

Synthesis of Polyaniline/Polytoluidine Block Copolymer via the Pernigraniline Oxidation State

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Abstract: Polyaniline was electrochemically synthesized in the emeraldine oxidation state and then converted to the pernigraniline oxidation state by applying an electric potential under optimized conditions. The stability/reactivity of polyaniline in the pernigraniline oxidation state was evaluated in various aqueous media. The products of the reduction of the pernigraniline oxidation state by *o*-toluidine were analyzed by gel permeation chromatography, ultraviolet–visible and infrared spectroscopies, and cyclic voltammetry. The results are consistent with the synthesis of a diblock copolymer of polyaniline/poly(*o*-toluidine) and also of some poly(*o*-toluidine) homopolymer in the emeraldine oxidation state as a side product.

Key words: polyaniline, pernigraniline oxidation state, copolymer, synthesis, electrochemistry.

1 INTRODUCTION

Polyanilines and their derivatives have been widely studied in the conducting polymer field owing to their promising physical properties and ease of doping in protonic acids. They are also soluble and can be prepared as free-standing films and fibers.^{1,2} The technological potential of conducting polymers, in general, can be enhanced if procedures are developed for preparing these materials in the versatile forms of composites, blends and copolymers.^{3–9} Attempts at randomly reacting aniline with other monomers for the formation of

copolymers have already been reported in the literature.^{10–15} However, in most cases no procedure is employed for separating the copolymer from the primary homopolymer. Furthermore, no evidence is usually presented to show that block copolymers were actually produced, and neither is the nature of the copolymers presumably formed clearly discussed.

It is shown, in this paper, that diblock copolymers may be synthesized from aniline and *o*-toluidine, by exploiting the high reactivity of the pernigraniline oxidation state.^{16–19} Pernigraniline is defined as the fully oxidized state of polyaniline that contains only imine structural units in the polymer backbone.^{20,21} The idea behind the copolymerization of aniline and *o*-toluidine arose from the observation that pernigraniline is an intermediate product in the conventional chemical synthesis of polyaniline,²² which can be reduced to the emeraldine oxidation state when excess monomer is present.^{23,24} As was previously proposed,^{15,23,24} pernigraniline may also be a sufficiently strong oxidizing

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agent to promote polymerization of aniline and therefore also the copolymerization of aniline with its derivatives.

2 EXPERIMENTAL

2.1 Electrochemical synthesis of polyaniline

Polyaniline (PAni) films were electropolymerized for 2 min at a constant applied potential of 0.75 V (using saturated calomel electrode, SCE), in a 1.0 M HCl solution containing 0.5 M freshly distilled aniline ($C_6H_5NH_2$). The electrochemical cell possessed a three-electrode configuration: a platinum (Pt) working electrode, a SCE reference electrode and a Pt counter electrode. Monitoring of the open circuit potential of the deposited PAni started immediately after the synthesis was terminated and continued until a constant value of ca. 0.43 V was observed. This potential is characteristic of the emeraldine oxidation state,²³ defined as the oxidation state in which the ratio of oxidized (imine structures) to reduced (amine) repeating units of the polymer backbone is equal to 0.5.²⁰ In a previous work²⁵ it was shown that polymers with weight-average molecular weights (\bar{M}_w) of 20 500, 26 500 and 40 800 g/mol were obtained at polymerization temperatures of 0, 25 and 44°C, respectively. In the experiments described in this paper, the polymer with the smallest \bar{M}_w (20 500) was used because it has, in principle, a greater probability of chain growth. Also, under these conditions the reproducibility was very satisfactory as deviations in \bar{M}_w between polymers obtained from different experiments were always below 5%.

