Communications to the Editor

Outer-Surface-Induced Crystallization of Semirigid Polymer Films

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Introduction. Rubbed polymer films are widely used in flat-panel liquid crystals (LC) displays; they are used to induce the alignment of LC molecules parallel to the sliding direction. From a large number of studies, it is now clear that the polymer chains near the surface are aligned during rubbing and act as a template that induces order within the LC layer via intermolecular interactions. This "epitaxial" model was confirmed by a wide set of experiments based on direct optical retardation measurements,[1,2] surface second harmonic generation,[2,3] grazing incidence X-ray diffraction (GIXD),[4] and near-edge X-ray absorption fine structure.[5] From optical retardation measurements, Van Aerle et al. proposed that the penetration depth of rubbing varies from 10 to 60 nm depending on the experimental conditions.[2] This proposal was further confirmed by GIXD experiments, which allows thickness mapping by varying the incidence angle of the X-ray beam.[4]

Studies of rubbed polymer thin films also reveal a relaxation phenomenon around the glass transition. In fact, when heated close to or slightly above the glass transition temperature (T_g), rubbed amorphous polystyrene (PS) films exhibit a drastic decrease of the surface roughness and a complete vanishing of the optical retardation.[6−8] From the thermal dependence of the surface relaxation, T_g was found to vary with film thickness. Furthermore, the study of PS thick films showed that molecules closer to the polymer−air interface relax more easily than bulk molecules.[6] In fact, there is a consensus to agree that, for free-standing and supported thin films, a decrease of T_g is associated with a decrease of the film thickness.[9−11] For instance, a decrease of T_g by about 40 deg was reported for supported PS thin films 10 nm thick.[11]

In this paper, we report on the influence of rubbing and surface relaxation of amorphous polymers on the cold-crystallization process. We selected polymers with relatively low T_g and able to partially crystallize from the glassy state: poly(ethylene terephthalate), PET, and poly(aryl ether ketone ketone), PEKK.[12] The surface relaxation and subsequent crystallization were investigated by FTIR spectroscopy, atomic force microscopy (AFM), and optical microscopy (OM) observations.

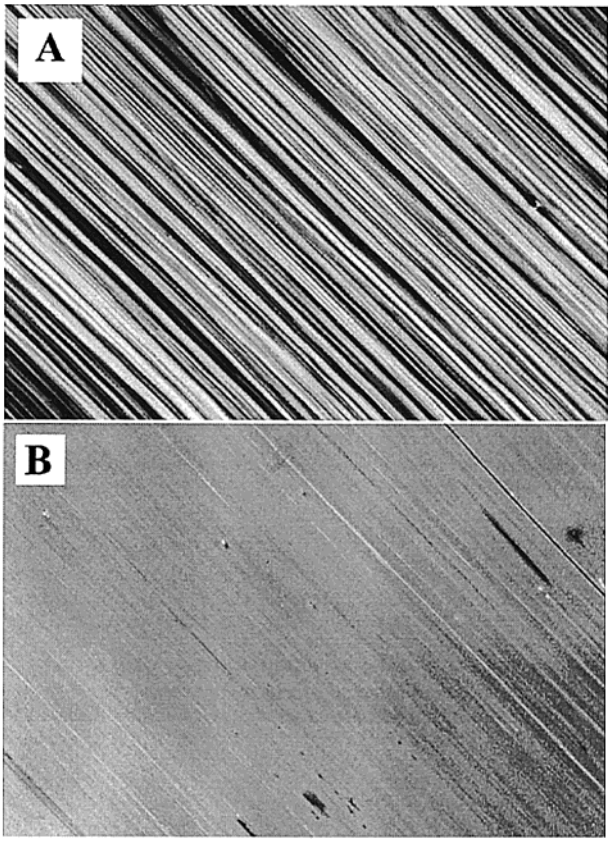
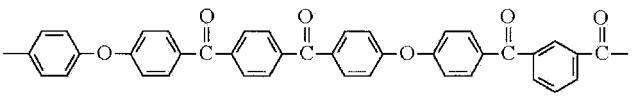


Figure 1. Optical micrographs, between crossed polars, of rubbed (a) and cold-crystallized (b) PET thin films. The rubbing conditions were the following: pressure = 20 g/cm^2, transport velocity = 1 cm/s, and rubbing distance = 60 cm. The crystallization was performed by heating the RUB films from 30 to 166 °C at 10 °C/min.

