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POLYPYRROLE GRAFTS SYNTHESIZED VIA ELECTROCHEMICAL POLYMERIZATION

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ABSTRACT

Electrically conducting polypyrrole grafts with poly[(methyl methacrylate)-co-(2-(N-pyrrolyl) ethyl methacrylate)] (PMMA-co-PEMA) were synthesized by constant potential electrolysis. Cyclic Voltammetry, DSC, TGA, SEM and elemental analysis were used in order to characterize the free standing films. Conductivities of the polymers were measured by a four-probe technique.

INTRODUCTION

Polypyrrole is a conducting polymer which can be electrochemically doped and undoped with electrolyte anions in aqueous and non-aqueous solutions. The quality and physical properties of electrodeposited PPy films are affected by the substrate, solvent, synthesis procedure, temperature, concentration, the nature of the electrolyte species and the type of the dopant in the film.

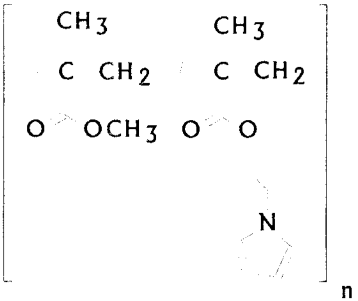
Since the first treatment on the synthesis of conducting polypyrrole (PPy) via the electrochemical oxidation of pyrrole [1], numerous studies have been reported concerning the conductive polymer synthesis [2-4]. The most successful method to form polymeric materials was found to be the electrochemical polymerization of pyrrole on an electrode coated with an insulating polymer [5-8]. An alternative method to composites had been utilized via grafting pyrrole on insulating polymers. Stanke *et al.* comparatively studied two synthetic ways to synthesize copolymers of methyl methacrylate(MMA) and 2-(N-pyrrolyl) ethyl methacrylate with pyrrole containing side groups [9]. MMA and 2-bromo ethyl methacrylate (BEMA) were copolymerized and a pyrrole moiety was introduced into the copolymer by using polymer analogous reaction [10]. It has been demonstrated that grafting between pyrrole and PMMA-co-PEMA-7 (7 mol percent PEMA content) can be achieved via oxidative polymerization of pyrrole with $FeCl_3$ in nitromethane, and these films were insoluble [11]. This copolymer had also been crosslinked via oxidative polymerization with $FeCl_3$ in nitromethane [12]. Recently, we have pointed out the electrochemical synthesis of graft polymers of methyl methacrylate-ethyl methacrylate units and pyrrole by using a two-step procedure [13]. In that, the grafting process has been carried out on a PMMA-co-PEMA coated electrode.

Here we studied the synthesis of graft polymers onto bare platinum electrodes in a medium containing the supporting electrolyte, pyrrole and the PMMA-co-PEMA insulating polymer. This method provides a single step procedure since the coating of the anode with the insulating polymers is not necessary.

EXPERIMENTAL

Materials

PMMA-co-PEMA copolymers were synthesized by methods reported earlier [9]. The structure of the copolymer is:



pristine polymer

The copolymers have two different structures in the sense that they differ in 2-(N-pyrrolyl) ethyl methacrylate content. Pyrrole (Merck) and acetonitrile (AN) (Merck) were used as received. Sodium p-toluene sulphonate was prepared by titrating p-toluene sulfonic acid monohydrate (Aldrich) with sodium hydroxide. Tetrabutylammonium tetrafluoroborate (TBAFB) was supplied by Aldrich.

Preparation of the Films

The syntheses of the films were carried out in a three electrode potentiostatic system under nitrogen atmosphere in aqueous acetonitrile (AN:H_2O:1:1). The working and counter electrodes were bare platinum foils with a 1.5 cm^2 area. The voltage was kept constant at 1.0 V versus Ag^o/Ag^+ (10^{-2} M) during the electrolyses. After the polymerizations, BF_4^- doped PPy/PMMA-co-PEMA films were washed with acetonitrile; p-TS^- doped films were washed with water and acetonitrile, and dried at 50°C. Polymerization time was about 20 minutes, and the concentrations of pyrrole and the electrolyte were 0.06 M and 0.1 M, respectively. 0.04 g of PMMA-co-PEMA-7 (7 mol% PEMA) or PMMA-co-PEMA-0.7 (0.7 mol% PEMA) were utilized in an electrolysis cell with 60 ml capacity.

