論文 / 著書情報
Article / Book Information

題目(和文)	触媒末端を有するハイパーブランチポリエーテルケトンの合成と特性評価
Title(English)	Synthesis and Characterization of Hyperbranched Aromatic Poly(ether ketone) Functionalized with Actively Catalytical Terminals
著者(和文)	ShiYing
Author(English)	Ying Shi
出典(和文)	学位:博士（工学）, 学位授与機関:東京工業大学, 報告番号:甲第9621号, 授与年月日:2014年9月25日, 学位の種別:課程博士, 審査員:柿本　雅明,手塚　育志,高田　十志和,早川　晃鏡,道信　剛志
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第9621号, Conferred date:2014/9/25, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

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Chapter 1 General Introduction

1.1 Hyperbranched polymer

Linear polymers are the most well-known and well-understood structures that is built from monomer units that connect one to the next to create a line. Branched polymers, however, have at least one point where a second chain of monomers branches off from the first chain. Generally, there are two types of polymers containing the branched units, that is, dendrimers and hyperbranched polymers (HBPs). HBPs are highly branched macromolecules with three-dimensional dentritic architecture, [1] they have unreacted branch points; therefore, the branch structure is irregular. In contrast, dendrimers are globular macromolecules that have highly ordered branch structure. (Figure 1.1)

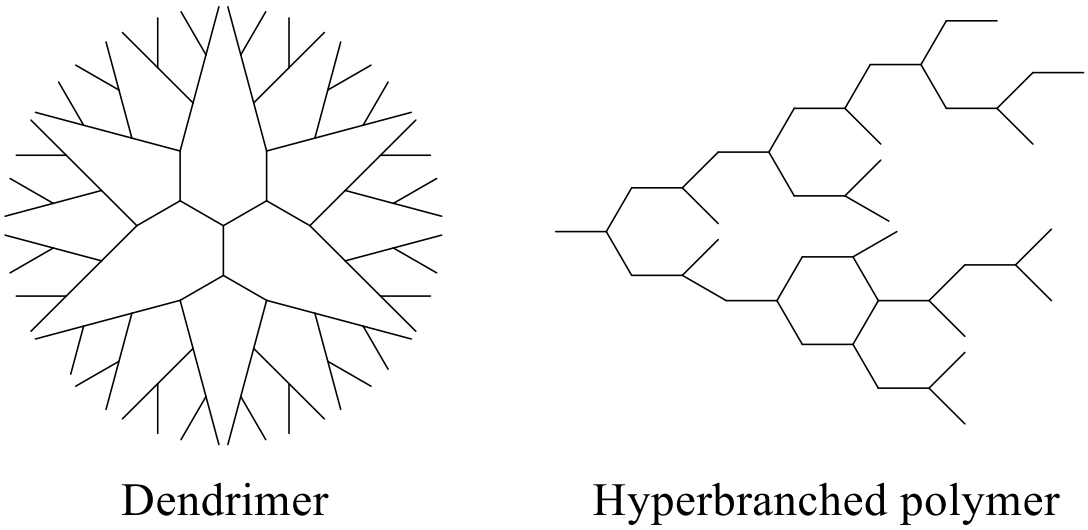


Fig 1.1 The structure of dendrimer and HBPs

In 1952, Flory demonstrated that highly branched polymers can be synthesized without any gelation. [2] In 1982, Krichedorf reported the copolymerization of AB and AB_2 monomers to form highly branched polyesters. [3] In 1988, Kim and coworkers defined HBPs when they synthesized a water soluble hyperbranched polyphenylene. [4-6] Since then, HBPs have become a hot field in polymer science and engineering.

Compared to the linear polymers, HBPs possess similar properties to dendrimers: weak molecular entanglement, low viscosity, high solubility and large numbers of functional groups, as they have numerous branching points and terminal groups. [7-12] Dendrimers with precise molecular weight and exact chemical units need to be constructed via multistep processes requiring isolation and purification in each step, [13-16] which requires laborious syntheses and is difficult to scale up. In contrast, HBPs can be prepared by one-step synthesis, which are suitable for large scale synthesis, although they consist of a mixture of different molecular weights. [17]

To date, the methodologies to prepare HBPs can be classified into several categories via the bottom up ideology [1,17,18]: (i) polycondension of AB_n monomers, ($n \geq 2$) [4,5,19,20]; (ii) self-condensing chain-growth polymerization of AB* monomers (including vinyl and cyclic molecules) [21-27]; (iii) polycondensation of symmetric monomer pairs (A_2 + B_3 methodology) [28,29]; (iv) polycondensation of asymmetric monomer pairs (coupling-monomer methodology) [30,31]. In the meantime, the first two can

be assigned as a single-monomer methodology (SMM), while the other two ranged as a double-monomer methodology (DMM).

Polycondensation of AB_n type monomer, which can minimize the risk of gelation, can provide various HBP structures by changing the structure of the AB_n monomers. As a result, this kind of monomers has been extensively studied. Various hyperbranched polymers such as polyphenylene [6], polyesters [32-35], polycarbonates [36,37], polyamides [38-40], polyimides [41-43], poly(ether sulfone)s [44,45] and poly(ether ketone)s [46-50] have been synthesized to date. However, a large scale production of such HBPs is quite limited, especially if the monomers are not commercially available and their synthesis involve tedious multistep procedures.

In contrast, the polycondensation of A_2 and B_3 with commercially available monomers has some advantages, such as facile preparation and scaling up, but the risk of gelation is unavoidable over a certain conversion in a 1:1 molar monomer feed ratio [51]. Kakimoto [28] et. al. reported a new approach to direct polycondensation of aromatic diamines (A_2) and trimesic acid (B_3) to synthesize hyperbranchend aromatic polyamides. Because of the formation of A'-ab-$(B')_2$ type intermediate, the reaction was kinetically controlled and proceeded without gelation.

Grafting the HBPs on solid substrate provide a promising application of HBPs. Surface composition, surface energy and some other physical properties of these materials can be modified to a desired physical state by

designing proper HBP structures. The modification can be done by "grafting from" or "grafting to" approaches (Figure 1.2). Both of them starts from introducing functional groups (X) onto the solid surface, and then the branch or core of HBPs is anchored on the surface by a covalent or noncovalent bond. The placement of HBPs on solid substrates is required for various prospective applications, such as sensing, catalysis, fouling, selective binding and lubrication. [17]

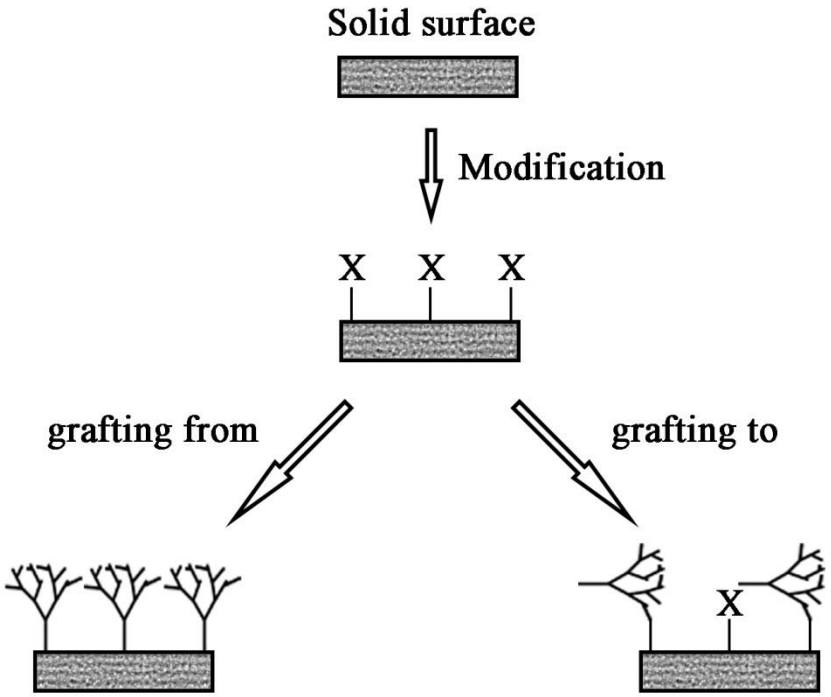


Fig 1.2 Surface modification approaches

1.2 TEMPO and some applications in oxidation and ATRP

Nitroxyl radicals (also called nitroxides) are *N*,*N*-disubstituted NO radicals with an unpaired electron delocalized between the nitrogen and the oxygen atom [52]. The delocalization of the unpaired electron is indicated

by the three resonance structures 1, 2, and 3 (Figure 1.3).

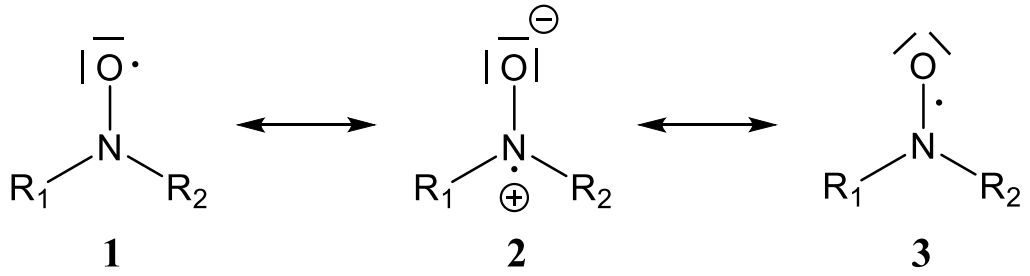


Fig 1.3 Resonance structures of nitroxyl radicals

2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), reported in 1960s, [53] and its analogues belong to this class of compounds. The NO-bond energy has been estimated to be 420 kJ/mol, approximately corresponding to the energy of one and a half bonds. The most striking features of these nitroxyl radicals is their high stability, which caused by a difficulty of self-reactions. [54]

TEMPO has been widely studied as an efficient catalyst for oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. With oxygen, TEMPO is oxidized to the oxoammonium ion which can also be generated by the disproportionation under acidic conditions (Figure 1.4). During the process of catalytic cycle, the hydroxylamine can be reoxidized in the presence of oxygen under basic conditions.

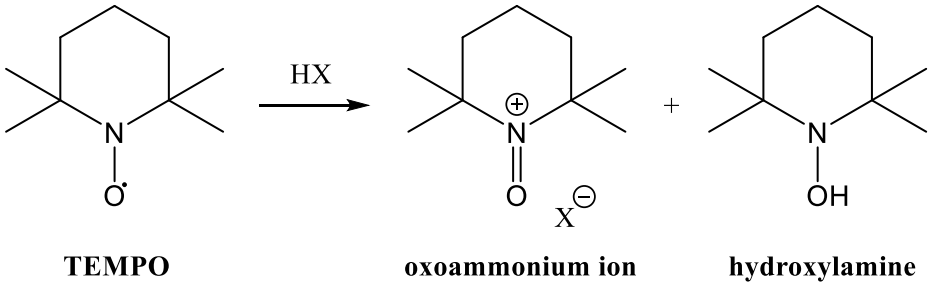
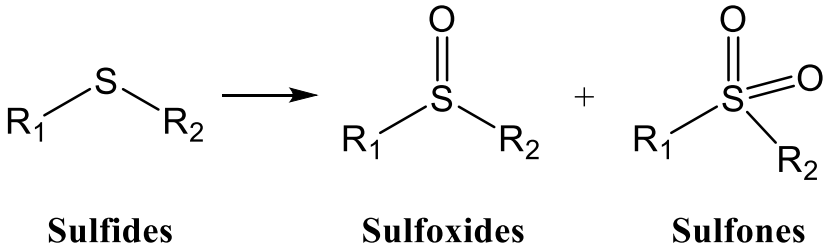


Fig 1.4 Disproportionation of TEMPO

A large number of different inorganic and organic cooxidants have been used for the regeneration of the oxoammonium ion from hydroxylamine, which will be discussed in 1.3-1.5.

TEMPO and its derivative are also capable of oxidizing sulfides to corresponding sulfoxides, and overoxidation to sulfones as well [55] (Figure 1.5). This reaction is conducted with the aid of transition metals and using H_2O_2 or NaOCl as oxidant. The addition of TEMPO enhanced the conversion and selectivity of sulfoxides, though the role is not yet understood.

R_1, R_2= alkyl, aryl, allyl



Sulfides **Sulfoxides** **Sulfones**

Fig 1.5 Oxidation of sulfides

TEMPO is also proposed to react with activated hydrocarbons by hydrogen abstraction, such as cyclohexene, acetonitrile or toluene. As a result, it has often been used as a radical scavenger.

Nitroxide-Mediated Polymerization is used in the preparation of various polymers by atom-transfer radical polymerization (ATRP), with adjustable molecular weights and lower polydispersities (PDI<1.5). These polymerizations use alkoxyamine type as an initiator/regulator and stopped

by simple separation of any remaining monomer. And then the macroalkoxyamines can be used as macroinitiators for subsequent block copolymerization. Even triblock copolymers can be prepared by this method. TEMPO has been used frequently to control the radical polymerization of styrene (Figure 1.6) and styrene derivatives. [52]

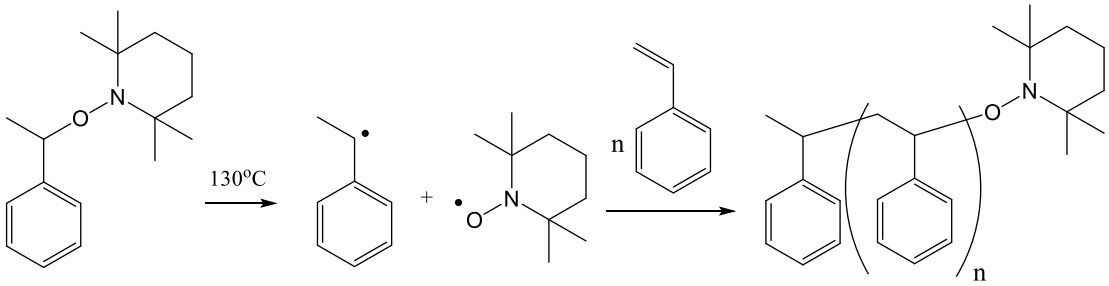


Fig 1.6 TEMPO Mediated Polymerization

1.3 Stoichiometric oxidation of alcohols mediated by TEMPO

TEMPO has been widely studied as an efficient catalyst for the oxidation of alcohols. With 1 mol % or even less amount, it can work selectively and conveniently that is competitive with metal-based catalyst. Sodium hypochlorite is widely used as a primary oxidant, and catalytic amounts of the bromide ion (such as KBr or NaBr) are often added to increase the reaction rate by generation of stronger oxidant, hypobromite [56] (Figure 1.7). Regeneration of the oxoammonium ion also can be accelerated by sonication. [57] By increasing the temperature and adjust pH value of the catalyst system, oxidation of primary alcohol groups in starch and methyl α-D-glucopyranoside can be performed in the absence of

sodium bromide. [58]

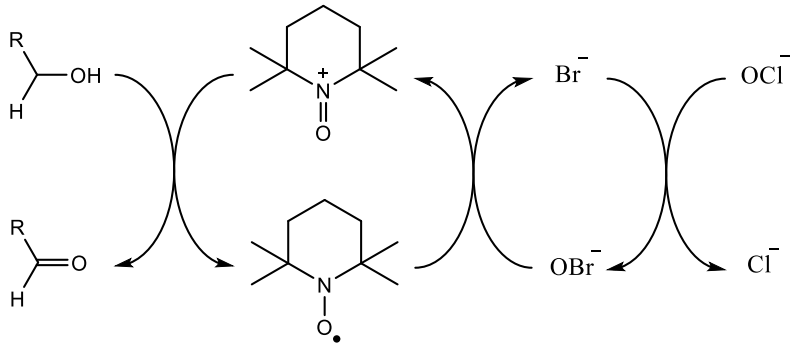


Fig 1.7 Scheme of TEMPO oxidation cycle with NaOCl/NaBr as primary oxidant

Other oxidants have also been successfully employed in the TEMPO mediated oxidation system. *m*-Chloroperbenzoic acid oxidizes secondary alcohols with catalytic amounts of *n*-Bu_4NBr. [59] Also, $KHSO_5$ was employed as primary oxidant in the presence of *n*-Bu_4NBr in nonaqueous media, toluene or dichloromethane. [60] As well, tert-Butyl hypochlorite, [61] $NaClO_2$, [62] *N*-chlorosuccinimide, [63] and some multicomponent, such as methyl trioxorhenium/HBr/TEMPO/H_2O_2 catalytic system [64] also show a good efficiency in primary oxidant.

1.4 Aerobic oxidation of alcohols involving mediated by TEMPO

The fine chemicals manufacturer employs the aerobic process developed by Neumann and co-workers for the synthesis of carbonyl compounds. [65] There are many reports utilizing TEMPO and transition metals as cocatalysts, such as $H_5PV_2Mo_{10}O_{40}$, [65] $FeCl_3/NaNO_2$, [66,67] $[RuCl_2(PPh_3)_3]$, [68] the couple $Mn(NO_3)_2/Co(NO_3)_2$ [69,70] or

$Mn(NO_3)_2/Cu(NO_3)_2$. [71] In these systems, alcohol is oxidized by oxoammonium ion, and the transition metals catalyze the reoxidation of hydroxylamine to generate oxoammonium ion, which is the rate-determining step of the reaction. Then the reduced metal is reoxidized by oxygen (Figure 1.8). [72]

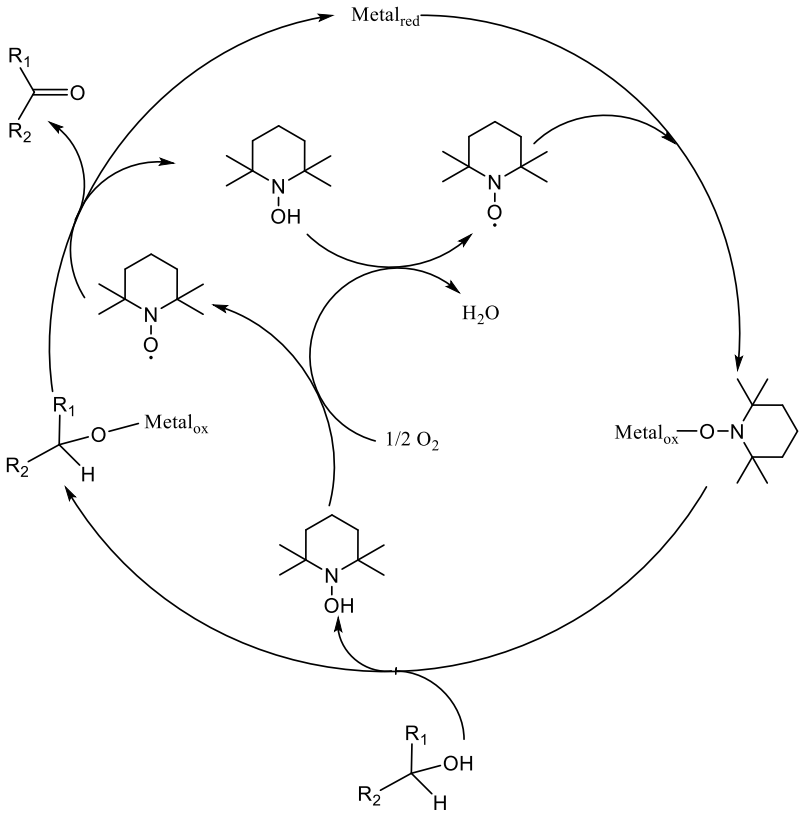


Fig. 1.8 Proposed mechanism for transition metal co-catalyzed aerobic alcohol oxidations

However, the water as a solvent can deactivate the catalyst by competing with the substrates and/or intermediates for vacant coordination sites on active metal catalysts. The deactivation may also leave heavy metals in the products. Thus there is an urgent need to develope an efficient nonmetallic catalyst system. Hu and coworkers [73] have reported

transition-metal-free systems, a TEMPO/Br_2/$NaNO_2$ system and its derivatives, as a more environmentally friendly catalytic system. In this system, oxoammonium ion oxidizes the alcohols and hydroxylamine is re-oxidized by O_2 via the intermediation of the Br_2/Br^- and NO_2/NO redox couples (Figure 1.9). [74,75] This system, however, often suffer from Br containing byproducts and the contamination from the NO_x species. [76]

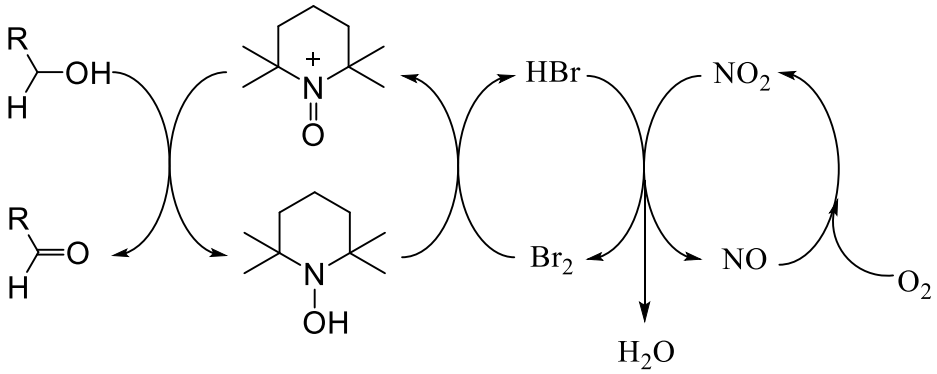


Fig 1.9 Proposed mechanism for TEMPO/Br_2/$NaNO_2$-catalyzed aerobic oxidation of alcohols

In order to suppress the hazardous nature of bromide, 1,3-Dibromo-5,5-dimethylhydantoin was introduced in to the system to replace bromide. [77] 1,3-Dibromo-5,5-dimethylhydantoin is easy to release HBrO under aqueous condition so water is introduced to the system as a solvent as well. The generated HBrO is consumed to oxidize TEMPOH to TEMPO cation in the catalyst cycle. The low concentration of HBrO suppresses the Br containing byproducts.

