New Thermotropic Liquid Crystal Polymers Containing the High Birefringence Cyanotolan Moiety

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ABSTRACT: The high birefringence cyanotolan moiety was employed to synthesize novel nematic homopolymers and, with (*S*)-(−)-1-phenylethanol, left-handed cholesteric copolymers without any other mesophases existing between T_g and T_c. The DSC thermograms revealed that at an increasing spacer length, T_g shows a monotonic decrease and T_c is governed by the oft-quoted odd–even effect. Both series of mesomorphic polymers were found to be readily soluble in common organic solvents, to be capable of vitrification with the glass transition above room temperature, to be thermally stable up to 250 °C, and not to absorb light in the visible and near-infrared region, all of which are desirable for optical applications.

I. Introduction

Primarily because of its relatively large optical birefringence and low viscosity, the cyanotolan moiety has been considered for electrooptical[1] applications. Moreover, the nitrotolan group is potentially suited for nonlinear optical[2,3] applications in view of its large molecular hyperpolarizability. It has been reported that cyanotolan carrying an alkoxy tail group shows a predominantly nematic mesophase, while a smectic mesophase may arise in addition with an alkyl tail group.[1,4,5] It would be of interest to explore to what extent one can take advantage of its nematogenicity in the design and synthesis of novel thermotropic liquid crystal polymers that may turn out to be useful for the fabrication of environmentally robust and durable optical devices. Moreover, there are benefits to be expected of a large optical birefringence value, which is expected to lessen the thickness requirement in a wave plate[6] and to broaden the selective wavelength reflection bandwidth in a cholesteric device.[7]

As part of our research on thermotropic liquid crystal polymers for a variety of potential optical device applications, such as linear polarization[8] based on nematic mesomorphism and circular polarization[9] based on cholesteric mesomorphism, the high birefringence cyanotolan moiety was considered for the synthesis of side-chain polymers that might satisfy the following optical material requirements: no light absorption in the visible and near-infrared region, readily soluble in common organic solvents, and capable of vitrification to eliminate the light scattering problem arising from crystallinity. Thus, homopolymers containing the cyanotolan moiety as well as copolymers containing both cyanotolan and chiral moieties as pendant groups were synthesized, and their thermotropic behavior and morphology were characterized using differential scanning calorimetry, DSC, and hot-stage polarizing optical microscopy. The selective wavelength reflection property of cholesteric copolymers was further characterized with UV–vis–near-IR spectrophotometry.

II. Experimental Section

Materials. 4-Iodophenol (99%), 3,4-dihydro-2*H*-pyran (97%), (trimethylsilyl)acetylene (98%), copper(I) iodide (99.999%), bis(triphenylphosphine)palladium(II) dichloride (98%), 4-bromobenzonotrile (99%), *n*-butyllithium (2.5 M in hexanes), zinc chloride (98%), tetrakis(triphenylphosphine)palladium(0) (99%), 4-hydroxybutyl acrylate (96%), pyridinium *p*-toluenesulfonate (98%), diethyl azodicarboxylate (>90%), triphenylphosphine (99%), and silica gel (40-μm flash chromatography packing) were all used as received from Aldrich Chemical Co. Solvent THF (100.0%, J. T. Baker) was dried by refluxing over sodium spheres in the presence of benzophenone, and methylene chloride (>99.5%, J. T. Baker) was dried by distillation over calcium hydride. Free radical initiator 2,2′-azobis(isobutyronitrile) (Chemical Dynamics Corp.) was recrystallized from diethyl ether before usage.

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 stability and phase transition temperatures were determined by TGA (DuPont 951) and DSC (DuPont 910 with Thermal Analyst 2100 System), respectively, with mesophase textures identified by polarizing optical microscopy (Leitz Orthoplan-Pol) equipped with a hot stage (FP82, Mettler) and a central processor (FP80, Mettler). The polymer products were further characterized in terms of molecular weight distribution, from which number- and weight-average molecular weights were calculated, using a GPC system comprising a Constametric III metering pump (Milton Roy), a V^4 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 polymer 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 (typically 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 chiral nematic copolymer product sandwiched between a pair of high quality glass substrates with a thickness on the order of 10 μm and annealed at 95% of its clearing temperature.

Synthesis of Monomers. The chiral monomer containing (*S*)-(−)-1-phenylethanol used in the present study was synthesized and characterized previously. Scheme I was followed for the synthesis of cyanotolan-containing nematogenic monomers with a spacer length ranging from 2 to 6. Illustrated as follows are the experimental procedures for the monomer carrying a spacer length of 4.

Intermediate I-1. A solution of 4-iodophenol (74.4 g) and 3,4-dihydro-2*H*-pyran (84.1 g) in 800 mL of dry methylene chloride containing pyridinium *p*-toluenesulfonate, PTTS (17.5 g), was stirred at room temperature for 5 h. Then the solution was diluted with ether and washed several times with half-saturated brine to remove the catalyst. Upon evaporation of the solvent, recrystallization from ethanol was accomplished to yield white chunky crystals of I-1 (90 g, 85%).

