Synthesis of Novel Polyimides Containing Side-Chain Azo-2-Naphthol Moieties

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ABSTRACT: An amine-ester derivative of isoeugenol was prepared in three steps. This amine-ester was converted to diazonium salt and subsequently was reacted with 2-naphthol and a novel isoeugenol ester-azo derivative as a new monomer was obtained in quantitative yield. This monomer was characterized by high-field ^{1}H-NMR, IR, and elemental analysis and then was used for the preparation of model compound and polymerization reactions. 4-Phenyl-1,2,4-triazoline-3,5-dione was allowed to react with this new monomer. The reaction was very fast and gave only one double adduct by Diels–Alder and ene pathways in excellent yield. The polymerization reactions of novel monomer with bistriazolinediones [bis(*p*-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)methane and 1,6-bis(3,5-dioxo-1,2,4-triazolin-4-yl)hexane] were carried out in *N,N*-dimethylacetamide at room temperature. The reactions were exothermic, fast, and gave novel heterocyclic polyimides by repetitive Diels–Alder-ene polyaddition reactions. Some structural characterization and physical properties of these novel heterocyclic polyimides are reported. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1942–1951, 2003

Key words: Diels–Alder polymers; bistriazolinediones; viscosity

INTRODUCTION

Aromatic polyimides are a very important class of polymeric materials of high performance for their excellent thermal and mechanical properties, good chemical resistance, high dimensional stability, and good electrical properties.[1–4] Because fully aromatic polyimides are intractable materials that do not melt before thermally decomposing, and do not dissolved in any organic solvents, copolyimides with a wide variety of molecular structure have been synthesized as a valuable alternative since 1960.[5–7] Classic polyimides, synthesized from dianhydrides of aromatic tetracarboxylic acids and diamines, show valuable properties, such as high glass-transition temperature (T_g) along with high decomposition temperatures, noncombustibility, and excellent mechanical properties. However, one major drawback was that they were typically insoluble in organic solvents and do not melt, which limits possible practical application. Several efforts have been made to obtain polyimides with good solubility while maintaining the excellent thermal and mechanical properties.[8–20] The synthesis of monomers with polar groups in the diamines or in the dianhydride molecules is one possible way of solving this problem. Another method for the synthesis of heterocyclic polyimides involves the cycloaddition reactions of bistriazolinediones with suitable dienes.[21–24]

Polymers containing the azo group can be used as dye materials. On the other hand, because of *cis* to *trans* isomerization about the diazo bond, which is responsible for the immediate optical properties, these polymers may potentially find applications such as optoelectronic devices, optical switches, optical data storage, halographic grating fabrication, liquid crystals, storage of light energy (to reappear as fluorescence, phosphorescence, and chemical or even mechanical energy), membranes, as a monolayer for Langmuir–Blodgett films, drug delivery systems, colored coatings, and colorants, particularly in textiles and as indicators.

In previous studies, we reported the synthesis of new aliphatic–aromatic polyimides by Diels–Alder-ene cycloaddition reactions.[25–29] In this investigation, we report the synthesis of novel heterocyclic polyimides containing the azo2-naphthol pendant group.

EXPERIMENTAL

Materials

Reagents were purchased from Fluka Chemie (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-deHaën AG (Seelze, Germany). 4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD) (**8**) and bistriazolinediones (**10**) and (**11**) were prepared according to published

Scheme 1
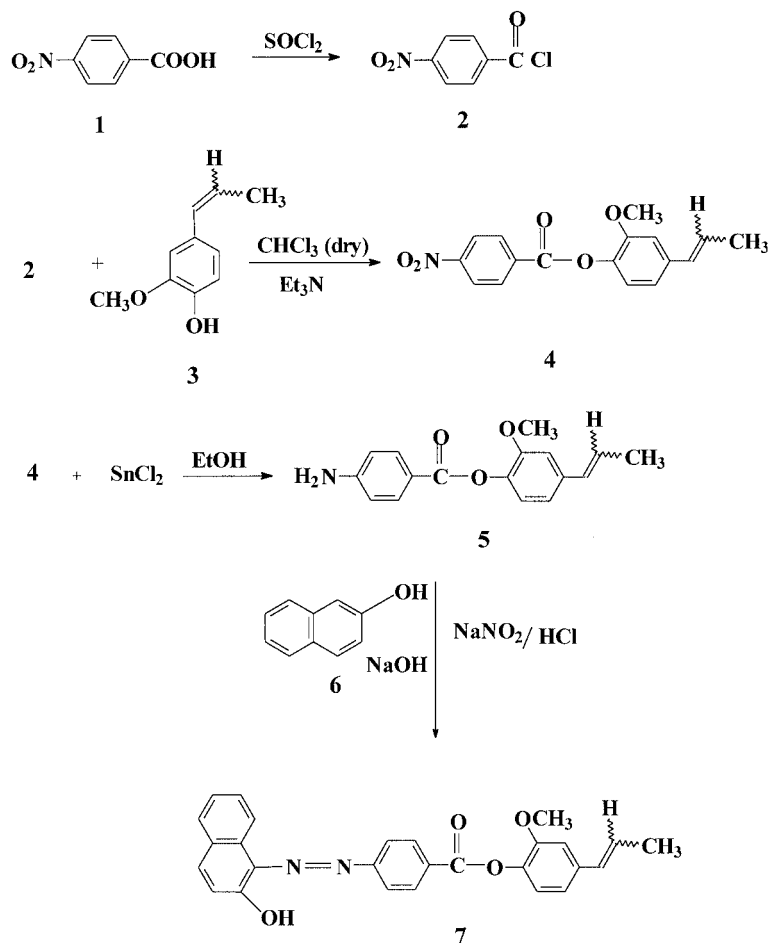
procedures.[30–32] N,N-Dimethylacetamide (DMAc) was dried over BaO, then distilled under reduced pressure. Compounds **1– 5** were synthesized according to our previous work.[29]

Techniques

IR spectra were recorded on a Shimadzu 435 IR spectrophotometer (Shimadzu, Kyoto, Japan). Spectra of solids were carried out using KBr pellets.

^{1}H-NMR 90-MHz spectra were recorded on a Varian EM-390 (Varian Associates, Palo Alto, CA) and 500-MHz spectrum on a Bruker (Germany) 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. Inherent viscosities were measured by a standard procedure using a Cannon Fensk routine viscometer (Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 (Poole, UK) system under N_2 atmosphere at a rate of 10°C/min. Elemental analyses were performed by Tarbiat Modarres University (Tehran, Iran).

