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Synthesis and characterization of new polyamide-imides containing pendent adamantyl groups

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Abstract

A new diimide-dicarboxylic acid, 4-(1-adamantyl)-1,3-bis(4-trimellitimidophenoxy)benzene (ADBTB), containing pendent adamantyl group was synthesized in three steps starting from adamantyl resorcinol. A series of new adamantyl-containing polyamide-imides (PAIs) were prepared by direct polycondensation of ADBTB and various aromatic diamines in *N*-methyl-2-pyrrolidinone (NMP) using triphenyl phosphite and pyridine as condensing agents. These PAIs produced had inherent viscosities of 0.72–0.94 dl g^{-1}. All the PAIs were readily dissolved in various solvents such as *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, pyridine, cyclohexanone and tetrahydrofuran. These PAIs were solution-cast from DMAc solutions into transparent, flexible, and tough films except for PAI-5 polymer film. Wide-angle X-ray measurement revealed that all the polymers were amorphous. These PAIs had glass transition temperatures between 230–254°C and 10% weight loss temperatures in the range of 467–491°C in nitrogen atmosphere. The polymer films had a tensile strength range of 67–110 MPa and a tensile modulus range of 2.1–2.6 GPa. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Adamantyl; Diimide-dicarboxylic acid; Polyamide-imide

1. Introduction

Aromatic polyimides are well recognized as a class of high performance materials due to their remarkable thermal and oxidative stabilities and excellent electrical and mechanical properties for long time periods of operation [1,2]. Unfortunately, strong interaction between polyimide chains and their rigid structure make them intractable. Poor thermoplastic fluidity and solubility are the major problems for wide application of polyimides. Thus, to overcome these processing problems various approaches have been carried out by incorporating flexible units such as –NHCO–, –O–, and $–SO_2–$, and some of which are commercialized [3,4].

Among them, polyamide-imide (PAI) is the most successful material, which combines the advantages of high-temperature stability and processability. In our previous studies, we have applied the phosphorylation polycondensation technique to prepare novel and soluble PAIs from imide-containing dicarboxylic acids and aromatic diamines [5–9]. This route provides significant advantages in manufacturing operations compared with conventional methods.

Adamantane is a highly symmetrical tricyclic hydrocarbon which consists of fused chair-form cyclohexane rings [10]. The unique structure of this substance is reflected in highly thermal and oxidative stabilities, and low hydrophobicity. Adamantane has been incorporated into many high-temperature polymers such as poly(ether ether ketone)s [11], polyamides [12,13], polyimides [13], polysulfones [11], and polycarbonates [14], subsequently producing increased thermal stability, solubility and glass transition temperature. However, there is limited literature reported on the synthesis and characterization of PAI containing adamantyl group.

In the present study, we report the synthesis and characterization of a series of new PAIs containing a pendent adamantyl group. A new adamantyl-containing diimide-dicarboxylic acid, 4-(1-adamantyl)-1,3-bis(4-trimellitimidophenoxy)benzene (ADBTB), was synthesized and polymerized with various synthesized diamines to obtain these PAIs. The crystallinity, solubility, thermal and tensile properties of these PAIs are also discussed.

2. Experimental

2.1. Materials

Adamantyl resorcinol (ADRL) was prepared by

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alkylating resorcinol with 1-bromoadamantane in refluxing benzene, m.p. 247–248°C (Lit. [11] 249–250°C). 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (DA-1) [15], 3,3′,5,5-tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]-propane (DA-2) [16], 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (DA-3) [17], 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene (DA-4) [18], 2,2′-dimethyl-4,4′-bis(4-aminophenoxy)biphenyl (DA-5) [19], and 2,2-bis[4-(4-aminophenoxy)phenyl]norbornane (DA-6) [20] were synthesized and purified in our laboratory according to the methods previously reported. Trimellitic anhydride (from Merck) was purified by sublimation. Triphenyl phosphite (from Merck) was used without purification. *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride before use.

