

Electrochemistry of the Films of a Novel Class C₆₀ Covalently Linked PPV Derivative: Electrochemical Quartz Crystal Microbalance Study in Acetonitrile Solutions of Tetra-*n*-butylammonium Cations

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ABSTRACT: The electrochemical behaviors of a novel class C₆₀ covalently linked PPV derivatives (*i.e.*, PPV-1-C₆₀ and PPV-2-C₆₀) in thin solid films as well as in solutions are reported. The first cathodic peak potentials of PPV-1-C₆₀ and PPV-2-C₆₀ have positive shifts by 30 and 50 mV, respectively, compared to pristine C₆₀ in formal cyclic voltammetry (CV). Simultaneous CV and piezoelectric microgravimetry of the drop-coated thin solid films of PPV-1-C₆₀ and PPV-2-C₆₀ in acetonitrile solutions of TBA⁺ counteractions

are strongly influenced by the structure of the polymer-C₆₀, including the length of the chain macromolecule and the steric hindrance effect. In addition, the atomic force microscopy (AFM) images of PPV-1-C₆₀ and PPV-2-C₆₀ films deposited on Au/quartz electrode both exhibit even distribution. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2737–2741, 2002

Key words: fullerenes; polymers; films

INTRODUCTION

The electrochemistry of fullerenes has been extensively investigated.^{1–4} The reports on the electrochemical behavior of pristine fullerenes and their derivatives dissolved in solutions have offered important information on the electronic structure of genuine fullerenes and their derivatives.^{2,3} Meanwhile, the electrochemical behavior of thin solid films of fullerenes has recently attracted much attention because of intrinsic interest in a new material and its applicability to batteries^{5,6} or sensing devices.⁷ These studies indicated the stability of fullerenes anions with respect to dissolution, countercation, and anion incorporation into the film, and moreover, the resulting changes of the film structure during the electrochemical processes.^{8–11}

Recently, the importance of organofullerenes in materials science has been recognized, but not much is known about their electrochemical properties in thin solid films,^{12,13} mainly because of the difficulty in synthesizing the organofullerenes in bulk quantities.

We have synthesized a novel class C₆₀ covalently linked PPV derivative (*i.e.*, PPV-1-C₆₀ and PPV-2-C₆₀)

(Fig. 1). The utilization of the strong photoluminescence of conjugated polymers of PPV for light-emitting devices have resulted in more research in the field of materials, that combine the electric and optical properties of semiconductors and metals with the attractive mechanical properties as well as processing properties of polymers.^{14–17} The polymer-C₆₀ system was used to prepare improved polymer photovoltaic cells with higher efficiency,^{18,19} being one of the most outstanding applications of fullerenes. Here, we report on the electrochemical behavior of these two C₆₀ covalently linked PPV derivatives both in thin solid films and in solutions by cyclic voltammetry (CV) as well as simultaneous CV and piezoelectric microgravimetry with an electrochemical quartz crystal microbalance (EQCM). The influences of the TBA⁺ cation and the structure of the C₆₀ covalently linked PPV derivatives on electrochemical behavior of the films and the film stability with respect to dissolution during electrochemical reduction and reoxidation are reported. In addition, the images of the thin films were examined by means of atomic force microscopy (AFM).

EXPERIMENTAL

PPV-1-C₆₀ and PPV-2-C₆₀ were synthesized and well characterized elsewhere.²⁰ Tetrabutylammonium hexafluorophosphate (TBAPF₆) purchased from Aldrich was dried for 6 h in vacuum prior to use. Acetonitrile

