Amino Acids (2010) 39:841–848
DOI 10.1007/s00726-010-0539-x

ORIGINAL ARTICLE

Construction of chiral polyesters from polycondensation of multifunctional monomer containing both flexible amino acid and rigid pendant groups with aromatic diols

Shadpour Mallakpour · Marziyeh Khani

Received: 17 October 2009 / Accepted: 20 February 2010 / Published online: 10 March 2010

Abstract A number of chiral wholly aromatic polyesters (PEs) with phthalimido and flexible chiral unit in the backbone were prepared from a chiral synthesized diacid monomer, 5-(3-methyl-2-phthalimidylpentanoylamino) isophthalic acid (**1**), and various aromatic diols via the polyesterification reaction. The tosyl chloride/pyridine/*N,N*-dimethylformamide (DMF) system was used as a condensing agent. All of the these polymers having bulky phthalimido and amino acid functionalities in the side chain showed excellent solubility and readily dissolved in various solvents such as *N*-methyl-2-pyrrolidinone, *N,N*-dimethylacetamide and DMF. Since, these chiral polymers have natural amino acids in the polymer architecture, they are expected to be biodegradable and therefore may be classified under eco-friendly polymers. They had useful levels of thermal stability associated with excellent solubility. Thermogravimetric analysis (TGA) showed that the obtained PEs are rather thermally stable, 10% weight loss temperatures in excess of 317°C, and char yields at 700°C in the nitrogen atmosphere higher than 24%. The resulting polymers were obtained in good yields with inherent viscosities ranging between 0.22 and 0.56 dL/g and were characterized with FT-IR, ^{1}H-NMR, elemental and TGA techniques.

Keywords Isoleucine · Inherent viscosity · Optically active polymers · Polycondensation · Polyesters

S. Mallakpour (✉) · M. Khani
Organic Polymer Chemistry Research Laboratory,
Department of Chemistry, Isfahan University of Technology,
84156-83111 Isfahan, I R Iran
e-mail: mallak@cc.iut.ac.ir; mallak777@yahoo.com;
mallakpour84@alumni.ufl.edu

Introduction

Polyesters (PEs) were in history the first category of synthetic condensation macromolecules and were investigated as part of Carothers' pioneering studies on polymerization in the 1930s (Edlund and Albertsson 2003). PEs are perfect for do-it-yourself, as well as in large industrial operations since they are simple to formulate, mix, and cure with a minimum of convoluted apparatus. They are becoming more and more popular because of their low cost, ease of application, and versatility. They find uses in, industrial construction, laminates, insulation, coatings, adhesives and molding compounds (Feldman and Barbalata 1996; Tawfik et al. 2003). A variety of combinations of reactant(s) and process conditions are potentially accessible to synthesize PEs (Odian 2004). PEs are classically prepared by stepwise polymerization of difunctional monomers of the AB type, i.e., hydroxy acids, or from a combination of AA and BB difunctional monomers. Polycondensation of difunctional monomers contain the esterification of diacids and diols, diacid chlorides and diols, or the ester interchange reaction of diesters and diols. (Edlund and Albertsson 2003; Kumar et al. 2003; Okada 2002; Vijayakumar et al. 2007). Aromatic PEs are known to be heat resistant and thermally stable macromolecules. Aromaticity in the PE backbone also tends to provide cured products that are more rigid (Flores and Balta Calleja 1998; Tawfik et al. 2003). Thermally stable PEs derived from isophthalic and terephthalic acids with bisphenol A have been commercialized (Tamami et al. 2004). However, these PEs encounter processing difficulties because of their high glass transition or melting temperatures joined with insolubility in the majority of organic solvents. Numerous approaches have been proposed to develop structurally modified polymers having increased solubility in order to improve their processability, whereas maintaining a good

thermal stability, based on the amalgamation of flexible segments in the macromolecule backbone, without sacrificing heat resistance (Bucio et al. 2005; Liaw and Chen 1996; Liaw et al. 2004, 2001; Zhang et al. 2005). The other strategy is the incorporation of pendant bulky groups along the polymer backbone, which results in a less ordered polymer matrix increasing the solubility characteristics with no affecting thermal and mechanical properties to a large extent (Ferrero et al. 2002; Sava et al. 2003). Recently, we have reported that PEs containing pendant bulky groups and flexible segments possess high thermal stability and enhanced solubility in organic solvents (Mallakpour and Sepehri 2008; Mallakpour and Seyedjamali 2008).

