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Synthesis and properties of polyimides derived from *N*-[4-(4-aminophenyloxy)phenyl]-4-aminophthalimide

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Abstract

A new phthalimide-containing diamine *N*-[4-(4-aminophenyloxy)phenyl]-4-aminophthalimide was synthesized and polymerized with various aromatic tetracarboxylic acid dianhydrides via one-step polycondensation in *p*-chlorophenol to produce high molecular weight polyimides. In comparison with the polymers based on 4,4′-oxydianiline (ODA), the polymers prepared in this work had comparable or slightly higher solubility in spite of the presence of one more rigid phthalimide group in the repeat unit. They showed much higher glass transition temperatures (263–338°C) and enhanced thermal stabilities observed from the temperatures (575–631°C) at 5% weight loss. Some of the polymers exhibited crystalline transitions even though they have bent groups and non-symmetric chain structure leading to irregular repeating sequences. © 2000 Published by Elsevier Science Ltd.

Keywords: Polyimide; Poly(etherimide); Polyphthalimide

1. Introduction

The synthesis of rigid, rod-like polyimides has been an important subject in polymer science for many years, as these polymers exhibit unique mechanical, chemical and thermal properties. However, in many cases, they are insoluble and do not melt below their decomposition temperature, which restricts their characterization, processing and application. Thus, many studies have focused on designing such chemical structures of the rigid aromatic backbone so as to obtain aromatic polymers that are processable by conventional techniques, while maintaining desirable properties. For example, bulky lateral substituents [1–5], flexible alkyl side chains [6–8], noncoplanar biphenyl moieties [9,10] as well as flexible alkyl or aryl ether spacers [11–13] have been used to enhance the solubility and thus processability.

Incorporation of aryl ether units is a particularly successful method for improving solubility with slight reduction in thermal properties. This trade-off is a natural outcome of the flexible linkages, which inhibit packing and decrease the coplanarity of the aromatic rings, thus reducing the interchain interaction to enhance solubility and increasing the segmental rotational motion to lower the T_g. On the other hand, incorporation of bulky pendant groups can impart a significant mobility, while providing good solubility due to decreased chain packing leading to crystallization.

In this connection, we became interested in the ability of a non-symmetrical diamine *N*-[4-(4-aminophenoxy)phenyl]-4-aminophthalimide (**3**) to influence the chain flexibility of aromatic polyimides, because this monomeric diamine incorporates both an aryl ether and a nonlinear 2,5-linked phthalimide group. The polyimides derived from **3** have the repeat unit structures of the corresponding polyimides prepared from 4,4′-oxydianiline (ODA), to which a phthalimide unit is added. By incorporating this non-symmetrical link to ODA–polyimides, enhanced solubilities but analogous T_g values were expected because the link might decrease interchain interactions, but increase chain rigidity. With these aims in mind, we report the synthesis of this diamine and its polyimides.

2. Experimental

2.1. Materials and measurement

p-Chlorophenol (PCP) was recrystallized from *n*-hexane [14]. Ammonium formate, 4-nitrofluorobenzene, 4-nitrophthalic anhydride, acetic acid, *n*-heptane and cyclohexane

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were used without purification. Pyromellitic dianhydride (PMDA) was purified by sublimation. 4,4′-Oxydi(phthalic anhydride) (ODPA), 3,3′,4,4′-biphenyltetracarboxylic acid dianhydride (BPDA) and 3,3′,4,4′-diphenylsulfonetetracarboxylic acid dianhydride (DSDA) were recrystallized from acetic anhydride and hexafluoroisopropylidene-4,4′-di(phthalic anhydride) (6FDA) and 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) from toluene. Other commercially available chemicals were used as received.

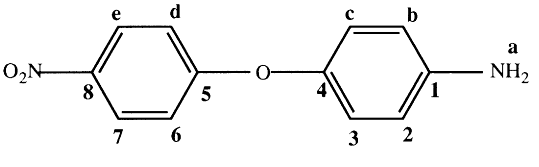
Melting points were determined using IA 9100 Digital melting point apparatus without correction. Elemental analyses were performed on a Carlo Erba EA 1108 microanalyzer. IR spectra were recorded on a Bio-Rad FTS 375C spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained from a 300 MHz Bruker AM 300 spectrometer at room temperature. Thermal analyses of polymers were carried out with a Perkin–Elmer PE PC Series TGA 7 thermogravimetric analyzer and DSC 7 thermal analyzer at a heating rate of 20°C/min under N_2. Wide-angle X-ray diffractograms were obtained using Ni-filtered CuK_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 NMP or H_2SO_4.

