Thermotropic Chiral−Nematic Poly(*p*-phenylene)s as a Paradigm of Helically Stacked π-Conjugated Systems

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As an emerging class of multifunctional optical materials, chiral−nematic poly(*p*-phenylene)s with cyanobiphenyl and (*S*)-1-phenylethyl pendants were synthesized and characterized. Nematic homopolymer was also synthesized for preparation into a uniaxially aligned film. Linearly polarized photoluminescence (LPPL) and FTIR dichroism revealed that both the conjugated backbone and the nematic pendant are oriented along the director with an orientational order parameter, $S = 0.62$ and 0.73, respectively. Films prepared with chiral−nematic copolymers were found to selectively reflect left-handed circularly polarized light in the ultraviolet, visible, and infrared region at a decreasing chiral content. The helically stacked poly(*p*-phenylene)s were further characterized in terms of circularly polarized photoluminescence (CPPL). On the basis of a recent theory, $S = 0.67$ was found for the orientational order of conjugated backbones within quasinematic layers comprising the chiral−nematic film. Within experimental uncertainty, the *S* values determined with the LPPL and CPPL techniques are in good agreement, thereby validating the proposed supramolecular structure on the basis of which theories governing light absorption, emission, and propagation in structured media were constructed.

I. Introduction

Conjugated polymers represent one of the most extensively investigated classes of advanced materials in the past two decades. Reasons for the extraordinary intensity of interest include the diverse structures and properties afforded by molecular design and synthesis, the ease of processing and low costs compared to inorganic materials, and the technological potential for advanced technologies, such as electronics, optics, photonics, and optoelectronics.[1] In particular, feasibility has been demonstrated with amorphous or crystalline conjugated polymers for light-emitting diodes,[2] organic lasers,[3] thin film transistors,[4] photoconductors,[5] and nonlinear optical devices.[6] Liquid crystalline conjugated polymers characterized by various modes of macroscopic order have added a new dimension in recent years. Mediated by nematic or smectic mesomorphism, axial alignment of π-conjugated segments has been shown to enhance electrical conductivity by orders of magnitude[7] and to induce linearly polarized light emission.[8] Conjugated polymers of the chiral−nematic (i.e., cholesteric) type, in which conjugated segments self-assemble into helically stacked, quasinematic layers, have remained literally unexplored. As a matter of fact, there exists only one paper at present[9] reporting loosely pitched conjugated systems. This is an emerging class of multifunctional optical materials potentially capable of selective reflection accompanied by circular polarization of incident unpolarized light,[10] circularly polarized luminescence,[11] and electrochromism inherent to π-con-

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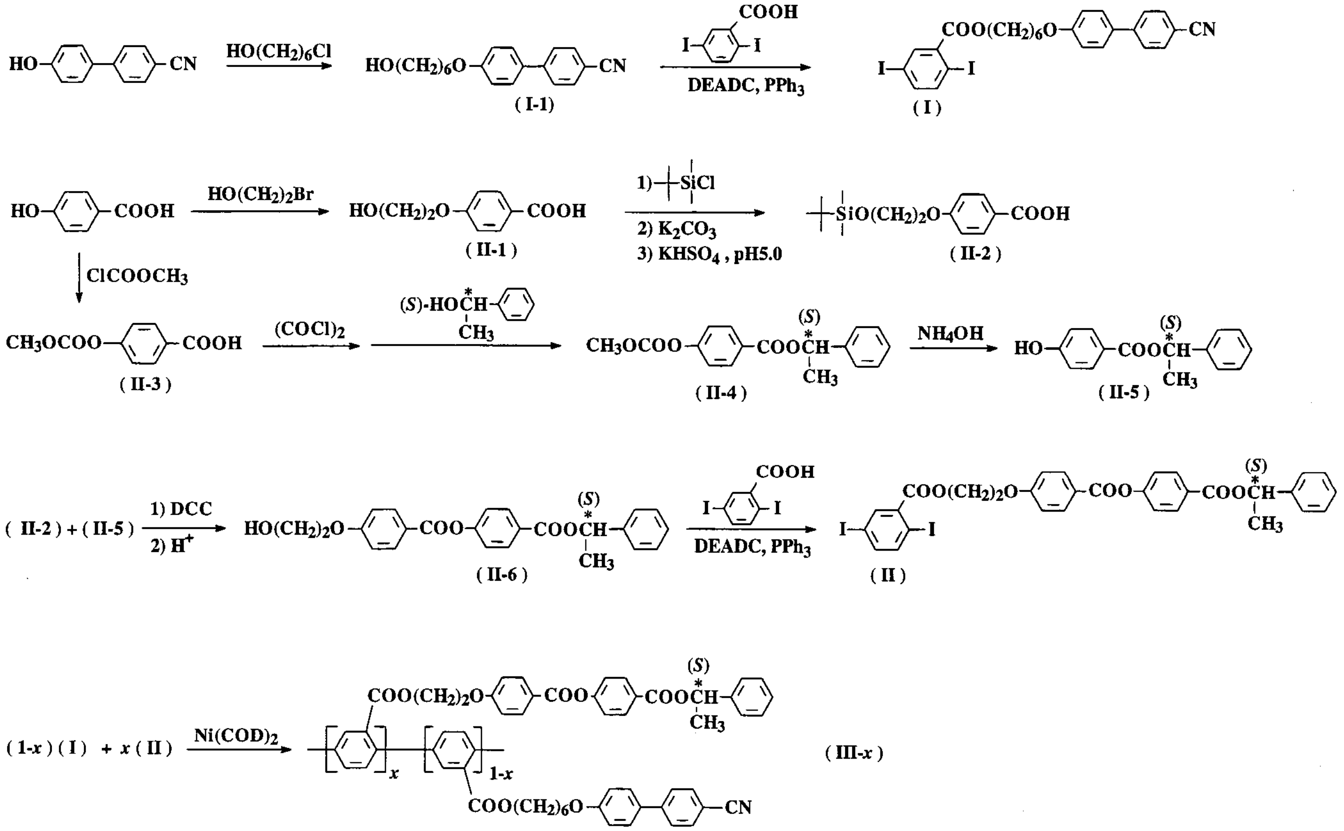
Scheme 1. Synthesis of Nematic and Chiral Monomers and of Nematic and Chiral−Nematic Poly(*p*-phenylene)s



