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

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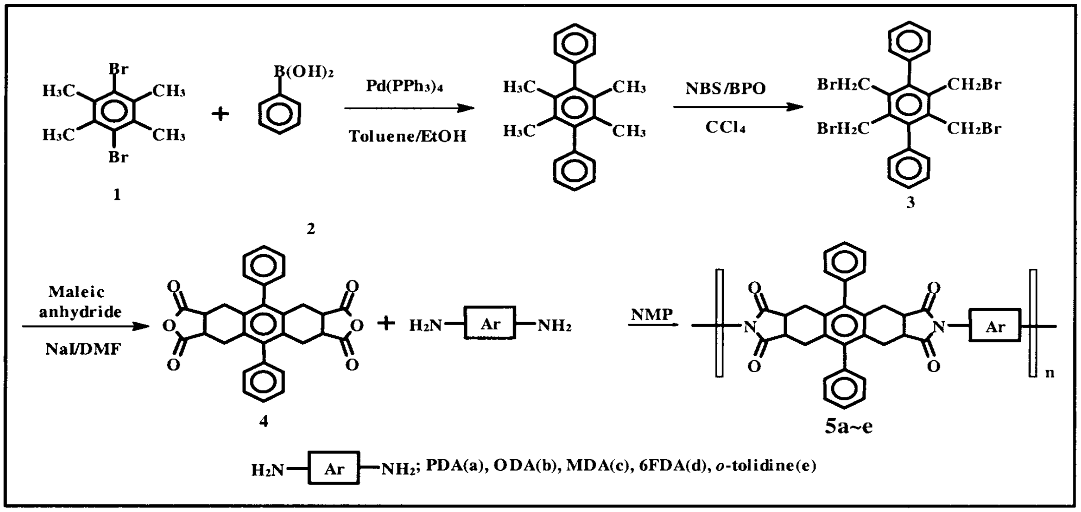
Summary

A new dianhydride containing pendent phenyl group and alicyclic unit was prepared by a bis-Diels-Alder reaction of 1,4-diphenyl-2,3,5,6-tetrakis(bromomethyl)benzene with maleic anhydride, and polymerized with various aromatic diamines in one step at high temperature in NMP. Polymers were soluble in NMP and their inherent viscosities were in the 0.29~0.47 dL/g range. Polyimides properties were investigated and discussed in terms of the chain structure resulting from the incorporation of different diamines.

Introduction

Aromatic polyimides are an important class of polymeric materials exhibiting not only excellent high-temperature stability but also electrical and mechanical properties [1,2]. Most of these materials, however, cannot be molded as polyimides but first be prepared as a soluble precursor poly(amic acid) and then processed into final form by thermal or chemical methods. Much effort, therefore, has been spent on synthesizing tractable, processable polyimides that reasonably maintain the desired properties. One of the more successful attempts to accomplish this goal is to incorporate aryl substituents. It is generally accepted that aryl substituents have a tendency to maintain good thermal properties. Especially, Harris et al. [3, 4] described the synthesis and properties of polyimides based on 3,6-diphenylpyromellitic dianhydride. Another approach is the use of alicyclic dianhydrides [5-12]. Recently, we have synthesized soluble polyimides using dianhydrides containing alicyclic structure and alkyloxy pendent groups [13]. Although the solubility of polyimides containing alkyoxy groups greatly was enhanced, the high temperature stability was sacrificed due to the presence of thermally fragile alkyloxy groups. In respect of these results, we design a novel dianhydride containing phenyl group as well as alicyclic unit. Therefore, we report here the synthesis of new polyimides derived from 9,10-diphenyl-

1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-dianhydride and investigation of resulting polyimides properties, such as thermal stability, solubility and structure.



Scheme 1. Synthetic route to monomer and polyimides

Experimental Part

Materials and Measurement

Dimethyl sulfoxide(DMSO) was used after drying over 4°C molecular sieves. DMF and NMP were distilled over MgSO4 and CaH2, respectively. Durene, bromine, and other reagents were used as received. 4,4'-Oxydianiline(ODA), 4,4'-(hexafluoroisopropylidene)dianiline(6FDA) were purified by sublimation. 4,4'-Methylenedianiline(MDA) and o-tolidine were recrystallized from water and ethanol, respectively. 1,4-Dibromodurene (1) was prepared according to the reported procedure [14]. Melting points were measured using IA 9100 Digital melting point apparatus without correction. Elemental analyses were performed on a Vario EL (Elementar) microanalyzer. FT-IR spectra of synthesized compounds were recorded on Mattson Infinity Gold series FT-IR spectrophotometer. 1H-, 13C-NMR and Heteronuclear Correlation (HETCOR) spectrum 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 N2. 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.)

