# Synthesis and Characterization of Soluble Conducting Polymers

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## ABSTRACT

Although conducting polymers have various potential applications, lack of solubility is an impediment in their direct application to material surfaces. Synthesis of alkyl pyrrole monomers and subsequent polymerization into soluble conducting polymers are aimed as alternatives to conventional methods of application of conducting polymers on substrates. Alkyl chains are attached to a pyrrole ring to produce solubility in the resulting conducting polypyrroles, which allow direct application of conductive polymer emulsions to any desired surface. Friedel-Crafts acylation of the tosyl-protected pyrrole provides high yields of the 3-acylated product. The conductivity values of poly-3- and 3, 4-substituted pyrroles are generally less than the unmodified polypyrrole. Increasingly bulkier groups attached to the pyrrole means lower conductivity of the resultant polymer. As the carbon chain length attached to the 3-position of pyrrole increases, the solubility also increases. However, the magnitude of change in conductivity of films and pellets of soluble conducting polypyrroles over the alkyl range is not significant.

*Keywords:* Composite, Fabric, Experimental, Surface Treatment

## 1. Introduction

Conducting polymers can be custom synthesized for a wide range of conductivities. This can be achieved by a selection of reactants, concentrations and synthesis parameters, such as time, temperature and pH, during the chemical or electrochemical polymerization process. The use of such conducting polymers to make conductive textiles is an exciting field that offers possibilities for potential intelligent material applications. As one of the most widely used amongst the heterocyclic conducting polymer family, polypyrrole can be readily applied to textiles.

The polymerization of pyrrole by chemical oxidation is usually achieved in organic solvents, but can be achieved in water (Bjorklund et al., 1984).

Oxidants that contain a counterion, such as iron (III) chloride ($FeCl_3$), oxidize pyrrole, initiate polymerization and provide the polymer with a chloride dopant. Previous research performed (Lin et al., 2005) has shown that with solution polymerization, the rate at which polypyrrole attaches to the textile surface (surface polymerization) is in competition with the bulk polymerization that occurs in the solution and subsequently deposits onto the surface (Fig.1). These bulk polymer deposits on the conducting polymer film are loosely bound and can be mostly removed by a thorough washing. In the case of fabrics, a complete removal of the bulk polymer particles may not be possible as they penetrate into the interstices of the fabric structure.



Mag = 1.00 K X    20μm
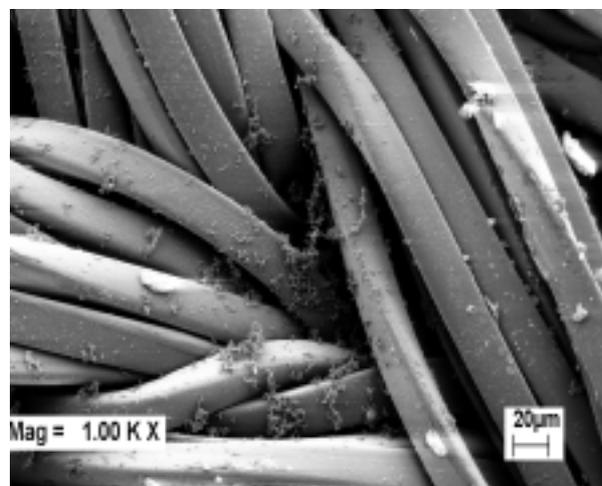
(a)

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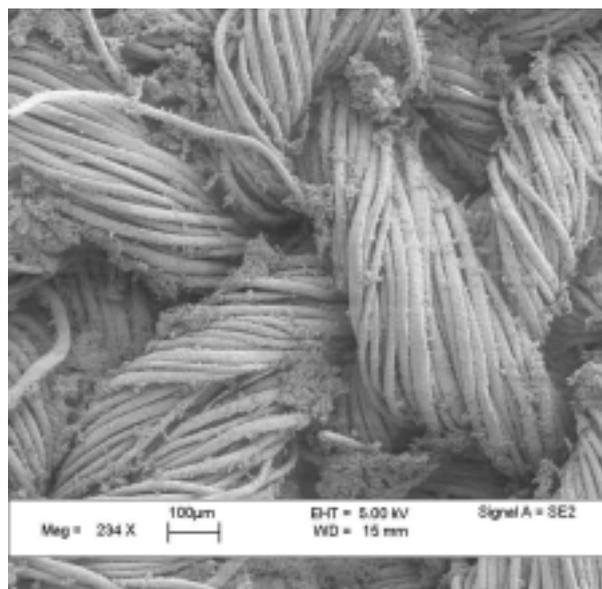
(b)

Fig. 1(a) Scanning electron micrographs of polypyrrole coating on polyester fibers, and

    (b) a wool fabric, applied by solution polymerization which reveals bulk polymer depositions on the fibre surfaces and in the interstices of the warp and weft threads.

