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ORIGINAL CONTRIBUTION

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Syntheses and properties of poly (amide–imide)s based on 5,5′-bis[4-(4-trimellitimidophenoxy)phenyl]-hexahydro-4,7-methanoindan and aromatic diamines

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Abstract A novel polymer-forming diimide–diacid, 5,5′-bis[4-(4-trimellitimido phenoxy)phenyl]-hexahydro-4,7-methanoindan (**II**), was prepared by the condensation reaction of 5,5′-bis[4-(4-aminophenoxy)phenyl]-hexahydro-4,7-methanoindan with trimellitic anhydride. A series of novel aromatic poly(amide–imide)s (PAIs) containing polycyclic cardo groups was prepared by the direct polycondensation of **II** with various aromatic diamines using phosphorylation techniques. The polymers had inherent viscosities between 0.71 and 0.96 dl/g. The polymers were soluble in polar solvents such as *N*-methyl-2-pyrrolidone, *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide, and could be cast from their DMAc solutions into transparent, flexible, and tough films, except for $\mathbf{III_a}$. These films had yield strengths of 85–114 MPa, tensile strengths of 77–102 MPa, an elongation at break of 8–17%, and initial moduli of 2.0–2.7 GPa. Wide-angle X-ray diffraction revealed that the polymers are amorphous. The glass-transition temperatures of the polymers were in the range 242–312 °C. All the PAIs exhibited no appreciable decomposition below 430 °C, and their 10%-weight-loss temperatures were in the range 484–507 °C in nitrogen and 494–515 °C in air.

Key words Poly(amide–imide) · Direct polycondensation · 5,5′-Bis-[4-(4-aminophenoxy)phenyl]-hexahydro-4,7-methanoindan · 5,5′-Bis[4-(4-trimellitimidophenoxy)phenyl]-hexahydro-4,7-methanoindan

Introduction

Aromatic poly(amide–imide)s (PAIs) are useful high-performance materials that exhibit better processing characteristics compared with polyimides of analogous structures [1]. A notable example is Torlon (Amoco Chemicals), a commercial PAI obtained from trimellitic anhydride chloride (TMAC) and 4,4′-methylenedianiline [2]. A number of PAIs have been synthesized through two main routes: via the amide–imide formation reaction of trimellitic anhydride (TMA), and through amide formation from imide-containing monomers, such as imide-containing dicarboxylic acid, or their acid chlorides [3]. One of the simpler approaches to prepare PAIs with high molecular weights is the direct polycondensation between imide-bearing dicarboxylic acid with aromatic diamine using the Yamazaki–Higashi phosphorylation technique [4–6]. The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages for the laboratory preparation of PAIs as well as of polyamides. Thus, several series of novel PAIs have been easily synthesized by this convenient technique in our laboratory [7–12]. Furthermore, this approach to PAI synthesis can offer us the option of introducing specific diamine residues between the amide or imide groups into the polymer backbone. The incorporation of such diamine residues may provide an easy method for controlling the physical properties of PAIs.

In previous articles [13–16], we demonstrated that the incorporation of aromatic cardo groups into the PAI backbone is one effective means of enhancing the solubility and lowering the transition temperature. Recently, a bisphenol, 5,5′-bis(4-hydroxylphenyl)-hexahydro-4,7-methanoindan [17, 18], which contained a special polycyclic cardo group, was used for the preparation of bis(ether amine) ($\mathbf{I_k}$) in our laboratory [19, 20]. Polyamides and polyimides derived from $\mathbf{I_k}$ exhibit good solubility in organic solvents by incorporating the nonplaner alicyclic cardo group into the rigid polymer chains [19, 20]. The present work deals with the synthesis and basic characterization of a novel series of PAIs derived from the imide ring-preformed dicarboxylic acid i.e. 5,5′-bis[4-(4-trimellitimidophenoxy)phenyl]-hexahydro-4,7-methanoindan (**II**).

Experimental

Materials

5,5′-Bis(4-hydroxylphenyl)-hexahydro-4,7-methanoindan from Acros), *p*-chloronitrobenzene, TMA (from Wako) and triphenyl phosphite (TPP from TCI) were used without purification.

Diamine monomers *p*-phenylene diamine ($\mathbf{I_a}$), *m*-phenylene diamine ($\mathbf{I_b}$), 4,4′-diaminophenyl methane ($\mathbf{I_c}$), 4,4′-diaminophenyl ether ($\mathbf{I_d}$), 3,4′-diaminophenyl ether ($\mathbf{I_e}$), 4,4′-diaminophenyl thioether ($\mathbf{I_f}$), and 1,4-bis(4-aminophenoxy)benzene ($\mathbf{I_g}$) were used directly as received from TCI. 1,3-Bis(4-aminophenoxy)benzene ($\mathbf{I_h}$), 2,2-bis[4-(aminophenoxy)phenyl]propane ($\mathbf{I_i}$), and 2,2-bis[4-(aminophenoxy)phenyl]hexafluoropropane ($\mathbf{I_j}$) were obtained from Chriskev and were used without futher purification.

