**Synthesis and Characterization of Isoregic Chiral Smectic Polyesters**

Feng Bai,† Liang-Chy Chien,*† Christopher Y. Li,‡ Stephen Z. D. Cheng,† and Rolfe Petschek§

Liquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, Ohio 44242, Maurice Morton Institute and Department of Polymer Science, University of Akron, Akron, Ohio 44325, and Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

Received March 17, 1999. Revised Manuscript Received May 10, 1999

We prepared a series of isoregic chiral smectic polyesters based on (R)-(−)-4′-(ω-[2-(p-hydroxy-o-nitrophenyloxy)-1-propoxy]-1-alkyloxy)-4-biphenylcarboxylic acid. The head-to-tail (p-hydroxybenzoic acid) type monomers enable us to proceed the isoregicly controlled polycondensation. All the monomers exhibited the chiral smectic C and nematic mesophases. The isoregic chiral smectic polyesters have good thermal stability and exhibit monolayered chiral smectic C and smectic A structures.

**Introduction**

There is intense interest in synthesizing liquid crystals with supramolecular structure to support the vastly growing optical thin films. Part of the stimulation for this research approach stems from the design of ferroelectric liquid crystal polymers (FLCPs) for optical thin films.1−3 However, there are only a few reported studies focusing on main-chain FLCPs.6,7 Besides the ferroelectric effect, liquid crystalline polyesters may be for optical thin-film applications, which is normally achieved by incorporating the molecular chirality and chromophore into the polymer backbone.6−13 Mesogenic polyesters provide virtually no limits in modifying the polymer chains; i.e., through the introduction of flexible chains as the side chains or between the mesogenic units, the introduction of lateral functional groups to the mesogens, or the addition of co-monomer to give co-polymers. Most of the synthesized MCLCPs systems have the mesogens randomly arranged along the polymer backbone. To maximize the dipole of a thin MCLCP film, it is necessary to apply electric field to establish a monodomain structure. The chiral smectic C mesogen can potentially exhibit ferroelectric properties with a monodomain structure.

In this paper, we report the synthesis and characterization of isoregic chiral smectic polyesters. The molecular design consists of an isoregicly arranged chiral center and a laterally attached dipolar group along the polymer backbone. A graphic illustration of this isoregic polymer structure is given as follows:

**Experimental Section**

**Materials.** Ethyl (S)-(−)-lactate ([α]D24 = −8.70°), 3,4-dihydro-2H-pyran, 4-hydroxy-4-biphenylcarboxylic acid, 4-hydroxy-3-nitroacetophenone, sodium iodide, m-chloroperbenzoic acid (mCPBA), diethyl azodicarboxylate (DEAD), triphenylphosphine, Amberlyst 15 ion-exchange resin, dibromoalkanes, 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyrididine (DMAP), p-toluenesulfonic acid (PTSA), anhydrous tetrahydrofuran (THF), absolute ethanol, anhydrous aceton, and dichloromethane were all purchased from Aldrich Chemical Company and were used as received. Sodium hydride was washed with hexane prior to use. Pyridine and acetonitrile were distilled and stored with 4 Å molecular sieves. Marlo-Martin and Block, A. Ind. Org. Ltd., New York, 1981.}

*Author for correspondence (lchien@corporo.kent.edu).
† Kent State University.
‡ University of Akron.
§ Case Western Reserve University.

therm-S was a gift from Higher Chemical Co. and was dried with sodium metal.

**Techniques.** The melting points of intermediates were determined on a Thomas-Hoover capillary melting apparatus and were uncorrected. Proton nuclear magnetic resonance (1H NMR) spectra were collected with a Varian NMR (200 MHz) using TMS as the internal standard. Infrared (IR) spectra were obtained using a Nicolet 550 Magma FT-IR spectrometer. The values of optical rotation were measured using an AA-10 Automatic Polarimeter. Elemental analyses were performed by Oneida Research Inc., Whitesboro, NY. Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC-7 equipped with a TAC-7 analyzer. Thermogravimetric analyses (TGA) were performed on a TA 2950 Thermogravimetric Analyzer. The optical textures of both monomers and polymers were studied using a Leitz Laborlux S polarizing microscope equipped with a Mettler FP52 hot stage and a Wild Leitz MP52 camera. Wide and small angle X-ray diffraction experiments were conducted using a Rigaku 12 kW rotating-anode generator coupled with a diffractometer.

