Macromolecules **1998,** *31,* 3391−3393

Synthesis and Characterization of Thermotropic Chiral-Nematic Polythiophenes

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Received January 21, 1998
Revised Manuscript Received April 3, 1998

Introduction. Over the past 2 decades π-conjugated polymers and oligomers have been extensively explored for various electronic and optical technologies. In particular, intensive efforts have been devoted to appraising the potential of these materials for use as thin film transistors,[1] light-emitting diodes,[2,3] and organic lasers,[4,5] for which polythiophene (PT) and poly(*p*-phenylenevinylene) (PPV) derivatives are among the most widely studied. Recently, liquid crystalline (LC) conjugated polymers with an above-ambient glass transition temperature, T_g, have emerged as a new class of materials. Various modes of order arising from molecular self-assembly in the mesomorphic temperature range can be frozen in ordered solid films, which offer unique properties induced or enhanced by order. Nematic and smectic conjugated polymers presenting a uniaxial and stratified molecular arrangement, respectively, have been demonstrated to be capable of linearly polarized photo- and electroluminescence (PL and EL).[6,7] A helical molecular arrangement readily accomplished through chiral-nematic (i.e., cholesteric) mesomorphism has also been shown to be capable of high degrees of circularly polarized PL[8] in comparison to a PT backbone carrying chiral pendants.[9] An integration of PT or PPV segments into chiral-nematic molecular structures represents a step toward improving charge injection and transport properties. To the best of our knowledge, no chiral-nematic LC polymers containing PT or PPV conjugated segments have been reported to date. In what follows, it will be demonstrated that chiral-nematic mesomorphism can be realized with a PT skeleton to which nematogenic and chiral pendants are chemically bonded.

Experimental Section. Reagents and Chemicals. Bis(1,5-cyclooctadiene)nickel(0), Ni(cod)$_2$, was acquired from Organometallics Inc. All other reagents and chemicals were used as received from Aldrich Chemical Co.: 4-hydroxy-4′-biphenylcarbonitrile (97%), 6-chlorohexanol (97%), cesium carbonate (99%), triphenylphosphine (PPh$_3$, 99%), diethyl azodicarboxylate (DEAD, 97%), *N*-bromosuccinimide (NBS, 99%), cholesterol (95%), ethyl isocyanatoacetate (95%), sodium hydroxide (95%), 1,5-cyclooctadiene (cod, 99%+), 2,2′-bipyridyl (bpy, 99%+), ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTA, 99%+).

Synthesis of Monomers and Polymers. Monomers **I** and **II** were synthesized according to Schemes 1 and 2 following established procedures.[10] Their chemical structures were elucidated by elemental analysis and ^{1}H NMR spectroscopy. Monomer **I**. Anal. Calcd for $C_{24}H_{21}NO_3SBr_2$: C, 51.17; H, 3.76; N, 2.49; S, 5.69; Br, 28.37. Found: C, 50.90; H, 3.66; N, 2.45; S, 5.79; Br, 28.98. Proton NMR spectral data (CDCl$_3$): δ 1.40−2.00 (m, 8H, $-(C\mathit{H}_2)_4-$), δ 4.05 (t, 2H, $ArOC\mathit{H}_2CH_2$), δ 4.35 (t, 2H, $CO_2C\mathit{H}_2CH_2$), δ 7.00 and 7.55−7.80 (4 sets of d, 8H, biphenyl aromatic *H*s), δ 7.35 (s, 1H, thiophene *H*). Monomer **II**. Anal. Calcd for $C_{35}H_{51}NO_4SBr_2$: C, 56.68; H, 6.93; N, 1.89; S, 4.32; Br, 21.55. Found: 56.81; H, 7.03; N, 2.01; S, 4.42; Br, 21.13. ^{1}H NMR spectral data (CDCl$_3$): δ 0.60−2.40 (m, 44H, cholesteryl *H*s), δ 4.00 (d, 2H, $O_2CC\mathit{H}_2NH$), δ 4.40−4.60 (m, 1H, $CO_2-C\mathit{H}-CH_2$ in cholesteryl ring), δ 5.05 (s, 2H, $ArC\mathit{H}_2O_2C$), δ 5.40 (m, 1H, $C{=}C\mathit{H}-$ in cholesteryl ring), δ 7.00 (s, 1H, thiophene *H*). Reaction Scheme 3 outlines the synthesis of a random copolymer (**III−*x***), where *x* denotes the chiral mole fraction. The experimental procedures reported by Yamamoto et al.[11] for polymerization, catalyzed by Ni(cod)$_2$ and bpy, and for product isolation and purification were followed with a typical yield of 70%.

