Vitrified Chiral−Nematic Liquid Crystalline Films for Selective Reflection and Circular Polarization

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Nematic and left-handed chiral−nematic liquid crystals comprising methoxybiphenylbenzoate and (*S*)−(−)-1-phenylethylamine pendants to a cyclohexane core were synthesized and characterized. Although pristine samples were found to be polycrystalline, thermal quenching following heating to and annealing at elevated temperatures permitted the molecular orders characteristic of liquid crystalline mesomorphism to be frozen in the glassy state. Left at room temperature for 6 months, the vitrified liquid crystalline films showed no evidence of recrystallization. An orientational order parameter of 0.65 was determined with linear dichroism of a vitrified nematic film doped with Exalite 428 at a mole fraction of 0.0025. Birefringence dispersion of a blank vitrified nematic film was determined using a phase-difference method complemented by Abbé refractometry. A series of vitrified chiral−nematic films were prepared to demonstrate selective reflection and circular polarization with a spectral region tunable from blue to the infrared region by varying the chemical composition. The experimentally measured circular polarization spectra were found to agree with the Good−Karali theory in which all four system parameters were determined a priori: optical birefringence, average refractive index, selective reflection wavelength, and film thickness.

I. Introduction

Liquid crystals are a unique class of organic materials capable of self-assembly into various molecular arrangements on a macroscopic scale. Specifically, a director defines the uniaxial molecular alignment characteristic of a nematic liquid crystal. A chiral−nematic (i.e., cholesteric) liquid crystal can be described as a stack of quasinematic layers, each characterized by its own director and all sharing a common surface normal referred to as the helical axis. From one layer to the next, the director makes an incremental rotation about the axis, resulting in right- or left-handed cholesteric mesomorphism, which is further characterized by a pitch length, p, the distance along the axis over which the director completes a 360° rotation. Under polarizing optical microscopy, the cholesteric mesophase is identifiable with two distinct textures, focal conic and Grandjean, depending on the orientation of the axis with the substrate. In the Grandjean mode, the axis is perpendicular to the substrate, giving rise to selective reflection. The selective reflection wavelength, λ_R, equals $0.5(n_e + n_o)p \cos \theta$,[1,2] where θ is the incidence angle, and n_e and n_o are the extraordinary and ordinary refractive index of the quasinematic layer. The experimentally observed bandwidth, $\Delta\lambda$, is approximately equal to $\lambda_R(\Delta n/\bar{n})$,[3] in which $\Delta n = n_e - n_o$ is the optical birefringence and $\bar{n} = (n_e + n_o)/2$ the average refractive index, both of the quasinematic layer. Furthermore, a left-handed film will selectively reflect the left-handed circularly polarized component of unpolarized, incident light without attenuating the right-handed circularly polarized component. The opposite is true of a right-handed film.

Therefore, a chiral−nematic liquid crystalline film is capable of selective reflection and circular polarization simultaneously: a single-handed film serving as a circular polarizer,[4] and a pair of right- and left-handed films as a notch filter.[5] Since the handedness of the reflected component from a chiral−nematic film can be reversed upon reflection from a mirror, unpolarized incident light can be converted into circularly polarized light in the forward direction at a nearly 100% efficiency.[4] These device concepts have been demonstrated

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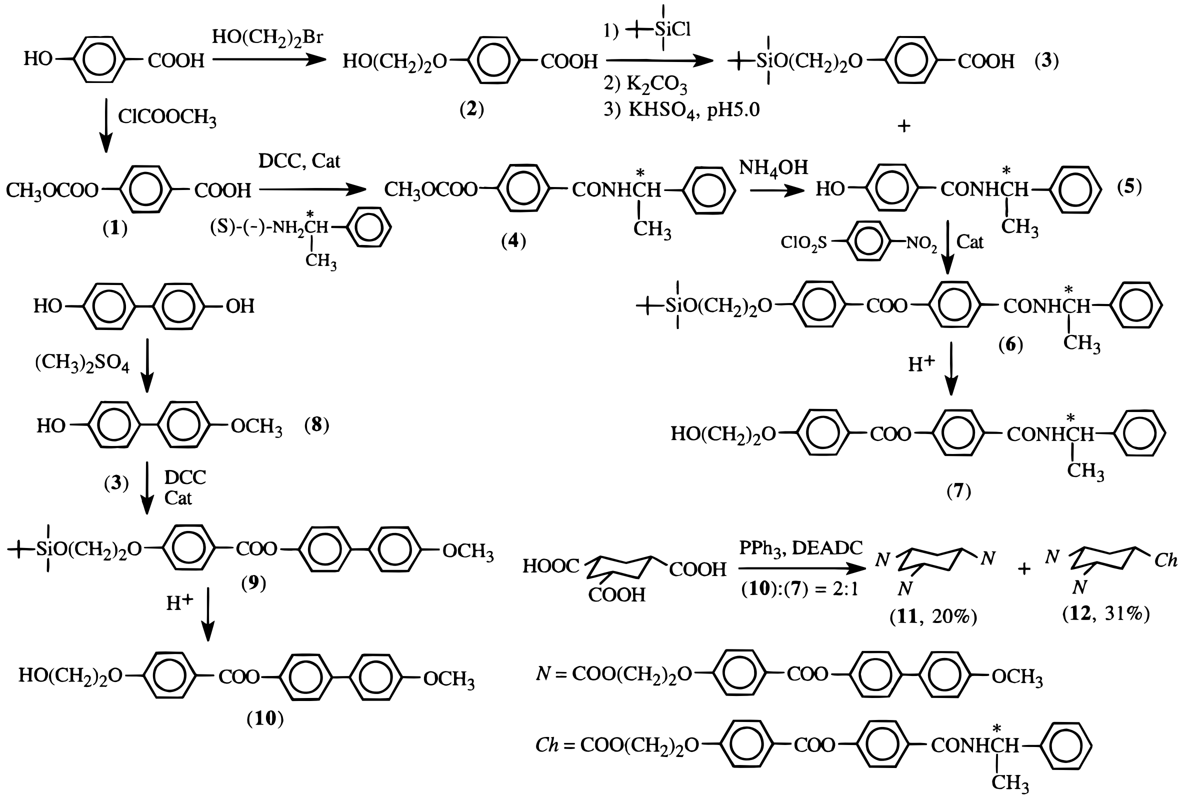
Scheme 1. Synthetic Routes for Nematic (11) and Chiral−Nematic (12) Glass-Forming Liquid Crystals



