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ORIGINAL ARTICLE

Synthesis and characterization of novel organosoluble and optically active aromatic polyesters containing L-methionine and phthalimide pendent groups

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Abstract 5-(4-Methylthio-2-phthalimidylbutanoylamino) isophthalic acid (**5**) as a novel diacid monomer containing phthalimide and flexible chiral groups was prepared by dehydration of L-methionine and phthalic anhydride followed by reacting with thionyl chloride and then treating with 5-aminoisophthalic acid (5AIPA) in dry *N,N*-dimethylacetamide (DMAc). A series of novel polyesters (PEs) containing phthalimide group was prepared by the reaction of diacid monomer **5** with several aromatic diols via direct polyesterification with tosyl chloride/pyridine/dimethylformamide (DMF) system as condensing agent. The resulting new polymers were obtained in good yields and inherent viscosities ranging between 0.21 and 0.51 $\mathrm{dLg^{-1}}$ were characterized with FT-IR, ^{1}H NMR, elemental and thermogravimetric analysis techniques. These polymers are readily soluble in polar organic solvents such as DMAc, DMF, dimethyl sulfoxide and protic solvents such as sulfuric acid. Specific rotation experiments demonstrate the optical activity induction due to successful insertion of L-methionine in the structure of pendent groups. Thermogravimetric analysis showed that the 10% weight loss temperature in a nitrogen atmosphere were more than 315°C, which indicates that the resulting PEs have good thermal stability.

Keywords L-methionine · Optically active polyester · Direct polycondensation

Introduction

Polyesters (PEs) are an important class of high performance and engineering materials, which find use in a number of diverse applications such as aviation, automobile and electronic industries due to their high temperature and chemical resistance (Zuev and Bertini 2006; Chern and Huang 1998; Chen at al. 2007). Among the PEs, aromatic ones have an importance as engineering plastics (Bohme et al. 2006; Mallakpour and Kolahdoozan 2007; Mallakpour and Rafiee 2007; Mallakpour and Rafiemanzelat 2007). On the other hand, during the last decade, resolution of racemic compounds attracted a great attention in analytical chemistry, especially in pharmaceutical analysis, because each enantiomer of the chiral drugs exhibits great differences in pharmacological, pharmacodynamic, and toxicological manners (Lancet and Kafri 2004; Huan-de et al. 2007; Millot 2003; Yoshimi et al. 2007). High-performance liquid chromatography (HPLC) using a chiral stationary phase is one of the most popular methods for the direct separation of chiral compounds (Kanazawa et al. 2006; Hohenesche et al. 2004; Davankov et al. 2003). Hitherto, several optically active polymers have been used for enantiomeric HPLC separation as the chiral stationary phase (Davankov et al. 2004; Furuta et al. 2000).

Although aromatic PEs with excellent pattern of physical and chemical properties are special candidates for chromatographic purposes, high melting or glass-transition temperatures and restricted solubility in organic solvents, due to their rigid structure, have limited their processability (Zuev and Bertini 2006; Mallakpour and Kolahdoozan 2007; Mallakpour and Rafiee 2007; Mallakpour and Rafiemanzelat 2007). In this regard, they exert a useful strategy, such as the use of monomer containing pendent groups, aimed for the improvement of solubility and

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processability of PEs, without significant decrease of thermal and mechanical properties (Tamami et al. 2004).

L-Methionine is one of the most essential amino acids that plays an important role in intracellular activities, such as synthesis of cysteine, carnitine, taurine, phosphatidylcholine, and other phospholipids (Wooley and Ziemer 2007), as well as in clinical applications (Zhang et al. 2007; Gu et al. 2006; Ghosh et al. 2006; Roje 2006). Furthermore radiolabeled L-methionine has been used in single-photon emission computed tomography (SPECT) and positron emission tomography (PET) methods for improvement of magnetic resonance imaging (MRI) techniques (Langen et al. 2006). Wide applications of methionine in various areas has been made it one of the most important industrial amino acids with a production of about 500,000 tons per year (Wittmann et al. 2006).

