

# Preparation and Characterization of New Organosoluble Polyamides with Good Thermal Properties Containing Photosensitive Group in the Main Chain

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**ABSTRACT:** In this article, we have successfully synthesized a new dicarboxylic acid, from the two step reactions. At first 4,4'-bis(1,2-diphenoxyethane) dialdehyde was synthesized from 1,2-dibromoethane and 4-hydroxybenzaldehyde, then 4,4'-bis(1,2-diphenoxyethane) diacrylic acid was synthesized from 4,4'-bis(1,2-diphenoxyethane) dialdehyde and malonic acid in a solvent free reaction. Four new organosoluble and thermally stable polyamides (PAs) with good inherent viscosities containing photosensitive groups were synthesized from the direct polycondensation reaction of 4,4'-bis(1,2-diphenoxyethane) diacrylic acid with four various aromatic diamines containing photosensitive group, by two different methods such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/

triphenyl phosphite (TPP)/calcium chloride (CaCl<sub>2</sub>)/pyridine (Py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (Py)/*N,N*-dimethylformamide (DMF) system. All of the above polymers were fully characterized by <sup>1</sup>H-NMR, FTIR, gel permeation chromatography (GPC), elemental analysis, inherent viscosity, solubility tests, UV-vis spectroscopy, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA). The resulted polyamides (PAs) have showed admirable good inherent viscosities, thermal stability and solubility. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** polyamide; organosoluble; thermally stable; polycondensation; malonic acid

## INTRODUCTION

Aromatic polyamides have excellent mechanical properties and thermal stability which make them useful as high-performance materials for advanced technologies and usually they are synthesized from aromatic diamines and aromatic dicarboxylic acids.<sup>1,2</sup> However, applications of polyamides are often restricted by problems in their fabrication such as poor solubility and high softening or melting temperatures caused by high crystallinity and high stiffness of the polymer backbone lead to difficult processability of resulting polyamides.

Much effort has been made to create structurally modified aromatic polyamides having better solubility and processability. Introduction of flexible chains in the polyamide backbone,<sup>3</sup> synthesis of polyamides with noncoplanar unit in the polymer chains,<sup>4</sup> preparation of copolymers such as poly(amide-imide)s,<sup>5–8</sup> poly(ester-imide)s,<sup>9</sup> poly(amide-ester-imide)s<sup>10</sup> and the introduction of bulky side groups in the polymer chains<sup>11–13</sup> resulted a series of modified polyamides.

Aromatic polymers that contain aryl ether linkages generally have lower glass transition temperatures, greater chain flexibility, and tractability these groups in the chain in compare to their corresponding polymers.<sup>14–16</sup> The lower glass transition temperatures and also improved solubility are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation.<sup>17</sup>

Polymers containing photosensitive moieties such as cinnamate, chalcone, coumarine, dibenzalacetone, and their derivatives both in main chain or side chain<sup>18–21</sup> have attracted great interest because of their potential use in various applications, the foremost of these including devices for optical data storage,<sup>22</sup> photoresists,<sup>23</sup> and photolithographic assemblies.<sup>24</sup> Moreover, the design and synthesis of polymers highly sensitive to light processing continue to be the most attractive targets because various material properties such as solubility can be improved by the incorporation of appropriate chemical structures into a polymer backbone.

A triphenyl phosphite (TPP)-activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki et al.<sup>25</sup> We describe here the preparation and basic characterization of thermally stable and organosoluble polyamides **10a–d** based on photosensitive group from the reaction of 4,4'-bis(1,2-diphenoxyethane)

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diacrylic acid **5** as a new diacid monomer with four synthesized aromatic diamines such as 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **9a**, 2,5-bis(4-aminobenzylidene)cyclopentanone **9b**, 2,6-bis(4-aminobenzylidene)cyclohexanone **9c** and 1,3-bis(4-aminophenyl)prop-2-en-1-one **9d** by two different methods such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl<sub>2</sub>)/pyridine (py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (py)/*N,N*-dimethylformamide (DMF) system.

## EXPERIMENTAL

### Materials

1,2-Dibromoethane, 4-hydroxybenzaldehyde, 4-nitrobenzaldehyde, malonic acid, acetone, cyclopentanone, cyclohexanone, 4-nitro acetophenone, and tosyl chloride (TsCl; from Merck) were used without further purification. Solvent: *N*-methyl-2-pyrrolidone (NMP; from Fluka), pyridine (from Acros), triphenyl phosphite (TPP; from Merck) and *N,N*-dimethylformamide (DMF; from Merck) were used as received. Commercially available calcium chloride (CaCl<sub>2</sub>; from Merck) was dried under vacuum at 150°C for 6 h.

### Techniques

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were reported in wave number (cm<sup>-1</sup>). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured at a concentration of 0.5 g/dL in DMF at 25°C by a standard procedure by using a Technico Regd Trad Mark Viscometer. Weight-average ( $\overline{M}_w$ ) and number-average ( $\overline{M}_n$ ) molecular weights were determined by gel permeation chromatography (GPC-Apparatur von Fa. Agilent Serie1100-RI -Detektor2 Zorbax PSM Trimodal-S-DMAc+2 vol % H<sub>2</sub>O+3 g/L LiCl, 0.5 mL/min, PVP-Standards). The eluents were monitored with a UV detector (JMST Systems, USA, VUV-24) at 254 nm. Polystyrene was used as the standard. UV-vis absorptions were recorded at 25°C in the 190–790 nm spectral regions with a Perkin-Elmer Lambda 15 spectrophotometer on DMF solution by using cell lengths of 1 cm. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N<sub>2</sub> atmosphere at rate of 10°C/min and differential scanning calorimeter (DSC) was conducted with a DSC Mettler 110

(Switzerland) at a heating and heating rate of 10°C/min in a nitrogen atmosphere. Elemental analyses were performed by Vario EL equipment.

