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Uniaxial Oriented Poly(*p*-phenylene) Fibrils and Films

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Introduction. Poly(*p*-phenylene) (PPP) prepared by electrochemical polymerization of benzene has been investigated for decades. In early studies, the formation of unidentified layers on the electrode[1] and of insoluble polyphenylenes which precipitated into the solution[2] was observed. Recently, new methods of electrosynthesis of polyphenylenes in various media were proposed. Most synthetic routes correspond to a direct oxidative coupling reaction of aromatic nuclei.[3–6] In these cases, superacids such as $SbF_5 + HF$, $CF_3CH_2SO_3H$, or aqueous HF were used for preparing polyphenylenes by oxidation of benzene. Other binary systems, such as CH_3NO_2 or $C_6H_5NO_2$ with benzene and $AlCl_3$ or BF_3, were also tested. However, no publications concerned the use of BF_3–ethyl ether solution (BFEE) containing a controlled amount of water (without adding other solvent) as the electrolyte for electropolymerization of benzene.

PPP is a conjugated polymer with a simple repeat chemical structure and has been widely investigated out of fundamental physical interest[6] and for practical applications.[7] However, those studies have been carried out mostly with compressed pellets of PPP powder which was synthesized from benzene with a Friedel–Crafts system. It is also reported that PPP films prepared by electrochemical polymerization of benzene are powderlike and lack flexibility.[5,8] Sato et al. prepared flexible PPP films by oxidation of benzene with $LiAsF_6 + CuCl_2$ in nitrobenzene or benzonitrile. These films were unoriented.[9] Homogeneous PPP films were also found to be formed in organic media such as CH_2Cl_2 and CH_3NO_2.[10] In this work, we used a solution of BFEE containing a controlled amount of water as both the solvent and catalyst for the electrochemical polymerization of benzene and surprisingly found that uniaxially oriented PPP fibers and films were obtained. They displayed anisotropic conductivity and were flexible in the direction parallel to the fiber axes.

Experimental Section. The electrochemical cell consisted of a classical three-electrode system connected to a PARC M273 potentiostat. All solutions were deaerated by a dry argon stream and maintained at a light overpressure during the experiments.

The working and the counter electrodes were separated from each other by a sintered-glass disk, which was made according to a published procedure.[11] The distance between these two electrodes was about 0.5 cm. Each of these two electrodes was made of 99.9% Pt sheet and had a size of 0.2 × 50 × 5 mm. The reference electrode was an Ag/AgCl (3.5 M KCl) electrode. The IR spectrum was obtained using a Nicolet 170SX FT-IR spectrometer. The transition spectrum was detected using the KBr pellet method. Surface reflection absorption spectra were obtained using PPP fiber as the sample; polarized IR radiation was used. Conductivity measurements were carried out by a conventional dc four-electrode technique.

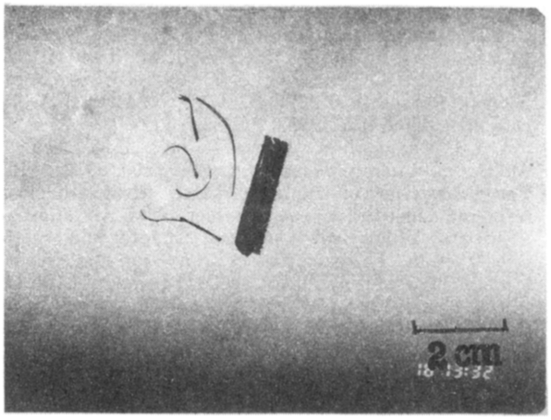

Figure 1. Photograph of the PPP film and fibers.