Over the past several years, sulfur-containing polymers have become increasingly more important due to their interesting properties such as reasonable hydrophilicity, complex-forming capability (Gal et al. 2007), high mechanical properties (Celli et al. 2007) and elevated refractive indexes (Mikroyannidis et al. 2004), which make them useful for a wide range of applications. In addition, because the sulfur atom in L-methionine can be converted to sulfoxide or sulfone (Schfneich 2005) derivatives, polymers containing L-methionine moieties are of interest in that they may similarly be converted to various functional polymers.

Because of the importance of optically active polymers and polymers with amino acid (especially L-metionine) moieties, in continuation of our study for preparation of optically active polymers (Mallakpour et al. 2003; Mallakpour and Kowsari 2004a, b; Mallakpour and Rafiemanzelat 2004; Mallakpour and Zamanlou 2004, Mallakpour and Kowsari 2005; Mallakpour and Rafiemanzelat 2005; Mallakpour and Kolahdoozan 2007; Mallakpour and Rafiee 2007; Mallakpour and Rafiemanzelat 2007), in this paper a new series of thermally stable and optically active aromatic PEs were synthesized using novel chiral diacid **5** containing L-methionine moiety in pendent group and several aromatic diols. *N,N*-dimethylformamide (DMF), tosyl chloride (TsCl) and pyridine (Py) system have been used as the condensing agents for direct polyesterification.

Materials and methods

Materials

All chemicals were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck. Phthalic anhydride (**1**) and bisphenol A **(6h)** were purified by recrystallization from chloroform and acetic acid-water, respectively. The other diols used were obtained without further purification.

Instruments

Proton nuclear magnetic resonance ^{1}HNMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument (Bruker, Rheinstetten, Germany) using DMSO-d$_6$ as solvent (by Sharif University of Technology). The FT-IR adsorption spectra were recorded on a Nicole Impact 400$_D$ IR spectrophotometer with KBr pallets. Vibration bands were reported as wavenumber (cm^{-1}). The band intensities were classified as weak (w), medium (m), strong (s), broad (br) and shoulder (sh). Inherent viscosities of polymer solution (0.5% w/v) in DMF were determined at 25°C by a standard procedure using a Cannon Fenske Routine viscometer (Cannon, Mainz, Germany). The specific rotations were measured by a Jasco polarimeter (Japan). Thermogravimetric analysis (TGA) data for the polymers were taken on Perkin-Elmer TGA 7 (Perkin-Elmer, Jugeshein, Germany) in nitrogen atmosphere at a heating rate of 10°C/min at the Research Institute of Petroleum Industry (Tehran, Islamic Republic of Iran). Elemental analyses were performed at Malek-Ashtar University of Technology (Tehran, Islamic Republic of Iran). Melting points were taken with a Gallenham melting point apparatus.

Synthesis of monomer

4-Methylthio-2-phthalimidylbutanoic acid (3)

One gram of phthalic anhydride (**1**) (6.75 mmol), 1.00 g (6.75 mmol) of L-methionine (**2**), 10 mL of acetic acid and a stirring bar were placed in a 25-mL round-bottomed flask. The mixture was refluxed for 24 h and then distilled under reduced pressure and trickled into a mixture of 50 mL water and 5 mL concentrated hydrochloric acid. A white precipitate formed was filtered and dried to give 1.85 g (98%) of imide acid **3**, mp 128–130°C, Lit: 129–131°C (Zeng et al. 2004) $[\alpha]_D^{25} = -24.72°$ (0.05 g in 10 mL of DMF).

FT-IR (KBr): 3323 (s, br), 2915 (m), 1757 (s), 1701 (s), 1393 (s), 1212 (m, sh), 1169 (m, sh), 1102 (m, sh), 1019 (m, sh), 890 (m, sh), 865 (m), 720 (s, sh), 623 (m), 529 (m, sh).

