

# High-quality poly(*p*-phenylene) film prepared by electrochemical polymerization of benzene at a stainless steel electrode

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Poly(*p*-phenylene) (PPP) film has been electrochemically deposited onto a stainless steel electrode surface by direct oxidation of benzene in BF<sub>3</sub>-diethyl ether solution at an applied potential of 1.7 V (vs Ag/AgCl). The morphology, conductivity and the mechanical property of the film were studied. As-grown PPP film has a conductivity of 2.7 S cm<sup>-1</sup>. It has a high modulus of 1.2 × 10<sup>10</sup> dyne cm<sup>-2</sup> and a large tensile strength of 550–650 kg cm<sup>-2</sup>. Furthermore, this film was flexible and could be easily cut into any shapes, such as fibres, circles, squares and triangles. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Amongst the conducting polymers, poly(*p*-phenylene) (PPP) has been known for many years. Its synthesis is normally achieved using the chemical method of Kovacic *et al.*<sup>1,2</sup>, which involves the reaction of benzene with AlCl<sub>3</sub>-CuCl<sub>2</sub> or other Friedel-Crafts catalysts; a non-melting insoluble dark brown powder is obtained as the product. It cannot be shaped by conventional polymer processing techniques. Since 1966, extensive work has been devoted to the electrochemical polymerization of benzene by several independent groups. In early studies, the formation of unidentified layers on the electrode<sup>3</sup> and of insoluble polyphenylenes which precipitated into the solution<sup>4</sup> were observed. Recently, new methods for electrochemical polymerization of benzene in various media were proposed<sup>5–10</sup>.

PPP is a conjugated polymer with a simple repeat chemical structure and has been widely investigated with respect to its fundamental electronic structure as a  $\pi$ -conjugated polymer<sup>11</sup> and for practical applications<sup>12</sup>. However, these studies were mostly carried out with compressed pellets of PPP powder which was chemically synthesized. The electropolymerization technique has many advantages over conventional chemical synthesis, because conducting polymer films can be deposited directly onto the electrode surface by anodic oxidation, which can be used without further changes as active material. It was also reported that PPP films prepared by electrochemical polymerization of benzene are powder-like and lack flexibility<sup>7,10</sup>. Sato and co-workers prepared a flexible PPP film by oxidation of benzene with LiAsF<sub>6</sub> + CuCl<sub>2</sub> in nitrobenzene or benzonitrile<sup>13</sup>. However, they did not characterize the film in detail.

The electrochemical polymerization of benzene has been successfully carried out by using a noble metal sheet (such as Pt, Au) or a glassy carbon as the electrode. However, these electrodes are too expensive for large-scale production and application. As far as the authors know, no work has been done towards the direct anodic oxidation of benzene onto a less noble metal or an alloy (such as stainless steel). One of the reasons is presumably related to the high oxidative potential<sup>4</sup> of the monomer. In this work, we used distilled BF<sub>3</sub>-diethyl ether containing a controlled amount of benzene as electrolyte for the electrochemical polymerization of benzene and surprisingly found that the obtained PPP film has a high strength and great flexibility. It can be easily cut by the conventional mechanical methods into a variety of structures, such as fibres, circles and triangles.

## EXPERIMENTAL

### Materials

BF<sub>3</sub>-diethyl ether (Huangyan Chem. Plant, China) was purified by distillation under reduced pressure. During the distillation process no special precautions were taken to avoid the absorption of the moisture from the air. Analytical grade benzene (Shanghai 2nd Chem. Co., China) was twice distilled before use.