Preparation of [2-methoxy-4-(1-propenyl)phenyl] 4-(2-azonaphthol) benzoate (7) (monomer)

Into a 25-mL beaker was dissolved 0.10 g (7.06×10^{-3} mol) of 2-naphthol (**6**) in 5 mL of 10% NaOH and 10 mL of water. Into another 25-mL beaker was dissolved 0.2 g (7.06×10^{-3} mol) of (**5**) in 2 mL of 30.5% HCl, 10 mL of water and minimun amount of acetone to get a homogeneous solution. While the acidic solution was being stirred, a solution of 0.054 g (7.77×10^{-3} mol) of sodium nitrate in 5 mL of water was added dropwise at 5°C. When about 90% of sodium nitrate solution was used, the starch/iodine test was done on the acidic solution between each addition of 4 drops. When the test became positive, the alkaline solution was added to the acidic solution in a period of 10 min at 5°C. The red solution was stirred in an ice bath for 30 min, then at room temperature for another 30 min. The solution was neutralized by addition of 10% NaOH to pH of 4–5. The resulting red solid was filtered off, washed with boiling water, then washed with boiling methanol, filtered off, and dried under vacuum at 100°C for 4 h to give 0.29 g (94%). Recrystallization from hot acetone gave a dark-red crystal, m.p. 201–203°C.
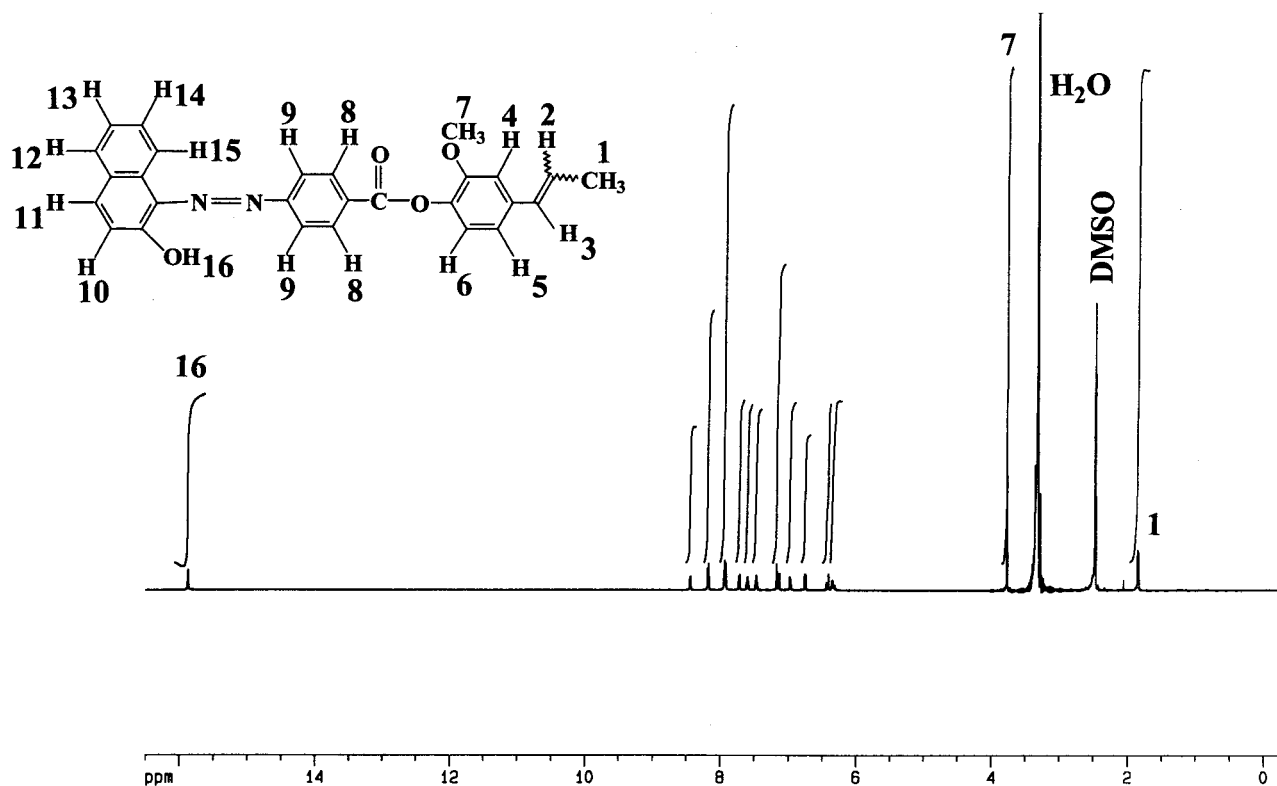
Figure 1 ¹H-NMR (500 MHz) spectrum of compound (**7**) in DMSO-d_6 at room temperature.