jugation.[12] Nonetheless, no existing conjugated polymers possess a tight enough pitch to show selective wavelength reflection in the visible region. In what follows we report on the synthesis and characterization of tightly pitched, chiral−nematic conjugated polymers with supramolecular structure fully characterized by polarized photoluminescence and infrared dichroism.

II. Experimental Section

Reagents and Chemicals. All chemicals, reagents, and solvents were used as received from the Aldrich Chemical Co. or VWR Scientific with the following exceptions. Bis(1,5-cyclooctadiene)nickel(0) (98+%, Strem Chemicals) was used without further purification. Tetrahydrofuran (99%) was dried by being refluxed over sodium in the presence of benzophenone until blue and then distilled. Silica gel 60 (EM Science, 230−400 mesh) was used for liquid chromatography.

Material Synthesis. Syntheses of monomers and polymers were performed following Scheme 1 with the experimental procedures as described in what follows.

4-(6-Hydroxyhexyloxy)-4′-cyanobiphenyl, (**I-1**). 4-Hydroxy-4′-cyanobiphenyl (4.92 g, 25.2 mmol), 6-chloro-1-hexanol (4.40 g, 32.2 mmol), cesium carbonate (9.18 g, 28.1 mmol), and potassium iodide (0.43 g, 2.6 mmol) were dissolved in 65 mL of DMF. The reaction mixture was stirred at 80 °C for 5 h. The resultant salt was removed by hot filtration. The filtrate was slowly added to 600 mL of water, and the crude product was collected for recrystallization from methanol to produce 5.75 g in 76% yield.

2,5-Diiodobenzoic Acid, 6-[4-(4′-Cyanobiphenyl)oxy]hexyl Ester (**I**). 2,5-Diiodobenzoic acid (6.65 g, 17.8 mmol), triphenylphosphine (5.33 g, 20.3 mmol), and **I-1** (5.00 g, 16.9 mmol) were dissolved in 85 mL of anhydrous tetrahydrofuran, to which diethyl azodicarboxylate (DEADC; 4.43 g, 25.4 mmol) was slowly added. Under argon the reaction mixture was stirred at room temperature overnight. Upon evaporation of the solvent under reduced pressure, the solid residue was dissolved in a small amount of methylene chloride for purification by flash column chromatography on silica gel, with a 98/2 mixture of methylene chloride and acetone as the eluent, followed by recrystallization from methanol to obtain 10.26 g in 93% yield. ^{1}H NMR: δ 8.08−7.00 (m, aromatic, 11H), 4.38 (t, COOCH_2, 2H), 4.04 (t, ArOCH_2, 2H), 1.86 (m, COOCH$_2$CH_2-(CH$_2$)$_2$CH_2CH$_2$OAr, 4H), 1.58 (m, COOCH$_2$CH$_2$(CH_2)$_2$CH$_2$CH$_2$-OAr, 4H). Anal. Calcd: C, 47.95; H, 3.56; N, 2.15; I, 38.97. Found: C, 47.98; H, 3.34; N, 2.21; I, 39.40.

4-(2-Hydroxyethyloxy)benzoic Acid, (**II-1**), *4-[2-[(tert-Butyldimethylsilyl)oxy]ethoxy]benzoic acid* (**II-2**), *4-Methoxycarbonyloxybenzoic Acid* (**II-3**), *4-Methoxycarbonyloxybenzoic Acid (S)-(−)-1-Phenylethyl Ester* (**II-4**), *and 4-Hydroxybenzoic Acid (S)-(−)-1-Phenylethyl Ester* (**II-5**). The synthesis of all the intermediates leading to the chiral monomer **II** except **II-6** has been reported previously.[13,14]

4-[(S)-(−)-1-Phenylethyl]-4-[(2-hydroxyethoxy)benzoyloxy]-benzoate (**II-6**). Intermediate **II-2** (9.62 g, 32.5 mmol) **II-5** (7.50 g, 30.8 mmol), *N,N′*-dicyclohexylcarbodiimide (DCC; 7.38 g, 35.8 mmol), and 4-pyrrolidinopyridine (0.46 g, 3.3 mmol) were dissolved in 60 mL of anhydrous tetrahydrofuran. The reaction mixture was stirred at room temperature overnight under nitrogen. Upon evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with a 75/25 mixture of methylene and *n*-hexane as the eluent. The resultant silyl ether was hydrolyzed by being stirred in a 60/20/20 mixture of acetic acid, tetrahydrofuran, and water. Upon neutralization with a NaHCO$_3$ solution, column chromatography was carried out on silica gel with methylene chloride containing 0.5% acetone as

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the eluent. Recrystallization from hexane containing 2% ethanol produced 7.50 g in 60%.

