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# Synthesis and properties of new AB-type semi-crystalline poly(ether imide)s

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## Summary

Two AB-type poly(ether imide)s were prepared by one-pot polyimidization in N-methyl-2-pyrrolidone(NMP)/pyridine or N,N-dimethylacetamide(DMAc)/$Et_3N$ solution in the presence of triphenylphosphite(TPP) activator. The polymers were obtained with inherent viscosities of 1.16(**5a**) and 0.54(**5b**) dL/g and were highly thermostable up to at least 552°C with 5% weight loss. The polymers showed chemical resistance against chloroform even at higher temperature but could readily be dissolved in m-cresol and concentrated sulfuric acid. Wide-angle X-ray diffractograms revealed that the polymers were semi-crystalline.

## Introduction

Aromatic polyimides such as Du Pont's Kapton have been known as high-performance polymers due to their excellent electrical, thermal and mechanical properties, and synthesized by polymerization of two difunctional monomers: a dianhydride and a diamine(1). Accordingly, much effort has been directed toward the design and synthesis of new dianhydrides and diamines. However, very few amino anhydride monomers and their corresponding polyimides are known and well characterized. This is presumable because those monomers can be hardly isolated in high purity due to the facile self-condensation between the amine and anhydride groups. In literature have been reported a few examples of AB-type poly(ether imide)s in which 4-(4-aminophenoxy)phthalic acid was used to prepare high molecular weight poly(ether imide) via two step procedure by the direct polycondensation in amide solvent with a mixture of triphenylphosphite and pyridine as a condensing agent, giving poly(ether amic acid), followed by thermal cyclodehydration(2). In addition, 4-aminophthalic anhydride and its many derivatives were used for polymerization(3). However, those monomers were difficult to polymerize to high molecular weight. Direct polymerization of dimethyl 4-[4-(4-aminophenoxy)phenyl-3,5,6-triphenylphthalate in m-cresol or neat only afforded a low molecular weight polyimide with an inherent viscosity of 0.13dL/g(4).

Recently, we reported a new method for high molecular weight poly(ether imide)s

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via direct polycondensation of AB-type monomers having amine hydrochlorides together with di(carboxylic acid) groups(5). These monomers were so stable that could be highly purified, and if the salts are deprotected to free amines by addition of tertiary amines such as $Et_3N$ or pyridine the amino groups start to react with the acid groups. And the low reactivity of the acid toward amino groups could be enhanced by triphenylphosphite activator which has been used for the synthesis of high molecular weight polyamides(6,7).

The goal of this ongoing research is to modify the structure of AB-type poly(ether imide)s to attain crystallinity, and to investigate the structure-property relation. This is important where the structure-property relation is not reliable yet, especially in AB-type polymers. In this article, we report the synthesis and polymerization of new AB-type monomers, and the properties of the corresponding AB-type poly(ether imide)s.

## Experimental part

*Materials and Measurements* : Dimethyl sulfoxide(DMSO) was used after drying over 4Å molecular sieves. NMP and DMAc were distilled over $CaH_2$ and pyridine dried in KOH before use. Anhydrous methanol, acetic acid, acetic anhydride, triphenylphosphite purchased all from Aldrich were used as received. Other reagents and solvents were used without further purification.

Melting points were determined using IA 9100 Digital melting point apparatus without correction. Elemental analyses were performed on a Carlo Erba EA 1108 microanalyzer. IR spectra(KBr pellets) were recorded on a Bio-Rad FTS 375C spectrophotometer. $^1$H- and $^{13}$C-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 scan rate of 20°C/min. under $N_2$. Inherent viscosities were determined using an Ubbelhode type viscometer at 25°C for 0.2g/dL solutions in concentrated $H_2SO_4$. Wide-angle X-ray diffractograms were obtained in a reflection mode using Ni-filtered Cu $K_\alpha$ radiation on a Rigaku Geiger Flex D-Max X-ray diffractometer.