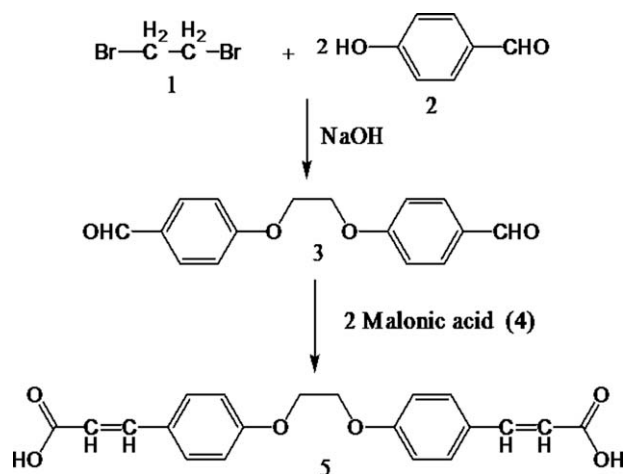
### Monomer synthesis

Synthesis of 4,4'-bis(1,2-diphenoxyethane) dialdehyde **3**

In a 250-mL round bottomed flask with dropping funnel fitted with a stirring bar were placed (4.06 g, 33.3 mmol) of 4-hydroxybenzaldehyde **2** and (2.60 g, 65.0 mmol) sodium hydroxide in 14.0 mL H<sub>2</sub>O. Then 16.8 mmol 1,2-dibromo ethane **1** was added into the reaction mixture slowly with stirring and the reaction mixture was refluxed for 3.5 h. After that (0.66 g, 16.5 mmol) NaOH was added and refluxing continuing for 2 h. Then the heating was removed, the stirring continued at room temperature for overnight. After that the white precipitate was filtered and washed with 15 mL methanol, the solid was dissolved in 34 mL H<sub>2</sub>O, by adding a solution of H<sub>2</sub>SO<sub>4</sub> (6 N) a white solid was precipitate, washed with the cold water and filtered at room temperature until 5.50 g (61%) white product was obtained. Mp: 210–212°C, FTIR (KBr): 3031 (w), 2963 (m), 2932 (w), 1814 (s), 1703 (s), 1689 (s), 1604 (m), 1671 (s), 1604 (m), 1412 (s), 1385 (s), 1292 (s), 1169 (m), 1040 (w), 847 (m), 769 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS)  $\delta$ : 4.27 (t, 4H), 7.14–7.16 (d, 4H), 7.84–7.87 (d, 4H), 9.86 (s, 2H) ppm. Elemental analysis: calculated for C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>: C, 71.10; H, 5.22, found: C, 71.03; H, 5.21.

Synthesis of 4,4'-bis(1,2-diphenoxyethane) diacrylic acid **5**

In a 100-mL beaker were placed (1.5 g, 5.55 mmol) of 4,4'-bis(1,2-diphenoxyethane) dialdehyde **3** and (1.15 g, 11.1 mmol) malonic acid **4** in 1 mL morpholine. The mixture compounds were heated until completely melted. Then the heating was removed and 20 mL HCl 5% was added in the reaction mixture slowly with stirring and the stirring continued at room temperature for 2 h. After that the white precipitate was filtered and washed with 20 mL H<sub>2</sub>O and washed with the cold water and filtered at room temperature until 1.61 g (82%) white product was obtained. Mp: 341–343°C, FTIR (KBr): 2400–3500 (s, br), 1689 (s), 1628 (s), 1601 (s), 1510 (s), 1427 (s), 1311 (s, sh), 1217 (m), 1172 (m), 1018 (s, br), 827 (m), 682 (w), 509 (w) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS)  $\delta$ : 4.37 (s, 4H), 6.36–6.41 (d, 2H), 7.01–7.05 (d, 4H), 7.52–7.57 (d, 2H), 7.64–7.66 (d, 4H), 12.5 (s, br, 2H) ppm. <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>)  $\delta$ : 168.31, 160.40, 144.15, 130.46, 127.53, 117.12, 115.32, 66.85 ppm. Elemental analysis: calculated for C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>: C, 67.79; H, 5.12, found: C, 67.34; H, 5.09.

