

New Poly(amide imide)s Containing Bis(4-trimellitimidophenyl) Sulfone and Hydantoin Moieties in the Main Chain: Synthesis and Properties

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ABSTRACT: Several new poly(amide imide)s were synthesized through the polycondensation reactions of bis(4-trimellitimidophenyl) sulfone [*N,N'*-(4,4'-diphenylsulfone) bistrimellitimide] with a number of hydantoin derivatives in a medium consisting of thionyl chloride, *N*-methyl-2-pyrrolidone, and pyridine. The polycondensations produced a series of novel poly(amide imide)s in high yields with inherent viscosities of 0.20–0.46 dL/g. The resulting poly(amide imide)s were characterized with elemental analysis, viscosity measurements, thermogravimetric analysis, deriv-

ative thermogravimetry, solubility testing, and Fourier transform infrared spectroscopy. All the polymers were soluble at room temperature in polar solvents such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, and *N*-methyl-2-pyrrolidone. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1776–1782, 2005

Key words: poly(amide imide)s; hydantoin moieties; solution polycondensation

INTRODUCTION

Aromatic polyimides are well known as high-performance polymeric materials because of their excellent thermal stability and balanced mechanical and electrical properties.^{1,2} They are finding numerous applications in the fields of adhesives, composites, fibers, films, and electrical materials.^{3,4} However, aromatic polyimides are difficult to process because of their high softening temperatures and limited solubility in organic solvents. Some methods are used to overcome these weak points, such as the addition of flexible linkages to the main chain^{5,6} and the introduction of substituted groups,⁷ flexible spacers,⁸ and heterocyclic moieties into the main chain.^{9,10} The synthesis of poly(amide imide)s (PAIs) with heterocyclic moieties is one method. In our previous work, we used this method to synthesize a series of new PAIs with modified properties.^{11–13} Furthermore, the insertion of sulfone groups into the polymer chain generally results in improved solubility, along with interesting properties, such as an increased glass-transition temperature and high thermooxidative stability.¹⁴ In this article, we

describe a series of novel PAIs containing bis(4-trimellitimidophenyl) sulfone and hydantoin moieties from the polycondensation reaction of *N,N'*-(4,4'-diphenylsulfone) bistrimellitimide (**3**) with six derivatives of hydantoins (**4a–4f**) with thionyl chloride, *N*-methyl-2-pyrrolidone (NMP), and pyridine as condensing agents.

EXPERIMENTAL

Materials

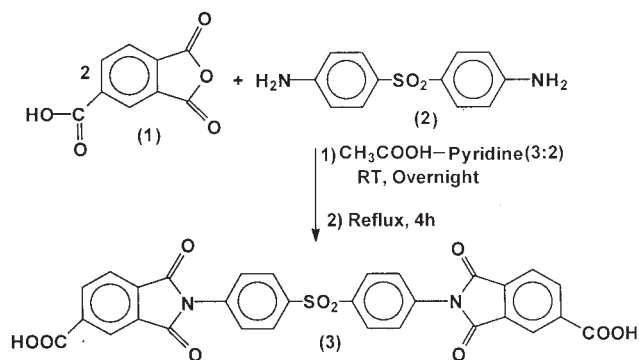
All chemicals were purchased from Merck Chemical Co. (Germany).

Techniques

¹H-NMR spectra were recorded on a Bruker 500-MHz instrument. Fourier transform infrared (FTIR) spectra were recorded on a Galaxy (England) FTIR 5000 spectrophotometer. Spectra of the solids were taken with KBr pellets. Vibrational transition frequencies were reported as wave numbers (cm⁻¹). The band intensities were designated as weak (w), medium (m), shoulder (sh), strong (s), or broad (br). The inherent viscosities were measured by a standard procedure with a Technico viscometer. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) data for the polymers were taken on a Mettler TA4000 system under an N₂ atmosphere at a rate of 10°C/min.

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Scheme 1

Differential scanning calorimetry was performed on a Stanton Redcraft STA-780 at a heating rate of 10°C/min in air. Elemental analyses were performed by Arak Petrochemical Co. (Arak, Iran).

