Surface Stability in Liquid-Crystalline Block Copolymers with Semifluorinated Monodendron Side Groups

Maoliang Xiang,† Xuefa Li,† Christopher K. Ober,*§ Kookheon Char,§ J an Genzer,† Eesan Sivaniah,† Edward J. Kramer,§,* and Daniel A. Fischer†,#

Materials Science & Engineering, Bard Hall, Cornell University, Ithaca, New York 14853-1501; Department of Materials, University of California at Santa Barbara, Santa Barbara, California 93106; Department of Chemical Engineering, University of California at Santa Barbara, Santa Barbara, California 93106; Materials Science & Engineering Laboratory, National Institute for Standards and Technology, Gaithersburg, Maryland 20899; and NSLS, Brookhaven National Lab, Upton, New York 11973

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ABSTRACT: Block copolymers with semifluorinated monodendron side groups were synthesized by attachment of a first generation 2- or 3-armed monodendron acid chloride to a hydroxylated poly(styrene-b-1,2/3,4-isoprene). A convergent growth strategy was developed to synthesize the monodendron groups in good yield using an approach that could be extended to higher generation monodendrons. High extents of attachment were achieved despite the steric effects of the bulky monodendron side groups. The resulting polymers formed a smectic B mesophase at room temperature as determined by WAXS data. The transition temperatures, mesophase range, and enthalpy of the smectic B— isotropic transition were all affected by side-group structural factors such as flexible spacer length, mesogen length, and monodendron core. The critical surface tensions of the resulting semifluorinated polymers were as low as ~8 mN/m as determined by Zisman analysis. Surface stability of polymer films in a polar liquid environment was strongly dependent on the extent of attachment exhibited by the semifluorinated groups. The monodendron –CF₂–– helix within 1 nm of the surfaces has a net orientation normal to the surface as measured by near-edge X-ray absorption fine structure (NEXAFS) methods, but the orientational order parameter S_helix is much higher for the 2-armed monodendrons than for the 3-armed monodendrons. In both cases S_helix seems insensitive to monodendron attachment density along the isoprene block. We suggest that packing frustration of the monodendron subunits produces surfaces with spontaneous curvature that differs depending on whether the monodendrons are 2- or 3-armed. The more highly curved surface topology of the 3-armed monodendrons may provide a partial explanation for its decreased orientational order.

Introduction

This paper describes the synthesis and surface properties of a series of block copolymers containing pendant semifluorinated groups with a monodendron structure. The synthetic procedure involved monodendron group attachment to the isoprene block of a presynthesized block copolymer of styrene and isoprene. This strategy aided processing and organic solvent solubility of these new fluorinated polymers. The resulting materials were examined using a variety of methods including near edge X-ray absorption fine structure (NEXAFS) and contact angle studies and were shown to have stable, nonreconstructing surfaces in polar aqueous environments. These polymers possess stable nonreconstructing surfaces that depend on the mesomorphic character of these side groups and their extent of attachment.

Creating a compliant (elastomeric) polymer surface that does not reconstruct in changing environments is normally a difficult challenge. Such behavior is, however, of great interest in many applications of synthetic polymers ranging from simple protective coatings to release agents to biologically stable surfaces. In particular, the materials with the most interest, those with low-energy surfaces, often have the greatest thermodynamic driving force for reconstruction when in contact with a polar liquid such as water. In the early 1960s, Zisman et al. showed that the critical surface energy of fluoropolymers such as perfluorooctyl methacrylate polymers can reach as low as 11 mJ/m². Lindner has, for example, recently synthesized a fluorinated silicone via the hydrosilylation reaction of fluorinated 1-olefins with poly(hydromethylsiloxane) and formed a material with a surface energy approaching 11 mJ/m² and at the same time demonstrated the feasibility of its nonwetting, low-energy surface to resist fouling by marine organisms. Thomas et al. reported that water- and oil-repellent surfaces could be obtained even though the incorporation of fluorinated monomer in a methacrylate copolymer was as low as 1.5 wt %. To the best of our knowledge, there is little information on long-term surface stability reported in these studies.

Silicone- and fluorine-containing polymers are usually quite susceptible to rapid surface rearrangement. Since our goal is the creation of low surface energy materials for long-term use in a polar environment, a critical question is how the surface properties of polymeric materials can remain stable. Several approaches to creating stable surfaces have been successfully examined previously and include the creation of a network scaffolding immediately below the low-energy surface and the stabilization of the surface using liquid crystalline groups. Of special interest are polymers with semifluorinated (SF) side groups, that is, short segments of alkyl and perfluoroalkyl groups of 5–10 carbons each.
The synthesis and structure of low molar mass semifluorinated materials were studied in detail by Rabolt et al.,7 who first recognized the mesogenic character of short $\text{CF}_2\text{-}$ segments. In subsequent study of several semifluorinated alkanes, Mahler8 and Viney9 generally found a common phase sequence on heating from a crystalline or highly ordered liquid crystalline phase to a smectic B phase. The properties of such semifluorinated materials can be used for tailoring surfaces by taking advantage of the stability of their ordered mesomorphic structure. In the case of semifluorinated LC groups, there is the advantage that not only does the surface resist reconstruction, but the mesomorphic structure is stable against surface reconstruction, because of sparse substitution.13 In other cases, the presence of underlying polar groups may lead to surface blooming and increase the polarity of surfaces.14 We have therefore explored a monodendron strategy to address these issues of surface coverage and polar group masking by using the monodendron’s larger surface coverage capability (see Scheme 1).

Dendrimers are a relatively new class of macromolecule. Recently monodendrons, a subunit of dendrimers, have been explored for surface modification. For example, monodendron monolayers have been successfully used as lithographic materials for patterning with SFM.15 The advantage of such materials is that each monodendron can cover a large area per attachment site with each monodendron acting as an “umbrella” to cover and protect its portion of surface. Our goal as described in this report has been to examine semifluorinated monodendrons for surface coverage and the formation of stable, hydrophobic surfaces. Achieving this requires that the liquid crystalline SF groups form regular, organized structures on the surface.

This paper describes our recent efforts to prepare and characterize semifluorinated LC monodendron surfaces. In the design of the monodendrons, an all aliphatic, phenyl-free structure (see Schemes 2 and 3) was chosen in order to ensure that the substructure was sufficiently flexible and decoupled from a polymer backbone to permit ordering at the fluorinated surface. Both the surface properties and surface coverage effectiveness of the monodendron structure on one block of a block copolymer were examined. The surface structure, morphology, and thermal behavior of these polymers were studied by a combination of advanced analytical techniques including transmission electron microscopy (TEM), NEXAFS, differential scanning calorimetry (DSC), and SFM. The effect of the chemical structure of the monodendron core, the length of the fluorinated mesogen, and the flexible $\text{CH}_2\text{-}$ spacer on the surface properties were of particular importance and are reported here.

