Synthesis and Characterization of Isoregic Chiral Smectic Polyesters

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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 isoregically 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 supermolecular 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.[1−7] 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 chomophore into the polymer backbones.[6−13]

Mesogenic polyesters provide virtually no limits in modifying the polymer chains; i.e., through the intro- duction 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 backbones. 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 isoregical chiral smectic polyesters. The molecular design consists of an isoregically arranged chiral center and a laterally attached dipolar group along the polymer backbone. A graphic illustration of this isoregical polymer structure is given as follow:
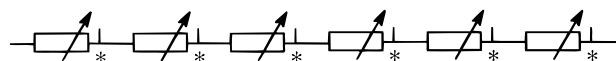
Experimental Section

Materials. Ethyl $(S)-(-)$-lactate ($[\alpha]_D^{24} = -8.70°$), 3,4-dihydro-2*H*-pyran, 4′-hydroxyl-4-biphenylcarboxylic acid, 4-hydroxyl-3-nitroacetophenone, sodium iodide, *m*-chloroperbenzoic acid (*m*CPBA), diethyl azodicarboxylate (DEAD), triphenylphosphine, Amberlyst 15 ion-exchange resin, dibromoalkanes, 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), *p*-toluenesulfonic acid (PTSA), anhydrous tetrahydrofuran (THF), absolute ethanol, anhydrous acetone, 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-

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therm-S was a gift from Huge 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 (^{1}H 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 Magna FT-IR spectrophotometer. The values of optical rotation were measured using an AA-10 Automatic Polarimeter. Elemental analyses were performed by Oneida Research Inc., Whitesboro, NY. Differential scaning 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′-[ω-(2-Hydroxyl-1-propyloxy)-1-octyloxy]-4-biphenylcarboxylate (13c).*[16] To a round-bottomed flask **10c** (4.00 g, 7.80 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 condensed under reduced pressure to afford 3.10 g (92.5%) of white solid: mp = 99−101 °C; TLC (petroleum/EtOAc, 4/1) R_f = 0.12; [α]$_D^{21}$ = +5.47° (*c* = 1.92, CHCl$_3$); IR (Nujol) 3426, 1720, 1608, and 1118 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.16 (d, 3H, *J* = 6.4 Hz, *CH$_3$*−C*H*−), 1.36−1.90 (m, 15H, −O−CH$_2$−*CH$_3$*, −O−CH$_2$−(*CH$_2$*)$_6$−CH$_2$−O−Ph−), 2.17 (s, 1H, −OH), 3.20 (m, 1H, one of −C*−CH$_2$−O−), 3.45 (m, 3H, one of −C*−CH$_2$−O−, −O−*CH$_2$*−(CH$_2$)$_6$−CH$_2$−O−Ph−), 4.00 (m, 3H, CH$_3$−*C*H*−, −O−CH$_2$−(CH$_2$)$_6$−*CH$_2$*−O−Ph−), 4.40 (q, 2H, *J* = 7.2 Hz, −O−*CH$_2$*−CH$_3$), 7.00 (d, 2H, *J* = 8.8 Hz, ArH, ortho to −OR), 7.58 (d, 2H, *J* = 8.8 Hz, ArH, meta to −OR), 7.64 (d, 2H, *J* = 8.6 Hz, ArH, meta to −COOC$_2$H$_5$), and 8.10 (d, 2H, *J* = 8.6 Hz, ArH, ortho to −COOC$_2$H$_5$); ^{13}C NMR (CDCl$_3$) δ 14.35, 18.55, 25.98, 26.04, 29.21, 29.31, 29.36, 29.61, 60.88, 66.40, 68.05, 71.40, 76.25, 76.24, 114.87, 126.35, 128.28, 128.49, 130.02, 132.19, 145.13, 159.34, and 166.58 ppm.

