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Synthesis and characterization of new soluble cardo poly(amide–imide)s derived from 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]norbornane

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Abstract

A series of new soluble poly(amide–imide)s were prepared from the diimide-dicarboxylic acid, 2,2-bis[4-(4-trimellitimidophenoxy) phenyl]norbornane, and various diamines by the direct polycondensation in *N*-methyl-2-pyrrolidinone containing $CaCl_2$, using triphenyl phosphite and pyridine as condensing agents. All the polymers were obtained in quantitative yields with inherent viscosities of 1.01–1.42 dL g^{-1}. Gel permeation chromatography (GPC) of the polymers showed number-average and weight-average molecular weight up to 67,300 and 118,000, respectively. The poly(amide–imide)s were amorphous and were readily soluble in various solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), pyridine, cyclohexanone and tetrahydrofuran. Tough and flexible films were obtained by casting their DMAc solution. The films had tensile strength of 89–110 MPa and a tensile modulus range of 1.8–2.2 GPa. The glass transition temperatures of the polymers were determined by DSC method and they were in the range of 265–295 °C. The polymers were fairly stable up to a temperature around or above 450 °C, and lose 10% weight in the range of 472–504 °C and 490–520 °C in nitrogen and air, respectively.

Keywords: Cardo; Poly(amide–imide)s; Direct polycondensation

1. Introduction

Aromatic polyimides possess many desirable characteristics such as high thermal stability and excellent physical properties. However, they are generally insoluble and infusible after conversion from their poly(amic acid) precursors [1–3]. Replacement of polyimides by copolyimides such as poly(amide–imide)s may be useful to tackle the intractability of polyimides. Poly(amide–imide)s are also expected to have the advantages of polyamides and polyimides, such as excellent mechanical and thermal properties as well as solvent resistance. A notable example is Torlon® (Amoco Chemicals Corporation) which was prepared from trimellitic anhydride (TMA) and various diamines [4].

Several approaches have been carried out successfully for the synthesis of poly(amide–imide)s [5–7]. Thus, the triphenyl phosphite promoted polycondensation for the synthesis of polyamides has been reported by Yamazaki and Higashi [8]. This technique has been extended for the synthesis of poly(amide–imide)s in our laboratory. The direct polycondensation route avoids the moisture-sensitive acid chloride or isocyanates used in the conventional methods, thus providing significant advantages in manufacturing operations.

It is known that the introduction of 'cardo' groups into the backbone of polymers is an effective approach for improving solubility and thereby processability of polyimides [9]. Cardo polymers exhibit a valuable set of properties: the combination of an increased thermal stability with an increased solubility in organic solvents [9–21]. In our previous works [22–24], we have found several means for the introduction of cardo groups such as cyclododecylidene, adamantane, tricyclo[5.2.1.0 [2,6]]decane, and *tert*-butylcyclohexylidene groups in the polymer backbone. In these attempts solubility of polyamides was enhanced while the high glass transition temperature and thermal stability were maintained.

In the present study, we will report the synthesis of a series of novel poly(amide–imide)s with pendent norbornyl

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groups along the polymer chain. The new diimide-dicarboxylic acid, 2,2-bis[4-(4-trimellitidophenoxy)phenyl]norbornane (**BTPN**), containing norbornyl group was first synthesized and polymerized with various diamines to prepare various novel poly(amide–imide)s. The incorporation of cardo and bulky norbornyl group into polyamide backbones is expected to increase the solubility, thermal and mechanical properties of the polymers. The characterization of new polymers such as crystallinity, thermal, physical and mechanical properties are also investigated.

2. Experimental

2.1. Materials

The starting diamine 2,2-bis[4-(4-aminophenoxy)phenyl]norbornane (**BAPN**) was synthesized according to the method reported in a previous study [23]. Trimellitic anhydride (from Merck) was purified by sublimation. *N*-Methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride prior to polymerization.