4-Methylthio-2-phthalimidylbutanoyl chloride (4)

Imide acid **3** weighing 1.5 g (5.37 mmol), 0.6 mL (8.4 mmol) of thionyl chloride and 5 mL of dichloromethane were placed in a 25-mL round-bottomed flask. The mixture was refluxed for 3 h. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed three times with *n*-hexane, producing 1.4 g (96%) of slightly yellow solid **4**. mp = 115–117°C $[\alpha]_D^{25} = -17.35°$ (0.05 g in 10 mL of DMF). FT-IR (KBr): 2900 (m), 1777(m, sh), 1715 (s, br), 1465 (m, sh), 1439 (m, sh), 1387 (s), 1287 (m), 1196 (m, sh), 1105 (s, sh), 993 (m, sh), 884 (m, sh), 713 (s, sh), 635 (m), 530 (w).

*5-(4-Methylthio-2-phthalimidybutanoylamino)isophthalic acid (**5**)*

A solution of 1.2 g (4.03 mmol) of 5AIPA and 5 mL of dry DMAc was placed in a 25-mL round-bottomed flask fitted with a magnetic stirrer. The reaction mixture was heated in an oil bath at 80°C for 0.5 h and cooled to room temperature (RT). The mixture of 1.2 g (4.03 mmol) of acid chloride **4** in 5 mL dry DMAc was added to this solution and stirred for 3 h at RT. A volume of 0.55 mL of triethylamine (TEA) was added to this mixture and heated at 80°C for additional 4 h. The solution was poured into a mixture of 50 mL water and 5 mL concentrated hydrochloric acid. The white precipitate was collected by filtration and washed thoroughly with water and dried at 70°C for 10 h, to give 1.52 g (95%) of compound **5**. Mp > 240°C dec. $[\alpha]_D^{25} = -23.05°$ (0.05 g in 10 ml of DMF). ^{1}H-NMR (500 MHz, DMSO-d$_6$): δ 2.05 (s, 3H), 2.33–2.56 (m, 4H), 5.05–5.06 (dd, br, 1H, $J_1 = 9.45$ Hz, $J_2 = 4.1$ Hz), 7.88–7.94 (m, 4H), 8.18 (s, 1H), 8.42 (s, 2H), 10.26 (s, 1H), 13.25 (s, 2H). ^{13}C-NMR (125 MHz, DMSO-d$_6$): 15.45 (CH$_3$), 28.84 (CH$_2$), 31.05 (CH$_2$), 53.19 (CH, chiral center), 124.15 (CH, aromatic), 125.32 (CH, aromatic), 125.81 (CH, aromatic), 132.49 (C, aromatic), 132.61 (CH, aromatic), 135.43 (C, aromatic), 140.10 (C, aromatic), 167.24 (C=O, imidic), 168.27 (C=O, acidic), 168.57 (C=O, amidic). IR (KBr): 3349 (s, br), 3089 (s), 1775 (s), 1713 (s, br), 1606 (s), 1551 (s), 1385 (s), 1203 (s, br), 1104 (m), 1086 (m), 905 (m), 876 (m), 759 (m), 720 (s), 666 (m), 530 (w).

Polymerization reactions

The PEs were prepared by the following procedure: for synthesis of polymer **7h**, a Py (0.50 mL) solution of tosyl chloride (TsCl) (0.26 g, 1.13 mmol), after 30 min stirring at RT, was treated with DMF (0.09 mL, 1.22 mmol) for 30 min and the resulting solution was added dropwise to a solution of diacid **5** (0.100 g, 0.226 mmol) in Py (0.50 mL). The mixture was maintained at RT for 30 min and then to this mixture, a solution of bisphenol A (**6h**) (0.0516 g, 0.226 mmol) in Py (0.50 mL) was added dropwise and the whole solution was stirred at RT for 30 min and at 120°C for 2 h. As the reaction proceeded, the solution became viscous. Then the viscous liquid was precipitated in 30 mL of methanol to give 0.144 g of polymer **7h** (95%). The other PEs **7a–7g** were prepared by a similar procedure. Elemental analysis data of monomer, **PE7a** and **PE7h** as the typical samples are shown in Table 1.

PE7a: Off white solid; FT-IR (KBr): 3463 (w, br), 2918 (w), 1740 (m), 1717 (s), 1485 (m, sh), 1384 (m, sh), 1338 (m), 1193 (s), 1162 (m, sh), 1012 (w, sh), 719 (w, sh).

