New Ferroelectric Liquid-Crystalline Polysiloxanes Containing Cyanohydrin Chiral Mesogens: L-Norleucine Series

I. G. Shenouda and L.-C. Chien*

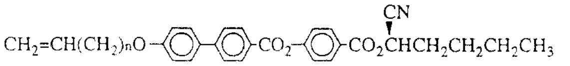
Liquid Crystal Institute and NSF ALCOM Center, Kent State University, Kent, Ohio 44242

Received March 11, 1993; Revised Manuscript Received June 24, 1993®

ABSTRACT: The synthesis and mesomorphic properties of three liquid-crystalline side-chain polymers with a cyanohydrin chiral center are described. The optically active cyanohydrin moiety was synthesized from the naturally occurring optically active amino acid L-Norleucine. The polysiloxanes were prepared by the hydrosilation of cyanohydrin monomers with poly(hydromethylsiloxane). All the polymers exhibit a wide range of the chiral smectic C phase (S_c*).

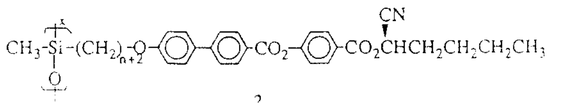
Introduction

Ferroelectricity in liquid crystals has gained considerable attention in the last few years in both basic research and potential technological applications. Of the various physical properties required of the ferroelectric liquid-crystalline (FLC) material, spontaneous polarization (Ps) is the most important for fast switching. A high Ps value and short response time could be achieved with materials having a dipolar chiral center connected directly to an aromatic core portion. The synthesis of chiral smectic C liquid crystal polymers having a chiral center in its side chain was first demonstrated by Shibaev et al.[1] and has been reviewed by Le Barny and Dubois.[2] The interest in ferroelectric liquid crystals and particularly in the S_c* phase increased substantially when a bistable fast-switching nonpolymeric display device operating in the S_c* phase was demonstrated.[3] Since then, the interest in these polymers lies in the possibility of having high values of spontaneous polarization (Ps).[4] Our previous series of FLCs with a cyanohydrin chiral center derived from the L-valine showed high Ps values over 500 nC/cm^2.[5] This paper describes the synthesis and properties of three monomers related to **1a–c** containing a cyanohydrin chiral center derived from the L-norleucine and their siloxane polymers **2a–c**.



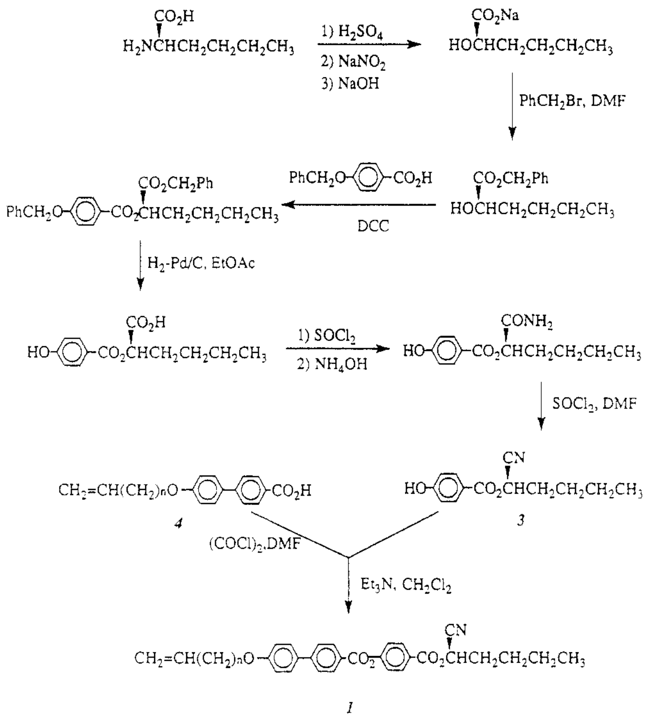
1

	a	b	c
n	2	4	9



2

Scheme I



Experimental Section

Characterization of Monomers and Polymers. The infrared spectra were run on a Pye-Unicam 3-200 spectrometer and NMR spectra on a Varian 200-MHz spectrometer. The purities of the monomers were checked using a Waters HPLC-600E with Waters 994 photodiode array detector. Transition temperatures for intermediates and monomers were determined using a Leitz-Laborlux S polarizing microscope fitted with a Mettler FP-5 heating stage, and for polymers they were determined using a Perkin-Elmer DSC-7 differential scanning calorimeter. The degree of polymerization for polymers was determined using a Waters 510 HPLC with a Waters 410 differential refractometer. X-ray diffraction patterns were obtained from a Siemens X-1000 system with a Laue camera using Ni-filtered Cu radiation on an unoriented sample at different temperatures after annealing at their phase transition temperature for 1 h.

