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Synthesis and characterization of polyimides from 9,10-diphenoxy-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetra-carboxylic 2,3:6,7-dianhydride

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Summary

A new dianhydride containing phenoxy groups and alicyclic unit was prepared by a bis-Diels-Alder reaction of 1,4-diphenoxy-2,3,5,6-tetrakis(bromomethyl)benzene with maleic anhydride, and polymerized with various aromatic diamines in one step at high temperature in NMP. All the polymers had good solubility toward polar solvents and their inherent viscosities were in the range of 0.31~0.53dL/g. Polyimides properties were investigated and discussed in terms of the chain structures resulting from the incorporation of different diamines. All the polyimides were thermostable up to 475°C with 10% weight loss and in DSC thermograms the polymers exhibited T_gs between 249 and 317°C.

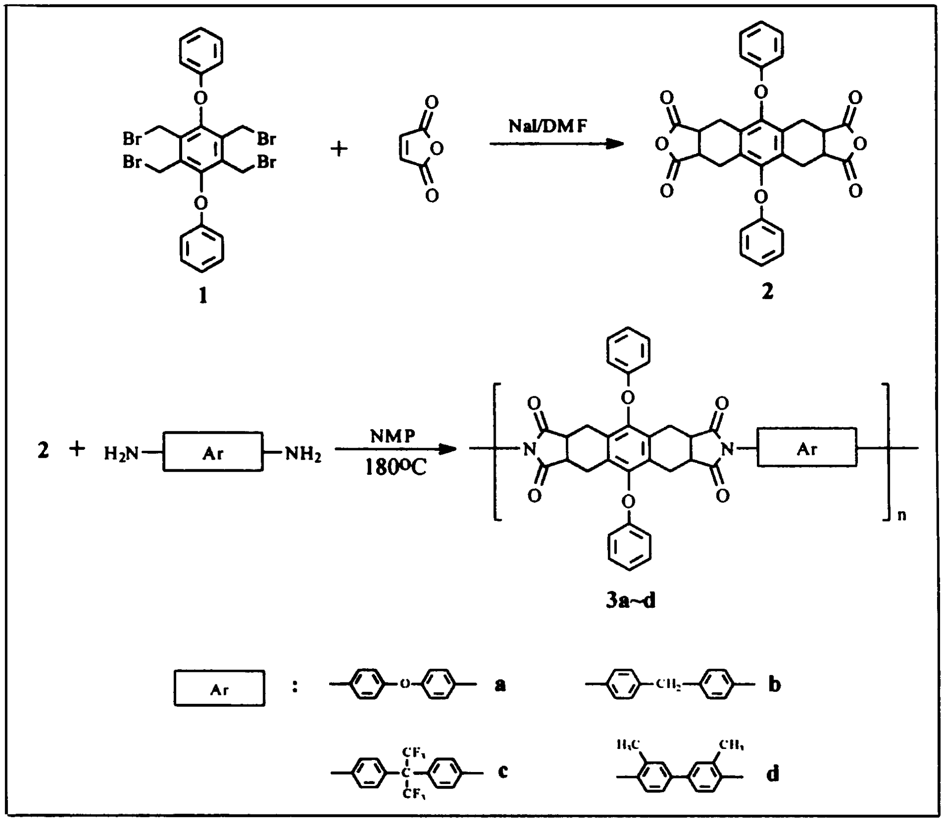
Introduction

The wide applications of aromatic polyimides in the electronics industry and others stem from their high thermal stability, chemical resistance and mechanical strength[1,2]. The rigid aromatic polyimides become improcessable and intractable after thermal curing (imidization) of the corresponding precursors and thus most polyimide fabrications such as coating and casting have to be conducted in precursor states, which is typical for these convertible polymers.