IR (KBr): 3400 (m, br), 3200–2500 (m, br), 1700 (s, br), 1600 (m), 1565 (m), 1550 (m), 1545 (m), 1510 (s), 1460 (m), 1450 (m), 1400 (m),1370 (w), 1320 (w, sh), 1300 (m), 1260 (s), 1200 (s), 1160 (s), 1140 (s), 1120 (s), 1070 (s), 1040 (m), 1010 (w), 980 (m), 960 (m), 960 (m), 900 (w), 870 (m), 830 (m), 780 (w), 750 (m), 680 (w), 610 (w), 540 (w), 490 (w) cm^{-1}. ¹H-NMR
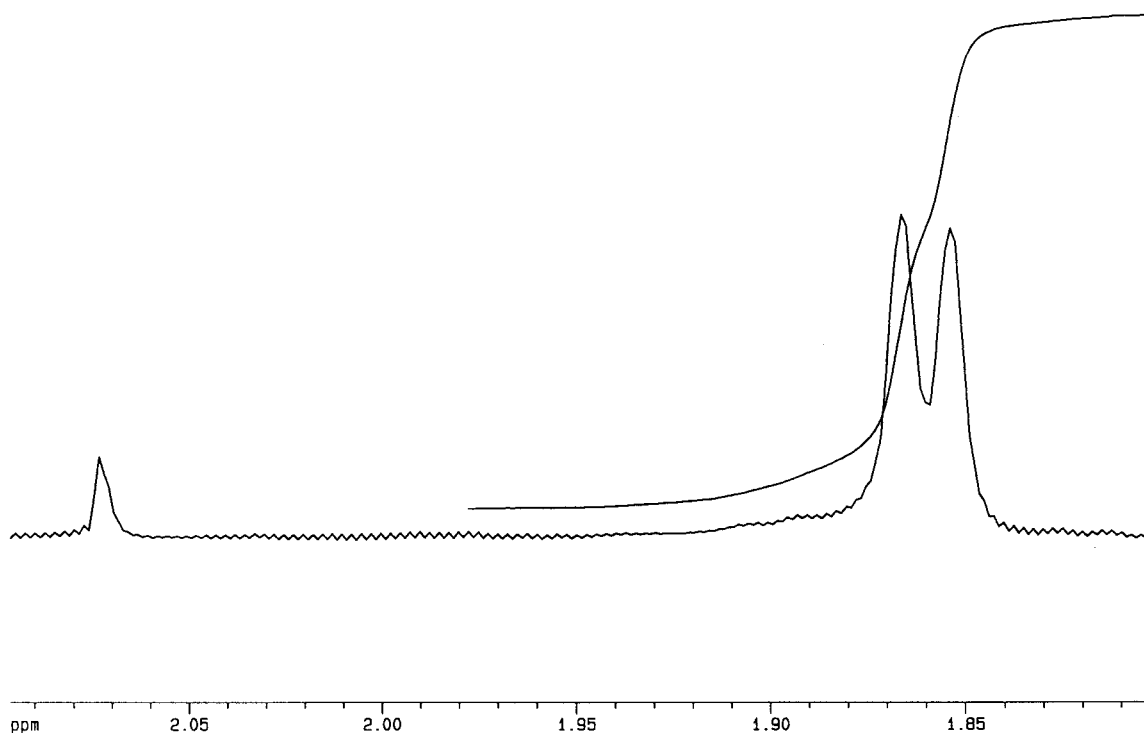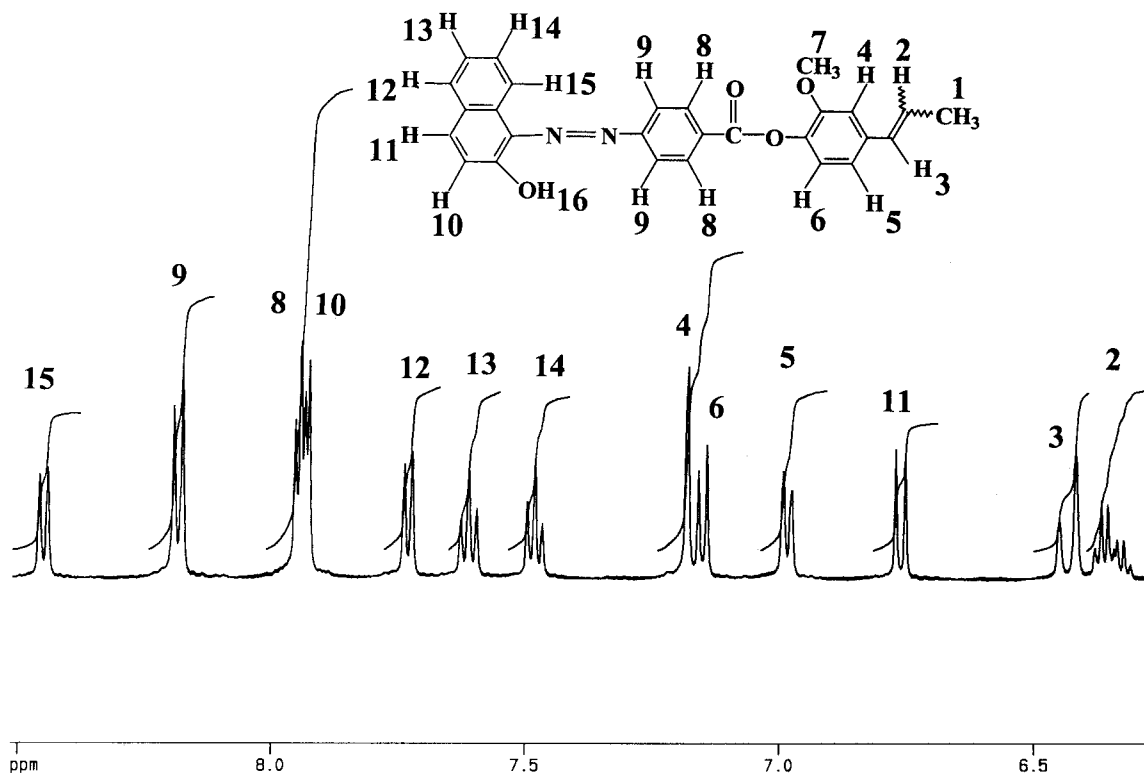

Figure 2 ¹H-NMR (500 MHz) spectrum of compound (**7**) in DMSO-d_6 at room temperature. Expanded region for the proton 1.

Figure 3 ^{1}H-NMR (500 MHz) spectrum of compound (**7**) in DMSO-d_6 at room temperature. Expanded region for the olefinic and aromatic protons.

(DMSO-d_6, TMS, 500 MHz): δ 1.85–1.87 (d, 3H, J = 6.21 Hz); 3.78 (s, 3H); 6.31–6.38 (doublet of quartet, 1H, J_1 = 16.08 Hz, J_2 = 6.21 Hz); 6.42–6.45 (d, 1H, J = 16.08 Hz); 6.75–6.77 (d, 1H, J = 9.54 Hz); 6.98–7.00 (d, 1H, J = 8.30 Hz); 7.15–7.1 (d, 1H, J = 8.10 Hz); 7.18 (s, 1H); 7.47–7.50 (t, H, J = 7.49 Hz); 7.60–7.63 (t, H, J = 7.42 Hz); 7.72–7.74 (d, H, J = 7.70 Hz); 7.93–7.95 (d, H, J = 8.45 Hz); 7.94–7.96 (d, H, J = 9.52 Hz); 8.18–8.20 (d, 1H, J = 8.62 Hz); 8.44–8.46 (d, 2H, J = 8.05 Hz); 15.88 (s, 1H). Anal. calcd for $C_{27}H_{22}N_2O_4$: C, 73.95%; H, 5.06%; N, 6.39%. Found: C, 73.63%; H, 5.19%; N, 6.37%.