Monomer synthesis

N,N'-(4,4'-Diphenylsulfone) bistrimellitimidic acid (3)

This compound was prepared according to a typical procedure shown in Scheme 1. Into a 250-mL, round-bottom flask (3.84 g, 20 mmol) with trimellitic dianhydride (1; 2.48 g, 10 mmol) and 4,4'-diaminodiphenyl sulfone (2), a 60-mL mixture of acetic acid and pyridine (3:2) and a stirring bar were placed. The mixture

was stirred at room temperature overnight and then refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in 100 mL of cold water; then, 5 mL of concentrated HCl was added. The solution was stirred until a yellow precipitate was formed, and then the precipitate was filtered off and dried to produce 5.07 g (85%) of 3 as white crystals.

mp: >300°C. FTIR (KBr, cm^{-1}): 3400–2500 (m, br), 1775 (w, sh), 1730–1700 (s, br), 1608 (m), 1506 (s), 1425 (w), 1392 (s), 1307 (s), 1300 (m), 1257–1200 (s, br), 1168 (m), 1118 (m), 1100 (m), 927 (w), 883 (w), 827 (m), 727 (m). $^1\text{H-NMR}$ [dimethyl sulfoxide- d_6 (DMSO- d_6), tetramethylsilane, δ]: 7.77–7.81 (d, 4H), 8.18–8.20 (d, 4H), 8.08–8.12 (d, 2H), 8.41–8.43 (d, 2H), 8.31 (s, 2H), 8.56 (s, br, 2H) ppm. ANAL. Calcd for $\text{C}_{30}\text{H}_{16}\text{N}_2\text{O}_{10}\text{S}$: C, 60.40%; H, 2.70%; N, 4.69%. Found: C, 60.7%; H, 2.9%; N, 4.4%.

5,5-Disubstituted hydantoin derivatives (4a–4f)

These compounds were prepared according to our previous works.¹⁵

Polymer synthesis

PAIs 5a–5f were prepared with the following general procedure (5a is used as an example). The imide dicarboxylic acid (3; 0.596 g, 1 mmol) was dissolved in 5

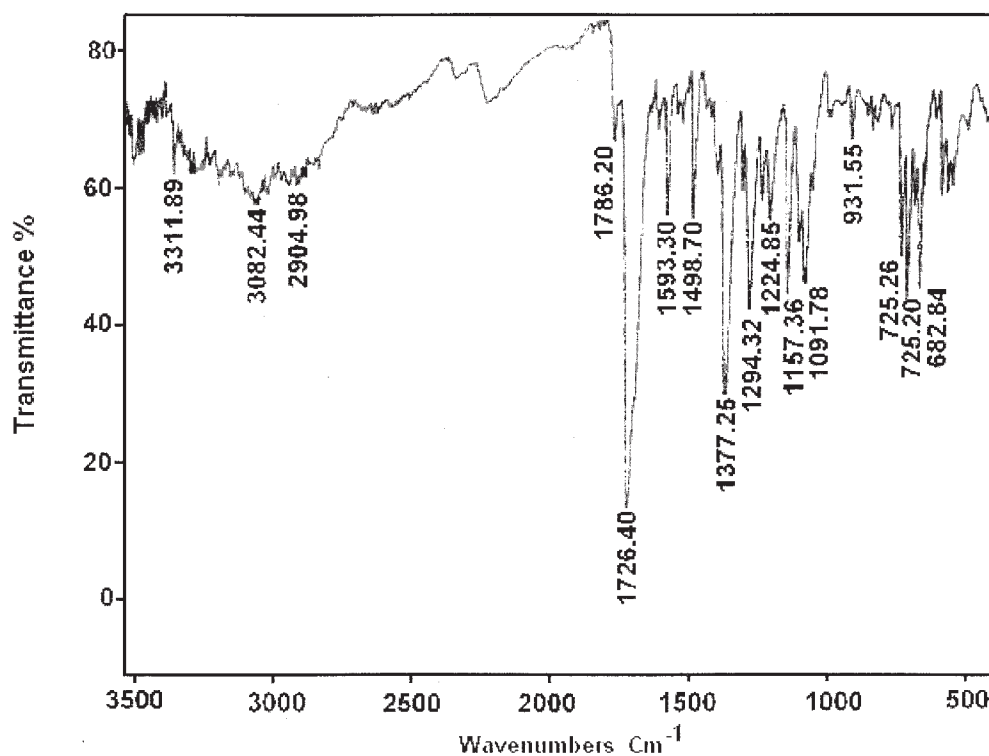


Figure 1 FTIR spectrum of imide acid 3.

