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Surface Characteristics of Polyfluorene Films Studied by Polarization-Dependent NEXAFS Spectroscopy

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ABSTRACT: The chemical composition and the preferential orientation of polymer segments at the surface of thin polyfluorene films have been investigated by carbon K-edge soft X-ray absorption spectroscopy, resolving the near-edge X-ray absorption fine structure (NEXAFS). The outermost surface layer of about 10 Å thickness exhibits a slight enrichment of alkyl side chains and a corresponding depletion of biphenyl groups. Moreover, at the film surface the plane of biphenyl rings comprising the polymer backbone is strongly oriented parallel to the film surface. This equilibrium surface characteristics of polyfluorene films are found to be caused mainly by the polymer/air interface rather than by the polymer/solid (silicon) interface. A significant reorientation of polymer segments occurs at the film surface upon rubbing with velour cloth, which results in a preferential orientation of polymer molecular axis (biphenyl ring axis) along the rubbing direction and a decrease in the in-plane orientation of biphenyl planes. Upon annealing a rubbed polyfluorene film in its nematic melt state, the rubbing-induced reorientation of polymer molecules disappears completely for a film of about 600 Å thickness, indicating that the rubbing-induced reorientation does not propagate much further beyond the surface region of polyfluorene films.

Introduction

Recently, polyfluorene and its derivatives generated enormous interest due to the attractive electroluminescence and charge mobility characteristics.[1−5] Polyfluorenes show good solubility and processability arising from the substitution at the remote C9 site. Moreover, the rigid biphenyl segments comprising the polymer backbone cause polyfluorenes to exhibit thermotropic liquid crystallinity.[5−10] This can be exploited to orient the polyfluorene molecules by annealing the polymer film in its nematic melt state upon a rubbed polyimide substrate to obtain highly anisotropic optical and electrical properties.[5−13] For such interesting electrooptical properties, the molecular structure at the surface of polyfluorene films is of crucial importance since the electronic properties of the polymer/conductor interface can vary strongly with the molecular structure at the polymer surface. Despite this importance, very little work has been carried out to understand the details of the surface characteristics of polyfluorene films and other electrooptically active polymers, considering the enormous amount of publications devoted to this type of polymer.

In this regard, the carbon K-edge soft X-ray absorption spectroscopy, resolving the near-edge X-ray absorption fine structure (NEXAFS), is uniquely suited to characterize the chemical composition and the molecular orientation in the outermost surface region of polymer films.[14] This experimental method measures the photon absorption cross section for the excitation of core electrons into unoccupied valence states. The unique surface sensitivity of NEXAFS spectroscopy stems from recording the absorption spectra by monitoring the electron yield signals, which are in good approximation proportional to the absorption coefficient.[14] The core electron vacancy created in the primary absorption process decays by either fluorescence or Auger decay, with Auger decay being the dominant decay mechanism for excitations in the soft X-ray region. Since the Auger electrons with kinetic energies of a few hundred electronvolts have short mean free paths in matter, an absorption spectrum recorded by monitoring the Auger electron yield (AEY), as indication of the occurrence of an absorption event, samples only the outermost top surface layer of about 10 Å.[15] In comparison, by monitoring all electrons escaping the sample surface, i.e., photo, Auger, and secondary electrons from the inelastic scattering cascade of scattered photo and Auger electrons, one samples deeper into the material. This technique is referred to as total electron yield (TEY), and its sampling depth in polymer materials is on the order of 100 Å.[15−17] Hence, by recording simultaneously the AEY and the TEY spectra, one can easily distinguish the characteristics of the outermost sample surface from those of the underlying regions.