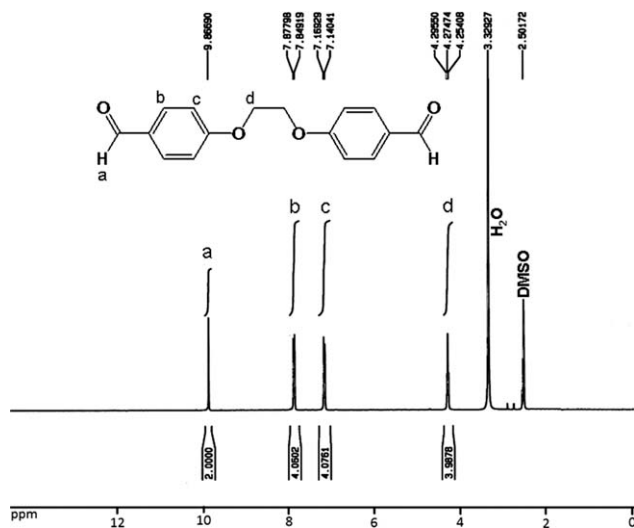


**Scheme 1** Synthesis of dicarboxylic acid 5.

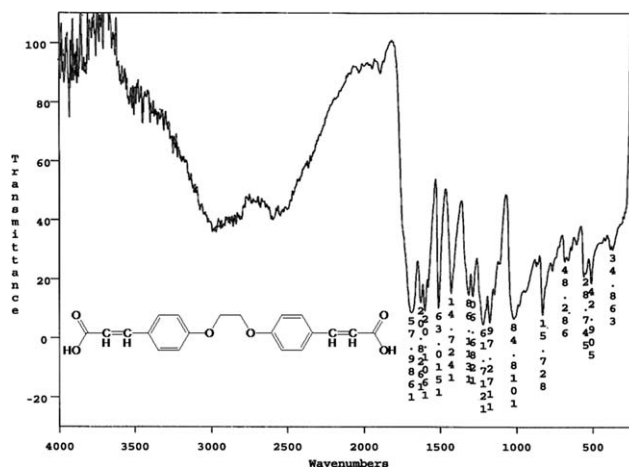
### Synthesis of aromatic diamines 9a–d

Aromatic diamines **9a–d** were synthesized by using two steps reaction.

**2,6-Bis(4-nitrobenzylidene)cyclohexanone 8c.** 0.548 g (5.6 mmol) of cyclohexanone **7c**, 1.691 g (11.2 mmol) of 4-nitrobenzaldehyde **6**, 15 mL of ethanol, and a stirring bar were placed into a 50-mL round-bottom flask. Then this mixture was heated in 50°C for 1 h and 5 mL of NaHCO<sub>3</sub> (1%) was added slowly at this temperature and refluxed for 3 h. Then the reaction mixture was cooled to ambient temperature and 50 mL cooled water was added. A yellow crude product formed and was collected by filtration, washed thoroughly with water, and dried to afford 1.67 g (82%). Mp: 251–253°C. FTIR (KBr): 3103 (w), 2922 (w) 1670 (m), 1589 (s, sh), 1512 (s), 1433 (w), 1342 (s), 1298 (s) 1265 (s), 1141 (s), 1107 (m), 1012 (m), 850 (m), 719 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>, TMS): δ; 7.46 (s, 2H), 7.27 (d, 4H), 6.59



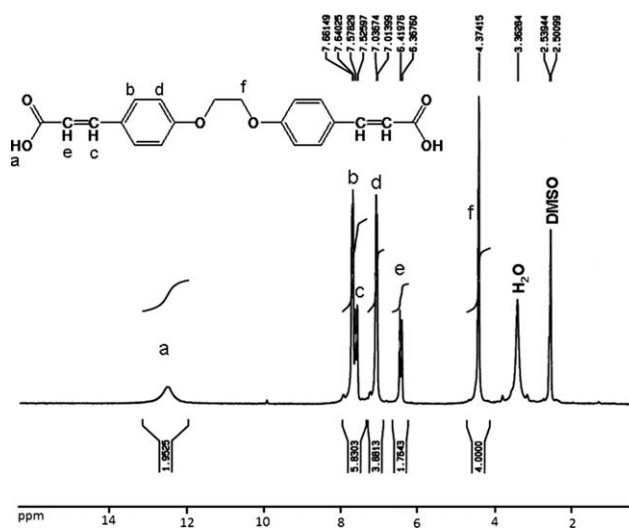
**Figure 1** <sup>1</sup>H-NMR spectrum of 4,4'-bis(1,2-diphenoxyethane) dialdehyde **3**.



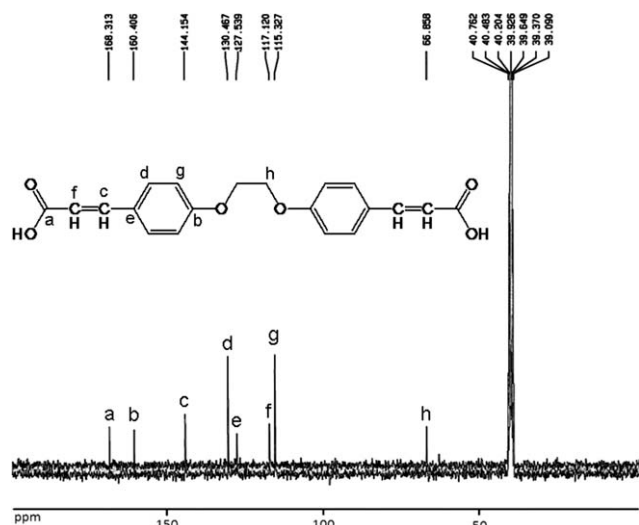
**Figure 2** FTIR spectrum of 4,4'-bis(1,2-diphenoxyethane) diacrylic acid **5**.

(d, 4H), 2.8 (s, 4H), 1.8 (s, 2H) ppm. Elemental analysis: calculated for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>: C, 65.93; H, 4.43; N, 7.69; found: C, 65.23; H, 4.41; N, 7.61.