Overall, efforts directed toward producing novel aromatic polyimides have emphasized the modification of structural factors directly affecting molecular regularity, rigidity, and cohesive energy density. Thus chemical modifications have mainly focused on the synthesis of new monomers that provide less molecular order, improved torsional mobility, and lower intermolecular interaction. From the various alternatives aimed at obtaining these targets, some general approaches have been universally adopted: (a) the introduction of aliphatic segments, (b) use of enlarged monomers containing angular bonds, (c) use of *meta*-substituted instead of *para*-substituted phenyl monomers and, (d) copolymerization of two or more dianhydrides and diamines. On the other hand, another approach to attaining an enhanced solubility was utilization of alicyclic dianhydrides such as bis(succinic anhydride)[3] or (4*arH*,8*acH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethannonaphthalene-2*t*,3*t*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride

[4], though thermal stability was expected to be compromised. In addition, the attachment of bulky aromatic substituents has been used extensively to prepare soluble rigid-rod polyamides[5,6] and polyimides [7,8]. On the basis of these concepts, successful results can be attained by using these approaches or by combining several of them [9].

The present work is a continuation of our research on preparing soluble polyimides. In previous works[13], we described the synthesis of soluble polyimides by introducing alkyloxy side groups along the polymer backbone as well as alicyclic units. In this article we report the synthesis and characterization of new polyimides containing phenoxy groups and alicyclic linkage in the main chain. Properties such as spectral characteristics, solubilities, thermal stabilities, phase transitions and crystallinities were comparatively studied.



Scheme 1. Synthetic Route to Monomer and Polymers

Experimental

Materials

DMF and NMP were distilled over $MgSO_4$ and CaH_2, respectively. Durene, bromine, and other reagents were used as received. 4,4'-Methylenedianiline(MDA) and *o*-tolidine were recrystallized from water and ethanol, respectively. 4,4'-Oxydianiline(ODA), 4,4'-(hexafluoroisopropylidene)dianiline(6FDA) were purified by sublimation. Copper bronze was purified by the following procedure. Copper bronze(10g) was treated with 100ml of 2% solution of iodine in acetone for 10min. The resulting product was filtered off and washed with 50ml of conc. HCl and acetone solution. The residual copper bronze was filtered and washed with acetone, then dried in a vacuum desiccator. The 1,4-dibromodurene was prepared according to the reported procedure[10]. 1,4-Dibromodurene: m.p.:199~200°C; FT-IR (KBr, cm^{-1}): 2920 (C-H stretch in $-CH_3$), 1411 and 1480 ($-CH_3$), 698 (Ar-Br); ^{1}H-NMR ($CDCl_3$, ppm): δ=2.46 (s, 12H); ^{13}C-NMR ($CDCl_3$, ppm): δ=22.7, 128.5 and 135.4.

Measurements

Melting points were measured using an IA 9100 Digital melting point apparatus without correction. Elemental analyses were performed on a Vario EL (Elementar) microanalyzer. The FT-IR spectra of synthesized compounds were recorded on a Mattson Infinity Gold series FT-IR spectrophotometer. ^{1}H-, ^{13}C-NMR spectra were obtained from a 300 MHz Bruker AM 300 spectroscope. 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 NMP. Wide angle X-ray diffractograms were taken in transmission mode using Ni-filtered CuKα radiation on an X-ray diffractometer consisting of an 18kW rotating anode X-ray generator operated at 50kV x 20mA (Rigaku Co.).

