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Living Anionic Polymerization of Styrenes Substituted with Electron-Withdrawing Groups

A Thesis Presented
To
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1994

TAKASHI ISHIZONE

Preface

The present studies in this thesis has been carried out under the guidance of Professor Seiichi Nakahama at the Department of Polymer Chemistry of Tokyo Institute of Technology during 1985-1993. The object of this thesis is concerned with the anionic living polymerization of novel styrene derivatives containing electron-withdrawing groups, leading to the syntheses of homopolymers and block copolymers with well-defined chain structures. The new class of reactivities for these monomers and their living polymers is demonstrated by using the results of block copolymerizations.

First of all, the author would like to express his sincere gratitude to Professor Seiichi Nakahama for his helpful guidance and advice throughout this work.

The author is deeply grateful to Associate Professor Akira Hirao for his constant advice and valuable suggestions together with continuous encouragement.

The author is much indebted to Drs. Kazuo Yamaguchi and Katsuhiko Takenaka for their useful discussions and technical instructions.

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Finally, the author wishes to express his deep gratitude to his parents for their constant encouragement.

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April, 1994

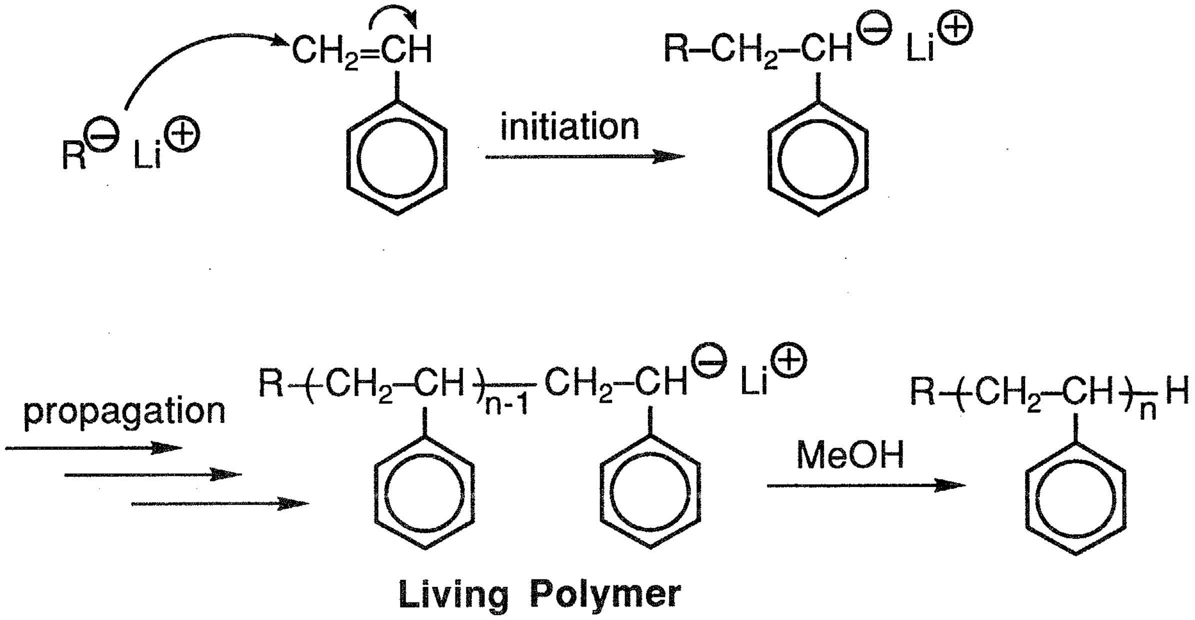
Contents

Chapter 1

General Introduction

Carbanions are highly reactive chemical species and have been widely used for organic synthesis.[1] The chemistry of carbanion has been intensively studied on the generating mechanism, the chemical structure, the coordination state, the substituent effects on stability and reactivity, and the mechanisms of carbanion-based reactions.[2] It still continues to attract a great deal of attention from the numerous researchers. It has been well known that the carbanion concerns with a number of important organic reactions as a reactive species, where a new carbon-carbon bond forms by its nucleophilic reaction.[3] The addition reaction of the carbanion toward the carbon-carbon double bond activated by the electron-withdrawing substituents, so-called the Michael addition or conjugate addition, is one of those organic reactions. In the reaction, both the nucleophilicity of the carbanions and the electrophilicity of the substrates such as α,β-unsaturated carbonyl compounds control the nature of reactions such as the selectivity, the conversion, and the yield of the reactants. In some cases, those reactions produce the polymeric products in good to quantitative yield by repeating addition of the newly formed carbanion to an another activated carbon-carbon double bonds. Even the inactive simple olefin such as ethylene undergoes the repeating addition reaction, where the carbanion successively acts as a reactive species to form the polymer, if one employs the strong nucleophile such as *n*-butyllithium as an initiator.[4] Hence, the carbanionic species have been realized to be very important to prepare the polymeric products as in the case of the organic synthesis.

Anionic living polymer, discovered by Szwarc in 1956,[5] is an interesting and versatile macromolecular carbanionic species also from the viewpoints of organic chemists due to the remarkable stability and high reactivity. The homogeneous anionic polymerization of styrene with organometallic reagents (*n*-butyllithium or metal naphthalenide) proceeds quantitatively to give a living polystyrene of an uniform chain length via the sequential monomer insertion to a carbon-metal bond of the active chain end (Scheme 1-1).



Scheme 1-1

There is a large influence stemmed from the discovery of this type of carbanions in the field of polymer synthesis by breaking a conventional concept as follows.[6] At first, the absence of termination reaction and chain transfer reactions enables the polymerization system to produce a polymer having a molecular weight predicted from a simple stoichiometry, based on the molar ratio of employed monomer to anionic initiator. Secondary, if the initiation step is sufficiently fast compared with the propagation step, the distribution of the degree of polymerization obeys Poisson distribution, *i.e.* extremely narrow distribution of the molecular weight. Furthermore, the nonterminating character of the growing chains in the anionic living polymer can lead to a successful synthesis of a block copolymer by sequential addition of different monomers after the complete consumption of the monomer fed first. Finally, the end-functionalized polymers can be also formed by the selective and quantitative termination of propagating carbanion with appropriate reagents.

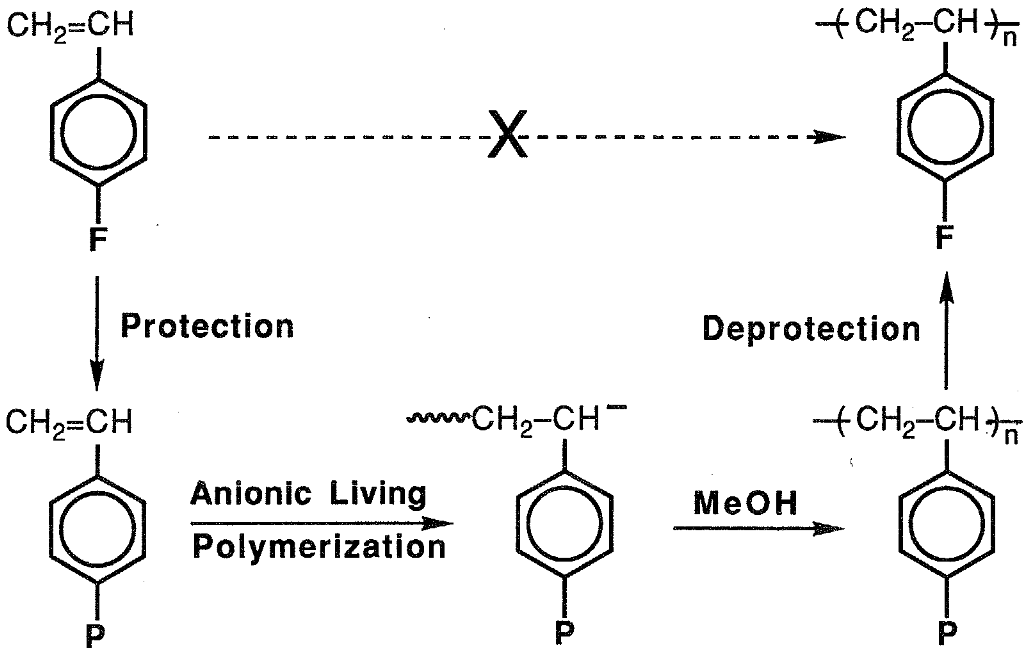
Hence, this anionic living polymerization system has strongly attracted polymer chemist's attention from both viewpoints of nature and mechanism of the polymerization system and above-mentioned unique synthetic attainment of the resulting polymers. The former interest particularly spread to the kinetic study of the polymerization system in 1960's mainly by measuring an absolute rate constant of the polymerization and an aggregation state of the propagating ends,[7] where a very important conception of the active chain end (contact ion pair, solvent-separated ion pair, and free ion) was proposed and actively controverted. The lack of side reactions in these polymerization systems has allowed the researchers to study the details of the pure chain propagation mechanism under the appropriate conditions. Nowadays, the above-mentioned classification of three states of the carbanion became popular and useful also for the better understanding of coordination state of the low-molecular weight organometallic compounds such as organolithiums[8] and lithium dialkylamides.[9]

On the other hand, the later interest strongly prompted synthetic polymer chemists to prepare the polymers of controlled architecture such as tailored block and graft copolymers,[10] star-branched polymers,[11] macrocyclics,[12] and end-functionalized polymers (telechelic polymer[13] and macromonomer[14]). In addition, it is evidently important from the industrial requirements that the lithium-initiated polymerization of dienes provides a valuable method to prepare the stereospecific polydienes constituted by 1,4-addition repeating microstructure.[15] Thus, the anionic living polymerization is the most powerful method to prepare a wide variety of polymers with precisely controlled molecular architecture such as molecular weight, molecular weight distribution, and copolymer composition and sequence. The nonterminating character of the propagating species leads to quantitative functionalization of the chain end and synthesizing of a tailor-made block copolymer.

In recent years, in addition to this anionic living polymerization, several different types of polymerization systems affording living polymers have been developed with the aim of fulfilling the favorable properties of the various polymers. These progressive examples involved cationic polymerization of electron rich olefins such as vinyl ethers[16] and isobutylene,[17] metathesis polymerization of cyclic olefins with transition metal,[18] coordination polymerization of α-olefins,[19] and so-called group transfer polymerizations of alkyl methacrylates[20] and trialkylsilyl vinyl ethers.[21] It was reported that, from each polymerization system, living polymers having different terminal active species yielded under the limited reaction conditions.

At this stage, the conventional anionic living polymerization of hydrocarbon monomers such as styrene and 1,3-butadiene is believed to be the best established method for synthesizing polymers having strictly controlled molecular weights (especially higher than 10^5) and extremely narrow molecular weight distributions, whereas the above-mentioned living polymerization systems have been newly developed. However, if one wishes to apply this elegant tool for the polymerization of functional monomers, the difficulty may be immediately encountered. Since the anionic living polymers are highly reactive and extremely susceptible to the proton sources such as water and alcohol, they are unfortunately incompatible with most functional groups used widely in the organic synthesis. This susceptibility makes an extension of the monomer range capable of living polymerization and a controlled synthesis of well-defined functional polymers very difficult. The anionic living polymerizations of polar monomers such as (meth)acrylic acid esters and vinylpyridines are somewhat troublesome because of the occurrence of side termination reactions to carbonyl moiety (C=O[22] and C=N[23] bond) and acidic α-proton.[24] A variety of modifications of initiating and polymerization systems[25–28] involving initiators, countercations, additives, solvents, and reaction temperature have been still examined with intensive efforts to polymerize ideally these polar monomers in a controlled fashion. Indeed, until the beginning of the 1980's, only a limited number of styrenes substituted with alkyl,[29] aryl,[30] and alkoxy[31] groups were known to afford the living polymers in addition to the conjugated hydrocarbon monomers, styrene, α-methylstyrene, 1,3-butadiene, and isoprene and some heterocyclic monomers.[32] Of course, the useful functional groups such as hydroxy, amino, carboxy, and formyl groups can not directly coexist with the organolithium compounds and can not tolerate the conditions typical for the anionic polymerization, resulting instantaneously in the chain termination reaction. Thus, due to the high reactivity of carbanions, the realization of living polymerization of monomers containing useful functional groups has been very difficult and slow in development.[33–35]

A significant improvement in the synthesis of novel anionic living polymer was made by Nakahama and co-workers in the early 1980's by the introduction of conception of the protecting groups into the anionic polymerization of functional monomers (Scheme 1-2).[36] Suitable selection of the protecting groups[37] for masking of the functional groups of the monomers is essential to achieve the living polymerization to allow the synthesis of polymers having desirable molecular weights and narrow molecular weight distributions. Subsequently, the complete removal of the protecting groups from the resulting polymer under mild conditions afforded the functional polymers of tailored chain lengths and distributions. The well-defined polymers, poly(4-hydroxystyrene),[38] poly(4-aminostyrene),[39] poly(4-carboxystyrene),[40] poly(4-formylstyrene),[41] poly(4-acetylstyrene),[42] poly(4-ethynylstyrene),[43] and poly(2-hydroxyethyl methacrylate)[44] have been successfully prepared via the above-mentioned synthetic route.



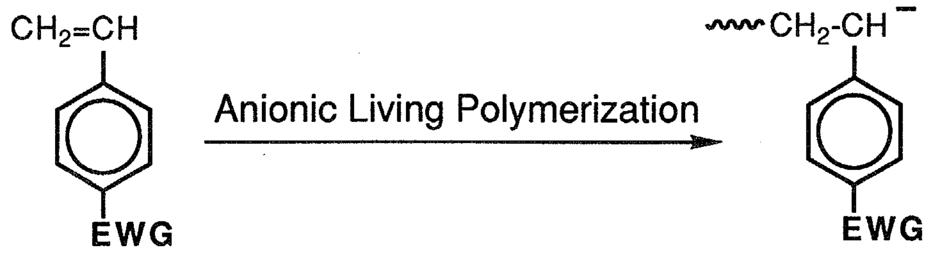
F: Functional Group, OH, NH_2, SH, CHO, $COCH_3$, COOH, $C{\equiv}C{-}H$
P: Protected Form of Functional Group

Scheme 1-2

Synthesis of Well-Defined Functional Polymers by Means of Anionic Living Polymerization

The persistency of the propagating carbanion of the resulting living polymers opens a way to the precisely controlled synthesis of block copolymers and end-functionalized polymers containing various functional groups in each monomer unit. Hence, this protection–living polymerization–deprotection strategy now has been extending to a wide area of polymer synthesis to prepare functional polymers possessing finely controlled chain structures regardless of the kind of polymerization mechanism.[45]

In this thesis, a newly developed strategy for the anionic living polymerization of styrene monomers containing functional groups is proposed through an introduction of electron-withdrawing groups into the *para* position of the styrene framework.[46] Although the employed electron-withdrawing groups, *N,N*-dialkylamide,[47] *tert*-butyl ester,[48] (trimethylsilyl)ethynyl,[43] *N,N*-dialkylsulfonamide,[49] and cyano,[50] are thought to be susceptible toward nucleophilic attack of the carbanionic species, these all substituted styrenes afford the stable anionic living polymers similar to living polystyrene (Scheme 1-3).



EWG : $-CONR_2$ $-COOR$ $-C{\equiv}C{-}SiMe_3$ $-SO_2NR_2$ $-C{\equiv}N$

Effect of Electron Withdrawing Group

1) High Electrophilicity of Vinyl Group
2) Low Nucleophilicity of Active Chain End

Scheme 1-3

The introduced substituents bring two effective characteristics into the anionic polymerization of these styrene derivatives to remarkably change the reactivities of the monomers and the living polymers.[51] One is a highly enhanced reactivity (electrophilicity) of those monomers under anionic conditions compared with that of styrene, because the electron-withdrawing group effectively reduces the electron density of the vinyl groups of these monomers. Even the anionic initiators of considerably low nucleophilicity, which are ineffective to initiate a polymerization of styrene, can be useful to initiate the polymerizations of these monomers quantitatively. The other is a reduced reactivity (nucleophilicity) of the terminal propagating carbanions of the resulting living polymers compared with that of anionic living polystyrene. The benzylic carbanions at the active chain ends are stabilized both by the electron-withdrawing effects and by the extended π-conjugated system involving the multiple bonds of C=O, C≡C, S=O, and C≡N of the functional groups.[52] This is evident from the crossover reactions of these living polymers and styrene monomer. The author believes that the later effect (reduced nucleophilicity), in particular, enables these functional monomers to produce the stable living polymers by suppressing the serious undesirable side reactions. It is also noteworthy that these living polymers are very important as new organometallic reagents containing widely available functional groups. Thus, the introduction of the electron-withdrawing groups into the monomer framework is very effective to change the monomer polymerizability under anionic mechanism and achieves a great success in the production of novel living polymers.

In this regard, it is very interesting to estimate the monomer reactivity of styrenes bearing electron-withdrawing groups, since the substituent effects will strongly affect the polymerization behaviors of these monomers. Several reports concerning the relationship between structure and reactivity have actually revealed the substituents effects of the 4-substituted styrenes on the various organic reactions such as methoxymercuration,[53] Diels-Alder reaction,[54] hydroboration,[55] free-radical addition,[56] and radical polymerization.[57] In addition, the reactivity of the employed styrenes may be evaluated in terms of their substituent effect which is generally accepted in physical organic chemistry. The methodology to measure the substituent effects of 4-substituted styrenes has been independently reported. The examples involved the Hammett σ-values, the ^{13}C NMR chemical shifts of β-carbons, and the π -electron densities by the semiemprical CNDO/2 and the ab initio calculations. In the framework of a series of *para*-substituted styrenes, Reynolds *et al.*[58] have reported that the ^{13}C NMR chemical shifts of β-carbons are precisely related to the π-electron densities at this site, calculated by the semiemprical CNDO/2 method. More recent ab initio calculation[59] has again confirmed this excellent linear relationship between the β-carbon chemical shifts and ab initio π-electron densities. As expected, compared with the π-electron density of the β-carbon of styrene, the values of 4-substituted styrenes having electron-donating and electron-withdrawing groups increased and decreased, respectively. Prior to these reports concerning with the correlation between the chemical shift and electron density, Dhami[60] has shown the similar good linear plot between the vinyl β-carbon shifts of styrenes and the Hammett σ-parameters covering the range from p-NMe_2 to p-NO_2. This linear relationship strongly supported that the substituent effects remarkably change the electron densities of the vinyl groups of functional styrenes. In other words, this means that the substituent effects can be estimated from the chemical shifts of the β-carbon of vinyl group in ^{13}C NMR spectra of 4-substituted styrenes.

Figure 1-1 presents a new plot between the β-carbon chemical shifts[61] for the 4-substituted styrenes including the monomers used in this thesis and the Hammett σ_p-values,[62] which have been recently measured by the author or reported in the literatures. This good linear relationship is consistent with the plot previously reported by Dhami.[60] As can be seen, all the chemical shifts of the vinyl β-carbons for styrenes *para*-substituted with electron-withdrawing groups (114.8–117.6 ppm) are apparently located at lower field than that of styrene (113.8 ppm). From this excellent linear plot, the Hammett σ_p-values for the electron-withdrawing groups of the monomers employed in this thesis can be evaluated to be 0.22–0.66. Furthermore, this means that the reactivities of substituted styrenes can be evaluated and arranged in reactivity order by measuring the chemical shifts of their vinyl β-carbons.

Likewise, the ^{13}C NMR chemical shift of the terminal benzylic carbanion of the resulting living polymers[63] might indicate the reactivity of the carbanion, although the data are not currently available. Moreover, it will be similarly possible to predict the reactivity of the living polystyrenes by calculating the

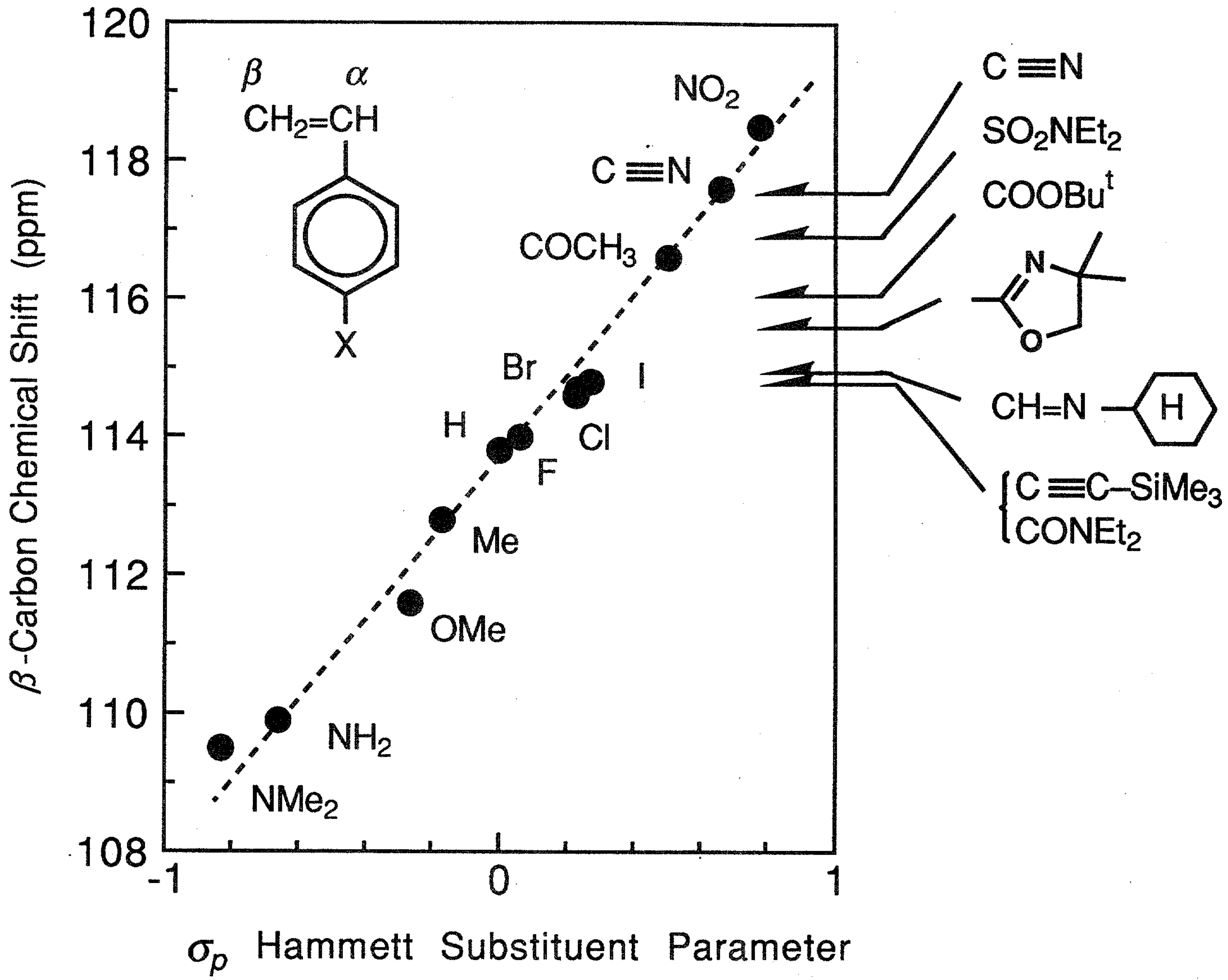


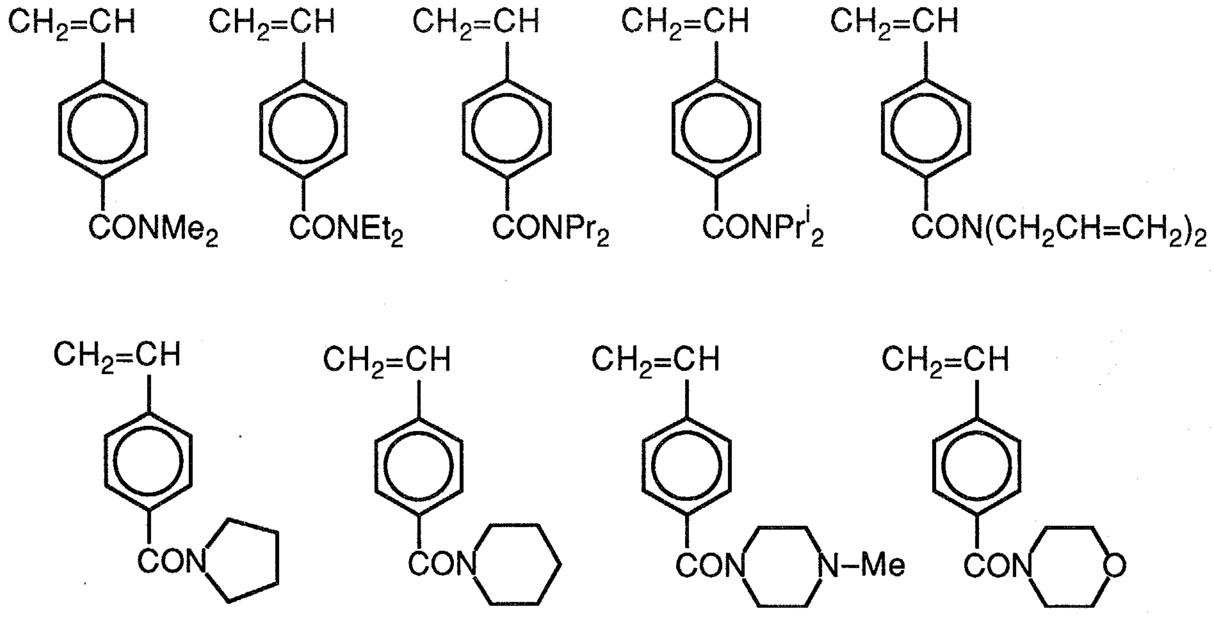
Figure 1-1. Plot of β-carbon chemical shifts of vinyl groups of *para*-substituted styrenes[61] vs. Hammett σ_p parameters.[62]

π-electron densities of the benzylic carbanions[64] by ab initio or semiemprical molecular calculations in the near future. Historically, the absolute rate constant of crossover reaction k_{AB} has been determined by Szwarc *et al.* from the kinetic study in the anionic copolymerization.[65] However, the k_{AB} values were observed for the limited range of monomers and complicated for the comprehensive discussion of the reactivities of the propagating carbanions. Thus, unfortunately, the reactivities of the various carbanion have not been thoroughly discussed and quantified until now.

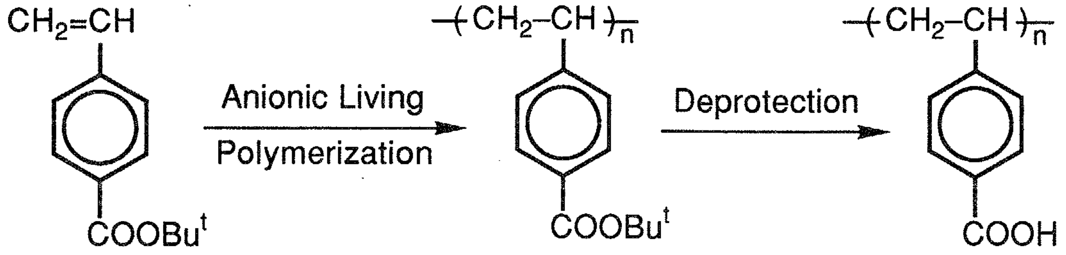
In this thesis, the author would like to propose new methodology to estimate systematically the reactivity of the propagating carbanions of the living polymers. The results of sequential block copolymerizations of the living polymers with different monomers are very useful to discuss the both reactivities of the monomers (electrophile) and the living polymers (nucleophile). Although the similar block copolymerizations of various monomers have been already reported by some researchers,[66] the discussions about the reactivities of the monomers and the living polymers are completely independent and the relationship of both reactivities is poorly understood. Moreover, the limited number of the employable monomers in the living polymerization has been a problem which makes the thorough discussions impossible. Here, the newly developed monomers capable of anionic living polymerization will extend the possibility of total discussion concerning the electrophilicity of these monomers and the nucleophilicity of the resulting polymers under the anionic conditions.

Under the above-described backgrounds, in this study, the anionic living polymerizations of five functional styrenes substituted with electron-withdrawing groups are demonstrated in Chapter 2 to Chapter 6, respectively. The well-defined novel homopolymers and block copolymers derived from these monomers are successfully synthesized by fine tuning of the polymerization conditions. As a summary of this subject, in Chapter 7, the sequential block copolymerizations of these styrene monomers and the conventional monomers (isoprene, styrene, 2-vinylpyridine, and *tert*-butyl methacrylate) are carried out in order to clarify the reactivity of these monomers and the resulting living polymers. The contents of each chapter are as follows.

Chapter 2 describes anionic polymerization of nine styrene monomers containing tertiary carboxylic amide groups, *N,N*-dialkyl-4-vinylbenzamides. The monomers possessed various functionalities such as linear and cyclic alkyl substituents, allyl group (carbon-carbon double bond), ether, and tertiary amine. The usual vinyl polymerization of the monomers proceeded quantitatively with anionic initiators to afford stable living polymers with predicted molecular weights and narrow molecular weight distributions. The electrophilic carbonyl group of the amide function for the monomers and the resulting polymers seems to be rather stable under anionic conditions.

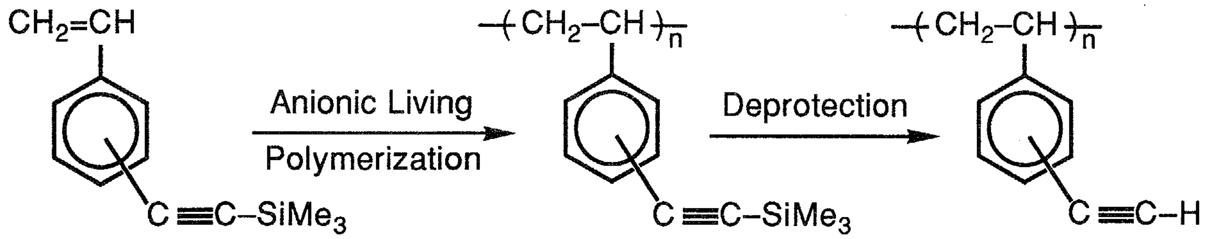


Chapter 3 demonstrates the elegant synthetic route of well-defined poly(4-vinylbenzoic acid) by means of anionic living polymerization of *tert*-butyl 4-vinylbenzoate and the subsequent deprotection reaction of the resulting polymer (Scheme 1-4). The complete controls for the polymerization of *tert*-butyl 4-vinylbenzoate are satisfactorily achieved by the suitable selection of the initiator and polymerization temperature. Polymerization behaviors of the other four ester monomers are discussed for a comparison.



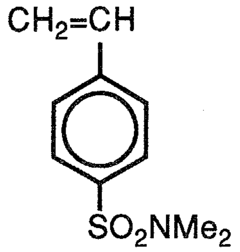
Scheme 1-4

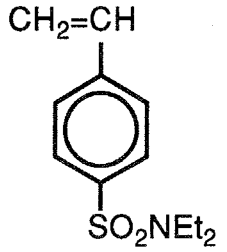
In Chapter 4, anionic polymerizations of 2-, 3-, and 4-[(trimethylsilyl)ethynyl]styrene are systematically investigated. Three isomeric poly(ethynylstyrene)s with controlled molecular structure can be synthesized by the complete deprotection of the trimethylsilyl group from the resulting polymers (Scheme 1-5).

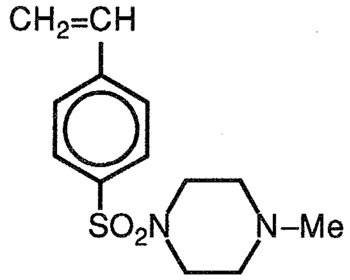


Scheme 1-5

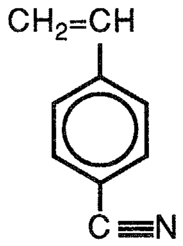
Chapter 5 deals with the anionic polymerization of three *N,N*-dialkyl-4-vinylbenzenesulfonamides. In each case, a stable living polymer is produced with conventional anionic initiators. This strongly indicates that the tertiary sulfonamide moiety is also intact toward the nucleophilic attack of the initiators and the propagating carbanion.

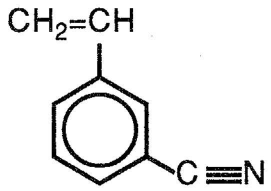


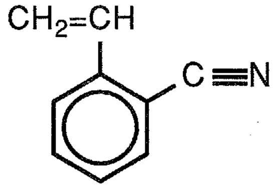




In Chapter 6, three mono-ring-substituted cyanostyrenes, 2-, 3-, and 4-cyanostyrene, are polymerized with anionic initiators. During the employed monomers in this thesis, since the electron-withdrawing effect of the cyano group is the strongest one, the polymerization behavior of cyanostyrenes may be dramatically affected. As a result, only *para*-substituted monomer ideally undergoes the anionic living polymerization, although the both polymerizations of *meta* and *ortho* isomers involve the undesirable side reactions.







Chapter 7 describes the anionic block copolymerization of above-mentioned styrene derivatives containing electron-withdrawing groups with the conventional comonomers. Several novel well-defined block copolymers can be synthesized by the sequential addition copolymerization of the monomers.

From the polymerization results, higher reactivities of the monomers and lowered nucleophilicities of their living polymers under anionic mechanism are demonstrated, compared with those of styrene and living polystyrene.

In summary, the major subjects of this thesis are anionic living homopolymerizations of novel styrene monomers bearing *N,N*-dialkylamide, *tert*-butyl ester, (trimethylsilyl)ethynyl, *N,N*-dialkylsulfonamide, and cyano groups and the evaluation of the reactivities of these monomers and the resulting living polymers from the results of the sequential block copolymerizations. The present novel living polymers having various electron-withdrawing groups are important as a new class of carbanion which shows remarkable stabilities and may contribute for a better understanding of the carbanionic chemistry. Moreover, the newly synthesized functional homopolymers and block copolymers possessing well-defined chain structures are hoped to play important roles in the future development of material science.

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Chapter 2

Living Anionic Polymerization of *N,N*-Dialkyl-4-vinylbenzamides

ABSTRACT: Anionic polymerization of *N*,*N*-dimethyl- (**1a**), *N*,*N*-diethyl- (**1b**), *N*,*N*-dipropyl- (**1c**), *N*,*N*-diisopropyl- (**1d**), and *N*,*N*-diallyl-4-vinylbenzamide (**1e**), *N*-(4-vinylbenzoyl)pyrrolidine (**1f**), *N*-(4-vinylbenzoyl)piperidine (**1g**) *N*-(4-vinylbenzoyl)-*N′*-methylpiperazine (**1h**), and *N*-(4-vinylbenzoyl)morpholine (**1i**) were carried out at –78°C in tetrahydrofuran (THF). The initiators involved lithium, sodium, and potassium naphthalenide, oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium, and cumylpotassium. Each of these polymerizations gave poly(**1**)s in quantitative yield. The polymerization reaction proceeded in a homogeneous system in the case of **1b-e** or **1g-h**, while poly(**1a**), poly(**1f**), and poly(**1i**) were precipitated during the polymerization. In each case, the obtained polymers had narrow molecular weight distributions and predictable molecular weights from the molar ratios of monomer to initiator, indicating that the anionic polymerization of **1**s proceeded without chain transfer and termination reactions to give a stable living polymer. New block copolymers, poly(**1a**-*b*-styrene-*b*-**1a**), poly(**1b**-*b*-styrene-*b*-**1b**), poly(**1h**-*b*-styrene-*b*-**1h**), poly(**1i**-*b*-styrene-*b*-**1i**), poly(**1b**-*b*-isoprene-*b*-**1b**), poly(**1f**-*b*-styrene-*b*-**1f**), and poly[(*tert*-butyl methacrylate)-*b*-**1b**-*b*-(*tert*-butyl methacrylate)], were synthesized by using these living systems. Poly(**1a**) was quantitatively converted into poly(4-vinylacetophenone) by reaction with methyllithium. Poly(**1b**) was metalated with *sec*-BuLi/*N*,*N*,*N′*,*N′*-tetramethylethylenediamine in THF and the resulting *ortho*-lithiated species were treated subsequently with trimethylsilyl chloride to transform into a polystyrene containing tertiary amide and trimethylsilyl group. Under acidic conditions (6 N HCl in 1,4-dioxane-water), quantitative hydrolysis of amide linkage for the poly(**1h**) was achieved to give a well-defined poly(4-vinylbenzoic acid).

Introduction

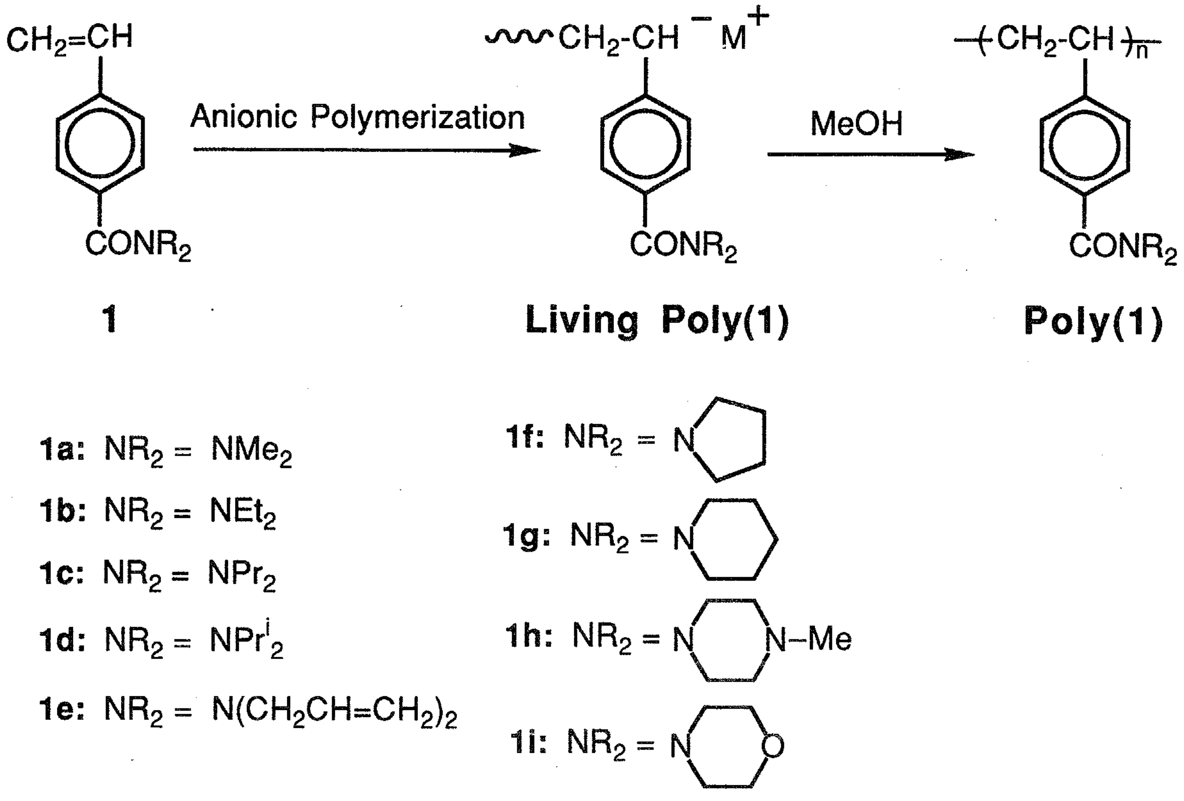
The control of polymerization affording macromolecules with regulated chemical structures is an exciting target in current polymer synthesis,[1] where the living polymer plays an important role to give block copolymers of various architectures, macromonomers, and telechelomers as well as homopolymers with well-defined chain structures. In addition, the development of new monomers affording living polymers is earnestly desired for the molecular design of new macromolecules having well-defined chain structures.

It has been recently demonstrated that anionic living polymerization of novel monomers having protected functions with suitable masking groups proceed under controlled conditions.[2] During the research, it has been found that several styrene derivatives *para*-substituted with electron-withdrawing groups such as imine,[3] ester,[4] oxazoline,[5] and cyano[6] yielded stable anionic living polymers. These polar groups are susceptible to the nucleophilic addition of anionic initiators, such as organolithium compounds and Grignard reagents.[7] However, these anionic species exclusively attack the vinyl groups of the monomers not the polar substituents to initiate the polymerization. Moreover, during the course of polymerization, the anionic chain ends of the polymers coexist with the polar functional groups to produce the living polymers with functions and well-defined structures. The electron-withdrawing groups are thought to play an important role in the stabilization of propagating chain ends.[3-6]

As another electron-withdrawing group, carboxylic acid amide might possibly show the similar behavior. Unfortunately, in the anionic polymerization of the vinyl monomers containing primary amide groups, such as 4-vinylbenzamide, vinyl polymerization (1,2-addition) and hydrogen-transfer polymerization (1,8-addition) proceed simultaneously, resulting in a polymer of mixed repeating units,[8] as was observed in the cases of acrylamide and methacrylamide.[9] Such diversity of the propagation reaction may be avoided by an employment of styrene derivatives with tertiary amide groups to obtain the polymer having uniform structure through anionic polymerization. Thus, the author here concentrates the study on the anionic polymerization of *N*,*N*-dialkyl-4-vinylbenzamides.

In the preceding paper,[10] it has been briefly reported the anionic polymerization of *N*,*N*-diisopropyl-4-vinylbenzamide (**1d**), bearing a sterically hindered tertiary amide group. The living nature of the anionic propagating chain end of poly(**1d**) in THF at –78°C was suggested by formation of the homopolymer and block copolymer with controlled chain structures. As described later in Chapter 3 in the anionic polymerization of alkyl 4-vinylbenzoate,[4] a bulky substituent like a *tert*-butyl group and a low polymerization temperature (–95°C) were required to realize the anionic living polymerization of the monomer containing polar ester moiety that might potentially be attacked by the nucleophilic propagating carbanion. Accordingly, in the anionic polymerization of *N*,*N*-dialkyl-4-vinylbenzamides, use of bulky substituents or severe control of reaction condition might also be required to avoid transfer and termination reactions.

The present chapter describes the anionic polymerization of nine *N*,*N*-dialkyl-4-vinylbenzamides (**1**) and discusses the steric effects of alkyl substituents on the stability of the anionic propagating chain end (Scheme 2-1). Furthermore, block copolymerizations of **1**s and three polymer reactions of the resulting poly(**1**)s are also carried out. In particular, a new styrene monomer bearing a tertiary *β*-amino amide, *N*-(4-vinylbenzoyl)-*N'*-methylpiperazine (**1h**) was purposely synthesized and polymerized to produce a well-defined poly(4-vinylbenzoic acid) by the hydrolysis of the resulting poly(**1h**).



Scheme 2-1

Results and Discussion.

2-1. Anionic Polymerization of *N*,*N*-Diethyl-4-vinylbenzamide (**1b**).

First of all, anionic polymerization of **1b** was carried out in THF at 14 to –78°C with various initiators such as lithium, sodium, and potassium naphthalenides, (1,1,4,4-tetraphenylbutanediyl)dilithium, oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium, and cumylpotassium. Typically, when **1b** was added to the alkali-metal naphthalenide solutions, a rapid color change from dark green to orange red occurred, indicating that the initiation reaction took place. The red coloration remained unchanged at –78°C even after 24 h and faded immediately on the addition of a small amount of methanol for quenching the polymerization. The polymer of white powder was quantitatively obtained after precipitation into a large excess of water and was purified by reprecipitation with a THF-hexane system and then freeze-dried from benzene. ^{1}H NMR spectrum of the resulting polymer shows the structure of the expected poly(*N*,*N*-diethyl-4-vinylbenzamide) as shown in Figure 2-1B. After the polymerization, signals due to vinyl protons (Figure 2-1A) of the monomer completely disappeared, and alternatively those of methylene and methine protons of the main chain were observed. In the ^{13}C NMR of the polymers, an amide carbonyl carbon at 170.9 ppm was detected in the same region of the monomer (171.0 ppm) and the resonances due to vinyl carbons of the monomer completely disappeared. The infrared spectrum of the polymer showed a strong absorption of the amide carbonyl group at 1636 cm^{-1}, whereas that of **1b** was observed at 1619 cm^{-1}. These spectroscopic observations indicate that anionic polymerization of **1b** takes place in the vinyl polymerization mode exclusively.

In each case, the yield of poly(**1b**) was quantitative. The number-average molecular weights of poly(**1b**)s were measured by VPO. Table 2-1 summarizes the results of the anionic polymerization of **1b**. The good agreements between the molecular weights of poly(**1b**)s measured and those calculated from the molar ratios of monomer to initiator were observed regardless of the initiators and countercations employed. The molecular weight distributions (MWDs) of all resulting poly(**1b**)s were very narrow in the molecular weight range 7000- 48 000. Even at higher polymerization temperatures, 0 and 14°C, nearly monodisperse polymers were obtained. The representative SEC curves of poly(**1b**)s produced at –78 and 14°C are shown in Figure 2-2. These results suggest that the anionic polymerization of **1b** proceeds without transfer and termination reactions even at room temperature. Moreover, to prove the living nature of the polymerization system at –78°C, the postpolymerization was carried out. The second-stage polymerization

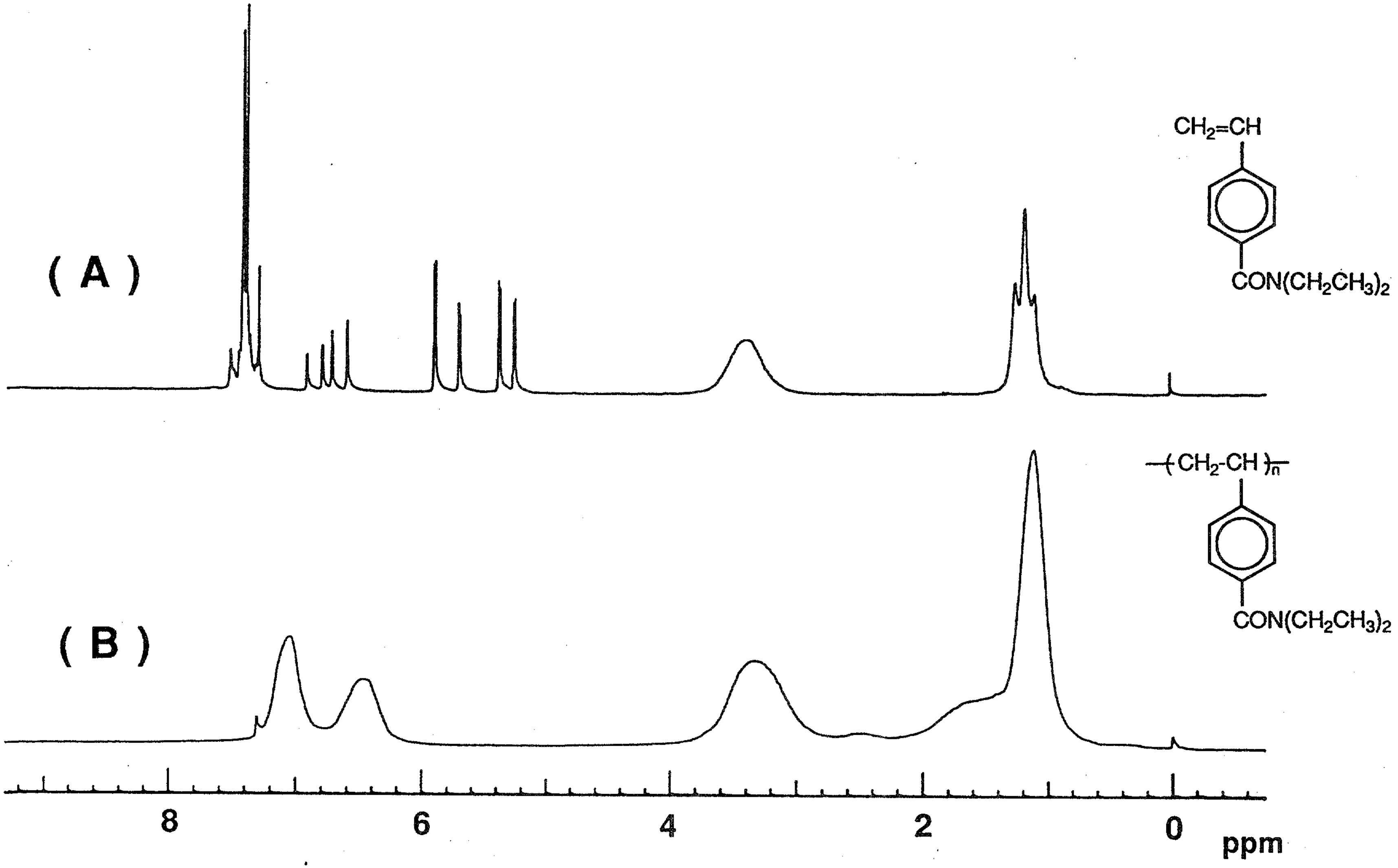


Figure 2-1. ^{1}H NMR spectra of **1b** (A) and poly(**1b**) (B) in $CDCl_3$.

Table 2-1

Anionic Polymerization of **1b** with Various Initiators in THF for 30–60 min[a]

run	**1b**, mmol	temp, °C	initiator, mmol	$10^{-3}M_n$ calcd[b]	$10^{-3}M_n$ obsd[c]	M_w/M_n
1	3.50	–78	Li-Naph[d], 0.108	13	12	1.13
2	3.05	–78	Li-Naph, 0.133/DPE[e], 0.251	9.7	7.2	1.09
3	3.92	–78	Li-Naph, 0.109/ α-MeSt[f], 0.883	17	14	1.06
4	3.59	–78	Na-Naph[g], 0.125	12	11	1.13
5	2.82	–78	Na-Naph, 0.103/ α-MeSt, 0.274	12	11	1.08
6	3.45	–78	K-Naph[h], 0.135	10	11	1.09
7	3.45	14	K-Naph, 0.0840/ α-MeSt, 0.360	18	12	1.13
8	4.95	0	K-Naph, 0.209/ α-MeSt, 0.451	9.7	10	1.09
9	3.88	–78	K-Naph, 0.152/ α-MeSt, 0.604	11	9.2	1.08
10	4.88	–78	K-Naph, 0.107/ α-MeSt, 0.699	20	17	1.07
11	5.40	–78	K-Naph, 0.0666/ α-MeSt, 0.461	35	33	1.13
12	6.40	–78	Cumyl-K[i], 0.0486/ α-MeSt, 0.171	36	36	1.09
13	7.17	–78	Cumyl-K, 0.0308/ α-MeSt, 0.449	48	48	1.08

[a] Yields of polymers were almost quantitative in all polymerizations. [b] M_n(calcd) = [monomer] × (MW of monomer) × f / [initiator] + MW of initiator, f = 1 or 2 corresponding to the functionality of the initiators. [c] M_n(obsd) was obtained by VPO in benzene solution. [d] Lithium naphthalenide. [e] 1.1-Diphenylethylene. [f] α-Methylstyrene. [g] Sodium naphthalenide. [h] Potassium naphthalenide. [i] Cumylpotassium.

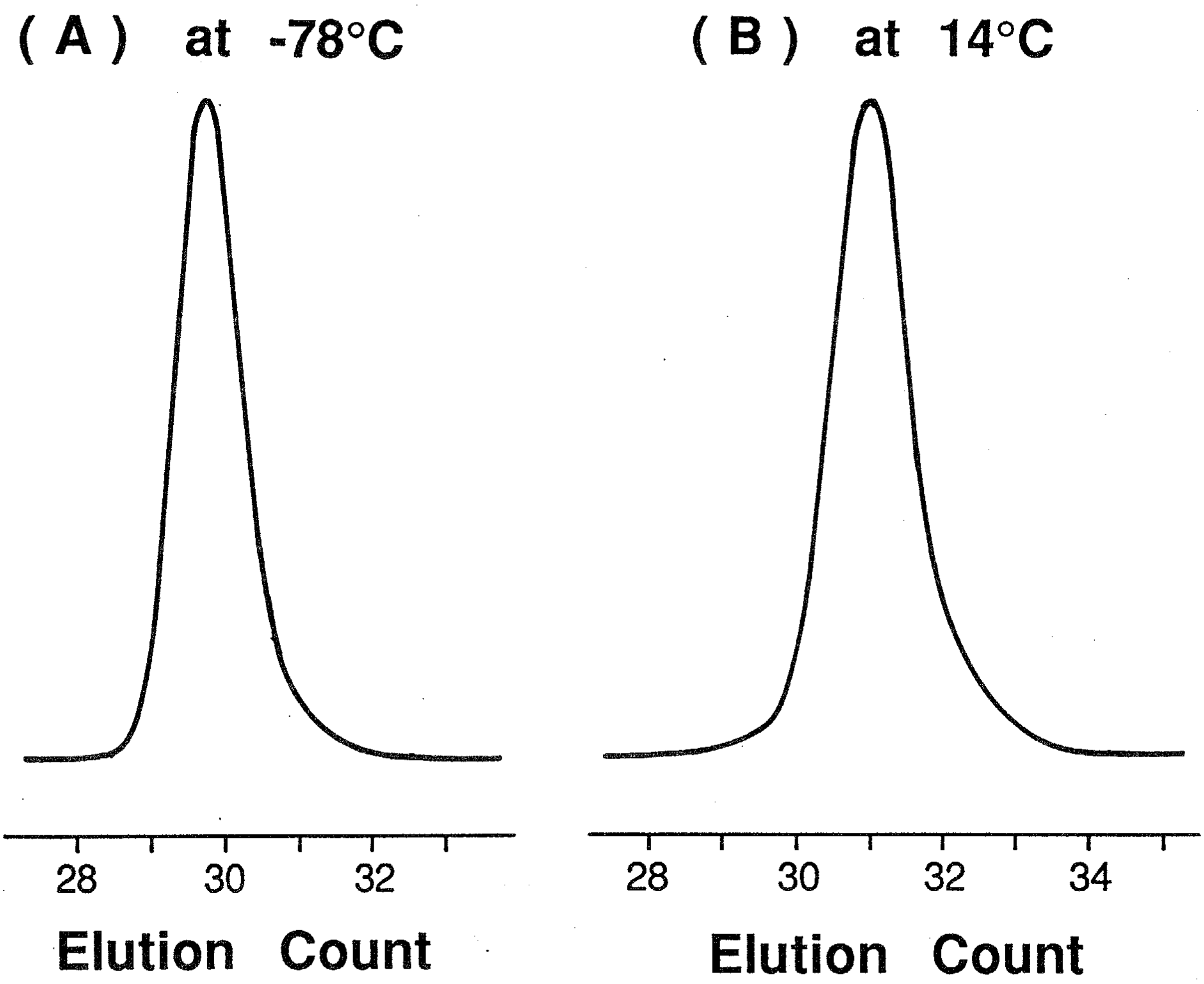


Figure 2-2. SEC curves of poly(**1b**) obtained with the potassium salts. Detailed data are shown in Table 2-1:
(A) run 13, at –78°C, M_n(obsd) = 48 000, M_w/M_n = 1.08;
(B) run 7, at 14°C, M_n(obsd) = 12 000, M_w/M_n = 1.13.

proceeded with a quantitative efficiency to produce a postpoly(**1b**) with a predictable molecular weight and a narrow MWD when **1b** was added to the THF solution of prepoly(**1b**) prepared from oligo(α-methylstyryl)dipotassium and **1b** at –78°C for 30 min. This indicates that the propagating chain end of **1b** completely survives at least at –78°C for 30 min. It is obvious from these results that the propagating carbanion of poly(**1b**) repeats 1,2-addition to the monomer vinyl group without carbonyl attack under the conditions employed here.

2-2. Anionic Polymerization of *N,N*-Dimethyl- (1a), *N,N*-Dipropyl- (1c), *N,N*-Diisopropyl- (1d), and *N,N*-Diallyl-4-vinylbenzamide (1e), *N*-(4-Vinylbenzoyl)pyrrolidine (1f), *N*-(4-Vinylbenzoyl)piperidine (1g), *N*-(4-vinylbenzoyl)-*N'*-methylpiperazine (1h), and *N*-(4-vinylbenzoyl)morpholine (1i).

In the series of the studies, it was already confirmed that the stable living polymers formed at –78°C from styrene derivatives containing electron-withdrawing groups, such as imino,[3] amide,[10] oxazolinyl,[5] and cyano.[6] As described in Chapter 3, additional results were obtained for the anionic polymerization of a styrene derivative with an ester moiety, *tert*-butyl 4-vinylbenzoate.[4] The living polymer was only stable below –95°C and caused the carbonyl attack to broaden the MWD even at –78°C. Moreover, the lithium salt initiators produced no polymer, although quantitative yields of polymers were achieved with sodium, potassium, and cesium salts as initiators. The polymerization of less-hindered methyl and allyl esters gave no polymeric products. Although isopropyl esters underwent anionic polymerization at least under a similar condition, polymers of broad MWD were produced in rather low yields, indicating that the propagating chain end of the polymer was quite unstable. In order to obtain a stable living polymer of the *tert*-butyl ester, polymerization required both bulkiness of the alkyl substituent of the ester group and a very low reaction temperature. In contrast, the living polymer derived from a tertiary amide counterpart, **1b**, which has relatively less-hindered substituents, survives even at room temperature. This might be explained by resistivity of amide toward nucleophilic attack.[11]

In this section, to investigate the limitation of living polymerization of **1**, the anionic polymerizations of the other seven analogues having various alkyl substituents on the nitrogen atom were carried out under the similar conditions. The results are discussed including those of *N,N*-diisopropyl-4-vinylbenzamide (**1d**), obtained previously.[10]

Upon addition of **1c-e** and **1g-h** to the initiators, the anionic polymerizations proceeded homogeneously, as did that of **1b**, to yield poly(**1**)s quantitatively. The polymers produced were found to have the repeating unit of 2,1-addition by ^{1}H and ^{13}C NMR, IR spectroscopic measurements, and elemental analysis. Typically, Figure 2-3A,B shows the ^{13}C NMR spectra of **1e** and poly(**1e**) obtained by anionic polymerization, respectively. The vinyl polymerization of **1e** exclusively proceeds and the pendant allyl groups on poly(**1e**) remain intact without nucleophilic attack from anionic initiator or active chain end at –78°C even for 24 h. As shown in Table 2-2, the polymers of **1c-e** and **1g-h** possess the predicted molecular weights based on monomer to initiator ratios and narrow MWDs. These results indicate the living character of anionic polymerizations of **1c-e** and **1g-h**, similarly to the case of **1b**.

1a, **1f**, and **1i** were similarly polymerized in THF at –78°C. In these cases, the orange polymers were immediately precipitated on addition of the monomers to anionic initiators with lithium and potassium countercations. The polymerization of **1a** proceeded slowly at –78°C compared with those of the other monomers, probably due to heterogeneity of the reaction system. The precipitation seemed to be caused by association of ionic species at chain terminals since the poly(**1a**) isolated readily and completely dissolved in THF at –78°C. Poly(**1a**) of quantitative yield was achieved at –78°C within 24 h.

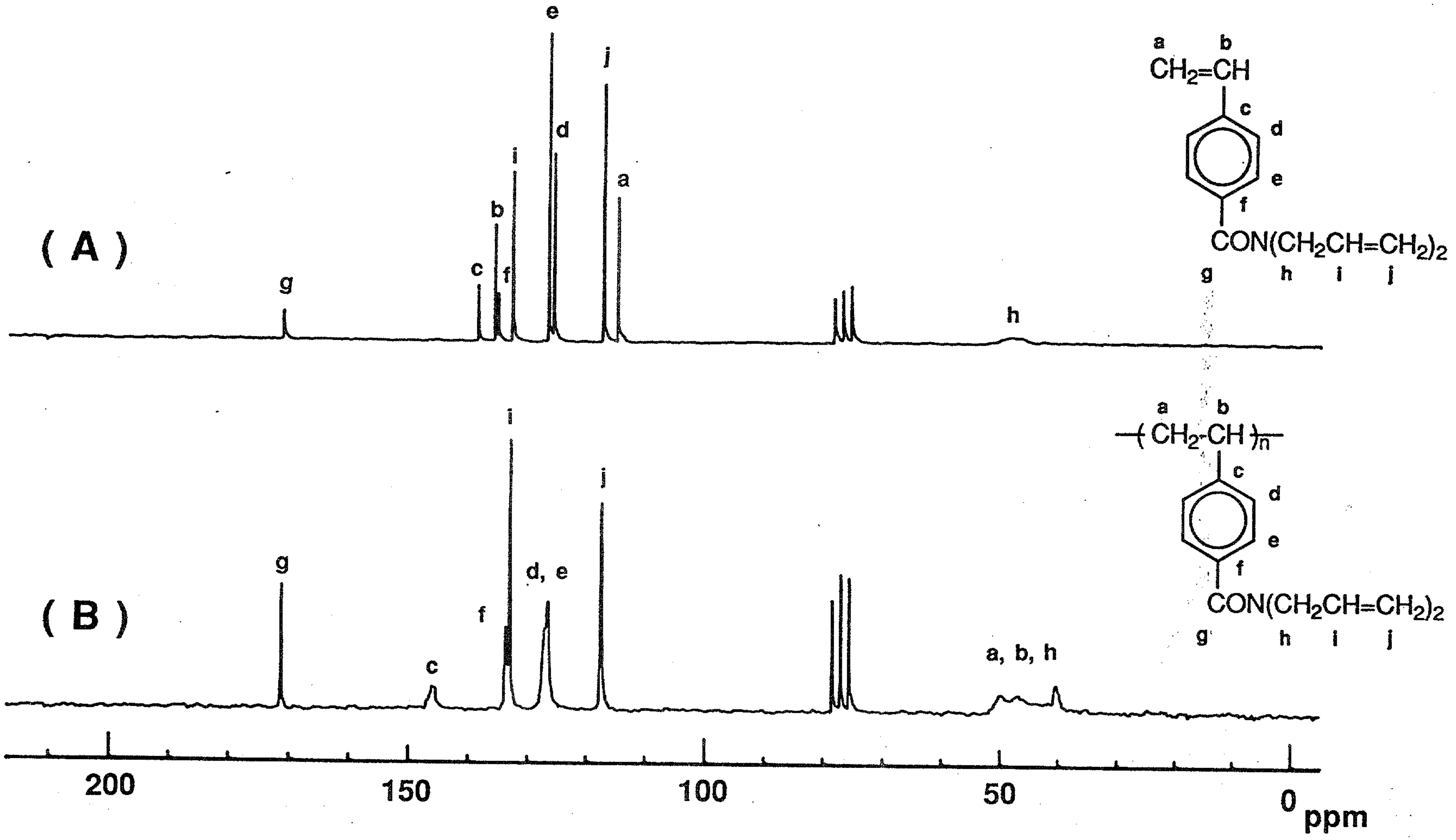


Figure 2-3. ^{13}C NMR spectra of **1e** (A) and poly(**1e**) (B) in $CDCl_3$.

