

Synthesis of Organosoluble and Optically Active Poly(ester-imide)s by Direct Polycondensation with Tosyl Chloride in Pyridine and Dimethylformamide

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Summary

4,4'-Oxydiphthalic anhydride (**1**) was reacted with L-methionine (**2**) in acetic acid and the resulting *N,N'*-(4,4'-oxydiphthaloyl)-bis-L-methionine diacid (**4**) was obtained in high yield. The direct polycondensation reaction of this diacid with several aromatic diols such as bisphenol A (**5a**), phenolphthalein (**5b**), 1,4-dihydroxyanthraquinone (**5c**), 4,4'-dihydroxydiphenyl sulfide (**5d**), 2,6-dihydroxytoluene (**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 the 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 0.21-0.71 dL/g. The polycondensation reactions were significantly affected by the amounts of DMF, molar concentration of monomers, TsCl and pyridine, aging time, addition time of diols, temperature and the reaction time. All of the above polymers were fully characterized by ¹H-NMR, FT-IR, elemental analysis and specific rotation. Some structural characterization and physical properties of these new optically active **PEI**s are reported.

Introduction

Recently, much attention on high-performance polymers that have excellent thermal stability and solubility has provided researchers with the impetus that has led to the discovery of a variety of thermostable and processable polymers. Polyimides are one of the high-performance polymeric materials, and are characterized by high thermal and thermo oxidative stability, good mechanical properties, and outstanding solvent resistance. However, poor solubility is a major problem for wide application of polyimides. Two typical successful approaches exist for increasing of the solubility and processability of polyimides without sacrificing their high thermal stability. First, synthesis of copolyimides such as poly(ester-imide)s and poly(amide-imide)s [1], Second, the introduction of flexible ether linkages noncoplanar and symmetric units and bulky pendant groups along the polymer backbones [2]. Direct polycondensation

as a mild condition method for the synthesis of polyamides and corresponding copolymers has been used in our laboratory [3-4]. In usual techniques for the preparation of polyesters, monomers such as diacid chlorides, diacetates and diesters 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. Several condensing agents suitable for the direct polycondensation reaction such as diphenyl chlorophosphate and arylsulfonyl chlorides [5-6] have been developed in the past decades. However, there are 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 DMF in pyridine 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 [7-8]. Synthesis of optically active polymers is an important field in macromolecular science as they find a wide variety of potential applications based on the chiral structure [9-11]. One of the most practical and widely accepted applications of chiral polymers is the use as chiral stationary phase for high-performance liquid chromatography (HPLC) for the separation of racemic compounds (resolution). Recently, we have synthesized optically active polymers by reaction of an optically active monomer with several diamines via solution polymerization [12-17]. In polycondensation reactions, we used amino acids as chiral inducing agents.

In the present study, we successfully prepared a series of optically active and thermally stable PEIs, by direct polycondensation of an optically active diacid and various aromatic diols using TsCl/DMF/Py systems as a condensing agent.

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.

Instruments

Proton nuclear magnetic resonance ($^1\text{H-NMR}$, 500 MHz) spectra were recorded on a Bruker (Germany) Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), and multiplet (m). FT-IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). 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 (Germany). Specific Rotations were measured by a Jasco Polarimeter (Japan). Thermal Gravimetric Analysis (TGA) and DSC data for polymers were taken on STA 625 in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. Elemental analysis were performed by Malek-Ashtar University of Technology, Tehran, I. R. Iran.

*Synthesis of monomer**N,N'-(4,4'-Oxydipthaloyl)-bis-L-methionine diacid (4)*

(1.00 g 3.22×10^{-3} mol) of 4,4'-oxydipthalic anhydride (**1**), (1.20 g, 8.05×10^{-3} mol) 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 was 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 was formed, and washed with cold water. It was dried under reduced pressure to give 1.72 g (93.5%) of compound **4**. mp 192-194°C, $[\alpha]_D^{25}$: -72.2° (0.050 g in 10 mL DMF); FT-IR (KBr, cm^{-1}): 3344 (m, br), 3064 (m), 2921 (w), 1779 (m), 1757 (s), 1703 (m), 1608 (m), 1474 (w), 1383 (s), 1265 (s), 1233 (w), 1183 (w), 1093 (m), 952 (w), 793 (m), 621 (m). $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ , ppm): 2.00-2.10 (s, 6H), 2.40 (m, 4H), 2.50 (m, 4H), 4.90-5.00 (m, 2H), 7.56-7.63 (dd, 2H, $J_1 = 10.0$ Hz, $J_2 = 5$ Hz), 7.62-7.64 (d, distorted, 2H), 7.98-8.00 (d, $J = 10.0$ Hz, 2H).

