

Synthesis and Properties of New Poly(amide imide)s Containing Trimellitic Rings and Hydantoin Moieties in the Main Chain under Microwave Irradiation

Khalil Faghihi, Mohsen Hajibeygi

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, 38156, Arak, Islamic Republic of Iran

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ABSTRACT: Trimellitic anhydride was reacted with 4,4'-diaminodiphenyl ether in a mixture of acetic acid and pyridine (3 : 2) at room temperature and was refluxed at 90–100°C, and *N,N'*-(4,4'-diphenylether) bistrimellitamide (3) was obtained in a quantitative yield. 3 was converted into *N,N'*-(4,4'-diphenylether) bistrimellitamide diacid chloride (4) by a reaction with thionyl chloride. Then, six new poly(amide imide)s were synthesized under microwave irradiation with a domestic microwave oven through the polycondensation reactions of 4 with six different derivatives of 5,5-disubstituted hydantoin in the presence of a small amount of a polar organic medium such as *o*-cresol. The

polycondensation proceeded rapidly and was completed within 7–10 min, producing a series of new poly(amide imide)s in high yields with inherent viscosities of 0.27–0.66 dL/g. The resulting poly(amide imide)s were characterized by elemental analysis, viscosity measurements, differential scanning calorimetry, thermogravimetric analysis, derivative 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. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3447–3453, 2004

INTRODUCTION

Microwave irradiation is being used in more and more applications in organic synthesis for the optimization and acceleration of chemical reactions.^{1–4} In some cases, microwave heating is superior to thermal heating, increasing the reaction rates and the selectivity and yields of target products and reducing tarring.⁵ Microwave energy is being investigated as a method for processing resins, such as epoxides,^{6,7} polyesters,⁸ polyurethanes,⁹ and more recently polyimides,^{10,11} because of its shorter processing time, its improved energy utilization, and the potential for lower processing temperatures and improved product uniformity. Recently, we used microwave irradiation for the synthesis of polyamides, poly(amide imide)s (PAIs), and poly(ester imide)s.^{12–17}

Aromatic polyimides are well known as high-performance polymeric materials because of their excellent thermal stability and balanced mechanical and electrical properties, and they have been used in adhesives, composites, fibers, films, and electrical materials.^{18,19} However, aromatic polyimides are difficult

to process because of their high softening temperatures and limited solubility in organic solvents. Some methods can be used to overcome these weak points, such as the addition of flexible linkages to the main chain²⁰ and the introduction of substituted groups,²¹ flexible spacers,²² and heterocyclic moieties to the main chain.²³ The synthesis of PAIs with heterocyclic moieties is one of the best methods. In our previous works, we used this method for the synthesis of a series of new PAIs with needed properties. In this study, we prepared a series of novel PAIs containing trimellitic rings and hydantoin moieties through the polycondensation reaction of *N,N'*-(4,4'-diphenylether) bistrimellitamide diacid chloride (4) with six different derivatives of 5,5-disubstituted hydantoin (5a–5h) under microwave irradiation.

EXPERIMENTAL

Apparatus

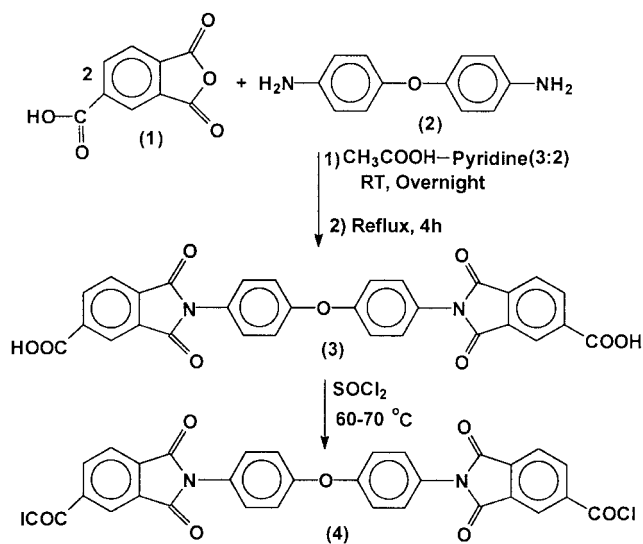
A Samsung domestic microwave oven (2450 MHz and 900 W) was used for the polycondensation reactions.

