Polymer Bulletin 59, 587–596 (2007)
DOI 10.1007/s00289-007-0802-9

Polymer Bulletin

Novel Optically Active Poly(amide-imide)s Derived from *N*-Trimellitylimido-*L*-Isoleucine and Different Diisocyanates

Shadpour Mallakpour (✉) and Marziyeh Khani

Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I.R. Iran
E-mail: MALLAK@CC.IUT.AC.IR; Fax: +98-311-3912350

Received: 4 June 2006 / Revised version: 10 June 2007 / Accepted: 17 June 2007

Summary

A new class of optically active poly(amide-imide)s was synthesized via direct solution polycondensation of different aliphatic and aromatic diisocyanates with a chiral diacid monomer. The polymerization of *N*-trimellitylimido-*L*-isoleucine **(TMIIL) (1)** as an aromatic-aliphatic diacid monomer with 4,4'-methylenebis(phenyl isocyanate) **(MDI) (2)** was carried out by graduate heating as well as refluxing method in the presence of pyridine **(Py)**, dibutyltin dilaurate **(DBTDL)**, triethylamine **(TEA)** as a catalyst and without catalyst, respectively. In these solution polycondensations we used amino acids as chiral inducing agents. The optimized polymerization conditions of **MDI** were used for the polymerization of isophorone diisocyanate **(IPDI) (3),** tolylene-2,4-diisocyanate **(TDI) (4)**, and hexamethylene diisocyanate **(HDI) (5)**. The resulting polymers have inherent viscosities in a range of 0.17-0.48 dL/g. These polymers are optically active, thermally stable and soluble in amide type solvents.

Keywords

poly(amide-imide)s; diisocyanate route; thermal gravimetric analysis (TGA); optically active polymers

Introduction

Numerous natural macromolecules, for instance DNA, cellulose and proteins are optically active, and a well proscribed polymer chain configuration makes them feasible to realize highly complicated functions [1]. Polymers with optically active possessions have found attractive uses, including chiral media for asymmetric synthesis, chiral phases for enantiomeric separations in chromatography techniques and polymeric chiral catalysts and so on [2-4]. In recent years more interest has been paid to the preparation and application of optically active macromolecules with chiral structures which are biologically very essential [5]. Many pathways to create stable optically active polymers with chiral structures have been proposed, such as the induction of an optically active substituent to the polymer side chain, and introduction of the chiroptical properties [6]. Lately some interesting procedures have been developed to synthesized optically active macromolecules having main-chain configurational chirality. For example, alternating copolymerization of olefins with CO provides a polyketone with stereogenic centers in the main chain [1].

Thermally stable macromolecules have received much attention over the past decade, due to increasing demands for high-performance polymers as replacement for ceramics or metals in the microelectronic, aerospace and automotive industries. Polyimides (PI)s and their copolymers are surely one of the most useful classes of high-performance polymers, which have found many uses in various industries [7,8]. Polyamides (PA)s on the other hand represent one of the most prevalent classes of macromolecules which are chemically stable against most organic solvents, alkaline mediums, fuels and concentrated acids. This offers an extensive range of applications in medicine, textile and car manufacturing industry [9]. Nevertheless, the poor solubility and also high softening temperatures or melting temperatures caused by their high crystallinity in addition of high stiffness of the polymer backbone lead to difficult processability for these macromolecules [10,11]. Because of these processing problems, much of research on aromatic PIs and PAs has been directed toward the improvement of processability while sustaining desirable properties of these polymers [8]. Poly(amide-imide)s (PAI)s are one of the classes of copolyimides, which combine the advantages of high-thermal stability and processability [12].

Copolyamides (COPA)s made from carbohydrate or amino acid based monomer also have received great attention. The interest for these COPAs arises not only for the fact that they are obtained from renewable feedstock, but also because of new properties that can be achieved upon the incorporation of carbohydrate units in the polymer main chain [13-18]. In fact most preparative method known for creating amide linkage are based on polycondensation between diamines and diacyl chlorides or direct polycondensation between diamines and diacids, but little work has been reported on the preparation of polyamides or copolyamides based on direct polycondensation between diacids and diisocyanates.