Synthesis of monomer

1,4-diphenyl-2,3,5,6-tertamethylbenzene (**2**)

Under nitrogen flow, a 250ml 3-neck flask was charged with 11.68g (40mmol) of dibromodurene, 120ml of toluene, 2.77g (6mol %) of Pd(PPh3)4, and 50ml of 2M aq. Na2CO3 solution. After addition of 10.97 g (89.96mmol) of phenylboronic acid in 20 ml of ethanol, the reaction mixture was refluxed for 24h. After cooling to room temperature, 5ml of 30 % H2O2 was carefully added and the mixture stirred for an additional hour. The organic layer was separated, the aqueous layer extracted twice with ether and the combined organic phases were dried with magnesium sulfate. After evaporation of the solvents, product was obtained by recrystallization in ethyl acetate. Yield: 68.7%; m.p.: 223~225°C .

IR (KBr):1952, 1882, 1816, 1765(all weak, terphenyl), 1598(s, aromatic), 965, 705cm-1(vs, para-disub.); 1H NMR (CDCl3): δ=1.95 (s, 12H), 7.20 (d, 4H), 7.36 (t, 2H), 7.43 (t, 4H); 13C NMR (CDCl3,): δ=19.6, 127.8, 129.8, 131.0, 133.4, 142.7, 144.3

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

In a 500ml 3-neck round bottom flask equipped with a N_2 inlet and magnetic stirrer were placed 130ml of carbontetrachloride, 26.13g (146.8mmol) of *N*-bromosuccinimide, 22.6mmol of 1,4-diphenyl-2,3,5,6-tetramethylbenzene (2) and added spatula tip of benzoyl peroxide(BPO). After refluxing under nitrogen atmosphere for 8h, succinimide by-produced was removed by hot filtration and carbon tetrachloride was evaporated. The product was recrystallized from EA/MeOH mixture to give fine crystals. Yield: 75%; m.p.: >300°C

IR (KBr); 3038(weak, $-CH_2-$), 1950, 1820 (all weak, terphenyl), 1591 645, 518cm^{-1}(m, C-Br); ^{1}H NMR ($C_2D_2Cl_4$): δ=4.57 (s, 8H), 6.89 (d, 4H, *J*=9Hz), 7.10 (t, 2H, *J*=9Hz), 7.34 (t, 4H, *J*=9Hz)

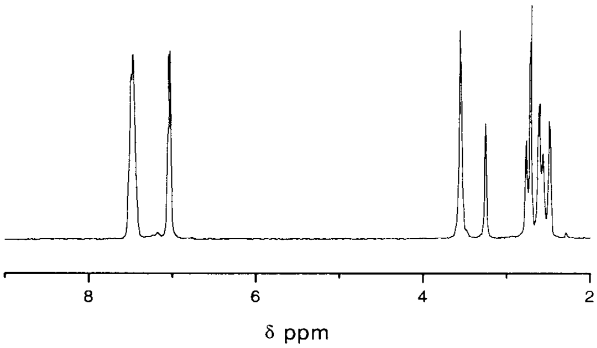


Figure 1. ^{1}H NMR spectrum of 4

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

11.17g (17.62mmol) of 1,4-diphenyl-2,3,5,6-tetrakis(bromomethyl)benzene (**3**), 6.04g (61.59mmol) of maleic anhydride and 26.41g (176.2mmol) of dried sodium iodide were placed in 250ml of round bottom flask filled with 70ml of freshly distilled DMF. The mixture was heated up to 85°C in a nitrogen flow for 36h. After cooling to room temperature, reaction mixture was poured into 10% of aqueous sodium bisulfite solution, and filtered off the precipitate. Crude product obtained was washed well with two portion of 100ml of distilled water and dried in vacuum.

Product was obtained by suction filtration followed by washing with diethyl ether and recrystallization from acetic anhydride to give crystals.