Experimental Section. a. Materials. PET samples were purchased from Aldrich and used without further purification. The PEKK samples were obtained by precipitation electrophilic polycondensation according to ref 12 and correspond to the following repeat unit:



The T_g of PET and PEKK samples are close to 80 and 160 °C, respectively. The polymer films were obtained by casting from dichloroacetic acid solutions onto glass slides and slow evaporation of the solvent at 100 °C overnight (these samples are called CAST). Before their use, the cast films were melted for 60 s and quenched in water (these amorphous samples were hereafter

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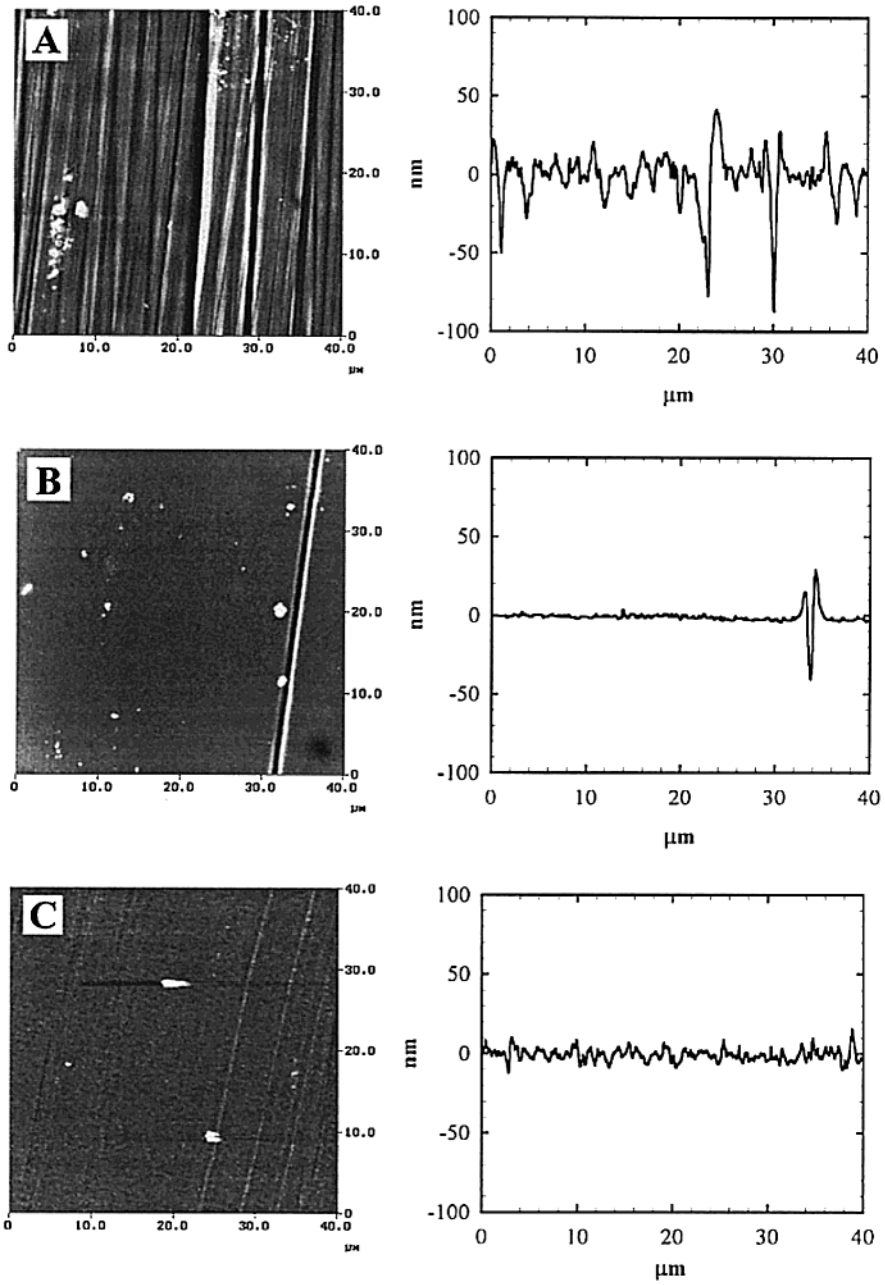