2,5-Diiodobenzoic Acid, 4′-{4″-[((S)-(−)-1‴-Phenylethyl)benzoyloxy]benzyloxy}-2-ethyloxy Ether (**II**). Chiral monomer **II** was prepared following the same procedure as for the nematic monomer **I**, except recrystallization from a 20/80 mixture of acetone and ethanol to obtain a 86% yield. ^{1}H NMR: δ 8.20−7.00 (m, aromatic, 16 H), 6.16 (q, $-\mathrm{COOC}H(\mathrm{CH}_3)$, 1H), 4.75 (t, $\mathrm{COOC}H_2$, 2H), 4.43 (t, $\mathrm{ArOC}H_2$, 2H), 1.70 (d, $\mathrm{CHC}H_3$, 3H). Anal. Calcd: C, 48.84; H, 3.17; N, 0.00; I, 33.29. Found: C, 49.03; H, 2.98; N, 0.00; I, 33.69.

Nematic and Chiral−Nematic Polymers **III-x**. The procedure for Ni(0)-mediated polymerization is illustrated with copolymer **III-0.23** as follows. Bis(1,5-cyclooctadiene)nickel(0) ($\mathrm{Ni(COD)_2}$; 0.84 g, 3.03 mmol), 2,2′-dipyridyl (0.47 g, 3.03 mmol), and 1,5-cyclooctadiene (0.33 g, 3.03 mmol) were dissolved in 8 mL of anhydrous DMF. To this solution were added **I** (0.90 g, 1.38 mmol) and **II** (0.45 g, 0.59 mmol). Precautions against oxygen and moisture were taken by preparing the reaction mixture in a glovebox. Polymerization was carried under argon at 55 °C overnight. The crude product was precipitated into 100 mL of methanol containing 2 mL of concentrated hydrochloric acid. The precipitate was filtered and washed sequentially with ethanol, basic EDTA, acidic EDTA, water, and ethanol. The resultant solid was slurried in methylene chloride, and the insolubles were filtered off. The methylene chloride solution was washed sequentially with basic EDTA, acidic EDTA, water, and brine before being dried over anhydrous $\mathrm{MgSO_4}$. The solution was reduced to 6 mL in volume for precipitation into 80 mL of methanol. A 0.61 g (59%) of copolymer **III-0.23** was collected. (**III-0.00**) ^{1}H NMR: δ 8.50−6.80 (m, aromatic, 11H), 4.50−3.70 (m, $\mathrm{COOC}H_2(\mathrm{CH}_2)_4\mathrm{C}H_2\mathrm{OAr}$, 4H), 2.00−1.00 (m, $\mathrm{COOCH}_2(\mathrm{C}H_2)_4\mathrm{CH}_2\mathrm{OAr}$, 8H). Anal. Calcd: C, 78.56; H, 5.84; N, 3.53. Found: C, 78.42; H, 6.03; N, 3.41. (**III-0.07**) ^{1}H NMR: δ 8.50−6.50 (m, aromatic, $x(26\mathrm{H}) + (1 - x)(11\mathrm{H})$), 6.14 (br, $-\mathrm{COOC}H(\mathrm{CH}_3)$, xH), 4.70−3.70 (m, $\mathrm{COOC}H_2$-$(\mathrm{CH}_2)_4\mathrm{C}H_2\mathrm{OAr}$ and $\mathrm{COO(C}H_2)_2\mathrm{OAr}$, $x(4\mathrm{H}) + (1 - x)(4\mathrm{H})$), 1.90−1.10 (m, $-\mathrm{C}H_3$ and $\mathrm{COOCH}_2(\mathrm{C}H_2)_4\mathrm{CH}_2\mathrm{OAr}$, $x(3\mathrm{H}) + (1 - x)(8\mathrm{H})$). Anal. Calcd: C, 78.07; H, 5.74; N, 3.20. Found: C, 77.60; H, 5.83; N, 3.12. (**III-0.12**) ^{1}H NMR: δ 8.50−6.50 (m, aromatic, $x(26\mathrm{H}) + (1 - x)(11\mathrm{H})$), 6.13 (br, $-\mathrm{COOC}H(\mathrm{CH}_3)$, xH), 4.70−3.70 (m, $\mathrm{COOC}H_2(\mathrm{CH}_2)_4\mathrm{C}H_2\mathrm{OAr}$ and $\mathrm{COO(C}H_2)_2\mathrm{OAr}$, $x(4\mathrm{H}) + (1 - x)(4\mathrm{H})$), 1.90−1.10 (m, $-\mathrm{C}H_3$ and $\mathrm{COOCH}_2(\mathrm{C}H_2)_4\mathrm{CH}_2\mathrm{OAr}$, $x(3\mathrm{H}) + (1 - x)(8\mathrm{H})$). Anal. Calcd: C, 77.77; H, 5.68; N, 3.01. Found: C, 77.46; H, 5.75; N, 3.01. (**III-0.17**) ^{1}H NMR: δ 8.50−6.50 (m, aromatic, $x(26\mathrm{H}) + (1 - x)(11\mathrm{H})$), 6.14 (br, $-\mathrm{COOC}H(\mathrm{CH}_3)$, xH), 4.70−3.70 (m, $\mathrm{COOC}H_2(\mathrm{CH}_2)_4\mathrm{C}H_2\mathrm{OAr}$ and $\mathrm{COO(C}H_2)_2\mathrm{OAr}$, $x(4\mathrm{H}) + (1 - x)(4\mathrm{H})$), 1.90−1.10 (m, $-\mathrm{C}H_3$ and $\mathrm{COOCH}_2(\mathrm{C}H_2)_4\mathrm{CH}_2\mathrm{OAr}$, $x(3\mathrm{H}) + (1 - x)(8\mathrm{H})$). Anal. Calcd: C, 77.55; H, 5.63; N, 2.86. Found: C, 76.87; H, 5.77; N, 2.67. (**III-0.23**) ^{1}H NMR: δ 8.50−6.50 (m, aromatic, $x(26\mathrm{H}) + (1 - x)(11\mathrm{H})$), δ 6.14 (br, $-\mathrm{COOC}H(\mathrm{CH}_3)$, xH), 4.70−3.70 (m, $\mathrm{COOC}H_2(\mathrm{CH}_2)_4\mathrm{C}H_2\mathrm{OAr}$ and $\mathrm{COO(C}H_2)_2\mathrm{OAr}$, $x(4\mathrm{H}) + (1 - x)(4\mathrm{H})$), δ 1.90−1.10 (m, $-\mathrm{C}H_3$ and $\mathrm{COOCH}_2(\mathrm{C}H_2)_4\mathrm{CH}_2\mathrm{OAr}$, $x(3\mathrm{H}) + (1 - x)(8\mathrm{H})$). Anal. Calcd: C, 77.06; H, 5.54; N, 2.54. Found: C, 76.53; H, 5.58; N, 2.49.