Table 2-2

Anionic Polymerization of **1a**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, and **1i** in THF[a]

	monomer			$10^{-3}M_n$		
run	mmol	temp(°C), time	initiator, mmol	calcd[b]	obsd[c]	M_w/M_n
14	**1a**, 2.64	19, 30 min	Li-Naph[d], 0.113/ α-MeSt[e], 0.358	9.0	8.1	1.11
15	**1a**, 2.37	0, 30 min	Li-Naph, 0.112/ α-MeSt, 0.367	8.2	7.8	1.12
16	**1a**, 2.49	–78, 30 min	Li-Naph, 0.106/ α-MeSt, 0.310	4.5	6.5	1.07
17	**1a**, 2.94	–78, 24 h	Li-Naph, 0.125/ α-MeSt, 0.364	8.9	9.5	1.12
18	**1a**, 6.01	–78, 24 h	Li-Naph, 0.0782/ α-MeSt, 0.711	29	34[f]	1.15
19	**1a**, 3.16	17, 30 min	K-Naph[g], 0.129/ α-MeSt, 0.430	9.4	9.9	1.19
20	**1a**, 4.09	0, 60 min	K-Naph, 0.117/ α-MeSt, 0.525	13	15[f]	1.55
21	**1a**, 4.63	–78, 24 h	K-Naph, 0.0916/ α-MeSt, 0.706	20	19[f]	1.94
22	**1c**, 2.74	–78, 2 h	Cumyl-K[h], 0.105	6.1	5.5	1.06
23	**1c**, 2.35	–78, 2 h	Cumyl-K, 0.0476	12	11	1.07
24	**1d**, 2.36	–78, 30 min	Li-Naph, 0.111/ α-MeSt, 0.305	11	10	1.08
25	**1d**, 4.42	–78, 30 min	K-Naph, 0.0981/ α-MeSt, 0.202	21	22	1.06
26	**1e**, 5.12	–78, 22 h	Li-Naph, 0.207/ α-MeSt, 0.506	12	12	1.12
27	**1e**, 3.93	–78, 30 min	K-Naph, 0.205/ α-MeSt, 0.727	9.5	9.3	1.07
28	**1e**, 5.55	–78, 30 min	K-Naph, 0.0999/ α-MeSt, 0.357	26	23	1.08
29	**1f**, 5.84	–78, 24 h	Cumyl-K, 0.133	8.9	8.0[f]	1.09
30	**1g**, 3.89	–78, 30 min	K-Naph, 0.103/ α-MeSt, 0.241	17	14	1.08
31	**1g**, 4.05	–78, 30 min	K-Naph, 0.0794/ α-MeSt, 0.262	23	22	1.08
32	**1h**, 3.05	–78, 24 h	Li-Naph, 0.124/ α-MeSt, 0.306	12	13[f]	1.13
33	**1h**, 2.88	–78, 30 min	Na-Naph, 0.145/ α-MeSt, 0.422	9.8	12[f]	1.08
34	**1h**, 2.62	–78, 30 min	K-Naph, 0.210/ α-MeSt, 0.543	6.4	8.4[f]	1.07
35	**1h**, 3.24	–78, 1 h	K-Naph, 0.151/ α-MeSt, 0.431	11	11[f]	1.06
36	**1h**, 6.11	–78, 2 h	K-Naph, 0.151/ α-MeSt, 0.548	20	20[f]	1.11
37	**1h**, 6.74	–78, 3 h	K-Naph, 0.0864/ α-MeSt, 0.290	37	38[f]	1.11
38	**1i**, 3.66	–78, 24 h	Li-Naph, 0.121/ α-MeSt, 0.318	14	14[f]	1.06

[a] Yields of polymers were almost quantitative except for the run.16, where the poly(**1a**) was produced in 51% yield. [b] M_n(calcd) = [monomer] × (MW of monomer) × f × (conversion of polymerization) / (100)[initiator] + MW of initiator, f = 1 or 2 corresponding to the functionality of the initiators. [c] M_n(obsd) was obtained by VPO in benzene solution. [d] Lithium naphthalenide. [e] α-Methylstyrene. [f] M_n(obsd) was obtained by SEC calibration using standard polystyrenes in DMF solution. [g] Potassium naphthalenide. [h] Cumylpotassium. [i] Sodium Naphthalenide

If the polymerization temperature is raised to 0°C or room temperature, the reactions proceeded in homogeneous orange-red solutions to consume **1a** completely in 30 min.

The poly(**1a**) and poly(**1i**) produced with lithium initiator and poly(**1f**) with potassium initiator have molecular weights[12] close to the calculated values and narrow MWDs regardless of reaction system, heterogeneous at –78°C or homogeneous at 0°C or room temperature (Table 2-2). This suggests that the propagating active end survives in the course of the polymerization, while longer time is required to complete the reaction in the heterogeneous system (run 16). In contrast, the poly(**1a**)s obtained with potassium initiators possessed somewhat broad MWDs compared with the case of lithium initiator, although the exact reason could not be clearly discussed at this stage.

Thus, formation of the living polymers of all eight styrene derivatives with tertiary amide groups is substantiated, in addition to the case of *N,N*-diisopropyl-4-vinylbenzamide (**1d**) previously reported.[10] The presence of carbon-carbon double bond (allyl group), tertiary amine, and ether functions in addition to the tertiary amide is not a problem in the polymerizations of **1e**, **1h**, and **1i**. In contrast to alkyl 4-vinylbenzoate, *N,N*-dialkyl-4-vinylbenzamides afford stable living polymers even at room temperature without steric protection of bulky alkyl group. This is consistent with the numerous reports that tertiary amides are more resistant to nucleophilic attack compared with esters.[11]

2-3. Block Copolymerization of 1 with Styrene, Isoprene, and *tert*-Butyl Methacrylate.

The most characteristic advantage of the living polymerization of **1** is that it is capable of the synthesis of various block copolymers having polar poly(**1**) segments with strictly controlled chain structure. In addition, the block copolymerizations may elucidate the relative reactivities of the monomer and the living end as well as the stability of the propagating end.

At first, ABA-type triblock copolymers containing poly(**1**) segments (A) as both terminal blocks were synthesized by addition of **1a**, **1b**, **1f**, **1h**, and **1i** to the living polystyrene (B) prepared with either lithium or potassium naphthalenide at –78°C in THF. The reactions proceeded homogeneously and quantitatively to yield block copolymers having predictable molecular weights and narrow MWDs as shown in Table 2-3. The content of poly(**1**) segment analyzed by ^{1}H NMR in each block copolymer agreed well with that calculated based on the molar ratio of the fed monomers. A well-defined block copolymer of **1b** and isoprene was also prepared in a similar manner.

Next, synthesis of the block copolymer with reversed sequence was attempted by addition of isoprene or styrene monomer to difunctional living poly(**1b**) at –78°C in THF. However, the living poly(**1b**) did not initiate the polymerization of isoprene to recover homopoly(**1b**) quantitatively. On the other hand, styrene monomer was polymerized with living poly(**1b**) to result in a mixture of virtual homopoly(**1b**) and block copolymer having a polystyrene segment of very high molecular weight.[13] The SEC and ^{1}H NMR analyses of the product reveal that only 2% of living poly(**1b**) reacts with styrene and the rest remains intact.

The polymerization of *tert*-butyl methacrylate (tBMA) was initiated with difunctional living poly(**1b**) to produce poly(tBMA-*b*-**1b**-*b*-tBMA) with regulated block length and narrow MWD in quantitative yield as shown in Table 2-3 (run 42). SEC analyses of the resulting polymers showed that the peak of the starting poly(**1b**) block shifted toward the higher molecular weight side without a shoulder at the elution count of the homopolymer as shown in Figure 2-4. In addition to the postpolymerization, this result strongly demonstrates that a stable living polymer of *N*,*N*-diethyl-4-vinylbenzamide forms at –78°C. The tailor-made triblock copolymer with different tertiary

Table 2-3

Block Copolymerization of **1**s with
Styrene, Isoprene, and *tert*-Butyl Methacrylate at –78°C in THF[a]

run	type	A monomer	B monomer	block copolymer (homopolymer)[b] $10^{-3}M_n$(calcd)	 $10^{-3}M_n$(obsd)	 M_w/M_n
39	A-B-A	**1a**	styrene	28 (15)	32 (17)	1.11 (1.13)
40	A-B-A	**1b**	styrene	31 (15)	32 (16)	1.06 (1.09)
41	A-B-A	**1b**	isoprene	30 (12)	27 (11)	1.08 (1.08)
42	B-A-B	**1b**	tBMA	19 (6.5)	23 (8.0)	1.13 (1.10)
43	A-B-A	**1f**	styrene	20 (9.5)	20 (10)	1.04 (1.08)
44	A-B-A	**1h**	styrene	25 (11)	23 (12)	1.07 (1.04)
45	B-A-B	**1h**	**1b**	17 (6.8)	17 (8.6)	1.09 (1.07)
46	A-B-A	**1i**	styrene	23 (10)	25 (11)	1.04 (1.05)

[a] Yields of polymers were nearly quantitative in each case.

[b] Homopolymers were obtained at the first-stage polymerization.

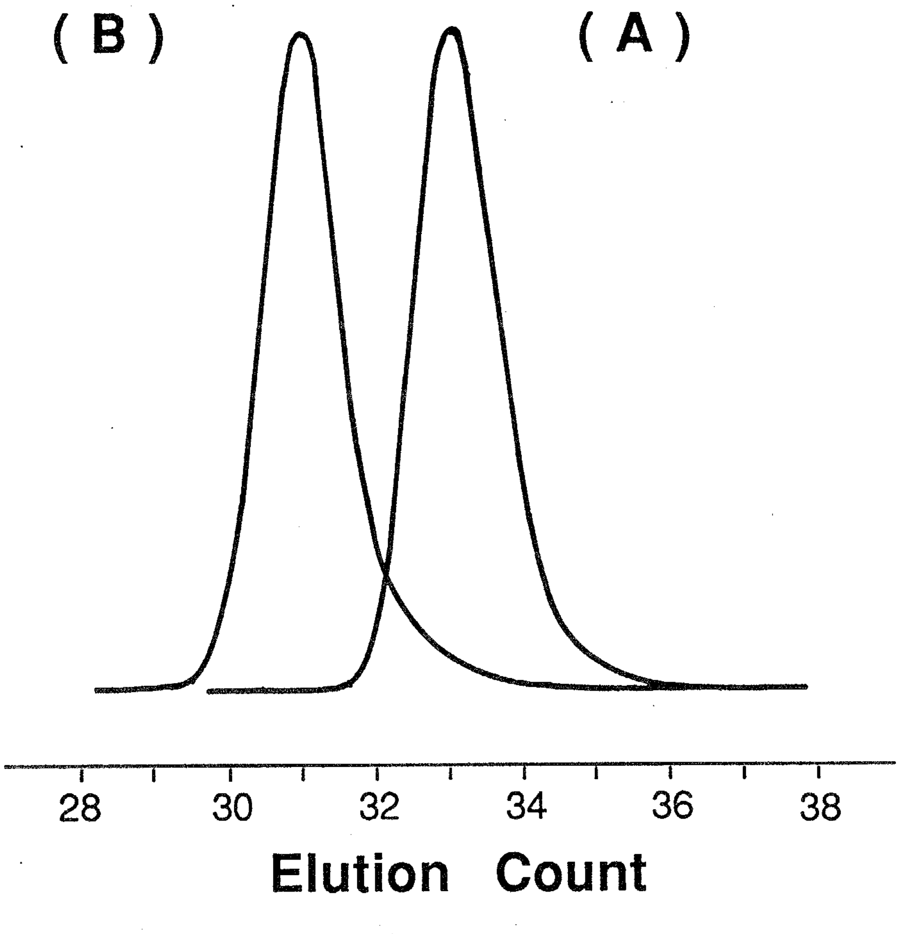


Figure 2-4. SEC curves of homopoly(**1b**) (A) at the first-stage polymerization and of poly(tBMA-*b*-**1b**-*b*-tBMA) (B):(Table 2-3, run 42):
peak A, M_n(obsd) = 8000, M_w/M_n = 1.10;
peak B, M_n(obsd) = 23 000, M_w/M_n = 1.13
(the second monomer was added 30 min after the first-stage polymerization).

amide functions was similarly synthesized by the sequential polymerization of **1h** and **1b**. This result also provides a direct evidence for the persistency of the propagating carbanion of the poly(**1h**) under the conditions, in THF at –78°C for 1 h. The piperazine amide in the resulting block copolymer could be chemoselectively hydrolyzed to give a novel block copolymer having carboxylic acid and *N,N*-diethylamide segments as discussed later.

Through the studies on the anionic polymerizations of *N*-(4-vinylbenzylidene)cyclohexylamine,[3a] *tert*-butyl 4-vinylbenzoate,[4] 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline,[5] and 4-cyanostyrene,[6] their active chain ends have been found to be stabilized by the electron-withdrawing effects of the substituents. The resulting living polymers are able to cause crossover reactions with these styrene derivatives and alkyl methacrylates to produce block copolymers but an ineffective to initiate styrene and isoprene. Similar results were obtained from the block copolymerizations of living poly(**1b**) with isoprene, styrene, and tBMA. The lowered nucleophilicity of the carbanion derived from **1b** is roughly estimated to be at the same level as those of the living polymers generated from those monomers having electron-withdrawing groups. More precise ranking of the reactivities of these new type carbanions is discussed in Chapter 7.

2-4. Solubility of poly(1)s.

As shown in Table 2-4, most poly(**1**)s are soluble in both polar and nonpolar solvents such as methanol, ethanol, *N,N*-dimethylformamide, THF, 1,4-dioxane, chloroform, and benzene. The wide solubilities of poly(**1**)s may be caused by the amphiphilic characters of the polymers with polar tertiary amide groups and nonpolar polystyrene backbones. Some steric effects on the solubilities of poly(**1**)s are observed. Surprisingly, poly(**1h**) was soluble in both neutral water and acidic aqueous medium but swelled in basic aqueous medium. This is probably due to the presence of β-amino functionality of

Table 2-4

Solubilities of Poly(**1**)s, and Polystyrene

solvent	poly(**1a**)	poly(**1b**)	poly(**1c**)	poly(**1d**)	poly(**1e**)	poly(**1f**)	poly(**1g**)	poly(**1h**)	poly(**1i**)	polystyrene
hexane	I	I	I	I	I	I	I	I	I	I
benzene	S[a]	S	S	S	S	S	S	I	I	S
carbon tetrachloride	I	S	S	S	S	I	S	S	I	S
chloroform	S	S	S	S	S	S	S	S	S	S
diethyl ether	I	Sw	S	S	Sw	I	I	I	I	S
ethyl acetate	Sw	S	S	S	S	Sw	Sw	S	I	S
1,4-dioxane	S	S	S	S	S	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S	S	S	S	S	S
N,*N*-dimethylformamide	S	S	S	S	S	S	S	S	S	S
ethanol	S	S	S	S	S	S	S	S	Sw	I
methanol	S	S	S	S	S	S	S	S	Sw	I
water	I	I	I	I	I	I	I	S	I	I
6 N HCl	S	S	I	I	I	S	Sw	S	I	I

I, insoluble; S, soluble; Sw, swelling. [a] Poly(**1a**) with molecular weight higher than 10 000 is not soluble in benzene.

amide group in addition to the polar tertiary amide group. Poly(**1i**) having ether linkage showed narrow solubility than those of other poly(**1**)s. Strong polarities of amide groups are reflected in the solubilities of poly(**1a**) and poly(**1f**), which are soluble even in 6 N HCl and insoluble in carbon tetrachloride and diethyl ether.

The glass transition temperatures (T_g) of poly(**1**)s were measured by differential scanning calorimetry as shown in Table 2-5. Some steric effects and effects of molecular weight on T_gs of poly(**1**)s are observed. Substitution of cyclic alkyl groups and increase of molecular weight of the polymer promote an increase of T_g values, as expected. The T_g values can be widely changed by the alkyl substituents of poly(*N*,*N*-dialkyl-4-vinylbenzamide)s from 60°C to 170°C.

The Mark-Houwink parameters, *K* and *a*, for poly(**1b**) in THF at 40°C were obtained by measuring intrinsic viscosities of five poly(**1b**) samples with M_ns ranging from 9200 to 48 000 (Table 2-6).[14, 15] The plots of log [η] versus log M_n lead to a good linear relationship given by

$$[\eta]\ \mathrm{THF}^{40^\circ\mathrm{C}} = (4.47 \times 10^{-4})M^{0.554}$$

Although a molecular weight range for meaningful *K* and *a* is somewhat narrow, the preliminary value of *a* for poly(**1b**) 0.55, suggests a rather small hydrodynamic volume of the polymer in THF, where the polystyrene (a = 0.72) chain expands in THF at 40°C. Accordingly, the molecular weight of poly(**1b**) tends to be underestimated in the SEC measurement by using the polystyrene standard calibration with THF as an eluting solvent as shown in Table 2-6.

Table 2-5

Glass Transition Temperatures (T_g) of Poly(**1**)s

polymer	$10^{-3}M_n$(obsd)	M_w/M_n	T_g (°C)
poly(**1a**)	9.5	1.12	141
poly(**1a**)	34	1.15	154
poly(**1b**)	7.2	1.09	99
poly(**1b**)	10	1.08	106
poly(**1b**)	33	1.13	106
poly(**1b**)	48	1.08	109
poly(**1c**)	11	1.07	74
poly(**1d**)	10	1.08	164
poly(**1e**)	23	1.08	61
poly(**1f**)	14	1.08	152
poly(**1g**)	22	1.08	136
poly(**1h**)	11	1.06	122
poly(**1h**)	38	1.11	133
poly(**1i**)	14	1.06	170

Table 2-6

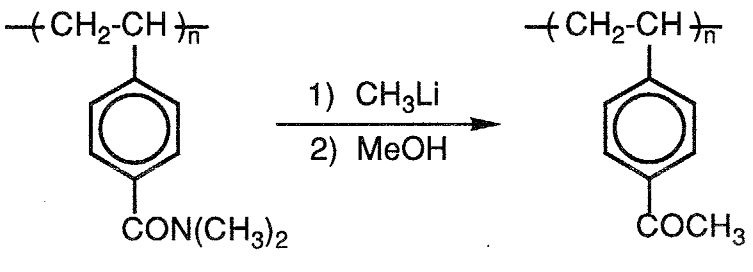
Values of Intrinsic Viscosities and Molecular Weights for Poly(**1b**)s

$[\eta]$ (THF 40°C) dL/g	M_n(VPO) × 10^{-3}	M_n(SEC) × 10^{-3} [a]	M_w/M_n
0.0736	9.2	8.4	1.08
0.0844	14	12	1.06
0.0964	17	14	1.07
0.147	33	25	1.13
0.176	48	30	1.08

[a] Molecular weight of poly(**1b**) estimated by SEC in THF using polystyrene standard calibration.

2-5. Reaction of Poly(**1a**) with Methyllithium.

Since several reactions of tertiary benzamides are known in the field of organic synthesis, further chemical modifications on the poly(**1**)s are expected to derive new functional polymers. Gschwend and his colleagues demonstrated that *N,N*-dimethylbenzamide was directly converted to acetophenone with methyllithium in good yield.[16] Under the similar condition they employed, poly(**1a**) was allowed to react with methyllithium to convert into poly(4-vinylacetophenone) as shown in Scheme 2-2.



Poly(1a)

Scheme 2-2

The IR spectrum of the polymer obtained shows the strong C=O stretching absorption of the ketone carbonyl group at 1680 cm^{-1}, whereas the amide carbonyl band at 1640cm^{-1} disappears. In the ^{13}C NMR spectrum, after polymer reaction, a signal responsible for the amide carbonyl carbon of poly(**1a**) at 171.1 ppm completely disappeared and resonances due to acetyl group newly appeared at 197.4 (C=O) and 26.3 ppm (CH_3) as shown in Figure 2-5. Furthermore, no nitrogen was detected by elemental analysis of the resulting polymer. All evidence for these analyses indicates the quantitative conversion of poly(**1a**) into poly(4-vinylacetophenone). Since the SEC curve of the polymer after reaction was narrow and unimodal as well as that before

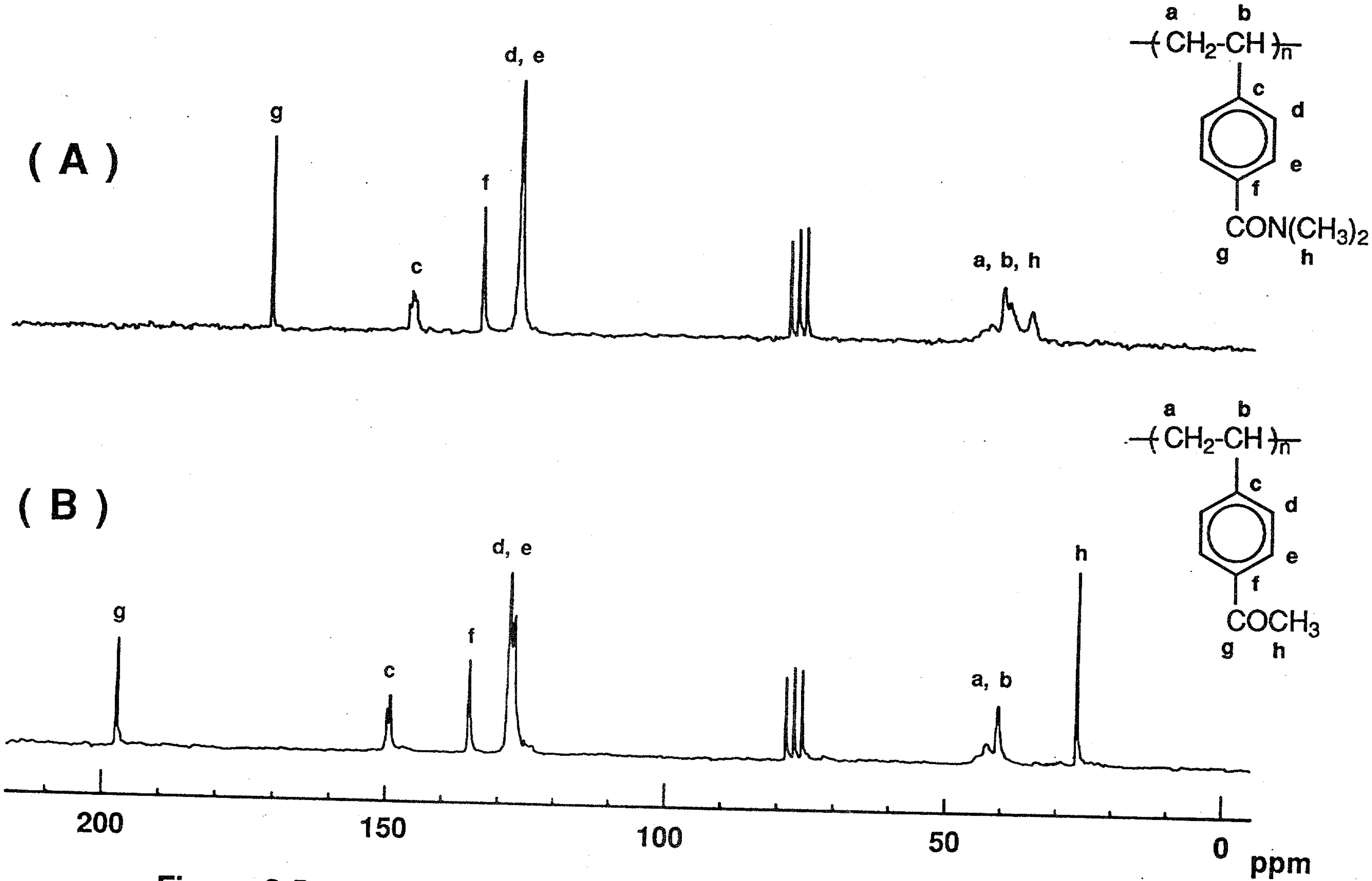
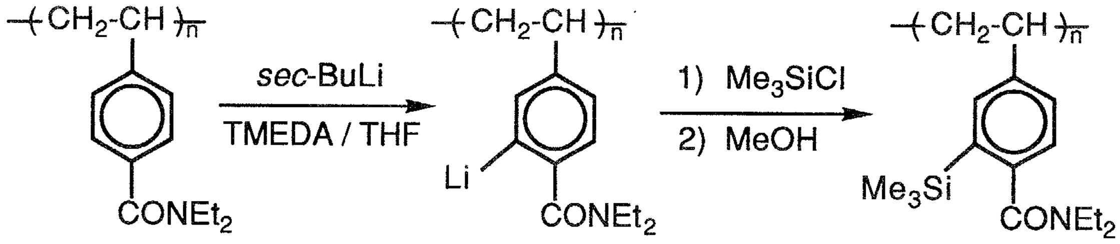


Figure 2-5. ^{13}C NMR spectra of the poly(**1a**) (A) and poly(4-vinylacetophenone) obtained by the polymer reaction (B) in $CDCl_3$.

reaction, the substitution reaction with methyllithium is considered not to accompany the cross-linking and degradation of the polymer backbone.

2-6. Aromatic Lithiation of Poly(**1b**).

The aromatic direct metalation reaction followed by electrophilic reaction is a useful method for efficient and regiospecific preparation of polysubstituted aromatic compounds.[17] Beak and Brown reported that the bulkier tertiary benzamides showed the excellent directing ability of *ortho*-lithiation.[18] In a similar manner, as shown in Scheme 2-3, lithiation of poly(**1b**) was carried out with *sec*-butyllithium/*N*,*N*,*N'*,*N'*-tetramethylenediamine (TMEDA) in THF at –78°C for 1 h followed by quenching with trimethylsilyl chloride to estimate the conversion of the reaction.



Poly(1b)

Scheme 2-3

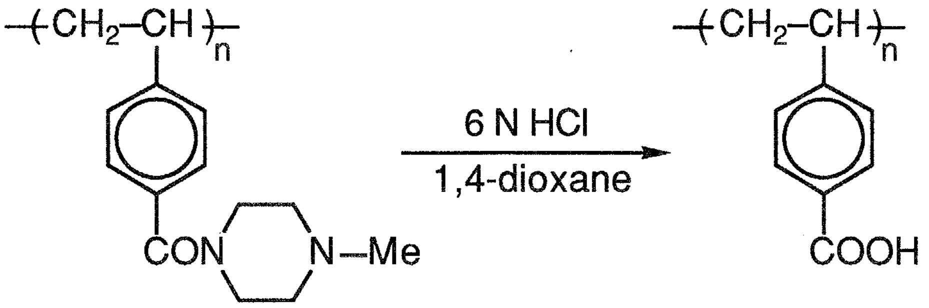
From ^1H NMR analysis, 80% of the polymer phenylene ring was substituted by a trimethylsilyl group at *ortho* position to amide functionality.[19] The SEC curve of the polymer still remained narrow and slightly shifted toward the higher molecular weight side, indicating the absence of cleavage of the main chain and cross-linking during the reaction. A variety of functional groups such as Br, CHO, and SR may be introduced into the polymers by the similar lithiation and the subsequent electrophilic reaction.[17]

2-7. Transformation of Poly(**1h**) into Poly(4-vinylbenzoic acid) by Deprotection of the Tertiary Amide Group.

Poly(4-vinylbenzoic acid) and the related polymers with carboxylic groups are a series of the most attractive functional polymers. Amide function of poly(**1**)s can be recognized as a precursor for the carboxylic acid by the hydrolyses. However, *N*,*N*-dialkylbenzamides are usually difficult to be converted into the carboxylic acids even under severe reaction conditions as previously pointed out.[17b, 17c] The acid hydrolyses of some poly(*N*,*N*-dialkyl-4-vinylbenzamide)s were actually performed with 6 N HCl in 1,4-dioxane or THF at the reflux temperatures. The hydrolysis for either poly(**1a**) or poly(**1i**) proceeded partially under the conditions and was far from complete even for 24 h. No detectable hydrolysis was observed when poly(**1b**) containing diethylamide moiety was employed. The results revealed that the acidic deprotection reactions toward usual poly(*N*,*N*-dialkyl-4-vinylbenzamide)s were not suitable to afford a pure poly(4-vinylbenzoic acid).

Recently, Comins and Brown have found that a series of the tertiary *β*-amino benzamides are readily hydrolyzed under the relatively mild conditions to afford the corresponding carboxylic acids in good to excellent yields.[20] Actually, the purposeful poly(**1h**) is readily hydrolyzed under acidic conditions (in aqueous 1,4-dioxane with 6 N HCl at 70°C for 12 h) (Scheme 2-4). The reported condition by Comins and Brown[20] was modified by using 1,4-dioxane as a solvent to keep the reaction system homogeneous. After the reaction, the polymer was quantitatively obtained by precipitation in water. Figure 2-6B shows the IR spectrum of the polymer obtained after hydrolysis, which is virtually consistent with that of the authentic poly(4-vinylbenzoic acid)s obtained by the deprotection of poly[2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline][5] or poly(*tert*-butyl 4-vinylbenzoate).[4] After hydrolysis, the strong absorption for amide C=O at 1636 cm^{-1} disappears and the characteristic C=O and O-H stretching absorptions of the carboxy group are newly observed at

1701 and 2500 - 3300 cm^{-1}. No observation of the signals corresponding to *N*-methylpiperazine after hydrolysis indicates strongly the complete hydrolysis of poly(**1h**) to benzoic acid moiety. This is more clear by the ^{13}C NMR spectrum which shows the carbonyl carbon at 170.6 ppm and neither the carbons of *N*-methylpiperazine at 46.0 and 55.0 ppm nor the amide carbonyl carbon at 170.0 ppm. The complete hydrolysis of poly(**1h**) to poly(4-vinylbenzoic acid) is thus obvious as indicated by the IR, ^1H and ^{13}C NMR spectroscopies. An additional evidence for the complete hydrolysis is provided by the fact that there is no nitrogen content in the elemental analysis of the resulting polymer.



Scheme 2-4

Since the hydrolyzed polymer was not eluted in the SEC measurement (DMF) probably due to the adsorption on the gel column, it was transformed into the methyl ester by treating with diazomethane.[4] Figure 2-7 shows the SEC profiles of the original poly(**1h**) and the methylated polymer. Even after two step polymer reactions, the polymer maintains unimodal and narrow MWD (M_w/M_n = 1.06) similar to that of the starting poly(**1h**) (M_w/M_n = 1.07), indicating there is no degradation and/or cross-linking of polymer chain during the two reaction steps from the hydrolysis to the methylation. This clearly indicates that the poly(4-vinylbenzoic acid) obtained by the hydrolysis

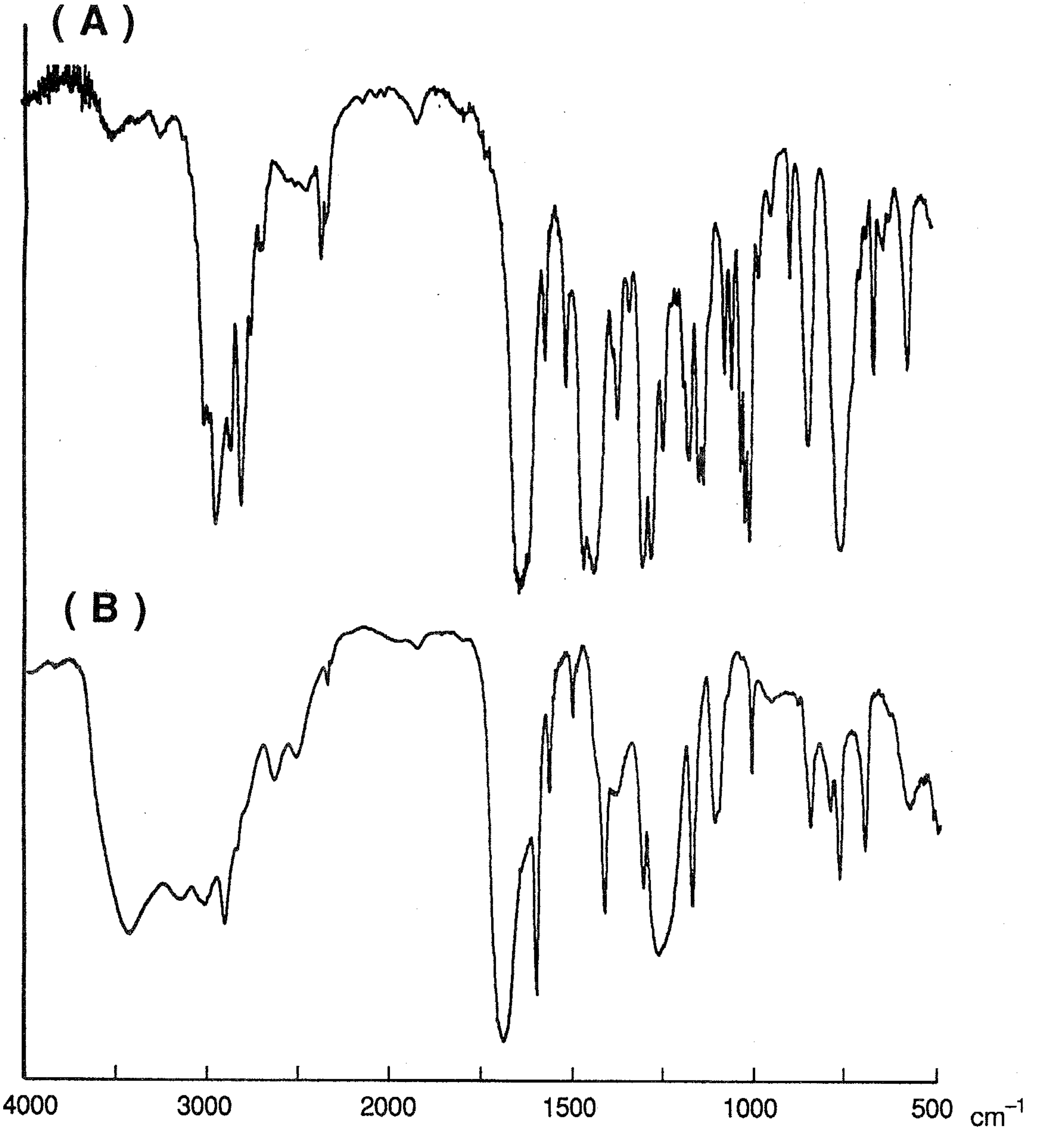


Figure 2-6. IR spectra of poly(**1h**) (A) and poly(4-vinylbenzoic acid) obtained by the acid hydrolysis of the poly(**1h**) (B).

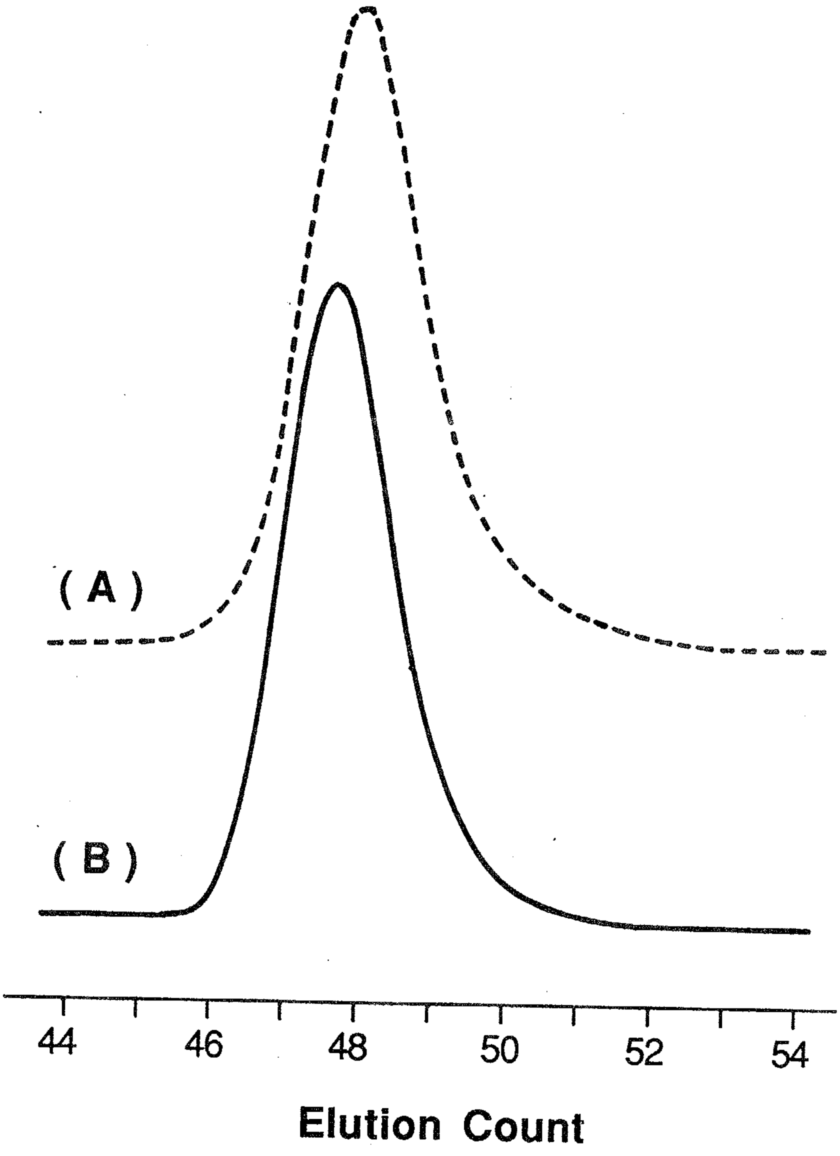


Figure 2-7. SEC (DMF) curves of poly(**1h**) (A); $M_w/M_n = 1.07$ and poly(methyl 4-vinylbenzoate) obtained by the hydrolysis and the subsequent methylation of the poly(**1h**) (B); $M_w/M_n = 1.06$.

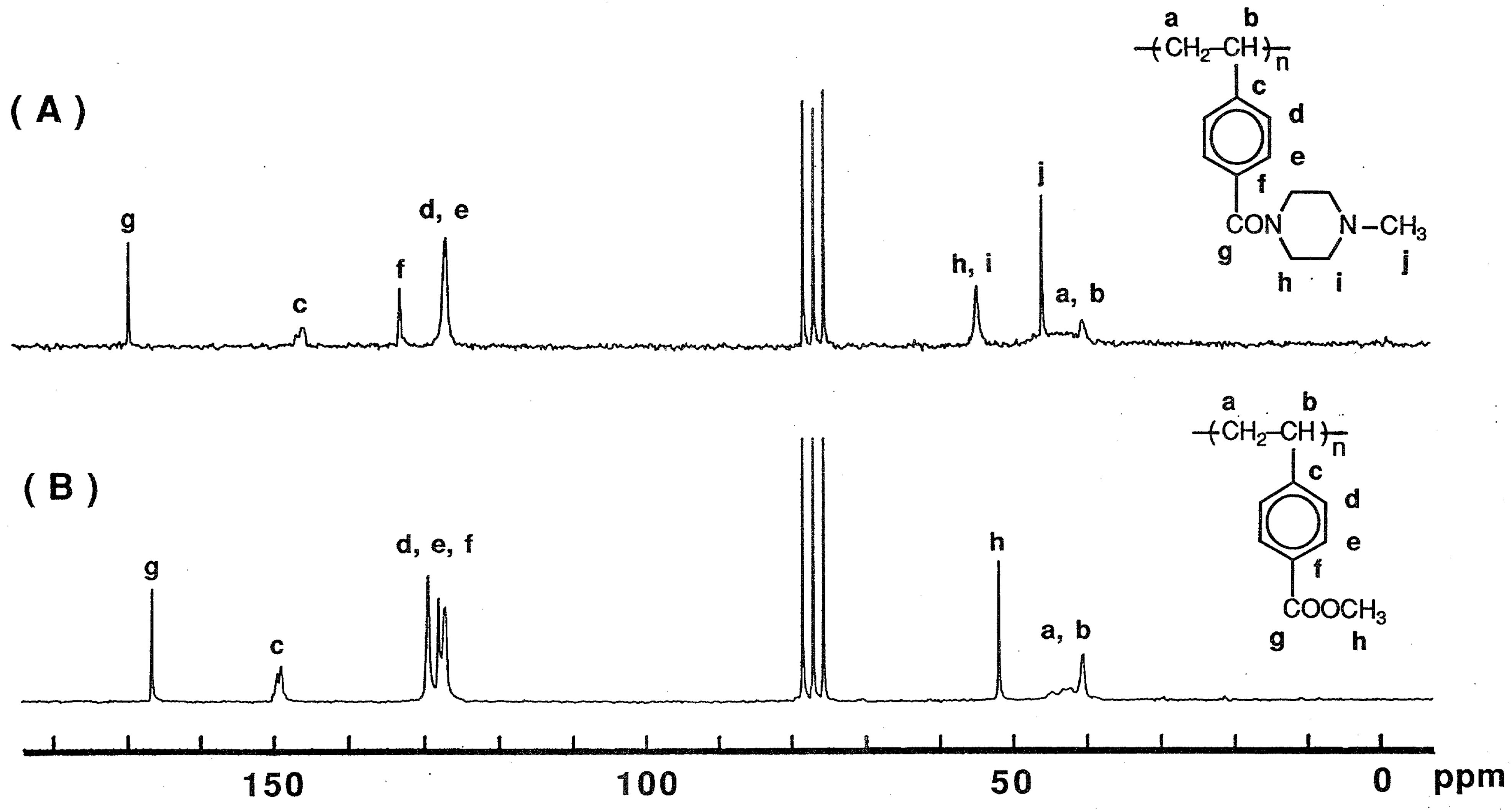
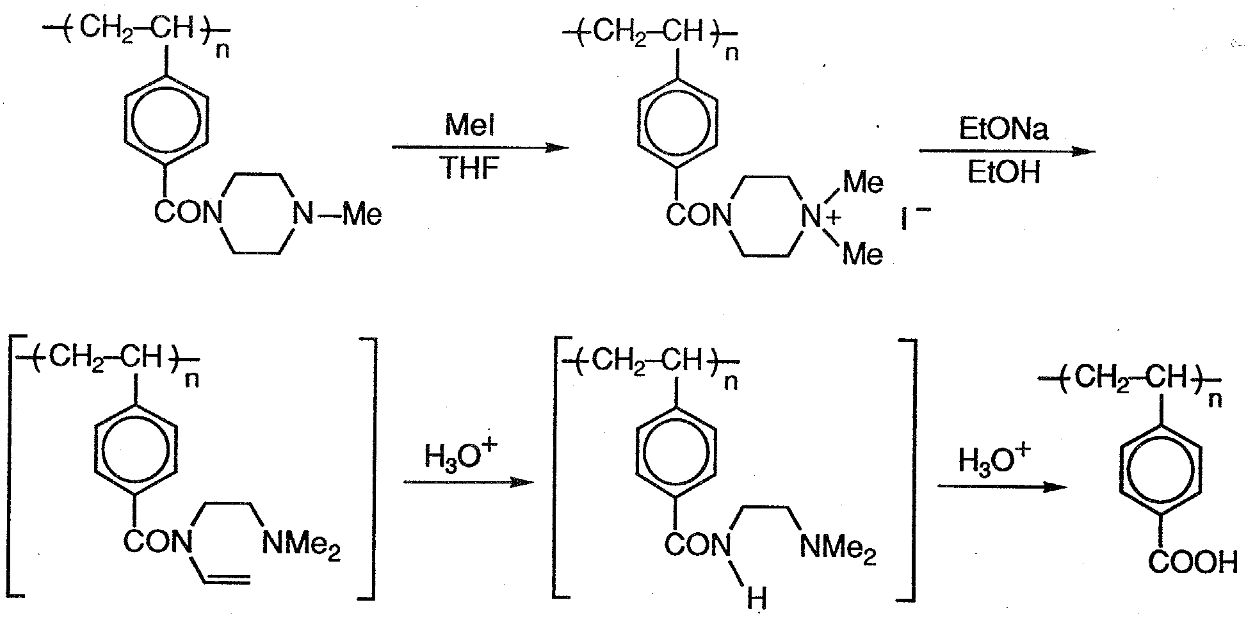


Figure 2-8. ^{13}C NMR spectra of poly(**1h**) (A) and poly(methyl 4-vinylbenzoate) (B) in $CDCl_3$.

retains the desired characteristics of main chain structures of the parent polymer, *e.g.* controlled molecular weight and narrow MWD. Figure 2-8A and 2-8B show the representative ^{13}C NMR spectra of the poly(**1h**) and the poly(methyl 4-vinylbenzoate). The remarkable changes in the spectra again support that both the deprotection reaction and the subsequent methylation reaction are unequivocally completed.

In addition to this direct acid hydrolysis, Comins and Brown reported that *β*-amino benzamides were hydrolyzed by a three-step, one-pot reaction involving methylation, elimination, and hydrolysis.[20] The corresponding benzoic acids were thereby obtained in excellent yields. Similarly, the hydrolysis of poly(**1h**) by the three-step, one-pot method, was attempted, taking advantage of the *β*-amine functionality of the polymer. This one-pot reaction successively involves quaternarization of *β*-amino function with methyl iodide, treatment with sodium ethoxide in ethanol to give enamide, and final acid hydrolysis of the enamide via the formation of secondary benzamide (Scheme 2-5). The starting polymer was treated with methyl iodide (80°C, 4 h), sodium ethoxide (80°C, 7 h), and then 6 N HCl (80°C, 24 h).



Scheme 2-5

The poly(4-vinylbenzoic acid) could be obtained nearly quantitatively also by this method. However, the ^{1}H and ^{13}C NMR spectra of the polymer indicated that the polymer was contaminated with a small amount of the ethyl ester unit probably produced by the nucleophilic attack of ethoxide anion to the quanternarized benzamide in the second step. Again, the MWD of the resulting polymer was revealed to be unchanged and narrow. Thus, although a further optimization of the reaction will be needed to obtain a pure poly(4-vinylbenzoic acid) in this synthetic route, this three step hydrolysis is also available, since the ethyl ester can be hydrolyzed under basic or acidic condition. The direct acid hydrolysis of the block copolymer, poly(**1b**-*b*-**1h**-*b*-**1b**), (Table 2-3, run 45) was also carried out. The analyses of ^{1}H and ^{13}C NMR spectroscopies presented a quantitative removal of *N*-methylpiperazine ring from poly(**1h**) segment. The *N*,*N*-diethylbenzamide function in the block copolymer was inert toward the acid hydrolysis under the conditions as well as that in the homopoly(**1b**). After methylation of the carboxy function, the SEC measurement revealed that the block copolymer kept an unimodal and narrow MWD (M_w/M_n = 1.08). Interestingly, these results clearly show that the acid hydrolysis of the block copolymer of **1h** and **1b** chemoselectively proceed only on the β-amino amide moiety of poly(**1h**) segment. The resulting well-defined block copolymer is a novel attractive material because it contains two different polar hydrophilic segments, *i.e.*, tertiary benzamide and benzoic acid moieties.

As a conclusion, an advantage of β-amino benzamide over the corresponding tertiary amides on the deprotection reaction is thus apparent. The β-amino group of the poly(**1h**) may promote the ease of acid hydrolysis due to electronic effects of the protonated amine moiety and due to the high solubility in the aqueous media as previously pointed out.[20] Hence, the method of anionic living polymerization of **1h** and possibly the related derivatives, followed by the hydrolysis of the resulting polymer may provide an alternative route to synthesize a well-defined poly(4-vinylbenzoic acid).

In the preceding works, it has also been successfully synthesized poly(4-vinylbenzoic acid) of predicted molecular weights by the anionic living polymerization of styrene derivatives containing both oxazoline[5] and *tert*-butyl ester[4] protecting groups and the subsequent removal of the protecting groups from the resulting polymers. The methods have, however, still some limitations with regard to the reaction conditions of living polymerization[4] and deprotection process.[5]

Compared with these synthetic routes, the presented methodology seemed to be moderately useful from the viewpoints of both steps. In particular, it should be recalled the synthetic advantages of the wide range of employable initiators for **1h** and the ease of one-pot acid hydrolysis of the poly(**1h**). Another advantage is that the chemoselective hydrolysis on the poly(**1h**) segment is possible for the block copolymer containing the other tertiary amide group to provide a new block copolymer which possesses poly(4-vinylbenzoic acid) segment and poly(*N*,*N*-dialkyl-4-vinylbenzamide) segment.

2-8. Conclusion.

This chapter has demonstrated that the anionic polymerizations of nine *para*-substituted tertiary amide styrenes, **1a-i**, proceed without any chain-termination reactions to give living polymers under appropriate conditions. Polymers with regulated chain lengths were synthesized. Furthermore, the living nature of these polymerizations makes the preparation of a variety of block copolymers having poly(*N*,*N*-dialkyl-4-vinylbenzamide) segments possible. It has also been demonstrated that the reactions with either poly(**1a**), poly(**1b**), and poly(**1h**) can lead to new functional polymers that retain the desirable characteristic of these parent polymers, *i.e.*, narrow MWD and controlled molecular weights.

Experimental Section

Materials. 4-Vinylbenzoic acid, kindly supplied from Hokko Chemical Industry Co., Ltd., was used without further purification. Diethylamine, dipropylamine, diisopropylamine, diallylamine, pyrrolidine, piperidine, *N*-methylpiperazine, mopholine, and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) were dried and distilled over calcium hydride under nitrogen. Dimethylamine was distilled from a 40 wt % aqueous solution through a column packed with potassium hydroxide and trapped with a dry ice-acetone bath under nitrogen over calcium hydride. *tert*-Butyl methacrylate, α-methylstyrene, styrene, and isoprene were distilled over calcium hydride. 1,1-Diphenylethylene (DPE), prepared by a literature method,[21] was purified fractional distillation and finally distilled from *n*-BuLi/pentane under vacuum. THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through vacuum line from sodium naphthalenide solution. Methyllithium (1.2 M solution) was prepared by the reaction of methyl iodide with lithium metal in ether. *sec*-BuLi as a 1.05 M solution in cyclohexane was purchased from Kanto Chemical Co., Ltd.,.

Initiators. Metal naphthalenides were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in THF. The oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared just prior to polymerizations from the corresponding metal naphthalenides and a 2-4 M quantity of α-methylstyrene at 20°C for 1 min and then at –78°C for 10 min. Cumylpotassium was prepared by the reaction of cumyl methyl ether with a potassium-sodium alloy in THF. These initiators were stored in ampules equipped with breakseals. The concentration of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.

4-Vinylbenzoyl Chloride. To a mixture of thionyl chloride (28 mL) and 4-*tert*-butylpyrocatecol (10 mg) under nitrogen in an ice bath was added 4-vinylbenzoic acid (13.1 g, 88.5 mmol) in small portions with stirring below 10°C for 4 h and at 40°C for 1 h to afford a homogeneous solution. After removal of unreacted thionyl chloride, distillation gave 13.3 g (79.9 mmol, 90%) of 4-vinylbenzoyl chloride as a colorless liquid at 72-73°C(0.3 mmHg) (lit.[22] 69.5-70.0°C(0.1 mmHg)): 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.44 and 5.88 (2d, 2H, J = 11 and 17 Hz, CH_2=), 6.72 (dd, 1H, -CH=), 7.38-8.03 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 118.3 (vinyl, CH_2=), 126.5 (Ar, C3), 131.7 (Ar, C2), 132.1 (Ar, C1), 135.3 (vinyl, -CH=), 144.4 (Ar, C4), 167.5 (C=O).

***N,N*-Dimethyl-4-vinylbenzamide (1a).** To a mechanically stirred solution of dimethylamine (10.2 g, 230 mmol) in dry ether (100 mL) under nitrogen, 4-vinylbenzoyl chloride (10.4 g, 62.5 mmol) in dry ether (50 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated ammonium salt was filtered off and the filtrate was washed two times with 1 N HCl (100 mL) and twice with saturated $NaHCO_3$ solution (100 mL), and then dried over anhydrous $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether three times to yield pure white crystal of **1a** (10.1 g, 57.7 mmol, 92%; mp 55-56°C): 90 MHz ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 6H, NCH_3), 5.31 and 5.79 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.74 (dd, 1H, -CH=), 7.41 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 37.5(broad, NCH_3), 115.0 (vinyl, CH_2=), 126.0 (Ar, C3), 127.4 (Ar, C2), 135.6 (Ar, C1) 136.1 (vinyl, -CH=), 138.7 (Ar, C4), 171.2 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1520, 1500, 1410, 1390, 1270, 1080, 940, 860, 850; Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40, H, 7.48, N, 8.00. Found: C, 75.16, H, 7.43, N, 7.89.

***N,N*-Diethyl-4-vinylbenzamide (1b).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (8.80 g, 52.9 mmol) and diethylamine (13.9 g, 190 mmol) in place of dimethylamine and recrystallization from petroleum ether gave 9.68 g (47.7 mmol, 90%, mp 57-58°C) of **1b** as a white crystal: 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.17 (t, 6H, J = 7 Hz, CH_3), 3.41 (broad, 4H, NCH_2), 5.30 and 5.78 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1H, -CH=), 7.38 (m, 4H, Ar); 23 MHz ^{13}C NMR δ 13.5 (CH_3), 41.3 (NCH_2), 114.8 (vinyl, CH_2=), 126.1 (Ar, C3), 126.6 (Ar, C2), 136.1 (vinyl, -CH=), 136.5 (Ar, C1), 138.3 (Ar, C4), 171.0 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1480, 1460, 1430, 1380, 1320, 1290, 1100, 1010, 920, 860; Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81, H, 8.43, N, 6.89. Found: C, 76.51, H, 8.71, N, 7.10.

***N,N*-Dipropyl-4-vinylbenzamide (1c).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (5.12 g, 30.8 mmol) and dipropylamine (9.63 g, 95.3 mmol) in place of dimethylamine. Evaporation and suction drying gave 6.76 g (29.3 mmol, 95%) of **1c** as a colorless oil: 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.88 (broad, 6H, CH_3), 1.60 (broad, 4H, CH_2), 3.31 (broad, 4H, NCH_2), 5.28 and 5.78 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1H, -CH=), 7.37 (m, 4H, Ar); 23 MHz ^{13}C NMR δ 10.9 (CH_3), 21.0 (CH_2), 48 (broad, NCH_2), 114.5 (vinyl, CH_2=), 125.8 (Ar, C3), 126.5 (Ar, C2), 135.9 (vinyl, -CH=), 136.4 (Ar, C1), 138.0 (Ar, C4), 171.2 (C=O); IR (KBr, cm^{-1}) 1630 (C=O), 1460, 1430, 1100, 910, 850; Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88, H, 9.15, N, 6.06. Found: C, 77.64, H, 9.23, N, 5.97.

***N,N*-Diisopropyl-4-vinylbenzamide (1d). 1d** was prepared according to the procedure previously described[10] and recrystallization from petroleum ether gave **1d** as a white crystal (75%, mp 82-83°C): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.34 (broad, 12H, CH_3), 3.69 (broad, 2H, NCH), 5.28 and 5.76 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1H, -CH=), 7.34 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3), 48.3 (NCH), 114.6 (vinyl, CH_2=), 126.0 (Ar, C3), 126.2 (Ar, C2), 136.1 (vinyl, -CH=), 137.8 (Ar, C1), 138.2 (Ar, C4), 170.6 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1450, 1370, 1340, 1040, 1010, 860, 840; Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88, H, 9.15, N, 6.06. Found: C, 77.89, H, 9.14, N, 6.35.

***N,N*-Diallyl-4-vinylbenzamide (1e).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (9.03 g, 54.2 mmol) and diallylamine (15.8 g, 163 mmol) in place of dimethylamine and recrystallization from petroleum ether(–20°C) gave 10.7 g (47.2 mmol, 87%, mp 16°C) of **1e** as a colorless crystal: 90 MHz ^1H NMR ($CDCl_3$) δ 3.95 (broad, 4H, NCH_2), 5.0-6.1 (overlapping m, 8H, allyl -CH=CH_2 and vinyl CH_2=), 6.73 (dd, 1H, -CH=), 7.41 (m, 4H, Ar); 23 MHz ^{13}C NMR δ 48 (broad, NCH_2), 115.0 (vinyl, CH_2=), 117.4 (allyl, CH_2=), 126.0 (Ar, C3), 126.8 (Ar, C2), 132.9 (allyl, -CH=), 135.3 (Ar, C1), 135.9 (vinyl, -CH=), 138.7 (Ar, C4), 171.3 (C=O); IR (KBr, cm^{-1}) 1640 (C=O), 1460, 1410, 1290, 1260, 990, 920, 850; Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26, H, 7.54, N, 6.16. Found: C, 79.24, H, 7.57, N, 6.27.

***N*-(4-Vinylbenzoyl)pyrrolidine (1f).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (9.65 g, 58.0 mmol) and pyrrolidine (11.9 g, 168 mmol) in place of dimethylamine and recrystallization from petroleum ether gave 6.45 g (32.1 mmol, 55%, mp 87-88°C) of **1f** as a white crystal: 90 MHz ^1H NMR ($CDCl_3$) δ 1.91 (broad, 4H, NCH_2CH_2), 3.54 (broad, 4H, NCH_2), 5.31 and 5.79 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1H, -CH=), 7.46 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 25.4 (broad, NCH_2CH_2), 47.8 (broad, NCH_2), 115.0 (vinyl, CH_2=), 125.9 (Ar, C3), 127.4 (Ar, C2), 136.0 (vinyl, -CH=), 136.3 (Ar, C1), 138.9 (Ar, C4), 169.2 (C=O); IR (KBr, cm^{-1}), 1610 (C=O), 1440, 1000, 900, 860, 850, 770, 730; Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58, H, 7.51, N, 6.96. Found: C, 77.89, H, 7.44, N, 6.90.

***N*-(4-Vinylbenzoyl)piperidine (1g).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (9.40 g, 56.5 mmol) and piperidine (13.8 g, 162 mmol) in place of dimethylamine and recrystallization from petroleum ether gave 10.2 g (47.3 mmol, 84%, mp 86-87°C) of **1g** as a white crystal: 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.64 (broad, 6H, $NCH_2CH_2CH_2$), 3.54 (broad, 4H, NCH_2), 5.30 and 5.78 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1H, -CH=), 7.39 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 24.5 ($NCH_2CH_2CH_2$), 26.0 (NCH_2CH_2), 46.0 (broad, NCH_2), 114.9 (vinyl, CH_2=), 126.1 (Ar, C3), 127.1 (Ar, C2), 135.7 (Ar, C1), 136.1 (vinyl, -CH=), 138.6 (Ar, C4), 169.9 (C=O); IR(KBr, cm^{-1}) 1620 (C=O), 1470, 1430, 1290, 1270, 1000, 920, 860, 730; Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10, H, 7.96, N, 6.51. Found: C, 78.02, H, 8.04, N, 6.41.

_N_-(4-Vinylbenzoyl)-_N'_-methylpiperazine (1h). To a mechanically stirred solution of *N*-methylpiperazine (21.3 g, 213 mmol) and triethylamine (67.4 g, 666 mmol) in dry ether (100 mL) under nitrogen, 4-vinylbenzoyl chloride (37.3 g, 224 mmol) in dry ether (80 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated ammonium salts were filtered off and the filtrate was washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with ether. The organic phase was combined and dried over anhydrous $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether ten times to yield pure white crystal of **1h** (17.0 g, 73.9 mmol, 35%; mp 48-49°C): 90 MHz ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H, CH_3), 2.39 (broad, 4H, CH_3NCH_2), 3.63 (broad, 4H, $CONCH_2$), 5.31 and 5.80 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.72 (dd, 1H, -CH=), 7.35-7.50 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 45 (broad, NCH_2), 45.8 (CH_3), 54.8 ($CONCH_2$), 115.0 (vinyl, CH_2=) 126.0 (Ar, C3), 127.2 (Ar, C2), 134.9 (Ar, C1), 135.9 (vinyl, -CH=), 138.7 (Ar, C4), 169.7 (C=O); IR (KBr, cm^{-1}) 1624 (C=O), 1459, 1432, 1297, 1271, 1166, 1134, 1001, 855, 779; Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01, H, 6.95, N, 12.16. Found: C, 73.50, H, 7.84, N, 12.32.

_N_-(4-Vinylbenzoyl)morpholine (1i). To a mechanically stirred solution of morpholine (45.1 g, 517 mmol) in dry ether (100 mL) under nitrogen, 4-

vinylbenzoyl chloride (16.0 g, 95.8 mmol) in dry ether (50 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated ammonium salts were filtered off and the filtrate was washed twice with 2 N HCl solution and twice with saturated $NaHCO_3$ solution and then dried over anhydrous $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether five times to yield pure white crystal of **1i** (10.7 g, 49.3 mmol, 51%; mp 57-58°C): 90 MHz ^1H NMR ($CDCl_3$) δ 3.67 (s, 8H, OCH_2CH_2N), 5.32 and 5.79 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 6.73 (dd, 1H, -CH=), 7.41 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 45.1 (NCH_2), 66.1 (OCH_2), 114.7 (vinyl, $CH_2{=}$), 125.6 (Ar, C3), 127.0 (Ar, C2), 134.0 (Ar, C1), 135.4 (vinyl, -CH=), 138.4 (Ar, C4), 169.3 (C=O); IR (KBr, cm^{-1}) 1629 (C=O), 1431, 1278, 1260, 1113, 1011, 907, 841; Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87, H, 6.96, N, 6.45. Found: C, 71.41, H, 7.14, N, 6.52.

Purification. After careful recrystallization, the purified monomer was dried over P_2O_5 for 48 h at ambient temperature in an apparatus equipped with a breakseal under vacuum (10^{-6} mmHg) and then diluted with THF. The resulting monomer solutions (0.3-0.5 M in THF) were stored at –30°C until ready to use for the anionic polymerization. The viscous liquid monomers, **1c** and **1e**, were dried under similar manner with ice bath cooling for 48 h and then diluted with THF.

Polymerization Procedures. All polymerizations were carried out at low temperature with shaking under high vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[23] The polymerization was quenched with methanol. The reaction mixture was concentrated, redissolved in THF and then poured into a large excess of water to precipitate the polymers. Polymers collected by filtration were purified by reprecipitation twice with a petroleum ether-THF system and by freeze-drying from benzene. Poly(**1**)s thus obtained were characterized by ^{1}H and ^{13}C NMR, IR and elemental analysis. The following is the full list.

