Synthesis of Novel Heterocyclic Polyimides Containing Trimellitimide Acid Moieties

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ABSTRACT: 4-Nitrobezoyl chloride **(2)** was reacted with isoeugenol in chloroform in the presence of triethyl amine and ester **(4)** was obtained in high yield. Ester **(4)** was reacted with $SnCl_2 \cdot 2H_2O$ to give amine-ester **(5)**, and subsequently was reacted with trimellitic anhydride **(6)** and novel isoeugenol ester-imide derivative **(7)**, as a new monomer was obtained in quantitative yield. Compound **(7)** was characterized by high-field ^{1}H–NMR, IR, and elemental analysis and then was used for the preparation of model compound **(9)** and polymerization reactions. 4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD) **(8)** was allowed to react with compound **(7)**. The reaction is very fast and gives only one double adduct **(9)** via Diels–Alder and ene pathways in excellent yield. The polymerization reactions of novel monomer **(7)** with bistriazolinediones [bis(*p*-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)methane **(10)** and 1,6-bis(3,5-dioxo-1,2,4-triazolin-4-yl-)hexane **(11)**] were carried out in *N*,*N*-dimethylacetamide (DMAc) at room temperature. The reactions are exothermic, fast, and gave novel heterocyclic polyimides **(12)** and **(13)** via repetitive Diels–Alder-ene polyaddition reactions. Some structural characterization and physical properties of these novel heterocyclic polyimides are reported. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1716–1725, 2001

Key words: trimellitic anhydride; Diels–Alder-ene polymerization; 4-phenyl-1,2,4-triazoline-3,5-diones; bistriazolinediones; inherent viscosity

INTRODUCTION

Aromatic polyimides are an important class of materials, having high temperature resistance and excellent mechanical properties.[1–4] Since fully aromatic polyimides are intractable materials that do not melt before thermally decomposing, and do not dissolve in any organic solvents, copolyimides with a wide variety of the 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) as well as 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, thus limiting possible practical applications. Several efforts have been made to obtain polyimides with good solubility while at the same time maintaining their 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. In previous studies, we introduced a new polymerization technique via Diels–Alder-ene cycloaddition reactions.[21–24] In this communication, we report the synthesis of novel heterocyclic polyimides containing a trimellitimide acid pendant group.

EXPERIMENTAL

Materials

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-de Haën AG (Seelze, Germany). 4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD) **(8)** and bistriazolinediones **(10)** and **(11)** were prepared according to published procedures.[12–14] DMAc (*N,N*-dimethylacetamide) was dried over BaO, then distilled under reduced pressure. Chloroform was dried over $CaCl_2$, then distilled at normal pressure.

Techniques

IR spectra were recorded on Shimadzu 435 IR spectrophotometer (Shimadzu, Japan). Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br).

Proton nuclear magnetic resonance (^{1}H–NMR) 90-MHz spectra were recorded on a Varian EM-390 (Varian Associates, Palo Alto, CA) and 500-MHz spectrum on 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. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 (England) System under N_2 atmosphere at a rate of 10°C/min. Elemental analyses were performed by Research Institute of Petroleum Industry (Tehran, Iran).

Preparation of 4-Nitrobenzoyl chloride (2)

A 5.0-g (0.03 mol) sample of 4-nitrobenzoic acid **(1)** was placed into a 50-mL round-bottom flask equipped with a condenser, to which 5.0 mL (6.80×10^{-2} mol) of freshly distilled thionyl chloride (excess amount) and 20.0 mL ethyl acetate were added. The mixture was refluxed until the suspension mixture was converted to a clear solution. The thionyl chloride was removed under reduced pressure, to leave 5.50 g (100.0%) yellow solid, m.p. 69–70°C.

IR (KBr): 3100 (w), 1740 (s), 1600 (s), 1510 (m), 1350 (s), 1320 (m), 1190 (s), 1260 (m), 1100 (m), 1040 (m), 880 (s, br), 840 (s), 690 (m), 640 (w) cm^{-1}.

Preparation of [2-Methoxy-4-(1-propenyl)phenyl] 4-Nitrobenzoate (4)

A 2.65-g (1.60×10^{-2} mol) sample of isoeugenol **(3)** and 8.0 mL of dry chloroform were placed into a two-necked round-bottom flask, to which a solution of 3.0 g (1.60×10^{-2} mol) of **(2)** in 10.0 mL of dry chloroform was added dropwise at 0°C over a period of 30 min. At the end of the addition the reaction mixture was stirred at 0°C for 1 h and then 2.25 mL (1.16×10^{-2} mol) of triethylamine in 3.0 mL of dry chloroform was added at 0°C over a period of 30 min. The reaction was stirred at room temperature for 24.0 h. Finally it was refluxed for 7.0 h. After addition of 10 mL of chloroform to the reaction mixture, extraction was done according to the following procedure: (1) 3 × 10 mL of 1% HCl solution, (2) 3 × 20 mL of 1% KOH solution (W/V), and (3) washing of the organic phase with distilled water until the extracted aqueous phase became neutral. The organic phase was dried over anhydrous sodium sulfate and chloroform was evaporated with a rotary evaporator, to leave 4.70 g (92.8%) of yellow solid. Recrystallization from methanol gave yellow crystals, m.p. 120–121°C.

