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Synthesis and properties of novel organosoluble polyimides derived from 1,4-bis[4-(3,4-dicarboxylphenoxy)]triptycene dianhydride and various aromatic diamines

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Abstract

A novel triptycene-based dianhydride, 1,4-bis[4-(3,4-dicarboxylphenoxy)]triptycene dianhydride, was prepared from 4-nitro-*N*-methylphthalimide and potassium phenolate of 1,4-dihydroxytriptycene (**1**). The aromatic nucleophilic substitution reaction between 4-nitro-*N*-methylphthalimide and **1** afforded triptycene-based bis(*N*-methylphthalimide) (**2**), which hydrolyzed and subsequently dehydrated to give the corresponding dianhydride (**3**). A series of new polyimides containing triptycene moieties were prepared from the dianhydride monomer (**3**) and various diamines in *m*-cresol via conventional one-step polycondensation method. Most of the resulting polyimides were soluble in common organic solvents, such as chloroform, THF, DMAc and DMSO. The polyimides exhibited excellent thermal and thermo-oxidative stabilities with the onset decomposition temperature and 10% weight loss temperature ranging from 448 to 486 °C and 526 to 565 °C in nitrogen atmosphere, respectively. The glass transition temperatures of the polyimides were in the range of 221–296 °C. The polyimide films were found to be transparent, flexible, and tough. The films had tensile strengths, elongations at break, and tensile moduli in the ranges 95–118 MPa, 5.3–16.2%, and 1.03–1.38 GPa, respectively. Wide-angle X-ray diffraction measurements revealed that these polyimides were amorphous.

Keywords: Polyimides; Triptycene; Solubility

1. Introduction

Aromatic polyimides are a class of high-performance polymers that have unique high temperature stability, excellent mechanical and electrical properties as well as excellent chemical resistance. Their applications range from electronics, separation membranes, and coatings to foams and fibers [1,2]. However, most of wholly aromatic polyimides have high melting or softening temperatures (T_ss) and are insoluble in most organic solvents because of the rigidity of the backbone and strong interchain interactions. These properties make them generally intractable or difficult to process, thus limiting their applications. Therefore, incorporating new functionalities to make polyimides more tractable without deteriorating their own excellent properties has become one important target of polyimides' chemistry [3–6]. It has been generally recognized that flexible linkages [7,8] or the bulky lateral groups [9–11] impart better solubility and melt-processing characteristics compared with polymers without these linkages. However, the decrease in mechanical properties on heating is almost always a consequence of the reduced chain stiffness or T_g. However, the attachment of bulky pendant phenyl groups can impart an increase in T_g by restricting the segmental mobility, while providing an enhanced solubility because of decreased packing density and crystallinity [12,13].

Triptycene (9,10-*o*-benzenoanthracene), for its three-dimensional rigid structure and readily derivative ability, has

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been found to have attractive applications in supramolecular chemistry [14,15] and materials science [16,17]. Perhaps the earliest explorations in the effects of triptycenes in polymers were investigations at DuPont in the late 1960s wherein triptycenes were incorporated into a wide range of polymer systems [18]. In that work, triptycenes were bridgehead substituted into the backbones of polyesters, polyamides, and polyurethanes. Very recently, Swager et al. have reported that the addition of triptycene units to polyester can increase the T_g and ductility of film samples also [19]. It is possible that the bulky triptycene groups prevented the formation of tightly aggregation and insertion of this thermally and oxidatively stable, rigid moiety into polymers may modify and improve physical properties such as enhanced thermal stability and glass transition temperature, increased chain stiffness, decreased crystallinity, and improved solubility. It is well known that polymers with good solubility, rigidity and large free volume are vital for application in gas separation membranes [1,2]. Bulky groups in the main chain generally tend to increase free volume and hence permeability coefficients. High chain stiffness is expected to result in relatively high permselectivities. Due to such structural feature of this triptycene, synthesizing and characterizing polyimides, as well as incorporating triptycene moieties into the backbone of the polyimides, are worth proceeding. So in this work, a new kind of triptycene-containing dianhydride, 1,4-bis[4-(3,4-dicarboxylphenoxy)]triptycene dianhydride, was synthesized successfully; meanwhile, a series of novel polyimides holding triptycene moieties in main chain were prepared from the resulting dianhydride monomer with various aromatic diamines via a conventional one-step method. It was expected that the introduction of triptycene structure as an anhydride unit could improve the solubility and increase T_g values of the polyimides. The rigid bulky triptycene units may decrease interchain interactions and the ability for polymer chains to pack while providing a barrier to segmental mobility, thus resulting in an enhanced solubility and an increased T_g for the polyimides. Physical, thermal, and optical properties of these polyimides were also investigated.

2. Experimental

2.1. Materials

m-Cresol was distilled under vacuum before use. *N*,*N*-Dimethylacetamide (DMAc) was dried over P_2O_5, then distilled under reduced pressure, and stored over 4 Å molecular sieves under nitrogen in the dark. Anthracene (97%), *p*-benzoquinone (98%), and 4-nitro-*N*-methylphthalimide (technical grade) were used as received from Aldrich. 4,4′-Oxydianiline (ODA) and 1,3-phenylenediamine (MPD) were purified by sublimation under vacuum. 4,4′-Methylenedianiline (MDA), 3,3′-dimethyl-4,4′-methylenedianiline (DMMDA), 2,2′-dimethyl-4,4′-biphenylenediamine (DMB) were purified by recrystallization from ethanol prior to use. 1,4-Bis(4-aminophenoxy)benzene (TPEQ) was synthesized according to the literature [20]. Other chemicals were used as received.