Preparation of model compound (9)

A solution of 0.1 g (2.28×10^{-3} mol) of monomer (**7**) in 2 mL of DMF was placed into a 10-mL round-bottom flask and was cooled in an ice bath, after which 0.079 g (4.56×10^{-3} mol) of PhTD (**8**) in 1 mL DMF was added dropwise. As the solution of PhTD was added, the red solution quickly decolored. The reaction mixture was stirred for 10 h at room temperature. The solution was precipitated in 100 mL of distilled water. The orange-red precipitate was filtered and dried, yielding 0.17 g (97%) of red solid. Recrystallization from acetic acid and water gave an orange-red powder, m.p. 174°C (dec.).
IR (KBr): 3450 (m, br), 3050 (w), 1775 (m), 1720 (s), 1620 (m), 1600 (m),1500 (s), 1450 (m), 1410 (s), 1310 (w), 1260 (s), 1230 (s, sh), 1200 (m), 1180 (m, sh), 1120 (s, sh), 1090 (w), 1060 (m), 1010 (w), 980 (m), 840 (m), 760 (s), 690 (w), 640 (m), 580 (w), 580 (w) cm^{-1}. ^{1}H-NMR (DMSO-d_6, TMS, 500 MHz): δ 1.28–

1.30 (d, 3H, J = 6.74 Hz); 3.73 (s, 3H); 4.89 (m, 1H), 5.49 (s, 1H); 6.73–6.75 (d, 1H, J = 9.60 Hz), 7.24 (s, 1H); 7.35–7.55 (m, 12H); 7.55–7.65 (t, 1H, J = 7.49 Hz); 7.92–7.94 (d, 1H, J = 7.72 Hz), 7.92–7.94 (d, 3H, J = 9.05 Hz), 8.19–8.20 (s and d overlapped, 2H, J = 8.50 Hz), 8.42–8.44 (d, 1H, J = 8.06 Hz), 10.56 (s, br, 1H), 15.86 (s, 1H). Anal. calcd for $C_{43}H_{32}N_8O_8$: C, 64.47%; H, 4.09%; N, 14.21%. Found: C, 64.77%; H, 4.34%; N, 13.50%.

Polymerization of bis(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl) methane (10) with (7)

Into a 10-mL round-bottom flask, 0.10 g (2.76×10^{-3} mol) of monomer (**7**) and 0.12 g (2.76×10^{-3} mol) of bis(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (BPMTD) (**10**) were mixed and 0.80 mL of dry DMAc was added. After 3 min two monomers were dissolved and the red color of BPMTD was faded completely. The solution became red and viscous and was stirred at room temperature for 2 h. The resulting viscous solution was precipitated in 20 mL of methanol. The red precipitate was filtered off and dried, yielding 0.18 g (82.0%) of red solid. $[\eta_{inh}]^{25}$ = 0.12 dL g^{-1} (0.50 g/dL in DMF).
IR(KBr): 3450 (m, br), 3200 (w, br), 3050 (w), 2900 (w) 1780 (m), 1720 (s, br), 1620 (m), 1600 (m), 1510 (s), 1450 (m, sh), 1410 (s), 1310 (w), 1260 (s), 1240 (s, sh), 1200 (m), 1150 (m), 1130 (m, sh), 1090 (m), 1060 (m), 1015 (m), 980 (m), 900 (w), 840 (m), 760 (m), 580 (w), 500 (w) cm^{-1}. Anal. calcd for
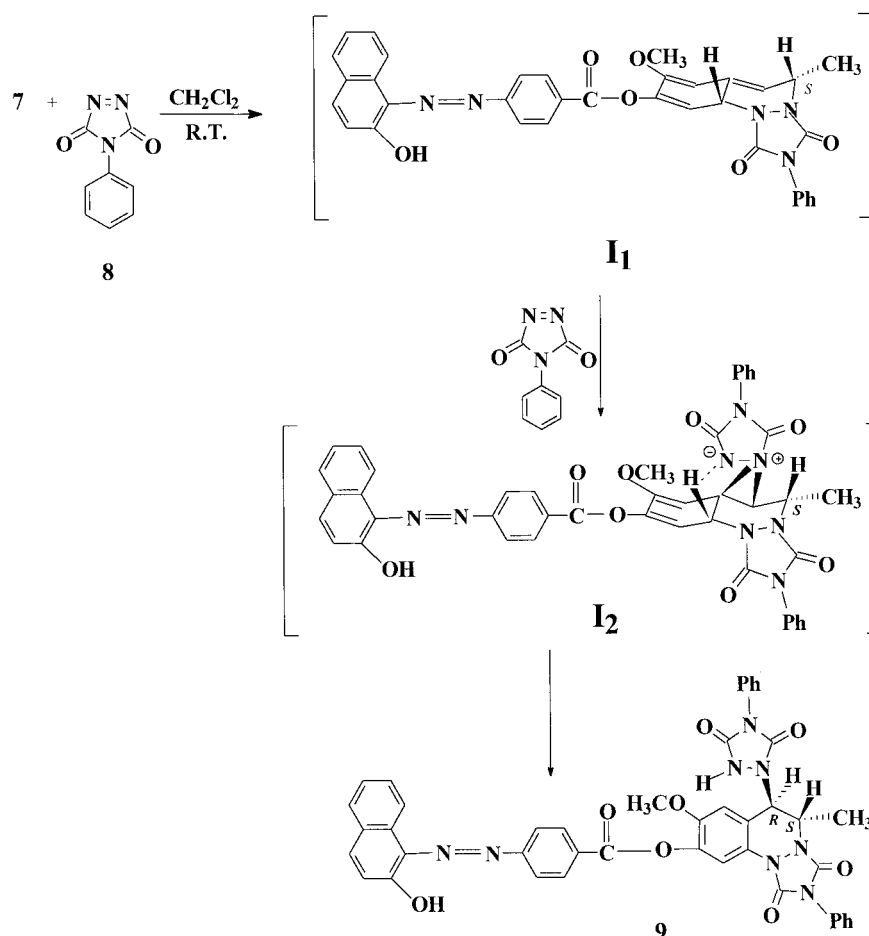
Scheme 2

$C_{44}H_{32}N_8O_8$ as repeating unit: C, 66.00%; H, 4.03%; N, 14.00%. Found: C, 63.60%; H, 4.34%; N, 13.62%.

Polymerization of 1,6-bis(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (11) with (7)

Into a 10-mL round-bottom flask, 0.16 g (3.57×10^{-3} mol) of monomer (7) and 0.10 g (3.57×10^{-3} mol) of 1,6-bis(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (HMTD) (11) were mixed and 0.8 mL of dry DMAc was added. After 5 min two monomers were dissolved and the pink color of HMTD was faded completely. The solution became viscous and was stirred at room temperature for 2 h. The resulting polymer was precipitated in 20 mL of methanol. The precipitate was filtered off and dried, yielding 0.21 g (82%) of orange-red solid. $[\eta_{inh}]^{25} = 0.16$ dL g^{-1} (0.50 g/dL in DMF). IR (KBr): 3450 (m, br), 3200 (m, br), 3050 (w), 2930 (m), 2850 (w), 1770 (m), 1710 (s, br), 1620 (m), 1600 (m), 1550 (w), 1500 (s), 1450 (s), 1420 (s), 1380 (m), 1320 (m), 1250 (s), 1200 (m), 1150 (s), 1060 (m), 1010 (m), 900 (w), 840 (m), 760 (m), 690 (w, sh), 590 (w), 500 (w) cm^{-1}. ANAL. calcd for $C_{37}H_{34}N_8O_8$ as repeating unit: C, 61.83%; H, 4.77%; N, 15.59%. Found: C, 60.24%; H, 5.00%; N, 15.44%.