2.2. Monomer synthesis

2.2.1. 2,2-Bis[4-(4-trimellitimidophenoxy)phenyl] norbornane (**BTPN**)

A flask was charged with 1.82 g (3.93 mmol) of 2,2-bis[4-(4-aminophenoxy)phenyl]norbornane (**BAPN**), 1.66 g (8.65 mmol) of trimellitic anhydride and 20 ml of glacial acetic acid. The heterogeneous mixture was refluxed for 12 h. The reaction mixture was filtered to yield a yellow solid, which was rinsed with ethanol to remove acetic acid. The obtained crude product was washed several times with ethanol, reprecipitated from tetrahydrofuran (THF) into *n*-hexane, dried in vacuum at 100 °C for 24 h and collected as yellow solid. Yield: 88%, mp 351 °C (by DSC). The IR spectrum (KBr) exhibited absorptions at 2500–3470 (–OH, carboxylic acid), 1770 (imide C=O), and 1723 cm^{-1} (imide C=O symmetrical stretching and acid C=O stretching). ^{1}H NMR (DMSO-d_6): δ (ppm) = 8.37 (d, 2H), 8.24 (s, 2H), 8.01 (d, 2H), 7.43 (d, 4H), 7.38 (d, 4H) 7.05 (d, 4H), 6.94 (d, 4H), 3.28–1.09 (m, 10H). ^{13}C NMR (DMSO-d_6): δ (ppm) = 175.7, 168.0, 167.5, 158.1, 155.1, 154.8, 149.1, 145.3, 137.9, 136.8, 136.0, 133.2, 130.5, 130.1, 129.5, 127.8, 124.9, 124.6, 119.8, 119.6, 55.6, 44.2, 43.4, 37.8, 30.1, 29.3, 28.9, 24.2; Anal. calcd for $C_{49}H_{34}O_{10}N_2$: C, 71.52%; H, 4.19%; N, 3.45%; found: C,71.42%; H, 4.27%; N, 3.31%.

2.3. Polymer Synthesis

2.3.1. Synthesis of polymer ***PAI-1***

A mixture of 0.3317 g (0.6 mmol) of diamine **DA-1**, 0.5187 g (0.6 mmol) of **BTPN**, 0.3 g of calcium chloride, 0.6 ml of triphenyl phosphite, 0.6 ml of pyridine, and 3 ml of NMP was refluxed for 3 h. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100 °C under vacuum. Yield: 98%. The inherent viscosity of the polymer in DMAc was 1.01 dL g^{-1}, measured at a concentration of 0.5 g dL^{-1} at 30 °C. The IR spectrum (KBr) exhibited absorptions at 3234 (N–H), 1768 (imide C = O), 1736 (C = O imide and amide) and 1367 cm^{-1}(C–N). ^{1}H NMR (DMSO-d_6): δ (ppm) = 10.83 (s, 2H), 8.56 (s, 2H), 8.09 (s, 2H), 8.01 (d, 2H), 7.60 (d, 4H), 7.44 (d, 4H), 7.22 (s, 4H), 7.17 (s, 4H), 7.15 (d, 12H), 7.01 (s, 4H), 2.87 (s, 2H), 2.33–1.16 (m, 10H). ^{13}C NMR (DMSO-d_6): δ(ppm) = 169.1, 169.0, 166.2, 164.8, 164.5, 164.2, 160.9, 159.3, 156.2, 154.0, 142.7, 137.8, 136.1, 136.0, 134.0, 133.6, 131.4, 130.9, 130.3, 128.9, 128.7, 125.3, 124.0, 122.0, 120.7, 120.5, 120.2, 120.1, 119.1, 56.5, 45.3, 38.7, 30.5, 30.3, 30.1, 29.9, 29.7, 29.5.

All other PAIs were prepared similarly.