### Electrochemical polymerization

The electrochemical synthesis and electrochemical examinations were performed in a one-compartment cell with the use of an EG&G potentiostat model 273 under computer control. The working and counter electrodes were AISI 304 stainless steel sheets (3 cm × 4 cm) placed 0.5 cm apart. The anodic potentials were measured vs a Ag/AgCl electrode (AgCl coated Ag directly in the solution). The stainless steel electrode was carefully polished with Al<sub>2</sub>O<sub>3</sub> (Presi, 1  $\mu$ m) before

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each synthesis. The electrolyte was  $\text{BF}_3$ -diethyl ether (no other solvent was added) containing 1.6 M benzene. All solutions were deaerated by a dry argon stream and maintained at a light overpressure during the experiments. The integrated charge passed during the film growth was used to control the thickness deposited films. The PPP films were peeled off the electrode surface and washed repeatedly with distilled ethyl ether, and then dried for 24 h at  $50^\circ\text{C}$  under vacuum before characterizations.

#### Tests and characterizations

The i.r. spectrum (KBr pellet) was obtained using a Nicolet 170 SX FTi.r. spectrometer. The film thicknesses were determined with a Heilderham thickness monitor. Dynamic property test was performed by a dynamic viscoelastometer Rheovibrom DDVII-EA over a range of temperature of  $30$ – $250^\circ\text{C}$  at a constant frequency of 3.5 Hz. Tensile strength of the film was measured by using an electronic drawing machine (WD-1, Changchun) at a stretching rate of  $0.5\text{ cm s}^{-1}$ . The differential scanning calorimetry (d.s.c.) test was carried out on a Perkin-Elmer thermal analysis calorimeter at a temperature scan rate of  $20^\circ\text{C min}^{-1}$ . Scanning electron microscopy pictures were taken using an X-560 electron micrographer.

## RESULTS AND DISCUSSION

#### Cyclic voltammograms

Cyclic voltammograms (CVs) of benzene at polished stainless steel electrode in  $\text{BF}_3$ -diethyl ether are shown in Figure 1A. The potential scans shown led to the formation of a film on the working electrode surface. The strong oxidation present at potentials greater than 1.5 V promoted polymer generation on the electrode (black with thickening deposit). As seen from this figure, a couple of peaks at about 0.4 and 1.5 V were attributed to the reduction and oxidation (doping and undoping) processes of the polymer. The increases of the redox wave currents of the polymer implied that the amount of the polymer on the electrode surface increased. On the other hand, the CV of distilled  $\text{BF}_3$ -diethyl ether showed no current waves in the same potential scale (Figure 1B), which demonstrated that the electrolyte and the stainless steel electrode were electrochemically inert during film growth.

#### I.r. spectrum

The transition i.r. spectrum of PPP (KBr pellet) is illustrated in Figure 2. The characteristic i.r. absorptions of PPP were located around  $650$ – $900\text{ cm}^{-1}$ . The absorption peak at  $805\text{ cm}^{-1}$  is due to the out-of-plane C–H vibration of *para*-disubstituted polyphenylene; the absorption peaks that appeared at 690 and  $754\text{ cm}^{-1}$  were attributed to the out-of-plane deformation C–H vibration of mono-substituted benzene ring (the terminal phenyl ring)<sup>14,15</sup>. Furthermore, in this spectrum no strong absorptions at 840 and  $860\text{ cm}^{-1}$  were detected, ascribable to trisubstituted and tetrasubstituted benzene, respectively. These results agree with those reported for chemically synthesized PPP<sup>16</sup>, and indicated that the principal structure of the polymer is poly(*p*-phenylene) without cross-linking. It is possible to estimate the degree of polymerization (DP) based on the ratios of the 805 and  $690\text{ cm}^{-1}$  intensities<sup>17</sup>.  $\text{DP} = 2I_{805}/I_{690} + 2$ , our