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Merck Chemical Co. (Germany).

Correspondence to: K. Faghihi (k-faghihi@araku.ac.ir).

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Scheme 1

Techniques

Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Spectra of the solids were obtained with KBr pellets. The vibrational transition frequencies are reported as wave numbers (cm^{-1}). The band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosity (η_{inh}) values were measured with a standard procedure with a Technico Regd Trad Merk viscometer. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) data for the polymers were obtained on a Mettler TA4000 system under N_2 at a rate of $10^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) was recorded on a Stanton Redcraft STA-780 at a heating rate of $10^\circ\text{C}/\text{min}$ in air. Elemental analyses were performed by Arak Petrochemical Co. (Arak, Iran).

Monomer synthesis

N,N'-(4,4'-diphenylether) bistrimellitamide diacid chloride (4)

This compound was prepared according to a typical procedure shown in Scheme 1.²⁴

N,N'-(4,4'-diphenylether) bistrimellitamide (3)

Into a 250-mL, round-bottom flask, 3.84 g (20 mmol) of trimellitic anhydride (1), 2.00 g (10 mmol) of 4,4'-diaminodiphenyl ether (2), 80 mL of a mixture of acetic acid and pyridine (3 : 2), and a stirring bar were placed. The mixture was stirred at room temperature overnight and then was 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; this yielded 4.95 g (90.3%) of yellow crystals (3).

mp: $392\text{--}394^\circ\text{C}$. FTIR (KBr): 3500–2800 (m, br), 1780 (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 cm^{-1} (m). ANAL. Calcd for $\text{C}_{30}\text{H}_{16}\text{N}_2\text{O}_9$: C, 65.71%; H, 2.92%; N, 5.10%. Found: C, 65.50%; H, 3.10%; N, 4.80%.

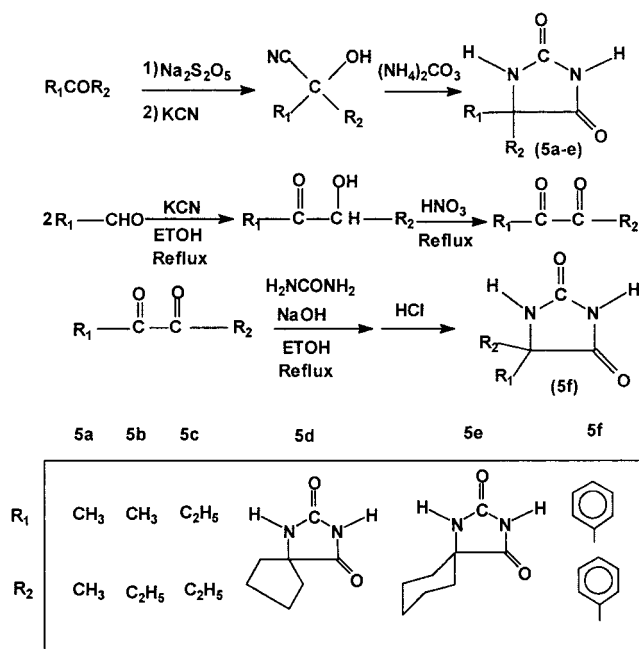
N,N'-(4,4'-diphenylether) bistrimellitamide diacid chloride (4)

Into a 100-mL, round-bottom flask were placed 3.00 g (5.47 mmol) of 3 and 20 mL of thionyl chloride. The mixture was heated in an oil bath up to 60°C until the suspension mixture was converted into a clear solution. Then, the solution was stirred overnight at room temperature. Unreacted thionyl chloride was removed under reduced pressure, and the residue was washed with dry *n*-hexane two times; this yielded 3.09 g (96.5%) of yellow crystals (4).