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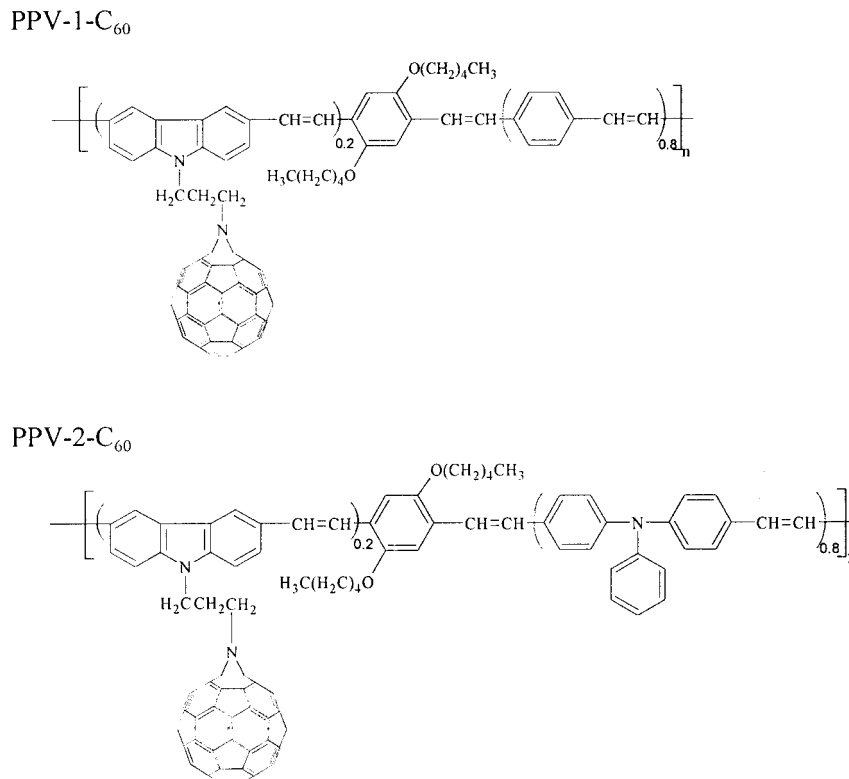


Figure 1 The structures of PPV-1-C₆₀ and PPV-2-C₆₀.

(CH₃CN) of a high-performance liquid chromatography (HPLC) grade was used as received, from Labscan Asia Co. (Thailand). Dichloromethane (CH₂Cl₂) (Park Co., Dublin, Ireland) was dried with 4 Å molecular sieve and refluxed for 6 h before distillation and then stored in the presence of unhydrated calcium chloride (CaCl₂). C₆₀ (99.9%) was provided by Perkin University.

Drop-coating is the most commonly used technique for the preparation of fullerene films for electrochemical studies.⁴ In our experiments, the thin solid films of these two kinds of C₆₀ covalently linked PPV derivatives were prepared by this method. The thin drop-coated solid films were cast directly onto the Au/quartz electrode from the casting solution. That is, a 6- μ l aliquot of CH₂Cl₂ containing PPV-C₆₀ derivative (~1 mM) was spread and evaporated repeatedly onto the Au electrode surface until a film covering the entire Au surface was obtained. The solvent was dried up rapidly by heating to form relatively fine smooth solid films. The surface coverage was about 5.1×10^{-9} mol cm⁻².

CV measurements were performed on a CHI705A electrochemical analyzer in a three-electrode cell. The working electrode was a 3-mm-diameter Pt disk. The auxiliary electrode consisted of a Pt plate. SCE was used as a reference electrode.

Simultaneous CV and piezoelectric microgravimetry measurements were carried out with a model 420

EQCM. An 8-MHz atom (AT)-cut quartz crystal resonator was used. Geometric area of the electrode was 0.196 cm². Mass sensitivity of this quartz crystal based on the Sauerbrey equation was 1.4 ng Hz⁻¹. The diameter of the quartz crystal was 13.7 mm. A central 5-mm-diameter circular gold spot served as the working electrode. Pt wire and a NaCl-saturated Ag/AgCl electrode were used as auxiliary and reference electrode, respectively. Each experiment was performed with a new Au quartz electrode.

All electrochemical experiments were performed under high-purity nitrogen atmosphere and at room temperature.

