Synthesis of Conducting PPy/pTHF Copolymers

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ABSTRACT: Living polytetrahydrofuran (pTHF) was terminated with the potassium salt of pyrrole to yield polymers with pyrrole end groups. Copolymerization of THF and pyrrole with short and long pTHF segments was achieved by constant potential electrolysis. Syntheses of the block copolymers were performed using tetrabutylammonium tetrafluoroborate, sodium perchlorate, and sodium *p*-toluenesulfonate as the supporting electrolytes. Characterization of the block copolymers were based on scanning electron microscopy, differential scanning calorimetry, thermal gravimetry analysis, cyclic voltammetry, and FTIR studies. No significant effect of the chain length on the properties of the copolymers was observed; however, use of different dopants resulted in different thermal and electrochemical behaviors, surface morphologies, and conductivities. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 713–720, 1999

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INTRODUCTION

In recent years, conducting polymers have attracted great interest due to their electrical, electrochemical, and optical properties.¹ They have possible widespread applications; however, those are limited in practical use as they are poor in mechanical and physical properties.^{2,3} To improve the processibility of conducting polymers, syntheses of polymer composites using an insulating polymer as the host matrix were considered. It was found that some electrochemically synthesized composites have different behavior than that of the simple mechanical mixture of the two polymers. For example, polypyrrole (PPy)/polycarbonate (PC) composites showed such behavior, which was ascribed to a better homogeneity, to a possible hydrogen bonding, and also to the formation of graft polymers to a certain extent.^{4,5} Recently,^{6–9} the formation of electrochemical block copolymers of PPy and poly[(methyl methacrylate)-*co*-(2-*N*-pyrrolyl)ethyl methacrylate] (PMMA-*co*-PEMA) was pointed out. The block copolymer synthesized had the same conductivity as that of the pure PPy; in addition, an increase in the thermal stability of the copolymer was observed.⁷

Living polymerization allows the preparation of various well-defined polymers with functional end groups. It has been shown that cyclic ethers such as tetrahydrofuran (THF) can be polymerized without chain transfer and termination under closely controlled conditions.¹⁰ Living ends of polytetrahydro-furan (pTHF) can react with nucleophiles and thus give rise to a variety of functional groups.^{11–15}

In this work, the synthesis and characterization of electrochemical block polymerization of pyrrole on pTHF with short and long chain lengths, prepared by taking advantage of living polymerization, were performed. Block copolymers were synthesized using three different electrolytes: tetrabutylammonium tetrafluoroborate (TBAFB), sodium perchlorate (NaClO₄), and sodium *p*-toluene sulfonate (PTS⁻). Characterization of the copolymers

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was done by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), FTIR, and cyclic voltammetry (CV). Electrical conductivities were determined by two-probe and four-probe techniques.

EXPERIMENTAL

Materials

THF (Merck, Dormstadt) was dried over KOH, distilled over sodium wire, and finally distilled over sodium/benzophenone ketyl prior to use. Dichloromethane (Fluka, Buchs) was treated with H_2SO_4 and washed with a Na_2CO_3 solution and water. After drying with CaCl₂, it was distilled over CaH₂ and stored over an activated molecular sieve (type 4A). Pyrrole (Merck, Dormstadt) was distilled before use. Dichloromethane (CH₂Cl₂) and acetonitrile (AN) were purchased from Merck and used without further purification. Sodium *p*-toluene sulfonate was prepared by titrating *p*toluene sulfonic acid monohydrate (Aldrich, Dorset) with sodium hydroxide. TBAFB was purchased from Merck and dried before use, and sodium perchlorate (Riedel-De Haen AG Seelze Hannover) was used as received.

Syntheses of Pyrrole-terminated pTHFs

The polymerization of THF was carried out in bulk at 25°C under a nitrogen atmosphere using methyl triflate. The coupling reaction between the living pTHF and the potassium salt of pyrrole was realized by adding an excess of a salt suspension in dichloromethane into the reaction mixture and stirring for 3 h. The reaction mixture was poured into a large amount of methanol/water (3:1, v/v). The solution was centrifuged to separate insoluble salts and cooled. Finally, the polymer was filtered and dried in a vacuum.

