

# Temperature Dependence of Molecular Orientation on the Surfaces of Semifluorinated Polymer Thin Films

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Received July 30, 1999. In Final Form: October 19, 1999

Near-edge X-ray absorption fine structure is used to investigate the temperature dependence of molecular orientation of semifluorinated liquid crystalline (SF-LC) mesogens, which are attached to the modified isoprene backbone of (i) a poly(1,2-isoprene) homopolymer and (ii) a diblock copolymer consisting of polystyrene and poly(1,2-isoprene) blocks. Our experiments reveal the existence of two temperature regions in which the surface orientation of the SF-LC mesogens changes abruptly, but even 30 K above the highest such temperature region the surface orientation does not become isotropic. The lower temperature surface transition for both homopolymer and block copolymer occurs close to the temperature of the bulk homopolymer smectic-B to smectic-A transition and well above the bulk smectic-B to smectic-A transition in the block copolymer. It seems to be controlled exclusively by the ordering phenomena originating from the surface. In contrast, the change in the surface organization of the SF-LC mesogens at higher temperatures can be associated with the bulk LC transition from the smectic-A to the isotropic phase.

## Introduction

The production of low-energy surfaces is the goal of much research on nonwetting and nonstick coatings.<sup>1–3</sup> Such surfaces are technologically useful in a variety of applications including lubricated surfaces and antifouling surfaces. Self-assembled monolayers (SAMs) of uniformly organized arrays of trifluoromethyl ( $-\text{CF}_3$ ) groups produce such surfaces<sup>4</sup> but are impractical for large-scale applications. A more effective approach is to harness the self-assembly behavior of semifluorinated (SF) liquid crystalline (LC) alkanes. The interplay between phase separation, caused by the strong incompatibility between fluoro- and hydrocarbon molecules, and the self-assembly

of the thermotropic LC mesogens present a useful tool to fine-tune the properties of these materials.

An equally important attribute of these surfaces is their stability and organization as a function of temperature. In addition to the normal disordering phenomena that accompany LC transitions, entropic and enthalpic forces arising from the surface proximity can drastically alter the nature of the resulting LC alignment. For example, the homeotropic (perpendicular to surface) or homeogeneous (parallel to surface) arrangement of mesogens depends strongly on a balance between the interaction of the mesogens with respect to the surface and their packing free energy in either of these states. There are abundant experimental studies on the organization of small molecule liquid crystals<sup>5–9</sup> as well as LC polymers at surfaces and interfaces.<sup>10–16</sup> However, the methods used previously (primarily ellipsometry and X-ray reflectometry) do not have sufficient surface sensitivity to reveal the homeo-

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tropic surface alignment of just the short LC-SF side chains of our polymers.

Near-edge X-ray absorption fine structure (NEXAFS) has a surface probing depth of only 1.5–2 nm.<sup>17</sup> Thus, along with glancing incidence X-ray diffraction<sup>18</sup> and X-ray photoelectron spectroscopy,<sup>19</sup> it is eminently suitable for the study of molecular orientation at polymer surfaces. Moreover, NEXAFS allows a simultaneous measure of orientation within the bulk of the sample. In the past, we utilized NEXAFS to study the room-temperature orientation of the pendent groups within fluorinated diblock copolymers.<sup>20,21</sup> In this paper, we report on the *in situ* measurement of loss of orientation in LC chains at polymer surfaces during thermal treatment.