Instead of Br_2, HCl/$NaNO_2$/TEMPO system [78] is reported to catalyze the selective aerobic oxidation of a broad range of primary and secondary

alcohols, which may contain carbon-carbon double bonds or N or S heteroatoms. The oxidation of NO by dioxygen in the presence of HCl regenerates NOCl, and the use of NOCl to oxidize TEMPOH plays a crucial role in the catalytic system (Figure 1.10). However, some acid sensitive substrate may be limited in this system because of the high loading of HCl (10–16 mol%).

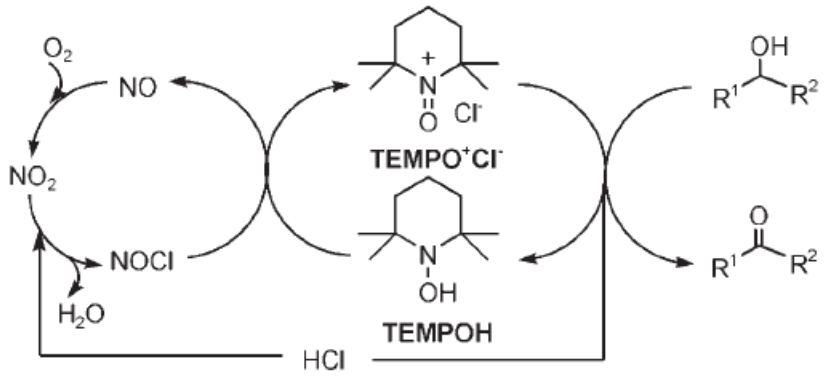


Fig 1.10 Proposed mechanism for TEMPO/HCl/$NaNO_2$-catalyzed aerobic oxidation of alcohols, [78] Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In addition, TEMPO/TBN double-component catalyst system has also been reported. [79] In this system, the organic nitrite *tert*-butyl nitrite (TBN), which is unstable under a high temperature and can release NO or NO_2, is served as an efficient NO source to activate molecular oxygen in the NO_2/NO redox couple with high volume efficiency. The formation of NO_x species is suppressed, because the generated NO is immediately consumed with sufficient molecular oxygen.

Kuang and coworkers [80] has presented a nitric acid assisted carbon-

catalyzed oxidation system (NACOS) using carbon-based materials as metal-free catalysts (Figure 1.11). This oxidation protocol can avoid halogen-containing by-products and shows good yields and selectivity to oxidize benzylic alcohols. In this system, the interaction of nitric acid and carbon strongly promotes the oxidative power with a mechanism based on *in-situ* recovery of nitric acid.

And then TEMPO is introduced to enhance this oxidation system by minimizing the use of nitric acid and solvents (even solvent free), expanding the substrate accessibility and improving the reactivity and selectivity. [81]

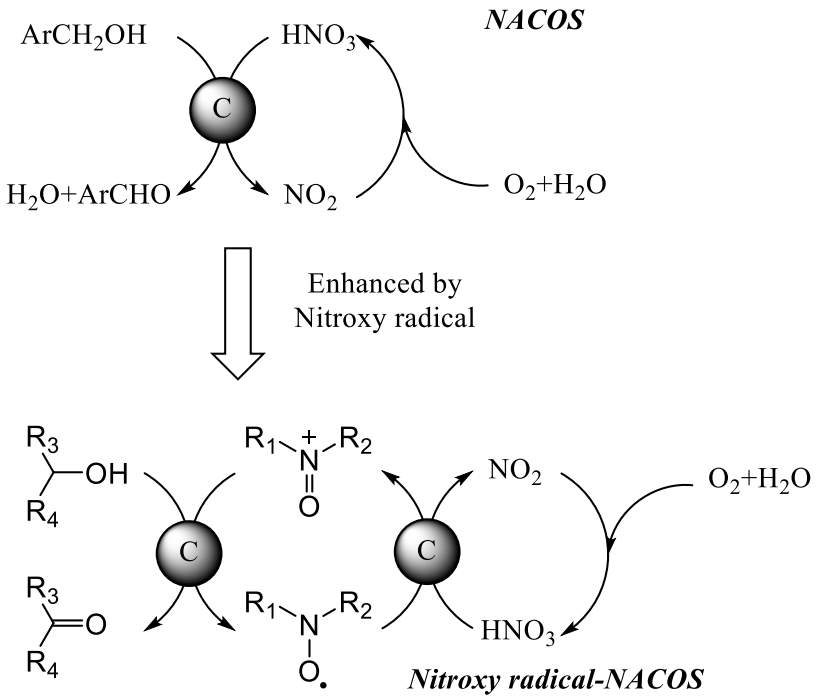


Fig 1.11 NACOS: Nitric acid carbon-catalyzed oxidation system

1.5 Immobilization of TEMPO on supports

Considering the high cost of TEMPO, the development of

heterogeneous TEMPO-based catalysts is desired. Heterogeneous catalyst has the advantage to be easily separated from the product and to be recyclable. One typical strategy is anchoring TEMPO on insoluble supports. Silica-supported TEMPO has been intensively studied as a heterogeneous catalyst which can be simply separated by filtration, for instance, silica sol-gels, [82,83] commercial silica beads [84] or mesoporous silica. [85,86]

For silica gels, the TEMPO is entrapped in a sol-gel matrix which work as a catalytic mediator and the matrix may affect the selectivity. Silica is usually modified with some functional groups, such as aminopropyl, which can react with oxo-derivatives of TEMPO. Mesoporous silica, such as SBA-15 and MCM-41, has a large surface area benefit from the mesoporous structure and can afford more activity site to link with TEMPO. Besides the silica supports, cross-linked polystyrene resins [87,88] and polyolefin fibers [89] are also used as insoluble supports. However, most of them suffer from low catalytic activity of the immobilized TEMPO or poor chemical stability of the polymer backbone under the severe oxidative conditions.

Another approach was to anchor TEMPO onto soluble supports, which can combine the benefit of homogeneous and heterogeneous. Such supports dissolve in the catalyst system to form a homogeneous condition, and then can be easily isolated from the products by changing the solubility

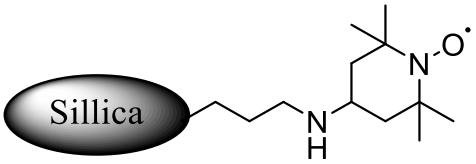
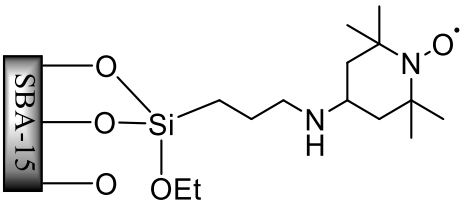
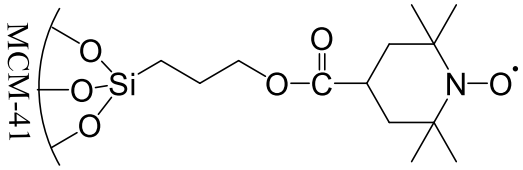
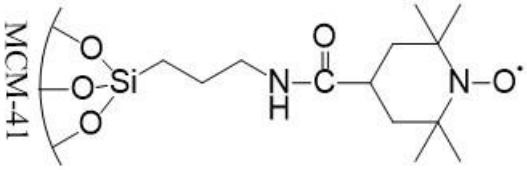
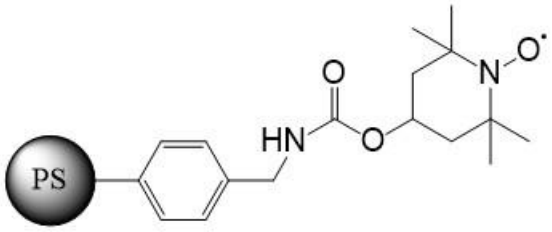
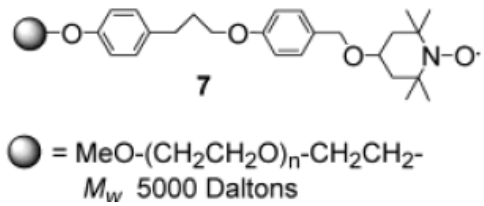
in different solution or magnetic fields.

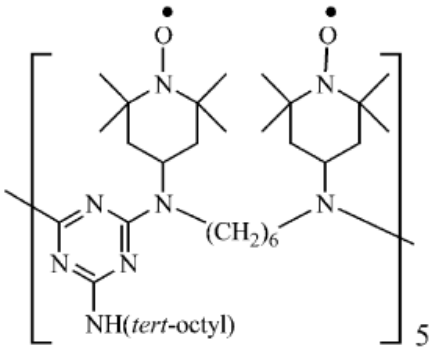
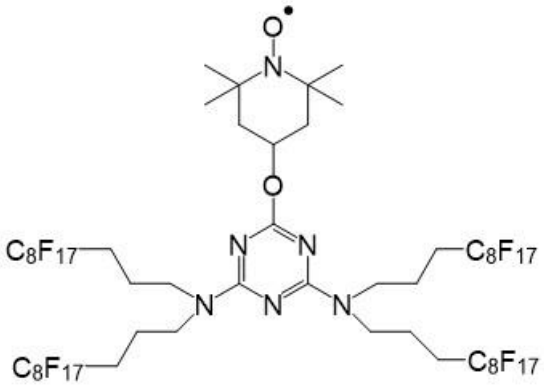
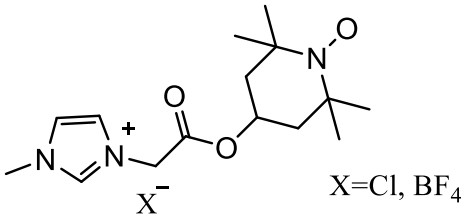
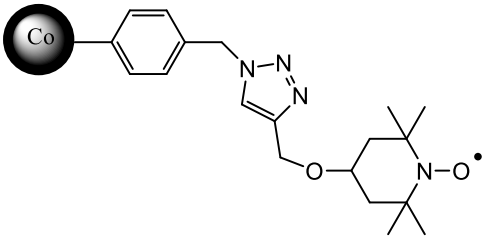
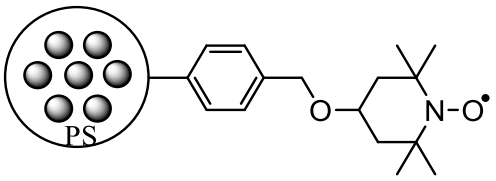
One type of widely discussed supports is polymer. Pozzi and co-workers [90] use poly(ethylene glycol) with a molecule weight about 5000 Daltons. The catalyst exhibits high activity with a NaOCl/KBr or bis(acetoxy)-iodobenzene system, and easily recycled in diethyl ester by filtration. Recycling experiments showed that PEG-TEMPO can work 6 times without loss of catalytic activity. In addition, they synthesized the perfluoroalkyl tag functionalized TEMPO working with $Co(NO_3)_2/Mn(NO_3)_2$ system to oxidize primary and secondary aliphatic alcohols [91]. The fluorous radical and related byproducts can be easily removed by phase separation or fluorous liquid-liquid extraction. Another structure of fluorous-tagged, F_{17}-CLICK-TEMPO, can be recovered using silica gel 60 and work 4 cycles without loss of activity.

TEMPO can also be conjugated to specific ionic liquids (IL) to form a structure [imidazolium-TEMPO]$^+X^-$.[92] The imidazolium cation is responsible for the IL-properties and X (halogenide) works as a co-catalyst with $NaNO_2$. And the IL-based catalyst can be recycled by phase separation for 4 times without loss of activity. Table 1.1 summarized important support-TEMPO and their catalyst systems.

Table 1.1 Structures of supported TEMPO and their catalyst systems

Structure of catalyst	TEMPO unit on supports / mmol	Catalyst system	Ref

	g^{-1}		
	0.50	NaOCl/KBr	84
	0.33	$NaNO_2$/$n$$Bu_4NBr$/$O_2$ TBN/O_2	85
	0.60	$CuCl/O_2$	86
	0.85	*m*-chloroperbenzoic acid	86
	1.59	NaOCl/KBr bis(acetoxy)-iodobenzene	87,88
 7 = MeO-$(CH_2CH_2O)_n$-CH_2CH_2- M_w 5000 Daltons	0.18	NaOCl/KBr bis(acetoxy)-iodobenzene	90

	3.20	NaOCl/KBr	72
Copyright © 2014 Journal of Molecular Catalysis A: Chemical			
	-	$Co(NO_3)_2/Mn(NO_3)_2$	91
Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim			
	-	$X/NaNO_2/O_2$	92
	0.10	NaOCl/KBr	93
	0.68	NaOCl/NaBr	94

As an alternative to solid matrix material, magnetic nanobeads have been also used as a support to immobilize TEMPO. Graphene-coated nanobeads with a magnetic cobalt core immobilized TEMPO was prepared by using a general applicable “click”-chemistry. [93] The catalyst can be rapidly collected by simple magnetic decantation. A magnetic polystyrene nanospheres (MPNs) also has been used as such type of supports. [94] In NaOCl/NaBr system, TEMPO/MPNs exhibits both similar versatility and efficiency to homogeneous TEMPO. The catalyst can be recycled over 20 times without loss of TEMPO radicals and degradation of MPNs.

Another approach has been reported that TEMPO ammonium salts were immobilized in commercially available saponite by a simple cation-exchange reaction. [95] The catalyst was successfully used as a recyclable catalyst for the oxidation in NaOCl/KBr system up to 10 runs.

1.6 Hyperbranched polymer for catalysis

Recently, HBPs have started to be utilized in catalyst field because of some unique advantages. Firstly, HBPs have a large number of end groups which can afford or introduce a large amount of catalytic functional groups. The synthesis process of HBPs is much easier than dendritic-like structures as well. Secondly, because of a low degree of entanglement of the hyperbranched structure, the end-groups can be well exposed and accessible for the reactants of catalytic reactions, which is benefit to the

work of catalytic functional groups. Moreover, the hyperbranched structure possesses a large free volume that could enhance mass transport of the reactants and products, which make it more efficient than other insoluble structures. Finally, the HBPs usually have a good solubility in organic solvent, as a result it can work as a homogeneous system in some conditions.

Van de Vyver et al. [96] have presented a water-soluble sulfonated hyperbranched poly(arylene oxindole) with high acidity to catalyze the reaction from cellulose to levulinic acid, and demonstrated a superior catalytic performance in terms of both activity and selectivity.

Nabae et al. [97] have synthesized a sulfonic acid functionalized hyperbranched poly(ether sulfone) and used it as a solid acid catalyst in esterification reaction of acetic acid and 1-butanol. After grafting the hyperbranched poly(ether sulfone) onto a carbon black, those materials show fairly good catalytic activity and promising recyclability for 5 runs.

In this thesis, hyperbranched poly(ether ketone) has been chosen to use in different catalytic reactions by introducing several different terminal groups.

1.7 Brief overview of this dissertation

The objective of this study is to introduce functional terminal groups on a novel designed hyperbranched aromatic poly(ether ketone) (HBPEK) to synthesize new catalysts with the benefit of hyperbranched structure. Moreover, the TEMPO terminated HBPEK was grafted to insoluble supports to form an insoluble catalyst.

Chapter 2 focuses on the synthesis of hyperbranched aromatic poly(ether ketone) (HBPEK) with carboxylic acid terminals. Weight-average molecular weight (Mw) was controlled by changing the reaction time and concentration of the monomer. And then, the terminal carboxylic acid function was converted to ethyl ester function, which lead to an obviously change of the polarity of polymer. The HBPEK with carboxylic acid terminals has been tested as a weak-acid catalyst for the hydrolysis of cellulose to glucose.

Chapter 3 discussed several kinds of monomer in order to synthesize a linear type or less branched type of poly(ether ketone) concluding 4-phenoxybenzonic acid, 4-phenoxy-1,3-benzenedicarboxylic acid, 4-phenoxyphthalic acid, 4-phenoxyphthalic anhydride and 4-phenoxyphthalic acid, 2-methyl ester. Those monomers are synthesized and characterized in detail in this chapter. However, except for the first one, all the other structures face a difficulty in polymerization, which proves the high activity of the AB_2 structure that we chose for the following catalyst

reactions.

Chapter 4 discusses the performance of HBPEK with TEMPO terminated as a catalyst for aerobic oxidation of benzyl alcohol. The procedure and TEMPO loading rate on HBPEK was discussed in detail. With a different catalytically active terminal, TEMPO, the polymer could have a wider range of application compared to Chapter 2. The TEMPO/HBPEK was used in aerobic oxidation of benzyl alcohol. Since the TEMPO/HBPEK is soluble in the current reaction condition, it has been grafted onto carbon black and polyimide particle to form a heterogeneous catalyst. The recyclability of these catalysts has been tested in the same reaction condition.

Considering the disadvantages of carbon black and polyimide particles investigated in Chapter 4 as insoluble supports, graphene, a carbon material with less surface radicals has been utilized in Chapter 5 to graft TEMPO/HBPEK as a new catalyst. Finally this catalyst has been used in aerobic oxidation of 2-adamantanol, which is harder to be oxidized than benzyl alcohol, to expand the usage of the catalyst.

The last chapter summaries the results obtain in each study and show some promotion possibilities for future work.

