

SELF-ASSEMBLED MULTILAYERS AND PHOTOLUMINESCENCE
PROPERTIES OF A NEW WATER-SOLUBLE POLY(PARA-PHENYLENE)

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ABSTRACT

This paper reports the synthesis and characterizations of a new water-soluble poly(para-phenylene) (PPP) and its applications in preparing self-assembled multi-layer films. This new water-soluble conducting polymer was prepared through the sulfonation reaction of poly(p-quarterphenylene-2,2'-dicarboxylic acid). The incorporation of sulfonate groups has dramatically improved PPP's solubility in water at a wide pH range, whereas previous PPP is only slightly soluble in basic solutions. Dilute aqueous solutions of this polymer with acidic, neutral or basic pH emit brilliant blue light while irradiated with UV light. The sulfonated PPP emits from 350 nm to 455 nm with a maximum intensity at 380 nm. Self-assembled multilayers of this sulfonated PPP were constructed with a positively charged polymer poly(diallyl dimethyl ammonium chloride) and characterized with various surface analyses. Conductive (RuO_2 and ITO), semiconductive (Si wafer), and non-conductive (SiO_2) substrates were used in the preparation of self-assembled multilayers. Electrical, optical and structural properties of these novel self-assembled thin films will be discussed.

INTRODUCTION

Conducting polymers are a novel class of conjugated materials which combine the electronic and optical properties of semiconductors and the processability of conventional polymers[1]. Conducting polymers, such as PPP or (poly(para-phenylene)), PPV or (poly(phenylene vinylene), and polythiophene, typically possess the delocalized π electrons in their polymeric backbones. These aromatic, rigid-rod polymers play an important role in some important technologies including smart and high performance molecular engineered materials[2] and polymer optoelectronic devices[3]. The organic electroluminescence device (LED) based on these conjugated conducting polymers have been studied extensively in the last decade. The blue-emission LEDs based on PPP was reported by Leising *et al.* in 1992[4]. Later on, Fou *et al.* reported the incorporation of self-assembled multilayer technology into the fabrication of LED's[5]. In general, the aforementioned unmodified PPP and cured PPV polymers are not soluble in water. To avoid using toxic and corrosive solvents, Novak *et al.* reported the first example of water soluble poly(para-phenylene) derivative[6] in 1991 which provides a new route to synthesize and process rigid-rod polymers in water. The molecular structure of this water-soluble poly(p-quarterphenylene-2,2'-dicarboxylic acid is illustrated in Figure 1(a). This polymer, however, is only slightly soluble in water in its salt form.

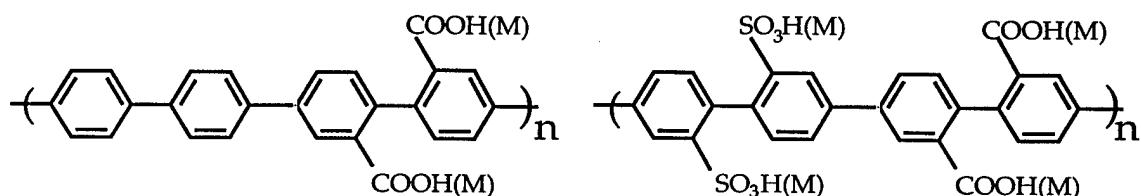


Figure 1(a). Poly(p-quarterphenylene-2,2'-dicarboxylic acid)

Figure 1(b). Poly(p-quarterphenylene-disulfonic-dicarboxylic acid)

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The mixture of dimethylformamide/aqueous solvent(25/75) was needed in order to prepare concentrated polymer solution for processing (>5% w/v). Thus, there is a need to prepare highly water-soluble, rigid-rod conducting polymers which can be processed entirely under environmentally benign conditions. Another important consideration is that the charged groups on the repeating unit of the polymer backbone can serve as anchor points in self-assembled thin film growth or LED's fabrications. It is anticipated that the increase in the number of charges on each monomeric unit of the polymer will provide stronger cation-anion attractions in the self-assembly process. In this paper, we report a new PPP polymer—poly(p-quaterphenylene-disulfonic-dicarboxylic acid (Figure 1(b)) through sulfonation of poly(p-quaterphenylene-2,2'-dicarboxylic acid). The sulfonated PPPso_3^- has enhanced solubility in aqueous solution and photoluminescent properties in both solution and solid state films. Self-assembled multilayer films of this new PPP are prepared and the structure of the films is characterized with X-ray reflectivity measurements.