Poly(1a): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.0-2.5 (m, 3H, CH_2CH), 3.0 (broad, 6H, NCH_3), 6.2-7.2 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 35-43 (overlapping, CH_2CH and NCH_3), 127 (Ar, C3 and C2), 133.7 (Ar, C1), 146.2 (Ar, C4), 171.1 (C=O); IR(KBr, cm^{-1}) 1640 (C=O), 1570, 1520, 1490, 1450, 1410, 1400, 1270, 1090, 850; Anal. Calcd for poly(**1a**), $(C_{11}H_{13}NO{\bullet}0.2H_2O)_n$: C, 73.88, H, 7.55, N, 7.83. Found: C, 73.70, H, 7.30, N, 7.05.

Poly(1b): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.8-2.0 (m, 9H, CH_3, CH_2CH), 3.3 (broad, 4H, NCH_2), 6.2-7.2 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 13.4 (CH_3), 39-44 (overlapping, CH_2CH and NCH_2), 126-128 (Ar, C3 and C2), 134.7 (Ar, C1), 145.9 (Ar, C4), 170.9 (C=O); IR(KBr, cm^{-1}) 1640 (C=O), 1470, 1460, 1430, 1380, 1360, 1320, 1290, 1100, 840; Anal. Calcd for poly(**1b**), $(C_{13}H_{17}NO{\bullet}0.1H_2O)_n$: C, 76.14, H, 8.45, N, 6.83. Found: C, 76.07, H, 8.39, N, 6.80.

Poly(1c): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.5-1.1 (m, 6H, CH_3), 1.1-2.0 (m, 7H, CH_2CH and CH_2), 2.9-3.6 (m, 4H, NCH_2), 6.2-7.3 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 11.3 (CH_3), 21.2 ($NCH_2\mathit{C}H_2$), 40-50 (overlapping, CH_2CH and NCH_2), 126-128 (Ar, C3 and C2), 135.0 (Ar, C1), 145.4 (Ar, C4), 171.5 (C=O); IR(KBr, cm^{-1}) 1640 (C=O), 1460, 1430, 1100; Anal. Calcd for poly(**1c**), $(C_{15}H_{21}NO)_n$: C, 77.88, H, 9.15, N, 6.06. Found: C, 78.56, H, 9.41, N, 5.27.

Poly(1d): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.9-1.9 (m, 15H, CH_2CH, CH_3), 3.6 (broad, 2H, NCH), 6.3-7.2 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3), 40-48 (overlapping, CH_2CH and NCH), 125-128 (Ar, C3 and C2), 136.6 (Ar, C1), 146.4 (Ar, C4), 170.9 (C=O); IR (KBr, cm^{-1}) 1640(C=O), 1440, 1370, 1340, 1040, 830; Anal. Calcd for poly(**1d**), $(C_{15}H_{21}NO{\bullet}0.1H_2O)_n$: C, 77.28, H, 9.17, N, 6.01. Found: C, 76.90, H, 8.83, N, 5.42.

Poly(1e): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.1-1.9 (m, 3H, CH_2CH), 3.5-4.2 (m, 4H, NCH_2), 5.0-5.3 (m, 4H, allyl CH_2=), 5.5-6.0 (m, 2H, allyl -CH=), 6.3-7.2 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40-50 (overlapping, CH_2CH and NCH_2), 117.5 (allyl, CH_2=), 126-128 (Ar, C3 and C2), 133.1 (allyl, -CH=), 133.8 (Ar, C1), 146.3 (Ar, C4), 171.3 (C=O); IR(KBr, cm^{-1}) 1640 (C=O), 1460, 1410, 1260, 930; Anal. Calcd for poly(**1e**), $(C_{15}H_{17}NO)_n$: C, 79.26, H, 7.54, N, 6.16. Found: C, 79.20, H, 7.55, N, 5.96.

Poly(1f): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.2-2.1 (m, 7H, CH_2CH and NCH_2CH_2), 3.1-3.8 (m, 4H, NCH_2), 6.3-7.3 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 24.1 and 26.1 (NCH_2CH_2), 40-46 (CH_2CH), 45.8 and 49.2 (NCH_2), 126.9 (Ar, C3 and C2), 134.4 (Ar, C1), 145.9 (Ar, C4), 169.0 (C=O); IR(KBr, cm^{-1}) 1610 (C=O), 1560, 1440, 850, 770, 720; Anal. Calcd for poly(**1f**), $(C_{13}H_{15}NO \bullet 0.3H_2O)_n$: C, 75.55, H, 7.61, N, 6.78. Found: C, 75.27, H, 7.50, N, 6.47.

Poly(1g): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.9-2.1 (m, 9H, CH_2CH and $CH_2CH_2CH_2$), 3.0-3.8 (m, 4H, NCH_2), 6.2-7.2 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 24.3 ($NCH_2CH_2\mathit{CH}_2$), 25.8 ($NCH_2\mathit{CH}_2$), 40-49 (overlapping, CH_2CH and NCH_2), 126.8 (Ar, C3 and C2), 133.7 (Ar, C1), 145.7 (Ar, C4), 169.8 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1440, 1280, 1110, 1000, 850; Anal. Calcd for poly(**1g**), $(C_{14}H_{17}NO \bullet 0.2H_2O)_n$: C, 76.82, H, 8.01, N, 6.40. Found: C, 76.94, H, 7.94, N, 6.33.

Poly(1h): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.0-2.7 (m, 10H, CH_2CH, CH_2NCH_3), 3.1-4.6 (m, 4H, $CONCH_2$), 6.2-7.3 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40-47 (m, CH_2CH, NCH_2), 46.0 (CH_3), 55.0 ($CONCH_2$), 127.3 (Ar, C3 and C2), 133.4 (Ar, C1), 146.5 (Ar, C4), 170.0 (C=O); IR (KBr, cm^{-1}) 1636 (C=O), 1431, 1295, 1273, 1142, 1129, 1015, 1002, 841; Anal. Calcd for poly(**1h**), $(C_{14}H_{18}N_2O \bullet 0.5H_2O)_n$: C, 70.26, H, 8.00, N, 11.71. Found: C, 70.03, H, 7.52, N, 10.76.

Poly(1i): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.8-2.2 (m, 3H, CH_2CH), 2.9-4.1 (broad, 8H, OCH_2CH_2N), 5.9-7.3 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40-47 (m, CH_2CH, NCH_2), 66.9 (CH_2O), 127.4 (Ar, C3 and C2), 133.1 (Ar, C1), 146.7 (Ar, C4), 170.1 (C=O); IR (KBr, cm^{-1}) 1636 (C=O), 1426, 1278, 1258, 1116, 1068, 1011, 839; Anal. Calcd for $(C_{13}H_{15}NO_2 \cdot 0.3H_2O)_n$: C, 70.19, H, 7.07, N, 6.30. Found: C, 70.10, H, 6.78, N, 5.98.

Reaction of Poly(1a) with Methyllithium. To a solution of poly(**1a**) (0.51 g, 2.9 mmol based on monomer unit) in dry THF (20 mL), methyllithium (20 mL of a 1.2 M ether solution, 24 mmol) was added dropwise at –78°C under nitrogen. The reaction mixture was allowed to stir at –78°C for 20 min and then at 0°C for 2 h to afford a homogeneous system. When the reaction was quenched with methanol at –78°C, a yield of dimethylamine was observed. To precipitate the polymer, the solution was poured into water. Subsequent reprecipitation and freeze-drying gave poly(4-vinylacetophenone) (0.33 g, 2.3 mmol based on monomer unit, 79%) characterized as follows. **Poly(4-vinylacetophenone)**: 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.1-1.8 (m, 3H, CH_2CH), 2.45 (broad, 3H, $COCH_3$), 6.2-7.7 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 26.3 (CH_3), 40-45 (CH_2CH), 126-129 (Ar, C3 and C2), 135.3 (Ar, C1), 149.4 (Ar, C4), 197.4 (C=O); IR(KBr, cm^{-1}) 1680 (C=O), 1610, 1420, 1360, 1270; Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16, H, 6.90, N, 0,00. Found: C, 81.57, H, 7.46, N, 0.00.

Aromatic Lithiation of Poly(1b) and Subsequent Reaction with Trimethylsilyl Chloride. To a solution of poly(**1b**) (0.20 g, 0.99 mmol based on monomer unit) and TMEDA (0.31 g, 2.7 mmol) in dry THF (20 mL), *sec*-BuLi (2.0 mL of a 1.05 M cyclohexane solution, 2.1 mmol) was added dropwise at –78°C under nitrogen. The reaction mixture was allowed to stir at –78°C for 1 h. Then trimethylsilyl chloride (1.1 g, 10 mmol) was added at once at –78°C. The color of solution changed from orange to yellow. After stirring for 1 h at –78°C, the reaction was quenched with

MeOH and the reaction mixture was poured into water for precipitation. The resulting polymer (0.25 g) was purified by reprecipitation from THF/hexane system and freeze-dried from benzene. Poly(**1b**) after polymer reaction: 90 MHz ^1H NMR ($CDCl_3$) δ 0.15 (broad s, $SiCH_3$), 0.8-2.0 (m, CH_2CH and CH_3), 2.9-3.6 (m, NCH_2), 6.2-7.8 (m, Ar).

Acid Hydrolysis of Poly(1h). A solution of 0.30 g (1.3 mmol based on a monomer unit) of poly(**1h**) in 1,4-dioxane (20 mL) and 6 N HCl (20 mL) was heated at 80°C for 12 h and then concentrated. The residue was poured into a large excess of water to precipitate of a polymer. The resulting polymer collected by filtration was rinsed with water and purified by the reprecipitations from MeOH-water system and finally freeze-dried from a solution of benzene containing a small amount of methanol. The polymer thus obtained was a white powder and characterized as a poly(4-vinylbenzoic acid) (0.16 g, 83%) by ^1H and ^{13}C NMR, and IR spectroscopy. The following is the full list.

90 MHz ^1H NMR (CD_3OD) δ 1.0-2.3 (m, 3H, CH_2CH), 6.3-7.8 (m, 4H, Ar); 23 MHz ^{13}C NMR (CD_3OD) δ 42-45 (m, CH_2CH), 128-133 (Ar, C1, C2, and C3), 153 (Ar, C4), 170.6 (C=O); IR (KBr, cm^{-1}) 1701 (C=O), 1609, 1421, 1273, 1180, 1118.

Three-step Hydrolysis of Poly(1h). To a solution of 0.50 g (2.2 mmol based on a monomer unit) of poly(**1h**) in THF (30 mL), 1.0 mL of methyl iodide (16 mmol) was added dropwise under nitrogen atmosphere at room temperature to yield the quarternary salts. The reaction mixture was heated at reflux for 4 h and concentrated, and to the residue was added sodium ethoxide (5.2 mmol) in absolute ethanol (30 mL). The reaction mixture was heated at reflux for 7 h and concentrated under reduced pressure. To the residue was added 6 N HCl (25 mL) and THF (25 mL), and the mixture was heated at reflux for 24 h to give a homogeneous solution. After concentration of reaction mixture, the polymer was similarly isolated as described above. It was found that the resulting poly(4-vinylbenzoic acid) (0.30 g, 91%) contained a small amount of its ethyl ester unit from the ^1H and ^{13}C NMR analyses.

Methylation of Poly(4-vinylbenzoic acid). The methylation of the carboxy group of the poly(4-vinylbenzoic acid) was performed with diazomethane in a mixed solvent of diethyl ether and benzene as described in Chapter 2.[4] The characteristic of the resulting poly(methyl 4-vinylbenzoate) is as follows. 90 MHz ^1H NMR ($CDCl_3$) δ 0.8-2.2 (m, 3H, CH_2CH), 3.9 (s, 3H, OCH_3), 6.8-7.9 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40-43 (CH_2CH), 52.1 (OCH_3), 126-131 (Ar, C1, C2, and C3), 149 (Ar, C4), 166.8 (C=O); IR (KBr, cm^{-1}) 1722 (C=O), 1609, 1436, 1283, 1182, 1105, 1019; Anal. Calcd for $(C_{10}H_{10}O_2{\bullet}0.2H_2O)_n$: C, 72.45, H, 6.32, N, 0.00. Found: C, 72.57, H, 6.78, N, 0.00.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.53MHz ^{13}C) in $CDCl_3$. Chemical Shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^1H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Size exclumsion chromatograms (SEC) for MWD determination were obtained at 40°C with a Toyosoda HLC-802 instrument with ultraviolet (254 nm) or refractive index detection. THF was a carrier solvent at a flow rate of 1.4 mL min^{-1}. SEC analyses for poly(**1a**), poly(**1h**), and poly(**1i**) were performed with a TOSOH HLC-8020 instrument equipped with two polystyrene gel columns (TOSOH $GMH_{XL} \times 2$) with ultraviolet (270 nm) or refractive index detection. DMF was a carrier solvent at a flow rate of 0.8 mL min^{-1}. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment of very exact temperature control. Intrinsic viscosities of poly(**1b**) and polystyrene were measured using an Ubbelohde type capillary viscometer at 40°C in THF.

The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC5200TA station. The samples were first heated to 240°C, cooled rapidly to –20°C, and then scanned again at a rate of 20°C/min.

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(12) In the cases of samples with molecular weights less than 10 000, the molecular weight of poly(**1a**) was measured by VPO in benzene. Since for poly(**1a**) with a molecular weight higher than 10 000 it was difficult to determine the molecular weight due to the insolubility in benzene,

those molecular weights were estimated by using the polystyrene standard calibration with SEC measurement in DMF.

(13) The product of block copolymerization was roughly separable by precipitation into methanol or Soxhhlet extraction. The filtrate was the virtual homopolymer of **1b**, which did not concern the block copolymerization, while the precipitate was block copolymer containing a polystyrene segment of very high molecular weight.

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(19) In this polymer reaction, the regioselectivity is not clear at this stage. In ^{13}C NMR spectrum of the resulting polymer, four signals of aromatic carbons of poly(**1b**) were split into complicated signals, indicating the substitution of aromatic rings of poly(**1b**).

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Chapter 3

Living Anionic Polymerization of *tert*-Butyl 4-Vinylbenzoate

ABSTRACT: Anionic polymerization of *tert*-butyl 4-vinylbenzoate (**1e**) was initiated in THF with oligo(α-methylstyryl)disodium, -dipotassium, and -dicesium as initiators to give poly(**1e**) in quantitative yield, whereas the lithium salts did not initiate the polymerization. At –78 and –40°C, broadening of the molecular weight distribution (MWD) of the poly(**1e**) resulted, which suggested that a termination reaction of the propagating end with the ester group of another polymer chain had occurred. At –95°C, with the potassium salts, the side reaction was suppressed to afford poly(**1e**) of a narrow MWD and of a predictable molecular weight from the mole ratio of monomer to initiator, indicating that the anionic polymerization of **1e** at –95°C gave a stable living polymer without chain transfer and termination reactions. New block copolymers, poly[(methyl methacrylate)-*b*-**1e**-*b*-(methyl methacrylate)], poly(**1e**-*b*-styrene-*b*-**1e**), and poly(**1e**-*b*-isoprene-*b*-**1e**) were prepared by means of this living system. The resulting poly(**1e**) was completely hydrolyzed with trimethylsilyl chloride/sodium iodide in a mixed solvent of acetonitrile and chloroform at ambient temperature for 10 min to give a corresponding poly(4-vinylbenzoic acid) with a well-defined chain structure.

Introduction

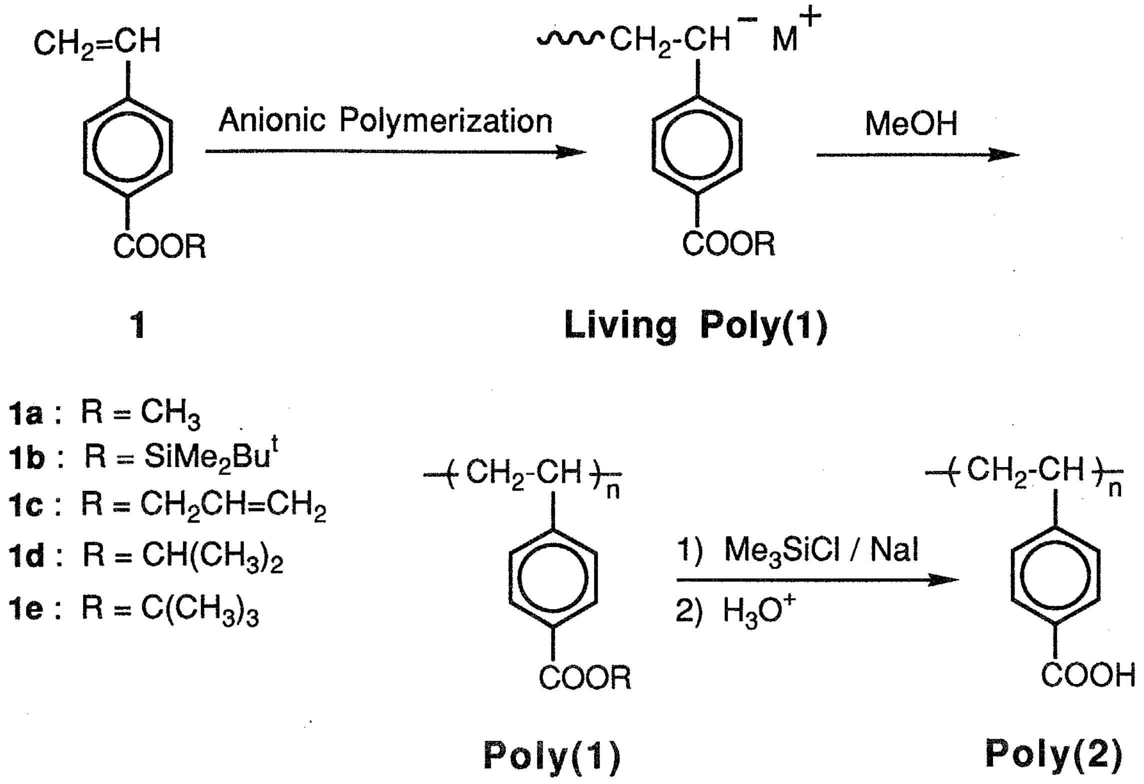
The pioneering discovery of Szwarc[1] in 1956 and the practical studies of Morton[2] in the 1960s on the anionic polymerizations of styrenes and dienes introduced the concept of living polymers. The utility of this method is derived from the absence of chain transfer and termination reactions, allowing the synthesis of polymers having predictable molecular weights and narrow molecular weight distributions. Anionic polymerizations of methacrylic acid esters such as methyl methacrylate (MMA) were also investigated under limited reaction conditions avoiding the deactivation of the propagating chain-end with carbonyl group.[3]

Generally, suitable choice of initiators, solvents, and reaction temperature is very important for the formation of living polymers from the monomers containing electron-withdrawing groups which might potentially have nucleophilic attack of the propagating carbanions. By the selection of suitable protective group and the control of reaction condition, it has been recently demonstrated the anionic living polymerization of styrene derivatives such as *N*-(4-vinylbenzylidene)alkylamine,[4] *N*,*N*-dialkyl(4-vinylbenzamide),[5] and 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline.[6] These polymerizations ideally proceeded in 2,1-addition mode and the propagating chain-ends did not react with the functional groups such as imine, amide, and oxazoline. The electron-withdrawing groups are thought to play an important role in the stabilization of living ends.

The present chapter deals with the study on the anionic polymerization of the styrene derivative containing ester group. If the ester carbonyl group coexists with anionic species such as Grignard reagent and organolithium compounds, the anionic polymerization of the monomers containing ester groups will proceed to afford a living polymer.

Parham and his co-workers demonstrated that stable aryllithium reagents were prepared by halogen-lithium exchange at very low temperature (–100°C) with a variety of aryl bromides containing reactive functional groups (COO^-, COOR, CN, CH_2Cl, CH_2CH_2Br).[7] At such a low temperature, the halogen-lithium exchange reaction was still rapid, and undesirable side reaction of the organolithium reagent might be inhibited. An aryllithium reagent was typically prepared by the reaction of *tert*-butyl 4-bromobenzoate with *n*-BuLi at –100°C, whereas less hindered methyl and isopropyl esters caused either self-condensation or reaction with unchanged bromoaryl ester.[8,9] The resulting aryllithium having *tert*-butyl ester group is so susceptible to temperature that the undesirable self-condensation proceeds at –78°C. Moreover, Beak and his co-workers demonstrated that the direct *ortho* lithiation of alkyl benzoate occurred regioselectively and that the nucleophilic addition to ester moiety could be suppressed by using sterically hindered organolithium reagents and bulkier alkyl group of ester.[10] These observations indicate that reaction temperature and steric effect of reactants are of importance in the synthesis of organolithium compound containing ester groups as models for living polymerizations.

In this chapter, the author investigates the anionic polymerization of 4-vinylbenzoate (**1**) in detail to produce a living poly(**1**) and the hydrolysis of the resulting poly(**1**) to synthesize a well-defined poly(4-vinylbenzoic acid), poly(**2**) (Scheme 3-1).



Scheme 3-1

Results and Discussion.

3-1. Polymerization of Methyl (1a), *tert*-Butyldimethylsilyl (1b), and Allyl (1c) 4-Vinylbenzoates.

Anionic polymerizations of 4-vinylbenzoates, such as allyl, vinyl, and 2-butyn-1-yl esters, were investigated by D'Alelio and Hoffend to afford the linear soluble polymers in tetrahydrofuran (THF) at –40°C with sodium naphthalenide as an initiator.[11] However, they did not mention the quantitative discussion of the molecular weight and the molecular weight distribution (MWD) of the polymers produced. The author here examined the anionic polymerizations of several 4-vinylbenzoates in detail and explored the possibility of anionic living polymerization of the monomers.

Anionic polymerizations of **1a**, **1b**, and **1c** were performed with various initiators, such as oligo(α-methylstyryl)dipotassium and sodium naphthalenide, in THF. As shown in Table 3-1, no polymer was obtained in each case. Steric hindrance of methyl group of **1a** seems to be insufficient to protect the carbonyl moiety from nucleophilic attack at the initiation step of the polymerization. Anionic polymerization of **1b** with bulky *tert*-butyldimethylsilyl group was not initiated and presumably terminated by nucleophilic attack of the initiator carbanion on the silicon atom. When **1c** was allowed to react with sodium naphthalenide in THF at –40°C, no polymer was obtained. This was contrary to the reports obtained by Hoffend and D'Alelio.[11] Under more preferable conditions, including high initiator level, low reaction temperature, and long reaction time, the polymerization of **1c** also did not proceed and the monomer was quantitatively recovered. These contrasting results will not be here further discussed in this thesis.

3-2. Anionic Polymerization of Isopropyl 4-Vinylbenzoate (1d).

Anionic polymerization of an alternative monomer, **1d**, an ester of a secondary alcohol, was initiated with oligo(α-methylstyryl)dipotassium in THF. In contrast to the results of **1a**, **1b**, and **1c**, poly(**1d**) was certainly produced in 25-70% yield. During the polymerization, characteristic dark red color of the reaction mixture maintained at –78°C and immediately disappeared by adding a few drops of methanol to quench the polymerization. Pouring the reaction mixture into an excess of methanol precipitated a white powder of poly(**1d**), which was purified by reprecipitation twice with a THF-methanol system. A typical ^{1}H NMR of poly(**1d**) is shown in Figure 3-1, where it is found that the considerable amount of pendant isopropyl ester groups are converted to methyl ester moiety by transesterification during the workup of polymer isolation. The ester exchange reaction, which presumably catalyzed with potassium methoxide formed by the termination reaction, was similarly observed in the recovered monomer. The corrected yields of poly(**1d**)s were not quantitative even after prolonged reaction time (20 h) and

Table 3-1

Anionic Polymerization of **1a**, **1b**, **1c**, and **1d** with Various Initiators in THF

monomer		condition			polymer	$10^{-3}M_n$		
type	mmol	temp, °C	time	initiator, mmol	yield, %	(calcd)[a]	(obsd)[b]	M_w/M_n
1a	3.06	–78	5 min	K-Naph,[c] 0.113 / α-MeSt,[d] 0.322	0			
1a	3.06	–78	24 h	K-Naph, 0.117 / DPE,[e] 0.286	0			
1b	2.75	–78	15 min	K-Naph, 0.166 / α-MeSt, 0.380	0			
1b	3.13	–78	30 min	K-Naph, 0.139 / DPE, 0.307	0			
1c	5.25	–78	5 min	K-Naph, 0.206 / α-MeSt, 0.513	0			
1c	3.39	–78	2 h	K-Naph, 0.122 / DPE, 0.360	0			
1c	6.03	–40	20 min	Na-Naph,[f] 0.195	0			
1d	3.22	–78	4 h	K-Naph, 0.138 / α-MeSt, 0.364	43	4.4	7.4	1.32
1d	3.30	–78	20 h	K-Naph, 0.126 / α-MeSt, 0.321	71	7.7	11	1.50
1d	3.59	–95	10 min	K-Naph, 0.115 / α-MeSt, 0.298	25	3.6	4.6	1.13
1d	3.41	–95	4 h	K-Naph, 0.116 / α-MeSt, 0.369	49	6.2	11	1.72

[a] M_n(calcd) = [monomer] × (MW of monomer) × 2 × (yield of polymer) / (100) [initiator] + MW of initiator.

[b] M_n(obsd) was obtained by SEC calibration using a standard polystyrenes. [c] Potassium naphthalenide.

[d] α-Methylstyrene. [e] 1,1-Diphenylethylene. [f] Sodium naphthalenide.

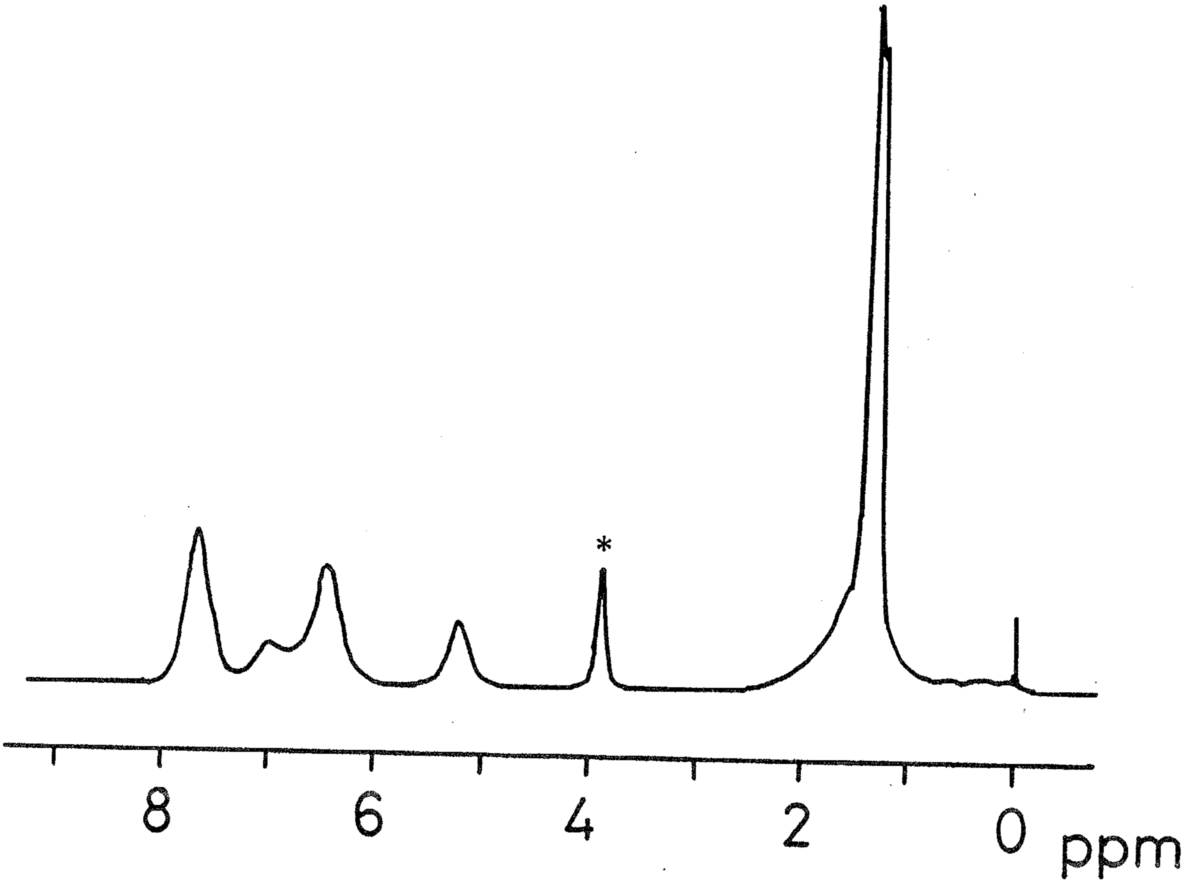


Figure 3-1. ^{1}H NMR spectrum of poly(**1d**). Peak attributable to methyl ester is marked with an asterisk (*).

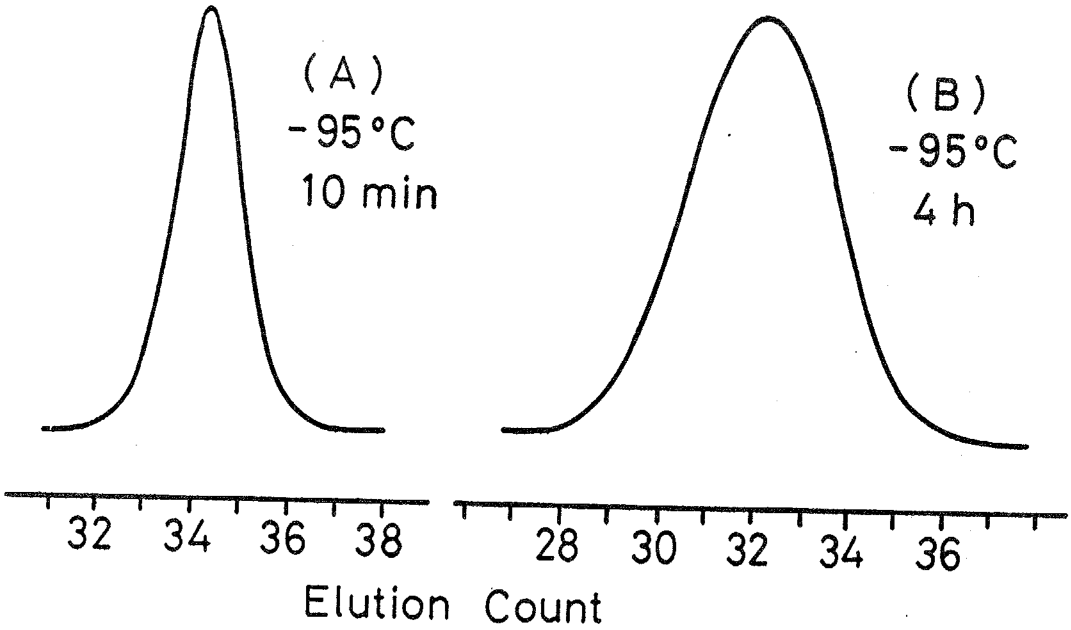


Figure 3-2. SEC curves of poly(**1d**)s obtained with the potassium salt:
(A) M_n(obsd)(SEC) = 4.6×10^3, $M_w/M_n = 1.13$;
(B) M_n(obsd)(SEC) = 11×10^3, $M_w/M_n = 1.72$.

the MWD are rather broad as shown in Table 3-1. These results reveal that anionic polymerization of **1d** unequivocally takes place contrary to the cases of **1a**, **1b**, and **1c**. The bulky isopropyl ester may to some extent prevent propagating chain-end from deactivation. However, occasional termination and transfer reactions still occur in the course of the polymerization of **1d**.

At –95°C for 10 min, nearly monodispersed poly(**1d**) was obtained. However, the MWD of the polymer broadened after 4 h as shown in Figure 3-2. The deactivation of propagating chain-end could not be suppressed by lowering the reaction temperature. Furthermore, in the case using lithium salts as initiators, poly(**1d**) was not virtually produced.

3-3. Anionic Polymerization of *tert*-Butyl 4-Vinylbenzoate (1e).

Anionic polymerization of **1e**, where ester carbonyl moiety was protected with bulkier alkyl group than that of **1d**, was carried out in THF with various initiators at –40 to –95°C. The initiators included oligo(α-methylstyryl)dilithium, -disodium, -dipotassium, and -dicesium and cumylpotassium. The reaction mixture showed a characteristic dark red color similar to that of living polystyrene during the course of the polymerization. The coloration remained unchanged at –78°C even after 20 h and disappeared immediately with a small amount of methanol as expected. The reaction mixture was poured into a large amount of methanol for precipitation of a polymer. The yielding polymer was purified by reprecipitation twice with a THF-methanol system and then freeze-dried from benzene. No transesterification of the pendant *tert*-butyl ester group of poly(**1e**) was observed during the polymer isolation process by means of ^{1}H and ^{13}C NMR spectroscopies, although the isopropyl ester group of poly(**1d**) was considerably converted into methyl ester under the similar conditions. Figures 3-6a and 3-7a show typical IR and ^{1}H NMR spectra of poly(**1e**), respectively.

As shown in Table 3-2, the remarkable effect of countercation on the polymerization was observed. By three initiators associated with lithium cation, poly(**1e**) was not formed as well as the polymerization of **1d**. Contrary to the case of lithium salt, sodium, potassium, and cesium salts gave poly(**1e**)s in good to quantitative yields. In most cases, the polymerization produced nearly monodispersed poly(**1e**) whose molecular weight observed agreed well with that calculated on the basis of the mole ratio of monomer to initiator. The rate of the polymerization for **1e** seemed to be significantly slow compared with that of anionic polymerization of styrene; the complete conversion of **1e** required about 40 min at –78°C.

At –78°C, the prolonged polymerization time leads to broadening of the size exclusion chromatography (SEC) curves of poly(**1e**) obtained under similar conditions as shown in Figure 3-3. A shoulder appears at the higher molecular weight side after 40 min and results in a bimodal peak after 20 h, where the summit of the higher molecular weight side corresponds to an about 2-fold higher molecular weight than the original one. This phenomenon suggests that the propagating chain-end of poly(**1e**) attacks the pendant ester group of another polymer chain. The polymerization system at –78°C affords a long-lived propagating species, but is not completely stable. At –40°C, the MWD of the polymer is already broad in 10 min with an increase in the termination reaction. In contrast, at –95°C, **1e** is completely transformed to the polymer which has a very narrow MWD even after 8 h. Hence, the side reaction seemed to be suppressed at –95°C for a long time. The stability of the carbanion is similar to that of aromatic organolithium reagents bearing electrophilic groups developed by Parham; *tert*-butyl 4-lithiobenzoate reacts with benzophenone to give a triarylcarbinol in good yield without self-condensation at –100°C, but attacks each other to form condensates when it is warmed to –78°C.[8,9] At –95°C, the anionic polymerizations produce poly(**1e**)s with the molecular weights in the range of 6500 - 59 000, which

Table 3-2 Anionic Polymerization of **1e** with Various Initiators in THF

	1e	condition			polymer	$10^{-3}M_n$		
run	mmol	temp, °C	time	initiator, mmol	yield, %	(calcd)[a]	(obsd)[b]	M_w/M_n
1	3.74	–78	30 min	*n*-BuLi, 0.0653 / α-MeSt,[c] 0.651	0			
2	3.76	–78	10 min	Li-Naph,[d] 0.137 / α-MeSt, 0.305	0			
3	3.12	–95	4 h	Li-Naph, 0.137 / DPE,[e] 0.187	0			
4	3.74	–78	10 min	Na-Naph,[f] 0.125 / α-MeSt, 0.305	80	10	14	1.18
5	2.87	–40	10 min	K-Naph,[g] 0.116 / α-MeSt, 0.244	100	11	16	1.59
6	4.77	–78	5 min	K-Naph, 0.173 / α-MeSt, 0.563	66	8.2	9.4	1.11
7	3.51	–78	40 min	K-Naph, 0.138 / α-MeSt, 0.339	100	11	10	1.18
8	2.19	–78	4 h	K-Naph, 0.113 / α-MeSt, 0.334	100	8.6	9.7	1.26
9	2.65	–78	20 h	K-Naph, 0.0921 / α-MeSt, 0.373	100	13	18	1.55
10	3.32	–95	8 h	K-Naph, 0.204 / α-MeSt, 0.378	100	7.1	6.5	1.10
11	3.29	–95	8 h	K-Naph, 0.145 / α-MeSt, 0.348	100	9.8	9.8	1.11
12	2.48	–95	4 h	K-Naph, 0.0944 / α-MeSt, 0.335	100	12	12	1.15
13	6.08	–95	8 h	K-Naph, 0.163 / α-MeSt, 0.302	100	16	13	1.12
14	5.69	–95	4 h	Cumyl K,[h] 0.0375 / α-MeSt, 0.350	61	20	19	1.09
15	8.35	–95	8 h	Cumyl K, 0.0404 / α-MeSt, 0.269	94	43	59	1.18
16	7.80	–95	12 h	Cumyl K, 0.0256 / DPE, 0.0333	100	63	18	1.55
17	2.87	–78	10 min	Cs-Naph,[i] 0.909 / α-MeSt, 0.314	51	7.4	7.3	1.08
18	4.26	–78	90 min	Cs-Naph, 0.164 / α-MeSt, 0.320	100	11	14	1.25

[a] M_n(calcd) = [monomer] × (MW of monomer) × f × (yield of polymer) / (100) [initiator] + MW of initiator, $f = 1$ or 2 corresponding to the functionality of the initiators. [b] M_n(obsd) was obtained by VPO in benzene solution. [c] α-Methylstyrene. [d] Lithium Naphthalenide. [e] 1,1-Diphenylethylene. [f] Sodium naphthalenide. [g] Potassium naphthalenide. [h] Cumylpotassium. [i] Cesium naphthalenide.

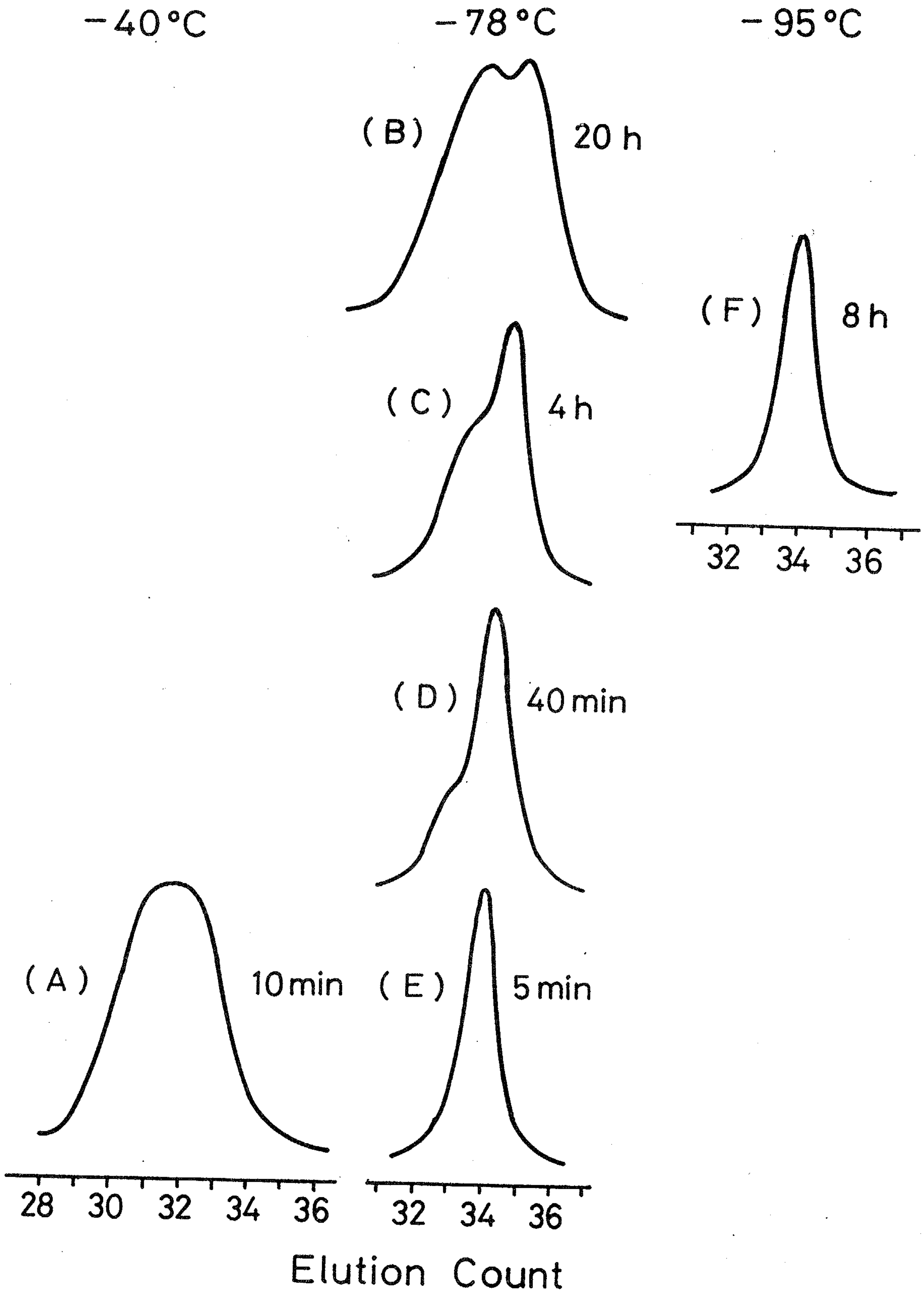


Figure 3-3. Effects of polymerization temperature and time on the MWD of poly(**1e**). Detailed data were shown in Table 3-2: (A) run 5, M_w/M_n = 1.59; (B) run 6, M_w/M_n = 1.11; (C) run 7, M_w/M_n = 1.18; (D) run 8, M_w/M_n = 1.26; (E) run 9, M_w/M_n = 1.55; (F) run 11, M_w/M_n = 1.11.

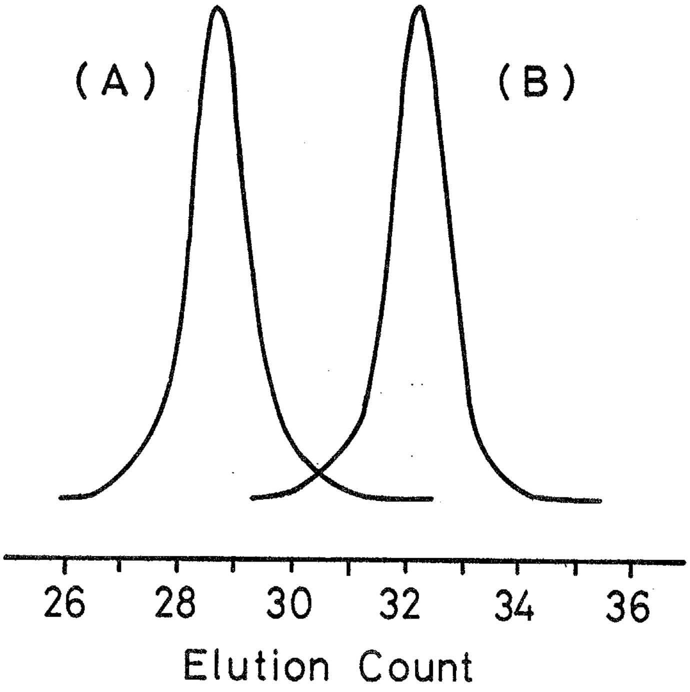


Figure 3-4. SEC curves of poly(**1e**)s obtained at –95°C. Detailed data were shown in Table 3-2: (A) run 14, M_n(obsd) = 19×10^3, M_w/M_n = 1.09; (B) run 16, M_n(obsd) = 59×10^3, M_w/M_n = 1.18.

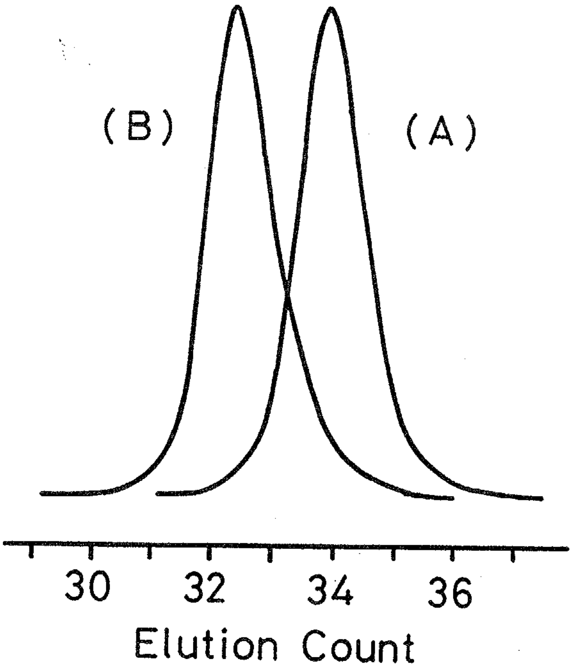


Figure 3-5. SEC curves of poly(**1e**)s obtained at –95°C:
the first polymerization (A), M_n(obsd) = 6.5×10^3, M_w/M_n = 1.10;
the second polymerization (B), M_n(obsd) = 13×10^3, M_w/M_n = 1.12.
(the second monomer was added after 4 h of the first addition).

agree fairly well with those calculated from the mole ratios of monomer to initiator. The M_w/M_n values of the resulting polymers are in the range of 1.09 - 1.18, indicating that the MWDs of the polymers are narrow. The representative SEC curves of poly(**1e**) obtained at –95°C are shown in Figure 3-4. These facts suggest that termination reaction is completely suppressed at –95°C to give a living end stabilized by electron-withdrawing ester group. Furthermore, to prove the living nature of the polymerization system of **1e**, the postpolymerization was carried out as follows. The first-stage polymerization was initiated with oligo(α-methylstyryl) -dipotassium at –95°C. After complete consumption of the monomer, the resulting polymerization mixture was divided into two portions. One was terminated with methanol, while monomer was again added to the other to propagate the second-stage polymerization at –95°C. In both cases, the poly(**1e**)s are obtained quantitatively, the SEC curves of which are very narrow as shown in Figure 3-5. The SEC curve of the postpolymer shifts toward higher molecular weights without a shoulder at the elution count of the prepoly(**1e**). The observed molecular weights of the pre- and postpolymers agree fairly well with the predicted ones. These results substantiate that a stable living polymer of *tert*-butyl 4-vinylbenzoate forms at –95°C, which is able to further propagate with quantitative efficiency.

It has been already confirmed that the anionic polymerizations of *N*-(4-vinylbenzylidene)cyclohexylamine,[4] *N,N*-dialkyl(4-vinylbenzamide),[5] and 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline[6] proceeded to afford stable living polymers at –78°C. Their propagating chain ends do not react with the functional groups, such as imine, amide, and oxazoline, at –78°C. This can be explained by stabilization of the carbanions with electron-withdrawing groups. However, the reaction of the propagating end of poly(**1e**) with pendant ester group partially occur even at –78°C. The different stabilities of their crucial propagating ends to the functional groups are of interest.

3-4. Block Copolymerization of **1e** with Methyl Methacrylate, Styrene, and Isoprene

In a similar manner to that of postpolymerization, the syntheses of block copolymers were attempted by the addition of the second monomer to the living poly(**1e**) prepared at –95°C. However, the living poly(**1e**) did not initiate the polymerizations of isoprene and styrene to recover homopoly(**1e**) without isoprene and styrene units in the polymer chain, whereas methyl methacrylatye (MMA), a more reactive monomer in anionic mechanism, reacted with living poly(**1e**) to yield the poly(MMA-*b*-**1e**-*b*-MMA) with regulated block length and narrow MWD as shown in Table 3-3.

Table 3-3

Block Copolymerization of **1e** with
Methyl Methacrylate, Isoprene, and Styrene at –95°C in THF

				block copolymer[a] (homopolymer)[b]		
run	type	A monomer	B monomer	$10^{-3}M_n$(calcd)	$10^{-3}M_n$(obsd)	M_w/M_n
19	B-A-B	**1e**	MMA	25 (7.1)	22 (6.8)	1.27 (1.10)
20	A-B-A	**1e**	styrene	25 (14)	25 (14)	1.13 (1.06)
21	A-B-A	**1e**	isoprene	27 (15)	25 (12)	1.13 (1.07)

[a] Yields of polymers were nearly quantitative in each case.

[b] Homopolymers were obtained at the first-stage polymerization.

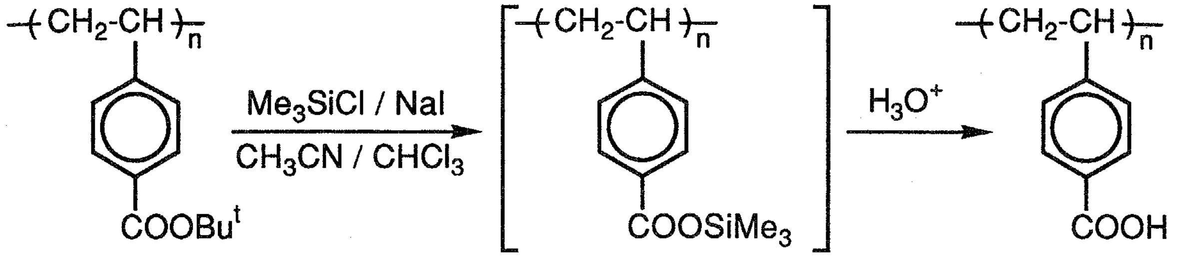
The reactivity of the carbanion derived from **1e** is supposed to be lowered on account of electron-withdrawing ester group. Similar behavior has been already observed in the series of the study on the anionic polymerization of styrene derivatives bearing electron-withdrawing groups at *para* position, *N*-(4-vinylbenzylidene)cyclohexylamine,[4] *N*,*N*-dialkyl-4-vinylbenzamide,[5] and 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline.[6] The carbanions derived from these monomers are able to initiate the polymerization of MMA but are virtually ineffective for initiating styrene and isoprene. Living poly(**1e**) also has a reactivity of this class.

On the other hand, the block copolymers with reversed block sequences having regulated molecular weights and narrow MWDs can be prepared by addition of **1e** to the living polymers of styrene and isoprene at –95°C (Table 3-3).

3-5. Deprotection of the Ester Group of Poly(1e)

In the hydrolyses of polymers with ester groups under acidic and basic conditions, some difficulties are occasionally encountered due to insolubility of the polymers in the reaction media. Recently, trimethylsilyl iodide (TMSI) has been proposed as an effective reagent for dealkylation of esters under neutral and mild conditions.[12] Bugner demonstrated the utility of TMSI in the hydrolysis of poly[(MMA)-*b*-(*tert*-butyl methacrylate)], where the *tert*-butyl ester moiety completely cleaved at ambient temperature, but the methyl ester was unreactive under the conditions, resulting in poly[(MMA)-*b*-(methacrylic acid)].[13] The stability of leaving carbocation in deprotection of the ester group may be responsible for this chemoselectivity.

The hydrolysis of poly(**1e**) was carried out by modifying Bugner's method. In place of TMSI, the author conveniently employed trimethylsilyl chloride (TMSCl) and sodium iodide, which yielded TMSI *in situ* in the reaction mixture.[14] Poly(**1e**) was treated with TMSCl and NaI at ambient temperature for 10 min in a mixture of acetonitrile and chloroform (Scheme 3-2).



Poly(1e) **Poly(2)**

Scheme 3-2

The product was isolated by precipitation in aqueous 0.1 N HCl solution and freeze-dried from 1,4-dioxane. IR, ^{1}H and ^{13}C NMR spectra of the polymer produced are identical with those of poly(4-vinylbenzoic acid), poly(**2**),[6] indicating that complete hydrolysis of *tert*-butyl ester of poly(**1e**) is achieved. As reported previously,[6] the poly(4-vinylbenzoic acid) obtained by the hydrolysis of the oxazoline protective group contained $^{7}/_{10}$ mole of water per each monomer unit. However, it is revealed from the elemental analysis of poly(**2**) prepared here that most water molecules can be removed from the polymer by thorough freeze-drying followed by heating at 60°C for 5 h. The characteristic C=O and O-H stretching absorptions of the carboxy group are observed at 1700 and 2500-3300 cm^{-1}, respectively, whereas the absorptions corresponding to the ester carbonyl group at 1710 cm^{-1} and the *tert*-butyl group at 1360 and 1690 cm^{-1} disappear as shown in Figure 3-6b. The ^{1}H NMR spectrum of poly(**2**) shows the signals responsible for the poly(4-vinylbenzoic acid) and the resonance corresponding to *tert*-butyl group of starting poly(**1e**) no longer exists (Figure 3-7b). Moreover, the ^{13}C signals due to *tert*-butyl ester group at 28.2 (C-CH_3), 80.7 (C-CH_3), and 165.5 ppm (C=O) thoroughly disappear and that of carboxy group (COOH) newly appears at 170.6 ppm. In contrast to the complete cleavage of the *tert*-butyl ester group, no hydrolysis of poly(**1d**) containing isopropyl ester group occurred under a similar condition even after 20 h. Because the carboxy group of the hydrolyzed polymer was adsorbed on the cross-linked polystyrene gel-column, the SEC measurement of poly(**2**) could not be directly performed. Hence, poly(**2**) was furthermore converted into poly(methyl 4-vinylbenzoate) by treating with diazomethane as described in the Experimental Section, to evaluate the degree of polymerization (DP) and M_w/M_n of poly(**2**), which were found almost unchanged compared with those of the poly(**1e**) before hydrolysis; DP and M_w/M_n of poly(**2**) and the corresponding poly(**1e**) (Table 3-2, run 12) are 59, 1.15 and 55, 1.18, respectively. These results strongly indicate that the quantitative hydrolysis of poly(**1e**) proceeds without any detectable degradation and cross-linking of main chain to afford the poly(4-vinylbenzoic acid) with a predictable molecular weight and a narrow MWD.

In a previous work[6] and a preceding Chapter 2, linear poly(4-vinylbenzoic acid)s with controlled chain structures were successfully synthesized by means of the anionic living polymerizations of 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline[6] and *N*-(4-vinylbenzoyl)-*N'*-methylpiperazine (Chapter 2) and the subsequent deprotections of the resulting polymers. The complete hydrolysis of oxazoline group required two step reaction including acid hydrolysis at 80-90°C for 10 h and subsequent saponification at 80-90°C for 6 h. The acid hydrolysis of *β*-amino benzamide linkage of the latter polymer quantitatively occurred in aqueous 1,4-dioxane with 6 N HCl at 70°C for 12 h. Compared with these processes, deprotection of poly(**1e**) advantageously proceeds under very mild conditions.

Furthermore, the hydrolysis of the block copolymers, poly(**1e**-*b*-styrene-*b*-**1e**) and poly(MMA-*b*-**1e**-*b*-MMA), was also carried out under the similar conditions. In both cases, the analyses by IR, ^{1}H and ^{13}C NMR spectroscopies showed quantitative cleavage of *tert*-butyl ester of poly(**1e**) block. ^{13}C NMR

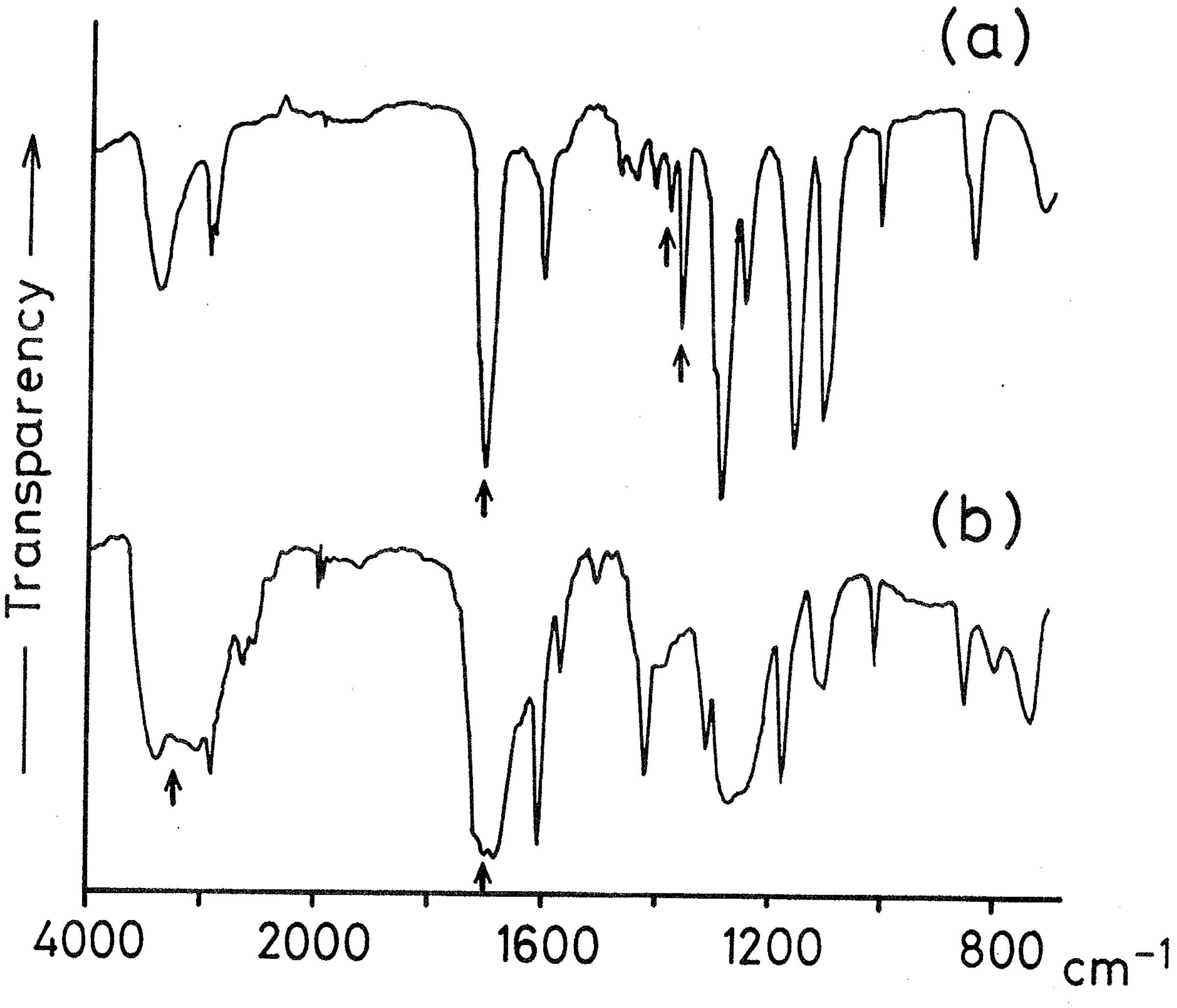


Figure 3-6. IR spectra of poly(**1e**) (a) and poly(**2**) (b).
The full elaboration on the absorption bands indicated by arrows is described in the Results and Discussion.

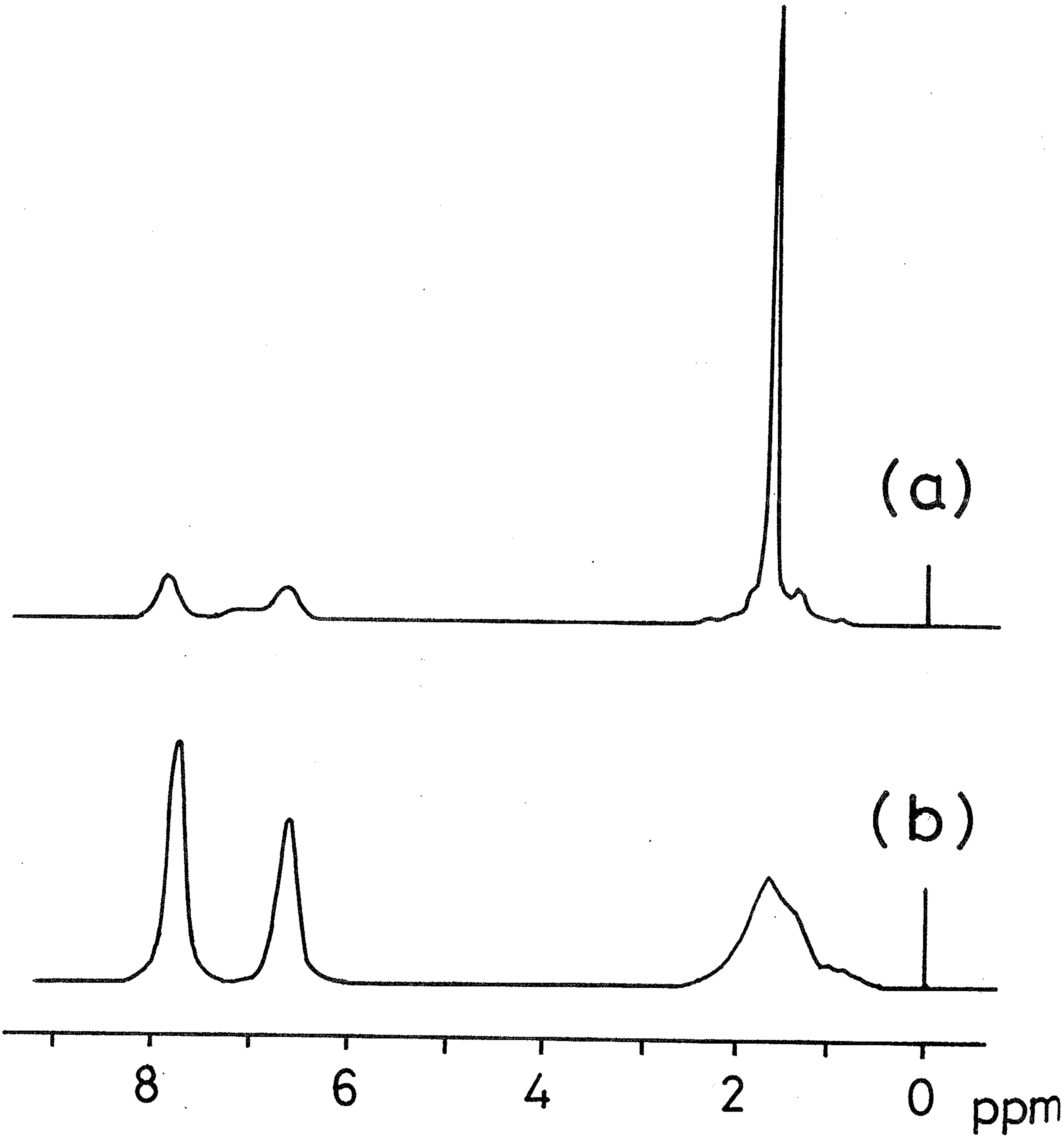


Figure 3-7. ^{1}H NMR spectra of poly(**1e**) (a) and poly(**2**) (b).

