

New Photosensitive Poly(amid-imide)s Containing Chalcone Moiety and Hydantoin Derivatives in the Main Chain: Synthesis and Characterization

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ABSTRACT: Six new poly(amid-imide)s containing chalcone and hydantoin moieties in the main chain were synthesized through the polycondensation reaction of 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone **6** with six hydantoin derivatives **7a-f** in a medium consisting of triphenyl phosphite, calcium chloride, pyridine, and *N*-methyl-2-pyrrolidone. The polycondensation reaction produced a series of novel poly(amid-imide)s **8a-f** in high yields with inherent viscosities between 0.26 and 0.42 dL/g. The resulting polymers were characterized by elemental analysis, vis-

cosity measurements, solubility test, thermo gravimetric analysis (TGA and DTG), FTIR, and UV-Vis spectroscopy. 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone **6** was prepared from a three-step reaction by using 4-nitro benzaldehyde **1** and 4-nitro acetophenone **2** as precursors. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1097–1103, 2009

Key words: chalcone moiety; poly(amid-imide)s; 4,4'-diamino chalcone; 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone; hydantoin derivatives

INTRODUCTION

Aromatic polyimides show high thermal stabilities, good mechanical properties, and chemical resistance, but their high softening or melting temperatures and poor solubility in common organic solvents cause their low processability and limit their applications.^{1,2} To overcome these drawbacks, many investigations were focused on the modifications of their chemical structure, for example, through the introduction of flexible linkages, asymmetric units, or bulky substituents into the polymer backbones.^{3–9} In addition, various copolyimides such as poly(amide-imide)s have been proposed in many reports.^{10–12} There is a growing interest in poly(amide-imide)s (PAIs) for a variety of applications as they retain good mechanical properties at high temperatures and show easier processability in comparison with other aromatic thermostable polymers such as polyamides and polyimides. They are finding numerous applications in adhesives, electronic wire enamel, injection-molding, extrusion products, and membranes.^{10,13–17} In our previous articles, we described synthesis and characterization of different poly(amide-imide)s containing heterocyclic segments in the main chain such as hydantoin, pyridyl, and tetrahy-

dropyrimidine rings with improved solubility and thermal properties.^{18–27}

Photosensitive polymers are widely used as polymeric photo resists in the field of microelectronics. They are of broad current interest because they possess a combination of good properties in dielectric constant, thermal stability, and sensitivity. On the other hand, a chalcone group as a classical photosensitive unit has been well studied and used in photo crosslinkable polymers because it affords high sensitivity to UV radiation and chemical resistance of the resultant polymers.^{28–31}

In this article, synthesis and characterization of a new series of PAIs containing chalcone moieties in the main chain from the polycondensation reaction of 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone **6** with six derivatives of hydantoins **7a-f** by using triphenyl phosphite and pyridine as condensing agents in *N*-methyl-2-pyrrolidone (NMP) as solvent was studied.

EXPERIMENTAL

Materials

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

Measurements

¹H-NMR spectra were recorded on a Bruker 300 MHz instrument. UV-vis absorptions were recorded at

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25°C in the 200–700 nm spectral region with a Perkin-Elmer Lambda 19 spectrophotometer on DMF solutions by using cell path lengths of 1 cm. Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed by using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Merk Viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken on a DuPont 2000 System V5.1A under N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed by the Research Institute of Petroleum Industry, Arak, Iran.

Monomer synthesis

Synthesis of 4,4'-dinitrochalcone 3

A mixture of 4-nitrobenzaldehyde **1** (1.83 g, 12 mmol), 4-nitroacetophenone **2** (2.00 g, 12 mmol), and 25 mL acetic anhydride was stirred and refluxed 12 h. Then, the mixture was poured into water, and the yellow-brown precipitate formed, the precipitate was filtered off, washed thoroughly with water and dried to afford 2.65 g **3** (yield 74%). A purified sample was obtained by recrystallization from DMF, Mp: 216–217°C, FTIR (KBr): 3113 (w), 1670 (m), 1573 (s), 1516 (s), 1319 (s, sh), 1288 (m), 1209 (s), 1026 (m, sh), 987 (m), 837 (s, sh), 787 (m), 742 (s), 682 (m) cm^{-1} .