Figure 2. AFM topographic images and representative height profiles of PEKK thin films: (a) rubbed amorphous film (RUB), (b) rubbed film relaxed at 172 °C (i.e., 10 °C above T_g) (ANN), and (c) cold-crystallized rubbed film (CCR) (heated from 100 to 260 °C at 10 °C/min). The grayscale ranges from 0 to 100 nm. The height profiles were recorded perpendicular to the rubbing direction.

called AMO). The melting temperatures were equal to 260 and 375 °C for PET and PEKK, respectively. Films thickness was estimated to be close to 1 μm. Unidirectional rubbing was performed with a velvet cloth and a homemade machine that allows a control of the pressure exerted on the film (here 20 g/cm^2), the transport velocity (≈1 cm/s), and the distance of rubbing (60 cm). Rubbed amorphous samples are called RUB. These RUB thin films were submitted to annealing at temperatures slightly above T_g, yielding surface relaxed samples (ANN). These ANN samples could then be heated at 10 °C/min and maintained at the final crystallization temperature (T_C) for 5 min to ensure cold crystallization of the polymer (CCR). The maximum T_C was set close to the maximum temperature of cold crystallization checked by DSC (T_C was set at 260 and 166 °C for PEKK and PET, respectively). The sample preparation can be summarized as

$$\text{CAST} \rightarrow \text{AMO} \rightarrow \text{RUB} \rightarrow \text{ANN} \rightarrow \text{CCR}$$

b. Measurements. The transition temperatures of the polymers were determined with a Perkin-Elmer Pyris 1 DSC with a heating rate of 20 °C/min. Thermal relaxation and crystallization were performed with a Mettler FP90 hot stage. Optical observations were carried out with a Leitz DMR microscope. The surface morphology of the films was studied with a Nanoscope III A AFM, operated in air, in tapping mode, with commercial 300 kHz tips. Under the conditions used, no tip-induced surface damage was observed. The surface roughness was calculated as the standard deviation of the height for the complete data set (rms roughness). Finally, polarized FTIR spectra were re-

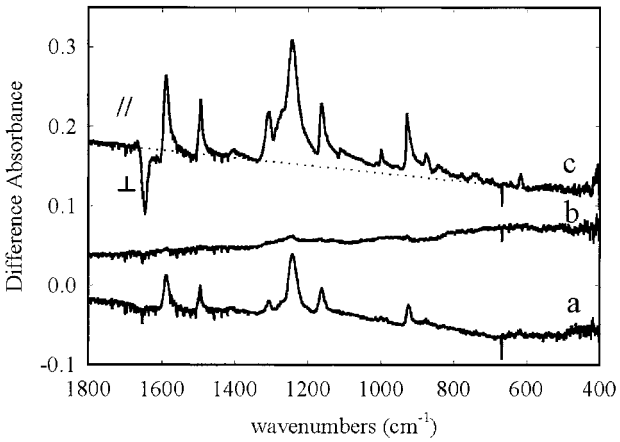

Figure 3. FTIR difference spectra of PEKK thin films obtained by subtracting the IR absorption spectrum with perpendicular polarization from the IR absorption spectrum with the beam polarized parallel to the rubbing direction: (a) rubbed amorphous film (RUB), (b) relaxed rubbed film (ANN), and (c) cold-crystallized rubbed film (CCR).

corded with a Bruker IFS113v spectrometer and an Au grid polarizer.

Results and Discussion. From OM observations, the CAST films are found to be semicrystalline. A subsequent melting/quenching process renders the film completely amorphous. The surface of these amorphous films (AMO) is featureless and smooth. Its rms roughness, as measured by AFM, is around 1 nm on a lateral scale of 10 μm.