2.2. Measurement

The FT-IR spectra were recorded on a Bio-Rad digilab Division FTS-80 spectrometer. ^{1}H NMR spectra were measured at 300 MHz on a Bruker AV300 spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on an Elemental Analyses MOD-1106. Inherent viscosities were determined on 0.5 g/dL concentration of polymer in DMAc using an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C. Molecular weight measurements were determined by gel permeation chromatography (GPC) and the GPC measurements were conducted at 35 °C with a Waters 410 GPC instrument equipped with two Waters Styragel columns (HT6E, HT3) and a differential refractometer detector. Chloroform was used as eluent at a flow rate of 1.0 mL/min. The molecular weights were calibrated against polystyrene standards. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC-7 system at a heating rate of 20 °C/min under both air and nitrogen atmosphere. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific™) in a tension mode at a heating rate of 3 °C/min and a frequency of 1 Hz from room temperature. Thermogravimetric analysis (TGA) was carried out with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. The mechanical properties of the films were measured on a mechanical tester Instron-1211 at a speed of 5 mm/min at 25 °C. UV–vis spectra were measured with a Shimadzu UV-2550 spectrometer in the transmittance mode. The X-ray diffraction data were collected on a Rigaku D/max-2500 X-ray diffractometer with a Cu Kα ($\lambda = 0.154$ nm) source, operated at 40 kV and 200 mA at 293 K.

2.3. Monomer syntheses

2.3.1. 1,4-Dihydroxytriptycene (**1**)

The bisphenol compound 1,4-dihydroxytriptycene was synthesized according to the literature [21]. Yield: 84%. M.p.: >300 °C (lit. [21], m.p. 338–340 °C dec). FT-IR (KBr pellet, cm^{-1}): 3286 (O–H), 1240 (asymmetry C–O stretching), 990 (symmetry C–O stretching). ^{1}H NMR (DMSO-d_6, δ ppm) 5.80 (s, 2H, C–H), 6.31 (s, 2H, Ar–H), 6.96–6.98 (m, 4H, Ar–H), 7.38–7.40 (m, 4H, Ar–H), 8.84 (s, 2H, OH). Anal. Calcd for $C_{20}H_{14}O_2$ (286.32): C, 83.90%; H, 4.93%. Found: C, 83.85%; H, 4.92%.

2.3.2. 1,4-Bis[4-(N-methyl-3,4-dicarboxylphenoxy)]-triptycene (**2**)

A solution of bisphenol (**1**) (4.29 g, 15 mmol) in DMAc (40 mL) and 2.5 g (18 mol) of anhydrous potassium carbonate was charged into a 100 mL three-necked round-bottomed flask, which was equipped with a mechanical stirrer and a Dean–Stark trap, nitrogen inlet and outlet; then 20 mL of toluene was added and the reaction flask was purged with dry N_2 for 30 min. The mixture was heated to 140 °C with stirring and maintained at this temperature for 3 h during which time the water was azeotropically removed. Toluene was then removed and the reaction mixture was cooled to room temperature. *N*-Methyl-4-nitrophthalimide (6.5 g, 31 mmol) was added, the temperature was gradually raised to 90 °C and maintained for 6 h. After cooling, the resulting solution was slowly added into 400 mL of water. The precipitated solid was collected by filtration. The crude product was recrystallized from chloroform to afford white crystalline bis(*N*-methylphthalimide) compound (**2**) (8.10 g, 89.3%). FT-IR (KBr pellet, cm^{-1}): 1769 (asymmetry C=O stretching), 1716 (symmetry C=O stretching), 1379 (C–N stretching), 1238 (asymmetry C–O stretching), 1010 (symmetry C–O stretching), 739 (imide ring deformation). ^1H NMR ($CDCl_3$, δ ppm) 3.23 (s, 6H, NCH_3), 5.57 (s, 2H, C–H), 6.80 (s 2H, Ar–H), 7.02–7.04 (m, 4H, Ar–H), 7.13–7.15 (dd, 2H, Ar–H), 7.22–7.24 (m, 4H, Ar–H), 7.39–7.40 (d, 2H, Ar–H), 7.82–7.84 (d, 2H, Ar–H). Anal. Calcd for $C_{38}H_{24}N_2O_6$ (604.61): C, 75.49%; H, 4.00%; N, 4.63%. Found: C, 75.60%; H, 4.05%; N, 4.52%.

*2.3.3. 1,4-Bis[4-(3,4-dicarboxylphenoxy)]-triptycene dianhydride (**3**)*

To a 15% KOH aqueous solution (60 mL) was added 12.1 g (20 mmol) of bis(*N*-methylphthalimide) compound (**2**). The mixture was refluxed for 48 h. After cooling to room temperature, the solution was adjusted to pH = 1.0 with 6 N HCl. The white precipitate was collected by filtration and dried in vacuum at 100 °C for 8 h. The resulting tetracarboxylic acid was dissolved in 20 mL acetic anhydride and then refluxed for 6 h. The white solids were filtered without cooling and washed with petroleum ether, then dried at 100 °C under vacuum for 8 h to give 10.4 g of white product. The yield was 90%. M.p.: >300 °C. FT-IR (KBr pellet, cm^{-1}): 1849 (asymmetry C=O stretching), 1775 (symmetry C=O stretching), 1278 (asymmetry C–O stretching), 1074 (symmetry C–O stretching). ^1H NMR (DMSO-d_6, δ ppm) 5.66 (s, 2H, C–H); 6.99–7.02 (m, 4H, Ar–H), 7.06 (s, 2H, Ar–H), 7.27–7.30 (m, 4H, Ar–H), 7.38–7.39 (d, 2H, Ar–H), 7.45–7.48 (dd, 2H, Ar–H), 8.10–8.13 (d, 2H, Ar–H). Anal. Calcd for $C_{36}H_{18}O_8$ (578.52): C, 74.74%; H, 3.14%. Found: C, 74.80%; H, 3.20%.

