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### Electrochemical Doping of Poly(*p*-Phenylene Vinylene) Thin Films

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## ELECTROCHEMICAL DOPING OF POLY(*p*-PHENYLENE VINYLENE) THIN FILMS

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### ABSTRACT

The electrochemical properties of poly(*p*-phenylene vinylene) (PPV) films, prepared via a water-soluble precursor, were investigated using chronocoulometry. The charging concentrations of 0.2- $\mu\text{m}$  thick PPV films leveled off within 500–600 seconds and was on the order of 1.0 charge per repeat unit when the magnitude of the potential steps from an initial potential of 0.0 V was 0.16 to 0.20 V beyond the anodic oxidative peak potential ( $E_p$ ). This indicates that PPV can be fully doped and may be a promising material for charge storage. The early stages of redox doping were studied, and the transfer coefficient ( $\alpha$ ) was estimated to be 0.4–0.9, which increased with an increase in the magnitude of the potential steps beyond  $E_p$ .

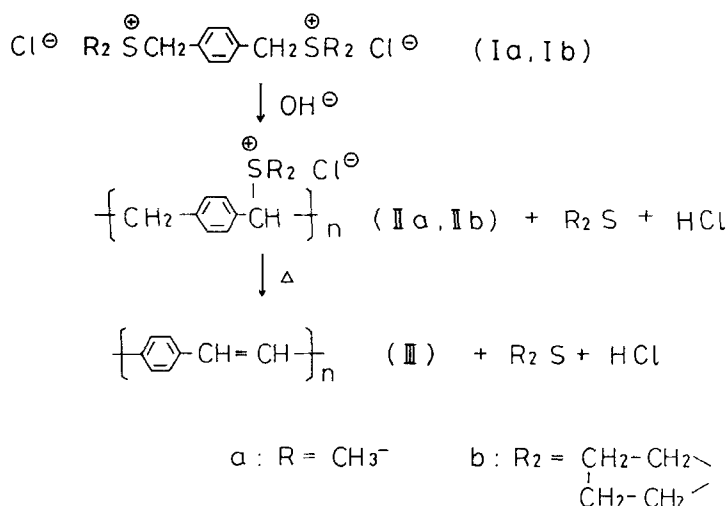
## INTRODUCTION

Many conductive polymers studied to date are completely infusible and insoluble in organic solvents. In order to obtain conductive polymer films, electrochemical polymerization has been developed as a useful technique. By this method, polythiophene, polypyrrole, and many other electroactive polymers have been prepared as highly conductive films directly in the doped state. Poly(3-methylthiophene) films, with conductivities in the range of 2000 S/cm, have been prepared by electrochemical polymerization under optimized conditions [1]. In early work, polypyrrole, poly(*N*-methylpyrrole), and poly(*N*-phenylpyrrole) films were prepared by electropolymerization of the corresponding pyrrole monomers [2]. Films of these polymers on platinum could be electrochemically driven between the oxidized form and the neutral form without evidence of decomposition. In these polymerizations, the electrical and electrochemical properties of the polymers are strongly influenced by a variety of factors, including solvent, temperature, electrolyte, and monomer concentration [3–5]. With these complexities, it is difficult to obtain electroactive polymers with controlled morphologies, and conductive polymer blend formation is limited to the use of soluble polyelectrolytes.

A route to processing conductive polymers from solution has been achieved by the development of soluble precursor polymers for polyacetylene [6], poly(*p*-phenylene) [7, 8] and poly(*p*-phenylene vinylene) (PPV) [9–11]. In the case of PPV, Wittig reaction of *p*-xylene bis(triphenylphosphonium chloride) with terephthalaldehyde resulted in the formation of low molecular weight polymers that could be doped to high levels of conductivity with AsF<sub>5</sub> [12, 13]. The polymerization of several bis-sulfonium salts yielded high molecular weight, water-soluble polyelectrolytes which generated PPV as films when exposed to elevated temperatures [9–11]. Electrical conductivity and ESR spectra were studied, and the band gap was evaluated to be 2.7 eV from absorption spectra [14]. Substitution with electron-donating groups substantially lowers the band gap [15] and enhances the conductivity to values as high as 10<sup>2</sup>–10<sup>3</sup> S/cm [16, 17]. Electrochemical doping studies of PPV, its derivatives, and model compounds have tended to focus on the reversibility of the redox behavior, the nature of the charge carriers formed, and the potential for using the polymer as an electrode in a secondary battery [14, 15, 17–23]. Preparing conductive and redox active polymer blends is also possible by utilizing the soluble precursor approach [24–26].

