A study of the kinetics of polymerization of aniline using proton NMR spectroscopy

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Abstract

The polymerization of aniline has been studied by monitoring monomer depletion using proton NMR spectroscopy. For precipitation polymerization at 298 K using $Na_2S_2O_8$ as oxidant an induction period of several minutes was observed, followed by relatively rapid polyaniline formation. In contrast, much slower polymerization was found using KIO_3 as oxidant. In both cases there is a significant residual NMR signal, even though a stoichiometric amount of oxidant was used. This was attributed to soluble aniline oligomers rather than unreacted aniline monomer. At 278 K the rate of polymerization is markedly slower for both oxidants. No significant differences were observed between the rates of precipitation polymerization and dispersion polymerization using a reactive poly(ethylene oxide)-based stabilizer. Faster reactions were observed when aniline was polymerized in the presence of ultrafine 20 nm silica particles to form polyaniline–silica colloidal nanocomposites. Polymerization was slower when aniline was polymerized in the presence of surfactant micelles to form surfactant-stabilized polyaniline particles; this is probably due to the high viscosity of the reaction solution. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Polyaniline and polypyrrole are both relatively air-stable organic conducting polymers [1]. They are usually chemically synthesized in aqueous solution as intractable 'bulk powder' precipitates, although several research groups have recently described the preparation of stable colloidal dispersions of polypyrrole and polyaniline particles [2–18]. Electropolymerization studies have been extremely useful in developing our understanding of the polymerization mechanism(s), although certain aspects remain controversial [19–29].

Various groups have studied the kinetics of the chemical polymerization of pyrrole and aniline with a wide range of experimental techniques. For example, the rate of pyrrole polymerization has been studied by: (i) monitoring the rate of monomer depletion using gas chromatography [30]; (ii) combined in situ Raman spectroscopy and potentiometry [31]; (iii) microcalorimetry measurements [32]. In addition, Bjorklund [33] has described the use of visible absorp-

tion spectroscopy to follow the kinetics of formation of methylcellulose-stabilized polypyrrole colloids. Aniline polymerization kinetics have been studied by monitoring the rate of monomer depletion using both linear sweep cyclic voltammetry [34] and gas chromatography [35]. Very recently Fu and Elsenbaumer [36] have reported a kinetic study based on a calorimetric method. Duran and co-workers [37] have explored the kinetics of polymerization of 2-pentadecylaniline at the air/water interface and have proposed a modified kinetic scheme based on that suggested by Tzou and Gregory [35] for the conventional polymerization of aniline.

In the present work ^1H NMR spectroscopy has been used to monitor the rate of depletion of aniline in DCl/D_2O solution. The precipitating polyaniline does not interfere since no NMR signal can be detected from the insoluble polymer. We have examined how the rate of polymerization of aniline is affected by: (i) the reaction temperature; (ii) the choice of oxidant; (iii) precipitation versus dispersion polymerization (i.e. whether the conducting polymer is formed as a bulk powder or as a stable colloidal dispersion). In the latter experiments three different dispersants were examined: a reactive

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poly(ethylene oxide)-based stabilizer, an ultrafine silica sol
and a small molecule surfactant.

2. Experimental

2.1. Materials

All chemicals were obtained from Aldrich and were used
as received unless otherwise stated. Aniline was distilled
under vacuum from zinc dust and stored under nitrogen in
the absence of light at $-18°C$. The ultrafine 'Nyacol' silica
sol was kindly donated as a 50 wt.% aqueous solution by
Nyacol Products and was used as received. Earlier electron
microscopy studies had indicated a mean silica particle diam-
eter of approximately 20 nm [17,18]. The reactive
poly(ethylene oxide)-based stabilizer (kindly donated by Dr
H.H. Kuhn of Milliken Research Corporation) contained a
single pendant aniline group per polymer chain and had a
molecular weight of 4900 g mol^{-1} as determined by end-
group analysis using UV spectroscopy [38].