## Experimental Section

**Synthesis and Characterization of Polymers.** The synthesis of polymers in which semifluorinated  $-\text{OCO}(\text{CH}_2)_{x-1}(\text{CF}_2)_y\text{F}$  side groups were attached to the isoprene backbone of either poly(1,2-isoprene) homopolymer (H-FyHx) or polystyrene-poly(1,2-isoprene), diblock copolymers (BC-FyHx) has been reported elsewhere.<sup>22</sup> The degree of substitution of SF side groups on the poly(1,2-isoprene) backbone was 100%, i.e., one SF side group per original pendent vinyl group of the poly(1,2-isoprene). In this paper we will be specifically referring to polymers H-F8H4 (degree of polymerization 107) and BC-F8H4 [degrees of polymerization of the polystyrene (PS) and poly(1,2-isoprene) (PI) blocks, 395 and 107, respectively], both containing the same pendent group  $-\text{OCO}(\text{CH}_2)_3(\text{CF}_2)_8\text{F}$ . For comparison purposes another fluorinated block was prepared from the same PS-PI diblock copolymer with a pendent group  $-\text{OCO}(\text{CF}_2)_8\text{F}$ . This block copolymer, which we designate BC-F8, shows no LC character at any temperature, despite having the same rigid, helical fluorinated end as BC-F8H4. Transmission electron microscopy and X-ray scattering show that the BC-F8H4 block copolymer adopts a lamellar morphology,<sup>22</sup> and scanning force microscopy reveals that the lamellae are oriented parallel to the surfaces of thin films.<sup>23</sup> The SF side groups are organized in a LC smectic-B ( $S_B$ ) phase at room temperature with the smectic layers arranged perpendicular to the PS-block/PI-block lamella interfaces.<sup>22</sup> There are transitions to smectic-A ( $S_A$ ) and isotropic (I) phases at 313 and 334 K, respectively, for BC-F8H4, while these transitions occur at higher temperatures (326 and 342 K) for H-F8H4.<sup>22</sup> Contact angle measurements revealed a very low surface energy ( $\approx 8 \text{ mJ/m}^2$ ) consistent with close packing of  $-\text{CF}_3$  groups at the surface for both BC-F8H4 and H-F8H4.<sup>22</sup> These results imply that the SF side groups in BC-F8H4 do not have the same orientation at the surface as they do in the bulk.

**NEXAFS.** The NEXAFS experiments involve the resonant X-ray excitation of a K- or L-shell electron to an unoccupied low-lying antibonding molecular orbital of  $\sigma$  or  $\pi$  symmetry,  $\sigma^*$  or  $\pi^*$ .<sup>17</sup> The initial-state K- or L-shell excitation gives NEXAFS its element specificity, while the final-state unoccupied molecular orbitals provide NEXAFS with its bonding or chemical selectivity. Because sharp core-level excitations for C and F occur in the soft X-ray spectral region, NEXAFS is an ideal technique for probing molecular orientations of SF side groups in semifluorinated polymers. Intensity measurement of the NEXAFS spectral

features is used to identify chemical bonds and their relative population density in the sample. Furthermore the average tilt,  $\langle \tau \rangle$ , of an oriented field of molecules at the surface can be determined by noting the resonant intensity variation as  $\theta$ , the angle between the polarization of the X-ray beam and the sample normal, is experimentally altered.<sup>24</sup> More details of this aspect of NEXAFS are to be found elsewhere.<sup>17,20,21</sup>

At its most detailed limit,  $\langle \tau \rangle$  is calculated by collecting the partial electron yield (PEY) intensities of a given sample at incremental sample-beam angles ( $\theta$ ). The resulting intensity variation for individual bonds, e.g., C–F, is then fit to a prescribed model for the bond orientation as a function of near surface depth,<sup>20,21</sup> ultimately revealing  $\langle \tau \rangle$ . In this paper  $\langle \tau \rangle$  for the SF part of the chain was determined rigorously from PEY data (for a range of  $\theta$  from 20° to 90°) for several semifluorinated polymers where the side-chain content was varied from nearly 100% fluorinated to nearly 100% hydrogenated. The  $\langle \tau \rangle$  was found to be a unique function of  $I_{\text{diff}}$ , the difference between the PEY  $\sigma_{\text{C-F}}^*$  intensities collected at  $\theta = 20^\circ$  and  $\theta = 90^\circ$ .<sup>21</sup> We have used this function in the present paper to determine the average tilt angle from  $I_{\text{diff}}$  measured as a function of temperature.

