

Chimia 47 (1993) 490-493
 © Neue Schweizerische Chemische Gesellschaft
 ISSN 0009-4293

Characterization of Low Temperature Soluble Polyaniline

Jeff C. Michaelson^{a)}, Augustin J. McEvoy^{a)*}, and Takeo Shimidzu^{b)}

Abstract. Because the charging of polyaniline films occurs in the bulk of the material rather than exclusively at the polymer-electrolyte interface, the use of thick polymer films for battery applications is justifiable. Here, we present a method for producing soluble polyaniline which can be cast to form free-standing films. Investigation by scanning electron microscopy (SEM) has shown that these films are significantly more compact than those made by standard electropolymerization.

Introduction

For over a decade, organic conducting polymers such as polyaniline (PANI) have been considered for application as the cathode material of secondary batteries. Much of the research has concentrated on developing polymer films which have the high electroactivity necessary to compete with conventional electrode materials. Due to this effort, reversible polyanilines with high conductivities and energy and charge densities have been produced. However, while the electrochemical properties have been greatly improved, other aspects such as thermal stability and mechanical properties have often been ignored. In particular, easily processible polyaniline films possessing a high degree of mechanical integrity, needed by industry to justify large-scale polyaniline battery production, have been quite elusive.

To produce such films, the polymer should be soluble in a common solvent which thereby permits the casting of free-standing films. Earlier, *Li et al.* [1] showed

that such PANI samples could be made by employing large organic protonic acids or by grafting the polymer with polyaminostyrene. More recently, a water-soluble conducting polyaniline has been reported, but this is in fact a poly(aniline propylsulfonate) [2]. Unsubstituted polyaniline produced by conventional electropolymerization or chemical oxidation, however, is known to be highly insoluble.

The reason is that, although PANI is considered to be formed by the head-to-tail coupling of aniline molecules and oligomers to form a simple linear chain (*Scheme*), the polymerization process is accompanied by a number of side reactions. For example, electrophilic substitution at the *ortho*-position, which has been estimated to account for 10% of all coupling reactions [3], naturally leads to chain branching. Incidentally, very high levels of chemical cross-linking in PANI has been observed when certain bi-functional species such as *para*-phenylenediamine (PPDA) have been introduced to the monomer solution [4].

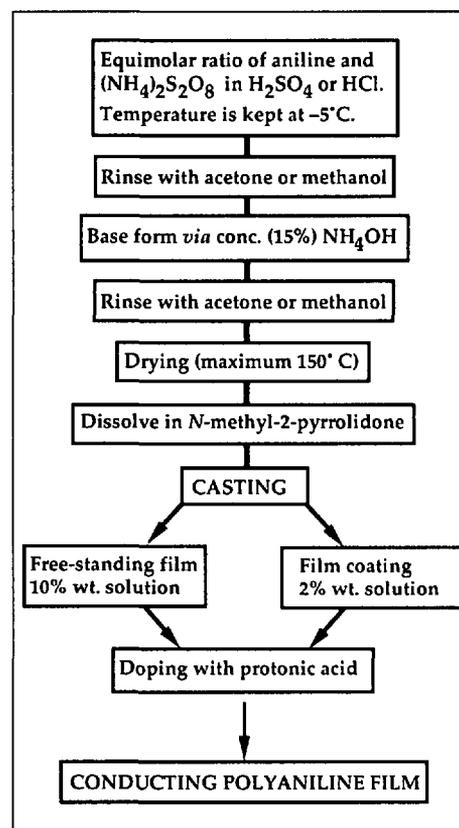


Fig. 1. Polymerization scheme for obtaining soluble polyaniline by low-temperature chemical oxidation

