Synthesis of Novel Optically Active Poly(ester imide)s by Direct Polycondensation Reaction Promoted by Tosyl Chloride in Pyridine in the Presence of *N,N*-Dimethyformamide

Shadpour Mallakpour,* Elaheh Kowsari

College of Chemistry, Organic Polymer Chemistry Research Laboratory, Isfahan University of Technology, Isfahan 84156–83111, Islamic Republic of Iran

Received 1 April 2005; accepted 20 September 2005
DOI 10.1002/app.23289

ABSTRACT: 4,4′-Hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (**1**) was treated with L-methionine (**2**) in acetic acid and the resulting 4,4′-(hexafluoroisopropylidene)-*N,N*′-bis(phthaloyl-L-methionine) diacid (**4**) was obtained in high yields. The direct polycondensation reaction of this diacid with several aromatic diols, such as bisphenol A (**5a**), phenolphthalein (**5b**), 1,4-dihydroxybenzene (**5c**), 4,4′-dihydroxydiphenyl sulfide (**5 d**), 4,6-dihydroxypyrimidine (**5e**), 4,4′-dihydroxydiphenyl sulfone (**5f**), and 2,4′-dihydroxyacetophenone (**5g**), was carried out in a system of tosyl chloride (TsCl), pyridine (Py), and *N,N*-dimethylformamide (DMF). The reactions with TsCl were significantly promoted by controlling alcoholysis with diols, in the presence of catalytic amounts of DMF, to give a series of optically active poly(ester imide)s, (PEI)s, with good yield and moderate inherent viscosity ranging from 0.43 to 0.67 dL/g. The polycondensation reactions were significantly affected by the amounts of DMF, molar concentration of monomers, TsCl and Py, aging time, temperature, and reaction time. All of the aforementioned polymers were fully characterized by ^{1}H NMR, FTIR, elemental analysis, and specific rotation. Some structural characterization and physical properties of these optically active PEIs are reported. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 455–460, 2006

Key words: poly(ester imide)s; optically active polymers; direct polycondensation

INTRODUCTION

Poly(ester imide)s (PEIs) are a class of macromolecules known for more than 35 years. They are used today in large tonnage as electrical insulating materials. The patent literature reviewed shows that predominant research activities in the past were focused on improving the electrical, thermal, and mechanical properties. In recent times, new applications for these polymers have been found, such as adhesives, printed circuit boards, membranes, and engineering thermoplastics. Excellent properties and easy processing will probably lead to a continuous growth of PEIs business.[1]

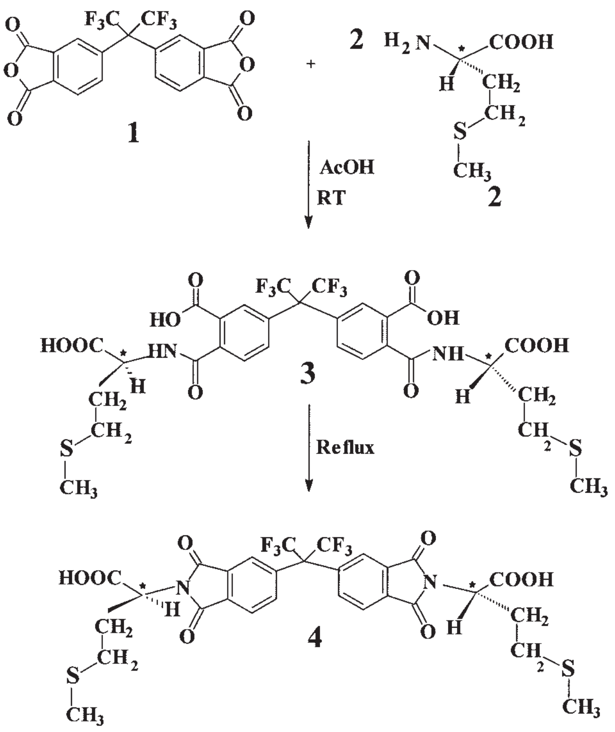
The polyesters are usually prepared by solution or by interfacial polymerization reaction between dicarboxylic acid chlorides and diols, and by an acid or phenyl ester exchange reaction of the acetate or ester of the acids under severe conditions (high temperature and reduced pressure). In these usual techniques, monomers such as acid chlorides, acetates, and esters should be prepared before polymerization. The processes, which are operative under mild conditions and adaptable to the direct polycondensations of free carboxylic acids and aromatic diols, can be a more useful technique for polyesterification. This method produces polymers with lower energy consumptions, thus lowering cost. Several condensing agents suitable for the direct polycondensation reaction, such as diphenyl chlorophosphate and arylsulfonyl chlorides,[2–3] have been developed in the past decades. However, there are a few which are well studied to the direct synthesis of the aliphatic and aliphatic–aromatic polyesters. It was found that Vilsmeier adduct, derived from arylsulfonyl chlorides and *N,N*-dimethylformamide (DMF) in pyridine (Py), was successfully used as a suitable condensing agent for the synthesis of aromatic polyesters by the direct polycondensation of aromatic dicarboxylic acids and bisphenols and also of hydroxybenzoic acids.[4–5] Direct polycondensation as a mild condition method for the synthesis of polyamides and corresponding copolymers has been used in our laboratory.[6–9]