**Experimental Section**

**Materials.** 5-Hexen-1-ol (99%), 9-decen-1-ol (98%), nitromethane, trisopropanol, 2,2-bis(hydroxymethyl)propiolic acid, tributyltin hydride, and 10% Pd/C were used as received from Aldrich. Azobis(isobutyronitrile) (AIBN) was recrystallized from acetone/ethanol at 0 °C. Benzyl bromide and benzyl chloride from Aldrich were passed through a short column of activated aluminum oxide to remove any inhibitor prior to

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**Scheme 1. Schematic of the Monodendron**

**Semifluorinated Side Groups Studied as Well as the Single Semifluorinated Side Group for Comparison. Note the Relative Size of the Monodendron Side Groups as Well as Their Larger Coverage Area**

![Scheme 1](Image 329x519 to 546x696)
their use. Perfluorooctyl iodide (97%) and perfluorodecyl iodide (97%) were purchased from Lancaster Synthesis Inc. and used without further purification.

The procedures for synthesis of the block copolymers with semifluorinated monodendron side groups are shown in Schemes 2–4. Anionic polymerization was first carried out (see...
was dried over MgSO4. Subsequently, the dichloromethane was evaporated, and the residual solid was purified by chromatography (ethyl acetate/hexane (v/v) 2/98–10/90). Compound 3 was then obtained as a white waxy solid in 90% yield.

Analysis of 2. 1H NMR (CDCl3): δ 1.0 (s, 3H, -CH3), 3.74 (d, 2H, -CH3OH), 3.97(d, 2H, -CH2OH), 5.20 (s, 2H, -OCH2Ph), 7.35 (bs, 5H, -C6H5).

Analysis of 3. A3 – FH10 1H NMR (CDCl3): δ 1.0 – 1.75 (m, 31H, -CH3 and -CH2), 2.04 (septet, 4H, -CH2CF2-), 2.24 (t, 4H, -CH2CO-), 4.24 (d, 4H, -CH2OOCR). 5.16 (s, 2H, -OCH2Ph), 7.34 (bs, 5H, -C6H5).

Synthesis of 2-Armed Monodendron. To a 3 oz glass bomb with 1.5 g of 3 were added 15 mL of ethyl acetate and 0.15 g of 10% Pd/C catalyst. The system was purged with hydrogen several times using a water aspirator and maintained at 50 psi hydrogen at room temperature (RT) for 1 h. After filtration, the solution was concentrated and vacuum-dried to give 4 in 95% yield as a white powder.

Analysis of 4. A2 – FHL10 1H NMR (CDCl3): δ 1.0 – 1.75 (m, 31H, -CH3 and -CH2), 2.04 (septet, 4H, -CH2CF2-), 2.24 (t, 4H, -CH2CO-), 4.28 (d, 4H, -CH2OOCR).

Synthesis of the Monodendron Acid Chloride (5). Compound 5 was prepared by reaction of the monodendron acid with thiouyl chloride. As an example, 0.5 mL of thiouyl chloride was added dropwise to a 10 mL round-bottomed flask charged with 1 g of monodendron 4. After reacting at room temperature for 30 min, the reaction was heated to and maintained at 40 °C for 6 h. The excess SOCl2 was removed by vacuum distillation at room temperature, followed by heating to 70 °C to give a yellowish solid, which was immediately used for attachment reaction without further purification.

General Procedure for Synthesis of 3-Arm Monodendron. The intermediates needed to make the 3-armed monodendron core (6–9) were synthesized as reported by Newkome et al.17 The characterization data are identical to those previously reported.

Synthesis of 3-Armed Monodendron Core (10). Catalytic hydrogenation was used to obtain the monacid triol (10). The same strategy was used for preparation of the 3-armed monodendron. To a 6 oz glass bomb containing 1.0 g of 9 were added 30 mL of absolute ethanol and 0.2 g of 10% Pd/C catalyst. The system was purged with hydrogen several times and vigorously stirred under 50 psi hydrogen at RT for 20 h. After filtration, the solvent was removed via vacuum distillation to give 10 in 90% yield as a white powder. In the 1H NMR spectrum, proton resonances at 4.49 ppm (s, 6H, -OCH2Ph) and 7.29 ppm (m, 15H, -C6H5) disappeared upon addition of D2O).

Analysis of 10. 1H NMR (DMSO-d6): δ 1.0 – 1.75 (m, 14H, -CH2Ph), 2.10 – 2.40 (m, 2H, -CH2COOH), 3.42 (t, 6H, -CH2OH), 3.39 (t, 3H, -CH3OH), disappeared upon addition of D2O.

Synthesis of Benzyl Group Protected 2-Armed Monodendron. Benzyl-2,2-bis[(hydroxymethyl)propionate (2) was synthesized by reaction of 2,2-bis[(hydroxymethyl)propionic acid (1) with benzyl bromide in the presence of KOH in DMF in 65% yield, as described elsewhere.13 The semifluorinated acid chlorides were synthesized from oxidation of semifluorinated alcohols, which can be readily prepared by the radical addition reaction of 1-iodoperfluoroalkane with alkene-1-ol, followed by treatment with thiouyl chloride. Details of this synthesis can be found in a previous publication.9

To a 50 mL flask were added both 20 mL of anhydrous THF and 2.5 mL of anhydrous triethylamine (18.0 mmol) through a septum to dissolve 1.073 g of 2 (9.6 mmol OH) and 56 mg of (dimethylaminopyridine) (DMAP) which were previously placed in the flask. Upon cooling to 0 °C in an ice bath, 11.52 mmol of freshly distilled semifluorinated acid chloride (20% excess) was added dropwise using a syringe, leading to immediate formation of a white precipitate. Once addition was finished, the reaction was kept at this temperature for an additional hour, and then the reaction completed by stirring at 40 °C overnight. The reaction mixture was treated with 0.5 mL of water and extracted with dichloromethane. The organic phase was separated and neutralized with 0.1 N HCl solution until it reached pH 3. After washing the organic phase twice with water and then twice with 5% NaCl solution, the organic phase contained at 50 psi hydrogen at room temperature (RT) for 1 h. After filtration, the solution was concentrated and vacuum-dried to give 4 in 95% yield as a white powder.

