

Thermal stability of electrochemically prepared polythiophene and polypyrrole

F MOHAMMAD*, P D CALVERT and N C BILLINGHAM

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

*Department of Applied Chemistry, Z. H. College of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, India

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Abstract. The degradation behaviour of electrochemically prepared polythiophene and polypyrrole has been studied by thermal gravimetric analysis technique. Studies on both the polymers show that they are more stable than polyacetylene but still undergo degradation reactions which involve two steps, viz. loss of dopant and then degradation of polymer backbone. The general features of degradation mechanisms are discussed.

Keywords. Conducting polymers; polythiophene; polypyrrole; TGA studies; degradation.

1. Introduction

Polymers undergo chemical reactions just like any typical low molecular weight compound, provided the reactants are made available at the reaction site. The process of deterioration of the useful polymer properties involving chemical reactions is defined as degradation. There are many external causes of degradation of polymeric materials such as heat, light, mechanical stress, oxygen, ozone, moisture, atmospheric pollutants, etc along with the factors effective at the time of processing. Also, the presence of reactive sites in the polymers such as peroxides, defects, chemically reactive groups, etc may degrade the polymer properties with or without the combination of external factors.

The emergence of direct and precursor route to polyacetylene films (Shirakawa and Ikeda 1971; Shirakawa *et al* 1977) and electrochemical polymerization of heterocyclics into polymer films such as polythiophene (Tourillon and Garnier 1982; Kaneto *et al* 1983) and polypyrrole (Dall'olio *et al* 1968; Diaz *et al* 1979; Street *et al* 1982) has triggered the investigation of these materials due to somewhat easier fabrication of experimental samples.

Knowledge of environmental stability and degradation behaviour is a prequalification for use of polymer films in many practical applications. This has led us to try to develop some chemical understanding of their stability and degradation behaviour in different environmental conditions.

2. Experimental

An evacuable electrochemical cell, assembled with platinum or indium–tin oxide conducting glass working electrode and aluminium counter electrode, was used for the preparation of oxidized polythiophene and polypyrrole films (Dall'olio *et al* 1968; Diaz *et al* 1979; Street *et al* 1982; Tourillon and Garnier 1982; Kaneto *et al* 1983). A current density of 9–12 mA/cm² was applied. Washing was done by extremely dry acetonitrile stored over

*For correspondence

freshly dried molecular sieves. Polymer films were further dried by pumping on vacuum line for about an hour prior to use. The thickness was estimated to be around 5 to 10 microns from the area and the weight of the polymer film. The TGA studies were performed on samples of as-prepared polythiophene and polypyrrole films in dry air as well as in nitrogen. Typically 5 to 8 mg samples were used and heated up to 700°C at a rate 30°C per min for the samples containing BF_4^- counterion and at a rate of 10°C per min in case of polythiophene containing ClO_4^- counterion. Isothermal TGA studies were carried out on as-prepared polythiophene (BF_4^-) and polythiophene (ClO_4^-) and their ammonia compensated counterparts in dry air. Typically 3 to 5 mg samples were heated at a rate of 100°C per min and then maintained at a desired temperature ranging from 372°C to 484°C. A Stanton Redcroft TGA instrument was used in these studies.

3. Results and discussion

Samples of polythiophene and polypyrrole containing various counterions and their ammonia compensated counterparts were examined in air and in nitrogen atmospheres both isothermally and with programmed temperature increase.

Thermogravimetric analysis of polythiophene (BF_4^-) and polypyrrole (BF_4^-) with programmed temperature increase reveals that polythiophene (BF_4^-) lost weight in two distinct steps. Step-1 is identical in nitrogen atmosphere and in air with a similar weight loss of 18% in the temperature range 70°C to 260°C. In step-2, the additional weight losses of 7% in nitrogen by 700°C and of 77% in air by 600°C were observed.

Polypyrrole (BF_4^-) lost weight in three rather indistinct steps in nitrogen as well as in air. Step-0 and step-1 are identical in nitrogen and air. Step-0 is very mild with a weight loss of 3% in the temperature range 45°C to 125°C in nitrogen and similar in air. Step-1 ranges from 125°C to 285°C with an additional weight loss of 19.5% in nitrogen and the same in air. Step-2 was monitored up to 700°C and found to be incomplete with further weight losses of 29% in nitrogen and 55% in air. The thermograms are shown in figure 1 and the results are given in table 1.