Syntheses of PPy/pTHF via Single-step Process

The syntheses of the polymers were performed in a conventional three-electrode electrochemical cell using platinum (Pt) electrodes (1.5 cm² each) as the working and the counterelectrodes. A Ag/ Ag+ $(10^{-2} M)$ was utilized as the reference electrode. A Wenking POS 73 potentiostat was used for the supply of a constant potential of 1.1 V in the electrosyntheses. The cell was kept at 0°C and purged with nitrogen during the polymerization. BF_4^- -doped and ClO_4^- -doped films were synthesized via a single-step process, in which polymerizations were carried out on a bare Pt electrode. A 60-mL solution of CH_2Cl_2 containing 100 mg of the pTHF polymer, a 0.05-*M* supporting electrolyte, and 0.02-*M* pyrrole was used as the electrolytic medium. In the case of ClO_4^- , a mixture of CH_2Cl_2 and AN (40% v/v) was used as the solvent. A sufficient amount of the films was obtained in 16 h when $BF_4^$ was used as the supporting electrolyte, with the time shortened to 2 h in the case of ClO_4^- .

Syntheses of PPy/pTHF via Two-step Process

PPy/pTHF grafts were prepared by the electrochemical polymerization of pyrrole onto a pTHFcoated electrode where PTS⁻ was used as the supporting electrolyte. The solvent was water (with 20% v/v AN) containing 0.05-*M* PTS⁻ and 0.02-*M* pyrrole. The pTHF polymers were dissolved in CH₂Cl₂ and coated on the Pt electrodes by dipping the electrode in the polymer solution and allowing the solvent to evaporate. Polymerization reactions lasted 2 h. The films were easily peeled off the electrode surface and washed with CH_2Cl_2 (for BF₄⁻-doped films), with AN (with ClO_4^- -doped ones), and with water (with PTSdoped ones) and dried under a vacuum.

Characterization

GPC analyses were performed with a setup consisting of a Waters 600 pump and two ultraStyragel columns (10^4 , 500 Å) with THF as the eluent at a flow rate of 1mL/min and a Waters differential refractometer (Model 410). UV spectra of the precursor polymers were taken by a Perkin–Elmer spectrophotometer.

For characterization of the PPy/pTHF copolymers, DSC, TGA, SEM, FTIR, and CV analyses were performed. Thermal behaviors of the films were analyzed by DSC (DuPont 2000) and TGA (TL-TGA 2000). SEM (JSM-6400) was used to observe the surface morphologies. FTIR spectra of the films were recorded on a Nicolet 510 FT spectrophotometer to investigate the formation of graft copolymers. To study the electroactivities of the monomer and the polymers, a HEKA potentiostat/galvanostat was utilized. Conductivities of the samples were measured using two-probe and four-probe techniques.

RESULTS AND DISCUSSION

Methyl trifluoromethane sulfonate (methyl triflate) has been described as an initiator which

Polymer	Time (min)	Conversion (%)	M_n	M_w/M_n
MT1	40	12	13,000	1.5
MT2	80	20	27,000	1.7

Table I	Bulk Polymerization	of THF	by	Methyl
Triflate	at 25°C			

[Methyl triflate] = 0.012 mol/L; [THF] = 12.3 mol/L.

leads to monofunctional living pTHF with low polydispersitiy.⁸ In this work, we employed this initiator in the polymerization of THF and electrochemically active pTHFs were obtained by terminating the living ends of a polymer with the potassium salt of pyrrole, according to Scheme 1.



The results are summarized in Table I. UV spectra of the polymers show the characteristic absorbance of the pyrrole moieties. According to the electroactivity of the terminal pyrrole moieties, as was demonstrated for poly(methyl methacrylate), the electrochemical method was employed in order to transform these polymers into block copolymers containing pyrrole and THF as depicted in Scheme 2.



Thermal Properties

The pristine polymers, MT1 and MT2, were resistant to heating up to about 200°C, after which they lost weight rapidly [Fig. 1(a)]. Grafting the precursor polymers with pyrrole caused them to lose weight at lower temperatures, but more gradually. As shown in Figure 1(b), BF₄⁻-doped PPy/ MT1 started to lose weight at the beginning of heating; there was 70% remaining at 230°C. However, after that, it lost weight more slowly. This behavior was somewhat between that of pure PPy and the pristine polymers, as BF₄⁻-doped pure PPy started to decompose at about 75°C. ClO_4^- doped films showed 70% remaining at 220°C andlost weight up to 600°C to 5% remaining [Fig. 1(c)].

