Synthesis and characterization of new AB-type poly(etherimide)s containing various naphthylene links

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Summary

New aromatic AB-type poly(etherimide)s containing various naphthylene links
were prepared by the self-condensation of [2-(3,4-dicarboxyphenyloxy)-3, 6 and
7-naphthyl]oxyanilines hydrochlorides and 5-(3,4-dicarboxyphenyl)oxy-1-naph-
thylamine hydrochloride. The polymerization performed in NMP/pyridine or
DMAc/Et$_3$N in the presence of triphenylphosphite(TPP) activator was found to
proceed to imide bond formation. Inherent viscosities of the polymers were in the
0.39-0.94dL/g range. Properties of the poly(etherimide)s were investigated and
discussed in terms of chain rigidity resulting from different naphthylene links. All
the poly(etherimide)s were highly thermostable up to 600°C with 10% weight loss
and showed chemical resistance against chloroform even at higher temperatures.

Introduction

Aromatic poly(etherimide)s are one of the most important classes of high-
performance polymers due to their excellent electrical, thermal and mechanical
properties(1-3). Most of them are AABB-type commonly prepared by the classical
two-step polyimidization of di(etheranhydride)s with diamines. However, little
efforts have been made for the synthesis of AB-type poly(etherimide)s which can
be obtained by self-condensation of amino(etheranhydride)s. This is presumably
because those monomers can be hardly isolated in high purity due to the facile
reaction between the amino and anhydride groups. In literature have been reported
a few examples of AB-type poly(etherimide)s in which aminodi(carboxylic
acid)s(4), aminodi(orthoester)s(5), 4-(4-aminophenoxy)phthalic anhydride hydro-
chloride(6) or 4-isocyanatophthalic anhydride(7) were used for polymerization.
There is another method of self-polymerization in which amine hydrochlorides
containing di(carboxylic acid) groups in the same molecules can be used. These
monomers are so stable that they can be highly purified and stored for prolonged
time in dry conditions without any special care. If the salts are deprotected to free
amines by addition of tertiary amines such as Et$_3$N or pyridine, the amino groups
start to react with the acid groups. However, this reaction proceeds very slow if
the water formed is not removed out of the reaction system efficiently by
evacuation at high temperatures. Recently a method of enormous speed-up of this
reaction at relatively lower temperatures has been developed by Higashi and

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Yamazaki(8,9) by using activators such as triphenylphosphite. This method needs not remove water formed.

In this article four new aromatic AB-type poly(etherimide)s containing various naphthylene links were prepared by deprotection and activated self-condensation of [2-(3,4-dicarboxyphenyloxy)-3, 6 and 7-naphthyl]oxyanilines hydrochlorides (**3a-c**) and 5-(3,4-dicarboxyphenyl)oxy-1-naphthylamine hydrochloride(**3d**) in the presence of triphenylphosphite and pyridine or Et_3N in NMP or DMAc. After structures of the polymers were characterized and their physical and thermal properties were measured, the effect of chain rigidity and substitution position of naphthylene links is discussed.

Experimental part

Materials and Measurement. DMSO was used after drying over 4Å molecular sieves. Anhydrous methanol, acetic acid, Na metal and TPP were used without further purification. NMP and DMAc were distilled over CaH_2 and pyridine over KOH before use. Other commercially available chemicals were used as received.

Melting points were determined using Haake-Buchler apparatus without correction. Elemental analyses were performed on a Carlo Erba EA 1108 microanalyzer. IR spectra(KBr pellets) were recorded on a Shimadzu FT-IR 4300 spectrophotometer. ^{1}H-NMR spectra were obtained from a 300 MHz Bruker AM 300 spectroscope at room temperature. Thermal analyses of polymers were carried out with a Perkin-Elmer PE PC Series TGA 7 thermogravimetric analyzer and a Perkin-Elmer PE PC Series DSC 7 thermal analyzer at a heating rate of 20°C/min. under N_2. Wide-angle X-ray diffractograms were obtained in a reflection mode using Ni-filtered Cu K_α radiation on a Rigaku Geiger Flex D-Max X-ray diffractometer. Inherent viscosities were determined using an Ubbelhode type viscometer at 25°C for 0.2 g/dL solutions in concentrated H_2SO_4.

