

Microphase-Stabilized Ferroelectric Liquid Crystals (MSFLC): Bistable Switching of Ferroelectric Liquid Crystal–Coil Diblock Copolymers

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A side-chain liquid crystal (LC) block copolymer with a ferroelectric smectic C* LC block has been shown to exhibit bistable switching behavior in electric fields. Ferroelectric switching was demonstrated for block copolymers with volume fractions of 0.58 and 0.52 liquid crystal block. SAXS and TEM showed that the bulk morphologies of these two materials were hexagonally packed minority amorphous polystyrene (PS) cylinders and alternating lamellar amorphous PS layers, respectively. Cross-sectional TEM of a 10 μm thick film of the 0.58 volume fraction liquid crystal material used for the optical switching studies showed the cylinders to be well aligned along the shear direction and orthogonal to the applied electric field direction. It is believed that switching is possible due to an unwinding of the pitch of the smectic C* phase due to the presence of the intermaterial dividing surface of the microphase-separated cylindrical domains of the block copolymer which spatially confine the mesophase. This interaction realizes the concept of a microphase-stabilized ferroelectric liquid crystal (MSFLC) device.

Introduction

Ferroelectric liquid crystals (FLC) have become a very active field of research since the first demonstration in 1980 that FLCs can be switched on microsecond time scales using a surface-stabilized FLC (SSFLC) arrangement.^{1,2} In such a device, the electric field switchable liquid crystals (LC) are used in their smectic C* phase, wherein the mesogens are arranged in layers with the molecular long axis tilted with respect to the layer planes but in which the helical arrangement of the layers has been physically unwound due to the preferential anchoring of the mesogens at the top and bottom surfaces of the device. The lack of a helical arrangement of the electrical dipoles induces a spontaneous global polarization in the mesogenic groups which can be switched with little molecular movement, making fast switching times possible.

The key to a working SSFLC device, therefore, is to make the cell gap on the order of the FLC supramolecular pitch. This gap is generally $\sim 1\text{--}2\ \mu\text{m}$ to maximize the bright and dark states. Unfortunately, this thin gap limits the display panel size due to difficulties in creating uniform spacing over large areas. Such cells also reportedly have poor shock resistance due to low mechanical robustness.³

As a result of the difficulties of using low molar mass Sc* liquid crystals in SSFLC applications, other alternatives are desirable. FLC-polymers³ with their combination of chiral mesogenic groups⁴ and macromolecular nature have been studied for possible display materials with improved properties. Scherowsky et al.⁵ have reported an FLC poly(acrylate) which has a switching time of 0.5–5 ms with a M_n of 15 000 at $\sim 120\text{--}130\ ^\circ\text{C}$. Takahashi et al.⁶ reported that FLCs with a poly(siloxane) backbone showed a 33-ms switching time at 43 $^\circ\text{C}$, which is similar to the value for

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conventional low molar mass nematic liquid crystals in the twisted nematic geometry. These reports indicate that FLC polymers can still have fast switching times if properly designed and processed. Zentel and Brehmer^{7,8} created FLC elastomers by photo-cross-linking monodomain FLC poly(siloxane)s in the bookshelf arrangement and systematically studied their switching properties. This interesting material shows great potential in applications for sensors and large displays due to the more robust nature of the elastomers. All these prior studies with polymer LC materials have been based on the SSFLC concept for low molar mass FLCs.^{1,2}

Recently there is growing interest in block copolymers with a liquid crystal block.^{9,10} Such systems offer unique opportunities for manipulating LC order due to the remarkable interplay between liquid crystallinity and phase-separated microdomain structures.^{11–16} Thus far only spherical, lamellar, and hexagonal cylinder phases of side-chain LC block-coil block copolymers have been observed,^{12,13} in contrast to the various novel morphologies (e.g., zigzag and arrowhead morphologies) which were discovered in rod LC block-coil block copolymers.^{16,17} Nevertheless, both types of LC block-coil block systems possess unique coupling of the LC orientation with the intermaterial dividing surface. In the case of the side-group LC (SGLC) polymers, the geometry at the intermaterial dividing surface (IMDS) between the mesogenic groups and the flexible spacer is key. This coupling offers opportunities for using simple polymer processing to control mesogenic group orientation, layer arrangement, and helical arrangement.

Omenat et al.¹⁸ first reported a series of side-group FLC-coil lamellar diblock copolymers using living cationic polymerization in which only monostable switching was observed. Zheng and Hammond¹⁹ have also recently synthesized and characterized a family of well-defined FLC-coil diblock copolymers employing living anionic polymerization; however, no switching data have been reported to date.¹⁹ In a preliminary publication, we have shown the bistable switching of a ferroelectric liquid crystal-coil (FLC-coil) diblock copolymer.^{14,20}

In this paper, we report in detail the concept of microphase-stabilized ferroelectric liquid crystals (MS-FLC)¹⁴ using FLC-coil diblock copolymers. The syn-

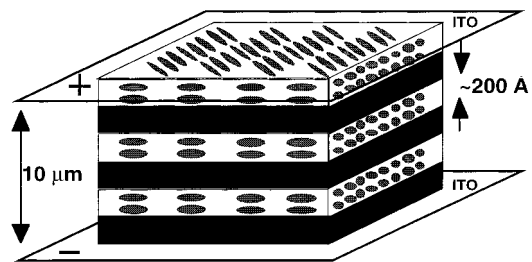


Figure 1. Microphase-stabilized ferroelectric liquid crystal (MSFLC). The lamellar microdomain morphology is shown. The black regions represent the coil block [e.g., poly(styrene)], and the white regions show the smectic C arrangement of the mesogens in the side-chain LC block. Other microdomain morphologies, such as coil block cylinders and FLC block cylinders, are also possibilities for MSFLC.

thesis and characterization of well-defined FLC-coil diblock copolymers as well as their electrooptical behavior are described. The MSFLC structure takes advantage of block copolymer microphase separation on domain scales in the range of 10–50 nm combined with ferroelectric liquid crystallinity. The small length scales of the interdomain spacings of block copolymers can be used to “unwind” the FLC supramolecular pitch for bistable switching. This concept is shown schematically in Figure 1. As well as controlling mesophase behavior by manipulating block copolymer microstructure, the MSFLC geometry offers advantages in controlling gap thickness, orientational stability, and mechanical properties without the necessity of using conventional surface orientation by substrates.