^{1}H-NMR (500 MHz, DMSO-d$_6$, TMS): 2.04 (s, 3H), 2.29–2.53 (m, 4H), 5.08–5.10 (m, 1H), 7.24–7.49 (m, 8H), 7.89–7.96 (m, 4H), 8.44 (s, 1H), 8.71 (s, 2H), 10.50 (s, 1H).

PE7b: Off white solid; FT-IR (KBr): 3353 (w), 3080 (w), 2917 (w), 1749 (s, sh), 1716 (s), 1674 (s), 1593 (s,), 1445 (m), 1384 (s), 1324 (m), 1200 (s), 1101 (m), 720 (w).

PE7c: Off white solid; FT-IR (KBr): 3365 (w, br), 3086 (w), 2920 (w), 1747 (m), 1717 (s, sh), 1609 (m), 1438 (m), 1384 (m), 1357 (m), 1249 (m), 1199 (s), 720 (m, sh).

PE7d: Off white solid; FT-IR (KBr): 3432 (s, br), 2919 (w), 1742 (m), 1717 (s, sh), 1633 (m), 1500 (m), 1384 (m), 1338 (w), 1212 (m), 1170 (s), 1101 (w), 720 (w), 529 (w).

PE7e: Off white solid; FT-IR (KBr): 3350 (w, br), 3071 (w), 2965 (w), 2920 (w), 1773 (w), 1718 (s, br), 1609 (w), 1552 (w), 1507 (m), 1381 (m), 1341 (m), 1195 (s), 1164 (m, sh), 1081 (m), 1012 (m), 715 (m).

PE7f: Off white solid; FT-IR (KBr): 3458 (w, br), 3074 (w), 2917 (w), 1743 (m), 1717 (s, sh), 1634 (m), 1600 (w), 1383 (m), 1195 (s), 1160 (s, sh), 1102 (m), 782 (w), 719 (w).

PE7g: Off white solid; FT-IR (KBr): 3359 (s, br), 3082 (w), 2919 (w), 1744 (m, sh), 1717 (s, sh), 1604 (w), 1551 (w), 1467 (m), 1383 (m, sh), 1337 (m), 1200 (s), 1105 (m), 1054 (m), 746 (w), 720 (w), 531 (w).

PE7h: Off white solid; FT-IR (KBr): 3355 (w, br), 3068 (w), 2966 (w), 2918 (w), 1776 (w), 1717 (s, br), 1603 (w), 1550 (w), 1504 (m), 1384 (m), 1337 (m), 1198 (s), 1168 (m, sh), 1078 (m), 1014 (m), 718 (m). ^{1}H-NMR (500 MHz, DMSO-d$_6$): 1.69 (s, 6H), 2.03 (s, 3H), 2.28–2.51 (m, 4H),

Table 1 Elemental analysis of monomer and typical PEs

Compound	Formula		Elemental analysis (%)		
			C	H	N
Monomer	$C_{21}H_{18}N_2O_7S$	Calcd	57.00	4.10	6.33
		Found	56.72	4.32	5.40
PE7a	$(C_{36}H_{30}N_2O_7S_2)_n$	Calcd	63.45	3.87	4.48
		Found	64.16	4.54	4.89
PE7h	$(C_{33}H_{24}N_2O_7S)_n$	Calcd	68.13	4.76	4.41
		Found	69.16	5.06	4.64

5.07 (m, 1H), 7.23–7.48 (m, br, 8H), 7.88–7.92 (m, 4H), 8.44 (s, 1H), 8.73 (s, 2H), 10.48 (s, 1H).

