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Conducting copolymers of polypyrrole/polytetrahydrofuran

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Summary

Bifunctional living polytetrahydrofuran (PTHF) was terminated with potassium salt of pyrrole to yield polymers with electrochemically active end groups. These polymers were employed in the second stage to obtain conducting polypyrrole/polytetrahydrofuran block copolymers with short and long polytetrahydrofuran segments by potentiostatic anodic polymerization of pyrrole in different electrolytic media. Syntheses of block copolymers were achieved in media where tetrabutylammonium fluoroborate, sodium perchlorate and sodium p-toluenesulfonate were used as the supporting electrolytes. Characterizations were based on DSC, TGA, SEM, FTIR, and CV analyses. No significant effect of the chain length of polytetrahydrofuran segments on the properties of the copolymers was observed; however, thermal, electrochemical behaviors, and surface morphologies of the films were greatly affected by the supporting electrolytes.

Introduction

In recent years, there has been growing interest in conducting polymers because of their wide range of potential applications in the areas such as rechargeable batteries (1,2), gas separation membranes (3), EMI shielding (4), and electrochromic display devices (5). Electrochemically prepared polypyrrole (PPy) is one of the well known one having high conductivity, environmental stability and ease of preparation. However, practical applications of the conducting polymers have been slow owing to certain deficiencies like poor mechanical properties and processibilities. Synthesis of conducting polymer composites was shown to be an effective way to compensate these deficiencies. By this way, materials having improved mechanical properties with little decrease in conductivities were obtained. Recently, many kinds of conducting polymer composites with insulating polymers like polyethylene (6), polyvinylchloride (7), polycarbonate (8) have been prepared. Another way of improving mechanical properties is to synthesize block copolymers. In recent works, it has been shown that electrochemically prepared block copolymers of PPy and poly [(methylmethacrylate)-co-(2-N-pyrrolyl)ethyl(methacrylate)] have the same conductivity as the pure PPy with an increase in the thermal stability (9). Polymeric initiators having functional groups become of interest in polymer synthesis (10). Most of the efforts for the preparation of polymeric initiators have focused on living polymerization techniques which involves quenching of living polymer ends with a reagent

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having functional groups (11-13). The functionality of the telechelic systems depends upon the functionality of the initiator, for doubly-ended telechelics bifunctional initiators are required. The anhydrides of very strong acids (e.g. triflic anhydride) are of typical cationic initiators fulfilling living conditions, and polymerization via these initiators yields a living polymer having cationic activity at each end (14). In this study, pyrrole terminated bifunctional PTHF was obtained by terminating living ends of a PTHF with a potassium salt of pyrrole.

Subsequently, we synthesized block copolymers of tetrahydrofuran and pyrrole with short and long tetrahydrofuran segments electrochemically by using bifunctional pyrrole terminated PTHF. Three different electrolytes were used in the syntheses of the polymers: tetrabutylammonium tetrafluoroborate (TBAFB), sodium perchlorate ($NaClO_4$) and sodium p-toluene sulfonate (PTS^-). Characterization of the films was done by differential scanning calorimetry (DSC) thermal gravimetry analysis (TGA), scanning electron microscopy (SEM), FTIR, and cylic voltammetry (CV). Electrical conductivities were determined by four-probe technique.

Experimental

Materials

Tetrahydrofuran (Merck) was dried over KOH, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use. Triflic anhydride (Fluka) was distilled under vacuum and kept over nitrogen. Dichloromethane (Fluka) was purified by conventional drying and distillation procedures and kept over activated molecular sieve (type 4A°). Pyrrole (Merck) was distilled before use. Dichloromethane (CH_2Cl_2) and acetonitrile (AN), purchased from Merck, were used without further purification. TBAFB (Merck) was dried and $NaClO_4$ (Riedel-De Haen AG Seelze Hannover) was used as received. PTS^- was prepared by titrating p-toluene sulfonic acid monohydrate (Aldrich) with sodium hydroxide.

Methods

Synthesis of pyrrole terminated polytetrahydrofuran was achieved as follows: The polymerization of THF was carried out in bulk at 25 °C under nitrogen atmosphere by using triflic anhydride to obtain bifunctional polymers. The coupling reaction between living PTHF and potassium salt of pyrrole was carried out by adding an excess of salt suspension in dichloromethane into the reaction mixture and stirring over night.