Experimental Section

1. Materials. All chemicals, including S-(+)-2-octanol (ee 95%), were purchased from Aldrich Chemicals and used without further purification unless noted. Methyl 3-nitro-4-hydroxybenzoate was purchased from Lancaster. The precursor poly(styrene-*b*-1,2- and -3,4-isoprene) (PSI) diblock copolymers were synthesized by conventional anionic polymerization followed by quantitative hydroboration/oxidation to convert the pendent double bonds to hydroxyl groups.¹³

2. Characterization. Structural characterization was done on bulk specimens using TEM and SAXS. X-ray analysis was performed both at the Cornell High Energy Synchrotron Source (CHESS) and at Brookhaven National Laboratory (BNL). SAXS data at CHESS were recorded at the F1 beamline with a CCD camera ($\lambda = 0.928 \text{ \AA}$). SAXS data at BNL were acquired at station X12B using a custom-built two-dimensional detector and an incident wavelength of $\lambda = 1.54 \text{ \AA}$. One of the switchable devices was also examined by cross-sectional TEM. For bulk films, samples were cast from toluene solutions and annealed at 120 °C for 7 days. A Reichert-Jung 4C-E ultramicrotome and Diatome diamond knife were used to cut sections at room temperature approximately 40 nm thick as estimated by interference color. Sections were floated on deionized water and picked up on carbon film covered copper mesh grids. The sections were stained by exposure to RuO₄ vapor at room temperature for 5 min. RuO₄ preferentially stains the polystyrene regions, and thus these appear dark in the TEM images. Bright-field TEM was performed using a JEOL 200CX electron microscope operated at 100 kV.

For TEM investigations of the MSFLC device, it was necessary to first remove the copolymer film from the ITO coated glass substrates. The electric field cell was opened at the glass-polymer interface, and the exposed copolymer film was coated with an approximately 100 Å thick layer of carbon to prevent infiltration of the embedding epoxy monomer. The embedding epoxy was next applied and cured. The bottom (i.e., second) glass substrate was then etched away from the

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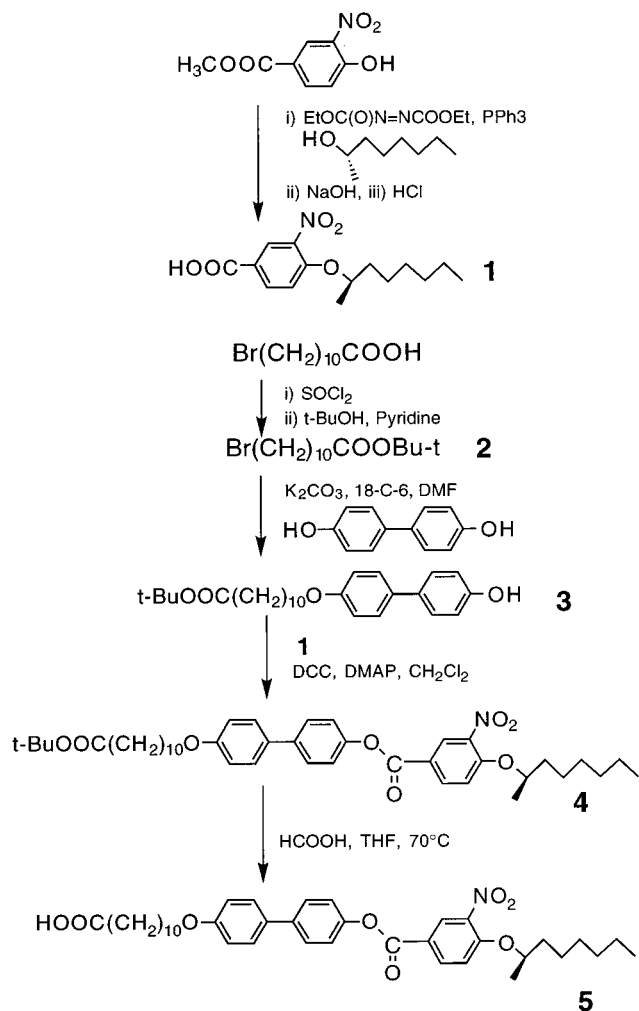


Figure 2. Synthetic scheme for functional chiral mesogenic group.

copolymer film with a 49% solution of HF for 5 h. FT-IR studies revealed that HF etching did not affect the FLC block copolymer. The film was then cleaned with an NaOH solution, followed by a HCl solution, and finally rinsed in H₂O. After this newly exposed copolymer film surface was carbon coated, it was fully embedded in epoxy, cured, and microtomed. The cutting orientations were chosen such that projections of the shear electric field and electric field neutral axis planes would be subsequently viewed in the TEM.

3. Switching Studies. For details of the electrooptical switching experiments see references 7 and 21. Due to the high viscosity of some block copolymers (e.g., SIC*10-41/63), the cell was taken apart to load the polymer, and uniaxial shear was performed at 140 °C (above the LC isotropization temperature but below the order-disorder transition temperature of the block copolymer) with a 10- μ m cell gap. The 10 μ m thick block copolymer films were hand sheared between two indium tin oxide (ITO) coated glass slides, which act as electrodes. Poling of the FLC domain with a 70 V/ μ m electric field was performed at a temperature near the S_C - S_A transition after cooling from the LC-isotropic state.

