

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Electropolymerization of Pyrrole on Cotton Fabrics

Surya Subianto^a; Geoffrey D. Will^a; Serge Kokot^a

^a Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, Brisbane, Australia

To cite this Article Subianto, Surya , Will, Geoffrey D. and Kokot, Serge(2005) 'Electropolymerization of Pyrrole on Cotton Fabrics', International Journal of Polymeric Materials, 54: 2, 141 – 150

To link to this Article: DOI: 10.1080/00914030390246252

URL: <http://dx.doi.org/10.1080/00914030390246252>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ELECTROPOLYMERIZATION OF PYRROLE ON COTTON FABRICS

Surya Subianto

Geoffrey D. Will

Serge Kokot

Centre for Instrumental and Developmental Chemistry,
Queensland University of Technology, Brisbane, Australia

Polypyrrole was electrochemically deposited onto cotton fabrics with the aid of a water-soluble adhesive. The conductivity and surface structure of the resultant polymer were studied, showing a templated dendritic growth on the surface of the cotton fabric. The mechanism for templated growth is discussed.

Keywords: electropolymerization, cotton, pyrrole, composite, conductivity, polypyrrole

INTRODUCTION

Over the last decade conducting polymers have been intensely investigated with specific focus on synthesis, characterization, processibility, and stability. Particular emphasis in the last few years has been directed toward applications, with an attempt to translate the versatility of conducting polymers into practical devices [1–5]. The ideal properties of a conducting polymer would result in a material with metallic conductivity and mechanical properties of a strong processible thermoplastic [6]. However, the reality is that most conducting polymers possess poor mechanical properties, rendering them unsuitable for many conventional industrial uses and processes [1]. Recently, the processability issue has been addressed by Garnier and co-workers through printing techniques [3] and Kim and co-workers by the incorporation of the conducting polymer into hydrogel composites [7].

Received 11 June 2003; in final form: 20 June 2003.

Address correspondence to Geoffrey D. Will, Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia. E-mail: g.will@qut.edu.au

In situ polymerization of polypyrrole and aniline onto materials with high surface area (textiles, membranes) has also been a source of commercial interest over the last 10 years by numerous groups [8–10]. More recently, modification of the synthesis of these polymers has produced soluble derivatives allowing in situ synthesis of the polymer in the same way as conventional thermoplastics [5].

Numerous composites made up of conducting polymers and structural synthetic polymers have been constructed and utilized in different ways such as in electromagnetic radiation shields by the U.S. military [9]. Generally, composite formation involves radical initiated polymerization in the presence of the structural material [11]. The integration of the structural material with the conducting polymer in this case is dependent on an absorption mechanism [11–14]. An alternative method is through the physical attachment of the textile substrate onto an electrode and electrochemically polymerizing through the textile network of the structural material [10,15]. The advantage with this method rests in the ultimate control of the rate of polymerization through the imposed electric current and the degree of conductivity via the dopant concentration.

This article reports the use of electrochemical polymerization of polypyrrole on/in to natural textiles through the surface modification of the anodes used. In using this technique it can be shown that the rate of polymerization has an inherent effect on the electrical properties of the final product. It is also shown that composite formation improves the mechanical properties of the conducting polymer. The nature and formation of the polypyrrole film are studied with the aid of scanning electron microscopy (SEM), which provides an insight into its polymerization on/in the cotton cellulose fabric structure in the presence and absence of the adhesive. In particular the authors follow and describe the growth stages of the polymer from the polymer film layer through the network of holes formed by the criss-crossing yarns to the formation of spherical dendrites.