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Chapter 2 Hyperbranched Aromatic Poly(ether ketone) with Carboxylic Acid Terminals as Catalyst for Hydrolysis of Cellulose

2.1 Introduction

In terms of the potential applications of hyperbranched polymers (HBPs), our research group has been particularly interested in hyperbranched aromatic polymers with acidic functional groups. Such polymers exhibit acidic functionality in various environments because of their high thermal and chemical stabilities. For instance, we have successfully synthesized a hyperbranched aromatic poly(ether sulfone) with sulfonic acid terminal groups and proposed it as a promising proton-conductive membrane for fuel cells, and a novel solid acid catalyst. [1-3]

Weakly-acidic groups, such as carboxylic acid as well as such strongly-acidic functional groups, are also of interest as the terminal functional groups of HBPs. There have been several studies reporting that weakly-acidic groups on carbon catalyze the hydrolysis of polysaccharides in water at 150-170 ℃. [4-6] One of the motivations to employ the weak acid groups is the stability of the acidic sites, whereas strong acids, such as sulfonic acid, which has been used after immobilized as a solid catalyst, [7-10] tend to be easily deactivated by impurities. Kobayashi et al. has proved

that neighboring carboxylic and phenolic groups synergistically work for the hydrolysis reaction. [5] If many carboxylic groups could be introduced on the terminals of a thermally stable HBPs, *e.g.*, hyperbranched poly(ether ketone) (HBPEK), the resulting material would be a quite active and stable catalyst for biomass conversion.

Shu [11] previously reported the synthesis of a HBPEK with carboxylic acid terminal groups through the polycondensation of an AB_2-type monomer, 5-phenoxyisophthalic acid. The activity of the B terminal was limited by steric hindrance because the two carboxyl groups were present on the same benzene ring, and resulted in a relatively low molecular weight (M_w) of less than 15000 Daltons.

In this chapter, we propose a symmetric AB_2 monomer, 4,4'-(*m*-phenylenedioxy)-bis(benzenecarboxylic acid), for the synthesis of hyperbranched aromatic poly(ether ketone) *via* Friedel-Crafts reaction as illustrated in Figure 2.1. Although this monomer is a known compound, [12, 13] it has not been utilized as an AB_2 monomer. The B terminals are expected to exhibit high reactivity due to the high flexibility derived from the ether bonds and less steric hindrance; therefore, higher molecular weights can be expected. Moreover, the B terminals can be utilized as a weak-acid terminal without any end-capping reaction. This study describes the details of the preparation of new HBPEK with various molecular weights and their physicochemical properties. Moreover, to investigate the

functionality of the terminal groups, a model catalytic reaction, the hydrolysis of cellulose to glucose, which is an important reaction in biomass conversion, was investigated using the prepared polymer.

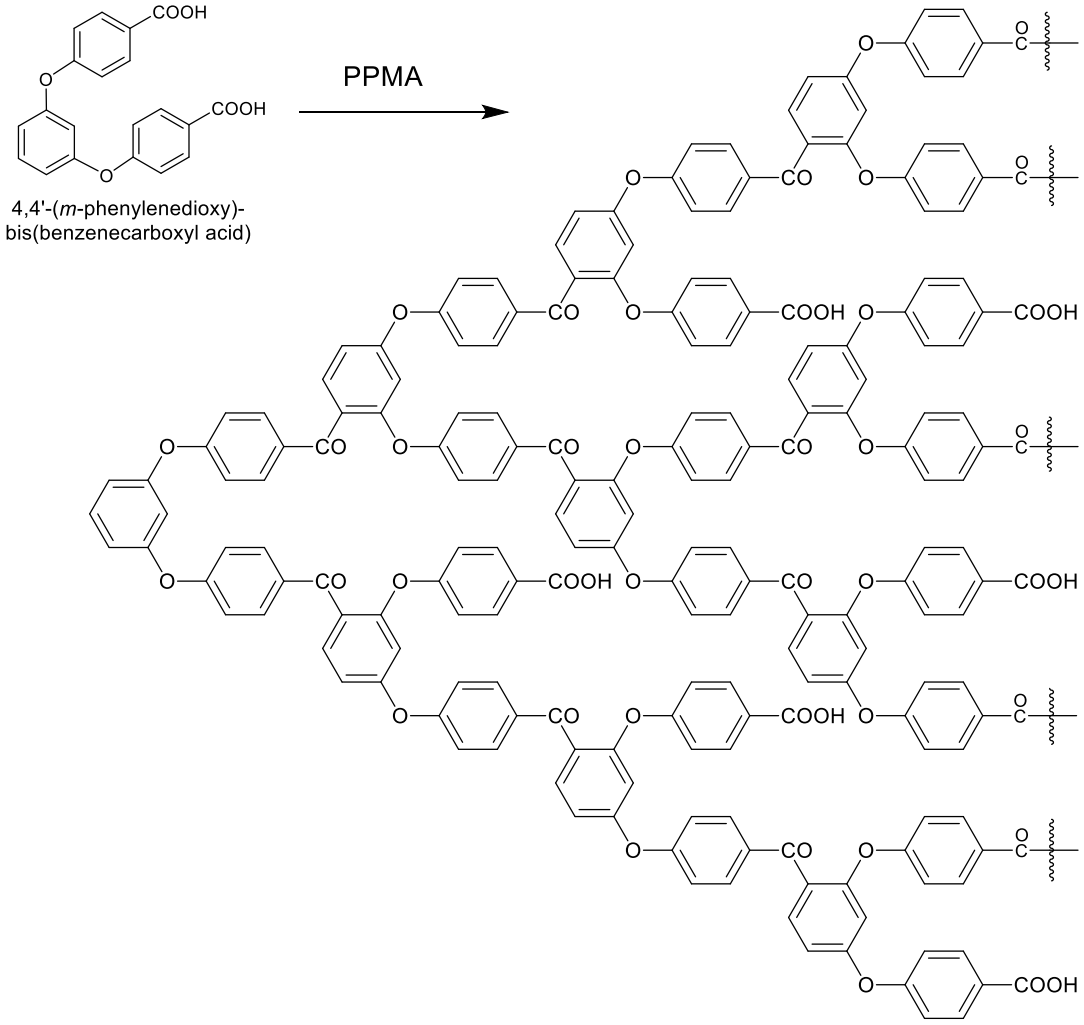


Fig 2.1 Structures of hyperbranched poly(ether ketone)

2.2 Experimental procedure

2.2.1 Materials

Resorcinol, 4-nitrobenzonitrile, methanesulfonic acid, thionyl chloride and triethylamine were purchased from TCI. Microcrystalline cellulose was purchased from Merck (Avicel, 102331). Potassium carbonate, potassium hydroxide, phosphorus pentoxide and distilled water were purchased from Wako. Phosphorous pentoxide/methanesulfonic acid (PPMA, 7.7 wt% phosphorus pentoxide solution in methanesulfonic acid, Eaton's reagent) was used immediately after preparation. All of the chemicals were used as received unless stated otherwise.

2.2.2 Measurements

Nuclear magnetic resonance (NMR) (^{1}H, 400 MHz) spectra were recorded for samples dissolved in chloroform-*d* or dimethyl sulfoxide-d_6 using a JEOL JNM-ECS 400 NMR spectrometer. FTIR spectra were recorded with a JASCO 4100 spectrometer using the KBr pellet method. Gel permeation chromatography (GPC) was performed using a Viscotek GPC-1000 system equipped with a TDA 302 triple detector and a TSK-GEL α-M column. DMF containing 0.05 M LiBr was used as the eluent. The weight-average molecular weight (M_w) was calculated from light scattering data. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere using a SII TGA 7300 system at a heating rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) was performed under nitrogen using a SII DSC 7020 system at a heating rate of 10°C min^{-1}. The inherent viscosity was measured with 0.5 g dL^{-1} of polymer solution in

dimethylacetamide (DMAc) using an Ostwald viscometer in a thermostatic bath at 30°C. The solubility of the polymer was qualitatively examined by adding 6 mg of polymer to 2 mL of solvents. The ion exchange capacity (IEC) was determined as follows: thirty milligrams of polymer sample was stirred in a 0.1 M NaOH solution (3 mL) overnight and then diluted to 10 mL with deionized water. The obtained solution was titrated with a 0.05 M HCl standard solution.

2.2.3 Synthesis of 4,4'-(m-phenylenedioxy)-bis benzenenitrile

In a 100-mL flask, resorcinol (1.11 g, 10.0 mmol) and 4-nitrobenzonitrile (3.02 g, 20.0 mmol) were dissolved in 60 mL of DMF. Then, potassium carbonate (6.98 g, 50 mmol) was added to the flask. The mixture was stirred at 120 °C for 48 h and then poured into 1000 mL of water. The product was collected by filtration, washed 3 times with water and then dried under vacuum. Yield: 90%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.64 (d, 4H), 7.43 (t, 1H), 7.06 (d, 4H), 6.93-6.90 (dd, 2H), 6.79 (s, 1H) (Figure 2.2).

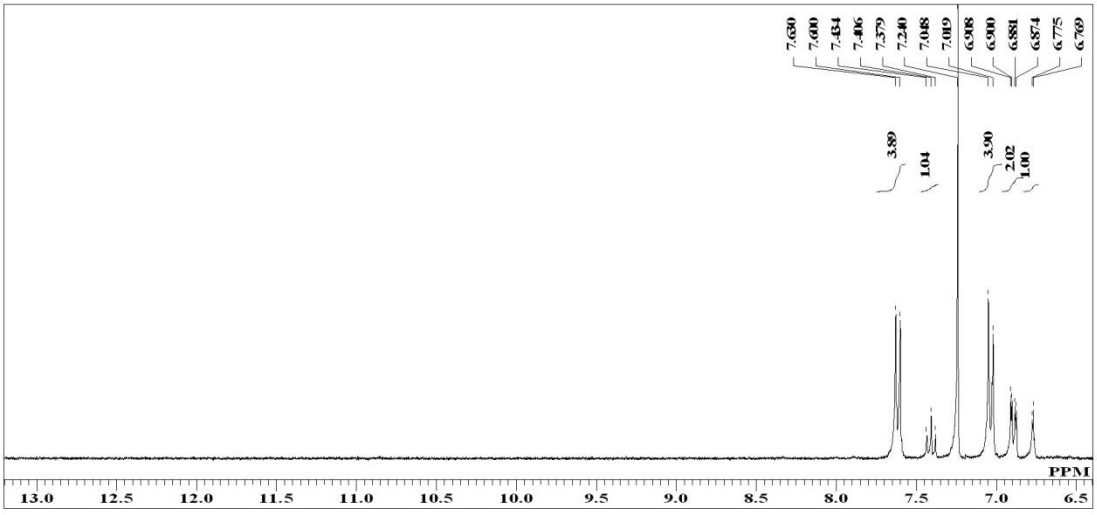


Fig 2.2 ^{1}H NMR of 4,4'-(*m*-phenylenedioxy)-bis benzenenitrile

2.2.4 Synthesis of 4,4’-(m-phenylenedioxy)-bis(benzenecarboxylic acid)(1)

In a 200-mL flask equipped with a reflux condenser, 4,4'-(m-phenylenedioxy)-bis benzenenitrile (1.56 g, 5 mmol) and potassium hydroxide (2.81 g, 50 mmol) were dissolved in 120 mL of a water/ethylene glycol (1:1, *v*:*v*) mixed solvent. The reaction mixture was refluxed at 136 ℃ for 4 h and then poured into 300 mL of water. The pH value of the solution was adjusted to 1 using a 1 M HCl aqueous solution. The crude product was collected by filtration and washed with diluted HCl aqueous and water. After recrystallization from aqueous acetic acid, a pink powdery product was obtained and dried under vacuum. Yield: 96%. ^{1}H NMR (DMSO-d_6, δ, ppm): 12.89 (s, 2H), 7.96 (d, 4H), 7.51 (t, 1H), 7.11 (d, 4H), 6.98-6.95 (dd, 2H), 6.89 (s, 1H, e) (Figure 2.3). IR (KBr, cm^{-1}): 1670 (C=O, stretching), 2500-3000 (O-H, vibration, broadband). (Figure 2.4) The TG

curve is shown in Figure 2.5.

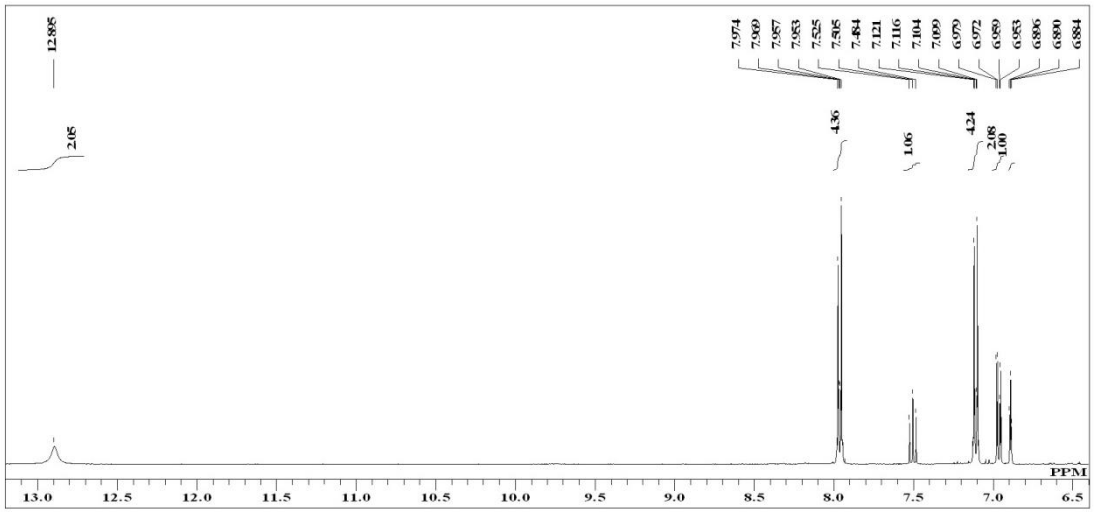


Fig 2.3 ^{1}H NMR of 4,4'-(m-phenylenedioxy)-bis(benzenecarboxylic acid)

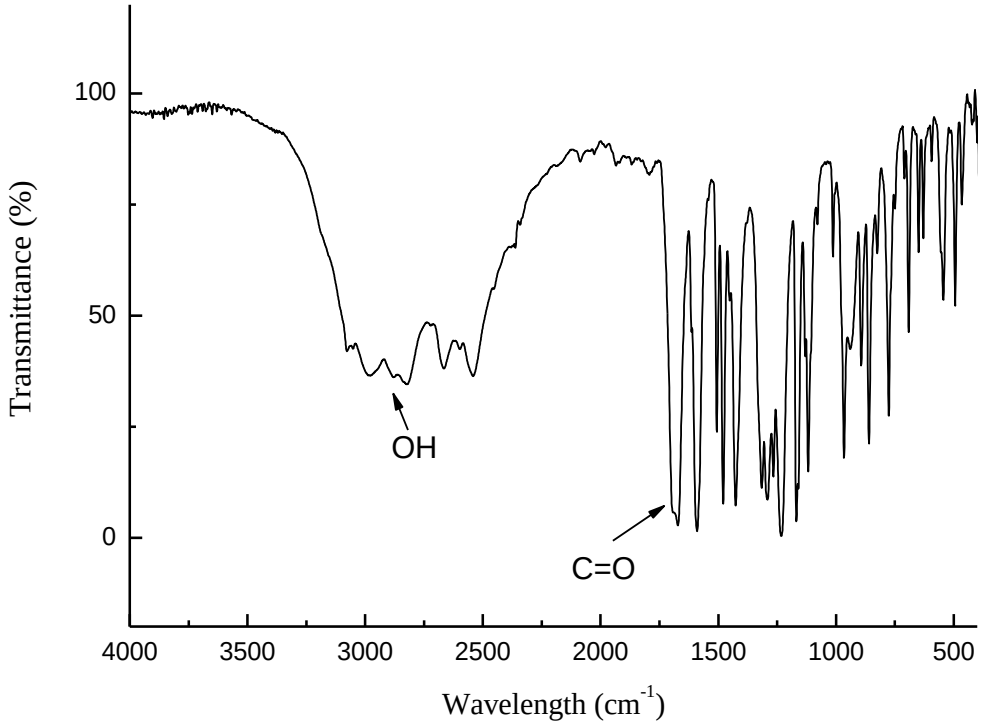


Fig 2.4 IR spectrum of 4,4'-(m-phenylenedioxy)-bis(benzenecarboxylic acid)

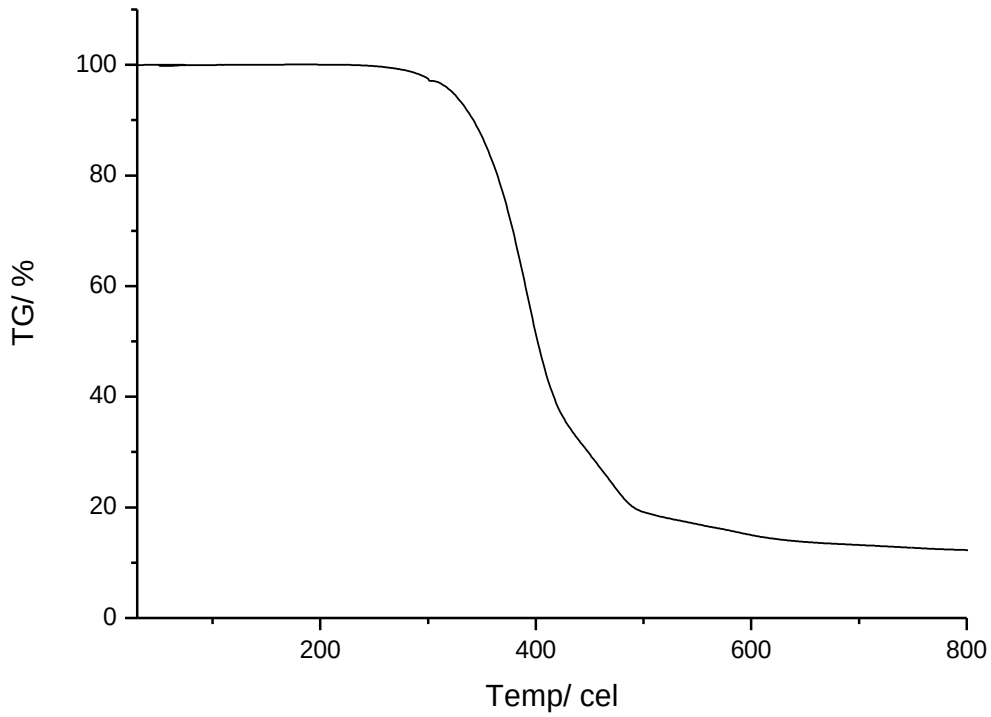


Fig 2.5 TG curve of 4,4'-(m-phenylenedioxy) -bis(benzenecarboxylic acid)

2.2.5 Synthesis of HBPEK with carboxylic acid terminal group (P2)

In a 5-mL flask, 0.3 g of monomer **1** was mixed with 2 mL of PPMA. [14,15] The reaction mixture was stirred at 110°C for 2 h, poured into water, washed with a large amount of water and then methanol, and finally dried at 80°C under vacuum. ^{1}H NMR was showed in Figure 2.6. IR (KBr, cm^{-1}): 1668 (C=O, stretching), 2500-3000 (O-H, vibration, broadband).