EXPERIMENT

The modified PPP bearing both sulfonate and carboxylate functional groups was prepared by the following route. In a typical experiment, the golden color powder of poly(p-quaterphenylene-2,2'-dicarboxylic acid) was slowly added into an aqueous solution containing 23% $\text{SO}_3^-/\text{H}_2\text{SO}_4$ (the ratio of polymer/ SO_3^- is 1:2.3) at 0°C degree under vigorous stirring. Upon the completion of the addition, the reaction solution was stirred at 0°C degree for an hour, and then was heated at 70°C for 7 hours. The product mixture was cooled down to room temperature and was neutralized by adding dilute KOH solution. The solvent in the mixture was removed under vacuum condition. The dried crude product was purified on a column packed with Florisil. Methanol was selected as eluent to collect the product. Final product was collected as yellow color powder.

Monosulfonated triphenylphosphine and its palladium catalyst, which are needed in the cross coupling polymerization, were synthesized according to the literature[7-8], while the monomers of 4,4'-dibromicdiphenic acid and bis(boronic acid) diphenyl were also synthesized and characterized by the reported methods[9-10]. The precursor polymer, poly(p-quaterphenylene-2,2'-dicarboxylic acid) used for sulfonation reaction, was obtained using the procedures reported by Novak *et al.*[6]. The purified product was characterized by 200 MHz ^1H NMR(D_2O) (Gemini NMR spectrometer) and IR (KBr pellet) (Bio-Rad-40). Absorption spectra were recorded using a Perkin-Elmer Lambda-19 UV/VIS/NIR spectrometer. Photoluminescence(PL) measurements on (un)sulfonated PPP solutions and self-assembled films were obtained using a SPEX Fluorolog Fluorometer.

The negatively charged PPPso_3^- polymer was assembled with a positive charged polymer poly(diallyl dimethyl ammonium chloride) or PDDA to form multilayers. The self-assembled multilayer of PDDA/ PPPso_3^- films and spin casted films were formed on various substrates; these include conductive RuO_2 and ITO, semiconducting Si wafer, and nonconductive quartz or glass substrates. The conductivity measurements were performed on a 100 PDDA/PPP bilayer film self-assembled on RuO_2 substrate. Self-assembled multilayer PDDA/PPP films on quartz and glass substrates were also characterized by UV-Visible absorption and photoluminescence measurements. Self-assembled PDDA/PPP multilayer films on Si(100) substrates were used for the X-ray reflectivity study which was carried out with an 18-kW rotating anode X-ray generator with a copper target and a four-circle diffractometer.

RESULTS AND DISCUSSION

The new sulfonated poly(para-phenylene) PPPso_3^- exhibits a high solubility in water at a wide range of pH including acidic, neutral, or basic conditions. It can be easily dissolved in water at pH values ranged from 1 to 14. This high solubility can be attributed to the increased numbers of negative charges on the repeating unit (possibly four negative charges on each repeating unit) of the sulfonated and carboxylated poly(para-phenylene) polymer. This highly water-soluble polymer was characterized by a number of techniques to confirm its composition and rod-like structure. ^1H NMR spectrum(D_2O) showed broad resonances ranged from 6.6 to 8.2 PPM, which can be attributed to the polymeric effect. The resolved vibronic features in the IR spectrum (KBr

pellet) displays expected bands at 1608, 1440, and 3448 cm^{-1} for -COOH vibrations, bands at 1440 and 1196 cm^{-1} for -SO₃H vibrations, bands at 3060, 1130 and 1046 cm^{-1} for Ar-H vibrations, and bands at 809 and 690 cm^{-1} for phenyl rings in PPP backbone.