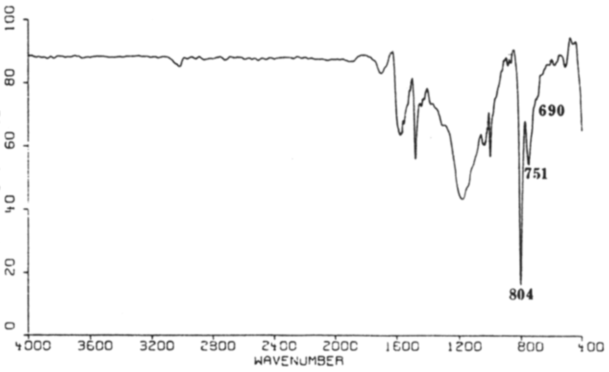

Figure 2. Transition FT-IR spectrum of PPP.

A BF_3–ethyl ether solution (chemical grade) was purchased from Shanghai 2nd Chemical Co. and purified by distillation under vacuum. Benzene (analytical grade) and water were twice distilled before use. Water was slowly dropped into the BFEE solution and mixed well by stirring. PPP fibers and films prepared in this experiment were repeatedly washed and then dried under vacuum at 80 °C for 24 h.

An amount of 1 mL of benzene was added into a 30 mL BFEE solution containing 0.3 mL of water and mixed by stirring. Then, a 2 V potential was applied for electrolysis. In a few seconds, many fine short, black polymer lines appeared on the working electrode surface. While electrolysis continued, these lines grew longer and broader. In about 3000 s, the short lines in vertical directions connected to form a long fiber. These fibers were parallel to each other, and the distances between two neighboring fibers were nearly the same. These fibers also grew in width during the electrolysis process, and they connected to form a film in about 8000 s. Figure 1 shows a photograph of the final PPP fibers and film.

Characterization and Properties of the PPP Fibers and Films. The transition IR spectrum of PPP is illustrated in Figure 2. The absorption band at 804 cm^{-1} is due to out-of-plane CH vibrations of para-disubstituted polyphenylenes, and the 751 cm^{-1} band and a shoulder band at about 690 cm^{-1} are typical of out-of-plane vibrations of the five adjacent hydrogens on the terminal phenyl rings.[12,13] The length of the PPP chains and the number of para coupling phenyl nuclei were estimated by analyzing the spectrum of PPP film between 810 and 680 cm^{-1}. The intensity ratio of bands 804 and 690 cm^{-1} ($R = I_{804}/I_{690}$) will tend to an infinite value as the number of phenyl nuclei increases. According to the published data,

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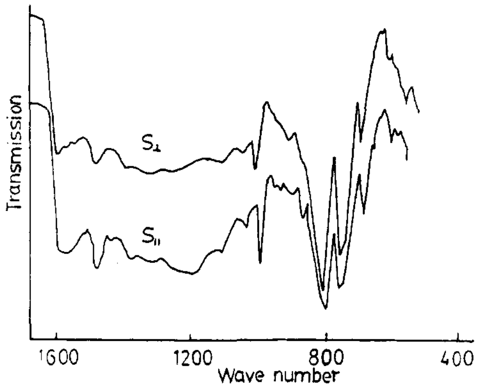

Figure 3. Polarized surface reflection–absorption IR spectra of the PPP fiber. $S_{\parallel}$: Spectrum recorded by locating the fiber axial direction parallel to IR rays. $S_{\perp}$: Spectrum recorded by locating the fiber axial direction perpendicular to IR rays.

R varies between 0.6 and 2 when the number of phenyl nuclei increases from 3 to 5.[11] Our results indicated the PPP obtained by electrochemical oxidation of benzene in BFEE containing 5 mM water, $R > 9$, which implied the repeat unit number of PPP is about 20. Furthermore, in this spectrum no strong absorptions at 840 and 860 cm^{-1} are detected, which are ascribed to trisubstituted and tetrasubstituted benzene, respectively. These results agree with those reported for chemically prepared PPP[14,15] and indicate that the principal structure of the polymer is poly(*p*-phenylene) without cross-linking.

