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Study on synthesis and characterization of novel optically active poly(amide-imide)s based on bis(*p*-aminobezoic acid)-*N*-trimellitylimido-S-valine via direct polycondensation

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Abstract: N-Trimellitylimido-S-valine (**3**) was prepared by reaction of trimellitic anhydride (**1**) with S-valine (**2**) in acetic acid solution at refluxing temperature. This diacid was reacted with thionyl chloride and *N*-trimellitylimido-S-valine diacid chloride (**4**) was obtained in quantitative yield. The reaction of this diacid chloride with *p*-aminobenzoic acid was carried out in dry tetrahydrofurane and bis(*p*-aminobenzoic acid)-*N*-trimellitylimido-S-valine (**5**) was obtained as a novel optically active amide-imide diacid monomer in high yield. The direct poly condensation of amide-imide diacid monomer with aromatic diamins such as 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ether, benzidine, 4,4'-diaminodiphenyl methane, 1,4-phenylene diamine and 2,5-diamino toluene was carried out in tosyl chloride/ pyridine/dimethylformamide system. The resulting novel optically active poly(amide-imide)s (PAIs) with inherent viscosities ranging from 0.24-0.76 dLg^{-1}, were obtained in good yield. All of these polymers were fully characterized with FT-IR spectroscopy and specific rotation. Some elemental analysis, thermal properties and ^{1}H-NMR of these new optically active PAIs are also reported.

Key Words: poly(amide-imide), direct polycondensation, TsCl/Py/DMF condensing agent, optically active polymers

Introduction

Polyimides (PIs) based on aromatic ring structures or their copolymers are well known as high performance polymers due to their excellent thermal and thermooxidative stabilities, outstanding mechanical and electrical properties, and therefore, all kinds of polyimides have been widely used in the fields of adhesives, composite matrices, fibers, films, foams, as well as microelectronic materials [1–4]. However these polymers are difficult to process because of their high softening temperatures and poor solubility in organic solvents. In order to improve the solubility and processability, several approaches have been proposed, based on the incorporation of flexible segments bearing ester, sulfone, amide, and ether moieties in the polymer backbone, without sacrificing the heat resistance [5-8]. Thus, several type of copolyimides such as poly(amide-imide)s (PAIs) which possess desirable characteristics between polyamides (PAs) and polyimides (PIs) such as high thermal stability and good mechanical properties as well as better processability have been developed.

Since chirality is a major concern in the modern pharmaceutical industry it has received much interest in recent years. This interest can be attributed largely to a heightened awareness that enantiomers of a racemic drug may have different pharmacological activities, as well as different pharmacokinetic and pharmacodynamic effects. The separation of chiral compounds has been of great interest because the majority of bioorganic molecules are chiral. Recent advances in asymmetric reactions and catalysis as well as in chiral separations have afforded a rapid increase in the number of commercially available optically active compounds and reagents [9, 10]. This situation will influence new methodologies for the preparation of optically active polymers (OAPs) in the coming century. Many chiral monomers could be prepared from these chiral chemicals. Recently, we have synthesized a variety of OAPs which in addition to inherent optical properties, their solubility was increased without significant loss of mechanical and thermal properties by incorporation of optically active segments in polymer's backbone, [11-13].

Various approaches have been devised thus far to prepare PAIs [14-16]. Among these procedures the processes which are operative under mild conditions and adaptable to the direct polycondensations of free carboxylic acids and aromatic diamines, could be more useful as a technique for polyamidation [17]. This method produces polymers with lower energy consumptions, thus lower in cost. Higashi et al. have developed several condensing agents suitable for the direct polycondensation reactions [18-22].

However, Vilsmeier adduct derived from arylsulfonyl chlorides and dimethyl formamide (DMF) in pyridine (Py) was successfully used as a suitable condensing agent for the synthesis of aromatic polyesters by the direct polycondensation of aromatic dicarboxylic acids and bisphenols [21]. In continuation of our attempt to develop new OAPs via direct polycondnsation [11-13], in this article we wish to report the application of this condensing agent for direct polyamidation of new optically active bis(*p*-aminobezoic acid)-*N*-trimellitylimido-S-valine (5) monomer with different aromatic diamines.

Results and discussion

Monomer synthesis

The unsymmetrical diacid compound **3** was synthesized by the condensation reaction of equimolar amounts of **1** and **2** in acetic acid. Chemical structure and purity of the monomer (**3**) were proved using IR, and ^{1}H-NMR spectroscopic techniques. The ^{1}H-NMR spectrum (300 MHz) of compound **3** is shown in Figure 1. The doublet in 4.48 ppm is assigned to the proton of chiral center.

The compound **3** was reacted with thionyl chloride, and the diacid chloride **4** was obtained in high yield. The chemical structure and purity of the optically active **4** were proved with FT-IR spectroscopy techniques. The reaction of **4** with *p*-aminobenzoic acid was performed in dry **THF** at 0^{o}C. The resulting novel optically active aromatic amide-imide diacid **5** was obtained in high yield (Scheme I), and its chemical structure and purity were confirmed with FT-IR and ^{1}H-NMR spectroscopy (Figure 2) techniques.

