

Electrochemical Polymerization of β -Naphthalene Sulfonic Acid

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ABSTRACT: β -Naphthalene sulfonic acid (β -NSA) has been electrochemically polymerized in a mixed electrolyte of boron trifluoride diethyl etherate (BFEE) solution mixed with a certain amount of trifluoroacetic acid (TFA) or concentrated sulfuric acid (SA). The poly(β -naphthalene sulfonic acid) (PNSA) film prepared from the medium of BFEE+TFA was partly soluble in methanol. On the other hand, the polymer obtained from the system of BFEE+SA was soluble in water and general polar organic solvents such

as methanol, alcohol, and acetone. The structure of PNSA was examined by infrared and UV spectra. Fluorescent spectral studies indicate that the polymer is a blue light emitter with fluorescence quantum efficiency of $\sim 4\%$. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1939–1944, 2004

Key words: electrochemistry; polymerization; structure; fluorescence

INTRODUCTION

Extensive work has been devoted to electrochemical synthesis of aromatic conductive polymers such as polypyrrole, polythiophene, and poly(*p*-phenylene) (PPP), etc.^{1–5} However, only a few publications concerned the electrochemical polymerization of naphthalene and its derivatives.^{6–8} On the other hand, it is known that free-standing polythiophene and PPP films with high qualities can be prepared by direct anodic oxidation of the corresponding monomers in boron trifluoride diethyl etherate (BFEE) and the oxidation potentials of the monomers can be greatly lowered.^{9,10} The addition of a strong acid, such as trifluoroacetic acid (TFA) or sulfuric acid (SA), to BFEE can further decrease the oxidation potential of benzene and improve the quality of PPP film.^{11,12} In this article, we report the direct electrochemical oxidative polymerization of β -naphthalene sulfonic acid in the mixed electrolytes of BFEE and TFA or SA. A new soluble conducting polymer with strong fluorescence in the blue light region was obtained.

EXPERIMENTAL

Materials

BFEE (Changyang Chem. Plant, Beijing) was purified by distillation. β -Naphthalene sulfonic acid (β -NSA;

Tongxia Yucai Fine Chemicals Plant, Beijing) was recrystallized from 1.0 mol L^{-1} aqueous HCl solution before use. TFA ($>98\%$) and SA ($>98\%$) were purchased from Beijing Jinlong Chemical Regent Co. and used as received. Commercial acetonitrile with purity higher than 99.9% was a product of Tianjing Siyou Biological and Medical Technology Co. (Tianjing, China). Tetrabutyl ammonium tetrafluoroborate (TBATBF, 98%) was a product of Fluka (Buchs, Switzerland) and was dried at 60°C for 24 h before use.

Electrosyntheses and polymer characterizations

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a Model 283 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. The working and counterelectrodes were two platinum sheets with surface area of 1.0 cm^2 each and were placed 1.0 cm apart. All the potentials were measured versus a saturated calomel electrode (SCE).

The typical electrolytic solution was pure BFEE or a mixture of BFEE and TFA or SA (volume percentage of acid was 0–80%) and contained 0.2 mol L^{-1} β -NSA. All solutions were deaerated by a dry nitrogen stream and maintained at a slight nitrogen overpressure during the experiments. Poly(β -naphthalene sulfonic acid) (PNSA) films were grown potentiostatically at 1.75 V (versus SCE) in BFEE+TFA or at 1.05 V (versus SCE) in BFEE+SA.

FT infrared spectra were taken by using a GX FT-infrared spectrometer (Perkin-Elmer) with KBr pellets. UV spectra were performed by using a UV-2100S

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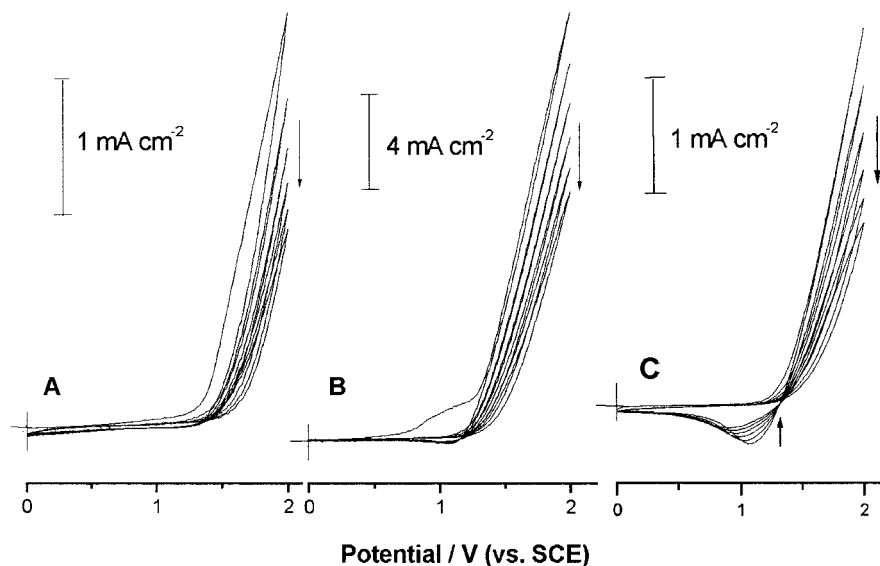