2.2. Monomer synthesis

*2.2.1. 4-(4-Nitrophenyloxy)aniline (**1**)*

A mixture of 5.46 g (0.05 mol) 4-aminophenol, 6.91 g (0.05 mol) anhydrous K_2CO_3 and 5.3 ml (0.05 mol) 4-nitrofluorobenzene in 70 ml DMAc was heated at 100°C for 20 h in nitrogen atmosphere. The color of the solution changed from yellow to dark brown as reaction proceeded. After cooling to room temperature, the reaction mixture was poured into 800 ml of water to form yellow solid. The solid was washed thoroughly with water, and then collected by filtration. The crude product was recrystallized from *n*-heptane.

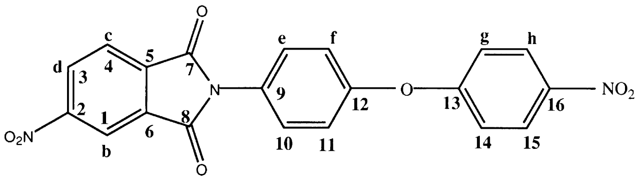
Yield: 86.9%, m.p.: 129°C. IR (KBr pellet) in cm^{-1}: 3446 and 3369 (NH_2), 1509 (benzene ring), 1341 (NO_2). ^{1}H-NMR(DMSO-d$_6$) in δ (ppm) and J(Hz): 8.22(2H, d, $J_{ed} = 9$, H-e), 7.02(2H, d, $J_{de} = 11$, H-d), 6.87(2H, d, $J_{cb} = 15$, H-c), 6.65(2H, d, $J_{bc} = 15$, H-b) and 5.18(2H, s, H-a). ^{13}C-NMR (DMSO-d$_6$) in δ (ppm): 164.5 (C-5), 146.7 (C-4), 143.5 (C-8), 141.3 (C-1), 126.0 (C-7), 121.4 (C-3), 116.0 (C-6) and 114.8 (C-2).



2.2.2. N-[4-(4-Nitrophenyloxy)phenyl]-4-nitrophthalimide (2)

In a flask equipped with a Dean–Stark trap and a stirrer were placed 3.40 g (17.3 mmol) 4-nitrophthalic anhydride, 100 ml acetic acid, 20 ml cyclohexane and 4.00 g (17.3 mmol) **1** and the mixture was heated at 110°C in nitrogen for 12 h. During this time, water formed was removed and trapped in a Dean–Stark tube quantitatively. On cooling to room temperature, yellow crystals were formed. They were collected by filtration. The filtrate was diluted with cool water and the precipitates formed were collected. The two solids were combined and recrystallized from acetonitrile.

Yield: 93.6%, m.p.: 205–206°C. IR (KBr pellet) in cm^{-1}: 1787 and 1725 (imide C=O), 1509 (benzene ring), 1387 (C–N–C) and 1345 (NO_2). ^{1}H-NMR (DMSO-d$_6$) in δ (ppm) and J (Hz): 8.70 (1H, d, $J_{dc} = 12$, H-d), 8.61(1H, s, H-b), 8.31–8.23 (1H + 2H, m, H-c, h), 7.60 (2H, d, $J_{gh} = 9$, H-g), 7.38 (2H, d, $J_{fe} = 9$, H-f) and 7.24 (2H, d, $J_{ef} = 9$, H-e). ^{13}C-NMR (DMSO-d$_6$) in δ (ppm): 165.4 (C-7), 165.1 (C-8), 162.3 (C-13), 154.1 (C-12), 151.5 (C-2), 142.5 (C-16), 136.2 (C-5), 132.9 (C-3), 129.7 (C-6), 129.3 (C-4), 128.3 (C-15), 126.2 (C-9), 124.8 (C-11), 120.6 (C-1), 118.1 (C-10) and 117.8 (C-14).



*2.2.3. N-[4-(4-Aminophenyloxy)phenyl]-4-aminophthalimide (**3**)*

A mixture of 1.62 g (4.0 mmol) **2**, 2.52 g (40.0 mmol) ammonium formate, 0.2 g 10% Pd–C and 30 ml DMAc was allowed to stir at ambient temperature in nitrogen atmosphere for 20 h. The reaction mixture was filtered to remove Pd–C and the filtrate was added to 700 ml water to obtain precipitates, which were filtered and dried. The crude product was recrystallized from methanol.

