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Synthesis and characterization of new poly(amide–imide)s containing 4,9-diamantane moieties in the main chain

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A series of new poly(amide–imide)s were synthesized by direct polycondensation of 4,9-bis(trimellitimido)-diamantane (**1**) with various aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) containing lithium chloride. The poly(amide–imide)s had medium and high number-average molecular weights (M_n) of 79 000–255 000. The new polycyclic monomer **1** was synthesized from 4,9-diaminodiamantane with trimellitic anhydride. Dynamic mechanical analysis (d.m.a.) revealed that the glass transition of the poly(amide–imide) derived from 4,4′-oxidianiline appeared at ~290°C. D.m.a. results also indicated that poly(amide–imide)s remained stable at high temperatures and maintained good mechanical properties ($G' > 10^8$ Pa) up to high temperature (300°C). Most of the poly(amide–imide)s were soluble in NMP, *N*-dimethylacetamide (DMAc) and *o*-chlorophenol. Most were cast into flexible films which had tensile strengths ranging from 35.6 to 52.5 MPa, elongation-to-breakage from 3.5 to 7.9%, and initial moduli from 1.9 to 2.1 GPa. The temperatures at 5% weight loss ranged from 423 to 435°C in air and from 438 to 471°C in N_2. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(amide–imide)s; diamantane; high transition)

INTRODUCTION

Thermally stable polymers have received extensive interest over the past decade, due to increasing demands for high-performance polymers as replacements for metals or ceramics in the automotive, aerospace and microelectronic industries. Polyimides are certainly one of the most successful classes of high-performance polymers and have found extensive use in those industries. However, most polyimides encounter processing difficulty due to their infusibility and poor solubility in organic solvents. Much effort has been devoted to making polyimides more tractable, soluble and processable without sacrificing their high-performance characteristics[1–6]. Copolymerization is one popular synthetic approach to improve processability and solubility of polyimides. Poly(amide–imide)s are one of the most successful classes of copolyimides, and they combine the advantages of high-temperature stability and processability.

Diamantane is a cycloaliphatic-cage hydrocarbon containing an 'extended-cage' adamantane structure[7,8]. Although diamantane has been investigated for many years, only a few examples of polymers based on diamantane are known[9–17]. Previously, the 1,4-, 4,9- and 1,6-diethynyldiamantanes were polymerized to yield clear thermoset resins that degraded between 518 and 525°C in air or helium[9]. In that work, colourless diamantane-based polybenzazoles were prepared via the established polyphosphoric acid polycondensation technique[10]. In addition, polycules based on diamantane have found specific applications in building dendritic materials[11]. Recently we reported that incorporation of diamantyl units into polyamides, poly(amide–imide)s and polyesters gave good thermal stability, good mechanical properties up to temperatures well above 350°C, and high glass transition temperatures[12–16]. From these results it can be concluded that the introduction of the diamantane units into the polymer backbone results in polymers with high thermal stability and retention of mechanical properties at high temperature.

This paper describes the synthesis of poly(amide–imide)s involving 4,9-bis(trimellitimido)diamantane (**1**) by direct polycondensation with aromatic diamines **2**, as shown in *Scheme 2*. In addition, the solubilities, dynamic mechanical properties and thermal properties of polymers **3** are investigated.

EXPERIMENTAL

Materials

4,4′-Oxidianiline ($\mathbf{2_a}$), 4,4′-methylene dianiline ($\mathbf{2_b}$), 1,3-phenylenediamine ($\mathbf{2_c}$), 4,4′-sulfonyldianiline ($\mathbf{2_d}$) and 1,4-phenylenediamine ($\mathbf{2_e}$) were purified by vacuum sublimation. Anhydrous LiCl (Merck) was dried in a vacuum oven at 150°C for 6 h and at 180°C for 10 h. NMP, DMAc and pyridine were purified by distillation under reduced pressure over calcium hydride, and stored over 4 Å molecular sieves. Trimellitic anhydride (TMA) was purified by sublimation. A polycyclic diamine, 4,9-diaminodiamantane, was synthesized starting from 4,9-dibromodiamantane in our previous study[18].

