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Conductive poly(α-ω-bis(3-pyrrolyl)alkanes) coated wool fabrics

Richard C. Foitzik, Akif Kaynak*, Frederick M. Pfeffer

a Deakin University, School of Engineering & Information Technology, Geelong, Victoria 3217 Australia
b Deakin University, School of Life and Environmental Science, Geelong, Victoria 3217 Australia

Abstract

Crosslinked poly(α-ω-bis(3-pyrrolyl)alkanes) were directly applied to woven wool substrates by either chemical, vapour or mist polymerization methods. Choice of dopant could greatly improve the surface resistance. The optimum coating on textiles with the lowest surface resistance, highest colour-fastness and stability was achieved using a mist polymerization method with 1,8-bis(pyrrolyl)octane, iron (III) chloride (FeCl₃) as the oxidant and p-toluene sulfonic acid sodium salt (pTSA) as the dopant.

Keywords: conducting polymers, cross-linked polymers, textiles, conductive textiles.

1. Introduction

Electrically conductive textiles has become a topic of research interest due to the versatility of these materials in areas such as electromagnetic shields and absorbers[1-3], sensors [4-12], and heated fabrics [13]. The coating of fabrics is often based on chemical polymerization of monomers such as pyrrole or aniline in the presence of textiles.

Recent publications on conducting polypyrrole coated yarns and fabrics, have outlined solution and vapour-phase chemical polymerization methods [13-16]. Direct coating of various substrates by solution, vapour and mist polymerization techniques using soluble poly(3-alkylpyrroles) have also been previously investigated by the authors.

* Corresponding Author. Tel.:+61 3 5227 2539; fax: +61 3 5227 2539.
Email address: akaynak@deakin.edu.au (A. Kaynak).
[17]. Directly applying an emulsion of soluble poly(3-alkylpyrrole) as a conductive paint to the textile surface eliminated the exposure of the substrate to damaging oxidizing agents, allowing the coating of more sensitive and delicate substrates [18].

The major impediments for commercial applications of conducting polymers have been brittleness, insolubility and unstable electrical properties. Some of these problems have been addressed to a certain extent: electrical stability has been improved through judicious choice of dopants and adjustment of synthesis parameters [19-21] whereas insolubility in organic solvents has been overcome by the synthesis of poly-3-alkylpyrroles [17-18].

There has been a limited number of publications on cross-coupled dimers of thiophene, in which the main dimers in question were linked through the 3-position such as α,ω-bis(thienyl)alkanes. These α,ω-bis(thienyl)alkane molecules, when polymerised, have been reported to have good conductivity and are highly flexible [22-28]. Work conducted in our laboratory has shown that the crosslinked pyrrole derivative α,ω-bis(pyrrolyl)alkanes (Fig.1), also produced conductive, highly flexible, polymer films [29] and in this publication we detail the conditions required for the coating of woven wool with poly(α,ω-bis(pyrrolyl)alkanes) to produce highly flexible conductive textiles.

![Chemical structure of α,ω-bis(pyrrolyl)alkanes](image)

**Fig.1. Chemicals structure of α,ω-bis(pyrrolyl)alkanes**

### 2. Experimental

#### 2.1 Chemicals and Instrumentation

All solvents used were AR grade or higher. All textiles were tested for abrasion resistance using a Martindale abrasion tester. Each specimen was tested for 2000 abrasion cycles with a pressure of 9 kPa. Scanning electron microscope (SEM) images
were recorded by a Leica S440 Scanning Electron Microscope. The SEM samples were prepared by sputter coating a thin layer of gold (~7-10 nm) onto the textile surface. Surface resistance was measured by a Fluke multimeter with a probe distance of 10.0 mm.

All samples used were 40 × 40 mm of a woven wool fabric, and cleaned prior to use by stirring for 3 hours in 1 L of water at 60°C with Decon 90 (2 mL). The pH of the solution was adjusted to 1 by addition of hydrochloric acid (HCl). The wool substrates were then washed with water followed by rinsing with acetonitrile. A fine mist or vapour of the dimer in ethanol was sprayed directly onto the textile samples by using a commercially available “Preval Sprayer ®”.

