# Electrochemical Polymerization of Toluene in the Mixed Electrolytes of Boron Trifluoride Diethyl Etherate and Trifluoroacetic Acid

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**ABSTRACT:** Poly(methylphenylene) (PMeP) films were prepared by direct oxidation of toluene in the mixed electrolytes of boron trifluoride diethyl etherate (BFEE) and trifluoroacetic acid (TFA). The oxidation potential of toluene in pure BFEE was measured to be 1.52 V versus saturated calomel electrode (SCE). This value was much lower than that determined in a neutral medium such as acetonitrile (2.13 V versus SCE). The introduction of TFA into BFEE decreased the oxidation potential of toluene and also improved the properties of as-formed polymer films. Infrared and Raman spectra confirmed the formation of PMeP films. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 189–195, 2004

**Key words:** films; electrochemical polymerization; conducting polymers; trifluoroacetic acid; Raman spectroscopy

## INTRODUCTION

Extensive work has been devoted to the synthesis of poly(paraphenylene),[1–6] one of the simplest conjugated polymers with high stability in its neutral state. However, only a few works have investigated the synthesis of conducting polymers from the derivatives of benzene, except polyaniline and poly(*p*-phenylene vinylene). On the other hand, the fabrication of new conducting polymers is of interest because of the potential applications of these materials. Previous studies indicated that electrodonating-group substitution on the backbones of conducting polymers could enhance the stability of radical cations or dications, thus improving the environmental stability of conducting polymers in doped states.[7–10] For example, conducting poly(3-methylthiophene) films have higher stability than that of conducting polythiophene films.[11] Therefore, a conducting polymer produced from toluene, one of the most important benzene derivatives, is expected to have better environmental stability than that of poly(*para*-phenylene). The anodic oxidation of concentrated solutions (0.5 mol/L) of toluene in anhydrous acetonitrile containing $Bu_4NBF_4$ (0.15 mol/L) led to the formation of a conductive PMeP film on the surface of a platinum electrode.[12] However, little study has been done on the electrochemistry and spectroscopic characterization of the as-formed polymers. Furthermore, the oxidation potential of toluene in acetonitrile was so high that side reactions may occur during the polymerization.

It is well known that freestanding polythiophene[13–17] and poly(paraphenylene) (PPP) films[4–6] with good mechanical properties can be prepared by direct anodic oxidation of the corresponding monomers in boron trifluoride diethyl etherate (BFEE) and their oxidation potential can be greatly reduced. The addition of a strong acid to BFEE, such as concentrated sulfuric acid (SA) or trifluoroacetic acid (TFA),[4–6,16,17] can further decrease the oxidation potentials of benzene or thiophenes and improve the quality of as-prepared polymer films. In this article, we report the direct electrochemical oxidative polymerization of toluene in the mixed electrolytes of BFEE and TFA.

## EXPERIMENTAL

### Materials

Toluene (analytical grade), purchased from Beijing Chemical Plant (Beijing, China), and boron trifluoride diethyl etherate (BFEE), a product of Beijing Changyang Chemical Plant (Beijing, China), were further purified by distillation. Chemically pure grade trifluoroacetic acid (TFA), a product of Beijing Hongyu Chemical and Engineering Co. (China), and commercial HPLC grade acetonitrile, a product of Tianjin Siyou Biomedical and Technological Co. (Tianjing, China), were used as received. Tetrabutylammonium tetraflu-

orobrate (TBATFB, 98%; Fluka, Buchs, Switzerland) was dried in vacuum at 60°C for 24 h before use.