Synthesis of 4,9-bis(trimellitimido)diamantane (1)

A flask was charged with 22 mL of *N,N*-dimethylformamide (DMF), 1.004 g (4.6 mmol) of 4,9-diaminodiamantane and 1.768 g (9.2 mmol) of TMA. The flask was

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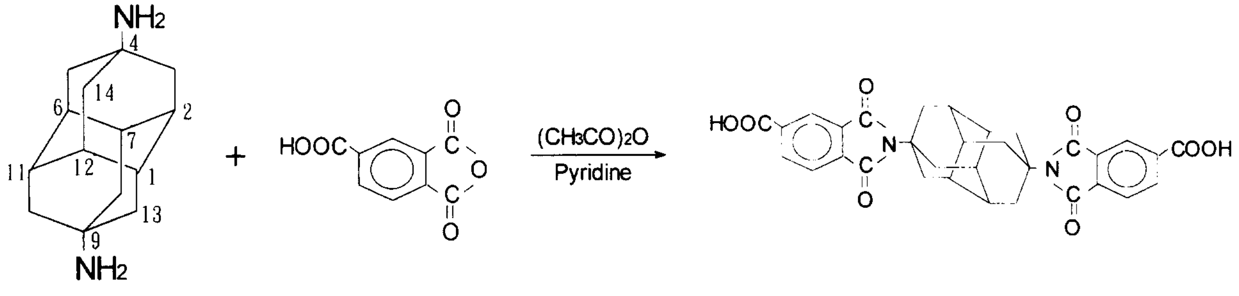


1

Scheme 1

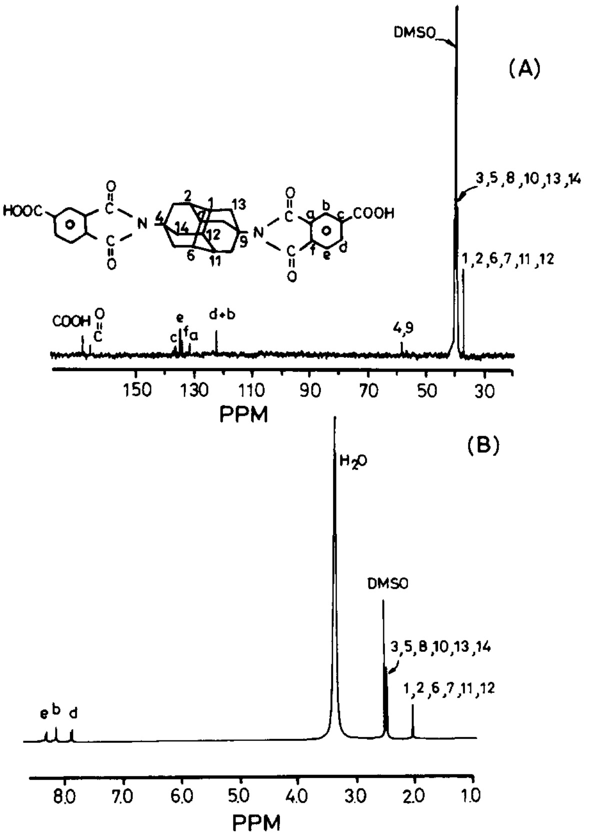


Figure 1 N.m.r. (DMSO-d$_6$) spectra of **1**: (A) ^{13}C (100 MHz); (B) ^{1}H (400 MHz)

stirred at room temperature for 6 h and nitrogen was passed through the solution. Then 6.4 mL of acetic anhydride was added, followed by 6.4 mL of pyridine; the clear solution was then heated by an oil bath at 150°C for 5 h. A yellowish precipitate that formed upon cooling was filtered off and washed several times with methanol and water. The product was purified by recrystallization with DMAc, and 1.34 g (49% yield) of **1** was obtained.

