POLYPYRROLE GRAFTS WITH POLY[(METHYL METHACRYLATE)-CO-(2-(N-PYRROLYL) ETHYL METHACRYLATE)]

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ABSTRACT

Conducting polymer grafts of pyrrole and poly[(methyl methacrylate)-co-(2-(N-pyrrolyl) ethyl methacrylate)] containing 0.7% PEMA units were prepared by potentiostatic anodic polymerization of pyrrole in different electrolytic media. Grafting between copolymer and pyrrole was achieved in media where tetrabutylammonium fluoroborate and sodium perchlorate were used as the supporting electrolytes. Characterizations were made by using FT-IR, DSC, TGA, SEM, CV, and elemental analysis. The conductivities of the resultant polymers seemed to be in the order of pure polypyrrole prepared under the same conditions. Copyright © 1997 Elsevier Science Ltd

KEYWORDS: A. organic compounds, C. differential scanning calorimetry (DSC), C. thermogravimetric analysis (TGA), D. electrical properties, D. electrochemical properties

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INTRODUCTION

Electronically conducting polymer films have attracted considerable attention in the electrochemical community due to the wide range of potential applications of these materials in electrocatalysis, molecular electronics, chemical and biosensor technologies, energy conversion, and storage. Polypyrrole (PPy) is one of the well-known conjugated heterocyclic polymers having high conductivity and environmental stability. It has been considered for use in many applications, including high energy batteries, electrochromic devices and modified electrodes [1]. A number of procedures have been proposed to prepare polypyrrole composites to improve the mechanical properties of polypyrrole.

PPy as a conductive polymer was electrochemically synthesized for the first time by Weiss et al. in 1965 [2] and later extensively studied by Diaz [3]. Conductive and free-standing films were obtained by potentiostatic anodic polymerization of pyrrole. Many research efforts also have been dedicated to obtaining stable, processable, and conductive polymeric materials [4].

Several composites of conducting polymers have been prepared for the simple reason of having polymers with good thermal and physical characteristics [5–7]. In some cases, however grafting to a certain extent between the insulating and the conducting polymer also has been observed [6–7].

In this work, we report on the electrochemical grafting of PPy and PMMA-co-PEMA-0.7, a special copolymer containing 0.7 mol% poly(ethylmethacrylate) units with a pendant pyrrole moiety [8–9]. This copolymer had been crosslinked via oxidative polymerization with $FeCl_3$ in nitromethane [10]. For copolymers in which the PEMA content is higher than 1 mol%, crosslinking between pendant pyrrole groups led to an increase in the glass transition temperature of the final product. Regarding the copolymers with less than 1 mol% PEMA units, crosslinking through the side groups was avoided. Furthermore, the oxidative grafting of pyrrole on the copolymer had been carried out [11], and it was found that copolymers with 0.7 mol% PEMA units were soluble.

EXPERIMENTAL

Materials. Sodium perchlorate (Aldrich), tetrabutylammonium tetrafluoroborate (Aldrich), pyrrole (Merck), and acetonitrile (AN) (Merck) were used as received. The synthesis of PMMA-co-PEMA-0.7 was reported earlier [8].

Synthesis of PPy/PMMA-co-PEMA-0.7. 0.5% (w/v) PMMA-co-PEMA-0.7 solution was prepared by dissolving the copolymer in acetonitrile. Prior to the electropolymerization of pyrrole, a platinum electrode was coated by dipping it several times into the solution of copolymer. Electrolytic films were synthesized in a three electrode–three compartment cell containing 0.024 M pyrrole in 0.1 M electrolyte solution. Electrolyses were done at a constant potential of 0.8 V versus Ag^0/Ag^+ (10^{-2} M) where the electrolytic medium was tetrabutylammonium tetrafluoroborate (TBFAB) and AN:H_2O, 16:84 (percent by volume). Electrolysis potential was 0.6 V versus Ag^0/Ag^+ (10^{-2} M) in the case of the $NaClO_4$-water medium. There was only 8% AN in this case which was used to swell the copolymer on the Pt electrode. Blank electrolyses (i.e., in the absence of pyrrole in the electrolytic medium) were carried out with PMMA-co-PEMA-0.7 coated electrodes to ensure that there were no

changes either chemically or gravimetrically in the polymer electrode. Several electrolyses with different feed pyrrole concentrations were run in order to determine the conductivities of the resultant polymers for both electrolytic media.

