Surface-Induced Ordering of an Aromatic Polyimide

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(Received 7 November 1990)

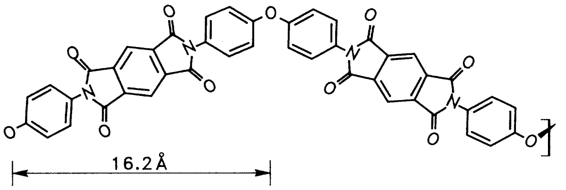
Grazing incidence x-ray diffraction has been used to characterize the near surface structure of an aromatic polyimide film. It is shown that within the first 90 Å from the surface the ordering of the polymer molecules is markedly enhanced. As the penetration depth of the x rays decreases, reflections characteristic of density correlations along the polymer chain axis shift to smaller scattering vectors and those indicative of intermolecular ordering become clearly evident. Thus, near the surface essentially *crystalline* order is seen.

PACS numbers: 61.41.+e, 61.30.Eb, 68.10.−m, 68.55.Jk

The structure of polymers near the vacuum/polymer interface is a subject of current theoretical and experimental interest. The presence of an interface places restrictions on the configurations and conformations of the nearby molecules, and, consequently, the structure of the polymer near the interface can be substantially altered.[1-3] Several studies have investigated structural changes at surfaces of crystalline elements,[4,5] elemental liquids,[6] liquid crystals,[7] polycrystalline oxides,[8] and amorphous alloys.[9] The nature of a surface structural change in polymers differs from those observed in other materials due to the linear *connectivity* of the monomers. The purpose of this study is to probe the effect of a free surface on the ordering of polymers. Characterizing the behavior of polymers near surfaces is critical for understanding interfacial mixing, surface tension, and interdiffusion of polymers and is of general importance to the numerous applications of polymers.

Recently, Martin, Berger, and Gardner[10] reported a high-resolution electron-microscopy study on the surface structure of polymers using thin droplets. The structural characterization of polymers near the air or vacuum interface for bulk specimens is difficult owing to the low atomic numbers of the constituents of the polymer molecules and the limitations of techniques available to provide such information. To our knowledge, the work presented herein represents the first successful effort made on the characterization of the ordering induced in bulk polymers by the presence of a surface. Grazing incidence x-ray scattering (GIXS) is used to assess the interchain and intrachain ordering of polymer molecules as a function of distance from the free surface.

Specifically, GIXS has been performed on films of the aromatic polyimide, poly(pyromelliticdianhydride oxydianiline), denoted PMDA-ODA. The chemical structure of PMDA-ODA is shown below. A film of the diethylester precursor of PMDA-ODA was spin coated onto a polished silicon substrate (7.5 cm in diameter by 5 mm thick) from a solution in *N*-methylpyrrolidone. This was gradually heated to 425 °C under a flowing nitrogen atmosphere to remove residual solvent and to cycloimidize the polymer to the corresponding polyimide.[11] X-ray-reflectivity studies and optical ellipsometry measurements showed that the film had a thickness of 2600 Å with a rms surface roughness of 8 ± 2 Å. The selection of this polymer was by no means arbitrary. It has been shown to exhibit a "liquid-crystalline-like" ordering in the bulk.[12,13] In addition to its widespread use in the microelectronics industry, PMDA-ODA also has excellent thermal and radiation stability as evidenced by the routine use of this polymer at storage-ring sources as window material (e.g., Kapton).



Experiments were performed on beam line X20C at the National Synchrotron Light Source[14] (NSLS) with an x-ray wavelength of 1.558 Å. The incident-beam optics consisted of a toroidal mirror, a pair of W/Si multilayers (*d* spacing of 22.3 Å with a 1% energy bandwidth), and slits for beam definition. Given the low scattering power of the constituents of the polymer and the inherent small scattering volume, the use of high-bandpass, multilayer crystals was essential to obtain a good signal-to-noise ratio. Slits in front of the mirror produced a 1-mrad horizontal divergence with a vertical divergence of < 0.5 mrad. The beam was spatially defined with slits just prior to the specimen to a size of 125 μm (horizontal) by 1.5 mm (vertical). Scattering measurements were performed with the specimen nearly vertical using a standard four-circle goniometer such that the direction of the scattering vector was essentially parallel to the film surface.[15] The scattered beam was collimated in the scattering plane with 1-mrad Soller slits and normal to the scattering plane with fixed slits that gave a resolution of 5 mrad. Scintillation counters were used for both the incident-beam monitor and the detector. Specimens were placed under a helium atmosphere to reduce air scattering and minimize degradation. It should be noted that no degradation of the specimen was observed in these experiments as evidenced by the excellent reproducibility of the scattering profiles at different times during the experiment.

