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Soluble poly(3-alkylpyrrole) polymers on films and fabrics

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Abstract

Conductive textiles with specific properties can be produced by the chemical polymerisation of a range of 3-alkylpyrroles in the presence of textiles. The morphologies of these coatings are altered from the traditional conductive coatings. Comparison using a SEM reveals substantial differences.

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1. Introduction

Conducting polymers can be synthesised to possess a wide range of conductivity values. This can be achieved by careful selection of reactant concentrations and synthesis parameters during chemical or electrochemical polymerisation processes [1-2].

The brittleness of conducting polymer films is a major impediment for their practical applications. This disadvantage can be circumvented by polymerising a thin conducting polymer film on a textile surface. The resulting fabrics possess excellent mechanical properties and also exhibit the wide range of conductivity levels available to the conducting polymer family [3].

Insolubility is the other major limitation of conducting polymers. Synthesis of soluble conducting polymers enables direct application of these polymers to any substrate using conventional printing techniques. Soluble conducting polymers are an exciting new field inspired by the advances in synthetic metals for devices such as solar cells, bio-actuators, diodes, transistors, electromagnetic interference shielding applications and conductive textiles [4-6].

Polypyrrole and polythiophene are amongst the most studied conjugated polymers because of their versatility and high electrical conductivity. Soluble conducting polymers are often N-doped polymers, where a dopant such as dodecylbenzene sulfonic acid (DBSA) is used [7]. Unfortunately attaching functional groups to the pyrrole nitrogen alters the polymer significantly, resulting in a decrease of conductivity by several orders of magnitude.

Although there have been reports of the synthesis of soluble polypyrroles, a detailed investigation into the coating of these polymers on fabrics has not been
attempted. Conductive textiles made by coating with intrinsically conducting polymers overcome the existing problems of poor mechanical properties and insolubility associated with free standing conducting polymer films. There have been some reports on the optimum conditions for surface polymerisation on textiles, using unaltered pyrrole monomer, the optimum dopant being anthraquinone-2-sulphonic acid (AQSA) [8-9].

The type of soluble polypyrrole that we are developing and present herein, are derived from monomers formed by the chemical addition of alkyl groups to the 3-position of pyrrole. Several such 3-alkylpyrroles have successfully been chemically polymerized by various research groups [10-12], and these polymers were found to be soluble in most polar organic solvents. Upon evaporation of solvent they exhibit film-forming properties [13]. In this work, we present the synthesis of 3-alkylpyrroles and investigate their polymerization on wool substrates.

2. Experimental

A three step process was used for the synthesis of the functionalised pyrroles (Scheme 1) [10]. Initially, a Friedel-Crafts acylation of the tosyl-protected pyrrole provided high yields of the 3-acylated product. Removal of the protecting group was achieved under basic conditions and finally, a Red-Al\textsuperscript{\textregistered} reduction yielded the desired 3-alkylpyrrole monomers.

Scheme 1. Synthesis of Poly(3-alkylpyrrole)s (i) AlCl\textsubscript{3}, 0°C, DCM, 2hrs.; (ii) NaOH, 110°C, 1,4-Dioxane, 14hrs.; (iii) RED Al, 0°C, THF, 3hrs.; (iv) FeCl\textsubscript{3}, R.T. CHCl\textsubscript{3}, 3hrs.

2.1. General Experimental

The product of each step was purified using column chromatography or distillation. All structure verified by Nuclear Magnetic Resonance (NMR).
Surface resistance measurements of soluble conductive polymer coated fabrics were performed using a Fluke multimeter with a probe distance of 1.0 cm. Solid pellets of polymers were formed by grinding the polymer and pressing into disks followed by four probe conductivity measurements on the resultant solid disks.

The solubility of polymers was tested by dissolving excess ground polymer powder in CHCl₃, then sonicating the solution for 1 hour before filtering with a scintillation funnel. Accurate volumes (2.00 cm³) of this solution at 25°C were then placed in dried pre-weighed vials, and the solvent removed under reduced pressure. The reported values are an average of 10 such experiments.

All chemicals were purchased from Sigma-Aldrich (> 99% purity). Solvents were distilled prior to use. All glassware was flame-dried prior to use and reactions conducted under a nitrogen atmosphere, where anhydrous conditions were required.

2.2. N-p Toluene Sulphonyl Pyrrole

A solution of pyrrole (33.56g, 0.50 mol) in dry THF (200 mL) was prepared at room temperature. Potassium metal (15.64g, 0.40 mol) was slowly added in small portions while stirring. The reaction was heated to reflux and left until all potassium had reacted. The reaction mixture was then cooled to room temperature before drier THF (200 mL) was added. To this solution, p-toluene sulphonyl chloride (76.26g, 0.40 mol) in THF (200 mL) was added dropwise over 30 minutes. The reaction was stirred for a further 18 hours, before being quenched with water (200 mL). The reaction mixture was filtered using a scintillation funnel and the solid washed with diethyl ether (2 × 100 mL). The organic phase was separated from the filtrate, dried (Na₂SO₄), and the solvent removed under reduced pressure. The resulting solid was recrystallised from methanol to yield the desired product as a white solid, 60.8g (69%).

