

Electrorheological properties of polypyrrole prepared by the action of mineral acids on pyrrole[†]

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Polypyrrole was prepared in high yield by the polymerisation of pyrrole in strongly acidic conditions using hydrofluoric, hydrochloric (at 20 °C and 100 °C), hydrobromic, nitric and orthophosphoric acids. The polymer products incorporated significant amounts of the anion from the acid used. The particulate morphology of the polymer products chiefly consisted of agglomerated μm -sized spheres. The rheological properties of dispersions of polymers prepared from pyrrole using hydrochloric and hydrobromic acids, suspended in 1-chloronaphthalene–1-bromonaphthalene, were found to be electric-field dependent. Fluids prepared from the polypyrrole products derived from hydrofluoric, nitric and orthophosphoric acids did not exhibit an electrorheological response.

The electrorheological (ER) effect involves the rapid and reversible modification of the flow properties of a fluid under the application of an external electric field, principally an increase in the viscosity and in the elastic modulus. There is considerable interest in these materials for possible uses as stop valves, clutches, brakes and dampers. Winslow first reported the ER effect in 1949,¹ using moist silica particles suspended in kerosene. Subsequently, other systems have been demonstrated to be ER active.^{2–4} Most ER fluids consist of suspensions of inorganic materials such as aluminosilicates in a continuous phase of an insulating fluid. In addition, these systems generally require the presence of significant amounts of polar solvents, such as water, to enhance particle polarisation, for an appreciable ER response. There are problems of settling out and abrasion with these inorganic materials, and the presence of water limits the working temperature range. Recently, it has been demonstrated that semiconducting organic polymers such as polyacenequinones,⁵ polyaniline⁶ and poly(*p*-phenylene)⁷ doped with copper(II) chloride or iron(III) chloride exhibit ER responses in the anhydrous state. These systems show considerable promise owing to the reduction of abrasion, and because of the wider range of fluids available for density matching with the dispersed phase. In this study it is demonstrated that materials prepared by the polymerisation of pyrrole in the presence of mineral acids possess electrorheological properties in the anhydrous state when dispersed in an appropriate fluid. These polymers are worthy of study owing to their ease of preparation and their low conductivities.

Experimental

Reagents

Pyrrole and mineral acids were purchased from the Aldrich Chemical Company (Dorset, UK). Pyrrole was distilled prior to use. Acid solutions (7.5 mol dm⁻³) were prepared by dilution of the appropriate general reagent grade concentrated acids.

Characterisation

Scanning electron microscopy (SEM) was carried out at the University of the West of England using an Hitachi S-450 scanning electron microscope, with an accelerating voltage of

10 kV. Samples were prepared for microscopy by sputter coating with gold, using an Emscope SC500 sputter coating unit. Microanalyses were carried out by the Microanalytical Department, School of Chemistry, Bristol University. X-Ray photoelectron spectroscopy (XPS) studies were carried out using a VG Scientific ESCALAB Mk II instrument. Lineshape analysis was performed on each peak in an attempt to resolve the broad signals. Al-K α radiation was used as the X-ray source. Bonding energies were adjusted so that the main C 1s peak occurred at 285.00 eV and atomic percentages were calculated from the peak areas using standard atomic sensitivity factors. The rheologies of the suspensions were tested using continuous shear viscometry, using a Bohlin VOR rheometer, with a measuring cell consisting of two 3 cm diameter, parallel stainless-steel plates, 1 mm apart, electrically isolated from the rest of the apparatus by ceramic spacers. A potential was applied to the upper plate *via* a fine gauge insulated wire. A flexible metal strip, in contact with the lower plate, was used as an earth. Potential was supplied using a Time Electronics (Tonbridge, Kent) multifunction ac–dc calibrator 9822 power supply. The current drawn was measured using a Fluke 8010A digital multimeter. Conductivity measurements were obtained from pressed pellets (10 tonnes pressure for 1 min) of the powdered, dried material. Both sides of each pellet were gold coated and the resistance measured with a Fluke 8010A digital multimeter. Conductivities were calculated using the surface area and thickness of each pellet.

