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Direct Polyamidation of *N,N'*-(4,4'-Hexafluoroisopropylidendiphthaloyl)-bis-L-isoleucine with Different Aromatic Diamines via Vilsmeier Adduct Derived from Tosyl Chloride and *N,N*-Dimethylformamide

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Summary

Various approaches have been carried out in the synthesis of poly(amide-imide)s. A well-developed solution polycondensation method has been used to prepare such copolymers either from a dianhydride containing a preformed amide group with a diamine or from a dicarboxylic acid containing a preformed imide ring with a diamine. Direct polycondensations of carboxylic acids and aromatic diamines can be a more useful technique for synthesis of poly(amide-imide)s **PAI**s. In this work, direct polymerization reaction of *N,N'*-(4,4'-hexafluoroisopropylidendiphthaloyl)-bis-L-isoleucine with several aromatic diamines such as 4,4'-diaminodiphenylsulphone (**4a**), 4,4'-diaminodiphenylmethane (**4b**), 4,4'-diaminodiphenylether (**4c**), 1,4-phenylenediamine (**4d**), 4,4'-diaminobiphenyl (**4e**), 1,3-phenylenediamine (**4f**), 2,4-diaminotoluene (**4g**), was performed in the presence of tosyl chloride (TsCl)/dimethylformamide (DMF)/pyridine (Py) as a condensing agent. The resulting **PAI**s were obtained in high yield and inherent viscosity. Some structural characterization and physical properties of these polymers have been studied and will be reported.

Introduction

Aromatic polyimides and polyamides are thermally stable polymers which have received much interest over the past decades due to increasing demands for high performance polymers as replacement for ceramics or metals in the microelectronic, aerospace and automotive industries [1-3]. **PAI**s have higher impact properties than other high performance polymers. **PAI**s resist many chemicals and solvents including aliphatic, aromatic and halogenated hydrocarbons, acids and weak bases. Since they are very resistant to gamma radiation, **PAI**s are used for parts exposed to nuclear radiation.

Synthesis of optically active polymers is an important field in macromolecular science as they find a wide variety of potential applications based on the chiral structure. An important field of application is chiral recognition. This ability of chiral polymers has been utilized in various forms of catalytic and separation chemistry. One of the most practical and widely accepted applications of chiral polymers is the use as chiral stationary phase (CSP) for high-performance liquid chromatography (HPLC) for the separation of racemic compounds (resolution)[4-7]. Recently, we have synthesized optically active polymers by reaction of an optically active monomer with several diamines via solution polymerization [8-15]. We use amino acids as chiral inducting agents. These materials are naturally occurring compounds therefore synthetic polymers based on amino acids are expected to be biodegradable and biocompatible. A Vilsmeier adduct derived from an arylsulfonyl chloride such as TsCl and DMF was successfully used by Higashi and co-workers for the direct synthesis of PAIs from aromatic dicarboxylic acids and aromatic diamines [16-18]. The reaction of the Vilsmeier adduct can activate carboxyl groups of dicarboxylic acids, thus, could be used for a wide variety of dicarboxylic acids.

This paper describes the synthesis and properties of novel optically active **PAI**s prepared from aromatic diamines and *N,N'*-(4,4'-hexafluoroisopropylidendiphthaloyl)-bis-L-isoleucine (**3**), as a novel monomer containing performed imide groups. Monomers bearing hexafluoroisopropyliden groups attract considerable attention because of the possibility to use in the preparation of **PAI**s with enhanced solubility, thermal stability and fire resistance and improved processibility. The use of monomers containing imide rings is one method for the preventing of partial of crosslinking in the course of reaction because it avoids high-temperature curing cycles and handling unstable intermediates such as polyamic acides [19-23]. Thus, we designed the above monomer with a preformed imide ring as an enlarged monomer containing an additional hexafluoroisopropyliden group and two chiral L-isoleucine groups, which also allows achieving chiral **PAI**s with appropriate molecular weight by direct polycondensation method.

Experimental

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-de Haen AG (Seelze, Germany) and Merck Chemical Co. 4,4'-diaminodiphenylmethane (**4b**) and 4,4'-diaminodiphenylether (**4c**) were purified by recrystallization from water. 1,4-phenylenediamine (**4d**), 4,4'-diaminobiphenylen (**4e**) and 1,3-phenylenediamine (**4f**) were purified by sublimation. The other diamines were used as obtained without further purification.

