Trimellitic anhydride (1) was reacted with L-isoleucine (2) in acetic acid and the resulting imide-acid \([N\text{-trimellitylimido-}L\text{-isoleucine}]\) (4) was obtained in high yield. The direct polycondensation reaction of this diacid with several aromatic diols such as bisphenol A (5a), phenolphthalein (5b), 4,4-di hydroxybiphenyl (5c), 4,4-di hydroxydiphenyl sulphide (5d), 4,4-di hydroxydiphenyl sulphone (5e) and 1,4-di hydroxyan thraquinone (5f) was carried out in a system of tosyl chloride (TsCl), pyridine (Py) and N,N-dimethylformamide (DMF). The reactions with TsCl were significantly promoted by controlling alcoholysis with diols in the presence of the catalytic amounts of DMF to give a series of optically active poly(ester-imide)s (PEI)s with good yield and moderate inherent viscosity ranging 0.18-0.28 dL/g. The polycondensation reactions were significantly affected by the amounts of DMF, molar concentration of monomers, TsCl and pyridine, aging time, addition time of diols, temperature and the reaction time. All of the above polymers were fully characterized by \(^1\)H NMR, IR, elemental analysis and specific rotation. Some structural characterization and physical properties of these optically active poly(ester-imide)s are reported.

**INTRODUCTION**

Polyimides have been widely studied for many years because of their high thermal stability, mechanical strength and good electrical properties. A drawback is however their poor solubility in most organic solvents which in combination with high temperature resistance, impair the processability of many polyimides. To solve these problems, amide, ester and urethane groups may be introduced into polyimide to form poly(amide-imide)s [1-2], poly(ester-imide)s [3-4] and poly(imide-
urethane)s [5-6] with improved solubility. Poly(ester-imide)s (PEIs) are well known for their thermal resistance coupled with easy processability [7-8]. Imide segments have also been incorporated into cross-linkable polyesters for the purpose of increasing the heat stability of resins and varnishes. Several strategies in synthesis of poly(ester-imide)s have been presented [9-10].

Direct polycondensation as a mild condition method for the synthesis of polyamides and corresponding copolymers has been used in our laboratory [11-14]. The usual route for the preparation of polyamides is the solution or interfacial reaction between dicarboxylic-acid chlorides and diols, and an acid or phenyl ester exchange reaction of the acetate or ester of the acids under severe conditions (high temperature and reduced pressure). In these usual techniques, monomers such as acid chlorides, acetates and esters should be prepared before polymerization. The processes which are operative under mild conditions and adaptable to the direct polycondensations of free carboxylic acids and aromatic diols, can be more useful technique for polyestcerification. Several condensing agents suitable for the direct polycondensation reaction such as diphenyl chlorophosphate and arylsulphonyl chlorides [15-16] have been developed in the past decades. However, there are few which are well studied to the direct synthesis of the aliphatic and aliphatic-aromatic polyesters. It was found that Vilsmeier adduct derived from arylsulphonyl chlorides and DMF in 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 and also of hydroxybenzoic acids [17-18].

L-isoleucine, one of the essential amino acid, has a strong hydrophobic nature and found naturally in the L-(+) form. It plays an important role in α-helix formation and stabilization of peptides and proteins [19]. Here, we used L-isoleucine amino acid as a biocompatible material as well as optically active pure and chemical functional group in the polymer backbone. Also we showed that easily available arylsulphonyl chloride such as TsCl is a very effective condensing agent for the direct synthesis of aliphatic-aromatic polyesters from aliphatic imide containing diacid and bisphenols in Py in the presence of DMF. In this study a series of new PEIs were synthesized by direct polycondensation from aromatic diols and imide dicarboxylic acid which is prepared from trimellitic anhydride and L-isoleucine aminoacid. The properties of these PEIs were also investigated. We also used triphenylphosphine oxide (TPPO) as another condensing agent but in this case satisfactory results were not obtained.

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. 1,4-Dihydroxyanthraquinone (5b) and Bisphenol A (5a) were purified by recrystalization from acetic acid and acetic acid-water respectively. The other diols were used as obtained without further purification.