IR (KBr): 3100 (w), 2950 (w), 1740 (s), 1600 (s), 1520 (s), 1460 (w, br), 1410 (m), 1350 (s), 1300 (w), 1390 (sh), 1260 (s), 1200 (m), 1150 (m), 1120 (m), 1060 (s), 1030 (m), 1010 (w), 960 (m), 870 (m), 1030 (m), 850 (m), 780 (w), 710 (s) cm^{-1}; ^{1}H–NMR (CDCl$_3$, TMS, 90 MHz): δ 1.7–1.9 (d, 3 H, $J = 6.0$ Hz); 3.7 (s, 3 H); 6.1–6.3 (m, 2 H); 6.7–7.1 (m, 3 H); 8.3 (s, 4 H); ANAL. calcd for $C_{17}H_{15}NO_5$: 65.17% C; 4.83% H; 4.47% N. Found: 65.00% C; 4.90% H; 4.50% N.

Reduction of [2-Methoxy-4-(1-propenyl)phenyl] 4-Nitrobenzoate (4)

A 3.0-g (9.57×10^{-3} mol) sample of compound **(4)** was placed into a 100-mL round-bottom flask

equipped with a condenser and nitrogen inlet, to which 10.8 g (4.80×10^{-2} mol) of $SnCl_2 \cdot 2H_2O$ (excess amount) and 50.0 mL of ethanol were added. The mixture was refluxed for 4.0 h until the suspension mixture became a clear solution. After cooling, the reaction mixture was poured into 50.0 g of ice with constant stirring, producing a yellowish precipitate. The pH was made basic (pH 10) by addition of 5% aqueous KOH and after 1 h at this pH, 5% HCl was added until the mixture reached a slightly basic pH 8. The mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous sodium sulfate. Evaporation of the solvent gave 2.60 g (96.3%) of [2-methoxy-4-(1-propenyl)phenyl] 4-aminobenzoate **(5)**. Recrystallization from acetone and water gave a white powder that was separated by filtration and dried under vacuum at 50°C for 5 h, m.p. 179–181°C.

IR (KBr): 3450 (m), 3350 (m), 2900 (w, br), 1670 (s), 1630 (m), 1590 (s), 1500 (s), 1440 (m, br), 1400 (m), 1260 (s, br), 1190 (s), 1150 (s), 1050 (w), 1020 (w), 950 (m), 860 (m), 830 (m), 780 (m), 760 (s), 690 (m), 630 (w) cm^{-1}; ^{1}H–NMR (CDCl$_3$, TMS, 90 MHz): δ 1.7–2.1 (d, 3 H, J = 6.0 Hz); 3.7 (s, 3 H); 5.8–6.2 (s, br, 2 H); 6.3–6.7 (m, 2 H); 6.7–6.8 (d, 2 H, J = 7.5 Hz); 6.9–7.3 (m, 3 H); 7.8–8.0 (d, 2 H, J = 7.4 Hz).

Preparation of [2-Methoxy-4-(1-propenyl)phenyl] 4-(Trimellitimide) Benzoate (7) (Monomer)

A 0.5-g (2.60×10^{-3} mol) sample of compound **(6)** was placed into a 50-mL round-bottom flask equipped with a condenser, to which 0.737 g (2.60×10^{-3} mol) of compound **(5)** and 8.0 mL of pyridine in 12.0 mL acetic acid were added. The reaction mixture was refluxed for 17.0 h and then the clear solution was concentrated up to 5.0 mL. The crude product (1.13 g, 94.9%) was recrystallized with acetone and water, m.p. 245°C (dec).

IR (KBr): 3200–2500 (m, br), 1700 (s, br), 1600 (m), 1500 (s), 1490 (w), 1430 (w), 1410 (w), 1360 (s), 1350 (s), 1270 (m, br), 1190 (m, br), 1120 (w), 1070 (s), 1040 (m), 1010 (w), 960 (m), 930 (m), 850 (s), 790 (m), 760 (s), 710 (s), 600 (w) cm^{-1}; ^{1}H–NMR (DMSO, TMS, 500 MHz): δ 1.85–1.89 (d, 3 H, J = 6.28 Hz); 3.80 (s, 3 H); 6.31–6.38 (doublet of quartet, 1 H, J_1 = 15.80 Hz, J_2 = 5.98 Hz); 6.41–6.45 (d, 1 H, J = 15.90 Hz); 6.98–7.00 (dd, 1 H, J_1 = 8.19 Hz, J_2 = 1.56 Hz); 7.15–7.17 (d, 1 H, J = 8.15 Hz); 7.18 (d, 1 H, J = 1.50 Hz); 7.71–7.73 (d, 2 H, J = 8.50 Hz); 8.09–8.11 (d, 1 H, J = 7.7 Hz); 8.25–8.26 (d, 2 H, J = 8.5 Hz); 8.32 (s, 1 H); 8.42–8.44 (d, 1 H, J = 7.7 Hz); 13.31–13.79 (s, br, 1 H). ANAL. calcd for C$_{26}$H$_{19}$NO$_7$: 68.27% C; 4.19% H; 3.06% N. Found: 68.20% C; 4.30% H; 3.00% N.
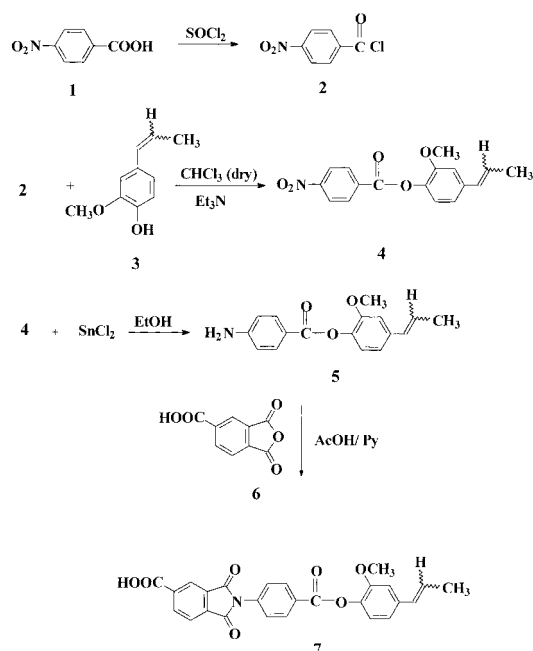
Scheme 1