To avoid bulk polymerized deposits on the surface, chemical vapor deposition (CVD) can be used (Mohammadi, 1986; Najar, 2007; Kaynak, 2008), where the textile surface is treated with an oxidizing agent, followed by exposure to a monomer in its vapor form, which is brought into contact by a carrier gas (Najar et al., 2007).

The vapor polymerization method shows no signs of bulk polymer and gives rise to a thinner coating with a smoother surface morphology. However, the vapor phase method produces a coating that has a slightly lower abrasion resistance (Foitzik et al., 2005).

Polypyrrole films can also be formed by electrochemical oxidation of a solution that contains pyrrole monomer and a specific electrolyte salt. The polymer films are formed on the electrode, which is usually platinum (Pt) in a one-cell compartment that contains a three electrode configuration (Bailey et al., 2000).

Electrochemical polymerization offers a greater control of the thickness, morphology and degree of doping. A disadvantage of the electrochemical method is that the sample size is limited by the size of the electrode in the cell.

The brittleness, insolubility and lack of long term electrical stability of conducting polymers hinder some of their applications. There are ways of circumventing some of these disadvantages, such as polymerization of conducting polymers onto textile surfaces to produce flexible conductive materials (Child et al., 1997), and synthesis of soluble conducting polymers and then, directly applying them onto the substrate surface. The electrical stability of conducting polymers can be improved to a certain extent by the use of specific dopants and/or adjustment of synthesis parameters (Heisey, 1993; Gazotti, 1993; Kaynak, 2001).

The research on soluble conducting polymers is motivated by the advances in synthetic metals for devices, such as electrochromic displays (Schwendeman et al., 2002), diodes (Pei et al., 2000), batteries (Shukla et al., 2000) and conductive textiles (Kaynak et al., 2003), and aims to offer an alternative to insoluble conducting polymers.

Soluble conductive polymers can be produced by a number of different processes, with chemical modification of the monomers as one of the most researched and commonly used processes. Polymerization of pyrrole occurs through the 2 and 5-position by using either electrochemical or chemical-polymerization methods (Ashraf et al., 1996; Krische et al., 1989).

Therefore, for the introduction of functional groups, only the nitrogen (*N*), and the 3 and 4-positions are available. For the textile field, it is preferable that the *N*-position is free to enable interaction of the polymer with fabric surfaces, as this is suggested to increase the binding strength of the coating (Kaynak et al. 2002; MacDiarmid et al., 1984).

Thus, the 3 and 4-positions are the only points available for functionalization. The type of soluble polymers presented in this paper are derived from monomers formed by the chemical addition of alkyl groups to the 3-position of the pyrrole monomer. Several 3-alkylpyrroles monomers have been successfully chemically polymerized by different research groups (Ruehe et al., 1989).

These resultant polymers were found to be soluble in most polar organic solvents and removal of these solvents by evaporation resulted in conductive films.

Although there have been reports of the synthesis of soluble polypyrroles, a detailed investigation into the coating of these polymers onto fabrics has not been attempted by other research groups. Chemical polymerization of the pyrrole monomer onto a surface involves exposure of the substrate material and equipment to damaging oxidizing agents. The polymerization reactions also need to be carried out under a ventilation system. As an alternative to this, soluble conducting polymers can be directly applied to any surface by conventional printing techniques, which avoid exposure of the surface to damaging oxidizing agents and eliminate the requirements for controlled laboratory conditions. Moreover, the soluble conducting poly-3-alkylpyrroles can be pre-packaged in aerosol cans or as commercially available paints, and applied directly to any surface in any desired pattern for applications that utilize electrical conductivity. In this paper, a method of chemical synthesis, and characterization of alkyl pyrroles are presented. The polymerization of alkyl pyrroles and coating methods of these soluble conducting polymers onto fabric surfaces will be the subjects of our subsequent paper.

## 2. Experimental

Solution-state nuclear magnetic resonance (NMR) is often used for the characterization of smaller organic and inorganic molecules that are soluble in deuterated solvents. Pyrrole is a symmetrical molecule (C2 symmetry as shown in Fig.2), therefore a $^{13}$C NMR spectrum reveals only two carbon resonance peaks at δ: 108 and 117 ppm (Jones, 1977).

