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Polymerization of 2-Pentadecylaniline Monolayers at Fluid Surfaces: Kinetics, Thermodynamics, and Mechanism

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Abstract: Monolayers of 2-pentadecylaniline were polymerized at the air/aqueous acid interface using ammonium persulfate as the oxidizing agent. Isotherms of 2-pentadecylaniline were measured on a 0.1 M sulfuric acid subphase at different temperatures. The mean molecular area at the surface pressure onset was found to increase with temperature. The effect of varying the applied surface pressure and temperature on the polymerization rate of 2-pentadecylaniline at the interface was investigated. Activation energy and other thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy of activation were calculated. The activation energy increased with increasing applied surface pressure. This result was interpreted in terms of intermolecular distances. The polymerization rate at the interface also increased with increasing applied surface pressure at a given temperature. Such experiments allowed the measurement of the activation area at a given temperature. The results cited above are used in interpreting the polymerization mechanism.

Introduction

Polyaniline is an electrically conducting polymer which has received much attention due to its chemical and thermal stability in the presence of oxygen and moisture even when doped.[1-4] Although first synthesized almost a century ago and known as "aniline black",[5-7] its potential electronic applications were not realized until its rediscovery by MacDiarmid *et al.*[8-13] It is also unique among all conducting polymers in that its electrical properties can be controlled by both the oxidation state of the main chain and the level of protonation.[14,15] It has also been found that polyaniline exhibits multiple color changes depending on both oxidation state and pH.[16-21] As a result, a number of potential applications have been reported for polyaniline.[11,22-34]

Polyaniline and its derivatives are generally synthesized by standard techniques in isotropic media. It can be prepared chemically using different oxidizing agents[8,35-38] or electrochemically in aqueous or nonaqueous media.[18,39-46] Synthesis of polyaniline by other methods such as gas-phase plasma techniques, polymerization in a two-phase system, and vapor deposition have been reported.[45,47] Another route toward the homogeneous polymerization of anilines involving a monomer–alkyl ligand complex has also been reported.[48]

Recently our group has polymerized some ortho-substituted anilines at the air/aqueous interface using the Langmuir–Blodgett (LB) technique.[49-52] In this technique, known amounts of amphiphilic monomer molecules are confined to a planar aqueous

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surface, which defines their orientation and intermolecular distances during the reaction. Since the surface is fluid, the molecules can be manipulated in a Langmuir trough yet are free to reorient within the monolayer upon reacting. The reaction then occurs under anisotropic conditions caused by the surface-oriented monomer. The polymer chains in the resulting monolayer may have enhanced long-range configurational, orientational, and positional ordering and higher anisotropic properties compared to those of polymers synthesized by conventional methods. The LB technique has further advantages: First, the average distance between reacting molecules can be easily changed by varying the temperature and applied surface pressure. Second, kinetics can be followed in real time by observing the change in the average surface area occupied by a monomer or repeating unit of the polymer backbone. Under conditions of constant surface pressure, this is analogous to volume dilatometry[53] in two dimensions, where the mean molecular area takes the place of the specific volume.

Although a large number of papers on the preparation and properties of polyaniline have been published, the kinetics and polymerization mechanism are still under discussion. After the formation of a dimer by coupling of two monomer radical cations, the method by which these species propagate to polymer is not clearly understood.[35,39,43,46,48,54–63]

In order to understand this reaction mechanism, it is important to know the nature of the activated complex (transition state). In classical synthetic techniques, the volume of activation is an experimentally accessible quantity which is easier to interpret than the free energy, enthalpy, or entropy of activation. Mechanistic interpretations of organic reactions using activation volumes have been reported in the literature.[64–67] In spite of its importance in the elucidation of reaction mechanisms, however, only a small amount of work dealing with activation volumes has been reported. This is, in part, because determining activation volumes requires difficult experiments at high pressures. Here, as already noted, the LB technique has a distinct advantage because the mechanically applied surface pressure can be easily changed. As a result, the measurement of the activation area is greatly simplified.

In this paper, we report the activation energy, entropy of activation, and activation area of the 2-pentadecylaniline polymerization reaction occurring at the air/aqueous solution interface. The results will be interpreted in terms of the polymerization mechanism.

Experimental Section

The monomer, 2-pentadecylaniline, was synthesized using a published procedure.[68] It was purified by silica gel column chromatography with toluene as the mobile phase. 4-Hexadecylaniline and 4-tetradecylaniline were purchased from Aldrich (97% purity) and used as received after confirming purity. Purity of the spread compounds was checked by TLC and ^{1}H and ^{13}C NMR. Spreading solutions were prepared by dissolving the monomer in chloroform (Fisher, spectra grade). Spreading solution concentrations ranged from 0.5 to 1.0 mg/mL. Ammonium persulfate (ACS grade) was purchased from Aldrich and used without further purification. Subphase solutions were prepared with ACS reagent-grade chemicals and highly purified water (Millipore, $\geq$18-MΩ resistance). Before the experiments were started, all subphase solutions were cleaned of any potential surface-active impurities by aspirating the surface on the Langmuir trough. The surface was then considered clean if no measurable surface pressure changes were observed within 2 min.

The experiments were carried out on a commercially available Langmuir trough LB5000 (KSV Instruments, Finland) equipped with a computerized control and one or two barriers. Surface pressures were measured using the Wilhelmy plate film balance method with a platinum plate which was carefully prewetted and zeroed in a clean subphase prior to measurement. The interior trough surfaces and barriers were made of Teflon. The trough and subphase temperature was controlled by passing water from a constant-temperature bath through channels below the trough. The subphase temperature was measured by placing either a calibrated thermometer or a Teflon-coated thermocouple into the subphase; temperature stability was typically ±0.1 °C.

Unless otherwise noted, all isotherms were measured on a 0.1 M sulfuric acid subphase with no added oxidizing agent. Known amounts of monomer solutions were spread on the subphase using a microliter Hamilton syringe. After spreading, chloroform was allowed to evaporate from the surface for about 2 min. The resulting monolayer was then compressed at a constant rate of surface area change (9 Å^2 molecule^{-1} min^{-1}) with the help of a barrier. The change in surface pressure versus mean molecular area was computer recorded. Measurements were repeated at least three times; isotherm repeatability was better than ±1 Å^2 at a given surface pressure.