In solution polymerization addition of anthraquinone-2-sulfonic acid (AQSA) or the p-toluene sulfonic acid (pTSA) dopants occurred before the reaction mixture was exposed to an oxidizing agent, whereas for the vapour and mist polymerization methods the dopant was mixed into the oxidizing solution and exposed to the textile sample simultaneously.

After the polymerization process all samples were soaked in an aqueous HCl solution at pH 1 for 10 minutes, then ethanol, followed by washing with copious amounts of water. The textile was dried under reduced pressure (0.1 mmHg) for 4 hrs before being tested for surface resistance and abrasion.

2.2. Solution polymerization of α,ω-bis(3-pyrrrolyl)alkanes onto woven wool

Solvent (water or chloroform) was placed in a flat dish with a large surface area (200 × 200 mm) to a depth to cover a flat wool sample (~0.5 g). To this solution a α-ω-bis(3-pyrrolyl)alkane [29] (5.0 mmol) and FeCl₃ (5.0 mmol) were added and mixed into the solution. The reaction mixture was subsequently left, and the solvent slowly evaporated. Evaporation of the solvent required varying lengths of time (1 hour to 3 days) depending on which was used. The textiles appeared to have films formed on the surface, resulting in a uniform coverage with low surface resistance.

2.3. Vapor polymerization of α,ω-bis(3-pyrrrolyl)alkanes to woven wool

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A clean wool sample was soaked in a solution of FeCl$_3$ in ethanol (50 g/L) and then dried rapidly with a heat gun leaving a yellow textile sample. The textile was then exposed to a $\alpha$-ω-bis(3-pyrrolyl)alkane vapour, which was produced using nitrogen as the carrier gas (solid dimers were dissolved in ethanol). The textile slowly turned black due to polymerization on the surface. The complete process of oxidizing the textile and exposing it to pyrrole vapour was repeated 5 times, to yield a black conductive textile.

2.4. Mist polymerization of $\alpha$,ω-bis(3-pyrrolyl)alkanes to woven wool

A clean wool sample was finely sprayed with FeCl$_3$ solution (50 g/L in ethanol), and dried rapidly with a heat gun to give a yellow coloured sample. The textile sample was then sprayed with the appropriate dimer (1:2 wt/wt in ethanol). The sample was slowly heated with a heat gun during which time the textile turned black due to polymerization on the surface. When the sample was completely dried, the entire process of oxidizing the textile and exposing it to pyrrole vapour was repeated 5 times, to yield a black conductive textile.

2.5. Aging studies of poly($\alpha$,ω-bis(3-pyrrolyl)alkane) coated wool fabrics

Textile samples were connected at different locations to two multimeters with probe distances of 10 mm. The samples were placed in an oven at 100°C and the initial surface resistance measured. Resistance measurements were taken every minute and an average was taken. The measurements were taken every minute for 30 minutes, then every 5 minutes, until the samples resistance became too high to record (>40 M Ohms/cm).

3. Results and discussion

Solution polymerization of $\alpha$,$\omega$-bis(pyrrolyl)alkanes onto textiles proved to be challenging. The traditional method involving the stirring of the dimer and oxidizing agent in the presence of textile [18] did not work for these cross-linked polymers as they
produced dendritic polymer particles in the solution that were easily washed off the textile surface. In this case, solution polymerization involving the evaporation of the solvent was essential for coating of textiles with a thin polymer film.

Coating textiles with poly(\(\alpha,\omega\)-bis(pyrrolyl)alkanes) by the evaporation of water produced a very brittle film on the textile surface. The flexibility of the textile was far greater than the coating, thus causing a multitude of cracks in the film and resulting in a discontinuous coating (Fig.2). On the other hand, applying \(\alpha,\omega\)-bis(pyrrolyl)alkanes by the solution polymerization method and leaving the reaction mixture until the chloroform has evaporated produced very different results as shown in Fig.3.

![Fig.2. Electron micrograph of 1,10-bis(pyrrolyl)decane applied to textiles by polymerization in water followed by the evaporation of water. Magnification 50 ×.](image)

Fig.2. Electron micrograph of 1,10-bis(pyrrolyl)decane applied to textiles by polymerization in water followed by the evaporation of water. Magnification 50 ×.

