

1-1-1998

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# Electrically Conductive Polymer Grafts Prepared by Electrochemical Polymerization of Pyrrole onto Poly[(methyl methacrylate)-co-(2-(N-pyrrolyl) Ethyl Methacrylate)] Electrodes

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Received 04.11.1997

Pyrrole was grafted on poly[(methyl methacrylate)-co-(2-(N-pyrrolyl) ethyl methacrylate)] (PMMA-co-PEMA) using constant potential electrolyses. The thermal stability of PMMA-co-PEMA was improved as a result of electrochemical grafting with pyrrole. The electrochemical behavior of the films was studied by cyclic voltammetry. Pyrrole was found to be electroactive on PMMA-co-PEMA electrodes.

## Introduction

Electrically conductive polymers have been the subject of a considerable amount of research because of their interesting and useful electronic, optical and redox properties<sup>1</sup>. Some of these materials have high conductivities with environmental stability. But many of these conjugated polymers are insoluble and difficult to process. Many studies have been conducted for the improvement of their processability by preparing composites<sup>2-5</sup>, and by blending<sup>6-8</sup> the conducting polymers with thermoplastic polymers. Stanke et.al. comparatively studied two synthetic ways to synthesize copolymers of methyl methacrylate (MMA) with 2-(N-pyrrolyl) ethyl methacrylate with pyrrole containing side groups<sup>9</sup>. MMA and 2- bromo ethyl

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methacrylate (BEMA) were copolymerized and a pyrrole moiety was introduced into the copolymer by using polymer analogous reaction<sup>10</sup>. It has also been demonstrated that grafting between pyrrole and PMMA-PEMA-7 can be achieved via oxidative polymerization of pyrrole with FeCl<sub>3</sub> in nitromethane<sup>11</sup>. This copolymer had also been self-crosslinked via oxidative polymerization with FeCl<sub>3</sub> in nitromethane<sup>12</sup>. An increase in the glass transition temperature of the final product was observed due to crosslinking between pendant pyrrole groups. Hallensleben et.al. copolymerized 2-(2-Thienyl) ethyl methacrylate (2-TEMA) with methyl methacrylate (MMA) and grafted thiophene onto PMMA-co-2TEMA, PMMA-co-3TEMA, PMMA-co-PEMA oxidatively<sup>13</sup>.

In this paper, we present the synthesis and characterization of electrochemical grafting of polypyrrole on PMMA-co-PEMA (copolymers containing 7% and 0.7% PEMA) using sodium p-toluene sulfonate as the supporting electrolyte in aqueous media.

## Experimental

### Materials

PMMA-PEMA copolymers were synthesized as described earlier<sup>13</sup>. 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.

### Synthesis of the Graft Films

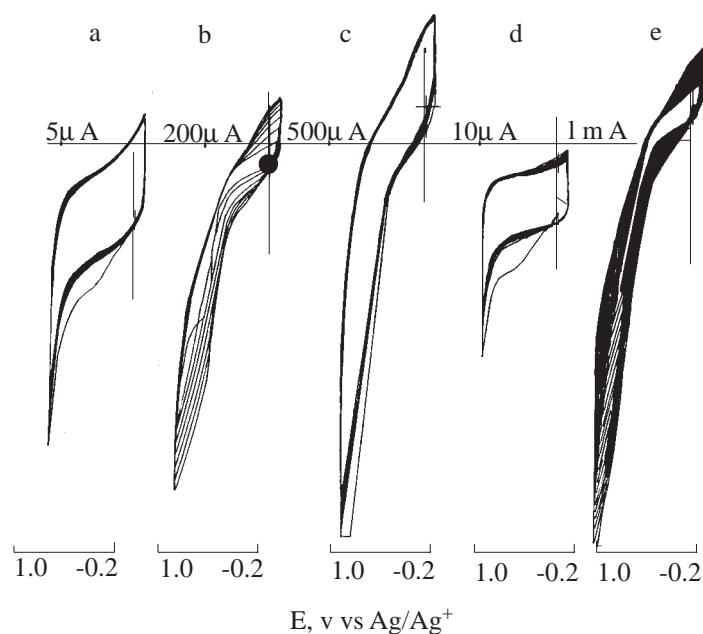
PPy/PMMA-co-PEMA grafts were prepared by electrochemical polymerization of pyrrole onto a PMMA-co-PEMA-coated electrode at a constant potential of 0.8 V versus Ag<sup>0</sup>/Ag<sup>+</sup> (10<sup>-2</sup>M) at room temperature under nitrogen atmosphere. The working and the counter electrodes were 1.5-cm<sup>2</sup> platinum foils, and the reference electrode was a Ag<sup>0</sup>/Ag<sup>+</sup> luggin capillary. The solvent-electrolyte couple was water (with 16% (v/v) acetonitrile)-sodium p-toluene sulphonate. Pyrrole and electrolyte concentrations were 0.05 M and 0.09 M, respectively. PMMA-co-PEMA (7% PEMA) and PMMA-co-PEMA (0.7% PEMA) were dissolved in acetonitrile and coated onto platinum electrodes by dipping the electrode in the polymer solution and allowing the solvent to evaporate. The coated electrode was then placed into the cell containing aqueous pyrrole solution with sodium p-toluene sulphonate, and electrolyses were carried out. After the polymerization, the films were washed with water and acetonitrile, and dried. Blank runs in the absence pyrrole were also done for both pristine copolymers to check their stability under electrolysis conditions.

