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Notes

Epitaxial Crystal Growth of Poly(*p*-oxybenzoate) on Highly Oriented Poly(tetrafluoroethylene) with Various Support Substrates

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Introduction

Poly(p-oxybenzoate) (POBA), a totally aromatic stiff-chain polymer, is expected to possess excellent thermal and mechanical properties.[1−3] It is known that the properties of polymers are improved by aligning the polymer chains in the specified direction. It is however difficult to prepare oriented films and fibers of POBA by conventional processing techniques, because POBA does not melt or dissolve in most of organic solvents. In our previous study, we achieved epitaxial growth of POBA on mica and potassium bromide (KBr) single crystal substrates by in-situ polymerization. The molecular chains of the POBA crystals align parallel to the substrate surface with azimuthal orientations.[4]

Recently Wittmann and co-workers have reported that a thin, uniaxially oriented film of poly(tetrafluoroethylene) (PTFE) was deposited by mechanically rubbing the polymer onto a smooth counterface such as glass or metal.[5−8] It was further shown that a surface of highly oriented PTFE films is able to induce epitaxial orientation in small organic molecules and polymers.[9−16] The unique property of the oriented PTFE films is possibly applied to produce oriented films of insoluble polymers.

This work aims at preparing uniaxially oriented films of intractable POBA by the epitaxial crystallization on highly oriented PTFE substrates. The influence of support substrates on the orientation of POBA films was also discussed.

Experimental Section

An oriented thin film of PTFE was prepared on the substrate surface by sliding the bulk piece of PTFE onto the support substrate. Polycrystalline calcium fluoride (CaF_2), single crystal potassium bromide (KBr), and quartz were used as supporting substrates. The substrate temperature was controlled at 320−330 °C. The in-situ preparation method of the POBA films on the solid substrates was described in a previous paper.[4] All samples were prepared at a reaction temperature of 320 °C. Table 1 summarizes the film thickness and substrate of each sample.

The polarized FTIR spectra were measured with a Bio-Rad FTS-60A/896 FTIR spectrometer equipped with a wire-grid polarizer and an infrared microscope. Samples were characterized by FTIR microspectroscopy. Polarized ultraviolet spectra were measured with a Shimadzu MPS-2000 spectrophotometer and a Glan-Thompson prism.

The morphology of the POBA crystals on the substrates was observed with a TOPCON DS-720 scanning electron microscope. The sample surface was coated with Pd−Pt before observation.

Results and Discussion

On PTFE/CaF_2 Substrates. A Polarized FTIR spectrum of sample 1 (PTFE/CaF_2) is shown in Figure 1. Some absorption bands, which are dependent on chain orientation, are categorized into groups of parallel bands and perpendicular bands, respectively, depending upon whether absorption happens when the polarization of the IR beam is parallel or perpendicular to the polymer chain. The absorption bands at 1599, 1510, 1158, 1059, and 1018 cm^{-1} are parallel bands, whereas the absorption bands at 1272, 1227, and 1089 cm^{-1} are perpendicular bands.

As seen in Figure 1, the parallel bands show strong light absorption in the spectrum measured with polarization parallel to the sliding direction, whereas the perpendicular bands are intensified in the spectrum with the opposite polarization. The polarized FTIR spectrum shows that the molecular chains of POBA are highly oriented in the sliding direction. The dichroic ratio of the 1018 cm^{-1} band amounts to 20. The second moment of orientation function is defined by

$$f = (3\langle \cos^2\theta \rangle - 1)/2 \quad (1)$$

where θ is the transition moment angle measured from the sliding direction of the PTFE substrate. The observed dichroic ratio corresponds to $f = 0.86$.

An SEM photograph of sample 1 (PTFE/CaF_2) is shown in Figure 2. The morphology of POBA is characterized by a smooth, oriented sheet, but small lump-like domains are scattered on the surface and align in the sliding direction.

On PTFE/Quartz Substrates. It is difficult to measure the polarized FTIR spectra of the samples on quartz substrate. In this work, the polarized ultraviolet (UV) spectroscopy was used to assess the molecular orientation of the samples on quartz. Figure 3 shows the polarized UV spectra of sample 2 (PTFE/quartz). The broadness of the absorption band is either caused by the electronic interaction among polymer chains in the solid phase or may come from the artifacts due to the light scattering although the sample is transparent in appearance. The large dichroism is observed in the region of the absorption peak; the strong light absorption is observed for the polarization parallel to the sliding direction, and the weak absorbance for the perpendicular polarization.