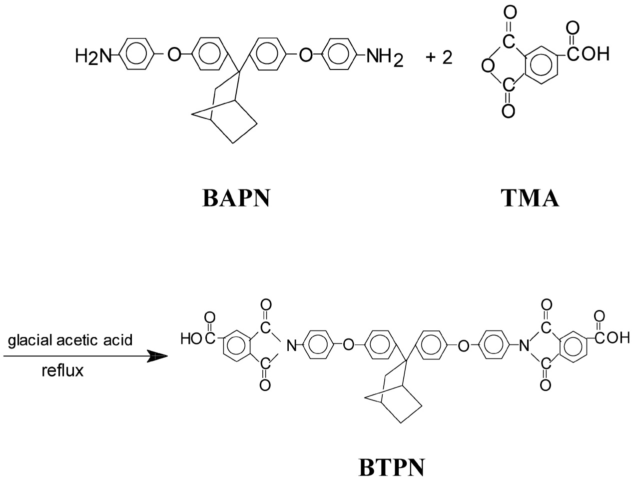
2.4. Measurements

Inherent viscosities of all polymers were measured using an Ubbelohde viscometer. Elemental analysis was performed on a Perkin–Elmer 2400 instrument. NMR spectra were obtained using a Jeol EX-400 operating at 399.65 MHz for proton and 100.40 MHz for carbon. Wide-angle X-ray diffraction patterns were obtained at room temperature with film specimens on an X-ray diffractometer (Philips model PW 1710) using Ni filtered Cu–Kα radiation (30 kV, 25 mA). Samples for thermogravimetric analysis (ULVAC, model 7000) were heated under nitrogen or air (60 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1}. Differential scanning calorimetry (DSC) was performed on a Du Pont 2000 differential scanning calorimeter. Mechanical properties were determined from stress–strain curves obtained on an Orientec Tensilon with a load cell of 10 kg. A gauge of 3 cm and a strain rate of 2 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens of dimensions 0.5 cm wide, 6 cm long, and ca. 0.05 mm thick. Weight-average ($\overline{Mw}$) and number-average molecular weights ($\overline{Mn}$) were determined by gel permeation chromatography (GPC). Four Shodex (KD-801, KD-802.5, KD-804, KD-805) columns 300 × 8.0 mm (4×10^6, 4×10^5, 2×10^4, 1500 Å in a series) were used for GPC analysis with *N*,*N*-dimethylformamide (DMF) (0.8 ml min^{-1}) as the eluent. The eluents were monitored with a RI detector (JASCO model 830). Polystyrene was used as the standard.

3. Results and discussion

3.1. Synthesis of monomer

The diimide-dicarboxylic acid monomer **BTPN** was prepared according to the route illustrated in Scheme 1. The norbornyl-containing diamine, 2,2-bis[4-(4-aminophenoxy) phenyl]norbornane (**BAPN**), was reacted with two mole equivalents of trimellitic anhydride in refluxing glacial acetic acid. The addition reaction between the amino and anhydride groups, as well as subsequent cyclodehydration reaction was carried out in the heterogeneous solution. After purification by rinsing with ethanol, the diimide-dicarboxylic acid monomer **BTPN** was reprecipitated from THF into *n*-hexane. The structure of the diimide-dicarboxylic acid monomer **BTPN** was confirmed by elemental analysis and IR and NMR spectroscopies. Elemental analysis data of 2,2-bis[4-(4-trimellitimidophenoxy)phenyl] norbornane (**BTPN**) are listed in the experimental section. The chemical structure of the newly synthesized monomer was confirmed by the good agreement of the elemental analysis values with those of the calculated values. The IR spectrum showed absorption bands around 2500–3470 (–OH, carboxylic acid), 1770 (imide C=O asymmetrical stretching), and 1723 cm^{-1} (imide C=O symmetrical stretching and acid C=O stretching), confirming the presence of imide ring and carboxylic acid groups in the structure. ^1H NMR and ^{13}C NMR spectral data of 2,2-bis[4-(4-trimellitimidophenoxy)-phenyl]norbornane (**BTPN**) are listed in the experimental section. It was observed that carbonyl carbons of carboxylic acid and imide groups resonate in the downfield at 175.7(imide), and 168.0 and 167.5 ppm(carboxylic acid), respectively. The resonance signals at downfield regions (8.37–8.01 ppm) in the ^1H NMR are ascribed to the protons of trimellitimido group. The area of integration for the protons is in accordance with the assignment. These results provide clear evidence to the proposed structure for the diimide-dicarboxylic acid monomer **BTPN**.



Scheme 1. Synthesis route for **BTPN**.

3.2. Synthesis of the poly(amide–imide)s

Direct polycondensation of a dicarboxylic acid with a diamine using triphenyl phosphite (TPP) and pyridine as condensing agent to form amide bonds is an efficient way to obtain polyamides of moderate to high degree of polymerization on a laboratory scale. This method was successfully applied to the preparation of PAIs (**PAI-1**–**PAI-5**) from diimide-dicarboxylic acid (**BTPN**) with various diamines (**DA-1**–**DA-5**) (Scheme 2). All the polymerizations in NMP proceeded homogeneously.