Ethyl (R)−(−)-4′-{ω-[2-(p-Acetoxy-o-nitrophenyloxy)-1-propyloxy]-1-octyloxy}-4-biphenylcarboxylate (14c).[17] To an ice bath cooled, 100 mL, round-bottomed flask were placed **12** (1.64 g, 8.30 mmol), **13c** (2.97 g, 6.92 mmol), triphenylphosphine (PPh$_3$) (2.54 g, 9.69 mmol), and anhydrous THF (60 mL). After the mixture was stirred for 10 min, diethyl azodicarboxylate (DEAD) (1.69 g, 9.69 mmol) in 10 mL of anhydrous THF was then added in a dropwise fashion. The reaction mixture was continuously stirred at 0 °C for 1 h, and then stirred at room temperature for additional 4 h. Removal of the solvent on a rotavap gave a solid residue. The crude was purified by column chromatography on silica gel using CH$_2$Cl$_2$ first and then EtOAc/CH$_2$Cl$_2$ (5:95, v/v) as the eluents to yield 2.94 g (70%) of yellow solid: mp = 49−51 °C; [α]$_D^{22}$ = −15.2°(*c* = 1.58, CHCl$_3$); TLC (CH$_2$Cl$_2$) R_f = 0.20; IR (Nujol) 1780, 1722, 1613, 1504, 1537, 1376, and 1200 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.32−1.90 (m, 18H, −O−CH$_2$−*CH$_3$*, *CH$_3$*−C*H*−, −O−CH$_2$−(*CH$_2$*)$_6$−CH$_2$−O−Ph−), 2.30 (s, 3H, CH$_3$−COO−), 3.40−3.70 (m, 4H, −C*−*CH$_2$*O−, −O−*CH$_2$*−(CH$_2$)$_6$−CH$_2$−O−Ph−), 4.00 (t, 2H, *J* = 6.4 Hz, −O−CH$_2$−(CH$_2$)$_6$−*CH$_2$*−O−Ph−), 4.40 (q, 2H, *J* = 7.2 Hz, −O−*CH$_2$*−CH$_3$), 4.60 (m, 1H, CH$_3$−*C*H*−), 7.00 (d, 2H, *J* = 9.0 Hz, ArH, ortho to −OR), 7.20 (m, 2H, ArH, meta to CH$_3$−COO− and para to −NO$_2$), 7.60 (m, 5H, ArH, ortho to −NO$_2$, meta to −OR and meta to −COOC$_2$-

