

A Conducting Polymer Film Stronger Than Aluminum

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Polythiophene (Pth) was electrochemically deposited onto stainless steel substrate from freshly distilled boron fluoride–ethyl ether containing 10 millimoles of thiophene per liter. The free-standing Pth film obtained at an applied potential of 1.3 volts (versus Ag/AgCl) had a conductivity of 48.7 siemens per centimeter. Its tensile strength (1200 to 1300 kilograms per square centimeter) was greater than that of aluminium (1000 to 1100 kilograms per square centimeter). This Pth film behaves like a metal sheet and can be easily cut into various structures with a knife or a pair of scissors.

Extensive work has been devoted to the synthesis of heteroaromatic conducting polymers, such as Pth (1–3), polypyrrole (4, 5), and polyaniline (6). The high electrical conductivity of these materials provides potential applications in fabricating many kinds of microelectrical devices (7–12). However, most electrically conductive polymers are brittle and have low mechanical strengths (13). Furthermore, these materials are insoluble and intractable or decompose before melting. Therefore, conventional polymer-processing techniques cannot be used in shaping these materials into a desired structure (14). Here, we describe a method for making high-quality Pth films. These films have great mechanical strengths and flexibility and can be easily cut by conventional mechanical methods into a variety of structures, such as fibers, circles, squares, and triangles.

Conductive Pth synthesis and electrochemical examinations were performed in a one-compartment cell with the use of an EG&G potentiostat model 273 under computer control (Princeton Applied Research). The working and counter electrodes were AISI 304 stainless steel (15) sheets (5 cm by 7 cm) placed 0.5 cm apart. The anodic potentials were measured versus an Ag/AgCl electrode. To provide a more general reference, we examined ferrocene-ferrocenium redox couple in freshly distilled boron fluoride–ethyl ether (BFEE), and its half-wave potential [$1/2(E_{p,a} + E_{p,c})$, where a = anodic and c = cathodic] was found at 0.331 V (versus Ag/AgCl). Thus, a correction of 0.069 V ($-0.331 + 0.400$ V) was needed to bring the measured potentials in BFEE originally versus Ag/AgCl to potentials versus the standard hydrogen electrode (16). The electrolyte solution was freshly distilled BFEE containing 10 mM thiophene. All solutions were deaerated by a dry argon stream and maintained at a light overpressure dur-

ing the experiments. The integrated charge passed during film growth was used to control the thickness of the deposited films (0.010 ± 0.002 mm). All of the films had been washed well with distilled ethyl ether and dried under vacuum at 80°C for 24 hours before our characterizations.

Cyclic voltammograms (CVs) of thiophene in BFEE are shown in Fig. 1A. The potential scans shown led to the formation of a film on the electrode surface (blue to black as the deposit thickened). The strong oxidation present at potentials greater than 1.0 V promoted polymer generation on the electrode. The polymer was reduced and oxidized between -0.4 and $+1.0$ V. The increases of the redox wave currents of the polymer implied that the amount of the polymer on the electrode increased. The CV of freshly distilled BFEE showed no current waves in the same potential scale (Fig. 1B), which demonstrated that the electrolyte and the electrode were electrochemically inert during film growth.

The surface-reflection infrared spectrum of the film obtained at 1.3 V (Fig. 2) showed aromatic ring stretching bands at 1541, 1430, and 1340 cm^{-1} . The C–C vibration and C–H deformation bands were

found at 1110 and 1040 cm^{-1} , respectively. The C–S stretching vibration band appeared at 642 cm^{-1} . Elemental analysis showed that the C:H atom ratio of this polymer was 4:1.83. These results confirmed that the polymer deposited on the electrode was disubstituted Pth with weak cross-linking. The doped polymer contained 56.56% carbon, and the Pth content in the film was calculated to be 96.15%; thus, its dopant content is 3.85%. We measured the current efficiency (that is, the current consumed by the growth of Pth relative to the total current passed in the cell) by weighting the polymer deposited on the electrode, according to Eq. 1

$$[(nFf_p w_p/M)/Q] \times 100\% \quad (1)$$

where F is the Faraday constant (96,500 C mol^{-1}), Q is the integrated charge passed in the cell during film growth (in coulombs), w_p is the net weight of doped polymer film (in grams), f_p is the Pth content of the film (which was determined by elemental analysis), n is the number of the electrons transferred per monomer attached to the polymer (according to the C:H atom ratio of the polymer described above, n is 2.17 for this case), and M is the molar mass of thiophene (in grams per mole). Thus, the current efficiency of the electrochemical polymerization of thiophene in freshly distilled BFEE is $\sim 94.2\%$.