2.2. Synthesis of monomer

2.2.1. 4-(1-Adamantyl)-1,3-bis(4-nitrophenoxy)benzene (ADBNB)

A mixture of ADRL (3.20 g, 13 mmol), *p*-chloronitrobenzene (4.53 g, 28.8 mmol), potassium carbonate (4.3 g, 31.2 mmol) and dry *N,N*-dimethylformamide (DMF, 30 ml) was refluxed for 8 h. The mixture was then cooled and poured into methanol–water (1:1 by volume). The crude product was recrystallized from glacial acetic acid to provide orange needles (m.p. 184–186°C) in 90% yield. The IR spectrum (KBr) exhibited absorptions at 1574 and 1341 cm^{-1} (NO_2), and 1222 cm^{-1} (C–O–C). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 162.78, 162.67, 155.07, 153.49, 142.90, 139.25, 129.31, 126.16, 125.94, 117.61, 117.14, 116.75, 113.66, 41.19, 36.81, 36.69, 28.78.

Anal. calcd for $C_{28}H_{26}O_6N_2$: C, 69.14%; H, 5.35%; N, 5.76%; found: C, 68.86%; H, 5.37%; N, 5.67%

2.2.2. 4-(1-Adamantyl)-1,3-bis(4-aminophenoxy)benzene (ADBAB)

Hydrazine monohydrate (10 ml) was added dropwise to a mixture of ADBNB, 6.0 g, (12.3 mmol), ethanol (25 ml), and a catalytic amount of 10% palladium on activated carbon (Pd/C, 0.05 g) at the boiling temperature. The reaction mixture was refluxed for 24 h, and ADBAB precipitated during this period. The mixture was then added to sufficient amount of ethanol to dissolve ADBAB and filtered to remove Pd/C. After cooling, the precipitated crystals were isolated by filtration and recrystallized from 1,2-dichlorobenzene. The yield was 79%; m.p. 176–178°C. The IR spectrum (KBr) exhibited absorptions at 3296, 3386 and 1614 cm^{-1} (N–H), and 1207 cm^{-1} (C–O–C). ^{13}C-NMR (DMSO-d_6): δ (ppm) = 158.41, 157.61, 146.30, 145.37, 145.33, 145.01, 132.61, 127.36, 120.67, 120.23, 114.98, 114.78, 109.32, 106.51, 40.64, 36.51, 35.86, 28.40. ^{1}H-NMR (DMSO-d_6): δ(ppm) = 7.10 (d,1H), 6.68–6.51 (m, 8H), 6.37 (d, 1H), 6.17 (s, 1H), 4.92 (s, 4H), 2.04–1.66 (m, 15H).

Anal. calcd for $C_{28}H_{30}O_2N_2$: C, 78.84%; H, 7.09%; N, 6.57%; found: C, 78.49%; H, 7.21%; N, 6.45%

2.2.3. 4-(1-Adamantyl)-1,3-bis(4-trimellitimidophenoxy)benzene (ADBTB)

A flask was charged with 0.73 g (1.73 mmol) of ADBAB, 0.68 g (3.54 mmol) of trimellitic anhydride, and 5 ml of DMAc. The mixture was stirred at room temperature for 5 h under argon atmosphere. To the solution 2.4 ml of acetic anhydride and 1.5 ml of pyridine were added with stirring at room temperature for 1 h and then the mixture was heated at 100°C for 4 h. The mixture was then cooled and poured into methanol. The yellowish precipitate, ADBTB, was filtered off. It was purified by extraction with hot ethanol using a Soxhlet extractor and subsequently dried in a vacuum oven at 70°C for 24 h. Yield: 83%, m.p. 338°C (by differential scanning calorimetry, DSC). The IR spectrum (KBr) exhibited absorptions at 2500–3500 cm^{-1} (–OH, carboxylic acid), 1770 cm^{-1} (imide C=O asymmetrical stretching), and 1715 cm^{-1} (imide C=O symmetrical stretching and acid C=O stretching). ^{13}C-NMR (DMSO-d_6): δ (ppm) = 165.98, 165.96, 165.94, 165.92, 165.43, 156.34, 155.78, 155.72, 154.79, 136.16, 135.96, 135.17, 134.58, 131.73, 128.81, 128.70, 128.34, 126.64, 126.33, 123.50, 123.09, 118.41, 118.15, 113.88, 111.21, 40.72, 36.36, 36.13, 28.33. ^{1}H-NMR (DMSO-d_6): δ (ppm) = 8.33 (d,2H), 8.18 (s, 2H), 7.97 (d, 2H), 7.42–7.31 (m, 5H), 7.11–7.01 (m, 4H), 6.79 (d, 1H), 6.51 (s, 1H).

