Properties of thermally treated polypyrroles

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The effect of thermal treatment on polypyrrole chloride and polypyrrole dodecyl sulphate has been studied. Changes in surface texture, electroactivity, composition and polarity after thermal treatment have been determined using scanning electron microscopy, cyclic voltammetry, fast atom bombardment mass spectrometry and gas chromatography, respectively.

(Keywords: polypyrrole; thermal stability; surface texture; electroactivity; composition; polarity)

INTRODUCTION

Thermal studies on conducting polymers not only facilitate a fundamental understanding of their properties, but also assist in the determination of the limitations and practical applications of these materials. Previous reports have indicated that most conducting polymers are very stable at room temperature[1]. However, at low temperatures (below room temperature), electrical conductivity and other physical properties are temperature-dependent[2,3]. After exposure to high temperatures, polypyrrole doped with perchlorate, tetrafluoroborate or hexafluorophosphate have been shown to lose conductivity and to decompose at about 150°C in air while toluene sulphonate-containing films did not decompose until 280°C (ref. 4). This previous work indicates that the counterion plays an integral role in polymer stability. It was revealed that the chemically synthesized, polypyrrole-I_2 complex was stable up to 184°C (ref. 5).

In this work the thermal stability and the properties of pyrrole chloride (PP/Cl) and polypyrrole dodecyl sulphate (PP/DS) have been investigated. Changes in surface properties, electrochemical activity and composition were characterized using scanning electron microscopy (SEM), cyclic voltammetry (CV) and fast atom bombardment mass spectrometry (FAB/MS), respectively. Changes in the polymer polarity were studied using gas chromatography after thermal treatment.

EXPERIMENTAL

Reagents

AR (analytical reagent) grade chemicals were used throughout this work unless stated otherwise. Pyrrole was distilled before use. The monomer solution for electropolymerization was 0.20 M pyrrole in purified water. Either 0.10 M sodium dodecyl sulphate or 0.20 M KCl was used as supporting electrolyte during polymer growth, whereas 1.0 M $NaNO_3$ was used as supporting electrolyte in the cyclic voltammetric experiments after polymer growth. Normal alkanes from C_6 to C_{11}, benzene, pyridine and 1-butanol were used as chromatographic test compounds. Reticulated vitreous carbon (RVC) with 100 pores per linear inch was obtained and pretreated in 6 M HCl for 3 h and rinsed with water.

Instrumentation

Thermal treatment and thermal gravimetry (TG) were carried out using a Rigaku analyser. Samples were purged with nitrogen during analyses. Fast atom bombardment mass spectra were obtained using a VG Analytical Model MM 12-12 mass spectrometer. Cyclic voltammetry was carried out using a Bioanalytical Systems CV-27 voltammograph. Scanning electron microscopy was performed using a Hitachi S-450 scanning electron microscope. Gas chromatography characterization was performed on a Varian Aerograph Model 1800 instrument. Electropolymerization was carried out using a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 179 digital coulometer.

Procedures

PP/DS and PP/Cl samples were electrodeposited galvanostatically (15 mA) and RVC cartridges (8.3 mg), (3 mm diameter, 18 mm length). The charge consumed was 31 C in the case of PP/DS (22.5 mg) and 33 C in the case of PP/Cl (9.0 mg). Stand alone PP/DS samples for TG analysis were obtained by electrochemical deposition onto a gold coated film using a current density of 1.0 mA cm^{-2}. All polymer samples were rinsed with water and dried in air at room temperature for at least 10 h.

Samples for SEM, CV and FAB/MS were prepared on RVC cartridges (6 mm diameter, 18 mm length), pretreated as above. PP/DS was grown galvanostatically using 0.75 mA cm^{-2} current density to a total charge of 8.0 C (5.5 mg). The samples were then rinsed with water and dried in air at room temperature for at least 10 h.

