Synthesis and Properties of Structurally Ordered Alicyclic Polyimides

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Keywords: alicyclic polyimide, structure-property relationship, structurally ordered polyimide, chiral polyimide

Main chain structurally ordered polycondensates are of interest from the viewpoint of structure-property relationship of polymers, and synthesis of such polymers have been extensively studied mainly in this decade.[1-9] The functional groups seen in the repeating unit of the structurally ordered polycondensates are amides or esters in most cases, and thioether[4,6], amine[4] and hydrazide[7-9] groups are also used. Ueda et al. have revealed that, by using an appropriately designed monomer, some of the structurally isomeric polycondensates show a distinct difference in the physical properties.[3-5]

Recently, we have reported on the synthesis of constitutionally isomeric head-to-head (HH), head-to-tail (HT) and random polyimides (PIs) using an unsymmetric alicyclic tetracarboxylic dianhydride, DAn (Figs. 1 and 2) [10]. For those PIs having \( p \)-phenylenediamine (PPD) moiety, no apparent difference was observed in physical properties. In this communication, we report a first example for the structurally isomeric PIs that show a different physical property.

We considered that the absence of the difference in the physical properties for the isomeric PI(DAn/PPD)s is due to their high rigidity. As both DAn and PPD have rigid framework, the resulting PIs are too rigid to show the difference in the physical properties which is caused by the structural isomerism. Therefore, in this study, we chose 4,4'-(oxydianiline (ODA) having an ether moiety as a flexible linkage.

We thought that a strictly ordered PI is not necessary and either an HH-rich or HT-rich PI would be sufficient in order to compare its physical properties with those for a random PI. Concerning this, we have already reported that an HH-rich poly(amide acid) (PAA) could be obtained in one pot via slow addition of the PPD solution to the DAn solution.[10]

The slow addition method for the preparation of structurally ordered polycondensates has been theoretically studied by Pino et al. [11,12]; a prerequisite is that at least one of the two bifunctional

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Received April 2, 2002
Accepted May 23, 2002
monomers show the differentiation in the reaction of the terminal functional groups. The dianhydride DAn has such a property although the reason is not yet clear; in the model reaction with aniline, the first amine attacks preferentially at an "a" position in Figure 1, and the second aniline molecule reacts predominantly at a "c" position.[13] On the basis of this background, we employed the one pot approach for the synthesis of a quasi ordered PI(DAn/ODA) (Figure 3).

The slow addition method was as follows: To a DMF (6 mL) solution of DAn (0.6721 g, 3.000 mmol) was added dropwise a half amount of a DMF (6 mL) solution of ODA (0.6010 g, 3.000 mmol) at 0°C. After 30 min, the rest of the ODA solution was added and the reaction was allowed to warm up to room temperature. The mixture was stirred for 48 h to give PAA(DAn/ODA), which was then chemically imidized at 140°C for 5 h using acetic anhydride and pyridine. The solution was poured into water to precipitate the PI(DAn/ODA). The degree of the imidization was determined to be >98% on the basis of a 1H-NMR analysis using DMSO-d6 as a solvent. Hereafter, the PAA and the PI thus obtained are called SAPAA and SAPI, respectively.

For the purpose of comparison, a random PI(DAn/ODA) was synthesized: To a solution of ODA was added DAn in one portion at room temperature to give a PAA(DAn/ODA). The PAA was then chemically imidized to give PI(DAn/ODA). The polymers obtained in this way are called OPPAA and OPPI, respectively.

1H NMR spectra of PAA and PI were compared because this analytical method was useful in the differentiation of the structure for the random and HH-rich PAA/PI in the case of the polymers prepared from DAn and PPD.[10] As shown in Figure 4, there observed a subtle difference in the shape of the peaks between the spectra of SAPAA and OPPAA, or those of SAPI and OPPI. The difference might be rationalized in relation to the order in the main chain structure, however, we could not evaluate the content of the HH-sequence from the spectra.