2.3. 3-Ketoalkylpyrrole
A solution of AlCl₃ (6.03 g, 45.20 mmol) in dry DCM (80 mL) was prepared at room temperature under a nitrogen atmosphere. To this, the appropriate acid chloride (1.1 mol equiv) in dry DCM (20 mL) was added portion wise. After 10 minutes the reaction was cooled to 0°C and a solution of N-tosyl-pyrrole (10.00 g, 45.20 mmol) in DCM (20 mL) was added dropwise over 5 minutes. This was stirred at 0°C for 2 hours before ice water was added and the product extracted using diethyl ether (3 × 50 mL). The organic portions were combined, dried (Na₂SO₄) and the solvent removed under reduced pressure. The resultant dark oil was redissolved in 1, 4 dioxane (200 mL) and to this a 5M NaOH in water (200 mL) was added and the mixture refluxed overnight. The mixture was cooled and extracted with diethyl ether (3×100 mL). The organics were combined, dried (Na₂SO₄) and the solvent removed under reduced pressure. The resulting solid was recrystallised from petroleum spirits to yield a white powder (66 – 99 %) (Table 1).

2.4. 3-Alkylpyrrole

Under a nitrogen atmosphere a solution of the appropriate 3-ketoalkylpyrrole (31.00 mmol) in THF (125 mL) was cooled to 0°C while stirring. A stirring solution of Red-Al® in toluene (65% wt/v, 19.95 g, 64.00 mmol) was added slowly. The solution was allowed to warm to room temperature and stirring continued for 3 hours. After heating the reaction mixture to 50°C for 1 hour, the solution was cooled to 0°C and cautiously hydrolysed by the slow addition of water (100 mL). The crude product was extracted with diethyl ether (3 × 50 mL) and dried (Na₂SO₄). The solvent was removed and the product was distilled at 0.01 mm Hg to yield a dark oil, or recrystallised from 1:1 hexane/dichloromethane to yield a white powder (55 – 80 %) (Table 1).

Table 1. Percentage Yields for all 3-ketoalkylpyrrole and 3-alkylpyrrole.

2.5. Solution Polymerisation
Solution polymerisation was conducted by stirring AQSA (1.22 mmol) in CHCl₃ (20 mL) with the appropriate 3-alkylpyrrole (2.44 mmol) for 10 minutes. FeCl₃ (4.88 mmol) was added portion-wise and the reaction left stirring for 3 hours. Solvent was removed in vacuo and the solid polymer which remained was ground finely then washed with copious amounts of water. The product was then tested for conductivity and solubility.

2.6. Textile Solution Polymerisation

Polymerisation on wool was carried out by stirring AQSA (1.22 mmol) in CHCl₃ (20 mL) with Decon 90, 3-alkylpyrrole (2.44 mmol) and clean wool (0.5 g) for 10 minutes. FeCl₃ (4.88 mmol) was added promptly and the reaction left stirring for 3 hours. The coated wool sample was removed and left to dry before being washed with copious amounts of water to remove excess iron (III) chloride.

3. Results and Discussion

Soluble polymers have been extensively documented with most exhibiting solubility in strong polar organic solvents [10-12]; however modified monomers have been designed for solubility in water [14-15]. For our research chloroform was used to compare our results with previous work [13, 16]. Furthermore, for the textile industry a water soluble coating would be undesirable. The length of the carbon chain is directly related to the solubility of the polymer as shown in Fig. 1. When the carbon chain is short (e.g. 4 or 5) the solubility is low. As the carbon chain length attached to the 3 position of pyrrole increases, the solubility increases respectively.

Fig. 1. Solubility of Poly(3-alkylpyrrole)s in chloroform.
Solution polymerisation of 3-alkylpyrrole in the presence of textiles such as wool produces polymer coated textiles. A photograph of wool fabrics coated with solution polymerized 3-alkylpolypyrrole can be seen in Fig. 2. The sequential images of uncoated and coated wool substrates shown in Fig. 2 indicate that poly(3-decanylpyrrole) \((n=10)\) resulted in the darkest coating and therefore it is a thicker coating. Consequently, the resulting fabric possesses higher conductivity compared to poly-3-dodecanylpyrrole \((n=12)\) and the lightest coated poly-3-behenylpyrrole \((n=22)\). This was also confirmed by surface resistance measurements.

Fig.2. From left to Right: Clean wool, wool coated by Poly(3-decanylpyrrole) \((n=10)\), Poly-3-dodecanylpyrrole \((n=12)\) and Poly-3-behenylpyrrole \((22)\) respectively.