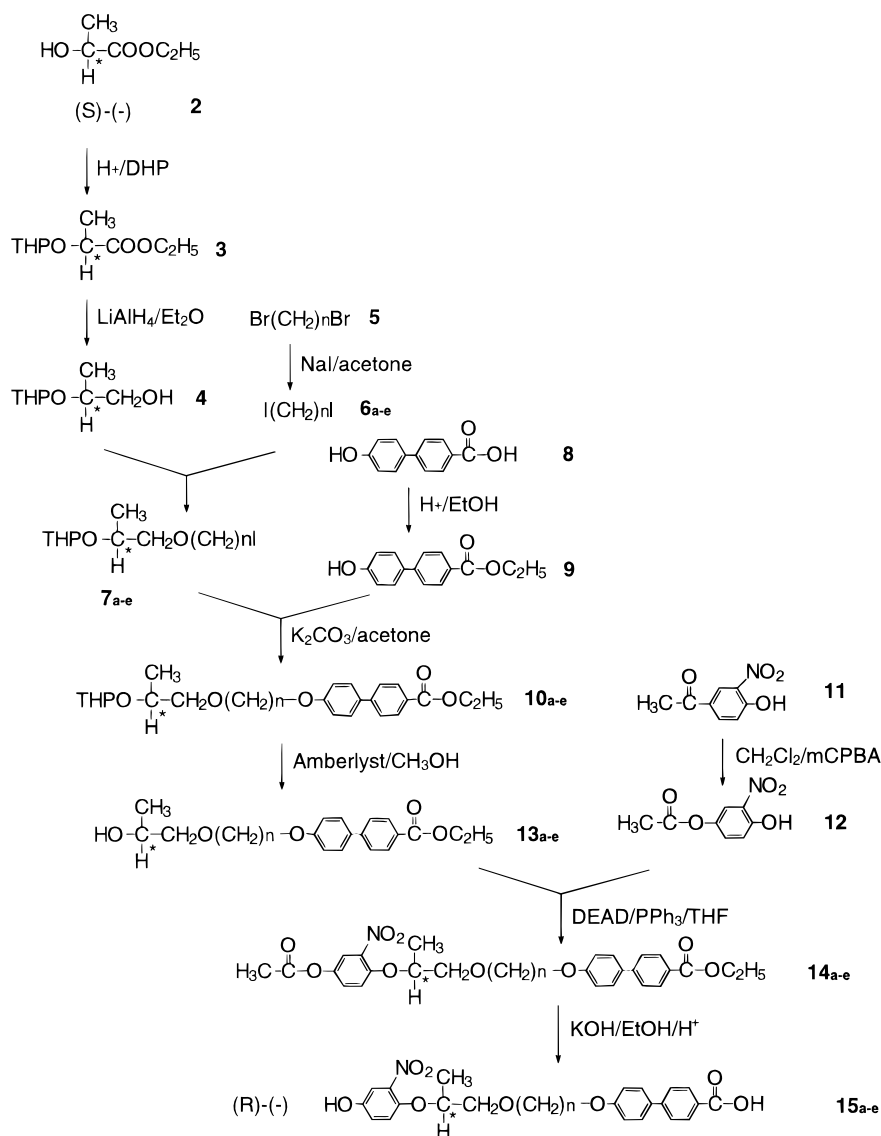(14) Ghirerdelli, K. *J. Am. Chem. Soc.* **1987**, *95*, 4987.

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H$_5$), and 8.10 ppm (d, 2H, *J* = 8.4 Hz, ArH, ortho to −COOC$_2$H$_5$); ^{13}C NMR (CDCl$_3$) δ 14.30, 17.00, 20.84, 25.89, 29.14, 29.24, 29.50, 60.82, 68.02, 71.74, 73.98, 76.99, 112.23, 114.83, 117.70, 118.66, 126.30, 128.23, 128.43, 129.97, 132.09, 142.97, 145.08, 149.57, 159.31, 166.54, and 169.02 ppm.

(R)−(−)-4′-{ω-[2-(p-Hydroxy-o-nitrophenyloxy)-1-propyloxy]-1-octyloxy}-4-biphenylcarboxylic Acid (15c). To a solution of **14c** (2.84 g, 4.67 mmol) in 60 mL of ethanol was added KOH (2.81 g, 70.1 mmol) in 15 mL of water. The mixture was stirred at room temperature for 24 h and then acidified with 10% aqueous hydrocloric acid. The yellow precipitate that formed was collected by filtration. The precipitate was dissolved in CH$_2$Cl$_2$, washed twice with water, and then dried over sodium sulfate. The crude was purified by column chromatography on silica gel using CH$_2$Cl$_2$ and acetone as the gradient eluents to yield 2.34 g (93.2%) of yellow solid: [α]$_D^{21}$ = −25.7° (*c* = 1.60, DMSO); TLC (EtOAc/hexane, 2:1) R_f = 0.21; IR (NaCl) 3421, 1678, 1611, 1503, 1537, 1336, and 1194 cm^{-1}; ^{1}H NMR (acetone-*d$_6$*) δ 1.26−1.90 (m, 15H, *CH$_3$*−C*H*−, −O−CH$_2$−(*CH$_2$*)$_6$−CH$_2$−O−Ph−), 3.40−3.60 (m, 4H, −C*−*CH$_2$*O−, −O−*CH$_2$*−(CH$_2$)$_6$−CH$_2$−O−Ph−), 4.06 (t, 2H, *J* = 6.4 Hz, −O−CH$_2$−(CH$_2$)$_6$−*CH$_2$*−O−Ph−), 4.60 (m, 1H, CH$_3$−*C*H*−), 7.07 (m, 3H, ArH, ortho to −OR, ortho to −NO$_2$), 7.25 (m, 2H, ArH, meta to −OH and para to −NO$_2$), 7.66 (d, 2H, *J* = 8.8 Hz, ArH, meta to −OR), 7.78 (d, 2H, *J* = 8.6 Hz, ArH meta to COOH), and 8.11 ppm (d, 2H, *J* = 8.0 Hz, ArH, ortho to −COOH); ^{13}C NMR (CDCl$_3$) δ 17.34, 26.66, 26.74, 29.93, 30.02, 30.36, 68.62, 71.89, 74.56, 74.66, 77.64, 111.39, 115.78, 120.46, 121.42, 127.05, 129.03, 129.47, 131.02, 132.61, 145.82, 151.93, 160.46, and 167.52 ppm. Elemental Analysis: Calcd for C$_{30}$H$_{35}$O$_8$N: C, 67.02; H, 6.56; N, 2.61. Found: C, 66.90; H, 6.47; N, 2.56.