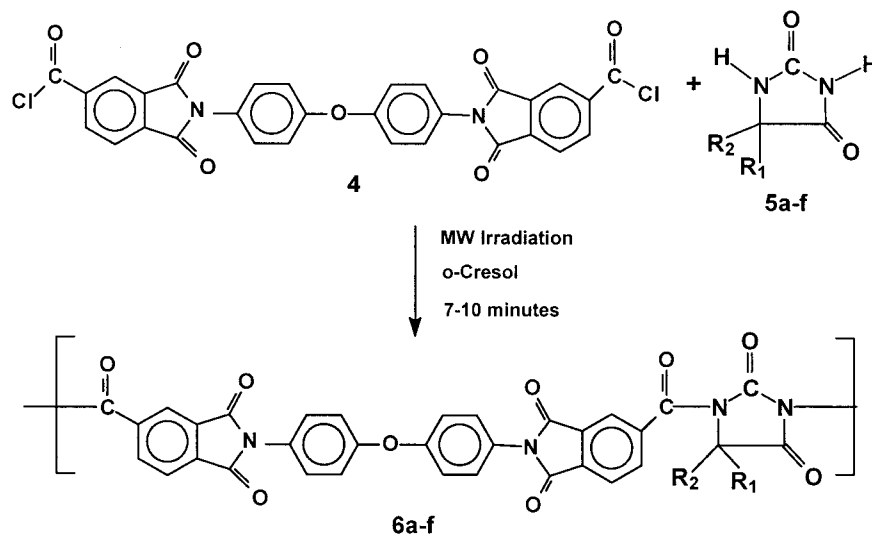
mp: $270\text{--}273^\circ\text{C}$, FTIR (KBr): 1780 (m, sh), 1757 (s, br), 1724 (s, br), 1504 (s), 1425 (w), 1379 (s), 1240–1220 (s, br), 1151 (m), 1111 (m), 1087 (m), 968 (m), 850–830 (m), 729 cm^{-1} (m). ANAL. Calcd for $\text{C}_{30}\text{H}_{14}\text{N}_2\text{O}_7\text{Cl}_2$: C, 61.56%; H, 2.39%; N, 4.78%. Found: C, 61.40%; H, 2.50%; N, 4.50%.

5,5-disubstituted hydantoin derivatives (5a–5f)

These compounds were prepared according to our previous works.¹⁵



Scheme 2



Scheme 3

Polymer synthesis

An equimolar mixture of **4** (0.585 g, 1.0 mmol) and 5,5-dimethyl hydantoin **5a** (0.128 g, 1.0 mmol) was placed in a porcelain dish, and the mixture was ground until a fine powder formed. Then, 1 mL of *o*-cresol was added to the mixture and mixed until a homogeneous solution formed. The reaction mixture was irradiated in a microwave oven at full power for 10 min and was then poured into 50 mL of methanol; the resulting polymer was filtered off and dried at 80°C for 12 h *in vacuo*. The yield was 0.60 g (94%) of a solid polymer (**6a**).

RESULTS AND DISCUSSION

Monomer synthesis

Hydantoin derivatives constitute an important class of heterocycles in medicinal chemistry because many derivatives have been identified that display interesting activities

against a broad range of biological targets.²⁵ Here, the 5,5-disubstituted hydantoin derivatives were synthesized in two ways. Hydantoin derivatives **5a–5e** were synthesized by the Bucherer–Berg method. They were prepared from the reactions of proper cyanohydrin derivatives with ammonium carbonate. The 5,5-diphenyl hydantoin derivative **5f** was prepared from condensation reactions of benzil with urea. Benzil was obtained from the oxidation of benzoin with concentrated nitric acid. Benzoin was also obtained from benzoin condensation of benzaldehyde (Scheme 2).

