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Preparation and properties of polyamides and polyimides from 4,4″-diamino-*o*-terphenyl

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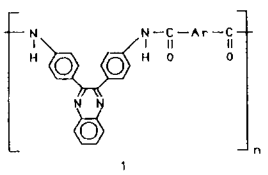
Polyamides and polyimides having 4,4″-*o*-terphenyldiyl units in the main chain were synthesized. The polyamides were prepared from 4,4″-diamino-*o*-terphenyl and aromatic dicarboxylic acids or aromatic dicarbonyl dichlorides. The polyimides were prepared from 4,4″-diamino-*o*-terphenyl and aromatic tetracarboxylic dianhydrides. Copolyamides and copolyimides were also prepared using 4,4″-diamino-*o*-terphenyl and other diamines. The T_g values of the polyamides were high (283–298°C). The polyamides were soluble in cyclohexanone and pyridine. The polyimides also possessed high T_g values (298–372°C). The solubilities of the polyimides, on the other hand, were poor. The introduction of *o*-terphenyl units into the main chain of the polyamides led to high thermal stability as well as good solubility.

(Keywords: polyamides; polyimides; 4,4″-diamino-*o*-terphenyl)

INTRODUCTION

We have previously reported upon the syntheses of the thermally stable and highly soluble polymers **1**, **2** and **4** having heterocycles in the main chain. Polyamides **1** and polyimides **4** having 2,3-quinoxalinediyl units[1,2] as well as polyamides **2** having 2-phenyl-4,5-imidazolediyl units[3] show high T_g values (>300°C). Introduction of 1,2-heteroarylene units leads to a zigzag main chain structure which increases the bulkiness and reduces the symmetry of the polymer chain. These effects, in general, improve the solubility but lower the thermal stability of the polymer. However, polymers **1**, **2** and **4** are not only thermally stable but are also soluble in many polar organic solvents. We attributed the high thermal stability of these polymers to the rigid aromatic structures and the dipole–dipole interactions of the heterocycles. In this paper, we report the preparation of aromatic polyamides **3** and polyimides **5** having 4,4″-*o*-terphenyldiyl units in the main chain, which have structures similar to those of the polymers **1**, **2** and **4** but have lower dipole moments, as well as the preparation of copolymers from 4,4″-diamino-*o*-terphenyl and other aromatic diamines in order to investigate the effects of the structure on the polymer properties.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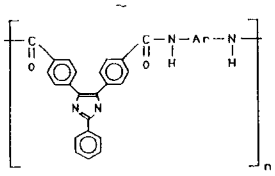
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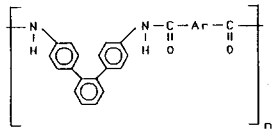
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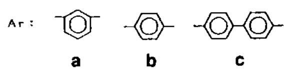

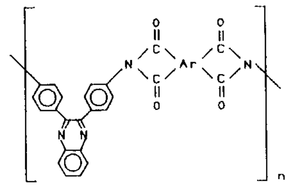
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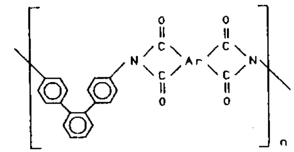
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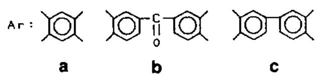

EXPERIMENTAL

*4,4″-Diamino-*o*-terphenyl 6*

Tin(II) chloride dihydrate (72.2 g) dissolved in 143 ml of hydrochloric acid was cooled to below −18°C under a nitrogen atmosphere. After 4,4″-dinitro-*o*-terphenyl[4]