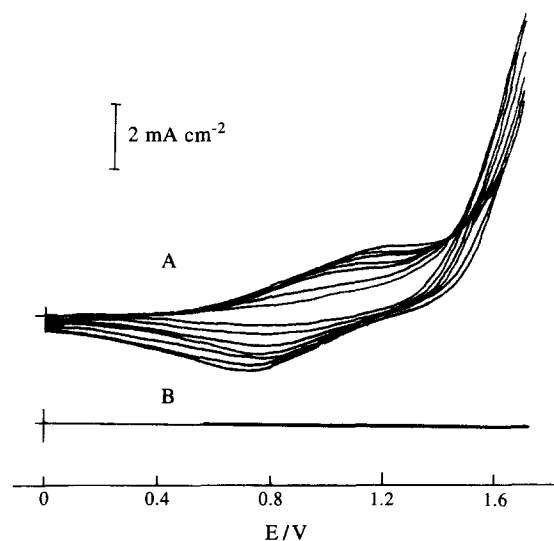


Figure 1 Cyclic voltammograms of 1.6 M benzene in distilled  $\text{BF}_3$ -diethyl ether (A), or pure  $\text{BF}_3$ -diethyl ether (B) on a stainless steel electrode and at a potential scan rate of  $0.1\text{ V s}^{-1}$

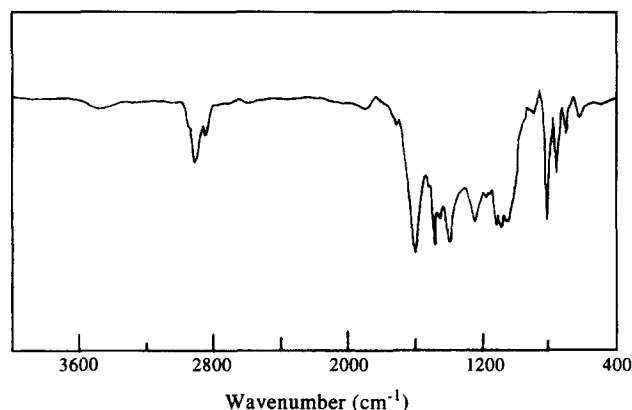


Figure 2 Transition FTi.r. spectrum of PPP prepared at 1.7 V vs Ag/AgCl

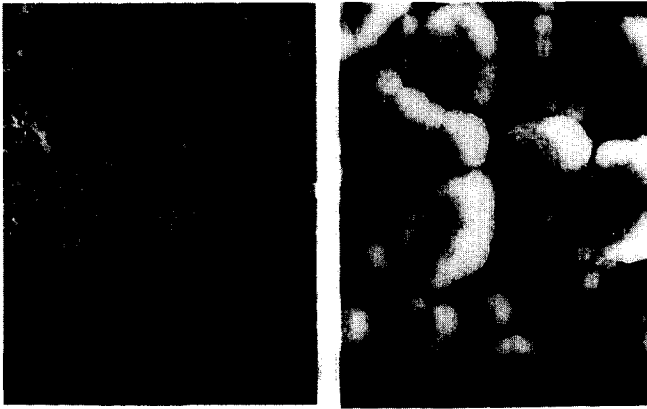
results indicated that PPP obtained by electrochemical polymerization of benzene in  $\text{BF}_3$ -diethyl ether had 11 repeat units. On the other hand, the peaks at  $2854$  and  $2922\text{ cm}^{-1}$  indicated that the as-grown PPP film was not completely aromatized, for these peaks were attributable to the C–H stretching vibration of alkanes. The structure of this part of the products was proposed by Toshima *et al.*<sup>18</sup>.