The preparation and application of optically active macromolecules are topics presently attracting much interest. This may occur primarily from their chiral structure which is common to naturally occurring macromolecules. Most of the naturally occurring polymers are optically active and some of them illustrate characteristic functionalities such as molecular recognition capacity and catalytic activity, due to their specific chiral structure as represented by genes and proteins. In synthetic polymer chemistry, it seems that one of the most challenging tasks is to construct functional polymeric systems that will be as effective as those in living systems, and the optically active synthetic macromolecules have today become of great curiosity and significance in this respect (Okamoto and Nakano 1994). In recent years, optically active polymers have attracted attention for their significant applications as catalysts for asymmetric synthesis and chiral stationary phases for the direct optical resolution of enantiomers and many publications on synthesis and characterization of such polymers have appeared in the literature (Chen et al. 2007; Itsuno 2005; Koyama et al. 1997; Samui et al. 2002). A large number of studies on chiral materials, reported in literature, are dedicated to amino acids and carbohydrates. The selection of amino acids is due to their availability with high optical purity and lower cost. These types of polymer also show biodegradability which could be listed as environmentally friendly materials (Bajgai et al. 2008; Bikiaris and Achilias 2008; Bordes et al. 2009; Hwang et al. 2006; Khang et al. 2003; Mallakpour and Sepehri 2008; Mallakpour and Seyedjamali 2008; Pan and Inoue 2009).

L-Isoleucine (ILE) is one of the three branched chain amino acids that are necessary to humans. Nevertheless, ILE is the only amino acid with an aliphatic side chain that has a stereocentre at the β-carbon. This carbon has an *R*-absolute configuration. This also implies that the ILE side chain can attain further out than that of its homologue (valine). For this reason, ILE in a protein may have not only the structural but also a functional role to play (Barroso et al. 2001; Mamer 2001). It is one of the vital amino acids to synthesize some hormones and enzymes. They are active site residues of enzymes, and assist in maintaining the exact conformation of enzymes by keeping them in their suitable ionic states (Kini et al. 2002). ILE can increase the protein integration and inhibit the protein from degradation. ILE has been extensively used as an additive in biological medicine, structuring project, photochemistry, electrochemistry, food industry and cosmetics. It is also used as feed additive and added to functional beverage (Murin et al. 2009; Peng et al. 2009). ILE has been used also in NMR structure determination (Barroso et al. 2001). It is also of great commercial interest as a food and feed additive because mammals are not able to prepare this essential amino acid. ILE is currently produced on a scale of about 400 tons per year (Kawabe et al. 2006; Sahm et al. 1999). This is the main nitrogen source in muscle (Doi et al. 2003).

In continuation of our previous works (Mallakpour and Khani 2007; Mallakpour and Kolahdoozan 2006; Mallakpour and Sepehri 2008; Mallakpour and Seyedjamali 2008, 2009; Mallakpour and Taghavi 2008; Mallakpour and Zadehnazari 2010) on synthesis and characterization of optically active polymers containing amino acid moeities, we wish here to report a successful use of 5-(3-methyl-2-phthalimidylpentanoylamino)isophthalic acid (**1**) for efficient synthesis of thermally stable, and optically active PEs. The reaction promoted by tosyl chloride (TsCl) in pyridine (Py) was applied to the direct polyesterification of diacid **1** with different aromatic diols.

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. 5-Aminoisophthalic acid was recrystallized from H_2O/*N,N*-dimethylformamide (DMF) (4/1) mixture. *N,N*-Dimethylacetamide (DMAc) was dried over BaO, followed by fractional distillation. Bisphenol A (2C) was purified by recrystallization from acetic acid/water. The other diols were used as obtained without further purification. (2*S*,3*S*)-5-(3-Methyl-2-phthalimidylpentanoylamino)isophthalic acid (**1**) as an optically active diacid monomer was synthesized according to our previous work (Mallakpour and Taghavi 2008). Melting point > 315°C, $[\alpha]_D^{25} = -27.3$ (0.05 g in 10 mL DMF).

Instrument and measurement

Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra were recorded in DMSO-d_6 and $CDCl_3$ solution

using a Bruker (Germany) Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), triplet (t) and multiplet (m). FT-IR spectra were recorded on a Nicolet impact 400_D IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Inherent viscosities were measured by a standard procedure using a Cannon-Fenske Routine Viscometer (Germany). Specific rotations were measured by a JASCO Polarimeter to spy incorporation of chiral structure in polymer backbone. Thermal gravimetric analysis (TGA) data for polymers were taken on a Perkin–Elmer Thermal Gravimetric Analyzer (Germany) under a nitrogen atmosphere at a heating rate of 10°C/min by the Research Institute of Polymer and Petrochemical of Iran (IPPI).

