

Rapid Synthesis of New Poly(amide-imide)s Based on N-(4-Carboxy phenyl) trimellitimide and Hydantoin Derivatives under Microwave Irradiation

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Six new poly (amide-imide)s (**6a-f**) were prepared under microwave irradiation by polycondensation reaction of diacid chloride (**4**) with 6 different derivatives of hydantoins (**5a-f**) using O-cresol as a microwave absorbent. These new PAIs were obtained in high yield and with inherent viscosities between 0.15 and 0.25 dL/g. The resulting poly(amide-imide)s were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA & DTG), solubility test, and FT-IR spectroscopy. N-(4-chlorocarbonyl phenyl) trimellitimide acid chloride (**4**) was prepared by a 2-step reaction. First trimellitic anhydride (**1**) was reacted with 4-amino benzoic acid (**2**) in acetic acid solution and the resulting imide-acid [N-(4-carboxy phenyl) trimellitimide] (**3**) was obtained in high yield. Then diacid (**3**) was converted to N-(4-chlorocarbonyl phenyl) trimellitimide acid chloride (**4**) by reaction with thionyl chloride in the presence of pyridine.

Key Words: Thermally stable polymers; icrowave irradiation; Poly (amide-imide); Hydantoin derivatives.

Introduction

Thermally stable polymers have received much interest over the past decade due to increasing demands for high-performance polymers as a replacement for ceramics or metals in the microelectronic, aerospace, and automotive industries. Polyimides and their copolymers are certainly one of the most useful classes of high-performance polymers that have found many applications in those industries.^{1,2} Aromatic polyimides are well known as high performance materials for their excellent thermal stabilities and balanced mechanical and electrical properties.³⁻⁵ Poor thermoplastic fluidity and solubility are the major problems for wide application

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of polyimides. However, poly(amide-imide)s (PAIs) are the most successful material, which combines the advantages of high-temperature stability and processability.⁶⁻⁷ A notable example is Torlon (Amoco Company), a commercial PAI obtained from trimellitic anhydride and 4,4'-diaminodiphenyl methane.⁸

In this article, we studied synthesis and characterization of 6 new poly(amide-imide)s (**6a-f**) containing a trimellitimide ring and hydantoin moieties in the main chain. The resulted PAIs (**6a-f**) were prepared from the polycondensation reaction of N-(4-chlorocarbonyl phenyl) trimellitimide acid chloride (**4**) with 6 different hydantoins derivatives (**5a-f**), such as hydantoin (**5a**), 5,5-dimethyl hydantoin (**5b**), 5-ethyl, 5-methyl hydantoin (**5c**), 5,5-diethyl hydantoin (**5d**), 5,5-spirocyclopantyl hydantoin (**5e**), and spirocyclohexyl hydantoin (**5f**), under microwave irradiation *o*-cresol as a microwave absorbent. These polymers have a heterocyclic ring such as a trimellitimide ring and hydantoin moieties in the main chain for improving solubility in organic solvents compared to aromatic poly(amide-imide)s. Hydantoin and hydantoin derivatives are important intermediates in the synthesis of several amino acids. In the chemical industry, various hydantoin derivatives are the basis of new generation of weatherproof high-temperature-stable epoxy resins.⁹

Also in recent years, organic reactions assisted by microwave irradiation have gained special attention. The reactions are very fast and are completed within a short period of time.¹⁰⁻¹² Recently, we have used microwave irradiation for the synthesis of organic compounds as well as macromolecules.¹³⁻¹⁶