Synthesis of 4,4'-diaminochalcone 4

Na_2S (2.00 g, 25 mmol) in 30 mL water was added to a mixture of 4,4'-dinitrochalcone **3** (0.50 g, 1.7 mmol) into 120 mL ethanol and stirred at 100°C for 12 h. After the solvent was removed using a rotary evaporator, an orange crude product formed and collected by filtration, then washed thoroughly with water and dried to produce 0.19 g of **4** (47% yield). Mp: 178–180°C. FTIR (KBr): 3431 (s), 3333 (s), 3225 (s), 1628 (s), 1593 (s, sh), 1512 (s), 1444 (m), 1356 (m), 1302 (m), 1234 (s), 1168 (s), 1033 (w), 977 (w), 817 (m), 611 (w), 513 (w), 430 (w) cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6), δ : 5.74 (s, 2H), 6.02 (s, 2H), 6.56–6.59 (m, 4H), 7.48–7.50 (m, 4H), 7.84–7.86 (d, 2H) ppm.

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$: C, 75.6; H, 5.9; N, 11.8; Found: C, 75.3; H, 5.8; N, 11.3.

Synthesis of 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone 6

4,4'-diaminochalcone **4** (1.00 g, 4.2 mmol), trimellitic dianhydride **5** (1.61g, 8.4 mmol), 20 mL of mixture

of acetic acid and pyridine (3 : 2 v/v) and a stirring bar were placed in a 250 mL round bottomed flask. The mixture was stirred for 12 h at room temperature and was refluxed for 4 h. The solvent was removed under reduced pressure, and residue was dissolved in 50 mL of cold water and 2 mL of concentrated HCl. The solution was stirred until a yellow precipitate was formed, and the precipitate was then filtered off and dried to give 2.20 g (89%) of compound **6**. Mp: 367–369°C, FTIR (KBr): 2837–3101 (m, br), 1782 (m), 1722 (s), 1695 (s), 1601 (s), 1512 (m), 1485 (w), 1423 (m), 1379 (s), 1305 (s), 1221 (s), 1182 (m), 1122 (m), 1097 (s), 1014 (w), 929 (w), 821 (m), 798(m), 719(s) cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6), δ :7.58–7.61 (d, 2H), 7.70–7.73 (d, 2H), 7.82–7.87 (d, 1H, $J_{\text{Trans}} = 15.5\text{Hz}$), 8.05–8.13 (m, 5H), 8.33–8.36 (m, 4H), 8.42–8.46 (m, 2H) ppm. Anal. Calcd for $\text{C}_{33}\text{H}_{18}\text{N}_2\text{O}_9$: C, 67.6; H, 3.1; N, 4.8; Found: C, 67.3; H, 3.0; N, 4.3.