## Preparation of Model Compound (9)

A solution of 0.1 g (2.18×10^{-4} mol) of monomer **(7)** in 0.50 mL of dry DMAc was placed into a 10-mL round-bottom flask, to which 0.076 g (4.36×10^{-4} mol) of PhTD **(8)** in 0.80 mL dry DMAc was added dropwise at room temperature. As the solution of PhTD was added, the red solution quickly decolored. The reaction mixture was stirred for 20 h at room temperature. The solution was precipitated in 20.0 mL of distilled water. The white precipitate was filtered and dried, leaving 0.104 g (84.3%) of white solid. Recrystallization from acetic acid and water gave white crystals, m.p. 158°C (dec).

IR (KBr): 3500–2500 (m, br), 1705 (s, br), 1600 (m), 1490 (s), 1390 (s, br), 1250 (m), 1170 (w), 1120 (m), 1090 (w), 1030 (m), 1065 (m), 1010 (s), 905 (m), 850 (m), 750 (s), 720 (m), 685 (m), 580 (w) cm^{-1}. ^{1}H–NMR (DMSO-d_6, TMS, 90 MHz): δ 1.1–1.4 (d, 3 H, J = 6.0 Hz); 3.9 (s, 3 H); 4.7–5.1 (m, 1 H); 5.4–5.6 (s, br, 1 H); 7.3 (s, 1 H); 7.5 (s, 5 H); 7.6 (s, 5 H); 7.8–7.9 (d, 2 H, J = 7.5 Hz), 8.2–8.7 (m, 7 H). ANAL. calcd for C$_{41}$H$_{29}$N$_7$O$_{11}$: 61.89% C; 3.67% H; 12.32% N. Found: 62.60% C; 3.80% H; 11.30% N.

## Polymerization of Bis(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl) Methane (10) with (7)

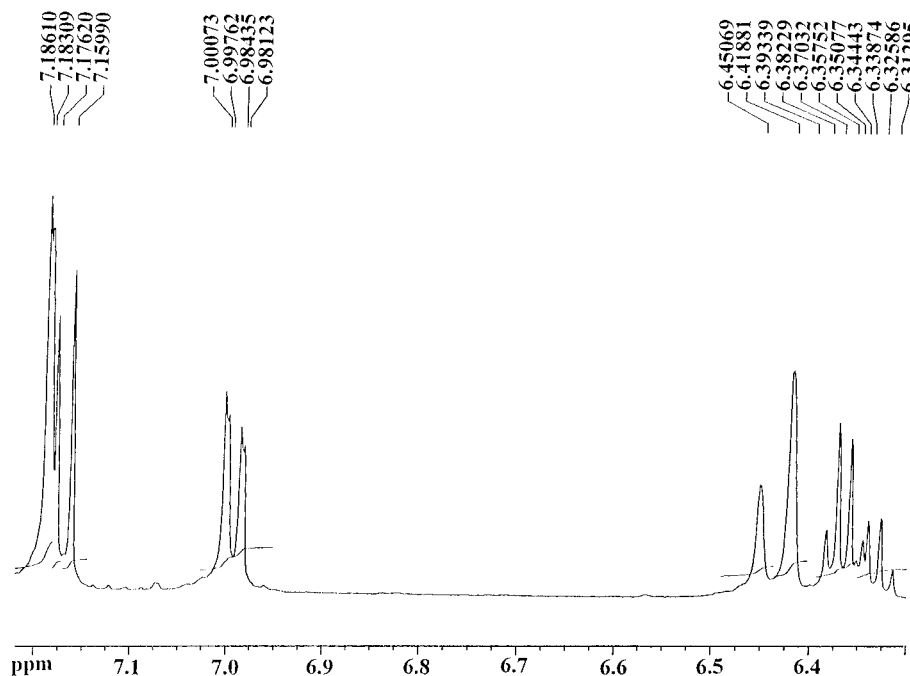Into a 10-mL round-bottom flask, 0.20 g (4.37×10^{-4} mol) of monomer **(7)** and 0.158 g (4.37
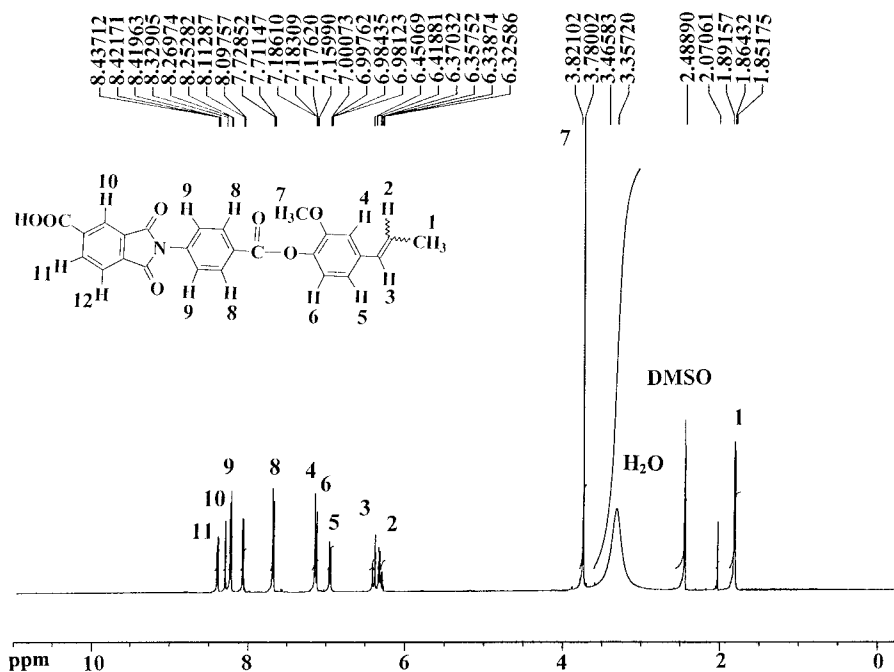
Figure 1 ^{1}H–NMR (500 MHz) spectrum of compound **(7)** in DMSO at room temperature. The COOH proton appeared between 13.31 and 13.79 as a broad peak.