2.2. NMR measurements

All polymerizations were carried out in a 250 MHz Bruker
NMR spectrometer at either 298 or 278 K in 1.2 M DCl/D$_2$O
solution in a 10 mm diameter NMR tube. For quantification
purposes a reference compound, sodium methanesulfonate,
was used. This reference was selected because its simple
methyl proton NMR signal was well separated from the
aromatic proton signal due to the aniline monomer. It was
also non-volatile and relatively inexpensive. However, in pre-
liminary studies, this compound became incorporated into
the precipitating polyaniline (presumably as a dopant anion)
and was thus depleted from solution [39]. In order to prevent
this, in subsequent experiments the reference was present as
a D$_2$O solution in a 5 mm NMR tube placed coaxially inside
the 10 mm tube. This assembly was rotated at 20 Hz during
each kinetic run; this was considered comparable to the effect
of magnetic stirring in a typical bench-scale synthesis. The
minimum delay time between the spectra was 3 s. Control
experiments carried out in the absence of oxidant confirmed
that such delay times did not produce any loss of NMR signal
intensity due to saturation effects. More than 40 single-scan
NMR spectra were acquired in the majority of the kinetics
experiments. Typical NMR spectra illustrating the depletion
of aniline monomer relative to the sodium methanesulfonate
reference are depicted in Fig. 1. The concentration of aniline
remaining in solution was determined from the ratio of the
NMR integral due to the aromatic protons of the aniline
monomer (δ 6.9 to 7.4) to that of the methyl protons of the
reference compound (δ 2.4 to 2.7).

2.3. Precipitation polymerization

Polyaniline was synthesized as a bulk powder precipitate
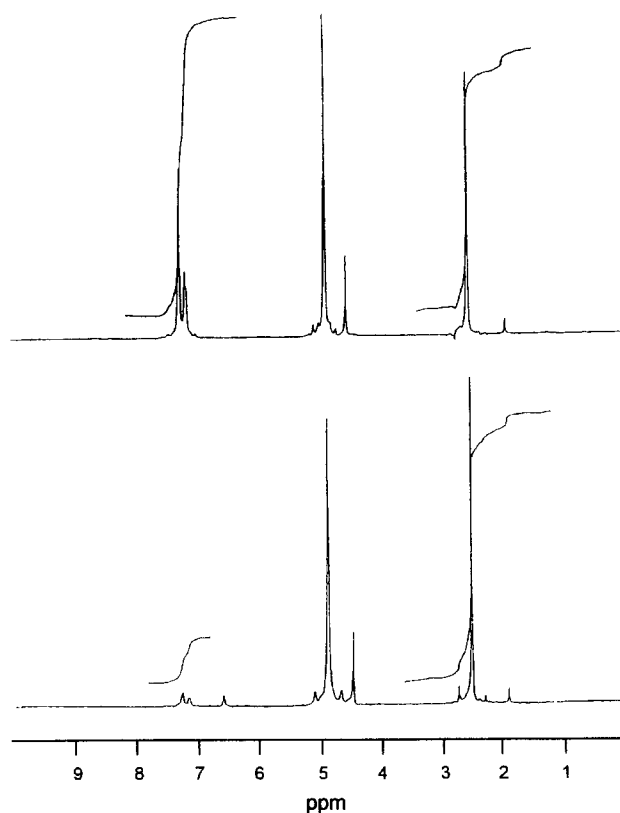at an initial monomer concentration of 0.10 M (1.00 vol.%)

Fig. 1. Two typical proton NMR spectra taken from a kinetic run of the
precipitation polymerization of aniline at 298 K. The reduced aromatic signal
after 20 min compared to that at the beginning of the reaction illustrates the
depletion of aniline monomer from solution.

using a stoichiometric amount of oxidant, either Na$_2$S$_2$O$_8$ or
KIO$_3$ [40–42]. Thus, the number of moles of oxidant used
was $2.5x/y$, where x is the number of moles of monomer and
y is the number of electrons involved in the redox half-equa-
tion of the particular oxidant. In the case of S$_2$O$_8$$^{2-}$, $y = 2$ but
for IO$_3$$^-$ it is not clear [42] whether y is actually 5 or 6; in
the present work we arbitrarily elected to take $y = 6$. Kinetic
runs were carried out at both 298 and 278 K and the total
volume of reaction solution was either 1.50 or 3.00 ml.

2.4. Dispersion polymerization

The colloidal conducting polymer syntheses were also car-
ried out using a stoichiometric oxidant/monomer ratio; each
system has been described in detail in earlier publications
[15,17,18,38,43–45]. The initial dispersant concentrations
used in the kinetic runs were 60, 40 and 60 g dm^{-3} for the
reactive poly(ethylene oxide)-based stabilizer, the 20 nm
silica sol and the sodium dodecylbenzenesulfonate surfactant,
respectively. As expected, the addition of the dispersing
agents produced no change in the pH of the initial solution.