The aqueous solution of sulfonated poly(para-phenylene) emits very brilliant blue light when irradiated by UV light. The emission spectrum of sulfonated PPP aqueous solution is compared with the emission spectrum for PPPCO₂⁻ solution in Figure 2 with the same concentration (10^{-3} M). Figure 3 displayed the photoluminescent spectra of a 100-bilayer-film of self-assembled PPP and PDDA. It is noticed that the introduction of -SO₃H(M) functional groups onto the polymer backbone caused the blue-shift for either absorption or photoluminescence spectrum. This phenomenon can be explained with either electron withdrawing effect or interruption of π -conjugation. It is more likely that the band gaps between conducting band and valence band is increased by the introduction of negatively charged electron withdrawing group such as -SO₃H(M). Comparing the blue shift effect for aqueous polymer solution, the effect is relatively small to the modified PPP/PDDA bilayer film. The explanation might be weak spatial interactions among the PPP layers through the PDDA linker. As shown in Figure 2, the carboxylated PPP emits blue light with a maximum intensity at about 430 nm, but the modified PPPSO₃⁻ with both sulfonate and carboxylate groups emits very brilliant blue light with maximum intensity at 380 nm and covered a narrow spectrum range from 355 to 450 nm. The emission spectrum of the 100-bilayer PDDA/PPP films has the maximum intensity at 411 nm (Figure 3) with a shoulder at about 430 nm.

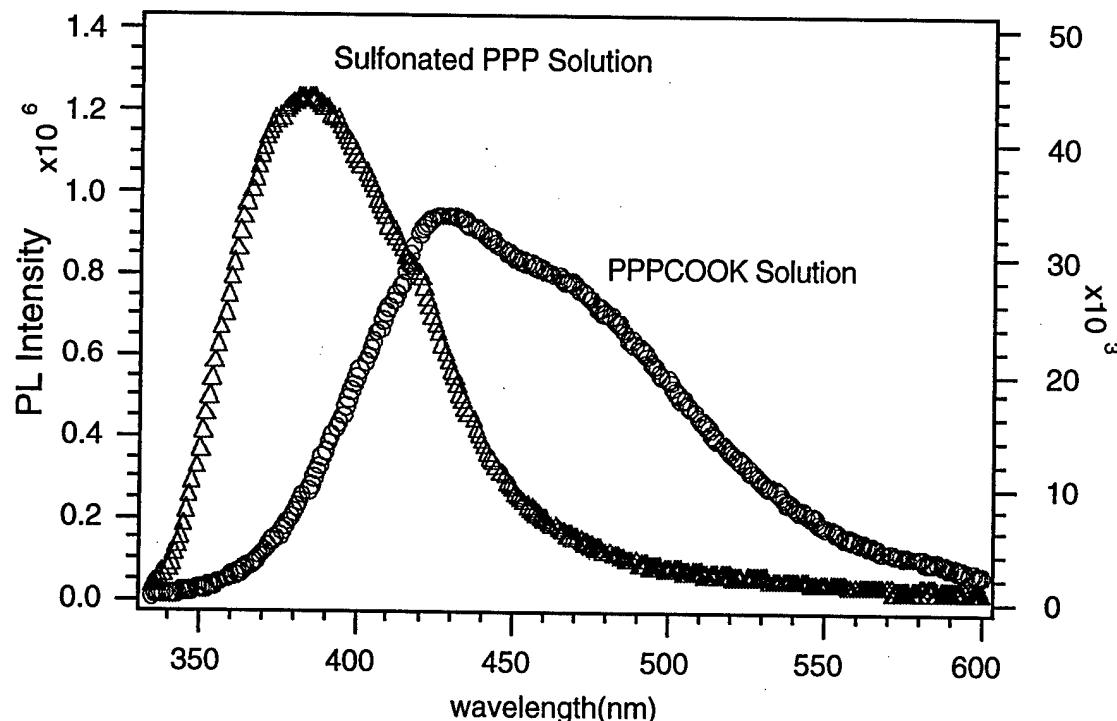


Figure 2. The solution emission spectra of poly(p-quarterphenylene- 2,2'-dicarboxylic acid (referred as PPPCO₂⁻) and Poly(p-quarterphenylene- disulfonic-dicarboxylic acid(referred as PPPSO₃⁻).