General Characterization Techniques. Chemical structures were elucidated with elemental analysis (performed by Oneida Research Services, Whitesboro, NY) and FTIR (Nicolet 20 SXC) and ^{1}H and ^{13}C NMR (Avance-400, Brüker) spectroscopic techniques. Thermal transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC-7) with a continuous $\mathrm{N_2}$ purge at 20 mL/min. Liquid crystal mesomorphism was characterized with a polarizing optical microscope (DMLM, Leica) equipped with a hot stage (FP82, Mettler) and a central processor (FP90, Mettler); the nematic and cholesteric mesomorphisms were identified with the threaded textures and oily streaks, respectively. Three PLgel mixed-C, 7.5 × 300 mm columns (Polymer Laboratories) were used in a size-exclusion chromatograph equipped with serially arranged UV−vis absorbance detector, 15° and 90° light scattering detector, differential viscometer, and differential refractometer, as described previously.[15] The size-exclusion chromatograph system was operated at 35 °C with uninhibited tetrahydrofuran as the eluent at a flow rate of 0.1 mL/min. A universal calibration curve was constructed using 15 polystyrene standards with a molecular weight ranging from 580 to 2 300 000. Samples in 100 μL were injected at a concentration of 2 mg/mL. The weight-average molecular weight was calculated from the 15° light scattering with correction for anisotropic scattering.

Preparation of Films and Characterization of Optical Properties. Optical elements for the order parameter measurement were fabricated using optically flat, calcium fluoride substrates (1.00 in. diameter × 0.04 in. thickness, Optovac) that are transparent from the infrared region down to 200 nm. Optical elements for the reflection, transmission, and circular polarization measurements were fabricated using optically flat, fused silica substrates (1.00 in. diameter × 1/8 in. thickness, Esco Products) transparent down to 200 nm. In both cases, the substrates were cleaned, spin-coated with Nylon 66, and then buffed with a velvet roller. Sandwiched films were prepared by melting the powders between two substrates at a temperature 20 °C above T_c followed by annealing 20 °C below T_c for 1 h with subsequent cooling at −10 °C/h to room temperature. The film thickness was controlled by glass fiber spacers (EM Industries) to within 4.1 ± 0.2 μm, as determined by the interference fringes from the air gap between the substrates using a UV−vis−near-IR spectrophotometer. Single-substrate films were prepared by spin-coating from a chloroform solution at 2500 rpm. Subsequent air-drying in a laminar flow hood for a few hours and vacuum-drying overnight at room temperature removed the last traces of solvent. The single-substrate film thickness was determined on a white light interferometer (Zygo New View 100).

Orientational order of the cyanobiphenyl pendant was characterized by linear dichroism using a FTIR spectrometer (Nicolet 20 SXC). Two measurements were performed with the transmission axis parallel and perpendicular to the nematic director (i.e., the buffing direction) of the sample. A UV−vis−near-IR spectrophotometer (Perkin-Elmer Lambda 9) was employed to measure light absorption and transmission (both at normal incidence) and reflection (at 15° incidence from the surface normal) at room temperature. An aluminum mirror served as a specular reflection standard, and the results were reported as percent reflectivity of incident unpolarized light. In all measurements, Fresnel reflections from the two air−glass interfaces were accounted for using a reference cell comprising an index-matching fluid sandwiched between two surface-treated substrates. Photoluminescence spectra were collected with a spectrofluorometer (Photon Technology International Quanta Master C-60SE). A liquid light guide (2 mm diameter × 1 m long, Photon Technology International) was used to direct the UV excitation source onto the center of the film through a glass filter (UG11, Schott Glass Technologies). The light guide also served as a polarization randomizer for the excitation source. In the case of circularly polarized photoluminescence (CPPL), polarization analysis was performed via a circular analyzer with maximum polarization efficiency greater than 99% at 425 nm. At 560 nm the efficiency dropped to 90%. In the case of linearly polarized photoluminescence (LPPL), two identical UV−vis linear polarizers were used for the polarization of the incident light and the analysis of the emitted light. Their efficiency was better than 99%, across a wide wavelength range, from 275 to 725 nm. All the polarized photoluminescence (both LPPL and CPPL) spectra were corrected for both the efficiency and the transmission dispersion of the analyzer. The order parameter governing the poly(*p*-phenylene) backbone was determined by the LPPL and CPPL spectra of a nematic and chiral−nematic film, respectively. In all cases, the order parameter was measured with an uncertainty of ±0.05 of the mean.