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Analysis of 10. 1H NMR (DMSO-d6): δ 1.0 – 1.75 (m, 14H, -CH2Ph), 2.10 – 2.40 (m, 2H, -CH2COOH), 3.42 (t, 6H, -CH2OH), 3.39 (t, 3H, -CH3OH), disappeared upon addition of D2O.

Synthesis of Benzyl Group Protected Triol (11). To a 100 mL round flask charged with 524 mg of 10 (2.0 mmol) and 220 mg of potassium bicarbonate (2.2 mmol, 10% in excess) was added 25 mL of anhydrous N,N-dimethylformamide (DMF). Upon addition of 0.285 mL of benzyl bromide (2.4 mmol, 20% in excess) in 1 mL of DMF through the septum, the reaction flask was wrapped with aluminum foil, and the reaction mixture was maintained at room temperature for 24 h. The potassium bicarbonate particles gradually become smaller over the course of the reaction. After the solvent was distilled under reduced pressure at 60 °C, the residue was subjected to column chromatography (from EtOAc to 10/90 methanol/EtOAc) to give 11 in 60% yield as colorless liquid.

Analysis of 11. 1H NMR (DMSO-d6): δ 1.0 – 1.75 (m, 14H, -CH2Ph), 2.10 – 2.40 (m, 2H, -CH2COOH), 3.32 (t, 6H, -CH2OH), 5.07 (s, 2H, -OCH2C6H5), 7.36 (bs, 5H, -C6H5).

Synthesis of 3-Armed Monodendron Acid Chloride (14). The benzyl protected monodendron (12) was synthesized in the same manner used to produce compound 3. For synthesis of compound 13, the same procedure for hydrogenation of 3 was also applied. However, in the case of compounds with -CF2- segments, 10 C long, a 1:1 mixture of dichloromethane and ethyl acetate was used instead of ethyl acetate.
alone as solvent in order to enhance the solubility of the resultant monodendron acid. The corresponding monodendron acid chloride 14 was made in a manner similar to the 2-armed synthesis. All acid chlorides were used immediately for the attachment reaction.

Analysis of 12, A3 –F8H10 –Bn 1H NMR (CDCl3): δ 1.0 – 1.75 (m, 56H, –CH2–), 2.05 (septet, 6H, –CF2CH2), 2.29 (t, 8H, –CH2COO–), 3.12 (s, 2H, –OCH2CH3), 3.76 (bs, 5H, –CH2S). Analysis of 13, A3 –F10H12 1H NMR (CDCl3): δ 1.0 – 1.75 (m, 56H, –CH2–), 2.05 (septet, 6H, –CF2CH2), 2.29 (t, 8H, –CH2COO–), 4.03 (t, 6H, –CH2OOC–).

**Synthesis of Block Copolymers with Semifluorinated Monodendron Side Groups.** The hydroxylated poly(styrene-b-1,2,3,4-isoprene) was synthesized via sequential anionic polymerization of the corresponding monomers of styrene and isoprene and followed by hydroboration and oxidation under mild conditions. These details have been reported elsewhere.5,18

Synthesis of single chain semifluorinated alcohols, acids, and acid chlorides was also reported in a previous publication.5

A 10 mL flask with 0.2 g of hydroxylated polymer and 5 mg of DMAP dissolved in 0.5 mL of pyridine and 2 mL of CH2Cl2, the desired amount of freshly prepared 50 wt% monodendron acid chloride (5 or 14) in CH2Cl2 was then injected slowly through a rubber septum. Immediate precipitation could be observed. After the reaction was stirred at RT overnight, in a mixture of these solvents depending on the extent of attachment and LC mesogen. This dissolution–precipitation cycle was repeated four more times. After further extraction with hexane for 24 h using a Soxhlet extractor, the polymer was dried overnight at 60 °C in a vacuum oven.

**Characterization of Polymers.** Gel permeation chromatography (GPC) with four Waters Styragel HT columns was run at 30 °C, with monodisperse polystyrene as standard. The extent of attachment of the fluorinated side groups was calculated from 1H NMR measurements that were carried out on a Varian 200 spectrometer. The thermal transitions were studied by differential scanning calorimetry (DSC) measurement using a Perkin-Elmer DSC-7 series instrument with a 10 °C/min heating and cooling rate.

Contact angles were determined with a NRL contact angle goniometer model 100-00 (Ramé-Hart Inc.) at room temperature. The samples were prepared by spinning 5 wt% copolymer/TFT solutions at a speed of 2500 rpm on a silicon wafer at room temperature or elevated temperature. Critical surface tensions were measured using linear alkanes and low molecular weight trimethylsilyl-terminated poly(dimethylsiloxanes) (Gestel Inc.) as standards.19

Bulk samples of these block copolymers were prepared for TEM and small-angle X-ray scattering (SAXS) studies of microdomain structures. Films of thickness ~1 mm were cast from 5 wt% solutions in TFT. The solvent was allowed to evaporate slowly for 1 week at room temperature. Then the as-cast film was dried thoroughly under vacuum at room temperature for 2 days to remove residual solvent and annealed at 145 °C under vacuum for 4 days to improve long-range order of the morphology. An annealing temperature of 145 °C was high enough (~40 °C) above the glass transition of the PS block to allow mobility of the chains.

The annealed as-cast film was used for X-ray studies without further processing. X-ray experiments were performed at the Cornell High Energy Synchrotron Source (CHESS). The X-ray wavelength and intensity and the distance between the sample and the detector were easily adjusted according to experimental need.

For TEM studies, small pieces of as-cast films were embedded in epoxy resin which was cured at 70 °C for 6 h to produce samples suitable for cross-sectional microtoming. Thin sections were microtomed at room temperature and stained with RuO4 for 15–20 min (RuO4 preferentially stains PS microdomains). 

Infrared spectra were measured with a Mattson 2020 Galaxy Series FTIR with 4 cm−1 resolution averaging 64 scans. Samples were either cast onto a NaCl crystal plate, pressed in a KBr pellet, or made in a thin liquid film between two NaCl crystal plates.