Measurements

Thermal gravimetry analysis (TGA) studies were recorded on a Du Pont 2000 instrument. Scanning electron microscope (SEM) (JSM-6400) was used to study the surface morphology of the films. Conductivities of the samples were measured using a four-probe technique. Cyclic voltammetry was utilized in order to study electroactivities of the monomer and the polymers. The multi-scan voltammograms were recorded in a potential range -0.2 to +1.4 V in 0.1 M electrolyte and 0.0036 M pyrrole solution.

RESULTS AND DISCUSSION

For both electrolyte systems, electrochemical polymerizations yielded free standing films that could be easily peeled off the electrode surface. When these films were washed with the solvent of pristine copolymer (acetonitrile) for 3 days and dried, there was only 8% weight loss for BF_4^- doped PPy/PMMA-co-PEMA-0.7 (0.7 mol percent PEMA content) films and no losses were found for the others. This may be interpreted as an indication of a chemical interaction between insulating and conducting polymers. This possibility can be checked with the help of cyclic voltammetry studies, since CV of pure polypyrrole is well defined in terms of reversibility and electroactivity. PMMA-co-PEMA-0.7 itself did not show any detectable redox peaks in aqueous p-TS$^-$ solution (AN:H_2O:1:1) (Figure 1a) whereas PMMA-co-PEMA-7 revealed a certain electroactivity (Figure 1c). This can be attributed to the presence of 7 mol percent of pyrrole moieties. However, this electroactivity disappeared for the successive runs which means that the possibility of self crosslinking through electrochemical coupling in the absence of pyrrole is unlikely. Cyclic voltammograms of the polymers in the presence of pyrrole indicated electroactivity increasing with the number of scans in a medium where NapTS was used as the electrolyte (Figures 1 b and d). In the TBAFB case, both copolymers gave redox activity, especially for PMMA-co-PEMA-7 due to the higher concentration of pyrrole moieties on the backbone (Figures 2 a and c). Redox activities were decreased for the multiple runs as was the p-TS$^-$ case. Cyclic voltammograms of PPy/PMMA-co-PEMA films indicated anodic and cathodic peak potentials both for PPy and PMMA-co-PEMA (Figures 2 b and d). Reversibility and increase in the height of redox peaks with increasing number of scans for all of the products show that PPy was also electroactive on the copolymer. After twenty runs, the cyclic voltammograms resemble that of pure polypyrrole, indicating the propagation of pyrrole polymerization through the pyrrole group on the PEMA backbone.

In thermal gravimetry analyses of the PMMA-co-PEMA.7 and PMMA-co-PEMA.0.7, the first derivative of the main weight loss is around 400°C. Triple weight loss patterns were recorded for the grafts and they were still remaining at 1070°C (Figures 3 and 4). However, double weight loss patterns were observed in the case of the graft films synthesized as a result of electropolymerization of pyrrole on the PMMA-co-PEMA coated electrodes [13, 14]. It was observed that the PPy/PMMA-co-PEMA films were thermally more stable than the pristine copolymers. The results of thermal gravimetry analysis can be seen from Table 1.

SEM photographs indicated that the films have very homogeneous surfaces and similar appearances were obtained for washed and unwashed films (Figures 5-8). This is a sign of propagation of Py chains on PMMA-co-PEMA rather than separate Ppy chains together with the insulating copolymer.

It was observed that the solution and electrode sides of the films have equal conductivities. Conductivities of the graft films were around 1.0 S/cm which are very close to pure PPy that was synthesized under same conditions. There is no difference between conductivities of PPy/PMMA-co-PEMA-7 and PPy/PMMA-co-PEMA-0.7 films and seems to be independent of the type of electrolyte.

