

# Synthesis and properties of new optically active and organosoluble poly(ester-imide)s containing L-valine moieties in the main chain by direct polycondensation reaction

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New optically active poly(ester-imide)s (PEIs) containing bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide in the main chain were prepared by the reaction of N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic)-bis-L-valine **4** as a diacid monomer with various aromatic diols **5a-g** 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 catalytic amounts of DMF, to give a series of optically active poly(ester-imide)s. The resulting new polymers were obtained in good yields and inherent viscosities, ranging between 0.36 and 0.62 dL g<sup>-1</sup>, and were characterized with FT-IR and <sup>1</sup>H-NMR spectroscopy, including specific rotation. All of these polymers were highly organosoluble at room temperature in solvents like N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), and sulfuric acid. The thermal stability of the resulting PEIs was evaluated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques under a nitrogen atmosphere, which indicated that the residual weight percent of the polymers at 600 °C was 43.69%-60.5% and showed that they are moderately thermally stable.

**Key Words:** Poly(ester-imide)s, direct polycondensation, optically active polymers, thermal properties

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## Introduction

High performance polymeric materials are currently receiving considerable attention for their potential applications in advanced technology demands. Aromatic polyimides are well-known high performance polymers that show excellent thermal, mechanical, and electrical properties.<sup>1,2</sup> However, applications may be rather limited due to their high softening or melting temperatures and their insoluble nature in most organic solvents.<sup>3</sup>

Modification of high performance materials by increasing the solubility and lowering the transition temperatures while maintaining thermal stability is of particular interest. Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyimides, many copolyimides, such as poly(amide-imide)s, poly(ester-imide)s, and other copolymers, have been prepared.<sup>4-9</sup>

Poly(ester-imide)s (PEIs) are a class of macromolecules known for more than 35 years. They are used today in large tonnage as electrical insulating materials. The patent literature reviewed shows that predominant research activities in the past were focused on improving the electrical, thermal, and mechanical properties. In recent times, new applications for these polymers have been found, such as adhesives, printed circuit boards, membranes, and engineering thermoplastics. Excellent properties and easy processing will probably lead to a continuous growth of the PEI business.<sup>10,11</sup>

Optically active polymers have also been found to have interesting applications because of their specific properties. For example, these polymers have the ability of molecular recognition, which leads to their use for stationary phases in chromatography methods for enantiomer separations.<sup>12-14</sup> They can also be used as chiral media for asymmetric synthesis, and chiral liquid crystals in ferroelectric and nonlinear optical devices.<sup>15</sup>

In this article, the synthesis and characterization of a new series of poly(ester-imide)s, **6a-g**, containing bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide in the main chain, was described. PEIs **6a-g** were synthesized by direct polycondensation reaction of diacid **4** with 4,4'-sulfonyldiphenol **5a**, bisphenol A **5b**, 1,5-dihydroxynaphthalene **5c**, 1,4-dihydroxyanthraquinone **5d**, phenolphthalein **5e**, hydroquinone **5f**, and resorcinol **5g** in a medium consisting of tosyl chloride (TsCl), pyridine (Py), and N,N-dimethylformamide (DMF). Results showed that these novel polymers with ester-imide groups and a bicyclo segment in the main chain had better solubility in organic solvents compared to aromatic polyimides.

## Experimental

### Materials

Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** (from Aldrich) and L-valine **2** (from Merck) were used without previous purification. Tosyl chloride (TsCl; from Merck), 4,4'-sulfonyldiphenol **5a**, bisphenol A **5b**, 1,5-dihydroxynaphthalene **5c**, 1,4-dihydroxyanthraquinone **5d**, phenolphthalein **5e**, hydroquinone **5f**, and resorcinol **5g** (from Merck), and solvents N,N-dimethylformamide (DMF; from Merck) and pyridine (from Acros) were used as received.

## Techniques

<sup>1</sup>H-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Galaxy series FT-IR 5000 spectrophotometer (England). Spectra of solids were obtained by using KBr pellets. Vibration transition frequencies were reported in wavenumbers (cm<sup>-1</sup>). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), or broad (br). Inherent viscosities were measured by a standard procedure using a Technico Registered Trade Mark viscometer. Specific rotations were measured by an A.KRÜSS polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 system, and differential scanning calorimetry (DSC) was conducted with a DSC Mettler 110 (Switzerland) at a heating and cooling rate of 10 °C min<sup>-1</sup> in a nitrogen atmosphere. Elemental analyses were performed with Vario EL equipment.

