Macromolecules **1998,** *31,* 7213−7217

Synthesis and Characterization of New Adamantane-Based Polyimides

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Received April 23, 1998; Revised Manuscript Received August 17, 1998

ABSTRACT: A new adamantane-based dietheramine, 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane, was prepared in two steps from chloro displacement of *p*-chloronitrobenzene with the potassium phenolate of 2,2-bis(4-hydroxyphenyl)adamantane, followed by hydrazine catalytic reduction of the intermediate dinitro compound. A series of polyimides with the adamantane-2,2-diyl unit as a cardo group was prepared from the adamantane-based dietheramine and various aromatic dianhydrides by a conventional two-stage synthesis in which the poly(amic acid)s obtained in the first stage were heated stage-by-stage at 150−270 °C to give the polyimides. The intermediate poly(amic acid)s had inherent viscosities between 0.82 and 1.66 dL/g. Except for the polyimide from pyromellitic dianhydride, all of the polyimides could be dissolved in NMP, and several polyimides also showed good solubility in other organic solvents. All of the polyimides were amorphous in nature as evidenced by X-ray diffractograms. The glass-transition temperatures (T_g) of these polyimides were recorded between 248 and 308 °C by differential scanning calorimetry (DSC), and the softening temperatures (T_s) determined by thermomechanical analysis (TMA) stayed in the range of 254−335 °C. Decomposition temperatures for 10% weight loss all occurred above 500 °C in both air and nitrogen atmospheres.

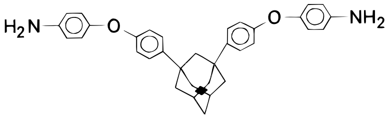
Introduction

Aromatic polyimides are well-known for their excellent characteristics such as mechanical and electrical properties, thermal stability, and chemical resistance.[1,2] However, most of them were insoluble and infusible, which limits their wide applications. Therefore, significant synthetic efforts have been carried out to improve processability and solubility of polyimides without compromising their attractive properties by the incorporation of flexible bridging links and/or bulky units into the rigid polyimide backbone or by attachment of bulky side groups.[3−8]

The introduction of cardo groups into the polymer chain of many polymer systems endows them with some specific properties such as enhanced thermal stability together with excellent solubility,[9] which is of particular importance in aromatic heterocyclic polymers with rigid chain. It has been demonstrated that incorporation of both ether and a cyclic side cardo group, such as a fluorene, a phthalide, or a phthalimidine group, into the macromolecular backbone resulted in aromatic polyimides with good thermal stability, high T_g, and excellent solubility in organic solvents.[3−6]

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a highly symmetrical tricyclic hydrocarbon which consists of fused chair-form cyclohexane rings.[10] It exhibits four bridgehead positions which are easily substituted using Friedel−Crafts alkylation. Substitution at the four bridgehead carbons allows for the formation of star polymers with a tetrahedral array of rigid arms, serving as molecular reinforcement. Some examples of these include polyaramids[11] and polybenzoxazoles[12] based on adamantane. Adamantane has also been inserted into the backbones of many polymers including polysulfones, polyesters, polyamides, and polyimides.[13−20] Insertion of this thermally and oxidatively stable, bulky, rigid, and hydrophobic moiety into polymers modifies and improves physical properties such as enhanced thermal stability and glass-transition temperature, increased chain stiffness, decreased crystallinity, improved solubility, and lowered dielectric constant values. Incorporation of pendant adamantyl groups into acrylates,[21−23] phenolics,[24] poly(phenylene)s,[25] poly(ether ether ketone)s,[26] and poly(benzyl ether)s[27] also results in a large increase in T_g, thermal properties, and solubility when compared to the unsubstituted polymer analogues. The rigidity and bulkiness of the adamantyl moiety greatly reduces chain mobility and inhibits chain packing. This increases T_g, lowers crystallinity, and enhances solubility. In addition, thermosetting polymers based on acetylene[28−30] or maleimide[31] derivatives of adamantane have been reported.