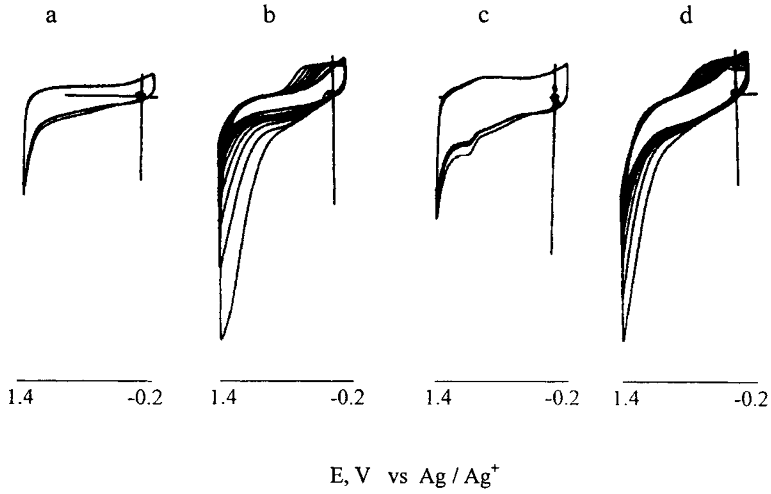


Figure 1. Cyclic voltammograms (NapTS) of
(a) PMMA-co-PEMA-0.7, (b) PPy/PMMA-co-PEMA-0.7,
(c) PMMA-co-PEMA-7, (d) PPy/PMMA-co-PEMA-7.

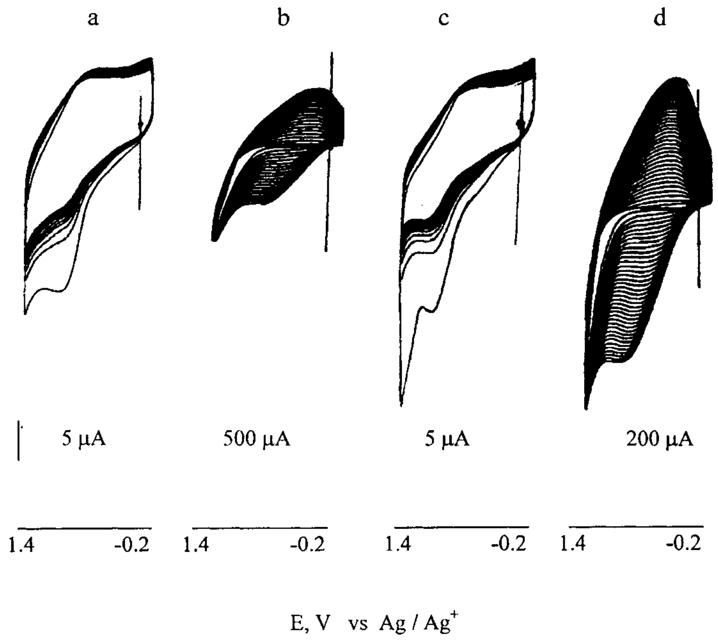


Figure 2. Cyclic voltammograms (TBAFB) of
(a) PMMA-co-PEMA-0.7, (b) PPy/PMMA-co-PEMA-0.7 ,
(c) PMMA-co-PEMA-7, (d) PPy/PMMA-co-PEMA-7.