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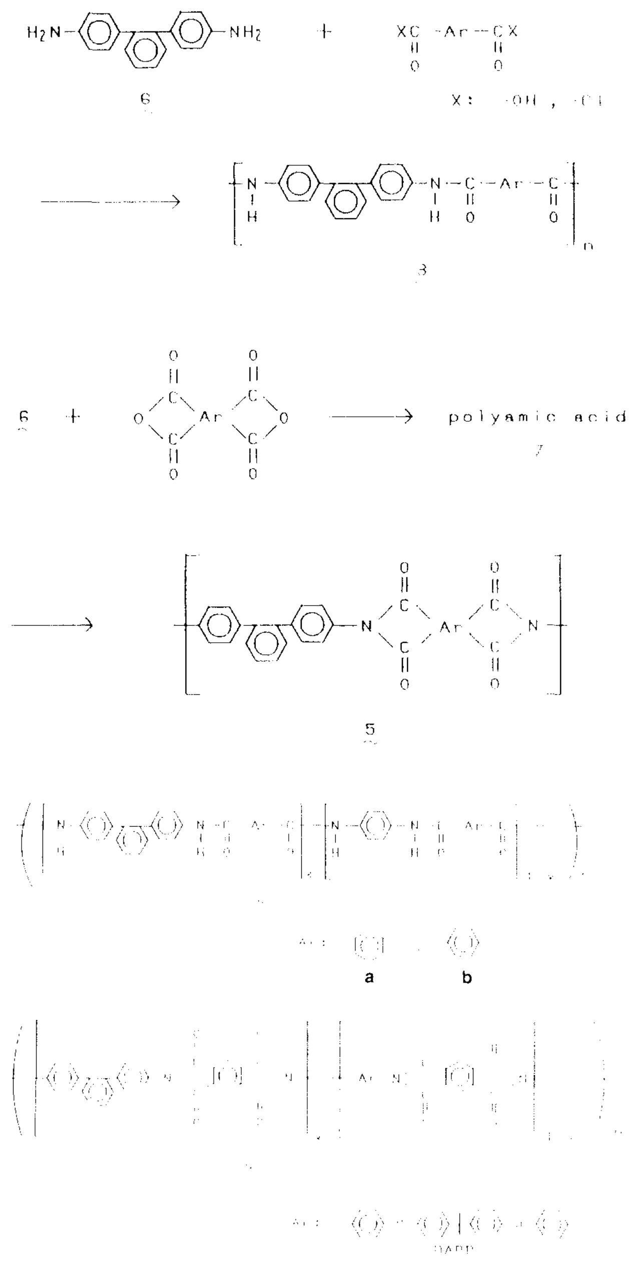


(15.0 g) was added, the reaction mixture was stirred and heated at 65°C for 9 h. The end point of the reaction was checked by dissolution of a portion of the reaction mixture when it was added to water. The mixture was cooled to room temperature and filtered. The salts were collected and dissolved in 200 ml of water. When the solution was poured into 200 ml of 20% NaOH solution, a white precipitate was formed. The precipitate was filtered, washed twice with 5% NaOH solution and three times with water and dried *in vacuo*. The product was recrystallized from anhydrous ethanol to give light-brown needles (65.9% yield), melting point (m.p.) 159.5–159.9°C (literature value[4] 149°C). I.r. (KBr, cm^{-1}) 3424 and 3352 (N–H). ^{13}C n.m.r. ($CDCl_3$, ppm) 114.7, 126.8, 130.4, 130.6, 132.2, 140.3 and 144.7. Analysis: calculated for $C_{18}H_{16}N_2$ (260.3): C, 83.04; H, 6.20; N, 10.76. Found: C, 82.80; H, 6.38; N, 11.00.

*4,4″-Bisbenzoylamino-*o*-terphenyl **10** (polyamide model)*

Into a 50 ml four-necked flask equipped with a reflux condenser and a nitrogen gas inlet were placed 1.83 g of **6**, 10.3 ml of dimethylacetamide (DMAc) and a magnetic stirrer bar. The mixture was cooled to −18°C and stirred until all the ingredients were dissolved. Then, propylene oxide (7.9 ml) was added. After stirring for 5 min, benzoyl chloride (2.45 ml) was added and the reaction mixture was stirred for 1 h. The mixture was then stirred at room temperature for 2 h and then poured into 400 ml of water. The precipitate was filtered, washed with 500 ml of 10% sodium carbonate solution and 500 ml of water, and dried *in vacuo*. The crude product was recrystallized from cyclohexanone (CHO) (85.1% yield, m.p. 323.4°C by thermogravimetry–differential thermal analysis (t.g.–d.t.a.)). I.r. (KBr, cm^{-1}) 1650 and 1522 (amide I, II). Analysis: calculated for $C_{32}H_{24}N_2O_2$ **10** (468.5): C, 82.03; H, 5.16; N, 5.98. Found: C, 82.00; H, 5.15; N, 6.02.

