

Synthesis and Properties of Novel Photosensitive Poly(amide-imide)s Containing Chalcone Moiety and Aromatic Diamines in the Main Chain

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Received 02.01.2008

Six new poly(amide-imide)s were synthesized by the polycondensation reaction of 1,3-bis[4,4'-bis(trimellityimido) phenyl]-2-propenone (**6**) with 3,3'-diamino diphenyl sulfone (**7a**), 4,4'-diamino diphenyl sulfone (**7b**), 4,4'-diamino diphenyl ether (**7c**), 1,5-diamino naphthalene (**7d**), 6-phenyl-1,3,5-triazine (**7e**), and 6-chloro-1,3-diazine (**7f**) in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. The polycondensation reaction produced a series of novel poly(amide-imide)s (**8a-f**) in high yield and with inherent viscosities between 0.42 and 0.62 dL/g. The resulting polymers were characterized by elemental analysis, viscosity measurement, solubility testing, thermo-gravimetric analysis (TGA & DTG), FT-IR, and UV-VIS spectroscopy.

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

Introduction

Aromatic polyimides have high thermal stability, good mechanical properties, and good chemical resistance, but because they soften or melt at high temperatures and have poor solubility in common organic solvents, they have low processability and limited use.^{1,2} To overcome these drawbacks, many investigations have focused on modification of their chemical structure; for example, through the introduction of flexible linkages, asymmetric units, or bulky substituents into their polymer backbones.³⁻⁸ In addition, various copolyimides, such as poly(amide-imide)s, have been proposed by many researchers.⁹⁻¹² 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 are more processable than other aromatic thermostable polymers, such as polyamides and polyimides.¹³ They are finding numerous uses in adhesives, electronic wire enamel, injection-molding, extrusion products, and membranes.^{14,15} In our previous reports we described the synthesis and characterization

of different poly(amide-imide)s that contain heterocyclic segments in the main chain, such as hydantoin, pyridyl, and tetrahydropyrimidine rings, with improved solubility and thermal properties.^{16–18}

Photosensitive polymers are widely used as polymeric photo resists in the field of micro-electronics. Currently, interest in them is widespread because they possess a combination of good properties in dielectric constant, and thermal stability and sensitivity. On the other hand, a chalcone group, as a classical photosensitive unit, has been studied extensively and used in photo crosslinkable polymers because it affords high sensitivity to UV radiation and chemical resistance of the resultant polymers.^{19–22}

The present study synthesized and characterized a new series of PAIs containing chalcone moieties in the main chain, which were obtained by the polycondensation reaction of 1,3-bis[4,4'-bis(trimellityimido)phenyl]-2-propanone (**6**) with 6 derivative aromatic diamines (**7a-f**) using N-methyl-2-pyrrolidone (NMP), triphenylphosphite, and pyridine as condensing agents.

Experimental

Materials

4-Nitrobenzaldehyde, 4-nitroacetophenone, Na₂S, 3,3'-diamino diphenyl sulfone, 4,4'-diamino diphenyl sulfone, 4,4'-diamino diphenyl ether, 1,5-diamino naphthalene, 6-phenyl-1,3,5-triazine, 6-chloro-1,3-diazine, triphenyl phosphite, pyridine, trimellitic anhydride, and calcium chloride were purchased from Aldrich Chemical Co. and Merck Chemical Co., and used without further purification. N,N-Dimethyl acetamide (DMAc), N-methyl-2-pyrrolidone, and acetic anhydride were purified by distillation under reduced pressure.

Measurements

¹H-NMR spectra were recorded with a Bruker 500 MHz instrument. Fourier transform infrared (FT-IR) spectra were recorded with a Galaxy series FT-IR 5000 spectrophotometer (England). Spectra of solids were obtained using KBr pellets. Vibrational transition frequencies are reported in wave number (cm⁻¹). Band intensities were characterized as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosity was measured by a standard procedure using a Technico[®] viscometer. Thermal gravimetric analysis (TGA) data for the polymers were obtained with a Mettler TA4000 system under an N₂ atmosphere at the rate of 10 °C/min. Elemental analyses were performed by the Research Institute of the Petroleum Industry, Tehran, I. R. 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 of acetic anhydride was stirred and then the mixture was refluxed overnight. The mixture was poured into water and a yellow-brown precipitate was 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; FT-IR (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), and 682 (m) cm⁻¹.