1,4-diphenoxy-2,3,5,6-tetramethylbenzene

The synthesis of 1,4-diphenoxy-2,3,5,6-tetramethylbenzene appears in the literature[10,11] and is presented in detail here. A 250ml three necked round bottom flask fitted with a condenser, nitrogen inlet tube, and magnetic stirrer was charged with 7g(0.024mol) of dibromodurene, 20g of phenol, 9.16g(0.05mol) of potassium carbonate, and 4.8g of copper bronze. The mixture was heated on an oil bath for 12 hours at 160°C. The hot maroon mixture was carefully poured into 200ml of an aqueous sodium hydroxide (20g) solution. Filtration provided a tan product mixed with copper. Recrystallization from ethanol produced cream-colored crystals.
Yield: 38%; m.p.: 180-181 °C; FT-IR (KBr, cm^{-1}): 2917 (C-H stretch in $-CH_3$), 1222 (aryl-aryl ether); ^{1}H-NMR ($CDCl_3$, ppm) : δ=2.07 (s, 12H), 6.79 (d, 4H, *J*=9Hz), 6.98 (t, 2H, *J*=9Hz) and 7.28 (t, 4H, J=9Hz); ^{13}C-NMR ($CDCl_3$, ppm): δ=13.4, 115.1, 121.6, 129.2, 130.1, 148.2 and 158.7.

*1,4-diphenoxy-2,3,5,6-tetrakis(bromomethyl)benzene(***1***)*

130ml of carbon tetrachloride, 26.13g(146.8mmol) of *N*-bromosuccinimide, 22.6mmol of 1,4-diphenoxy-2,3,5,6-tetramethylbenzene and a spatula tip of benzoyl peroxide(BPO) were placed in a 500ml three necked round bottom flask equipped with a N_2 inlet and magnetic stirrer. After refluxing under nitrogen atmosphere for 8 hours, the succinimide by-product was removed by hot filtration and the carbon tetrachloride was evaporated. The product was recrystallized from an EA/MeOH mixture to give fine crystals.

Yield: 75%, m.p.: 198.5~199.5°C; FT-IR(KBr, cm^{-1}): 3038 (C-H stretch in $-CH_3$), 1591 (aromatic), 1197 (aryl-aryl ether) 527,589 (C-Br); ^{1}H-NMR ($CDCl_3$, ppm): δ=4.57 (s, 8H), 6.89 (d, 4H, *J*=9Hz), 7.10 (t, 2H, *J*=9Hz) and 7.34 (t, 4H, *J*=9Hz); ^{13}C-NMR ($CDCl_3$, ppm): δ=22.6, 115.7, 123.5, 130.5, 134.3, 149.5 and 157.9.

*9,10-diphenoxy-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-dianhydride(**2**)*

11.17g(17.62mmol) of 1,4-diphenoxy-2,3,5,6-tetrakis(bromomethyl)benzene(**1**), 6.04g(61.59mmol) of maleic anhydride and 26.41g(176.2mmol) of dried sodium iodide were placed in a 250ml round bottom flask filled with 70ml of freshly distilled DMF. The mixture was heated up to 85°C in a nitrogen flow for 36 hours. After cooling to room temperature, the reaction mixture was poured into 10% aqueous sodium bisulfite solution, and filtered off the precipitate. The crude product obtained was washed thoroughly twice with a 100ml of distilled water and then dried in a vacuum. Product was obtained by suction filtration followed by washing with diethyl ether and recrystallization from acetic anhydride to produce crystals.

Yield: 35%, m.p.: 338.6°C (measured by DSC); FT-IR (KBr, cm^{-1}): 1843 and 1777 (C=O stretch in cyclic anhydride), 1210 (aryl-aryl ether); ^{1}H-NMR ($C_2D_2Cl_4$, ppm): δ=2.63 (d, 4H, $J_{geminal}$=15Hz), 3.26 (d, 4H, $J_{geminal}$=15Hz), 3.47 (broad s, 4H), 6.69 (d, 4H, *J*=9Hz), 7.07 (t, 2H, *J*=9Hz) and 7.32 (t, 4H, *J*=9Hz); ^{13}C-NMR ($C_2D_2Cl_4$, ppm): δ=22.8, 39.6, 114.6, 122.4, 128.6, 129.9, 145.8, 157.9 and 172.8

Polymerization

A typical polymerization procedure is as follows. To a solution of 2mmol of diamine in freshly distilled NMP, equimolar dianhydride was added at room temperature under argon atmosphere with the 10% solid content (w/v). The reaction mixture was heated at 70~80°C over 2hours and kept at that temperature another for 2hours. Then the solution temperature was slowly raised to 180°C and kept there for an additional 12 hours. Polymerization was performed under a gentle argon stream to remove the water produced during imidization. The resulting solution was poured into the excess methanol and filtered. The precipitated polymers were washed several times with boiling methanol, and then dried at 100°C for 12hrs *in vacuo*.