## Monomer synthesis

N,N-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-valine **4** was synthesized according to previous work.<sup>14</sup>

## Polymer synthesis

The PEIs were prepared by the following procedure: For synthesis of polymer **6g**, a solution of pyridine (0.15 mL, 1.9 mmol) with TsCl (0.09 g, 0.460 mmol), after 30 min of stirring at room temperature, was treated with DMF (0.15 mL, 1.86 mmol) for 30 min and the mixture was added dropwise to a solution of diacid **4** (0.083 g, 0.186 mmol) in pyridine (0.15 mL). The mixture was maintained at room temperature for 20 min and then a solution of resorcinol **5g** (0.02 g, 0.186 mmol) in pyridine (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. The viscous liquid was then precipitated in 50 mL of methanol to yield 0.086 g (89%) of polymer **6g**.

## Results and discussion

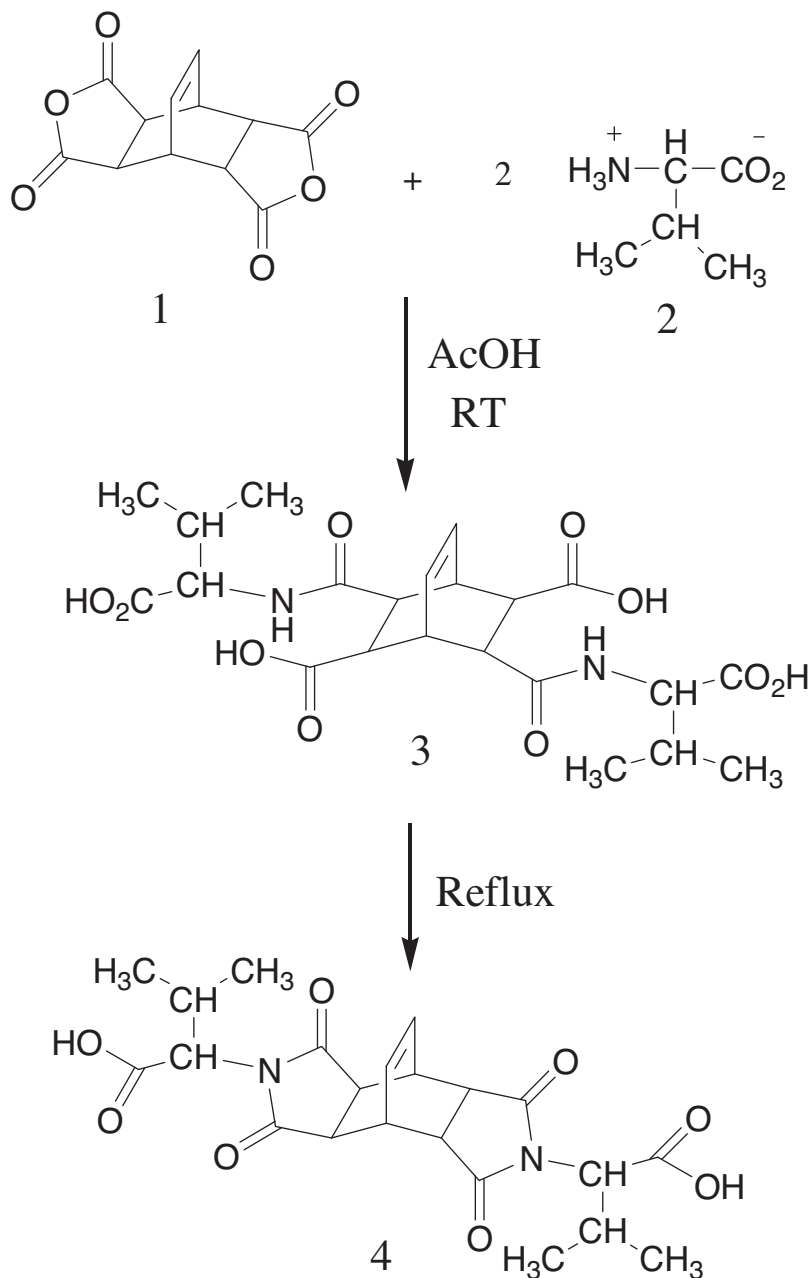
### Monomer synthesis

N,N-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-valine diacid **4** was prepared in a single step, as shown in Scheme 1. The asymmetric diacid **4** was synthesized by the condensation reaction of 2 equimolar amounts of L-valine **2** with one equimolar amount of dianhydride **1** in acetic acid. Dissolving the residue in cold water gave a gummy-like solid that broke with the addition of concentrated HCl and gave a white-colored solid.

