Communications to the Editor

Curable Aromatic Polyimides Containing Enaminonitrile Groups

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Among thermally stable polymers, aromatic polyimides find many applications in electronics and composites, because of their high glass transition temperature (T_g), outstanding chemical stability, and mechanical properties. However, their high T_g and insoluble nature in most organic solvents make them difficult to fabricate. Generally, the processing of polyimides has been accomplished through the soluble poly(amic acid) precursor, which has some problems such as hydrolytic instability of the poly(amic acid), corrosion of copper interconnecting metal, and generation of water during the cure process. To address these problems, several approaches for soluble polyimides including introduction of a flexible linkage or bulky substituents on the main chain and use of noncoplanar or unsymmetrical monomers have been developed. However, the approaches for soluble polyimides through structural modification are often accompanied by deterioration of some physical properties.

Poly(enaminonitrile)s (PEANs) which were synthesized by J. A. Moore show hydrolytic stability, excellent thermal properties, and good solubility in organic solvents, and can be cured thermally without evolution of volatile byproducts to the insoluble polymers. Bulky enaminonitrile groups not only enhance the solubility of polymers but also increase the thermal stability, T_g and chemical resistance of polymers through curing without any volatile byproducts. Several aromatic polyamides containing enaminonitrile groups were synthesized, but unsymmetrical diamines with one enaminonitrile unit have not been reported. In this communication, we describe our successful attempt to obtain a soluble polyimide by using an unsymmetrical diamine monomer containing a curable enaminonitrile unit.

The diamine monomers containing one enaminonitrile unit were prepared from (chloro-4-nitrophenylmethylidene)propanedinitrile (1) in two steps, as shown in Scheme 1.

(Chloro-4-nitrophenylmethylidene)propanedinitrile (1) was prepared according to the previously reported procedure. The product 1 was reacted with 4-nitroaniline in a polar aprotic solvent in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as an acid acceptor to form the nitro compounds 2 and 3. Complete reduction of the dinitro compounds was found to be difficult with a palladium catalyst, presumably because of the complexation of palladium with the reactant or the product. However, the nitro compounds were hydrogenated successfully with stannous chloride/HCl to give the corresponding diamine monomers 4 and 5 with 84 and 75% yields, respectively. The above result revealed
the hydrolytic stability of the enaminonitrile group in HCl solution. The chemical structure of the monomers were confirmed by spectral analyses.

The model reaction was conducted to investigate the reactivity of the diamine monomers and to obtain a model compound as a reference material for structural analysis and curing reaction. Diamine monomer 4 was reacted with monofunctional phthalic anhydride in m-cresol in the presence of a catalytic amount of isoquinoline at 190 °C. The water generated during the imidization was removed by azeotropic distillation of chlorobenzene and water. Diimide model compound was obtained quantitatively (Scheme 2).

The structure of model compound 6 was confirmed with IR and 1H NMR analyses. FTIR spectrum of 6 shows absorption bands at 1782, 1718, 1375, and 719 cm⁻¹ corresponding to the C=O imide asymmetric and symmetric stretching, C=N imide stretching, and C=O imide bending, respectively, and at 2206 cm⁻¹ corresponding to the CN stretching. 1H NMR spectrum of 6 shows a peak at 11.01 ppm corresponding to the enaminonitrile proton (−NH−C(=C(CN))−). Also, thermal behavior of the diimide model compound was examined with DSC. DSC analysis showed two melting points at 358 and 442 °C, and irreversible exothermic transition between 360 and 400 °C, due to the curing of the enaminonitrile groups in the model compound 6. It seems that upon initial melting, the compound undergoes the exothermic curing and immediately crystallizes, resulting in a second melting. The exothermic peak was completely absent, and only the second melting point was observed when the sample was cooled and rescanned.

Polymerization of the diamine monomer 4 with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) or 4,4'-oxydiphenic anhydride (ODPA) was carried out via one-pot solution imidization method, but precipitation occurred during the imidization in both N-methylpyrrolidone (NMP) and m-cresol solvents. Polymerization of the diamine monomer 4 with ODPA in N,N-dimethylacetamide (DMAc) via chemical imidization method was also attempted, but only a low molecular weight polymer having inherent viscosity of 0.18 dL/g (DMAc, 30 °C) was obtained. However, polymerization of the diamine monomer 5 with commercially available dianhydrides, pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), hexafluorisopropylidene diphthalic anhydride (6FDA), BTDA, and ODPA via the one-pot solution imidization method in NMP proceeded homogeneously, and high molecular weight polymers were obtained in quantita-

![Scheme 2](4554CommunicationsToTheEditor.png)

![Scheme 3](4554CommunicationsToTheEditor.png)

<table>
<thead>
<tr>
<th>polymer</th>
<th>[η] ( \text{dL/g} )</th>
<th>( \text{T}_{\text{exo}} ) (°C)</th>
<th>( \text{T}_{\text{dec}} ) (°C)</th>
</tr>
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<tr>
<td>7</td>
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<td>519</td>
</tr>
<tr>
<td>9</td>
<td>0.45</td>
<td>555</td>
<td>507</td>
</tr>
<tr>
<td>10</td>
<td>0.54</td>
<td>548 (567)( ^{\text{c}} )</td>
<td>514</td>
</tr>
<tr>
<td>11</td>
<td>0.46</td>
<td>524</td>
<td>512</td>
</tr>
</tbody>
</table>

\( ^{\text{a}} \) Intrinsic viscosity in DMAc (0.5 g/dL) at 25 °C. \( ^{\text{b}} \) \( T_{\text{exo}} \) (5% weight loss temperature) was measured by TGA at a heating rate of 10 °C/min. \( ^{\text{c}} \) Measured by TGA at a heating rate of 10 °C/min in nitrogen. \( ^{\text{d}} \) Measured by DSC at a heating rate of 10 °C/min in nitrogen. \( ^{\text{e}} \) \( T_{\text{dec}} \) (5% weight loss temperature) after curing at 450 °C was measured by TGA at a heating rate of 10 °C/min.
In summary, the diamine monomers containing one enaminonitrile unit were synthesized and polymerized by the Brain Korea 21 project. Supporting Information Available: Text giving synthesis of the diamine monomer 4 and figures showing FTIR, 1H NMR, 13C NMR, and DSC curves of model compound 6 and polymer 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information Available: Text giving synthetic procedures and figures showing FTIR, 1H NMR, 13C NMR, and HRMS spectra of monomers 4 and 5 and IR and 1H NMR spectra and DSC curves of model compound 6 and polymer 9. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