PTS⁻-doped pure PPy was more resistant to heating when compared to BF_4^- and ClO_4^- -doped ones, as with graft copolymers. The behavior of PTS⁻-doped PPy/MT1 is shown in Figure 1(d). A weight loss of 20% at about 300°C was significant.

DSC thermograms for the precursor polymers were obtained via heating from -60 to 100° C at a rate of



Figure 1 Thermal gravimetric analysis of (a) MT1, (b) BF_{-}^{4} -doped PPy/MT1, (c) ClO_{-}^{4} -doped PPy/MT1, and (d) PTS⁻-doped PPy/MT1.



Figure 2 DSC thermograms of (a) MT1, (b) BF_4^- -doped PPy/MT1, (c) ClO_4^- -doped PPy/MT1, and (d) PTS⁻-doped PPy/MT1.

10°C/min. A well-defined melting peak appeared at 44°C for MT1 and 38°C for MT2. After a cooling step, the polymers were heated again, andthe melting peaks shifted to 30°C for both [Fig. 2(a)].

 BF_4^- -doped PPy/MT1 showed two broad melting peaks in the first heating, as shown in Figure 2(b). The first peak was attributed to the presence of PPy, because a similar peak was observed in



Figure 2 (Continued from the previous page)

the PPy DSC thermogram. The second one should belong to PPy/MT1. The second heating curve showed a transition at 240°C and at 422°C, which was observed in all of the second heating thermograms of the graft copolymers. ClO_4^- -doped PPy/MT1 and PPy/MT2 showed a large exothermic peak due to the decomposition of ClO_4^- [Fig. 2(c)]. In the second heating curves, at 102°C, an endothermic peak and two transitions at 251 and 429°C were observed. PTS⁻-doped



Figure 3 SEM photographs (1000 magnification) of (a) the electrode side of BF_4^- doped PPy/MT2, (b) the solution side of BF_4^- -doped PPy/MT2, (c) the electrode side of PTS)-doped PPy/MT1, (d) the solution side of PTS⁻-doped PPy/MT1, (e) the electrode side of ClO_4^- -doped PPy/MT1, and (f) the solution side of ClO_4^- -doped PPy/MT1.

PPy/MT1 is shown in Figure 2(d). The transitions of PPy/MT2 were very close to PPy/MT1 in the first heating curve. However, additional transitions at about 70 and 150°C were observed in the second run for PPy/MT2.

Morphologies of the Films

The SEM micrographs of the BF_4^- -doped PPy/MT1 revealed that the solution and the electrode sides

were not similar in appearance. The electrode side of the polymer was rough; the solution side had globules of PPy with voids in between. The BF_{-}^4 doped PPy/MT2's electrode side was smooth in contrast to the solution side, where small globules of PPy came together with a chainlike structure forming voids in between [Fig. 3(a,b)].

Micrographs of the PPy/MT1 PTS⁻-doped copolymer revealed that the surface appearance of the electrode and the solution sides of the films



Figure 4 Cyclic voltammograms of (a) PTS-doped PPy, (b) PTS-doped PPy/MT2, (c) BF_4^- -doped Ppy, and (d) BF_4^- -doped PPy/MT2.

were quite different. Pyrrole groups at the end of the insulating polymer chain grew toward the solution, giving rise to a cauliflowerlike surface which was very similar to the appearance of pure PPy^{16} [(Fig. 3(c,d)]. The PPy/MT2 PTS^- -doped copolymer had similar surface appearances.

Unlike BF_4^- and PTS^- -doped grafts, ClO_4^- doped PPy/MT1 had a corrugated electrode surface [Fig. 3(e)]. Formation of PPy was clearly observed from the solution side of the film [Fig. 3(f)]. PPy/MT2 had a smooth appearance of the electrode side and a cauliflowerlike appearance of the solution side.

Use of different electrolytes resulted in different sizes of PPy grains. Films doped with $BF_4^$ had the smallest-size PPy grains, doping with ClO_4^- resulted in relatively larger grains, and the PTS^- -doped one had the largest PPy grains [Fig. 3(b,d,f)].