pristine polymer   electrolytic polymer
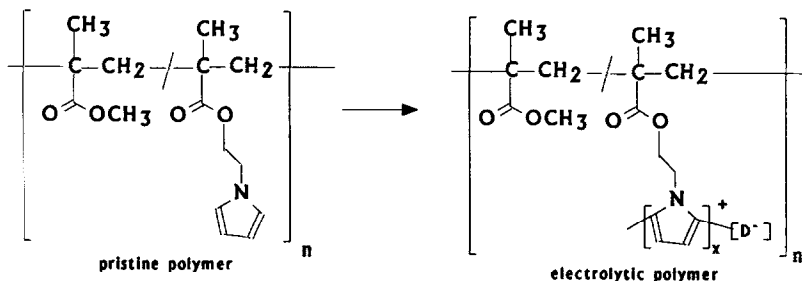
Electrochemical Studies. The electroactivities of the polymers were investigated by cyclic voltammetry between -0.2 and 1.1 V (versus Ag/Ag^+) in an electrolytic medium containing 0.1 M electrolyte and 0.0036 M pyrrole solution for both systems (TBAFB and $NaClO_4$). The cyclic voltammogram for the first route was obtained where the copolymer and TBAFB were present as dissolved in AN. The working electrode was a platinum wire. On the other hand, the voltammogram of the second route was taken in $NaClO_4$-H_2O medium (with a small amount of AN) and the working electrode in this case was a copolymer-coated platinum wire.

Measurements. Conductivities of the samples were measured by the four-probe technique. FT-IR (Nicolet 510) and scanning electron microscopy (JSM-6400) were used in order to characterize the polymer and the graft films. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were recorded on a Du Pont 2000 instrument. Elemental analyses were carried out with LECO CHNS 900 and LECO VHF 925 instruments.

RESULTS AND DISCUSSION

As soon as the polymerization started, the formation of black PPy on the surface of electrode could visually be observed. After a sufficient period of polymerization time (30 min), the film was successfully peeled off from the electrode. Both BF_4^- and ClO_4^- doped films were left in AN for 2 days after the polymerization. The polymer was filtered and put into fresh acetonitrile every other 2 hours until constant weight. It was found that they were only partially dissolved in AN (about 15%). Although AN is a suitable solvent for PMMA-co-PEMA-0.7, it seems that the remaining copolymer is still in the final product either through a chemical interaction between the two components or through a physical adsorption.

FT-IR spectra of the free-standing films showed characteristic bands of both PPy and the precursor polymer. Some of the observed peaks are C–H stretching at 2960 cm^{-1}, C=O band at about 1720 cm^{-1}, ring –C=C stretching at 1500 cm^{-1}, and C–O stretching at 1150 cm^{-1}. Moreover, disappearance of C–H bending vibration of N-monosubstituted pyrroles at 725 cm^{-1} supports the grafting of pyrrole on the copolymer backbone.

Cyclic voltammograms of the films indicated that both the copolymer and the electrolytic film were electroactive. In the cyclic voltammogram of PPy at bare electrode, the oxidation
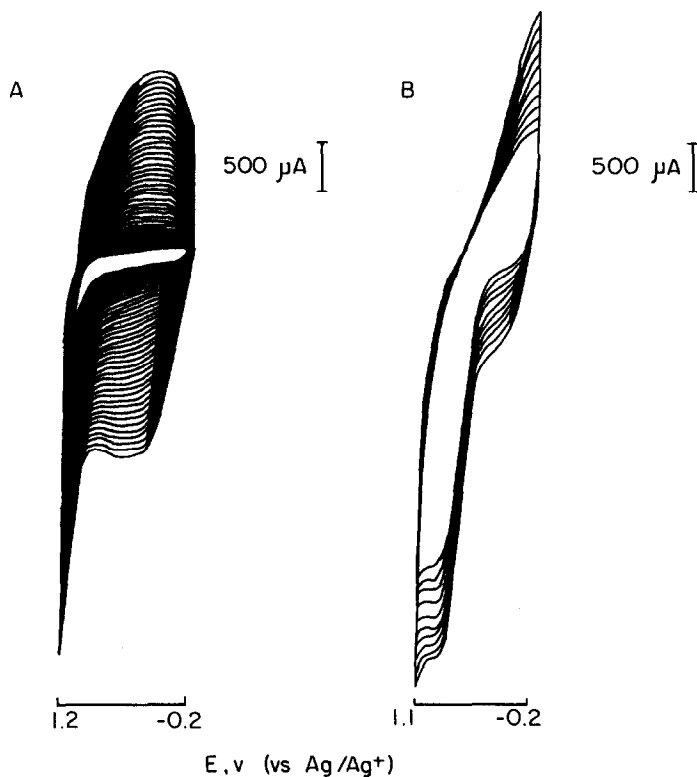
FIG. 1