![Fig.3. Electron micrograph of 1,10-bis(pyrrolyl)decane applied to textiles by polymerization in chloroform followed by the evaporation of chloroform. Magnification 100 ×.](image)

Fig.3. Electron micrograph of 1,10-bis(pyrrolyl)decane applied to textiles by polymerization in chloroform followed by the evaporation of chloroform. Magnification 100 ×.
The coating produced by the evaporation of chloroform appeared to fuse the textile strands together, this in turn allowed a greater flexibility of the coating, which appeared to have no cracks (unlike the coatings formed by solution polymerization in water). Unfortunately the complete evaporation of the solvent took 7 days before the coating transformed from a viscous, sticky polymer to a solid surface that could be handled.

The vapour polymerization method was tested for the application of the \( \alpha,\omega \)-bis(pyrrolyl)alkane dimers to textile surfaces. The coatings that were cast onto the surface were discontinuous, having localized areas of polymer build-up. In this case, the distribution of polymer onto textile surfaces did not improve with multiple coatings, as with the poly(3-alkylpyrroles) [18]. Various oxidizing agents were trialled with different surface treatments and wetting agents but none prevailed. This method produced poor coatings and the textile required exposure to vapour for 3 hours for each coating, which was very costly due to the large amount of N\(_2\) gas used.

The polymerization of \( \alpha,\omega \)-bis(pyrrolyl)alkanes directly onto textiles was best achieved by applying a fine mist of the dimer onto a pre-oxidised surface. The surface morphology of the resultant \( \alpha,\omega \)-bis(pyrrolyl)alkane polymers can be seen in Figs. 4 and 5. The surface of the textile appears to be coated with a thick ‘paint’, with the excess paint welling up into the gaps between the wool strands in the woven textile.

The mist method gave a homogeneous coating and the solvent used to dilute the \( \alpha,\omega \)-bis(pyrrolyl)alkane dimer had a large influence on the overall appearance of the coated textile. The optimum solvent for the mist polymerization method of these cross-coupled dimers was ethanol. The ratio of the dimer to solvent used was 1:20 (wt:wt).

Production of a homogenous textile coating also depended on the thickness of each individual coating and the drying time between coats. It was crucial that multiple thin coats were applied to the textiles as these produced textiles with a greater coating fastness. Applying thicker coatings can be accompanied by bulk polymerization, which results in the settlement of loosely bound bulk polymer particles as flakes on the textiles surface.
A slightly bubbled effect in the appearance of the polymer surface formed by mist polymerization is shown in Fig.4. Unlike the synthesis of polymer films using organic solvents, this coating has only a small number of crevices, possibly due to the thinner coats, which do not allow the build up of localised un-polymerised dimers in solvent, thus encapsulation of solvents in the polymer is prevented.

The fusion of the textile strands shown in Fig.4 is indicative of a strong binding between the polymer and the fibres. The crack free surfaces also suggest that the surface coating is strongly bound and/or the polymer has a high degree of flexibility. The flexibility and handling of the coated wool fabric did not appear to be significantly different from that of untreated woven wool. Therefore it is proposed that the flexibility of the polymer is much greater when cast from an organic solvent such as ethanol rather
than water. Previous investigations have also identified ethanol as being superior to water for the purpose of forming polymer films using this method [29]. It is assumed that the organic solvents are better for the polymerization process due to the solubility of the dimers, also unlike water, organic solvents are not repelled by any lanolin or wax residues residing in the woven wool substrates.

From conductivity tests previously reported for these dimers [29], it was decided that 1,8-bis(pyrrolyl)octane \( (n=8) \) was the optimum chain length for our investigations. Three factors led to this conclusion: the high yield produced, the greater degree of the dimer stability and the conductivity could be greatly increased with a judicious choice of dopant [29].

Conductive textiles produced by the mist polymerization of 1,8-bis(pyrrolyl)octane have a lower surface resistance than the septane and nonane derivatives. However, this was not the most conductive polymer trialled. The poly(1,5-bis(pyrrolyl)pentane) dimer produced a textile with the lowest surface resistance for all the samples produced by using a Cl\(^-\) (FeCl\(_3\)) dopant.

