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Polycondensation Reaction of *N,N′*-(4,4′-Oxydiphthaloyl)-bis-*L*-isoleucine Diacid Chloride with Aromatic Diamines

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ABSTRACT

4,4'-Oxydiphthalic anhydride **(1)** was reacted with L-isoleucine **(2)** in acetic acid and the resulting imide-acid **(3)** was obtained in high yield. The diacid chloride **4** was obtained from diacid derivative **(3)** by reaction with excess thionyl chloride. The polycondensation reaction of diacid chloride **4** with several aromatic diamines such as 4,4'-sulphonyldianiline **(5a)**, 4,4'-diaminodiphenyl methane **(5b)**, 4,4'-diaminodiphenylether **(5c)**, *p*-phenylenediamine **(5d)**, *m*-phenylenediamine **(5e)**, and 4,4'-diaminobiphenyl **(5f)** was accomplished by two conventional methods: low temperature solution polycondensation and short period reflux conditions. In order to evaluate conventional solution polycondensation reaction methods with microwave-assisted polycondensation, the reactions were also carried out under microwave conditions in the presence of small amount of *o*-cresol that acts as a primary microwave absorber. The reaction mixture was irradiated for 6 min with 100% of radiation power. A series of new optically active poly(amide-imide)s **(PAIs)** with inherent viscosity ranging from 0.22-0.44 dL/g has been prepared with high yield. All of the above polymers were fully characterized by FTIR, elemental analyses and specific rotation techniques.

Key Words:
polycondensation;
reflux conditions;
physical properties;
specific rotation;
elemental analyses;
amino acid.

INTRODUCTION

Aromatic polyimides are certainly one of the most successful classes of high-performance polymers widely used in the microelectronics. However, most polyimides encounter processing difficulty due to their rigidity and poor solubility in organic solvents. The incorporation of flexible bridging groups and introduction of bulky substituents into the polymer structure are some of the approaches used to make polyimides more tractable and soluble. Copolymerization is another synthetic

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approach used to obtain processable and soluble polyimides. Poly(amide-imide) **PAI**s are one out of many successful classes of copolyimides, which combine the advantages of high-temperature stability and processability [1-2].

The synthesis of novel optically active polymers has attracted the attention of

Many research groups due to their potential applications, chiral molecules are used in a number of interesting applications: in catalysis for asymmetric induction in organic synthesis, in chiral separations, and in ferroelectric and nonlinear optical applications [3-7].

Enantioseparations are becoming increasingly important because the Food and Drug Administration (FDA) has declared if a drug is chiral, the biological effects of both enantiomers must be determined. Many procedures for resolutions of *D,L*-amino acids have been documented on an analytical scale. The biological activity of chiral substances often depends upon their stereochemistry, since the living body is a highly chiral environment. A large percentage of commercial and investigational pharmaceutical compounds are enantiomers, and many of them show significant enantio selective differences in their pharmacokinetics and pharmacodynamics. The importance of chirality of drugs has been increasingly recognized, and the consequences of using them as racemates or as enantiomers has been frequently discussed in the pharmaceutical literature during recent years. With increasing evidence of problems related to stereoselectivity in drug action, enantioselective analysis by chromatographic methods has become the focus of intensive research of separation scientists. During the past decade attention has been paid to fabrication of chiral separation materials. One of the most appealing optically active polymers as chiral stationary phases for a high chiral recognition ability in high-performance liquid chromatography (HPLC) to resolve a wide range of racemates or chiral media for asymmetric synthesis, then the synthesis of optically active polymers is the newly considerable topics, which have been paid more attention. Recently, we have synthesized optically active polymers by different methods [8-10].

In this contribution, production of new optically active PAIs containing 4,4'-oxydiphthalic anhydride and *L*-isoleucine moieties by conventional solution polymerization is described and is compared with microwave-assisted polycondensation reaction method.