3. Results

Initially, we thought that precipitating polyaniline might
interfere with the NMR instrument's magnetic field homo-

geneity, leading to distortion of the NMR spectrum and unreliable peak integrals. Thus, we originally intended to study only the kinetics of formation of conducting polymer colloids. However, preliminary experiments showed that the NMR spectra were not adversely affected by polyaniline precipitation so the kinetics of formation of 'bulk powder' polyaniline were also examined.

In many conducting polymer syntheses reported in the literature an excess of either the oxidant or (more typically) the monomer has been used. In our research we have focused on the synthesis of stable colloidal dispersions (rather than precipitated bulk powders) of conducting polymers. In the course of this work we have found that too high a polymerization rate often leads to precipitation of the colloidal particles. Since this is obviously undesirable, we have generally used stoichiometric oxidant/monomer molar ratios. This ensures the minimum rate of polymerization for a given overall yield of conducting polymer. In view of our earlier work, the present study was also carried out using stoichiometric amounts of oxidant and monomer. The same conditions were selected by Wei's group [34] and Fu and Elsenbaumer [36] on the basis of similar arguments.

Tzou and Gregory [35] recently examined the kinetics of aniline polymerization at 277 K using gas chromatography to monitor the rate of monomer depletion. They proposed a semi-empirical kinetic model in which the consumption of aniline involves a slow, homogeneous reaction with the oxidant, and a much faster heterogeneous reaction with the precipitating polyaniline phase. This led them to propose the following empirical rate equation, which was based in part on an earlier kinetic study by Wei's group [20]:

$$-d[AN]/dt = k_1[AN][APS] + k_2[AN][P] \tag{1}$$

where [AN], [APS] and [P] are the concentrations of aniline, $(NH_4)_2S_2O_8$ and polyaniline, respectively, and k_1 and k_2 are constants. k_2 is a composite quantity containing a contribution from the specific surface area of the precipitating polymer.

Since [AN], [APS] and [P] are functions of the reaction stoichiometry of the initial reagent concentrations, Eq. (1) can be integrated and fitted to experimental data, using k_1 and k_2 as variables. It was claimed that this approach gives good fits and that k_1 was primarily affected by the initial reactant concentrations and the presence of catalyst, whereas k_2 depended on the acid concentration and the presence of added colloidal substrates. In general, k_2 was found to be two to three orders of magnitude larger than k_1.

Examination of Tzou and Gregory's paper shows that they made a minor error in their mathematical derivation. In the Appendix of Ref. [35] it is stated (see Eq. (A-2) in that paper) that the oxidant concentration at any given time during the polymerization is given by

$$[APS] = [APS]_o - ([AN]_o - [AN])/1.25 \tag{2}$$

where the factor of 1.25 arises because one mole of aniline is consumed by 1.25 moles of APS (a two-electron oxidant).

Substitution from Eq. (2) allowed Eq. (1) to be integrated in terms of two variables, β_1 and β_2, which were defined by

$$\beta_1 = 0.80k_1 - k_2 \text{ and } \beta_2 = k_1[APS]_o - \beta_1[AN]_o$$

In fact, the correct expression should be

$$[APS] = [APS]_o - 1.25([AN]_o - [AN]) \tag{3}$$

This error inevitably leads to incorrect expressions for both β_1 and β_2. Using Eq. (3), the correct formulae for β_1 and β_2 are

$$\beta_1 = 1.25k_1 - k_2 \text{ and } \beta_2 = k_1[APS]_o - \beta_1[AN]_o \tag{4}$$

The integrated rate equation is unchanged and is given by

$$[AN]/[AN]_o = \beta_2/(\beta_1[AN]_o(\exp(\beta_2 t) - 1) + \beta_2\exp(\beta_2 t)) \tag{5}$$

However, the relationship between the fitting parameters β_1 and β_2 is now given by Eq. (4).