4,9-Bis(trimellitimido)diamantane (**1**): m.p. 431°C (by d.s.c.). I.r. (KBr): 2970, 2915, 1625, 1766, 1385, 1180, 732 cm^{-1}. M.s. (EI): *m/z* 566 (M$^+$, 100). ^{1}H n.m.r. (400 MHz, DMSO-d$_6$): δ 2.02 (s, 6H, H-1, 2, 6, 7, 11, 12), 2.46 (s, 12H, H-3, 5, 8, 10, 13, 14), 7.87 (d, $J = 7.56$, 2H, ArH), 8.14 (s, 2H, ArH), 8.31 (d, $J = 8.00$, 2H, ArH). ^{13}C n.m.r. (100 MHz, DMSO-d$_6$): δ 36.73 (C-1, 2, 6, 7, 11, 12), 38.92 (C-3, 5, 8, 10, 13, 14), 57.99 (C-4,9), 122.21 (d, Ar), 122.31 (d, Ar), 131.39 (s, Ar), 134.13 (s, Ar), 134.61 (d, Ar), 136.41 (s, Ar), 165.36 (C=O), 167.94 (COOH). Analysis (wt%): calculated for $C_{32}H_{26}N_2O_8$: C, 67.78; H, 4.59; N, 4.95; found: C, 67.59; H, 4.70; N, 4.87.

Polymerization

Poly(amide–imide) **3$_a$** from **1** and **2$_a$** (typical example): a mixture of 1.133 g (2.0 mmol) of **1**, 0.40 g (2.0 mmol) of **2$_a$**, 1.0 g of LiCl, 1.230 g (4.0 mmol) of triphenyl phosphite, 4 mL of pyridine and 16 mL of NMP was heated and stirred at 110°C for 12 h. The polymer solution obtained was trickled on to 500 mL of methanol, giving rise to a fibrous, yellowish precipitate, which was thoroughly washed with methanol and hot water, collected by filtration and dried. The yield was nearly quantitative. The inherent viscosity of the polymer **3$_a$** was 1.72 dL g^{-1}, measured at 0.5 g dL^{-1} concentration in NMP containing dissolved 5% w/v LiCl at 30°C. The i.r. spectrum of **3$_a$** exhibited absorptions at 3450 cm^{-1} (N–H str.), 1775 and 1710 cm^{-1} (imide, C=O str.), 1665 cm^{-1} (amide, C=O str.), 1340 cm^{-1} (imide, C–N str.) and 720 cm^{-1} (imide ring deformation), i.e. characteristic of the imide and amide groups.