### Measurements

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) studies were recorded on a Du Pont 2000 instrument. Scanning electron microscope (SEM) (JSM-6400) was used to observe the surface morphology of the films. Conductivities of the samples were measured by four-probe technique. Cyclic voltammetry was used in order to study electroactivities of the monomer and polymers. The multiscan voltammograms of the copolymers were recorded on potential range -0.2 to +1.0 V in 0.09 M electrolyte. Accordingly similar runs were repeated in the presence of 0.0036 M pyrrole solution.

## Results and Discussion

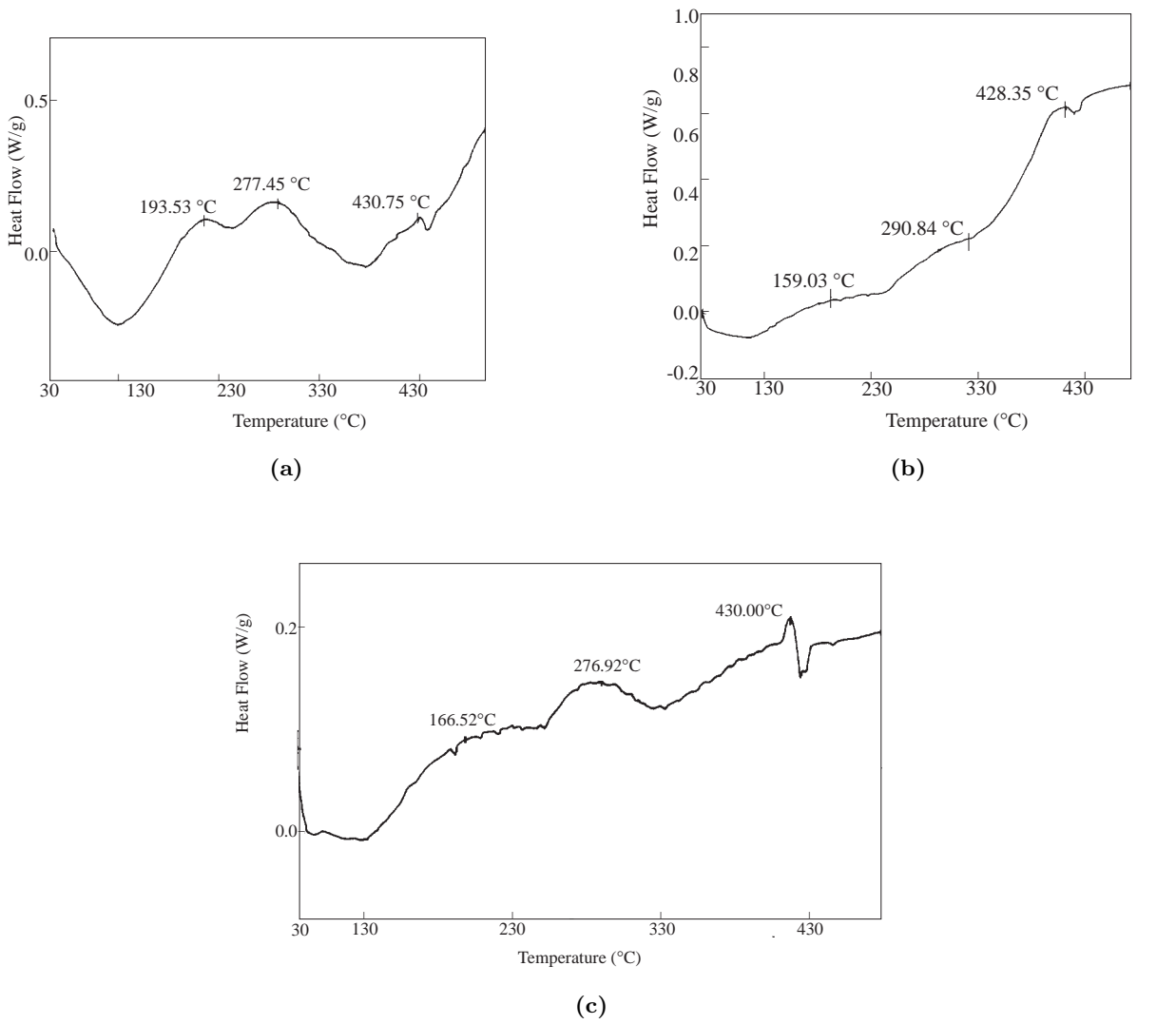
Free standing black films were easily peeled off of the electrode surface. When these films were washed with the solvent of pristine copolymer (acetonitrile) for 3 days and dried, only 10% of the PPy/PMMA-co-PEMA.7 and 6% of the PPy/PMMA-co-PEMA.0.7 