The solution was centrifuged to separate insoluble salts and polymers were poured into a large amount of MeOH/water (3:1, v/v). and cooled down for precipitation. Finally, precipitated polymer was filtered off and dried under vacuum.

Polypyrrole (PPy)/ polytetrahydrofuran (PTHF) block copolymers were synthesized via single step and double step procedures. In the former, syntheses were carried out on a bare platinum electrode in a medium containing the supporting electrolyte, pyrrole and the pristine polymer. In the latter procedure, coating of the anode with the insulating polymer was required, that is the polymerization of pyrrole was conducted on a PTHF coated Pt electrode.

All syntheses were carried out in a conventional three electrode electrochemical cell using platinum (Pt) electrodes (1.5 cm^2 each) as the working and the counter electrodes. The reference electrode was a Ag/Ag^+ (10^{-2} M). Syntheses of the polymers were performed at a constant potential of 1.1 V (supplied by a Wenking POS 73 potentiostat) and under nitrogen atmosphere. The temperature was kept at 0 °C during electrolysis.

When TBAFB and $NaClO_4$ were used as the supporting electrolytes, single step procedure was followed. In the case of TBAFB, a 60-mL solution of CH_2Cl_2 containing 100 mg PTHF, 0.02 M pyrrole and 0.05 M electrolyte was used. Sufficient amount of films were obtained in 10 hours. Syntheses of the ClO_4^- doped films were performed under similar conditions; however, 60 mL CH_2Cl_2 (60 % v/v) and AN (40 % v/v) mixture rather than a solution of CH_2Cl_2 was used. 2 hours were enough to obtain sufficient amount of films.

PPy/pTHF PTS^- doped polymers were synthesized by the electrochemical polymerization of pyrrole onto a PTHF coated electrode, i.e., via double step procedure. The solvent was water (with 20 % v/v AN) containing 0.05 M PTS^- and 0.02 M pyrrole. PTHF polymers were dissolved in CH_2Cl_2 and coated on Pt electrodes by dipping the electrode in the polymer solution and allowing the solvent to evaporate. The reaction lasted for 2 hours.

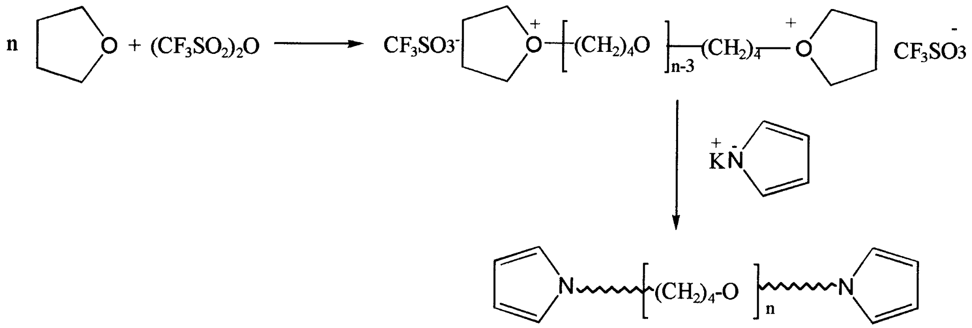
Characterization

GPC analysis were performed with a set up consisting of a Waters 600 pump and 2 ultrastyragel columns (10^4, 500 A°) with THF as the eluent at a flow rate of 1 mL/min and Waters differential refractometer (model 410). Molecular weights were calculated with the aid of PST standards. UV spectrum of polymers were measured by Perkin Elmer UV Lambda 2 spectrometer. ^{1}H-NMR spectra were taken on a Bruker Am 400 type instrument using $CDCl_3$ as a solvent and TMS as an internal standart.