Polymer synthesis

The PEs were prepared by the following procedure: for synthesis of polymer **PE3C**, A Py (0.20 mL) solution of TsCl (0.26 g; 1.23×10^{-3} mol), after 30 min stirring at room temperature (RT), was treated with DMF (0.09 mL; 1.22×10^{-3} mol) for 30 min and the resulting solution was added dropwise to a solution of diacid **1** (0.103 g; 2.44×10^{-4} mol) in Py (0.20 mL). The mixture was maintained at room temperature for 30 min, then to this mixture, a solution of bisphenol A (2C) (0.056 g; 2.44×10^{-4} mol) in Py (0.20 mL) was added dropwise 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 30 mL of methanol to give 0.127 g of polymer **PE3C** (80% yield). The other PEs were prepared by a similar procedure.

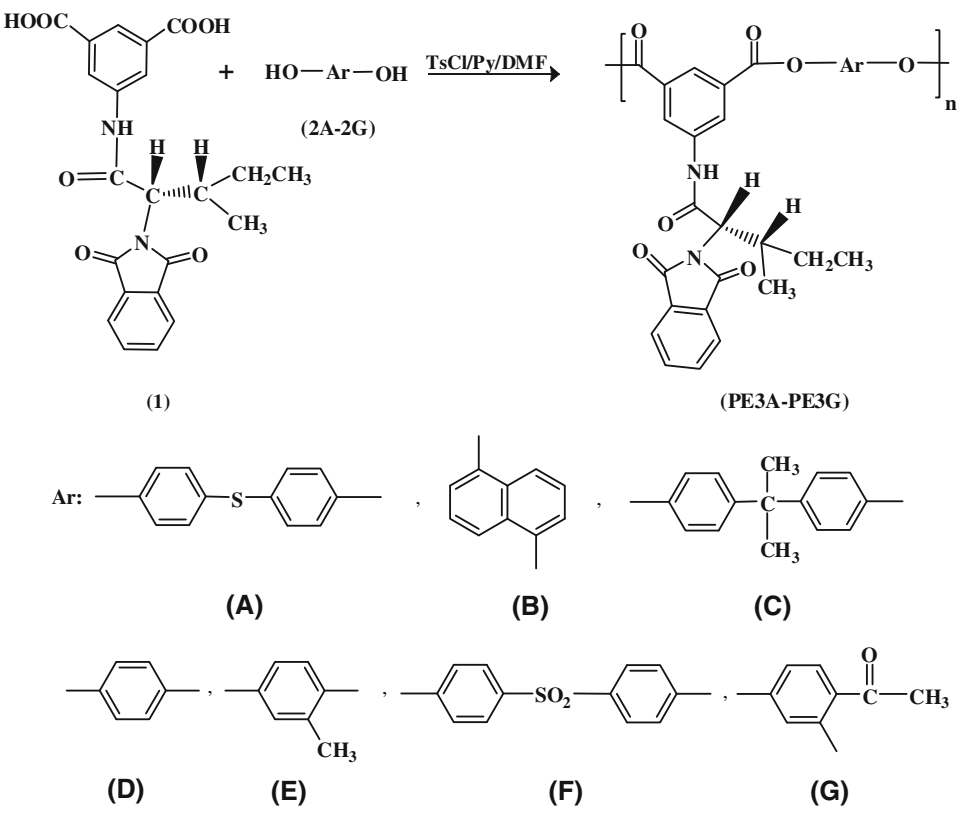
Result and discussion

Monomer synthesis

(2*S*,3*S*)-5-(3-Methyl-2-phthalimidylpentanoylamino)isophthalic acid (**1**) was prepared by a previous procedure (Mallakpour and Taghavi 2008).