Elemental analysis $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_9\text{S}_2$ (572): Cal. C, 54.54; H, 4.22; N, 4.89. Found: C, 54.69; H, 4.20; N, 4.99.

Polymerization

The PEIs were prepared by the following procedure. For synthesis of polymer **6a**, pyridine (0.05 mL, 6.6×10^{-4} mol) solution of TsCl (0.082 g, 4.35×10^{-4} mol) after 30 min stirring at room temperature, was treated with DMF (0.14 mL, 1.74×10^{-3} mol) for 30 min and the solution was added dropwise to a solution of diacid **4** (0.1 g, 1.74×10^{-4} mol) in pyridine (0.05 mL). The mixture was maintained at room temperature for 20 min and then to this mixture, a solution of bisphenol A (**5a**) (0.039 g; 1.74×10^{-4} mol) in pyridine (0.05 mL) was added dropwise at room temperature and the whole solution was stirred at 120°C for 2h. As the reaction proceeded, the solution became viscous. Then the viscous liquid was precipitated in 40 mL methanol to yield 0.10 g (73.2%) of the polymer **6a**. FT-IR (KBr, cm^{-1}): 3068 (s), 1772 (s, sh), 1718 (s), 1609 (s), 1505 (s), 1473 (s), 1381 (s), 1168 (s), 892 (m), 749 (w), 691 (w). $^1\text{H NMR}$ (500 MHz, DMSO- d_6 , δ , ppm): δ 1.50 (s), 2.00 (s, br), 5.40 (s, br), 6.60 (s), 7.0 (s, br.), 7.20 (s) 7.60 (d), 8.0 (s).

Elemental analysis $\text{C}_{41}\text{H}_{36}\text{N}_2\text{O}_9\text{S}_2$ (764): Cal. C, 64.39; H, 4.71; N, 3.66. Found: C, 63.80; H, 4.90; N, 3.50.

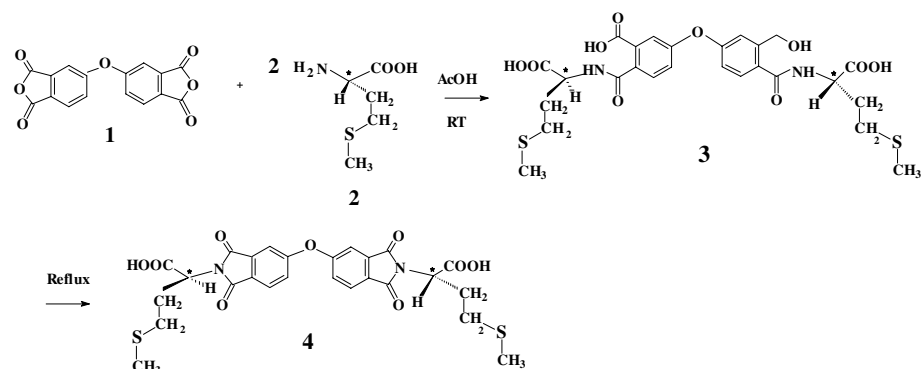
The other PEIs **6a-6g** were prepared with a similar procedure.

Results and Discussion*Monomer synthesis*

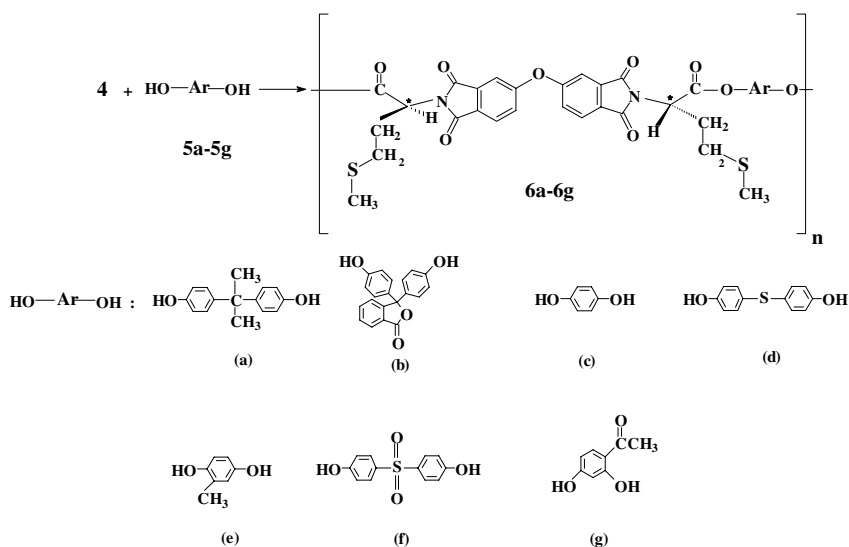
The asymmetric diacid **4** was synthesized by the condensation reaction of dianhydride **1** with two moles of L-methionine (**2**). In this reaction the intermediate amic acid was not isolated and ring closure for the formation of imide ring was carried out under refluxing conditions (Scheme 1).