Characterization

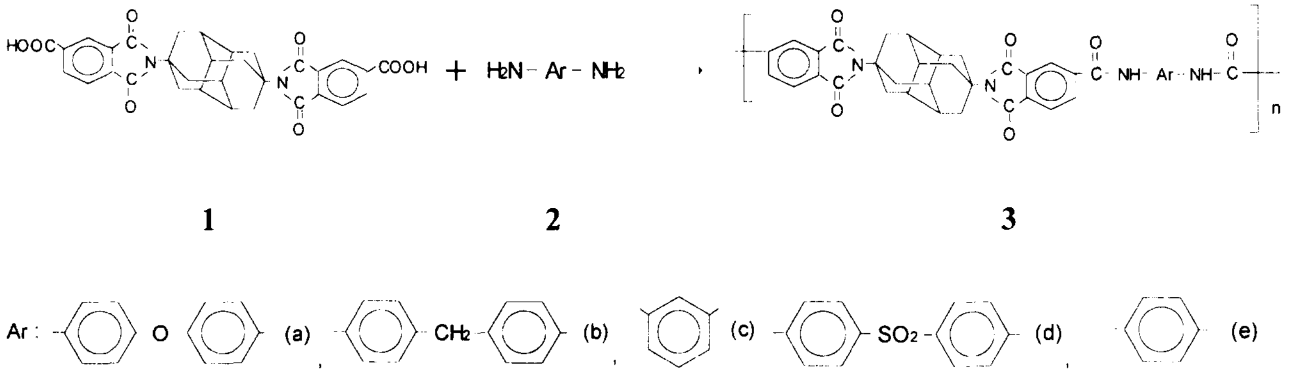
A Bio-Rad FTS-40 *FT*i.r. spectrophotometer was used to record spectra (KBr pellets). In a typical experiment, an average of 20 scans per sample was made. MS spectra were obtained by using a JEOL JMS-D300 mass spectrometer. ^{1}H and ^{13}C n.m.r. spectra were recorded on a Bruker AM-400 Fourier transform nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as the internal standard. A Perkin-Elmer 240C elemental analyser was used for elemental analysis. The melting points were obtained by a standard capillary melting point apparatus. Inherent viscosities of all polymers were determined at 0.5 g dL^{-1} concentration using an Ubbelohde viscometer. Gel permeation chromatography (g.p.c.) on soluble polymers was performed on an Applied Biosystem at 70°C with two PLgel 5 μm mixed-C columns in the NMP–LiBr (0.06 mol L^{-1}) solvent system. The flow rate was 0.5 mL min^{-1}, detection was by u.v. and calibration was performed with polystyrene standards. Qualitative solubility was determined using 0.01 g of polymer in 2 mL of solvent.

A Du Pont 9900 differential scanning calorimeter and a Du Pont 9900 thermogravimetric analyser were then used to study the transition data and thermal decomposition temperature of all the polymers. The differential scanning calorimeter (d.s.c.) was run under a nitrogen stream at a flow rate of 30 mL min^{-1} and a heating rate of 20°C min^{-1}.

Table 1 Effect of reaction parameters on polymerization[a]

	Reaction conditions			Polymer		
Part	Monomer[b] (mol L^{-1})	Reaction temp. (°C)	Reaction time (h)	Yield (%)	η_{inh}^{c} (dL g^{-1})	Remark[d]
I	0.05	130	12	98.8	1.04	S
	0.08	130	12	99.5	1.06	S
	0.10	130	12	99.4	1.23	S
	0.12	130	12	99.2	1.23	S
	0.15	130	12	97.9	1.08	S
II	0.10	100	12	99.6	1.58	S
	0.10	110	12	99.7	1.72	S
	0.10	120	12	99.4	1.40	S
	0.10	130	12	99.4	1.23	S
	0.10	140	12	99.0	1.27	S
III	0.10	110	8	99.7	1.62	S
	0.10	110	12	99.7	1.72	S
	0.10	110	16	97.3	1.48	S

[a] Reaction conditions: pyridine/NMP ratio, 0.25; $P(OC_6H_5)_3$/**1** ratio, 2; concentration of LiCl 5% w/v
[b] [**1**] = [**2$_a$**]
[c] Measured at 30°C at concentration 0.5 g dL^{-1} in NMP containing 5% w/v LiCl
[d] S, homogeneous solution



Scheme 2

The thermogravimetric (t.g.) analyses were determined under a nitrogen flow of 50 mL min^{-1} with a heating rate of 20°C min^{-1}. Dynamic mechanical analyses (d.m.a.) were performed on a Du Pont 9900 thermal analyser system. Samples 10 mm long, 2 mm wide and ~0.065 mm thick were used. The dynamic shear modulus was measured in a resonance mode. Wide-angle X-ray diffraction measurements were performed on a Philips PW 1730-10 X-ray diffractometer using Cu Kα radiation.

Tensile properties were determined from stress–strain curves with a Toyo Baldwin Instron UTM-III-500 with a load cell of 10 kg at a drawing speed of 5 cm min^{-1}. Measurements were performed at 28°C with film specimens (~0.1 mm thick, 1.0 cm wide and 5 cm long) and an average of at least five individual determinations was obtained.