All isobaric stability measurements were made on a 0.1 M sulfuric acid subphase with no added oxidizing agent. Isobaric stability is defined here as the change in average surface area with time at a constant applied surface pressure. In these experiments, solutions were spread as described above. The resulting monolayer was compressed at 9 Å^2 molecule^{-1} min^{-1} until the desired surface pressure was reached. The applied surface pressure was kept constant during the experiment by displacing the barrier. After constant surface pressure was reached, the change in mean molecular area with time was recorded. Experiments were repeated at least three times; area change repeatability at a given time was better than ±5%.

All polymerization reactions were also carried out at constant applied surface pressure. In these experiments, the monomer was spread on a subphase consisting of a mixture of 0.1 M sulfuric acid and 0.03 M ammonium persulfate. Ammonium persulfate acts as an oxidizing agent, and it has been used for chemical polymerization of aniline and derivatives of aniline.[8,10,44,60] After spreading the monomer solution, chloroform was allowed to evaporate from the interface for 2 min. The resulting monolayer film was then compressed (90 Å^2 molecule^{-1} min^{-1}) until the desired applied surface pressure was reached. The pressure was kept constant during the entire reaction by changing the barrier position. The polymerization reaction was monitored either by measuring the change in mean molecular area or by measuring the average barrier speed. A reaction time of zero was taken to be the point at which the surface pressure reached the desired value. After the polymerization and between each experiment, the trough was cleaned first with a mixture of chloroform and ethanol and then, several times, with purified warm water. Polymerization experiments were repeated at least three times at surface pressures of 10 and 20 mN/m and twice at pressures of 15 and 30 mN/m. Typical repeatability of the time and magnitude of the barrier speed maximum at a given condition was better than ±2%.

Results and Discussion

Isotherms. Isotherms of 2-pentadecylaniline measured on a 0.1 M sulfuric acid subphase at three different temperatures (10, 25, and 40 °C) and on pure water at 25 °C are shown in Figure 1. In all experiments, no surface pressure was measurable at mean molecular areas higher than 90 Å^2/molecule. We will refer to the area at which the pressure becomes measurable as the surface pressure onset. The onsets for 2-pentadecylaniline on water and 0.1 M sulfuric acid at 25 °C were 47.7 and 74.6

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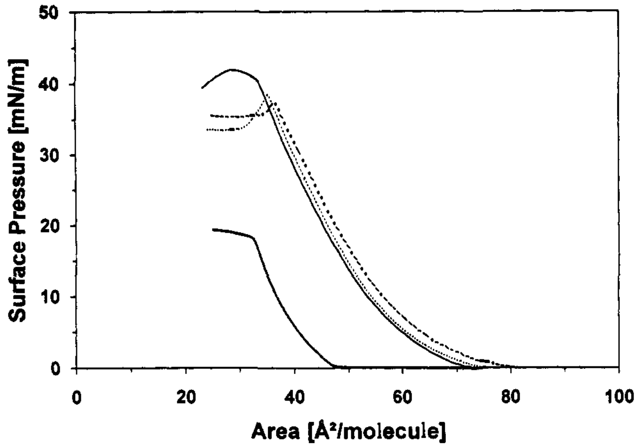

Figure 1. Surface pressure vs area isotherms of 2-pentadecylaniline on water (boldface curve) at 25 °C and on a 0.1 M H_2SO_4 subphase at 10 °C (—), 25 °C (···), and 40 °C (- - -). Monolayers were compressed from one side only with a compression speed of 9 Å² molecule⁻¹ min⁻¹.

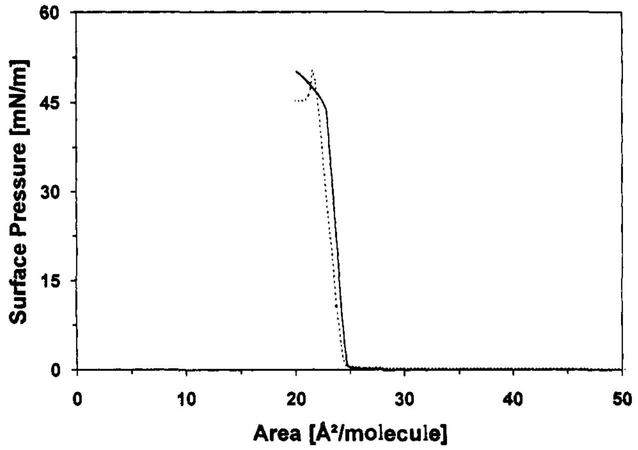

Figure 2. Surface pressure vs area isotherms of 4-hexadecylaniline on water (···) and on a 0.1 M H_2SO_4 (—) subphase at 25 °C. Monolayer films were compressed from one side only with a compression speed of 9 Å² molecule⁻¹ min⁻¹.

Å²/molecule, respectively. Upon further compression, a monotonic increase in surface pressure was observed at all conditions investigated. Mean molecular areas at the collapse point for 2-pentadecylaniline on water and 0.1 M sulfuric acid were 32.5 and 35.2 Å²/molecule, respectively, at 25 °C. The isotherms show that the films are highly compressible and that the compressibility increases with subphase acidity, while the collapse area is not highly affected. Compression and subsequent expansion also showed little hysteresis below the collapse pressure at all temperatures. The isotherms show that the mean molecular area at the surface pressure onset (73.7, 74.6, and 84.4 Å²/molecule at 10, 25, and 40 °C, respectively) as well as at any given surface pressure increases as the subphase temperature increases. Otherwise, isotherms at different temperatures look similar except in the collapse region. The collapse pressure (41.4, 39.2, and 37.6 mN/m for 10, 25, and 40 °C at 9 Å² molecule⁻¹ min⁻¹ compression speed) decreases slightly as the temperature increases. In addition, isotherms at 25 and 40 °C have well-defined collapse points while the isotherm at 10 °C has a broad collapse region. This may be due to different collapse mechanisms.

The temperature effects cited above are expected when the monolayer is in a liquid expanded state. At surface areas greater than 90 Å²/molecule, molecules at the interface are thought to be lying flat, far apart from each other, with negligible interaction between them. Brewster angle microscopy,[69,70] a powerful technique for looking at monolayer morphology and homogeneity, performed on a 2-pentadecylaniline monolayer at the air/0.1 M sulfuric acid interface showed that the film was homogeneous, not birefringent, and free from domains during compression from 90 Å²/molecule until collapse. At higher surface pressures, the change in surface area with temperature is likely to be due to an increase in the van der Waals repulsion, causing the aniline molecules to occupy a larger surface area.

