PYROLYSIS OF BF$_4^-$ DOPED POLYPYRROLE BY DIRECT INSERTION PROBE PYROLYSIS MASS SPECTROMETRY

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ABSTRACT

A systematic structural and thermal characterization of conducting polypyrrole doped with BF$_4^-$ was performed using a direct insertion probe pyrolysis mass spectrometry technique. The effect of dopant concentration on the structure and stability was investigated not only by analyzing samples with different doping levels, but also analyzing the dedoped polypyrrole sample. To get a better understanding, the changes in structure and stability upon overoxidation and thermal aging were also studied. During pyrolysis, mainly three thermal decomposition stages were observed. The first stage below 100°C was associated with evolution of adsorbed water, the solvent acetonitrile, tetrabutylammonium ion, and unreacted pyrrole. The dopant peaks such as BF$_3$, BF$_2$, and BF were recorded at moderate temperatures around 250°C, whereas, polypyrrole peaks showed up in the last stage above which is 300°C. It has been observed that at high BF$_4^-$ concentrations aromatic structure was enhanced contrary to what was observed for p-toluene sulfonic acid doped polypyrrole in our previous studies.

Key Words: Polypyrrole; BF$_4^-$ as dopant; Thermal degradation; Mass spectrometry

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INTRODUCTION

There have been many studies related to structure [1-5], effects of doping level and dopant on conductivity [6-8] and stability [9-16] of polypyrrole, PPY. The electrical conductivity for the quinoid form is found to be larger than that for the aromatic form. Thus, the quinoid form is assigned to the doped state whereas the aromatic form is assigned to the undoped state [1-3]. Yet, Forsyth *et al.* proposed that the polypyrrole structure is counterion (dopant) dependent and only some counterions favor the quinoid structure [2]. The higher conductivities of polypyrrole films prepared with large organic counterions such as dodecyl sulfate or p-toluene sulfonate compared to those prepared with inorganic dopants also suggest counterion dependence of the structure. M. Kikuchi *et al.* showed in their solid state ^{15}N NMR spectroscopy study that the extent of quinoid structure increased by doping [3]. However, Sun *et al*. observed that H_2SO_4, KI and several other doping agents initially caused an increase in the conductivity, but beyond a certain dopant concentration the conductivity decreased [6]. In addition, it has also been determined that when $AlCl_3$, $KBrO_3$, or HNO_3 were used the conductivity decreased with the increase in dopant concentration.

In many spectrometric studies a decrease in conductivity in the presence of hydroxide and carbonyl groups in the polymer backbone was detected. The oxidation in aqueous electrolytes was basically associated with water attack at the pyrrole radical cations yielding hydroxide and carbonyl groups [2]. It is clear from the literature results that thermo-oxidative degradation mechanisms of PPY are complex and depend on various factors. In a previous pyrolysis mass and FTIR spectroscopy studies on p-toluene sulfonic acid doped polypyrrole, we have determined that polypyrrole prepared in aqueous media contains a high concentration of oxygen defects even if the synthesis potential is kept low and have shown that the extent of overoxidation associated with ketone formation increases with the increase in synthesis potential and thermal aging [9].

In this work, a systematic structural and thermal characterization of conducting polypyrrole doped with BF_4^- was performed using a direct insertion probe pyrolysis mass spectrometry technique. The effect of dopant concentration on structure and stability was investigated not only by analyzing samples with different doping levels, but also by analyzing dedoped polypyrrole samples. To get a better understanding the changes in the structure and stability upon overoxidation and thermal aging were also studied.

EXPERIMENTAL

Electrochemical Synthesis of Polypyrrole

Polypyrrole was electrochemically prepared using the system discussed in our previous studies [5, 17]. The concentration of vacuum distilled pyrrole (Aldrich) was 0.02 M (1.2 mmol). The electrolysis was performed using 1.2 cm^2

platinum electrodes in acetonitrile at room temperature at 1.1 V vs. Ag/Ag$^+$ reference electrode using tetrabutyl ammonium tetrafluoroborate (TBAFB) as the supporting electrolyte. A PPY doped with 0.05 M BF$_4^-$, (HB-PPY) and PPY doped with 10^{-3} M BF$_4^-$ (LB-PPY) were obtained as free standing black films in 3 hours and 12 hours of electrolyses, respectively. The reduced, dedoped sample (DB-PPY) was obtained by the reduction of HB-PPY at –1.1 V vs. Ag/Ag$^+$ for 6 hours. Overoxidized PPY sample (OB-PPY) was synthesized by applying electrolysis potential of 2.0 V keeping the other experimental conditions constant. A PPY sample prepared at 1.1 V was thermally aged at 120°C for three days in air, and named as TB-PPY. All the PPY samples were washed with acetonitrile to remove physically adsorbed TBAFB. Samples were dried in high vacuum and kept under nitrogen atmosphere.