Very recently, Chern and Shiue[20] have demonstrated that soluble polyimides with high T_g's and low dielectric constants could be prepared from 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane and selected aromatic tetracarboxylic dianhydrides. The present work examines 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane-based polyimides in order to understand how molecular mobility and packing behavior are affected as related to solubility and thermal properties. The adamantane-2,2-diyl cardo units decrease the ability for polymer chains to pack while providing a barrier to segmental mobility and, thus, may result in an increased T_g and an enhanced solubility to the polyimides.



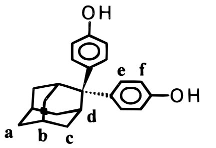
Experimental Section

Materials. 2-Adamantanone (Aldrich), phenol (Wako), zinc chloride ($ZnCl_2$; Wako), potassium carbonate (K_2CO_3; Fluka),

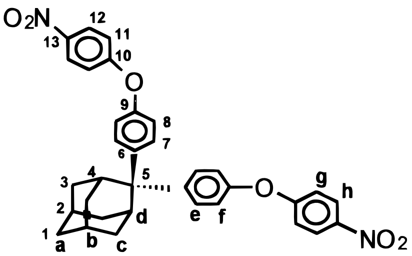
10.1021/ma980649c CCC: $15.00

p-chloronitrobenzene (TCI), 10% palladium on charcoal (Pd/C; Fluka), and hydrazine monohydrate (Wako) were used as received. *N*,*N*-Dimethylformamide (DMF; Fluka) and *N*,*N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Reagent grade aromatic tetracarboxylic dianhydrides such as 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA; **4b**, from Oxychem), diphenyl sulfone-3,3′,4,4′-tetracarboxylic dianhydride (DSDA; **4e**, from New Japan Chemical Co.), 4,4′-oxydiphthalic dianhydride (OPDA; **4c**, from Oxychem), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **4f**, from Hoechst Celanese) were used as received, whereas pyromellitic dianhydride (PMDA; **4a**, from Aldrich) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; **4d**, from Aldrich) were recrystallized from acetic anhydride prior to use. According to a well-developed method,[32−34] 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**4g**) (mp 183 °C) and 2,2-bis[4-(3,4-dicarboxyphenoxy)-phenyl]adamantane dianhydride (**4h**) (mp 227 °C) were prepared in three main steps starting from the nucleophilic nitrodisplacement reaction of 4-nitrophthalonitrile with 2,2-bis(4-hydroxyphenyl)propane and 2,2-bis(4-hydroxyphenyl)adamantane (**1**), respectively, in DMF in the presence of potassium carbonate. Details of the synthesis and characterization data of the new adamantane-based dianhydride **4h** have been described in a separate article.[35]

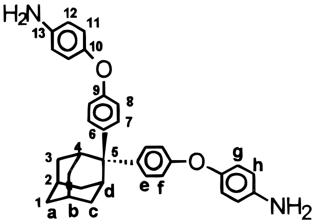
Synthesis of 2,2-Bis(4-hydroxyphenyl)adamantane (1). In a 500-mL flask, 50.0 g (0.3328 mol) of 2-adamantanone and 6 g of $ZnCl_2$ were stirred in 94 g (0.1 mol) of molten phenol. The mixture was heated at approximately 60 °C on an oil bath, and then dry hydrogen chloride was bubbled in for about 4 h. The reaction system became dark brown. The reaction solution was diluted with 100 mL of ethanol, and then 150 mL of water was added to precipitate a white solid. The crude product was recrystallized from ethanol to afford colorless needle crystals of pure diol **1**. Yield: 20.6 g (19.3%); mp 316 °C (lit.[18] 316−318 °C). IR (KBr): 3356 cm^{-1} (O−H). ^1H NMR (400 MHz, DMSO-d_6): $\delta = 8.26$ (s, −OH, 2H), 7.13 (d, H_e, 4H), 6.56 (d, H_f, 4H), 3.17 (d, H_d, 2H), 1.89 (d, H_c, 4H), 1.71 (d, H_b, 2H), 1.62 ppm (complex, H_a + H_c, 6H). Anal. calcd for $C_{22}H_{24}O_2$ (320.43): C, 82.46; H, 7.55. Found: C, 81.78; H, 7.53.