#### Film morphologies and d.c. conductivity

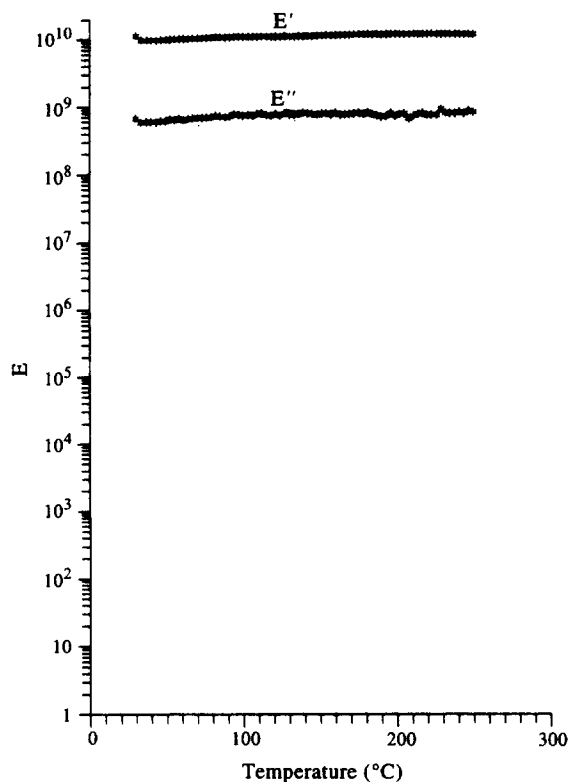
Figure 3 presents the scanning electron microscopy pictures of the PPP film prepared at 1.7 V vs Ag/AgCl. These pictures showed the morphologies of the two sides of PPP film were different. The side contacted to the electrode is relatively flat and compact (Figure 3A). However, the side exposed to the solution is rough and irregular (Figure 3B). The conductivity of this film, measured by the conventional four-electrode technique, was  $2.7\text{ S cm}^{-1}$ .

#### Mechanical tests

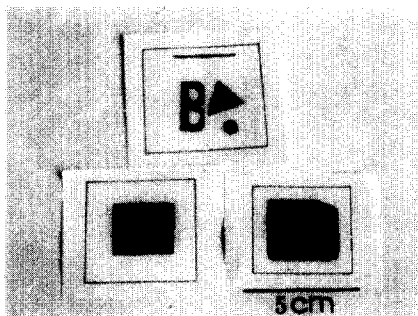
The tensile strength of this film was measured as  $600 \pm 50\text{ kg cm}^{-2}$  at a stretching rate of  $0.5\text{ cm min}^{-1}$ . This value was much higher than those of some widely



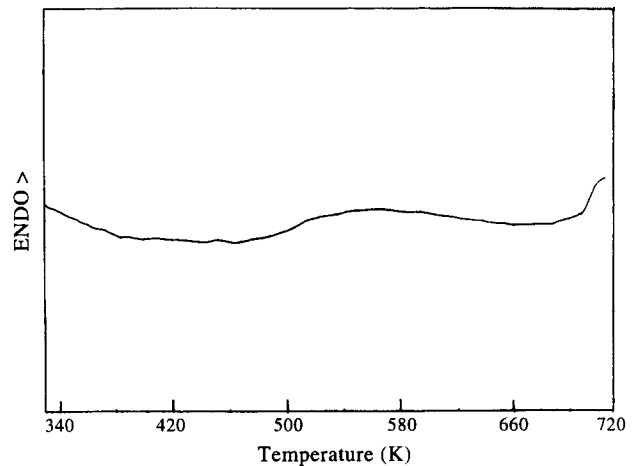
**Figure 3** Scanning electron micrographs of the PPP film: (A) the side in contact with the electrode; (B) the side in contact with the solution



**Figure 4** Dynamic mechanical test diagram of a PPP film with a thickness of  $0.019 \pm 0.002$  mm



**Figure 5** Photograph of free-standing PPP films shaped into various shapes with a knife



**Figure 6** D.s.c. curve of PPP film

used engineering plastics such as poly(propylene) ( $260 \text{ kg cm}^{-2}$ ) and poly(vinyl acetate) ( $300 \text{ kg cm}^{-2}$ )<sup>19</sup>. *Figure 4* shows the dynamic mechanical test diagrams of the as-grown PPP film. The experiment was carried out in a temperature range of 30–250°C. It is clear from this figure, the obtained film has a high real modulus ( $E'$ ) of  $1.2 \times 10^{10} \text{ dyne cm}^{-2}$  and loss modulus ( $E''$ ) of  $8.0 \times 10^9 \text{ dyne cm}^{-2}$  at room temperature, and they were almost unchanged in the test temperature scale. According to these experimental results, the modulus of the film was comparable to those of poly(methyl methacrylate) and polystyrene, and much higher than those of polyethylene and polypropylene. Furthermore, this film was flexible and can be shaped into various shapes by a knife or a pair of scissors (*Figure 5*).