Thermal Analysis

The direct insertion probe mass spectrometry system consists of a 5973 HP quadrupole mass spectrometry with a mass range of 10-700 amu coupled to a SIS direct insertion probe. The maximum temperature that can be attained is 445°C. Thermal decomposition of the samples was studied at a heating rate of 10°C/min. Mass spectra were acquired at a rate of 2 scans/s using 70 eV electrons. Experiments were repeated decreasing ionization energy to 19 eV to minimize dissociation of thermal decomposition products in the ion source of the mass spectrometry system.

Thermogravimetry analysis, TGA were performed using a Perkin Elmer TGA system at a heating rate of 10°C/min in the range of 25 to 1000°C under the flow of N$_2$.

RESULTS AND DISCUSSION

Thermal decomposition product peaks started to appear in the pyrolysis mass spectra even at initial stages. Yet, the main decomposition was occurred above 200°C in accordance with TGA results [18, 19]. The total ion-temperature profiles (variation of ion yield as a function of temperature) of decomposition products of all the samples showed several shoulders pointing out that the polymer samples were inhomogeneous. Actually, there exists mainly three decomposition stages. In the first stage below 100°C only low mass fragments were observed. Among these, the peaks at 41, 26, and 15 amu showed similar behavior in the low temperature ranges below 80°C. These peaks were assigned directly to fragments due to dissociative ionization of adsorbed solvent acetonitrile namely, CH$_3$CN$^+$, CN$^+$, and CH$_3$. Alkyl amine, and hydrocarbon peaks such as peaks at m/z = 185 amu due to N(C$_4$H$_9$)$_3$, and 57 amu due to (C$_4$H$_9$), were also present indicating the adsorbtion of tetrabutylammonium ion N(C$_4$H$_9$)$_4^+$ ion on the polymer matrix although polymer films were washed several times with acetonitrile and dried

under vacuum. Both the solvent and $N(C_4H_9)_4^+$ based peaks dissappeared in the thermally aged TB-PPY sample supporting our assignments.

H$_2$O based peaks were also quite intense especially at initial stages. Since syntheses were carried in nonaqueus media under N_2 atmosphere, their origin can not be due to adsorbed water on the polymer samples during preparation. Actually, H$_2$O based peaks are always present in the background due to the desorption of water adsorbed on the metal surfaces of the mass spectrometry and pyrolysis systems under high vacuum conditions. Yet, their existence in the high-temperature pyrolysis mass spectra can be attributed to presence of oxygen defects along the polymer chains.

In the second stage of thermal decomposition dopant based peaks were detected. The peaks at m/z= 68, 49, and 30 attributed to BF_3, BF_2, and BF, respectively were among the most intense and appeared in the pyrolysis mass spectra starting from initial stages and reached their maximum values around 250°C. Formation of HF mainly occurred at high temperatures and discussed in detail in a previous study [17]. The dopant related peaks followed completely different paths. We proposed flouride substitution on the pyrrole ring during electrolysis considering HF evolution at high temperatures even from the dedoped sample. The dopant based peaks were observed at significantly higher temperatures in the p-toluene sulfonic acid doped polypyrrole samples around 340°C. Thus, it may be concluded that the interaction between BF_4^- and the host polymer is weaker compared to that of between p-toluene sulfonate ion and polypyrrole.

In the last stage of degradation besides the HF peaks, pyrolysis mass spectra involved features that may directly be attributed to the fragmentation of polypyrrole chain. Actually, these peaks were quite weak and observed in a broad temperature range. Peaks at 67 amu due to monomer M, and at 66 amu due to [M-H] were present. The contribution of $^{1°}BF_3$ peak to the monomer peak at 67 amu was obvious and seemed to be more efficient around 250°C. Appearance of polypyrrole based peaks in a broad temperature range may directly be related to the presence of low molecular weight oligomers and polydispersity of the sample. Presence of unreacted pyrrole adsorbed during synthesis was identified in the first degradation stage below 100°C. Very weak dimer and trimer peaks were also detected in the high temperature range above 340°C. Peaks at 26 (C_2H_2, CN) and 27 amu (C_2H_3, HCN) being significantly intense at high temperatures may be associated with the cleavage of the pyrrole ring.