Moreover, in the case of the carbon K absorption edge in molecular systems like polymers, the NEXAFS is dominated by resonances arising from the transition of C 1s core electrons into unoccupied molecular orbitals of π and σ symmetry.[14] Since these orbitals are oriented with respect to the molecular axis, the absorption probability for linearly polarized X-rays depends on the relative orientation of the molecular axis and the electric field vector of the incident X-ray.[14,16,17] Therefore, the

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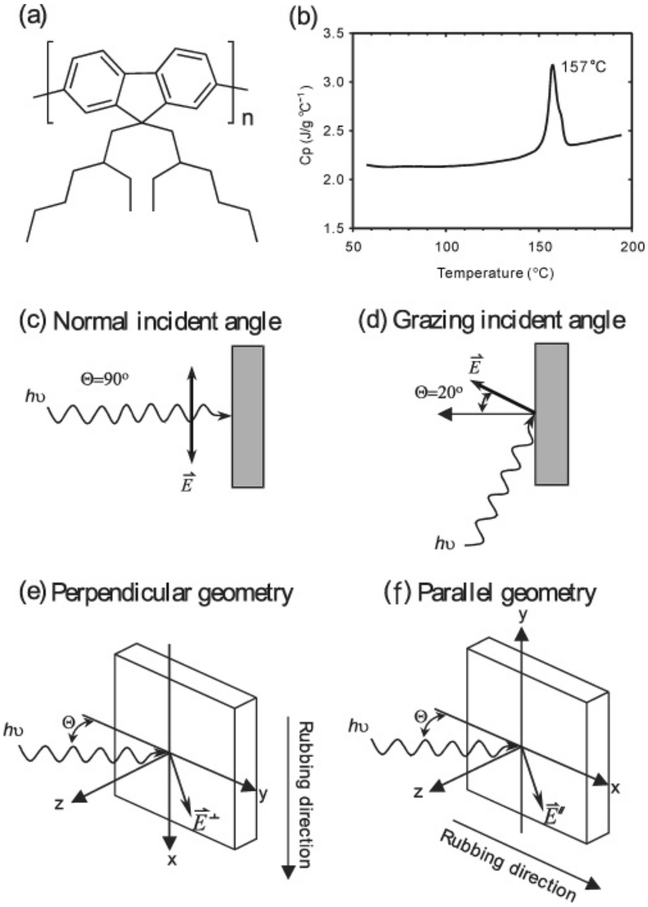

Figure 1. Molecular structure of poly(9,9-bis(2-ethylhexyl)-fluorene-2,7-diyl) used in this work (a); a typical DSC thermogram of the polyfluorene sample used (b); and the schematics of the experimental geometries illustrating the orientation of the electric field vector with respect to the film surface and the rubbing direction (c)−(f).

dependence of the intensity of a particular absorption resonance on the polarization direction of the electric field of incident X-ray reveals the preferential orientation of the molecular groups contributing to the observed absorption resonance. From this observed polarization dependence one can derive the order parameters, which describe quantitatively the average molecular orientation.

In this work, we have investigated the chemical composition and the molecular orientation at the surface of polyfluorene films, employing NEXAFS spectroscopy. Moreover, we also investigated the molecular reorientation caused by rubbing the free surface of polyfluorene films with velour cloth and explored the depth of the reoriented region by monitoring the change in the NEXAFS spectra upon annealing a rubbed thin film in its nematic melt state, since the reoriented region of sufficient depth could highly align the whole film upon bringing the rubbed film into its nematic melt.

Experimental Section

Materials. Poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) with a molecular weight of M_w = 65 600 (PDI = 2.0), measured by gel permeation chromatography (GPC) with polystyrene standards, was employed in our study. This particular polyfluorene, with the molecular structure illustrated in Figure 1a, was selected since it has become most popular among the various polyfluorenes due to the color stability of electroluminescence and the good alignment characteristics on rubbed polyimide substrates.[5,12,13] This polymer exhibits a melting transition into a nematic phase at 157 °C as well documented by differential scanning calorimetry (DSC), shown in Figure 1b, and polarized optical microscopy. Also, the glass transition temperature (T_g) of the nematic melt of this polymer is expected at 64 °C, upon extrapolation of the well-defined T_gs of oligofluorenes.[18] A series of four thin film samples were prepared by spin-coating on silicon wafers from a 5 wt % solution of the polymer in toluene. This yielded films with thickness of about 600 Å as measured by ellipsometry. All samples were vacuum-dried at room temperature (25 °C) for 1 day. Then, three of the samples were annealed for 1 h at 170 °C, which is well above the nematic transition temperature of the polymer. Two of these three samples were subsequently rubbed with a velour cloth to cause molecular reorientation at the film surface. Finally, one of the rubbed thin films was annealed again for 1 h at 170 °C in its nematic melt state.