For x rays the index of refraction of a material is slightly less than unity and is given by[16]

$$n = 1 - \delta - i\beta , \qquad (1)$$

where

$$\delta = N_0 \rho_{\mathrm{el}} \lambda^2 r_0 / 2\pi , \quad \beta = \lambda\mu/4\pi ,$$

where N_0 is Avogadro's number, ρ_{el} is the molar electron density, r_0 is the classical electron radius, λ is the x-ray wavelength, and μ is the attenuation coefficient. For angles of incidence, α, less than the critical angle, $\alpha_c = (2\delta)^{1/2}$, x rays are totally externally reflected and the transmitted wave is evanescent and decays exponentially into the film. It is this evanescent wave that is diffracted by the material.[17] The penetration depth $d(\alpha)$ characterizing the exponential decay of the intensity is shown in Fig. 1 as a function of α for PMDA-ODA ($\mu = 10.0$ cm^{-1}, $\rho = 1.42$ g/cm^3, $\alpha_c = 0.18°$, and a wavelength of 1.558 Å). Scattering measurements were performed as a function of q $[=(4\pi/\lambda)\sin\theta]$ at constant values of α to control the penetration depth.

Typical GIXS profiles are shown in Fig. 2 for α above and below α_c. The data have been offset for clarity. In Fig. 2 $d(\alpha = 0.185°)$ is greater than 10^4 Å which is greater than the total film thickness. Consequently, this profile represents the bulk scattering of PMDA-ODA and is in good agreement with previous work.[13] As $d(\alpha)$ decreases for the smaller values of α, distinct changes are seen in the scattering profiles. In general, for $q > 0.8$ Å reflections appear which are not seen in the bulk and the reflections seen for $q < 0.8$ Å shift to smaller q. These results show unequivocally that, for $d(\alpha) \lesssim 90$ Å, the PMDA-ODA molecules pack more efficiently and the ordering is markedly improved.

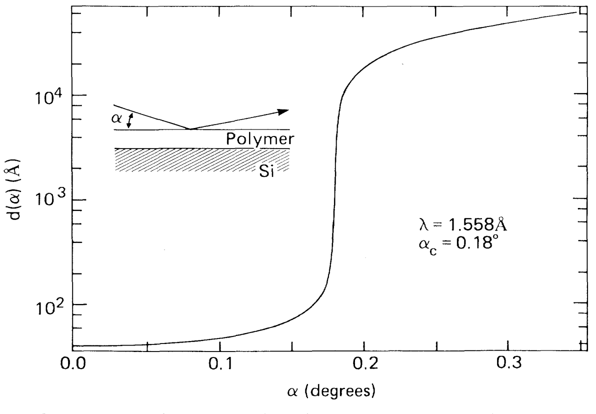


FIG. 1. Variation of the incident x-ray penetration depth for polyimide as a function of the angle of incidence. Below the critical angle α_c, the penetration depth ranges between 50 and 100 Å, while above α_c, it is nearly equal to the attenuation length times $\sin\alpha$.