2.2 Conversion to the pernigraniline state

The polyaniline (PAni) deposited films were deprotonated for 2 h in 0.1 M ammonium hydroxide (NH_4OH) to the emeraldine base form and then carefully and repeatedly washed with ether and methylene chloride, respectively, until a clear solution was observed. Although PAni is known to be insoluble in this solvent, this procedure was used to remove any soluble fraction of low molecular weight polyaniline ($\bar{M}_w < 2000$ g/mol). The PAni on the Pt electrode was converted to the pernigraniline state (changing from greenish to bluish) by applying an electric potential of 0.8 V for 5 s in an aqueous 1.0 M HCl solution at 0°C. This short time was sufficient for the conversion, as observed by the current measured for this system that presented a sharp peak and remained constant after 2 s. If this voltage is applied for periods longer than 5 s, charges apparently begin to be stored in the polymer and the open circuit potential values become greater than 0.8 V (characteristic of the pernigraniline state^{23,24}). The polymer thus obtained was isolated by a procedure similar to that used in the

chemical synthesis,^{21,24} i.e. deprotonation with 0.1 M NaOH (0°C) followed by repeated washing in doubly distilled water (0°C), acetonitrile and ether, respectively.

2.3 Pernigraniline reactivity

In order to evaluate its stability/reactivity, the polyaniline in the pernigraniline state, isolated as described above, was immersed for 16 h in various aqueous media: 1.0 M HCl/25°C; 1.0 M HCl/0°C; 1.0 M HCl/0°C + 0.5 M aniline; and 1.0 M HCl/0°C + 0.5 M *o*-toluidine ($CH_3C_6H_4NH_2$). The open circuit potential decay of the deposited pernigraniline film was monitored. The resulting polymer was deprotonated as already described, and then extensively washed using several baths of ether and methylene chloride, respectively. The soluble and insoluble polymer fractions obtained were then dried for further analysis.

2.4 Analysis

The molecular weights were determined by gel permeation chromatography (GPC) using a Waters instrument and polystyrene standards with molecular weights in the range 3250–2 950 000 g/mol. A solution of 0.5% LiCl in NMP was used as the solvent for both the GPC calibration and molecular weight measurements. Ultraviolet–visible (UV–Vis) spectra of the polymers in solution were obtained with a Perkin–Elmer Lambda9 spectrometer. The infrared (FTIR) spectra of the samples in the form of a KBr pellet were obtained in the transmission mode using a Perkin–Elmer model 1760 spectrometer. The electrochemical studies were performed using a PAR model 173 potentiostat in conjunction with a PAR model 175 Universal Programmer. The cyclic voltammograms in blank solution (in 1.0 M HCl) were obtained after preconditioning the PAni deposited on the Pt electrode for 10 cycles between –0.1 V and 0.35 V versus SCE.

3 RESULTS AND DISCUSSION

In this section the aim is to show that the highly reactive pernigraniline state can be obtained by applying an electric potential to the emeraldine film and that, owing to the strong oxidizing properties of pernigraniline, it can be used for copolymerizing *o*-aniline with *o*-toluidine. Open circuit potential (V_{oc}) measurements show that stable pernigraniline films can be obtained in an aqueous solution at low temperature. The V_{oc} potential of pernigraniline films remains reasonably constant (at the characteristic value of pernigraniline) for long periods of time in a 1.0 M HCl solution at 0°C (Fig. 1(a)). At room temperature, on the other hand, pernigraniline undergoes a reduction reaction in a 1.0 M HCl solution. The V_{oc} potential falls from 0.8 V to 0.5 V

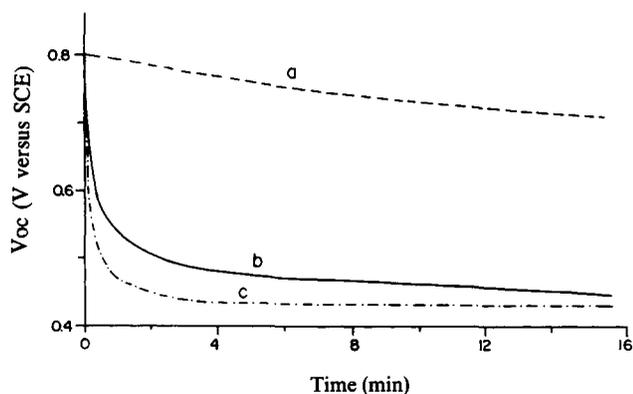


Fig. 1. Open circuit potential (V_{oc}) versus time for the reaction of polyaniline in the pernigraniline oxidation state with the following solutions: (a) 1.0 M HCl/0°C; (b) 1.0 M HCl/0°C + 0.5 M *o*-toluidine; (c) 1.0 M HCl/25°C.