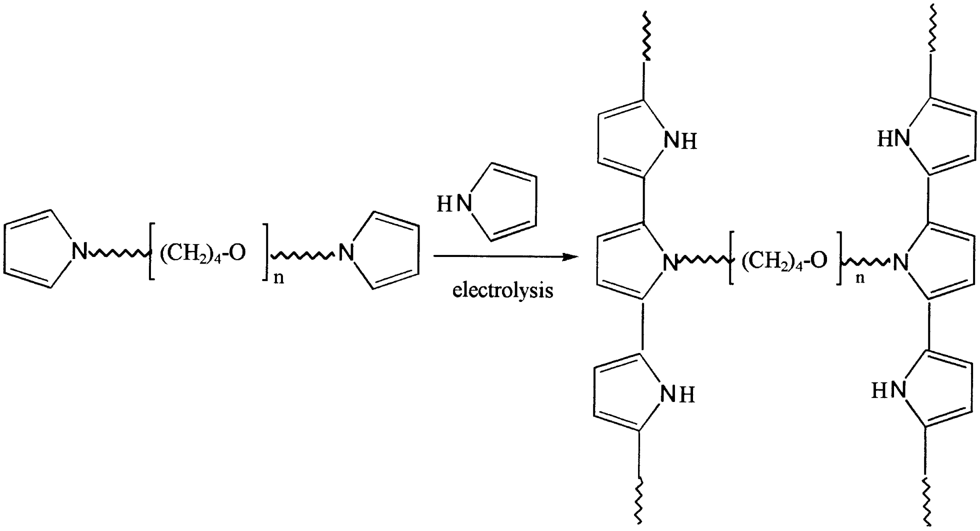
DSC studies were carried out under nitrogen atmosphere at a heating rate of 10°C/min by using a Du Pont 2000 instrument. Thermal behaviors of the films were also analyzed by TGA (Du Pont 960), conditions similar to that of DSC studies were provided. SEM was performed using a Jeol JSM 6400 Scanning Electron Microscope. Despite their intrinsically conducting nature, all specimens were coated with gold prior to examination. FTIR spectra of the films were recorded on a Nicolet 510 FT-spectrometer to investigate the formation of graft copolymers. Cyclic voltammetry experiments were carried out with a HEKA potentiostat/galvanostat. Conductivities were measured via 4- probe technique.

Results and Discussion

Trifluoromethane sulfonic anhydride (triflic anhydride) has been described as an initiator which leads to bifunctional living polytetrahydrofurans (14). In this work, bulk polymerization of THF was initiated by 1.2×10^{-2} mol/L and 2.44×10^{-2} mol/L triflic anhydride in the synthesis of PTHF1 and PTHF2 at 25°C separately. Living ends of the polymers were terminated with potassium salt of pyrrole to yield electrochemically active-bifunctional PTHF's; PTHF1 (Mn:30000, Mw/Mn:1.3) with 10 % conversion, and PTHF2 (Mn: 13750, Mw/Mn:1.5) with 20 % conversion at the end of 20 and 35 minutes, respectively. The content of pyrrole moiety is about 2.01 and 1.98 for per PTHF1 and PTHF2 chains, respectively,as calculated by ^{1}H-NMR using the peak areas ratio of the protons of pyrrole at 6.4-7.1 ppm and the protons of OCH_2 of PTHF at 3.4 ppm. These results and increase in molecular weight distribution (Mw/Mn≅1.1) during functionalization suggests that functionalization was quantitative in spite of slow termination reaction. UV spectra of polymers show characteristic absorbance of pyrrole moieties.



As regards to the electroactivity of the terminal pyrrole moieties, as was demonstrated for polymethylmethacrylate, electrochemical method was employed in order to transform these polymers into block copolymers containing pyrrole and tetrahydrofuran segments as depicted below.



Electrochemical synthesis of block copolymers yielded free standing black films which were easily peeled off from the electrode surface. The mechanical properties of block copolymers were quite different from the polypyrrole homopolymer. The polytetrahydrofurane-polypyrrole block copolymers produced rubbery films. These films were soft but retained their shape when cut into strips. When these films were washed with the solvent of pristine copolymer (dichloromethane) for three days and dried, PPy/PTHF1 films showed a weight loss of 9 %, 5.5 % and 2.5 %, when BF_4^-, ClO_4^- and PTS^- were used as the supporting electrolytes, respectively. PPy/PTHF2 films doped with BF_4^-, ClO_4^- and PTS^- lost 10 %, 3 % and 2 % of their original weights, respectively. Therefore, the remaining insulating polymer should have incorporated in the conducting polymer through the growing pyrrole chain.

DSC of the pristine polymers showed only a well-defined, sharp melting peak at 43 °C for PTHF1 (fig 1a) and at 38 °C for PTHF2. In the second heating, after the samples were cooled from 90 °C to –60 °C, the melting peaks were at 30 °C for the both (fig 1a).