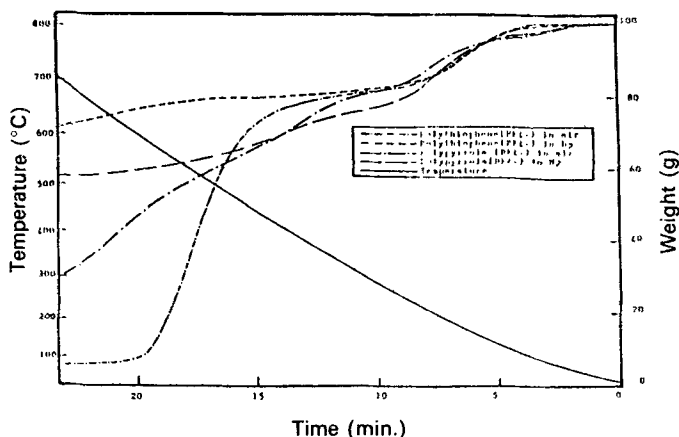


Figure 1. Thermograms of polythiophene and polypyrrole containing BF_4^- counterion in air and nitrogen.

Isothermal TGA studies of as-prepared polythiophene (BF_4^-) and polythiophene (ClO_4^-) and their ammonia compensated counterparts in air were carried out in the temperature range 372°C to 484°C . Plots of $\log W/W_0$ against time followed straight line characteristic of a first-order weight loss as shown in figure 2. Table 2 gives the rate constants of first order weight loss as estimated from $\log W/W_0$ versus time plots at various temperatures from different thiophene samples. The activation energy was calculated to be 94.5 kJ/mol from the slope of the Arrhenius plot shown in figure 3.

Table 1. Observed weight loss for 5–10 μm thick films of as-prepared PTh- BF_4 and PPy- BF_4 in various steps during programmed heating.

Step	PTh- BF_4		PPy- BF_4	
	Air	N_2	Air	N_2
Step-0	Temp. range($^\circ\text{C}$)		45–125	45–125
	Weight loss(%)		3.0	3.0
Step-1	Temp. range($^\circ\text{C}$)	70–260	70–260	125–285
	Weight loss(%)	18	18	19.5
Step-2	Temp. range($^\circ\text{C}$)	260–600	260–700	285–700
	Weight loss(%)	77	7	22.5
Residue(%)	5	75	55	29
Total	100	100	100	100

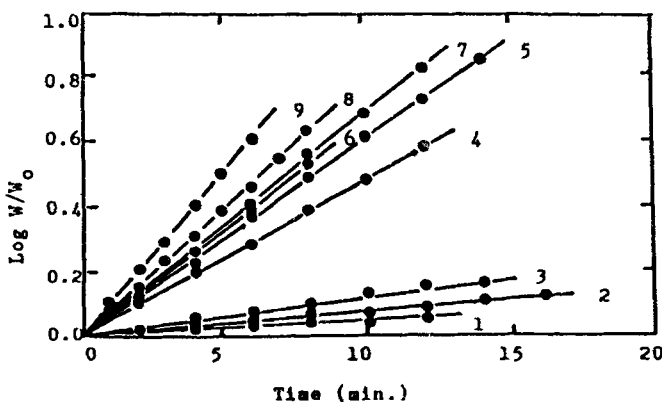


Figure 2. First-order weight loss of polythiophene on isothermal heat treatment. 1, NH_4OH compensated polythiophene with BF_4^- at 377°C ; 2, as-prepared polythiophene with BF_4^- at 372°C ; 3, NH_4OH compensated polythiophene with ClO_4^- at 400°C ; 4, NH_4OH compensated polythiophene with BF_4^- at 462°C ; 5, as-prepared polythiophene with ClO_4^- at 475°C ; 6, as-prepared polythiophene with BF_4^- at 464°C ; 7, NH_4OH compensated polythiophene with ClO_4^- at 475°C ; 8, as-prepared polythiophene with ClO_4^- at 475°C ; and 9, NH_4OH compensated polythiophene with BF_4^- at 483°C .

Table 2. First-order rate constants estimated from the logarithmic plots of the weight loss for as-prepared and ammonia compensated polythiophene containing various counterions during isothermal heating in a TGA instrument in the temperature range 372–483°C.

