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

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Six new poly(amide-imide)s were synthesized by the polycondensation reaction of 1,3-bis[4,4′-bis(trimellitylimido) 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(amide-imide)s; 4,4′-diamino chalcone; 1,3-bis[4,4′-bis(trimellitylimido) 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.\textsuperscript{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.\textsuperscript{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(trimellitimidio)phenyl]-2-propenone (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, Na\textsubscript{2}S, 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**

\textsuperscript{1}H-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\textsuperscript{-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\textsuperscript{®} viscometer. Thermal gravimetric analysis (TGA) data for the polymers were obtained with a Mettler TA4000 system under an N\textsubscript{2} 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\textsuperscript{-1}.   

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Synthesis of 4,4'-diaminochalcone (4)

Na$_2$S (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 derivatized 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-d$_6$), 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 C$_{15}$H$_{14}$N$_2$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(trimellitylimido)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-d$_6$), 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 C$_{33}$H$_{18}$N$_2$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 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(trimellitylimido)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 NO$_2$ groups (Figure 1).
4,4′-Diaminochalcone (4) was produced by the reduction of 4,4′-dinitrochalcone (3) in the presence of Na2S. The chemical structure and purity of compound 4 was determined by elemental analysis, and FT-IR 1H-NMR spectroscopic techniques. The 1H-NMR spectrum of compound 4 showed 2 singlet peaks at \( \delta = 5.74 \) and \( \delta = 6.02 \) ppm, which were assigned to the \( \text{H}_9 \) and \( \text{H}_8 \) protons of the \( \text{NH}_2 \) groups. Peaks at \( \delta = 6.56-6.59, \delta = 7.48-7.50, \) and \( \delta = 7.84-7.86 \) ppm were assigned to the \( \text{H}_f, \text{H}_e, \text{H}_b, \text{H}_c, \text{H}_d, \) and \( \text{H}_a \) 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 \( \text{NH}_2 \) groups, and an absorption band at 1628 cm\(^{-1} \) due to the carbonyl group (Figure 3).
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 $^1$H-NMR spectroscopic
techniques. The $^1$H-NMR spectrum of diacid (6) showed peaks at $\delta = 7.58$-$7.61$ and $\delta = 7.70$-$7.73$ ppm as 2 doublet peaks for $H_l$ and $H_k$, and several peaks at $\delta = 8.08$-$8.13$, $\delta = 8.33$-$8.36$, and $\delta = 8.42$-$8.46$ 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 $\delta = 7.82$-$7.87$ and $\delta = 8.05$-$8.08$ 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 2800-3150 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 (trimellityimido) phenyl]-2-propenone (6).](image)

**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 0.42-0.62 dL/g.
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Figure 5. $^1$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.

<table>
<thead>
<tr>
<th>Diamines</th>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$\eta_{inh}$(dL/g) $^a$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>8a</td>
<td>80</td>
<td>0.42</td>
<td>Red</td>
</tr>
<tr>
<td>7b</td>
<td>8b</td>
<td>85</td>
<td>0.46</td>
<td>Red</td>
</tr>
<tr>
<td>7c</td>
<td>8c</td>
<td>88</td>
<td>0.50</td>
<td>Light orange</td>
</tr>
<tr>
<td>7d</td>
<td>8d</td>
<td>89</td>
<td>0.49</td>
<td>Light orange</td>
</tr>
<tr>
<td>7e</td>
<td>8e</td>
<td>90</td>
<td>0.52</td>
<td>Dark orange</td>
</tr>
<tr>
<td>7f</td>
<td>8f</td>
<td>95</td>
<td>0.62</td>
<td>Dark orange</td>
</tr>
</tbody>
</table>

$^a$Measured 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 1370-1380 and 710-730 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).

![FT-IR spectrum of PAI 8e.](image)

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Formula</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>C(<em>{45})H(</em>{26})N(<em>{4})O(</em>{9})S ((798.79)_n)</td>
<td>Calc. 67.7</td>
<td>Found 66.9</td>
<td>3.3</td>
</tr>
<tr>
<td>8b</td>
<td>C(<em>{45})H(</em>{26})N(<em>{4})O(</em>{9})S ((798.79)_n)</td>
<td>Calc. 67.7</td>
<td>Found 67.9</td>
<td>3.3</td>
</tr>
<tr>
<td>8c</td>
<td>C(<em>{43})H(</em>{24})N(<em>{4})O(</em>{7}) ((708.68)_n)</td>
<td>Calc. 72.9</td>
<td>Found 72.3</td>
<td>3.1</td>
</tr>
<tr>
<td>8d</td>
<td>C(<em>{45})H(</em>{26})N(<em>{4})O(</em>{8}) ((750.72)_n)</td>
<td>Calc. 71.9</td>
<td>Found 71.0</td>
<td>3.5</td>
</tr>
<tr>
<td>8e</td>
<td>C(<em>{45})H(</em>{23})N(<em>{7})O(</em>{7}) ((737.68)_n)</td>
<td>Calc. 68.4</td>
<td>Found 69.3</td>
<td>3.1</td>
</tr>
<tr>
<td>8f</td>
<td>C(<em>{37})H(</em>{19})N(<em>{6})O(</em>{7})Cl ((695.04)_n)</td>
<td>Calc. 63.9</td>
<td>Found 63.2</td>
<td>2.7</td>
</tr>
</tbody>
</table>
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 ($n \rightarrow \pi^*$).

**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 °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 °C for these PAIs are summarized in Table 3. Polymer 8a began to decompose at 385 °C, lost 5% of its weight due to decomposition at 385 °C, and lost 52% of its original weight due to decomposition by 600 °C. Polymer 8e began to decompose at 290 °C and lost 5% of its weight at 290 °C. Only 12% of its original weight remained at 600 °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.
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![Graph showing TGA and DTG thermogram of PAI 8e.]

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

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T$_{5}$(°C)$^a$</th>
<th>T$_{10}$(°C)$^b$</th>
<th>Char Yield$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>385-390</td>
<td>400-405</td>
<td>52%</td>
</tr>
<tr>
<td>8e</td>
<td>290-295</td>
<td>305-310</td>
<td>12%</td>
</tr>
</tbody>
</table>

$^a$Temperature at which 5% and 10% weight loss was recorded by TGA at the heating rate of 10 °C min$^{-1}$ in N$_2$, respectively.

$^b$Percentage 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.

References