In this work we wish to describe the synthesis and characterization of a set of new organosoluble, thermally stable and optically active PAIs made from diacid containing *L*-isoleucine and trimellitic anhydride **(TMA)** with several readily available diisocyanates by conventional solution polymerization through diisocyanate route.

Experimental

Materials

Reagents were purchased from Fluka, Aldrich and Riedel-deHaen AG. Pyridine **(Py)**, *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and 1-methyl-2-pyrrolidone (NMP) were dried over BaO and then were distilled under reduced pressure. 4,4'-methylenebis(phenylisocyanate) **(MDI) (2)** (Aldrich) was used as received. **TMA** was recrystallized in acetic acid/acetic anhydride mixture (3/1) and dried under vacuum at 60°C for 6h. *N*-trimellitylimido-*L*-isoleucine **(TMIIL) (1)** was prepared as described previously in glacial acetic acid [19]. The yield of the diacid **1** was 95%, m.p = 198°C (dec), and $[\alpha]_D^{25}$ = -62.73 (0.0504 g in 10 mL of DMF).

Equipments

Proton nuclear magnetic resonance (^{1}H-NMR, 300 MHz) spectra were recorded in DMSO-d_6 solution using a Bruker (Germany) Avance 300 instrument at Shahid Beheshti University, Tehran, Iran. Multipilicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd) 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}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon-Fenske Routine Viscometer (Germany). Specific rotations were measured by a JASCO Polarimeter. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a PerkinElmer Thermal Gravimetric Analyzer (Germany) under a nitrogen atmosphere at a heating rate of 10°C/min, and the first run of Differential Scanning Calorimetry (DSC) data were recorded on a DSC–PL-1200 instrument under a nitrogen atmosphere at a heating rate of 10°C/min by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Elemental analyses were also performed by IPPI.

Polymerization of TMIIL (1) with MDI (2)

The following procedures were applied to all polymerizations.

Method I: In a 25 mL round bottom flask **MDI (2)** (0.0820 g, 3.27×10^{-4} mol) was added to a solution of **TMIIL (1)** (0.1000 g, 3.27×10^{-4} mol) in 0.18 mL of NMP. The mixture was stirred at room temperature (RT) then triethylamine **(TEA)** (0.018 g, 2.78×10^{-5} mol) was added. The solution was stirred for 1h at RT, 3h at 60°C, then it was heated gradually from 60°C to 90°C during of 8h, 2h at 100°C, and finally 2h at 120°C. During of this period 0.2 mL of NMP was added. The reaction mixture was poured into 10 mL of methanol to precipitate the polymer. The solid was filtered off, dried to give 0.0825 g (54 %) of yellow solid **PAI1A**. This polymerization was also repeated using **Py** and dibutyltin dilaurate **(DBTDL)** as catalysts, and without catalyst, respectively.

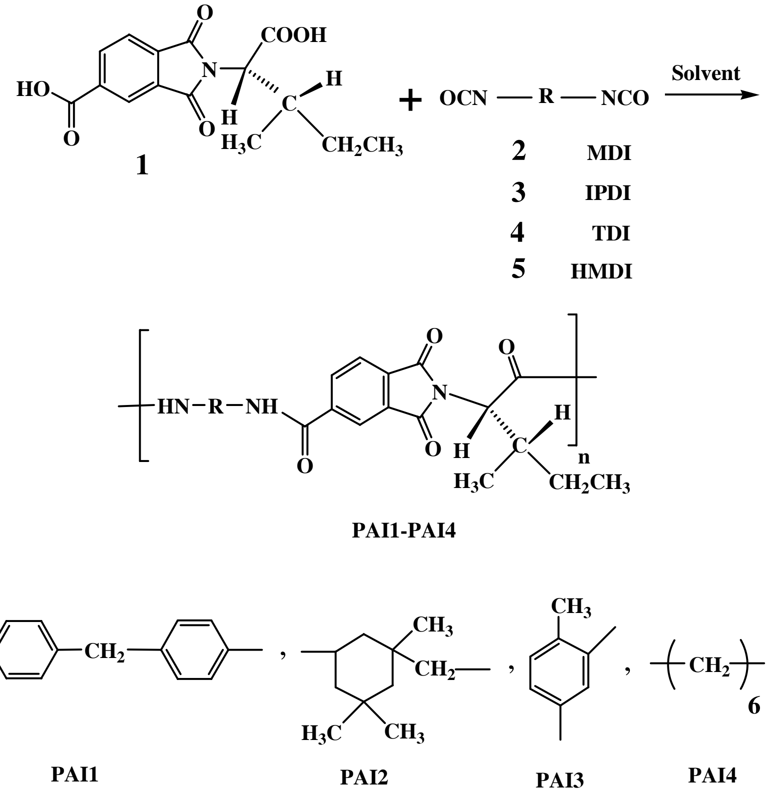
Method II: In a 25 mL round bottom flask **TMIIL (1)** (0.0908 g, 2.97×10^{-4} mol) was heated up to 180°C in the presence of one drop of NMP, then **MDI (2)** (0.0744 g, 2.97×10^{-4} mol) was added and the clear reaction mixture was stirred at 180°C for 1 min. The temperature was decreased to 60°C and **Py** (0.05 ml, 5.95×10^{-4} mol) was added. Then it was heated gradually from 60°C to 90°C during of 8h, 2h at 100°C, and finally 2h at 120°C. The reaction mixture was poured into 10 mL of methanol to precipitate the polymer. The solid was filtered off, dried to give 0.0870 (62 %) of gray solid **PAI1F**.