Results and discussion

Monomer synthesis

Condensation of compounds **1** with **2** in equimolar ratio under acetic acid reflux condition produced imide acid **3**. Reaction progress was followed using thin layer chromatography (TLC) technique and melting point of compound **3** was also compared with the literature (Zeng et al. 2004). The compound **3** was treated with thionyl chloride in dichloromethane to give corresponding acid chloride **4** in quantitative yield. Disappearance of broad peak around 2,400–3,400 cm^{-1} in FT-IR spectrum confirms the complete conversion of imide acid **3** to acid chloride **4**. The reaction of 5AIPA with compound **4** in DMAc in the presence of TEA gave the novel chiral diacid **5** in high yield. ^{1}H-NMR, ^{13}C-NMR (Fig. 1, 2) and FT-IR spectroscopies and elemental analysis confirm the chemical structure of diacid **5** (Scheme 1).

Polymer synthesis

Vilsmeier adduct was used as a condensing agent for the polymerization reaction of novel chiral diacid **5** with aromatic diols **6a–6h** which is illustrated in Scheme 2. Sulfonium salt (**I**) was prepared by dissolving TsCl in Py and stirring for 0.5 h (aging time) followed by addition of DMF and stirring for 0.5 h until Vilsmeier adduct (**II**) was formed, which has been suggested before (Higashi et al. 1984; Higashi and Tobe 2001; Mallakpour and Rafiee 2007; Mallakpour and Rafiemanzelat 2007; Mallakpour and Kolahdoozan 2007). The reaction mixture was transferred into a Py solution of diacid **5** for another 0.5 h then a solution of diol in Py was added and the whole reaction mixture kept at RT for 0.5 h and at 120°C for 2 h (Scheme 3). All the reaction parameters such as aging times, reaction time, temperature and molar ratio of chemical additives to diacid have significant effect on the reaction progress, which were optimized in previous work (Mallakpour and Kolahdoozan 2006) and used for direct polyestrification of diacid **5**.