in about 20 s and remains constant after *c.* 5 min at around 0.43 V (Fig. 1(c)). This indicates that a ring chlorination reaction might have occurred, resulting in a polymer in the emeraldine oxidation state, in a similar way to that reported elsewhere.²⁶

When pernigraniline films are placed in a 1.0 M HCl solution in the presence of *o*-aniline or *o*-toluidine, they also undergo a reduction reaction even at low temperatures. This is illustrated in Fig. 1(b), where the open circuit potential, V_{oc} , of the polymer film in the presence of *o*-toluidine is seen to decrease to the potential char-

acteristic of the emeraldine oxidation state, despite the low value of the temperature (0°C). The occurrence of such a reaction corroborates earlier work²³ in which pernigraniline was formed during chemical synthesis and then reduced to the emeraldine salt form in the presence of excess monomer.

There are, in principle, two possibilities for the product(s) formed from the reaction (see Fig. 2) between pernigraniline and *o*-toluidine under the conditions described above: (i) homopolymerization of *o*-toluidine and (ii) copolymerization. Combinations of these two cases are also possible.

The mechanisms inherent in these reactions are essentially the same as those proposed by Wei *et al.*¹⁰ for the polymerization of aniline. It is believed that copolymerization also occurs via an electrophilic attack of toluidine monomers by pernigraniline species in the form of diimines or nitrenium ions, the latter being produced by deprotonation. The monomers are thus added to the polymer chain ends, leading to a linear polymer. This is supported by experimental evidence,^{2,10} which indicates the predominance of *para*-coupling reactions of aniline monomers with the growing polymer chain ends. Consequently, branching or grafting reactions are negligible, probably due to steric hindrance, and not considered in the mechanisms reported in the literature.^{2,10}

The possibilities presented in Fig. 2 have been checked by investigating the nature of the products formed after the reduction reaction (repeated three times) of pernigraniline by GPC, UV-Vis, and FTIR