Yield: 74.6%, m.p.: 246–247°C. Elemental analysis for $C_{20}H_{15}N_3O_3$ (MW = 345.3) in wt.%: Calc. C 69.56, H 4.38, N 12.17 and found C 69.55, H 4.53, N 12.20. IR (KBr pellet) in cm^{-1}: 3446 and 3365 (NH_2), 1763 and 1705 (imide C=O), 1501 (benzene ring) and 1393 (C–N–C). ^{1}H-NMR (DMSO-d$_6$) in δ (ppm) and J (Hz) (See Fig. 2): 7.57 (1H, d, $J_{cd} = 9$, H-c), 7.29 (2H, d, $J_{ef} = 15$, H-e), 6.99 (1H, d, $J_{bd} = 3$, H-b), 6.95 (2H, d, $J_{fe} = 15$, H-f), 6.86 (1H, q, $J_{dc} = 15$, $J_{db} = 3$, H-d), 6.83 (2H, d, $J_{gh} = 15$, H-g), 6.62 (2H, d, $J_{hg} = 12$, H-h) 6.56 (2H, s, H-a) and 5.04 (2H, s, H-i). ^{13}C-NMR (DMSO-d$_6$) in δ (ppm): 168.4 (C-7), 168.0 (C-8), 159.2 (C-12), 156.1 (C-1), 146.6 (C-13), 146.0 (C-16), 135.2 (C-5), 129.6 (C-3), 126.8 (C-4), 126.1 (C-9), 122.0 (C-11), 117.9 (C-2), 117.2 (C-14), 117.1 (C-10), 115.8 (C-15) and 107.9 (C-6).

Table 1
Yield, inherent viscosity (η_{inh}), elemental analysis and solubility of polymers

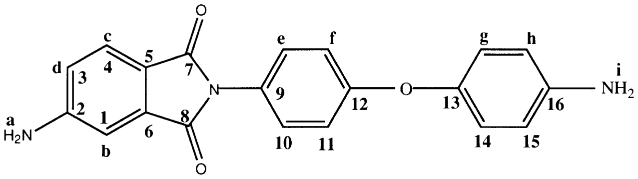
Polymer code	Yield (%)	η_{inh} (dl/g)	Elemental analysis (wt.%)[a]			Solubility[b]		
			C	H	N	H_2SO_4	*m*-Cresol	NMP
O-4	95	–	69.80(69.80)	2.77(2.81)	6.78(6.74)	++	++	++
T-4	99	0.62[c]	70.37(70.10)	2.71(2.75)	6.65(6.68)	++	+	++
F-4	99	–	62.16(62.10)	2.30(2.27)	5.51(5.58)	++	+	+
P-4	99	0.97[c]	68.32(68.41)	2.48(2.52)	7.99(7.90)	+++	–	–
S-4	99	0.81[d]	64.77(64.50)	2.57(2.60)	6.29(6.25)	+++	+	++
B-4	98	1.83[c]	71.65(71.63)	2.84(2.87)	6.96(6.92)	+++	+	+

[a] Values in the parentheses are calculated ones.

[b] +++: Soluble at room temperature, ++: soluble on heating, + : slightly soluble or swellable, –: insoluble.

[c] Measured from 0.2 g/dl H_2SO_4 at 25°C.

[d] Measured from 0.2 g/dl NMP at 25°C.



2.3. Polymer synthesis

As a typical procedure for the preparation of polymers, the polymerization of **3** with ODPA is given. ODPA (0.4290 g (1.50 mmol)) was added to a stirred solution of 0.5180 g (1.5 mmol) **3** in 12.84 g PCP at 100°C in nitrogen atmosphere. The mixture was heated to 180°C for 1 h and maintained at that temperature for 24 h under stirring in nitrogen flow. The obtained polymer solution was coated on a Petri dish to form a liquid film. This was heated under vacuum at 110°C for 1 h and then the temperature was gradually elevated to 300°C and kept for 1 h. To completely remove PCP, the film taken off was treated with hot water. It was dried at 100°C for 1 day in a vacuum oven. The other polymers were prepared in the similar manner from **3** with other tetracarboxylic dianhydrides. The reaction yields and the elemental analyses of all polymers are given in Table 1.