with fluid films, for which λ_R is known to be sensitive to extrinsic factors, such as temperature variation and mechanical perturbation. To surmount these limitations, we have developed vitrifiable liquid crystals (VLCs)[6] as a new class of optical materials with an above-ambient glass transition temperature, T_g, and an elevated clearing temperature, T_c. One unique feature of VLCs is that the molecular order can be frozen in the solid state, thereby rendering device robustness. In particular, both right- and left-handed materials were made available using a pair of enantiomers as the chiral building block.[7] In the present study, nematic and left-handed chiral−nematic VLCs were synthesized based on a cyclohexane core with methoxybiphenylbenzoate and (*S*)−(−)-1-phenylethylamine pendants. Vitrified liquid crystalline films were also prepared for the characterization of linear dichroism, birefringence dispersion, selective reflection, and circular polarization.

II. Experimental Section

Reagents and Chemicals. All chemicals, reagents, and solvents were used as received from the Aldrich Chemical Company or VWR Scientific with the following exceptions. Exalite 428 (>98%) was received from Exciton, Inc., and tetrahydrofuran (99%) was dried by refluxing over sodium in the presence of benzophenone until blue then distilled. Silica gel 60 (EM Science, 230−400 mesh) was used for liquid chromatography unless noted otherwise.

Material Synthesis. Synthesis and purification of intermediates and final products were carried out following Scheme 1. All the intermediates were verified with ^{1}H NMR spectroscopy and thin-layer chromatography before proceeding further. Experimental procedures are described in what follows.

*4-[(Methoxycarbonyl)oxy]benzoic Acid (**1**).* To a solution of sodium hydroxide (18.75 g, 469 mmol) in water (500 mL) was added 4-hydroxybenzoic acid (22.4 g, 162 mmol). The solution was then cooled to −5 °C before methyl chloroformate (25.0 g, 265 mmol) was added slowly to prevent temperature rise. The resulting slurry was stirred for 4 h followed by adjusting its pH to 5.0 with hydrochloric acid (36 wt %). The crude product formed as the precipitate, which was purified by recrystallization from ethanol to give 21.7 g (68%).

*4-(2-Hydroxyethoxy)benzoic Acid (**2**).* In ethanol (200 mL) and water (20 mL) were dissolved 4-hydroxybenzoic acid (44.0 g, 289 mmol), potassium hydroxide (40.27 g, 610 mmol), and potassium iodide (4.0 g). Under reflux conditions 2-bromoethanol (25 mL, 353 mmol) was added over 1 h. The reaction was allowed to continue for 24 h under reflux. The solid was removed by filtration, and the filtrate was evaporated under vacuum followed by dilution with water (350 mL) and subsequent acidification with hydrochloric acid. The white precipitate, which formed as a result, was filtered and recrystallized from ethanol:water (1:1) to give 27.5 g (52%).

*4-[2-[(tert-Butyldimethylsilyl)oxy]ethoxy]benzoic Acid (**3**).* In 110 mL anhydrous *N*,*N*-dimethylformamide were dissolved **2** (22.51 g, 124 mmol) and *tert*-butyldimethylsilyl chloride (40.1 g, 266 mmol), to which imidazole (32.65 g, 480 mmol) was quickly added. After stirring overnight, the reaction mixture was shaken with diethyl ether (250 mL) and water (700 mL). The ether layer was washed with saturated sodium bicarbonate and dried over anhydrous magnesium sulfate. An oil (60 mL) was obtained upon removing ether by evaporation under vacuum. The oil was dissolved in methanol (600 mL) and tetrahydrofuran (200 mL) followed by stirring with a solution of potassium carbonate (20.16 g, 146 mmol) in water (100 mL) for 1 h. The volume of the solution was reduced by 75% via evaporation under vacuum. The pH of the solution was adjusted to 5.0 with 1 M aqueous solution of potassium hydrogen sulfate. The solid was collected by filtration and washed with water before dissolving in methylene chloride. The solution was dried over anhydrous magnesium sulfate for evaporation to dryness. Recrystallization from hexane:ethyl acetate (3:1) yielded 27.0 g (74%).