III. Results and Discussion

The molecular structures of nematic and chiral monomers, **I** and **II** as well as nematic and chiral−nematic

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Table 1. Number- and Weight-Average Molecular Weights and Thermotropic Properties of Poly(*p*-phenylene)s

polymer	$\bar{M}_n$[a] (SEC)	$\bar{M}_w$[a] (SEC)	$\overline{DP}$[b]	$\bar{M}_w$[c] (LS)	DSC (°C)[d]
III-0.00	3380	6320	9	6760	*G* 66 *N* 165−196 *I*
III-0.07	5440	10000	13	10600	*G* 72 *Ch* 168−195 *I*
III-0.12	7050	14500	17	15200	*G* 75 *Ch* 162−192 *I*
III-0.17	3900	8100	9	8170	*G* 70 *Ch* 147−175 *I*
III-0.23	4610	10400	11	10300	*G* 73 *Ch* 153−181 *I*[†]

[a] Number- and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, calculated from the molecular weight distribution measured by SEC with universal calibration using polystyrene standards. [b] Number-average degree of polymerization, $\overline{DP} = \bar{M}_n/\bar{M}_1$, where $\bar{M}_1$ is the nominal molecular weight of a "chiral−nematic repeat unit", i.e., the molecular weights of chiral and nematic repeat units weighted with mole fraction. [c] $\bar{M}_w$ evaluated with the integrated 15° LS signal and the mass injected; agreement between SEC and LS indicating the absence of polymer aggregation. [d] Samples preheated to 200 °C with subsequent cooling to room temperature for gathering heating scans at 20 °C/min on a differential scanning calorimeter; glass transition temperature, T_g, reported as the inflection point across the step change, and clearing temperature, T_c, as the range over which nematic or cholesteric mesomorphism vanishes into an isotropic fluid.

poly(*p*-phenylene)s **III-*x*** were elucidated with analytical as well as ^{1}H NMR spectral data. The chiral mole fraction, *x*, was calculated from the intensities of the two sets of ^{1}H NMR signals centered around δ 6.14 and between δ 4.70 and δ 3.70 ppm. The structures of poly(*p*-phenylene)s were further elucidated with ^{13}C NMR spectra of **I**, **II**, **III-0.00**, and **III-0.23**, which are provided as Supporting Information. On the basis of the accepted Ni(0)-catalyzed polymerization mechanism[16] and reduction with hydrogen chloride as part of the workup procedure,[17] it is believed that the resultant poly(*p*-phenylene)s are terminated with hydrogen atoms. In the presence of ester linkages other than those directly attached to the backbone, the degree of regioregularity could not be assessed with ^{1}H NMR or ^{13}C NMR spectroscopy. However, a multitude of peaks between δ 166.0 and δ 168.8 in the ^{13}C NMR spectrum of nematic homopolymer **III-0.00** seems to indicate the absence of regioregularity[18] in the resultant polymers. The average molecular weight of a repeat unit in **III-*x***), $\bar{M}_1$, was calculated using the molecular weights of monomers **I** and **II** less iodine atoms. Number- and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, were determined from the molecular weight distribution measured with size-exclusion chromatography (SEC) based on universal calibration using polystyrene standards. The ratio, $\bar{M}_n/\bar{M}_1$, yields the number-average degree of polymerization, $\overline{DP}$. The light scattering (LS) signal observed at 15° was employed for an independent evaluation of M_w. The results are presented in Table 1. The fact that the M_w values measured by size-exclusion chromatography agree with those by light scattering to within ±5% on average suggests the absence of aggregation in solution. The depicted polymer structures are consistent with analytical data for which the calculation was performed using the chiral mole fraction determined with ^{1}H NMR spectroscopy and the number average degree of polymerization determined with size-exclusion chromatography and on the basis of the observation that hydrogen atoms represent the end groups. Also reported in Table 1 are the glass transition temperature, T_g, and the nematic-to-isotropic or cholesteric-to-isotropic transition (i.e., clearing) temperature, T_c, based on the 20 °C/min heating scans of samples preheated to 200 °C with subsequent cooling to room temperature.

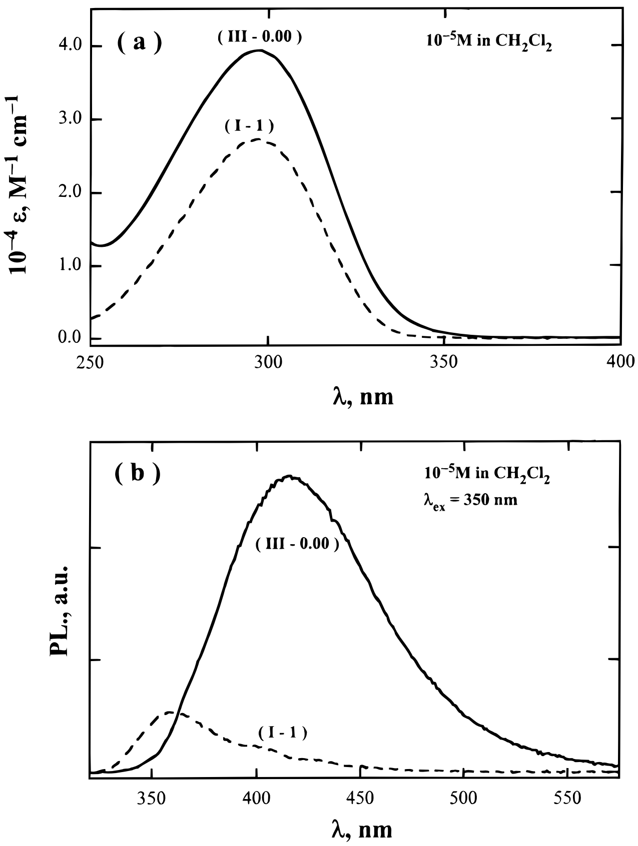

Figure 1. Absorption (a) and photoluminescence (b) spectra of nematic pendant, **I-1**, and nematic homopolymer, **III-0.00**, in methylene chloride at 10^{-5} M repeat units.