× 10^{-4} mol) of bis(*p*-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (BPMTD) **(10)** were mixed, after which 0.70 mL of dry DMAc was added. After 5 min two monomers were dissolved and the red color of BPMTD had faded completely. The solution became pale orange viscous and was stirred
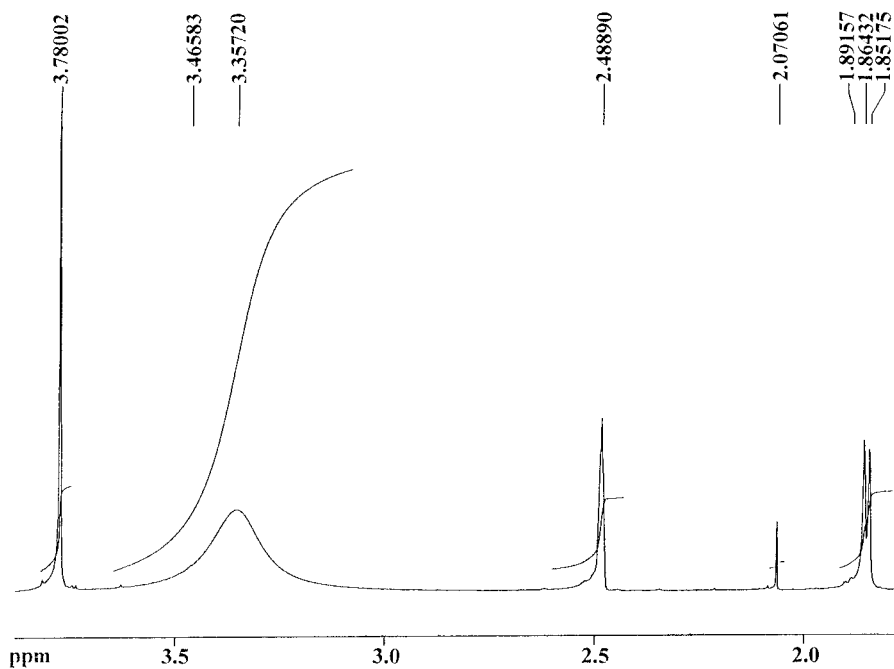
Figure 2 ^{1}H–NMR (500 MHz) spectrum of compound **(7)** in DMSO-d_6 at room temperature. Expanded region for protons 1 and 7.
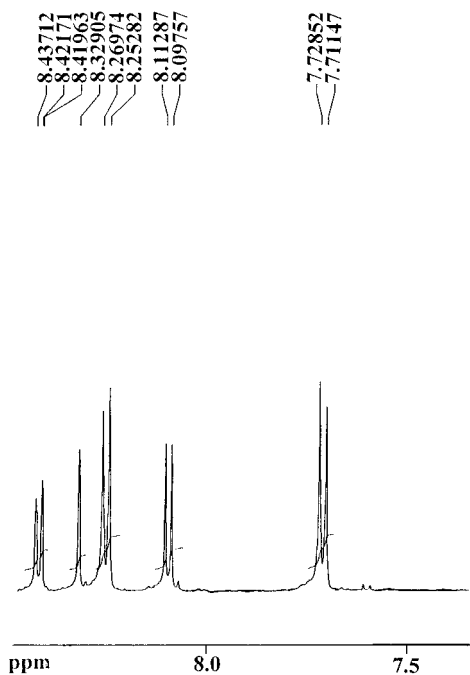
7.18610
7.18309
7.17620
7.15990