Our experimental data are qualitatively similar to those of Tzou and Gregory [35], in that there is an induction period followed by relatively rapid polymerization. The conversion curves obtained from the NMR measurements could usually be fitted using Eq. (5) with β_1 and β_2 as adjustable parameters; Fig. 2 shows a typical example for the precipitation polymerization of aniline at 278 K. Judging from the data 'scatter' the random errors associated with the NMR method are comparable to those incurred using gas chromatography as described by Tzou and Gregory. The reproducibility of the NMR conversion curves was generally good, although it was found that the k_2 values calculated using Eq. (5) were more reliable than the k_1 values. These rate constants were generally of a similar order of magnitude to those calculated by Tzou and Gregory, who also reported that the experimental error associated with k_1 was relatively high. Closer comparison between these authors' rate constants and our own precipitation polymerization data is very difficult due to dif-
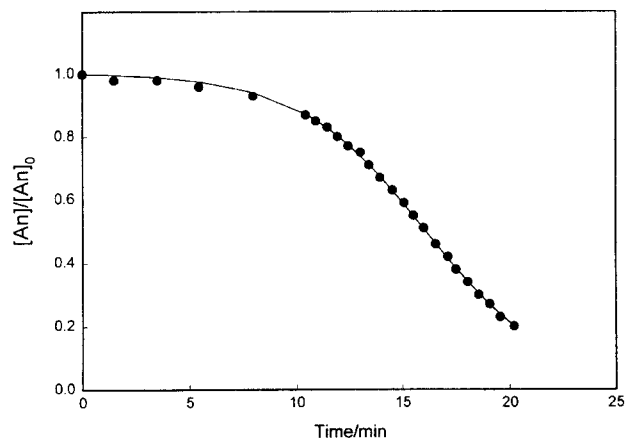

Fig. 2. Comparison of conversion data (filled circles) obtained by proton NMR spectroscopy for the precipitation polymerization of aniline at 278 K, with $Na_2S_2O_8$ as oxidant, and the curve (continuous line) calculated from Eq. (5) using β_1 and β_2 as adjustable parameters. k_1 and k_2 are 0.011 and 3.05 l mol^{-1} min^{-1}, respectively.

Table 1
Summary of kinetic data for aniline polymerization

Reaction type	Temperature (K)	Dispersant	k_1 ($\times 10^3$ M^{-1} min^{-1})	k_2 (M^{-1} min^{-1})
Precipitation	278	none	5.2	3.1
Dispersion	278	silica sol	0.23	7.1
Dispersion	278	PEO–An [a]	38	1.9
Precipitation	298	none	47	6.8
Dispersion	298	silica sol	23	8.8
Dispersion	298	PEO–An [a]	45	6.7
Dispersion	298	SDS	0.88	3.7

[a] PEO–An denotes the reactive poly(ethylene oxide)-based stabilizer of molecular weight 4900 g mol^{-1}, see Section 2.

ferences in both the absolute and relative reactant concentrations, HCl concentration and reaction temperature.

Tzou and Gregory's experiments [35] used a 1:1 oxidant/aniline molar ratio in order to avoid side reactions, such as over-oxidation of aniline. Thus, their observation of excess, unreacted aniline monomer at long reaction times is presumably due to their oxidant-deficient oxidant/monomer ratio. For reasons stated earlier, a stoichiometric ratio was used in our studies but a residual NMR signal, apparently due to unreacted monomer, was still observed even at long reaction times. It is possible that this excess 'monomer' signal is in part due to soluble aniline dimer and higher oligomers; according to Wei's group [34] such species have similar NMR signals to aniline. These workers used linear sweep voltammetry to show the presence of aniline dimer in the reaction solution at stoichiometric oxidant/monomer molar ratios. However, this species remained at a relatively low steady-state concentration for most of the polymerization and never exceeded 3% of the residual aniline concentration.

The gas chromatography method favoured by Tzou and Gregory analyses specifically for aniline monomer. Since our NMR-derived conversion curves are generally in good agreement with Tzou and Gregory's data this suggests that poly-

aniline formation is highly unlikely to proceed via step polymerization. With this mechanism the majority of the aniline monomer would be converted into (soluble) aniline oligomers during the early stages of the polymerization. These soluble oligomers would be erroneously detected as unreacted monomer by NMR but not by gas chromatography; thus, discrepancies might reasonably be expected between these two techniques, particularly at low conversions. In fact, the observed close agreement indicates that the aniline is converted directly into relatively high molecular weight (insoluble) polyaniline, which is consistent with the chain polymerization mechanism postulated by Wei's group [34].