EXPERIMENTAL

The preparation of conducting polymer films with and without a natural fiber support were carried out using pyrrole (Aldrich, 98%), p-toluenesulphonic acid (Aldrich, 99%) as dopant/electrolyte at the indicated concentrations in an aqueous solution. Galvanostatic electrochemical synthesis was carried out by the oxidative polymerization of polypyrrole using a two-electrode electrochemical cell employing a stainless steel (type-304) anode in conjunction with a stainless steel mesh (type-304) cathode. The cell was arranged such that polymerization

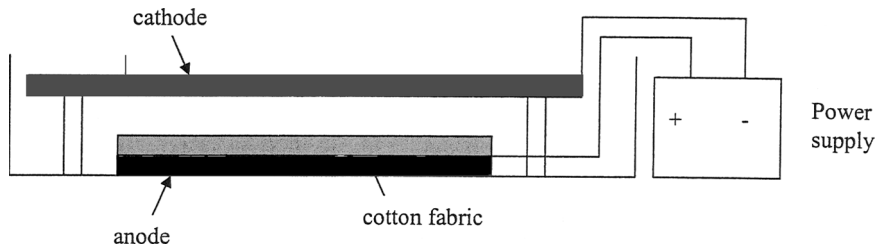


FIGURE 1 A two-electrode electrochemical setup for polymerization of polypyrrole.

occurred in a horizontal orientation with the cathode suspended above the anode (see Figure 1). Current and voltage were controlled and monitored in the cell using a Parameters 8040 multimeter connected to a Thandar TS3021S 30V/2A power supply.

Electropolymerization was carried out for 4 to 6 h. In the case of a supported polymer film, cotton fabric was attached to the anode by means of a water-based adhesive (Henkel Pritt stick) with a second layer of adhesive applied to the external surface of the fabric. For comparison, polymer films were also produced in the presence of cotton fabric without adhesive by physically pressing the textile to the surface of the anode. Unsupported films were prepared using the same apparatus but in the absence of both adhesive and cotton fabric. All polymerizations were carried out at room temperature (25°C).

Films were peeled from the electrode using a scalpel, washed with deionized water, and air dried before testing. If films were not immediately tested they were stored in a darkened desiccator.

Conductivity of the resulting films was measured using the two-point probe method. SEM micrographs of the supported and unsupported films were measured with a JEOL JSM-35 CF scanning electron microscope.

RESULTS AND DISCUSSION

Nature and Properties of the Polypyrrole Film

The polypyrrole formed on cotton fabric grew as a film of even thickness on the electrode and appeared to be mechanically attached to the cotton by polymerizing in between the yarns and finally through the cotton fabric as dendrites. In contrast to the dendritic surface, a smooth polypyrrole film was formed at the surface of the stainless steel electrode. It was noted that the quality and uniformity of the film

TABLE 1 Conductivities of Films Prepared in 0.2 M Pyrrole, 0.5 M p-Toluenesulphonic Acid in Aqueous Solution at Indicated Polymerization Currents

Polymerization current density (A/cm ²)	Resistance (Ω /cm ²)
2	0.75
3	1.19
5	210

depended highly on the polymerization current and the evenness of the adhesive layer, with low current and a thin, even layer of adhesive producing the films with best physical properties. This result reflects the dependence of electrochemical polymerization on the rate of diffusion of the pyrrole from the bulk solution to the growing polymer tip [15]. Similar to results obtained by various groups [16–22], the conductivity of the polymer increases with increasing dopant concentration and decreasing polymerization current (see Tables 1 and 2). This is due to a higher number of charge carriers in the polymer as the dopant concentration increases and higher degree of crystallinity in the polymer structure as it is formed more slowly at lower currents.

It was found that the conductivity of the films supported on the cotton fabric were lower than that of the free standing film (see Table 3). This could be attributed to the more irregular structure of the film on the cotton, therefore increasing the number of defects and barriers to the movement of electrons. This result is supported by the hopping mechanism proposed to be the limiting step in the conduction of electricity through a conducting polymer [17,21,23]. It would be expected that the cotton, which is an insulator, would decrease the interaction between polymer chains as a result of its presence. Therefore, the result is a decreased probability of electrons hopping from one polymer chain to the next, leading to a decrease in the conductivity of the composite.