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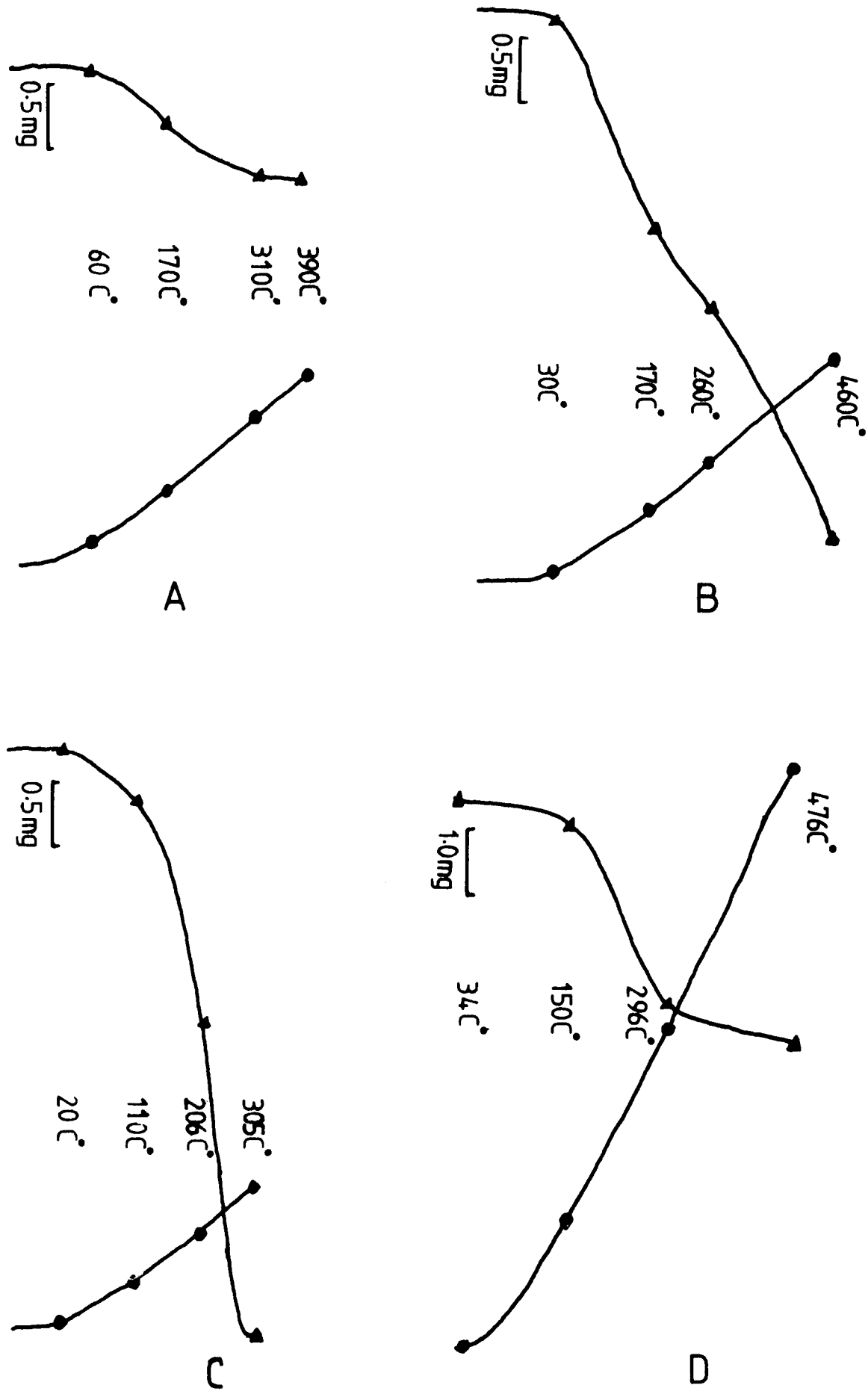

Figure 1 Thermal stability of conducting polymers. Sample A, 18 mm × 3 mm diameter RVC (8.3 mg); B, PP/Cl/RVC (17.3 mg); C, PP/DS/RVC (30.8 mg); D, PP/DS (7.1 mg); cartridge in an aluminium pan; reference, aluminium pan; heating rate, 20°C min^{-1}; ●, temperature profile; ▲, weight loss

Thermal treatment experiments were carried out using a temperature programmer to increase temperatures from room temperature to the required temperature at 10°C min^{-1}. The temperature was then held at the maximum temperature for about 20 min. After this treatment, the sample was divided into sections as required for SEM, CV and FAB/MS analysis.