(R)−(−)-4′-{ω-[2-(p-Acetoxy-o-nitrophenyloxy)-1-propyloxy]-1-octyloxy}-4-biphenylcarboxylic acid (16c). To a 50 mL, round-bottom flask fitted with a magnetic stirring bar and a condenser were placed zinc chloride (0.60 g, 4.1 mmol), acetic anhydride (16.10 g, 147.1 mmol), and **15c** (2.00 g, 3.71 mmol). The mixture was then heated at 50 °C overnight. After the mixture was allowed to cool to room temperature, it was poured into vigorously stirred ice water (~100 mL), extracted with methylene chloride, and then dried over sodium sulfate. Removal of solvent under reduced pressure yielded a residue as pale yellow solid. The residue was purified by column chromatography on silica gel using a gradient eluent from CH$_2$-Cl$_2$ to CH$_2$Cl$_2$/EtOAc (70/30, v/v) to afford 1.48 g (66%) of light yellow solid: mp = 177 °C; [α]$_D^{21}$ = −15.8° (*c* = 0.42, CHCl$_3$); TLC (EtOAC/hexane, 2:1) R_f = 0.08; IR (NaCl) 3400, 1765, 1683, 1611, 1505, 1538, and 1189 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.20−1.90 (m, 15H, *CH$_3$*−C*H*−, −O−CH$_2$−(*CH$_2$*)$_6$−CH$_2$−O−Ph−), 2.30 (s, 3H, CH$_3$−COO−), 3.46−3.70 (m, 4H, −C*−*CH$_2$*O−, −O−*CH$_2$*−(CH$_2$)$_6$−CH$_2$−O−Ph−), 4.00 (t, 2H, *J* = 6.4 Hz, −O−CH$_2$−(CH$_2$)$_6$−*CH$_2$*−O−Ph−), 4.60(m, 1H, CH$_3$−*C*H*−), 6.98 (d, 2H, *J* = 8.8 Hz, ArH, ortho to −OR), 7.20−7.32 (m, 2H, ArH, meta and para to −NO$_2$), 7.53−7.70 (dm, 5H, *J* = 8.6 Hz, ArH, ortho to −NO$_2$, meta to −OR, and meta to −COOH), and 8.18 ppm (d, 2H, *J* = 8.6 Hz, ArH, ortho to −COOH); ^{13}C NMR (CDCl$_3$) δ 16.97, 20.88, 25.79, 29.02, 29.13, 29.47, 67.95, 71.67, 74.04, 77.00, 114.92, 117.69, 118.72, 126.47, 127.06, 127.28, 128.34, 130.72, 131.93, 143.00, 146.06, 149.57, 159.48, 169.12, and 171.84. Elemental Analysis: Calcd for C$_{32}$H$_{37}$O$_9$N: C, 66.30; H, 6.44; N, 2.42. Found: C, 66.42; H, 6.33; N, 2.26.