The electronic structure of *p*-hydroxybenzoic acid units was studied by the complete neglect of differential overlap (CNDO) molecular orbital calculations.[17] Two electronic transitions are expected in the wavenumber region below 45 000 cm^{-1}. The lowest electronic transition is weak, but the second transition has the higher absorption intensity with the transition moment parallel to the molecular chain axis. Therefore, the parallel dichroism of the polarized UV spectra shows that the

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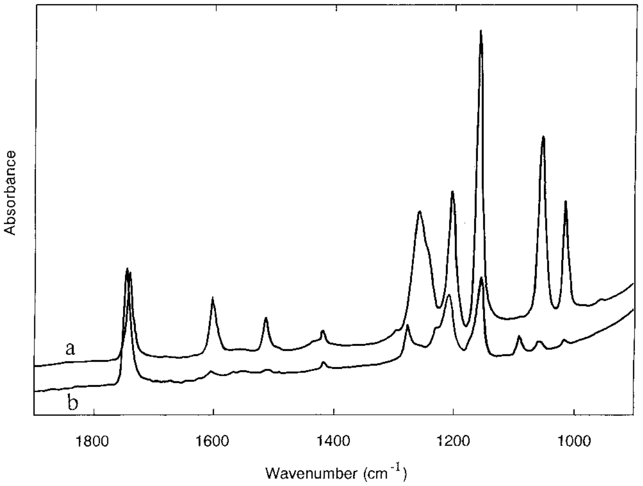

Figure 1. Polarized FTIR spectra of Sample 1 (PTFE/CaF_2): the polarization direction is (a) parallel and (b) perpendicular to the sliding direction.

Table 1. Substrate and Film Thickness of Samples

sample no.	substrate	film thickness (nm)
1	PTFE/CaF_2	150−200
2	PTFE/Quartz	20−40
3	PTFE/KBr	110−150

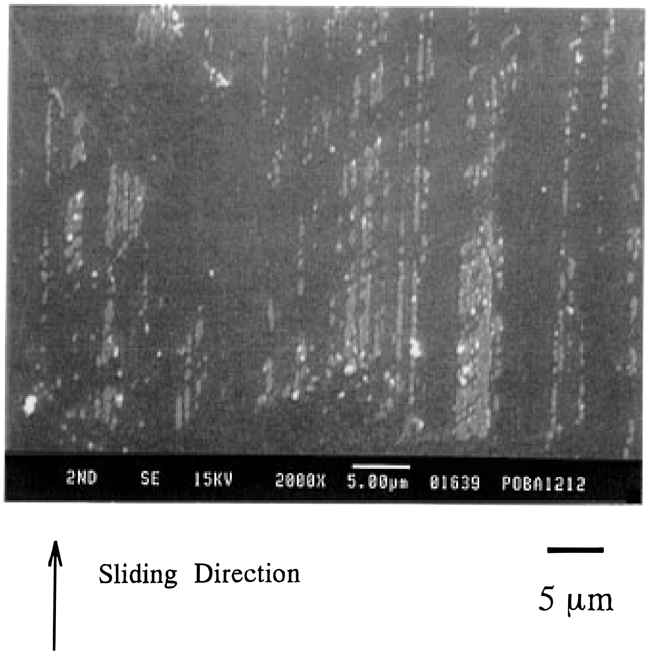

Figure 2. SEM photograph of sample 1 (PTFE/CaF_2).

molecular chains of POBA follow the orientation direction of the PTFE molecular chains.

On PTFE/Single Crystalline KBr Substrate. Figure 4 shows an AFM photograph of PTFE mechanically deposited on the cleaved KBr surface. The sliding direction of the PTFE bar was parallel to one crystal axis of KBr. The individual molecular chains are clearly seen in the AFM image and align in the sliding direction with an interchain spacing of 0.556 nm. Bunn and Howells reported that the molecular chains of PTFE were packed in the hexagonal lattice and that the interchain distance in the crystalline state was 0.554 nm.[18] The mechanically deposited PTFE on KBr has a similar structure to that of the hexagonal crystal phase in the bulk sample.