**Sample Preparation.** Thin films ( $\approx 50 \text{ nm}$  thick) of the polymers were spun-cast from  $\alpha, \alpha, \alpha$ -trifluorotoluene ( $\text{C}_6\text{H}_5\text{CF}_3$ ) solutions onto silicon wafers and annealed at 423 K for 4 h before being mounted onto a heating stage within the analysis chamber. The NEXAFS experiments were carried out on the NIST/Dow materials characterization end-station (U7A) at the National Synchrotron Light Source at Brookhaven National Laboratory. While more in-depth information regarding the instrument can be found elsewhere,<sup>20,21</sup> the most pertinent details are as follows: The degree of polarization of the X-ray beam was  $\approx 85\%$  and the incident photon energy resolution and approximate intensity were 0.2 eV and  $5 \times 10^{10}$  photons/s at 490 eV, respectively. The fluorescence yield (FY) and the partial electron yield (PEY) signals are collected by using a proportional gain counter and a channeltron electron multiplier, respectively. By simultaneously collecting the FY and PEY signals, whose probing depths are  $\approx 200 \text{ nm}$  and  $\approx 2 \text{ nm}$ , respectively, both the bulk and the near-surface structures of the film are examined. The heating stage, positioned on a goniometer that controls  $\theta$ , maintains the sample temperature constant to within  $\pm 1.5^\circ$  of the set point. The samples were left at each heating temperature for  $\approx 15 \text{ min}$  before the collection of a NEXAFS spectrum at  $\theta = 90^\circ$  and  $\theta = 20^\circ$ . A fresh area of the sample was exposed to the 1 mm X-ray beam spot for each heating increment to minimize possible beam damage effects.

## Results and Discussion

Figure 1a shows the room-temperature PEY NEXAFS spectra at the C 1s edge from the BC-F8H4 sample measured at  $\theta = 90^\circ$  and  $\theta = 20^\circ$ . The increase of the PEY  $\sigma_{\text{C-H}}^*$  and  $\sigma_{\text{C-F}}^*$  intensities and simultaneous decrease of the PEY  $\sigma_{\text{C-C}}^*$  intensity as  $\theta$  is increased is easily rationalized by considering the alignment of the incident X-ray polarized electric field vector with the net  $\sigma^*$  orbital vector arising from each of these types of bonds. In fact, such behavior will only be present within well-oriented surfaces and the differential intensity,  $I_{\text{diff}}$ , (shown graphically in Figure 1a) is used as a quantitative indicator of the degree of surface orientation present. The fact that the PEY  $\sigma_{\text{C-H}}^*$  and  $\sigma_{\text{C-F}}^*$  intensities are larger while the PEY  $\sigma_{\text{C-C}}^*$  intensity is smaller at  $\theta = 90^\circ$  than at  $\theta = 20^\circ$  means qualitatively that the entire SF component has its long axis aligned more nearly normal than parallel to the sample surface.

(24) The tilt angle determined from NEXAFS represents an *average* value. There is no straightforward way to discriminate between the case of all chains homogeneously tilted by the same angle and the case of a disordered system with a broad distribution of tilt angles. Moreover, due to the nature of the polarization dependencies of the NEXAFS signal intensities, one cannot distinguish between a completely disoriented sample and a sample whose chains are all tilted by  $54.7^\circ$ , the so-called magic angle (see ref 17).