Chromatographic packing materials for gas chromatography were prepared by electrodeposition of PP/DS on crushed, acid-washed RVC particles (60–120 mesh) using a cell developed previously[6]. The packings were washed with AR grade acetonitrile and distilled water then packed into a 2 m × 3 mm i.d. glass coil column. In total, approximately 4.9 g PP/DS/RVC with 622 C charge/g RVC was employed in each column.

Gas chromatographic characterization was carried out after conditioning the column for 10 h at the required temperature. The dead time (t_M) was measured by injecting methane, and the retention time (t_R) of the test compounds was recorded using a stopwatch. Capacity factors (k') were calculated according to $k' = (t_R - t_M)/t_M$, and retention indices and McReynolds' constants were calculated as has been described previously[7].

RESULTS AND DISCUSSION

Polymer samples for thermal analysis were electrodeposited onto RVC cartridges. Preliminary results revealed that the RVC itself lost about 14% of its initial weight when exposed to temperatures between room temperature and 310°C, and at temperatures greater than 310°C no further weight loss was recorded (*Figure 1A*).

Upon exposure of the polymer (PP/Cl) coated RVC to increasing temperatures, a continuous weight loss was observed from 25°C to 460°C (*Figure 1B*). About 30% of the polymer weight was lost when the polymer was heated to 460°C. The weight loss may have been due to the volatilization of oligomers, since polypyrrole has a large molecular weight distribution[1]. Alternatively, the weight loss may have been due to the oxidation of polypyrrole at high temperatures, which is known to cause release of counterions from the polymer[1]. The continuous weight loss observed when PP/Cl was exposed to higher temperatures may have been due to the release of the Cl^- counterion, which could be released as HCl.

Similar results were obtained when a sample of RVC coated with PP/DS was exposed to higher temperatures (*Figure 1C*). However, a more dramatic weight loss was observed at temperatures greater than 180°C. This was found to correspond with the decomposition of DS^- itself. About 20% of the polymer weight was lost when the polymer was heated to 305°C. In order to examine the cause of weight loss, stand alone PP/DS were used in this experiment. It was found that the weight loss from the polymer was approximately equal to the total weight of DS^- counterions. At temperatures greater than 300°C, the polymer became thermally stable even up to 476°C (*Figure 1D*). Similar results have been reported previously using polypyrrole *p*-toluene sulphonate[8].

Given the more marked weight losses observed with PP/DS, further characterization was carried out on this polymer.

Thermal treatment and changes in surface properties

Scanning electron micrographs indicated that after coating with the polymer the smooth surface, initially observed with bare RVC, assumed a rougher appearance, and that after thermal treatment at elevated temperatures the appearance of the surface experienced further changes (*Figure 2b*). Specifically, the higher the temperature at