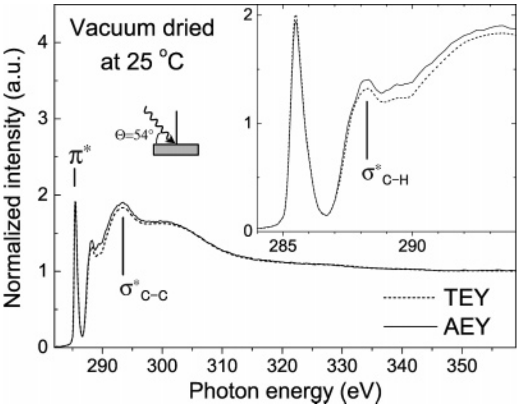

Figure 2. Normalized carbon K-edge NEXAFS spectra of a spin-coated polyfluorene film after vacuum-drying at 25 °C, recorded by monitoring simultaneously Auger (AEY) and total electron yield (TEY) in the magic angle geometry (Θ = 54°).

NEXAFS Measurements. The NEXAFS measurements were performed at the spherical grating beamline 10-1 of the Stanford Synchrotron Radiation Laboratory (SSRL) with a photon energy resolution of about 80 meV around the C K absorption edge. The refocusing optics were defocused to blur the beam spot on the sample to about 2 mm × 2 mm, thereby rendering sample damage effects insignificant. Nevertheless, every spectrum has been recorded on a fresh sample spot. As illustrated in Figure 1c,d, the spectra were obtained for X-ray incidence angles at normal (Θ = 90°) to grazing incidence (Θ = 20°). The orthogonal spectra corresponding to the electric field vector parallel and perpendicular to the sample surface can easily be derived from the measured spectra.[14] For the rubbed samples, additional polarization-dependent spectra were obtained with the normal incidence (Θ = 90°), for the incident electric field vector parallel and perpendicular to the rubbing direction, respectively, as shown in parts e and f of Figure 1. The spectra shown here have been corrected for the finite polarization degree (80%) of the incident X-ray beam, and hence we discuss throughout the paper as if they were measured with 100% polarized incident beam. Moreover, the spectral intensities have been normalized to show the C K-edge absorption per average carbon atom as discussed in detail elsewhere.[14,17]

Results and Discussion

The AEY and TEY NEXAFS spectra of the polyfluorene film dried in a vacuum at 25 °C are plotted in Figure 2. Annealing the vacuum-dried sample for 1 h at 170 °C in the nematic melt did not cause any change in both spectra. Therefore, the spectra in Figure 2 may be considered to represent the equilibrium surface structure of polyfluorene films. Here, it is of interest to note that the equilibrium polymer/vacuum (air) interface is already reached upon drying the spin-coated

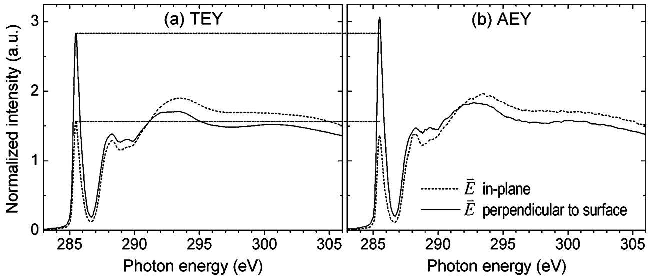

Figure 3. Polarization-dependent carbon K-edge NEXAFS spectra of a spin-coated polyfluorene film after vacuum-drying at 25 °C, recorded with the electric field vector of the incident X-ray along the in-plane (dashed line, E parallel to film surface) vs the out-of-plane of the film direction (solid line, E perpendicular to surface). The peak intensities of the NEXAFS spectra recorded by means of the TEY (a) and the AEY (b) are compared by drawing thin horizontal lines.