The polarized surface reflection–absorption FT-IR spectra (RPS) of PPP fiber are shown in Figure 3. $S_{\parallel}$ is the spectrum recorded by locating the fiber axial direction parallel to the incident IR rays, and $S_{\perp}$ is recorded by positioning the fiber axial direction vertical. The infrared dichroic ratio R is equal to $A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are measured absorbances of the electric vector parallel and perpendicular, respectively, to the fiber axial direction. As described above, 804 cm^{-1} is the out-of-plane vibration of the CH in the chain backbone. The vertical vibrational electromagnetic wave of the polarized IR ray supported this vibration. Therefore, the 804 cm^{-1} band was strengthened, and the R of this band was measured to be about 0.65. A similar behavior was also found for the bands at 750 and 690 cm^{-1}. R of the band at about 1000 cm^{-1}, characterizing the aromatic in-plane hydrogen-bending vibration,[16] is larger than 1 (calcd 1.28). These results strongly support the uniaxial molecular orientation of PPP chains.

The dynamic mechanical test diagrams of the PPP film, both parallel and perpendicular to the orientation directions, are shown in Figure 4. The PPP film has high strength in the parallel direction. Dynamic mechanical tests were carried out in the temperature range of 25–250 °C (Figure 4A). Its real modulus (E'), loss modulus (E''), and loss tangent (Δ) are measured to be in the ranges of $(5.0–6.3) \times 10^9$ dyn/cm^2, $(1.2–6.2) \times 10^8$ dyn/cm^2, and 0.02–0.04, respectively, along the fiber direction. Furthermore, in this direction, the tensile strength of the film was about 78 kg/cm^2 and the elongation at break was about 5.1%. On the other hand, in its perpendicular direction, this film was weak and broken easily, especially at high temperatures. Therefore, a dynamic mechanical test was performed only in the temperature scale of 25–50 °C. Its E', E'', and Δ were found to be in the range of $(6.0–7.1) \times 10^8$ dyn/cm^2, $(3.8–5.0) \times 10^7$ dyn/cm^2, and 0.05–0.075, respectively (Figure 4B). The tensile strength of this film in the perpendicular direction was about 6.7 kg/cm^2, and the elongation at break was about 4.8%. These results revealed that the PPP film was well oriented, and the orientation increased the E', E'', and impact strength of the film in the parallel direction but, by contrast, decreased the loss tangent. Conductivity measurements also showed that the PPP film was anisotropic. In the direction of orientation, its conductivity was measured to be 0.465 S cm^{-1}. However, in the perpendicular direction, its conductivity was lower than 1.2×10^{-5} S cm^{-1}.

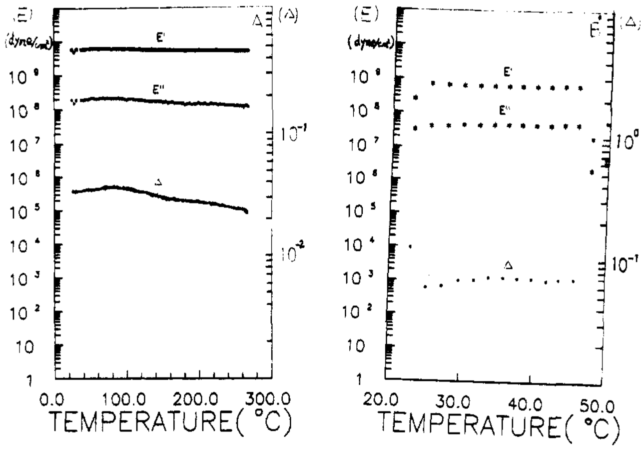

Figure 4. Dynamic mechanical test diagrams of a PPP film: (A) In the direction parallel to orientation. (B) In the direction perpendicular to orientation.

The water content in the BFEE solution and mechanical stirring influence strongly the parallel arrangement of fibers. The PPP fibers with the best quality could be obtained only by using the BFEE solution containing about 5 mM water as the electrolyte. The underlying forces leading to molecular orientation are still not clear now, and further work is needed.

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