TABLE 2 Conductivities of Films Prepared at 100 mA/cm² and 0.6 M Pyrrole with the Indicated Concentration of Dopant, p-Toluenesulphonic Acid

Dopant concentration (M)	Resistance (Ω /cm ²)
0.01	0.44
0.02	0.033
0.05	0.0059

TABLE 3 Conductivities of Free Standing and Composite Films Prepared in 0.2M Pyrrole, 0.01 M p-Toluenesulfonic Acid at 100 mA for 2.5 h

Film type	Resistance (Ω/cm^2)
Free standing film	0.077
Film on cotton	1.60

Morphology Studies of the Cotton/Polypyrrole Composite

The SEM micrographs (Figure 2) reveal that a thick film growth through the cotton is present when adhesive is used, with less ordering compared to the free-standing film. It also shows that the polymer does not coat the individual cotton fibers but rather fills the gap between the yarns. Mechanical interlocking between the polymer and the cotton yarns is therefore responsible for the improved mechanical properties. This observation is in contrast to that observed for conducting polymers formed chemically in the presence of supporting fibers where the polymer was shown to form a continuous coating on the supporting fiber through an adsorption mechanism [11–14].

The growth pattern of the polymer on the surface of the free-standing and supported films were shown to be distinctly different (see Figure 3). The free-standing films produce granular dendrites, which seem to be made of small spherulites growing together, whereas the film on the adhesive-coated cotton fabric produces porous, hollow dendrites.

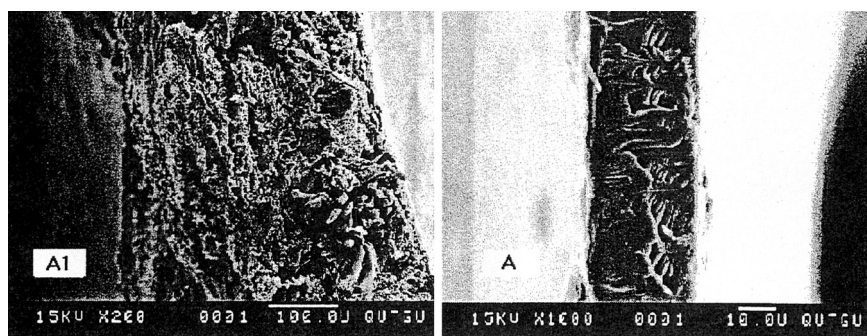


FIGURE 2 SEM images of the cross section of electrochemically polymerized polypyrrole films on cotton fabric (A1) and freestanding film (A) (Polymerization conditions: 100 mA/cm² from a 0.2 M polypyrrole, 0.02 M p-toluenesulfonic acid aqueous solution for 4 h).