**2,6-Bis(4-aminobenzylidene)cyclohexanone 9c.** To solution 0.8 g (10.2 mmol) of Na<sub>2</sub>S and 0.35 g (4.16 mmol) of NaHCO<sub>3</sub> in 5 mL water, 10 mL methanol was added. The mixture stirred for 30 min in room temperature. The precipitate was filtered, then the filtrate was added to mixture 0.28 g (0.770 mmol) of 2,6-bis(4-nitrobenzylidene) cyclohexanone **8c**, and 15 mL methanol, and stirred for 3 h under reflux conditions. The mixture was concentrated using rotary evaporator, and the residue poured into water, a dark red crude product formed and was collected by filtration, washed thoroughly with water, and dried to afford 0.21 g (91%). Mp: 285–287°C. FTIR (KBr): 3348 (m), 3223 (w), 2930 (w), 1628 (s, sh), 1579 (s), 1512 (s), 1435 (m), 1344 (w), 1286 (s), 1161 (s), 968 (m), 829 (m), 495 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR (300 MHz,



**Figure 3** <sup>1</sup>H-NMR spectrum of 4,4'-bis(1,2-diphenoxyethane) diacrylic acid **5**.



**Figure 4**  $^{13}\text{C}$ -NMR spectrum of 4,4'-bis(1,2-diphenoxyethane) diacrylic acid **5**.

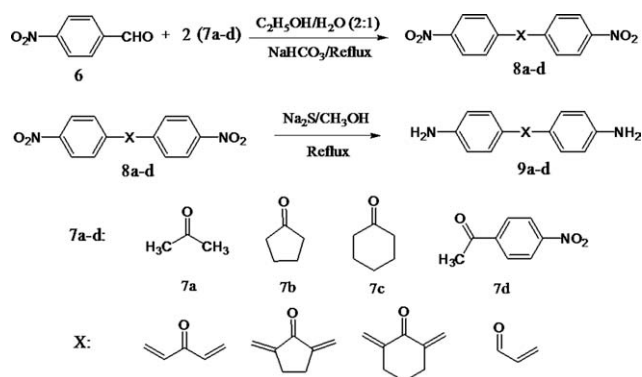
DMSO- $d_6$ , TMS):  $\delta$ : 7.47 (s, 2H), 7.27 (s, 4H), 6.61 (s, 4H), 5.95 (s, br, 4H), 2.82 (s, 4H), 1.70 (s, 2H) ppm.  $^{13}\text{C}$ -NMR (300 MHz, DMSO- $d_6$ ):  $\delta$ : 188.39, 149.91, 136.85, 132.93, 131.61, 123.77, 114.24, 28.67, 23.16 ppm. Elemental analysis: calculated for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$ : C, 78.92; H, 6.62; N, 9.20; found: C, 78.56; H, 6.61; N, 9.16.

### Polymer synthesis

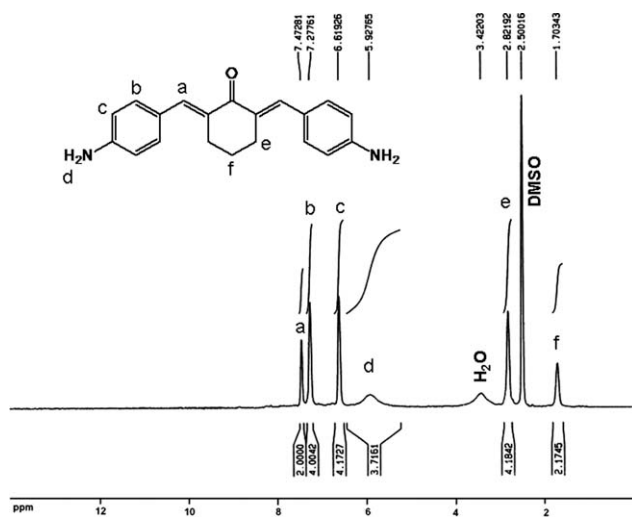
Polyamides **10a–d** were synthesized by two different methods that as an example the preparation of PA **10a** explains in the following. PA **10a** was prepared from the reaction of 4,4'-bis(1,2-diphenoxyethane) diacrylic acid **5** with 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **9a** by two different methods.

**Method A:** Direct polycondensation in a medium consisting of N-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride ( $\text{CaCl}_2$ )/pyridine (Py)

Totally, 0.23 g (0.662 mmol) dicarboxylic acid **5**, 0.174 g (0.662 mmol) 1,5-bis(4-aminophenyl)penta-



**Scheme 2** Synthesis of diamines **9a–d**.



**Figure 5**  $^1\text{H}$ -NMR spectrum of diamine **9c**.

1,4-dien-3-one **9a**, 0.1 g (0.9 mmol) calcium chloride, 0.84 mL (3.00 mmol) triphenyl phosphite, 0.1 mL of pyridine and 2 mL N-methyl-2-pyrrolidone (NMP) were placed into a 25-mL round-bottomed flask, which was fitted with a stirring bar. The reaction mixture was heated under reflux on an oil bath at  $110^\circ\text{C}$  for 8 h. Then, the reaction mixture was poured into 50 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly with hot methanol and dried at  $60^\circ\text{C}$  for 12 h under vacuum to leave 0.341 g (92%) cream solid polymer **10a**.