The NEXAFS experiments were carried out on the NIST/Dow materials characterization end station on the U7A beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. A toroidal mirror spherical grating monochromator gives this beamline an incident photon energy resolution and intensity of 0.2 eV and 5 × 1010 photons/s, respectively, for an incident photon energy of 30 eV and a typical storage ring current of 500 mA. The X-rays are elliptically polarized, with the electric field vector E dominantly in the plane of the storage ring (polarization factor = 0.85). The monochromator energy and resolution were calibrated by comparing the transmission spectrum from gas-phase carbon monoxide with electron energy loss reference data.

For the NEXAFS experiments polymer films approximately 200 nm thick were prepared by spin-casting onto silicon wafers from trifluorotoluene solutions and annealed for 6 h in a vacuum at 150 °C. A goniometer stage allowed the angle of the sample surface with regard to the polarization vector of the soft X-rays to be varied between 20° and 90°. Our NEXAFS experiments measure the resonant soft X-ray excitation of a carbon 1s electron to an α orbital, an unoccupied low-lying antibonding molecular orbital with α symmetry.14 Since the 1s → α resonant excitations are governed by dipole selection rules, the transitions are polarized; i.e., their intensity varies as a function of the direction of the electric field vector E of the incident X-ray photon relative to the long axis of the α orbital of the final state. In our experiments we detect the resonant excitation by monitoring the emission of Auger electrons from the near-surface region of the polymer film. These Auger electrons form most of the partial electron yield (PEY) signal that is collected using a channeltron electron multiplier that has an adjustable entrance grid bias (EBG). Auger electrons that have lost significant energy in emerging from more than 2 nm below the surface are discriminated against by increasing the negative EGB on the channeltron detector. To eliminate the effect of incident beam intensity fluctuations and monochromator absorption features, the PEY signal was normalized by the incident beam intensity obtained from the photoyield of a clean gold grid.

**Results and Discussion**

Direct syntheses of fluorinated block copolymers have been reported by a number of living polymerization methods. However, direct anionic polymerization of fluorinated monomers cannot be readily undertaken due to their poor solubility in common solvents at low temperature as well as the sensitive character of chemical functions associated with many fluorinated groups. In this study, the semifluorinated monodendron groups were therefore attached to preformed polymers using the esterification chemistry that has been successfully demonstrated with styrene-modified diene block copolymers.5 A great advantage of this postpolymerization chemistry is that a single base polymer with a well-defined block copolymer architecture can be reliably prepared in a large quantity via living anionic polymerization and then modified with different side groups. This approach enables the direct comparison of different side groups on the same polymer backbone.

**Synthesis of Semifluorinated Monodendrons.** In this paper, a protection–deprotection procedure and convergent growth strategy were used for synthesis of the target monodendrons. The large differences in
molecular weight and polarity between products and starting materials or byproducts made purification much simpler. In the synthetic schemes employed, two major reaction steps, esterification of protected intermediates and deprotection via hydrogenation, were used. Ester formation was carried out in very high yield through acid chloride chemistry in the presence of base (triethylamine or pyridine) and (dimethylamino)pyridine (DMAP) catalyst. A benzyl function was used as a protecting group because it can be cleanly and quantitatively removed by catalytic hydrogenation. In addition, this hydrogenation step does not cleave the ester bonds formed between the monodendron core and the single semifluorinated segments. On the basis of these reaction steps, we have successfully synthesized 2-armed and 3-armed single generation semifluorinated monodendrons in good yields.

Prior to producing the 2-armed monodendron, we recognized that 4 can also be obtained from the direct one-step reaction of 1 and a semifluorinated acid chloride. However, there are possible acid chloride exchange reactions, and as a consequence, an intermolecular esterification reaction may occur between two molecules of 1. In addition, the final monodendron acid is extremely difficult to separate from any free semifluorinated acid produced from the excess semifluorinated acid chloride, because the physical properties of these two acids are very similar. Despite the three reaction steps involved in Scheme 1, the benzyl-protected monodendron is easily purified from the single semifluorinated acid by chromatography in step two. Because of the inexpensive starting material 1 and the efficient esterification and debenzylation reactions, this multistep scheme is considered to be much better than the direct reaction in making the pure monodendron.

For the synthesis of the 3-armed monodendron core, the first three steps were adapted from ref 17. Quantitative hydrogenation of the benzyl ester at relatively low pressure was used in the final step. Absolute ethanol was chosen as the solvent since the resulting product 10 was expected to be very hydrophilic. Because of the relatively high reactivities of both hydroxyl and carboxyl groups in 10 and the low vapor pressure of ethanol, it was necessary to avoid high reaction temperatures during the removal of the solvent in order to prevent any possible side reactions such as unwanted esterification. However, this reaction has the additional advantage of easy workup and pure product formation because the activated carbon present as the catalyst support can absorb impurities in the starting material.

For the reasons mentioned above, the monodendron core 10 was converted to its benzyl ester 11 within 24 h of synthesis to avoid any side reactions during storage. Initially, we used the same reaction conditions (KOH/DMF, 100 °C) as for the 2-armed monodendron reaction. However, the resultant product was a viscous liquid. 1H NMR analysis showed the existence of both benzyl and other aliphatic esters. A possible cause was the vigorous reaction conditions used. An efficient method of esterification has been reported by Pfeffer et al. through alkylation of carboxylate salts with alkyl halides in dipolar aprotic solvents. To avoid side reactions, very mild reaction conditions (KHCO3, C6H5CH2Br, RT) were chosen. The corresponding potassium monodendron carboxylate, which is formed in situ using potassium bicarbonate, reacts immediately with the more reactive benzyl bromide (instead of benzyl chloride) to give the corresponding benzyl group protected triol. Dark reaction conditions were used to reduce the possibility of photolysis of benzyl bromide and to make final separation easier. Irreversible evolution of carbon dioxide favors product formation. Thin-layer chromatography (TLC) was used to monitor the conversion of the acid to benzyl ester. Through combination of both reduced base strength and reaction temperature, no evidence of ester formation between the hydroxyl and carboxyl groups was detected in 1H NMR measurement. The polarity difference between 10 and 11 makes separation simple by chromatography. For the case of the 3-armed monodendron 13 with a −CF2− length of 10, the resultant monodendron was insoluble in ethyl acetate. It was necessary to reduce the polarity of the solvent by using a mixed solvent of dichloromethane and ethyl acetate.