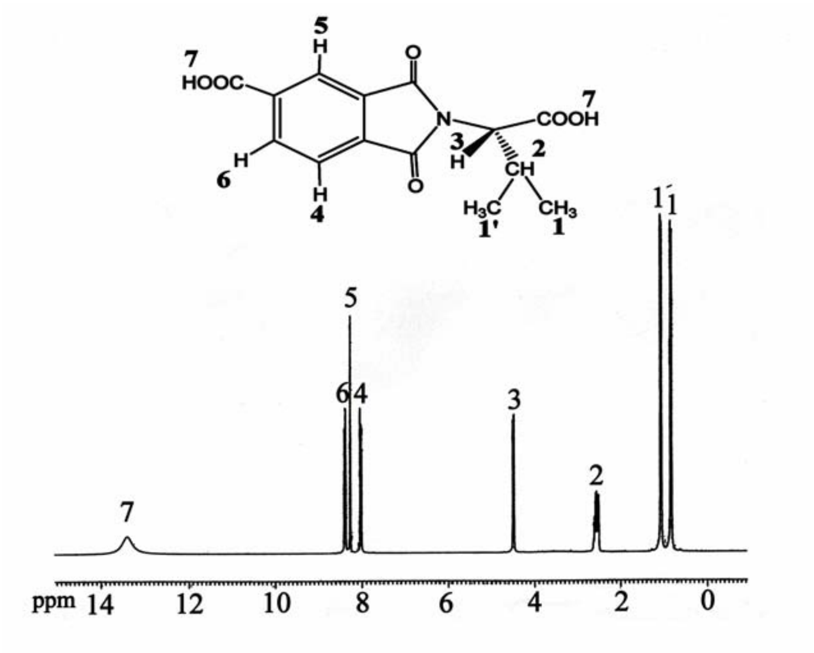
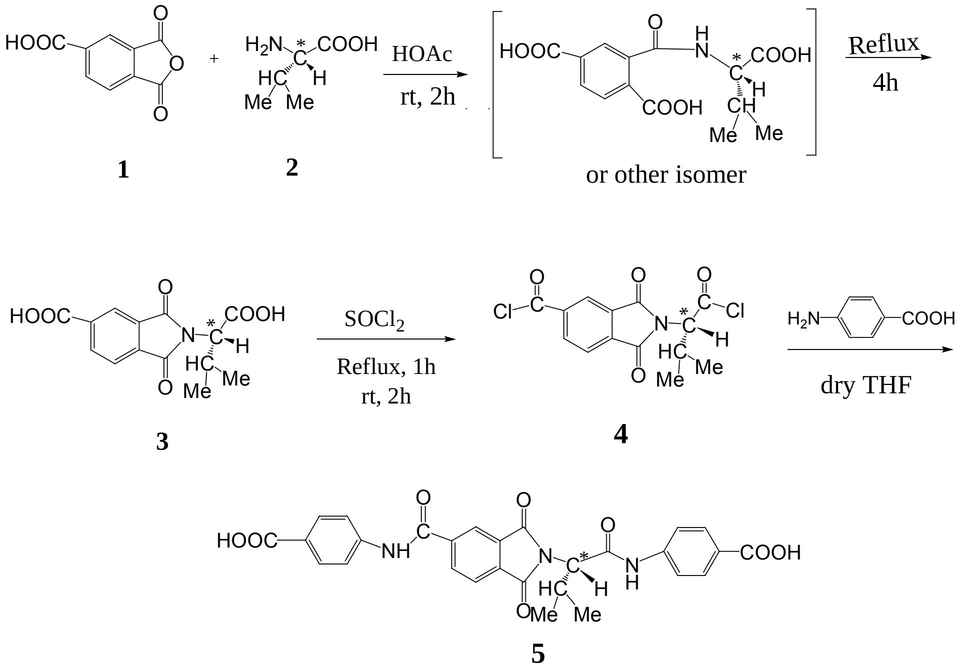


Fig. 1. ^{1}H-NMR (300MHz) Spectrum of compound **3** in DMSO-d$_6$ at RT.



Scheme I. Synthesis of N-trimellitylimido-S-valine (**3**) and *N*-trimellityl imido-S-valine-bis(*p*-aminobenzoic acid) (**5**).