Experimental

Apparatus

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

Materials

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

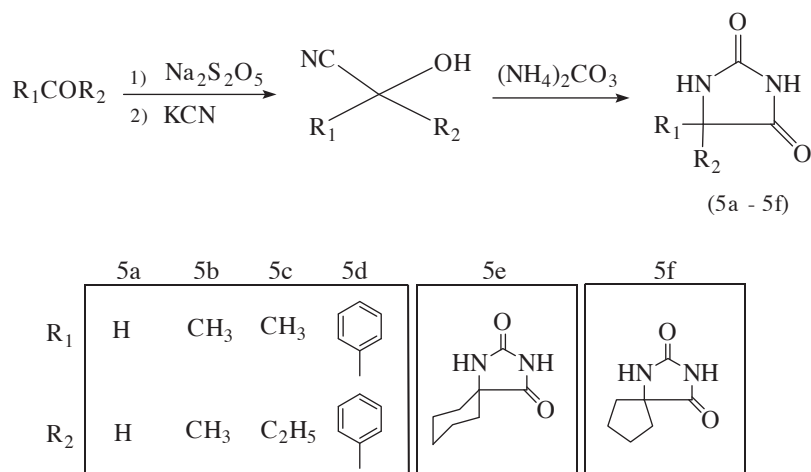
Techniques

Fourier transform infrared (FT-IR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were obtained using KBr pellets. Vibrational transition frequencies were reported in wave number (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). The $^1\text{H-NMR}$ spectrum (300 MHz) was recorded on a Bruker Avance 300 spectrometer (Germany). Inherent viscosities were measured by a standard procedure using a Technico® Viscometer. Thermal gravimetric analysis (TGA and DTG) data for polymers were recorded on a Mettler TA 4000 System under N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed by Arak Petrochemical Company, Arak, Iran.

Monomer synthesis

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

Hydantoin derivatives were prepared according to our previous work.¹³ Chemical reactions involved are shown in Scheme 1.



Scheme 1

N-(4-chlorocarbonyl phenyl)-trimellitimide acid chloride (4)

This compound was prepared according to a typical procedure as shown in Scheme 2.

N-(4-carboxy Phenyl) trimellitimide (3)

Trimellitic anhydride (**1**) (1.92 g, 10 mmol), 4-amino benzoic acid (**2**) (1.33 g, 10 mmol), and 32 mL of acetic acid were added into a 250 mL round-bottomed flask, and a reflux system was set up. The mixture was stirred overnight at room temperature and then refluxed for 8 h at 130 °C. The solvent was removed under reduced pressure until a white-cream precipitate formed. Then 100 mL of water and 5 mL of concentrated HCl were added into the flask. The mixture was stirred vigorously, filtered off, and dried to give 2.84 g (91%) of compound (**3**). Mp: 375–377 °C. FT-IR (KBr): 2800-3100 (m, br), 1782 (w), 1724 (s), 1685 (s), 1601 (s), 1425 (s), 1377 (s), 1298 (s, sh), 1296 (m), 1091 (m), 925 (w), 854 (w), 769 (m), 723 (s), 507 (w) cm⁻¹. ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.61-7.64 (d, 2H,); 8.08-8.12 (dd, 3H,); 8.33 (s, 1H); 8.42-8.45 (dd, 1H,) ppm. Analysis: Calculated for C₁₆H₉NO₆: C, 61.74; H, 2.91; N, 4.50; found: C, 61.40; H, 2.80; N, 4.30.

N-(4-chloro carbonyl phenyl) trimellitimide acid chloride (4)

Into a 100 mL round-bottomed flask were placed (2.00 g, 6.43 mmol) of diacid (**3**) and 20 mL of thionyl chloride. The mixture was heated in an oil bath up to 100 °C until the suspension mixture converted to 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 twice, yielded to a cream precipitate (**4**).

Mp: 181–183 °C. FT-IR (KBr): 3040(w), 1786(s), 1730(s), 1597(m), 1514(m), 1317(s, br), 1216(m), 1174(s), 1156(m), 1087(s), 972(m), 894(m), 856(s), 834(s), 709(m), 694(m), 674(m) cm^{-1} . Analysis: Calculated for $\text{C}_{16}\text{H}_7\text{NO}_4$: C, 55.20; H, 2.03; N, 4.02; found: C, 55.30; H, 2.20; N, 3.90.

Polymer synthesis

An equimolar mixture of diacid chloride (**4**) (0.17 g, 0.48 mmol) and 5-spiro cyclohexyl hydantoin (**5e**) (0.08 g, 0.48 mmol) were placed in a porcelain dish, and the mixture was grounded until a fine powder formed. Then 0.3 mL of *o*-cresol was added to the mixture and mixed until a homogeneous solution formed, which was irradiated in a microwave oven at full power for 11 min. Then 25 mL of methanol was added to the reaction mixture, the resulting polymer was filtered off and dried at 60 °C for 12 h in vacuum. The yield was 0.18 g (83%) of a white solid polymer (**6e**).