## Film preparation

The electrochemical polymerization and examinations were performed in a one-compartment cell by the use of a potentiostat–galvanostat (Model 283, EG&G Princeton Applied Research, division of AMETEK, Paoli, PA) under computer control. For electrochemical examinations, Pt wires (with surface areas of 0.4 and 0.6 cm$^2$) were used as the working and counterelectrodes, respectively. In the case of film synthesis, the working electrode was a platinum plate (5 × 5 mm) and the counterelectrode was a stainless steel sheet (AISI 304, 18 × 10 mm) placed 10 mm apart, which before each polymerization, were carefully polished with abrasive paper (1200 mesh), cleaned with water and acetone successively, then dried by a blower. All potentials were referred to a saturated calomel electrode (SCE). The typical electrolytic solutions were BFEE mixed with 0–30% (by volume) TFA. All solutions were deaerated by bubbling dry N$_2$ gas for 5 min before each experiment and a slight overpressure was maintained during the experiment.

The polymer films were grown potentiostatically. Their thickness was controlled by the total charges passed through the cell and the charge values were read directly from *I–t* curves by computer. After polymerization, the films were scraped from the electrode surfaces then washed repeatedly with acetone to remove the electrolyte and monomer. For electrochemical studies, polymer-coated Pt electrodes were rinsed with acetone and dried by a blower. The dedoping of polymer films was performed at a constant potential of 0 V versus SCE in BFEE until the current density was close to zero.

The doping levels (*f*) of as-grown polymer films were determined electrochemically by using the following equation[18,19]:

$$f = [2Q_o/(Q_d - Q_o)] \times 100\%$$

where $Q_d$ is the total charges used for polymer deposition and $Q_o$ is the total charges of the oxidized species in the polymer films.

## Characterizations

For infrared spectral studies, polymer films were dedoped with 25% ammonia for 3 days, then washed repeatedly with distilled water and acetone. Finally, they were dried under vacuum at 60°C for 24 h. The infrared (IR) spectra were recorded by using KBr pellets of the polymers on an Avatar 360 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). Raman spectra were recorded by using a microscopic confocal Raman spectrometer (RM 2000; Renishaw plc, Gloucestershire, UK) using a 633-nm laser beam and a charge-coupled detector (CCD) with 4 cm$^{-1}$ resolution. The spectra were recorded by using a 50× objective and the laser power was always kept very low (~ 0.1 mW) to avoid destruction of the samples. Scanning electron micrographs were taken under a KY2800 electron micrographer (Scientific Instrumental Plant of Chinese Academy of Sciences, Beijing, China).

## RESULTS AND DISCUSSION

### Electrochemical oxidative polymerization of toluene

Figure 1 shows the anodic polarization curves of toluene in the mixed electrolytes of BFEE and TFA. The oxidation onset of toluene was initiated at 1.52 V in pure BFEE [Fig. 1(a)], which was lower than that of benzene in BFEE (1.75 V versus SCE).[4–6] This is mainly explained by the substitution effect of the electro-donating methyl group, which can decrease the resonance energy of the benzene ring. However, the polymer prepared in this medium adhered to the electrode surface so weakly that most of it precipitated to the bottom of the cell or dispersed in the solution.

The addition of 5% TFA (by volume) into BFEE decreased the oxidation potential of the monomer to about 1.49 V [Fig. 1(b)]. With the increase of TFA volume content in the mixed electrolytes, the oxidation potential of the monomer can be decreased further to 1.39 V (Fig. 1). All these values are much lower than the oxidation potential of toluene in acetonitrile containing 0.1 mol L$^{-1}$ TBATFB (2.13 V versus SCE), as shown in the inset of Figure 1. According to Figure 1, at a given applied potential, the current density of the monomer oxidation increases with the increase of TFA content, indicating the increase of polymerization rates. These are mainly attributed to the strong acid forming a π-complex with the monomer, which reduced the resonance of the aromatic ring and also increased the stability of the radical cations.[6]