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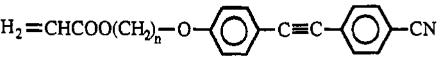
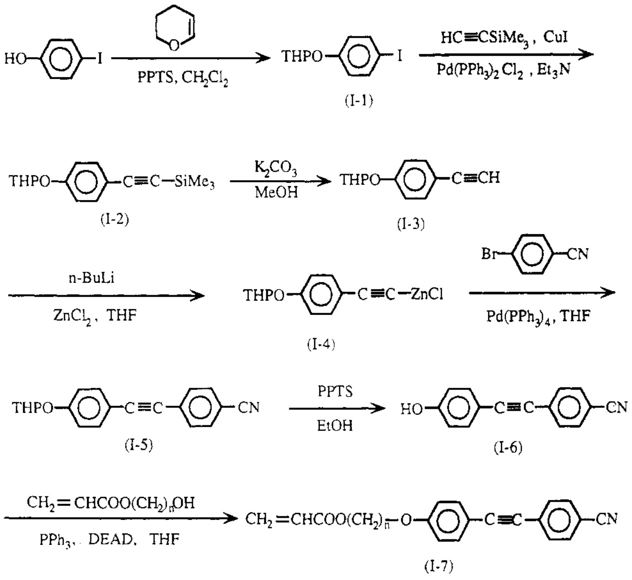
Table I. Elemental Analysis and Phase Transition Temperatures of Acrylate Monomers Containing the Cyanotolan Group


(I)

	n = 2			n = 3			n = 4			n = 6		
	C	H	N	C	H	N	C	H	N	C	H	N
calcd	75.70	4.73	4.41	76.12	5.14	4.23	76.50	5.51	4.06	77.19	6.17	3.75
obsd	75.57	4.74	4.41	76.36	5.19	4.17	76.76	5.45	4.04	76.85	6.09	3.66
phase transitions[a]	$\mathrm{C} \underset{92.0\ ^\circ\mathrm{C}}{\overset{110.5\ ^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$			$\mathrm{C} \underset{90.5\ ^\circ\mathrm{C}}{\overset{93.1\ ^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$			$\mathrm{C} \xrightarrow{73.0\ ^\circ\mathrm{C}} \mathrm{I}$ $\mathrm{I} \xrightarrow{62.0\ ^\circ\mathrm{C}} \mathrm{N}$ $\mathrm{N} \xrightarrow{43.0\ ^\circ\mathrm{C}} \mathrm{C}$			$\mathrm{C} \underset{66.7\ ^\circ\mathrm{C}}{\overset{71.0\ ^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$		

[a] Observed with a hot-stage polarizing optical microscope at a heating and cooling rate of 5 °C/min. Symbols: C, crystalline; N, nematic; I, isotropic.

Scheme I. Synthesis Scheme for Cyanotolan-Containing Nematogenic Monomers



PPTS——Pyridinium p-toluenesulfonate
PPh$_3$——Triphenylphosphine
DEAD——Diethyl azodicarboxylate

Intermediate I-2. To a mixture of I-1 (25 g) and (trimethylsilyl)acetylene (12 g) in 300 mL of triethylamine were added bis(triphenylphosphine)palladium(II) dichloride (1 g) and copper(I) iodide (0.133 g). The reaction mixture was stirred under nitrogen at room temperature for 3 h before the solvent was removed under reduced pressure. The residue was extracted with 500 mL of petroleum ether, and the solution was filtered, washed with water, and then dried over anhydrous MgSO$_4$. Upon evaporating the solvent, the brown crude product was purified by flash chromatography on silica gel using 1:15 diethyl ether/petroleum ether as the eluent. The pale yellowish product was recrystallized to yield white chunky crystals of I-2 (15 g, 66%).

Intermediate I-3. I-2 (5.0 g) and anhydrous potassium carbonate (1.0 g) were dissolved in 100 mL of methanol, and the solution was stirred for 2 h. The solvent was then evaporated, and the residue was dissolved in 200 mL of petroleum ether followed by washing with water and drying over anhydrous MgSO$_4$. Recrystallization from ethanol gave white chunky crystals of I-3 (3.62 g, 98%).

Intermediate I-4. To a solution of I-3 (3.4 g) in 10 mL of anhydrous THF at 0 °C was added *n*-butyllithium (0.078 g) in hexanes (2.5 M). The solution was stirred for 5 min prior to adding anhydrous zinc chloride (2.29 g) dissolved in anhydrous THF (20 mL). The mixture was stirred at room temperature for an additional 15 min.

