

# Synthesis of Novel Photoactive Heterocyclic Polyimides Containing Naphthalene Moieties via Cycloaddition Reactions

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**ABSTRACT:** 1-Naphthylacetic acid (**1**) was reacted with thionyl chloride and 1-naphthylacetyl chloride (**2**) was obtained in a quantitative yield. The reaction of this acid chloride (**2**) with isoeugenol (**3**) was performed in chloroform and a novel isoeugenol ester derivative (**4**) as a monomer was obtained in a high yield. The compound (**4**) was characterized by <sup>1</sup>H-NMR, IR, mass, and elemental analyses and then was used for the preparation of a model compound (**6**) and polymerization reactions. 4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD) (**5**) was allowed to react with compound (**4**). The reaction is very fast and gives only one double adduct (**6**) via Diels–Alder and ene pathways in an excellent yield. The polymerization reactions of the novel monomer (**4**) with bistriazolinediones [bis-(*p*-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)methane (**7**) and 1,6-bis-(3,5-dioxo-1,2,4-triazolin-4-yl)hexane] (**8**) were carried out in *N,N*-dimethylacetamide (DMAc) at room temperature. The reactions are exothermic and fast and gave novel heterocyclic polyimides containing a naphthalenic pendant group (**9**) and (**10**) via repetitive Diels–Alder-ene polyaddition reactions. Stereochemical analysis of the model compound and fluorimetric studies of the model compound as well as polymers were done conclusively. Excimer formation of the polymers and its effect on fluorescence emission were investigated and some structural characterization and physical properties of these novel heterocyclic polyimides are reported. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 527–536, 2000

**Key words:** 1-naphthylacetyl chloride; Diels–Alder-ene polymerization; 4-phenyl-1,2,4-triazoline-3,5-diones; bistriazolinediones; inherent viscosity; photoactive polymers

## INTRODUCTION

Most fluorescent polymers obtained by polymerization are essentially the copolymers of low mo-

lecular weight luminophores, containing vinyl groups, and conventional unsaturated compounds. The derivatives of naphthalene, anthracene, pyrene, other condensed aromatic hydrocarbons, and some heteroaromatic hydrocarbons such as carbazole and pyrazoline are more considerable in the preparation of photoluminescence polymers. These polymers have been widely used in several industries. Some of their applications are as (i) ionizing radiation recording materials, (ii) luminescent solar concentrators, (iii) materials for lasers, (iv) materials for the paints

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and varnish industries, (v) luminescent photolayers, and (vi) luminescent probes in fiber-optic sensors.<sup>1</sup> In the course of our study, polymers bearing naphthalene groups are considered, and several research investigations on fluorimetric studies of polymer-bearing naphthalene groups already exist.<sup>2–8</sup>

In previous articles, we introduced a new polymerization technique via Diels–Alder-ene cycloaddition reactions.<sup>9–12</sup> In this article, we wish to report the synthesis of novel photoactive and moderately thermally stable polymers with a fluorescent property containing a naphthalenic pendant group.

## EXPERIMENTAL

### Materials

Reagents were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Dorset, England), and Riedel-deHaen AG (Seelze, Germany). 4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD) (**5**) and bis-triazolinediones (**7**) and (**8**) were prepared according to published procedures.<sup>12–14</sup> *N,N*-Dimethylacetamide (DMAc) was dried over BaO, then distilled under reduced pressure. Chloroform was dried over CaCl<sub>2</sub>, then distilled at normal pressure.

### Techniques

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) 90-MHz spectra were recorded on a Varian EM-390 and a 500-MHz spectrum on a Bruker Advance 500. Multiplicities of proton resonances are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublet (dd), and broad (br). Tetramethylsilane (TMS) was used as an internal reference.

IR spectra were recorded on a Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumbers (cm<sup>-1</sup>). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk routine viscometer. Specific rotations were measured by a Perkin–Elmer-241 polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 System under a N<sub>2</sub> atmosphere

at a rate of 10°C/min. The fluorescence spectra were recorded on Shimadzu RF-5000 spectrofluorophotometer. Elemental analysis were performed by the Research Institute of Petroleum Industry, Tehran, I.R. Iran.

### Preparation of 1-Naphthylacetyl Chloride (2)

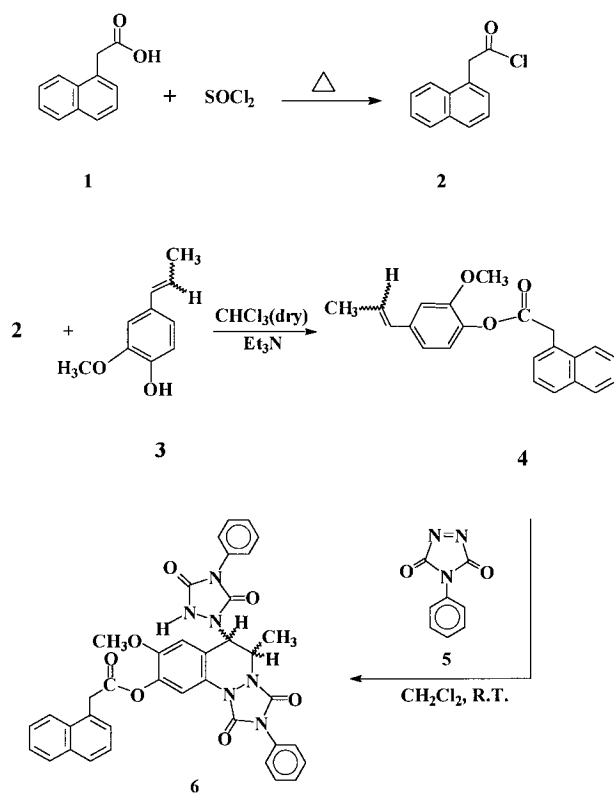
1-Naphthylacetic acid (**1**), 0.50 g ( $2.69 \times 10^{-3}$  mol), was placed into a 25-mL round-bottomed flask equipped with a condenser and 3.0 mL ( $4.11 \times 10^{-2}$  mol) of freshly distilled thionyl chloride (excess amount) was added. The mixture was heated on a waterbath up to 50°C, until the suspension mixture was converted to a clear solution. After dissolution was completed, the solution was stirred for 1 h. The thionyl chloride was removed under reduced pressure, to leave 0.55 g (100.0%) viscous liquid.