Characterization Techniques. Chemical structures were elucidated with elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, New York), the FTIR (Nicolet 20 SXC) and ^{1}H NMR (QE−300, GE) spectroscopic techniques. The chiral mole fraction, *x*, of polymers was also determined with an integration of relevant signals, and the values were found to be fairly close to the feed composition. Thermal transition temperatures were determined by DSC (Perkin-Elmer DSC-7) with a continuous nitrogen purge at 20 mL/min. Liquid crystalline mesomorphism was identified with a polarized optical microscope (Leitz Orthoplan-Pol) equipped with a hot stage (FP82, Mettler) and a central processor (FP80, Mettler). A UV−vis spectrophotometer (Lambda 9, Perkin-Elmer) was used to gather absorption spectra in dilute solution. A gel permeation chromatograph was employed to determine the molecular weight distribution with reference to polystyrene standards, from which the number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were calculated.

Results and Discussion. Thermotropic properties of mesogenic monomers **I** and **II**, a nematic homopolymer (**III-0.00**), an amorphous copolymer (**III-0.42**), and three cholesteric copolymers, (**III-0.07**, **-0.16**, and **-0.29**), are presented in Table 1. As illustrated in Figure 1 for **III-0.42**, the ^{1}H NMR spectrum is simply a composite of those of the two monomers; the absence of monomer peaks in the GPC chromatogram is a further evidence of chemical purity. All these polymers were found to be readily soluble in common organic solvents: methylene chloride, chloroform and tetrahydrofuran. DSC thermograms of the pristine samples of **I** and **II** revealed melting points of 79 and 95 °C, respectively, without showing any mesophases up to 150 °C. Subsequent cooling at a rate of −20 °C/min to −65 °C produced

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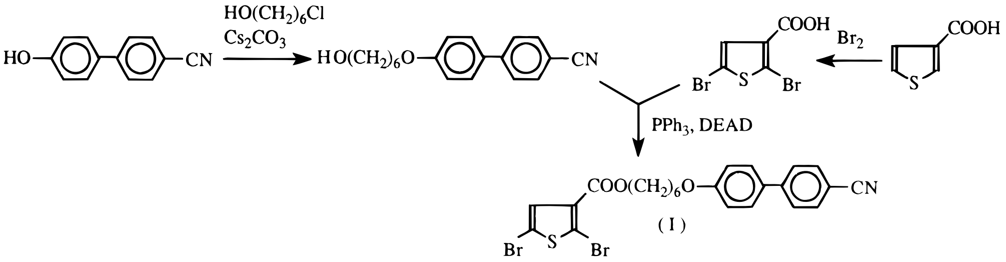
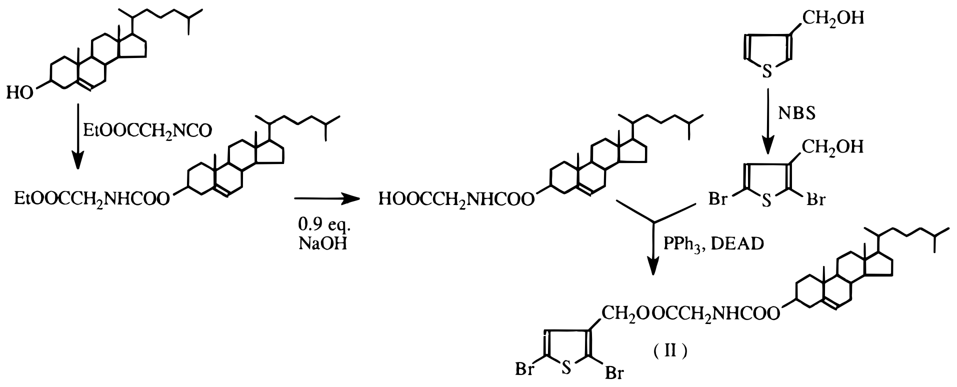
S0024-9297(98)00073-4 CCC: $15.00