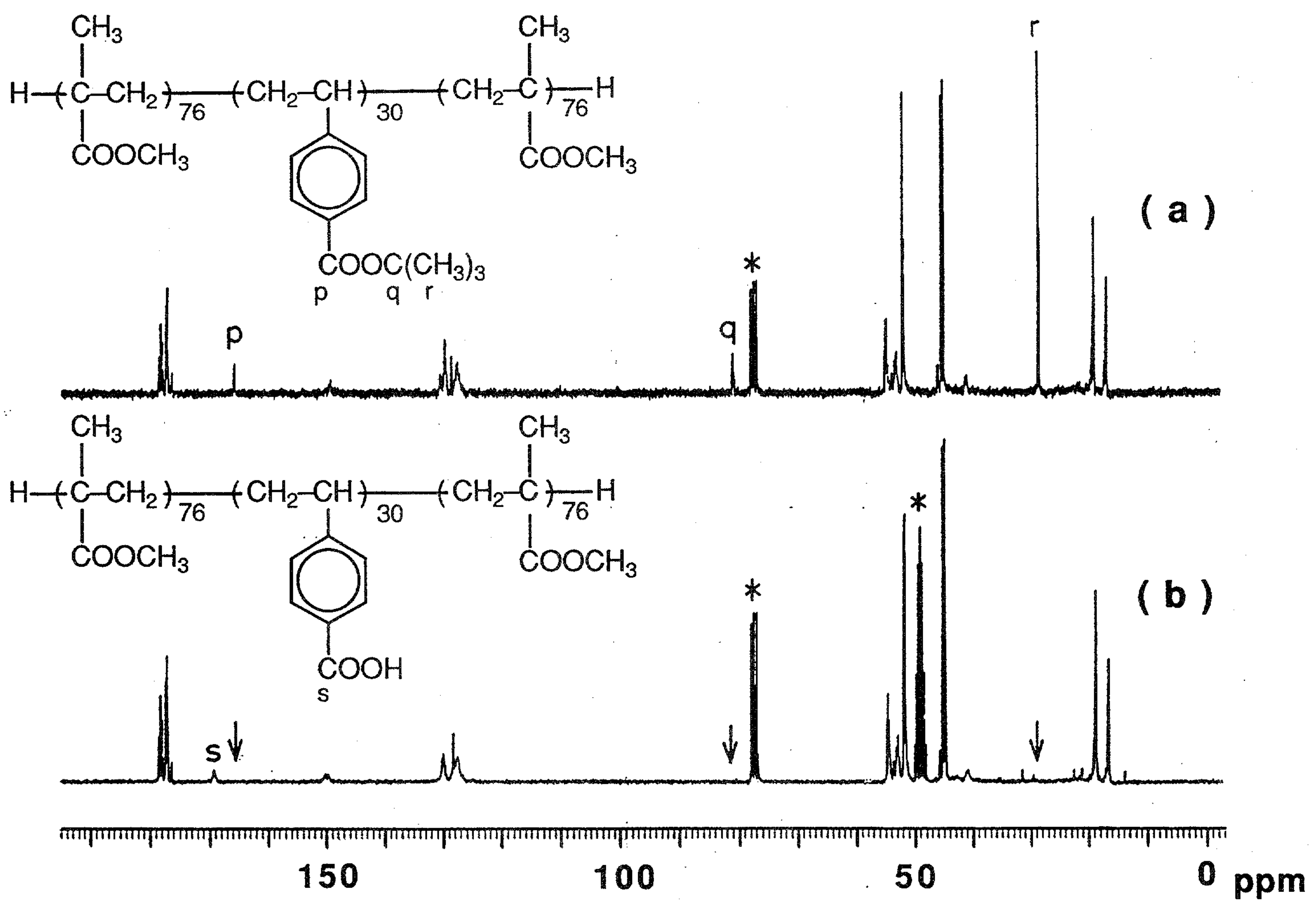


Figure 3-8. ^{13}C NMR spectra of the block copolymer (Table 3-3, run 1) before hydrolysis in $CDCl_3$ (a) and the hydrolyzed one in the mixed solvent of $CDCl_3$ and CD_3OD (b). After hydrolysis, peaks, p, q, r, corresponding to the *tert*-butyl ester carbons disappear as indicated by arrows and new signal, s, due to carboxy carbon appears. Peaks attributable to solvent are marked with asterisks (*).

spectra (Figure 3-8) clearly show that the highly chemoselective hydrolysis of the block copolymer with MMA occurs similar to the result of Bugner.[13] The signals due to *tert*-butyl ester of poly(**1e**) segment in the block copolymer are no longer present, whereas those of poly(methyl methacrylate) segment are unchanged. These high reactivity and chemoselectivity to the ester function clearly demonstrate the utility of TMSI in the synthesis of amphiphilic block copolymer with controlled structure.

3-6. Solubility of the Polymers.

Table 3-4 summarizes the solubilities of the polymers synthesized in this chapter. Poly(alkyl 4-vinylbenzoate)s have similar solubilities to that of polystyrene. In contrast, hydrophilic poly(**2**) is soluble in methanol, ethanol, THF, *N*,*N*-dimethylformamide and insoluble in nonpolar solvents. The block copolymer of 4-vinylbenzoic acid and styrene shows the intermediate solubility and is particularly dissolved in mixtures of polar and nonpolar solvents: benzene/methanol, chloroform/methanol, and diethyl ether/methanol.

The glass transition temperatures (T_gs) of the polymers were measured by differential scanning calorimetry. The T_gs of poly(**1a**), poly(**1d**), and poly(**1e**) were 133, 127, and 163°C, respectively. These values for polystyrenes bearing ester functional groups were apparently higher than that of polystyrene (T_g = 100°C).

Table 3-4

Solubilities of Poly(4-vinylbenzoic acid), Poly(4-vinylbenzoate)s, Block Copolymer, and Polystyrene[a]

solvent	polymer					
	poly(**2**)	poly(**1a**)	poly(**1d**)	poly(**1e**)	block copolymer[b]	polystyrene
hexane	I	I	I	I	I	I
benzene	I	S	S	S	I	S
carbon tetrachloride	I	S	S	S	I	S
chloroform	I	S	S	S	Sw	S
diethyl ether	I	S	S	S	I	S
ethyl acetate	I	S	S	S	Sw	I
1,4-dioxane	Sw	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S	S
N,*N*-dimethylformamide	S	S	S	S	S	S
ethanol	S	I	I	I	Sw	I
methanol	S	I	I	I	Sw	I
water (basic)	I	I	I	I	I	I
water (acidic)	Sw	I	I	I	I	I

[a] I, insoluble; S, soluble; Sw, swelling.

[b] $(\mathbf{2})_{30}$–$(\text{styrene})_{130}$–$(\mathbf{2})_{30}$: obtained by the hydrolysis of block copolymer shown in Table 3-3, run 20.

3-7. Conclusion.

At –95°C, the anionic polymerization of *tert*-butyl 4-vinylbenzoate, **1e**, constructs a stable living polymer inhibiting the undesirable side reactions.[15] The bulkiness of the ester alkyl group and the electron-withdrawing effect of ester group seem to play an important role in the stabilization of the living end. From this living polymerization system, poly(**1e**)s and the block copolymers with well-defined chain structures are synthesized. Finally, the resulting poly(**1e**) is completely hydrolyzed under a mild condition to afford poly(4-vinylbenzoic acid) with controlled chain length.

Experimental Section

Materials. 4-Vinylbenzoic acid kindly supplied from Hokko Chemical Industry Co., Ltd., was used without further purification. α-Methylstyrene, styrene, isoprene, and MMA was distilled over calcium hydride. 1,1-Diphenylethylene (DPE) prepared by a literature procedure[16] was purified by fractional distillation and was finally distilled together with THF from benzylmagnesium chloride under vacuum. THF used as a solvent in all polymerization experiments was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through a vacuum line from sodium naphthalenide solution.

Initiators. Cumylpotassium was prepared by the reaction of cumyl methyl ether with potassium-sodium alloy in THF at room temperature for 10 h followed by filtration of the reaction mixture. Metal naphthalenides were prepared by the reactions of a small excess naphthalene with the corresponding alkali metal in THF. Initiators were stored in ampules equipped with breakseals at –30°C. The oligo(α-methylstyryl)dilithium, -disodium, -dipotassium, and -dicesium were freshly prepared just prior to polymerization from the corresponding metal naphthalenides and a 2-4 M quantity of α-methylstyrene at 20°C for 1 min and then at –78°C for 10 min. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed tube under vacuum.[17]

4-Vinylbenzoyl Chloride. To a mixture of thionyl chloride (28 mL) and 4-*tert*-butylpyrocatecol (10 mg) under nitrogen in an ice bath was added 4-vinylbenzoic acid (13.1 g, 88.5 mmol) in small portions with stirring below 10°C for 4 h and at 40°C for 1 h to afford a homogeneous solution. After removal of unreacted thionyl chloride, distillation gave 13.3 g (79.9 mmol, 90%) of 4-vinylbenzoyl chloride as a colorless liquid at 79-83°C (0.5 mmHg) (lit.[18] 69.5-70.0°C (0.1 mmHg)): 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.44 and 5.88 (2d, 2H, J = 11 and 17 Hz, CH_2=), 6.72 (dd, 1H, -CH=), 7.38-8.03 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 118.3 (vinyl, CH_2=), 126.5 (Ar, C3), 131.7 (Ar, C2), 132.1 (Ar, C1), 135.3 (vinyl, -CH=), 144.4 (Ar, C4), 167.5 (C=O).

Methyl 4-Vinylbenzoate (1a). To a mechanically stirred mixture of dry methanol (3.0 mL, 74 mmol) and triethylamine (10 mL) in dry ether (50 mL) under nitrogen, 4-vinylbenzoyl chloride (9.25 g, 55.6 mmol) in dry ether (30 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated salt was filtered off and the filtrate was washed three times with 0.5 N HCl (100 mL) and twice with saturated $NaHCO_3$ solution (100 mL), and then dried over $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether three times to yield pure white crystal of **1a** (7.24 g; 44.7 mmol; 80%; mp 35-36°C): 200 MHz ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3H, OCH_3), 5.39 and 5.86 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.75 (dd, 1H, -CH=), 7.44-8.02 (m, 4H, aromatic); 50 MHz ^{13}C NMR ($CDCl_3$) δ 51.8 (OCH_3), 116.2 (vinyl, CH_2=), 125.9 (Ar, C3), 129.1 (Ar, C1), 129.7 (Ar, C2), 135.9 (vinyl, -CH=), 141.7 (Ar, C4), 166.5 (C=O).

***tert*-Butyldimethylsilyl 4-Vinylbenzoate (1b).** To a stirred mixture of 4-vinylbenzoic acid (5.0 g, 34 mmol) and imidazole (6.0 g, 88 mmol) in dry *N,N*-dimethylformamide (DMF) (80 mL) under nitrogen, *tert*-butyldimethysilyl chloride (6.7 g, 45 mmol) in dry DMF (20 mL) was added dropwise in an ice bath and then stirred overnight at room temperature. After removal of DMF under vacuum, distillation of the residue gave a liquid containing imidazole hydrochloride at 100-110°C (1 mmHg). To remove the solid salt, hexane was added to the mixture, and the liquid layer was separated by decantation. After removal of hexane, distillation gave 2.6 g (9.9 mmol, 29%) of **1b** as a colorless liquid at 103-105°C (1 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 6H, $SiCH_3$), 1.01 (s, 9H, $SiCCH_3$), 5.36 and 5.83 (2d, 2H, J = 11, 18 Hz, CH_2=), 6.75 (dd, 1H, -CH=), 7.39-8.02 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ -4.6 ($SiCH_3$), 18.0 (SiC), 25.8 (CH_3), 116.5 (vinyl, CH_2=), 126.2 (Ar, C3), 126.9 (Ar, C1), 130.5 (Ar, C2), 136.2 (vinyl, -CH=), 142.0 (Ar, C4), 166.4 (C=O).

Allyl 4-Vinylbenzoate (1c). The reaction was performed according to the procedure for **1a** using allyl alcohol (4.7 g, 81 mmol) in place of methanol and distillation gave 10.7 g (57.0 mmol, 77%) of **1c** as a colorless liquid at 96-106°C (1 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 4.82 (broad d, 2H, OCH_2), 5.2-6.2 (overlapping m, 5H, $-OCH_2-CH{=}CH_2$ and CH_2=), 6.75 (dd, 1H, J = 11 and 18 Hz, -CH=), 7.41-8.07 (m, 4H, aromatic); 50 MHz ^{13}C NMR ($CDCl_3$) δ 65.4 (OCH_2), 116.3 (vinyl, CH_2=), 118.0 (allyl, CH_2=), 126.0 (Ar, C3), 129.7 (Ar, C1), 129.8 (Ar, C2), 132.2 (allyl, -CH=), 135.9 (vinyl, -CH=), 141.9 (Ar, C4), 165.7 (C=O).

Isopropyl 4-Vinylbenzoate (1d). The reaction was performed according to the procedure for **1a** using isopropanol (12.0 g, 200 mmol) in place of methanol and distillation gave 10.3 g (54.4 mmol, 79%) of **1d** as a colorless liquid at 69-70°C (0.5 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.38 (d, 6H, J = 6Hz, CH_3), 5.25 (hepta, 1H, J = 6Hz, $CHCH_3$), 5.37 and 5.85 (2d, 2H, J = 11 and 17 Hz, CH_2=), 6.76 (dd, 1H, -CH=), 7.40-8.04 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 67.9 (OCH), 115.9 (vinyl, CH_2=), 125.8 (Ar, C3), 129.5 (Ar, C2), 129.9 (Ar, C1), 135.9 (vinyl, -CH=), 141.5 (Ar, C4), 165.3 (C=O).

***tert*-Butyl 4-Vinylbenzoate (1e).** To a mechanically stirred mixture of *tert*-butyl alcohol (100 mL), potassium *tert*-butoxide (180 mmol) and dry ether (50 mL) under nitrogen, 4-vinylbenzoyl chloride (13.3 g, 79.9 mmol) in dry ether (30 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The mixture was washed twice with 2 N HCl (100 mL) and twice with saturated $NaHCO_3$ solution (100 mL), and then dried over $MgSO_4$. After removal of ether, distillation gave 14.0 g (68.5 mmol, 86%) of **1e** as a colorless liquid at 82-84°C (0.8 mmHg): 200 MHz ^1H NMR ($CDCl_3$) δ 1.60 (s, 9H, CCH_3), 5.36 and 5.84 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.75 (dd, 1H, -CH=), 7.41-7.96 (m, 4H, aromatic); 50 MHz ^{13}C NMR ($CDCl_3$) δ 28.3 (CH_3), 80.8 ($OCCH_3$), 116.0 (vinyl, CH_2=), 125.9 (Ar, C3), 129.6 (Ar, C2), 131.2 (Ar, C1), 136.1 (vinyl, -CH=), 141.4 (Ar, C4), 165.4 (C=O).

Purification. In order to remove impurities in monomer, phenylmagnesium chloride (5 mL, 0.25 M solution in THF) was added to *tert*-butyl 4-vinylbenzoate (6.1 g, 30 mmol) at –78°C under a degassed condition in an all-glass apparatus equipped with breakseals and the mixture was stirred for 10 min. It was then degassed again and distilled on a vacuum line into the ampules fitted with breakseals. The other liquid monomers were also purified in a similar manner. The resulting monomer solutions, the concentrations of which were 0.4-0.6 M in THF, were stored at –30°C until they were ready to use for anionic polymerization.

The purified crystalline of methyl 4-vinylbenzoate was dried over P_2O_5 for 48 h in an apparatus equipped with a breakseal under vacuum (10^{-6} mmHg) and then diluted with THF to use for the anionic polymerization.

Polymerization Procedures. All the polymerizations were carried out at low temperatures with shaking under vacuum in the all-glass apparatus equipped with breakseals as previously reported.[17] Hexane-acetone (1:1) cooled with liquid nitrogen at –95°C and dry ice-acetone at –40 and –78°C were used as refrigerants. After the polymerization systems were kept at various temperatures for the required time, the reaction was terminated with methanol. The reaction mixture was concentrated by evaporation and poured into methanol to precipitate polymers, and then the polymers were collected by filtration and freeze-dried from benzene. Poly(**1d**) and poly(**1e**) obtained were characterized by IR, ^{1}H and ^{13}C NMR spectroscopies.

Poly(1d): IR 1710 cm^{-1} (C=O), 1350, 1370 cm^{-1} (isopropyl, C-H deformation); 90 MHz ^{1}H NMR ($CDCl_3$) (Figure 3-1) δ 0.9-2.1 (m, 9H, CH_3 and CH_2CH), 5.2 (m, 1H, $CHCH_3$), 6.2-7.8 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 22.0 (CH_3), 40-42 (CH_2CH), 68.2 (OCH), 126-131 (Ar, C1, C2, C3), 149 (Ar, C4), 165.7 (C=O).

Poly(1e): IR (Figure 3-6a) 1710 cm^{-1} (C=O), 1360, 1390 cm^{-1} (*tert*-butyl, C-H deformation); 90 MHz ^{1}H NMR ($CDCl_3$) (Figure 3-7a) δ 1.0-2.1 (m, 12H, CH_3 and CH_2CH), 6.3-7.8 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 28.2 (CH_3), 40-42 (CH_2CH), 80.7 ($OCCH_3$), 126-131 (Ar, C1, C2, C3), 149 (Ar, C4), 165.5 (C=O); Anal. Calcd for poly(**1e**) $(C_{13}H_{16}O_2)_n$: C, 76.44; H, 7.90; N, 0.00. Found: C, 76.38; H, 7.89; N, 0.00.

Deprotection of Poly(1e). To a stirred mixture of poly(**1e**) (0.45 g, 2.2 mmol based on monomer unit) and sodium iodide (2.0 g, 14 mmol) in acetonitrile (10 mL) and chloroform (20 mL) was added 2.0 mL (15 mmol) of trimethylsilyl chloride at once at room temperature. The reaction mixture immediately turned yellow, and the white precipitate of sodium chloride appeared. After 10 min, the mixture was concentrated by evaporation, redissolved in THF, and poured into 0.1 N HCl containing $Na_2S_2O_3$ for decolorination to precipitate the polymer. The obtained polymer was purified by reprecipitation from THF-water and THF-hexane system, and then freeze-dried from 1,4-dioxane containing a small amount of methanol. A pure white powder (0.27 g, 82%, 1.8 mmol based on monomer unit) of poly(4-vinylbenzoic acid) was obtained: IR (Figure 3-6b) 3300-2500 cm^{-1} (O-H), 1700 cm^{-1} (C=O); 90 MHz ^{1}H NMR (CD_3OD) (Figure 3-7b) δ 1.0-2.3 (m, 3H, CH_2CH), 6.3-7.8 (m, 4H, aromatic); 23 MHz ^{13}C NMR (CD_3OD) δ 42-45 (CH_2CH), 128-133 (Ar, C1, C2, C3), 153 (Ar, C4), 170.6 (C=O); Anal. Calcd for $(C_9H_8O_2)_n$: C, 72.96; H, 5.44; N, 0.00. Found: C, 72.37; H, 5.98; N, 0.00.

Methylation of Poly(4-vinylbenzoic acid), Poly(2). To a suspension of poly(2) (0.18 g, 1.2 mmol based on monomer unit) in benzene (30 mL) was added diazomethane[19] (8.5 mmol) in ether (20 mL) by small portions at room temperature. As the methylation proceeded, the polymer dissolved into the solution with yielding bubble of nitrogen. The homogeneous yellow reaction mixture was kept in a well-ventilated hood overnight at room temperature. After the addition of acetic acid to quench unreacted diazomethane, the reaction mixture was concentrated by evaporation and poured into methanol. The polymer was recovered by filtration, redissolved in THF, and reprecipitated into methanol. The yield of polymer was fairly good (0.18 g, 90%). The polymer was identified as poly(methyl 4-vinylbenzoate) by the IR, ^{1}H and ^{13}C NMR spectroscopic measurements: IR 1720 cm^{-1} (C=O); 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.8-2.2 (m, 3H, CH_2CH), 3.9 (broad s, 3H, OCH_3), 6.8-7.9 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40-42 (CH_2CH), 52.1 (OCH_3), 126-131 (Ar, C1, C2, C3), 149 (Ar, C4), 166.8 (C=O).

Measurements. Infrared spectra (KBr disc) were recorded on a Jasco IR-G spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^{1}H, 22.53 MHz ^{13}C), a JEOL FX-200 (199.56 MHz ^{1}H, 50.18 MHz ^{13}C), and a JEOL GSX-270 (67.80 MHz ^{13}C) in $CDCl_3$ or CD_3OD. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Size exclusion chromatograms (SEC) for molecular weight distribution determination were obtained at 40°C with Toyo Soda HLC-802 instrument with ultraviolet or refractive index detection. THF was the carrier solvent at a flow rate of 1.4 mL min^{-1}. Vapor pressure osmometry (VPO) measurements for number average molecular weight determination were made with a Corona 117 instrument in benzene solution with highly sensitive thermoelectric couple and equipment of very exact temperature control. The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC 5200TA station. The samples were first heated to 240°C, cooled rapidly to –20°C, and then scanned again at a rate of 20°C min^{-1}.

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Chapter 4

Living Anionic Polymerizations of 2-, 3-, and 4-(Trimethylsilyl)ethynylstyrene

ABSTRACT: The anionic polymerizations of the three ethynylstyrenes protected with a trimethylsilyl group have been carried out in THF at –78°C with a variety of initiators. The monomers involve 4-(trimethylsilyl)ethynylstyrene (**1**), 3-(trimethylsilyl)ethynylstyrene (**2**), and 2-(trimethylsilyl)ethynylstyrene (**3**) that are isomers with different substituent positions. They are found to undergo anionic living polymerization. The polymers from **1** and **3** were observed to have molecular weights predictable from monomer to initiator ratios and narrow molecular weight distributions ($M_w/M_n < 1.14$). From the *meta* isomeric monomer, **2**, on the other hand, the poly(**2**)s with somewhat broad molecular weight distributions ($M_w/M_n = 1.22 - 1.39$) were obtained, although their observed molecular weights were agreed with those predicted. Complete deprotection of the silyl groups from the polymers provides the poly(2-, 3-, and 4-ethynylstyrene)s with well-regulated chain lengths, identical to those of the parents poly(**1**), poly(**2**), and poly(**3**). The poly(4-ethynylstyrene) thus obtained can be quantitatively brominated to give a poly[4-(1,2-dibromoethenyl)styrene] which still retains a narrow distribution of the molecular weight. Some novel block copolymers with a high degree of block integrity are synthesized by using these new living polymers. They are poly[(2-vinylpyridine)-*b*-**1**-*b*-(2-vinylpyridine)], poly(**1**-*b*-styrene-*b*-**1**), poly(**1**-*b*-isoprene-*b*-**1**), poly(**2**-*b*-styrene-*b*-**2**), poly(MMA-*b*-**3**-*b*-MMA), and poly(**3**-*b*-styrene-*b*-**3**).

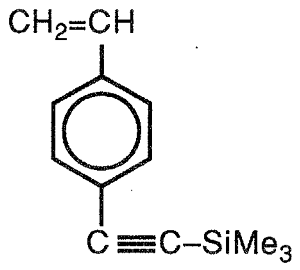
Introduction

In order to synthesize well-defined functional polymers with precisely regulated polymer chain lengths, it has been recently developing a new strategy which combines both the methods of protection and anionic living polymerization of functional monomers.[1] The reason to protect the functional groups is that conventional anionic living polymers from styrene and 1,3-dienes do not tolerate to most of functional groups. The strategy involves protection of the functional group of a monomer and the anionic living polymerization of the protected monomer, followed by deprotection to regenerate the original functional group. If this route could successfully be executed, the resulting polymer would have a functional group in each monomer unit and desirable characteristics of the parent living polymer with respect to the main chain structure.

Through the pioneering work, Nakahama and his co-workers have successfully synthesized a variety of polystyrene derivatives mainly *para*-substituted with functional groups such as OH,[2,3] CH_2CH_2OH,[4,5] NH_2,[6,7] CH_2NH_2 and $CH_2CH_2NH_2$,[8] CHO,[9-11] $COCH_3$,[12] COOH,[13,14] and poly(2-hydroxyethyl methacrylate)[15]. Similarly, other research groups also have synthesized poly(4-vinylphenol)[16,17] and poly(methacrylic acid).[18,19] Clearly, this protection–anionic living polymerization–deprotection strategy becomes generally and versatilely used for synthesizing such functional polymers.

As a part of this program to investigate the more general applicability of the above-mentioned strategy, this chapter focused on a polymerization of ethynylstyrenes. For the attempted synthesis of poly(ethynylstyrene)s, both the C-H and the C≡C bonds of ethynyl functions may require protection before their anionic polymerizations. It is known that the proton of C≡C-H bond is relatively acidic ($pK_A = 25$) to destroy the highly nucleophilic anionic initiators used for styrene derivatives.[20] Moreover, the C≡C bond is believed to be susceptible to addition reactions as well as polymerization.[21] Among a number of known protecting groups,[22] the trimethylsilyl group would be the most suitable one for this purpose, since it was reported that the Si-C≡C bonds were stable toward carbanionic species[23] but readily cleaved with F^- [24] or OH^-.[25] In addition, the introduction of a trimethylsilyl group into *β*-position of ethynyl function may become more resistant to undesirable nucleophilic addition reaction and anionic polymerization.

This chapter deals with the anionic living polymerization of 4-(trimethylsilyl)ethynylstyrene (**1**). In addition, the corresponding *meta* and *ortho* isomers, (**2**) and (**3**), are synthesized and their anionic polymerization are attempted at the aim for examining the general effectiveness of silyl protection under the anionic polymerization conditions.



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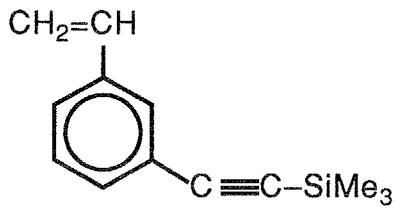

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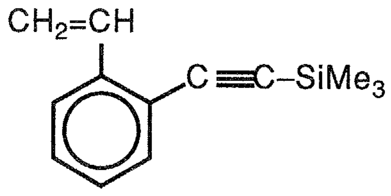

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Results and Discussion.

4-1. Anionic Polymerization of 1. At first, to examine the anionic polymerizability of **1**, the polymerization of **1** was carried out with a variety of anionic initiators. The employed initiators included oligo(*α*-methylstyryl)lithium and -dipotassium, *n*- and *sec*-butyllithium (*n*-BuLi and *s*-BuLi), and potassium naphthalenide.

The reaction mixtures always exhibit a brownish red and dark red in the cases of lithium salt and potassium salt, respectively, which indicate production of polystyryl anions from **1**. The characteristic colors remained unchanged at –78°C even after 24 h, but immediately disappeared by quenching a few drops of degassed methanol. The polymers were obtained quantitatively in all runs under the conditions. From the analytical results of ^{1}H, ^{13}C NMR, and IR, it is obvious that the anionic polymerization of **1** proceeds in a vinyl polymerization mode exclusively to afford the expected poly[4-(trimethylsilyl)ethynylstyrene]. Furthermore, no cleavage of the Si-C bond was observed by the same analyses after purification of the polymer by reprecipitation thrice using a THF-methanol system. The purified polymers were therefore directly characterized by SEC and VPO in the form of poly[4-(trimethylsilyl)ethynylstyrene].

Table 4-1 summarizes the molecular weights and molecular weight distributions shown by M_w/M_n values of the resulting polymers. The SEC analyses revealed unimodal and symmetrical peaks with narrow distributions for all polymer samples. The M_w/M_n values were less than 1.1. As can be seen in Table 4-1, the number-average molecular weights (M_n) measured by VPO are in fair agreement with those values predicted from [M] to [I] ratios in most cases.

The higher molecular weights tend to have more deviation from the calculated values. For example, a M_n was obtained to be 99 000 by VPO in the polymer with M_n calculated as 77 000. Since this polymer sample still possessed a narrow molecular weight distribution, trace impurities in the monomer would cause some loss of initiator before propagation reaction, so that the molecular weight would be somewhat higher than expected. More rigid purification of **1** may possibly be required to obtain the polymers with M_n values of 10^5 order.

Table 4-1

Anionic Polymerization of **1** in THF at –78°C for 0.5-1 h[a]

run	**1**	initiator		α-methylstyrene	$10^{-3}M_n$		
	mmol	type	mmol	mmol	calcd[b]	obsd[c]	M_w/M_n[d]
1	3.08	K-Naph[e]	0.105	0.322	12	10	1.04
2	3.14	K-Naph	0.0998	-	13	14	1.09
3	3.72	K-Naph	0.0633	0.319	25	25	1.04
4	3.17	*s*-BuLi[f]	0.0572	-	11	12	1.10
5	3.09	*n*-BuLi[g]	0.0497	-	12	17	1.09
6	3.69	*n*-BuLi	0.0456	0.304	17	15	1.04
7	5.04	Li-Naph[h]	0.0915	0.327	23	21	1.13
8	2.85	*s*-BuLi	0.0241	0.356	25	28	1.03
9	2.91	*s*-BuLi	0.0196	0.246	31	39	1.04
10	4.93	*s*-BuLi	0.0245	0.317	42	40 (39)[i]	1.08
11	3.38	*s*-BuLi	0.00921	0.257	77	99 (98)[i]	1.07

[a] Yields of polymers were quantitative in all runs. [b] M_n calcd was calculated from [M] to [I] ratio. [c] M_n obsd was obtained by VPO in benzene. [d] M_w/M_n was determined by SEC using polystyrene calibration. [e] Potassium naphthalenide. [f] *sec*-Butyllithium. [g] *n*-Butyllithium. [h] Lithium naphthalenide. [i] Values were M_ws obtained by light scattering in benzene at 25°C.

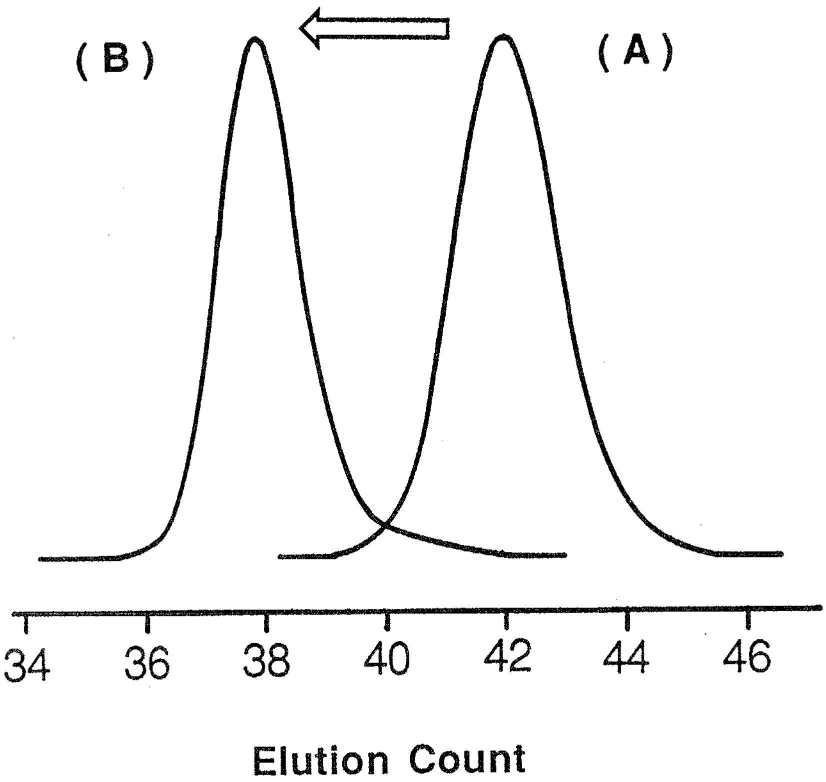


Figure 4-1. SEC curves of poly(**1**)s obtained at –78°C: (A) the first-stage polymerization, M_n(obsd) = 7500, M_w/M_n = 1.05; (B) the second-stage polymerization, M_n(obsd) = 18 000, M_w/M_n = 1.04 (the second feed of monomer was added 30 min after the first-stage polymerization).

It is of great importance to elucidate the stability of the growing chain for proof of livingness of the polymerization. For this purpose, postpolymerization is one of the most suitable method. After the first polymerization of **1** with oligo(α-methylstyryl)dipotassium at –78°C for 30 min, the second feed of **1** was then added to the reaction mixture. It was allowed to stand an additional 30 min to complete the further polymerization. Both pre- and postpolymers were obtained quantitatively. As shown in Figure 4-1, the peak of postpolymer shifts completely to a higher molecular weight side and no peak is observed at all in the molecular weight region of the prepolymer. Both the pre- and postpolymers are found to possess the desirable M_n values and narrow molecular weight distributions. Evidently, the propagating polymer chain end is stable at –78°C at least for 30 min and is capable of initiating further polymerization quantitatively. This result as well as the results on molecular weight and the distribution clearly confirms the living character of the anionic polymerization of **1**. Accordingly, the trimethylsilyl group perfectly protects the terminal ethynyl function of 4-ethynylstyrene during the course of the anionic living polymerization. Furthermore, narrow distributions of molecular weight offer convincing evidence that the initiation reaction must be sufficiently rapid under these conditions.

4-2. Anionic Polymerizations of 2 and 3.

In order to examine the effectiveness of the trimethylsilyl protecting group for other ethynylstyrenes, the corresponding *meta* and *ortho* substituted monomers, **2** and **3**, were synthesized and their anionic polymerizations were attempted under exactly the same conditions.

The anionic polymerization of the *meta* isomeric monomer, **2**, was carried out in THF at –78°C with either oligo(α-methylstyryl)dilithium or the dipotassium salt. A characteristic brownish red color was observed in each of the polymerization mixtures. Yields of polymers were quantitative after 30 min. Occurrence of the vinyl polymerization of **2** was clearly ascertained by the IR, ^1H and ^{13}C NMR analyses. The Me_3Si-C bond was observed to be stable and intact after a purification workup.

The results are summarized in Table 4-2, which includes the M_n and M_w/M_n values. A comparison for the M_n value of each polymer shows that the values observed are in good agreement with those calculated within experimental error. The SEC traces of polymers all show unimodal and quite symmetrical peaks, although the molecular weight distributions are observed to be somewhat broad, the M_w/M_n values being in the range from 1.22 to 1.39. To ascertain the living character of the polymerization of **2**, the postpolymerization was carried out similar to the case of **1**. Yields of pre- and postpolymers were quantitative. The SEC analyses of both polymers showed that the peak of postpolymer shifted to a higher molecular weight side, although the peaks of pre- and postpolymers were relatively broad and therefore overlapped each other to some extents. Both the pre- and postpolymers were found to possess predictable molecular weights. The result of postpolymerization suggests that the active propagating chain end from **2** appears stable and initiates the further polymerization. These results as well as the red coloration in the polymerization systems indicate that the anionic polymerization of **2** has living nature.

As will be mentioned in the section on the synthesis of block copolymers, the resonance effect and electron-withdrawing nature[28] of (trimethylsilyl)ethynyl group may significantly influence both the reactivities of **1-3** and the active growing chain ends of the resulting living polymers. Moreover, those effects must be different by the position of substituent. It seems that somewhat broad molecular weight distributions of the poly(**2**)s can be due to a slow initiation compared to the propagation reaction, since both the reaction rates may be caused by the above-mentioned effects.

Similarly, the anionic polymerization of the *ortho* substituted monomer, **3**, was carried out at –78°C in THF with oligo(α-methylstyryl)lithium, -dilithium, or -dipotassium. Upon addition of **3** to the initiator solutions, an immediate and characteristic color change from dark red to dark violet occurred in all the cases. Yields of polymers were quantitative after 30 min. The expected vinyl polymerization and no cleavage of Si-C bond are clearly demonstrated by the analyses of IR, ^{1}H, and ^{13}C NMR. The results of the polymerization are summarized again in Table 4-2.

Table 4-2

Anionic Polymerizations of **2** and **3** in THF at –78°C for 0.5 h[a]

run	monomer	initiator		α-methylstyrene	$10^{-3}M_n$		
	mmol	type	mmol	mmol	calcd[b]	obsd[c]	M_w/M_n[d]
12	**2**, 2.86	K-Naph	0.111	0.310	11	13	1.22
13	**2**, 3.80	Li-Naph	0.161	0.358	10	11	1.28
14	**2**, 3.32	Li-Naph	0.0635	0.351	22	21	1.39
15	**3**, 2.73	K-Naph	0.113	0.332	10	10	1.08
16	**3**, 3.88	K-Naph	0.101	0.270	16	15	1.10
17	**3**, 3.03	K-Naph	0.0568	0.295	23	19	1.10
18	**3**, 2.35	*s*-BuLi	0.0458	0.314	11	13	1.10
19	**3**, 2.86	Li-Naph	0.0969	0.255	12	10	1.14

[a] Yields of polymers were quantitative in all runs.

[b] M_n calcd was calculated from [M] to [I] ratio.

[c] M_n obsd was obtained by VPO in benzene.

[d] M_w/M_n was determined by SEC using polystyrene calibration.

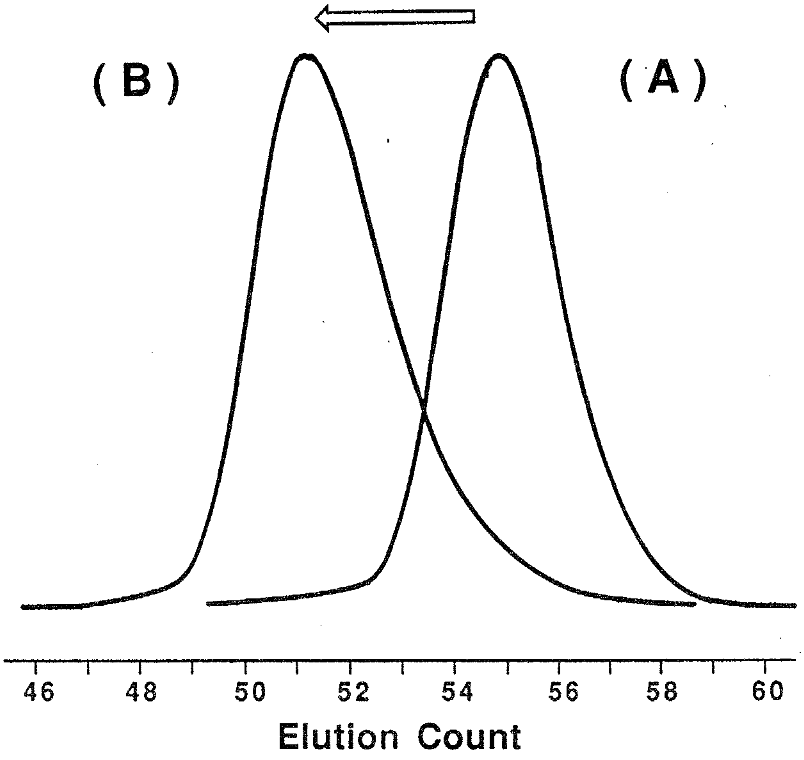


Figure 4-2. SEC curves of poly(**3**)s obtained at –78°C: (A) the first-stage polymerization, M_n(obsd) = 5900, M_w/M_n = 1.06; (B) the second-stage polymerization, M_n(obsd) = 12 000, M_w/M_n = 1.10 (the second feed of monomer was added 30 min after the first-stage polymerization).

As can be seen, there is a fair agreement between the M_n values calculated and observed by VPO. Narrow molecular weight distributions for all samples are realized by the SEC measurement. The M_w/M_n values were observed to be 1.08 - 1.14. These results indicate the living polymerization of **3** under the conditions. The success of the postpolymerization of **3** also provides a direct evidence of the living polymerization (Figure 4-2). The effectiveness of trimethylsilyl protection for *p*-, *m*-, and *o*-ethynylstyrenes is thus evident in their anionic living polymerizations.

The success of anionic living polymerization of the *ortho* substituted monomer is of particular interest,[26] because it is possible to obtain the stereoregulated polymers with well-regulated chain lengths. In fact, the splitting of C1 carbon of the aromatic ring of the 2-ethynylstyrene unit appears different from those of the *meta* and *para* derivatives, although more detailed information by high resolution NMR will be needed to discuss this.

4-3. Block Copolymerizations of 1-3 with Isoprene, Styrene, 2-Vinylpyridine, and Methyl Methacrylate.

One of the most characteristic advantages of living polymerization is to provide the best method for creating block copolymers with precisely controlled chain structures and compositions. In addition to such a synthetic utility, the block copolymerization by using living polymers has another important aspect, that relative reactivities of monomers and the living growing chain ends can be elucidated from the effectiveness of copolymerization. Furthermore, the result may also give direct information on the stability of living polymer at the first-stage. In this section, the block copolymerizations of **1**-**3** with isoprene, styrene, 2-vinylpyridine (2VP), and methyl methacrylate (MMA) have been performed to examine the synthetic possibility of novel block copolymers with poly(ethynylstyrene) block segments. The reactivities of **1**-**3** and their living polymers are also discussed from the results of the block copolymerizations.

At first, an ABA triblock copolymer of **1** (A monomer) with styrene (B monomer) was synthesized by the addition of **1** to the difunctional living polystyrene initiated with potassium naphthalenide in THF at –78°C. The polymerization proceeded quantitatively to yield the expected block copolymer having a predictable molecular weight and composition and a narrow molecular weight distribution as shown in Table 4-3. The SEC trace also demonstrated the successful block copolymerization by the observation that the peak of block copolymer shifted completely to higher molecular weight side and that it was a symmetrical unimodal peak with a narrow distribution

(Figure 4-3). Similarly, a well-defined ABA block copolymer of poly(**1**-*b*-isoprene-*b*-**1**) was synthesized. Furthermore, novel ABA triblock copolymers containing poly(**2**) and poly(**3**) segments as terminal A blocks were also successfully synthesized by the addition of **2** and **3** to the difunctional living polystyrene in a manner similar to the case of **1**. Their well-defined and regulated structures are demonstrated by VPO, SEC, and ^{1}H NMR analyses. The poly(**2**-*b*-styrene-*b*-**2**) was observed to possess a somewhat broad molecular weight distribution, the M_w/M_n being 1.24, as would be expected from the result of homopolymerization of **2**.

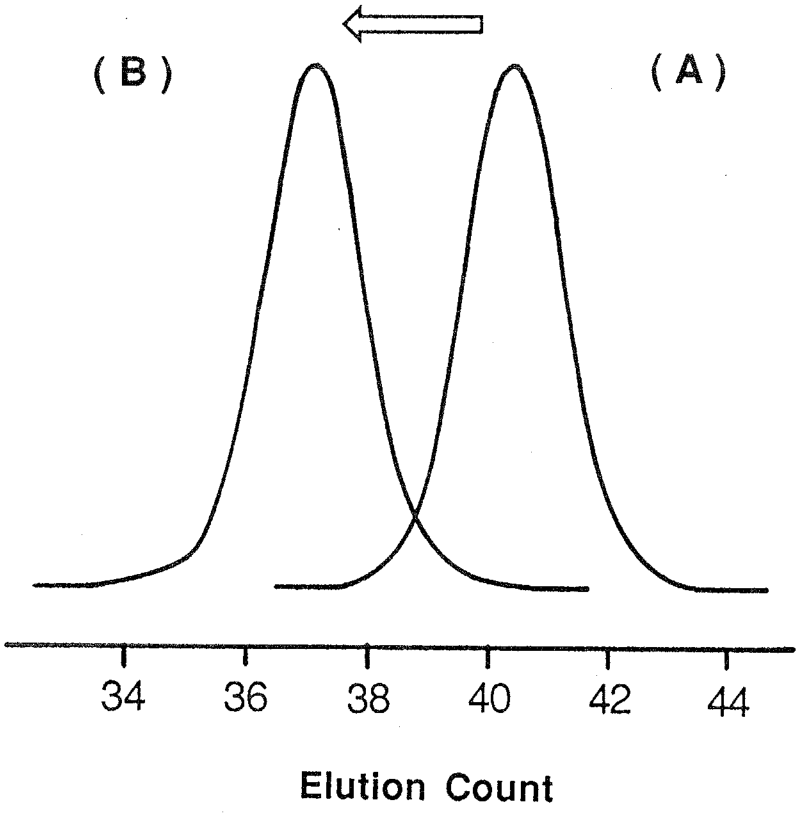


Figure 4-3. SEC curves of polystyrene at the first-stage polymerization (A) and poly(**1**-*b*-styrene-*b*-**1**) obtained at –78°C (B) (Table 4-3, run 21): peak A, M_n(obsd) = 10 000, M_w/M_n = 1.03; peak B, M_n(obsd) = 22 000, M_w/M_n = 1.03 (the second monomer was added 30 min after the first-stage polymerization).

Table 4-3

Block Copolymerization of **1**, **2**, and **3** with Isoprene, Styrene, 2-Vinylpyridine (2VP), and Methyl Methacrylate (MMA) in THF at –78°C[a]

			A	B	block copolymer (homopolymer[b])		
run	initiator	block type	monomer	monomer	$10^{-3}M_n$(calcd)[c]	$10^{-3}M_n$(obsd)[d]	M_w/M_n[e]
20	K-Naph	A-B-A	**1**	isoprene	23 (14)	26 (15)	1.05 (1.05)
21	K-Naph	A-B-A	**1**	styrene	21 (12)	22 (10)	1.06 (1.03)
22	*s*-BuLi/DPE[f]	B-A	**1**	2VP	22 (8.4)	g (7.8)	g (1.04)
23	Li-Naph	B-A-B	**1**	2VP	21 (9.7)	19 (6.7)	1.09 (1.10)
24	K-Naph	A-B-A	**2**	styrene	30 (9.3)	28 (8.2)	1.24 (1.09)
25	K-Naph	A-B-A	**3**	styrene	19 (9.6)	18 (9.8)	1.06 (1.10)
26	Li-Naph/α-MeSt[g]	B-A-B	**3**	MMA	20 (7.5)	24 (9.0)	1.18 (1.12)

[a] Yields of polymers were quantitative in all runs. [b] Homopolymers were obtained by the first-stage polymerization.
[c] M_n(calcd) was calculated from [M] to [I] ratio. [d] M_n(obsd) was obtained by VPO.
[e] M_w/M_n was determined by SEC using polystyrene calibration. [f] 1,1-Diphenylethylene. [g] α-Methylstyrene.

An attempt to synthesize the block copolymer failed by the sequential addition of **1** to the living polymer of 2-vinylpyridine (2VP) initiated with 1,1-diphenyl-3-methylpentyllithium from *sec*-BuLi and 1,1-diphenylethylene. The yield of polymer was 100% in this case. However, a bimodal distribution curve was observed in the SEC curve. The first peak eluted at low molecular weight region was consistent with that of homopolymer of 2VP polymerized at the first-stage. There appeared a second peak at the high molecular weight region which resulted from the polymerization of **1** initiated with the living poly(2VP). This peak may correspond to a block copolymer of 2VP and **1** with a higher molecular weight poly(**1**) segment than expected. It is possible to speculate that the carbanion produced from 2VP is not nucleophilic enough to polymerize **1** quantitatively, but still has the ability to initiate the polymerization of **1** very slowly. As soon as the initiation of **1** starts only a small extent from the living poly(2VP), the newly formed polystyryl anion from **1** polymerizes the monomer to consume rapidly. Residual unreacted living poly(2VP) remains even after the conclusion of the second-stage polymerization of **1**. It is obvious from the result that the living poly(2VP) shows low reactivity toward **1**.

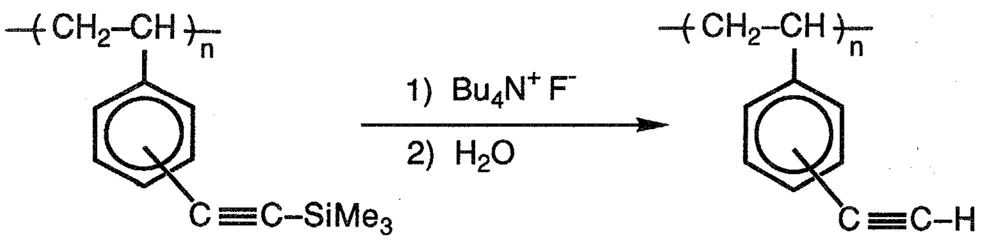
Next, the synthesis of the block copolymer with reversed sequence was attempted by addition of isoprene, styrene, or 2VP to the difunctional living polymer of **1**. The living poly(**1**) could not initiate the polymerization of isoprene at all and the homopolymer of **1** was quantitatively recovered. Styrene was polymerized with the living poly(**1**) with low efficiency, resulting in a mixture of virtual homopolymer and the block copolymer having a polystyrene segment of very high molecular weight. Thus, the synthesis of BAB block copolymers failed by the sequential addition of either isoprene or styrene to the living poly(**1**). These results indicate that the living polymer from **1** is not sufficiently nucleophilic to initiate the polymerization of either isoprene or styrene, although the latter appears to react slowly with the living polymer. On the other hand, the polymerization of a more anionically reactive 2VP occurred quantitatively to produce the poly(2VP-*b*-**1**-*b*-2VP) with a predictable molecular weight and a narrow molecular weight distribution. The SEC analysis showed that the peak of the starting poly(**1**) shifted completely to a higher molecular weight side. No peak corresponding to the homopolymer was observed.

The syntheses of a BAB triblock copolymer were also attempted by using the living poly(**3**) with styrene or MMA as a second monomer. Again, difficulty was encountered to polymerize styrene with living poly(**3**). A low initiation efficiency of the living polymer toward styrene was indicated by the analytical results of the resulting polymer. This phenomenon is very similar to the one which occurs in the living poly(**1**)-initiated polymerization of styrene as mentioned before. On the other hand, MMA was quantitatively polymerized with the difunctional living polymer of **3**. The VPO and ^{1}H NMR analyses of the resulting polymer strongly confirm a formation of poly(MMA-*b*-**3**-*b*-MMA) with desirable segment lengths. This is further supported by the observation of SEC that the resulting polymer possesses a symmetrical unimodal peak and no peak corresponding to the homopolymer.

Thus, in this chapter, some novel block copolymers with poly(ethynylstyrene) segments were successfully synthesized. However, it is observed that the sequential addition with certain combinations of **1**, **2**, or **3** and conventional monomers imposes the restriction to "reversible" block copolymerization where both the A and B blocks can initiate each other. For example, the living polymer of **1** has little or less ability to initiate the polymerization of isoprene or styrene but not vice versa. From the results of block copolymerizations obtained here, it is definite that **1** is an anionically more reactive monomer than isoprene and styrene while the living poly(**1**) is less reactive than those living polymers from isoprene and styrene. The anionic reactivities of **1** and the living polymer seem to be roughly located near that of 2VP, although a low reactivity of living poly(2VP) toward **1** has been demonstrated. This may be caused by the electron-withdrawing nature of the (trimethylsilyl)ethynyl group,[27] which enhances the reactivity of monomer by reducing the electron density of β-carbon of the vinyl group and, on the other hand, reduces the nucleophilicity of the propagating carbanion of the resulting living polymer by a similar effect. The resonance effect may also play an important role in determining their reactivities. On the reactivities among **1-3**, it can be concluded from the results that they are approximately the same, but a more detailed experiment is necessary for this discussion.

4-4. Deprotection of Trimethylsilyl Group from Poly(1-3)s.

As mentioned in the preceding section, the (trimethylsilyl)ethynyl functions of the polymers of **1-3** stayed intact during the purification step of polymers. These polymers can therefore be directly characterized in their forms by SEC, VPO, and NMR analyses. On the other hand, it was found that the Si-C bonds of polymers were readily and completely cleaved by treating with $(C_4H_9)_4NF$ in THF in a manner similar to that previously reported in the case of low molecular weight analog.[28] For example, the poly(**1**) was treated with $(C_4H_9)_4NF$ in THF at 0°C for 1 h and the mixture was poured into methanol to precipitate the polymer as shown in Scheme 4-1. The yield was quantitative assuming complete conversion to poly(4-ethynylstyrene).



poly(**1**) : *para*
poly(**2**) : *meta*
poly(**3**) : *ortho*

Scheme 4-1

The IR spectrum of the resulting polymer showed new bands at 2109 and 3294 cm^{-1} characteristic of $\nu_{C\equiv C}$ and $\nu_{C\text{-}H}$ and complete disappearance of the absorptions at 759, 868, 1250 cm^{-1} and 2159 cm^{-1} due to $\delta_{Si\text{-}Me}$ and $\nu_{C\equiv C\text{-}SiMe}$, respectively. Examination of the resulting polymer by ^{1}H NMR spectroscopy clearly showed resonances assigned to poly(4-ethynylstyrene) as shown in Figure 4-4. A resonance of the trimethylsilyl group at 0.24 ppm was no longer present in the spectrum, whereas the terminal ethynyl proton appeared instead at 3.04 ppm. It was found that the integral ratio of ethynyl to aromatic protons was exactly 1 : 4 as expected. The ^{13}C NMR also gave the consistent analytical result. It is clear from these results that complete deprotection is achieved to afford poly(4-ethynylstyrene) under the condition employed.

The SEC profile of the resulting poly(4-ethynylstyrene) demonstrated that the shapes of chromatograms before and after deprotection were indeed identical (Figure 4-5). The deprotected sample still possessed a narrow molecular weight distribution ($M_w/M_n = 1.04$) and eluted in a slightly lower molecular weight side than that of the parent polymer. This indicates no detectable side reactions leading to main chain degradation and/or chain branching during the deprotection step. Similarly, complete conversion of either poly(**2**) or poly(**3**) was achieved into poly(3-ethynylstyrene) or poly(2-

ethynylstyrene). Again their molecular weight distributions unchanged after deprotection, indicating no side reactions during the deprotection process.

Table 4-4 summarizes the solubilities of poly(**1**), poly(**2**), and poly(**3**), and the three poly(ethynylstyrene)s thus obtained after deprotections. It is generally observed that these polymers show a solubility similar to that of polystyrene and are soluble in common organic solvents such as benzene, diethyl ether, 1,4-dioxane, THF, ethyl acetate, chloroform, and acetone but insoluble in ethanol, methanol, and water. Interestingly, solubility changed from the protected polymers to deprotected ones. For example, the polymers from **1-3** are soluble in hexane but insoluble in dimethyl sulfoxide. By contrast, the deprotected polymers showed the opposite solubility in both solvents, *e.g.*, soluble in dimethyl sulfoxide, but insoluble in hexane. Little difference in the solubility was observed among the polymers with different substituent positions.

The glass transition temperatures (T_g) of all polymer samples were measured by differential scanning calorimetry, since most were new polymers and no data on their T_g values were available. The results are summarized in Table 4-5. The values of T_g of *para*-substituted poly(**1**) were higher than those of poly(**2**) and poly(**3**). As expected, the T_g values tend to increase with an increase of the molecular weight of the polymer. With poly(ethynylstyrene)s, their T_g values are found to decrease to a large extent in comparison with their parent polymers.

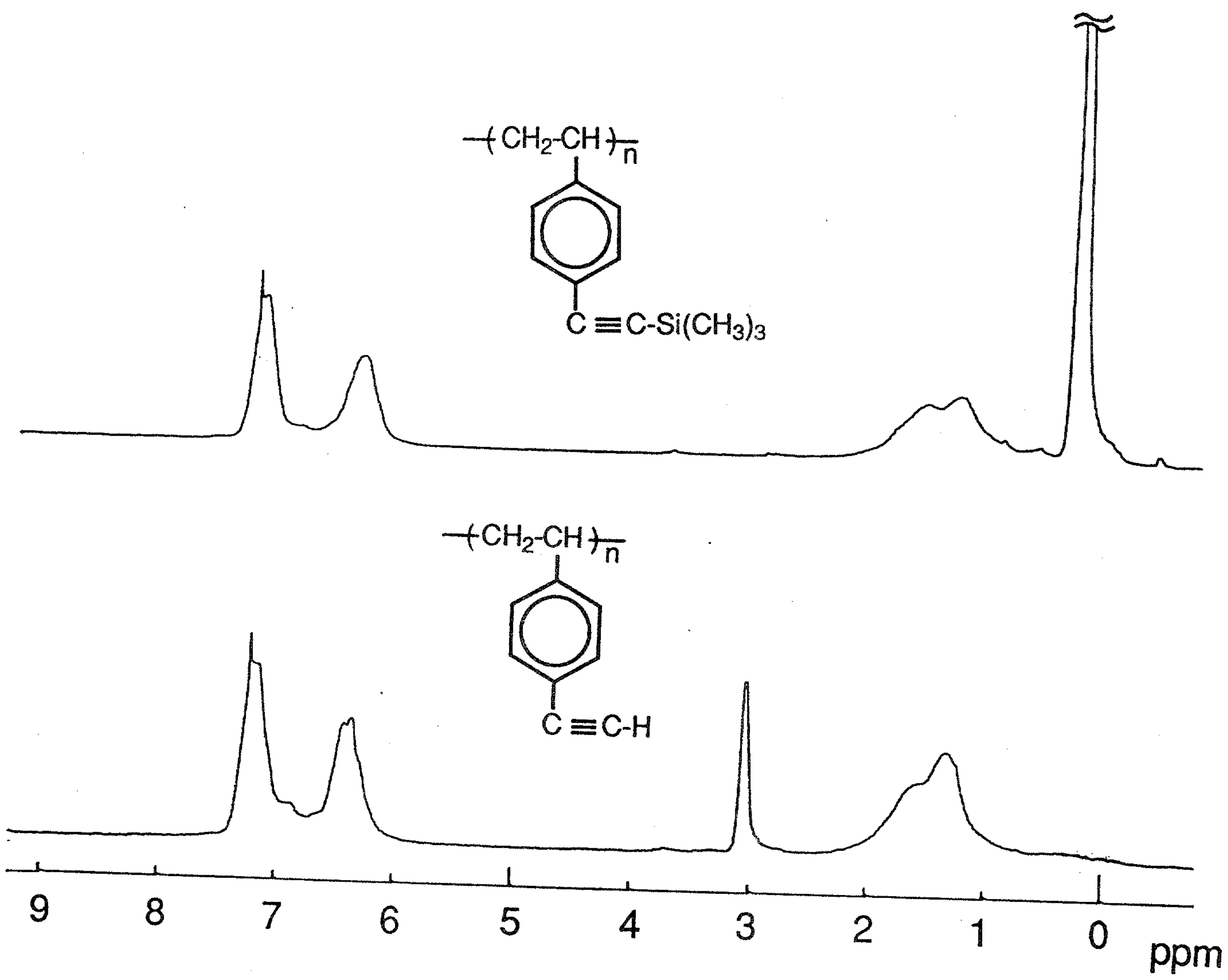


Figure 4-4. ^1H NMR spectra of poly(**1**) (A) and poly(4-ethynylstyrene) after deprotection (B) in $CDCl_3$.

Table 4-4

Solubilities of Poly(**1**), Poly(**2**), Poly(**3**), and Poly(ethynylstyrene)s[a]

solvent	poly(**1**)	poly(**2**)	poly(**3**)	poly(4ESt)[b]	poly(3ESt)[c]	poly(2ESt)[d]
hexane	S	S	S	I	I	I
benzene	S	S	S	S	S	S
diethyl ether	S	S	S	S	S	S
ethyl acetate	S	S	S	S	S	S
chloroform	S	S	S	S	S	S
acetone	S	S	S	S	S	S
1,4-dioxane	S	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S	S
N,*N*-dimethylformamide	S	S	I	S	S	S
dimethyl sulfoxide	I	I	I	S	S	S
ethanol	I	I	I	I	I	I
methanol	I	I	I	I	I	I
water	I	I	I	I	I	I

[a] S, soluble; I, insoluble. [b] Poly(4-ethynylstyrene); $M_n = 12\,000$.
[c] Poly(3-ethynylstyrene); $M_n = 13\,000$. [d] Poly(2-ethynylstyrene); $M_n = 13\,000$.

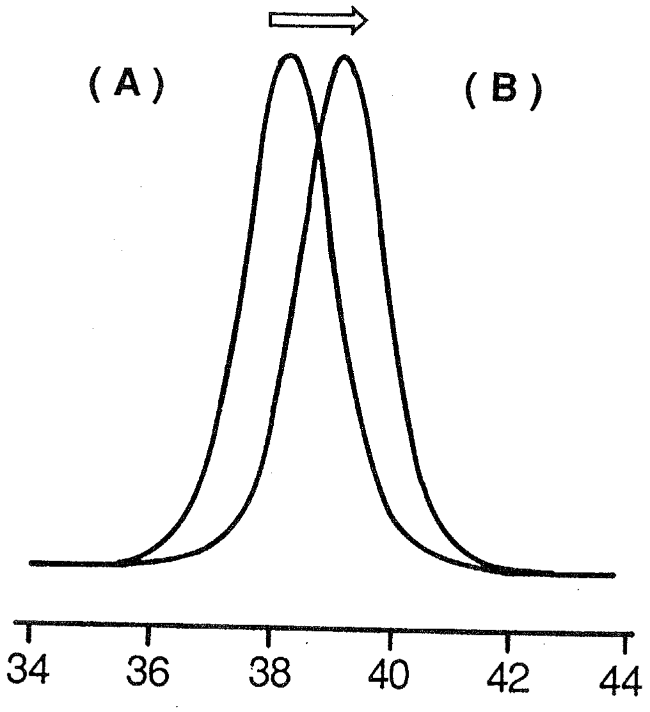


Figure 4-5. SEC curves of poly(**1**) (A) and poly(4-ethynylstyrene) after deprotection (B): peak A, M_n(obsd) = 14 000, M_w/M_n = 1.04; peak B, M_n(obsd) = 12 000, M_w/M_n = 1.04.