3. Results and discussion

3.1. Monomer synthesis

A new phthalimide-containing diamine was synthesized

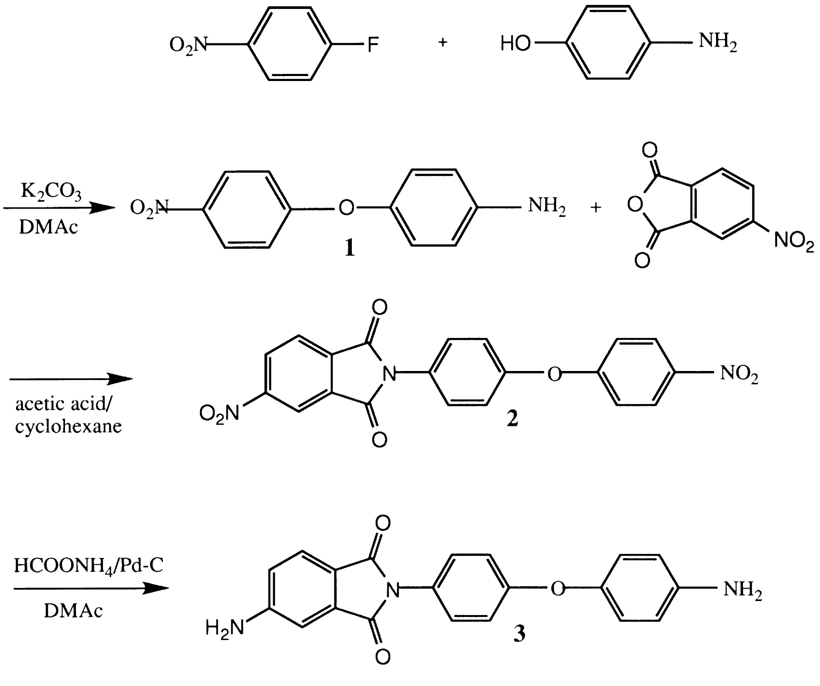


Fig. 1. Monomer synthesis.

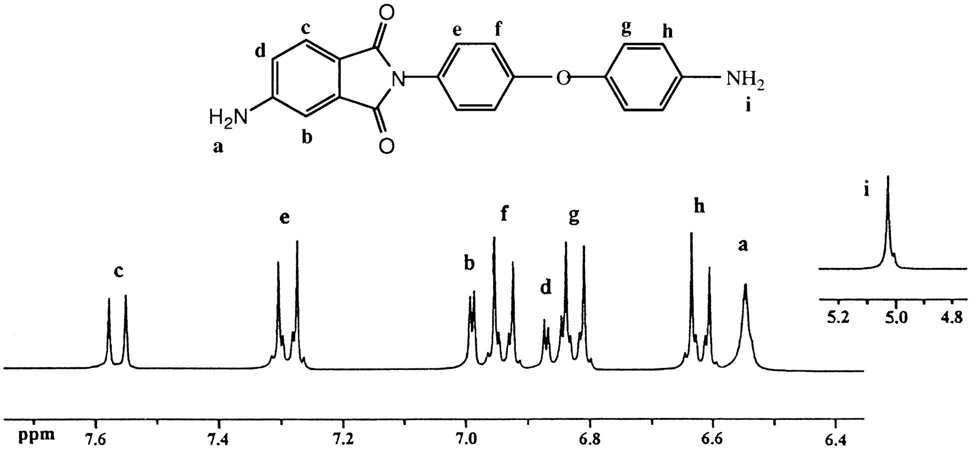


Fig. 2. ^{1}H-NMR spectrum of **3** in DMSO-d_6.

according to the reaction sequence of Fig. 1. Thus, the raw material **1** was obtained by nucleophilic substitution reaction of 4-nitrofluorobenzene with 4-aminophenol. Monomer **3** was prepared by condensation of 4-nitrophthalic anhydride with 4-(4-nitrophenyloxy)aniline in acetic acid–cyclohexane mixture, followed by reduction of the dinitro compound using ammonium formate in DMAc at room temperature. The new diamine was purified by recrystallization from methanol. It was a bright yellow solid, and could be handled and purified in air for a prolonged time without any signs of deterioration.

The structure of this diamine was confirmed by elemental analysis, IR and ^{1}H- and ^{13}C-NMR spectroscopy. As observed in Section 2, the elemental analysis values of diamine are well coincident with the calculated values and all the NMR peaks could be exactly assigned. The ^{1}H-NMR spectrum shown in Fig. 2 exhibits the peaks assignable for two different amino groups at around 6.56 and 5.04 ppm. This difference in chemical shift means that each amino group should have different reactivity, leading to the internal copolymerization effect [15]. This internal copolymerization effect will be discussed later in greater detail.