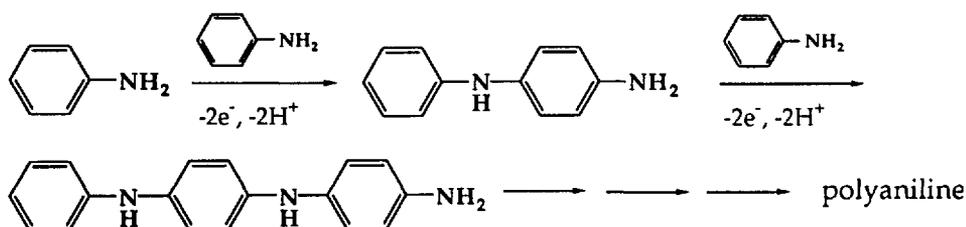
Furthermore, physical cross-linking may occur in the microcrystalline domain where two or more different polymer chains become bound together [5]. This results in a higher degree of polymer crystallinity which can be observed by the improvement in certain mechanical properties such as tensile strength. The overall polymer conductivity may also rise. However, due to this crystal alignment, the overall polymer solubility will normally suffer. This can be explained by considering the rise in cross-linking as an increase in the overall size of the macromolecular entity which consequently hinders the solvent from forming an effective solvation shell around the polymer.

Typically, the side reactions which result in PANI chemical cross-linking have activation energies that are substantially higher than that needed for simple chain propagation. Therefore, by lowering the temperature of the reaction vessel for chemical polymerization, all high-energy reactions can be statistically suppressed, and the polymer chains will have a predomi-

*Correspondance: Dr. A.J. McEvoy

a) Institut de chimie-physique II
 Ecole Polytechnique Fédérale de Lausanne
 CH-1015 Lausanne

b) Division of Molecular Engineering
 Graduate School of Engineering
 Kyoto University
 Kyoto 606, Japan



nantly linear character. *MacDiarmid* and coworkers [5] have already reported that PANI samples prepared by chemical oxidation at -30° have molecular weights of 400.000 g/mol with no appearance of crystallinity. During electrodeposition, however, the temperature affects only the aniline diffusivity so that lower temperatures result in lower monomer concentrations near the working electrode and thus slower polymerization rates; no macrostructural changes are expected.

Experimental

All chemicals were purchased from *Fluka* and used as received, the sole exception being aniline which was also doubly distilled under reduced pressure. The aq. monomer soln., 0.2M aniline/1M HCl, was deaerated with Ar for several h prior to polymerization. In the co-polymerization experiments, the monomer soln., furthermore, contained 5.0×10^{-4} M PPDA. For low-temperature polymerization, a second soln. containing 0.2M ammonium peroxydisulfate (APD) in 1M HCl was prepared and deaerated.

For comparison purposes, PANI samples were made by standard cyclic sweep electropolymerization (denoted as echem-PANI) using a single compartment 3-electrode cell under potentiostatic control (*PAR model 273* potentiostat) as described in detail in [6]. The reference electrode was a *saturated calomel electrode* (SCE) and a Pt foil was used as the counter electrode. The working electrode substrate was a polished 1 cm² Pt foil for electrochemical characterization while conductive *indium tin oxide* (ITO) glass slides were used for the SEM investigation.

Room-temp. chemical oxidation was achieved by adding 0.92 g (4 mmol) of APD to 20 ml of the monomer soln. The rapid appearance of a dark green color indicated that polyaniline (chem-PANI) had been formed. The resulting polymer deposited onto ITO slides which were suspended in the reaction vessel while heating gradually to 35° to evaporate the solvent.

Low-temp. chemical polymerization was accomplished following the scheme shown in *Fig. 1*. Prior to polymerization, the monomer and APD solns. were first cooled to -10° in a dry ice bath. Then, 10 ml of each soln. were mixed by adding the APD soln. dropwise while keeping the aniline soln. at -5° . Over the following several h, the formation of polymeric material was observed. These large suspended particles were then rinsed with acetone and collected by vacuum filtration to give an emerald-colored gel. The polymer gel, converted to the base form by treatment with conc. NH_4OH which removed any trapped counterions, then became rich blue. A second rinsing process followed. This material was then dried at 100° for 24 h to form a powder which was readily soluble in *N*-methyl-2-pyrrolidone (NMP). Polyaniline films (It-PANI) were made from a 10% (by wt.) polymer soln. which was heated to 130° in order to substantially raise the viscosity so that the casting of thick films was possible. The polymer-coated ITO slides (1 cm²) were further baked at 100° prior to further characterization.

SEM investigation was carried out with a *Cambridge Instruments model 360* scanning elec-

tron microscope. The quantity of electroactive polymer present can be estimated faradaically by the area of the oxidation peak centered at +200 mV in the voltammogram. For the comparison SEM images shown in *Fig. 4*, this is ca. 3 mC/cm². All electrochemical characterization was accomplished using the same 3-electrode system as that employed for electrodeposition.