4. Synthesis Of Functional Mesogen. The carboxylic acid containing a chiral mesogenic group was synthesized according to Figure 2. Compound **1** (mp 55–56 °C; lit.⁷ 48–50 °C) was synthesized using the Mitsunobu reaction²² as previously reported by Zentel and co-workers.^{7,21}

Synthesis of Br(CH₂)₁₀COOBu-t (2). Compound **2** was synthesized by coupling the corresponding acid chloride (5 g,

17.6 mmol) with excess *tert*-butyl alcohol in the presence of pyridine and 4-(dimethylamino)pyridine (DMAP) as a catalyst. THF was used as solvent. Purification was carried out by distillation under reduced pressure. Yield: 55%. Bp 135 °C/0.2 mmHg.

Synthesis of HO-PhPh-O(CH₂)₁₀COOBu-t (3). 1,4-Biphenol (12.2 g, 65.4 mmol) was put into a 500-mL flask, followed by the addition of 3.9 g of anhydrous K₂CO₃ (28.3 mmol), 100 mg of 18-crown-6, 20 mg of KI, and 150 mL of anhydrous DMF. The solution was then heated to 95 °C for 15 min. To this solution, 7.8 g of Br(CH₂)₁₀COOBu-t (21.8 mmol) in 15 mL of DMF was added dropwise. The solution was then stirred at 95 °C for 12 h. After cooling, the mixture was then poured into 400 mL of water which contained 2 mL of acetic acid. The white precipitates formed were filtered and washed with water extensively. After drying in a vacuum oven overnight, the product was purified via flash column chromatography using 1/3 (v/v) ethyl acetate/hexane as elution solvent; 7.0 g of product (**3**) was obtained. Yield: 75.2%. Mp 83 °C. ¹H NMR (CDCl₃): δ 7.46 (2H, d, aromatic), 7.41 (2H, d, aromatic), 6.93 (2H, d, aromatic next to -OR), 6.90 (2H, d, aromatic next to -OH), 5.14 (1H, s, -OH), 3.96 (2H, t, next to ether linkage), 2.21 (2H, t, next to carbonyl group), 1.79 (2H, m, -OCH₂CH₂-), 1.58 (2H, m), 1.46 (9H, s, *t*-butyl group), 1.32 (12H, m, CH₂'s in the spacer).

Synthesis of C₈H₁₇*-O-Ph(3-NO₂)COO-PhPh-O(CH₂)₁₀-COO-Bu-t [C*10-Ester] (4). A mixture of 2.07 g (7.05 mmol) of **1**, 3.0 g (7.05 mmol) of **3**, and 123 mg (0.84 mmol) of 4-(dimethylamino)pyridine (DMAP) was put into a 150-mL flask (flask A) and dried under vacuum for 2 h, after which 60 mL of methylene chloride was added to dissolve these reactants. In flask B, 1.74 g (8.46 mmol) of 1,3-dicyclohexylcarbodiimide (DCC) was dissolved in 15 mL of anhydrous methylene chloride. The DCC solution in flask B was then slowly transferred via a cannula into flask A (which had been cooled at 0 °C). White precipitates came out soon, and the solution was kept stirring overnight. The white precipitate was filtered, and the filtrate was then rotovaped to dryness and purified by flash chromatography using 1/5 (v/v) ethyl acetate/hexane as elution solvent. Yield: 4.3 g (86.6%). Mp 47 °C. ¹H NMR (CDCl₃): δ 8.64 (1H, s, aromatic next to -NO₂); 8.35 (1H, d, aromatic, para position to NO₂), 7.60 (2H, d, aromatic in central biphenyl group, meta position to the central ester bond), 7.50 (2H, d, aromatic in the biphenyl group, meta position to the spacer group), 7.22 (2H, d, aromatic in biphenyl group, next to central ester bond), 7.18 (1H, d, aromatic, meta position to NO₂), 6.99 (2H, d, aromatic, next to the spacer group), 4.68 (1H, m, proton in the chiral center), 4.00 (2H, t, next to ether linkage with biphenyl group), 2.20 (2H, t, next to carbonyl group), 1.40 (9H, s, *t*-butyl group), 1.74–1.30 [m, 38H, including 1.40 (9H, s, *t*-butyl group) and 1.39 (3H, d, methyl group next to the chiral center)], 0.95 (3H, t, methyl group).

Synthesis of C*10-Acid (5) (see Figure 2). Deprotection of the *tert*-butyl group was performed using formic acid in THF solution at 70 °C for 2 h. The conversion is almost quantitative with no influence on the central ester bond. Mp 110 °C. [α]_D²⁰ = +2.50°. ¹H NMR (CDCl₃): δ very similar to those of C*10-ester (**4**) except that the peak at 1.40 ppm (*t*-butyl group) disappeared, while the peak at 1.39 ppm (the methyl group next to the chiral center) became clear; the CH₂ next to the carboxylic acid group shifted to 2.38 ppm (2H, t) from 2.20 ppm.

Synthesis of Mesogenic Acid Chloride.¹³ The C*10-acid was converted to acid chloride using oxalyl chloride. Recrystallization was performed 3 or 4 times with 10/1 (v/v) hexane/toluene mixed solvent, and K₂CO₃ fine powder was used to absorb any polar impurities.