The morphology of PPV-1-C₆₀ film and PPV-2-C₆₀ film was studied by atomic force microscopy (AFM) with the use of a HL-II style computerized scanning probe microscope.

RESULTS AND DISCUSSION

Electrochemistry in solutions

Figure 2 displays the CV behaviors of PPV-1-C₆₀, PPV-2-C₆₀, and C₆₀ in CH₂Cl₂ with 0.1M TBAPF₆. Three one-electron reversible diffusion-controlled processes are observed within the accessible potential window of the solvent. The E_{1/2} values for the first redox couples of PPV-1-C₆₀ and PPV-2-C₆₀ have positive shifts by 30 and 50 mV, respectively, compared to the

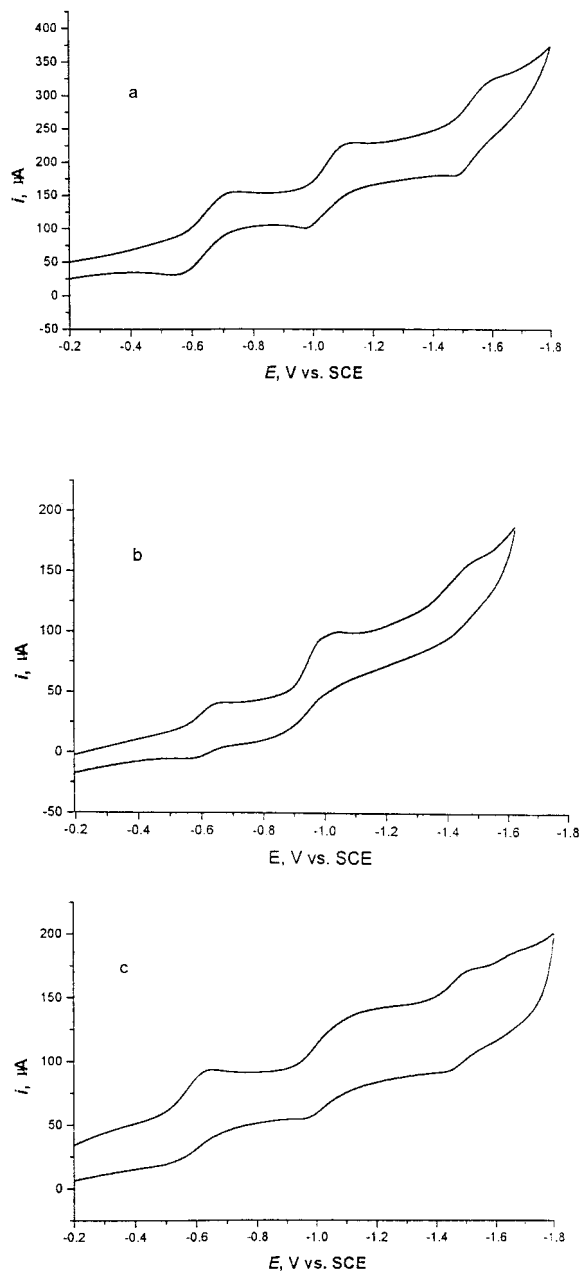


Figure 2 Cyclic voltammograms at a Pt working electrode for ~ 1 mM C₆₀(a) and PPV-1-C₆₀ (b) and PPV-2-C₆₀ (c) in CH₂Cl₂ with 0.1M TBAPF₆. Potential scan rate, 50 m V s⁻¹.

$E_{1/2}$ values of the corresponding C₆₀ couples. This implies that these two C₆₀ covalently linked PPV derivatives are better electron acceptors than pristine C₆₀.