EXPERIMENTAL

Materials

4,4'-Diaminodiphenylmethane **(5b)** and 4,4'-diaminobiphenyl **(5f)** was purified by recrystallization from water. 4,4'-Diaminodiphenylether **(5c)**, 1,4-phenylenediamine **(5d)**, 1,3-phenylenediamine **(5e)**, were purified by sublimation. 4,4'-Oxydiphthalic anhydride dianhydride was supplied from T.C.I Chemical Co (Japan). *N,N*-Dimethylacetamide (**DMA**c) was dried over BaO, then distilled in vacuum. The other chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany) were used as obtained without further purification.

Apparatus

The apparatus used for the polycondensation was a Samsung microwave oven (2450 MHz, 900 W). Proton nuclear magnetic resonance ^{1}HNMR (500 MHz) spectra were recorded on a Varian EM-390 (Varian Assosciates, Palo Alto, CA) and Bruker, Advance 500 instrument (Germany), respectively. Proton resonance is designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). FTIR Spectra were recorded on (Jasco-680, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fenske Routine Viscometer (Germany). Specific rotations were measured by Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on TGA 7 Perkin Elmer (Germany) in nitrogen atmosphere at a rate of 40°C/min. Elemental analysis were performed by Malek-Ashtar University of Technology, Tehran, I.R. Iran.

Monomer Synthesis

*N,N'-(4,4'-Oxydiphthaloyl)-bis-L-isoleucine Diacid (**3**)*

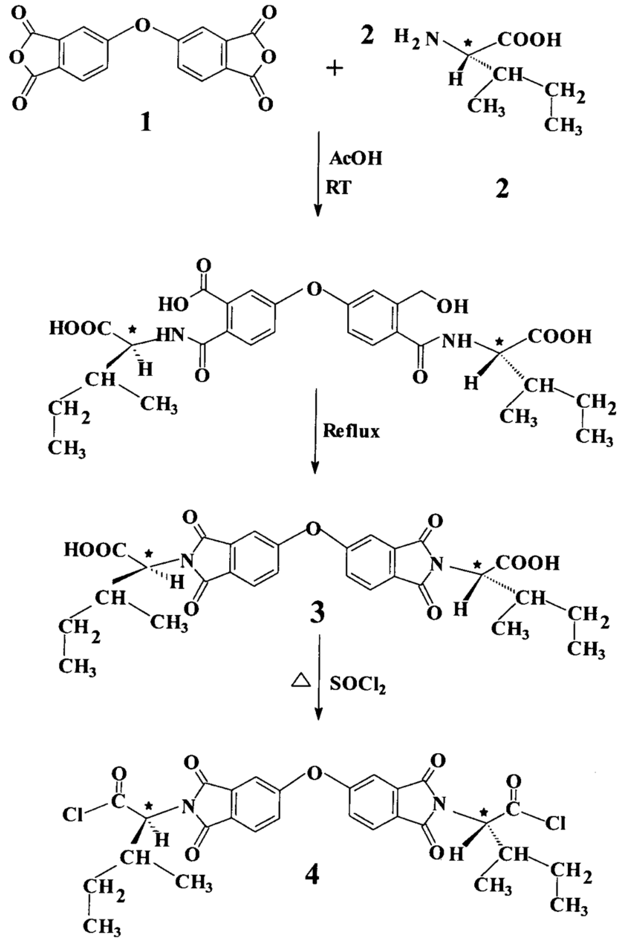
One gram (3.22×10^{-3} mol) of **1**, 0.93 g (7.08×10^{-3} mol) of **2**, 30 mL of acetic acid and a stirring bar were placed into a 50-mL round-bottomed flask. The mixture was stirred at room temperature for 3 h and then was refluxed for 8 h. The solvent was removed under reduced pressure and 5 mL of cold concentrated HCl was added to the residue. A white precipitate was formed and washed with cold water. It was removed under pressure to give 1.69g (98.2 %) of compound **3**. Mp = 112-114°C,[α]= -153.08° (0.050 g in 10 mL DMF); FTIR (KBr): 2968.9 (s, br), 1777.1 (m), 1718.3 (s), 1610.3 (s), , 1379.9 (s), 1275.7 (m), 1080.9 (m), 751.2 (w), cm^{-1}; ^{1}H NMR (DMSO-d$_6$, TMS, 500 MHz): δ 0.70-0.84 (t, 6H), 1.01-1.04 (d, 6H, J = 6.66 Hz), 1.45-1.49 (m, 2H), 2.30-2.39 (m, 2H), 4.50-4.51 (d, 2H, J = 8.00 Hz), 7. 59-7.61 (dd, 2H, J_1 = 8.10 Hz, J_2 = 2.20 Hz), 7.63-7.64 (d, 4H, J = 1.96 Hz), 7.97-7.98 (d, 2H, J =8.13 Hz) ppm. Elemental analysis: Calcd. for $C_{28}H_{28}N_2O_9$: C, 62.69%; H, 5.26%; N, 5.22%; Found: C, 62.63%; H, 5.31%; N, 5.44%.