3.2. Polymer synthesis

The diamine monomer was polymerized with six different aromatic tetracarboxylic dianhydrides as depicted in Fig. 3. The polymerizations were carried out via one-step method in 10% (w/v) monomer concentrations because the

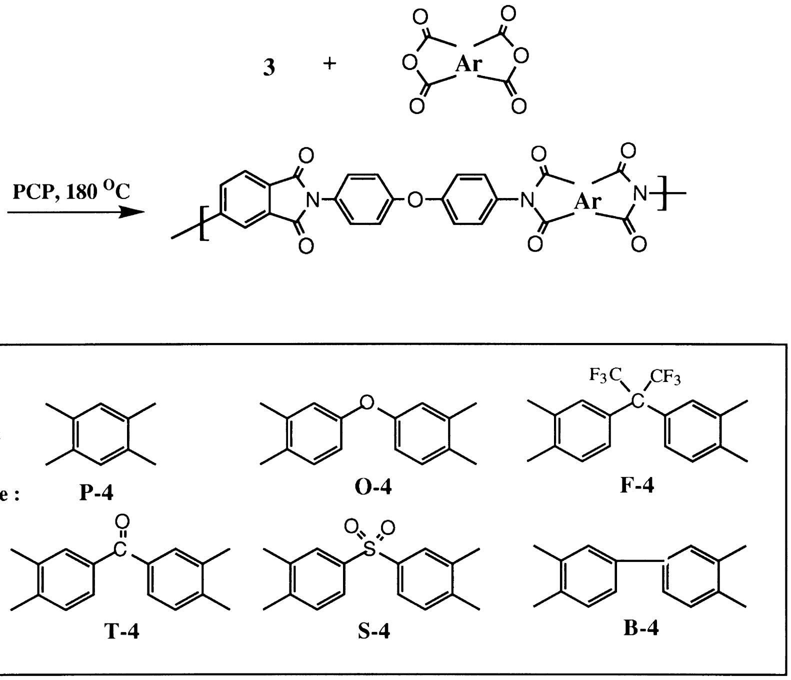


Fig. 3. Polymer synthesis.

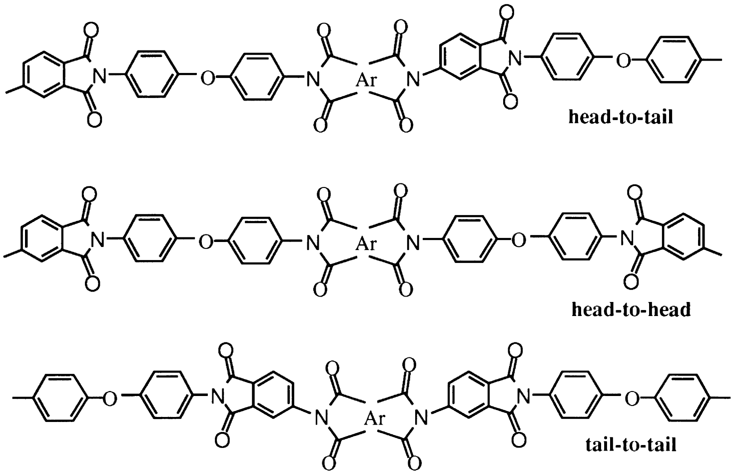


Fig. 4. Three different triad structures.

non-symmetric nature of the diamine monomer was expected to impart sufficient solubility to fully imidized polymers. Furthermore, amino group directly attached to imide ring was considered to have lower reactivity toward anhydride than the one attached to 4-oxyphenylene ring, and hence the two-step method could produce low molecular weight poly(amic acid)s. The reaction mixtures were heated at 180°C for 24 h, with water removal by PCP azeotrope. Most polymers remained in solution throughout the polymerization, thus permitting an increase of their molecular weights and giving viscous solutions, except the polymer from PMDA, which precipitated during the polymerization.

As already mentioned above, the two amino groups of monomeric diamine must have different reactivity, which leads to internal copolymerization. This reaction behavior should result in the random head-to-tail, head-to-head and tail-to-tail triad orientation in consecutive repeating units along the polymer main chain, as shown in Fig. 4. In head-to-tail sequence the aromatic tetracarboxydiimide ring is linked to a 4-phenylene ring and in tail-to-tail orientation with two phthalimido rings. These three structures are naturally different in rigidity and degree of bending, but because they all should be present mixed up along polymer chains, they lead to backbone randomization. This backbone randomization should make a contribution to the high solubility of polymers. In spite of this randomization the main chain of PMDA–polyimide (**P-4**) is so highly rigid that it did not dissolve in the polymerization system.

The polymer films were flexible and creasable without cracking, indicating that high molecular weight polymers had been obtained. The polymerization yields were almost quantitative, and elemental analyses shown in Table 1 as well as IR spectroscopy verified the structures of the polymers as proposed.