Due to the benefits of controlled morphology through solution and thermal processing, combined with the reversible electrochemical properties and relatively high oxidation potential of the polymer, we undertook a study to determine some of the fundamental characteristics of PPV electrodes. In this study we report on electrochemical doping of PPV films and blends. PPV could be cycled between the doped and undoped states without decomposition. Using chronocoulometry, saturation charging levels on the order of one charge per PPV unit were obtained, indicating that PPV could be fully doped.

In general, two types of *p*-xylene bis-sulfonium chloride monomers are used for PPV synthesis [27], as illustrated in Scheme 1. The reaction of **I** with an equivalent amount of sodium hydroxide leads to polymerization to yield a precursor polyelectrolyte **II**. Subsequent heat treatment of **II** yields PPV, **III**. However, there is a large difference in the reactivity to thermal elimination between **IIa** and **IIb**.



SCHEME 1.

Complete elimination could only be achieved at temperatures above 350°C for **IIa** with a high probability of some thermal degradation. A more efficient elimination of **IIb** occurs at temperatures around 210°C. Higher elimination temperatures also make it difficult to prepare conductive polymer blends when the blended polymers do not have a high thermal stability. Therefore, we have used **Ib** as the starting material for the PPVs studied here.

## EXPERIMENTAL

$\alpha,\alpha'$ -Dichloro-*p*-xylene, tetrahydrothiophene (THT), and poly(ethylene oxide) (PEO,  $M_w = 2 \times 10^5$ ) were used as received. Lithium perchlorate ( $\text{LiClO}_4$ ) and sodium perchlorate ( $\text{NaClO}_4$ ) were dried under vacuum at room temperature. Acetonitrile was distilled from phosphorus pentoxide. Other solvents were used as received.

In a 250-mL three-necked flask equipped with a stirrer and a condenser,  $\alpha,\alpha'$ -dichloro-*p*-xylene (4.38 g, 25 mmol) was reacted with THT (6.60 g, 75 mmol) and methanol (50 mL). After heating with stirring at 50°C for 20 hours, the solution was evaporated and a white crystalline powder was obtained. Yield: 8.17 g (93%). The water-soluble bis-sulfonium salt obtained was purified by reprecipitation into cold acetone (0°C). The mixture was stirred in an ice bath for 0.5 hour and subsequently filtered. The white solid obtained was washed with acetone and dried under vacuum at room temperature until two sequential weighings were constant.

The purified bis-sulfonium salt (3.51 g, 10 mmol) was dissolved in water (200 mL), placed in a three-necked flask, cooled in an ice bath, and thoroughly flushed with nitrogen. A solution of deoxygenized sodium hydroxide (1 N, 10 mL) was cooled to 0°C and added via a dropping funnel to the sulfonium salt solution with

continuous nitrogen flushing. After 40 minutes the solution was quenched with hydrochloric acid (1 N, 7.5 mL). The neutralized solution was dialyzed for 3 days using Spectra/Por 3 (MWCO 3500) against deionized water to remove the low molecular weight products, sodium chloride, and unreacted monomeric sulfonium salt.

A free-standing precursor film was obtained by casting the polyelectrolyte solution on a glass plate which had been rinsed with dimethyldichlorosilane. IR (film): 3023(m), 2943(m), 1513(s), 1416(m), 963(w), 831(m), 631(m), 551(m)  $\text{cm}^{-1}$ . The precursor film was treated at 210°C for 4 hours under nitrogen to obtain a PPV film. IR (film): 3023(m), 1695(w), 1593(m), 1513(s), 1416(m), 963(s), 831(s), 551(m)  $\text{cm}^{-1}$ .