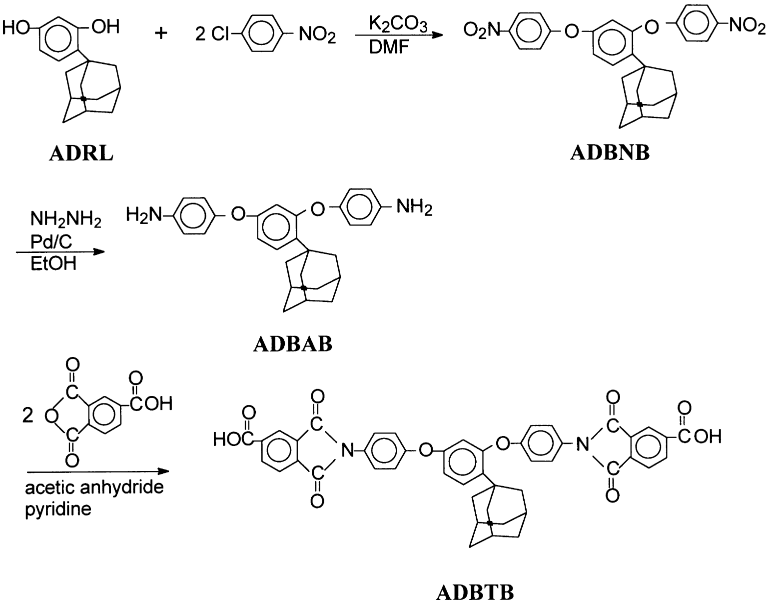
Anal. calcd for $C_{46}H_{34}O_{10}N_2$: C, 71.31%; H, 4.42%; N, 3.62%; found: C, 71.61%; H, 4.21%; N, 3.33%

2.3. Preparation of polymer

A mixture of 0.542 g (0.7 mmol) of diimide-dicarboxylic acid ADBTB, 0.362 g (0.7 mmol) of diamine DA-1, 0.25 g of calcium chloride, 0.6 ml of triphenyl phosphite, 0.6 ml of pyridine, and 3.0 ml of NMP was heated with stirring at 100°C for 2 h under argon stream. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, producing a yellow stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100°C under vacuum for 24 h. The inherent viscosity of the polymer was 0.72 dl g^{-1}. The IR spectrum (film) exhibited absorptions at 1768, 1715, 1670 cm^{-1} (C=O) and 3292 cm^{-1} (N–H). All the other PAIs were prepared using a similar procedure.

2.4. Measurements

IR spectra were recorded in the range 4000–400 cm^{-1} on a JASCO IR-700 spectrophotometer. The inherent viscosities of all polymers were measured in DMAc at a concentration 0.5 g dl^{-1} at 30°C using the Ubbelohde viscometer. Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer (Philips model PW 1710) using Ni-filtered CuKα radiation (35 kV, 25 mA). The scanning rate was



