

Thionyl Chloride/Pyridine System as a Condensing Agent for the Polyesterification Reaction of *N,N'*-(4,4'-oxydipthaloyl)-bis-*L*-leucine and Aromatic Diols

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Received 19 October 2005; accepted 14 March 2006

ABSTRACT

N,*N'*-(4,4'-Oxydipthaloyl)-bis-*L*-leucine (**4**) was prepared as an aliphatic optically active diacid monomer from treatment of 4,4'-oxydipthalic anhydride (**1**) with *L*-leucine (**2**). The direct polyesterification reaction of this diacid with several commercially available aromatic diols was performed in a system of thionyl chloride and pyridine (Py). Polycondensation was carried out by varying the initial reaction time of thionyl chloride, Py, and diacid (aging time), the reaction temperature, and the time of heating. A series of optically active poly(ester-imide)s (**PEI**)s were obtained in high yield and inherent viscosities under optimum conditions. All of the above polymers were fully characterized by ¹HNMR, FTIR, elemental analysis and specific rotation techniques. Some structural characterization and physical properties of these optically active **PEI**s are reported. The resulting **PEI**s show good solubility and thermal stability.

Key Words:

poly(ester-imide)s;
thionyl chloride;
optically active polymers;
direct polycondensation;
thermally stable polymers.

INTRODUCTION

The separation of chiral compounds has been of great interest because the majority of bioorganic molecules are chiral. Living organisms, for example, are composed of chiral biomolecules such as amino acids, sugars,

proteins and nucleic acids. In nature these biomolecules exist in only one of the two possible enantiomeric forms, e.g., amino acids in the *L*-form and sugars in the *D*-form. Because of chirality, living organisms show different

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biological responses to one of a pair of enantiomers in drugs, pesticides, or waste compounds. Chirality is a major concern in the modern pharmaceutical industry [1]. Separation of enantiomers can be done simultaneously by high performance liquid chromatography (HPLC) [2]. One of the most appealing features of optically active polymers as chiral stationary phase is the high chiral recognition ability in chiral HPLC. Therefore, the synthesis and application of chiral polymers are active research areas. Recently, we have synthesized optically active polymers by different methods [3-8].

Direct polycondensation methods have been developed by several investigators and especially by Higashi [9,10]. In direct polycondensation, preparation and separation of acid chlorides are not necessary and the reactions proceed as one pot reaction using the free carboxylic acid, diamines, and compounds such as arylsulphonyl chlorides [11-13], triphenylphosphite [14-16], LiCl [16], phosphorous-oxychloride [13], etc. Direct polycondensation as a mild condition method for the synthesis of polyamides and corresponding copolymers has been used in our laboratory [17-20].

In continuation of our previous works on preparation and characterization of optically active polymers, we report here a facile method for efficient synthesis of thermally stable and optically active PEIs. The reaction promoted by thionyl chloride in Py was applied to the direct polyesterification of diacid (**4**) with aromatic diols.

EXPERIMENTAL

Materials

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

Apparatus

Proton nuclear magnetic resonance ^1H 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 as wavenumber (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 Perkin-Elmer TGA 7 (Perkin-Elmer, Jugeshein, Germany) in nitrogen atmosphere at a rate of $20^\circ\text{C}/\text{min}$. Elemental analysis were performed at Malek-Ashtar University of Technology and Research Institute of Petroleum Industry (Tehran, Islamic Republic of Iran).

Synthesis of Monomer

N,N'-(4,4'-oxydipthaloyl)-bis-*L*-leucine (**4**) was prepared according to our previous work [21].

Polymerization

The PEIs were prepared by the following procedure: For synthesis of polymer **6c**, pyridine (0.5 mL) was added to a cold thionyl chloride (0.05 mL, 0.80 mmol) in an ice-water bath, the mixture was kept at this temperature for 10 min. the diacid solution, (0.2 g, 0.37 mmol) in Py (0.5 mL), was added slowly for 10-20 min and then the cooling bath was removed, and the reaction mixture was stirred at room temperature for 30 min. 1,4-Dihydroxybenzene (**5c**) (0.04 g, 0.37 mmol) in Py (0.5 mL) was added to the mixture all at once, and the whole solution was heated at 80°C for 4 h. Then the viscous liquid was precipitated in 40 mL of methanol to yield 0.20 g (89.2%) of the polymer (**6c**).