Figure 1 Successive voltammograms of 0.2 mol L^{-1} β -NSA in pure BFEE (A) and in the mixed electrolytes of BFEE+TFA with volume ratio of 1 : 1 (B) and 1 : 2 (C) at a potential scan rate of 50 mV s^{-1} .

UV-visible spectrometer (Shimadzu). Fluorescent spectrum was carried out by using a Perkin-Elmer LS 50B luminescence spectrometer. Fluorescence quantum efficiency of the polymer was measured by using a FS 850 (Hitachi) fluorescence spectrometer via a published procedure.¹³ The conductivity of as-formed PNSA was measured by a conventional four-probe technique. Scanning electron micrographs were taken by using a KY2800 electron micrograph (Scientific Instrumental Plant of Chinese Academy of Sciences).

RESULTS AND DISCUSSION

Electrochemical polymerization

Figure 1 shows the successive cyclic voltammograms (CVs) of 0.2 mol L^{-1} β -NSA in pure BFEE and in the media of BFEE mixed with TFA. The oxidation potential of the monomer in pure BFEE was found at about 1.5 V and the current density of the anodic current wall decreases quickly with the increase of CV scanning number. This is mainly due to a thin polymer film coated on the electrode surface and its conductivity is much lower than that of the platinum electrode. No apparent redox waves of the polymer was found, indicating only a trace amount of the polymer was formed. The main features of the CVs of β -NSA in BFEE+TFA (2 : 1, by volume; not shown here) was similar to those of Figure 1(A). However, a reduction wave of the polymer was found at around 1.0 V. Indeed, a dark film was observed on the surface of working electrode. The CV of β -NSA in BFEE containing 50% [by volume, Fig. 1(B)] TFA showed an oxidation wave of the polymer at around 1.0 V on the first cycle; however, it disappeared on the successive cy-

cles, indicating that the polymer can not be synthesized in this medium in a large amount. BFEE containing 67% TFA was tested to be the best medium for polymer growth [Fig. 1(C)]. While the oxidation potential of the monomer in the medium of BFEE + 67% was measured to be as low as 1.0 V, the polymerization rate is fairly low. To obtain a sufficient amount of polymer for characterization, the monomer was electrolyzed potentiostatically at 1.75 V. As-formed PNSA obtained at 1.75 V was a flat film with weak strength. It cracked easily during the drying process as shown in the scanning electron micrograph of Figure 2. The film was in the doped state and dark blue in color. However, it quickly changed into golden yellow in air. The polymer was insoluble in strong polar solvents such as water and dimethyl sulfoxide, and also insoluble in weak polar or nonpolar solvents such as acetone, tetrahydrofuran, and benzene. However, it can be partly ($\sim 70\%$, by weight) dissolved in methanol or ethanol. A flat and compact semitransparent golden yellow film could be obtained by casting the methanol solution of the soluble part of the polymer. The conductivity of the film was measured to be 0.95 S cm^{-1} . However, it decreased quickly in air and measured only $1.1 \times 10^{-2} \text{ S cm}^{-1}$ after 5 days. It should be noted here that β -NSA cannot be electrochemically polymerized in the convenient neutral solvents such as acetonitrile, mainly due to the low solubility of the monomer.

