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New Thermotropic Chiral Nematic Polymers. 3. Copolymers Containing a Cyanobiphenyl Group and (*S*)-(−)-1-Phenylethanol or (*S*)-(−)-1-Phenylethylamine

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I. Introduction

Thermotropic chiral nematics in thin films on the order of 10 μm possess a unique optical property, selective wavelength reflection, that forms the basis of a number of potential applications including circular polarizers, notch filters, beamsplitters,[1-3] and so on. More specifically, polarization of light and selective wavelength reflection are both crucial to the development of high efficiency liquid crystal color display and projection systems.[4] Instead of low molar mass chiral nematics, thermotropic copolymers have been actively pursued as an alternative in view of the possibility of achieving long-term mesophase stability and optical characteristics desired for passive device applications.[5] Of all the polymeric systems, including main- and side-chain homopolymers and copolymers, that have been reported in the literature,[6] side-chain copolymers seem to have received the most attention presumably because of the apparent flexibility and versatility in molecular design.

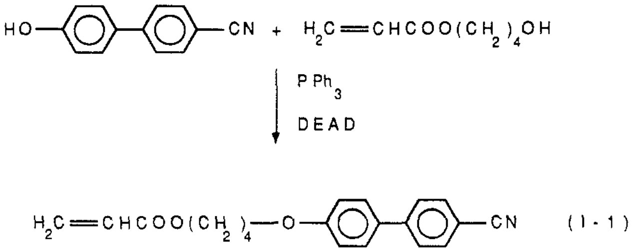
In a recent series of papers,[7-11] we have reported successful synthesis of both right- and left-handed thermotropic chiral nematic copolymers using pairs of enantiomers. Our attempt to interpret handedness from a chiral/nematic molecular interaction perspective strictly of a steric nature has also met with some success. Nevertheless, from a fundamental standpoint, it is fair to point out that an understanding of helical sense as a function of molecular structure is still lacking at the present time, let alone other factors relevant to cholesteric mesomorphism such as helical twisting power and selective wavelength reflection bandwidth. It is hoped that the synthesis and characterization of new copolymer systems will contribute to an improved understanding of structure–property relationships by providing a more extensive empirical database that will be employed to validate theoretical or simulation approaches.

Cyanobiphenyl is a relatively high birefringent group which is known to contribute to the formation of low molar mass liquid crystals;[12,13] it was found to exhibit a nematic mesophase between the glass transition and clearing temperatures in side-chain polyacrylates with spacer lengths in the 2–6 range.[14] However, there exists only one report on the formation of a chiral nematic copolymer with cholesterol as the chiral moiety.[15] Since several chiral building blocks other than cholesterol have been found to possess strong helical twisting powers with selected nematogenic monomers,[9-11] it would be of interest to explore a cyanobiphenyl group as a building block for the synthesis of new chiral nematic copolymers.