Techniques

Proton nuclear magnetic resonance (\(^{1}\)H NMR, 500 MHz) spectra were recorded on a Bruker (Germany) Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). IR Spectra were recorded on Shimadzu 435 IR spectrophotometer (Shimadzu, Japan). The spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumbers (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-Fensk Routine Viscometer (Germany). Specific rotations were measured by a Perkin Elmer-241 Polarimeter (Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-50 in nitrogen atmosphere at a rate of 10°C/min. Elemental analyses were performed by Malek-Ashtar University of Technology, (Tehran, Iran).

Monomer Synthesis

\(N\)-Trimellitylimido-L-isoleucine (4) was prepared according to our previous work [13]. Here, we used acetic acid as a solvent.

Polymer Synthesis

The PEIs were prepared by the following procedure:
For synthesis of polymer (6a), A Py (0.15 mL; 7.6 × 10^{-3} mol) solution of TsCl (0.1623 g; 8.5×10^{-4} mol) after 30 min stirring at room temperature, was treated with DMF (0.05 mL; 6.5×10^{-4} mol) for 30 min and the solution was added dropwise to a solution of diacid (4) (0.1 g; 3.9×10^{-3} mol) in Py (0.15 mL). The mixture was maintained at room temperature for 20 min and then to this mixture, a solution of bisphenol A (5a) (0.047 g; 3.9×10^{-3} mol) in Py (0.15 mL) was added dropwise at room temperature and the whole solution was stirred at 120°C for 2 h. As the reaction proceeded, the solution became viscous. Then the viscous liquid was precipitated in 30 mL of methanol to yield 0.1301 g (80%) of the polymer 6a. Mp = 220-225°C, IR (KBr): 2950(s), 1780(s, sh), 1740 (s, sh), 1720 (s), 1600 (m, br), 1500 (s), 1460 (m), 1380 (s), 1340 (s, sh), 1280 (s), 1240 (s), 1200 (s), 1160 (s), 1100 (s), 1080 (s), 1050 (s), 1010 (s), 920 (m), 850 (m), 810 (m), 720 (s), 540 (w) cm^{-1}. 

{1}H NMR (500 MHz, DMSO-d_{6}, TMS, δ, ppm): 0.78-1.15 (m, 6H), 1.15-1.30 (m, 1H), 1.45-1.80 (m, 7H), 2.32-2.49 (m, 1H), 4.98-5.18 (d, 1H), 6.83-7.42 (m, 8H), 8.13-8.62 (m, 3H).

The other PEIs (6b-6f) were prepared with a similar procedure.

**Polymer 6b**
IR (KBr): 3400 (H_{2}O), 2950 (m), 1770 (s), 1720 (s), 1600 (m), 1500 (s), 1460 (m), 1380 (s), 1280 (m), 1240 (s), 1200 (s), 1160 (s), 1100 (s), 1050 (m), 1020 (w), 970 (m), 920 (m), 720 (s) cm^{-1}.

**Polymer 6c**
IR (KBr): 2950 (m), 1780 (s, sh), 1740 (s, sh), 1720 (s), 1600 (m, br), 1500 (s), 1380 (s), 1340 (m, sh), 1280 (s), 1240 (s), 1190 (s), 1160 (s), 1090 (m), 1050 (m), 1000 (m), 800 (m), 720 (s) cm^{-1}.

**Polymer 6d**
IR (KBr): 3400 (m, br, H_{2}O), 2950 (m), 1780 (s, sh), 1740 (s, sh), 1720 (s), 1580 (m), 1480 (s), 1420 (w), 1380 (s), 1320 (m), 1280 (s), 1240 (s), 1200 (s), 1160 (s), 1090 (m), 1050 (m), 1010 (m), 920 (w), 800 (w), 720 (s) cm^{-1}.

**Polymer 6e**
IR (KBr): 3400 (m, br, H_{2}O), 2950 (m), 1780 (s, sh), 1740 (s, sh), 1720 (s), 1580 (m), 1480 (m), 1380 (s), 1320 (m), 1280 (s), 1240 (s), 1200 (s), 1150 (s), 1100 (s), 1050 (m), 1010 (m), 920 (w), 830 (m, br), 720 (s), 680 (m), 560 (m, br) cm^{-1}.