As shown in the micrograph of Figure 1a, rubbing of AMO thin films with a velvet cloth clearly induces a strong birefringence and the formation of grooves parallel to the rubbing direction. The topography of rubbed PEKK films measured by AFM further confirms the optical observations and previous measurements. Indeed, grooves typically 10−20 nm high (a few exceed 100 nm) are formed parallel to the sliding direction (Figure 2a). The rms roughness is about 10 nm on a 10 μm scale. It is noteworthy that the shape of the grooves also exhibits ridges at the border typical of a strong plastic deformation of the surface. In addition to the topography effects, FTIR difference spectra of rubbed PEKK films demonstrate the orientation of the chains parallel to the rubbing direction (Figure 3a). The assignment of the observed IR bands to molecular modes is made according to the previous FTIR study of oriented PEEK films epitaxially grown on PTFE substrates.[13] The ν_{CO} IR mode (1646 cm^{-1}) has a transition moment perpendicular to the chain axis while several IR bands, appearing at 1164, 1244, 1308, and 1590 cm^{-1}, correspond to aromatic ring modes parallel to the chain axis. In Figure 3a, these parallel modes are clearly polarized along the rubbing direction, confirming the orientation of PEKK chains in the RUB samples. Similar AFM and FTIR results were obtained for PET and PEKK thin films. Therefore, our observations indicate that relatively low-T_g amorphous polymers behave in a similar way as polyimide layers.[2,4,5]

These rubbed PET and PEKK thin films also undergo surface relaxation upon annealing. As shown in Figure 2b, RUB surfaces relax at temperatures slightly above T_g. This relaxation is accompanied by a drastic decrease of the surface roughness, below 1 nm on a 10 μm scale. Only the deepest grooves still remain discernible on the surface, with their depth strongly attenuated relative to RUB samples. The IR difference spectra confirm the relaxation process: the IR dichroism completely vanishes for ANN films (Figure 3b), indicating that the polymer chains are almost randomly oriented.

The most striking feature concerning these films appears during the heating of ANN samples (i.e., after the surface relaxation). When apparently unoriented and featureless ANN films are cold-crystallized, uniform orientation typical of stretched or epitaxially crystallized polymers are observed in the CCR samples thus obtained (Figure 1b). In contrast, it should be noted that cold crystallization of unrubbed amorphous films yields completely different morphologies, with a few spherulites dispersed in an amorphous matrix. The very low number of heterogeneous nuclei, observed for unrubbed samples, is in complete disagreement with an orientation mechanism based on the parallel alignment of tiny crystallites upon rubbing. The IR difference spectra recorded for these CCR films, given in Figure 3c, confirm the high degree of molecular orientation achieved during the cold crystallization. In the same way as above, the observed dichroism shows that the polymer chains in the semicrystalline films are parallel to the initial rubbing direction (Figure 3c). This IR dichroism is even more pronounced than for initial RUB films. The corresponding AFM image (Figure 2c) shows that the crystallized CCR films exhibit appreciable corrugation likely to be due to the presence of crystalline domains; consistently, the surface roughness increases to 3−4 nm.

These observations clearly indicate that an "epitaxial" mechanism is at work, the orientation being transferred to the bulk samples via the nucleation/growth of polymer crystals from preoriented nuclei located at the surface. It thus appears that the surface relaxation does not completely erase the molecular orientation induced by the rubbing process. However, it is essential to note that the part of the samples that remains oriented after the surface relaxation is extremely low, since IR dichroism measurements are typical of unoriented films (Figure 3b). The origin of the preexisting nuclei oriented along the rubbing direction could be accounted for by considering the increase in chain mobility at the air−polymer interface.[6,8,11] Oriented crystalline aggregates could therefore develop simultaneously to the surface relaxation process around T_g, these aggregates acting as nuclei during the macroscopic cold crystallization of the polymer films.

Conclusions. Our observations demonstrate that *crystallization* (i.e., the formation of either crystalline aggregates or transient ordered structures) occurs during the surface relaxation at temperatures close to bulk T_g. In agreement with an increase of segmental mobility (i.e., a decrease of T_g) at the air−polymer interface, the crystallization range is extended to low temperatures by several tens of degrees for such semirigid polymers.

However, prior to giving a definite interpretation of these observations, the influence of molecular orientation on the crystallization of polymers has to be established. At first sight, it appears as quite evident that the macroscopic bulk drawing and microscopic surface rubbing have common manifestations: orientation, annealing, crystallization, and relaxation mechanisms.[14,15] But major differences remain; i.e., the drawing procedure delays the appearance of crystallinity after the end of the process, with a minimum critical draw ratio, whereas the surface rubbing involves a progressive emergence of oriented crystalline aggregates further

used as critical nuclei to induce the macroscopic oriented crystallization of the whole film. However, the above-mentioned studies could be used as guidelines to characterize the relaxation and/or crystallization processes associated with the surface rubbing of such polymer thin films.

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