The electrochemical behavior of β -NSA in BFEE+SA is similar to that in BFEE+TFA. However, at a given applied potential, the polymerization rate in the former medium was much higher than that in the latter system. As a result, the polymer sample can be prepared at a low potential of 1.05 V. The as-grown

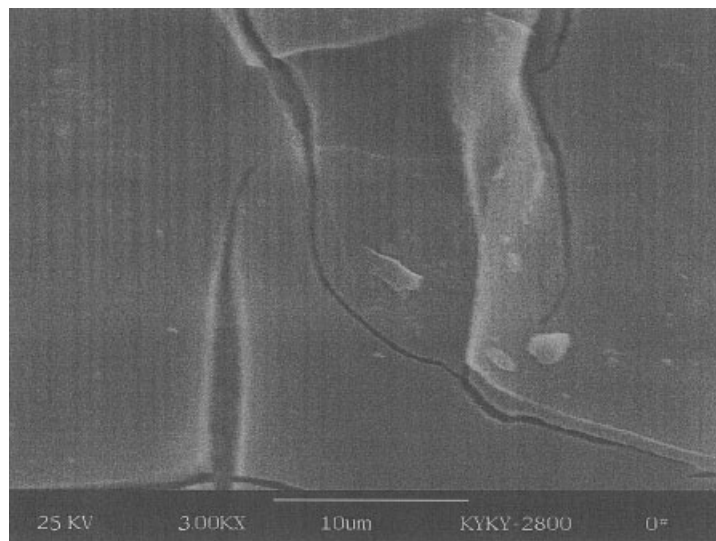


Figure 2 Scanning electron micrograph of a PNSA film coated on the electrode surface.

PNSA film was completely soluble in water and the usual polar organic solvents such as methanol and acetone. This is mainly because of the finding that a low applied potential resulted in the formation of the polymer with low molar mass.

Electrochemistry of PNSA film

The electroactivity of PNSA film was tested in a concentrated H_2SO_4 solution after rapid washing with

diethyl ether. Figure 3 shows the CV of PNSA deposited electrochemically from the medium of BFEE+50% SA, and in concentrated SA. The steady-state CV presents broad anodic and cathodic peaks. The currents are proportional to the scan rate (Fig. 3, inset), indicating a redox couple attached to the electrode.¹ Furthermore, these films can be cycled repeatedly between the conducting (oxidized) and insulating (neutral) state with no significant decomposition of the materials.

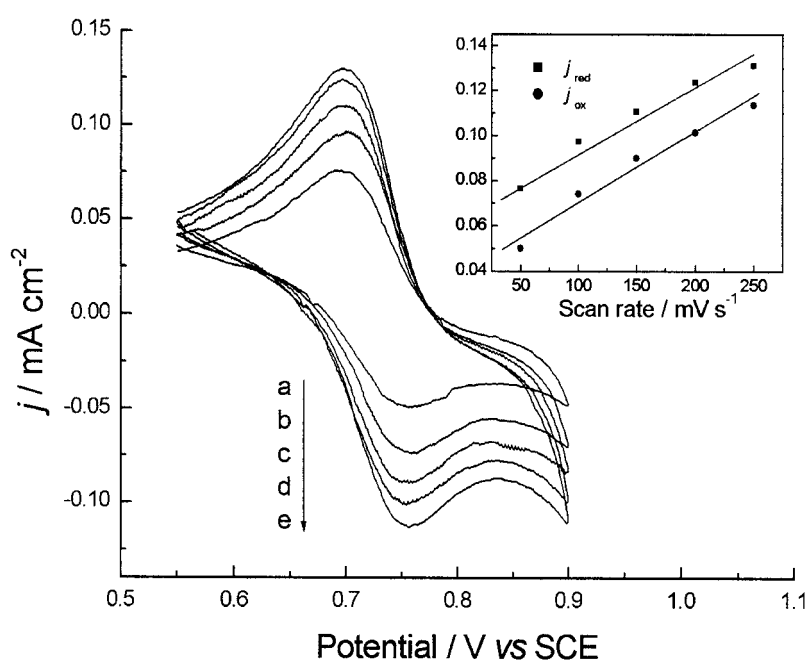


Figure 3 Cyclic voltammograms of PNSA film in concentrated SA at potential scan rates of 50 (a), 100 (b), 150 (c), 200 (d), 250 mV s^{-1} (e). Inset: plots of anodic or cathodic peak current density versus potential scan rate.