3a) FT-IR (KBr, cm^{-1}): 1780 and 1711 (C=O, imide I), 1386 (C-N-C, imide II), 1596 (aromatic), 1165 (C-O-C); Elemental analysis for $(C_{42}H_{30}N_2O_7)_n$ Calc. C 74.76 H 4.48 N 4.15 Found C 74.69 H 4.44 N 4.33

3b) FT-IR (KBr, cm^{-1}): 1781 and 1714 (C=O, imide I), 1380 (C-N-C, imide II), 1596 (aromatic), 1168 (C-O-C); Elemental analysis for $(C_{43}H_{32}N_2O_6)_n$ Calc. C 76.77 H 4.79 N 4.15 Found C 75.71 H 4.64 N 4.02

3c) FT-IR (KBr, cm^{-1}): 1790 and 1717 (C=O, imide I), 1379 (C-N-C, imide II), 1597 (aromatic), 1172 (C-O-C); Elemental analysis for $(C_{45}H_{30}N_2O_6F_6)_n$ Calc. C 66.83 H 3.73 N 3.46 Found C 66.35 H 3.55 N 3.50

3d) FT-IR (KBr, cm^{-1}): 1781 and 1715 (C=O, imide I), 1379 (C-N-C, imide II), 1597 (aromatic), 1177 (C-O-C); Elemental analysis for $(C_{44}H_{34}N_2O_6)_n$ Calc. C 76.95 H 4.99 N 4.07 Found C 76.25 H 4.87 N 3.96

Results and discusstion

Monomer Synthesis

Monomeric dianhydride was prepared by the bis-Diels-Alder reaction from maleic anhydride and 1,4-diphenyloxy-2,3,5,6-tetrakis(bromomethyl)benzene, as shown in Scheme 1, which had been synthesized from durene as a starting material *via* consecutive bromination, coupling with phenol by Ullmann ether synthesis in the presence of activated copper and side chain bromination using NBS. In each step, synthesized compounds were separated, purified and identified by spectroscopic means. 1,4-Dibromodurene was synthesized in CH_2Cl_2 at reflux temperature, with a 92% yield, and a melt temperature of 199~200°C[10]. An Ullmann reaction was carried out in a phenol as a solvent at 160°C using activated copper. It was important that the activated copper bronze was used immediately after preparation or no product would be obtained by the Ullmann reaction. The spectroscopic information such as the FT-IR and NMR were in excellent agreement with those of established literature[11]. Bis-Diels-Alder addition was employed to build the desired framework from tetrabenzyl bromide with maleic anhydride as a dienophile in freshly distilled DMF[12]. After the reaction, the reaction mixture was poured into a 10% aqueous sodium bisulfite solution to decolorize, and the crude diadduct was filtered and recrystallized in acetic anhydride. The yield of the crude product was over 40% and the final product was further purified by recrystallization to give a polymerizable monomer with a yield of 35%. The structure of this monomer was characterized by the spectroscopic analysis. In the FT-IR spectrum, the monomer showed C=O stretching bands at 1843 and 1777cm^{-1}, characteristic of cyclic dianhydride. In the ^{1}H-NMR spectrum, the structure of the monomer was confirmed by aromatic region of 6.69, 7.07, 7.32 ppm and aliphatic region of 2.63 and 3.26 ppm splited with 15Hz of geminal coupling constant.