**Previous name*: Shadpour E. Mallakpour.

Correspondence to: S. Mallakpour (mallak@cc.iut.ac.ir).

Contract grant sponsor: Management and Programming Organization, Iran.
Contract grant sponsor: Center of Excellency in Chemistry Research (IUT).

Journal of Applied Polymer Science, Vol. 101, 455–460 (2006)



Scheme 1 Synthesis of monomer **4**.

Polymers with optically active properties have found interesting applications, such as chiral phase for enantiomeric separations in chromatography methods or chiral media for asymmetric synthesis.[10–15] Recently, we have synthesized optically active polymers by reaction of optically active monomers via solution polymerization and direct polycondensation.[16–23] In polycondensation reactions, we use amino acids as chiral inducting agents. These materials are naturally occurring compounds, and therefore synthetic polymers based on amino acids are expected to be biodegradable and biocompatible.

In continuing our interest in preparing novel optically active PEIs bearing amino acid units, we studied the solution polycondensation of aliphatic dicarboxylic acid and aromatic diols using TsCl/DMF/Py as a condensing agent, which produce new optically active and organosoluble PEIs.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Co. Bisphenol A (**5a**) was purified by recrystallization from acetic acid–water. The other diols were used as obtained without further purification.

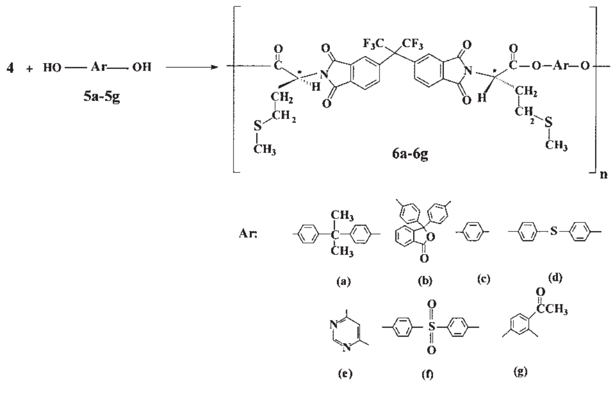
Measurements

Proton nuclear magnetic resonance ^{1}H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument (Bruker, Rheinstetten, Germany). The proton resonances were designated as singlet (s), doublet (d), and multiplet (m). Fourier transform infrared (FTIR) spectra were recorded on a Jasco 680 spectrophotometer (Jasco, Japan). Spectra of solids were obtained with KBr pellets. Vibration bands were reported in wavenumbers (cm^{-1}). The band intensities were classified as weak (w), medium (m), strong (s), and broad (br). The inherent viscosities were measured 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 a Perkin–Elmer TGA 7 (Perkin–Elmer, Jugeshein, Germany) in nitrogen atmosphere at the rate of 20°C/min. Elemental analysis were performed at Malek-Ashtar University of Technology (Tehran, Islamic Republic of Iran).