Method III: In a 25 mL round bottom flask a solution of **TMIIL (1)** (0.1114 g, 3.65×10^{-4} mol) in 0.08 mL of dry DMAc and **Py** (0.02 mL, 1.89×10^{-4} mol) was stirred at RT for 0.5h, then a solution of **MDI (2)** (0.0913 g, 3.65×10^{-4} mol) in 0.08 mL of dry DMAc was added. The reaction mixture was refluxed by a heating mantel under a nitrogen atmosphere. After 5 min. a very viscose solution was formed. Then 10 mL of methanol was added and under vigorous trituration the polymer was precipitated. The solid was filtered off, dried to give 0.1302 g (76%) of white solid **PAI1G**. The above polymerization was repeated, but the reaction mixture was refluxed in DMAc in the presence of **DBTDL** or **TEA** as a catalyst and without any catalyst, respectively. For each method the optimized reaction conditions according to reaction catalysts were used for the polymerization of **TMIIL (1)** with other diisocyanates.

Results and Discussion

Polymerization Reactions

Monomer **1** was synthesized according to the reported procedure [19]. The polymerization of monomer **1** with diisocyanates was carried out under conventional solution polymerization techniques with three different methods in the presence of different catalysts and without catalyst to afford **PAI1-PAI4** (Scheme **1**).



Scheme 1. Polycondensation reactions of monomer **TMIIL (1)** with **MDI (2)**, **IPDI (3)**, **TDI (4),** and **HDI (5)**.

The results obtained under different reaction conditions, for polymerization of **TMIIL (1)** with **MDI (2)** are summarized in table 1. These new polymers were obtained in good yields and possessed inherent viscosities ranging from 0.29 to 0.44 dL/g. In method **I** the reaction mixture was heated gradually from RT up to 120°C in the presence of **Py**, **DBTDL**, **TEA** and without catalyst, respectively. NMP and 2 % W/W of $CaCl_2$ in NMP (NMP 2%) were used as reaction solvents. The polymers **PAI1A-PAI1E** were obtained in moderate yields and inherent viscosities. In method **II** the reaction mixture after melting in 180°C, cooled until 60°C then was heated gradually up to 120°C in the presence of **Py** as a catalyst. The polymer **PAI1F** was obtained in moderate yield and inherent viscosity. Method **II** gave better results for **PAIs** based **MDI** than other diisocyanates. In method **III** the reaction mixture was refluxed in DMAc. The resulting polymers **PAI1G-PAI1J** show good to high yields and moderate inherent viscosities. The polymerization of monomer **1** with **MDI (2)**, by method **III** gave better results in terms of yields, than method **I** (Table 1).