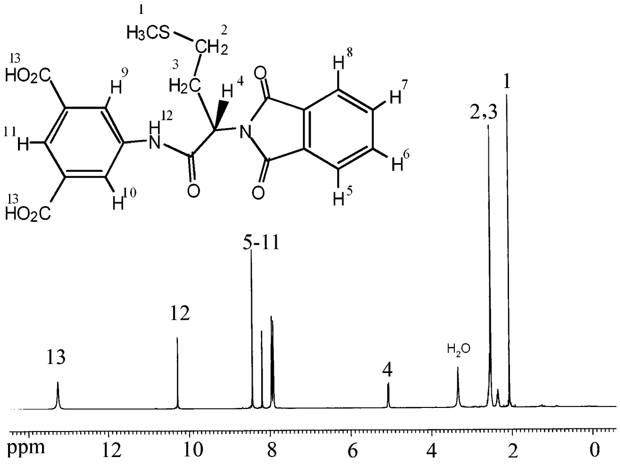


Fig. 1 ^{1}H NMR spectrum of monomer **5**

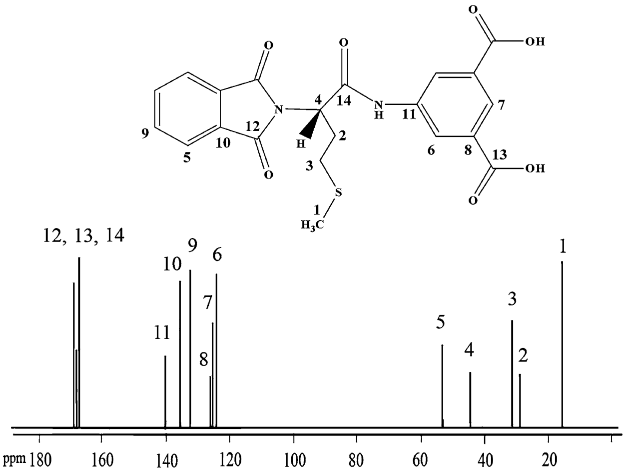


Fig. 2 ^{13}C NMR spectrum of monomer **5**

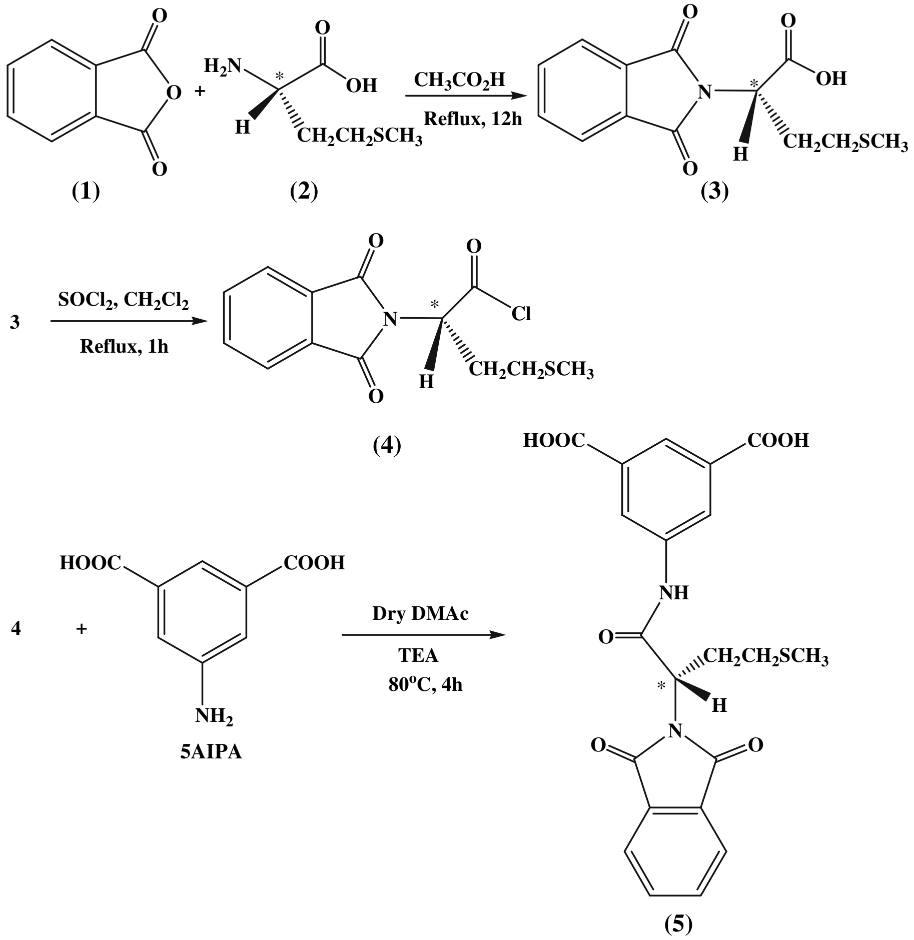
Various aromatic PEs have been synthesized in high yields and with medium inherent viscosities. Some physical properties of these optically active PEs are summarized in Table 2. The inherent viscosities and yields of the synthesized polymers were in the range of 0.21–0.51 dL/g and 77–95%, respectively. Optical activity of the synthesized PEs was proved by measuring their specific rotations (Table 2).

In comparison with our pervious work on optically active polyesters (Mallakpour and Rafiee 2007; Mallakpour and Rafiemanzelat 2007; Mallakpour and Kolahdoozan 2007), we obtained comparable yields and inherent viscosities, whereas these novel polyesters showed higher optical rotations.