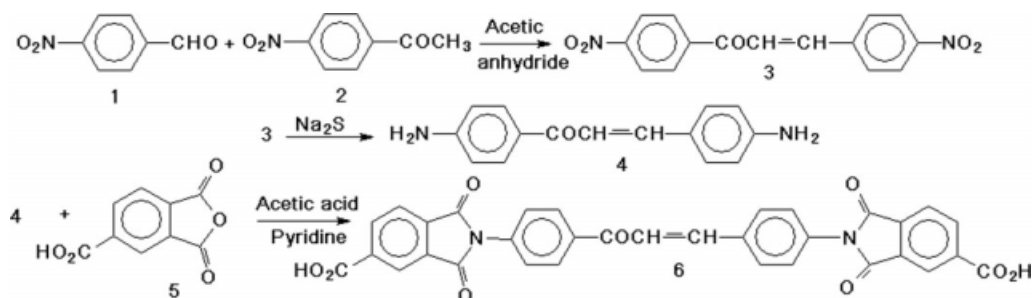
Polymer synthesis

The PAIs **8a-f** were prepared by the following general procedure (using polymer **8a** as an example). Into a 25-mL round-bottomed flask that was fitted with a stirring bar were placed hydantoin **7a** (0.01 g, 0.16 mmol), diacid **6** (0.09 g, 0.16 mmol), calcium chloride (0.50 g, 0.90 mmol), triphenyl phosphite (0.42 mL, 1.50 mmol), pyridine (0.09 mL) and *N*-methyl-2-pyrrolidone (0.40 mL). The mixture was heated under reflux on an oil bath at 60°C for 1 h, then at 90°C for 2 h, and at 130°C for 8 h. The reaction mixture was poured into 25-mL of methanol. The precipitated polymer was collected by filtration and washed thoroughly with methanol and was dried at 60°C for 12 h under vacuum to leave 0.08 g (81%) of yellow solid polymer **8a**.

RESULTS AND DISCUSSION

Monomer synthesis

1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone **6** was prepared from a three step reaction, as shown in Scheme 1. First, 4,4'-dinitrochalcone **3** was prepared from the aldol condensation reaction of 4-nitro benzaldehyde **1** with 4-nitro acetophenone **2**. FTIR spectrum of compound **3** showed a peak at 1670 cm^{-1} , which was assigned to the carbonyl group and two absorption bands at 1516 and 1319 cm^{-1} due to the NO_2 groups. 4,4'-diaminochalcone **4** was produced from the reduction of the 4,4'-dinitrochalcone **3** in the presence of Na_2S . The chemical structure and purity of the compound **4** was determined by using elemental analysis, FTIR, and $^1\text{H-NMR}$ spectroscopic techniques. The $^1\text{H-NMR}$ spectrum of compound **4** showed two singlet peaks



Scheme 1 Preparation of 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone **6**.

at $\delta = 5.74$ and $\delta = 6.02$ ppm, which were assigned to the H_g and H_h protons of the NH_2 groups. Peaks between $\delta = 6.56$ – 6.59 , $\delta = 7.48$ – 7.50 and $\delta = 7.84$ – 7.86 ppm were assigned to the H_f , H_e , H_b , H_c , H_d and H_a proton of the phenyl rings and vinyl moiety (Fig. 1). The FTIR spectrum of compound **4** showed a broad peak between 3200 and 3450 cm^{-1} , which was assigned to the NH_2 groups and absorption band at 1628 cm^{-1} due to the carbonyl group.

Finally, compound **6** was synthesized through the condensation reaction of diamine **4** with trimellitic anhydride **5** in a mixture of acetic acid and pyridine (3 : 2). Dissolving the residue in cold water produced a gummy solid that provided a yellow solid with the addition of concentrated HCl. The chemical structure and purity of the compound **6** was determined by using elemental analysis, FTIR and 1H -

NMR spectroscopic techniques. The 1H -NMR spectrum of diacid **6** showed peaks at $\delta = 7.58$ – 7.61 and $\delta = 7.70$ – 7.73 ppm, as two doublet peaks for H_l and H_k and several peaks between $\delta = 8.08$ – 8.13 , $\delta = 8.33$ – 8.36 and $\delta = 8.42$ – 8.46 ppm, as multiplies which were assigned to the $H_{l'}$, $H_{g'}$, $H_{f'}$, $H_{e'}$, $H_{d'}$, $H_{c'}$, H_b and H_a of protons of the phenyl rings, respectively, and peaks between $\delta = 7.82$ – 7.87 and $\delta = 8.05$ – 8.08 ppm, which were assigned to the H_i and H_j protons of the vinyl group. Finally, a broad peak at $\delta = 14.0$ ppm was assigned for protons of the COOH groups (Fig. 2). The FTIR spectrum of compound **6** showed a broad peak at 2800 – 3150 cm^{-1} , which was assigned to the COOH group. Several absorption bands appeared at 1782 , 1722 , 1379 , 798 , and 719 cm^{-1} , which were characteristic peaks for the imide ring. Hydantoin constitute an important