RESULTS AND DISCUSSION

Monomer and model compounds studies

In previous studies we reported the preparation of novel optically active and photoactive and also flame retardant[21–29] polymers by tandem Diels–Alder-ene polymerization reactions. We also proposed a reasonable mechanism for this type of reactions. In this work we report the synthesis of azodye polyimides by tandem Diels–Alder-ene polymerization reactions. Thus monomer (7) as a red crystal was synthesized from the reaction of 2-naphtol (6) with compound (5) (**Scheme 1**).

The reaction occurred by diazonium salt of compound (5) and gave monomer (7) in high yield. The structure of monomer (7) was characterized by ^{1}H-NMR (Fig. 1), IR, and elemental analysis. As shown in Figure 2, the methyl group [CH$_3$(**1**)] appeared as a doublet, according to its coupling with H(2). The[CH$_3$(**7**)] was observed at 3.78 ppm, which appeared as a singlet.

In Figure 3, the expanded regions are shown for the olefinic and aromatic regions. H(2) was coupled with
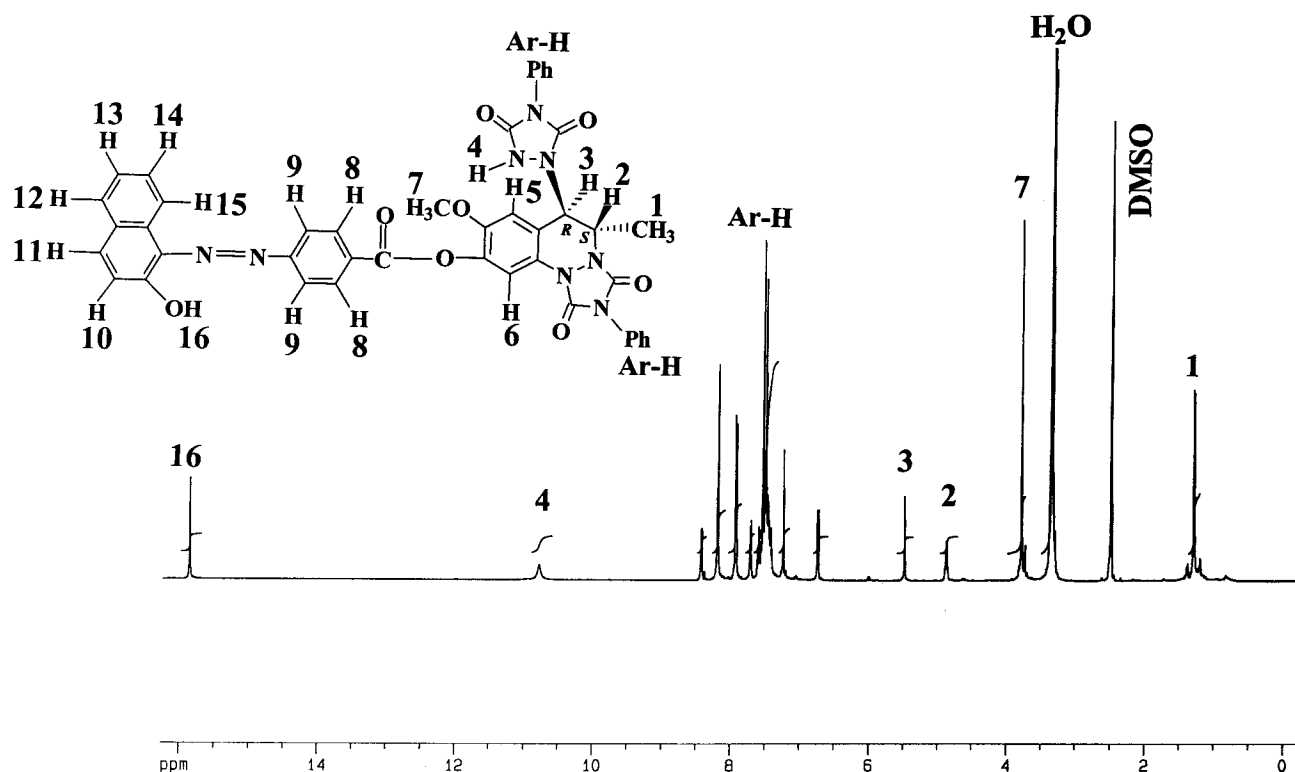
Figure 4 ^{1}H-NMR (500 MHz) spectrum of compound (**9**) in DMSO-d_6 at room temperature.

H(3) with $J = 16.08$ Hz and then coupled with [CH$_3$(**1**)] with $J = 6.21$ Hz. H(3) appeared as a doublet, according to its coupling with H(2). Also in this figure, the aromatic protons and their multiplicity are shown. It is interesting to mention that the OH on the naphthalene system was observed at 15.88 ppm. This downfield observation is attributed to intramolecular H-bonding of OH with the azo group. The UV-visible spectrum of this monomer was measured in DMF solution, showing λ_{max} at 498.2 nm (C $= 5.70 \times 10^{-6}$ mol L^{-1}, $\epsilon = 2.14 \times 10^4$ M^{-1} cm^{-1}).

The monomer (**7**) was reacted with two moles of PhTD (**8**) in DMF at room temperature. The reaction was very fast and gave only one adduct (**9**) by Diels–Alder-ene reactions (**Scheme 2**). The first step of the reaction is [4 + 2] Diels–Alder cycloaddition reaction, which leads to the formation of intermediate (**I$_1$**). This intermediate is so reactive that it cannot be isolated and subsequently undergoes ene reaction with a second mol of PhTD through intermediate (**I$_2$**)^{29} (**Scheme 2**). Although it has been observed that in a chiral environment only one diastereomer was formed,$^{25-27}$ in this case, because of an achiral environment, racemic mixtures are formed. Therefore, the resulting adduct (**9**) does not show optical rotation.