The $^1$H spectra shows 3 resonance peaks at δ 6.32, 6.71 and 7.99 ppm, which have an integral ratio of 2:2:1. Due to the symmetry, protons H2 and H5 are equivalent. Likewise, protons H3 and H4 are equivalent and the proton on the nitrogen is singular. Due to the symmetry of this molecule, any modifications to the 3-position disrupt the symmetry, and 4 carbon peaks for each carbon in the pyrrole molecule are then observed.
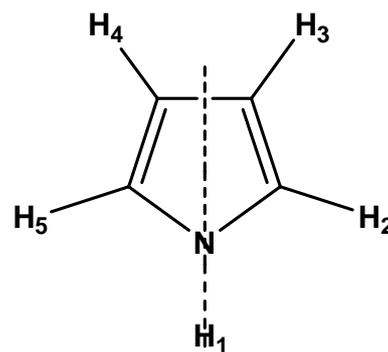


Fig. 2. Symmetry of pyrrole

Elemental analysis gives the exact percentage of each element in a sample. Carbon, hydrogen and nitrogen are three elements which are generally measured and the experimental values are compared to an exact calculated percentage composition of the product. Purification of the sample is essential prior to analysis. This is one of the main methods of characterization used to determine the synthesis of new structures, and is especially useful for insoluble samples due to the ability to test samples in a gas, liquid or solid state. This technique is important for this research due to the large number of new insoluble compounds that were formed.

Scanning electron microscopy (SEM) allows the surface morphology of the samples to be viewed. Synthesis parameters, such as temperature, time, agitation, type and concentration of the reactants, and pH of the solution, affect the surface morphology of the conducting polymer films (Kaynak, 1997; Kaynak et al., 2003).

Any alterations on the monomer structure, such as attachment of functional groups to the 3-position, also causes changes in the surface morphology of the resultant polymer. Most of the samples were sputter coated by gold to obtain a conductive surface.

Conductivity of the coated textiles could not be determined as the thickness of the polymer coating cannot be accurately measured. Therefore, the electrical property of coated fabrics was expressed as resistance. However, prior to textile coating applications, pellets of alkyl polypyrroles were prepared and conductivity measurements were carried out by using a modified 4-probe to accommodate the small pellets with the following equation:

$$\rho = \frac{wt}{d}\left(\frac{\Delta V}{I}\right) = \frac{1}{\sigma} \qquad (\Omega.m)$$

where w, t and d are the sample width, thickness and inner electrode separation. I and $\Delta V$ are the current supplied and measured potential drop, respectively.

## 2.1 Synthesis of N-tosyl Pyrrole

Protection of the nitrogen group on the pyrrole ring is essential for the chemical modification of pyrrole in the 3- and 4-positions; it also deactivates the 2- and 5-positions which prevents polymerization. The synthesis of N-protected pyrrole by using a benzyl sulphate group was described (Zeilikin et al., 1999) where a one-pot method that utilizes inexpensive potassium hydroxide (KOH) in place of potassium metal to attach the benzyl sulphate group in high yields (Fig.3) is used. Modifications to this procedure were made in which a solution of pyrrole, KOH

and tosyl chloride in Tetrahydrofuran (THF) was heated for four hours, cooled and a simple ether/$H_2O$ extractive workup afforded excellent yields of tosyl pyrrole after recrystallization from methanol.
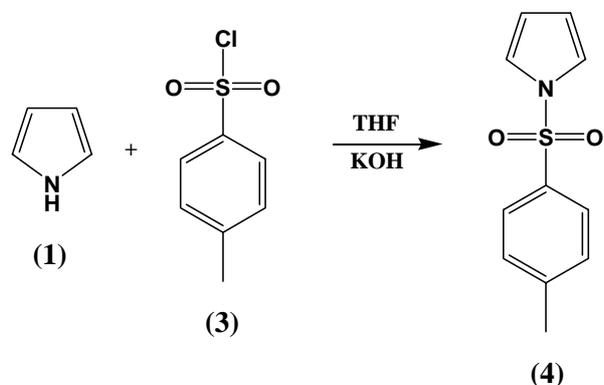