Blend films were prepared by mixing the polyelectrolyte solution with PEO and subsequent casting in vacuum at room temperature as reported previously [24–26]. After heat treatment at 210°C for 4 hours under nitrogen, PPV:PEO blends were obtained. The PPV and PPV:PEO blends were prepared on either platinum plates (0.5 cm  $\times$  0.5 cm) or indium-tin oxide glass (ITO, 0.7 cm  $\times$  1.2 cm) to investigate their redox behaviors. The amount of PPV cast on each electrode was  $2.5 \times 10^{-7}$  mol/cm<sup>2</sup> to yield film thicknesses of 0.2  $\mu\text{m}$ .

FT-IR spectra were measured using a Bio-Rad/Digilab Model FTS-40 spectrophotometer. UV-Vis-NIR spectra were carried out on a Varian Model 2300 spectrophotometer. The electrochemical experiments were performed using a Princeton Applied Research Model 273 Potentiostat with a Houston Instruments Model 200XY Recorder. Cyclic voltammograms were measured in 0.1 mol/L NaClO<sub>4</sub> or LiClO<sub>4</sub> solution in acetonitrile.

Double potential step chronocoulometric experiments were carried out in 0.1 mol/L NaClO<sub>4</sub> solution in acetonitrile. The film was initially equilibrated at 0.0 V to ensure it was in the fully reduced state. The oxidative potentials ( $E_t$ ) chosen were 0.04, 0.08, 0.12, 0.16, and 0.20 V greater than the anodic oxidative peak potential ( $E_p$ ) of the film. After oxidation, the film was returned to the reduced state at 0.0 V.

## RESULTS AND DISCUSSION

### Preparation of PPV and Its Properties

The change in the IR spectra of a PPV film during heat treatment at 210°C for 4 hours under nitrogen indicates that the elimination reaction of the polyelectrolyte **IIb** could be carried out to a high degree of conversion. The same thermal treatment of PPV precursor polymer:PEO blends gave PPV:PEO polymer blends. Judging from the changes in the IR spectra, no thermal degradation of either PPV or PEO occurred under these conditions [26]. The UV-Vis-NIR spectra of a dark yellow PPV film exhibited a strong peak at 3.0 eV, which is due to the  $\pi$ - $\pi^*$  transition of the polymer [14]. The band gap energy was estimated to be 2.4 eV from the onset of the absorption.

Figure 1 shows the cyclic voltammograms of PPV and PPV:PEO blends on Pt. In both cases the amount of PPV cast on the working electrodes was the same ( $2.5 \times 10^{-7}$  mol/cm<sup>2</sup>) in order to compare the current responses. In Fig. 1(a) an anodic shoulder was found at 0.7 V vs Ag/Ag<sup>+</sup> and a cathodic peak at 0.46 V. In