Figure 2 shows isotherms of a homologue of the para isomer, 4-hexadecylaniline, on water and 0.1 M sulfuric acid subphases at 25 °C. The para isomer spread well and gave reproducible isotherms which showed little hysteresis upon expansion below collapse. The surface pressure onsets were 24.6 and 24.9 Å²/molecule on water and 0.1 M sulfuric acid at 25 °C. Collapse was observed at areas of 21.6 and 22.8 Å²/molecule, respectively. 4-Tetradecylaniline was investigated, and its isotherms showed similar surface areas in its condensed region. Isotherms of 4-hexadecylaniline were also obtained on aqueous HCl and NaOH subphases. The surface pressure onsets on water as well as on 0.1 M HCl and 0.001 M NaOH subphases were very similar. The 0.1 M HCl subphase results agreed, within experimental error, with results previously reported by Adam.[71] At 1 M HCl concentration, the results differed from those reported by another group,[72] though at surface pressures higher than 30 mN/m, the monolayer appeared to show condensed phases in both studies. It should be mentioned that *n*-alkylamines, under acidic conditions, are also known to have similar surface areas in the condensed region of the isotherm.[73,74]

Comparing the ortho and para compounds on water reveals a difference of more than 20 Å²/molecule in the onset areas. Additionally, the isotherm of 4-hexadecylaniline shows a compressibility substantially lower than that of the ortho-substituted monomer. The observed surface areas and low compressibility imply that the alkyl side chains of the para-substituted monomer are well-aligned and tightly packed near its collapse point. This type of packing is possible when the chains are in a predominantly *trans* conformation. The isotherm of 2-pentadecylaniline indicates that it is highly compressible, and the higher surface areas observed near collapse indicate that the side chains do not achieve a close-packed conformation. In addition, the surface pressure onset occurred at a larger area than in 4-hexadecylaniline. As 2-pentadecylaniline and 4-hexadecylaniline are chemically similar, the difference in the surface pressure onset is due largely to the substitution position.

A small area increase was observed for the para compound upon decreasing the subphase pH. Nonetheless, in 0.1 M sulfuric acid the monomer is protonated and exists as an anilinium cation. This result implies that the surface pressure observed upon compression is not strongly affected by Coulombic repulsion between anilinium ions. Therefore the increase in the surface pressure onset of the ortho-substituted monomer with subphase acidity is unlikely to arise from similar Coulombic repulsion between protonated head groups. If this were the case, the surface pressure onset for the para-substituted monomer should also shift to substantially higher areas with increasing subphase acidity.

The details of molecular arrangements which lead to monolayer behavior are not well-known. It has been shown that, in condensed films, molecules have close-packed, well-aligned conformations with high positional and orientational order, while in gaseous films they are widely separated with no long-range orientational or positional order. Apparently, the molecular conformation in these expanded films is intermediate between these two extremes.[75]

In the case of the ortho-substituted monomer, it is likely that the polar amine group is hydrated and disposed toward the aqueous

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Table I. Stability of 2-Pentadecylaniline Monolayers on a 0.1 M Sulfuric Acid Subphase at Different Temperatures and Surface Pressures[a]

appl surf. press. (mN/m)	temp (°C)	change in area in 15 min (Å^2/molecule)
30	10	0.86
	25	1.43
	32.5	2.36
	40	6.16
10	10	0.23
	25	0.44
	40	1.9

[a] These values were calculated 5 min after the surface pressure reached the measurement value.

subphase, while the alkyl side chain is "dewetted" during compression and likely to be oriented away from the surface toward the air.[50] As the amine and alkyl groups are attached to adjacent ring carbons, the first few carbons of the alkyl chain probably adopt *gauche* conformations to allow the chain to leave the water surface. Once protonated by an acidic subphase, the conformation of 2-pentadecylaniline molecules may change due to hydration forces which would tend to pull the anilinium ion formed further downward into the subphase and cause more *gauche* conformations in the alkyl side chain, increasing the net surface area occupied per monomer.

In the case of the para-substituted moiety, the amine group is easily disposed toward the subphase due to its favorable position on the aromatic ring. For steric reasons, the plane of the aromatic head group is expected to be perpendicular to the air/water interface instead of lying flat on the surface. The alkyl side group is able to protrude from the plane of the interface and pack in a largely *trans* conformation. Packing of the para compound in acidic solution is quite similar. This accounts for the differences between the isotherms of 2- and 4-substituted anilines in aqueous and acidic subphases.

Isobaric Stability. Isobaric stability experiments were performed on a 0.1 M sulfuric acid subphase at different temperatures and applied surface pressures. Measurements were started 5 min after the surface pressure reached the desired value to allow the molecules to relax and equilibrate. Stability values, shown in Table I, are the changes in the apparent mean molecular areas measured every 15 min, a time period selected because most of the polymerization reactions reached their maximum rate before this time. Stability at a given surface pressure decreases with increasing temperature and increases with decreasing pressure at a given temperature. Results also indicate that the 2-pentadecylaniline does not form a stable Langmuir film at 40 °C and 30 mN/m of surface pressure. Polymerization of 2-pentadecylaniline under these conditions was not successful. Under all other conditions, the isobaric creep values were sufficiently small to make rate constant calculations possible.

Polymerization. Figure 3 shows monolayer polymerization results for 2-pentadecylaniline at 20 mN/m of surface pressure and 25 °C. The polymerization was carried out on a subphase containing a mixture of 0.1 M H_2SO_4 and 0.03 M $(NH_4)_2S_2O_8$. The reaction was monitored by measuring the change in mean molecular area and the average barrier speed (the rate of barrier displacement needed to maintain isobaric conditions) with time. The monotonic decrease in area during polymerization is due to the replacement of van der Waals radii by covalent bonds between monomer molecules and changes in their conformation.[49,50] It should be noted that the surface area after polymerization in Figure 3 is in close agreement with the isotherms of Figure 2. Also, after polymerization, the monolayer film could be expanded and recompressed below collapse repeatedly with very little hysteresis. During polymerization, the average barrier speed increased from an initial value of zero, reached a maximum value, and then decreased to a zero or negligible value. Almost no induction period was observed before the barrier speed increased.