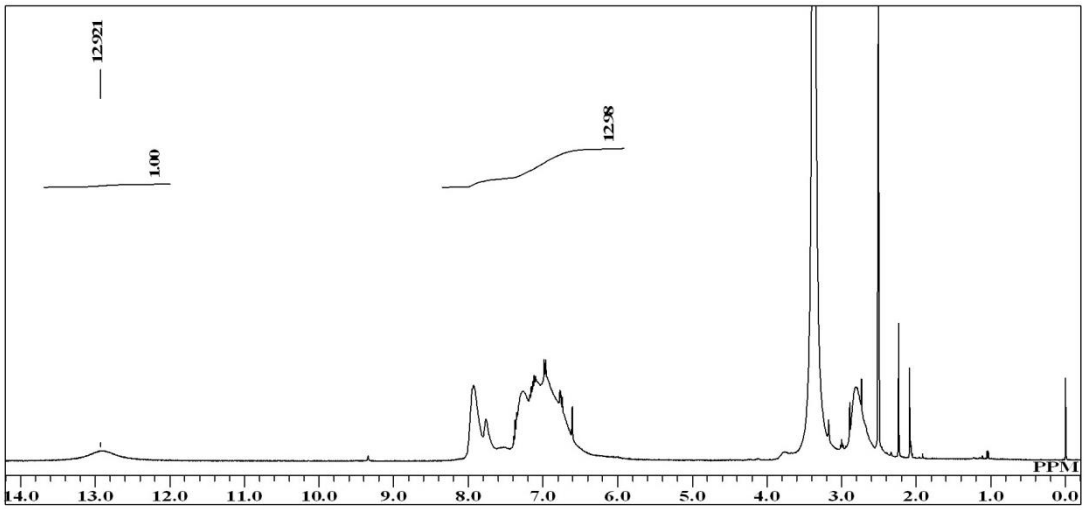


Fig 2.6 ^{1}H NMR of HBPEK **P2**

2.2.6 Synthesis of HBPEK with ethyl ester terminal group (P3)

To a 5-mL flask equipped with a reflux condenser was added 0.3 g of polymer, and then 1.5 mL of thionyl chloride was added drop-wise while stirring. The mixture was gently heated at 100 ˚C for 1 h (1 mL of thionyl chloride was added after 20 min) and then distilled at 70 ˚C under atmospheric pressure to remove excess thionyl chloride. Then, the bath temperature was slowly increased to 130 ˚C under vacuum until the product, carbonyl chloride-terminated polymer, was fully dried. Ethanol (3 mL) and triethylamine (0.5 mL, 3.4 mmol) were added to the same flask. The mixture was refluxed at 80 ˚C for 4 h and distilled at 95 ˚C under reduced pressure. The obtained product was washed with water and methanol and then dried under vacuum. IR (KBr, cm^{-1}): 1716 (C=O, stretching), 2497, 2604, 2942, 2978, (CH_2, CH_3, stretching), 3421 (overtone of C=O stretching vibration). ^{1}H NMR was shown in Figure 2.7.

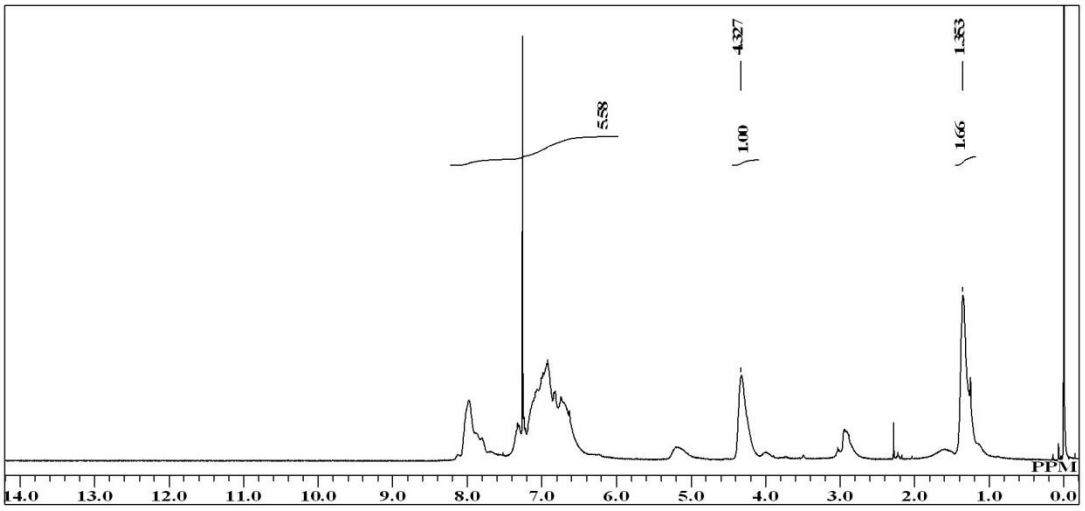


Fig 2.7 ^{1}H NMR of HBPEK P3

2.2.7 Hydrolysis of cellulose

As a pretreatment, microcrystalline cellulose (9.72 g) and **P2** (1.49 g, acid: 3.73 mmol) were milled together with alumina balls (1.5 cm, 2 kg) in a ceramic pot (3.6 L) at 60 rpm for 48 h. The hydrolysis of cellulose was conducted in a Hastelloy C22 high-pressure reactor (MMJ-100, OM-LabTech, 100 mL). The milled sample (374 mg; containing 324 mg of cellulose and 50 mg of catalyst (acid: 0.125 mmol)) and 40 mL of distilled water were added to the reactor. The temperature was increased to 230 °C in approximately 17 min and then rapidly cooled to 50 °C by flowing air. After the reaction, the solid and liquid phases were separated by centrifugation and decantation. The reaction products in the liquid phase were analyzed by high-performance liquid chromatography [HPLC; Shimadzu LC10-AT*VP* with refractive and ultraviolet (210 nm) detectors] with a Shodex SUGAR SH-1011 column (ø8 × 300 mm, mobile phase:

water at 0.5 mL min^{-1}, 50 °C) and a Phenomenex Rezex RPM-Monosaccharide Pb++ column (ø7.8 × 300 mm, mobile phase: water at 0.6 mL min^{-1}, 70°C). The conversion of cellulose was determined from the weight difference in the solid fraction before and after the reaction.

2.3 Results and Discussion

2.3.1 Synthesis of HBPEK.

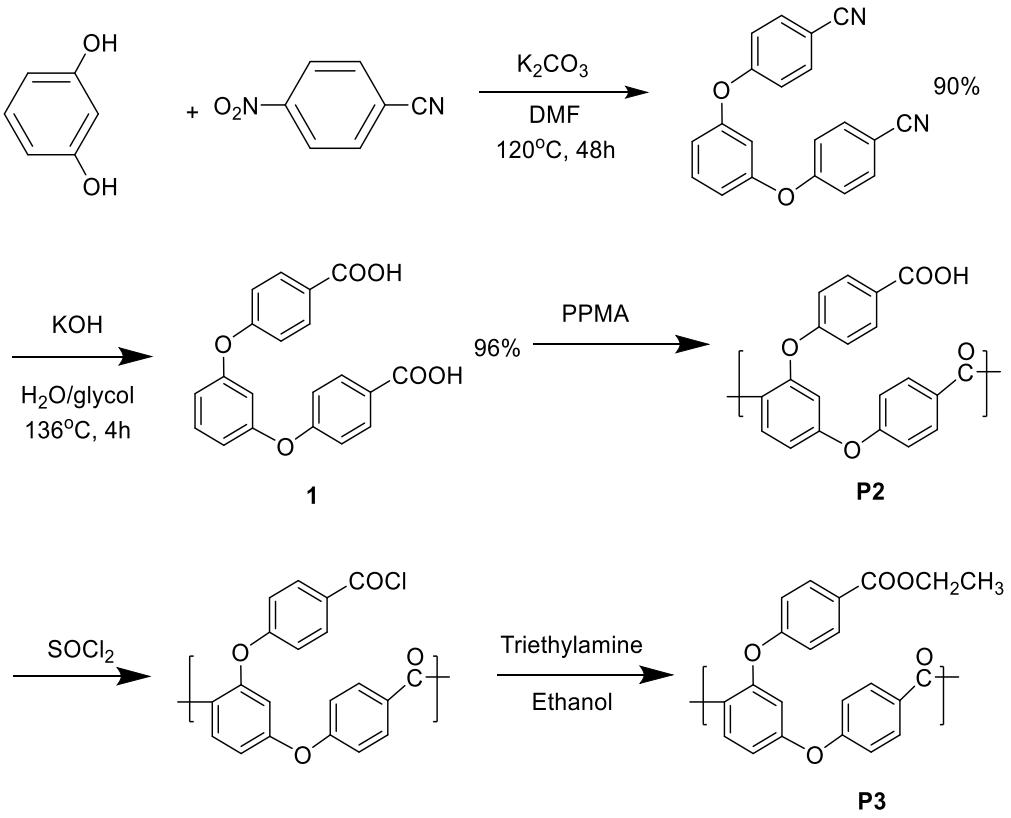
The hyperbranched aromatic poly(ether ketone) was synthesized as shown in Scheme 2.1. The AB_2 monomer, 4,4'-(m-phenylenedioxy)-bis(benzenecarboxylic acid), was prepared *via* a simple route starting from resorcinol and 4-nitrobenzonitrile with a yield of greater than 86%. [16] The structure of **1** was confirmed by ^1H NMR (Figure 2.8a). The polycondensation of the monomer was conducted in PPMA at 110 ℃, which afford the hyperbranched polymer (**P2**). Figure 2.8b shows the ^1H NMR spectrum of **P2**. After polymerization, the peak of carboxylic acid (f, 12.89 ppm) decreased and a new peak (g, 7.28 ppm) appeared, suggesting a successful polycondensation.

The solubility of monomer in different organic solution are listed in Table 2.1. Since **1** and **P2** show different solubility in methanol, it was used to purify the synthesized polymer.

Table 2.1 Solubility of monomer **1** and **P2**

Solvent	Monomer **1**	Polymer **P2**
THF	+	+

Ethyl acetate	-	-
Toluene	-	-
Methylene Chloride	-	-
Chloroform	-	-
DMAc	+	+
DMF	+	+
DMSO	+	+
Hexane	-	-
Acetone	-	-
Methanol	+	-



Scheme 2.1 Synthesis and structures of HBPEK with carboxylic acid and ethyl ester as the terminal groups.

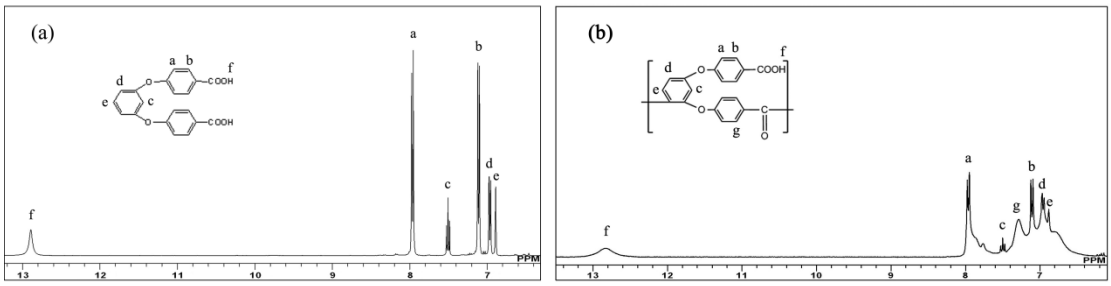


Fig 2.8 ^{1}H NMR (DMSO-d_6) of monomer **1** (a) and polymer **P2** (b).

Because the GPC for **P2** was difficult due to the presence of numerous carboxylic acid groups, the terminal functional groups were converted into ethyl ester (**P3**) and analyzed by GPC (Table 2.2). Figures 2.6 and 2.7 show the ^{1}H NMR spectra of **P2** and **P3** of entry 2, suggesting a fully conversion of terminal groups. Compared to **P2**, the peak of carboxylic acid (12.89 ppm) disappeared and the peaks of ethyl ester (4.33 ppm and 1.35 ppm with a ratio of 2:3) appeared which confirmed a successful terminal conversion. The IR spectra of **P2** and **P3** were shown in Figure 2.9. The CH_2, CH_3, stretching peaks appear at 2497, 2604, 2942, 2978 cm^{-1} in **P3**.

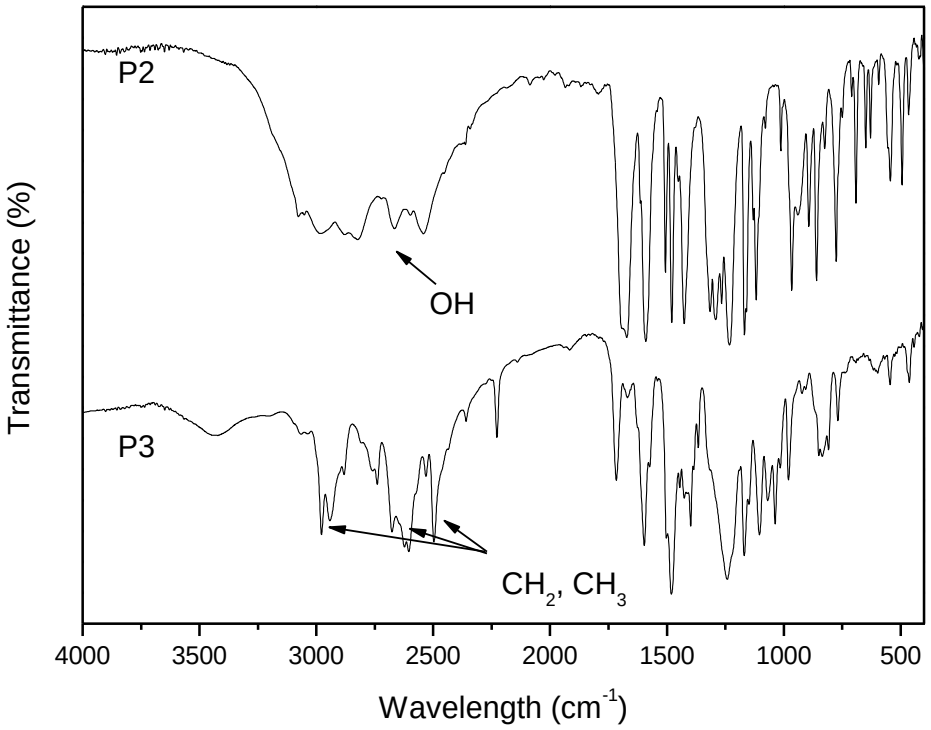


Fig 2.9 IR spectra of **P2** and **P3**

The GPC result suggests that the molecular weight of the HBPEK can be controlled in the range of 42000 to 159000 Daltons by changing the polymerization conditions. It is remarkable to nobe that clearly higher molecular weights have been achieved here in comparison to previously reported work: M_w < 15000 from 5-phenoxyisophthalic acid. [11] This high molecular weight is most likely due to the higher reactivity of the B terminal of monomer **1**.

Table 2.2 Synthesis of HBPEK under different conditions

Entry[a]	PPMA /mL	T/ ℃	Time /h	M_w[b]	Yield	$\eta_{inh,P2}$[c]	$\eta_{inh,P3}$[c]	IEC /mol kg^{-1}
1	3	110	2	42000	84	0.101	0.067	2.8
2	2	110	2	74000	84	0.127	0.081	2.5
3	2	110	6	123000	94	0.133	0.085	2.3
4	2	110	10	159000	92	0.171	0.112	2.2

[a]The amount of monomer **1**: 300 mg.

[b]Determined by GPC eluted with DMF containing lithium bromide (0.05 mol/L).

[c]Measured at a concentration of 0.5 g dL^{-1} in DMAc at 30 ℃.

2.3.2 Physicochemical property.

The inherent viscosities of **P2** and **P3** were measured using an Ostwald viscometer, and the results are shown in Table 2.2. The **P2** polymers show inherent viscosities in the range of 0.101-0.171 dL g^{-1} in DMAc, and the corresponding ethyl ester-terminated **P3** polymers show inherent viscosities in the range of 0.067-0.112 dL g^{-1}. These low viscosity values are most likely due to the quite low degree of entanglement of the HBPs. The difference between the viscosities of **P2** and **P3** resulted from the different polarities of the terminal groups.

Table 2.3 shows the solubilities of the HBPs from entry 1. P2 is

soluble in basic aqueous solutions, tetrahydrofuran and some polar aprotic solvents, such as DMSO and DMF, and it is partially soluble in acetone and insoluble in dichloromethane, chloroform, and toluene, among others. However, **P3** is soluble in dichloromethane, chloroform and acetone and partially soluble in toluene and THF. It is important to note that the aromatic poly(ether ketone) dissolved in several solvents due to the introduction of the hyperbranched structure, whereas typical linear aromatic poly(ether ketone)s are generally known to be insoluble polymers in most solvents. [17]

Table 2.3 Solubility of HBPEK[a]

	NMP	DMAc	DMSO	DMF	THF	Acetonitrile
P2	++	++	++	++	++	-
P3	++	++	++	++	±	-
	Acetone	Dichloromethane	Chloroform	Hexane	Ethyl acetate	Acetone
P2	±	-	-	-	-	±
P3	++	++	++	-	-	++
	Toluene	MeOH	EtOH	Deionized water	0.1M NaOH solution	Tetramethylammonium hydroxide solution
P2	-	-	-	-	+	±
P3	±	-	-	-	-	-

[a] ++, soluble at room temperature; +, soluble on heating; ±, partially soluble; -, insoluble even on heating

The thermal stabilities of **P2** and **P3** were examined by TGA under a nitrogen atmosphere (Figure 2.10 and 2.11). The weight losses of **P2** and **P3** begin at approximately 150 and 200 °C, respectively. These initial weight losses are most likely due to the decomposition of the terminal functional groups. The 10% of weight-loss temperatures of all P2 and P3 polymers are greater than 300 °C, suggesting that the poly(ether ketone) backbone possesses high thermal stability. Differential scanning calorimetry (DSC) measurements for **P2** and **P3** were performed over the temperature range of -30-200 °C. No glass transition temperature was observed, suggesting that the glass transition temperatures of these polymers may be greater than 200 °C.

