Iranian Journal of Organic Chemistry Vol. 2, No. 4 (2010) 479-485

Preparation and characterization of optically active polyamides containing natural L-leucine amino acid linkages

Shadpour Mallakpour[1,2*] and Mohammad Dinari[1]
[1]Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I. R. Iran.
[2]Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan, 84156-83111, I. R. Iran

Abstract: Step-growth polymerization reactions of chiral diacid monomer containing phthalimide and flexible chiral groups with different commercially available diisocyanates were carried out under oil bath heating at 120 °C in tetrabutylammonium bromide as a modern green solvent or in *N*-methylpyrrolidone as a traditional solvent. Different optically active and thermally stable polyamides were obtained in high yields and moderate inherent viscosities.

Keywords: Polycondensation reaction, Polyamides, Thermally stable polymers, Molten tetrabutylammonium bromide, Green chemistry

Introduction

Polymerization of chiral monomer is one of the most normally used approaches to prepare optically active polymers [1]. Numerous methods have been reported for the preparation of chiral polymers including amalgamation of amino acids into the polymer backbone or side chains [2]. Amino acids have been frequently employed as chiral sources in the synthesis of chiral polymers due to their accessibility and biological relevance. It can produce new biomaterials with a wide range of properties that can be easily adjusted by varying the components in the building block of the macromolecular backbone during synthesis [3-5]. Chiral polymers, counting those bearing main or side chain amino acid units have found successful uses in the pharmaceutical industry for enantio-selective separation of drugs, high performance liquid chromatography as chiral stationary phase, chiral liquid crystals and biomedical devices, etc [6,7].

Polyamides PAs are a class of engineering macromolecules that play an imperative role in modern industrial and commercial applications [8].

In recent years, sustained efforts have been devoted to rendering PAs more degradable, to extend their applications to new fields demanding materials with lower environmental impact or exhibiting biodegradable and biocompatible properties [9]. In the case of the synthetic PAs, only those containing the naturally occurring (L)-α-amino acids, being structurally close to the natural polypeptides, possess potentially degradable linkages that make them suitable as biomaterials [10,11].

The applications of aromatic PAs were limited owing to their infusibility and insolubility which make them difficult to process. One attractive synthetic route for these types of polymers is incorporation of bulky pendent groups along the polymer backbone to improve the solubility and processability [12].

Volatile organic compounds are the most usually used solvents in solution polymerizations, owing to their compatibility with monomers and simplicity of separation, even with their well-documented health and environmental concerns [13]. Because of the health and environmental concerns associated with volatile organic compounds, substitute solvents which are more environmentally benign are being investigated as potential replacements. Ionic liquids ILs have potential as volatile organic compounds alternatives and have received much interest recently for environmentally benign processing, including reactions and separations

---

*Corresponding author. Tel: +98 311 391 3267; Fax: +98 311 391 2350; E-Mail: *mallak@cc.iut.ac.ir, mallak777@yahoo.com, mallakpour84@alumni.ufl.edu*

[14,15]. ILs have become the focus of many examinations because of many good properties like, low flammability, negligible vapor pressure, high ionic conductivity, broad liquid temperature ranges and an excellent ability to dissolve organic compounds [16,17]. This unique set of properties has earned ILs recognition as environmentally benign alternatives to traditional organic solvents [18]. Then again, the synthesis of polymers in ILs media is also of significant scientific interest. Direct polycondensation reaction in ILs is a recently developed method of polymerization. The polyamidations in ILs proceed as one pot path-way reactions and have the advantages of direct polycondensation [19-21].

In previous study, we reported the synthesis and characterization of optically active PAs under microwave irradiation by different methods [22,23]. During this study, we successfully synthesized a series of optically active and thermally stable PAs containing phthalimide moieties and L-leucine amino acid linkages in the side chain via step-growth polymerization reaction of the chiral diacid monomer with a variety of diisocyanates by a one-step procedure using tetrabutylammonium bromide TBAB as a green media. Furthermore, the solubility, thermal and physical properties of these PAs are presented in this article.