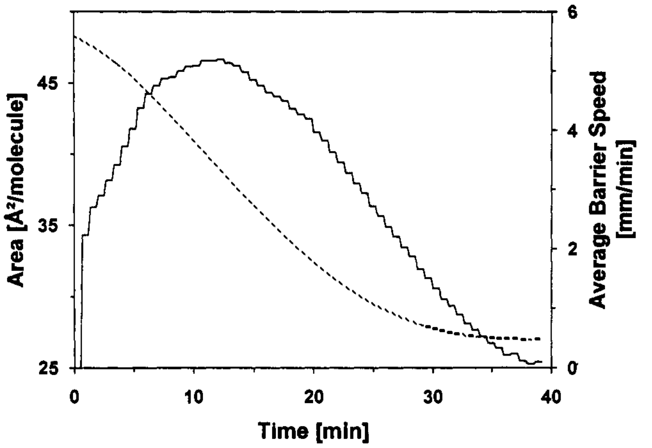

Figure 3. Area (- - -) and average barrier speed (—) vs time during the Langmuir film polymerization of 2-pentadecylaniline at 25 °C and 20 mN/m applied surface pressure. The subphase was a mixture of 0.1 M H_2SO_4 and 0.03 M $(NH_4)S_2O_8$. Initial compression speed was 90 Å^2 molecule^{-1} min^{-1}.

When the change in the area with time was negligible or the barrier speed dropped to zero, the reaction was considered completed. Thus, this technique allows the study of the reaction kinetics in real time by observing the change in the average surface area occupied by a monomer or repeating unit of the polymer backbone.

Aniline and substituted anilines are known to undergo polymerization via an oxidative coupling mechanism. It has also been reported that the dimer, trimer, oligomers, and higher polymers have lower oxidation potentials than the monomer. So, once oligomers are formed in the reaction medium they can oxidize faster than the monomer and the reaction rate accelerates. Thus, when aniline is polymerized by classical techniques, two phenomena have been observed: an induction period of the order of 10–30 min and, then, an acceleration in the overall reaction rate. By adding catalytic amounts of dimer to a reaction medium containing monomer, Wei and co-workers found that the polymerization could be carried out below the oxidation potential of aniline and the induction period decreased.[62]

The above mentioned increase in the overall polymerization rate from its initial value has been termed "auto-acceleration".[59,61] As shown in Figure 3, auto-acceleration is also seen during the Langmuir film polymerization of 2-pentadecylaniline. A difference observed between this method and classical aniline polymerization, however, is that there is almost no induction period.

The maximum values of the barrier speed and the corresponding area were chosen to calculate the polymerization rate and the rate constant. The barrier speed maximum was used because it is reproducible and gives an estimation of the overall reaction kinetics at the air/aqueous solution interface.

The rate constant was derived as follows. The relationship between the average barrier speed, BS, and the change in the mean molecular area with time, $\partial A/\partial t$, is given by

$$\mathrm{BS} = (L/A_0)\, \partial A/\partial t \qquad (1)$$

where L is the length of the trough and A_0 is the initial mean molecular area. But $L/A_0 = N/W$; therefore

$$\mathrm{BS} = (N/W)\, \partial A/\partial t \qquad (2)$$

where N is the number of monomer molecules spread on the subphase and W is the width of the trough.

According to Gee and Rideal,[76–78] the rate at which a monolayer polymerizes at an air/aqueous acid interface can be expressed as

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(76) Gee, G.; Rideal, E. K. *Trans. Faraday Soc.* **1935**, *31*, 969.
(77) Gee, G. *Trans. Faraday Soc.* **1936**, *32*, 187.
(78) Gee, G. *Proc. R. Soc. London* **1936**, *A153*, 129.

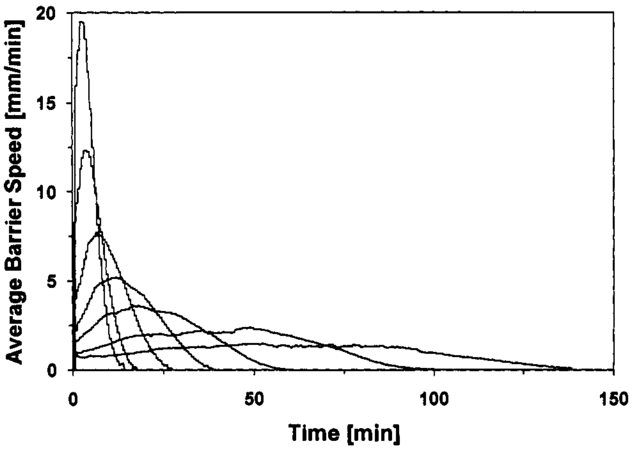

Figure 4. Average barrier speed vs time during the Langmuir film polymerization of 2-pentadecylaniline at 20 mN/m applied surface pressure and different temperatures. The subphase was a mixture of 0.1 M H_2SO_4 and 0.03 M $(NH_4)S_2O_8$. Initial compression speed was 90 Å^2 molecule^{-1} min^{-1}. Curves correspond to temperatures of 10, 15, 20, 25, 30, 35, and 40 °C from right to left, respectively.

$$\partial A/\partial t = k[(A_0 - A)(A - A_\infty)/(A_0 - A_\infty)] \tag{3}$$

where A is the mean molecular area at any time during the reaction, k is the rate constant at a given pressure and temperature, and A_∞ is the mean molecular area of the product.

Equation 3 was derived using the following assumptions. Products remain at the interface during the reaction. Molecular areas of reactants and products are additive. Coupling of monomers, or of a monomer to a growing polymer chain, or of one reactive chain to another, results in a constant area change. Reactant concentrations are a constant in the vicinity of the reacting molecules.

By combining eqs 2 and 3, one obtains the following:

$$\mathrm{BS} = (N/W)k[(A_0 - A)(A - A_\infty)/(A_0 - A_\infty)] \tag{4}$$

$$\therefore\ k = [10^{14}W(\mathrm{BS})/N][(A_0 - A_\infty)/(A_0 - A)(A - A_\infty)] \tag{5}$$

The units of k in eq 5 are found to be min^{-1}, which indicates that the reaction follows first-order kinetics. Both chemical and electrochemical polymerizations of aniline, however, have been found to be first order in monomer concentration and concentration of polymer formed.[61,63] In the monolayer polymerization, though, the rate constant is normalized by the monomer concentration and thus it follows pseudo-first-order kinetics.

Activation Energies. In order to elucidate the effect of temperature on polymerization kinetics, reactions were carried out at different temperatures and at 20 mN/m surface pressure. The results are shown in Figure 4.

It can be seen from the figure that the maximum barrier speed increases and the time required to complete the reaction decreases with the subphase temperature. According to the Arrhenius law,

$$\ln k = \ln A - E_a/RT \tag{6}$$

a plot of ln k vs T^{-1}(K^{-1}) for the Langmuir film polymerization of 2-pentadecylaniline is shown in Figure 5.