### Polymer synthesis

In this work, the Vilsmeier adduct was used for the polycondensation of aromatic diacid and aromatic diols in the following way (Scheme 2): TsCl was dissolved in Py to yield sulfonium salt, and after a certain period of aging time, the solution was treated with DMF for 30 min to form the Vilsmeier adduct, as proposed by Higashi et al.<sup>16,17</sup> The reaction mixture was added to a solution of diacid in Py to form activated acid. After 30 min, a solution of diol in Py was added, and the whole solution was maintained at room temperature and then at an

elevated temperature for a period of time. For direct polycondensation of monomer **4**, the reported optimized conditions were selected and polymerization was carried out under these conditions<sup>18,19</sup> (Scheme 2).

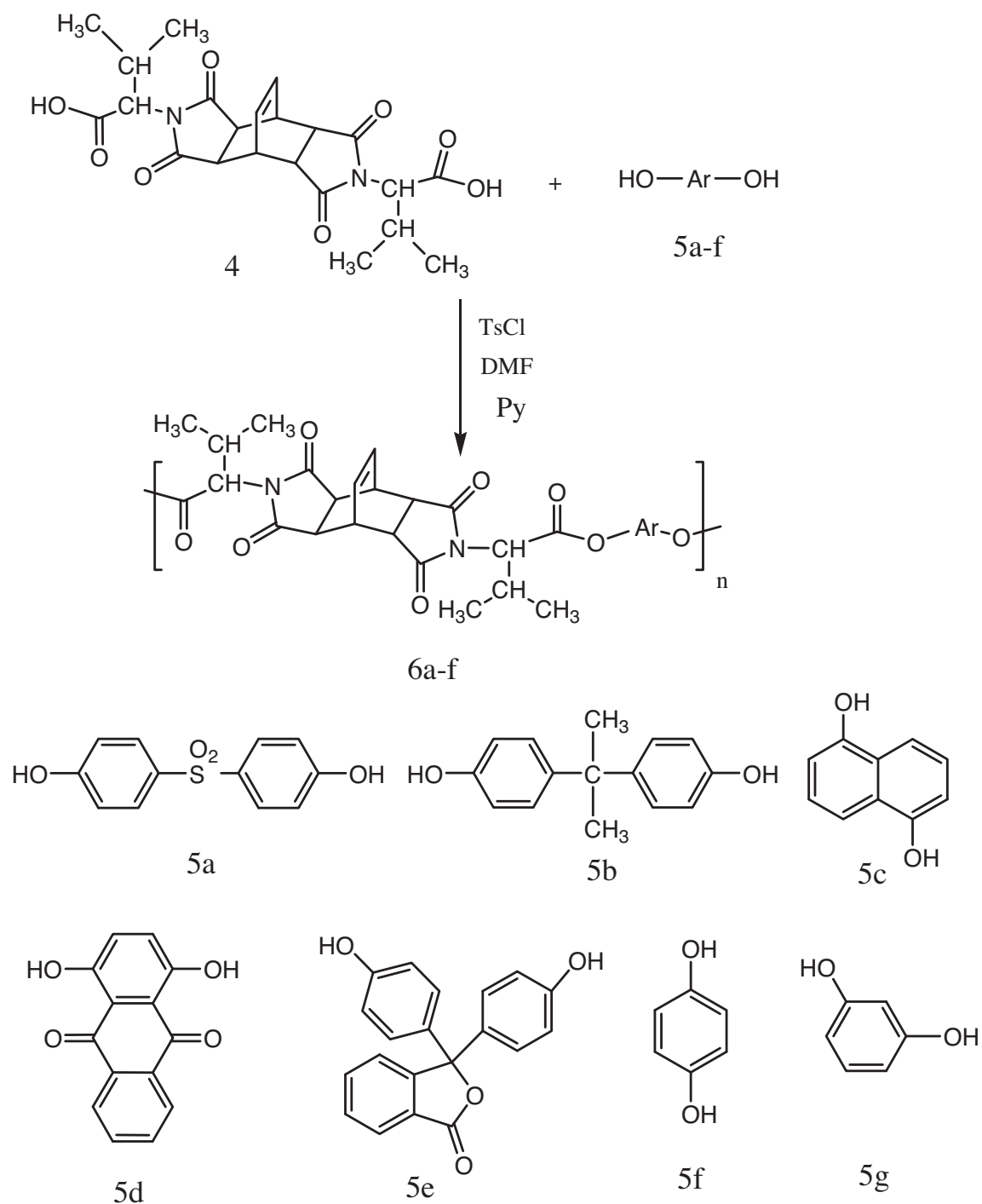


**Scheme 1.**

The structures of these polymers were confirmed as PEIs by means of FT-IR spectroscopy and elemental analyses. FT-IR spectroscopies of all PEIs are listed in Table 1.

The representative FT-IR spectrum of PEI **6a** is shown in Figure 1. The polymer showed the C=O asymmetric stretching of imide and ester at  $1774\text{ cm}^{-1}$ , the C=O symmetric stretching of imide and ester

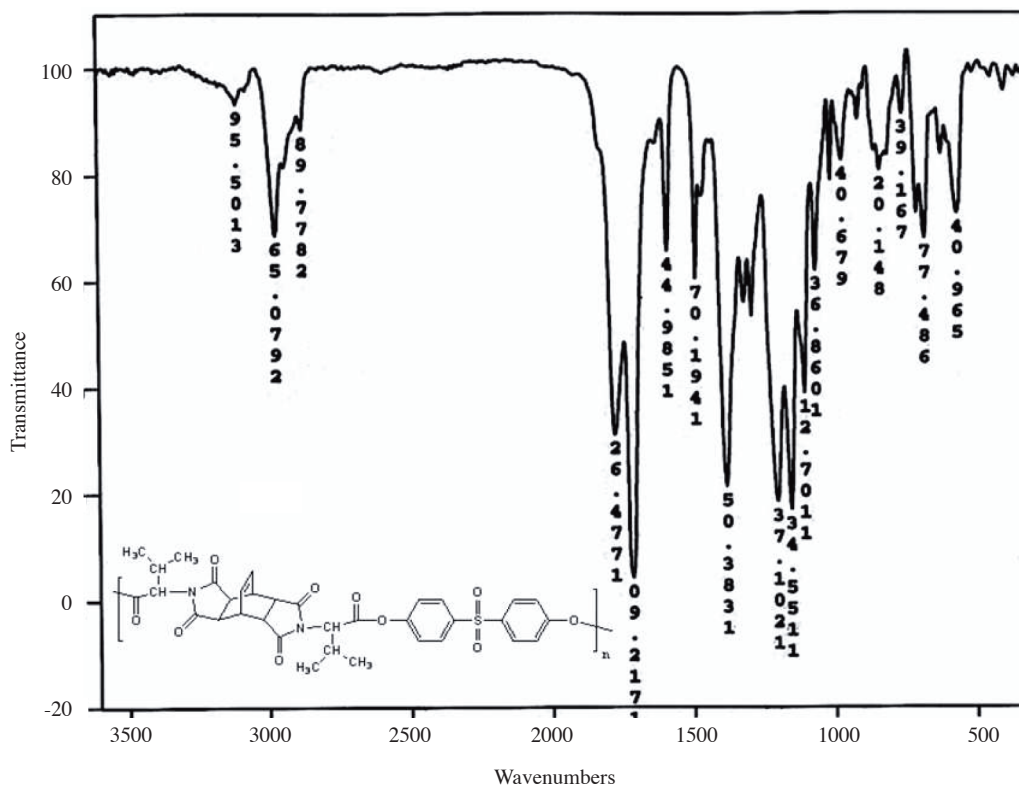
groups at  $1712\text{ cm}^{-1}$ , the C-N stretching at  $1383\text{ cm}^{-1}$ , and the C-O-C stretching at  $1201\text{-}1068\text{ cm}^{-1}$ . All of these PEIs exhibited strong absorption around  $1383$  and  $729\text{ cm}^{-1}$ , which shows the presence of the heterocyclic imide groups.



