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Polymerization of aniline using mixed oxidizers

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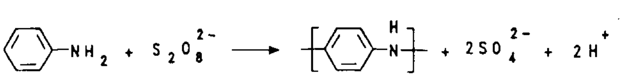
Potentiometric and calorimetric measurements on aniline polymerized by persulfate reveal an induction period, which may be decreased or eliminated by the addition of ceric (Ce^{IV}) ion. The addition of the second oxidizer appears to promote nucleation. The molecular weight and electrical conductivity of the resulting polyaniline were measured. Substantial shortening of the reaction time and improvement of polymer conductivity may be realized with the addition of 0.1–1% Ce^{IV} co-oxidizer in the standard polymerization technique using persulfate. Ultraviolet/visible spectroscopy of polymer solutions suggests that significant oxidative degradation is responsible for poor conductivity of polymer made using large amounts of Ce^{IV}.

(Keywords: polyaniline; kinetics; conducting polymer)

INTRODUCTION

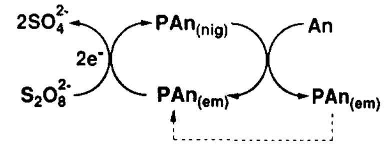
The polyanilines form a versatile collection of conjugated, conductive polymers that are easily synthesized by aqueous solution polymerization to yield high-molecular-weight materials[1]. Polyaniline in the neutral emeraldine form is soluble in a variety of solvents[2], and the electrically conductive emeraldine salts are soluble when the counterion is derived from a lipophilic organic acid[3]. The processibility of polyaniline has catalysed research into novel blends and composites[4] with useful electrical[5] and optical properties[6].

Polyaniline (PAn) is widely prepared by the oxidation of aniline (An) by persulfate in aqueous acid[7]:



In this reaction, 2 mol of electrons are required to couple each mol of monomer and an additional 0.5 mol are consumed to yield the final polymer in the emeraldine form. Ths use of lower temperatures leads to polyaniline with higher molecular weight and improved mechanical and electrical properties[8].

Detailed studies on the mechanism of chemical[9–11] (electrochemical[12–14]) polymerization of aniline have revealed that oxidation of aniline by persulfate (a bare electrode) is much slower than oxidation by polyaniline in a high oxidation state. In the major propagation step, polyaniline in the pernigraniline oxidation state acts as an intermediate for the oxidation of aniline, as illustrated by the scheme below[9,11,13]:



Pernigraniline may be isolated during the course of the reaction[15]. It is proposed that the reactive polymer species is a nitrenium ion[10,16], which performs an electrophilic attack on aniline monomer. As discussed by Wei *et al.*[10,17], the selective oxidation of aniline by polymer, and subsequent incorporation into the growing polymer chain, represents an unusual class of addition polymerization. Since the oxidation product is polyaniline itself, one expects, and observes, autoacceleration in the reaction kinetics (see the dotted line in the scheme above). The rate behaviour has been described[11,13] by equations of the form:

$$-\mathrm{d}[\mathrm{An}]/\mathrm{d}t = k_1[\mathrm{An}] + k_2[\mathrm{An}][\mathrm{PAn}]$$

where k_1 and k_2 are rate constants for the formation of PAn in the absence and presence, respectively, of PAn; k_2 was found to be two to four orders of magnitude larger than k_1 for heterogeneous solution polymerization and electrochemical polymerization[11,13].

Because the presence of polymer is required for a significant rate of polymerization, an induction period is typically observed for solution polymerization of aniline by persulfate. During the course of our studies into the kinetics of this polymerization process[18], we found a consistent induction period in the reaction, which became more pronounced at lower temperatures. Presumably, during the induction period a small 'seed'

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population of polymer particles grows. Tzou and Gregory[11] showed that the addition of polyaniline to a reaction mixture essentially eliminated the induction period.

We wished to circumvent the induction period through the use of an auxiliary oxidizing agent that would produce a small amount of polyaniline rapidly. The effect would be to increase the rate constant k_1 to a high value, removing it as rate-limiting at the beginning of the polymerization. We decided to employ various amounts of cerium(IV) ion as an auxiliary oxidizing agent, since polymerization with this oxidant is extremely rapid. The techniques we used to follow the polymerization included potentiometry and temperature measurements, both introduced for the aniline/persulfate system by MacDiarmid and coworkers[15,19]. Raman spectroscopy may also be employed[18].