7.00073
6.99762
6.98435
6.98123

6.45069
6.41881
6.39339
6.38229
6.37032
6.35752
6.35077
6.34443
6.33874
6.32586
6.31295

ppm   7.1   7.0   6.9   6.8   6.7   6.6   6.5   6.4

Figure 3 ^{1}H–NMR (500 MHz) spectrum of compound **(7)** in DMSO-d_6 at room temperature. Expanded region for protons 2, 3, 4, 5, and 6.

at room temperature for 20 h. The resulting viscous solution was precipitated in 30 mL of methanol. The yellow precipitate was filtered off and dried, leaving 0.34 g (95.0%) of yellow solid. $[\eta_{inh}]^{25} = 0.21$ dL g^{-1} (0.50 g/dL in DMF).

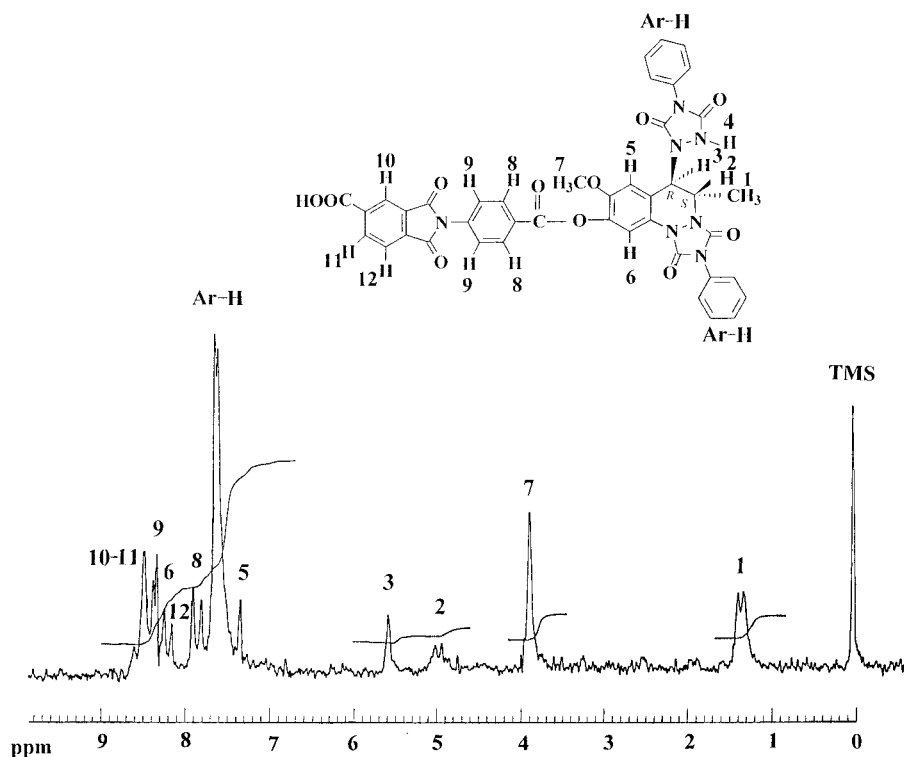IR(KBr): 3500–2500 (m, br), 1700 (s, br), 1600 (w), 1500 (s), 1400 (m), 1380 (m, br), 1250 (m), 1210 (w), 1170 (w),

8.43712
8.42171
8.41963
8.32905
8.26974
8.25282
8.11287
8.09757

7.72852
7.71147

ppm   8.0   7.5

Figure 4 ^{1}H–NMR (500 MHz) spectrum of compound **(7)** in DMSO-d_6 at room temperature. Expanded region for protons 8, 9, 10, 11, and 12.
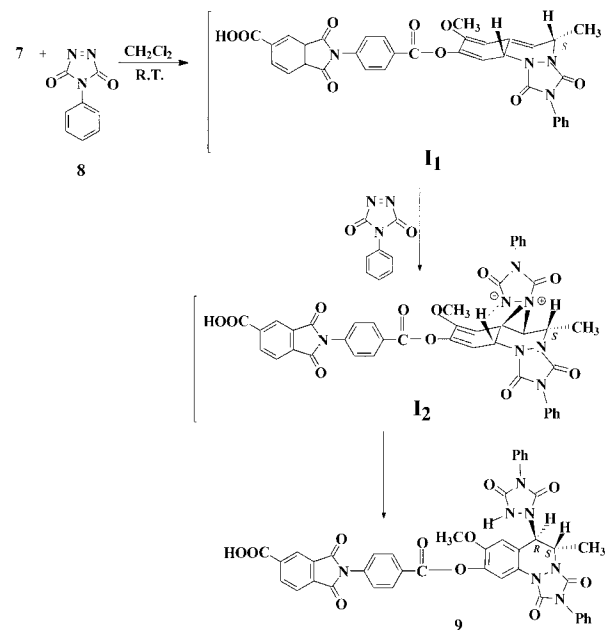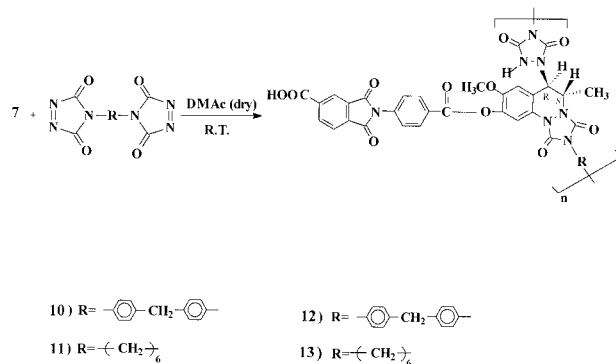
Scheme 2

