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Effect of synthesis conditions on the properties of wet spun polypyrrole fibres

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ABSTRACT

High molecular weight doped polypyrrole (PPy) has been synthesized by the incorporation of the di(2-ethylhexyl) sulfosuccinate dopant anion which renders the polymer soluble in various organic solvents. The intrinsic viscosity of PPy solutions show that the molecular weight of PPy is very sensitive to the polymerization temperature. A significant increase in molecular weight was achieved by reducing the polymerization temperature from 0 to −15 °C. The resultant solutions were amenable to a wet-spinning process that produced continuous, doped polypyrrole fibres. The ultimate tensile strength, elastic modulus and elongation at break of the higher molecular weight fibres were 136 MPa, 4.2 GPa and 5%, respectively. These values were 500%, 250% and 280% higher than obtained from the lower molecular weight fibers. X-ray diffraction showed that the low temperature PPy powder exhibited a similar degree of ordering to the standard PPy powder. UV and FT-IR spectroscopy showed that the conjugation length of PPy could be increased significantly depending on the polymerization conditions. Cyclic voltammetry demonstrated the electroactivity of the polypyrrole fibres. These fibres are likely to be important for bionic, electronic textile, artificial muscles, battery and sensor applications.

1. Introduction

Although polymers dominate the general fibre and textile industries they have had little impact on applications that require electrically conducting or electronic properties. Conducting polymer fibres are likely to be important for electronic textile applications as they allow the possibility to incorporate desirable features like chemical sensing or actuation that are not feasible with metallic fibres. However, the production of continuous conducting polymer fibres has proved difficult as their common forms are not soluble, and cannot be processed by melt techniques like extrusion. Some success was previously achieved using polyaniline, however, polyaniline is less environmentally stable, less biocompatible and produces limited actuation compared to polypyrrole. Polypyrrole (PPy) is a well known conducting polymer that is already used in a range of applications including battery electrodes [1], gas sensors [2], biological sensors [3], ion-sieving, corrosion protection [4], microwave shielding [5,6], e-Textiles and artificial muscles [1,7–12]. In addition, polypyrrole manufactured by conventional chemical and electrochemical methods is normally insoluble in ordinary organic solvents [13] and this intractability has been attributed to the presence of strong interchain interactions [14]. Consequently, PPy films are normally prepared electrochemically with the size of the film restricted to the electrode area, although slow production of PPy tape has been demonstrated using a rotating anode apparatus [15].

Recently the availability of soluble PPy [16] has enabled the production of PPy fibres for the first time [17]. The incorporation of di(2-ethylhexyl) sulfosuccinate (DEHS) dopant anion renders the polymer soluble in polar and also weakly polar or non-polar solvents such as n-methyl pyrrolidine (NMP), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and m-cresol [16]. The interaction of the DEHS dopant with doped PPy chains is illustrated in Scheme 1. The first PPy fibres were found to show adequate conductivity (1–3 $S\,cm^{-1}$) and were moderately electroactive. The fibres, however, were brittle which limited their applicability.

Increasing the molecular weight of soluble PPy is one of the most likely ways to improve the properties of the PPy fibres. In previous work it was found that oxidant concentration, polymerization temperature, and polymerization time are the key factors that determine the molecular weight and resultant electrical conductivity and solubility of the PPy-DBSA (dodecylbenzenesulfonic acid) [18]. The electrical conductivity of PPy-DBSA increased with increasing oxidant concentration and with decreasing polymerization temperature [18]. The increased conductivity obtained by polymerization of PPy at lower temperature and with higher oxidant/monomer (pyrrole) mole ratio was caused by the increased number of radical cations of PPy monomer or oligomer resulting from the raised oxidant concentration, which increased the PPy chain length. Furthermore, polymerization temperature controls the reaction rate, which should be slowed down to obtain a molecular structure with high linearity. In addition, it was reported that

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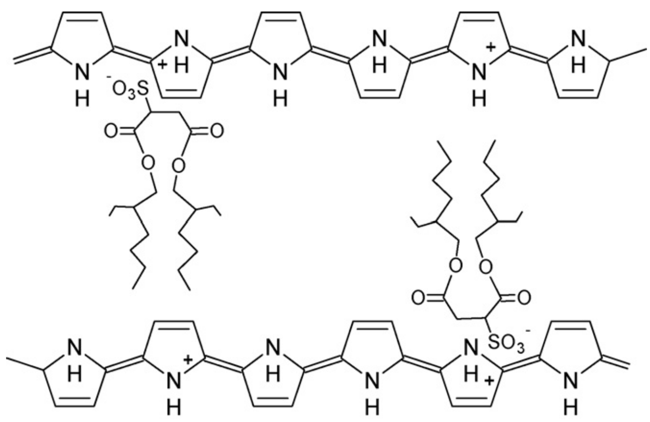

Scheme 1. Schematic diagram showing interaction between $DEHS^-$ and oxidised polypyrrole.

polymerization time significantly affected the electrical conductivity and solubility of the PPy-DBSA. Doping level as well as the apparent yield, defined as the ratio of PPy-DBSA/monomer feed, increased with increasing polymerization time over the range from 5 min to 4 h. However, longer polymerization times produced little increase in the doping level [18].