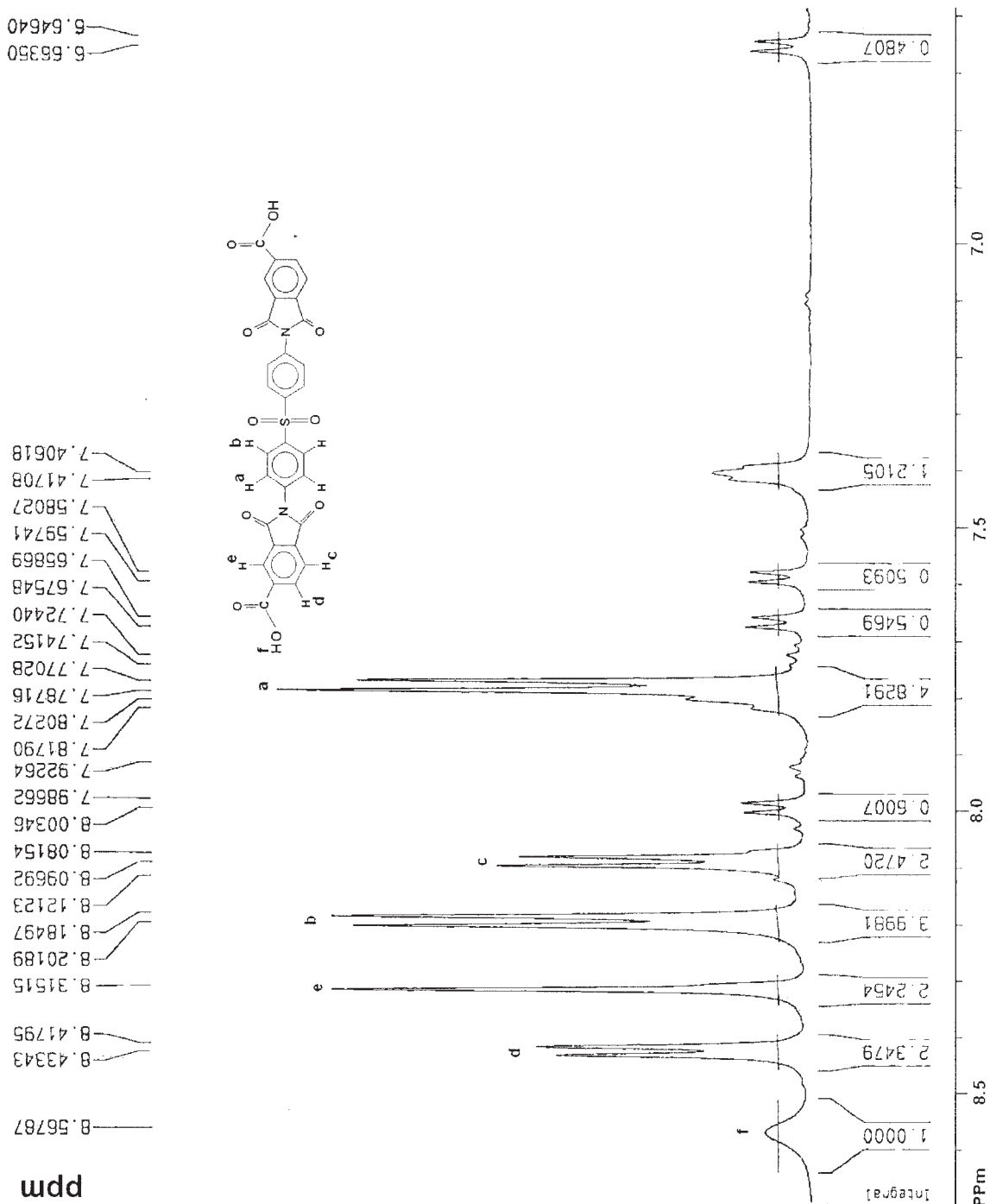
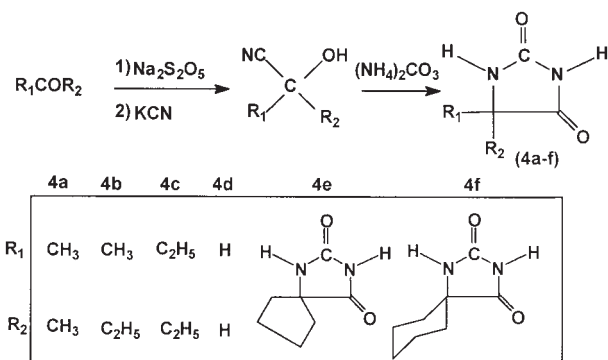


Figure 2 ¹H-NMR spectrum of imide acid 3.