For the solid pellets of poly(3-alkylpyrrole) the increase in solubility with the increasing carbon chain length is accompanied by a decrease in conductivity. However, the magnitude of change in conductivity over the alkyl range is very small \((0.5-3.0 \text{ S/cm})\) (Fig. 3).

Fig. 3. Conductivity vs. Alkyl Chain Length for solid conductive pellets of poly(3-alkylpyrrole).

When coated on fabrics conducting polymers give a lower conductivity than when polymerized as films. This lower conductivity is due to the low thickness of the coatings and the fibrous nature of textiles. The surface resistance measurements were taken when the fabrics were relaxed. If the fabrics are stretched, the loose weave of the wool fabric is compressed, due to this compression each strand of wool coated with the conducting polymer is drawn closer, and is postulated to creating better
electrical contact between fibres, hence their surface resistance reduce by two orders of magnitude.

Fig. 4. Surface Resistance vs. Alkyl Chain Length of poly(3-alkylpyrrole)s on wool. Probe separation=10 mm.

Alkyl chain length also has an influence on the conductivity of the polymer. As seen in Fig. 4, the surface resistance increases rapidly when the carbon chain is increased over 14. For the purpose of conductive textiles, taking into account the solubility and conductivity, it was found that the optimum carbon chain lengths were between n=10 and n=14, giving a relatively high conductivity and solubility, while the fabrics retain their advantageous mechanical properties. The increase in the surface resistance with the attachment of alkyl groups may be attributed to the rearrangement of the conjugated system in the polymer by twisting out of alignment. The consequence of this lack of optimal conjugation is a drop in conductivity [10, 16-19]. Poly-3-behenylpyrrole (n=22) does not conduct on the surface of wool when the fabric is relaxed, although when tension is placed on the fabric a very low conductivity can be measured.

Fig. 5. Electron micrograph of a chemically polymerized 3-decanylpyrrole on wool. Magnification: 1000 X. 3-Decanylpyrrole, AQSA, FeCl₃, 2:1:4 respectively. Polymerized 4 Hours at 25°C.

Fig. 6. Electron micrograph of a chemically polymerized 3-decanylpyrrole. Magnification: 5000X. 3-Decanly pyrrole, AQSA, FeCl₃, 2:1:4 Respectively. Polymerized 4 Hours at 25°C.
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Fig. 8. Electron micrograph of a polypyrrole. Magnification 1090 X. Pyrrole, AQSA, FeCl₃. 2:1:4 Respectively. Polymerized 4 Hours at 25°C.

Fig. 9. Electron micrograph of a polypyrrole. Magnification: 9490 X. Pyrrole, AQSA, FeCl₃. 2:1:4 Respectively. Polymerized 4 Hours at 25°C.

Figures 5, 6 and 7 show electron micrographs of chemically polymerized 3-decanylpyrrole at increasing magnifications. As the soluble conductive polymer dries, it forms a solid layer that binds the fibres together, acting like conductive glue. The loosely bound bulk polymerized dendritic particles of traditional solution polymerisation cannot be seen in these images. Such dendritic polymer particles are formed in solution (bulk polymerisation) and deposit on the conducting polymer layer on the substrate. These particles are not adherent to the polymer coating and can be washed off. Figures 8 and 9 show these dendritic depositions on traditional solution polymerized polypyrrole coatings on wool fabrics. The bulk polymerized dendritic polymer particles can be clearly seen in the higher magnification SEM micrograph in Fig. 9. It is not easy to completely wash these particles off the surface of the coating as some of these particles get trapped in the interstices of the fabric structure and such loosely bound particles are not desirable in practical applications. Thus the SEM observations indicate that polymers formed from soluble polymers possess superior coating properties with no dendritic polymer particles. Although the surface bonding appears to be greater for the poly(3-decanylpyrrole) polymer, the surface resistance is higher than polypyrrole coated fabrics.

At higher magnifications, as in Figures 6 and 7, it can be clearly seen that the coating is aerated. The formation of this unusual morphology is due to the slow
evaporation of the solvents as the polymer dries whereas the conventional solution
chemical polymerisation of pyrrole on to a substrate results in a random deposition of
polypyrrole particles from the solution on the existing polypyrrole coating (Figures 8
and 9).

4. Conclusions

In this work, we have synthesised 3-alkylpyrroles and polymerized them on wool
substrates. The solubility of the polymer increased while the conductivity of the
coated fabric decreased with the alkyl chain length and the optimum carbon chain
lengths were between 10 to 14. Surface morphology of the soluble alkyl pyrroles were
different from traditional polypyrrole coatings. The conductivity of solid films was
much less affected by the alkyl chain length compared to that of fabrics coated by
soluble poly(3-alkylpyrrole)s. This is attributed to the lower thickness of the coatings
on the fabrics compared to that of conductive polymer pellets and also the fibrous
nature of the fabrics.
Acknowledgments

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References

Figure and Table Captions

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n = 4, 5, 6, 8, 10, 12, 14, 16, 22
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