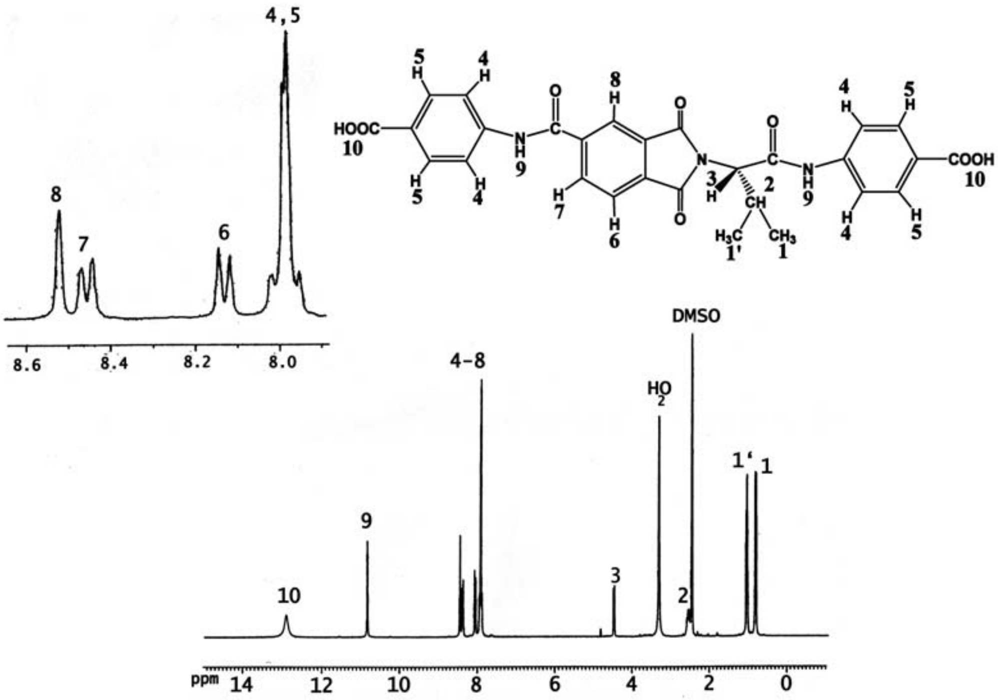
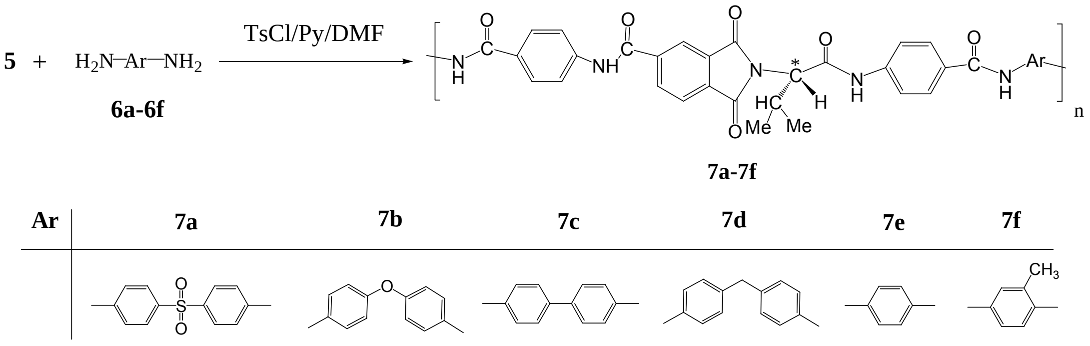


Fig. 2. ^{1}H-NMR (300MHz) Spectrum of monomer **5** in DMSO-d_6 at RT.

Polymer Synthesis

PAEIs **(7a-7f)** were synthesized by the direct polycondensation reactions of an equimolar mixture of monomer **(5)** with several different aromatic diamines **(6a-6f)** in a system of TsCl/Py/DMF (Scheme II).



Scheme II: Polycondensation reactions of monomer **5** with aromatic diamines.

In this work for the polycondensation of aliphatic-aromatic diacids and aromatic diamines, a Vilsmeier adduct was prepared by dissolving tosyl chloride (TsCl) in a mixed solvent of Py and DMF. The polycondensation was carried out in the following way: TsCl was dissolved in pyridine and after a certain period (aging time) the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After 30 min, a solution of diamine in Py was added and the whole solution was maintained at room temperature and elevated temperature for a period of time.

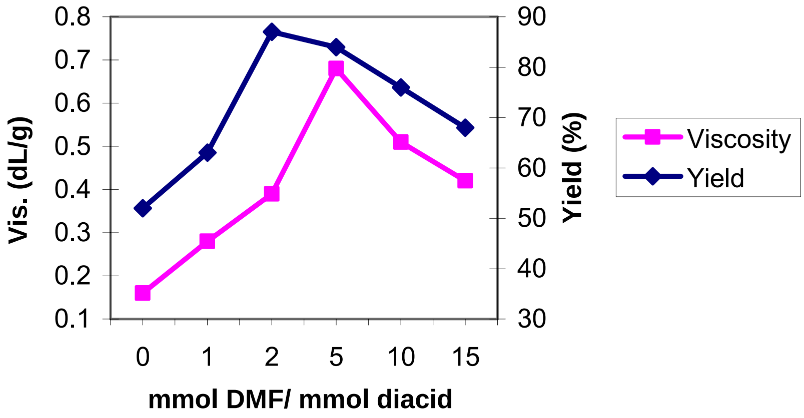


Fig. 3. Effect of the molar ratio of DMF to diacid added to TsCl/Py on the η_{inh} a yield of PAI-7a prepared using TsCl/DMF/Py.