IR(KBr): 3050 (w), 2900 (m), 1800–1780 (s), 1600 (m), 1510 (m), 1390 (m), 1310 (w), 1260 (m), 1210 (w), 1190 (w), 1160 (w), 1080 (w), 1050 (m), 1020 (s), 950 (s), 860 (w), 810 (sh), 780 (s), 750 (m), 730 (sh), 690 (m), 610 (sh), 580 (m) cm<sup>-1</sup>.

### Preparation of [2-Methoxy-4-(1-propenyl)phenyl]1-naphthylacetate (4) (Monomer)

Isoeugenol (**3**), 0.40 g ( $2.46 \times 10^{-3}$  mol), and dry chloroform, 3.0 mL, were placed into a two-necked round-bottomed flask and a solution of 0.42 g ( $2.05 \times 10^{-3}$  mol) of (**2**) in 3.0 mL of dry chloroform was added dropwise at 0°C in a period of 30 min. At the end of the addition, the reaction mixture was stirred at 0°C for 1 h and then 1.0 mL ( $7.17 \times 10^{-3}$  mol) of triethylamine in 2.0 mL of dry chloroform was added at 0°C in a period of 30 min. The reaction was stirred at room temperature for 20.0 h. Finally, it was refluxed for 4.0 h. After addition of 20 mL of chloroform to the reaction mixture, extraction was done according to the following manner: (i) 2 × 10 mL distilled water (ii) 6 × 20 mL of 1% KOH solution (w/v), and (iii) washing of the organic phase with distilled water until the extracted aqueous phase becomes neutral. The organic phase was dried over sodium sulfate and chloroform was evaporated with a rotary evaporator. Recrystallization from carbon tetrachloride gave 0.52 g (76.5%) of white crystals, mp 83–85°C.

IR (KBr): 3050 (w), 3000 (w), 2950–2900 (w), 2870 (w), 2850 (w), 1750 (s), 1600 (m), 1520 (s), 1460–1400 (m, br), 1390 (sh), 1370 (w), 1350 (w), 1330 (sh), 1300 (m), 1270 (m), 1250 (m), 1200 (s), 1150 (m), 1110 (s), 1030 (m), 980 (m), 970 (sh), 900 (m), 870 (m), 840 (w),



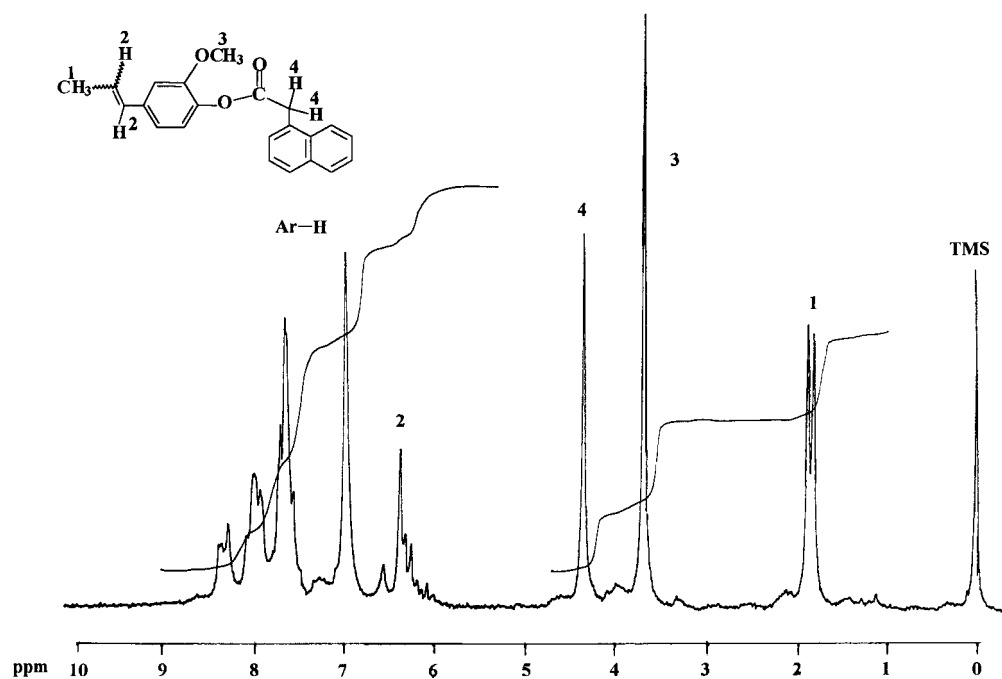
780 (s), 760 (m), 740 (w), 720 (sh)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS, 90 MHz):  $\delta$  1.7–1.9 (d, 3H); 3.6–3.8 (s, 3H); 4.4–4.6 (s, 2H); 6.0–6.4 (m, 2H); 6.8–7.0 (s, 3H); 7.4–8.4 (m, 7H).

ANAL. Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_3$ : C, 79.49%; H, 6.07%. Found: C, 78.80%; H, 6.10%.