Results and Discussion

Electrochemical cycling of polyaniline films produced by the three different polymerization methods are shown in *Fig. 2*. The It-PANI film (*Fig. 2C*) is quite electroactive showing a well-defined redox system between 0 and 250 mV with a second system, although less pronounced, at the anodic potential limit. This electrochemical behavior is markedly similar to that of the electrodeposited polymer (*Fig. 2A*). Although the relative size of the redox wave depends on the quantity of material deposited, it is still quite clear that the cyclic voltammograms of the chem-PANI sample exhibit a much broader redox system, indicative of slower transport of charge carriers within the polymer matrix.

It is already known that the type of counterion employed can influence the charge-transfer kinetics of the electrolyte solution. During normal electrodeposition, this effect can be observed by measuring changes in the initial nucleation rate as a function of the counterion employed. Comparison of the role of the counterion for the electrochemical behavior of It-PANI is shown in *Fig. 3*. Cyclic voltammograms taken in 1M HClO_4 (*Fig. 3B*) show much greater peak separation for both polyaniline redox systems indicating slower charge exchange.

Electron micrographs comparing the morphology of conventional echem-PANI with that of It-PANI are shown in *Fig. 4*. The echem-PANI surface macrostructure is highly fibrous in nature with an average fiber thickness of ca. 100 nm. Furthermore, as *Desilvestro* and *Scheifele* [7] have recently shown, this macrostructure does not vary significantly with the counterion employed. The morphology of chem-PANI samples also show a fine fibrillar character [6]. The It-PANI films, on the other hand, are extremely compact and show no distinguishing features at low magnification (*Fig. 4A*), while at higher magnifications, the presence of a densely matted structure is observed (*Fig. 4C*). Correlating morphology with the observed electrochemical behavior, we can conclude that charge transfer can occur through the bulk of the polymer material rather than exclusively at the polymer-electrolyte interface.

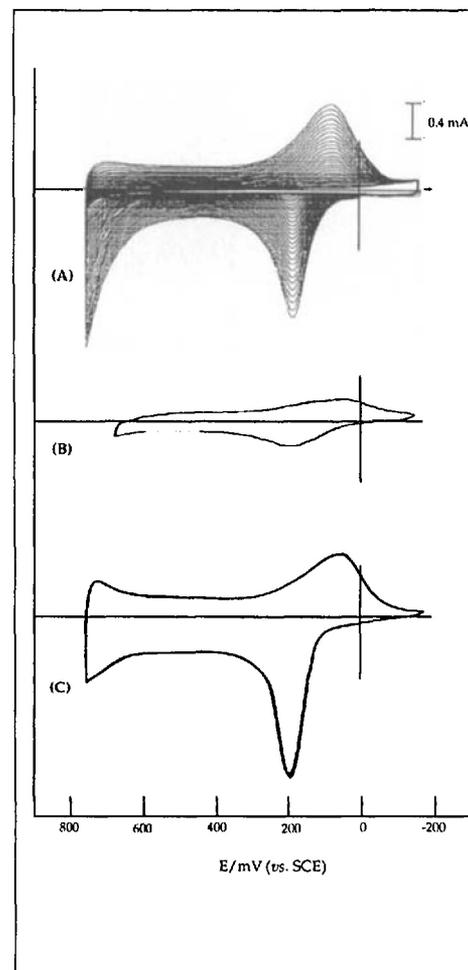


Fig. 2. Cyclic voltammograms obtained: (A) during the electrochemical polymerization of aniline; (B) following standard chemical preparation of PANI; and (C) following low-temperature chemical preparation of soluble PANI. Note: (B) and (C) were cycled in 1M HCl.