Simultaneous CV and piezoelectric microgravimetry of films

EQCM is a very powerful technique to elucidate the process of dissolution and deposition of the film on the electrode surface and processes of doping and dedoping cation into and out of the film. We examined

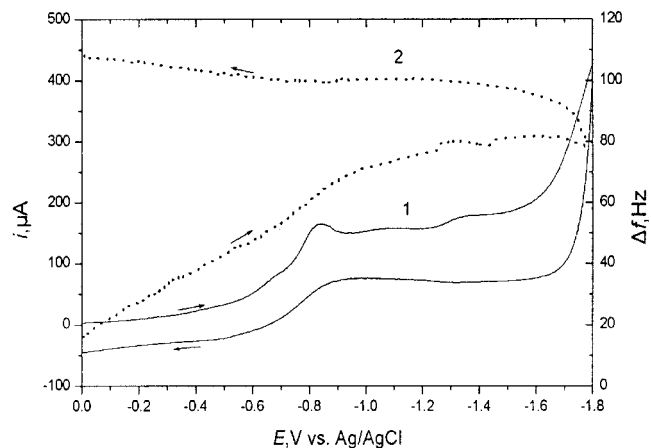


Figure 3 Simultaneous recorded for PPV-1-C₆₀ film drop-coated onto Au/quartz electrode: cyclic voltammogram (curve 1) and frequency change (curve 2) versus potential traces for acetonitrile solution with 0.1M TBAPF₆. Potential scan rate, 100 m V s⁻¹.

the electrochemical behavior of PPV-1-C₆₀ and PPV-2-C₆₀ in films and the stability of the films with respect to dissolution by using EQCM. Simultaneously recorded CV and the frequency change versus potential curves for the films, cast on the Au/quartz electrode, are shown in Figures 3 and 4. Experiments were performed in acetonitrile solutions. In some cases, pronounced differences were observed for the CV curves of the first and subsequent cycles. For clarity, only the first CV cycle and the corresponding microgravimetrogram are presented. For different films of the same adduct, both voltammograms and microgravimetrogram were quite reproducible. That is, peak potentials and the peak height ratios were similar.

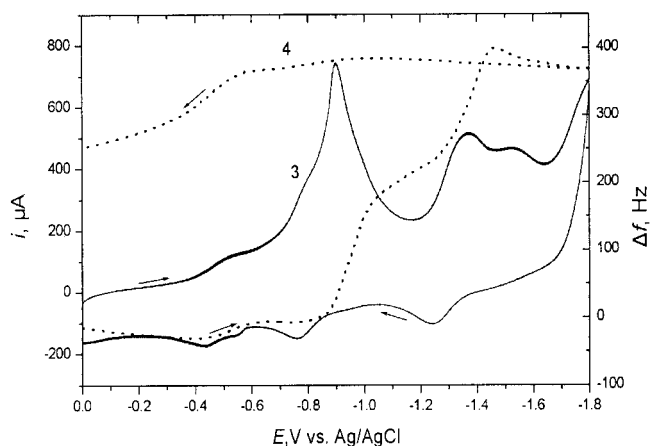


Figure 4 Simultaneous recorded for PPV-2-C₆₀ film drop-coated onto Au/quartz electrode: cyclic voltammogram (curve 3) and frequency change (curve 4) versus potential traces for acetonitrile solution with 0.1M TBAPF₆. Potential scan rate, 100 m V s⁻¹.

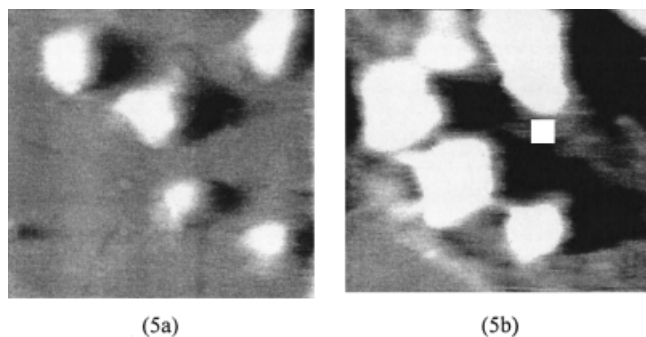


Figure 5 AFM image (3000×3000 nm), taken in air, of the surface of PPV-1-C₆₀ film (5a) and PPV-2-C₆₀ film (5b) on Au/quartz electrode.