NMP as a solvent and **TEA** as a catalyst and without catalyst conditions were selected to investigate the outcome of method **I**, for the reaction of monomer **1** with other diisocyanates. According to the tables 1-4, in the case of method **I**, **PAI**s-based **MDI** provided higher viscosities than the **PAI**s-based **IPDI**, **TDI**, and **HDI**, respectively. The method **III**, has comparable results for the polymerization reactions of monomer **1** with **TDI** and **IPDI**, but it shows a distinct effect on the polymerization of **PAI**s-based **HDI**, the linear aliphatic flexible diisocyanate.

Under reflux conditions the unsymmetric diisocyanates such as **IPDI** and **TDI** gave lower viscosities, compared to the symmetric diisocyanates **MDI** and **HDI**. It could be pertained to the better possibility of chain arrangement and chain growth. It was shown that there was no distinct effect on the polymer chain growth by changing in the polarity of reaction solvent (**PAI3A/PAI3B**). Tables 1-4 show when **MDI** and **HDI** were used under refluxing conditions, better results in terms of yield and inherent viscosity were obtained. Therefore symmetric diisocyanates provide better chain growth. It is interesting to mention that polymer made by different methods (Tables 1-4) shows different optical rotation and this is consistent for the all types of diisocyanates. These could be explained in terms of that optical rotation is highly dependent to the overall structure and regularity of the resulting polymer chains.

Table 1. Reaction conditions for the polymerization of monomer **TMIIL(1)** with **MDI (2)** by different methods and some physical properties of **PAI1A-PAI1J**[a].

Polymer	Method	Catalyst	Reaction time	Yield (%)	η (dL/g)	$[\alpha]_D^{25,g}$	$[\alpha]_{Hg}^{25,h}$
PAI1A	**I**[b]	TEA	A	53	0.44[e]	-	+40.04
PAI1B	**I**[b]	No Cat	A	77	0.37[e]	-5.63	+17.53
PAI1C	**I**[b]	DBTDL	A	70	0.30[f]	-	+34.15
PAI1D	**I**[b]	Py	A	64	0.36[e]	-	+45.10
PAI1E	**I**[c]	Py	A	65	0.34[f]	+1.68	+11.53
PAI1F	**II**	Py	A	62	0.37[f]	-	+48.20
PAI1G	**III**[d]	Py	5 min.	76	0.29[e]	+6.39	+15.96
PAI1H	**III**[d]	TEA	3 min.	76	0.31[f]	-	+76.04
PAI1I	**III**[d]	DBTDL	7 min.	97	0.29[e]	-1.44	+2.52
PAI1J	**III**[d]	No Cat	5 min.	77	0.35[e]	-	+30.06

Method I: Graduate heating at different temperature, **Method II**: Graduate heating at different temperature in the presence of small amount of solvent, **Method III**: Refluxing, [a]all of these polymers were precipitated in methanol, [b]NMP was used as a solvent, [c]NMP 2% was used as a solvent, [d]DMAc was used as a solvent, [e]measured at a concentration of 0.5 g/dL in DMF at 25°C, [f]measured at concentration of 0.5 g/dL in DMF containing 0.2% W/W LiCl (soluble fraction) at 25°C, [g]measured under the condition the same as viscosity, [h]wide range was used (no filter was used for the Hg lamp), A: 1h RT; 3h 60°C; 8h 80-90°C; 2h 100°C; 2h 120°C.

Table 2. Reaction conditions for the polymerization of monomer **TMIIL (1)** with **IPDI (3)** by different methods and some physical properties of **PAI2A-PAI2F**[a].

Polymer	Method	Catalyst	Reaction time	Yield (%)	η (dL/g)[e]	$[\alpha]_D^{25,f}$	$[\alpha]_{Hg}^{25,g}$
PAI2A	**I**[b]	TEA	A	99	0.27	-1.16	+4.13
PAI2B	**I**[c]	TEA	A	69	0.29	+10.09	+45.92
PAI2C	**I**[b]	No Cat	A	98	0.26	-2.15	+11.18
PAI2D	**II**	TEA	A	88	0.21	+8.61	+8.06
PAI2E	**III**[d]	DBTDL	5 min.	99	0.13	+7.46	+8.95
PAI2F	**III**[d]	No Cat	8 min.	92	0.13	+6.89	+11.47