2.4. Polyimide syntheses

A typical polymerization procedure is as follows. To a 100 mL three-necked round-bottomed flask were added 0.2003 g (1.00 mmol) of 4,4′-oxydianiline (ODA) and 8 mL of *m*-cresol which was equipped with a mechanical stirrer, nitrogen inlet and outlet. The reaction flask was purged with dry N_2 for 30 min. The mixture was stirred until the complete dissolution of diamine, then 0.5785 g (1.00 mmol) of powdered dianhydride (**3**) and five drops of isoquinoline were added. The mixture was stirred at 100 °C until the complete dissolution of solids and maintained at this temperature for 2 h. Then the temperature of the oil bath was gradually raised to 180 °C. The reaction mixture was stirred on the conditions for 15 h under the steady flow of nitrogen and then poured into ethanol. The precipitate was filtered off, washed freely with ethanol, extracted with ethanol in a Soxhlet extractor for 6 h and dried in vacuum at 80 °C for 24 h, to afford powdered polyimides **4a–f** in 94–98% yield.

2.5. Spectroscopic data of the polymers

*2.5.1. Polyimide **4a***

This polyimide was synthesized from 4,4′-methylenedianiline (MDA) and dianhydride (**3**). The yield was 97%. FT-IR (KBr pellet, cm^{-1}): 1778 (asymmetry C=O stretching), 1724 (symmetry C=O stretching), 1372 (C–N stretching), 744 (C=O bending). ^1H NMR ($CDCl_3$, δ ppm): 3.95 (s, 2H, CH_2), 5.50 (s, 2H, C–H), 6.74 (s, 2H, Ar–H), 6.92–6.94 (m, 4H, Ar–H), 7.10–7.11 (m, 6H, Ar–H), 7.15–7.18 (m, 10H, Ar–H), 7.82–7.85 (d, 2H, Ar–H). Anal. Calcd for $C_{49}H_{28}N_2O_6$ (740.75): C, 79.45%; N, 3.78%; H, 3.81%. Found: C, 79.38%; N, 3.73%; H, 3.80%.

*2.5.2. Polyimide **4b***

This polyimide was synthesized from 4,4-oxydianiline (ODA) and dianhydride (**3**). The yield was 98%. FT-IR (KBr pellet, cm^{-1}): 1779 (asymmetry C=O stretching), 1723 (symmetry C=O stretching), 1373 (C–N stretching), 743 (C=O bending). ^1H NMR (DMSO-d_6, δ ppm): 5.74 (s, 2H, C–H), 7.02 (m, 6H Ar–H), 7.24–27 (m, 4H, Ar–H), 7.32–7.34 (m, 8H, Ar–H), 7.50–7.53 (m, 4H, Ar–H), 7.97–8.00 (d, 2H, Ar–H). Anal. Calcd for $C_{48}H_{26}N_2O_7$ (742.75): C, 77.62%; N, 3.77%; H, 3.53%. Found: C, 77.04%; N, 3.76%; H, 3.57%.

*2.5.3. Polyimide **4c***

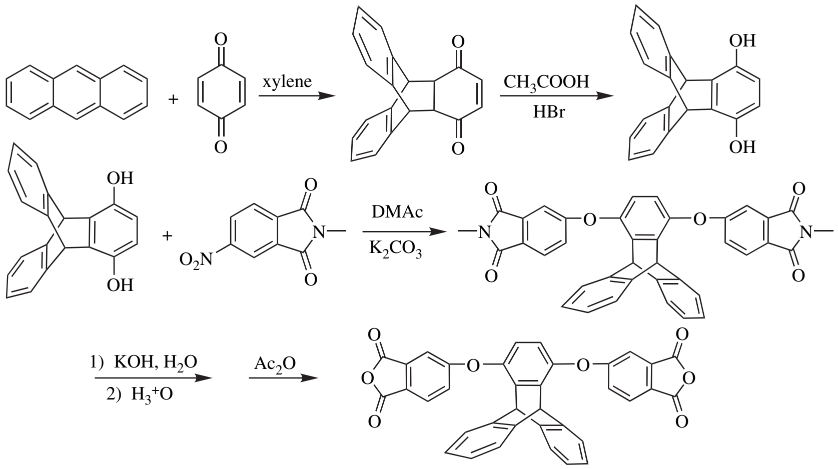
This polyimide was synthesized from 3,3-dimethyl-4,4-methylenedianiline (DMMDA) and dianhydride (**3**). The yield was 96%. FT-IR (KBr pellet, cm^{-1}): 1778 (asymmetry C=O stretching), 1723 (symmetry C=O stretching), 1374 (C–N stretching), 748 (C=O bending). ^1H NMR ($CDCl_3$, δ ppm): 2.04 (s, 6H, CH_3), 3.86 (s, 2H, CH_2), 5.40 (s, 2H, C–H), 6.64 (s, 2H, Ar–H), 6.82–6.84 (m, 4H, Ar–H), 6.97–7.08 (m, 14H, Ar–H), 7.72–7.75 (d, 2H, Ar–H). Anal. Calcd for $C_{51}H_{32}N_2O_6$ (768.81): C, 77.68%; N, 3.64%; H, 4.19%. Found: C, 78.05%; N, 3.68%; H, 4.20%.