Under optimum conditions, one would be able to enhance the kinetics of polymerization without compromising the physical properties of the final polymer. We thus characterized the materials obtained using viscosity and u.v.-vis. measurements, and determined conductivities of cast films.

EXPERIMENTAL

The method for preparing polyaniline in the protonated emeraldine form was adapted from the procedure described by MacDiarmid *et al.*[7]. The reaction medium was 1.0 M aqueous perchloric acid and the concentrations of aniline and ammonium persulfate in the reaction mixture were 0.44 M and 0.10 M, respectively. Mixing occurred in a beaker immersed in a −4.5°C ice bath and the total solution volume was 25 ml. The persulfate was substituted by increasing amounts of cerium(IV) (as $(NH_4)_2Ce(NO_3)_6$), with two ceriums replacing one persulfate (since the former is a one-electron oxidant and the latter consumes two electrons). The percentage of cerium reported represents mole percentage of persulfate substituted. Thus, 100% Ce^{IV} yields a Ce^{IV} concentration of 0.20 M. The total reaction time was 60 min, after which the product was filtered and washed with 600 ml acid, 600 ml water, followed by 750 ml of 0.10 M ammonium hydroxide. The polymer was resuspended in 500 ml of 0.10 M NH_4OH and the pH was adjusted to ca. 8 by adding 1.0 M NH_4OH. After 3 to 5 h the polymer was washed with 750 ml 0.1 M NH_4OH. The undoped polyaniline (emeraldine base) paste was freeze-dried, then further dried in a vacuum oven at 60°C for 12 h. (*Caution*: doped polyaniline containing perchlorate as counterion should not be dried.)

Dried emeraldine base (EB) was redissolved in 1-methyl-2-pyrrolidinone (NMP) to make 1% w/w solutions. Insoluble material was removed by passing the solution through 1.5 μm glass microfibre filter. The amount of insoluble material was typically very small, in the range of 1–4% of the total polymer. Films of EB were cast onto silanized glass at 60°C under vacuum. The free-standing films (ca. 50 μm thick) were cut into strips and immersed into hydrochloric acid for 5 h for protonic acid doping. Four-point conductivity measurements were then performed on protonated polymer. Viscosities of 0.14% w/w solutions of EB in NMP were determined using a Cannon–Feuske viscometer (150 × 127) thermostated to 24°C. U.v.-vis. absorption spectra of 0.0016% w/w EB in NMP were recorded on a Cary 4 spectrometer over the range 260 to 860 nm. Molecular weight was determined using a Perkin Elmer 250 solvent delivery module fitted with a Styragel (divinylbenzene-crosslinked polystyrene) column, and a PE 290 u.v.-vis. detector. The mobile phase was dimethylformamide and the flow rate was 1.0 ml min^{-1}. Sample concentrations were 0.1% w/w and polystyrene standards were used to calibrate the molecular weight.

In situ potentiometry was performed with a Keithley 617 electrometer connected to a platinum wire sealed in glass and a calomel reference electrode. Temperature was recorded using a thermocouple in a thin glass sheath and a digital thermometer reading to 0.1°C.

RESULTS AND DISCUSSION

Polymerization

Both *in situ* analytical techniques revealed significant acceleration in polymerization kinetics on addition of co-oxidant, even for very small concentrations of Ce^{IV} (see *Figures 1* and *2*). Substitution of only 0.01 mol% persulfate by Ce^{IV} (0.3 mg Ce^{IV}, giving a concentration of 2×10^{-5} M) resulted in a decrease of the time required for complete reaction by almost one-half. Further additions of Ce^{IV} resulted in faster reactions, although the effect is not as dramatic (for example, 1.0% substitution decreased the overall reaction time to one-third that for pure persulfate).