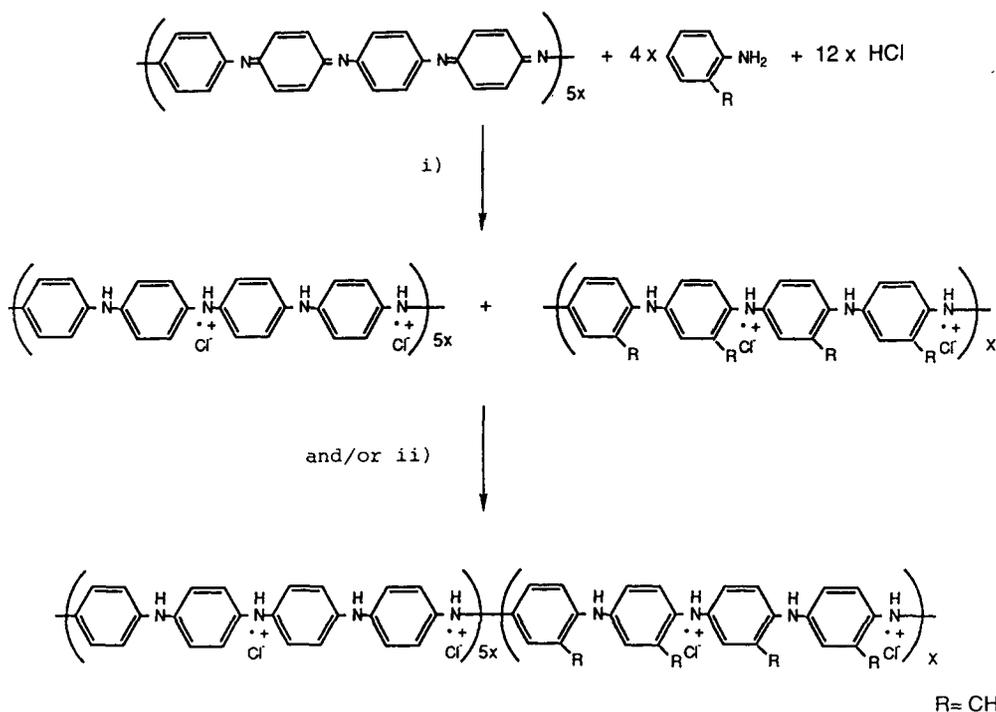


Fig. 2. Possible products formed from the reaction of polyaniline in the pernigraniline oxidation state and *o*-toluidine monomers in aqueous 1.0 M HCl at 0°C.

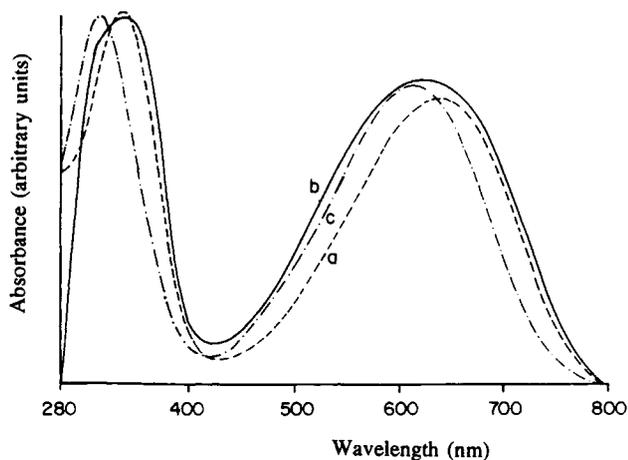


Fig. 3. UV-Vis absorption spectra in NMP solution of (a) PANi; (b) PANi/poly(*o*-toluidine); (c) poly(*o*-toluidine).

spectroscopies and cyclic voltammetry. It should be pointed out that, in contrast with previous work,¹⁵ in the study presented here the polymer in the pernigraniline state was actually isolated.

The first possibility mentioned above cannot be the only process to occur, since a fraction of a methylene chloride-soluble material reappeared after the reduction of pernigraniline. As the PANi film had been previously washed with methylene chloride, any soluble fraction was eliminated prior to the experiments with *o*-toluidine. The UV-Vis spectrum of the soluble fraction mentioned shows a maximum absorption (λ_{\max}) peak at 602 nm, which is similar to the value obtained for poly(*o*-toluidine) polymers in the emeraldine oxidation state (see Fig. 3). GPC analysis (Table 1) confirmed that a polymer (rather than an oligomer) of \bar{M}_w 11 800 g/mol was formed.

The remaining insoluble fraction could then be a blend of PANi and poly(*o*-toluidine), pure PANi or a copolymer. A blend would be formed only if the washing in methylene chloride was inefficient, thus allowing unbound homopolymer to be entangled with the insoluble material. The formation of such a blend is unlikely, as the procedure used here involves a suitable interfacial reaction (between Pt-deposited PANi and the monomer in solution) which minimizes the physical anchoring of any soluble polymer.

TABLE 1. Molecular weights (g/mol) of the polyanilines and derivatives prepared

Polymer type	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
PAni	20 500	12 600	1.55
Soluble fraction	11 800	8 300	1.42
PAni/PoTol ^a	25 100	16 100	1.56
PAni/PAni	29 800	17 200	1.73

^a PAni = polyaniline; PoTol = poly(*o*-toluidine).