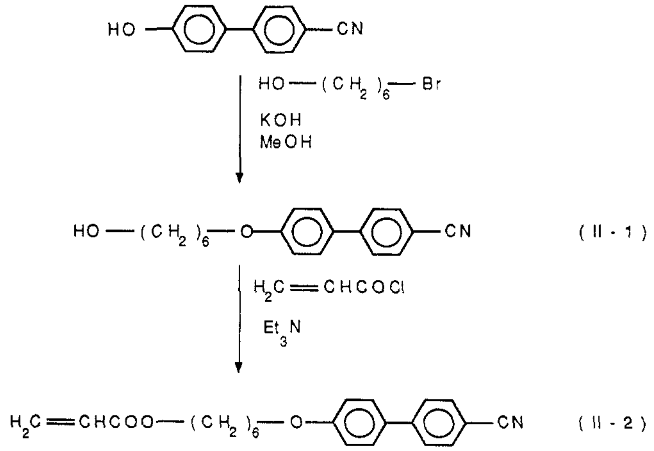
II. Experimental Section

Materials. 4-Hydroxybutyl acrylate (96%), 6-bromohexanol (95%+), acryloyl chloride (98%), diethyl azodicarboxylate (>90%), triphenylphosphine (99%), potassium hydroxide (85%+), and silica gel (40-μm flash chromatography packing), all received from Aldrich Chemical Co., plus anhydrous sodium sulfate (99.5%, J. T. Baker), 4-hydroxy-4′-cyanobiphenyl (95%+, TCI America), and triethylamine (99%, Fisher Scientific) were used as received without further purification. Solvents including tetrahydrofuran (100.0%), methylene chloride (>99.8%) were supplied by J. T. Baker through VWR Scientific; THF was further dried by refluxing over sodium spheres in the presence of benzophenone. Free radical initiator 2,2′-azobis(isobutyronitrile) (Chemical Dynamics Corp.) was recrystallized from diethyl ether before usage.

Scheme I. Synthesis of Nematogenic Monomer I-1 with Spacer Length *n* = 4



Scheme II. Synthesis of Nematogenic Monomer II-2 with Spacer Length *n* = 6



Characterization Techniques. Chemical structures of monomers and polymers were elucidated with FTIR (Nicolet 20 SXC) and proton-NMR (QE-300, GE) spectroscopic techniques, and thermal transition temperatures were determined by DSC (DuPont 910 with Thermal Analyst 2100 System) with mesophase textures identified by polarizing optical microscopy (Leitz Orthoplan-Pol) equipped with a hot stage (FP82), Mettler) and a central processor (FP800, Mettler). The copolymer products were further characterized in terms of molecular weight distribution, from which number and weight averages were calculated, using a GPC system comprising a Constametric III metering pump (Milton Roy), a V⁴ absorbance detector (ISCO), and two PLgel columns of 500 and 10 000 Å (Hewlett Packard) in series housed in a column oven (Jones Chromatography) set at 40 °C. Note that the reported copolymer molecular weights are equivalent to those of polystyrene standards (Pressure Chemical Co.). The chiral mole fractions in the copolymer products were determined via an integration of appropriate proton-NMR signals (1 wt % in $CDCl_3$). For the determination of selective reflection wavelength, a spectrophotometer (Perkin-Elmer Lambda 9) was employed to gather a UV–vis–near-IR spectrum on an optical element containing a copolymer product sandwiched between a pair of microscope slides with a thickness on the order of 10 μm and annealed at 95% of its clearing temperature.

Synthesis of Monomers. The two chiral monomers containing (*S*)-(−)-1-phenylethanol and (*S*)-(−)-1-phenylethylamine used in the present study were synthesized and characterized previously.[9] Schemes I and II were followed for the synthesis of cyanobiphenyl-containing nematogenic monomers, and the procedures are as outlined below.

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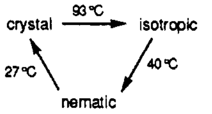
Table I. Elemental Analysis, Proton-NMR Spectral Data, and Phase Transition Temperatures of Nematogenic Monomers[a]

	nematogenic monomer (I-1)	nematogenic monomer (II-2)
	Elemental Analysis	
C, H, N calcd	74.75, 5.96, 4.36	75.62, 6.63, 4.00
C, H, N obsd	74.70, 5.97, 4.33	75.78, 6.73, 3.98
	Proton-NMR (δ, ppm)	
	1.92 [m, 4H, $-(CH_2)_2-$], 4.06 (t, 2H, $-CH_2-O-$phenyl), 4.27 (t, 2H, $-CH_2-O-CO-$), 5.85 and 6.44 (m, 2H, $H_2C=$), 6.16 (m, 1H, $H_2C=CH-COO-$), 6.97–7.71 (m, 8 arom ^{1}Hs)	1.40–1.89 [m, 8H, $-(CH_2)_4-$], 4.03 (t, 2H, $-CH_2-O-$phenyl), 4.20 (t, 2H, $-CH_2-O-CO-$), 5.83 and 6.43 (m, 2H, $H_2C=$), 6.13 (m, 1H, $H_2C=CH-CO_2-$), 6.94–7.69 (m, 8 arom ^{1}Hs)
	Phase Transitions	
		$\text{crystal} \underset{59\,°C}{\overset{73\,°C}{\rightleftharpoons}} \text{isotropic}$

[a] Observed with a hot-stage polarizing optical microscope at a heating and cooling rate of 5 °C/min.