Synthesis. The synthesis of the L-norleucine FLC series was carried out as shown in Scheme I. The detailed synthesis of 4-carboxy-4′-(4-butenyloxy)biphenyl (**4a**), 4-carboxy-4′-(6-hexenyloxy)biphenyl (**4b**), and 4-carboxy-4′-(11-undecenyloxy)biphenyl (**4c**) has been reported in a previous publication.[5]

(*S*)-1-Cyanopentyl 4′-Hydroxybenzoate (3). This compound was prepared in the same manner as mentioned in a previous publication,[5] using L-norleucine. Yield: 72.7%. IR (Nujol, cm^{-1}): 3300, 1730. NMR ($CDCl_3$): δ 0.95 (t, 3H, CH_3), 1.37–1.61 (m, 4H, C_2H_4), 1.99–2.10 (m, 2H, $CHCH_2$), 5.55 (t, 1H, CO_2CH), 6.90 (d, 2H, Ar), 7.95 (d, 2H, Ar).

Preparation of Monomer 1a. The acid **4a** (1.15 g, 4.3 mmol) was initially converted into the acid chloride by reacting with oxalyl chloride (1.1 g, 8.6 mmol) and sieve-dried dimethylformamide (2 drops) in sieve-dried benzene (15 mL) for 3 h at room temperature. The excess oxalyl chloride and the solvent were removed by distillation under reduced pressure. The crude acid chloride residue was dissolved in sieve-dried dichloromethane (10 mL) and added dropwise to a cold solution (0–5 °C) of compound **3** (1.0 g, 4.3 mmol) and sieve-dried triethylamine (TEA;

---

* Author to whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts*, August 15, 1993.