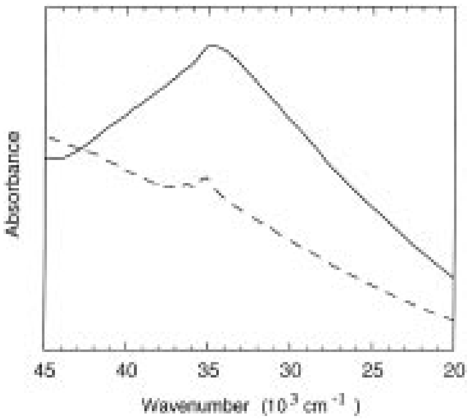

Figure 3. Polarized UV spectra of sample 2 (PTFE/quartz): the polarization direction is parallel (—) and perpendicular (- -) to the sliding direction.

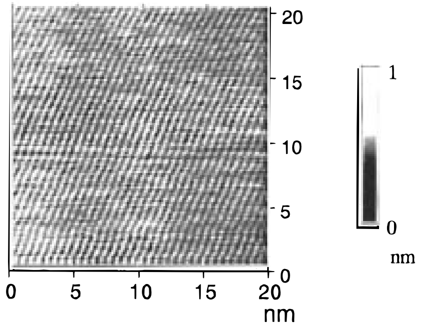

Figure 4. High magnification AFM image of mechanically deposited PTFE on KBr substrate.

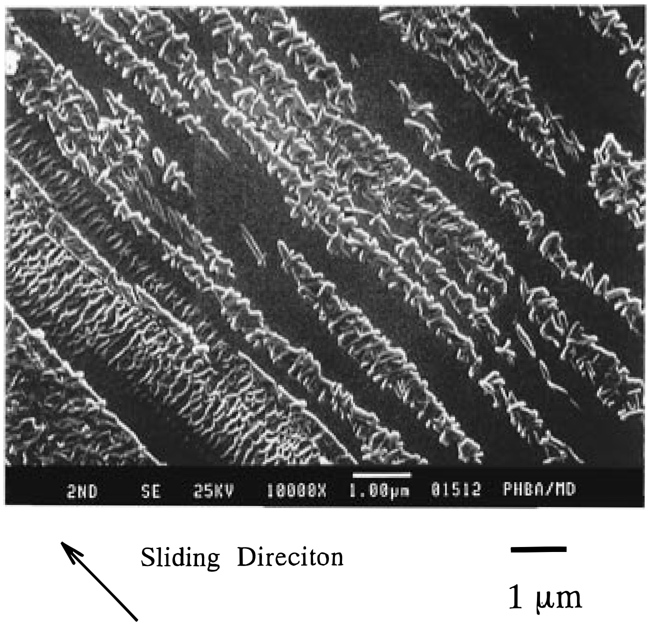

Figure 5. SEM photograph of sample 3 (PTFE/KBr).

On the other hand, the polarized FTIR spectra of sample 3 (PTFE/KBr) show that the POBA films on PTFE/KBr are approximately isotropic. The dichroic ratios of the parallel bands are as low as 1.0−1.1. Although the PTFE molecular chains are highly oriented in the sliding direction, the POBA chains do not follow the orientation direction of PTFE chains.

An SEM photograph of sample 3 (PTFE/KBr) is shown in Figure 5. Some POBA crystals are seen to grow from the area of cracks among PTFE strips, and the POBA crystal arrays align parallel to the deposition direction. In between the POBA crystal arrays the KBr substrate is covered by crack-free PTFE.

Single crystal KBr is expected to have very high free surface energy due to the strong ionic bonds and high bonding density of the single crystal.[19] As seen in Figure 5, POBA nucleations start on the cracks among PTFE strips as a consequence of preferred nucleation on the high free surface energy sites of KBr rather than on the PTFE, which has a low free surface energy.[7] As crystal growth proceeds, the POBA crystals, which are initially grown from cracks, grow over to cover the overall PTFE surfaces merging into the center of the smooth PTFE strips. Even further nuclei growth onto the PTFE surface mostly retains the original epitaxial orientations of POBA on KBr.

Conclusions

The highly oriented films of intractable POBA were shown to be prepared by the in-situ epitaxial polymerization on the highly oriented PTFE film. The morphology of POBA crystals was however affected by the kinds of supporting substrate for the mechanically transferred PTFE film. The molecular chains of POBA are highly oriented parallel to the PTFE chain direction on well-prepared PTFE/CaF_2 and PTFE/quartz substrates. On the other hand, the POBA film is almost isotropic on a PTFE/KBr substrate, in which the crystal growth from the cracks among PTFE strips dominates the morphology of POBA films.

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