The effect of temperature on the precipitation polymerization of aniline using $Na_2S_2O_8$ as oxidant is shown in Fig. 3. The rate constants calculated from these conversion curves are summarized in Table 1: the value of k_1 increases almost ten-fold on going from 278 to 298 K, whereas k_2 about doubles. The two conversion curves are qualitatively similar, but there is a much longer induction period at 278 K compared to that observed at 298 K. The level of residual aniline 'monomer' is approximately 10% for the 298 K polymerization but around 20% for the 278 K polymerization. The reason for this difference is not clear at present.
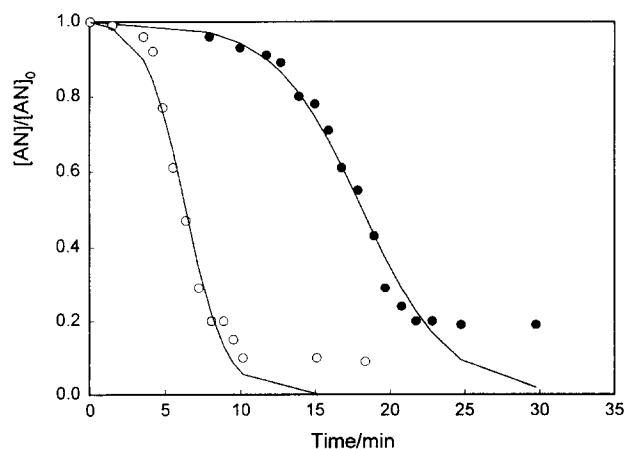

Fig. 3. Effect of temperature on the polymerization of aniline using $Na_2S_2O_8$ as oxidant: in each case the points are experimental and the continuous line is calculated from Eq. (5); (open circles) 298 K, $k_1 = 0.047$ l mol^{-1} min^{-1}, $k_2 = 6.8$ l mol^{-1} min^{-1}; (filled circles) 278 K, $k_1 = 0.005$ l mol^{-1} min^{-1}, $k_2 = 3.1$ l mol^{-1} min^{-1}.
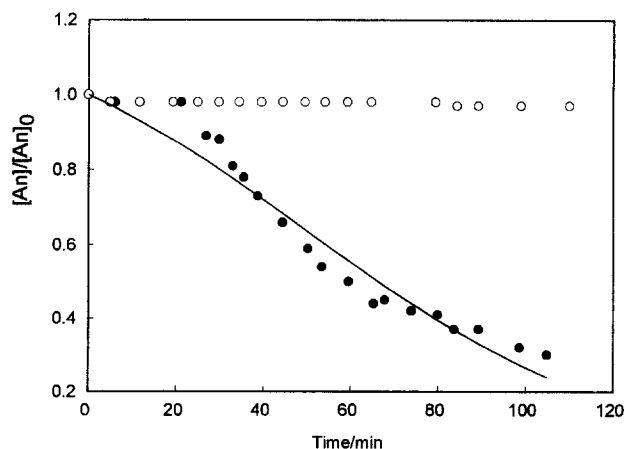

Fig. 4. Effect of reaction temperature on the kinetics of polymerization of aniline using KIO_3 as oxidant: (open circles) 278 K; (filled circles) 298 K. The continuous line is the best-fit line from Eq. (5), $k_1 = 0.12$ l mol^{-1} min^{-1}, $k_2 = 0.26$ l mol^{-1} min^{-1}.

Conversion versus time curves for the precipitation polymerization of aniline at 278 and 298 K using KIO_3 as oxidant are shown in Fig. 4. At 298 K the rate of polymerization is significantly slower than that found with $Na_2S_2O_8$ as oxidant, with only approximately 50% of the aniline monomer being consumed within the first hour. Surprisingly, there is a very marked temperature dependence for aniline polymerization using KIO_3: at 278 K the rate of polymerization is negligible, with less than 5% monomer depletion even after 2 h. Although the data are qualitatively similar to those for $Na_2S_2O_8$, it was not possible to obtain a satisfactory fit using Eq. (5). Thus, it appears that the polymerization of aniline follows a different kinetic law for the KIO_3 oxidant.