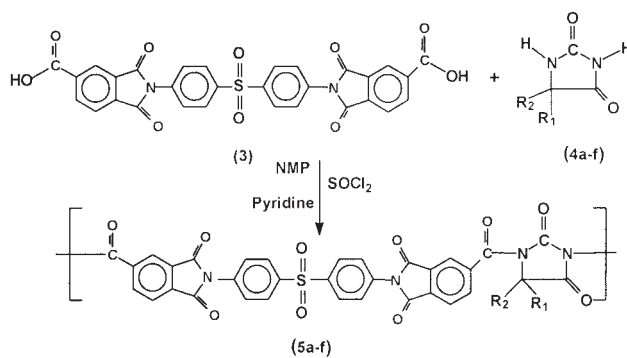
Scheme 2

mL of NMP in a dry three-necked flask. The solution was cooled to -10°C ; then, thionyl chloride (SOCl_2) (0.298 g, 2.5 mmol) was added, and the mixture was stirred for 2 min. 5,5-Dimethyl hydantoin **4a** (0.128 g, 1 mmol) and pyridine (0.198 g, 2.5 mmol) were then added to the mixture. It was stirred for 15 h at 0°C and then for 2 h at room temperature. The viscous reaction mixture was poured into 25 mL of methanol (MeOH). The precipitated polymer (**5a**) was collected by filtration and was dried at 80°C for 8 h *in vacuo*; 0.42 g (61%) of solid polymer was produced.

RESULTS AND DISCUSSION

Monomer synthesis

3 was prepared in a one-pot reaction sequence, as shown in Scheme 1. **3** was synthesized through the condensation reaction of 2 equiv of **1** with 1 equiv of **2** in a mixture of acetic acid and pyridine (3:2). Dissolving the residue in cold water produced a gummy solid that provided a white solid with the addition of concentrated HCl. The chemical structure and purity of **3** were proved with elemental analysis, FTIR, and $^1\text{H-NMR}$ spectroscopy techniques. The $^1\text{H-NMR}$ spectrum of compound **3** showed two doublet peaks between 7.77–7.81 and 8.18–8.20 ppm, which were assigned to the H_a and H_b protons of the phenyl rings, respectively. Peaks between 8.08–8.43 and 8.41–8.43 ppm (two doublets) were assigned to the H_c and H_d protons of the imide rings, respectively. The singlet peak at 8.31 ppm was assigned to H_e protons of the imide rings. Finally, a broad peak at 8.56 ppm was assigned to H_f protons of the COOH groups (Fig. 1). The FTIR spectrum of compound **3** showed a broad peak between 2800 and 3500 cm^{-1} , which was assigned to the COOH groups. Several absorption bands appeared at 1786, 1726, 752, and 729 cm^{-1} , which were characteristic peaks for the imide rings. Also, the absorptions found at 1377 and 1157 were characteristic peaks for the SO_2 group (Fig. 2):



Scheme 3

TABLE I
Synthesis and Some Physical Properties of 5a–5f

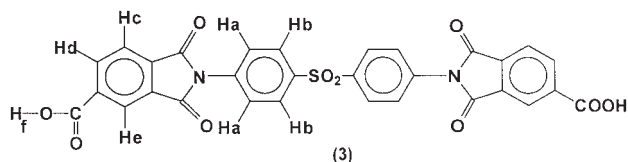
Polymer	Hydantoin moieties	Yield (%)	η_{inh} (dL/g) ^a
5a	4a 	83	0.30
5b	4b 	79	0.39
5c	4c 	85	0.46
5d	4d 	78	0.20
5e	4e 	77	0.32
5f	4f 	82	0.30

η_{inh} = inherent viscosity.