*N,N'-(4,4'-Oxydiphthaloyl)-bis-L-isoleucine Diacid Chloride (**4**)*
One gram (1.86 x 10^{-3} mol) of compound **3**, 2.0 mL of thionyl chloride were placed into a 25-mL round-bottomed flask. The mixture was stirred at room temperature for 0.5 h until the suspension mixture was converted to a clear solution. Unreacted thionyl chloride was removed under reduced pressure and was washed with fresh dry ether three times, to leave 1.03 g (96.1%) of pale yellow solid. Mp = 75°C (decomposed),$[\alpha]^{25}_{D}$= 163.2°(0.050 g in 10 mL DMF); FTIR (NaCl): 2981.4 (w), 1775.1 (m), 1718.2 (s), 1609.3 (w), 1496.5 (w), 1382.7 (s), 1274.7 (w), 1239.0 (m), 1062.9 (m), 914.1 (w), 874.6 (w), 747.3(m), 700.0 (m), 671.1 (w) cm^{-1}; Elemental analysis: Calcd. for $C_{28}H_{26}N_2O_7Cl_2$: C, 58.64%; H, 4.57%; N, 4.88%; Found: C, 58.60%; H, 4.59%; N, 4.96%.

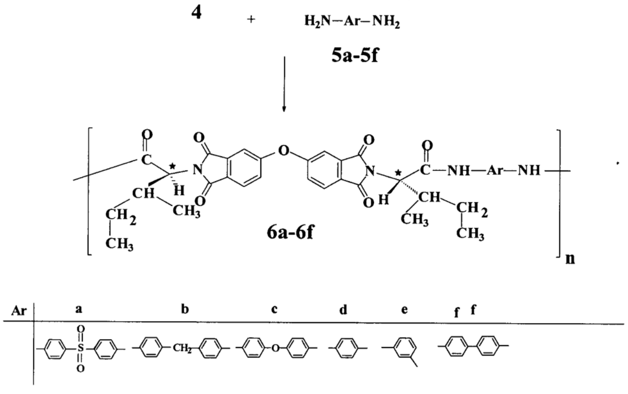
Polymerization

All of the polymers were synthesized with three different methods:

Method I: Low Temperature Solution Polycondensation
Using polymer **6aI** as an example, in the present approach, 0.20 g (3.48 × 10^{-4} mol) of diacid chloride **4** was cooled to -5.0°C, and then was added to a stirred solution (0.0863 g, 3.48 × 10^{-4} mol) of diamine **5a** in 0.25 mL of *N*-methylpyrrolidone (**NMP**). After the reagents were dissolved completely, 0.05 mL of trimethylsilyl chloride (TMSC) was added and the reaction mixture was allowed to proceed for 2 h under a blanket of nitrogen. Then the temperature was raised to room temperature. The reaction mixture was stirred for 5 h. The viscous solution was poured into 40 mL of



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



Scheme II. Ploycondensation reactions of monomer **4** with aromatic diamines.

