Thermochemistry and Kinetics of Chemical Polymerization of Aniline Determined by Solution Calorimetry

Yueping Fu and Ronald L. Elsenbaumer*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065

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The thermochemistry and reaction kinetics of oxidative chemical polymerization of aniline (AN) with ammonium peroxydisulfate (APS) in various aqueous acids, concentrations, and oxidant/aniline ratios are reported. The polymerization was found to be a highly exothermic reaction leading to the formation of the emeraldine form of polyaniline with an enthalpy change of −105 kcal/mol of AN when aniline is in excess. Overoxidation with APS in excess caused the formation of higher oxidation states of polyaniline as well as polymer chain hydrolysis and chlorine substitution. The reaction kinetics were found to be different between polymerizations in highly acidic and relatively neutral pH's, though the reaction enthalpy was the same. *In situ* UV spectra of the polymerization showed that emeraldine was rapidly formed in acidic media, whereas low molecular weight products were produced in relatively neutral media. The polyaniline produced using excess aniline and highly acidic media showed the highest conductivity. An empirical relationship was found that relates the reaction induction period to the starting concentration of aniline in aqueous HCl solutions. A strong dependence of the induction period on the nature of the acid used in the polymerization was also found.

Introduction

Polyaniline, which exists in various oxidation states, can be synthesized by the oxidative chemical or electrochemical polymerization of aniline (AN). As a member of the conducting polymer family, polyaniline has been extensively studied because it can be readily doped to the metallic conducting regime by protonic acids, because it is processable in selected solvent systems, and because of its promise of industrial applications.[1-6] Although much work has been devoted to the study of polyaniline, many aspects of aniline polymerization are still not well understood.

The base form of polyaniline has the generalized composition $[-(B-NH-B-NH-)_y-(B-N{=}Q{=}N-)_{1-y}-]_n$, where B denotes a benzenoid unit and Q a quinoid unit. The terms leucoemeraldine (LEB), emeraldine (EB), and pernigraniline (PNB) refer to the different oxidation states of the undoped polymer where $y = 1$, 0.5, and 0, respectively. Bond-energy calculations indicate that the chemical polymerization of aniline with APS to give a head-to-tail polymer results in a large negative enthalpy change. For example, the calculated enthalpy change for the formation of LEB and EB are about −83 and −77 kcal/mol of AN, respectively. Since the conductive form of polyaniline contains both benzenoid and quinoid segments with additional structural features such as conjugation and protonation, the usefulness of such calculations is limited to merely a semiquantitative enthalpy change estimation, neglecting the additional stabilization due to conjugation and polymer backbone protonation. Because the final polymer product also can be in various oxidation states (quinoid-to-benzenoid ratio), the stoichiometry leading to products in these different oxidation states will be different, as will the overall enthalpy change of the polymerization reaction.

It is reported that the oxidative polymerization of aniline by a chemical oxidant at ambient temperature can be a highly exothermic reaction.[7] The primary goal of this investigation was to study the thermochemistry of the oxidative polymerization of aniline with ammonium peroxydisulfate (APS) as a function of pH, nature of the acid, concentration of initial aniline monomer, and concentration ratio of APS/AN to help elucidate mechanistic information about the polymerization reaction.

Experimental Section

The polymerization of aniline was carried out in a solution calorimeter (Parr 1451) with the starting solution temperature at 24 °C. Aniline (Aldrich Chemical Co., reagent grade) was dissolved in 80.0 mL of a protonic acid solution in a glass dewar, ammonium peroxydisulfate (Aldrich Chemical Co., reagent grade) was dissolved in 20.0 mL of the same acid solution, warmed to 24 °C, and then transferred to a sealed glass cell which was immersed in the aniline solution. After both reactants came into thermal equilibrium, the reactants were mixed and the polymerization reaction started by depressing a push rod to drop the ammonium peroxydisulfate solution into the surrounding aniline solution. The polymerization then proceeded to completion under stirring action of the rotating cell. Throughout the polymerization reaction, temperatures in the calorimeter were sensed by a thermistor and recorded on a strip-chart recorder.

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1994.

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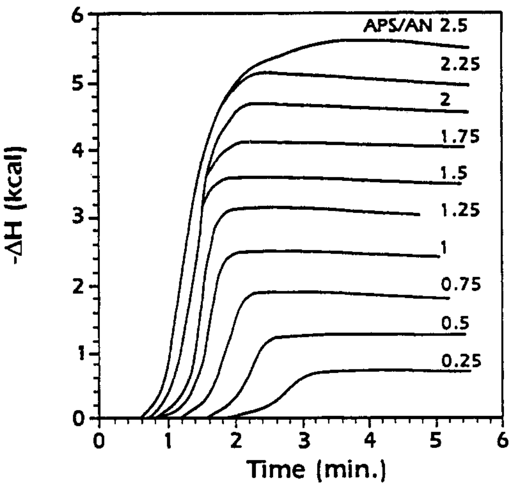

Figure 1. Enthalpy change vs time profiles for reactions using different [APS]/[AN] ratios. Initial [AN] was 0.300 M in 1.00 M [HCl].