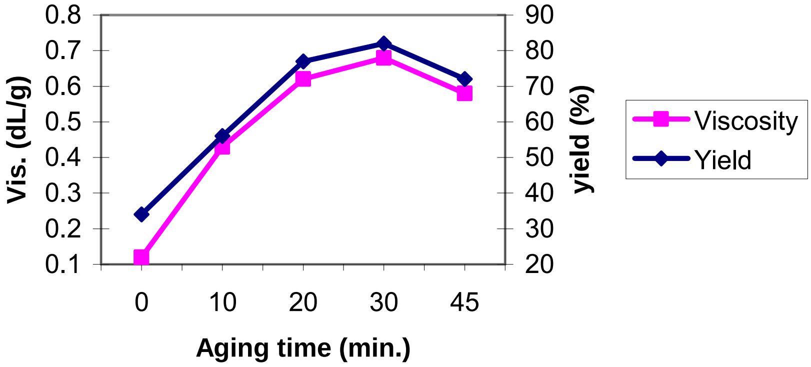


Fig. 4. Effect of aging time of TsCl in pyridine on the η_{inh} and yield of PAI-**7a** prepared using TsCl/DMF/Py.

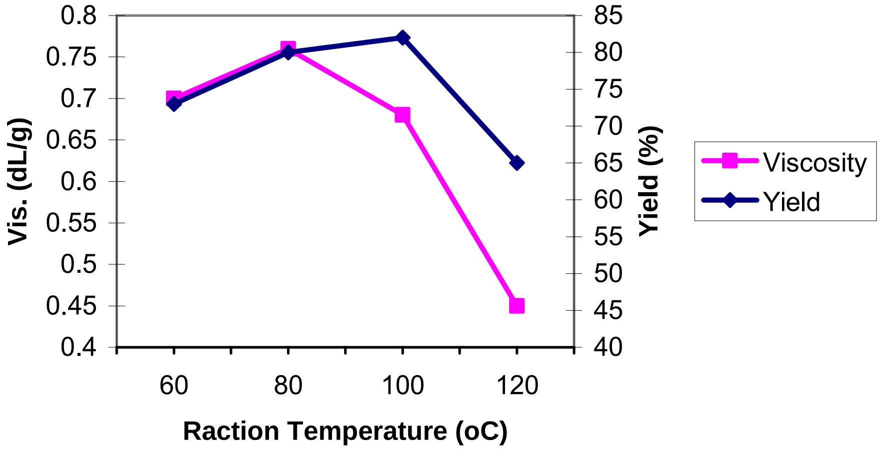


Fig. 5. Effect of reaction temperature on the η_{inh} and yield of PAI-**7a** prepared using TsCl/DMF/Py.

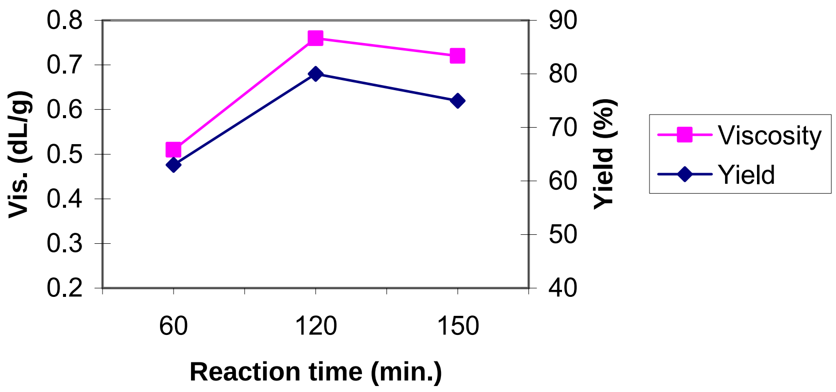


Fig. 6. Effect of reaction time on the η_{inh} and yield of PAI-**7a** prepared using TsCl/DMF/Py.

Tab. 1. The optimum conditions for the preparation of PAIs

Optimum Condition	
TsCl/Diacid (mol/mol)	5.0
Py/Diacid (mol/mol)	30
DMF/Diacid (mol/mol)	5.0
Aging Time (min)	30
Reaction Temperature (^{o}C)	80
Reaction Time (h)	2.0

Polycondensation was carried out by varying the aging time of the initial reaction of TsCl and Py, the molar ratio of DMF to diacid, the reaction time and reaction temperature. All of these parameters had critical effect on the polymer chain growth (Figures 3-6). The outcome of Figures 3-6 is in Table 1 which shows the optimum condition for polymerization.

The synthesis and some physical properties of these novel optically active PAIs are listed in Table 2. The inherent viscosities of the resulting polymers under optimized conditions were in a range of 0.24-0.76 dL/g and the yields were 66-86%. All of the PAIs are optically active.

Polymer characterization

The structures of these polymers were confirmed as PAIs by means of FTIR spectroscopy and elemental analyses. The FTIR spectra of all polymers showed absorptions around 3335 cm^{-1} (N-H) and the two overlapped carbonyl (amide and imide C=O) absorptions at 1777, 1719 and 1675cm^{-1}. All of these PAIs exhibited absorption at 1370-1380 and 715-725 cm^{-1} that showed the presence of the imide heterocycle in these polymers. The polymer (**7a**) showed characteristic absorptions at 1247 and 1150 cm^{-1} due to the sulfone moiety (SO_2 stretching). As an example, the IR spectrum of PAI-7f (Figure 7) showed the characteristic absorptions of imide and ester groups occurred around 1778, 1716 and 1652 cm^{-1}, characteristic to carbonyls stretching of imide and amide, respectively.