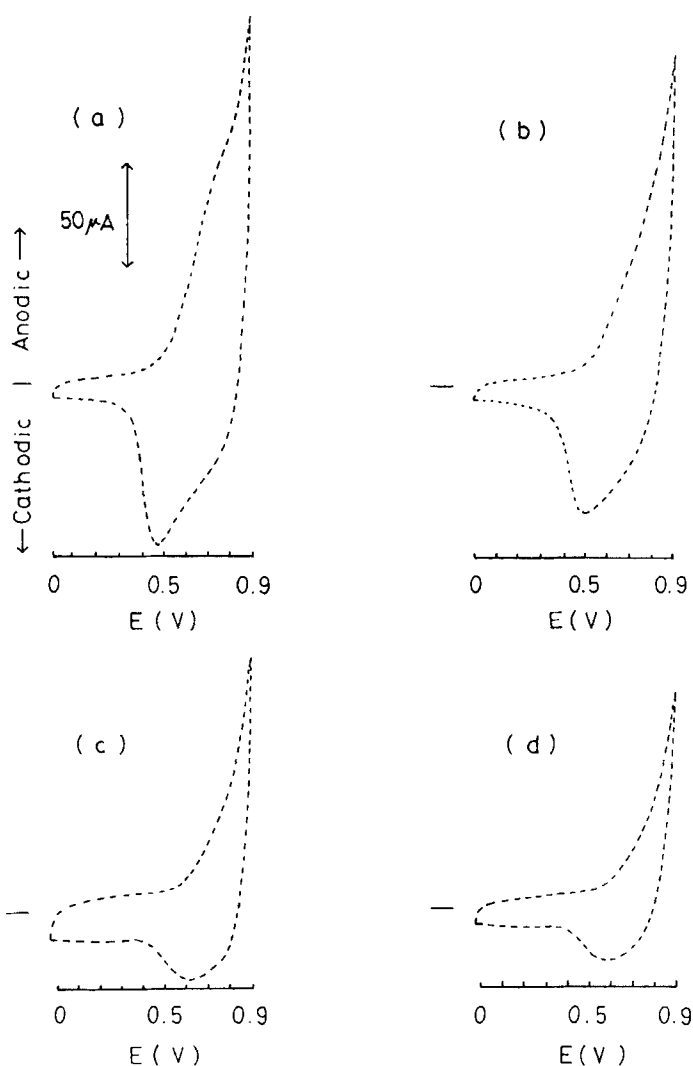


FIG. 1. Cyclic voltammograms of PPV and PPV:PEO (50:50) blend films. Scan rate: 100 mV/s. (a) PPV- $\text{NaClO}_4$ , (b) PPV- $\text{LiClO}_4$ , (c) PPV:PEO (50:50)- $\text{NaClO}_4$ , (d) PPV:PEO (50:50)- $\text{LiClO}_4$ .

the neutral state the film was yellow in color, and in the doped state it was black. In the other cases the current responses were quite similar with cathodic peaks observed around 0.5 V, although anodic shoulders were not found. In all cases the expected color change was observed and the current response was stable as the PPV was repeatedly doped and undoped. Scanning in the anodic region above 1.0 V caused a decrease in current with repetitive scanning because the films were overoxidized. Such a loss of electroactivity has also been found for polythiophenes [28–30] and polypyrrole [31]. For this reason the potential was always kept lower than 0.9 V to avoid deactivation of the film.

### Chronocoulometry

Chronocoulometric studies yield important information on charging rate and mechanisms of transport in conductive polymers [32, 33]. By developing an understanding of these charging and discharging processes, along with the effect of film thickness and morphology, the inherent limitations, the possibility for optimizing conductive polymer redox processes is possible. Figure 2 shows the chronocoulometric response for a PPV film on Pt as a function of the magnitude of the potential steps beyond the polymer's oxidative peak potential ( $E_f - E_p$ ) from an initial reductive potential of 0.0 V.  $E_f - E_p$  is the difference between the final applied potential and the polymer's oxidative peak potential as determined by cyclic voltammetry. The rate of oxidation increased with an increase in the magnitude of the potential step. At  $E_f - E_p = 0.20$  V, 13.9 C/mmol PPV was passed after 10 seconds of oxidation of a 0.2- $\mu\text{m}$  film which was equivalent to about 14% oxidation of the PPV repeat units. As a comparison, the amount of charge passed after 1 second with a potential step of 0.2 V for polypyrrole was equivalent to approximately 33% oxidation of the monomer unit [33]. The slower charging rate for PPV can be attributed to the difference in film morphologies. Electrochemically prepared polypyrrole film have open and porous structures, while the PPV films studied here are dense and space filling.

Charge ( $\log Q$ ) vs  $\log t$  plots (Figs. 3-5) were generated from the chronocoulograms, and they show that the charge passed varies as  $t^\alpha$  where  $\alpha$  is the transfer

