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Correlation of Surface and Bulk Order in Low Surface Energy Polymers

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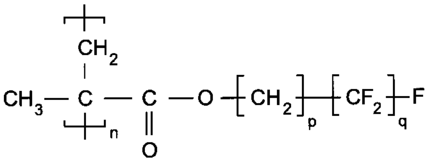
Low surface energy coatings or antiwetting agents play an essential role in microelectronics, antifogging, and antifouling applications and even have promising medical applications.[1] Currently, perfluoroalkyl-substituted polymethacrylates (PFPMs) are widely in use, and the antiwetting properties of these and related polymers[2,3] are believed to arise from the segregation of CF_3 groups to the surface. Such polymers are known to exhibit various ordered bulk phases (crystalline, smectic A, smectic B, nematic, and isotropic), depending on the number of CF_2 units in the side groups.[4,5] So far, the search for possible correlations between the bulk structure/order and the surface energy[3,6] has been impeded by a missing link, namely, knowledge of the surface structure. It is clear that the surface energies are determined by the structures present in the top layer (1 nm or less from the air surface), and such information has been lacking for all but a few systems.[7] Thus, in lieu of a scientific understanding of how bulk structures and properties influence surface energies, the design of improved coatings has been largely empirical.

We have investigated polymers with the same polymethacrylate backbone but with different perfluoroalkyl side groups of the form



$$\left[-CH_2-C(CH_3)\left(C(=O)-O-(CH_2)_p-(CF_2)_q-F\right)-\right]_n$$

The polymer with $(CH_2)_2(CF_2)_8F$ side groups (F8) exhibits a smectic A order at room temperature. Around 80 °C it undergoes a smectic A to a nematic (or cybotactic nematic) transition and around 120 °C a nematic to isotropic transition. In comparison, the polymer with $(CH_2)(CF_2)_7F$ (F7) exhibits a nematic phase at room temperature and a nematic to isotropic transition around 75 °C. In contrast, no ordered phase is seen for the polymer with $(CH_2)_2(CF_2)_6F$ (F6) side groups.[4] The change in bulk order from isotropic to nematic to smectic A is accompanied by a change in surface energy from 10.0 dyn/cm (F6) to 9.0 dyn/cm (F7) to 8.0 dyn/cm (F8) at 20 °C. Therefore, the three PFPMs are well-suited to investigate the relationship between bulk order, surface order, and surface energies.

The polymer samples were prepared by atom transfer radical polymerization (ATRP) of the monomers, obtained from an esterification reaction of methacryloyl chloride with corresponding alcohols, to obtain high molecular weight samples with a relatively narrow molecular weight distribution.[8] The polymers were soluble in hexafluorobenzene and purified by reprecipitation in chloroform and methanol. The intrinsic viscosities of the polymers in hexafluorobenzene were found to be high, ca. 1.5 dL/g at 30 °C, indicating high molecular weight characteristics (>100 000). Thin polymer films were deposited on silicon wafers by spin-coating using hexafluorobenzene as solvent. We do not observe any thickness effects in the studied range of some 10 nm to a few microns.

The surface energy was determined with the Zisman plot method from the measured contact angles for several liquids.[9] The contact angles remained constant over time for the F8 and F7 samples, but the value for the F6 sample had to be measured immediately due to the partial solubility of the polymer. An accuracy better than ±0.02 dyn/cm is indicated by the Zisman plots, which is significantly better than the observed decrease in surface energy with increasing number of CF_2 groups in the side chains. The bulk phase behavior was determined in the temperature range of 20−140 °C by X-ray diffraction experiments and hot-stage polarized optical microscopy studies of miscibility behavior with perfluoroalkyl ethers which are completely miscible at the ambient.

NEXAFS measurements were carried out at the Stanford Synchrotron Radiation Laboratory using nearly linear polarized soft X-rays from the wiggler beam line 10-1, which is equipped with a spherical grating monochromator. Prior to the measurements reported here a detailed study of radiation damage effects was conducted, and the photon flux density was decreased to about 3×10^9 photons/s into a 2×2 mm^2 spot on the sample, with an energy resolution of about 80 meV at the C K-edge. Under these conditions the radiation damage effects were negligible over the 15 min time period of a NEXAFS spectrum, and each NEXAFS spectrum was recorded on a new spot on the same sample. Polarization-dependent NEXAFS spectra[10] were recorded at normal X-ray incidence ($\alpha = 90°$) with the electric field vector $\vec{E}$ parallel to the sample surface and at grazing X-ray incidence ($\alpha = 20°$) with $\vec{E}$ oriented 70° from the surface, i.e., $\vec{E}$ oriented 20° from the surface normal. We simultaneously measured NEXAFS spectra by means of Auger electron yield (AEY) and total electron yield (TEY) detection, which sample about 1 and 10 nm from the free polymer surface, respectively.[11] The spectra were normalized to the incident photon flux and per C atom, as discussed elsewhere.[12]

In Figure 1 we compare room temperature AEY and TEY NEXAFS spectra of F7, corresponding to a magic angle geometry[12] that eliminates molecular orientation effects. The spectral peaks are due to transitions of C 1s core electrons into unoccupied molecular orbitals, and our peak assignment agrees with that in the literature.[7,13] Because of the magic angle geometry and the different sampling depth of AEY and TEY, these spectra