*2.5.4. Polyimide **4d***

This polyimide was synthesized from 2,2′-dimethyl-4,4′-biphenylenediamine (DMB) and dianhydride (**3**). The yield was 96%. FT-IR (KBr pellet, cm^{-1}): 1778 (asymmetry C=O stretching), 1721 (symmetry C=O stretching), 1368 (C–N stretching), 746 (C=O bending). ^1H NMR ($CDCl_3$, δ ppm): 2.12 (s, 6H, CH_3), 5.50 (s, 2H, C–H), 6.74 (s, 2H, Ar–H), 6.96–6.99 (m, 4H, Ar–H), 7.14–7.27 (m, 10H, Ar–H), 7.31–7.32 (d, 2H, Ar–H), 7.42–7.45 (d, 2H, Ar–H), 7.82–7.85 (d, 2H, Ar–H). Anal. Calcd for $C_{50}H_{30}N_2O_6$ (754.78): C, 79.57%; N, 3.71%; H, 4.01%. Found: C, 79.79%; N, 3.54%; H, 4.05%.

*2.5.5. Polyimide **4e***

This polyimide was synthesized from 1,4-bis(4-aminophenoxy)benzene (TPEQ) and dianhydride (**3**). The yield was 97%. FT-IR (KBr pellet, cm^{-1}): 1778 (asymmetry C=O



Scheme 1. Synthesis of triptycene-containing dianhydride (**3**).

stretching), 1724 (symmetry C=O stretching), 1377 (C–N stretching), 745 (C=O bending). ^{1}H NMR ($CDCl_3$, δ ppm): 5.47 (s, 2H, C–H), 6.73 (s, 2H, Ar–H), 6.94–7.14 (m, 18H, Ar–H), 7.32–7.40 (m, 6H, Ar–H), 7.82–7.84 (d, 2H, Ar–H). Anal. Calcd for $C_{54}H_{30}N_2O_8$ (834.82): C, 77.69%; N, 3.36%; H, 3.62%. Found: C, 77.30%; N, 3.39%; H, 3.60%.

2.5.6. Polyimide *4f*

This polyimide was synthesized from 1,3-phenylenediamine (MPD) and dianhydride (**3**). The yield was 94%. FT-IR (KBr pellet, cm^{-1}): 1780 (asymmetry C=O stretching), 1724 (symmetry C=O stretching), 1357 (C–N stretching), 744 (C=O bending). ^{1}H NMR ($CDCl_3$, δ ppm): 5.50 (s, 2H, C–H), 6.75 (s, 2H, Ar–H), 6.93–6.95 (m, 5H, Ar–H), 7.12–7.18 (m, 7H, Ar–H), 7.40–7.41 (d, 2H, Ar–H), 7.46–7.49 (d, 2H, Ar–H), 7.82–7.85 (d, 2H, Ar–H). Anal. Calcd for $C_{42}H_{22}N_2O_6$ (650.63): C, 77.53%; N, 4.31%; H, 3.41%. Found: C, 77.81%; N, 4.28%; H, 3.40%.

2.6. Preparation of polyimide film

A 5–7 wt% solution of polymer in DMAc was prepared and filtered through a 0.2 μm syringe filter to remove the insoluble materials and dust particles. The solution was then poured on a leveled clean glass plate. The casting process took about 8 h at 60 °C. The resulting film samples were dried at 80 °C for 2 h, 100 °C for 2 h and 200 °C for 12 h.

3. Results and discussions

3.1. Synthesis of dianhydride monomer (*3*)

In the present work, we successfully synthesized a new triptycene-containing dianhydride, 1,4-bis[4-(3,4-dicarboxyphenoxy)phenoxy]triptycene dianhydride through a four-step synthetic route starting from anthracene and *p*-benzoquinone, as shown in Scheme 1. First, bisphenol 1,4-dihydroxytriptycene (**1**) was prepared according to the literature [21]. A adduct was formed from anthracene and *p*-benzoquinone via Diels–Alder reaction and subsequent rearrangement reaction using acetic acid/HBr as catalyst afforded high yield diphenol. Then the bis(phthalimide) compound 1,4-bis[4-(*N*-methyl-3,4-dicarboxylphenoxy)]triptycene (**2**) was readily synthesized from the nitro displacement of *N*-methyl-4-nitrophthalimide by the phenoxide ion of diphenol (**1**) in good yield. After that, the bis(phthalimide) compound (**2**) was hydrolyzed by 15% aqueous solution of KOH and subsequently acidified with hydrochloric acid to give tetracarboxylic acid, which was chemically cyclodehydrated with acetic anhydride to afford the targeted compound 1,4-bis[4-(3,4-dicarboxylphenoxy)]triptycene dianhydride (**3**) in a 90% yield. FT-IR, ^{1}H NMR spectroscopies and elemental analyses confirmed the structures of the monomers (**3**). The ^{1}H NMR spectrum of the dianhydride monomer (**3**) is shown in Fig. 1.