0024-9297/93/2226-5020$04.00/0

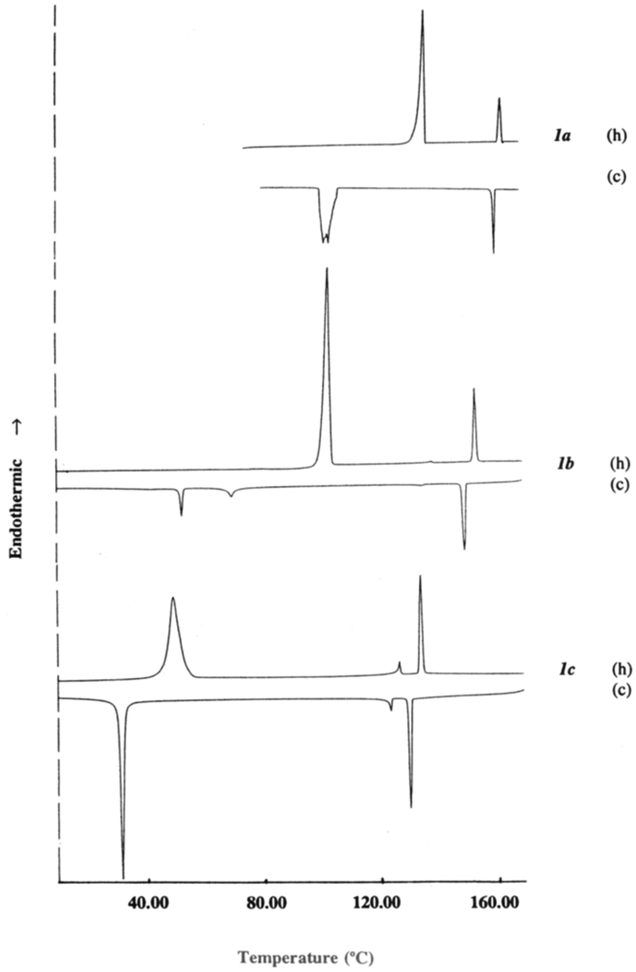


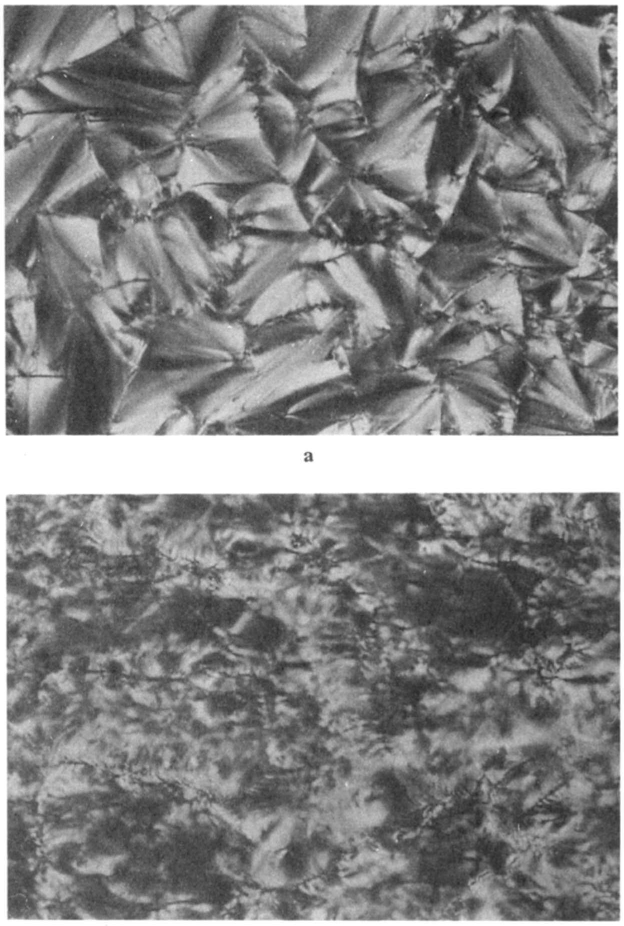
Figure 1. DSC thermograms of monomers **1a–c**: (h) represents the heating curve, and (c) represents the cooling curve.

1 mL) in sieve-dried dichloromethane (10 mL). The reaction mixture was stirred at room temperature overnight, washed with 5% hydrochloric acid and water, dried ($MgSO_4$), and filtered. The solvent was removed from the filtrate, and the remaining crude product was purified by column chromatography on silica gel (60–100 mesh). Elution with dichloromethane gave the pure product, which was recrystallized from EtOH to give compound **1a**. Yield: 1.8 g (87.0%). IR (Nujol, cm^{-1}): 1720, 1640. NMR ($CDCl_3$): δ 0.97 (t, 3H, CH_3), 1.38–1.66 (m, 4H, C_2H_4), 2.00–2.12 (m, 2H, $CHCH_2$), 2.53–2.63 (m, 2H, $CH_2{=}CHCH_2$), 4.08 (t, 2H, $ArOCH_2$), 5.10–5.24 (m, 2H, $CH_2{=}CH$), 5.60 (t, 1H, CHCN), 5.82–6.05 (m, 1H, $CH_2{=}CH$), 7.01 (d, 2H, Ar), 7.37 (d, 2H, Ar), 7.60 (d, 2H, Ar), 7.70 (d, 2H, Ar), 8.15 (d, 2H, Ar), 8.23 (d, 2H, Ar).

Preparation of Monomer 1b. This compound was prepared in the same manner as compound **1a**. Yield: 95.9%. IR (Nujol, cm^{-1}): 1730, 1640. NMR ($CDCl_3$): δ 0.97 (t, 3H, CH_3), 1.38–1.67 (m, 6H, C_3H_6), 1.77–1.88 (m 2H, CH_2), 2.01–2.20 (m 4H, C_2H_4), 4.03 (t, 2H, $ArOCH_2$), 4.96–5.10 (m, 2H, $CH_2{=}CH$), 5.60 (t, 1H, CHCN), 5.97 (m, 1H, $CH_2{=}CH$), 7.00 (d, 2H, Ar), 7.37 (d, 2H, Ar), 7.60 (d, 2H, Ar), 7.70 (d, 2H, Ar), 8.15 (d, 2H, Ar), 8.23 (d, 2H, Ar).