Experimental

Apparatus and Reagents

Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra were recorded in DMSO-d_6 solution using a Bruker (Germany) Avance 500 instrument. Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). FT-IR spectra were recorded on Jasco-680 (Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 gdL^{-1} at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). Quantitative solubility was determined with 0.005 g of the polymer in 1 mL of the solvent. Thermal gravimetric analysis (TGA) data for polymers were taken on a Perkin Elmer (Pyris 1) instrument in a nitrogen atmosphere at a rate of 10 °C/min. Elemental analyses were performed by the Iranian Polymer and Petrochemical Institute, Tehran, Iran.

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. *N*-Methyl-2-pyrrolidone (NMP) *N,N*-dimethylformamide (DMF), pyridine (Py), and triethylamine (TEA) was dried over BaO and then were distilled under reduced pressure. TBAB with m.p = 100-103 °C was purchased from Merck Co. (Darmstadt, Germany) and was used without further purification.

Monomer synthesis

An optically active diacid monomer 5-(4-methyl-2-phthalimidylpentanoylamino)iso-phthalic acid was synthesized according to our previous study [22].

Polymer synthesis

Polymers were synthesized by two different methods:

Method A: Polymerization under oil bath heating in molten TBAB as a reaction medium

The **PA1-PA10** were prepared by the following general procedure: as an example for the preparation of **PA1**, a mixture of 0.10 g (2.36 × 10^{-4} mol) of diacid **1** and 0.30 g (9.42 × 10^{-4} mol) of TBAB was ground until a powder was formed. Then 0.02 mL (1.80 × 10^{-4} mol) of dibutyltin dilaurate (DBTDL) as a catalyst was added and it was transferred into a 25 mL round-bottom flask. 0.06 g (2.36 × 10^{-4} mol) of 4,4'-methylenebis(phenyl isocyanate) MDI (2) was added to the mixture and it was heated until homogeneous solution was formed. Then the solution was stirred for 12 h at 120 °C, and the viscous solution was precipitated in 30 mL of methanol. The white solid was filtered off and dried to give 0.148 g (93%) of white **PA1**. The above polymerization was repeated with Py or TEA as a catalyst, and without catalyst.

Method B: Polymerization under oil bath heating in NMP as a solvent

The **PA11-PA20** were prepared by the following general procedure: as an example for the preparation of **PA11**, a mixture of 0.10 g (2.36 × 10^{-4} mol) of diacid **1**, 0.18 mL of NMP and 0.02 mL (1.80 × 10^{-4} mol) of DBTDL as a catalyst was placed into a 25 mL round-bottom flask. Then 0.06 g (2.36 × 10^{-4} mol) of MDI was added to the mixture. It was heated until homogeneous solution was formed. The solution was stirred for 1 hr at RT, 3 h at 60 °C, 8 h at 80 °C, and then it was heated gradually from 100 to 120 °C during 4 h. After this period, 0.20 mL of NMP was added.

Then the viscous solution was precipitated in 30 mL of methanol. The white solid was filtered off and dried to give 0.15 g (94%) of white **PA11**. The above polymerization was repeated with Py or TEA as a catalyst, and without catalyst.

For each method, the optimized reaction conditions according to reaction time and reaction catalysts were selected for the polymerization of diacid monomer 1 with other diisocyanates such as isophorone diisocyanate (IPDI) 3, toluylene-2,4-diisocyanate (TDI) 4 and hexamethylene diisocyanate (HDI) 5.

PA1: FT-IR Peaks (cm^{-1}): 3311 (s), 3125 (w, sh), 2957 (s), 2853 (m), 1779 (s), 1720 (m), 1671 (m), 1644 (s), 1594 (w), 1555 (s), 1509 (m), 1466 (w), 1411 (m), 1380 (s), 1361 (m), 1323 (m), 1237 (m), 1075 (w), 1018 (w), 962 (w, br), 879 (w), 857 (w), 832 (w), 814 (w), 779 (w), 753 (w), 717 (w), 472 (w). ^{1}H-NMR Peaks (ppm): 0.89 (d, 6H, CH_3, J = 7.21 Hz), 1.41-1.43 (m, H, CH), 2.10-2.13 (m, 1H, CH_2), 2.21-2.24 (m, 1H, CH_2), 3.82-3.84 (m, 2H, CH_2), 4.93-4.95 (dd, 1H, CH, J_1 = 6.64, J_2 = 6.92 Hz), 7.30(d, 4H, CH, J = 8.23 Hz), 7.62 (d, 4H, CH, J = 8.23 Hz), 7.67 (s, 1H, CH), 7.86-7.89 (distorted dd, 4H, CH, J_1 = 9.34, J_2 = 10.21 Hz), 8.45-8.47 (m, br, 2H, CH), 10.21 (s, br, NH),10.35 (s, br, NH). Elemental analysis calculated for $(C_{35}H_{30}N_4O_5)_n$ (586.64 g/mol)$_n$: Calcd. C 71.65, H 5.15, N 9.55; Found C 70.85, H 4.28, N 9.17.