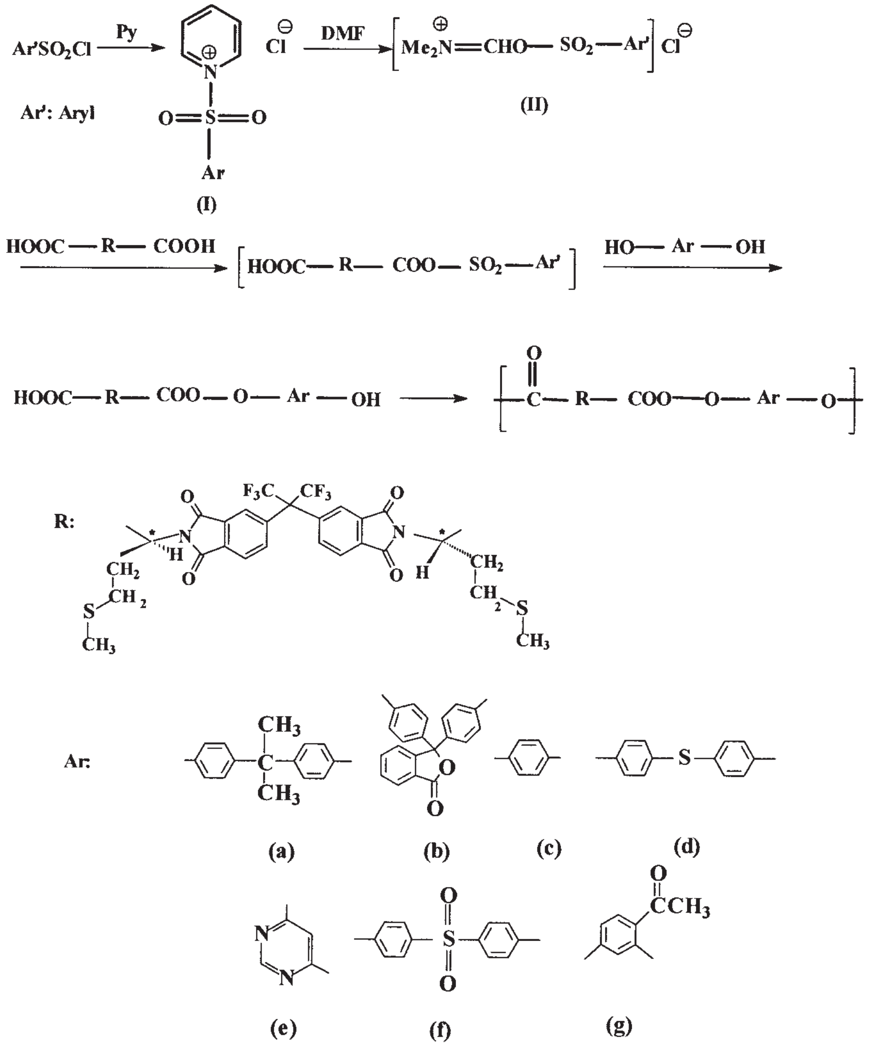
Monomer synthesis

Preparation of 4,4′-(hexafluoroisopropylidene)- *N,N′* -bis(phthaloyl-L-METHIONINE), DIACID (**4**)

1.00 g (2.2 mmol) of 4,4′-hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride),(**1**), 0.82 g (5.5 mmol) of L-methionine (2), 30 mL of acetic acid, and a stirring bar were placed into a 50 mL round-bottomed flask. The mixture was stirred at room temperature for 3 h and then refluxed for 8 h. The solvent was removed under reduced pressure, and 5 mL of cold concentrated HCl was added to the residue. A white precipitate formed was washed with cold water, and dried under reduced pressure to give 1.47 g (93.2%) of compound **3**. mp: 136–138°C, $[\alpha]_D^{25} = -82.2$ deg/dm/g cm^3 (0.050 g in 10 mL DMF).



Scheme 2 Polycondensation reactions of monomer **4** with aromatic diols.