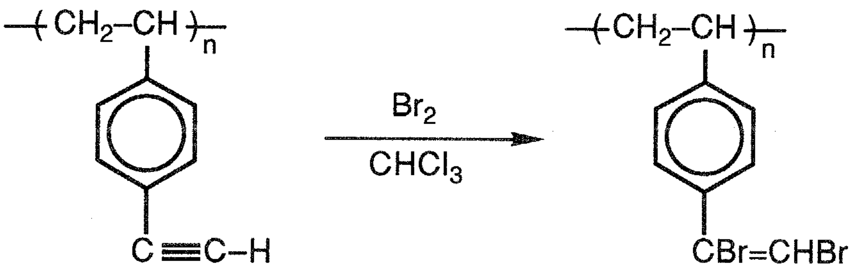
Table 4-5

Glass Transition Temperatures (T_g) of Poly(**1**), Poly(**2**), Poly(**3**), and Poly(ethynylstyrene)s

polymer	$10^{-3}M_n$(obsd)	M_w/M_n	T_g (°C)
poly(**1**)	10	1.04	157
poly(**1**)	14	1.09	159
poly(**1**)	21	1.13	165
poly(**2**)	13	1.22	115
poly(**2**)	21	1.39	119
poly(**3**)	10	1.08	112
poly(**3**)	19	1.10	118
poly(4-ethynylstyrene)	14	1.13	90
poly(3-ethynylstyrene)	14	1.39	69
poly(2-ethynylstyrene)	13	1.10	82

4-5. Bromination of Poly(4-ethynylstyrene).

Since many reactions of ethynyl group are known in organic synthesis, further chemical modifications of the poly(ethynylstyrene)s by means of these reactions are expected to derive other new functional polymers. Among the known reactions, the author has chosen here the electrophilic bromination reaction by which bromine is added to the carbon-carbon triple bond of poly(4-ethynylstyrene). The dibromo adducts are usually formed, but bromoalkynes are sometimes produced in the bromination of terminal acetylenes.[29]



Scheme 4-2

The poly(4-ethynylstyrene) was allowed to react with a slight excess bromine in chloroform at room temperature (Scheme 4-2). The polymer was isolated by precipitation in methanol. The yield of the polymer was almost quantitative based on the formation of dibromo adduct. The IR spectrum of the polymer obtained showed that the two sharp bands at 3294 and 2109 cm^{-1} characteristic to ν_{C-H} and $\nu_{C\equiv C}$ disappeared completely, while new absorptions at 1654 cm^{-1} for $\nu_{C=CH}$, 1582 cm^{-1} for $\nu_{=C-Br}$, and 689 cm^{-1} for ν_{C-Br} appeared. In the ^1H NMR spectrum, a resonance for ethenyl proton appeared at 7.80 - 5.80 ppm, although it was overlapped by aromatic protons. As expected, the signal at 3.04 ppm corresponding to the terminal ethynyl proton completely disappeared. It was found that the integral ratio of ethenyl and aromatic protons to methylene and methine protons of main chain was exactly 5 : 3.

^{13}C NMR spectral analysis did not show the signals due to ethynyl carbons at 83.8 and 77.1 ppm at all but the newly appeared resonances responsible for dibromoethenyl group at 131.1, 108.5 ppm and at 121.7, 102.7 ppm for cis and trans ArCBr=CHBr, respectively. All signals assigned in the spectrum are clearly consistent with the expected structure of poly[4-(1,2-dibromoethenyl)styrene]. The C, H, and Br percentages found by elemental analysis agreed well with those calculated as mentioned in the Experimental Section. Thus, quantitative transformation of poly(4-ethynylstyrene) into poly[4-(1,2-dibromoethenyl)styrene] is evident.

Interestingly, the shapes of SEC peaks of the polymers before and after bromination were almost identical, indicating that the poly[4-(1,2-dibromoethenyl)styrene] retained a narrow molecular weight distribution of the parent polymer. All these results indicate that the bromination reaction proceeds cleanly under the conditions employed here. Accordingly, the bromination of poly(4-ethynylstyrene) provides a new route to obtain well-defined poly[4-(1,2-bromoethenyl)styrene]s with regulated chain lengths.

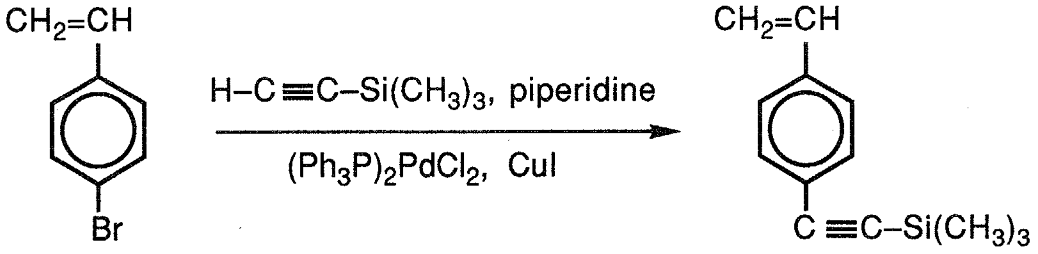
4-6. Conclusions.

The results described in this chapter demonstrate that the well-defined poly(ethynylstyrene)s are synthesized by the anionic living polymerization of ethynylstyrenes through the trimethylsilyl protection for terminal ethynyl functions, followed by complete deprotection. As a result, poly(4-ethynylstyrene), poly(3-ethynylstyrene), and poly(2-ethynylstyrene) were obtained by this method. Some novel block copolymers with these poly(ethynylstyrene) segments are also synthesized. In addition, the bromination of poly(4-ethynylstyrene) is found to proceed quantitatively to provide a well-defined poly[4-(1,2-dibromoethenyl)styrene] with a narrow molecular weight distribution.

Experimental Section

Materials. (Trimethylsilyl)acetylene and bis(triphenylphoshine)palladium(II) chloride were kindly supplied by Shinetsu Chemical Industry and N. E. Chemcat. respectively. They were used without further purification. Piperidine was distilled over CaH_2 under an atmosphere of nitrogen. Styrene, α-methylstyrene, methyl methacrylate, and isoprene were washed with 10% NaOH and water and were dried over $MgSO_4$ for overnight. After filtration, they were dried over CaH_2 and distilled under nitrogen atmosphere. Styrene and α-methylstyrene were distilled on a high vacuum line after addition of appropriate amounts of benzylmagnesium chloride. Methyl methacrylate was distilled over trihexylaluminium on a high vacuum line. Isoprene was distilled from its *n*-butyllithium solution on a high vacuum line. 2-Vinylpyridine was distilled twice over KOH and then over CaH_2 under nitrogen atmosphere. These monomers were diluted with tetrahydrofuran (THF) and divided into several ampoules with break-seals on the vacuum line. THF was refluxed over sodium wire and distilled from its $LiAlH_4$ solution under nitrogen atmosphere. It was finally distilled from its sodium naphthalenide solution on the vacuum line. Commercially available *n*- and *sec*-butyllithium were used without further purification. Metal naphthalenides were prepared by the reactions of naphthalene with the corresponding alkali-metals in THF at room temperature for 10 h in a sealed reactor with break-seals on the vacuum line. A slightly excess naphthalene was generally used in the reaction. After filtration, their concentrations were determined by colorimetric titration using 1-octanol from characteristic green to colorless end-point in the sealed reactors via break-seals. Living oligomers of α-methylstyrene were prepared just prior to the polymerization from the metal naphthalenides or butyllithiums and 2-5 times molar excess of α-methylstyrene in THF at 25°C for 1 min and –78°C for 10-30 min.

4-(Trimethylsilyl)ethynylstyrene (1). **1** was synthesized by modifying the reaction previously reported as shown in Scheme 4-3.[30] A dry piperidine (730 mL) solution of 2-bromostyrene (33.20 g, 181 mmol), bis(triphenylphosphine)palladium (II) chloride (4.14 g, 5.89 mmol), and copper(I) iodide (0.14 g, 0.73 mmol) was prepared and a nitrogen was then bubbled through this solution for 2 h. (Trimethylsilyl)acetylene (21.41 g, 218 mmol) was added dropwise to the solution at 50°C and the mixture was stirred at 50°C for additional 6 h under an atmosphere of nitrogen. After filtration of the precipitated piperidinium salt, the solvent was evaporated. The residue was washed with water and extracted with hexane (200 mL x 5). The extract was dried over Na_2SO_4. After filtration and evaporation, column chromatography on silica gel with hexane as an eluent yielded the desired product of **1**. It was further purified by fractional distillation at 68-69°C (0.33 mmHg) to give 16.20 g (80.9 mmol, 45 %) of **1** as a colorless liquid: ^1H NMR (90 MHz, $CDCl_3$) δ 7.48-7.25 (m, 4H, Ar), 6.69 (dd, 1H, -CH=), 5.75, 5.28 (2d, 2H, J = 17 and 11 Hz, CH_2=), 0.25 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 137.8 (Ar, C1), 136.3 (-CH=), 132.2 (Ar, C3), 126.1 (Ar, C2), 122.5 (Ar, C4), 114.8 (CH_2=), 105.2 (ArC≡), 94.8 (≡CSi), 0.1 ($SiCH_3$); IR (neat, cm^{-1}) 760, 866, 1250 (C-Si), 912 ($CH=CH_2$), 2156 (C≡C).



1

Yield 45%

Scheme 4-3

3-(Trimethylsilyl)ethynylstyrene (2). **2** was obtained by the reaction of 3-bromostyrene (12.1 g, 66.0 mmol) with (trimethylsilyl)acetylene (7.78 g, 79.2 mmol) by a method similar to that in the case of **1**. After **2** was isolated by column chromatography, it was further purified by fractional distillation at 91.0-91.5°C (3.5 mmHg) to give 10.1 g (50.5 mmol, 77 %) of **2** as a colorless liquid: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.52-7.30 (m, 4H, Ar), 6.67 (dd, 1H, -CH=), 5.75, 5.27 (2d, 2H, J = 18 and 11 Hz, CH_2=), 0.26 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 137.8 (Ar, C1), 136.2 (-CH=), 131.3 (Ar, C4), 129.9 (Ar, C2), 128.5 (Ar, C6), 123.5 (Ar, C3), 114.7 (CH_2=), 105.1 (ArC≡), 94.3 (≡CSi), 0.1 ($SiCH_3$); IR (neat, cm^{-1}) 759, 842, 1250 (C-Si), 920 (CH=CH_2), 2150 (C≡C).

2-(Trimethylsilyl)ethynylstyrene (3). **3** was obtained by the reaction of 2-bromostyrene (12.1 g, 66.0 mmol) with (trimethylsilyl)acetylene (7.78 g, 79.2 mmol) by a method similar to that in the case of **1**. After **3** was isolated by column chromatography, it was further purified by fractional distillation at 84.5-86.0°C (3.5 mmHg) to give 5.84 g (29.2 mmol, 44 %) of **3** as a colorless liquid: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.62-7.02 (m, 5H, Ar and -CH=), 5.85, 5.35 (2d, 2H, J = 18 and 11 Hz, CH_2=), 0.26 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 139.4 (Ar, C1), 135.0 (=CH-), 132.9 (Ar, C3), 128.7 (Ar, C5), 127.4 (Ar, C4), 124.6 (Ar, C6), 121.9 (Ar, C2), 115.6 (CH_2=), 103.5 (ArC≡), 99.2 (≡CSi), 0.1 ($SiCH_3$); IR (neat, cm^{-1}) 843, 868, 1250 (C-Si), 914 (CH=CH_2), 2156 (C≡C).

Homopolymerization. The monomers **1-3** were degassed and stirred over finely ground CaH_2 overnight and were distilled on a vacuum line into the round-bottomed flask equipped with breakseals. After adding 3-5 mol% of benzylmagnesium chloride in THF into the monomer through the breakseal, the mixture was stirred for 1 h at room temperature and then distilled on a vacuum line into the breakseal-attached round-bottomed flask prewashed with sodium naphthalenide in THF. The monomer was diluted to 0.2-0.5 M solutions with THF and stored at –30°C until ready for polymerization. All polymerizations were carried out at –78°C for 0.5 - 1 h with shaking under a high vacuum condition (10^{-6} mmHg) in an all-glass apparatus equipped with breakseals in the usual manner.[3] The desired charge of monomer in THF was added to the THF solution of initiator with strong shaking. Both the solutions must be kept at –78°C. The polymerization was terminated with a few drops of degassed methanol after an appropriate time. The polymer was then precipitated by pouring the mixture into a large amount of methanol. It was purified by reprecipitation twice from THF solution to methanol and freeze-dried from the benzene solution. The polymers thus obtained were characterized by ^{1}H and ^{13}C NMR and IR spectroscopies.

Poly(1): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.35-7.00 (br s, 2H, Ar), 6.60-6.10 (br s, 2H, Ar), 2.10-0.90 (m, 3H, CH_2CH), 0.24 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 145.3 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 120.8 (Ar, C4), 105.5 (ArC≡), 93.7 (≡CSi), 43.6 (CH), 40.6 (CH_2), 0.2 ($SiCH_3$); IR (KBr, cm^{-1}) 759, 868, 1250 (C-Si), 2159 (C≡C).

Poly(2): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.55-6.05 (m, 4H, Ar), 2.30-0.80 (m, 3H, CH_2CH), 0.21 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 144.8 (Ar, C1), 130.9 (Ar, C2), 130.0 (Ar, C4 and C5), 128.2 (Ar, C6), 123.0 (Ar, C3), 105.7 (ArC≡), 93.6 (≡CSi), 43.0 (CH), 40.4 (CH_2), 0.3 ($SiCH_3$); IR (KBr, cm^{-1}) 759, 842, 1250 (C-Si), 2156 (C≡C).

Poly(3): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.65-6.25 (br s, 4H, Ar), 3.25-2.10 (m, 1H, CH), 1.90-0.80 (m, 2H, CH_2), -0.03 (br s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 147.5 (Ar, C1), 133.3 (Ar, C3), 128.5 (Ar, C5), 126.9 (Ar, C6), 125.1 (Ar, C4), 122.5 (Ar, C2), 104.7 (ArC≡), 97.2 (≡CSi), 47.0 (CH), 40.8 (CH_2), 0.3 ($SiCH_3$); IR (KBr, cm^{-1}) 841, 868, 1250 (C-Si), 2154 (C≡C).

Block Copolymerization. Block copolymerizations were carried out by the sequential addition of different two monomers. The first-stage polymerization was carried out in THF at –78°C in a manner similar to the homopolymerization and somewhat sampled to determine the characteristics. The second block was prepared by adding an appropriate amount of second monomer to the residual living polymer produced in the first-stage polymerization. After quenching with degassed methanol, the polymer was precipitated in methanol, purified by reprecipitation twice and then freeze-dried. Yields were quantitative in all runs. They were characterized by IR, ^{1}H and ^{13}C NMR, SEC, and VPO.

Deprotection of Poly[(trimethylsilyl)ethynylstyrene]s. Poly(**1**) (0.320 g, 1.6 mmol based on (trimethylsilyl)ethynylstyrene unit) was dissolved in dry THF (10 mL) and the solution was cooled at 0°C. $(C_4H_9)_4NF$ in THF (1.0 M, 3.3 mL) was added to the solution and the mixture was stirred at 0°C for 1h. The polymer was precipitated in methanol and purified twice by reprecipitation using a THF-methanol system. The yield of polymer was quantitative. The polymer was identified as poly(4-ethynylstyrene) from the following analyses.

Poly(4-ethynylstyrene): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.40-6.20 (m, 4H, Ar), 3.04 (s, 1H, C≡CH), 2.30-0.70 (m, 3H, CH_2CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 145.8 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 119.9 (Ar, C4), 83.8 (ArC≡), 77.1 (≡CH), 43.0 (CH), 40.8(CH_2); IR (KBr, cm^{-1}) 2109 (C≡C), 3294 (≡CH). Similarly, the deprotection of trimethylsilyl groups from poly(**2**) and poly(**3**) was carried out. Yields of polymers were quantitative in both cases. They were identified as poly(3-ethynylstyrene) and poly(2-ethynylstyrene), respectively. The analytical results are as follows:

Poly(3-ethynylstyrene): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.55-5.95 (m, 4H, Ar), 3.01 (s, 1H, C≡CH), 2.30-0.60 (m, 3H, CH_2CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 144.7 (Ar, C1), 131.2 (Ar, C2), 130.1 (Ar, C4 and C5), 128.3 (Ar, C6), 122.0 (Ar, C3), 84.0 (ArC≡), 77.1 (≡CH), 43.0(CH), 40.5(CH_2); IR (KBr, cm^{-1}) 2108 (C≡C). 3293 (≡CH).

Poly(2-ethynylstyrene): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.10-6.20 (m, 4H, Ar), 3.35-2.00 (m, 1H, CH), 2.54 (s, 1H, C≡CH), 2.00-0.80 (br s, 2H, CH_2); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 148.8 (Ar, C1), 132.4 (Ar, C3), 128.6 (Ar, C5), 127.2 (Ar, C6), 125.2 (Ar, C4), 121.6 (Ar, C2), 82.6 (ArC≡), 80.5 (≡CSi), 41.6 (CH), 37.7(CH_2),; IR (KBr, cm^{-1}) 2104 (C≡C). 3296 (≡CH).

Bromination of Poly(4-ethynylstyrene). The reaction was carried out in a manner similar to the previous method reported.[31] To a stirred solution of poly(4-ethynylstyrene) (0.120 g, 0.94 mmol based on ethynylstyrene unit) in $CHCl_3$ (12 mL) was added dropwise bromine in $CHCl_3$ (0.09 M, 12 mL) at 25°C. The mixture was stirred for an additional 30 min at room temperature. The polymer was precipitated in methanol and purified by thrice reprecipitation using a THF-methanol system. A yield of polymer was quantitative. The polymer was identified to be poly[4-(1,2-dibromoethenyl)styrene] by IR, ^1H and ^{13}C NMR, and elemental analysis: ^1H NMR (90 MHz, $CDCl_3$) δ 7.80-5.80 (overlapping m, 5H, Ar and =CHBr), 2.70-0.80 (m, 3H, CH_2CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 146.1 (Ar, C1), 136.0 (Ar, cis C4), 134.8 (Ar, trans C4), 131.1 (cis ArCBr=), 129.5 (Ar, C3), 127.8 (Ar, C2), 121.7 (trans ArCBr=), 108.5 (cis =CHBr), 102.7 (trans =CHBr), 43.2 (CH), 40.7 (CH_2); IR (KBr, cm^{-1}) 689 (C-Br), 1582 (=C-Br), 1654 (C=CH). Anal. Calcd for $(C_{10}H_8Br_2)_{3.08}(C_9H_{10})_{0.322}$: C, 43.75; H, 3.04; Br, 53.22. Found: C, 43.71; H, 3.10; Br, 53.21. The (C_9H_{10}) shown here was the residue of initiator (α-methylstyrene).

Measurements. Infrared (IR) spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz for ^1H and 22.5 MHz for ^{13}C). Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^1H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard, respectively. Size-exclusion chromatograms (SEC) were obtained at 40°C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, G3000H_{XL}) with ultraviolet (254 nm) or refractive index detection. THF was the carrier solvent at a flow rate of 1.0 mL/min. Vapor pressure osmometry (VPO) measurement was made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment of very exact control of temperature. Laser light scattering measurements for weight-average molecular weight (M_w) determination were performed at 25°C with an Ootsuka Electronics SLS-600R instrument in benzene solution. The glass transition temperature (T_g) was measured by differential scanning calorimetry using a Seiko Instruments SSC/5200. The samples were first heated to 200°C, cooled rapidly to room temperature, and then scanned again at a rate of 20°C/min.

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molecular weight distribution in very low yield and did not proceed at all, respectively, probably due to the serious side reactions.

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Chapter 5

Living Anionic Polymerization of *N,N*-Dialkyl-4-vinylbenzenesulfonamides

ABSTRACT: Anionic polymerizations of *N*,*N*-dimethyl-4-vinylbenzenesulfonamide (**1a**) and *N*,*N*-diethyl-4-vinylbenzenesulfonamide (**1b**), and *N*-methyl-*N'*-[(4-vinylphenyl)sulfonyl]piperazine (**1c**) were carried out at –78°C in tetrahydrofuran. The initiators included potassium naphthalenide, oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium, (1,1,4,4-tetraphenylbutanediyl)dilithium and -dipotassium, [1,1-bis[4'-(trimethylsilyl)phenyl]hexyl]lithium, and [1,1,4,4-tetrakis[4'-(trimethylsilyl)phenyl]butanediyl]dipotassium. These polymerizations gave poly(**1**)s in quantitative yields. In all cases, the obtained polymers had narrow molecular weight distributions ($M_w/M_n < 1.15$) and molecular weights predicted from the molar ratio of monomer to initiator, indicating that the anionic polymerizations of these monomers gave stable living polymers. Novel block copolymers, poly(**1b**-*b*-styrene-*b*-**1b**), poly(**1b**-*b*-isoprene-*b*-**1b**), poly(**1b**-*b*-2-vinylpyridine-*b*-**1b**), poly(2-vinylpyridine-*b*-**1b**-*b*-2-vinylpyridine), poly[(methyl methacrylate)-*b*-**1b**-*b*-(methyl methacrylate)], poly[(*tert*-butyl methacrylate)-*b*-**1b**-*b*-(*tert*-butyl methacrylate)], and poly(**1c**-*b*-styrene-*b*-**1c**) were synthesized using these living systems.

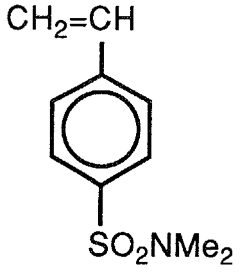
Introduction.

The anionic living polymerization of styrene is undoubtedly the best established method to prepare polymers with strictly controlled chain structures.[1] Actually, the molecular weights of polystyrene can be precisely controlled in a wide range (10^3 – 10^6) by this method. These samples possess very narrow molecular weight distributions (MWDs). In addition, well-defined block copolymers and end-functionalized polystyrenes are readily synthesized by the use of living polystyrene. Unfortunately, only a very limited number of styrene derivatives were amenable to this living polymerization method until the beginning of the 1980s. The reliable examples were alkyl[2] and aryl[3] substituted styrenes and styrene derivatives having alkoxy[4] and *N,N*-dimethylamino groups.[5] The styrenes *para*-substituted with SiR_3,[6] GeR_3,[7] and $SnPh_3$[8] were also reported to undergo anionic living polymerization. Under specific conditions, the living polymer of 4-bromostyrene was possibly prepared in 1983.[9] However, styrenes with potentially useful functional groups are believed not to yield living polymers by anionic methods. This is because these groups are normally incompatible with both highly reactive anionic initiators and propagating chain ends in the anionic living polymerization of styrene.

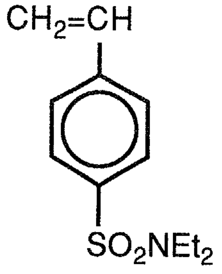
In order to overcome this difficulty, Nakahama and his co-workers have introduced a protective method into the anionic polymerization of functional styrene derivatives.[10] The method involves the suitable protection of functional groups and anionic living polymerization of the protected styrene monomers, followed by complete deprotection. According to their strategy, several successful examples have been demonstrated in the last ten years.[10]

More recently, it has been found a very interesting fact that a family of styrene derivatives *para*-substituted with electron-withdrawing groups undergo anionic living polymerization without difficulty.[11] These monomers include *N*-alkylimine,[12] *N,N*-dialkylamide,[13] oxazoline,[14] *tert*-butyl ester,[15] and nitrile.[16] Thus, it has been successfully synthesized new types of polystyrenes with these functional groups in each monomer unit. The polystyrenes possess nearly monodispersed distributions of molecular weight and controllable molecular weights. However, the success of living polymerization of these styrene derivatives is very surprising, since their functional groups are known to readily react with nucleophiles such as organolithium compounds, whose reactivities are similar to those of the anionic initiators and active propagating chain ends formed in the anionic polymerization of styrene. The reason for this success may be due to the stabilization of propagating polystyryl carbanions by the electron-withdrawing effects of these substituents. Moreover, the extension of the π-conjugation system of benzylic carbanion (polystyryl carbanion at the propagating chain end) may also play an important role in the stabilization to produce living polymers from the monomers of this class.

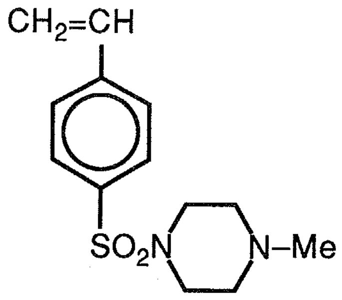
As an extension of a series of studies on the anionic polymerization of monomers containing electron-withdrawing groups, the author describes in this chapter the anionic polymerization of styrene derivatives *para*-substituted with tertiary sulfonamide groups. The monomers employed are *N*,*N*-dimethyl-4-vinylbenzenesulfonamide (**1a**) and *N*,*N*-diethyl-4-vinylbenzenesulfonamide (**1b**), and *N*-methyl-*N'*-[(4-vinylphenyl)sulfonyl]piperazine (**1c**).



1a



1b



1c

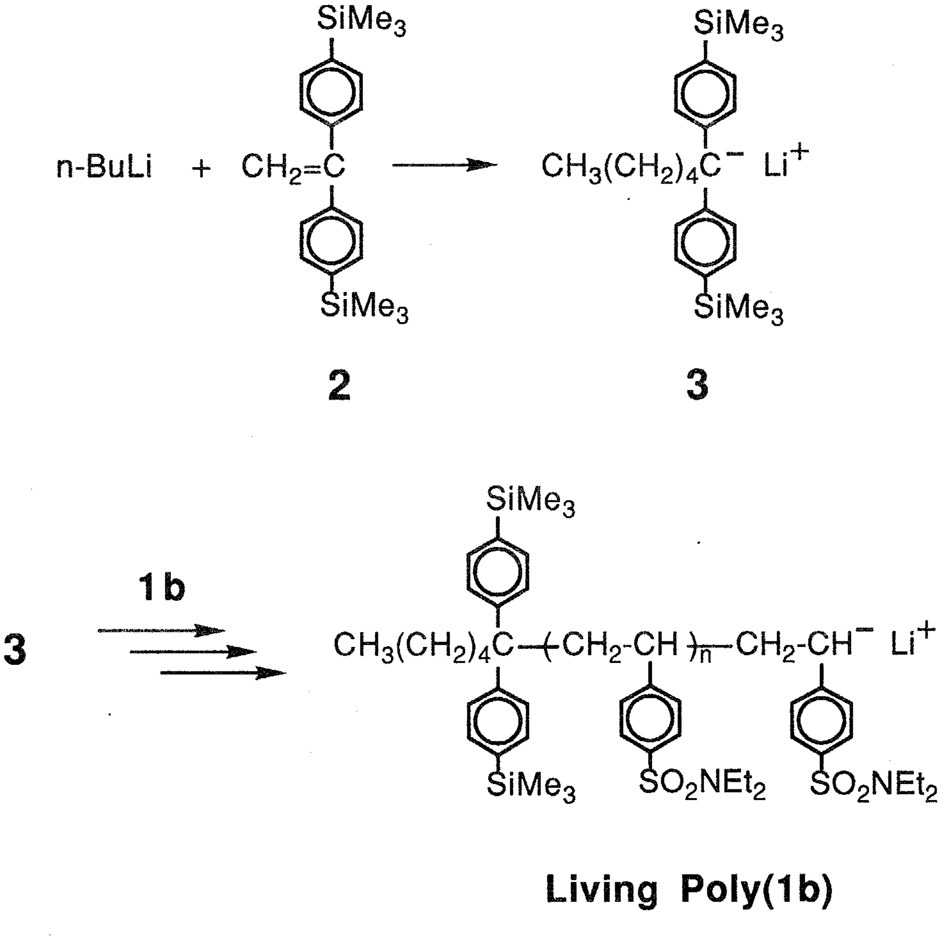
Results and Discussion.

The tertiary sulfonamide group is a well-known electron-withdrawing group. In fact, the Hammett σ-value of the *N,N*-dimethylsulfonamide group is reported to be 0.9.[17] This value means that the sulfonamide can compete in terms of electron-withdrawing character with cyano and nitro groups, whose σ-values are 0.69 and 0.80,[17] respectively. Reynolds *et al.*[18] reported that the evaluations of substituent effects were realized from the chemical shifts of the β-carbon of the vinyl group in ^{13}C NMR spectra of 4-substituted styrenes. By using the chemical shifts of β-carbons of **1a-c**, the Hammett σ-values of the *N,N*-dialkylsulfonamide groups of these monomers could be estimated to be between 0.60 and 0.70, which are again comparable to those of cyano and nitro groups.

N,N-Dialkylsulfonamides are reported to be relatively stable to very strong nucleophiles like organolithium compounds. For example, some tertiary sulfonamides are observed to be compatible with organolithium compounds.[19] In fact, methyllithium has a half-life of 14 h even at room temperature in *N,N*-diethyl-trimethylmethanesulfonamide. Hauser and his co-workers[20] characterized proton-lithium exchange reaction between *N,N*-dimethylbenzenesulfonamide and *n*-butyllithium (*n*-BuLi) at 0°C in THF-hexane. The important point of this reaction is that no sulfonyl attack by *n*-BuLi occurs but the *ortho*-lithiated compounds yield efficiently in the reaction. Furthermore, the resulting *ortho*-lithiated compounds with tertiary sulfonamide groups are quite stable and widely used in various organic syntheses.[21-30] These observations strongly indicate that the sulfonamide moiety can coexist with the carbanionic species, which can be regarded as models for the living polymers. Therefore, in great expectation of success, the author could perform the anionic polymerizations of a series of styrene monomers containing electron-withdrawing tertiary sulfonamide functionalities, **1**.

5-1. Anionic Polymerization of *N,N*-Diethyl-4-vinylbenzenesulfonamide (1b).

First of all, the anionic polymerization of **1b** (*N,N*-diethyl-substituted derivative) was carried out at –78°C in THF with the use of [1,1-bis[4'-(trimethylsilyl)phenyl]hexyl]lithium (**3**, Scheme 5-1), and [1,1,4,4-tetrakis[4'-(trimethylsilyl)phenyl]butanediyl]dipotassium (**4**) as initiators. They were prepared by reactions of 1,1-bis[4'-(trimethylsilyl)phenyl]ethylene (**2**) with *n*-BuLi in THF/pentane, and **2** with potassium naphthalenide in THF, respectively.



Scheme 5-1

Upon adding **1b** to rose red initiator solutions, the color changed rapidly to orange red (Li^+ counterion) or dark red (K^+ counterion). The resulting characteristic color remained unchanged at –78°C, even after 4 h. It disappeared immediately upon adding a few drops of methanol for termination, indicating the presence of styryl carbanionic species derived from **1b**. The polymer was obtained quantitatively by precipitation into a large excess of water. The resulting polymer was purified by reprecipitations with a THF(soluble)-hexane(precipitate) system.

Figure 5-1 presents the ^{1}H NMR spectra of **1b** (A) and the resulting polymer (B) initiated with **4**. In comparison of the spectrum of A with that of B, the signals (5.3-6.8 ppm) of vinyl group of the monomer completely disappeared and the broad signals corresponding to CH_2–CH of the polymer main chain (0.8-2.1 ppm) appeared. The trimethylsilyl protons of the initiator residues (0.15 ppm) were also observed in the spectrum of the polymer. Similarly, in the ^{13}C NMR spectrum of the polymer, signals due to the secondary and tertiary carbons of the polymer main chain were observed and signals for vinyl carbons (117.0 and 135.4 ppm) were absent. In the infrared spectrum of the polymer, the absorptions corresponding to the vinyl group of the monomer at both 990 and 850 cm^{-1} thoroughly disappeared. In addition, the strong absorptions of the $-SO_2-$ linkage at 1333 and 1155 cm^{-1} were observed, slightly shifted toward higher wave number from those of the monomer. From these results, it is obvious that anionic polymerization of **1b** proceeds exclusively in the vinyl polymerization mode to afford the expected poly(*N,N*-diethyl-4-vinylbenzenesulfonamide).

Table 5-1 summarizes the polymerization results of **1b**. In all cases, the yield of poly(**1b**) was quantitative. The size exclusion chromatography (SEC) of each polymer exhibited unimodal distribution of molecular weight both in DMF and THF as eluents. The polydispersity indices, M_w/M_n values, of the resulting polymers are determined to be in the range 1.03-1.15, indicating narrow MWDs of all poly(**1b**)s. It is observed that the number-average molecular weights calculated from the molar ratios of monomer to initiator in the feed are in proportion to those estimated by the SEC calibration using standard polystyrenes. However, the M_n values thus obtained by SEC both in THF and DMF deviated from the calculated ones (Table 5-1). In THF, the molecular weights by SEC were approximately two thirds of the calculated values. In contrast, the relationship was opposite in DMF and the M_n values were about 1.4 times the theoretical ones.

Therefore, an alternative method has been utilized to determine the absolute molecular weights of the polymers. It is a trimethylsilyl end group analysis which will be described later in Chapter 6 in detail.[16] The polymers initiated with either **3** or **4** had trimethylsilyl protons of the initiator residues at their chain ends or in the middle of their polymer chains,[31] as can be seen in Figure 5-1B. By using the relative NMR intensities of trimethylsilyl to aromatic protons in the polymer samples, the M_n(NMR)s of poly(**1b**) were determined. Actually, this method was found to be very effective to determine the M_n values of poly(4-cyanostyrene)[16] and poly(methyl methacrylate).[32] As can be seen in Table 5-1, good agreements between the M_n(NMR)s thus obtained and molecular weights calculated from the molar ratios of monomer to initiator are observed in the cases both of mono- and difunctional initiators.

The weight-average molecular weights of some samples were also determined by light scattering measurements. They are comparable to the weight-average molecular weights calculated from the M_n(NMR)s and the MWDs by SEC. These predicted molecular weights and values of M_w/M_n (1.08-1.14) of the poly(**1b**)s strongly suggest that the anionic polymerization of **1b** is free from termination and chain transfer reactions, characteristic of the living nature of the polymerization system. In addition, the closeness between M_w(LS)s and M_n(NMR)s, considering the narrow MWDs, supports the reliability of the molecular weights determined by the end group analysis.

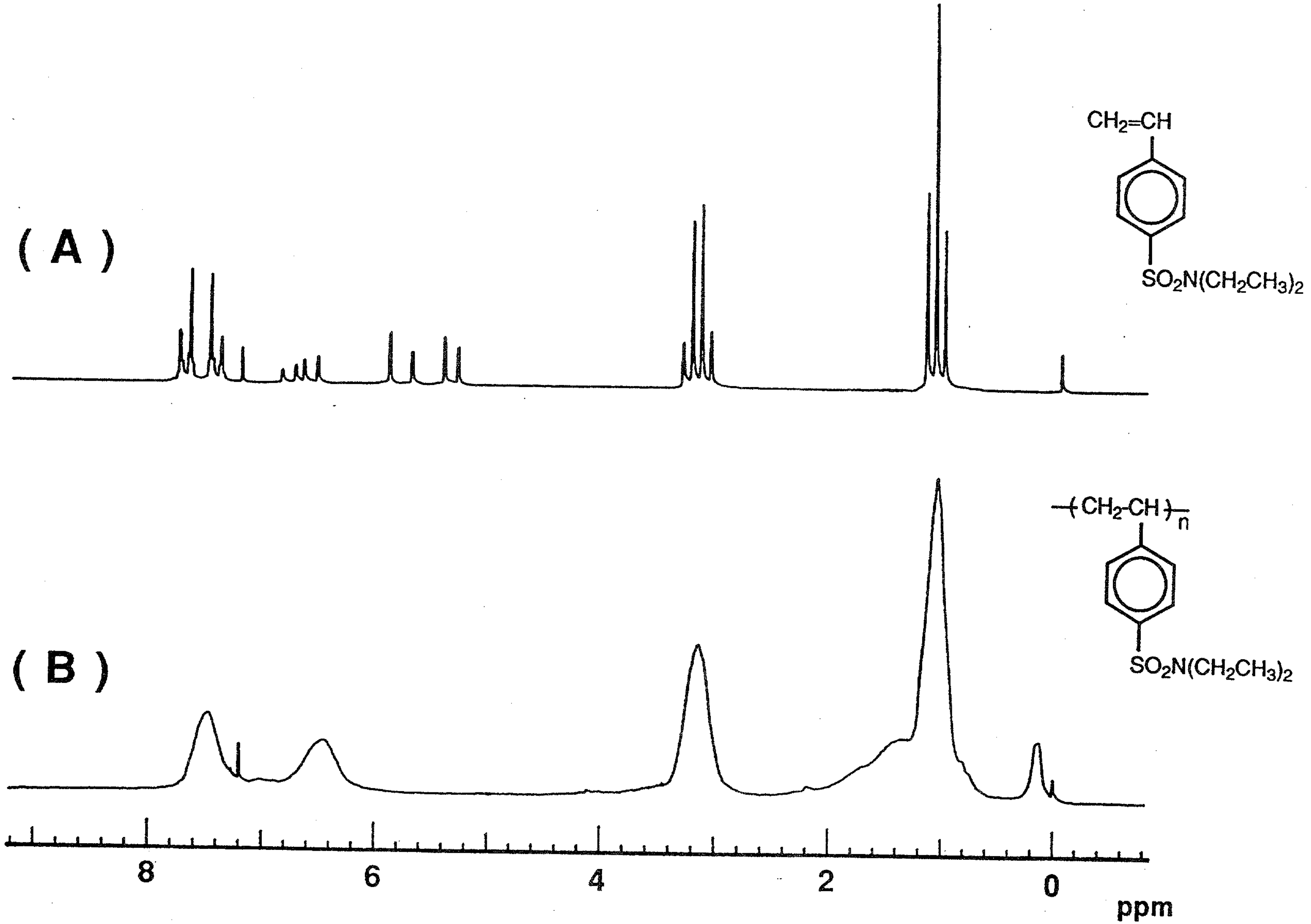


Figure 5-1. ^{1}H NMR spectra of **1b** (A) and poly(**1b**) obtained with **4** as an initiator (B) in $CDCl_3$. The trimethylsilyl protons the initiator residues (at 0.2 ppm) appear to have expected intensity in the spectrum of the polymer (Table 5-1, run 2).

Table 5-1

Anionic Polymerization of **1b** in THF at –78°C for 0.5-4 h[a]

	1b		$10^{-3}M_n$ (M_w/M_n)					
run	mmol	initiator, mmol	calcd[c]	NMR	GPC(THF)[d]	GPC(DMF)[e]	$10^{-3}M_w$(LS)[b]	M_w(LS)/M_n(NMR)
1	3.56	K-Naph,[f] 0.234/ **2**, 0.444	7.9	6.8	5.2 (1.15)	13 (1.14)	6.9	1.01
2	4.19	K-Naph, 0.146/ **2**, 0.216	14	14	9.1 (1.12)	20 (1.13)	18	1.29
3	5.67	K-Naph, 0.107/ **2**, 0.174	26	27	16 (1.11)	35 (1.12)	35	1.30
4	7.43	*n*-BuLi, 0.0622/ **2**, 0.148	27	28	16 (1.05)	35 (1.08)		
5	6.89	*n*-BuLi, 0.0493/ **2**, 0.134	33	38	22 (1.06)	44 (1.09)	50	1.32
6	6.04	*n*-BuLi, 0.0322/ **2**, 0.0450	45	59	48 (1.03)	91 (1.08)	70	1.19

[a] Yields of polymers were almost quantitative in each case. [b] M_w(LS) was obtained by light scattering in THF at 25°C. [c] M_n(calcd) = [monomer] × (MW of monomer) × f / [initiator] + MW of initiator; $f = 1$ or 2, corresponding to the functionality of the initiators. [d] M_n(SEC(THF)) was obtained by SEC calibraton using standard polystyrenes in THF solution. [e] M_n(SEC(DMF)) was obtained by SEC calibraton using standard polystyrenes in DMF solution. [f] Potassium naphthalenide.

From comparison of the predicted M_n(NMR) values with M_n(SEC)s in THF and DMF, they were correlated by the following equations, which are practically useful to estimate the molecular weights of poly(**1b**) samples:

$$M_n(\text{obsd}) = 1.18 \times M_n(\text{SEC(THF)}) + 5970 \quad (1)$$

$$M_n(\text{obsd}) = 0.653 \times M_n(\text{SEC(DMF)}) + 2880 \quad (2)$$

Next, to examine the scope of the initiators, **1b** was anionically polymerized with various initiators, such as potassium naphthalenide, 1,4-dilithio- and 1,4-dipotassio-1,1,4,4-tetraphenylbutanes, and oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium in THF at –78 to 0°C for 30 min. A nearly quantitative yield of polymer was obtained in each case. The molecular weights of the polymer samples were determined using the above-mentioned SEC calibration for poly(**1b**) in DMF (equation (2)). The polymers of **1b** prepared at –78°C possess the predicted molecular weights and narrow MWDs in all cases with different initiator countercations and functionalities, as shown in Table 5-2. The polymer obtained at 0°C had also the predicted molecular weight, and the polydispersity index was slightly broad (M_w/M_n = 1.23).

Since it is also of great importance to estimate the stability of the active chain end for the proof of livingness of polymerization, postpolymerization was carried out (see Experimental Section in detail). After the first polymerization of **1b** with oligo(α-methylstyryl)dipotassium at –78°C for 30 min, the second feed of **1b** was added to the reaction mixture and then reacted for 30 min to complete the further polymerization. The postpolymer was quantitatively obtained after quenching as well as the prepolymer. From the SEC curve of the postpolymer shown in Figure 5-2, it was observed that the peak of prepolymer disappeared and that the peak of postpolymer shifted to higher molecular weight side. Furthermore, the resulting postpolymer possessed the desirable molecular weight and a narrow MWD. Consequently, it is clearly evident that the propagating carbanion of living poly(**1b**) is stable at –78°C at least for 30 min and initiates further polymerization. This complete survival of the terminal carbanion is a satisfactory result to synthesize the tailor-made block copolymers of **1b**.

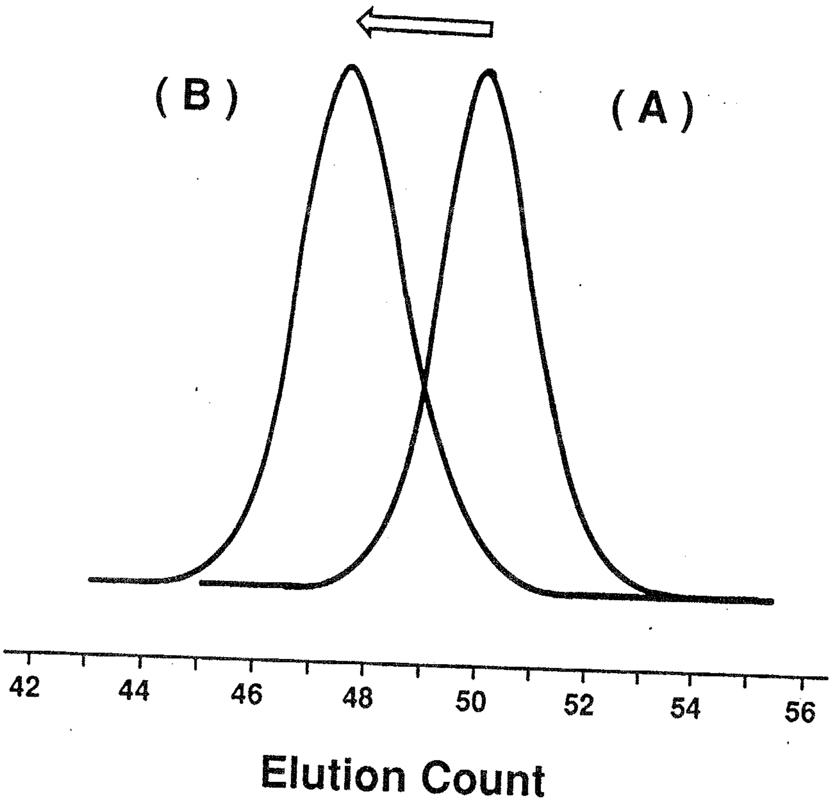


Figure 5-2. SEC curves (DMF) of poly(**1b**)s obtained at –78°C: the first polymerization (A), M_n(obsd) = 12,000, M_w/M_n = 1.05; the second polymerization (B), M_n(obsd) = 19,000, M_w/M_n = 1.08 (the second monomer was added 30 min after the first addition).

5-2. Anionic Polymerization of *N*,*N*-Dimethyl-4-vinylbenzenesulfonamide (1a) and *N*-Methyl-*N'*-[(4-vinylphenyl)sulfonyl]piperazine (1c).

The anionic polymerization of two additional related monomers, **1a** and **1c**, was attempted to evaluate the effect of the *N*-alkyl substituent on the polymerization. The polymerization of these monomers was similarly carried out at −78°C for 20 h in THF. The polymers were produced in quantitative yields in all cases. It should be mentioned that, whereas the polymerization of **1a** always suffered from the precipitation of polymer during the polymerization under the experimental conditions, the polymer of the quantitative yield was produced.[33] Occurrence of the vinyl polymerization of **1a** and **1c** was ascertained by ^{1}H NMR, ^{13}C NMR, and IR spectroscopic measurements. The resulting polymers from both **1a** and **1c** possess the molecular weights close to the calculated values as shown in Table 5-2. The SEC traces of polymers in DMF were unimodal and represented the narrow MWD; the values of M_w/M_n were around 1.10. These results indicate the living character of the anionic polymerizations of **1a** and **1c** as well as of **1b**.

Thus, the achievement of anionic living polymerization of **1a-c** provides for a valuable extension of monomers capable of living anionic polymerization. The high stability of living poly(**1a-c**) might be explained by the resistivity of tertiary sulfonamide toward nucleophilic attack[19-30] and by the stabilization of active chain-ends with the strongly electron-withdrawing sulfonamide groups as discussed in the next section.

Table 5-2 Anionic Polymerization of **1a**, **1b** and **1c** in THF[a]

run	monomer, mmol	temp(°C), time	initiator, mmol	$10^{-3}M_n$		M_w/M_n[d]
				calcd[b]	obsd[c]	
7	**1a**, 1.37	−78, 20 h	K-Naph[e], 0.0499 / **2**, 0.181	12	10[f]	1.10
1	**1b**, 3.56	−78, 30 min	K-Naph, 0.234 / **2**, 0.444	7.9	6.8[f]	1.14
2	**1b**, 4.19	−78, 30 min	K-Naph, 0.146 / **2**, 0.216	14	14[f]	1.13
3	**1b**, 5.67	−78, 30 min	K-Naph, 0.107 / **2**, 0.174	26	27[f]	1.12
4	**1b**, 7.43	−78, 80 min	*n*-BuLi, 0.0622 / **2**, 0.148	27	28[f]	1.08
5	**1b**, 6.89	−78, 4 h	*n*-BuLi, 0.0493 / **2**, 0.134	33	38[f]	1.09
6	**1b**, 6.04	−78, 60 min	*n*-BuLi, 0.0322 / **2**, 0.0450	45	59[f]	1.08
8	**1b**, 2.48	0, 30 min	K-Naph, 0.100 / α-MeSt,[g] 0.269	13	14	1.23
9	**1b**, 4.95	0, 60 min	K-Naph, 0.124 / α-MeSt, 0.263	20	22	1.23
10	**1b**, 2.88	−78, 30 min	K-Naph, 0.0941	15	17	1.11
11	**1b**, 2.43	−78, 30 min	Li-Naph[h], 0.0851 / α-MeSt, 0.273	14	16	1.10
12	**1b**, 2.43	−78, 30 min	Na-Naph,[i] 0.102 / α-MeSt, 0.394	12	12	1.12
13	**1b**, 2.66	−78, 30 min	K-Naph, 0.0871 / α-MeSt, 0.277	15	19	1.12
14	**1b**, 2.70	−78, 30 min	Li-Naph, 0.101 / DPE,[j] 0.177	13	16	1.12
15	**1b**, 2.75	−78, 30 min	K-Naph, 0.0977 / DPE, 0.180	13	16	1.11
16	**1c**, 3.14	−78, 20 h	*n*-BuLi, 0.103 / **2**, 0.186	8.5	10[f]	1.08
17	**1c**, 4.35	−78, 20 h	*n*-BuLi, 0.0598 / **2**, 0.171	20	26[f]	1.10
18	**1c**, 4.16	−78, 20 h	Cumyl-K[k], 0.0744 / DPE, 0.0968	15	15	1.09

[a] Yields of polymers were almost quantitative in each case. [b] M_n(calcd) = [monomer] × (MW of monomer) × f / [initiator] + MW of initiator; $f = 1$ or 2, corresponding to the functionality of the initiators. [c] M_n(obsd) was determined by equation (2) using the SEC calibration of poly(**1b**)s in DMF solution. [d] M_w/M_n was obtained by SEC in DMF solution. [e] Potassium naphthalenide. [f] M_n(obsd) was obtained by ^{1}H NMR spectrum. [g] α-methylstyrene. [h] Lithium naphthalenide. [i] Sodium naphthalenide. [j] 1,1-Diphenylethylene. [k] Cumylpotassium.

Table 5-3

Solubilities of Poly(**1**)s and Polystyrene[a]

solvent	poly(**1a**)	poly(**1b**)	poly(**1c**)	polystyrene
hexane	I	I	I	I
benzene	I	I	I	S
carbon tetrachloride	I	I	I	S
diethyl ether	I	I	I	S
ethyl acetate	I	I	I	S
chloroform	I	S	S	S
acetone	I	S	S	S
1,4-dioxane	I	S	I	S
tetrahydrofuran	I	S	S	S
N,N-dimethylformamide	S	S	S	S
dimethyl sulfoxide	Sw	S	S	I
ethanol	I	I	I	I
methanol	I	I	I	I
water	I	I	I	I
6 N HCl	I	I	Sw	I

[a] I, insoluble; S, soluble; Sw, swelling.

Table 5-3 summarizes the solubilities of poly(**1a**-**c**) obtained in this study. It is generally observed that poly(**1a**-**c**) are insoluble in common organic solvents such as benzene, carbon tetrachloride, diethyl ether, and ethyl acetate. The range of useful solvents of poly(**1a**-**c**) is more limited than that of polystyrene. The high polarity of tertiary sulfonamide moieties of the polymers may promote the solubilities of poly(**1a**-**c**) in polar solvents. Among the resulting poly(**1a**-**c**), the poly(**1a**) particularly shows limited solubility in the various solvents. It is soluble only in polar *N,N*-dimethylformamide and only swells even in dimethyl sulfoxide. The poly(**1c**) is of interest, because it contains a tertiary amino moiety on the piperazine ring in each monomer unit in addition to the polar sulfonamide moiety. This polymer may be converted into tailor-made polyelectrolytes through the quarternization of the tertiary amino group. In fact, the poly(**1c**) swells in 6 N HCl, probably due to the protonation of tertiary amino function on the piperazine ring.

The glass transition temperatures (T_gs) of all polymer samples were determined by differential scanning calorimetry. The T_gs of poly(**1a**), poly(**1b**), and poly(**1c**) were 187°C, 140°C, and 171°C, respectively. As expected, these values were higher than that of polystyrene (T_g = 93°C) with comparable molecular weight.

5-3. Block Copolymerization of 1b and 1c with Styrene, Isoprene, 2-Vinylpyridine, Methyl Methacrylate, and *tert*-Butyl Methacrylate.

The success of living polymerization of **1a**-**c** opens the way for synthesis of block copolymers with strictly controlled chain structures, which are of interest as new heterophase materials containing polar poly(**1**) segments.

At first, the synthesis of an ABA type triblock copolymer, poly(**1b**-*b*-styrene-*b*-**1b**), was carried out by the sequential polymerization of styrene and

1b with potassium naphthalenide at –78°C in THF. Both steps of the polymerizations proceeded to attain 100% conversions of styrene and **1b**. The ^{1}H NMR analysis showed good agreement between the molar ratio of monomer units of both polymer segments and the initial molar ratio of the monomers. The SEC curve of the copolymer shifted toward higher molecular weight region from that of the styrene homopolymer (Figure 5-3). As shown in Table 5-4, the resulting polymer was found to have the predicted molecular weight and a relatively narrow MWD. Consequently, the polymer is the expected ABA triblock copolymer with well-defined block lengths. Similarly, a tailor-made poly(**1c**-*b*-styrene-*b*-**1c**) could be synthesized quantitatively by addition of **1c** to the difunctional living polystyrene.

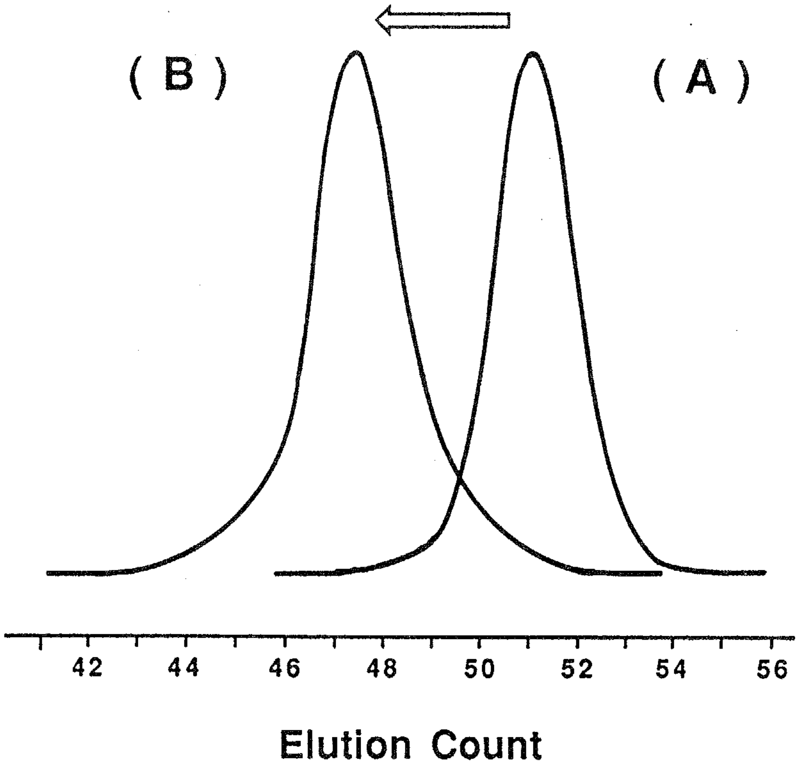


Figure 5-3. SEC curves (DMF) of polystyrene (A) at the first polymerization and poly(**1b**-*b*-styrene-*b*-**1b**) (B): peak A, M_n(obsd) = 12,000, M_w/M_n = 1.08; peak B, M_n(obsd) = 19,000, M_w/M_n = 1.12 (the second monomer was added 10 min after the first addition).

Table 5-4

Block Copolymerization of **1b** and **1c** with Styrene, Isoprene, 2-Vinylpyridine, Methyl Methacrylate, and *tert*-Butyl Methacrylate at –78°C in THF[a]

run	counter-cation	block	A monomer	B monomer	block copolymer (homopolymer[b])		
					$10^{-3}M_n$(calcd)[c]	$10^{-3}M_n$(obsd)[d]	M_w/M_n
19	K^+	A-B-A	**1b**	Styrene	22 (13)	19 (12)	1.12 (1.08)
20	K^+	A-B-A	**1b**	Isoprene	21 (11)	23 (13)	1.16 (1.09)
21	Li^+	A-B-A	**1b**	2VP	21 (9.5)	20 (9.5)	1.16 (1.09)
22[e]	Li^+	B-A-B	**1b**	MMA	17	16	1.16
23	K^+	B-A-B	**1b**	*t*BuMA	26 (12)	23 (12)	1.10 (1.08)
24	Li^+	B-A-B	**1b**	2VP	21 (12)	21 (13)	1.17 (1.15)
25	K^+	A-B-A	**1c**	Styrene	21 (12)	22 (11)	1.05 (1.05)

[a] Yields of polymers were nearly quantitative in each case. Difunctional initiators were used in all block polymerizations. [b] Homopolymers were obtained at the first-stage polymerization. [c] M_n(calcd) = [monomer] × (MW of monomer) × 2 / [initiator] + Mw of initiator. [d] The molecular weights of the block copolymers were determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analysed by ^{1}H NMR.

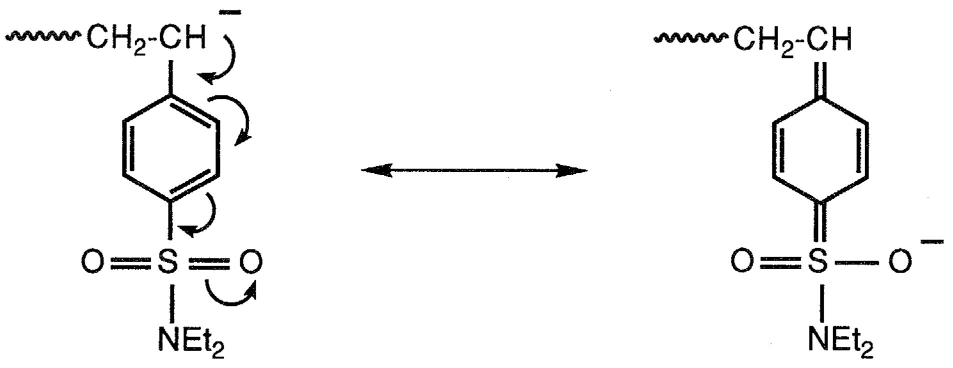
[e] Homopolymer of **1b** was not isolated in this case.

To examine the feasibility of synthesis of other block copolymers, two additional polymerizations were performed by using difunctional living polymers of isoprene and 2-vinylpyridine (2VP) as polymeric initiators of **1b**. Both triblock copolymers, *i.e.*, poly(**1b**-*b*-isoprene-*b*-**1b**) and poly(**1b**-*b*-2VP-*b*-**1b**) were synthesized in quantitative yield. It was found that they had the predictable segment compositions as well as the regulated chain lengths. The results are also listed in Table 5-4 (runs 20 and 21).

Next, the synthesis of the triblock copolymer with reversed sequence of a BAB type, where A was poly(**1b**) and B was an other polymer segment, was attempted. Either isoprene or styrene was added to the difunctional living polymer of **1b** prepared as described in the preceding section. Virtually, no further polymerization occurred in either case, even after several hours in THF at –78°C. Homopolymers of **1b** and the unreacted monomers were quantitatively recovered from the polymerization systems. Thus, the living poly(**1b**) could not initiate the polymerizations of either isoprene or styrene at –78°C. On the other hand, more anionically reactive monomers, such as 2VP, methyl methacrylate (MMA), and *tert*-butyl methacrylate (tBuMA), were quantitatively polymerized with difunctional living poly(**1b**). The SEC and NMR analyses of the resulting polymers indicate that they are block copolymers with desirable segment lengths.

The crossover reaction of **1b** to and from the living polymers of various monomers not only makes available the controlled synthesis of block copolymers containing poly(**1b**) segments, but also elucidates the relative reactivities of the monomers and the carbanions of the living polymers. The living poly(**1b**) is able to initiate the polymerization of 2VP and alkyl methacrylates but is ineffective toward the initiation of styrene and isoprene. In contrast, both living polymers of styrene and isoprene have abilities to initiate the polymerization of **1b**. Accordingly, the living poly(**1b**) has a lower reactivity than living polystyrene and polyisoprene.

These results clearly demonstrated that the electron-withdrawing sulfonamide group significantly affects the reactivity of the living carbanion derived from **1b**. The electron density of the terminal carbanion is decreased by the electron-withdrawing effect of sulfonamide, resulting in the lower nucleophilicity of living poly(**1b**) than that of living polystyrene. In addition to this, it have been proposed that the SO_2 moiety adjacent to the aromatic ring tends to accept negative charge and stabilize the carbanion adjacent to the ring through π-electron resonance analogous to carbonyl, cyano, and nitro moieties.[34] According to the proposal, the extension of the π-conjugated system of the benzylic carbanion may also stabilize the propagating carbanion due to the resonance effect of the *para*-substituted sulfonamide group (Scheme 5-2). Such a stabilized carbanion may react with various monomers having electron-withdrawing groups to allow the anionic polymerizations in a living fashion. In fact, the anionic living polymerizations of styrene derivatives bearing electron-withdrawing groups have become possible. The monomers are *N*-alkylimine, *N,N*-dialkylamide, oxazoline, tert-butyl ester, and nitrile as mentioned in the Introduction.[11-16] More accurate evaluation of the reactivities of new carbanions derived from these monomers is the subject of Chapter 7.



Scheme 5-2

5-4. Conclusion.

This chapter demonstrated that three *N*,*N*-dialkyl-4-vinylbenzenesulfonamides, **1a-c**, were anionically polymerized to afford new types of living polymers. This is the first example of anionic living polymerizations of the styrene derivatives containing of *N*,*N*-dialkylsulfonamide groups. (*N*,*N*-Dialkylamino)sulfonyl functional groups in the monomers and the polymers tolerate the initiation and the repeated propagation reactions during the course of anionic living polymerization. By means of the living polymerization of **1a-c**, homopolymers and the block copolymers with controlled molecular weights and narrow MWDs (M_w/M_n = 1.03 - 1.17) are quantitatively synthesized.

Experimental Section

Materials. Sodium *p*-styrenesulfonate purchased from Tokyo Kasei Co. Ltd. was used without further purification. *N*,*N*-Dimethylformamide (DMF) was dried and distilled from calcium hydride under vacuum. Dimethylamine was distilled under nitrogen from a 40 wt % aqueous solution through a column packed with potassium hydroxide and trapped over calcium with a dry ice-acetone bath. Diethylamine and *N*-methylpiperazine were dried and distilled over calcium hydride under nitrogen. Methyl methacrylate, *tert*-butyl methacrylate, α-methylstyrene, styrene, and isoprene were dried over calcium hydride and distilled on the vacuum line. 2-Vinylpyridine was dried with potassium hydroxide and then distilled from calcium hydride under vacuum. 1,1-Diphenylethylene (DPE), prepared by a literature method,[35] was purified by fractional distillation and finally distilled from *n*-BuLi/pentane under vacuum. Tetrahydrofuran (THF) used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through the vacuum line from sodium naphthalenide solution. Trimethylsilyl chloride, 1,4-dichlorobenzene, and ethyl acetate was purified by standard techniques.[36]

Initiators. Commercially available *n*-BuLi was used without purification and it was diluted by *n*-heptane. Metal naphthalenides were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether with sodium-potassium alloy in THF at room temperature. The oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared just prior to polymerizations from the corresponding metal naphthalenides and a 2-4 molar excess of α-methylstyrene at 20°C for 1 min and then at –78 °C for 10 min. These initiators were stored in ampules equipped with breakseals. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[37]

4-(Trimethylsilyl)chlorobenzene. To a suspension of dry, clean magnesium turnings (10.50 g, 432 mmol) in dry THF (30 mL) at reflux temperature under nitrogen, 1,4-dichlorobenzene (30.04 g, 204 mmol) in dry THF (100 mL) was added dropwise over 30 min. After a further 8 h at reflux, the reaction mixture was cooled to 0°C. To the reaction mixture, trimethylsilyl chloride (26.0 mL, 205 mmol) was added dropwise over 30 min with cooling in an ice bath and then stirred overnight at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 4-(trimethylsilyl)chlorobenzene (14.9 g, 80.7 mmol, 40%, bp 52-53°C/1.2 mmHg). 90 MHz ^1H NMR ($CDCl_3$) δ 0.00 (s, 9H, $SiCH_3$), 7.10-7.26 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ -1.1 ($SiCH_3$), 128.1 (Ar, C2), 134.8 (Ar, C3), 135.2 (Ar, C1), 138.8 (Ar, C4); IR (KBr, cm^{-1}) 2958, 1577, 1484, 1381, 1251, 1085, 1016, 841, 810, 756, 736; Anal. Calcd for $C_9H_{13}SiCl$: C, 58.51, H, 7.09, Cl, 19.19. Found: C, 58.36, H, 7.06, Cl, 19.35.

