Monitoring the chemical polymerization of aniline by open-circuit-potential measurements

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We present the first open-circuit-potential (OCP) study of the chemical polymerization of aniline in the presence of various aromatic additives and demonstrate the feasibility of monitoring the polymerization rate by the OCP technique. With $(NH_4)_2S_2O_8$ as oxidant, there are three stages in the OCP–reaction time plots. The time ($t_1 + t_2$) needed for completion of the first two stages is inversely related to the rate of polymerization. The presence of *p*-aminodiphenylamine, *N,N'*-diphenylhydrazine, benzidine and *p*-phenylenediamine reduces the $t_1 + t_2$ value and therefore increases the rate of polymerization. In contrast, the presence of *p*-hydroquinone increases the $t_1 + t_2$ value and thus reduces the polymerization rate. These preliminary results are consistent with the kinetics and mechanism of the electrochemical polymerization of aniline.

(Keywords: conducting polymers; polyaniline: open-circuit potentials)

Polyaniline, an important electrically conducting polymer, can be prepared by either electrochemical or chemical oxidation of aniline monomer (for reviews, see refs 1 and 2). The electrochemical process can be monitored easily but it usually offers low yields of the polymer. On the other hand, the chemical process affords higher yields and is suitable for industrial production of polyaniline, but the rate of polymerization is difficult to monitor. Based mainly on kinetic studies of the electrochemical polymerization of aniline, we proposed a new mechanism for aniline polymerization[3–8]. In this mechanism, the growth of polymer chains is achieved mainly via electrophilic aromatic substitution on neutral monomers by the oxidized growing polymer chain ends. The polymerization process is neither a classical step nor a classical chain polymerization, but something in between, which we tentatively named 'the non-classical chain polymerization'; it has been found to be applicable to the oxidative polymerization of other aromatic monomers such as thiophene and pyrrole as well[9–13]. Guided by this mechanism, we have invented a new method for the synthesis of polyaniline, in which a small amount of aromatic additive, such as *p*-aminodiphenylamine, *N,N'*-diphenylhydrazine, benzidine, etc., is introduced to the aniline polymerization system[3–8]. In the presence of these additives, the rate of polymerization is greatly increased and lower applied potentials can be used to minimize undesirable side reactions. In contrast to the electrochemical polymerization, the kinetics of chemical polymerization of aniline have been investigated to a much lesser extent. There are a few reports on the kinetics of chemical polymerization of aniline using techniques such as linear sweeping voltammetry, precipitation and solution calorimetry[3,14,15]. A convenient, *in situ* method is needed for monitoring the chemical polymerization process, particularly the fast reactions in the presence of the additives and the initial stage of the polymerization.

The open-circuit-potential (OCP) measurement has been an important technique for investigating various electrochemical processes, such as corrosion of metals[16,17], photoelectronic effects in semiconducting materials[18] and secondary batteries[19]. The OCP usually reflects the complex discharging phenomena that are associated with the potential relaxation within the electrical double layer of an electrode[20] and/or with the pseudo-capacitor effect of chemisorbed electroactive intermediates in the electrode process[21]. Experimental set-ups are usually designed to attain an equilibrium situation, where all anodic and cathodic reactions proceed at an equal finite rate. Consequently, the net current flow is zero and the voltage corresponding to this zero current is defined as the open-circuit potential. Recently, the OCP technique has been employed in the synthesis of electroactive polymers, such as polypyrrole[22,23] and polyaniline[24,25]. The results obtained by Manohar *et al.*[25] are particularly interesting: they found that the fully oxidized pernigraniline is the intermediate of the chemical polymerization of aniline in association with the OCP measurements.