While the potentiometry gave a good measure of the end of the reaction, indicated by a sharp drop in the potential, the beginning of the reaction is hard to discern. A clearer picture of the reaction kinetics is provided by the (crude) calorimetric measurements. These results, summarized in *Table 1*, indicate an induction period in the polymerization of aniline by persulfate. This is also seen in Raman scattering measurements[18]. High concentrations of Ce^{IV} lead to rapid reactions, with pure Ce^{IV} effecting essentially instantaneous polymerixation (the heat of polymerization for this quasi-adiabatic process is approximately 80 kJ mol^{-1}). The evidence points towards nucleation, resulting in a

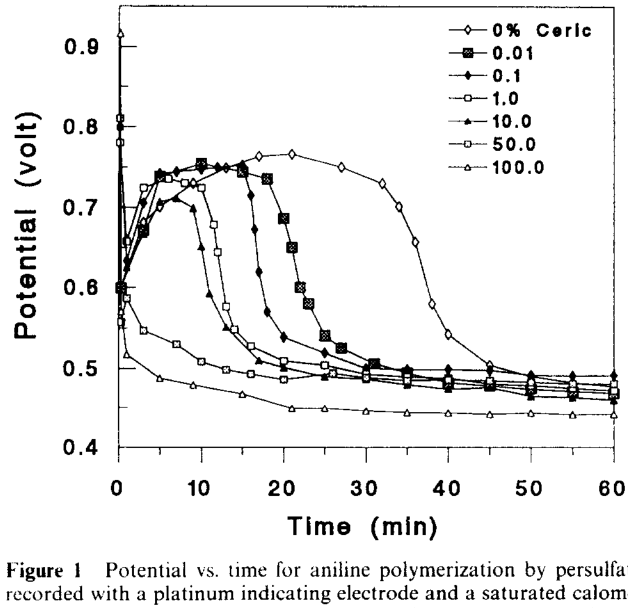


Figure 1 Potential vs. time for aniline polymerization by persulfate recorded with a platinum indicating electrode and a saturated calomel reference. Various mole percentages of persulfate have been substituted by Ce^{IV}

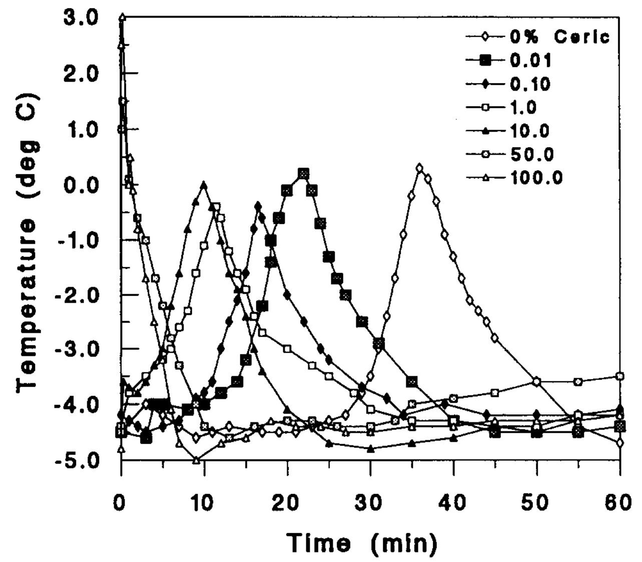


Figure 2 Temperature vs. time for aniline polymerization. Conditions as in *Figure 1*

Table 1 Yield, and times for maximum temperature and fall in potential for aniline polymerized with various mole percentages of cerium substituting for persulfate

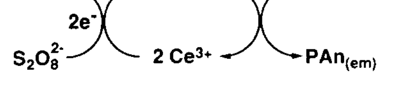
Ceric ion (mol%)	Yield (%)	$T_{\text{temp max}}$ (min)	$T_{E\frac{1}{2}\text{fall}}$ (min)
0	87	36	37
0.01	91	22	21.5
0.1	80	16	16
1.0	80	12	12.5
10.0	89	10	10
50.0	50	0.1	0.1
100	52	–[a]	0.1

[a] Instant

significant induction period, as a rate-limiting process in polymerization of aniline by persulfate. The Ce^{IV} presumably produces an initial population of oligomeric polyaniline molecules. Further oxidation of aniline by persulfate occurs more rapidly at these nucleation sites.