The resultant system **III-*x*** represents conjugated polymers functionalized with nematic and chiral-nematic mesogens, the latter being a mixture of the nematic and chiral pendants depicted as **I-1** and **II-6**, respectively, in Scheme 1. Through such functionalization, the conjugated segments are induced to align in a manner dictated by the pendant groups. The orientation of the pendants with respect to the backbone remains to be probed with spectroscopic techniques. The fact that the nematic and chiral pendants do not crystallize independently of the poly(*p*-phenylene) backbone suggests some extent of coupling between two structural elements through the methylenic spacer. In fact, the hybrid system **III-*x*** was found to undergo glass transition, thereby permitting the liquid crystalline order achieved in the mesomorphic melt state (viz., between T_g and T_c) to be frozen in the vitreous state upon cooling. The UV−vis absorption and photoluminescence spectra are compiled in Figure 1 for the nematic precursor depicted as **I-1** in Scheme 1 and the nematic homopolymer **III-0.00** in methylene chloride at 10^{-5} M. The chiral precursor **II-7** is not included in Figure 1 because it was found to have a UV absorption cutoff at 325 nm and to be nonfluorescent with excitation at 350 nm. Figure 1a

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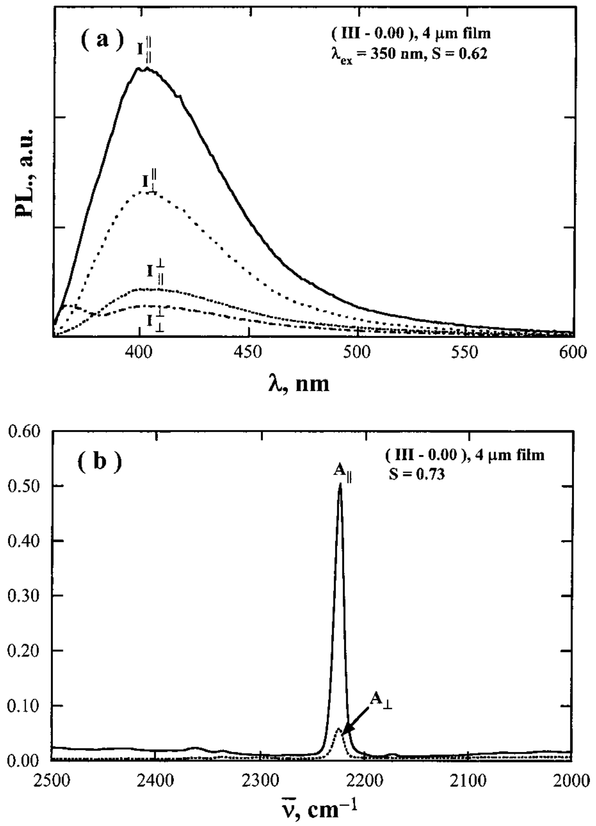

Figure 2. (a) Linearly polarized photoluminescence and (b) FTIR dichroism of a film of nematic homopolymer **III-0.00** for the evaluation of the orientational order parameter governing the conjugated backbone and the nematic pendant, respectively.

indicates that the nematic pendant is essentially nonabsorbing above 340 nm in comparison to the backbone. Excited with λ_{ex} = 350 nm, the poly(*p*-phenylene) backbone showed an emission peak at 410 nm, whereas the cyanobiphenyl group produced a minor emission peak at 360 nm, as shown in Figure 1b.

Anisotropic light absorption and emission involving an axially aligned film were characterized to independently evaluate the orientational order of the conjugated backbone and that of the nematic pendant. A 4 μm thick film was prepared with **III-0.00** between two surface-treated calcium fluoride substrates for the characterization of LPPL. One characteristic of these substrates is the direction in which the nylon alignment coating is buffed with a velvet roller. The buffing direction defines the "nematic director". All the nematic and chiral−nematic films prepared for the present work are contained between two substrates with their directors parallel to each other. The results are shown in Figure 2a, in which the emission intensity is presented with reference to the director. As an example, $I^{\parallel}_{\perp}$ denotes the emission intensity linearly polarized parallel to the director with UV excitation linearly polarized perpendicular to the director. The observed LPPL spectra indicate that the emission intensities parallel to the director are consistently higher than those perpendicular regardless of the polarization state of the excitation source. On the basis of the available data on *p*-terphenyl and other linear luminophores,[19] it is believed that the absorption and emission transition moments of poly(*p*-phenylene) lie parallel to its long axis. It is thus concluded that the axis of poly(*p*-phenylene) lies parallel to the director. On the basis of the linearly polarized intensities observed at 410 nm, the orientational order paramenter, *S*, was evaluated at 0.62 using eq 39 in ref 20 based on a theory of LPPL. Orientational order of the nematic pendant was probed by FTIR dichroism involving the stretching vibration of C≡N (at 2224 cm^{-1}), as shown in Figure 2b. The absorbances parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the nematic director were used to calculate the dichroic ratio, $R = A_{\parallel}/A_{\perp}$, from which the orientational order parameter emerged, $S = (R - 1)/(R + 2)$, with its transition moment lying parallel to the long molecular axis of the cyanobiphenyl group.[20] It was found that $S = 0.73$, indicating that the pendant is also oriented along the director.