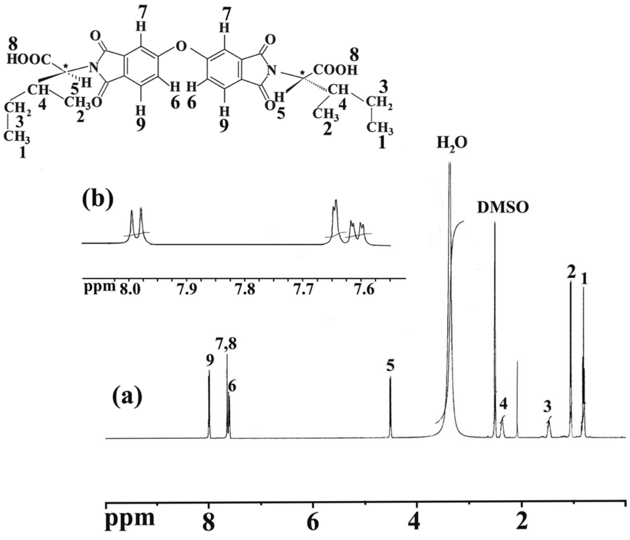


Figure 1. (a) ^{1}H NMR Spectrum of diacid **3** in DMSO-d$_6$ at rt. (b) Expanded region for the aromatic protons (δ =7.6-8.0 ppm).

methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.214 (82.3%) of solid polymer **6aI**; FT-IR (KBr): 3378.7 (m, br), 3069.2(m), 2967.0(m), 1778.1 (s), 1718.3 (s), 1592.9 (s), 1519.6 (m), 1381.7 (s), 1233.3(m), 829.2 (m), 750.2(m), 553.5 (w) cm^{-1}.

The other PAIs (6bI-6fI) were prepared with analogus procedures.

*Polymer **6bI***

FTIR (KBr): 3365.2(m, br), 2965(m), 1777.1(m), 1717.3(s), 1607.4 (m), 1513.85 (w), 1473.4 (w), 1379.8 (s), 1232.3 (s), 1075.1(w), 1021 (w), 845.6(w), 749.2 (m) cm^{-1}.

*Polymer **6cI***

FTIR (KBr): 3366.1 (m, br), 2965.0 (m), 1777.1 (m), 1717.3 (s), 1608.3 (m), 1499.4 (s), 1380.8 (s), 1232.3 (m), 1075.1 (m), 749.2 (w), 670.1 (w) cm^{-1}.

*Polymer **6dI***

FTIR (KBr): 3377.7 (m, br), 3069.2(m), 2966.0(m), 1777.1 (s), 1717.3 (s), 1591.9 (s), 1519.6 (m), 1381.7 (s), 1233.3(m), 829.2 (m), 749.2(m), 5525 (w) cm^{-1}.

*Polymer **6eI***

FTIR (KBr): 3366.1 (m, br), 2966.9 (m), 1777.1 (w), 1717.3 (s), 1608.3 (w), 1541.8 (m), 1381.75 (s), 1273.7 (m), 1024.0 (w), 848.5 (w), 749.2 (w) cm^{-1}.

Table 1. Some physical properties of **PAIs (6aI-6fI)** prepared by method I.

Diamine	Polymer				
	Polymer	Yield (%)	η_{inh}(dL/g)^a	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{25}$
5a	**6aI**	82. 3	0. 34	-55.5	-60.3
5b	**6bI**	93. 2	0. 42	-48.1	-56.9
5c	**6cI**	87. 3	0. 26	-19.2	-27.1
5d	**6dI**	77. 2	0. 33	-9.7	-16.3
5e	**6eI**	68. 6	0. 29	-18.3	-25.3
5f	**6fI**	95. 3	0. 39	-40.2	-57.3

(a) Measured at a concentration of 0.5 g/dL in DMF at 25°C. $[\alpha]_\lambda^{to}$ = Specific rotation = deg dm^{-1} g^{-1} cm^3.