*Synthesis of 4-[4-(N-phenyl)phthalimidyloxy-(2,3-, 2,6- and 2,7-naphthylene)-oxy]acetanilides(**2a, 2b** and **2c**) and 5-[4-(N-phenyl)phthalimidyloxy]naphthyl-1-acetamide(**2d**)* : 5.2mmol **1a**, **1b**, **1c** or **1d** were reacted with 5.2mmol $NaOCH_3$ in 30mL anhydrous methanol by stirring for 2h at room temperature under a N_2 stream. After methanol was completely distilled out by vacuum, the remnants were dissolved in 40mL DMSO containing 5.2mmol 4-nitro-N-phenylphthalimide and heated at 80°C for 48h. The mixtures were cooled and poured into 600mL water. The precipitates formed were collected and recrystallized from acetonitrile. Yield(%) : **2a** ; 60.3, **2b** ; 63.0, **2c** ; 64.1, **2d** ; 56.4. M.p.(°C) : **2a** ; 254, **2b** ; 256, **2c** ; 218, **2d** ; 302.

*Synthesis of [2-(3,4-dicarboxyphenyloxy)-3, 6 and 7-naphthyl]oxyanilines hydro-chlorides(**3a, 3b** and **3c**) and 5-(3,4-dicarboxyphenyl)oxy-1-naphthylamine hydro-chloride(**3d**)* : A mixture of 1.94mmol **2a**, **2b**, **2c** or **2d**, 40mL ethylene glycol, 8mL water and 2.5g KOH was placed in a 100mL flask equipped with a Dean-Stark trap and refluxed under nitrogen for 24h to remove aniline azeotropically. After cooled, the solution was acidified with concentrated hydrochloric acid to form white precipitates. The precipitates were purified by recrystallization from

ethanol/water mixture to obtain white powders.

3a : yield ; 86.6%, ^{1}H-NMR(DMSO-d$_6$, ppm) ; 7.89-7.77(m:4H), 7.46-7.42(m: 2H), 7.21(s:1H), 7.16-7.12(m:2H), 6.81-6.78(d:2H) and 6.68-6.65(d:2H). Elemental analysis ; calc. (C$_{24}$H$_{18}$N$_1$O$_6$Cl$_1$, wt. %) : C 63.80, H 4.02, N 3.10, found : C 63.72, H 3.96, N 3.23.

3b : yield ; 87.7%, ^{1}H-NMR(DMSO-d$_6$, ppm) ; 7.92-7.87(q:2H), 7.83-7.80(d:1H), 7.62-7.61(d:1H), 7.31-7.26(m:2H), 7.24-7.23(d:1H), 7.17-7.14(q:2H), 6.91-6.87(d:2H) and 6.75-6.71(d:2H). Elemental analysis ; calc. (C$_{24}$H$_{18}$N$_1$O$_6$Cl$_1$, wt. %) : C 63.80, H 4.02, N 3.10, found : C 64.06, H 3.90, N 3.17.

3c : yield ; 84.1%, ^{1}H-NMR(DMSO-d$_6$, ppm) ; 8.00-7.93(t:2H), 7.83-7.81(d:1H), 7.49-7.48(d:1H), 7.24-7.15(m:5H), 6.91-6.87(d:2H) and 6.75-6.71(d:2H). Elemental analysis ; calc. (C$_{24}$H$_{18}$N$_1$O$_6$Cl$_1$, wt. %) : C 63.80, H 4.02, N 3.10, found: C 64.20, H 4.03, N 3.12.

3d : yield ; 72.5%, ^{1}H-NMR(DMSO-d$_6$, ppm) ; 8.04-8.01 (d:1H), 7.80-7.72(q:1H), 7.44-7.38(t:1H), 7.30-7.18(m:2H), 7.07-7.01(m:3H) and 6.76-6.73(d:1H). Elemental analysis ; calc. (C$_{18}$H$_{14}$N$_1$O$_5$Cl$_1$, wt. %) : C 60.10, H 3.92, N 3.89, found: C59.98, H 3.86, N 4.09.

Polymerization : In a flask fitted with a magnetic stirrer 2.21mmol of the monomers **3a**, **3b** or **3c** were dissolved in 10mL anhydrous NMP/pyridine(4:1 v/v ratio), but the monomer **3d** in 10mL anhydrous DMAc/Et$_3$N(4:1 v/v ratio), and 2.21mmol TPP were added in one portion at room temperature. Upon heating the mixture changed to reddish brown color. Polymerization was continued with stirring at 150℃ for 24h forming a viscous solution. After cooled, polymer was obtained by precipitating into excess methanol, washing and thoroughly extracting in hot acetone and drying for 48h at 100℃ under vacuum.

4a : yield ; 90%. IR(KBr, cm^{-1}) : 1778 & 1723(C=O imide I & II), 1598(bz. ring) and 1377(C-N-C). Elemental analysis ; calc. ((C$_{24}$H$_{13}$N$_1$O$_4$)$_n$, wt. %) : C 75.99, H 3.45, N 3.69, found : C 74.52, H 3.40, N 3.43.