Scheme 3 Mechanism of activation of diacid **4** by Vlismeier adduct, derived from TsCl and DMF.

FTIR (KBr): 2919 (m, br), 1778 (m), 1717 (s), 1624 (m), 1436 (w), 1384 (s), 1257 (s), 1211 (m), 1143 (m), 1093 (m), 964 (m), 850 (m), 630 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 2.00 (s, 6H, CH_3—S), 2.40 (m, 4H, CH_2), 2.5 (m, 4H, CH_2—S), 4.96–4.98 (m, 2H, CH—N), 7.54–7.60 (s, 2H Ar—H), 7.89–7.90 (d, 2H, J = 5.0 Hz, Ar—H), 8.07–8.09 (d, 2H, J = 10.0 Hz, Ar—H), 13.25 (s, br, 2H, COOH). $C_{29}H_{24}F_6N_2O_8S_2$ (706.55): Calcd C, 49.29; H, 3.42; N, 3.96. Found: C, 49.21; H, 3.43; N, 4.11.

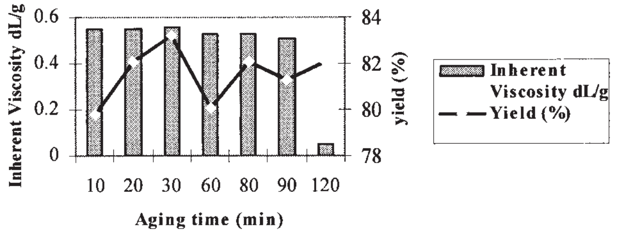


Figure 1 Effect of aging condition of TsCl in Py on the inherent viscosity and yield of PEI **6a** at 120°C for 2 h. (For TsCl = 0.70 mmol, diacid = 0.14 mmol, DMF = 1.4 mmol.)

Polymer synthesis

The PEIs were prepared by the following procedure: For synthesis of polymer **6a**, A Py (0.10 mL, 1.2 × 10^{-3} mol) solution of tosyl chloride (TsCl, 0.13 g, 7.0 × 10^{-4} mol), after 30 min stirring at room temperature, was treated with DMF (0.10 mL, 1.4 × 10^{-3} mol) for 30 min, and the solution was added dropwise to a solution of diacid **4** (0.1 g, 1.40 × 10^{-4} mol) in Py (0.10 mL). The mixture was maintained at room temperature for 20 min, and then to this mixture, a solution of bisphenol A (**5a**) (0.031 g, 1.40 × 10^{-4} mol) in Py (0.10 mL) was added dropwise at room temperature, and the whole solution was stirred at 120°C for 2 h. As the reaction proceeded, the solution became viscous. Then, the viscous liquid was precipitated in 40 mL of methanol to yield 0.105 g (83.2%) of the polymer **6a**.

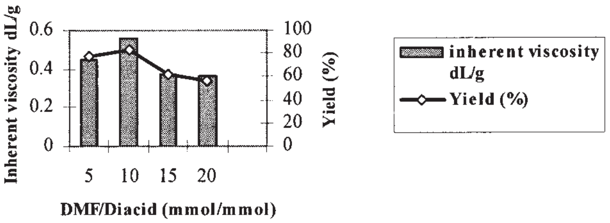


Figure 2 Effect of the amount of DMF added to TsCl on the inherent viscosity and yield of PEI **6a** at 120°C for 2 h, with aging time of 30 min. (For TsCl = 0.70 mmol, diacid = 0.14 mmol.)

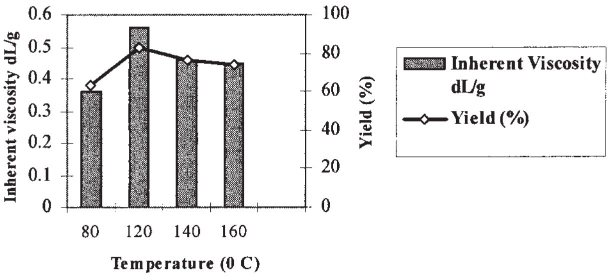


Figure 4 Effect of temperature on the inherent viscosity and yield of PEI **6a** at 2 h, with aging time of 30 min. (For TsCl = 0. 7 mmol, diacid = 0.14 mmol, DMF = 1.4 mmol.)