RESULTS AND DISCUSSION

Monomer synthesis

A new polycyclic monomer, 4,9-bis(trimellitimido)-diamantane (**1**), was synthesized according to the route shown in *Scheme 1*. **1** was prepared from 4,9-diaminodiamantane and TMA by refluxing in DMF, using acetic anhydride and pyridine as condensing agents, with 49% yield. On the basis of the shielding effect of carbon and protons, the individual positions of chemical shifts for carbons and protons of compound **1** were assigned in *Figure 1*. However, the protons for acid groups of **1** in the ^{1}H n.m.r. spectrum were not observed. This absence is probably due to the fast exchange of these protons with moisture associated with the solvent. The elemental analysis, the characteristic peaks in the n.m.r. spectra and the characteristic bands in the i.r. spectrum accord sufficiently with the presumed structure of **1**.

Effect of reaction parameters on the inherent viscosity of 3$_a$

Part I in *Table 1* reveals that the inherent viscosity of **3$_a$** increased with increasing monomer concentration up to 0.10M. However, a higher concentration of monomer (0.15M) did not continue to increase the inherent viscosity of **3$_a$**. This is possibly because the higher concentration of monomer had an adverse effect in the solubility of **3$_a$**. Part II in *Table 1* also indicates that the inherent viscosity of **3$_a$** increased with increasing reaction temperature up to 110°C. However, decreased inherent viscosities were obtained when the reaction was performed above 110°C. This decrease in viscosity might be due to an adverse effect on the complex form derived from LiCl and phenol at an excessively high temperature, subsequently causing side reactions to increase[19]. Part III in *Table 1* shows that the inherent viscosity of 3_a was high at all three reaction times. However, the polymer obtained at 12 h had the greatest inherent viscosity among the three reaction times. From these results, it can be inferred that the most favourable conditions for this system are a monomer concentration of 0.10M, a reaction temperature of 110°C and a reaction time of 12 h.

Synthesis of poly(amide–imide)s

Various new poly(amide–imide)s **3** were prepared from **1** with aromatic diamines **2**, by using the most favourable conditions for the reaction with 4,4′-oxydianiline ($\mathbf{2_a}$), as shown in *Scheme 2*. Polycondensation results are listed in *Table 2*. All poly(amide–imide)s were obtained in nearly quantitative yield. Most of the poly(amide–imide)s **3**, except $\mathbf{3_e}$, had medium and high inherent viscosities, ranging from 0.50 to 1.72 dL g^{-1}. According to g.p.c. data, poly(amide–imide)s **3** had medium and high molecular weights, ranging from 79000 to 255000. The unsatisfactory results obtained from *p*-phenylenediamine ($\mathbf{2_e}$) were caused by the poor solubility of $\mathbf{3_e}$. I.r. spectroscopy confirmed the formation of poly(amide–imide)s **3**. *FT*i.r. spectra of the poly(amide–imide)s detected characteristic bands appearing at 3300–3455 cm^{-1} (amide, N–H str.), 1765–1775 cm^{-1} (imide, C=O str.), 1660–1670 cm^{-1} (amide, C=O str), 1340–1350 cm^{-1} (imide, C–N str.) and 720–730 cm^{-1} (imide ring deformation).