**Method B:** Direct polycondensation in a tosyl chloride (TsCl)/pyridine (Py)/N,N-dimethylformamide (DMF) system

A solution of 0.1 mL pyridine, 0.078 g (0.411 mmol) TsCl after 30 min stirring at room temperature was treated with 0.1 mL (1.36 mmol) DMF for additional 30 min. The reaction mixture was added dropwise to a solution 0.048 g (0.137 mmol) of dicarboxylic acid **5** in 0.1 mL pyridine. The mixture was maintained at room temperature for 30 min, and then to this mixture, a solution 0.036 g (0.137 mmol) 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one **9a** in 0.4 mL of Pyridine was added dropwise and the whole solution was stirred at room temperature for 30 min and at  $100^\circ\text{C}$  for 2 h. As the reaction proceeded, the solution became viscous, then was precipitated in 30 mL of methanol and filtered off, dried under vacuum to leave 0.056 g (71%) brown solid polymer **10a**.<sup>5</sup>

**Polymer 10a**, FTIR(KBr): 3369 (m, br), 2945 (m, sh), 1697 (s, br), 1590 (m), 1518 (s), 1386 (m, sh), 1319 (m, sh), 1178 (m), 1105 (w), 979 (w), 835 (w)  $\text{cm}^{-1}$ .

**Polymer 10b**, FTIR(KBr): 3367 (m, br), 2922 (m, sh), 1690 (s), 1656 (s), 1589 (s), 1514 (s), 1380 (w, sh), 1356 (s), 1249 (m), 1172 (s), 985 (w), 727 (m), 590 (w)  $\text{cm}^{-1}$ .

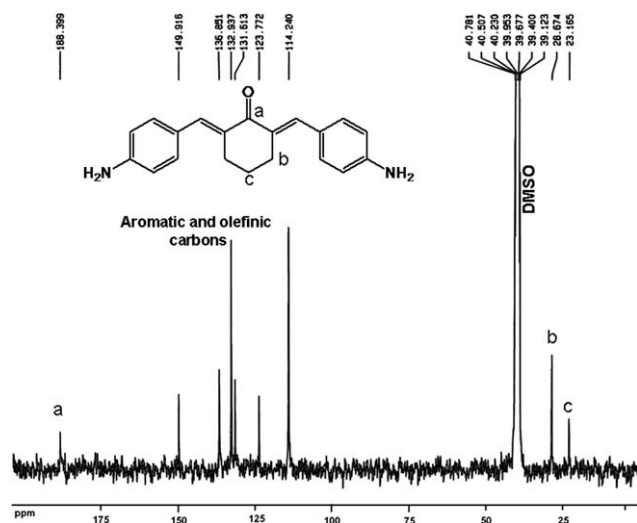


Figure 6  $^{13}\text{C}$ -NMR spectrum of diamine 9c.

**Polymer 10c**, FTIR(KBr): 3342 (m, br), 2966 (m), 1685 (s, br), 1671 (s), 1593 (s), 1516 (s), 1380 (s), 1350 (s), 1251 (s), 1170 (s), 1078 (m), 985 (m), 835 (m), 729 (m), 532 (m)  $\text{cm}^{-1}$ .

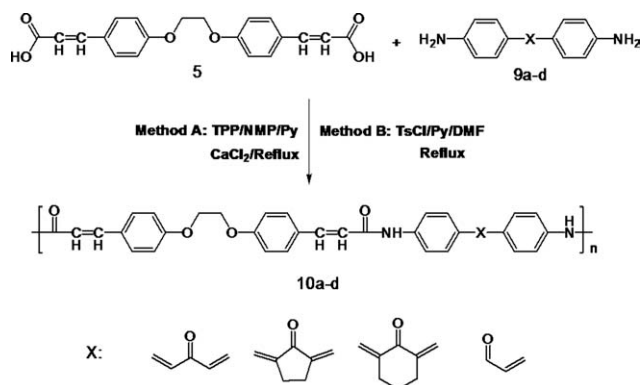
**Polymer 10d**, FTIR(KBr): 3327 (m, br), 2972 (m), 1688 (s), 1658 (s), 1593 (s), 1516 (s), 1383 (s), 1209 (s), 1074 (s), 937 (s), 765 (m), 727 (w), 690 (m), 509 (w)  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

### Monomer synthesis

Dicarboxylic acid **5** was synthesized by using two step reactions. At first 4,4'-bis(1,2-diphenoxyethane) dialdehyde **3** was prepared from the reaction of one equimolar 1,2-dibromoethane **1** and two equimolar 4-hydroxybenzaldehyde **2** in aqueous solution of sodium hydroxide. Then dialdehyde compound **3** was reacted with 2 equimolar of malonic acid **4** in a solvent free reaction and 4,4'-bis(1,2-diphenoxyethane) diacrylic acid **5** at presence of morpholine. Diacid **5** was synthesized by this method with good yield and facile condition (Scheme 1).

The chemical structure and purity of dialdehyde compound **3** were confirmed with elemental analysis,  $^1\text{H}$ -NMR and FTIR spectroscopy and dicarboxylic



Scheme 3 Synthesis of PAs 10a–d by two different methods.

acid compound **5** were proved with elemental analysis, FTIR,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR spectroscopy. The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

The  $^1\text{H}$ -NMR spectrum of 4,4'-bis(1,2-diphenoxyethane) dialdehyde **3** shows a singlet peak at 9.86ppm related to aldehyde protons and peaks at 7.41–7.16 ppm and 7.84–7.87 ppm ( $J = 8.5$  Hz) were assigned to H(b) and H(c) related to aromatic protons (Fig. 1).