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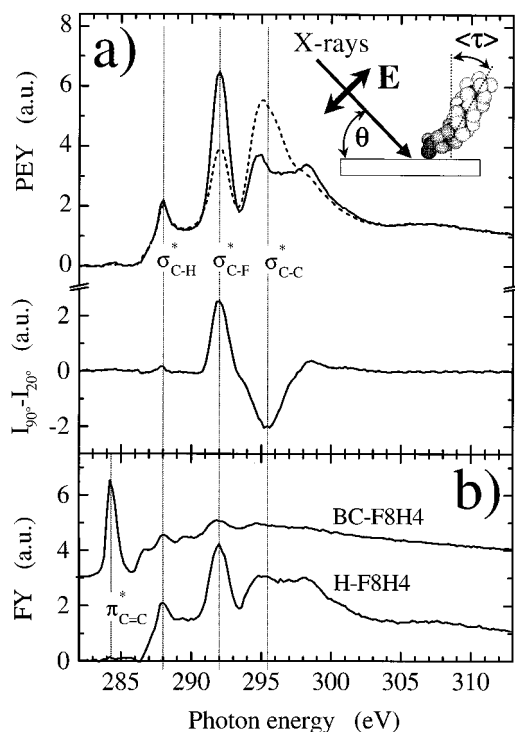
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**Figure 1.** (a) PEY NEXAFS spectra from BC-F8H4 at two different sample orientations with respect to the X-ray beam,  $\theta$  (solid line,  $\theta = 90^\circ$ ; dashed line,  $\theta = 20^\circ$ ). The inset shows schematically the sample geometry. Also marked in the figure are the positions of the  $1s \rightarrow \sigma^*$  transitions for the C-H, C-F, and C-C bonds. The bottom part of panel a shows the difference spectrum obtained by subtracting the dashed line data from the solid line data. (b) FY NEXAFS spectra from H-F8H4 and BC-F8H4 (the latter has been offset along the intensity axis for clarity) recorded at  $\theta = 90^\circ$ . Also marked in the figure are the positions of the  $1s \rightarrow \sigma^*$  transitions for the C-H, C-F, C-C, and  $1s \rightarrow \pi^*$  C=C bonds.

The near-surface composition consists primarily of the low surface energy SF component of the diblock copolymer, as shown by the comparison of the typical PEY and FY NEXAFS data (Figure 1) from BC-F8H4 and H-F8H4 collected at  $\theta = 90^\circ$ . Since the transitions that give rise to the FY signal follow the same selection rules as those of PEY signal, peaks corresponding to the  $1s \rightarrow \sigma^*$  transitions for the C-H, C-F, and C-C bonds are present in both bulk and surface spectra. However, an additional peak in the BC-F8H4 FY spectrum is present at  $\approx 284.3$  eV and can be assigned to originate from the  $1s \rightarrow \sigma^*$  transition of the PS phenyl ring. This observation indicates that there is no PS present within a region from the surface comparable with the escape depth of the Auger electrons ( $\approx 2$  nm), a distance in fact comparable to the length of the SF side chains.

These observations (full surface coverage of the SF-LC side chains and orientation of these side chains roughly normal to the surface) rule out for our SF-LC block copolymers molecular organization schemes such as those found by Wong et al.<sup>12</sup> for their LC-block copolymers based on PChEMA LC-mesogens, models in which the normal symmetric block copolymer morphology in thin films (stacks of lamellae parallel to the surface) changes to a morphology where the lamellae are perpendicular to the surface, allowing the PChEMA LC-mesogens to lie parallel to the lamellae and still be homeotropic (perpendicular to surface). In our case we presume that the very low surface energy of the SF-LC homeotropic surface as compared to the much higher surface energy of the PS block stimulates

the full coverage of the surface by the SF-LC block and the orientation of the PS lamellae parallel to the surface.