PA7: FT-IR Peaks (cm^{-1}): 3339 (s, br), 2931 (s), 2857 (m), 1775 (w), 1719 (s), 1670 (s), 1523 (s), 1467 (w), 1384 (s), 1254 (m), 1210 (m), 1094 (m), 904 (w), 876 (w), 769 (w), 720 (m), 661 (w), 530 (w). ^{1}H-NMR Peaks (ppm): 0.86 (d, 6H, CH_3, J = 7.14 Hz), 1.49-1.52 (m, CH), 2.01-2.04 (m, 1H, CH) 2.17-2.19 (m, 1H, CH) 2.24 (s, 1H, CH_3), 4.93-4.95 (dd, 1H, CH, J_1 = 5.68, J_2 = 6.81 Hz), 7.43 (d, 2H, CH, J = 8.23 Hz), 7.57 (s, 1H, CH), 7.68 (d, 4H, CH, J = 7.50 Hz) 7.85 (s, 1H, CH), 8.41 (s, br, 2H, CH), 10.01 (s, br, NH), 10.48 (s, br, NH). Elemental analysis calculated for $(C_{29}H_{26}N_4O_5)_n$ (510.54 g/mol)$_n$: Calcd. C 68.22, H 5.13, N 10.97; Found C 67.97, H 5.45, N 10.43.

PA15: FT-IR Peaks (cm^{-1}): 3369 (m, br), 3100 (m, sh), 2957 (s), 1776 (w), 1719 (s), 1665(s), 1523 (m), 1467 (w), 1384 (m), 1309 (w), 1254 (m), 1210 (m), 1095 (m), 769 (w), 720 (m), 611 (m), 531 (w).

PA19: FT-IR (KBr): FT-IR Peaks (cm^{-1}): 3339 (s, br), 2931 (s), 2857 (m), 1776 (w), 1719 (s), 1674 (s, br), 1599 (s), 1544 (s), 1447 (m), 1421 (s), 1383 (s), 1322 (m), 1303 (m), 1266 (m), 1222 (s), 1119 (w), 1071 (w, br), 1001 (w), 901 (w), 878 (w), 778 (w), 753 (w), 718 (m).