Direct polycondensation of polyamide

A typical procedure was as follows. Into a four-necked 10 ml reaction tube equipped with a reflux condenser, a mechanical stirrer and a nitrogen gas inlet were placed 0.0671 g of calcium chloride, 0.0221 g of lithium chloride and 0.5 ml of 1-methyl-2-pyrrolidone (NMP). The mixture was heated with stirring under a nitrogen atmosphere until the salts were dissolved. After the mixture had cooled to room temperature, pyridine (Py) (0.22 ml) and triphenyl phosphite (0.525 ml) were added. Then, diamine **6** (0.2603 g), isophthalic acid (0.1661 g) and more NMP (0.6 ml) were added. The reaction mixture was heated at 115°C for 5 h with stirring. It was then cooled and poured into aqueous methanol (1:1 by volume). The precipitate was collected on a glass filter (3G), washed with methanol in reflux and dried *in vacuo* (97.0% yield, $\eta_{\mathrm{inh}} = 0.31\ \mathrm{dl\,g^{-1}}$ ($0.5\ \mathrm{g\,dl^{-1}}$ concentrated H_2SO_4 at 30°C)).

Low temperature solution polycondensation of polyamide

A typical procedure was as follows. Into a 10 ml reaction tube equipped with a nitrogen gas inlet and a calcium chloride tube were placed 0.1537 g of lithium chloride, 0.2603 g of diamine **6** and 2.0 ml of NMP. The salts were allowed to dissolve, and to the cooled (−20°C) solution were added 0.2030 g of isophthaloyl dichloride and 0.78 ml of propylene oxide (PO). The mixture was stirred at −20°C for 1 h, then at −10 to −15°C for 1 h, and finally at room temperature for 5 h. The reaction mixture was then poured into aqueous methanol (1:1 by volume). The precipitate was collected with a glass filter (3G) and then dried *in vacuo* at 60°C (85.3% yield, $\eta_{\mathrm{inh}} = 0.46\ \mathrm{dl\,g^{-1}}$ ($0.5\ \mathrm{g\,dl^{-1}}$ concentrated H_2SO_4 at 30°C)).

N,N″-o-*Terphenyl-4,4″-diyldiphthalic imide **11** (polyimide model)*

Into a four-necked 10 ml reaction tube equipped with a mechanical stirrer and a nitrogen inlet with a calcium chloride tube were placed 0.5206 g of diamine **6** and 3.0 ml of DMAc. The mixture was cooled to −15°C and phthalic anhydride (0.5295 g) was added. The mixture was stirred at that temperature for 1 h and then at room temperature for 4 h. The resulting solution was spread onto a glass plate and the solvent was removed at 60°C. The film thus obtained was dried *in vacuo* at 60°C. Thermal cyclodehydration was performed at 200°C for 2 h in a nitrogen atmosphere and then at 300°C. The product was recrystallized from dimethylformamide (DMF) (22.5 ml g^{-1}), and further purified by sublimation (65.4% yield, m.p. 307°C (t.g.–d.t.a., light-yellow powder)). I.r. (KBr, cm^{-1}) 1778, 1722 (C=O) and 1376 (C–N). Analysis: calculated for $C_{34}H_{20}N_2O_4$ **11** (520.49): C, 78.45; H, 3.87; N, 5.38. Found: C, 78.47; H, 3.90; N, 5.27.

Ring-opening polyaddition and cyclodehydration of polyimide 5

A typical procedure was as follows. Into a four-necked 10 ml reaction tube equipped with a mechanical stirrer and a nitrogen inlet with a calcium chloride tube were placed 0.2603 g of diamine **6** and 1.0 ml of NMP. To the cooled (– 18°C) solution were added 0.1281 g of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BTDA) and 1.0 ml of NMP. The mixture was stirred at room temperature for 5 h and then allowed to stand overnight. A 0.50 ml portion of the reaction mixture was removed for viscosity measurement. The remaining mixture was spread onto a glass plate and the solvent was removed at 70°C. The film obtained was dried *in vacuo*. Thermal cyclodehydration of the polyamic acid **7** was performed by heating at 180°C for 2 h and then at 350°C. As soon as the temperature reached 350°C, the product was taken out of the electric furnace and cooled to room temperature. The inherent viscosity of the polyamic acid was 0.32 dl g^{-1} (0.5 g dl^{-1} NMP at 30°C).

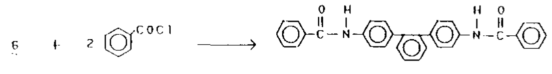
Measurements

Glass transition temperatures were obtained by differential scanning calorimetry (d.s.c.) on a Rigakudenki 8055D1. Decomposition temperatures were obtained by t.g.–d.t.a. on a Mac Science 2000. I.r. spectra were recorded on a Hitachi 270-30 spectrophotometer. ^{13}C n.m.r. spectra were recorded at 125 MHz on a Nihondenshi JNM-GSX500 spectrometer.