4b : yield ; 90%. IR(KBr, cm^{-1}) : 1774 & 1716(C=O imide I & II), 1598(bz. ring) and 1374(C-N-C). Elemental analysis ; calc. ((C$_{24}$H$_{13}$N$_1$O$_4$)$_n$, wt. %) : C 75.99, H 3.45, N 3.69, found : C 76.65, H 3.48, N 3.96.

4c : yield ; 89%. IR(KBr, cm^{-1}) : 1776 & 1720(C=O imide I & II), 1606(bz. ring) and 1371(C-N-C). Elemental analysis ; calc. ((C$_{24}$H$_{13}$N$_1$O$_4$)$_n$, wt. %) : C 75.99, H 3.45, N 3.69, found : C 75.62, H 3.43, N 3.76.

4d : yield ; 86%. IR(KBr, cm^{-1}) : 1778 & 1720(C=O imide I & II), 1602(bz. ring) and 1366(C-N-C). Elemental analysis ; calc. ((C$_{18}$H$_9$N$_1$O$_3$)$_n$, wt. %) : C 75.26, H 3.16, N 4.88, found : C 74.77, H 3.43, N 5.08.

Results and discussion

Monomer synthesis : Monomers(**3a-c**) were prepared by nitro-displacement reaction of N-phenyl-4-nitrophthalimide with sodium 3, 6 and 7-(4-acetamidophenyloxy)-2-naphtholates followed by basic hydrolysis of the N-phenylimide groups(11) and acidification with HCl, as shown in Scheme 1. The three raw materials 3, 6 and 7-(4-acetamidophenyloxy)-2-naphthols had been synthesized by reaction of excess sodium 2,3-, 2,6- and 2,7-dinaptholates with 4-

nitrofluorobenzene followed by reduction of the nitro groups(12) and acetylation of the amino groups formed by the reduction. Monomer **3d** was synthesized from sodium 5-acetamido-1-naphtholate and 4-nitro-N-phenylphthalimide followed by acidification with HCl. 4-Nitro-N-phenylphthalimide was obtained from 4-nitrophthalic anhydride as described previously(13). All the monomers were purified to polymerization grade by recrystallization from aqueous ethanol solutions. They were so hygroscopic that they had to be stored in strictly dry conditions. Their melting points could not be measured due to decomposition before melting. The intermediates and final products were identified by FTIR and ^{1}H-NMR spectroscopy, although these data are given only for the monomers.
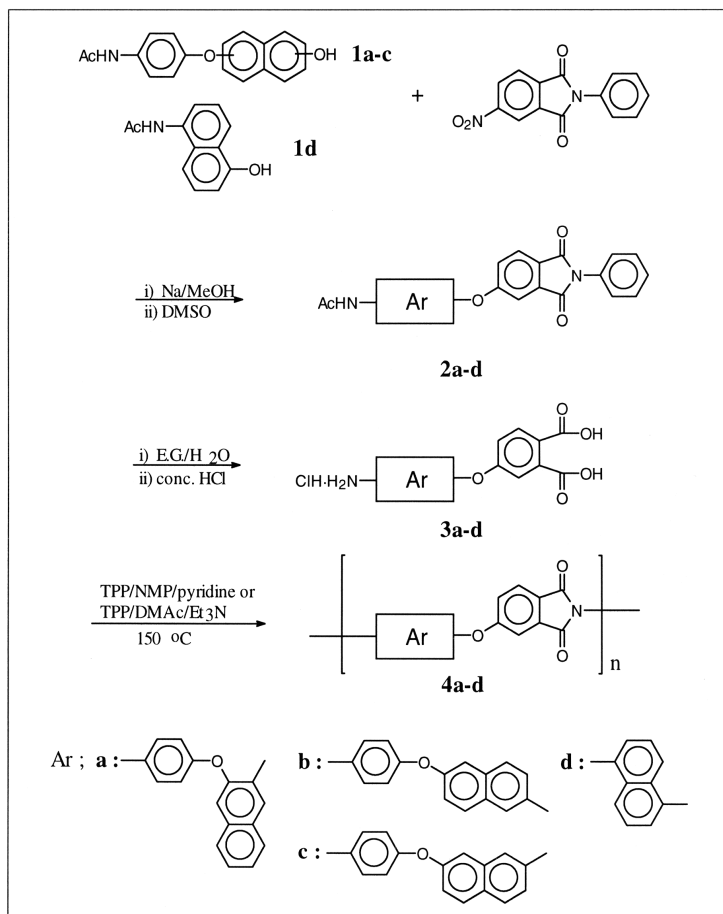
Scheme 1. Polymer synthesis.