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*(S)−(−)-1-(Phenylethyl)-4-[(methoxycarbonyl)oxy]benzamide (**4**).* *N*,*N*-Dicyclohexylcarbodiimide (11.57 g, 56.1 mmol) and 4-pyrrolidinopyridine (0.75 g, 5.1 mmol) were dissolved, with chilling in an ice bath, in anhydrous tetrahydrofuran (200 mL). To this solution was added **1** (10.0 g, 51.0 mmol) followed by (*S*)−(−)-1-phenylethylamine (6.18 g, 51.0 mmol). The reaction mixture was stirred overnight, and the resulting precipitate was filtered off. The filtrate was evaporated under vacuum and then dissolved in methylene chloride. The solution was then shaken with water and subsequently with 10% aqueous sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate for evaporation to dryness. The solid was recrystallized from ethanol to yield 6.10 g (40%).

*(S)−(−)-1-(Phenylethyl)-4-hydroxybenzamide (**5**).* To a solution of **4** (2.64 g, 8.8 mmol) in ethanol (150 mL) was added 30% ammonium hydroxide (25 mL) at room temperature. The reaction mixture was stirred for 1 h before adjusting its pH to 5.0 with hydrochloric acid. The solution was then filtered, diluted with chloroform, and washed with water. The organic layer was dried over anhydrous sodium sulfate and then evaporated under vacuum to yield 1.82 g (85%).

*(S)−(−)-1-(Phenylethyl)-4-[[4-[2-[(tert-butyldimethylsilyl)oxy]ethoxy]benzoyl]oxy]benzamide (**6**).* In anhydrous tetrahydrofuran (250 mL) and acetonitrile (40 mL) were dissolved **5** (9.50 g, 32 mmol), (dimethylamino)pyridine (0.85 g, 7 mmol), and triethylamine (9 mL, 0.0646 mol), and then 4-nitrobenzenesulfonyl chloride (7.1 g, 32 mmol) was added. After stirring at room temperature for 40 min, the reaction mixture was submerged in an ice bath for 10 min before a solution of (**5**) (7.24 g, 30 mmol) in anhydrous tetrahydrofuran (90 mL) was added dropwise over a period of 20 min. The reaction mixture was then stirred overnight at room temperature before filtering off insolubles. The filtrate was diluted with methylene chloride and shaken with saturated sodium bicarbonate. After the solution was dried over anhydrous magnesium sulfate, the organic layer was evaporated to dryness. The crude product was purified by column chromatography on silica gel with a gradient elution using methylene chloride followed by 5% acetone in methylene chloride. Hexane was added to the resulting concentrated solution to induce crystallization of 9.9 g (63%). An additional 1.0 g (7%) was obtained by repeating column chromatography of the mother liquor.

*(S)−(−)-1-(Phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide (**7**).* In tetrahydrofuran (200 mL) was dissolved **6** (10.9 g, 20.9 mmol) followed by an addition of 1.2 M aqueous hydrochloric acid (5 mL). The reaction mixture was stirred overnight. Powdered sodium bicarbonate (about 1 g) was then added, and most of the solvent was evaporated off. The resulting slurry was shaken with methylene chloride (150 mL) and three batches of water (3 × 100 mL) followed by concentrated brine (100 mL). The organic layer was dried over anhydrous magnesium sulfate. Filtration followed by evaporation to a concentrated solution with subsequent dilution with acetone:ethanol (1:1) afforded product (6.50 g) of good purity. Column chromatography of the mother liquor on silica gel with 5% acetone in methylene chloride as eluent yielded additional pure product, producing a total of 7.75 g (91%).

*4-Hydroxy-4′-methoxybiphenyl (**8**).* To a solution of sodium hydroxide (8.6 g, 215 mmol) in water (80 mL) was added 4,4′-dihydroxybiphenyl (20 g, 107 mmol). Dimethyl sulfate (13.5 g, 107 mmol) was then added, and the resultant slurry was stirred at room temperature for 4 h. The solid was collected by filtration, washed with 10% aqueous sodium hydroxide, and then dissolved in boiling water. The trace amount of insoluble 4,4′-dimethoxybiphenyl was separated by hot filtration. Dilute hydrochloric acid (5 wt %) was then added to the solution upon which the product precipitated. The crude product was collected by filtration and washed with water. Recrystallization from ethanol yielded 16 g (74%).