Instruments

Proton nuclear magnetic resonance (^{1}H NMR, 300 MHz) spectra were recorded on a Bruker (Germany) Avance 300 instrument. Multipilicities of proton resonances were designated as singlet (s), doublet (d) and multiplet (m). Fourier transform infrared (FT-IR) spectra were recorded on (Jasco-680, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). The inherent viscosities were measured by a standard procedure using a Cannon-Fensk Routine Viscometer (Canon, Maine, Germany). The specific Rotations were measured with a Jasco Polarimeter. Thermal Gravimetric Analysis (TGA) and DSC data for polymers were taken on STA 625 in nitrogen atmosphere at a heating rate of 20 °C/min. Elemental analysis were performed by Polymer and Petrochemical Institute (Tehran, Islamic Republic of Iran).

Synthesis of Monomer

Peparation of N,N'-(4,4'-Hexafluoroisopropylidendiphthaloyl)-bis-L-isoleucine *(**3**).* Into a 50-mL round-bottomed flask 1.00 g (1.49×10^{-3} mol) of 4,4'-(hexafluoroisopropyliden)-2,2'-bis-(phthalic acid anhydride) (**1**), 0.48 g (3.72×10^{-3} mol) of L-isoleucine (**2**), 30 mL of acetic acid and a stirring bar were placed. The mixture was stirred at room temperature for 6 h and then was refluxed for 24 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, washed with cold water, it was removed under reduced pressure to give 1.35 g [89.6% of compound (**3**)] mp: 104-106 °C, $[\alpha]_D^{25}$: –32.2 ° (0.050 g in 10 mL, DMF); FT-IR (KBr): 3300 (m, br), 2969 (m, br), 1780 (m), 1724 (s), 1644 (m), 1381 (s), 1256 (s), 1211 (s), 1142 (m), 1105 (m), 966(w), 746(w), 724 cm^{-1} (m). ^{1}H-NMR (300 MHz, TMS, DMSO-d_6): δ 0.82 (t, 6H, *J* = 7.32 Hz), 1.11 (d, 6H, *J* = 6.69 Hz), 1.51-1.59 (m, 4H), 2.42-2.50 (m, 2H), 4.62 (d, 2H, *J* = 8.01 Hz), 7.89 (s, 2H), 8.03 (d, 2H, *J* = 8.04 Hz), 8.98 (d, 2H, *J* = 8.04), 10.11 (s, 2H) ppm. MS: m/z = 672, 671 (M^+).

Polymer Synthesis

The **PAI**s were prepared by the following procedure: For the synthesis of polymer **5d**, A Py (0.15 mL, 0.19×10^{-2} mol) solution of TsCl (0.84 g, 1.78×10^{-3} mol) after 20 min stirring at room temperature, was treated with DMF (0.27 mL, 3.7×10^{-3} mol) for 30 min and the solution was added dropwise to a solution of diacid **3** (0.1 g, 1.49×10^{-4} mol) in Py (0.15 mL). The mixture was maintained at room temperature for 20 min, and then to this mixture, a solution of 1,4-phenylenediamine (**4d**) (0.016 g, 1.49×10^{-4} mol) in Py (0.15 mL) was added dropwise at room temperature, the whole solution was stirred at 120 °C for 2h. As the reaction proceeded, the solution became viscous. Then, the viscous liquid was precipitated in 40 mL of methanol to yield 0.0926 g (84%) of polymer **5d**.

Elemental analysis. Calcd. For polymer **5d** ($C_{37}H_{32}F_6N_4O_6$): C, 61.32%; H, 4.45%; N, 7.73%. Found: C, 60.34%; H, 4.58%; N, 7.60%., Correction: C, 61.03%; H, 4.52%; N, 7.68% (for moisture contact content = 1.1).

Moisture Content (%) = $\frac{(\mathbf{W - W_0})}{\mathbf{W_0}} \times 100$, 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. Corrected value for C and N = Found value $\times \frac{(100 + \textbf{moisture content})}{100}$, and

Corrected value for H = Found value $\times \frac{(100 - \textbf{moisture content})}{100}$.