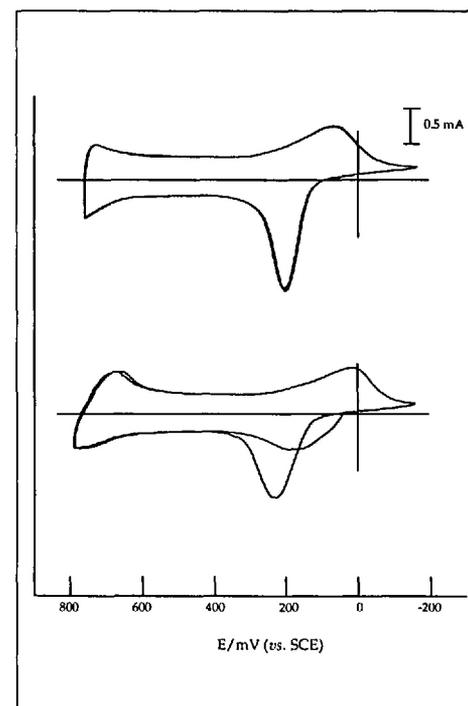


Fig. 3. Characteristic cyclic voltammograms of polyaniline free-standing films obtained following low-temperature chemical preparation of soluble PANI where the electrolyte is: (A) 1M HCl; and (B) 1M HClO4

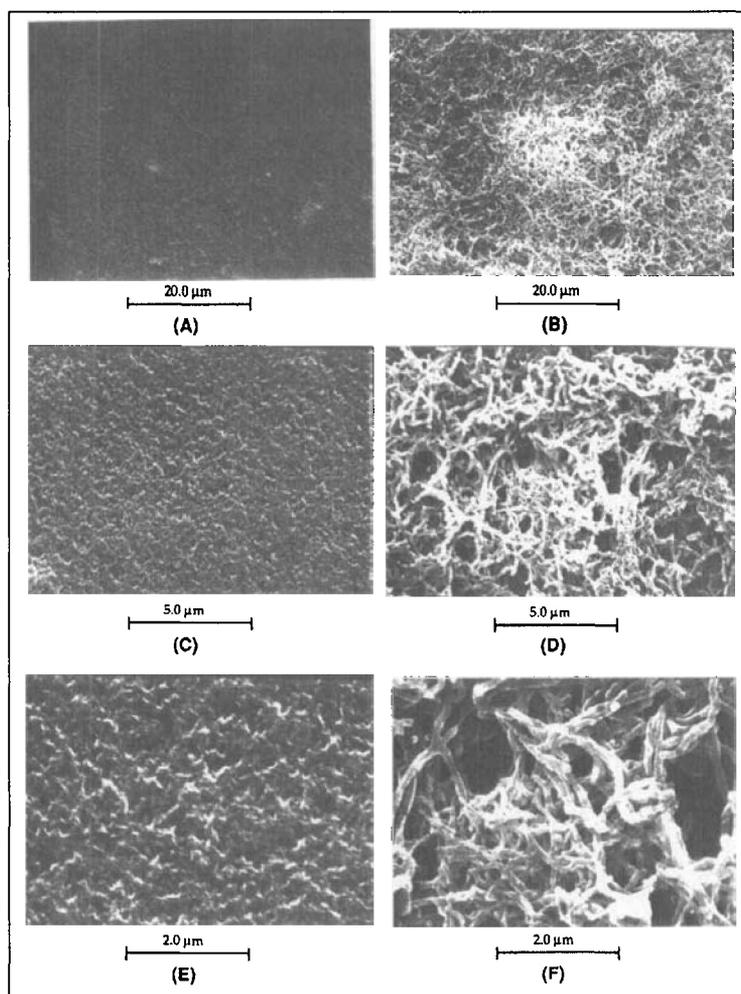


Fig. 4. SEM Micrographs at three magnifications of: (A, C, E) a cast polyaniline film ($\sim 3 \text{ mC/cm}^2$) which has been produced by low-temperature chemical oxidation; and (B, D, F) a PANI sample ($\sim 30 \text{ mC/cm}^2$) obtained by electrochemically cycling a 0.2 M aniline/ 1 M HCl aqueous solution between -180 and $+780 \text{ mV}$. In both cases, the substrate was ITO glass.