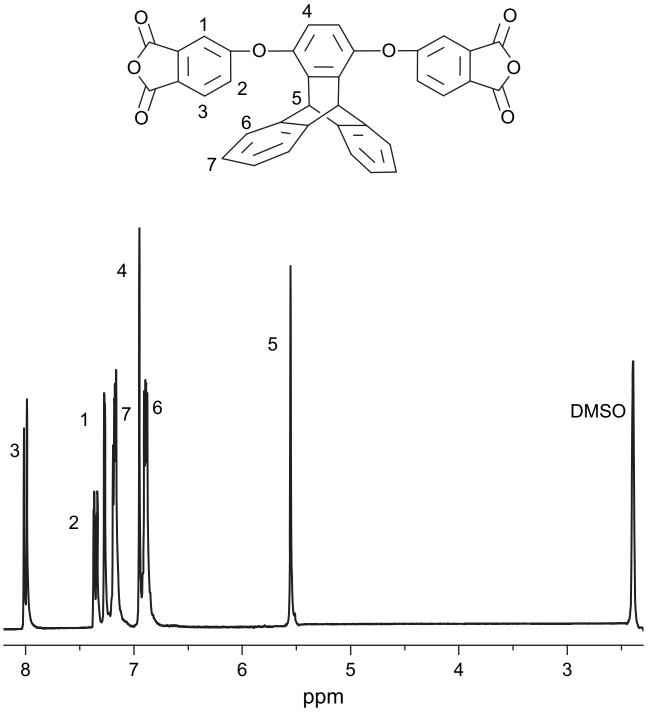
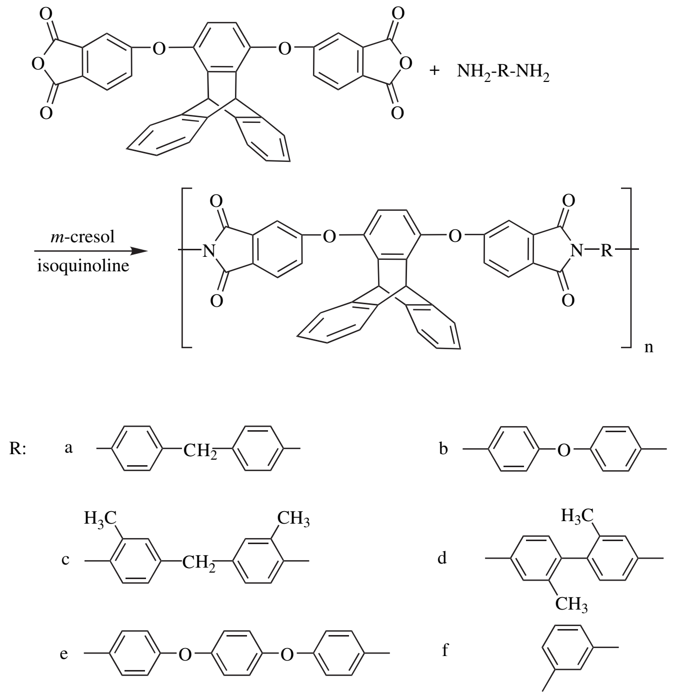


Fig. 1. ^{1}H NMR spectrum of triptycene-containing dianhydride (**3**) in DMSO-d_6.



Scheme 2. Synthesis of polyimides **4a–f** derived from triptycene-containing dianhydride (**3**).

3.2. Synthesis chemistry of the polyimides

Six triptycene-containing polyimides **4a–f** were synthesized derived from triptycene-containing dianhydride monomer with various aromatic diamines by a conventional one-step procedure at a high temperature in *m*-cresol with a catalytic amount of isoquinoline (Scheme 2). The polymerizations were carried out with 10% (w/v) solid concentrations. The triptycene-containing dianhydride monomer was dissolved slightly in *m*-cresol at room temperature so the reaction mixture was initially heated to 100 °C for the solid to dissolve completely and maintained at this temperature for 2 h, the solution were then heated at 180 °C for 15 h. Water formed during the imidization was continuously removed with a stream of nitrogen. In all of the reactions, homogeneous solutions were obtained. The polyimide products were isolated by precipitation in ethanol. The polymers were purified by extracting with ethanol in a Soxhlet extractor for 6 h and dried in vacuum at 80 °C for 24 h. The experimental data are summarized in Table 1. As can be seen in Table 1, the polyimides were synthesized in high yields (94–98%). All polyimides (**4a–f**) had inherent viscosities in the range of 0.45–0.74 dL/g in DMAc. The gel permeation chromatographic (GPC) measurements for five $CHCl_3$ soluble polyimides (**4a**, **4c–f**) demonstrated that polymers exhibited weight average molecular weights (M_ws) and polydispersities (M_w/M_ns) in the ranges 4.3–7.3 × 10^4 g/mol and 2.39–2.76 based on polystyrene standard, respectively.

The chemical structures of polyimides were characterized by FT-IR, ^1H NMR and element analysis. All of the polyimides showed characteristic imide absorption bands at 1778–1780 cm^{-1} attributed to the asymmetric carbonyl stretching vibrations and at 1721–1724 cm^{-1} attributed to the symmetric carbonyl stretching vibrations. The absorption bands at 1357–1377 cm^{-1} were assigned to C–N stretching vibrations, and the C=O bending absorption bands were also detected in the range of 743–748 cm^{-1}. Fig. 2 depicts a typical ^1H NMR spectrum of the triptycene-containing polyimide (**4b**), in which all the protons in the polymer backbone can be assigned. The composition of chain unit of six polyimides was confirmed by elemental analysis (Table 1) results because those found from it are in accordance with those calculated.