The heat capacity of the calorimeter was calibrated by dissolving the standardizing reagent [tris(hydroxymethyl)amino]methane (TRIS) in dilute hydrochloric acid (0.1 M) for which the amount of heat evolved is well established. The heat capacity of the calorimeter containing 100 mL of 0.1 M HCl solution was found to be 120.8 ± 0.2 cal/°C.

The undoped forms of polyaniline were obtained by treating acidic polymerization products with 0.1 M NH_4OH aqueous solution for ca. 20 h. Both the doped and undoped forms of polyaniline were vacuum dried at room temperature for ca. 24 h. Infrared spectra were obtained by using a Digilab FTS-40 FTIR spectrophotometer utilizing the diffuse reflectance technique (DRIFT) on samples in a powdered KBr dispersion. Electronic absorption spectra were obtained on a Varian Cary 5 UV-VIS-NIR spectrophotometer. Elemental analyses were performed in-house on a Perkin Elmer 2400 CHN Analyzer or were sent out to Quantitative Technologies, Inc. (Whitehouse, NJ). Conductivity measurements were made using a DC four-in-line-probe method (compressed pellets).

Results and Discussion

Stoichiometric Polymerization of Aniline. A set of thermograms from reactions using various APS/AN ratios are shown in Figure 1. Related thermal data are shown in Table 1 and plotted in Figure 2. As shown in Figure 2A, the heat given off for polymerization of aniline increases proportionally with increasing oxidizing agent (APS) concentration, though there is a break point at APS/AN = 1.25 which separates the plot into two linear parts. One can also see from the enthalpy data in Table 1 that the heats of reaction per mole of reactant are very consistent throughout the range of APS/AN ratios of 0.25–1.25. As shown from early studies,[8-11] when the polymerization is carried out with an excess of aniline under acidic conditions, i.e., APS/AN < 1.25, the final polymerization product is in the form of emeraldine. From titrimetric estimation,[8] the APS was essentially all consumed in the polymerization. FTIR spectra of undoped polymers were found to be nearly identical for the polymers produced at APS/AN = 0.75 and 1.25. Also, the results of elemental analysis of

Table 1. Heats Evolved from the Reaction of Aniline with APS at Different APS/AN Ratios

	[APS]/[AN][a]									
	0.250	0.500	0.750	1.00	1.25	1.50	1.75	2.00	2.25	2.50
ΔT (± 0.05 °C)	5.250	10.35	15.50	20.75	26.00	30.35	34.50	39.13	43.58	47.43
$q = \Delta T\lambda$[b] (kcal)	0.634 ± 0.006	1.251 ± 0.006	1.873 ± 0.007	2.507 ± 0.007	3.141 ± 0.008	3.666 ± 0.008	4.168 ± 0.009	4.727 ± 0.010	5.265 ± 0.010	5.730 ± 0.011
$\Delta H = -q$/APS[c] (kcal/mol of APS)	-84.5 ± 1.4	-83.4 ± 0.7	-83.2 ± 0.5	-83.6 ± 0.4	-83.8 ± 0.3	-81.5 ± 0.3	-79.4 ± 0.3	-78.8 ± 0.3	-78.0 ± 0.3	-76.4 ± 0.3
$\Delta H = -q$/AN[d] (kcal/mol of AN)	-105 ± 2	104 ± 1	-104 ± 1	104 ± 1	-105 ± 1	-122 ± 1	139 ± 1	-158 ± 1	176 ± 1	-191 ± 1

[a] In 1.0 M HCl with initial [AN] = 0.300 M. [b] Heat capacity of calorimeter containing 100 mL of 0.10 M HCl, λ = 120.8 ± 0.2 cal/°C. [c] Heat evolved per mole of APS consumed. Errors correspond to absolute standard deviations. [d] Heat evolved per mole of AN consumed (knowing that 1 mol of aniline is consumed for every 1.25 mol of APS added as determined by the break point in the plot of q vs [APS]/[AN]).