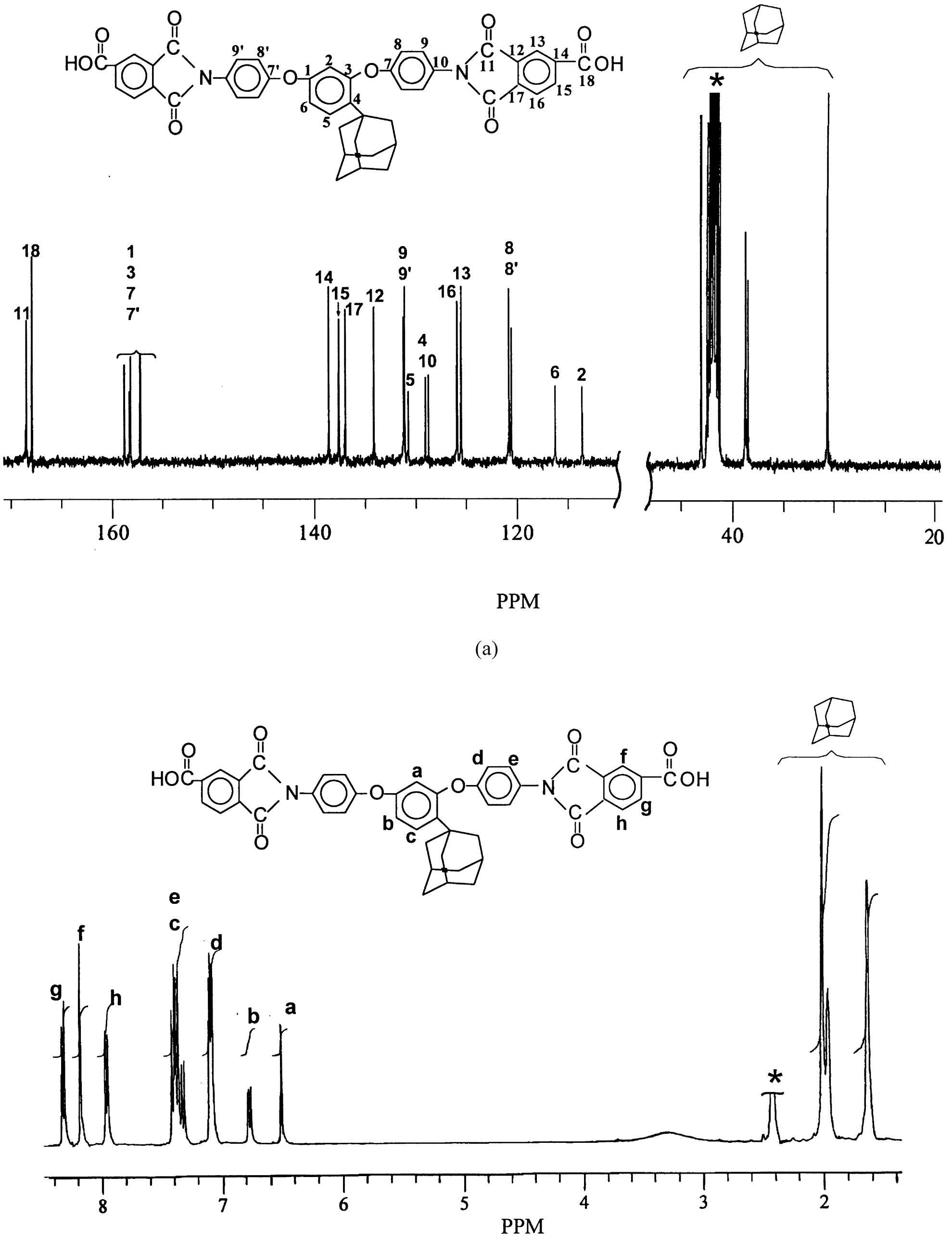
Scheme 1.

3°C min^{-1}. Samples for thermogravimetric analysis (Du Pont 2200) were heated under nitrogen or air (60 cm^3 min^{-1}) at a heating rate of 10°C min^{-1}. The DSC analysis was performed on a DuPont 2100 differential scanning calorimeter. Tensile properties were determined from stress–strain curves obtained with an Orientec Tensilon with a load cell of 10 kg. A gauge of 3 cm and a strain rate of 20 mm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (4 mm wide, 6 cm long, and ca. 0.1 mm thick).