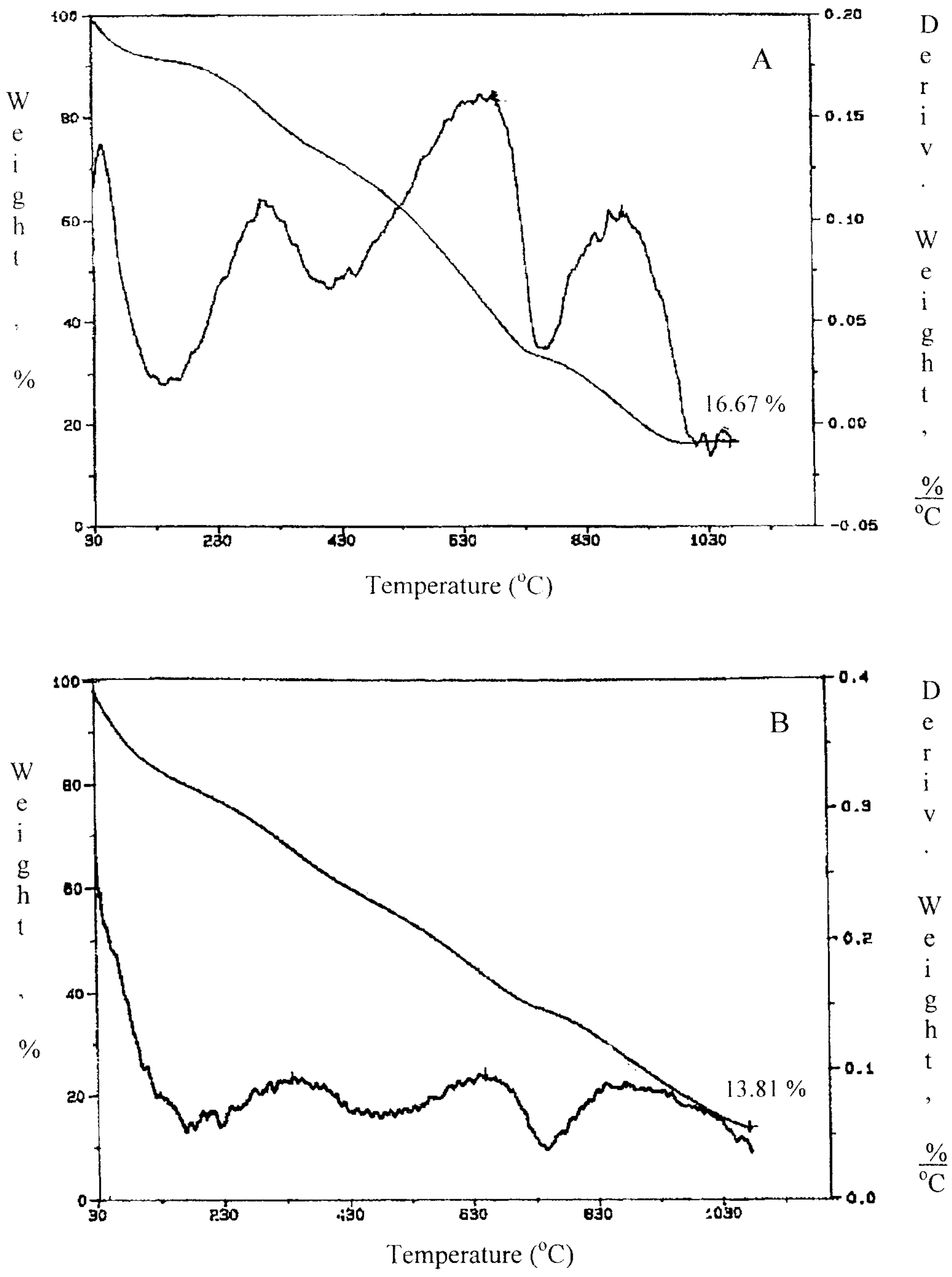


Figure 3. Thermal gravimetric analyses of (a) BF_4^- doped PPy/PMMA-co-PEMA-7, (b) BF_4^- doped PPy/PMMA-co-PEMA-0.7.