#### Preparation of Model Compound (6)

A solution of 0.22 g ( $6.47 \times 10^{-4}$  mol) of (4) in 2 mL of methylene chloride was placed into a 25 mL round-bottomed flask and 0.23 g ( $1.29 \times 10^{-3}$  mol) of PhTD (5) in 10 mL of methylene chloride was added dropwise at room temperature. As the solution of PhTD was added, the red solution quickly decolorized. The reaction mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure and the residue was dried to give 0.45 g (100.0%) of a white solid. Recrystallization from acetic acid and water gave white crystals, with a decomposition temperature of 125°C.

IR (KBr): 3500–3300 (w, br), 3100 (sh), 3000 (m), 2900 (sh), 1740 (s), 1720–1670 (s, br), 1580 (m), 1490 (s), 1430–1380 (s, br), 1300 (m), 1260 (m), 1220 (m), 1160 (w), 1150 (sh), 1000 (s), 1030 (m), 1010 (m), 900 (m), 860 (m), 780 (s), 750 (s), 710 (sh), 680 (m)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$  TMS, 500 MHz):  $\delta$  1.22–1.24 (d, 3H,  $J = 6.76$  Hz); 3.71 (s, 3H); 4.49 (s, 2H), 4.82–4.86 (doublet of quartet, 1H,  $J = 6.76, 1.56$  Hz); 5.43 (d, 1H,  $J = 1.56$  Hz); 7.14 (s, 1H); 7.40–7.61 (m, 14H); 7.88–8.08 (m, 3H).



**Figure 1**  $^1\text{H-NMR}$  (90 MHz) spectrum of compound (4) in  $\text{CCl}_4$  at RT.

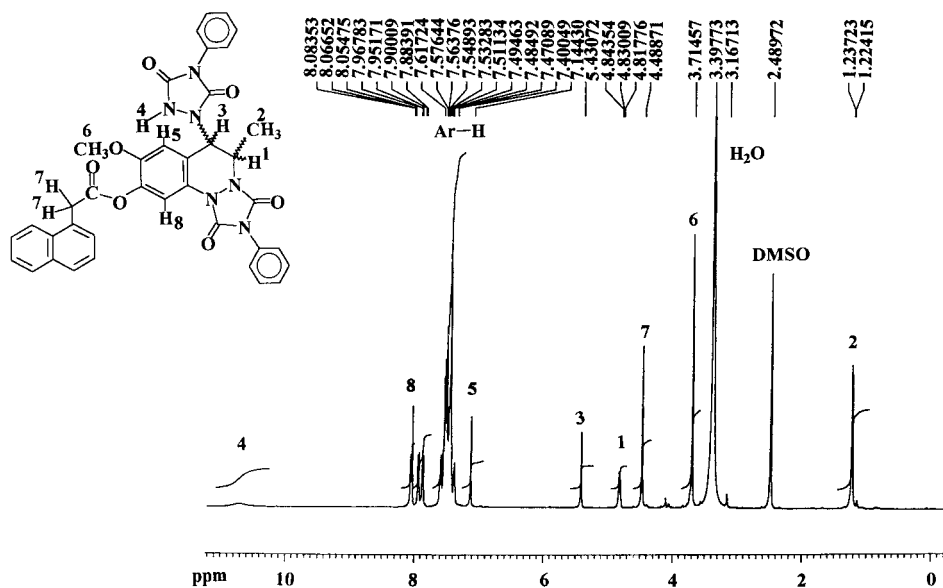


Figure 2  $^1\text{H-NMR}$  (500 MHz) spectrum of compound (6) in  $\text{DMSO-}d_6$  at RT.

ANAL. Calcd for  $\text{C}_{38}\text{H}_{30}\text{N}_6\text{O}_7$ : C, 66.85%; H, 4.43%; N, 12.31%. Found: C, 66.80%; H, 4.40%; N, 12.00%.

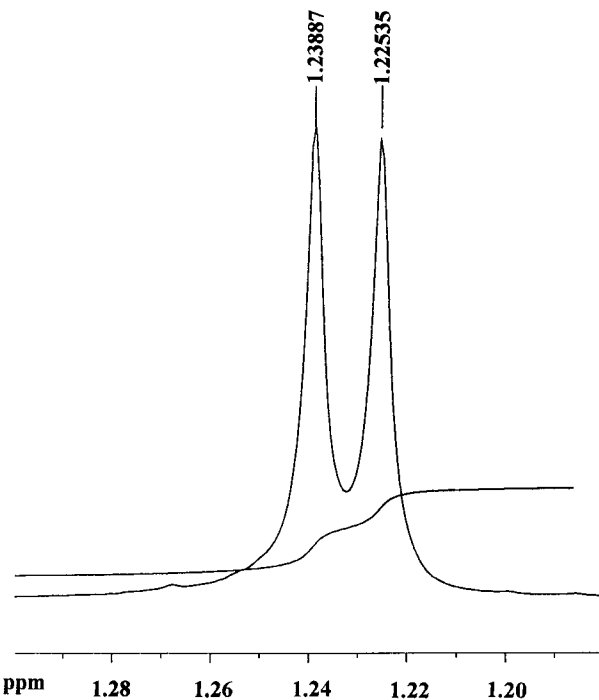


Figure 3  $^1\text{H-NMR}$  (500 MHz) spectrum of compound (6) in  $\text{DMSO-}d_6$  at RT. Expanded region for the proton #2.