The PAIs were obtained in almost quantitative yields (yields were above 95%), and had inherent viscosity values ranging between 1.01–1.42 dL g^{-1} (Table 1). Number-average ($\overline{Mn}$) and weight-average ($\overline{Mw}$) molecular weights of the polymers were found to be in the range of 33,000–67,300 and 55,400–118,000, respectively (Table 1). The structure of PAIs was confirmed by elemental analysis and IR and NMR spectroscopies.

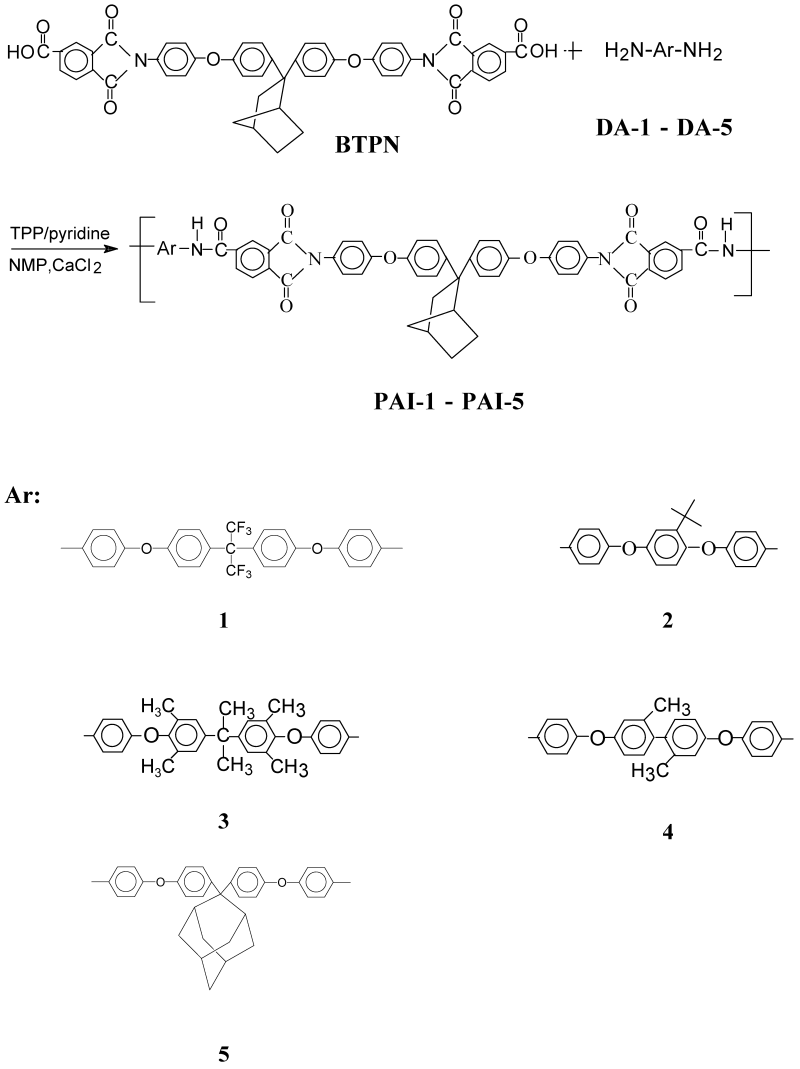
Elemental analysis data of poly(amide–imide)s are listed in the Table 1. The chemical structures of these newly synthesized polymers were confirmed by the good

Table 1
Inherent viscosity, molecular weight and elemental analysis of various poly(amide–imide)s

Polymer code	η_{inh}[a] (dL g^{-1})	$\overline{Mn}$[b] ($\times 10^{-4}$)	$\overline{Mw}$[b] ($\times 10^{-4}$)	$\overline{Mw}/\overline{Mn}$[b]	Elemental analysis (%)			
						C	H	N
PAI-1	1.01	3.72	6.36	1.71	Calcd	70.59	3.90	4.33
					Found	68.10	3.82	4.33
PAI-2	1.18	6.73	11.8	1.75	Calcd	75.92	4.85	4.99
					Found	74.93	5.05	4.38
PAI-3	1.19	3.30	5.54	1.68	Calcd	77.40	5.20	4.51
					Found	75.71	4.73	4.65
PAI-4	1.42	3.85	6.47	1.68	Calcd	76.91	4.65	4.78
					Found	75.59	5.33	4.32
PAI-5	1.10	3.85	6.35	1.65	Calcd	77.98	5.12	4.38
					Found	74.61	4.86	4.65

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

[b] Measured by GPC in DMF, polystyrene was used as standard.