Figure 2a shows the PEY  $I_{\text{diff}}$  for  $\sigma_{\text{C-F}}^*$  and  $\sigma_{\text{C-C}}^*$  obtained from spectra of BC-F8H4 (circles). At room temperature, the SF-LC chains on the sample surface are oriented and reveal, in agreement with previous data,<sup>20,21,25</sup> that  $\langle \tau \rangle$  of the rigid, helical fluorinated part of the SF-LC chain is  $29^\circ \pm 3^\circ$ .<sup>20,21,25,26</sup> While  $\langle \tau \rangle$  was determined from the PEY  $I_{\text{diff}}$  for  $\sigma_{\text{C-F}}^*$  alone, the PEY  $I_{\text{diff}}$  for  $\sigma_{\text{C-C}}^*$  is consistent with the  $\langle \tau \rangle$  reported, the major uncertainty being how the orientation of the  $-(\text{CH}_2)-$  portion of the SF component is connected to that of the rigid  $-(\text{CF}_2)-$  helix. Note also the point at room temperature for BC-F8 (squares). This block copolymer, which has no LC character, shows almost no orientation of its rigid  $-(\text{CF}_2)-$  helix.

More significantly, Figure 2a also shows a decrease in the degree of surface ordering as the temperature increases. Moreover, the decrease in  $I_{\text{diff}}$  from the  $\sigma_{\text{C-F}}^*$  and the increase in  $I_{\text{diff}}$  from the  $\sigma_{\text{C-C}}^*$  are not continuous and one can distinguish two regimes over which  $I_{\text{diff}}$  changes significantly, delineating regions where the orientation of near-surface C-F and C-C bonds remains relatively constant or decreases slowly. These discontinuities (corresponding to the changes in  $\langle \tau \rangle$  of  $\approx 7^\circ$  and  $\approx 5^\circ$ , respectively) occur at temperatures that are close to the bulk  $S_B-S_A$  and  $S_A-I$  LC phase transitions, respectively, determined previously by differential scanning calorimetry (DSC).<sup>22</sup> Similar behavior is observed also for the H-F8H4 sample, as is shown in Figure 2b. Remarkably, for both the copolymer and homopolymer there is still a significant degree of organization at the polymer surfaces at elevated temperatures, where by comparison X-ray diffraction results<sup>22</sup> reveal a complete loss of LC ordering within bulk samples. More quantitatively,  $\langle \tau \rangle$  for both polymers is  $\approx 45^\circ$  at sample temperatures approximately 20 K above the bulk isotropic transition; still some  $10^\circ$  below the nominal value ( $\approx 55^\circ$ ) for complete disorder. This retention of orientation above the  $S_A-I$  bulk transition for both the BC-F8H4 and H-F8H4 is clearly a consequence of the LC crystalline character of the SF mesogens and not due simply to the fluorinated  $-(\text{CF}_2)_8\text{F}$  group being anchored on the surface by favorable surface interactions. Our NEXAFS experiments on BC-F8, a block copolymer with a  $-\text{OCO}(\text{CF}_2)_8\text{F}$  side group (F8), reveal no LC phases and almost no surface orientation of the F8 side group even at room temperature as shown in Figure 2a.<sup>20,21,25</sup>