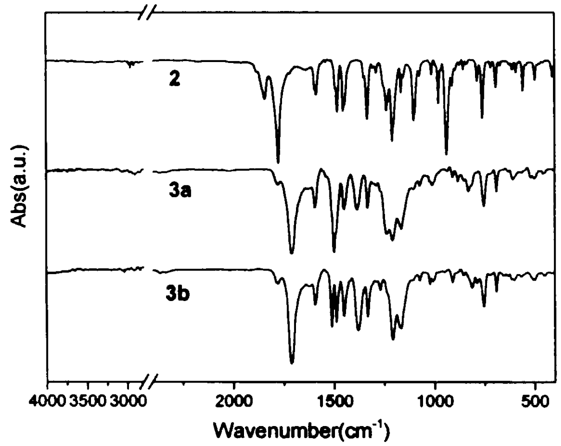


Figure 1. FT-IR Spectra of monomer(**2**) and polyimides(**3a**,**3b**)

Polymerization and characterization

Polyimidizations were carried out in one step, and the synthetic route of the polyimides from the anhydride(**2**) with various aromatic diamines being illustrated in Scheme 1. All the reactions proceeded homogeneously without gelation or precipitation of the resultant polymers. The resultant viscous polyimide solution was diluted with 3ml of NMP and poured into methanol while the stirring vigorous. The polyimides obtained were characterized by FT-IR spectroscopy and elemental analysis. In FT-IR spectra measured in transmission mode, three characteristic peaks of imide (C=O; imide I and C-N-C ; imide II), but no amine and acid peaks confirmed complete imidization (Figure 1). The elemental analysis values confirm to chemical structures of polymers.

Solution properties

To obtain first-hand information of molecular weight of the polymers obtained, their inherent viscosities were measured in NMP and summarized in Table 1. It shows that the viscosities lie in the 0.31~0.53 dL/g range, indicating that the polymers have medium to reasonable high molecular weights. The solubilities of polyimides toward various kinds of organic solvents were tested qualitatively. All the polymers prepared have excellent solubility toward polar solvents such as NMP and *m*-cresol.

Table 1. Inherent Viscosities and Solubilities

Polymer code	η_{inh}(dL/g)$^{(a)}$	Solubility$^{(b)}$				
		$CHCl_3$	DMAc	NMP	*m*-cresol	H_2SO_4
3a	0.34	-	+	++	++	++
3b	0.40	-	+	++	++	++
3c	0.31	-	+	++	++	++
3d	0.53	-	+	+	+	++

(a) Inherent viscosities were measured in 0.2g/dL in NMP at 25℃

(b) – Insoluble, + slightly soluble at r.t., ++ soluble at r.t.

This may be due to the amorphous nature of these polymers, as evidenced by X-ray diffractograms discussed later. The solubility behavior of the new polyimides derived from the dianhydride(**2**) and aromatic diamines was compared with that of polyimides based on 3,6-diphenoxypyromellitic dianhydride[11] without alicyclic unit; it was found that the solubility of the new polyimides was significantly enhanced by the

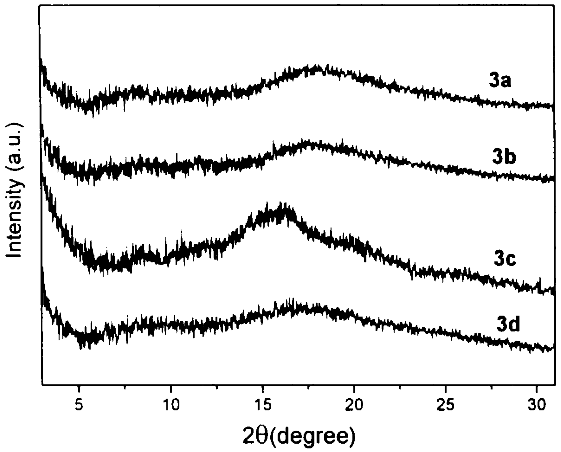


Figure 2. X-ray Diffractograms of polyimides

introduction of alicyclic unit into the polymer backbone as well as bulky phenoxy groups.