Commercially available anhydrous $CaCl_2$ was dried under vacuum at 180 °C for 10 h before use. *N*-Methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide (DMF) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Monomer synthesis

5,5′-Bis[4-(4-aminophenoxy)phenyl]-hexahydro-4,7-methanoindan ($\mathbf{I_k}$)

As reported previously [19, 20], 5,5′-bis(4-hydroxylphenyl)-hexahydro-4,7-methanoindan, *p*-chloronitrobenzene, and K_2CO_3 were reacted in the molar ratio of 1/2/2 at 160 °C in DMAc to provide the intermediate dinitro compound (yield: 83%; m.p. 175–176 °C). Following reduction with hydrazine and Pd/C in a suitable solvent (ethanol), the diamine ($\mathbf{I_k}$) was formed with 92% yield. (m.p. 188–190 °C).

5,5′-Bis[4-(4-trimellitimidophenoxy)phenyl]-hexahydro-4,7-methanoindan

A mixture of 3.84 g (20 mmol) TMA and 5.02 g (10 mmol) $\mathbf{I_k}$ was dissolved in 30 ml dry DMF at 60 °C and stirred for 1 h. About 20 ml toluene was then added and the mixture was heated under reflux for 3 h until about 0.51 ml water had been azeotropically distilled off with a Dean–Stark trap. Heating was continued to distill off the residual toluene. After cooling the yellow precipitate of **II** was separated by filtration and was washed with methanol. The product was dried in a vacuum, and the mass of the solid thus obtained was 8.08 g (95% yield); m.p. 277–279 °C.

^1H NMR [500 MHz, dimethyl sulfoxide (DMSO)-d$_{6,\delta}$): 0.89 (1H, m, H-20b), 1.02 (2H, m, H-18b, 19b), 1.20 (1H, d, *J* = 10.1 Hz, H-23b), 1.40 (1H, d, *J* = 10.1 Hz, H-23a), 1.57 (1H, m, H-19a), 1.78 (4H, m, H-18a, 20a, 21, 22), 2.07 (1H, m, *J* = 4.0 Hz, H-17), 2.25 (2H, m, H-18b, 18a), 3.04 (1H, s, H-16), 6.92 (4H, d, *J* = 13.5, H-9, 9′), 7.08 (4H, m, H-12, 12′), 7.39 (8H, m, H-8, 8′, 13, 13′), 8.03 (2H, d, *J* = 12.9, H-5, 5′), 8.27 (4H, s, H-2, 2′), 8.38 (4H, d, *J* = 12.9, H-6, 6′).

^{13}C NMR (500 MHz, DMSO-d$_{6,\delta}$): 26.90 (C-19), 31.48 (C-23), 31.59 (C-20), 31.95 (C-18), 41.73 (C-17), 42.06 (C-22), 43.17 (C-24), 47.56 (C-21), 48.67 (C-16), 54.55 (C-15), 118.31, 118.46, 118.61, 118.68 (C-9, C-9′, C-12, C-12′), 123.41, 123.71 (C-8, C-8′), 126.58, 126.69 (C-5, C-5′), 128.41 (C-2, C-2′), 128.94 (C-13, C-13′), 129.23 (C-6, C-6′), 131.97 (C-3, C-3′), 134.81 (C-1, C-1′), 135.41 (C-4, C-4′), 136.50 (C-7, C-7′), 143.68, 147.57 (C-14, C-14′), 153.20, 153.60 (C-10, C-10′), 156.31, 156.49 (C-5, C-5′), 165.78, 166.29 (C=O).

($C_{52}H_{38}N_2O_{10}$) (850.88)
Calculated C 73.40 H 4.50 N 3.29
Found C 73.32 H 4.56 N 3.25

Polymerization

A typical example of polycondensation is described as follows. A mixture of 0.521 g (0.625 mmol) **II**, 0.314 g (0.625 mmol) $\mathbf{I_k}$, 0.25 g $CaCl_2$, 2.5 ml NMP, 0.6 ml pyridine, and 0.4 ml TPP was heated with stirring at 100 °C for 3 h. The highly viscous polymer solution obtained was trickled into 400 ml stirred methanol. The stringy polymer precipitated was washed thoroughly with methanol and hot water, collected by filtration, and dried at 100 °C under vacuum. The yield was quantitative. The inherent viscosity of the polymer, measured at a concentration of 0.5 g/dl in DMAc at 30 °C, was 0.92 dl/g.

Other PAIs, ($\mathbf{III_{a-j}}$), were synthesized analogously. The synthesis conditions and the inherent viscosities of the polymers obtained are summarized in Table 1.