films were lost by weight. We believe the remaining insulating polymers were incorporated through the growing pyrrole chain. In cyclic voltammetry studies both PMMA-co-PEMA.7- and PMMA-co-PEMA.0.7-coated electrodes indicated electroactivity only in the first cycle (Figures 1a and d). However, this electroactivity was absent in successive runs. This may well mean that the possibility of self crosslinking through electrochemical coupling in the absence of pyrrole is unlikely. On the other hand, when pyrrole was added to solution, PMMA-co-PEMA coated electrodes revealed increasing electroactivity with the reaction time (Figures 1b and e), the cyclic voltammograms exhibited pyrrole-like behavior with further scans.



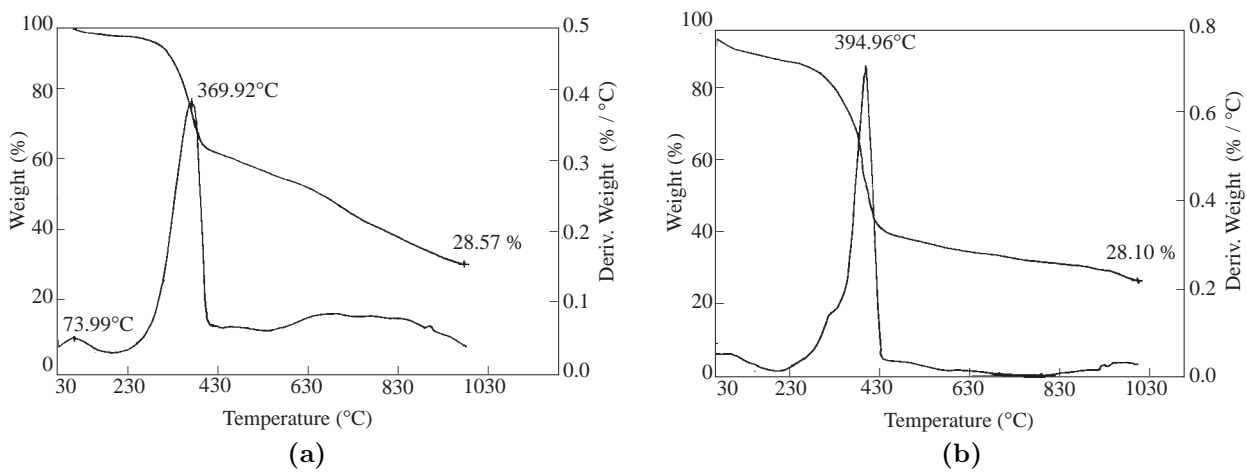
**Figure 1.** Cyclic voltammograms of (a) PMMA-co-PEMA-7, (b) PPy/PMMA-co-PEMA-7, (c) polypyrrole, (d) PMMA-co-PEMA-0.7, (e) PPy/PMMA-co-PEMA-0.7