**Synthesis of Monomer.** Ethyl (S)-(−)−4′-[2-(2-Hydroxy-1-propionyl)-1-octyloxy]-4-biphenylcarboxylate (13c). To a round-bottomed flask 10c (4.00 g, 7.85 mmol) were added Amberlyst 15 (0.40 g), and molecular sieve-dried methanol (40 mL). After the mixture was stirred at 0 °C for 1 h, it was allowed to warm to room temperature and stirred for additional 4 h. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The light yellow precipitate that formed was collected by filtration. The precipitate was dissolved in CH2Cl2, washed twice with water, and then dried over sodium sulfate. The crude product was recrystallized from CH2Cl2 and hexane to obtain 13c (0.25 g, 91% yield). Spectral data: IR (KBr, cm−1): 3432, 1683, 1611, 1505, 1538, and 1189; 1H NMR (acetonitrile-4d6) δ 1.26−1.19 (15H, CH3−CH2−), 0.20−0.18 (15H, CH3−CH2−), 7.07 (7H, ArH, meta to −OH and para to −NO2), 7.67 (2H, J = 8.8 Hz, ArH, meta to −OR), 7.78 (2H, J = 8.6 Hz, ArH meta to COOH), and 8.11 ppm (2H, J = 8.0 Hz, ArH, ortho to −COOH); 13C NMR (CDCl3) δ 16.34, 30.36, 65.09, 71.19, 74.57, 74.77, 74.87, 75.64, 76.64, 77.64, 111.39, 115.78, 120.46, 126.30, 128.23, 128.43, 129.97, 132.09, 142.97, 145.08, 149.57, 159.31, 166.54, and 169.02 ppm. To a solution of 14c (2.84 g, 4.67 mmol) in 60 mL of ethanol was added K2CO3 (2.81 g, 0.11 mol) in 15 mL of water. The mixture was stirred at room temperature for 24 h and then acidified with 10% aqueous hydrochloric acid. The yellow precipitate that formed was collected by filtration. The precipitate was dissolved in CH2Cl2, washed twice with water, and then dried over sodium sulfate. The crude product was purified by column chromatography on silica gel using CH2Cl2 and acetone as the gradient eluents to yield 2.34 g (93.2%) of yellow solid: 1H NMR (acetone-d6) δ 1.26−1.19 (15H, CH3−CH2−), 0.20−0.18 (15H, CH3−CH2−), 7.33−7.36 (10H, CH3−CH2−), 7.07−7.10 (7H, ArH, meta to −OH and para to −NO2), 7.67 (2H, J = 8.8 Hz, ArH, meta to −OR), 7.78 (2H, J = 8.6 Hz, ArH meta to COOH), and 8.11 ppm (2H, J = 8.0 Hz, ArH, ortho to −COOH); 13C NMR (CDCl3) δ 16.34, 30.36, 65.09, 71.19, 74.57, 74.77, 74.87, 75.64, 77.64, 111.39, 115.78, 120.46, 126.30, 128.23, 128.43, 129.97, 132.09, 142.97, 145.08, 149.57, 159.31, 166.54, and 169.02 ppm. Elemental Analysis: Calculated for C30H35O8N: C, 67.02; H, 6.56; N, 2.61. Found: C, 66.90; H, 6.47; N, 2.56.}


(16) Borgini, A.; Cardillo, G.; Orena, M.; Sandri, S. Synthesis 1979, 618.