Cyclic voltammogram of (A) PPy/PMMA-co-PEMA-0.7 in TBAFB-acetonitrile and (B) pyrrole on a PMMA-co-PEMA-0.7 coated electrode in $NaClO_4$-water medium.

peak is at about 0.55 V on the anodic sweep and the corresponding reduction peak is at about 0.25 V on the cathodic sweep. Multisweep cyclic voltammograms of PPy/PMMA-co-PEMA-0.7 in the TBAFB-acetonitrile and $NaClO_4$-water media are given in Figure 1. In the first case, oxidation peaks of PMMA-co-PEMA-0.7 and PPy are at 0.35 V and 0.65 V, respectively (Fig. 1A). The corresponding cathodic peaks are at 0.1 V and 0.25 V. Thin films of PPy which less than 0.1 μm are electroactive and can be switched between oxidized and neutral state at about 0.1 V versus SCE [12]. In aprotic solvents and in the absence of oxygen, the reaction is coulombically reversible and the film can be switched between the two oxidation states repeatedly without the decay of the electroactivity. Reversibility was observed for PPy/PMMA-co-PEMA-0.7 electrode, indicating the existence of a possible reaction between the copolymer and pyrrole. In the case of the $NaClO_4$-water system (there exists a small amount of acetonitrile to swell the copolymer), the anodic peak potentials are 0.2 V and 0.8 V (Fig. 1B). These reversible peaks reveal that pyrrole is also electroactive on the copolymer-coated electrode. Shifts in the Ep_a and Ep_c of the substrate suggest a different process than the pure pyrrole polymerization on the metal electrode.

   The glass transition temperature of PMMA-co-PEMA-0.7 is 130°C (Fig. 2A). However, thermal behaviors of the products were different than that of the pure copolymer (Fig. 2). Endothermic transitions at 93, 223, and 426°C were revealed for the BF_4^- doped films. This
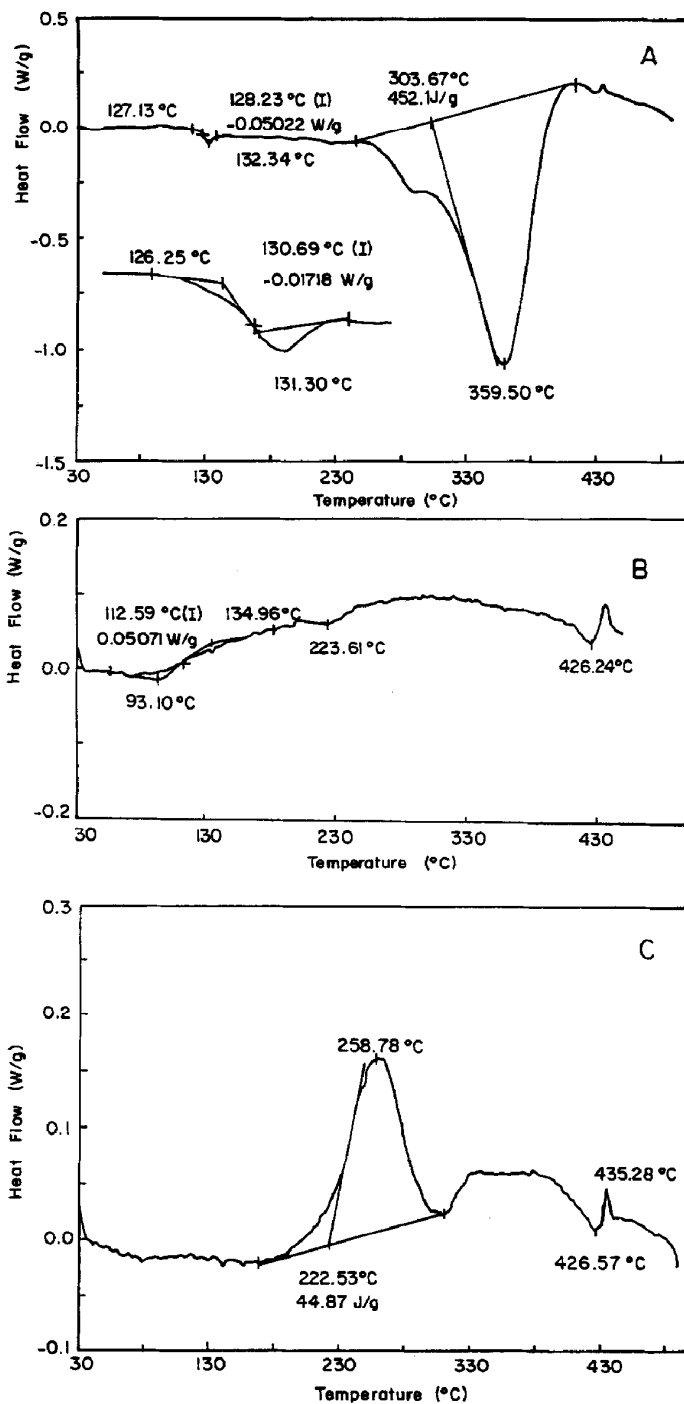
FIG. 2