The molecular structure of (**9**) was studied by elemental analysis IR and ^{1}H-NMR spectroscopy. The IR spectrum of compound (**9**) showed two peaks at 1775 and 1720 cm^{-1} for the carbonyl groups. These consti-

tute the characteristic pattern for the urazole moiety. The ^{1}H-NMR spectra of compound (**9**) (Figs. 4 and 5) showed peaks for [CH$_3$(**1**)], which appeared as a doublet according to its coupling with H(2) with $J = 6.74$ Hz. In the region 4.89 ppm H(2) was shown as a multiplet as a result of coupling with H(3) and [CH$_3$(**1**)] and H(3) appeared at 5.49 ppm as a broad singlet, attributed to the small coupling constant. The peak at 10.56 ppm is related to N–H of the urazole group (proton number 4). It is also interesting to mention that the OH on the naphthalene system was observed at 15.86 ppm. This downfield observation is attributed to intramolecular H-bonding of OH with the azo group. This data also show that the very reactive PhTD did not react with the OH group of the naphthalene system. In Figure 6 expanded regions are shown for the aromatic regions, which are consistent with the structure of (**9**). The UV-visible spectrum of this model compound was also measured in DMF solution and show λ_{max} at 484.5 nm (C $= 3.68 \times 10^{-5}$ mol L^{-1}, $\epsilon = 2.51 \times 10^4$ M^{-1} cm^{-1}). Compound (**9**) was used as a model compound for the studies of polymerization reactions.

Polymerization reactions

Two bistriazolinediones, BPMTD (**10**) and HMTD (**11**), were selected as bisdienophilies for the polymerization reactions. Thus, the reaction of BPMTD (**10**) with
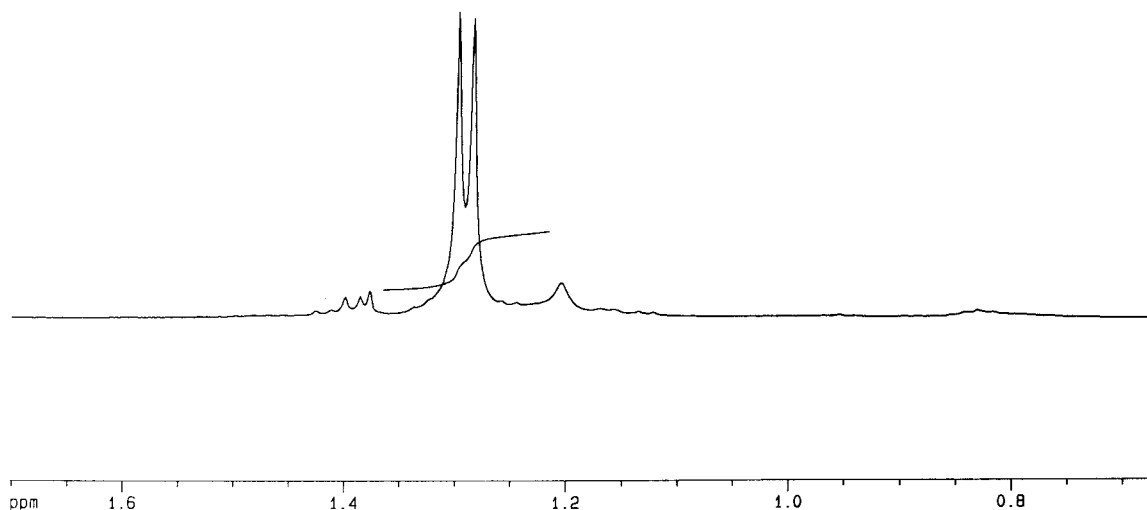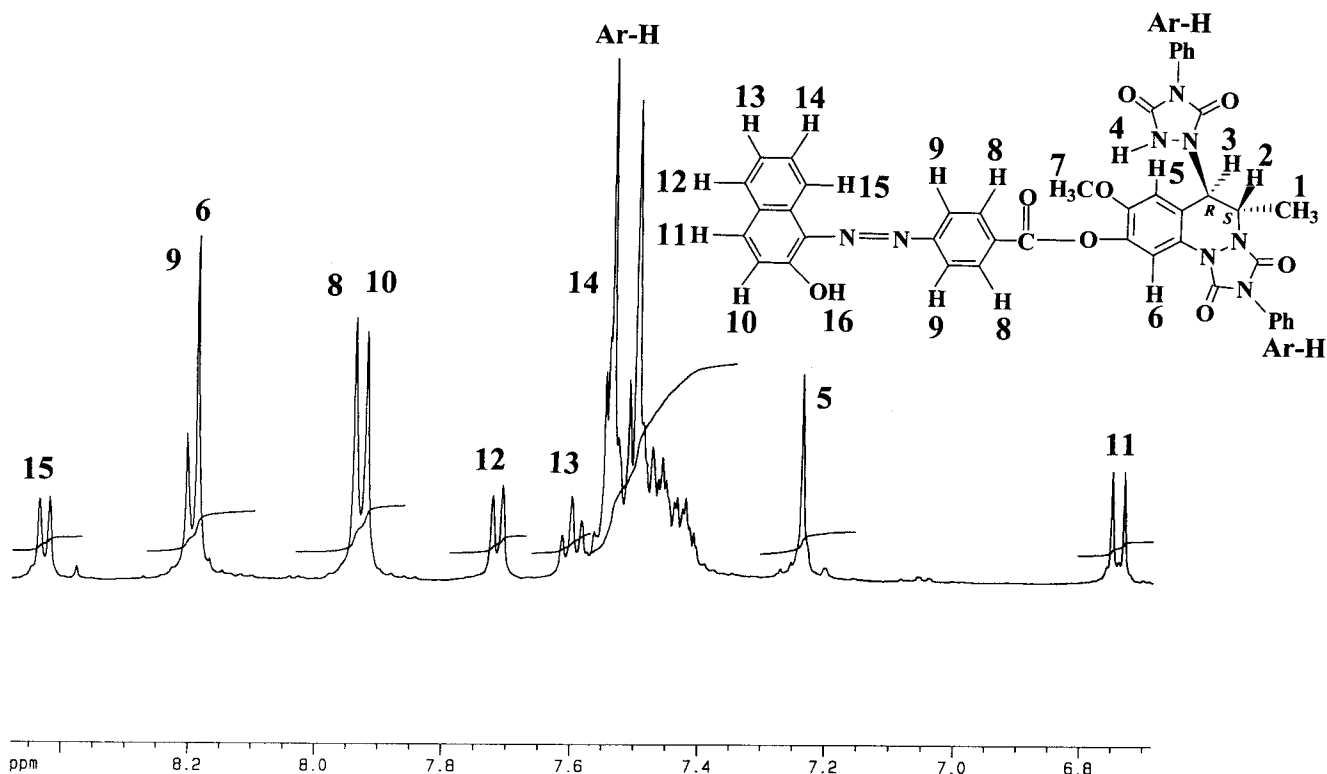
Figure 5 ^{1}H-NMR (500 MHz) spectrum of compound (**9**) in DMSO-d_6 at room temperature. Expanded region for the proton 1.

monomer (**7**) was carried out in DMAc solution at room temperature (**Scheme 3**).