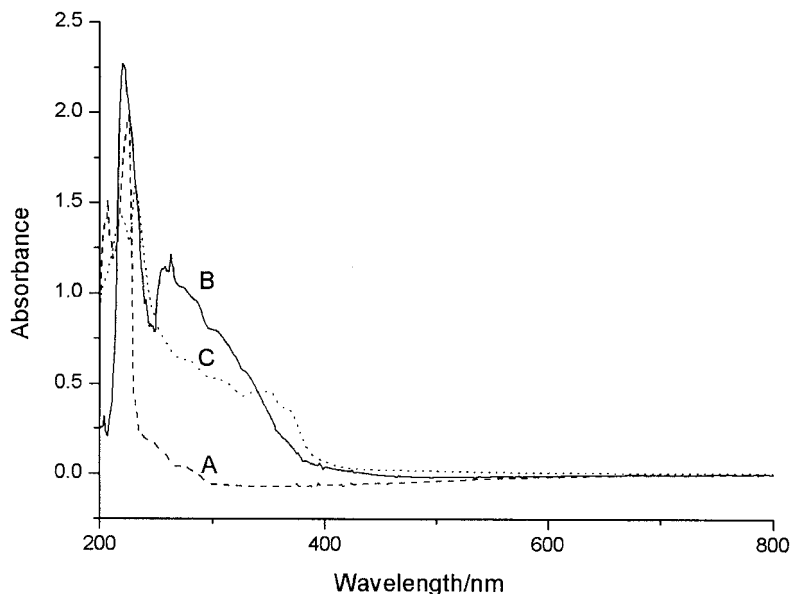


Figure 4 UV-visible spectra of β -NSA (A) and PNSA prepared by using BFEE+TFA (1 : 2, v/v) (B) or BFEE+SA (1 : 1, v/v) (C) as electrolytes. Solvent: methanol.

Structure of poly(β -naphthalene sulfonic acid)

Figure 4 illustrates the UV-visible spectra of the monomer β -NSA (A), and the soluble part of PNSA prepared by electropolymerization of 0.2 mol L^{-1} β -NSA in BFEE+TFA (1 : 2, v/v) at 1.75 V (B) or in BFEE+SA (1 : 1, v/v) at 1.05 V (C) (methanol was used as the solvent). The UV spectrum of the monomer shows peaks at 207 and 226 nm [Fig. 4(A)]. The spectrum of the polymer shown in Figure 4(B) has a much broader band with several fine structures at 200, 260, and 300 nm. The overall absorption tails off to about 550 nm. The longer wavelength indicated longer polymer sequences.^{14,15} The UV spectral results confirmed that a conjugated polymer with broad molar mass distribution was obtained. Furthermore, the conjugated sequence length of the polymer synthesized in BFEE+SA is almost the same as the soluble part of the polymer obtained from the medium of BFEE+TFA, because the spectral features of Figure 4(C) are nearly the same as Figure 4(B).

The typical transmission infrared spectra of the monomer (A) and the polymers (B, C) are illustrated in Figure 5. In the spectrum of the monomer, the broad peak centered at 3400 cm^{-1} is associated with the sulfonic acid group. The sharp peak at $\sim 3030 \text{ cm}^{-1}$ is assigned to the $=\text{C}-\text{H}$ winding stretching of the benzene ring. The $\text{C}=\text{C}$ stretching peaks appeared at 1649 and 1503 cm^{-1} . The peaks at 1290- and 1038-cm^{-1} bands are also attributed to the sulfonic groups. The 1187- and 1096-cm^{-1} peaks are related to the $\text{C}-\text{C}$ bonds of the naphthalene rings. The peaks at the frequencies lower than 900 cm^{-1} are assigned to $\text{C}-\text{H}$

winding stretching bands of naphthalene rings.¹⁶ The 744-, 825-, and 890-cm^{-1} peaks are attributed to 4, 2, and 1 adjacent hydrogen atoms, respectively.¹⁷ In the spectrum of the polymer, the characteristic bands of the naphthalene ring and sulfonic acid group are still found and also confirm the formation of PNSA. The bands are relatively broad mainly because the polymer has a broad chain length distribution. In spectrum B, the peaks at the frequencies lower than 900 cm^{-1} are weak, indicating the molar mass of the polymer is relatively high because of a low content of $\text{C}-\text{H}$ bonds. However, in spectrum C, there are medium strong peaks at 850 and 890 cm^{-1} and the peak at 744 cm^{-1} disappeared. This implied that the polymer was formed by $\text{C}-\text{C}$ coupling at the 5,8 positions of β -NSA ring.

The excitation spectrum of the soluble PNSA has several peaks and the maximum absorption is at 278 nm, as shown in Figure 6. A dominant maximum at 430 nm and several weaker bands around 350 nm characterize the emission spectrum. These results indicate that the polymer is a good blue light emitter. Its quantum efficiency was measured to be $\sim 4\%$.