Polymerization : To obtain high molecular weight polymers by condensation reaction between an amino group and a phthalic acid group at sufficiently high speed without removing the formed water out of the polymerization reaction system, triphenylphosphite(TPP)-activated polycondensation method was taken.

Polymers **4a**, **4b** and **4c** were prepared in NMP/pyridine and polymer **4d** in DMAc/Et$_3$N solution in the presence of equimolar amount of TPP activator at 150°C, as shown in Scheme 1. Because the polymerization systems contain large amounts of TPP, it had to be thoroughly removed to obtain highly purified polymers by reprecipitating the crude polymers in large excess of methanol and washing and thoroughly extracting with hot acetone.

Characterization : Structures of the polymers thus obtained were characterized by elemental analysis and FTIR spectroscopy. In Figure 1 is reproduced an IR spectrum of the sample **4c** together with that of its monomer **3c**. From Figure 1 it is readily to confirm that monomer **3c** exhibits C=O stretching band at 1700 cm^{-1} which is characteristic of a carboxylic acid, while polymer **4c** shows absorption bands which are characteristic of imide ring, such as those appearing at 1776 and 1720 cm^{-1} (C=O imide I & II) and 1371 cm^{-1}(C-N-C stretching). This fact indicates that the activated polymerization did not proceed only to polyamidation giving rise to poly(amic acid)s, but further to polyimidization accompanied by a subsequent cyclodehydration. At moment we can not say if this cyclization has taken place by a chemical action of TPP or a thermal action.

To make a further confirmation if the imidization proceeds only partially or completely, a model study has been carried out for the reaction between phthalic acid and aniline hydrochloride in the exactly same conditions as polymerization reaction. This experiment gave only N-phenylphthalimide, meaning that the reaction proceeds to complete imidization. Complete imidization could be confirmed once again from TGA investigations, which will be discussed later. Although this paper does not describe how the activator TPP is involved in direct imidization, we could prepare AB-type poly(etherimide)s by one-step polymerization reaction between amino groups and diacid groups.
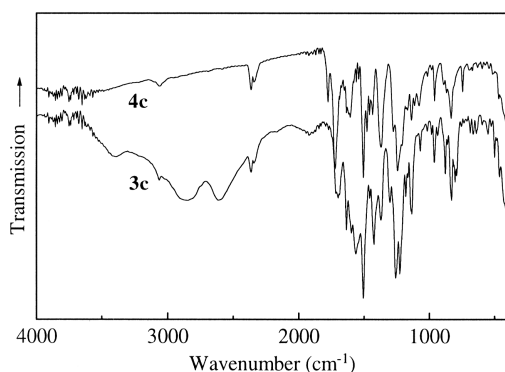
Solution properties : To obtain a first-hand information of molecular weight of the polymers obtained, their inherent viscosities were measured in concentrated sulfuric acid and are summarized in Table 1. It shows that the viscosities lie in the 0.39-0.94 dL/g range, indicating that the polymers have quite reasonably high molecular weights. To check their solvent resistances, solubilities in various solvents were measured

Figure 1. IR spectra of **4c** and **3c**.

and summarized also in Table 1. As it shows, all the polymers have excellent chemical resistance against chloroform even on heating, but they are vulnerable in m-cresol and concentrated sulfuric acid at room temperature.

Table 1. Inherent viscosities and solubilities of polymers.

Polymer code	η_{inh} [a] (dL/g)	CHCl$_3$	pyridine	NMP	m-cresol	H$_2$SO$_4$
4a	0.40	-	-	++	+++	+++
4b	0.94	-	-	++	+++	+++
4c	0.39	-	-	++	+++	+++
4d	0.53	-	-	++	+++	+++

a) Determined at 25°C in concentrated sulfuric acid(0.2g/dL).
- : insoluble, ++ : soluble on heating, +++ : soluble at r.t.

Thermal stability : Thermal resistances of the polymers were measured by TGA and evaluated by temperatures of 10% weight losses(T_{10}) and residual weights at 800°C(R_{800}), as summarized in Table 2. As Table 2 shows, all the polymers have T_{10}s higher than 600°C and R_{800}s higher than 60%, indicating that these polymers are highly thermostable and probably self-extinguishable. In many naphthylenic polymers 1,2-linked ones are commonly much less thermostable than others(14,15). However, **4a** shows only a slightly lower T_{10} value(603°C) than others, but this value is still higher than analogous AABB-type poly(etherimide)s derived from 2,3-di(4-aminophenyloxy)naphthalene and various aromatic dian-hydrides(523-578°C range)(16). **4d** has an extraordinarily high T_{10} and R_{800} values, presumably because it has only one ether group in its repeat unit, while the others have two.