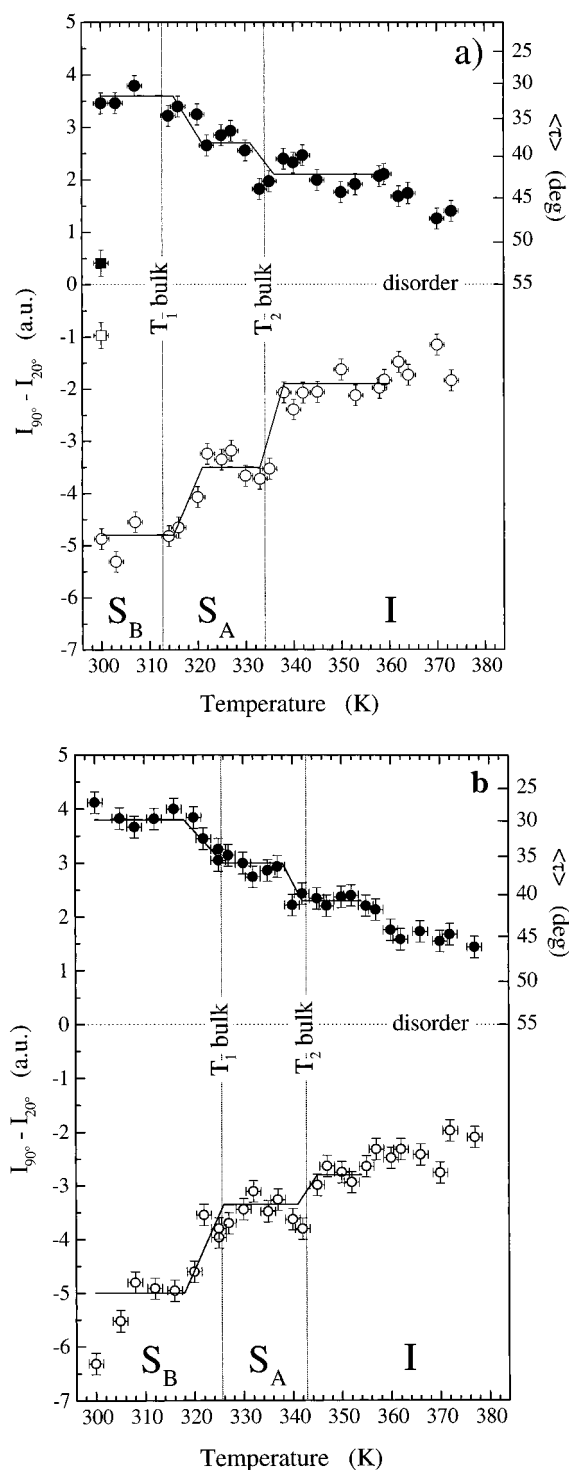
Comparing Figure 2 panels a and b, we note that the first drop in orientation upon heating occurs at nearly the same temperature ( $\approx 321$  K) for both H-F8H4 and BC-F8H4, a temperature that is lower than the bulk  $S_B-S_A$  transition in the H-F8H4 but higher than that in BC-F8H4. Because the DSC heating rate ( $\approx 10$  K/min) at which the bulk  $S_B-S_A$  transition was measured is much higher than the very slow effective heating rate of the NEXAFS experiments, it is rational to assume that the bulk  $S_B-S_A$  transition and the drop in the surface orientation coincide for the H-F8H4 and the drop in surface orientation for BC-F8H4 occurs well above its bulk  $S_B-S_A$  transition.<sup>27</sup> Such an idea is reasonable since the lateral confinement

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(26) The average surface tilt of the SF-LC mesogens was independent of whether the SFP was a diblock copolymer or a homopolymer. Nor it did not depend on whether the surface topology of the SF-diblock was smooth or rough due to the formation of islands or holes.

(27) Had the DSC data been collected at lower heating rates, one might expect lower transition temperatures. The NEXAFS data are highly repeatable and were collected over heating and cooling regimes.





**Figure 2.** Temperature dependence of  $I_{\text{diff}}$  for  $\sigma_{\text{C-F}}^*$  (closed symbols) and  $\sigma_{\text{C-C}}^*$  (open symbols) signals in the difference spectra of (a) BC-F8H4 (circles) and BC-F8 (squares) and (b) H-F8H4 (circles). The vertical lines denote the temperatures associated with the  $S_B - S_A$  ( $T_1$ ) and  $S_A - I$  ( $T_2$ ) LC transitions in the bulk of the BC-F8H4 and H-F8H4. The horizontal line represents the value of the peak areas in a completely disordered sample (or a sample with an average chain tilt of  $54.7^\circ$ ). The solid lines are drawn through the data simply as a guide to the eye and should not be used to obtain accurate transition temperatures or even to imply the existence of sharp (first-order) transitions.

of the  $S_B$  layers by the perpendicular block copolymer lamellae must be responsible for the decrease in the bulk  $S_B - S_A$  transition from H-F8H4 to BC-F8H4. At the surface of BC-F8H4, however, the  $S_B$  layers lie along the surface

and are thus unconfined by the BC-F8H4 lamellae. Hence, the  $S_B - S_A$  transition in the outer layer of the BC-F8H4 should be very similar to that in H-F8H4, as observed. Thus, we conclude that the drop in orientation observed with NEXAFS at 321 K is a  $S_B - S_A$  transition in the surface.