Table 2. Some physical properties of **PAIs (6aII-6fII)** prepared by method II.

Diamine	Polymer				
	Polymer	Yield (%)	η_{inh}(dL/g)^a	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{25}$
5a	**6aI**	97.0	0. 40	-53.5	-60.9
5b	**6bI**	91. 6	0. 31	-43.1	-59.2
5c	**6cI**	74. 3	0. 28	-14.2	-20.3
5d	**6dI**	71. 3	0. 22	-7.8	-12.5
5e	**6eI**	69. 8	0. 35	-10.3	-18.4
5f	**6fI**	92. 4	0. 44	-34.1	-50.2

(a) Measured at a concentration of 0.5 g/dL in DMF at 25°C. $[\alpha]_\lambda^{to}$ = Specific rotation = deg dm^{-1} g^{-1} cm^3.

Table 3. Some physical properties of **PAIs (6aIII-6fIII)** prepared by method III.

Diamine	Polymer				
	Polymer	Yield (%)	η_{inh}(dL/g)^a	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{25}$
5a	**6aI**	90. 0	0. 34	-76.4	-90.2
5b	**6bI**	72. 4	0. 31	-44.9	-55.8
5c	**6cI**	84.3	0. 29	-24.3	-30.3
5d	**6dI**	88. 5	0. 27	-13.5	-22.6
5e	**6eI**	76. 2	0. 34	-11.8	-18.2
5f	**6fI**	90. 3	0. 38	-22.6	-30.3

(a) Measured at a concentration of 0.5 g/dL in DMF at 25°C. $[\alpha]_\lambda^{to}$ = Specific rotation = deg dm^{-1} g^{-1} cm^3.

Table 4. Elemental analysis of **PAIs (6aI-6fI)**.

Polymer	Formula		Elemental analysis (%)			Moisture content (%)[a]
			C	H	N	
6aI	$(C_{40}H_{36}N_4O_9S)_n$	Calcd	64.16	4.84	7.48	0.41
	$(748.8)_n$	Found	63.69	4.81	7.89	
		Corr[b]	63.95	4.79	7.92	
6bI	$(C_{41}H_{38}N_4O_7)_n$	Calcd	70.47	5.48	8.01	0.11
	$(698.7)_n$	Found	71.81	5.80	8.31	
		Corr[b]	71.87	5.79	8.31	
6cI	$(C_{40}H_{36}N_4O_8)_n$	Calcd	68.56	5.18	7.99	0.21
	$(700.6)_n$	Found	68.81	5.20	7.41	
		Corr[b]	68.95	5.18	7.42	
6dI	$(C_{34}H_{32}N_4O_7)_n$	Calcd	67.09	5.20	9.20	0.10
	$(608.6)_n$	Found	67.19	5.31	9.35	
		Corr[b]	67.25	5.31	9.35	
6eI	$(C_{34}H_{32}N_4O_7)_n$	Calcd	67.09	5.30	9.20	0.42
	$(608.6)_n$	Found	67.31	5.30	9.33	
		Corr[b]	67.59	5.27	9.36	
6fI	$(C_{40}H_{36}N_4O_7)_n$	Calcd	70.16	5.29	8.18	0.52
	$(684.6)_n$	Found	70.81	5.30	8.91	
		Corr[b]	70.52	5.27	8.94	

(a) Moisture content (%) = × [(W-W_0)/W_0] 100, W = weight of polymer sample after standing at room temperature and W_0= weight of polymer sample after dried in vacuum at 100°C for 10 h.

(b) Corrected value for C and N = found value × (100 + moisture content)/100, and corrected value for H = Found value × (100 - moisture content)/100.

*Polymer **6fI***

FTIR (KBr): 3327.5 (m, br), 2965.0 (m), 1776.1 (m), 1717.3 (s), 1607.3 (w), 1498.4(m), 1377.9 (s), 1233.3(w), 1075.1 (m), 813.8 (w), 749.2 (w), 670.1 (w) cm^{-1}.