*Synthesis of 4-(4-Acetamido-3-methylphenoxy)-N-phenylphthalimide*(**3a**):

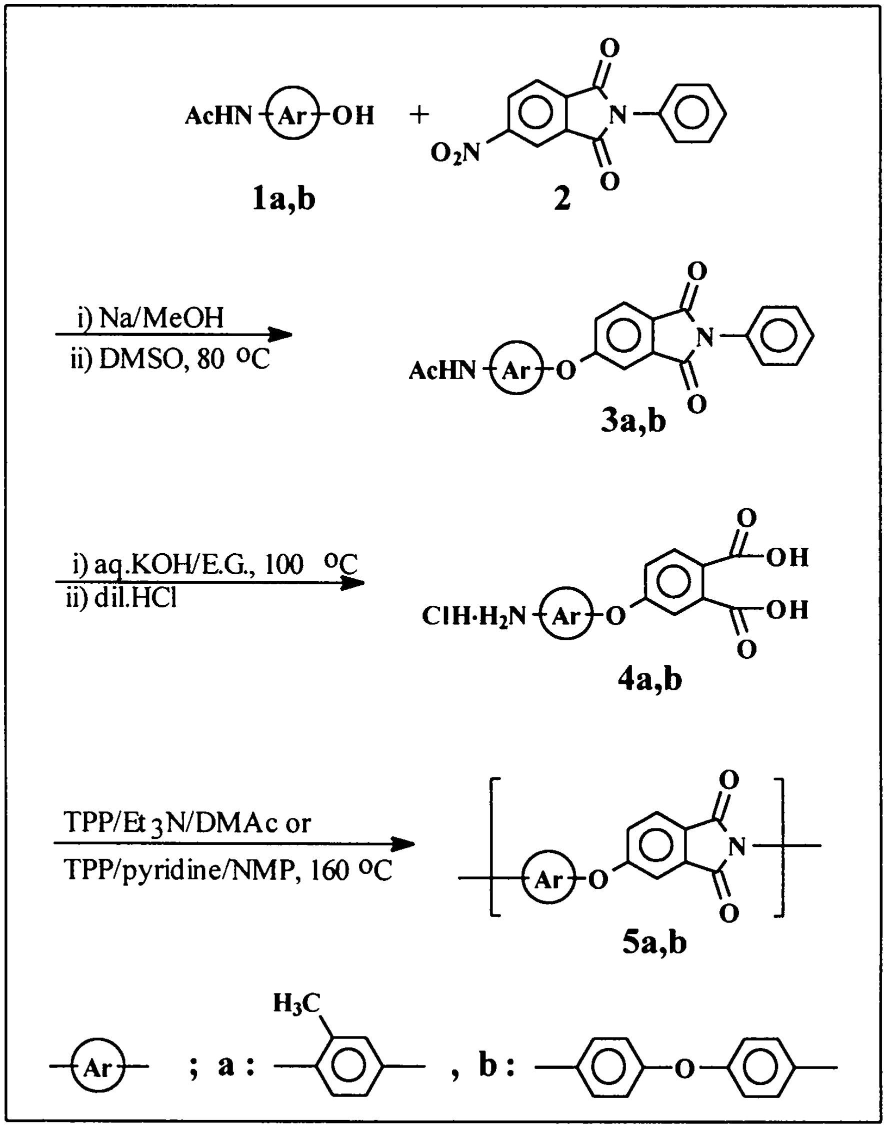
0.86g(5.2mmol) **1a** were reacted with 0.28g(5.2mmol) $NaOCH_3$ in 30mL anhydrous methanol by stirring for 2h at room temperature under nitrogen. After methanol was completely distilled out by vacuum, the remnants were dissolved in 40mL DMSO containing 1.39g(5.2mmol) 4-nitro-N-phenylphthalimide and heated at 80°C for 24h. The mixture was cooled and poured into 700mL water. The precipitates formed were collected and recrystallized from ethanol. **3b** was synthesized by the same procedure. Yield; 71.5%, m.p. 279°C. $^1$H-NMR(DMSO-$d_6$): $\delta$=9.36(s;1H), 7.97-7.95(d;1H), 7.55-7.50(m;3H), 7.46-7.39(m;4H), 7.32-7.31 (d;1H), 7.08-7.04(d;1H), 7.02-6.98 (q;1H), 2.23(s;3H) and 2.08(s;3H). $^{13}$C-NMR (DMSO-$d_6$): $\delta$=168.5, 166.6, 166.5, 163.4, 151.5, 134.5, 134.4, 134.1, 132.1, 129.1, 128.3, 127.5, 127.1, 126.1, 125.3, 122.8, 122.1, 117.9, 111.4, 23.4 and 18.1.