The peaks occurring at 0.401 and 0.782 Å^{-1} correspond to electron density correlations parallel to the chain axis which, from unit-cell studies on highly stretched PMDA-ODA,[18-20] correspond to the (002) and (004) reflections of an orthorhombic unit cell where the c axis is in the chain direction. Features of these reflections are worth noting from the GIXS studies. Both (002) and (004) reflections shift to smaller q as the measurements become surface sensitive. Shown in Fig. 3 are the Bragg spacings of these reflections as a function of $d(\alpha)$. For $d(\alpha) \gtrsim 90$ Å the spacings are constant at 15.67 and 8.04 Å. However, as $d(\alpha)$ decreases, both spacings increase with the (002) reflection increasing more rapidly which corresponds to an increase in the ratio of the Bragg spacings from 1.95 to 1.97. The maximum value of the (002) spacing is 16.05 ± 0.05 Å which is only slightly less than the projection of the planar zigzag conformation of the molecule onto the chain axis in the crystalline state.[14] Also, with decreasing α the FWHM of the (002) reflection decreases from 0.056 ±0.002 Å to 0.051 ± 0.002 Å, whereas, due to the weakness of the (004) reflection, the FWHM of the

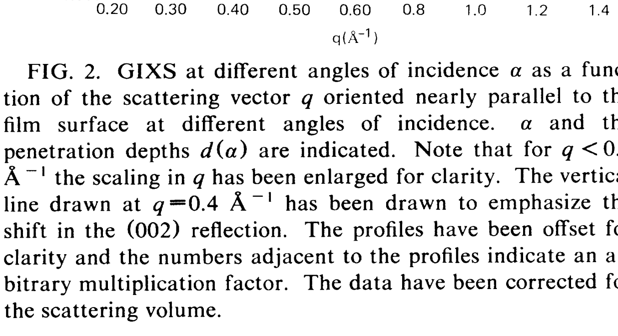


FIG. 2. GIXS at different angles of incidence α as a function of the scattering vector q oriented nearly parallel to the film surface at different angles of incidence. α and the penetration depths $d(\alpha)$ are indicated. Note that for $q < 0.6$ Å^{-1} the scaling in q has been enlarged for clarity. The vertical line drawn at $q = 0.4$ Å^{-1} has been drawn to emphasize the shift in the (002) reflection. The profiles have been offset for clarity and the numbers adjacent to the profiles indicate an arbitrary multiplication factor. The data have been corrected for the scattering volume.

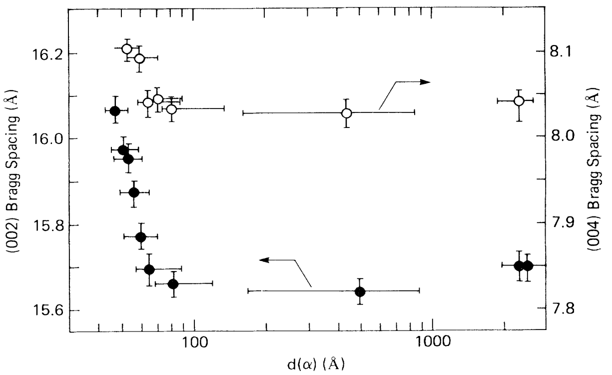


FIG. 3. Bragg spacings corresponding to the (002) (●) and (004) (○) reflections for PMDA-ODA as a function of incident-beam penetration depth. The vertical error bars were determined from the standard deviation in the peak position of fitted profiles to the experimental data, whereas the horizontal error bars show the range of penetration depths for a given α with a 1-mrad angular divergence.

(004) reflection remained constant at 0.063 ± 0.004 Å. The measured intensity at any α is an integral over the sample volume. Since the (002) reflection shifts to smaller scattering vectors with decreasing α, an asymmetry in the shape of the reflection might be expected due to different contributions from the surface and bulk at different α's. However, the shift is much smaller than the FWHM of the reflection and the asymmetry is too small to be observed.

The ratio of the Bragg spacings of (00*l*) reflections is expected to be nonintegral due to the modulation of the intensity by the form factor over the finite width of the reflections. However, calculation of the form factor using the parameters published by Takahashi, Yoon, and Parrish[13] results in a ratio of the (002) and (004) spacings that is greater than 2.[21] Thus, the form factor cannot account for the observations in this study. Possible explanations for the values found are disorder within the crystalline structure or the superpositioning of reflections from crystalline and noncrystalline regions. The exact origin is not known and is currently under investigation.