The FTIR spectrum of dicarboxylic acid **5** shows a broad peak at 2400–3500  $\text{cm}^{-1}$ , which were assigned to the OH related to carboxylic acid groups in this compound and strong peak at 1689  $\text{cm}^{-1}$  related to carbonyl groups (Fig. 2). Also  $^1\text{H}$ -NMR spectrum of dicarboxylic acid **5** showed two peaks as a doublet of doublet at 7.01–7.03 ppm and 6.64–6.66 ( $J = 6$  Hz) were assigned to the H(b) and H(d) related to aromatic protons and two peaks as a doublet of doublet at 6.36–6.41ppm and 7.52–7.57 ppm ( $J = 15$  Hz) were assigned to the H(c) and H(e) related to olefinic protons. A broad singlet peak at 12.52 ppm related to carboxylic acid protons (Fig. 3). Also  $^{13}\text{C}$ -NMR spectrum of dicarboxylic acid **5** showed eight different carbon atoms (Fig. 4).

The aromatic diamines **9a–b** and **9d** are synthesized previously,<sup>6,18,19</sup> but diamine **9c** is a new

TABLE I  
Syntheses and Some Physical Properties of New PAs 10a–d by Methods A and B

Diamine	Polymer	Yield (%)		$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>		Color <sup>b</sup>	
		Method A	Method B	Method A	Method B	Method A	Method B
9a	10a	92	71	0.68	0.34	C	B
9b	10b	93	75	0.61	0.31	C	DR
9c	10c	90	78	0.79	0.44	PY	R
9d	10d	95	70	0.71	0.31	Y	B

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>b</sup> C, cream; B, brown; DR, dark red; PY, pale yellow; R, red; and Y, yellow.

TABLE II  
Number-Average and Weight-Average Molecular Weights of PAs 10a–d by Methods A and B

Diamine	Polymer	Method A			Method B		
		$\overline{M}_n$ ( $10^4$ ) <sup>a</sup>	$\overline{M}_w$ ( $10^4$ ) <sup>a</sup>	PDI <sup>b</sup>	$\overline{M}_n$ ( $10^4$ ) <sup>a</sup>	$\overline{M}_w$ ( $10^4$ ) <sup>a</sup>	PDI <sup>b</sup>
9a	10a	1.8	4.1	2.2	1.0	2.5	2.5
9b	10b	1.5	3.1	2.0	0.9	2.4	2.6
9c	10c	2.4	5.1	2.1	1.2	2.8	2.3
9d	10d	1.9	4.6	2.4	0.8	2.3	2.8

<sup>a</sup> Measured by GPC in DMAc, poly(vinylpyrrolidone) was used as standard.

<sup>b</sup> Poly dispersity index.

compound that is synthesized for this work. Diamines 9a–d were synthesized by using a two-step reaction. At first dinitro compounds 8a–d were prepared from the reaction of two equimolar 4-nitrobenzaldehyde 6 with one equimolar of compounds containing carbonyl group such as acetone 7a, cyclopentanone 7b, cyclohexanone 7c and 4-nitro acetophenone 7d in ethanol/water (2 : 1) and NaHCO<sub>3</sub>. Then dinitro compounds 8a–d were reduced by using Na<sub>2</sub>S (Scheme 2).

The chemical structure and purity of dinitro compounds 8a–d were proved with elemental analysis, <sup>1</sup>H-NMR and FTIR spectroscopy and diamine compounds 9a–d were proved with elemental analysis, FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy. The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

As an example, The FTIR spectrum of diamine 9c showed two peaks at 3348 and 3223 cm<sup>-1</sup>, which were assigned to the NH<sub>2</sub> groups. Also <sup>1</sup>H-NMR spectrum of diamine 9c showed two peaks at 7.27 ppm and 6.61 related to aromatic protons and a peak as a singlet at 7.47 ppm, which was assigned to the H(a) related to olefin protons. Also a singlet and broad peak at 5.92 ppm which was assigned to the H(d) protons of the NH<sub>2</sub> groups. Peaks at 2.82 and 1.70 ppm (as a singlet) which were assigned to the H(e) and H(f) protons of the methylene groups (Fig. 5). Also <sup>13</sup>C-NMR spectrum of diamine 9c showed nine different carbon atoms (Fig. 6).

TABLE III  
Elemental Analysis of PAs 10a–d

Polymer	Formula		C%	H%	N%
10a	C <sub>37</sub> H <sub>30</sub> N <sub>2</sub> O <sub>5</sub> (582.64) <sub>n</sub>	Calcd.	76.27	5.19	4.81
		Found	75.46	5.01	4.78
10b	C <sub>39</sub> H <sub>32</sub> N <sub>2</sub> O <sub>5</sub> (608.68) <sub>n</sub>	Calcd.	76.96	5.30	4.60
		Found	75.23	5.22	4.56
10c	C <sub>40</sub> H <sub>34</sub> N <sub>2</sub> O <sub>5</sub> (622.71) <sub>n</sub>	Calcd.	77.15	5.50	4.50
		Found	76.31	5.34	4.53
10d	C <sub>35</sub> H <sub>28</sub> N <sub>2</sub> O <sub>5</sub> (556.61) <sub>n</sub>	Calcd.	75.52	5.07	5.03
		Found	74.11	5.01	5.03

## Polymer syntheses

In this article, we synthesized organosoluble and thermally stable PAs 10a–d containing photosensitive group in the backbone by the direct polycondensation reactions of diacid 5 with four aromatic diamines 9a–d by two different methods such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl<sub>2</sub>)/pyridine (py) (method A, Scheme 3) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (py)/*N,N*-dimethylformamide (DMF) system (method B, Scheme 3).

