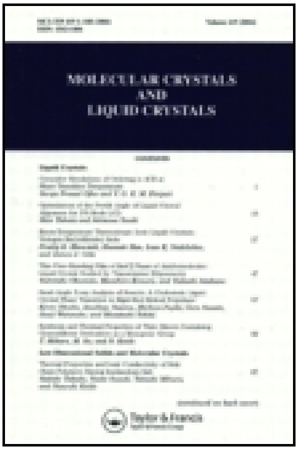

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Formation of Polypyrrole Copolymer in PSPMS Precursor Film by Electrochemical Polymerization

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Formation of Polypyrrole Copolymer in PSPMS Precursor Film by Electrochemical Polymerization

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The electrochemical copolymerization process of polypyrrole (PPy)in the PSPMS precursor film has been discussed. Constant potential electrolysis and SEM experiments showed that pyrrolyl groups in the precursor were oxidized to form grafting centers and PPy grew through the film.

Keywords: Polypyrrole; Electrochemical copolymerization; SEM; PSPMS

INTRODUCTION

PPy is a well-known conducting polymer having simple structure, high electronic conductivity, long term stability and excellent electrochromic properties, which could fit to advanced optoelectronic device applications. However, not many of applications are reported in these days, because this polymer is not easy to fabricate. The appearance of soluble PPy seems to overcome this difficulty, but it still shows weak mechanical properties.

In this view, composite formation or copolymerization rises as a main issue in conducting polymer chemistry. We have reported several times about composite formations and copolymerizations of PPy to fill out its complements[1]. In this paper, we have tried to elucidate the electrochemical copolymerization process of PPy in the poly(styrene-co-pyrrolylmethyl styrene) (PSPMS) precursor films.

EXPERIMENTAL

A Potentiostat and a cell equipped with platinum disc working, platinum plate counter, and Ag/AgCl (saturated KCl) reference electrodes were employed for the constant potential electrochemical polymerization. The Pt electrodes covered with PSPMS precursor or poly(styrene-co-chloromethyl styrene) (PSCMS) matrix films were electrolyzed in a mixture solution of acetonitrile and dichloromethane keeping pyrrole(0.1M) and $LiClO_4$(0.1M)[2]. SEM images were obtained from the films taken out of the Pt electrodes. Conductivity was measured using four-point probe method.

RESULTS AND DISCUSSION

Current transients in the constant potential electrolysis of PSPMS precursor films are shown in Fig. 1. Each curve shows a current maximum and a

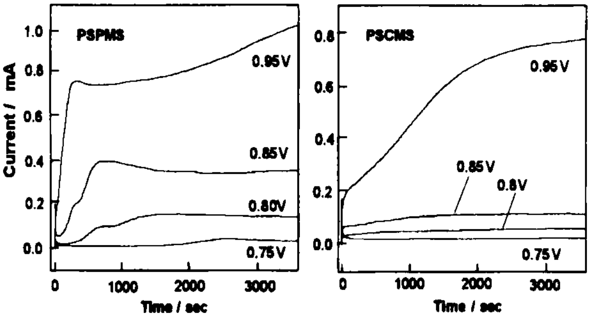

FIGURE 1. Chronoamperograms of Pt electrodes covered with PSPMS or PSCMS films in 0.1 M pyrrole solution.

plateau except the one for 0.75V. This type of transient strongly implies that two different species are involved in the polymerization process. Potential of 0.75 V is able to oxidize only the pyrrole species between Pt electrode and PSPMS film and form PPy growing centers . As the growing centers expand and coalesce, the current reaches a maximum and decays as $t^{-1/2}$[3]. Potentials higher than 0.75V are able to form the grafting centers at pyrrolyl groups of the precursor in addition to PPy formation at the interface region and their transients show both of current plateau and maximum. On the other hand, PSCMS transients, except 0.95V, show only a broad maximum due to the formation of PPy at the interface region, because the matrix has no pyrrolyl group to form the centers.

Results from SEM and conductivity measurements support the above explanation. SEM image in Fig.2 (A) shows that PSPMS film at 0.75V has small black spots irregularly distributed underneath the film. When the potential is increased, the black spots of growing centers are formed at

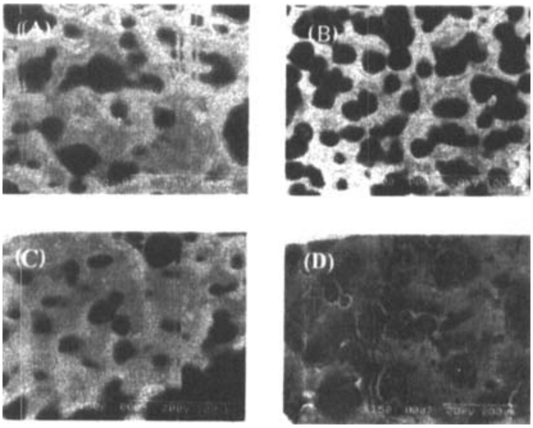

FIGURE 2. SEM images. (A) PSPMS at 0.75V, (B) PSPMS at 0.85V, (C) PSCMS at 0.80V, and (D) PSCMS at 0.95 V

interface and inside of the precursor and grow three dimensionally. Low potential electrolysis of PSCMS matrix film shows only PPy centers at interface as in (C). Applying the highest potential to PSCMS induces PPy to grow out of the matrix films (D). Conductivity changes of the electrolyzed PSPMS and PSCMS are compared in Fig. 3. The conductivity in PSPMS increases abruptly at low potential region due to the existence of the copolymerized PPy. A comparable conductivity only at 0.95V in PSCMS implies that PPy has been formed at the interface region only.

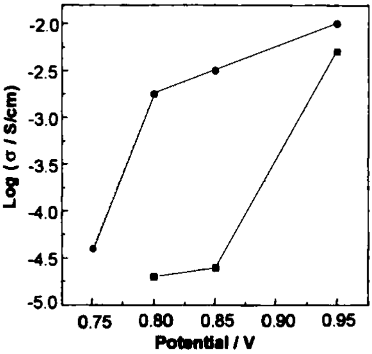

FIGURE 3. Solution side conductivity of the PSPMS(●) and PSCMS(■) at different electrolytic potentials.

Acknowledgments

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