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Thesis

Studies on Highly Birefringent Liquid Crystals

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Chapter 1 Introduction

1.1 General introduction

Liquid crystals which exhibit high birefringence (Δn) are useful components of liquid crystal mixtures. They are employed in high response super twisted nematic (STN) with a narrow cell gap as Δn moderators as well as in conventional STN. The setting value of Δn is around 0.15～0.18 so that liquid crystals with medium Δn of about 0.2 must be contained in such mixtures. Recently, the remarkable development of multimedia technology has created a strong demand for high performance mobile displays. High Δn liquid crystals are attractive materials for bright reflective displays including PDLCDs[1][2], cholesterics[3], holographic switching devices[4] and directional reflectors[5][6]. High Δn enhances the light scattering efficiency, which improve the brightness of PDLCDs or holographic PDLCDs. Concerning cholesteric LCDs and directional reflectors, the reflection bandwidth is proportional to the liquid crystal birefringence. Then high Δn produces the wideband reflection or decreases the thickness of the devices. Besides display applications, these materials are thought to be applicable to laser beam steering[7] and infrared spatial modulators[8].

This research was performed for the purpose of developing practical high Δn liquid crystals. Δn of liquid crystals have been studied extensively. Before starting on a molecular design of high Δn liquid crystals, we should review the relationship between molecular properties and macroscopic optical anisotropy.

The nematic phase behaves as optically uniaxial media and the optic axis is parallel to the director. Generally, in uniaxial materials there are two principal refractive indices.

The refractive index of the ordinary ray (n_o) is measured for light waves the electric vector of which vibrates perpendicularly to the optical axis. The refractive index of the extraordinary ray (n_e) corresponds to light waves where the electric vector is parallel to the optic axis. The birefringence (n_e-n_o) of liquid crystals is the result of parallel alignment of elongated molecules, which possess an anisotropy of polarizability. It is plausible that the magnitude of the birefringence is determined by the polarizability anisotropy of the molecules and by the molecular orientational order described by the order parameter S.
If the principal refractive indices n_e and n_o are correlated with the molecular polarizability anisotropy $\alpha_l - \alpha_t$ (α_l; longitudinal polarizability, α_t;transversal polarizability), it must be taken into consideration that the local field which acts on the molecules within the condensed phase differs from the applied external field. There are different theoretical approximations to describe this local field in nematic liquid crystals.

For the purpose with a merely qualitative interpretation of the experimental result, it is sufficient to use the equations of Vuks [9]. Although an isotropic local field is assumed, these equations are often applied in optical studies of liquid crystals:

$$\frac{(n_e^2-1)}{\bar{n}^2+2} = \frac{\rho N_A \alpha_{\parallel}}{3M\varepsilon_0} \qquad (1)$$

$$\frac{(n_o^2-1)}{\bar{n}^2+2} = \frac{\rho N_A \alpha_{\perp}}{3M\varepsilon_0} \qquad (2)$$

where $\rho$is density; M is molar mass, N_A is Avogadro number, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are average polarizabilities of liquid crystals parallel and perpendicular to the optic axis, respectively.

They can be expressed by the longitudinal ($\alpha_{\parallel}$) and transversal ($\alpha_{\perp}$) of the molecules

$$\bar{\alpha}_{\parallel} = \bar{\alpha} + \frac{2}{3}(\alpha_l - \alpha_t)S \qquad (3)$$

$$\bar{\alpha}_{\perp} = \bar{\alpha} - \frac{1}{3}(\alpha_l - \alpha_t)S \qquad (4)$$

where S is the order parameter and $\bar{\alpha}$ is the average polarizability $\bar{\alpha}$=1/3 (α_1 + 2 α_t). By setting S=0 in Eq. (3) or Eq (4) and substituted them into Eq(1) or Eq(2), respectively, an expression which correlates the refractive index n_i of the isotropic liquid with the average polarizability $\bar{\alpha}$;

$$\frac{(n_i^2 - 1)}{(\bar{n}^2 + 2)} = \frac{\rho N_A \bar{\alpha}}{3M\varepsilon_0} \qquad (5)$$

Using Eqs.(1)-(4) we also obtain

$$\frac{(n_e^2 - n_o^2)}{(\bar{n}^2 + 2)} = \frac{\rho N_A (\alpha_l - \alpha_t)S}{3M\varepsilon_0} \qquad (6)$$

These equations will be used to interpret the experimental results.

As can be seen from Eq.(6), Δn of nematic is governed by molecular polarizability, number density and order parameter. For increasing anisotropy of polarizability, π-conjugated core structures have been employed. [10]. A considerable number of π-conjugated compounds have been developed as high Δn liquid crystals[11]-[14]. Tolane is one of the most common core structures for high Δn liquid crystal compounds and it is used as a component of practical liquid crystal mixtures. Δn of

these compounds are about 0.2 ~0.25 which are high enough as components for STN liquid crystal mixtures designed with Δ n of around 0.15. For the use of PDLC or optical devices as reflectors, higher Δ n materials are needed. Diphenyl-diacetilene, modified tolane and phenylacetylene compounds were reported as very high Δn liquid crystals[15]-[19]. Their Δn are around 0.4 which is larger than conventional tolanes. However, compounds with high Δn are generally thought to have problems such as high melting points, poor solubility with other liquid crystal mixtures and insufficient photostability. Fused rings were incorporated into the core part in an attempt to obtain higher values of Δ n. 2,6-Disubstituted naphthyl-ethynyl moieties were synthesized and investigated [20]. They exhibited high Δn values of about 0.3, but showed a high temperature nematic phase. 2,6-Naphthynyl-2,5-pyridinyl ethynes exhibited similar properties. Terminal groups which could contribute towards a high values of Δn were also investigated. 2,6-Disubstitued naphthyl homologues containing a terminal cyano-substituent have high Δn values of over 0.4 [21]. Isothiocyanato-substituted biphenyls were synthesized and the terminal group was shown to give a higher Δ n than a cyano group [22]. Unfortunately, compounds containing these moieties exhibited high melting points and low solubilities.

On the basis of such past studies, we developed colorless high Δn liquid crystals with practical nematic temperature and stability. In the following section, our strategy of molecular design and preliminary study of high Δ n liquid crystals are explained.

1.2 Preliminary study of high birefringence liquid crystals

In the development of very high Δn liquid crystals, not only the achievement of high Δn but also practical properties such as liquid crystal temperature, solubility and durability are important.

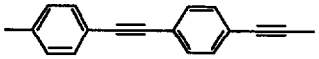
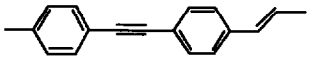
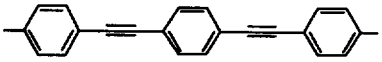
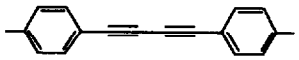
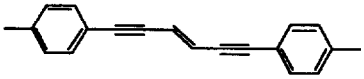
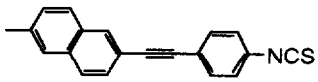
To decide the starting compound of this study, we will look back at high Δn liquid crystals reported before [11-13,23-25]and the interpretation of birefringence [22]. The representative high Δn liquid crystals reported before are shown in TABLE1-1.

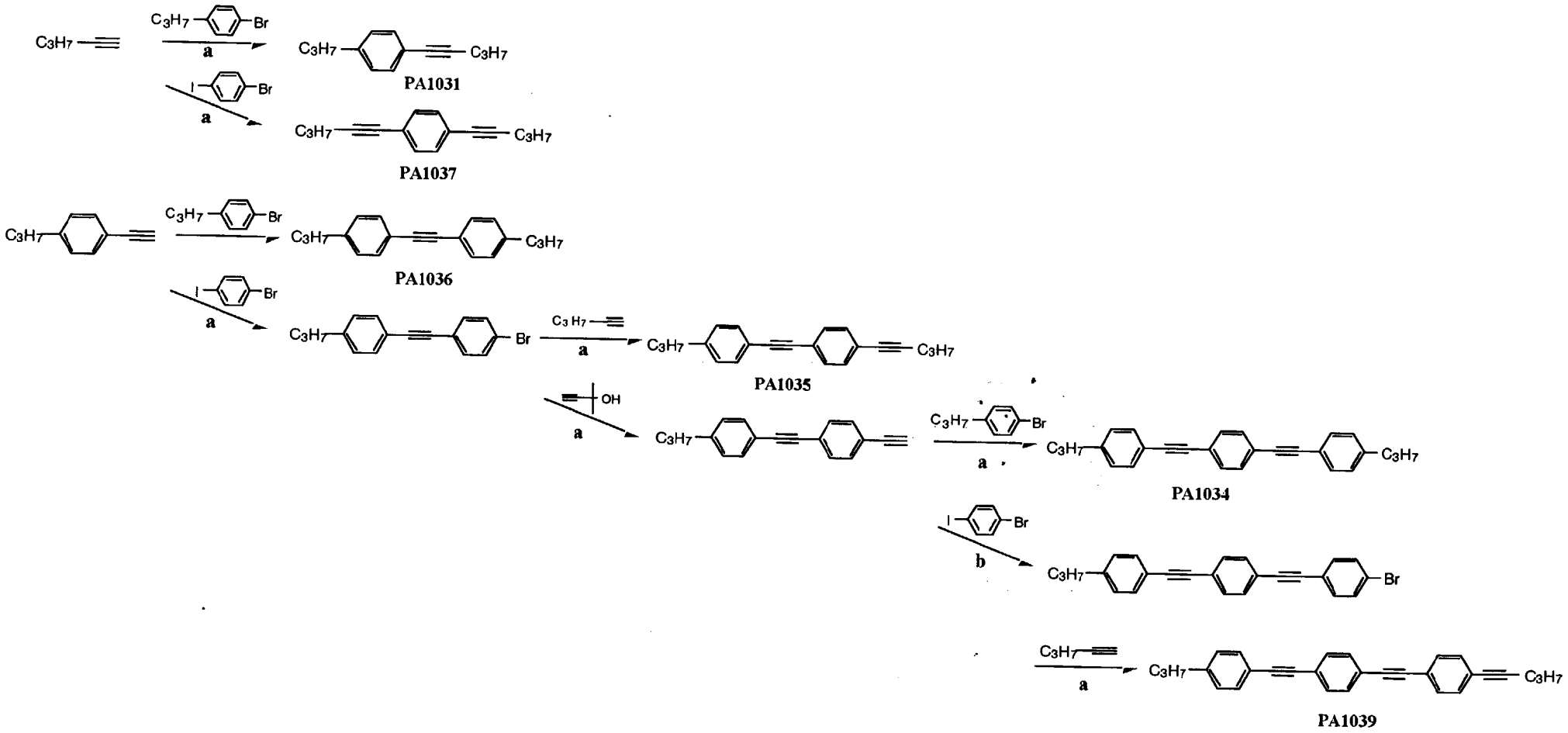
The composition unit for high Δn, phenyl ring and acetylene unit, is considered to be important. A phenyl ring is the most basic part of all liquid crystal molecules for producing mesophases. On the other hand, acetylene group contributes to increase the anisotropy of polarizability effectively because the polarizability along to the axis perpendicular to molecular long axis is almost zero. For these reasons, we selected phenylacetylene unit as a high Δn molecular part. In order to investigate the starting core structure of high Δn liquid crystals, we synthesized and evaluated the basic properties of phenylacetylene homologues which had different lengths of this unit.

1.2.1 Synthesis

The synthesis routes of phenylacetylene derivatives are shown in SCHEME 1-1. The compounds investigated here were synthesized by coupling of bromide intermediates and ethynyl intermediates. The structures of final compounds and various synthetic intermediates were characterized by ^{1}H-NMR spectroscopy. All spectra were recorded in $CDCl_3$ with TMS as internal standard. They exhibited ^{1}H NMR spectra (UNITY300, Varian 300 MHz) which are in accordance with their structures. Mass spectra (SX102, JEOL) were also measured

TABLE 1-1 Examples of high Δn liquid rystals

Core structures	References
	H.Takatsu et al, Mol. Cryst. Liq. Cryst.,141,279(1986)
	JP89-879,Chisso Corp.
	JP94-245992,Sumitomo Chemical Co.,LTD
	JP88-133577,Chisso Corp.
	Wu,S.T. et al ,J.Appl.Phys.,65.4372(1989)
	Y. Goto, T. Inukai, A. Fujita and D. Demus, Mol.Cryst. Liq. Cryst., 260, 23(1995)
	A.J. Seed et al ,J. Mater. Chem., 10, 2069(2000)



SCHEM 1-1

a $CuI/PdCl_2(PPh_3)_2$/triethylamine, **b** $CuI/PdCl_2(PPh_3)_2$/DMF

and they coincided with their predicted molecular weight. All compounds of these series were more than 99 percent pure according to HPLC(ODS A-212 column,Sumika Chemical Analysis Service).

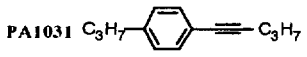
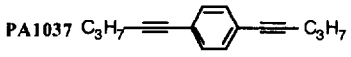
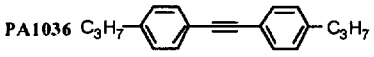
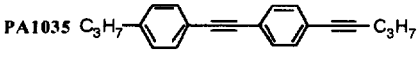
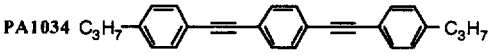
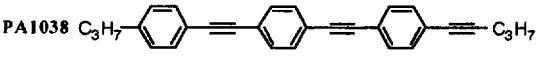
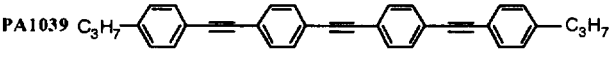
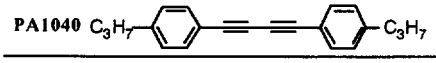
1.2.2 Influences of core structures on physical properties

The phase sequences and transition temperatures of phenylacetylene homologues are shown in TABLE 1-2. The melting points of these compounds and nematic tendencies increased with the increase in the number of phenylacetylene unit. 1 and 2-ring compounds did not exhibit liquid crystal phases, but 3-ring compounds showed enantiotropic liquid crystal phases. Δn also increased with the increase of the unit number as expected. Diacetylene types showed higher melting points and larger Δn compared with phenylacetylene types in which the number of phenyl rings and etynyl groups are the same. 3-Ring compounds exhibited broad nematic phase and large Δn. Δn's of these compounds were larger than that of conventional tolane (**PA1036**) because of extension of π-conjugation by introducing ethynyl or ethenyl group.

We calculated polarizabilities of compounds, which were investigated here by MOPAC93 (AM1 method). $\Delta\alpha$ was defined as follows. $n_{\parallel}^2-n_{\perp}^2$ and calculated $\Delta\alpha$ were plotted in FIGURE 1-1. The birefringence was almost proportional to $\Delta\alpha$, but the plots showed some scatter. In the case of 1-ring compounds, Δn values were lower than that of 2-ring compounds which have almost the same $\Delta\alpha$ values. It is considered that 1-ring compounds have lower order parameters compared with 2-ring compounds therefore $n_{\parallel}^2-n_{\perp}^2$ were reduced.

Concerning the effect of lateral fluorinated

TABLE 1-2 Phase sequences, transition temperatures and birefringence

Compounds	Phase sequences /°C	Δn [1)]
PA1031 	(-50<) I	0.000
PA1037 	K · 47 · I	0.115
PA1036 	K · 73 · I	0.264
PA1035 	K · 99 · I	0.351
PA1034 	K · 170 · Sx · 178 · N · 245 · I	0.496 [2)]
PA1038 	K · 194 · N · 265 · I	- [3)]
PA1039 	K · 230 · Sx · 246 · N · 310 · I	- [3)]
PA1040 	K · 108 · N · 133 · I	0.410

1)Extrapolated values from liquid crystal (10wt%) mixed in nematic host MJ931381 (at 20 °C and 589 nm)
2)Extrapolated values from liquid crystal (5wt%) mixed in nematic host MJ931381
3)Insoluble in MJ931381

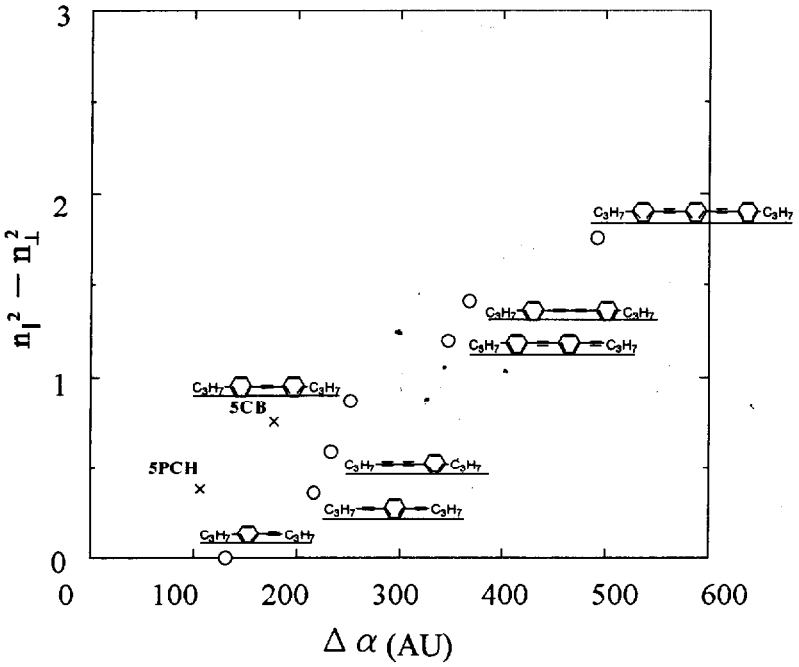
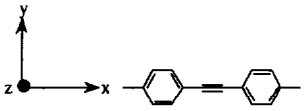


FIGURE 1-1 Plots of refractie index vs anisotropy of polarizability

The polarizability was calculated by MOPAC93

$$\Delta\alpha = \alpha_x - \frac{(\alpha y + \alpha z)}{2}$$

αx ; Polaizability along the molecular long axis
αy、αz ; Polaizability along the molecular short axis



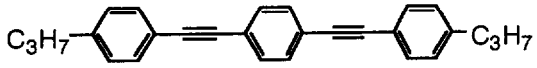
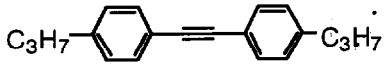
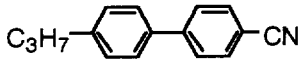
substituents on order parameters, it was confirmed that a non-substituted compound exhibited higher order parameters compared with a laterally fluorinated compound by using C-13NMR[26]. Therefore, the Δ n of substituted alkenyltolanes and alkynyltolanes were considered to posses different values of order parameters in the mixtures at 20℃ and these compounds which had almost the same $\Delta\alpha$ exhibited different values of $n_{\parallel}^2-n_{\perp}^2$.

1.2.3 Durability and UV-visible absorption spectra

High birefringence liquid crystals generally have problems of durability; especially photostability is a problem because of the red-shift of UV absorption induced by extension of conjugated length. We estimated the stabilities before deciding the target core structure of development of high Δn liquid crystals.

In the former section, the 3-ring phenylacetylene compound **PA1034** was found to be very high Δn and wide nematic phase. The photo and heat durability of **PA1034** were also estimated and compared with conventional liquid crystalline compounds. The residual rates after the tests are shown in TABLE 1-3. **PA1034** exhibited good durabilities almost same as **PA1036** which is a conventional high Δn tolane or 5CB. In comparison with UV-Visible absorption spectra, **PA1034** showed a longer absorption edge than **PA1036**, which means **PA1034** absorbs larger energy of irradiated light (see FIGURE 1-2). Because of this, 3-ring phenylacetylene core was thought to have excellent stability. **PA1039**, which has more phenylacetylene units than **PA1034**, exhibited longer absorption edge. However, **PA1039** with 4 phenyl rings and 3 acetylene groups was still colorless. From a practical point of view, the phenylacetylene series was thought to be

TABLE 1-3 Stabilties of the 3-ring phenylacethylene liquid crystal

Compounds		Residual rate (%) 1*	2**
PA1034		100	92.4
PA1036		99.2	99.6
3CB		100	99.4

*; After the irradiation test
**; After the heat test

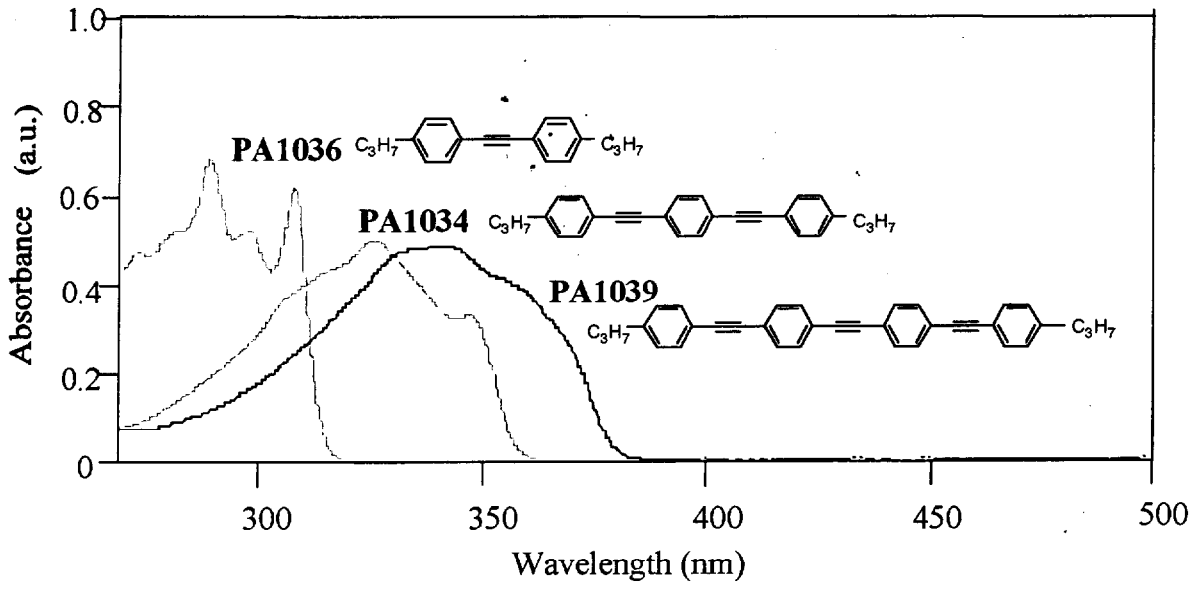


FIGURE 1-2 UV-VIS absorption spectra of phenylacetylene compounds

worth investigating for high Δn liquid crystals.

1.3 Contents of this thesis

As the results of the preliminary study, we believed that 3-ring phenylacethylene is highly worth further investigating high Δn liquid crystals. In chapter 2, the full-scale investigation of 3-ring phenylacethylenes is explained. A variety of the homologues were synthesized and their properties were evaluated to find out effects of positions of substituents, terminal groups and substituted groups on the thermal, the optical and other physical properties. Other phenylacethylene homologues containing heterocyclic rings were also investigated to obtain higher Δn liquid crystals than 3-ring phenylacethylenes. A molecular design of colorless high Δn liquid crystals and new compounds based on this design are shown in chapter 4. The origin of the high birefringence is also discussed.

Liquid crystals which are used for practical purposes are generally composed of more than ten compounds. This enables them to adjust a lot of properties to their specification. Therefore, various kinds of liquid crystalline compounds are needed for preparing liquid crystal mixtures with controlled physical properties. We have also developed new core substituted phenylacetylene homologues with a cycrohexyl group. It is known that cyclohexyl or cyclohexylethyl groups might have the effect of lowering or widening nematic range. Therefore these types of compounds are commonly used as components of practical liquid crystal mixtures. We reported the synthesis and physical properties of new phenylacetylene derivatives with cyclohexyl and cyclohexylethyl groups in chapter 4.

For extending the application of high Δn liquid crystals, a photopolymerizable function was introduced to these materials. Liquid crystal monomers, which have one polymerizable group,

have been well studied because pendant type polymers function as switching devices and optical standing films. Recently liquid crystal monomers, which had two polymerizable groups, have been investigated. These types of polymers, whose nematic orientations were frozen by photopolymerization, were called in-situ photopolymerized polymers [27-31]. They are more advantageous for static uses, such as optical films. 3-Ring phenylbenzoate monomers with one or two polymerizable groups and their polymers have already been studied systematically. In those studies the relationship between the optical properties of monomers and those of polymers was complicated. We applied the high Δn core structures which were obtained while investigating low weight molecular types to the photopolymerizable liquid crystal monomers with diacrylate groups. In chapter 5, we report the evaluation of physical properties of new photopolymerizable 3-ring phenylacethylene diacrylate monomers and their polymer networks.

References of Chap. 1

[1] J. L. Fergason, 1986, SID Digest '86, 68

[2] J. W. Doane, N. A. Vaz, B. G. Wu, and S. Zumer, 1986, Appl. Phys. Lett.,**48**,269

[3] J.Li, C.Hoke, D. S.Fredly and P. J. Bos, 1996, SID'96 DIGEST, 265

[4] R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia and T. J. Bunning, Chem. Mater., 1993, **5**, 1533

[5] C. C. Bowley, H. Yuan and G.P. Crawford, Mol. Cryst. Liq. Cryst.,1999, **331**, 209

[6] T. Tokumaru, K Iwauchi, Y. Higashigaki and M. Matsuura, 1999, Proc. of Anglo-Japanese Seminar on liquid Crystals'99,72

[7] P. F. Mcmanamon, E. A. Watson, T. A. Dorschner and L. J. Barnes, 1993, Opt. Eng., **32**,2657

[8] S. T. Wu, U. Efron, J. Grinberg and L. D. Hess, 1985, SID Tech. Dig., **16**,262

[9] M.F.Vucks, Opt. & Spectroscopy, 1966,20,361

[10] S. T. Wu, 1995, Mol. Cryst. Liq. Cryst.**261**,79

[11] H. Takatsu, K. Takeuchi, Y. Tanaka and M. Sasaki, 1986, Mol. Cryst. Liq. Cryst., **141**, 279

[12] S. T. Wu, U. Finkenzeller and V. Reiffenrath, 1989, J.Appl.Phys., 65, 4372

[13] Y. Goto, T. Inukai, A. Fujita and D. Demus, 1995, Mol.Cryst. Liq. Cryst., **260**, 23

[14] JP96-47950,1996, Chisso Corp

[15] M.D.Wand, R.Vohra and S.Monahan, 1993, Liq. Cryst., **15**, 2, 269

[16] A.Fujita,A.Matsui,K.Miyazawa,Y.Goto,E.Nakagawa and D.Demus, 1994, 20th Liquid Crystal Conference of Japan, 2G 406

[17] M.J.Goulding, S.Greenfield, D.Coates and R.Clemitson, 1993, Liq. Cryst., **14**, 5, 1397

[18] S.T.Wu, J.D.Margerum, M.S.Ho, M.Fung, C.S.Hsu, S.M..Chen

and K.T.Tsai, 1995, Mol.Cryst.Liq. Cryst., **261**, 79

[19] S.T.Wu, C.S.Hsu, and K.F.Shyu, 1999, Applied Physics Letters, **74**, 3, 344

[20] M. Hird, K. J. Toyne and G. W. Gray, 1993, Liq. Cryst. **14**, 3, 741

[21] M. Hird, K. J. Toyne, G. W. Gray, S. E. Day and D. G. McDonnel, 1993, Liq. Cryst., **15**, 2, 123

[22] M. Hird, A. J. Seed, K. J. Toyne, J. W. Goodby, W. Gray and D. G. McDonnel, 1993, J.Mater. Chem., **3**,8,851

[23] JP89-879,1989, Chisso Corp.

[24] JP94-245992,1994.Sumitomo Chemical Co.,LTD

[25] JP88-133577,1988, Chisso Corp.

[26] M.L.Manuson, B.M.Fung and M.Schadt, 1995, Liq. Crysta.,19,3,333

[27] D. J. Broer, H. Finkelmann and K. Kondo, 1988, Makromol. Chem.,**189**,185

[28] D. J. Broer, G. N. Mol and G. Challa, 1989, Makromol. Chem.,**190**,19

[29] D. J. Broer, J. Boven, G. N. Mol and G. Challa, 1989, Makromol. Chem.,**190**,2255

[30] D. J. Broer, R. A. M.Hikmet and G. Challa, 1989, Makromol. Chem.,**190**,3201

[31] D. J. Broer, G. N. Mol and G. Challa, 1990, Makromol. Chem.,**192**,59

Chapter 2 Development of high Δn liquid crystals with wide nematic range and high miscibility
- 3-ring phenylacetylene liquid crystals-

2.1 Introduction

In Chapter 1, we focused on the 3-ring phenylacethylene (**3PA**) core as a starting structure of research and development of practical high Δn liquid crystals. **PA1034**, which is 3-ring phenylacethylene compound containing n-propyl terminal chains, exhibited very high temperature nematic phase around 200℃. The relationship between chemical constitutions and mesophase behaviors was well studied and modifications of molecular design toward lowering the temperature range of liquid crystal phase have been proposed. From the theory about the effect of length-to breadth ratios of molecules on this property [1], introducing lateral substituents are often adopted to decrease the melting and clearing points.

In order to understand the mesophase behavior of mesogens with lateral alkyl substituents, a lot of liquid crystalline compounds containing a lateral group were synthesized and evaluated. A homologue of 2-substituted 1,4-phenylene bis (benzoates) is one of the most well-studied series. In this series the alkyl group lowered nematic temperature. The clearing point decreased as the length of alkyl chain became longer, but the melting point decreased and increased alternately with increasing the alkyl chain length in the region of long chain.

A fluoro group is also one of the most useful lateral substituent for special features as electron-attraction which may give compounds of high dielectric anisotropy, a depression of melting point and so on [2].

This chapter focused on the modification of the **3PA**

homologues for the purpose of lowering nematic phase. Firstly, the effect of some substituents in the terminal ring were investigated. Secondly, the influence of substituted position of a methyl group, which was the most effective substituent for the improvement of the properties in the former investigation, was examined. Lastly, **3PA**s with different types of substituents in the best position were synthesized and the effects on the physical properties were investigated.