DSC thermogram of (A) PMMA-co-PEMA-0.7, (B) PPy/PMMA-co-PEMA-0.7 (BF_4^- doped), and (C) PPy/PMMA-co-PEMA-0.7 (ClO_4^- doped).
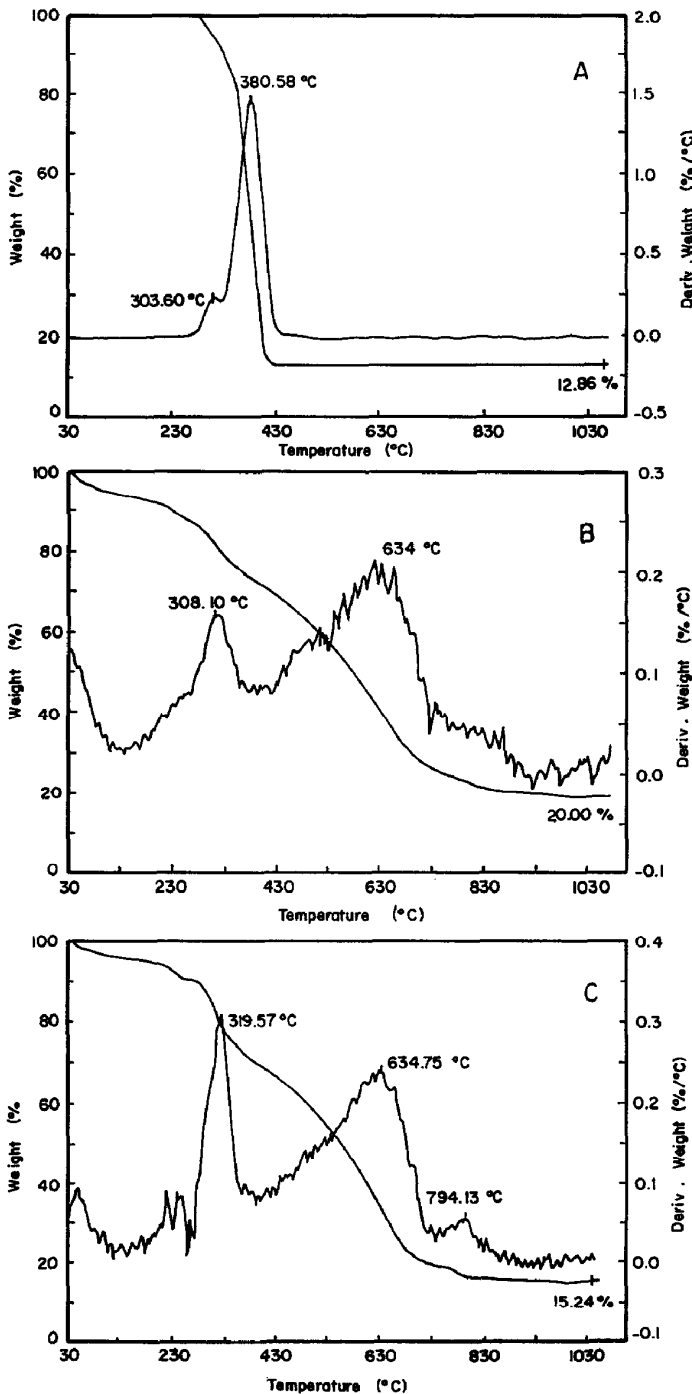
FIG. 3