#### Thermal test

The d.s.c. test diagram of the obtained PPP film shows a weak and broad transition between 205 and 365°C (*Figure 6*). However, no decomposition of the film was found as the temperature increased up to about 440°C, indicating the film has a high thermal stability.

#### CONCLUSIONS

High-quality PPP film was obtainable with the use of distilled  $\text{BF}_3$ -diethyl ether containing 1.6 M benzene as electrolyte and polished stainless steel as the working electrode and at an applied potential of 1.7 V (vs Ag/AgCl). The film prepared under these conditions was shiny and very flexible. It can be easily cut into any shape with conventional mechanical methods. The as-grown film had high tensile strength and modulus, its tensile strength was greater than that of some widely used engineering plastics such as polypropylene and poly(vinyl acetate). In addition, the film had a high thermal stability.

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REFERENCES

1. Kovacic, P. and Kyriakis, A., *J. Am. Chem. Soc.*, 1963, **85**, 454.
2. Speight, J. G., Kovacic, P. and Koch, F. W., *J. Macromol. Sci.*, 1971, **C5**, 295.
3. Shepard, A. F. and Dannels, B. F., *J. Polym. Sci., Polym. Chem. Ed.*, 1966, **4**, 511.
4. Osa, T., Yildiz, A. and Kuwana, T., *J. Am. Chem. Soc.*, 1969, **91**, 3994.
5. Rubinstein, I., *J. Electrochem. Soc.*, 1983, **130**, 1506.
6. Brilmyer, G. and Jasinski, R., *J. Electrochem. Soc.*, 1982, **129**, 1950.
7. Kaeriyama, K., Sato, M., Someno, K. and Tanaka, S., *J. Chem. Soc., Chem. Commun.*, 1984, 1199.
8. Goldenberg, L. M., Aeiyaich, S. and Lacaze, P. C., *J. Electroanal. Chem.*, 1992, **335**, 151.
9. Soubiran, P., Aeiyaich, S., Aaron, J. J., Delamar, M. and Lacaze, P. C., *J. Electroanal. Chem.*, 1988, **251**, 89.
10. Ye, J. H., Chen, Y. Z. and Tian, Z. W., *J. Electroanal. Chem.*, 1987, **229**, 215.
11. Crecelius, G., Stamm, M., Fink, J. and Ritsko, J., *J. Phys. Rev. Lett.*, 1983, **50**, 1498.
12. Shacklette, L. W., Elsenbaumer, R. L., Chance, R. R., Sowa, J. M., Ivory, D. M., Miller, G. G. and Baughman, R. H., *J. Chem. Soc., Chem. Commun.*, 1982, 381.
13. Sato, M., Tabata, M., Kaneto, K. and Yoshino, K., *J. Electroanal. Chem.*, 1985, **195**, 203.
14. Hsing, C. F., Khoury, I., Bezcar, M. D. and Kovacic, P., *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 3313.
15. Rao, C. N. R., *Chemical Applications of Infrared Spectroscopy*. Academic Press, New York, 1963, p. 164.
16. Brown, C. E., Jones, M. B. and Kovacic, P., *J. Polym. Sci., Polym. Lett.*, 1980, **18**, 653.
17. Jones, M. B., Kovacic, P. and Lanska, D., *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**, 89.
18. Toshima, N., Kanada, K., Koshirai, A. and Hirai, H., *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2551.
19. Brandup, J. and Immergut, E. H. (ed.), *Polymer Handbook*. John Wiley & Sons, New York, 1975, pp. V-23, V-51.