Polymer synthesis

According to our previous results,^{12–17} PAIs **6a–6f** were synthesized through microwave-assisted polycondensation reactions of equimolar mixtures of monomer **4** with six different derivatives of 5,5-disubstituted hydantoin (**5a–5f**) in the presence of *o*-cresol, as shown in Scheme 3. *o*-Cresol was used as a polar

TABLE I
Synthesis and Some Physical Properties of PAIs 6a–6f

Polymer	Microwave irradiation time (min)	Temperature (°C) ^a	Yield (%)	η_{inh}^b (dL/g)
6a	10	140	94	0.66
6b	8	140	84	0.52
6c	7	140	92	0.55
6d	7	140	86	0.44
6e	8	140	90	0.50
6f	10	140	85	0.42

The power of microwave irradiation was 900 W

^a Temperature of reaction mixture under microwave irradiation

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

TABLE II
Elemental Analysis of PAIs 6a–6f

Polymer	Formula		C(%)	H(%)	N(%)
6a	$C_{35}H_{20}N_4O_9$ (640.35) _n	Calcd	65.64	3.12	8.74
		Found	66.40	3.80	7.80
6b	$C_{36}H_{22}N_4O_9$ (654.36) _n	Calcd	66.07	3.36	8.55
		Found	67.30	3.50	8.10
6c	$C_{37}H_{24}N_4O_9$ (668.37) _n	Calcd	66.48	3.59	8.37
		Found	65.50	3.30	7.60
6d	$C_{37}H_{22}N_4O_9$ (666.37) _n	Calcd	66.68	3.30	8.40
		Found	65.80	3.20	8.00
6e	$C_{38}H_{24}N_4O_9$ (680.38) _n	Calcd	67.07	3.52	8.23
		Found	66.80	3.90	7.60
6f	$C_{45}H_{24}N_4O_9$ (764.45) _n	Calcd	70.69	3.14	7.32
		Found	69.30	3.30	6.90

