

# Synthesis and Characterization of Novel Optically Active and Flame-Retardant Heterocyclic Polyimides

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**ABSTRACT:** Tetrachlorophthalic anhydride (**1**) was reacted with L-leucine (**2**) in toluene solution at refluxing temperature in the presence of triethylamine and the resulting imide-acid (**4**) was obtained in quantitative yield. The compound (**4**) was converted to the *N*-(tetrachlorophthaloyl)-L-leucine acid chloride (**5**) by reaction with thionyl chloride. The reaction of this acid chloride (**5**) with isoeugenol (**6**) was carried out in chloroform and novel optically active isoeugenol ester derivative (**7**) as a chiral monomer was obtained in high yield. The compound (**7**) was characterized by <sup>1</sup>H-NMR, IR, Mass and elemental analysis, and then was used for the preparation of model compound (**10**) 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 diastereomer of (**10**) 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 (**11**) and 1,6-bis-(3,5-dioxo-1,2,4-triazolin-4-yl)hexane] (**12**) were carried out in *N,N*-dimethylacetamide (DMAc) at room temperature. The reactions are exothermic, fast, and give novel optically active polymers (**13**) and (**14**) via repetitive Diels–Alder-ene polyaddition reactions. The resulting polymers are optically active, thermally stable, and flame resistant. All of the above compounds were fully characterized by IR, <sup>1</sup>H-NMR, elemental analysis, and specific rotation. Some structural characterization and physical properties of these novel heterocyclic polyimides are reported. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 240–248, 2000

**Key words:** Diels–Alder-ene polymerization; *N*-(tetrachlorophthaloyl)-L-leucine acid chloride; optically active polymers; 4-phenyl-1,2,4-triazoline-3,5-diones, bistriazolinediones, inherent viscosity, diastereoselectivity; fire-resistant polymers

## INTRODUCTION

Aromatic polyimides and heterocyclics are known as high-performance polymer materials for their excellent electrical and mechanical properties, outstanding solvent resistance, and high thermal and thermo-oxidative stability.<sup>1,2</sup> Polyimides with a

wide variety of chemical structures have been reported that have excellent thermal stability and chemical resistance.<sup>3–15</sup> Classic polyimides, synthesized from dianhydrides of aromatic tetracarboxylic acids and diamines, show valuable properties, such as high glass transition temperatures ( $T_g$ ), 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.<sup>16–28</sup> The syn-

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thesis 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. 4-Substituted-1,2,4-triazoline-3,5-diones and bistriazolinediones are among the most reactive dienophiles,<sup>29–40</sup> enophiles,<sup>34–40</sup> and electrophiles.<sup>41–43</sup> Styrene undergoes facile reaction with triazolinediones as well as bistriazolinediones, and in the latter case, lead to polymer formation via double Diels–Alder and Diels–Alder-ene sequences.<sup>44</sup> The reaction of 1,1-diphenylethylene (DPE) with maleic anhydride have been reported to give only double Diels–Alder adduct.<sup>45–48</sup> The reaction takes place at elevated temperature. Recently, we reported<sup>49</sup> that the DPE undergoes reaction with triazolinediones as well as bistriazolinediones at room temperature, and gives novel small molecules and polymers via Diels–Alder-ene and double Diels–Alder reactions. Polymerization of triazolinediones with *trans*-stilbene and *trans*-3,3-dichloro-1-phenyl-1-propene<sup>50,51</sup> also gave polymers via Diels–Alder-ene and double Diels–Alder reactions. We have also reported the polymerization reaction of 2-methoxy-4-propenylphenyl methylcarbamate,<sup>38</sup> which gives polymers by Diels–Alder-ene reactions pathways.

Although the synthesis and application of optically active polymers have been studied a long time ago, more attention has been paid to this topic recently.<sup>52–55</sup>

In previous articles, we have reported the synthesis of two optically active polymers via continuous Diels–Alder-ene reactions for the first time.<sup>56,57</sup> In this article, we wish to report the synthesis of new optically active polymers containing four chlorine atoms via the above novel method. These novel polymers have flame-retardant properties as well as being thermally stable.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Fluka Chemical Co., Aldrich Chemical Co., and Riedel-deHaen AG. 4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD) (**8**) and bis-triazolinediones (**11**) and (**12**) were prepared according to published procedures.<sup>38</sup> DMAc (*N,N*-dimethylacetamide) was dried over BaO and then was distilled under reduced pressure. Chloroform was washed with wa-

ter, dried over CaCl<sub>2</sub>, and then distilled at normal pressure.

### Techniques

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR, 90 MHz, 250 MHz) spectra were recorded on either a Varian EM-390 or Bruker Advance DPX 250-MHz instrument. 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 Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave numbers (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. Differential Scanning Calorimetric (DSC) data for polymers were taken on a Mettler TA4000 System instrument under N<sub>2</sub> atmosphere at a rate of 20°C/min. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Mettler TA4000 System. Elemental analysis were performed by Research Institute of Petroleum Industry, Tehran, I.R. Iran.