The effect of a rapid oxidant to produce an initial population of polyaniline particles is in accord with published mechanisms[9–14] describing the polymerization of aniline by persulfate (see above). It should be noted that the presence of surface is also sufficient to accelerate the polymerization of aniline under the conditions described, leading to the well known observation that polyaniline rapidly coats articles immersed in the polymerizing solution[15,20]. A quantitative evaluation of the coating process is provided by *in situ* quartz crystal microbalance measurements of film thickness[18].

Both 'seeding' and providing extended surface area emphasize the kinetic nature of the induction process. Persulfate is a very strong oxidizing agent[21] ($E^{\ominus} = 2.01$ V), stronger than Ce^{IV} ($E^{\ominus} = 1.6$ V), but the electron-transfer kinetics of Ce^{IV} are much faster. A possible acceleration mechanism could be built upon Ce^{IV} acting as an intermediate:



In this case Ce^{IV} is truly catalytic. However, at least two pieces of evidence point away from this mechanism. First, for a catalytic reaction (outside of the diffusion-controlled domain) one would expect the reaction kinetics to have a first-order dependence on the Ce^{IV} concentration. While Ce^{IV} significantly decreases the reaction time, the effect is not proportional to concentration. For example, the polymerization time decreases from 22 min to 10 min for a factor of 1000 increase in Ce^{IV} concentration. Secondly, once the reaction has started, the temperature vs. time plots are similar in slopes and shapes for all but the highest concentration of Ce^{IV}, indicating the induction period to be the major variable. The highest concentrations of Ce^{IV} (50% and 100%) are sufficient to oxidize all the aniline present, which would not allow the slower oxidation by persulfate (second term in the equation above) to manifest itself.

Material properties

Acceleration of the overall polymerization time would clearly be advantageous in the large-scale production of polyaniline. An important question would be whether the strategy detailed here leads to materials with different physical properties. We determined molecular weight via viscosity measurements and gel permeation chromatography. Conductivity measurements on cast films were intended to reveal correlations between synthesis conditions and electrical properties. The results are discussed with reference to the work of Cao *et al.*[8], who performed extensive studies on the influence of polymerization conditions on the properties of polyaniline.

Viscosity measurements are useful for indicating rough trends in molecular weight. Our viscometry, summarized in *Figure 3*, suggested a complex dependence of molecular weight on co-oxidant concentration, with a maximum at 1–10% Ce^{IV}. It is known, however, that the molecular-weight distribution in polyaniline is typically bimodal[22–24]. A small fraction of high-molecular-weight polymer could dominate the viscosity. G.p.c. of our

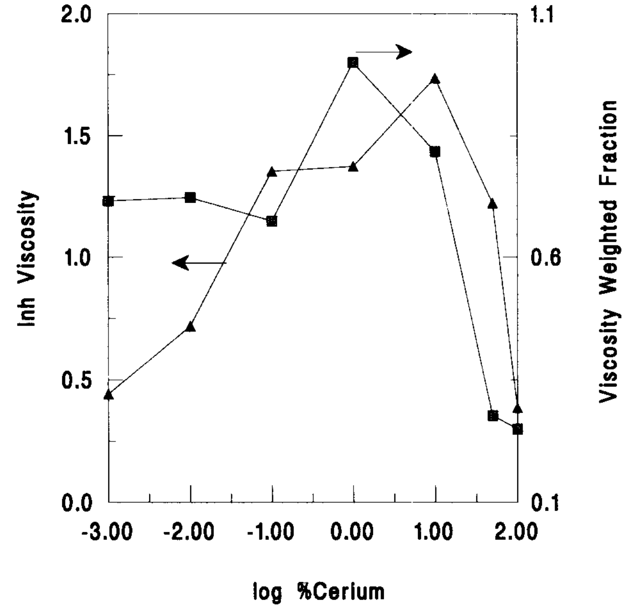


Figure 3 Inherent viscosity of emeraldine base in NMP, and relative viscosity weighted for molecular weight, as a function of percentage of cerium substituting for persulfate