5. Synthesis Of FLC-Coil Diblock Copolymers.¹³ After vacuum drying, the acid chloride was used right away for attachment to the hydroxylated PSI block copolymers (Figure 3). A 20–30% excess of acid chloride relative to hydroxyl groups was used. For details of this synthesis, see reference.¹³ The final FLC-coil block copolymer was purified

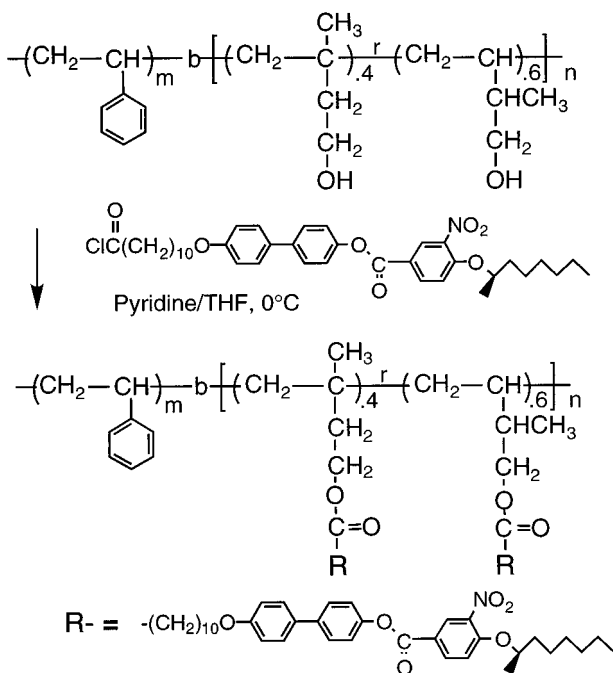
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Table 1: Summaries of FLC Homopolymers and FLC-Coil Diblock Copolymers

sample	wt fraction (LC%)	theoretical M_n (PS/FLC) ^a	GPC (M_w/M_n) ^b	thermal transitions ^c	ΔH (J/g) ^d	morphology
IC*10-117	100	0/117K	93K (1.60)	$g55 S_C^* 105 S_A^* 140 I$	8.6	
IC*10-17	100	0/17K	17K (1.12)	$S_C^* 122 S_A^* 133 I$	7.9	
SIC*10-107/50	30	107/50K	125K (1.09)	$g102 S_C^* 112 S_A^* 117 I$		lam, 552 Å
SIC*10-176/110	38	176K/110K	214K (1.16)	$g102 S_C^* 117 S_A^* 127 I$	3.7	lam
SIC*10-46/54	54	46K/54K	90K (1.12)	$g102 S_C^* 118 S_A^* 130 I$	2.3	lam, 452 Å
SIC*10-66/100	60	66K/100K	124K (1.23)	$g102 S_C^* 116 S_A^* 127 I$	2.8	coil cyl
SIC*10-41/63	61	41K/63K	67K (1.12)	$g102 S_C^* 118 S_A^* 130 I$	2.1	coil cyl, 408 Å ^e

^a The absolute M_n of the polystyrene precursor was measured by GPC using polystyrene standards. The LC block was measured by ¹H NMR. ^b GPC calibration is vs polystyrene standards. ^c From DSC second heating. ^d ΔH ($S_A^*-T_i$ transition) is normalized according to the weight fraction of FLC block. ^e Data from SAXS D₁₀₁₀.

**Figure 3.** Synthetic scheme for FLC-coil diblock copolymers.

by Soxhlet extraction with 95% ethanol (for 24–48 h) until no small molecule mesogen could be detected by TLC and GPC.

Results and Discussion

Synthesis. The basic mesogenic group used (Figure 2) has been previously employed in several small molecule^{23,24} and polymer systems.^{21,25} This new structure required the presence of a carboxylic acid for attachment to the hydroxylated polymer backbone. After DCC coupling (Figure 2), the *t*-butyl group was deprotected with formic acid without any adverse effect on the central ester bond.

The attachment of the mesogenic group was very efficient using acid chloride chemistry (with a 20–30% excess relative to hydroxyl groups), and ¹H NMR analysis showed more than 95% conversion of the hydroxyl groups. The properties of the synthesized FLC homopolymers and FLC-coil diblock copolymers used in this study are summarized in Table 1. Samples are

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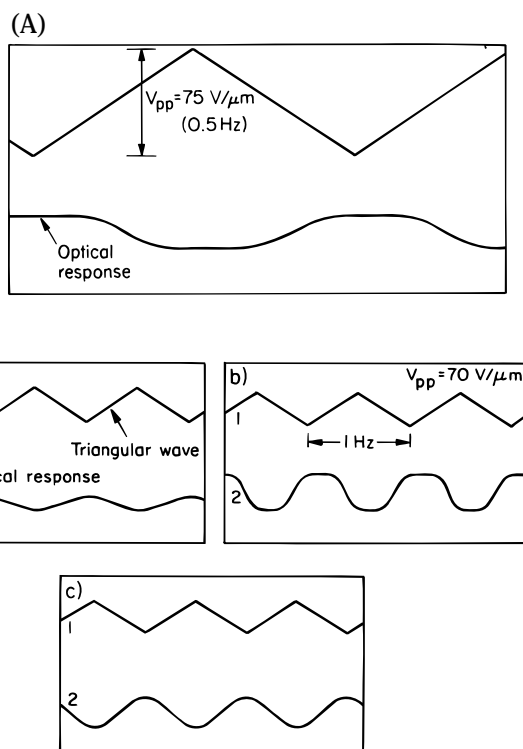


Figure 4. Electrooptical response (lower curve) of FLC block copolymers to an applied triangular wave (upper curve). (A) SIC*10-46/54 (lamellar) at 114 °C, $V_{pp} = 750$ V (0.5 Hz), 10- μ m cell. (B) SIC*10-41/63 (coil cylinder in an FLC matrix). $V_{pp} = 700$ V (1.0 Hz), 10- μ m cell, (a) 110 °C with quiescent preparation, (b) 110 °C after shearing (S_C^* phase), and (c) 120 °C (S_A^*).

referred to as SIC*10-*x*/*y* in which SI stands for styrene–isoprene block copolymer precursor, C*10 stands for the chiral mesogenic group with a 10 methylene group spacer, *x* stands for the M_n of PS (kg/mol), and *y* stands for the M_n of FLC block (kg/mol), respectively.