#### Polymerization of Bis(*p*-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (7) with (4)

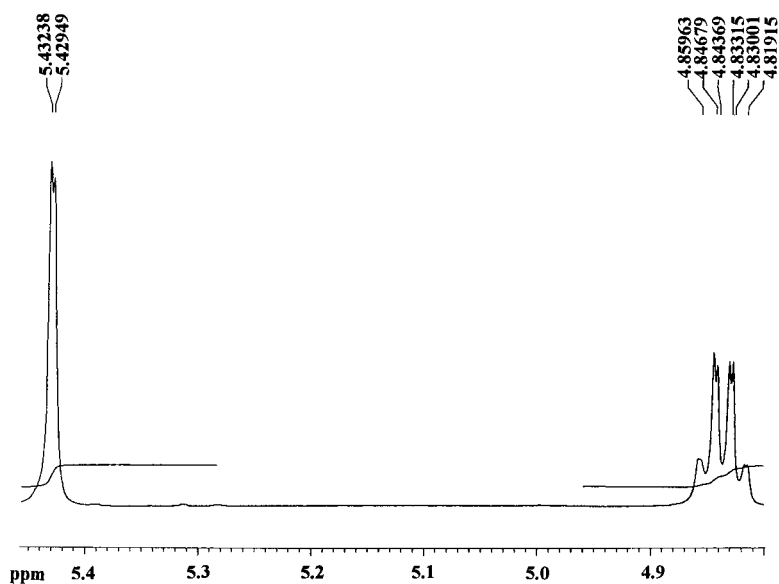
Into a 25-mL round-bottomed flask, 0.11 g ( $3.28 \times 10^{-4}$  mol) of (4) and 0.12 g ( $3.28 \times 10^{-4}$  mol) of bis-(*p*-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (BPMTD) (7) were mixed and 0.5 mL of dry DMAc was added. After about 10 min, the two monomers were dissolved and the red color of BPMTD was faded completely. The solution became pale orange and viscous and was stirred at room temperature for 20 h. The resulting viscous solution was precipitated in 50 mL of distilled water. The yellow precipitates were filtered and dried to leave 0.22 g (96.6%) of a yellow solid.  $[\eta]_{\text{inh}}^{25} = 0.27 \text{ dL g}^{-1}$  (0.51 g/dL in DMF).

IR(KBr): 3500–3400 (w, br), 3050–2850 (w, br), 1760 (m), 1710–1690 (s, br), 1620–1600 (m, br), 1510 (s), 1410–1390 (s, br), 1310 (w), 1260 (m), 1250–1230 (m, br), 1170 (w), 1120–1100 (m, br), 1040 (m), 1020 (m), 900 (w), 880 (w), 850 (w), 780 (m)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , TMS, 90 MHz):  $\delta$  1.1–1.3 (d, br); 3.5–3.8 (s, br); 4.0–4.2 (s, br); 4.3–4.5 (s, br); 4.6–5.0 (m, br); 5.4–5.5 (br); 6.9–7.8 (m, br); 7.9–8.2 (m, br); 10.5–11.0 (br).

ANAL. Calcd for  $\text{C}_{39}\text{H}_{30}\text{N}_6\text{O}_7$  as repeating unit: C, 67.43%; H, 4.35%; N, 12.10%. Found: C, 65.50%; H, 4.70%; N, 11.30%.

#### Polymerization of 1,6-Bis-(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (8) with (4)

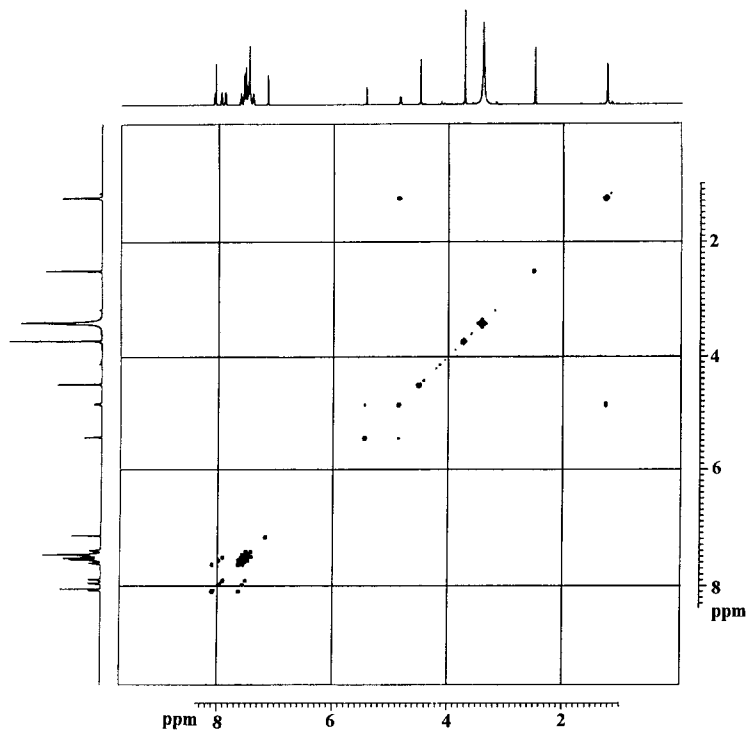
Into a 25-mL round-bottomed flask, 0.11 g ( $3.27 \times 10^{-4}$  mol) of (4) and 0.09 g ( $3.27 \times 10^{-4}$  mol) of