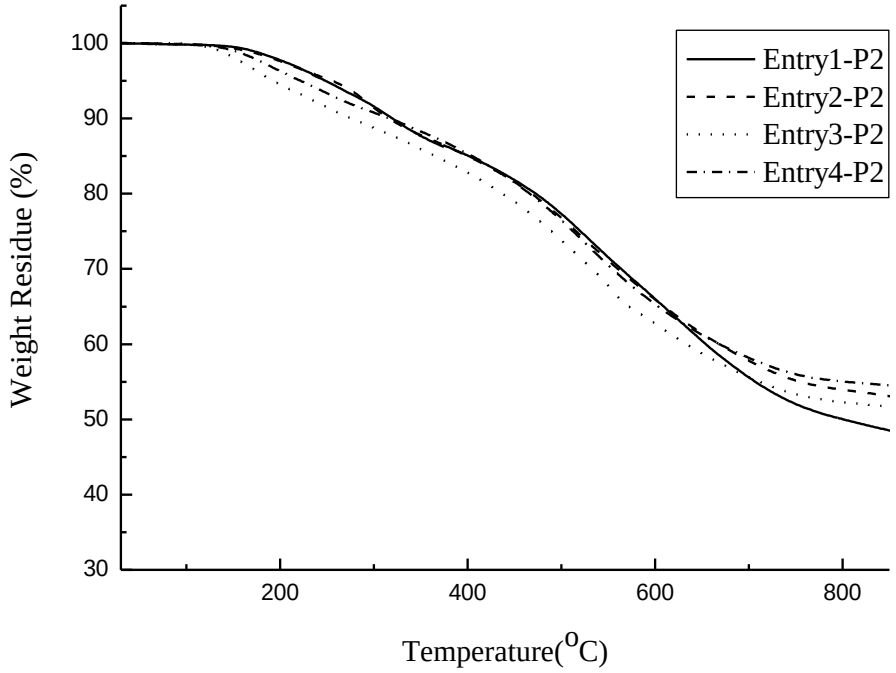


Fig 2.10 TG curve of entry 1-4 with carboxylic acid terminal groups

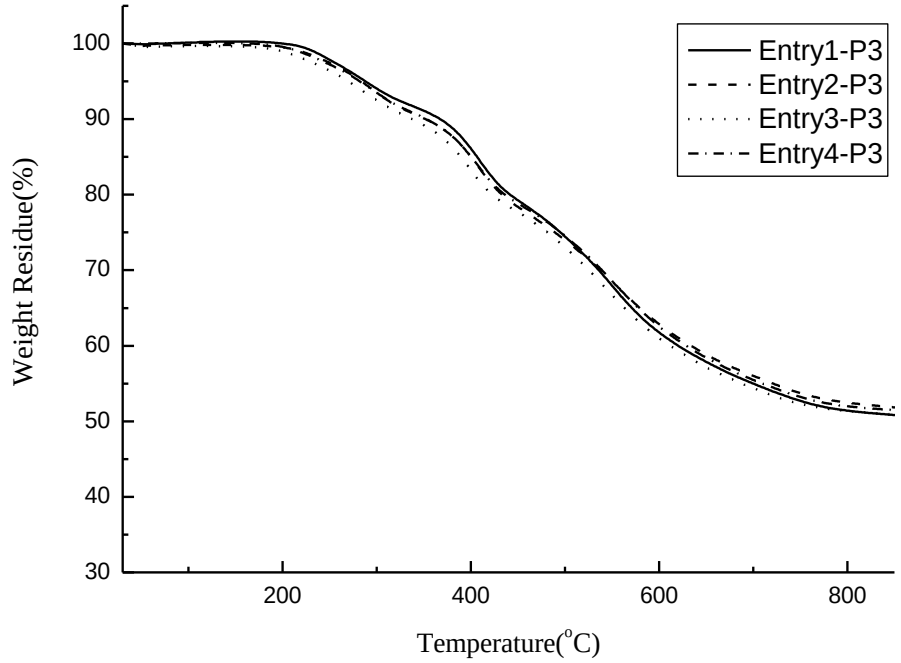


Fig 2.11 TG curve of entry 1-4 with ethyl ester terminal groups

2.3.3 Functionality of the carboxylic acid terminals.

The ion exchange capacity of **P2** was evaluated by acid-base titration, and the results are shown in Table 2.2. Entry 1 shows an IEC of 2.8 mol kg^{-1}, whereas the theoretical value is 2.9 mol kg^{-1}. As the weight-average molecular weight increases, the amount of titrated carboxylic acid decreases. Presumably, some terminal groups are hidden in the polymer matrix or a cross-linking reaction decreased the number of terminals as the molecular weight increased (Figure 2.12).

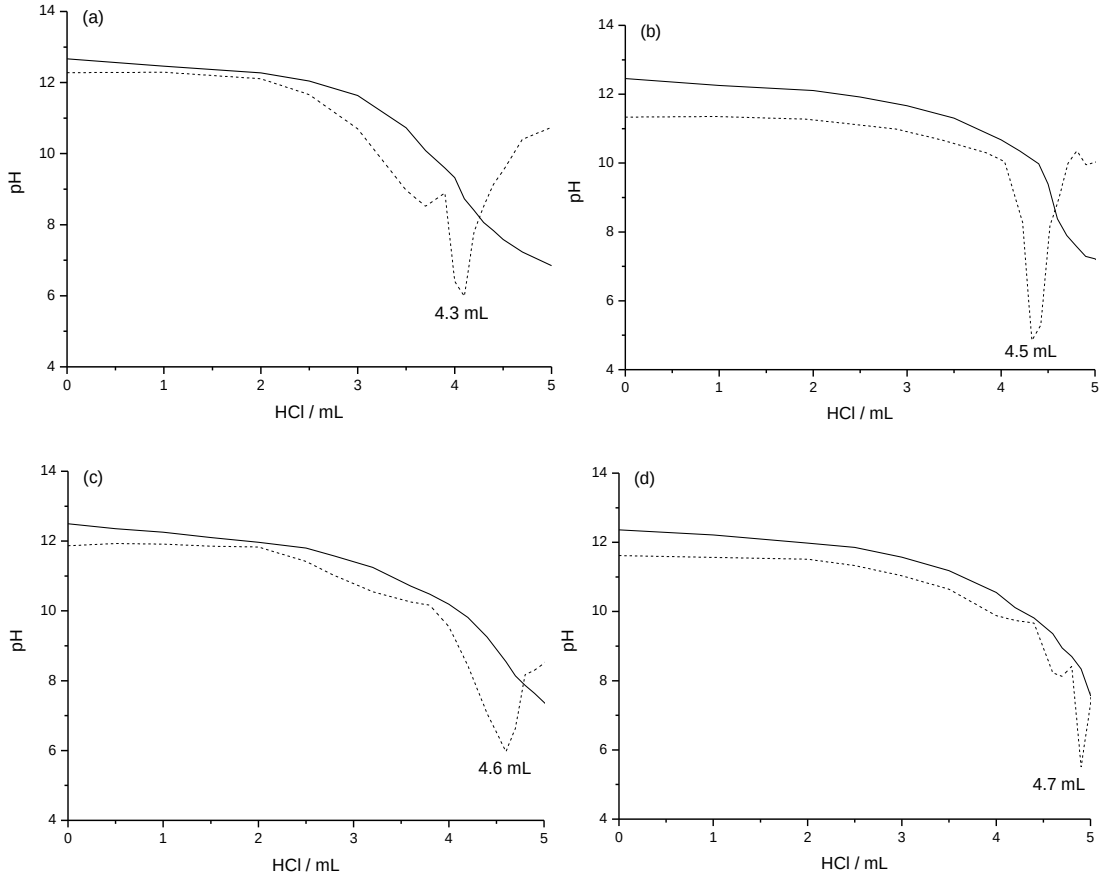
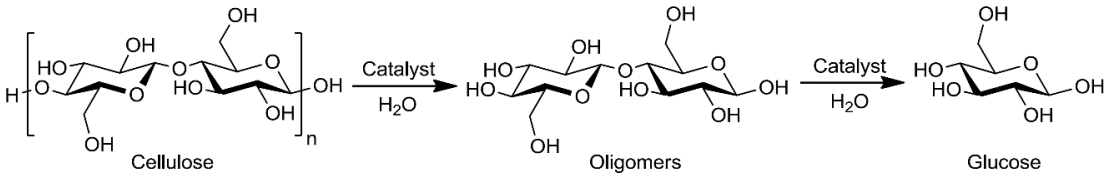


Fig 2.12 Titration result of P2 (a) entry 1; (b) entry 2; (c) entry 3; (d) entry 4

The hydrolysis of cellulose was employed as a catalytic reaction (Scheme 2.2) to investigate the functionality of the terminal groups of **P2** from entry 2. Table 2.4 summarizes the results of the catalytic reaction. **P2** clearly shows a higher conversion of cellulose than the blank test. The conversion of cellulose and the yield of glucose reached 53% and 16%, respectively, after the reaction period. The turnover number (TON) was 1.6, which was calculated from the difference between the glucose yields of **P2** and blank, whereas a control experiment with benzoic acid showed a TON of 2.3. These experimental results suggest that the carboxylic acid groups

on the terminals of the HBPEK functioned as a weak-acid catalyst. The present results suggest that **P2** has potential applications as a heterogeneous catalyst, although the solubility and catalytic activity of the polymer requires optimization.



Scheme 2.2 Hydrolysis of cellulose to glucose.

Table 2.4 Hydrolysis of cellulose by **P2** from entry 2.[a]

Entry	Catalyst	Conv. /%	Yield /%C							TON[i]
			Glc[b]	Olg[c]	Man[d]	Frc[e]	Lev[f]	5-HMF[g]	Others[h]	
1	None	27	4.6	15	0.6	0.5	0.2	1.8	4.8	-
2	**P2**	53[j]	16	22	0.9	1.1	0.8	3.8	8.7	1.6
3	Benzoic acid	53	19	21	1.1	1.4	1.0	4.2	5.2	2.3

[a] Cellulose 324 mg, **P2** 50 mg or benzoic acid 14 mg, distilled water 40 mL, 230 °C.

[b] Glucose.

[c] Degree of polymerization = mainly 2-6.

[d] Mannose.

[e] Fructose.

[f] Levoglucosan.

[g] 5-Hydroxymethylfurfural.

[h] (conversion) − (total yield of shown products).

[i] Turnover number for production of glucose.

[j] For estimation of conversion, we hypothesized that none of **P2** dissolved into water.

2.4 Conclusions

A new type of HBPEK that possesses carboxylic acid terminal groups has been successfully synthesized via a one-step polycondensation of a symmetric AB_2 monomer **1**, using PPMA as a condensing agent and solvent. The weight-average molecular weight can be controlled in the range of 4.2×10^4 to 1.6×10^5 Daltons by changing the polymerization conditions. The HBPEK exhibited good solubility in organic solvents, and the solubility could be changed by converting the terminal groups. TGA suggested that these polymers possessed good thermal stability. The catalytic activity of the carboxylic acid terminal groups was demonstrated by the hydrolysis of cellulose. Considering the development possibilities for carboxylic acid functionality, the present hyperbranched poly(ether ketone)s have potential for a wide range of applications.

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Chapter 3 Exploration of Various Monomer Structures for Different Branching Structures of Aromatic Poly(ether ketone)

3.1 Introduction

In the last chapter, a novel hyperbranched aromatic Poly(ether ketone) (HBPEK) has been synthesized *via* a one-step polycondensation of a symmetric AB_2 monomer, 4,4′-(*m*-phenylenedioxy) -bis(benzenecarboxylic acid). Compared to another AB_2 monomer, 5-phenoxyisophthalic acid reported by Shu et al. [1], this monomer exhibits much higher activity. Under the same polycondensation condition, 4,4′-(*m*-phenylenedioxy)-bis(benzenecarboxylic acid) reach to a molecular weight (M_w) of 42000 Daltons in 2 h, whereas Shu et al. monomer needed 10 h to obtain a low M_w of 14300 Daltons. The huge difference shows the branching structure obviously affect the reaction activity of monomers.

In this chapter, several structures of AB and ABB′ monomers, including those supposed to result in linear or less branched structures, are explored in order to introduce various branching structures to the poly(ether ketone) functionalized with carboxylic acid groups. One purpose of this chapter is to compare the polymerizability of various potential monomers. Moreover, if one could synthesized various poly(ether ketone)s with various branching structures with similar density of

functionalities, the effect of branching structure for the application in catalysis could be experimentally proved. Figure 3.1 shows the structure of monomers discussed in this chapter.

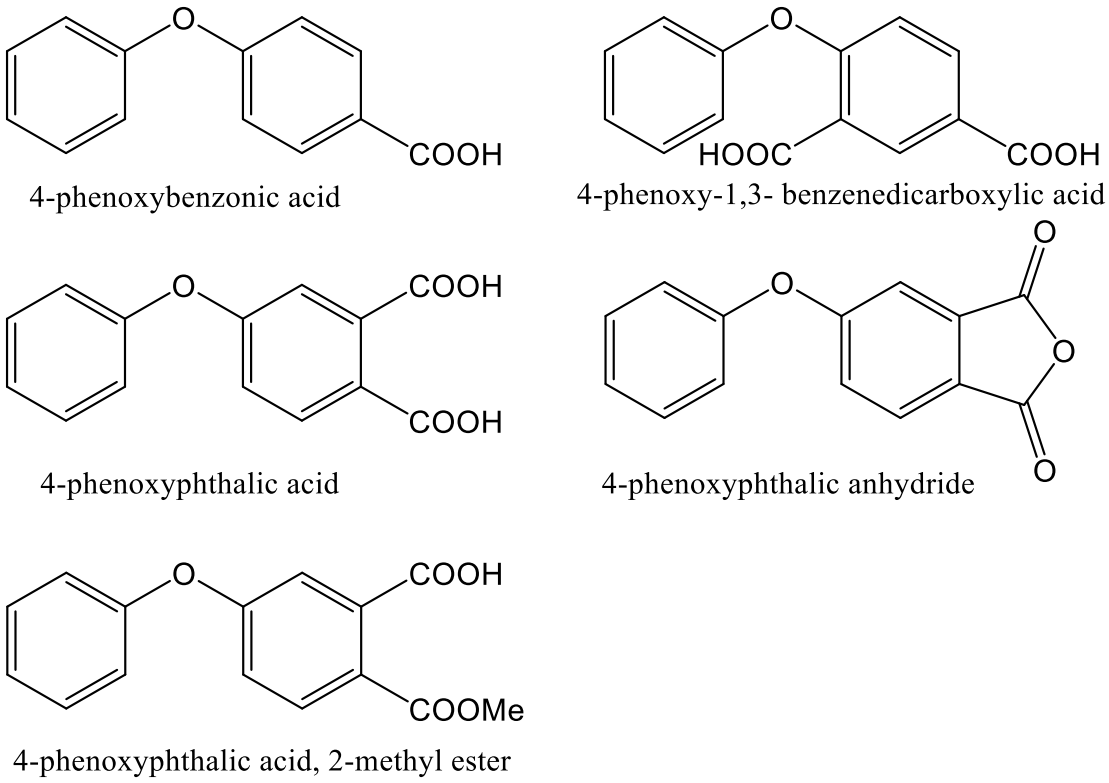


Fig 3.1 Structure of various monomers discussed in this chapter

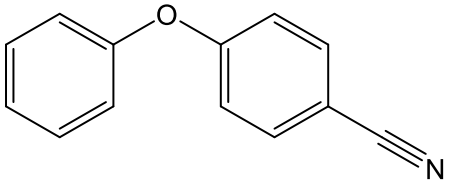
3.2 Experimental procedure

3.2.1 Materials

Phenol, 4-nitrobenzonitrile, 4-bromoisophthalic acid, methanesulfonic acid, thionyl chloride and triethylamine were purchased from TCI. 4-phenoxyphthalonitrile was purchased from Aldrich. Potassium carbonate, potassium hydroxide, phosphorus pentoxide and distilled water were purchased from Wako. Phosphorous pentoxide/methanesulfonic acid

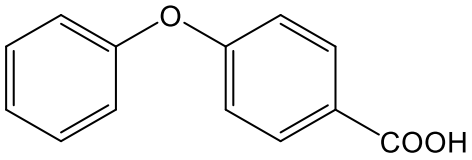
(PPMA, 7.7 wt% phosphorus pentoxide solution in methanesulfonic acid) was used immediately after preparation. All of the chemicals were used as received unless stated otherwise.

3.2.2 Synthesis of 4-phenoxybenzonitrile



In a 100-mL flask, phenol (9.41 g, 10.0 mmol) and 4-nitrobenzonitrile (1.51 g, 10.0 mmol) were dissolved in 40 mL of DMF. Then, potassium carbonate (3.49 g, 25 mmol) was added to the flask. The mixture was stirred at 120 ℃ for 48 h and then poured into 1000 mL of water. The product was collected by filtration, washed 3 times with water and then dried under vacuum. Yield: 74%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.60 (s, 2H), 7.42 (s, 2H), 7.26 (s, 2H), 7.02 (s, 3H).

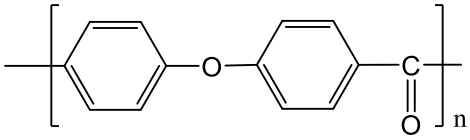
3.2.3 Synthesis of 4-phenoxybenzonic acid



In a 200-mL flask equipped with a reflux condenser, 4-phenoxybenzonitrile (1.59 g, 10 mmol) and potassium hydroxide (1.69 g, 30 mmol) were dissolved in 60 mL of a water/ethylene glycol (1:1 volume) mixed solvent. The reaction mixture was refluxed at 136 ℃ for 4 h and then poured into 300 mL of water. The pH value of the solution was

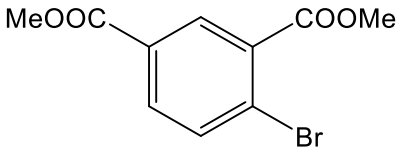
adjusted to 1 using a 1 M HCl aqueous solution. The crude product was collected by filtration and washed with diluted hydrochloric acid and water. After recrystallization from aqueous acetic acid, a powdery product was obtained and dried under vacuum. Yield: 95%. ^{1}H NMR (DMSO-d_6, δ, ppm): 12.89 (s, 1H), 8.07 (d, 2H), 7.41 (d, 2H), 7.23 (t, 1H), 7.01-7.00 (d, 2H).

3.2.4 Synthesis of linear poly(ether ketone)



Different conditions of polycondensation with PPMA have been tried. After reaction, the mixture was poured into water, washed with a large amount of water and then methanol, and finally dried at 80 ℃ under vacuum.

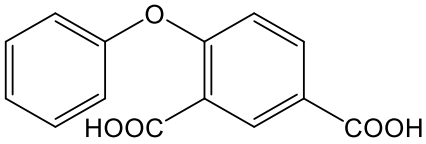
3.2.5 Synthesis of Dimethyl 4-bromoisophthalate



The synthesis was achieved as reported. [2] Briefly, to a suspension of 4-bromoisophthalic acid (9.8 g, 40 mmol) in MeOH (150 mL) at 0 ℃ was added thionyl chloride (140 mmol) drop wise. The reaction was stirred for 24 h, then filtered and concentrated. The resulting oil was put into CH_2Cl_2 (250 mL), and washed with saturated $NaHCO_3$ solution (2 x 35 mL). The organic solvent was collected, dried over anhydrous Na_2SO_4, and removed

under vacuum to give a white powder. Yield: 86 %. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.44 (d, 1H), 7.98-7.96 (d, 1H), 7.77-7.75 (d, 1H), 3.97-3.94 (d, 6H) (Figure 3.1)

3.2.6 Synthesis of 4-phenoxy-1,3- benzenedicarboxylic acid



In a 100-mL flask, phenol (9.41 g, 10.0 mmol), potassium carbonate (2.79 g, 20 mmol) and 5 mL toluene were added in 60 mL of *N*-methyl-2-pyrrolidone (NMP). The mixture was stirred at 120 ℃ for 2 h to evaporate toluene with water in the system. Then, dimethyl 4-bromoisophthalate (4.37 g, 16.0 mmol) was added to the flask. The mixture was stirred at 190 ℃ for 72 h and then poured into 300 mL of water. The pH value of the solution was adjusted to 1 using a 1 M HCl aqueous solution. The crude product was collected by filtration and washed with diluted hydrochloric acid and water. After recrystallization from aqueous acetic acid, a powdery product was obtained and dried under vacuum. Yield: 51%. ^{1}H NMR ($CDCl_3$, δ, ppm): 13.16 (s, 2H), 8.07-8.04 (d, 1H), 7.46-7.41 (d, 2H), 7.22-7.19 (t, 1H), 7.06-7.05 (d, 2H), 6.98-6.96 (d, 1H).

3.2.7 Polycondensation of 4-phenoxy-1,3- benzenedicarboxylic acid

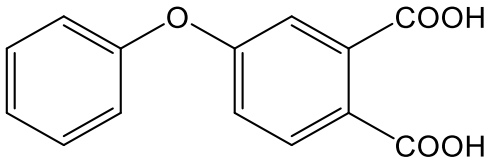
Different conditions of polycondensation with PPMA have been tried. After reaction, the mixture was poured into water, washed with a large amount of water and then methanol, and finally dried at 80 ℃ under

vacuum.

3.2.8 Terminal groups' modification to ethyl ester terminal groups

To a 5-mL flask equipped with a reflux condenser was added 0.3 g of polymer, and then 1.5 mL of thionyl chloride was added drop wise while stirring. The mixture was gently heated at 100 ℃ for 1 h (1 mL of thionyl chloride was added after 20 min) and then distilled at 70 ℃ under atmospheric pressure to remove excess thionyl chloride. Then, the bath temperature was slowly increased to 130 ℃ under vacuum until the product, carbonyl chloride-terminated polymer, was fully dried. Ethanol (3 mL) and triethylamine (0.5 mL, 3.4 mmol) were added to the same flask. The mixture was refluxed at 80 ℃ for 4 h and distilled at 95 ℃ under reduced pressure. The obtained product was washed with water and methanol and then dried under vacuum. IR (KBr, cm^{-1}): 1716 (C=O, stretching), 2500-3000, (CH_2, CH_3, stretching).