LC Phase Behavior. All homopolymers and block copolymers showed broad S_C^* and S_A^* mesophase ranges. Slight pressure on a heated sample in a hot stage revealed a softening temperature (T_g) of ~ 55 °C for the FLC homopolymer with a M_n of 17 000 g/mol. Typical DSC traces for the FLC-coil diblock copolymers are shown in Figure 6. For sample SIC*10-41/63, a T_g for the PS block is observed at 102 °C; an S_C^* to S_A^* phase transition is observed at 118 °C as later confirmed by electrooptical switching studies; the clearing transition temperature was 130 °C, but the T_g of the FLC

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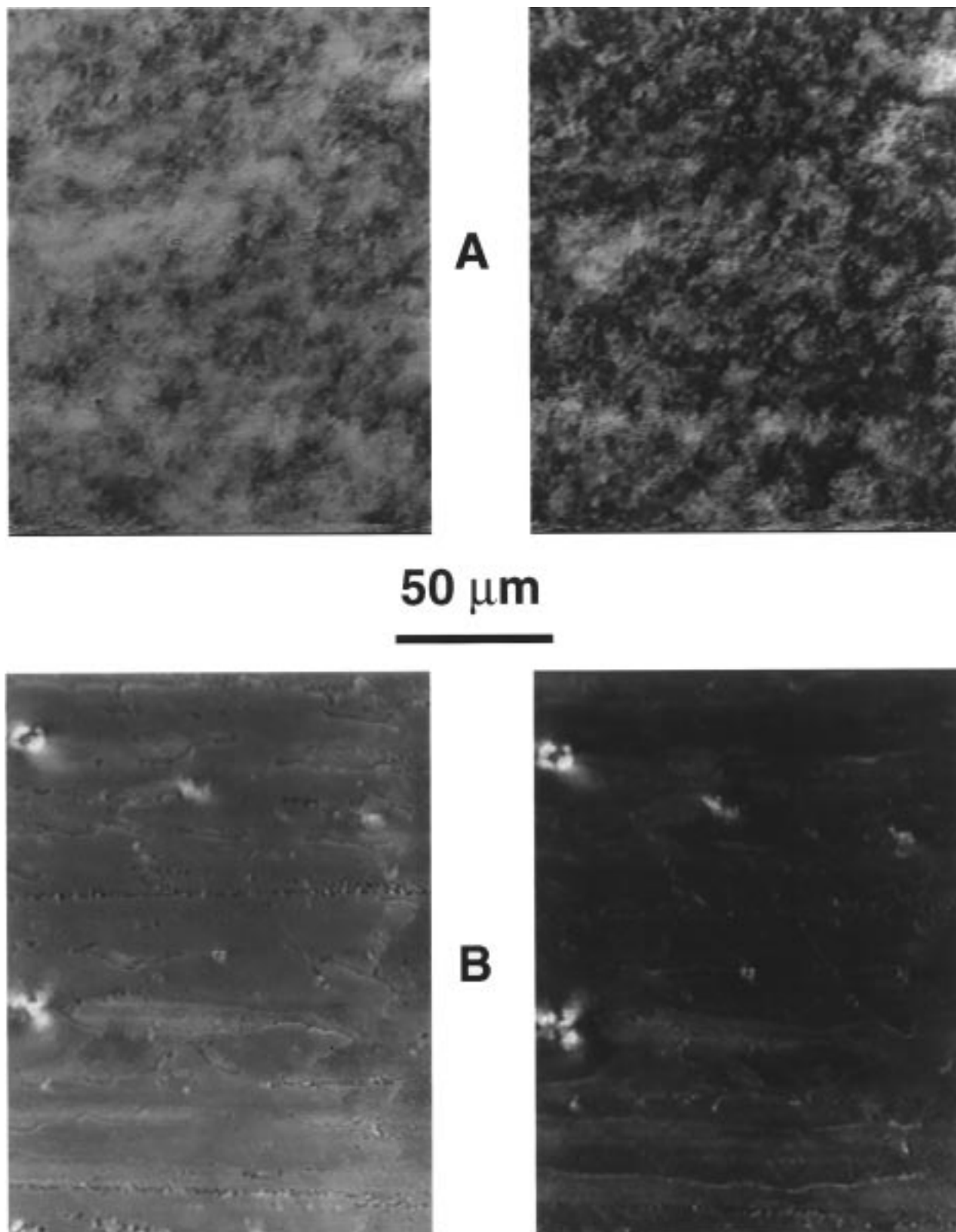


Figure 5. Polarized optical microscopy images of the two switching states exhibited by (A) SIC*10-46/54 and (B) SIC*10-41/63 under an electric field.

block could not be easily detected. The order–disorder transition (ODT) temperature for SIC*10-41/63 is higher than 210 °C (80 °C higher than T_i) as indicated by temperature-dependent SAXS studies.²⁶

Switching Studies. Details of the electrooptical switching experiments have been reported earlier.^{7,21} To introduce the polymers into the cell, a commercial

ferroelectric LC cell was opened to load the polymer, and uniaxial shear was applied by hand to a sample 10 μm thick between two indium tin oxide (ITO) coated glass slides at 140 °C (above the LC isotropization temperature but below the order–disorder temperature of the block copolymer). Poling of the FLC domain with a 70 V/ μm electric field was performed at a temperature

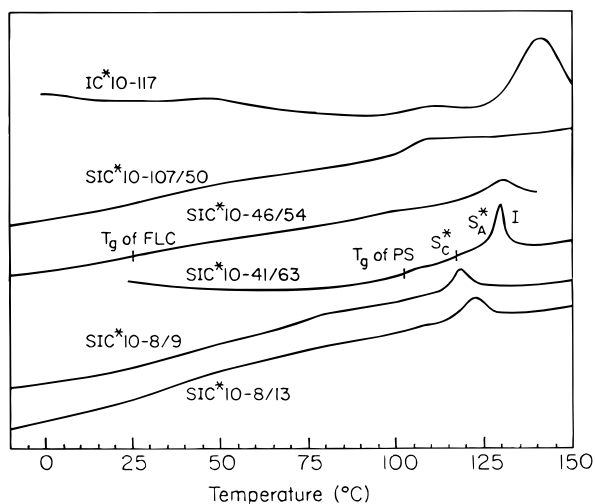


Figure 6. DSC traces of FLC-coil diblock copolymers. Curves are for second heating runs with a 10 °C/min heating rate.