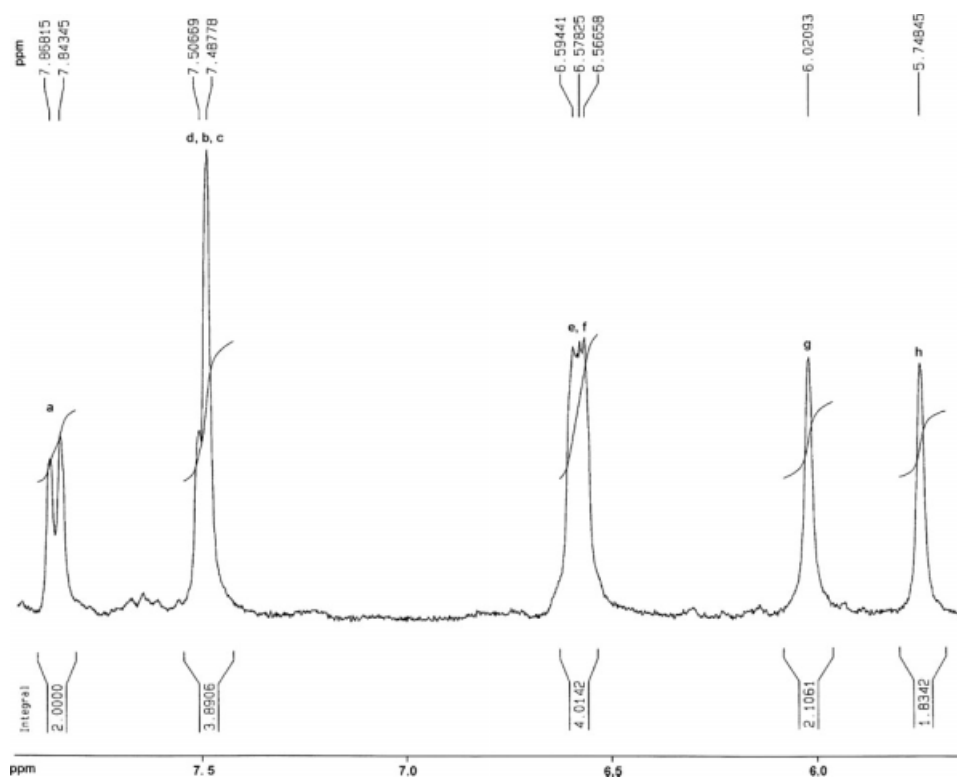


Figure 1 1H -NMR spectrum of 4,4'-diaminobenzylideneacetophenone **4**.