### Preparation of *N*-(tetrachloro phthaloyl) *L*-Leucine (**4**)

Into a 250-mL round-bottomed flask 2.0 g (7.00 × 10<sup>-3</sup> mol) of tetrachloro phthalic anhydride (**1**), 0.92 g (7.00 × 10<sup>-3</sup> mol) of *L*-leucine (**2**), 100 mL of toluene, 1.0 mL (7.00 × 10<sup>-3</sup> mol) of triethylamine, and a magnetic stirrer were placed. The stirrer was started, and the mixture was refluxed under a Dean-Stark apparatus for 10 h. The solvent was removed under reduced pressure, and the remaining solid was dried. Five milliliters of concentrated HCl was added, and a pale-yellow precipitate was formed, filtered off, and dried, to give 2.8 g (100%) of compound (**4**). m.p. = 134–136°C, [α]<sub>D</sub><sup>25</sup> = -33.78° (0.521 g in 100 mL DMF); IR (KBr): 3300–3000 (m, br), 2950 (s), 2800 (m), 1780 (s), 1780 (s), 1740–1700 (s, br), 1490 (s), 1470–1450 (s, br), 1390 (s), 1370–1350 (s,br), 1280 (s), 1230 (w), 1200 (m), 1160 (s), 1100–1080 (s, br), 1070 (s), 1010 (m, br), 930–920 (m, br), 910 (m), 800–780 (s), 760 (m), 740 (s), 650 (sh), 620 (m) cm<sup>-1</sup>; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS, 250 MHz): δ 0.92–0.95 (3H), 1.57 (m, 1H), 1.84–1.94 (m, 1H), 2.12–2.22 (m, 1H), 4.84–4.91 (dd, 1H, *J* = 6.0 Hz), 13.37 (br, 1H) ppm. Anal. calcd. for

$C_{14}H_{11}Cl_4NO_4$ : 42.14% C; 2.78% H; 3.51% N.  
Found: 42.00% C; 2.80% H; 3.40% N.

**Preparation of N-(tetrachloro phthaloyl) L-Leucine Acid Chloride (5)**

0.5 g ( $1.25 \times 10^{-3}$  mol) of (4) was placed into a 25-mL round-bottomed flask equipped with a condenser and 2.0 mL ( $1.68 \times 10^{-2}$  mol) of freshly distilled thionyl chloride (excess amount) was added. The mixture was heated on a water bath up to 50°C, until the suspension mixture was converted to a clear solution. After dissolution was completed, the solution was stirred for 1.5 h. The excess amount of thionyl chloride was removed under reduced pressure, to leave a viscous liquid which was crystallized in  $CCl_4$  (as solvent) and *n*-hexane (as nonsolvent) to give 0.49 g (93.5%) of white crystals of (5), m.p. = 118–120°C.  $[\alpha]_D^{25} = -30.91^\circ$  (0.537 g in 100 mL DMF); IR (KBr): 2950 (m), 2900 (sh), 2880 (w), 2850 (w), 1800 (s), 1780 (s), 1720 (s), 1570 (w), 1460 (m), 1450 (w), 1380 (s), 1370 (s), 1350–1340 (s,br), 1290 (w), 1230 (w,br), 1200 (m), 1160 (m), 1120 (w), 1090 (m), 1060 (m), 990 (m), 970 (w), 900 (m), 850 (m), 830 (m), 790 (m), 770 (s), 730 (s), 630 (w), 600 (m)  $cm^{-1}$ ;  $^1H$ -NMR ( $CCl_4$ , TMS, 90 MHz):  $\delta$  0.80–1.10 (d, 6H,  $J = 4.5$  Hz); 1.20–2.50 (m, br, 3Hz); 5.10–5.30 (dd, 1H,  $J_1 = 9.0$  and  $J_2 = 6.0$  Hz). Anal. calcd. for  $C_{14}H_{10}Cl_5NO_3$ : 40.24% C; 2.41% H; 3.35% N. Found : 40.00% C; 2.40% H; 3.00% N.

**Preparation of 2-Methoxy-4-(1-propenyl)phenyl-2(S)-N-(tetrachloro phthaloyl)-4-methyl pentanoate (Chiral Monomer) (7)**

To a solution of 0.28 g ( $1.69 \times 10^{-3}$  mol) of isoeugenol (6) in 4 mL of dry chloroform into a two-necked round-bottomed flask, 0.49 g ( $1.17 \times 10^{-3}$  mol) of optically pure compound (5) in 4 mL of dry chloroform was added dropwise at 0°C in a period of 30 min. At the end of addition, the reaction mixture was stirred at 0°C for 1 h, and then 0.50 mL ( $6.92 \times 10^{-3}$  mol) of triethylamine in 2 mL of dry chloroform was added dropwise in a period of 30 min. After completion of addition, the reaction was stirred at room temperature for 20 h. Finally, it was refluxed for 2 h. Extraction, after addition of 20 mL chloroform to the reaction mixture was done according to the following manner: (a)  $2 \times 20$  mL of distilled water, (b)  $5 \times 10$  mL of 1% KOH solution (W/V), and (c) washing of the organic phase with distilled water until the extracted aqueous phase becomes neutral. The organic phase was dried over sodium sulfate and evaporated with rotary evapo-