Synthesis of 2,2-Bis[4-(4-nitrophenoxy)phenyl]adamantane (2). In a 500-mL round-bottomed flask, 10 g (0.031 mol) of adamantane-bisphenol **1** and 9.9 g (0.0628 mol) of *p*-chloronitrobenzene were dissolved in 150 mL of dry DMF. Then, 9 g (0.0652mol) of anhydrous potassium carbonate was added, and the suspension solution was refluxed at 140 °C for 10 h. The mixture was allowed to cool and then poured into 600 mL of methanol/water (1:1 by volume) to precipitate a yellow solid which was collected by filtration, repeatedly washed with methanol and water, and dried. The crude product was recrystallized from DMF/water to afford 14.5 g (82%) of pale-yellow crystals: mp 238 °C. IR (KBr): 1586 (asym. $-NO_2$ str.), 1342 (sym. $-NO_2$ str.), 1248 cm^{-1} (C−O−C). ^1H NMR (400 MHz, DMSO-d_6): δ 8.12 (d, H_h, 4H), 7.44 (d, H_e, 4H), 6.44 (two overlapped AB doublets, H_f + H_g, 8H), 3.21 (d, H_d, 2H), 1.95 (d, H_c, 4H), 1.78 (d, H_b, 2H), 1.71 (d, H_c, 4H), 1.66 ppm (d, H_a, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.39 (C^9), 149.93 (C^{10}), 143.69 (C^{13}), 140.74 (C^6), 126.15 (C^7), 124.31 (C^{11}), 118.64 (C^8), 115.62 (C^{12}), 48.36 (C^5), 36.07 (C^1), 31.46 (C^3), 34.18 (C^4), 25.52 ppm (C^2). Anal. calcd for $C_{34}H_{30}N_2O_6$ (562.62): C, 72.59; H, 5.37; N, 4.98. Found: C, 72.30; H, 5.51; N, 5.00.



Synthesis of 2,2-Bis[4-(4-aminophenoxy)phenyl]adamantane (3). In a 1-L flask, 14 g (0.02488 mol) of dinitro compound **2** and 0.1 g of 10% Pd/C were suspended in 200 mL of ethanol, 300 mL of tetrahydrofuran (THF), and 50 mL of hydrazine monohydrate. The suspension solution was refluxed for 10 h, and then the resulting clear, hot solution was filtered to remove Pd/C. The filtrate was concentrated to $^1/_2$ of its original volume and then poured into 150 mL of distilled water. The precipitated colorless crystals were isolated by filtration, thoroughly washed by water, and dried in a vacuum; mp 240 °C. Yield: 11.5 g (92%). IR (KBr): 3458 (asym. $-NH_2$ str.), 3372 (sym. $-NH_2$ str.), 1237 cm^{-1} (C−O−C). ^1H NMR (400 MHz, DMSO-d_6): δ 7.28 (d, H_e, 4H), 6.67 (two overlapped AB doublets, H_f + H_g, 8H), 6.55 (d, H_h, 4H), 4.89 (quadrupole broadening, NH_2, 4H), 3.17 (d, H_d, 2H), 1.89 (d, H_c, 4H), 1.72 (d, H_b, 2H), 1.65 (d, H_c, 4H), 1.62 ppm (d, H_a, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.95 (C^9), 145.29 (C^{10} + C^{13}), 141.71 (C^6), 126.71 (C^7), 120.98 (C^{11}), 115.90 (C^8), 114.77 (C^{12}), 49.02 (C^5), 37.48 (C^1), 32.77 (C^3), 31.04 (C^4), 26.83 ppm (C^2). Anal. calcd for $C_{34}H_{34}N_2O_2$ (502.65): C, 81.24; H, 6.82; N, 5.57. Found: C, 80.89; H, 6.91; N, 5.56.