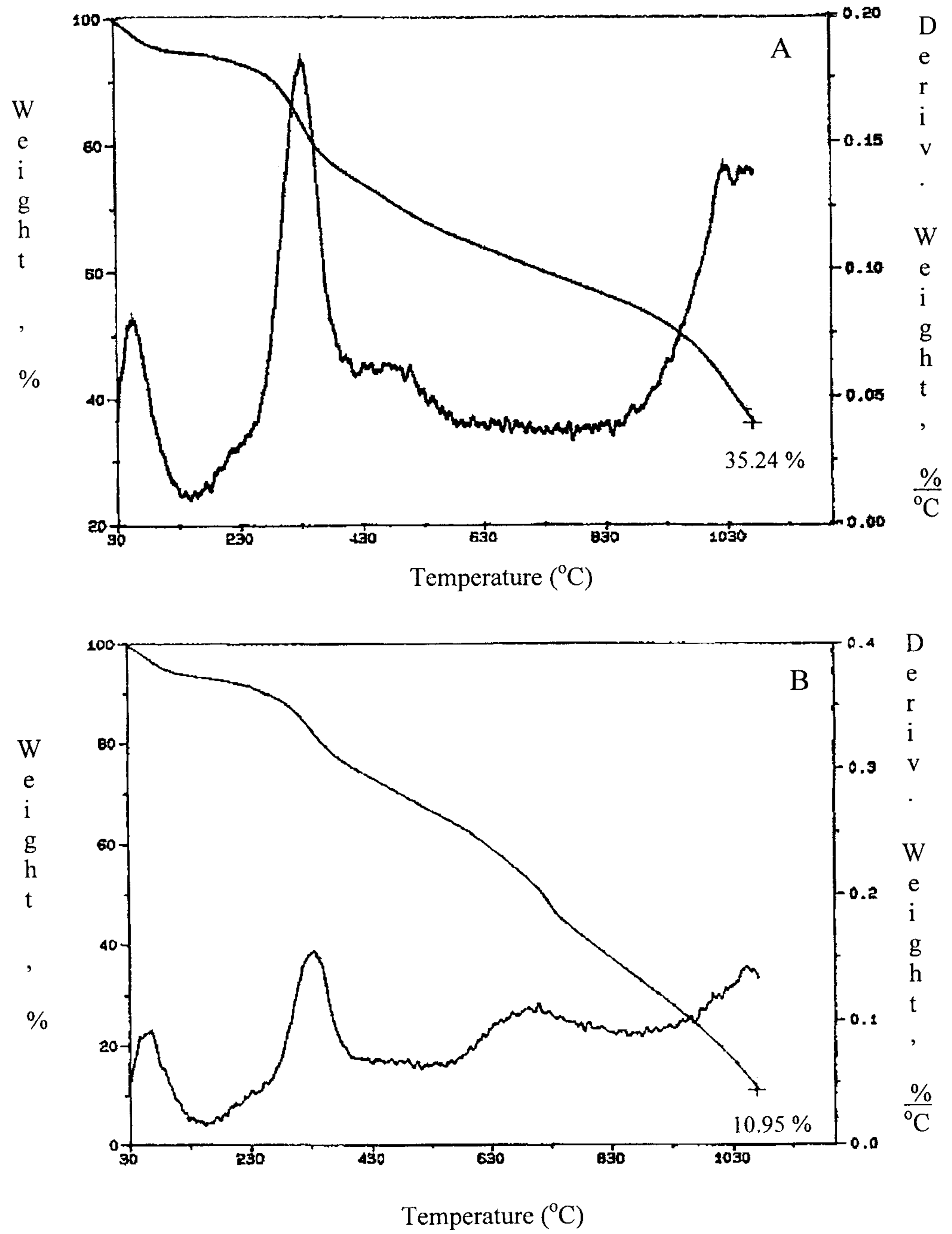


Figure 4. Thermal gravimetric analyses of (a) p-TS$^-$ doped PPy/PMMA-co-PEMA-7, (b) p-TS$^-$ doped PPy/PMMA-co-PEMA-0.7.

TABLE 1. The Results of Thermal Gravimetry Analysis of the Films Synthesized Via Single-Step Process[a]

p-TS$^-$ doped PPy/PMMA-co-PEMA-0.7	19 % at 336 °C	34 % at 728 °C	36 % at 1030 °C	11 % remained at 1080 °C
p-TS$^-$ doped PPy/PMMA-co-PEMA-7	17 % at 333 °C	10 % at 530 °C	38 % at 1000 °C	35 % remained at 1070 °C
BF$_4^-$ doped PPy/PMMA-co-PEMA-0.7	32 % at 338 °C	24 % at 638 °C	30 % at 880 °C	14 % remained at 1070 °C
BF$_4^-$ doped PPy/PMMA-co-PEMA-7	18 % at 300 °C	41 % at 682 °C	24 % at 930 °C	17 % remained at 1070 °C

a: Percentages of weight loss at indicated temperatures

Elemental analyses of the films also support the idea of grafting of pyrrole onto the backbone of the copolymer. Calculations based on the ratio of dopant anions to N mol percentages give reasonably average degree of doping and the chain length of pyrrole on the polymer backbone. The results indicated that the chain length of p-TS$^-$ doped polypyrrole grafted on PMMA-co-PEMA is longer than BF$_4^-$ doped ones. The average number of pyrrole rings was found to be 110 for p-TS$^-$ doped PPy/PMMA-co-PEMA-0.7 and 355 for PPy/PMMA-co-PEMA-7. These numbers were 112 for the BF$_4^-$ doped PPy/PMMA-co-PEMA-0.7 and 220 for PPy/PMMA-co-PEMA-7 films. Doping levels were different for each film; 24 % for p-TS$^-$ doped PPy/PMMA-co-PEMA-0.7, 30 % for PPy/PMMA-co-PEMA-7, 32% for BF$_4^-$ doped PPy/PMMA-co-PEMA-0.7 and 19% for PPy/PMMA-co-PEMA-7.

As a result, single-step electrochemical polymerization is also feasible for the synthesis of electrically conducting, homogeneous PPy/PMMA-co-PEMA films as well as the two-step (copolymer coating on anode) process.