**Synthesis of Semifluorinated Block Copolymers.** Several factors, such as monodendron attachment chemistry, the type of monodendron, and the solvent system, were examined for their influence on the attachment efficiency of the semifluorinated monodendron. The use of acid chloride (5 or 14) for attachment to the hydroxylated block copolymer backbone was found to be the most efficient reaction. Complete removal of excess thionyl chloride from the monodendron acid chloride was critical in order to avoid chlorination of any hydroxyl group on the polymer backbone during the attachment reaction. Because of the large molecular weight of the monodendron acid chloride, we elected to heat the resultant acid chloride above its melting point under vacuum to remove residual thionyl chloride rather than risk partial hydrolysis during recrystallization.

The type of monodendron affects attachment efficiency. Under the best conditions, an attachment ratio (defined as the percentage conversion from hydroxyl group to monodendron ester) as high as ~80% could be reached for the 2-armed monodendron and up to ~60% for the 3-armed monodendron, even though an excess of monodendron acid chloride was used. Because of the bulkiness and solubility of the monodendron group, we believe steric hindrance played a significant role in attaining high conversion and restricted further attachment. The reaction medium had an important effect on the attachment ratio as well. Attachment in dichloromethane or THF lead to low conversion, simply because of the low solubility of the resultant polymer in such solvents. Immediate addition of a nonpolar solvent, such as trifluorotoluene (TFT), leads to precipitation of the starting hydroxylated polymer, which is quite polar. As a result, a two-stage procedure was developed to achieve higher attachment levels. In the first stage, excess pyridine was used as a hydrochloric acid acceptor and a solvent for the hydroxylated polymer. Because of the low solubility of the monodendron acid chloride, the reaction system gradually gelled, indicating the occurrence of the attachment reaction. In the second stage after the initial 12 h reaction period, some of hydroxyl groups have been converted to the less polar monodendron ester. It was usually necessary at that point to increase the reaction temperature and add nonpolar solvent, such as TFT, to enhance the solubility of the resulting polymer and achieve higher attachment levels.

Attachment of monodendron side groups could be confirmed by the downfield shift of the CH3O− group on the isoprene block by ~0.4 ppm, which indicates the formation of monodendron ester from the corresponding...
Table 1. Molecular Weight and Composition Analysis of Semifluorinated Block Copolymers with FxHy Single and Monodendron Side Groups

<table>
<thead>
<tr>
<th>polymera</th>
<th>side group</th>
<th>starting PS/PI</th>
<th>attachment ratio</th>
<th>calc'd MW of final polymer</th>
<th>absd from GPC</th>
<th>peaks</th>
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<tr>
<td>BC-0.99F8H10</td>
<td>F8H10</td>
<td>41.1K/7.3K</td>
<td>full</td>
<td>41.1K/70.6K</td>
<td>81.0K</td>
<td>two</td>
</tr>
<tr>
<td>BC-0.52F8H10</td>
<td>F8H10</td>
<td>41.1K/7.3K</td>
<td>51.9%</td>
<td>41.1K/41.2K</td>
<td>3000K</td>
<td>one</td>
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<tr>
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<td>A3-F8H10</td>
<td>38.2K/6.7K</td>
<td>58.5%</td>
<td>38.2K/121.4K</td>
<td>66K/96K</td>
<td>two</td>
</tr>
<tr>
<td>BC-3A0.56F8H10</td>
<td>A3-F8H10</td>
<td>66K/5.5K</td>
<td>56.2%</td>
<td>66K/96K</td>
<td>66K/96K</td>
<td>two</td>
</tr>
</tbody>
</table>

a BC denotes block copolymer, FxHy refers to the composition of the semifluorinated group, and 0.2z indicates the extent of attachment on the hydroxylated backbone.

Figure 1. GPC traces of semifluorinated block copolymers with 3-armed monodendron and single SF side groups with different extents of attachment (measurements made in THF) showing both free chains and micellar structures: BC-0.99F8H10 (- - -), BC-0.52F8H10 (---), and BC-3A0.59F8H10 (-----).

A polymer (BC-0.99F8H10) with single semifluorinated side groups. It is known that micellization of block copolymers generally occurs in a solvent that is selective for one block but is a poor solvent for the other block.22 The higher molecular weight peak observed in Figure 1 is associated with micelle formation while the lower molecular weight peak is due to the isolated block copolymer molecules. For comparison, we synthesized polymer with single semifluorinated side groups (BC-0.52F8H10) with a similar attachment ratio (but clearly lower F content) to a polymer with 3-armed monodendrons (BC-3A0.59F8H10), so that it had the same molar ratio of residual OH groups, as listed in Table 1. BC-0.52F8H10 does not form micelles under these conditions as judged from the GPC trace (Figure 1), while the polymer with semifluorinated monodendron side groups (BC-3A0.59F8H10) shows very strong micellization behavior with only a small fraction of free polymer chains. The ratio of micellar to free chains of this polymer is higher than BC-0.99F8H10 (full attachment), as can be seen from Figure 1. The overall content of −CF2− groups in a polymer plays a very important role in this micellization behavior since the residual OH group content remains the same. Prior published work has shown that no micellization occurs if the −CF2− length is 6 or less, independent of the extent of attachment. Details of the micellar structure are being investigated by light scattering and other methods. Even though the presence of micelles can be readily demonstrated in many of these polymers, the surface properties did not depend on the casting solvent.

LC Behavior in a Monodendron Structure

Dendrimers and monodendrons have recently received intense study either as single molecular species or attached to polymer chains to form so-called bottle brush polymers. Focusing on fluorinated dendrimer structures, DeSimone and co-workers have reported fourth generation poly(ethyleneimine) with a “CO2-philic” shell derived from a heptamer acid fluoride of hexafluoropropylene oxide that act as excellent surfactants in CO2 media. Percec and co-workers have reported the self-assembly behavior of a homopolymer with semifluorinated monodendron side groups. However, its LC mesophase was quite weak as judged by its low Φlon−isotropic transition enthalpy (0.2–0.3 kcal/mol repeat unit). The same research group also synthesized a series of semifluorinated tapered monodendrons, which were capable of forming supramolecular columnar structures with a hexagonal columnar LC phase, and studied the fluorophobie effect on the self-assembly behavior compared with their hydrocarbon analogues. Since the fluorinated segments were connected to an aromatic core group, the ability of the SF structure to spontaneously organize into an ordered surface was unclear.