Method I: Graduate heating at different temperature, **Method II**:Graduate heating at different temperature in the presence of small amount of solvent, **Method III**: Refluxing, [a]all of these polymers were precipitated in water and methanol (50:50) except **PAI2D** that was precipitated in water, [b]NMP was used as a solvent, [c]NMP 2% was used as a solvent, [d]DMAc was used as a solvent, [e]measured at a concentration of 0.5 g/dL in DMF at 25°C, [f]measured under the condition the same as viscosity, [g]wide range was used (no filter was used for the Hg lamp), A: 1h RT, 3h 60°C, 8h 80-90°C, 2h 100°C, 2h 120°C.

Table 3. Reaction conditions for the polymerization of monomer **TMIIL (1)** with **TDI (4)** by different methods and some physical properties of **PAI3A-PAI3F**[a].

Polymer	Method	Catalyst	Reaction time	Yield (%)	η (dL/g)[e]	$[\alpha]_D^{25,f}$	$[\alpha]_{Hg}^{25,g}$
PAI3A	**I**[b]	TEA	A	46	0.24	-6.82	+7.87
PAI3B	**I**[c]	TEA	A	77	0.24	-5.22	-0.09
PAI3C	**I**[b]	No	A	89	0.25	-6.05	-7.78
PAI3D	**II**	TEA	A	66	0.21	+8.95	+12.9
PAI3E	**III**[d]	No	5 min.	96	0.19	+12.61	+14.85
PAI3F	**III**[d]	DBTDL	3 min.	94	0.28	+7.23	+8.37

Method I: Graduate heating at different temperature, **Method II**:Graduate heating at different temperature in the presence of small amount of solvent, **Method III**: Refluxing, [a]all of these polymers were precipitated in water except **PAI3E** that was precipitated in a mixture of water and methanol (50:50), [b]NMP was used as a solvent, [c]NMP 2% was used as a solvent, [d]DMAc was used as a solvent, [e]measured at a concentration of 0.5 g/dL in DMF at 25°C, [f]measured under the condition the same as viscosity, [g]wide range was used (no filter was used for the Hg lamp), A: 1h RT, 3h 60°C, 8h 80-90°C, 2h 100°C, 2h 120°C.

Table 4. Reaction conditions for the polymerization of monomer **TMIIL (1)** with **HDI (5)** by different methods and some physical properties of **PAI4A-PAI4E**[a].

Polymer	Method	Catalyst	Reaction time	Yield (%)	η (dL/g)	$[\alpha]_D^{25,f}$	$[\alpha]_{Hg}^{25,g}$
PAI4A	**I**[b]	TEA	A	57	0.25[d]	-	+47.23
PAI4B	**I**[b]	No Cat	A	54	0.17[e]	+28.29	-38.24
PAI4C	**II**	TEA	A	93	0.19[e]	-4.32	+12.95
PAI4D	**III**[c]	DBTDL	6 min.	54	0.47[e]	+15.12	+15.10
PAI4E	**III**[c]	No Cat	7 min.	97	0.48[e]	+7.44	+12.94

Method I: Graduate heating at different temperature, **Method II**:Graduate heating at different temperature in the presence of small amount of solvent, **Method III**: Refluxing, [a]all of these polymers were precipitated in a mixture of water and methanol (50:50) except **PAI4E** that was precipitated in water, [b]NMP was used as a solvent, [c]DMAc was used as a solvent, [d]measured at a concentration of 0.5 g/dL in DMF containing 0.4% W/W LiCl (soluble fraction) at 25°C, [e]measured at a concentration of 0.5 g/dL in DMF at 25°C, [f]measured under the condition the same as viscosity, [g]wide range was used (no filter was used for the Hg lamp), A: 1h RT, 3h 60°C, 8h 80-90°C, 2h 100°C, 2h 120°C.

The solubility properties of **PAI**s were studied in different solvents. The polymers are soluble in amide type solvents such as NMP, DMF, DMAc and partially soluble in DMSO. They are insoluble in solvents such as water, methanol, acetone, cyclohexane and chloroform.