Table 1 Effiect of reaction conditions on the preparation of poly (amide–imide)s. In each polymerization 0.625 mmol **II** and diamines, and 0.4 ml triphenyl phosphite were used. Reaction temperture = 100 °C; reaction time = 3 h

Polymer	Amount of reagents		Polymer	
	N-methyl-2-pyrrolidone (ml)	$CaCl_2$ (g)	Pyridine (ml)	η_{inh}[a] (dl/g)
$\mathbf{III_a}$	3.5	0.34	0.8	0.71[b]
$\mathbf{III_b}$	2.5	0.25	0.7	0.77
$\mathbf{III_c}$	3.2	0.30	0.8	0.84
$\mathbf{III_d}$	3.2	0.30	0.8	0.91
$\mathbf{III_e}$	2.5	0.25	0.6	0.76
$\mathbf{III_f}$	2.8	0.27	0.7	0.73
$\mathbf{III_g}$	3.0	0.30	0.8	0.96
$\mathbf{III_h}$	2.5	0.25	0.6	0.82
$\mathbf{III_i}$	2.5	0.25	0.6	0.89
$\mathbf{III_j}$	2.5	0.25	0.6	0.79
$\mathbf{III_k}$	2.5	0.25	0.6	0.92

[a] Measured at a polymer concentration of 0.5 g/dl in *N*,*N*-dimethylacetamide (*DMAc*) at 30 °C

[b] Measured at a polymer concentration of 0.5 g/dl in DMAc +0.5 wt% LiCl at 30 °C

Measurements

Melting points were measured in capillaries with a Yamato melting point apparatus (model MP-21) without correction. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WB/DMX-500 SB FT-NMR spectrometer operating at 30 °C with tetramethylsilane as an internal standard. Elemental analyses were run on a Perkin–Elmer model 2400 CHN analyzer. The inherent viscosities of all the polymers were measured at a concentration of 0.5 g/dl with a Cannon–Fenske viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 10 ± 2 mg samples heated in flowing air or nitrogen (50 cm^3/min) at a heating rate of 20 °C/min. The differential scanning calorimetry (DSC) traces were recorded with a Sinku–Riko 7000 differential scanning calorimeter coupled to a TA-7000 thermal analyzer in flowing nitrogen (30 cm^3/min) at a heating rate of 20 °C/min. An Instron universal tester (model 1130) with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick); an average of at least six individual determinations was used.

Results and discussion

Monomer synthesis

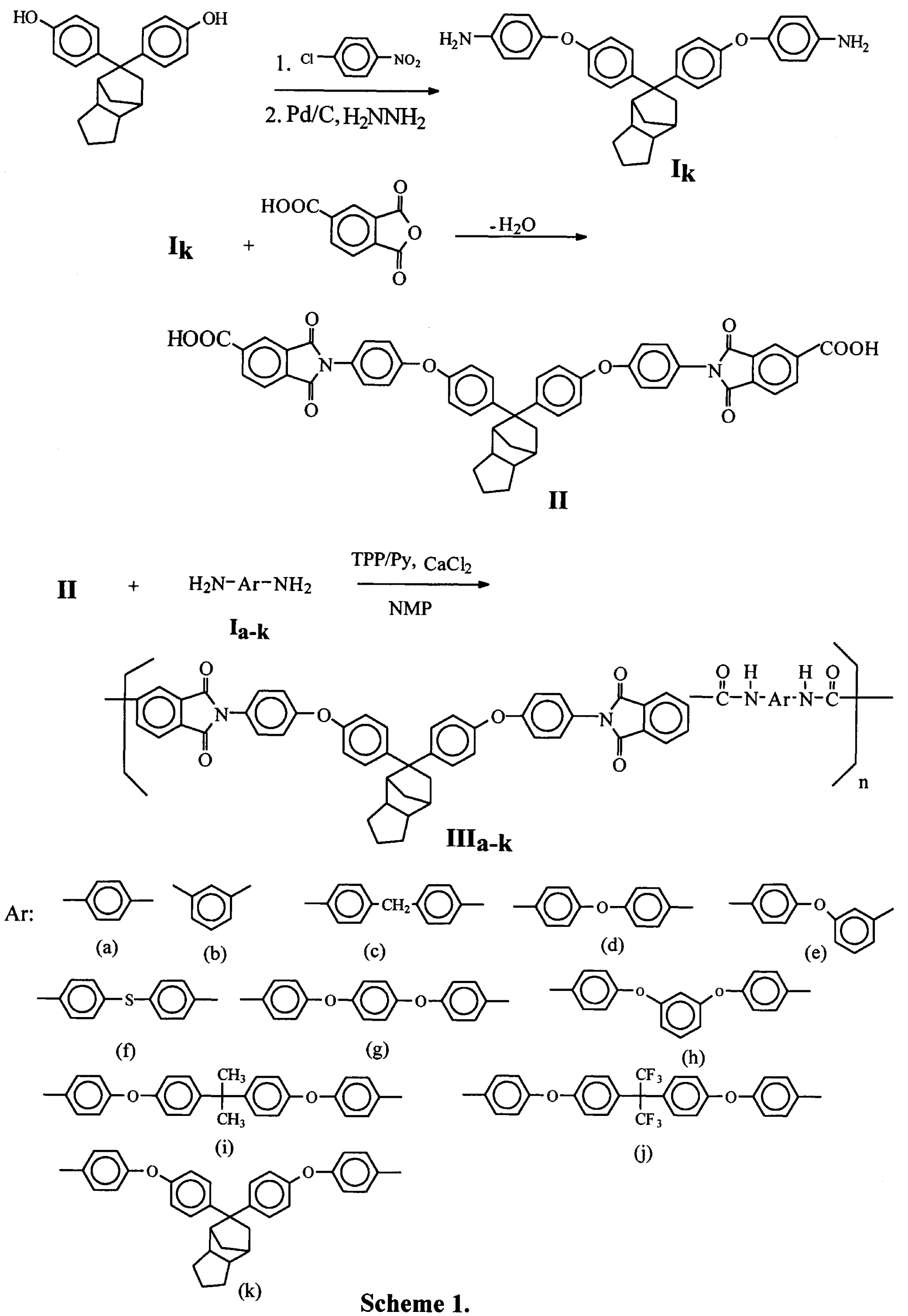
II was synthesized from the condensation of $\mathbf{I_k}$ with TMA as shown in Scheme 1. The complete cyclization of the intermediate amic acid was achieved by toluene–water azeotropic distillation. The IR spectrum of **II** exhibited a characteristic absorption at 3440 cm^{-1} due to carboxylic acid –OH. The coupled carbonyl stretching vibrations of the imide rings appeared at 1785 and 1720 cm^{-1}. The ^{1}H NMR spectrum of **II** is shown in Fig. 1. The spectrum is divided into two parts: one part corresponds to the aliphatic ring protons in the upfield region; the other corresponds to the aromatic protons in the downfield region. Proton signals H-6,6′ (8.38 ppm), H-2,2′ (8.27 ppm) and H-5,5′ (8.04 ppm) present in the most downfield part of the spectrum are caused by the electron-withdrawing effect of the carbonyl group present in the structure. The chemical shifts of H-9,9′ and H-12,12′ are 6.92 and 7.08 ppm, and the upfield shifting of their positions may be due to the electron-donating phenoxyl groups present in the ortho positions. The signals from the aliphatic protons present in the upfield region were more complicated than those of the aromatic protons, and were assigned as described in the Experimental section and in Fig. 1. In the ^{13}C NMR spectrum (Fig. 2), the aliphatic carbons appeared as ten peaks in the upfield region and were in good agreement with the predicted structure. Because of their asymmetric structure, the peaks of the aromatic rings were more complicated than predicted from the symmetric structure; however, they caused no problems for the structural assignment.