rator to leave 0.61 g (96.5%) of yellow solid. Recrystallization from hot ethanol as solvent and water as nonsolvent gave yellow crystals of (7), m.p. = 78–80°C.  $[\alpha]_D^{25} = -22.64^\circ$  (0.530 g in 100 mL DMF). IR (KBr): 3000 (sh), 2950 (m), 2850 (m), 1780–1760 (s,br), 1720 (s), 1590 (m), 1500 (s), 1460–1440 (m,br), 1390 (s), 1370–1350 (s), 1300 (w), 1260 (m), 1200–1180 (m,br), 1140–1120 (m,br), 1030 (m), 960 (m), 860–840 (m,br), 780 (w), 770 (s), 760 (sh), 730 (s)  $cm^{-1}$ ;  $^1H$ -NMR ( $CCl_4$ , TMS, 90 MHz):  $\delta$  0.8–2.8 (m, 12H), 3.7–4.0 (d, 3H), 5.1–5.4 (dd, 1H,  $J_1 = 9.0$  and  $J_2 = 6.0$  Hz), 6.0–6.5 (m, 2H), 6.8–7.1 (m, 3H). Mass for  $C_{24}H_{21}Cl_4NO_5$ : *m/e* (rel. intensity): 549 (M+6, 0.2); 547 (M+4, 0.8); 545 (M+2, 1.7); 543 (M<sup>+</sup>, 1.2); 380 (0.9); 360 (0.2); 358 (2.0); 356 (8.9); 354 (18.0); 352 (14.1); 324 (0.4); 304 (0.1); 302 (1.3); 300 (5.5); 298 (11.1); 296 (8.8); 292 (0.2); 290 (1.4); 288 (6.1); 286 (12.5); 284 (10.1); 248 (0.2); 246 (0.6); 244 (1.5); 242 (3.0); 240 (2.5); 220 (0.4); 218 (0.6); 216 (1.7); 214 (3.4); 212 (2.7); 164 (100.0); 163 (5.2); 117 (1.2); 116 (0.9); 75 (0.4); 56 (2.4); 41 (35.6). Anal. calcd. for  $C_{24}H_{21}Cl_4NO_5$ : 52.87% C; 3.88% H; 2.57% N. Found : 52.80% C; 4.00% H; 2.20% N.

**Preparation of Model Compound (10)**

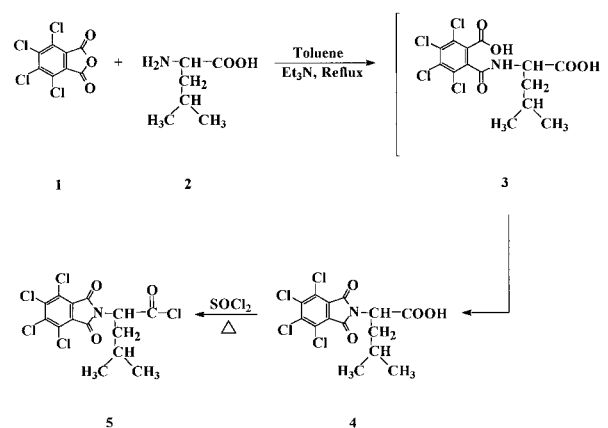
Into a 25-mL round-bottomed flask was placed a solution of 0.30 g ( $5.54 \times 10^{-4}$  mol) of (7) in 5 mL of methylene chloride and 0.19 g ( $1.10 \times 10^{-3}$  mol) of PhTD (8) in 9 mL of methylene chloride was added dropwise at room temperature. As soon as the PhTD solution was added, its red color was diminished. The mixture was stirred for overnight (15 h). At the end of reaction time the solvent was removed under reduced pressure and the residue was dried under vacuum, to give 0.48 g (98.0%) of white solid. Recrystallization from hot ethanol, gave white crystals of the model compound (10), m.p. > 165°C (dec.).  $[\alpha]_D^{25} = -8.40$  (0.524 g in 100 mL DMF). IR (KBr): 3500 (m, br), 3200–3050 (m, br), 2950 (m), 2900 (sh), 2880 (w), 1780–1760 (s, br), 1740–1700 (s, br), 1600–1590 (w), 1520–1500 (s, br), 1430–1340 (m, br), 1270–1260 (w, br), 1200–1120 (w, br), 1050 (w), 1020 (w), 920–910 (w, br), 760 (w, br), 730 (w), 670 (w), 660–580 (w, br)  $cm^{-1}$ .  $^1H$ -NMR (DMSO-*d*<sub>6</sub>, TMS, 250 MHz):  $\delta$  0.92–0.96 (q, 6H), 1.23–1.26 (d, 3H,  $J = 5.0$  Hz), 1.63 (br, 1H), 1.97 (br, 1H), 2.24 (br, 1H), 3.71 (s, 3H), 4.83–4.86 (q, 1H,  $J = 5.0$  Hz), 5.30–5.35 (dd, 1H,  $J_1 = 9.0$  and  $J_2 = 6.0$  Hz), 5.44 (s, 1H), 7.13 (s,1H), 7.48–7.58 (m, 10H), 8.12 (s, 1H), 10.72 (br, 1H). Anal. calcd. for  $C_{40}H_{31}Cl_4N_7O_9$ : 53.65% C; 3.49% H; 10.95% N. Found: 53.60% C; 3.60% H; 10.40% N.