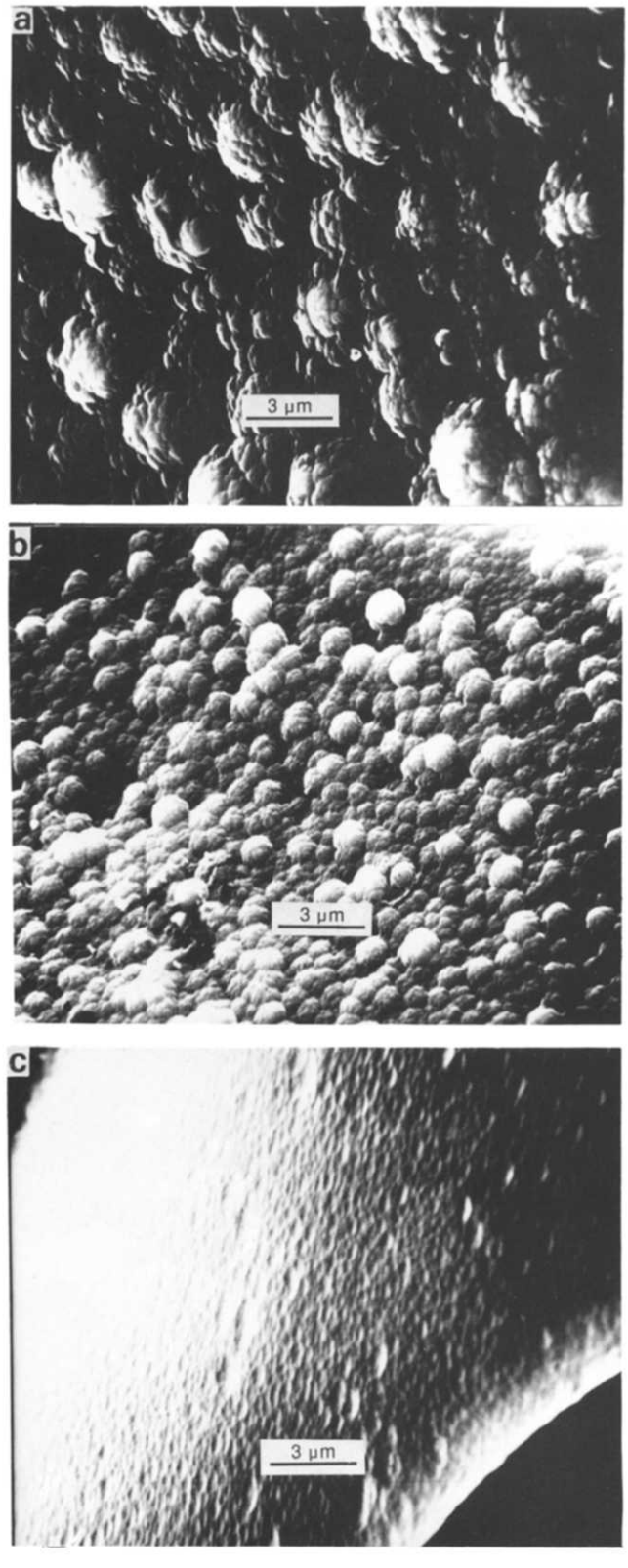

Figure 2 Surface texture of PP/DS/RVC after thermal treatment. SEMs: A, without heating; B, heated to 212°C; C, heated to 370°C; heating rate, 10°C min^{-1}; rest time at maximum temperature, 20 min

Table 1 Ion intensity of FAB/MS peaks obtained from PP/DS after heating to different temperatures. (Heating rate, 10°C min^{-1}; time at maximum temperature, 20 min)

Temperature (°C)	Mass number				
	80 (SO_3^{2-})	81 (HSO_3^-)	96 (SO_4^{2-})	97 (HSO_4^-)	265 (DS^-)
25	340	0	191	513	322
173	406	10	187	498	200
212	301	16	84	295	8
240	141	6	40	115	0
263	181	6	13	49	0

