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ORIENTED FILMS OF POLY(*p*–PHENYLENE) BY FRICTION–DEPOSITION AND ORIENTED GROWTH IN POLYMERIZATION

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Abstract Oriented films of poly(*p*–phenylene) (PPP) were prepared by two methods. One was the friction–deposition technique, in which sliding the solid PPP on the substrate at a controlled temperature afforded a highly oriented film on the surface. In another method, when the friction–deposited film was immersed into the reaction mixture, benzene was polymerized into the oriented PPP film on the friction–deposited substrate. Both oriented films of PPP were characterized by electron microscope and polarized spectroscopic methods.

INTRODUCTION

Poly(*p*–phenylene) (PPP) has been obtained by chemical oxidation in the powder state, and by electro–oxidization in the film. Because it is insoluble and infusible, it is difficult to control the higher–order structure of polymer. In this work, we attempt to orient PPP.

Recently, a sophisticated technique has been reported by Wittmann and Smith[1], in which a highly oriented film of poly(tetrafluoroethylene) has been mechanically deposited onto a smooth counterface by dragging the polymer. By this technique they obtained the highly oriented films from the solid polymer.

We have applied the friction-deposition technique to a so-called untractable powder polymer, such as poly(dimethylsilylene)[2]. Now, we prepared an oriented film of PPP by friction-deposition. However, the film was very thin and nonuniform. In order to increase the film thickness, PPP was newly polymerized on the friction-deposited film.

Oriented films were characterized by a polarized microscope, transmission electron microscope (TEM), polarized ultraviolet absorption spectroscopy (UV), polarized infrared absorption spectroscopy (IR), and polarized fluorescence spectroscopy.

EXPERIMENTAL

Friction-deposition

PPP was synthesized from benzene, aluminum chloride and copper(Ⅱ) chloride by the method of Kovacic and Kyriakis[3]. Elemental analysis showed that 3.7% of hydrogen had been substituted by chlorine. The brown powder of PPP was compressed into a black-purple disk at about 5kg/cm^2. Sliding the PPP disk on the smooth counterface such as a quartz plate at a controlled temperature (160-235°C) afforded an oriented layer of the polymer on the surface.

Oriented Growth in Polymerization

The friction-deposited PPP film on a substrate was put into the mixture of benzene, aluminum chloride and copper(Ⅱ) chloride, and then polymerization was started by heating. When the substrate was picked up, a red-brown PPP film covered on the friction-deposited film. The polymerized film was washed in benzene, boiling hydrochloric acid, and water, in that order.

Measurements

Transmission electron micrographs were taken by a Hitachi H-9000 with an acceleration voltage of 300 kV. The specimen for TEM was covered with carbon for reinforcement, separated from the substrate on water surface, and scooped up

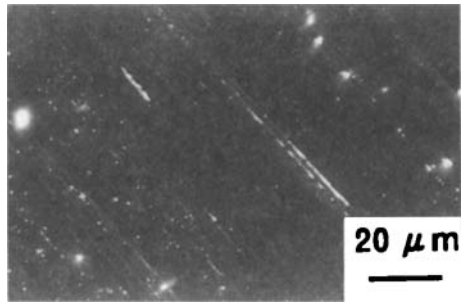

FIGURE 1 An optical micrograph of friction-deposited PPP on quartz substrate prepared at 170°C with crossed polarizers.

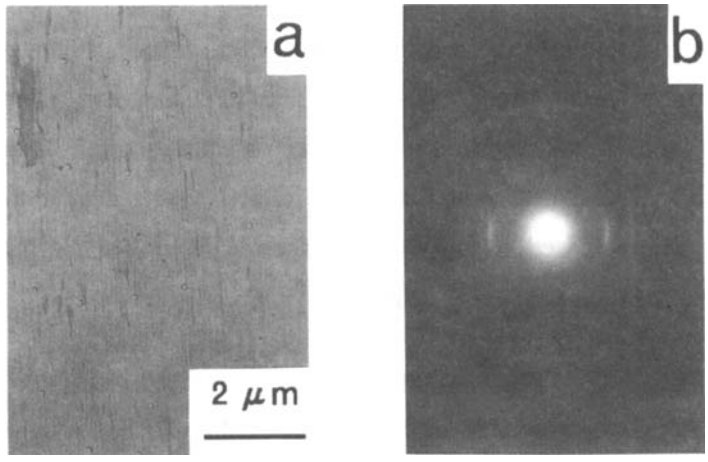

FIGURE 2 (a) An electron micrograph and (b) an electron diffraction pattern of friction-deposited PPP on quartz prepared at 175°C.

onto an electron microscopic grid.

Polarized UV spectra were measured by a Shimadzu MPS2000 spectrophotometer equipped with a Glan-Thompson prism polarizer. Polarized IR spectra were measured by a BIO-RAD FTS-60A/896 FT-IR spectrometer with a wire-grid polarizer. The specimen deposited on KBr disk substrate was used for IR measurements, and quartz substrates were used for UV spectroscopy.

RESULTS AND DISCUSSION

Friction-deposited film of PPP

When PPP disk was slid on the smooth substrates, such as quartz plate, highly oriented layer was obtained on the surface of the substrates. The polymer layer could be deposited when the substrate temperature was higher than 160°C. However, the film was not uniform (FIGURE 1). The electron micrograph showed the discontinuity of the film and very anisotropic morphology (FIGURE 2a). The electron diffraction pattern was a fiber diagram (FIGURE 2b), suggesting that the film was oriented and crystalline.