Yield: 35%; m.p.: >350°C ; IR(KBr): 1839(s, C=O), 1777 cm^{-1} (vs, cyclic anhydride; ^{1}H NMR (DMSO-d_6 at 120°C) : δ=2.59 (d, 4H, $J_{geminal}$=15Hz), 2.77 (d, 4H, $J_{geminal}$=15Hz), 3.56 (broad s, 4H), 7.03(d, 4H), 7.44~7.52(m, 6H); ^{13}C NMR (DMSO-d_6 at 120°C): δ=32.4, 46.4, 133.2, 134.0, 135.4, 137.9, 143.8, 145.0, 179.7

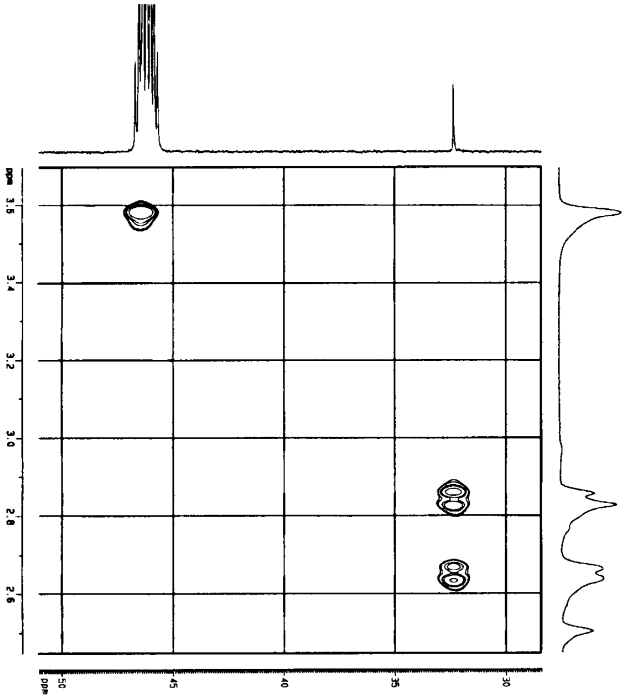


Figure 2. HETCOR NMR spectrum of **4** (DMSO-d_6, at 120°C)

Synthesis of polymers

The synthesis of polyimides is given below as a general procedure. To a 50ml round bottom flask was added 4,4'-methylenedianiline (0.124g, 0.627mmol) and 9,10-dipheny-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetrtracarboxylic 2,3:6,7-dianhydride (**4**) (0.3g, 0.627mmol), and 3.8ml of distilled NMP. The flask was purged with argon and the solution was stirred for 2h under an argon atmosphere at room temperature. The reaction system was heated to 180°C for 12h. The reaction mixture was cooled and precipitated into a large excess of methanol. The precipitated polymers were separated by filtration and washed several times with boiling methanol and then dried at 160°C for 12h in vacuo.

5a: Yield: 97%; IR (KBr): 1780 and 1711 (C=O, imide), 1386 cm^{-1} (C-N-C) $(C_{36}H_{26}N_2O_4)_n$ $(550.6)_n$:Calcd. C 78.52, H 4.75, N 5.08; Found C 77.69, H 4.84, N 4.94.

5b: Yield: 99%; IR (KBr): 1776 and 1710 (C=O, imide), 1377 cm^{-1} (C-N-C) $(C_{42}H_{30}N_2O_5)_n$ $(642.7)_n$:Calcd. C 78.48, H 4.70, N 4.35;Found C 78.02, H 4.64, N 4.33.

5c: Yield: 98%; IR (KBr): 1778 and 1710 (C=O, imide), 1380 cm^{-1} (C-N-C) $(C_{43}H_{32}N_2O_4)_n$ $(640.7)_n$:Calcd. C 80.60, H 5.03, N 4.37; Found C 79.71, H 4.94, N 4.42.

5d: Yield: 94%; IR (KBr): 1781 and 1712 (C=O, imide), 1380 cm^{-1} (C-N-C) $(C_{45}H_{30}N_2O_4F_6)_n$ $(776.7)_n$:Calcd. C 69.58, H 3.89, N 3.60;Found C 69.35, H 3.95, N 3.31.

5e: Yield: 95%; IR (KBr): 1778 and 1710 (C=O, imide), 1385 cm^{-1} (C-N-C) $(C_{44}H_{34}N_2O_4)_n$ $(654.8)_n$:Calcd. C 80.71, H 5.23, N 4.27; Found C 79.35, H 4.97, N 3.96.