^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 0.70–1.10 (distorted, dd, 12H), 1.50 (m, 2H), 1.80-1.90 (s, br, 2H), 1.90-2.20 (s, br, 2H), 5.30-5.40 (m, 2H), 6.73-7.11 (m, 4H), 7.59-7.66 (distorted d, 4H), 8.00 (s, br, 2H) ppm.

FTIR (KBr): 2960 (s), 1768 (s, sh), 1720 (s), 1610 (s), 1500 (s), 1473(s), 1380 (s), 1173 (s), 858 (m), 781 (w), 671 (w) cm^{-1} . Elemental analysis: Calcd.

for $C_{34}H_{30}N_2O_9$: C, 66.88%; H, 4.91%; N, 4.59%.
Found: C, 65.70%; H, 5.00%; N, 4.20%.

The other **PEIs 6a, 6b** and **6d-6h** were prepared with analogous procedure.

Polymer (6a)

FTIR (KBr): 2961(s), 1766 (s, sh), 1720 (s), 1610 (m, br), 1505 (m), 1473 (m), 1380 (s), 1274 (s), 1170 (s), 1080 (m), 941 (w), 854 (w), 746 (m), 553 (w) cm^{-1} .

Polymer (6b)

FTIR (KBr): 2959 (s), 1775 (s, sh), 1720 (s, sh), 1610 (m), 1505 (s), 1440 (w), 1380 (s), 1167 (s), 1082 (s), 1017 (m), 929 (w), 846 (m), 745 (m), 539 (w) cm^{-1} .

Polymer (6d)

FTIR (KBr): 2914 (m), 1780 (s, sh), 1718 (s, sh),

1608 (s), 1485 (s), 1437 (s), 1380 (s), 1195 (s), 1012 (w), 892 (w), 507 (w) cm^{-1} .

Polymer (6e)

FTIR (KBr): 1780 (s, sh), 1719 (s, sh), 1383 (s), 1235(w), 1210 (m), 746 (w) cm^{-1} .

Polymer (6f)

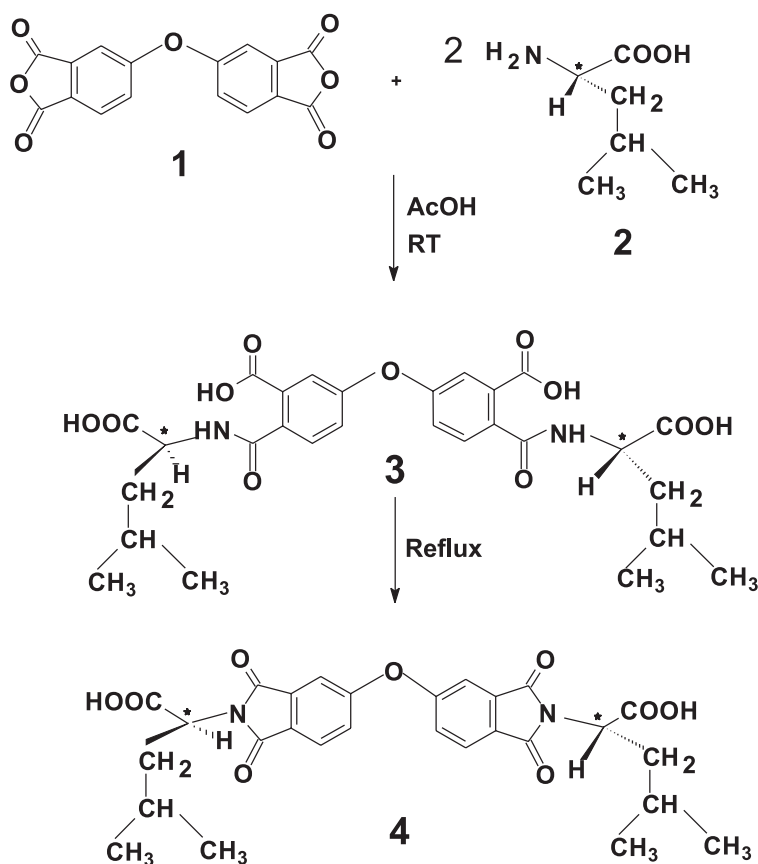
FTIR (KBr): 2959 (m), 1780 (s, sh), 1717(s, sh), 1610 (s), 1474 (s), 1381 (s), 1014 (m), 711 (m, br), 568 (m) cm^{-1} .