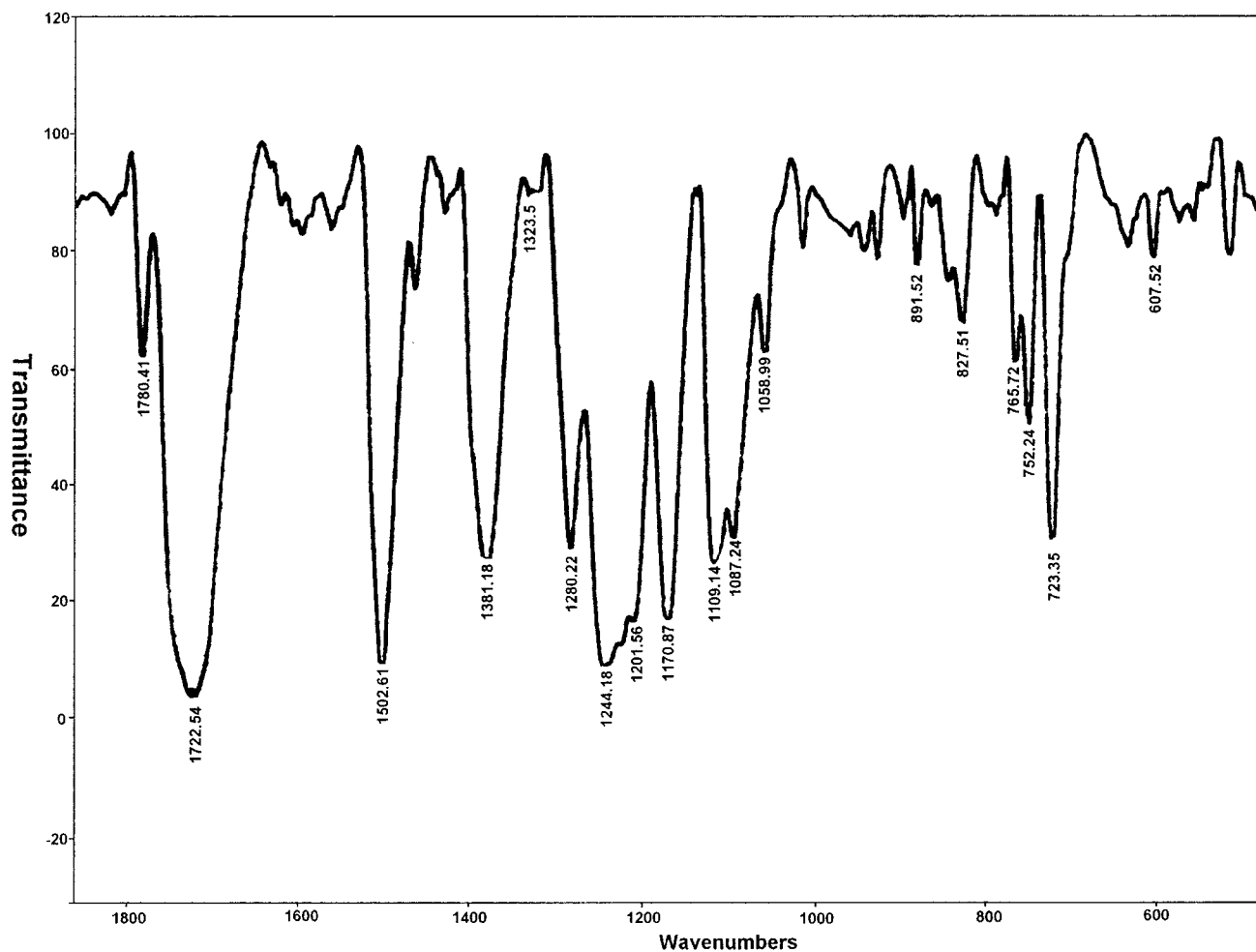


Figure 1 FTIR spectrum of polymer 6d.

organic medium, acting as a primary microwave absorber and as a solvent for both the starting monomers and the resulting polymers. This allowed effective homogeneous heating of the reaction mixture, and so a polycondensation reaction occurred, leading to poly-

mer formation. The optimum reaction time (irradiation time) was 7–10 min. Below this time, the given polymers had lower η_{inh} values, and above this time, the materials degraded.

TABLE III
Solubility of PAIs 6a–6f

Solvent	6a	6b	6c	6d	6e	6f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	+	+	+	+	+	+
CHCl ₃	+	+	+	+	+	+
Acetone	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
MeOH	–	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–	–
H ₂ O	–	–	–	–	–	–

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

Polymer characterization

The syntheses and some physical properties of PAIs 6a–6f are summarized in Table I. These polymers had η_{inh} values of 0.27–0.66 dL/g and were yellow. These

TABLE IV
Thermal Behavior of PAIs 6a and 6c

Polymer	T_g	T_5 (°C)	T_{10} (°C)	Char yield ^a
6a	156	285–290	430–435	10
6c	160	310–315	420–425	12

T_g = Glass-transition temperature; T_5 and T_{10} = temperature at which 5 and 10 weight loss were recorded by TGA at heating rate of 10°C/min in N₂, respectively.

^a Percentage weight of material left undecomposed after TGA analysis at 600°C.