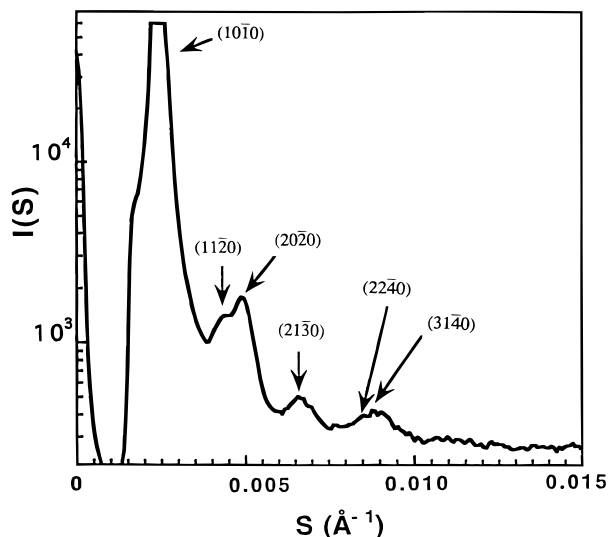


Figure 7. Line scan of SAXS pattern of sample SIC*41/63.

near the S_C^* – S_A^* transition after cooling from the LC-isotropic state.

Very high M_n FLC-coil block copolymers, such as SIC*10-66/100 (lamellar; see Table 1), were extremely viscous. No switching could be observed even at voltages as high as ~ 800 V across the 10- μm film. Of the five block copolymer samples studied, block copolymers SIC*46/54 (lamellar) and SIC*10-41/63 (coil cylinder) represent the first bistable switchable FLC-coil block copolymers. With SIC*46/54 in a 10- μm cell, bistable switching was observed at ~ 114 °C (S_C^* mesophase) with a voltage (V_{pp}) of 750 V (0.5 Hz) (see Figure 4A) to produce a switching speed in the range of hundreds of milliseconds, which is slower than low molar mass ferroelectric liquid crystals. The switching speed appears to be caused by a combination of both the distance between amorphous domains and the attachment of the mesogenic groups to a polymer backbone. This bistable switching behavior can be explained by the concept of microphase-stabilized FLC (MSFLC) geometry as shown in Figure 1. The layers of the PS block microdomain (thickness ~ 250 Å) unwind the FLC supramolecular pitch. More remarkably, the coil cylinder morphology also showed bistable switching properties. In cells

prepared by sandwiching the sample in the isotropic phase between two glass plates *without shearing*, SIC*10-41/63, an FLC-coil diblock copolymer with a PS coil cylinder morphology, showed only electroclinic switching over the entire S_C^* temperature range [Figure 4B(a)]. It is noteworthy, however, that the electroclinic switching was observed even below the glass transition temperature of the PS blocks. This demonstrates that the presence of the glassy PS domains does not significantly hinder the motion of the mesogenic groups in an applied field. After *shear* alignment processing, the optical response of SIC*10-41/63 became rectangular [Figure 4B(b)], indicating two stable ferroelectric switching states. Bistable switching was observed over the entire temperature range of the S_C^* phase. On heating into the S_A^* phase the response became electroclinic again [Figure 4B(c)]. The two bistable switching states observed using polarized optical microscopy (POM) are shown in Figure 5.

Because the block copolymer microstructure of the unsheared cell consists of unoriented polydomains, apparently the FLC monodomain bookshelf structure necessary for bistable switching is not formed. Therefore, shearing must be performed before monodomain orientation of the FLC becomes possible. This is consistent with our previous results which indicate that an LC-coil block copolymer must be oriented to align and lock-in the orientation of the LC mesogen.^{13,15} To understand the change in switching behavior due to shearing, the nature of the mesophase and the block microstructure were examined in detail.

Microdomain Morphology. WAXD showed that all samples contained a smectic LC phase with d spacings of 33.2, 21.3, and 13.3 Å [which indexes to the (200), (300), and (500) reflections from the smectic layers, respectively] and a broad peak at 4.4 Å (for the average inter-mesogen spacing). Molecular modeling reveals a fully extended side-group length of 38.2 Å. This indicates a smectic bilayer repeat of 66.4 Å with a tilt angle of 30° at room temperature. SAXS and TEM were used to determine the bulk morphologies of these samples. We were unable to directly measure the SAXS patterns of the 10 μm thick films employed by switching studies due to their limited thickness. SAXS patterns of static toluene cast copolymer SIC*10-41/63 after annealing for 4 days at 140 °C are shown in Figure 7. This copolymer exhibits peaks with q_n/q_1 ratios of 1.0, 1.88, 2.08, 2.75, and 3.63, corresponding approximately to 1.0, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, and $\sqrt{13}$ peaks of hexagonally packed cylindrical morphology with an intercylinder domain spacing of 472 Å. The SIC*10-46/54 copolymer exhibits peaks with q_n/q_1 ratios corresponding to approximately 1.0, 2, 3, and 4. This indicates a lamellar microstructure with a domain spacing of 550 Å. The TEM images of microtomed sections of the quiescently cast and annealed bulk SIC*10-46/54 film show alternating layers of the dark RuO_4 -stained polystyrene and lighter, unstained liquid crystal blocks (see Figure 8).