Thermogravimetric analysis of (A) PMMA-co-PEMA-0.7, (B) PPy/PMMA-co-PEMA-0.7 (BF_4^- doped), and (C) PPy/PMMA-co-PEMA-0.7 (ClO_4^- doped).
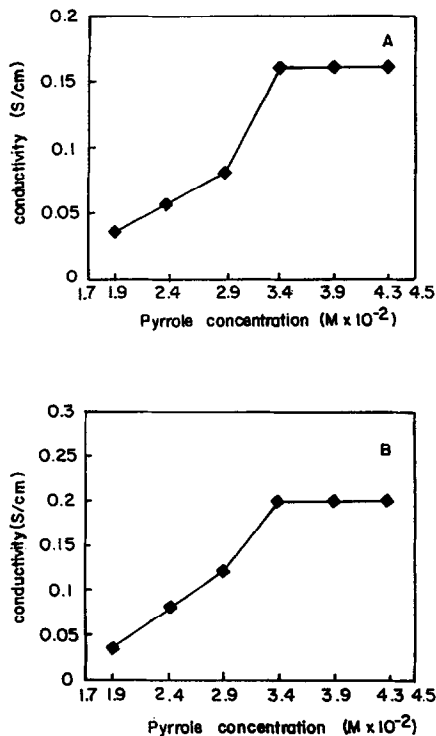
FIG. 4

Conductivity versus feed pyrrole for (A) PPy/PMMA-PEMA-0.7 (BF_4^- doped) and (B) PPy/PMMA-PEMA-0.7 (ClO_4^- doped).

behavior was not observed when the copolymer was oxidatively crosslinked in the absence of pyrrole [10]. Thus, the thermal behaviors of polypyrrole grafted copolymer and the crosslinked copolymer are quite different. Another aspect is the presence of the 93°C peak, which is quite lower than the Tg of the pristine copolymer. It seems like there exists a substantial difference between $FeCl_3$ grafting and electrochemical grafting of polypyrrole onto the copolymer. Although the dopant is different (BF_4^-), this may not account for the difference. We believe that the electrochemical method is more selective and the chain length of the pyrrole on the backbone is shorter. In the case of the ClO_4^- doped film, an exothermic peak was observed at around 222°C corresponding to the degradation of perchlorate (Fig. 2C).