3.3. Polymer properties

3.3.1. Polymer solubility

The new triptycene-containing polyimides can be dissolved in organic solvents to afford homogeneous polymer solution. The solubility of all the polyimides was determined by 10% solid content at room temperature or upon heating. The solubilities of the resulting polyimides in several organic solvents

Table 1
Inherent viscosity, molecular weight and elemental analysis of polyimides

Polymer	η_{inh}[a] (dL/g)	Elemental analysis (%)					GPC[b] data		
		Formula of PI (formula weight)		C	H	N	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n
4a	0.58	$(C_{49}H_{28}N_2O_6)_n$ $(740.75)_n$	Calcd	79.45	3.81	3.78	1.92	5.28	2.76
			Found	79.38	3.80	3.73			
4b	0.65	$(C_{48}H_{26}N_2O_7)_n$ $(742.75)_n$	Calcd	77.62	3.53	3.77	–	–	–
			Found	77.04	3.57	3.76			
4c	0.62	$(C_{51}H_{32}N_2O_6)_n$ $(768.81)_n$	Calcd	77.68	4.19	3.64	2.56	6.71	2.62
			Found	78.05	4.20	3.68			
4d	0.70	$(C_{50}H_{30}N_2O_6)_n$ $(754.78)_n$	Calcd	79.57	4.01	3.71	2.75	6.56	2.39
			Found	79.79	4.05	3.54			
4e	0.74	$(C_{54}H_{30}N_2O_8)_n$ $(834.82)_n$	Calcd	77.69	3.62	3.36	2.94	7.25	2.47
			Found	77.30	3.60	3.39			
4f	0.45	$(C_{42}H_{22}N_2O_6)_n$ $(650.63)_n$	Calcd	77.53	3.41	4.31	1.58	4.25	2.69
			Found	77.81	3.40	4.28			

The symbol "–" signifies not measured.

[a] Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

[b] With respect to polystyrene standards, with $CHCl_3$ as the eluent.

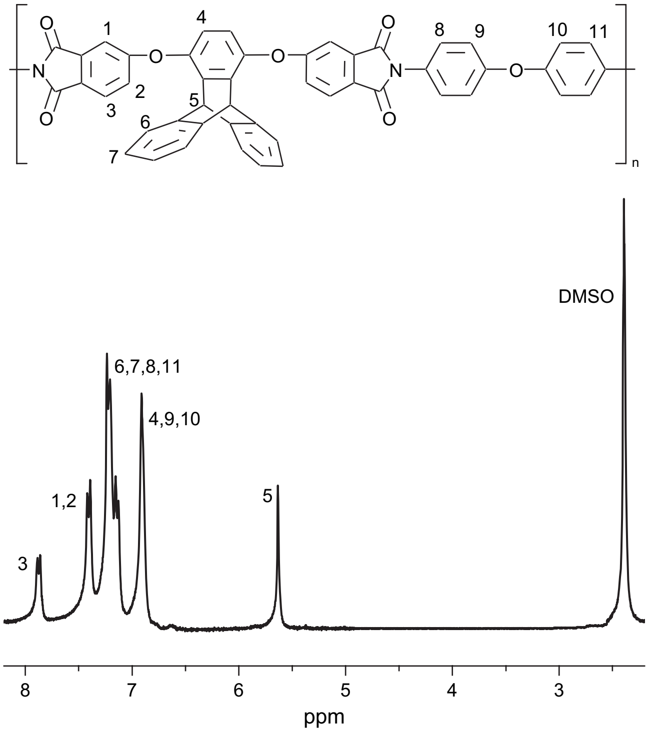


Fig. 2. ^{1}H NMR spectrum of polyimide **4b** in DMSO-d_6.

are summarized in Table 2. The solubility varies depending upon the diamine used. The new triptycene-containing polyimides, except **4b** and **4d**, were easily dissolved both in polar solvents, such as DMF, DMAc, DMSO, NMP and *m*-cresol, and in less polar solvents, such as THF, CH_2Cl_2, chloroform and TCE at room temperature. Polyimides **4b** and **4d** were dissolved in polar solvents, such as DMF, DMAc, DMSO, NMP and *m*-cresol, upon heating, but polyimide **4d** was partially dissolved in common organic solvents, such as THF, CH_2Cl_2, chloroform and TCE and **4b** slightly dissolved, even upon heating. The good solubility of these polyimides can be attributed to the presence of flexible aryl ether linkages and bulky side substituents, together with the incorporation of bulky alicyclic units of the triptycene structure. The poor solubility of polyimide **4d** can be explained by the rigid and symmetric nature of its diamine moiety.

Table 2
Solubility[a] of polyimides

Polymers	THF	CH_2Cl_2	$CHCl_3$	TCE[b]	DMF	DMAc	DMSO	NMP	*m*-cresol
4a	+	+	+	+	+	+	+	+	+
4b	−	−	−	+h	+h	+h	+h	+h	+h
4c	+	+	+	+	+	+	+	+	+
4d	±	±	±	+h	+h	+h	+h	+h	+h
4e	+	+	+	+	+	+	+	+	+
4f	+	+	+	+	+	+	+	+	+

[a] The solubility was determined at 10% solid content; +, soluble at room temperature, the solid polymer was completely dissolved in the solvent to afford a clean, homogeneous solution; +h, soluble upon heating; ±, partially soluble at room temperature. −, insoluble; the solid polymer did not dissolve in the solvent.