IR spectra of polymers showed characteristic absorption bands associated with the imide structure at around 1780, 1720, 1370 and 720 cm^{-1}, together with the absence of characteristic double peaks for amino group and of $C=O$ peak for amic acid. The experimental results support the formation of fully imidized polymers with suggested structures.

3.3. Solution properties

The inherent viscosities determined for the polymer films except **O-4** and **F-4** gave values in the 0.62–1.83 dl/g range, reflecting high molecular weights of the polymers. **O-4** and **F-4** did not completely dissolve even in concentrated H_2SO_4 at room temperature. Upon heating for longer time, the solutions became deeply colored, but only very low inherent viscosity values around 0.07 dl/g could be attained. This may result from decomposition of the polymers by the concentrated H_2SO_4 at higher temperature as generally known. In that sense, the lowest value of **T-4** could be explained in terms of partial decomposition because its solution could be prepared only by gentle heating.

Table 2
Phase transition and thermal stability of polymers

Polymer	Phase transition [a]		Thermal stability[b]		
	T_g (°C)	T_m (°C)	T_5 (°C)[c]	T_{max} (°C)[d]	R_{900} (%)[e]
O-4	284(270)	410	613	641	61
T-4	287(272)	–	593(545)	655	60
F-4	338(287)	–	587	666	57
P-4	− (400)	–	623(550)	663	58
S-4	324(293)	–	575(485)	639	57
B-4	263(262)	372	631(555)	659	66

[a] Measured from DSC under nitrogen at a heating rate of 20°C/min in nitrogen. Values indicated in the parentheses are those for polymers based on ODA reported in the literature [16–18].

[b] Measured from TGA under nitrogen at a heating rate of 20°C/min in nitrogen. Values indicated in the parentheses are those for polymers based on ODA reported in the literature [16–18].

[c] Temperature at 5% wt. loss.

[d] Maximum degradation temperature obtained from the differential curve.

[e] Residual weight at 900°C.

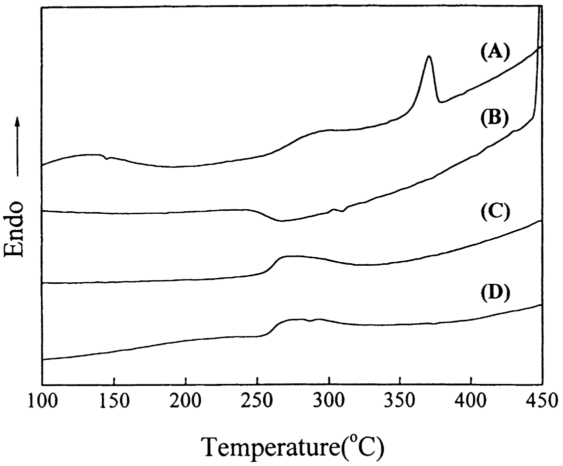


Fig. 5. DSC thermograms of **B-4**: (A) first heating scan; (B) first cooling scan; (C) second heating scan; and (D) third heating scan.

The solubility behavior of the polymers was examined for the film samples in excess solvents and the results are listed in Table 2. The polymers could be dissolved more or less in *m*-cresol, NMP and concentrated sulfuric acid at room temperature or by heating, but they were not soluble in DMSO, DMAc and $CHCl_3$ even on heating for prolonged time. When our polymers were compared with the polymers based on ODA [16–18], they showed higher solubility in the tested solvents. This result implies that the bent structure of 2,5-linked phthalimide and the random sequence resulting from internal copolymerization exert a very favorable effect on enhancing polymer solubility. The enhancing effect is more remarkable when we consider that the solubility tests were performed with polymer film samples, which in general, dissolve more slowly than their powder samples.

3.4. Thermal stability

The thermal stability of the polymers was measured by TGA and evaluated by the temperature at 5% weight loss (T_5), maximum degradation temperature ($T_{\max}$) and residual weight at 900°C (R_{900}), as listed in Table 2. All the polymers showed a similar TGA pattern with no significant weight loss below 400°C in nitrogen. They exhibited extremely high T_5 values ranging from 577 to 631°C. On scanning the TGAs, **P-4** started to lose its weight at around 300°C while the other polymers at 400°C. This implies that it still contains a small amount of trapped PCP. **P-4** precipitated out during polymerization and, therefore, it could not have sufficiently high molecular weight. This low molecular weight portion must degrade away at lower temperature. Nevertheless, when compared with the ODA–polyimides as shown in the Table 2, the polymers of the present work reveal much higher T_5 values (>48–90°C). This result could be attributable for the incorporation of rigid 2,5-linked phthalimide group in the main chain. R_{900} varied from 57 to 66%.