(17) For a review, see: Mitsunobu, O. Synthesis 1981, 1.

followed by a high vacuum (1–2 mmHg) for 1 h. The solution was allowed to cool to room temperature, diluted with methylene chloride, and then precipitated in hexane. The solid obtained upon centrifugation was dissolved in THF and precipitated in a mixture of hexane/acetone (9:1, v/v) three times. The obtained polymer was dried at 70 °C (25 mmHg) for 3 days. Polymers 1c and 1e were prepared by the same method.

Method B (1b). To a flame dried, two-necked, round-bottom flask equipped with a magnetic stirring bar were introduced monomer 15b (2.10 g, 4.00 mmol), DPTS (1.25 g, 4.00 mmol), dried dichloromethane (40 mL), and distilled pyridine (1 mL) under nitrogen. After the mixture was stirred about 10 min at room temperature, 1,3-dicyclohexylcarbodiimide (1.65 g, 8.00 mmol) dissolved in 10 mL of dried dichloromethane was then added through syringe. The resultant mixture was stirred at room temperature overnight and then poured into 400 mL of methanol. The precipitate that formed was collected by filtration, washed with THF, and then dried at 65 °C (25 mmHg) for 4 days. Polymer 1d was prepared in a similar way.

Results and Discussion

Synthesis of Monomers 15a–e. All monomers were synthesized following the synthetic route outlined in Scheme 1. Starting from commercially available ethyl-(S)–(−) lactate, intermediates 3 and 4 were obtained according to the literature. Intermediate 6 was afforded quantitatively by carrying out the Finklstein reaction on dibromoalkanes 5. Subsequently, the intermediate 7 was prepared from alkylation of intermediate 4 with alkyl halides 6. The alkylation of 9 and 7 in the presence of excess potassium carbonate in anhydrous acetone yielded intermediate 10. Deprotection of 10 was easily accomplished in methanol using the macromolecular resin Amberlyst 15 as a catalyst. The functional group transformation, by means of Baeyer–Villiger oxidation with starting material 11, resulted exclusively in the desired ester 12 as yellow needles. Monomer precursors 14 were readily obtained by coupling intermediates 12 and 13 using the Mitsunobu reaction. The targeted monomers 15a–e were obtained by hydrolyzing the corresponding precursor 14a–e with an alkaline solution and followed by an acidification.

Synthesis and Properties of Polymers 1a–e. Polymerization of p-hydroxybenzoic acid to yield high molecular weight polymers directly from hydroxy acid monomers has been a subject of study for over 100 years.
years. A series of studies by Higashi et al. showed that direct polymerization of hydroxy acid monomers is possible under mild conditions by using diphenylchlorophosphonic acid derivatives as a condensing agent. The results indicated that this method was quite successful for small monomers. After several trials, we were unable to succeed in accomplishing the polymerization, probably because of the size of our monomers. It was reported by Economy et al. that p-hydroxy acid polymer can be prepared from its hydroxy or carboxylic acid derivatives directly, but harsh reaction conditions have to be used, such as a high temperature (about 300–350 °C). The use of good heat transfer fluid such as Marlotherm-S, a commercial aromatic solvent, however, can significantly reduce the temperature. By using this heat transfer fluid and surface-treated magnesium, we were able to successfully polymerize monomers in solution (method A, Scheme 2). The polycondensation was monitored by constantly checking the FT-IR spectrum of the shift of the carbonyl group absorption peak from 1690 to 1734 cm$^{-1}$, corresponding to benzoic acid and benzoate, respectively. The polymers obtained by method A polycondensation. Polymers 1b and 1d were obtained as pale yellow solids using method B.

The physical properties such as molecular weights, intrinsic viscosities, elemental analyses, and thermal analyses of polymers are summarized in Table 1. Polymers 1b and 1d have much higher molecular weights than those of polymers 1a, 1c, and 1e. The molecular weight of polymer 1b is so high, exhibiting low solubility in common organic solvents such as tetrahydrofuran, N,N-dimethylacetamide, and N-methylpyrrolidinone. The good thermal stability of polymers is a key to their applications as NLO materials (Table 1). The thermal stability for polymers is similar regardless the difference in spacer length and functional groups and linkages.