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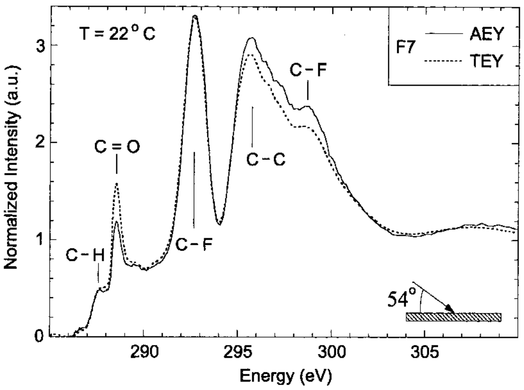

Figure 1. Room temperature AEY and TEY spectra of F7, corresponding to a magic angle geometry. The segregation of CF_3 groups to the polymer surface is demonstrated by the increased intensity between 295 and 300 eV in the more surface-sensitive AEY spectrum and the decreased intensity of the C=O peak.

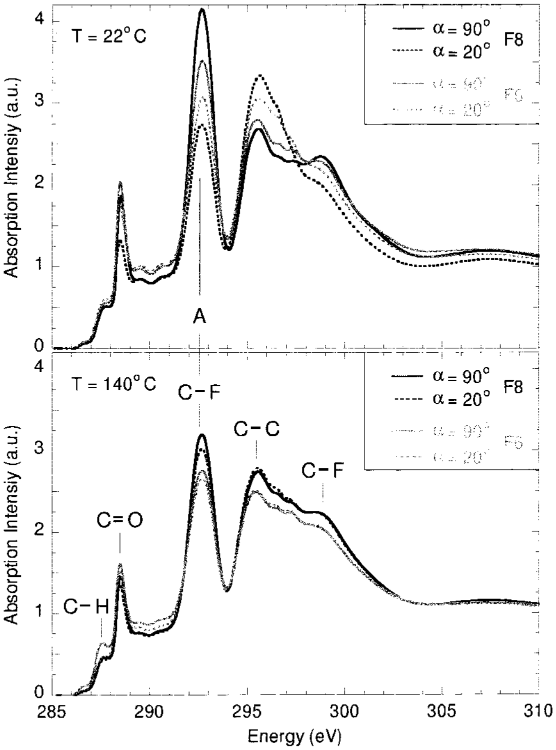

Figure 2. Polarization-dependent C K-edge NEXAFS spectra for F6 and F8 recorded at room temperature and 140 °C by means of TEY detection. The peak assignment is in agreement with the literature.[7,13]

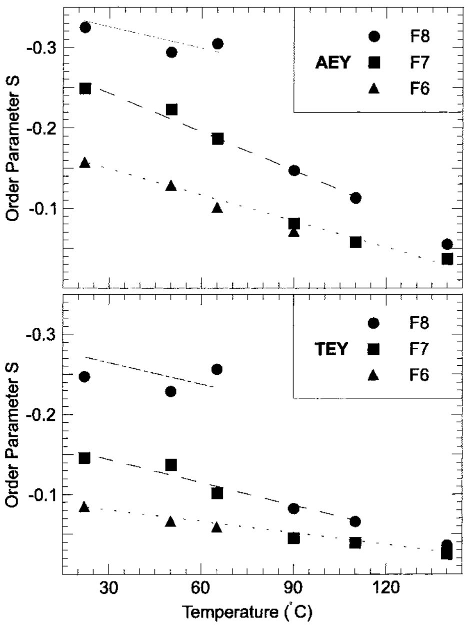

Figure 3. Temperature dependence of the order parameter *S*. The values derived from the angular dependence of peak A (Figure 2) in the AEY and TEY spectra describe the order within the first 1 and 10 nm below the surface, respectively. The dashed line connects points corresponding to nematic bulk phases in F7 (below 80 °C) and F8 (above 80 °C), and the dotted line connects points corresponding to isotropic bulk phases in F6 (whole temperature range) and F7 (above 80 °C).

give the average chemical composition within the top 1 nm (AEY) and the top 10 nm layer (TEY). The higher intensity in the AEY spectrum in the 295−300 eV region proves an enrichment of the surface with CF_3 groups whose spectral signature[14] is superimposed on the dominant resonances due to the CF_2 groups in the 290−300 eV region. This assignment is supported by the lower AEY intensity of the C=O peak around 288 eV associated with the ester link of the side chains to the polymer backbones, indicating a depletion of polymer backbones in the surface region.

TEY NEXAFS spectra of F8 and F6 recorded at room temperature and 140 °C are shown in Figure 2 for the two experimental geometries. The polarization dependence shows that within the first 10 nm of the free surface the C−F bonds of the CF_2 groups are preferentially oriented parallel to the surface, while the C−C bonds of the perfluoroalkyl side chains are preferentially oriented perpendicular to the surface.[7,13] The polarization dependence of the spectra of F7 falls in between that of F6 and F8. The surface-sensitive AEY NEXAFS spectra for the respective samples exhibit a significantly enhanced polarization dependence, which reveals a greater order at the surface than in the bulk. This is in accordance with the enrichment of the top surface region with CF_3 groups which, especially in the case of the isotropic bulk phase of F6, generates the preferential orientation of the side chains.