Polymer syntheses

A series of novel PAIs, $\mathbf{III_{a-k}}$, containing an $\mathbf{I_k}$ unit was synthesized from **II** and various aromatic diamines, $\mathbf{I_{a-k}}$, by direct polycondensation using TPP as a promoter in NMP in the presence of pyridine and $CaCl_2$ at 100 °C (Scheme 1). The conditions for the preparation of the PAIs are summarized in Table 1. All the polymers were obtained in almost quantitative yields with inherent viscosities of 0.71–0.96 dl/g. Generally, the molecular weight of the polymers obtained from the phosphorylation reaction is highly dependent on the reactant concentration. In this system, **II** exhibited good solubility in organic solvents; thus the reaction conditions were dependent on the diamines used. A larger amount of solvent and $CaCl_2$ were needed for the preparation of $\mathbf{III_a}$. This was because of the poor solubility of the polymer which contained a *p*-phenylene unit in the diamine moiety. The monomer concentrations for producing $\mathbf{III_{d,g}}$ were lower than those for $\mathbf{III_{e,h}}$ due to the presence of para phenoxyl groups in the diamine residues. For the syntheses of $\mathbf{III_{i,j,k}}$, smaller amounts of NMP and $CaCl_2$ were needed, probably due to the good solubility of diamines associated with isopropyl, hexafluoroisopropyl or bulky alicyclic cardo groups. The results of the elemental analyses of all the PAIs are listed in Table 2. In all cases, however, the carbon values were found to be lower than the calculated values for the proposed structures. This can possibly be attributed to the hygroscopic nature of amide groups of these PAIs. The intakes of water were in the range 2.08–3.70%, and were calculated from the weight change of the vacuum-dried polymer samples after being exposed in air at room temperature. When the values were corrected by eliminating the amount of absorbed water, the correction values were in good agreement with the calculated ones.