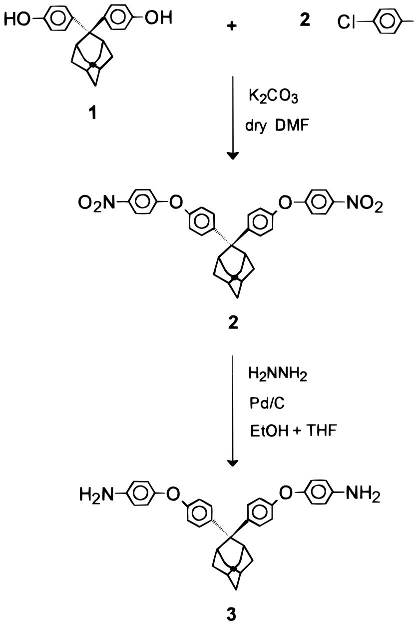


Synthesis of Polyimides. A typical polymerization procedure is as follows. Adamantane-dietheramine **3** (0.6094 g, 2.124 mmol) was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.3907 g (2.124 mmol) of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**4d**) was added in one portion. The mixture was stirred at room temperature for 2 h. The inherent viscosity of the resulting poly(amic acid) **5d** was 1.21 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The polymer solution obtained was poured into a $\varphi = 9$-cm glass culture dish, which was placed in an 80 °C oven overnight to remove the solvent. The semidried poly(amic acid) film was further dried and transformed into polyimide by sequential heating at 150 °C for 20 min, 180 °C for 20 min, 220 °C for 20 min, 250 °C for 20 min, and 270 °C for 20 min. By being soaked in hot water, a flexible polyimide film of **6d** self-stripped off the glass surface.

IR of **5d** (film): 3000−3500 (O−H, N−H str.), 1719 (C═O, carboxylic acid), 1603 (C═O, amide), 1237 cm^{-1} (C−O str.). IR of **6d** (film): 1781 (asym. C═O str.), 1729 (sym. C═O str.), 1498, 1600 (arom. C═C), 1380 (C−N), 1241 (C−O), 1170, and 722 cm^{-1} (imide ring deformation).

Characterization. IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were measured on a JEOL EX-400 NMR spectrometer with perdeuteriodimethyl sulfoxide (DMSO-d_6) as an external reference, working at 400 and 100 MHz, respectively. Elemental analyses were run in a Perkin-Elmer model 2400 C, H, N analyzer. The inherent viscosities were measured with an Ubbelohde viscometer at 30 °C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 thermal analyzer was used to determine the thermal

Scheme 1



transitions. The heating rate was 20 °C/min. Glass-transition temperatures (T_g) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quick cooling. Thermomechanical analysis (TMA) was conducted with a Rigaku TMA 8140 coupled to a Rigaku TAS-100 thermal analysis station with a penetration probe of 1.0-mm diameter and using an applied constant load of 5 g at a scan rate of 10 °C/min. The TMA experiments were conducted in duplicate. Softening temperatures (T_s) were taken as the intersection of the extrapolation of the baseline with the extrapolation of inflection from the second TMA traces. Thermogravimetry (TG) was conducted with a DuPont 951 Thermogravimetric Analyzer coupled to a DuPont 2000 Thermal Analyst. Experiments were carried out on 9−11-mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20 °C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu Kα radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5-40°$. An Instron universal tester model HT-9102 (Hung Ta Instrument Co., Taiwan) with a load cell of 10 kg was used to study the stress−strain behavior of the polymer films (6 cm long, 0.5 cm wide, and about 0.1 mm thick), using a gauge length of 2 cm and 5 cm/min rate of extension. An average of at least five individual determinations was used.