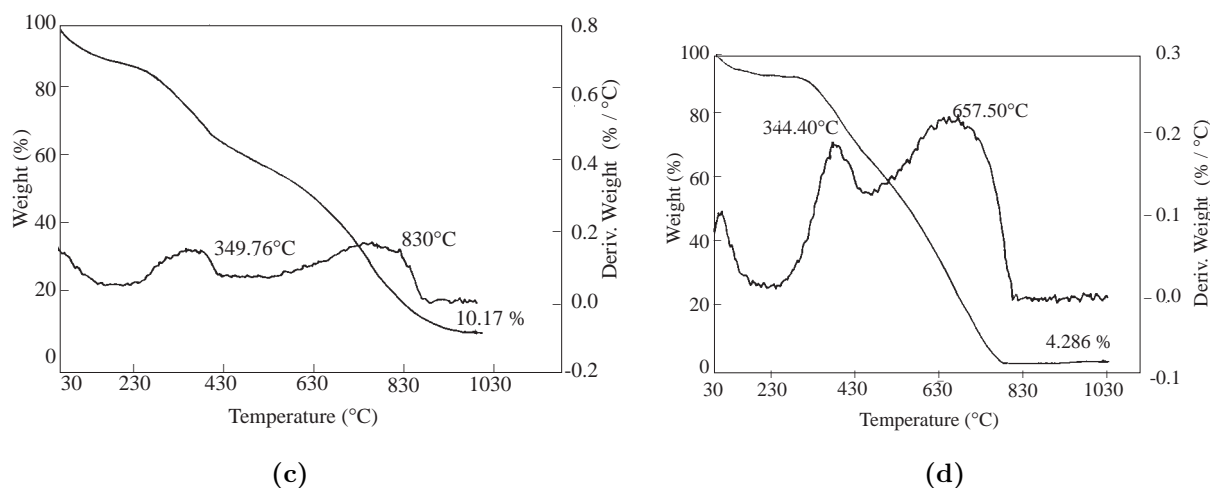
The glass transition temperature ( $T_g$ ) of PMMA-co-PEMA.7 is  $122^\circ\text{C}$  and the melting point ( $T_m$ ) is  $370^\circ\text{C}$ <sup>12</sup>.  $T_g$  and  $T_m$  values for PMMA-co-PEMA.0.7 are  $132^\circ\text{C}$  and  $367^\circ\text{C}$ <sup>11</sup>. The graft films (PPy/PMMA-co-PEMA) of each copolymer have transitions around  $160^\circ\text{C}$ ,  $280^\circ\text{C}$ , and  $430^\circ\text{C}$ , and no decomposition was observed (Fig. 2).

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  $400^\circ\text{C}$ . However, for the p-TS<sup>-</sup> doped graft films there exist 10% and 4% remnants even at  $1030^\circ\text{C}$  (Figures 3c and d). PPy/PMMA-co-PEMA.7 lost 35% at  $349^\circ\text{C}$  and 55% at around  $830^\circ\text{C}$ . While the grafts show double weight loss patterns, the simple mechanical mixtures of PPy and PMMA-co-PEMA have single weight loss patterns with 28% residue at  $1030^\circ\text{C}$  (Figures 3a and b)