Structural Characterization of PAIs

The resulting polymers were characterized by FT-IR, ^{1}H-NMR spectroscopy and elemental analyses. The results are shown in tables 5 and 6. The ^{1}H-NMR spectra of **PAI1A** and **PAI4E** showed all peaks for the aliphatic as well as aromatic protons that confirms their chemical structures (Table 5). Figure 1 shows the ^{1}H-NMR of **PAI4E** as an example.

The FT-IR spectra of resulting **PAI**s showed the presence of the characteristic peaks of amide and imide functions and the absence of the original peaks arising from the COOH and NCO groups in the corresponding diacid **1** and diisocyanates precursors

Table 5. ^{1}H-NMR and FT-IR characterization of **PAI1-PAI4**.

Polymer	Spectra data	
PAI1	**FT-IR Peaks (cm^{-1}):** 3322 (m, br, N-H stretching), 3123 (w, C-H aromatic), 2925 (w, C-H aliphatic), 1786 (w, C=O imide, Asymmetric stretching), 1720 (s, C=O imide, symmetric stretching), 1667 (s, C=O amide, stertching), 1383 (m, CNC axial stretching), 1197 (m, CNC transverse stretching), 734 (w, CNC out-of-plane bending).	**^{1}H-NMR Peaks (ppm):** 0.83 (distorted dd, 3H, CH_3), 1.07 (distorted d, 3H, CH_3), 1.50-1.90 (m, 2H, CH_2), 3.35 (m, 1H, CH), 3.78 (s, 2H, CH_2), 4.47 (d, 1H, J = 6.99 Hz, CH), 7.11 (d, 4H, J = 7.36 Hz, MDI), 7.35 (d, 4H, J = 7.36 Hz, MDI), 7.70-8.40 (m, 3H, Ar-H, TMA), 8.70 (s, br, 1H, NH), 10.50 (s, 1H, NH).
PAI2	**FT-IR Peaks(cm^{-1}):** 3378 (s, br, N-H stretching), 3052 (s, C-H aromatic), 2923 (s, C-H aliphatic), 1783 (w, C=O imide, Asymmetric stretching), 1724 (s, C=O imide, symmetric stretching), 1652 (m, C=O amide, stertching), 1381 (m, CNC axial stretching), 1178 (w, CNC transverse stretching), 742 (m, CNC out-of-plane bending).	
PAI3	**FT-IR Peaks(cm^{-1}):** 3328 (m, br, N-H stretching), 3084 (w, C-H aromatic), 2931 (s, C-H aliphatic), 1786 (m, C=O imide, Asymmetric stretching), 1720 (s, C=O imide, symmetric stretching), 1654 (s, C=O amide, stertching), 1383 (s, CNC axial stretching), 1204 (w, CNC transverse stretching), 734 (m, CNC out-of-plane bending).	
PAI4	**FT-IR Peak(cm^{-1}):** 3318 (m, br, N-H stretching), 3112 (m, C-H aromatic), 2930 (m, C-H aliphatic), 1765 (m, C=O imide, Asymmetric stretching), 1717 (s, C=O imide, symmetric stretching), 1665 (s, C=O amide, stertching), 1375 (w, CNC axial stretching), 1197 (w, CNC transverse stretching), 723 (m, CNC out-of-plane bending).	**^{1}H-NMR Peak (ppm):** 0.74-0.95 (m, 6H, CH_3), 1.25-1.75 (m, 10H, CH_2), 2.85-2.90 (distorted t, 4H, CH_2), 3.35 (m, br, 1H, overlapped with H_2O, CH), 4.40 (d, br, 1H, CH), 7.85-8.35 (m, 3H, Ar–H, TMA), 8.00-8.85 (s, br, 2H, NH).

(Table 5). For example the FT-IR spectrum of **PAI1A** exhibited characteristic absorption bands of the amide group around 3322 (N–H stretching) and 1667 cm^{-1} (C=O stretching), together with peaks at 1786 (C=O asymmetric stretching), 1720 (C=O symmetric stretching), 1383 (CNC axial stretching), 1197 (CNC transverse stretching), 734 (CNC out-of-plane bending) cm^{-1} for the imide heterocyclic ring.

Table 6. Elemental analysis of **PAI**s.