Polymer (6g)

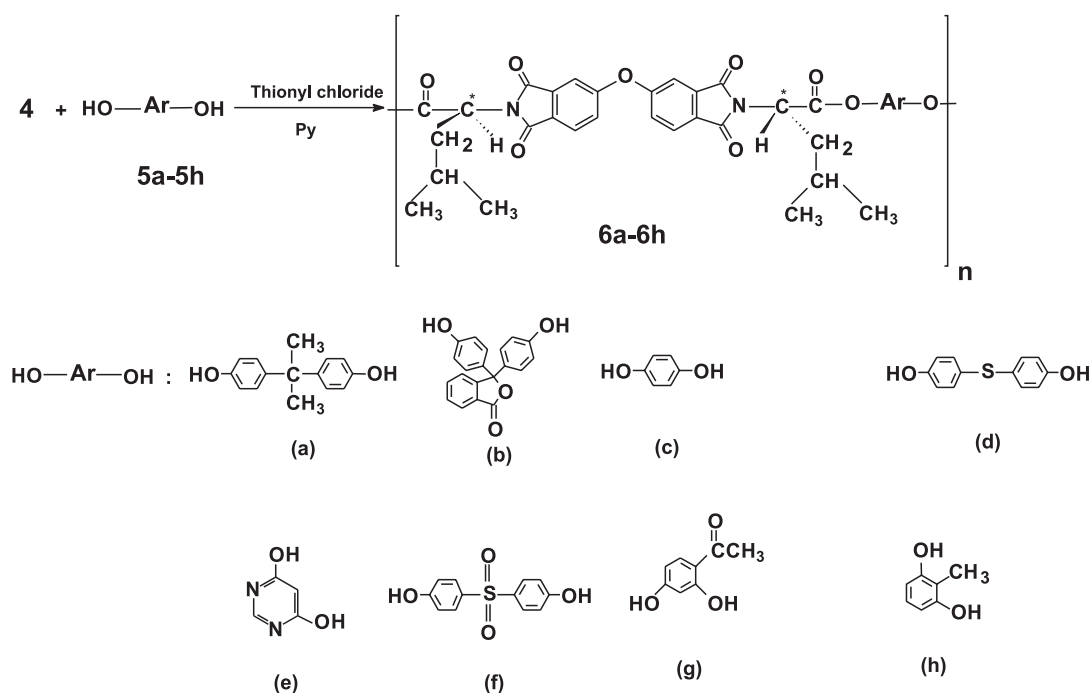
FTIR (KBr): 2959 (m), 1774 (s, sh), 1720 (s, sh), 1382 (s), 1234 (w), 747(w) cm^{-1} .

Polymer (6h)

FTIR (KBr): 2360 (w), 1770 (m, sh), 1720 (s, sh), 1382 (s), 1275 (w), 746 (w), 699 (w) cm^{-1} .



Scheme I. Synthesis of aliphatic diacid monomer **4**.



Scheme II. Polyesterification reactions of monomer **4** with aromatic diols under thionyl chloride/Py system.

RESULTS AND DISCUSSION

Monomer Synthesis

N,N'-(4,4'-Oxydipthaloyl)-bis-*L*-leucine (**4**) was synthesized according to our previous work [5] as shown in Scheme I.

Polymer Synthesis

PEIs **6a-6h** were synthesized by the direct polycondensation reactions of an equimolar mixture of monomer (**4**) with several different aromatic diols

(**5a-5h**) in a system of thionyl chloride and Py (in Scheme II).

Thionyl chloride reacts with Py to form 1-chlorosulfinyl pyridinium chloride (compound 1 or 2 in Scheme III), which is converted into compound 3 by the reaction with additional Py (Scheme III), as has been proposed as an intermediate in thionyl chloride/Py system [21].

The reaction promoted by thionyl chloride in Py was applied to the direct polyesterification of optically active diacid (**4**) with aromatic diols. Polycondensation

Table 1. Effect of aging condition of thionyl chloride in pyridine and diacid on the inherent viscosity and yield of PEI **6c** at 80°C.