*4-[4-(4-Acetamidophenoxy)phenoxy]-N-phenylphthalimide*(**3b**):

Yield; 80.3%, m.p. 253-254°C. $^1$H-NMR(DMSO-$d_6$): $\delta$=9.98(s;1H), 7.97-7.94 (d;1H), 7.64-7.60(d;2H), 7.56-7-51(d,2H), 7.46-7.40(m;4H), 7.36-7.35(d;1H), 7.23-7.19(d;2H), 7.11-7.03(t;4H) and 2.04(s;3H). $^{13}$C-NMR(DMSO-$d_6$): $\delta$=168.3, 166.6, 166.4, 163.5, 154.9, 151.6, 149.7, 135.7, 134.4, 132.1, 129.1, 128.2, 127.5, 126.0, 125.3, 122.6, 122.2, 120.9, 119.7, 119.7, 111.3 and 24.1.

*Synthesis of 4-(4-Amino-3-methylphenoxy)phthalic acid hydrochloride*(**4a**):

A mixture of 1.50g(3.88mmol) **3a**, 40mL ethylene glycol, 10mL water and 2.5g KOH was placed in a 100mL flask equipped with a Dean-stark trap and heated to 100°C under nitrogen for 24h to remove aniline azeotropically. After cooled, the solution was filtered and acidified with dilute hydrochloric acid to form white precipitates. The precipitates were collected and recrystallized from ethanol. The other monomer **4b** was prepared by the same procedure as above. Yield; 72.3 %. $^{1}$H-NMR(DMSO-$d_6$): $\delta$=7.76-7.73(d;1H), 7.01-6.98(q;1H), 6.96-6.95(d;1H), 6.79-6.78 (d;1H), 6.73-6.72(d;2H) and 2.08(s;3H). $^{13}$C-NMR(DMSO-$d_6$): $\delta$=169.0, 167.6, 161.4, 145.1, 143.3, 136.9, 131.8, 124.6, 123.9, 122.5, 119.0, 117.5, 115.7, 115.3 and 17.7. Anal. $(C_{15}H_{14}N_1O_5Cl_1)_n$ (323.7)n Calc. C 55.66 H 4.36 N 4.33 Found C 55.58 H 4.29 N 4.30.



Scheme 1. Polymer synthesis.

*4-[4-(4-Aminophenoxy)phenoxy]phthalic acid hydrochloride* (**4b**):
Yield; 72.3%. $^{1}$H-NMR(DMSO-$d_6$): $\delta$=7.80-7.77(d;1H), 7.12-7.05(m;4H), 6.97-6.94(d;2H), 6.86-6.83 (d;2H) and 6.70-6.67(d;2H). $^{13}$C-NMR(DMSO-$d_6$): $\delta$=168.7, 167.6, 160.2, 155.8, 149.3, 147.1, 143.6, 136.9, 132.0, 125.8, 121.9, 120.9, 118.5, 118.2 and 116.3. Anal. $(C_{20}H_{16}N_{1}O_{6}C_{l})_n$ $(401.8)_n$ Calc. C 59.79 H 4.01 N 3.49 Found C 59.74 H 4.40 N 3.60.

*Polymerization* : After 1.0g(3.09mmol) **4a** was dissolved in 15mL NMP/pyridine(6.5/1 v/v), 0.8095mL(3.09mmol) TPP was added in one portion with stirring. The solution was heated at 160°C for 24h, cooled to room temperature and precipitated by pouring into 400mL methanol. The yellow precipitates were filtered, washed with hot acetone and finally vacuum-dried at 80°C for 24h to give **5a**. The other polymer **5b** was prepared from 1.0g(2.49mmol) **4b** in 30mL DMAc containing 0.35mL $Et_3N$ and 0.655mL (2.49mmol) TPP.

*Poly[4-{[(2-methyl)-1,4-phenylene}oxyphthalimide]*(**5a**):
Yield; 87%, IR(KBr); 1779 & 1721(C=O imide I & II), 1607(bz. ring) and 1374 cm$^{-1}$(C-N-C). Anal. $(C_{15}H_{9}N_{1}O_{3})_n$ $(251.2)_n$ Calc. C 71.72 H 3.61 N 5.58 Found C 71.61 H 3.69 N 5.55.

*Poly[4-(1,4-phenyleneoxy-1,4-phenylene)oxyphthalimide]*(**5b**):
Yield; 85%, IR(KBr); 1775 & 1713(C=O imide I & II), 1619(bz. ring) and 1378 cm$^{-1}$(C-N-C). Anal. $(C_{20}H_{11}N_{1}O_{4})_n$ $(329.3)_n$ Calc. C 72.95 H 3.37 N 4.25 Found C 73.05 H 3.46 N 4.30.