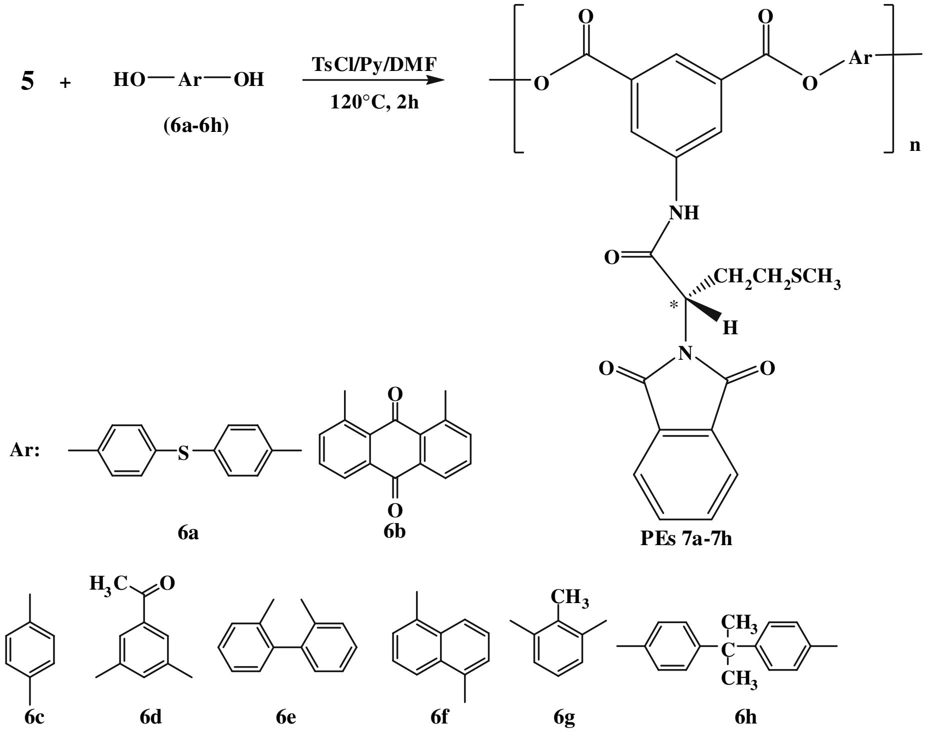
Thermal properties

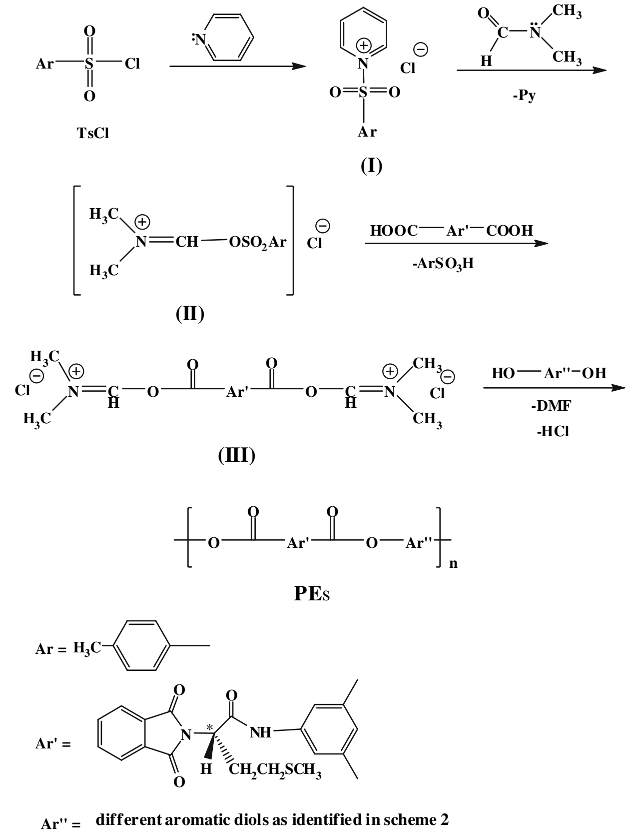
The thermal properties of **PE7a** and **PE7h** were evaluated by means of TGA/DTG in a nitrogen atmosphere at a heating rate of 10°C/min. The temperature of 5 and 10% weight loss together with char yield at 600°C have been calculated by means of thermograms, and used as criterion for evaluation of thermal stability of the polymers. Figure 3 shows the TGA thermograms of **PE7a** and **PE7h**. These

Scheme 1 Synthesis of 4-methylthio-2-phthalimidylbutanoic acid (**3**) and 5-(4-methylthio-2-phthalimidylbutanoylamino) isophthalic acid (**5**)



Scheme 2 Polyesterification reactions of monomer **5** with aromatic diols





Scheme 3 Mechanistic representation of polycondensation reaction of monomer **5** with aromatic diols using TsCl/Py/DMF as a condensing agent

polymers are stable about 300°C. The thermoanalysis data of these polymers are summarized in Table 3. The **PE7h** show better thermal stability compared to **PE7a**. This may be attributed to higher inherent viscosity of **PE7h** in comparison to **PE7a**. It can be predicted that the aromatic polymer's backbone increases the stability of the polymers towards heating.