Results and Discussion

Monomer Synthesis. The new adamantane-based dietheramine **3** was prepared from *p*-chloronitrobenzene and 2,2-bis(4-hydroxyphenyl)adamantane (**1**) using a two-step synthetic route as outlined in Scheme 1, where the adamantane-bisphenol **1** was prepared by a common bisphenol synthesis method[36] from the condensation of 2-adamantanone with excess phenol in the presence of an acidic condensing agent. In the first step, the adamantane-bisphenol **1** and *p*-chloronitrobenzene were condensed in the presence of potassium carbonate in DMF, giving rise to the bis(4-nitrophenoxy) compound **2**. The intermediate dinitro compound **2** was then catalytically reduced to the adamantane-dietheramine **3** using hydrazine as the reducing agent and palladium as the catalyst. The yield was high (92%), and the purity was also high enough for the preparation of polymers with high molecular weights. The structures of dinitro compound **2** and diamine **3** were confirmed by elemental analysis, IR, and NMR results.

Table 1. Inherent Viscosities of Poly(amic acid)s and Film Quality of Polyimides

poly(amic acid)s		polyimides		
code	η_{inh}[a] (dL/g)	code	η_{inh}[b] (dL/g)	film quality[c]
5a	1.58	**6a**		highly brittle
5b	1.31	**6b**	0.63	flexible
5c	0.96	**6c**	1.03	flexible
5d	1.21	**6d**		flexible
5e	1.66	**6e**	0.47	slightly brittle
5f	1.21	**6f**	0.42	slightly brittle
5g	0.82	**6g**	0.70	flexible
5h	0.98	**6h**	0.63	flexible

[a] Measured at 0.5 g/dL in DMAc at 30 °C. [b] Measured at 0.5 g/dL in NMP at 30 °C. [c] Films were obtained by sequential heating of the poly(amic acid) films at 150 °C for 20 min, 180 °C for 20 min, 220 °C for 20 min, 250 °C for 20 min, and 270 °C for 20 min.

Table 2. Solubility Behavior of Polyimides[a]

polymer code	solvents[b]						
	NMP	DMAc	DMF	DMSO	*m*-cresol	THF	$CHCl_3$
6a	−	−	−	−	−	−	−
6b	+	−	−	−	+	−	−
6c	+	+h	+h	−	−	−	+
6d	+h	−	−	−	−	−	−
6e	+	+	+	+h	+	+	+
6f	+	+	+	+h	−	+	+h
6g	+	+h	+h	−	+	+	+
6h	+	+h	−	−	+	+h	+

[a] Solubility: +, soluble at room temperature; +h, soluble on heating; −, insoluble even on heating. [b] NMP: *N*-methyl-2-pyrrolidone. DMAc: *N,N*-dimethylacetamide. DMF: *N,N*-dimethylformamide. DMSO: dimethyl sulfoxide. THF: tetrahydrofuran.

Polymer Synthesis. New adamantane-based polyimides **6a**−**h** were prepared from dietheramine **3** and various aromatic tetracarboxylic dianhydrides **4a**−**h** by a conventional two-step method in which the first step was formation of the poly(amic acid) (Scheme 2). As shown in Table 1, the poly(amic acid) precursors **5a**−**h** exhibited inherent viscosities ranging from 0.82 to 1.66 dL/g and could afford free-standing films by solution casting, indicative of the formation of moderate to high molecular weight polymers. The imidization step was carried out by thermal dehydration of poly(amic acid)s by sequential stage-by-stage heating to 270 °C. Most of polyimides were soluble in polar solvents such as NMP. Therefore, the characterization of inherent viscosity was carried out without any difficulty, and the inherent viscosities of soluble polyimides were in the range of 0.42−1.03 dL/g. Probably due to the structural rigidity of the polymer chain, the film of polyimide **6a** derived from PMDA became brittle during thermal cure. The polymer films of **6e** and **6f** cracked upon creasing, possibly attributable to the increased stiffness of the polymer chains caused by the presence of polar sulfonyl and hexafluoroisopropylidene groups together with the rigid adamantane-2,2-diyl unites. The other polyimide films are flexible and tough and can be creased without cracking.