Characterization of polymers

The solubilities of these polymers were tested in various solvents. *Table 3* summarizes those results. Poly(amide–imide)s **3**, except $\mathbf{3_c}$ and $\mathbf{3_e}$, were soluble in NMP, DMAc and *o*-chlorophenol. When NMP and DMAc were added with 3% w/v LiCl, the solubilities of most of the poly(amide–imide)s, except $\mathbf{3_e}$, were markedly enhanced. Poly(amde–imide) $\mathbf{3_e}$ had the worst solubility among the polymers **3**. This inferiority is attributed to the fact that polymer $\mathbf{3_e}$ contains relatively rigid and symmetrical *p*-phenylene groups. X-ray diffraction results, as discussed below, also revealed that $\mathbf{3_e}$ had the highest crystallization tendency among the polymers **3**. The poly(amide–imide)s **3** were structurally characterized by X-ray methods. Poly(amide–imide) $\mathbf{3_e}$ had a semicrystalline pattern and exhibited crystalline peaks (2θ) at around 17° and 21°, as shown in *Figure 2*. The other polymers **3** had nearly the same semicrystalline patterns with broad peaks appearing at ~17° (2θ). Opaque films of **3** also suggests that these polymers are semicrystalline structures.

The mechanical properties were determined with an Instron machine. The tensile properties of the poly(amide–imide)s **3** are summarized in *Table 4*. Poly(amide–imide)s **3** had tensile strengths of 35.6–52.5 MPa, elongation-to-break values of 3.5–7.9%, and initial moduli of 1.9–2.1 GPa. However, this observation contradicts the original expectation that the high tensile strengths of the poly(amide–imide)s $\mathbf{3_a}$, $\mathbf{3_b}$ and $\mathbf{3_c}$ are not obtained by virtue of their high inherent viscosities. Such a contradiction is attributed to defects possibly arising in these films due to casting from their DMAc or NMP solution containing LiCl.

Thermal analysis was performed by d.s.c., d.m.a. and t.g.a. *Table 5* summarizes the results. The temperatures of poly(amide–imide) **3** at 5% weight loss ranged from 423 to

Table 2 Synthesis of poly(amide–imide)s[a]

Polymer	Yield (%)	η_{inh}[b] (dL g^{-1})	M_n[c] (10^4)	M_w/M_n	Remark[d]
$\mathbf{3_a}$	99.7	1.72	20.5	3.86	S
$\mathbf{3_b}$	98.5	1.18	17.4	3.02	S
$\mathbf{3_c}$	99.1	0.97	25.5	3.57	S
$\mathbf{3_d}$	97.8	0.50	7.9	3.48	S
$\mathbf{3_e}$	93.2	0.12[e]			P

[a] [1] = [2] = 0.1M; Pyridine/NMP = 0.25; $P(OC_6H_5)_3$/1 = 2.0; LiCl = 5% w/v; temperature = 110°C; time = 12 h

[b] Measured at 30°C at concentration 0.5 g dL^{-1} in NMP containing 3% w/v LiCl

[c] By g.p.c. (relative to polystyrene)

[d] Appearance of polymerization system: S, homogeneous solution; P, polymer precipitation

[e] Measured at 30°C at concentration 0.5 g dL^{-1} in H_2SO_4

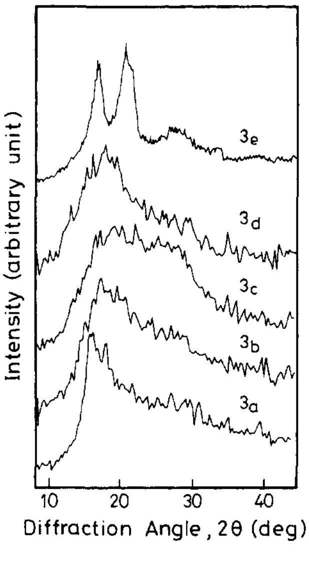


Figure 2 Wide-angle X-ray diffraction curves of poly(amide–imide)s

Table 3 Solubilities of poly(amide–imide)s

	Solvent[a]					
Polymer	NMP	DMAc	DMF	*o*-Chlorophenol	NMP-LiCl[b]	DMAc-LiCl[b]
$\mathbf{3_a}$	+ +	+ −	−	+ +	+ +	+ +
$\mathbf{3_b}$	+ +	+ −	−	+ +	+ +	+ +
$\mathbf{3_c}$	+ −	+ −	−	−	+ +	+ +
$\mathbf{3_d}$	+ +	+ +	+ −	+ +	+ +	+ +
$\mathbf{3_e}$	+ −	−	−	−	+ −	+ −