Preparation of the polymers

Product 1. An aqueous solution of pyrrole (250 cm³, 0.75 mol dm⁻³) was added rapidly to a stirred solution of hydrochloric acid (1000 cm³, 7.5 mol dm⁻³) at 20 °C. Stirring was continued for 12 h, after which time the resulting product was filtered off, extensively washed with distilled water (3000 cm³), and dried *in vacuo* at 70 °C for 5 h, yielding 7.89 g of a dark red–brown powder (product 1).

Product 2. Product 1 (4.00 g) was heated *in vacuo* for 72 h at 180 °C, yielding 2.81 g of a fine black powder (product 2).

Product 3. An aqueous solution of pyrrole (250 cm³, 0.75 mol dm⁻³) was added rapidly to a stirred solution of hydrochloric acid (1000 cm³, 7.5 mol dm⁻³) at 100 °C. Stirring was continued for 10 min, after which time the resulting product was filtered off. The same washing and drying procedures were carried out as for product 1, yielding 8.53 g of a brown powder (product 3).

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Product 4. An aqueous solution of pyrrole (250 cm³, 0.75 mol dm⁻³) was added rapidly to a stirred solution of nitric acid (1000 cm³, 7.5 mol dm⁻³) at 20 °C. The reaction continued for 8 h, after which time the precipitate was filtered. Washing and drying procedures were carried out as for product 1, yielding 10.56 g of a dark brown powder (product 4).

Product 5. An aqueous solution of pyrrole (100 cm³, 0.75 mol dm⁻³) was added rapidly to a stirred solution of hydrofluoric acid (400 cm³, 7.5 mol dm⁻³) at 20 °C. No product was apparent after 24 h, and stirring was continued for 96 h, after which time the precipitate was filtered off, washed with distilled water (2000 cm³) and dried *in vacuo* at 70 °C for 5 h, yielding 1.63 g of a fine brown powder (product 5).

Product 6. An aqueous solution of pyrrole (50 cm³, 0.75 mol dm⁻³) was added rapidly to a stirred solution of orthophosphoric acid (200 cm³, 7.5 mol dm⁻³) at 20 °C. No product was apparent on stirring for 24 h; on stirring for a further 72 h a dark red intractable gelatinous mass was obtained. Removal of acid was carried out by vigorous stirring of the gel in distilled water (1000 cm³), followed by decantation of the supernatant liquid. This process was repeated several times. The washed gel was filtered and dried *in vacuo* at 70 °C for 8 h, to yield a black powder. Residual acid was removed by stirring the solid product in distilled water (200 cm³), followed by filtration. This process was repeated several times. The solid product was then filtered and dried *in vacuo* at 70 °C for 5 h, to yield a black powder, mass 2.03 g (product 6).

Product 7. An aqueous solution of pyrrole (44 cm³, 0.75 mol dm⁻³) was added rapidly to a stirred solution of hydrobromic acid (177 cm³, 7.5 mol dm⁻³) at 20 °C. Stirring was continued for 8 h, after which time the precipitate was filtered, washed with distilled water (2000 cm³) and dried *in vacuo* at 70 °C for 5 h, yielding 1.71 g of a fine brown powder (product 7).

Preparation of suspensions for ER testing

Samples of products 1–7 were ground in a vibratory ball mill for 40–60 min. The resulting particle size and morphology were determined by SEM. The suspending fluid used was a mixture of 1-chloronaphthalene and 1-bromonaphthalene, in the ratio 0.56:1 v/v, with a density of 1.30 g cm⁻³. This was found to be a suitable density match for the materials tested. For products 1–7, test fluids were prepared by suspending 0.60 g of solid material in 2.00 cm³ of the 1-chloronaphthalene–1-bromonaphthalene mixture (designated 30% suspensions). In addition, for product 1, suspensions were prepared with 0.20, 0.40 and 0.80 g of solid in 2.00 cm³ of fluid (designated 10%, 20% and 40% suspensions).