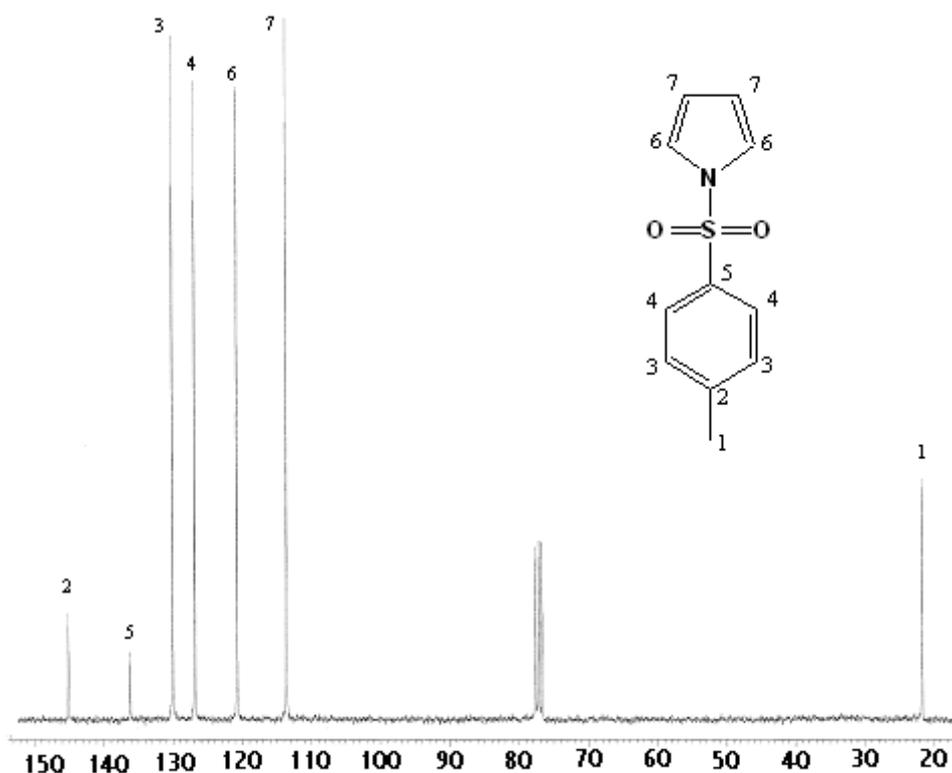Fig.3. Synthesis of N-tosyl pyrrole (4) using potassium hydroxide.



Fig. 4. $^{13}$C NMR spectra of N-tosyl pyrrole.

A $^{13}$C NMR spectrum of N-tosyl pyrrole is shown in Fig. 4. There are a total of 11 carbons in N-tosyl pyrrole, but the NMR spectra only shows 7 due to the $C_2$ mirror plane symmetry of this molecule. Modifications made to N-tosyl pyrrole, such as the substitution of an alkyl group to the 3-position, can be observed in the $^{13}$C NMR spectrum due to the change in the symmetry of the molecule.

The main method used for the addition of alkyl groups to the 3-position of N-tosyl pyrrole is the Friedel-Crafts acylation method, in which an acid chloride was dissolved in a solution in the presence of aluminium chloride ($AlCl_3$), which removes the chloride of the acid chloride to produce $AlCl_4^-$ and the resonance stabilized acylium ion (Smith et al., 2000) (Fig.5). After the addition of N-tosyl pyrrole to the reaction mixture that contained the acylium ion, the latter is attacked by the pyrrole, and after re-aromatization of which, an aromatic ketone is produced.
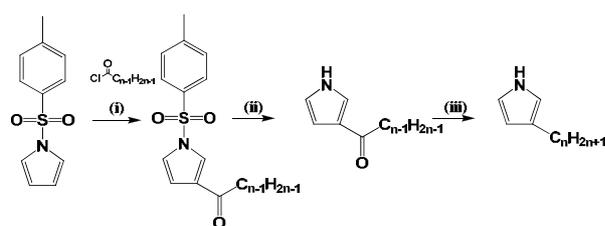


Fig. 5. Synthesis of 3-alkylpyrroles:
   (i)   $AlCl_3$, 0°C, DCM, 2 hrs.;
   (ii)  NaOH, $H_2O$, 110ºC, 1,4-dioxane, 14 hrs.;
   (iii) Red Al®, 0ºC, THF, 3 hrs.

The removal of the protecting group was achieved by refluxing the N-tosyl-3-n-alkanoylpyrroles in 1, 4-dioxane overnight with an aqueous NaOH solution (5 M) (Fig.5). The products were extracted from the reaction mixture using dichloromethane (DCM). Column chromatography was employed to purify the products. To remove the small amount of polymer which was responsible for the dark color of the product, vacuum filtration through silica gel was employed. Compounds were obtained as white solids that were stable and showed no signs of degradation over time.