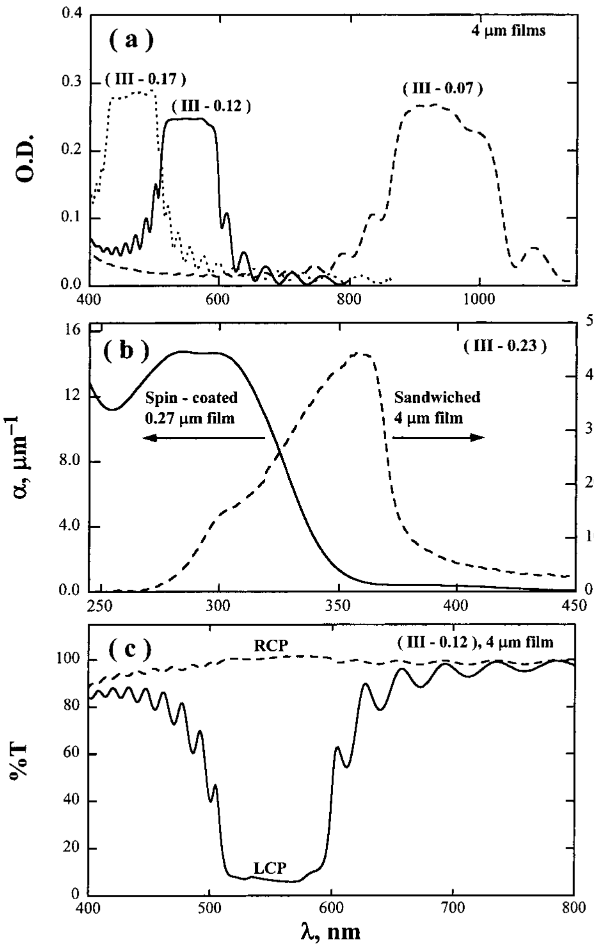

Figure 3. Optical properties of thin films prepared with chiral−nematic copolymers: (a) selective reflection spectra measured in terms of optical density for **III-0.17**, **III-0.12**, and **III-0.07**; (b) absorption coefficient, α, and reflection spectrum measured in terms of reflectivity, %*R*, for **III-0.23**; (c) transmittances of the right- and left-handed circularly polarized (RCP and LCP) light propagating through **III-0.12**.

To appraise the ability of **III-*x*** to form vitrified chiral−nematic films, 4 μm thick films were prepared for the characterization of selective wavelength reflection. Comprising a helical stack of quasinematic layers, a chiral−nematic film is capable of selective reflection

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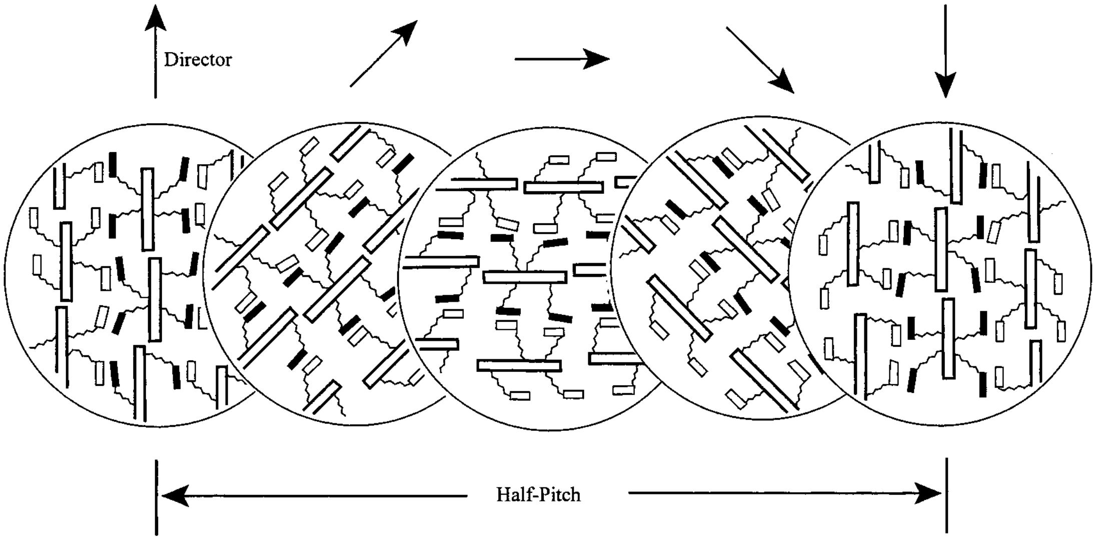

Figure 4. A schematic diagram of the supramolecular structure of a chiral−nematic film with its quasinematic director undergoing a counterclockwise rotation, as stipulated by the left-handed helical structure determined in Figure 3c. Within each layer, the backbone and the nematic pendant are oriented along the director. Note the antiparallel arrangement of nematic pendants, shown as small filled and open rectangles, from neighboring conjugated backbones. The pitch length is defined as the distance along the surface normal to quasinematic layers over which the director completes a 360° rotation.