Polymer	Formula		C%	H%	N%
PAI1	$C_{28}H_{25}N_3O_4$	Calcd.	71.93	5.39	8.99
	467.18 g/mol	Found	70.58	5.31	10.44
PAI4	$C_{21}H_{27}N_3O_4$	Calcd.	65.44	7.06	10.90
	385.46 g/mol	Found	63.40	7.23	11.09

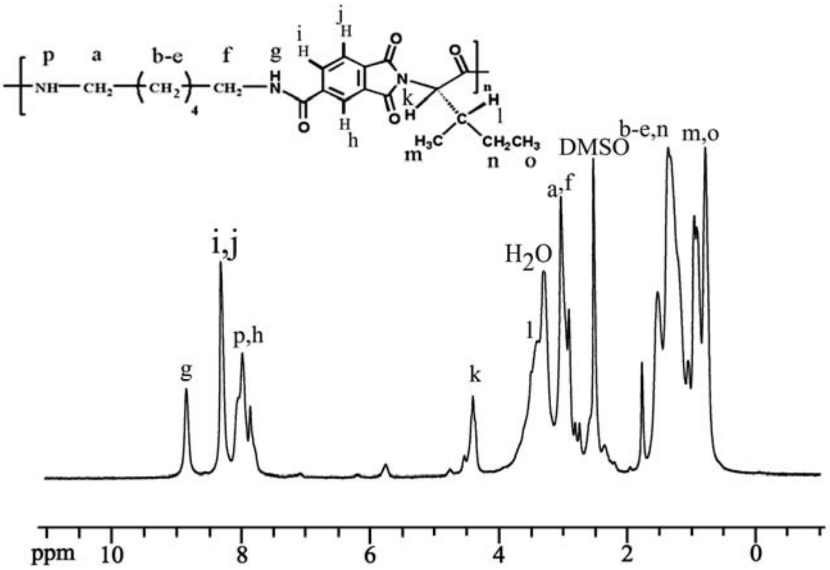


Figure 1. ^{1}H NMR (300MHz) spectrum of **PAI4E** in DMSO-d6 at RT.

The elemental analyses results are also in good agreement with calculated values of carbon, hydrogen and nitrogen in the polymers (Table 6).

Thermal Properties

The thermal behaviors of the resulting **PAI**s were examined by TGA (Figure 2) and DSC. TGA results for **PAI1A**, **PAI3F** and **PAI4E** are shown in Table 7. The TGA curves for all samples show a smooth, stepwise manner, suggesting a two-step thermal degradation. The 5% and 10% weight loss (T_5, T_{10}) of the polymers and residue at 600°C (char yield) are used as criterions for their thermal stability by TGA (Table 7). Because of the both of PAI2 and PAI4 based on aliphatic diisocyanate, it is expected that these polymers show similar thermal assets.

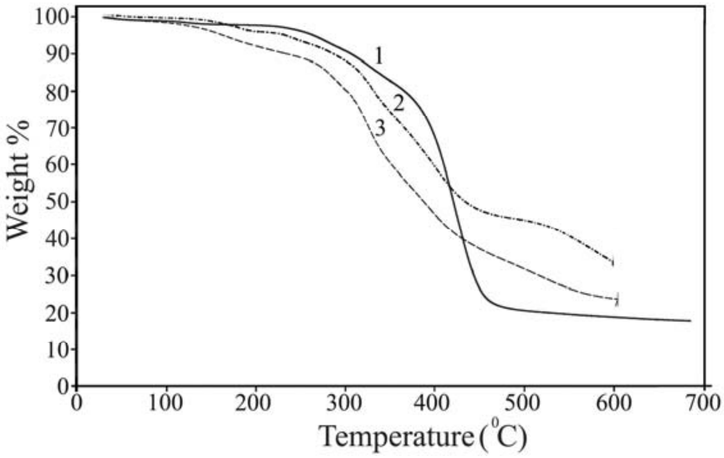


Figure 2. TGA thermograms of **PAI4E (1)**, **PAI3F (2)** and **PAI1A (3)** under a nitrogen atmosphere at heating rate of 10°C/min.