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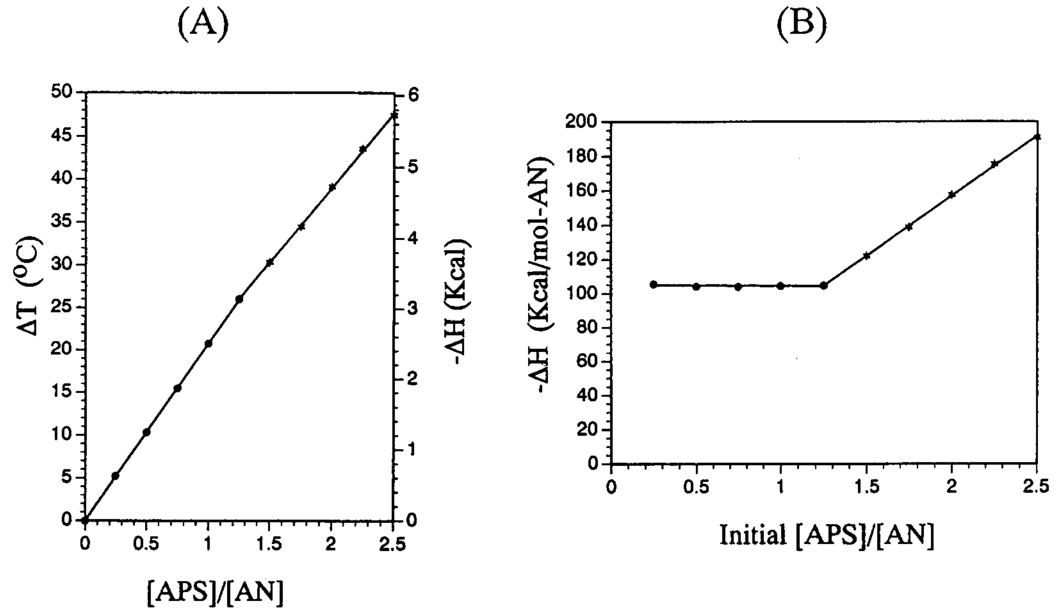


Figure 2. (A) Relationship between heat evolved and [APS]/[AN] ratio. Initial [AN] was 0.300 M in 1.0 M [HCl]. (B) Enthalpy change per mole of AN vs initial [APS]/[AN] ratios.

Table 2. Elemental Analysis of Neutralized, Dried Polymers Obtained from Polymerizations Using Different [APS]/[AN] Ratios, Where Initial [AN] Is 0.300 M and [HCl] Is 1.00 M

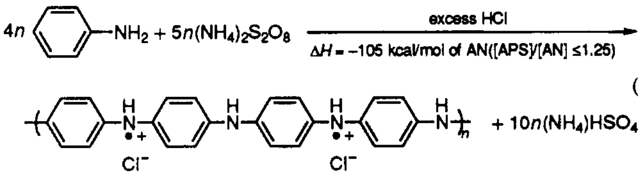
[APS]/[AN]	C (%)	H (%)	N (%)	Cl (%)	total (%)[a]	empirical formula[b]
0.75	77.70	4.76	14.80	0.24	97.50	$C_{24.0}H_{17.5}N_{3.9}O_{0.5}$
1.25	73.75	4.52	13.60	1.42	93.29	$C_{24.0}H_{17.5}N_{3.8}O_{1.6}$
2.50	57.74	3.07	10.04	17.82	88.67	$C_{24.0}H_{15.2}N_{3.6}O_{3.6}Cl_{2.5}$

[a] Total of C, H, N, and Cl. [b] Oxygen by difference.

Table 3. Conductivities of Polyaniline Samples Obtained from Polymerizations Using Different APS/AN Ratios; [HCl] at 1.00 M and Initial [AN] at 0.300 M

[APS]/[AN]	0.75	1.25	2.50
σ (S/cm)	9.1	7.2	0.001

undoped polymers and conductivities of doped polymers synthesized at different APS and AN ratios are shown in Tables 2 and 3. It is evident that polymers prepared using ratios of [APS]/[AN] = 0.75 and 1.25 have very similar elemental compositions and conductivities. The heat of reaction per mole of APS added remains remarkably constant up to an APS/AN ratio of 1.25 and then falls off above this ratio. This "titration experiment" provides evidence for the stoichiometry of the reaction to be 1.25 mol of APS to 1.0 mol of aniline and strongly suggests that one and the same product (polymer and oxidation state) is made throughout the stoichiometric range of APS/AN less than or equal to 1.25. This stoichiometry is consistent with the product being the protonated emeraldine form of polyaniline, and the stoichiometric reaction equation can be written as



(1)

Figure 2B also shows that the enthalpy of the reaction based on the amount of aniline consumed in the reaction remains very constant up to an APS/AN ratio of 1.25. The observed enthalpy change of −105 kcal/mol of AN in this APS/AN range is much larger than that calculated based solely on bond energy considerations. The larger observed reaction enthalpy is most likely resulting from a large conjugation contribution along the polymer backbone. It is not predominately arising from protonation of neutral polyaniline, since the heat evolved for the protonation of EB was determined to be only 5 kcal/mol of aniline repeat units.