In order to evaluate the orientation of friction-deposited film, polarized UV spectra and IR spectra were measured. The PPP film had a broad peak at 389nm in the UV spectrum. The polarized spectra showed large dichroism (FIGURE 3). The film absorbed only the parallel polarized light to the sliding direction. The polarized IR spectra also showed dichroism for the absorption band at 1481, 1000, and 806cm^{-1} (FIGURE 4).

Oriented growth in Polymerization

Several authors[4] reported that monomers epitaxially aligned on substrates were polymerized to highly ordered polymer. Recently, Sano *et al.*[5] obtained polymer films epitaxially grown on graphite during polymerization. Wittman and Smith[1] reported oriented polymerization of poly(*p*-xylylene) on friction-deposited poly(tetrafluoroethtlene). Now, we attempted homoepitaxial growth of PPP in

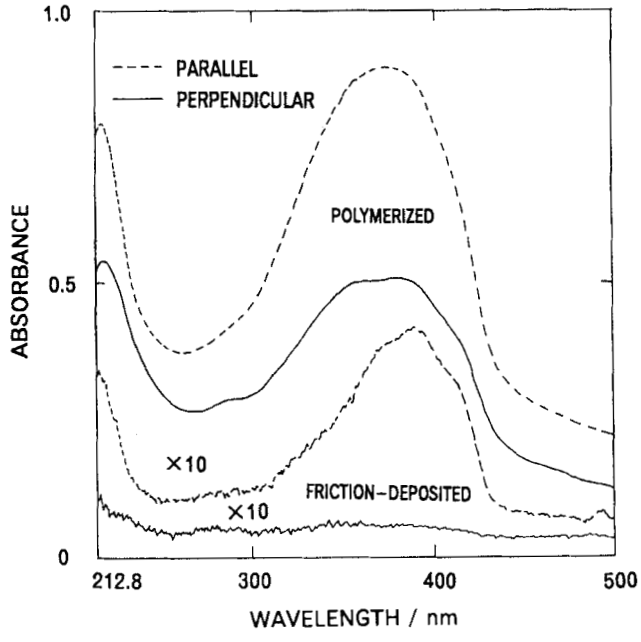

FIGURE 3 Polarized UV spectra of PPP film; friction–deposited (lower ×10) and oriented growing in polymerization (upper). The solid and dashed lines represent the polarization perpendicular and parallel to the sliding direction, respectively.

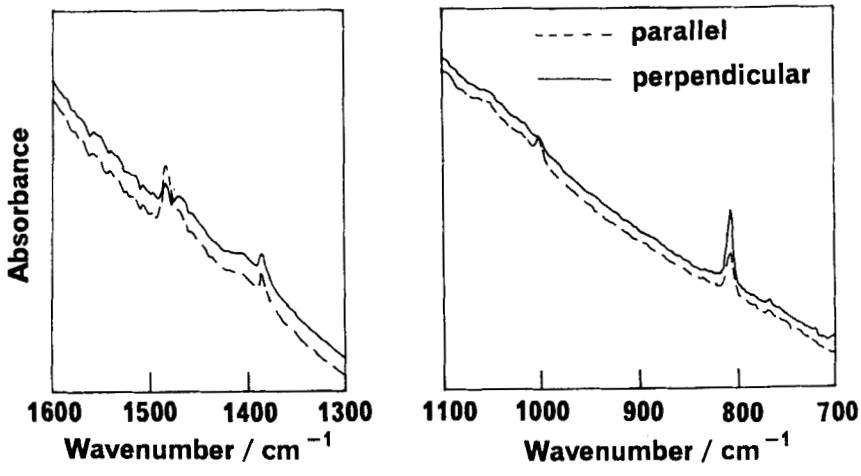

FIGURE 4 Polarized IR spectra of friction–deposited film on KBr disk prepared at 179°C. The solid and dashed lines represent the polarization perpendicular and parallel to the sliding direction, respectively.

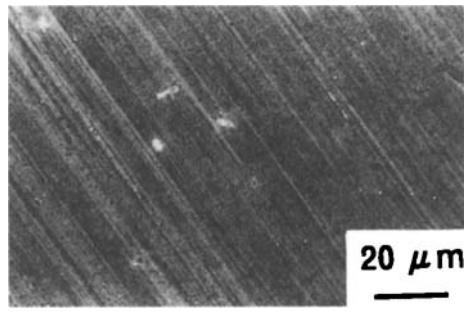

FIGURE 5 An optical micrograph of polymerized PPP film on friction-deposited PPP with crossed polarizers.

polymerization. When the friction-deposited PPP film was immersed into the reaction mixture, PPP was newly deposited on the friction-deposited PPP substrate in polymerization. This film was more continuous than friction-deposited one (FIGURE 5). The polarized UV spectra showed that the polymerized film was oriented (FIGURE 3). The degree of orientation of polymerized film was lower than that of the friction-deposited film. However, the distinct dichroism of UV spectra remained even though the original spectra of the friction-deposited film was subtracted from the spectra of the polymerized film. Therefore, the film newly deposited during polymerization was obviously oriented. As an absorption peak was blue-shifted, it was expected that the polymerized film had lower molecular weight than powder.

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