Scheme 2.

**Table 1.** FT-IR characterization of PEIs **6a-g**.

| Polymer   | Spectral data  |
|-----------|--|
| <b>6a</b> | <b>FT-IR peaks (cm<sup>-1</sup>):</b> 3105 (w), 2970 (m), 1774 (m), 1712 (s), 1589 (w), 1491 (w), 1383 (s), 1201 (m), 1155 (m), 1107 (w), 976(w), 761 (w), 684 (w).            |
| <b>6b</b> | <b>FT-IR peaks (cm<sup>-1</sup>):</b> 2940 (m), 1770 (m), 1712 (s), 1589 (s), 1494 (w), 1384 (s), 1302 (m), 1140 (m), 1076 (w), 846 (m), 729 (m), 578 (w).                     |
| <b>6c</b> | <b>FT-IR peaks (cm<sup>-1</sup>):</b> 2968 (m), 1776 (m), 1710 (s), 1633 (w), 1514 (w), 1462 (w), 1386 (s, br), 1199 (s), 1068 (w), 839 (m), 761 (w), 688 (w).                 |
| <b>6d</b> | <b>FT-IR peaks (cm<sup>-1</sup>):</b> 3061 (w), 2968 (m), 1776 (w), 1712 (s), 1678 (m), 1639 (w), 1591 (m), 1464 (m), 1383 (s), 1321 (w), 1201 (m), 1113 (w), 723 (w).         |
| <b>6e</b> | <b>FT-IR peaks (cm<sup>-1</sup>):</b> 3059 (w), 2958 (w), 1776 (m), 1712 (s, br), 1632 (m), 1591 (m), 1481 (m), 1383 (m), 1246 (w), 1109 (m), 729 (w), 698 (m), 501 (w).       |
| <b>6f</b> | <b>FT-IR peaks (cm<sup>-1</sup>):</b> 3105 (w), 2972 (w), 1774 (m), 1712 (s), 1589 (m), 1494 (w), 1384 (s), 1300 (w), 1140 (m), 1103 (w), 848 (m), 729 (m), 611 (w).           |
| <b>6g</b> | <b>FT-IR peaks (cm<sup>-1</sup>):</b> 3095 (w), 2966 (w), 1776 (m), 1710 (s), 1589 (m), 1494 (w), 1384 (s), 1300 (w), 1140 (m), 1103 (w), 1008 (w), 848 (m), 729 (m), 611 (w). |



**Figure 1.** FT-IR spectrum of PEI **6a**.

The  $^1\text{H-NMR}$  spectra of PEIs **6a** and **6d** showed peaks that confirmed their chemical structures (Figures 2 and 3). Figure 5 displays the  $^1\text{H-NMR}$  spectrum of PEI **6a**; 2 peaks of the aromatic protons related to diphenyl sulfone appeared at 7.23-7.28 and 8.02-8.04 ppm. Olefin protons H (c) in bicyclo appeared at 5.96-6.09 ppm, and the peak in the region of 4.67-4.72 ppm was assigned to the chiral center proton in the main chain of the polymer. Figure 6 displays the  $^1\text{H-NMR}$  spectrum of PEI **6d**. The aromatic protons appeared in the region of 7.33-8.18 ppm, the olefin protons H (d) in bicyclo appeared at 6.04-6.15 ppm, and the peak in the region of 4.69-4.75 ppm was assigned to the chiral center proton in the main chain of the polymer. The decaying peak related to carboxylic acid protons and hydroxyl protons in the  $^1\text{H-NMR}$  spectra confirmed the proposed structure for these polymers.