FTIR (KBr): 2968 (s), 1780 (s, sh), 1724 (s), 1625 (m, br), 1505 (s), 1437(m), 1382 (s), 1208 (s), 1106 (s), 1016 (s), 963 (m), 847 (m), 745 (m), 569 cm^{-1} (w). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.50 (s, br), 2.00 (s, br), 2.00–2.80 (m), 5.40 (s, br), 6.70 (s,br), 6.90 (s), 7.10 (s), 7.83 (d, distorded), 8.10 (s) ppm.

Elem. Anal. Calcd. for $C_{44}H_{36}F_6N_2O_8S_2$: C, 58.8%; H, 4.0%; N, 3.1%. Found: C, 58.5%; H, 4.2%; N, 3.1%. The other PEIs (**6b–6g**) were prepared with similar procedures.

Polymer **6b**. FTIR (KBr): 2918 (s), 1723(s), 1505(m), 1381 (s), 1210(s), 1015(m), 966 (m), 847 (m), 543 cm^{-1} (w).

Polymer **6c**. FTIR (KBr): 2918 (m), 1780 (s, sh), 1723 (s, sh), 1626 (m), 1501(s), 1438 (m), 1381 (s), 1190 (s), 1160 (s), 1090 (m), 1015 (m), 963 (m), 846 (m), 745 (m), 523 cm^{-1} (m).

Polymer **6d**. FTIR (KBr): 2918 (m), 1780 (s, sh), 1723 (s, sh), 1626 (m), 1501 (s), 1438 (w), 1381 (s), 1190 (s), 1090 (m), 1015 (w), 963 (m), 846 (w), 745 (w), 722 cm^{-1} (s).

Polymer **6e**. FTIR (KBr): 2918 (m), 1780 (s, sh), 1724 (s, sh), 1436 (w), 1382 (m), 1255 (s), 1210 (m), 1107 (w), 965 (w), 847 (w), 746 (w), 722 cm^{-1} (m).

Polymer **6f**. FTIR (KBr): 2950 (m), 1780 (s, sh), 1719 (s, sh), 1586 (s), 1488 (s), 1148(s, sh), 723 (m, br), 553 cm^{-1} (s).

Polymer **6g**. FTIR (KBr): 2919 (m), 1724 (s, sh), 1382 (s), 1254 (s), 964 (s), 746 (m), 722 (s), 569 cm^{-1} (w).

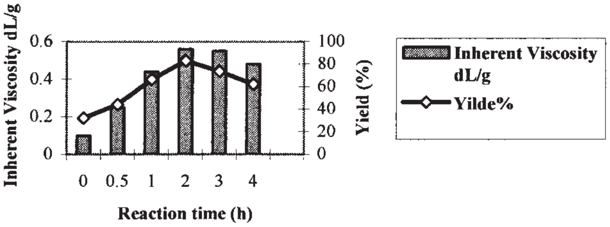


Figure 3 Effect of reaction time on the inherent viscosity of PEI **6a** at 120°C for 2 h, with aging time of 30 min. (For TsCl = 0.70 mmol, diacid = 0.14 mmol, DMF = 1.4 mmol.)

RESULTS AND DISCUSSION

Monomer synthesis

The asymmetric diacid compound **4** was synthesized by the condensation reaction of dianhydride **1** with two moles of L-methionine, **2** (Scheme 1). In this process, the intermediate, amic acid, was not isolated, and ring closure for the formation of imide ring was carried out under refluxing conditions.