*4′-(Methoxybiphenyl) 4-[2-[(tert-butyldimethylsilyl)oxy]ethoxy]benzoate (**9**).* Anhydrous tetrahydrofuran (40 mL) was added to **3** (5.00 g, 16.9 mmol), **8** (3.73 g, 18.5 mmol), *N*,*N*-dicyclohexylcarbodiimide (4.00 g, 19.4 mmol), and 4-pyrrolidinopyridine (0.25 g, 1.7 mmol). A mostly clear solution was obtained before a large amount of precipitate formed. After the solution was stirred for 4 h, the insolubles were filtered and washed with tetrahydrofuran. The filtrate was evaporated to dryness and then redissolved in methylene chloride. The solution was shaken with 5% acetic acid (100 mL) and then with water before drying over anhydrous magnesium sulfate. The solution was reduced in volume before adding methanol to produce a slurry, which was heated and hot filtered to yield 5.5 g (68%).

*4′-(Methoxybiphenyl) 4-(2-hydroxyethoxy)benzoate (**10**).* To ethanol (550 mL) were added **9** (25.1 g, 52.1 mmol) and *p*-toluenesulfonic acid monohydrate (4.62 g, 18.3 mmol) to produce a slurry, which was stirred at 55 °C for 5 h. The solid product collected by filtration produced a slurry in boiling acetone (400 mL), which upon cooling yielded 15.3 g (80%).

*Vitrifiable Nematic and Chiral−Nematic Liquid Crystals (**11** and **12**).* In a mixed solvent of anhydrous tetrahydrofuran (30 mL) and anhydrous *N*,*N*-dimethylformamide (8 mL) were dissolved **7** (1.00 g, 2.47 mmol), **10** (1.80 g, 4.94 mmol), triphenylphosphine (2.02 g, 7.79 mmol), and *cis*-1,3,5-cyclohexanetricarboxylic acid (0.537 g, 2.48 mmol), under argon. Diethyl azodicarboxylate (1.3 mL, 8.26 mmol) was then added dropwise to the solution. The solution was stirred overnight at room temperature. The white precipitate collected by filtration was identified as a crude product, **11**, which was purified by a short silica gel column (40−140 mesh) with a gradient elution from pure methylene chloride to 2.5% acetone in methylene chloride. The filtrate of the reaction mixture was reduced in volume by evaporation under vacuum for precipitation into ethanol. The collected solid was dissolved in methylene chloride for column chromatography on silica gel with a gradient elution from methylene chloride to 10% acetone in methylene chloride. Two reasonably pure fractions were obtained. One of the fractions containing mostly **11** was further purified by recrystallization from hot methylene chloride. The other fraction containing mostly **12** was further purified by a short silica gel column (40−140 mesh) followed by precipitation into methanol. Overall, **11** was obtained in 0.61 g (20%), and **12** in 1.01 g (31%). For compound **11**, ^{1}H NMR ($CDCl_3$) spectral data: δ 1.50−2.60 (m, *cis*-cycloxhexane, 9H), 3.88 (s, $OC\mathbf{H}_3$, 3H), 4.30 (t, $COO{-}C\mathbf{H}_2CH_2O$, 6H), 4.52 (t, $COOCH_2C\mathbf{H}_2O$, 6H), 6.90−8.62 (m, aromatic, 36H). Anal. Calcd for $C_{75}H_{66}O_{18}$: C, 71.76; H, 5.30; N 0.00. Found: C, 70.91; H, 5.22; N 0.04. For compound **12**, ^{1}H NMR ($CDCl_3$) spectral data: δ 1.52−2.60 (m, *cis*-cycloxhexane and $CHC\mathbf{H}_3$, 12H), 3.88 (s, $OC\mathbf{H}_3$, 3H), 4.30 (t, $COOC\mathbf{H}_2CH_2O$, 6H), 4.52 (t, $COOCH_2C\mathbf{H}_2O$, 6H), 5.37 (m, $N\mathbf{H}$, 1H), 6.36 (m, $C\mathbf{H}CH_3$, 1H), 6.90−8.24 (m, aromatic, 37H). Anal. Calcd for $C_{77}H_{69}NO_{18}$: C, 71.34; H, 5.36; N 1.08. Found: C, 70.79; H, 5.10; N 1.07.

Molecular Structures, Thermotropic Properties, and Morphology. Chemical structures were elucidated with elemental analysis (performed by Oneida Research Services, Whitesboro, NY), FTIR (Nicolet 20 SXC) and ^{1}H NMR (QE-300, GE) spectroscopic techniques. Thermal transition temperatures were determined by DSC (Perkin-Elmer DSC-7) with a continuous N_2 purge at 20 mL/min. Liquid crystal mesomorphism was characterized with a polarizing optical microscope (Leitz Orthoplan-Pol) equipped with a hot stage (FP82, Mettler) and a central processor (FP80, Mettler); the nematic and cholesteric mesomorphism were identified with the threaded textures and oily streaks, respectively. The morphology of pristine and thermally processed samples were analyzed with X-ray diffractometry (XRD). The diffraction data were collected in reflection mode geometry using a Siemens D500 θ/θ Bragg−Brentano diffractometer equipped with an Anton−Paar HTK temperature stage and a Braun position-sensitive detector. The source was a copper X-ray tube filtered with nickel foil. Samples were prepared as powders on a platinum heating strip and analyzed as-received at 26 °C. The samples were then heated to 220 °C, quenched to 26 °C at a rate of −60 °C/min, followed by XRD data collection at 26 °C. All XRD experiments were performed under dry N_2.