The successive cyclic voltammograms (CVs) of 1 mol L$^{-1}$ toluene in the mixed electrolytes on Pt electrode are illustrated in Figure 2. As can be seen from Figure 2(a), on the first CV cycle the current densities on the reverse scan were higher than those on the forward scan (in the potential region of 1.4–1.8 V). The formation of this loop can be explained as a characteristic of the nucleation process,[20] and appeared only on the first cycle. As the CV scan continues, the color of the solution close to the working electrode changed slightly from colorless to blue, indicating that part of the monomer was oxidized into oligomers and the oligomers were dissolved or dispersed into the electrolyte. Simultaneously, a polymer film was formed on the working electrode surface because of the strong
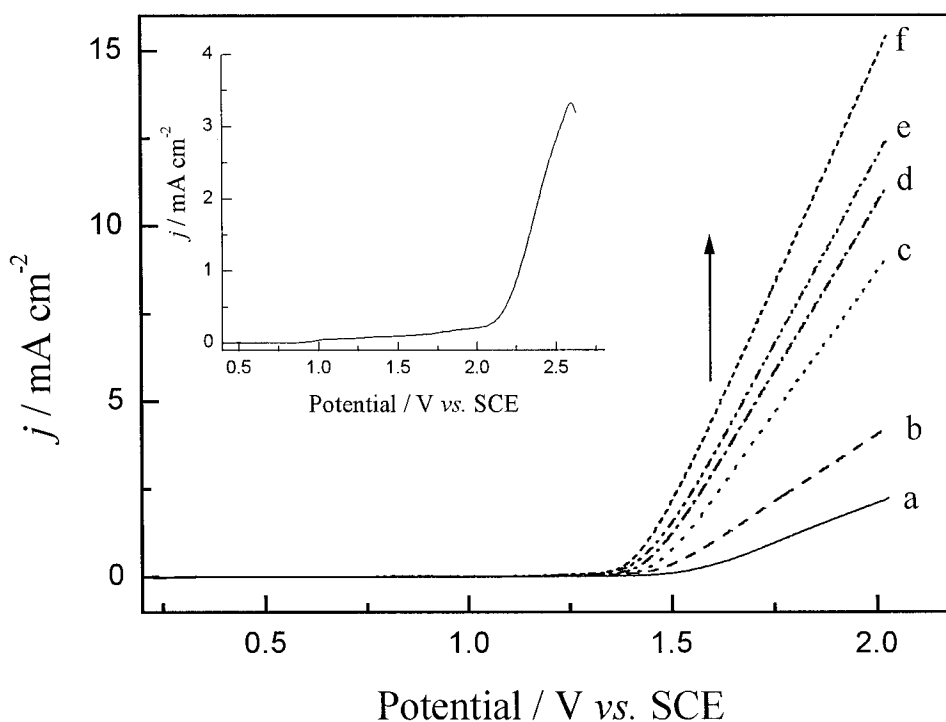
**Figure 1** Anodic polarization curves of 1 mol L$^{-1}$ toluene in the mixed electrolytes of BFEE containing TFA (in vol %): (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 30%; and in acetonitrile + 0.1 mol L$^{-1}$ TBATFB (inset). Potential scan rate: 20 mV s$^{-1}$.

oxidation presented at the potentials higher than 1.52 V (blue to black as the deposit thickened). The cyclic voltammogram shows a strong hysteresis between the positive and the negative scans as the CV proceeds. The polymer was reduced and oxidized in the potential scale of 0.64 and 1.21 V. The increase of the redox wave currents implied that the amount of the polymer on the electrode increased. The potential shift of the wave current maximum provides information about the increase the electrical resistance in the polymer film and the overpotential needed to overcome the resistance.[21]

BFEE exists in diethyl ether as a polar molecule, $[(C_2H_5)_3O^+]BF_4^-$, which furnishes a conducting medium.[22] However, the conductivity of freshly distilled BFEE is relative low ($\sim$ 380 $\mu$S cm$^{-1}$). This factor, together with the high oxidation potential of toluene, caused the deposition rate of polymer in pure BFEE to be fairly low. When a small amount of TFA (5%) was introduced into BFEE, the conductivity of the mixed electrolytes increased significantly ($\sim$ 3450 $\mu$S cm$^{-1}$).[16] Furthermore, the addition of TFA into BFEE may lead to the formation of $\pi$-complexes between the monomer and the strong acid.[23] These two factors result in decreasing the oxidation potential of toluene and increasing the polymerization rate. With the increase of TFA content in the mixed electrolytes, the solution conductivity increased gradually.[16] As a consequence of the wave current density increment of the

polymer film between the two neighboring CV cycles becoming increasingly larger (Fig. 2), the accompanying redox processes became increasingly reversible.