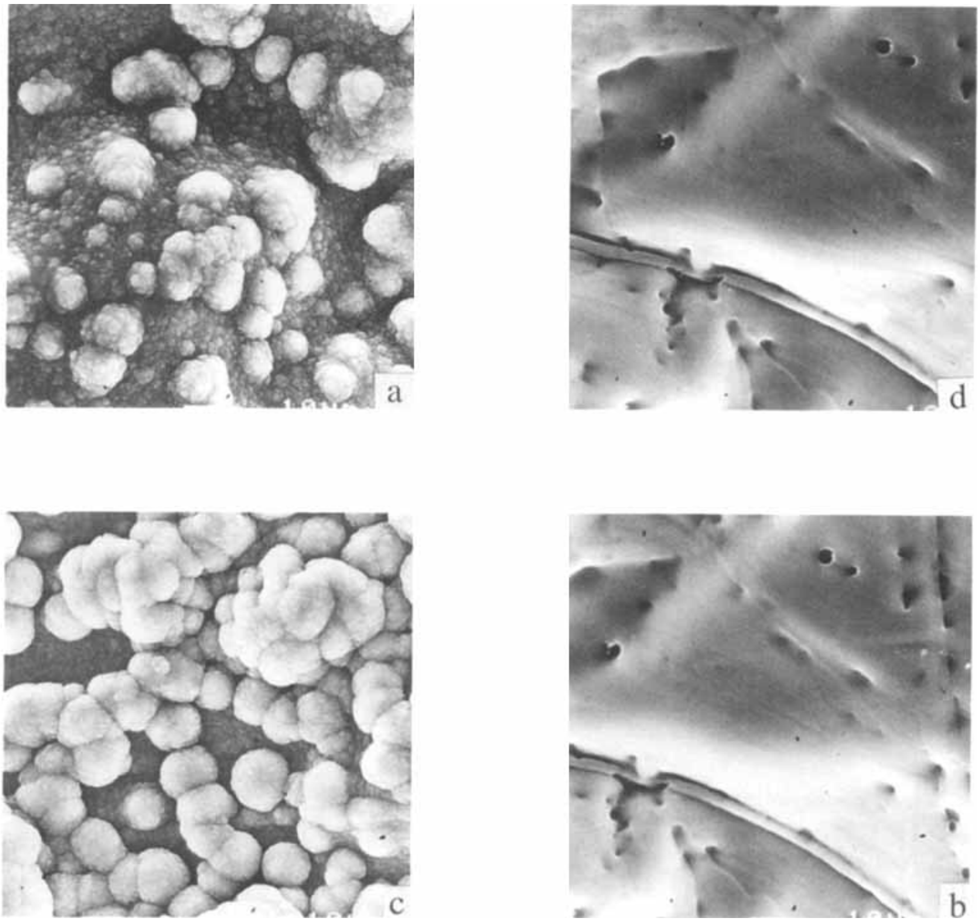


Figure 5. SEM photographs (1000 magnification) of BF_4^- doped polymers:
a) the solution side of PPy/PMMA-co-PEMA-0.7,
b) the electrode side of PPy/PMMA-co-PEMA-0.7,
c) the solution side of washed PPy/PMMA-co-PEMA-0.7,
d) the electrode side of washed PPy/PMMA-co-PEMA-0.7.