**Figure 2.** DSC thermograms of (a) polypyrrole, (b) PPy/PMMA-co-PEMA-0.7, (c) PPy/PMMA-co-PEMA-7

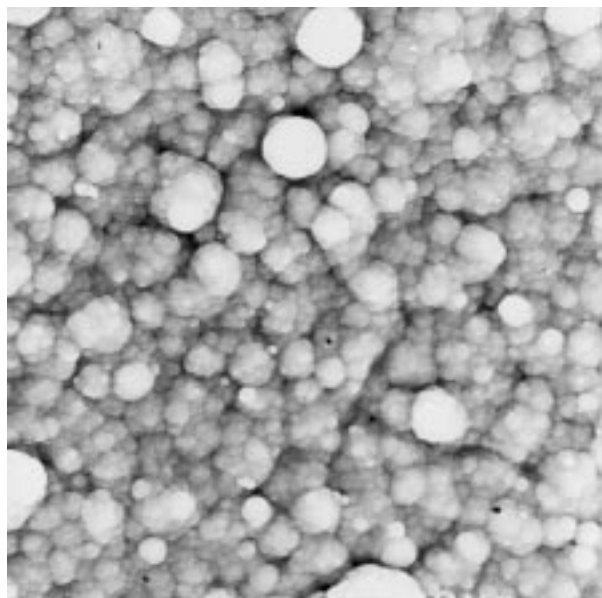




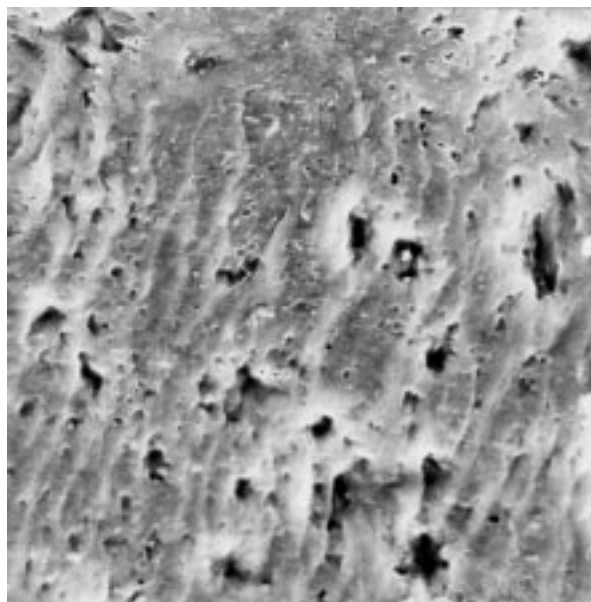
**Figure 3.** Thermal gravimetric analyses of (a) mechanical mixture of PPy and PMMA-co-PEMA-7, (b) mechanical mixture of PPy and PMMA-co-PEMA-0.7, (c) PPy/PMMA-co-PEMA-7, (d) PPy/PMMA-co-PEMA-0.7.

SEM photographs indicated the films to have very homogeneous surfaces, and similar appearances were obtained for washed and unwashed films (Figures 4 and 5). Solution sides of the films have regular spherical morphologies.

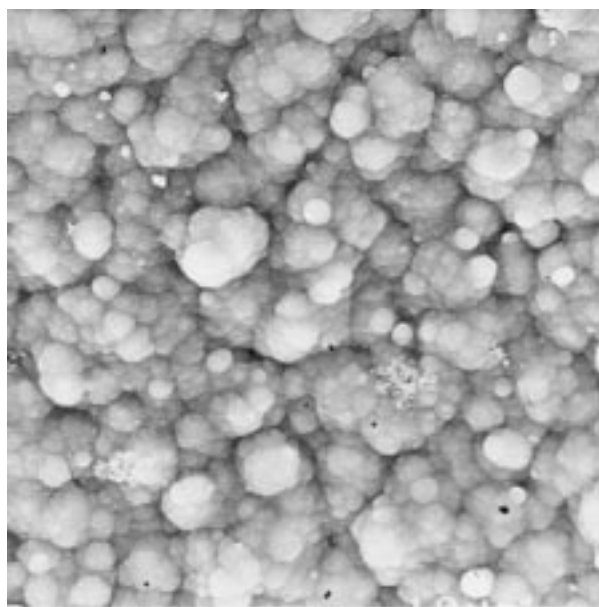
Conductivities of the  $p\text{-TS}^-$  doped graft films were around 1.0 S/cm, which is very close to that of PPy synthesized under same conditions. There is no difference between the conductivities of PPy/PMMA-co-PEMA-7 and PPy/PMMA-co-PEMA-0.7 films.