**Polymer 6f**
IR (KBr): 3400(m, br, H_{2}O), 2950 (m), 1780 (s, sh), 1750 (s, sh), 1720 (s), 1670 (s), 1640 (s), 1590 (s), 1460 (s), 1420 (m), 1380 (s), 1360 (s), 1320 (m), 1270 (s), 1240 (s), 1210 (s), 1180 (s, sh), 1160 (s), 1100 (m), 1070 (m), 1040 (m), 1020 (m), 860 (m), 780 (m, br), 720 (s) cm^{-1}.

**RESULTS AND DISCUSSION**

**Monomer Synthesis**
N-Trimellitylimido-L-isoleucine (4) was synthesized according to our previous work [13] (Scheme I).

**Polymer Synthesis**
PEIs (6a-6f) were synthesized by the direct polycondensation of 

![Scheme I. Synthesis of monomer 4.](image)
Polycondensation reactions of an equimolar mixture of monomer (4) with several different aromatic diols (5a-5f) in a system of TsCl/Py/DMF (Scheme II).

In this work for the polycondensation of aliphatic-aromatic diacids and aromatic diols, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polycondensation was carried out in the following way: TsCl was dissolved in Py 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 a period of time a solution of diol in Py was added and the whole solution was maintained at elevated temperature for several hours. Polycondensation was carried out by varying the aging time of the initial reaction of TsCl and Py, the amount of DMF, the molar ratio of TsCl/diacid, Py/diacid, the time of diol addition and the time of heating. All of these parameters had critical effect on the polymer chain growth (Tables 1-5).

The synthesis and some physical properties of these novel optically active PEIs are listed in Table 6. The inherent viscosities of the resulting polymers under optimized condition were in a range of 0.18-0.28 dL/g and the yields were 60-95%. All of the PEIs are optically active.

Triphenylphosphine oxide (TPPO) was also tested...
as another condensing agent but satisfactory results were not obtained.

**Polymer Characterization**

The formation of PEIs was confirmed by IR spectroscopy analysis. As an example, the IR spectrum of PEIs (6d) (Figure 1) showed the characteristic absorptions of imide and ester groups occurred around 1780, 1720 cm⁻¹, peculiar to carbonyls stretching of imide and ester, respectively. All of these PEIs exhibited absorption at 1380 cm⁻¹ and 720 cm⁻¹, that show the presence of the imide heterocycle in these polymers.

The ¹H NMR spectrum (500 MHz) of polymer (6d) has been shown in Figure 2.

In the ¹H NMR spectrum of polymer (6d), the absorption of aromatic protons (H₆, H₇, H₈) appeared in a range of 8.12-8.64 ppm. The other aromatic protons (H₅) appeared as multiplets in a range of 6.86-7.44 ppm. The proton of the chiral center (H₄) appeared as a doublet (d) at 5.11 ppm. Absorption of another chiral proton (H₃) appears as a multiplet from 2.32 to 2.48 ppm.

The peaks of diastereotopic protons of CH₃ (H₂) appeared as a doublet of doublet which is splitted as multiplets in a range of 1.41 ppm. Absorption of the CH₃ protons (H₁) appears as a triplet for proton (H₁) and a doublet for proton (H₂) which both have split by diastereotopic protons and the chiral center proton to multiplets from 0.78 to 1.14 ppm.

The ¹H NMR spectrum of PEI (6a) is shown in Figure 3. Elemental analysis values of the resulting polymers are listed in Table 7. PEIs derived from monomer (4) may range in colour from white to green.

The solubility of PEIs was tested quantitatively in

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**Table 5.** The optimum conditions for the preparation of PEIs.

<table>
<thead>
<tr>
<th>Optimum condition</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TsCl/diacid (mol/mol)</td>
<td>2.6</td>
</tr>
<tr>
<td>Py/diacid (mol/mol)</td>
<td>6.0</td>
</tr>
<tr>
<td>DMF (mmol)</td>
<td>0.65</td>
</tr>
<tr>
<td>Aging time (min)</td>
<td>30</td>
</tr>
<tr>
<td>Addition time of diol (min)</td>
<td>20</td>
</tr>
<tr>
<td>Reaction time (h)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Table 6.** Synthesis and some physical properties of PEIs (6a-6f).