Synthesis of 4,4'-diaminochalcone (4)

Na₂S (2.00 g, 25 mmol) in 30 ml of water was added to a mixture of 4,4'-dinitrochalcone (**3**) (0.50 g, 1.7 mmol) and 120 mL of ethanol, and stirred for 12 h at 100 °C. After the solvent was removed using a rotary evaporator, an orange crude product was formed and collected by filtration, washed thoroughly with water, and dried to produce 0.19 g of (**4**) (47% yield). mp: 178-180 °C; FT-IR (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), and 430 (w) cm⁻¹. ¹H-NMR (DMSO-d₆), δ: 5.74 (s, 2H), 6.02 (s, 2H), 6.56-6.59 (m, 4H), 7.48-7.50 (m, 4H), and 7.84-7.86 (d, 2H) ppm.

ANAL. Calcd for C₁₅H₁₄N₂O: 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 anhydride (**5**) (1.61 g, 8.4 mmol), a 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 overnight at room temperature and was then refluxed for 4 h. The solvent was removed under reduced pressure and the 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. The precipitate was then filtered off and dried to give 2.20 g (89%) of compound **6**. mp: 367-369 °C; FT-IR (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), and 719(s) cm⁻¹. ¹H-NMR (DMSO-d₆), δ: 7.58-7.61 (d, 2H), 7.70-7.73 (d, 2H), 7.82-7.87 (d, 1H, *J*_{trans} = 15.5 Hz), 8.05-8.13 (m, 5H), 8.33-8.36 (m, 4H), and 8.42-8.46 (m, 2H) ppm. ANAL. Calcd for C₃₃H₁₈N₂O₉: 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 fitted with a stirring bar were placed 3,3'-diamino diphenyl sulfone (**7a**) (0.04 g, 0.16 mmol), diacid (**6**) (0.09 g, 0.16 mmol), calcium chloride (0.50 g, 0.90 mmol), triphenyl phosphate (0.42 mL, 1.50 mmol), pyridine (0.09 mL), and N-methyl-2-pyrrolidone (0.40 mL). The mixture was heated under reflux in an oil bath at 60 °C for 1 h, at 90 °C for 2 h, and then at 130 °C for 8 h. The reaction mixture was then poured into 25 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with methanol, and dried at 60 °C for 12 h under vacuum to leave 0.10 g (80%) of a yellow solid polymer (**8a**). The PAIs (**8a-f**) were then analyzed by FT-IR.

Results and Discussion**Monomer Synthesis**

1,3-Bis [4,4'-bis(trimellityimido)phenyl]-2-propenone (**6**) was prepared from the 3-step reaction shown in Scheme 1. First, 4,4'-dinitrochalcone (**3**) was prepared from the aldol condensation reaction of 4-nitro acetophenone (**1**) with 4-nitro benzaldehyde (**2**). The FT-IR spectrum of compound **3** showed a peak at 1670 cm⁻¹, which was assigned to the carbonyl, and 2 absorption bands at 1516 and 1319 cm⁻¹ due to the NO₂ groups (Figure 1).

