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Characterization of Conducting Copolymer of Pyrrole via Pyrolysis Mass Spectrometry

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In this work, structural and thermal characterization of BF_4^- doped copolymer of pyrrole (PPy) with 2-methylbutyl-2-(3-thienyl)acetate prepared by electrochemical polymerization were performed via a pyrolysis mass spectrometry technique. The pyrolysis mass spectrometry data of the copolymer PPy/PMBTA, and the homopolymers; polypyrrole, PPy, and poly(2-methylbutyl-2-(3-thienyl)acetate), PMBTA were analyzed and compared. It has been determined that when the electrochemical polymerization of pyrrole was achieved on a PMBTA coated anode through the thiophene moieties of PMBTA, thermal stability of PMBTA chains increased slightly and the decomposition of both units followed quite similar pathways indicating an increase in the thermal stability of PMBTA chains unlike what was observed for PTSA doped PPy/PMBTA copolymer.

Keywords: pyrolysis; polypyrrole; copolymer; conducting polymers

1 Introduction

Electrochemical polymerization has been extensively used for preparing conducting polymer films such as polypyrrole. The great interest focused on polypyrrole is due not only to its good stability, but also to its ability to switch between oxidized and reduced states leading to conducting or insulating polymer films (1, 2) and its several applications such as elastic textile composites of high electrical conductivity, supercapacitors for energy storage and secondary batteries and enhancement of shear strength and toughness of graphite fibers (3–5).

The synthesis conditions and the nature of the supporting electrolyte used during electropolymerization strongly affect the electrochemical, mechanical, and other properties of the polymer films. The mechanical properties of polypyrrole films have already been the topic of various studies (6–10). In order to improve the mechanical properties of conductive polymers either structural modification of monomers or preparation of block and graft copolymers of conducting polymers with certain insulating polymer matrices having good mechanical properties have been achieved (11–13). For this purpose, we have attempted to polymerize thiophene and pyrrole through the heterocyclic end groups of some insulating polymers in our recent studies (14–16).

Although, the research on conducting polymers increased significantly during the last decades, the structural characterization of the samples by classical spectrometry techniques is still limited. It has been shown that pyrolysis mass spectrometry techniques offer an alternative way for polymer structure and composition analyses (17–19).

In this work, the structural and the thermal characterization of BF_4^- doped copolymer prepared by electrochemical polymerization of pyrrole (Py) on poly(2-methylbutyl-2-(3-thienyl)acetate) (MBTA) coated electrode has been performed via direct insertion probe pyrolysis mass spectrometry technique and the results were compared with those of polypyrrole (PPy), and poly(2-methylbutyl-2-(3-thienyl)acetate) (PMBTA). The results were also compared with those obtained for (PTSA), a copolymer doped with p-toluene sulfonic acid, in order to investigate the effect of dopant on the thermal characteristics.

2 Experimental

2.1 Synthesis

We have discussed the synthesis of (S)-2-methylbutyl-2-(3-thienyl)acetate (MBTA) in detail in our previous studies (15, 16). The crude product was purified by passing through a silica gel column using hexane as the eluent. The polymerization of the monomer was achieved by constant current electrolysis in a one compartment cell consisting of platinum working and counter electrodes, in

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dichloromethane-tetrabutylammonium tetrafluoroborate, $N(C_4H_9)_4BF_4$, (TBAFB), solvent electrolyte system. Scheme 1 represents the galvanostatic polymerization of the monomer, MBTA.

Homopolymerization of pyrrole (0.02 M) was achieved in an aqueous solution of 0.05M TBAFB using two Pt foil electrodes (1.5 cm^2) as the working and counter electrodes and a Ag/Ag^+ as the capillary reference electrode by a Wenking POS 73 Potentiostat at 1.1 V. Pyrrole (0.02 M) was electrochemically polymerized on a PMBTA coated anode through the thiophene moieties using similar conditions as for the preparation of PPy. The expected mechanism is shown in Scheme 2.