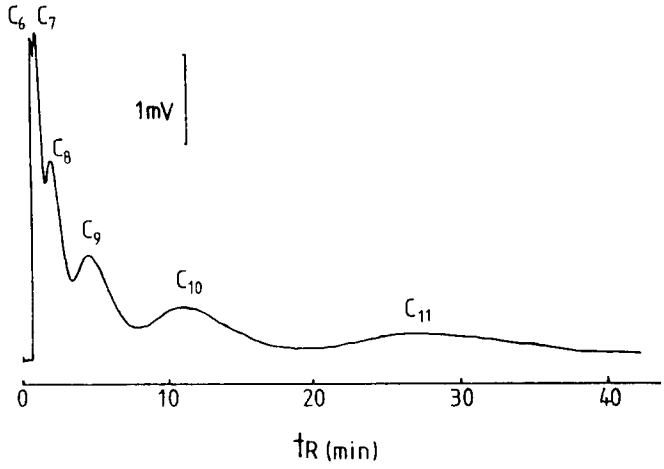

Figure 3 Gas chromatogram using polypyrrole stationary phase. Column, 2 m × 3 mm i.d. glass tube packed with PP/DS/RVC particle (60–120 mesh); column temperature, 120°C; carrier gas, N_2 at 30 ml min^{-1}; detector, FID 10^{-10} A/mv; attenuation, 16; condition temperature, 150°C

which the polymer was treated, the smoother the polymer surface (*Figure 2c*).

Thermal treatment and chemical composition

Fast atom bombardment mass spectra were obtained for PP/DS samples treated at various temperatures. The DS^- fragment (M/C = 265) on the FAB/MS disappeared when the polymer was treated at temperatures greater than approximately 180°C. At these temperatures DS^- broke down to form smaller anionic species that were still retained in the polymer (*Table 1*).

Thermal treatment and polarity changes

The effect of thermal treatment on the surface characteristics was also investigated using the polymer as a stationary phase in gas chromatography. Changes in surface properties were then determined using a series of molecular probes. This approach has become known as inverse chromatography[9].

Initially, non-coated RVC particles conditioned at 180°C were employed as the packing material and no retention was observed for each of the test compounds investigated. However, retention of the molecular probes was obtained after coating the RVC particles with the polypyrroles. A typical chromatogram is shown in *Figure 3*.

It was found that the effect of thermal treatment on the retention of test compounds was significant (*Table 2*). After conditioning columns at elevated temperatures, retention on PP/DS/RVC increased markedly. This was presumed to have been due to changes in the polymer polarity during treatment at higher temperatures. Alternatively, treatment at higher temperatures could increase the specific surface area, and as a result increase the retention.

McReynolds constants are used as indicators of the polarity of a stationary phase, compared with a non-polar squalene phase[7]. The McReynolds constants for benzene and 1-butanol (*Table 3*) indicated that polypyrrole was a polar stationary phase after conditioning at 150°C. Failure to elute another McReynolds test probe, pyridine, again suggested that the stationary phase was highly polar. After treatment at higher temperatures, the stationary phase became more polar, i.e., the McReynolds constant for benzene and butanol increased. As shown above, DS^- was released from the polymer at higher temperatures. DS^- contains a large non-polar dodecyl group that would impart hydrophobic character to the polymer. Loss of DS^-, therefore, would result in the stationary phase becoming more polar.

Electroactivity

Changes in the electrochemical behaviour of polypyrrole with thermal treatment were characterized using cyclic voltammetry (*Figure 4*). After treatment at elevated temperatures, the oxidation/reduction responses became smaller and eventually disappeared. The changes in electroactivity after thermal treatment further confirmed that PP/DS underwent chemical changes when treated at elevated temperatures. Electroactivity, which is usually associated with the polymer conductivity and switching properties, deteriorated gradually after treatment at high temperatures.

Using cyclic voltammetry, the first cycle revealed a large reduction peak about −0.34 V, and then an oxidation peak at −0.73 V was observed. The process was somewhat irreversible, and was probably due to the following reactions:

$$\text{Reduction:}\quad PP^+DS^- + e^- \rightarrow PP^\circ + DS^- \qquad (1)$$

$$\text{Oxidation:}\quad PP^\circ - e^- + C^- \rightarrow PP^+C^- \qquad (2)$$

where PP°, DS^- and C^- are the free reduced polymer,

Table 2 Effect of the conditioning temperature on chromatographic capacity factors. (Carrier gas N_2 at 30 ml min^{-1}; FID detector; column was 40% (w/w) PP/DS on RVC; conditioning time 0 h)