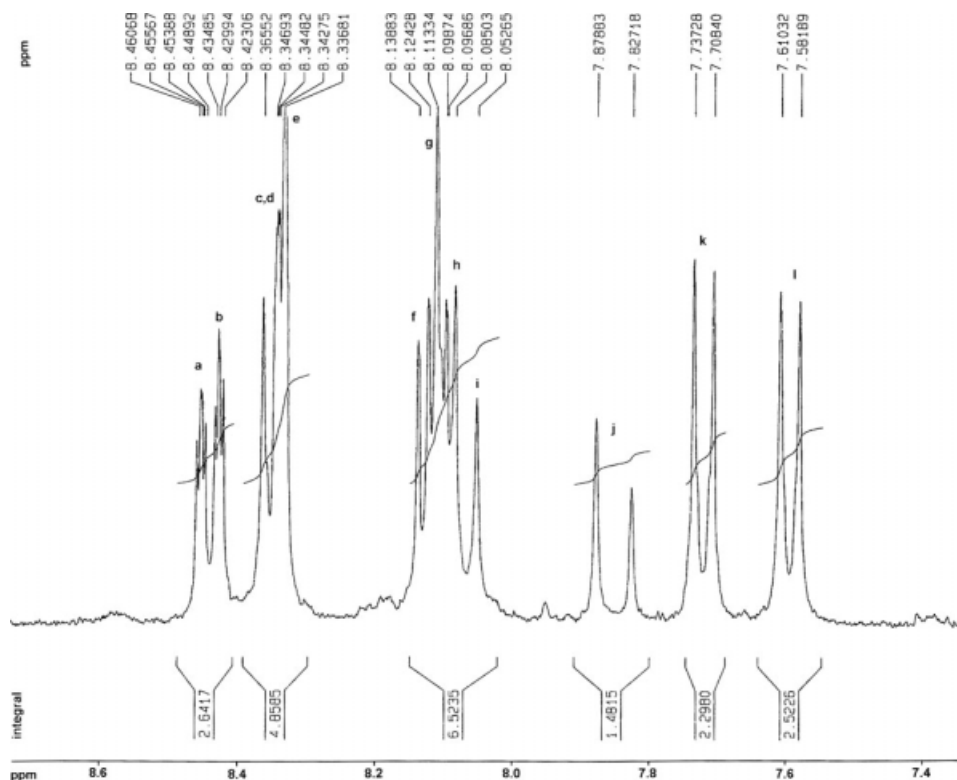


Figure 2 ¹H-NMR spectrum of 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propenone 6.

class of heterocyclic compound in medicinal chemistry because many derivatives have been identified to display interesting activities against a broad range of biological targets.^{32,33} 5,5-Disubstituted hydantoin derivatives were synthesized by the Bucherer-Berg method. By using this method, hydantoin compounds **7a-f** (Scheme 2) were prepared through the reaction of cyanohydrin derivatives with ammonium carbonate.³⁴

Polymer synthesis

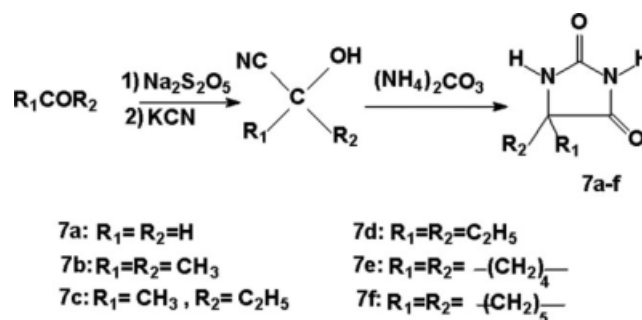
PAIs **8a-f** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **6** with hydantoin derivatives **7a-f** with triphenyl phosphate, calcium chloride, and pyridine as condensing agents in NMP as solvent (Scheme 3). The syntheses and some physical properties of these PAIs **8a-f** are given in Table I. The entire polycondensation readily proceeded in a homogeneous solution. Tough and stringy precipitates formed when the viscous PAIs solution were obtained in moderate to good yields and had inherent viscosities of 0.26–0.42 dL/g.

Polymer characterization

The syntheses and some physical properties of PAIs **8a-f** are summarized in Table I. These polymers had inherent viscosities of 0.26–0.42 dL/g. Inherent vis-

cosities of resulting PAIs **8a-f** were measured by a standard procedure using a Technico Regd Trad Merk Viscometer at a concentration of 0.5g/dL in DMF as solvent at 25°C.