Method II: High Temperature Solution Polycondensation

Polymer **6aII** is used as an example. 0.20 g (3.48×10^{-4} mol) of diacid chloride **4**, 0.0863 g (3.48×10^{-4} mol) of diamine **5a** were placed and then 0.25 mL of DMAc and 0.05 mL of TMSC was added into a 5-mL round-bottomed flask. The mixture was refluxed for 1 min. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.23 g (91.0 %) of polymer **6aII**.

The other PAIs **6bII-6fII** was prepared in procedures similar to that described above.

Table 5. Elemental analysis of **PAIs (6aI-6fI)**.

Polymer	T_5 (°C)[a]	T_{10}(°C)[b]	Char yield (%)[c]
6aI	263	300	10
6dI	300	312	19

(a) Temperature at which 5% weight loss was recorded by TGA at heating rate of 40°C/min in N_2; (b) Temperature at which 10% weight loss was recorded by TGA at heating rate of 40°C/min in N_2; (c) Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in N_2.

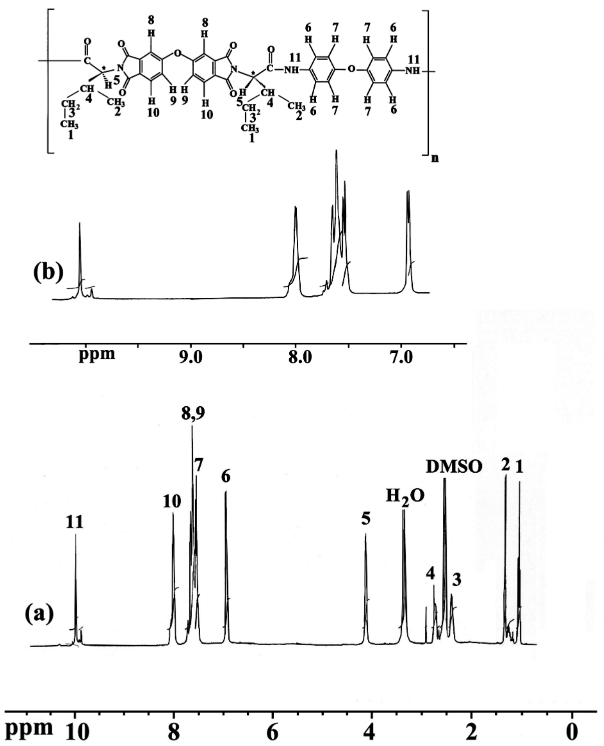


Figure 2. (a) ^{1}H NMR (500 MHz) Spectrum of **PAI-6cI** in DMSO-d_6 at rt, (b) expanded region for the aromatic protons (δ =6.5-10.0 ppm).

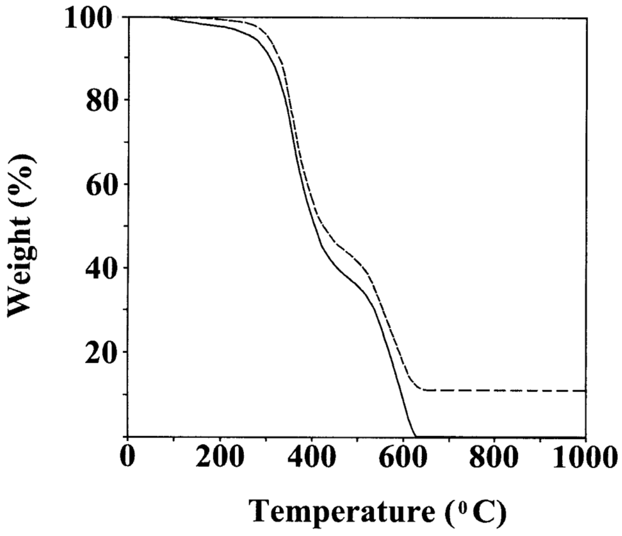


Figure 3. TGA of PAI-**6aI** (—) and PAI-**6dI** (- - -) with a heating rate of 40°C/min and chart speed 10 mm/min in nitrogen atmosphere.