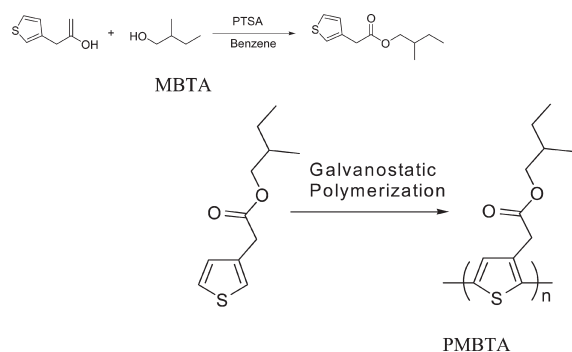
2.2 Analysis

5973 HP quadruple mass spectrometry system is coupled to a JHP SIS direct insertion probe for thermal analyses. Samples (0.01 mg) were pyrolyzed in flared glass sample vials. The temperature was increased at a rate of $10^\circ\text{C}/\text{min}$ up to $30\text{--}450^\circ\text{C}$, the maximum attainable temperature. 70 eV EI mass spectra were recorded at a scan rate of 2 scans/s during the pyrolysis. Pyrolysis experiments were repeated using different samples of the same polymer films and films obtained from parallel electrochemical polymerization processes.

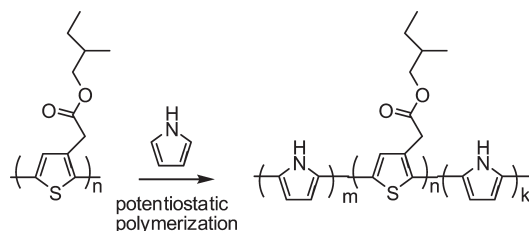
Conductivity of the samples was measured using a four probe technique as 1×10^2 , 8×10^{-3} , and $2 \times 10^{-2}\text{ Scm}^{-1}$ for BF_4^- doped PPy, PMBTA, and PPy/PMBTA, respectively.

3 Results and Discussions

It is known that when the thermal degradation proceeds through a depolymerization mechanism, the mass spectrum of the monomer and the pyrolysis mass spectra of the corresponding polymer are almost identical. A depolymerization mechanism is likely for straight chain polymers that do not involve labile side chains and linkages or crosslinked structure. In general, thermal degradation mechanisms of conducting polymers are usually complex, not only due to the presence of dopant, but also the network structure usually these polymers possess. Thus, for a reliable analysis of a



Sch. 1. Synthesis of (S)-2-methylbutyl 2-(3-thienyl)acetate (MBTA) and its homopolymer.



Sch. 2. The expected mechanism for the synthesis of PPy/PMBTA.

conducting copolymer by pyrolysis MS technique, the pyrolysis mass spectra of all the reactants and the related homopolymers must be studied (16, 20). The mass spectrum of (S)-2-methylbutyl-2-(3-thienyl)acetate (MBTA) involves peaks due to C_2H_2OH ($m/z = 43\text{ Da}$), $C_4H_3SCH_2$ ($m/z = 97\text{ Da}$), $C_4H_3SCH_2COOH$ ($m/z = 142\text{ Da}$), $COOH$ ($m/z = 45\text{ Da}$), C_5H_{11} ($m/z = 71\text{ Da}$) reflecting the classical ester, hydrocarbon and thiophene fragmentation patterns. On the other hand, the spectrum of pyrrole shows the molecular ion peak at $m/z = 67\text{ Da}$ (the base peak), and intense peaks at 41, 39 and 28 Da due to C_2H_2NH , C_3H_3 and $CHNH$. The mass spectrum of the supporting electrolyte is mainly dominated with peaks due to dissociative ionization of tetrabutylammonium cation, peaks at $m/z = 100, 142, 185,$ and 242 Da are due to $N(C_4H_9)C_2H_5$, $N(C_4H_9)_2CH_2$, $N(C_4H_9)_3$, and $N(C_4H_9)_4$ respectively. Actually, the doped polymer samples should only involve the anion BF_4^- , not the counter ion tetrabutylammonium cation.

In our previous work, we determined that BF_4^- doped PPy decomposes mainly in three stages; the first stage below 100°C was associated with evolution of adsorbed water, the solvent, acetonitrile, tetrabutylammonium ion, and unreacted pyrrole (14). The second stage at moderate temperatures, around 250°C was attributed to the degradation of dopant ion yielding product peaks due to BF_3 , BF_2 , and BF , and the third stage is due to decomposition of polypyrrole.