Nematogenic Monomer I-1. 4-Hydroxy-4′-cyanobiphenyl (3.8 g), triphenylphosphine (4.42 g), and 4-hydroxybutyl acrylate (2.04 g) were dissolved in 20 mL of anhydrous THF to prepare a solution, to which 40 mL of an anhydrous THF solution of diethyl azodicarboxylate (2.91 g), abbreviated as DEAD in Scheme I, was added dropwise. The reaction mixture was stirred at room temperature overnight and then concentrated under reduced pressure. The solid residue was dissolved in 100 mL of methylene chloride, and the solution was shaken with an equal volume of water. The organic portion was washed again with water and then dried over anhydrous Na_2SO_4 before the crude product was collected by removing the solvent under reduced pressure. The product was further purified by flash chromatography on silica gel with methylene chloride as the eluent. Recrystallization from methanol gave shiny white crystals of I-1 (3.27 g, 71%).

Intermediate II-1. 4-Hydroxy-4′-cyanobiphenyl (5.03 g) and potassium hydroxide (1.73 g) were dissolved in 30 mL of methanol, and the solution was brought to reflux before 6-bromohexanol (5.15 g) in 11 mL of methanol was added. Chloroform (100 mL) and water (100 mL) were added to the reaction mixture at the end of the reaction followed by extractions with chloroform, and the crude product was collected by evaporating the solvent under reduced pressure after drying over anhydrous Na_2SO_4. Following recrystallization from acetone, flash chromatography on silica gel was accomplished using a 10:1 methylene chloride/methanol mixture as the eluent to yield II-1 (4.17 g, 55%).

Nematogenic Monomer II-2. II-1 (4.94 g) and triethylamine (2.02 g) were dissolved in 15 mL of dry THF, to which a solution of acryloyl chloride (1.65 g) in 10 mL of dry THF was added dropwise. To the reaction mixture were added 75 mL each of methylene chloride and water, and the organic layer was dried over anhydrous Na_2SO_4. The crude product was isolated by evaporating the solvent and then flash chromatographed on silica gel with methylene chloride as the eluent. Further purification was accomplished by recrystallization from methanol to yield shiny white crystals (4.11 g, 70%).

Free Radical Copolymerization: Copolymer P-2 with x = 0.15. In 2 mL of dry THF were dissolved II-2 (0.40 g), methacrylate chiral monomer containing (*S*)-(−)-1-phenylethanol (0.055 g), and initiator 2,2′-azobis(isobutyronitrile) (2 mg). The solution was stirred at 60 °C under nitrogen for 3 days. The product was isolated by precipitation with cold methanol and further purified with repeated dissolution–precipitation cycles to yield copolymer P-2 (0.382 g, 84%). The vacuum dried sample was found to have a weight-average molecular weight of 14 800 with a polydispersity index of 2.5, and the chiral mole fraction, x, was determined to be 0.15 on the basis of proton-NMR spectroscopy. The DSC thermogram showed a T_g at 29 °C and a T_c at 83 °C with the mesophase identified to be cholesteric by polarizing optical microscopy. A purified and thoroughly dried copolymer sample was placed between a pair of microscope slides, heated beyond T_c, then cooled to 76 °C following by shearing to encourage alignment, and finally left at 76 °C to anneal overnight. The UV-vis-near-IR spectrum of the annealed optical element gave a λ_R value of 550 nm.

