

Conducting Polymer Grafts of Polypyrrole

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Received 30.04.1997

Conducting polymer grafts of pyrrole with poly[(methyl methacrylate)-co-(2-(N-pyrrolyl) ethyl methacrylate)] were synthesized via electrochemical polymerization of pyrrole in different media. Samples were characterized by SEM, thermal analysis and conductivity measurements.

Introduction

Electronically conducting polymers have attracted considerable attention in the last two decades due to their potential applications in molecular electronics and sensor technologies. Polypyrrole is one of the most studied polymers owing to its high conductivity and environmental stability. Numerous chemical¹⁻⁴ and electrochemical⁵⁻¹⁰ procedures have been employed to prepare polypyrrole composites in efforts to improve its mechanical and physical properties.

Synthesis of poly(methyl methacrylate-co-2-(N-pyrrolyl) ethyl methacrylate-g-pyrrole) through chemical oxidative polymerization has been extensively studied by Stanke et al¹¹⁻¹⁴. In achieving this, poly[(methyl methacrylate)-co-(2-(N-pyrrolyl) ethyl methacrylate)] had been synthesized in two different compositions in terms of PEMA content, namely 7 and 0.7 percent by mole.

In this study, pyrrole was grafted on these copolymers via constant potential electrolyses in several different electrolysis media. PMMA-co-PEMA-g-pyrrole grafts were prepared by polymerizing pyrrole onto copolymer coated electrodes. Three different electrolytes were utilized for that purpose.

Experimental

Materials

PMMA-co-PEMA polymers were synthesized as described earlier¹¹. Pyrrole (Aldrich), acetonitrile (AN)(Aldrich) were used as received. Sodium p-toulene sulfonate (pTS) was prepared by titrating p-toluene sulfonic acid (Aldrich) with NaOH. NaClO₄ and tetrabutylammonium tetrafluoroborate (TBAFB)(Aldrich) were used after drying.

Synthesis of Graft Films

The copolymers (with 7 and 0.7 percent PEMA content) were coated on 1.5 cm² platinum foils by dip coating from its solution (chloroform). The counter electrode was 1.5 cm² Pt foil and the reference electrode was Ag/Ag⁺ (10⁻² M). Pyrrole and electrolyte concentrations were 0.05M. Following ca. 2 h. of electrolyses at +0.8 V vs Ag/Ag⁺ the free standing films were washed with acetonitrile and dried. Blank runs in the absence of pyrrole were done for both copolymers to ensure the stability of them under given conditions.

The three solvent-electrolyte couples for different experiment were: 1) water(16% AN-to swell the polymers on the electrode surface)-pTS, 2) AN-TBAFB, 3) water (16%AN)-NaClO₄

Measurements

Differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA) studies were recorded on a Du Pont 2000 instrument. Scanning electron microscope (SEM), JSM-6400, was used to analyze the surface morphology of the film. Conductivity measurements were done using a standard four probe technique.

Results and Discussion

Free standing graft films can easily be peeled off from the electrode surface. Upon washing with chloroform for several days (at least 3) only under 10 % weight losses were recorded for electrolytic films. However, gravimetry studies before and after potentiostatic electrolyses revealed that the graft films contain 50% insulating polymer by weight. Thus remaining copolymers must have been incorporated in the polypyrrole chain.

DSC studies are collected in Table 1 for several electrolyses conditions i.e., graft films with various dopant ions.

Table 1. DSC Results for graft polymers obtained at different conditions. Endotherms in °C

	AN/pTS	H ₂ O/NaClO ₄	AN/TBAFB
PMMA-co- PEMA.7.-g-Py*	160, 280, 430	371, 425	230, 425
PMMA-co- PEMA.0.7-g-Py**	160, 280, 430	222, 425	93, 223, 426

*T_g:122, T_m: 370

**T_g:132, T_m: 370

Presence of several endo terms reveals that a different species were formed during pyrrole electrolyses. Pyrrole, however, is thermally inert up to 500 °C with the exception of the ClO₄⁻ doped one.

Thermal gravimetry studies show that the resulting graft polymer are far more thermally stable compare to the pristine copolymers (Table 2).

For PMMA-co-PEMA.7 and PMMA-co-PEMA.0.7, the first main weight loss is around 370 °C. On the other hand, for the pTS doped films there exists 10% remainings even after 1000 °C. PMMA-co-PEMA.0.7-g-Py lost 10 % at 344 °C and 30 % at 675 °C. Similarly, PPMMA-co-PEMA.7.-g-Py lost 10% at 344 °C and 55 & at 830 °C.

Prechlorate and tetrafluoroborate ion doped films show the same trend, i.e. higher stability after incorporating pyrrole chain (Table 2).

Table 2. Thermal Gravimetry Results on Electrolytic Films. Percent Weight Losses at Given Temperatures.

	AN/pTS	H ₂ O/NaClO ₄	AN/TBAFB
PMMA-co-	10% 344°C;	5% 290°C;	5% 317°C;
PEMA.7.-g-Py*	55% 830°C	50% 710°C	50% 680°C
PMMA-co-	10% 344°C;	10% 320°C;	10% 317°C;
PEMA.0.7-g-Py**	30% 675°C	40% 630°C	40% 630°C

*40% 369°C

**50% 394°C

Scanning electron micrographs yield valuable information about the homogeneity and the formation of grafts. According to our previous studies^{10,15}, among the composites manufactured by the electrolytic polymerization of pyrrole on an insulating polymer (e.g. polybisphenol carbonate, aliphatic polyamides, polyimides, polyaryl ether ketones), polypyrrole was found to be rich on the electrode side of the film whereas the film itself was homogeneous. This picture is not valid only if there exists an interaction between the two polymers (the insulating and the conducting). Although the structures are not defined yet, it is well established that lack of such an interaction results in simple mixtures of the two components as shown by the removal of the insulating component upon washing. In this case, we not only have the same micrographs for both side of the films, but also the washing process does not interfere with the morphology of the films, i.e., washed and unwashed samples of the same films do have the same micrographs.

Conductivities of the electrolytic films stand yet for another proof of the interaction between the insulating and conducting polymers. Even 50 percent percolation cannot decrease the conductivities by more than one order of magnitude compared to pure polypyrrole synthesized under same conditions (Table 3).

Table 3. Conductivities of the Films (S/cm)

	AN/pTS	H ₂ O/NaClO ₄	AN/TBAFB
PMMA-co-	1	0.7	0.7
PEMA.7.-g-Py			
PMMA-co-	1	0.2	0.2
PEMA.7.-g-Py			
PPy	10	5	5

Conclusion

It was shown that electrochemical grafting of pyrrole on an insulating polymer can be achieved provided that the latter contains pyrrole moieties and is hosted by a metal electrode. Thus, diffusion problems that may arise in the case where the polymerization was carried out in a solution with both components are dissolved can be avoided. The resulting polymers are shown to be more heat resistant compared to the pristine insulating polymers.

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