However, in other work by Percec,33 dendrimers with conventional mesogenic groups and linking spacers were
The transition enthalpy and thus the stability of the growing from 5.2 J/g (CH2 6) to 10.3 J/g (CH2 10). This increase was found in the single SF side group case which grew dramatically from 2.0 to 7.0 J/g. A similar enthalpy of transition for the SF side group in the 3-armed series is used. Lattermann and co-workers reported the structure when the appropriate dendrimer architecture was used. They showed that a mesogenic group can pack into an ordered hexagonal columnar (Colh) or enantiotropic Colh phase in the presence of a rigid aromatic core and the attachment ratio. It can be assigned to a transition from the smectic B mesophase to the isotropic state. This is different from the behavior of single SF side groups attached to the same block copolymer in which two transitions were observed. One possible explanation for this difference is that introduction of a monodendron structure disturbs the formation of a mesophase. However, both the enthalpy of transition and the transition temperature are sensitive to not only the structure of the semifluorinated unit, even though the attachment ratio is the same range. From a structural viewpoint, the difference between the 3-armed and 2-armed monodendron cores is caused by the additional CH2 groups in the 3-armed case which provide extra conformational flexibility for the fluorinated segments to order into a well-ordered mesophase.

As can be seen from Table 2, the transition temperature for the 3-armed monodendron polymer is almost 25 °C higher than that for the corresponding 2-armed one, and the transition enthalpy for the 3-armed series is also much higher, if the attachment ratio is kept in the same range. From a structural viewpoint, the difference between the 3-armed and 2-armed monodendron cores is caused by the additional CH2 groups present in the 3-armed case which provide extra conformational flexibility for the fluorinated segments to order into a well-ordered mesophase.

In addition, the attachment ratio was found to affect the transition enthalpy (3.9 J/g for BC-3A0.24F8H10 (24% attachment) versus 10.1 J/g for BC-3A0.53F8H10 (53% attachment)) but have little effect on transition temperature (55.6 °C for BC-3A0.24F8H10 versus 62.4 °C for BC-3A0.53F8H10). The monodendron side groups can form a similar, stable mesophase even at relatively low attachment levels; however, a lower transition enthalpy is an indication of decreased stability of the mesophase in the bulk. From the discussion above, it is believed that the CH2 spacer plays an important role in determining the transition enthalpy while the −CF2−mesogen influences mostly the transition entropy (and thus the transition temperature without changing the transition enthalpy). In the next section, we discuss how this LC behavior affects the surface properties of a polymer film.

### Solid State Properties of the Semifluorinated Polymers

The morphology of these polymers was examined by X-ray diffraction and transmission electron microscopy (TEM). BC-2A0.66F8H10, a 2-armed monodendron block copolymer, was selected as a representative polymer for thorough study. As shown in Figure 2, a highly ordered smectic mesophase is observed by WAXD analysis. Three orders of reflection can be clearly seen at spacings of 40, 20, and 13 Å and were assigned to the smectic layers. The two sharp, oriented outer arcs with a d spacing of 4 Å can be identified as the intermesogen spacing. The sharpness of the two outer arcs shows that d spacing between mesogens is very uniform and that they are oriented normal to the layers of the smectic mesophase. This feature is characteristic of a smectic B mesophase for this block copolymer. The theoretical length of this mesogen is about 21 Å estimated by computer simulation. Thus, within each layer of the mesophase, a model with two mesogens arranged head-to-head to make up the 40 Å layer thickness is consistent with observation.

TEM images of this sample (Figure 3) revealed a microphase-separated, highly organized and hexagonally packed cylinder morphology with PS cylinders placed in a fluorinated LC matrix, as expected from the

<table>
<thead>
<tr>
<th>polymer</th>
<th>monodendron</th>
<th>attachment ratio (%)</th>
<th>T (°C)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-2A0.62F8H6</td>
<td>A2F8H6</td>
<td>68.2</td>
<td>30.9</td>
<td>2.0</td>
</tr>
<tr>
<td>BC-2A0.66F8H10</td>
<td>A2F8H10</td>
<td>66.3</td>
<td>47.8</td>
<td>7.0</td>
</tr>
<tr>
<td>BC-2A0.38F10H10</td>
<td>A2F10H10</td>
<td>38.0</td>
<td>67.7</td>
<td>3.5</td>
</tr>
<tr>
<td>BC-3A0.24F8H10</td>
<td>A3F8H10</td>
<td>23.7</td>
<td>55.6</td>
<td>3.9</td>
</tr>
<tr>
<td>BC-3A0.53F8H10</td>
<td>A3F8H10</td>
<td>53.1</td>
<td>62.4</td>
<td>10.1</td>
</tr>
<tr>
<td>BC3A0.58F10H10</td>
<td>A2F8H10</td>
<td>57.5</td>
<td>95.4</td>
<td>11.6</td>
</tr>
</tbody>
</table>

*BC denotes block copolymer, FxHy refers to the composition of the semifluorinated group, and 0.2z indicates the extent of attachment on the hydroxylated backbone. Molecular weight of the starting PS/P1 block copolymers is 36.2K/67.2K.
estimated volume fractions of the LC block ($f_{\text{LC}} = 59.2\%$). The domain spacing (distance between cylinders) obtained from TEM was $670\ \text{Å}$, with a cylinder radius $R$ of $\sim 260\ \text{Å}$. The dark edge of the cylinder is believed to arise from preferential staining along the microstructure interface due to fast diffusion through the LC domain and slow diffusion into the PS one. To confirm this morphology, a two-dimensional SAXS pattern (Figure 4) was recorded. This highly oriented X-ray pattern also showed that macroscopically aligned films could be prepared by a simple solvent-casting process. A one-dimensional line scan of this pattern (Figure 5) clearly showed peaks of 100, 110 (as a shoulder), 200, and 210 indices in a ratio of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, which is characteristic of hexagonally packed structures. The domain spacing calculated from SAXS of $680\ \text{Å}$ is in good agreement with TEM data.

Unlike coil–coil block copolymers, the side chain 2-armed monodendron LC–coil block copolymer can self-assemble on several length scales. Within the LC microdomains, which are discussed in the next section, the side-chain LC mesogens form a confined smectic B mesophase as shown by DSC and WAXS. To understand how the mesophase is aligned with respect to the microdomain structure, additional two-dimensional X-ray patterns (Figure 6) of the same macroscopically oriented film were taken. This pattern shows a set of inner Bragg reflections resulting from the hexagonally packed cylinders and a pair of outer reflections resulting from the smectic B mesophase. Obviously, the smectic layer reflections are perpendicular to the PS–cylinder reflections. From Figure 2, we know that mesogen alignment is perpendicular to the smectic layers. As a result, the X-ray studies demonstrate that these side chain LC mesogens have a homogeneous boundary condition in the bulk with respect to the intermaterial dividing surface and are oriented in the axis direction
of the cylinders. Combining the WAXS, SAXS, and TEM results for this block copolymer, we propose a schematic molecular model shown in Figure 7, which illustrates the packing between the side group LC monodendrons and the coil chains. This packing behavior is consistent with observations made by others and us for polymers with single LC side groups but is remarkable in view of the fact this complex structure is observed with side group monodendrons. It should be noted that not all side group LC block copolymers show this orientation in thin film studies.