To further investigate these novel conductive textiles, multiple dopants were investigated and the results are shown in Fig.6. In contrast to expected results the AQSA dopant produced a textile that had a higher surface resistance than the chloride dopant. The AQSA dopant has been frequently documented as being a dopant that produces higher conductivity values than the Cl\(^-\) residue dopant from polymerization by FeCl\(_3\) [1,13,14,16,20,30-35].
Fig. 6. Surface resistance of textiles coated with poly(α,ω-bis(pyrrolyl)alkanes) by mist polymerization in the presence of specific dopants.

The surface resistance of the AQSA doped conductive textiles rises as the carbon chain increases to n=8 (Fig. 6). This follows the trends of poly(3-alkylpyrroles) and is indicative of the high level of twisting of the conjugated \( \pi \) system of polypyrrole. The surface resistance peaks at n=8 and is followed by a drop in surface resistance with increasing alkyl cross-coupler length and to the best of our knowledge such a trend has not been observed before. It is hypothesised that after n=8, the increasing length of the carbon chain facilitates the encapsulation of the bulky AQSA dopant.

A tosyl dopant (\( p \)-toluene sulfonic acid (pTSA) sodium salt) gave contrasting results to those of the AQSA dopant. Indeed pTSA was the optimum dopant tested providing a highly conductive textile in all cases. The same trend as for the FeCl\(_3\) doped polymers was observed however, the anomaly at n=8 was more defined (Fig. 6). The tosyl doped poly(1,8-bis(pyrrolyl)octane) provided material with the lowest resistance out of the entire series investigated, producing a textile with a high degree of flexibility and a surface resistance of \( \sim 76 \) k Ohms/cm.
Aging studies of the textiles coated by mist polymerization of poly(α,ω-bis(pyrrolyl)alkanes) were performed by first cleaning the samples of all ferric impurities and drying under reduced pressure. The samples were heated to 100°C and surface resistance measurements were recorded every minute for the first 30 minutes then at intervals of 5 minutes for a further 30 minutes using a two probe multimeter. The results obtained for the homologous series followed the same trend, the only difference observed being the time taken for the deterioration of conductivity for each polymer. The general trends of the results obtained from the aging studies can be seen in Fig.7.

![Figure 7](image_url)

Fig. 7. Aging studies of textiles coated with poly(1,8-bis(pyrrolyl)octane) aged at 100°C.

All the coated textiles tested for age related degradation lose conductivity slowly (0~3 minutes), this is due to the textile warming to the elevated temperature. The rate of degradation intensifies from this point on with a large increase in resistance observed between 8 and 13 minutes (Fig.7). The Cl\textsuperscript{−} doped conductive textile showed a rapid and complete deterioration (i.e. resistance >40 M Ohms/cm) within 21 minutes.

The textile coated with AQSA doped polymer exhibited total deterioration as well, however this process took longer than the standard Cl\textsuperscript{−} doped polymer (Fig.7). These results are surprising since the AQSA dopant has been found to produce thermally stable, low resistance, conductive textiles when unfunctionalised polypyrrole is used [13-14,21].
The tosyl dopant again provided the best resistance to electrical degradation with the large decrease in the rate of degradation after approximately 30 minutes. There was a slight decrease in surface resistance between 30 and 60 minutes however, this was insignificant and cannot be shown on the scale in Fig.7. All the textile samples prepared by the polymerization in the presence of the tosyl dopant produced similar results.

The total degradation of the Cl⁻ and AQSA doped conductive polymer coated textiles occurred at different times for the different length of the carbon cross-coupler alkyl chain. Longer alkyl chain resulted in quicker total deterioration of the conductivity of the polymer coated textiles (Fig.8).

![Fig.8. Time taken for total degradation by aging studies at 100°C of textiles coated with poly(α,ω-bis(pyrrrolyl)alkanes).](image)

The conductive surface coating of textiles coated by poly(α,ω-bis(pyrrrolyl)alkanes), when applied by mist polymerization, had a greater fastness than those formed by solution polymerization. The results from Martindale abrasion testing can be seen in Fig.9. The poly(1,8-bis(pyrrrolyl)octane) coated textile on the left (mist polymerization) retained a larger portion of the coated polymer, easily visualised by the darker residual colour.
The textile coated by solution polymerization of poly(1,8-bis(pyrrolyl)octane) had poor fastness. SEM observations of the coating surfaces produced by this polymer revealed brittle coatings on the textile surface. As a result, after only a few seconds on the Martindale instrument it was visible that the weakly bound bulk polymer films peeled off, revealing the light color of the untreated textile (Fig. 9).