Method III: Polymerization under Microwave Irradiation

The PAIs were prepared by the following general procedure (using polymer **6aIII** as an example). 0.20 g (4.00×10^{-4} mol) of diacid chloride **4** and 0.0866 g (4.00×10^{-4} mol) of diamine **5a** were placed into a porcelain dish. After the reagents were completely ground, 0.25 mL of o-cresol as a solvent and 0.05 mL of TMSC was added. The mixture was grounded for 5 min. The reaction mixture was irradiated in the microwave oven for 4 min with 100% of the power of microwave apparatus. The resulting product was isolated by adding methanol and triturating, following by filtration and was dried at 80°C for 10 h under vacuum to leave 0.243 g (90.0%) of solid **6aIII**.

RESULTS AND DISCUSSION

Monomer Synthesis

The diacid **3** was synthesized by the condensation reaction of anhydride **1** with two moles of *L*-isoleucine (**2**). In this reaction the intermediate amic acid was not isolated and ring closure for the formation of imide ring was performed under refluxing conditions.

Diacid chloride **4** was obtained by reaction of thionyl chloride with diacid **3**. The chemical structure and purity of the compounds **3** and **4** were confirmed using elemental analysis, FTIR and ^{1}H NMR spectroscopic techniques (Scheme I).

The FTIR spectrum of compound **3** exhibit a broad and strong peak at 3500-2500 cm^{-1}, which was assigned to the COOH groups and two absorption bands at 1770 and 1705 cm^{-1}, which are characteristic peaks for imide rings.

The disappearance of strong acidic hydroxyl peak in FTIR spectrum of compound **4** approved a complete conversion of diacid **3** to diacid chloride **4**.

The ^{1}H NMR spectrum (500 MHz) of compound **3** are displayed in Figure 1. The distorted quartet in 4.50 ppm is assigned to the protons of the chiral center, which appeared as distorted doublet of doublet by the two-diastereotopic protons.

Polymer Synthesis

The polymerization of diacid chloride **4** with aromatic diamines **5a-5f** was accomplished under low temperature (method I) and reflux condition (method II). In method I polycondensation reaction was performed in cold NMP solution (-5°C) in the presence of a small amount of TMSC (Scheme II). In this method the polymerization reactions occurred at lower temperature in a period of 2 h. In method II polycondensation reactions were proceeded rapidly at the reflux temperature of solvent in 1 min. We obtained comparable yields and viscosity of **PAIs 6a-6f** from methods I and II then compared with microwave-assisted polymerizations. The reaction yields and some physical data of the solution polycondensations are listed in Tables 1 and 2.

In order to compare conventional solution polycondensation reaction methods with microwave-assisted polycondensation, the reactions were also carried out under microwave conditions in the presence of small amount of *o*-cresol that acts as a primary microwave absorber.

The reaction mixture was irradiated for 6 min with 100% of radiation power. At higher radiation times dark products were obtained, and on the other hand under low radiation times or power, reactions gave low yield and viscosity. TMSC activates the diamine monomers [11]. The reaction yields and some physical data for **PAIIIs 6aIII-6fIII** are listed in Table 3.

Polymers Characterization

The structures of these polymers were confirmed as **PAI**s by means of elemental analysis, FTIR and ^{1}H NMR spectroscopy. Elemental analysis data of the resulting polymers are listed in Table 4.

FTIR Spectra of all polymers show the characteristic absorption peaks for the imide ring at 1700 and 1778 cm^{-1} due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N-H groups appeared around 3360 cm^{-1} (hydrogen band) and 1519-1541 cm^{-1} (amide II band). All of them exhibited strong absorptions at 1380 cm^{-1} and 749-891 cm^{-1} show the presence of the imide heterocycle ring in these polymers.