**Polymerization of Bis(*p*-3,5-dioxo-1,2,4-triazoline-4-ylphenyl) methane (BPMTD) (11) with Monomer (7)**

Into a 25-mL round-bottomed flask, 0.20 g ( $3.67 \times 10^{-4}$  mol) of monomer (7) and 0.13 g ( $3.67 \times 10^{-4}$  mol) of monomer BPMTD (11) were mixed and 0.9 mL of dry DMAc was added. After about 6 min, two monomers were dissolved and the solution became pale brown and viscous. The mixture was stirred at room temperature for overnight (15 h). The resulting viscous solution was precipitated in 50 mL of distilled water, filtered off, and dried to leave 0.30 g (90.9%) of yellow solid.  $[\alpha]_D^{25} = -10.19^\circ$  (0.530 g in 100 mL DMF);  $[\eta]_{inh}^{25} = 0.12$  dL  $\cdot$  g $^{-1}$  (0.503 g/dL in DMF); IR (KBr): 3450 (sh), 3300–3200 (m, br), 2950 (m), 2900 (m), 2850 (sh), 1780–1760 (s, br), 1730–1710 (s, br), 1600 (m, br), 1510 (s), 1420–1400 (m, br), 1390–1380 (m), 1370 (sh), 1350 (sh), 1300 (w), 1260 (w), 1200 (w), 1140 (w), 1120 (w), 1030–1010 (w, br), 960 (w), 850 (w), 780 (sh), 760 (sh), 740 (m)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO- $d_6$ , TMS, 90 MHz):  $\delta$  0.80–2.70 (m, br); 2.80–4.60 (m, br); 4.70–5.00 (br); 5.20–5.60 (br); 6.90–8.00 (m, br); 8.10–8.30 (s, br); 10.30–11.00 (br). Anal. calcd. for  $\text{C}_{41}\text{H}_{31}\text{Cl}_4\text{N}_7\text{O}_9$ : 54.26% C; 3.44% H; 10.80% N. Found: 54.40% C; 3.90% H; 8.90% N.

**Polymerization of 1,6-Bis-(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (HMTD) (12) with Monomer (7)**

Into a 25-mL round-bottomed flask, 0.16 g ( $2.91 \times 10^{-4}$  mol) of monomer (7) and 0.08 g ( $2.91 \times 10^{-4}$  mol) of monomer HMTD (12) were mixed and 0.8 mL of dry DMAc was added. In about 12 min two monomers were dissolved completely, and the solution became pale orange and viscous. The solution was stirred overnight (15 h) at room temperature and the resulting polymer was precipitated in 50 mL of distilled water, filtered off, and dried, to give 0.22 g (90.0%) of white solid.  $[\alpha]_D^{25} = -19.73^\circ$  (0.294 g in 100 mL DMF);  $[\eta]_{inh}^{25} = 0.07$  dL  $\cdot$  g $^{-1}$  (0.405 g/dL in DMF); IR (KBr): 3490 (m), 3300–3050 (m, br), 2950 (m), 2900 (m), 2850 (w), 1780–1760 (s, br), 1720–1680 (s, br), 1600–1590 (w, br), 1510 (m), 1460–1440 (m, br), 1420 (w), 1260–1240 (w, br), 1200 (w), 1150 (w, br), 1120 (w, br), 1030 (w), 960 (w, br), 850 (w, br), 780 (sh), 760 (sh), 740 (m)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO- $d_6$ , TMS, 90 MHz):  $\delta$  0.80–2.70 (m, br); 3.00–4.00 (m, br); 5.10–5.40 (br); 6.40–6.60 (s, br); 7.00–7.30 (m, br); 9.70–10.40 (br). Anal. calcd. for  $\text{C}_{34}\text{H}_{33}\text{Cl}_4\text{N}_7\text{O}_9$ : 49.47% C; 4.03% H; 11.88% N. Found: 50.60% C; 4.50% H; 9.40% N.