Polymer (6a)

FT-IR (KBr): 3063 (w), 2966 (w), 1782 (w), 1728 (s), 1613 (w), 1606 (w), 1512 (m), 1379 (s), 1271 (s), 1222 (m), 1129 (m), 1078 (w), 725 (m) cm^{-1} .

Polymer (6b)

FT-IR (KBr): 3109 (w), 2969 (w), 1782 (w), 1730 (s), 1512 (w), 1377 (m), 1271 (m), 1222 (m), 1116 (w), 856 (m, br), 725 (m) cm^{-1} .

Polymer (6c)

FT-IR (KBr): 3053 (w), 1778 (m), 1730 (s), 1597 (m), 1504 (w), 1373 (s), 1205 (m), 1172 (m), 1078 (s), 972 (m), 887 (m), 829 (s, sh) cm^{-1} .

Polymer (6d)

FT-IR (KBr): 3090 (w), 1782 (w), 1730 (s), 1599 (w), 1485 (w), 1377 (m), 1271 (m, sh), 1221 (m), 1165 (w), 854 (w), 725 (m) cm^{-1} .

Polymer (6e)

FT-IR (KBr): 1776 (m), 1728 (s), 1606 (m), 1514 (m), 1379 (s), 1271 (s), 1219 (s), 1170 (s), 1111 (s), 1074 (s), 763 (m), 731 (m) cm^{-1} .

Polymer (6f)

FT-IR (KBr): 3109 (w), 2958 (w), 1778 (w), 1728 (s), 1603 (w), 1512 (w), 1379 (m, br), 1271 (m, sh), 1221 (m), 1169 (m), 856 (w), 725 (m) cm^{-1} .

Results and Discussion

Monomer synthesis

N-(4-chloro carbonyl phenyl) trimellitimide acid chloride (**4**) was prepared in a 2-step reaction as shown in Scheme 2. Diacid (**3**) was synthesized by condensation reaction of 1 equimolar amount of anhydride (**1**) with 1 equimolar amount of 4-amino benzoic acid (**2**) in acetic acid which gives a white solid after extracting the solvent and adding HCl and water. The resulting diacid (**3**) was converted to its diacid chloride derivative (**4**) by reaction with thionyl chloride. Monomer (**4**) was purified by washing with n-hexane. The chemical structure and purity of monomers (**3**) and (**4**) were determined using elemental analysis, FT-IR and $^1\text{H-NMR}$ spectroscopic techniques. FT-IR spectrum of compound (**3**) showed a broad peak between 2800 and 3100 cm^{-1} , which was related to COOH groups. Two absorption bands around 1780 and 1724 cm^{-1} were characteristic peaks for asymmetric and symmetric stretching carbonyl band of imide ring, respectively, and absorption bands around 1377, 1091, and 723 cm^{-1} were characteristic peaks for imide ring deformation (Figure 1).