This plot is linear, indicating that the reaction obeys the Arrhenius law. The activation energy was calculated from the slope according to eq 6. As shown in Table II, the activation energy at 20 mN/m was 66 kJ/mol.

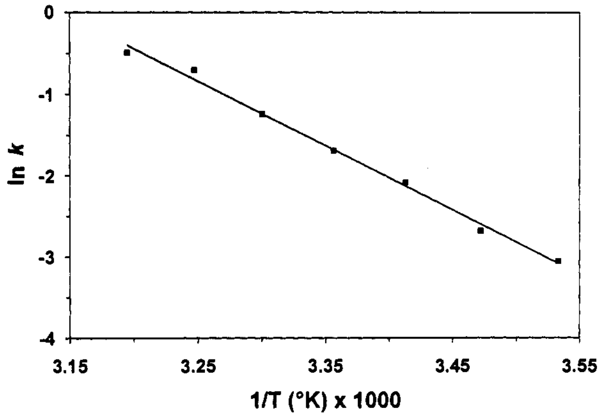

Figure 5. ln k vs $1/T$ (K^{-1}) plot for monolayer polymerizations at 20 mN/m applied surface pressure. A linear regression method was used to draw a straight line from experimental data.

Table II. Rate Constants and Thermodynamic Parameters for Polymerization of 2-Pentadecylaniline at Different Temperatures and Surface Pressures[a]

	temp (°C)	rate constant k (min^{-1}) 20 mN/m	15 mN/m	10 mN/m	30 mN/m
	10	0.0471			0.1277
	15	0.0685	0.0909	0.0786	0.1689
	20	0.1243	0.1301	0.1055	0.2372
	25	0.1837	0.1815	0.1505	0.3530
	30	0.2894	0.2956	0.2325	0.5464
	35	0.4971	0.4200	0.3261	
	40	0.6119		0.4400	
E_a (kJ/mol)		66	57	53	
pre-exp		7.2×10^{10}	2.11×10^9	3.52×10^8	
$\Delta H^\ddagger$ (kJ/mol)		62	53	50	
$\Delta S^\ddagger$ (J/K mol)		−87	−114	−127	
$\Delta G^\ddagger$ (kJ/mol)		87	87	88	

[a] The polymerization reactions were carried out on a subphase of 0.1 M sulfuric acid and 0.03 M ammonium persulfate.

This calculated activation energy is reasonable and falls within the range obtained by other research groups for the polymerization of unsubstituted aniline. The activation energies for aniline polymerized electrochemically and chemically have been found to be 64 and 87 kJ/mol, respectively.[61,48] However, the monomer used in this study was ortho substituted with an alkyl side chain and thus chemically different. Previous studies have also shown that the monomer film does not polymerize measurably without applied surface pressure.[49] Furthermore, the Langmuir polymerization of ortho-substituted anilines is independent of the alkyl side chain length in the range of 13–17 carbon atoms at applied pressures of 10, 20, and 30 mN/m. Thus, the steric bulk of the side chain does not appear to affect the monomer reactivity in the monolayer in this case. This can be understood as follows. As discussed in the isotherm section above, for Langmuir monolayers, the applied surface pressure dehydrates large portions of the alkyl side chain, therefore removing it from the vicinity of the reaction center. As such, activation energies similar to those of unsubstituted anilines are not surprising.

One might anticipate a lower activation energy for aniline monolayer polymerization as compared with a solution since the monomer is essentially pre-oriented before reaction. This might favor low energy pathways to the activated complex. In fact, the polymerization is completed faster in the monolayers than in solution, while the activation energies are similar. However, large changes in reaction rates may also occur because of differences in the pre-exponential factor. These differences result from losses in degrees of freedom for reactants and activated complexes in the monolayer compared with the solution or from changes in collision frequency. The reactants and activated complex in the monolayer have one degree of translational freedom and two degrees of rotational freedom, less than in bulk or solution. Thus the pre-exponential term is larger for a reaction in two dimensions than for a reaction in three dimensions. This, according to eq 6, causes the observed rate increase since activation energies for both cases are similar. Furthermore, systematic studies of other reactions in Langmuir monolayers of nonpolymeric compounds have not shown differences in activation energies between the monolayer and the bulk.[79] The large increase in the monolayer

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(79) Macritchie, F. *Chemistry at Interfaces*; Academic Press, Inc.: New York, 1990; p 41.

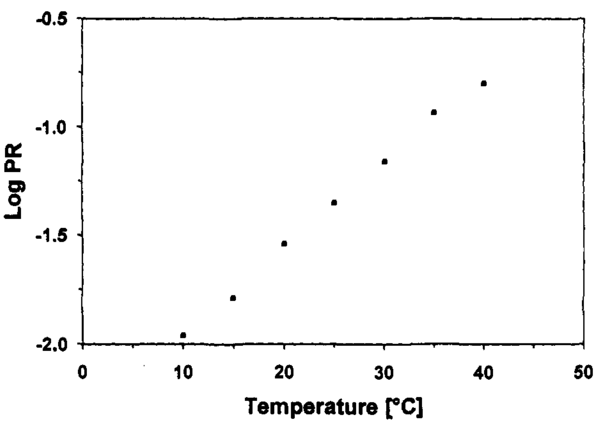

Figure 6. Logarithm of polymerization rate (PR) vs temperature for monolayer polymerization reactions at 20 mN/m surface pressure.

pre-exponential factor may be a reason for no induction period for the monolayer polymerization reaction.

Figure 6 shows a plot of the logarithm of polymerization rate (PR) versus T (°C). PR was calculated from the maximum barrier speeds using the following equation:[50]

$$PR = [10^{14}W(BS)]/[N(\Delta A)] \qquad (7)$$

where ΔA is the area change during the reaction in Å^2/molecule.

The units of PR are found to be reactions per minute. The polymerization rate increases monotonically with temperature. Such behavior is in agreement with the electrochemical results of Wei *et al.*[61] but differs from that predicted by Contractor *et al.*[80]

Langmuir film polymerization is one of the few techniques that allows the distance between reacting molecules to be varied while anisotropic orientations are maintained. In fact, it can be seen from Figure 1 that changing the applied surface pressure between 1 and 35 mN/m causes the monomer surface concentration to vary between 0.014 and 0.027 molecules/Å^2 on a 0.1 M H_2SO_4 subphase at 25 °C. Such concentration changes cannot be achieved easily by varying the pressure in a three-dimensional solution. From Figure 1, it can be seen that the surface concentration can also be varied, under isobaric conditions, by changing the subphase acidity (0.019 and 0.027 molecule/Å^2 at 10 mN/m surface pressure on 0.1 M H_2SO_4 and water at 25 °C, respectively). In this study, the monomer surface concentration was varied by changing the surface pressure. To measure the effect of the pressure (or surface concentration) on the activation energy, the polymerization of 2-pentadecylaniline was carried out at 10 mN/m, a lower pressure, as described above.