The ^{1}H NMR spectrum (300 MHz) of polymer **(7b)** is shown in Figure 8. In the ^{1}H NMR spectrum of polymer **(7b),** appearance of the N-H proton of amide groups at

10.25, 10.85 ppm indicates two amide groups in the polymer chain. The absorption of aromatic protons appeared at a range of 6.95-8.51 ppm. The proton of the chiral center appeared at 4.63 ppm. The peaks of C-H bonding to chiral center appeared as a multiple 2.55-2.95 ppm. The absorption of the CH_3 protons groups appeared at 0.86, 1.09 ppm.

Tab. 2. Synthesis and some physical properties of PAIs **(7a-7f)**

diamine	**Polymer**					
	Polymer	**Yiled(%)**	η_{inh}**(dL/g)**[a]	$[\alpha]^{25,b}_{Na,589}$	$[\alpha]^{25,b}_{Hg}$	**Color**[c]
6a	**7a**	86	0.76	-6.5	-7.1	OW
6b	**7b**	71	0.41	-19.2	-18.0	P
6c	**7c**	85	0.38	-19.7	-24.9	Y
6d	**7d**	70	0.37	-22.6	-28.3	Y
6e	**7e**	75	0.47	-16.7	-18.4	PY
6f	**7f**	66	0.24	-17.5	-24.3	PY

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C.
[b] Measured at a concentration of 0.5 g/dL in DMF at 25°C.
[c] OW= off-white, P= pink, Y= yellow , PY=pale yellow.

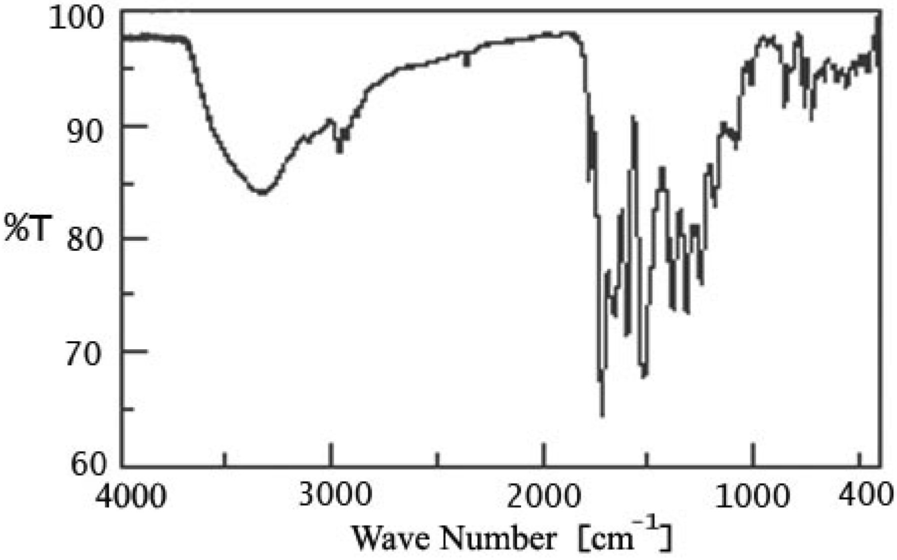


Fig. 7. FT-IR (KBr) spectrum of PAI-**7f.**

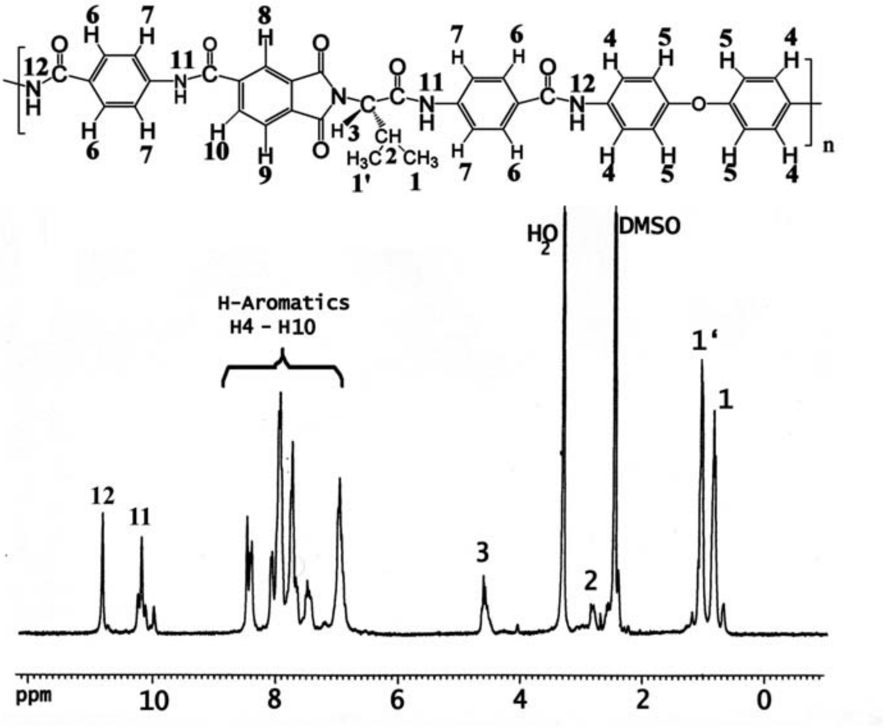


Fig. 8. ^{1}H-NMR (300MHz) Spectrum of PAI- **7b** in DMSO-d_6 at RT.