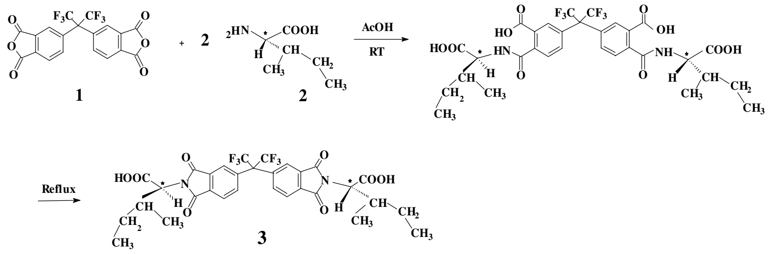
FT-IR (KBr): 3427 (m), 2967 (m), 1779 (m), 1724 (s), 1518 (s), 1382 (s), 1256 (s), 1210 (w), 724 cm^{-1} (m).

The other **PAI**s (**5a-5c, 5e-5g**) were prepared with a similar procedure.

Result and Discussion

Monomer synthesis

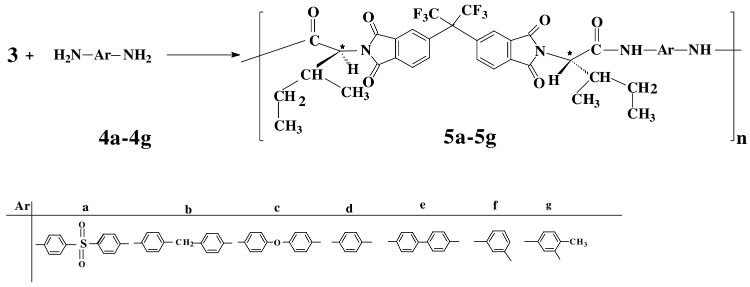
The asymmetric diacid compound **3** was synthesized by the condensation reaction of dianhydride **1** with two moles of L-isoleucine (**2**). In this process the intermediate amic acid was not isolated and ring closure for the formation of imide ring was carried out under refluxing conditions. The resulting novel monomer **3** was fully characterized by FT-IR, ^{1}H NMR and Mass spectroscopy.



Scheme 1. Synthesis of monomer **3**.

Polymer Synthesis

PAIs **5a-5g** were synthesized by the direct polyesterification reactions of an equimolar mixture of monomer **3** with several different aromatic damine **4a-4g** in a TsCl/Py/DMF system (Scheme 2).



Scheme 2. Polycondensation reaction of monomer **3** with aromatic diamine.

The polymerization reaction was carried out in the following way: TsCl was dissolved in Py and after a certain period of time about 20 min (aging time) the solution was treated with DMF. The reaction mixture was added to a solution of aliphatic diacid **3** in Py. After a period of time a solution of diamine in Py was added and the whole solution was maintained at elevated temperature for 2 h. Polycondensation of diacid 3 with aromatic diamines was carried out by varying the aging time of the initial reaction of TsCl and Py, TsCl was dissolved in Py at room temperature and kept at this temperature for a certain period of time (10-40 min) (figure 1). According to figure1 the suitable aging time is 20 min. The yield and viscosity of the resulting PAIs were affected by the amount of DMF. From this data it is clear that a ratio of DMF/diacid should be about 25, in order to obtain polymers with high yield and inherent viscosity. Further addition of DMF did not improve the molecular weights and yields (figure 2). The effect of reaction time on inherent viscosity and yield of resulting **PAI**s is shown in figure 3. From this information an appropriate reaction time of 2 h is required to get **PAI**s with high yield and inherent viscosity. The polycodensation reaction was also carried out at 120 ºC [4].

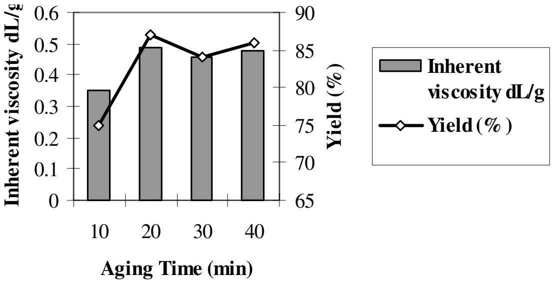


Figure 1. Effect of aging condition of TsCl in Py on the inherent viscosity and yield of the **PAI 5d** for 2 h at 120 °C (For 0.1 g diacid and 0.27 mL of DMF).