These polymers confirmed to be PAIs with FTIR spectroscopy and elemental analyses (Table II). A representative FTIR spectrum of PAI **8e** is shown in Figure 3. PAI **8e** had absorption bands between 1780 and 1710 cm^{-1} due to imide and amide carbonyl groups. Absorption bands around 1370–1380 and 710–730 cm^{-1} demonstrated the presence of the imide heterocyclic ring in this polymer. Also the elemental analyses of the resulting polymers are in good agreement with the calculated values for the



Scheme 2 Synthesis of hydantoin derivatives **7a-f**.

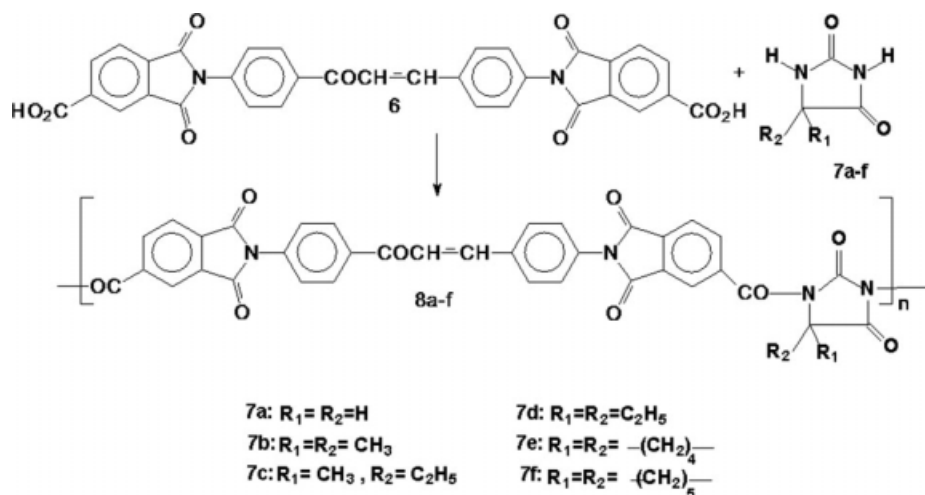
Scheme 3 Preparation of poly(amide-imide)s **8a-f**.

TABLE I
Synthesis and Some Physical
Properties of Polyamide **8a-f**

Hydantoins	Polymer	Yield (%)	η_{inh} (dL/g) ^a
7a	8a	81	0.26
7b	8b	88	0.34
7c	8c	80	0.27
7d	8d	78	0.32
7e	8e	75	0.36
7f	8f	96	0.42

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

proposed structures (Table II). Results show solubility of PAIs **8a-f** determined quantitatively by dissolving 20 mg of solid polymer in 2 mL of organic solvents. It can be seen that PAIs **8a-f** containing hydantoin moiety in the main chain showed good solubility in polar solvents, such as NMP, DMAc, DMF, and DMSO. These polymers are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water in room temperature.

Also, the UV-vis absorption spectrum of diacid **6** and PAIs **8a** in DMF are shown in Figures 4 and 5. From their UV-vis spectra presented in Figures 4 and 5, it is readily seen that the absorption of PAIs **8a** at 355 nm appeared at a much longer wavelength than that diacid **6** at 330 nm. The attachment of the chalcone unit on the polymer main chain was causes a bathochromic strong shift on $n \rightarrow \pi^*$ transition in this polymer.

Thermal properties

The thermal properties of PAIs **8a** and **e** as two samples 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 III (Fig. 6). The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 600°C for them are summarized in Table III. These polymers exhibited good resistance to thermal decomposition up to 275–295°C in nitrogen and began to decompose gradually above that