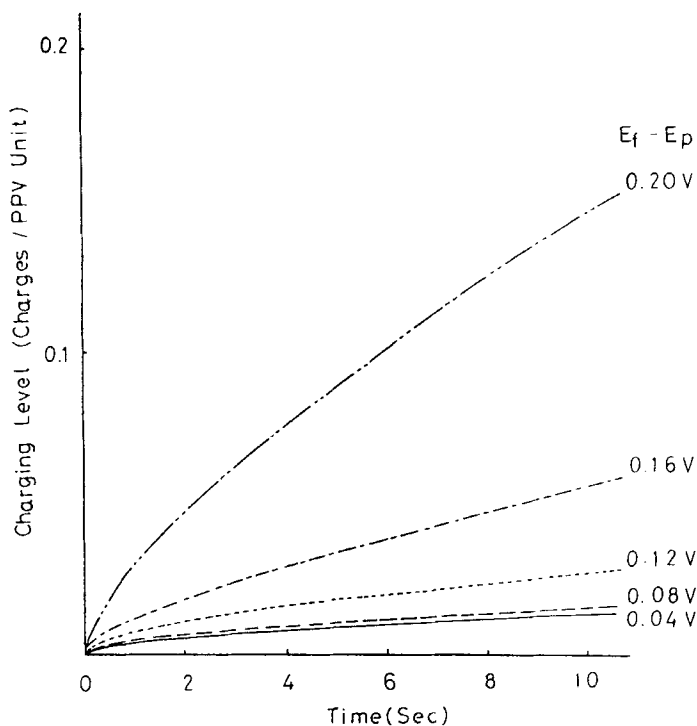


FIG. 2. Chronocoulometric response as a function of the magnitude of the potential step for PPV on Pt.

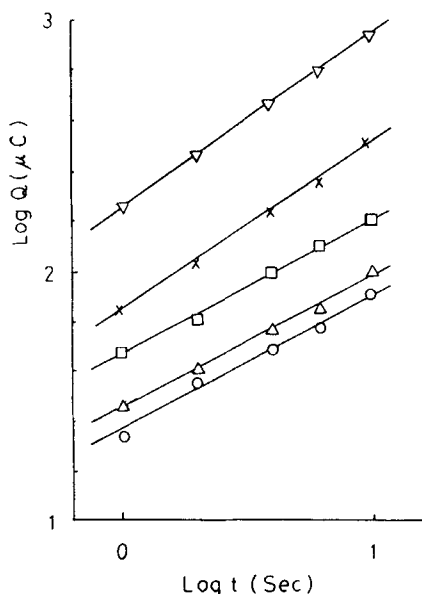


FIG. 3.  $\text{Log } Q$  vs  $\text{log } t$  plots of PPV on Pt. The magnitude of the potential steps were ( $\circ$ ) 0.04 V, ( $\triangle$ ) 0.08 V, ( $\square$ ) 0.12 V, ( $\times$ ) 0.16 V, ( $\nabla$ ) 0.20 V.

coefficient. The charge results and transfer coefficients for three different PPV electrodes are shown in Table 1. When using PPV/Pt, these slopes fall in the range of 0.52 to 0.70 as is typical for irregular electrode surfaces [34]. With smaller potential steps ( $E_f - E_p \leq 0.12$  V) these slopes were lower, tending to approach a value of 0.5, which is expected for Cottrell behavior. The transfer coefficient increased with an increase in the magnitude of the potential step, which might be brought about by a morphological change during doping at higher potentials. This deviation from Cottrell behavior is also observed for PPV/ITO and PPV:PEO/Pt electrodes which show increasing  $\alpha$  as a function of the potential step.

While this consistent change of  $\alpha$  with applied field suggests that the mechanism for charge transport in each electrode is similar, the overall doping rates are quite different. Correlation of the charge passed per PPV unit at a specific time (10 seconds) and  $E_f - E_p$  demonstrates this as illustrated in Table 1. For PPV/ITO, 10 seconds of doping at  $E_f - E_p = 0.2$  V yielded 8.63 C/mmol PPV, which corresponds to a charging level of 9%. This shows the importance of the PPV/substrate electrode interface since (as noted earlier) PPV/Pt doped to 14% under identical conditions. It is possible that the more polar and rougher ITO surface provides better contact with the precursor polyelectrolyte and, ultimately, PPV.