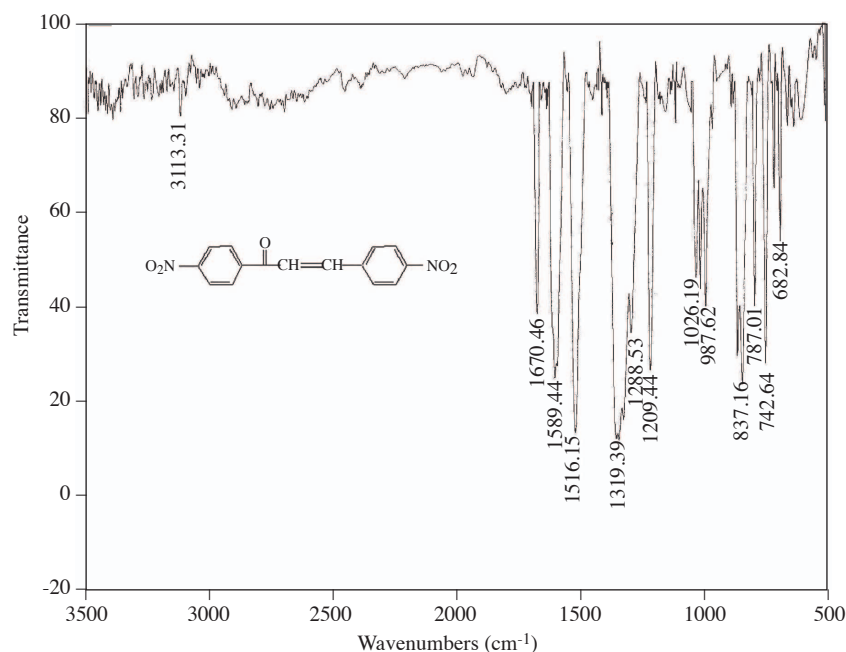
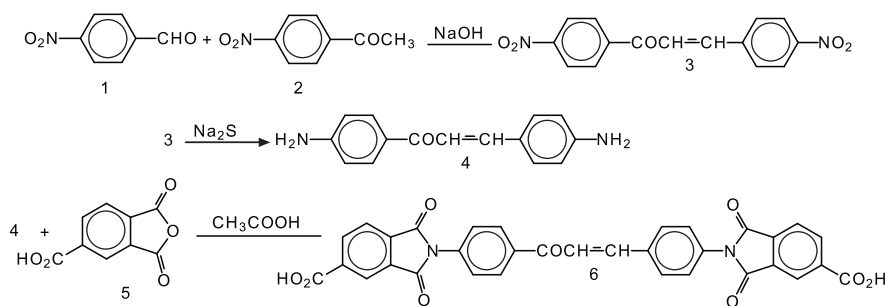


Figure 1. FT-IR spectrum of 4,4'-dinitrochalcone (**3**).



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

4,4'-Diaminochalcone (**4**) was produced by the reduction of 4,4'-dinitrochalcone (**3**) in the presence of Na_2S . The chemical structure and purity of compound **4** was determined by elemental analysis, and FT-IR $^1\text{H-NMR}$ spectroscopic techniques. The $^1\text{H-NMR}$ spectrum of compound **4** showed 2 singlet peaks 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 at $\delta = 6.56$ - 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 protons of the phenyl rings and vinyl group (Figure 2). The FT-IR spectrum of compound **4** showed a broad peak between 3200 and 3450 cm^{-1} , which was assigned to the NH_2 groups, and an absorption band at 1628 cm^{-1} due to the carbonyl group (Figure 3).

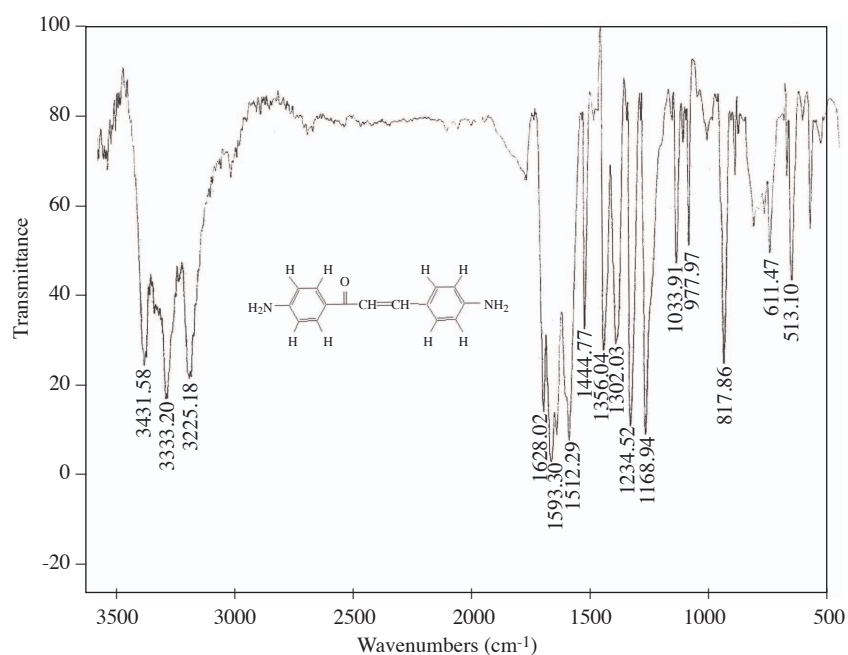


Figure 2. FT-IR spectrum of 4,4'-diaminochalcone (**4**).