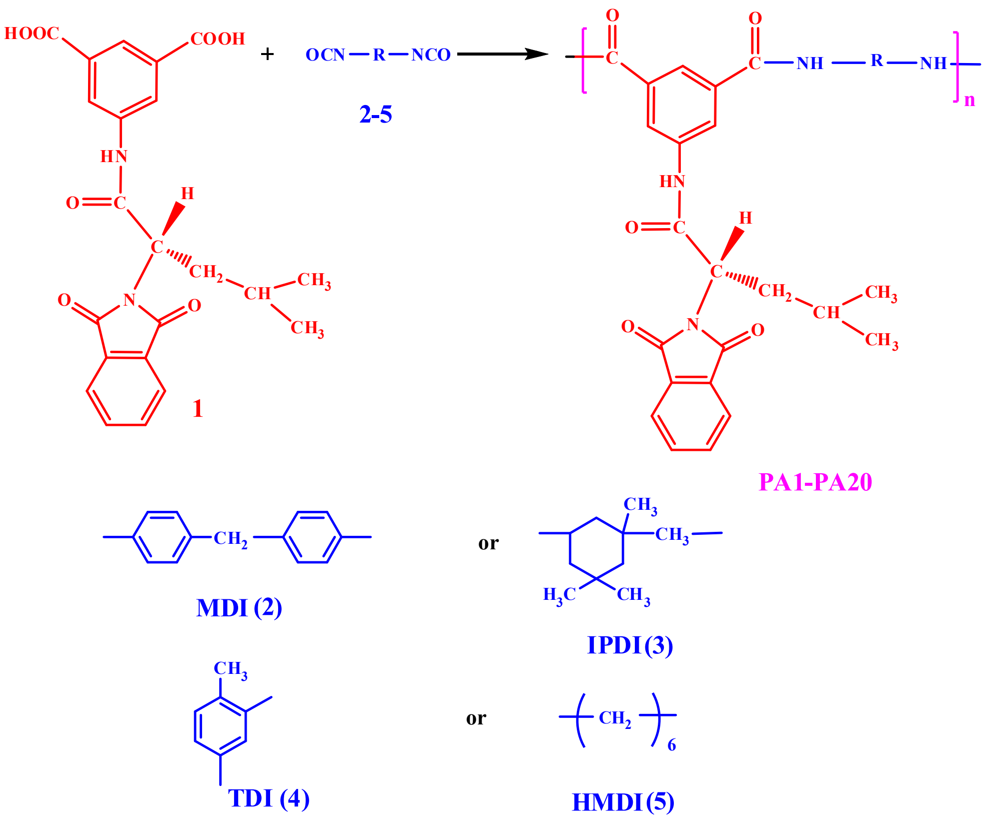
Results and Discussion

Polymer synthesis

The employment of environmentally benign reaction media is very necessary in view of today's environment-conscious outlooks. The application of organic solvents, which are most often used for conventional polymerization media, has several shortcomings like flammability, toxicity, and volatility, which increases the potential hazard of environmental pollution due to solvent loss. The utilize of green solvents such as ILs shows to eliminate these weaknesses, while retaining the advantages of common organic solvents or even ensuring better conditions. In the current investigation, in order to extend the employment of ILs in polymers synthesis, molten TBAB was used as solvent for the formation of optically active PAs by the polymerization reaction of diacid 1 with different diisocyanates. As a result, we decided to synthesize optically active PAs having L-leucine amino acid via step-growth polymerization of chiral diacid 1 with readily accessible diisocyanates under oil bath heating at 120 ^{o}C in TBAB (Method A) and in NMP as a common organic solvent (Method B) as shown in Scheme **1**.

In method A, at first, polycondensation reaction of diacid 1 with MDI 2 were examined in molten TBAB by using different catalyst for the formation of **PA1-PA4** through heating the reaction mixture at 120 ^{o}C for 12 h. To find the best catalyst in these reactions and effect of these catalysts on the viscosity and yield of the resulting polymers, the reaction of diacid 1 with MDI in the presence of DBTDL, Py, TEA, and without catalyst has been performed and the result are shown in Table **1**. According to the Table **1**, the resulting PAs have good yields and moderate viscosities, especially in the case of DBTDL and no catalyst conditions. Then, the polymerization reactions of 1 with other diisocyanates like TDI (3), IPDI (4), and HDI (5) were also performed with the same methods according to the optimized conditions. These polymers were obtained in almost quantitative yields and possessed inherent viscosities ranging from 0.36 to 0.61 dL/g (Table **1**).

With the aim of comparison of this method with a classical instance, the step-growth polymerization reactions have been examined using NMP as a common organic solvent. The reaction mixture was carried out under gradual heating from room temperature (RT) up to 120 ^{o}C (Method B). To find the best catalyst in these reactions, the reaction of diacid 1 with MDI was performed in the presence of DBTDL,



Scheme 1: Polycondensation reactions of diacid **1** with several diisocyanates.