Conditioning temperature (°C)	k' of n-hexane at 180°C
200	0.64
250	1.67
300	37.9

Table 3 Selectivity changes due to thermal treatment of stationary phases[a]. (Carrier gas, N_2 at 30 ml min^{-1}; FID detector; column was 40% (w/w) PP/DS on RVC)

Condition temperature (°C)		150	200
Retention index	Benzene	791 (138)[b]	836 (138)[b]
	1-Butanol	1003 (413)[b]	–[c]

[a]Column temperature: 120°C
[b]McReynolds constants
[c]Retention time too high

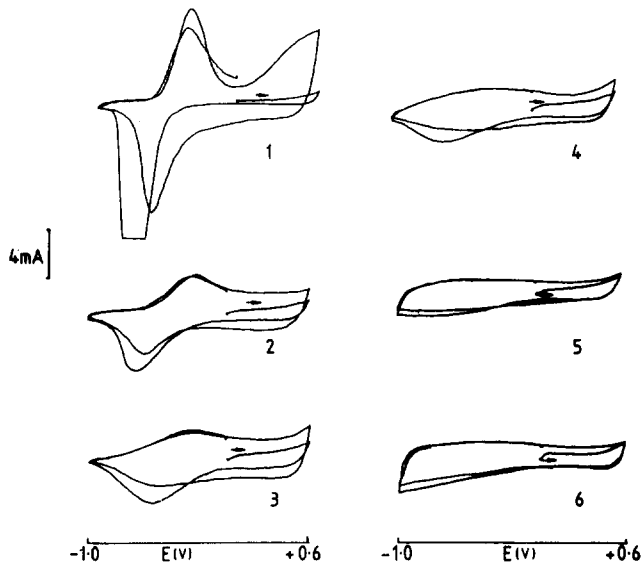

Figure 4 Changes in electrochemistry of PP/DS/RVC after thermal treatment. Reference electrode, Ag/AgCl (3 M NaCl); auxiliary electrode, RVC; scan rate, 50 mV s^{-1}; potential range, −1.00 to +0.60 V; supporting electrolyte, 0.1 M $NaNO_3$; CVs on PP/DS/RVC: 1, without heating; 2, heated to 173°C; 3, heated to 21°C; 4, heated to 240°C; 5, heated to 313°C; 6, heated to 370°C; heating rate, 10°C min^{-1}; rest time at maximum temperature, 20 min

dodecyl sulphate ion and supporting electrolyte anion, respectively. Since released DS^- diffused into the solution and was replaced by C^-, the process appeared to be irreversible.

However, subsequent scans showed a more reversible process since the ratio of oxidation and reduction peak currents was closer to unity, and the differences in peak potentials was smaller. This may have been due to the fact that with subsequent scans it became more difficult to release the DS^- anion. This has been reported by other workers[10,11].

The changes in cyclic voltammetry after thermal treatment confirmed that some DS^- was released. This was reflected in lost electroactivity after treatment at higher temperatures. Despite this loss of electroactivity the polymer coating did not become totally insulating, as revealed in the cyclic voltammograms.

CONCLUSION

PP/Cl and PP/DS both decomposed at elevated temperatures. Weight loss from PP/Cl/RVC was initiated at relatively low temperatures, and proceeded rapidly at temperatures greater than about 180°C. Weight loss of PP/DS started at 180°C. At temperatures greater than 300°C, no further weight loss was recorded for PP/DS. The surface texture of the polymer changed at elevated temperatures: the higher the temperature the smoother the surface became. The polymer became less electroactive after treatment at elevated temperatures: the redox properties of the polymer disappeared gradually due to the thermal degradation of the polymer. The counterions were released from the polymer at high temperatures. The polarity of the polymer, indicated by chromatographic data of the test compounds, changed after treatment at elevated temperatures.

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