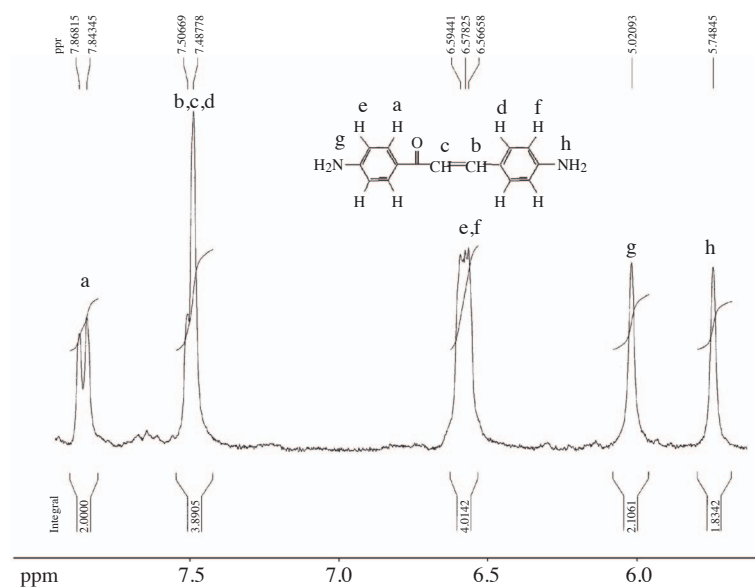
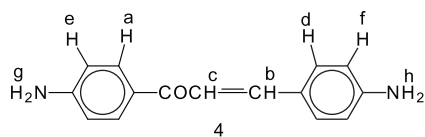
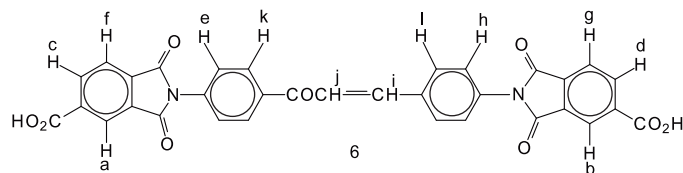


Figure 3. $^1\text{H-NMR}$ spectrum of 4,4'-diaminochalcone (**4**).



Finally, compound **6** was synthesized by 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 after the addition of concentrated HCl. The chemical structure and purity of compound **6** was determined by elemental analysis, and FT-IR and $^1\text{H-NMR}$ spectroscopic

techniques. The $^1\text{H-NMR}$ spectrum of diacid (**6**) showed peaks at $\delta = 7.58\text{-}7.61$ and $\delta = 7.70\text{-}7.73$ ppm as 2 doublet peaks for H_l and H_k , and several peaks at $\delta = 8.08\text{-}8.13$, $\delta = 8.33\text{-}8.36$, and $\delta = 8.42\text{-}8.46$ ppm as multiples that were assigned to the H_h , H_g , H_f , H_e , H_d , H_c , H_b , and H_a protons of the phenyl rings, and peaks at $\delta = 7.82\text{-}7.87$ and $\delta = 8.05\text{-}8.08$ ppm that 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 to the protons of the COOH groups (Figure 4).



The FT-IR spectrum of compound **6** showed a broad peak at $2800\text{-}3150\text{ cm}^{-1}$, which was assigned to the COOH groups. Several absorption bands appeared at 1782 , 1722 , 1379 , 798 , and 719 cm^{-1} , which were characteristic peaks for the imide ring (Figure 5).