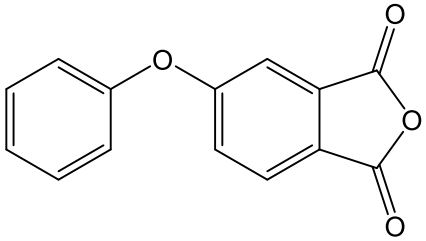
3.2.9 Synthesis of 4-phenoxyphthalic acid



In a 200-mL flask equipped with a reflux condenser, 4-phenoxyphthalonitrile (2.40 g, 10 mmol) and potassium hydroxide (2.81 g, 50 mmol) were dissolved in 120 mL of a water/ethylene glycol (1:1, *v*:*v*) mixed solvent. The reaction mixture was refluxed at 136 ℃ for 4 h and then poured into 300 mL of water. The pH value of the solution was

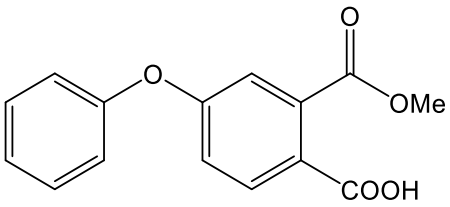
adjusted to 1 using a 1 M HCl aqueous solution. The crude product was collected by filtration and washed with diluted hydrochloric acid and water. After recrystallization from aqueous acetic acid, a light green powdery product was obtained and dried under vacuum. Yield: 96%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.76 (d, 1H), 7.47 (t, 2H), 7.25 (t, 1H), 7.14-7.10 (m, 3H), 7.07 (d, 1H).

3.2.10 Synthesis of 4-phenoxyphthalic anhydride



In a 200-mL flask equipped with a reflux condenser, 4-phenoxyphthalic acid (2.58 g, 10 mmol) was mixed with 100 mL of dried Dichloromethane (DCM). [3] After stirring at 70 °C for 10 min, phosphorus pentoxide (5.68 g, 20 mmol) was added to the mixture. After 3 h, the 4-phenoxyphthalic acid was dissolved in the solution. Then the clear solution was collected by filtration and evaporated to obtain a powdery product. Yield: 70%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.74 (d, 1H), 7.48-7.44 (t, 2H), 7.26-7.22 (t, 1H), 7.13-7.04 (m, 4H).

3.2.11 Synthesis of 4-phenoxyphthalic acid, 2-methyl ester



In a 200-mL flask equipped with a reflux condenser, 4-phenoxyphthalic anhydride (1.20 g, 5 mmol) was dissolved in 40 mL of methanol and refluxing for 30 min.[4] The solvent was then evaporated and a viscous liquid compound was collected after drying under vacuum. Yield: 60%. (Figure 3.6) ^{1}H NMR ($CDCl_3$, δ, ppm): 7.84-7.80 (d, 1H), 7.48-7.44 (t, 2H), 7.27-7.23 (t, 1H), 7.16-7.04 (m, 4H), 3.76-3.74 (d, 3H).

3.2.12 Polycondensation of 4-phenoxyphthalic acid

In a 5-mL dry flask, 0.3 g of 4-phenoxyphthalic acid was mixed with 2 mL of PPMA. The reaction mixture was stirred at 110 ℃ for 24 h, poured into water, filtration, and washed with 100 mL of methanol.

3.2.13 Polycondensation of 4-phenoxyphthalic acid, 2-methyl ester

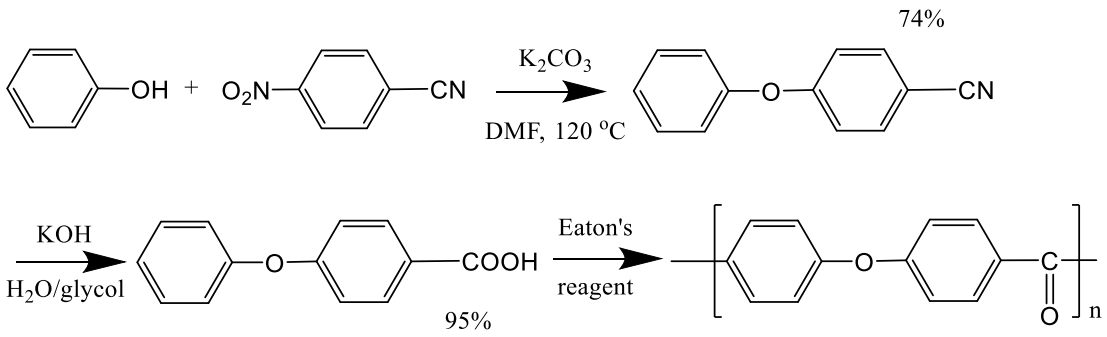
In a 5-mL dry flask, 0.3 g of 4-phenoxyphthalic acid, 2-methyl ester was mixed with 2 mL of PPMA. The reaction mixture was stirred at 110 ℃ for 24 h, poured into water, filtration, and washed with 100 mL of methanol.

3.2.14 Polycondensation of 4-phenoxyphthalic anhydride

In a 5-mL dry flask, 4-phenoxyphthalic anhydride (0.3 g) and $Sc(OTf)_3$ (0.092 g, 0.15 molar eq) was mixed with 1.3 mL of nitrobenzene.[5-8] The reaction mixture was stirred at 130 ℃ for 24 h, poured into methanol to precipitate.

3.3 Results and Discussion

3.3.1 4-phenoxybenzonic acid



Scheme 3.1 Synthesis scheme of 4-phenoxybenzonic acid

4-phenoxybenzonic acid is a known compound [9,10] and its structure was confirmed by ^{1}H NMR according to the reference. The synthesis scheme was shown in Scheme 3.1.

For polymerization of the linear poly(ether ketone), several different conditions has been tried, as listed in Table 3.1

Table 3.1 Polycondensation conditions with PPMA for 4-phenoxybenzonic acid

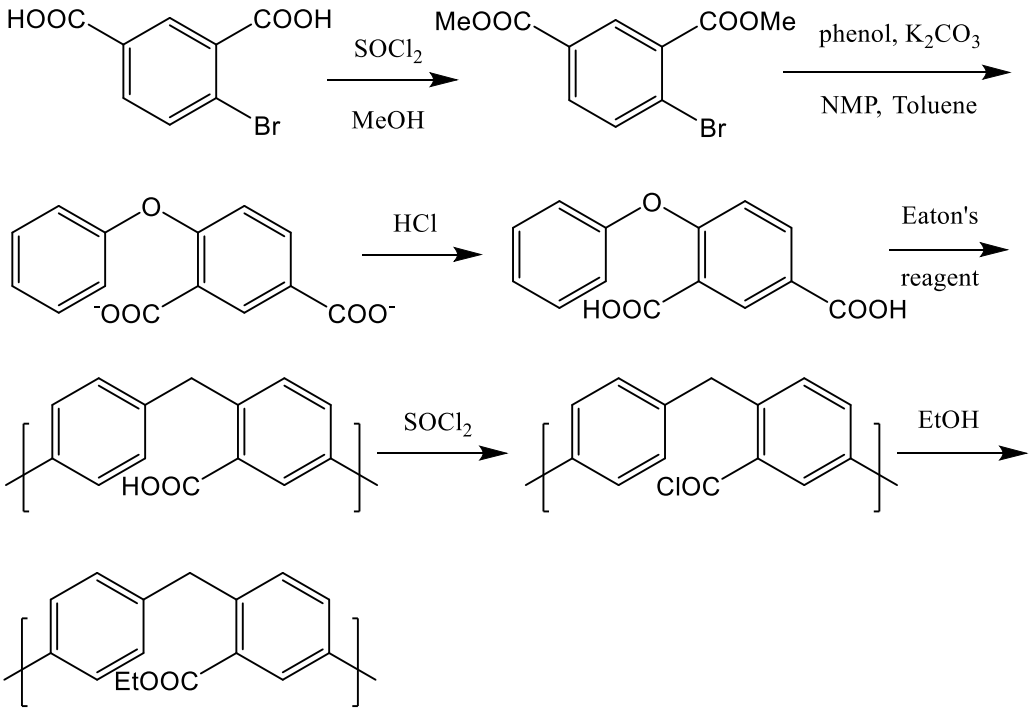
Entry	Monomer / g	Eaton's reagent / mL	Temperature / ℃	Time / h
1	0.2	3	110	5
2	0.2	3	100	3
3	0.2	3	100	2
4	0.2	3	100	1

After reaction, all the products were insoluble in any solvents, which prevent the characterization by NMR or GPC. Thus, no future consideration of this polymerization system was done.

3.3.2 4-phenoxy-1,3- benzenedicarboxylic acid

Because of the solubility problem of the linear structure, some side

carboxylic acid terminals were introduced to improve the solubility. As a result, we chose 4-phenoxy-1,3-benzenedicarboxylic acid as an ABB' type of monomer. The design of synthesis scheme was shown in Scheme 3.2.



Scheme 3.2 Synthesis pathway of 4-phenoxy-1,3-benzenedicarboxylic acid and polymerization

3.3.2.1 Characterization of monomer

The first step of Scheme 3.2 was confirmed by ^{1}H NMR (Figure 3.2). The peak of methyl ester appears at 3.94-3.97 ppm, with a ratio of 6.

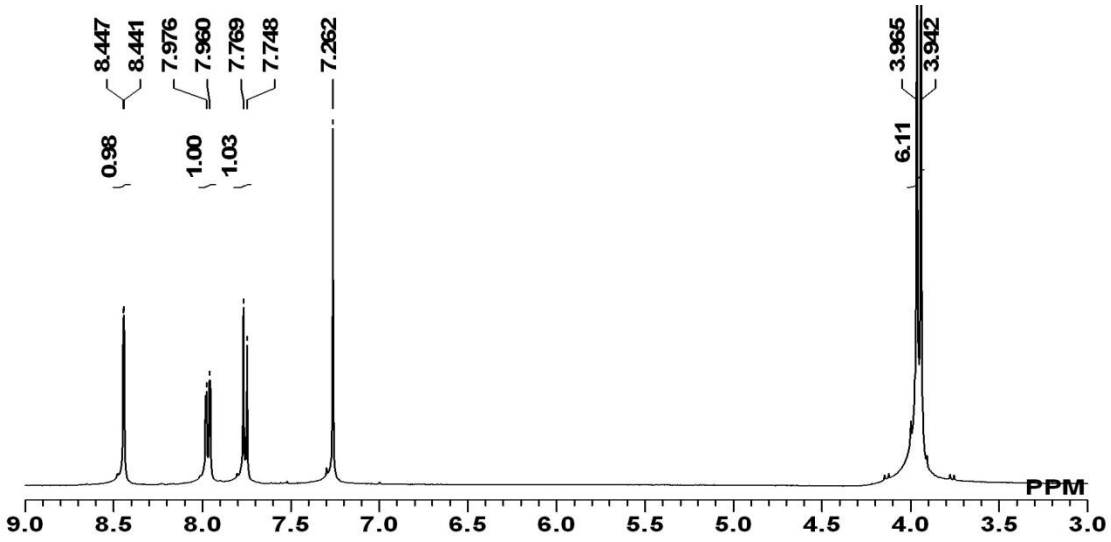


Fig 3.2 ^{1}H NMR of dimethyl 4-bromoisophthalate

After the second step and acidification by HCl solution, ^{1}H NMR, ^{13}C NMR and IR spectrum of the production were shown in Figure 3.3, 3.4 and 3.5 respectively. The hydroxy broad band from 2500 to 3000 confirmed the terminal conversion to carboxylic acid groups. The successful synthesis was confirmed according to the reference [2].

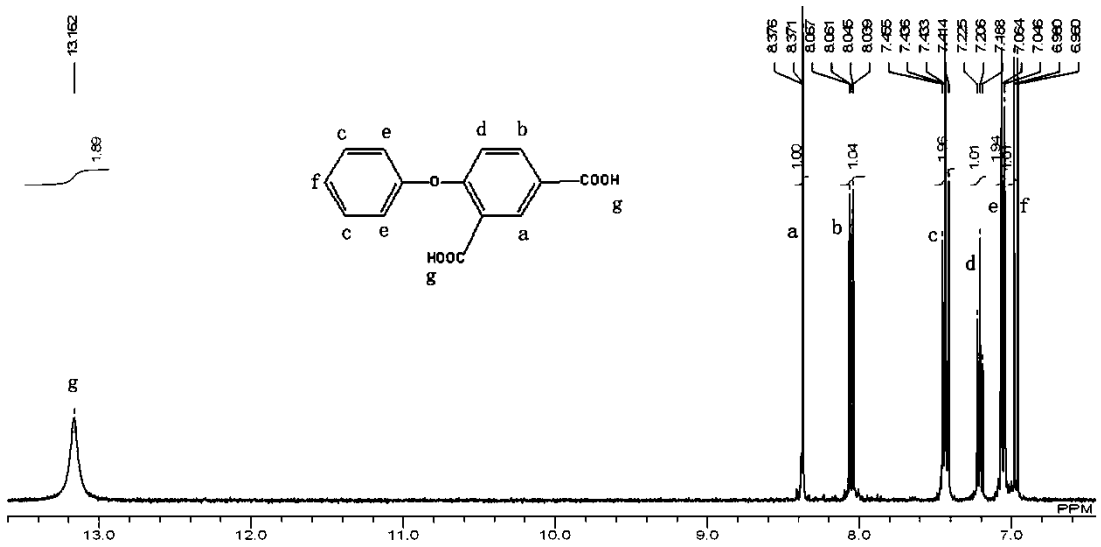


Fig 3.3 ^{1}H NMR spectrum of 4-phenoxy-1,3-benzenedicarboxylic acid

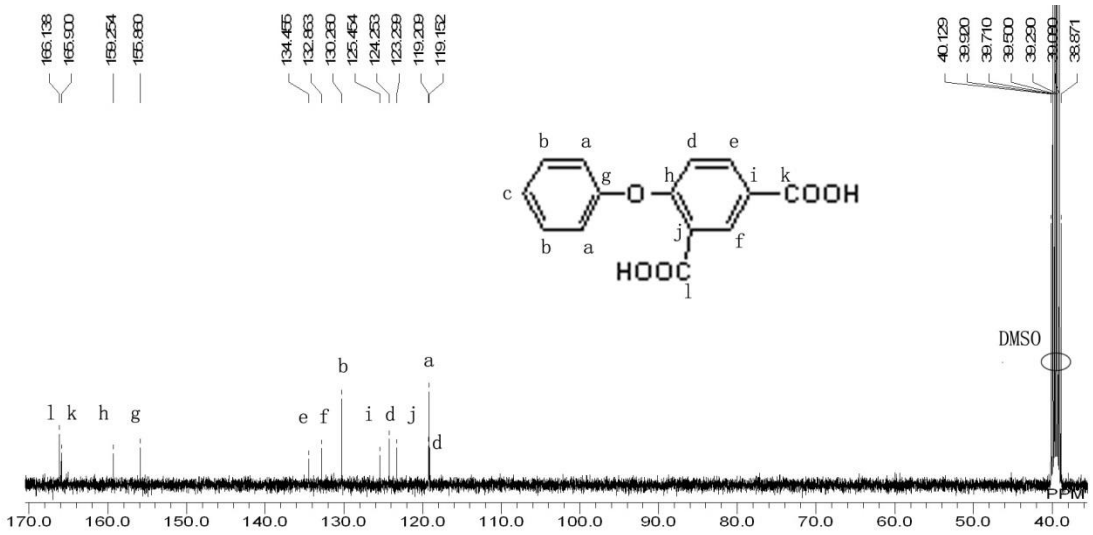


Fig 3.4 ^{13}C NMR spectrum of 4-phenoxy-1,3-benzenedicarboxylic acid

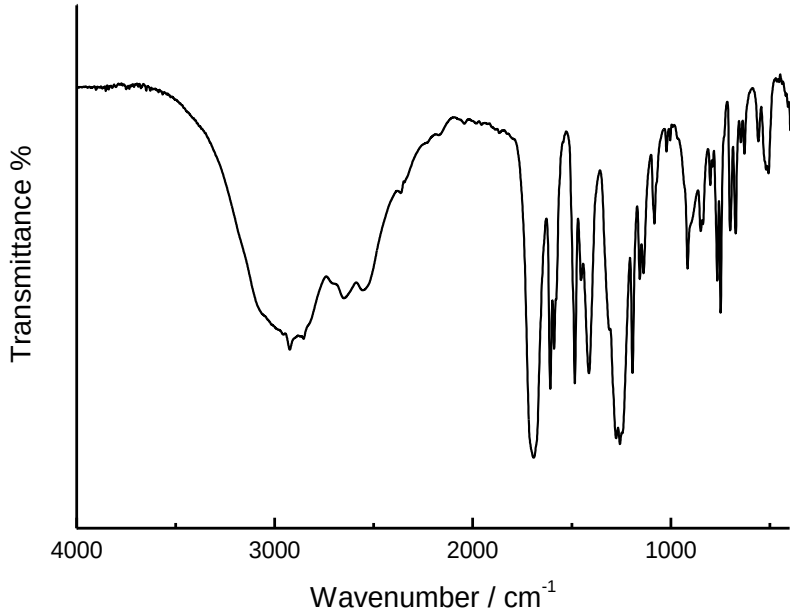


Fig 3.5 IR spectrum of 4-phenoxy-1,3- benzenedicarboxylic acid

3.3.2.2 Polycondensation with PPMA

Polycondensation was attempted with PPMA (Eaton's reagent) under the conditions summarized in table 3.2. GPC results for the 8 samples were listed in Fig 3.6. From the RI line, the product was shown as a mixture of different compounds containing only a small amount of high molecular

compound. It proves that the polycondensation reaction stopped at an early stage so that the monomer is quite hard to grow to high molecular weight.