Results and Discussion

Although the oxidative polymerisation of pyrrole to produce polypyrrole has been widely studied,^{8–10} there are few reports of the polymerisation of pyrrole mediated by mineral acids.^{11–14} The properties of polypyrrole obtained by oxidative polymerisation and under acid conditions are different: the former is a highly conjugated material which in the oxidised form may have conductivities in excess of 10 S cm⁻¹, whereas the latter is insulating, with limited conjugation along the polymer chain because of ring opening and the presence of hydrogenated pyrrole units. Lamb and Kovacic¹³ studied the polymerisation of pyrrole with trichloroacetic acid. Rapid quenching of the reaction mixture was found to lead to the isolation of an oligomer as the major product, identified as 2,5-bis(2-pyrrolyl)pyrrolidine. The authors suggested that the formation of polypyrrole in acidic solution proceeds through this trimer,

with protonated trimer species attacking pyrrole or trimer molecules. Polypyrrole was therefore assumed to essentially consist of alternating pyrrole and pyrrolidine units. Elemental analyses also indicated the presence of appreciable amounts of oxygen, with minor amounts of chlorine. Salmon *et al.*¹⁴ obtained yellow, insulating films of polypyrrole by the treatment of an ethanolic pyrrole solution with aqueous sulfuric acid. From elemental analyses and IR spectra, it was suggested that the material consisted of chains of saturated or partially saturated pyrrolidine units and pyrrole units terminating in pyrrolidinone moieties. It was proposed that under the acidic conditions present during polymerisation, a proportion of the pyrrolidine nitrogens became protonated, leading to a cationic polymer backbone. Evidence for the incorporation of sulfate counter-ions in the polymer film was obtained from elemental analyses and IR spectroscopy.

In our study, we have extended the range of acids shown to polymerise pyrrole. Aqueous pyrrole solutions were added to 7.5 mol dm⁻³ acids to obtain a final 6 mol dm⁻³ acid concentration. Brown polymer products were obtained using 6 mol dm⁻³ hydrochloric, hydrofluoric, hydrobromic and nitric acids at room temperature (products 1, 5, 7 and 4), and 6 mol dm⁻³ hydrochloric acid at 100 °C (product 3). The reaction with 6 mol dm⁻³ orthophosphoric acid led to the formation of a red–brown gel, which on work-up gave a black powder (product 6). Polymer product formation was much slower using the weaker hydrofluoric and orthophosphoric acids. The material obtained by thermal degradation¹⁵ of product 1 was also a black powder (product 2). In all cases the materials were insoluble in common solvents. Conductivities of compressed discs of all the polymers were less than 10⁻⁸ S cm⁻¹. SEM images obtained for products 1, 2, 4 and 7 showed a similar polydisperse spherical morphology, with particle diameters in the range 1–4 µm. The spheres appear to be fused together. Fig. 1 shows an SEM image of product 1. In contrast, the material obtained from polymerisation carried out in hydrochloric acid at 100 °C (product 3) consisted of irregular particles with an average size of 20 µm.

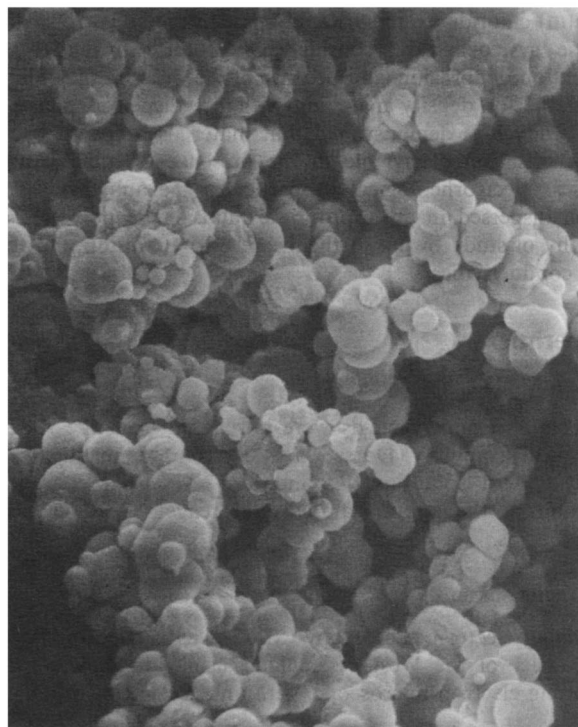


Fig. 1 SEM image of product 1 (scale bar = 5 µm)