Py, TEA, and without catalyst. The results are summarized in Table **2**. The yield and inherent viscosity of the obtained polymers by this method were in the range of 78-93% and 0.25-0.58 dL g^{-1} respectively. The results are comparable with method A. It is interesting to mention that when NMP was used as a solvent, which is volatile, and will cause a change in the concentration of reaction mixture during polymerization process and lead to the formation of polymers with lower yields and inherent viscosity. When polymerization reaction was performed in molten TBAB, viscous solutions were formed and the resulting polymers were never precipitated, whereas precipitation was observed during of conventional method in NMP as a solvent. The aforementioned results demonstrate that in method A by replacement of a volatile and toxic organic solvent in the polymerization with a nonvolatile solvent will reduce losses through evaporation, and it is important that ILs are chemicals that can be used as solvents in green chemistry processes. The ability of ILs to dissolve monomers as well as polymers to provide homogeneity and easily separate from resulting polymers, are some other advantages of using IL systems. The incorporation of a chiral unit into the polymer backbone was confirmed by measuring the specific rotations of polymers (Tables **1** and **2**).

Polymer characterization

FT-IR and ^{1}H-NMR study

The structures of polymers were confirmed as **PA**s by means of elemental analysis, FT-IR and ^{1}H-NMR (500 MHz) spectroscopy. FT-IR spectra of all polymers show the characteristic absorption peaks for the imide ring at 1765 and 1710 cm^{-1} due to the symmetrical and asymmetrical carbonyl stretching vibrations. All of them exhibited medium absorptions at 1384 cm^{-1} and 718-720 cm^{-1} that show the presence of the imide heterocycle ring in these polymers. The wide bands which appeared at 3331-3310 cm^{-1} were attributed to the NH stretching vibration in amide group. Characteristic absorptions appeared at 1670-1660 cm^{-1} due to the carbonyl stretching vibration (amide I) and at 1530-1520 cm^{-1} due to NH deformational vibration (amide II).

In the ^{1}H-NMR spectra of these polymers, the absorption of the diastereotopic CH_3 protons groups of L-leucine appeared as a broad multiplet peak at 0.89-0.94 ppm. The resonance of the diastereotopic hydrogens bonded to neighbor carbon of chiral center appeared in the range of 2.05-2.07, 2.24-2.26 ppm as two discrete multiplets peaks. The proton of the chiral center appeared as multiplets in the range of 4.97-5.00 ppm. The resonance of aromatic protons appeared in the range of 7.03-8.31 ppm. Appearances of the N-H protons of amide groups at 10.30 and 10.45 ppm as two peaks indicate the presence of amide group in the polymers side chain, as well as main chain. The aforementioned results show that PAs were synthesized successfully. The ^{1}H-NMR data of **PA1** and **PA7** are presented in the experimental sections.

Table 1. Some physical properties of **PA1-PA10** prepared by method A using TBAB as a green media

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh}^{a} (dL/g)	$[\alpha]_D^{25, a}$
PA1	MDI	DBTDL	80	0.61	-31.34
PA2	MDI	No cat	79	0.57	-27.32
PA3	MDI	Py	76	0.46	-30.56
PA4	MDI	TEA	74	0.46	-28.32
PA5	IPDI	DBTDL	85	0.49	-21.45
PA6	IPDI	No cat	79	0.47	-28.31
PA7	TDI	DBTDL	79	0.48	-27.80
PA8	TDI	No cat	83	0.36	-37.16
PA9	HDI	DBTDL	80	0.45	-38.60
PA10	HDI	No cat	68	0.39	-41.26

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

Table 2. Some physical properties of PA11-PA20 prepared by method B using NMP as a solvent.

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh}^{a} (dL/g)	$[\alpha]_D^{25, a}$
PA11	MDI	DBTDL	93	0.58	-28.54
PA12	MDI	No cat	84	0.57	-24.32
PA13	MDI	Py	79	0.49	-20.54
PA14	MDI	TEA	80	0.46	-28.51
PA15	IPDI	DBTDL	84	0.31	-20.66
PA16	IPDI	No cat	78	0.25	-17.16
PA17	TDI	DBTDL	91	0.51	-48.66
PA18	TDI	No cat	78	0.47	-52.31
PA19	HDI	DBTDL	81	0.47	-38.66
PA20	HDI	No cat	78	0.45	-41.26