**Table 1. Physical Properties of Polymers 1a–e**

<table>
<thead>
<tr>
<th>polymer</th>
<th>n</th>
<th>M$_n$</th>
<th>DP</th>
<th>$\eta$ (g$^{-1}$dL$^{-1}$)</th>
<th>MWD</th>
<th>$T_{5%}$ (°C)</th>
<th>yield (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a$^b$</td>
<td>6</td>
<td>9900</td>
<td>18</td>
<td>24.5</td>
<td>1.9</td>
<td>322</td>
<td>55.3</td>
<td>68.40</td>
<td>68.70</td>
<td>5.95</td>
</tr>
<tr>
<td>1b$^c$</td>
<td>7</td>
<td>3100</td>
<td>15</td>
<td>15.1</td>
<td>1.5</td>
<td>313</td>
<td>55.4</td>
<td>69.78</td>
<td>69.28</td>
<td>6.61</td>
</tr>
<tr>
<td>1c$^d$</td>
<td>9</td>
<td>16000</td>
<td>5</td>
<td>12</td>
<td>1.7</td>
<td>313</td>
<td>40.0</td>
<td>70.18</td>
<td>69.39</td>
<td>6.81</td>
</tr>
<tr>
<td>1d$^e$</td>
<td>7</td>
<td>9000</td>
<td>12</td>
<td>16.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

M$_n$: number average molecular weight determined by GPC in THF relative to polystyrene standards. DP: degree of polymerization. $\eta$: viscosity (25°C in THF). MWD: molecular weight distribution. $T_{5\%}$: temperature obtained at which 5% weight loss with a heating rate 10°C/min under nitrogen. Polymers obtained by method A polycondensation. Polymers obtained by method B polycondensation.

**Mesomorphic Behavior of Monomers and Polymers.** The liquid-crystalline behavior of monomers 15a–e, investigated by DSC and polarizing optical microscopy, is summarized in Table 2. All the monomers exhibit chiral smectic C (S$_C^{\ast}$) and nematic phases with Schlieren optical texture when viewed the samples through crossed polarized light. Figure 1 shows the textures S$_C^{\ast}$ and chiral nematic (N$^\ast$) phases of monomer 1e.
The formation of pitch bands or dechiralization lines were not observed in the defect texture because the high viscosity of oligomer (formed by means of hydrogen bonding) stabilizes the nematic defects. This phenomenon is identified by the defects with strength larger than 1, e.g., $S_2$, $S_3$, or higher from the photomicrograph, which is normally observed in nematic high-molecular-mass liquid crystals. The nematic to isotropic transition temperatures for monomers 15b and 15d are higher than monomers 15c and 15e, because the monomers with odd number of methylene spacer have higher molecular anisotropy. $^{24-28}$

The mesomorphic properties of polymers 1a–e are summarized in Table 3. The mesophase was determined from polymer samples sandwiched between two glass plates and separated by 10 $\mu$m glass spacers. The liquid crystalline behavior of these isoregic chiral polyesters is similar, which they exhibit a glass transition, $S_*$, and smectic $S_{A*}$ phases. However, the transition temperatures are in a size regime where there is strong glass transition, taken from the halfway between the extrapolated tangent to the baselines above and below the glass transition region. $S_{C*}$: chiral smectic C phase. $S_{A*}$: chiral smectic A phase.