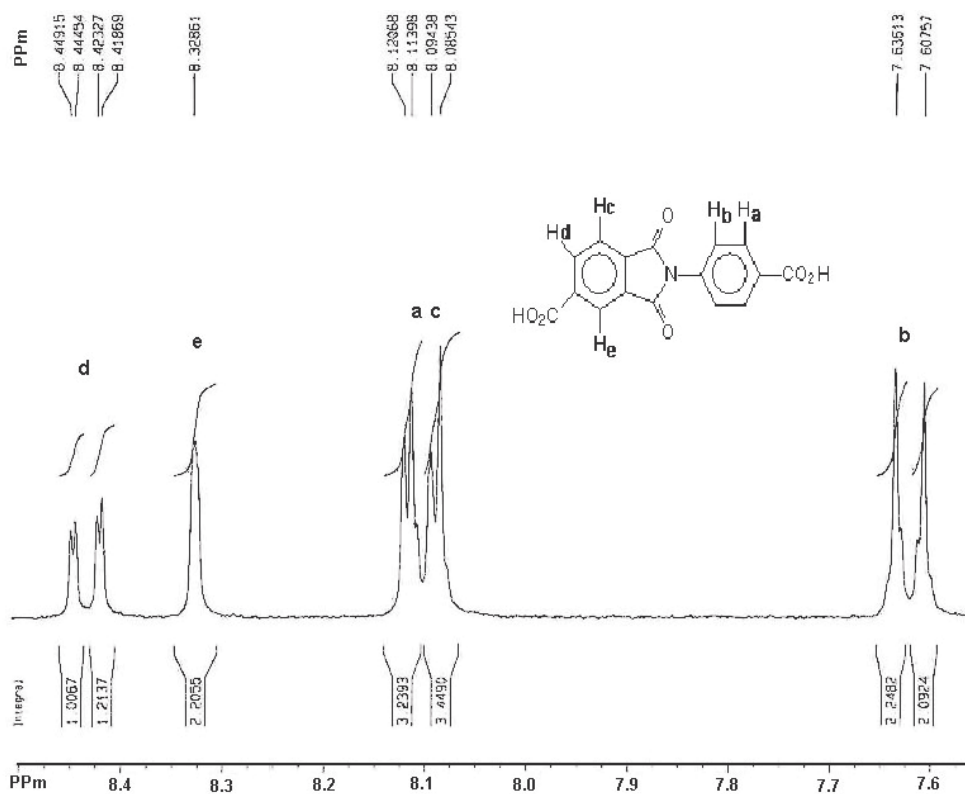
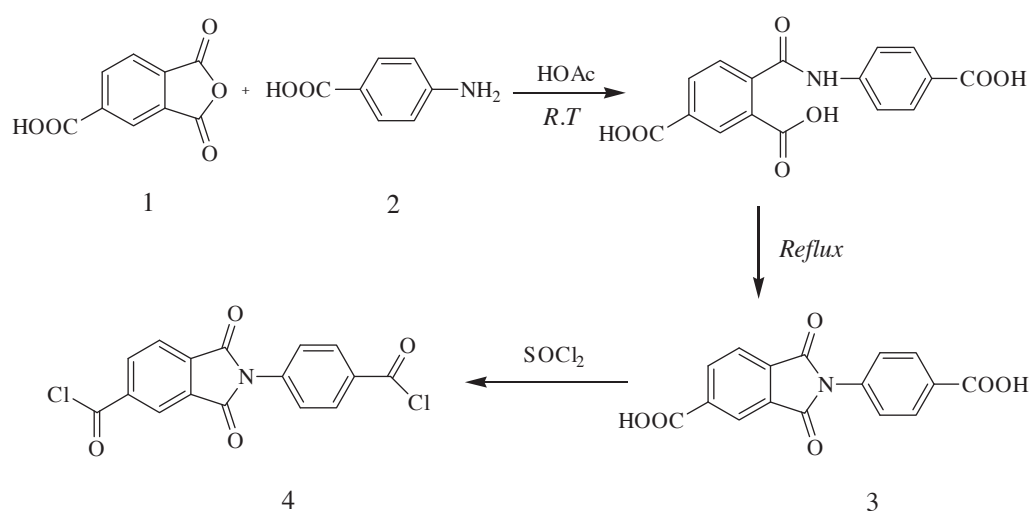


Figure 1. FT-IR spectrum of diacid (**3**).

The $^1\text{H-NMR}$ spectrum of compound (**3**) showed peaks between 7.60 and 7.63 ppm as a “doublet”, which was assigned to H(b), the peaks between 8.08 and 8.12 ppm as “doublet of doublet” - assigned to H(a) and H(c), the peak at 8.32 ppm as “singlet” - assigned to H(e), and the peaks between 8.41 and 8.44 ppm as “doublet of doublet” was assigned to H(d) (Figure 2).