The polymerization reaction is very fast and the resulting polymer (**12**) was obtained as a red solid. The structure of polymer (**12**) was characterized by elemental analysis and IR spectrum, which are in agreement with structure (**12**). The IR spectrum of polymer (**12**) showed two peaks at 1780 and 1720 cm^{-1} for the carbonyl groups. These constitute a characteristic pattern for the urazole moiety. The other peaks resemble the IR spectrum of the model compound. The UV-visible spectrum of this polymer was measured in DMF solution and show λ_{max} at 488.2 nm (C = 6.24 $\times$ 10^{-6} mol L^{-1}, ϵ = 4.47 $\times$ 10^4 M^{-1} cm^{-1}). Polymer

Figure 6 ^{1}H-NMR (500 MHz) spectrum of compound (**9**) in DMSO-d_6 at room temperature. Expanded region for the aromatic protons.
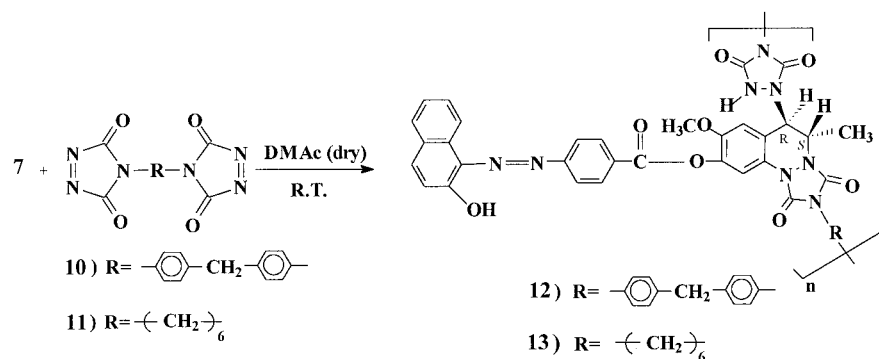
Scheme 3

(**12**) is soluble in polar solvents such as DMAc, H$_2$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 (**11**) with monomer (**7**) was also performed in DMAc solution at room temperature. The resulting polymer (**13**) was obtained as an orange-red solid. The IR spectrum (Fig. 7) of polymer (**13**) resembles that of model compound (**9**); therefore structure (**13**) was assigned to it (**Scheme 3**). Elemental analysis of polymer (**13**) is in agreement with the assigned structure of (**13**). This polymer shows solubility similar to that of polymer (**12**). The UV-visible spectrum of this polymer was also measured in DMF solution, showing λ_{max} at 482.2 nm (C = 7.51×10^{-6} mol L^{-1}, $\epsilon = 5.43 \times 10^4$ M^{-1} cm^{-1}). These polymers have low inherent viscosities, which show the formation of low molecular weight polymers. Reaction conditions and some physical properties for these novel polymers are summarized in Table I.

Thermal properties

Thermal gravimetric analyses of polymers (**12**) and (**13**) show that they are rather thermally stable. For polymer (**12**) the TGA thermogram (Fig. 8) reveals a 5% weight loss at 225°C and the residual weight percentage at 600°C is 42.60%. There are two domains of weight loss according to the DTG thermogram. The first begins at 28.7°C and ends at 113.0°C. The peak temperature during this weight loss is at 43.0°C. This loss could be the result of solvent or water loss. The second begins at 113.0°C and ends at 795.0°C. The peak temperature during this weight loss is at 307.3°C.
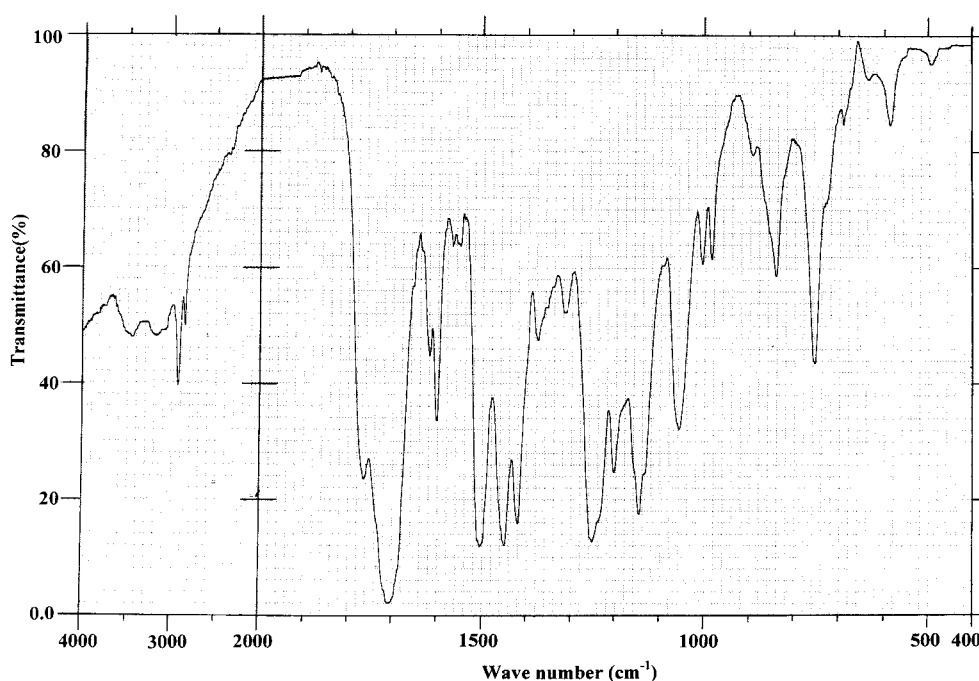

Figure 7 IR (KBr) spectrum of polymer (**13**).