[b] 1,1′,2,2′-Tetrachloroethane.

3.3.2. Thermal and mechanical properties

Thermal and mechanical properties of polyimides **4a–f** are summarized in Table 3. Thermal properties of the polyimides were evaluated by means of differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). DSC was used to determine the glass transition temperature (T_g) values of the polyimides with a heating rate of 20 °C/min in nitrogen, the T_g of polymer could be read in the second heating trace of DSC (Fig. 3). The T_g of the polyimides was in the range of 221–296 °C, which depended on the chemical structure of aromatic diamine component. Among all the polyimides synthesized, polyimide **4d** showed the highest T_g of 296 °C, which can be attributed to the rigid diamine moieties in the polymer backbone. On the contrary, polyimide **4f** showed the lowest T_g of 221 °C due to the relative flexible polymer chain. Cella and Faler reported a spirobisindane dietheranhydride (SBIDA) synthesized from 5,5′-dihydroxy-3,3,3′,3′-tetramethyl-1,1″-spirobisindane and 4-nitro-*N*-methylphthalimide [22]. Chao and Barren reported on the synthesis and properties of polyimides based on SBIDA [23]. It was found that the polyimide made from SBIDA and an aromatic diamine had a higher glass transition temperature than the polyimide made from bisphenol A dietheranhydride and the same diamine. It is conceivable that the structural rigidity of SBIDA contributes to the increase in the glass transition temperature of those polyimides. In comparison with SBIDA, the triptycene tetraetheranhydride (**3**) is more rigid than SBIDA due to the rotation around carbon–carbon bond being restricted for the formation of triptycene. Therefore, the polyimides from **3** showed an increased T_g than these from SBIDA. For example, the T_g value of polyimide **4b** (279 °C) is about 30 °C higher than that of polyimide from SBIDA and ODA (252 °C).

Fig. 4 displays the dynamic storage modulus (E'), loss modulus (E'') and tan δ as a function of temperature for two polyimides **4c** and **4e**. Regarding the peak temperature in the tan δ curves as the glass transition temperature (T_g) of these polyimides, the polyimide **4c** exhibited a T_g at 289 °C and **4e** at 244 °C. The T_g values obtained by DMTA were comparable to that measured by DSC method.

For evaluating thermal and thermo-oxidative stabilities of the polyimides, Table 3 also gives the onset decomposition temperature and the temperature at 10% weight loss in air and in nitrogen, respectively, i.e. T_d and T_{10} values. The T_d and T_{10} values of the polyimides were in the range 425–468 °C and 504–556 °C in air, while those of them were in the range 448–486 °C and 526–565 °C in nitrogen atmosphere. Representative TGA diagram of polyimide **4b** (a) in air and (b) in nitrogen is shown in Fig. 5.

The mechanical properties of the polyimide films **4a–f** are also summarized in Table 3. The films had tensile strengths of 95–118 MPa, an elongation at break in the range of 5.3–16.2%, and a tensile modulus in the range of 1.03–1.38 GPa. Most of the polymer films exhibited high tensile strength, indicating that they are strong materials.

Table 3
Thermal and mechanical properties of polyimides

Polymers	T_g (°C)		T_d[c] (°C)		T_{10}[d] (°C)		Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
	DSC[a]	DMTA[b]	Air	N_2	Air	N_2			
4a	270	273	455	471	529	547	112	1.22	11.8
4b	279	286	464	482	556	561	118	1.38	12.1
4c	275	289	425	448	504	526	104	1.20	10.8
4d	296	312	434	450	523	536	102	1.15	5.3
4e	273	244	468	486	546	565	96	1.03	16.2
4f	221	230	440	452	528	548	95	1.05	9.4

[a] From the second trace of DSC measurements conducted at a heating rate of 20 °C/min.
[b] Measured by DMTA at 1 Hz and at a rate of 3 °C/min.
[c] Onset decomposition temperature in TGA at 10 °C/min heating rate.
[d] 10% weight loss temperature in TGA at 10 °C/min heating rate.

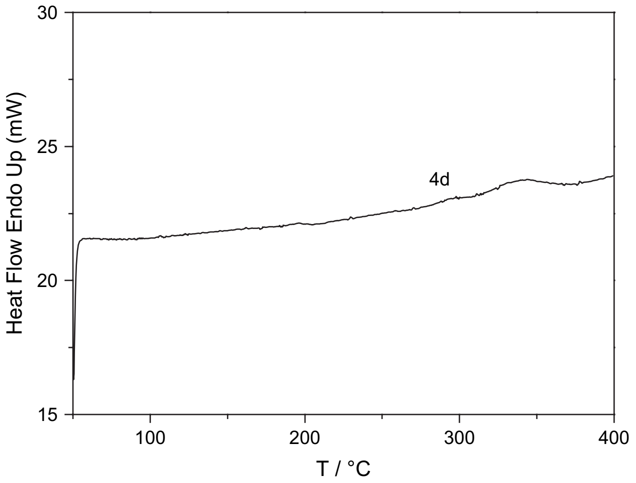


Fig. 3. DSC curves of polyimide **4d**.