Polymer synthesis

PEIs (**6a–6g**) were synthesized by the direct polyesterification reactions of an equimolar mixture of the monomer **4** with several different aromatic diols (**5a–5g**) in a system of TsCl/Py/DMF (Scheme 2). In this work, for the polycondensation of aliphatic diacids and aromatic diols, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polymerization reaction was carried out in the following way: TsCl was dissolved in Py, and after a certain period (aging time), the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After a period of time, a solution of diol in Py was added, and the whole solution was maintained at elevated temperature for several hours. Polycondensation was carried out by varying the aging time of the initial reaction of TsCl and Py. TsCl dissolves endothermically in Py, probably to form a sulfonium salt of Py(I) (Scheme 3). Its formation before addition of DMF seemed to be essential to obtain reproducible data. Using aging for 30 min, the polymer of reproducibly moderate inherent viscosity was obtained (Fig. 1). The reaction of the sulfonium

TABLE I
The Optimum Conditions for the Preparation of PEIs

TsCl/diacid (mol/mol)	5
Py/diacid (mol/mol)	26
DMF/diacid (mol/mol)	10
Aging time (min)	30
Reaction time (h)	2

TABLE II
Some Physical Properties of PEIs 6a–6g Synthesized under Optimum Conditions

	Polymer							
Diols	Polymer code	Yield (%)	η_{inh} (dL/g)	$[\alpha]^{25}_{589}$	$[\alpha]^{25}_{577}$	$[\alpha]^{25}_{546}$	$[\alpha]^{25}_{435}$	$[\alpha]^{25}_{365}$
5a	6a	83.2	0.56	−20.2	−16.4	−18.2	−28.3	—
5b	6b	86.3	0.63	−14.2	−13.9	−14.2	−18.6	—
5c	6c	76.3	0.43	−14.5	−11.2	−16.3	−21.3	—
5d	6d	85.6	0.55	−19.5	−16.7	−19.2	−28.3	−20.1
5e	6e	52.4	0.49	−30.1	−23.3	−28.3	−33.8	—
5f	6f	92.3	0.48	−23.1	−21.3	−23.2	−29.4	—
5g	6g	63.3	0.67	−20.1	−19.2	−20.3	−24.5	−12.1

salt (I) with DMF to form a Vilsmeier adduct (II) (Scheme 3)[3] seemed to complete after more than 30 min, at room temperature, and nearly 10 equivalence amount of diacid, amount of DMF, was sufficiently added to produce the polymer of high inherent viscosity. Further addition did not improve the inherent viscosity and yield (Fig. 2), but in cases involving extremely high contents of Py or DMF, less favorable results were obtained. The reaction was also run at different reaction time, and the highest viscosity was obtained at a reaction time of 2 h (Fig. 3). The best temperature for PEI synthesis was 120°C, and moderate inherent viscosities of PEIs were obtained at this temperature (Fig. 4).

The optimum conditions for the preparation of PEIs are listed in Table I. The synthesis and some physical properties of these novel optically active PEIs are listed in Table II. The inherent viscosities of the resulting polymers under optimized condition were in a range of 0.43–0.67 dL/g, and the yields were 52–92%. All of the PEIs are optically active.

Polymer characterization

The formation of PEIs was confirmed by FTIR spectroscopy analysis. The FTIR spectrum of PEI **6a** showed the characteristic absorptions of imide and ester groups occurred around 1780 and 1724 cm^{-1}, peculiar to carbonyls stretching of imide and ester, respectively. All of these PEIs exhibited absorption at 1380 and 722 cm^{-1}, which show the presence of the imide heterocycle in these polymers. The ^1H NMR spectrum (500 MHz) of polymer **6a** has been shown in Figure 5. The absorption of aromatic protons (H_9, H_{10}) appeared in the range of 7.70–8.40 ppm. The other aromatic protons ($H_{8,}$ H_7, H_6) appeared as singlet in the range of 6.50–7.50 ppm. The proton of the chiral center (H_5) appeared as a broad singlet band at 5.30–5.50 ppm. Absorption of the CH_3 protons (H_1) appeared as a singlet for proton (H_1) and (H_2) at 1.40–2.20 ppm.