polyfluorene film at 25 °C, which is well below the predicted glass transition of this polymer at 64 °C.[18]

The peak at 285.5 eV originates from the excitation of C 1s electrons belonging to the carbon atoms of the aromatic biphenyl rings into the π^* orbital of these rings.[14,19,20] The absorption structure at about 288 eV belongs to the excitation into σ^* orbitals of C−H bonds. And the broad structure in the spectrum centered around 294 eV is associated with the excitation of C 1s electrons into σ^* orbitals of carbon−carbon bonds. We note that while the first resonance at 285.5 eV is associated uniquely with the carbon atoms of the biphenyl rings, contributions from all carbon atoms overlap in the higher energy part of the absorption spectrum. In particular, both the biphenyl rings[19] and alkyl groups[20] contribute to the small peak at 289.5 eV. Hence, we will concentrate in the following discussion mainly on the intensity variations of the first resonance at 285.5 eV, which indicates the changes in the concentration and the orientation of the biphenyl rings. Note that they are the molecular groups most relevant for the important electrooptical properties.

The spectra shown in Figure 2 correspond to the magic angle geometry; i.e., the X-ray incidence angle relative to the film surface is $\Theta = 54°$ as illustrated in Figure 2. They have been obtained from the measurements at $\Theta = 20°$ and $\Theta = 90°$ and checked with the measurements at $\Theta = 49.8°$, the magic angle corresponding to the finite polarization (80%) of the incident beam. Therefore, these spectra are not affected by any orientation effects[14] and solely reveal the chemical composition of the top 10 Å (AEY) and 100 Å (TEY) surface layer, respectively.[15] Comparison of the two spectra shows a decreased intensity of the biphenyl aromatic carbons and a higher relative intensity for C−H and aliphatic C−C bonds in the AEY spectrum than those in the TEY spectrum. This indicates that there is a slight enrichment of the alkyl side chains and a corresponding depletion of biphneyl groups at the film surface.

Next, the preferential orientation of polyfluorene segments at the surface of the polyfluorene films has been characterized by the polarization-dependent NEXAFS spectra shown in Figure 3. Again, the vacuum-dried (25 °C) sample and the sample subsequently annealed in the nematic melt (170 °C) show the identical results. The TEY and AEY spectra plotted by the dotted lines correspond to the electric field vector of the incident X-ray oriented parallel to the film surface (normal X-ray incidence with $\Theta = 90°$), while the solid lines show the spectra for the incident electric field vector perpendicular to the film surface (derived "0° incidence"). The significantly increased intensity of the aromatic (biphenyl) ring π^* resonance in the 0° incidence spectrum indicates that the π orbitals are preferentially oriented perpendicular to the film surface. Since the π orbitals are oriented perpendicular to the plane of the biphenyl ring, this shows that the biphenyl planes exhibit a preferential in-plane orientation parallel to the film surface. Moreover, the absorption anisotropy or the dichroism is greater for the more surface-sensitive AEY spectra (Figure 3b), as compared with the deeper sampling TEY spectra (Figure 3a). This indicates that the preferential in-plane orientation of biphenyl planes is stronger at the film surface than in the underlying region. Therefore, one can conclude that the preferential in-plane orientation of the biphenyl rings of polyfluorene segments is caused by the polymer/air interface, rather than by the polymer/solid (silicon) interface. This is a quite important result.

Combining the NEXAFS results concerning the chemical composition and the preferential orientation, we can summarize that the surface layer of the polyfluorene film is slightly enriched with aliphatic side chains. This should not result in an electrically insulating layer at the polymer film surface, since the segregation is very weak, and the biphenyl planes are preferentially oriented parallel to the film surface for favorable charge transfer into the polymer film.