In an attempt to improve the doping rate, a PPV:PEO/Pt (50:50 wt%) was investigated. At  $E_f - E_p = 0.20$  V and  $t = 10$  seconds, the charging level was 5%, which is lower than that found for either PPV/Pt or PPV/ITO. Schlenoff et al. reported that the rates of electrochemical doping of PPV were strongly increased by PEO blend formation for thick films [24]. In those studies the rates were measured on films with thicknesses of 10–50  $\mu\text{m}$ , and doping proceeded very slowly for PPV



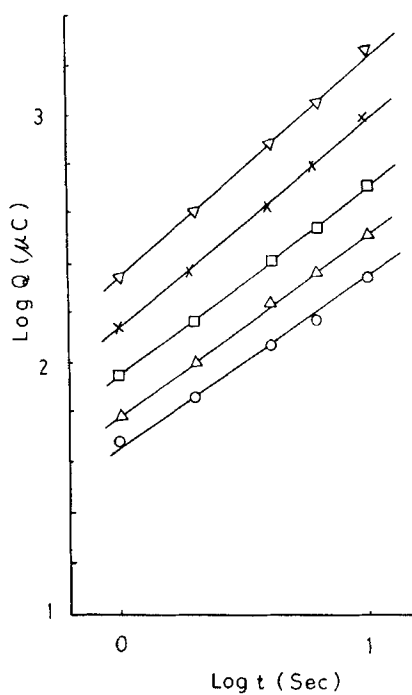


FIG. 4.  $\text{Log } Q$  vs  $\text{log } t$  plots of PPV on ITO. The magnitude of the potential steps were (○) 0.04 V, (△) 0.08 V, (□) 0.12 V, (×) 0.16 V, (▽) 0.20 V.

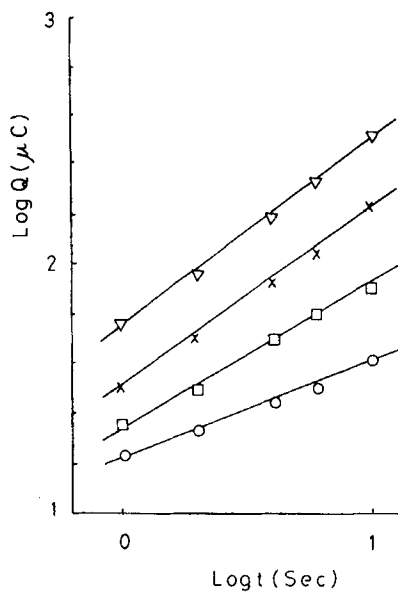


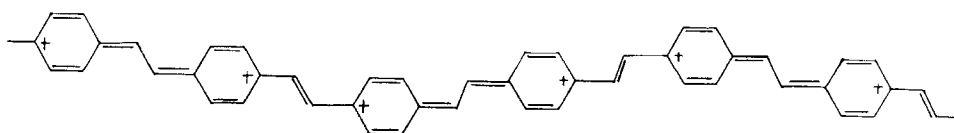
FIG. 5.  $\text{Log } Q$  vs  $\text{log } t$  plots of PPV:PEO (50:50) blend on Pt. The magnitude of the potential steps were (○) 0.04 V, (○) 0.08 V, (□) 0.12 V, (×) 0.16 V, (▽) 0.20 V.

TABLE 1. Charging Rate Data for PPV Films and Blends

$E_t - E_p$ in V	Polymer								
	PPV			PPV/ITO			PPV:PEO (50:50 wt%)		
	$\alpha$	$Q$ at 10 s in $\mu Q$	$Q$ /mol at 10 s in C/mmol	$\alpha$	$Q$ at 10 s in $\mu Q$	$Q$ /mol at 10 s in C/mmol	$\alpha$	$Q$ at 10 s in $\mu Q$	$Q$ /mol at 10 s in C/mmol
0.04	0.52	80	1.26	0.65	224	1.06	0.39	42	0.66
0.08	0.52	97	1.53	0.74	340	1.60	0.39	42	0.66
0.12	0.52	166	2.61	0.77	552	2.60	0.58	81	1.28
0.16	0.66	340	5.35	0.84	1040	4.91	0.71	168	2.65
0.20	0.70	880	13.9	0.89	1830	8.63	0.75	318	5.01

alone because the electrolyte was not able to penetrate the thick films well. The inclusion of a PEO phase enhanced the electrode polarity and allowed faster change and ion transport. In the experiments described here on thin films, thicknesses are approximately  $0.2 \mu\text{m}$ , the film could be doped quite easily without PEO, and using PEO blends did not increase the doping rates.