## Results and discussion

*Synthesis and Characterization* : Monomers(**4a,4b**) were prepared by nitro-displacement reaction of 4-nitro-N-phenylphthalimide with sodium 4-(4-acetamidophenyloxy)phenolate and 4-acetamido-3-methylphenolate followed by basic hydrolysis of N-phenylimide and amide group(8), as shown in Scheme 1. The raw material **1b** had been prepared by the reaction of excess hydroquinone with 4-nitrofluorobenzene followed by reduction of the nitro group and acetylation of the amino group formed by the reduction(9). 4-Nitro-N-phenylphthalimide was obtained from 4-nitrophthalic anhydride with aniline as described previously(10). Monomers were purified to polymerization grade by recrystallization. The structures of the intermediate compounds and final products were confirmed by means of elemental analysis and IR and NMR spectroscopy. As shown in the Experimental part, the elemental analysis values of monomers agreed well with the calculated values of their structures. Their melting points could not be measured due to decomposition before melting.

New AB-type poly(ether imide)s were synthesized by the one-pot polycondensation in a polar aprotic solvent such as DMAc and NMP, which involved the polyamidation and subsequent cyclodehydration. For the regeneration of free amino group, $Et_3N$(DMAc) or pyridine(NMP) was used. Polymers were thoroughly purified by precipitating from large excess of methanol and repeated washing with hot acetone. Structures of the polymers thus obtained were characterized by IR spectroscopy and elemental analysis. In IR spectra, the polymer **5b** shows only the absorption bands at 1775 & 1713cm$^{-1}$(C=O imide I & II) and 1378cm$^{-1}$(C-N-C stretching) associated with imide ring, whereas monomer

**4b** exhibits the C=O stretching band at 1709cm$^{-1}$ which is characteristic of a carboxylic acid with the appearance of overlapped amine hydrochloride and acid in the 3300-2500cm$^{-1}$ region. In addition, there were no peaks attributable to NH or COOH observable in amic acid, as was found in our previous works(5). These facts indicate that the activated polycondensation involved polyamidation and subsequent effective cyclodehydration. Moreover, in model imidizations of N-phenylphthalamic acid in the presence of TPP we obtained the cyclized imide product N-phenylphthalimide quantitatively even at such lower temperature as 50°C, which will be reported in detail in a separate paper. Although the present investigation does not describe the mechanistic aspect, we could obtain AB-type poly(ether imide)s by one-pot polymerization reaction between amino and diacid groups.

*Properties of Polymers* : The inherent viscosities of the polymers were 1.16(**5a**) and 0.54(**5b**) dL/g, as measured in 0.2g/dL conc. $H_2SO_4$ solution at 25°C, showing that they were high molecular weight polymers although they were polymerized with very low monomer concentration such as 6.7(**5a**) or 3.3(**5b**)wt.%. The solubility behavior of the polymers was determined for the as-polymerized powder samples in excess solvents. As listed in Table 1, they had high chemical resistance to common organic solvents, but readily dissolved in m-cresol and sulfuric acid. It is notable that the polymer **5a** was soluble on heating in m-cresol, while the polymer without methyl pendant(Ref. II) was soluble only in sulfuric acid(11). The enhanced solubility may be due to the fact that the methyl pendant inhibits close packing of polymer chains, hence becomes more vulnerable to solvents.

Table 1. Viscosity and solubility of polymers.

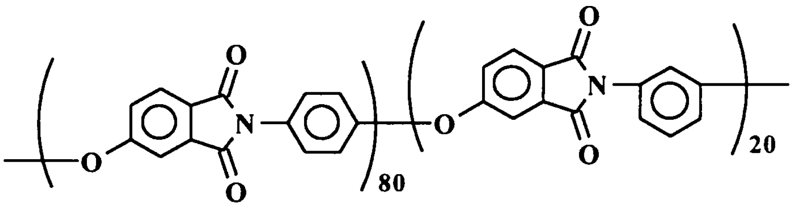
| Polymer code | $\eta_{inh}$ $^{a)}$ (dL/g) | Solubility $^{b)}$ | | | | |
|---|---|---|---|---|---|---|
| | | $CHCl_3$ | DMSO | NMP | MC | $H_2SO_4$ |
| **5a** | 1.16 | - | - | - | + | ++ |
| **5b** | 0.54 | - | - | - | ++ | ++ |

a) determined at 25°C in conc. $H_2SO_4$(0.2g/dL),
b) ++: soluble at room temperature, +: soluble on heating, -: insoluble, MC: m-cresol.