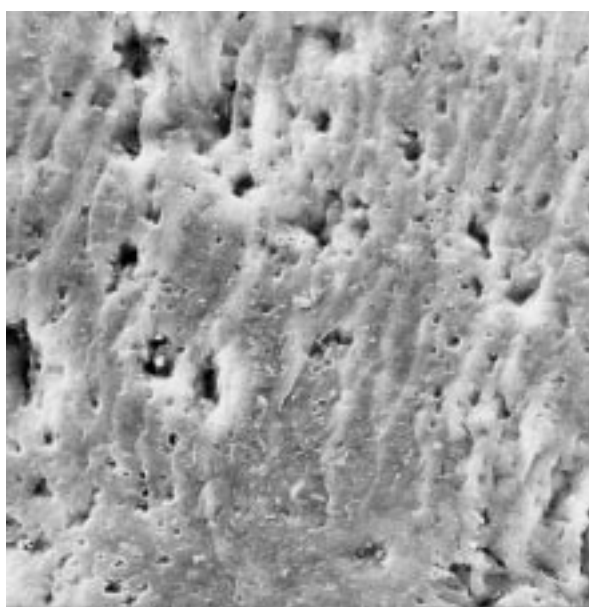
(a)



(b)

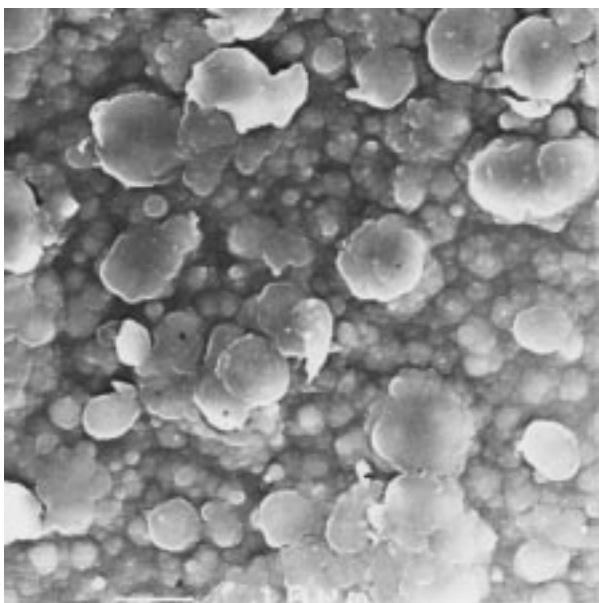


(c)

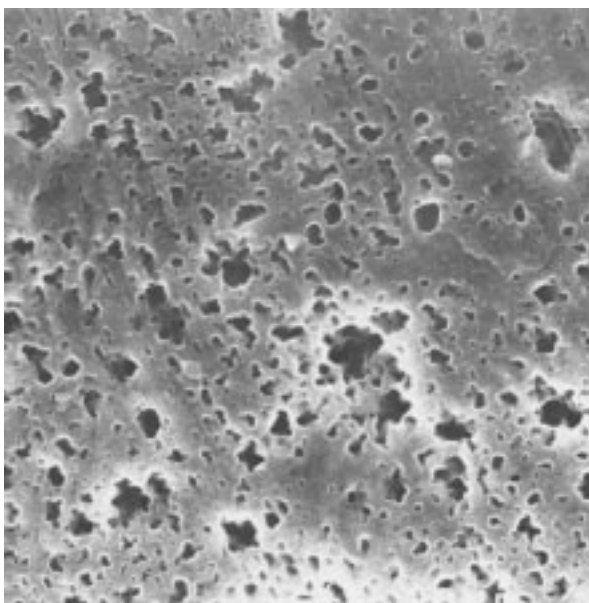


(d)