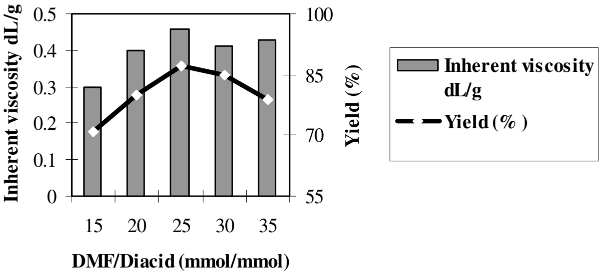


Figure 2. Effect of the amount of DMF added to TsCl/Py on the inherent viscosity and yield the **PAI 5d** for 2 h at 120 °C (For 0.1 g diacid).

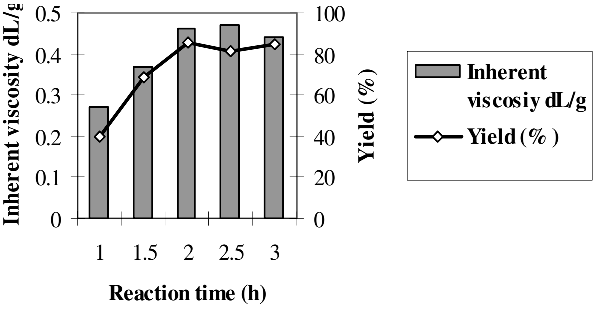


Figure 3. Effect of reaction time on the inherent viscosity and yield of the **PAI 5d** at 120 °C (For 0.1 g diacid and 0.27 mL of DMF).

Table 1. The optimum conditions for the preparation of **PAI**s

Optimum Condition	
TsCl/Diacid (mol/mol)	12.0
Py/Diacid (mol/mol)	6.2
DMF/ Diacid (mol/mol)	25
Aging Time (min)	20
Reaction Time (h)	2.0

The optimum conditions for the preparation of **PAI**s are demonstrated in table 1.

The synthesis and some physical properties of these novel optically active **PAI**s are listed in table II. The inherent viscosities of the resulting polymers under optimized condition were in a range of 0.46-0.61 dL/g and the yields were 75-88%. All of the **PAI**s show rotations of plane of polarized light, therfore are optically active.

Structural Characterization of Polymer

The formation of **PAI**s was confirmed by FT-IR spectroscopy analysis. The FT-IR spectrum of **PAI**s **5d** show the characteristic absorptions of imide and amide groups occurred around 1779, 1724 cm^{-1}, peculiar to carbonyls stretching of imide and ester, respectively. All of these **PAI**s exhibited absorption at 1382 cm^{-1} and 724 cm^{-1}, that show the presence of the imide heterocycle in these polymers. The ^{1}H NMR spectrum (300 MHz) of polymer **5d** is presented in figure 4.

Table 2. Some physical properties of **PAI**s **5a-5g.** Synthesized under optimum conditions

Diamines	Polymer	Yield (%)	η_{inh}(dL/g)	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{25}$
4a	5a	75	0.49	-3.4	-3.1
4b	5b	87	0.58	-8.6	-9.1
4c	5c	88	0.57	-12.1	-15.3
4d	5d	84	0.61	-9.3	-12
4e	5e	85	0.50	-15.7	-18.3
4f	5f	83	0.62	-22.1	-32.1
4g	5g	75	0.46	-14.0	-15.3