In method A for direct polycondensation used TPP/Py/CaCl<sub>2</sub> as activating agent that was shown in Scheme 3. The entire polycondensation reaction readily proceeds in a homogeneous solution, tough, and stringy precipitates formed when the viscous PAs solution was obtained in good yields. Also the resulting polymers have a range of color between cream and yellow. In method B for the direct polycondensation of diacid 5 and aromatic diamine 9a–d, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polycondensation was carried out as the following way: TsCl was dissolved in Py and after a certain period of time (aging time), the solution was treated with DMF for 30 min. The reaction mixture was added to

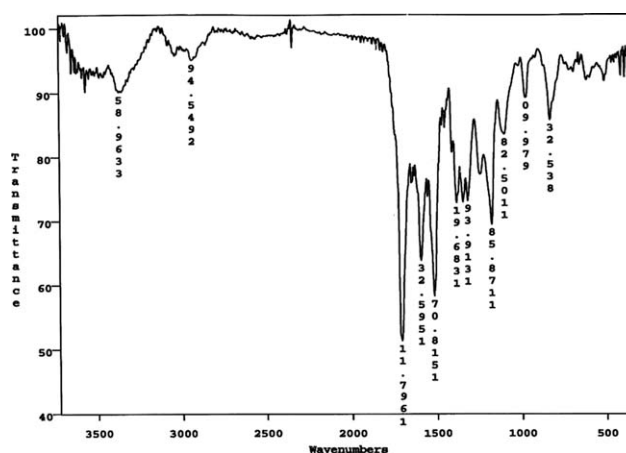


Figure 7 FTIR Spectrum of PA 10b.

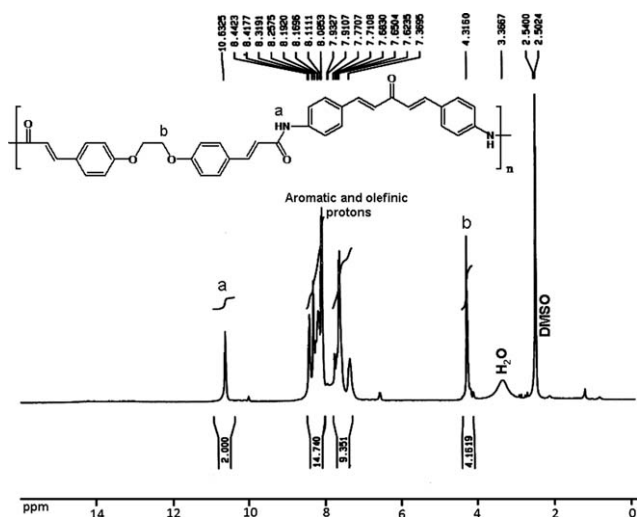


Figure 8  $^1\text{H-NMR}$  Spectrum of PA 10a.

a solution of diacid in Py. After 30 min, a solution of diamine in Py was added and the whole solution was maintained at room temperature, and then elevated temperature for 2 h. Less than this time, the polymers obtained will have lower inherent viscosities, and more than this time, the materials will be degraded. Also the resulting polymers have a range of color between red and brown. The syntheses and some physical properties of these new PAs 10a–d by methods A and B are given in Table I.

Also, these synthesized polymers exhibited number-average molecular weights ( $\overline{M}_n$ ) and weight-average molecular weights ( $\overline{M}_w$ ) in method A in the range of  $1.5\text{--}2.4 \times 10^4$  and  $3.1\text{--}5.1 \times 10^4$  and in method B in the range of  $0.8\text{--}1.2 \times 10^4$  and  $2.3\text{--}2.8 \times 10^4$ , respectively, as measured by GPC, relative to PVP (Poly(vinylpyrrolidone)) standards (Table II). Although PAs 10a–d obtained in a shorter period by method B, but these polymers obtained with higher inherent viscosities, good yields and higher weight-

average ( $\overline{M}_w$ ) and number-average ( $\overline{M}_n$ ) molecular weights by method A.

### Polymer characterization

The elemental analyses of the resulting PAs 10a–d were in good agreement with the calculated values for the proposed structure (Table III).

The structure of these polymers was confirmed as PAs by means of FTIR spectroscopy and elemental analyses. The representative FTIR spectrum of PA 10b was shown in Figure 7. The polymer exhibited characteristic absorption band at  $1697\text{ cm}^{-1}$  for the amide groups (C=O stretching vibration),  $1595\text{ cm}^{-1}$  (C=C stretching vibration). The absorption bands of amide groups appeared at  $3369\text{ cm}^{-1}$  (N–H stretching).

The  $^1\text{H-NMR}$  spectrum of PA 10a showed peaks that confirm its chemical structure that displays in Figure 8. The aromatic and olefin protons appeared in the region of 7.36–8.44 ppm. The protons related to methylene group appeared in the region of 4.31 ppm and the peak in the region of 10.63 ppm is assigned for N–H amide groups in the polymer backbone.