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

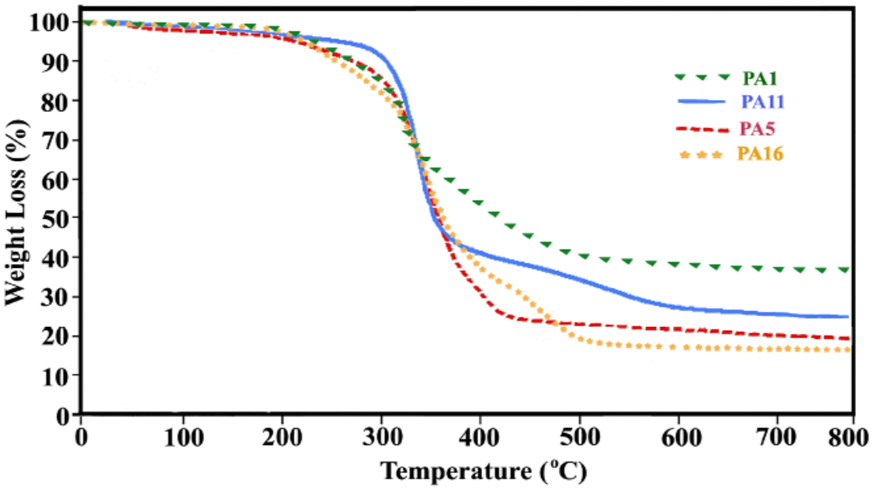
Solubility of PAs

One purposes of this study was producing modified PAs with enhanced solubility. Because of flexible bulky groups in polymer's pendent, these polymers are expected to have higher solubility. The solubility of PAs was tested in various solvents. Almost all of the PAs are soluble in organic polar aprotic solvents such as DMF, *N,N*-dimethylacetamide, dimethyl sulfoxide, NMP and polar protic solvents such as H_2SO_4 at room temperature, and are insoluble in solvents like chloroform, methylene chloride, methanol, ethanol and water. The incorporation of bulky side groups into the polymer structure, reduces molecular packing, and restricts the formation of interchain hydrogen bonds, which are responsible of the PAs intractability.

Thermal Properties

Thermal stability plays an important role in determining both technological applications and processing conditions of polymeric materials. TGA was used to evaluate the thermal properties of the resulting PAs. The thermal behavior data of some of the polymers such as: PA1, PA5, PA11 and PA16 are given in Table **3**. The thermal stabilities of these PAs were evaluated by TGA under nitrogen with a 5 and 10% weight-loss temperature (T_5, T_{10}) and residue at 800 °C (char yield) for comparison and the results are reviewed in Table **3**. The decomposition temperatures at a 10% weight loss of above polymers were recorded in the range of 257-302 °C under nitrogen atmosphere. According to these results, it is clear that the **PA1** and **PA11** (based on MDI) have higher thermal stability than **PA5** and **PA16** (based on IPDI). It might be related to aromatic, rigid structure of diisocyanate for **PA1** and **PA11** compare to aliphatic, flexible structure of diisocyanate for **PA5** and **PA16**. Fig. 1 shows the TGA thermograms of these PAs.

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation [24]. LOI = 17.5 + 0.4 CR, where CR = char yield. All of the polymers had LOI values calculated based on their char yield at 800 °C. On the basis of LOI values, such macromolecules can be classified as elfextinguishing polymers.



Figures 1: TGA thermograms of PA1, PA5, PA11 and PA16 under N_2 atmosphere and a heating rate of 10 °C/min.

Table 3. Thermal properties of PAs

Polymer	Decomposition Temperature (°C)		Char Yield (%)[b]	LOI[c]
	T_5 [a]	T_{10} [a]		
PA1	241	296	36	32
PA5	230	286	20	25.5
PA11	247	302	27	28
PA16	221	257	16	24

[a] Temperature at which 5 % and 10 % weight loss were recorded by TGA at heating rate of 10 °C min^{-1} in a N_2 atm.

[b] Weight percent of the material left undecomposed after TGA at maximum temperature 800 °C in a N_2 atm.

[c] Limiting Oxygen Index (LOI) evaluating at char yield at 800 °C.