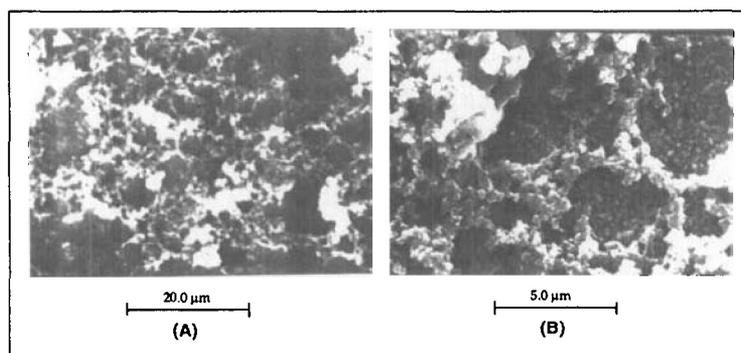


Fig. 5. SEM Micrographs of a cast polymer film made from the low temperature chemical oxidation of an aqueous 0.1 M aniline/ 1 M HCl solution containing $2.5 \times 10^{-4} \text{ M}$ para-phenylene diamine. Substrate was ITO glass.

Using the above method for producing It-PANI, thick polymer films may be cast which, when placed in acidic soln., can easily be detached from the substrate to give free-standing films. Gustafsson and co-workers [8] have used a similar recipe to make PANI-based electrodes which provide hole-injection for LED devices. Klavetter and Cao [9] have shown that following the initial oxidation and dedoping processes, the It-PANI gel may be transferred to a nonaq. CH_2Cl soln. containing a small amount of dodecylbenzylsulfonic acid. This polymer is highly soluble in xylene. Incidentally, neither echem-PANI nor chem-PANI showed any in-

crease in solubility in the presence of surfactants such as dodecylbenzylsulfonic acid, sodium dodecyl sulfonate, or Triton-X100.

It has already been reported that small amounts of para-phenylene diamine (PPDA) added to the aniline monomer solution can greatly affect the resulting polymer either during electrochemical [4] or chemical [6] polymerization. Due to the lower oxidation potential of PPDA, the rate of aniline polymerization is greatly accelerated and the two amino groups offer themselves to chemical cross-linking within the polymer matrix. The final polymer morphology becomes much more

fibrous, with the single fiber diameter being ca. 1/10 as thick as in a normal PANI fiber.

When low-temperature polymerization is attempted in the presence of $5 \times 10^{-4} \text{ M}$ PPDA, the rather flat macrostructure is replaced by a morphology containing islands of fibrous growth (see Fig. 5). Furthermore, there is no noticeable incubation period; instead, green polymer product is observable immediately after the APD solution is first introduced. The polymerization acceleration effect of PPDA is, therefore, clearly maintained at low temperatures.

Conclusions

While conventional chemical preparation of polyaniline offers a means for producing the polymer in bulk, the resulting polymer shows slower charge transfer than that of electrodeposited PANI. Low-temperature chemical preparation of PANI, however, produces nearly the same electrochemical behavior. Furthermore, It-PANI is soluble in NMP and can, therefore, be used to cast free-standing films which would be directly applicable to secondary batteries.

This research was sponsored by the Swiss Federal Office of Education and Science (BBW). At the time of this work, Prof. Shimidzu was a visiting professor at the Institut de chimie-physique, EPFL. The authors appreciate the constant interest and support of Prof. Michael Grätzel.

Received: September 2, 1993

- [1] S. Li, Y. Cao, Z. Xue, *Synth. Met.* **1987**, *20*, 141.
- [2] J.-Y. Bergeron, J.-W. Chevalier, L. H. Dao, *J. Chem. Soc., Chem. Commun.* **1990**, 180.
- [3] A. Thyssen, A. Hochfeld, R. Kessel, A. Meyer, J. W. Schultze, *Synth. Met.* **1989**, *29*, E357.
- [4] C. Mailhé-Randolph, A. J. McEvoy, *Ber. Bunsenges. Phys. Chem.* **1989**, *93*, 905.
- [5] E. J. Oh, Y. Min, J. M. Weisinger, S. K. Manohar, E. M. Scherr, P. J. Priest, A. G. MacDiarmid, A. J. Epstein, *Synth. Met.* **1993**, *55*, 977.
- [6] J. C. Michaelson, A. J. McEvoy, N. Kuramoto, *J. Electroanal. Chem.* **1990**, *287*, 191.
- [7] J. Desilvestro, W. Scheifele, *J. Mater. Chem.* **1993**, *3*, 263.
- [8] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Heeger, *Nature* **1992**, *357*, 477.
- [9] F. Klavetter, Y. Cao, *Synth. Met.* **1993**, *55*, 989.