Polymer Characterization. The solubility behavior of polyimides was determined for the film samples in excess solvents. As listed in Table 2, except for the polyimide (**4a**) derived from PMDA, all of the polyimides were soluble at least in NMP. The polyimides derived from the dianhydrides having flexible bridging groups, such as O, $C(CF_3)_2$, SO_2, and $C(CH_3)_2$ groups, and bulky units like adamantylidene between aromatic rings

Scheme 2

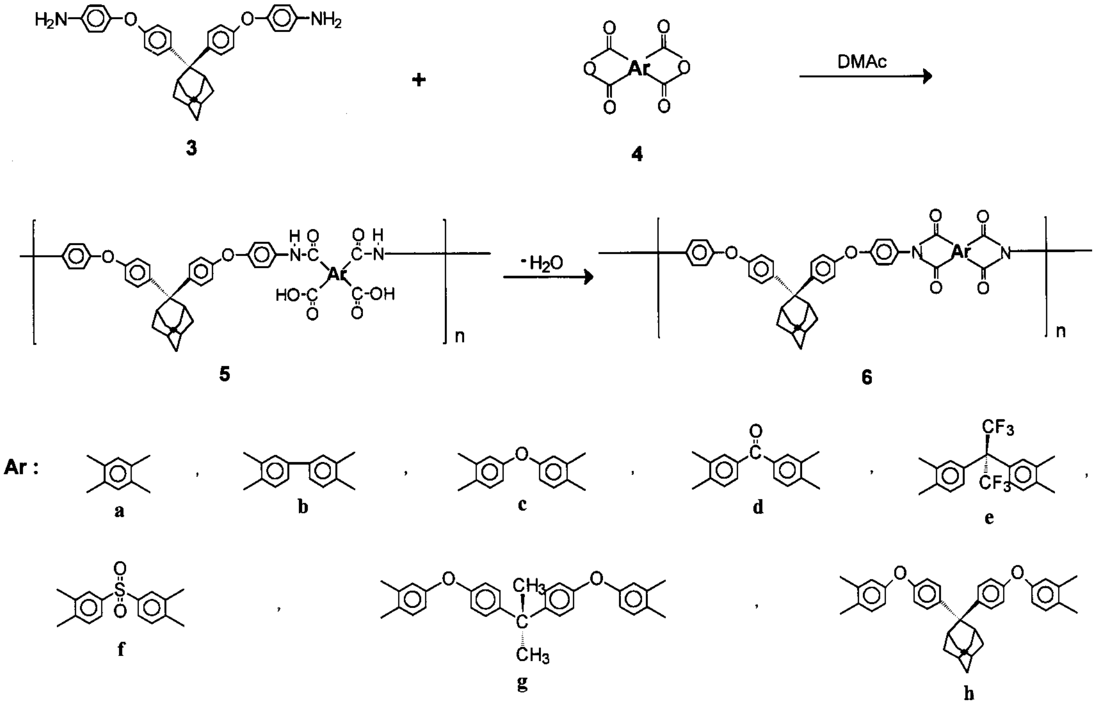


Table 3. Tensile and Thermal Properties of Polyimide Films

polymer code	tensile properties: strength at break (MPa)	tensile properties: elongation at break (%)	T_g[a] (°C)	T_s[b] (°C)	decomposition[c] temperature (°C): in N_2	decomposition[c] temperature (°C): in air	char yield[d] (%)
6a			*e* (330)	335	531	518	56
6b	87	7	308 (292)	306	546	535	53
6c	113	10	293 (268)	288	538	531	53
6d	98	9	289 (272)	286	529	525	60
6e			300 (284)	290	541	534	55
6f			303	308	508	508	34
6g	97	9	248	254	532	524	40
6h			296	293	523	518	41

[a] Baseline shifts in the second heating DSC traces, with a heating rate of 20 °C/min. Values indicated in the parentheses are those for the isomeric polyimides based on 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane reported in ref 20. [b] Softening temperatures measured by TMA (penetration method) with a load of 5 g at a heating rate of 10 °C/min. [c] Temperature at which 10% weight loss was recorded by TG at a heating rate of 20 °C/min. [d] Residual weight % when heated to 800 °C in nitrogen. [e] No discernible transitions were observed.