Table 3.2 Polycondensation conditions of 4-phenoxy-1,3-benzenedicarboxylic acid with PPMA

Entry	Monomer / g	Eaton's reagent / mL	Temperature / ℃	Time / h
1	0.22	2	110	2
2	0.22	2	110	4
3	0.22	2	110	6
4	0.22	2	110	14
5	0.22	2	110	24
6	0.22	2	110	48
7	0.22	1	110	48
8	0.22	3	130	24

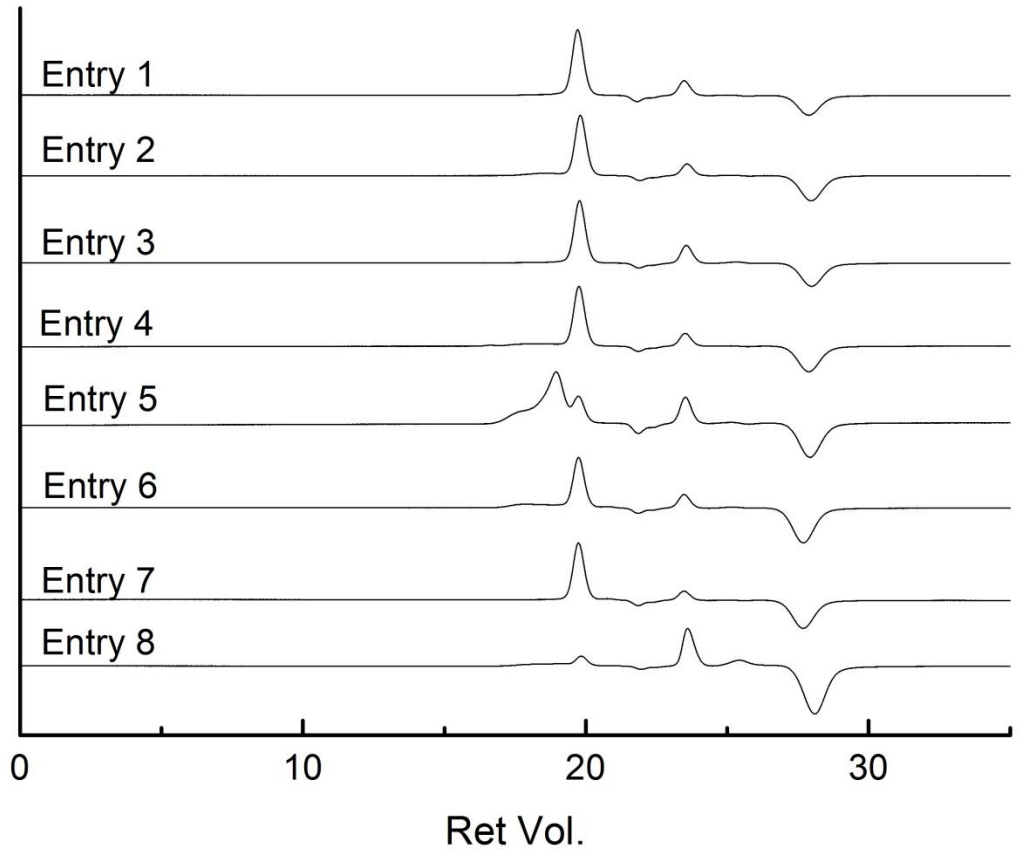


Fig 3.6 RI line of GPC result of entry 1-8

^{1}H NMR of entry 8 is shown in Figure 3.7. The peaks are still sharp

and the similar results also appeared in the other products of entry 1-7. In order to get more information of the product, ^{13}C NMR and 2D NMR were used to analyze the ABB' monomer and product after polymerization.

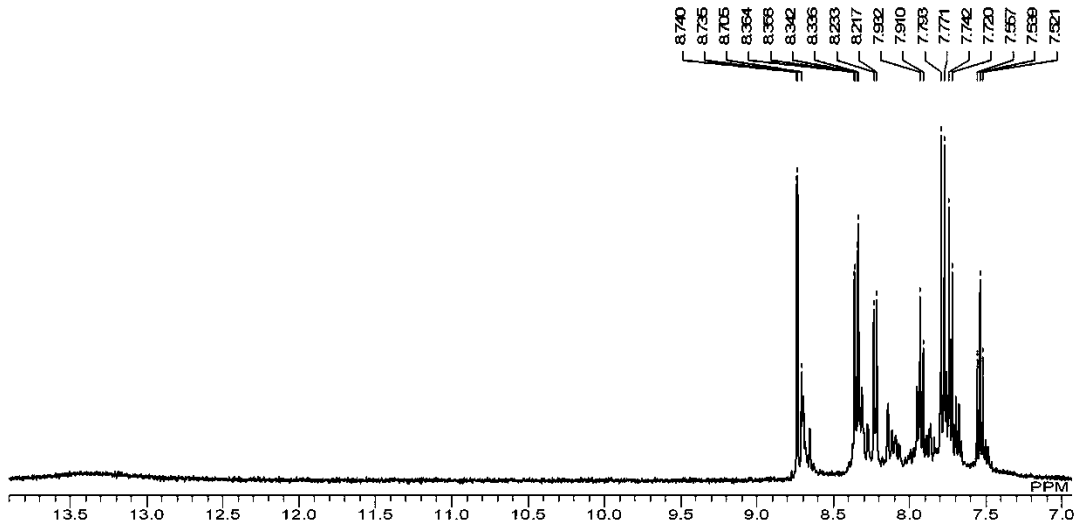


Fig 3.7 ^{1}H NMR spectrum of the result of entry 8 in Table 3.2

Figure 3.8 show the 2-D NMR of the monomer, the peaks have been assigned on the Figure. 2-D NMR of entry 3 was shown in Figure 3.9. For our designed polymer, the 2b and 2b' peaks are almost equal and should be close. However, in Figure 3.9, they are not equal position. So we reassigned the peaks (shown in Figure 3.10) and found the formation of Xanthone-2-carboxylic acid is much easier than polymerization and then the byproduct stops the polymerization reaction in an early stage. As a result, the structure of ABB' monomer required to be changed to avoid the intramolecular condensation. At last, the position of side carboxylic acid was moved that another ABB' monomer, 4-phenoxyphthalic acid [4] was chosen.

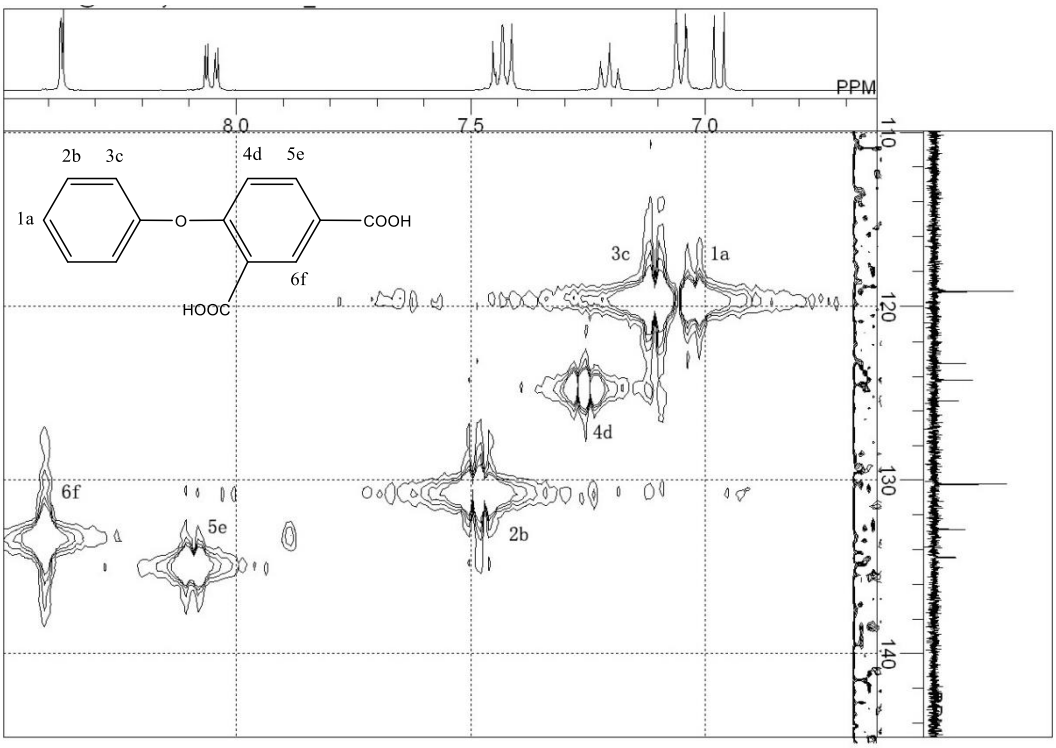


Fig 3.8 2-D NMR spectrum of the ABB’ monomer

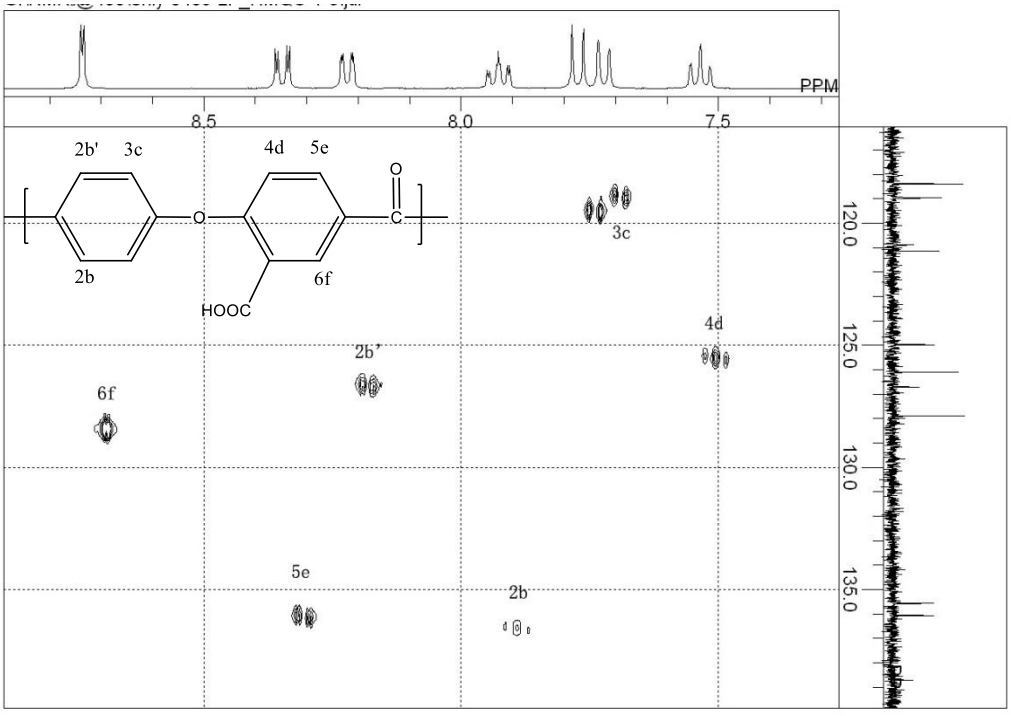


Fig 3.9 2-D NMR spectrum of the ABB’ monomer with peak assigned as the design.

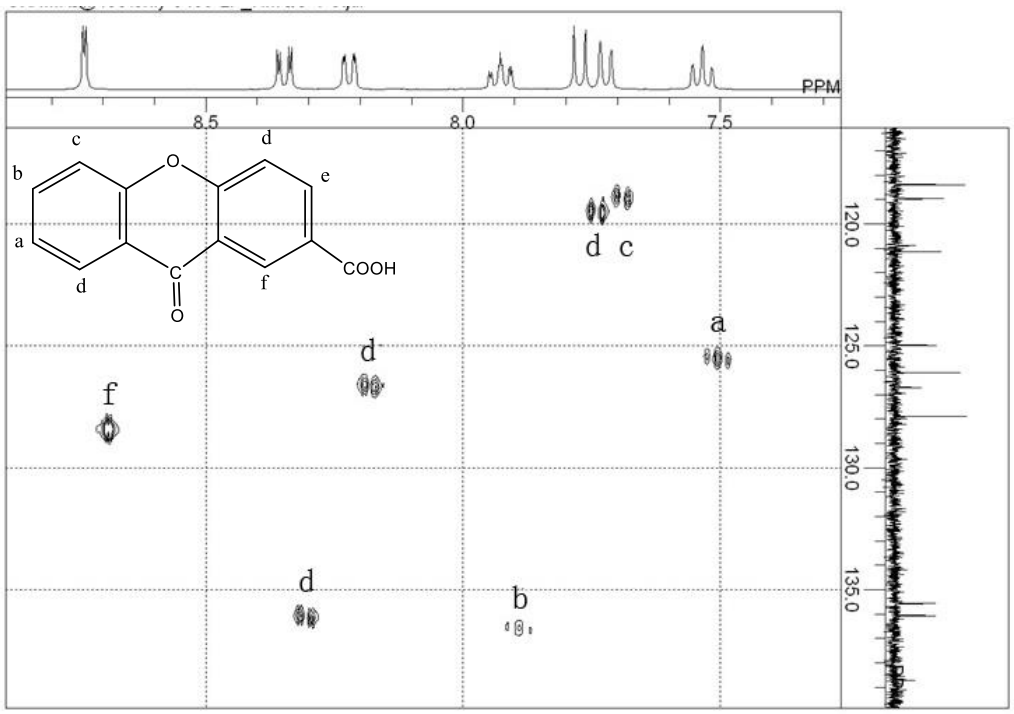
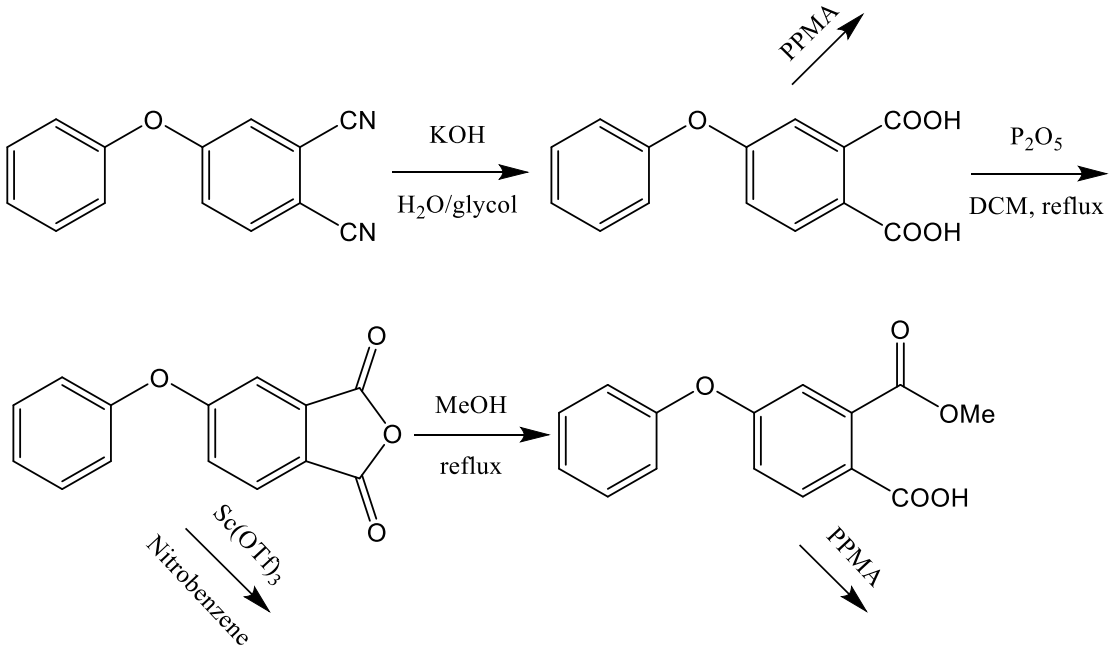


Fig 3.10 2-D NMR spectrum of the ABB' monomer with proper peak assignment

3.3.3 4-phenoxyphthalic acid

The synthesis route to obtain the 4-phenoxyphthalic acid and derivatives is shown in Scheme 3.3.



Scheme 3.3 Synthesis of 4-phenoxyphthalic acid and derivatives

3.3.3.1 Characterization of monomer

The ^{1}H NMR spectrum of 4-phenoxyphthalic acid is shown in Figure 3.11. The peak positions on benzene ring confirmed the compound, however, the carboxylic acid peak cannot be observed.

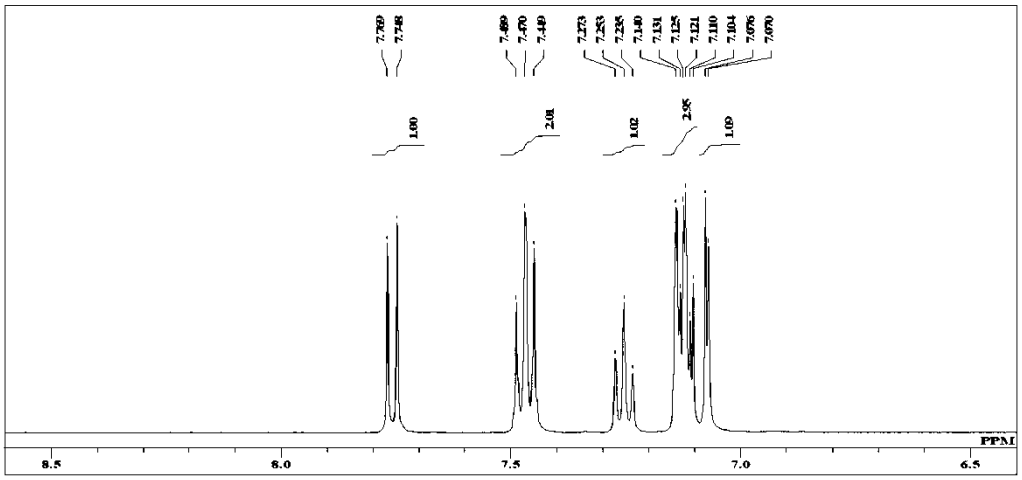


Fig 3.11 ^{1}H NMR of 4-phenoxyphthalic acid

IR spectra of 4-phenoxyphthalonitrile and 4-phenoxyphthalic acid were shown in Figure 3.12. In the spectrum of 4-phenoxyphthalic acid, the C≡N stretching at 2240 disappeared and an O-H broad bond around 2500 cm^{-1} appeared which proved a successful changing of terminal groups.

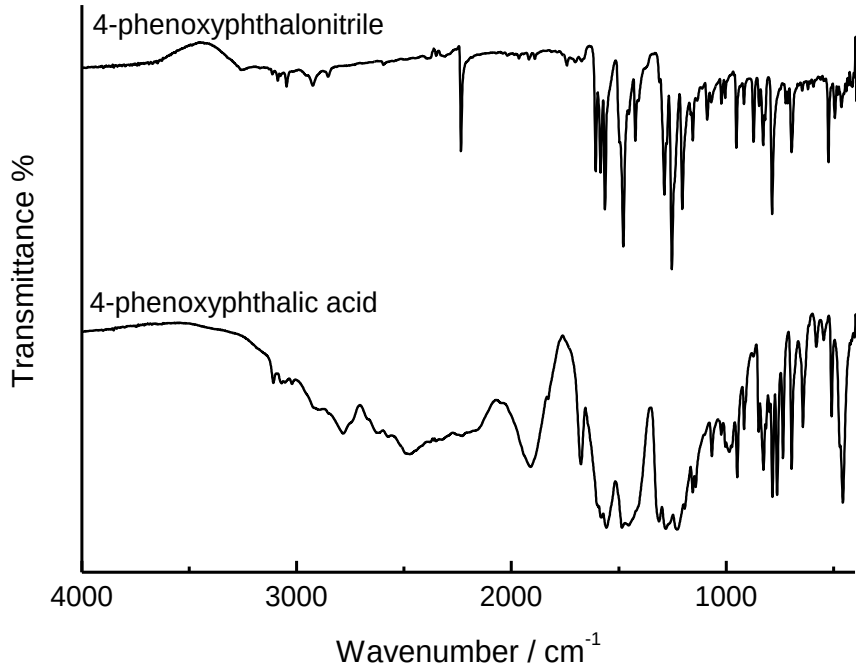


Fig 3.12 IR spectra of 4-phenoxyphthalonitrile and 4-phenoxyphthalic acid

3.3.3.2 Polycondensation with PPMA

The synthesized 4-phenoxyphthalic acid was used as an ABB' monomer for polymerization with PPMA. After reaction at 110 ℃ for 24 h, the product was totally dissolved in methanol. Because of the insolubility of HBPEK in methanol, the less branched polymer, which is supposed to be harder to dissolve in organic solvents, should be insoluble in methanol as well. As a result, this monomer is not easy to be polymerized; and it will stop at only oligomer stage.

3.3.4 4-phenoxyphthalic anhydride

The ^{1}H NMR spectrum of 4-phenoxyphthalic anhydride is shown in Figure 3.13.