TABLE II
Elemental Analysis of PAIs **8a-f**

Polymer	Formula		C%	H%	N%
8a	$C_{36}H_{18}N_4O_9$ (650.56) _n	Calc.	66.5	2.8	8.6
		Found	65.9	3.0	8.2
8b	$C_{38}H_{22}N_4O_9$ (678.61) _n	Calc.	67.3	3.3	8.3
		Found	68.2	3.0	8.6
8c	$C_{39}H_{24}N_4O_9$ (692.64) _n	Calc.	67.6	3.5	8.1
		Found	67.0	3.1	7.6
8d	$C_{40}H_{24}N_4O_9$ (706.67) _n	Calc.	67.9	3.7	7.9
		Found	66.9	3.1	7.0
8e	$C_{40}H_{24}N_4O_9$ (704.65) _n	Calc.	68.2	3.4	7.9
		Found	69.3	2.8	8.6
8f	$C_{41}H_{26}N_4O_9$ (718.68) _n	Calc.	68.5	3.6	7.8
		Found	68.0	3.0	8.2

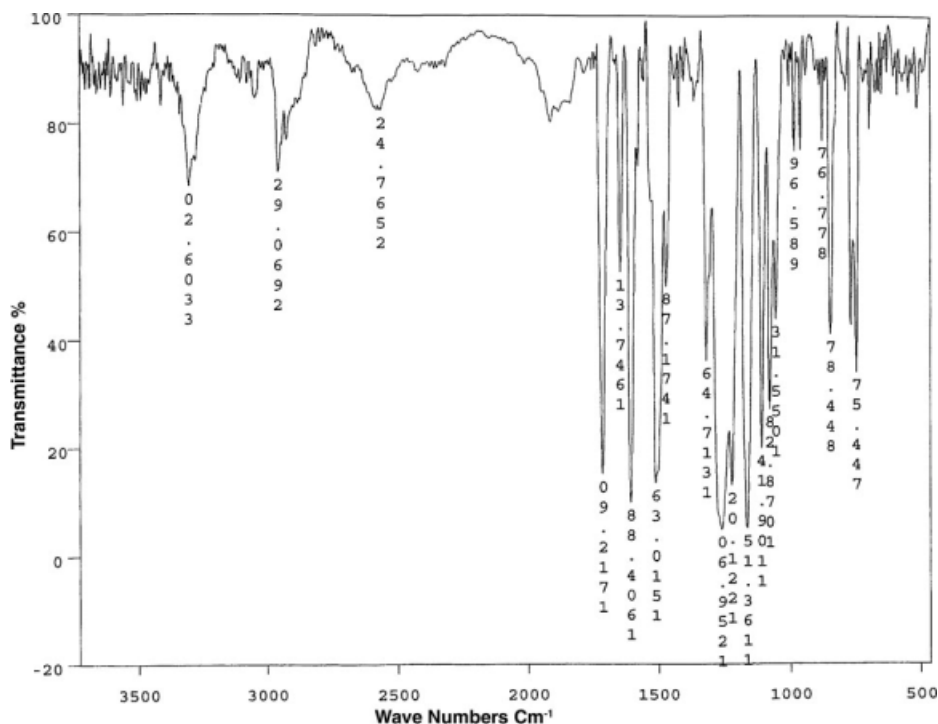


Figure 3 FTIR spectrum of PAI 8e.

temperature. T_5 for them ranged from 275 to 295°C and T_{10} ranged from 290 to 300°C, and the residual weight for these polymers at 600°C ranged from 0 to 9% in nitrogen. Results show that PAIs 8e containing 5,5-spirocyclopantyl hydantoin moiety in the main chain has higher thermal stability in compare with other polymers because it has a rigid structure in position of 5 of hydantoin ring.

CONCLUSIONS

This work involved the syntheses of several new PAIs 8a-f through solution polycondensation reaction of 6 with six hydantoin derivatives 7a-f with triphenyl phosphite, calcium chloride, and pyridine as condensing agents in NMP as solvent. These PAIs

were soluble in various organic solvents and had moderate thermal stability. The presence of hydantoin into the backbone increased the solubility of these polymers. PAIs with the chalcone unit in the main chain used in photocrosslinkable polymer.