**Scheme 1**

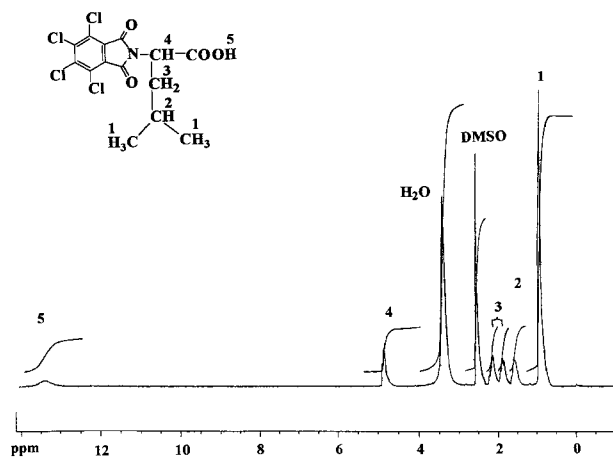
## RESULTS AND DISCUSSION

In previous articles<sup>56,57</sup> we reported the synthesis of some novel optically active polymers that were prepared through synchronous Diels–Alder and ene reactions of newly synthesized monomers with bis triazolinediones. Also, the mechanism of formation of only one diastereomer through these type of the reactions have been discussed (100% d.e.). In this article, we wish to report for the first time the preparation and polymerization of another new monomer that gives fire retardancy and thermal properties to its corresponding optically active heterocyclic polyimides.

The reaction of tetrachlorophthalic anhydride (1) with L-leucine (2) produces the amic acid (3) (Scheme 1).

Amic acid (3) was not isolated, and was dehydrated *in situ* to give its corresponding imide (4) in high yield. The compound (4) was separated and identified by high-field  $^1\text{H-NMR}$  (Fig. 1), IR spectroscopy, and also elemental analysis. The white crystals of acid chloride (5) were prepared from the reaction of (4) with thionyl chloride under neat reaction condition. The structure of (5) was characterized by spectroscopic methods ( $^1\text{H-NMR}$ , IR) and elemental analysis. The acid chloride (5) was reacted with a mixture of *cis* and *trans* isoeugenol (6), and the chiral monomer (7) obtained in high yield (Scheme 2).

The purity and structure of the new chiral monomer (7) were confirmed by  $^1\text{H-NMR}$  and elemental analysis. As we used *cis* and *trans* mixture of isoeugenol (6), two diastereomer must be formed in the course of the reaction, that is L-*cis* and L-*trans*. The presence of these two diastereomers could be observed by  $^1\text{H-NMR}$  spectrum (Fig. 2). The methoxy group is assigned as two

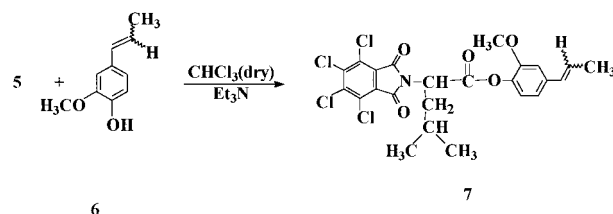


**Figure 1**  $^1\text{H-NMR}$  (250 MHz) spectrum of compound (4) in  $\text{DMSO-}d_6$  at rt.

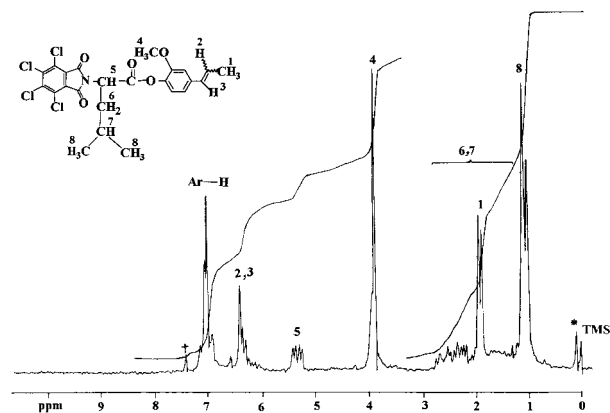
singlets between 3.7–4.0 ppm. This evidence proves the presence of two diastereomers. The mixture of diastereomeric forms of chiral monomer (7) was used in the next reactions without separation.

To obtain more information about polymerization reaction, we prepared the model compound (10). The reaction of chiral monomer (7) with phenyl triazolinedione (8) was performed in dichloromethane at room temperature, and the compound (10) was obtained in high yield with 100% conversion. This reaction passes through a two-step pathway. The first step is a Diels–Alder reaction between (7) as a diene, and (8) as a dienophile. Stereochemical studies that have been mentioned before<sup>57</sup> reveal that both of diastereomeric forms (7) (*L-cis* and *L-trans*) produce only one reactive diastereomer as an intermediate (9), shown in Scheme 3.

This intermediate (9) is so reactive that it undergoes ene reaction simultaneously to produce model compound (10). The proposed mechanism for the next step is the formation of an aziridinium imide (AI), which is syn and at the same side of the allylic hydrogen. High-field  $^1\text{H-NMR}$  studies from the crude product of (10) reveals the formation of only one diastereomer (Fig. 3). This