CONCLUSION

β -NSA can be electrochemically polymerized in the mixed electrolytes of BFEE and TFA or SA. The as-grown polymer film prepared from the medium of BFEE+TFA was in the doped state and black in color. However, it changed into golden yellow after several minutes in air. The golden yellow film formed by

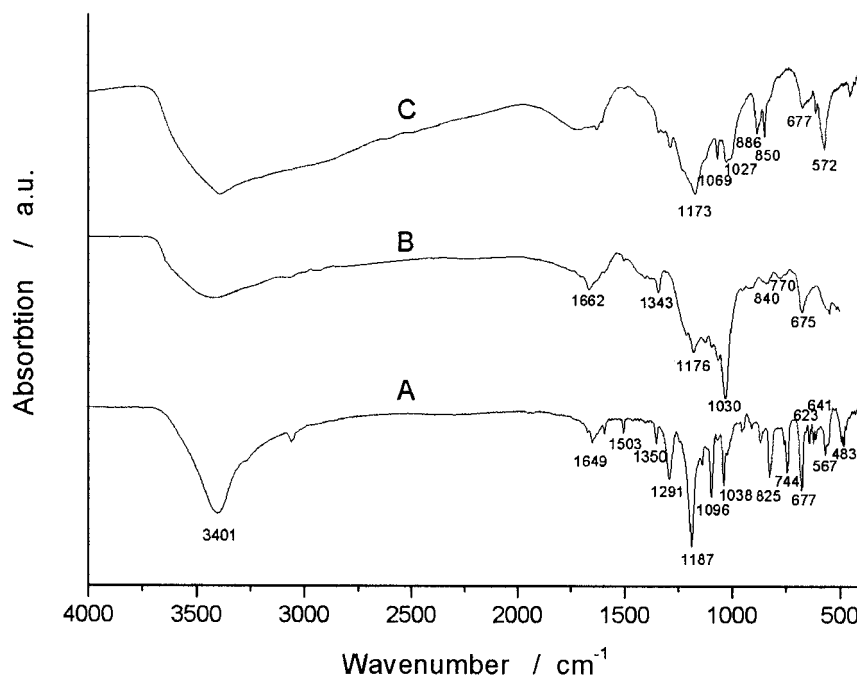


Figure 5 FT-infrared spectra of β -NSA (A) and PNSA prepared by using BFEE+TFA (1 : 2, v/v) (B) or BFEE+SA (1 : 1, v/v) (C) as electrolytes.

casting the solution of soluble part of PNSA had a conductivity of 0.95 S cm^{-1} , while it decreased to $\sim 0.01 \text{ S cm}^{-1}$ after 5 days. The polymer synthesized in BFEE+SA had a structure similar to that of the soluble

part of the polymer prepared in BFEE+TFA. It was soluble in water and methanol. The PNSA prepared by this technique had a strong fluorescence in the blue light region with a quantum efficiency of $\sim 4\%$.

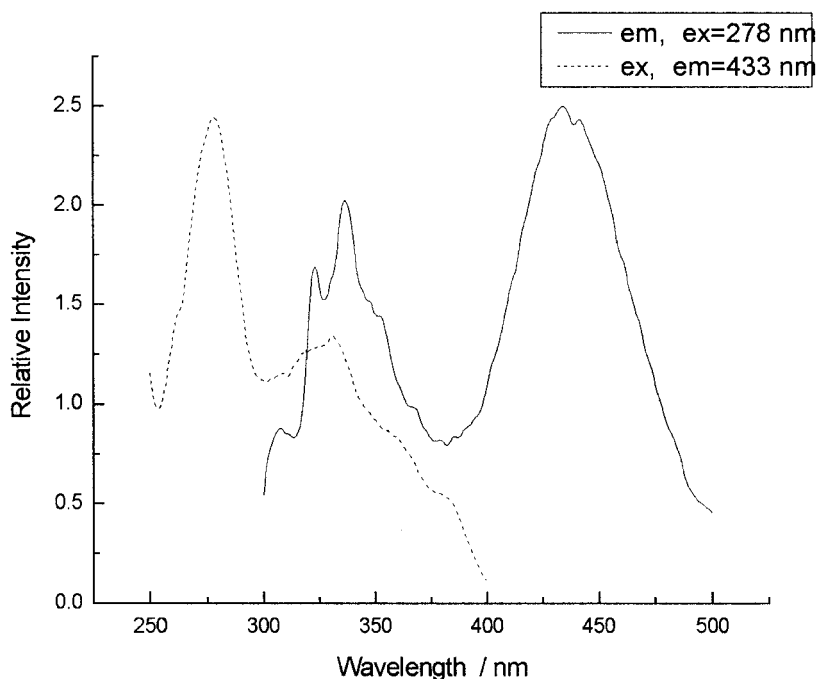


Figure 6 Excitation (left) and fluorescence (right) spectra of PNSA prepared by using BFEE+TFA (1 : 2, v/v) as electrolyte. Solvent: methanol.

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