The conversion curve for the dispersion polymerization of aniline at 298 K using the poly(ethylene oxide)-based steric stabilizer is shown in Fig. 5. Data for a precipitation polymerization under the same conditions in the absence of any steric stabilizer are also presented for comparison. The data (see Table 1) show virtually identical kinetics for these two runs, apart from the final monomer concentration. The higher residual aniline level observed for the dispersion polymerization is most likely due to some of the $Na_2S_2O_8$ being used up in oxidizing the pendant aniline groups of the polymeric stabilizer. Visible absorption spectroscopy studies by Tadros et al. [15] have previously confirmed that such stabilizer 'activation' occurs. Inspection of the contents of the NMR tube after the kinetic measurements revealed that a stable colloidal dispersion of polyaniline particles with no signs of macroscopic precipitation was obtained in the dispersion polymerization experiment. Thus, in this case, the overall rate of dispersion polymerization of aniline is very similar to the rate of precipitation polymerization.

The conversion curve for the dispersion polymerization of aniline at 278 K using the ultrafine silica sol as a dispersant is shown in Fig. 6. Again, a precipitation polymerization experiment carried out under the same conditions in the absence of any silica sol is also presented. Clearly, the rate of dispersion polymerization is significantly faster in the presence of the high surface area colloidal substrate. Similar results were reported by Tzou and Gregory [35], although in their case the colloidal alumina particles did not prevent macroscopic precipitation of the polyaniline. Inspection of the rate constants presented in Table 1 shows that k_1 is significantly reduced in the presence of the silica sol, whereas k_2 increases by a factor of nearly four. Tzou and Gregory also concluded that the increased rate of polymerization was primarily due to an increase in k_2. This is reasonable since k_2 is a composite rate constant which contains a surface area term. As expected, inspection of the NMR tube after the kinetic run revealed a colloidally stable dispersion of polyaniline–silica nanocomposite particles. Thus, for this 'heterogeneous' dispersion polymerization the rate of polymerization of aniline is significantly faster than that found for either precipitation polymerization or 'homogeneous' dispersion polymerization.
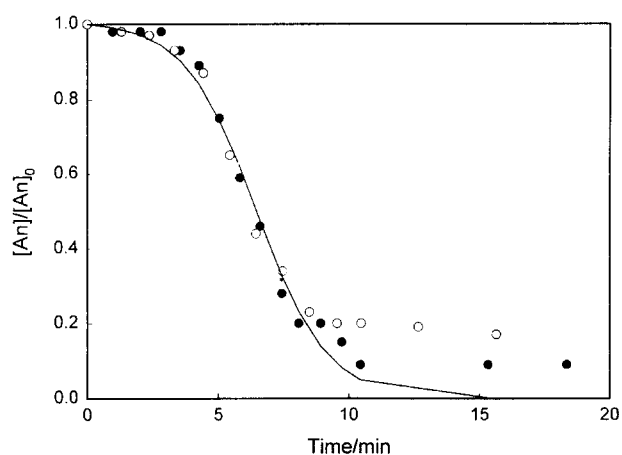

Fig. 5. Conversion curves for the dispersion polymerization of aniline at 298 K using a reactive poly(ethylene oxide) stabilizer and $Na_2S_2O_8$ as oxidant (open circles) and the precipitation polymerization of aniline under the same conditions in the absence of any stabilizer (filled circles). The continuous line is calculated from Eq. (5) using the data from the dispersion polymerization, $k_1 = 0.0450 \, l \, mol^{-1} \, min^{-1}$, $k_2 = 6.7 \, l \, mol^{-1} \, min^{-1}$.
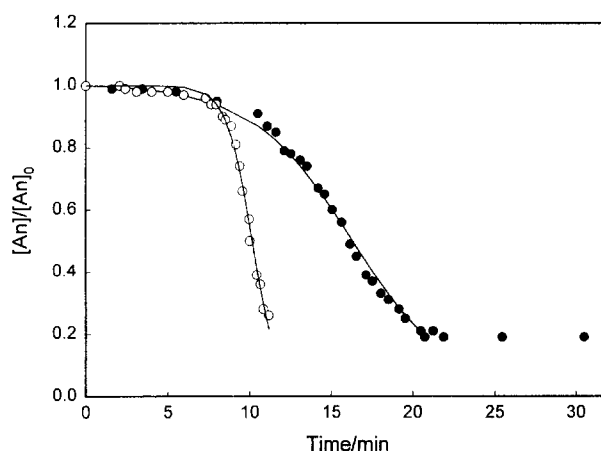

Fig. 6. Comparison of the conversion curves obtained for the dispersion polymerization of aniline at 278 K using an ultrafine silica sol with $Na_2S_2O_8$ as oxidant (open circles) and the precipitation polymerization of aniline under the same conditions in the absence of any silica sol (filled circles). The continuous lines are calculated from Eq. (5) (dispersion reaction $k_1 = 2.3 \times 10^{-4} \, l \, mol^{-1} \, min^{-1}$, $k_2 = 7.1 \, l \, mol^{-1} \, min^{-1}$; precipitation reaction $k_1 = 0.012 \, l \, mol^{-1} \, min^{-1}$, $k_2 = 2.9 \, l \, mol^{-1} \, min^{-1}$).