Pyrolysis mass spectrometry analyses also indicated a three stage thermal decomposition for BF_4^- poly(2-methylbutyl 2-(3-thienyl)acetate), PMBTA which is basically a 3-substituted thiophene polymer (16, 20). At temperatures around $180\text{--}190^\circ\text{C}$, evolution of the counter ion of the electrolyte trapped by the polymer, around 240°C decomposition of supporting electrolyte, BF_4^- and around 440°C , thermal degradation products of the polymer itself were detected. The pyrolysis mass spectra of PMBTA showed no resemblance to that of the monomer. A multi-step degradation mechanism that started by the loss of side chains and the cleavage of labile C-O bonds was assigned for the thermal decomposition of the polymer. Although, the generation of thiophene and its dimer were significant at moderate temperatures, that of H_2S can only be detected at elevated temperatures. In our previous studies on pyrolysis of polythiophene, PTh, the H_2S yield was higher than that of the thiophene and this behavior was explained by a network structure (21, 22). Yet, for PTh samples, evolutions of H_2S and

thiophene were detected in the same temperature region. The results also indicated that for this particular thiophene derivative, PMBTA the extent of the network structure is limited.

The thermal decomposition of the copolymer occurred in a broad temperature range above 200°C. In Figure 1, total ion current (variation of total ion yield as a function of temperature) curves for BF₄ doped PPy, PMBTA and PPy/PMBTA copolymer are shown. The low temperature peaks due to evolution of unreacted MBTA and adsorbed counter ion were significantly diminished for this sample pointing out the desorption of adsorbed MBTA, and TBAFB adsorbed on the matrix polymer during the electrochemical polymerization of pyrrole.

Single ion evolution profiles of some characteristic products due to decomposition of dopant and each component of the copolymer namely, BF₂ (m/z = 49 Da) pyrrole (m/z = 67 Da), pyrrole dimer (m/z = 131 Da), C₄H₇ (m/z = 55 Da) and (CH₂)C₄H₃S (m/z = 97 Da) are shown in Figure 2. The evolution profiles of PMBTA based products from the copolymer shifted to higher temperatures compared to PMBTA indicating an increase in thermal stability of PMBTA due to copolymerization of Py. Inspection of single ion pyrograms also pointed out that the thermal decomposition of both units followed very similar paths unlike what was observed for PTSA doped PPy/PMBTA copolymer.

In Figure 3, evolution profiles of characteristic degradation products such as pyrrole (m/z = 67 Da), pyrrole dimer (m/z = 131 Da), C₄H₇ (m/z = 55 Da) and (CH₂)C₄H₃S (m/z = 97 Da) and H₂S detected during the pyrolysis of PTSA and BF₄ doped PPy/PMBTA are shown. C₇H₇ (m/z = 91 Da) and BF₂ (m/z = 49 Da) fragments, being the

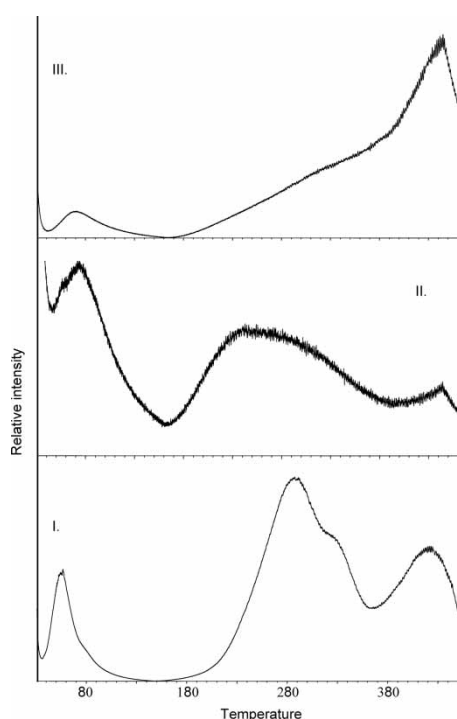


Fig. 1. The TIC curves and of BF₄ doped I. PMBTA, II. PPy and III. PPy/PMBTA.

