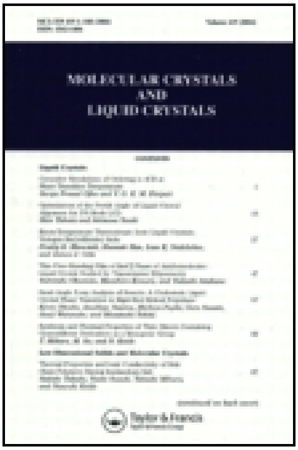

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Growth of Poly(pyrrole) Copolymer Films by Electrochemical Method and their Electrical Conductivity

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Growth of Poly(pyrrole) Copolymer Films by Electrochemical Method and Their Electrical Conductivity

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Growth of conductive copolymer PPy-g-PVC film via electrochemical route was discussed. The growing feature was dependent on electrolytic state. Optimum conditions for the copolymerization were found. Electrical conductivity of the copolymer was 10 times greater than that of the composite.

Key words: electrochemical polymerization; PVC-g-PPy copolymer; electrolytic condition; Chronoamperogram; electrical conductivity

INTRODUCTION

The π system of conducting polymers stands for having electric conductivity, and their redox reactivity allows them being applied to dynamic devices[1,2]. Chemical and electrochemical synthetic routes are well known. The former fits for producing massive products of poor physical and redox properties. The latter produces film type product having excellent redox reactivity but the yield is generally limited. A lot of studies concerning enhancement of physical and redox properties of conducting polymers were reported. Holdcroft reported the application of soluble poly(3-hexyl thiophene) to LED[3]. Lee showed PPy/PAN composite has good physical properties[4]. We also reported electrochemical properties of soluble poly(pyrrole)[5] and the usage of a modified PVC as a grafting center for poly(pyrrole)[6]. In this study, we tried to extend our previous work to elucidate the growth of the copolymer on the modified PVC film and find out the optimum conditions for preparation.

EXPERIMENTAL

Chemicals used in this study were ACS grade. Pyrrole was purified using an aluminum oxide (activated, 150 mesh, $155m^2/g$) column. A BAS 100/W potentiostat equipped with a Pt disk working ($0.78cm^2$), a Pt plate counter, and a Ag/AgCl (sat'ed KCl) reference electrodes was used for electrolysis. The electrochemical cell was purged and blanketed with dried N_2 prior to use.

The PVC precursor[6] films were spin-casted on the Pt working electrode. Dipping the electrode into polymerization solutions, potential cycle or constant potential was applied. Conductivity of the resulting films was measured with a Keithley 236 source and measure unit adopting a home made four-point probe.

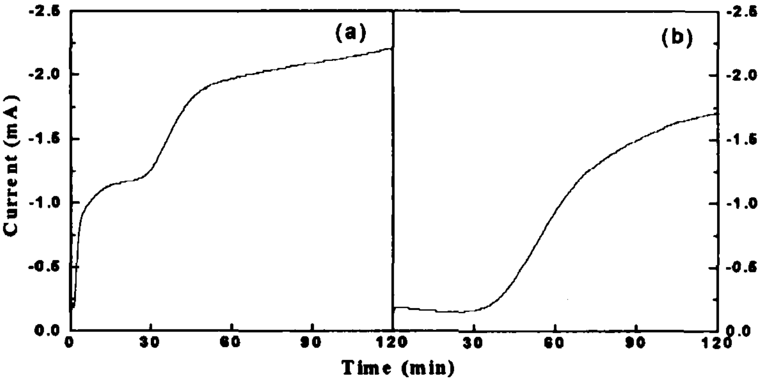

FIGURE 1. Chronoammperograms of the Pt electrode covered with (a) modified PVC and (b)PVC using 0.1M pyrrole in Acn solution of $LiClO_4$

RESULTS AND DISCUSSION

Constant potential polymerization has been performed to realize the growth of the copolymer. Current change in Fig. 1(a) shows sharp initial increase and next increase at 30min. In (b), little initial and large second increases at 40min are appearing. One can easily note the initial polymerization in (a) is occurring homogeneously inside the precursor film and later the PPy is growing out of the film, but in (b) initially little amount is formed, subsequently PPy formed at outside of the film. This matches well with the CV results in our previous study[6]. Dopant size effect was tested using ClO$_4^-$, BF$_4^-$, and tosylate ions. Only small dopants can produce reasonable $I_{p,a}$ values. $I_{p,a}$ is also proportional to electrolyte concentration in Fig. 2 (a), because the solution R is reduced. $I_{p,a}$ also increases rapidly in the solutions having monomer concentration greater than 0.3M in (b).

Conductivity is varying with the polymerization time. Fig. 3 shows the conductivity increases up to 5 S/cm at 60 min and saturated. This coincides with the results in Fig. 1(a). After 60 min, thick poly(pyrrole) is growing out of

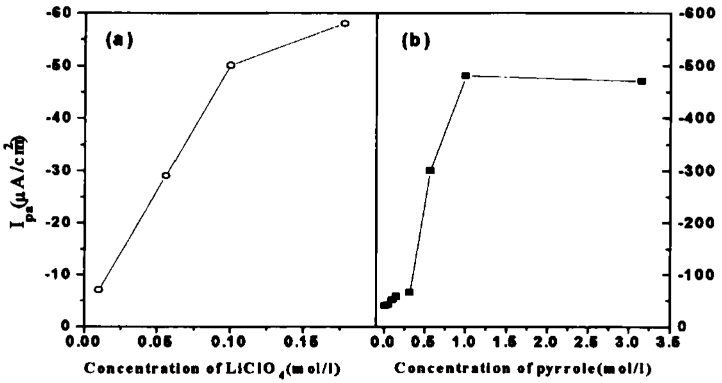

FIGURE 2. Dependence of oxidation peak current($I_{p,a}$) on electrolytic concentration (a) and monomer concentration, LiClO$_4$ used.

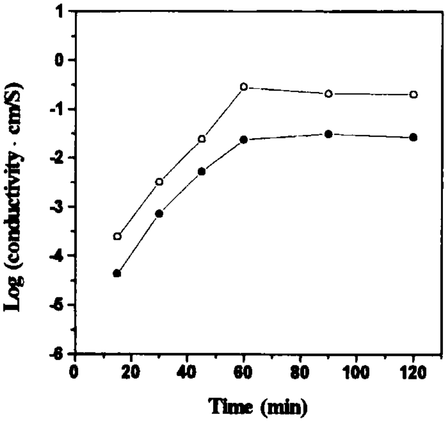

FIGURE 3. Conductivity of PPy copolymer (o), and composite(•)

the film. The composite shows similar conductivity trend. The electrical conductivity of the copolymer is 10 times greater than that of the composite.

CONCLUDING REMARKS

Electrochemical polymerization is able to produce homogeneous copolymer with the modified PVC matrix. Monomer concentration of 0.3M gives good growing rate. 5 S/cm is found to be the best conductivity for the copolymer and this is 10 times greater than that of simple composite of PPy/PVC.

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