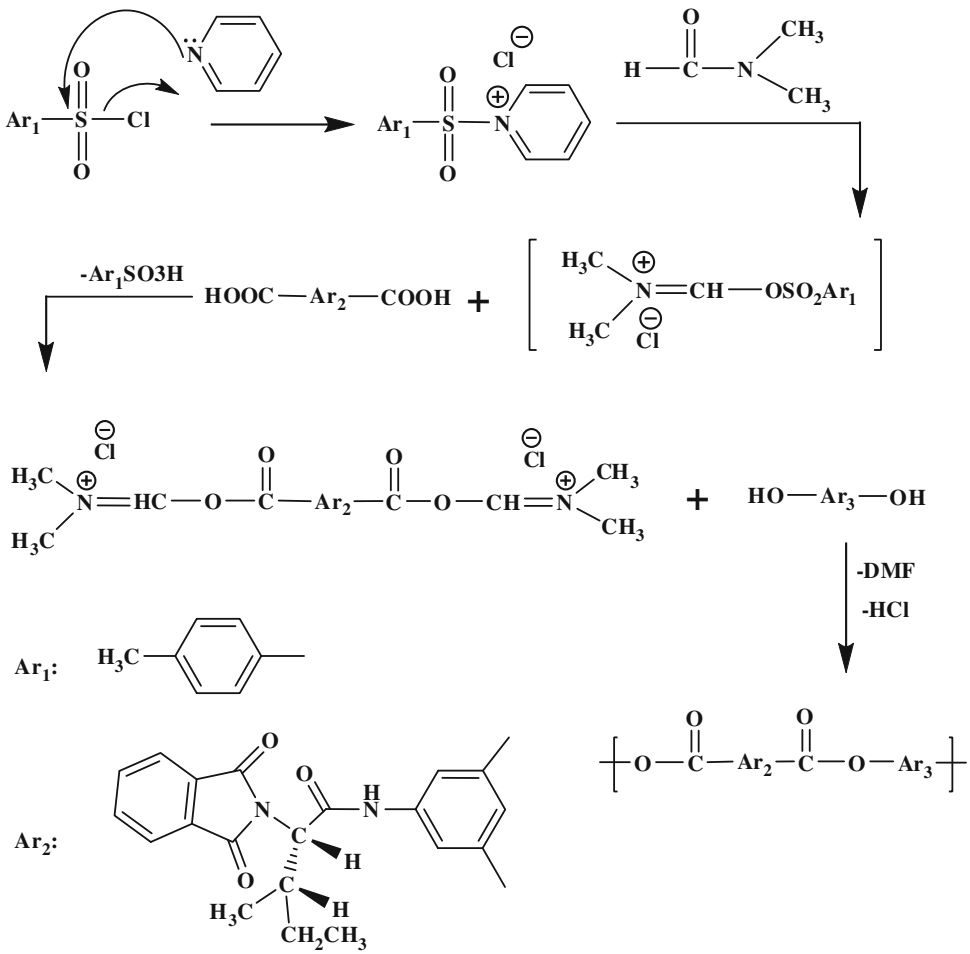
Polymer synthesis

In this work, new wholly aromatic polyesters with phthalimido pendant group were synthesized with the aim of achieving better solubility and thermal stability. The Vilsmeier adduct was used for the polycondensation of optically active and aromatic diacid and diols in the following way: TsCl was dissolved in Py and after a certain period of time (aging time) the solution was treated with



Scheme 1 Polycondensation reactions of monomer **1** with different diols

Scheme 2 Mechanism of polycondensation reaction of diacid **1** with aromatic diols



Ar_3: Aromatic moeities of diols

DMF for several times to form Vilsmeier adduct (Schemes 1, 2) as proposed by Higashi et al. (Higashi and Tobe 2001). 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 an elevated temperature for several hours. All the reaction parameters such as aging times, reaction time, temperature and molar ratio of chemical additives to diacid which have considerable effect on the reaction progress were optimized in previous work (Mallakpour and Kolahdoozan 2006). The synthesis and some physical properties of these novel optically active PEs are listed in Table 1. The inherent viscosities of the resulting polymers under optimized conditions were in the range of 0.22–0.56 dL/g and the yields were 70–86%. The incorporation of a chiral unit into the polymer backbone was confirmed by measuring the specific rotations of polymers with different source lamps (Table 1). As shown in Table 1 all of the obtained polymers show optical rotation and therefore are optically active.

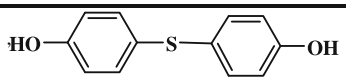
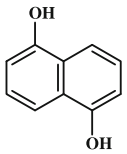
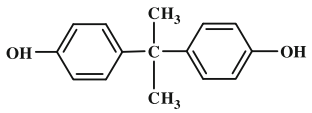
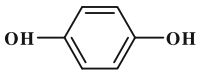
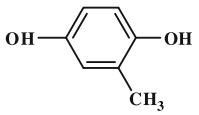
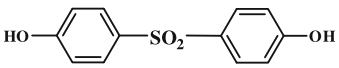
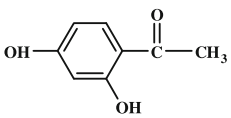
Thermal stability

The thermal properties of **PE3C** and **PE3D** were evaluated by 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 700°C has been calculated by means of thermograms, and used as a criterion for the evaluation of thermal stability of the polymers. Figure 1 shows the TGA thermograms of **PE3D**. The thermoanalysis data of these polymers are summarized in Table 2. The 10% weight loss temperature of these polymers was more than 314°C. The **PE3D** shows a better thermal stability compared to a **PE3C**. This may be attributed to a higher inherent viscosity of **PE3D** in comparison to **PE3C**.