Polymer synthesis

PEIs **6a-6g** were synthesized by the direct polycondensation reactions of an equimolar mixture of monomer **4** with several different aromatic diols **5a-5g** in a system of TsCl/Py/DMF (Scheme 2).



Scheme 1. Synthesis of monomer **4**.



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

In this work for the polycondensation of aliphatic diacids and aromatic diols, a Vilsmeier adduct was prepared by dissolving tosyl chloride (TsCl) in a mixed solvent of pyridine and DMF. The polycondensation was carried out in the following way: TsCl was dissolved in pyridine 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 pyridine. After a period of time a solution of diol in pyridine 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 pyridine, the amount of DMF, the molar ratio of TsCl/diacid, pyridine/diacid, the time of diol addition and the time of heating. All of these parameters had critical effect on the polymer chain growth (Figure 1-4).

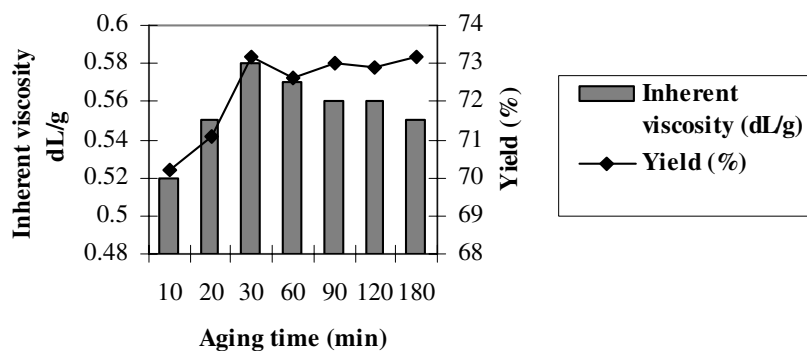


Figure 1. Effect of aging condition of TsCl in pyridine on the inherent viscosity and yield of PEI (6a) at 120°C for 2 h (For TsCl = 0.435 mmol, Diacid = 0.174 mmol, DMF = 1.74 mmol and Pyridine = 2 mmol).

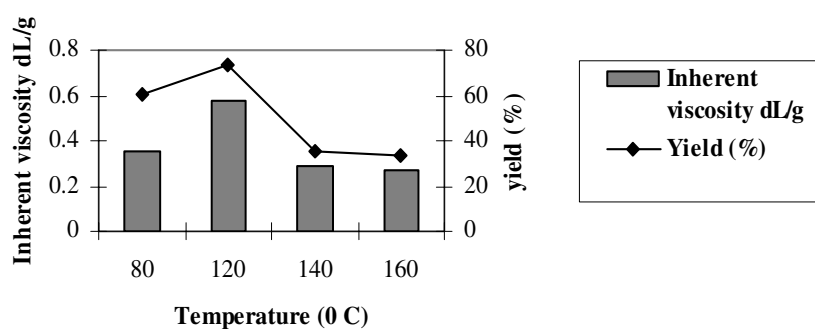


Figure 2. Effect of temperature on the inherent viscosity and yield of PEI (6a) at 2 h with aging time 30 min. (For TsCl = 0.435 mmol, Diacid = 0.174 mmol, DMF = 1.74 mmol and Pyridine = 2 mmol).

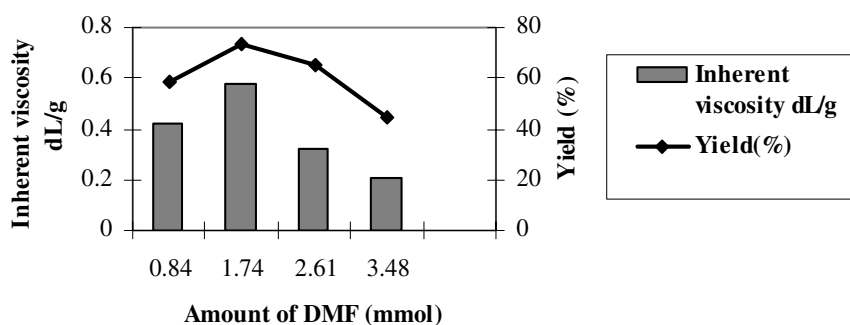


Figure 3. Effect of the amount of DMF added to TsCl on the inherent viscosity and yield of PEI (6a) at 120 °C for 2 h with aging time 30 min. (For TsCl = 0.435 mmol, Diacid = 0.174 mmol and Pyridine = 2 mmol).