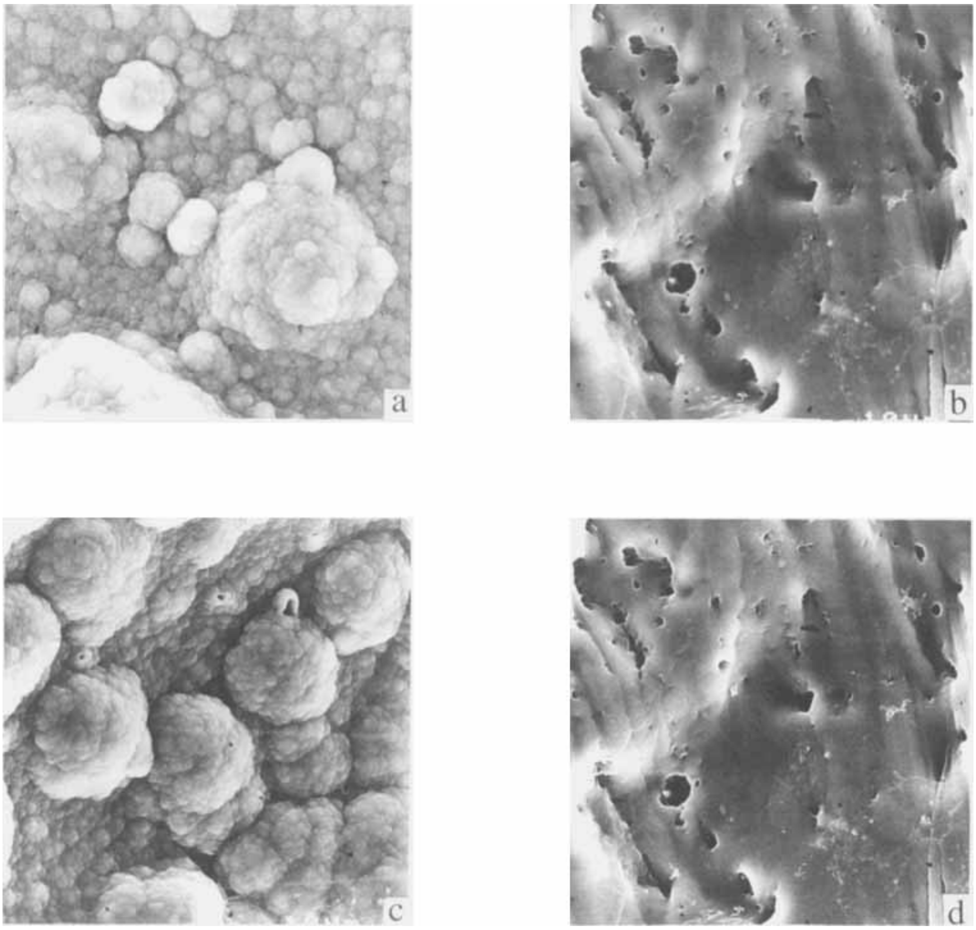


Figure 6. SEM photographs (1000 magnification) of p-TS$^-$ doped polymers:
a) the solution side of PPy/PMMA-co-PEMA-0.7,
b) the electrode side of PPy/PMMA-co-PEMA-0.7,
c) the solution side of washed PPy/PMMA-co-PEMA-0.7,
d) the electrode side of washed PPy/PMMA-co-PEMA-0.7.