Scheme 2. Synthesis of Poly(amide–imide)s.

agreement of the elemental analysis values with those of the calculated values. IR spectra of these PAIs showed the characteristic absorptions of imide groups at 1768, 1736 cm^{-1}, and those of the amide group around 3234 cm^{-1}. The NMR spectral data of polymer **PAI-1** are listed in the experimental section. The resonance signal at 169.1 and 169.0(imide) and 164.8 ppm (amide) in the ^{13}C NMR are ascribed to the carbon of imide and amide group, respectively. The transparent, tough and flexible polymer films obtained by casting their DMAc solutions were further characterized by wide-angle X-ray measurement and mechanical analysis.

Table 2
Solubility of various poly(amide–imide)s

Polymer code	Solvent[a]				
	DMF	DMSO	Pyridine	Cyclohexanone	THF
PAI-1	++	+	++	++	+ −
PAI-2	++	+ −	++	+ −	−
PAI-3	++	+	++	+ −	+ −
PAI-4	++	+ −	++	+ −	−
PAI-5	++	+ −	++	+ −	−

DMF, *N*,*N*-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran.

[a] Solubility: ++ soluble at room temperature; + soluble on heating at 70 °C; + − partially soluble at 70 °C; − insoluble at 70 °C.

3.3. Properties of polymers

Solubilities of the PAIs in several organic solvents at 3.0% (w/v) are summarized in Table 2. Remarkably, all these PAIs were easily soluble at room temperature in polar solvents such as *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as well as in less polar solvents such as pyridine, cyclohexanone and even tetrahydrofuran. The excellent solubility of these PAIs could be attributed to the presence of the norbornane groups, which inhibit the dense packing of the polymer chains. Therefore, the solvent molecule could easily penetrate into the polymer chains [22].

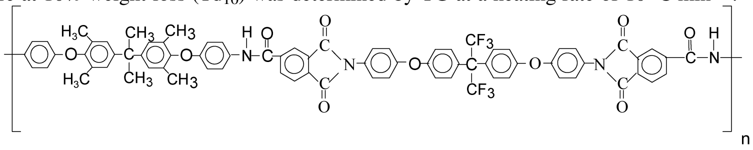
Table 3
Thermal and mechanical properties of various poly(amide–imide)s

Polymer code	T_g[a] (°C)	Td_{10}[b] (°C) In nitrogen	In air	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
PAI-1	267	504	504	94	9	1.9
PAI-2	265	480	490	89	8	1.8
PAI-3	276	472	498	92	9	1.9
PAI-4	273	498	520	100	9	2.0
PAI-5	295	494	511	110	10	2.2
Ref[c]	242	455	–	90	9	1.8

[a] From DSC measurements conducted at a heating rate of 10 °C min^{-1}.

[b] Temperature at 10% weight loss (Td_{10}) was determined by TG at a heating rate of 10 °C min^{-1}.

[c] Ref:



The wide-angle X-ray diffraction patterns of PAIs indicated that the polymer films were highly amorphous. The highly amorphous nature of the polymers could be attributed to the structural modification through the incorporation of the bulky pendent norbornyl groups. The incorporation of bulky pendent norbornyl groups might decrease the inter-molecular forces between the polymer chains due to a less dense packing of polymer chain as compared to the unsubstituted polymers [9,22]. Therefore, crystallization tendency is markedly lowered and the solubilities are significantly enhanced.