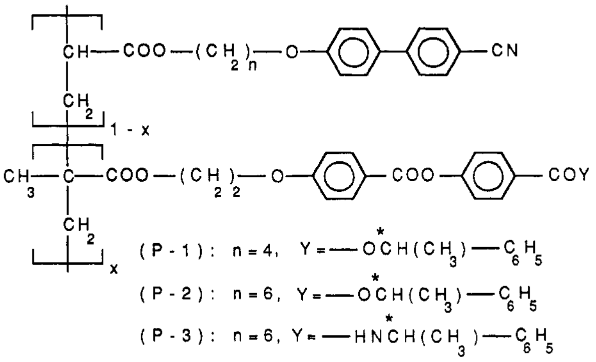


Figure 1. Chemical structures of copolymers P-1, P-2, and P-3 synthesized for the present study.

III. Results and Discussion

Acrylate monomers containing the cyanobiphenyl group with spacer lengths of 4 and 6, synthesized according to Schemes I and II, respectively, were characterized by elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, NY), proton-NMR and FTIR spectroscopies, DSC, and polarizing optical microscopy. The structures of these two nematogenic monomers are consistent with NMR and FTIR spectra and with the results of elemental analysis listed as part of Table I, which also contains information on phase transitions and proton-NMR spectral data (1 wt % in $CDCl_3$).

Copolymer structures are defined in Figure 1 in terms of spacer length and chiral moiety. The acrylate/methacrylate mixed backbone structure was adopted in favor of a pure acrylate or methacrylate backbone structure for two reasons: one is to have T_g near or above the ambient temperatures, and the other is to broaden the mesophase temperature range. Indeed, the pure methacrylate backbone structure was found to give a rather narrow mesophase temperature range, which was known to render molecular alignment difficult to achieve via thermal annealing.[10] As a result of the preferred backbone structure, copolymerization involving acrylate and methacrylate monomers was not expected to yield a chemically uniform product because of unequal reactivity ratios. No attempts were made in this work to investigate possible effects of compositional heterogeneity and copolymer molecular weight on the observed thermotropic and optical properties.

Table II. Characterization Data for Copolymer P-1, P-2, and P-3

copolymer	chiral,x	T_g (°C)	T_c (°C)	ΔH_c (J/g)	M_w	M_w/M_n	λ_R[a] (nm)
P-1	0.11	30	76	1.2	6550	2.1	880
P-1	0.15	40	76	0.93	9110	2.0	470
P-2	0.04	21	86	1.9	7060	1.9	960
P-2	0.15	29	83	1.3	15300	2.4	550
P-3	0.04	18	74	2.4	6900	1.9	1180
P-3	0.07	31	83	1.5	11700	2.2	670

[a] Note that optical elements prepared for the measurement of λ_R were all annealed at 98% T_c.

The second heating scans at 20 °C/min with nitrogen purge at 50 mL/min were consistently collected from DSC experiments. Summarized in Table II are the experimentally determined values for chiral mole fraction, glass transition and clearing temperatures, selective reflection wavelength, weight-average molecular weight, and polydispersity index. Oily streaks characteristic of a cholesteric mesophase were observed with polarizing optical microscopy for all copolymer samples between T_g and T_c. As previously reported by Platé and Shibaev,[15] cholesterol was found to be capable of producing a chiral nematic copolymer with λ_R = 555 nm at x = 0.55 with the same nematogenic monomer. In contrast, the presently reported chiral nematic copolymers yield the same λ_R values at x values less than 0.15, suggesting that, with the cyanobiphenyl-containing nematogenic monomers, both (*S*)-(–)-1-phenylethylamine and (*S*)-(–)-1-phenylethanol possess a stronger helical twisting power than cholesterol. On the basis of the optical elements prepared and characterized previously[9–11] in terms of selective reflection property and handedness, copolymers P-1, P-2, and P-3 were all found to result in left-handed structures with the specified enantiomers. In view of the relatively high birefringent cyanobiphenyl moiety[12,13] and an accepted theory governing selective reflection,[16] these materials are expected to exhibit broad-band characteristics, which is presently being investigated in terms of polymer structure and thermal annealing at decreasing temperatures from the clearing point.

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