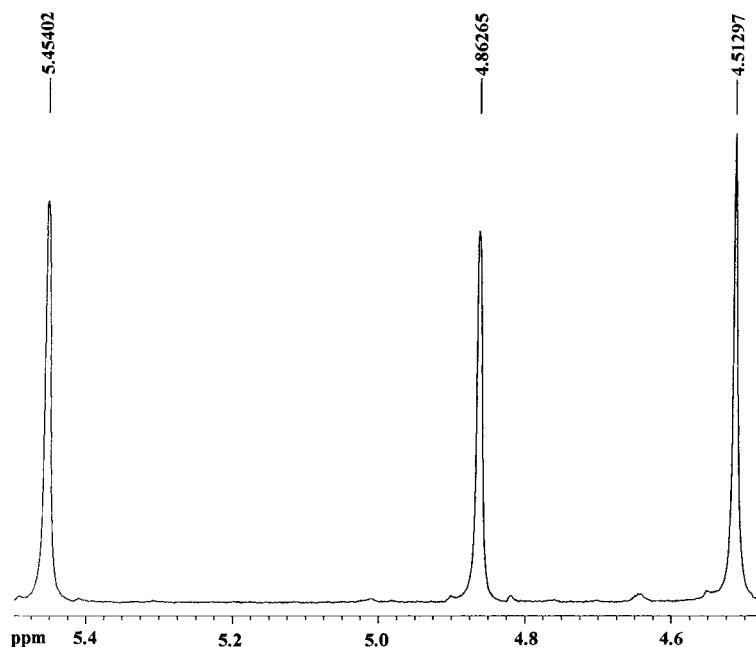
**Figure 4**  $^1\text{H-NMR}$  (500 MHz) spectrum of compound (**6**) in  $\text{DMSO-}d_6$  at RT. Expanded region for protons #1 and 3.

1,6-*bis*-(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (HMTD) (**8**) were mixed and 0.4 mL of dry DMAc was added. In about 15 min, the two monomers were dissolved and the pink color of HMTD was

faded completely. The solution became viscous and was stirred at room temperature for 20 h. The resulting polymer was precipitated in 50 mL of distilled water. The white precipitate was filtered



**Figure 5** Two-dimensional  $^1\text{H-NMR}$  (500 MHz) spectrum of compound (**6**) in  $\text{DMSO-}d_6$  at RT.



**Figure 6** Decoupled  $^1\text{H-NMR}$  (500 MHz) spectrum of compound (**6**) in  $\text{DMSO-}d_6$  at RT. Expanded region for the protons #7, 1, and 3 after decoupling of proton #2.

and dried to give 0.19 g (94.8%) of a white solid.  $[\eta]_{\text{inh.}}^{25} = 0.21 \text{ dL g}^{-1}$  (0.57 g/dL in DMF).

IR(KBr): 3500–3400 (w, br), 3200–3050 (w, br), 2900 (m), 2850 (w), 1760 (s), 1710–1680 (s, br), 1620 (sh), 1510 (s), 1450 (s), 1420 (s), 1370–1350 (w, br), 1310 (w), 1250–1240 (m, br), 1180–1160 (w, br), 1110 (m), 1010 (w), 900 (w), 870 (w), 850 (w), 780 (m), 730 (sh)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , TMS, 90 MHz):  $\delta$  1.0–1.8 (m, br); 3.1–3.7 (m, br); 4.2–4.5 (s, br); 4.5–4.8 (m, br); 5.1–5.3 (br); 6.9–7.0 (s, br); 7.3–7.6 (br); 7.7–8.2 (m, br); 10.0–10.3 (br).

ANAL. Calcd for  $\text{C}_{32}\text{H}_{32}\text{N}_6\text{O}_7$ : C, 62.73%; H, 5.27%; N, 13.72%. Found: C, 62.80%; H, 5.50%; N, 13.30%.

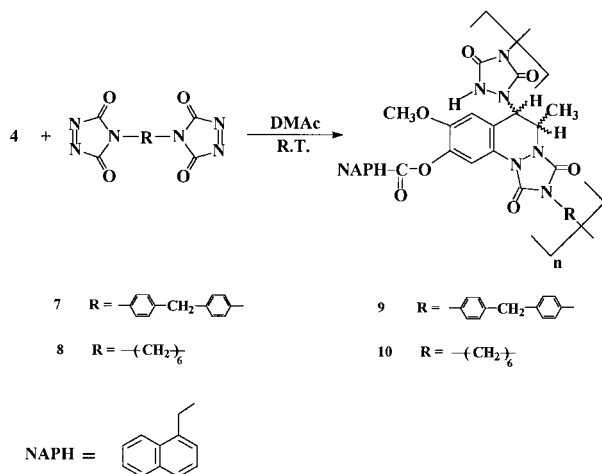
**Table I** Solubility of Polymers (**9**) and (**10**)

Solvent	Polymer ( <b>9</b> )	Polymer ( <b>10</b> )
$\text{H}_2\text{SO}_4$	+	+
Acetic acid	–	+ <sup>a</sup>
DMSO	+	+
DMF	+	+
$\text{H}_2\text{O}$	–	–
Methanol	–	–
Ethanol	–	–
Acetone	–	–
$\text{CHCl}_3$	+	–
$\text{CH}_2\text{Cl}_2$	+	–
THF	+	–
Diethyl ether	–	–
$\text{CCl}_4$	–	–
Toluene	–	–
Cyclohexane	–	–
n-Hexane	–	–

The above polymers which were not soluble, kept at room temperature for 15 h and also heated at boiling point of water, but still were not dissolved.

+ : Soluble at room temperature; – : insoluble.

<sup>a</sup> After swelling in the solvent for 15 h at room temperature.