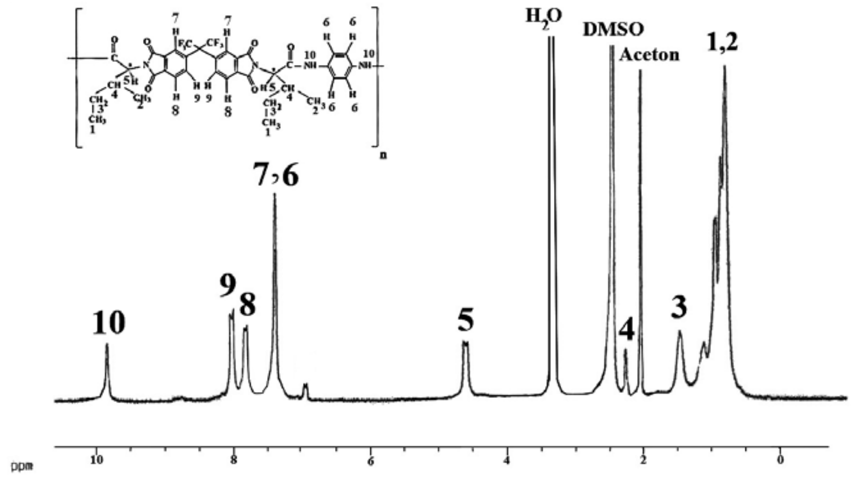


Figure 4. ^{1}H NMR (300 MHz) spectrum of **PAI 5d** in DMSO-d_6 at rt.

*Solubility of **PAIs***

The solubility of **PAI**s was tested quantitatively in various solvents. All of the **PAI**s are soluble in organic solvents such as DMF, *N,N*-dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Thermal properties

The thermal stability of the **PAI**s **5a** and **5d** were characterized by TGA and DSC conducted in nitrogen, at a heating rate of 20°C/min. The thermal stability are very good. Typical TGA curve of representative **PAI 5d** is shown in Figure 5. The temperatures of 5% and 10% weight loss together with char yield at 600 °C for **PAI**s **5a** and **5d** have been calculated from their thermograms. From these data it is clear that the resulting polymers are thermally stable, but the thermal stability is limited by the presence of the aliphatic segment. The thermo analyses data of **PAI**s **5a** and **5d** are summarized in Table 3. It is clear from obtained data that polymer containing SO_2 group with higher T_5 and T_{10} is more stable.

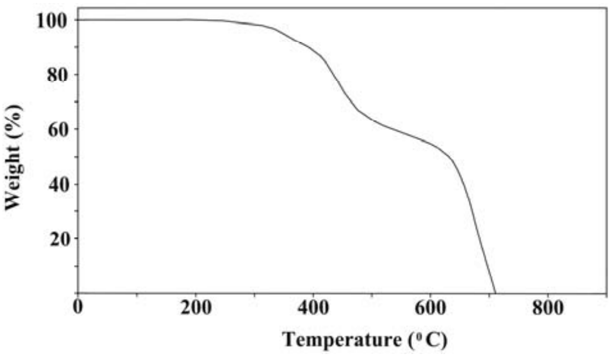


Figure 5. TGA of **PAI 5d** and with a heating rate of 20°C/min in nitrogen atmosphere.

Table 3. Thermal Properties of **PAI**s **5a** and **5d**

Polymer	T_0 (°C)[a]	T_5 (°C)[b]	T_{10} (°C)[c]	Char Yield (%)[d]	Tg (°C)
5a	341	372	389	22	185
5d	293	363	413	56	-

[a] The initial decomposition temperature by TGA at heating rate of 20 °C/min in N_2.
[b] Temperature at which 5% weight loss was recorded by TGA at heating rate of 20 °C/min in N_2.
[c] Temperature at which 10% weight loss was recorded by TGA at heating rate of 20°C/min in N_2.
[d] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600 °C in N_2.

Conclusion

In the present study, we successfully prepared a series optically active aliphatic-aromatic **PAI**s having L-isoleucine and 4,4'-(hexafluoroisopropylidene)-2,2'-bis-(phthalic acid anhydride) moieties by direct polycondensation method. The polycondensation lead to the formation of polymers having inherent viscosity ranging from 0.46-0.61 dL/g. We carried out the direct polycondensatin reaction of aliphatic-aromatic imide containing diacid and aromatic diamines using TsCl/DMF/Py as condensing agent to prepare new aliphatic-aromatic **PAI**s. The influence of aging time, amount of DMF, concentration of monomers and condensing agents, addition time of aromatic diamines and reaction time on the physical properties of the resulting polymers were investigated. Flourine containing **PAI**s exhibit a higher thermal stability than non-fluorine bearing polymer with comparable structure. The excellent thermal stability of these **PAI**s could be attributed to CF_3 groups [24]. Furthermore, the resulting optically active **PAI**s contain amino acid linkages, could be biocompatible and biodegradable.

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