Characterization

The resulting PEs were characterized by FT-IR spectroscopy, ^{1}H-NMR spectroscopy and elemental analysis. The structures of these polymers were confirmed as PEs by

Table 1 Reaction conditions for the polymerization of monomer **1** with different diols and some physical properties of PEs

Polymer	Diols	Yield (%)	η (dL/g)	$[\alpha]_{D\ c}^{25}$	$[\alpha]_{Hg\ c,d}^{25}$
PE3A		70	0.22[a]	−12.4	−48.4
PE3B		85	0.30[a]	−22.6	−27.2
PE3C		80	0.45[b]	−25.7	−15.2
PE3D		86	0.56[a]	−20.6	+40.9
PE3E		87	0.24[a]	−15.4	−28.5
PE3F		72	0.24[a]	+25.6	−44.9
PE3G		82	0.23[a]	−15.6	−50.2

TsCl/DMF/Py was used as a condensing agent

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

[b] Measured at concentration of 0.5 g/dL in DMF containing 2% W/W LiCl (soluble fraction) at 25°C

[c] Measured under the condition the same as viscosity

[d] Wide range was used (no filter was used for the Hg lamp)

means of FT-IR spectroscopy. The FT-IR spectra of all polymers showed absorptions around 3,335 cm^{-1} (N–H) and two overlapped carbonyl (ester and imide C=O) absorptions at 1,717 cm^{-1}. All of these PEs exhibited absorptions at 1,370–1,380 and 715–725 cm^{-1} which show the presence of the imide heterocycle in these polymers. The FT-IR spectrum of **PE3C** is shown in Fig. 2.

The ^{1}H-NMR spectrum of **PE3C** showed peaks that confirms its chemical structure (Fig. 3). It showed peak for CH_3 (1) which appeared as distorted t at 0.82 ppm. Peaks for CH_3 (2) appeared as doublet at 1.02 ppm according to their coupling with CH (5). The Peaks in the region of 1.49–1.61 ppm are related to diastereotopic hydrogens of CH_2 (3,3′) which appeared as multiplet. In the spectrum of **PE3C**, CH_3 protons of bisphenol A appeared at 1.69 ppm as a single peak. Peak in the region of 2.59–2.64 ppm are related to CH_2 (5). Peak at 4.69 ppm is assigned for CH (6) which appeared as doublet. The aromatic protons appeared in the region of 7.22–8.69 ppm. The peaks in the region of 10.53 ppm are assigned for NH of amide group.

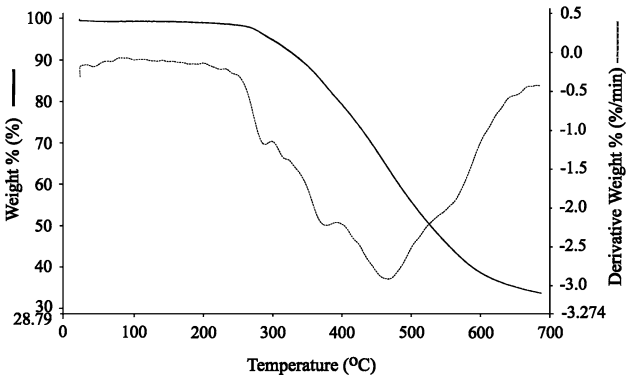


Fig. 1 TGA thermogram of **PE3D** under a nitrogen atmosphere at heating rate of 10°C/min

^{1}H-NMR Peaks (ppm) for **PE3D**

0.85–0.92 (distorted t, 3H, CH_3), 1.04 (distorted d, 3H, CH_3), 1.18–1.50 (m, 2H, CH_2), 2.90–2.94 (m, 1H, CH), 4.71 (distorted d, 1H, CH), 6.82–7.93 (8H, Ar–H), 8.97 (s, 1H, Ar–H), 9.53 (s, 2H, Ar–H), 10.54 (s, 1H, NH).