RESULTS AND DISCUSSION

4,4″-Diamino-*o*-terphenyl **6** was prepared using a two-step reaction from *o*-terphenyl. Nitration of *o*-terphenyl was carried out according to the method of Garapon and Stille[5]. Catalytic reduction of 4,4″-dinitro-*o*-terphenyl in the presence of Raney nickel catalyst has been reported[4] to give **6**. In the present work, however, the reduction was carried out using a more convenient $SnCl_2$–HCl system. The reaction product was recrystallized from anhydrous ethanol. The melting point (159.5–159.9°C) of the obtained product did not agree with the literature value[4] (149°C), but the reduction product was identified as diamine **6** by ^{13}C n.m.r. and i.r. spectroscopy as well as by elemental analysis.

Prior to polymerization, model reactions were performed as follows



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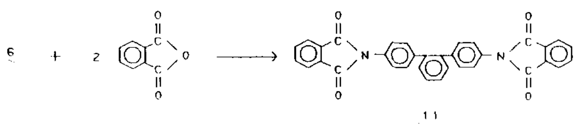

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The model products **10** and **11** were obtained in 85% yield and 65% yield, respectively. Their structures were confirmed by spectroscopic data as well as by elemental analysis.

Poly(imino-4,4″-*o*-terphenyldiyliminocarbonylarylenecarbonyl)s **3a**–**3c** were prepared by direct polycondensation[6,7] of 4,4″-diamino-*o*-terphenyl **6** with aromatic dicarboxylic acids, e.g. isophthalic acid, terephthalic acid and 4,4′-biphenyldicarboxylic acid. Polyamides **3a**–**3c** were also synthesized from diamine **6** and aromatic dicarbonyl dichlorides by conventional low temperature solution polycondensation using propylene oxide[8] or lithium carbonate[9] as the hydrogen chloride acceptor. The results for the polycondensations are shown in *Table 1*. All polyamides were obtained in quantitative yields. Polyamides prepared by low temperature solution polycondensation showed higher inherent viscosities than the polyamides obtained by direct polycondensation.

The solubilities of the polyamides are summarized in *Table 2*. Polyamide **3a** was soluble in all the polar solvents used except formic acid, and its solubility was as good as that of polyamide **1a** or **2a**. Polyamide **3b** was soluble in all the polar solvents used except pyridine, cyclohexanone and formic acid. But in comparison to polyamides **1b** and **2b**, the solubility of polyamide **3b** was a little lower. On the contrary, polyamide **3c**, of which the solubility was poor, was merely soluble in concentrated sulfuric acid and hexamethylphosphoric triamide (HMPA). Its solubility was much lower than that of polyamide **3a** or **3b**, which may be attributed to a decrease in the number of *o*-terphenyl groups in the repeat units owing to the use of a dicarboxylic acid with a higher molecular weight. Moreover, the solubility of **3c** was also much lower than that of **1c** or **2c**. From these results, it can be seen that there was a trend for the solubility of a polyamide having heterocyclic units in the main chain to be superior to that of a polyamide not having these units. This trend can probably be attributed to the polarity of the heterocyclic units in the polyamide main chain.

The thermal properties of the polyamides are summarized in *Table 3*. The T_g values of polyamides **3** were above 280°C but 30–80°C lower than those of polyamides **1** and **2**, which suggests that dipole–dipole interactions between the polymer chains in polyamides **1** and **2** contribute to the high T_g values. The temperatures at which 5% weight loss were observed with thermogravimetry

Table 1 Results of preparations of polyamides 3

Polymer	Method[a]	Yield (%)	η_{inh}[b] (dl g^{-1})
3a	DP	97.0	0.31
	LS1	85.3	0.46
	LS2	91.4	0.58
3b	DP	96.7	0.27
	LS1	93.5	0.36
	LS2	89.8	0.48
3c	DP	95.5	0.33
	LS1	97.7	0.80
	LS2	95.8	0.35

[a] DP, direct polycondensation; LS1, low temperature solution condensation (PO); LS2, low temperature solution condensation (Li_2CO_3)
[b] Inherent viscosity measured in H_2SO_4 (0.50 g dl^{-1}) at 30°C