Table 2 Molecular weights, distributions and weight fractions of polyanilines

Ceric ion (mol%)	Low-*MW* fraction			High-*MW* fraction	
	M_w	M_n	M_w/M_n	Wt%	M_w
0	31 800	17 700	1.8	5.7	410 000
0.01	30 400	17 600	1.7	7.4	350 000
0.1	30 400	17 600	1.7	5.7	360 000
1.0	31 200	17 400	1.8	8.5	720 000
1.0	27 700	12 600	2.2	6.7	650 000
5.0	10 600	6 600	1.6	2.2	290 000
100	9 700	5 600	1.7	1.9	250 000

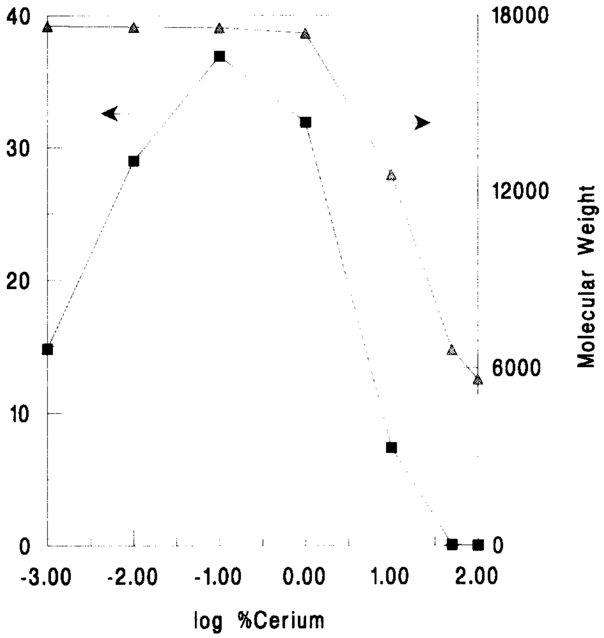


Figure 4 Conductivity of doped films of polyaniline, and molecular weight of the major weight fraction vs. percentage of Ce^{IV} co-oxidant used during synthesis

polymer displayed a bimodal distribution with most of the polymer to be found in the lower-molecular-weight fraction. The results are summarized in *Table 2*, which lists molecular weights and weight fractions. It is apparent that the molecular weight of almost all of the polymer is unaffected by the presence of the co-oxidant up to ca. 10% Ce^{IV}. There does appear to be a maximum in the high-molecular-weight fraction at 1–10% Ce^{IV}, which could be responsible for the maximum observed in *Figure 3*. The relative viscosity of polymer was weighted for the different fractions according to the following:

$$\text{relative weighting} = W_1(M_{w1})^{0.8} + W_2(M_{w2})^{0.8}$$

where W_1 and W_2 are the weight percentages of the lower and higher fractions, M_{w1} and M_{w2} are their molecular weights and the exponent of 0.8 is chosen to reflect the weight dependence of the viscosity of a stiff polymer[25]. This relative weighting is also depicted in *Figure 3* and serves to explain the appearance of a maximum in the viscometry. It was not possible to relate inherent viscosity measurements to conductivity, and such a correlation is best done only for process control under a limited range of conditions. It should be noted that recent comparisons of polyaniline g.p.c. with other techniques suggest that the high-molecular-weight fraction may be the result of aggregation of smaller chains[26].

Although molecular weight is relatively independent of co-oxidant over a wide range, the conductivity was found to be very sensitive to the synthesis conditions. In particular, at Ce^{IV} concentrations greater than ca. 1% the conductivity drops precipitously, as depicted in *Figure 4* (conductivity values for 50 and 100% Ce^{IV} are 0.05 and $0.005\,\Omega^{-1}\,cm^{-1}$, respectively). Inspection of the molecular-weight data for these higher Ce^{IV} concentrations would not lead one to expect a large decrease in conductivity: the polymers have molecular weights that are one-third of those obtained with lower Ce^{IV} concentrations. The conductivity of polyaniline is known to be roughly proportional to molecular weight up to $MW \sim 100\,000$[27].