1,1-Bis(4'-trimethylsilylphenyl)ethylene (2). To a suspension of dry, clean magnesium turnings (3.19 g, 131 mmol) in dry THF (10 mL) at reflux temperature under nitrogen, 4-(trimethylsilyl)chlorobenzene (16.2 g, 87.6 mmol) in dry THF (50 mL) was added dropwise over 30 min. After a further 8 h at reflux, the reaction mixture was cooled to 0°C. To the reaction mixture, dry ethyl acetate (3.48 g, 39.5 mmol) was added dropwise with cooling in an ice bath and then stirred for 1 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and concentrated under reduced pressure.

To the residue, 20% H_2SO_4 (26 mL) was added and then the resulting mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature to give a yellow solid. The solid was taken up in ether (100 mL), and the solution was washed twice with water, five times with saturated $NaHCO_3$ solution, and twice with water. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give slightly yellow solids (9.42 g, 74%). The solids were recrystallized from methanol three times to yield pure white crystals of **2** (3.77 g, 11.6 mmol, 29%): mp 112.0-113.0°C. 90 MHz ^1H NMR ($CDCl_3$) δ 0.28 (s, 18H, $SiCH_3$), 5.48 (s, 2H, $CH_2=$), 7.37-7.55 (m, 8H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ -1.0 ($SiCH_3$), 114.0 ($CH_2=$), 127.7 (Ar, C2), 133.3 (Ar, C3), 139.9 (Ar, C1), 141.9 (Ar, C4), 150.2 (-C=); IR (KBr, cm^{-1}) 2955, 1247, 1118, 1085, 914, 857, 831, 753, 727; Anal. Calcd for $C_{20}H_{28}Si_2$: C, 74.00, H, 8.69. Found: C, 73.82, H, 8.90.

After careful recrystallization, **2** was finally distilled from *n*-BuLi/pentane in an apparatus equipped with a breakseal under vacuum and then diluted with dry THF. The resulting THF solution (0.05 M) of **2** was used in the anionic polymerization.

4-Vinylbenzenesulfonyl Chloride. To thionyl chloride (65 mL) under nitrogen in an ice bath was added sodium *p*-styrenesulfonate (26.3 g, 128 mmol) in small portions with stirring below 10°C for 10 min. To the resulting suspension, dry DMF (35 mL) was added dropwise under cooling. The reaction system became homogeneous and it was stirred for 6 h at room temperature. The reaction mixture was stand in a refrigerator overnight and poured into ice water to quench unreacted thionyl chloride. The aqueous solution was extracted three times with diethyl ether and the combined organic layer was washed three times with water and then dried over $MgSO_4$.

Concentration of the organic solution under reduced pressure gave a solution of 4-vinylbenzenesulfonyl chloride (23.6 g, 116 mmol, 91%) in ether.[38] The resulting solution was used without further purification in the following reaction with dialkylamine, because the sulfonyl chloride tended to spontaneously polymerize in high concentration. 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.55 and 5.96 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.80 (dd, 1H, -CH=), 7.56-8.04 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 119.4 (vinyl, CH_2=), 127.2 (Ar, C2 and C3), 134.8 (vinyl, -CH=), 143.0 (Ar, C1), 144.5 (Ar, C4); IR (KBr, cm^{-1}) 1593, 1374, 1190, 1173, 1082, 988, 927, 844, 651.

***N,N*-Dimethyl-4-vinylbenzenesulfonamide (1a).**[39-41] To a mechanically stirred solution of dimethylamine (18.2 g, 404 mmol) in dry ether (80 mL) under nitrogen, 4-vinylbenzenesulfonyl chloride (26.10 g, 129 mmol) in dry ether (30 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated ammonium salt was filtered off, and the filtrate was washed twice with 2 *N* HCl, twice with saturated $NaHCO_3$ solution, and twice with water and then dried over $MgSO_4$. Concentration of the organic solution under reduced pressure gave yellow colored crystals of **1a** (20.7 g, 98.1 mmol, 76%). Five recrystallizations from methanol gave 1.6 g (7.7 mmol, 6%) of **1a** as pure white crystals: mp 64.0-64.5°C. (lit. [37], mp 63-63.5°C) 90 MHz ^{1}H NMR ($CDCl_3$) δ 2.71 (s, 3H, NCH_3), 5.44 and 5.89 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.78 (dd, 1H, -CH=), 7.50-7.80 (m, 4H, aromatic); 23MHz ^{13}C NMR ($CDCl_3$) δ 37.9 (NCH_3), 117.4 (vinyl, CH_2=), 126.6 (Ar, C3), 128.0 (Ar, C2), 134.5 (Ar, C4), 135.3 (vinyl, -CH=), 141.8 (Ar, C1); IR (KBr, cm^{-1}) 1596, 1453, 1397, 1337, 1189, 1162, 1092, 992, 953, 935, 851, 710; Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85, H, 6.20, N, 6.63, S, 15.17. Found: C, 56.52, H, 6.32, N, 6.51, S, 14.47.

N,N-Diethyl-4-vinylbenzenesulfonamide (1b).

Method A. The same procedure was followed as described for **1a** using 4-vinylbenzenesulfonyl chloride (9.03 g, 37.8 mmol) and diethylamine (6.90 g, 94.5 mmol) in place of dimethylamine and recrystallizations from petroleum ether gave 7.37 g (30.8 mmol, 81%) of **1b**.

Method B. To a mechanically stirred solution of diethylamine (9.60 g, 132 mmol) and 5% NaOH solution (200 mL), 4-vinylbenzenesulfonyl chloride (26.30 g, 130 mmol) in ether (100 mL) was added dropwise with cooling in an ice bath over 30 min and then stirred vigorously overnight at room temperature. The aqueous layer was extracted three times with diethyl ether. The combined ether layer was washed twice with 2 *N* HCl, twice with saturated $NaHCO_3$ solution, and twice with water and then dried over $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether gave **1b** (25.60 g, 107 mmol, 84%) as white crystals: mp 74.5-75.0°C. 90 MHz ^1H NMR ($CDCl_3$) δ 1.13 (t, 6H, $J = 7$ Hz, CH_3), 3.24 (q, 4H, NCH_2), 5.41 and 5.85 (2d, 2H, $J = 11$ and 18 Hz, $CH_2=$), 6.75 (dd, 1H, -CH=), 7.45-7.81 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 42.0 (NCH_2), 117.0 (vinyl, $CH_2=$), 126.6 (Ar, C3), 127.3 (Ar, C2), 135.4 (vinyl, -CH=), 139.3 (Ar, C4), 141.4 (Ar, C1); IR (KBr, cm^{-1}) 1596, 1469, 1331, 1200, 1152, 1089, 1019, 990, 933, 850, 700; Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22, H, 7.16, N, 5.85, S, 13.40. Found: C, 60.17, H, 7.44, N, 5.78, S, 13.07.

N-Methyl-N′-[(4-vinylphenyl)sulfonyl]piperazine (1c). To a mechanically stirred solution of N-methylpiperazine (13.40 g, 134 mmol) and 5% NaOH solution (200 mL), 4-vinylbenzenesulfonyl chloride (27.14 g, 134 mmol) in ether(100 mL) was added dropwise with cooling in an ice bath over 30 min and then stirred vigorously overnight at room temperature. The aqueous layer was extracted three times with diethyl ether. The combined ether layer was washed three times with water and then dried over $MgSO_4$. Concentration of the organic solution under reduced pressure gave slightly yellow crystals of **1c** (30.2 g, 114 mmol, 89%). Recrystallization from ethanol ten times gave **1c** (4.30 g, 16.2 mmol, 12%) as pure white crystals: mp 115.5-116.5°C. 90 MHz ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H, NCH_3), 2.50 (t, 4H, $J = 5$ Hz, CH_2NCH_3), 3.06 (t, 4H, $J = 5$ Hz, SO_2NCH_2), 5.44 and 5.87 (2d, 2H, $J = 11$ and 18 Hz, CH_2=), 6.76 (dd, 1H, -CH=), 7.48-7.76 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 45.5 (NCH_3), 45.7 (CH_2NCH_3), 53.9 (SO_2NCH_2), 117.3 (vinyl, CH_2=), 126.5 (Ar, C3), 128.0 (Ar, C2), 134.2 (Ar, C4), 135.2 (vinyl, -CH=), 142.0 (Ar, C1); IR (KBr, cm^{-1}) 2851, 1596, 1453, 1350, 1331, 1286, 1168, 1152, 1095, 942, 848, 733; Anal. Calcd for $C_{13}H_{18}N_2O_2S$: C, 58.62, H, 6.81, N, 10.52, S, 12.04. Found: C, 58.50, H, 6.57, N, 10.43, S, 11.34.

Monomer Purification. After careful recrystallization, the purified monomer was dried over P_2O_5 for 48 h at ambient temperature in an apparatus equipped with a breakseal under vacuum (10^{-6} mmHg) and then diluted with dry THF. The resulting monomer solutions (0.3-0.5 M in THF) were stored at –30°C until ready to use for the anionic polymerization.

Polymerization Procedures. All polymerizations were carried out at low temperature with shaking under high vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[37] The polymerization was quenched with methanol. The reaction mixture was concentrated, redissolved in THF and then poured into a large excess of water to precipitate the polymers. Polymers collected by filtration were purified by reprecipitation twice with a petroleum ether-THF system. Poly(**1**)s thus obtained were characterized by ^{1}H and ^{13}C NMR, IR and elemental analysis. The following is the full list.

Poly(1a): 90 MHz ^{1}H NMR (DMF-d_7) δ 1.2-2.2 (m, 3H, CH_2CH), 2.6 (broad, 6H, NCH_3), 6.5-7,8 (m, 4H, aromatic); 23 MHz ^{13}C NMR (DMF-d_7) δ 38 (NCH_3), 41-46 (CH_2CH), 128-130 (Ar, C2 and C3), 133.6 (Ar, C1), 150.4 (Ar, C4); IR (KBr, cm^{-1}) 2926, 1598, 1459, 1413, 1340, 1163, 1092, 952, 777; Anal. Calcd for poly(**1a**), $(C_{10}H_{13}NO_2S)_n$: C, 56.85, H, 6.20, N, 6.63, S, 15.17. Found: C, 57.39, H, 6.19, N, 6.34, S, 13.44. T_g = 187°C.

Poly(1b): 90 MHz ^1H NMR ($CDCl_3$) δ 0.8-2.1 (overlapping m, 3H, CH_2CH), 1.1 (broad, 6H, CH_3), 3.2 (broad, 4H, NCH_2), 6.3-7,8 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 41-43 (CH_2CH), 42.1 (NCH_2), 127.1 and 127.8 (Ar, C2 and C3), 138.9 (Ar, C1), 148.9 (Ar, C4); IR (KBr, cm^{-1}) 2978, 2936, 1598, 1333, 1202, 1155, 1092, 1019, 935, 785, 700; Anal. Calcd for poly(**1b**), $(C_{12}H_{17}NO_2S)_n$: C, 60.22, H, 7.16, N, 5.85, S, 13.40. Found: C, 59.84, H, 7.22, N, 5.47, S, 12.90. T_g = 140°C.

Poly(1c): 90 MHz ^1H NMR ($CDCl_3$) δ 1.1-3.4 (overlapping m, 3H, CH_2CH), 2.24 (s, 3H, NCH_3), 2.49 (broad, 4H, $\mathit{CH_2}NCH_3$), 2.98 (broad, 4H, SO_2NCH_2), 6.5-7.8 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 41-46 (CH_2CH), 45.8 (NCH_3 and $\mathit{C}H_2NCH_3$), 54.1 (SO_2NCH_2), 127-129 (Ar, C2 and C3), 134.1 (Ar, C1), 149.6 (Ar, C1); IR (KBr, cm^{-1}) 2886, 2798, 1598, 1455, 1380, 1288, 1168, 1152, 1087, 948, 787, 726; Anal. Calcd for poly(**1c**), $(C_{13}H_{18}N_2O_2S)_n$: C, 58.62, H, 6.81, N, 10.52, S, 12.04. Found: C, 58.29, H, 6.74, N, 9.72, S, 11.34. T_g = 171°C.

Postpolymerization. In the all-glass apparatus in vacuo, by the reaction of oligo(α-methylstyryl)dipotassium and **1b** in THF at –78°C for 30 min the prepoly(**1b**) was quantitatively prepared and somewhat sampled to determine the characteristics. To the residual reaction mixture at –78°C, the second feed of **1b** in THF solution was again added and reacted for 30 min to complete the further polymerization. After quenching with methanol, both pre- and postpolymer were obtained in quantitative yield. In both cases of postpolymerization at 0°C and that carried out with lithium counter cation at –78°C, similar results were obtained. Block copolymerizations of **1**s were performed in a similar manner.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^{1}H, 22.53MHz ^{13}C) in $CDCl_3$ or DMF-d_7. Chemical Shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Chemical shifts of poly(**1a**) were reported in ppm downfield relative to DMF-d_7 (δ 8.05) for ^{1}H NMR and (δ 162.5) for ^{13}C NMR as standard. Size exclusion chromatograms (SEC) for MWD determinations of poly(**1**)s were obtained at 40°C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) with ultraviolet (254 nm) or refractive index detection. THF or DMF was the carrier solvent at a flow rate of 0.8 mL min^{-1}. Laser light scattering measurements for weight-average molecular weight determination were performed at 25°C with an Ootsuka Electronics SLS-600R instrument in THF solution. The glass transition temperature was measured by differential scanning calorimetry using a Perkin Elmer DSC7 apparatus and analyzed by a Perkin Elmer PC Data Station. The samples were first heated to 200°C, cooled rapidly to room temperature, and then scanned again at a rate of 20°C min^{-1}.

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(31) The 18 (initiator **3**) or 36 (initiator **4**) trimethylsilyl protons of these initiator residues in the polymers provide valuable probes for determining number-average molecular weights by ^{1}H NMR analysis. The propagating carbanion of poly(**1b**) caused no crossover reaction with **2** due to the low nucleophilicity, which indicated that the polymer contained no 1,1-bis[4'-(trimethylsilyl)phenyl]ethylene unit other than the initiator residue.

(32) Using **3** as an initiator, poly(methyl methacrylate) with a narrow MWD ($M_w/M_n = 1.02$) and a predicted molecular weight (M_n(obsd) = 12 000 and M_n(calcd) = 12 000) was quantitatively produced in THF at –78°C. From this experiment, it is clear that **3** is a good initiator for living polymerization of methyl methacrylate.

(33) It should be mentioned that **1a** in a bulk and in a solution show the high polymerization tendency in a wide range of concentrations and temperature.[39] It is therefore necessary for purification of the monomer to take care of recrystallization.

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Chapter 6

Anionic Polymerizations of 2-, 3-, and 4-Cyanostyrene

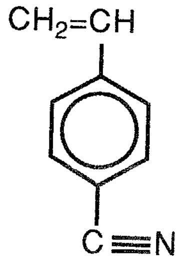
ABSTRACT: Anionic polymerizations of 4-cyanostyrene (**1**), 3-cyanostyrene (**2**), and 2-cyanostyrene (**3**) were carried out in tetrahydrofuran (THF). The initiators included lithium naphthalenide, potassium naphthalenide, oligo(α-methylstyryl)dilithium and -dipotassium, (1,1,4,4-tetraphenylbutanediyl)dilithium and -dipotassium, [1,1-bis[4'-(trimethylsilyl)phenyl]hexyl]lithium, and [1,1,4,4-tetrakis[4'-(trimethylsilyl)phenyl]butanediyl]dipotassium. The polymerization of **1** proceeded quantitatively with each of these initiators at –78°C for 2 h. The resulting polymers all possessed molecular weights predicted from the molar ratios of monomer to initiator and narrow molecular weight distributions (MWDs). The persistency of propagating activity at the chain end of poly(**1**) was confirmed by the quantitative initiation efficiency in the postpolymerization at –78°C. These results strongly indicated that the anionic polymerization of **1** afforded a stable living polymer under the conditions. The Mark-Houwink equation for poly(**1**), $[\eta] = 1.004 \times 10^{-4} M^{0.749}$ (in *N,N*-dimethylformamide at 40°C), was correlated. New block copolymers, poly(**1**-*b*-styrene-*b*-**1**) and poly[(methyl methacrylate)-*b*-**1**-*b*-(methyl methacrylate)] could be synthesized by using living polymerization system of **1**. The results of both polymerization of **2** and **3** were not very satisfactory from a view point of living polymerization. The polymerization of **2** did not occur at –78°C at all, but proceeded quantitatively with warming to –30°C. However, undesirable side reactions might considerably occur at this temperature from the fact that the resulting poly(**2**) had somewhat broad MWD. The anionic polymerization of **3** gave polymeric products having low molecular weights only in a 30% yield even for longer reaction time of 200 h at –78°C. The resulting poly(**3**)s were found to have again broad MWDs.

Introduction

It has been recently reported anionic polymerizations of a series of *para*-substituted styrenes containing electron-withdrawing groups[1] such as *N,N*-dialkylamide,[2] *N*-alkylimino,[3] trimethylsilylethynyl,[4] oxazolinyl,[5] *tert*-butyl ester,[6] and *N,N*-dialkylsulfonamide.[7] The vinyl polymerizations of these monomers proceeded quantitatively and the resulting polymers had predicted molecular weights based on molar ratios of monomer to initiator and narrow molecular weight distributions (MWDs). The propagating carbanions at the chain ends maintained quantitative activities promoting the further polymerization to produce the well-defined block copolymers after the complete consumption of the monomers. These results clearly demonstrated that the stable living polymers yielded in the polymerization reactions of these functional monomers. This is a surprising finding because these polar electron-withdrawing groups are usually believed to be susceptible to the nucleophilic attack of anionic initiators and propagating chain end. The success of the living polymerization of these monomers may be due to the stabilization of carbanions at their active chain ends by these electron-withdrawing groups. Furthermore, the extension of the π-conjugated system of terminal benzylic carbanion[8] may also provide an additional effect to stabilize the propagating carbanion due to the resonance effect of the *para*-substituted electron-withdrawing groups. Thus, the electron-withdrawing group plays a very important role to yield the stable propagating chain-end of living polymer.

This success suggested the possible extension to the styrenes with another electron-withdrawing group. This chapter deals with a cyano group as an electron-withdrawing group for extension of the investigations concerning the anionic living polymerizations of functional styrenes. Since the cyano group is known to show a strongly electron-withdrawing effect and involve carbon-nitrogen triple bond containing π-conjugated electron,[9] the similar polymerization behavior may be expected in the polymerization of cyanostyrenes.

In this chapter, the author describes the anionic living polymerization of **1** under various conditions including the synthesis of block copolymer containing poly(**1**) segment. The anionic polymerizations of two additional positional isomers of cyanostyrene, 3-cyanostyrene (**2**) and 2-cyanostyrene (**3**) are also carried out, because it is expected that the position of cyano group on aromatic ring may affect their polymerization behaviors.



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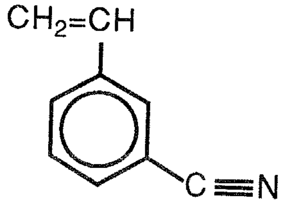

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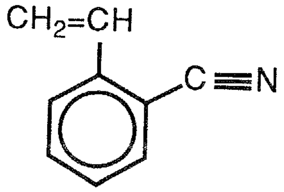
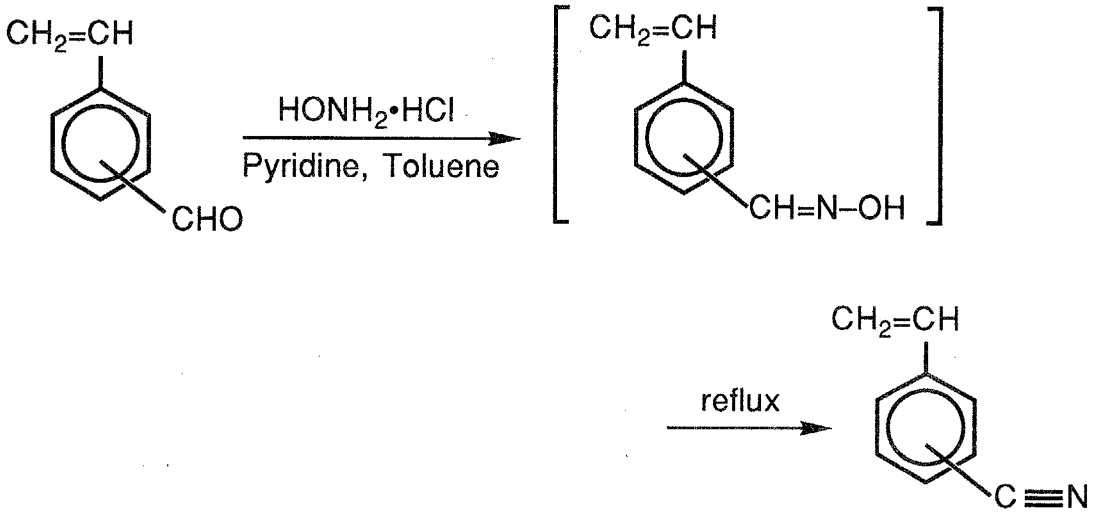


3

Results and Discussion.

6-1. Syntheses of Cyanostyrenes.

Cyanostyrenes were previously prepared by the coupling reaction of arylbromide[10] or diazonium salt[11] and cuprous cyanide. Unfortunately, these synthetic methods involved the use of highly toxic cuprous cyanide and the yields of products were moderate. An alternative method was here developed to synthesize cyanostyrenes by using modified reaction reported by Saednya.[12] The reaction involves an one-pot synthesis of cyanostyrenes from the corresponding formylstyrenes, which proceeds via the formation of oxime *in situ* and the subsequent dehydration of the resulting oxime as shown in Scheme 6-1. Yields of cyanostyrenes were usually fairly good in these two-step reactions. The resulting nitrile monomers were thoroughly purified by several fractional distillations over calcium hydride *in vacuo*. Then the monomers were finally distilled over phenylmagnesium chloride on the vacuum line to attain the sufficient purity of monomers for the anionic polymerization.



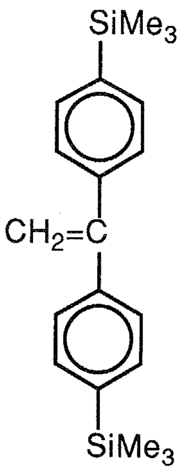
1 : *para* 69%
2 : *meta* 72%
3 : *ortho* 60%

Scheme 6-1

6-2. Anionic Polymerization of 4-Cyanostyrene (1).

As mentioned in the Introduction, cyano group is a well-known electron-withdrawing group.[9] The strong electron-withdrawing nature is clear from the fact that the Hammett σ-value of cyano group is estimated to be in the range of 0.64 - 0.70.[13] Reynolds *et al.*[14] reported that the substituents effects could be evaluated from the chemical shift of the β-carbon of vinyl group in ^{13}C NMR spectra of 4-substituted styrenes. In fact, the chemical shift of the vinyl β-carbon of 4-cyanostyrene (117.6 ppm) considerably shifts toward lower field from that of styrene (113.8 ppm).[15] The Hammett σ-value of cyano group of **1** can also be estimated to be 0.75 from the chemical shift, which again suggests the strong electron-withdrawing character of cyano group of **1**. Accordingly, the electron-withdrawing cyano group may decrease the electron density of the vinyl group through the π-conjugated system, resulting in high reactivity of **1** in the anionic polymerization. For example, Q and e values for 4-cyanostyrene are reported to be 1.67 and 0.325, respectively.[16] As expected, the positive e value for **1** ($e = 0.33$) clearly supports the low electron density on the vinyl β-carbon and the higher reactivity of **1** than styrene ($e = -0.8$) in the anionic polymerization. In addition to this, the extension of the conjugated system of monomer molecule is apparent from the large Q value ($Q = 1.67$) compared with that of styrene ($Q = 1.0$). Thus, the strong electron-withdrawing effect of cyano group will significantly enhance the reactivities of cyanostyrenes in their polymerization reactions.

The anionic polymerization of **1** was first investigated in THF at −78°C with [1,1-bis[4'-(trimethylsilyl)phenyl]hexyl]lithium and [1,1,4,4-tetrakis[4'-(trimethylsilyl)phenyl]butanediyl]dipotassium as initiators.[17] These initiators were prepared at −78°C in THF by the reactions of either *n*-butyllithium (*n*-BuLi)/heptane or potassium naphthalenide/THF and 1,1-bis[4'-(trimethylsilyl)phenyl]ethylene (**4**).



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On the addition of **1** to the initiator solution, the color of reaction mixture changed from rose red into dark red which resembles that of living polystyrene. The coloration was maintained during the course of polymerization until it was quenched with methanol. In some polymerization systems aiming at the syntheses of high molecular weight polymers, although the polymers precipitated as the reaction proceeded, 100% conversions of **1** always attained in 20 h. The polymers were quantitatively obtained after precipitating the polymerization mixture into methanol. In the ^{1}H NMR spectrum of the resulting polymer, the signals corresponding to the vinyl protons of **1** completely disappear and the broad signals due to the polymer backbone are observed. Typical ^{13}C NMR spectra of **1** and poly(**1**) are shown in Figure 6-1. After the polymerization, the signals corresponding to the vinyl carbons (117.6 and 135.2 ppm) completely disappear and alternatively those of methylene and methine carbons of polymer main chain newly appear at 40-44 ppm. The signal due to the cyano carbon at 119.2 ppm is observed unchanged in the same region of the monomer (118.7 ppm). In the infrared spectrum of the polymer exhibits the strong and characteristic C≡N stretching absorption at 2230 cm^{-1}, whereas the absorptions due to the vinyl deformation at 923 and 990 cm^{-1} no longer exist. These spectroscopic observations of the polymer suggest the expected structure of poly(**1**) obtained by the vinyl polymerization.

Table 6-1 summarizes the results of anionic polymerization of **1**. The molecular weights and their distributions of the poly(**1**)s were first measured by size exclusion chromatography (SEC) calibrated by the standard polystyrenes using DMF as an eluent. All the SEC curves of poly(**1**) showed sharp and unimodal peaks. The polydispersity indices (M_w/M_n) were within 1.1. However, the relative molecular weights of poly(**1**)s estimated from SEC calibration do not agree with the calculated values based on the molar ratio of monomer to initiator. They all present the values approximately 3 times

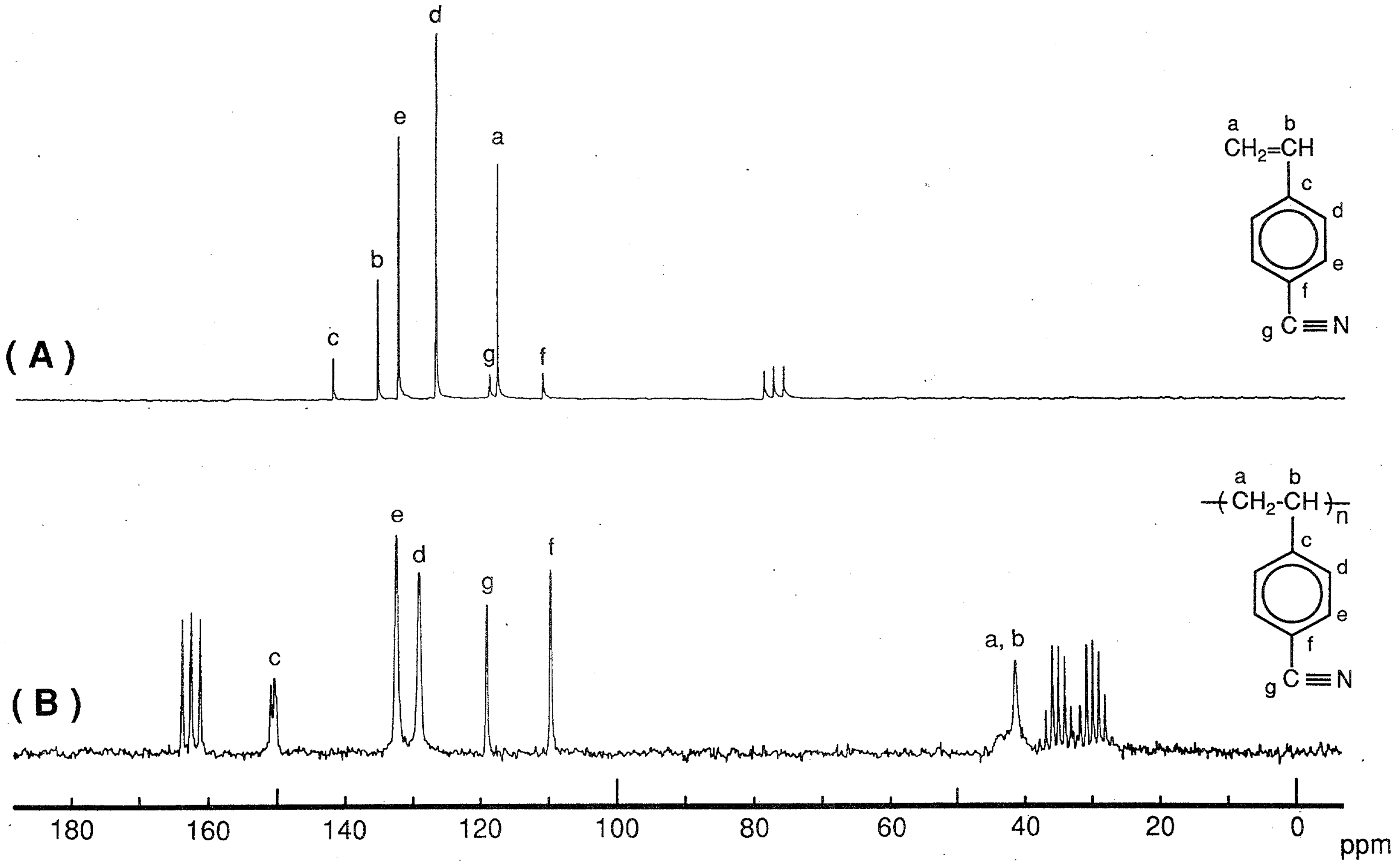


Figure 6-1. ^{13}C NMR spectra of **1** in $CDCl_3$ (A) and of poly(**1**) in DMF-d_7 (B).

Table 6-1

Anionic Polymerization of **1** in THF at –78°C for 1-20 h[a]

	1		$10^{-3}M_n$				
run	mmol	initiator, mmol	calcd[b]	NMR	SEC[c]	M_w/M_n[d]	M_w(LS)[e]
1	3.74	K-Naph[f], 0.127 / **4**, 0.172	8.2	8.7	23	1.07	
2	5.36	K-Naph, 0.117 / **4**, 0.157	12	13	33	1.07	
3	7.01	K-Naph, 0.0970 / **4**, 0.228	19	20	45	1.07	
4	9.85	*n*-BuLi, 0.0402 / **4**, 0.0414	32	30	80	1.05	38
5	10.3	*n*-BuLi, 0.0453 / **4**, 0.135	30	33	94	1.04	
6	11.6	*n*-BuLi, 0.0285 / **4**, 0.0289	53	61	140	1.06	66
7	18.3	*n*-BuLi, 0.0239 / **4**, 0.0244	99	122	270	1.09	137

[a] Yields of polymers were almost quantitative in each case. [b] M_n(calcd) = [monomer] × (MW of monomer) × f / [initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [c] M_n(SEC) was obtained by SEC calibration using standard polystyrenes in DMF solution. [d] M_w/M_n was estimated from SEC calibration for poly(**1**) as shown in an equation (1). [e] M_w(LS) was obtained by light scattering in DMF at 25°C. [f] Potassium naphthalenide.

higher than the calculated ones. As discussed later, these deviations are probably due to the difference of hydrodynamic volume between poly(**1**) and polystyrene in DMF solution at 40°C. The constancy of the M_n(GPC)/M_n(calcd) ratio over the whole range of molecular weights suggests the livingness of this polymerization system, but more accurate method for determination of the molecular weights is necessary before any firm conclusion can be made.

For the accurate determination of the number-average molecular weights of the end-labeled polymers, ^{1}H NMR spectroscopy is proposed as a very useful method.[18] To estimate the molecular weights of poly(**1**) from the end group analysis by using NMR spectrum, novel anionic initiators containing trimethylsilyl protons as an NMR probe was synthesized by the reaction of **4** and either *n*-BuLi or metal naphthalenides.[17] With these initiators, seven samples of poly(**1**) were here prepared. Comparing the relative integrated intensity between the trimethylsilyl protons and the aromatic or the methylene and methine protons of the poly(**1**) main chain, the reproducible values of M_n were actually obtained within ± 10%. These M_n(NMR)s of poly(**1**)s fairly agree well with the theoretical values predicted from the initial molar ratios of monomer to initiator as can be seen in Table 6-1. Thus, the good agreement of two values and linear relationship between M_n(NMR) and M_n(GPC) give the following equation useful to estimate the practical molecular weights of poly(**1**) samples.

$$M_n(\text{obsd}) = 0.459 M_n(\text{GPC}) - 3820 \qquad (1)$$

The M_w/M_n values were estimated by using the above calibration for poly(**1**) and those were listed in Table 6-1. These values are again within 1.1, which strongly indicate that all the polymers have narrow MWDs. In addition, the weight-average molecular weights of three poly(**1**) samples were independently determined by light scattering measurement. The values, M_w(LS)s, are also listed in Table 6-1. These absolute values of M_w(LS)s are close to the weight-average molecular weights estimated from the M_n(NMR)s and their MWDs by SEC. This closeness supports the reliability of molecular weights obtained from the end group analysis by ^{1}H NMR. Accordingly, these controlled molecular weights in the range of 8700 - 122 000 and narrow MWDs substantiate that the anionic polymerization of **1** is free from termination and transfer reactions, *viz.*, living character of the polymerization.

Effect of Anionic Initiator. The polymerization of **1** was performed with various anionic initiators at –78°C in order to examine the scope of living system. The results were listed in Table 6-2. The employed anionic initiators included lithium naphthalenide and potassium naphthalenide, (1,1-diphenylhexyl)lithium, cumylpotassium, oligo(α-methylstyryl)dilithium and -dipotassium, and (1,1,4,4-tetraphenylbutanediyl)dilithium and -dipotassium. With these initiators, the polymerizations of **1** quantitatively proceeded at –78°C within 2 h. The molecular weights of the resulting poly(**1**)s were determined by using an above-mentioned SEC calibration curve. Every poly(**1**)s thus obtained had predictable molecular weights from the ratios between monomers to initiators and very narrow MWDs (M_w/M_n = 1.05 -1.09). Consequently, the anionic living polymerizations of **1** are also realized in these polymerization systems at –78°C in THF. The initiators available for the living polymerization are widely ranged in chemical species (radical anion and carbanion), reactivities (metal naphthalenide and carbanions capped with α-methylstyrene or 1,1-diphenylethylene) countercations (lithium and potassium), and functionalities (monofunctional and difunctional). Unfortunately, the poly(**1**) directly initiated with *n*-BuLi was found to have a molecular weight significantly higher than the predicted value, although its MWD was very narrow (run 8). In this case, *n*-BuLi, a highly reactive

Table 6-2 Anionic Polymerization of **1** in THF[a]

	1			$10^{-3}M_n$		
run	mmol	temp(°C), time(h)	initiator, mmol	calcd[b]	obsd[c]	M_w/M_n[c]
8	3.98	–78, 2	*n*-BuLi, 0.0445	12	18	1.05
9	9.08	–78, 2	*n*-BuLi, 0.0946 / DPE,[d]	13	14	1.05
4	9.85	–78, 20	*n*-BuLi, 0.0402 / **4**, 0.0414	32	30	1.05
5	10.3	–78, 20	*n*-BuLi, 0.0453 / **4**, 0.135	30	33	1.04
6	11.6	–78, 20	*n*-BuLi, 0.0285 / **4**, 0.0289	53	61	1.06
7	18.3	–78, 20	*n*-BuLi, 0.0239 / **4**, 0.0244	99	122	1.09
10	3.68	–78, 0.5	Li-Naph,[e] 0.0881	11	8.7	1.07
11	3.84	–78, 0.5	Li-Naph, 0.0844 / α-MeSt,[f] 0.205	12	12	1.07
12	6.93	–78, 0.5	Li-Naph, 0.171 / DPE, 0.234	11	11	1.07
13	9.37	–78, 2	Cumyl-K,[g] 0.0842 / DPE,	15	15	1.09
14	7.97	–78, 2	Cumyl-K, 0.0427 / DPE,	24	27	1.06
15	9.15	–78, 12	Cumyl-K, 0.0281 / DPE,	42	37	1.07
16	3.79	–78, 0.5	K-Naph,[h] 0.0962	10	9.2	1.07
17	3.54	–78, 0.5	K-Naph, 0.0786 / α-MeSt, 0.229	12	12	1.06
18	5.26	0, 1	K-Naph, 0.143 / DPE, 0.201	9.9	11	1.49
19	3.84	–30, 1	K-Naph, 0.0991 / DPE, 0.290	10	12	1.07
20	4.23	–78, 0.5	K-Naph, 0.102 / DPE, 0.248	11	9.3	1.08
1	3.74	–78, 1	K-Naph, 0.127 / **4**, 0.172	8.2	8.7	1.07
2	5.36	–78, 1	K-Naph, 0.117 / **4**, 0.157	12	13	1.07
3	7.01	–78, 4	K-Naph, 0.0970 / **4**, 0.228	19	20	1.07

[a] Yields of polymers were almost quantitative in each case. [b] M_n(calcd) = [monomer] × (MW of monomer) × f / [initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [c] M_n(obsd) and M_w/M_n were estimated from the SEC calibration using several poly(**1**) samples in DMF solution. [d] 1,1-Diphenylethylene. [e] Lithium naphthalenide. [f] α-Methylstyrene. [g] Cumylpotassium. [h] Potassium naphthalenide.

nucleophile, may attack the cyano carbon of the monomer at the initiation step even at –78°C to some extents. Then, the decrease of concentration of the propagating carbanion at the initiation reaction increased the molecular weight of the resulting polymer but did not affect the MWD.

Effect of Polymerization Temperature. As described above, when the anionic polymerization of **1** was carried out at –78°C, the MWDs of the resulting poly(**1**)s were narrow in all cases. With raising the polymerization temperature to –30°C, a polymer having a narrow MWD and a predicted molecular weight was still obtained (run 19). By contrast, a broadening of the MWD (M_w/M_n = 1.49) occurred when the polymerization was carried out at 0°C. This is probably due to the undesirable side reaction of the propagating species during the course of polymerization at temperatures over 0°C. Nucleophilic attack of the propagating carbanion on the cyano groups might occur at this temperature. It should be mentioned that the suitable choice of the reaction temperature below 0°C is necessary for complete control of the polymerization of **1**.

Postpolymerization. Evidence for the living polymerization of **1** is also provided by the postpolymerization of **1** in THF at –78°C. After **1** was completely polymerized with (1,1,4,4-tetraphenylbutanediyl)dilithium for 30 min, the second feed of **1** was added to the polymerization system. The mixture was allowed to stand for an additional 30 min to complete the second polymerization. The conversion of each polymerization was quantitative. The pre- and postpolymer possessed the molecular weights, 7000 (M_w/M_n = 1.04) and 16 000 (M_w/M_n = 1.05), closed to the respective theoretical values, 6800 and 16 000. It was found that the SEC curve of the prepolymer shifted toward that of the postpolymer on the higher molecular weight side, maintaining the sharp shape of the chromatogram (Figure 6-2). These results indicate that the active chain end of living poly(**1**) is stable at −78°C at least for 30 min and is able to initiate further polymerization with quantitative efficiency. It was ascertained that the propagating chain end of poly(**1**) containing potassium countercation was stable under the identical condition, when cumylpotassium was employed as an initiator of **1**. Accordingly, the both lithium and potassium cation are able to promote the anionic living polymerization of **1**.

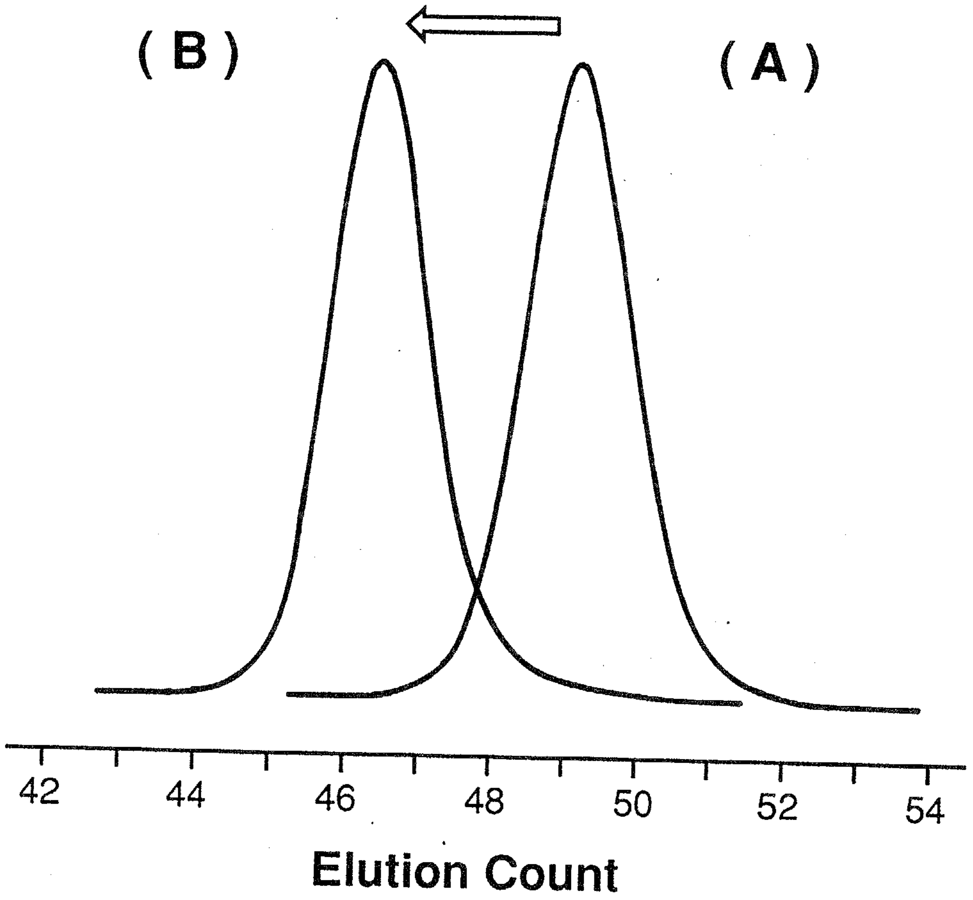


Figure 6-2. SEC curves of poly(**1**)s obtained at −78°C: the first-stage polymerization (A), M_n(obsd) = 7000, M_w/M_n = 1.04; the second-stge polymerization (B), M_n(obsd) = 16 000, M_w/M_n = 1.05 (the second feed of monomer was added 30 min after the first-stage polymerization).

The results obtained here clearly demonstrated that the anionic living polymerization of **1** could be attained under the various conditions. This success of living polymerization is a surprising fact judging from the numerous reports concerning the nucleophilic attack of cyano group by carbanionic species similar to the initiators used here.[19]

6-3. Anionic Polymerization of 2-Cyanostyrene (3) and 3-Cyanostyrene (2).

The results in the preceding section have clearly shown that the anionic polymerization of 4-cyanostyrene proceeded well to yield the stable living polymer under the various conditions. In this section, anionic polymerizations of the *ortho* and *meta* isomers (**3** and **2**) were carried out and the positional effects of cyano substituent on their polymerization behaviors were discussed. It is well known that the position of the substituent on the aromatic ring in organic aromatic compounds significantly influences the acidity, reactivity, and regioselectivity toward several reactions due to their electronic effects. If there is little or no steric effect of the substituent, the electronic substituent effects of *para* and *ortho* isomers would be analogous to the situation found in organic reactions. This means that 2- and 4-cyanostyrene will promote similar polymerization behaviors. On the other hand, in the case of *meta* isomer, only an inductive effect (no resonance effect) of the cyano group would be expected.

First, the anionic polymerization of the *ortho* isomer, **3**, was carried out under conditions identical to those used for the *para* isomer, **1**, as shown in Table 6-3. An immediate color change of the reaction mixture from dark red to bright red was observed at –78°C on the addition of **3** to the initiator solution, but the resulting red color faded within 1 min. Most of the unreacted monomer was recovered from the reaction system in each polymerization. Polymeric product was obtained in a low yield after the

Table 6-3

Anionic Polymerization of **3** and **2** in THF

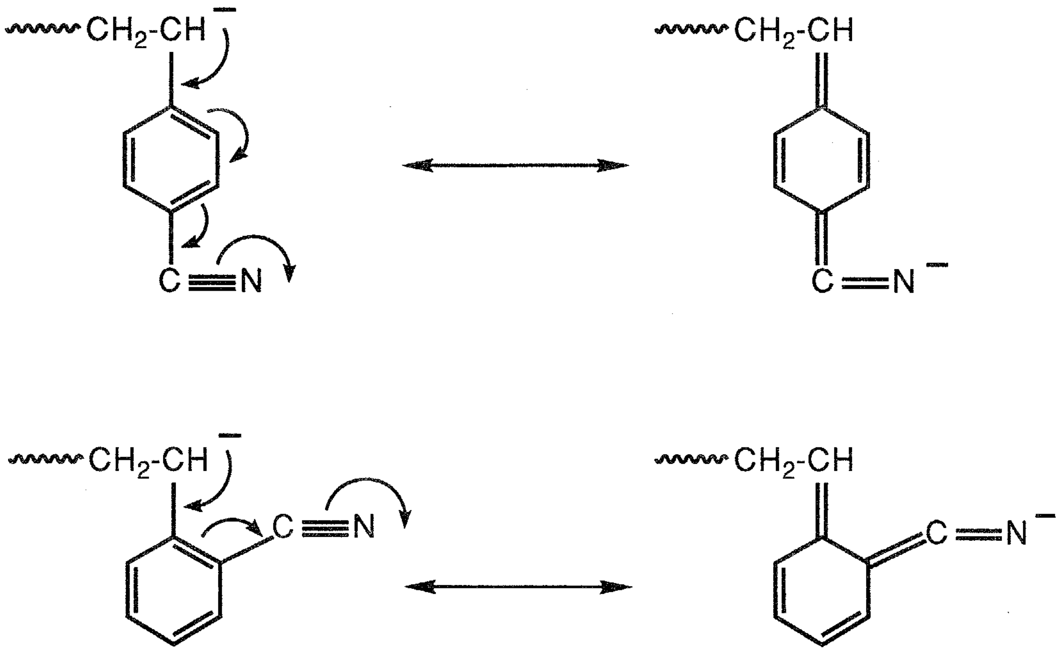
run	monomer, mmol	temp (°C), time (h)	initiator, mmol	yield, %	$10^{-3}M_n$		M_w/M_n[b]
					calcd[a]	obsd[b]	
21	**3**, 5.03	–78, 0.5	K-Naph,[c] 0.119 / α-MeSt,[d] 0.306	17	2.5	2.7	1.32
22	**3**, 5.02	–78, 20	K-Naph, 0.113 / DPE,[e] 0.119	15	2.1	6.5	1.42
23	**3**, 4.75	–78, 200	K-Naph, 0.121 / DPE, 0.206	30	3.4	2.8	1.78
24	**3**, 4.83	–78, 20	Li-Naph,[f] 0.115 / DPE, 0.192	8	1.2		
25	**3**, 4.94	–30, 3	K-Naph, 0.126 / DPE, 0.210	11	1.5	2.4	1.29
26	**2**, 4.88	–78, 0.5	K-Naph, 0.116 / **4**, 0.191	0			
27	**2**, 4.73	–78, 20	K-Naph, 0.139 / DPE, 0.200	0			
28	**2**, 5.57	–78, 400	K-Naph, 0.124 / DPE, 0.169	0			
29	**2**, 3.20	–78, 20	Li-Naph, 0.0843 / **4**, 0.167	0			
30	**2**, 3.92	–30, 0.5	K-Naph, 0.0899 / DPE, 0.178	27	3.4	2.7	1.06
31	**2**, 3.28	–30, 3	K-Naph, 0.106 / DPE, 0.221	100	8.0	7.1	1.15
32	**2**, 6.09	–30, 20	K-Naph, 0.157 / **4**, 0.272	100	10	11	1.16
33	**2**, 6.02	–30, 5	K-Naph, 0.0657 / DPE, 0.215	40	9.6	11	1.16
34	**2**, 4.42	–30, 20	K-Naph, 0.0407 / DPE, 0.139	100	28	24	1.19

[a] M_n(calcd) = [monomer] × (MW of monomer) × 2 × yield / [initiator] + MW of initiator. [b] M_n(obsd) and M_w/M_n were obtained by the SEC calibration using standard polystyrenes in THF solution. [c] Potassium naphthalenide. [d] α-Methylstyrene. [e] 1,1-Diphenylethylene. [f] Lithium naphthalenide.

reaction solution was poured into methanol. ^{1}H NMR and SEC analyses ascertained that the methanol-insoluble part was a poly(**3**) with a low molecular weight and a broad MWD. Attempts to polymerize **3** both for a long time (run 23) and at a higher temperature (run 25) were not successful in the quantitative synthesis of the polymers with well-defined chain structures. Poly(**3**) with a broad MWD was produced at most in 30% yield even after 200 h at –78°C with (1,1,4,4-tetraphenylbutanediyl)dipotassium. These findings indicate that the active chain-end of the poly(**3**) produced may be unstable and a side reaction considerably occurs at the early stage of the polymerization. The susceptibility of the *ortho* isomer to the side reaction can be accounted for by an intramolecular side reaction, which includes nucleophilic attack of the propagating carbanion on the cyano group located near the carbanion.

Next, the polymerization of the *meta* isomer, **2**, was investigated under the identical conditions (Table 6-3). An immediate color change of the reaction mixture again took place on the addition of **2** to (1,1,4,4-tetraphenylbutanediyl)dipotassium at –78°C. In this case, the mixture maintained the red coloration during the reaction, but the monomer was quantitatively recovered after 0.5–20 h. No polymerization of **2** was found to occur under the conditions where the quantitative polymerization of the *para* isomer was attained. Furthermore, no polymeric products were obtained at –78°C even after 400 h. When the polymerization temperature was raised from –78°C to –30°C, the polymerization of **2** proceeded. The rate of polymerization seemed to be slow even at –30°C from the fact that the yield of polymer was only 27% after 30 min. A longer time of 3 h was required for a quantitative conversion (run 31). The chemical structure of the resulting polymer was ascertained as the poly(**2**) produced by the vinyl addition from the analyses of NMR and IR spectra. No heterogeneous structure was observed within the range of the spectroscopic measurements. The molecular weights of the polymers estimated by SEC fairly agreed with the values calculated from the ratios of consumed monomers to initiators. The MWD of the resulting polymer was unimodal and narrow when the polymerization was carried out for 30 min, although its molecular weight and yield were low (run 30). However, in the case of the polymerization for a longer time, the MWDs became somewhat broader, particularly after the complete consumption of the monomer. Although M_w/M_n values were within 1.2, a bimodal peak with a tailing on the low molecular weight side was observed in the SEC chart (runs 31–34). These phenomena suggest that side reactions slowly occur during the course of polymerization of **2** at –30°C, whereas the polymerization proceeds quantitatively. The side reactions are probably due to the inter- and intramolecular nucleophilic attacks of the propagating carbanion on the cyano functionality.

From the polymerization results of **1**-**3**, it is evident that the position of cyano group seriously affects their polymerization reactions. Only the *para* isomer is capable of the anionic living polymerization. Undoubtedly, the propagating carbanion stabilized by the *para*-substituted electron-withdrawing cyano group greatly contributes to form the living polymer in the polymerization of **1**. In contrast to the *para* isomer, both *meta* and *ortho* isomers cause the undesirable side reactions in greater or lesser degree. As shown in Scheme 6-2, in the cases of **1** and **3**, the cyano groups on the benzenoid system can accept negative charge partly to stabilize the benzylic carbanions through π-electron resonance.[8] The inductive effect of the cyano group also tends to stabilize the both propagating carbanions. Thus, a similar electronic effect promoting the stabilization will be expected in the polymerizations of *para* and *ortho* isomers. However, in the case of the propagating terminal of *ortho* isomer, since the cyano group was located near the reactive benzylic carbanion, intramolecular nucleophilic attack of the carbanion on the cyano group might occur at an early stage of the polymerization. This serious side reaction resulted in a low yield of poly(**3**) with a broad MWD. In the case of **2**, the resonance effect of the cyano group is negligible, since the terminal benzylic carbanion of the *meta* isomer can not conjugate with the cyano substituent. Only the inductive effect of the group contributes a stabilization of the active chain end. The stabilization seems not to be enough for achieving the living polymerization of *meta* isomer. The considerable amount of termination reactions might occur during the polymerization, although one could obtain the poly(**2**) in quantitative yield by the long time reaction.



Scheme 6-2

As mentioned in the Introduction, it has been reported the successful examples of anionic living polymerization of styrene derivatives *para*-substituted with some electron-withdrawing functionalities.[1-7] From the results obtained in this section, it seems that the success of the living polymerization of *para* isomer does not always mean that the *meta* and *ortho* isomers will also undergo living polymerization. Therefore, the polymerization chemistry of the ring-substituted styrenes is complicated and is of great interest to clarify the features totally. The modification of the reaction conditions would be required for the anionic living polymerization of the *meta* and *ortho* isomers containing the various functional groups.

6-4. Block Copolymerization of 1 with Styrene and Methyl Methacrylate (MMA).

Interest in block copolymers has recently increased because of their properties as an interfacial agent between the incompatible homopolymers[20] as well as their ordered morphologies observed in bulk. The success of living polymerization of 4-cyanostyrene opens the way to the controlled synthesis of novel block copolymers containing polar poly(**1**) segments.

First, the synthesis of triblock copolymer was demonstrated by the sequential addition of styrene and **1** with a difunctional initiator. Styrene was first polymerized with potassium naphthalenide in THF at −78°C, and then **1** was added to the reaction mixture. Both the first and second polymerizations smoothly proceeded and the yields of polymers were quantitative. Figure 6-3 shows SEC curves of the starting polystyrene and the polymer obtained after the second polymerization. Obviously, the SEC curve of the polystyrene shifted toward the higher molecular weight region after an addition of **1**. The content of poly(**1**) segment in the resulting polymer agreed with the calculated values based on the molar ratio of both fed monomers from the analysis of ^{1}H NMR. As shown in Table 6-4, the resulting polymer had a controlled molecular weight in accord with the calculated value and narrow MWD as well as homopolystyrene obtained at the first-stage polymerization. These findings suggest that the polymer is the expected ABA type triblock copolymer, poly(**1**-*b*-styrene-*b*-**1**), with a desirable chain structure.

Table 6-4

Block Copolymerization of **1** with Styrene and Methyl Methacrylate at –78°C in THF[a]

run	counter-cation	block sequence	A monomer	B monomer	block copolymer (homopolymer[b])		
					$10^{-3}M_n$		
					calcd[c]	obsd[d]	M_w/M_n[e]
35	K^+	A-B-A	**1**	Styrene	22 (12)	21 (12)	1.07 (1.04)
36[f]	K^+	A-B-A	**1**	Styrene	23 (13)	25 (14)	1.09 (1.07)
37[g]	K^+	B-A-B	**1**	Styrene	24 (9.4)	9.0[g] (9.0)	1.06[g] (1.06)
38	Li^+	B-A-B	**1**	MMA	25 (9.7)	26 (9.6)	1.11 (1.06)

[a] Yields of polymers were nearly quantitative in each case except for run 37. Difunctional initiators were used in all block copolymerizations. [b] Homopolymers were obtained at the first-stage polymerization. [c] M_n(calcd) = [monomer] × (MW of monomer) × 2 / [initiator] + MW of initiator. [d] The molecular weights of the block copolymers were dertermined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analysed by ^{1}H NMR. [e] M_w/M_n was obtained by SEC calibraton using standard polystyrenes in DMF solution. [f] After an end capping of the difunctional living polystyrene with 1,1-diphenylethylene, block copolymerization was carried out by the addition of **1** in THF to the reaction mixture. [g] Homopoly(**1**) and unreacted styrene monomer were quantitatively recovered from the reaction mixture.

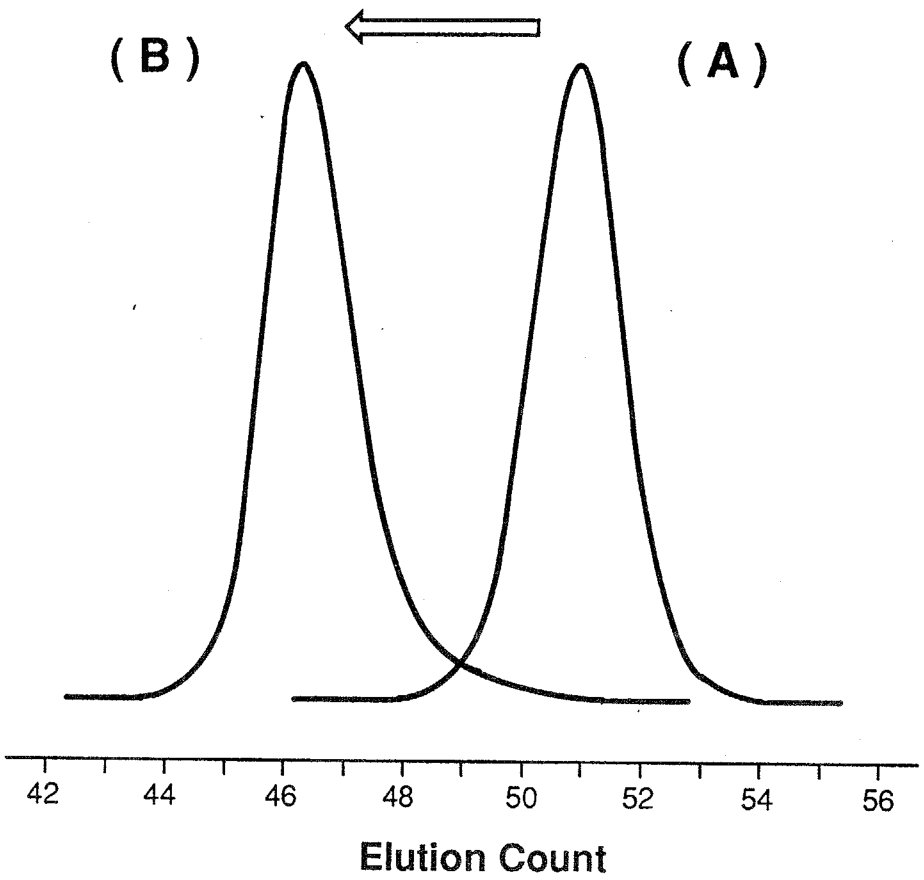


Figure 6-3. SEC curves of polystyrene at the first-stage polymerization (A) and of poly(**1**-*b*-styrene-*b*-**1**) obtained at –78°C (B) (Table 6-4, run 35): peak A, M_n(obsd) = 12 000, M_w/M_n = 1.04; peak B, M_n(obsd) = 21 000, M_w/M_n = 1.07 (the second monomer was added 30 min after the first-stage polymerization).

Next, the synthesis of triblock copolymer of **1** and styrene with a reversed sequence was attempted. In this case, styrene monomer was added to the living poly(**1**) produced with (1,1,4,4-tetraphenylbutanediyl)dipotassium. However, virtual homopoly(**1**) and the unreacted styrene monomer were quantitatively recovered from the reaction mixture after the reaction for 2 h in THF at –78°C (Table 6-4, run 37). This means that the living poly(**1**) could not initiate the polymerization of styrene at all under the conditions. The contrasting results of two block copolymerizations of **1** with styrene clearly show that the living poly(**1**) has a significantly lower nucleophilicity than that of styrene. It is obvious that the electron-withdrawing cyano group decreases the electron density of the terminal carbanion, resulting in the low nucleophilicity of living poly(**1**) as mentioned before.

With the use of more reactive methyl methacrylate (MMA) instead of styrene as the second monomer, MMA could be quantitatively initiated and polymerized by the propagating carbanion of living poly(**1**). The resulting triblock copolymer, poly(MMA-*b*-**1**-*b*-MMA), had a narrow MWD and a predictable molecular weight as expected.

During the recent research, similar phenomena were found in the anionic living polymerizations of a series of styrenes *para*-substituted with electron-withdrawing groups.[1-7] In the anionic polymerization of these monomers, the lowered reactivities of living polymers were similarly ascertained by the crossover reaction of the living carbanion and the various monomers as discussed in Chapter 7 in detail. These stabilized carbanions may permit various styrene monomers containing electrophilic functionalities to undergo the living polymerization.

Table 6-5

Solubilities of Poly(cyanostyrene)s, Block Copolymer, and Polystyrene[a]

solvent	polymer				
	poly(**1**)	poly(**2**)	poly(**3**)	block copolymer[b]	polystyrene
hexane	I	I	I	I	I
benzene	I	I	Sw	Sw	S
carbon tetrachloride	I	I	I	I	S
diethyl ether	I	I	S	I	S
ethyl acetate	I	I	Sw	Sw	S
chloroform	Sw	S	S	Sw	S
acetone	S	S	Sw	S	S
methyl ethyl ketone	S	S	Sw	S	S
1,4-dioxane	I	I	S	Sw	S
tetrahydrofuran	Sw	S	S	S	S
N,*N*-dimethylformamide	S	S	S	S	S
dimethyl sulfoxide	S	S	S	S	I
nitromethane	S	S	I	S	I
acetonitrile	S	S	I	I	I
ethanol	I	I	I	I	I
methanol	I	I	I	I	I
water	I	I	I	I	I

[a] I, insoluble; S, soluble; Sw, swelling. [b] Block copolymer of **1** and styrene shown in Table 6-4, run 35.