Reduction of the ketone group to an alkane using a commercially available Red Al® solution (Ruehe et al., 1989) is a quick, high yielding, one step

process to obtain the desired 3-alkylpyrroles. Purification of the smallers monomers (n = 2-4) was done by distillation using a Kügelröhr bulb oven, and placing the sample under reduced pressure at various temperatures. Column chromatography was used for the purification of larger monomers (n >4) due to thehigh boiling points of these monomers. The heating required to distil them caused decomposition/uncontrolled polymerization of the products.

Polymerization of the 3-alkylpyrrole derivatives in the presence of $FeCl_3$ occurred readily to produce black soluble conductive polymers. The 3-alkylpyrrole was stirred in an organic solvent (typically, chloroform ($CHCl_3$)) at room temperature and $FeCl_3$ was added (Fig.6). This reaction mixture was left stirring for several hours before the solvent was removed and the resulting black polymer washed with copious amounts of water.
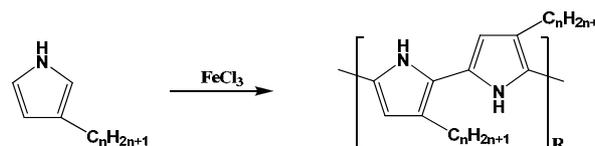


Fig. 6. Polymerization of 3-alkylpyrroles.

## 3.   Results and Discussion

Friedel-Crafts acylation of the tosyl-protected pyrrole provided high yields of the 3-acylated product, where the number of carbon atoms, n, was greater than 6. A shorter chain length of the acid chloride means a greater reactivity of acetyl (n = 2), butyryl (n = 4), valeryl (n = 5) and hexeryl (n = 6) chlorides. To obtain high yields for the acylation of these lower carbon chain acid chlorides, inert conditions are essential.

The conductivity values of poly-3- and 3, 4-substituted pyrroles are generally less than the unmodified polypyrrole. Increasingly bulkier groups attached to the pyrrole means lower conductivity of the resultant polymer. This is due to the bulky groups twisting the polymer chain out of alignment. This can be seen in the molecular model of poly-3-butylpyrrole in Fig.7. With no groups attached, polypyrrole has a flat overlapping conjugated π system.
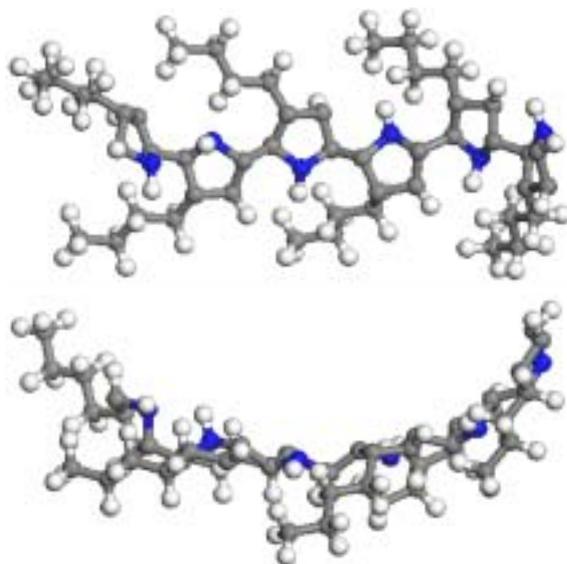
Fig. 7. Molecular model of poly-3-butylpyrrole.

Other physical properties we have introduced to conducting polymers by modifications to the monomer units include solubility, cross-linking, colour and chirality. Conducting polymers, such as polypyrrole, are generally insoluble black materials. Alkyl chains are introduced to produce soluble polymers, which allow the application of emulsions of soluble polymers to different substrates without the exposure of damaging chemicals.

Characterization of 3-n-alkyl pyrroles is accomplished by using $^{13}$C and $^{1}$H NMR. An alkyl chain greater than 5 carbons in length creates an overlap in the $^{13}$C spectra. A large peak emerges at δ ~30 ppm and is assigned to the long extending carbon chain. After a certain chain length is reached, these peaks all have the same chemical shift (δ) in the NMR spectra, as they are all chemically very similar. Each monomer is further characterised by $^{1}$H NMR and an elemental analysis.

## 3.1 Solubility and Conductivity of Poly (3- alkylpyrroles)

Soluble polymers have been documented, and most exhibit solubility in strong polar organic solvents (Ashraf et al., 1996).