Table 2 Synthesis and some physical properties of **PE7a–h**

Diol	Polymer	Yield (%)	η_{inh} (dL/g)[a]	$[\alpha]^{25,b}_{Na,589}$	Color
6a	**PE7a**	86	0.37	−30.15	OW
6b	**PE7b**	77	0.21	−15.52	OW
6c	**PE7c**	78	0.22	−18.77	OW
6d	**PE7d**	81	0.25	−18.39	OW
6e	**PE7e**	80	0.28	−21.41	OW
6f	**PE7f**	89	0.37	−17.90	OW
6g	**PE7g**	86	0.33	−18.82	OW
6h	**PE7h**	95	0.51	−15.22	OW

OW Off white

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C

[b] Measured at a concentration of 0.5 g/dL in DMF at 25°C

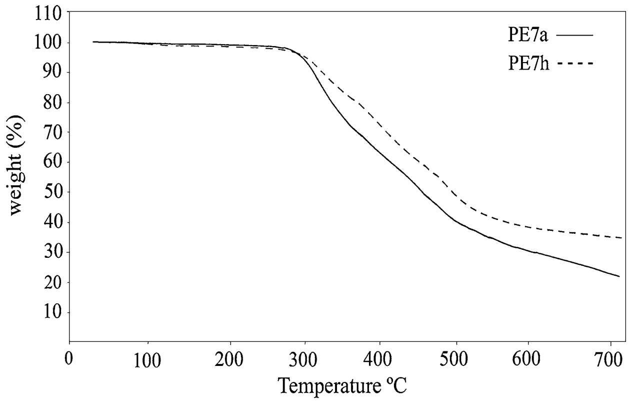


Fig. 3 TGA thermograms of **PE7a** and **PE7h** under N_2 atmosphere and a heating rate of 10°C/min

Table 3 Thermal behavior of aromatic **PE7a** and **PE7h**

Polymer	Decomposition temperature (°C) T_5^a	Decomposition temperature (°C) T_{10}^b	Char yield (%)[c]
PE7a	296	314	28
PE7h	300	325	37

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate 10°C/min in a nitrogen atmosphere

[b] Temperature at which 10% weight loss was recorded by TGA at heating rate 10°C/min in a nitrogen atmosphere

[c] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in a nitrogen atmosphere

Solubility of PEs

Solubility of PEs, **7a–h** at RT have been investigated in various solvents such as dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), DMF, DMAc, acetone, cyclohexane, chloroform, methanol and water. The solubility data are shown in Table 4. Higher solubility of PEs can be interpreted by the effects of flexible amide and imide groups in polymers structure.

Table 4 Solubility of **PE7a–h**

Solvent	PE7a	PE7b	PE7c	PE7d	PE7e	PE7f	PE7g	PE7h
DMSO	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+	+
DMAc	+	+	+	+	+	+	+	+
Acetone	−	−	−	−	−	−	−	−
Cyclohexane	−	−	−	−	−	−	−	−
Chloroform	−	−	−	−	−	−	−	−
Methanol	−	−	−	−	−	−	−	−
Water	−	−	−	−	−	−	−	−

Concentration: 5 mgmL^{-1}, +soluble at RT, −insoluble

Conclusions

In this study we have successfully synthesized a novel chiral dicarboxylic acid **5**, containing L-methionine based optically active pendent group. A series of novel optically active aromatic PEs was prepared by the direct polycondensation of compound **5** with various aromatic diols using TsCl/DMF/Py as a condensing agent. Furthermore the perturbation of the strong interchain attractions by insertion of L-methionine based pendent groups is the cause for increasing the solubility of PEs while good thermal stability is not disturbed. Optical activity of novel synthesized PEs makes them a suitable candidate for chromatographic applications as a chiral stationary phase for resolution of racemic mixtures. Biodegradability of these optically active PEs, because of the existence of amino acid moieties in the polymers structure, can be the subject of further investigations.

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