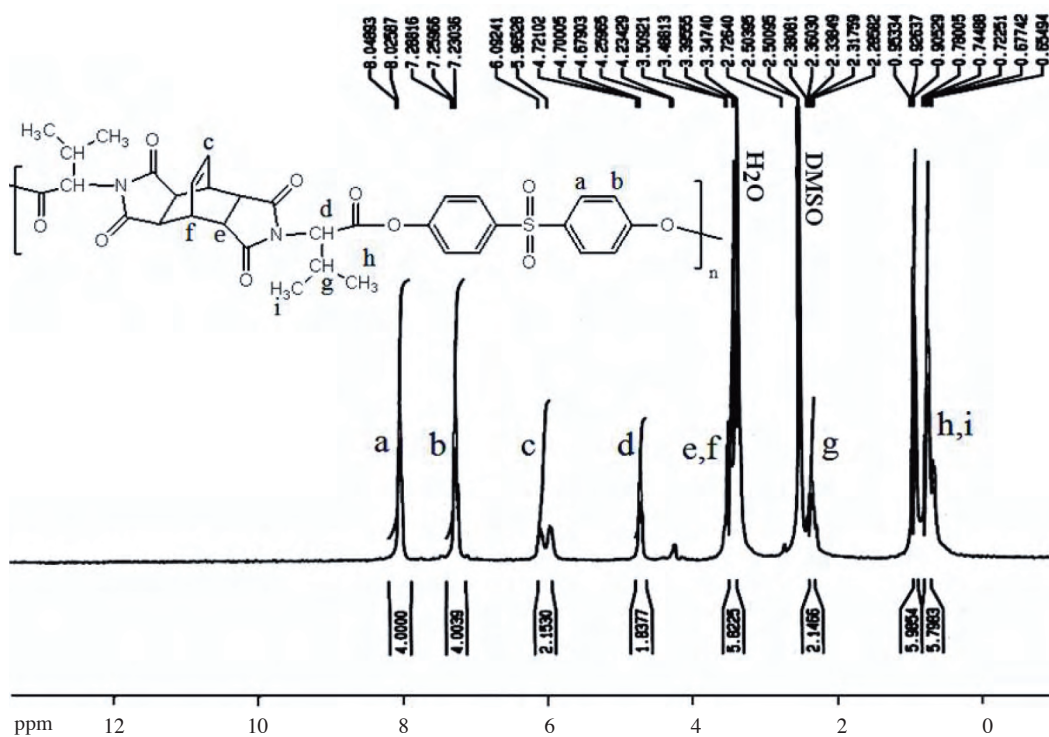


Figure 2.  $^1\text{H-NMR}$  spectrum of PEI **6a**.

## Polymer characterization

Synthesis and some physical properties of PEIs **6a-g** are summarized in Table 2. These polymers have inherent viscosities in the range of 0.36-0.62 dL g $^{-1}$ . The incorporation of the chiral unit into the polymer structure was confirmed by measuring the specific rotations based on the optically active nature of these PEIs at a concentration of 0.5 g dL $^{-1}$  in DMF at 25 °C. They may be potentially useful materials for column packing in HPLC techniques for resolution of racemic mixtures.

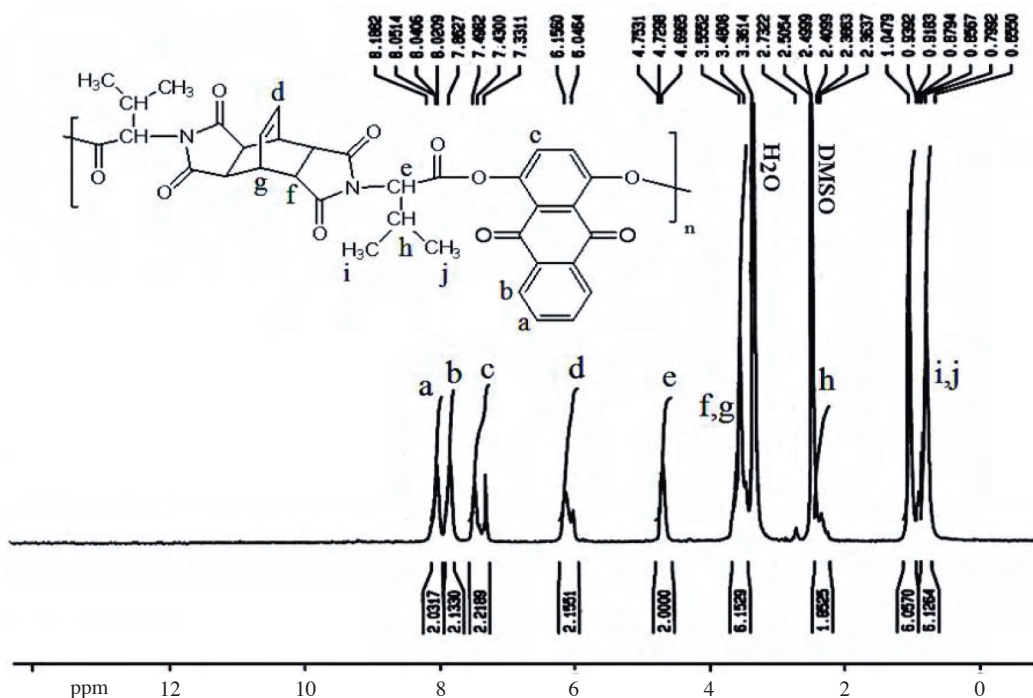

 Figure 3. <sup>1</sup>H-NMR spectrum of PEI 6d.