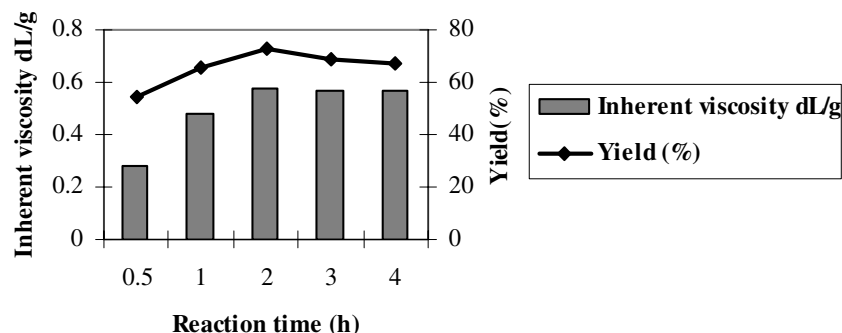


Figure 4. Effect of reaction time on the inherent viscosity of **PEI (6a)** at 120 °C for 2 h with aging time 30 min. (For TsCl = 0.435 mmol, Diacid = 0.174 mmol, DMF = 1.74 mmol and Pyridine = 2 mmol).

The optimum conditions for the preparation of **PEIs** are demonstrated in Table 1.

Table 1. The optimum conditions for the preparation of **PEIs**

Optimum Condition	
TsCl/Diacid (mol/mol)	2.5
Py/Diacid (mol/mol)	12
DMF/ Diacid (mol/mol)	10
Aging Time (min)	30
Reaction Time (h)	2

The synthesis and some physical properties of these novel optically active **PEIs** are listed in Table 2. The inherent viscosities of the resulting polymers under optimized condition were in a range of 0.21-0.71 dL/g and the yields were 51-90%. All of the **PEIs** are optically active.

Table 2. Some physical properties of **PEIs 6a-6g**. Synthesized in the optimum conditions.

Diols	Polymer							
	Polymer code	Yield (%)	η_{inh} (dL/g)	$[\alpha]_{589}^{25}$	$[\alpha]_{577}^{25}$	$[\alpha]_{546}^{25}$	$[\alpha]_{435}^{25}$	$[\alpha]_{365}^{25}$
5a	6a	73.2	0.58	-36.2	-30.5	-32.4	-40.1	-12.1
5b	6b	90.1	0.71	-18.3	-11.1	-16.2	-23.6	-
5c	6c	51.1	0.21	-17.3	-6.8	-11.3	-18.3	-
5d	6d	86.6	0.66	-46.7	-26.2	-43.8	-51.3	-
5e	6e	82.3	0.63	-42.1	-32.1	-36.3	-50.1	-
5f	6f	80.0	0.48	-41.3	-38.1	-41.2	-44.6	-
5g	6g	72.3	0.46	-12.2	-10.6	-12.3	-18.2	-

Structural Characterization of Polymer

The formation of **PEIs** was confirmed by FT-IR spectroscopy analysis. The FT-IR spectrum of **PEIs 6a** showed the characteristic absorptions of imide and ester groups occurred around 1772, 1718 cm^{-1} , peculiar to carbonyls stretching of imide and ester,

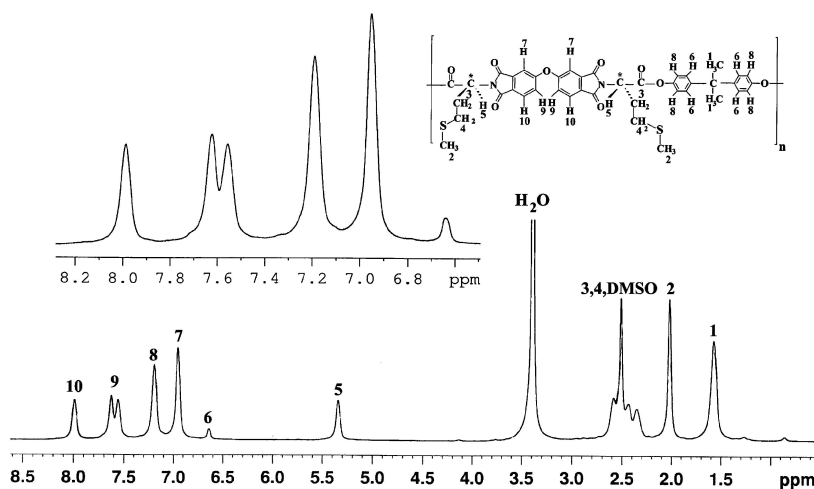


Figure 5. ^1H NMR (500 MHz) spectrum of **PEI 6a** in $\text{DMSO-}d_6$ at rt.

respectively. All of these **PEIs** exhibited absorption at 1380 cm^{-1} and $691\text{--}749\text{ cm}^{-1}$, that show the presence of the imide heterocycle in these polymers. The ^1H NMR spectrum (500 MHz) of polymer **6a** has been shown in figure 1.