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C

TABLE II
Elemental Analysis of 5a–5f

Polymer	Formula		C (%)	H (%)	N (%)
5a	$C_{35}H_{20}N_4O_{10}S$ (688.60) _n	Calcd	61.04	2.92	8.13
		Found	62.2	2.8	7.9
5b	$C_{36}H_{22}N_4O_{10}S$ (702.63) _n	Calcd	61.54	3.15	7.97
		Found	62.2	3.4	7.2
5c	$C_{37}H_{24}N_4O_{10}S$ (716.66) _n	Calcd	62.01	3.37	7.81
		Found	62.8	2.9	7.1
5d	$C_{33}H_{16}N_4O_{10}S$ (660.55) _n	Calcd	60.00	2.44	8.47
		Found	61.1	2.8	8.0
5e	$C_{37}H_{22}N_4O_{10}S$ (714.64) _n	Calcd	62.18	3.10	7.83
		Found	62.9	3.6	7.0
5f	$C_{38}H_{24}N_4O_{10}S$ (728.67) _n	Calcd	62.63	3.31	7.68
		Found	63.6	3.1	6.7



Hydantoin constitutes an important class of heterocycles in medicinal chemistry because many derivatives have been identified that are active against a broad range of biological targets.¹⁶ 5,5-Disubstituted hydantoin derivatives were synthesized by the Bucherer–Berg method. With this method, hydantoin compounds 4a–4f (Scheme 2) were prepared through

the reactions of cyanohydrin derivatives with ammonium carbonate.

Polymer synthesis

PAIs 5a–5f were synthesized by the direct solution polycondensation reactions of an equimolar mixture of 3 with the hydantoin derivatives 4a–4f with thionyl chloride, NMP, and pyridine as condensing agents (Scheme 3). The syntheses and some physical properties of these PAIs 5a–5f are given in Table I. The entire polycondensation readily proceeded in a homogeneous solution. Tough and stringy precipitates formed when the viscous PAIs solutions were trickled into stirred MeOH. All the polymers were obtained in moderate-to-good yields and had inherent viscosities of 0.20–0.46 dL/g.

Polymer characterization

The syntheses and some physical properties of PAIs 5a–5f are summarized in Table I. These polymers had inherent viscosities of 0.20–0.46 dL/g and were white. These polymers were confirmed to be PAIs with FTIR spectroscopy and elemental analyses (Table II). A representative FTIR spectrum of PAI 5e is shown in Figure 3. This polymer had absorption bands between 1780 and 1710 cm^{-1} due to imide and amide carbonyl groups. Absorption bands around 1390–1380 cm^{-1} and 730–710 demonstrated the presence of the imide

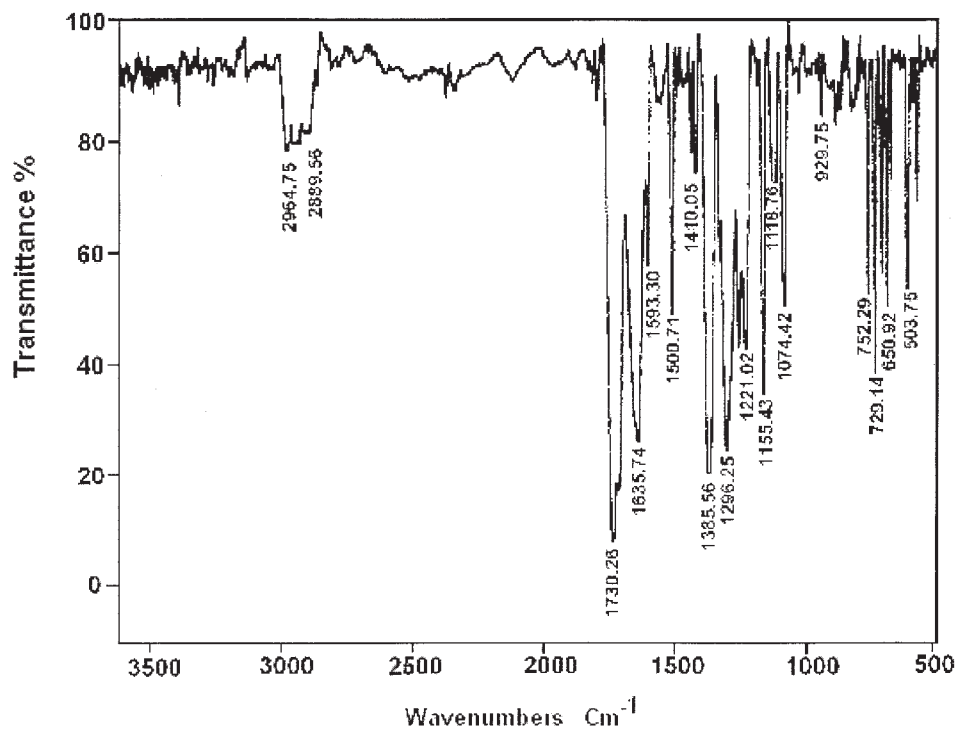


Figure 3 FTIR spectrum of PAI 5e.