The conversion curves for the dispersion polymerization of aniline at 298 K in the presence and absence of sodium dodecylbenzenesulfonate (SDS) are presented in Fig. 7. (The aromatic protons in the SDS ($\delta = 7.7$) are clearly distinguishable from the signals due to the aniline ($\delta = 7.0$–7.3) so that there is no interference.) It is evident that the time to reach a given conversion is much longer in the presence of the surfactant stabilizer. However, this effect results almost entirely from the longer induction time; the gradients of the conversion curves are similar after the induction period. This is reflected in the values of the rate constants; k_1 is 25 times smaller in the presence of the surfactant, whereas k_2 is lower by a factor of 2.4. The dispersion polymerization gave a colloidally stable dispersion of surfactant-stabilized polyani-
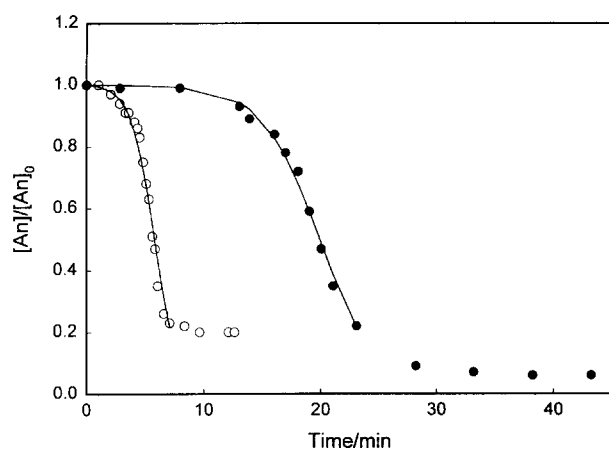
Fig. 7. Conversion curves for the dispersion polymerization of aniline at 298 K using a sodium dodecylbenzenesulfonate surfactant stabilizer in conjunction with the $Na_2S_2O_8$ oxidant (filled circles), and the precipitation polymerization of aniline under the same conditions in the absence of any surfactant (open circles). The continuous lines are calculated from Eq. (5) (dispersion reaction $k_1 = 9 \times 10^{-4}$ l mol^{-1} min^{-1}, $k_2 = 3.7$ l mol^{-1} min^{-1}; precipitation reaction $k_1 = 0.023$ l mol^{-1} min^{-1}, $k_2 = 9.1$ l mol^{-1} min^{-1}).

line particles judged by visual inspection. Polymerizations at 278 K with SDS did not give stable dispersions.

4. Discussion and conclusions

4.1. Applicability of the NMR spectroscopy

We have shown that NMR is a convenient technique for monitoring the kinetics of polymerization of aniline. Both precipitation and dispersion polymerization reactions were analysed and the quality of the kinetic data is comparable to that obtained by Tzou and Gregory using gas chromatography.

In view of the stoichiometric oxidant/monomer molar ratios used in our study the residual 'aniline' signal, which apparently remains at the end of the polymerization, is attributed to the formation of soluble aniline dimer and higher oligomers. The good agreement of our data with the results from other techniques suggests that the contribution of such species is small. In particular, the observed induction period is not due to a step-reaction polymerization leading initially to soluble oligomers, since similar induction times are seen by chromatographic analysis of monomer depletion.

The main limitation of NMR spectroscopy is its sensitivity to paramagnetic species such as Fe^{3+}, Cu^{2+}, V^{5+}, Ce^{4+}, $Cr_2O_7^{2-}$, etc., which excludes many of the common oxidants for aniline polymerization. The selected oxidants, $Na_2S_2O_8$ and KIO_3, were particularly suitable because no significant polymerization occurred for several minutes after addition of the aniline monomer. This allowed proper optimization of the spectrometer prior to spectral accumulation. Using $(NH_4)_2S_2O_8$ as oxidant in place of $Na_2S_2O_8$ gave a complex signal, due to the quadrupolar NH_4^+ cation, which partially

obscured the aniline monomer signal. Thus, $Na_2S_2O_8$ was the preferred oxidant.