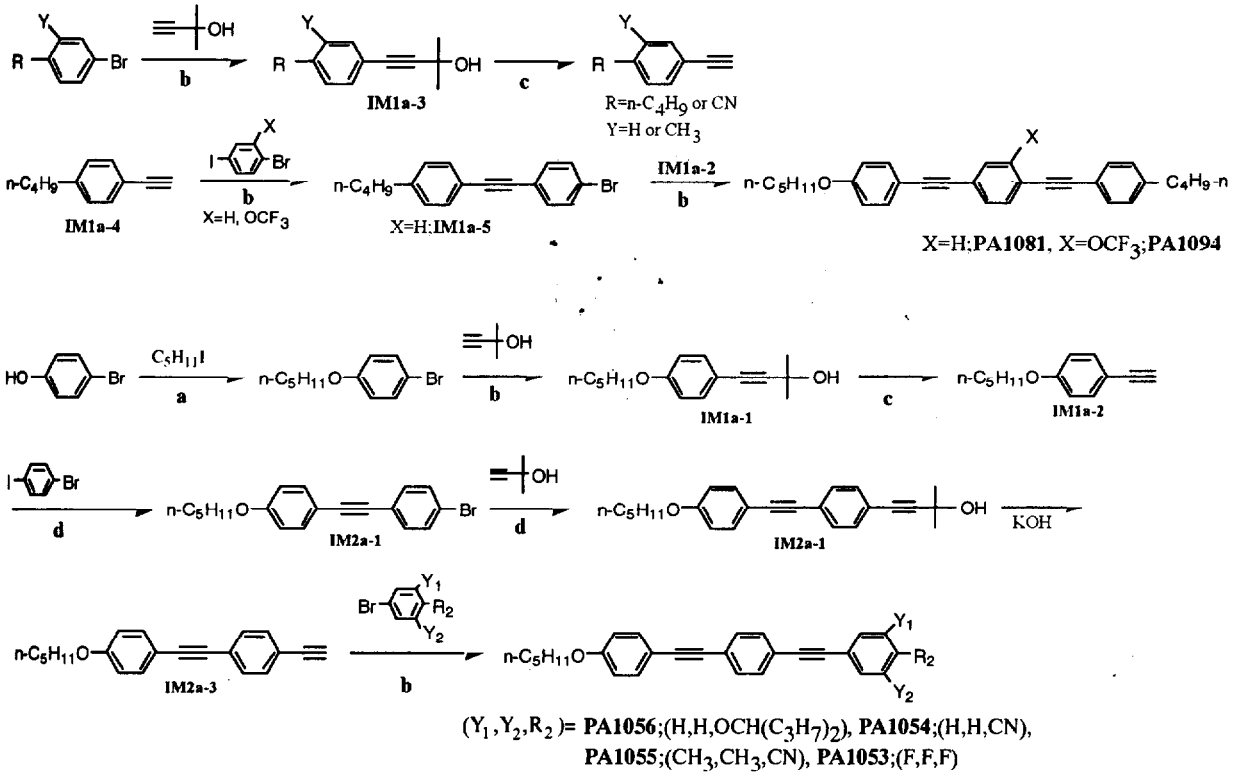
2.2.Experimental

2.2.1 Synthesis

The preparative routes for the **3PA** homologues including some intermediates are shown in SCHEM 2-1 ~ SCHEME 2-3. The structures of the final compounds and various synthetic intermediates were characterized by ^{1}H-NMR spectroscopy; all spectra were recorded in $CDCl_3$ with TMS as internal standard. All ^{1}H NMR spectra (UNITY300, Varian 300 MHz) were in accordance with the proposed structures. Mass spectra (SX102, JEOL) were also measured and identified the predicted molecular weights. The purity of each compound was verified by HPLC analysis (ODS A-212 column, Sumika Chemical Analysis Service) and the purity of all compounds were confirmed to be as high as 99 % except for **PA1121** (94.6 %) and **PA1123** (98.3 %).

2.2.2 Measurement of physical properties

Transition temperatures and phase sequences were measured using a Mettler FP82 hotstage and control unit in conjunction with an optical microscope (OPTIPHOT2-POL, Nikon) and these were confirmed using differential scanning calorimetry (DSC-200, Seiko Instruments Inc.). Refractive indices were evaluated as extrapolated values from mixtures containing a 10wt% solution of each test compound in MJ931381 (Merck Japan).

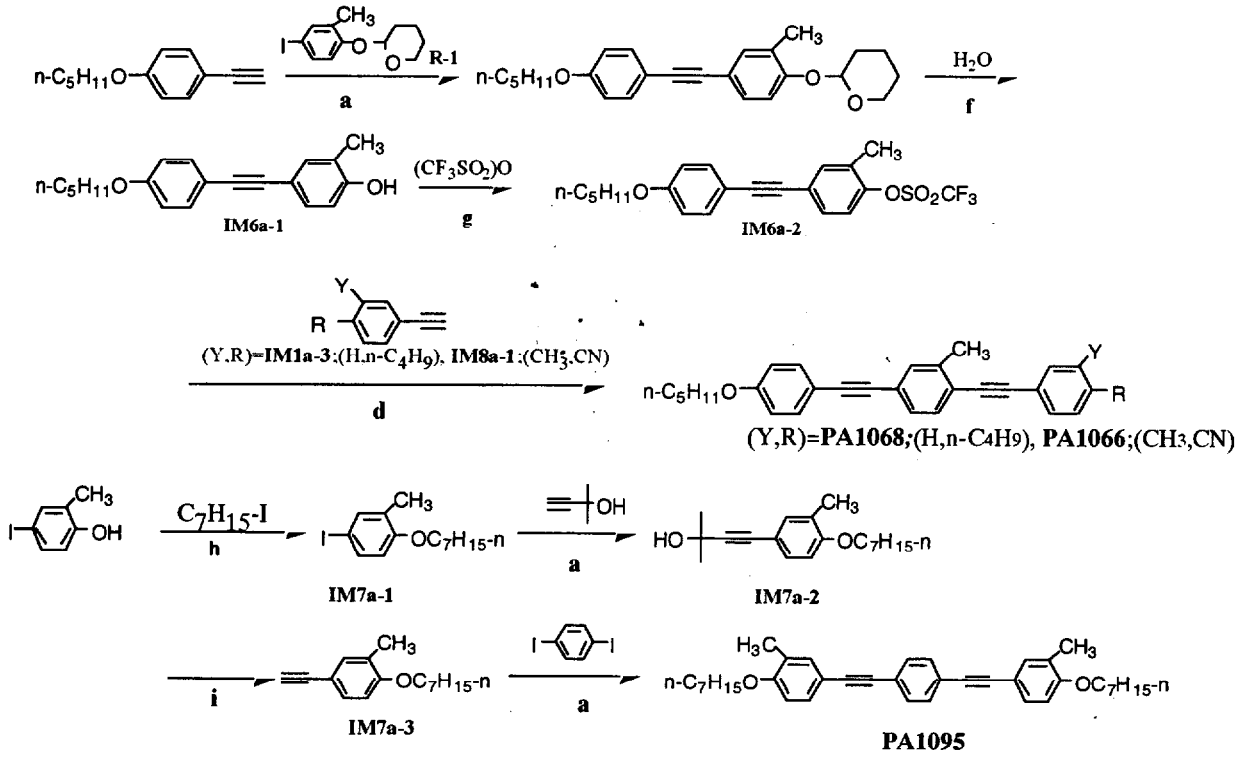


(Y_1, Y_2, R_2)= **PA1056**;(H,H,$OCH(C_3H_7)_2$), **PA1054**;(H,H,CN), **PA1055**;(CH_3,CH_3,CN), **PA1053**;(F,F,F)

SCHEME 2-1

a K_2CO_3/2-butanone **b** $PdCl_2(PPh_3)_2$/PPh_3/CuI / triethylamine

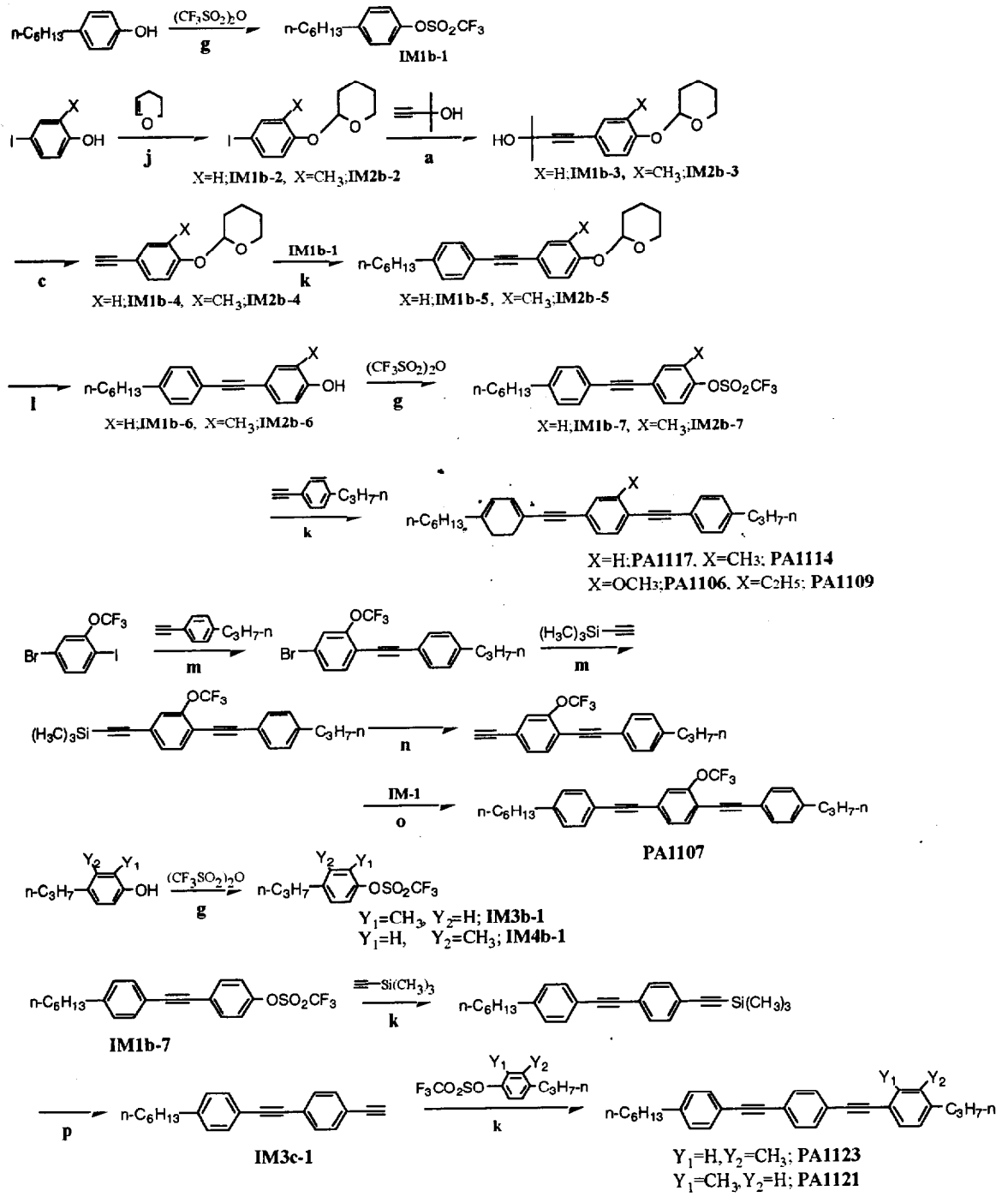
c NaOH/Toluene **d** $PdCl_2(PPh_3)_2$ / CuI / triethylamine **e** toluene / KOH



SCHEME 2-2

f *p*-toluenesulfonic acid **g** pyridine / 4-pyrrolidin-1-pyridine

h Na_2CO_3 / methylethylketone **i** NaOH / Toluene



SCHEME2-3

j *p*-toluenesulfonic acid / chroloform **k** $PdCl_2(PPh_3)_2$/ triethylamine/DMF

l *p*-toluenesulfonic acid / methanol **m** $PdCl_2(PPh_3)_2$ / PPh_3 / CuI / triethylamine

n methanol/KOH **o** $PdCl_2(PPh_3)_2$/ triethylamine **p** Na_2CO_3 / ethylacetate / ethanol

An Abbe refractometer (2T, ATAGO) with a sodium lamp (589 nm) was used to measure the refractive indices of the mixtures at 20 ℃. The birefringence of single compounds was also measured by hollow prism method [3]. The setup for the measurement is shown in FIGURE 2-1. A temperature controlled parallel aligned wedge cell, which was set on a rotational stage equipped with a stepping motor (D80, Suruga Seiki) and encoder system (resolution; 1 arcsec, K1 and CR-16, Canon), was used for the measurement. Each reflection angle of the incident He-Ne laser (λ = 633 nm) light, polarized perpendicular and parallel to the rubbing direction was measured for the calculation of n_o and n_e.

Order parameters were estimated by measuring polarized IR absorption spectra (FTIR, Magna860, Nicolet). 10 μm thick homogeneously aligned cells were prepared for this measurement; the substrates were CaF_2 plates coated with polyimide (LX-1800, Hitachi Chemicals) and rubbed in one direction. Order parameters were calculated from the dichroic ratio [4] of the acetylene C≡C stretching absorption peaks at around 2220cm^{-1}, according to the equation S=(D-1)/(D+2), where D is a dichroic ratio, S is an order parameter.

The viscosity was also estimated as extrapolated values from the same mixtures used for the Δn evaluation using a microviscometer (AMV-200, DMA48 for the measurement of density, Anton Parr KG) at 20 ℃. The stabilities were estimated by the same method explained in Chap.1.

2.3 Terminal substituted series

2.3.1 Mesogenic properties

Phase sequences, transition temperatures and associated enthalpies for compounds **PA1081** ~ **PA1053** are listed in TABLE 2-1. Compound **PA1081**, which has linear terminal alkoxy and

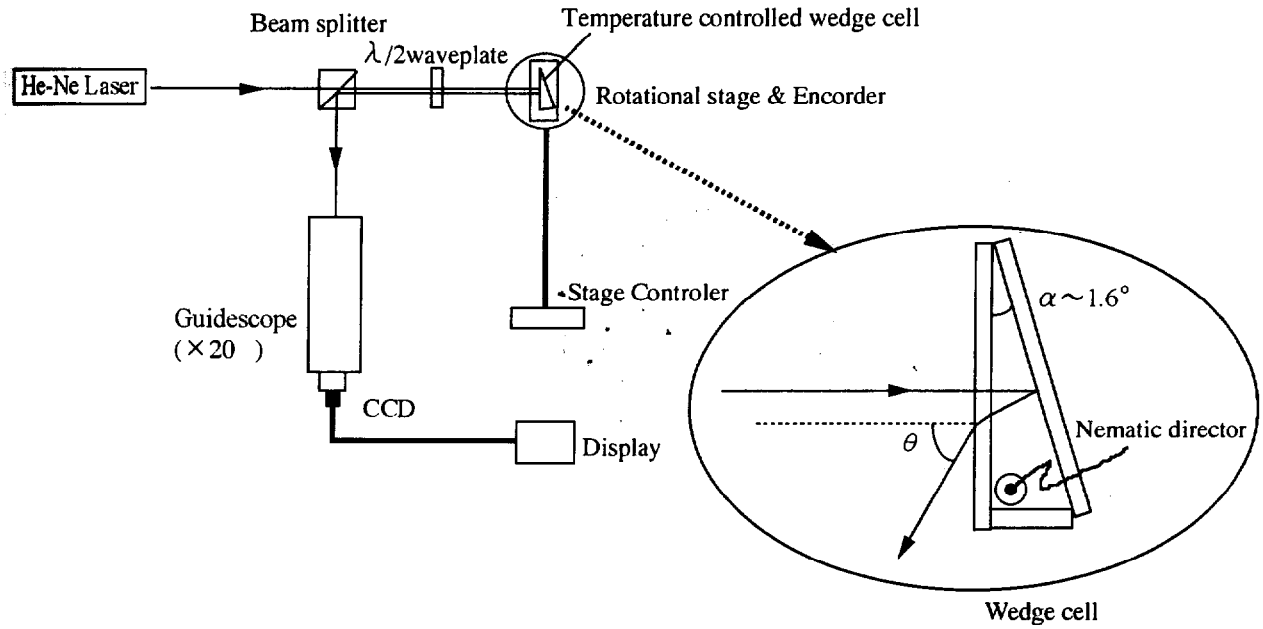
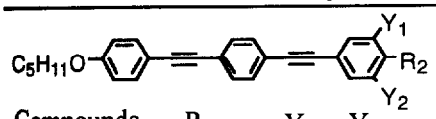


FIGURE 2-1 Optical setup for refractive index measurement

TABLE 2-1 Transition temperatures and enthalpies for the 3PA homologues.



Compounds	R_2	Y_1	Y_2	Transition temperatures (°C) and enthalpies(in square brackets[], kJ/mol) K	S_X	S_A	N	I
PA1081	C_4H_9	H	H	·	·	162[19.4]	· 234 [1.4]	·
PA1056	$OCH(C_3H_7)_2$	H	H	· 143[32.5] (	· 119[16.3])			·
PA1054	CN	H	H	.		199 [18.8]	· 297 [1.5]	·
PA1055	CN	CH_3	CH_3	.		149[37.6]	· 160 [0.5]	·
PA1053	F	F	F	· 129 [18.8] (	· 101[3.3])	· 168[2.4]	· 179[0.54]	·

Pharenthese () denote a monotropic transition.
K: crystal, Sx; unassigned smectic phase, SA; smectic A phase, N; nematic phase, I; isotropic

a midpoint of 200 ℃. In order to reduce this temperature, the core part or/and terminal chains of the compounds were modified. The introduction of a branched terminal alkoxy chain (**PA1056**) or fluorine substituents (**PA1053**) was effective in lowering the liquid crystal temperatures. Terminal CN group increased T_{NI} and melting point in comparison of **PA1054** and **PA1081**. However these properties of **PA1055** with lateral methyl groups were far lower than those of **PA1054**. In comparison these compounds, lateral methyl and fluorine substituents particularly decreased the clearing (T_{NI}) and melting points effectively. Similar effects of lateral fluoro and alkyl substituents have been reported [5], suggesting that these groups are capable of disrupting the intermolecular crystalline packing as well as increasing the breadth of the molecules. The transition enthalpies associated with the nematic-isotropic transitions were smaller than those seen for compounds without lateral substituents, indicating a lower degree of interaction between the molecules in the mesophases.

The effects of these modifications on the phase sequences differed. Compound **PA1056**, containing a branched alkoxy group, did not exhibit nematic phase while fluoro substitution (**PA1053**) induced smectic behaviour in addition to the nematic phase. The incorporation of lateral methyl groups (**PA1055**) did not change the phase sequence.

2.3.2 Physical properties

The optical properties, the calculated anisotropic polarizabilities ($\Delta\alpha$) and the viscosities are listed in TABLE 2-2. Most of the compounds exhibited high Δn values of over 0.4. The compounds containing nitrile groups showed very high Δn values of 0.5-0.6. Fluoro substituents, branched alkoxy chains and methyl groups decreased Δn compared with that of the analogous non-laterally substituted compound even though

TABLE 2-2 Optical property and viscosity the **3PA** homologs

Compounds	no[1)]	ne[1)]	Δn[1)]	α[2)] [A.U.]	$\Delta\alpha$[3)] [A.U.]	η[1)] [mPa · s]
PA1081	1.519	1.966	0.448	359	525	-
PA1056	1.532	1.888	0.356	397	562	-
PA1054	1.513	2.114	0.601	342	558	-
PA1055	1.542	2.012	0.470	362	555	1050
PA1053	1.511	1.922	0.410	508	328	84

1) Optical properties(at 20℃ and λ=589nm) and visocosity(at 20℃) were extrapolated values of the mixture [liquid crystal(10wt %) and MJ931381 (90wt %)]
2) Average polarizability calculated by MOPAC93
3) $\Delta\alpha=\alpha x-(\alpha y+\alpha z)/2$
αx ; Polaizability along the molecular long axis
αy、αz ; Polaizability along the molecular short axis

chains and methyl groups decreased Δn compared with that of the analogous non-laterally substituted compound even though the $\Delta\alpha$ values were similar.

In order to study the effects of the substituents on the properties, the temperature dependence of Δn and order parameters of the pure compounds were measured (see FIGURE 2-2 and 2-3 respectively). The dependence of Δn on chemical structure was the same as seen for Δn estimated by extrapolation from mixtures with a host nematic.

The order parameters of the non-substituted compounds (**PA1081** and **PA1054**) were almost the same, but introducing methyl groups resulted in decreased values. The calculated value of $\Delta\alpha$ for **PA1054** was the largest of all the compounds. Substituents decreased $\Delta\alpha$ because the lateral groups increased the polarizability perpendicular to the long axis of the molecule. It is well known that Δn is determined by $\Delta\alpha$ and the order parameter, such that incorporating substituents decreases Δn because of the reduction in $\Delta\alpha$ and the order parameter. In the case of Δn estimated by extrapolation from mixtures, the lowering of T_{NI} also caused the decrease in the order parameter at the temperature at which Δn was estimated.

The viscosities of these series were slightly higher than those for the 3-ring phenylcyclohexyl compounds [6]. The effect of the substituents on the viscosity was almost the same as for conventional liquid crystals; specially lower viscosity is observed with fluoro groups and higher viscosities with nitrile substituents.

2.4 Effect of lateral substituent position of the methyl groups on physical properties

As the introduction of methyl groups was effective in lowering the nematic temperature range but with only a small

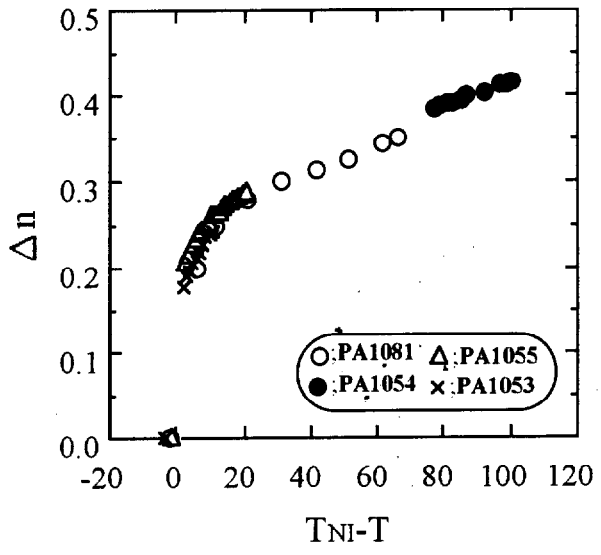


FIGURE2-2. The effect of substituent group on birefringence

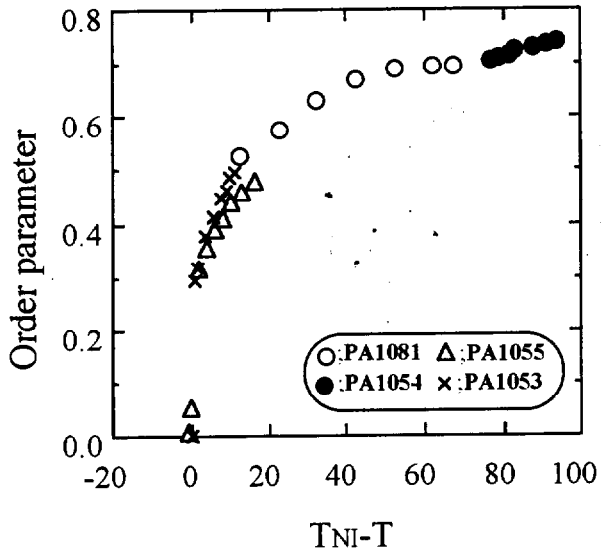


FIGURE 2-3 The effect of substituent group on order parameters

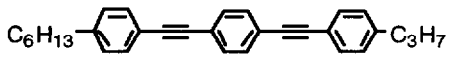
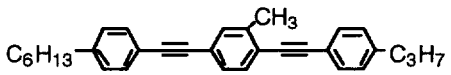
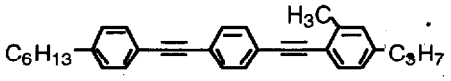
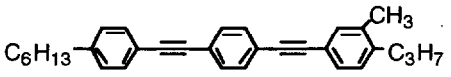
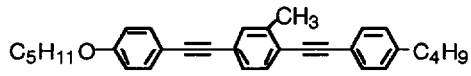
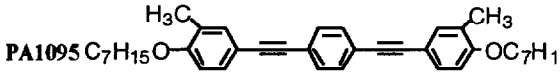
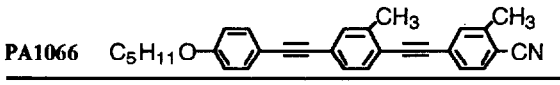
decrease in Δ n, we synthesized a variety of 3-ring phenylacetylene compounds with lateral methyl groups. The effects of the position and number of substituents on the physical properties were investigated in order to establish the optimum structual modification for these homologues.

2.4.1 Mesogenic properties

The phase sequences, transition temperatures and associated enthalpies are listed in TABLE 2-3. A comparison of the transition temperatures for **PA1117** $\sim$ **PA1123**, reveals that the most effective substitution position for lowering the nematic temperature range was the central ring. The behaviour of T_{NI} and the melting point(T_m) was different: T_m increased in the order **PA1114** (substituted center ring) < **PA1121** (substituted terminal ring) < **PA1123** (substituted terminal ring) < **PA1117** (non-substituted) , whereas T_{NI} increased in the oeder **PA1123** < **PA1114** < **PA1121** < **PA1117**. In the case of the alkyl-alkoxy compounds (**PA1068** $\sim$ **PA1066**), a similar trend was observed.

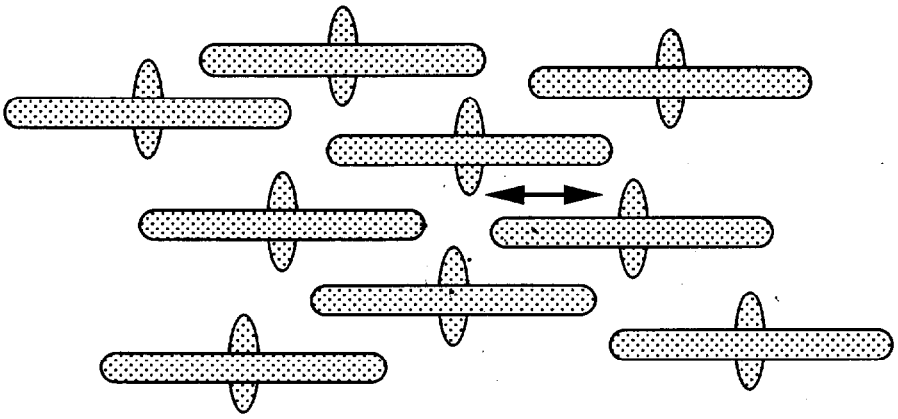
Molecular theories of the nematic phase have been extensively studied and T_{NI} is determined by some very delicate balance between repulsive and attractive forces [7]. The substitution at position A (see FIGURE 2-4) decreased the interaction area of the mesogenic cores to the greatest extent because the substituent is in the center of the core, and hence the melting point was lowest in this group. Substitution at position C retains a larger interaction area between the molecules than for substitution at position A, and therefore the melting point decreases. Substitution at position A increased the distance between molecules but the molecular shape was almost symmetrical and so they behaved like linear molecules. As a result, T_{NI} was not low compared with those

TABLE 2-3 The effects of substituted position of a methyl group on physical properties

Compounds		Transition temperatures (℃) and enthalpies(in square brackets[], kJ/mol)		
		K	N	I
PA1117		· 147[18.6]	· 209 [1.2]	·
PA1114		· 57 [14.4]	· 169 [1.3]	·
PA1121		· 67 [13.5]	· 176 [1.0]	·
PA1123		· 85 [30.9]	· 143 [0.9]	·
PA1068		· 83 [16.4]	· 201 [1.4]	·
PA1095		· 146 [54.8]	· 162 [1.8]	·
PA1066		· 106 [39.0]	· 191 [0.7]	·

K: crystal, N; nematic phase, I; isotropic

Substituted position; A type



Substituted position; C type

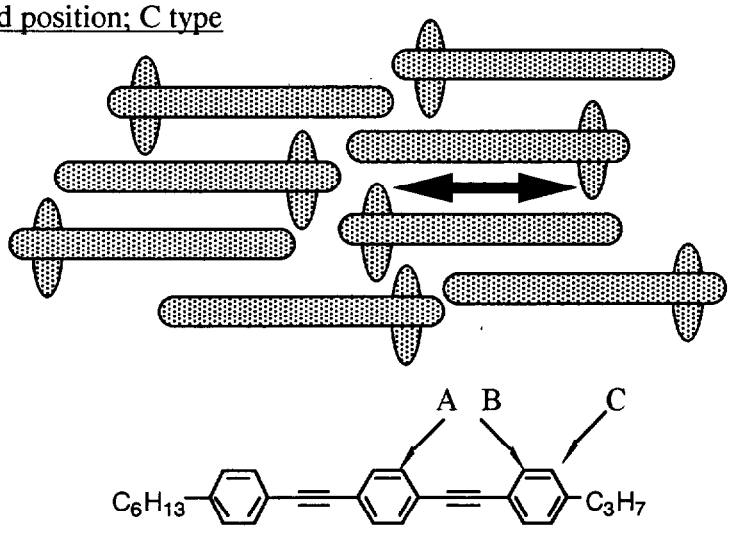


FIGURE 2-4 Schematic presentation of the core substitued 3PA compounds

for positions B and C. Substitution at position C destroyed the symmetry of molecular shape. The interaction area of the mesogenic cores was larger than for compounds substituted in positions A or B, and therefore the melting point of this compound was the highest. On the other hand, the excluded volume presumably increased because of the wedge-like molecular shape. As a result T_{NI} was lowered by the greatest amount. The large excluded volume may also result in the lowering of the order parameter.

The temperature dependence of the order parameter of **PA1117** ~ **PA1123** and **PA1068** ~ **PA1066** are shown in FIGURE 2-5. The order parameter of **PA1123** was lower than those of **PA1114** or **PA1121**, supporting the suggestion that the excluded volume effect is important. In the case of the alkoxy type (**PA1068**) and cyano substituents (**PA1066**), similar thermal properties were observed.

Compound **PA1095**, which has two methyl substituents, one in each terminal ring, exhibited almost the same values of order parameters as that of the non-substituted compound. This is not inconsistent with the excluded volume model. In the case of **PA1095**, it is considered that symmetrical substitution keeps the order parameter higher because the symmetrical molecular shape behaved as a simple rod-like molecule containing no substituent.