There is clear evidence from the microanalytical data that acid treatment of pyrrole results in products which have an increase in the carbon:nitrogen ratio relative to the monomer starting material (Table 1). The use of orthophosphoric acid resulted in the greatest loss of nitrogen. Ring opening and subsequent loss of nitrogen from the polymer is the most likely explanation for these results. The high acid concentrations would also be expected to cause protonation of non-aromatic nitrogen atoms, with the concomitant incorporation of the respective anion into the polymer. XPS was undertaken for products 1 and 2. Chlorine was shown to be present solely in the anionic state. The inclusion of halogen, nitrate and phosphate in the polymers was also supported by the micro-analytical data.

The polymer products resulting from the acid polymerisation from pyrrole were thoroughly dried. They were then successfully ground up in a ball mill to μm -sized particles.

The rheological properties of these dispersions in the presence and absence of an electric field were evaluated by trapping the dispersions, in turn, between two parallel stainless steel discs separated by a 1 mm gap, the rotation of one of the discs being electrically controllable.

The electrorheological activity of the dispersions of each polymer in 1-chloronaphthalene–1-bromonaphthalene at a 30% loading (0.60 g in 2.00 cm³) was assessed at a constant shear rate of 0.990 s⁻¹, to determine which dispersions were worthy of further study. Measurements of shear stress were obtained in the absence of an electric field, and for ac (50 Hz) and dc electric fields of up to 500 V mm⁻¹. Those fluids prepared from products 2, 4, 5 and 6 gave no response, even at the highest field strength. After testing suspensions of products 4 and 6 under dc fields, examination of the rheometer plates revealed the coating of particles on the cathode. The bulk of the fluid appeared depleted of the disperse phase. This effect must be due to electrophoresis. A similar effect has been noted for fluids based on zeolite particles.¹⁶ This is unlikely to account for the lack of ER response, since no response was observed with ac field conditions. Suspensions of products 1, 3 and 7 gave appreciable increases in developed shear stress with increasing field strength. The material derived from hydrochloric acid at room temperature (product 1) showed the greatest response, with the product derived from hydrochloric acid at 100 °C showing a lesser response. The material derived from the hydrobromic acid polymerisation of pyrrole showed a much smaller ER effect (Fig. 2). Clearly the differing methods of polymer preparation have a profound effect on the ER response of the dispersions. The lack of knowledge of the polymer structures, however, prevents structure/activity relationships being made. Cation exchange resins with different halide counter-ions have been utilised for ER research.¹⁷ The same trend of ER response was observed as for polypyrrole with different counter-ions, the greatest effect being observed for chloride, followed by bromide and then fluoride.

Table 1 Elemental ratios (derived from microanalytical data) for a range of polypyrrole polymers

product	elemental ratios				
	C	H	N	O ^a	anion
1	4	5.97	0.81	0.41	0.33 (Cl)
2	4	3.2	0.69	0.56	0.23 (Cl)
3	4	5.6	0.64	0.74	0.33 (Cl)
4	4	3.58	1.1	2.28	— ^b
5	4	5.14	0.7	0.86	0.42 (F)
6	4	4.88	0.65	1.46	0.03 (PO ₄)
7	4	4.87	0.78	0.47	0.27 (Br)

^a Oxygen values were obtained by difference. ^b Nitrate ratio not obtained.