For this investigation, $CHCl_3$ is used to compare our results with previous work (Masuda et al., 1989).

The solubility of the polymers is tested by dissolving a ground polymer powder in $CHCl_3$, and then the solution was sonicated for 1 hour before it was filtered with a scintillation funnel. Accurate volumes (2.00 $cm^3$) of this solution at 25$^o$C were then placed in dried pre-weighed vials, and the solvent was removed under reduced pressure. This was repeated 10 times for each sample with the mass of the polymer recorded each time, and an average taken. The results showed that the length of the carbon chain is directly related to the solubility of the polymer. As the carbon chain length attached to the 3-position of pyrrole increases, the solubility also increases. The increase in solubility with an increasing carbon chain length is accompanied by a slight decrease in conductivity exhibited by their solid films. However, the magnitude of change in conductivity over the alkyl range is very small (0.5-3.0 S/cm) (Fig.8).
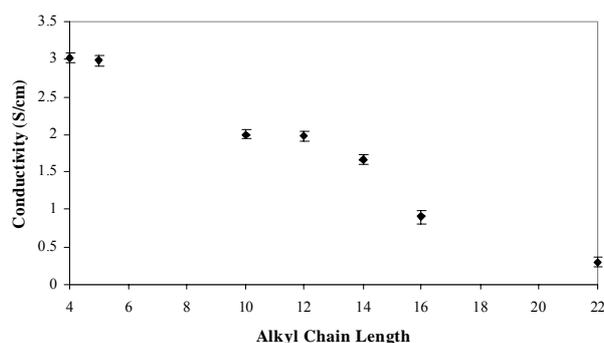


Fig. 8. Conductivity vs. alkyl chain length for solid conductive pellets of poly (3-n- alkylpyrrole).

A study of the homologous series of n-alkyl pyrroles shows an increase in solubility and a decrease of conductivity with increasing chain length (Fig.9).
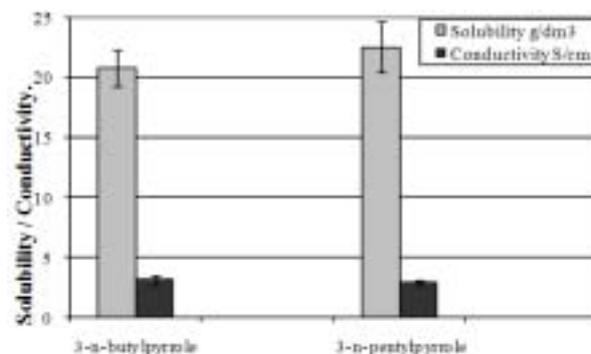


Fig. 9. Comparison of the conductivity and solubility between the polymers formed from 3-n-butyl, 3-n-pentylpyrroles.

## 4. Conclusion

The lack of solubility of conducting polymers is tackled by synthesizing alkyl pyrrole monomers, and the chemical polymerization of which results in soluble alkyl polypyrrole conducting polymers. In this work, we have focused on the synthesis and chemical characterization of alkyl pyrroles. In addition, we have polymerized alkyl pyrroles into soluble alkyl polypyrroles and finally, characterized the resulting polymers with respect to solubility and conductivity. Methods of direct application onto textile surfaces and characterization of the coated textiles are the subjects of the second part of this work and presented in a subsequent article. Alkyl chains are attached to a pyrrole ring to produce soluble conducting polymers, which allow direct application of polymer emulsions to any desired surface. The synthesis of a family of 3-alkylpyrroles which range from ethyl (n=2) to behenyl (n=22), using Friedel-Crafts acylation, is achieved in high yields and purity. The products are tested by an analysis of $^{13}C$ NMR spectra at each stage of the monomer synthesis. The polymerization of the 3-alkylpyrrole derivatives in the presence of $FeCl_3$ occurs readily to produce black soluble conductive polymers. The experiments show that the length of the carbon chain affects the solubility of the polymer. As the carbon chain length attached to the 3-position of pyrrole increases, the solubility also increases. However, the conductivity decreases slightly with an increase in the alkyl chain length. The bulkier groups attached to the pyrrole ring have an effect of lowering the conductivity of the resulting polymer. This is attributed to the side groups which twist the polymer chain out of alignment. However, the conductivity of solid films is much less affected by the alkyl chain length compared to that of fabrics coated by soluble poly(3-alkylpyrroles), the results of which will be discussed in the subsequent paper. The conductivity of poly-3- and 3,4-substituted pyrroles is generally less than the unmodified polypyrrole.

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