In contrast the drop in surface orientation at higher temperatures, 334 K for BC-F8H4 and 340 K for H-F8H4, cannot be a surface smectic transition as the layer does not become isotropic. The fact that the drop in surface orientation coincides closely with the bulk transition in both BC-F8H4 and HF8H4 suggests that the decrease is due to the disordering produced in the surface layer when the subsurface mesogens become isotropic. Whether this disordering is mediated by the polymeric connection between surface and bulk or whether it is due to direct mesogen-mesogen interaction is not clear. What is clear is that the surface does not become isotropic at the bulk  $S_A - I$  transition and that the surface mesogen orientation persists well above this temperature.

The persistence of smectic surface layers to temperatures above the bulk  $S_A$  to isotropic transition is well documented in small-molecule liquid crystals,<sup>5-9</sup> so our observation that surface order of the SF groups exists at temperatures where the bulk is isotropic is not unexpected. In small-molecule liquid crystals these smectic surface structures do not persist for more than 10 K above the bulk  $S_A$  to isotropic transition temperature  $T_{\text{SI}}$ . In contrast here we see surface order that persists more than 30 K above  $T_{\text{SI}}$ . Elben and Strobl<sup>11</sup> observed similarly persistent smectic surface layers in the isotropic phase of side-chain LC polymers, where the mesogenic side chains did not contain fluorine. It seems likely, therefore, that stability of the smectic surface layers in isotropic side-chain LC polymers is due to connection of the surface mesogens to a polymer backbone rather than to some specific strong interaction of the mesogen with the surface. Such a hypothesis is supported by observations that attachment of mesogens to a polymer backbone can alter the anchoring of such mesogens at the surface.<sup>28</sup>

Finally, we comment on the difference between the organization of the SF mesogens attached to our polymer backbone and small-molecule mesogens (HMF) with one alkyl and one perfluoroalkyl tail. Such HMF molecules show smectic-A layering in the bulk in which the perfluoroalkyl tail points randomly to one or the other side of each smectic layer.<sup>29</sup> Surface tension measurements on free-standing, multilayer films of such HMF molecules have been interpreted by assuming a similar random placement of perfluoroalkyl and alkyl tails on the surface.<sup>30</sup> Without necessarily completely endorsing this interpretation (the surface tension of molecules with two perfluoroalkyl tails is very similar to that of HMF molecules), we note that our NEXAFS results rule out a mixed surface for our SF polymers. The SF molecules cannot point randomly out of and into the surface without strongly deforming the polymer backbone to which they are attached.

In summary, we have observed the orientation of LC semifluorinated mesogens attached to a block copolymer and a homopolymer as the temperature is increased through the bulk  $S_B - S_A$  and  $S_A - I$  transitions. A loss of the mesogen orientation is observed at a temperature

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corresponding closely to the homopolymer  $S_B-S_A$  transition, suggesting that the lamellar structure of the block copolymer does not significantly affect the order in the  $S_B$  surface layer. The surface orientation does not become isotropic at the  $S_A-I$  transition of the bulk but persists to much higher temperatures. We argue that the decrease in surface mesogen orientation observed near the bulk  $S_A-I$  transition results from the disordering effects of the bulk on the surface layer.

**Acknowledgment.** This research was supported by the Office of Naval Research, Grant No. N00014-92-J-1246 and the Division of Materials Research, NSF

Polymers Program, Grant DMR92-23099. Partial support from Division of Materials Research, NSF Polymer Program, Grant DMR93-214573, is also appreciated. We thank M. Xiang, S. Yang, and B. Glösen (Cornell University) for their assistance during the course of the experiments. NEXAFS experiments were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

LA9910327