Table 7. Thermal properties of **PAI1A**, **PAI3F**, **PAI4E**

Polymer	T_5 (°C)[a]	T_{10} (°C)[b]	Char Yield(%)[c]
PAI1A	175	225	25
PAI3F	214	285	32
PAI4E	265	310	21

[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 600°C under a nitrogen atmosphere.

The thermal behavior of **PAI1A**, **PAI4E** as an example was studied by DSC. In the case of **PAI1A** no transition associated with softening was observed. In the case of **PAI4E** two transition around 130°C and 190°C were observed, which could be related to Tg and Tm respectively.

Conclusions

Several new optically active **PAI**s with inherent viscosities ranging between 0.17 and 0.48 dL/g were synthesized by direct solution polycondensation methods. Thus, the optically active *N*-trimellitylimido-*L*-isoleuceine **(TMIIL) (1)** as a monomer was reacted with some aromatic as well as aliphatic diisocyanates according to isocyanate route. This method is a convenient technique for the preparation of novel optically active **PAI**s, in addition in this method we eliminate the use of diamines and we do not need to activate diacid monomer. Among four different diisocyanates were used, **MDI** and **HDI** gave better yields and inherent viscosities. Although different organic and organometallic catalysts and no catalyst were used, but we obtained comparable results, so the reaction could be performed under no catalyst conditions to lower the cost. The presence of flexible *i*-butyl side chain, amide groups and aliphatic linkages in the final macromolecules were lead to improved solubility, while maintaining moderate thermal properties. The resulting polymer show optical rotation, therefore are optically active and they have potential to be used as chiral stationary phase in gas chromatography for the separation of racemic mixtures. The resulting polymers contain amino acid moiety, so they could be classified under environmentally friendly polymers.

Acknowledgements. 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 Center of Excellency in Sensors Research (IUT) is gratefully acknowledged. Useful help from Miss F. Rafiemanzelat, Z. Rafiee and Mr M. Kolahdoozan (IUT) is also acknowledged.

References

1. Itsuno S. (2005) Prog. Polym. Sci. 30: 540.
2. Limousin C, Cleophax J, Loupy A, Petti A. (1998) Tetrahedron 54: 13567.
3. Loupy A, Regnier S. (1999) Tetrahedron Lett. 40: 6221.
4. Chtti S, Bortolussi M, Loupy A, Blais JC, Bogdal D, Majdoub M. (2002) Eur. Polym. J. 38: 1851.
5. Nakanot OY. (1994) Chem. Rev. 94: 349.
6. Jeong YS, Goto H , Iimura S, Asano T, Akagi K. (2006) Curr. Appl. Phys. 6 (5): 960.
7. Mallakpour SE, Hajipour AR, Roohipour-fard R. (2000) Eur. Polym. J. 36: 2455.
8. Jinghe Z, Mingyan Z, Qibin J, Shujin Z, Tiequan D, Binfen C, Qingquan L. (2006) Mat. Lett. 60: 585.
9. Weidnera SM, Justa U, Wittkea W, Rittigb F, Gruberb F,.Friedricha JF. (2004) Int. J. Mass. Spect. 238: 235.
10. Kim YJ, Chung IS, In I, Kim SY. (2005) Polymer 46: 3992.
11. Mehdipour-Ataei SH, Sarrafi Y, Hatami M. (2005) Eur. Polym. J. 41: 2887.
12. Liaw DJ, Chen WH. (2006) Polym. Degrad. Stab. 91(8): 1731.
13. Alla A, Oxelbark J, Rodrıguez-Galan A, Munoz-Guerra S. (2005) Polymer 46: 854.
14. Mallakpour SE, Hajipour AR, Vahabi R. (2002) J. Appl. Polym. Sci. 84: 35.
15. Mallakpour S, Kowsari E. (2005) Iranian Polym. J. 14(1): 81.
16. Mallakpour S, Kowsari E. (2005) Polym. Bull. 53: 169.
17. Mallakpour S, Rafiemanzelat F. (2005) Eur. Polym. J. 41: 2945.
18. Mallakpour S, Rafiee Z. (2004) Iranian Polym. J. 13: 225.
19. Mallakpour S, Hajipour AR, Shahmohammadi M H. (2003) J. Appl. Polym. Sci. 89: 116.