The typical chronoamperograms of the oxidation of toluene in pure BFEE and in mixed electrolyte of BFEE + 10% TFA are demonstrated in Figure 3(a) and (b), respectively. As can be seen from this figure, in pure BFEE, the current density of polymer growth decreased rapidly within 1200 s. After this time, the curve becomes almost stable at 0.8 mA cm$^{-2}$, although the applied potential was as high as 2.33 V. The doping level of as-formed polymer film was measured to be only about 3%. The current decreases are mainly attributed to the poor conductivity of the polymer films.

On the other hand, in BFEE + 10% TFA, the $I$–$t$ curve shows an increasing tendency after a slight decrease in the transitory period (400 s), indicating that the introduction of TFA into BFEE improved the conductivity of the polymer. In this case, the doping level of as-formed polymer film was determined to be about 11%, much higher than that of the films produced in pure BFEE.

### Electrochemistry of as-grown poly(methylphenylene) films

The electrochemical behavior of as-grown PMeP films deposited potentiostatically from the mixed electro-
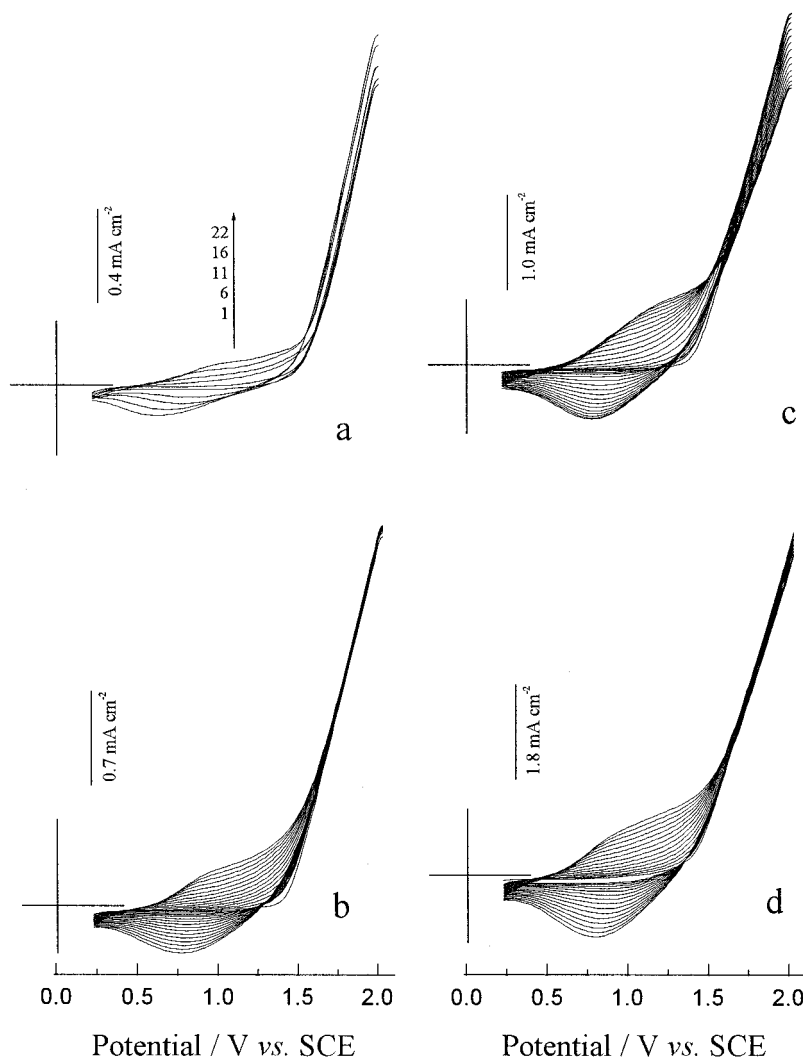
**Figure 2** Cyclic voltammograms of 1 mol dm$^{-3}$ toluene in (a) pure BFEE, or in mixed electrolytes of (b) BFEE + 5% TFA, (c) BFEE + 10%, or (d) BFEE + 20%. Potential scan rate: 20 mV s$^{-1}$.