In Figure 1, ion-temperature profiles of 66 (monomer-H), 131 (dimer-H), 26 and 27 amu fragments observed during pyrolysis of LB-PPY, HB-PPY, DB-PPY, and OB-PPY samples are shown. Two maxima around 375 and 440°C were detected. These values are in very good agreement with our previous pyrolysis results of p-toluene sulfonic acid doped polypyrrole indicating that thermal stability of the polypyrrole chain does not depend on the dopant [6]. Note the trends in the ion-temperature profiles of 26 and 27 amu peaks. Taking the fragmentation of tetrabutylammonium salt, the solvent and the pyrrole into account only the high temperature bands with maxima at 375 and 440°C were attributed to fragments
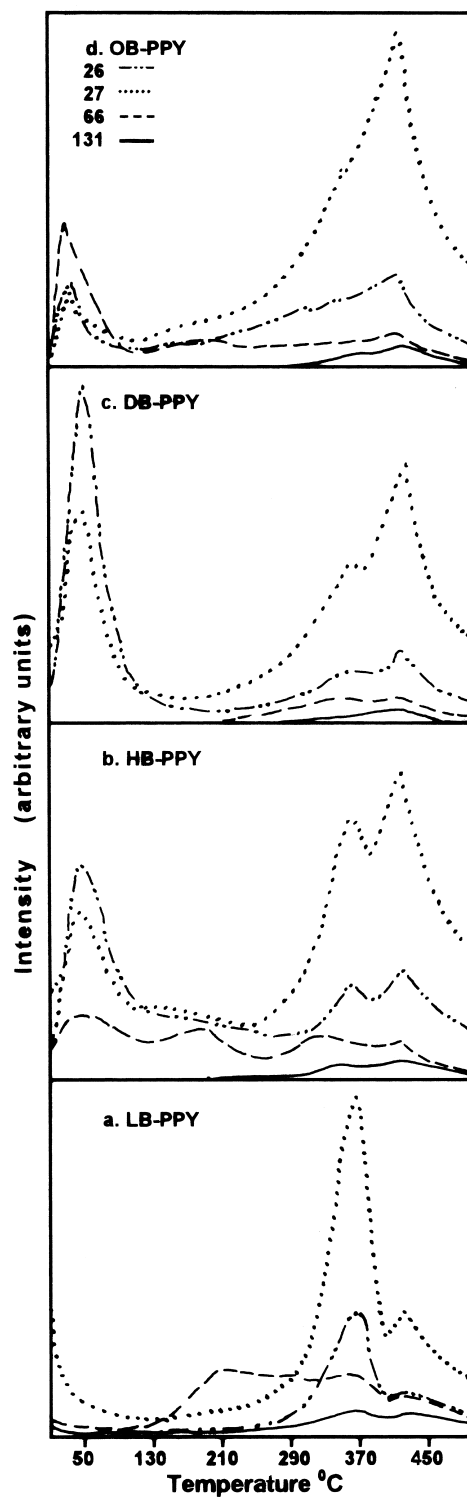
Figure 1. Ion-temperature profiles of 26, 27, 66, and 131 amu peaks associated with pyrrole decomposition observed during thermal degradation of a. LB-PPY; b. HB-PPY; c. OB-PPY; d. TB-PPY.

due to cleavage of the polypyrrole. Upon thermal aging, low temperature bands disappeared supporting our proposal.