For charge compensation, either the counteranion must enter the fullerene film during its electroreduction or the film is removed from the electrode surface. In our experiments, the TBA⁺ cations were selected for the study, because this cation was known to affect the electrochemistry of fullerene films in a certain way.⁸

For PPV-1-C₆₀ (Fig. 3), three cathodic peaks or shoulders are recorded in its CV curve, but only two electrooxidation anodic peaks are present after the positive scan reversal. Therefore, the cathodic peaks must originate from the electroreductions of both the surface confined fullerenes and the fullerene anions dissolved from the film during the film electroreduction. A decrease of mass accompanies the electroreduction of the film. The film starts to dissolve at the beginning of the cathodic scan. Up to ~ -0.85 V (*i.e.*, the potential of the first cathodic peak), the degree of the dissolution is relieved because the TBA⁺ cation ingresses into the film for charge compensation. During the anodic scan, with the TBA⁺ cation's egressing into the solution, the mass of the film keeps on decreasing. These phenomena can be explained by considering the structure of PPV-1-C₆₀. The polymer-C₆₀ is a long chain macromolecule; therefore, once the fullerene anions dissolve into the solution from the film during the electroreduction, there are difficulties for these anions to redeposit onto the electrode surface. This leads to the continuous mass decrease of the film.

In contrast to the behavior of PPV-1-C₆₀ films, four well-defined cathodic and four anodic peaks are seen for PPV-2-C₆₀ in the TBA⁺ solution (Fig. 4). The first cathodic peak, at ~ -0.5 V, is accompanied by a slight mass change. Presumably, the mass decrease of the film due to partial dissolution is almost compensated by the mass increase due to the TBA⁺ cation entering the film. The second cathodic peak, at ~ -0.9 V, is associated with a mass decrease, indicating that the film dissolution prevails over the cation entrapment. Eventually, the film is completely dissolved. In the positive scan, the mass does not change in the potential range of the first and second anodic peaks. How-

ever, the mass increase in the potential range of the $-2/-1$ electrooxidation can be ascribed to the redeposition of the film. Similar to PPV-1-C₆₀, the length of the molecular chain also is a main factor affecting the behavior of the PPV-2-C₆₀ film upon electroreduction. In addition, there are three benzene rings in the unit adjacent to the vinylene in the structure of the PPV-2-C₆₀ macromolecule, so the influence of steric hindrance is another important factor that should be taken into account. Under the condition of a relatively strong steric effect, the large counteranion TBA⁺ cannot easily ingress into the film for charge compensation. As a result, the mass of the film decreases during the electrochemical process.

AFM measurement

Further information about the PPV-1-C₆₀ film and PPV-2-C₆₀ film is obtained from AFM. Figure 5 shows their topographic images. The panel of PPV-1-C₆₀ film [Fig. 5(a)] and the panel of PPV-2-C₆₀ film [Figure 5(b)] show that both are distributed evenly. The size of the PPV-1-C₆₀ group and PPV-2-C₆₀ group determined by these AFM images are about 390 and 460 nm, respectively.

CONCLUSIONS

Compared to the pristine C₆₀, the first cathodic peaks of PPV-1-C₆₀ and PPV-2-C₆₀ are both shifted positively in formal CV behavior in solution. Simultaneous CV and piezoelectric microgravimetry of the drop-coated films of PPV-1-C₆₀ and PPV-2-C₆₀ in acetonitrile solutions reflect the charge transfer accompanied by mass transfer across the film-solution interface. PPV-1-C₆₀ and PPV-2-C₆₀ are both chain polymers. The length of the macromolecules chain as well as the steric hindrance effect are two important factors that affect the stability of the films. Moreover, the AFM images of the PPV-1-C₆₀ film and PPV-2-C₆₀ film deposited on the Au/quartz electrode both exhibit even distribution.

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