When the oxidizing agent APS was present in excess, i.e., APS/AN > 1.25, the amount of heat evolved increased with an increase in concentration of APS but less slowly than observed at APS/AN < 1.25. This implies that the reaction stoichiometry has changed. Genies *et al.*[11] chemically synthesized polyaniline by oxidation of aniline with APS in quantities corresponding to APS/AN ratios of 0.31, 0.625, 1.25, and 2.5 to investigate how polymer molecular weight changes as a function of oxidant-to-aniline ratio. They found a bimodal molecular weight distribution of polymer where the more concentrated the oxidant, the more important the higher molecular weight fraction. They interpreted the bimodal distribution as arising from cross-linked and non-cross-linked polymer fractions. Wei *et al.*[12] first observed a bimodal distribution of molecular weights from the polymerization of aniline where they have correlated the higher molecular weight fraction with the level of aniline conversion. From FTIR spectra on neutralized samples, when APS is in excess (APS/AN = 2.5), we did not find peaks positioned near 890 cm^{-1}, which is the region characteristic for C–H out-of-plane bending on 1,2,4-trisubstituted benzene rings and

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would indicate the level of cross-linking.[13,14] However, the spectrum for the sample prepared at APS/AN = 2.5 does show a new peak at 1650 cm^{-1}, possibly arising from a carbonyl group. Elemental analysis on this sample shows the following result: 57.74% C, 3.07% H, 10.04% N, 17.82% Cl, and 11.33% O (remaining difference). This confirms earlier findings that when APS is used in excess, overoxidation causes backbone ring chlorination, and the formation of polyaniline in a high oxidation state that is degraded by hydrolysis with the formation of quinone end groups.[15,16]

Kinetic Modeling of Aniline Polymerization. Polymerization mechanisms and reaction kinetics of aniline in aqueous solution have recently been investigated by several groups.[17-24] Most of these studies dealt with polyaniline prepared by electrochemical polymerization, and several possible polymerization mechanisms were reported.[7] Gregory *et al.*[23] studied chemical polymerization of aniline in acidic aqueous media with and without substrates and proposed the semiempirical kinetic equation

$$-\mathrm{d}[\mathrm{AN}]/\mathrm{d}t = k_1[\mathrm{AN}][\mathrm{APS}] + k_2[\mathrm{AN}][\mathrm{P}] \qquad (2)$$

where [P] = equivalent concentration of polymer. They reported that the value for k_2 depended primarily on acid concentration, while k_1 was affected by the presence of catalyst and the initial reactant concentration; k_2 has a value about 2–3 orders of magnitude higher than k_1, indicating that polymerization occurs much faster on precipitated polymer than on monomer. Under our reaction conditions, the reaction temperature increases as the polymerization proceeds, and the temperature change of the reaction medium can be as high as 26 °C. Since the reaction rate constant is dependent on temperature, accurate kinetic modeling is not possible in our system. Still, our results appear to qualitatively fit the empirical kinetic equation 2. As seen in Figure 1, the induction period for polymerization is reduced as the concentration of oxidizing agent APS increases. During the induction period, the second term in eq 2 is very much smaller than the first term because the concentration of polymer ([P]) is extremely small. So, the reaction in the induction period is mainly governed by the first term, which is first order in concentration of aniline and first order in concentration of APS. As soon as oligomer is formed, the second term becomes dominant, which does not include the oxidizing agent concentration. Most of the reaction heat for this polymerization reaction is given off at the second step, and this temperature "jump" is finished almost within the same time period for reactions using widely different APS/AN ratios.

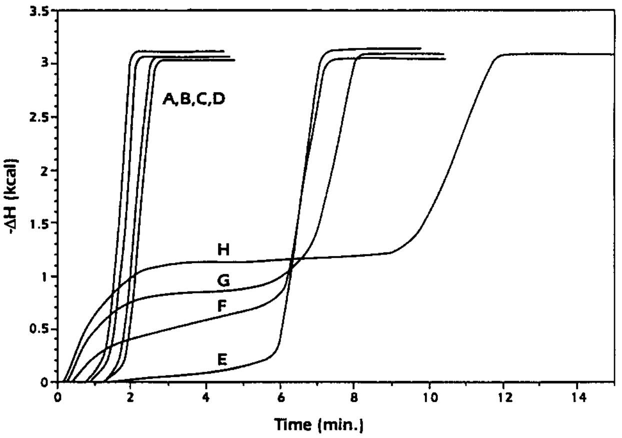

Figure 3. Enthalpy change vs time profiles for polymerization of aniline in different acid concentrations. Ratio of [APS]/[AN] was initially 0.375 M/0.300 M. Curves were obtained with initial acid concentrations (initial pH) of (A) 3.00 M (<0), (B) 1.00 M (0.5), (C) 0.50 M (1.0), (D) 0.40 M (1.9), (E) 0.30 M (4.3), (F) 0.20 M (4.7), (G) 0.10 M (5.0), (H) 0.010 M (6.1).