Properties of polymers

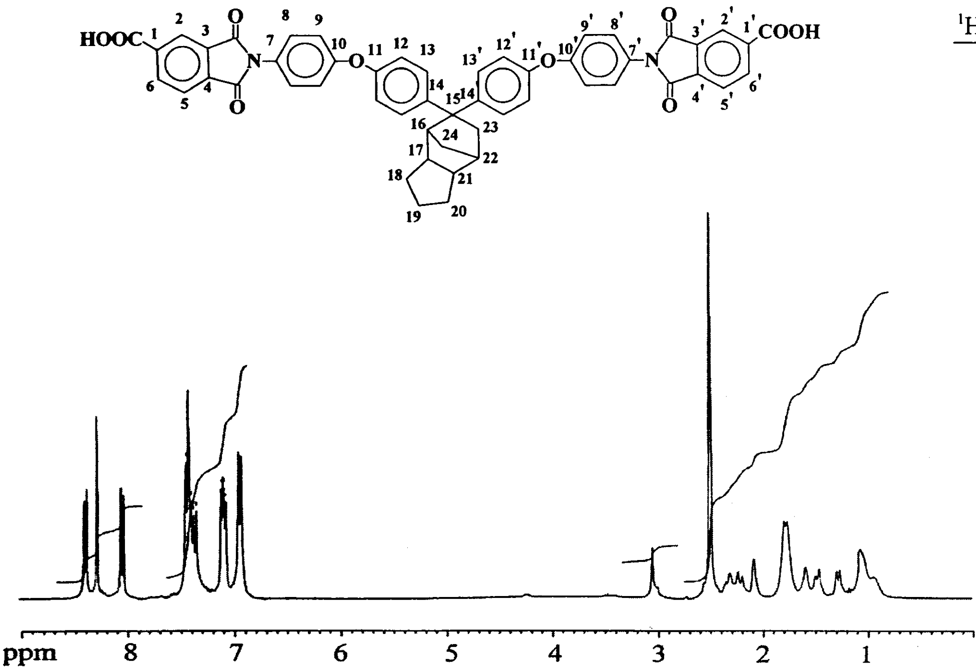
The qualitative solubilities of the PAIs are listed in Table 3. Except for $\mathbf{III_a}$, which can only dissolve in concentrated H_2SO_4 and DMAc + 5% LiCl, the polymers show good solubility in polar organic solvents such as NMP, DMAc and DMF. Polymer $\mathbf{III_b}$, formed by replacing the *p*-phenylene unit of $\mathbf{III_a}$ by a *m*-phenylene unit, is easily soluble in the test solvents. Because the solubility of the meta linkage is better than that of the para linkage, $\mathbf{III_{e,h}}$ exhibited better solubility properties than $\mathbf{III_{d,g}}$ in non-amide-type solvents such as DMSO, pyridine, *m*-cresol and tetrahydrofuran (THF). That good solubilities of $\mathbf{III_{i,j,k}}$ were obtained in all the test solvents, even in low-polarity solvents such as THF at room temperature, may be due to the flexible isopropyl, hexafluoroisopropyl or bulky polycyclic groups in the polymer chain.



Scheme 1.

The crystallinity of the PAIs was evaluated by X-ray diffraction measurements with 2θ scattering angles from 5°–40°. All the polymers showed amorphous characteristics and exhibited no observable reflection peak in the testing range. This characteristic is governed by the structural modification through the incorporation of the bulky polycyclic group into the polymer structures.

All the PAIs were cast into films from polymer solutions of DMAc, except for $\mathbf{III_a}$. The tensile properties of the polymer films are summarized in Table 4. These films had yield strengths of 85–114 MPa, tensile