Intermediates I-5 and I-6. To the solution containing I-4 cooled to 0 °C were added sequentially a solution of 4-bromobenzonitrile (3.07 g) in anhydrous THF (20 mL) and that of tetrakis(triphenylphosphine)palladium(0) (0.5 g) in anhydrous THF (20 mL), both at 0 °C, to obtain I-5, which was not isolated. Instead, 30 mL of 1 N HCl solution and 10 g of ammonium chloride were added to form two clearly separated layers, which were stirred at room temperature for another 3 h to deprotect the hydroxyl group. The two layers were separated upon shaking with 50 mL of petroleum ether, and the aqueous portion was extracted with petroleum ether. The organic portions were combined, washed with a saturated aqueous solution of sodium bicarbonate, and dried over anhydrous MgSO$_4$. After the solvent was evaporated under reduced pressure, the brown residue was purified by flash chromatography on silica gel with methylene chloride as the eluent. The yellowish product was recrystallized from chloroform to give white flakes of I-6 (2.35 g, 64%).

Nematogenic Monomer I-7. Diethyl azodicarboxylate, DEAD (1.91 g), in 10 mL of anhydrous THF is added slowly to a mixture containing I-6 (2.0 g), 4-hydroxybutyl acrylate (1.56 g), triphenylphosphine (2.87 g), and 20 mL of anhydrous THF. The reaction mixture was stirred at room temperature for 5 h and then concentrated under reduced pressure followed by flash chromatography on silica gel with methylene chloride as the eluent. The crude product was recrystallized from ethanol to give white flakes of I-7 (2.0 g, 64%).

Free-Radical Polymerization: Copolymer I with x = 0.07 as an Example. I-7 (0.433 g), the chiral monomer containing (*S*)-(−)-1-phenylethanol (0.0464 g), and 2,2′-azobis(isobutyronitrile), AIBN (1 mg), were dissolved in anhydrous THF (1.5 mL). The reaction mixture was stirred under nitrogen at 60 °C for 2 days. The copolymer product was isolated and purified by repeated dissolution–precipitation cycles using methanol as the nonsolvent, and the chemical structure was elucidated with NMR and FTIR spectroscopies including a comparison to monomer spectra. The thoroughly dried product (0.15 g, 30%) was analyzed by GPC, DSC, and polarizing optical microscopy. About a 20-mg sample was placed between a pair of glass substrates, heated beyond T_c, then cooled to 85 °C followed by shearing to encourage alignment, and finally left at 85 °C to anneal overnight for characterization with UV–vis–near-IR spectrophotometry.

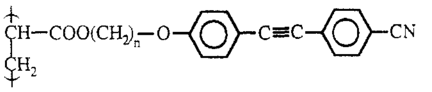
III. Results and Discussion

Tables I and II summarize the analytical results of nematogenic monomers in terms of elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, NY), hot-stage polarizing optical microscopy, and proton-NMR spectroscopy. Note that the nematogenic monomer with spacer length 4 showed monotropic nematic mesomorphism, whereas other spacer lengths gave no mesophase at all under hot-stage polarizing optical microscopy at a heating and cooling rate of 5 °C/min, which is consistent with DSC thermograms for all four monomers. However, homopolymers with all spacer lengths were found to give a glass transition followed by a nematic to isotropic transition, as revealed by the second DSC heating scans at 20 °C/min with nitrogen purge at 50 cc/min; the characteristic Schlieren texture was evident from the optical element (annealed at 95% of the clearing point) observed under polarizing optical microscopy. Further-

Table II. Proton-NMR Spectral Data for Acrylate Monomers Containing the Cyanotolan Group

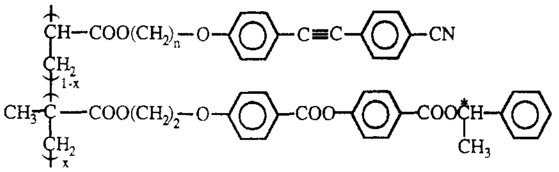
$n = 2$	$n = 3$	$n = 4$	$n = 6$
4.28 (t, 2H, $-CH_2O-$)	2.16–2.25 (m, 2H, $-CH_2-$)	1.84–1.96 (m, 4H, $-[CH_2]_2-$)	1.47–1.96 (m, 8H, $-[CH_2]_4-$)
4.57 (t, 2H, $-CO_2CH_2-$)	4.10 (t, 2H, $-CH_2O-$)	4.05 (t, 2H, $-CH_2O-$)	4.01 (t, 2H, $-CH_2O-$)
5.87–6.50 (m, 3H, $H_2C{=}CH-$)	4.37 (t, 2H, $-CO_2CH_2-$)	4.30 (t, 2H, $-CO_2CH_2-$)	4.22 (t, 2H, $-CO_2CH_2-$)
6.93–7.66 (m, 8 arom ^{1}Hs)	5.83–6.47 (m, 3H, $H_2C{=}CH-$)	5.84–6.47 (m, 3H, $H_2C{=}CH-$)	5.83–6.46 (m, 3H, $H_2C{=}CH-$)
	6.89–7.62 (m, 8 arom ^{1}Hs)	6.92–7.67 (m, 8 arom ^{1}Hs)	6.91–7.67 (m, 8 arom ^{1}Hs)