6-5. Some Physical Properties of Poly(cyanostyrene)s.

The three poly(cyanostyrene)s obtained in this chapter were white powder and could be cast into a transparent and brittle film from their solutions. Table 6-5 summarizes the solubilities of the resulting polymers and the block copolymer containing poly(**1**) segments. Some positional substituents effects on the solubilities of polymers are observed. Poly(**1**) and poly(**2**) show similar solubilities in most solvents examined here. They are insoluble in nonpolar solvents such as benzene, carbon tetrachloride, diethyl ether, 1,4-dioxane, and ethyl acetate but soluble in polar solvents such as dimethyl sulfoxide, nitromethane, and acetonitrile. Chloroform and THF are useful solvents for the poly(**2**) but they are ineffective for the poly(**1**). The strong dipole moment or high polarity of the cyano group of both polymers may promote these solubilities, particularly in the polar solvents which can not dissolve polystyrene. On the other hand, the solubility of poly(**3**) was different from the solubilities of poly(**1**) and poly(**2**) but rather resembled with the solubility of polystyrene, although the influence of low molecular weight of poly(**3**) sample might be observed in the solubility. As expected, the block copolymer, poly(**1**-*b*-styrene-*b*-**1**) shows solubilities intermediate between those of poly(**1**) and polystyrene.

Although poly(**1**)s have been prepared by the free-radical polymerization of 4-cyanostyrene,[10, 11] the information of molecular weights is not available and the MWDs of those polymer samples might be very broad. Since the anionically-synthesized poly(**1**)s had confirmed molecular weights and narrow MWDs, intrinsic viscosities of seven poly(**1**) samples were measured in DMF at 40°C to estimate the physical property of poly(**1**) in solution. The $[\eta]$ values and molecular weights of the polymer samples are shown in Table 6-6. It should be mentioned that these values are preliminary ones because the molecular weight range is rather limited for precise discussion. The plot of log $[\eta]$ and log M_n(NMR) gave a linear relationship in this molecular weight region as follows.

$$[\eta]_{\mathrm{DMF}}^{40^{\circ}\mathrm{C}} = (1.004 \times 10^{-4})\, M_n(\mathrm{NMR})^{0.749} \quad \text{for poly(1)}$$

The Mark-Houwink parameters, K and a, for poly(**1**) were hence estimated to be 1.00×10^{-4} and 0.75, respectively. The equation for polystyrene was also determined under the same conditions by using commercially available standard sample of M_n in the range $(5.11 - 294) \times 10^3$ with polydispersity indices of 1.01 -1.04.[21]

$$[\eta]_{\mathrm{DMF}}^{40^{\circ}\mathrm{C}} = (3.865 \times 10^{-4})\, M_n^{0.582} \quad \text{for polystyrene}$$

The value of a for poly(**1**) is 0.75, indicating that DMF is a good solvent for poly(**1**). By contrast, polymer chain of polystyrene ($a = 0.58$) contracted in DMF. These a values suggest that in DMF poly(**1**) has a larger hydrodynamic volume than polystyrene. This difference is accounted for the higher polarity of poly(**1**) containing cyano group than that of polystyrene. The molecular weights of poly(**1**)s are thereby always overestimated by using the polystyrene calibration of SEC measurements in DMF as shown in Table 6-6.

The glass transition temperatures (T_gs) of the resulting poly(**1**)s were measured by differential scanning calorimetry (DSC) (Table 6-7). Since the poly(**1**) samples used here had very narrow MWDs, they were suitable for the accurate discussion concerning T_g values. In fact, the molecular weight dependence of T_g is clearly observed in the T_g measurement of poly(**1**). T_g increases with molecular weight of poly(**1**) and becomes constant at about 180°C over the molecular weight of 30 000. This T_g of 180°C is obviously higher than the reported T_g value of poly(4-cyanostyrene) obtained by free-

Table 6-6

Values of Intrinsic Viscosities and Molecular Weights for Poly(**1**)s

Sample	$[\eta]$	$10^{-3}M_n$		
run	(DMF 40°C), dL/g	obsd	SEC[a]	M_w/M_n
1	0.0902	8.7	23	1.07
2	0.121	13	33	1.07
3	0.155	20	45	1.07
4	0.242	30	80	1.04
5	0.257	33	94	1.05
6	0.338	61	140	1.06
7	0.663	122	270	1.09

[a] Molecular weights of poly(**1**)s were estimated by the SEC calibration using standard polystyrenes in DMF at 40°C.

Table 6-7

Glass Transition Temperatures of Poly(**1**)s[a]

$10^{-3}M_n$	M_w/M_n	Tg, °C
8.7	1.07	161
13	1.07	158
14	1.07	157
20	1.07	174
30	1.04	179
61	1.06	179
122	1.09	181

[a] Glass transition temperature was measured in the second heating scan at a rate of 20°C/min.

radical polymerization (T_g = 120°C).[22] On the other hand, the T_g s of poly(**2**) and poly(**3**) could be measured to be 131°C and 137°C, respectively. The value for poly(**3**) is a preliminary one because its molecular weight is relatively low (M_n = 6500) for the estimation of T_g. However, these T_g values were lower than that of *para* isomer but significantly higher than that of polystyrene (T_g = 101°C) with nearly comparable molecular weight. The introduction of polar cyano group into aromatic ring may promote the higher T_g s of poly(cyanostyrene)s than that of polystyrene. Poly(**1**-*b*-styrene-*b*-**1**) showed two endothermic DSC peaks at 152°C and 106°C, corresponding to the T_g s of the poly(**1**) segment and the polystyrene block, respectively. Similarly, poly(MMA-*b*-**1**-*b*-MMA) exhibited T_g s at 169°C and 113°C, which were derived from the poly(**1**) and PMMA segment. These observations indicate that these triblock copolymers cause microphase separation in the bulk.

6-6. Conclusion.

This chapter has demonstrated the substituent effects on the anionic polymerizations of three cyanostyrenes. 4-Cyanostyrene is quantitatively polymerized with various anionic initiators to afford a stable living polymer. The living system leads to the perfect controls of the molecular weights and their distributions of the resulting polymers. On the other hand, the living polymerizations of 2- and 3-cyanostyrene are not achieved because of the undesirable side reactions during the polymerization. The success of the living polymerization of **1** may be due to the stabilization of growth center of the living poly(**1**) by the electron-withdrawing effect of *para*-substituted cyano group.

Experimental Section

Materials. 4-Chlorostyrene, kindly supplied from Hokko Chemical Industry Co., Ltd., was used without further purification. *N,N*-Dimethylformamide was dried and distilled from calcium hydride under vacuum. Commercially available 3-bromoacetophenone, 2-bromobenzaldehyde, toluene, pyridine, and hydroxylamine hydrochloride were used without purification. 4-(Trimethylsilyl)chlorobenzene was synthesized by the Grignard reaction of 1,1-dichlorobenzene and trimethylsilyl chloride as previously described in Chapter 4. Ethyl acetate was purified by standard techniques.[23] Styrene and α-methylstyrene were distilled over calcium hydride and finally distilled from benzylmagnesium chloride under vacuum. Methyl methacrylate was distilled over calcium hydride and finally distilled from triethylaluminum on the vacuum line.[24] 1,1-Diphenylethylene (DPE), prepared by a literature method,[25] was purified by fractional distillation and finally distilled from *n*-BuLi/heptane under vacuum. THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through a vacuum line from sodium naphthalenide solution.

Initiators. Commercially available *n*-butyllithium (1.6 M hexane solution) was diluted by *n*-heptane and used for the anionic polymerization. Metal naphthalenides were prepared by the reactions of a small excess molar quantity of naphthalene with the corresponding alkali metal in THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether with sodium-potassium alloy in THF at room temperature. The oligo(α-methylstyryl)dilithium and -dipotassium were freshly prepared just prior to polymerizations from the corresponding metal naphthalenides and a 2–4 M quantity of α-methylstyrene at 20°C for 1 min and then at –78°C for 10 min. These initiators were stored at –30°C in ampules equipped with breakseals. The concentration of initiators was determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[26]

1,1-Bis[4'-(trimethylsilyl)phenyl]ethylene (4). To a suspension of dry, clean magnesium turnings (3.19 g, 131 mmol) in dry THF (10 mL) at reflux temperature under nitrogen, 4-(trimethylsilyl)chlorobenzene (16.2 g, 87.6 mmol) in dry THF (25 mL) was added dropwise over 30 min. After a further 8 h at reflux, the reaction mixture was cooled to 0°C. To the reaction mixture, dry ethyl acetate (3.48 g, 39.5 mmol) was added dropwise with cooling in an ice bath and then stirred for 1 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and concentrated under reduced pressure.

To the residue was added 20% H_2SO_4 (26 mL), and the resulting mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature to give a yellow solid. The solid was taken up in ether (100 mL), and the solution was washed twice with water, five times with saturated $NaHCO_3$ solution, and twice with water. The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure to give a slightly yellow solid (9.42 g, 74%). The solid was recrystallized from methanol three times to yield a pure white crystal of **4** (3.77 g, 11.6 mmol, 29%): mp 112.0-113.0°C; 90 MHz ^1H NMR ($CDCl_3$) δ 0.28 (s, 18H, $SiCH_3$), 5.48 (s, 2H, CH_2=), 7.37-7.55 (m, 8H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ -1.0 ($SiCH_3$), 114.0 (CH_2=), 127.7 (Ar, C2), 133.3 (Ar, C3), 139.9 (Ar, C1), 141.9 (Ar, C4), 150.2 (-C=); IR (KBr, cm^{-1}) 2955, 1247, 1118, 1085, 914, 857, 831, 753, 727; Anal. Calcd for $C_{20}H_{28}Si_2$: C, 74.00, H, 8.69. Found: C, 73.82, H, 8.90.

After careful recrystallization, **4** was finally distilled from *n*-BuLi/pentane in an apparatus equipped with a breakseal under high vacuum and then diluted with dry THF. The resulting THF solution (0.05 M) of **4** was used in the anionic polymerization.

3-Bromostyrene.[27] To a solution of $NaBH_4$ (2.45 g, 64.7 mmol) in ethanol (130 mL), 3-bromoacetophenone (25.83 g, 130 mmol) was added dropwise under cooling in an ice bath. After stirring for 2 h at room temperature, the reaction mixture was poured into cold 2 N HCl (100 mL) and extracted three times with diethyl ether. The organic layer was washed with saturated $NaHCO_3$ solution and brine and then dried over anhydrous $MgSO_4$. The organic phase was combined and concentrated under reduced pressure to give a rough 3-bromophenylmethylcarbinol.

To a heated mixture of $KHSO_4$ (2.98 g, 21.9 mmol) and 4-*tert*-butylcatechol (10 mg) at 230°C under reduced pressure (120 mmHg), the carbinol was added dropwise over 1 h. The carbinol was immediately dehydrated and the product was azeotropically distilled through the condenser. The distillate was extracted three times with diethyl ether and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 3-bromostyrene (12.67 g, 69 mmol, 53%, bp 31-32°C/0.5 mmHg): 90 MHz ^1H NMR ($CDCl_3$) δ 5.29 and 5.72 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.68 (dd, 1H, -CH=), 7.08-7.55 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 115.3 (vinyl, CH_2=), 122.8 (Ar, C3), 124.9 (Ar, C6), 129.1 (Ar, C2), 130.0 (Ar, C5), 130.6 (Ar, C4), 135.5 (vinyl, -CH=) 139.7 (Ar, C1).

2-Bromostyrene.[27] To a mixture of methyltriphenylphosphonium bromide (51.1 g, 143 mmol) and potassium *tert*-butoxide (28.7 g, 255 mmol), 120 mL of dry THF was added at room temperature under nitrogen. To the mixture under cooling in an ice bath, 2-bromobenzaldehyde (24.96 g, 135 mmol) was added dropwise over 30 min. After stirring for 1 h at 0°C, the reaction mixture was quenched with water (150 mL) and the layers were separated. The aqueous layer was extracted three times with dichloromethane. The combined organic phase was concentrated by evaporation and poured into diethyl ether to precipitate triphenylphosphine oxide. After filtration, the filtrate was concentrated and purified by flash chromatography (petroleum ether, silica gel). After concentration of the effluent, the residue was distilled under vacuum to give a colorless liquid of 2-bromostyrene (17.50 g, 96 mmol, 71%, bp 57-58°C/6 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.36 and 5.69 (2d, 2H, J = 11 and 17 Hz, CH_2=), 7.10(dd, 1H, -CH=), 7.09-7.59 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 116.7 (vinyl, CH_2=), 123.7 (Ar, C2), 126.9 (Ar, C5), 127.5 (Ar, C6), 129.1 (Ar, C4), 132.9 (Ar, C3), 135.9 (vinyl, -CH=) 137.6 (Ar, C1).

4-Formylstyrene.[28] To a suspension of dry, clean magnesium turnings(8.42 g, 347 mmol) in dry THF (50 mL) at reflux temperature under nitrogen, 4-chlorostyrene (31.84 g, 230 mmol) in dry THF (150 mL) was added dropwise over 30 min. After a further 30 min at reflux, the reaction mixture was cooled to 0°C. To the reaction mixture, dry DMF (21.20 g, 290 mmol) was added dropwise with cooling in an ice bath and then stirred for 2 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 4-formylstyrene (25.71 g, 195 mmol, 85%, bp 55-57°C/0.5 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.43 and 5.90 (2d, 2H, J = 11 and 18 Hz, =CH_2), 6.78 (dd, 1H, -CH=), 7.71 (m, 4H, aromatic), 9.98 (s, 1H, -CHO); 23 MHz ^{13}C NMR ($CDCl_3$) δ 117.2 (vinyl, =CH_2), 126.7 (Ar, C2), 130.0 (Ar, C3), 135.9 (vinyl, -CH=), 138.0 (Ar, C4), 143.5 (Ar, C1), 191.6 (CHO).

3-Formylstyrene.[28a] All the attempts to synthesize 3-formylstyrene from the Grignard reaction between 3-chlorostyrene and DMF were unsuccessful. The Grignard reagent of 3-chlorostyrene showed a high tendency to spontaneously polymerize as reported previously.[28a] Even Rieke's method[29] using the highly activated magnesium gave quantitatively insoluble polymer. The author hence utilized 3-bromostyrene for the synthesis of 3-formylstyrene by way of the organomagnesium reagent.

To a suspension of dry, clean magnesium turnings (5.96 g, 245 mmol) in dry THF (120 mL) under cooling in an ice bath under nitrogen, 3-bromostyrene (29.56 g, 162 mmol) in dry THF (40 mL) was added dropwise over 30 min. Stirring was continued for 2 h at room temperature. To the reaction mixture, dry DMF (30.56 g, 419 mmol) was added dropwise at 0°C, and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was washed with saturated $NaHCO_3$ solution and with brine and then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 3-formylstyrene (16.10 g, 122 mmol, 75%, bp 47-49°C/0.5 mmHg (lit. [28a], bp 74-78°C/1 mmHg)): 90 MHz ^1H NMR ($CDCl_3$) δ 5.37 and 5.85 (2d, 2H, J = 11 and 17 Hz, CH_2=), 6.80 (dd, 1H, -CH=), 7.49-7.91 (m, 4H, aromatic), 10.03 (s, 1H, CHO); 23 MHz ^{13}C NMR ($CDCl_3$) δ 115.7 (vinyl, CH_2=), 127.1 (Ar, C2), 128.9, 129.2, and 131.9 (Ar, C4, C5, and C6), 135.6 (vinyl, -CH=), 136.7 (Ar, C3), 138.5 (Ar, C1), 192.1 (CHO).

2-Formylstyrene.[28a] A procedure similar to that described above for 3-formylstyrene was followed using magnesium (3.12 g, 130 mmol), DMF (19.43 g, 266 mmol) and 2-bromostyrene (16.08 g, 88 mmol) in place of 3-bromostyrene. Distillation in vacuo gave 9.35 g (71 mmol, 85%, bp 61.5-62.0°C/0.5 mmHg (lit. [28a], bp 113-115°C/18 mmHg)) of 2-formylstyrene as a colorless liquid: 90 MHz ^1H NMR ($CDCl_3$) δ 5.49 and 5.67 (2d, 2H, J = 11 and 17 Hz, CH_2=), 7.30-7.86 (m, 5H, aromatic and -CH=), 10.26 (s, 1H, CHO); 23 MHz ^{13}C NMR ($CDCl_3$) δ 119.2 (vinyl, CH_2=), 132.9 (Ar, C2), 133.7 (vinyl,

-CH=) 127.3, 127.9, 131.1, and 133.3 (Ar, C3, C4, C5, and C6), 140.4 (Ar, C1), 192.2 (CHO).

4-Cyanostyrene (1)[10] was prepared by the modified method according to the procedure reported by Saednya.[12] To a mixture of hydroxylamine hydrochloride (13.91g, 200 mmol), pyridine (31.60 g, 400 mmol), and 4-*tert*-butylcatechol (10 mg), was added 4-formylstyrene (25.74 g, 195 mmol) in one portion at room temperature. After 3-5 min of stirring, toluene (200 mL) was added and the mixture was heated for 10 h under reflux with azeotropic separation of water by means of a Dean-Stark water trap. The cooled solution was filtered from pyridinium chloride. The filtrate was washed twice with 1 N HCl, twice with saturated $NaHSO_3$ solution, and twice with H_2O, and dried over anhydrous $MgSO_4$. After removal of toluene under vacuum, distillation gave 17.24 g (134 mmol, 69%) of **1** as a colorless liquid at 56-58°C/0.3 mmHg (lit. [10a], bp 102-104°C/9 mmHg) : 90 MHz ^1H NMR ($CDCl_3$) δ 5.45 and 5.87 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.75 (dd, 1H, -CH=), 7.43-7.68 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 110.9 (Ar, C4), 117.6 (vinyl, CH_2=), 118.7 (CN), 126.6 (Ar, C2), 132.2 (Ar, C3), 135.2 (vinyl, -CH=), 141.8 (Ar, C1); IR (KBr, cm^{-1}) 2228 (CN), 1629, 1606, 1506, 1406, 1285, 1176, 1116, 990, 923, 847; Anal. Calcd for C_9H_7N: C, 83.69, H, 5.46, N, 10.85. Found: C, 83.29, H, 5.49, N, 10.81.

3-Cyanostyrene (2).[30] The same procedure was followed as described above for **1** using hydroxylamine hydrochloride (8.55 g, 123 mmol), pyridine (19.5 mL, 244 mmol), toluene (150 mL), and 3-formylstyrene (16.10 g, 122 mmol) in place of 4-formylstyrene. Distillation in vacuo gave 11.36 g (88.1 mmol, 72%, bp 33-34°C/0.3 mmHg (lit. [30], bp 83°C/3.5 mmHg)) of **2** as a colorless liquid: 90 MHz ^1H NMR ($CDCl_3$) δ 5.41 and 5.78 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1H, -CH=), 7.27-7.68 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 112.7 (Ar, C3), 116.5 (vinyl, CH_2=), 118.5 (CN), 129.3 (Ar, C5), 129.6 (Ar, C6), 130.2 (Ar, C2), 130.9 (Ar, C4), 134.7 (vinyl, -CH=), 138.6 (Ar, C1); IR (KBr, cm^{-1}) 2231 (CN), 1635, 1598, 1577, 1479, 1397, 1280, 990, 920, 897, 802; Anal. Calcd for C_9H_7N: C, 83.69, H, 5.46, N, 10.85. Found: C, 83.07, H, 5.93, N, 10.76.

2-Cyanostyrene (3).[31] The same procedure was followed as described above for **1** using hydroxylamine hydrochloride (5.31 g, 76.4 mmol), pyridine (13.0 mL, 165 mmol), toluene (120 mL), and 2-formylstyrene (9.35 g, 70.8 mmol) in place of 4-formylstyrene. Distillation in vacuo gave 5.50 g of **3** (42.6 mmol, 60%, bp 42-43°C/0.4 mmHg (lit. [31], bp 53°C/0.15 mmHg)) as a colorless liquid: 90 MHz ^1H NMR ($CDCl_3$) δ 5.52 and 5.92 (2d, 2H, $J = 11$ and 18 Hz, CH_2=), 7.09 (dd, 1H, -CH=), 7.25-7.72 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 110.9 (Ar, C2), 117.5 (CN), 118.7 (vinyl, CH_2=), 125.3, 127.8, 128.9, and 131.9 (Ar, C3, C4, C5, and C6), 132.6 (vinyl, -CH=), 140.4 (Ar, C1); IR (KBr, cm^{-1}) 2226 (CN), 1630, 1598, 1566, 1479, 1450, 1286, 1210, 985, 927, 772, 754; Anal. Calcd for C_9H_7N: C, 83.69, H, 5.46, N, 10.85. Found: C, 83.39, H, 5.42, N, 10.73.

Monomer Purification. After careful fractional distillation, the purified cyanostyrenes were sealed off under a degassed condition in an apparatus equipped with a breakseal in the presence of CaH_2. The monomer was stirred for 24 h at ambient temperature and then distilled from CaH_2 on a vacuum line into ampules fitted with breakseal. Next, to remove impurities in the monomer, phenylmagnesium chloride (5.0 mL, 0.20 M solution in THF) was added to the monomer (5.88 g, 46 mmol) at −78°C under vacuum (10^{-6} mmHg), and the mixture was stirred for 30 min at ambient temperature. It was distilled again under vacuum into the apparatus equipped with a breakseal and diluted with dry THF. The resulting monomer solutions (0.3-0.5 M in THF) were stored at −30°C until ready to use for the anionic polymerization.

Polymerization Procedures. All polymerizations were carried out at low temperature with shaking under high vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[26] The polymerization reaction was quenched with methanol. The reaction mixture was dissolved by the addition of DMF and then poured into a large excess of methanol to precipitate the polymer. Polymers collected by filtration were purified by reprecipitation twice with either a methanol-DMF (for poly(**1**)) or a methanol-THF (for poly(**2**) and poly(**3**)) system. Polymers thus obtained were characterized by ^{1}H and ^{13}C NMR, and IR spectroscopy, and elemental analysis. The following is the full list.

Poly(4-cyanostyrene): 90 MHz ^{1}H NMR (DMF-d_7) δ 1.4-2.5 (m, 3H, CH_2-CH), 6.7-7.7 (m, 4H, aromatic); 23 MHz ^{13}C NMR (DMF-d_7) δ 40-44 (m, CH_2-CH), 109.8 (Ar, C4), 119.2 (CN), 129.2 (Ar, C2), 132.6 (Ar, C3), 150.5 (Ar, C1); IR (KBr, cm^{-1}) 2228 (CN), 1672, 1607, 1505, 1453, 1416, 1177, 1018, 836; Anal. Calcd for $(C_9H_7N\cdot 0.2H_2O)_n$: C, 81.42, H, 5.62, N, 10.55. Found: C, 81.60, H, 5.34, N, 10.90.

Poly(3-cyanostyrene): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.6-2.7 (m, 3H, CH_2-CH), 6.2-7.9 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40-45 (m, CH_2-CH), 112.7 (Ar, C3), 118.3 (CN), 128-133 (Ar, C2, C4, C5, C6), 145 (Ar, C4); IR (KBr, cm^{-1}) 2928, 2229 (CN), 1601, 1582, 1482, 1433, 1248, 896, 848, 797; Anal. Calcd for $(C_9H_7N\cdot 0.1H_2O)_n$: C, 82.54, H, 5.54, N, 10.70. Found: C, 82.38, H, 5.72, N, 9.59.

Poly(2-cyanostyrene): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.2-3.0 (m, 3H, CH_2-CH), 6.5-7.9 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40-43 (m, CH_2-CH), 112 (Ar, C2), 118 (CN), 125-128, 133, 147 (Ar, C1); IR (KBr, cm^{-1}) 2931, 2223 (CN), 1599, 1574, 1526, 1484, 1448, 1336, 1163, 1031, 759; Anal. Calcd for $(C_9H_7N\cdot 0.2H_2O)_n$: C, 81.42, H, 5.62, N, 10.55. Found: C, 81.87, H, 5.62, N, 9.58.

Postpolymerization. In the all-glass apparatus in vacuo, the first-stage polymerization of **1** was carried out with (1,1,4,4-tetraphenylbutanediyl)dilithium as an initiator in THF at −78°C for 30 min. After sampling to determine the characteristics of the first-stage polymer, to the residual polymerization system, the second feed of **1** was added and reacted for 30 min to complete the further polymerization. After quenching with methanol, both pre- and postpolymer of **1** were quantitatively obtained. Both polymers possessed narrow MWDs and predictable molecular weights, as expected. With use of potassium initiator (cumylpotassium capped with 1,1-diphenylethylene), a similar result was obtained.[10] Block copolymerizations of **1** were performed in a similar manner.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^{1}H, 22.53 MHz ^{13}C) in $CDCl_3$ or DMF-d_7. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Chemical shifts of poly(**1**) were reported in ppm downfield relative to DMF-d_7 (δ 8.05) for ^{1}H NMR and (δ 162.5) for ^{13}C NMR as standard. Size exclusion chromatograms (SEC) for MWD determinations of polymers were obtained at 40°C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, and G3000H_{XL}) with ultraviolet (270 nm in DMF or 254 nm in THF) or refractive index detection. DMF (for poly(**1**)) or THF (for poly(**2**) and poly(**3**)) was the carrier solvent at a flow rate of 1.0 mL min^{-1}. Laser light scattering (LS) measurements for weight-average molecular weight determination of poly(**1**) were performed at 25°C with an Ootsuka Electronics DSL-600R instrument in DMF solution. Intrinsic viscosities of poly(**1**) and polystyrene were measured by using an Ubbelohde type capillary viscometer at 40°C in DMF. The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC5200TA station. The samples were first heated to 240°C, cooled rapidly to –20°C, and then scanned again at a rate of 20°C min^{-1}.

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Chapter 7

Anionic Block Copolymerization of Styrene Derivatives *Para*-Substituted with Electron-Withdrawing Groups

ABSTRACT: The anionic block copolymerizations between six styrene derivatives *para*-substituted with electron-withdrawing groups and four conventional comonomers (isoprene, styrene, 2-vinylpyridine (2VP), and *tert*-butyl methacrylate (tBMA)) were mainly carried out with oligo(α-methylstyryl)dipotassium in tetrahydrofuran (THF) at –78°C by sequential addition of two monomers. The six styrene monomers employed were *N*,*N*-diethyl-4-vinylbenzamide (**1**), *N*-(4-vinylbenzylidene)cyclohexylamine (**2**), 2-(vinylphenyl)-4,4-dimethyl-2-oxazoline (**3**), *tert*-butyl 4-vinylbenzoate (**4**), *N*,*N*-diethyl-4-vinylbenzenesulfonamide (**5**), and 4-cyanostyrene (**6**). From the analyses of the copolymerization products, the results of crossover reactions were classified into four categories as follows: (a) successful synthesis of a block copolymer with a narrow molecular weight distribution and a controlled segment composition, (b) synthesis of a block copolymer having a relatively broad molecular weight distribution, (c) examples proceeding with a low initiation efficiency and/or including some side reactions at the second-stage polymerization, and (d) no polymerization at the second stage. From the results, higher reactivities of **1**-**6** and lower nucleophilicities of their living polymers have been demonstrated, compared with those of styrene monomer and living polystyrene. Both of these characteristic features may be accounted for by the strong electron-withdrawing effects of the substituents of **1**-**6**. For example, the polymerizations of **1**-**6** were initiated with the low nucleophilic living polymers derived from 2VP and tBMA. By contrast, the living polymers derived from **1**-**6** were ineffective in initiating further polymerizations of isoprene and styrene. Thus, the anionic polymerizability of **1**-**6** can be evaluated as being between those of 2VP and alkyl methacrylates. The reactivity ranking of **1**-**6** can also be estimated from the chemical shifts of the vinyl β-carbons for these *para*-substituted styrenes in the ^{13}C NMR spectra, which is consistent with the present copolymerization results.

Introduction

Although a variety of living polymerization systems has been developed, particularly for over the past few years,[1] the conventional anionic living polymerization method of conjugated hydrocarbon monomers such as styrene, 1,3-butadiene, and isoprene is believed to be still the most established method from the viewpoint of synthesizing polymers with precisely controlled molecular weights and extremely narrow molecular weight distributions.[2] The highly reactive but stable carbanionic character of the living polymers from these monomers also provides the best method for synthesizing well-defined block copolymers. In fact, many previous reports demonstrate that block copolymers obtained by this method could have been of very good uniformity.[3] On the other hand, a major drawback of these living polymers is their intolerance to most polar functional groups. This means that limitations are encountered when one attempts the anionic living polymerization of styrene and 1,3-diene monomers with functional groups.

As one solution to overcome this longstanding problem,[4] the author has deliberately introduced an electron-withdrawing group into the phenyl ring of a styrene monomer to change the reactivities of the monomer and the resulting living polymer.[5] It was particularly anticipated that the nucleophilicity of the carbanion at the growing chain end of the living polymer would be lowered by reducing the electron density on the carbanion through the electron-withdrawing effect, thereby allowing the electron-withdrawing group to coexist with the carbanion of lowered reactivity. Actually, the following styrene derivatives have been found to undergo anionic living polymerization without problem. They are the styrenes *para*-substituted with *N,N*-diethylamide (**1**),[6] *N*-cyclohexylimino (**2**),[7] oxazolinyl (**3**),[8] *tert*-butyl ester (**4**),[9] *N,N*-diethylsulfonamide (**5**),[10] and cyano (**6**)[11] groups, which are normally susceptible to react with living polystyrene (Chart 7-1). This success of living polymerization may be attributed to the decrease of electron densities on the propagating carbanions of the living polymers. In these cases, resonance stabilization of the carbanions through extended π-conjugated systems[12] involving the multiple bonds of C=O, C=N, S=O, and C≡N and the benzene rings also plays an important role for the success of the living polymerization. The reduced reactivity of these living polymers is evident from crossover reactions with styrene. Thus, the developed methodology, *para*-substitution with electron-withdrawing groups, opens a route for providing new anionic living polymers containing polar groups showing an electron-withdrawing character.[5-11]

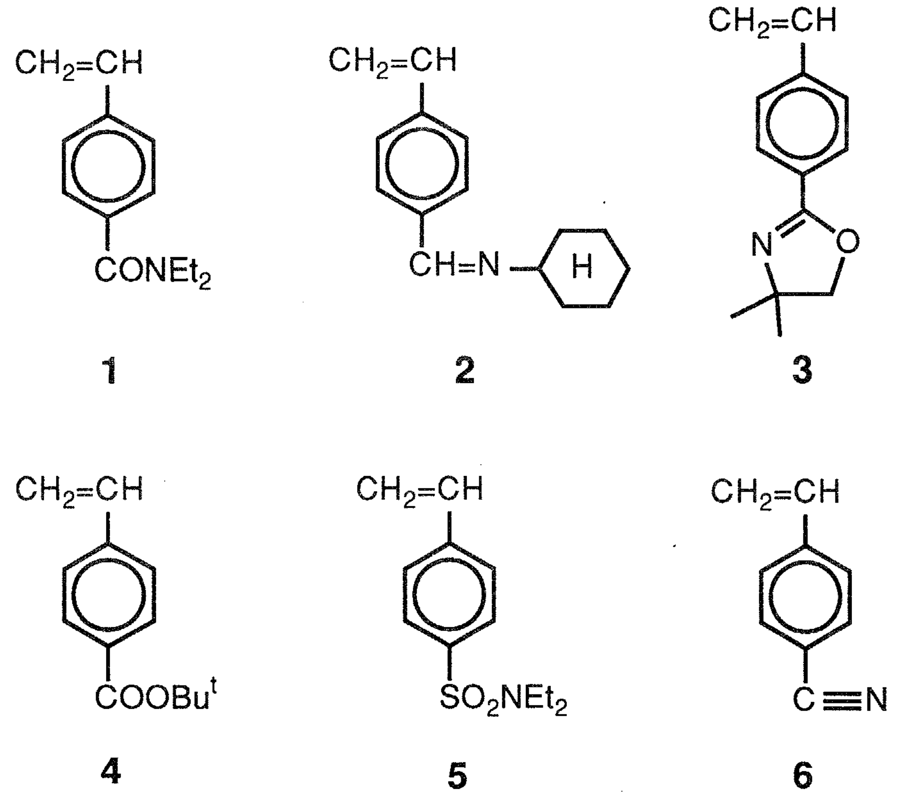


Chart 7-1

In contrast to the reduced reactivity of the carbanions, these styrenes become more anionically reactive than styrene in principle by a similar electron-withdrawing effect. This is strongly supported by the fact that weak nucleophilic initiators, which do not initiate styrene polymerization[13], can initiate **1-6** to afford polymers. Furthermore, all of the ^{13}C NMR chemical shifts of the vinyl β-carbons of these monomers appeared in lower field than that of styrene, indicating the decreased electron densities of the vinyl groups in **1-6**. This observation also suggests the higher reactivities of **1-6** toward nucleophilic attack under anionic polymerization conditions. Accordingly, the introduction of an electron-withdrawing group may influence both the reactivities of the carbanions produced and the monomers themselves.

In the preliminary experiments on the block copolymerizations of styrene with **1**, (Chapter 2[6] **3**,[8] **4**, (Chapter 3)[9] **5**, (Chapter 5)[10] and **6**, (Chapter 6)[11] it has been found that these monomers and their living polymers do not behave as styrene and living polystyrene. Their different behaviors led the author to investigate the block copolymerizations using these monomers in detail. The resulting information seems to be very important not only to clarify the anionic polymerizabilities of **1-6** but also to synthesize block copolymers especially by the sequential addition of different monomers.

This chapter deals with the results of thorough investigations into the block copolymer syntheses of **1-6** with four conventional monomers capable of producing anionic living polymers, namely isoprene, styrene, 2-vinylpyridine (2VP), and *tert*-butyl methacrylate (tBMA) (Chart 7-2). The overall objectives of this work are the following: (1) to evaluate the reactivities of **1-6** and their living polymers by crossover block copolymerization and (2) to explore the possibility of synthesizing block copolymers with the polar functional groups shown here.

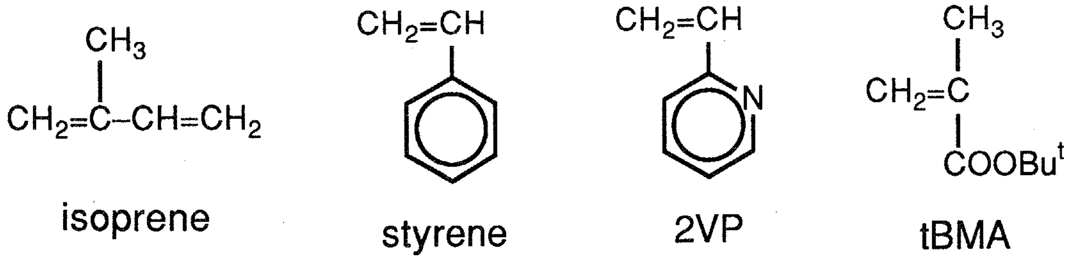


Chart 7-2

Experimental Section

Monomers and Solvents. The six *para*-substituted styrene derivatives, **1**,[6] **2**,[7] **3**,[8] **4**,[9] **5**,[10] and **6**,[11] were synthesized according to the preceding papers, respectively. Isoprene, styrene, and α-methylstyrene were distilled over calcium hydride and finally distilled from benzylmagnesium chloride under vacuum. 1,1-Diphenylethylene was purified by fractional distillation over calcium hydride and finally distilled from *n*-BuLi under vacuum. 2-Vinylpyridine (2VP) was first dried with potassium hydroxide and then distilled over calcium hydride under vacuum. *tert*-Butyl methacrylate (tBMA) was distilled over calcium hydride and finally distilled from trioctylaluminum on the vacuum line.[14] The monomers were diluted by dry THF as 0.3-0.8 M solutions and were stored at –30°C in glass ampules equipped with breakseals until ready to use for the anionic polymerizations. THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled over lithium aluminum hydride and finally through a vacuum line from its sodium naphthalenide solution. Heptane was refluxed and distilled over *n*-BuLi and finally distilled through the vacuum line in the presence of (1,1-diphenylhexyl)lithium.

Initiators. Potassium naphthalenide and lithium naphthalenide were prepared by the reaction of a small excess molar quantity of naphthalene with the corresponding alkali metal in THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether with sodium-potassium alloy in THF at room temperature. Commercially available *n*-BuLi (1.6 M hexane solution) was diluted by heptane and used for the anionic polymerization. These initiators were stored at –30°C in ampules equipped with breakseals. The oligo(α-methylstyryl)dilithium and -dipotassium were freshly prepared just prior to polymerizations from the corresponding metal naphthalenides and a 2-4 M quantity of α-methylstyrene at 20°C for 1 min and then at –78°C for 10 min. The (1,1,4,4-tetraphenylbutanediyl)dipotassium was similarly prepared by the reaction of potassium naphthalenide and 1,1-diphenylethylene. The concentration of initiators was determined by a colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum as previously reported.[15]

Polymerization Procedures. All of the block copolymerizations were carried out at –78 to –95°C with shaking under high vacuum conditions in the all-glass apparatus equipped with breakseals. The first monomer was polymerized to complete the first-stage polymerization under the appropriate conditions as shown in Table 7-1. In the presented conditions, a stable living polymer was obtained from each monomer. The conversions of the first monomers were always quantitative under the conditions. After an aliquot of the reaction mixture was withdrawn for the analysis of the homopolymer at the first-stage polymerization, the second monomer was then added to the residue of the reaction system. After the polymerization system was allowed to stand under the appropriate conditions according to the second monomer as listed also in Table 7-1, the second-stage polymerization was terminated with methanol. The reaction mixture was poured into a large excess of a suitable solvent to precipitate the polymer. The conversion of the second monomer and the yield of the resulting polymeric product were first checked to estimate the character of the second-stage polymerization. The copolymerization products collected by filtration were then analyzed by size exclusion chromatography (SEC) either in THF or in DMF solution. The molecular weights and the distributions of the first-stage polymers were determined by the SEC calibration curves for each homopolymer. The molecular weight distribution of the block copolymer was directly estimated from the SEC calibration using standard polystyrenes. In most cases, the molecular weights of the block copolymers were determined by using the molecular weight of the homopolymer and the molar ratios of the monomer units in the copolymer analyzed by ^{1}H NMR spectroscopy.

Table 7-1

Reaction Conditions of Various Monomers
for the Block Copolymerization in THF[a]

	first-stage polymerization[b]		second-stage polymerization[c]	
Monomer	initiator system	condition	countercation	condition
Isoprene	K-Naph[d]	–78°C, 4 h	K^+	–78°C, 4 h
Styrene	K-Naph or Cumyl-K[e]	–78°C, 10 min	K^+	–78°C, 2 h
			Li^+	–78°C, 2 h
2VP[f]	Li-Naph[g] / DPE[h]	–78°C, 1 h	Li^+	–78°C, 2 h
	K-Naph / DPE	–78°C, 1 h	K^+	–78°C, 2 h
1	K-Naph / α-MeSt[i]	–78°C, 30 min	K^+	–78°C, 1 h
	Li-Naph / α-MeSt	–78°C, 30 min	Li^+	–78°C, 1 h
2	K-Naph / α-MeSt	–78°C, 30 min	K^+	–78°C, 1 h
	Li-Naph / α-MeSt	–78°C, 4 h	Li^+	–78°C, 4 h
3	K-Naph / α-MeSt	–78°C, 10 min	K^+	–78°C, 1 h
	Li-Naph / α-MeSt	–78°C, 10 min	Li^+	–78°C, 2 h
4[j]	K-Naph / α-MeSt	–95°C, 4 h	K^+	–95°C, 4 h
5	K-Naph / α-MeSt	–78°C, 30 min	K^+	–78°C, 2 h
	Li-Naph / α-MeSt	–78°C, 30 min	Li^+	–78°C, 2 h
6	K-Naph / DPE	–78°C, 30 min	K^+	–78°C, 2 h
	Li-Naph / DPE	–78°C, 30 min	Li^+	–78°C, 2 h
tBMA	K-Naph / α-MeSt	–78°C, 2 h	K^+	–78°C, 2 h
	n-BuLi / DPE	–78°C, 2 h	Li^+	–78°C, 2 h

[a] Under these conditions, the polydipersity index (M_w/M_n) of the resulting polymers at the first-stage was within 1.2. [b] Reaction conditions of monomers to produce their living homopolymer quantitatively. [c] Reaction conditions of monomers for the second-stage polymerization corresponding to the used counter cation. [d] Potassium naphthalenide. [e] Cumylpotassium. [f] By using the initiator containing potassium countercation, the polydispersity index of the resulting poly(2VP) was around 1.3. [g] Lithium naphthalenide. [h] 1,1-Diphenylethylene. [i] α-Methylstyrene. [j] By using the initiators containing lithium countercation, no poly(**4**) was produced under various conditions; see ref. 9.

Typical Procedure of Block Copolymerization (Table 7-2, run 22). Polymerization of styrene (7.51 mmol) was carried out with potassium naphthalenide (0.133 mmol) as an initiator in THF (16.0 mL) at –78°C *in vacuo* for 10 min in the all-glass apparatus equipped with breakseals. To determine the characteristics of the first-stage polymer, an aliquot of the reaction mixture (3.7 mL) was withdrawn. Precooled 4-cyanostyrene at –78°C (**6**, 3.98 mmol, 0.743 M solution in THF) was quickly added to the residual THF solution (12.3 mL) of the difunctional living polystyrene (central block) and the mixture was kept at –78°C for 30 min to complete the second-stage polymerization. After quenching with methanol, both homopolystyrene (0.19 g) and the copolymerization product (1.13 g) were quantitatively obtained by pouring them into a large excess of methanol. The composition of the copolymerization product was analyzed by ^{1}H NMR spectroscopy. The segment ratio between the polystyrene block and the poly(**6**) block in the copolymer agreed well with the calculated value from the molar ratio of the fed monomers. As shown in Figure 7-1 and in Table 7-3 (run 22), the homopolymer and the copolymer possessed molecular weights of 12 000 (M_w/M_n = 1.04) and 21 000 (M_w/M_n = 1.07), close to the theoretical values, 12 000 and 22 000, respectively. These results strongly indicate that the polymer obtained after the second-stage is an expected A-B-A type triblock copolymer, poly(**6**-*b*-styrene-*b*-**6**). This block copolymer showed two glass transition temperatures at 152°C and 106°C,[11] corresponding to those of the poly(4-cyanostyrene) terminal segments and the central polystyrene block, indicating microphase separation in the bulk.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz, ^{1}H, 22.53 MHz, ^{13}C) in $CDCl_3$ or DMF-d_7. Chemical shifts are reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^{1}H NMR and relative to $CDCl_3$ (δ 77.1) for ^{13}C NMR. Chemical shifts in DMF-d_7 are reported in ppm downfield relative to DMF-d_7 (δ 8.05 for ^{1}H

NMR and δ 162.5 for ^{13}C NMR). Infrared spectra (KBr disk) were measured on a JEOL JIR-AQS20M FT-IR spectrophotometer. Size exclusion chromatograms (SEC) for the determination of the molecular weight distributions of the polymers were mainly obtained at 40°C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) with an ultraviolet (270 nm in DMF or 254 nm in THF) or a refractive index detector. THF or DMF was the carrier solvent at a flow rate of 1.0 mL min^{-1}. The glass transition temperature of the polymer was measured by differential scanning calorimetry using a Seiko Instruments DSC220 apparatus. The polymer sample was first heated to 240°C, cooled rapidly to –20°C, and then scanned at a rate of 20°C min^{-1}.

Results and Discussion

7-1. Sequential Polymerizations of Conventional Monomers with their Living Polymers.

As mentioned in the Introduction, the method of anionic living polymerization allows one to synthesize well-defined block copolymers in which each block has a predictable molecular weight and a narrow molecular weight distribution. However, this method, in some cases, may yield different results, depending on the order in which the monomers are added. For example, the sequential addition of styrene at first and then tBMA provides a well-defined block copolymer, but not vice versa. Thus, considerable care is needed for sequential addition of different monomers to synthesize block copolymers.

Such a restriction observed in the block copolymerization, however, may offer an advantage to estimate the reactivities of the monomers and the resulting living polymers. Therefore, the sequential block copolymerization with different monomers is a good probe to clarify the reactivities of new monomers as well as the resulting new living polymers. The new monomers **1-6** were used here in addition to four conventional monomers and block copolymerizations among these monomers were attempted for understanding the reactivities as well as for synthesizing a variety of novel block copolymers.

Before discussing this study, the author should recall the addition order of four conventional monomers from the results on block copolymerizations among these monomers, although some examples were independently reported in the previous works[2, 3, 16-19]. Table 7-2 shows the practical polymerization results under the specified conditions according to the standard as mentioned later. As can be seen, well-defined block copolymers were synthesized by the sequential polymerization of isoprene at first and then styrene and vice versa. Accordingly, they are mutually replaceable in the sequential addition. These results from the presented data are consistent with the previous works reported so far.[2,3] Furthermore, several researchers have actually demonstrated that their living polymers can initiate the polymerizations of both 2VP[16, 17] and tBMA[18] to produce the desired block copolymers.[20] These results again agree with the data shown here.

On the other hand, in the block polymerizations of isoprene and styrene by using the living polymer derived from 2VP, the results were completely different from the above ones . No polymerization of isoprene occurred with the living poly(2VP) at –78°C. The crossover reaction of styrene with living poly(2VP) is somewhat complicated (run 6). Styrene could be initiated from the living poly(2VP) only with a low efficiency, and the conversion of styrene was low and far from quantitative under the polymerization conditions. Size exclusion chromatography (SEC) analysis of the copolymerization product showed a multimodal peak with a broad distribution. Since it was previously reported that the pyridine ring was susceptible to react with the carbanionic species,[21] the nature of the polymerization result could be speculated as follows: living poly(2VP) reacted very slowly with styrene to transform the

Table 7-2 Anionic Block Copolymerization of Isoprene, Styrene, 2-Vinylpyridine (2VP), and *tert*-Butyl Methacrylate (tBMA) at –78°C in THF

						block copolymer (homopolymer[a])		
						$10^{-3}M_n$		
run	counter-cation	block sequence	1st monomer (A)	2nd monomer (B)	yield[b] %	calcd[c]	obsd[d]	M_w/M_n
1[e]	K^+	B-A-B	isoprene	styrene	100	17 (6.9)	21[f]	1.14
2[g]	K^+	B-A-B	isoprene	tBMA	100	24 (13)	28 (14)	1.08 (1.09)
3[e]	K^+	B-A-B	styrene	isoprene	100	24 (12)	26[f]	1.06
4	K^+	A-B	styrene	tBMA	100	12 (6.9)	14 (7.1)	1.07 (1.12)
5[h]	K^+	B-A-B	2VP	isoprene	0	26 (12)	h (9.6)	h (1.18)
6[i]	Li^+	B-A-B	2VP	styrene	11	23 (11)	11 (8.2)	1.44 (1.06)
7	Li^+	B-A-B	2VP	tBMA	100	24 (11)	20 (10)	1.23 (1.05)
8[h]	K^+	B-A-B	tBMA	isoprene	0	23 (11)	h (9.8)	h (1.10)
9[h]	K^+	B-A-B	tBMA	styrene	0	31 (16)	h (16)	h (1.18)
10[h]	Li^+	B-A-B	tBMA	2VP	0	27 (10)	h (9.2)	h (1.06)

[a] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases.

[b] Yield of the second-stage polymerization.

[c] $M_n(\text{calcd}) = [\text{monomer}] \times (\text{MW of monomer}) \times f / [\text{initiator}] + \text{MW of initiator unit}$. $f = 1$ or 2, corresponding to the functionality of the initiators.

[d] The molecular weight of the block copolymers were determined by using the molecular weight of homopolymer and the molar ratios of monomer units in the block copolymer analysed by ^1H NMR.

[e] Homopolymer of the first monomer was not isolated in these cases.

[f] The molecular weight of block copolymer was directly estimated from the SEC calibration using polystyrene standards.

[g] The second-stage polymerization was carried out after end-capping of the living polymer with 1,1-diphenylethylene.

[h] No polymerization proceeded at the second-stage, resulting in a quantitative recovery of the homopolymer of the first monomer.

[i] Side reaction may occur during the second-stage polymerization.

styryl anion at the growing chain end to a small extent, and the newly formed polystyryl anion might possibly attack the pyridine ring to terminate the propagation reaction before complete consumption of styrene. Thus, the attempt to synthesize the well-defined block copolymer by this addition order was not successful. Compared with the reactivities of living poly(2VP) toward isoprene and styrene as described above, it is certain that styrene is more anionically reactive than isoprene. The block copolymerizations of these combinations impose the additional restrictions that (a) isoprene or styrene must be polymerized first and (b) 2VP should be added to the resulting living polymers, since the anion of poly(2VP) is not sufficiently nucleophilic to initiate quantitatively the polymerizations of isoprene and styrene.

The living polymer of 2VP could initiate the polymerization of tBMA quantitatively to afford the block copolymer with a well-defined structure as reported recently by Hogen-Esch,[19] while the sequential addition of tBMA at first and then 2VP resulted in a quantitative recovery of homopoly(tBMA) as shown in run 10. No polymerization of 2VP took place with living poly(tBMA). These results indicate that the living polymer of 2VP is more reactive than that of tBMA and the synthesis of block copolymer must proceed in the order of 2VP as a first monomer and then tBMA addition. As can be expected, the living poly(tBMA) has no ability to initiate the polymerizations of both isoprene and styrene.

It is obvious from the results of block copolymerizations that the nucleophilicity of living polymer appears to increase in the order: living polyisoprene = living polystyrene > living poly(2VP) > living poly(tBMA). In contrast, the reactivity (or electrophilicity) of monomer is reversed as expected. *i.e.* tBMA > 2VP > styrene > isoprene. In this regard, it is interesting to examine the reactivities of **1-6** and their anionic living polymers in the sequential block copolymerization, since the electron-withdrawing groups introduced can expect to affect considerably their reactivities.

7-2. Sequential Polymerizations of 1-6 with Living Polymers derived from Conventional Monomers.

In this section, the sequential polymerizations of **1-6** were carried out with the anionic living polymers from isoprene, styrene, 2VP, and tBMA as initiators. In other words, **1-6** are employed as second monomers in the sequential polymerization to synthesize block copolymers. From the analyses of the polymeric products including the yield, the molecular weight, the molecular weight distribution, and the composition, the reactivities of **1-6** under the anionic conditions are discussed.

For an easy comparison, the conditions of living polymerization of **1-6** were standardized as much as possible. All of the polymerizations were investigated in THF at –78°C except for the polymerizations of *tert*-butyl 4-vinylbenzoate (**4**), which were performed at –95°C to avoid the significant side reactions at –78°C previously reported.[9] The anionic initiator used mainly was oligo(α-methylstyryl)dipotassium, which was prepared from potassium naphthalenide and α-methylstyrene in THF just prior to the polymerization. The anionic polymerization of 4-cyanostyrene (**6**) was initiated with (1,1,4,4-tetraphenylbutanediyl)dipotassium to prevent the cyano group from the nucleophilic attack by using a bulky diphenylethylene-capped carbanion. The corresponding lithium salt was employed in the polymerizations using 2VP,[19, 21] since the polymers with relatively broad molecular weight distributions were obtained with the initiator bearing K^+. The first monomer was polymerized for the appropriate reaction time (Table 7-1), and an aliquot of the mixture was withdrawn to analyze the first polymer. Then the second monomer was added to the residue of the mixture and allowed to stand under the appropriate conditions (Table 7-1). In some cases, the living polymers of isoprene and styrene were capped with 1,1-diphenylethylene to avoid attack of the polar functional groups of **1-6** before the second monomers were polymerized.[22] The resulting carbanion thus formed is a sterically hindered poorer nucleophile than the uncapped anions. It is, however, believed to be more reactive than the carbanions derived from 2VP and tBMA. Therefore, comparison is possible taking this into consideration. The results are summarized in Table 7-3 where M_n and M_w/M_n values of the polymers at the first and second polymerizations are listed. Yields refer to the polymer yields at the second-stage of polymerization.

As can be seen, living polymers of isoprene and styrene are capable of initiating **1-6** to quantitatively afford the polymers in all runs, although the 1,1-diphenylethylene-capped anion is often employed. The polymerization mixtures always became dark red upon addition of **1-6**, which remained unchanged until quenching with methanol. In the ^{1}H NMR spectra of the resulting polymers, signals corresponding to either polyisoprene or polystyrene and poly(**1-6**) were observed. The compositions determined from the integral ratios of the NMR signals are nearly equal to those calculated from both monomers fed. In every case, the M_n value of the resulting polymer is in good agreement with that predictable from monomers to initiator ratio. All of the SEC traces of the resulting polymers revealed sharp single peaks and the absence of any peaks at the elution counts for the homopolymers of the first monomers. The M_w/M_n values were around 1.1 for all polymer samples, indicating that the copolymers possessed narrow molecular weight distributions. As a typical example, Figure 7-1 shows both chromatograms of the starting polystyrene and the resulting block copolymer of styrene and **6**. These analytical results clearly indicate the quantitative formation of B-A-B type triblock copolymers with the desired and well-defined structures. Accordingly, the polymerization by sequential addition of isoprene or styrene and each of **1-6** quantitatively proceeds to synthesize successfully tailor-made block copolymer in every combination.

Table 7-3

Anionic Block Copolymerization of **1** - **6** with Living Polymers Derived from Isoprene, Styrene, 2VP, and tBMA at –78°C in THF[a]

						block copolymer (homopolymer[b])		
	counter-	block	1st monomer	2nd monomer	yield[c]	$10^{-3}M_n$		
run	cation	sequence	(A)	(B)	%	calcd[d]	obsd[e]	M_w/M_n
11	K^+	B-A-B	isoprene	**1**	100	30 (12)	27 (11)	1.08 (1.08)
12	K^+	B-A-B	isoprene	**2**	100	22 (11)	19 (14)	1.08 (1.08)
13	K^+	B-A-B	isoprene	**3**	100	29 (16)	28 (15)	1.11 (1.08)
14[f]	K^+	B-A-B	isoprene	**4**	100	27 (15)	25 (12)	1.13 (1.07)
15[f]	K^+	B-A-B	isoprene	**5**	100	21 (11)	23 (13)	1.16 (1.09)
16[f]	K^+	B-A-B	isoprene	**6**	100	25 (14)	23 (12)	1.15 (1.08)
17	K^+	B-A-B	styrene	**1**	100	31 (15)	32 (16)	1.06 (1.09)
18	K^+	B-A-B	styrene	**2**	100	23 (12)	25 (13)	1.11 (1.06)
19	K^+	B-A-B	styrene	**3**	100	25 (11)	27 (11)	1.12 (1.09)
20[f]	K^+	B-A-B	styrene	**4**	100	25 (14)	25 (14)	1.13 (1.06)
21	K^+	B-A-B	styrene	**5**	100	22 (13)	19 (12)	1.12 (1.08)
22	K^+	B-A-B	styrene	**6**	100	22 (12)	21 (12)	1.07 (1.04)
23[f]	K^+	B-A-B	styrene	**6**	100	23 (13)	25 (14)	1.09 (1.07)
24	Li^+	B-A-B	2VP	**1**	100	25 (12)	21 (13)	1.14 (1.11)
25	Li^+	B-A-B	2VP	**2**	100	18 (9.1)	18 (8.7)	1.15 (1.13)
26	Li^+	B-A-B	2VP	**3**	100	23 (13)	22 (12)	1.06 (1.05)

Table 7-3 (Continued)

						block copolymer (homopolymer^b)		
						$10^{-3}M_n$		
run	counter-cation	block sequence	1st monomer (A)	2nd monomer (B)	yield^c %	calcd^d	obsd^e	M_w/M_n
27	K$^+$	B-A-B	2VP	4	100	22 (12)	20 (15)	1.36 (1.27)
28	Li$^+$	B-A-B	2VP	5	100	21 (9.5)	20 (9.5)	1.16 (1.09)
29	Li$^+$	B-A-B	2VP	6	100	23 (8.6)	19 (7.9)	1.11 (1.07)
30^g	K$^+$	B-A-B	tBMA	1	100	27 (16)	g (15)	g (1.23)
31^g	K$^+$	B-A-B	tBMA	2	100	22 (10)	g (10)	g (1.13)
32^g	K$^+$	B-A-B	tBMA	3	100	22 (11)	g (8.5)	g (1.12)
33	K$^+$	B-A-B	tBMA	4	100	23 (11)	28 (9.1)	1.17 (1.12)
34	K$^+$	B-A-B	tBMA	5	100	23 (13)	20 (12)	1.14 (1.12)
35	K$^+$	B-A-B	tBMA	6	100	22 (10)	18 (6.8)	1.06 (1.08)

[a] Polymerization reaction concerning monomer (**4**) was carried out at –95°C to avoid the serious side reaction; see ref. 9. [b] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [c] Yield of the second-stage polymerization. [d] M_n(calcd) = [monomer] × (MW of monomer) × 2 / [initiator] + MW of initiator unit. [e] The molecular weight of the block copolymers were determined by using the molecular weight of homopolymer and the molar ratios of monomer units in the block copolymer analysed by ^{1}H NMR. [f] The second-stage polymerization was carried out after end-capping of the living polymer with 1,1-diphenylethylene. [g] Initiation efficiency of the crossover reaction was moderate (50-60%) resulting in a copolymerization product showing bimodal and broad molecular weight distribution, which was consisted of a virtual homopolymer and a block copolymer having high molecular weight.

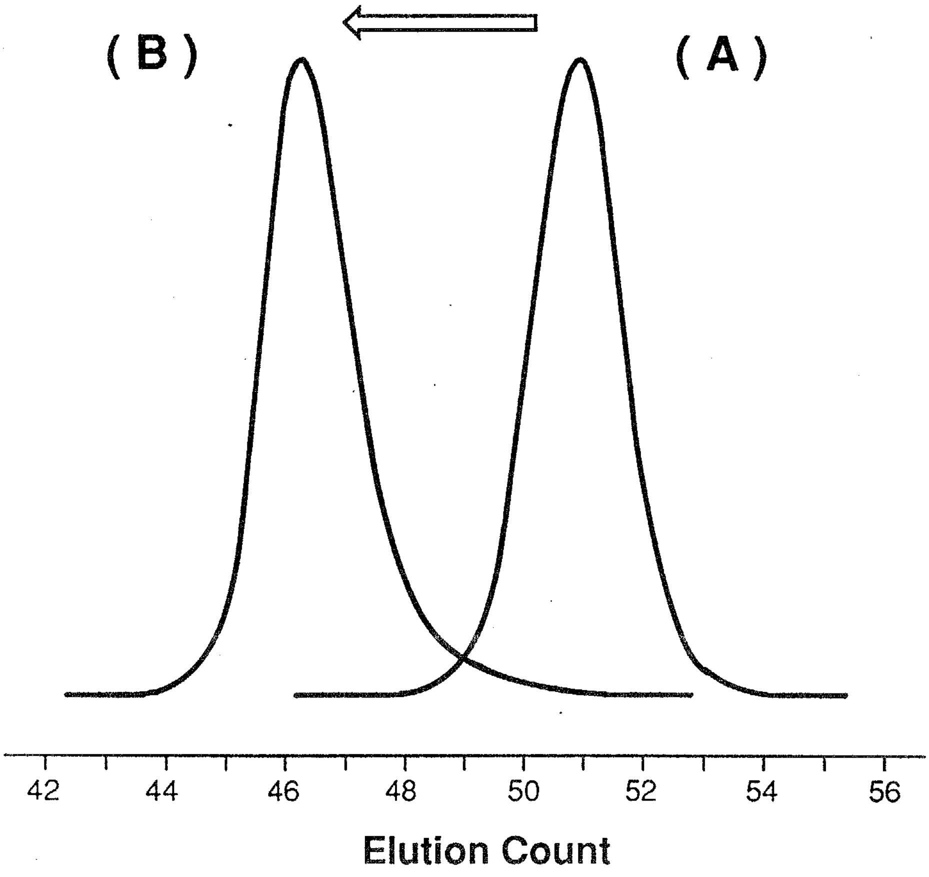


Figure 7-1. SEC curves (DMF) of polystyrene at the first-stage polymerization (A) and of poly(**6**-*b*-styrene-*b*-**6**) (B) (Table 7-3, run 22): peak A, M_n(obsd) = 12 000, M_w/M_n = 1.04; peak B, M_n(obsd) = 21 000, M_w/M_n = 1.07.

Next, the polymerization of **1-6** with living poly(2VP) were attempted. Unfortunately, homopolymers of 2VP having relatively broad molecularweight distributions were always obtained by the polymerization of 2VP with organopotassium initiators in THF at –78°C. Therefore, the living poly(2VP) bearing Li^+ by initiation with (1,1,4,4-tetraphenylbutanediyl)dilithium was instead synthesized. The resulting polymers of 2VP thus obtained at the first-stage were always found to possess narrow molecular weight distributions and predictable molecular weights.

Contrary to the expectation, each of these styrene derivatives containing electron-withdrawing groups can undergo anionic polymerization quantitatively with living poly(2VP). This is also inferred from the color changes of the reaction systems observed during polymerizations. The dark red color, typical of the polystyryl anions from **1-6**, appeared immediately upon addition of **1-6** to living poly(2VP). Successful syntheses of well-defined block copolymers by this sequential order were clearly evidenced from the sharpness of the single peaks and the absence of homopolymers in their SEC charts as well as the fact that the M_n values and the compositions agreed with those predicted within experimental accuracy. It should be noted that the living poly(2VP) bearing K^+ was used in the polymerization of **4** (Table 7-3, run 27), since no appreciable homopolymerization of **4** was previously observed to occur with the anionic initiators with Li^+ as a countercation under various conditions.[9] As expected, the resulting polymers at the first- and second-stage possessed somewhat broad molecular weight distributions, the M_w/M_n values being 1.27 and 1.36, respectively. It is believed from the analytical results that a block copolymer with the desired structure is also formed in this polymerization.