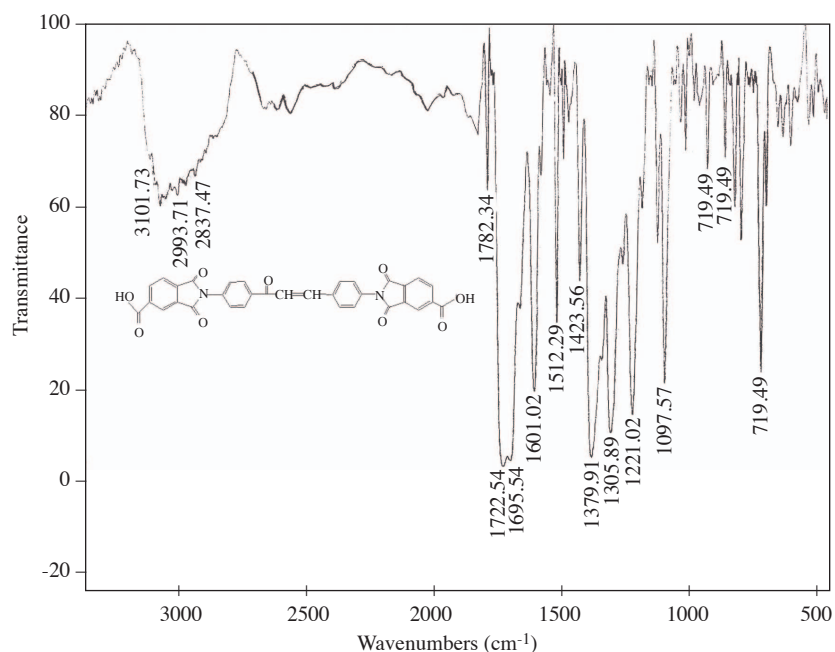


Figure 4. FT-IR spectrum of 1,3-bis[4,4'-bis(trimellitylimido)phenyl]-2-propenone (**6**).

Polymer Synthesis

PAIs **8a-f** were synthesized by the direct solution polycondensation reaction of an equimolar mixture of (**6**), with diamines (**7a-f**) and triphenyl phosphate, NMP, calcium chloride, and pyridine as condensing agents (Scheme 2).

The synthesis and some physical properties of PAIs **8a-f** are given in Table 1. The entire polycondensation readily proceeded in a homogeneous solution. Tough and stringy precipitates formed when the viscous PAI solutions were obtained in moderate to good yields, with inherent viscosities of $0.42\text{-}0.62\text{ dL/g}$.

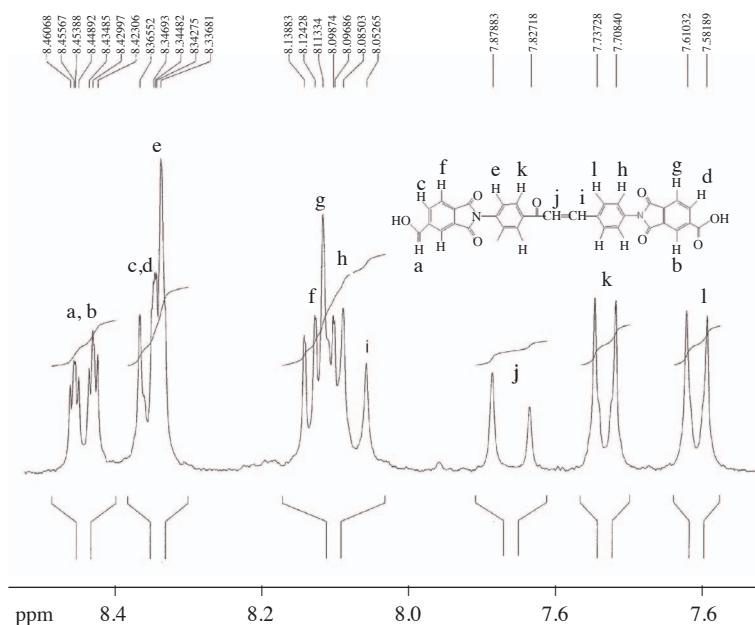
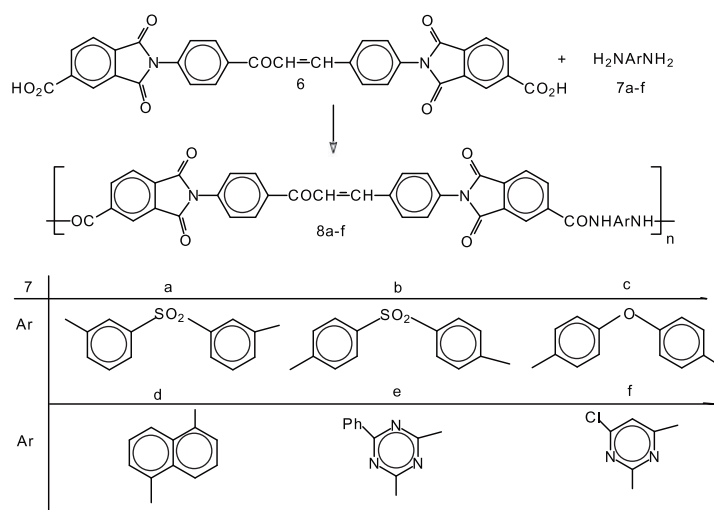