Conclusions

In this study, a series of optically active aromatic and aliphatic PAs having natural L-leucine amino acid were synthesized under oil bath heating at 120 °C by two different methods via solution polycondensation reactions of an equimolar mixture of chiral diacid monomer **1** with different diisocyanates in TBAB and NMP as solvents and in the presence of several catalysts. The best results were obtained from the reaction of monomer **1** with MDI by both methods in the presence of DBTDL and no catalyst conditions. A comparable result on the isolated yields and inherent viscosities was obtained using TBAB or NMP as a reaction medium. The resulting polymers have inherent viscosities in the range of 0.25-0.63 dL/g. The incorporation of phthalimide and L-leucine groups, through an amide unit into PAs backbone gave polymers with remarkable solubility in common organic solvents. The outcome existing here also express obviously that the phthalimide linkage in the polymer side chain outstandingly enhanced the solubility and thermal stability of the polymers. Because of the existence of amino acids in the polymer pendant group these polymers are expected to be biodegradable and optically active.

Acknowledgment

We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), for financial support. Further financial support from National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Research (IUT) are also gratefully acknowledged

References

[1] J. Zhi, Z. Zhu, A. Liu, J. Cui, X. Wan, Q. Zhou, *Macromolecules* **2008**, 41, 1594-97.

[2] E. C. Buruiana, T. Buruiana, L. Hahui, *Photochem, J. Photobiol A: Chemistry* **2007**, 189, 65-72.

[3] G. Qing, T. Sun, Z. Chen, X. Yang, X. Wu, Y. He, C*hirality* **2008**, 21, 363-74.

[4] S. L. Bourke, J. Kohn, *Adv. Drug Delivery Rev.* **2003**, 55, 447-466.

[5] D. J. Liaw, F. C. Chang, J. H. Liu, K. L. Wang, K. Faghihi, S. H. Huang, K. R. Lee, J. Y. Lai, *Polym. Degrad. Stab.* **2007**, 92, 323-329

[6] Z. Fu, X. Xi, L. Jiang, Z. Shen, *React. Funct. Polym.* **2007**, 67, 636-43.

[7] L. Feng, J. Hu, Z. Liu, H. Zhao, G. Liu, *Polymer* **2007**, 48, 3616-23.

[8] S. Mallakpour, M. Dinari, *J. Polym. Environ.* **2010**, 18, 705-713

[9] M. Mancera, I. Roffe, S. S. J. Al-Kass, M. Rivas, J. A. Galbis, *Macromolecules* **2003**, 36, 1089-1097.

[10] A. Okamura, T. Hirai, M. Tanihara, T. Yamaoka, *Polymer* **2002**, 43, 3549-3553.

[11] D. Kiely, L. Chen, T. Lin, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 38, 594-603.

[12] Y. Saegusa, T. Tomita, *Macromol. Rapid Commun.* **2000**, 21, 1072-1078.

[13] A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, R. D. Rogers, *Chem. Comm.* **2001**, 101, 135-136.

[14] A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin, R. D. Rogers, *Industrial Engineering Chem.* **2000**, 39, 3596-3604.

[15] A. E. Visser, R. P. Swatloski, R. D. Rogers, *Green Chem*. 2001, 3, 1-6.

[16] A. J. Carmichael, M. J. Earle, J. D. Holbrey, P. B. McCormac, K. R. Seddon, *Org. Lett.* **1999**, 1, 997-1000.

[17] M. J. Earle, P. B. McCormac, K. R. Seddon, *Green Chem*. **1999**, 1, 23-25.

[18] T. L Greaves, C. J. Drummond, *Chem. Rev*. **2008**, 108, 206-237.

[19] S. Mallakpour, M. Dinari, *Iran. Polym. J.* **2010**, 19, 983-1004.

[20] S. Mallakpour, E. Kowsari, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, 43, 6545-6553.

[21] P. Kubisa, *Prog. Polym. Sci.* **2004**, 29, 3-12.

[22] S. Mallakpour, M. Dinari, *Polym. Adv. Technol.* **2008**, 19, 1334-1342.

[23] S. Mallakpour, M. Dinari, *J. Appl. Polym. Sci.* **2009**, 112, 244-253.

[24] D. W. Van Krevelen, P. J. Hoftyzer, Properties of polymers, Elsevier Scientific Publishing, New York, **1976**.