The monodomain processing^{28–30} of FLC-coil diblock copolymers is a key step for MSFLC. TEM images of

(28) Hadziioannou, G.; Mathis, A.; Skoulios, A. *Colloid Polym. Sci.* **1979**, *257*, 136.

(29) Albalak, R. J.; Thomas, E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32*, 341.

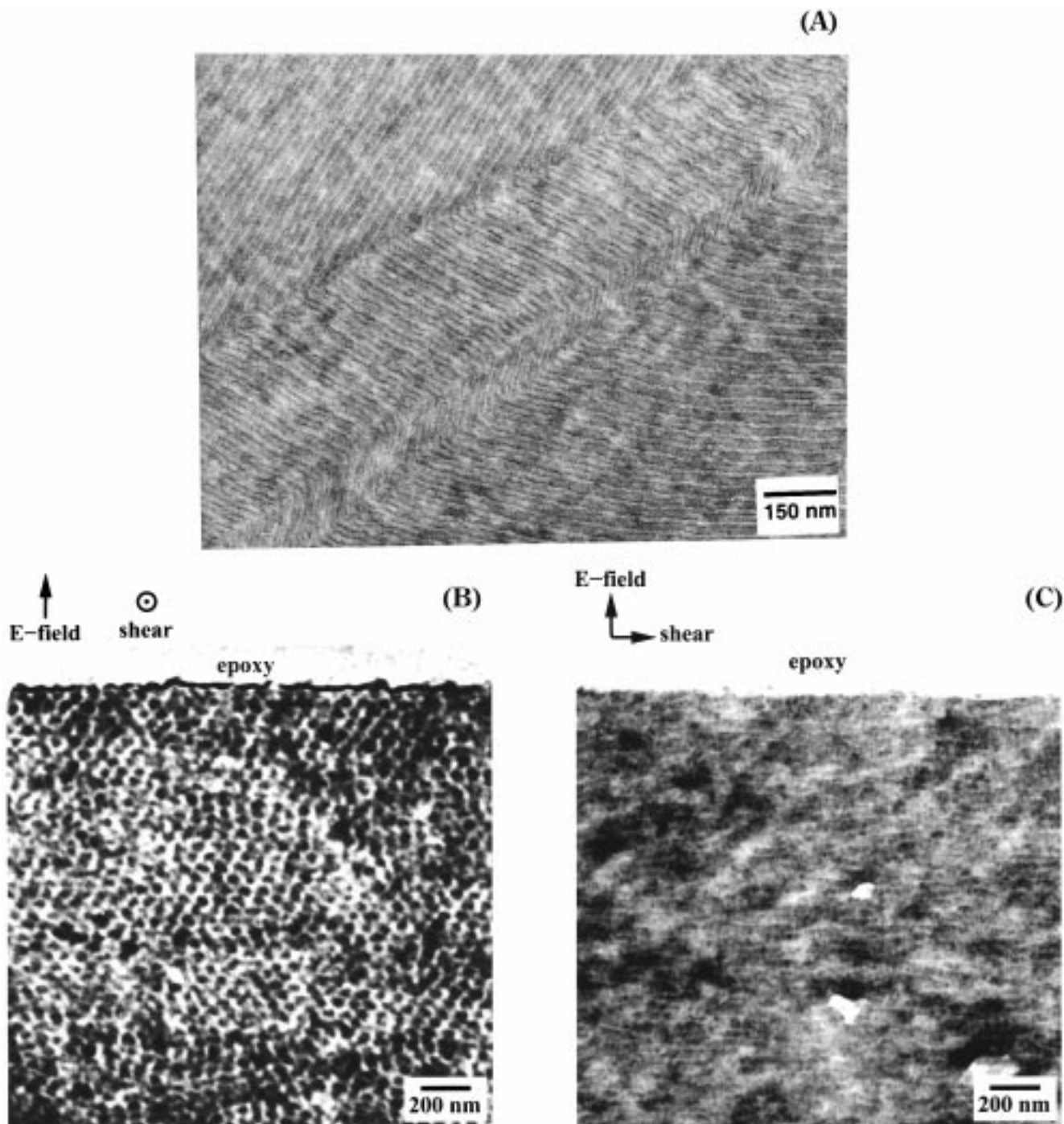


Figure 8. TEM micrographs of SIC*10-46/54 and SIC*10-41/63 MSFLC cell. (A) Bright-field image of RuO_4 -stained bulk film showing a region containing a tilt grain boundary of the lamellar structure. (B) View along the shear axis and perpendicular to the electric field of a copolymer with composition (PI-LC)/PS = 63 000/41 000 which exhibited bistable switching. This bright-field image shows dark end-on polystyrene cylinders in a liquid crystal matrix oriented in the shear direction. (C) View perpendicular to both the shear axis and the electric field of a copolymer with composition (PI-LC)/PS = 63 000/41 000. This image shows a transverse view of the polystyrene cylinders oriented in the shear direction in the liquid crystal matrix.

the SIC*10-41/63 MSFLC copolymer film used for the optical switching experiments are shown in Figure 8B,C. Viewing the near-surface region of the film along the shearing direction shows dark circular regions on an approximate hexagonal lattice in a lighter matrix (Figure 8B). The dark regions correspond to the RuO_4 -stained polystyrene. The diameter and LC spacing of the PS cylinders leads to an LC matrix volume fraction

of 0.63, which compares well with the value of 0.58 calculated on the basis of known composition. Images of sections cut so as to contain the shear axis and electric field directions display dark stripes of RuO_4 -stained polystyrene oriented with their axes parallel to the shear direction in the near-surface region (Figure 8C). The cylinders are not as straight and as continuous as

(30) Winey, K. I.; Patel, S. S.; Larson, R. G.; Watanabe, H. *Macromolecules* **1993**, *26*, 2542.