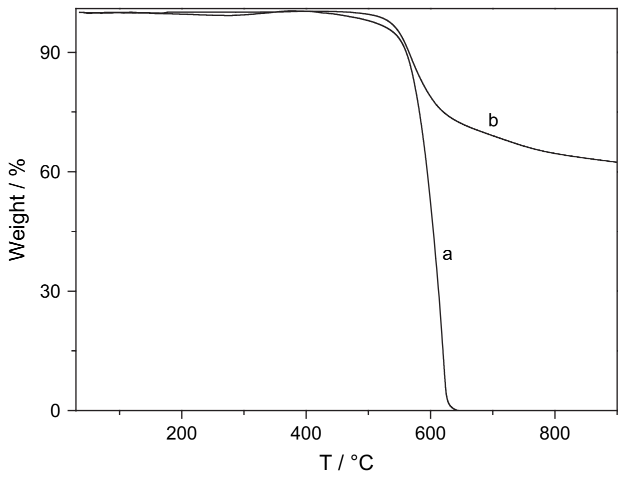


Fig. 5. TGA diagram of polyimide **4b** (a) in air and (b) in nitrogen.

3.3.3. Optical properties

Transmission UV–vis spectra were measured for the thin films of all polyimides. Typical UV–vis spectra of some representative polyimide films are illustrated in Fig. 6. All polyimide films exhibited cut-off wavelengths (λ_0) shorter than 400 nm and high optical transparency with the 80% transmission wavelength above 600 nm except **4f**. The cut-off and 80% transmission wavelengths for the polyimide films are listed in Table 4.

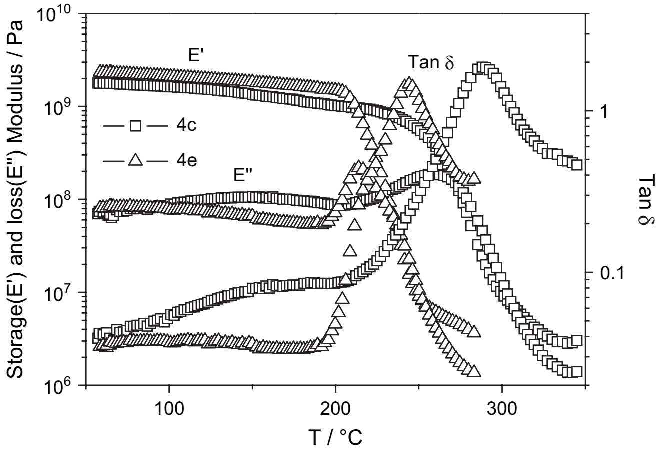


Fig. 4. Dynamic modulus as a function of temperature for films of polyimides **4c** and **4e**.

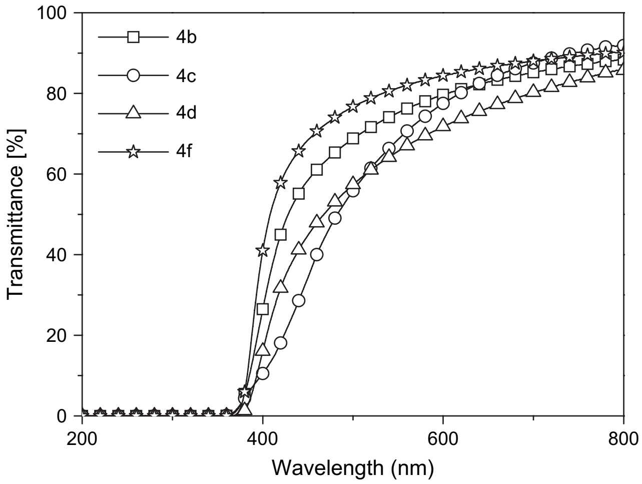


Fig. 6. UV–vis spectra of the polyimides.

Table 4
The cut-off and 80% transmission wavelengths of polyimide films

Polymers	Cut-off wavelength λ_0 (nm)	80% Transmission wavelength (nm)
4a	373	620
4b	367	605
4c	360	618
4d	375	697
4e	372	619
4f	366	533

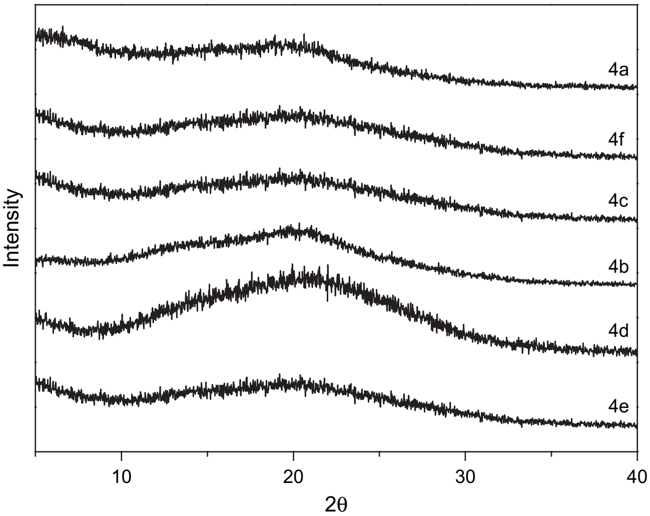


Fig. 7. Wide-angle X-ray diffractograms of polyimides.

Crystallinity of the polyimides was evaluated by wide-angle X-ray diffraction experiments. Fig. 7 displays the diffraction patterns for the polyimides. All the polyimides showed amorphous diffraction patterns.

4. Conclusions

A novel dianhydride having triptycene unit was synthesized, characterized and applied to polyimide preparation. The resulting polyimides had good solubility in common organic solvents and could be cast into transparent and strong films. They also exhibited high T_gs and good thermal stability. The polyimides containing a rigid triptycene moiety and a large free volume could be a good candidate for membrane application. The investigation of their gas separation properties is in progress.

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