Critical Surface Tension. The critical surface tension of these polymers and their stability were evaluated and are reported in Table 3. It is well-known that the contact angle of a liquid on a given low-energy surface usually increases with surface tension except when the liquid has a tendency to dissolve or reorganize the surface molecules of the wetted solid. Using as standards a series of linear alkanes and two low molecular weight trimethylsilyl-terminated poly(dimethysiloxanes) with known surface tension, the advancing contact angles were measured. Values of critical surface tension were extrapolated from Zisman plots of cos(θ) versus surface tension as shown in Figure 8.

Provided that −CF₂− lengths longer than eight were used, it was found that all block copolymers with monodendron side groups have surface energies in the range 7–9 mJ/m² regardless of the extent of attachment (which varied from 25% to 70%) or the monodendron structure. These values are comparable to values obtained for similar block copolymers with single semifluorinated side groups and are very close to the known critical surface tension of a uniform −CF₃ surface formed by monolayers of perfluorocarbon acids (e.g., 8.6 mJ/m² for perfluorohexanoic acid and 7.9 mJ/m² for perfluorooctanoic acid). Since those monolayers

Table 3. Water Contact Angles and Critical Surface Tensions of Selected Semifluorinated Block Copolymers Polymers with Monodendron Side Groups

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monodendron</th>
<th>Attachment Ratio (%)</th>
<th>Advancing Angle (deg)</th>
<th>Receding Angle (deg)</th>
<th>Critical Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-2A0.62F8H6 A₂-F₈H₆</td>
<td>68.2</td>
<td>121</td>
<td>103</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>BC-2A0.66F8H10 A₂-F₈H₁₀</td>
<td>66.3</td>
<td>121</td>
<td>108</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>BC-2A0.38F10H10 A₂-F₁₀H₁₀</td>
<td>38.0</td>
<td>122</td>
<td>110</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>BC-3A0.24F8H10 A₃-F₈H₆</td>
<td>23.7</td>
<td>117</td>
<td>98</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>BC-3A0.53F8H10 A₃-F₈H₁₀</td>
<td>53.1</td>
<td>120</td>
<td>108</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>BC3A0.58F10H10 A₃-F₁₀H₁₀</td>
<td>57.5</td>
<td>124</td>
<td>110</td>
<td>7.7</td>
<td></td>
</tr>
</tbody>
</table>

a BC denotes block copolymer, FₙHₙ refers to the composition of the semifluorinated group, and 0.22 indicates the extent of attachment on the hydroxylated backbone.
have vertically oriented and closely packed perfluorinated chains, we may infer that these polymer surfaces have similar orientation and packing of their perfluorinated segments and that hydrophobic \(-\text{CF}_3\) groups are well organized on the surface, while the more hydrophilic OH and ester groups are almost completely hidden by the low surface energy monodendron structure.

**Effect of Side Groups on the Temporal Stability of the Surface.** For a hydrophobic coating material used under a polar environment, it is very important to understand the long-term surface stability of these polymer films. For this purpose, partially substituted block copolymers with single semifluorinated side groups were synthesized for comparison with polymers having 2-armed and 3-armed monodendrons. The attachment ratios for all side group types were controlled to be \(-55\%\) so that the residual OH molar ratio in all polymers remained the same. Obviously, the fluorinated unit content in each polymer is quite different; i.e., 3-armed polymers have the highest content, while the single chain polymers have the lowest. The contact angle changes versus immersion time of polymer films in water over a 2 week period are shown in Figure 9.

The advancing contact angle for single semifluorinated side groups drops slightly over this period, while only 12° and 5° respectively for the 2-armed polymer and 3-armed polymers. A similar situation is found for the receding contact angle. From DSC measurements, the semifluorinated chains in the partially substituted single SF group polymers (BC-0.52F8H10) are unable to form a well-ordered smectic mesophase as demonstrated by both transition temperature and enthalpy. The surface structure of these semifluorinated polymers was further characterized by near edge X-ray absorption fine structure (NEXAFS) analysis. Details of this work appear elsewhere.\(^{12,34,35}\) The orientation of the semifluorinated units in the near surface region (upper 2 nm) was examined by partial electron yield signals. From these we conclude that the surface is entirely dominated by the fluorocarbon segments and that their net orientation in the surface region is toward the surface normal, thus forming a \(-\text{CF}_3\) surface. This fact can be established...
of the 1s core electron, consist almost exclusively of the semifluorinated iso-
surface of any of these samples; i.e., the sample surfaces in the NEXAFS data. Figure 11a shows the partial electron yield (PEY) signal as a function of soft X-ray photon energy over the region of the C K-edge for the single SF group substituted block copolymer while parts b and c of Figure 11 show similar data for the 2-armed and 3-armed monodendrons (BC-2A0.66F8H10 and BC-3A0.59F8H10), respectively. Two curves are shown on each plot, one corresponding to an angle $\theta$ between the electric field vector $\mathbf{E}$ of the polarized X-ray beam and the sample normal of 90° and one corresponding to an angle $\theta$ of 20°. Although the 1s to $\pi^*$ ($E = 284.5$ eV) resonant transition is the strongest feature of the X-ray fluorescence yield spectrum of each of these samples, there is only a small 1s to $\pi^*$ PEY signal from the phenyl rings of the polystyrene (PS) block in any of these plots. The absence of this resonance in the PEY spectrum means that these bonds have some net orientation normal to the sample surface. These results are consistent with previous ones on the semifluorinated LC block copolymers and indicate that the rigid $-\text{CF}_2-$ helix is, on the average, oriented normal to the sample surface. The degree of that orientation or the orientational order, however, is clearly different for the different samples. The surface of the 3-armed monodendrons is clearly less oriented than that of the 2-armed monodendrons while the surface of the 2-armed monodendrons is about as oriented as those of the single SF group substituted block copolymer.