The effects of rubbing polyimide surfaces with velour cloth, a widely used method to align the nematic liquid crystals for liquid crystal displays, were well characterized by the previous AFM[21] and NEXAFS studies.[17,22] Previous studies showed that the rubbing process orients the polyimide molecules on the film surface, and the anisotropic anchoring energy resulting from such orientated molecules on polyimide surfaces leads to a large-scale monodomain alignment of nematic liquid crystals. As mentioned in the Introduction, highly oriented polyfluorene films were obtained by aligning them in the nematic melt state on the same rubbed polyimide substrates. However, the polyimide alignment layer is not practical for electrooptical applications of polyfluorenes since polymides are generally excellent electrical insulators. In this regard, one way of overcoming this problem would be to rub the polyfluorene surface such that the oriented layer comprises a significant fraction of the thin films. If this is achieved, annealing the rubbed polyfluorene thin films in the nematic melt state would then result in highly oriented monodomain films. In other words, employing the rubbing procedure one can explore the depth of rubbing-induced molecular orientation in polymer films and possibly obtain thin polyfluorene films with highly anisotropic electrooptical properties.

Figures 4 and 5 show the variation in the AEY NEXAFS spectra as a well-equilibrated polyfluorene film is rubbed and then subsequently annealed in the nematic melt at 170 °C. The absorption dichroism shown by the two normal incidence ($\Theta = 90°$) spectra in Figure 4b, recorded with the electric field vector lying in the film plane and oriented parallel (dotted line) and perpendicular (solid line) to the rubbing direction, respectively, clearly demonstrates that the rubbing procedure causes the molecular reorientation in the film surface. (For clarity, see the experimental geometries

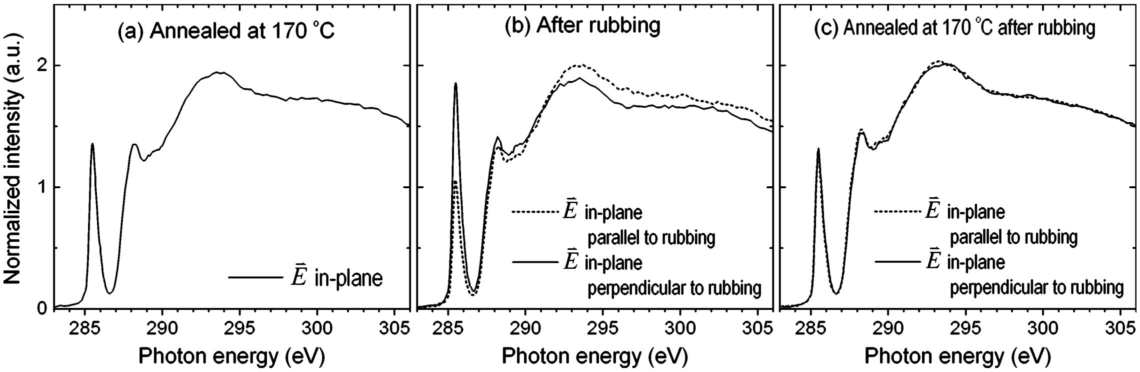

Figure 4. Polarization-dependent carbon K-edge AEY NEXAFS spectra of the polyfluorene film for the incident electric field vector in the plane of the film and oriented parallel and perpendicular to the rubbing direction, respectively. The isotropic in-plane distribution of the annealed equilibrium sample (a) is changed by the rubbing process (b) but is fully restored upon annealing the rubbed film in its nematic melt state (c).