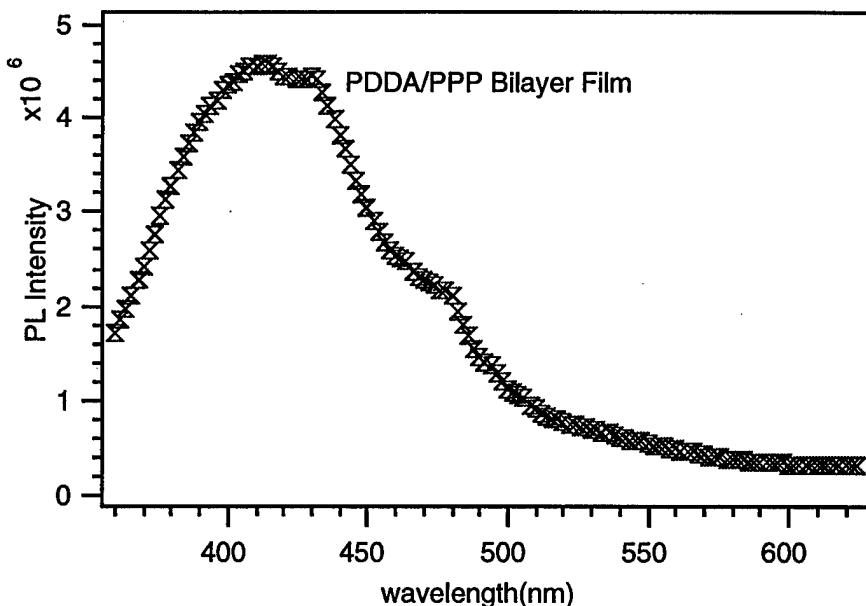


Figure 3. The emission spectrum of the 100-bilayer PDDA/PPP film

In an attempt to build high quality multilayer films, the modified PPP bearing carboxylate groups was used first. However, it failed to yield good quality films due to the use of mixture aqueous and organic solvent. The possible reasons for this failure might be that the organic solvent such as DMF may cause desorption of the deposited bilayers. The sulfonated PPP, however, is very soluble in water and can be successfully employed to build up multilayer films. Several factors were considered to play important roles in such kind of self-assembly process. First, the number of net negative charges on each repeating structural unit in the polymer was doubled, the increased negative charges provided stronger chemical forces for this conducting polymer to bind with positively charged polymer linkers. Second, the incorporation of more negatively charged functional group dramatically increased the solubility of sulfonated PPP in water at ambient pHs so that the use of polar organic solvent in self-assembly was eliminated avoiding desorption of the films from the substrate surface.

Figure 4 shows the electron-depth-density profile of a bilayer film of PDDA/PPP which was derived from the analysis of the X-ray reflectivity measurement shown in the figure inset. The reflectivity is the ratio of the intensities of the X-rays reflected from the sample to that which illuminate the sample. Such measurements can be fitted to calculations of reflectivity profiles from model systems (such as that shown in figure 4) using the Parratt-formalism [11]. The best fitting model is one of a substrate terminated with a native oxide of a thickness of 7.1 Å and a roughness of 2.4 Å (rms). The modeled PDDA layer was 17.4 Å thick and had a surface roughness of 1.2 Å. These values are similar to those of a previous study of PDDA and NiPc [12]. The sulfonated PPP layer deposited on the PDDA layer was 12.5 Å thick and has a slightly larger roughness (2.3 Å) than the PDDA-layer.

The X-ray study was sensitive to a scattering contrast between the PDDA and sulfonated PPP layers, whereas previously no scattering contrast was determined between PDDA and NiPc [12]. The difference in the scattering contribution in the present system suggests that the single layers which comprise the bilayer of PDDA and PPP are distinct (not intermixed).