exhibited higher solubility and were soluble even in less polar solvents such as THF and chloroform. In general, this series of adamantane-based polyimides revealed a relatively higher solubility as compared to their isomeric polymers based on 1,3-bis[4-(4-aminophenoxy)phenyl]-adamantane reported in the literature.[20] The enhanced solubility may be due to the fact that the polymer chain based on the 2,2-isomer is more “kinked” than for the 1,3-isomer because the phenyl rings are connected to the same carbon. The bulky, kinked 2,2-adamantylidene unit inhibits close packing of polymer chains and, thus, enhances solubility of the polymers.

The crystallinity of the polyimides was evaluated by wide-angle X-ray diffraction experiments. It was found that all the polyimides showed a completely amorphous diffraction pattern due to the reason cited above. Some good-quality polyimide films were subjected to a tensile test, and the results are shown in Table 3. The polyimide films behave as strong and hard materials with the tensile strength and elongation to break between 87 and 113 MPa and 7%–10%, respectively.

Thermal properties of all of the polyimides were evaluated by thermogravimetry (TG), differential scanning calorimetry (DSC), and thermomechanical analysis (TMA). Some thermal behavior data of all of the polymers are also compiled in Table 3. All of the polyimides showed a similar TG pattern with no significant weight loss below 500 °C in air or nitrogen, but with more than 40% residue remaining when heated to 800 °C in nitrogen. The 10% weight loss temperatures of these polymers varied in the range of 508–535 °C in air and 508–546 °C in nitrogen.

The T_g's of these polyimides were recorded in the range of 248–308 °C, depending on the exact structure of the repeating unit. The softening temperatures (T_s, which may be considered as apparent T_g) of the polymer films measured by TMA were recorded between 254 and 335 °C. In most cases, the T_s values measured by TMA are comparable to the T_g values determined by DSC. As can be expected, the PMDA-derived polyimide **6a** exhibited the highest T_s due to the most rigid dianhydride structure. Incorporation of flexible linkages such as ether and isopropylidene groups into the macromolecular backbone generally leads to a decreased T_g or T_s; for example, polyimide **6g** revealed the lowest T_g and T_s in this series of polyimides.

A comparison with some adamantane-1,3-diyl isomeric polyimides reveals that the 2,2-catenation increases the T_g by 16−25 °C. Differences in barriers to molecular motion apparently are responsible for the difference in T_g. The bisphenol phenyl rings of the 1,3-isomer are relatively free to rotate around the bond axes, while those of the 2,2-isomer are constrained in their relative position and rotational freedom by steric interactions. The fact that adamantane-2,2-diyl cardo unit has a greater stiffening effect on the polymer backbone than its counterpart, adamantance-1,3-diyl, has been previously noted by Pixton and Paul.[18] They observed that the T_g of polysulfone with adamantane-2,2-diyl cardo units was 55 °C higher than that of polysulfone with adamantane-1,3-diyl units. As compared with the polyimides with fluorene-9,9-diyl unit,[3] a more common cardo structure, most of the corresponding polyimides with adamantane-2,2-diyl unit showed slightly lower T_g values by approximately 2−12 °C.

Conclusions

A new adamantane-based dietheramine, 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane, was synthesized from readily available reagents in three main steps. A series of high molar mass polyimides have been synthesized from this dietheramine monomer and various aromatic tetracarboxylic dianhydrides. All of the polyimides were noncrystalline. Most of the polyimides were organic-soluble and exhibited valuable properties such as good mechanical properties, high thermal stability, and moderate to high T_g's. As compared with their analogues prepared from 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane, this series of polyimides showed an enhanced solubility and T_g.

Acknowledgment. The authors are grateful to the National Science Council of the Republic of China for the financial support of this work.

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MA980649C