It could be argued that the polymer made with higher Ce^{IV} concentrations is in a higher or lower oxidation state, beyond the optimum emeraldine form, and is thus less conducting. It is known that conducting polymers, including polyaniline, possess a doping 'window' for maximum conductivity[28,29]. It is possible to differentiate between oxidation states of polyaniline with absorption spectroscopy. The u.v.-vis. spectra of neutral (base form) polyaniline samples in NMP are depicted in *Figure 5*. Masters *et al.*[30] report a λ_{max} for emeraldine base at around 630 nm, whereas the λ_{max} for pernigraniline is ca. 530 nm. While the λ_{max} of samples made with higher Ce^{IV} concentrations are blue-shifted, the conversion from emeraldine base to pernigraniline has been shown to occur without passing through an intermediate oxidation step[31]. Thus, if pernigraniline were being formed, one would not expect a monotonic shift in λ_{max}, rather the appearance of a new absorption maximum at 530 nm and an isosbestic point at 550 nm[31]. The u.v.-vis. spectroscopic evidence points towards a decrease in the effective conjugation length, probably through the formation of oligomers as supported by the g.p.c. data.

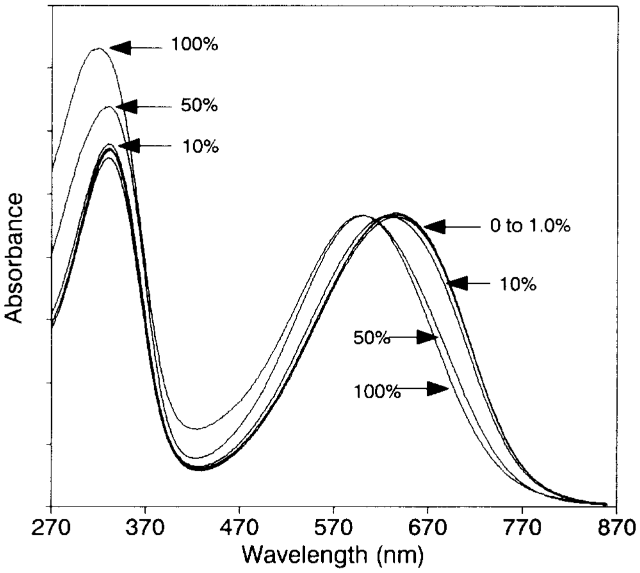


Figure 5 U.v.-vis. absorption spectra in NMP of emeraldine base synthesized with different concentrations of cerium. Spectra have been normalized via the absorption maximum at 570–670 nm

An indication of the degree of oxidation is provided by comparing the infra-red absorption bands at 1500 and 1598 cm^{-1}, which arise from the benzenoid diamine unit and the quinoid diimine unit, respectively[24,32]. Such a comparison (spectra not shown) reveals bands of approximately equal intensity for 0% Ce^{IV}. Substitution of cerium leads to a small increase in the ratio of 1500 to 1598 cm^{-1}. The maximum ratio, for 100% Ce^{IV}, is about 1.3, suggesting a less-than-optimum doping level.

The initial 130% increase in conductivity depicted in *Figure 4* is harder to explain, but is a result, we believe, of more rapid polymerization. The less time polyaniline is exposed to persulfate, the less possibility there is for oxidative degradation. Exposure of polyaniline to highly oxidizing potentials is known to degrade its electrical and mechanical properties[33–35]. Since aniline is present in excess under the conditions used here, persulfate is consumed by the end of the polymerization period.

In conclusion, the addition of small amounts of co-oxidants will substantially decrease the induction period for aniline polymerization by persulfate. Once the reaction has started, the rate appears to be independent of the amount of co-oxidant, suggesting nucleation as a rate-limiting step. Solution and electrical properties depend on co-oxidizer concentration, and significant benefits in reaction time and electrical properties can be gained simply by adding 0.1% Ce^{IV} to a persulfate system. Interestingly, aniline that has been exposed to ambient for some time develops a yellow discoloration, due presumably to air oxidation. This material exhibits a considerably reduced induction period. For reproducible kinetics it is thus necessary to control the purity of the starting material.

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