Scheme 1



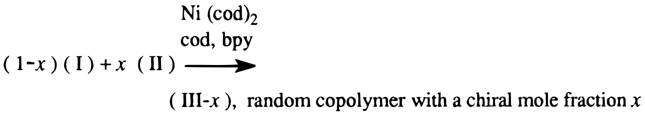
(I)

Scheme 2



(II)

Scheme 3



$$(1\text{-}x)(\text{I}) + x\,(\text{II}) \xrightarrow[\text{cod, bpy}]{\text{Ni (cod)}_2} (\text{III-}x),\ \text{random copolymer with a chiral mole fraction } x$$

Table 1. Properties of Thiophene Monomers I and II and Polythiophenes (III-*x*) with a Chiral Mole Fraction *x*[a]

material system	$\bar{M}_n$	$\bar{M}_w$	transition temps (°C)[b]
I	NA	NA	G, −4, N, 33, I
II	NA	NA	G, 30, Ch, 42, I
III-0.00	2635	4244	G, 74, N, 144, I
III-0.07	1734	2082	G, 61, Ch, 112, I
III-0.16	3861	22554	G, 90, Ch, 132, I
III-0.29	3814	17235	G, 88, Ch, 116, I
III-0.42	3882	10585	G, 95, I

[a] Number- and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$ in g/(g mol), were calculated using the molecular weight distributions determined by GPC with reference to polystyrene standards. [b] Thermotropic transition temperatures were determined with DSC heating scans at 20 °C/min of quenched glassy samples with nematic and cholesteric mesophases idetified by threaded textures and oily streaks, respectively. Symbols: G, glassy; N, nematic; Ch, cholesteric, I, isotropic.

nematic and cholesteric glasses out of **I** and **II** with T_g located at −4 and +30 °C, respectively. As indicated by thermal transition temperatures, polymerization of **I** and **II** results in an elevation in both T_g and T_c with an increased separation between the two temperatures. The reported nematic and cholesteric mesophases were identified by the threaded textures and oily streaks, respectively. Figure 2 shows the oily streaks exhibited by **III-0.07** processed and annealed into a 14 μm film. It should be remarked that a prior effort to synthesize thiophene homopolymer carrying pendant cyanobiphenyl groups produced a mostly insoluble sample, and the soluble part was found to be infusible.[12]

The UV−vis absorption spectra of all samples in methylene chloride at high dilution (~10^{-5} M) are compiled in Figure 3, in which the molar extinction coefficient, ϵ, was calculated on the basis of thiophene repeat units. As revealed by spectra a and b, monomers **I** and **II** are both completely transparent in the spectral region above 350 nm. Monomer **II** has an absorption maximum at 255 nm that can be attributed to the $\pi-\pi^*$ transition of the thiophene unit. Therefore, the broad absorption peaks between 350 and 500 nm observed for all polymers arise from the formation of thiophene backbones. The absorption maxima between 285 and 300 nm originate in the $\pi-\pi^*$ transition of the cyanobiphenyl group. Note the decreasing ϵ with an increasing x, suggesting self-consistency of the data on UV−vis absorption and number-average molecular weight of polymer samples. Because of the relatively low $\bar{M}_n$ of **III-0.07**, the absorption band is blue-shifted in comparison to those of the rest of polymers. An alternative approach to chiral-nematic conjugated polymers as presently pursued would be doping conjugated segments into a chiral-nematic host. Two problems may arise: destruction of mesomorphism by the dopant and phase separation because of limited miscibility. The present work represents a more desirable approach to multifunctional polymers, especially at a high content of conjugated segments. The conjugated segments can be oriented helically with a tunable pitch length by adjusting the chiral mole fraction. We are working on dichroism and polarized luminescence using glassy

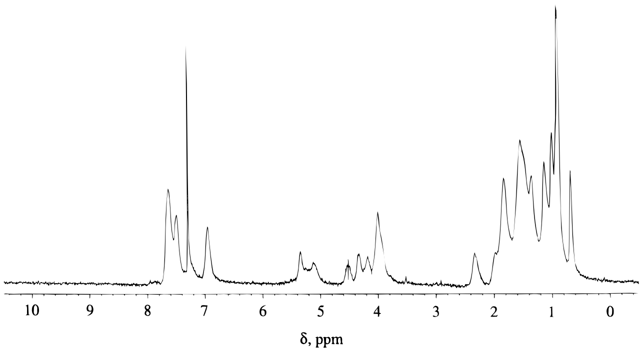


Figure 1. ^{1}H NMR spectrum of copolymer **III-0.42** in $CDCl_3$.