Examination of the ion-temperature profiles of polypyrrole based peaks prepared using two different dopant concentrations pointed out that the relative intensity of high temperature shoulder at 440°C increased significantly with the increase in dopant concentration (Figure 1). The increase in the relative intensities of fragment peaks attributed to the decomposition of pyrrole ring was more drastic. At this temperature, the relative intensity of 66 amu peak was enhanced by a factor of 1.7, while those of 26 and 27 amu peaks were increased more than a factor of 3 with respect to the base peak. It is known that polypyrrole predominantly has aromatic or quinoid structure. Among these two fundamental structures, the aromatic form corresponds to the undoped state and the quinoid form corresponds to the doped state. In a recent study on p-toluene sulfonic acid doped polypyrrole we have assigned the high temperature shoulder to the aromatic structure and the band with maximum at 370°C to the quinoid structure [5]. A decrease in the relative intensity of the shoulder with the increase in dopant concentration has been observed indicating that the extent of quinoid structure was increased with the increase in dopant concentration. Thus, present results are contrary to our previous findings. There have been various studies in the literature indicating that polypyrrole structure is counterion (dopant) dependent and only some counterions favor the quinoid structure [2, 6]. Furthermore, decreases in conductivity beyond a certain dopant concentration have been observed. In our case, an increase in conductivity with the increase in the dopant concentration was recorded; conductivity was 10^{-2} Scm^{-1} for LB-PPY and 10^1 Scm^{-1} for HB-PPY. Thus, one possibility may be that the quinoid structure was favored at low BF$_4^-$ concentrations and formation of aromatic structure was enhanced at high dopant concentrations. However, taking into account the significant increase in the relative intensities of peaks related to oxidation and/or overoxidation (Table 1), it may also be suggested that another possibility is the increase in the extent of oxidation of the pyrrole ring for this sample. The decrease in the relative intensity of the band at 370°C assigned to the quinoid structure for the sample synthesized at 2 V and for the dedoped sample was in accordance with our previous results. These results confirmed that overoxidation diminishes the growth of quinoid structure and dedoping causes the loss of quinoid structure more readily.

In general, it is also known that the films polymerized at high potentials show more crosslinking and more structural defects [7-8]. Thus, the increase in the relative intensities of 26, and 27 amu peaks for the OB-PPY sample indicated that the cleavage of the pyrrole ring was enhanced possibly due to the existence of structural defects and in the extent of crosslinking that would inhibit depolymerization reactions reactions producing mostly monomer and low molecular weight oligomers.

Since all the samples except TB-PPY were freshly prepared in the absence of air and H$_2$O, oxidation of the polymer should be negligible. Of course, it is

Table 1. Some Characteristic Ions and Their Relative Intensity Observed from HB PPY, DB-PPY, OB-PPY and TB-PPYT in the High Temperature Range

| m/z		LB-PPY		HB-PPY		DB-PPY		OB-PPY		TB-PPY	
		370°C	440°C	370°C	440°C	370°C	440°C	370°C	440°C	370°C	440°C
18	H_2O	2538	2528	8129	7392	9448	10000	4578	4944	8878	7610
20	HF	7607	10000	10000	9093	9888	8052	10000	8830	10000	8934
26	C_2H_2, CN	275	111	384	349	440	683	526	703	357	292
27	C_2H_3, HCN	727	267	1107	1455	1600	2904	1446	2484	1126	1126
28	C_2H_4, CO, N_2	1286	711	4460	4964	8030	8953	2765	3533	5683	5762
30	BF	468	105	487	488	356	305	280	161	393	133
44	CO_2	1414	682	2205	2215	2747	2445	1463	983	9713	7037
49	BF_2	6203	1494	7010	3956	223	83	3901	1078	950	506
66	M-H	151	80	149	140	333	247	178	261	90	74
68	BF_3	638	148	607	497	265	152	360	256	227	92
131	D-H	56	43	76	87	93	110	88	157	37	49
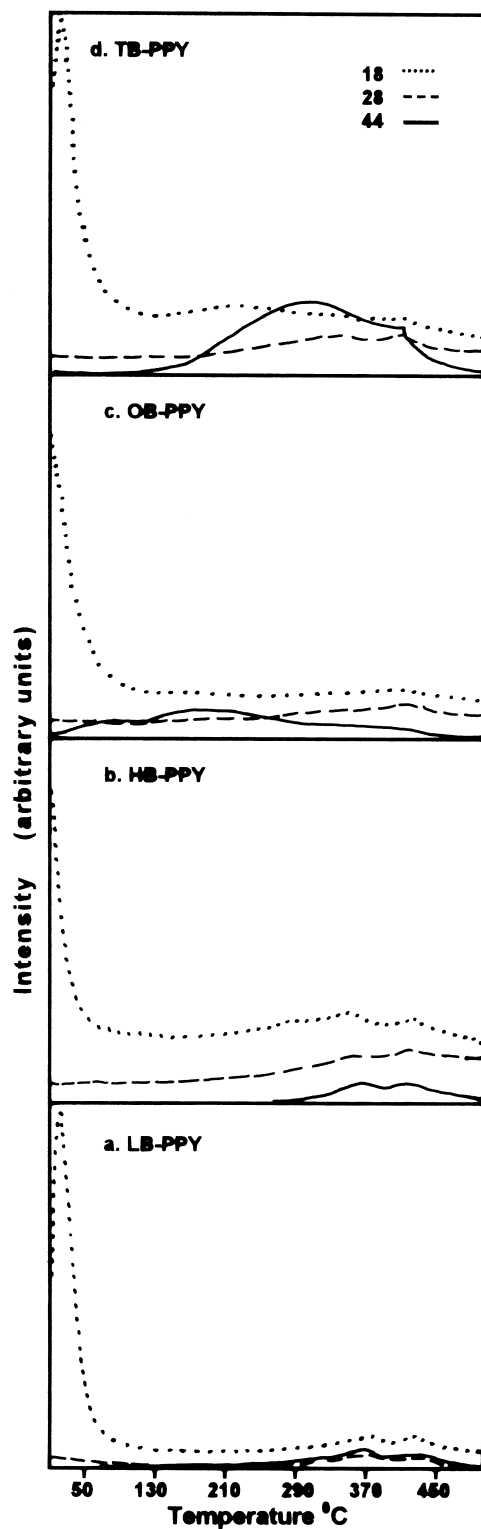
Figure 2. Ion-temperature profiles of 18, 28, and 44 amu peaks observed during thermal degradation of a. LB-PPY; b. HB-PPY; c. OB-PPY; and d. TB-PPY.