The Pth film obtained at 1.3 V was very shiny and metallic. The two side surfaces of the film were very smooth and compact, as confirmed by its scanning electron microscopy images. The conductivity of this film, measured by the conventional four-electrode technique, was 48.7 S cm^{-1} . The tensile strength of this film was measured to be 1250 ± 50 kg cm^{-2} [with the use of an electronic stretching machine (WD-1, Changchun) at a stretching rate of 5 cm min^{-1}], and its elongation at the break was about $4.3 \pm 0.5\%$. An aluminum sheet (99.99 weight %) with a thickness of 0.010 mm was also tested under the same conditions for comparison, and its tensile

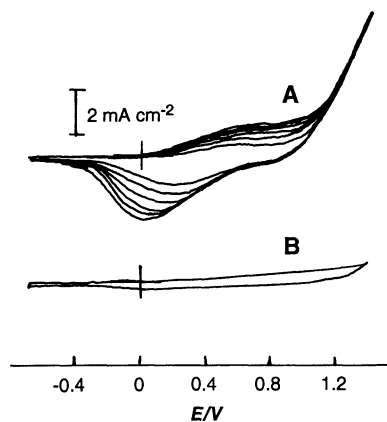


Fig. 1. Cyclic voltammograms of freshly distilled BFEE containing 10 mM thiophene (A) or pure BFEE (B) on stainless steel and a potential scan rate of 0.2 V s^{-1} .

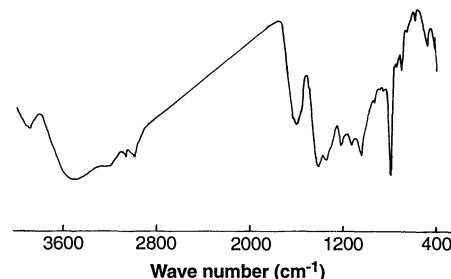


Fig. 2. Surface-reflection infrared spectrum of a free-standing Pth film (0.010 ± 0.002 mm in thickness) prepared at 1.3 V with the use of stainless steel as the substrate and freshly distilled BFEE and 10 mM thiophene as the electrolyte.

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strength was measured to be $1000 \pm 50 \text{ kg cm}^{-2}$. This value is lower than that for the Pth film, although the elongations at the break of these two materials are nearly the same. The stress-strain curve of the Pth film did not show a yield point like an aluminum sheet would. The real modulus of this Pth film at room temperature was $8.4 \times 10^{10} \text{ dyne cm}^{-2}$, and the loss modulus was $4.3 \times 10^9 \text{ dyne cm}^{-2}$ (measured by a dynamic viscoelastometer Rheovibron DDVII-EA at a frequency of 3.5 Hz). These two moduli showed only a little drop when the test temperature increased from 25°C to 250°C (Fig. 3). This polymer film has good flexibility and can be cut like a metal sheet with a knife or a pair of scissors into a variety of structures (Fig. 4).

The quality of the conductive polymer film prepared by electrochemical methods depends strongly on various experimental parameters, such as the properties of the substrate (17), the solvent (3), the applied potential (18), and the concentration of the monomer (19, 20). We will discuss each of these factors here. The possibility of electrochemical deposition of Pth onto different substrates depends largely on the width of the "electrochemical window" that these materials exhibit in different electrolytes (18). Pth has been successfully grown on platinum from relatively concentrated solutions of thiophene in acetonitrile (21) or in liquid SO_2 containing a supporting electrolyte (22). The competing electrochemical reactions in which the electrode itself, the electrolyte, or both undergo electrochemical deposition can be the major limitation in electrochemical deposition of Pth on

substrates other than platinum in the same media. In freshly distilled BFEE, the oxidation potential of the thiophene monomer is $\sim 1.0 \text{ V}$ (versus Ag/AgCl), as shown in Fig. 1A. This value is much lower than that of thiophene in other systems ($>1.65 \text{ V}$, versus $0.01 \text{ M Ag}^+/\text{Ag}$) (1–3, 22).