Figure 5. $^1\text{H-NMR}$ spectrum of 1,3-bis[4,4'-bis(trimellitylimido) phenyl]-2-propenone (**6**).



Scheme 2. Preparation of poly (amide-imide)s (**8a-f**).

Table 1. Synthesis and some physical properties of PAIs **8a-f**.

Diamines	Polymer	Yield (%)	η_{inh} (dL/g) ^a	Color
7a	8a	80	0.42	Red
7b	8b	85	0.46	Red
7c	8c	88	0.50	Light orange
7d	8d	89	0.49	Light orange
7e	8e	90	0.52	Dark orange
7f	8f	95	0.62	Dark orange

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

Polymer Characterization

The polymers had inherent viscosities of 0.42-0.62 dL/g and were confirmed to be PAIs by FT-IR spectroscopy and elemental analysis. Transparent, flexible, and orange-to-red films could be cast from the DMAc or NMP solutions of the resultant polymers. PAIs **8a-f** were orange to red (Table 1).

A representative FT-IR spectrum of PAI **8e** is shown in Figure 6. PAI **8e** had absorption bands between 1780 cm^{-1} and 1710 cm^{-1} due to imide and amide carbonyl groups. Absorption bands around $1370\text{-}1380$ and $710\text{-}730\text{ cm}^{-1}$ demonstrated the presence of an imide heterocyclic ring in this polymer. The other spectra showed similar patterns. The elemental analyses of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table 2).

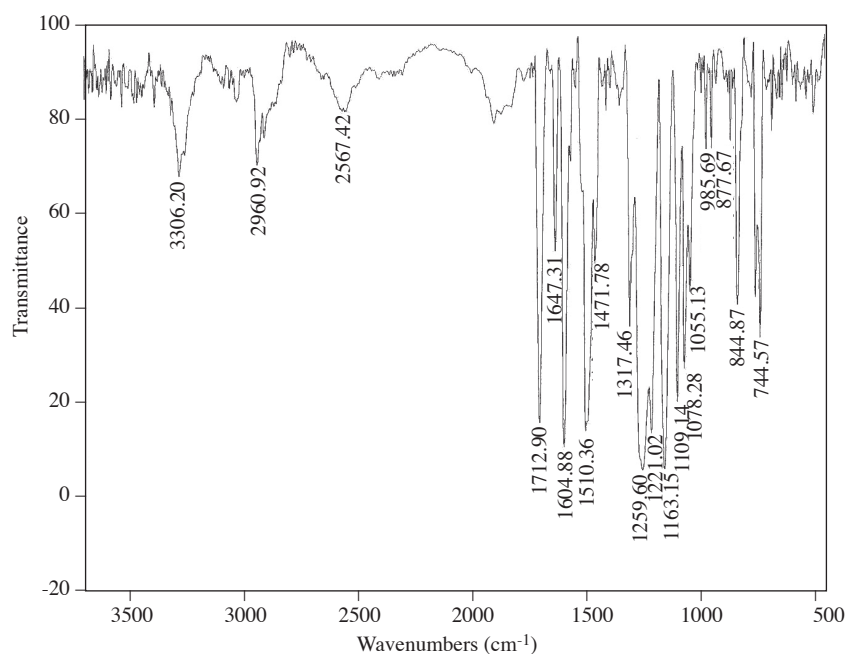


Figure 6. FT-IR spectrum of PAI **8e**.