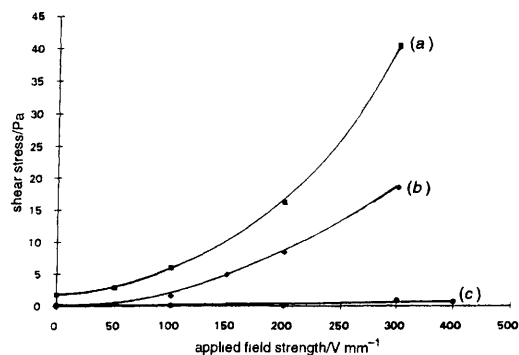


Fig. 2 Shear stress vs. applied electric field (dc) for products 1 (a), 3 (b) and 7 (c) (shear rate 0.990 s⁻¹)

The effect of different sample loading on the ER response was examined using 10, 30 and 40% suspensions of product 1 (Fig. 3). These data show clearly the increase in ER activity at greater solid loadings. This correlation is broadly in line with results obtained by other workers utilising different fluids.¹⁸

The most promising disperse phase (product 1) was selected for further study, using a 40% mass/volume loading. The current density drawn using this fluid under a range of dc electric fields is shown in Fig. 4. This parameter is of importance with respect to Joule heating and power consumption. At the highest field tested (500 V mm⁻¹), a current density of 0.85 mA cm⁻² was obtained. In contrast, Gow and Zukoski⁶ quote current densities for polyaniline-based fluids (volume fraction 0.018, field strength 500 V mm⁻¹) of between 10⁻² and 1 mA cm⁻², although it should be noted that the significance of this comparison is questionable owing to the difference in sample loadings. Meaningful comparisons of our results with current densities quoted in the literature cannot be made since most literature values have been obtained at higher electric field strengths.

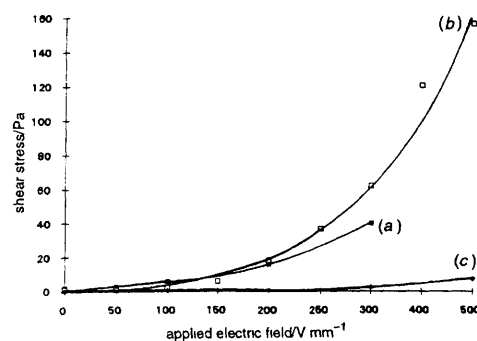


Fig. 3 Shear stress vs. applied electric field (dc) for 30% suspensions of product 1 (shear rate 0.990 s⁻¹): (a) 40% loading; (b) 30% loading; (c) 10% loading

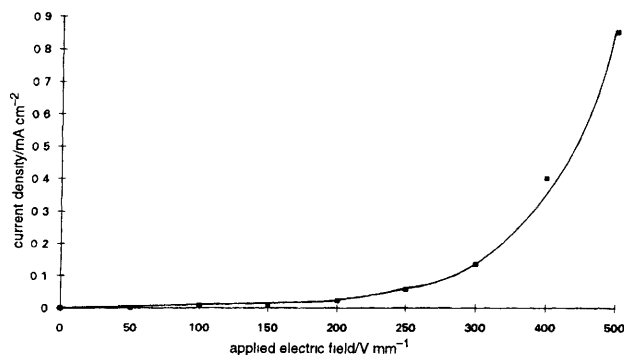


Fig. 4 Current density vs. applied electric field (dc) for a 40% suspension of product 1 (shear rate 0.990 s⁻¹)

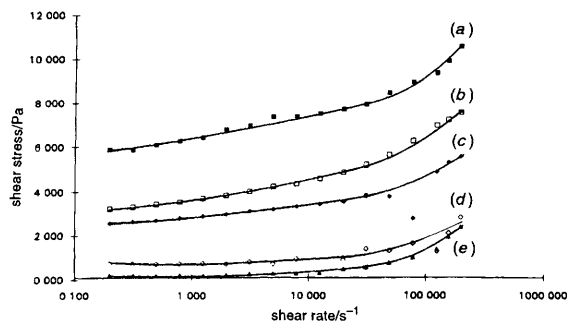


Fig. 5 Shear stress vs shear rate for a 40% suspension of product 1, at different applied ac electric fields (a) 600, (b) 500, (c) 400, (d) 200 V mm⁻¹, (e) no field

Shear stress data as a function of shear rate were obtained for a suspension of product 1 (40% loading) in the absence of an electric field and for ac fields of 200, 400, 500 and 600 V mm⁻¹ (Fig 5) it can be seen that the behaviour of the fluid under each applied field is broadly similar, with an approximately linear increase in developed shear stress with increasing shear rate, over the range of shear rates tested. The enhanced shear stresses, as defined by the difference between the developed shear stress with and without the electric field, is broadly independent of the shear rate over the range tested. This, for instance, is in contrast to hydrated lithium poly(methacrylate)¹⁹ which shows a *ca* ten-fold reduction in shear stress with an applied field of 400 V mm⁻¹ for a change in shear rate from 0.2 to 6 s⁻¹.