In the thermogravimetric analysis of PMMA-co-PEMA-0.7, there existed about 10% weight loss at 303°C and 78% loss at 380°C (Fig. 3A). For the BF_4^- doped polymer, 30% weight loss at 308°C and 50% weight loss at 630°C were recorded (Fig. 3B). In addition to these weight losses, an additional 5% weight loss was observed at 794°C for the ClO_4^- doped polymer (Fig. 3C). It is thus safe to say that PPy/PMMA-co-PEMA-0.7 polymers are thermally more stable than the PMMA-co-PEMA-0.7 copolymer, although the onset of decomposition is above 300°C for the pure copolymer, whereas about 200°C for the electrolytic film. This low onset decomposition of the electrolytic film arises from the decomposition of the units with long polypyrrole chains.
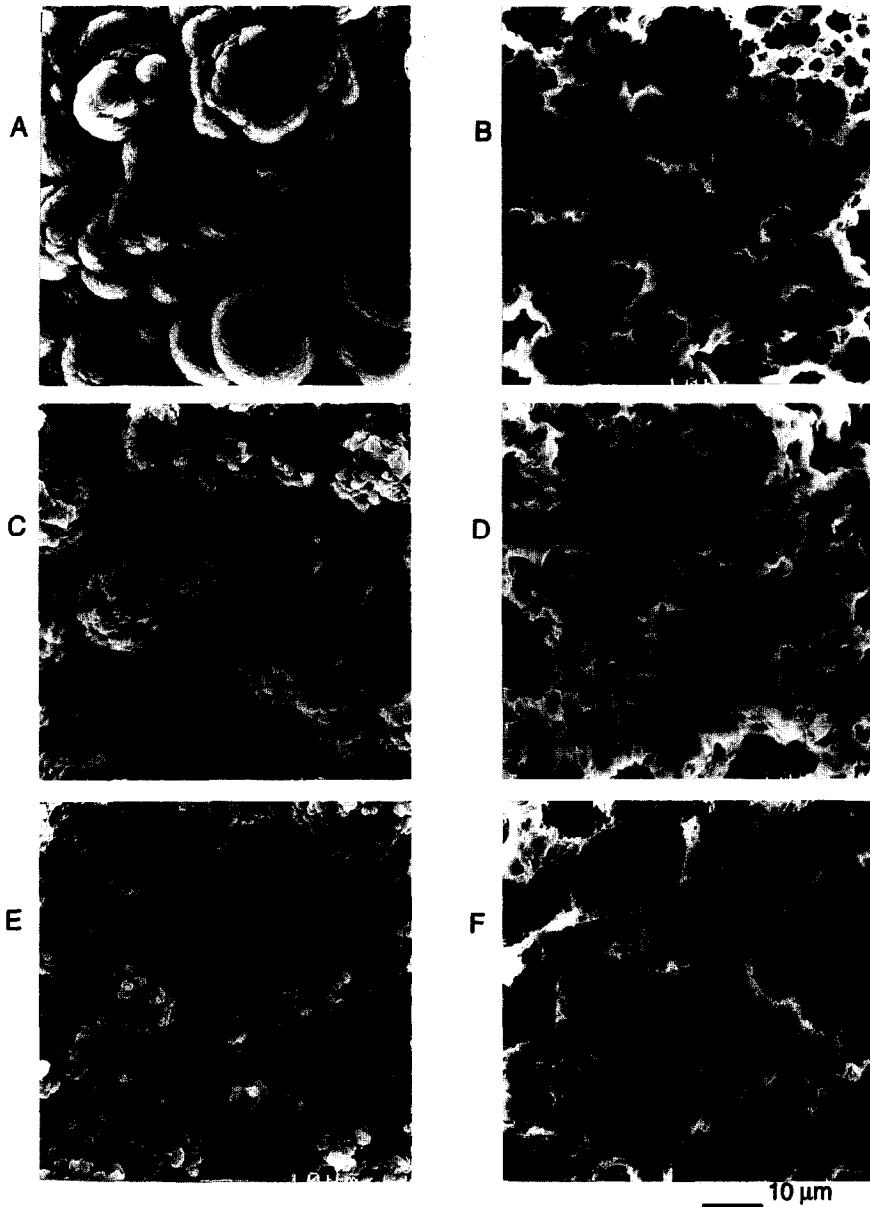
FIG. 5