Some elemental analyses values of the resulting polymers are listed in Table 3.

Tab. 3. Elemental Analysis of PAIs **(7a, 7d).**

Polymer	Formula		Elemental Analysis (%)			Moisture Intake(%)[a]
			C	H	N	
8a	$(C_{40}H_{31}N_5O_8S)_n$	Calcd	64.77	4.21	9.44	1.7
	$(741.8)_n$	Found	63.29	4.50	9.10	
		Corr[b]	64.37	4.42	9.25	
8d	$(C_{41}H_{33}N_5O_6)_n$	Calcd	71.19	4.81	10.12	1.4
	$(691.7)_n$	Found	69.88	4.99	9.98	
		Corr[b]	70.85	4.92	10.12	

[a] Moisture Intake(%)=$(W-W_0)/W_0\times100$, W= weight of polymer sample after standing at room 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 intake) /100, and Corrected value for H= Found value temperature × (100 - moisture intake) /100.

The solubility of PAIs was tested quantitatively in various solvents. All of the PAIs are soluble in organic solvents such as DMF, DMAc, DMSO, 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 properties of PAI-7a and PAI-7d were evaluated by means of TGA in nitrogen atmosphere at a heating rate of 10°C/min. The temperature at 5% and 10% weight loss, together with char yield at 500°C and 700°C have been calculated by means of thermograms. The Figures 9 and 10 show the TGA thermogram of PAI-7a and PAI-7d. The thermoanalysis data of these polymers are summarized in Table 4. On the other hand, because the sulfone group increases thermal stability in comparison to methylene group, some differences in thermal stability were observed between the polymers containing these groups. The TGA measurement of the polymers revealed that theses polymers exhibited excellent thermal stability.

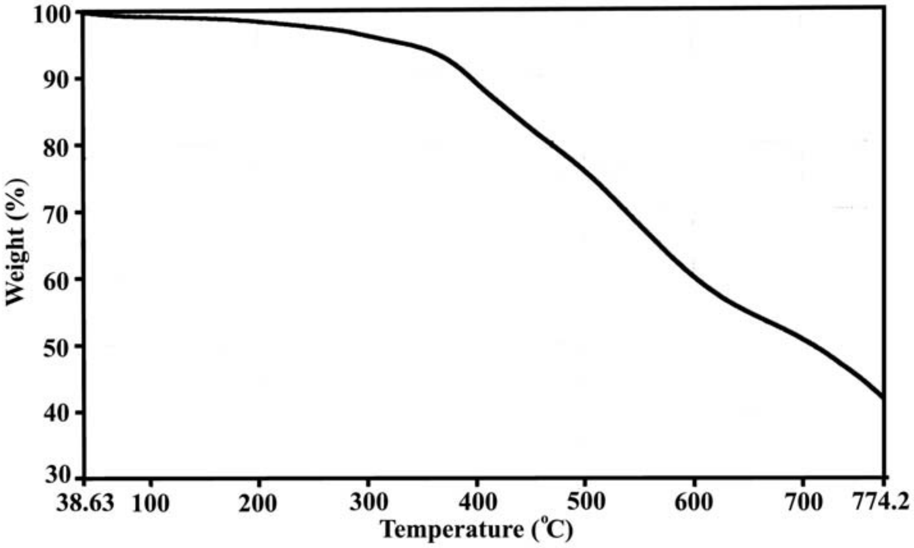


Fig. 9. TGA thermograms of PAI-**7a** in a N_2 atmosphere and heating rate of 10 °C/min.

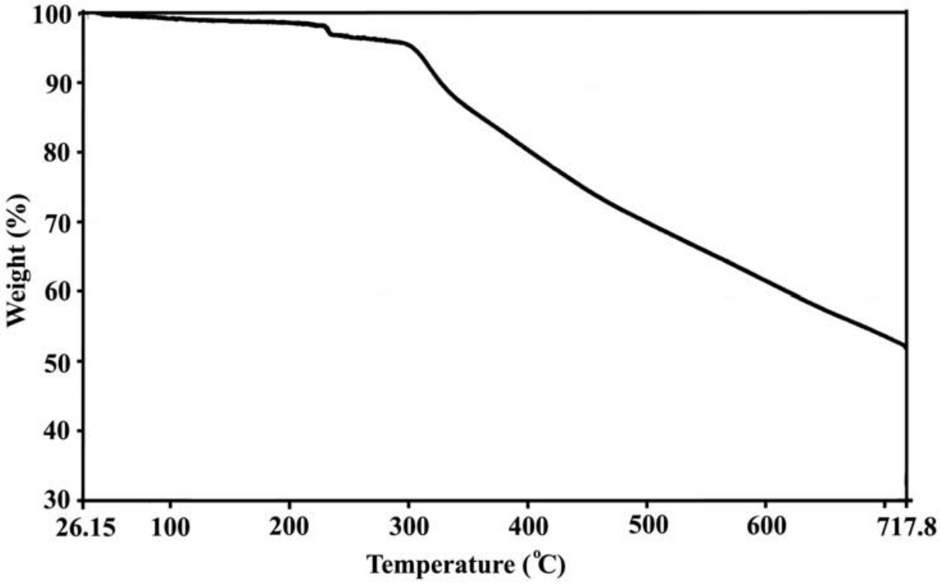


Fig. 10. TGA thermograms of PAI-**7d** in a N_2 atmosphere and heating rate of 10 °C/min.