The conductive textiles produced by mist polymerization showed a greater resistance to abrasion. The bulk polymer that built up between the wool strands remained intact. The SEM image in Fig. 10 indicates that the higher surfaces were the only part of the wool, from which the conductive coating was removed. The bottom half of this image is the strands of wool which was exposed to abrasion testing, and it can be seen that there is evidence of abrasion due to the removal of some of the polymer coating.
Due to the effortless removal of polymer film formed by solution polymerization the resultant abraded sample became non-conductive. The only abraded samples that remained conductive were those formed by mist polymerization. Nevertheless, the conductivity decreased by approximately two orders of magnitude. The results for the Cl- doped textiles are shown in Fig.11. The other dopants tested gave similar increases in the surface resistance. The conductivity of the abraded samples decreased as the cross-coupled alkyl chain length increased. It was found that the conductivity of the tosyl doped samples was the highest compared to the FeCl₃ and AQSA doped samples.

![Surface resistance of wool coated with poly(α,ω-bis(pyrrolyl)alkanes) before and after abrasion testing.](image)

Fig.11. Surface resistance of wool coated with poly(α,ω-bis(pyrrolyl)alkanes) before and after abrasion testing.

4. Conclusion

The fabrication of textiles coated with poly(α,ω-bis(pyrrolyl)alkanes) was attempted by solution, vapour and mist polymerization methods. Unlike the poly(3-alkylpyrroles) with varying alkyl chain lengths these poly(α,ω-bis(pyrrolyl)alkanes) were insoluble,
therefore direct application as paint could not be attempted. Unlike many other pyrrole derivatives, suspension of textiles in an organic solvent (CHCl₃, Ethanol etc.) in the presence on the dimers and oxidizing agent (FeCl₃) did not produce coatings on wool. The textiles sample was placed in the smallest amount of the solvent possible with the dimer and oxidizing agent, and the solvent is left to evaporate leaving a thin film on the textile surface. The resultant conductive textiles produced using the solution polymerization of α,ω-bis(pyrrolyl)alkanes gave not only high surface resistance, but these coatings had poor fastness to wool resulting in a non-conductive textile after the abrasion testing.

Mist polymerization on the wool substrate gave the best results for the synthesis of poly(α,ω-bis(pyrrolyl)alkane) coated textiles. This method gave a homogeneous coating on wool and the coated textiles had the highest conductivity when compared to those produced by solution polymerization and vapour polymerization. Fastness of these polymer coatings was the best of any the methodologies trialled. The absorption of the un-reacted dimers into the textiles strands is believed to be the reason for such good attraction of the polymer to the substrate surface.

Conductive textiles coated with poly(1,8-bis(pyrrolyl)octane) had the second highest conductivity, only succeeded by poly(1,5-bis(pyrrolyl)pentane). As shown in Fig.6, poly(1,8-bis(pyrrolyl)octane) was unique in regards to the conductivity trend of the homologues series and is the optimum dimer not only for conductivity but also for its high synthetic yields and abrasion resistance.

Surface resistance of conductive textiles was greatly reduced by the aid of specific dopants. Compared to the standard Cl– dopant. The AQSA dopant increased the surface resistance, reversing the traditional role of this dopant. However, the tosyl dopant decreased the surface resistance proving to be the best dopant tested in this investigation.

Aging studies proved the importance of dopants such as the tosyl sodium salt. Rapid deterioration of the poly(1,8-bis(pyrrolyl)octane) was observed with the standard Cl– dopant. It was also shown that by using the AQSA dopant the rate of degradation is halved. The tosyl dopant allowed the textile sample to stabilise and remain conductive even after 1 hour at 100°C.
The best conductive textile produced from this homologous series was poly(1,8-bis(pyrrolyl)octane) combined with the tosyl dopant. This combination produced the most stable textile with the highest conductivity. Variation in the dopants used and the possibility of electrochemical polymerization are some areas of interest that need more investigation.

The synthesis of the new series of the poly(α,ω-bis(pyrrolyl)alkanes) has opened up an area of research into conductive polymers. Their thin film forming abilities combined with the high degree of flexibility makes them an area of ongoing interest and further results in this field will be reported in due course.

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