2.4.2 Birefringence and Viscosity

The birefringence and viscosities of these compounds are listed in TABLE 2-4; the temperature dependence of Δn, measured for the pure compounds is also shown in FIGURE 2-6. Δn for the pure compounds slightly decreased on introducing methyl groups. However, no dependence of substituent positions on Δn was observed. In the case of Δn estimated by extrapolation from the mixture with a nematic host, substituent position A

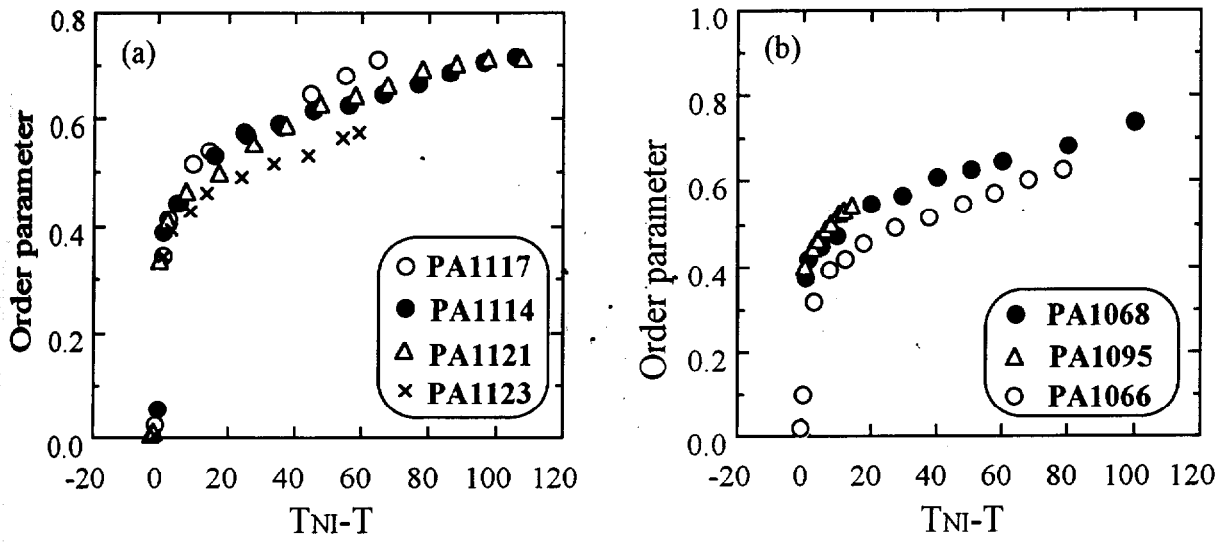


FIGURE 2-5 The effect of substituted position of methyl group on order parameters (a) alkyl type and (b) alkoxy type

TABLE2-4 Physical properties of methy substitued 3PA homologues

Compounds	no*	ne*	Δn*	η* [mPa · s]
PA1117	1.515	1.947	0.432	84
PA1114	1.524	1.944	0.419	119
PA1121	1.527	1.914	0.388	195
PA1123	1.528	1.932	0.404	104
PA1068	1.522	1.954	0.432	156
PA1095	1.514	1.876	0.362	-
PA1066	1.537	2.027	0.490	1157

*:Optical properties(at 20℃ and λ=589nm) and visocosity(at 20℃) were extrapolated values of the mixture [liquid crystal(10wt %) and MJ931381 (90wt %)]

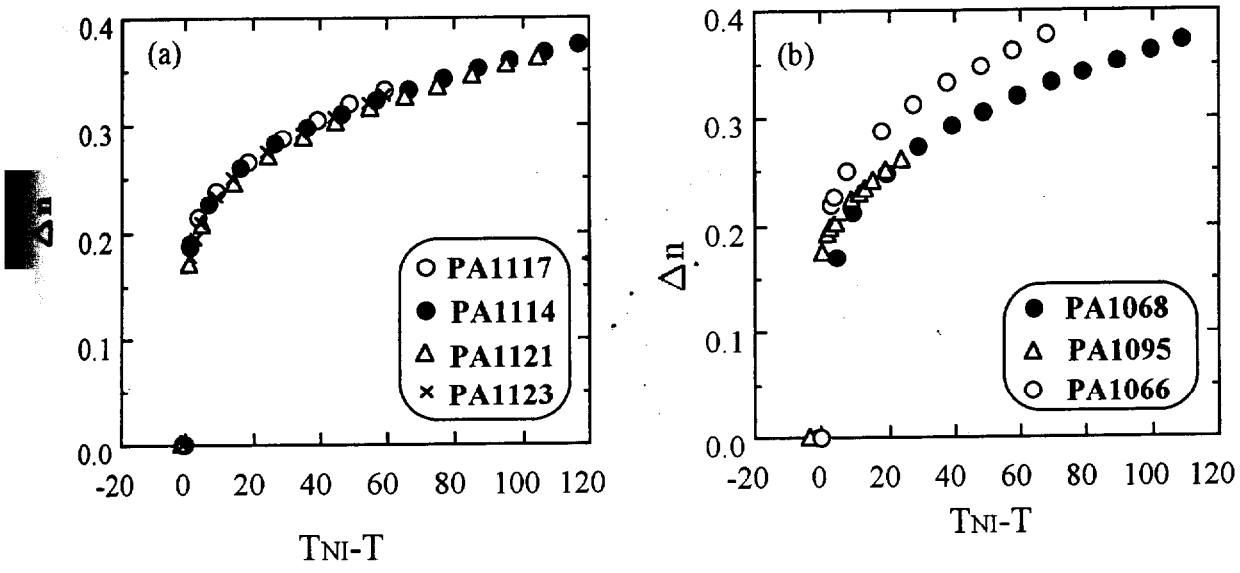


FIGURE 2-6 The effect of substituted position of methyl group on birefringence (a) alkyl type and (b) alkoxy type

(**PA1114** or **PA1068**) exhibited the highest values for the methyl substituted homologues.

The viscosities of these were also the lowest. From these viewpoints, position A was the most useful substituent position in the case of these 3-ring phenylacetylene homologues.

2.5 Effect of central ring substituents on physical properties

2.5.1 Mesogenic properties

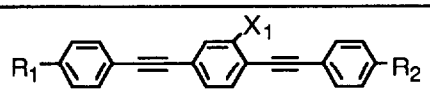
The phase transition temperatures and associated enthalpies of the compounds with a substitued central ring in the core part are listed in TABLE2-5. The nematic temperature was lowered by introducing a lateral substituent in both cases of alkyl-alkyl and alkyl-alkoxy terminal chains. The effect of the kind of substituents on liquid crystal temperature was different. The methyl group lowered the melting(m.p.) and clearing points(T_{NI}) and extended the nematic range. Other substituents also lower m.p. and T_{NI}, but they reduced their nematic ranges. Trifluoro methoxy and ethyl substituents lowered nematic temperature drastically. **PA1109** with ethyl substituent exhibited wide nematic range including room temperature. **PA1106** which had a methoxy group exhibited higher m.p. and lower T_{NI} than other types, as a result, the nematic range became very narrow.

2.5.2 Physical properties

Δn of **3PA**s estimated from the mixtures are listed in TABLE 2-6. These compounds exhibited very high Δn value of about 0.4. Δn was decreased by the substituents in the order H > CH_3 > C_2H_5 > OCF_3 > OCH_3.

Temperature dependence of Δn and the order parameter (S) of pure compounds were also measured and the values at T_{NI}- T = 100 are shown in TABLE2-7. The Δn and S were reduced by introduction of substituents, but trifluoromethoxy group did

TABLE2-5 Phase transition temperatures and enthalpies for the 3PA homologs.



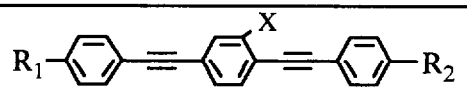
Compounds	R1	R2	X1	Transition temperatures (°C) and enthalpies(kJ/mol)
PA1094	$C_5H_{11}O$	C_4H_9	OCF_3	K [40.4] 60 N [1.7] 162 I
PA1106	C_6H_{13}	C_3H_7	OCH_3	K [28.6] 86 N [1.1] 108 I
PA1107	C_6H_{13}	C_3H_7	OCF_3	K [23.8] 34 N [1.1] 85 I
PA1109	C_6H_{13}	C_3H_7	C_2H_5	K [15.3] 16 N [1.5] 115 I
PA1108	C_6H_{13}	CN	C_2H_5	K [25.8] 74 N [1.3] 149 I

TABLE2-6 Physical properties of substituted **3PA** derivatives

	Optical anisotropy[1]			Viscosity[2]
	no	ne	Δn	[mPas]
PA1094	1.502	1.875	0.374	100
PA1107	1.498	1.844	0.346	56
PA1106	1.534	1.923	0.389	353
PA1109	1.528	1.907	0.379	94
PA1108	1.532	1.993	0.462	231

1) Extrapolated values(at 20℃ and λ=589nm)
the mixture [liquid crystal(10wt%) and MJ931381 (90wt%)]
2) Extrapolated values(at 20℃) of the mixture [liquid crystal(10wt%) and MJ931381 (90wt%)]

TABLE2-7 Physical properties of **3PA** homologs



	R1	R2	X	Δn(exp)[1]	S[1]	α[2]	Δα[3]	Δn(calc)[4]
PA1081	$C_5H_{11}O$	C_4H_9	H	0.383	0.76	359	525	0.580
PA1068	$C_5H_{11}O$	C_4H_9	CH_3	0.363	0.70	368	522	0.484
PA1094	$C_5H_{11}O$	C_4H_9	OCF_3	0.382	0.76	378	525	0.492
PA1117	C_6H_{13}	C_3H_7	H	0.363	0.76	349	502	0.560
PA1114	C_6H_{13}	C_3H_7	CH_3	0.361	0.70	358	499	0.467
PA1107	C_6H_{13}	C_3H_7	OCF_3	0.363	0.77	366	494	0.473
PA1106	C_6H_{13}	C_3H_7	OCH_3	0.339	0.59	363	494	0.389
PA1109	C_6H_{13}	C_3H_7	C_2H_5	0.362	0.69	366	489	0.434

1)Experimental datas at TNI-T=100
2) $\alpha=(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$
3) $\Delta\alpha=\alpha_{xx}-(\alpha_{yy}+\alpha_{zz})/2$
4)Calculated by Vucks low

not affect these properties. Introducing a non-polar substituent to the lateral position increased the free volume of the molecule so that it may cause mobility along n-director to increase and S to decrease. However, in the case of polar substituent group like trifluoromethoxy, the interaction of core part covered the effect of increasing free volume. As a result S was hardly affected.

Visocity of these homologues was slightly higher than those of conventional 2-ring type liquid crystals (see TABLE2-6). Introducing substituent groups increased viscosity, but trifluoromethoxy group decreased the viscosity remarkably. The viscosity of trifluoromethoxy type was lower than ethyl, methoxy or non-substituted type. It was considered that not only bulkiness of substituent group but also fluorine atoms reduced the interaction of molecules and induced lower viscocious property.

2.6 Conclusions

Substitued 3-ring phenylacetylene homologues have been synthesized and evaluated. In the investigation of modifying the terminal ring, it was found that methyl substituent was effective in lowering the nematic temperature range with keeping high Δn compared with a fluorine group or introducing a branched terminal chain. With these results, we studied the effect of the position of the methyl substituent on the physical properties. The most effective methyl substituent position for improving the nematic range was the central ring. Based on the estimated values of Δn, and the measured order parameters and viscosities, the best substituent position is also on the central ring.

These results led us to investigate the **3PA** homologues with different types of substituent. Introduing trifluoromethoxy

group was effective for lowering nematic range and viscosity. Therefore this type of compound was useful for preparing practical liquid crystal mixtures.

References of Chap. 2

[1] D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill ed., 1998, Handbook of Liquid Crystals, vol.2B (WILEY-VCH-Verlag, GmbH), 835

[2] D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill ed., 1998, Handbook of Liquid Crystals, vol.2B (WILEY-VCH-Verlag, GmbH),

[3] D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill ed., 1998, Handbook of Liquid Crystals, vol. 2A (WILEY-VCH-Verlag, GmbH), 129

[4] M. P. FONTANA, B. ROSI, N. KIROV and I. DOZOV, 1986, Phys. Rev. A, **33**,6,4132

[5] D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill ed., 1998, Handbook of Liquid Crystals, vol. 2B (WILEY-VCH-Verlag, GmbH), 835

[6] V. Reiffenrath, J. Krause, H. J.Plach and G. Weber, 1989, Liq. Cryst, **5**,159

[7] D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill ed., 1998, Handbook of Liquid Crystals, vol. 1 (WILEY-VCH-Verlag, GmbH), 56

Chapter 3 Development of colorless high Δn liquid crystals -phenylacetylene liquid crystals with heterocyclic groups-

3.1 Introduction

In Chap. 1 and Chap.2, high Δn liquid crystals of phenylacetylene homologues were developed. They exhibited Δn values of 0.4 ~ 0.5 and good stabilities. It was also successful in the improvement of liquid crystal temperature and solubilities by introducing lateral substituents. However, the values of such Δn are not enough large to prepare liquid crystal mixtures with high Δn over 0.5.

Most of high Δn liquid crystals reported before including phenylacetylene derivatives contained only carbon, hydrogen, oxygen and fluorine atoms. Recently liquid crystalline compounds with heterocyclic groups have been studied not for display use but other applications. Thiophenyl liquid crystalline compounds were developed as nonlinear optics materials [1]. Benzothiazolyl compounds have been studied as photoconductive materials [2]-[3]. High Δn liquid crystals containing naphtalene ring and isothiocyanato group were also reported [4]. Hetero atoms are expected to increase Δn because of more number of electrons than that of carbon; that contributes the increase of the polarizability. A condensed ring is also expected to increase the Δn because polarizability is larger than that of a phenyl ring. In order to obtain higher Δn liquid crystals, heterocyclic groups were introduced to the phenylacetylene core.

In this section, we synthesized and evaluated the physical properties of thiophenyl acetylene, benzothiazolyl acetylene

and dibenzothiophenyl acetylene compounds for the investigation of the effect of these hetero-rings on optical properties.

3.2 Experimental

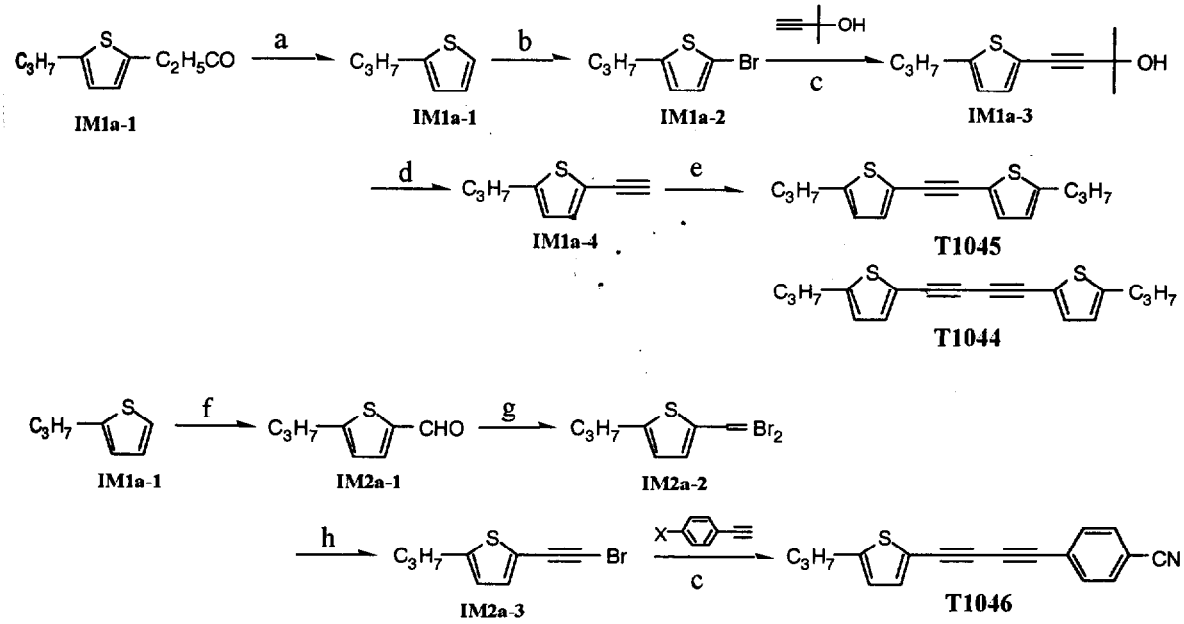
The preparative routes for the thiophenyl acetylene and benzothiazolyl acetylene derivatives including some intermediates are shown in SCHEM 3-1 ~ SCHEME 3-4 respectively. The characterization of structures of final compounds and various synthetic intermediates were examined by the same method explained in Chap.2.

Transition temperatures, phase sequences, refractive indices and viscosity were also evaluated by the same method in Chap.2. UV and visible spectra were measured with U-3500 (Hitachi) spectrometer. The samples were prepared by adding each compound (about 0.1mg) to DMF(10ml, spectrum grade). A quartz cell with 1cm thickness was used for this measurement.

3.3 Results and discussion

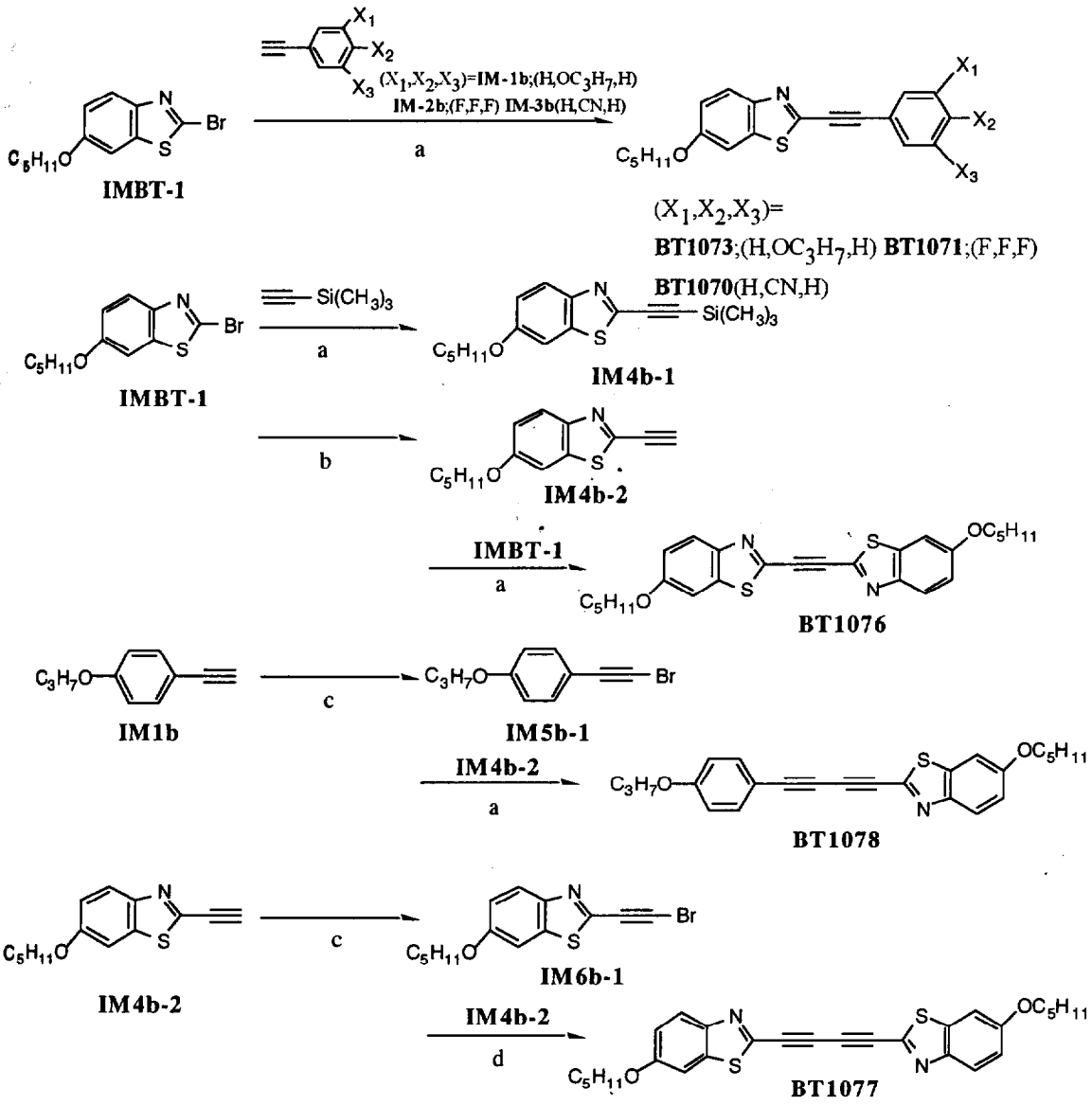
3.3.1 Thiophenylacetylene derivatives

The phase transition temperatures, associated enthalpies and refractive indices of the thiophenyl acetylene derivatives are listed in TABLE 3-1. Analogous phenylacetylene derivatives (**PA1036** and **PA1040**) are included for comparison. The thiophenylacetylene-based compounds are poorer liquid crystals with low liquid crystallinity than the corresponding phenylacetylene-based compounds. Compounds **T1045** and **T1044** did not exhibit liquid crystallinity while **T1046** showed only a monotropic nematic phase. The melting points of the



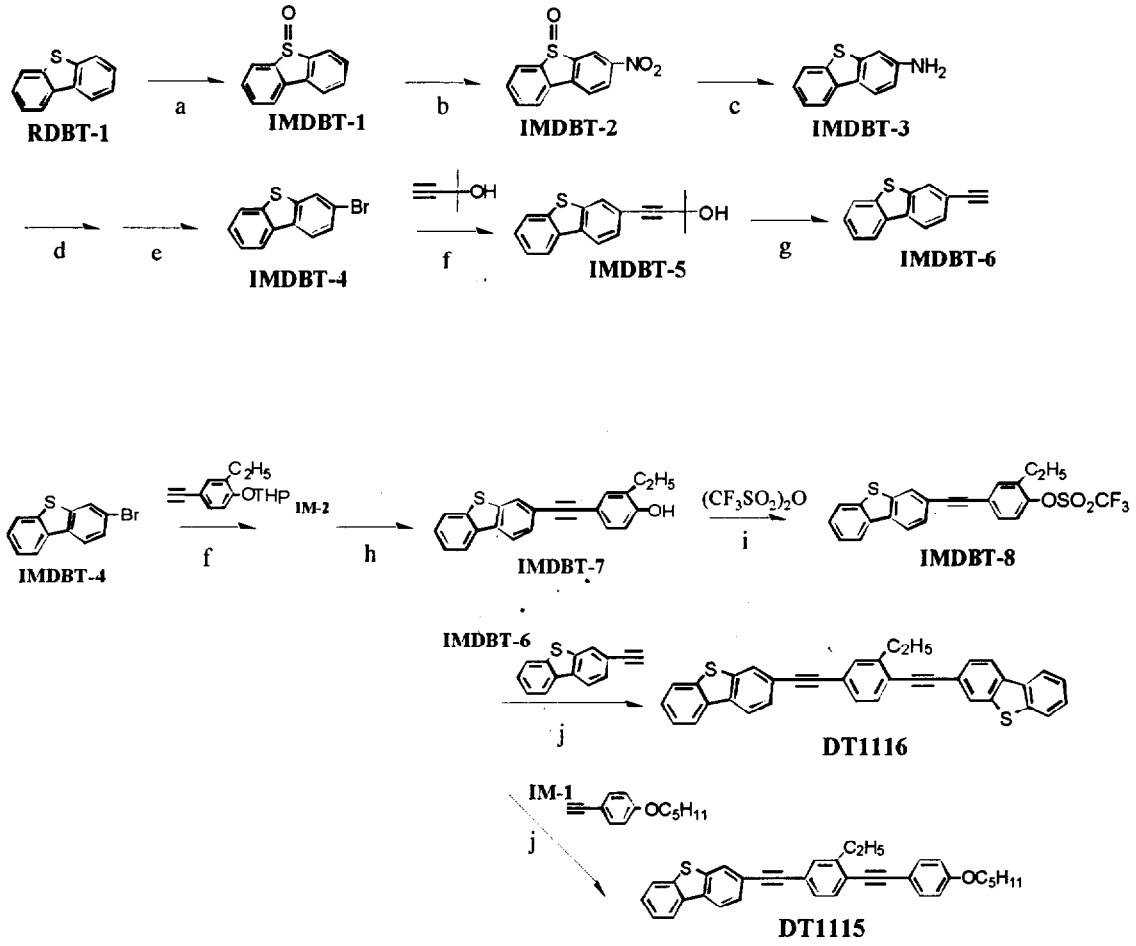
SCHEME 3-1

a NH_2NH_2 / KOH , b Br_2/Methanol , c CuI / $PdCl_2(PPh_3)_2$ / Triethylamine, d KOH / Toluene ,
e CuI /$PdCl_2(PPh_3)_2$, Air / NH_4OH / Ethanol ,f DMF / $POCl_3$, g Zn / PPh_3 / CBr_4 / CH_2Cl_2 , h NaOH / PEG400



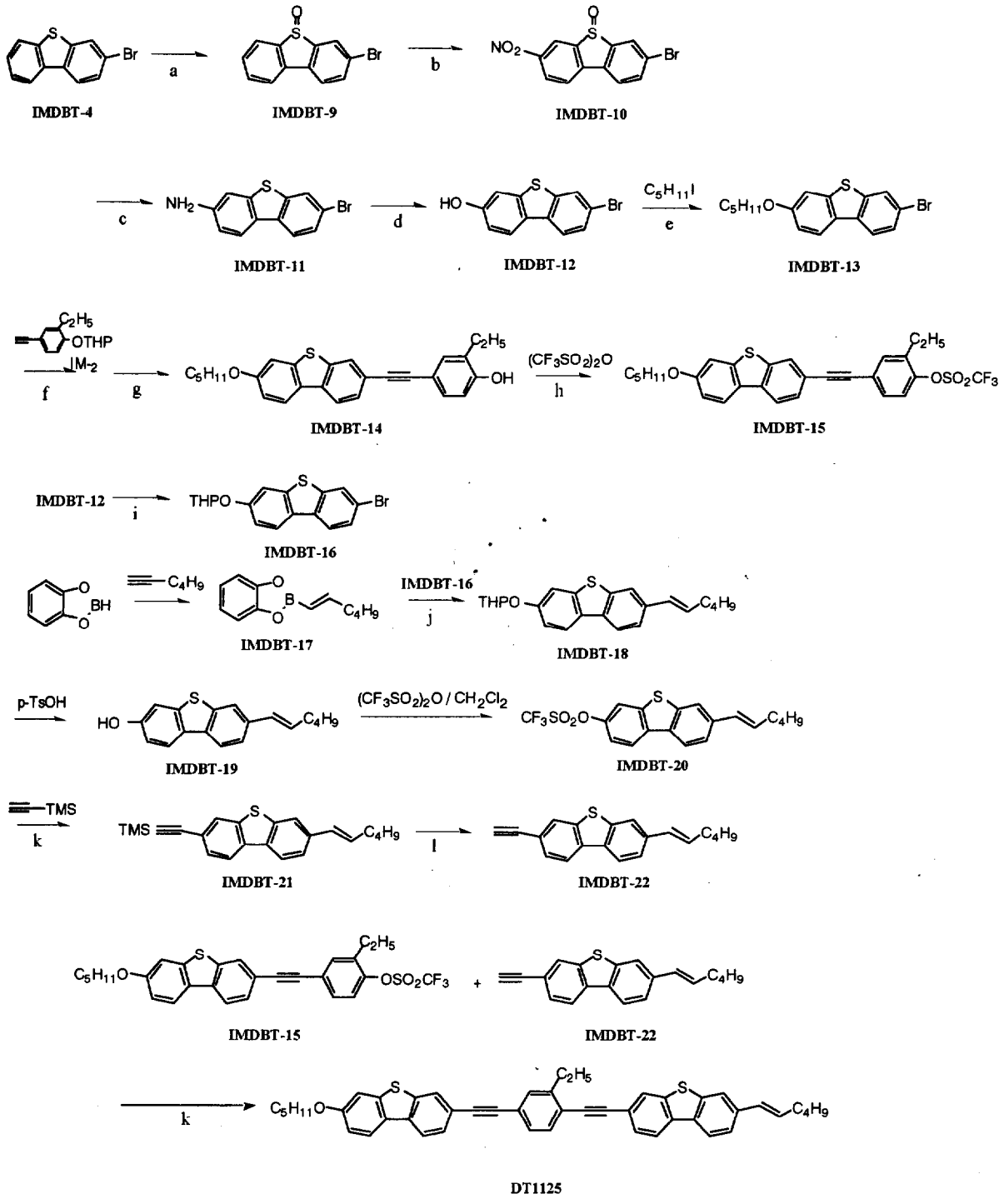
SCHEME 3-2

a $PdCl_2(PPh_3)_2PPh_3$ / CuI / Triethylamine, b K_2CO_3 / Methanol, c KOH, Br_2,
d CuCl / NH_2OH-HCl / CH_3NH_2 / Methanol



a Cl_2 / H_2O , b HNO_3 / H_2SO_4 / CH_3COOH , c $SnCl_2$ / HCl , d $NaN0_2$ / H_2SO_4 , e CuBr / HBr
f $PdCl_2(PPh_3)_2$ / PPh_3 / CuI / Triethylamine, g KOH / Toluene , h p-Toluenesulphonic acid / methanol
i 4-pyroridinopyridine / pyridine , j $PdCl_2(PPh_3)_2$ / PPh_3 / CuI / DMF,

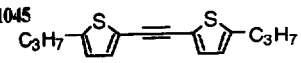
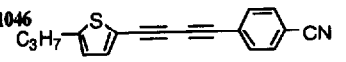
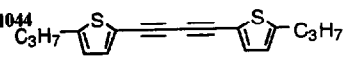
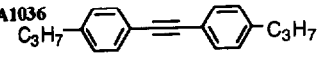
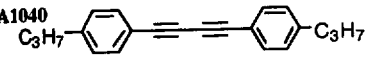
SCHEME 3-3



SCHEME 3-4

/ H_2O, b HNO_3 / H_2SO_4 / CH_3COOH, c $SnCl_2$ / HCl, d $NaNO_2$ / H_2SO_4, e K_2CO_3 / ethylmethyl ketone.
$Cl_2(PPh_3)_2$ / PPh_3 / CuI / Triethylamine, g p-Toluenesulphonic acid / methanol,
yrrolidin-1-yl pyridine / pyridine / dichrolomethane, i DHP / p-TsOH, j $PdCl_2(PPh_3)_2$ / Na_2CO_3, .
$Cl_2(PPh_3)_2$ / Triethylamine, l K_2CO_3 / methanol / THF

TABLE 3-1 Physical properties of thiophene homologues.