Figure 5 ^{1}H–NMR (90 MHz) spectrum of model compound **(9)** in DMSO-d_6 at room temperature. The peaks for COOH and NH protons are very broad and were not detected.

1110 (w), 1070 (w), 1050 (m), 870 (w), 750 (w), 710 (w) cm^{-1}. ^{1}H–NMR (DMSO-d_6, TMS, 90 MHz): δ 1.1–1.4 (d, br, 3 H); 1.8–1.9 (s, DMAc); 1.9–2.0 (s, DMAc); 3.8 (s, br, 3 H); 4.1 (s, br, 2 H); 4.6–5.1 (m, br, 1 H); 5.4–5.6 (s, br, 1 H); 7.1–7.3 (s, br, 1 H); 7.3–7.6 (s, br, 8 H); 7.7–8.0 (d, br, 2 H); 8.1–8.6 (m, br, 6 H); 10.6–10.9 (s, br, N—H and COOH); 11.0–11.2 (s, br, N—H and COOH). ANAL. calcd for C$_{43}$H$_{29}$N$_7$O$_{11}$ as repeating unit: 63.00% C; 3.57% H; 11.96% N. Found: 61.70% C; 3.90% H; 10.90% N.

Scheme 3

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, 0.20 g (4.37 × 10^{-4} mol) of monomer **(7)** and 0.122 g (4.37 × 10^{-4} mol) of 1,6-bis(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (HMTD) **(11)** were mixed, after which 0.6 mL of dry DMAc was added. After 5 min two monomers were dissolved and the pink color of HMTD had faded completely. The solution became viscous and was stirred at room temperature for 20 h. The resulting polymer was precipitated in 30 mL of methanol. The white precipitate was filtered off and dried, to give 0.29 g (90.06%) of white solid. [η$_{inh}$]^{25} = 0.23 dL g^{-1} (0.50 g/dL in DMF).

IR (KBr): 3600–2500 (m, br), 2905 (m), 1700 (s, br), 1600 (m), 1510 (m), 1450 (m, br), 1420 (m, br), 1360 (m), 1250 (m), 1205 (w), 1160 (m), 1120 (w), 1060 (m), 1050 (w), 930 (w), 890 (w), 850 (m), 750 (m), 720 (m) cm^{-1}. ^{1}H–NMR (DMSO-d_6, TMS, 90 MHz): δ 1.0–2.0 (m, br, 11 H); 3.1–3.6 (m, br, 4 H); 3.7–3.9 (s, br, 3 H); 4.5–4.8 (m, br, 1 H); 5.2–5.4 (s, br, 1 H); 7.0–7.3 (s, br, 1 H); 7.7–8.0 (d, br, 2 H); 8.1–8.6 (m, br, 6 H); 10.7–11.7 (s,

Table I   Reaction Conditions and Some Physical Properties for Polymers (12) and (13)

Property	Polymer (12)	Polymer (13)
Reaction solvent	DMAc	DMAc
Fading time[a]	5 min	5 min
Nonsolvent	Methanol	Methanol
Yield (%)	95.0	90.06
T_w[b]	262.5°C	266.6°C
$[\eta_{inh}]^{25}$ (dL g^{-1})	0.21[c]	0.23[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.

br, N—H and COOH). ANAL. calcd for $C_{36}H_{31}N_7O_{11}$ as repeating unit: 58.62% C; 4.24% H; 13.29% N. Found: 57.70% C; 4.50% H; 12.90% N.

RESULTS AND DISCUSSION

Monomer and Model Compounds Studies

In previous studies we reported the preparation both of novel optically active and photoactive[21–23] polymers and of flame retardant[24] polymers via tandem Diels–Alder-ene polymerization reactions. We also proposed a reasonable mechanism for these types of reactions. Monomer (7) was synthesized from the reaction of trimellitic anhydride (6) with compound (5) (**Scheme 1**). 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) and [CH3 (7)] was observed at 3.80 ppm, which appeared as a singlet. In Figure 3 expanded regions are shown for H (2) and H (3). H (2) was coupled with H (3), with $J = 15.80$ Hz, and then coupled with [CH3 (1)], with $J = 6.40$ Hz. H (3) appeared as a doublet according to its coupling with H (2). Also in Figure 3, there is a doublet of doublet pattern for H (5) with $J_1 = 8.19$ Hz, $J_2 = 1.56$ Hz, and two doublets for H (6) and H (4) with $J = 8.15$ and 1.50 Hz, respectively. In Figure 4, protons H (8) and H (9) appeared at 7.71 and 8.25 ppm, respectively, with $J = 8.5$ Hz. Also, H (12) and H (11) were observed as two doublets according to their coupling with each other in regions 8.11 and 8.42 ppm, respectively, with $J = 7.70$ Hz. H (10) is shown as a singlet at 8.33 ppm.