We also examined the polymerization of pyrrole in D_2O using $Na_2S_2O_8$. However, this reaction was so fast that more than 80% of the pyrrole signal had disappeared within the first minute, which was the minimum time required for optimization of the NMR spectrometer [45]. The rate of pyrrole polymerization in the presence of added surfactant was much slower and therefore more amenable to NMR analysis. However, experiments without oxidant confirmed [45] that the aromatic pyrrole protons exchanged with the D_2O, thus leading to an artificial reduction in the NMR peak integral of the pyrrole monomer. Although the time scale for H/D exchange was slower than the rate of polymerization, it was sufficiently fast to be a source of error. No further studies on pyrrole polymerization were attempted.

4.2. Polymerization kinetics

As discussed above, the kinetics of consumption of aniline monomer in both precipitation and dispersion polymerizations with $Na_2S_2O_8$ as oxidant are fitted well by the two rate constant kinetic model of Tzou and Gregory, as expressed in Eq. (1). This model assumes that the initial oxidation of aniline by the oxidant is slow compared to the oxidation of aniline by oxidized polymer, leading to an induction period.

Table 1 summarizes our best-fit values of the two rate constants, k_1 and k_2, for the reactions studied here. It should be emphasized that the influence of variations in the two rate constants is very different. Although their effects are interdependent, k_1 dominates the induction period and has rather little effect on the later rate. Only order of magnitude variations in k_1 are significant. In contrast, k_2 dominates the rapid polymerization phase of the reaction and quite small (less than one order of magnitude) changes in k_2 are significant. Both k_1 and k_2 are important in the auto-accelerating phase. For these reasons, curve fitting gives values of k_2 which are more precise than those for k_1.

As expected, precipitation polymerizations were slower at 278 than at 298 K. This was particularly marked with KIO_3, for which the rate of precipitation polymerization was negligible at 278 K.

Since k_2 is a composite quantity which describes a heterogeneous reaction, it might be expected that addition of dispersing agents, giving higher specific surface areas, would lead to an increase in k_2. If the dispersing agent does not influence the initial oxidation of aniline then it should not change k_1.

Tzou and Gregory [35] found that the polymerization of aniline is accelerated by the presence of 0.3 μm alumina particles and that the major effect was a large increase in k_1, leading to a much shorter induction time, with only a slight increase in post-induction period rate, reflected in almost no change in k_2. They suggested that the main effect is a catalytic influence of the alumina on the initial oxidation of aniline, probably through some sort of adsorption effect. However,

there is no indication in Ref. [35] of what effect the alumina had on the particle size of the polyaniline.

Our experiments with silica sols (Table 1 and Fig. 6) give slightly different results. At both temperatures k_1 is lowered by the presence of the silica, implying that it retards the initial oxidation of the aniline. However, the effect is more than compensated by an increase in k_2, which causes more rapid polymerization once polyaniline appears in the solution. The overall result of slow initiation and rapid polymerization is an induction period, followed by the sharp onset of rapid polymerization.

A different effect was seen when SDS was used as the dispersion stabilizer, although experiments could only be done at the higher temperature. Here again, k_1 is lowered by the stabilizer, implying that it retards the inital oxidation of the aniline. In this case the effect is reinforced by a decrease in k_2, which causes slower polymerization once polyaniline appears in the solution. The overall result is a longer induction period, followed by slower polymerization. It is not entirely clear why this should occur. However, in order to get stable polyaniline dispersions it was necessary to use a high (60 g 1^{-1}) concentration of SDS, which gives a highly viscous, micellar solution, whose increased viscosity may account for the slower polymerization.

The kinetics of dispersion polymerization using a reactive poly(ethylene oxide)-based stabilizer are very similar to those found for precipitation polymerization under identical conditions in the absence of any stabilizer. At 298 K the reaction rate is unaffected by the stabilizer, despite the fact that a colloid is formed rather than a precipitate. Polymerization at 278 K is slightly slower in the presence of the dispersing agent, though the induction time is shortened.

In conclusion, although the NMR technique is limited to those oxidants which do not contain or produce paramagnetic species, it is a very successful method for monitoring polymerization in appropriate cases.

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