In this paper, we present the first OCP study of the chemical polymerization of aniline in the presence of aromatic additives under various reaction conditions, and demonstrate that the rate of polymerization can be readily monitored with the OCP technique. In our experiments, the OCP of the chemical polymerization of aniline was measured as a function of time on a single-compartment two-electrode cell:

Pt/analyte solution//reference electrode (SCE)

The reference electrode was a saturated calomel electrode (SCE) and a platinum wire was used as the working electrode. The potential was recorded with an EG&G PAR 273 potentiostat/galvanostat. The analyte solution

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was the system for the chemical polymerization of aniline, which consisted of doubly distilled aniline, 0–2 mol% (relative to aniline concentration) of *p*-aminodiphenylamine, *p*-phenylenediamine, *N,N'*-diphenylhydrazine, *p*-hydroquinone (all from Aldrich) or benzidine (Sigma), and an oxidant: $(NH_4)_2S_2O_8$, $Na_2Cr_2O_7$ or KIO_3 (all from EM Science) in aqueous 1 M HCl. The amount of aniline monomer was in excess to the oxidant. Typically, in each polymerization, 20 ml of 0.1 M aniline and an appropriate amount of the additive in 1 M HCl aqueous solution was stirred in a 100 ml beaker, which was placed in a water-bath at room temperature. After the value of OCP became constant at about 0.44 V vs. SCE under stirring, 20 ml of 0.1 M $(NH_4)_2S_2O_8$ in 1 M HCl was added to the aniline solution in one portion. With stirring, continuous measurement of OCP and temperature was performed every 15 s throughout the course of polymerization. The potential readings were generally reproducible to ±0.05 V from parallel experiments.

A typical plot of OCP against reaction time is shown in *Figure 1* along with the temperature change during the chemical polymerization of aniline using ammonium persulfate as oxidant. There are three distinct stages in this OCP–time profile, similar to those observed by Manohar *et al.*[25]. The durations of these stages are labelled as t_1, t_2 and t_3, respectively. The OCP for ammonium persulfate alone in 1 M HCl was found to be 1.03 V vs. SCE and was essentially independent of time and concentration. On the other hand, the OCP of pure aniline in 1 M HCl solution was about 0.4 V vs. SCE, which was an equilibrium potential reading for the protonated aniline monomer after a time lapse of 1 h. This value was independent of aniline concentration in the range of 0.1–0.5 M. When the persulfate solution was added to the aniline solution with stirring, an immediate change of OCP was recorded. After the short and unstable region (~15 s), the OCP increased continuously to a plateau at 0.78 V in 4 min (t_1). We postulate that in this stage the persulfate ions may dissociate into radical anions ($SO_4^{\bullet -}$) and anion (SO_4^{2-}) in the presence of the aniline monomer (i.e. M_x, $x=1$) and subsequently form oligomers (M_x, $x>1$), which function as reducing agents. Some of the possible redox reactions are listed below:

$$M_x + S_2O_8^{2-} \rightarrow M_x^{\bullet +} + SO_4^{2-} + SO_4^{\bullet -}$$

$$M_x + SO_4^{\bullet -} \rightarrow M_x^{\bullet +} + SO_4^{2-}$$

$$M_x^{\bullet +} + S_2O_8^{2-}\ (\text{or } SO_4^{\bullet -}) \rightarrow M_x^{2+} + SO_4^{2-} + SO_4^{\bullet -}$$

The oxidized M_x species (or their nitrenium forms) could react with neutral aniline monomers via an electrophilic aromatic substitution mechanism[3] to accomplish a chain-growth step leading to M_{x+1}. Accompanying the OCP change, the colour of the reaction system showed a continuous change. We have monitored the reaction system with u.v.–vis. spectroscopy and confirmed the existence of various oligomeric species during this reaction stage[26].

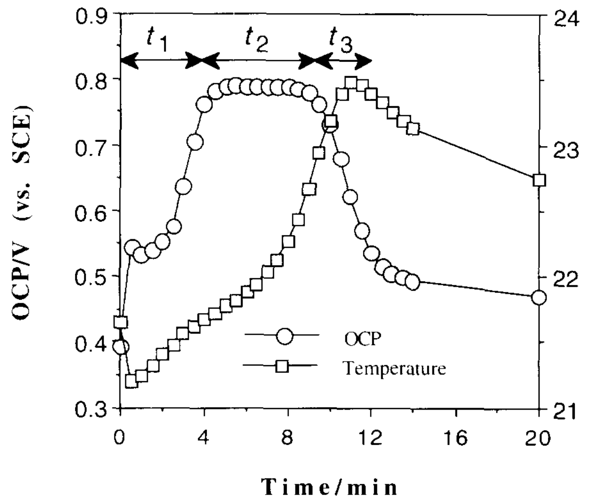

Figure 1 The OCP–time profile of chemical polymerization of aniline with ammonium persulfate as oxidant in aqueous 1 M HCl. The temperature change during the reaction was also measured