Compounds	Transition temperatures (℃) and enthalpies(in square brackets[], kJ/mol) K N I	ne [1)]	no[1)]	Δn[1)]	Δα[2)]
T1045 	· 7[22.9] ·	1.732	1.575	0.157	241
T1046 	· 114 [37.9](· 107 [0.1]) ·	2.078	1.560	0.518	401
T1044 	· 12[23.4] ·	1.911	1.584	0.327	363
PA1036 	· 73 [20.2] ·	1.781	1.518	0.264	251
PA1040 	· 108 [25.4] · 133 [1.4] ·	1.935	1.526	0.410	368

Pharenthese () denote a monotropic transition.
K : crystal, N : nematic phase, I : isotropic

1) Optical properties(at 20 ℃ and λ=589nm) were extrapolated values of the mixture [liquid crystal (10 wt %) and MJ931381 (90 wt %)]
2) Anisotropy of calculated polarizability by MOPAC 93
$\Delta\alpha=\alpha x-(\alpha y+\alpha z)/2$
αx ; Polaizability along the molecular long axis
αy、αz ; Polaizability along the molecular short axis

thiophenylacetylene series are lower than corresponding phenylacetylenes and; they exhibit good solubility with other nematic mixtures.

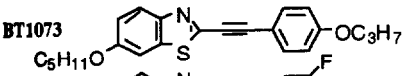
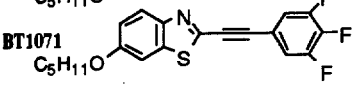
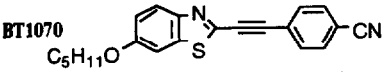
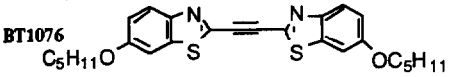
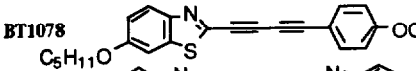
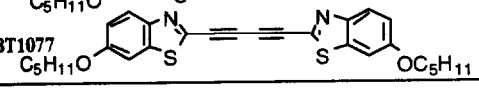
The values of Δn for the thiophenylacetylene series were around 0.3, which is moderately high. Δn was reduced by exchanging the phenyl group for a thiophenyl ring because of the reduction in the polarizability. As shown in TABLE 3-1, the anisotropic polarizabilities of the thiophenylacetylene homologues are lower than those of phenylacetylene homologues.

3.3.2 Benzothiazolylacetylene derivatives

The physical properties of the benzothiazolylacetylene homologues are listed in TABLE 3-2. They exhibit higher melting points and lower liquid crystal phase transition temperatures than the phenylacetylene and thiophenylacetylene homologues. Compounds **BT1073** to **BT1076** and **BT1077** did not exhibited liquid crystal phases. The transition enthalpies were larger than those of the reference compounds. The condensed ring increased the interaction area of the cores giving higher melting points ans reduced liquid crystalline behaviour. **BT1078** shows an enantiotropic nematic phase, but decomposes at 159℃; **BT1077** decomposes at 158℃ prior to melting. He compounds containing a diacetylene fragment were less thermally stable than those having an acetylene linkage(**BT1073 ~BT1076**).

Δn was increased by exchanging the phenyl group for a benzothiazole ring. The fluorine-substituted compound (**BT1071**) showed a low Δn, while alkoxy substituents gave high Δn values of 0.3 ~ 0.5. As $\Delta \alpha$ increased on adding benzothiazole ring, so did Δn. Compounds **BT1070** and **BT1076**

TABLE 3-2 Physical properties of the benzothiazole homologues.

Compounds	Transition temperatures (℃) and enthalpies(in square brackets[], kJ/mol) K	N	I	ne[1]	no[1]	Δn[1]	Δα[2]
BT1073 	· 115 [43.2]		·	1.878	1.543	0.335	395
BT1071 	· 97 [31.9]		·	1.780	1.540	0.240	351
BT1070 	· 162 [50.2]		·	-	-	-	-
BT1076 	· 176 [65.9]		·	-	-	-	-
BT1078 	· 116 [39.6]	· decomposed at 159℃		2.057	1.554	0.503	530
BT1077 	decomposed at 158℃			2.015	1.537	0.478	636

K : crystal, N : nematic phase, I : isotropic

1) Optical properties (at 20 ℃ and λ = 589 nm) were extrapolated values of the mixture [liquid crystal (10 wt %) and MJ931381 (90 wt %)]

2) Anisotropy of calculated polarizability by MOPAC 93

$\Delta\alpha = \alpha x - (\alpha y + \alpha z)/2$

αx ; Polaizability along the molecular long axis

αy、αz ; Polaizability along the molecular short axis

showed poor solubility in the host nematic, and thus, Δn values could not be estimated.

The benzothiazolylacetylene and thiophenylacetylene derivatives were yellow or brownish in colour. The absorption spectra of these series had longer absorption edges than that of even the colourless three-ring phenylacetylene compound which has a higher Δn value of 0.43 [9] (see FIGURE 3-1). It is considered that the conjugated hetero rings raise the HOMO level; indeed the calculated HOMO levels of these compounds are -8.40 eV (**T1045**) and -8.47 eV (**BT1073**), which are higher, than that of **PA1036** (-8.56 eV). Therefore, the absorption spectra shifts to longer wavelengths on substituting the phenyl ring with a hetero ring.

3.3.3 Dibenzothiophenyl acetylene derivatives

As has been investigated in 3.3.1 and 3.3.2, introducing hetero atoms was effective for increasing $\Delta\alpha$ and Δn. However, it was thought to induce a red shift of the UV-Vis absorption spectra because the HOMO level is raised. It is important to restrain the decrease in the HOMO-LUMO gap in the design of high Δn liquid crystalline compounds with heterocyclic rings. In order to obtain colourless high Δn liquid crystals, new molecules having dibenzothiophenyl rings were designed, synthesized and investigated.

3.3.3.1 Molecular designs

Refractive index is determined by polarizability and number density as expressed by Vuks equation [10]. Increasing the polarizability along the molecular long axis is effective for increasing Δn. We introduced dibenzothiophenyl rings

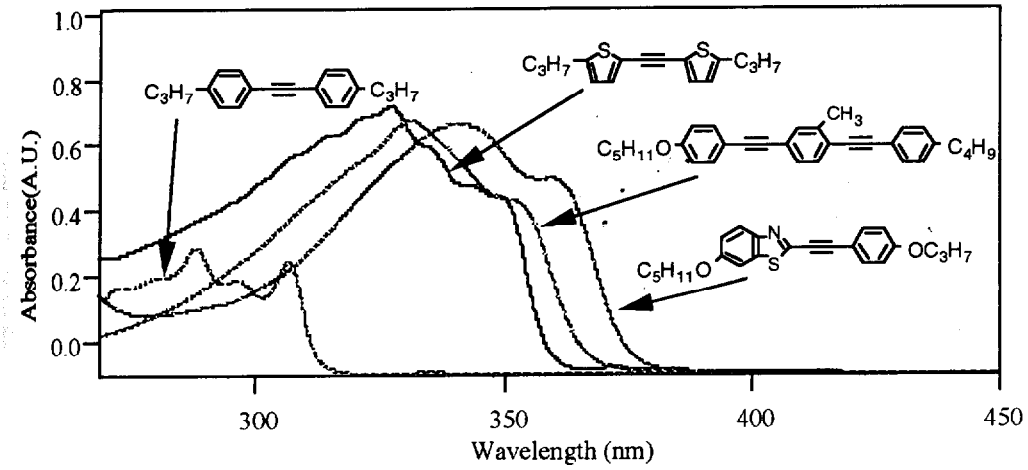


FIGURE 3-1 The effect of heterocyclic groups on UV-VIS absorption spectra

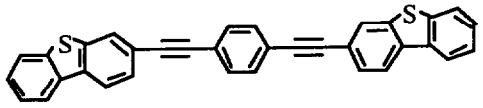
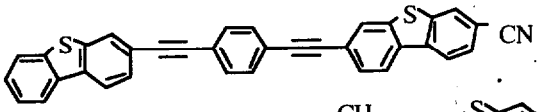
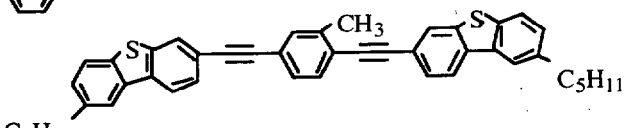
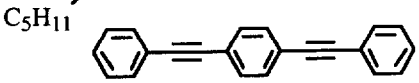
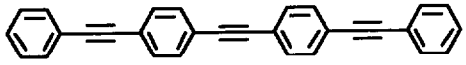
with larger Δn than a phenyl ring because they were expected to cut the conjugation system in the molecule because of the different HOMO level from that of the phenyl ring. Before synthesis started, anisotropy of polarizability and UV-Vis absorption spectra had been calculated. From the results of the calculations (see TABLE 3-3), it was predicted that the dibenzothiophenyl series would exhibit larger $\Delta\alpha$ and almost the same absorption edge as 3-ring and 4-ring acetylenes.

The molecular orbitals of HOMO and HOMO-2 of model molecule **1** are shown in FIGURE 3-2. HOMO-2 is the next-but-one lower energy level because of degeneration of HOMO and the next lower HOMO. The HOMO is localized at the dibenzothiophenyl rings. On the other hand, HOMO-2 is delocalized over the whole molecule. It might be speculated that dibenzothiophenyl series exhibit high $\Delta\alpha$ because of the conjugated nature of HOMO-2 and short wavelength absorption because of the localized HOMO.

3.3.3.2 Physical properties of dibenzothiophenyl acetylene derivatives

Chemical structures and physical properties of the dibenzothiophenylacetylene homologues are listed in TABLE 3-4. **DT1116** containing two dibenzothiophenyl rings exhibited a high melting point and a wide range enantiotropic nematic phase. In the measurement by DSC, only the transition from the crystal to the nematic phase was observed on the heating cycle from room temperature to 330 ℃. **DT1115** with one dibenzothiophenyl ring exhibited lower melting point of 134 ℃ and a wide nematic phase range. **DT1125** with an alkenyl group connected directly to the core part exhibited a high melting point like **DT1116** and had a smectic phase. This phase was thought to be highly

TABLE 3-3 Calculation of polarizability and absorption wavelength of model molecules

model molecules	$\Delta\alpha$ (a.u.)[1]	Abs.(nm)[2]
model 1 	755	361
model 2 	819	368
model 3 	808	364
R1 	426	358
R2 	681	374

1) Calculated by MOPAC93 (revision number 2)
2) Calculated by MOPAC-RPA program, Single CI [13]

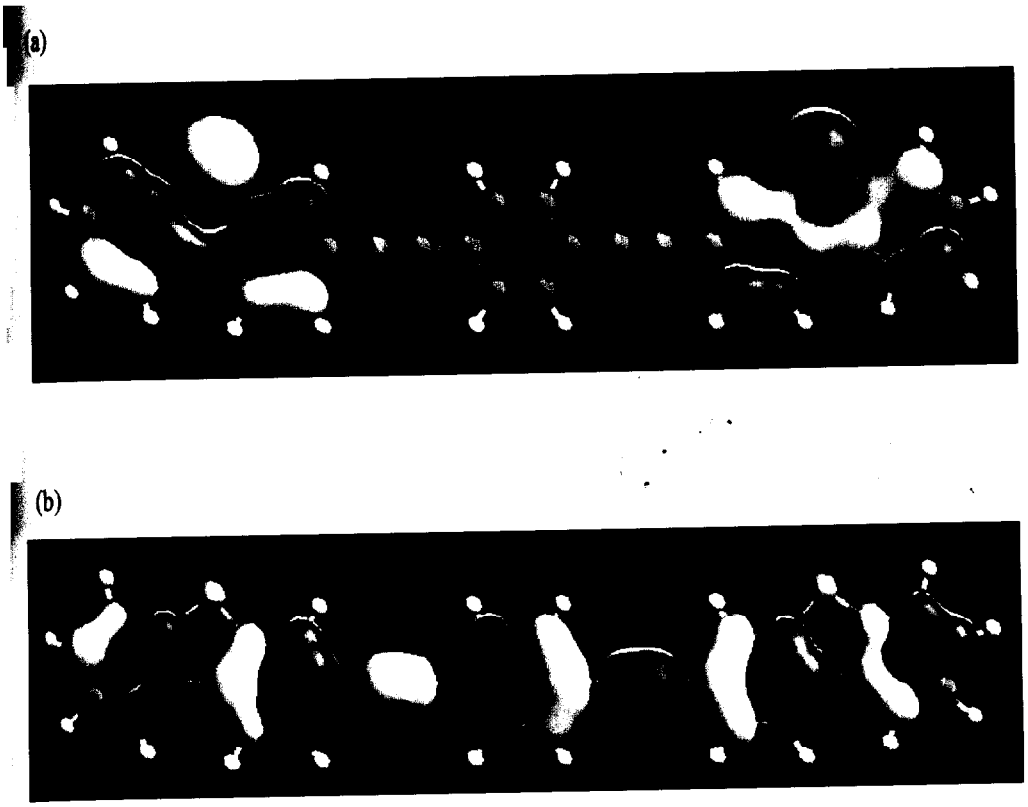
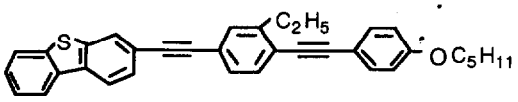
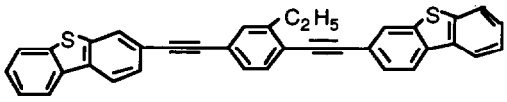
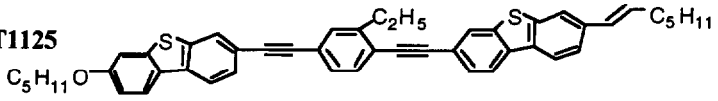


FIGURE 3-2 Image of MO of the model molecule 1
(a) HOMO (b) HOMO-2

TABLE 3-4 Transition temperatures of dibenzothiophenyl derivatives

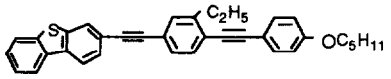
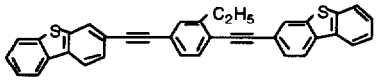
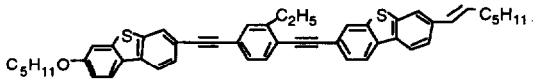
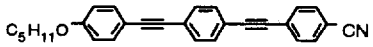
Compounds		Transition temperatures(℃)
DT1115		K · 134 · N · 253 · I
DT1116		K · 227 · N >300
DT1125		K · 225 · Sx >300

ordered, but could not properly be assigned simply by observation of the texture using the polarizing microsope.

Extrapolated Δ n values of the dibenzothiophenyl homologues were very high as expected (see TABLE 3-5); **DT1116** and **DT1125** had values of over 0.6. When E9 was used as a host mixture (E9 has a higher T_{NI} than MJ931381), the extrapolated Δn of **DT1116** was over 0.7. Refractive indices for **DT1115** and **DT1116** were measured using the single compounds as shown in FIGURE 3-3. They also exhibited very high Δn as single pure compounds , especially **DT1116** with Δ n over 0.5. The calculated $\Delta\alpha$ are increased by exchanging a phenyl ring for a dibenzo-thiophenyl ring (see TABLE 3-6). The order parameter of **DT1115** was slightly larger than that of the simple phenylacetylene compound **PA1109** (see FIGURE 3-4), but the difference was so small that mainly the increase of $\Delta\alpha$ must contribute to the increase in Δn. **DT11125** also exhibited high Δn over 0.6, but the alkenyl group did not contribute the increase of Δn.

Absorption spectra of compounds **DT1116**, **DT1115** and **PA1054** are shown in FIGURE 3-5. The spectral edges are all shorter than 400nm, the shortest limit of the visible range. **DT1116** with two benzothiophenyl rings is colourless. The plots of the shortest absorption edge of each compounds to Δn are shown in FIGURE 3-6. The compounds used in this plots are shown in TABLE 3-7. The transition energy was almost proportional to Δn in the phenylacetylene series. Thiophenyl series and benzothiazolyl series exhibited smaller energy than phenylacetylene plots as menthioned in chapter2. However dibenzothiophenyl series showed larger Δn with almost same transition energy as phenylacetylene series.

TABLE 3-5 Optical properties of dibenzothiophenyl derivatives

Compounds		n_e [1)]	n_o [1)]	Δn [1)]	n_e [2)]	n_o [2)]	Δn [2)]
DT1115		2.093	1.563	0.530	2.158	1.541	0.617
DT1116		2.223	1.590	0.633	2.332	1.589	0.743
DT1125		2.181	1.551	0.631			
PA1054		—[3)]	—[3)]	—[3)]	2.128	1.534	0.594

1) Optical properties(at 20℃ and λ=589nm) were extrapolated values of the mixture [liquid crystal(5wt%) and MJ931381 (95wt%)]
2) Optical properties(at 20℃ and λ=589nm) were extrapolated values of the mixture [liquid crystal(5wt%) and E9 (95wt%)]
3) Insolble in the host mixture

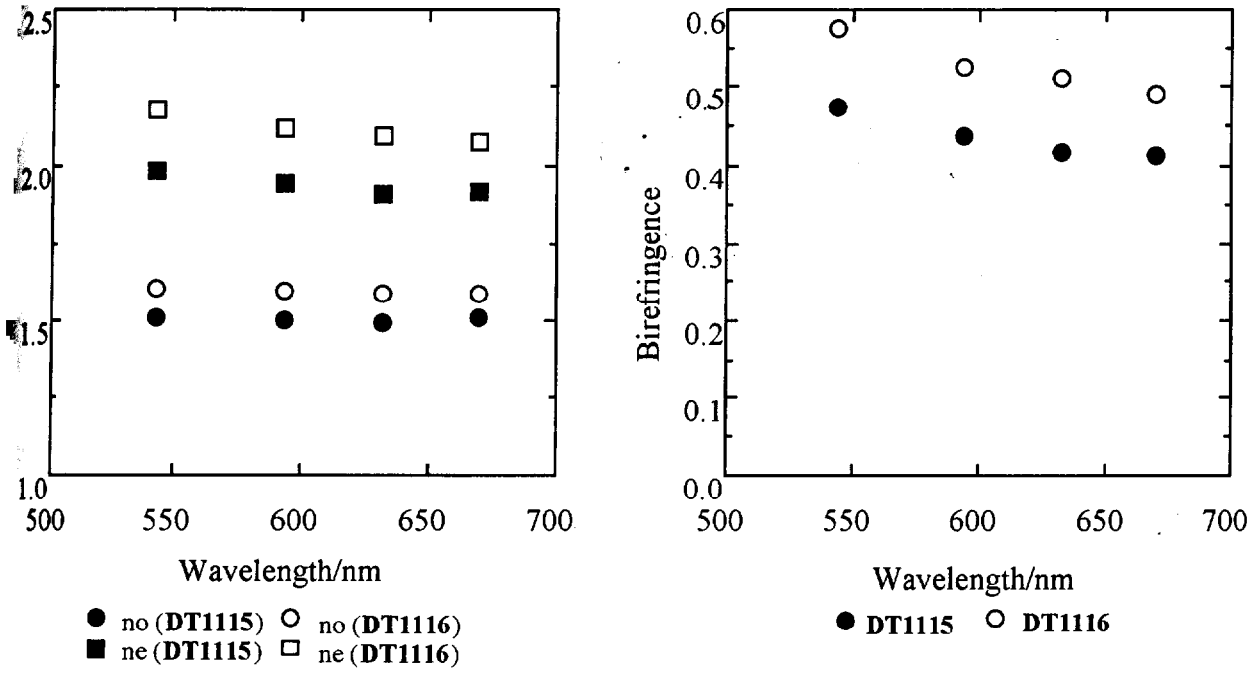


FIGURE 3-3 Refractive indices and birefringence of **DT1115** and **DT1116**

TABLE 3-6 Calcurated polarizabilities of dibenzothiophenyl derivatives

	α_{xx}	α_{yy}	α_{zz}	$\Delta\alpha$
DT1115	870	338	98	652
DT1116	977	380	68	753
DT1125	1251	456	146	950
PA1109	692	288	118	489
PA1054	714	232	80	558

αxx ; Polaizability along the molecular long axis
αyy、αzz ; Polaizability along the molecular short axis
$\Delta\alpha=\alpha xx-(\alpha yy+\alpha zz)/2$

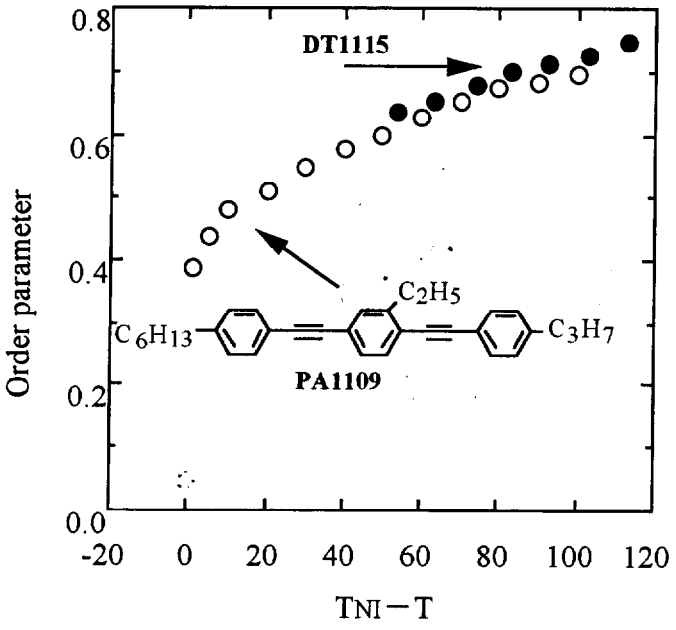


FIGURE 3-4 Order parameter of **DT1115**

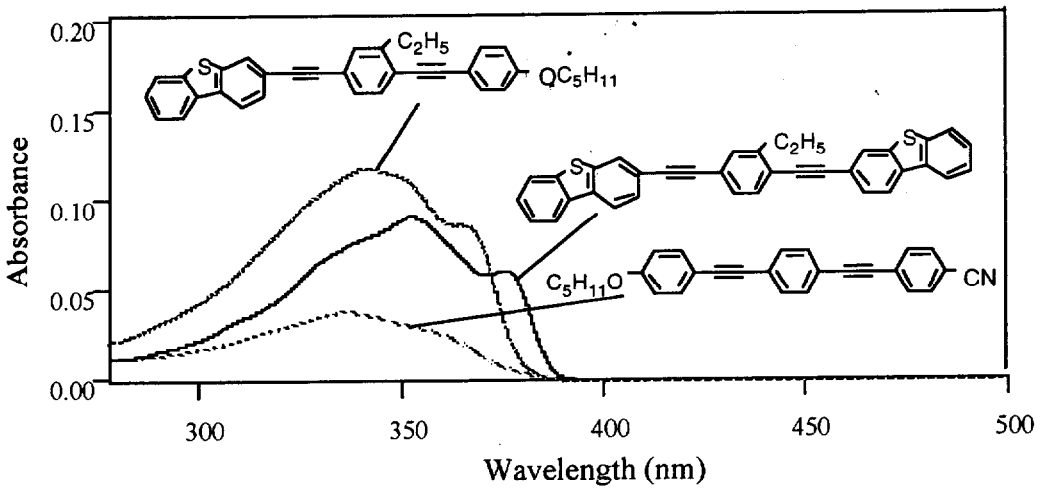


FIGURE 3-5 The effect of the dibenzothiophenyl ring on UV-VIS absorption spectra

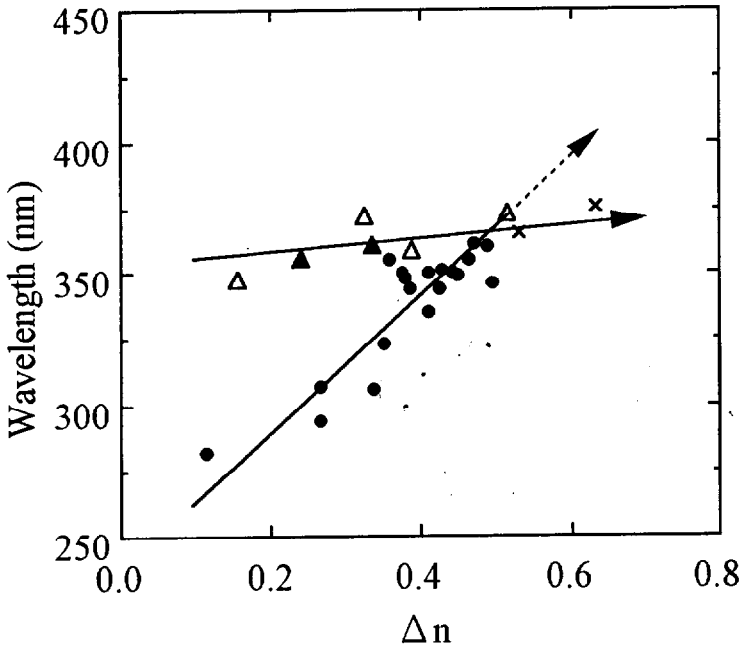
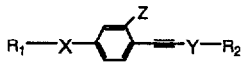
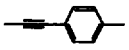
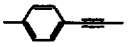
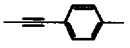
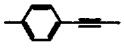
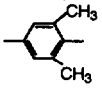
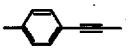


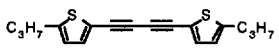
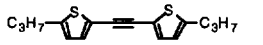
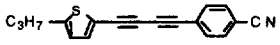
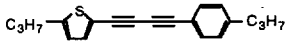
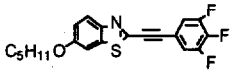
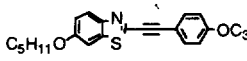
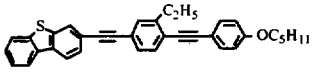
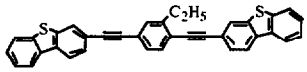
FIGURE 3-6 Plots of Δn vs transition energy of high Δn liquid crystalline compounds

• Phenylacethylenes Δ Thiophenylacethylenes ▲ Benzothiazolylacethylenes × Dibenzothiophenylacethylenes

TABLE 3-7 Δn and absorption edge of compounds



X	Y	Z	R_1	R_2	Δ n	Abs (nm)
		H	C_3H_7	C_3H_7	0.115	282
		↑	↑	↑	0.264	294
	↑	↑	CN	↑	0.335	306
		↑	C_3H_7	↑	0.410	336
		↑	↑	↑	0.264	307
		↑	↑	↑	0.351	323
		↑	↑	OC_5H_{11}	0.385	344
	↑	↑	OC_3H_7	OC_3H_7	0.424	344
		↑	↑	↑	0.496	346
↑	↑	↑	OC_5H_{11}	C_4H_9	0.448	350
↑		↑	↑	F	0.410	350
↑		↑	↑	CN	0.470	361
↑		↑	↑	$O(C_3H_7)_2$	0.356	356
↑	↑	CH_3	↑	OCF_3	0.375	350
↑		↑	↑	CN	0.490	361
↑		↑	↑	F	0.442	350
↑	↑	↑	↑	C_4H_9	0.430	352
		C_2H_5	C_6H_{13}	CN	0.462	356
↑	↑	↑	↑	C_3H_7	0.379	349

	Δ n	Abs (nm)
	0.327	372
	0.157	348
	0.518	373
	0.391	359
	0.240	355
	0.335	360
	0.530	366
	0.633	376

Dibenzothiophenyl series exhibited shorter absorption spectra than the expectation from the large Δn.

The durability of **DT1115** and **DT1116** was estimated by the same method explained in Chap.1. They exhibited good stability as same as 3-ring phenyl acetylene series (see TABLE 3-8).

3.3.3.3 Analysis of the contribution to birefringence

Some semi-empirical models exist for describing the refractive index dispersions of liquid crystals [11]. Three absorption bands (one $\sigma \rightarrow \sigma^*$ and two $\pi \rightarrow \pi^*$ transition bands) have been correlated with the refractive indices to identify the physical origins responsible for the observed values. In this section, the dependence of the refractive indices on the absorption wavelengths of **DT1115** and **DT1116** was measured and analyzed in order to confirm the origin of the physical features of dibenzothiophenylacetylenes, which exhibited very high Δn and no colour.

(1) Three-band model

A semi-empirical formula correlating with the microscopic molecular polarizabilities ($\alpha_{e,o}$) of a liquid crystal with the macroscopic refractive indices was obtained from the Vucks equation and the semi-empirical relationship between n_e and n_o [12]:

$$n_e = M\alpha_e + \left[1 + (M\alpha_e)(M\alpha_o)\right]^{\frac{1}{2}} \quad (1a)$$

$$n_o = M\alpha_o + \left[1 + (M\alpha_o)(M\alpha_e)\right]^{\frac{1}{2}} \quad (1b)$$

TABLE 3-8 Durabilities of Dibenzothiophenyl derivatives

Compounds	Residual rate (%)	
	1*	2**
DT1115	98	99
DT1116	99	99
DT1125	88	96

*; After the irradiation test
**; After the heat test

where M=1.4(4πN/3) and N is the number of molecules per unit volume. Equation (1) can be expanded by a power series to the first order since both $M\alpha_e$ and $M\alpha_o$ are much less than unity

$$n_e \cong 1 + M\alpha_e\left(1+\frac{1}{2}M\alpha_e+\cdots\right) \quad (2a)$$

$$n_o \cong 1 + M\alpha_o\left(1+\frac{1}{2}M\alpha_o+\cdots\right) \quad (2b)$$

At the off-resonance region, molecular polarizability ($\alpha_{e,o}$) is related to the resonance absorption wavelength λ_i and associated oscillator strength $(f_{e,o})_i$ as

$$\alpha_{e,o}(\lambda) \approx \sum_i (f_{e,o})_i \frac{\lambda^2\lambda_i^2}{\lambda^2-\lambda_i^2} \quad (3)$$

In the three-band model, one $\sigma\rightarrow\sigma^*$ transition (designated as the λ_0 band and two $\pi\rightarrow\pi^*$ transitions (designated as the λ_1 and λ_2 bands with $\lambda_2 > \lambda_1$) are considered. The λ_0 band appears in the vacuum UV region; its actual wavelength has not been measured, but is expected to locate at around 120nm. There are many σ electrons available in a liquid crystal molecule, so that the transition intensity should be very strong. The λ_1 band of several conjugated liquid crystal molecules occurs at about 200 nm; it consists of two closely overlapped bands. Considering all three bands, we derive the following expressions for refractive indices:

$$n_e \cong 1 + g_{0,e}\frac{\lambda^2\lambda_0^2}{\lambda^2-\lambda_0^2} + g_{1,e}\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + g_{2,e}\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2} \quad (4a)$$

$$n_o \cong 1 + g_{0,o}\frac{\lambda^2\lambda_0^2}{\lambda^2-\lambda_0^2} + g_{1,o}\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + g_{2,o}\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2} \quad (4b)$$

Where $g_i \sim Nz_if_i$ are proportionality constants; Z_0 is the number of responsible σ electrons, and $Z_1=Z_2$ is the number of π electrons in liquid crystal compounds. This g_i determines the temperature effect of the refractive indices. In the visible region, $\lambda >> \lambda_0$ so that the second terms in Eqs. (4a) and (4b) are reduced to constants: $n_{oe} = g_{0e}\lambda_{02}$ and $n_{oo}=g_{oo}\lambda_{20}$ which are independent of wavelength, but are dependent on temperature. Furthermore, the ratios $g_{2e}/g_{1e} = m_e$ and $g_{2o}/g_{1o} = m_o$ of a liquid crystal can be obtained from the measured polarized absorption spectrum. Therefore, Eqs.(4a) and (4b) are simplified to

$$n_e \cong 1 + n_{0,e} + g_{1,e}\left(\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + m_e\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2}\right) \quad (5a)$$

$$n_o \cong 1 + n_{0,o} + g_{1,o}\left(\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + m_o\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2}\right) \quad (5b)$$

The three-band model as described in Eq.(5) also involves two parameters (n_{0e} and g_{1e} for n_e, n_{0o} and g_{1o} for n_o). These two parameters can be evaluated by simply measuring the refractive indices of a liquid crystal at two different wavelengths. Once these two unknowns are obtained, the wavelength dependent refractive indices of the liquid crystal can be calculated and the contribution of each band to the overall refractive index can be evaluated

quantitatively.