Figure 7 shows results for 2-pentadecylaniline polymerization at different temperatures and at 10 mN/m surface pressure. The barrier speed vs time plot shows a trend similar to that for the monolayer polymerization at 20 mN/m. From eq 7, it was also calculated that the polymerization rate increases with temperature.

A plot of ln k vs T^{-1} (K^{-1}) for the polymerization of 2-pentadecylaniline at 10 mN/m also exhibits a straight line, giving an activation energy of 53 kJ/mol according to eq 6. The activation energy thus decreased by 13 kJ/mol when the applied surface pressure was reduced by 10 mN/m (or the surface concentration was reduced by a factor of 0.85). Reductions in activation energies with decreases in interfacial pressure have also been reported for other reactions,[81,82] though their interpretation remains unclear. In this case, three possible explanations can be given as follows.

Figure 1 shows that decreasing the surface pressure at a given temperature increases the average distance between reacting molecules (for example, surface areas are 37.04 and 71.43 Å^2/molecule at 35 and 1 mN/m surface pressure, respectively). Thus, molecules have more freedom to change their orientation at low pressures, and they can reorient to lower energy conformations not possible at higher pressures. Second, an increase in the average distance between reacting molecules increases the probability of a persulfate ion diffusing to the interface and thus being able to oxidize monomer or growing polymer chain ends. Third, changes in the surface pressure may change the nature of the hydration shell around a monomer or growing chain end, thus modifying the reaction pathway by effectively changing the nature of the "solvent" around the aniline head group.

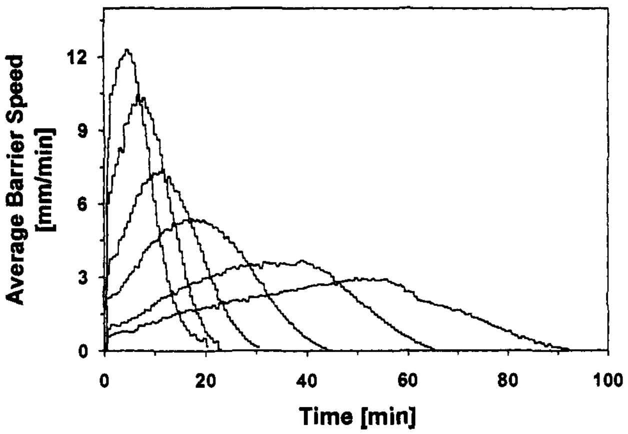

Figure 7. Average barrier speed vs time during the Langmuir film polymerization of 2-pentadecylaniline at 10 mN/m surface pressure and different temperatures. The subphase was a mixture of 0.1 M H_2SO_4 and 0.03 M $(NH_4)S_2O_8$. Initial compression speed was 90 Å^2 molecule^{-1} min^{-1}. Curves correspond to temperatures of 15, 20, 25, 30, 35, and 40 °C from right to left, respectively.

A decrease in activation energy generally results in an increased reaction rate. In this study, however, the opposite effect is observed; the polymerization rate was found to increase with an increase in the applied surface pressure at a given temperature. This indicates that the polymerization rate is dominated by the pre-exponential term in eq 6 and not by the activation energy.

The pre-exponential term has two components: a steric factor and a collision frequency. At low surface pressures, molecules have more freedom to reorient to a sterically favorable position; thus the change in the steric factor should lead to an increase in the reaction rate. Yet the overall reaction rate was found to increase with surface pressure, even though the activation energy increased. This indicates that the collision frequency is the dominant component in the pre-exponential term.

An increase in the polymerization rate with pressure can be explained in terms of the collision frequency as follows. The collision frequency depends upon the population of molecules in a given area. The increase in the surface pressure at a given temperature increases the number of molecules per area and thus the collision frequency. Pre-exponential terms for the monolayer polymerization of 2-pentadecylaniline at 20 and 10 mN/m pressure were calculated from the intercepts of ln k vs T^{-1} (K^{-1}) plots. Values of the pre-exponential term for reactions at 20 and 10 mN/m pressure were 7.2×10^{10} and 3.5×10^{8}, respectively. For a gas-phase reaction, the pre-exponential term is used to measure the collision frequencies. In this study, the monolayer polymerization reaction occurs in a liquid expanded state, not a gas. For such a case, the pre-exponential term cannot be used for a quantitative measurement of the collision frequencies. Nonetheless, qualitative comparisons can be made. For the monolayer polymerization at 20 mN/m, the pre-exponential term is 200 times greater than that for the reaction at 10 mN/m surface pressure. This argument can be used as an explanation for the increase in reaction rate with surface pressure at a given temperature.

The rationale presented above was further checked by carrying out the reaction at an intermediate surface pressure, 15 mN/m.

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(80) Gholamian, M.; Contractor, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *252*, 291.

(81) Davies, J. T. *Trans. Faraday Soc.* **1949**, *45*, 448.

(82) Alexander, A. E.; Rideal, E. K. *Proc. R. Soc. London* **1937**, *A163*, 70.

Results in Table II show that the polymerization rate increases with surface pressure even though there is an increase in the activation energy. These results provide further support for the above argument.

The reaction at 30 mN/m surface pressure also showed that the polymerization rate increases with temperature. The reaction at this pressure did not follow the Arrhenius law, however. Instead, a concave upward deviation from the straight line was observed. This indicates that at 30 mN/m the activation energy and the pre-exponential factor are temperature dependent and these values cannot be directly compared with those at other conditions.

Activation Enthalpies, Entropies, and Areas. From the activation energy, other thermodynamic parameters such as activation enthalpy ($\Delta H^‡$), activation entropy ($\Delta S^‡$), and Gibbs free energy of activation ($\Delta G^‡$) can be calculated. Of the two principal activation parameters, enthalpy and entropy, it is the entropy that can be used as a probe of important mechanistic details.[83] Whereas activation enthalpy is calculated from the temperature dependence of the reaction rate, the entropy is deduced from the absolute value of the rate constant once the enthalpy is known. It has been shown that the activation enthalpy can be calculated from the Arrhenius activation energy by subtracting the RT term:[83]

$$E_a = \Delta H^‡ + RT \tag{8}$$

where E_a is the activation energy, $\Delta H^‡$ is the activation enthalpy, R is the gas constant, and T is the absolute temperature.