Thermal properties of the polymers were evaluated by thermogravimetric analysis(TGA) and differential scanning calorimetry(DSC), as shown in Table 2. The polymers showed a similar TGA pattern with no significant weight loss below 500°C in nitrogen, but with more than 51% residue remaining when heated to 800°C, meaning that they were highly thermostable. The 5% weight loss temperatures were 552°C(**5a**) and 578°C(**5b**), and maximum degradation temperatures 578°C(**5a**) and 601°C(**5b**). The $T_g$s of these polymers were recorded at 307°C(**5a**) and 220°C(**5b**). The polymer **5a** exhibited higher $T_g$ due to the rigid structure, but this $T_g$ value seemed to be lowered when compared to the polymer without methyl pendant(Ref. II) that showed no transitions before degradation. This is very interesting because the introduction of short methyl pendant adjacent to imide carbonyl groups on the polymer main chain generally leads the increase of $T_g$ due to the blocking of the rotation around C-N bond. However, the length of repeat unit of **5a** is relatively short therefore the volume effect of methyl pendant could be a dominant factor leading to an increase in chain mobility. And much lower $T_g$ value of the polymer **5b** could be ascribable in terms of incorporation of flexible ether linkage.

These polymers also exhibited the crystalline transition endotherms characteristic of semi-crystalline polymers. The melting temperatures were detected at 464°C(**5a**) and 380°C(**5b**), respectively. The melting temperature of **5a** might be significantly lowered when compared to the polymer Ref. II. Because Ref. II is believed to have much higher $T_m$ values from the fact that the copolymer Ref. I showed melting transition at 460°C(11). The lowered melting temperature may be due to a less packing of its polymer backbone. This is quite reasonable because the presence of noncoplanar conformation due to the methyl pendant decreases the intermolecular forces between the polymer chains, subsequently causing a decrease in crystallinity. In fact, the crystallinity of **5a** was somewhat low ca. 60%. Their endothermic peaks which were appeared on first heating scan were not shown upon cooling and second heating scans even after annealing above their $T_g$s for several hours, meaning that the crystallization rate is much slow.

**Ref. I**



**Ref. II**

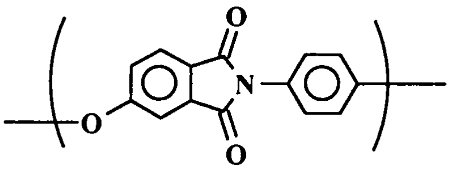


Table 2. Thermal properties of polymers [a].

| Polymer code | $T_g$(°C) | $T_m$(°C) [b] | Thermal stability | | |
|---|---|---|---|---|---|
| | | | $T_5$(°C) [c] | MDT(°C) [d] | $R_{800}$(%) [e] |
| **5a** | 307 | 464 | 559 | 594 | 57 |
| **5b** | 220 | 380 | 612 | 634 | 51 |

a) obtained at a heating rate of 20°C/min. under $N_2$, b) obtained from 1st heating scan, c) temperature at 5% weight loss, d) maximum degradation temperature, e) residue at 800°C.

The crystallinity of the polymers was examined by wide-angle X-ray diffraction experiments. The as-polymerized powders were employed as the samples at room temperature. As shown in Figure 1, both polymers exhibited several strong reflections around $2\theta$ = 12, 17, 22(**5a**), and 6, 17, 19, 26, 27, 28 degree(**5b**), indicating of higher crystallinity which has already been detected in DSC studies.

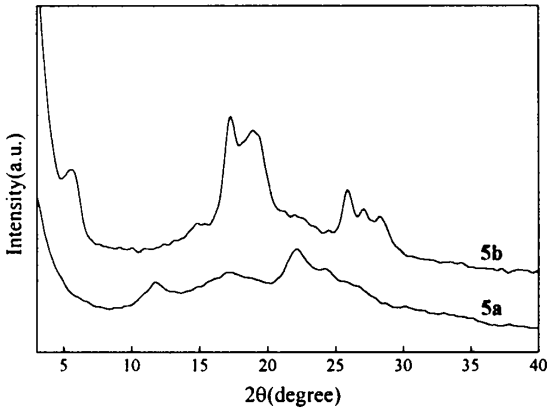


Figure 1. X-ray diffractograms of polymers.

It is worth while to consider the effect of ether links or short pendant groups on crystallizability of the AB-type poly(ether imide)s main chain. It is generally known that ether links or pendant groups provide such strongly bent chain structure that the chain can hardly pack tight, consequently result to flexible main chain structures. However, these polymers(**5a,b**) were found to overcome the packing disturbance arising from ether links or short pendant groups together with another bent structure of 4-oxyphthalimide moiety, indicating the existence of strong interchain attractions and to some degree, chain linearity, both facilitating chain packing.

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