Table III. Thermal Properties and Molecular Weights of Nematic Homopolymers Containing the Cyanotolan Side Group


(II)

spacer n	T_g (°C)	T_c (°C)	ΔH_c (J/g)	M_w	M_w/M_n
2	69	114	2.3	7 470	1.8
3	53	99	0.75	14 800	1.8
4	42	129	3.2	12 400	2.0
6	33	129	2.7	11 700	1.4

Table IV. Thermal and Optical Properties and Molecular Weights of Chiral Nematic Copolymers Containing Cyanotolan and 1-Phenylethanol as Pendant Groups


(III)

spacer n	chiral x	T_g (°C)	T_c (°C)	ΔH_c (J/g)	M_w	M_w/M_n	λ_R (nm)
2	0.05	76	112	2.5	11 900	1.7	840
3	0.05	58	85	0.5	8 980	1.6	*a*
4	0.05	45	117	1.7	12 200	2.3	920
4	0.07	43	104	1.3	10 800	2.3	770
4	0.13	48	94	1.4	13 700	2.2	450
6	0.08	34	116	2.0	17 500	2.1	1140

[a] The cholesteric mesophase was identified with polarizing optical microscopy, but the selective wavelength reflection property could not be determined because of the relatively narrow mesophase temperature range that prevents adequate molecular alignment from being achieved via annealing.

more, the TGA scans at 10 °C/min with nitrogen purge at 50 cc/min indicated that these nematic homopolymers are thermally stable up to 250 °C. It was also found that these nematic polymers are readily soluble in THF and methylene chloride, and UV–vis spectra of the resultant solutions showed no light absorption at a wavelength greater than or equal to 370 nm. Compiled in Table III are thermal properties and molecular weight information for the nematic homopolymers. Note that T_g undergoes a monotonic decrease with increasing spacer length, while T_c clearly shows an odd–even effect, as previously reported for nematic homopolymers containing the cyanobiphenyl side group.[10]

Free-radical polymerization of the nematogenic monomers depicted as part of Table I with a previously synthesized and characterized chiral comonomer containing (*S*)-(−)-1-phenylethanol[11] was conducted to yield a series of chiral nematic side-chain copolymers with the general structure shown in Table IV. As a result of the acrylate/methacrylate mixed backbone structure, the copolymerization reaction was not expected to yield a chemically uniform product because of the unequal reactivity ratios. No attempts were made in this work to examine the possible effects of compositional heterogeneity and copolymer molecular weight on the resultant thermotropic and optical properties. The second DSC heating scans at 20 °C/min with nitrogen purge at 50 cc/min revealed a glass transition followed by a first-order phase transition, and relevant characterization data are summarized in Table IV. The Grandjean texture was consistently observed under polarizing optical microscopy for all these copolymers as the sample was thermally annealed between T_g and T_c. Although minor variations in T_g and T_c with chiral mole fraction within spacer length 4 are noticed, that T_g decreases with increasing spacer length and that T_c follows the odd–even effect with spacer length, are both evident from the thermal data compiled in Table IV, which also contains information on molecular weight and selective reflection wavelength. It is noted that no more than 15 mol % chiral content is needed for selective reflection to occur at 400 nm in the case of copolymer III with $n = 4$ as opposed to at least 25 mol % in all formerly reported chiral nematic copolymers.[11-16] By comparing to the previously reported chiral nematic copolymers, it was found that (*S*)-(−)-1-phenylethanol gives left-handed copolymers containing the pendant cyanotolan group, which is consistent with the molecular interaction model depicted in Figure 1 of ref 11.

IV. Summary

The cyanotolan moiety was employed to synthesize novel nematic homopolymers and cholesteric copolymers using (*S*)-(−)-1-phenylethanol as the chiral building block. These thermotropic liquid crystal polymers were found to possess properties desirable for optical applications, such as absence of light absorption in the visible region, solubility in common organic solvents, capability for vitrification, and stability against thermal decomposition up to 250 °C. In both series of polymers, T_g was found to decrease monotonically with increasing spacer length, while T_c showed an oft-quoted odd–even effect. Because of the high optical birefringence value of the cyanotolan group, it is expected that the presently reported materials will be particularly useful for linear as well as circular polarization of incident light. Characterization of parameters pertinent to practical applications, such as index of refraction, optical birefringence, and order parameter of properly aligned samples, is in progress, and the results will be reported in a future communication.

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