Scanning electron micrograph of (A) solution side of pure PPy (BF_4^- doped), (B) electrode side of pure PPy (BF_4^- doped), (C) solution side of unwashed PPy/PMMA-co-PEMA-0.7 (BF_4^- doped), (D) electrode side of unwashed PPy/PMMA-co-PEMA-0.7 (BF_4^- doped), (E) solution side of washed PPy/PMMA-co-PEMA-0.7 (BF_4^- doped), and (F) electrode side of washed PPy/PMMA-co-PEMA-0.7 (BF_4^- doped).
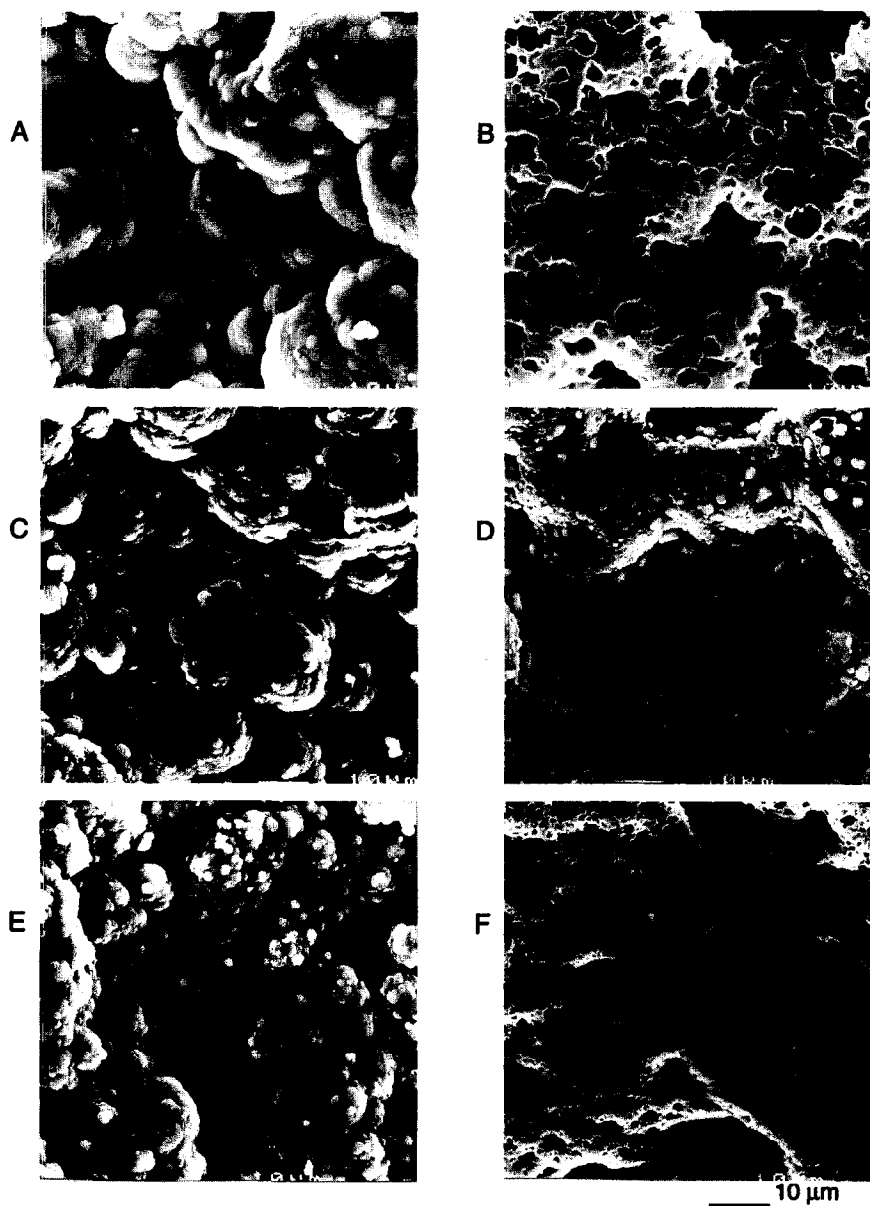
FIG. 6

Scanning electron micrograph of (A) solution side of pure PPy (ClO_4^- doped), (B) electrode side of pure PPy (ClO_4^- doped), (C) solution side of unwashed PPy/PMMA-co-PEMA-0.7 (ClO_4^- doped), (D) electrode side of unwashed PPy/PMMA-co-PEMA-0.7 (ClO_4^- doped), (E) solution side of washed PPy/PMMA-co-PEMA-0.7 (ClO_4^- doped), and (F) electrode side of washed PPy/PMMA-co-PEMA-0.7 (ClO_4^- doped).

As a result of elemental analyses, doping levels were found to be 20% and 3% for BF_4^- and ClO_4^- ions, respectively. The polypyrrole chain grafted onto the polymer backbone in the first case is believed to be longer than that of the second one. The number of pyrrole rings incorporated to the copolymer was found to be about 80 in BF_4^- doped PPy/PMMA-co-PEMA films, but about 60 for the ClO_4^- doped films.

Conductivities of the products and pure polypyrrole were in the same order of magnitude. As a result of electrolyses with various volumes of feed pyrrole, the threshold concentration was found to be 3.4×10^{-2} M, which corresponds to the threshold conductivity of 0.2 S/cm for both TBAFB and $NaClO_4$ systems (Fig. 4). That means that above this feed concentration, conductivity of the resultant film does not change by increasing the concentration of pyrrole in the electrolysis medium.

Pure PPy (Figs. 5A and 5B) and the graft films (5C and 5D) have similar morphologies for both the solution and the electrode sides of the electrolytic films, although the solution side of the graft film is not exactly the same as that of the pure polypyrrole synthesized under the same conditions. When the graft films were washed with AN (Figs. 5C and 5D), the surface appearances of both sides of the films did not change much, which may be considered as an indication for the presence of pyrrole chains attached to the backbone of PMMA-co-PEMA-0.7. The same argument is also valid for perchlorate-doped films (Fig. 6).

Conductive PPy/PMMA-co-PEMA-0.7 films were synthesized as a result of potentiostatic electropolymerization of pyrrole on PMMA-co-PEMA-0.7 coated electrodes. The results revealed that grafting pyrrole onto the copolymer was feasible. Moreover, thermal stability of the copolymer was improved via grafting with polypyrrole.

ACKNOWLEDGMENTS

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