Table 2 Solubilities[a] of polyamides

Polymer	CHO	Py	*m*-Cre[b]	DMAc	NMP	HMPA	DMF	HCOOH	DMSO[c]	H_2SO_4	Ref.
1a	−	±	+	+	+	+	+	±	(+)	+	1
1b	−	SW	+	+	+	+	SW	±	(+)	+	
1c	−	−	+	+	+	+	±	±	(+)	+	
2a	±	+	+	+	+	±	+	+	+	+	2
2b	±	+	+	+	+	±	+	+	+	+	
2c	±	+	+	+	+	±	+	+	±	+	
3a	(+)	+	+	+	+	+	+	−	+	+	
3b	(±)	−	(+)	+	+	+	(+)	−	+	+	
3c	−	−	−	−	−	+	−	−	−	+	

[a] The symbols have the following meanings: +, soluble; ±, partially soluble; −, insoluble; SW, swelling; ( ), soluble on heating
[b] *m*-Cresol
[c] Dimethyl sulfoxide

Table 3 Thermal properties of polyamides

Polymer	T_g^a (°C)	T_d^b (°C)	Ref.
1a	314	473	1
1b	357	464	
1c	377	497	
2a	343	483	2
2b	361	487	
2c	358	487	
3a	283	442	
3b	289	462	
3c	298	486	

[a] Measured by d.s.c. ($\Delta T = 10\,K\,min^{-1}$) under a nitrogen atmosphere
[b] Temperature at which a 5% weight loss was observed with t.g. under nitrogen ($\Delta T = 10\,K\,min^{-1}$)

(T_d values) for polyamides **3** were similar to those for **1** and **2**.

The copolyamides **8** were prepared from isophthaloyl dichloride or terephthaloyl dichloride and mixtures of diamine **6** and *p*-phenylenediamine. Copolyamides **8** were obtained in quantitative yields using low temperature solution polycondensation. The solubilities of copolyamides **8** are summarized in *Table 4*. The higher the content of 4,4″-*o*-terphenyldiyl units in the copolyamide, the higher the solubility. For example, while polyamide **8a** without 4,4″-*o*-terphenyldiyl units was soluble only in concentrated sulfuric acid, copolyamide **8a** containing 25% 4,4″-*o*-terphenyldiyl units was soluble also in DMAc, NMP and HMPA. Copolymers **8b** were expected to have poor solubility because of the rigid structure of the terephthaloyl unit, but copolyamide **8b** having 75% 4,4″-*o*-terphenyldiyl units was soluble in NMP and HMPA, indicating that the introduction of 4,4″-*o*-terphenyldiyl units into the main chain of the polymer leads to improved solubility over that effected by the phenylene linkage. The thermal properties of copolyamides **8** are shown in *Table 5*. The T_g and T_d values of copolyamides **8** were high ($T_g > 270°C$, $T_d > 440°C$). The introduction of 4,4″-*o*-terphenyldiyl units into the main chain, as opposed to the introduction of 1,4-phenylene or 1,3-phenylene units, was expected to lower the thermal stability. But even when the content of 4,4″-*o*-terphenyldiyl units in the copolyamides was increased, the thermal stabilities of copolyamides **8** were little affected.

Polyimides **5** were prepared using a two-step procedure[10]. Polyamic acids **7**, prepared by ring-opening polyadditions of diamine **6** to tetracarboxylic dianhydrides, were cyclodehydrated with heating. Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BPDA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BTDA) were used as the tetracarboxylic dianhydrides. Since the use of DMAc as a solvent caused precipitation of the polymer, NMP was used instead. The results of polymerizations of **6** with tetracarboxylic dianhydrides are summarized in *Table 6*. The inherent viscosities of all the polyamic acids were lower than those of polyamides **3**. Thermal cyclodehydration of polyamic acids **7** was performed at 180°C for 2 h and then at 300°C for 1 h under nitrogen. Completion of cyclodehydration was confirmed by the presence in the i.r. spectrum of absorptions at 1778, 1722 (imide C=O) and 1376 cm^{-1} (imide C–N).