Therefore, Pth can be deposited onto various metallic substrates, such as Pt, Al, Zn, *p*-Si, *n*-Si, and stainless steel from this electrolyte. Experimental results showed that the Pth deposited on platinum (99.99 weight %) adhered firmly to the electrode and could be detached only with great difficulty (23, 24). The free-standing film stripped from the platinum electrode had many defects, and they greatly decreased the film strength. In fact, the tensile strength of the Pth film deposited onto platinum at 1.3 V was measured to be only $280 \pm 50 \text{ kg cm}^{-2}$. The Pth films have weak interactions at the surfaces of Al (99.99 weight %), Zn (99.99 weight %), stainless steel (AISI 304), and boron-doped $\langle 111 \rangle$ *p*-type monocrystalline silicon ($3.44 \text{ ohm} \cdot \text{cm}$). They can be easily peeled off these electrodes by hand. However, the electrochemical stability of the less noble metals (including Zn, Al, and Si) in BFEE was much lower than that of stainless steel. The dissolution of the electrodes led to the formation of Pth films with many pores. Actually, the tensile strengths of the Pth films obtained from these three substrates (Al, Zn, and Si) were never greater than 800 kg cm^{-2} . Stainless steel is the best electrode we tested for preparing high-strength Pth film.

High applied potentials support the degradation of the polymer and the side reactions of the electrolytes and electrodes (20). These factors resulted in lowering the conductivity and strength of conductive polymer films. The potentials used for electrolysis of thiophene in acetonitrile or liquid SO_2 were very high, and no high-quality Pth films were obtained in those systems. The low oxidation potential of thiophene

in BFEE favored the formation of films with high quality. Although Pth can be deposited onto stainless steel at a potential as low as 0.8 V, this low applied potential led to a polymerization rate of thiophene that was too low to compete the side reactions. The film obtained at 0.8 V was very poor and could not even be stripped from the electrode to a free-standing state. These results are consistent with those reported by Gratzl and co-workers (18). As a result, in BFEE 1.3 V is the most suitable applied potential for making high-quality Pth films.

Freshly distilled BFEE is very stable at potentials between -1.0 and 2.5 V , and the side reactions of this electrolyte during electrochemical polymerization can be neglected. On the other hand, the strong electrophilic property of this Lewis acid strongly catalyzed the deprotonation of thiophene on the electrode, which resulted in a very low oxidation potential of this monomer. The addition of a small amount of water into the electrolyte can improve the conductivity of this medium; however, it also increases the degradation of polymer and other side reactions. Experimental results demonstrated that when BFEE containing 2 mM water was used instead of freshly distilled BFEE, the current efficiency of the electrolysis process was decreased from 94.2% to $\sim 76\%$. The conductivity and tensile strength of the Pth film prepared at 1.3 V were also decreased from 48.7 S cm^{-1} and 1250 kg cm^{-2} to 6.0 S cm^{-1} and 440 kg cm^{-2} , respectively.

Electrochemical polymerization of aromatic monomers follows an anion radical mechanism (25). The increase in monomer concentration of the electrolyte will increase the probability of chain transfer between the monomer and the growing polymeric species. These reactions will shorten the polymer chain length of the film. In addition, the high polymer deposition rate in concentrated monomer electrolytes favors the formation of rougher and irregular Pth films with more defects. In other media

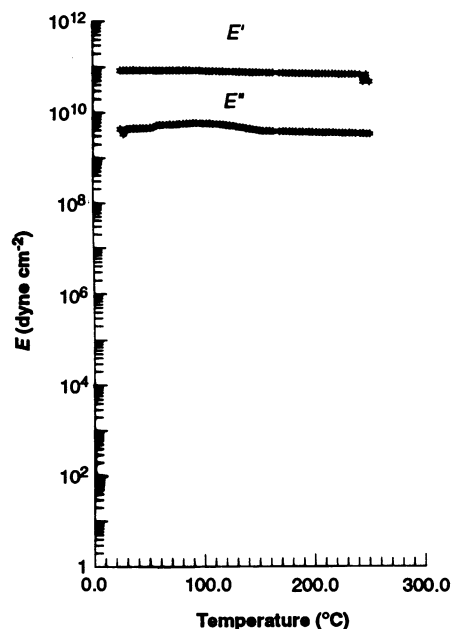


Fig. 3. Dynamic mechanical test diagrams of a Pth film (same as in Fig. 2) peeled off stainless steel.