**Scheme 2**

**Table II** Reaction Conditions and Some Physical Properties for Polymers (9) and (10)

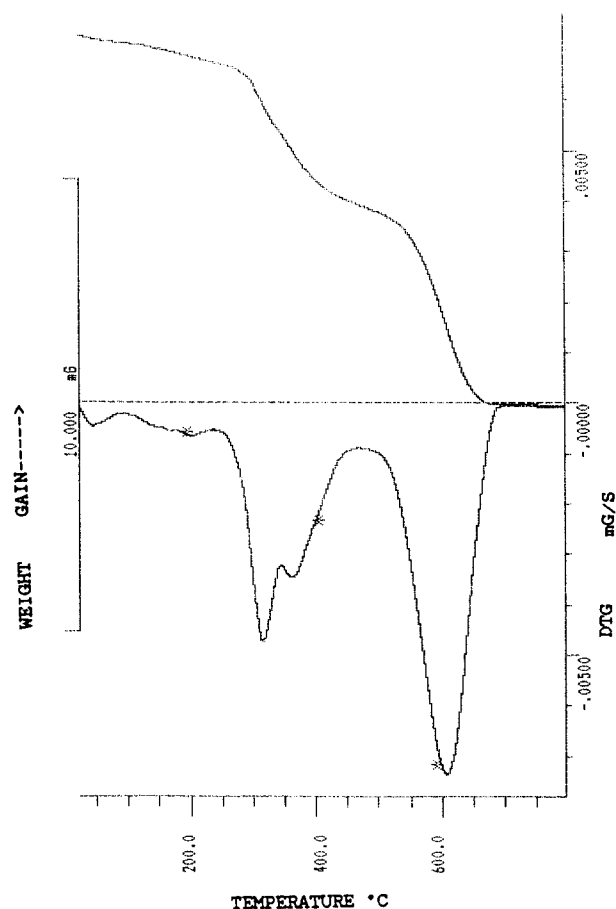
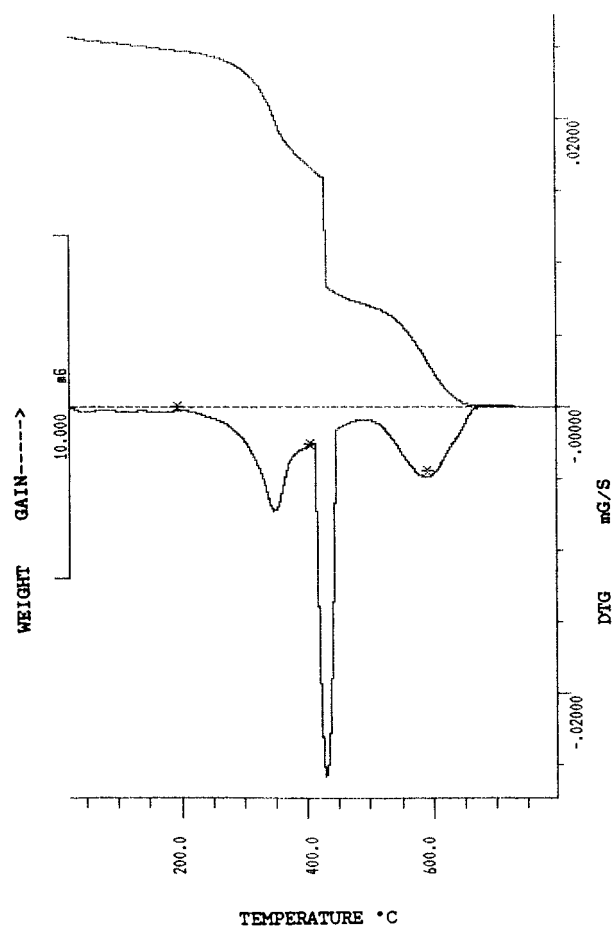
Polymer	(9)	(10)
Reaction solvent	DMAc	DMAc
Fading time <sup>a</sup>	10 min	15 min
Nonsolvent	Water	Water
Yield %	96.6	94.8
$T_w^b$	233°C	225°C
$[\eta]_{inh.}^{25}$ (dL g <sup>-1</sup> )	0.27 <sup>c</sup>	0.21 <sup>d</sup>

<sup>a</sup> Time for disappearance of triazoline diones colors.<sup>b</sup> Temperature for 5% weight loss.<sup>c</sup> Measured at a concentration of 0.51 g/dL in DMF at 25°C.<sup>d</sup> Measured at a concentration of 0.57 g/dL in DMF at 25°C.

## RESULTS AND DISCUSSION

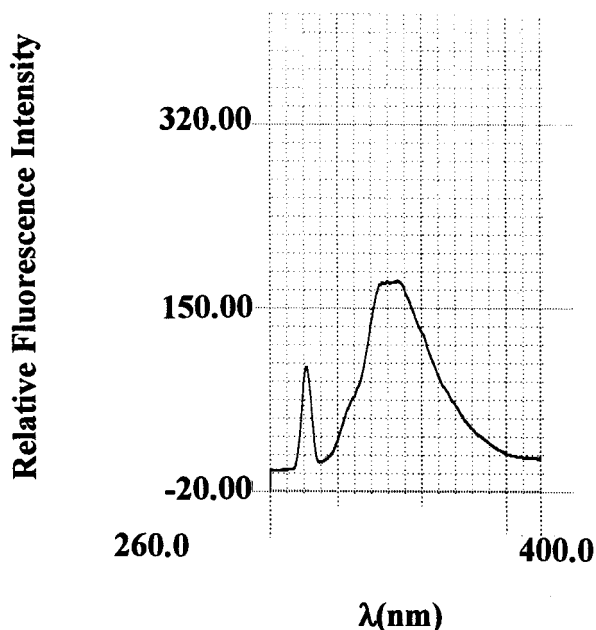
### Model Compound Studies

In previous articles, we reported the preparation of novel optically active<sup>9,10</sup> and also flame-retar-

**Figure 7** TGA and DTG thermograms of polymer (9).**Figure 8** TGA and DTG thermogram of polymer (10).

dant<sup>11</sup> polymers via tandem Diels–Alder-ene polymerization reactions. We also proposed a reasonable mechanism for these types of reactions. The monomer (4) containing a photoactive naphthalene pendant group was synthesized from the reaction of acid chloride (2) with isoeugenol (3) (Scheme 1). The structure of monomer (4) was characterized by <sup>1</sup>H-NMR (Fig. 1), IR, and elemental analysis.