4-(Dimethylamino)pyridinum 4-Toluenesulfonate (DPTS). This catalysis was prepared according to literature:[18] yield 3.10 g (94.5%); mp = 165−167 °C (reported 165 °C).

Synthesis of Polymers. *Method A (1a).* To a flame-dried polymerization tube was added monomer **16a** (0.15 g, 0.27 mmol), 1.5 mL of Marlotherm-S, a small piece of 10% hydrochloric acid-washed magnesium metal, and a magnetic bar. After the solution was heated and kept at 180 °C for 20 h under nitrogen, a low vacuum (~60 mmHg) was applied for 2 h

(18) Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65.

Scheme 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 dicloromethane 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.[14,15] Intermediate **6** was afforded quantitatively by carrying out the Finklstein reaction on dibromoalkanes **5**.[16] 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.[16] 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** was readily obtained by coupling intermediates **12** and **13** using the Mitsunobu reaction.[17] 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
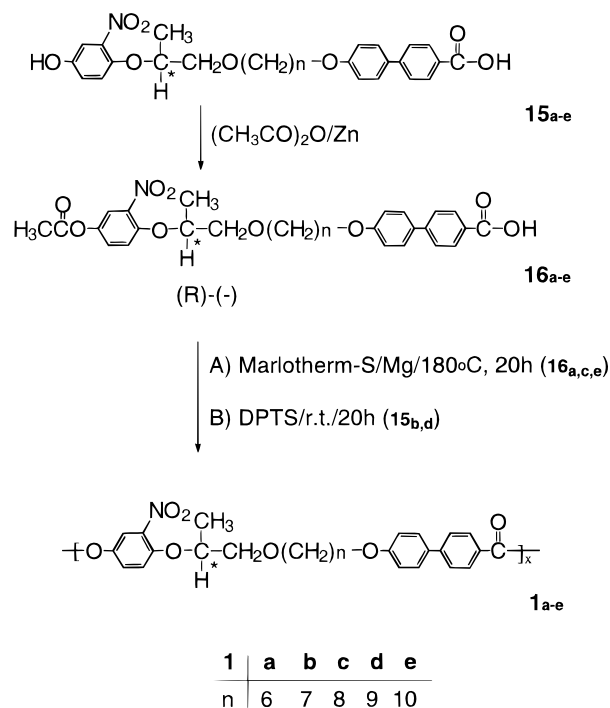
Table 1. Physical Properties of Polyesters 1a−e[a]

polymer	n	M_n	DP	η (g^{-1}dl)	MWD	T_{d_5} (°C)	yield (%)	C (%) calcd	C (%) exp	H (%) calcd	H (%) exp.	N (%) calcd	N (%) exp.
1a[b]	6	9900	18	24.5	1.9	322	55.3	68.40	68.70	5.95	6.38	2.85	2.37
1b[c]	7	−	>30	−	−	325	69.0	68.90	68.76	6.18	6.25	2.77	2.76
1c[b]	8	3100	5	15.1	1.5	313	45.0	69.35	69.16	6.40	6.03	2.70	2.76
1d[c]	9	16000	30	−	1.5	325	55.4	69.78	69.28	6.61	6.63	2.62	2.63
1e[b]	10	7000	12	16.9	1.7	313	40.0	70.18	69.39	6.81	6.89	2.56	2.25

[a] M_n: number average molecular weight determined by GPC in THF relative to polystyrene standards. DP: degree of polymerization. η: viscosity (25 °C in THF). MWD: molecular weight distribution. T_{d_5}: temperature obtained at which 5% weight loss with a heating rate 10 °C/min under nitrogen. [b] Polymers obtained by method A polycondensation. [c] Polymers obtained by method B polycondensation.