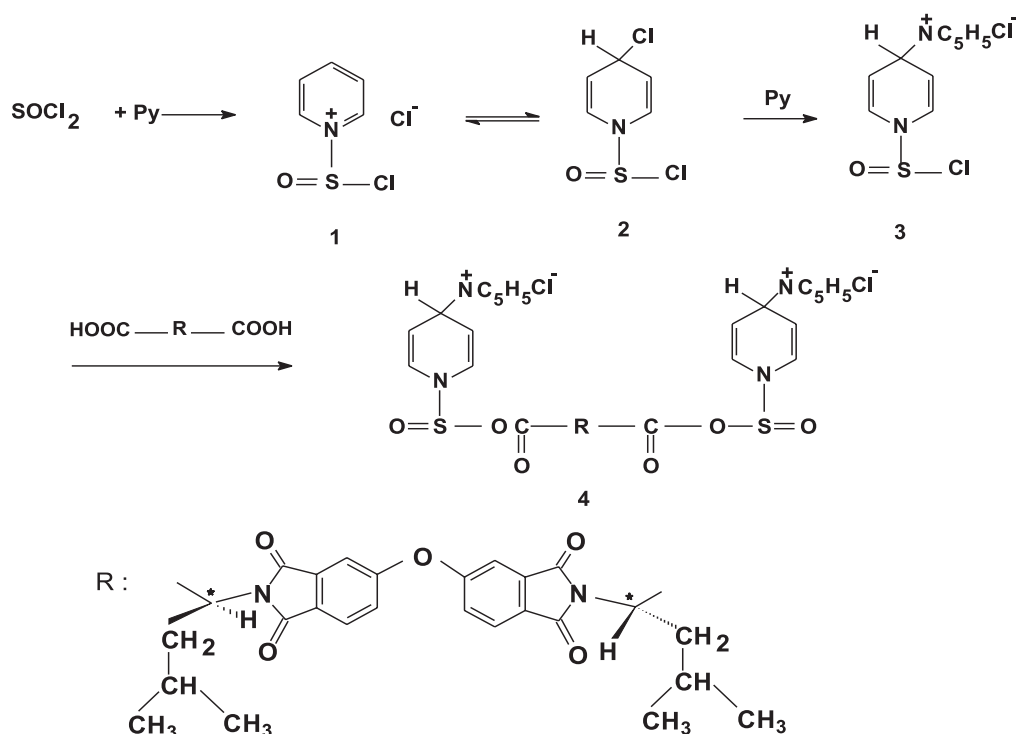
Aging time (min)	η_{inh} (dL/g)	Yield (%)
0	No polymer	-
10	0.34	75.3
20	0.45	85.3
30	1.0	95.3
60	0.98	81.1

Diacid = 0.37, Diol = 0.37, and Thionyl chloride = 0.8 mmol; reaction time = 4 h.

Table 2. Effect of temperature on the inherent viscosity and yield of PEI **6c** prepared using thionyl chloride/pyridine.

Temperature (°C)	η_{inh} (dL/g)	Yield (%)
25 (r. t.)	0.22	44.3
80	1.0	93.2
100	0.72	81.1
120	0.55	95.3
140	0.50	64.3

Diacid = 0.37, Diol = 0.37, and Thionyl chloride = 0.8 mmol; Aging time = 30 min; reaction time = 4 h.



Scheme III. The mechanism of activation of diacid **4** by thionyl chloride and Py system.

was performed by varying the initial reaction time of thionyl chloride, Py and diacid (aging time) (Table 1), the reaction temperature (Table 2), and the time of heating (Table 3). Thionyl chloride dissolves endothermically in Py, probably to form the 1-chlorosulphonyl pyridinium chloride intermediate (1 or 2). The reaction of the intermediate 2 with diacid forms an intermediate 4 (Scheme III). The inherent viscosity of the **PEIs** was affected by the

Table 3. Effect of reaction time on the inherent viscosity and yield of **PEI 6c** prepared using thionyl chloride/pyridine at 80°C.