TABLE I
Reaction Conditions and Some Physical Properties for Polymers 12 and 13

Property	Polymer	
	12	**13**
Reaction solvent	DMAc	DMAc
Fading time[a]	3 min	5 min
Nonsolvent	Methanol	Methanol
Yield %	82.0	82.0
T_w[b]	225°C	265°C
$[\eta_{inh}]^{25}$ (dL g^{-1})	0.12[c]	0.16[c]

[a] Time for disappearance of triazolinediones colors.
[b] Temperature for 5% weight loss.
[c] Measured at a concentration of 0.50 g/dL in DMF at 25°C.

For polymer (**13**) the TGA thermogram (Fig. 9) shows a 5% weight loss at 265.0°C and the residual weight percentage at 600°C is 35.03%. In this polymer one main weight loss domain is observed according to the DTG thermogram. The starting temperature is 94.7°C and the end temperature is 787.7°C, with a peak temperature of 289.0°C. These polymers show a substantial weight loss at 280°C. This could be attributable to

retro-Diels–Alder reactions and decomposition of the resulting adducts.

CONCLUSIONS

Compound (**7**) is an interesting novel monomer containing 2-naphthol azo moieties. This monomer reacts very quickly with 2 mol of PhTD by Diels–Alder-ene reactions and gives only one product in high yield. Thus, it can act as a difunctional monomer AA′, in which the second functionality is produced during the course of reaction. The reaction of this monomer with bistriazolinediones gave novel heterocyclic polyimides by tandem Diels–Alder-ene reactions. These polymers have OH and NH as well as C═O functional groups and they can readily form H-bonding and make a physical network. On the other hand, the presence of these functional groups will make these polymers crosslinkable.
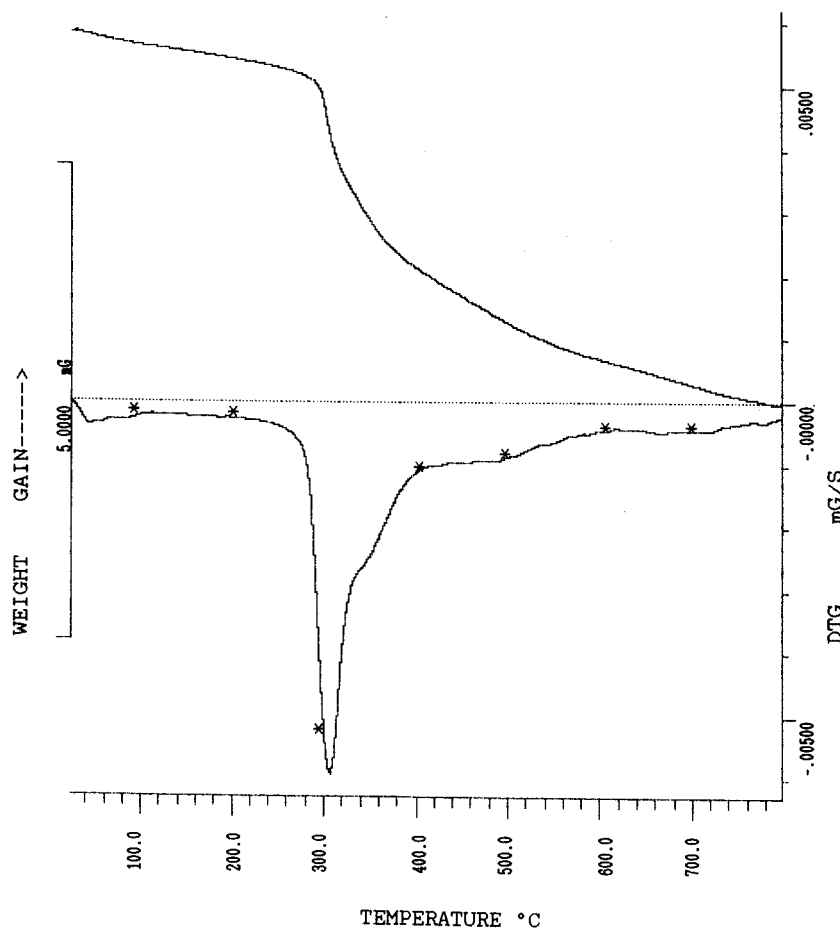
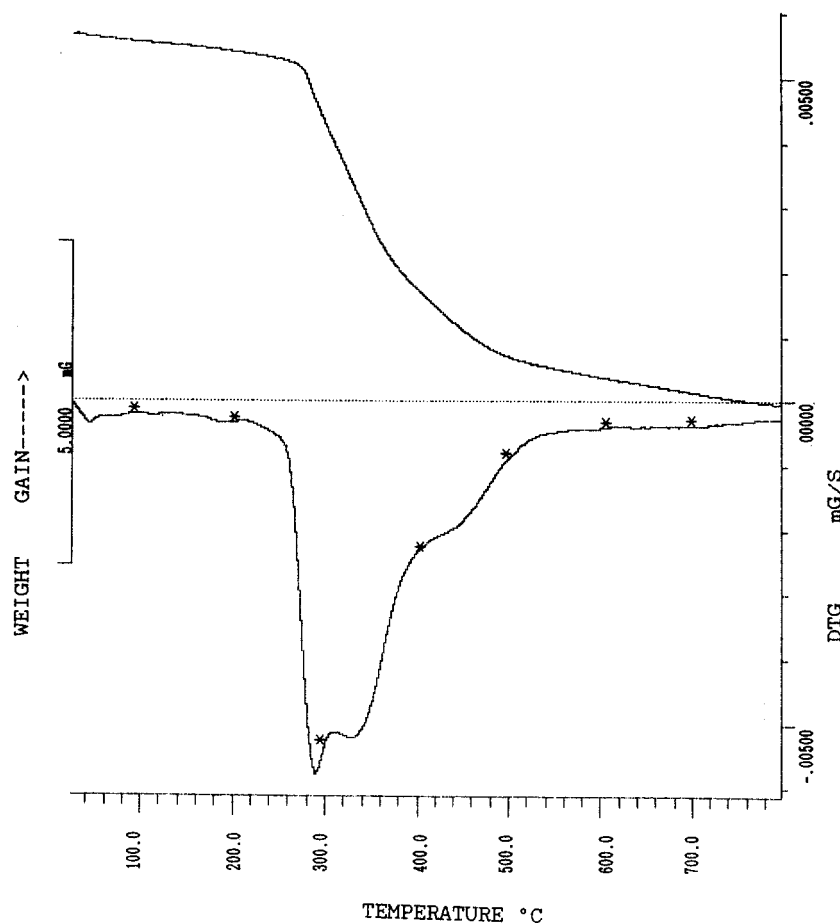**Figure 8** TGA and DTG thermograms of polymer (**12**).

Figure 9 TGA and DTG thermograms of polymer (**13**).

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