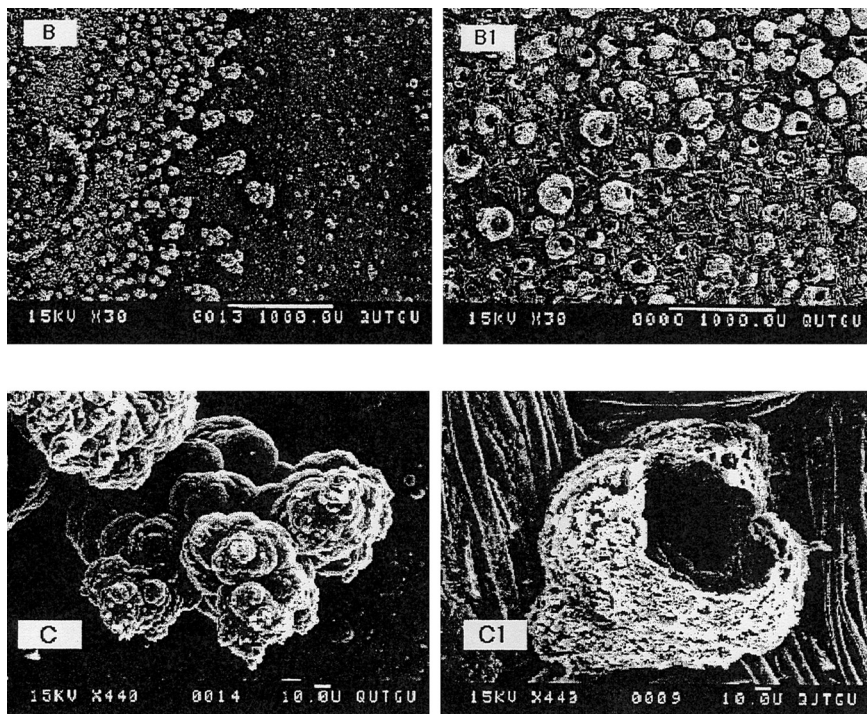


FIGURE 3 Dendrite on free standing film (B, C) and film on cotton (B1, C1) (Polymerization conditions: 100 mA/cm^2 from a 0.2 M polypyrrole, 0.02 M p-toluenesulfonic acid aqueous solution for 4 h.

It can be seen from Figure 3 that the growth pattern for the polymer is significantly different depending on the presence or absence of the cotton fabric and the adhesive. When the adhesive and cotton are present at the anode the dendrite has a hollow sponge-like appearance (Figure 3(C1)). This structure may have arisen due to the structure of the cotton fabric and the adhesive [8–9]. It has been observed previously that templated growth of conducting polymers can occur at the surface of synthetic fibers. In these studies the polymers were synthesized chemically and the mechanism for the templated polymerization was thought to have resulted from the adsorption of the monomer onto the surface of the substrate [11–14]. A similar mechanism could exist here whereby the monomer adsorbs on the surface of the cotton resulting in a high concentration of reactant or a preferential nucleation site, and thus a route for accelerated electrochemical polymerization. Further, the polymer appears to grow only initially from

the electrode surface [24,25] and then it propagates from the outer edge of the growing conducting polymer. This could be seen as a consequence of the conducting properties of the polymer and indicates that electrons are being transferred from the electrode through the polymer to the growing tip.

The polypyrrole grown through the yarn substrate does so preferentially on the yarn's surface following the contour, forming hollow square bases, which grows further into a circular "bloom." As the electrochemical polymerization proceeds the "bloom" closes off, resulting in a roughly spherical hollow structure. Figure 4 shows the possible steps in the growth of a dendrite through the gaps between yarn fibers, taken from various areas of Figure 3(B1).

A adhesive-coated cotton fabric sample subjected to electrochemical polymerization for periods up to 10 h showed hollow structures similar to that in the micrograph in Figure 4. The growth of hollow structures was uniform with most of the structures similar in size. However, they did not grow evenly across the surface, resulting in dark patches on the cotton surface. The proposed reason for this behavior is the uneven distribution of the adhesive underneath the cotton, resulting in differing resistance to monomer diffusion and therefore different rates of polymerization at that point.

A further comparison between polypyrrole grown through cotton fabric in the presence and absence of adhesive reveals an interesting change in the growth pattern. SEM micrographs reveal that the adhesive plays an important role in the incorporation of the polypyrrole in the cotton fabric. When the cotton was only attached to the electrode without any adhesive similar to the method used by Bhadani et al. [10], (see Figure 5.) the polypyrrole film grows underneath the cotton fabric and does not become incorporated between the yarns. The attachment of the polypyrrole onto the fabric results from the forced growth of the dendrites through the fabric rather than incorporation of the polymer into the structure of the yarns. The adhesive also

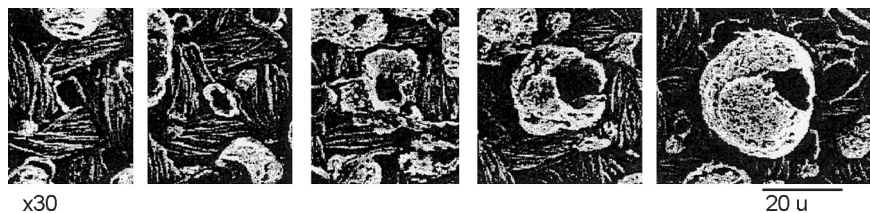


FIGURE 4 Polymer dendrite growth (taken from different areas on the polymer in micrograph Figure 3 B1).