Reaction time (h)	η_{inh} (dL/g)	Yield (%)
0.5	0.55	63.1
1.0	0.62	79.3
2.0	0.76	84.1
3.0	0.78	89.3
4.0	1.05	96.2
5.0	0.88	92.3

Diacid = 0.37 mmol, Diol = 0.37, and Thionyl chloride = 0.8 mmol; Aging time = 30 min.

reaction time of Py, thionyl chloride, and diacid (aging time) suggesting that the formation of intermediate **4** (Scheme III) should be completed before addition of diol (Table 1). Using aging time of 30 min, the obtained polymer had the reproducible moderate inherent viscosity. The reaction was run at different temperature (Table 2). The best temperature for **PEI** synthesis was 80°C, and the **PEIs** obtained at this temperature had moderate inherent viscosities. The reaction was also run at different reaction time (Table 3) and the highest viscosity was obtained at the reaction time of 4 h.

The optimum conditions for the preparation of **PEIs** are demonstrated in Table 4. Some physical

Table 4. Optimum conditions for the preparation of **PEIs**.

Optimum condition	
Thionyl chloride/Diacid (mol/mol)	2.2
Aging time (min)	30
Reaction time (h)	4.0

Table 5. Some physical properties of **PEIs 6a-6h** synthesized under the optimum conditions.

Diols	Polymer				
	Polymer	Yield (%)	$\eta_{inh}(dL/g)^a$	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{25}$
5a	6a	96.2	1.00	-0.2	-0.85
5b	6b	94.1	0.70	-7.2	-15.3
5c	6c	89.2	0.67	-3.25	-8.24
5d	6d	95.6	0.55	-7.26	-5.35
5e	6e	78.0	0.56	-3.27	-6.20
5f	6f	69.2	0.57	-0.35	-0.81
5g	6g	85.5	0.80	-6.38	-7.33
5h	6h	90.4	0.86	-5.56	-4.84

(a) Measured at a concentration of 0.5 gL⁻¹ in DMF at 25°C.

$[\alpha]_{\lambda}^{25}$ = Specific Rotation = deg dm⁻¹ g⁻¹ cm³

properties of these novel optically active **PEIs** are listed in Table 5. The inherent viscosities of the resulting polymers under optimized condition were in the range of 0.55-1.0 dL/g. All of these **PEIs** show optical rotations, therefore, they are optically active.

In order to see the efficiency of this method with the other condensing agent such as TsCl/DMF/Py system [22], we compared these two methods in

preparation of the **PEIs** and the results are summarized in Table 6. Direct polyestification in method A showed a series of advantages including improved reaction yield and higher molecular weights of the resulting **PEIs**.

FTIR and ¹H NMR Data

The formation of **PEIs** was confirmed by FTIR and

Table 6. Comparative physical properties data referring to the two methods synthesized under optimum conditions.

Diols	Polymer				
	Polymer	Yield (%) ^a	$\eta_{inh}(dL/g)^a$	Yield (%) ^b	$\eta_{inh}(dL/g)^b$
5a	6a	96.2	1.00	85.3	0.48
5b	6b	94.1	0.70	92.3	0.64
5c	6c	89.2	0.67	65.6	0.56
5d	6d	95.6	0.55	86.0	0.53
5e	6e	78.0	0.56	69.3	0.36
5f	6f	69.2	0.57	90.1	0.55
5g	6g	85.5	0.80	72.4	0.49
5h	6h	90.4	0.86	79.3	0.78

(a) Method A: Direct polyesterification of imide containing diacid and aromatic diols using thionyl chlorid/pyridine as condensing agent. (b) Method B: The direct polyesterification of dicarboxylic acid and aromatic diols using TsCl/DMF/Py as a condensing agent [23].

Table 7. Thermal properties of **PEIs 6e** and **6f**.

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char yield (%) ^c
6e	433	553	73
6f	343	450	55

(a) Temperature at which 5% weight loss was recorded by TGA at heating rate of 20°C/min in N₂.

(b) Temperature at which 10% weight loss was recorded by TGA at heating rate of 20°C/min in N₂.

(c) Percentage weight of material left undecomposed after TGA analysis at maximum temperature 800°C in N₂.

¹HNMR spectroscopy analysis which are similar to those analysis in previous work [23].

Solubility Behaviour

Solubility behaviour of polymers was tested in various solvents which were similar to those solvent in ref. [23].

Thermal Properties

Thermal properties of **PEIs** were studied by means of TGA conducted under nitrogen atmosphere, at a heating rate of 20°C/min. The temperature at which the decomposition began never gets below 300°C. Several thermal regions were selected on TGA curves for comparison of the relative thermal stabilities of **PEIs**. These are polymer decomposition temperatures (PDT)s, char yield at 800°C (%Y). PDT₁₀ refers to the temperature at which 10% weight loss occurs for the polymer, and PDT₅ is the temperature corresponding to the temperature at which 5% weight

loss occurs for the polymer decomposition.