Scheme 2

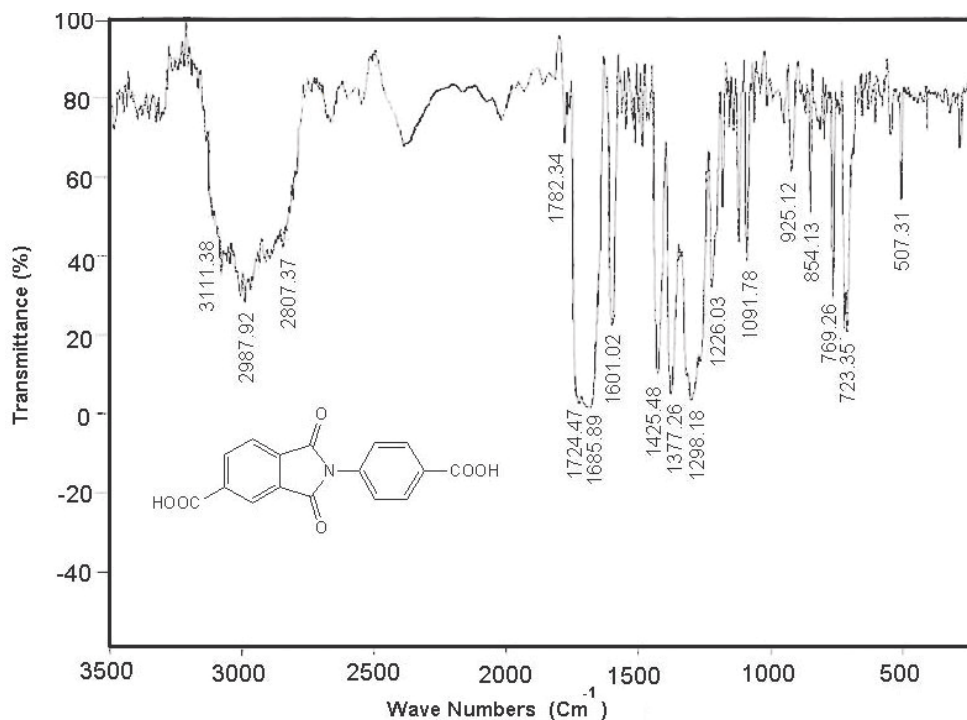


Figure 2. ¹H-NMR spectrum of diacid (3) (300 MHz).

The FT-IR spectrum of compound (4) confirmed a complete conversion from diacid (3) to diacid chloride (4). A broad peak at 2800-3100 cm⁻¹ indicating carboxylic acid group of diacid (3) has been faded out and, because of the electron withdrawing character of the Cl group, carbonyl peaks of the diacid chloride at 1778 and 1755 cm⁻¹, in comparison with its starting diacid at 1695 cm⁻¹, were shifted to a higher frequency (Figure 3).