Counterion	Temperature (°C)	k_1 (s ⁻¹)
BF ₄ ^{-b}	377	2.50×10^{-4}
BF ₄ ^{-a}	372	2.66×10^{-4}
ClO ₄ ^{-b}	400	4.83×10^{-4}
BF ₄ ^{-b}	462	1.84×10^{-3}
ClO ₄ ^{-a}	475	2.12×10^{-3}
BF ₄ ^{-a}	464	2.44×10^{-3}
ClO ₄ ^{-b}	475	2.64×10^{-3}
ClO ₄ ^{-a}	475	2.94×10^{-3}
BF ₄ ^{-b}	483	3.97×10^{-3}

^aAs-prepared

^bAqueous ammonia compensated.

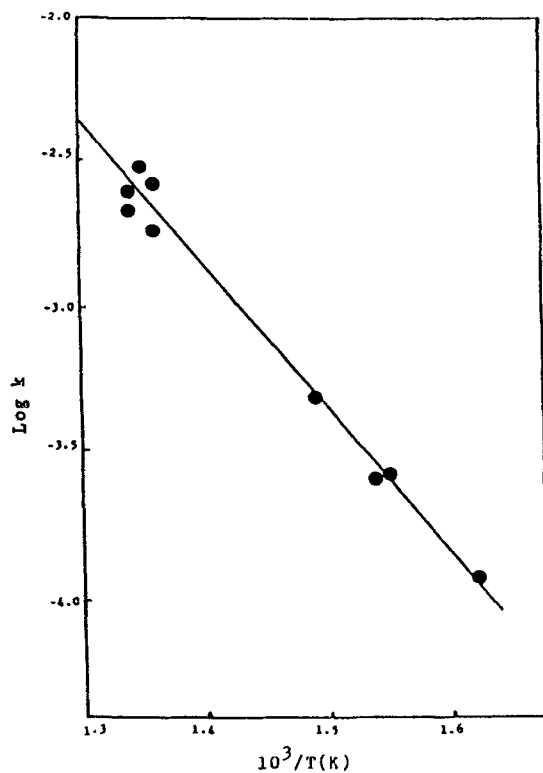
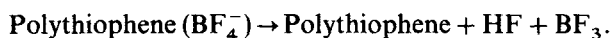


Figure 3. Arrhenius plot of first-order rate constants of isothermal weight loss of polythiophene.

It is evident from TGA studies that degradation of polythiophene involves two steps depending upon the experimental temperature. In step-1, a similar weight loss of 18% in air as well as in nitrogen with programmed temperature increase is observed whereas a massive weight loss is the main characteristic of step-2. Step-0 with a 3% weight loss in polypyrrole (BF_4^-) seems to be due to the removal of trapped moisture which is also supported by our electrical conductivity loss studies (Mohammad 1988) by the consistency of the temperature range from 45°C to 125°C and also by the work of Wynne and Street (1985). The presence of moisture could not be confirmed in our FTIR studies (Mohammad *et al* 1994) due to the presence of a strong and broad band in the -OH absorption region.

Step-1 seems to correspond to the loss of the counterion by some complex chemical reaction but without any loss of conjugation as reported in our UV-VIS studies with a corresponding change in the colour to red and green in polythiophene and polypyrrole respectively (Mohammad *et al* 1989, 1993). The dopant concentrations (mol ratio) of 0.21 and 0.19 [excluding 3% moisture in case of polypyrrole (BF_4^-)] for polythiophene (BF_4^-) and polypyrrole (BF_4^-) respectively as estimated from weight loss studies are in agreement with the reported y values (Diaz 1981; Cao *et al* 1985), but are greater than our electrochemically estimated y values (Mohammad *et al* 1990). Erlandsson *et al* (1985) proposed the formation of OH-counterion in polypyrrole and also observed the formation of BF_3 and HF by mass spectrometry. In our opinion, the formation of HBF_4 with or without carboxylate as an end group is most consistent with the FTIR spectra of aged polythiophene (BF_4^-) at 80°C as shown in figure 4 (Mohammad *et al* 1994). This process of counterion loss may be given by the following total chemical reaction, analogous to what we have observed in our compensation studies (Mohammad *et al* 1989):



Step-2 corresponds to the oxidative degradation reactions of polymer backbone producing segments of various conjugation lengths (Mohammad *et al* 1993) and may