The monomer (4) was reacted with two mol of PhTD (5) in a methylene chloride solution at room temperature. The reaction is very fast and gave only one adduct via Diels–Alder-ene reactions (Scheme 1). The molecular structure of (6) was studied by high-field <sup>1</sup>H-NMR spectroscopy (Fig. 2). As shown in Figure 3, the methyl group [CH<sub>3</sub>(2)] appeared as a doublet according to its coupling with H(1). Also, in Figure 4, an expanded region for H(1) and H(3) are shown. H(1) was coupled with [CH<sub>3</sub>(2)] with  $J = 6.76$  Hz and weakly coupled with H(3) with  $J = 1.56$  Hz. This



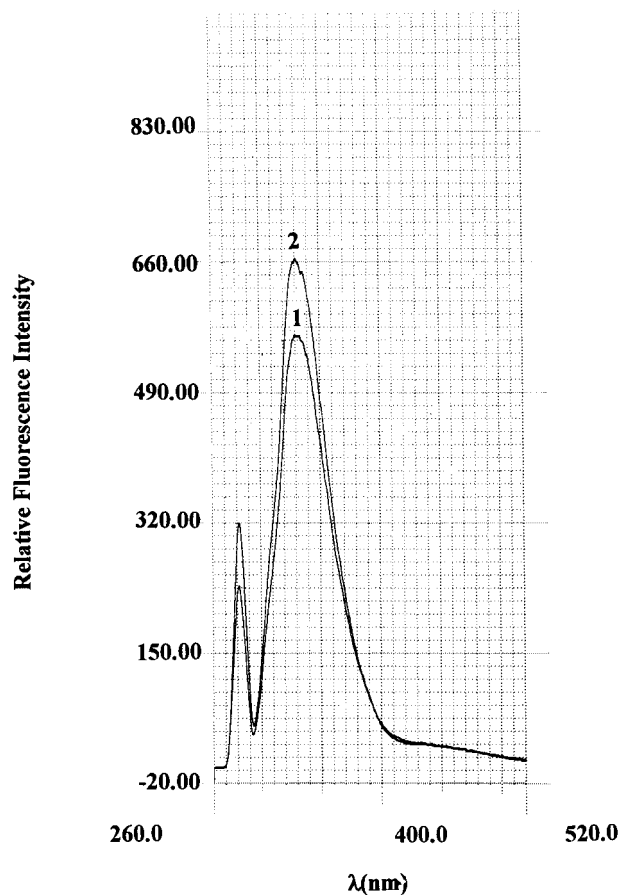
**Figure 9** Fluorescence spectrum of polymer (9) in DMF ( $9.1 \times 10^{-9}$  M),  $\lambda_{\text{ex}} = 283.2$  nm at RT.

weak coupling is in regard to the *cis* conformation of H(1) and H(3) with a dihedral angle of near  $90^\circ$ . This is also observable for H(3) in the region of 5.429–5.432 ppm, which has appeared as a doublet with  $J = 1.56$  Hz. However, its COSY (Fig. 5) and decoupled spectra (Fig. 6) confirm the correlation between H(1) and H(3). In Figure 6, the proton at 1.25 ppm ( $[\text{CH}_3(2)]$ ) was decoupled and its coupling with H(1) was excluded. So, the proton H(1) appeared as a singlet. This spectral evidence revealed that the model compound (6) exists as a pair of an enantiomeric form of four possible diastereomers. Also, the model compound (6) solution in DMF does not show any optical rotation, which confirms the results obtained by the above  $^1\text{H-NMR}$  studies. The compound (6) was used as a model compound for the polymerization reaction.

### Polymerization Reactions

Two bistriazolinediones, BPMTD (7) and HMTD (8), were selected as bisdienophiles for the polymerization reactions. Thus, the reaction of BPMTD (7) with monomer (4) was carried out in a DMAc solution at room temperature (Scheme 2). The polymerization reaction is very fast and the resulting polymer (9) was obtained as a pale yellow solid. The structure of polymer (9) was char-

acterized by IR and  $^1\text{H-NMR}$  spectra, which are in agreement with structure (9). Although the  $^1\text{H-NMR}$  spectrum of the polymer is broad, it resembles the spectrum of the model compound (6). The elemental analysis of the polymer (9) also confirms this structure. Polymer (9) is soluble in polar solvents such as DMAc,  $\text{H}_2\text{SO}_4$ , DMF, and DMSO and is insoluble in solvents such as methanol, ethanol, diethyl ether, *n*-hexane, and water. The reaction of other bistriazolinedione HMTD (8) with monomer (4) was also performed in a DMAc solution at room temperature. The resulting polymer (10) was obtained as a white solid. The IR and  $^1\text{H-NMR}$  spectra of polymer (10) resemble those of the model compound (6); therefore, structure (10) was assigned to it (Scheme 2). The solubility characteristics of polymer (9) and polymer (10) are listed in Table I. The reaction conditions and some physical properties for these novel photoactive polymers are summarized in Table II.



**Figure 10** Fluorescence spectra of polymer (10) in DMF,  $\lambda_{\text{ex}} = 283.2$  nm at RT. **1** at  $C = 9.1 \times 10^{-8}$  M and **2** at  $C = 9.1 \times 10^{-9}$  M.