Table 2. Yields and some physical properties of PEIs 6a-g.

| Diol | Polymer | Yield (%) | $\eta_{inh}$ (dL g <sup>-1</sup> ) <sup>a</sup> | $[\alpha]_D^{25}$ <sup>a</sup> | Color      |
|------|---------|-----------|---|--------------------------------|------------|
| 5a   | 6a      | 93        | 0.59  | +84                            | White      |
| 5b   | 6b      | 91        | 0.62  | +91                            | White      |
| 5c   | 6c      | 73        | 0.56  | +54                            | Gray       |
| 5d   | 6d      | 91        | 0.41  | +31                            | White      |
| 5e   | 6e      | 78        | 0.39  | +28                            | Gray       |
| 5f   | 6f      | 92        | 0.47  | +76                            | White      |
| 5g   | 6g      | 89        | 0.43  | +57                            | Light Gray |

<sup>a</sup> Measured at a concentration of 0.5 g dL<sup>-1</sup> in DMF at 25 °C.

The elemental analyses of the resulting PEIs, 6a-g, were in good agreement with the calculated values for the proposed structure (Table 3).

The solubility of these polymers was tested qualitatively in various solvents at room temperature. These series of polymers were easily soluble in polar amide-type solvents, whose polarities were in the order of NMP, DMAc, DMF, and other aprotic polar solvents such as DMSO. The good solubility of these polymers might be due to the presence of the easily soluble groups of bicyclo units in diimide-diacid 4. The solubility of the poly(ester-imide)s was greatly improved by the introduction of bicyclo units into the polymer backbones (Table 4).



**Table 3.** Elemental analysis of PEIs **6a-g**.

| Polymer   | Formula  |        | C%    | H%   | N%   |
|-----------|--|--------|-------|------|------|
| <b>6a</b> | C <sub>34</sub> H <sub>32</sub> N <sub>2</sub> O <sub>10</sub> S | Calcd. | 61.68 | 4.88 | 4.24 |
|           | (660.69) <sub>n</sub>  | Found  | 61.36 | 4.83 | 4.02 |
| <b>6b</b> | C <sub>37</sub> H <sub>38</sub> N <sub>2</sub> O <sub>8</sub>    | Calcd. | 69.58 | 6.00 | 4.39 |
|           | (638.71) <sub>n</sub>  | Found  | 69.11 | 5.57 | 4.01 |
| <b>6c</b> | C <sub>32</sub> H <sub>30</sub> N <sub>2</sub> O <sub>8</sub>    | Calcd. | 67.36 | 5.30 | 4.91 |
|           | (570.59) <sub>n</sub>  | Found  | 66.78 | 5.01 | 4.70 |
| <b>6d</b> | C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>10</sub>   | Calcd. | 66.46 | 4.65 | 4.31 |
|           | (650.63) <sub>n</sub>  | Found  | 65.84 | 4.06 | 4.23 |
| <b>6e</b> | C <sub>42</sub> H <sub>36</sub> N <sub>2</sub> O <sub>10</sub>   | Calcd. | 69.22 | 4.98 | 3.84 |
|           | (728.24) <sub>n</sub>  | Found  | 67.52 | 4.70 | 3.01 |
| <b>6f</b> | C <sub>28</sub> H <sub>28</sub> N <sub>2</sub> O <sub>8</sub>    | Calcd. | 64.61 | 5.42 | 5.38 |
|           | (520.18) <sub>n</sub>  | Found  | 63.88 | 5.35 | 5.18 |
| <b>6g</b> | C <sub>28</sub> H <sub>28</sub> N <sub>2</sub> O <sub>8</sub>    | Calcd. | 64.61 | 5.42 | 5.38 |
|           | (520.18) <sub>n</sub>  | Found  | 63.38 | 5.32 | 5.06 |