**Scheme 2**



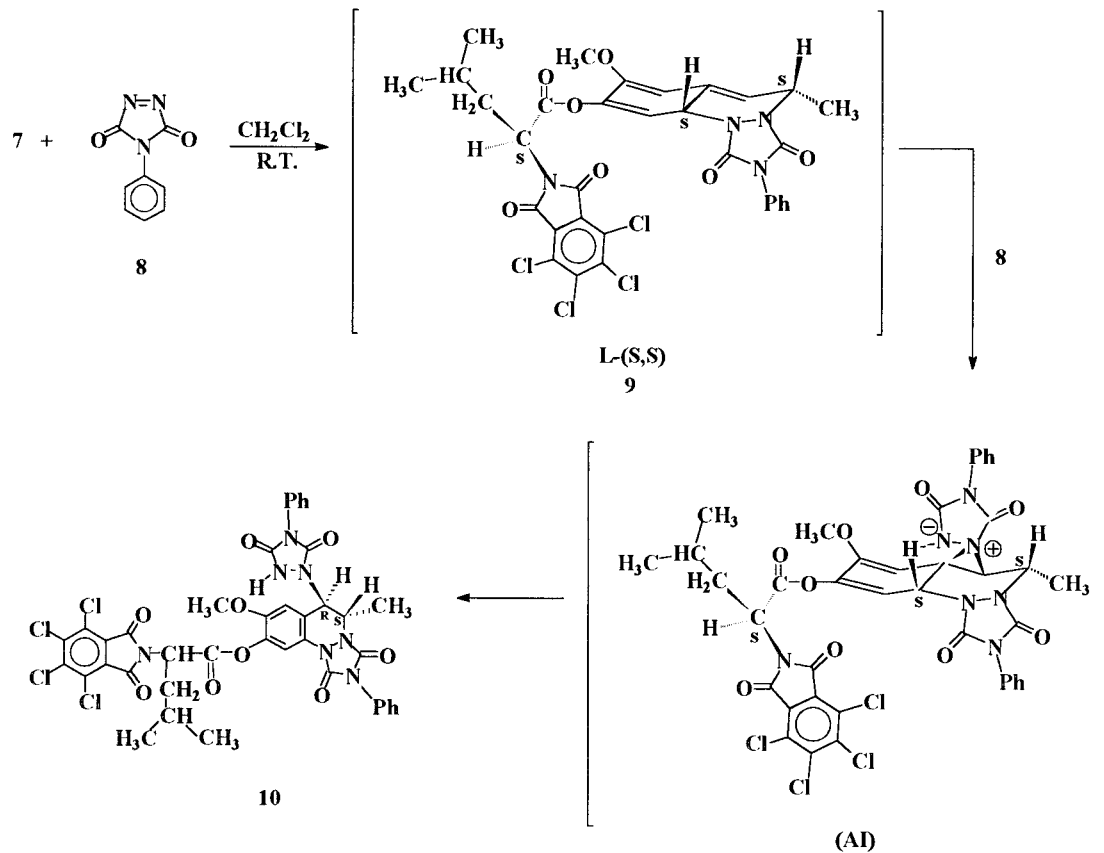
**Figure 2**  $^1\text{H-NMR}$  (90 MHz) spectrum of compound (7) in  $\text{CCl}_4$  at rt.\* This peak is due to silicon grease.

claim is due to the presence of only one doublet of doublet between 5.30–5.35 ppm related to H-8, which is also proved by its expanded  $^1\text{H-NMR}$  spectra (Fig. 4). The expanded region of the  $^1\text{H-NMR}$  spectra show that there is one doublet at 1.23–1.26 ppm, which is assigned to H-1 (Fig. 5), and a singlet at 3.71 ppm, which belongs to H-6 (Fig. 6).

### Polymerization Reactions

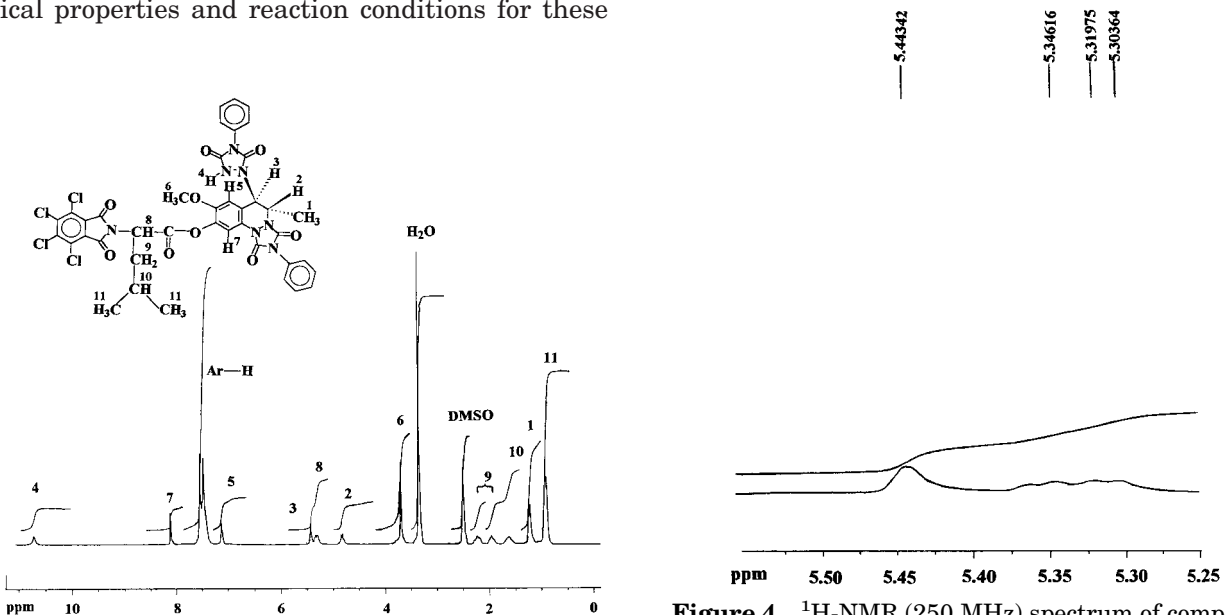
The step-growth polymerization reaction of monomer BPMTD (11) with chiral monomer (7) (1 : 1 molar ratio) was carried out in DMAc solution at room temperature (Scheme 4). The reaction is very fast and gives a viscous yellow solution.