The results are summarized in Table 7. Figure 1 shows the TG curves of **PEIs 6e** and **6f** which reveals that **PEI 6e** has a better thermal stability than **PEI 6f**.

CONCLUSIONS

In this investigation several optically active aliphatic-aromatic **PEIs** having moieties of *N,N'*-(4,4'-oxydipthaloyl)-bis-*L*-leucine were successfully synthesized by direct polycondensation method. The results clearly show that the obtained **PEIs** have either excellent solubility in various polar solvents and high thermal stability. Direct polycondensation was carried out by using aliphatic-aromatic imide containing diacid and aromatic diols using thionyl chloride/Py as condensing agent to prepare aliphatic-aromatic **PEIs**.

The effects of aging time, reaction temperature, and reaction time were investigated on the physical properties of the resulting polymers. For comparison, direct method A and direct method B (TsCl/Py/DMF) were used. Direct method A showed a series of advantages including improved reaction yield, higher molecular weights of the **PEIs**, and lower reaction temperature.

ACKNOWLEDGEMENT

We wish to express our gratitude to the Research Affairs Division of Isfahan University of Technology (IUT), Isfahan, for financial support. Further financial support from Center of Excellency in Chemistry Research (IUT) is gratefully acknowledged.

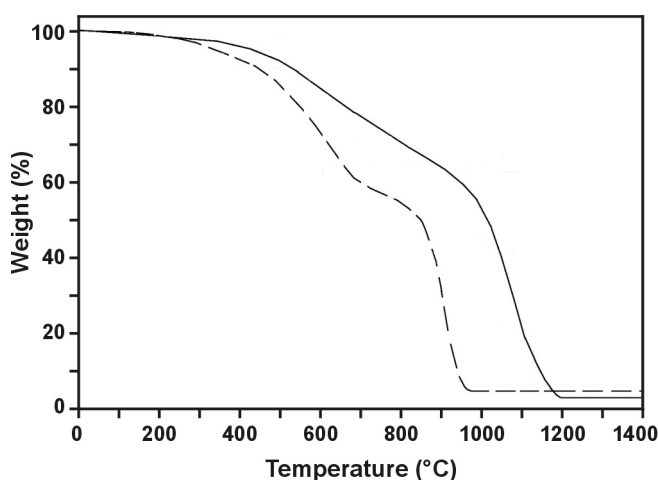


Figure 1. TGA of **PEI 6e** (—) and **PEI 6f** (----) with a heating rate of 20°C/min in nitrogen atmosphere.