As the reaction proceeded, the potential reached a steady plateau of about 0.78 V. Small green/blue particles started to appear in the solution and on the Pt electrode. These particles are the pernigraniline form of polyaniline according to Manohar *et al.*[25]. The polymerization may proceed upon pernigraniline chains to afford polymer chains of higher molecular weights. In the presence of persulfate, these new polymer chains may be oxidized to pernigraniline again. This process is repeated until all the persulfate oxidants are consumed at the end of the plateau region (t_2). The completion of the main chain-growth process is consistent with our observation that the temperature of the system reached a maximum immediately after the time t_2 (*Figure 1*). Furthermore, we have found that either an increase in $[(NH_4)_2S_2O_8]$ or a decrease in [aniline] always results in higher t_1+t_2 values. We conclude that the time elapsed at the end of the plateau (i.e. t_1+t_2) should reflect the rate of persulfate consumption and therefore the rate of the overall aniline polymerization process. In the third stage (t_3), the OCP decays rapidly from around 0.78 V to 0.5 V in about 3 min (*Figure 1*). If more time is allowed, the potential relaxes eventually to around 0.44 V, a value that is close to the OCP of suspended particles or thin film of emeraldine in 1 M HCl. This process is believed to involve further polymerization of aniline with pernigraniline as the oxidant (instead of the persulfate) while the pernigraniline is reduced to the emeraldine form of polyaniline[25]. The polymerization in this stage may not affect the overall rate significantly, judging from our observation that the t_3 value varied little with the reaction conditions in this study.

In the presence of various aromatic additives, including *p*-aminodiphenylamine, *N,N'*-diphenylhydrazine, benzidine, *p*-phenylenediamine and *p*-hydroquinone, in a concentration range of 0.05–2 mol% with respect to the concentration of aniline, the plots of OCP against time for the chemical oxidative polymerization of aniline are very similar to that shown in *Figure 1*. They all exhibit the three-stage potential–time profiles. In all cases, the reaction temperature peaked at the end of the OCP plateau (i.e. the end of t_2). In the presence of these additives (except *p*-hydroquinone), the persulfate was consumed much sooner (i.e. lower t_1+t_2 values) and therefore the rate of polymerization was greater than the system in the absence of additives (*Figure 1*). An increase in the additive concentration resulted in a decrease in the t_1+t_2 value. As a typical example, the OCP–time plot for the system containing 0.2 mol% of *p*-phenylenediamine is given in *Figure 2*. The t_1+t_2 value for this system is reduced to 6 min, in comparison with 9 min for the aniline

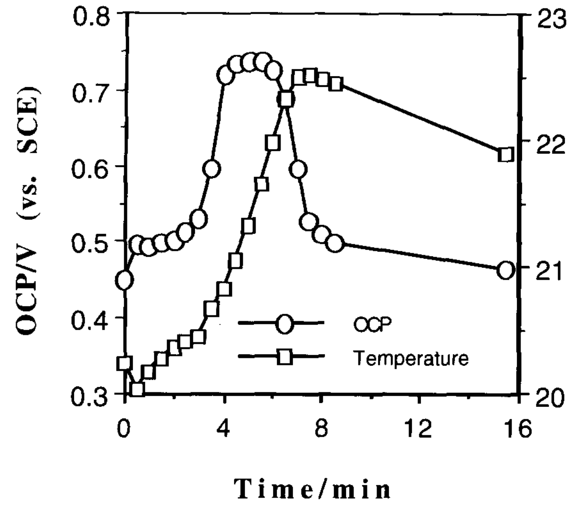

Figure 2 Plot of OCP and temperatures as functions of reaction time for the chemical polymerization of aniline with ammonium persulfate as oxidant in the presence of 0.2 mol% of *p*-phenylenediamine