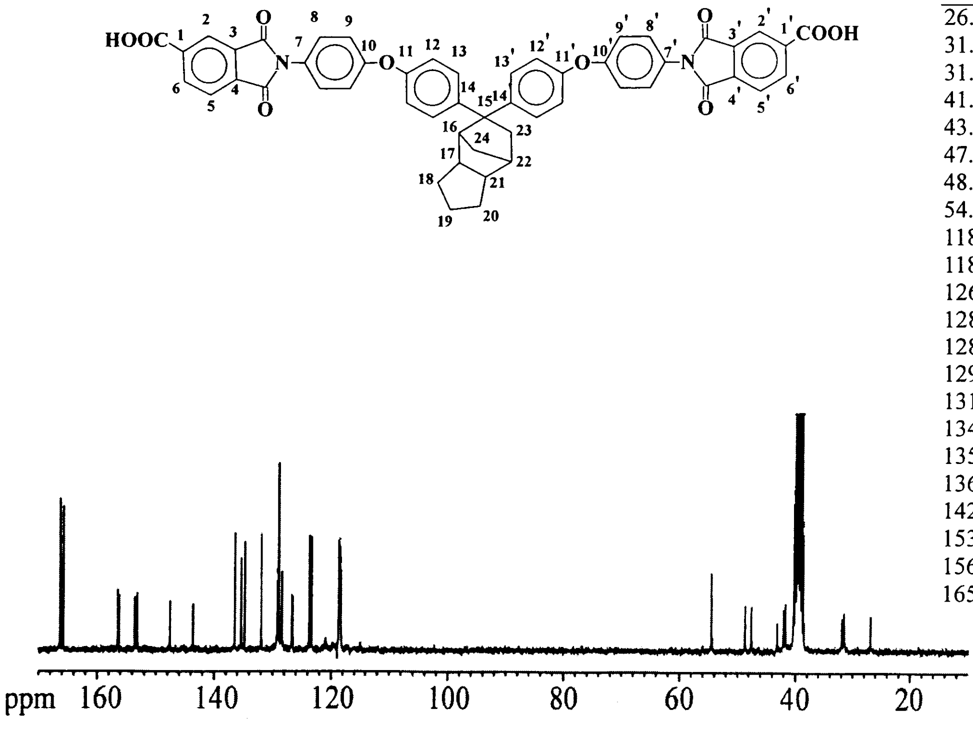


^{1}H-NMR(ppm)	atom (H)
0.89	20b
1.02	18b, 19b
1.20	23b
1.40	23a
1.57	19a
1.78	18a, 20a, 21, 22
2.07	17
2.25	24a, 24b
3.04	16
6.92	9, 9’
7.08	12, 12’
7.39	8, 8’, 13, 13’
8.03	5, 5’
8.27	2, 2,
8.38	6, 6’

Fig. 1 ^{1}H NMR spectrum of **II** dimethyl sulfoxide (*DMSO*)-d$_6$

strengths of 77–102 MPa, elongations-to-break of 8–17%, and initial moduli of 2.0–2.7 GPa. Under tension, over half the polymer films, those from **III**$_{c,e,g,h,j,k}$, behave as ductile materials with a yield point and a moderate elongation-to-break. In general, the tensile properties of the polymers were dependent on two factors: the structure or the molecular weight of the polymers. A higher degree of polymerization results in higher tensile strengths in polymer films such as **III**$_g$, **III**$_i$ and **III**$_k$: their tensile properties are as good as Torlon.

Fig. 2 ^{13}C NMR spectrum of **II** (DMSO-d$_6$)



^{13}C-NMR(ppm)	atom (C)
26.90	19
31.48	23
31.95	18
41.73	21
43.17	22
47.56	17
48.67	16
54.55	15
118.31, 118.46	9, 9’
118.61, 118.68	12, 12’
126.58, 126.69	8, 8’
128.41	5, 5’
128.94	2, 2’
129..23	13, 13’
131.97	6, 6’
134.81	3, 3’
135.41	1, 1’
136.50	7, 7’
142.68, 147.57	14, 14’
153.20, 153.60	10, 10’
156.31, 156.49	11, 11’
165.78, 166.29	C=O

Table 2 Elemental analysis of poly(amide–imide)s

Polymer	Formula (Molecular weight)	Elemental analysis (%)[a]				Moisture intake (%)[b]
			C	H	N	
$\mathbf{III_a}$	$(C_{58}H_{42}N_4O_8)_n$	Calc	75.48	4.59	6.07	
	$(922.30)_n$	Found	73.27	4.63	5.92	2.80
		Corrected	75.32	4.50	6.08	
$\mathbf{III_b}$	$(C_{58}H_{42}N_4O_8)_n$	Calc	75.48	4.59	6.07	
	$(922.30)_n$	Found	73.09	4.66	5.90	3.36
		Corrected	75.55	4.50	6.09	
$\mathbf{III_c}$	$(C_{65}H_{48}N_4O_8)_n$	Calc	77.06	4.78	5.53	
	$(1012.35)_n$	Found	74.56	4.90	5.39	3.25
		Corrected	76.98	4.74	5.56	
$\mathbf{III_d}$	$(C_{64}H_{46}N_4O_9)_n$	Calc	75.73	4.57	5.52	
	$(1014.33)_n$	Found	74.11	4.77	5.40	2.08
		Corrected	75.65	4.67	5.51	
$\mathbf{III_e}$	$(C_{64}H_{46}N_4O_9)_n$	Calc	75.73	4.57	5.52	
	$(1014.33)_n$	Found	73.08	4.81	5.32	3.46
		Corrected	75.61	4.65	5.50	
$\mathbf{III_f}$	$(C_{64}H_{46}N_4O_8S)_n$	Calc	74.55	4.50	5.43	
	$(1030.30)_n$	Found	72.11	4.74	5.30	3.32
		Corrected	74.51	4.59	5.48	
$\mathbf{III_g}$	$(C_{70}H_{50}N_4O_{10})_n$	Calc	75.94	4.55	5.06	
	$(1106.35)_n$	Found	73.10	4.66	4.89	2.89
		Corrected	75.76	4.53	5.03	
$\mathbf{III_h}$	$(C_{70}H_{50}N_4O_{10})_n$	Calc	75.94	4.55	5.06	
	$(1106.35)_n$	Found	73.10	4.58	4.96	3.70
		Corrected	75.81	4.48	5.13	
$\mathbf{III_i}$	$(C_{79}H_{60}N_4O_{10})_n$	Calc	77.44	4.94	4.75	
	$(1124.43)_n$	Found	75.42	5.02	4.66	2.81
		Corrected	77.54	4.88	4.79	
$\mathbf{III_j}$	$(C_{79}H_{54}F_6N_4O_{10})_n$	Calc	71.17	4.08	4.20	
	$(1332.37)_n$	Found	68.95	4.19	4.04	3.23
		Corrected	71.18	4.08	4.17	
$\mathbf{III_k}$	$(C_{86}H_{68}N_4O_{10})_n$	Calc	72.16	4.79	3.91	
	$(1316.46)_n$	Found	69.59	4.90	3.79	3.59
		Corrected	72.08	4.73	4.92	