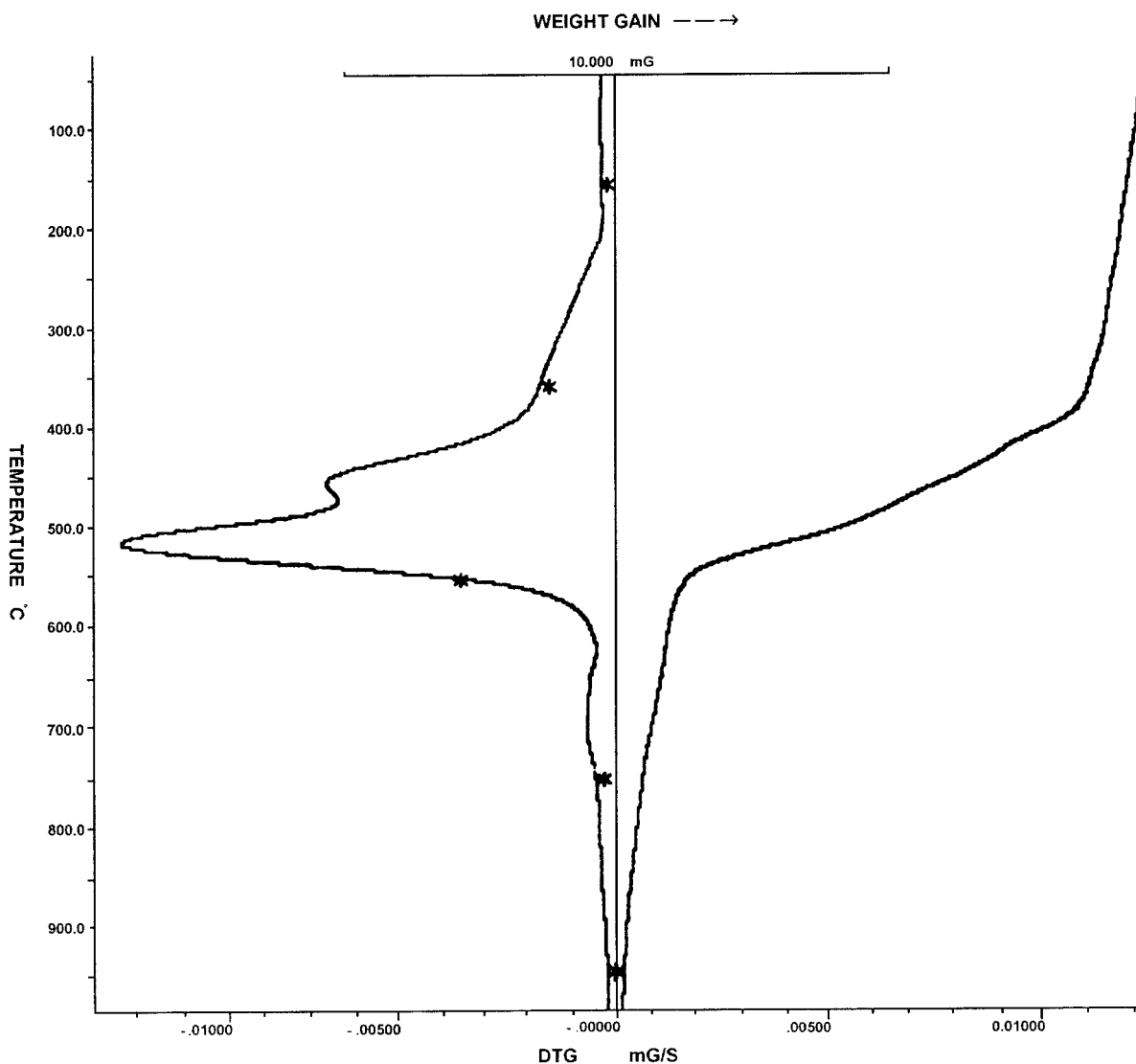


Figure 2 TGA and DTG thermogram of polymer 6a.

polymers were confirmed to be PAIs by means of FTIR spectroscopy and elemental analyses (Table II). A representative FTIR spectrum of polyamide **6d** is shown in Figure 1. Absorption bands can be seen between 1780 and 1710 cm^{-1} due to imide and amide carbonyl groups. Absorption bands around 1390 – 1380 and 730 – 710 cm^{-1} show the presence of the imide heterocyclic ring 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 **6a**–**6f** was investigated with 0.01 g of a polymeric sample in 2 mL of a solvent. All of these PAIs were soluble in organic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and

chloroform at room temperature, and they were insoluble in solvents such as acetone, methylene chloride, methanol, ethanol, and water (Table III). The improved solubility of these PAIs, in comparison with the solubility of polyimides prepared from **1** and aromatic diamines, can be explained by the presence of the hydantoin moieties in the main chain.

