Chiral Mesophase Derived from Achiral Polymers with Banana-Shaped Mesogens and Their Model Compounds

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Abstract
In this work, we report the synthesis and characterization of benzene-ester-ether polymers that consist of banana-shaped mesogens in their backbone. Two parts of the key structure of five-ring bent-core mesogens were modified by connecting different angles of central unit (Ar), and introducing lateral substances into the outer ring (X). The synthetic details include (1) placing the diaryldiethoxymethylene unit as a flexible spacer, (2) possessing 2,3- or 2,7-naphthylene, or 1,2-phenylene connection on the central unit, and (3) introducing fluorine or chlorine substituent ($X = F$ or $Cl$) into the outer phenylene unit.

1. Introduction
Non-conventional liquid crystalline molecules with banana-shaped or bent-core mesogens have revealed unique insights into mesomorphism and its associated electro-optic properties. For instance, adaxial banana-shaped molecules could form chiral mesophases with spontaneous polarization in the layer plane [1-4]. In spite of vigorous theoretical work and many experimental efforts, the existence of biaxial nematic phases has not been proved distinctively in low molar mass thermotropic liquid crystals. While there are a considerable number of studies concerned with low molar mass banana-shaped or bent-core molecules, little attention has been given to polymeric materials containing banana-shaped or bent-core mesogenic unit in the backbone.

In 2002, we first reported the synthesis and properties of the new main-chain liquid crystalline poly(azomethines) with banana-shaped mesogen [5]. In 2004 [6] and 2004 [7], Galli and coworkers have reported the so-called banana polymers consisting of a regular alternation of a banana unit and flexible spacer in the main chain synthesized by the acyclic diene metathesis polymerization. In 2004, we first reported the main chain polymers containing banana-shaped mesogens could form B phases [8].

In this study, new poly(azomethine-esters) varying the bend-angle of a central core in the mesogen were synthesized and the effects on the liquid crystalline properties were investigated. In addition, the liquid crystalline behavior of the banana-shaped mesogen with all ester-linking group will be included and discussed in comparison with that of the poly(azomethine-esters).

2. Experimental

Synthesis. The polymers were synthesized through the synthetic route as shown in Schemes 1-4 [7]. Since the synthetic procedures used to prepare the polymers were essentially the same, one representative polymer is given in the following section.

First, 1,2-phenylene bis(4-formyl benzoyl) was prepared by reaction of catechol and 4-formyl benzoyl chloride in tetrahydrofuran with triethylamine at 0°C. Next, dodecane-1,2-bis(4-nitrophenyl), which was prepared by the nucleophilic substitution reaction of dodecane-1,2-diol (p-nitrobenzenediazonium), was used with PDCl in EtOH to dodecane-1,2-bis(p-nitrophenyl). Finally, the polymer was prepared by poly-condensation reaction between amine and dialdehyde monomers.

IR (KBr pellet, cm⁻¹): 3079 (aromatic = CH, ν), 2926, 2852 (aliphatic CH, ν), 1738 (C=O, ν), 1684 (C=N, ν), 1621, 1506 (aromatic C=C, ν). ¹H NMR (CDCl₃, δ ppm): 9.53 (H, s, N=CH), 8.51-8.74 (4H, d, ArH), 8.64-8.58 (4H, ArH), 8.10-8.02 (4H, ArH), 7.93 (1H, br s, ArH), 7.77-7.41 (7H, m, ArH), 4.40 (4H, t, OCH₂), 2.2 (4H, br s, OCH₂Ph). ¹³C NMR (CDCl₃): 1.71 (OCH₂).
Table 1. Designation of polymers containing bent-core mesogens with Ar/X

<table>
<thead>
<tr>
<th>X</th>
<th>Ar</th>
<th>(2,7)</th>
<th>(2,3)</th>
<th>(1,2)</th>
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<tbody>
<tr>
<td>H</td>
<td>5a</td>
<td>5b</td>
<td>5c</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>5d</td>
<td>5e</td>
<td>5f</td>
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<tr>
<td>Cl</td>
<td>5g</td>
<td>5h</td>
<td></td>
<td>5i</td>
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</table>

3. Results and Discussion
All polymers were only soluble in a strong acid such as H₃SO₄, CF₃CO₂H etc. The solution viscosities were measured on 0.16 g/dl solution in H₂SO₄ at 30°C, and the values are in the range of 0.59-0.79 dl/g. All of the polymers are semi-crystalline. The melting temperatures (T_m) of polymers are ranged from 188 °C to 229 °C depending on the structure (see Table 2). Polymer derived from 2,7-naphthalendiol could not show the melting transition before thermal degradation, while polymers derived from 2,3-naphthalendiol seem to form H-phase according to polarizing microscopic observation (see Figure 3). Polymer derived from 1,2-phenylenediol showed an optical texture corresponding to smectic phase, and as a shear is applied a more distinctive broken fan texture was observed (see Figure 4).

4. Conclusion
By DSC measurement and cross-polarizing microscopic observation, it was concluded that polymers with Ar/X = 1,2/H and 2,3/H form smectic phases, and polymers with Ar/X = 2,3/F and 2,3/Cl form B phases: polymer with Ar/H = 2,7/H showed thermal decomposition before melting.

5. Acknowledgements
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6. References

Table 2. Yield, thermal transition temperature, and enthalpy change

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (wt%)</th>
<th>η_{pol} (dl/g)</th>
<th>T_{m1} (°C)</th>
<th>ΔH_{m1} (J/g)</th>
<th>T_{m2} (°C)</th>
<th>ΔH_{m2} (J/g)</th>
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<tbody>
<tr>
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<td>-</td>
<td>-</td>
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<tr>
<td>5b</td>
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<tr>
<td>5d</td>
<td>89.5</td>
<td>0.79</td>
<td>-</td>
<td>156</td>
<td>15.1</td>
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</tr>
<tr>
<td>5e</td>
<td>85.6</td>
<td>0.62</td>
<td>190</td>
<td>225</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Cross-polarized optical micrographs for (a) polymer 5e with Ar/X = 2,7/H on heating: taken at (a) 150°C, (b) 200°C and (c) 250°C, and (d) after shearing at 250°C.