**Table 4.** Solubility of PEIs **6a-g**.

| Solvent                         | <b>6a</b> | <b>6b</b> | <b>6c</b> | <b>6d</b> | <b>6e</b> | <b>6f</b> | <b>6g</b> |
|---------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| DMAc                            | +         | +         | +         | +         | +         | +         | +         |
| DMSO                            | +         | +         | +         | +         | +         | +         | +         |
| DMF                             | +         | +         | +         | +         | +         | +         | +         |
| NMP                             | +         | +         | +         | +         | +         | +         | +         |
| MeOH                            | -         | -         | -         | -         | -         | -         | -         |
| EtOH                            | -         | -         | -         | -         | -         | -         | -         |
| CHCl <sub>3</sub>               | -         | -         | -         | -         | -         | -         | -         |
| CH <sub>2</sub> Cl <sub>2</sub> | -         | -         | -         | -         | -         | -         | -         |
| H <sub>2</sub> O                | -         | -         | -         | -         | -         | -         | -         |

+: Soluble at room temperature.

-: Insoluble at room temperature.

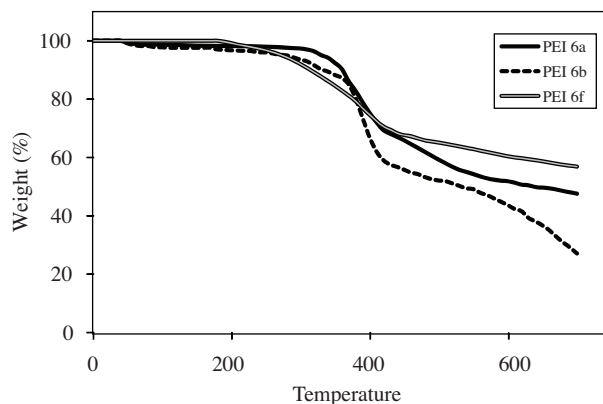
The thermal properties of PEIs **6a**, **6b**, and **6f** were investigated by TGA and DTG in a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup> as a model for prepared poly(ester-imide)s, and the thermal data are summarized in Table 5 and Figure 4. The initial decomposition temperatures for 5% and 10% weight losses (T<sub>5</sub> and T<sub>10</sub>) and the char yield at 600 °C are also summarized in Table 5. The polymers exhibited good resistance to thermal decomposition, up to 270-330 °C in nitrogen, and began to decompose gradually above those temperatures. T<sub>5</sub> for these polymers ranged from 275 to 335 °C, and T<sub>10</sub> ranged from 315 to 365 °C. The residual weights for the polymers at 600 °C were 43.69%, 51.75%, and 60.5% in nitrogen.

**Table 5.** Thermal behavior of PEIs **6a**, **6b**, and **6f**.

| Polymer   | T <sub>5</sub> (°C) <sup>a</sup> | T <sub>10</sub> (°C) <sup>b</sup> | T <sub>g</sub> (°C) | Char yield (%) <sup>c</sup> |
|-----------|----------------------------------|-----------------------------------|---------------------|-----------------------------|
| <b>6a</b> | 330-335                          | 360-365                           | 211                 | 51.75                       |
| <b>6b</b> | 270-275                          | 335-340                           | 188                 | 43.69                       |
| <b>6f</b> | 270-275                          | 310-315                           | 197                 | 60.5                        |

<sup>a,b</sup>Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub>.

<sup>c</sup>Weight percentage of material left after TGA analysis at maximum temperature 600 °C in N<sub>2</sub>.



**Figure 4.** TGA curves of PEIs **6a**, **6b**, and **6f**.

## Conclusion

A new series of PEIs, **6a-g**, containing bicyclo rings and L-valine moieties, were synthesized by the direct polycondensation reaction of diacid **4** with various aromatic diols **5a-g**. These PEIs are optically active, soluble in various organic solvents, and have good thermal stability. Optically active, thermally stable, and organosoluble properties can make these polymers attractive for practical applications such as processable high performance engineering plastics, construction of chiral media for asymmetric synthesis, chiral stationary phases for resolution of racemic mixtures by chromatographic techniques, and chiral liquid crystals in ferroelectrics and nonlinear optical devices.

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