Tab. 4. Thermal properties of some aromatic PAIs.

Polymer	T_5[a](°C)	T_{10}[b](°C)	**Char Yield(%)**[C]	**Char Yield(%)**[C]
7a	358	395	76	51
7b	310	326	71	54

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate of 10 °C/min in a N_2 atmosphere.

[b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 10 °C/min in a N_2 atmosphere.

[c] Weight percent of the material left undecomposed after TGA at maximum temperature 500 °C in a N_2 atmosphere.

[d] Weight percent of the material left undecomposed after TGA at maximum temperature 700 °C in a N_2 atmosphere.

Conclusions

Direct polyamidation reaction of monomer **5** with several aromatic diamines furnished novel optically active PAIs containing S-valine amino acid moiety using TsCl/ DMF/ Py as a condensing agent. The influences of aging time, amount of DMF, reaction time and temperature on the physical properties of the resulting PAIs were investigated. The main advantages of this polycondensation reaction are that in this procedure we do not need to prepare diacid chloride, which saves time and energy. These OAPs are thermally stable and have good solubility. In addition because of the existence of amino acid in the polymer backbone these polymers are expected to be biodegradable and therefore are classified under environmentally friendly polymers. Since the resulting polymers are optically active and have good thermal stability they have potential to be used as chiral stationary phase in GC for the separation of racemic mixtures.

Experimental

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co.) Trimellitic anhydride **(1)** was purified with acetic anhydride in boiling acetic acid. 4,4'-diaminodiphenylsulfone (**6a**) was used as obtained without further purification. Benzidine (**6c**) and 4,4'-diaminodiphenyl methane (**6d**) was purified by recrystallization from ethanol and water respectively. 4,4'-Diaminodiphenylether (**6b**), *p*-phenylenediamine (**6e**), and 2,5-diaminotoluene (**6f**) were purified by sublimation.

Techniques

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. 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 wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured using a Cannon-Fensk Routine Viscometer (Germany) at concentration of 0.5 g/dL at 25°C. Specific Rotations were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a rate of

10^{o}C/min. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran.

Monomer synthesis

- N-Trimellitylimido-S-valine (**3**)

Into a 250 mL round-bottomed flask 3.00 g (1.56×10^{-2} mol) of trimellitic anhydride **(1)**, 1.83 g (1.56×10^{-2} mol) of S-valine **(2)**, 120 mL of acetic acid and a stirring bar were placed. The solution was stirred for 2 h to yield amic acid and then the mixture was refluxed for 4 h. The solvent was removed under reduced pressure and to the residue 100 mL of cold water was added. The solution was then decanted, and 5 mL of concentrated HCl was added. A white precipitate was formed, filtered off and dried, to give 4.42 g (91.5%) of diacid **(3)**. Recrystallization from methanol/water gave white crystals, mp 186-188°C, $[\alpha]_D^{25}$ = -23.2 (0.050 g in 10 mL DMF); FT-IR (KBr): 2400-3400 (br), 1780 (m, sh), 1722 (s, sh), 1486 (w), 1422 (m), 1383 (s), 1289 (s), 1257 (m), 1173 (w), 1095 (w), 928(m), 878 cm^{-1} (w). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 0.82 (d, 3H, J = 6.7 Hz), 1.05 (d, 3H, J = 6.6 Hz), 2.55 (m, 1H), 4.48 (d, 1H, J = 7.7 Hz), 8.01 (d, 1H, J = 7.7 Hz), 8.25 (s, 1H), 8.37 (d, 1H, J = 7.7 Hz), 13.39 (s, 2H) ppm.

- N-Trimellitylimido-S-valine diacid chloride (**4**)

Into a 50 mL round-bottom flask, 1.00 g (3.43×10^{-3}) of *N*-trimellitylimido-S-valine **(3)**, 10 mL (an excess amount) of thionyl chloride, and a stirring bar were placed. The stirring started and the mixture was refluxed for 1 h. Then the reaction mixture was stirred at room temperature for 2 h. The thionyl chloride was removed via distillation and 20 mL of *n*-hexane was added, the mixture heated, *n*-hexane distilled off, and the solid collected and dried in vacuo to give 1.02 g (90%) of a white solid. mp 42°C**,** $[\alpha]_D^{25}$= -25.6 (0.050 g in 10 ml DMF); FT-IR (KBr): 2959 (m), 1779 (m,sh), 1721 (s), 1431 (w), 1382 (m), 1289 (m), 1252 (m), 1203 (m), 1104 (w), 1074 (w), 1019 (w), 916 (w), 728 cm^{-1} (m).