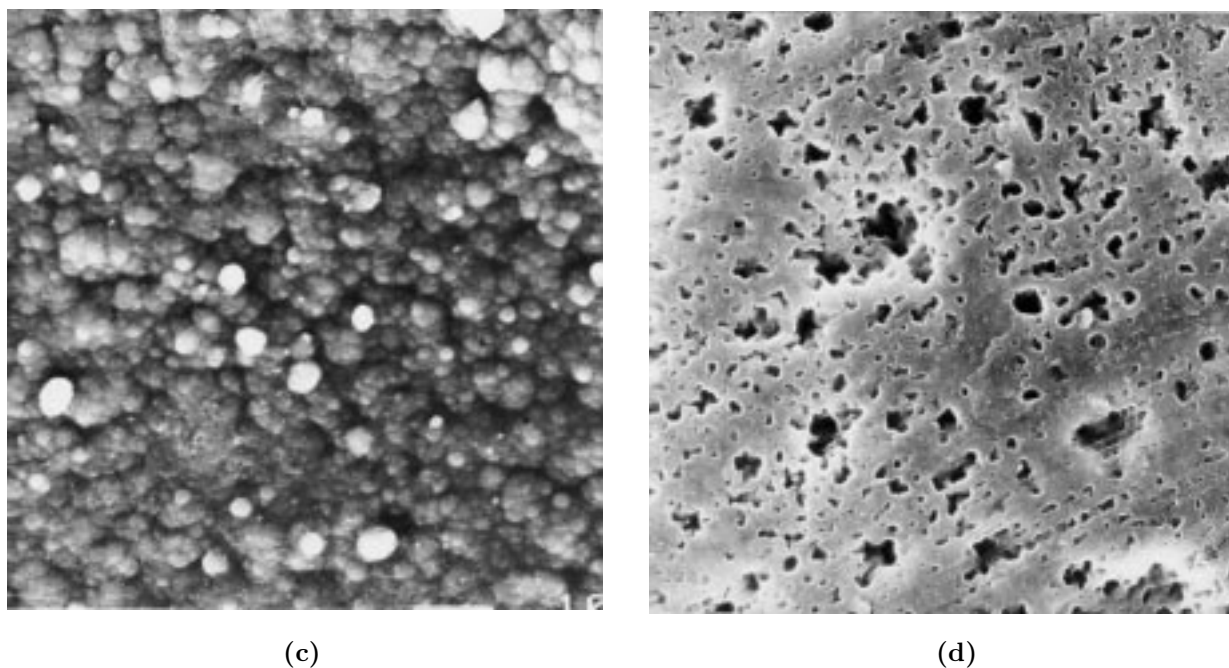
**Figure 4.** SEM photographs (1000 magnification) of (a) unwashed PPy/PMMA-co-PEMA-7 solution side, (b) unwashed PPy/PMMA-co-PEMA-7 electrode side, (c) washed PPy/PMMA-co-PEMA-7 solution side, (d) washed PPy/PMMA-co-PEMA-7 electrode side.



(a)



(b)



**Figure 5.** SEM photographs (1000 magnification) of (a) unwashed PPy/PMMA-co-PEMA-0.7 solution side, (b) unwashed PPy/PMMA-co-PEMA-0.7 electrode side, (c) washed PPy/PMMA-co-PEMA-0.7 solution side, (d) washed PPy/PMMA-co-PEMA-0.7 electrode side.

## Conclusion

Syntheses of electrically conductive polymer grafts of PPy on PMMA-co-PEMA in the presence of sodium p-toluene sulphonate as the electrolyte were achieved. Both of the copolymers (without pyrrole) indicated poorly defined electroactivities for the first runs only. However, PPy showed reversible peaks on both of the copolymer coated electrodes. The PPy/PMMA-co-PEMA films behaved more like polypyrrole as the PPy chain grew longer on the copolymer backbone. PPy/PMMA-co-PEMA.0.7 exhibited a narrower oxidation peak area than PPy/PMMA-co-PEMA.7 because of the lower concentration of pyrrole moieties on the backbone.

DSC studies of the films revealed that the thermal behaviors of the grafts were quite different than that of the pure copolymers. TGA thermograms of the mechanical mixtures and the grafts were different from each other, as indicated by different weight loss patterns. It was observed that the PPy/PMMA-co-PEMA films were thermally more stable than the pristine copolymers.

SEM studies revealed PPy to grow uniformly on PMMA-co-PEMA since the washed and unwashed electrolytic films have similar surface morphologies. This idea is further supported by conductivity measurements of the films. They have conductivities as high as the pure polypyrrole synthesized under same conditions.

## Acknowledgements

The authors gratefully acknowledge financial support by TUBA and TBAG-1422 Grants.



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