Preparation of Monomer 1c. This compound was prepared in the same manner as compound **1a**. Yield: 96.4%. IR (Nujol, cm^{-1}): 1730, 1640. NMR ($CDCl_3$): δ 0.97 (t, 3H, CH_3), 1.32–1.65 (m, 16H, C_8H_{16}), 1.74–1.90 (m, 2H, CH_2), 2.01–2.11 (m, 4H, C_2H_4), 4.01 (t, 2H, $ArOCH_2$), 4.90–5.03 (m, 2H, $CH_2{=}CH$), 5.60 (t, 1H, CHCN), 5.72–5.94 (m, 1H, $CH_2{=}CH$), 7.07 (d, 2H, Ar), 7.37 (d, 2H, Ar), 7.60 (d, 2H, Ar), 7.70 (d, 2H, Ar), 8.15 (d, 2H, Ar), 8.23 (d, 2H, Ar).

Synthesis of Polymers 2a–c. A stirred mixture of monomer **1** (1.0 mmol), poly(methylhydrosiloxane) (0.9 mmol), 5% hexachloroplatinic acid in isopropyl alcohol (2 drops) , and sodium-dried toluene (5 mL) was heated under N_2 and anhydrous conditions at 110 °C for 24 h. The solvent was removed under reduced pressure and the crude polymer purified by precipitation from solution in dichloromethane by the addition of petroleum ether or methanol. The polymer was isolated by centrifugation and this procedure repeated until the product was shown by TLC to be free from monomer.


a

b

Figure 2. Photomicrographs of monomer **1c**: (a) focal-conic fan texture of the smectic A phase; (b) broken fan texture of the smectic C phase.

Results and Discussion

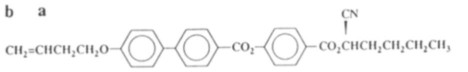
Liquid-Crystalline Behavior of Monomers 1a–c. Monomers **1a–c** were characterized, and their properties are reported. The DSC thermogram of **1a–c** is shown in Figure 1. The heating cycle thermogram of **1c** contained two endotherms of the phase transitions. A small endotherm ($\Delta H = 0.97$ J/g) indicates the second-order phase transition of the chiral smectic C phase to smectic A phase. The large endotherm ($\Delta H = 7.78$ J/g) is the phase transition of the smectic A to isotropic phase. Upon heating monomer **1c** on the hot stage of the polarizing microscope, the focal-conic fan texture of smectic C and A appeared. On cooling from the isotropic state to 134 °C, the focal-conic fan texture of the smectic A phase appeared (Figure 2a). On continued cooling to 127 °C, a broken fan and straited texture appeared in (Figure 2b). These reversible observations indicate that monomer **1c** is an enantiotropic liquid crystal. Both monomers **1a** and **1b** exhibit the supercooling behavior. Monomer **1b** exhibits a monotropic smectic B phase. The thermal stability of the S_c* phase increases with an increase of the flexible chain length. The transition temperatures of the three synthesized monomers are summarized in Table I.

Polymers. The prepared polymers are soluble in common solvents. The degree of polymerization of these

Table I. Transition Temperatures of Monomers *1a–c*[a]

		transition temp (°C)				
monomer	*n*	K	B	C*	A	I
1a	2	116.0			137.0	165.6
1b	4	55.3	(72.7)	103.5	137.7	153.4
1c	9	36.6		52.8	127.6	134.3

[a] K, crystal; C*, chiral smectic C; A, smectic A; I, isotropic phase.