TABLE III
Solubility of 5a–5f

Solvent	5a	5b	5c	5d	5e	5f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
Acetone	+	+	+	+	+	+
CHCl ₃	–	–	–	–	–	–
THF	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
MeOH	–	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–	–
H ₂ O	–	–	–	–	–	–

+ = soluble at room temperature; – = insoluble at room temperature.

heterocycle in this polymer. The other spectra showed similar patterns (see the appendix).

The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table II).

The solubility of PAIs 5a–5f was investigated with 0.01-g polymeric samples in 2 mL of a solvent. All these PAIs were soluble in organic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), DMSO, NMP, tetrahydrofuran (THF), and chloroform at room temperature and were insoluble in solvents such as acetone, methylene chloride, MeOH, ethanol (EtOH), and water (Table III). That the solubility of these PAIs was better than that of polyimides prepared from **1** and aromatic diamines can be explained by the presence of hydantoin moieties in the main chain.

Thermal properties

The thermal properties of PAIs 5a–5f were investigated with TGA and DTG in a nitrogen atmosphere at a rate of heating of 10°C/min, and the thermal data are summarized in Table IV (Figs. 4 and 5). The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yields at

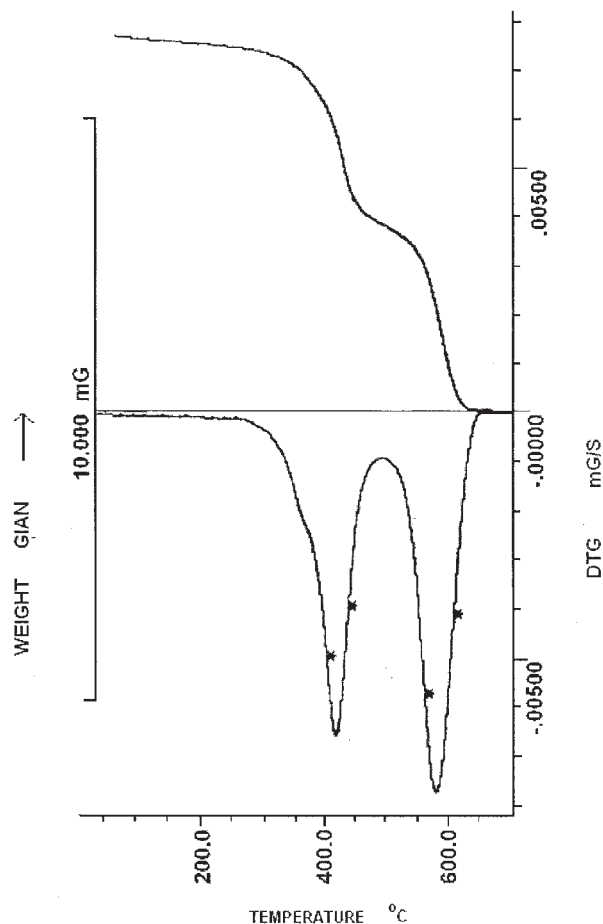


Fig 4. TGA and DTG thermogram of PAIs 5a

Figure 4 TGA and DTG thermogram of PAI 5a.

600°C for 5a–5f are summarized in Table IV. These polymers exhibited good resistance to thermal decomposition, up to 310–355°C in nitrogen, and began to decompose gradually above that temperature. T_5 for all the polymers ranged from 315 to 360°C, and the residual weight for these polymers at 600°C ranged from 11 to 20% in nitrogen.

CONCLUSIONS

This work involved the syntheses of several new PAIs (5a–5f) through solution polycondensation reactions of **3** with six hydantoin derivatives (4a–4f) with thionyl chloride, NMP, and pyridine as condensing agents. These PAIs were soluble in various organic solvents and had moderate thermal stability. The introduction of hydantoin moieties into the backbone increased the solubility of these polymers. These properties could make these PAIs attractive for practical applications, such as processable high-performance engineering plastics.