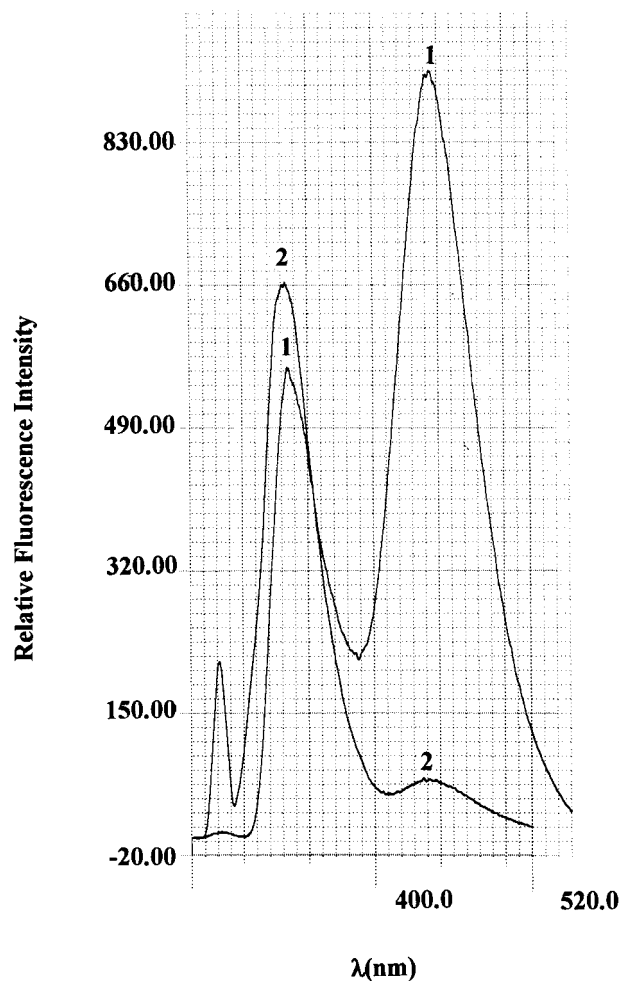


### Thermal Properties

Thermal gravimetric analysis (TGA) of polymers (9) and (10) show that they are moderately thermally stable. For polymer (9), the TGA thermogram (Fig. 7) reveals a 5% weight loss at 233°C and the residual weight percent at 500°C is 66.4%. There are two domains of weight loss according to the DTG thermogram. The first begins at 98°C and ends at 469°C. The peak temperature during this weight loss is at 315°C. The second one begins at 469°C and ends at 692°C. The peak temperature during this weight loss is at 608°C. For polymer (10), the TGA thermogram (Fig. 8) shows a 5% weight loss at 225°C and the residual weight percent at 500°C is 17.6%. Here, three main weight-loss domains are observed according to the DTG thermogram. For the first one, the starting temperature is 28.7°C, the end temperature is 414°C, and the peak temperature is 348°C. The second starts at 414°C and ends at 487°C. The peak temperature is 428°C. The last main weight loss starts at 487°C and ends at 674°C and the peak temperature is 590°C.

### Fluorimetric Studies

According to the UV-vis spectra of polymers (9, 10) in DMF, the  $\lambda_{\text{max}}$  at 283.2 nm was chosen, in which the maximum absorption was observed. The solutions were excited at this wavelength that is in the region of excitation for the naphthalenic moiety. This naphthyl pendant group is responsible for the luminophore properties of the resulting polymers. For polymer (9), at very low concentrations (up to  $9.1 \times 10^{-8}$  molar) with  $\lambda_{\text{ex}} = 283.2$  nm, only fluorescence emission at 336.0 nm ( $\lambda_{\text{em}} = 336.0$  nm) was observed (Fig. 9). For polymer (10), the above results were also obtained (Fig. 10). For instance, when the concentration of the polymer (9) solution increases (above  $9.1 \times 10^{-7}$  molar), another fluorescence emission at 443.2 nm appeared (Fig. 11). However, the emission at 443.2 nm and  $1 \times 10^{-3}$  molar concentration becomes the predominant emission in comparison to 336.0 nm emission (Fig. 11). This interesting behavior of the polymer solution and appearance of an extra emission is related to the excimer formation of naphthalenic pendant groups in the polymer main chain, which has been reported earlier.<sup>1,3</sup> It has been proved that polymers show normal fluorescence at a shorter wavelength and a broad excimer emission band lying at longer wavelengths.<sup>15</sup> Also, the intensity



**Figure 11** Fluorescence spectra of polymer (9) in DMF,  $\lambda_{\text{ex}} = 283.2$  nm at RT. 1 at  $C = 9.1 \times 10^{-3}$  M and 2 at  $C = 9.1 \times 10^{-7}$  M.

ratio of these bands is dependent on the concentration of solution. It is noteworthy that the polymer film exhibits only excimer fluorescence. So, according to the above discussion, the exceeding of the excimer emission intensity to the normal fluorescence emission of polymer (9) solution at  $1 \times 10^{-3}$  molar concentration is conceivable. The high tendency of the polymer chain to align these naphthalenic pendant groups comes back to the presence of rigid biphenyl methane group in the polymer backbone. This is responsible for the predomination of the excimer emission to the normal fluorescence emission.

### CONCLUSIONS

The present work has shown that compound (4) is an interesting novel photoactive monomer. This

monomer reacts very fast with 2 mol of PhTD via Diels–Alder-ene reactions and gives only one product in high yeild. Thus, it can act as a difunctional photoactive monomer AA' in which the second functionality is produced during the course of the reaction. The reaction of this monomer with bistriazolinediones gave novel photoactive, heterocyclic polyimides via tandem Diels–Alder-ene reactions. The resulting polymers are thermally stable and show fluorescence emission phenomena. They also show the excimer formation due to naphthalenic pendant groups in the polymer main chain. This is the first report of the synthesis of novel photoactive polymers with the above properties via a cycloaddition polymerization reaction. Furthermore, the method of preparation of this type of polymers is simple, very fast, and quantitative.

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