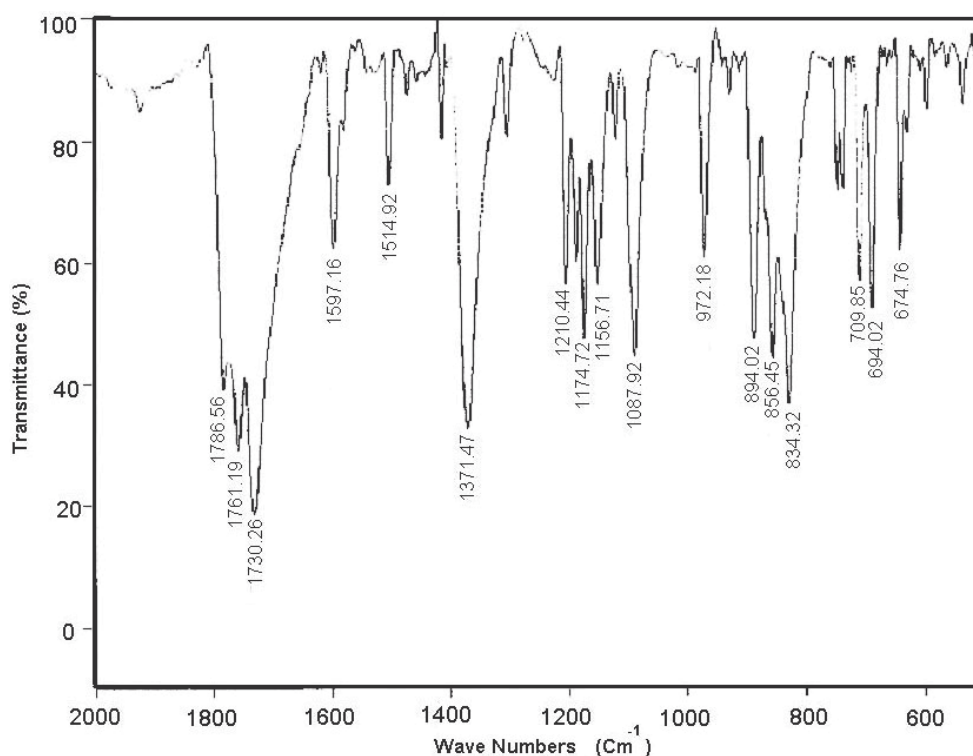
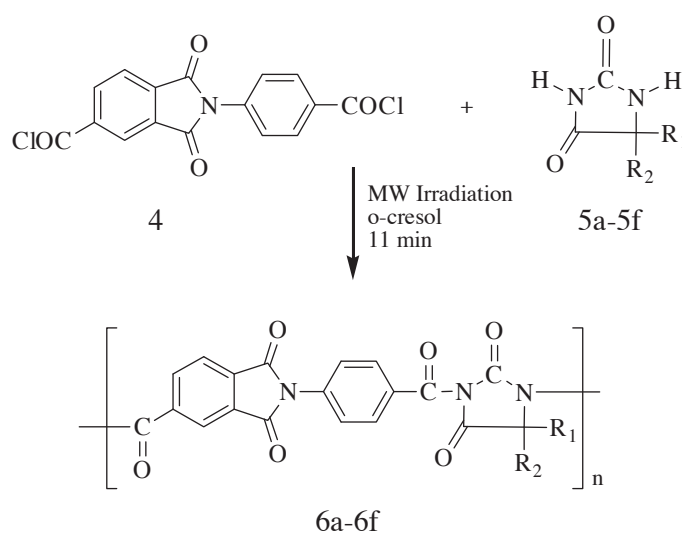


Figure 3. FT-IR spectrum of diacid chloride (4).



Scheme 3

Polymer synthesis

PAIs (**6a-f**) were synthesized by microwave-assisted polycondensation reactions of an equimolar mixture of monomer (**4**) with 6 different derivatives of 5,5-disubstituted hydantoin compounds (**5a-f**) in *o*-cresol as organic solvent using a domestic microwave oven as shown in Scheme 3. *o*-Cresol was used as an organic

medium that acts as a primary microwave absorber and as a solvent for both of the starting monomers and the resulting polymers, which allows induction of effective homogeneous heating of the reaction mixture and thereby subsequent polycondensation reaction leading to the polymer formation. The optimum period of reaction time (irradiation time) was found to be 11 min and below this time will give polymers with lower inherent viscosities and above this time materials will be degraded.

Polymer characterization

Synthesis data and some physical properties of the **PAIs (6a–f)** are summarized in Table 1. These polymers have inherent viscosities in the range of 0.15–0.22 dLg⁻¹. All of the **PAIs** derived from monomer (4) have off-white color. The structure of resulting polymers was confirmed as **PAIs** by means of FT-IR spectroscopy and elemental analysis. A representative FT-IR spectrum of the **PAI (6a)** is shown in Figure 4. This spectrum includes absorption bands around 1700–1780 cm⁻¹ due to amide and imide carbonyl linkages of hydantoin and imide rings in the main chain. Absorption bands around 1360–1390 cm⁻¹ and 760–730 cm⁻¹ show the presentation of imide heterocyclic moiety in this polymer. Other spectra have a similar pattern.