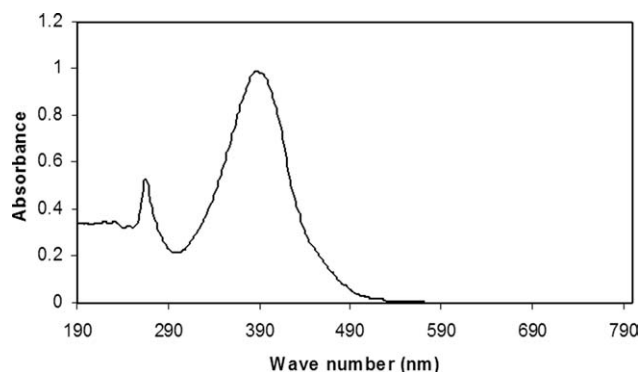
### Solubility of polymers

One of the main objectives of this study was producing modified polyamides with improved solubility. The incorporation of monomers with dibenzalacetone and chalcone moieties prevents an efficient molecular packing and restricts the formation of interchain hydrogen bonds, which are responsible of the PAs intractability. Also these polymers are expected to have higher solubility. The solubility of PAs 10a–d was investigated as 0.01 g of polymeric sample in 2 mL of solvent. Remarkably, all of these PAs were easily soluble at room temperature in

TABLE IV  
Solubility of PAs 10a–d

Solvent	10a	10b	10c	10d
H <sub>2</sub> SO <sub>4</sub>	++	++	++	++
DMAc	++	++	++	++
DMSO	++	++	++	++
DMF	++	++	++	++
NMP	++	++	++	++
THF	+	+	+	+
Pyridine	+	+	++	++
Cyclohexanone	+–	+–	+	+
CHCl <sub>3</sub>	–	–	–	–
Acetone	–	–	–	–
EtOH	–	–	–	–
MeOH	–	–	–	–
H <sub>2</sub> O	–	–	–	–

Solubility: ++: soluble at room temperature; +: soluble on heating at 70°C; +–: partially soluble on heating at 70°C; –: insoluble on heating.



**Figure 9** UV-vis absorption spectrum of PA **10c** in DMF solution.

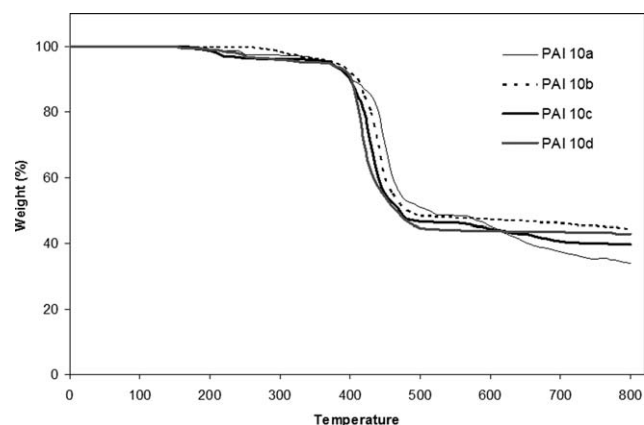
aprotic polar solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), soluble on heating at 70°C and partially soluble on heating at 70°C in tetrahydrofuran (THF), pyridine (Py), and cyclohexanone, and insoluble in solvents such as acetone, chloroform, ethanol, and methanol (Table IV).

#### UV-vis absorption characteristics

The photosensitive property of the new polyamides **10a–d** in the DMF solution was studied by a UV spectrophotometer. All polymer solutions exhibit two same positions of absorption maximum in UV-vis spectra around 270 nm and 375 nm. The UV-vis absorption spectrum of PA **10c** in *N,N*-dimethylformamide is shown in Figure 9. The spectrum of PA **10c** exhibited two typical peaks at 266.71 nm and 393.47 nm.

#### Thermal properties

TGA and derivative of thermogravimetric (DTG) analysis at a rate of 10°C/min in a nitrogen atmosphere were utilized to examine the thermal properties of these PAs, and the obtained results are sum-



**Figure 10** TGA curves of PAs **10a–d**.

**TABLE V**  
Thermal Behavior of PAs **10a–d**

Polymer	$T_g^a$	$T_5$ (°C) <sup>b</sup>	$T_{10}$ (°C) <sup>b</sup>	Char yield <sup>c</sup>
<b>10a</b>	205	370	400	34.1
<b>10b</b>	210	380	410	44.4
<b>10c</b>	210	375	400	39.7
<b>10d</b>	190	370	405	42.9

<sup>a</sup> Glass transition temperature was recorded at a heating rate of 10°C/min in a nitrogen atmosphere.

<sup>b</sup> Temperature at which 5 or 10% weight loss was recorded by TGA at a heating rate of 10°C/min under N<sub>2</sub>.

<sup>c</sup> Weight percentage of material left after TGA analysis at a maximum temperature of 800°C under N<sub>2</sub>.

marized in Table IV. Figure 10 shows TGA results of PAs **10a–d**, respectively.

The thermal stability of the polymers was studied on the basis of 5 and 10% weight losses ( $T_5$  and  $T_{10}$ , respectively) of the polymers and the residue at 800°C (char yield). The results revealed that the PAs were thermally stable up to 370°C. TGA data showed that the resulting polymers were good thermally stable. Also the DSC analyses for these synthesized PAs showed  $T_g$  around 190–210°C (Table V). Polyamide **10a** has the lowest char yield in comparison other polymers. This low char yield can be due to presence of acetone moiety in structure of polymer **10a**.

#### CONCLUSIONS

In this article, we have successfully synthesized 4,4'-bis(1,2-diphenoxyethane) diacrylic acid, containing ether linkages and olefinic groups, and also aromatic diamines **9a–d** containing photosensitive group. A series of new organosoluble and thermally stable PAs **10a–d** with good inherent viscosity were prepared by the direct polycondensation from dicarboxylic acid **5** with various aromatic diamines **9a–d** by two different methods. The results presented herein also clearly demonstrate that incorporating the aromatic structure in the backbone of polymer and several functional groups remarkably enhanced the thermal stability of the new polymers. Because of presence dibenzalacetone moiety and ether group in polymer backbone, these PAs had good solubility in organic solvents. These properties could make these PAs attractive for practical applications such as processable high-performance engineering plastics.

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