3. Results and discussion

3.1. Synthesis of diimide-dicarboxylic acid

The synthetic route to the new adamantyl-containing diimide-dicarboxylic acid monomer, ADBTB, is shown in Scheme 1. The bisphenol compound, adamantyl resorcinol (ADRL), was prepared by alkylating resorcinol with 1-bromoadamantane in refluxing benzene without adding any catalyst [11]. The compound ADRL was reacted with *p*-chloronitrobenzene in the presence of potassium carbonate and afforded the dinitro compound ADBNB. It was obtained in high yield (90%) and purified by recrystallizing in glacial acetic acid. The catalytic hydrogenation of dinitro compound ADBNB to the diamine compound ADBAB was accomplished by using hydrazine monohydrate and catalytic amount of Pd/C as a reducing agent. The structures of these compounds were confirmed by elemental analyses as well as IR and NMR spectroscopy. For instance, the reduction of dinitro compound to the diamine could be monitored by IR spectroscopy. The dinitro compound ADBNB showed characteristic absorptions at 1341 and 1574 cm^{-1} associated with the nitro group, whereas the diamine compound ADBAB lacked these absorption bands. The latter displayed new absorptions at 3296 and 3386 (N–H stretching) and 1614 cm^{-1} (N–H deformation), respectively. The diimide-dicarboxylic acid compound, ADBTB, was prepared by the condensation of ADBAB with two mole equivalents of trimellitic anhydride. ADBAB was reacted with trimellitic anhydride in DMAc to form an amic acid intermediate at room temperature. A subsequent cyclodehydration reaction was carried out by adding dehydrating agents such as a mixture of acetic anhydride and pyridine. The IR spectrum of ADBTB showed absorption bands around 3500–2500 (COOH), 1770 (symmetric imide C=O stretching), 1715 (acid C=O stretching and asymmetric imide C=O stretching), and 1374 cm^{-1} (imide ring vibration, axial), confirming the presence of imide ring and carboxylic acid groups in the structure. ^{13}C-NMR spectrum (Fig. 1(a)) of ADBTB reveals that carbonyl carbons of carboxylic acid and imide groups resonate in the downfield at 165.43 and 165.98 ppm, respectively. The chemical shifts in the upfield region (40.72–28.33 ppm) are ascribed to the resonance of aliphatic adamantyl group. In the ^{1}H-NMR spectrum (Fig. 1(b)), the resonance signal in the downfield region (8.33–7.97 ppm) is ascribed to the protons of trimellitimido group. The area of integration for the protons is in accordance with the assignment. However, the proton for carboxylic acid group of ADBTB in the ^{1}H-NMR spectrum was not observed. This was probably due to the fast exchange of this proton with the trace amount of moisture associated with the solvent [5,6].The results provided further clear evidence that the diimide-dicarboxylic acid monomer prepared herein correlated with the proposed structure.



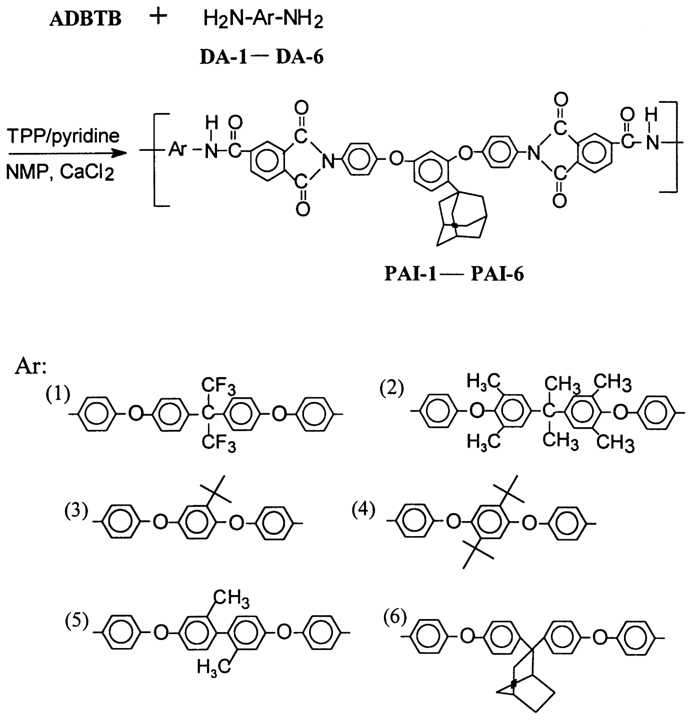
(a)

(b)

Fig. 1. NMR spectra of diimide-dicarboxylic acid ADBTB in DMSO-d_6: (a) ^{13}C-NMR; and (b) ^{1}H-NMR ($*$: solvent peak).