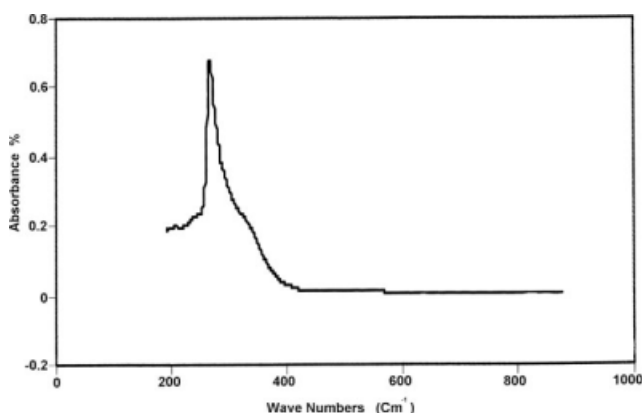


Figure 4 UV spectrum of diacid 6.

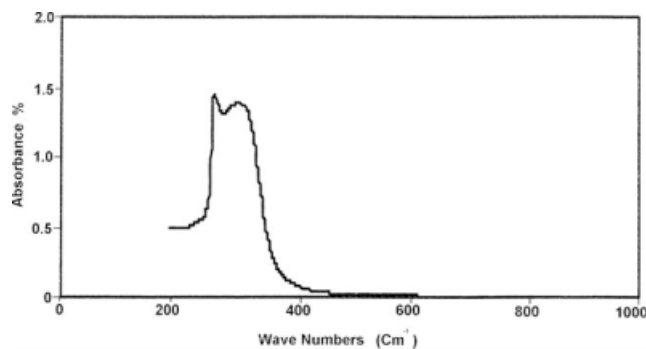


Figure 5 UV spectrum of PAI 8a.

TABLE III
Thermal Behavior of PAIs 8a-f

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield ^c
8a	275–280	290–295	0
8e	295–300	300–305	9%

^{a,b} Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N₂, respectively.

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

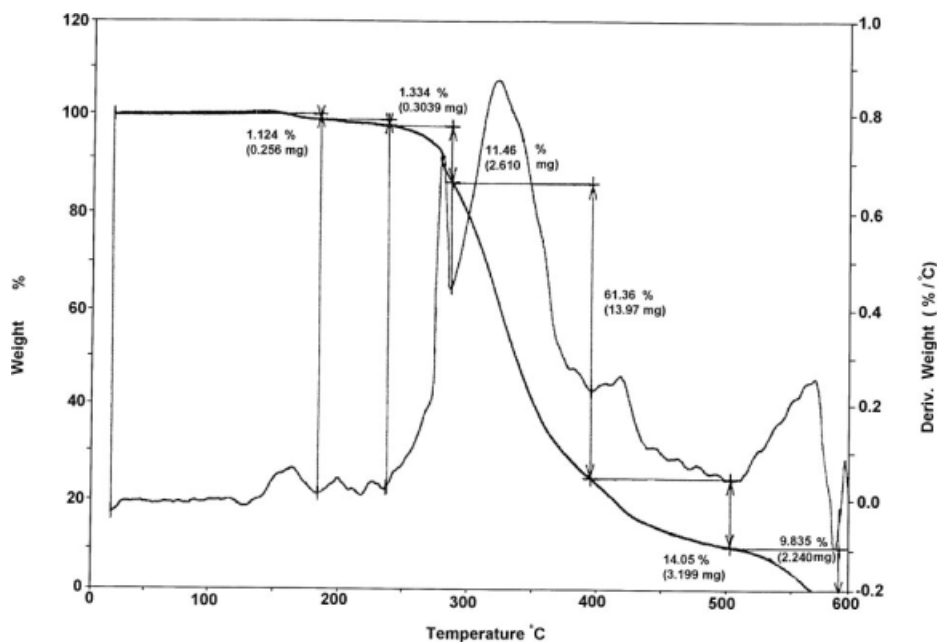


Figure 6 TGA and DTG thermogram of PAI 8a.

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