

# Terminal End Group Chemistry Affects Order At Side Chain Liquid Crystalline Polymer Surfaces

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**Introduction:** Materials having low surface energy may be formed using fluorinated polymers such as poly(tetrafluoroethylene) (PTFE) and fluorinated ester side chain acrylic and methacrylic polymers or fluorinated block copolymers. It is well known that some of the important factors in the behavior of low-energy surfaces include both the precise nature of the atoms populating a surface and their physical arrangement. Fluorinated polymers having  $-\text{CF}_3$  end groups have been shown to have a lower surface energy than PTFE. However, in most fluorinated polymers, a potential problem in many applications has been the stability of these low-energy surfaces and their tendency to undergo surface reconstruction in polar environments, e.g., in water. We have synthesized families of semifluorinated diblock copolymers [SFDs] that combine the low surface energy, the rigidity and the self-organizing properties of fluorinated alkanes together with the structural stability and morphological control provided by diblock co-polymers. One such family whose bulk morphological and liquid crystalline structure and properties have been determined consists of poly(styrene)-poly(isoprene) di-block copolymers where the isoprene block has semi-fluorinated side groups  $[-\text{CO}-(\text{CH}_2)_x-1-(\text{CF}_2)_y\text{F}]$  attached to it. In these experiments we have observed the effects of substituting one atom (H) for an F on the terminal  $-\text{CF}_3$  end group, i.e. we made semifluorinated side groups with  $-\text{CF}_2\text{H}$  end groups.

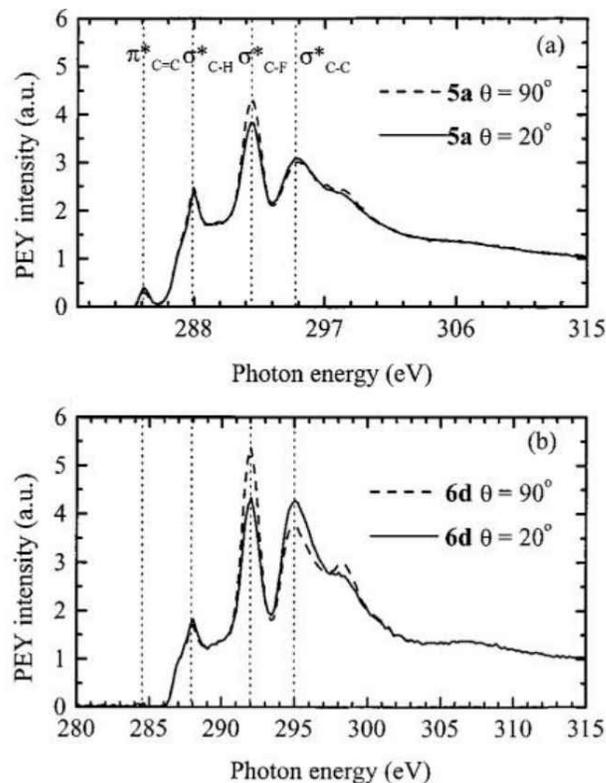
**Methods and Materials:** From plots of the partial electron yield PEY vs.  $\sin^2\theta$  where  $\theta$  is the angle between the electric vector of the X-ray beam and the sample normal, we determine the degree of ordering of the fluorinated alkanes at the surfaces by extracting the  $\text{CF}_2$  helix order parameter  $S_{\text{CF}_2 \text{ Helix}}$ . The orientational order parameter  $S_{\text{CF}_2 \text{ Helix}}$  ranges from  $-0.5$  for all helices oriented parallel to the surface to  $0$  for no orientational order to  $1$  for all helices oriented normal to the surface. We correlate this with measurements of the critical surface tension, and the stability of the water contact angles with time of water exposure.

**Results:** The NEXAFS results (**Figure 1**) show that while the surface coverage of semifluorinated groups is roughly the same regardless of whether the ends are  $-\text{CF}_3$  or  $\text{CF}_2\text{H}$ , there is much less orientational order for semifluorinated side chains with  $-\text{CF}_2\text{H}$  end groups than for those with  $-\text{CF}_3$  end groups [1]. For example for the polymers in **Figure 1**, we find  $S_{\text{CF}_2 \text{ Helix}} = 0.240 \pm 0.04$  for helices with  $-\text{CF}_3$  end groups but  $S_{\text{CF}_2 \text{ Helix}} = 0.114 \pm 0.03$  for helices with  $-\text{CF}_2\text{H}$  end groups. Similar effects are seen for semifluorinated side groups with 8 rather than 6  $-\text{CF}_2$ -units. Large changes in critical surface tension, from  $\sim 8$  mN/m for  $-\text{CF}_3$  end groups to  $\sim 18$  mN/m for  $-\text{CF}_2\text{H}$  end groups, accompany these changes in surface orientational order. In addition we find that after long time water exposure, the  $-\text{CF}_2\text{H}$  surfaces reconstruct to more hydrophilic ones even though surfaces of the analogous polymers with  $-\text{CF}_3$  end groups are quite stable. The ease of surface reconstruction is probably related to the relatively poor orientational order of the  $-\text{CF}_2\text{H}$  surfaces observed by NEXAFS.

**Conclusions:** The substitution of a single atom on the end of a semifluorinated side group can cause large changes in surface energy, surface orientational order and stability of polymer surfaces.

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**References:** [1] T. Hayakawa *et al.* *Macromolecules*, **33** 8012-8019 (2000).



**Figure 1.** NEXAFS partial electron yield intensity versus X-ray photon energy for angles  $\theta$  between the electric field vector and the sample normal of 20 and 90°. a.) sample 5a ( $-\text{CF}_2\text{H}$  end groups). b.) sample 5b ( $-\text{CF}_3$  end groups).