Table 2 Thermal properties of **PE3C** and **PE3D**

Polymer	T_5 (°C)[a]	T_{10} (°C)[b]	Char yield (%)[c]
PE3C	287	314	24
PE3D	300	343	25

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

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

[c] Weight percentage of material left undecomposed after TGA analysis at a temperature of 700°C under a nitrogen atmosphere

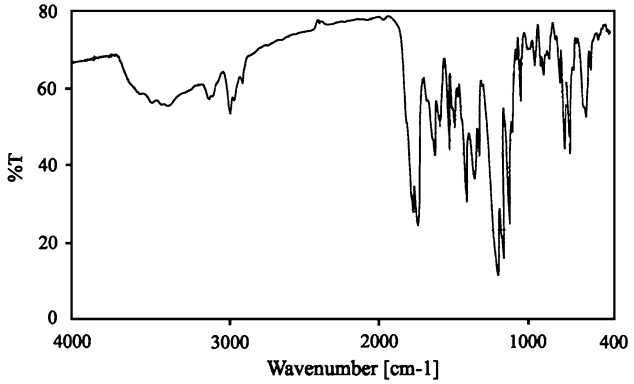


Fig. 2 FT-IR (KBr) spectrum of **PE3C**

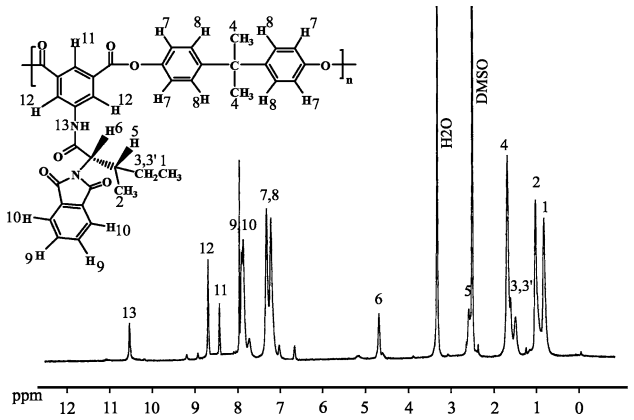


Fig. 3 ^{1}H-NMR (500 MHz) spectrum of **PE3C** in DMSO-d_6 at RT

It was observed that the obtained CHN values have good agreement with calculated percentage of carbon, hydrogen and nitrogen contents in the polymer repeating units (Table 3).

Solubility properties of PEs

The solubility properties of PEs were studied in different solvents. These polymers are soluble in amide type solvents such as 1-methyl-2-pyrrolidone (NMP), DMF and DMAc. They are insoluble in solvents such with lower polarities as water, methanol, chloroform and dichloromethane. Improved solubility of the PEs in organic solvents are attributed to facilitating the diffusion of organic solvents among the polymer chains that is a result of existence of bulky pendant groups along the polymer backbone which avoided the effective chain packing through hydrogen bonds that are characteristics of amide functional groups.

Conclusion

From the results obtained in this research, the following conclusions can be reached.

We have successfully used a novel chiral aromatic dicarboxylic acid (**1**), containing a rigid phthalimido and flexible amino acid pendant group for the synthesis of a series of novel optically active wholly aromatic PEs by the direct polycondensation with various aromatic diols using TsCl/DMF/Py as a condensing agent. The introduction of flexible pendant moieties and phthalimido group into the backbone of these polymers remarkably enhanced the solubility while maintaining good thermal stability of the new polymers. Wholly aromatic backbones of PEs provide some superior properties such as stability toward thermal shocks and at last, organosolubility of PEs removes the processing difficulties which are regularly associated with handing out of this important type of macromolecules. From the chemical point of view the ester group imparts to the polymer's main chain increased sensibility to hydrolysis that can cause chain breaking. In addition, because of the existence of amino acids in the polymer pendant group

Table 3 Elemental analysis of PEs

Polymer	Formula	C%		H%		N%	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
PE3C	$C_{37}H_{32}N_2O_7$ 616.66 g/mol	72.07	71.88	5.23	5.06	4.54	4.98
PE3D	$C_{28}H_{22}N_2O_7$ 498.48 g/mol	67.46	66.98	4.45	4.24	5.62	5.93

these polymers are expected to be biodegradable and therefore could be classified under eco-friendly polymers. Optical activities of resulting PEs make them the potentially useful candidates for the new chiral stationary phases in HPLC techniques.

Acknowledgments We wish to express our gratitude to the Research Affairs Division, Isfahan University of Technology (IUT), Isfahan, for partial financial support. Further financial support from National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged. We also like to thank Dr Z. Rafiee and Mr. M. Dinari.