Equation 8, however, is valid only when there is no volume change during activated complex formation. If the volume change during the formation of an activated complex is significant, then eq 8 can be modified as follows:

$$E_a = \Delta H^‡ - P\Delta A^‡ + RT \tag{9}$$

where P is the applied surface pressure and $\Delta A^‡$ is the activation area, defined as the area change during the formation of the activated complex from reactants.

The $P\Delta A^‡$ term can be calculated using the following equation:

$$\ln k = k_0 - [(\Delta A^‡)/RT]P \tag{10}$$

where k_0 is the rate constant at zero surface pressure.

It can be seen that the effect of the applied surface pressure on the reaction rate depends on the sign as well as the magnitude of $\Delta A^‡$. If $\Delta A^‡$ is negative (i.e., there is a decrease in area when the activated complex is formed), increasing the surface pressure should increase the rate constant, and conversely if $\Delta A^‡$ is positive. In order to evaluate $\Delta A^‡$ and the pressure effect on the polymerization rate, monolayer polymerizations of 2-pentadecylaniline were carried out at different pressures and at 25 °C. Typical barrier speed results as a function of time are shown in Figure 8. Results indicate that the barrier speed maximum increases with the pressure at a given temperature. Figure 9 shows a plot of ln k vs applied surface pressure calculated from the maximum barrier speed and the corresponding area. The linear increase with pressure indicates that the area decreases during the formation of the activated complex.

In order to evaluate the magnitude of $\Delta A^‡$, ln k was plotted against the pressure as shown in Figure 9. According to eq 10, the slope is equal to $-(\Delta A^‡)/RT$. The value obtained for $\Delta A^‡$ was -16 Å^2/molecule. This is a large negative number.

It has been reported that unimolecular reactions result in small, generally positive, activation volumes, whereas bimolecular additions give activation volumes that are negative by at least several cubic centimeters per mole.[64] Evans and Polanyi pointed out that two distinct effects must be considered in connection with the interpretation of volumes of activation.[84] First, there may be a change, due to structural factors, in the area of the reactants themselves as they pass into the activated state. Bimolecular reactions lead to a decrease in area, while unimolecular reactions lead to an increase. Second, area changes can result from reorganization of the solvent molecules. Studies on classical reactions have led to the conclusion that, for reactions in which ions or relatively strong dipoles are involved, the solvent effects are generally more important than the structural ones.[85,86] By analogy, the negative value (-16 Å^2/molecule) of the activation area in this polymerization indicates that the activated complex is bimolecular in nature.

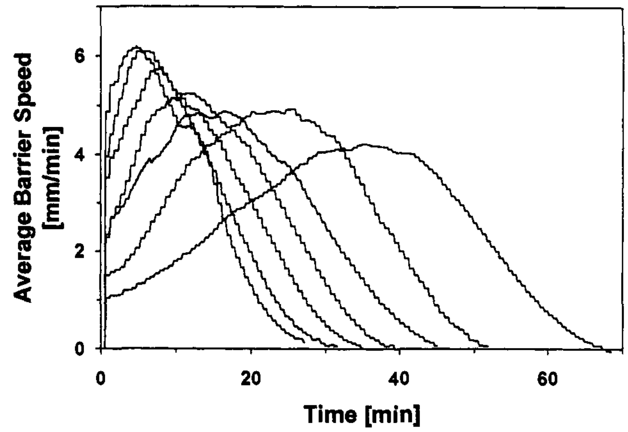

Figure 8. Average barrier speed vs time during the Langmuir film polymerization of 2-pentadecylaniline at 25 °C and various applied surface pressures. The subphase was a mixture of 0.1 M H_2SO_4 and 0.03 M $(NH_4)S_2O_8$. Initial compression speed was 90 Å^2 molecule^{-1} min^{-1}. Curves correspond to surface pressures of 5, 10, 15, 20, 25, 30, and 35mN/m from right to left, respectively.

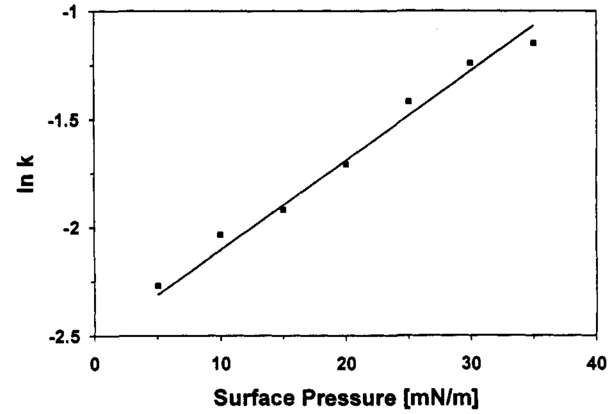

Figure 9. ln k vs surface pressure (mN/m) for monolayer polymerization reactions at 25 °C. A linear regression method was used to draw a straight line from experimental data.

A negative activation area can also be due to an approach of species with like charges during the formation of the activated complex. Hamann and his co-workers[85,87] have described this phenomenon as follows. If a reaction occurs with an intensification of the electric field (as when two ions of the same sign come together, or separate, or two neutral molecules react to form a polar activated complex), there will be a net contraction due to the binding of solvent molecules and therefore an increase in reaction rate with pressure. The effect of pressure may thus be interpreted in terms of the *electrostriction* of the solvent around ions and dipoles. So the large negative activation area and increase in reaction rate with applied surface pressure in this reaction indicate not only that the activated complex is bimolecular but also that like charges approach during activated complex formation.

By substitution of the value of the activation area in eq 9, enthalpies of activation were calculated and, from them, other

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[83] Lewis, E. S., Ed. *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; John Wiley and Sons Inc.: New York, 1974; Part 1, Vol. 6, p 421.

[84] Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 144.

[85] Buchanan, J.; Hamann, S. D. *Trans. Faraday Soc.* **1953**, *49*, 1425.

[86] Burris, C. T.; Laidler, K. J. *Trans. Faraday Soc.* **1955**, *51*, 1497.

[87] David, H. G.; Hamann, S. D. *Trans. Faraday Soc.* **1954**, *50*, 1188.

thermodynamic parameters such as Gibbs free energies of activation and, more significantly, the entropies of activation. These are shown in Table II. Clearly, the entropies of activation are negative, indicating the activated complex is more ordered than the reactant molecules. It was also found that the entropy of activation decreased as the reaction pressure decreased. This finding provides further evidence that the pre-exponential term, rather than the activation energy term, is the dominant factor in determining the rate of reaction.