Monomer (7) was reacted with 2 mol of PhTD (8) in dry DMAc at room temperature. The reaction is very fast and gave only one adduct via Diels–Alder-ene (9) reactions (**Scheme 2**). The first step of the reaction is the [4 + 2] Diels–Alder cycloaddition reaction, which leads to the formation of intermediate (I_1). This intermediate is extremely reactive, such that it cannot be isolated, and subsequently undergoes ene reaction with the second mole of PhTD through intermediate (I_2)[21] (**Scheme 2**). Although it has been observed that, in a chiral environment, only one diastereomer was formed,[21,22,24] in this case, as a result 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 ^{1}H–NMR spectroscopy (Fig. 5). The [CH$_3$ (1)] appeared as a doublet according to its coupling with H (2), with $J = 6.0$ Hz. In the region between 4.7 and 5.1 ppm H (2) appeared as a multiplet, as a result of coupling with H (3) and [CH$_3$ (1)], and between 5.4 and 5.6 ppm, H (3) appeared as a singlet. Although the absorption bonds for OH and NH were observed in the IR spectrum, in the ^{1}H–NMR spectrum signals for these protons were not detected. This observation could result from the broadness of the signals. Compound (9) was used as a model compound for the polymerization reaction studies.

Table II   Solubility of Polymers (12) and (13)

Solvent	Polymer (12)	Polymer (13)
H_2SO_4	+[a]	+
Acetic acid	−[a]	+
DMSO	+	+
DMF	+	+
H_2O	−	−
Methanol	−	−
Ethanol	−	−
Acetone	−	−
CHCl$_3$	−	−
CH$_2$Cl$_2$	−	−
THF	+	−
Diethyl ether	−	−
CCl$_4$	−	−
Toluene	−	−
Cyclohexane	−	−
n-Hexane	−	−

[a] +, soluble at room temperature; −, insoluble at room temperature.
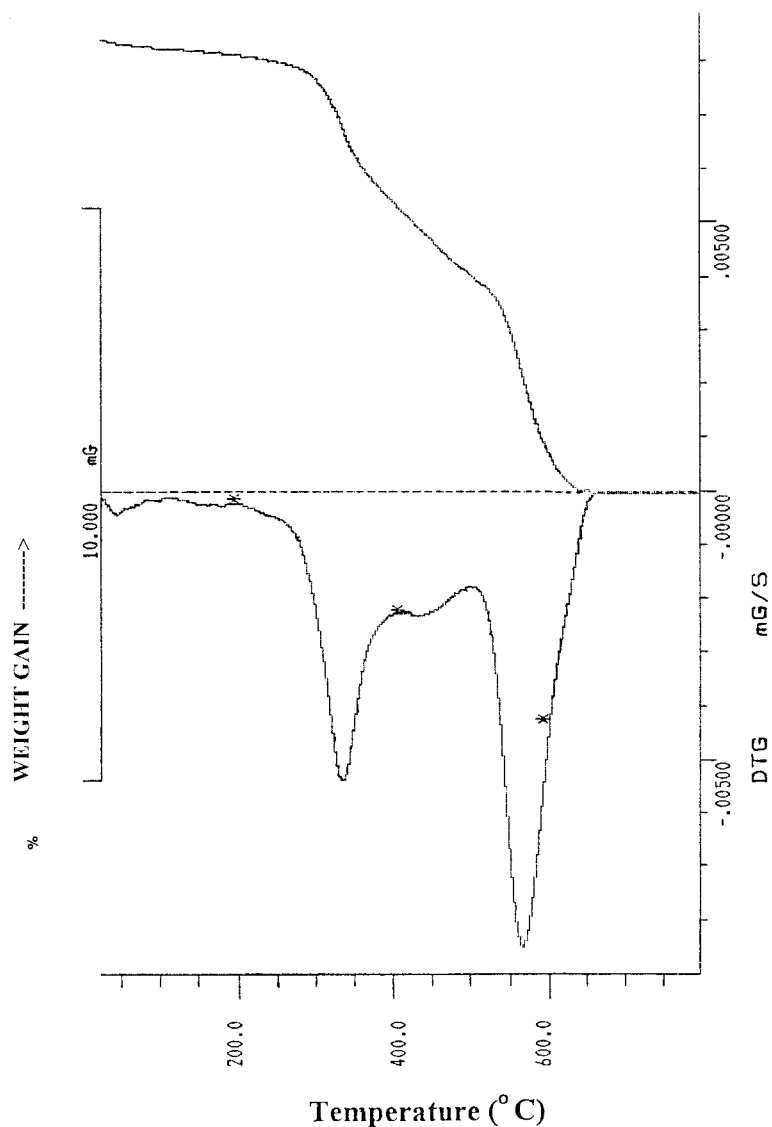
Figure 6 TGA and DTG thermograms of polymer **(12)**.