References

Bajgai MP, Aryal S, Lee DR, Park SJ, Kim HY (2008) Physicochemical characterization of self-assembled poly(ε-caprolactone) grafted dextran nanoparticles. Colloid Polym Sci 286:517–524

Barroso MN, Cerutti ES, Rodriguez AM, Jauregui EA, Farkas O, Perczel A, Enriz RD (2001) Side-chain conformations for selected backbone conformations of *N*-acetyl-L-isoleucine-*N*-methylamide and *N*-acetyl-L-nor-isoleucine-*N*-methylamide. An exploratory ab initio study. J Mol Struct (Theochem) 548:21–37

Bikiaris DN, Achilias DS (2008) Synthesis of poly(alkylene succinate) biodegradable polyesters, Part II: mathematical modelling of the polycondensation reaction. Polymer 49:3677–3685

Bordes P, Pollet E, Averous L (2009) Nano-biocomposites: biodegradable polyester/nanoclay systems. Prog Polym Sci 34:125–155

Bucio E, Fitch JW, Venumbaka SR, Cassidy PE (2005) Synthesis and properties of aliphatic spirodilactam diphenol containing polyesters. Polymer 46:3971–3974

Chen J, Zhou Y, Nan Q, Ye X, Sun Y, Zhang F, Wang Z (2007) Preparation and properties of optically active polyurethane/TiO_2 nanocomposites derived from optically pure 1,1′-binaphthyl. Eur Polym J 43:4151–4159

Doi M, Yamaoka I, Fukunaga T, Nakayama M (2003) Isoleucine, a potent plasma glucose lowering amino acid, stimulates glucose uptake in C2C12 myotubes. Biochem Biophys Res Commun 312:1111–1117

Edlund U, Albertsson AC (2003) Polyesters based on diacid monomers. Adv Drug Deliver Rev 55:585–609

Feldman D, Barbalata A (1996) Synthetic polymers, technology, properties, applications. Chapman and Hall, London

Ferrero E, Espeso JF, Campa JGDL, Abajo JD, Lozano AE (2002) Synthesis and characterization of aromatic polyamides containing alkylphthalimido pendent groups. J Polym Sci Part A Polym Chem 40:3711–3724

Flores A, Balta Calleja FJ (1998) Mechanical study of sintered aromatic polyesters as revealed by microindentation measurements. J Mater Sci 33:3567–3571

Higashi F, Tobe A (2001) A new polycondensation involving dicarboxylic acids with differently activated carboxyl groups by TsCl/DMF/Py. Macromol Chem Phys 202:745–749

Hwang KJ, Park JW, Kim I, Ha CS (2006) Effect of a compatibilizer on the microstructure and properties of partially biodegradable LDPE/aliphatic polyester/organoclay nanocomposites. Macromol Res 14:179–186

Itsuno S (2005) Chiral polymer synthesis by means of repeated asymmetric reaction. Prog Polym Sci 30:540–558

Kawabe M, Sano M, Hagiwara A, Tamano S, Suzuki S, Shirai T (2006) Lack of carcinogenicity of L-isoleucine in F344/DuCrj rats. Food Chem Toxicol 44:278–285

Khang G, Rhee JM, Jeong JK, Lee JS, Kim MS, Cho SH, Lee HB (2003) Local drug delivery system using biodegradable polymers. Macromol Res 11:207–223

Kini AK, Farokhi SA, Nandibewoor ST (2002) A comparative study of ruthenium(III) catalysed oxidation of L-leucine and L-isoleucine by alkaline permanganate. A kinetic and mechanistic approach. Transit Metal Chem 27:532–540

Koyama E, Sanda F, Endo T (1997) Polycondensations of hydroxycarboxylic acids derived from optically active aminoalcohols and acid anhydrides—syntheses of functional poly(ester-amide)s. J Polym Sci Part A Polym Chem 35:345–352

Kumar R, Tyagi R, Parmar VS, Samuelson LA, Kumar J, Watterson AC (2003) Enzymatic synthesis of multi-component copolymers and their structural characterization. Mol Divers 6:287–295

Liaw DJ, Chen PS (1996) Preparation and properties of polyesters derived from 4,4′-sulfonyl dibenzoyl chloride by solution polycondensation. J Polym Sci Part A Polym Chem 34:885–891

Liaw DJ, Hsu JJ, Liaw BY (2001) Synthesis and characterization of new soluble cardo polyesters derived from 1, 1-bis-[4-(4-chlorocarboxyphenoxy)phenyl]-4-tert-butylcyclohexane with various bisphenols by solution polycondensation. J Polym Sci Part A Polym Chem 39:2951–2956