<table>
<thead>
<tr>
<th>Diol</th>
<th>Polymer</th>
<th>Yield (%)</th>
<th>η_{inh} (dL/g)</th>
<th>[α]_{D}^{25}</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>6a</td>
<td>80</td>
<td>0.20</td>
<td>+14.6</td>
<td>W</td>
</tr>
<tr>
<td>5b</td>
<td>6b</td>
<td>80</td>
<td>0.18</td>
<td>+14.2</td>
<td>W</td>
</tr>
<tr>
<td>5c</td>
<td>6c</td>
<td>89</td>
<td>0.25</td>
<td>+8.3</td>
<td>OW</td>
</tr>
<tr>
<td>5d</td>
<td>6d</td>
<td>92</td>
<td>0.28</td>
<td>+15.6</td>
<td>PY</td>
</tr>
<tr>
<td>5e</td>
<td>6e</td>
<td>95</td>
<td>0.24</td>
<td>+16.8</td>
<td>W</td>
</tr>
<tr>
<td>5f</td>
<td>6f</td>
<td>60</td>
<td>0.24</td>
<td>+17.1</td>
<td>G</td>
</tr>
</tbody>
</table>

(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) W= white, OW= off white, PY= pale yellow, G= green.

**Table 7.** Elemental analysis of PEIs (6a-6f).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Formula</th>
<th>Element analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>(C₃₀H₂₇NO₆)ₙ</td>
<td>C 72.42 H 5.47 N 2.82</td>
</tr>
<tr>
<td></td>
<td>(498)ₙ</td>
<td>Calcd</td>
</tr>
<tr>
<td>6b</td>
<td>(C₂₂H₂₅NO₆S)ₙ</td>
<td>Calcd</td>
</tr>
<tr>
<td></td>
<td>(488)ₙ</td>
<td>Found</td>
</tr>
<tr>
<td>6d</td>
<td>(C₂₂H₂₅NO₆S)ₙ</td>
<td>Calcd</td>
</tr>
<tr>
<td></td>
<td>(520)ₙ</td>
<td>Found</td>
</tr>
<tr>
<td>6e</td>
<td>(C₂₁H₁₇NO₆)ₙ</td>
<td>Calcd</td>
</tr>
<tr>
<td></td>
<td>(379)ₙ</td>
<td>Found</td>
</tr>
<tr>
<td>6f</td>
<td>(C₃₇H₃₆N₂O₆)ₙ</td>
<td>Calcd</td>
</tr>
<tr>
<td></td>
<td>(636)ₙ</td>
<td>Found</td>
</tr>
</tbody>
</table>

---

Figure 1. IR (KBr) spectrum of PEI (6d).

Figure 2. ¹H NMR spectrum of polymer (6d).

Figure 3. ¹H NMR spectrum of polymer (6a).
Figure 2. $^1$H NMR (500 MHz) spectrum of PEI (6d) in DMSO-d$_6$ at room temperature.

Figure 3. $^1$H NMR (500 MHz) spectrum of PEI (6a) in DMSO-d$_6$ at room temperature.
various solvents and are listed in Table 8. All of the PEIs are soluble in organic solvents such as DMF, N,N-dimethyl acetamide (DMAc), dimethyl sulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and H2SO4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

### Thermal Properties

The thermal properties of PEI (6d) was evaluated by means of TGA/DTG in nitrogen atmosphere. The PEI (6d) exhibited good resistance to thermal decomposition between 210 and 230°C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for this polymer was 260°C, the temperature of 10% weight loss ranged from 310°C and the residual weight for this polymer at 600°C was 12.42% under nitrogen atmosphere. The TGA curve of PEI (6d) has been shown in Figure 4.

### CONCLUSION

In this study for the first time we carried out direct polycondensation of aliphatic-aromatic imide containing diacid and aromatic diols using TsCl/DMF/Py as condensing agent to prepare new aliphatic-aromatic poly(ester-imide)s. The influence of aging time, amount of DMF, concentration of monomers and condensing agents, addition time of aromatic diols and reaction time on the physical properties were investigated.

### ACKNOWLEDGMENTS

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### REFERENCES