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

Thermal properties

The thermal properties of the polymers, **6c** and **6f** was studied by TGA and DSC conducted in nitrogen at a heating rate of $20^\circ\text{C}/\text{min}$. Typical TGA curves of representative polymers are shown in Figures 6 and 7. The temperatures of 5% and 10% weight loss together with char yield at 600°C for **PEIs 6c** and **6f** have been calculated from their thermograms. From these data it is clear that the resulting polymers are thermally stable. The thermo analyses data of **PEIs 6c** and **6f** are summarized in Table 3. It is clear from obtained data that polymer containing SO_2 group with higher T_5 and T_{10} is more stable. Polymer with polar sulfone group also show higher T_g value.

Table 3. Thermal properties of **PEIs 6c** and **6f**

Polymer	T_5 ($^\circ\text{C}$) ^a	T_{10} ($^\circ\text{C}$) ^b	T_g ($^\circ\text{C}$) ^c	Char Yield (%) ^d
6cI	247	302	159	54
6fI	268	343	180	32

^a Temperature at which 5% weight loss was recorded by TGA at a heating rate of $20^\circ\text{C}/\text{min}$ in N_2 .

^b Temperature at which 10% weight loss was recorded by TGA at a heating rate of $20^\circ\text{C}/\text{min}$ in N_2 .

^c DSC was recorded at a heating rate of $20^\circ\text{C}/\text{min}$ in N_2 .

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

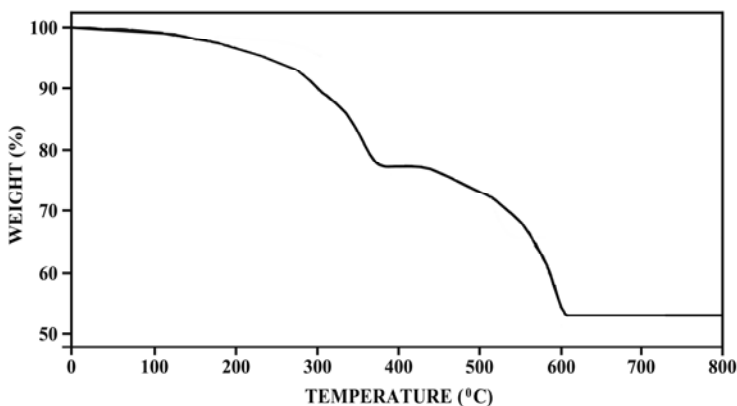


Figure 6. TGA of PEI 6c and with a heating rate of 20°C/min in nitrogen atmosphere.

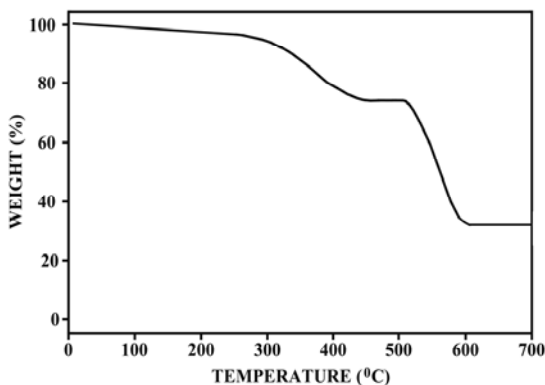


Figure 7. TGA of PEI 6f and with a heating rate of 20°C/min in nitrogen atmosphere.

Conclusion

A series of optically active aliphatic-aromatic PEIs having L-methionine and *N,N'*-(4,4'-oxydipthaloyl)-bis-L-methionine diacid moieties was synthesized by direct polycondensation method. The resulting PEIs have both excellent solubility in various polar solvents and thermal stability. Direct polycondensation was carried out by using 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, concentration of monomers and condensing agents, addition time of aromatic diols and reaction time on the physical properties was investigated. This method is a very useful technique for the preparation of optically active PEIs which prevents the use of diacid chloride and is very efficient in terms of cost and energy. Furthermore, the resulting optically active PEIs containing amino acid linkages, so could be biocompatible and biodegradable.

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