We tried to find a difference in 13C NMR spectra for OPPI and SAPI, however, they were quite similar to each other. For example, in the carbonyl carbon region there observed only four peaks for both PIs, and the chemical shifts of them were virtually identical to each other. This is in contrast to the fact that many of the structurally isomeric polycondensates have been successfully distinguished by means of 13C NMR spectra.[1,3-8]

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Table 1. Inherent viscosity and molecular weight of polyimidesa)

<table>
<thead>
<tr>
<th></th>
<th>[η]b)</th>
<th>M_n/10^3</th>
<th>M_w/10^3</th>
<th>M_n/M_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPPI</td>
<td>0.32</td>
<td>5.0</td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>SAPI</td>
<td>0.25</td>
<td>2.7</td>
<td>1.3</td>
<td>2.1</td>
</tr>
<tr>
<td>OPPPIc)</td>
<td>0.37</td>
<td>4.8</td>
<td>2.4</td>
<td>2.0</td>
</tr>
<tr>
<td>SAPIC)</td>
<td>0.22</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

a) Estimated by GPC based on polystyrene standards.  
   b) At 30°C in DMF at a concentration of 0.5 g dL-1.  
   c) n.m. = not measured.

Next, isolation of the intermediate in the slow addition method was attempted. The slow addition was performed in acetone using 1.0 equiv. of DAn and 0.5 equiv. of ODA. After the removal of the solvent, the residual solid was analyzed and was proved to be a 2:1 adduct of DAn and ODA by means of mass spectrum. 1H NMR (not shown) of this compound showed fairly simple pattern which might be due to a symmetric structure of the adduct. This is an indirect proof for the formation of HH-rich polymer for the slow addition method.
On the other hand, DAn is a chiral molecule. It would be of interest to examine the structure-property relationship of PIs in the viewpoint of chirality.

We prepared (-)-DAn, mp 196-197°C and \([\alpha]_D^{20} = -14.0^\circ\), via an asymmetric Diels-Alder reaction of itaconic acid derivative. By using this optically active DAn, we prepared optically active version of OPPI and SAPI with ODA. Such PIs are indicated as OPPI* and SAPI*. The synthesis of the (-)-DAn will be published elsewhere.

<table>
<thead>
<tr>
<th>Table 2. Solubility and glass transition temperature for PIs</th>
<th>Solvent(^{a,b)} \phantom{123})</th>
<th>(T_g , ^{\circ}C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>DMSO</td>
<td>DMAc</td>
</tr>
<tr>
<td>OPPI</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>SAPI</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>OPPI*</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>SAPI*</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

\(^{a)} 5 \text{ mg of the sample was dissolved to } 1 \text{ mL of the solvent. \text{++: soluble,)): partially soluble,} \\
\text{+--: swelling, --: insoluble.} \text{ b) DMSO: dimethylsulfoxide, DMAc: } N,N\text{-dimethylacetamide,} \\
\text{Py: pyridine, DIOX: 1,4-dioxane, ACTN: acetone.} \text{ c) Determined by DSC analysis at a} \\
\text{heating rate of } 20^\circ\text{C/min.} \\

The results for the synthesis of structurally isomeric PIs are shown in Table 1.

Solubility of the PIs toward various solvents was tested. As shown in Table 2, there was a difference in the solubility for 1,4-dioxane and chloroform. However, it was difficult to correlate the solubility with the polymer structure.

The difference in the glass transition temperature of the PIs was clear-cut (Table 2). There was a tendency that the \(T_g\) of SA- and OP-series are different from each other while the \(T_g\) of the PIs having racemic DAn unit was similar to that for the PIs derived from optically active DAn.

In summary, it was clarified for the first time that the structurally isomeric, amorphous alicyclic polyimides show a difference in their physical properties by using an appropriate monomer.

Acknowledgements

We are grateful to JSR corporation for the financial support of this work.

References