For a quantitative analysis of the molecular orientation, we have utilized peak A in Figure 2 which predominantly originates from transitions into molecular orbitals of the CF_2 groups. This peak is located on a nearly constant background following the preceding C−H and C=O resonances. After subtraction of this background we can use the angular dependence of the peak A intensity to determine the molecular orientation factors f_i ($i = x, y, z$), which describe the relative alignment of the C−F bonds along the carthesian axes *i*, without actual knowledge of the orientation function itself.[10] If we choose the *z* axis of our coordinate system along the surface normal, we have $f_x = f_y = (1 - f_z)/2$ because of uniaxial symmetry about *z*, and the order parameter *S* is given by $S = (3f_z - 1)/2$. The order parameter *S* therefore measures the degree of preferential orientation of the molecular C−F bonds relative to the surface normal. With our definition, perfect alignment of the C−F bonds of the CF_2 groups along the surface normal corresponds to $S = 1$, parallel to the surface corresponds to $S = -0.5$, and a random orientation is characterized by $S = 0$.

The order parameters of the C−F bonds in F6, F7, and F8 as a function of temperature are shown in Figure 3. On top we show the order parameters determined

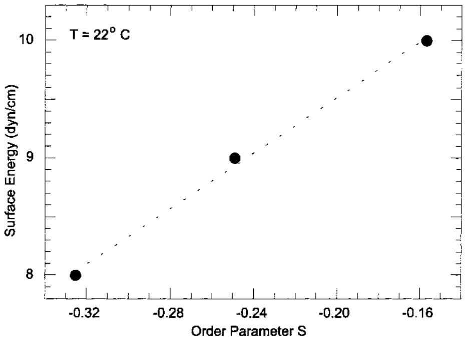

Figure 4. Correlation between order parameter *S* (derived from peak A (Figure 2) in the AEY spectra) and surface energy at room temperature.

from the AEY spectra, corresponding to the molecular orientation within 1 nm of the surface, and at the bottom those obtained from the TEY spectra, reflecting the orientation within 10 nm. Comparing the room temperature values of the order parameter of the three different films, one finds the expected decrease of the absolute value of *S* with decreasing degree of the bulk order, *S* being the largest for the well-ordered smectic film, lower for the nematic, and the lowest for the film with the isotropic bulk phase.

Figure 3 also shows that the absolute values of order parameters derived from the AEY data are larger than those from the TEY data. This indicates that, in general, the surface has a higher degree of order than the bulk, independent of the bulk phase. Even for F6, with an isotropic bulk phase, the segregation of CF_3 groups at the surface gives rise to a significant surface order. Assuming for simplicity an exponential decay of the surface order toward the isotropic bulk value ($S = 0$), we can estimate a decay length for the F6 sample from the AEY and TEY order parameters.[11] Including estimates of uncertainties in the AEY (1−2 nm) and TEY sampling depths (7.5−10 nm), we obtain a 1/e decay length in the range of 5−10 nm for the surface order in F6 at room temperature.

For F8 and F7 the determination of a decay length is limited by the unknown order parameter of the nonisotropic bulk phases. The experimentally determined ratio of surface to bulk order parameter, however, gives an upper limit of around 20 nm for the order decay length.

In Figure 4 the room temperature order parameters of the surface-sensitive AEY data, taken from Figure 3, are plotted versus the surface energies determined by the Zisman plot method. The good correlation between the surface energy and the side chain orientation shows that the segregation of the terminal CF_3 groups, which are mainly responsible for the low surface energy, is enhanced by the orientation of the perfluoroalkyl side chains.

One notices in Figure 3 that for all samples the side chain orientation decreases with increasing temperature. This is caused by thermally activated molecular motions and decreasing density. For F8 and F7 the surface order exhibits an apparently discontinuous decrease at the bulk phase transition temperatures near 80 °C. This demonstrates unambiguously that for a given polymer the surface order is determined by the bulk order.

More importantly, however, one observes that the order parameter for F8 in the nematic phase above 80 °C follows the extrapolated curve for the nematic phase of F7 below 80 °C (dashed lines in Figure 3). Similarly, the order parameter for F7 in the isotropic phase above 80 °C follows the curve for the isotropic F6 phase (dotted lines). This establishes a more general correlation between surface order and the nature of the bulk phase; i.e., our results show that, in general, a liquid crystalline bulk phase causes a higher surface order than an isotropic bulk phase. Thus, the bulk phase ultimately determines the achievable surface order.

In summary, we have established a link between the surface energy and the structural order in the surface region which is found to be limited by the bulk phase behavior.

Note Added in Proof. During the referee process of this manuscript the work of Genzer et al.[15] has been published. The temperature dependence of the surface order of liquid crystalline semifluorinated groups, attached to the poly(1,2-isoprene) backbone, presented in that work supports the findings discussed here.

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