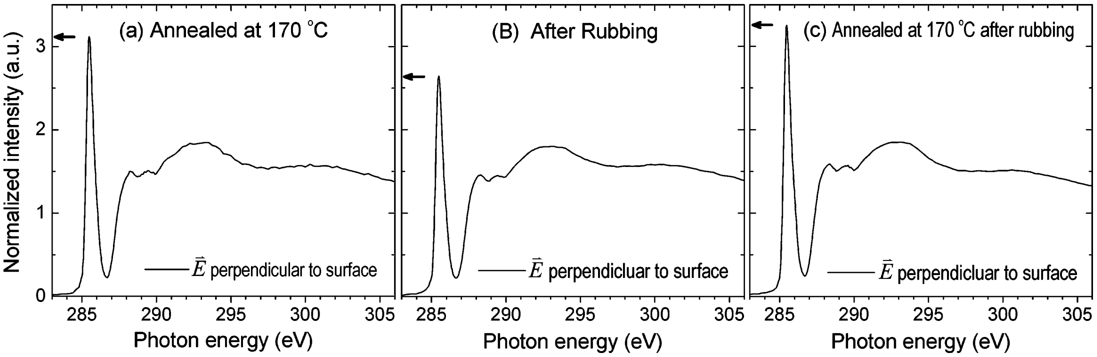

Figure 5. Carbon K-edge AEY NEXAFS spectra of the polyfluorene film for the incident electric field vector oriented perpendicular to the film surface. The preferential orientation of the biphenyl rings parallel to the film surface in the annealed equilibrium sample (a) is reduced by the rubbing process (b), but is fully recovered upon annealing of the rubbed film in the nematic melt state (c), as shown by the arrows denoting the peak intensity at 285.5 eV.

Table 1. Quantitative Comparison of Uniaxial Order Parameter S^a and Biaxiality P^b Determined from the NEXAFS Spectra Shown in Figures 3−5

	AEY	TEY
spin-coated film dried in a vacuum at 25 °C	0.29	0.21
film annealed in the nematic melt at 170 °C	0.30	0.22
rubbed film	0.23 ($P = 0.21$)	0.17 ($P = 0.12$)
film rubbed and then annealed in the nematic melt at 170 °C	0.34	0.21

[a] S describes the order parameter of ring transition vectors of the biphenyl groups with respect to surface normal of the film. [b] P denotes the in-plane order parameter of the biphenyl ring-axis with respect to the rubbing direction.

sketched in Figure 1e,f with $\Theta = 90°$.) It is clearly seen that the biphenyl ring π^* resonance with the incident electric field vector perpendicular to the rubbing direction has nearly twice the intensity of that with the incident electric field parallel to the rubbing direction. Therefore, we can conclude that the rubbing procedure results in a significant reorientation of the biphenyl ring axis of the polymer backbone along the rubbing direction.

For the same rubbed sample, the spectra derived for the incident electric field vector perpendicular to the film surface ($\Theta = 0°$) in Figure 5 show that the intensity of the biphenyl π^* resonance is lower than that for the initial equilibrated film. This shows that the rubbing-induced orientation of the biphenyl ring axis, or the polymer molecular axis, along the rubbing direction is accompanied by a small decrease in the preferential in-plane orientation of the biphenyl planes parallel to the film surface. (The quantitative comparison listed in Table 1 will be discussed later.)

Upon bringing the rubbed polyfluorene film to its nematic melt state, the two NEXAFS spectra recorded with the incident electric field vector lying in the film plane and oriented parallel (solid) and perpendicular (dashed line) to the rubbing direction, respectively, show the same results as seen in Figure 4c. Therefore, the rubbing-induced molecular reorientation completely disappears, and the initial equilibrium structure is fully restored. Also, the preferential in-plane orientation of biphenyl planes parallel to the film surface, which is reduced by the rubbing process, fully recovers to the equilibrium state upon annealing the rubbed film in the nematic melt (see Figure 5 and Table 1).

The complete recovery of the initial equilibrium spectra upon bringing the rubbed sample to the nematic melt further confirms that the results presented in Figures 2 and 3 truly represent the equilibrium surface structures of polyfluorene films. Moreover, this complete recovery indicates that the rubbing-induced reorientation of polymer surface does not penetrate deep enough into the film. Considering that the thickness of the investigated polyfluorene film is ca. 600 Å, the depth of the reoriented region seems to be much smaller than this film thickness and most likely confined within the top ca. 100 Å. Therefore, further work is underway to determine the depth of the rubbing-induced reorientation region employing films of varying thicknesses and also to devise novel methods which will extend the reorientation depth sufficiently so as to exploit it as a template for the alignment of the whole film instead of the electrically insulating polyimide alignment layers.