FTIR Analysis

FTIR spectra of the MT1 and MT2 insulating polymers have the same characteristic bands. C—O—C asymmetric stretching was observed as an intense band at 1113 cm⁻¹. Two bands (2940 and 2866 cm⁻¹) arose as the result of aliphatic CH₂ vibrations. A less intense band at 1681 cm⁻¹ due to the C—C ring stretching vibration and the one at 1366 cm⁻¹ due to C—N stretching have proved the presence of the pyrrole end group.

Both the PPy/MT1 and PPy/MT2 copolymers (doped with BF_4^-) showed the characteristic bands of the pristine polymers. In addition, an intense band at 1084 cm⁻¹ was observed, indicating the presence of BF_4^- anions in the polymer chain.

PPy/MT1 and PPy/MT2 ClO_4^- -doped copolymers had spectra indicating the presence of MT1 and MT2, that is, an intense C—O—C asymmetric stretching band at 1112 cm⁻¹ was observed. Furthermore, bands at 632 and 1087 cm⁻¹ arose due to the presence of the ClO_4^- anion. PTS⁻doped polymers had a very crowded appearance between 1700 and 500 cm⁻¹; they also revealed the characteristic bands of the pristine polymers.

Electrochemical Behavior of the Films

Cyclic voltammetry analyses of MT1 and MT2 showed that they were not electroactive, because no detectable redox peak was observed with any of the systems described above. This result indicated that crosslinking through the pyrrole moieties of the precursor polymers was impossible. When pyrrole was added to the solution, the situation changed, the electroactivity increasing with the number of scans.

Cyclic voltammetry experiments were performed with a potential scan from -0.1 to +1.5 V for the bare Pt and -0.1 to +1.3 V for the MT2coated electrode in the presence of PTS⁻ The two

Conducting Polymer	Conductivity (S/cm)
$PPy BF_{4}^{-}$	0.56
$PPy/MT1 BF_4$	0.55
$PPy/MT2 BF_4$	0.14
$PPy ClO_4^-$	0.085
$PPy/MT1 ClO_4^-$	$5.5 imes10^{-3}$
PPy/MT2 ClO ₄	$9.2 imes10^{-3}$
PPy PTS ⁻	0.090
PPy/MT1 PTS ⁻	0.032
PPy/MT2 PTS ⁻	0.065

Table II Conductivities of BF_4^- , ClO_4^- , and PTS^- -doped Films

cyclic voltammograms with Pt and MT2/Pt as the working electrodes are compared in Figure 4(a,b). The anodic peak potential of the bare Pt electrode shifting toward to +1.1 V with repeated cycling could not be observed in the multisweep cyclic voltammogram of the MT2-coated electrode. This indicated that PPy chains should grow through the insulating polymer chain, forming a graft copolymer.

The cyclic voltammogram of PPy/MT2 was obtained in a solution where BF_4^- was used as the supporting electrolyte. Figure 4(c) shows the CV of PPy at the bare Pt electrode in the range of -0.2 to +1.4 V. A different electroactive behavior of PPy in the presence of MT2 was revealed from the comparison of Figure 4(c,d). In the cathodic sweep, the reduction peak for pure PPy was not observed for MT2/PPy. ClO_4^- -doped PPy and PPy/ MT2 did not show well-defined oxidation and reduction peaks.

Conductivities of the Films

In contrast to the chain length, the electrolyte type significantly changed the conductivities. The highest conductivity, very close to that of pure PPy, was shown by BF_4^- -doped polymers. Values of 0.55 and 0.14 S/cm were obtained for PPy/MT1 and PPy/MT2, respectively. The lowest conductivity was shown by ClO_4^- -doped films; the order of magnitude was 10^{-3} S/cm for both films. When PTS⁻ was used as the supporting electrolyte, films had conductivity values of about 0.02 S/cm, which was also the conductivity of the PTS⁻ doped pure PPy (Table II).

CONCLUSIONS

Pyrrole moieties were incorporated into pTHF using a living polymerization technique. The electropolymerization capability of these polymers provides a versatile method for preparing conducting block polymers with insulating pTHF segments.

The growth of PPy through the pyrrole moiety of the insulating polymer chain was indicated. Another indication was that the chain length of the insulating polymer did not influence thermal or electrochemical behaviors, surface morphologies, or conductivities of the copolymers significantly. However, the presence of different electrolytes during electrochemical preparation strongly affects the properties of the polymer films. As a future work, syntheses of PPy-pTHF polymers containing terminal pyrrole groups at both ends will be considered.

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