Extended period chronocoulometry was carried out to determine the extent and the end point of the charging process since the maximum charging level is a factor when considering the application of conductive polymers to energy storage devices. Figure 6 shows the extended period chronocoulograms of a PPV film as a function of the magnitude of the potential steps. As expected, the charging rates and maximum doping levels accessible increase with an increase in the potential steps. When the magnitudes of the potential steps were 0.16 and 0.20 V, the doping level was on the order of 1.0 charge per repeat unit, which suggests that PPV can be fully doped as indicated by Structure IV.



(IV)

When considering PPV or any other conductive polymer as a potential energy storage material for rechargeable batteries, the maximum accessible doping levels are quite important. The energy density of our fully doped PPV electrode is estimated to be  $532 \text{ W}\cdot\text{h/kg}$  if lithium and lithium perchlorate are used as anode and electrolyte, respectively. This value is much higher than those reported so far for polypyrrole ( $297 \text{ W}\cdot\text{h/kg}$ ) [35] and polyaniline ( $382 \text{ W}\cdot\text{h/kg}$ ) [36]. While this work indicates that high charge levels are possible in thin films, the charging process is quite slow.

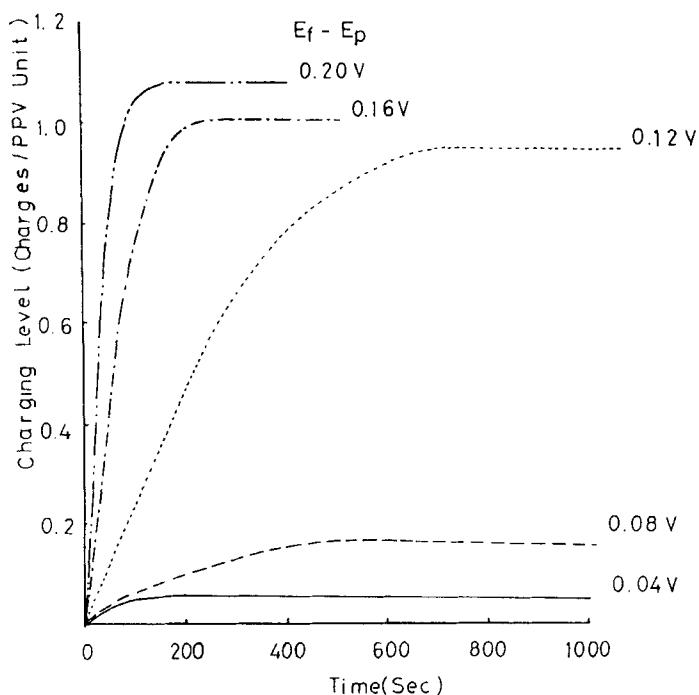


FIG. 6. Extended period chronocoulometry as a function of the magnitude of the potential steps for PPV on Pt.

### CONCLUSION

The electrochemical doping of PPV films was investigated. PPV films can be cycled between the doped and undoped states without decomposition. Using chronocoulometry, saturation charging levels on the order of one charge per PPV unit were obtained, indicating that PPV can be fully doped and may be a promising material for charge storage, although the charge transport process is slow.

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### REFERENCES

- [1] J. Roncali, A. Yassar, and F. Garnier, *J. Chem. Soc., Chem. Commun.*, p. 589 (1988).
- [2] A. F. Diaz, J. I. Castille, J. A. Logan, and W. Y. Lee, *J. Electroanal. Chem.*, 129, 113 (1981).