Preparation of Vitrified Liquid Crystalline Films. Optically flat fused silica substrates (1 in. diameter × $^1/_8$ in. thickness, EscoProducts) transparent down to 200 nm were cleaned, spin-coated with Nylon 66, and uniaxially buffed using a polyaramide roller. Elements for most optical characterization were fabricated by sandwiching powdered VLC material between two surface-treated substrates with the buffing directions parallel to each other. The film thickness was defined by 14-μm glass fiber spacers (Bangs Laboratories). The actual thickness was determined using interference fringes of the air gap between the substrates gathered with a spectrophotometer (Perkin-Elmer Lambda 9). Chiral−nematic devices were assembled by melting the crystalline powder at 210 °C. The devices were then transferred onto a hot-plate set at 130 °C for shearing to induce alignment followed by annealing for 3 min before quenching to room temperature. Nematic devices were assembled and annealed at 250 °C for 1 h followed by quenching to room temperature. Both the nematic and chiral−nematic VLC films prepared with the procedures as described were found to be nearly monodomain under polarizing optical microscopy with a magnification factor of 100. Optical elements for Abbé refractometry were prepared using a high (SF_6, $n_D = 1.805$) with a low (CaF_2, $n_D = 1.430$) index substrate, both treated the same way as described above.

Optical Properties of Vitrified Liquid Crystalline Films. A UV−vis−NIR spectrophotometer (Perkin-Elmer Lambda 9) was used to characterize selective reflection, circular polarization, UV−vis linear dichroism, and birefringence dispersion of VLC films. Fresnel reflections from air−glass and glass−air interfaces were eliminated through the use of a reference cell comprising an index-matching fluid ($n_D = 1.500$ at 25 °C, Cargille Laboratories) sandwiched between two surface-treated substrates. Selective reflection was characterized using unpolarized incident light, and circular polarization using right- and left-handed circularly polarized incident light generated by a combination of a linear polarizer (HPN′B, Polaroid) and an achromatic quarter waveplate (Meadowlark Optics). The light source of the instrument was found to be linearly polarized to some extent because of the grating system in the spectrophotometer. To minimize potential artifacts, measurements were carried out with the buffing direction of the cell oriented vertically and horizontally. The arithmetic average of the two transmittances was reported as the selective reflection and circular polarization spectra.[8] Orientational order of Exalite 428, as a dopant with rodlike molecules, was characterized by UV−vis linear dichroism. A lightly doped nematic VLC film was scanned with its director parallel and perpendicular to the maximum transmission axis of the linear polarizer. A blank nematic VLC film was also prepared for background correction, resulting in linear dichroism of the dopant. Abbé refractometry was employed for the measurement of n_e and n_o. A refractometer (Bellingham and Stanley, Model 60/HR) with a high index prism ($n_D = 1.916$) provided n_e and n_o at $\lambda_D = 589.6$ nm for a vitrified nematic film at 20 °C. Calibration was performed with a fused silica optical flat with $n_D = 1.458$. Good optical contact between fused silica and the prism was ensured using 1-bromonaphthalene ($n_D = 1.657$), and between the SF_6 substrate and the prism using a contact fluid with $n_D = 1.810$. The retardance calculated with optical birefringence, film thickness, and wavelength was used as a data point in the phase-difference technique[9] to determine the wavelength dependence of optical birefringence. This method involved spectrophotometric characterization of a nematic film placed between a polarizer and an analyzer. The director of the nematic film was oriented at 45° with respect to the polarization plane of the polarizer. Two measurements were carried out with the polarization plane of the analyzer parallel and perpendicular to that of the polarizer, yielding $T_{\|}$ and $\mathrm{T}_{\perp}$, respectively.

III. Results and Discussion

Vitrifiable chiral−nematic liquid crystals consist of a volume-excluding central core to which nematogenic and chiral pendants are chemically bonded.[7] Although all three structural elements are crystalline as separate entities, the hybrid system readily forms macroscopically ordered glass on cooling without residual crystallinity or a tendency toward spontaneous crystallization.[10] This new material class is further characterized by ease of processing into optical-quality thin films because of favorable rheological properties[11] and expedited defect annihilation upon thermal annealing in comparison to polymeric counterparts.[12] Nematic compound **11** and chiral−nematic compound **12**, as depicted in Scheme 1, were mixed at various ratios via codissolution in methylene chloride followed by drying in vacuo. The thermotropic data based on the DSC second heating scans at 50 °C/min of thermally quenched samples are presented in Table 1 for I through V. It is demonstrated that material systems I through IV are capable of glass formation without residual crystallinity or thermally induced recrystallization. In contrast, a thermally quenched sample of V undergoes recrystallization upon heating at 50 °C/min. Note the decreasing T_g and increasing T_c with a decreasing content of chiral−nematic (**12**) component in the blend. To unravel the morphology and long-term stability against recrystallization, X-ray diffraction (XRD) patterns of both pristine and thermally quenched samples were collected at 26 °C. Representative data are shown in Figure 1 for I and V: the pristine sample is crystalline and the thermally quenched sample is glassy. Left at 26 °C for six months, the thermally processed samples of I and V showed no evidence of recrystallization from the quenched glassy state. It is noted that samples II, III, and IV behaved similarly to I.