Thermal properties

The thermal properties of two PAIs, **6a** and **6c**, were investigated with DSC, TGA, and DTG in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$, and the thermal data are summarized in Table IV. All of these polymers showed similar decomposition behaviors (Figs. 2 and 3). The initial decomposition temperatures, 5 and 10% weight losses, and char yields at 600°C for PAIs **6a** and **6c** are summarized in Table IV.

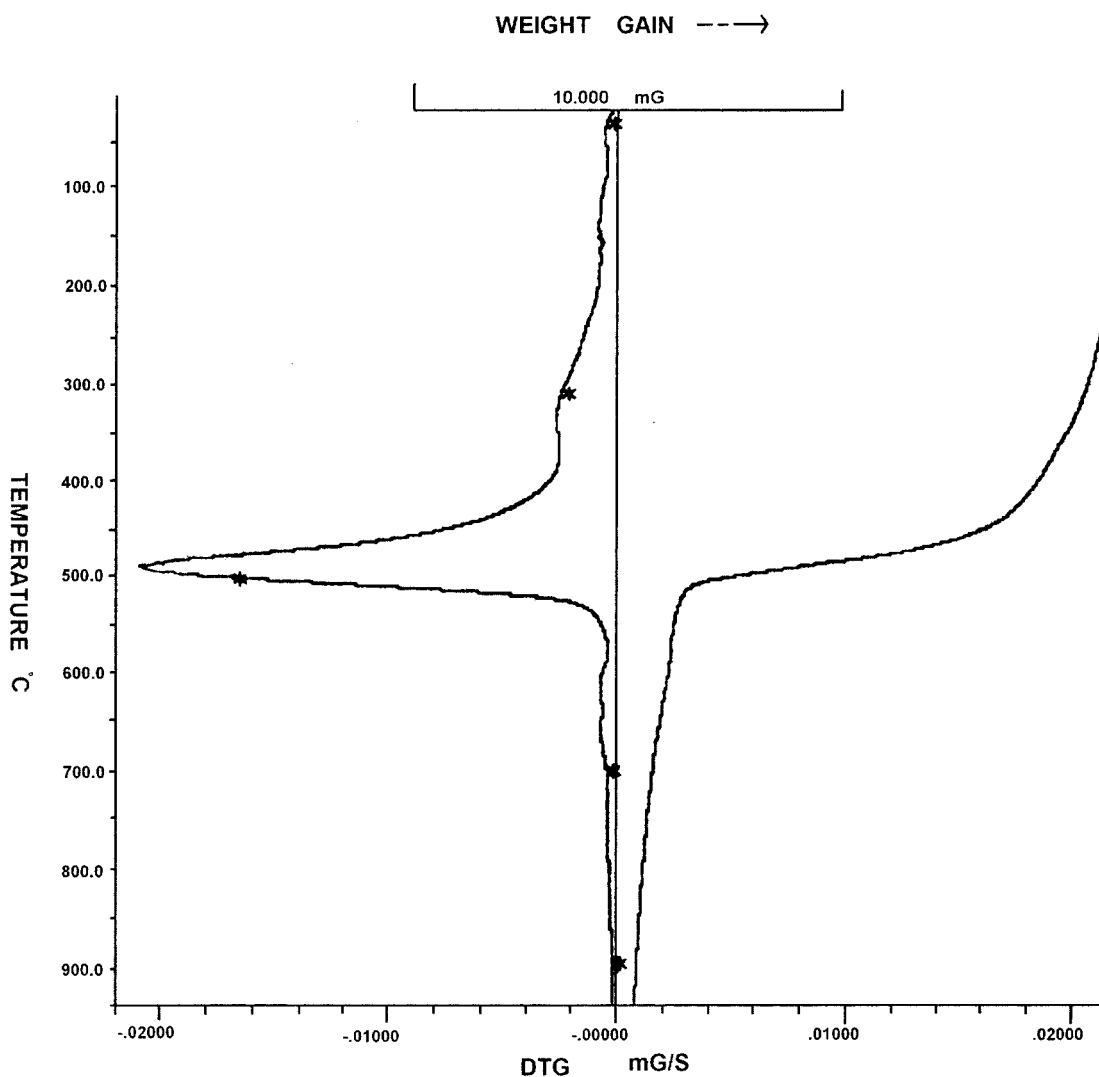


Figure 3 TGA and DTG thermogram of polymer 6c.

These polymers exhibited good resistance to thermal decomposition up to 220–255°C in nitrogen and began to decompose gradually above that temperature. The 5% weight-loss temperature for all the polymers ranged from 250 to 280°C, and the residual weight for these polymers at 600°C ranged from 18.60 to 27.61% in nitrogen.

CONCLUSIONS

In this study, we synthesized several new PAIs (6a–6f) through the microwave-assisted polycondensation reaction of monomer 4 with six different derivatives of hydantoin compounds (5a–5f). These new PAIs are soluble in various organic solvents and have good thermal stability. The introduction of hydantoin moieties into the backbone increases the solubility of these polymers. These properties could make these PAIs attractive for practical applications such as process-