The influence of acid concentration on the polymerization of aniline is shown in Figure 3. Although the thermograms differ very much from low acid concentrations to high ones, the heat of the polymerization is exactly the same. FTIR spectra indicate that the final polymer products synthesized in acidic and relatively neutral media have similar structures. However, the polymerization kinetics are very different, possibly indicating a change in polymerization mechanism as a result of the change in pH of the reaction media. At low acid concentrations (pH ≥ 4.2; Figure 3, curves E–H), the polymerization proceeds in two steps, where each step gives off varying amounts of heat depending on the acid-to-aniline ratio. Very short induction times appear with these reactions, although there is a long delay between the first heat evolution and the second. This delay time is clearly dependent on pH of reaction media. Also, heat is given off more slowly in the first step, this means that polymerization goes slowly and may indicate that proton transfer is important.[7] UV–vis solution spectra of the aniline polymerization in acidic media (pH < 2) and relatively neutral media (pH > 5) are shown in Figures 4 and 5, respectively. In the acidic reaction media, two peaks at 330 and 640 nm were observed. The absorption at 330 nm is from the π–π^* excitation of the para-substituted benzene segment (–B–NH–B–NH–B–), and the absorption at 640 nm is from the excitation of the quinone diimine structure (–N═Q═N–).[24,25] However, in neutral media, the UV–vis spectra are different. An absorbance first appears at ~430 nm and the intensity increases as the reaction proceeds. Studies were recently carried out on oligomers of polyaniline in order to understand how the UV spectra of the polymer changes as a function of the oxidation states of polyaniline.[24-28] For example, *N*-phenyl-*p*-phenylenediamine (B–NH–B–

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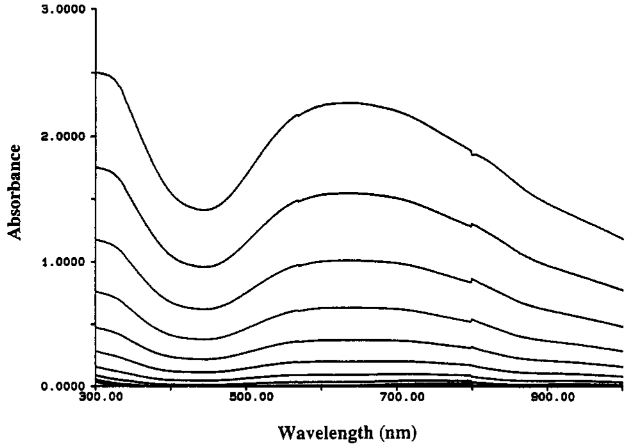

Figure 4. UV–vis solution spectra of *in situ* polymerized aniline in aqueous 1 M HCl, where initial [APS]/[AN] = 0.018 75 M/0.015 M; each scan interval was 2 min.

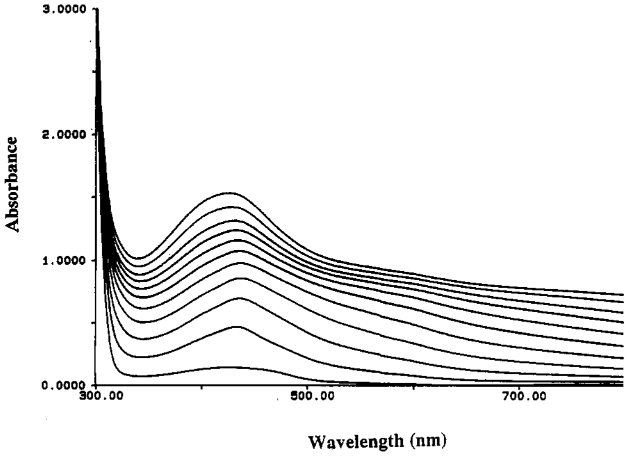

Figure 5. UV–vis "solution" spectra of *in situ* polymerized aniline in dilute acid (0.005 M HCl, initial pH 5.1) with initial [APS]/[AN] = 0.018 75 M/0.015 M; each scan interval was 2 min.