Table 2. Elemental analysis of PAIs **8a-f**.

Polymer	Formula		% C	% H	% N
8a	$\text{C}_{45}\text{H}_{26}\text{N}_4\text{O}_9\text{S}$ (798.79) _n	Calc.	67.7	3.3	7.0
		Found	66.9	3.0	6.6
8b	$\text{C}_{45}\text{H}_{26}\text{N}_4\text{O}_9\text{S}$ (798.79) _n	Calc.	67.7	3.3	7.0
		Found	67.9	3.1	6.4
8c	$\text{C}_{43}\text{H}_{24}\text{N}_4\text{O}_7$ (708.68) _n	Calc.	72.9	3.4	7.9
		Found	72.3	3.1	7.3
8d	$\text{C}_{45}\text{H}_{26}\text{N}_4\text{O}_8$ (750.72) _n	Calc.	71.9	3.5	7.5
		Found	71.0	3.0	7.1
8e	$\text{C}_{42}\text{H}_{23}\text{N}_7\text{O}_7$ (737.68) _n	Calc.	68.4	3.1	13.3
		Found	69.3	2.6	12.6
8f	$\text{C}_{37}\text{H}_{19}\text{N}_6\text{O}_7\text{Cl}$ (695.04) _n	Calc.	63.9	2.7	12.1
		Found	63.2	2.1	11.8

The solubility of PAIs **8a-f** was investigated with 0.01 g of polymeric samples in 2 mL of solvent. All the above-mentioned polymers dissolved in organic solvents, such as DMF, DMAC, DMSO, and NMP, at room temperature and were insoluble in such solvents as chloroform, methylene chloride, methanol, ethanol, and water.

Additionally, the UV-VIS absorption spectrum of PAI **8e** in N,N-dimethyl formamide is shown in Figure 7. The spectrum of PAI **8e** exhibited 2 typical peaks at 270 nm ($\pi \rightarrow \pi^*$) and 350 nm ($n \rightarrow \pi^*$).

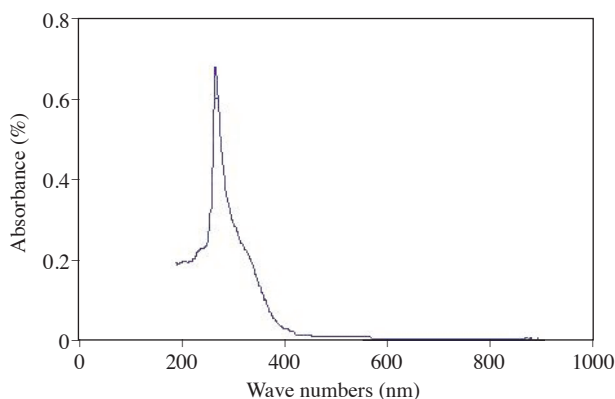


Figure 7. UV spectrum of PAI **8e**.

Thermal Properties

The thermal properties of PAIs **8a** and **8e** were investigated by TGA and DTG in a nitrogen atmosphere at the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$; the thermal data are summarized in Table 4 (Figures 7 and 8). The initial decomposition temperatures for 5% and 10% weight loss (T_5 and T_{10}), and the char yields at $600\text{ }^{\circ}\text{C}$ for these PAIs are summarized in Table 3. Polymer **8a** began to decompose at $385\text{ }^{\circ}\text{C}$, lost 5% of its weight due to decomposition at $385\text{ }^{\circ}\text{C}$, and lost 52% of its original weight due to decomposition by $600\text{ }^{\circ}\text{C}$. Polymer **8e** began to decompose at $290\text{ }^{\circ}\text{C}$ and lost 5% of its weight at $290\text{ }^{\circ}\text{C}$. Only 12% of its original weight remained at $600\text{ }^{\circ}\text{C}$. The results of the present study show that PAI **8a**, with a sulfone moiety, demonstrated greater thermal decomposition than PAI **8e**, which had a naphthyl moiety in the main chain.