TABLE 2. Half-wave potential ($E_{1/2}$) data obtained from cyclic voltammetry and maximum absorption peak of the lower energy UV-Vis transition

Polymer type	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	λ_{\max} (nm/eV)
PAni	0.12	0.75	634 (1.96)
PoTol	0.19	0.60	610 (2.03)
PAni/PoTol	0.16	0.72	623 (1.99)
PAni/PAni	0.13	0.76	636 (1.95)

The presence of poly(*o*-toluidine) in the insoluble fraction rules out the possibility of having only pure PANi, as demonstrated by the UV-Vis (in NMP) and FTIR spectroscopies and cyclic voltammetry analyses. This insoluble fraction must therefore be a diblock copolymer of polyaniline/poly(*o*-toluidine), which is confirmed by the presence of bound poly(*o*-toluidine) according to the characterization described below. FTIR results indicate the presence of *o*-toluidine by the increase in the peaks at 818, 2865 and 2936 cm^{-1} , assigned to the *o*-methyl group.^{24,27} Figure 3 shows that the maximum in the UV-Vis spectrum was shifted to a higher energy ($\lambda_{\max} = 623 \text{ nm}$), as would be expected²⁰ for the copolymerization of polyaniline with poly(*o*-toluidine) (PANi/PoTol). Cyclic voltammetry results presented in Table 2 show that the sample PANi/PoTol presents $E_{1/2}$ values between those obtained for the pure homopolymers, consistent with previous work.¹⁰ The formation of a diblock copolymer is also corroborated by GPC. A typical gel permeation chromatogram of a sample of the fraction insoluble in methylene chloride is presented in Fig. 4. The observed monomodal pattern for the molecular weight distribution is consistent with a copolymer rather than with a mixture of two homopolymers. Also, the GPC results presented in Table 1 indicate that an increase in molecular weight (c. 25%) occurred, showing that the increase

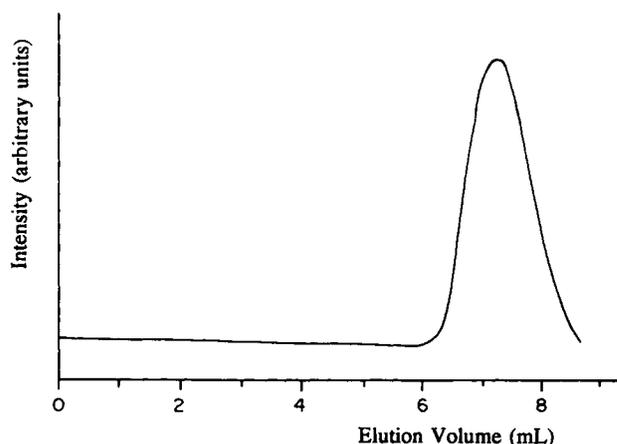


Fig. 4. Gel permeation chromatogram of polyaniline/polytoluidine block copolymer; polystyrene standards, 0.5% LiCl/NMP.

in the polymer chain size must have been promoted by copolymerization with *o*-toluidine.

The procedure presented here may also be employed as a method to increase the molecular weight of the electrochemically synthesized polymer. If aniline is used instead of *o*-toluidine, the M_w of the parent polyaniline presents an increase of ca. 33%, as shown in Table 1 (PAni/PAni). The UV-Vis and cyclic voltammetry results (Table 2) obtained for PAni/PAni are identical, within experimental error, to those of the as-synthesized parent PAni.

4 CONCLUSIONS

Polyaniline in the pernigraniline oxidation state can be conveniently synthesized electrochemically from aniline, and the rate of its decomposition in aqueous HCl can be sufficiently reduced at 0°C to permit a study of its reaction with aniline and with *o*-toluidine.

The pernigraniline oxidation state is a sufficiently strong oxidation agent to oxidatively polymerize aniline and also *o*-toluidine to the emeraldine oxidation state, while it is itself reduced to the emeraldine oxidation state. When *o*-toluidine is used, significant quantities of a block copolymer of polyaniline and poly(*o*-toluidine) are formed.

This new route may also be of interest for the fabrication of Langmuir-Blodgett films from conducting polymers, as copolymers may be produced which possess chain blocks of different hydrophobicity and size.

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