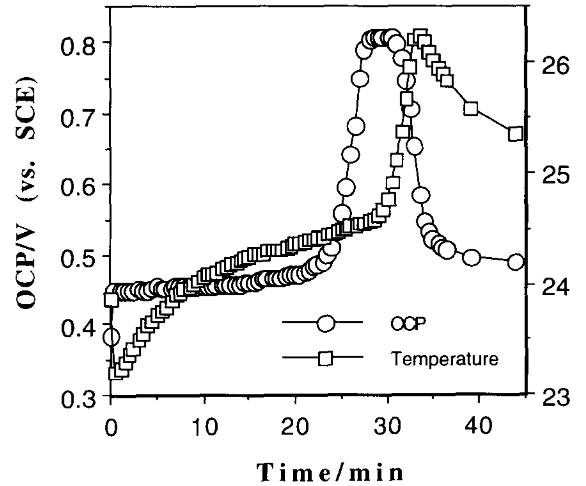

Figure 3 Plot of OCP and temperature as functions of reaction time for the chemical polymerization of ailine with ammonium persulfate as oxidant in the presence of 0.2 mol% of *p*-hydroquinone

polymerization without additive. Thus the presence of such a small amount of additive facilitates the polymerization process by 30%. In the case of *p*-hydroquinone as additive (*Figure 3*), the t_1+t_2 value is 31 min, indicating that *p*-hydroquinone significantly reduces the rate of polymerization. Higher concentrations of *p*-hydroquinone were found to lead to still higher t_1+t_2 values. All these results are in excellent agreement with the kinetic studies of electrochemical polymerization of aniline and with the mechanism proposed for the polymerization[3-8].

In the absence of additives, the slowest step in the polymerization of aniline is the oxidation of aniline monomer to form dimeric species (i.e. *p*-aminodiphenylamine, *N,N'*-diphenylhydrazine and benzidine) because the oxidation potential of aniline is higher than those of the dimers, subsequently formed oligomers and polymer. Upon formation, the dimers are immediately oxidized and then react with an aniline monomer via an electrophilic aromatic substitution followed by further oxidation and deprotonation to afford the trimers. This process is repeated, leading eventually to the formation of polyaniline. The observed rate-enhancement in the presence of *p*-aminodiphenylamine, *N,N'*-diphenylhydrazine, benzidine and *p*-phenylenediamine is attributed to two major factors: (1) all these additives have lower oxidation potentials than aniline, and (2) the oxidized additives can undergo electrophilic substitution reactions with aniline monomer to result in polymer growth, which effectively by-passes the rate-determining step. In contrast, though hydroquinone also has a lower oxidation potential than aniline, the oxidized hydroquinone cannot undergo electrophilic substitution with aniline. Hence, hydroquinone only consumes oxidant and reduces the rate of aniline polymerization. We have also studied the oxidative polymerization systems with other oxidants, including $Na_2Cr_2O_7$ and KIO_3. The OCP–time profiles are quite similar to that with persulfate as oxidant, except that t_1 values are near zero in these systems.

In summary, we have demonstrated the feasibility of monitoring the chemical oxidative polymerization of aniline with or without additives by simple, *in situ* OCP measurements. The time needed for complete consumption of the oxidant (i.e. t_1+t_2) is inversely related to the rate of polymerization. The presence of *p*-aminodiphenylamine, *N,N'*-diphenylhydrazine, benzidine and *p*-phenylenediamine significantly reduces the t_1+t_2 value, and thus increases the rate of polymerization. In contrast, the presence of *p*-hydroquinone drastically increases the t_1+t_2 value and thus reduces the polymerization rate. The results are consistent with kinetic studies of the electrochemical polymerization of aniline and with the mechanism we have proposed for the polymerization. Further investigation is in progress in an effort to develop a better understanding of the complex redox processes that might contribute to the observed OCP values, and to obtain kinetic parameters systematically for the chemical polymerization of aniline.

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