Volumes and entropies of activation have been used by Whalley to elucidate reaction mechanisms.[64] In this study, the activation area was used as a criterion to understand the mechanism since the analogous activation volumes are more reliable than activation entropies in interpreting the type of reaction taking place. This is because activation entropies are quite sensitive to factors such as the loosening or strengthening of chemical bonds, whereas volumes depend to a much greater extent on electrostriction effects than anything else. Therefore, volume changes are more constant for a given reaction than entropies, and thus, volumes lead to more clear-cut conclusions about the processes taking place.[88] Activation areas will be used in a similar manner below.

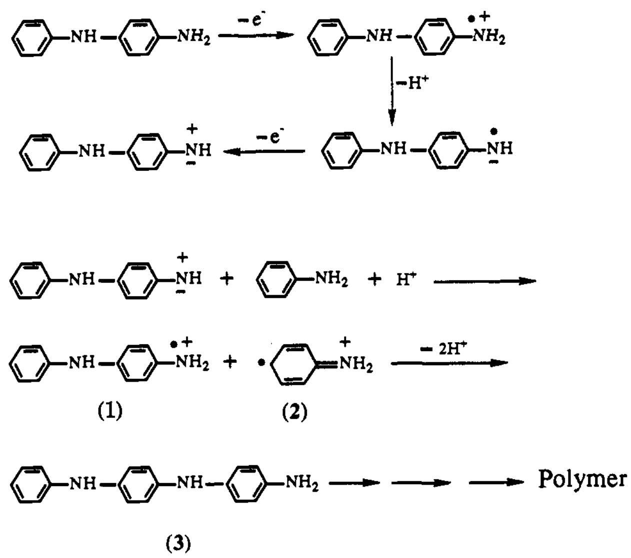
Mechanism. Most authors agree that the first step in aniline polymerization is the formation of a radical cation[45] ($BNH_2^{\bullet+}$, where B = benzene ring). This radical cation is delocalized over the benzene ring. Two such radical cations combine to form a dimer. The existence of three types of dimeric species, such as *N*-(*p*-aminophenyl)phenylamine (head-to-tail coupling), benzidine (tail-to-tail coupling), and *N,N'*-diphenylhydrazine (head-to-head coupling), have been verified experimentally. The relative concentrations of these species in the reaction medium are thought to depend upon reaction conditions. In a moderately acidic medium, for example, *N*-(*p*-aminophenyl)phenylamine is known to be the major species.[45] Oxidation potentials of oligomers are lower than those of the monomers.[62] So dimers and higher species are reoxidized faster than additional monomer molecules.

Once a dimer is formed in the reaction mixture, the mechanism by which these species propagate to form a polymer molecule is not very well understood. Wei proposed that the dimer loses two electrons to form a diiminium dication or a stable nitrenium cation (BNH^+) which could be readily generated from the deprotonation of the diiminium ions.[62] The presence of the stable nitrenium cation in the reaction medium was reported by Genies and Lapkowski.[56] According to Wei and co-workers, electrophilic attack of either a diiminium dication or a nitrenium cation on a neutral aniline molecule would accomplish a polymer growth step. The subsequent oligomers also have lower oxidation potentials than aniline, and the reaction proceeds, leading eventually to the final polymer.

It is not clear, however, whether an oxidized polymer molecule directly reacts with a neutral aniline or if it catalytically oxidizes the neutral aniline and then adds together. Both routes have been suggested,[63] but neither has been confirmed.

Since in monolayers the alkyl substituent has a negligible effect on the reactivity of the aniline head group and because certain experimental signatures of the monolayer polymerization mechanism are similar to those seen in chemical and electrochemical methods, the above findings and other studies can be used to propose a reaction mechanism in both monolayer and solution polymerization reactions. The mechanism shown in Scheme I is proposed for the growth of a polymer molecule. We believe that the oxidized polymer molecule does not directly couple to the neutral aniline monomer. Rather, neutral aniline molecules are catalytically oxidized near the polymer in the presence of acid. The combination of the resulting two radical cations (**1** and **2**) leads to the formation of the activated complex, which then looses two protons to form an oligomer (**3**). If the addition occurs by the mechanism proposed by Wei et al., a large negative value of the activation area should not be observed, as charge intensification during activated complex formation is not possible. The neutral polymer segment shown in our mechanism is then quickly reoxidized to the emeraldine form commonly observed upon polymerization.[8]

Scheme I



As proposed, the above mechanism should lead to polymer growth intermediate between classical step growth and chain growth mechanisms. During the reaction, though, the higher molecular weight species diffuse more slowly, decreasing their probability of colliding which would tend to favor monomer colliding with them. For this reason, the overall polymerization should be more akin to chain rather than step growth.

Conclusions

Comparison of the isotherms of 2-pentadecyl- and 4-hexadecylaniline on water and 0.1 M sulfuric acid provides a description of the conformation of 2-pentadecylaniline at the air/aqueous acid interface. Monolayers of 2-pentadecylaniline were highly compressible and showed little hysteresis upon compression and subsequent expansion below the collapse point. The monolayer of 2-pentadecylaniline was in the liquid expanded state, and no phase transition was observed during compression at all temperatures investigated. Isobaric creep measurements on 2-pentadecylaniline at different temperatures and applied surface pressures showed sufficient monolayer stability to carry out polymerization reactions at the interface. The reaction rate at a given surface pressure was found to increase with increasing subphase temperature. Also, the rate was found to increase with increases in surface pressure at a given temperature. From Arrhenius plots at different applied surface pressures, activation energies and other thermodynamic parameters such as activation enthalpies, activation entropies, and Gibbs free energies of activation were calculated. The activation energy for the polymerization of 2-pentadecylaniline at the interface was found to decrease with decreasing surface pressure. The activation area, an important criterion in interpreting reaction mechanisms, was calculated by carrying out polymerization reactions at different applied surface pressures. Results showed that the activated complex was bimolecular in nature. In the mechanism, we believe that the oxidized polymer molecule, instead of adding to the neutral aniline monomer, catalytically oxidizes the neutral molecule of aniline in the presence of acid. Combination of the resulting radical cations (**1** and **2**) leads to the formation of a growing polymer chain by losing two protons.

Acknowledgment. We wish to acknowledge financial support from the Office of Naval Research and technical assistance from KSV Instruments, Finland.

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[88] Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row, Publishers, Inc.: New York, 1987; p 209.