lyte of BFEE + 30% TFA was studied in the same monomer-free electrolyte (Fig. 4). The CVs are characterized by two well-defined redox waves with current maxima, $I_{pa}$ and $I_{pc}$, proportional to the potential scan rate in the range of 50 to 250 mV s$^{-1}$ (Fig. 4, inset). The linear relation between scan rate and peak current indicates that a redox couple is fixed on the electrode.[24,25]

**Spectral studies**

Figure 5 illustrates the infrared spectrum of a PMeP film prepared from the medium of 1 mol L$^{-1}$ toluene in BFEE containing 30% TFA. The spectrum shows the C—H out-of-plane deformation bands at frequencies of 884 and 819 cm$^{-1}$, attributed to 1,2,4-trisubstituted benzene rings,[26] and confirmed the polymerization of toluene and that the polymer had a linear structure. The two peaks at about 1376 and 1450 cm$^{-1}$ can be

assigned to the symmetric and antisymmetric bending of methyl C—H bonds, respectively. The strong and sharp peak at 1603 cm$^{-1}$ is related to the C=C bonds of benzene rings. Furthermore, a broad shoulder peak centered at 1693 cm$^{-1}$ was also found. This is possibly attributable to overoxidation of the polymers in the mixed electrolytes, resulting in the formation of carboxyl groups on the polymer chains.

Raman spectroscopy has been tested to be an effective approach for the characterization of conducting polymers, especially in doped and dedoped states.[9,10,27–30] Figure 6 shows the Raman spectrum of PMeP film prepared from BFEE containing 30% TFA and 1 mol L$^{-1}$ toluene potentiostatically at 1.73 V (versus SCE). It is clear from this figure that the Raman features of PMeP are similar to those of the Raman spectrum of poly(paraphenylene).[28] The band at about 1595 cm$^{-1}$ can be assigned to aromatic benzene ring stretching vibration.[28] The 1323 cm$^{-1}$ band
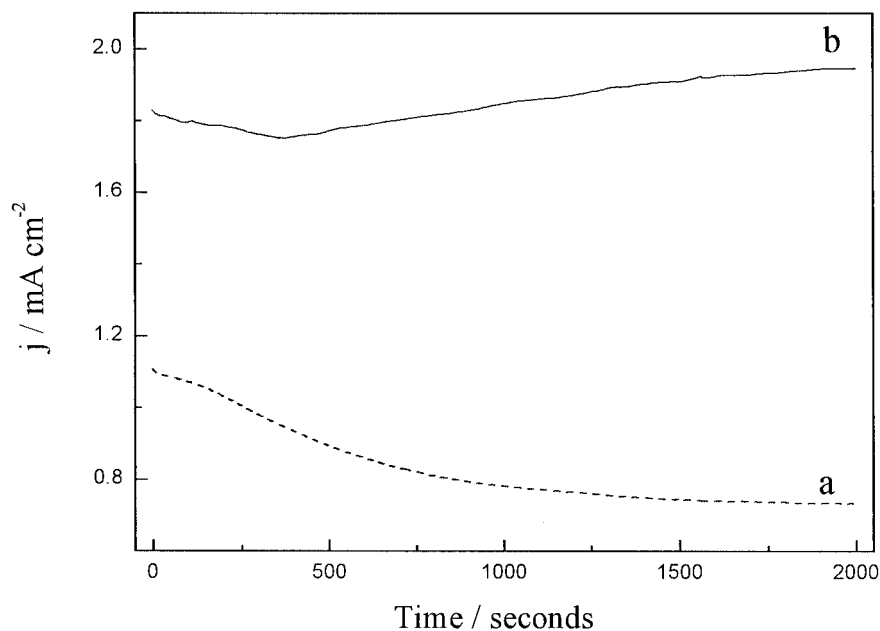
**Figure 3** Chronoamperograms for the oxidation of 1 mol L$^{-1}$ toluene in (a) pure BFEE and in (b) mixed electrolyte of BFEE + 10% TFA at constant applied potentials of 2.33 and 1.83 V versus SCE, respectively.

can be attributed to in-phase inter-ring C—C stretching of polarons of the polymer. All the spectral results described above confirmed the formation of poly(m-ethylphenylene) from toluene.