Thermal properties of the PAIs were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are tabulated in Table 3. Glass transition temperatures (Tg's) of PAIs were found to be in the range of 265–295 °C. No melting endotherm was observed in the DSC curves. As expected **PAI-5**, due to the presence of rigid adamantane group it exhibited a higher Tg (295 °C) than commercial PAI, Aron (Amoco, Tg = 272 °C) [24] while **PAI-3** and **PAI-4** showed Tg similar to that of the latter. In general, the chain rigidity increases due to the pendent cardo group, which restricts the free rotation of the polymer backbone. Hence, the polymers showed high glass transition temperature [9,24–26]. TGA measurement was conducted in nitrogen and in air atmospheres. The polymers exhibited a one-step pattern of decomposition with no significant weight loss below 450 °C in nitrogen and air. As listed in Table 3, the temperatures at 10% weight loss (Td_{10}), examined by TG analysis, showed values ranging from 472–504 °C in nitrogen and 490–520 °C in air. Representative TGA diagram of **PAI-4** (a) in air and (b) in nitrogen are shown in Fig. 1.

The higher Td_{10} in air may be due to oxidation of alicyclic norbonyl groups, to form carbonyl (C=O) and hydroxy (O–H) groups causing weight gain [27,28]. Polymer **PAI-4** containing biphenyl unit had the highest

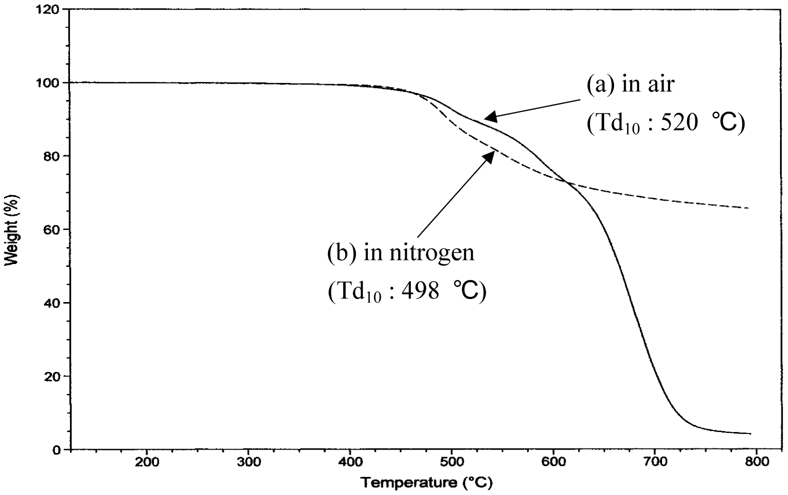
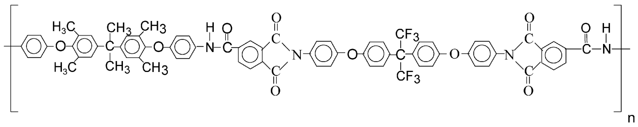


Fig. 1. The thermogravimetric analysis diagram of **PAI-4** (a) in air (—); (b) in nitrogen (···).

thermal stability in nitrogen and air atmospheres. For comparison, the thermal properties of an analogous polymer **Ref** having hexafluoroisopropylidene groups [29], which was derived from **DA-3** are also listed in Table 3. It was observed that the polymer **PAI-3** showed higher Tg value and thermal decomposition temperatures (Td_{10} values) than polymer **Ref**. That is, the norbornyl-containing poly(amide–imide)s showed better thermal stability than those bearing hexafluoroisopropylidene units. Obviously, the incorporation of the norbornyl group into the polymer backbone has enhanced the thermal resistance.

Ref:



The mechanical properties of the PAIs films are also summarized in Table 3. The films had tensile strength of 89–110 MPa, an elongation at break range of 8–10%, and a tensile modulus range of 1.8–2.2 GPa. Most of the polymer films exhibited high tensile strength, indicating that they are strong materials.

4. Conclusions

A New norbornyl-containing diimide-dicarboxylic acid monomer **BTPN** was successfully prepared in high purity and used to synthesize a series of poly(amide–imide)s (PAIs). These PAIs exhibited excellent solubility in various organic solvents and polymer films could be obtained by casting their DMAc solutions. The PAIs were amorphous and showed good mechanical properties as well as high thermal stability. The norbornyl-containing poly(amide–imide)s showed better thermal stability than those bearing hexafluoroisopropylidene and biphenyl units. These poly(amide–imide)s could be considered as new processable high-performance polymeric materials.

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