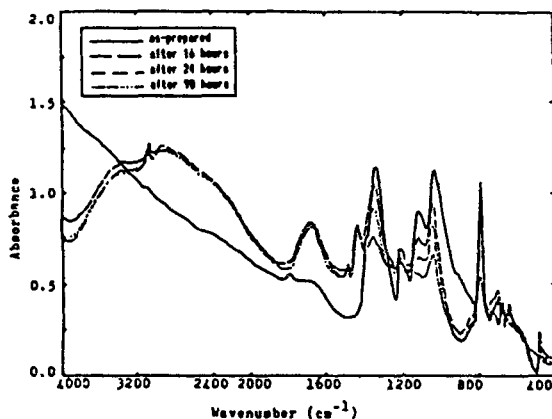
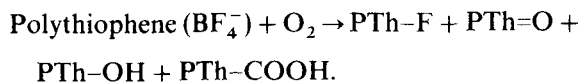


Figure 4. Effect of aging on FTIR spectra of BF_4^- containing polythiophene at 80°C in air.

involve substitution, addition and chain scission. The presence of resonances due to broad H-bonded $-\text{OH}$ and $\text{C}=\text{O}$ groups in the FTIR spectra of degraded polythiophene (BF_4^-) (Mohammad 1988) are further supported by the work of Hahn *et al* (1986) on polypyrrole. An overall chemical reaction for the oxidative degradation of polythiophene (BF_4^-) may be given by the following equation:



Oxidative degradation of most polymers proceeds via chemical reactions of peroxy radicals. Yang and Chien (1985) reported autooxidation of polyacetylene, a typical unsaturated polymer with a long conjugated system, and a value of $9 \times 10^{-7} \text{ mol(g)s}^{-1}$ for the rate constant at 70°C and 760 torr O_2 . By analogy with polyacetylene, we expect to find that polythiophene and polypyrrole will also be rather oxygen-sensitive and will degrade with or without loss of conjugation involving addition to $\text{C}=\text{C}$ bonds, substitution and chain scission. Figure 5 shows the proposed mechanism for the various competing degradation reactions which is supported by our FTIR (Mohammad 1988; Mohammad *et al* 1994) and UV-VIS studies (Mohammad *et al* 1993).

4. Conclusion

The degradation of polythiophene and polypyrrole occurs in two steps: step-1 corresponds to decomposition of dopant counterion and step-2 corresponds to oxidative degradation of polymer backbone. However, polypyrrole seems to contain about 3% moisture as evident from step-0. Oxidative degradation seems to follow first-order kinetics of weight loss with an activation energy of 94.5 kJ/mol in isothermal TGA experiments. There is no doubt that polythiophene and polypyrrole are much more stable than polyacetylene and may be capable of retaining their initial electrical

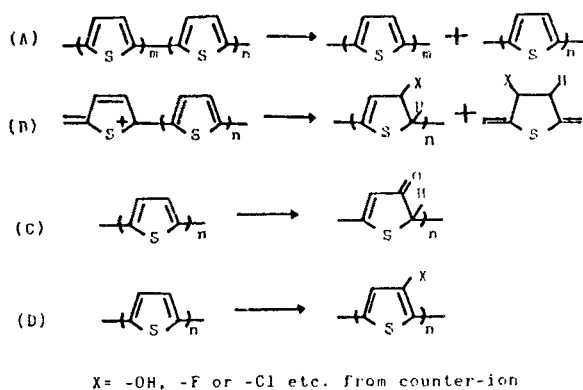


Figure 5. Oxidative degradation of polythiophene. (A) Random chain scission accompanied with loss of conjugation, (B) random chain scission with addition on $\text{C}=\text{C}$ bond leading to loss of conjugation and (C) addition on $\text{C}=\text{C}$ bond without chain scission leading to loss of conjugation and (D) substitution on $\text{C}=\text{C}$ bond without chain scission leading to the retention of conjugation.

properties for long periods (months or years) in ambient atmosphere but there are evidences of chemical reactions in both the polymers. Although the study of degradation has barely begun, we can identify several processes which can contribute to the instability and degradation of conducting polymers such as (i) reaction of main chain with oxygen leading to irreversible loss of conjugation and conductivity, (ii) reaction of the main chain with its counterion again leading to irreversible loss of conjugation and conductivity, (iii) reaction with oxygen or counterions at hetero-atoms without loss of conjugation but with modification of the electronic structure of the polymer and (iv) reversible or partly reversible undoping reactions of the conjugated system by moisture.

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