To quantify these statements, we have analyzed these NEXAFS data as described in the Appendix to determine the uniaxial order parameters $S_{\text{CF}}$ and $S_{\text{CC}}$ of the CF and CC bonds of the surface. These range from +1 (a bond axis completely aligned along z) to $-1/2$ (a bond axis lying in the plane of the surface) and are equivalent to the Hermans orientation function of X-ray diffraction. These are shown in Figure 12. In addition, we have computed from these the uniaxial orientational order parameter $S_{\text{helix}}$ of the $-\text{CF}_2-$ helix as well as the average angle between the helix and the surface normal. These are given in Table 4 along with the other order parameters. It can be seen that the CF and CC order parameters for all samples are comparable in magnitude but different in sign, with $S_{\text{CF}}$ being negative and $S_{\text{CC}}$ being positive. The $-\text{CF}_2-$ helix order parameter computed from $S_{\text{CF}}$ is approximately 0.26 for both the two single SF side group block copolymers and the two 2-armed monodendron block copolymers even though the two polymers with single SF side groups and the two polymers with 2-armed monodendrons have quite different attachment ratios (0.99 for BC-0.99F8H10 vs 0.52 for the BC-0.52F8H10 and BC-2A0.66F8H10 vs 0.34 for the BC-2A0.34F8H10). Therefore, even large differences in attachment ratio do not seem to produce large differences in orientational order of the semifluorinated mesogen surfaces. The surface orientational order parameter of the $-\text{CF}_2-$ helix for the two block copolymer with attached 3-armed mono-
dendrons, however, is significantly smaller, about 0.17. The smaller CF helix order parameter for the 3-armed monodendron surfaces may be related to the fact that these surfaces show roughness on a scale of about 10 nm (observed by SFM) that is significantly larger than that for the 2-armed monodendron and single SF side group surfaces. The 3-armed SF monodendron polymers have a surface consisting of spherical humps about 10 nm in diameter. This topography may be due to spontaneous curvature of the surface region caused by the frustration introduced by attaching these bulky monodendrons to the polymer backbone. The observed effect of these surface textures on wetting is negligible, since all these polymer surfaces show similar advancing and receding water contact angles on fresh exposure to water. The spontaneous curvature may however affect the NEXAFS results, since the extra surface roughness should introduce an extra source of orientational disorder. In addition, the packing frustration that we speculate gives rise to the fine scale surface topology may introduce an extra splay in the surface smectic director that will result in poorer orientational order.

Conclusions

In summary, a series of styrene-modified diene block copolymers with low surface energy, semifluorinated monodendron side groups were prepared and studied by a variety of methods. A general procedure for synthesizing low-energy surface forming semifluorinated monodendrons has been developed which can be extended to the synthesis of higher generation monodendrons. The surface of the block copolymer films examined in this study is largely made up of a uniform −CF3 layer and typically has surface energies of only 7−9 mJ/m2. The molecular structure of the monodendrons plays an important role in surface stability. In particular, the linking of the monodendron core and the fluorinated mesogen by a flexible group determines the temperature and enthalpy of a smectic B−isotropic transition present in these polymers, which in turn controls resistance to surface reconstruction. With sufficiently long methylene spacers and mesogenic groups, the polymer film surface is stabilized by the LC mesophase and can resist reconstruction in water even with hydrophilic OH groups lying just beneath the surface. Studies of the effect of degree of substitution on surface stability showed that the more arms on the monodendron, the more it could tolerate partial substitution and still form a stable low-energy surface. Thus, the use of the semifluorinated monodendron structure is a promising strategy for creation of stable, low-surface-energy materials with strong subsurface polar group masking ability.

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Appendix: The Orientational Order Parameter

The orientational order is found by first using the method of Outka and co-workers37 to fit the PEY NEXAFS spectra as a series of Gaussian curves representing the different 1s → σ* transitions and a step function corresponding to the excitation edge of carbon. The magnitudes of these Gaussians are taken to be the intensities I(θ) of the various 1s → σ* transitions. Using the notation of Stöhr and Samant,38 the molecular orientation factors fxy, fyz, and fz for the C−F and C−C bonds are defined as follows:

\[
f_z = \int \cos^2 \alpha \, f(\alpha) \, d\Omega
\]

\[
f_x = f_y = \frac{1 - f_z}{2}
\]

where z is an axis normal to the film surface and x and y are orthogonal axes in the plane of the surface while \( \alpha \) is the angle between the axis of the σ* orbital (\( \sigma \) bond axis) and z. The molecular axis distribution function \( f(\alpha) \) is normalized so that \( \int f(\alpha) \, d\Omega = 1 \) and thus \( f_z + f_x + f_y = 1 \). A uniaxial orientation order parameter S is then defined as

\[
S = \frac{1}{2}(3f_z - 1)
\]

where S ranges from +1 (\( \sigma \) bond axis completely aligned along z) to −1/2 (\( \sigma \) bond axis lying in the plane of the surface). It is assumed that there is isotropy in the plane of the surface; i.e., there is no preferred direction in the plane. The order parameter defined in this way is analogous to the Hermans orientation parameter of X-ray diffraction.36 Regardless of the amount of orientation of the \( \sigma \) bond normal to the plane, the PEY intensity I(θ) is predicted to have the following form:

\[
I(\theta) = A + B \sin^2 \theta
\]
from the values of A and B as follows:

\[
S = -\frac{P^{-1}B}{3A + (3 - P^{-1})B}
\]

(3)

where P is the polarization factor of the X-ray beam (0.85 in our case).

Previously we reported the average tilt angle \(\langle \tau_{\text{F-helix}} \rangle\) of the fluorocarbon helix part of single semifluorinated groups with respect to the surface normal34 which was calculated on the basis of the "building block model".37,39 This average tilt angle is directly related to the orientational order parameter of the C–F bonds, \(S_{\text{CF}}\), as follows:

\[
S_{\text{CF}} = \frac{1}{2} \frac{3}{2} \sin^2 \langle \tau_{\text{F-helix}} \rangle - 1
\]

(4)

Inversion of eq 4 yields \(\langle \tau_{\text{F-helix}} \rangle\) values from values of \(S_{\text{CF}}\), and these values of \(\langle \tau_{\text{F-helix}} \rangle\) are also given in Table 4. Finally, the order parameter \(S_{\text{helix}}\) of the fluorocarbon helix part of single semifluorinated molecules follows:

\[
S_{\text{helix}} = -2S_{\text{CF}}
\]

References and Notes

(3) Thomas, R. R.; Anton, D. R.; Graham, W. F.; Darman, M. J.; Sauer, B. B.; Stika, K. M.; Swartzfager, D. G.

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