(31) We employ characteristic dimensions determined from WAXS and SAXS which do not suffer from specimen and domain dimensional changes due to image projection, beam damage, and staining in TEM.

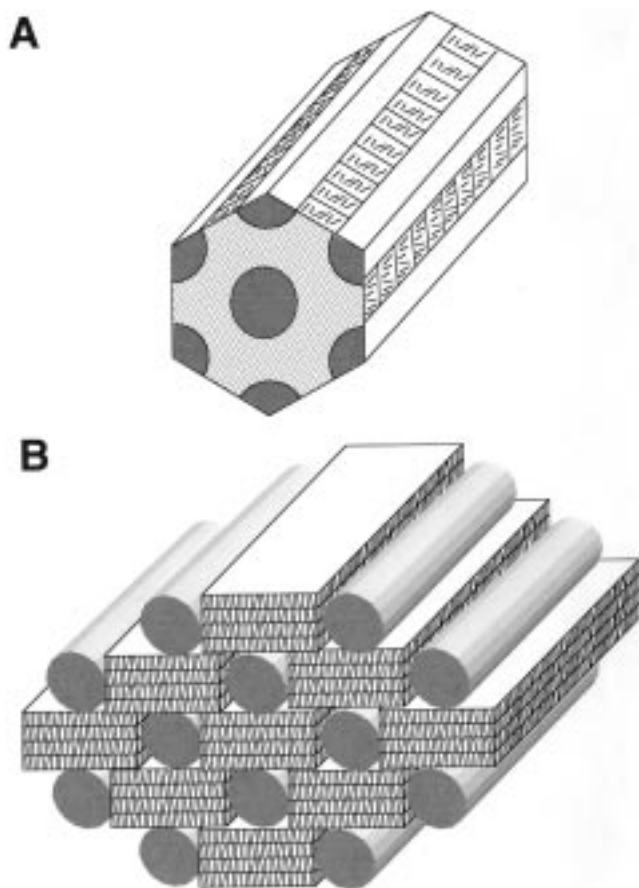


Figure 9. Possible packing models for coil cylinder morphology with a tilted smectic mesophase. (A) The mesogens form bilayers which are oriented parallel to the (0001) planes of the hexagonal structure. The mesogens are shown parallel to the cylinders with a homogeneous anchoring condition. (B) The mesogens form bilayers which are oriented parallel to the (10 $\bar{1}$ 0) planes of the hexagonal structure. The mesogens have a highly variable angle with respect to the surface of the cylinders.

in typical noncrystalline coil-coil block copolymers. Further into the interior of the 10 μm thick film, the orientation of the cylinders is somewhat less well organized with grains of cylinders less well aligned than in the near-surface regions.

These results indicate that, in addition to lamellae, cylinders can also be used to untwist the FLC supramolecular helix to permit bistable switching as proposed in the MSFLC concept. The observation of bistable switching in the minority polystyrene cylinder block copolymer morphology is especially interesting if we consider that the liquid crystal domain is the continuous matrix domain. Various possible models can be envisioned for the packing of the mesogens, the smectic layers, and the PS cylinders. The characteristic length scales are approximately 40 \AA (mesogen), 70 \AA (smectic bilayer), 320 \AA (cylinder diameter), and 470 \AA (intercylinder center-to-center spacing), respectively.³⁰ Two possible structures are depicted in Figure 9. The smectic bilayer structure of the LC block must somehow be accommodated into the block copolymer suprastructure. One possibility is shown in Figure 9A where the bilayers organize perpendicular to the cylinder axis; another possibility is shown in Figure 9B where the

side-chain mesogens form bilayers which are oriented parallel to the axes of the PS cylinders. This figure was difficult to prepare, suggesting that any structure must have a very complex molecular architecture. In both arrangements the microphase-separated structure serves to unwind the helix of the smectic C* state. Due to the incompatibility of the tilt angle of the mesogens with the orientation of the IMDS, distortions and defects must occur. Examples would include curvature of the layers, variation of the mesogen tilt angle near the IMDS as well as structural variation from region to region (to accommodate total bilayer thickness and intercylinder spacing), and disclination defects aligned parallel to the cylinders. The relatively low heat of transition for the S_A^* to I transition (about 1/3) for the block copolymers relative to that of the homopolymer IC* material also suggests that a lower order parameter and more defects are present in the LC domains in the block copolymer than in the LC homopolymer. In either case, the presence of the very high surface-to-volume ratio of the microphase-separated block copolymer structure inhibits the helix formation of the smectic C* state and allows for bistable switching. In the first microstructural model, the helical twist is prohibited by a preferred anchoring condition of the mesogens with respect to the IMDS, whereas the limited number of layers between cylinders prohibits the twist in the second model.

Conclusions

A series of well-defined FLC-coil diblock copolymers were synthesized via polymer analogous reactions. Microdomain structures were evaluated by X-ray scattering and TEM. The concept of microphase-stabilized FLC (MSFLC) was demonstrated and confirmed by the bistable switching of FLC-coil diblock copolymers with lamellar and with coil cylinder (in a FLC matrix) morphologies. The combination of ferroelectric liquid crystallinity and block microphase separation offers opportunities for advanced materials with tailored properties. Compared with SSFLC, MSFLC offers larger gap thickness, improved mechanical properties, and excellent shock resistance. This study shows great potential of such materials for flat panel display applications and other areas. Future work will concentrate on single-crystal processing of FLC-coil copolymer and switching studies of blends with low molar mass FLCs.

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