**CONCLUSIONS**

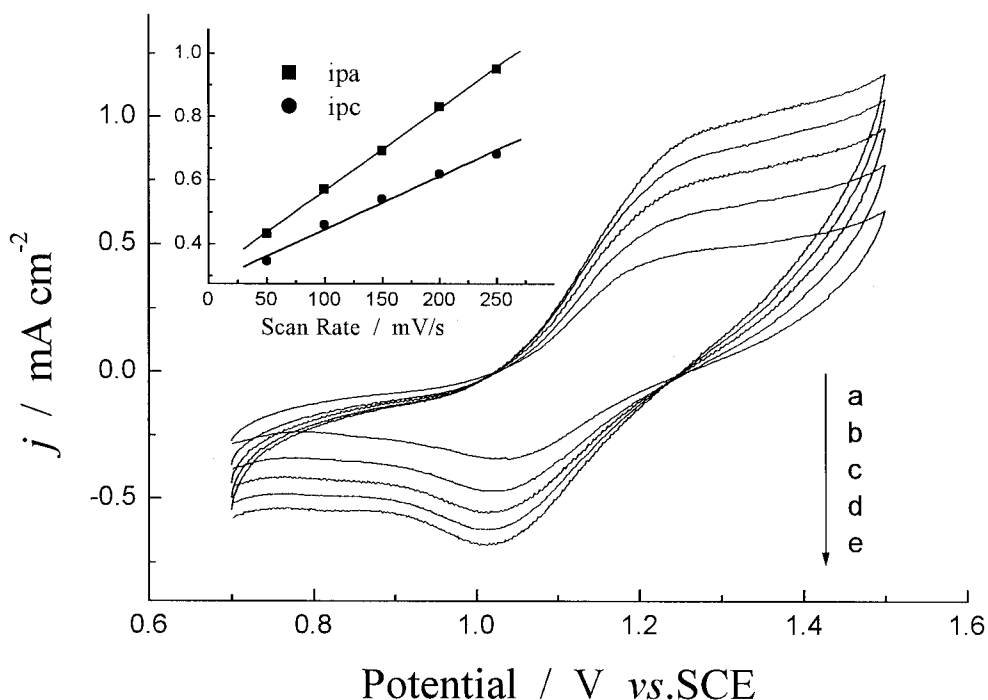Toluene can be electrochemically polymerized in the mixed electrolytes of BFEE and TFA and substrate-