years.[19] A series of studies by Higashi et al.[21] showed that direct polymerization of hydroxy acid monomers is possible under mild conditions by using diphenylchlorophosphate as a condensing agent.[20a] 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.[21] 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,[22] 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 **16a,c,e** 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 polymerization rate can be significantly increased by adding trace amount of magnesium metal. Presumably, the propagation phenomenon could be due to the formation of nucleophilic species, a carboxylate anion, which can attack the electrophilic carbonyl carbon of another molecule to give another nucleophilic species, a phenoxy anion. The nucleophilic attack of this species onto the more electrophilic carbon of the mixed anhydride resulted in the formation of an ester, accompanying the release of the leaving group CH_3COO^-. This leaving group can easily take a proton from a carboxylic acid group to form acetic acid as a byproduct and generate a new nucleophilic species, at the same time keeping the chain continuously growing. The resultant polymers **1a**, **1c**, and **1e** are found to have low molecular weights ($M_n < 10\,000$) and are difficult for preparing fibers and thin films. An alternative polycondensation method[13c,18] for preparing isoregic chiral polyesters were employed using catalyst 4-(dimethylamino)pyridinium 4-toluene-

Scheme 2

sulfonate (DPTS) (method B, Scheme 2). 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 **1a−e** 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 **1a−e** is a key to their applications as NLO materials (Table 1). The thermal stability for polymers **1a−e** is similar regardless the difference in spacer length and molecular wieght. This phenomenon can be easily understood, since the polymers **1a−e** have the same functional groups and linkages.

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*) and nematic phases with Schlieren optical texture when viewed the samples through crossed polarized light. Figure 1 shows the textures S_C* and chiral nematic (N*) phases of monomer

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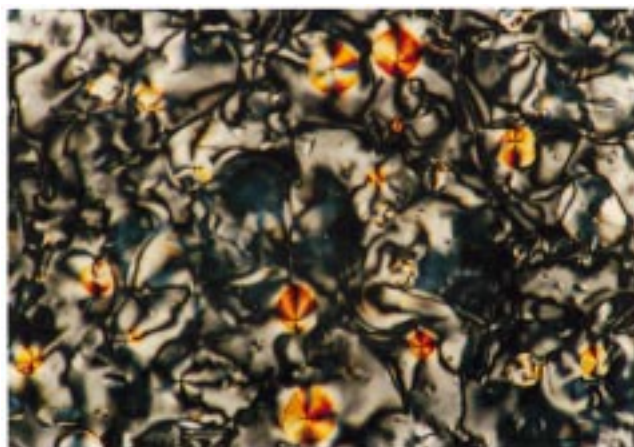(21) Economy, J.; Storm, R. S.; Matkovich, V. I.; Nowak, B. E.; Cottis, S. G. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2207.
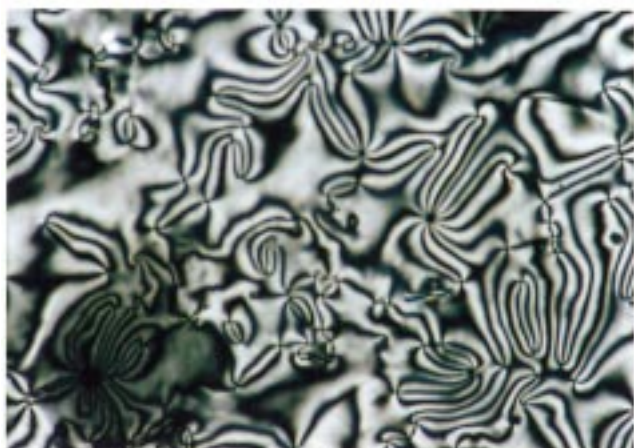(22) Kricheldorf, H. R.; Adebah. T. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 159.