REFERENCES

1. Collins A. N., Sheldrake G.N., Crosby J., *Chirality In Industry*, John Wiley, New York, (1994).
2. Subramanian G., *Chiral Separation Techniques*, WILEY-VCH, New York (2001).
3. Mallakpour S., Kowsari E., Preparation and characterization of optically active and organosoluble poly(amide-imide)s from polycondensation reaction of *N,N'*-(4,4'-sulphonedipthaloyl)-bis-*L*-isoleucine diacid with aromatic diamines, *Polym. Adv. Technol.*, **16**, 466–472, 2005.
4. Mallakpour S., Kowsari E., Synthesis and properties of novel soluble and thermally stable optically active poly(amide-imide)s from *N,N'*-(4,4'-oxydipthaloyl)-bis-*L*-phenylalanine diacid chloride and aromatic diamines, *Polym. Bull.*, **54**, 147–155, 2005.
5. Mallakpour S., Kowsari E., Soluble novel optically active poly(amide-imide)s derived from *N,N'*-(4,4'-oxydipthaloyl)-bis-*L*-leucine diacid chloride and various aromatic diamines: Synthesis and characterization. *J. Appl. Polym. Sci.*, **96**, 435–442, 2005.
6. Mallakpour S., Kowsari E., Microwave-assisted and conventional polycondensation reaction of optically active *N,N'*-(4,4'-sulphonedipthaloyl)-bis-*L*-leucine diacid chloride with aromatic diamines, *J. Appl. Polym. Sci.*, **91**, 2991–3000, 2004.
7. Mallakpour S., Zamanlou M.R., Synthesis of new optically active poly(amide-imide)s containing EPICLON and *L*-phenylalanine in the main chain by microwave irradiation and classical heating., *J. Appl. Polym. Sci.*, **91**, 3281–3291, 2004.
8. Mallakpour S., Kowsari E., Synthesis and characterization of novel, optically active poly(amide-imide)s from *N,N'*-(4,4'-sulfonyldipthaloyl)-bis-*L*-phenylalanine diacid and aromatic diamines under microwave irradiation, *J. Polym. Sci. Pol. Chem.*, **41**, 3974–3988, 2003.
9. Higashi F., Nishi T., High-molecular-weight poly(p-phenyleneterephthalamide) by CaCl_2 promoted direct polycondensation with thionyl chloride in *N*-methylpyrrolidone, *J. Polym. Sci. Pol. Chem.*, **26**, 3235–3240, 1988.
10. Higashi F., Kubayashi A., Direct polyamidation with phosphorus oxychloride in pyridine, *J. Polym. Sci. Pol. Chem.*, **27**, 507–513, 1989.
11. Higashi F., Mashimo T., Direct polyamidation with tosyl chloride in pyridine by formamide catalyzed alcoholysis, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 2999–3005, 1985.
12. Higashi F., Akiyama N., Takashi I., Koyama T., Direct polyamidation of aromatic dicarboxylic acids bisphenols with tosyl chloride and *N,N*-dimethylformamide in pyridine, *J. Polym. Sci. Pol. Chem. Ed.*, **22**, 1653–1660, 1984.
13. Higashi F., Yamada Y., Hoshio A., Direct polyamidation of hydroxybenzoic acids by use of diphenyl chlorophosphate in the presence of *N,N*-dimethylformamide, *J. Polym. Sci. Pol. Chem. Ed.*, **22**, 2181–2187, 1984.
14. Yang C., Lin J., Syntheses and properties of aromatic polyamides and polyimides derived from 9, 9-bis [4-(p-aminophenoxy) phenyl] fluorine, *J. Polym. Sci. Pol. Chem.*, **31**, 2153–2163, 1993.
15. Kasashima Y., Kumada H., Yamamoto K., Akutsa F., Naruchi K., Miura M., Preparation and properties of polyamides and polyimides from 4,4'-diamino-*o*-terphenyl, *Polymer*, **36**, 645–650, 1995.
16. Diakoumakos C. D., Mikroyannidis J.A., Unsaturated polyamides prepared from 3-amino-*r*-4-carboxycinnamic acid and their heat curing to thermally stable resins, *Polymer*, **36**, 387–392, 1995.
17. Mallakpour S. E., Hajipour A.R., Roohipour Fard R., Direct polycondensation of *N*-trimellitylimido-*L*-leucine with aromatic diamines, *Eur. Polym. J.*, **36**, 2455–2462, 2000.
18. Mallakpour S. E., Hajipour A.R., Vahabi R., Synthesis and characterization of novel poly(amide-imide)s based on bis(p-amidobenzoic acid)-*n*-trimellitylimido-*L*-leucine, *J. Appl. Polym. Sci.*, **84**, 35–43, 2002.
19. Mallakpour S. E., Hajipour A. R., Shahmohammadi M. H. Direct polycondensation of *N*-trimellitylimido-*L*-isoleucine with aromatic diamines, *J. Appl. Polym. Sci.*, **89**, 116–122, 2003.
20. Mallakpour S.E, Hajipour A. R., Shahmohammadi M. H., Novel optically active poly(amide-imide)s from *N*-Trimellitylimido-*S*-valine and aromatic diamines by direct polycondensation reaction, *Iran. Polym. J.*, **11**, 425–431, 2002.

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21. Higashi F., Mashimo T., Takahashi I., Preparation of aromatic polyesters by direct polycondensation with thionyl chloride in pyridine, *J. Polym. Sci. Pol. Chem.*, **24**, 97-102, 1986.
 22. Mallakpour S., Kowsari E., Direct polycondensations of *N,N'*-(4,4'-oxydiphthaloyl)-bis-*L*-leucine diacid by use of tosyl chloride in the presence of *N,N*-dimethylformamide, *Polym. Adv. Technol.* , **16**, 795-799, 2005.