The resulting solution was precipitated in water and the polymer (13) obtained as a yellow solid. The structure of the resulting polymer was characterized by  $^1\text{H-NMR}$  and IR spectra, which are in agreement with structure (13).  $^1\text{H-NMR}$  spectrum of the polymer (13) is broad but, it resembles the spectrum of the model compound (10). Elemental analysis of polymer (13) also confirms its structure. The polymer (13) shows optical rotation and, therefore, is optically active. The reaction of monomer HMTD (12) with chiral monomer (7) was also performed in DMAc solution at room temperature, and the resulting polymer (14) was obtained as a white solid. IR and  $^1\text{H-NMR}$  spectra of polymer (14) resemble those of the model compound (10); therefore, structure (14) was assigned to it (Scheme 4). The polymer (14) also shows optical rotation. The above polymers are formed via Diels–Alder–ene reaction, and elemental analysis data confirm their structure. A small pellet of the above polymers was made by compression molding, and the resulting pellets



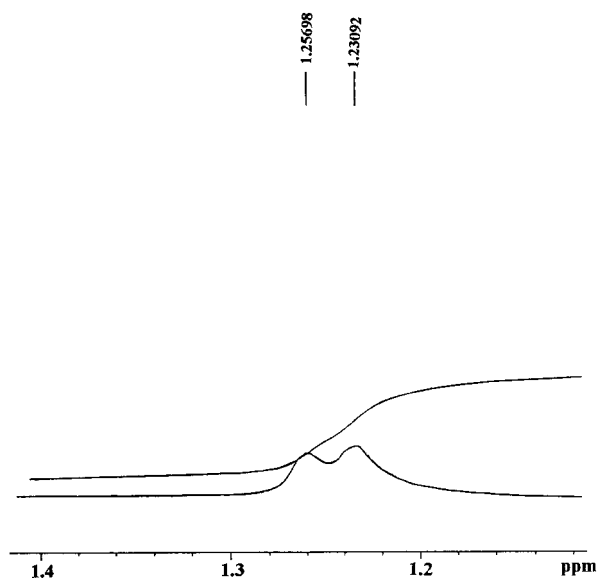
Scheme 3

were placed on the flame, they catch fire and immediately act as self-extinguisher; therefore, they have flame-retardant properties. Some physical properties and reaction conditions for these



**Figure 3**  $^1\text{H-NMR}$  (250 MHz) spectrum of compound (10) in  $\text{DMSO-}d_6$  at rt.

**Figure 4**  $^1\text{H-NMR}$  (250 MHz) spectrum of compound (10) in  $\text{DMSO-}d_6$  at rt. Expanded region for the proton #8.

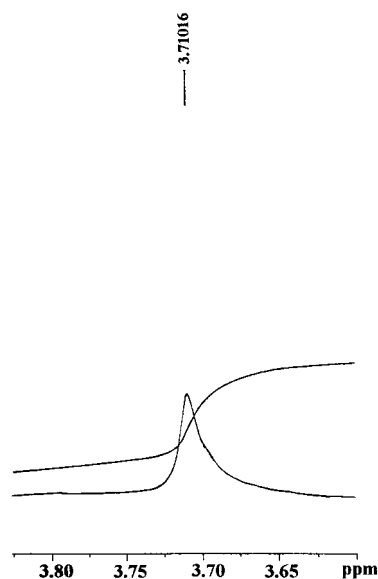


**Figure 5**  $^1\text{H-NMR}$  (250 MHz) spectrum of compound (10) in  $\text{DMSO-}d_6$  at rt. Expanded region for the proton #1.

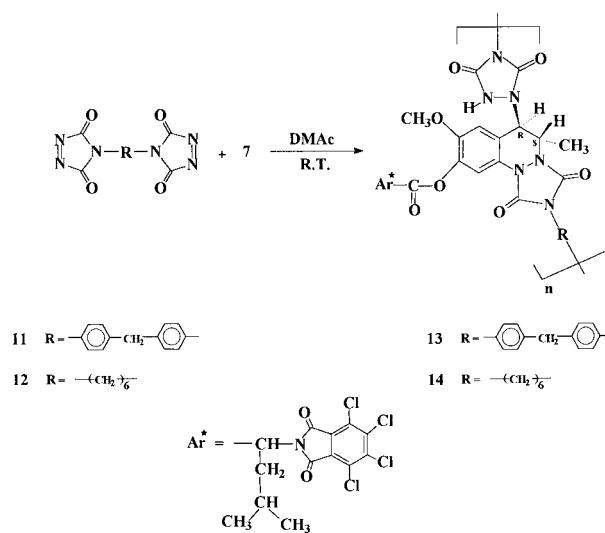
novel optically active polymers are summarized in Tables I and II.