Results and Discussion

Synthesis

Monomeric dianhydride **4** was prepared via several steps. 1,4-Diphenyl-2,3,5,6-tetramethylbenzene **2** was prepared by Suzuki-Miyaura coupling using $Pd(PPh_3)_4$ as a catalyst under a nitrogen atmosphere. The product was purified by recrystallization from ethyl acetate. The IR spectrum of compound **2** showed the C-H stretching band at around $3000cm^{-1}$, and characteristic peaks were ranged from 1800 to $2000cm^{-1}$ due to the terphenyl unit. Side chain bromination was carried out in CCl_4 using NBS/BPO system. During the reaction, the color of reaction mixture turned into white meaning that the NBS involved was almost consumed. DMSO-$_{d6}$ dissolved the compound **3**, but in DMSO compound **3** was decomposed slowly to corresponding aldehyde [15, 16]. The ^{1}H NMR spectrum was taken in $C_2D_2Cl_4$.

Dianhydride **4** was synthesized from compound **3** with maleic anhydride by bis-Diels-Alder reaction in freshly distilled DMF under NaI as in situ generator of diene. The final monomer was purified in acetic anhydride under N_2 atmosphere and confirmed by spectroscopic analysis. IR spectrum of compound **4** showed the typical bands of cyclic anhydride at 1839 and $1777cm^{-1}$. NMR spectrum of compound 4 was interpreted easily by aid of HETCOR spectrum. The peak at 32.4 ppm is correlated with two protons at 2.59 and 2.77 ppm in which they were splited by geminal proton ($J_{geminal}$=15Hz) and their integration corresponds to 8 protons. The peak at 46.4 ppm correlates with the broad singlet at 3.56 ppm representing 4 protons. On the basis upon their HETCOR NMR spectrum, monomer **4** is thought to have bis-endo configuration [20].

The polyimides having alicyclic unit and pendent phenyl group were synthesized through one-step polyimidization as shown in Scheme 2. Polyimides derived from ODA, MDA and 6FDA were homogenous through the reaction, but polymer solutions from PDA and *o*-tolidine showed turbidity during polyimidization. The powdery polyimides were characterized by IR spectroscopy and elemental analysis. Though the polyimides **5a** and **5e** were precipitated during polyimidization reaction, IR spectra showed no trace of amine and acid peaks indicating the polyimides were fully imidized. The others also confirmed by the peaks at around 1780 and 1710cm^{-1} ascribed to the stretching of carbonyl group and C-N-C stretching at 1380cm^{-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 structure.

Table 1. Solution properties of polyimides.

Polymer Code	η_{inh} (dL/g)$^{(a)}$	Solubility$^{(b)}$				
		$CHCl_3$	DMAc	NMP	*m*-cresol	H_2SO_4
5a	0.32	-	+	+	+	++
5b	0.42	-	+	++	+	++
5c	0.47	-	+	++	+	++
5d	0.36	-	+	++	+	++
5e	0.29	-	+	+	+	++

(a)**5b~d**: 0.2g/dL in NMP at 25°C , **5a** and **5b** in conc. H_2SO_4 at 25°C

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

Properties of polyimides

Table 1 presents the solution behavior of polyimides prepared. The polyimides **5b**, **5c** and **5d** were readily soluble in NMP and concentrated H_2SO_4. They also slightly dissolved upon heating in *m*-cresol and DMF, while they were insoluble in chloroform. In contrast, the polyimides **5a**, **5e** derived from more rigid diamines dissolved at ambient temperature only in concentrated H_2SO_4. The good solubilities to the NMP were maintained regardless of different kinds of pendent groups, phenyl or phenoxy or alkyloxy[13]. This means that the alicyclic moiety in the main chain is a potent influence on the solubility of polyimide. The Inherent viscosity (η_{inh}) values of **5b**, **5c** and **5d** lie in the range of 0.36~0.47dL/g as listed in Table 1. As expected , **5d** showed lowest inherent viscosity value because 6FDA is generally less reactive towards anhydrides due to the presence of electron-withdrawing hexafluoroisopropylidene moiety. Since **5a** and **5e** were partially soluble in NMP, their η_{inh} were determined in concentrated H_2SO_4 with 0.32 and 0.29dL/g, respectively.