Based on these prior studies, the polymerization conditions were further modified in an attempt to produce high molecular weight PPy-DEHS that could be wet spun into fibres. The aim of the current study was to prepare PPy-DEHS fibres from polymer produced at low polymerization temperatures and to characterize the structure and properties of the polymer and fibres formed.

2. Experimental

2.1. Materials

Di-(2-ethylhexyl) sulfosuccinate sodium salt (Na^+DEHS^-), ammonium peroxydisulfate (APS), dichloroacetic acid (DCAA, 98%), and dimethylformamide (DMF) were supplied by Sigma–Aldrich and used as received. Pyrrole monomer (95%, Aldrich) was used after distillation.

2.2. Polypyrrole synthesis

Pyrrole (0.4 M) and DEHS (0.15 M) were mixed in distilled water (400 ml) including 20% (v/v) ethanol to reduce the freezing point. The solution was prepared with mechanical stirring and cooled to −15 °C. APS (0.2 M) dissolved in 100 ml distilled water was added during ~15 min with mechanical stirring to the pyrrole/DEHS solution. The reaction mixture was held at −15 °C for 24 h with mechanical stirring. The precipitate of DEHS doped PPy was washed several times with distilled water then purified by centrifugation at 4000 rpm for 20 min. The resultant wet PPy powder (65% by weight of polymer) was stored at −30 °C before use because it was found that the solubility of dried PPy was decreased significantly. PPy-DEHS prepared as above is referred to here as “low temperature PPy-DEHS”, while the term “standard PPy-DEHS” refers to polymer prepared at 0 °C using previously described methods [17]. For further comparison purposes, a third polymer was synthesized using the standard method at 0 °C but without the DEHS dopant.

2.3. Fibre spinning

The fibre spinning solution was prepared by slowly adding 2.5 g of wet PPy (65% PPy) to 10 g DCAA over a period of 1 h with vigorously stirring. The spinning solution was stirred for another 2 h (200 rpm) at 20 °C. Finally, a further 1 h of stirring under a dynamic vacuum ensured a bubble free solution ready for fibre spinning.

Prior to spinning, the solution was passed through a 200 μm filter using a nitrogen (N_2) pressure vessel. The filtered solution was transferred to a syringe and a syringe pump was used to drive the spinning solution through a single hole spinneret with D = 400 μm and finally to the coagulation bath. The bath contained 40% (v/v) DMF in water at 20 °C. The syringe pump was adjusted to 100 ml/h to control the injection rate for the spinning dope. The fibre was held in the coagulation bath for 30 min, where the fibre solidified. The fibre was then kept for 24 h in a water bath to reduce the solvent content, and then for 24 h in air at room temperature.

In some cases the fibre was further treated by hot drawing. A dynamic mechanical analyzer (DMA, TA Instruments) was used to heat the fibre to 100 °C and then stretch the fibre to the desired strain (without breakage). Such drawn fibres were cooled and further evaluated.

2.4. Instrumentation

For electron microscopy, fibre samples were cut after cooling in liquid N_2 to obtain circular undamaged cross-sections. Small pieces of fibre were fixed vertically on an aluminum stub using conductive glue. A sputter coater (Dynavac) was used for coating a thin layer of gold on the cross-section and side wall of the fibres (35 mA for 12 s under 200 mbar Ar). A Leica Stereoscan 440 Scanning Electron Microscope (SEM) was used for morphological studies of the fibres.

Tensile testing was carried out using TA Instruments DMA. For tensile testing, a 10 mm gauge length of fibre was stretched at 25 °C and at a strain rate of 500 μm/min until the sample failed.

The electrical conductivity of the fibres was measured using an in-house built four point probe. The electrodes consisted of four parallel rods at a spacing of 0.33 cm; the fibres were connected to the parallel rods using silver paint (obtained from SPI). A constant current was applied between the two outer electrodes using a Potentiostat/Galvanostat (Princeton Applied Research Model 363). The potential difference between the inner electrodes was recorded using a digital multimeter 34401A (Agilent).

The dynamic solvation diameter of PPy dispersions in DCAA were measured using dynamic light scattering (ZS, Malvern, UK). A red laser beam of 632 nm (He/Ne) was used. This system uses the NIBS (non-invasive back scatter) technology where the back scatter at 173° is detected. The use of NIBS technology reduces multiple scattering effects since scattered light does not have to travel through the entire sample, so that the size distribution at higher concentrations of sample can be measured.

A three electrode electrochemical cylindrical cell (15 mm × 50 mm) coupled to a Bioanalytical Systems (Model CV27) potentiostat was used for cyclic voltammetry. A 10 mm fibre was used as the working electrode with an Ag/AgCl reference electrode and a Pt mesh counter electrode.

Viscometry measurements were performed using an Ubbelohde type viscometer from Cannon Instrument Co. The temperature of the viscometer was maintained by immersing the apparatus in a constant-temperature water bath regulated by Julabo temperature controller. The viscosity of the spinning solution was also recorded using an Anton Paar viscometer (physical MCR 301) using Rheoplus software.

X-ray diffraction was performed using a GBC-MMA diffractometer with Cu Kα radiation and graphite monochromator. Powder and fibre samples were dispersed on the surface of glass substrates. The long axis of the fibres was made parallel to the beam direction. Ultra violet–visible–near infrared spectra were obtained using a Cary 5000 spectrophotometer. The TGA characteristics of PPy powder, fibres and dopant (DEHS) were studied from room temperature