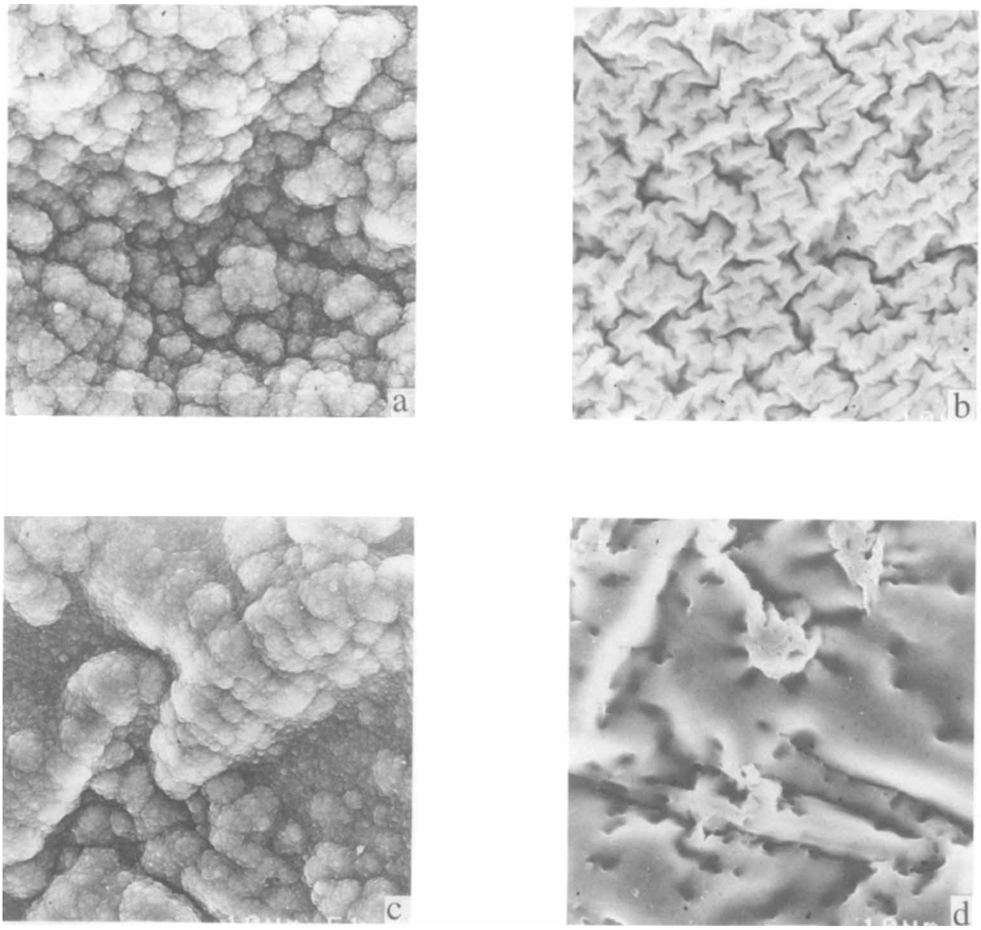


Figure 7. SEM photographs (1000 magnification) of BF_4^- doped polymers:
a) the solution side of PPy/PMMA-co-PEMA-7,
b) the electrode side of PPy/PMMA-co-PEMA-7,
c) the solution side of washed PPy/PMMA-co-PEMA-7,
d) the electrode side of washed PPy/PMMA-co-PEMA-7.

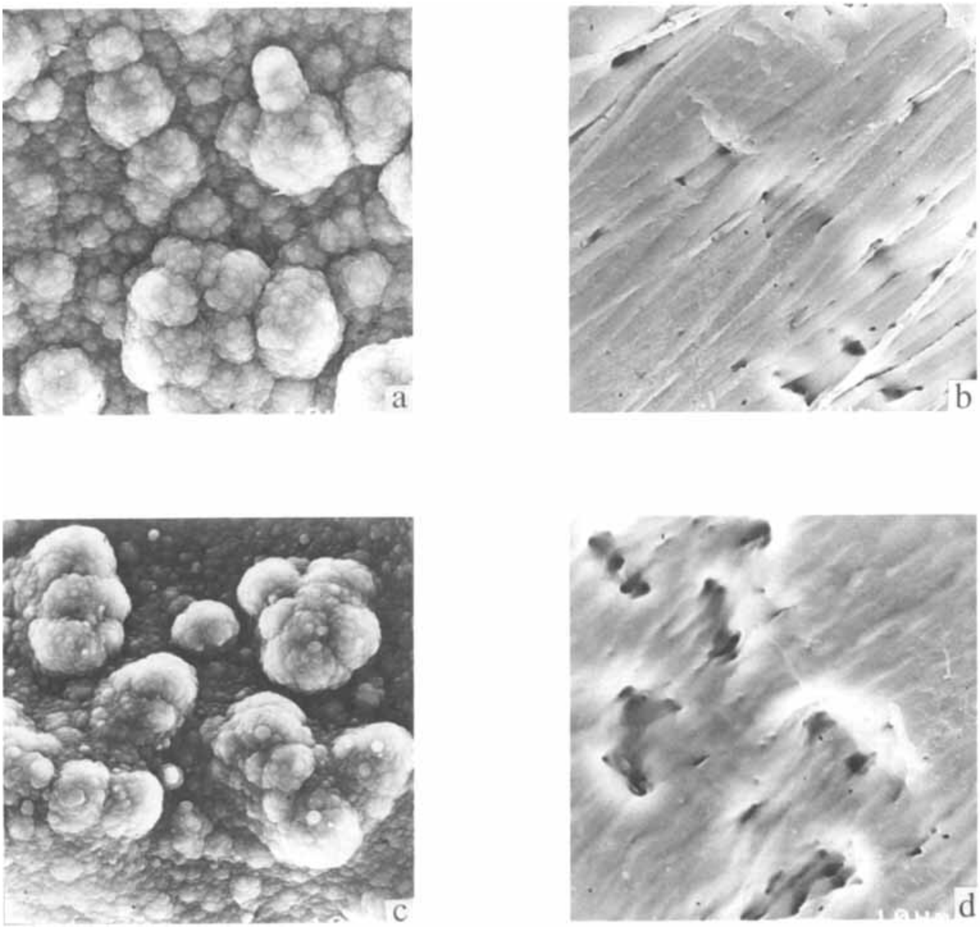


Figure 8. SEM photographs (1000 magnification) of p-TS$^-$ doped polymers:
a) the solution side of PPy/PMMA-co-PEMA-7,
b) the electrode side of PPy/PMMA-co-PEMA-7,
c) the solution side of washed PPy/PMMA-co-PEMA-7,
d) the electrode side of washed PPy/PMMA-co-PEMA-7.

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