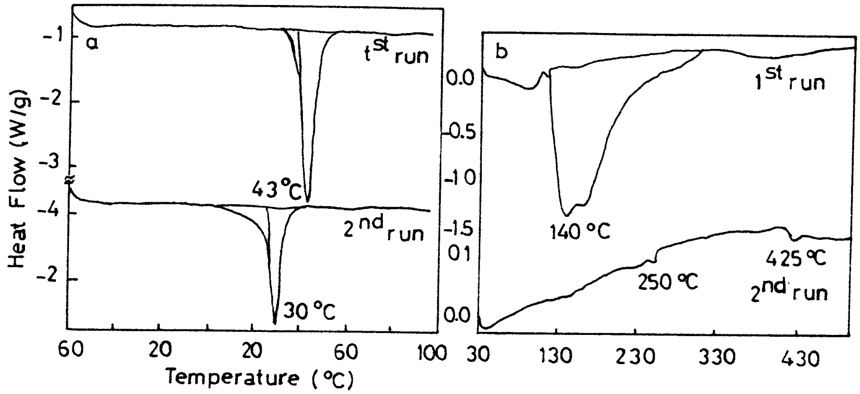


Figure 1. DSC thermograms of a) PTHF1, b) BF_4^- doped pure polypyrrole.

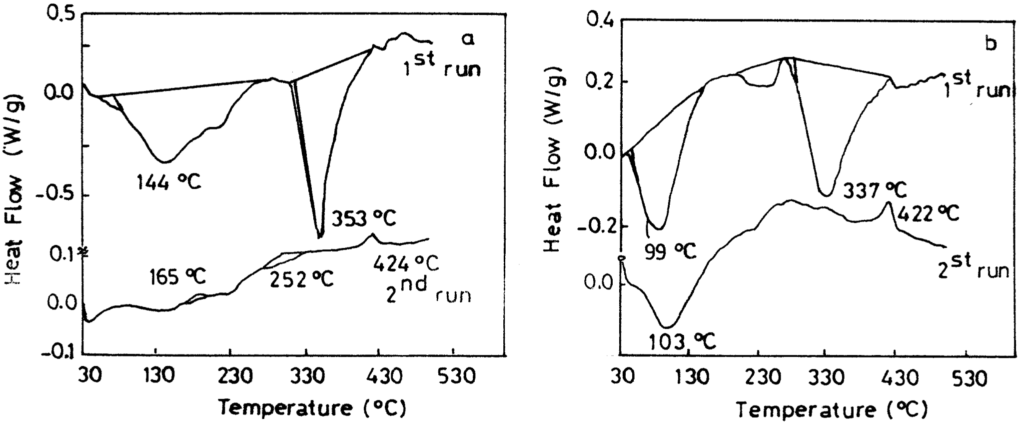


Figure 2. DSC thermograms of (a) BF_4^- doped PPy/PTHF1, (b) PTS^- doped PPy/PTHF1