Liaw DJ, Fan CL, Lin CC, Wang KL (2004) Synthesis and characterization of new soluble poly(esterimide)s containing noncoplanar 2,2′-dimethyl-4,4′-biphenylene unit. J Appl Polym Sci 92:2486–2493

Mallakpour S, Khani M (2007) Novel optically active poly(amide-imide)s derived from *N*-trimellitylimido-L-isoleucine and different diisocyanates. Polym Bull 59(5):587–596

Mallakpour S, Kolahdoozan M (2006) Preparation and characterization of novel optically active poly(amide-ester-imide)s based on bis(*p*-aminobenzoic acid)-*N*-trimellitylimido-*S*-valine via direct polyesterification. Iran Polym J 15:307–315

Mallakpour S, Sepehri S (2008) Synthesis and characterization of new optically active polyesters by step-growth polymerization of novel aromatic (2*S*)-4-[(4-methyl-2-phthalimidyl-pentanoylamino)benzoylamino]isophthalic acid with aromatic diols. J Appl Polym Sci 110(5):2942–2949

Mallakpour S, Seyedjamali S (2008) Synthesis and characterization of novel organosoluble and optically active aromatic polyesters containing L-methionine and phthalimide pendent groups. Amino Acids 34(4):531–538

Mallakpour S, Seyedjamali H (2009) Fast synthesis of optically active polyamides containing L-methionine linkages in ionic liquid via a microwave-assisted process. Colloid Polym Sci 287:1111–1116

Mallakpour S, Taghavi M (2008) A facile, microwave-assisted synthesis of novel optically active polyamides derived from 5-(3-methyl-2-phthalimidylpentanoylamino) isophthalic acid and different diisocyanates. Eur Polym J 44:87–97

Mallakpour S, Zadehnazari A (2010) Microwave irradiation as a versatile tool for increasing reaction rates and yields in synthesis of optically active polyamides containing flexible L-leucine amino acid. Amino Acid (in press)

Mamer OA (2001) Initial catabolic steps of isoleucine, the *R*-pathway and the origin of alloisoleucine. J Chromatogr B 758:49–55

Murin R, Mohammadi G, Leibfritz D, Hamprecht B (2009) Glial metabolism of isoleucine. Neurochem Res 34:194–204

Odian G (2004) Principles of polymerization. Wiley Interscience, New York

Okada M (2002) Chemical syntheses of biodegradable polymers. Prog Polym Sci 27:87–133

Okamoto Y, Nakano T (1994) Asymmetric polymerization. Chem Rev 94:349–372

Pan P, Inoue Y (2009) Polymorphism and isomorphism in biodegradable polyesters. Prog Polym Sci 34:605–640

Peng Z, Fang J, Li J, Liu L, Du G, Chen J, Wang X, Ning J, Cai L (2009) Combined dissolved oxygen and pH control strategy to improve the fermentative production of L-isoleucine by *Brevibacterium lactofermentum*. Bioprocess Biosyst Eng (in press)

Sahm H, Eggeling L, Morbach S, Eikmanns B (1999) Construction of L-isoleucine overproducing strains of *Corynebacterium glutamicum*. Naturwissenschaften 86:33–38

Samui AB, Ratna D, Chavan JG, Deb PC (2002) Modification of epoxy resin with optically active carboxylic acid. J Appl Polym Sci 86:2523–2529

Sava I, Iosip MD, Bruma M, Hamciuc C, Robison J, Okrasa L, Pakula T (2003) Aromatic polyamides with pendent acetoxybenzamide groups and thin films made therefrom. Eur Polym J 39:725–738

Tamami B, Yeganeh H, Kohmareh GA (2004) Synthesis and characterization of novel polyesters derived from 4-aryl-2,6-bis(4-chlorocarbonyl phenyl) pyridines and various aromatic diols. Eur Polym J 40:1651–1657

Tawfik SY, Asaad JN, Sabaa MW (2003) Effect of polyester backbone structure on the cured products properties. Polym Test 22:747–759

Vijayakumar CT, Sivasamy P, Rajkumar T (2007) Synthesis and characterization of 1,3-bis(2-hydroxyethoxy) benzene based saturated and unsaturated polyesters. Eur Polym J 43:3028–3035

Zhang S, Li Y, Yin D, Wang X, Zhao X, Shao Y, Yang S (2005) Study on synthesis and characterization of novel polyimides derived from 2,6-bis(3-aminobenzoyl) pyridine. Eur Polym J 41:1097–1107