Table 2. Phase Transition Temperatures of Monomers
15a−e[a]

monomer	n	transition temperature (°C)						
15a	6	K	127.2	S_C^*	171.6	N[*]	178.8	I
15b	7	K	128.0	S_C^*	179.8	N[*]	187.2	I
15c	8	K	130.8	S_C^*	181.1	N[*]	185.7	I
15d	9	K	136.0	S_C^*	178.5	N[*]	189.0	I
15e	10	K	142.0	S_C^*	185.4	N[*]	187.9	I

[a] K: crystal. S_C^*: chiral smectic C. N: nematic. I: isotropic phase.

Table 3. Phase Transition Temperatures of Polyesters
1a−e[a]

polymer	n	transition temperature (°C)						
1a	6	g	45.1	S_C^*	102.0	S_A^*	140.5	I
1b	7	g	49.2	S_C^*	134.5	S_A^*	173.2	I
1c	8	g	50.9	S_C^*	123.7	S_A^*	159.0	I
1d	9	g	39.4	S_C^*	140.6	S_A^*	182.9	I
1e	10	g	37.0	S_C^*	101.3	S_A^*	147.0	I

[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.

15d, respectively. 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., $S = 2, 3$, 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.[23−28]

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 μm glass spacers. The liquid crystalline behavior of these isoregic chiral polyesters is similar, which they exhibit a glass transition, S_C^*, and smectic S_A^* phases. However, the transition temperatures are in a size regime where there is strong

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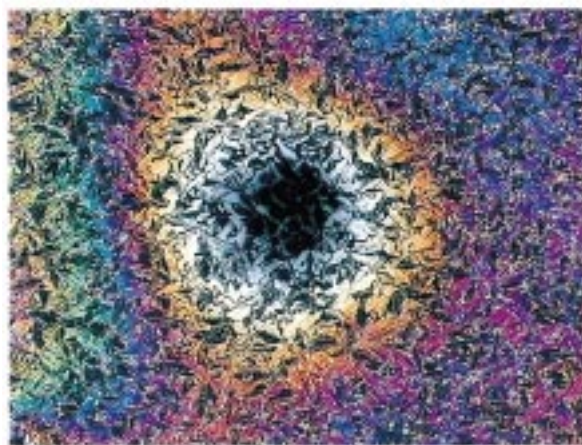
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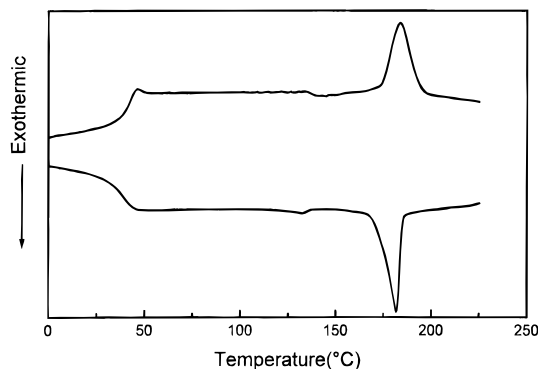
Figure 3. DSC heating and cooling traces of polymer *1d*, obtained at a cooling rate of 20 °C/min.

Figure 4. Wide-angle X-ray diffraction patterns of polymer *1d*, measured at a rate of 20 °C/min from cooling.

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.
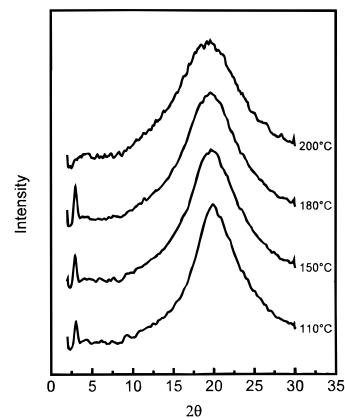
Conclusions

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 for 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.

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