3.2. Synthesis of PAIs

The new polyamide-imides (PAIs) were prepared by phosphorylation polycondensation of diimide-dicarboxylic acid ADBTB with various synthesized aromatic diamines using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). The yield, inherent viscosity and film quality of the polymers are summarized in Table 1. All the polycondensations proceeded readily in a homogeneous solution. Tough and stringy precipitates formed when the viscous polymer solutions were trickled into the stirring methanol. All the polymers were obtained in high yields (95–98%), and the inherent viscosities were 0.72–0.94 dl g^{-1} which were measured in DMAc solutions. The transparent, tough and flexible polymer films, except PAI-5 film, were obtained by casting from their DMAc solutions. These polymer films were further characterized by X-ray measurement and mechanical analysis. The IR spectra of these PAIs revealed the characteristic absorptions of imide groups at 1768, 1717 and 1366 cm^{-1}, and those of the amide groups around 3290 and 1670 cm^{-1}. For comparison, polymer Ref having no adamantyl substituent was prepared to



Scheme 2.

examine the influence of the adamantyl group on the polymer solubility and thermal stability.

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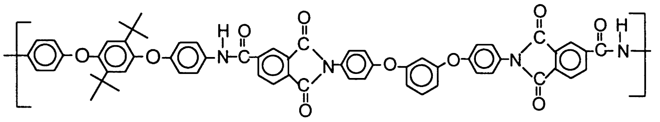

3.3. Polymer characterization

The crystallinity of the PAIs was estimated by means of wide-angle X-ray diffractograms. The X-ray diffractograms of these polymer films revealed that all the PAIs exhibited amorphous patterns. The amorphous behavior of these PAIs is attributed to the bulky substituent groups which significantly increased the disorder in chains and, therefore, caused less chain packing [21]. In addition, the adamantyl group also decreases the intermolecular force such as hydrogen bonding between the polymer chains, subsequently causing a decrease in crystallinity. The wide-angle X-ray diffraction diagrams of PAI-4 and Ref are illustrated in Fig. 2. It was observed that polymer PAI-4 showed a fair amorphous pattern. However, Ref having no adamantyl group showed a weak crystalline pattern with a reflection

Table 1
Preparation and solubility of various polyamide-imides (abbreviations: DMAc, *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; THF: tetrahydrofuran)

Polymer code	Yield (%)	η_{inh}[a] (dl g^{-1})	Film quality	Solubility[b]						
				DMAc	DMF	DMSO	Pyridine	Cyclohexanone	THF	Chloroform
PAI-1	95	0.72	Tough and flexible	++	++	++	++	++	++	+ −
PAI-2	96	0.73	Tough and flexible	++	++	++	++	++	++	+ −
PAI-3	96	0.79	Tough and flexible	++	++	+	++	++	++	+ −
PAI-4	98	0.94	Tough and flexible	++	++	+	++	+	++	+ −
PAI-5	97	0.83	Brittle	++	++	+	++	++	++	+ −
PAI-6	96	0.75	Tough and flexible	++	++	+	++	++	++	+ −
Ref	98	1.01	Tough and flexible	++	++	+ −	+	−	−	−

[a] Measured in DMAc at a concentration of 0.5 g dl^{-1} at 30°C.

[b] Solubility: + + :soluble at room temperature; +: soluble on heating at 60°C; + − : partial soluble at 60°C; −: insoluble.

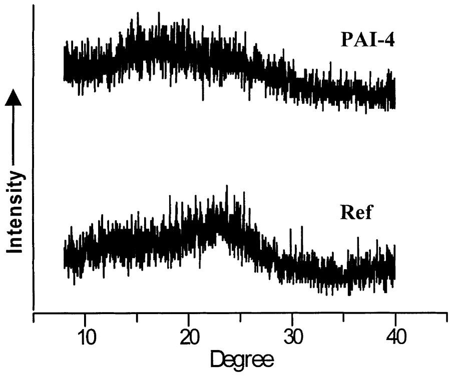

Fig. 2. Wide-angle X-ray diffractograms of PAI-4 and Ref.

peak around $2\theta = 23°$. Obviously, the incorporation of the adamantyl group effectively reduced the crystallinity of the polymer.