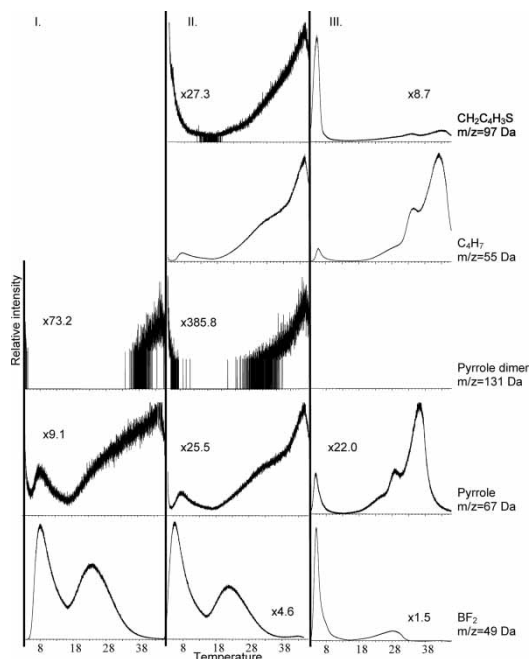


Fig. 2. Single ion pyrograms of some selected degradation products of BF₄ doped I. PPy II. PPy/PMBTA and III. PMBTA.

most abundant products due to loss of dopants from PTSA and BF₄ doped copolymers, respectively are also included for comparison. It is clear that evolution of PTSA related products occurred at significantly higher temperatures

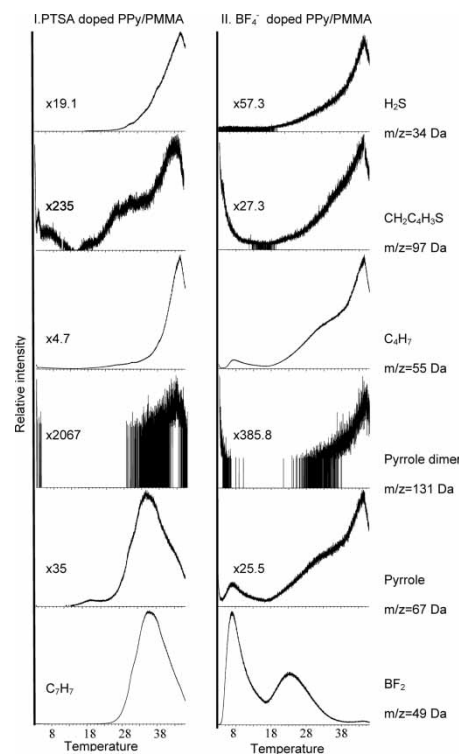


Fig. 3. Single ion pyrograms of some selected degradation products of I. PTSA doped PPy/PMBTA, and II. BF₄ doped PPy/PMBTA.

compared to BF_4^- related ones. The maxima in the evolution profiles of C_7H_7 and BF_2 were at 350 and 240°C, respectively. This result indicated that the PTSA as a dopant is more effective and PTSA doped samples can retain their conductivity at higher temperatures.

Evolution of H_2S was recorded for both samples in the final stage of pyrolysis due to the decomposition of the thiophene ring. Yet, for PTSA doped sample, the relative yield of H_2S compared to other thiophene consisting fragments, such as $(\text{CH}_2)\text{C}_4\text{H}_3\text{S}$, was significantly high. The $\text{H}_2\text{S}/(\text{CH}_2)\text{C}_4\text{H}_3\text{S}$ peak ratios were 12.4 and 0.47 for PTSA and BF_4^- doped samples, respectively. Its high yield could be attributed to the decomposition of dopant p-toulene sulfonate. However, its evolution profile was totally different than the rest of the PTSA based products such as tropylium ion and mainly generated in the region where decomposition of polymers was recorded (Figure 3). It can be concluded that some chemical reactions have taken place between the PTSA and the polymers and/or pyrrole yielding sulphur containing chains. Actually, for PTSA doped copolymer evolution of pyrrole was detected in the lower temperature ranges compared to BF_4^- doped copolymer. This may be an indication of presence of low molecular weight oligomers. Thus, it can further be concluded that although a stronger interaction between dopant and the polymer existed for PTSA doped copolymer, reactions of dopant with the monomer and/or polymer lead to substitution reactions depressing the growth of the polymer.

4 Conclusions

Pyrolysis mass spectrometry analyses of BF_4^- doped PPy/PMBTA copolymer revealed that unlike the PTSA doped PPy/PMBTA copolymer, the decomposition of both units followed quite similar pathways indicating an increase in thermal stability of PMBTA chains.

5 Acknowledgments

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