(2) Analysis of refractive indices

The data used for the analysis are listed in TABLE 3-9. The parameters m_e and m_o are calculated from the polarized absorption spectra as shown in FIGURES 3-7 and 3-8. These data were measured by mixing 1 wt% of each compound in a host liquid crystal mixture A at room temperature. The compositions of the mixture A are shown in TABLE 3-10. In this study, the ratio of m_e and m_o was treated as constant for simplicity [11].

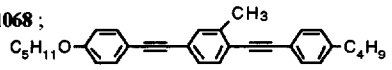
Once m_e and m_o are known, the number of adjustable parameters of the three-band model is reduced to two. FIGURES 3-9 and 3-10 show, respectively, the fittings of the experimental results for **DT1115** at 150℃ and **DT1116** at 230 ℃ to the three-band model; the fittings were very good. The contributions of each band, defined as in equations (5), to the total refractive indices of the compounds were evaluated by using of the fitting parameters of $n_{ie,o}$ and $g_{ie,o}$. From the results, the λ_0 band makes a greater contribution to refractive indices than the sum of the λ_1 and λ_2 bands (see FIGURES 3-11 and 3-12). The contribution of λ_1 band to n_o was slightly larger than that of λ_2. Contrary to this, the λ_2 band makes more contribution to n_e and Δn than λ_1. The contribution of λ_2 to Δn of **DT1116** was smaller than that of **DT1115**.

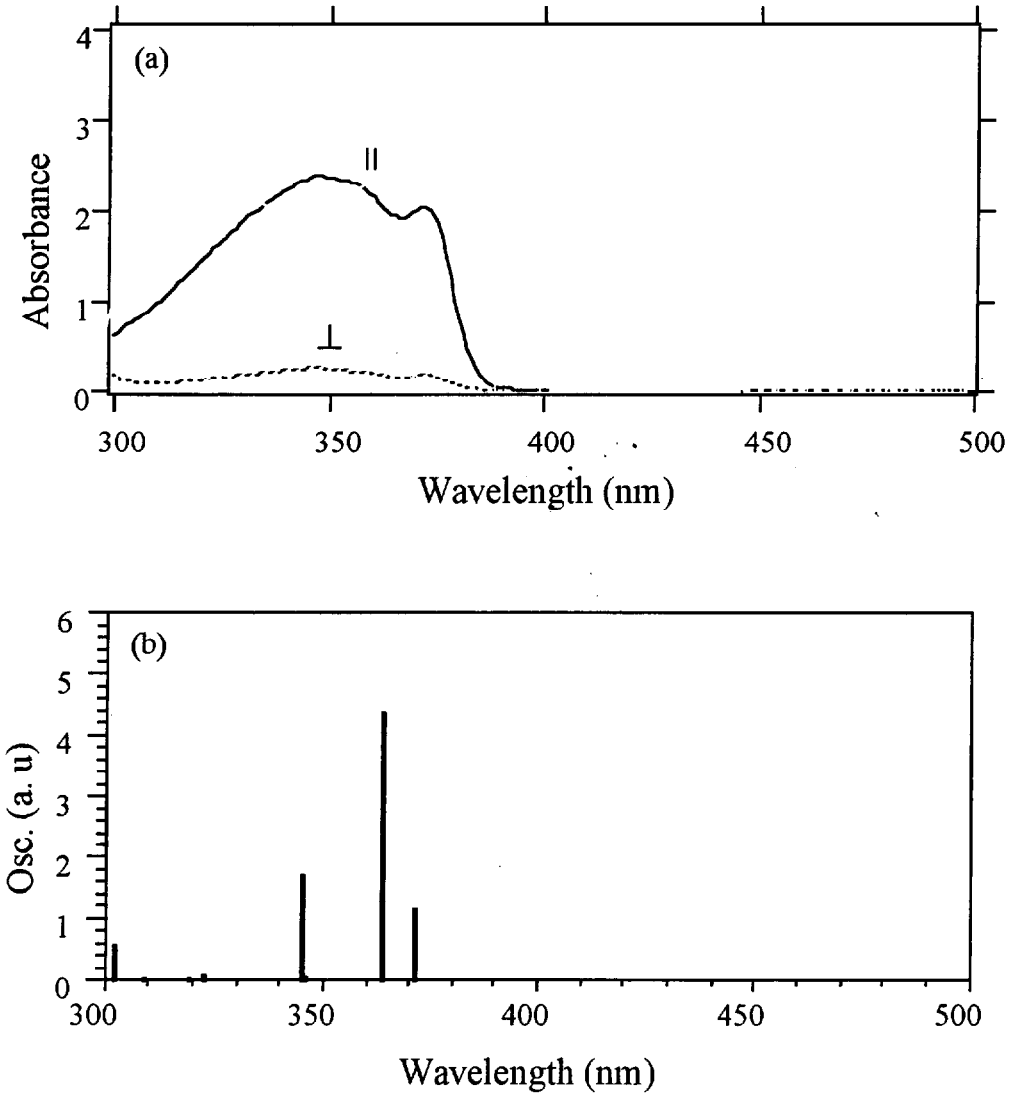
The contribution of each MO to Δn was estimated by using the assignment of the calculated transitions[13]. The calculated transitions are listed in TABLE 3-11. The MO numbers of the HOMO of **DT1115** and **DT1116** were 91 and 89 respectively. The transitions from the HOMO mainly

TABLE 3-9 Refractive indices and dicroic ratio of polarized UV spectra of dibenzothiophenyl derivatives

	DT1115 (at 150°C)			**DT1116** (at 230°C)			**PA1068** (at 90°C)		
Wavelength /nm	n_o	n_e	Δn	n_o	n_e	Δn	n_o	n_e	Δn
670	1.536	1.959	0.422	1.581	2.073	0.492	1.499	1.870	0.372
632.8	1.538	1.974	0.436	1.584	2.096	0.512	1.501	1.880	0.380
594	1.540	1.997	0.457	1.590	2.116	0.526	1.502	1.896	0.395
543.5	1.551	2.041	0.490	1.602	2.178	0.577	1.509	1.930	0.421
m_o		0.65			0.65			0.83	
m_e		0.85			0.81			0.91	

PA1068;





GURE 3-7 Absorption spectra of **DT1115**
(a) Polarized spectra of **DT1115** in MIXTURE A (b) Calculated spectraum

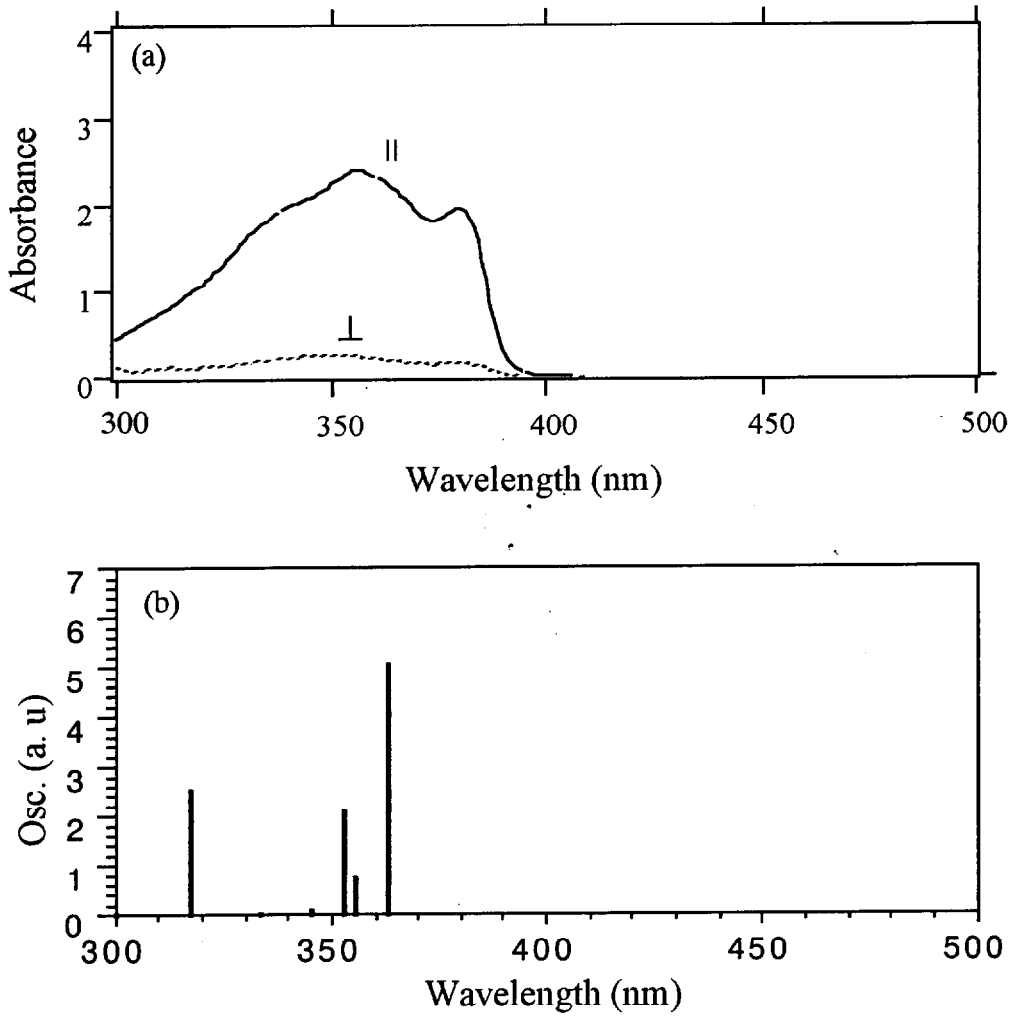
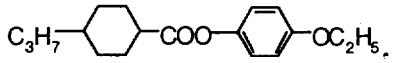
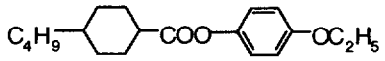
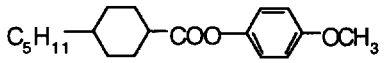
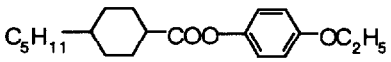
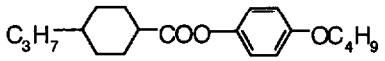


FIGURE 3-8 Absorption spectra of **DT1116**
(a) Polarized spectra of **DT1116** in MIXTURE A (b) Calculated spectrum

TABLE 3-10 Constituents and physical properties of MIXTURE A

Constituents	Concentration (mol%)
	18.3
	21.0
	20.9
	13.3
	26.5

Physical properties

$$K \xrightarrow{2} N \xrightarrow{75} I$$

Δn=0.088 (20℃、633nm)

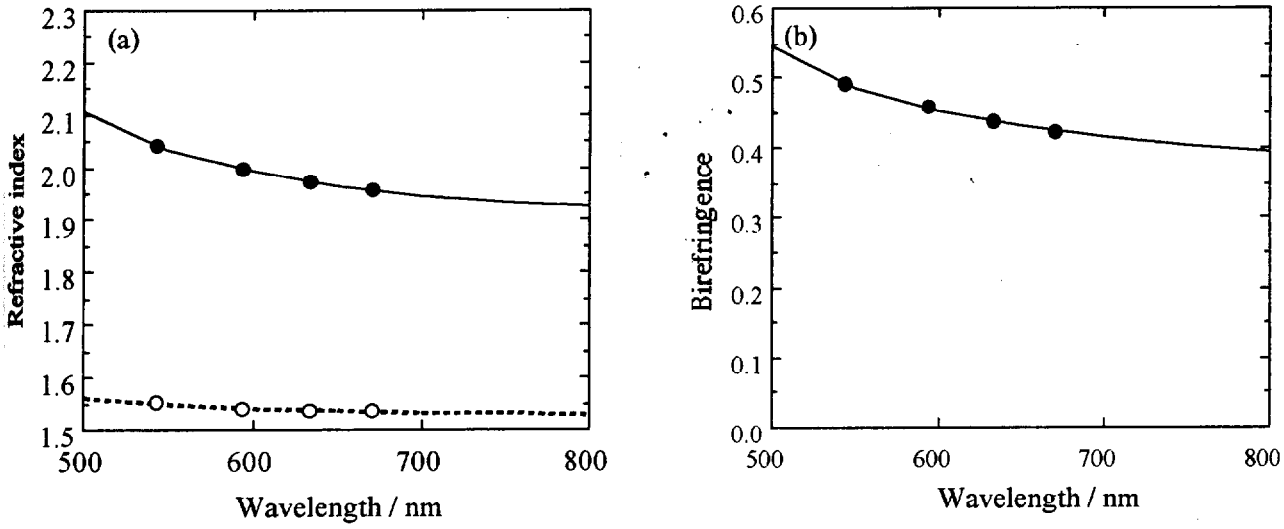


FIGURE 3-9 Wavelength dependence of refracrive indices and birefringence of **DT1115** at 150℃. Dots are experimental data. Solid or dashed lines are the fitting curves (Eq.5).

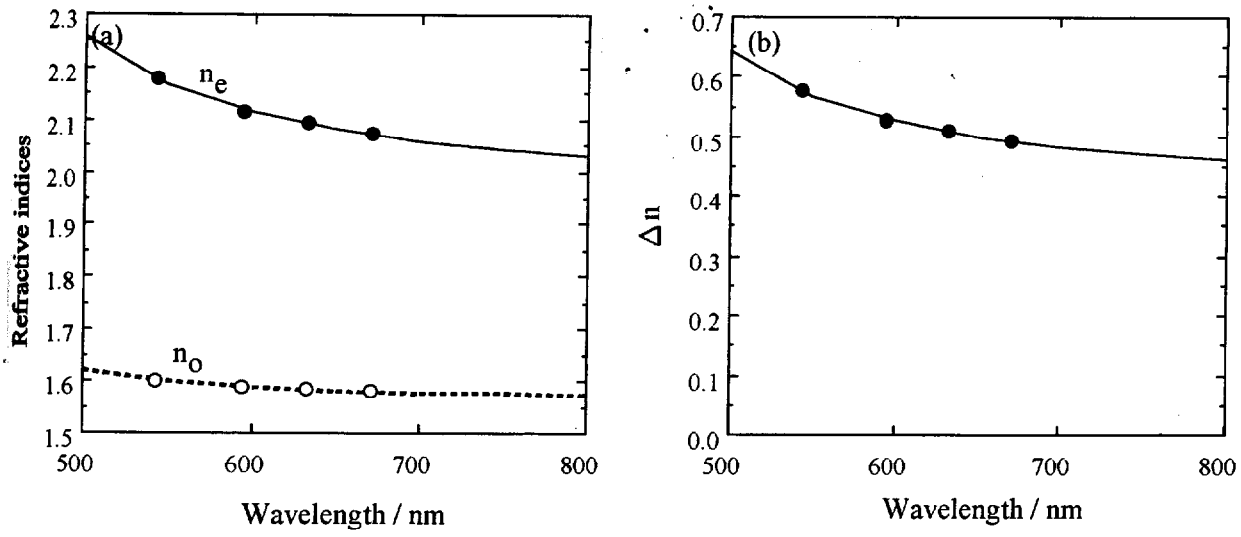


FIGURE 3-10 Wavelength dependence of refracrive indices and birefringence of **DT1116** at 230℃. Dots are experimental data. Solid or dashed lines are the fitting curves (Eq.5).

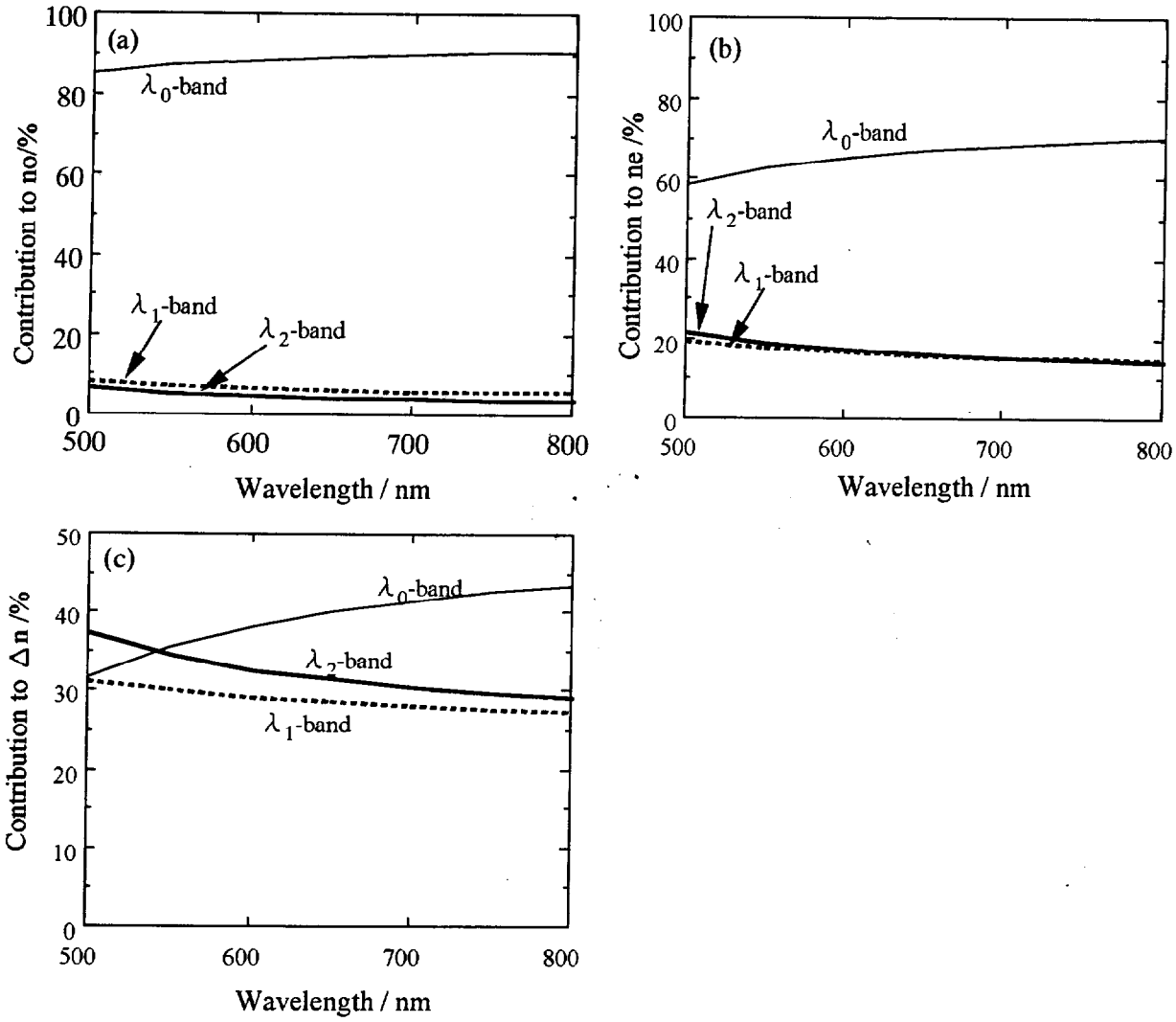


FIGURE 3-11 Contribution of each band to refractive indices and birefringence of **DT1115**

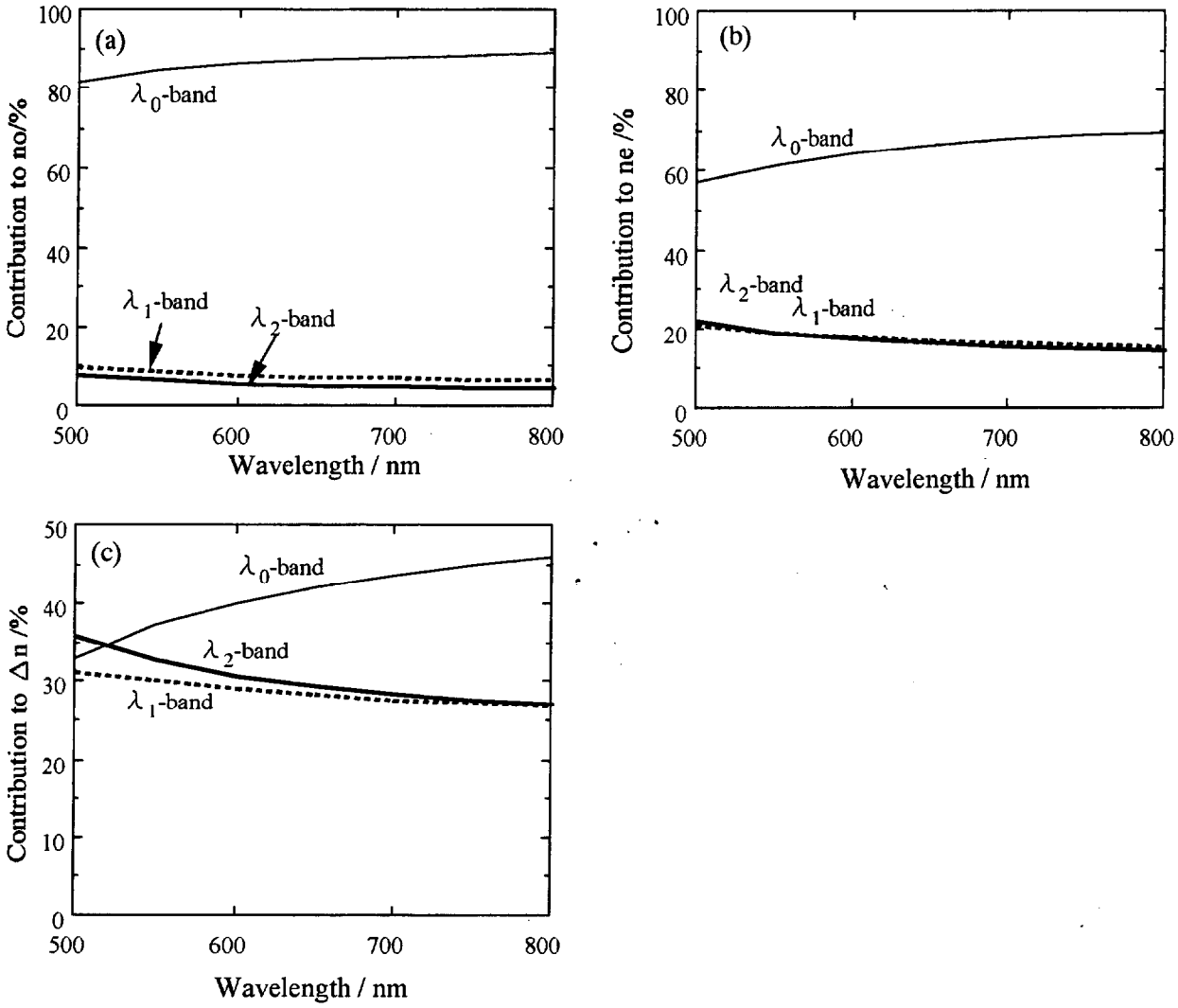


FIGURE 3-12 Contribution of each band to refractive indices and birefringence of **DT1116**

TABLE 3-11 Transition energy and contribution of **DT1115** and **DT1116**

DBT1115				**DBT1116**			
Transition energy (nm)		Contribution		Transition energy (nm)		Contribution	
Abs.	Calc.	MO number	%	Abs.	Calc.	MO number	%
372	371	91--> 92	46.7	380	363	87--> 90	40.0
		91--> 93	15.1			86--> 91	14.5
		89--> 94	10.7			89--> 90	10.9
		90--> 93	8.1			88--> 91	7.9
		90--> 94	5.7			85--> 92	4.9
		91--> 95	1.9			88--> 90	4.5
		89--> 93	1.8			89--> 91	2.5
		84--> 98	1.8			86--> 93	2.4
		88--> 94	1.7			89--> 92	2.1
		89--> 92	1.3			87--> 92	2.0
						87--> 94	1.6
347	364	90--> 92	52.7			85--> 94	1.2
		89--> 93	12.0			88--> 93	1.1
		91--> 93	7.2			84--> 95	1.0
		91--> 94	6.3				
		89--> 92	5.9	356	353	87--> 90	22.9
		88--> 95	3.2			88--> 91	21.1
		88--> 93	1.8			89--> 90	9.7
		89--> 94	1.7			86--> 93	6.2
		87--> 97	1.2			86--> 91	5.9
						89--> 91	5.9
						89--> 92	5.3
						88--> 90	4.9
						87--> 94	3.9
						85--> 92	2.8
						88--> 92	2.5
						89--> 94	1.7
						85--> 94	1.4

contributed to the λ_2 transition with respect to **DT1115**.

However, in the case of **DT1116**, the contribution of the transition from the MO lower than HOMO was the largest. The contribution rates of each MO to Δn at 600 nm are summarized in TABLE 3-12. **PA1068**, which is a three-ring phenylacetylene, was analyzed in the same way for comparison. The main origins of Δn for **DT1115** and **DT1116** were MOs lower than the HOMO and this resulted in the combination of large Δn and lack of colour. In contrast to this, **PA1068** which is a simple π-conjugated compound showed a main contribution from the HOMO.

From the analysis of the contribution of each band to Δn, it has confirmed that the molecular design involving the combination of the dibenzothiophenyl ring and the ethynyl group has been successful in increasing Δn, while restraining the red-shift of the UV absorption spectra.

3.4 Conclusions

We synthesized new thiopheny acetylene and benzothiazolyl acetylene homologues, and evaluated their thermal and optical properties in the comparison with phenyl acetylene homologues. These series had poor liquid crystallinity when compared with phenyl acetylene type. The conjugated hetero ring systems shifted UV absorption spectra to the visible region, as a result they showed yellow or brownish colour.

The thiophenylacetylenes exhibited low melting points and poor liquid crystallinity. Δn was also lower because of lower anisotropy of polarizability. Exchanging of the phenyl ring to a benzothiazole ring was effective to increase

TABLE 3-12 Contribution rates of each MO to Δn at 600nm

MO level [1)]	Contribution rate (%)		
	DT1115	**DT1116**	**PA1068**
HOMO	13.0	11.3	22.9
HOMO-1	19.9	11.1	4.8
HOMO-2	10.2	20.1	12.3
HOMO-3	2.0	8.8	2.1
HOMO-4	0.4	3.1	3.2
HOMO-5	0.0	0.3	0.5

1) HOMO-X; X is the MO number from HOMO
(ex. HOMO-1 is the second HOMO)

Δn, but it decreased the liquid crystallinity. The benzothiazole type did not exhibit a liquid crystal phase without the compounds with a diacetylene unit. However they decomposed at around 150℃. Further research on improvement of liquid crystallinity, heat stability and colour of materials would be needed if incorporating heterocyclic rings to the conjugated core part.

On the basis of the investigation of thiophenylacetylene and benzothiazolylacetylene series, new heterocyclic molecules, which were expected to give high $\Delta\alpha$ and short UV absorption spectra, were designed. The dibenzothiophenylacetylene homologues exhibited wide nematic phase ranges and very high Δn over 0.6 and values of 0.5 by direct measurements. The compound with two dibenzothiophenyl rings was colourless, so that we have succeeded in obtaining colourless super-high Δn liquid crystals. We also analyzed the contribution of the transition band to the refractive indices and birefringence.

References of Chap. 3

[1] H.H.B. Meng, L.R. Dalton and S.T. Wu, 1994, Mol. Cryst. Liq. Cryst.,**259**,303

[2] S.T.Wu, J.D.Margerum, M.S.Ho, M.Fung, C.S.Hsu, S.M..Chen and K.T.Tsai, 1995, Mol.Cryst.Liq. Cryst.,**261**,79

[3] C.S.Hsu, K.T.Tsay, A.C.Chang, S.R.Wang and S.T.Wu, 1995, Liq. Cryst., **19**,4,409

[4] K.J. McEwan, S.Day, D.G.MaCdonnel and K.J.Harrison, 1992, SPIE-Int. Soc. Opt. Eng.,**1692**,118

[5] M.Funahashi and J.Hanna, 1996, Jap. J.Appl. Phys., **35**, L703

[6] M.Funahashi and J.Hanna, 1997, Phy. Rev. Lett., **78**, 11, 2184

[7] C.Sekine, K.Fujisawa, N.Konya and M.Minai, 1998, JP98-43289

[8] C.Sekine, K.Fujisawa, N.Konya and M.Minai, 1999, Mol. Cryst. Liq. Cryst.,**332**,235

[9] C.Sekine, K.Fujisawa, K.Iwakura and M.Minai, Mol. Cryst. Liq. Cryst., in press

[10] M.F.Vuks, Opt. Spektrosk.,1966, **20**, 644

[11] S.T.Wu, J. Appl. Phys. 1991, **69**,4,2080

[12] S.T.Wu, Phys. Rev. A, 1986, **33**,1270

[13] S.Kawauchi, H.Muta, M.Satoh, J.Komiyama, J.Watanabe, Y.Tamura, K.Mori and K.Suzuki, 2000, Nonlinearoptics, **26**,91

Chapter 4 Development of high Δn liquid crystal mixtures with wide nematic range

-phenylacetylene-based homologue containing a cyclohexyl group-

4.1 Introduction

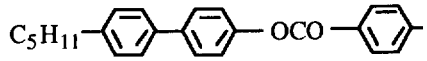
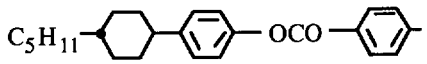
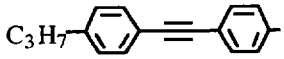
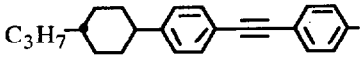
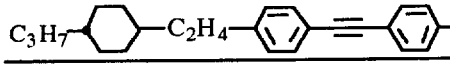
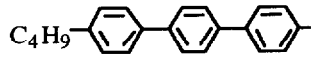
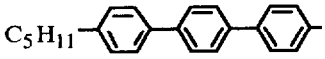
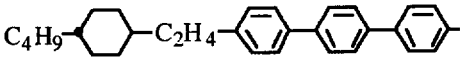
In Chap.2, we described new high birefringence 3-ring phenylacetylene compounds, which reduced problems like high melting point or poor solubility by the introduction of a substituent into the central core ring [1-4]. A range of liquid crystalline compounds is needed, however, for the formulation of liquid crystal mixtures having controllable physical properties. Different type liquid crystals from the 3-ring phenylacetylenes were also developed in Chap. 3. Some of them are expected to be effective components of high Δn liquid crystal mixtures, since they exhibit very high Δn. However they have relatively high nematic temperature so that another component which lowers the liquid crystal temperature are needed.