The ^{1}H NMR spectra of **PAI-6cI** are shown in Figure 2. The pattern of spectra is similar to those of monomer diacid chloride and corresponding diamine.

These polymers are soluble in organic polar solvents such as DMAc, DMF and even in less polar solvents like o-cresol. But these polymers are insoluble in solvents such as chloroform, methanol, acetonitril, cyclohexane and water.

Thermal Properties

The thermal stability of some **PAI**s was investigated by thermogravimetric analysis (TGA) mesurments. Typical TGA curves of representative polymers are shown in Figure 5. The temperatures of 5% and 10% weight loss together with char yield at 600°C for **PAI**s **6aI** and **6dI** have been calculated from their thermograms. The Figure 3 shows the TGA curve for **PAI-6aI** and **6dI**. The thermoanalyses data of **PAI**s **6aI** and **6dI** are summarized in Table 5.

CONCLUSION

Several new optically active aliphatic-aromatic **PAI**s having *L*-isoleucine and 4,4'-oxydiphthalic anhydride moieties were synthesized by three methods. The polycondensation leads to the formation of polymers having inherent viscosity ranging from 0.22-0.44 dL/g. We obtained comparable results from these methods with microwave-assisted polymerization. The above results demonstrate that microwave heating is an efficient method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. The resulting **PAI**s are thermally stable and are readily soluble in common organic solvents. The synthetic polymers are expected to have a potential as packing materials in column chromatography.

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REFERENCES

1. Mittal K.L., *Polyimides, Synthesis, Characterization and Application,* Plenum, New York (1984).
2. Yang C.P., Wei C.S., Synthesis and characterization of two polytrimellitamideimide series with different segment order by direct polycondensation, *J. Appl. Polym. Sci.,* **82**, 1556-1567 (2001).
3. Hudlicky V.P., Hudlicky T., Synthesis of chiral ADMET polymers containing repeating D-chiro-inositol units derived from a biocatalytically prepared diene diol, *Tetrahedron*, **60**, 641-646 (2004).

4. Collins A.N., Sheldrake G.N., Crosby J., Chirality in Industry, New York, John Wiley, 2 (1994).
5. Seino M., Oishi M., Imae I., Kawakami Y., Formation of poly(silsequioxane) gel containing optically active 1,3-dimethyl-1,3-diphenyl-disiloxane as a connecting unit, *Polym. J.,* **34**, 43-(2002).
6. Nishio Y., Chiba R.,Miyashita Y., Oshima K., Miyajima T., Kimura N., Suzuki H., Salt addition effects on mesophase structure and optical properties of aqueous hydroxypropyl cellulose solutions, *Polym. J.,* **34**, 149-157 (2002).
7. Hopkins T.E., Pawlow J.H., Koren D.L., Deters K.S., Solivan S.M., Davis J.A., Gomez J.F., Wagener K.B., Chiral polyolefins bearing amino acids, *Macromolecules,* **34**, 7920-7922 (2001).
8. Mallakpour S.E, Kowsari E., Microwave-assisted and conventional polycondensation reaction of optically active *N,N′*-(4,4′-sulphonediphthaloyl)-bis-*L*-leucine diacid chloride with aromatic diamines, *J. Appl. Polym. Sci.,* **91**, 2991-3000 (2004).
9. Mallakpour S.E., 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).
10. Mallakpour S.E, Kowsari E., Synthesis and characterization of novel, optically active poly(amide-imide)s from N′,N-(4,4′-sulfonediphthaloyl)-bis-*L*-phenylalanine diacid and aromatic diamines under microwave irradiation, *J. Polym. Sci. Ser. A,* **41**, 3974-3988 (2003).
11. Becker K.H., Schmidt H.W., Para-linked aromatic poly(amic ethyl ester)s: Precursors to rod-like aromatic polyimides, synthesis and imidization study, *Macromolecules,* **25**, 6784-6790 (1992).