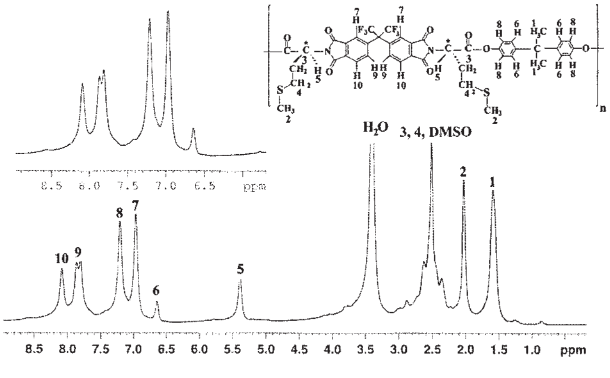


Figure 5 ^1H NMR (500 MHz) spectrum of PEI **6a** in DMSO-d_6 at room temperature.

The solubility of polymer

The solubility of PEIs was tested quantitatively in various solvents and is listed in Table III. All of the PEIs are soluble in organic solvents, such as DMF, *N,N*-dimethyl acetamide, dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone and H_2SO_4 at room temperature, and are insoluble in solvents, such as chloroform, methylene chloride, methanol, ethanol, and water.

TABLE III
Solubility of PEIs 6a-6g[a]

Solvent	6a	6b	6c	6d	6e	6f	6g
DMAc	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+
H_2SO_4	+	+	+	+	+	+	+
MeOH	−	−	−	−	−	−	−
EtOH	−	−	−	−	−	−	−
$CHCl_3$	−	−	−	−	−	−	−
CH_2Cl_2	−	−	−	−	−	−	−
H_2O	−	−	−	−	−	−	−

[a] Concentration, 10 mg/mL; (+) soluble at room temperature; (−) insoluble at room temperature.

Thermal properties

The thermal stability of the polymers, **6a**, **6b**, **6f**, and **6g**, was characterized by TGA, conducted in nitrogen, at a heating rate of 20°C/min.The highest thermal stability was shown by PEI **6f**. This behavior could be a consequence of the sulfone moieties present in the main chain of the polymer. Typical TGA curves of representative polymers are shown in Figure 6. The temperatures of 5 and 10% weight loss together with char yield at 600°C for PEIs **6a**, **6b**, **6f**, and **6g** have been calculated from their thermograms. From these data, it is clear that the resulting polymers are thermally stable. The thermoanalyses data of **6a**, **6b**, **6f**, and **6g** are summarized in Table IV.

CONCLUSIONS

In the present study, we successfully prepared a series of optically active aliphatic–aromatic PEIs having L-methionine and 4,4′-hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) moieties by direct polycondensation method. The polycondensation leads to the formation of polymers having inherent viscosities ranging from 0.43 to 0.67 dL/g. We carried out direct polyesterification reaction of aliphatic–aromatic imide containing diacid and aromatic diols using TsCl/DMF/Py as condensing agent to prepare new aliphatic–aromatic PEIs. The influence of aging time, amount of DMF, reaction time, and reaction temperature on the physical properties of the resulting polymers was investigated.

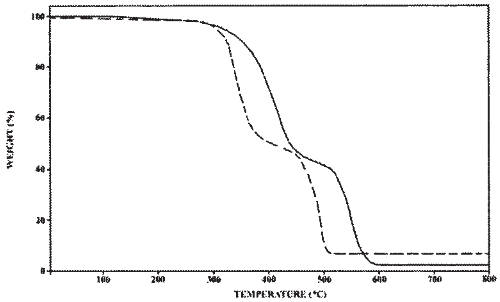


Figure 6 TGA of PEI **6b** (----) and PEI **6f** (——) with a heating rate of 20°C/min in nitrogen atmosphere.

TABLE IV
Thermal Properties of PEIs 6a, 6b, 6f, and 6g

Polymer	T_0[a] (°C)	T_5[b] (°C)	T_{10}[c] (°C)	Char yield[d] (%)
6a	210	245	305	8
6b	300	314	335	4.6
6f	314	328	362	3
6g	200	290	330	45

[a] The initial decomposition temperature by TGA at a heating rate of 20°C/min in N_2.

[b] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 20°C/min in N_2.

[c] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 20°C/min in N_2.

[d] Percentage weight of material left undecomposed after TGA analysis at a maximum temperature of 600°C in N_2.

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