[a] For C and N: corrected value = found value × (100% + moisture intake %). For H: corrected value = found value × (100% − moisture intake %)

[b] Moisture intake (%) = $(W - W_0)/W_0 \times 100\%$, where W is the weight of the polymer sample after standing at room temperature for 3 days and W_0 is the weight of the polymer sample after being dried in a vacuum at 100 °C for 12 h

Table 3 Solubility[a] of polymers in various solvents: DMAc, *N*-methyl-2-pyrrolidone (*NMP*), *N*,*N*-dimethyl formamide (*DMF*), dimethyl sulfoxide (*DMSO*), pyridine (py), *m*-cresol and tetrahydrofuran (*THF*)

Polymer	Solvent							
	DMAc	DMAc +5% LiCl	NMP	DMF	DMSO	Py	*m*-Cresol	THF
$\mathbf{III_a}$	–	+	+–	–	–	–	–	–
$\mathbf{III_b}$	+	+	+	+	+	+	+	+
$\mathbf{III_c}$	+	+	+	+	+–	+	+	–
$\mathbf{III_d}$	+	+	+	+	+–	+–	+–	–
$\mathbf{III_e}$	+	+	+	+	+	+	+	+
$\mathbf{III_f}$	+	+	+	+	+	+	+	+–
$\mathbf{III_g}$	+	+	+	+	+–	+–	+–	–
$\mathbf{III_h}$	+	+	+	+	+	+	+	+
$\mathbf{III_i}$	+	+	+	+	+	+	+	+
$\mathbf{III_j}$	+	+	+	+	+	+	+	+
$\mathbf{III_k}$	+	+	+	+	+	+	+	+

[a] Solubility: (+) soluble at room temperature, (+–) partially soluble or swelling and (–) insoluble

Table 4 Tensile properties of polymers

Polymer[a]	Strength at yield (MPa)	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
III$_b$	–	93	11	2.1
III$_c$	85	79	13	2.2
III$_d$	–	87	10	2.0
III$_e$	99	85	17	2.3
III$_f$	–	94	10	2.2
III$_g$	113	102	13	2.5
III$_h$	85	77	16	2.2
III$_i$	–	99	12	2.3
III$_j$	93	85	14	2.2
III$_k$	114	102	15	2.7
Torlon[b]	–	97	7	2.3

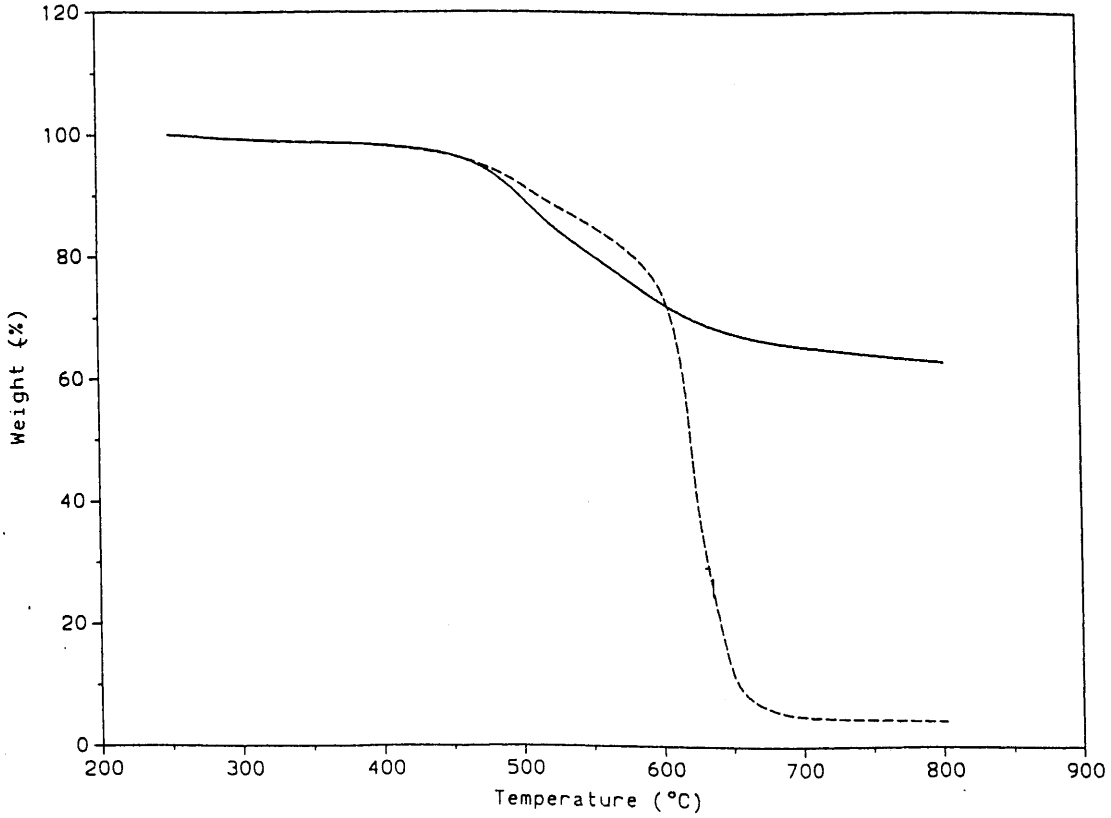
[a] Films were cast from a polymer solution of DMAc
[b] The inherent viscosity of Torlon was 0.71 dl/g measured in DMAc