In our studies on fluids based on products 1, 3 and 7, it was found that for sample loadings of 10 and 20%, and for dc field strengths of below 200 V mm⁻¹, the response was reproducible and reversible, with a rapid increase in developed shear stress to a stable value. However, for sample loadings of 30% and above, and for dc electric fields of above 200 V mm⁻¹, the enhancement of shear stress upon application of the field was not constant, tending to decay with time. This was most apparent for the case of a suspension of product 1 (40% loading, 500 V mm⁻¹ dc field, shear strain rate 0.990 s⁻¹), where application of the field produced a rapid increase in shear stress to approximately 250 Pa, the shear stress then falling to the zero-field shear stress over a period of 60 s. This effect was not found in the case of ac electric fields, where repeated cycling of this suspension with an electric field of 750 V mm⁻¹ gave steady and repeatable enhanced shear stress values.

Conclusion

Novel polymers were prepared by hydrofluoric, hydrobromic and orthophosphoric acid treatment of pyrrole. Significant ER responses were observed for dispersions of polypyrrole obtained by the action of hydrochloric acid on pyrrole. A lesser effect was observed for the polymer obtained by the hydrobromic acid-mediated polymerisation of pyrrole. These materials represent a new class of polymers which may be used as components for the formulation of anhydrous ER fluids. They merit further investigation because of their facile synthesis and their significant ER responses.

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References

- 1 W M Winslow, *J Appl Phys*, 1949, **20**, 1137
- 2 Y F Deinega and G V Vinogradov, *Rheol Acta*, 1984, **23**, 636
- 3 H Block and J P Kelly, *J Phys D*, 1988, **21**, 1661
- 4 K D Weiss, J D Carlson and J P Coulter, *Journal of Intelligent Material Systems and Structures*, 1993, **4**, 13
- 5 H Block, J P Kelly, A Qin and T Watson, *Langmuir*, 1990, **6**, 6
- 6 C J Gow and C F Zukoski IV, *J Colloid Interface Sci*, 1990, **136**, 175
- 7 T Shiga, A Okada and T Kurauchi, *Macromolecules*, 1993, **26**, 6958
- 8 K K Kanazawa, A F Diaz, W D Gill, P M Grant, G B Street, G P Gardini and J F Kwak, *Synth Met*, 1980, **1**, 329
- 9 J Mansouri and R P Burford, *J Mater Sci*, 1994, **29**, 2500
- 10 S Pouzet, N LeBoly, A Ricard and F Jousse, *Synth Met*, 1993, **55–57**, 1069
- 11 M Dennstedt and F Voigtlander, *Chem Ber*, 1894, **27**, 476
- 12 H A Potts and G F Smith, *J Chem Soc*, 1957, 4018
- 13 B Lamb and P Kovacic, *J Polym Sci Polym Chem Ed*, 1980, **18**, 1759
- 14 M Salmon, K K Kanazawa, A F Diaz and M Krounbi, *J Polym Sci Polym Lett Ed*, 1982, **20**, 187
- 15 S J Hawkins and N M Ratchffe, *J Polym Chem Part A*, 1996, in press
- 16 K Negita and Y Ohsawa, *J Phys II (France)*, 1995, **5**, 883
- 17 N Sugimoto, *Bull Jpn Soc Mech Eng*, 1977, **20**, 1476
- 18 P J Burchill, *Mater Forum*, 1991, **15**, 197
- 19 L Marshall, C F Zukoski IV and J W Goodwin, *J Chem Soc Faraday Trans 1*, 1989, **85**, 2785

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