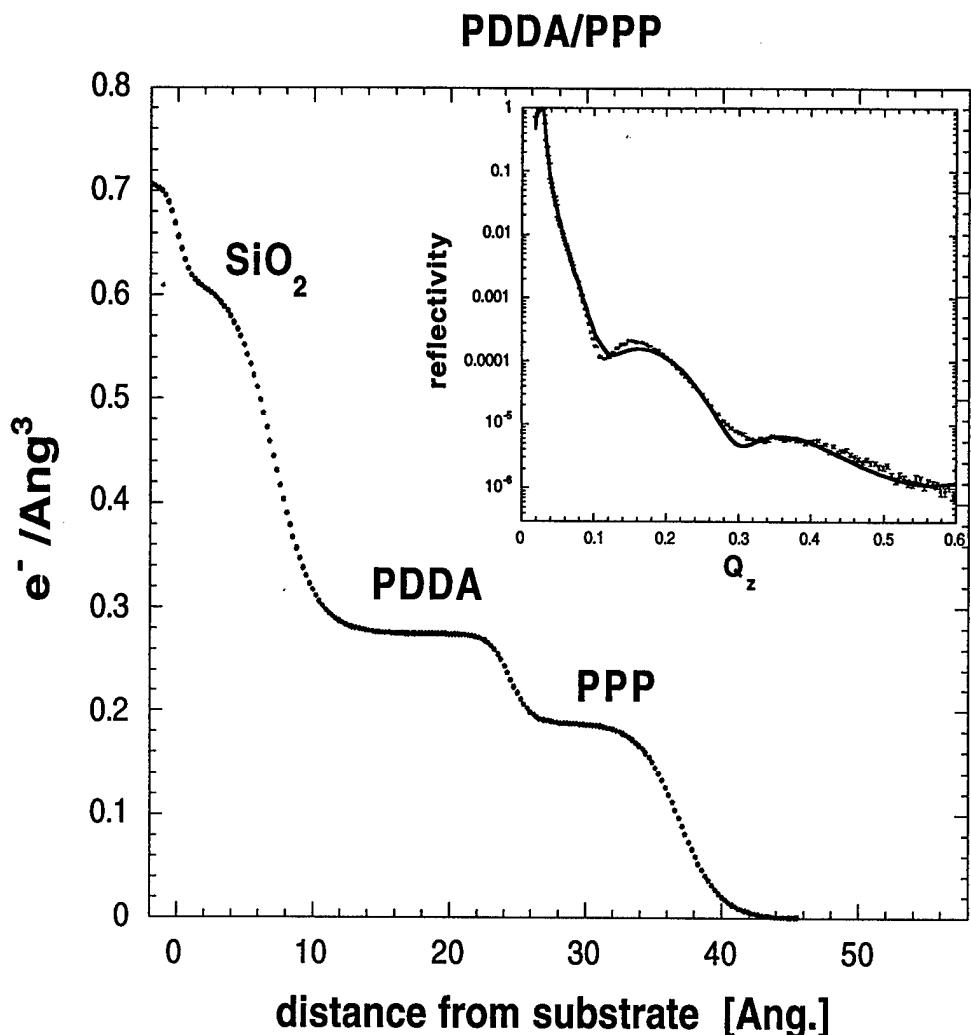


Figure 4 The electron density profile of a PDDA/PPP bilayer film on Si(100) derived from an X-ray reflectivity measurement (shown in the inset)

CONCLUSION

Through the chemical modification of poly(p-quarterphenylene-2,2'-dicarboxylic acid), a newly prepared Poly(p-quarterphenylene-disulfonic-dicarboxylic acid) shows a promising solubility in water at a wide range pH values (ranged from 1 to 14), which can be self-assembled at an environmentally benign condition. The brilliant blue luminescence was observed when the aqueous Poly(p-quarterphenylene-disulfonic-dicarboxylic acid) was irradiated using UV-light. The incorporation of electron withdrawing group $-\text{SO}_3\text{H}(\text{M})$ into the rigid polymer backbone caused the blue shift in both absorption and emission spectrum while compared to poly(p-quarterphenylene-2,2'-dicarboxylic acid). Photoluminescence was also observed when a self-assembled multilayer PDDA/PPP film or a spin coated film was exposed to the UV-light. Finally, the thin-film structure of a PDDA/PPP bilayer was determined by X-ray reflectivity.

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