Table 1. Thermotropic and Selective Reflection Properties of the Nematic (11) and Chiral−Nematic (12) Blends That Have Been Thermally Processed

sample	mole fraction (**12**)	transition temp[a] (°C)	thickness[b] (μm)	λ_R[c] (nm)
I	1.00	*G* 77 *Ch* 147 *I*	14.5 ± 0.3	410
II	0.95	*G* 75 *Ch* 154 *I*	14.2 ± 0.1	434
III	0.61	*G* 68 *Ch* 202 *I*	14.4 ± 0.2	714
IV	0.39	*G*67 *Ch* 235 *I*	14.4 ± 0.1	1210
V	0.00	*G* 64, 95 K_1 130 K_2 180 *N* 279 *I* [d]	13.9 ± 0.3	∞

[a] Thermal transition temperatures determined from the DSC second heating scans at 50 °C/min of samples preheated to 250 °C followed by quenching at −60 °C/min to −30 °C; the nematic and cholesteric mesophases were identified as threaded textures and oily streaks, respectively, under polarizing optical microscopy. Symbols: *G*, glassy; *K*, crystalline; *Ch*, cholesteric; *N*, nematic; *I*, isotropic. [b] Thickness of vitrified films determined with interference fringes of the air gap surrounding the film contained between two substrates. The reported mean and standard deviation were based on several measurements around the film on a single optical element. [c] Values of λ_R determined as the center wavelength of the selective reflection band shown in Figure 4 with nematic film representing a limiting case of infinite λ_R. [d] The second heating scan of sample V at 50 °C/min showed glass transition at 64 °C followed by crystallization at 95 °C, crystalline modification at 130 °C, melting into a nematic liquid crystal at 180 °C, and clearing at 279 °C.

To probe the molecular order in a vitrified nematic film of V, Exalite 428 was employed as a guest at a mole

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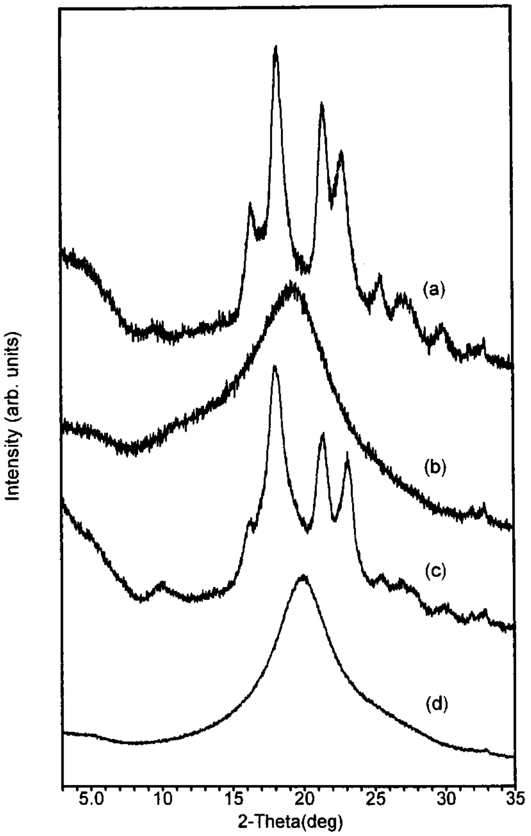

Figure 1. X-ray diffraction patterns: (a) Pristine powder of I at 26 °C; (b) I heated to 220 °C then quenched at −60 °C/min to 26 °C; (c) Pristine powder of V at 26 °C; (d) V heated to 220 °C then quenched at −60 °C/min to 26 °C. Scans a and c reveal the polycrystalline nature of pristine samples, while scans b and d confirm the glassy characteristic of the thermally processed, nematic, and chiral−nematic samples.

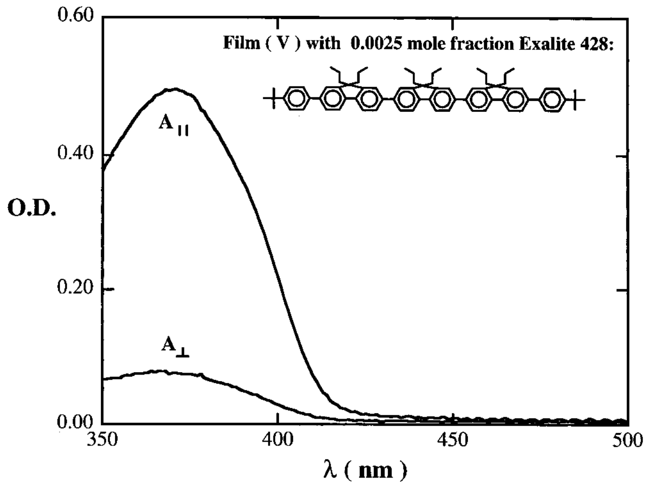

Figure 2. Linear dichroism of Exalite 428 doped at a mole fraction of 0.0025 in unaxially aligned nematic film V, 14.0 μm thick: $A_{\|}$ and $A_{\perp}$ are the absorbances measured parallel and perpendicular, respectively, to the nematic director defined by the buffing direction on the substrate.