For $q > 0.08$ Å^{-1} pronounced changes are observed in the GIXS as a function of $d(\alpha)$. Above α_c the GIXS of PMDA-ODA is characterized by weak, diffuse reflections centered at $q \sim 1.02$ and 1.15 Å^{-1}. These reflections can be attributed to interchain packing or density correlations between neighboring chains with average spacings of 6.2 and 5.5 Å, respectively. The latter reflection may also contain contributions from the (006) reflection which should be observed at 1.18 Å. From Fig. 2, as $d(\alpha)$ decreases, distinct reflections appear at 0.985 and 1.041 Å^{-1} and become sharper as $d(\alpha)$ decreases. In fact, at $d(\alpha) \sim 60$ Å the FWHM of the reflection is 0.042 Å^{-1} which corresponds to a distance of at least 150 Å over which the ordering along the chain is coherent.[22] The positions of these reflections did not change with $d(\alpha)$. The positions of the two reflections are consistent with the (101) and (102) reflections of the crystalline PMDA-ODA.[18] The appearance of these reflections for shallow penetration depths clearly shows an enhanced local ordering of the PMDA-ODA molecules near the surface that is induced by the presence of the air/polymer interface. From the FWHM of the reflections it is also clear that adjacent polymer chains are, effectively, in crystallographic register with one another over relatively large distances.

For partially ordered materials it is important to distinguish between orientation and ordering, since both can cause variations in the intensities measured at a particular azimuthal angle, i.e., the angle of inclination from the surface plane. In the bulk, polyimide films prepared on a substrate exhibit a pronounced orientation of the chain axes parallel to the film surface.[23] For this PMDA-ODA film, the local orientation of the molecule [i.e., the orientation of chain segments giving rise to the (002) reflection] was investigated in both the surface-sensitive mode and with bulk penetration. The variation in the integrated intensity of the (002) reflection with respect to the azimuthal angle was basically the same in both cases. This means that within the first ~55 Å of the surface there is *not* a marked increase in the local orientation of the chain segments. Given the existing orientation of the chain axes parallel to the film surface in the bulk, this result is consistent with theoretical arguments.[1-3]

The FWHM of the (002) reflection changes only slightly with decreasing penetration depth which shows that the coherence length does not change significantly. This implies that there is not a significant fraction of extended, planar zigzag conformations of the molecule near the surface. This does not mean that the average molecular orientation does not change near the surface since the (002) reflection arises from only portions of the chain. However, since the (002) spacing increases as the surface is approached, *locally*, a planar zigzag conformation of the molecule is assumed. This differs from the bulk conformation where slight rotations of the repeat unit about the oxygen atom in the chain, i.e., the oxygen atom in the diphenyl ether moiety, produce a nonplanar molecular conformation thereby reducing the projection of the repeat unit onto the chain axis and, consequently, reducing the (002) spacing. Another marked difference between the PMDA-ODA molecules near the surface and those in the bulk is the lateral registry of the molecules. Near the surface essentially crystalline registry is seen laterally which extends over ~150 Å.

The local ordering of the polymer chains at the surface should give rise to an increase in the density of the film which may be observable by specular reflectivity measurements. This is currently under investigation. As evidenced by the low value of the surface roughness (8 ± 2 Å), the packing of the chains must be such as to minimize the surface area and, consequently, the surface energy. The low value of the surface roughness also shows that the crystalline structure at the surface does not assume the classical lamellar structure seen in typical semicrystalline polymers. This would give rise to a significant roughening of the surface[10,24] which is not seen here.

In summary, GIXS measurements on polymers have been presented which clearly demonstrate that the presence of an interface can markedly alter the ordering of the molecules. It has been shown that reflections characteristic of crystalline PMDA-ODA molecules are present at the surface and that this ordering extends ~90 Å into the bulk of the specimen. In addition, the lateral registry of the molecules parallel to the surface of the film extends over relatively large distances of ~150 Å.

We wish to thank G. B. Stephenson and J. Jordan-Sweet for their assistance at NSLS and Professor A. Bienenstock for insightful comments and criticisms of this work. T.P.R. acknowledges the support of the Department of Energy, Office of Basic Energy Sciences, Grant No. FG03-88ER45375. B.J.F. acknowledges the support of the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences through the Stanford Synchrotron Radiation Laboratory. This research was carried out (in part) at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

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