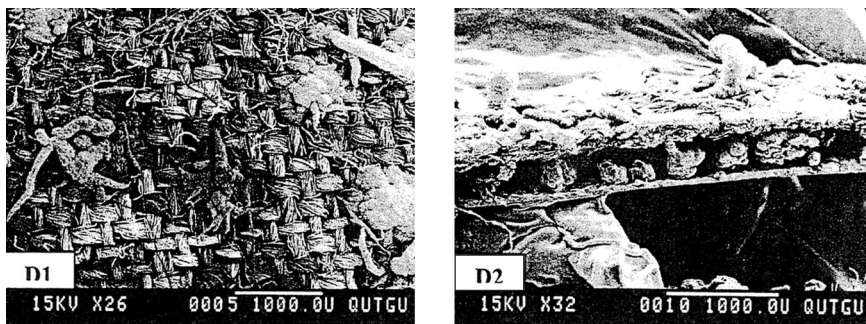


FIGURE 5 Polypyrrole film grown with cotton fabric attached to the electrode without the adhesive present. D1 shows the dendrite growth through the fabric, where as D2 shows the cross section of the fabric with a distinct polypyrrole layer formed at the electrode side of the fabric.

affects the dendrite formation, so that the polypyrrole film grown without adhesive present results in non-uniform dendritic growth with a granular structure similar to those formed in a free-standing film. Figure 5(D2) demonstrates the formation of a film at the electrode followed by the growth of individual dendrites through the textile. The evidence of a two-layered structure in Figure 5(D2) is in stark contrast to that of the composite formed in the presence of the adhesive, Figure 2(A), where the incorporation of the polymer into the textile structure results in a significantly more uniform composite.

CONCLUSION

The authors have successfully electrochemically polymerized polypyrrole through derivatized cotton fabric forming a highly uniform composite material. The resulting mechanical properties of the composite film were improved with a notable difference between it and a free-standing polypyrrole film. In agreement with the literature [17–18,26] the resistance of the composite films was shown to decrease with increasing dopant concentration and increase with decreased polymerization rate. The conductivity of composite films compared to free-standing films was observed to decrease as a result of the inclusion of the insulating cotton fibers.

The mechanism for growth of the polymer appears to follow the template laid out by the yarns in the cotton fabric. It is proposed that this is due to the adsorption of monomer to the surface of the yarns and subsequent polymerization along the areas of high concentration of monomer. The polymer appears to propagate from the growing

polymer end, forming hollow spheres as they emerge on the solution side of the cotton fabric. This templated growth was seen to be distinctly different from that of a free-standing film in which growth appears to progress through spherical nodes. Films prepared with an added adhesive showed significantly better structural uniformity than those prepared without. This is a noteworthy result as it indicates that the adhesive has a significant templating effect on the growth of the polymer.

The simplicity of the process and the significant improvements in the mechanical properties of the composite and its uniformity indicate the potential benefits of this process over more conventional means. The processibility, control of the rate of polymerization, and the dopant concentration all contribute to tuning the electrical properties of the composite and are thus major benefits of this method of preparation.