This is in sharp contrast to the polymerization of either isoprene or styrene with living poly(2VP) where either no polymerization or slow reaction occurs as mentioned before. The results of block copolymerizations obtained here indicate that the reactivities of **1-6** seems to be at least comparable to that of 2VP and more anionically reactive than those of isoprene and styrene, although they are the styrene derivatives. Clearly, introduction of the electron-withdrawing groups into the styrene framework reduces the charge densities of the vinyl groups of **1-6**, allowing these monomers to become more reactive than styrene itself in the anionic polymerization.

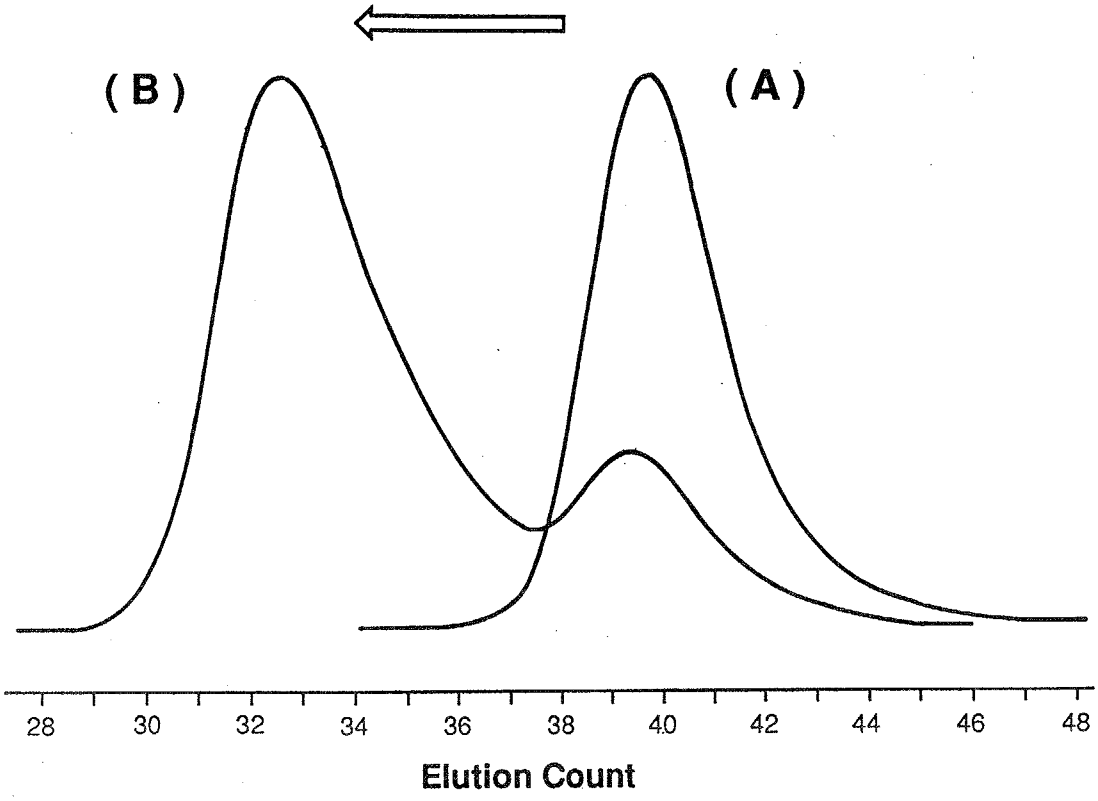


Figure 7-2. SEC curves (THF) of poly(tBMA) at the first-stage polymerization (A) and of the copolymerization product after the second-stage polymerization of **2** in THF at –78°C for 1 h (B) (Table 7-3, run 31): peak A, M_n(obsd) = 10 000, M_w/M_n = 1.13; peak B, M_w/M_n = 1.57.

Finally, attempts of the sequential polymerizations were carried out by addition of tBMA as a first monomer and then **1-6**. The most interesting aspect of the polymerization is whether the further polymerizations of **1-6** can proceed with the low nucleophilic carbanion produced from tBMA. The difunctional living polymer of tBMA was successfully synthesized by the polymerization of tBMA with oligo(α-methylstyryl)dipotassium in THF at –78°C for 2 h. The control of molecular weight and the narrow molecular weight distribution were actually attained under the polymerization conditions.

Upon addition of **1-3** to the living poly(tBMA), the color of the reaction mixture slowly changed from pale violet to orange red, and a quantitative conversion was realized for each case. The copolymerization products were obtained in quantitative yield. However, the SEC charts always showed bimodal peaks of broad molecular weight distributions. A typical example is shown in Figure 7-2. The peaks at the low molecular weight side are corresponding to homopolymers of tBMA, which are not involved in the initiation of **1-3**. The nonquantitative initiation of the second monomer may result in the formation of the block copolymer which was observed in the higher molecular weight region of Figure 7-2. The copolymerization products are therefore estimated to consist of virtual homopolymers of tBMA and the block copolymers containing poly(**1-3**) segments of higher molecular weights than expected.

From these results, it can be concluded that the initiation reactions of **1-3** occur slowly with living poly(tBMA) and the residual monomers are consumed rapidly by the newly formed living polymers from **1-3**. Some of unreacted living poly(tBMA) still remains even after the conclusion of polymerizations of **1-3**. Accordingly, the synthesis of well-defined block copolymer is not successful by the sequential addition of tBMA and **1-3** in this order. However, it is surprising that the styrene derivatives of **1-3** can be initiated with the propagating carbanion of living poly(tBMA), even though their initiation efficiencies are not quantitative. For example, the estimated efficiency of the crossover initiation reaction of **2** with living poly(tBMA) was ca. 60%. The contrasting result of no polymerization of 2VP with living poly(tBMA) indicates that **1-3** may be more reactive than 2VP. It is of course certain that they are anionically less reactive than tBMA.

More surprising are the results of the polymerizations of the sequential addition of **4-6** to the living poly(tBMA). Upon addition of **4-6** to living poly(tBMA), the colors of the polymerization systems changed immediately from pale violet to bright red, characteristic to the polystyryl anions produced from **4-6**. The red coloration remained unchanged at –78°C after 2 h, indicating no side reactions of the polar substituents with the active growing ends. All of the conversions of **4-6** were quantitative.

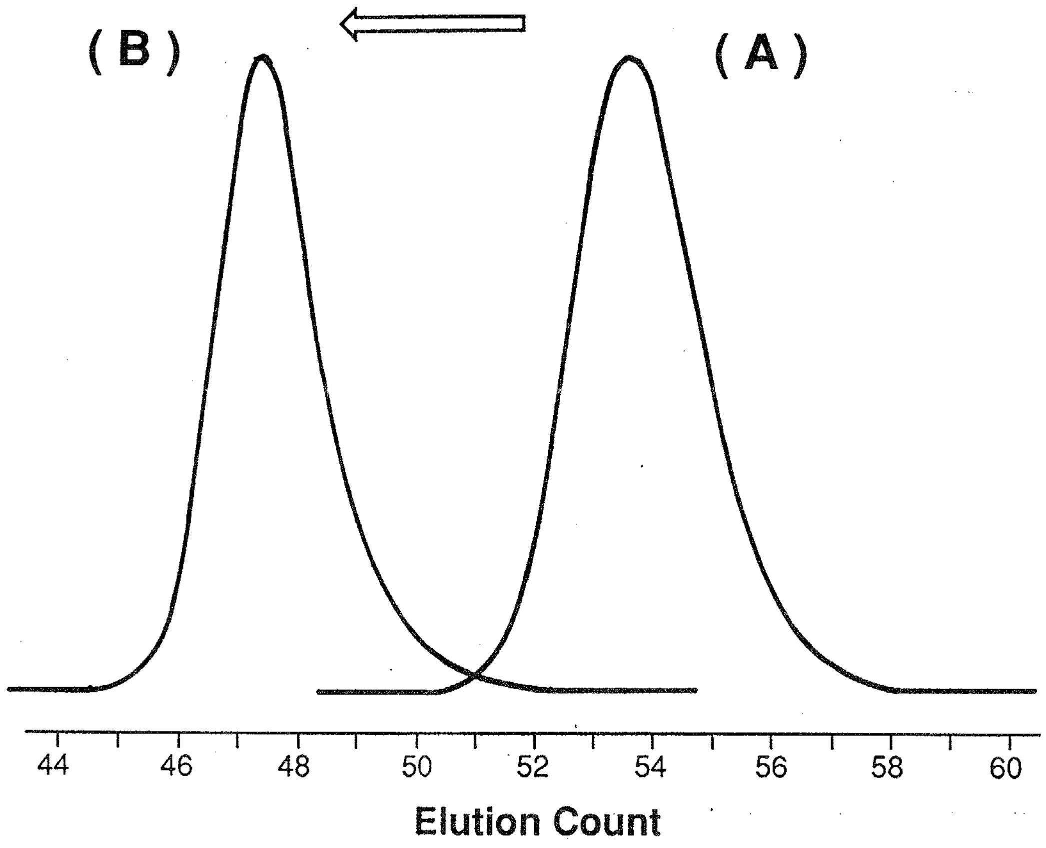


Figure 7-3. SEC curves (DMF) of poly(tBMA) at the first-stage polymerization (A) and of poly(**6**-*b*-tBMA-*b*-**6**) (B) (Table 7-3, run 35): peak A, M_n(obsd) = 6800, M_w/M_n = 1.08;
peak B, M_n(obsd) = 18 000, M_w/M_n = 1.06.

The compositions of the resulting polymers were analyzed by ^{1}H NMR and agreed well with the calculated values of both monomers fed. The observed molecular weights were in close accord with the theoretical ones assuming the living polymerizations of **4-6** at the second-stage. The SEC analyses exhibited that the resulting polymers all possessed narrow molecular weight distributions eluted at the higher molecular weight sides without the corresponding homopolymers of tBMA. A representative chromatogram is shown in Figure 7-3, which offers convincing evidence of the formation of the B-A-B triblock copolymer of tBMA and **6**, poly(**6**-*b*-tBMA-*b*-**6**), with a well-defined chain structure. It is obvious from these results that the second-stage polymerizations of **4-6** proceed in a living manner with the carbanion of living poly(tBMA) to afford tailor-made pure block copolymers. Thus, the anionic block copolymerization behaviors of **4-6** are apparently different from those of **1-3** as mentioned before.

Considering the results of block copolymerizations using **1-6**, the monomers of **4-6** can be classified as anionically more reactive monomers than **1-3**. The reactivities of **4-6** might be comparable to that of tBMA and are undoubtedly much higher than that of 2VP, although they are styrene derivatives. It is also interesting that the monomer reactivity can be changed by the electron-withdrawing groups introduced, varying the anionic reactivity from styrene to tBMA. From all the results in this section, the order of monomer reactivity (or in other words, the electrophilicity of the monomer) can be evaluated. Thus, the reactivity by the effect of the monomer skeleton and the electron-withdrawing group introduced is increased as follows: isoprene < styrene < 2VP < **1-3** < tBMA ≅ **4-6**

7-3. Sequential Polymerizations of Conventional Monomers with Living Poly(1-6)s.

In the preceding section, the anionic block copolymerizations by sequential addition of **1-6** to the living polymers from conventional monomers such as isoprene, styrene, 2VP, and tBMA has been discussed. Successful synthesis of block copolymers and evaluation of the monomer reactivity have been demonstrated. In particular, the reactivities of **1-6** are found to be remarkably enhanced by introducing electron-withdrawing groups into the phenyl ring of styrene. This section evaluates the nucleophilicities of the living polymers derived from **1**-**6** by the sequential addition of isoprene, styrene, 2VP, or tBMA to the living poly(**1**-**6**)s. The difunctional living polymers bearing K^+ were prepared from **1**-**6** and used to synthesize block copolymers with isoprene, styrene, and tBMA. The living polymers with Li^+ were employed for the synthesis of block copolymers using 2VP to avoid broadening of the molecular weight distribution of the resulting poly(2VP) block. The results are summarized in Table 7-4.

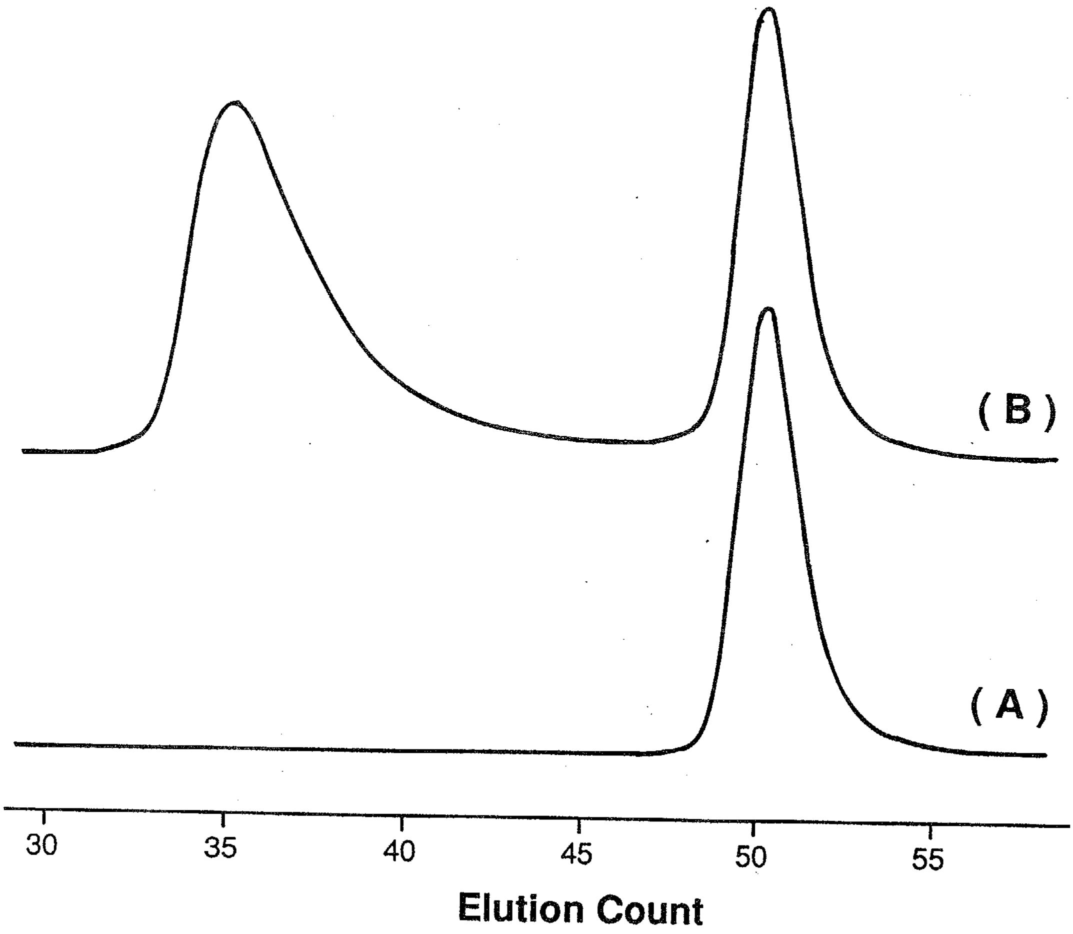


Figure 7-4. SEC curves (THF) of poly(**1**) at the first-stage polymerization (A) and of the copolymerization product after the second-stage polymerization of styrene in THF at –78°C for 2 h (B) (Table 7-4, run 42):
peak A, M_n(obsd) = 12 000, M_w/M_n = 1.09.

Table 7-4

Anionic Block Copolymerization of Isoprene, Styrene, 2VP, and tBMA with Living Poly(**1** - **6**) at –78°C in THF[a]

						block copolymer (homopolymer[b])		
	counter-	block	1st monomer	2nd monomer	yield[c]	$10^{-3}M_n$		
run	cation	sequence	(A)	(B)	%	calcd[d]	obsd[e]	M_w/M_n
36[f]	K$^+$	B-A-B	**1**	isoprene	0	27 (11)	f (8.5)	f (1.08)
37[f]	K$^+$	B-A-B	**2**	isoprene	0	22 (8.1)	f (8.4)	f (1.13)
38[f]	K$^+$	B-A-B	**3**	isoprene	0	36 (10)	f (10)	f (1.03)
39[f]	K$^+$	B-A-B	**4**	isoprene	0	43 (13)	f (12)	f (1.19)
40[f]	K$^+$	B-A-B	**5**	isoprene	0	19 (7.7)	f (7.6)	f (1.12)
41[f]	K$^+$	B-A-B	**6**	isoprene	0	42 (11)	f (9.3)	f (1.08)
42[g]	K$^+$	B-A-B	**1**	styrene	100	28 (15)	g (12)	g (1.09)
43[g]	K$^+$	B-A-B	**2**	styrene	100	21 (8.3)	g (7.0)	g (1.04)
44[g]	K$^+$	B-A-B	**3**	styrene	100	19 (7.0)	g (7.0)	g (1.02)
45[f]	K$^+$	B-A-B	**4**	styrene	0	23 (9.8)	f (9.8)	f (1.11)
46[f]	K$^+$	B-A-B	**5**	styrene	0	18 (8.9)	f (9.5)	f (1.15)
47[f]	K$^+$	B-A-B	**6**	styrene	0	24 (9.4)	f (8.8)	f (1.06)
48	Li$^+$	B-A-B	**1**	2VP	100	26 (9.0)	24 (9.5)	1.16 (1.10)
49	Li$^+$	B-A-B	**2**	2VP	100	20 (7.7)	19 (9.6)	1.26 (1.14)
50	Li$^+$	B-A-B	**3**	2VP	100	24 (9.6)	21 (9.0)	1.08 (1.05)
51[h]	K$^+$	B-A-B	**4**	2VP	100	17 (7.5)	41[i] (8.5)	1.90 (1.20)
52	Li$^+$	B-A-B	**5**	2VP	100	21 (12)	21 (13)	1.17 (1.15)

Table 7-4 (Continued)

run	counter-cation	block sequence	1st monomer (A)	2nd monomer (B)	yield[c] %	block copolymer (homopolymer[b])		
						$10^{-3}M_n$		
						calcd[d]	obsd[e]	M_w/M_n
53[j]	Li$^+$	B-A-B	**6**	2VP	100	21 (12)	j (10)	j (1.09)
54	K$^+$	B-A-B	**1**	tBMA	100	19 (6.5)	15 (7.5)	1.13 (1.10)
55	K$^+$	B-A-B	**2**	tBMA	100	25 (12)	23 (12)	1.07 (1.10)
56	K$^+$	B-A-B	**3**	tBMA	100	18 (8.9)	17 (8.4)	1.08 (1.03)
57	K$^+$	B-A-B	**4**	tBMA	100	27 (7.8)	27 (9.0)	1.24 (1.15)
58	K$^+$	B-A-B	**5**	tBMA	100	26 (12)	23 (9.9)	1.10 (1.08)
59	K$^+$	B-A-B	**6**	tBMA	100	16 (8.8)	16 (8.5)	1.17 (1.11)

[a] Polymerization reaction concerning monomer (4) was carried out at –95°C to avoid the serious side reaction; see ref. 9. [b] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [c] Yield of the second-stage polymerization. [d] M_n(calcd) = [monomer] × (MW of monomer) × 2 / [initiator] + MW of initiator unit. [e] The molecular weight of the block copolymers were determined by using the molecular weight of homopolymer and the molar ratios of monomer units in the block copolymer analysed by ^{1}H NMR. [f] No polymerization proceeded at the second-stage, resulting in a quantitative recovery of the homopolymer of the first monomer. [g] Initiation efficiency of the crossover reaction was low (2-10%) resulting in a copolymerization product showing bimodal and broad molecular weight distribution, which was consisted of a virtual homopolymer and a block copolymer having very high molecular weight. [h] Side reaction may occur during the second-stage polymerization. [i] The molecular weight of block copolymer was directly estimated from the SEC calibration using polystyrene standards. [j] The insoluble products was quantitatively obtained from the reaction mixture probably due to the crosslinking reaction of the polymer.

As was seen at first, all of the living polymers prepared from **1**-**6** were found not to initiate the polymerization of isoprene at all even for longer reaction times (runs 36-41). Each of the homopolymers of **1**-**6** was quantitatively recovered in every polymerization.

Next, with the use of styrene as a second addition monomer, complete conversions of styrene were realized with the living polymers of **1**-**3**. The SEC traces of the resulting products always showed two separated peaks which resulted from the virtual homopolymers of **1**-**3** and the block copolymers having very high molecular weight polystyrene segments, respectively. Figure 7-4 shows a SEC curve in the polymerization of styrene with living poly(**1**), typical for the slow initiation with rapid consumption of the second monomer by the newly formed carbanion. Only a portion of the living poly(**1**-**3**)s may react (2-10%) slowly with styrene to produce polystyryl anion and the newly formed anion polymerize rapidly to consume styrene completely. Residual unreacted living polymers remain after the consumption of styrene. Accordingly, the carbanion at the active growing end of **1**, **2**, or **3** shows only a low reactivity toward styrene. By contrast, no polymerization occurred at all between styrene and the living polymers from **4**-**6** (runs 45-47).

These observations confirm that the nucleophilicities of the living polymers from **1**-**6** are much lower than those of living polyisoprene and living polystyrene, possibly due to a reduction of the electron densities on the carbanions by the electron-withdrawing effect of the substituents. It would appear obvious from the crossover reactions with styrene that the carbanions derived from **1**-**3** are more reactive than those from **4**-**6**, as might be expected from these monomer reactivities. In any event, a well-defined block copolymer synthesis has not been feasible by this sequential addition order; *i.e.*, **1**-**6** is added first and isoprene or styrene is then added. The synthesis must be carried out in the reversed addition order as mentioned before in Table 7-3.

Next, the sequential polymerizations using more anionically reactive monomers such as 2VP and tBMA were attempted. The polymerizations of both 2VP and tBMA were found to proceed quantitatively with the living polymers of **1**-**6**. The block copolymers with regulated segments and compositions have been successfully synthesized in any combinations except for 2VP and either living poly(**4**) or living poly(**6**).

As mentioned before, no polymerization of **4** was observed with anionic initiators with Li^+.[9] Therefore, the polymerization of living poly(**4**) bearing Li^+ with 2VP could not carried out. Instead, the living poly(**4**) bearing K^+ was employed for the sequential polymerization of 2VP as shown in run 51. Although the polymer yield was quantitative in this case, the molecular weight distribution by SEC was broad. The observed molecular weight was definitely higher than the predicted value. In this case, undesirable side reactions may occur during the second-stage of the polymerization of 2VP.

The polymerization of 2VP with living poly(**6**) for 2 h always gave an insoluble polymeric material quantitatively based on the weights of fed monomers. It probably involves a cross-linking reaction between the cyano group in poly(**6**) and the carbanion of the newly produced living poly(2VP). This side reaction might possibly occur slowly, compared to the polymerization, since a soluble polymer was obtained when a similar polymerization was terminated in a short time. In this case, therefore, the first addition should be 2VP and then **6** to achieve the successful synthesis of block copolymer (Table 7-3, run 29).

As mentioned in the preceding section, it has been observed that the sequential polymerizations by all the combinations of **1**-**6** with living poly(2VP) provide the desired block copolymers. It is also found that the well-defined block copolymers are possibly synthesized by the sequential additions of **4-6** to living poly(tBMA), while the carbanion of living poly(tBMA) is not sufficiently nucleophilic to initiate quantitatively the polymerizations of **1-3**. Accordingly, among the monomers **1-3**, **5**, and 2VP as well as the monomers **4-6** and tBMA, "reversible" block copolymerization is possible where both A and B blocks can initiate each other. Either A-B-A or B-A-B triblock copolymers with desired compositions are arbitrarily synthesized only by changing the addition order of the monomers. On the other hand, in the combination of tBMA and **1-3**, there is a restriction. "Unilateral" block copolymerization is only possible where the living polymers of **1-3** can initiate tBMA with quantitative efficiency, but not vice versa.

From the results obtained in this section, it is possible to compare the nucleophilic reactivities of the living polymers. The following is the decreasing order of reactivity:

living polyisoprene = living polystyrene
> living poly(2VP) = living polymers from **1-3**
> living poly(tBMA) = living polymers from **4-6**

This reactivity order of living polymer is seen to be almost opposite of the monomer reactivity discussed before. This may be reasonable since the electron-withdrawing nature also reduces the electron densities on the propagating benzylic carbanions to stabilize in a similar manner. It therefore seems possible to predict the nucleophilicity of the propagating carbanion of the living polymers from the reactivity of the employed monomers and vice versa. From the ranking between the living polymers of **1-6**, the strength of the electron-withdrawing effect for the substituents introduced is also significant with respect to the reactivity of the living carbanion derived from the monomer.

7-4. Sequential Polymerizations of 1-6 with Living Poly(1-6)s.

This section establishes whether "reversible" or "unilateral" block copolymerization is possible among the six styrenes with electron-withdrawing groups, **1**-**6**. The results are summarized in Table 7-5.

As can be seen in runs 60-64, the block copolymerizations with living poly(**1**) successfully occur without regard of which monomer from **2** to **6** is added sequentially. Quantitative yields of polymers and the results of good agreement between the calculated and observed M_n values as well as the narrow molecular weight distributions were obtained in all combinations. The SEC charts showed that the resulting polymers all had symmetrical unimodal peaks with narrow distributions, the M_w/M_n values being less than 1.2. These confirm quantitative production of the pure block copolymers with well-defined structures by this sequential route.

Similarly, the living polymers of **2**, **3**, and **5** initiated quantitatively the polymerizations of **1**-**6** to afford well-defined block copolymers of the same grade. For example, Figure 7-5 and 7-6 show the SEC chromatograms of block copolymers obtained from the reversed addition polymerization of **1** and **3** to oligo(α-methylstyryl)dipotassium in THF at –78°C. These two SEC curves clearly support that the order of addition of these two monomers does not affect the polymerization results. Thus, the tailor-made A-B-A and B-A-B triblock copolymers, poly(**3**-*b*-**1**-*b*-**3**) and poly(**1**-*b*-**3**-*b*-**1**), can be synthesized only by changing the order of addition of two comonomers. Consequently, the sequential addition is mutually replaceable; *i.e.*, reversible block copolymerization is possible among the monomers **1**-**3** and **5**. This polymerization behavior of **5** is totally unexpected, considering from the observations that the reactivities of monomer and the carbanion can be roughly classified between **1**-**3** and **4**-**6**, which will be discussed in more detail.

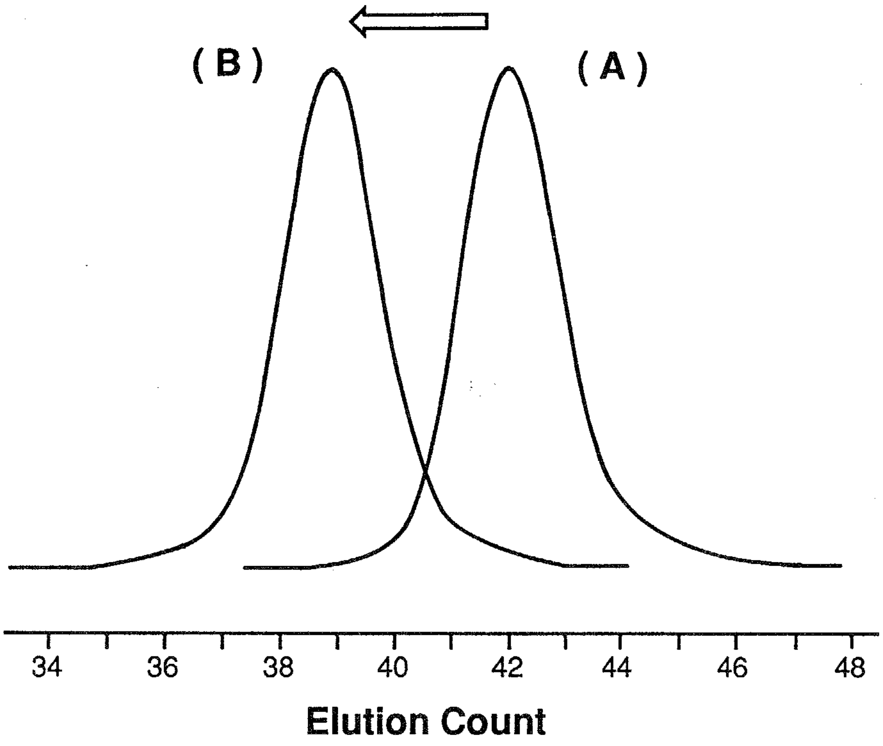


Figure 7-5. SEC curves (THF) of poly(**1**) at the first-stage polymerization (A) and of poly(**3**-*b*-**1**-*b*-**3**) (B) (Table 7-5, run 61):
peak A, M_n(obsd) = 11 000, M_w/M_n = 1.06;
peak B, M_n(obsd) = 19 000, M_w/M_n = 1.07.

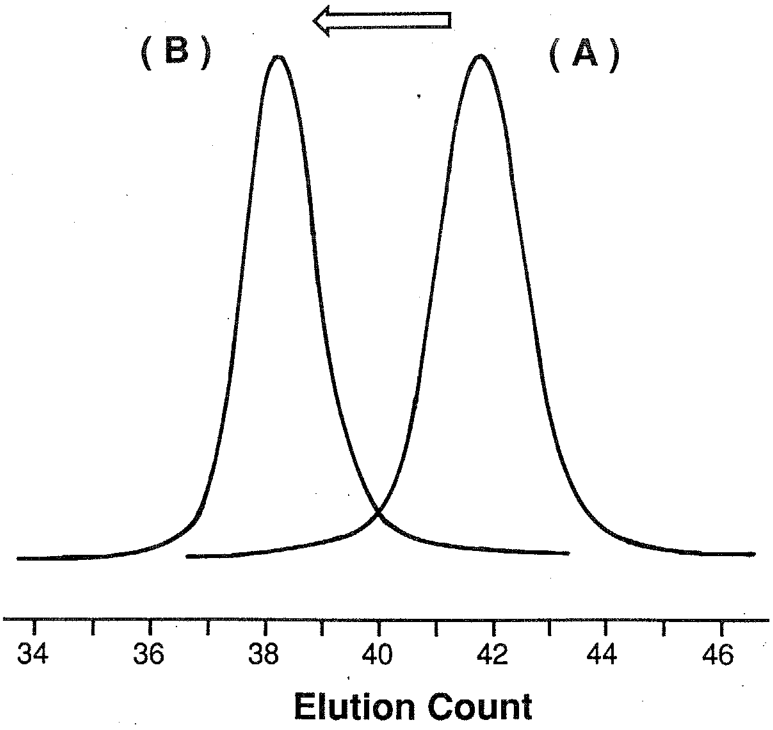


Figure 7-6. SEC curves (THF) of poly(**3**) at the first-stage polymerization (A) and of poly(**1**-*b*-**3**-*b*-**1**) (B) (Table 7-5, run 70):
peak A, M_n(obsd) = 9000, M_w/M_n = 1.06;
peak B, M_n(obsd) = 16 000, M_w/M_n = 1.05.

Table 7-5 Anionic Block Copolymerization of **1** - **6** with Living Poly(**1** - **6**)s at –78°C in THF[a]

						block copolymer (homopolymer[b])		
	counter-	block	1st monomer	2nd monomer	yield[c]	$10^{-3}M_n$		
run	cation	sequence	(A)	(B)	%	calcd[d]	obsd[e]	M_w/M_n
60	K^+	B-A-B	**1**	**2**	100	17 (7.4)	15 (7.6)	1.12 (1.10)
61	K^+	B-A-B	**1**	**3**	100	19 (10)	19 (11)	1.07 (1.06)
62	K^+	B-A-B	**1**	**4**	100	23 (9.1)	17 (8.7)	1.13 (1.08)
63	K^+	B-A-B	**1**	**5**	100	18 (7.8)	16 (7.8)	1.16 (1.07)
64[f]	K^+	B-A-B	**1**	**6**	100	17 (9.3)	16	1.05
65	K^+	B-A-B	**2**	**1**	100	16 (7.7)	16 (8.5)	1.10 (1.10)
66[f]	K^+	B-A-B	**2**	**3**	100	17 (9.8)	14	1.04
67[f]	K^+	B-A-B	**2**	**4**	100	21 (11)	17	1.11
68[f]	K^+	B-A-B	**2**	**5**	100	15 (7.2)	14	1.08
69[f]	K^+	B-A-B	**2**	**6**	100	19 (10)	16	1.12
70	K^+	B-A-B	**3**	**1**	100	21 (8.9)	16 (9.0)	1.05 (1.06)
71[f]	K^+	B-A-B	**3**	**2**	100	17 (7.6)	15	1.04
72[f]	K^+	B-A-B	**3**	**4**	100	18 (8.3)	16	1.09
73[f]	K^+	B-A-B	**3**	**5**	100	20 (9.4)	19	1.08
74	K^+	B-A-B	**3**	**6**	100	19 (9.0)	16 (9.0)	1.07 (1.09)
75	K^+	B-A-B	**4**	**1**	100	12 (6.7)	13 (6.8)	1.11 (1.18)
76[g]	K^+	B-A-B	**4**	**2**	0	24 (10)	g (10)	g (1.08)
77[f, h]	K^+	B-A-B	**4**	**3**	100	17 (10)	18[i]	j
78	K^+	B-A-B	**4**	**5**	100	15 (6.0)	18 (7.1)	1.19 (1.12)
79[f]	K^+	B-A-B	**4**	**6**	100	21 (12)	20	1.12
80	K^+	B-A-B	**5**	**1**	100	16 (8.6)	15 (8.5)	1.16 (1.14)

Table 7-5 (Continued)

						block copolymer (homopolymer[b])		
	counter-	block	1st monomer	2nd monomer	yield[c]	$10^{-3}M_n$		
run	cation	sequence	(A)	(B)	%	calcd[d]	obsd[e]	M_w/M_n
81[f]	K^+	B-A-B	**5**	**2**	100	22 (9.4)	22	1.19
82[f]	K^+	B-A-B	**5**	**3**	100	22 (12)	20	1.14
83	K^+	B-A-B	**5**	**4**	100	14 (6.2)	13 (6.7)	1.22 (1.09)
84[f]	K^+	B-A-B	**5**	**6**	100	19 (9.0)	18	1.09
85[g]	K^+	A-B	**6**	**1**	0	18 (10)	g (10)	g (1.10)
86[h]	K^+	B-A-B	**6**	**2**	24	19 (9.7)	7.4[i] (6.5)	j (1.05)
87[k]	K^+	B-A-B	**6**	**3**	100	19 (9.3)	k (7.4)	k (1.05)
88[f]	K^+	B-A-B	**6**	**4**	100	21 (9.2)	16	1.13
89	K^+	B-A-B	**6**	**5**	100	19 (11)	18 (8.3)	1.07 (1.09)

[a] Polymerization reaction concerning monomer (**4**) was carried out at –95°C to avoid the serious side reaction; see ref. 9. [b] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [c] Yield of the second-stage polymerization. [d] $M_n(\text{calcd}) = [\text{monomer}] \times (\text{MW of monomer}) \times f / [\text{initiator}] + \text{MW of initiator unit}$. $f = 1$ or 2, corresponding to the functionality of the initiators. [e] The molecular weight of the block copolymers were determined by using the molecular weight of homopolymer and the molar ratios of monomer units in the block copolymer analysed by ^{1}H NMR. [f] Homopolymer of the first monomer was not isolated in these cases. [g] No polymerization proceeded at the second-stage, resulting in a quantitative recovery of the homopolymer of the first monomer. [h] Side reaction may occur during the second-stage polymerization. [i] The molecular weight of block copolymer was directly estimated from the SEC calibration using polystyrene standards. [j] A multimodal peak or long tailing of the SEC chromatogram of the product was observed. [k] Initiation efficiency of the crossover reaction was moderate (ca. 80%) resulting in a copolymerization product showing bimodal molecular weight distribution.

With use of living poly(**4**) as an initiator, well-defined block copolymers were obtained by the sequential addition of **1**, **5**, or **6** to this living polymer. On the other hand, some difficulties were encountered in the cases where **2** and **3** were added to living poly(**4**). In the first case, no appreciable polymerization of **2** occurred at all and homopoly(**4**) was recovered quantitatively. The possibilities of side reactions among the carbanions and polar groups may be ruled out from the observations that the red color of living poly(**4**) remains unchanged after addition of **2** and the block copolymerization by reversed addition takes place without problem. It can be therefore concluded that the carbanion derived from **4** is not capable of initiating the polymerization of **2** under the specific condition at –95°C. For the latter case, the polymerization of **3** was found to proceed quantitatively, but the resulting block copolymer had a broad molecular weight distribution in this case. A multimodal peak was observed by SEC, indicating that the competitive side reactions like ester attack occurred to some extent during the course of the polymerization of **3** with living poly(**4**).

When living poly(**6**) was used in block copolymerization, unsatisfactory results were obtained with **1**-**3** as second monomers. No polymerization of **1** was found to occur at all from the fact that the homopolymer at the first-stage and the monomer unreacted were quantitatively recovered. A low conversion of 24% could be achieved by the second polymerization of **2** with living poly(**6**). The SEC chromatogram of the resulting polymer possessed a long low-molecular-weight tailing. Termination was strongly suggested at the second-stage of polymerization of **2**. Although the polymerization of **3** proceeded quantitatively from living poly(**6**), the resulting product was a polymer with a bimodal distribution, indicating a mixture of homopoly(**6**) and the block copolymer. The results clearly indicate low reactivities of living poly(**6**) toward **1**, **2**, and **3**, respectively. The low reactivity of living poly(**6**) has thus far prevented the synthesis of well-defined block copolymers by the sequential addition order as shown here. At the sequential addition using living poly(**6**) as an initiator, only combinations of **4** and **5** with living poly(**6**) provide block copolymers having a high degree of block integrity. This is evidenced by the SEC analyses of the resulting polymers which show sharp single peaks eluted on the higher molecular weight sides and the absence of any peaks corresponding to homopolymers.

From the observation at both sequential additions with the living polymers from **4** and **6**, it offers the choice of reversible addition of the following monomer pairs: **1** and **4**, **4** and **5**, **4** and **6**, and **5** and **6**. In the other pairs – **1** and **6**, **2** and **4**, **2** and **6**, **3** and **4**, and **3** and **6** – these types of block copolymer impose the additional restrictions that (a) the low reactive monomer of **1**, **2**, or **3** must be polymerized first and (b) either **4** or **6** is then added to the resulting living polymers. The synthesis of block copolymer must proceed in this order. Furthermore, the reactivities of living poly(**6**) toward monomers **1**-**3** clearly indicate that living poly(**6**) has the lowest nucleophilicity among the living polymers derived from the present six styrene derivatives with electron-withdrawing groups. In comparison with the reactivity of living poly(2VP), living poly(**6**) is evidently much less reactive. Surprisingly, living poly(**6**) appears to have a lower nucleophilicity than living poly(tBMA), which initiates the polymerization of **1** as mentioned before. It can be concluded from the results obtained in this section that reversible block copolymerization among **1**-**6** is possible for most monomer pairs.

Since it is difficult from Tables 7-2 to 7-5 to see a full view of the block copolymerizations obtained here, all block copolymerization results[23] were classified into four categories for easy comparison. A summary is listed in Table 7-6. The first symbol (+++) indicates a successful example of block copolymerization to afford a well-defined block copolymer. The second one (++) means that a sequential block copolymerization occurs with quantitative efficiency, but the resulting block copolymer has a relatively broad

Table 7-6 Summary of the Results of Block Copolymerization (Crossover Reaction) between Various Monomers and Their Living Polymers[a]

	Monomer Reactivity[b]									
Reactivity of Living Polymer	Isp	St	2VP	**1**	**2**	**3**	**4**	**5**	**6**	tBMA
Poly(Isp)$^{-}$ [c]	+++[d]	+++	+++[e]	+++	+++	+++	+++	+++	+++	+++
Poly(St)$^{-}$ [c]	+++	+++[d]	+++[f]	+++	+++	+++	+++	+++	+++	+++
Poly(2VP)$^{-}$	–	SR[g]	+++[d]	+++	+++	+++	++	+++	+++	++
Poly(**1**)$^{-}$	–	+	+++	+++[d]	+++	+++	+++	+++	+++	+++
Poly(**2**)$^{-}$	–	+	++	+++	+++[d]	+++	+++	+++	+++	+++
Poly(**3**)$^{-}$	–	+	+++	+++	+++	+++[d]	+++	+++	+++	+++
Poly(**4**)$^{-}$	–	–	SR[g]	+++	–	SR[g]	+++[d]	+++	+++	++
Poly(**5**)$^{-}$	–	–	+++	+++	+++	+++	+++	+++[d]	+++	+++
Poly(**6**)$^{-}$	–	–	SR[h]	–	SR[g]	+	+++	+++	+++[d]	+++
Poly(tBMA)$^{-}$	–	–	–	+	+	+	+++	+++	+++	+++[d]

+++: Quantitative initiation efficiency resulting in the block copolymers with narrow molecular weight distributions ($M_w/M_n <$ 1.2). ++: Quantitative initiation efficiency, the polydispersity index (M_w/M_n) of the resulting block copolymer was 1.2 - 1.4. +: Initiation efficiency of the crossover reaction was not quantitative (2-80%) resuting in a mixture of homopolymer and block copolymer, showing bimodal and broad molecular weight distribution. –: No reaction between the living polymer and the second monomer occurred resulting in a quantitative recovery of homopolymer of the first monomer.

[a] Most data from Table 7-2 – 7-5. [b] β-Carbon chemical shift of monomer (in ppm): isoprene, 113.5 and 116.7; styrene, 113.8; 2VP, 118.1; (**1**), 114.8; (**2**), 114.9; (**3**), 115.3; (**4**), 116.0; (**5**), 117.0; (**6**), 117.6; tBMA, 124.0. [c] Including the results by using the polymeric carbanion capped with 1,1-diphenylethylene. [d] Postpolymerization. [e] Ref. 16. [f] Ref. 17. [g] These polymeric products had multimodal and broad molecular weight distributions probably due to the serious side reaction. [h] An insoluble product was quantitatively obtained from the reaction mixture probably due to the crosslinking reaction of the polymer.

distribution of molecular weight (M_w/M_n = 1.2 - 1.4). The third one (+) means that the second-stage polymerization takes place with low initiation efficiency, generally resulting in a mixture of virtual homopolymer and the block copolymer with undesirable structures. The last symbol (–) shows no polymerization at the second-stage. From Table 7-6, the reactivities of monomers and the resulting living polymers are clearly demonstrated. It is especially useful for judgment of the sequential addition order between different monomers in synthesizing a block copolymer.

A wide variety of novel block copolymers have thus been successfully synthesized by using **1**-**6**, isoprene, styrene, 2VP, and tBMA, although the order of addition of monomers is not exchangeable in some combinations. Most of the resulting block copolymers have an excellent degree of block integrity with respect to composition, structure, molecular weight, and molecular weight distribution. The method developed here also is valuable in the synthesis of block copolymers where each or both blocks have polar functional groups in all monomer units.

The *N*-cyclohexylimino,[7] oxazolinyl,[8] and *tert*-butyl ester[9] pendant groups on the polymers have been previously reported to be readily deprotected under mild conditions to generate quantitatively more useful formyl[7] and carboxyl functions.[8,9] The cyano group may also be transformed into many other functional groups, *e.g.*, COOH and CH_2NH_2. Thus, many new block copolymers with other functional groups can be prepared from the block copolymers developed here. The presence of such functionalities in block copolymers may provide practical special advantages in a variety of fields.

Narrow molecular weight distribution is desirable in the synthesis of a block copolymer, although it is not a criterion of living polymerization as emphasized by Quirk.[24] Molecular weight distribution of the resulting polymer is known to be generally sensitive to the polymerization conditions, such as structure and countercation of the initiator, ligand, solvent, and temperature. As mentioned before, the standard conditions of anionic polymerization were employed as much as possible to compare easily the results of block copolymerization. No attempt was made to optimize the condition for each of the monomers used here. It would be therefore potentially possible to make the distributions of molecular weight listed in Table 7-2 – 7-5 narrower by optimizing the polymerization conditions for each of the cases.

7-5. Evaluation of Monomer Reactivity for 1-6 by ^{13}C NMR Measurement.

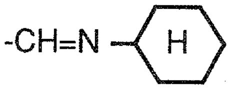
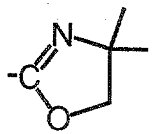
In the preceding sections, the reactivities of new styrene derivatives, **1-6**, as well as the resulting living polymers have been evaluated by the results of sequential block copolymerization. Their reactivities are found to be in the range between those of 2VP and tBMA. However, more detailed information on the reactivities of **1-6** and their living polymers is not available from the above results.

There have been several previous reports concerning the reactivities of 4-substituted styrenes estimated by means of various organic reactions such as methoxymercuration,[25] Diels-Alder reaction,[26] free-radical addition reaction,[27] and hydroboration.[28] These reports have revealed the relationship between structure and reactivity and demonstrated that the introduced substituents remarkably affect the reactivities of styrenes. As a generally established parameter to account for the substituent effects, the Hammett σ value[29] has been effectively employed in these reactions of 4-substituted styrenes.[25-28]

The ^{13}C NMR chemical shifts for aromatic compounds has also been well utilized to determine the electronic effect of the substituent on the phenyl ring for many years. Actually, Dhami and Stothers[30] pointed out a good linear relationship between the Hammett σ parameter and the β-carbon NMR

Table 7-7

Hammett Substituent Parameter and ^{13}C NMR Chemical Shift of Vinyl β-Carbon for 4-X-Substituted Styrenes

X	C_β[a]	σ_p[b]	X	C_β[a]	σ_p[b]	X	C_β[a]	σ_p[b]
NMe_2	109.3[c]	–0.83	$CONEt_2$ (1)	114.8		SO_2NEt_2 (5)	117.0	
OMe	111.6	–0.27	 (2)	114.9		C≡N (6)	117.6	0.66
Me	112.8[c]	–0.17	 (3)	115.3		NO_2	118.5	0.78
H	113.8	0.00	$COOBu^t$ (4)	116.0				
Cl	114.4	0.23	COOMe	116.2	0.45			
Br	114.6	0.23	COMe	116.6	0.50			

[a] In $CDCl_3$ in ppm. [b] Ref. 29a. [c] Ref. 32.

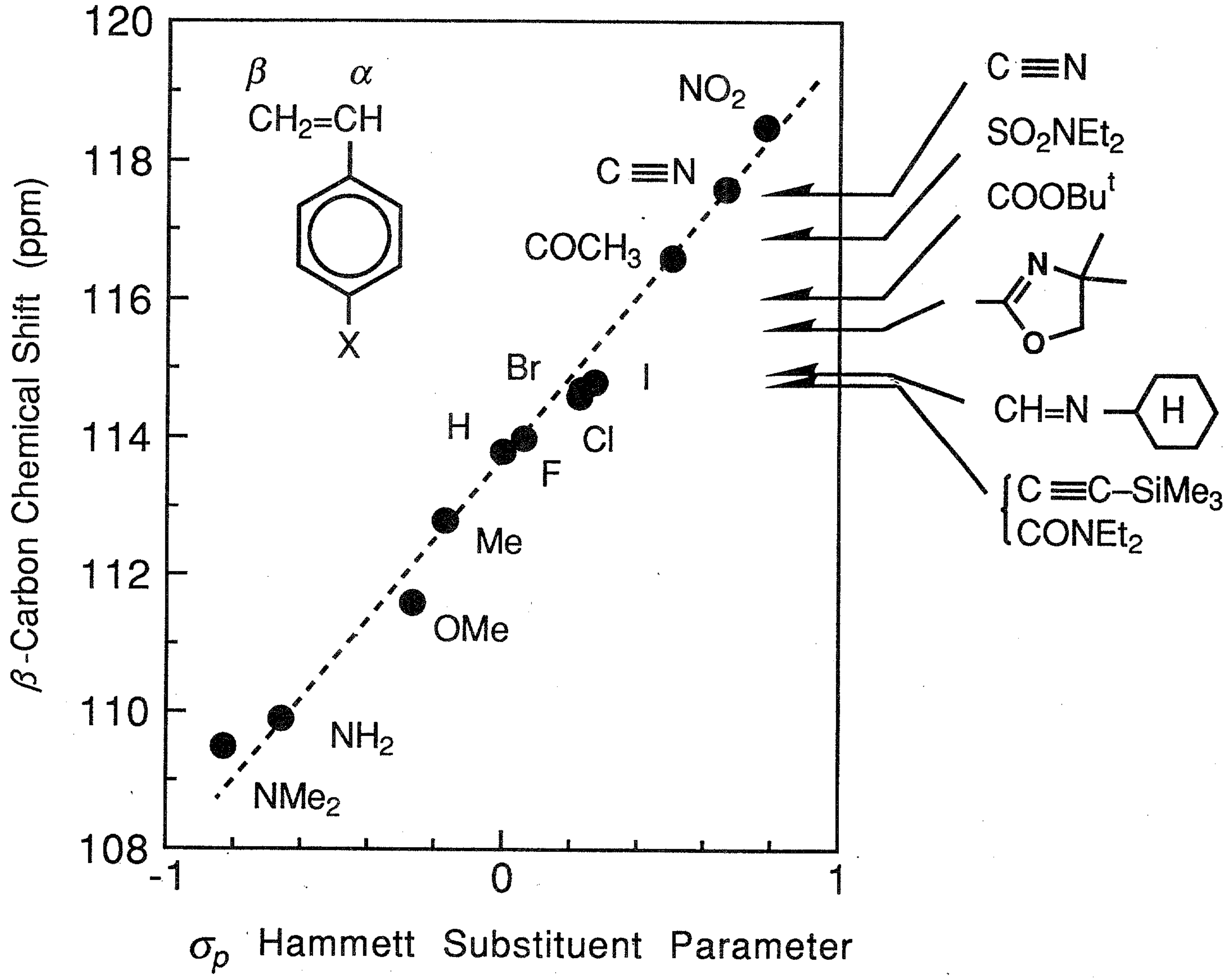


Figure 7-7. Plot of β-carbon chemical shifts of vinyl groups of *para*-substituted styrenes[32] vs. Hammett σ_p parameters.[29a]

chemical shifts of the vinyl group of seven 4-substituted styrenes in the range from Me_2N to NO_2 substituents. Figure 7-7[31] certainly shows a similar linear plot by using the newly reported chemical shifts[32] and substituent values.[29a] More interestingly, Reynolds and co-workers[33] have reported that the chemical shifts of β-carbons of 4-substituted styrenes are precisely related to the π -electron densities at this site calculated by the semiemprical CNDO/2 method. Recent ab initio calculations[34] have again confirmed this linear relationship between the β-carbon chemical shifts and the ab initio π -electron densities. It is therefore possible that the π -electron densities on the vinyl β-carbon which might reflect monomer polymerizability of **1-6** are estimated from their values of chemical shifts of the β-carbons. This means that the reactivities of **1-6** can be evaluated and arranged in reactivity order by measuring the chemical shifts of their β-carbons. The chemical shifts of the β-carbons of **1-6** and some styrene derivatives as references are listed in Table 7-7 in addition to the reported Hammett substituent values.[29a]

As can be seen, the values for **1-6** (114.8 - 117.6 ppm) are considerably shifted to lower field than that of styrene (113.8 ppm), as would be expected. This clearly indicates that the π -electron densities on the vinyl β-carbons of **1-6** are decreased to a variety of extents by introducing electron-withdrawing substituents and, in other words, their reactivities increase more than that of styrene under the anionic polymerization condition. The reactivity order increases as follows:

styrene < **1** < **2** < **3** < **4** < **5** < **6**

Similarly, the ^{13}C chemical shift of the terminal benzylic carbanion of the resulting living polymers[35] might indicate the reactivity of the carbanion, although the data are not currently available. As discussed before, the reactivities of the carbanions from **1-6** can be estimated to be in the opposite order of the monomer reactivity. The electron-withdrawing effect of the introduced substituents might contribute to both the enhancement of the monomer reactivity and the stabilization of the propagating carbanion in the same order of strength. Therefore, the reactivity of the carbanion at the growing chain end would be completely opposite to that obtained for the monomer:

living polystyrene > living poly(**1**) > living poly(**2**)
> living poly(**3**) > living poly(**4**) > living poly(**5**)
> living poly(**6**)

As mentioned before, both the reactivities of **1-6** and their carbanions were examined by the results of block copolymerization among these and conventional monomers. It has been observed that the reactivities of the monomers and the carbanions increase as styrene < **1-3** < **4-6** and carbanion from **6** < carbanions from **4** and **5** < carbanions from **1-3** < styryl anion in these orders, respectively. Evidently, the trends agree very well with those evaluated by the chemical shifts of the β-carbons of **1-6** and styrene.

7-6. Conclusion

This chapter established synthetic achievement of a series of novel block copolymers with strictly controlled chain architecture by the living block copolymerizations between six 4-substituted styrenes containing electron-withdrawing groups, **1-6**, and four conventional monomers. It is evident from the results of crossover reactions that the introduced electron-withdrawing groups play very important roles both in the enhancement of monomer reactivity and in the stabilization of the propagating carbanions of the living polymers. The anionic polymerizabilities of **1-6** are apparently higher than that of styrene and are evaluated as being between those of 2VP and tBMA.

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Chapter 8

Conclusions

Chapter 1. General Introduction.

In this chapter, the chemistry of anionic living polymerization was reviewed particularly from the synthetic point of view. The present problems on a controlled synthesis of polymers bearing functional groups under the anionic conditions were pointed out. A new synthetic strategy for the anionic living polymerization of styrene derivatives containing functional groups was proposed by means of an introduction of electron-withdrawing groups into the styrene framework.

Chapter 2. Anionic Living Polymerization of *N,N*-Dialkyl-4-vinylbenzamides.

The anionic polymerizations of nine *para*-substituted tertiary amide styrenes quantitatively proceeded without chain transfer and termination reactions to give stable living polymers. Polymers with regulated chain lengths and narrow molecular weight distributions were actually synthesized. Furthermore, the living nature of these polymerizations made the preparation of a variety of block copolymers having poly(*N,N*-dialkyl-4-vinylbenzamide) segments possible. It was also demonstrated that three polymer reactions, nucleophilic substitution of poly(**1a**), aromatic lithiation of poly(**1b**), and acid hydrolysis of poly(**1h**), could lead to new functional polymers that retained the well-defined characteristic of these parent polymers.

Chapter 3. Anionic Living Polymerization of *tert*-Butyl 4-Vinylbenzoate.

At –95°C, the anionic polymerization of *tert*-butyl 4-vinylbenzoate constructed a stable living polymer inhibiting the undesirable side reactions. The polymerization results of sterically less-hindered methyl, allyl, and isopropyl esters of 4-vinylbenzoate were unsuccessful from the viewpoint of a living polymerization. The bulkiness of the ester alkyl group and the electron-withdrawing effect of the ester group played an important role in the stabilization of the propagating carbanion. The resulting polymer was completely hydrolyzed with trimethylsilyl chloride / sodium iodide under mild conditions to afford poly(4-vinylbenzoic acid) with a predictable molecular weight and a narrow molecular weight distribution.

Chapter 4. Anionic Living Polymerizations of 2-, 3-, and 4-(Trimethylsilyl)ethynylstyrene.

The new linear poly(4-ethynylstyrene), poly(3-ethynylstyrene), and poly(2-ethynylstyrene) were synthesized by the anionic living polymerizations of (trimethylsilyl)ethynylstyrenes, followed by the complete deprotections of the resulting polymers. These polymers possessed ethynyl (carbon-carbon triple bond) substituents in each monomer unit and the predicted molecular weights. Novel tailor-made block copolymers containing poly(ethynylstyrene) segments were also synthesized by the sequential polymerization of protected (trimethylsilylethynyl)styrenes and the other monomer. Finally, the bromination reaction of poly(4-ethynylstyrene) quantitatively proceeded to provide a poly[4-(1,2-dibromoethenyl)styrene] having a controlled chain length.

Chapter 5. Anionic Living Polymerization of *N*,*N*-Dialkyl-4-vinylbenzenesulfonamides.

Three *N*,*N*-dialkyl-4-vinylbenzenesulfonamides were anionically polymerized to afford new types of living polymers with controlled molecular weights and narrow distributions ($M_w/M_n = 1.1$). (*N*,*N*-Dialkylamino)sulfonyl functional groups in the styrene monomers and the polymers tolerated the initiation and the repeated propagation reactions during the course of anionic living polymerization.

Chapter 6. Anionic Polymerizations of 2-, 3-, and 4-Cyanostyrene.

This chapter demonstrated the substituent effects on the anionic polymerizations of three ring-substituted cyanostyrenes. 4-Cyanostyrene was quantitatively polymerized with various anionic initiators to afford a stable living polymer. The living system led to the perfect controls of the molecular weights and their distributions of the resulting polymers. On the other hand, the living polymerizations of 2- and 3-cyanostyrene were not achieved because of the undesirable side reactions during the polymerization. The success of the living polymerization of 4-cyanostyrene was due to the stabilization of growth center of the living polymer by the electron-withdrawing effect of *para*-substituted cyano group.

Chapter 7. Anionic Block Copolymerization of Styrene Derivatives *Para*-Substituted with Electron-Withdrawing Groups.

The sequential anionic block copolymerizations between six *para*-substituted styrenes containing electron-withdrawing groups and four conventional monomers (isoprene, styrene, 2-vinylpyridine, and *tert*-butyl methacrylate) were carried out to evaluate the reactivities of the monomers and the resulting living polymers. A series of novel block copolymers having strictly controlled chain architecture were actually synthesized. It was evident from the results of crossover reactions that the introduced electron-withdrawing groups played very important roles both in the enhancement of monomer reactivity and in the stabilization of the propagating carbanions of the living polymers. The anionic polymerizabilities of the new styrene monomers were apparently higher than that of styrene and were ranked between those of 2-vinylpyridine and *tert*-butyl methacrylate.

In summary, it was evident from the results of the block copolymerization that the introduction of electron-withdrawing groups into the styrene framework could efficiently change the both reactivities of *para*-substituted styrene monomers and the resulting living polymers. The newly proposed strategy for the anionic living polymerization of styrene derivatives containing functional groups was successfully achieved to form the polystyrenes *para*-substituted with *N,N*-dialkylamide, *tert*-butyl ester, (trimethylsilyl)ethynyl, *N,N*-dialkylsulfonamide, and cyano groups.

The contribution to the field of material science is expected by these successful syntheses of functional homopolymers and block copolymers possessing well-defined chain structures. The present novel living polymers having various electron-withdrawing groups are important as a new class of carbanion which shows remarkable stabilities and may open a bright route to the future development of carbanionic chemistry as well as the synthetic polymer chemistry.

List of Publications

Chapter 1 (Review)

Anionic Living Polymerization of Styrenes Containing Electron-withdrawing Groups
S. Nakahama, T. Ishizone, A. Hirao
Makromol. Chem., Macromol. Symp., **67**, 223-236 (1993)

Chapter 2

1) Anionic Polymerization of Monomers Containing Functional Groups. 3.
Anionic Living Polymerization of *N,N*-Dialkyl-4-vinylbenzamides
T. Ishizone, S. Wakabayashi, A. Hirao, S. Nakahama
Macromolecules **24**, 5015-5022 (1991)

2) Protection and Polymerization of Functional Monomers. 22.
Anionic Synthesis of Well-defined Poly(4-vinylbenzoic acid) by Means of Anionic Living Polymerization of *N*-(4-Vinylbenzoyl)-*N'*-methylpiperazine, Followed by Deprotection
T. Ishizone, H. Kurosawa, A. Hirao, S. Nakahama
Makromol. Chem. in press.

Chapter 3

Protection and Polymerization of Functional Monomers. 13.
Anionic Living Polymerization of *tert*-Butyl 4-Vinylbenzoate
T. Ishizone, A. Hirao, S. Nakahama
Macromolecules **22**, 2895-2901 (1989)

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1) Protection and Polymerization of Functional Monomers. 16.
Anionic Living Polymerization of 4-[(Trimethylsilyl)ethynyl]styrene
T. Ishizone, A. Hirao, S. Nakahama, T. Kakuchi, K. Yokota, K. Tsuda
Macromolecules **24**, 5230-5231 (1991)

2) Protection and Polymerization of Functional Monomers. 19.
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Anionic Living Polymerization of (Trimethylsilyl)ethynylstyrenes
K. Tsuda, T. Ishizone, A. Hirao, S. Nakahama, T. Kakuchi, K. Yokota
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Chapter 5

Anionic Polymerization of Monomers Containing Functional Groups. 4.
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Chapter 6

1) Anionic Polymerization of Monomers Containing Functional Groups. 2.
Anionic Living Polymerization of 4-Cyanostyrene
T. Ishizone, A. Hirao, S. Nakahama
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2) Anionic Polymerization of Monomers Containing Functional Groups. 5.
Anionic Polymerizations of 2-, 3-, and 4-Cyanostyrene
T. Ishizone, K. Sugiyama, A. Hirao, S. Nakahama
Macromolecules **26**, 3009-3018 (1993)

Chapter 7

Anionic Polymerization of Monomers Containing Functional Groups. 6.
Anionic Block Copolymerization of Styrene Derivatives
para-Substituted with Electron-withdrawing Groups
T. Ishizone, A. Hirao, S. Nakahama
Macromolecules **26**, 6964-6975 (1993).

Other Publications (Not included in this thesis)

1) Protection and Polymerization of Functional Monomers. 15. Anionic Living Polymerizations of 2-(3-Vinylphenyl)-1,3-dioxolane and Related Monomers
T. Ishizone, R. Kato, Y. Ishino, A. Hirao, S. Nakahama
Macromolecules **24**, 1449-1454 (1991)

2) Synthesis of Polymers with Carboxy End Groups by Reaction of Polystyryl Anions with 4-Bromo-1,1,1-trimethoxybutane
A. Hirao, H. Nagahama, T. Ishizone, S. Nakahama
Macromolecules **26**, 2145-2150 (1993)

3) Anionic Polymerization of Monomers Containing Functional Groups. 7. Anionic Polymerizations of *N*-Alkyl-4-vinylbenzylideneamines
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Macromolecules **26**, 6976-6984 (1993).

4) Synthesis of Polystyrene Having an Aminoxy Terminal by the Reaction of Living Polystyrene with an Oxoaminium Salt and with the Corresponding Nitroxyl Radical
E. Yoshida, T. Ishizone, A. Hirao, S. Nakahama, T. Takata, T. Endo
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Review

Anionic Living Polymerization: Recent Progress
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Kaigai Koubunshi Kenkyu **38**, 18-19 (1992)