- [3] S. Tanaka, M. Sato, and K. Kaeriyama, *Makromol. Chem.*, **185**, 1295 (1984).
- [4] M. Sato, S. Tanaka, and K. Kaeriyama, *Synth. Met.*, **14**, 279 (1986).
- [5] M. Martinez, J. R. Reynolds, S. Basak, D. A. Black, D. S. Marynick, and M. Pomerantz, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 911 (1988).
- [6] J. H. Edwards and W. J. Feast, *Polym. Commun.*, **21**, 595 (1980).
- [7] D. G. H. Ballard, A. Courtis, I. M. Shirley, and S. C. Taylor, *J. Chem. Soc., Chem. Commun.*, p. 954 (1983).
- [8] V. Chaturvedi, S. Tanaka, and K. Kaeriyama, *Ibid.*, p. 1658 (1992); *Macromolecules*, **26**, 2607 (1993).
- [9] R. A. Wessling and R. G. Zimmerman, US Patents 3,401,152 (1968) and 3,706,677 (1972).
- [10] I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Polym. Commun.*, **25**, 327 (1984).
- [11] F. E. Karasz, J. D. Capistran, D. R. Gagnon, and R. W. Lenz, *Mol. Cryst. Liq. Cryst.*, **118**, 327 (1985).
- [12] G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, *Polym. Commun.*, **20**, 1441 (1979).
- [13] K. D. Gourley, C. P. Lillya, J. R. Reynolds, and J. C. W. Chien, *Macromolecules*, **17**, 1025 (1984).
- [14] K. Yoshino, T. Takiguchi, S. Hayashi, D. H. Park, and R. Sugimoto, *Jpn. J. Appl. Phys.*, **25**, 881 (1988).
- [15] H. Eckhardt, L. W. Shacklette, K. Y. Jen, and R. L. Elsenbaumer, *J. Chem. Phys.*, **91**, 1303 (1989).
- [16] I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Synth. Met.*, **17**, 639 (1987).
- [17] J. B. Schlenoff, J. Obrzut, and F. E. Karasz, *Phys. Rev.*, **B40**, 11822 (1989).
- [18] J. Obrzut and F. E. Karasz, *J. Chem. Phys.*, **87**, 6178 (1987).
- [19] J. Heinze, J. Mortensen, K. Mullen, and R. Schenk, *J. Chem. Soc., Chem. Commun.*, p. 701 (1987).
- [20] A. Pron, F. Genoud, M. Nechstein, and A. Rousseau, *Synth. Met.*, **31**, 147 (1989).
- [21] J. D. Stenger-Smith, R. W. Lenz, and G. Wegner, *Polymer*, **30**, 1048 (1989).
- [22] T. Kawai, T. Iwasa, T. Kuwabata, M. Onoda, and K. Yoshino, *Jpn. J. Appl. Phys.*, **29**, 1833 (1990).
- [23] C. W. Spangler and T. J. Hall, *Synth. Met.*, **44**, 85 (1991).
- [24] J. B. Schlenoff, J. M. Machado, P. J. Glatkowski, and F. E. Karasz, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 2247 (1988).
- [25] J. M. Machado, F. E. Karasz, and R. W. Lenz, *Polymer*, **29**, 1412 (1988).
- [26] J. M. Machado, J. B. Schlenoff, and F. E. Karasz, *Macromolecules*, **22**, 1964 (1989).
- [27] R. W. Lenz, C.-C. Han, J. Stenger-Smith, and F. E. Karasz, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 324 (1988).
- [28] J. R. Reynolds, S.-G. Hsu, and H. J. Arnott, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 2081 (1989).
- [29] E. W. Tsai, S. Basak, J. P. Ruiz, J. R. Reynolds, and K. Rajeshwar, *J. Electrochem. Soc.*, **136**, 3683 (1989).
- [30] B. Krische and M. Zagorska, *Synth. Met.*, **28**, C257 (1989).

- [31] F. Beck, P. Braun, and M. Oberst, *Ber. Bunsenges. Phys. Chem.*, *91*, 967 (1987).
- [32] P. G. Pickup and R. A. Osteryoung, *J. Electroanal. Chem.*, *195*, 271 (1985).
- [33] J. R. Reynolds, N. S. Sundaresan, S. Basak, M. Pomerantz, and C. K. Baker, *Ibid.*, *250*, 355 (1988).
- [34] R. de Levie, *Adv. Electrochem. Electrochem. Eng.*, *6*, 329 (1967).
- [35] H. Münstedt, G. Köhler, H. Möhwald, D. Naegle, R. Bitthin, G. Ely, and E. Meissner, *Synth. Met.*, *18*, 259 (1987).
- [36] T. Osaka, S. Ogano, K. Naoi, and N. Oyama, *J. Electrochem. Soc.*, *136*, 306 (1989).

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