[a] Solubility: + +, soluble at room temperature; +, soluble on heating at 60°C; + −, partly soluble on heating at 60°C; −; insoluble on heating at 60°C. DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide

[b] Concentration of LiCl 3% w/v

Table 4 Tensile properties of polymer films

Polymer[a]	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
$\mathbf{3_a}$[b]	52.5	7.9	1.9
$\mathbf{3_b}$	46.3	6.6	1.9
$\mathbf{3_c}$	49.6	5.6	2.0
$\mathbf{3_d}$	35.6	3.5	2.1

[a] Films cast from polymer solution of DMAc containing 3% w/v LiCl
[b] Films cast from polymer solution of NMP containing 3% w/v LiCl

Table 5 Thermal properties of poly(amide–imide)s

Polymer	T_g[a] (°C)	T_g[b] (°C)	T_5[c] (°C) In N_2	T_5[c] (°C) In air	T_d[d] (°C) In N_2	T_d[d] (°C) In air
$\mathbf{3_a}$	295	290	463	435	537	452
$\mathbf{3_b}$	–[e]	–	464	427	524	445
$\mathbf{3_c}$	–	–	455	423	524	450
$\mathbf{3_d}$	–	–	438	427	507	457
$\mathbf{3_e}$	–	–	471	433	531	451

[a] Glass transition measured by d.s.c.
[b] Glass transition measured by d.m.a.
[c] Temperature of 5% weight loss recorded by t.g. at a heating rate of 20°C min^{-1}
[d] Maximum decomposition temperature of polymer films recorded by t.g. at a heating rate of 20°C min^{-1}
[e] Not found

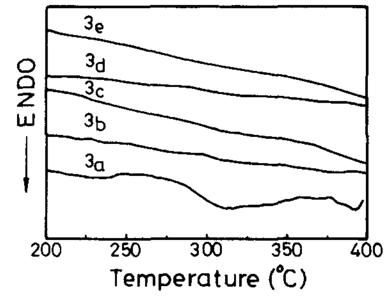


Figure 3 D.s.c. thermograms of poly(amide–imide)s in nitrogen atmosphere at a heating rate of 20°C min^{-1}

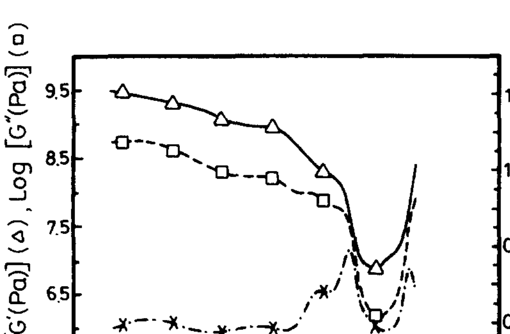


Figure 4 Dynamic mechanical analysis curves for $\mathbf{3_a}$ at a heating rate of 5°C min^{-1}

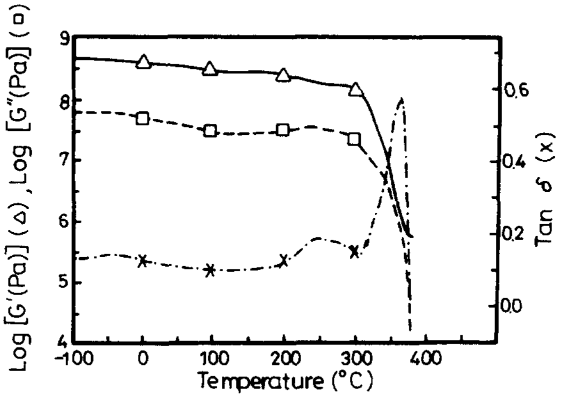


Figure 5 Dynamic mechanical analysis curves for $\mathbf{3_b}$ at a heating rate of 5°C min^{-1}