3.5. Phase transition

The phase transitions of the synthesized polymers were investigated by DSC in nitrogen atmosphere and the results are listed also in Table 2. T_gs were in the range 263–338°C, but no T_g was detectable for **P-4**. The higher T_gs of the polymers from PMDA and 6FDA are explainable in terms of the rigidity of pyromellitimide unit and dipolar interaction of the hexafluoroisopropylidene group, respectively. Among the aromatic dianhydrides used, the T_gs of their polymers increased in the order of: BPDA < ODPA < BTDA < DSDA < 6FDA ≈ PMDA.

DSC thermograms of **B-4** is reproduced in Fig. 5. As seen from Fig. 5, **B-4** displays a small but distinctive endothermic peak at 372°C in the first heating scan, meaning that it has crystalline nature. From the endothermic peak, the value of ΔH_m and ΔS_m was calculated to be as low as 3700 and 5700 J mol^{-1} K^{-1}, respectively. Because the analogous polymer based on ODA is known to be completely amorphous, these values could not be compared with those of ODA polyimide, but the above small numerical values indicates that **B-4** in as-polymerized state has only very low crystallinity. As curves (B), (C), and (D) of Fig. 5 show, the sample once molten does not exhibit any endotherm upon cooling or reheating even after annealing for prolonged time and only T_g at around 263°C remained observable. This behavior implies that the rate of crystallization might be extremely low or the as-polymerized sample might have only such loosely developed crystal structure that it is hard to reform. Similar phenomenon was observed in **O-4** having ΔH_m and ΔS_m values of 11 200 and 16 400 J mol^{-1} K^{-1}, respectively, at 410°C. Concerning **P-4**, one can easily expect that it would be crystalline due to its linearity or pyromellitimido unit. However, it did not show any endotherm up to 500°C. This fact implies that its melting temperature, if any, might be higher than 500°C or its degradation temperature.

It was surprising that **B-4** and **O-4** in their as-polymerized state have small, but distinctive crystallinity. As already pointed out, the present polyimides are comparable to ODA–polyimides, which have one additional phthalimido unit in their repeat unit. The phthalimide unit is rigid, but bent because it is 1,2,4-substituted. Its rigidity might make a positive, but its bent structure a negative contribution to crystal formation. Therefore, it can be deduced that in **B-4** and **O-4**, the rigidity effect of phthalimido unit is slightly more dominant than the bent structure effect. In addition, as already shown in Fig. 4, the non-symmetric diamine monomer leads to the internal copolymerization effect [15] upon polymerization in consecutive repeating units along the polymer chain. Therefore, the crystallizability of **O-4** and **B-4** poses a similar question from crystallization of random copolymers. Here, crystallinity may be brought about through lateral juxtaposition of parts of the chains having same sequence, which was proposed and experimentally evidenced by Windle et al. [19,20]. In this connection, the

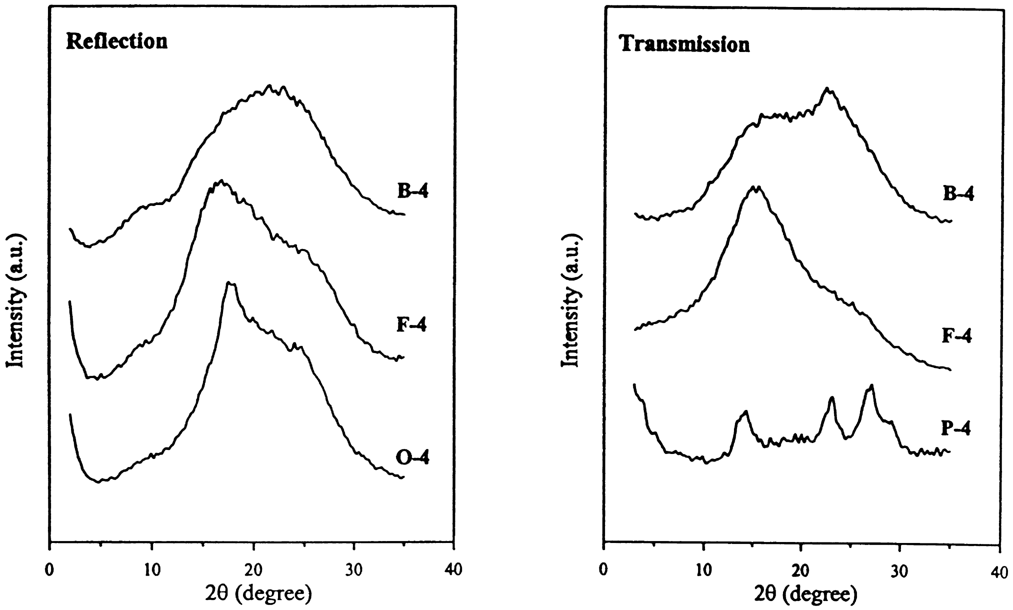


Fig. 6. Wide-angle X-ray diffractograms of polymers.

fact that they once molten did not slow any endothermic peaks upon reheating can be explainable by the view point that the probability of finding a given sequence of congruent units would strongly decrease once the polymers are molten.