able high-performance engineering plastics. In addition, the results demonstrate that microwave heating is an efficient method (shorter reaction time and high energy efficiency) for polycondensation reactions. We are currently using this method for the synthesis of novel polymers and the modification of polymers.

APPENDIX: FTIR ANALYSES OF PAIS 6a–6f

Polymer 6a

FTIR (KBr): 1780 (m, sh), 1722 (s, br), 1502 (s), 1381 (m), 1284 (m), 1250–1220 (s, br), 1170 (s), 1108 (m), 1100 (m), 827 (w), 756 (m), 723 cm^{-1} (m).

Polymer 6b

FTIR (KBr): 1780 (m, sh), 1724 (s, br), 1597 (w), 1502 (s), 1381 (m, br), 1284 (m), 1250–1220 (s, br), 1170 (s), 1106 (m), 1100 (m), 829 (w), 752 (m), 725 cm^{-1} (m).

Polymer 6c

FTIR (KBr): 1781 (m, sh), 1724 (s, br), 1502 (s), 1381 (m), 1284 (m), 1245–1220 (s, br), 1170 (s), 1116 (m), 1100 (m), 1058 (w), 879 (w), 827 (w), 752 (m), 723 cm^{-1} (m).

Polymer 6d

FTIR (KBr): 1780 (m, sh), 1730–1720 (s, br), 1502 (s, br), 1381 (m), 1280 (s, sh), 1250–1220 (s, br), 1170 (s), 1109 (m), 1087 (s), 1058 (m), 891 (w), 827 (w), 756 (m), 723 cm^{-1} (m).

Polymer 6e

FTIR (KBr): 1780 (m, sh), 1730–1720 (s, br), 1502 (s, br), 1381 (m), 1280 (m), 1250–1220 (s, br), 1170 (s), 1116 (m), 1087 (m), 1058 (w), 890 (w), 829 (w), 756 (w), 725 cm^{-1} (m).

Polymer 6f

FTIR (KBr): 1782 (m, sh), 1735–1720 (s, br), 1595 (w), 1505 (s), 1382 (m), 1284 (m), 1250–1220 (s, br), 1170 (s), 1116 (m), 1100 (m), 1058 (w), 879 (w), 827 (w), 756 (m), 723 cm^{-1} (m).

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