- N-Trimellitylimido-S-valine-bis(p-aminobenzoic acid) **(5)**

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 1.00 g (3.05×10^{-3} mol) diacid chloride **(5)** in 5 mL of tetrahydrofuran (THF). The reaction mixture was cooled in an ice water bath. To this solution 0.46 g (3.35×10^{-3} mol) *p*-aminobenzoic acid in 7 mL THF was added dropwise. The mixture was stirred in ice bath for 2 h and at room temperature overnight. The resulting mixture was poured into 100 mL of water. The precipitate was collected by filtration and washed thoroughly with water and dried at 70^{o}C for 10 h, to yield 1.36 g (84%) of diacid **(6)**. mp >270°C (dec), $[\alpha]_D^{25}$ = -19.6 (0.050 g in 10 mL DMF); FT-IR (KBr): 2400-3400 (br), 1776 (m, sh), 1714 (s, br), 1599 (s), 1519 (s), 1422 (s, sh), 1377 (m), 1315 (m), 1248 (s, sh), 1179 (m), 1083 (m, sh), 1019 (w), 851 (m), 800 (m), 770 cm^{-1} (m). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 0.85 (d, 3H, J = 6.7 Hz), 1.07 (d, 3H, J = 6.6 Hz), 2.56 (m, 1H), 4.66 (d, 1H, J = 7.7 Hz), 7.92–8.49 (m,11H), 10.86 (s, 2H), 12.93 (s, 2H) ppm.

Elemental analysis: calculated for $C_{28}H_{23}N_3O_8$, C (63.51%), H (4.38%), N (7.94%); Found, C (63.08%), H (4.48%), N (7.68%).

Polymer Synthesis

The PAIs were prepared by the following procedure: For synthesis of polymer **(7a)**, A pyridine (0.15 mL; 1.9 × 10^{-3} mol) solution of TsCl (0.180 g; 9.5 × 10^{-4} mol) after 30 min stirring at room temperature, was treated with DMF (0.07 mL; 9.45 × 10^{-4} mol) for 30 min and the solution was added dropwise to a solution of diacid **5** (0.100 g; 1.89 × 10^{-4} mol) in Py (0.15 mL). The mixture was maintained at room temperature for 30 min and then to this mixture, a solution of 4,4'-diaminophenylsulfone **(6a)** (0.047 g; 1.89 × 10^{-4} mol) in **Py** (0.15 mL) was added dropwise at room temperature and the whole solution was stirred at room temperature for 30 min and at 80°C for 2h. As the reaction proceeded, the solution became viscous. Then the viscous liquid was precipitated in 30 mL of methanol to yield 0.127 g (86%) of the polymer **7a**. IR (KBr): 3347 (br), 2965 (m, sh), 1777 (m), 1718 (s), 1679 (s), 1591 (s), 1525 (s, sh), 1507 (s, sh), 1404 (m), 1380 (m), 1318 (s), 1247 (s), 1182 (m), 1150 (m), 1106 (m), 1033 (w, sh), 838 (m), 760 (w), 727 (m) cm^{-1}.

The other PAIs (**7b-7f**) were prepared with a similar procedure.

-Polymer **7b**

IR (KBr): 3330 (br), 2966 (w), 1777 (m), 1718 (s), 1669 (s), 1598 (s), 1498 (s, sh), 1407 (m), 1373 (m), 1318 (m), 1219 (m, sh), 1099 (w, sh), 1012 (w), 876 (m), 850 (m, sh), 761(m), 725 (m) cm^{-1}.

-Polymer **7c**

IR (KBr): 3343 (br), 2965 (w), 1778 (m), 1719 (s, sh), 1663 (m), 1595 (s), 1503 (s, sh), 1377 (m), 1318 (m), 1244 (m), 1171 (m), 1083 (w, sh), 1033 (w), 851 (w), 816 (m), 725 (m) cm^{-1}.

-Polymer **7d**

IR (KBr): 3312 (br), 2965 (w), 1777 (m), 1718 (s), 1662 (s), 1598 (s), 1512 (s, sh), 1410 (m), 1380 (m), 1319 (s), 1252 (m), 1183 (w, sh), 1099 (w, sh), 1018 (w, sh), 855 (w), 761 (w, sh), 726 (w) cm^{-1}.

-Polymer **7e**

IR (KBr): 3313 (br), 2964 (w), 1777 (m), 1716 (s), 1656 (m), 1597 (m), 1515 (s), 1406 (m), 1379 (m), 1316 (m), 1249 (m), 1181 (w), 1079 (w, sh), 1010 (w), 827 (m), 760 (w), 723 (w) cm^{-1}.

-Polymer **7f**

IR (KBr): 3337 (br), 2966 (w), 1778 (m), 1716 (s), 1652 (m, sh), 1597 (s), 1520 (s, sh), 1383 (m), 1317 (m), 1249 (m), 1185 (w), 1075 (w, sh), 851 (w), 761 (w), 724 (w) cm^{-1}.

Acknowledgments

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