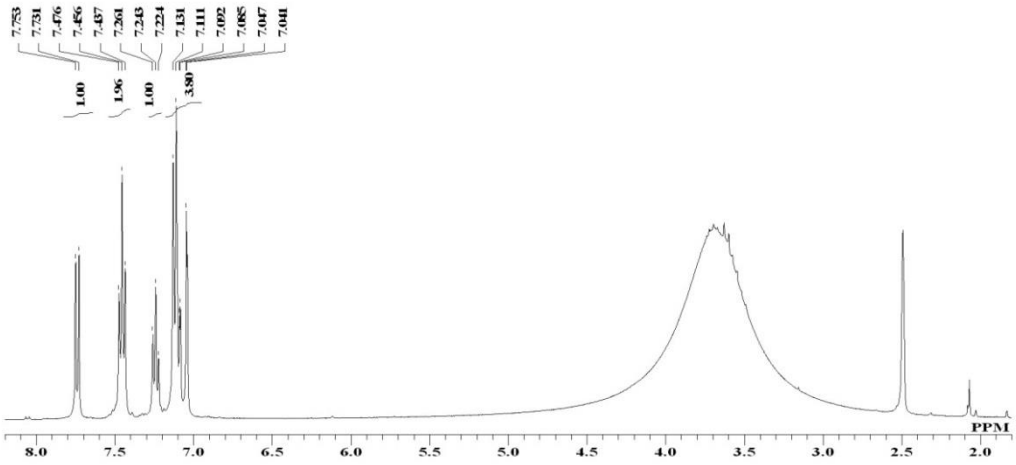


Fig 3.13 ^{1}H NMR of 4-phenoxyphthalic anhydride

The polycondensation by Friedel-Crafts reactions from 4-phenoxyphthalic anhydride has also been tried to react at 130 ℃ for 24 h. However, the product totally dissolved in methanol. The condensation seems not strong enough to get a polymer.

3.3.5 4-phenoxyphthalic acid, 2-methyl ester

3.3.5.1 Characterization of monomer

The synthesis of 4-phenoxyphthalic acid, 2-methyl ester is shown in Scheme 3.3, through anhydride and then esterification by methanol. ^{1}H NMR of the 4-phenoxyphthalic acid, 2-methyl ester structure is shown in Figure 3.14. The ester peak at 3.10 ppm was observed with a ratio about 3, despite of the overlap with water peak.

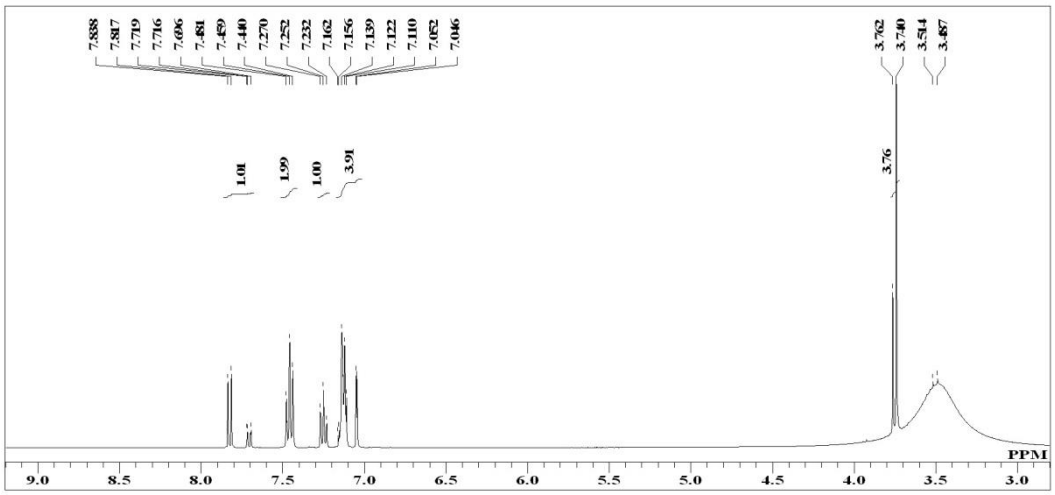


Fig 3.14 ^{1}H NMR of 4-phenoxyphthalic acid, 2-methyl ester

3.3.5.2 Polycondensation with PPMA

Considering the two carboxylic acids have equal chance to react with another molecule to form an irregular growing that may reduce the polymerization to work, the side carboxylic acid was protected and the polymerization was attempted again. The 4-phenoxyphthalic acid, 2-methyl ester was used as an AB monomer for polycondensation with PPMA. After 12 h, a small amount of insoluble product was collected. The product was characterized by NMR, IR and GPC directly. The results are shown in Figure 3.15-3.17. The peak of NMR is quite weak because of the limited solubility in DMSO. After reaction, all aromatic peaks around 6.5-8.0 gather together and the methyl ester peak at 3.7 ppm still can be observed. In IR spectrum, the CH_3 peaks around 3000 cm^{-1} are observed, as well as C=O stretching of ester at 1740 cm^{-1}.

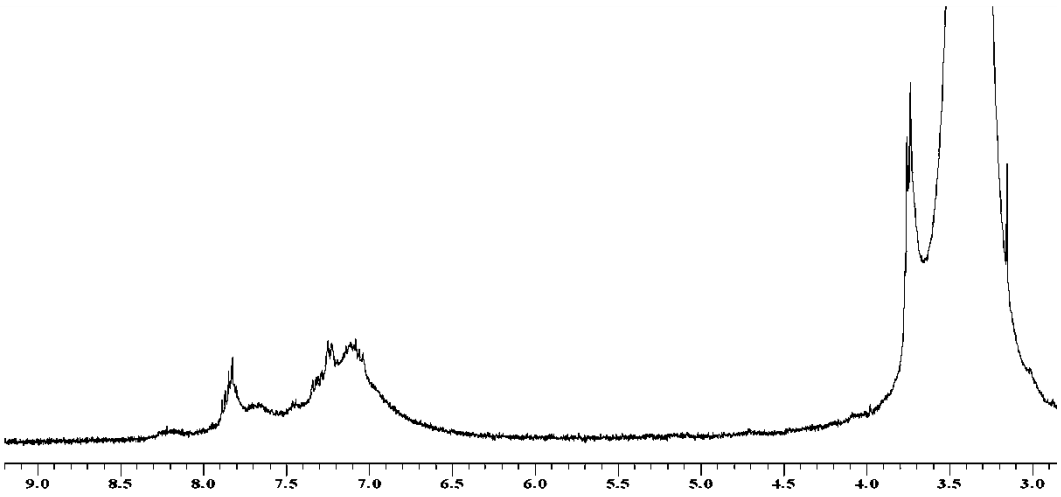


Fig 3.15 ^{1}H NMR of the compound polymerized from 4-phenoxyphthalic acid, 2-methyl ester.

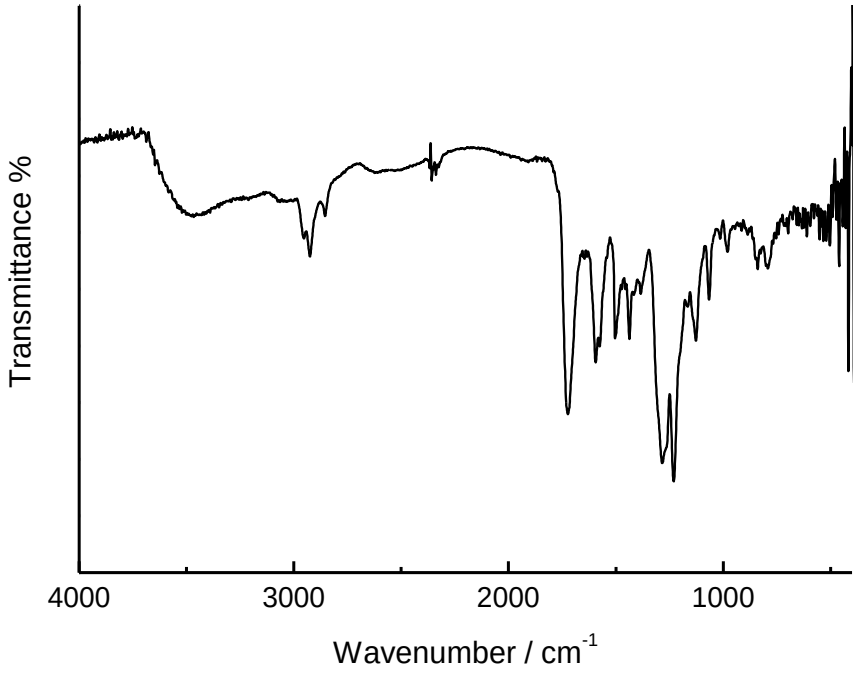


Fig 3.16 IR spectrum of the compound polymerized from 4-phenoxyphthalic acid, 2-methyl ester.

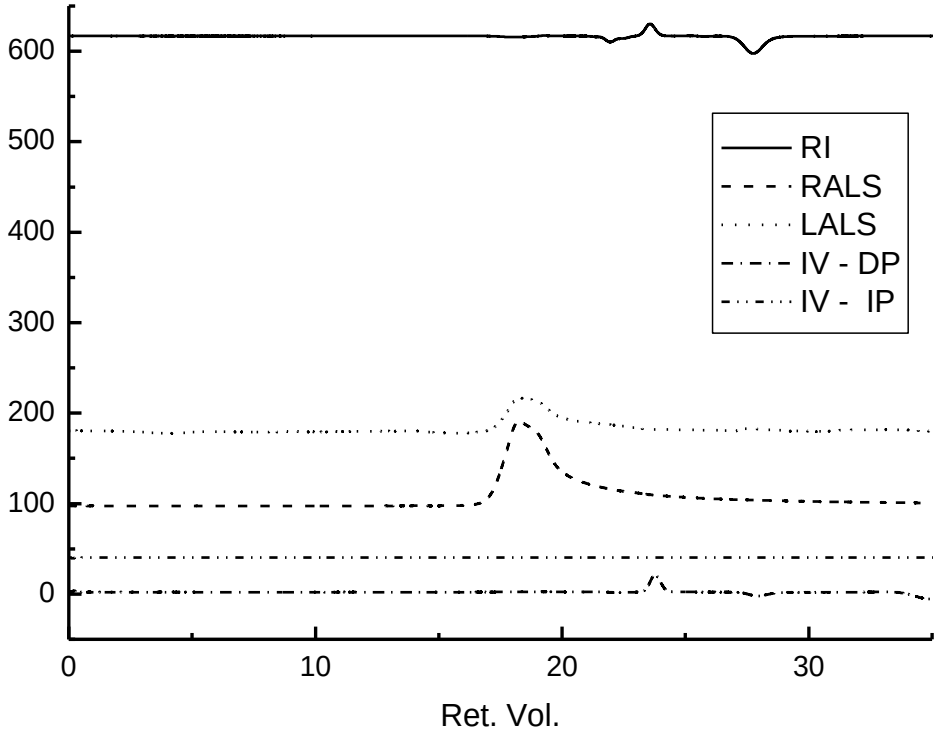


Fig 3.17 GPC spectrum of the compound polymerized from 4-phenoxyphthalic acid, 2-methyl ester.

From GPC result, no polymer derived single peak can be observed on the RI and IV-DP line. As a result, the compound is still oligomer instead of polymer.

3.3.6 Precipitation yield from all the monomers

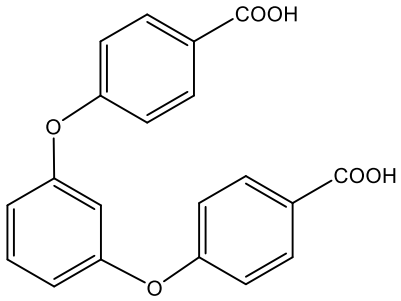
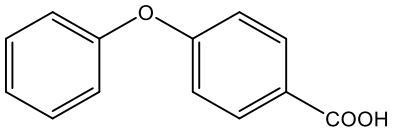
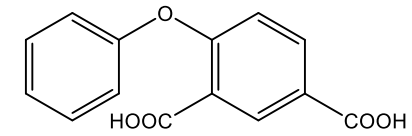
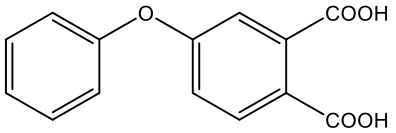
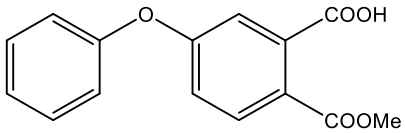
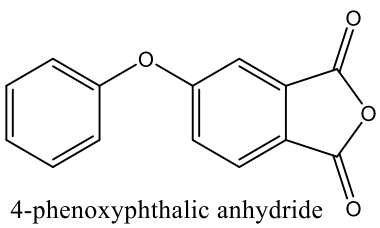
All the products after polycondensation reaction have been poured into methanol to precipitation, and the yield from each monomer was collected in Table 3.3.

By comparing the precipitation yield of all the structures, the AB_2 type with the highest yield is proved to be the most activate structure which is suitable for the utilization as catalyst.

3.4 Conclusions

In this chapter, several kinds of structure with carboxylic acid terminal for AB or ABB’ monomers were successfully synthesized. The AB monomer can be polymerized but the resulting polymer was insoluble in any solvent. Introducing of side carboxylic acid terminal groups on the ether ketone backbone will increase the solubility; however, the polyrmerization of such monomers failed. It can be concluded 4,4’-(m-phenylenedioxy)-bis(benzenecarboxylic acid) is a quite suitable monomer for the synthesis of the poly(ether ketone) functionalized with carboxylic acid group.

Table 3.3 Precipitation yield from all the monomers have been tried.

Structrue of monomers	Polycondensation conditon	Precipitation yield with methanol	Main product
 4,4'-(m-phenylenedioxy)-bis(benzenecarboxylic acid)	PPMA	84%	Hyperbarnched polymer
 4-phenoxybenzonic acid	PPMA	-	Insoluble polymer
 4-phenoxy-1,3-benzenedicarboxylic acid	PPMA	47%	Xanthone-2-carboxylic acid
 4-phenoxyphthalic acid	PPMA	0	Oligomer
 4-phenoxyphthalic acid, 2-methyl ester	PPMA	15%	Oligomer
 4-phenoxyphthalic anhydride	$Sc(OTf)_3$	0	Oligomer

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Chapter 4 Hyperbranched Aromatic Poly(ether ketone) with TEMPO Terminals as Heterogeneous Catalyst for Aerobic Oxidation of Benzyl Alcohol

Chapter 5 Hyperbranched Aromatic Poly(ether ketone) with TEMPO Terminals Grafted onto Graphene as Heterogeneous Catalyst for Aerobic Oxidation of 2-Adamatanol

Chapter 6 Summary and Conclusion

In the previous chapters, a series of hyperbranched aromatic poly(ether ketone) based catalysts have been synthesized and applied to several different catalytic reactions. They represent the major efforts of my research work, that is, to explore the utilization of hyperbranched polymers in catalysis. The hyperbranched structure has many potential advantages, for example, its numerous end groups can afford or introduce more catalytic functional groups than common used polymer supports. The end-groups can be well exposed and accessible for the reactants due to low degree of entanglement of HBPs. Moreover, its large free volume can enhance mass transport. However, it is still a quite new research area that has not been well studied up to date, so this research is full of challenge and already shown promising results.

In this study, a novel hyperbranched aromatic poly(ether ketone) with carboxylic acid terminal groups has been synthesized in Chapter 1. The conversion of terminals was proved to be efficient to change the physicochemical property (such as polarity and solubility, thermal stability) of the prepared polymer. Catalytic activity of the carboxylic acid terminal groups on hyperbranched poly(ether ketone) was demonstrated by the

hydrolysis of cellulose, which proved the potential of this structure for a wide range of applications

In order to explore the effect of different structure and find the optimal one for the following catalyst study, in Chapter 3, various monomer structures have been designed for linear or less branched structure. The side carboxylic acid terminal groups showed a considerable influence on the activity and solubility of the system. By comparing the yield of polymerization of various structures, the originally designed AB_2 monomer shows an outstanding high activity for polymerization, and that was utilized in the following study for catalysis.

In Chapter 3, the carboxylic acid terminal groups have been changed to TEMPO terminals *via* an amide bond. Since TEMPO is a widely used nitroxyl radical in many reactions, TEMPO/HBPEK has the potential to work in various systems, and such immobilization will enable to recycle the catalyst, which is economically and environmentally prefered. In this chapter, TEMPO/HBPEK has been well characterized with a TEMPO loading over 2 mmol g^{-1} and used for the aerobic oxidation of benzyl alcohol in a halogen free green system. A good catalytic activity and selectivity has been proved as well as a promising recyclability by grafting onto carbon black and polyimide particles. However, there are still several disadvantages of carbon black and polyimide particles as catalyst supports. As to the carbon black, some unknown surface species could deactivate

TEMPO terminals during the recycling test. Polyimide particles, though without such problem, tends to be stuck on glassware and bring a difficult to recycle. Considering such disadvantages, more suitable supports need to be introduced.

Hereby, in Chapter 5, graphene, a carbon, theoretically without radicals and easy to be collected, has been introduced to form a heterogeneous catalyst of TEMPO/HBPEK/graphene. Moreover, 2-adamantanol was used as a more challenging reactant in the aerobic oxidation compared to Chapter 4. The TEMPO/HBPEK/graphene, with a TEMPO loading about 1.0 mmol g^{-1}, shows good recyclability and activity for at least 5 runs. The performance of the 2-adamantanol oxidation also proved the potential for different substrates.

List of Publications

Journal Articles

[1] Y. Shi, Y. Nabae, T. Hayakawa, H. Kobayashi, M. Yabushita, A. Fukuoka, M. Kakimoto, Polymer J. (2014) DOI: 10.1038/pj.2014.62.

In considering

[2] Ying Shi, Yuta Nabae, Teruaki Hayakawa, and Masa-aki Kakimoto. Hyperbranched aromatic poly(ether ketone) functionalized with tempo as a heterogeneous catalyst for aerobic oxidation of alcohols. Applied Catalysis A, submitted.

[3] Ying Shi, Yuta Nabae, Teruaki Hayakawa, and Masa-aki Kakimoto. Graphene modification with hyperbranched poly(ether ketone) as heterogeneous catalyst. Chemical Communications, submitted.

International Conference Presentation

[1] Synthesis of a Hyperbranched Aromatic Polyether ketone Functionalized with Catalytically Active Terminal Groups

Ying Shi, Yuta Nabae, Teruaki Hayakawa, and Masa-aki Kakimoto.

2012 Asia-Pacific Polyimides and High Performance Polymers Symposium, Taibei, Taiwan, November **2012.**

[2] Metal-Free Aerobic Oxidation of Alcohols Using an Aromatic

Polyether Ketone Supported Organocatalyst

Ying Shi, Yuta Nabae, Teruaki Hayakawa, and Masa-aki Kakimoto.

The Seventh Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT7), Kyoto, Japan, June **2014.**

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Acknowledgements

First, I want to give my sincere gratitude to my supervisor, Prof. Kakimoto, who gave me the opportunity to study in his laboratory and a lot of guidance when I face difficulty in my research work. His geniality and patient encouraged me a lot and brought me many good memories.

Also, I need to give sincere thanks to Assistant Prof. Nabae, who taught me a lot of things not only for academic but also for my life. His conscientious and precise attitude influenced me a lot and make me start to understand the way Japanese working, step by step, steadily toward the success.

And then, I appreciate to all the members in our laboratory, who always be kind and patient for me, a foreigner cannot handle Japanese well, and bring me a nice experience in Japan for these three years.

As well, I want to thank Assistant Prof. H. Kobayashi, Prof. Fukuoka's group in Hokkaido University for the help of hydrolysis reaction, and center for Advanced Materials Analysis that help me do the SEM & TEM characterization.

Lastly, I would like to thank my referees, Prof. Takata, Prof. Tezuka, Associate Prof. Michinobu, and Associate Prof. Hayakawa. Thanks for the review and many good suggestions they gave me.