New core-substituted phenylacetylene-based homologues containing a cyclohexyl group have been also developed. It is known that cyclohexyl or cyclohexylethyl groups can have the effect of lowering or widening the nematic range, see TABLE 4-1, and these types of compounds are commonly used as components in practical liquid crystal mixtures. In this chapter synthesis and physical properties of new phenylacetylene derivatives containing cyclohexyl and cyclohexylethyl groups are reported.

4.2 Experimentals

The preparative routes for the cyclohexyl and

TABLE 4-1 Examples of liquid crystals with a cyclohexyl group

Compounds	Transition temperatures / ℃	Ref.
	K · 101 · N · 166 · I	[5]
	K · 59 · N · 158 · I	[6]
	K · 22(N · 15) · I	[7]
	K · 87 · N · 201 · I	[8]
	K · 42.5 · S · 90 · N · 158.8 · I	[9]
	K · 208 · S · 218 · I	[10]
	K · 192 · SA · 213 · I	[11]
	K · 149.8 · S · 215.5 · S · 263.0 · N · 267.0 · I	[12]

Pharenthese () denote a monotropic transition.
K : crystal, S : smectic phase (not identified in detail) , N : nematic phase, I : isotropic

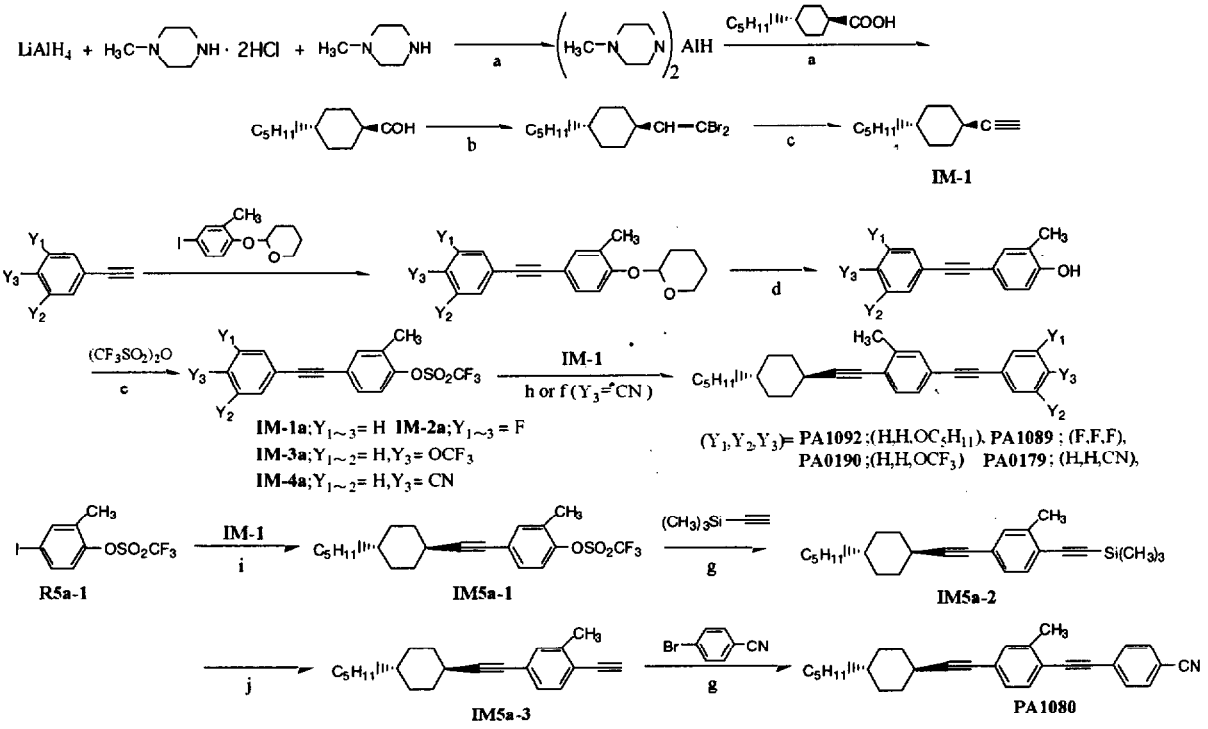
cyclohexylethyl derivatives including various intermediates are shown in schemes 4-1 and 4-2, respectively. The structures of the final compounds and various synthetic intermediates were characterized by the same method mentioned in Chap.2. All compounds of these series were more than 99 percent pure according to HPLC (ODS A-212 column, Sumika Chemical Analysis Service). Physical properties were also evaluated by the same method in Chap. 2.

4.3 Results and discussion

4.3.1 Physical properties of cyclohexyl series

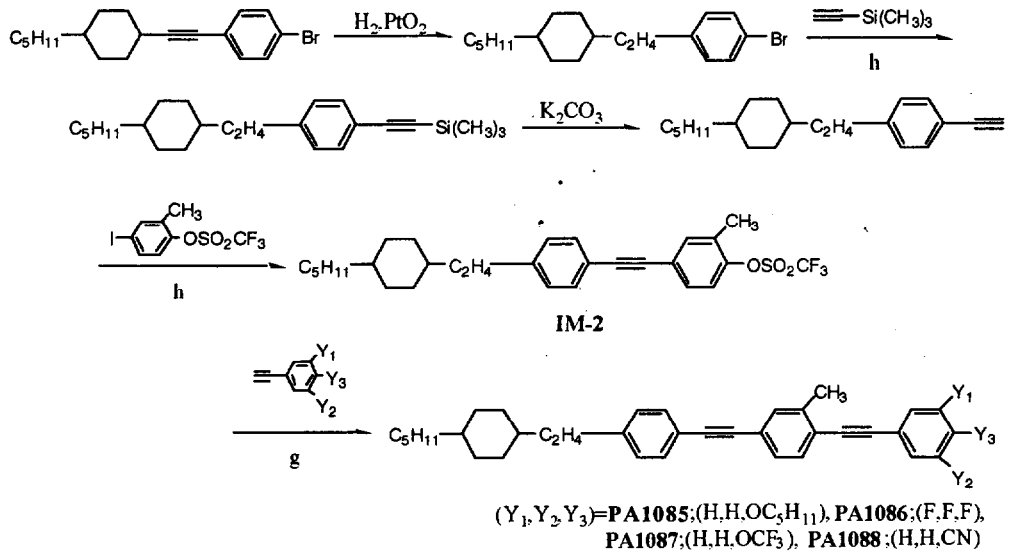
The phase transition temperatures, enthalpies and birefringence (Δn) of cyclohexyl series (**CABAB**) are listed in TABLE 4-2. Tolane and three-ring phenylacetylene-based compounds are also included for comparison. The compounds shown in TABLE 4-2 exhibited nematic enantiotropic phases. Exchanging a phenyl ring with a cyclohexyl ring lowered the liquid crystal temperature range compare for example **PA1092** with **PA1068**. It was considered that this was a result of the reduction in the anisotropic polarizability arising from the decrease in the conjugation length within these aromatic system. Compound **PA1090**, containing a trifluoromethoxy terminal group, exhibited a smectic A phase. The effects of the terminal groups were almost the same as observed for three-ring phenylacetylene-based compounds [13]. This series exhibits small heats of fusion when compared with other high Δn type liquid crystals. Therefore the **CABAB** series is expected to provide useful components for liquid crystal mixtures from the view point of solubility.

The values Δn and viscosity for the **CABAB** series are shown in TABLE 4-3. The birefringence of these compounds is around 0.3, which is moderately high. The value of Δn was reduced on exchanging the phenyl group with a cyclohexyl ring because



SCHEME 4-1 The synthesic route of ***CABAB*** *homologues*

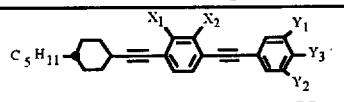
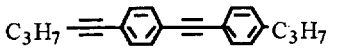
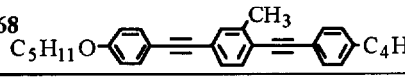
a Dry THF b Zn / PPh_3 / CBr_4 / CH_2Cl_2 c *n*-BuLi,H_2O d H_2O/Methanol/*p*-toluenesulphonic acid e Pyridine,4-pyroridinopyridine
f $PdCl_2$ (PPh_3) / PPh_3 / Triethylamine g $PdCl_2(PPh_3)$/PPh_3/Triethylamine/DMF h $PdCl_2(PPh_3)$ / PPh_3 / CuI / Triethylamine
i $PdCl_2(PPh_3)$ / PPh_3 / CuI / Triethylamine / Ethylacetate j K_2CO_3/Methanol



SCHEME 4-2 The synthesic route of **CEBABAB** homologues

g $PdCl_2(PPh_3)$ / PPh_3 / Triethylamine / DMF h $PdCl_2(PPh_3)$/PPh_3/CuI/Triethylamine

TABLE 4-2 Phase transition temperatures and enthalpies for the **CABAB** homologues.

Compounds						Transition temperatures (°C) and enthalpies(in square brackets[], kJ/mol)			
	X_1	X_2	Y_1	Y_2	Y_3	· K	S_A	N	I
PA1092	CH_3	H	H	H	OC_5H_{11}	· 79 [26.9]		· 191 [1.5]	·
PA1089	CH_3	H	F	F	F	· 56 [21.9]		· 98 [0.4]	·
PA1090	CH_3	H	H	H	OCF_3	· 65 [24.0]	· 93 [0.09]	· 167 [1.0]	·
PA1079	CH_3	H	H	H	CN	· 78 [29.0]		· 228 [3.6]	·
PA1080	H	CH_3	H	H	CN	· 88 [25.5]		· 212 [1.0]	·
Reference **PA1035**						· 99 [32.9]			·
PA1068						· 83 [16.4]		· 201 [1.4]	·

Pharenthese () denote a monotropic transition.
K: crystal, S_A; smectic A phase, N; nematic phase, I; isotropic

TABLE 4-3 Physical properties of the **CABAB** homologues

Compounds	n_o	n_e	Δn	η [mPa · s]
PA1092	1.502	1.801	0.299	220
PA1089	1.499	1.746	0.247	144
PA1090	1.481	1.752	0.272	88
PA1079	1.512	1.877	0.365	181
PA1080	1.515	1.885	0.370	258
PA1035	1.524	1.875	0.351	-
PA1068	1.525	1.955	0.430	156

Optical properties (at 20℃ and λ = 589 nm) and viscosity (at 20 ℃) were extrapolated values of the mixture [liquid crystal (10wt%) and MJ931381 (90wt%)]

of the reduction in the conjugation length. The presence of fluorine and trifluoromethoxy groups also reduced Δn, whereas the presence of the cyano group increased Δn compared with that of the corresponding materials containing an alkoxy group. FIGURE 4-1 shows the temperature dependence of Δn measured for individual compounds. This figure shows essentially the same trends as found for the extrapolated values obtained from the mixtures. Compounds **PA1089** and **PA1090**, however, exhibited almost the same value of Δn as **PA1092** , which differs from the behavior of the Δn values evaluated using mixtures. The difference in Δn between the values obtained for individual compounds and mixtures was caused by the difference in T_{NI}. FIGURE 4-2 shows the temperature dependence of the order parameter of each compound. The order parameter was not affected by either the terminal groups or the core structure.

The viscosity of the cyclohexyl-containing compounds was larger than that of the corresponding phenyl homologue (compare **PA1092** with compound **PA1068**). The effect of the terminal group on the viscosity was similar to that seen for previously studied series, e.g., OCF_3 reduced the viscosity while an alkyl group increased it.

4.3.2 Physical properties of cycrohexylethyl series

The phase transition temperatures and associated enthalpy of cyclohexylethyl series (**CEBABAB**) are listed in TABLE 4-4. Compounds **PA1085**～**PA1088** exhibit enantiotropic liquid crystal phases. Compounds **PA1085** and **PA1088** exhibit only a nematic phase, whereas compounds **PA1086** and **PA1087** exhibit a smectic A phase. The presence of a cyclohexylethyl group increased T_{NI} remarkably and in a similar manner as seen for other series, see TABLE 4-1. Compound **PA1088** exhibits a nematic phase at temperatures higher than 300℃. The melting points were not greatly changed by introducing the cyclohexylethyl group.

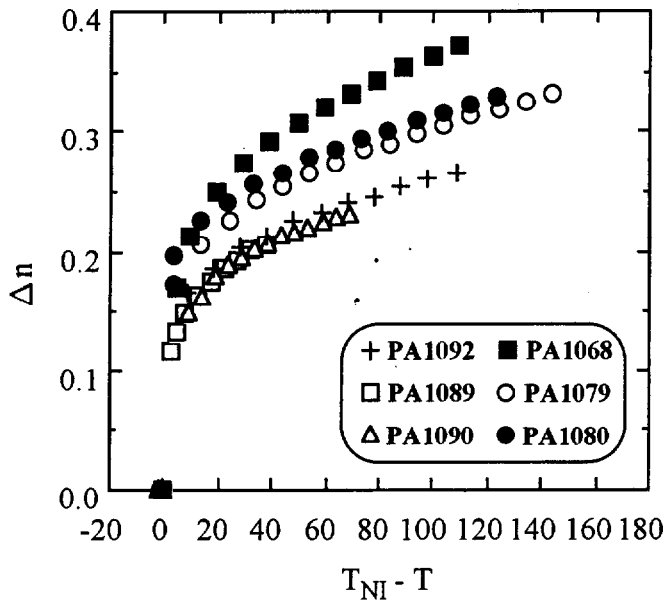


FIGURE 4-1 Temerature dependence of Δn of **CABAB** homologues

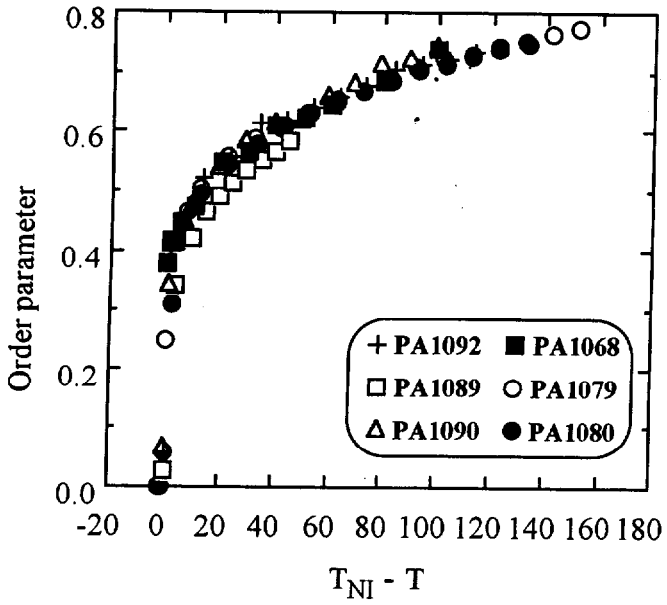
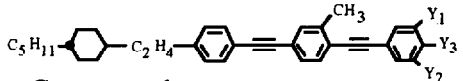


FIGURE4-2 Temerature dependence of order parameter of **CABAB** homologues

TABLE 4-4 Phase transition temperatures and enthalpies for the **CEBABAB** homologues.



Compounds	Y_1	Y_2	Y_3	Transition temperatures (°C) and enthalpies(in square brackets[], kJ/mol) K	S_A	N	I
PA1085	H	H	OC_5H_{11}	· 108[26.2]		· 267[3.0]	·
PA1086	F	F	F	· 102[30.7](· 100 [2.0])		· 220[3.1]	·
PA1087	H	H	OCF_3	· 97[26.4]	· 216[0.17]	· 259[2.9]	·
PA1088	H	H	CN	· 115[29.3]		· <300	

Pharenthese () denote a monotropic transition.
K: crystal, S_A; smectic A phase, N; nematic phase, I; isotropic

The enthalpies associated with the nematic-isotropic transition were smaller than those exhibited by the three-ring phenylacetylene series.

The values of birefringence and viscosity for the **CEBABAB** series are shown in TABLE 4-5. The values of Δn for this series were found to be around 0.35～0.45. Thus, Δn was reduced by introducing the cyclohexylethyl group. The effects of the terminal groups were essentially the same as those observed for the three-ring phenylacetylene-based compounds [3]. The presence of a fluorine atom or trifluoromethoxy group decreased Δn while a CN group increased Δn. FIGURE 4-3 shows temperature dependence of Δn measured for individual compounds. As for the **CEBABAB** series, the terminal group did not affect Δn without CN group type. These data also showed essentially the same trends as those observed for the extrapolated values of Δn measured using mixtures. But the cyclohexylethyl-containing compounds exhibited lower values of Δn than the corresponding three-ring phenylacetylene-based materials. FIGURE 4-4 shows the temperature dependence of the order parameter for the individual compounds. The order parameter was not significantly changed on varying the terminal groups or by introducing cyclohexylethyl groups.

The viscosity of the **CEBABAB** series was lower than that of either the three-ring phenylacetylene-based materials or the **CABAB** series. It was considered that the flexibility of the C-C bond of the ethyl group decreased the molecular interactions.

TABLE 4-5 Physical properties of the **CEBABAB** homologues

Compounds	n_o	n_e	Δn	η [mPa·s]
PA1085	1.510	1.896	0.386	131
PA1086	1.507	1.857	0.350	114
PA1087	1.492	1.847	0.356	59
PA0188	1.515	1.983	0.467	290

Optical properties (at 20 ℃ and λ = 589nm) and viscosity (at 20℃) were extrapolated values of the mixture [liquid crystal (10wt %) and MJ931381 (90wt %)]

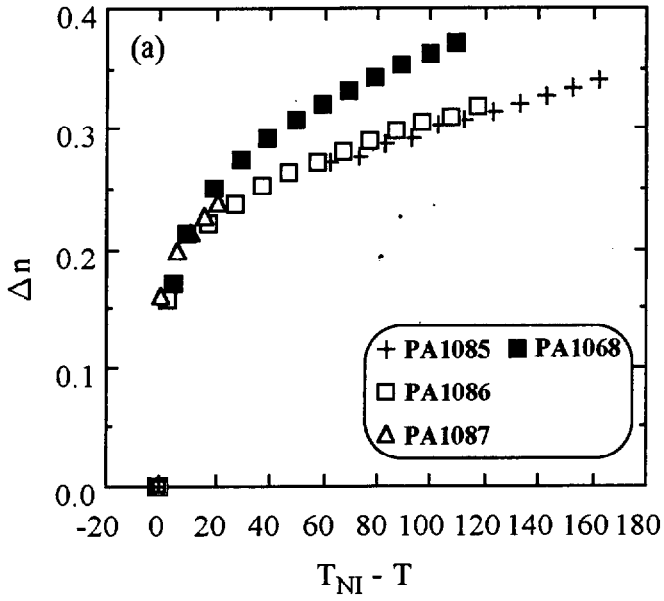


FIGURE 4-3 Temerature dependence of Δn of **CEBABAB** homologues

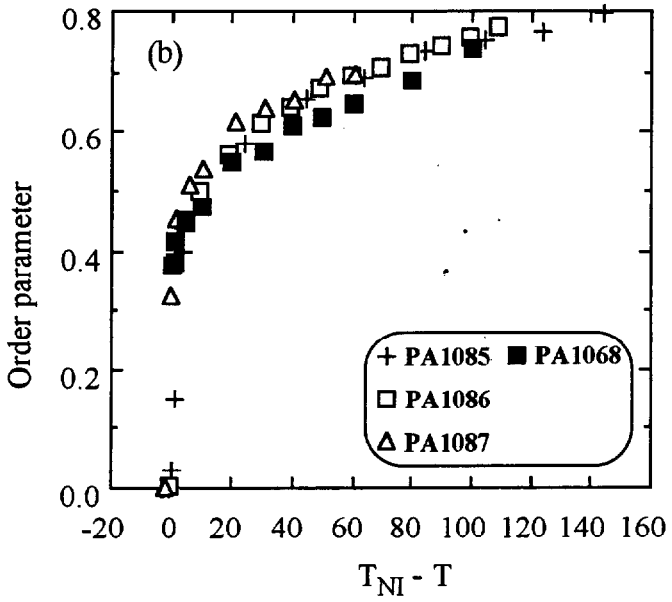


FIGURE 4-4 Temerature dependence of order parameters of **CEBABAB** homologues

4.3.3 Birefringence and polarizability

In order to understand the effects of cyclohexyl and cyclohexylethyl groups on Δn, Δn was calculated using the equations proposed by Vuck [13].

$$\frac{(n_e^2-1)}{n^2+2}=\frac{N}{3\varepsilon_0}(\alpha+\frac{2\Delta\alpha S}{3}) \qquad (1)$$

$$\frac{(n_o^2-1)}{n^2+2}=\frac{N}{3\varepsilon_0}(\alpha-\frac{\Delta\alpha S}{3}) \qquad (2)$$

where $n^2=(n_e^2+2n_o^2)/3$. $\Delta\alpha$ denotes the anisotropic molecular polarizability, α is the molecular polarizability, S is the order parameter, ε_o is the static dielectric constant and N is the number of molecules per unit volume. $\Delta\alpha$ and α were calculated using MOPAC93(AM1 method) for an isolated molecule. The number density was approximated using the group contribution method of Fedors [14]. It is known that the calculated polarizability obtained using the AM1 method is useful in predictions of Δn [15,16]. The trends of the effects of cyclohexylethyl group on the experimental Δn were almost the same as seen for the calculated values. Therefore, the decrease of Δn on introducing either a cyclohexyl or cyclohexylethyl group was caused by the change in the polarizability.

The values of Δn estimated from the extrapolation of the values for 10% mixtures are plotted against the calculated values in FIGURE4-5. It was assumed that there was no significant difference between the order parameters of compounds in the mixture. An order parameter of 0.7 was used in the calculations. For reference in the region of low birefringence, the values of Δn for 4-cyano-4'-penthylbiphenyl, **5CB**, and 4-(trans-4-penthylcyclohexyl)benzonitlile, **5PCH**, are also plotted. The experimental and calculated values of

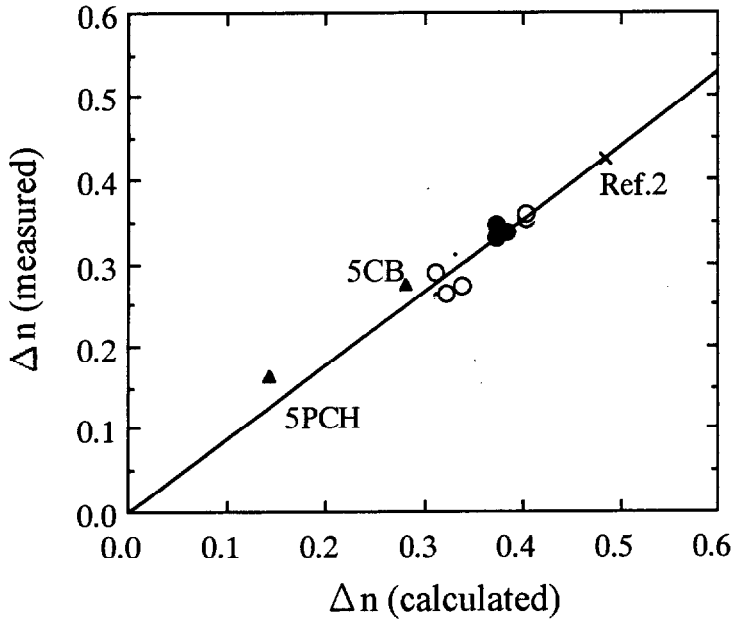


FIGURE4-5 Measured optical birefringence Δn vs calculated values

○ ; CABABs ●; CEBABABs × ; 3-ring phenylacetylene

Δn show a good linearly proportional relationship.

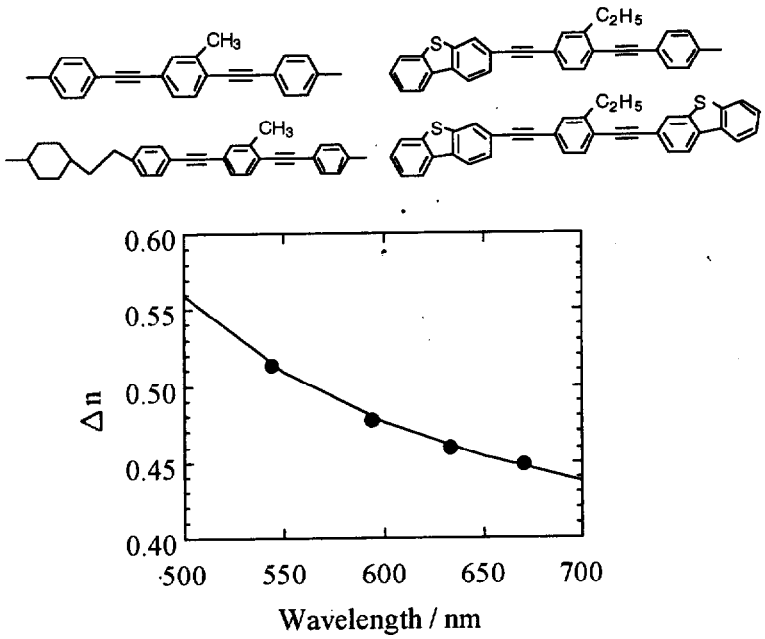
4.4. The preparation of high Δn liquid crystal mixture

In the investigation explained in Chap.2 ~ Chap.4, a variety of high Δn liquid crystal compounds were obtained. In this section, an example of high Δn room temperature nematic mixture is introduced.

The three-ring phenylacetylene-based compounds were used as main components because of high Δn and wide nematic temperature. The cyclohexylethyl compounds (**CEBABAB** series) were effective in decreasing the lower limit of nematic temperature. The dibenzotyophenylacetylne compounds increased the value of Δn by adding only small amount of them to the mixture. The birefringence of the liquid crystal mixture containing these compounds is shown in FIGURE 4-6. It exhibited wide nematic range including the room temperature and very high Δn value of over 0.5 at 20℃.

4.5. Conclusions

The synthesis and characterization of cyclohexyl and cyclohexylethyl-containing phenylacetylene-based compounds have been described. They exhibited wide nematic phases and moderately high Δn values. The order parameter was not affected by introducing either a cyclohexyl or a cyclohexylethyl group and the values expected for Δn based on calculated polarizabilities were obtained experimentally.



Nematic Phase ; ~175℃

Δn=0.51

FIGURE 4-6 Components and physical properties of the high Δn room temperature liquid crystal mixture

References of Chap. 4

[1] C.Sekine, K.Fujisawa, N.Konya and M.Minai, 1998, JP 98-43289

[2] C.Sekine, K.Fujisawa, N.Konya and M.Minai, 1999, Mol. Cryst. Liq. Cryst., **332**, 235

[3] C.Sekine, K.Fujisawa, N.Konya and M.Minai, 1998, Proc. of IDW98, p839

[4] C.Sekine, K.Fujisawa, N.Konya and M.Minai, 1999, Proc. of IDW99, p411

[5] LiqCryst 3.4 Database of Liquid Crystalline Compounds, 2000, Computer Software, Fujitsu Kyusyu System Engineering Ltd.

[6] M.Koden, T.Kuratate, M.Shiomi, F.Funada, H.Inoue, K.Tsuchiya, A.Sugiura, T.Fujii, 1990, EP414.230

[7] H.Takatsu, M.Sasaki ,Y.Tanaka, and H.Sato, 1988, US4726910

[8] H.Takatsu, K.Takeuchi, Y.Tanaka and M.Sasaki, 1986, Mol. Cryst. Liq. Cryst., **141**, 279

[9] Y.Goto, K.Kitano, and T.Ogawa, 1989, Liq. Cryst., **5**, 225

[10] H.Schubert, H.J.Lorenz, R.Hoffmann. and F.Franke, 1966, Z. Chem., **6**, 337

[11] G.W.Gray, M.Hird, and K.J.Toyne, 1991, Mol. Cryst. Liq. Cryst., **204**, 43

[12] A.Boller, M.Petrzika, A.Germann, and M.Schadt, 1984, EP110.205

[13] M.F.Vucks, Opy. & Spectroscopy, 1966, **20**, 361

[14] R.F.Fedors, 1974, Polym.Eng.Sci., **14**, 147

[15] D.Demus and T.Inukai, 1999, Liq. Cryst., 26, 9, 1257

[16] M.Klasen, M.Bremer, A.Gotz, A.ManabeA. S.Naemura and K.Tarumi, 1998, Jpn. J.Appl.Phys., **37**, L945

Chapter 5 Development of high Δn photopolymerizable liquid crystals

5.1 Introduction

Polymerizable liquid crystals are useful for many applications of electronic devices. Many types of liquid crystal monomers, oligomers and polymers have been investigated for use of as LCD components [1-3]. Liquid crystal monomers, which have one polymerizable group, have been and continue to be extensively studied because pendant-type polymers have application potential in switching devices and as optical free standing films. Cyanobiphenyl-containing materials, which are representative nematic compounds, were investigated and the physical properties of the monomers and polymers were compared [4]. The birefringence was reduced by polymerizations because the orientational order decreased. Recently liquid crystal monomers containing two polymerizable groups have been investigated. This type of polymer, for which nematic orientations are frozen by photopolymerization, are called in situ photopolymerized polymers [5-9]. These materials are better suited for static applications, such as optical films. Three-ring phenylbenzoate monomers with either one or two polymerizable groups and their polymers were systematically studied. This revealed that the relationships between the optical properties of the monomers and polymers are complex.