Finally, one can quantify the preferential orientation of a molecular ensemble by introducing the tensorial order parameter $\overleftrightarrow{Q}$, which is derived from the observed linear dichroism signal, as discussed elsewhere.[22−24] Employing the coordinate system (x, y, z) with $+x$ along the rubbing direction, y in the film plane perpendicular to the rubbing direction, and z along the surface normal (see Figure 1), the order parameter of the polymer surface is diagonal:

$$\overleftrightarrow{Q} = \begin{pmatrix} -\frac{1}{2}(S+P) & 0 & 0 \\ 0 & -\frac{1}{2}(S-P) & 0 \\ 0 & 0 & S \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(3f_x - 1) & 0 & 0 \\ 0 & \frac{1}{2}(3f_y - 1) & 0 \\ 0 & 0 & \frac{1}{2}(3f_z - 1) \end{pmatrix}$$

Here, f_x, f_y, and f_z are the orientation factors, which describe the relative orientation of the molecular axes with respect to the three orthogonal axes. From these one can estimate the uniaxial order parameter S (in-plane vs out-of-plane anisotropy) and the biaxiality P (in-plane anisotropy).[22−24] For an isotropic, random orientation the uniaxial order parameter S takes a value of 0, while $S = 1$ (or $S = -0.5$) corresponds to all the molecular axes aligned perfectly parallel (or perpendicular) to the major symmetry axis. The uniaxial order parameter S derived from the polarization-dependent NEXAFS spectra dominated by the biphenyl ring π^* resonance of polyfluorene films refer to the orientation of the ring transition vector with respect to the surface normal of the film as the major axis. The biaxiality P caused by rubbing represents the extent of biphenyl ring axis orientation along the rubbing direction. The uniaxial order parameters for all the polyfluorene films, derived from the spectra in Figures 3−5 according to refs 22−24, are listed in Table 1, together with the biaxiality P obtained for the rubbed films. Generally, the order parameters are quite significant and are always greater for the AEY spectra than those for the TEY spectra, indicating that the degree of molecular orientation is largest at the film surface and decreases with the increasing depth. The quantitative comparison also shows the effect of rubbing on the order parameters S and P and the recovery to the equilibrium state upon annealing in the nematic melt state.

Conclusion

We have employed carbon K-edge soft X-ray absorption spectroscopy, resolving the near-edge X-ray absorption fine structure (NEXAFS), and carried out a detailed investigation of the chemical composition and the preferential orientation of polymer segments at the surface of thin polyfluorene films, since such surface characteristics are critically relevant to the electronic properties of the polymer/electrode interfaces. The outermost surface layer of about 10 Å exhibits a slight enrichment of alkyl side chains and a corresponding depletion of biphenyl groups. More important, on the film surface the plane of biphenyl rings comprising the polymer backbone is strongly oriented parallel to the film surface. This equilibrium surface structure of polyfluorene films is obtained upon drying the spin-coated films at room temperature, substantially below the glass transition temperature (64 °C) of the polymer, and is caused mainly by the polymer/air interface rather than by the polymer/solid (silicon) interface. This is an important result that needs further consideration. A significant reorientation of polymer segments occurs at the film surface upon rubbing with velour cloth, which results in preferential orientation of biphenyl ring axis along the rubbing direction and a small decrease in the in-plane orientation of biphenyl planes. Moreover, the extent of molecular orientations has been quantified by the uniaxial order parameter around the surface normal of the film and the biaxiality caused by the rubbing procedure. Upon bringing a rubbed polyfluorene film to its nematic melt state, the rubbing-induced reorientation of polymer molecules disappears completely for a film of about 600 Å thickness. This indicates that the rubbing-induced reorientation does not propagate deep into the film and is most likely confined within the top ca. 100 Å. Therefore, further work is underway to determine the depth of the rubbing-induced reorientation region and also to extend the reorientation depth sufficiently so as to exploit it as a template for the alignment of the whole film, and the key results will be reported shortly elsewhere.

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