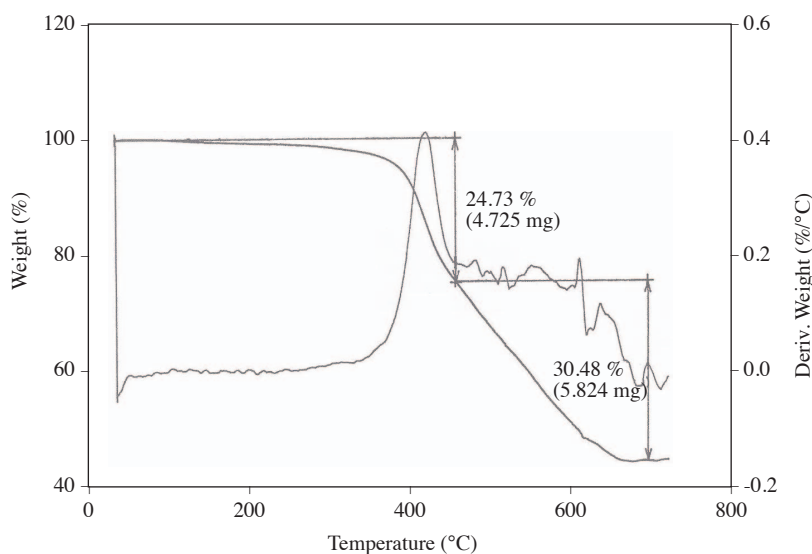


Figure 8. TGA and DTG thermogram of PAI **8a**.

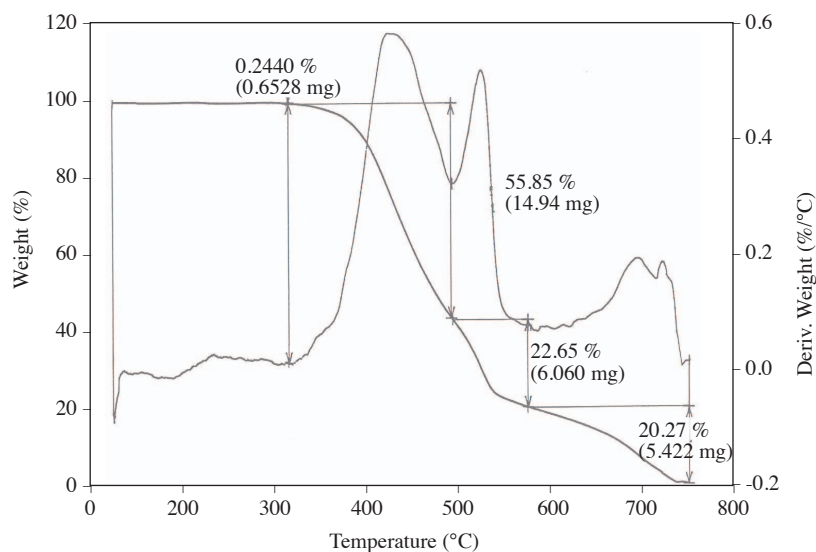


Figure 9. TGA and DTG thermogram of PAI **8e**.

Table 3. Thermal behavior of PAIs **8a** and **8e**.

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield ^c
8a	385-390	400-405	52%
8e	290-295	305-310	12%

^{a,b}Temperature at which 5% and 10% weight loss was recorded by TGA at the heating rate of 10 °C min⁻¹ in N₂, respectively. ^cPercentage of material (by weight) left undecomposed after TGA analysis at 600 °C.

Conclusion

The present study involved the synthesis of several new PAIs (**8a-f**) by the solution polycondensation reaction of **6** with 6 aromatic diamines (**7a-f**), and triphenyl phosphite, NMP, calcium chloride, and pyridine as condensing agents. These PAIs were soluble in various organic solvents and had moderate thermal stability. The presence of heterocyclic and aromatic compounds in the backbone increased the solubility of these polymers. PAIs with a chalcone moiety in the main chain were used in the preparation of the photocrosslinkable polymer.

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