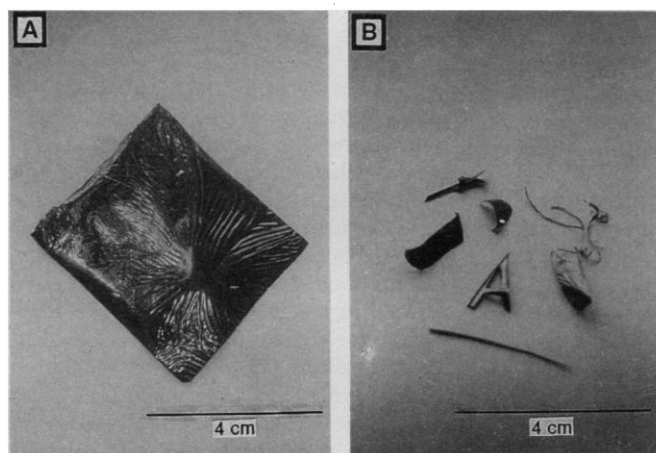


Fig. 4. A free-standing Pth film (same as in Fig. 2) peeled off stainless steel (A) and shaped into various shapes with a knife (B).

such as acetonitrile, Pth can be successfully deposited on platinum only from a relatively concentrated monomer solution. On the contrary, in freshly distilled BFEE, the monomer concentration may be as low as 2 mM. Indeed, high-quality Pth films were obtained only by ensuring that the monomer concentration was lower than 10 mM. The Pth film with the highest quality was obtainable only with the use of freshly distilled BFEE (with a monomer concentration lower than 10 mM) as the electrolyte and stainless steel as the substrate and at an applied potential of 1.3 V (versus Ag/AgCl). The film prepared at this condition was shiny and metal-like, and its strength was greater than that of aluminum and it could be cut into a variety of structures with mechanical methods.

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26. This work was supported by the research foundation of the national key laboratory of coordination chemistry of Nanjing University.

15 August 1994; accepted 23 November 1994

Simultaneous Studies of Reaction Kinetics and Structure Development in Polymer Processing

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The simultaneous time-resolved study of structure development and reaction kinetics during polymer processing is an experimental method that has great potential in developing a deeper understanding of the parameters that govern the formation of structure and therefore polymer properties. A combination of synchrotron radiation small-angle x-ray scattering and Fourier-transform infrared spectroscopy experiments have been performed on a series of model segmented block copolyurethanes. These studies confirm that the driving force for structure development in polyurethanes is the thermodynamics of phase separation rather than hydrogen bonding.

One significant advantage of using synchrotron radiation small-angle x-ray scattering (SAXS) beam lines for polymer processing studies is that the high x-ray intensity allows time-resolved x-ray scattering experiments on polymers to be performed with a resolution comparable to the time scales used in the processing of such polymers. This provides a useful insight into the morphological changes that take place in the materials during processing.

When time-resolved SAXS experiments are done simultaneously with additional experimental techniques, a wealth of informa-

tion can be derived from a single sample, and the artifacts introduced by the combination of two independent experiments are avoided (that is, temperature- or thermal-history differences and inaccuracies in the time correlations between the experiments). Successful experiments using the concept of combined techniques have been reported in recent years. The SAXS technique, wide-angle x-ray scattering, and differential scanning calorimetry have all been combined in a single experiment (1, 2), and so has light scattering and SAXS (3).

For the reactive processing of polymers

(that is, all thermosetting materials), understanding of the development of structure and properties during polymerization requires a transformation of data from the (experimental) time domain into the (molecular) conversion domain because many processes involve a chemical quench from the one-phase region to the two-phase region of a ternary phase diagram. In the conversion domain, the evolution of structure may be related to the increase of molecular weight, which locates a material in a phase diagram independently of reaction kinetics.

Fourier-transform infrared spectroscopy (FTIR) is a widely used tool in the characterization of polymers (4), especially for following the reaction kinetics and phase-separation dynamics during reaction-induced phase transformations (5). The FTIR technique has proven most successful in the special case of segmented urethane block copolymers, where the soft and hard block sequences can undergo microphase separation and subsequent hydrogen bonding. The technique is used to determine the chemical reaction kinetics from the decrease in the isocyanate absorbance and to find the hydrogen bonding dynamics from the subtleties of the carbonyl absorbances (6–9). In most reports (6–9), determination of hydrogen bonding has been associated with the onset of phase separation. Independent SAXS studies attempting to reproduce the FTIR conditions (10) indicate that microphase separation determined directly by SAXS may precede hydrogen bonding. However, the difference in conversion between the phase separation and hydrogen bonding, as probed by the two independent techniques, is at the limit of the error between experiments, ~2%. Whether microphase separation precedes hydrogen bonding is of fundamental scientific and technological importance in the processing of polyurethane materials (the annual market is 10⁷ metric tons per year). The combination of time-resolved FTIR with x-ray scattering techniques is therefore an excellent tool for the study of these phase transitions, providing a correlation between reaction kinetics and structure development or other morphological changes.

We have developed equipment that al-

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