The solubility behavior of all PAIs and Ref is also summarized in Table 1. It was observed that all the adamantyl-containing PAIs exhibited good solubility in a variety of solvents such as DMAc, DMF, dimethyl sulfoxide (DMSO), pyridine, cyclohexanone and tetrahydrofuran at room temperature or upon heating at 60°C. In contrast, polymer Ref having no adamantyl substituent showed less solubility than polymer PAI-4. This result demonstrates that the PAIs with adamantyl substituent displayed good solubility in organic solvents owing to the presence of the bulky substituent. The bulky substituent probably disturbs dense chain packing of the polymer chain; consequently, the solvent molecules can penetrate easily to solubilize the chain. It is worth noting that the PAIs herein showed slightly higher solubility compared to their analogous PAIs containing *tert*-butyl substituent [5]. This shows that the adamantyl group in the polymer side chain has more effect on enhancing solubility of the polymers than the *tert*-butyl group. The higher stiffness of the adamantyl substituent, compared with the *tert*-butyl group, should be responsible for this result.

The thermal properties of these PAIs are summarized in Table 2. All the PAIs displayed distinct glass transitions on the second heating DSC traces, whereas endotherms or exotherms are completely lacking. These PAIs had glass transition temperatures (T_gs) in the range of 230–254°C. Notably, PAI-4 polymer having two butyl substituents gives a higher T_g than PAI-3 which has only one butyl substituent. This is due to the fact that PAI-4 polymer containing symmetric di-*tert*-butyl substituents packs efficiently while the polymer containing unsymmetric mono *tert*-butyl substituent packs quite loosely. Therefore, PAI-4 has smaller free volume and higher T_g than PAI-3 [7,22].

The TGA traces reveal that all the PAIs do not decompose around or below 450°C in nitrogen and air atmosphere. Their decomposition temperatures of 10% weight loss (T_{d10}) were in the range of 467–491°C in nitrogen. The thermal properties of polymer Ref are also listed in Table 2. It was found that Ref displayed lower T_g and T_{d10} values than polymer PAI-4, indicating that incorporating adamantyl group into polymer backbone imparts greater thermal stability of polymers.

The mechanical properties of the polymer films are also summarized in Table 2. They had tensile strength of 67–110 MPa, elongation at break of 5–11%, and tensile modulus of 2.1–2.6 GPa. It was observed that PAI-4 containing symmetric di-*tert*-butyl substituents on the polymer chain showed high tensile strength value and the highest tensile modulus.

4. Conclusions

This study had successfully synthesized a new diimide-dicarboxylic acid, ADBTB, containing a rigid and bulky adamantyl pendent group. A series of novel PAIs were prepared by the direct polycondensation from the diimide-dicarboxylic acid with various diamines. These PAIs exhibited amorphous nature as well as mechanical properties. The results presented herein also demonstrate clearly that incorporating the adamantyl group into the polymer backbone remarkably enhanced the solubility and thermal stability of the polymers.

Table 2
Thermal and mechanical properties of various polyamide-imides

Polymer code	T_g[a] (°C)	T_{d10}[b] (°C)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
PAI-1	230	489	87	7	2.1
PAI-2	238	467	93	8	2.1
PAI-3	244	470	110	11	2.3
PAI-4	254	481	103	8	2.6
PAI-5	233	491	–[c]	–[c]	–[c]
PAI-6	241	470	67	5	2.1
Ref	243	469	94	10	2.3

[a] Glass transition temperature (T_g) measured by DSC at a heating rate of 20°C min^{-1}.

[b] Temperature at which 10% weight loss (T_{d10}) was recorded on TGA at a heating rate of 10°C min^{-1}.

[c] Polymer film was too brittle to be measured.

Acknowledgements

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