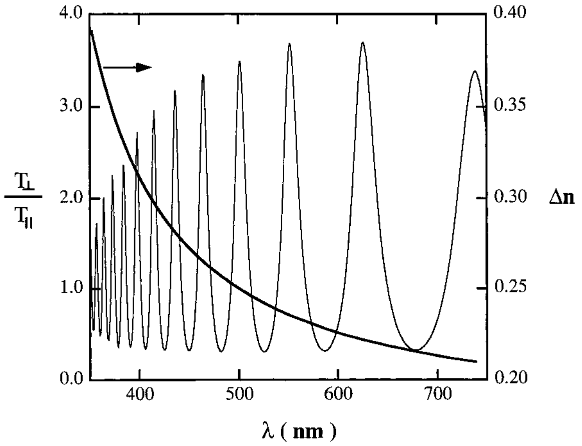

Figure 3. Birefringence dispersion, $\Delta n(\lambda)$, determined with $T_{\perp}/T_{\|}$ measured as a function of wavelength on a spectrophotometer for a 13.9 μm thick nematic film V.

fraction of 0.0025. The rodlike molecular shape of Exalite 428, as depicted in Figure 2, suggests its ability to align with the nematic director. The UV−vis absorption spectra were gathered both parallel and perpendicular to the nematic director. With a blank film of V prepared under the same condition as the doped film for background correction, the linear dichroism of unaxially oriented Exalite 428 is presented in Figure 2. Note the absorption maximum at 370 nm, which is fairly close to 366 nm observed in methylene chloride at a concentration of 10^{-5} M. The absorbances parallel ($A_{\|}$) and perpendicular ($A_{\perp}$) to the director were used to calculate the dichroic ratio, $R = A_{\|}/A_{\perp} = 6.5$, from which the orientational order parameter was determined: $S = (R - 1)/(R + 2) = 0.65$, indicating a high degree of alignment of the guest with the nematic director of the host. The blank nematic film of V was further characterized in terms of Δn and $\bar{n}$. Refractometric measurements produced $\bar{n} = 1.67$ and $\Delta n = 0.23$ at 589.6 nm. This birefringence value was employed to determine the dispersion of birefringence via the measurement of $T_{\perp}/T_{\|}$ as a function of λ, which yielded $\Delta n(\lambda)$ based on a phase-difference technique.[9] The results are displayed in Figure 3. The Δn values at selected wavelengths evaluated from the dispersion curve were used for the interpretation of circular polarization by chiral−nematic films containing the same nematogen within the framework of the Good−Karali theory.[13]

Four vitrified chiral−nematic films were prepared, with thicknesses reported in Table 1, for the characterization of selective reflection and circular polarization. The selective reflection spectra resulting from unpolarized incident light are compiled in Figure 4; note the observed optical densities that are close to the theoretical limit of 0.30 with a perfectly aligned, single-handed film. The ease of film preparation, in particular the 3-min annealing time, is in sharp contrast to polymeric materials which produce inferior optical density even upon annealing for up to a week; ref 14 provides an extensive survey on prior research on chiral−nematic copolymers. The center wavelength identified as λ_R was found to obey the correlation, $\lambda_R \chi_{ch} = 144 \pm 9$ nm, where the mole fraction of chiral pendant, χ_{ch}, equals $^1/_3$ of the mole fraction of **12** listed in Table 1. That the reflection band is broader at a longer wavelength is consistent with $\Delta\lambda/\lambda_R \cong \Delta n/\bar{n}$ established for chiral−nematic films.[3] With circularly polarized incident light, the performance of chiral−nematic films as circular polarizers was evaluated. All four chiral nematic films were found to be highly transmissive to right-handed circularly polar-

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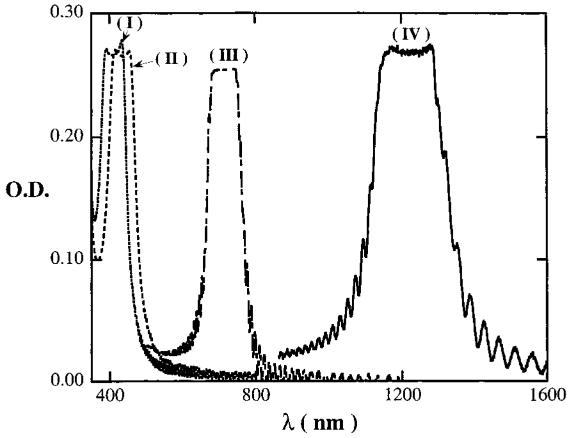

Figure 4. Selective reflection spectra of chiral−nematic films I through IV, with thicknesses as reported in Table 1, measured with unpolarized incident light. Note that an optical density of 0.30 is expected of a perfectly aligned, single-handed chiral−nematic film.