High birefringence (Δ n) liquid crystals are useful materials for application in reflective-type LCDs, spatial light modulators, compensation films, reflectors and polarizers [10-12]. The fabrication of such optical components, requires high Δ n polymerizable liquid crystal monomers. We have studied three-ring phenylacetylene

compounds as high Δn liquid crystals having improved liquid crystal temperature range, solubility and photostability [13-15]. On the basis of the results obtained in Chap. 2 and Chap.3, we have incorporated the core structures of these series into photopolymerizable liquid crystal monomers. In this Chap., we report the physical properties of new photopolymerizable three-ring phenylacetylene (3PA) diacrylate monomers and of their polymeric networks.

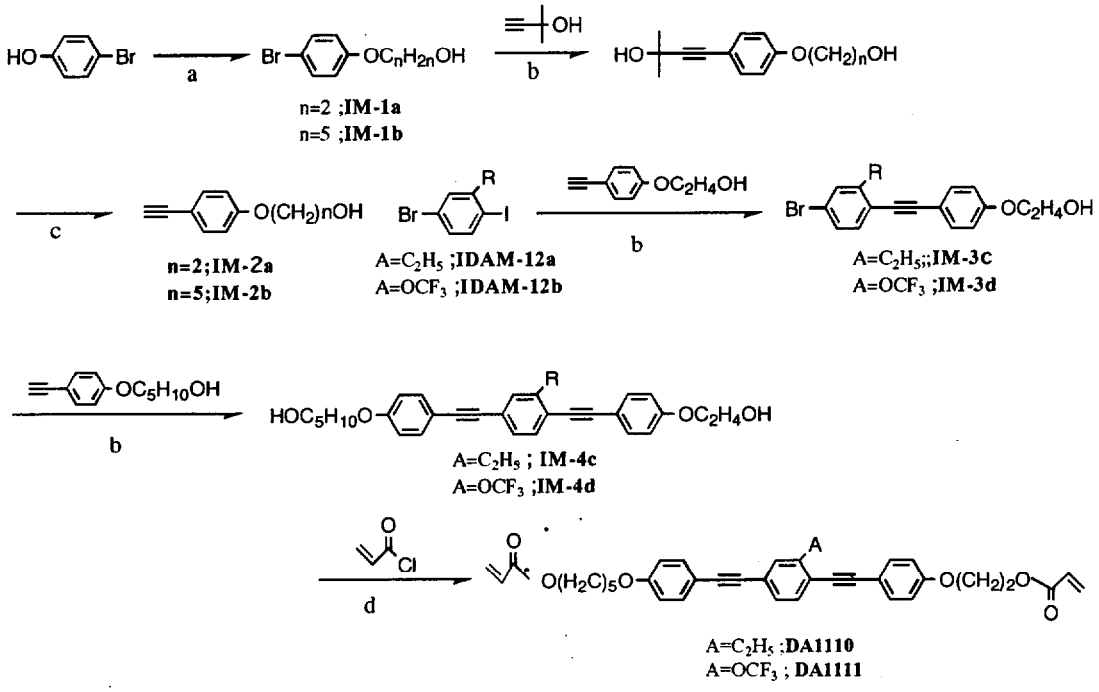
5.2 Experimental

We synthesized the three-ring phenylacetylene derivatives and a dibenzothiophenylacethylene compound as shown in reactional SCHEME 5-1 ~ 5-3 and SCHEME 5-4 respectively. All compounds investigated here were synthesized by coupling of acrylic chloride with hydroxyl derivatives. The structures of final compounds and various synthetic intermediates were confirmed by the same method menthioned in Chap.2. All spectra were recorded in $CDCl_3$ with TMS as internal standard. They exhibited ^1H NMR spectra (UNITY300, Varian 300 M Hz) which are in accordance with their structures. Mass spectra (SX102, JEOL) were also measured and they coincided with their predicted molecular weight. All compounds of this series were more than 99 percent pure according to HPLC(ODS A-212 column, Sumika Chemical Analysis Service).

Physical properties were also evaluated by the same method as Chap.2.

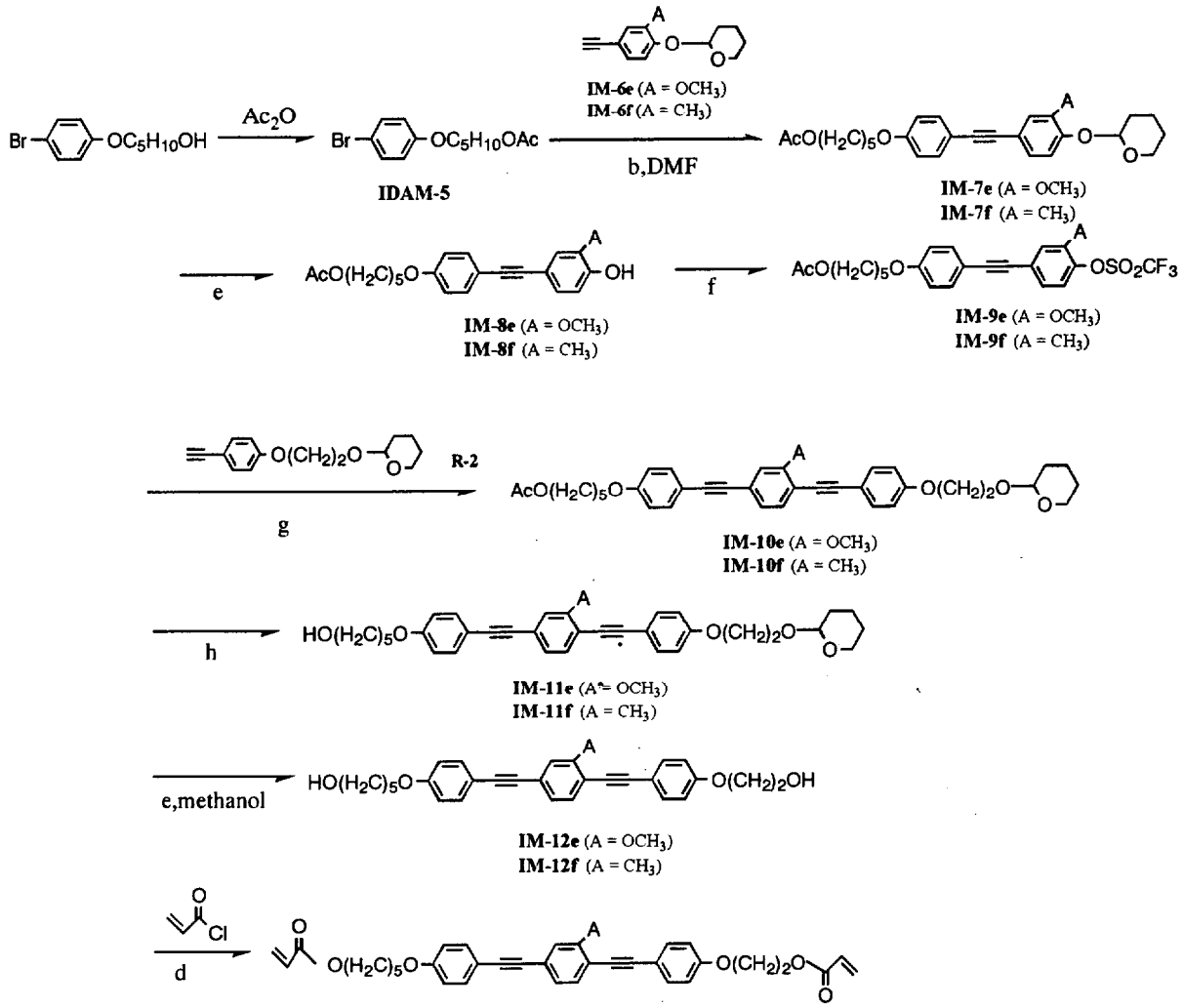
5.3 Physical properties of three-ring phenylacethylene-based diacrylates containing substituents

The phase transition temperatures of the acrylic



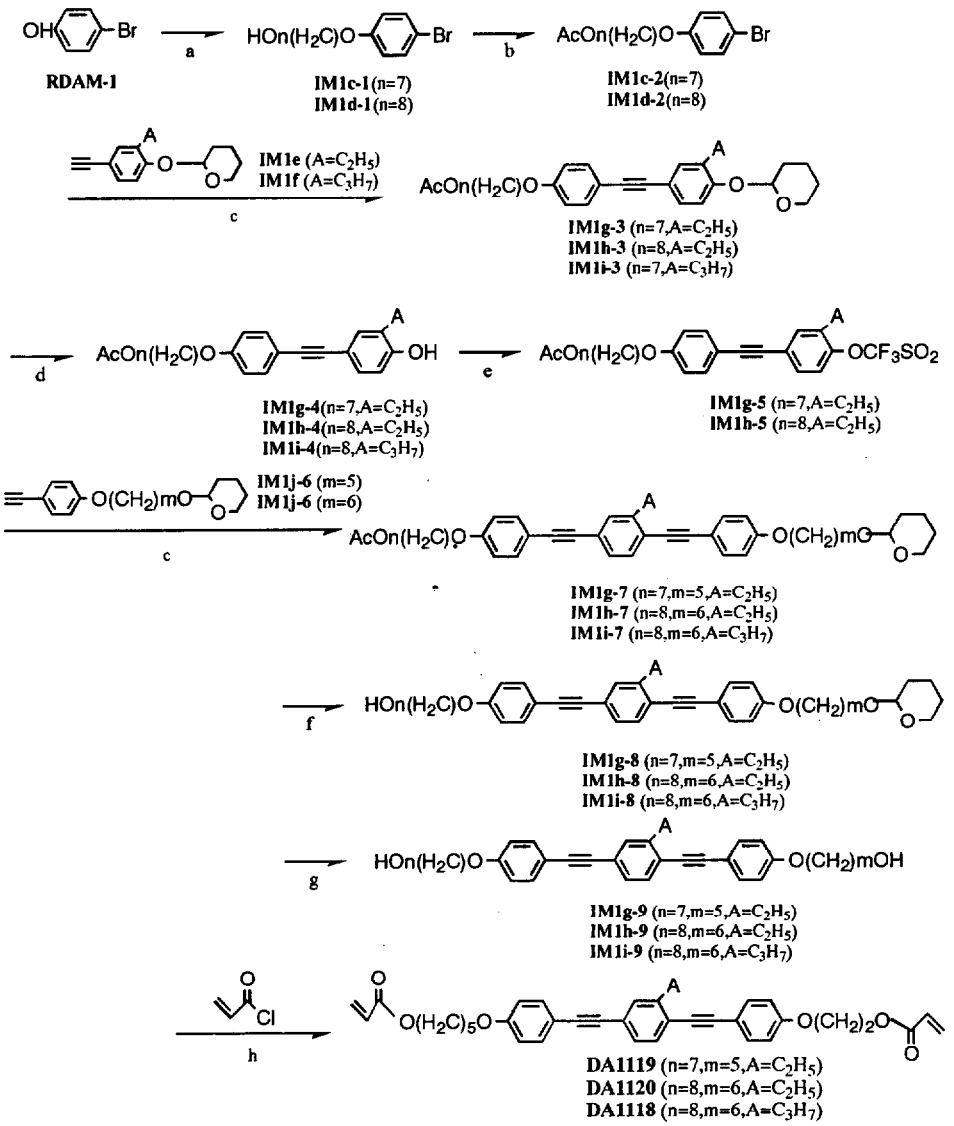
a $Br(CH_2)_5OH$ / K_2CO3, b $PdCl_2(PPh_3)_2$ / PPh_3 / Triethylamine / CuI c NaOH / Toluene d THF

SCHEME 5-1



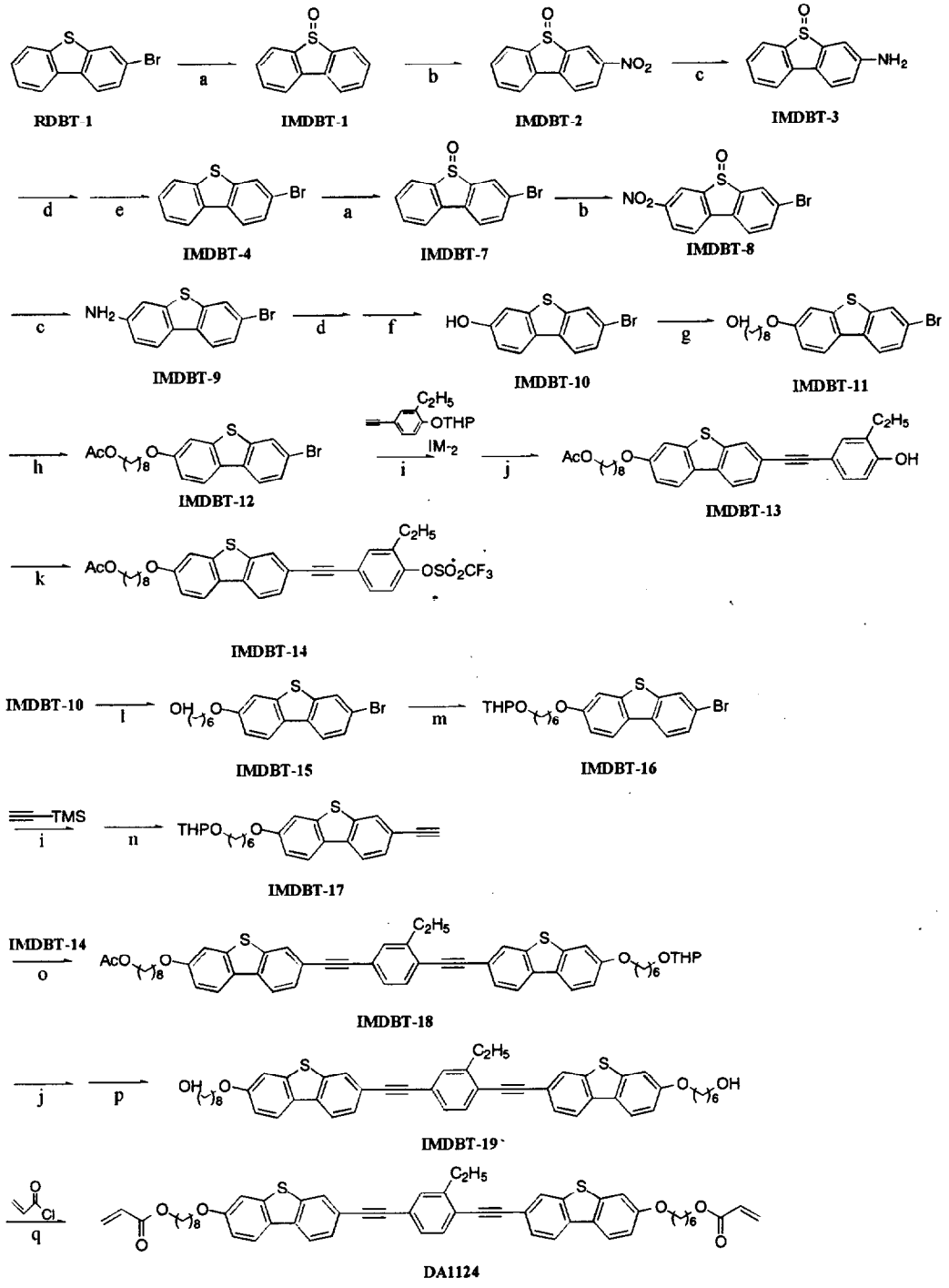
e *p*-Toluenesulfonic acid / methanol f $(CF_3SO_2)_2O$ / pyridine / 4-pyrrolydin-1-yl pyridine
g $PdCl_2(PPh_3)_2$ / triethylamine / DMF h $LiAlH_4$/THF

SCHEME5-2



SCHEME 5-3

a $Br(CH_2)_nOH$ / K_2CO_3, b Ac_2O, c $PdCl_2(PPh_3)_2$ / PPh_3 / Triethylamine / DMF, d PTS/Methanol
e $(CF_3SO_2)_2O$ / 4-pyrrolydin-1-yl pyridine / Pyridine, f LAH/THF, g PTS / $CHCl_3$ / Methanol, h Triethylamine / THF



SCHEME 5-4

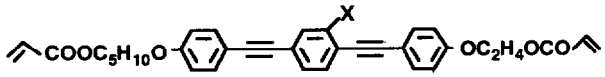
a Cl_2 / H_2O, b HNO_3 / H_2SO_4 / CH_3COOH, c $SnCl_2$ / HCl, d $NaNO_2$ / H_2SO_4, e CuBr / HBr, f H_2SO_4 / H_2O,
g $BrC_8H_{16}OH$ / K_2CO_3, h AcCl / Triethylamine, i $PdCl_2(PPh_3)_2$ / PPh_3 / Triethylamine / CuI, j p-TsOH,
k $(CF_3SO_2)_2O$ / pyridine, l $Br(CH_2)_6OH$ / K_2CO_3, m DHP / p-TsOH, n K_2CO_3, o $PdCl_2(PPh_3)_2$ / Triethylamine,
p $LiAlH_4$, q Triethylamine

phenylacetylene monomers are listed in TABLE 5-1. All of them exhibited a nematic phase. Compound **DA1110** (X = C_2H_5) and **DA1113** (X = CH_3) exhibited enantiotropical nematic phases. The presence of an acrylic terminal group narrowed the nematic range compared with the non-acrylic homologues [18]. As shown in FIGURE 5-1, the effects of the substituent group (X) on the transition temperatures of the liquid crystal phases were similar to those observed for compounds with alkyl terminal chains [18].

The Δn values of these monomers were high at around 0.35; acrylic groups tended to lower Δn as estimated from the mixtures with the host nematic, as shown in FIGURE 5-1. A comparison of Δn, measured for single compounds, for the acrylic and non-acrylic compounds is shown in FIGURE 5-2. There were no differences between these compounds, and so the lower Δn values estimated from the mixtures (see FIGURE 5-1) were a result not of the difference in polarizability but of the decreeas in T_{NI} of the mixtures with the host nematic at 20℃.

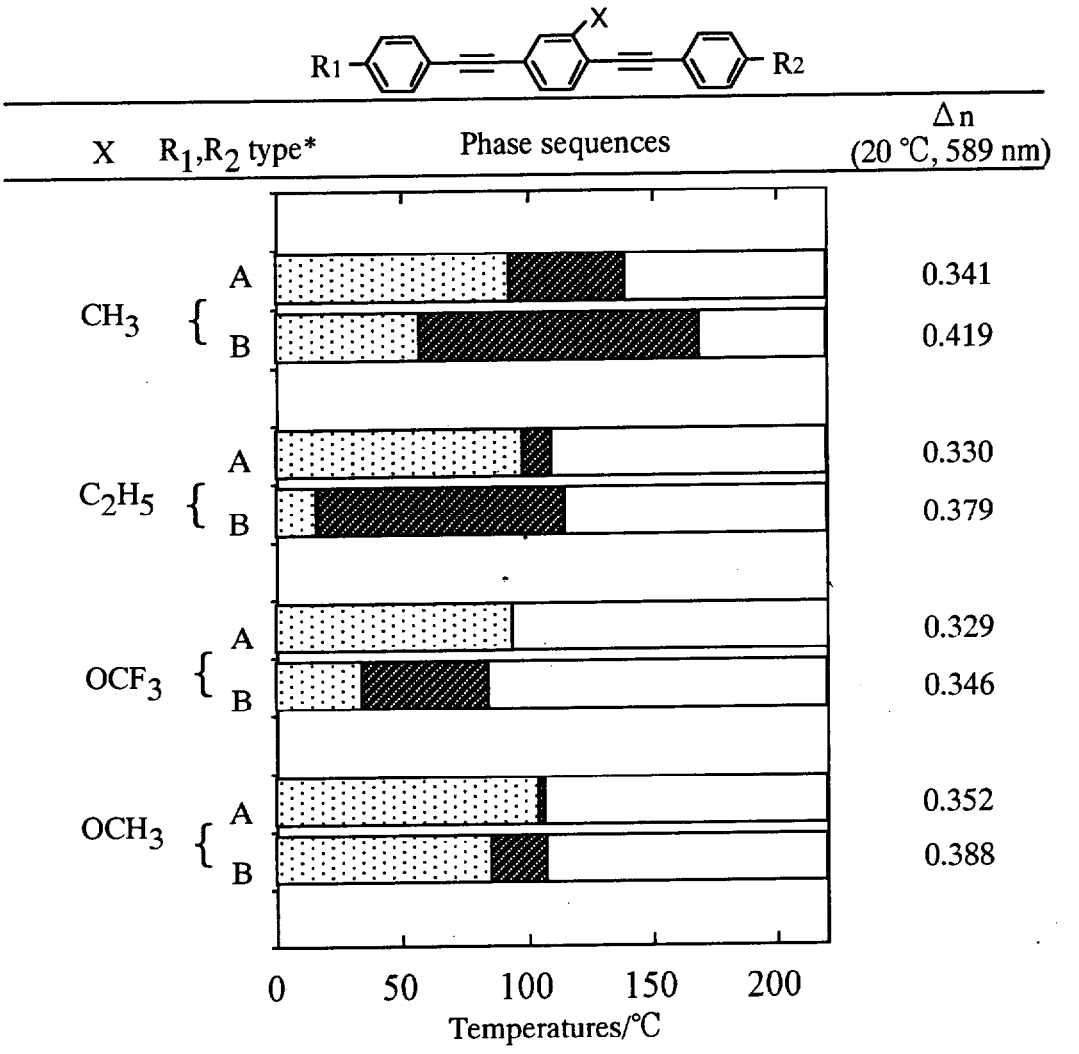
Compounds **DA1110** and **DA1113**, which exhibited an enantiotropic nematic phase, were polymerized in order to evaluate the physical properties of the corresponding polymers. FIGURE 5-3 shows the refractive indices (at 633 nm) before and after the polymerization of **DA1110**. Compound **DA1110** with 1wt% Irgacure 651 as photoiniciator was irradiated with a high pressure mercury lamp (1.4 J/cm^2) in a cell with rubbed polyimide as the alignment layers at 105℃ in the nematic phase. Polymerization was confirmed by the IR spectrum, and specially the band associated with the acrylate C=C double bonds disappeared. The optical texture after polymerization was homogeneous and almost the same as that of the monomer. Defects were not generated by polymerization and no haze was observed. Therefore, the arrangements of the cores was thought to be retained and significant shrinkage was not

TABLE5-1 Phase sequences refractive indices and Δn of the phenylacetylene monomers



	X	Transition temperatures / ℃	n_o [1)]	n_e [1)]	Δn [1)]
DA1110	C_2H_5	K・98・N・110・I	1.523	1.854	0.330
DA1111	OCF_3	K・94・(N・91) I	1.504	1.833	0.329
DA1112	OCH_3	K・105・N・107・I	1.525	1.877	0.352
DA1113	CH_3	K・93・N・140・I	1.516	1.857	0.341

1) Extrapolated values (20 ℃, 589 nm) of the mixture (monomer (10 wt%) and MJ931381 (90 wt%))



*; Type A; $R_1 = OC_5H_{10}OCOCHCH_2$, $R_2 = OC_2H_4OCOCHCH_2$

Type B; $R_1 = C_6H_{13}$, $R_2 = C_3H_7$

⊡ ;Crystal phase, ▨ ;Nematic phase, □ ;Isotropic phase

FIGURE 5-1 Effect of acrylic groups on transition temperatures and birefringence

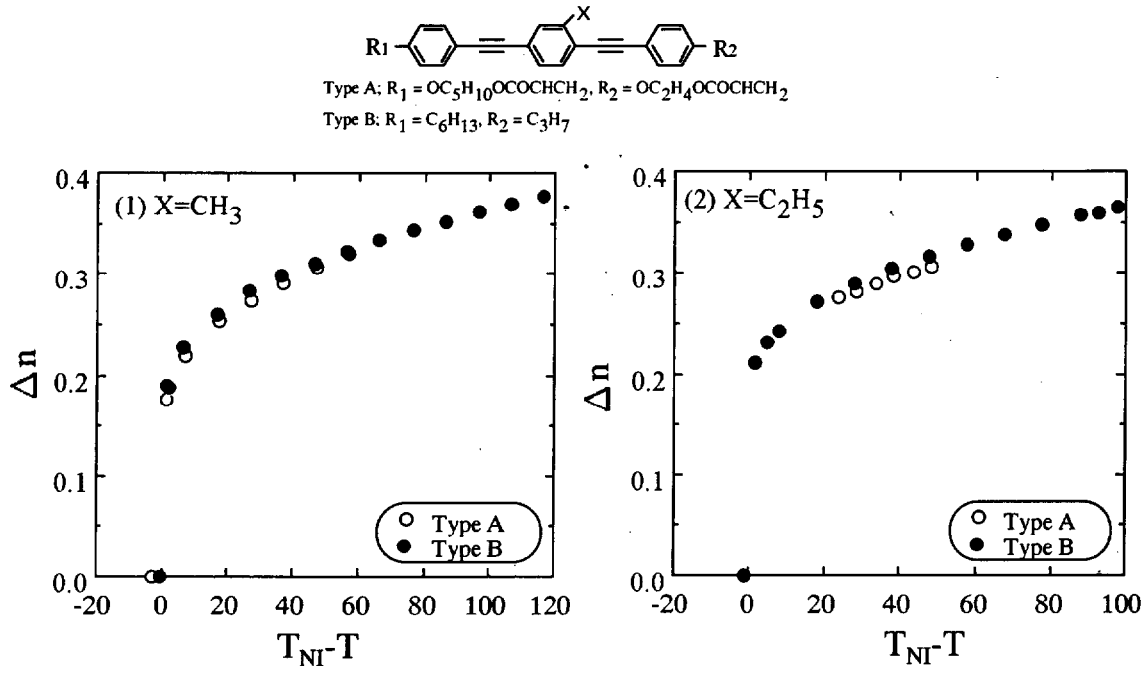


FIGURE 5-2 Effect of acrylic groups on birefringence (1) X=CH_3, (2) X=C_2H_5

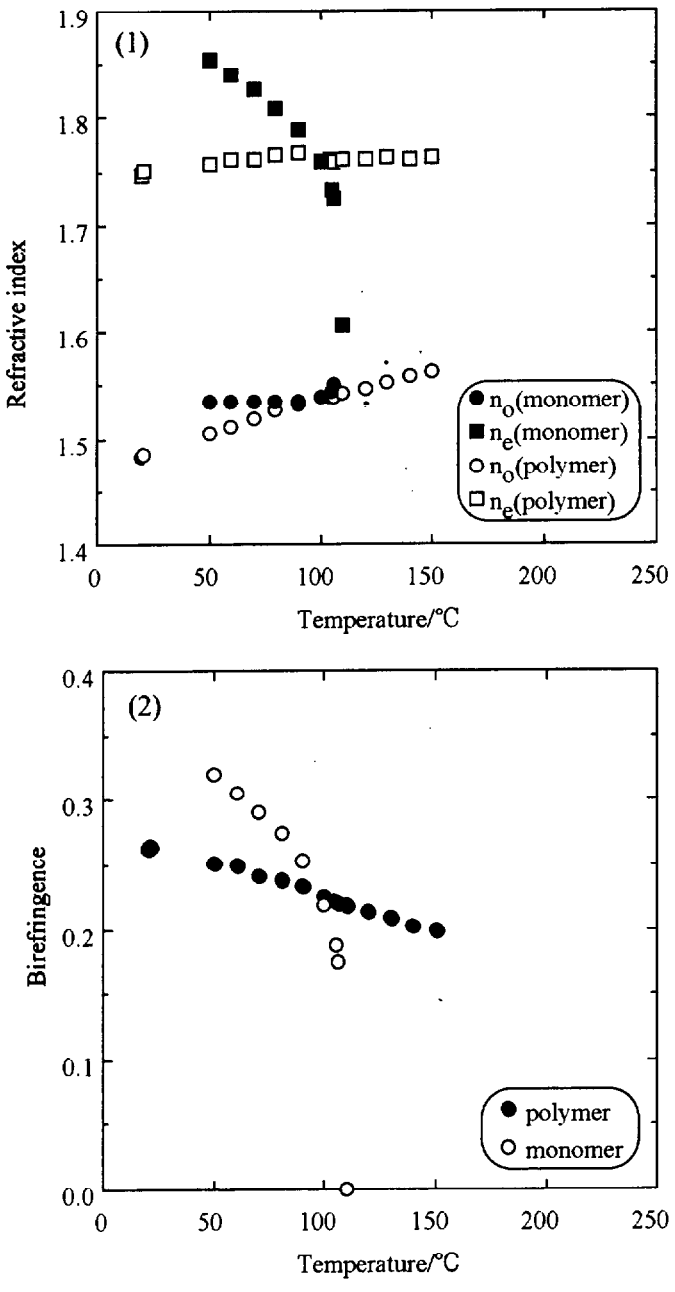


FIGURE 5-3 Refractive index (1) and birefringence (2) of diacrylate monomer **DA1110** and its crosslinked polymers

observed. The temperature dependences of n_e and Δn were smaller than those of the monomer. The values of Δn, n_o and n_e of the monomer were almost captured by polymerization, which is consistent with the observation that no textural changes occur after polymerization.

The order parameter of compound **DA1110** is shown in FIGURE 5-4. The temperature dependence of the order parameter also decreased after polymerization. The order parameter at the polymerization temperature was captured in the polymer and it showed similar behavior after polymerization as the refractive indices.

Compound **DA1113** had a wider nematic range than **DA1110** and thus was polymerized at two different temperatures, 105 and 140 ℃. The polymerization conditions were the same as that used to polymerize **DA1110**. As shown in FIGURE 5-5, Δn of polymer **DA1113** (irradiated at 105 ℃) was essentially the same as the value of the monomer at the polymerization temperature, but n_o decreased and n_e also became slightly smaller on polymerization. The order parameter of polymer **DA1113** was almost the same as that of the monomer at 105 ℃ (see FIGURE 5-6). It was considered that the orientational order in the nematic phase was essentially captured after polymerization with regard to monomer **DA1113**, as for **DA1110**. The dicroic ratio of the C=C double bond of monomer **DA1113** in IR spectrum was negative so that the contribution of the bond to n_o as clearly decreased by polymerization. A decrease in n_e was also apparent for the same reason.