Polymerization Reactions

Two bistriazolinediones, BPMTD **(10)** and HMTD **(11)**, were selected as bisdienophilies for the polymerization reactions. Thus, the reaction of BPMTD **(10)** with 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 pale-yellow solid. The structure of polymer **(12)** was characterized by IR and ^{1}H–NMR spectra, which are in agreement with structure **(12)**. Although the ^{1}H–NMR spectrum of the polymer is broad, it resembles the spectrum of model compound **(9)**. The elemental analysis of polymer **(12)** also confirms this structure.

Polymer **(12)** is soluble in polar solvents such as DMAc, H_2SO_4, DMF, and DMSO, but 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 a white solid. The IR and ^{1}H–NMR spectra of polymer **(13)** resemble those of model compound **(9)**; therefore, structure **(13)** was assigned to it (**Scheme 3**). Reaction conditions and some physical properties for these novel polymers are summarized in Table I. The solubility characteristics of polymer **(12)** and polymer **(13)** are listed in Table II.
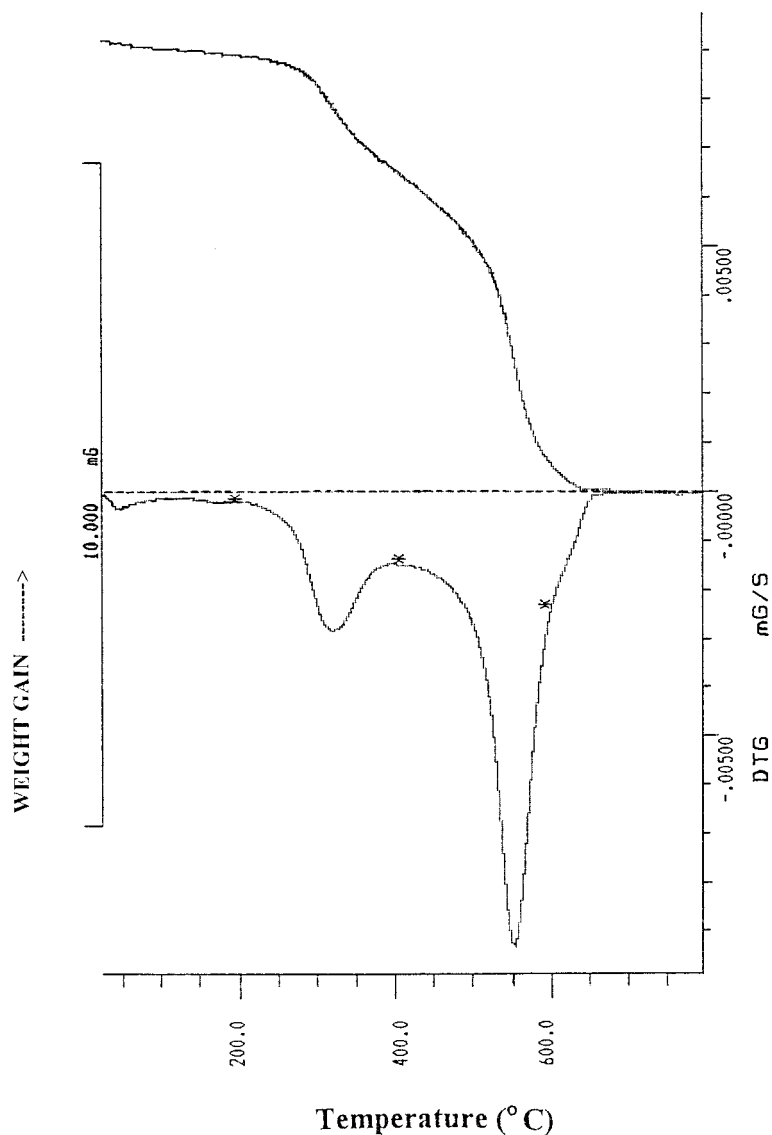
Figure 7 TGA and DTG thermograms of polymer **(13)**.

Thermal Properties

Thermal gravimetric analysis (TGA) of polymers **(12)** and **(13)** shows that they are rather thermally stable. For polymer **(12)** the TGA thermogram (Fig. 6) reveals 5% weight loss at 262.5°C and the residual weight at 500°C is 45.71%. There are two domains of weight loss according to the DTG thermogram. The first begins at 28.7°C and ends at 399.0°C; the peak temperature during this weight loss is at 322.0°C. The second begins at 399.0°C and ends at 655.7°C; the peak temperature during this weight loss is at 553.0°C. For polymer **(13)** the TGA thermogram (Fig. 7) shows 5% weight loss at 266.6°C and the residual weight at 500°C is 48.60%. Also in this polymer two main weight-loss domains are observed according to the DTG thermogram. For the first one, the starting temperature is 116.7°C, the end temperature is 505.3°C, and the peak temperature is 336.7°C. The second starts at 505.3°C and ends at 659.3°C; the peak temperature is 567.7°C.

CONCLUSIONS

Compound **(7)** is an interesting novel monomer containing trimellitimide acid moieties. This monomer reacts very fast with 2 mol of PhTD via

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 via tandem Diels–Alder-ene reactions. The resulting polymers are rather thermally stable. Furthermore, these polymers have COOH 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 makes these polymers crosslinkable.

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