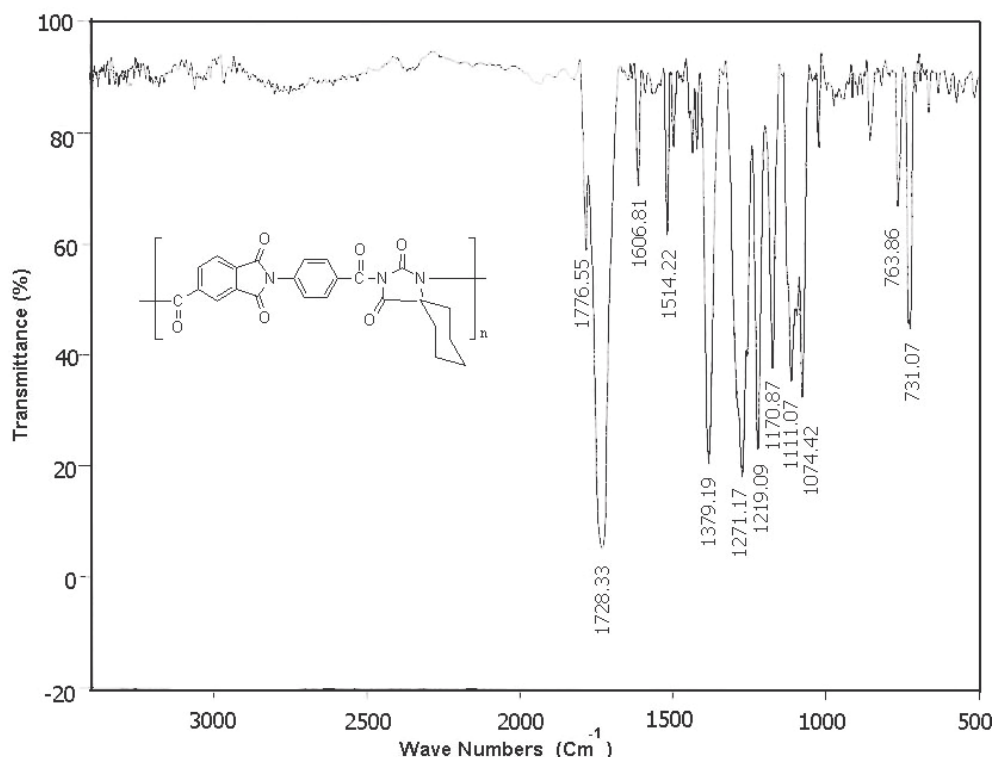


Figure 4. FT-IR spectrum of poly(amide-imide) (**6a**).

The elemental analysis values of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table 2).

Table 1. Synthesis data and some physical properties of PAIs (6a-f).

5.5-Disubstituted hydantoin	Polymer	Temp.(°C) ^a	Yield (%)	η_{inh} (dL/g) ^b
5a	6a	160	92	0.1
5b	6b	160	81	0.14
5c	6c	160	78	0.22
5d	6d	160	78	0.2
5e	6e	160	83	0.16
5f	6f	160	81	0.12

^aThe power of microwave irradiation was 900 W and temperature at which polymerization reaction occurred under microwave irradiation ^b Measured at concentration of 0.5 g/dL in DMF at 25 °C

Table 2. Elemental Analysis of Poly (amide-imide)s (6a-f).

N%	H%	C%		Formula	Polymer
11.2	2.4	60.8	Calc.	C ₁₉ H ₉ N ₃ O ₆	6a
10	2	61	Found.	(375.2) _n	
10.42	3.22	62.5	Calc.	C ₂₁ H ₁₃ N ₃ O ₆	6b
10	3	61	Found.	(403.3) _n	
10	3.6	63.3	Calc.	C ₂₂ H ₁₅ N ₃ O ₆	6c
9.2	3	62	Found.	(417.3) _n	
7.9	3.2	70.6	Calc.	C ₃₁ H ₁₉ N ₃ O ₆	6d
7	2.5	69	Found.	(529.4) _n	
9.5	3.8	65	Calc.	C ₂₄ H ₁₇ N ₃ O ₆	6e
8.6	3	64	Found.	(443.3) _n	
9.8	3.5	64.3	Calc.	C ₂₃ H ₁₅ N ₃ O ₆	6f
9	3	63	Found.	(429.3) _n	

The solubilities of the poly (amide-imide)s (**6a-f**) were investigated. All of the polymers are soluble in organic solvents, such as DMF, DMAc, DMSO, and NMP at room temperature, and are insoluble in solvents such as methanol, ethanol, chloroform, and water.

