Hyperbranched Aromatic Polyimides from Self-Polycondensation of ABB' Monomer

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Introduction
Aromatic polyimides are well known as important high performance polymers owing to their outstanding thermal and mechanical properties. One major problem in polyimides is their poor processability caused by low solubility in organic solvents and high melting or softening temperatures. Recent developments have shown that hyperbranched polymers have better solubility than their corresponding linear analogues due to their branched structure. Besides having good solubility, hyperbranched polymers can be easily prepared from a one-step process and possess intriguing properties, such as one-step preparation and multi-functionality, which make them interesting for a number of applications. [1]

Hyperbranched polymers are typically synthesized by the polymerization of symmetric ABₙ type monomer [2]. However, there are no papers related to the synthesis of hyperbranched polymers from asymmetric ABB' monomer, which has different reactivity on the B group. We have reported the synthesis of linear semi-crystal polyimide (PI-AB) derived from AB monomer [3] and hyperbranched polyimide (PI-AB₂) derived from ABB monomer [4].

In this paper, we report the preparation of soluble hyperbranched aromatic polyimides via a polyamic acid methyl ester precursor. The precursor was prepared from the self-polycondensation of an ABB' type monomer, isomeric mixture of 4-(2,4-diaminophenoxy) diphenyl ether-3',4'-dicarboxylic acid methyl ester (I), with one phthalic acid methyl ester group and two amine groups of different reactivity.

Results and Discussion
A novel ABB' monomer, isomeric mixture of 4-(2,4-diaminophenoxy) diphenyl ether-3',4'-dicarboxylic acid methyl ester (I), was successfully prepared by six steps similar to the synthesis of AB type monomer in reference 3. From the ¹H-NMR spectrum, the ratio of the two isomers for p-, m-methyl ester substitution was 1:3.

As shown in Scheme 1, the self-polycondensation of ABB' monomer (I) was carried out in the presence of (DBOP) as a condensing agent in NMP at room temperature for 4hr to obtain the precursor PAME. The PAME had a weight-average molecular weight (Mw) of 22000 and polydispersity index (Mw/Mn) of 1.8 determined by GPC measurement with laser light scattering, UV and viscosity detectors. The inherent viscosity (ηinh) was 0.3 dL/g in NMP. The Mark-Houwink-Sakurada (η=KMⁿ) coefficient, α, calculated from TriSEC was 0.72. In general, α lies between 0.5 and 1.0 for randomly coiled linear polymers. For hyperbranched polymers, the coefficient α is less than 0.5. [1] Therefore, this suggests that PAME has more entanglement than hyperbranched polymer derived
Scheme 1. Synthesis of Polymides

from AB₂ monomer. The degree of branching (DB) of hyperbranched polymers was calculated according to Frey equation [5]. For hyperbranched polymer synthesized from ABB' monomer, there are two types of linear unit: para-amine reacted linear unit (Lₚ) and ortho-amine reacted linear unit (Lₒ).

DB=2D/(Lₚ+2D)=2D/(Lₒ+Lₚ+2D) (Frey eq)

From the ¹H-NMR spectrum, the DB of PAME calculated from the integration ratio of peaks for the characteristic amide proton (10.14 ppm for linear unit Lₚ and Lₒ, and 10.49 and 10.05 ppm for dendritic unit) is 0.07. The low DB indicates the different reactivity on B group.

The end groups of PAME were modified with acetyl chloride and benzoyl chloride. The acetylamide end-modified (PAME-a) and benzamide end-modified (PAME-b) precursors were then converted into end-modified polyimides (PI-a and PI-b) by cycloolysis in the presence of acetic anhydride and pyridine in NMP at 100°C for 24hr. Pouring the resulting solution into 0.1 wt% LiCl/CH₂OH and reprecipitating from NMP solution into 0.1 wt% LiCl/CH₂OH, we obtained the light yellow powdery products at 92-94% yield. In the IR spectra, two peaks characteristic of imide groups were clearly detected at 1721 and 1776 cm⁻¹, and the absorption assigned to amide group remained at 1679 cm⁻¹. It was concluded that treatment with acetic anhydride and pyridine can quantitatively convert the polymeric acid ester precursors (PAME-a and PAME-b) to the hyperbranched polymides possessing acetamides end group (PI-a) and benzoyl amide end group (PI-b). The properties of polyimides are summarized in Table 1. From DSC analyses, we can see that glass transition temperatures of the resulting polyimides depended on the modified end groups. The 5% thermal loss temperatures were observed at ca. 400°C for the hyperbranched polyimides (PI-AB₂, PI-a and PI-b) and 556°C for the linear polyimide (PI-AB). The result suggests that the initial degradation starts from the amide in end group. The hyperbranched polyimides exhibited good solubility compared with linear polyimide, and the solubility is dependent on the modified end groups.

In summary, we have successfully prepared hyperbranched polyimides via a polyamic acid methyl ester, which was prepared by self-polycondensation of an ABB' monomer 1. The resulting polyimides have low DB and higher Mark-Houwink-Sakurada coefficient, α, meaning that the polymers have higher entanglement. Also, the resulting polyimides exhibited good solubility and, like the hyperbranched polyimides prepared from AB₂ monomer could be modified by changing end groups.

**Table 1. Properties of Polymides**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tₛ¹/Tₛ²⁺ (°C)</th>
<th>Solubility³⁺⁺⁻⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-AB��</td>
<td>198/556</td>
<td>-</td>
</tr>
<tr>
<td>PI-AB₂戓</td>
<td>193/395</td>
<td>+</td>
</tr>
<tr>
<td>PI-a</td>
<td>201/399</td>
<td>+</td>
</tr>
<tr>
<td>PI-b</td>
<td>217/402</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ determined by DSC at a heating rate of 10°C in nitrogen on 2ndheating ² determined by TG at a heating rate of 10°C in nitrogen ³(+)soluble ⁴(-)insoluble d from ref.3 e from ref.4

**References**