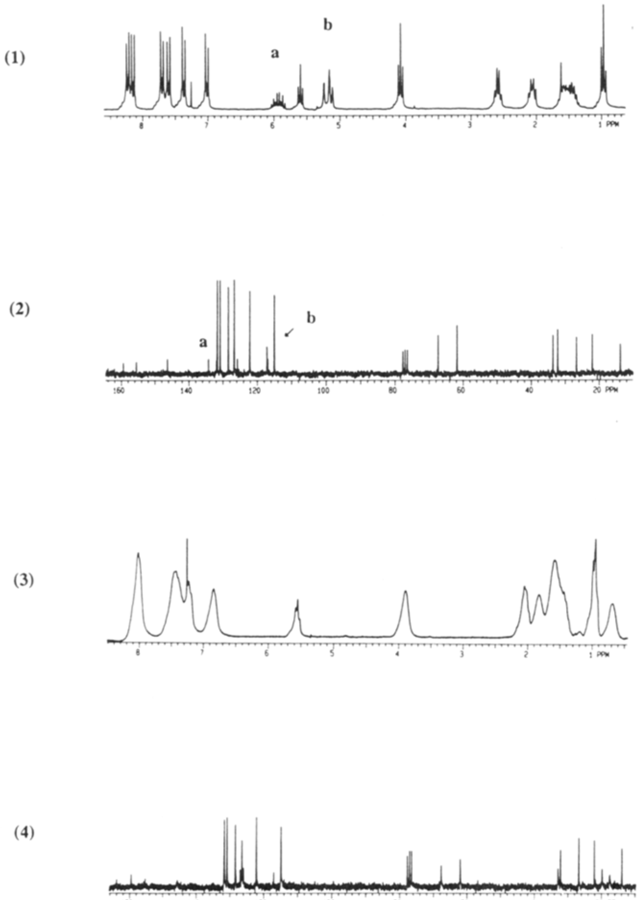


Figure 3. ^{1}H and ^{13}C NMR spectra of monomer **1a** (1 & 2) and polymer **2a** (3 & 4).

Table II. Transition Temperatures of Polymers *2a–c*[a]

polymer	*n*	transition temp
2a	2	K 43.9 C* 91.0 A 202.3 I
2b	4	g 30.6 C* 221.6 I
2c	9	g 26.2 K 73.4 C* 252.0 I

[a] g: glass transition.

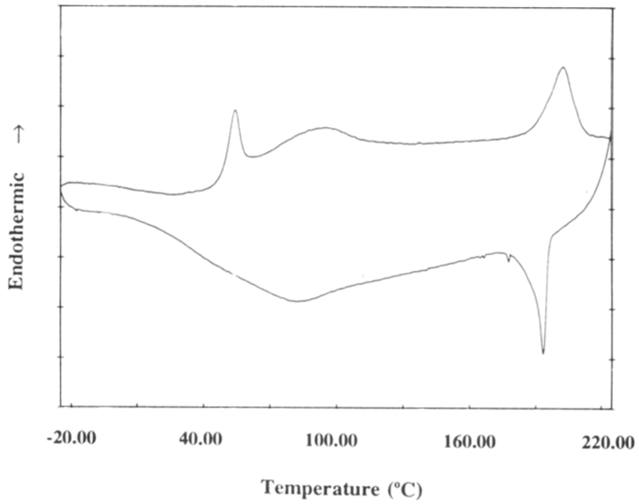


Figure 4. DSC thermogram of polymer **2a**.

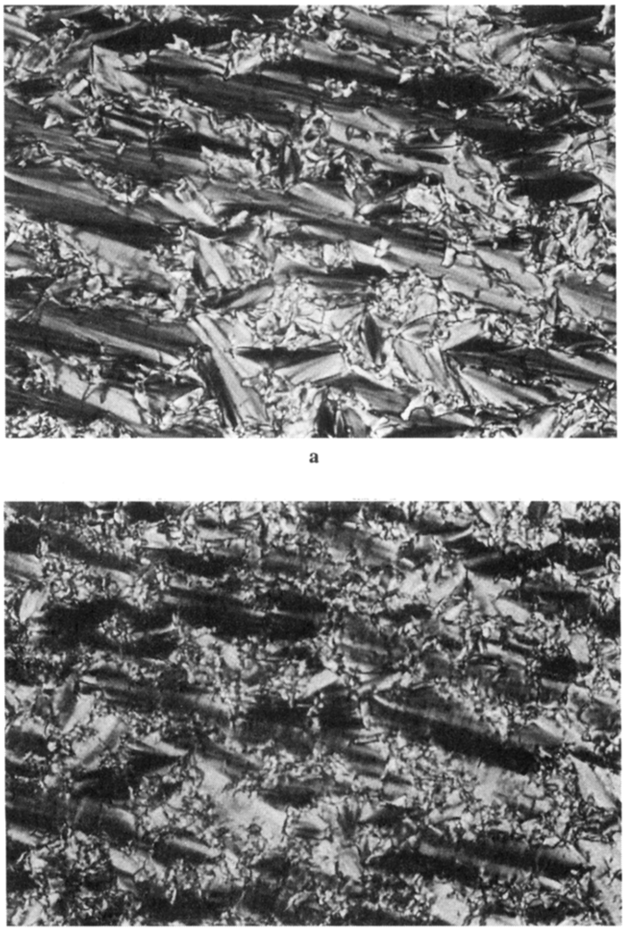


Figure 5. Photomicrographs of polymer **2a**: (a) focal-conic fan texture of the smectic A phase; (b) broken fan texture of the smectic C phase.