Thermal properties

The thermal properties of 3 samples of resulting polymer (**6a,d,f**) were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of 10 °C/min⁻¹ and the thermal data are summarized in Table 3 (Figure 5). The initial decomposition temperatures of 5% and 10% weight losses (T₅ and T₁₀) and the char yield at 600 °C for (**6a, d & f**) are summarized in Table 3. These polymers exhibited good resistance to thermal decomposition up to 245-355 °C in nitrogen and began to decompose gradually above that temperature. T₅

for polymers (**6a**, **6d** & **6f**) ranged from 245 to 355 °C and T_{10} for all polymers ranged from 305 to 410 °C, and the residual weight for these polymers at 600 °C ranged from 41% to 62% in nitrogen (Table 3). Results show that PAIs (**6f**) containing 5,5-spirocyclohexyl hydantoin moiety in the main chain has higher thermal stability compared with other polymers because it has a rigid structure in position of 5 of hydantoin ring.

Table 3. Thermal behavior of PAIs (6a, d, f).

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char Yield ^c
6a	245-250	350-360	60 %
6d	250-255	305-310	41 %
6f	355-360	410-415	62 %

^{a,b}Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N₂ respectively. ^cPercentage weight of material left under composed after TGA analysis 600 °C.

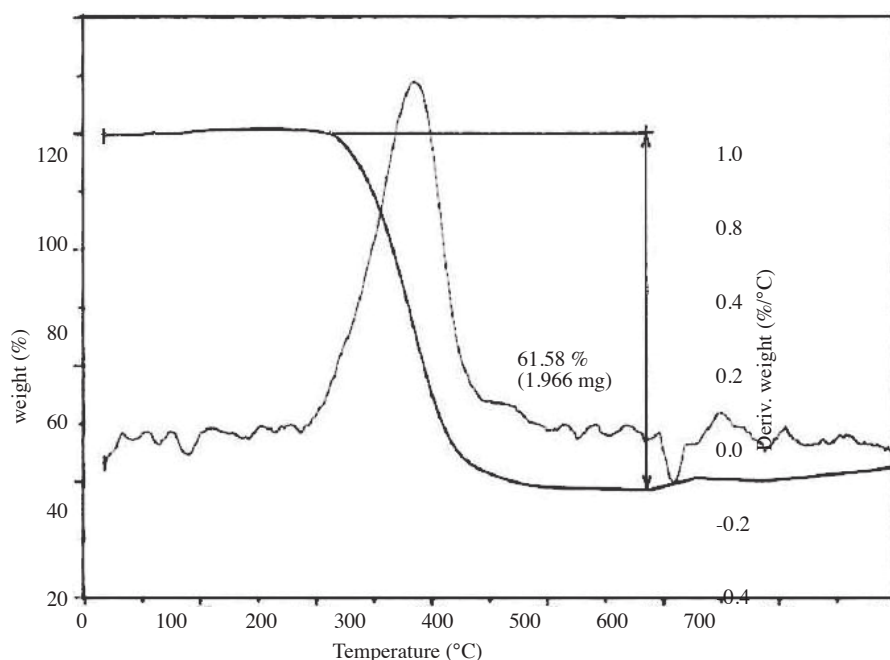


Figure 5. TGA and DTG thermogram of poly(amide-imide) (**6d**).

Conclusion

This work involved the syntheses of several new PAIs (**6a-f**) through the microwave-assisted polycondensation reaction of N-(4-chlorocarbonyl phenyl)-trimellitimide acid chloride (**4**) with 6 different derivatives of 5,5-disubstituted hydantoin compounds (**5a-f**) in o-cresol as organic solvent using a domestic microwave oven. These new PAIs are soluble in various organic solvents and have a good thermal stability. These properties could make these PAIs attractive for practical applications, such as processable high-performance engineering plastics.

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