On scanning TGAs any weight decreases below 200°C were carefully checked, because these weight losses could be tied with water removal from cyclo-dehydration reaction of poly(amic acid) contained, but no such weight losses were observed at all. This result forms an additional confirmation that the activated polymerization led to complete imidization.

Table 2. Thermal properties of polymers.

Polymer code	T_g(°C) [a]	Thermal stability in nitrogen [b]	
		T_{10}(°C)	R_{800}(%)
4a	227	603	62
4b	259	626	67
4c	270	622	63
4d	N/O [c] , 475(T_m)	677	71

a) & b) Obtained from DSC and TGA at a heating rate of 20°C/min.
under nitrogen, respectively.
c) Not observed.

Phase transitions : These were investigated by DSC in nitrogen atmosphere and the T_g values measured for annealed samples are summarized in Table 2.

Polymers **4a**, **4b** and **4c** revealed no other transitions than T_gs in the 227-270°C range, indicating that they must be amorphous. Their amorphous structures could also be confirmed by X-ray studies, which will be discussed later. However, **4d** showed no T_g but a T_m at 475°C in spite of repeated scannings, meaning that it has much stiffer backbone and some crystallinity. This behavior could also be ascribable for the presence of less number of ether bonds in its repeat unit.

It is interesting to consider the effect of isomeric naphthylene links on flexibility and conformation of the poly(etherimide) main chain. The 2,3-naphthylene unit provides such strongly bent chain structure that the chains can only hardly pack tight, and it should result to a much more flexible main chain structure than 2,6- or 2,7-naphthylene links. This surmise is really evidenced experimentally by the lowest T_g value. In contrast to 2,3-, 2,6-naphthylene link is almost linear and 2,7-link is slightly bent, and **4b** must have the higher T_g than **4c**, but as to see in Table 2, **4b** has 11 °C lower than **4c**. This negligible difference in T_g might be explained by the fact that both polymers have almost the same chain linearity in their stable conformations, as clearly to see in Figure 2.
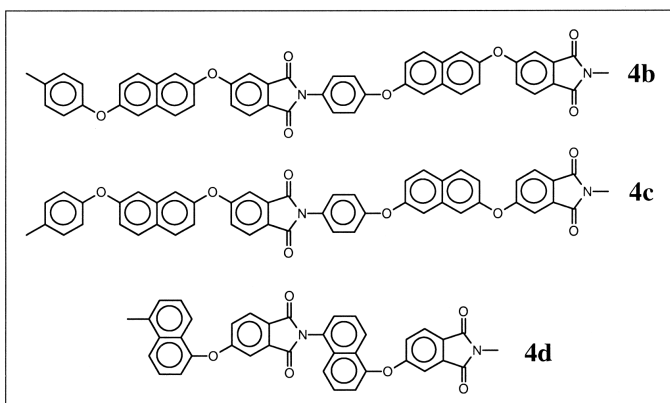

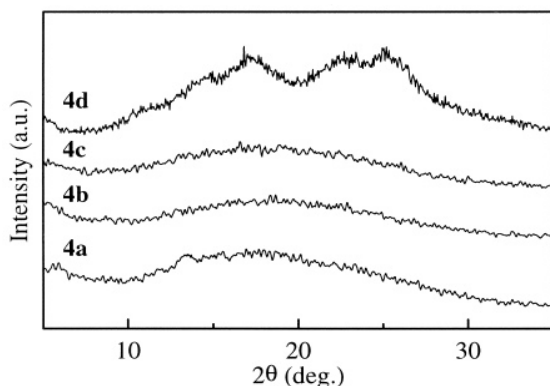Figure 2. Chain structure of **4b**, **4c** and **4d**.

Figure 3. WAXS diffractograms of **4a-d**.

Crystallinity : By wide-angle X-ray diffractometry the crystallinity of the as-polymerized samples was investigated in a reflection mode at room temperature and the diffractograms obtained are reproduced in Figure 3. It clearly shows that **4a**, **4b** and **4c** has no distinctive peaks but only a broad halo. But **4d** has several peaks recognizable near $2\theta = 15$, 17, 22 and 26

degree, meaning that it has a crystallinity, which has already been detected in DSC studies. Existence of the crystallinity in spite of two bent structures around the two ether links seems to result from chain linearity (Figure 2) as well as from a strong interchain attraction, both facilitating chain packing. This strong attraction arises from strong hydrophobic interaction between the fused aromatic rings.

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