Table 5 Thermal properties of polymers

Polymer	Thermogravimetric analysis			
	Differential scanning calorimetry	Decomposition temperature (°C)[b]		Wt% residue at 800 °C in N_2
	T_g^a (°C)	In N_2	In air	
III$_a$	312	495	502	64.3
III$_b$	264	491	498	65.8
III$_c$	296	486	496	64.3
III$_d$	303	499	505	63.5
III$_e$	264	486	494	63.2
III$_f$	273	484	501	60.3
III$_g$	286	501	509	62.5
III$_h$	275	490	496	60.4
III$_i$	273	502	508	62.3
III$_j$	242	507	515	61.5
III$_k$	287	487	503	62.7
Torlon	288	526	518	59.4

[a] From the second-heating differential scanning calorimetry traces conducted at a heating rate of 15 °C/min in nitrogen
[b] Temperature at which a 10% weight loss was recorded by thermogravimetric analysis at a heating rate of 20 °C/min

Fig. 3 Thermogravimetric analysis curves of poly(amide–imide) **III$_g$** at a heating rate of 20 °C/min under nitrogen (–) and air (- - - -) atmospheres



The thermal properties of the polymers were evaluated by means of TGA and DSC. The thermal behavior data of all PAIs are listed in Table 5. The 10% weight loss temperatures (T_ds) were recorded in the range 484–507 °C in nitrogen and 494–515 °C in air. The char yields at 800 °C in nitrogen of all the polymers were above 50%. The TGA curves of the typical polymer **III$_g$** shown in Fig. 3 indicated high thermal stability with no significant weight loss up to approximately 430 °C under a nitrogen or an air atmosphere. As shown in Fig. 3, T_d

is higher under air than under nitrogen between 500–630 °C. The other polymers in the **III** series also show similar phenomena to $\mathbf{III_g}$. This is probably caused by the crosslinking reaction of the alicyclic ring during the oxidative degradation under air, which raised the T_ds of the polymers. The T_ds of $\mathbf{III_{d,g}}$ are about 10 °C higher than those of $\mathbf{III_{e,h}}$ under nitrogen: the para linkage of the phenoxyl group probably induces better thermal resistance properties. Polymers $\mathbf{III}_{\mathbf{g,i,j}}$ had good thermal stability; $\mathbf{III_j}$, which contained the hexafluoroisopropyl units, had the highest T_d. These new PAIs did not show much decrease in thermal stability when compared with Torlon.

The thermal transition data of the PAIs are also summarized in Table 5. After quenching, the glass-transition temperatures (T_gs) could be easily observed in the second-heating DSC traces and were in the range 242–312 °C. The highest T_g was observed for $\mathbf{III_a}$, which contained a *p*-phenylene unit within the diamine moiety, and was probably due to **IIIa** having the most symmetric structure. Similarly, the T_gs of $\mathbf{III_{d,g}}$ are about 15 °C higher than those of $\mathbf{III_{e,h}}$. The lowest T_g, associated with $\mathbf{III_j}$, is attributed to the presence of the flexible hexafluoroisopropyl group which reduced the packing density of the polymer chains. The T_g of $\mathbf{III_k}$ is higher than those of $\mathbf{III_{i,j}}$ due to the presence of more cardo groups interrupting the rotation of the polymer chain.

Conclusion

A novel polycyclic-cardo-group-containing diimide–diacid (**II**) was prepared by the condensation of a cardo-group-containing bis(ether amine) ($\mathbf{I_k}$) with TMA. The imide–imide–amide–amide type of the alternating copolymer could be easily obtained by the direct polycondensation of **II** and aromatic diamines. Almost all the polymers were soluble in polar solvents such as NMP, DMAc and DMF, and could be cast from these solvent into transparent, flexible, and tough films which exhibited good tensile properties. These PAIs also possessed high thermal stability below 430 °C under a nitrogen or an air atmosphere.

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