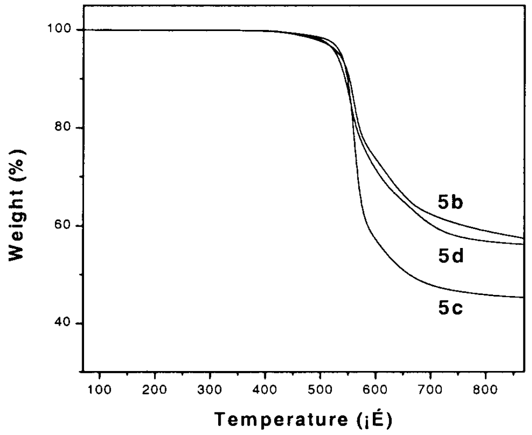


Figure 2. TGA pyrograms of **5b**, **5c** and **5d**

The thermal stability of polymers was measured by TGA and their results are depicted in Table 2. Thermal analysis revealed that the polyimides were highly thermostable and that the onset temperatures of decomposition all lie above 532°C in spite of the presence of alicyclic units in the polymer backbone. When the calculated wt.-% of phenyl group is compared with the corresponding ones at T_{d1} and T_{d2} in experimental data, which showed no significant correlation with each other. From these facts, it could be deduced that thermal bond scissions occurred regardless of pendent group or main chain. The overall weight losses in nitrogen up to 900°C are in the range of 37.9~54.9%. As expected, **5e** revealed highest char yield.

Table 2. Thermal stabilities of polyimides.

Polymer Code	T_g(°C)$^{(a)}$	Thermal stability in $N_2$$^{(b)}$				
		T_o(°C)	T_{10}(°C)	T_{d1}(°C)	T_{d2}(°C)	R_{900}(%)
5a	-	546	557	572	657	48.9
5b	350	543	557	566	617	57.0
5c	342	550	556	567	620	45.1
5d	324	532	548	560	640	56.0
5e	-	542	566	579	650	62.1

(a)Determined by 2nd heating at the rate of 20°C /min. in a N_2 atmosphere (b) T_o :Onset temp. of degradation; T_o :Temp. at 10% weight loss; T_{d1}:1st Max. decomposition temp.; T_{d2} :2nd Max.decomposition temp. ; R_{900}:Residue at 900°C

Phase transitions of polymers were evaluated by DSC, and listed in Table 2. Glass transition temperatures(T_gs) were obtained from second heating scans of as-polymerized **5a~e** samples at 20°C /min. of heating rate. Polyimide **5d** has the lowest T_g at 324°C , and followed by **5c** and **5b** at 342 and 350°C , respectively. The T_gs of **5a** and **5e** could not be detected and no additional endothermic transitions up to 400°C . This fact implies that their melting

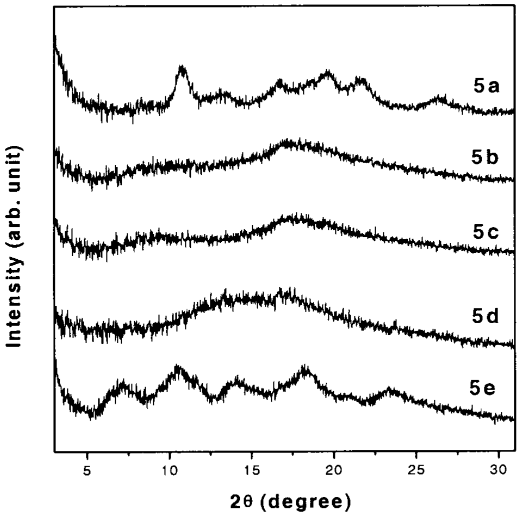


Figure 4. X-ray diffractograms of polyimides

temperatures might be higher than 400°C or their degradation temperatures, although their semi-crystalline nature were confirmed by X-ray diffraction experiment. In comparison with our previous results[13] of polyimides containing phenoxy group as pendent, the T_0s were greatly increased by about 100°C due to the thermally stable phenyl groups, and also the T_gs of the polyimides were about 70°C greater than the polyimides based on phenoxy pendent group.

Figure 4 presents the wide-angle X-ray diffractograms of the powdery polyimide samples. For **5b**, **5c** and **5d,** the reflection pattern exhibited only broad halo centered at around 2θ=18.2°, consecutively showing no regularly ordered structure. This is mainly because of interference of chain packing by pendent phenyl groups and presence of kink moiety in counter diamines. Moreover, the amorphous character of **5b~d** is in agreement with their enhanced solubility. For the polyimides **5a** and **5e** from more rigid diamines, several strong reflections around 2θ=10.8, 13.2, 16.7, 19.6 21.6 and 26.3° for **5a** and 2θ=7.2, 10.7, 14.1, 18.3, 23.4° for **5e** were measured. The high level of crystallinity associate with **5a** and **5e** may attributable to the existence of the rigid and coplanar moiety in polyimide backbone, leading to better packing of polymer chain. But, because this preliminary result is not enough to interpret the exact structure, a more detailed study of the chain packing is necessary.

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