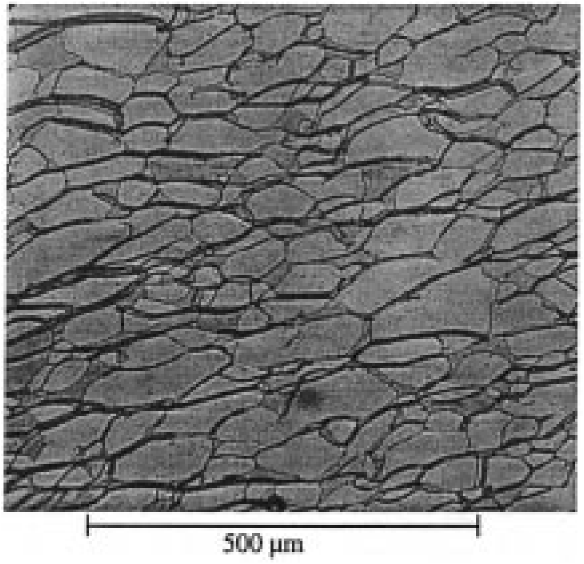


Figure 2. Oily streaks exhibited by copolymer **III-0.07** processed into a 14 μm thick film.

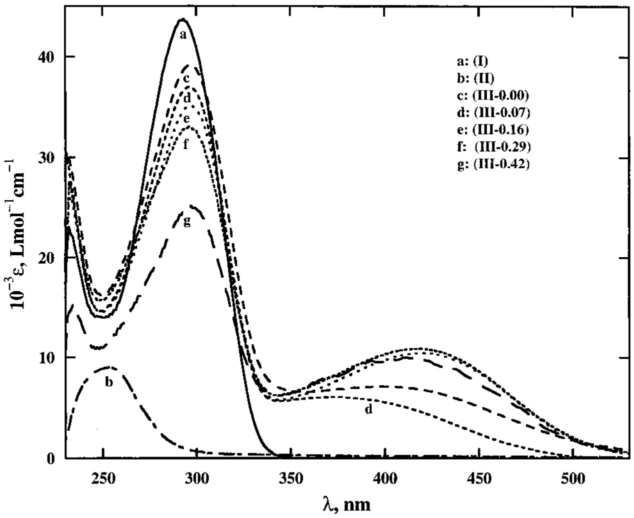


Figure 3. UV−vis absorption spectra of monomers and polymers in CH_2Cl_2 at concentrations on the order of 10^{-5} M (in thiophene repeat units).

nematic and chiral-nematic polymer films, and the results will be reported in a forthcoming paper.

Summary. A new series of thermotropic chiral-nematic thiophene copolymers was synthesized and characterized. The presence of conjugated thiophene segments was supported by UV−vis absorption spectra and GPC data. This class of materials allows for a spontaneous assembly of the conjugated thiophene segments into a uniaxial and helical arrangement via nematic and chiral-nematic mesomorphism, respectively. The resultant macroscopic order can be frozen into a glassy state with a T_g above 60 °C and a T_c above 110 °C depending on the chiral mole fraction and the number of repeat units in the conjugated segments. Work on dichroism and luminescence using well-aligned glassy films is in progress.

Acknowledgment. The authors wish to express their gratitude for the support of this work by the National Science Foundation under CHE-9120001. In addition, B.M.C. and S.H.C. were supported by NSF under CTS-9500737; K.L.M. and S.H.C. were also supported by the Department of Energy, Division of Inertial Confinement Fusion under Cooperative Agreement No. DE-FC03-92SF19460 with the Laboratory for Laser Energetics.

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