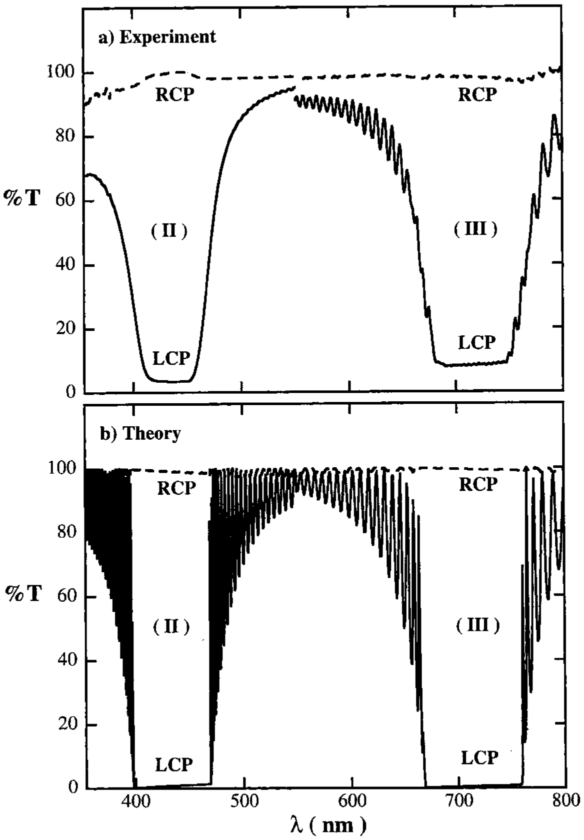

Figure 5. Circular polarization spectra of chiral−nematic films II and III, 14.2 and 14.4 μm, respectively: (a) Experimental results with right- and left-handed circularly polarized (RCP and LCP) incident light; (b) theoretical prediction based on the Good−Karali theory with $\lambda_R = 434$ nm, $\bar{n} = 1.70$, and $\Delta n = 0.28$ for film II, and $\lambda_R = 714$ nm, $\bar{n} = 1.66$ and $\Delta n = 0.21$.

ized (RCP) incident light and highly reflective to left-handed circularly polarized (LCP) incident light, as illustrated in Figure 5a for films II and III. Note the poor transmission in the spectral region below 400 nm due to light absorption of the film. Thus, (*S*)−(−)-1-phenylethylamine causes left-handed twisting of quasinematic layers comprising these chiral−nematic films following a commonly accepted convention.[15] Similar behaviors have been observed[16] without theoretical interpretation using vitrifiable liquid crystalline materials reported earlier.[7]

The circular polarization spectra were further interpreted with the Good-Karali theory[13] governing the propagation of light through a chiral−nematic film. The theory contains four parameters: $\bar{n}$, Δn, λ_R, and film thickness, all estimated a priori in the present treatment. As an approximation, $n_o = 1.56$ measured with refractometry at 589.6 nm was applied across the spectral region. This can be justified by the general observation that the dispersion of Δn is predominated by that of n_e in nematic liquid crystals.[17] Therefore, the birefringence dispersion curve presented in Figure 3 together with a constant n_o was used to determine Δn and $\bar{n}$ at selected λ_Rs. For films II and III with $\lambda_R = 434$ and 714 nm, n and Δn were estimated at 1.70 and 0.28, and 1.66 and 0.21, respectively. The comparison made in Figure 5b indicates good agreement between the theoretical prediction and experimental observation of circular polarization. The fact that the transmittance of the LCP incident light through a left-handed chiral−nematic film falls short of the predicted 0% is an indication of less than perfect order in which all helical axes are oriented perpendicularly to the substrate.

IV. Conclusions

Nematic and left-handed chiral−nematic liquid crystals, with methoxybiphenylbenzoate and (*S*)−(−)-1-phenylethylamine pendants to a cyclohexane core, were successfully synthesized and purified. The thermotropic properties and solid morphology of the pure components and their blends were characterized with differential scanning calorimetry, polarizing optical microscopy, and X-ray diffractometry. Vitrified films were prepared for the characterization of orientational order, optical birefringence, selective reflection and circular polarization using linear dichroism, a phase-difference technique, and UV−vis−NIR spectrophotometry with and without polarization control and analysis. The main observations are summarized as follows:

(1) Pristine samples of nematic and chiral−nematic compounds were found to be polycrystalline. Heating pristine samples up to 250 °C followed by thermal annealing and then quenching to room temperature produced morphologically stable liquid crystalline glasses.

(2) Exalite 428, a UV dye with a rodlike molecular shape, was doped in a vitrified nematic film at a mole fraction of 0.0025 for the characterization of linear dichroism, resulting in an order parameter of 0.65.

(3) Optical birefringence of a blank nematic film was determined across the spectral region from 400 to 700 nm using a phase-difference technique complemented with Abbé refractometry at 589.6 nm.

(4) Nearly monodomain chiral−nematic films were prepared following the thermal processing as described in 1 above. By blending nematic and chiral−nematic compounds, the spectral region of selective reflection

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and circular polarization can be readily tuned from blue to the infrared region.

(5) The experimentally observed circular polarization spectra were found to agree very well with the Good−Karali theory with all system parameters determined a priori: optical birefringence, average refractive index, selective reflection wavelength, and film thickness.

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