REFERENCES

- [1] Aldissi, M. et al., *Crit. Rev. Surf. Chem.* **3**, 13 (1993).
- [2] Arango, A. C., Johnson, L. R., Bliznyuk, V. N., Schlesinger, Z., Carter, S. A., and Horhold, H. H. *Adv. Mater. (Weinheim, Ger.)* **12**, 1689 (2000).
- [3] Garnier, F., Hajlaoui, R., Yassar, A., and Srivastava, P. *Science (Washington, D.C.)* **265**, 1864 (1994).
- [4] Hutchison, A. S., Lewis, T. W., Moulton, S. E., Spinks, G. M., and Wallace, G. G. *Synth. Met.* **113**, 121 (2000).
- [5] Segawa, H., Wu, F. P., Nakayama, N., Maruyama, H., Sagisaka, S., Higuchi, N., Fujitsuka, M., and Shimidzu, T. *Synth. Met.* **71**, 2151 (1995).
- [6] MacDiarmid, A. G. *Synth. Met.* **84**, 27 (1997).
- [7] Kim, B. C., Spinks, G., Too, C. O., Wallace, G. G., and Bae, Y. H. *React. Funct. Poly.* **44**, 31 (2000).
- [8] Kuhn, H. H., Kimbrell, W. C., Worrell, G., and Chen, C. S. *Annu. Tech. Conf. Soc. Plast. Eng.* **49**, 760 (1991).
- [9] Kuhn, H. H., Kimbrell, W. C., Fowler, J. E., and Barry, C. N. *Synth. Met.* **57**, 3707 (1993).
- [10] Bhadani, S. N., Kumari, M., Gupta, S. K., and Sahu, G. C. *J. App. Poly. Sci.* **61**, 207 (1996); Bhadani, S. N., Gupta, S. K., Sahu, G. C., and Kumari, M. *J. App. Poly. Sci.* **64**, 1073 (1997); Bhadani, S. N., Gupta, S. K., Sahu, G. C., and Kumari, M., *J. Poly. Mat.* **13**, 61 (1996).
- [11] Gregory, R. V., Kimbrell, W. C., and Kuhn, H. H. *J. Coated Fabr.* **20**, 167 (1991).
- [12] Gregory, R. V., Kimbrell, W. C., and Kuhn, H. H. *Synth. Met.* **28**, 823 (1989).
- [13] Kuhn, H. H., Kimbrell, W. C., and Gregory, R. V. (1991). *Properties of Polypyrrole Treated Textiles for Advanced Application*. In *Search of Excellence* (ANTEC, Brookfield Center, Conn., USA, SPE).
- [14] Kimbrell, W. C., Gregory, R. V., and Kuhn, H. H. (1989). *Conductive Textile composites* In *Electronic materials and processes* (3rd International SAMPE Electronics Conference, Society for the Advancement of Material and Process Eng., Covina, CA, USA).
- [15] Li, S., Macosko, C. W., and White, H. S. *Science* **259**, 957 (1993).
- [16] Jerome, C. and Jerome, R. *Angew Chem. Int. Ed. Eng.* **37**, 2488 (1998).

- [17] Chandrasekhar, P. (1999). *Conducting polymers, fundamentals and applications: A practical approach* (Dordrecht: Kluwer Academic).
- [18] Aldissi, M. (1989). *Inherently Conducting Polymers* (Noyes Data Corporation, New Jersey).
- [19] Kupila, E. K. and Kankare, J. *Synth. Met.* **82**, 89 (1996).
- [20] Davidson, R. H., Hammond, L., Turner, A., and Wilson, A. *Synth. Met.* **81**, 1 (1996).
- [21] Schmeiber, D. B., Bartl, A., Dunsch, L., Naarman, H., and Gopel, W. *Synth. Met.* **93**, 43 (1998).
- [22] Drekylev, P. G., Granstrom, M., Ingnas, O., Guaratne, L., Senadeera, G., Skaarup, S., and West, K. *Polymer* **37**, 2609 (1996).
- [23] Joo, J., Lee, J. K., Baeck, J. S., Kim, K. H., Oh, E. J., and Epstein, J. *Synth. Met.* **117**, 45 (2001).
- [24] Otero, T. F., Santamaria, C., and Bunting, R. K. *J. Electroanal. Chem.* **380**, 291 (1995).
- [25] Sadki, S. S., Schottland, P., Brodie, N., and Saboraud, G. *Chem. Soc. Rev.* **29**, 283 (2000).
- [26] Nalwa, H. S. (Ed.), (1997). *Conductive Polymers: Synthesis and Electrical Properties. Handbook of Organic Conductive Molecules and Polymers*, Vol. 2 (John Wiley & Sons, Chicester).