NH_2) is a dimer of aniline with an absorption peak around 300 nm. When this compound is oxidized to *N*-phenyl-1,4-benzoquinone diimine (B–N=Q=NH), it has an absorption peak around 430 nm. The absorption peak for the quinoid unit (–N=Q=N–) is red shifted as the chain length increases.[25] To obtain an intermediate from neutral reaction media, a reaction was quenched with aqueous ammonium hydroxide solution at the beginning of the polymerization. Isolated material exhibited a low melting point (~220 °C) and UV–vis spectrum with an absorption maximum at 430 nm (Figure 6). This material is characteristic of low molecular weight polyaniline oligomer with an oxidation state higher than that of emeraldine base.[26] The conductivities of protonated polymers synthesized at different acid concentrations are shown in Table 4. One can see that as the acid concentration of the reaction medium decreases (pH increases), the conductivities of the fully doped products decreases, where conductivities drop off rapidly for polymers prepared at pH's > 4.6, the pK_a of aniline. The low conductivity of doped polymers from reaction media with pH > 4 is possibly caused by the observed low molecular weight and high oxidation state of the products. Low molecular weight polymers reduce in-chain conjugation lengths, and polyaniline in high oxidation states is not very conductive.[26,29]

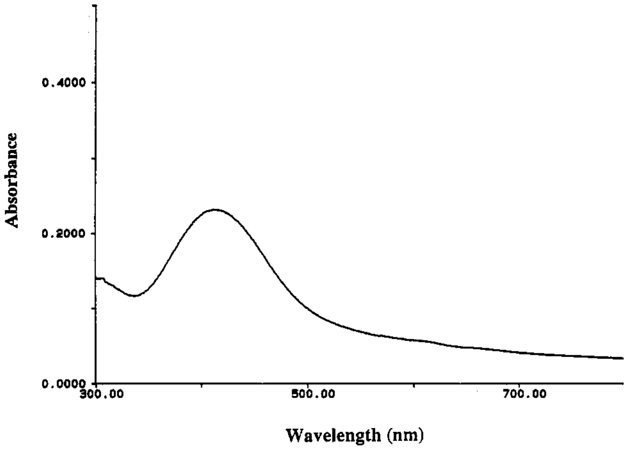

Figure 6. UV–vis spectrum of neutralized intermediate quenched from the polymerization of aniline (0.300 M) with APS (0.375 M) in 0.010 M aqueous HCl solution (initial pH 6.1).

Table 4. Conductivities of Polyaniline Samples (Pressed Pellets) Synthesized at Different Acid Concentrations, [APS]/[AN] at 0.375 M/0.300 M

[HCl] (M)	1.00	0.50	0.40	0.30	0.20	0.10	0.01
initial pH	0.5	1.0	1.9	4.2	4.7	5.0	6.1
σ (S/cm)[a]	6.4	4.9	2.5	1.5	0.53	0.1	0.036

[a] After treating with 1.0 M HCl for ca. 6 h and vacuum drying.

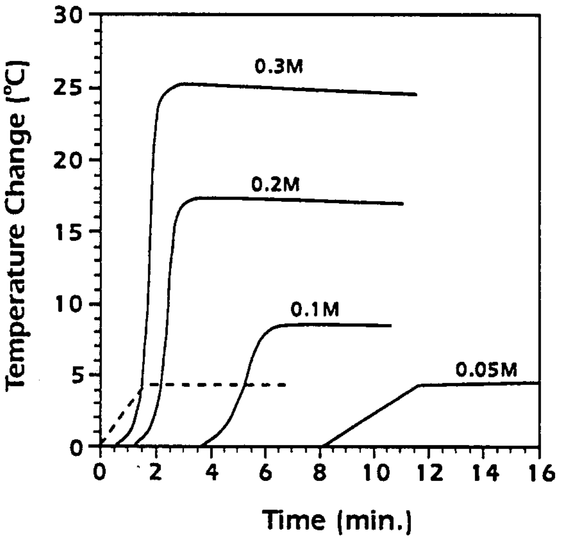

Figure 7. Temperature vs time profiles for reactions of aniline with APS in 1.00 M HCl at different initial aniline concentrations; initial ratio of [APS]/[AN] was 1.25/1.00. Curves were obtained for reactions at aniline concentrations of (A) 0.300 M, (B) 0.200 M, (C) 0.100 M, (D) 0.050 M. The dashed curve is for the same reaction as (D) with *N*-phenyl-*p*-phenylenediamine present at 0.005 M.

Figure 7 shows reaction thermograms obtained with different initial aniline monomer concentrations in acidic media. The initial molar ratio of APS to AN was kept constant (1.25), and the total heat given off was found to be directly proportionally to the initial aniline concentration, as shown by the data in Table 5. This is further evidence that AN is stoichiometrically transformed into polymer. As seen in Figures 7 and 8, the larger the concentration of reactants, the less the induction time, and the shorter the time taken for the major exotherm.