Table 4 Solubilities of copolyamides **8**

Polymer	x^a	CHO	Py	*m*-Cre	DMAc	NMP	HMPA	DMF	HCOOH	DMSO	H_2SO_4
8a	1.00	+	+	+	+	+	+	+	−	+	+
	0.75	±	+	+	+	+	+	+	−	+	+
	0.50	−	+	+	+	+	+	+	−	+	+
	0.25	−	−	±	+	+	+	−	−	±	+
	0	−	−	−	−	−	−	−	−	−	+
8b	1.00	(±)	−	(+)	+	+	+	(+)	−	+	+
	0.75	−	−	−	±	+	+	−	−	±	+
	0.50	−	−	−	−	±	−	−	−	±	+
	0.25	−	−	−	−	−	−	−	−	−	+
	0	−	−	−	−	−	−	−	−	−	+

[a] Molar fraction of repeat units containing *o*-terphenyldiyl groups

Table 5 Some results for copolyamides **8**

Polymer	x	Yield (%)	η_{inh} (dl g^{-1})	T_g (°C)	T_d (°C)
8a	1.00	91.4	0.58	283	444
	0.75	100.0	0.54	275	454
	0.50	97.6	0.54	279	448
	0.25	97.1	0.72	277	451
	0	86.1	1.24	277	464
8b	1.00	89.8	0.48	298	486
	0.75	79.9	1.41	–[a]	462
	0.50	90.8	0.94	–[a]	472
	0.25	90.2	0.77	–[a]	493
	0	91.3	0.57	–[a]	503

[a] Not observed

Table 6 Results of preparations of polyamic acids **7**

Polymer	η_{inh} (dl g^{-1})	Colour
7a	0.34	Yellow
7b	0.29	Yellow
7c	0.32	Yellow

As shown in *Table 7*, the solubilities of polyimides **5** are rather poor; polyimide **5a**, in particular, was soluble only in concentrated sulfuric acid, and its solubility was lower than that of polyimide **4a**. The solubility of **5b** was as low as that of **4b**, and a similar result was also obtained with regard to the solubility of **5c**.

The thermal properties of polyimides **5** are summarized in *Table 8*. Compared with polyimides **4**, polyimides **5** have lower T_g values. The decreased dipole moment due to the introduction of 4,4''-*o*-terphenyldiyl units apparently leads to lower T_g values.

Copolymerizations were conducted using **6** and 4,4'-isopropylidenebis(1,4-phenylenoxy)dianiline (DAPP). The results are summarized in *Table 10*. The inherent viscosities of the copolyimides were much improved. The solubilities of copolyimides **9** are summarized in *Table 9*. Generally, the introduction of flexible units such as ether and propylidene units into the polymer backbone improves the solubility of the polymers, but even copolyimide 9 containing 75% DAPP was insoluble in all solvents other than concentrated sulfuric acid, which suggests that the structure of the imide unit is so

Table 7 Solubilities of polyimides

Polymer	CHO	Py	*m*-Cre	DMAc	NMP	HMPA	DMF	HCOOH	DMSO	H_2SO_4	Ref.
4a	–	–	±	–	±	–	±	±	±	+	3
4b	–	±	±	–	±	–	–	±	±	+	
4c	–	–	+	–	±	–	–	±	–	+	
5a	–	–	–	–	–	–	–	–	–	+	
5b	–	±	(±)	(±)	(±)	–	(±)	–	±	+	
5c	–	(SW)	+	–	(±)	–	(SW)	–	–	+	

Table 8 Thermal properties of polyimides

Polymer	T_g[a] (°C)	T_d[b] (°C)	Ref.
4a	380	539	3
4b	326	545	
4c	351	556	
5a	372	563	
5b	298	561	
5c	319	571	

Table 9 Solubilities of copolyimides **9**

Polymer	x[a]	CHO	Py	*m*-Cre	DMAc	NMP	HMPA	DMF	HCOOH	DMSO	H_2SO_4
9	1.00	–	–	–	(SW)	–	–	–	–	–	+
	0.75	–	–	–	–	(±)	–	–	–	–	+
	0.50	–	–	(SW)	(SW)	(±)	–	–	–	–	+
	0.25	–	(SW)	–	(SW)	(±)	–	–	–	–	+
	0	(±)	–	–	(SW)	(±)	–	–	–	–	+

[a] Molar fraction of repeat units containing *o*-terphenyldiyl groups

Table 10 Some results for copolyimides **9**

Polymer	x	η_{inh} (dl g^{-1})	T_g (°C)	T_d (°C)
9	1.00	0.34	372	563
	0.75	0.57	351	534
	0.50	0.84	329	523
	0.25	1.05	309	515
	0	1.39	289	507

rigid and symmetrical that the introduction of 4,4″-*o*-terphenyldiyl units into the main chain does not improve the solubility. The thermal properties of copolyimides **9** are summarized in *Table 10*. As the content of **6** in the mixture of diamines increases, the value of T_d also increases. This was attributed to the increased rigidity of the main chain.

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