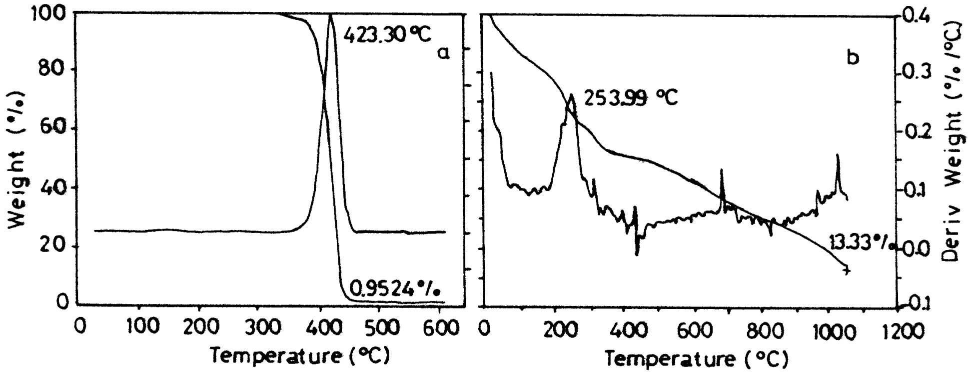


Figure 3. TGA of (a)PTHF1, (b) BF_4^- doped PPy/PTHF1

DSC of the copolymer films were fairly complicated as shown in fig.2. PPy/PTHF1 and PPy/PTHF2 films showed similar thermal behaviors. The broad endothermic peak at 144°C for PPy/PTHF1 was attributed to the decomposition of PPy was also evident from fig.1b. A large broad exothermic peak at about 270°C was due to the ClO_4^- in PPY/PTHF films. Fig. 2b reveals the thermal behavior of a film obtained via double step procedure (PPy/PTHF-PTS doped). The thermogravimetric scans of PTHF1 and PTHF2 showed that, they were somewhat stable to heating up to the decomposition temperature. 423°C for PTHF1 and 429°C for PTHF2 after which losing weight rapidly (fig.3a). Pure PPy BF_4^- doped film; however, lost its weight rapidly at about 70°C to 60% remaining and then gradually lost its weight to 15% remaining at 760°C. BF_4^- doped PPy/PTHF1 and PPY/PTHF2 showed a thermal stability somewhat between the pristine polymers and pure polypyrrole. Double weight loss patterns were observed for the both, at 98°C up to 73 % remaining and 260°C up to 55 % remaining (fig.3b). The first loss might be due to the decomposition of polypyrrole, the other might be due to the copolymer. ClO_4^- doped PPy/PTHF1 and PPy/PTHF2 showed a single weight loss pattern, 60 % remaining at 263°C for PPy/PTHF1 and 277°C for PPy/PTHF2. There was a more gradual decrease in weight when compared to BF_4^- doped ones. The highest resistance to heat was revealed by PTS^- doped films. About 80% remaining at 338°C for PPy/PTHF1, and slow weight loss pattern after that was observed.

FTIR spectra of PTHF1 and PTHF2 insulating polymers had almost the same characteristic bands. C-O-C asymmetric streching was observed at 1113 cm^{-1} most intensely. Three bands between 2939 cm^{-1} and 2795 cm^{-1} arouse as a result of aliphatic C-H strechings. C=C ring streching at 1455 cm^{-1} and C-N streching at 1244 cm^{-1} proved the presence of pyrrole moieties in the pristine polymers. Both PPy/PTHF1 and PPy/PTHF2 doped with BF_4^- showed the characteristic bands of insulating polymers. In addition, an intense band at 1082 cm^{-1} indicated the presence of BF_4^- anions in the polymer chain. PPy/PTHF1 and PPy/PTHF2 ClO_4^- doped copolymers showed aliphatic C-H streching and C-O-C asymmetric streching bands. In addition, three bands between 1150 cm^{-1} and 1084 cm^{-1} and the one at 628 cm^{-1} arouse as a result of PPy-counterion interactions. PTS^- doped polymers have had a very crowded appearance between 1700 cm^{-1} and 500 cm^{-1} and they also showed the characteristic bands of pristine polymers.

Scanning electron microscopy studies (SEM) revealed that PPy/PTHF1 and PPy/PTHF2 films had no significant difference in surface morphologies, in contrast to different dopants. Solution sides of ClO_4^- and PTS^- doped films had cauliflower-like surfaces, in addition, even worm-like forms were observed in the case of PTS^- doped ones. BF_4^- doped films showed no significant difference between solution and electrode sides, even the formation of cauliflower-like structures on the solution side could not have been observed. This is most unusual since pristine polypyrrole films with any dopant reveal cauliflower-like structures on solution sides.

Cylic voltammetry studies indicated that PTHF1 and PTHF2 did not show any detectable redox peaks with any of the systems described. The pristine polymers were not electroactive; however, in the presence of pyrrole, an electroactivity with the number of scans was observed, in a medium where BF_4^-, ClO_4^- were used as the electrolytes. As a result, possibility of self crosslinking through the pyrrole moieties in the absence of pyrrole was unlikely. BF_4^- doped PPy/PTHF1 and PPy/PTHF2 showed no well-defined oxidation peaks. However, an oxidation peak at about 0.65 V was observed for both polymers in the presence ClO_4^-. The voltammograms were similar in appearance to that of ClO_4^- doped pure PPy. PTS^- doped PPy/PTHF1 and PPy/PTHF2 showed a well-defined oxidation peak at 0.9 V which disappeared after successive runs, electroactivity decreased down to a certain point and then became constant. This behavior was attributed to the presence of water in the system. Pure PPy showed a similar behavior.

Conductivities of the products and pure PPy were in the same order of magnitude. All of the films had conductivity values between 0.2 and 0.9 S/cm.

Conclusion

Chain length of the polytetrahydrofuran segments did not influence thermal, electrochemical behaviors, surface morphologies and conductivities significantly. However, those properties were strongly affected by using different electrolytes in the syntheses of conducting polymers. The pristine Ppy films synthesized via same methods using the same supporting electrolytes are different from the PPy/PTHF electrolytic films in terms of thermal and SEM analyses.

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