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Table 5. Heat Produced from the Polymerization of Aniline at Various Initial Aniline Monomer Concentrations in 1.00 M HCl, Where Initial [APS]/[AN] Was Constant at 1.25/1

[AN] (M)	0.050	0.100	0.200	0.300
ΔT (± 0.05 °C)	4.25	8.75	17.5	26.0
q (kcal)	0.513 ± 0.006	1.06 ± 0.006	2.11 ± 0.007	3.14 ± 0.008
$\Delta H = -q/\text{AN}$ (kcal/mol of AN)	−103 ± 2	−106 ± 2	−106 ± 2	−105 ± 2
$\Delta H = -q/\text{APS}$ (kcal/mol of APS)	−82.1 ± 1.5	−84.6 ± 1.5	−84.6 ± 1.5	−83.8 ± 1.5

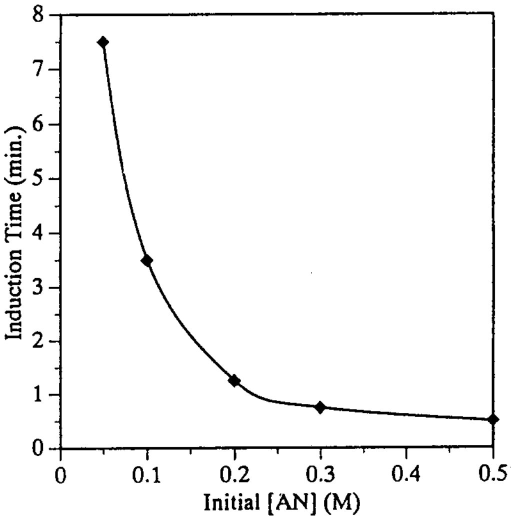

Figure 8. Plot of induction time vs initial aniline concentration in 1.00 M HCl with initial [APS]/[AN] = 1.25/1.00. Points are from Figure 7; the solid curve is the empirical fit to the data using eq 3.

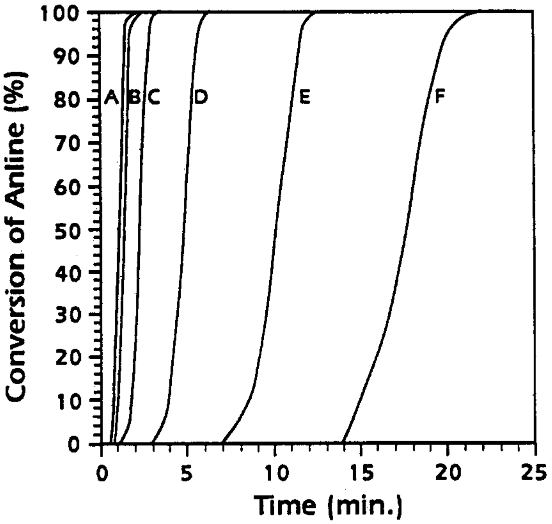

Figure 9. Plot of conversion vs time for reactions using different initial aniline monomer concentrations in 1.00 M HCl; initial molar ratio of [APS]/[AN] = 1.25/1.00. Plots correspond to initial aniline concentrations of (A) 0.500 M, (B) 0.300 M, (C) 0.200 M, (D) 0.100 M, (E) 0.050 M, and (F) 0.030 M.

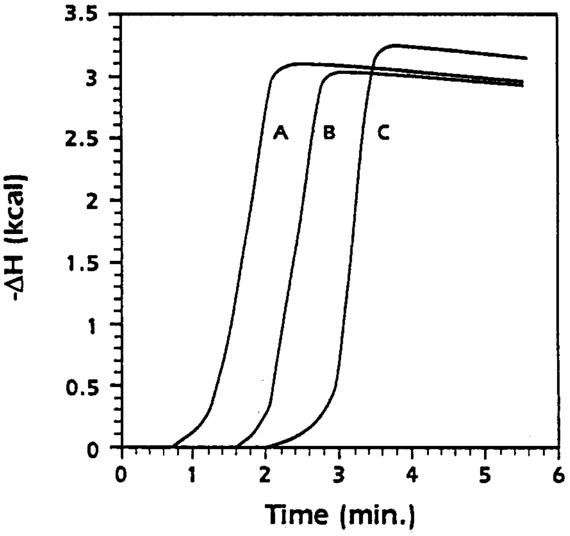

Figure 10. Reaction thermograms for the polymerization of aniline in various acid media, where the initial [APS]/[AN] ratio was 0.375 M/0.300 M. Polymerizations were run in (A) 1.00 M HCl, (B) 1.00 M H_2SO_4, and (C) 1.00 M p-$CH_3C_6H_4SO_3H$.