**Figure 4** Cyclic voltammograms of a PMeP film in mixed electrolyte of BFEE + 30% TFA at potential scan rates (in mV s$^{-1}$) of: (a) 50, (b) 100, (c) 150, (d) 200, and (e) 250. The PMeP film was electrochemically grown in BFEE at a constant applied potential of 1.73 V versus SCE for 114 mC cm$^{-2}$.
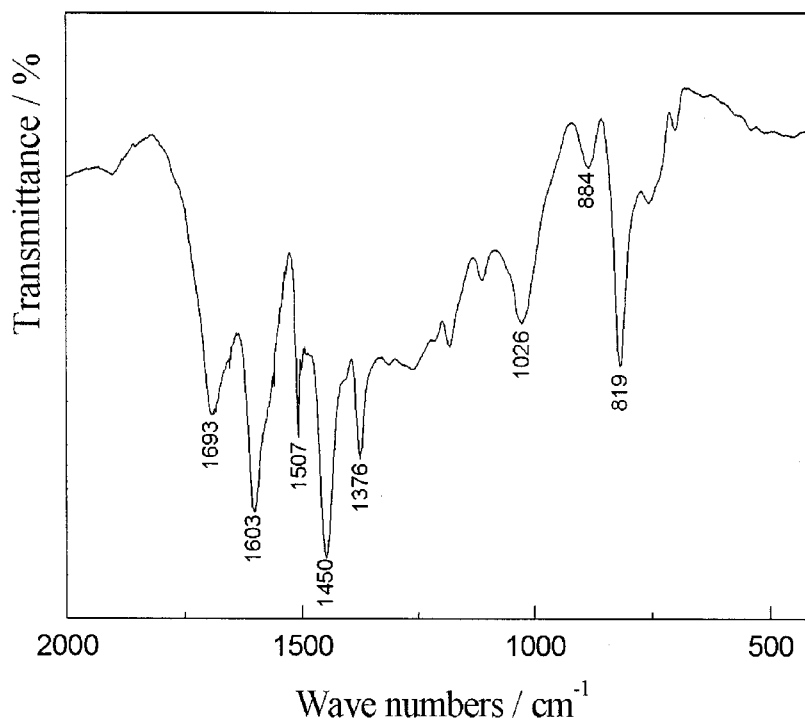
**Figure 5** FTIR spectra of a PMeP film prepared by using BFEE + 30% TFA as mixed electrolyte at a constant applied potential of 1.73 V versus SCE after treatment with 25% aqueous ammonia for 3 days.

supported poly(methylbenezene) films were obtained. The oxidation potential of the monomer in pure BFEE was found to be as low as 1.52 V versus SCE. The addition of TFA into pure BFEE not only decreased the oxidation potential of the monomer but also enhanced the adhesive properties of as-formed polymer
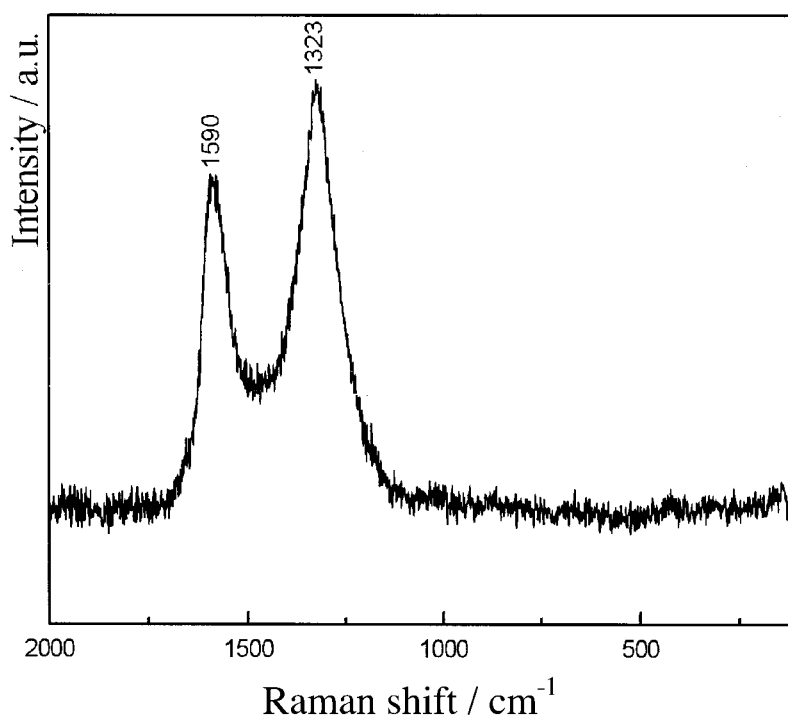


**Figure 6** Excited Raman spectrum (633 nm) of a PMeP film prepared electrochemically in mixed electrolyte of BFEE + 30% TFA at constant applied potential of 1.73 V versus SCE.

films on a platinum electrode. As-formed PMeP films showed electroactivity and spectral studies confirmed the formation of PMeP films with linear chain structures.

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