**Table 2. Phase Transition Temperatures of Monomers 15a–e**

<table>
<thead>
<tr>
<th>monomer</th>
<th>n</th>
<th>transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15a</td>
<td>6</td>
<td>K 127.2 $S_{C*}$ 171.6 N* 178.8 I</td>
</tr>
<tr>
<td>15b</td>
<td>7</td>
<td>K 128.0 $S_{C*}$ 179.8 N* 187.2 I</td>
</tr>
<tr>
<td>15c</td>
<td>8</td>
<td>K 130.8 $S_{C*}$ 181.1 N* 185.7 I</td>
</tr>
<tr>
<td>15d</td>
<td>9</td>
<td>K 136.0 $S_{C*}$ 178.5 N* 189.0 I</td>
</tr>
<tr>
<td>15e</td>
<td>10</td>
<td>K 142.0 $S_{C*}$ 185.4 N* 187.9 I</td>
</tr>
</tbody>
</table>


**Table 3. Phase Transition Temperatures of Polyesters 1a–e**

<table>
<thead>
<tr>
<th>polymer</th>
<th>n</th>
<th>transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>6</td>
<td>g 45.1 $S_{C*}$ 102.0 $S_{A*}$ 140.5 I</td>
</tr>
<tr>
<td>1b</td>
<td>7</td>
<td>g 49.2 $S_{C*}$ 134.5 $S_{A*}$ 173.2 I</td>
</tr>
<tr>
<td>1c</td>
<td>8</td>
<td>g 50.9 $S_{C*}$ 123.7 $S_{A*}$ 159.0 I</td>
</tr>
<tr>
<td>1d</td>
<td>9</td>
<td>g 39.4 $S_{C*}$ 140.6 $S_{A*}$ 182.9 I</td>
</tr>
<tr>
<td>1e</td>
<td>10</td>
<td>g 37.0 $S_{C*}$ 101.3 $S_{A*}$ 147.0 I</td>
</tr>
</tbody>
</table>

$^a$ g: glass transition, taken from the halfway between the extrapolated tangent to the baselines above and below the glass transition region. $S_{C*}$: chiral smectic C phase. $S_{A*}$: chiral smectic A phase.

**Figure 1.** Photomicrographs (200×) of monomers 15d: (a) the Schliren texture of $S_{C*}$ phase at 166 °C and (b) the Schliren texture of nematic phase at 188 °C.

**Figure 2.** Photomicrographs (200×) of polymers 1d, obtained from cooling the isotropic melt into (a) the focal conic fan texture of $S_{A*}$ phase at 166 °C and (b) the broken fan texture of $S_{C*}$ phase at 100 °C.
molecular weight dependence. Cooling polymer 1d from the isotropic melt, a focal conic fan texture of $S_{A^*}$ phase was observed at 166 °C (200×, as shown in Figure 2a). When the sample was further cooled, a broken fan texture was observed at 100 °C indicating a $S_{C^*}$ phase (Figure 2b). It is worth noting that the birefringence change results from a distribution of polymer molecule alignment from homeotropic to planar. Figure 3 shows the DSC heating and cooling traces of polymer 1d, scanned at a rate of 20 °C/min. The smectic structures of polyesters 1a–e were further confirmed with wide-angle X-ray diffraction (WAXD) studies. The WAXD patterns of polymer 1d, measured at a cooling rate of 20 °C/min from cooling, are shown in Figure 4. The layer spacings for $S_{A^*}$ and $S_{C^*}$ structures are 29.6 and 29.1 Å, respectively. Molecular modeling of polymer 1d (performed on a commercial software) shows the length of a fully extended individual repeat unit is 29.5 Å, indicating that the isoregic smectic polyesters 1a–e have a monolayered two-dimensional structure.

**Conclusions**

We synthesized a series of new liquid-crystalline polyesters having the chiral centers and dipolar groups isoregically arranged along the polymer backbones. The head-to-tail (p-hydroxybenzoic acid) type monomers enable us to proceed the isoregically controlled polycondensation. Compared to that of magnesium catalyst method, the DPTS-catalyzed polymerization method presents a better means to obtain higher molecular weight polyesters. All the monomers exhibit the $S_{C^*}$ and nematic phases, while the isoregic chiral polyesters show a monolayered $S_{C^*}$ and $S_{A^*}$ phases.

**Acknowledgment.** This research was supported in part by the NSF ALCOM Center Grant DMR 89-20147. CM990159E