These observations are again qualitatively consistent with the kinetic model (eq 2). Curve fitting (correlation coefficient is 0.999) shows that the induction time, t_{in}, is inversely proportional to the initial aniline concentration, and the relation can be expressed as

$$t_{\text{in(min)}} = 0.40/[\text{AN}]_0 - 0.525 \qquad (3)$$

for aniline polymerized in HCl solution with an APS to AN ratio of 1.25:1. We expect similar linear relationships to exist for reactions using other APS to AN ratios <1.25:1. This suggests that the rate of formation of the initiating species causing the rapid exothermic polymerization is second order. This would be qualitatively consistent with the formation of an aniline dimer as the initiating species. If this assumption is correct, then by the addition of a small amount of aniline dimer, *N*-phenyl-*p*-phenylenediamine, to the reaction mixture before the addition of APS, the time required for the onset of the exothermic polymerization reaction should be dramatically reduced.[31-35] This is what has been observed, as shown by the dashed curve in Figure 7, which is the thermogram for the same reaction as for curve D but with a small amount of the aniline dimer present (0.005 M). With the dimer present, the induction time is essentially zero. The induction time was also found to be very dependent on the nature of the acid used (*vide infra*).

Assuming that the heat produced is directly proportional to the conversion of monomer to the polymer, one can use the thermal data to determine aniline conversion versus time, as shown in Figure 9. The shapes of the curves in Figure 9 are qualitatively very similar to those obtained by Gregory *et al.*[23] However, precise kinetic models can not be obtained from our data because of the widely varying reaction temperatures. Nonetheless, monitoring the heat of reaction should allow one to essentially follow continuously the conversion of aniline to polymer in the reaction.

Figure 10 displays reaction thermograms from reactions run using different acid media: HCl, H_2SO_4, and p-$CH_3C_6H_4SO_3H$ (PTSA), all at concentrations of 1.0 M. The heat of polymerization was found to be similar for all

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three acid systems. Observed minor differences may be caused by some slight morphological differences (degree of crystallinity) and molecular packing arrangements in the lattice between samples polymerized in the presence of different acid (dopant) types. In this respect, it is noteworthy that the heat of polymerization of aniline in PTSA is slightly greater than that for HCl and H_2SO_4. This suggests that polyaniline doped with PTSA might be more stable than the corresponding HCl- and H_2SO_4-doped complexes of polyaniline, which in fact has been observed.[30] Careful inspection of these curves reveals that both the onset for polymerization and the rate of polymerization depend on the chemical nature of the acid medium. The most pronounced effect is on induction time where the larger the acid counter ion (Cl^- vs $H_2SO_4^-$ vs $CH_3C_6H_4SO_3^-$), the longer the induction time. This suggests that the rate-limiting step in the polymerization of aniline in acidic media might involve diffusion of tight ion pairs of an oxidized aniline species (radical cation) and the acid anion. Thus, diffusion of these species to form the aniline dimer, *N*-phenyl-*p*-phenylenediamine (or its oxidized form) might be the rate-limiting step for the exothermic polymerization of aniline since it is known that oxidative polymerization of aniline occurs readily in the presence of *N*-phenyl-*p*-phenylene diamine.[31-35]

Conclusions

Chemical oxidative polymerization of aniline is a highly exothermic reaction, with an enthalpy change of −105 ± 1 kcal/mol of AN. Although the heat of reaction is largely invariant, the final polymer product is heavily dependent on the reaction conditions, such as APS to AN ratio and acid concentrations. The thermograms of polymerization of aniline show that the polymerization rate is dependent on the initial AN and APS concentrations. The larger the concentration of AN and/or APS, the less the induction time. The observed induction period for reactions in 1 M HCl with an [APS]/[AN] ratio of 1.25 follows the relationship $t_{in} = 0.40/[AN]_0 - 0.525$. The addition of *N*-phenyl-*p*-phenylenediamine results in the complete elimination of the induction period. In other acidic media, induction times are different and are dependent on the nature of the acid anion. Larger anions provide longer induction times. It is postulated that the rate-limiting step is the formation of an aniline dimer from oxidized aniline monomers.

The thermograms from aniline polymerization at various acid concentrations are dramatically different. In the acidic reaction media, the polymerization is finished essentially in one step. However, in relatively neutral reaction media, the reaction appears to proceed in two steps, and more slowly. UV–vis spectra during polymerization suggests that the products formed in neutral media are low molecular weight oligomers of aniline, whereas in acidic media the emeraldine form of polyaniline is rapidly formed.

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