polymers is 35, according to the siloxane polymers used in the polymerizations. The NMR spectra of the polymers were obtained and used to compare with those of the monomers (see Figure 3). The transition temperatures for these polymers are summarized in Table II. A DSC thermogram of polymer **2a** is shown in Figure 4. Polymer **2a** showed three endotherms and two exotherms and a glass transition in the second heating and cooling cycles. The first endotherm is the crystal to chiral smectic C transition; the second endotherm is the chiral smectic C to smectic A transition; and the third endotherm is the smectic A to isotropic transition. The phase identifications were also verified by the polarizing optical microscopy study. Figure 5a shows the photomicrographs of polymer **2a** obtained 10 °C below the melting temperature with annealing on a hot stage. The typical fan texture is observed indicating the smectic A phase. Figure 5b was taken at the chiral smectic C transition temperature where the broken fan texture was shown. All the synthesized polymers exhibited enantiotropic liquid-crystalline behavior.

An X-ray diffraction study was carried out for polymer **2a** at different temperatures. The X-ray patterns (Figure

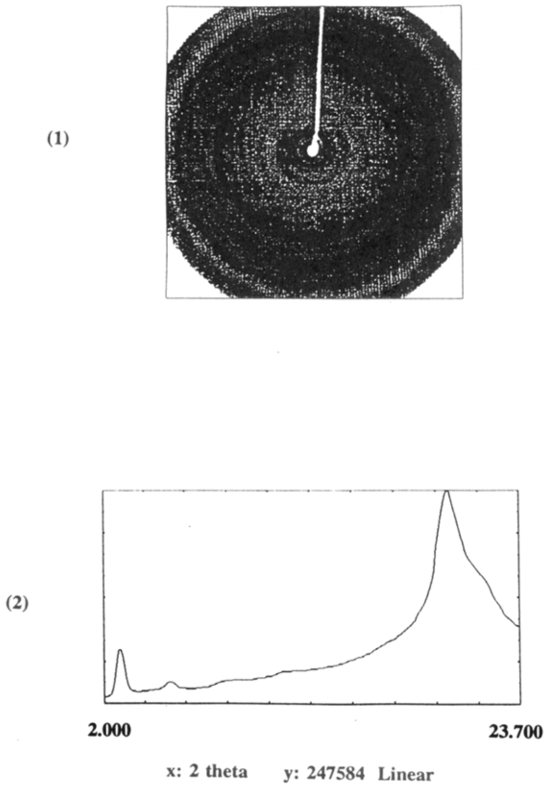


Figure 6. WAXD patterns of a S_c* phase of the unoriented polymer **2a**.

6) of a S_c* phase of unoriented polymer **2a** showed two rings (one sharp inner ring and one diffused outer ring) at 90 °C. The small-angle reflections correspond to Bragg spacings of 30 Å for the layers. The calculated length of the side group is 31.8 Å. The result leads to a tilted single layer structure for the S_c* phase.

Conclusion

Both the polymers and monomers exhibited enantiotropic liquid-crystalline mesophases. The liquid-crystalline temperature ranges of the monomers increase with an increase of the spacer length, while all the polymers have wide mesophase ranges. WAXD verified the Bragg layer spacing for the smectic polymers. These new ferroelectric liquid-crystalline materials with a strong dipolar group attached to a chiral center are expected to exhibit a very large polarization. The studies of ferroelectric properties, spontaneous polarization, tilt angle, and memory switching time, of these new ferroelectric materials are in progress.

Acknowledgment. This research is supported in part by the NSF ALCOM center (Grant No. DMR 89-20147) and the Ohio Research Challenge on Polymer Liquid Crystal Synthesis. We acknowledge the ALCOM-NCIPT Resource Facility Center and Dr. L. Chen in the X-ray diffraction study.

References and Notes

(1) Shibaev, V.; Kozlovsky, M.; Beresnev, L.; Blinov, L.; Plate, A. *Polym. Bull.* **1984**, *12*, 299.
(2) Le Barny, P.; Dubois, J. C. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie and Sons Ltd.: Glasgow, U.K., 1989.
(3) Clark, N.; Largerwall, S. U.S. Patent 4367924, 1980.
(4) Meyer, R.; Liebert, L.; Strezlecki, L.; Keller, P. *J. Phys. Lett (Paris)* **1975**, *36*, L69.
(5) Chien, L.-C.; Shenouda, I. G.; Saupe, A.; Jákli, A. *Liq. Cryst.*, in press.