Δn, n_e and the order parameters of polymer **DA1113** (irradiated at 140 ℃) were smaller than those of the polymer irradiated at 105 ℃, but they increased compared with the monomer values at the irradiation temperature 140 ℃. Monomer **DA1113** began its transition from nematic to isotropic phase at

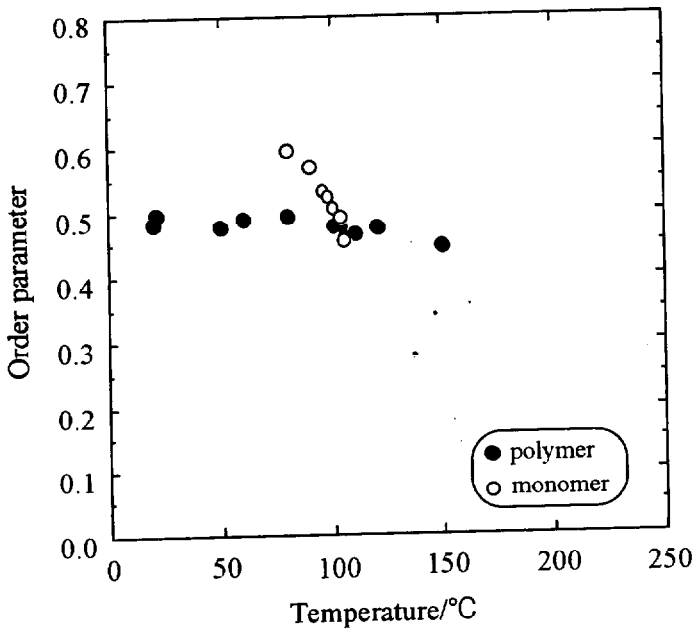


FIGURE 5-4 Order parameter of diacrylate monomer **DA1110** and its crosslinked polymers

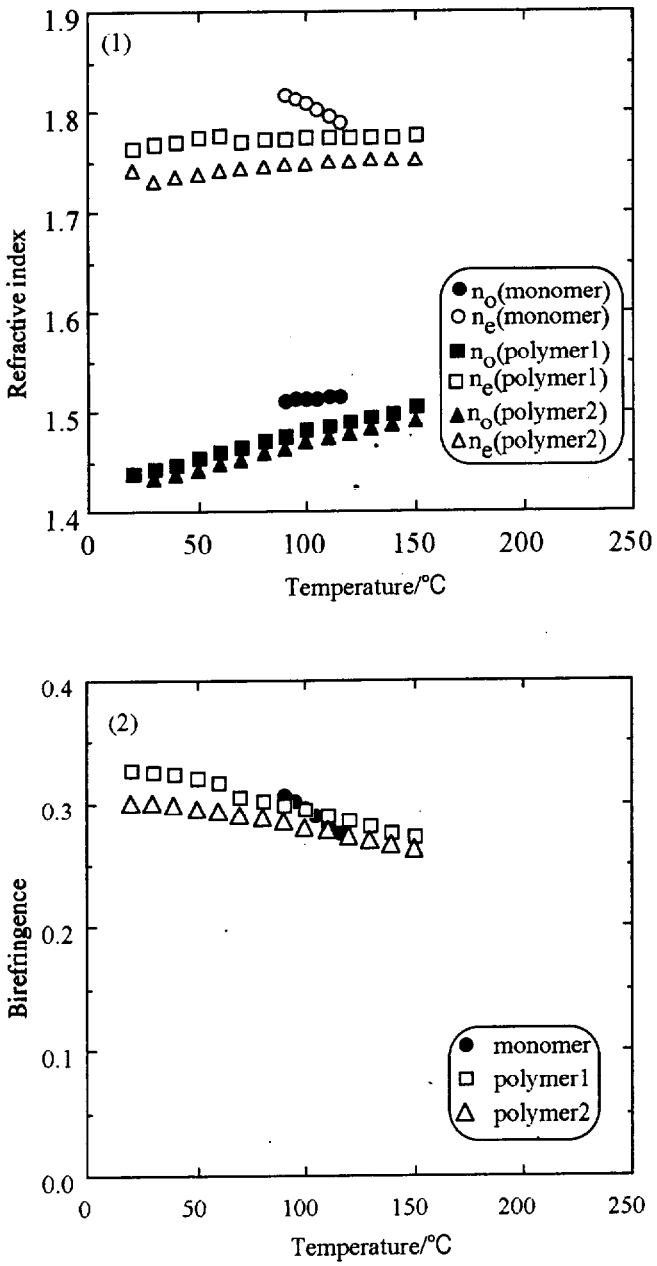


FIGURE 5-5 Refractive index (1) and birefringence (2) of diacrylate monomer **DA1113** and its crosslinked polymers
polymer1 ; irradiated at 105°C, polymer2 ; irradiated at 140°C

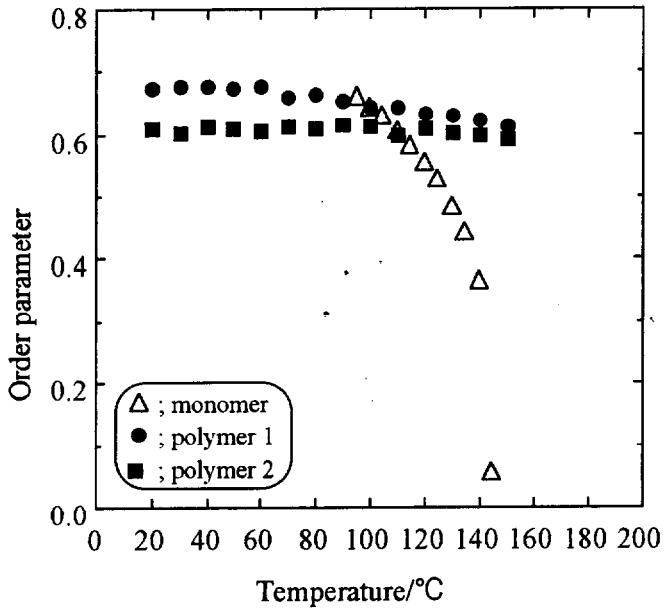


FIGURE 5-6 Order parameter of diacrylate monomer **DA1113** and its crosslinked polymers

polymer1 ; irradiated at 105°C, polymer2 ; irradiated at 140°C

140 ℃, but exhibited a narrow transition range. Thus the orientation was increased by polymerization in the co-existence of nematic and isotropic phases.

Δn and the order parameter of the polymer varied with polymerization temperature; the lower temperature gave the higher Δn and order parameter. The orientation at photopolymerization was almost fixed such that Δn and order parameter varied with polymerization temperature.

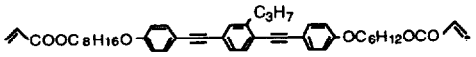
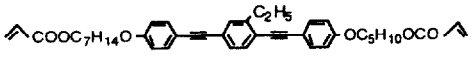
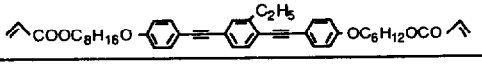
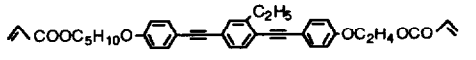
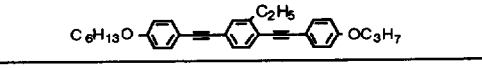
5.4 Modification of terminal and substituent groups of the three-ring phenylacetylene diacrylates

In order to obtain lower and wider nematic phase, the length of terminal groups and substituent alkyl groups were modified. Phase sequences and transition temperatures of new three-ring phenylacetylene diacrylates are shown in TABLE 5-2. The nematic phase decreased as the length of terminal chains increased. **DA1120** exhibited lower nematic 38 ～ 104 ℃ compared with **DA1110** (nematic; 98 ～ 110 ℃) or **DA1119** (nematic; 54 ～ 114 ℃). **DA1118** containing longer terminal chains exhibited wider and lower nematic phase. Longer chain of core substituents also lowered the nematic phase. The melting point of **DA1118** with propyl substituent was 36℃, and the nematic phase was so stable that once it melt from crystal phase to nematic, the nematic was kept for very long time over a few months at room temperature.

Birefringence of **DA1118** ～ **DA1120** were very high around 0.3, but Δn lowered as longer chain of terminal groups. The difference of Δn between ethyl and propyl lateral core substituents was small.

Each monomer with 1 % photoiniciator (Irgacure 651) was put into a cell coated with rubbed polyimide as the alignment layers and irradiated with a high pressure mercury lamp (200

TABLE5-2 Phase sequences refractive indices and Δn of the modified phenylacetylene monomers

	Compounds	Phase transitions / ℃	n_o [1)]	n_e [1)]	Δn [1)]
DA1118		K · 39 · N · 82 · I	1.518	1.813	0.295
DA1119		K · 54 · N · 114 · I	1.514	1.845	0.331
DA1120		K · 38 · N · 104 · I	1.514	1.818	0.304
(ref.) **DA1110**		K · 98 · N · 110 · I	1.523	1.854	0.330
PA1109		K · 16 · N · 115 · I	1.528	1.907	0.379

1) Extrepolated values (20 ℃, 589 nm) of the mixture (monomer (10 wt%) and MJ931381 (90 wt%))

W / cm^2, 72 sec) at temperatures of nematic phase. The polymerization was confirmed by the IR spectrum as the absorption of the acrylate C=C double bonds disappeared. The textures of **DA1118** ~ **DA1120** after polymerization were homogeneous same as **DA1110** or **DA1113**.

The values of Δn before and after polymerization were shown in FIGURE 5-7. Δn of monomers were decreased as the terminal chains became longer, which was the same trend of the Δn estimated from the mixtures with the host nematic. Δn of polymers were changed with the polymerization temperatures. Order parameters before and after polymerization showed similar behaviors as Δn (see FIGURE 5-8).

Haze after polymerization was shown In TABLE 5-3. All of the polymers showed very small haze under 5 % as same with observation. The three-ring phenylacethylene diacrylate series have a merit of small disorder after polymerization.

5.5 Dibenzothiophenylacetylene diacrylate

In the investigation of low molecular weight liquid crystals (see section 3.3.3 in chapter 3), new high Δn core dibenzothiophenylacethylene was developed. The new core was applied to photopolymerizable liquid crystalline materials. The diacrylate compound synthesized here and physical properties are shown in FIGURE 5-9. **DA1124** exhibited wide nematic phase from 124 ℃ to over 300℃. The Δn of the monomer was 0.41, which was higher than those of phenylacethylene diacrylate series. Δn before and after polymerization was also shown in FIGURE 5-9. **DA1124** with 3 % irgacure 651 was prepared and polymerized at 125 ℃ by the same condition mentioned in section 5.3. The textures after polymerization was homogeneous same as phenylacethylene diacrylate series. Δn of the **DA1124** polymer was very high 0.35 which was slightly lower than that of the monomer.

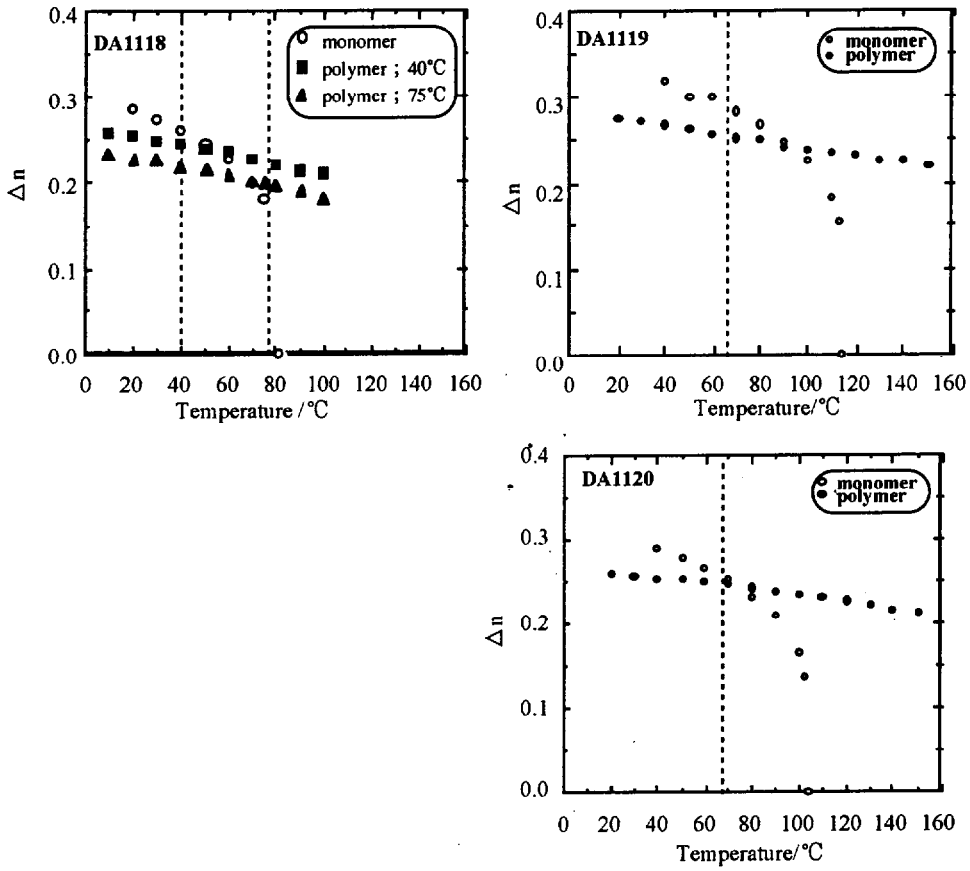


FIGURE 5-7 Birefringence of the diacrylate monomers and their crosslinked polymers (broken lines show the irradiated temperatures)

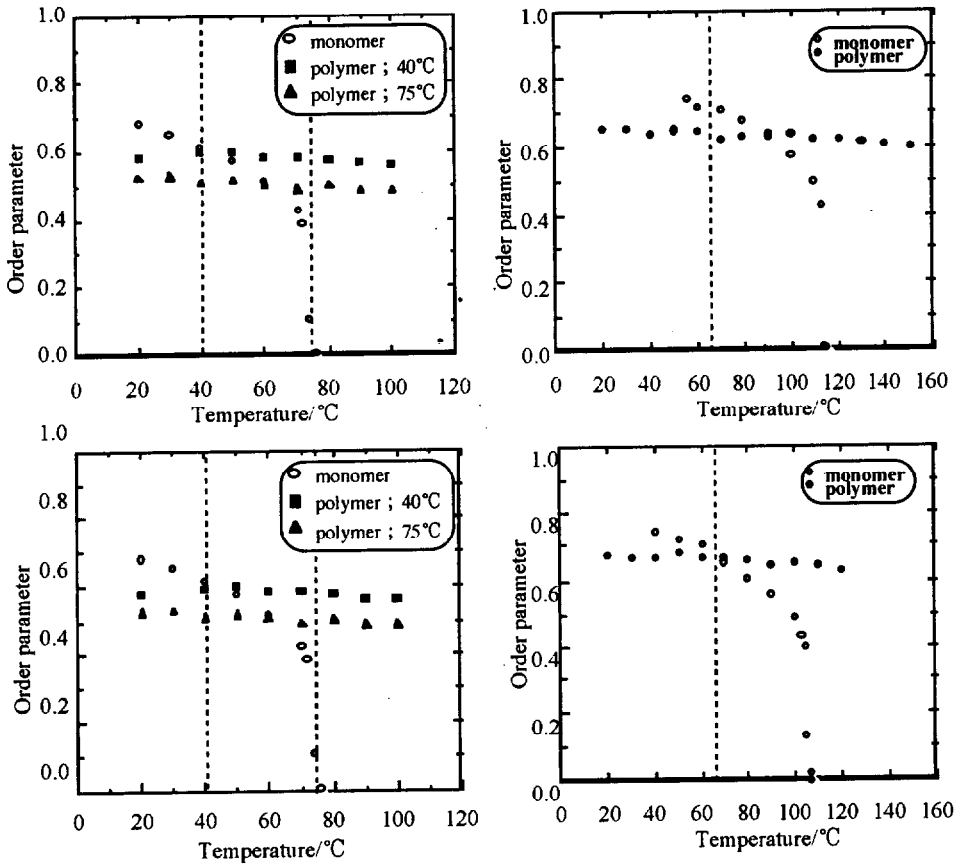


FIGURE 5-8 Order parameters of the diacrylate monomers and their crosslinked polymers (broken lines show the irradiated temperatures)

TABLE 5-3 Haze of the 3PA polymer

Sample No	Haze (%)
DA1118	0.7
DA1119	2.8
DA1120	3.1

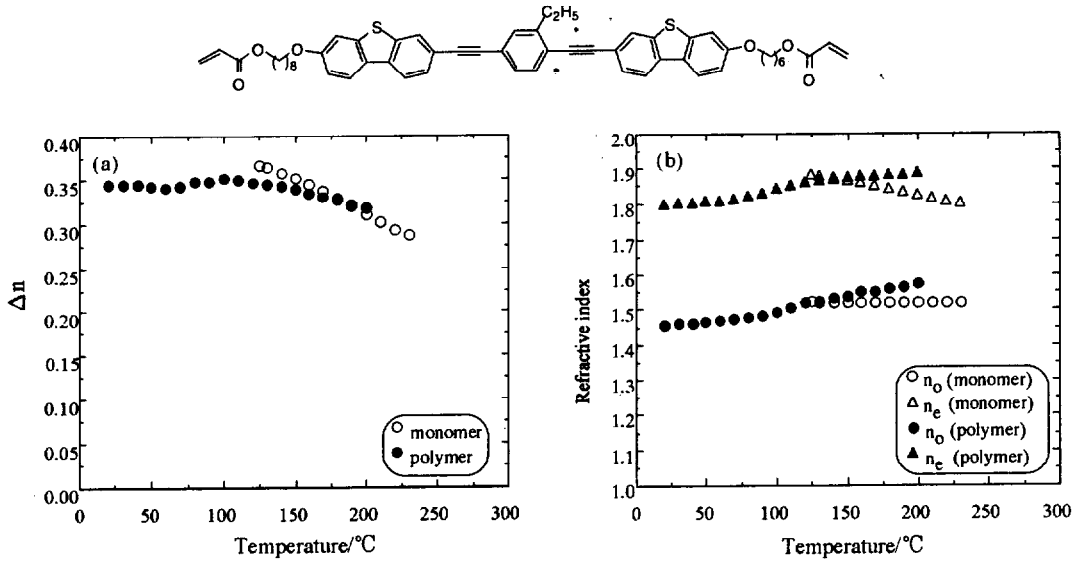


FIGURE 5-9 Refractive inidices and birefringence of the diacrylate monomer **DA1124** and their crosslinked polymers irradiated temperature; 125 °C

In order to obtain high Δn polymer, a mixture of **DA1124** and **DA1113** (the highest Δn 3-ring phenylacethylene diacrylate monomer) was prepared to lower the polymerization temperature. The mixture of **DA1124** : **DA1113** = 65.7 : 34.3 exhibited nematic phase from 90 to 232 ℃. This mixture was polymerized at 100℃ by the same condition of **DA1124**. The value of Δn after polymerization was over 0.4 (see FIGURE 5-10)

5.6 Conclusions

The synthesis and characterization of photopolymerizable phenylacetylene and dibenzothiophenylacetylene liquid crystals have been described. The compounds evaluated here exhibited a nematic phase and high birefringence as expected from the corresponding alkyl containing homologues. The homogeneous alignment of the monomers was retained after polymerization such that the birefringence and the order parameters were almost fixed at the values of the monomers. The haze of the polymers was also very small under 5 %. Therefore, Δn and S varied with polymerization temperature and hence, the higher Δn value was obtained by polymerization at lower temperature.

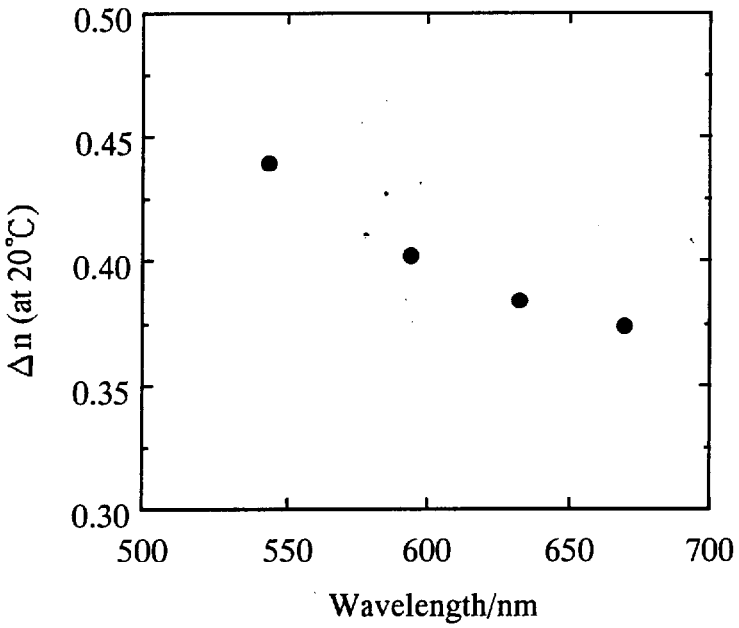


FIGURE 5-10 Birefringence of the diacryrate polymer (**DA1113+DA1124**) mixture irradiated temperature; 100℃

References of Chap. 5

[1] D. J. Broer, J. A. M. M.van Harren, G. N. Mol and F. Leenhouts, 1995, SID'95, Asia Display, 735

[2] A.Stohr and P.Strohriegl, 1997, Mol. Cryst. Liq. Cryst., **299**, 211

[3] R.A.M.Hikmet and H.Kemperman, 1999, Liq. Cryst., **26**, 11,1645

[4] N.A.Plte, R.V.Talroze and V.P.Shibaev, 1987, Makromol. Chem.,Macromol. Symp., **12**,203

[5] D. J. Broer, H. Finkelmann and K. Kondo, 1988, Makromol. Chem.,**189**,185

[6] D. J. Broer, G. N. Mol and G. Challa, 1989, Makromol. Chem.,**190**,19

[7] D. J. Broer, J. Boven, G. N. Mol and G. Challa, 1989, Makromol. Chem.,**190**,2255

[8] D. J. Broer, R. A. M.Hikmet and G. Challa, 1989, Makromol. Chem.,**190**,3201

[9] D. J. Broer, G. N. Mol and G. Challa, 1990, Makromol. Chem.,**192**,59

[10] S. T. Wu, 1995, Mol. Cryst. Liq. Cryst., **261**,79

[11] H. Takatsu, K. Takeuchi, Y. Tanaka and M. Sasaki, 1986, Mol. Cryst. Liq. Cryst., **141**, 279

[12] S. T. Wu, U. Finkenzeller and V. Reiffenrath, 1989, J.Appl.Phys.,**65**.4372

[13] JP98-43289,1998, Sumitomo Chemical Co.,Ltd

[14] C. Sekine, K. Fujisawa, N. Konya, and M. Minai, 1998, Liquid Crystal Conference of Japan, 2B11

[15] C. Sekine, K. Fujisawa, N. Konya, and M. Minai, 1998, Proc. IDW99, 411

[16] D. Demus, J. Goodby, G. W. Gray, H.-W.Spiess and V. Vill ed., 1998, Handbook of Liquid Crystals, vol. 2A, WILEY-VCH-Verlag, GmbH

[17] M. P. Fontana, B. Rosi, N. Kirov and I. Dozov, 1986, Phys. Rev. A, **33**,6,4132

[18] C. Sekine, K. Iwakura, M. Minai and K. Fujisawa, Mol.Cryst.Liq.Cryst., in press

Chapter 6 Summary

In this thesis, novel high birefringence liquid crystals are designed, synthesized and evaluated in order to develop optical materials which are expected to be useful for brilliant and low power consumption reflective LCDs. Practical properties as liquid crystal temperature and durability are also focused in this investigation.

The background of the study and the preliminary study of high birefringence liquid crystals are presented in Chap.1. In order to investigate the starting core structure of high Δ n liquid crystals, we synthesized phenyl acetylene homologues which had different lengths of units and evaluated the basic properties. 3-Ring phenylacetylene compound exhibited wide nematic phase and high Δn over 0.4. It also showed good durability and was colorless. Therefore, we believe that 3-ring phenylacetylene is highly worth further investigation for high Δn liquid crystals.

Chap.2 focuses on the modification of 3-ring phenyl acetylenes to improve the liquid crystal temperature and solubility with keeping high Δn. In the investigation of modified terminal ring, it was found that methyl substituent was effective for lowering nematic range with keeping high Δ n compared with fluorine group or introducing a branched terminal chain. With these results we studied the effect of the substituted position of methyl group on their physical properties. The most effective methyl substituted position for improving nematic temperature was core center ring. From the estimation of Δn, order parameter and viscosity, the best substituent position was the same.

These results led us to the investigation of different type of substituents. Introducing trifluoromethoxy group was

effective for lowering nematic range and viscosity. Therefore this type compound was useful for preparing of practical liquid crystal mixtures.

In Chap.3, We synthesized new thiopheny acetylene and benzothiazolyl acetylene homologues, and evaluated their thermal and optical properties in the comparison with phenyl acetylene homologues. These series had poor liquid crystallinity when compared with phenyl acetylene type. The conjugated hetero ring systems shifted UV absorption spectra to the visible region, as a result they showed yellow or brownish colour.

On the basis of the investigation of thiophenyl acetylene and benzothiazolyl acetylene series, new heterocyclic molecules, which were expected to show high $\Delta\alpha$ and short UV absorption spectra, were designed. Dibenzothiophenyl acetylene homologues exhibited wide nematic phase and very high Δn over 0.6. They exhibited high Δn over 0.5 even as single compounds. The compounds with two dibenzothiophenyl rings was colourless, so that we succeeded in obtaining colourless super high Δn liquid crystals. We also analyzed the contribution of transition band to refractive indices and birefringence. From the analysis, dibenzothiophenyl compounds were thought to be designed as expectation.

In Chap.4, cyclohexyl and cyclohexylethyl phenyl-acetylene homologues are synthesized and evaluated for the purpose of obtaining components for preparing liquid crystal mixtures. Both type of them exhibited wide nematic phase and moderate high Δn. Order parameters were not affected by introducing cyclohexyl or cyclohexyl-ethyl groups so that values expected for Δn from calculated polarizabilities were actually obtained.

In Chap.5, photopolymerizable phenylacetylene liquid crystals are synthesized and evaluated. The compounds

evaluated here exhibited a nematic phase and high birefringence as expected from the alkyl type homologues. The homogeneous alignment of monomers was kept after polymerization so that the birefringence and order parameters were almost fixed at the values of the monomers. The hazes of the polymers were also very small under 5 %. Therefore Δn and S were varied with polymerized temperature so that higher Δn was obtained by polymerization at lower temperature.

New dibenzothiophenylacetylene core were also applied to photopolymerizable liquid crystals. This monomer exhibited high Δn and wide nematic temperature. High Δn polymer over than Δn of 0.4 was obtained using the 3-ring phenylacetylene and the dibenzothiophenylacetylene diacrylate monomers.

List of publications

Original

1. "Optical anisotropy of phenylacetylene homologues", Chizu Sekine, Koichi Fujisawa, Yukari Fujimoto and Masayoshi Minai, Mol. Cryst. Liq. Cryst.**332**, 235-242 (1999).<<Chap.1>>

2. "High birefringence phenylacetylene liquid crystals with low viscosity", Chizu Sekine, Koichi Fujisawa, Kazunori Iwakura and Masayoshi Minai, Mol. Cryst. Liq. Cryst.**364**, 711-718 (2001) <<Chap.2>>

3. "Synthesis and properties of Some novel high birefringence phenylacethylene liquid crystal materials with lateral substituents", Chizu Sekine, Naoto Konya, Masayoshi Minai and Koichi Fujisawa, Liq. Cryst.,**28**, 9,1375-1387 (2001) <<Chap. 2>>

4. "Synthesis and properties of high birefringence liquid crystals; thiophenylacethylene and benzothiazolyl -acethylene derivatives", Chizu Sekine, Naoto Konya, Masayoshi Minai and Koichi Fujisawa, Liq. Cryst., **28**,9, 1361-1367 (2001). <<Chap. 3>>

5. "Novel high birefringence dibenzothiophenylacetylene liquid crystals", Chizu Sekine, Kazunori Iwakura, Masayoshi Minai and Koichi Fujisawa, Liq. Cryst., **29**,3, 355-367 (2002). <<Chap. 3>>

6. "Synthesis and physical properties of high birefringence phenylacetylene liquid crystals containing a cyclohexyl group", Chizu Sekine, Naoto Konya, Masayoshi Minai and Koichi Fujisawa, Liq. Cryst., **28**, 10, 1495-1503 (2001). <<Chap. 4>>

7. "High Birefringence photopolymerizable phenylacetylene liquid crystals", Chizu Sekine, Kazunori Iwakura, Masayoshi Minai and Koichi Fujisawa, Liq. Cryst., **28**, 10, 1505-1512 (2001). <<Chap. 5>>

Review

1."Highly anisotropic molecular materials for LCDs", Toshihiko Tanaka, Chizu Sekine, Toru Ashida, Masamitsu Ishitobi, Naoto Konnya, Masayoshi Minai and Koichi Fujisawa, Mol. Cryst. Liq. Cryst.,**346**,209 (2000)

2."超高屈折率異方性液晶"、関根千津、石飛昌光、南井正好、藤沢幸一、月刊ディスプレイ、8, 1, 69-77 (2002)

Reference

1. "Physical properties of new phenylpyrimidine type ferroelectric liquid crystals", Chizu Sekine, Takeshi Tani, Kayoko Ueda, Koichi Fujisawa, Takayuki Higashii, Isao Kurimoto, Shoji Toda, Naoyuki Takano, Yukari Fujimoyo, and Masayoshi Minai, Ferroelectrics, **148**, 203-212 (1993)

2. "Physical Properties of novel biphen
yl and phenylpyrimidine type ferroelectric liquid crystals", Kayoko Ueda, Chizu Sekine, Takeshi Tani, Koichi Fujisawa, Takayuki Higashii, Isao Kurimoto, Shoji Toda, Naoyuki Takano, Yukari Fujimoto, and Masayooshi Minai, Ferroelectrics, **148**, 213-222 (1993)

3. " Synthesis and physical properties of new biphenyl and phenylpyrimidine type ferroelectric liquid crystals", Takayuki Higashii, Isao Kurimoto, Shoji Toda, Naoyuki Takano, Yukari Fujimoto, Masayooshi Minai, Chizu Sekine, Takeshi Tani, Kayoko Ueda, and Koichi Fujisawa, Ferroelectrics, **148**, 169-178 (1993)

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