3.6. Crystallinity

An attempt was made to estimate the crystallinity of the polymers by wide-angle X-ray measurements. All the measurements were made in $\theta/2\theta$ mode at room temperature. The 2θ scan data were collected at 0.05° interval and the scan speed was 1° (2θ)/min. For most polymers, the reflection patterns are featureless, showing only broad amorphous halos. However, **O-4** interestingly showed distinctive reflections indicative of low crystallinity as shown in Fig. 6, whereas analogous polymer derived from ODA is known to be completely amorphous.

For **B-4**, the reflection pattern exhibited only broad halo centered at around $2\theta = 21.6°$, consecutively showing no regularly ordered structure. But the transmission mode revealed a distinctive peak at $2\theta = 22.5°$ as well as an amorphous halo. This means that the rigid polymer chains in the film are packed more regularly in the horizontal direction of film than in thickness direction. Furthermore, this diffraction peak supports that the endothermic peak in the first heating scan could be a true melting process. Similar phenomenon was observed for **F-4**, although it did not show any endothermic peak in DSC.

For **P-4**, the diffraction pattern was obtained with powder sample in a transmission mode. It has multiple peaks at $2\theta = 14.1°$ (6.3 Å), 23.0° (3.9 Å) and 27.0° (3.3 Å), together with the shoulder peak adjacent to the 27° peak which was considered to be the overtone of the 14.1° peak. The high level of crystallinity associated with **P-4** may be attributable to the existence of the rigid, nearly planar 4-pyromellitimidophthalimide units in polymer backbone, leading to better packing of polymer chains. In the diffraction pattern, all the recorded peaks could be satisfactorily indexed by assuming an orthorhombic unit cell of dimension: $a = 6.3$ Å, $b = 3.9$ Å and $c = 22.6$ Å. The repeating unit length (22.6 Å) could be optimized by computer simulation. The density was calculated to be 1.60 g/ml that is usual in crystalline polyimides, and could be in good agreement with the measured value (1.50 g/ml) with only slight deviation caused by the calculation based on the perfect crystal. Therefore, the measure density supports that **P-4** has the proposed orthorhombic crystal structure.

4. Conclusions

A new diamine *N*-[4-(4-aminophenyloxy)phenyl]-4-aminophthalimide was prepared from raw materials comprising 4-aminophenol, 4-nitrofluorobenzene and 4-nitrophthalic anhydride and polymerized with six different aromatic tetracarboxylic dianhydrides to obtain high molecular weight polyimides. The polyimides prepared are structurally equivalent to 4,4′-oxydianiline (ODA)-based polyimides having one more phthalimido group incorporated in the repeat unit. All the polyimides except those derived from pyromellitic dianhydride (PDMA) and hexafluoroisopropylidene-4,4′-diphthalic anhydride (6FDA) were generally more soluble than ODA–polyimide in highly polar organic solvents and sulfuric acid. These enhanced solubilities were presumed to be ascribable to the presence of the additional bent phthalimido structures and random chain sequences comprising head-to-tail, head-to-head and tail-to-tail triads formed by internal copolymerization resulting from different reactivity of two non-symmetric amino groups. Insolubility of PMDA– and 6FDA–polyimide (**P-4** and **F-4**) might be explained by the very high rigidity and very strong dipolar interaction, respectively. Thermal stabilities of the polymers as judged from T_g and temperature at 5% degradation were distinctively higher than the ODA–polyimides perhaps due to increased chain rigidity exerted by phthalimido groups additionally incorporated. X-ray diffractograms showed that **P-4** is highly crystalline with orthorhombic structure and **O-4**, **F-4** and **B-4** only slightly crystalline. The high crystallinity of **P-4** is ascribable to its chain linearity and rigidity. The low crystallinity of **B-4**, **F-4** and **O-4** might result from lateral juxaposition of parts of the chains having same sequence. The low crystallinity of **B-4** and **O-4** could be detected by first scan of DSC, but it disappeared on rescans, presumably because their crystals are only loosely formed and/or their crystallization rates are extremely low.

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