obvious that peaks due to H$_2$O, N$_2$, CO, O$_2$ and CO$_2$ as background gases should be present in each pyrolysis mass spectrum without background subtraction. Taking desorption of these species from the probe itself at initial stages into account it is expected that their intensities should be constant above 100°C in stabilized vacuum conditions. To get a better insight on oxidation processes, the ion-temperature profiles of H$_2$O, CO and CO$_2$ were studied (Figure 2). The weak bands in the region associated with polypyrrole degradation indicated oxidation of the pyrrole ring at least to a certain extent. The increase in relative intensities of these peaks with the increase in dopant concentration may be attributed to possibility of H-bonding with the dopant. The CO$_2$ formation from the OB-PPY and TB-PPY samples increased significantly at moderate temperatures pointing out the presence of carbonyl groups. In a previous study, we have studied the oxidation of p-toluene sulfonic acid doped polypyrrole prepared in aqueous media and showed that the oxidation of pyrrole ring occurs even at low synthesis potentials and the extent of overoxidation associated with ketone formation increases with thermal aging. Present results indicated that polymer samples were easily oxidized by atmospheric oxygen and carbonyl formation enhanced in the presence of structural defects. Intense CO$_2$ absorption was observed in the FTIR spectra of evolved gases from OB-PPY and TB-PPY samples collected in an evacuated IR gas cell supporting mass spectral results.

The relative intensities of some selected peaks recorded during pyrolysis of BF$_4^-$ doped polypyrroles are collected in Table 1.

Similar results were obtained when pyrolysis experiments were repeated decreasing ionization energy to minimize fragmentation in the ion source.

CONCLUSION

It is observed that pyrolysis of BF$_4^-$ doped polypyrrole mainly occurs in three regions. The low temperature peaks below 100°C were associated with adsorbed water, the solvent acetonitrile, tetrabutylammonium ion, and the unreacted pyrrole. The dopant peaks such as BF$_3$, BF$_2$, and BF were recorded around 250°C. On the other hand the decomposition product peaks of polypyrrole showed up at temperatures above 300°C. It has been observed that at high BF$_4^-$ concentrations aromatic structure was enhanced contrary to what was observed for p-toluene sulfonic acid doped polypyrrole samples, most probably due to higher extent of oxidation. Although counterion dependence of structure was noted, considering the results obtained in previous studies it may be proposed that thermal stability of both of the polypyrrole forms are independent of the type of the dopants involved and doping levels studied. Last but not least, features indicating oxidation of the pyrrole ring were determined indicating high reactivity towards atmospheric O$_2$ and/or water.

ACKNOWLEDGMENTS

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