### Thermal Properties

The thermal behavior data of the polymers (13) and (14) were obtained from their DSC and TGA (Figs. 7 and 8) thermograms. The DSC Thermograms (Fig. 7) show that they have almost the



**Figure 6**  $^1\text{H-NMR}$  (250 MHz) spectrum of compound (10) in  $\text{DMSO-}d_6$  at rt. Expanded region for the proton #6.



**Scheme 4**

same differential scanning calorimetric characteristics. For polymer (13), there is an endothermic transition at  $287^\circ\text{C}$ , which would relate to its glass transition temperature ( $T_g$ ), and an exothermic transition with a maxima at  $353^\circ\text{C}$  owing to decomposition of the polymer through the bond breakage. These transition could be seen for polymer (14), first at  $229^\circ\text{C}$ , and second at  $342^\circ\text{C}$ . TGA thermograms (Fig. 8) of the above polymers reveal that they are thermally stable. Polymers (13) and (14) show the 5% weight loss at 298

**Table I** Solubility of Polymers (13) and (14)<sup>a</sup>

Solvent	Polymer (13)	Polymer (14)
$\text{H}_2\text{SO}_4$	+	+
Acetic acid	-	+
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	-	-
<i>n</i> -Hexane	-	-

+ : Soluble at room temperature; - : Insoluble.

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

**Table II** Reaction Conditions and Some Physical Properties for Polymers (13) and (14)

Polymer	(13)	(14)
Reaction solvent	DMAc	DMAc
Fading time <sup>a</sup>	6 min	12 min
Nonsolvent	Water	Water
Yield %	90.9	90.0
$T_g$	287°C	229°C
$T_w^b$	298°C	275°C
$[\alpha]_D^{25}$	-10.19 <sup>c</sup>	-19.73 <sup>e</sup>
$[\eta]_{inh}^{25}$ (dL · g <sup>-1</sup> )	0.12 <sup>d</sup>	0.07 <sup>f</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 0.530 g/dL in DMF at 25°C.

<sup>d</sup> Measured at a concentration of 0.503 g/dL in DMF at 25°C.

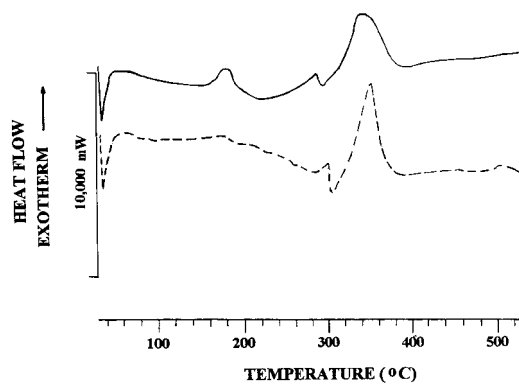
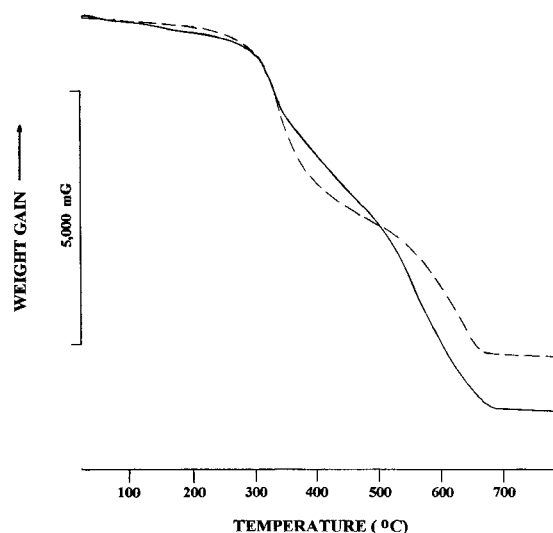
<sup>e</sup> Measured at a concentration of 0.294 g/dL in DMF at 25°C.

<sup>f</sup> Measured at a concentration of 0.405 g/dL in DMF at 25°C.

and 275°C, respectively. The residual weight percents for these polymers at 625°C are 5.1 and 4.4%.

## CONCLUSIONS

Novel optically active monomer (7) has been synthesized in three steps. This monomer reacts very fast with 2 mol of PhTD, and gives only one diastereomer. The reaction of this monomer with bistriazolinediones gave novel, optically active, heterocyclic polyimides via tandem Diels-Aldere reactions. The resulting polymers are thermally stable and flame retardant.

**Figure 7** DSC thermograms of polymers (13) (---) and (14) (—).**Figure 8** TGA thermograms of polymers (13) (---) and (14) (—).

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