with simultaneous circular polarization of incident unpolarized light.[10] The result is that the incident intensity is equally divided between the reflected and the transmitted components with opposite handedness in circular polarization. Thus, an optical density of 0.30 is expected of unpolarized light at normal incidence on a perfectly ordered chiral−nematic film. Polymers **III-*x*** were found not to absorb light in the visible or infrared region, where the observed attenuation of incident light can be attributed to reflection. As shown in Figure 3a, chiral−nematic films prepared with **III-*x*** were found to have an increasing selective reflection wavelength, λ_R, at a decreasing x value. At $x = 0.23$ a selective reflection band was observed in the ultraviolet region, part of which was diminished by light absorption between 300 and 350 nm, as shown in Figure 3b. Traditionally, handedness of the helical stack is defined by that of the reflected circularly polarized component.[22] Whereas handedness of a chiral−nematic film is related to the absolute configuration of the chiral pendant, no correlation between the two has been established.[23] To determine the handedness presented by films of **III-*x*** containing (*S*)-(−)-1-phenylethanol, the transmittances of both left- and right-handed circularly polarized light at normal incidence were measured, as illustrated with a film of **III-0.12** in Figure 3c. Since left-handed circularly polarized light is selectively reflected, it is concluded that the film prepared with **III-*x*** presents a left-handed, helical stack of quasinematic layers. Within each layer, both the poly(*p*-phenylene) backbone and the cyanobiphenyl pendant are oriented parallel to the director, as evidenced by LPPL of the nematic film prepared with **III-0.00**. Thus, the supramolecular structure of a chiral−nematic film is as depicted in Figure 4, with the chiral pendants (not shown) providing the rotation between adjacent quasinematic layers. The schematic diagram also reflects the lack of regioregularity and the antiparallel arrangement of cyanobiphenyl pendants from neighboring poly(*p*-phenylene) backbones.

To determine the orientational order parameter governing the helically stacked π-conjugated segments, a 4 μm thick film of **III-0.07** was prepared for the characterization of CPPL. With unpolarized excitation at 350 nm targeting the poly(*p*-phenylene) backbone, an emission peak emerged between 350 and 550 nm, which is far removed from the selective reflection band centered at 945 nm of the **III-0.07** film. At normal incidence of both excitation and emission, left- and right-handed circularly polarized emission intensities, I_L and I_R, were measured for the calculation of the degree of circular polarization, $g_e \equiv 2(I_L - I_R)/(I_L + I_R)$.

The experimental setup described previously[24] was simplified with a liquid light guide directing the excitation source directly onto the film. On the basis of the CPPL spectra, $g_e = -0.35$ was evaluated at 410 nm. The fact that a significant extent of CPPL resulted from emission outside the selective reflection band can be attributed to the circular polarization of linearly polarized emission originating in all quasinematic layers.[24] For light emission outside the selective reflection band of a chiral−nematic film, a CPPL theory has been constructed and validated with experimental observations without resorting to adjustable parameters.[20] The observed g_e value was employed to evaluate S governing the helically stacked poly(*p*-phenylene) backbones as the predominant light emitter with excitation at 350 nm, according to Figure 1b. To accomplish this, the average refractive index ($\bar{n}$) and the optical birefringence (Δn) of the quasinematic layer at both the excitation and emission wavelengths were determined a priori. The optical properties of a nematic homopolymer **III-0.00**, reported previously[9] served as the basis for parameter estimation: $\bar{n} = 1.75$ and $\Delta n = 0.30$ at 350 nm and $\bar{n} =$

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1.63 and $\Delta n = 0.25$ at 410 nm. In addition, the average absorbance per unit thickness reported previously[9] for the nematic homopolymer, 0.651 μm^{-1} at 350 nm, was adopted here as another input parameter. With the absorption and emission transition moments lying along the conjugated backbone, the agreement between the predicted and the observed g_e values was secured with $S = 0.67$. Thus, the orientational order characterizing quasinematic layers comprising a chiral−nematic film is consistent with that observed in a nematic film, $S = 0.62$, within an experimental uncertainty of ±0.05.

Summary

A series of poly(*p*-phenylele)s functionalized with nematic and chiral pendants were synthesized and characterized as a novel class of multifunctional optical materials. Elemental analysis and ^{1}H and ^{13}C NMR spectroscopic techniques were employed to determine the lack of regioregularity with hydrogen atoms as the terminal groups to poly(*p*-phenylene)s. The degree of polymerization was found to vary from 9 to 17 by size-exclusion chromatography with universal calibration. A uniaxially aligned film was prepared with homopolymer to assess the orientation of the conjugated backbone and the nematic pendant with reference to the nematic director as defined by the direction of buffing on the substrates. With an excitation source at 350 nm, LPPL revealed the alignment of the conjugated backbone with the nematic director and an orientational order parameter, $S = 0.62$. The cyanobiphenyl pendant was found to align with the nematic director as well, as shown by FTIR dichroism of the C≡N stretching vibration observed at 2224 cm^{-1}, resulting in $S = 0.73$. At a decreasing chiral mole fraction, films prepared with chiral−nematic copolymers showed a selective reflection band in the ultraviolet to visible and infrared regions. Moreover, the chiral−nematic film was found to consist of a left-handed helical stack of quasinematic layers with (*S*)-(−)-1-phenylethanol as the chiral moiety. The supramolecular structure representing the chiral−nematic film was further characterized with CPPL. On the basis of a recent theory, the orientational order of the conjugated backbone was evaluated at $S = 0.67$. The agreement between the *S* values determined with the LPPL and CPPL techniques, 0.62 versus 0.67 within experimental uncertainty, validates the proposed supramolecular structure on the basis of which theories governing light absorption, emission, and propagation in structured media were constructed.

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Supporting Information Available: ^{13}C NMR spectra of **I**, **II**, **III-0.00**, and **III-0.23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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