The crystallinity of the prepared polyimides was measured by wide-angle X-ray diffraction scans (Figure 2). These diagrams revealed that polyimides containing phenoxy groups and alicyclic units were amorphous(**3a**,**3b**,**3d**) or semi-crystalline(**3c**). This is reasonable because the presence of bulky phenoxy groups and flexible alicyclic units induce looser chain packing and revealed a large decrease in crystallinity. Thus, the amorphous structure or low crystallinity of these polymers was reflected in their good solubility.

Table 2. Thermal properties of polyimides

Polymer code	T_g(℃)$^{(a)}$	Thermal stability in N_2				
		T_o(℃)$^{(b)}$	T_{10}(℃)$^{(c)}$	T_{d1}(℃)$^{(d)}$	T_{d2}(℃)$^{(e)}$	R_{900}(%)$^{(f)}$
3a	284	471	495	498	661	51.4
3b	249	454	475	503	626	47.9
3c	266	457	481	463	661	42.3
3d	317	474	497	497	645	57.5

(a) Determined by 2nd heating at the rate of 20℃/min in a N_2 atmosphere

(b) Onset Temperature of degradation (c) Temperature at 10% weight loss

(d), (e) 1st, 2nd Max. decomposition temperature (f) Residue at 900℃

Thermal behaviors of the polymers were evaluated by DSC and TGA. As a representative example, the TGA and DSC curve of the polyimide(**3b**) obtained from the dianhydride(**2**) and MDA are shown in Figure 3, and thermal behavior data of the polymers are summarized in Table 2. The T_gs of amorphous and semi-crystalline polyimides were observed in the range of 251~316°C, depending on the structure of diamine component and decreased with the decreasing of rigidity of the polymer backbone. In addition, **3d** had higher T_g than the others by about 50°C. This phenomenon can be attributed to the more rigid structure of counter diamine, *o*-tolidine.

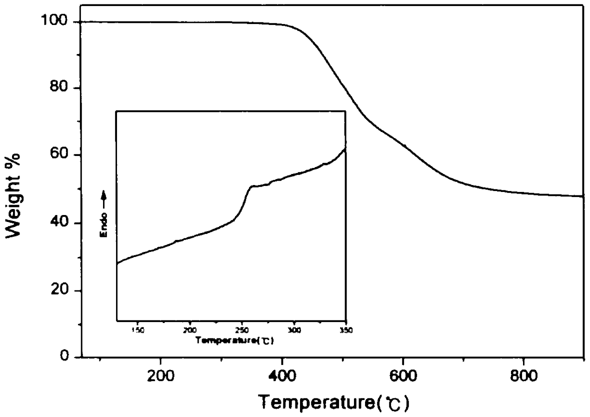


Figure 3. TGA and DSC curve of polyimide(**3b**)

All the polyimides showed similar patterns in the TGA pyrograms. Due to the incorporation of thermally labile phenoxy groups, all the polyimides prepared showed two-step weight loss behavior.

The prepared polyimides were thermally stable up to about 475°C according to T_{10}, and drastic degradation(T_{d1}) occurred in the range of 463~503°C, which was followed by the second slight degradation(T_{d2}) above 600°C. The first maximum degradation might be originated from the split of phenoxy groups, which was confirmed by theoretical calculation of weight loss at that temperature. That is, the theoretical values well coincided with experimental value within ±2% error bound. The amount of carbonized residue(R_{900}) of these polymers in a nitrogen atmosphere was in the range of 41.3~57.5 weight% even at 900°C, showing intrinsically high fire-retardant characteristics.

Overall, their thermal stabilities were improved by the introduction of alicyclic unit and the bulky phenoxy pendent groups compared to those of polyimides[13] having alicyclic units and thermally fragile alkoxy side groups. In addition, good solubilities of polyimides were maintained regardless of different kinds of side groups, alkoxy and phenoxy one. This means the alicyclic units in the main chain can play an important role in increasing the solubility of polyimides

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