TABLE IV
Thermal Behavior of 5a–5f

Polymer	T_5 (°C) ^a	T_{10} (°C) ^a	Char yield ^b
5a	355–360	400–405	11
5b	320–325	340–345	13
5c	330–335	390–395	16
5d	310–315	350–355	18
5e	350–355	390–395	20
5f	325–330	370–375	12

^a Recorded by TGA at heating rate of 10°C/min in N₂.

^b Weight percentage of material left undecomposed after TGA at 600°C.

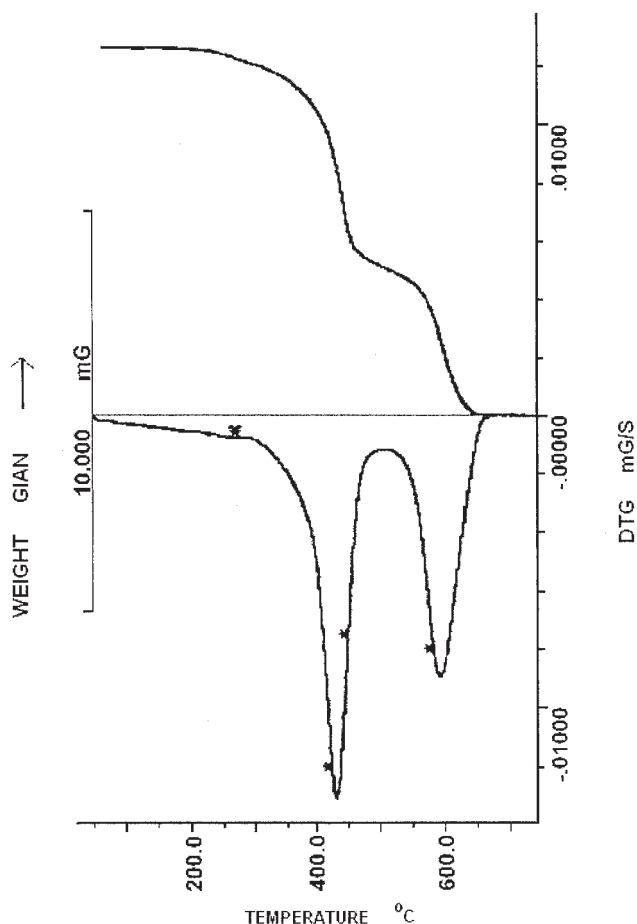


Fig. 5 TGA and DTG thermogram of PAIs 5e

Figure 5 TGA and DTG thermogram of PAI 5e.

APPENDIX

Polymer 5a

FTIR (KBr, cm^{-1}): 2952 (w), 2857 (w), 1730 (s), 1710 (s, sh), 1633 (m), 1500 (s), 1385 (s), 1296 (m), 1221 (m), 1155 (m), 1074 (m), 750 (m), 729 (m).

Polymer 5b

FTIR (KBr, cm^{-1}): 2945 (w), 1730 (s), 1712 (s, sh), 1633 (m), 1593 (w), 1498 (m), 1387 (s), 1296 (m), 1221 (m), 1155 (m), 1075 (m), 752 (m), 727 (m), 682 (m).

Polymer 5c

FTIR (KBr, cm^{-1}): 2946 (w), 1732 (s), 1712 (s, sh), 1635 (m), 1593 (w), 1500 (m), 1385 (s), 1296 (m), 1221 (m), 1155 (m), 1109 (m), 752 (m), 729 (m), 682 (m).

Polymer 5d

FTIR (KBr, cm^{-1}): 2954 (w), 2859 (w), 1730 (s), 1710 (s, sh), 1635 (m), 1593 (w), 1500 (m), 1410 (w), 1385 (s), 1296 (m), 1221 (m), 1155 (m), 1110 (m), 752 (m), 729 (m), 680 (m).

Polymer 5e

FTIR (KBr, cm^{-1}): 2962 (w), 2889 (w), 1730 (s), 1710 (s, sh), 1635 (m), 1593 (w), 1500 (m), 1410 (w), 1385 (s), 1296 (m), 1221 (m), 1155 (m), 1108 (m), 1074 (m), 752 (m), 729 (m).

Polymer 5f

FTIR (KBr, cm^{-1}): 2962 (w), 2880 (w), 1730 (s), 1710 (s, sh), 1635 (m), 1593 (w), 1500 (m), 1410 (w), 1385 (s), 1296 (m), 1221 (m), 1155 (m), 1118 (m), 1074 (m), 752 (m), 729 (m), 682 (w).

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