435°C in air and from 438 to 471°C in N_2. As for the d.s.c. experiments, initial heating of the samples was curtailed a 300°C. In addition, T_g and other thermal properties were evaluated according to the d.s.c. curves of the second heating. *Figure 3* shows that most of the poly(amide–imide)s **3**, except $\mathbf{3_a}$, did not display a typical glass transition in the temperature range between 30 and 400°C. However, poly(amide–imide) $\mathbf{3_a}$ showed a typical glass transition at 295°C.

More detailed information can be obtained from the dynamic mechanical behaviour of the films as a function of temperature. Films of ~65 μm thickness were studied in the temperature range between −100 and 400°C. The mechanical relaxation spectrum of $\mathbf{3_a}$ is shown in *Figure 4*. Based on the tan δ and G'' peaks, four profound relaxations appeared at −50, 170, 290 and 350°C. The low transition of −50°C is a typical relaxation of polyamides. This relaxation is attributed to a mechanism of motion (rotation) of the amide bonds together with water molecules that are bonded to them[20–22]. The second relaxation, at ~170°C, was observed in G'' and tan δ. However, this relaxation is associated without any effect on the G' value. The relaxation in poly(amide–imide)s is probably related to the rotation of rigid segments of the *p*-phenylene and amide groups around 'hinges' such as –O– and –CH_2– in diamines. Such a transition was also observed in other related polymers[20–22]. The third relaxation, at ~290°C, was observed in G'' and tan δ. Moreover, this transition is associated with a ~0.75 order-of-magnitude step decrease in G'. This relaxation is probably due to the glass relaxation process. The glass relaxation temperature of $\mathbf{3_a}$ correlates well with the typical glass transition at ~295°C as obtained by d.s.c. The last relaxation, at ~350°C, is associated with a ~1.35 order-of-magnitude step decrease in G'. This relaxation is probably due to the α relaxation. *Figure 4* also indicates that the diamantane-based poly(amide–imide) $\mathbf{3_a}$ exhibited good retention of storage modulus at a high temperature, > 310°C.

The mechanical relaxation spectrum of $\mathbf{3_b}$ is shown in *Figure 5*. Based on the tan δ and G'' peaks, three relaxations occurred at −50, 250 and 360°C. Two lower relaxations of $\mathbf{3_b}$ resemble those of $\mathbf{3_a}$. However, the second relaxation of $\mathbf{3_b}$ shifted to 250°C. The last relaxation, at ~360°C, is also due to the α relaxation. However, the glass relaxation of $\mathbf{3_b}$ was not observed. This absence is possibly because the glass relaxation of polymer $\mathbf{3_b}$ nearly approached its α relaxation. In addition, polymer $\mathbf{3_b}$ also exhibited good retention of storage modulus (> 10^8 Pa) at a high temperature, > 300°C.

CONCLUSIONS

According to the results obtained, introduction of a diamantyl unit into the poly(amide–imide)s backbone yielded poly(amide–imide)s with good thermal stability and good retention of storage modulus approaching the thermal decomposition temperature. The poly(amide–imide)s had medium and high molecular weights, ranging from 79 000 to 255 000. Most of the poly(amide–imide)s were soluble in NMP, DMAc and *o*-chlorophenol. Poly(amide–imide)s **3** had tensile strengths of 35.6–52.5 MPa, elongation-to-breakage values of 3.5–7.9%, and initial moduli of 1.9–2.1 GPa. D.m.a. results indicated that polymers $\mathbf{3}_a$ and $\mathbf{3}_b$ exhibit good retention of storage modulus ($> 10^8$ Pa) at high temperatures, > 300°C. The glass transition of polymer $\mathbf{3}_a$ was observed at ~290°C by d.m.a. and d.s.c.

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