Surface Behavior and Polymerization of 2- and 3-(1-Octadecynyl)aniline at the Air−Aqueous Interface

L. J. Kloeppner, J. H. Batten, and R. S. Duran*

Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

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ABSTRACT: The surface behavior of 2- and 3-(1-octadecynyl)aniline (2ODA and 3ODA) was studied in Langmuir films and compared to that of 2- and 3-pentadecylaniline (2PDA and 3PDA), which was previously reported. Surface pressure (π) and potential (ΔV) vs mean molecular area (A) isotherms of these substituted anilines were generated, and the results were, in part, attributed to the orientation of the aromatic rings at the interface. Using well-established methods, 2ODA and 3ODA were polymerized at the air−aqueous interface, and the reactivities of the aniline derivatives were studied at different surface pressures. It was found that the initial rate constant (k') for the polymerization of 2ODA was significantly greater than that of 2PDA, but autoacceleration was not detected. The reaction rates are explained in part by molecular orientational differences at the air−aqueous interface. The polymerization rates of 3ODA and 3PDA were comparable, which is probably due to similar headgroup orientation at the air−aqueous interface.

Introduction

The Langmuir film technique is a unique method by which the polymerization of amphiphilic monomers can be studied at the air−aqueous interface. The advantage of this technique is that the molecules are held in a well-defined orientation[1] while the polymerization kinetics are observed in real time.[2] Our group has studied the Langmuir film polymerization and kinetics of 2- and 3-pentadecylaniline (2PDA and 3PDA) and found that the *o*-alkylaniline was more reactive at higher surface pressures.[3,4] The results indicate that at higher surface pressures the monomer was oriented similar to the resulting polymer and was therefore more reactive. Thus, if the orientation of the reactive group could be more effectively controlled, reactivity may also be controlled.

One way of achieving a desired orientation may be to synthesize a molecule with a structure more conducive to polymerization. For an aniline-type monomer, orientational control may be accomplished by designing a surfactant with an inflexible component, such as an acetylene, on the aliphatic chain adjacent to the anilinium group. The length of the rigid acetylene unit is estimated to be ca. 4.27 Å (two single and one triple bond), while that of a single C−C bond is 1.54 Å. The longer pendant group should act as a simple nanoscopic arm to convert some of the laterally applied surface pressure to torque about the aromatic ring of the anilinium group. An inflexible triple bond should thus alter the orientation of the anilinium group in the Langmuir film, which should also change the monomer's reactivity.

Figure 1 illustrates the predicted relative conformation of the anilinium group in a Langmuir film as surface pressure is increased. When the ortho-substituted aniline is compressed, it is proposed that the ammonium group will be favorably aligned for polymerization with the para position on an adjacent anilinium group. The hydrophobic chain with the triple bond may assist in orienting the monomer at the interface. The reactivity of the meta-substituted surfactant may also be affected by the presence of the triple bond, but the anticipated outcome is less predictable.

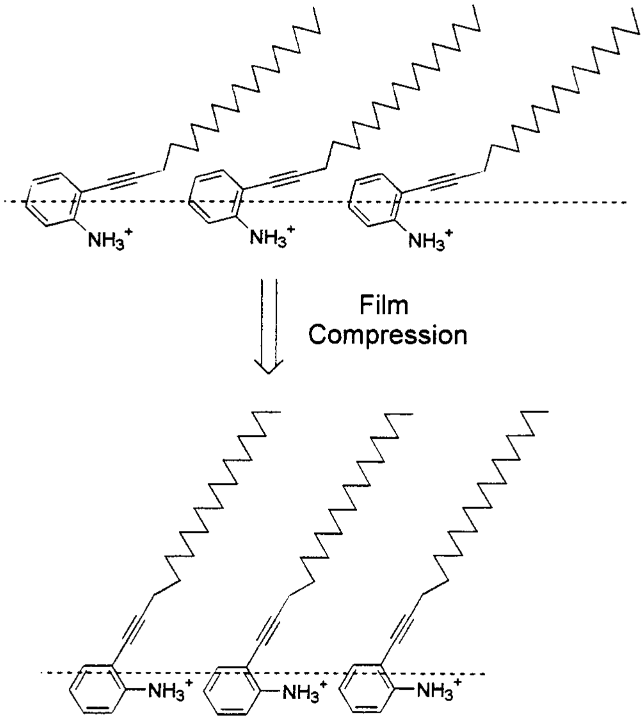

Figure 1. Cartoon of the predicted conformational change of 2ODA at the air−aqueous interface during compression.

This paper explores the polymerization of 2- and 3-(1-octadecynyl)aniline (2ODA and 3ODA) at the air−aqueous interface. The surface behavior and polymerization kinetics of these monomers are compared with the Langmuir film polymerization of 2PDA and 3PDA, which was previously reported.[3]

Experimental Section

The monomers 2PDA and 3PDA were prepared by a method previously reported.[3,5] A modified literature procedure was

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used to prepare 2ODA and 3ODA.[6] 1-Octadecyne was provided by Farchan Laboratories, Gainesville, FL. All other reagents were purchased from Aldrich or Fisher and were used without further purification.

General Procedure for the Synthesis of 2ODA and 3ODA. Bromoaniline (2.22 g, 12.9 mmol), 1-octadecyne (3.59 g, 14.4 mmol), triphenylphosphine (171 mg, 0.653 mmol), cupric acetate dihydrate (42.6 mg, 0.235 mmol), and palladium dichloride (22.7 mg, 0.128 mmol) were suspended in 50 mL of freshly distilled diisopropylamine. The flask was flushed with argon and heated to 80 °C for 4 h. Upon completion (determined by TLC), the reaction mixture was cooled, and the white precipitate that formed was filtered and discarded. The solvent was removed under reduced pressure, and the crude mixture was passed through silica gel using methylene chloride as the eluant. Further purification was achieved by column chromatography (silica gel/hexane:methylene chloride, 60:40).

2-(1-Octadecynyl)aniline (2ODA). The yield was 41% (1.84 g, 5.26 mmol). The white solid melted at 29.5−30.0 °C. ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (t, 3H), 1.28 (bs, 24H), 1.47 (m, 2H), 1.63 (m, 2H), 2.47 (t, 2H), 4.00 (bs, 2H), 6.70 (m, 2H), 7.09 (t, 1H), 7.25 (d, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 14.09$, 19.62, 22.67, 28.97, 29.15, 29.35, 29.54, 29.68, 31.91, 95.79, 108.99, 114.09, 117.81, 128.74, 131.98, 147.55. FTIR (KBr): 3483, 3389, 2919, 2837, 1607, 1484, 1454, 1302, 1266, 1149, 743 cm^{-1}. MS (FAB) exact mass calcd: $(m + 1)$ 342.3161. Found: 342.3179. Anal. Calcd for $C_{24}H_{39}N$: C, 84.39; H, 11.51; N, 4.10. Found: C, 84.43; H, 12.09; N, 3.89.

3-(1-Octadecynyl)aniline (3ODA). The yield was 36% (1.62 g, 4.68 mmol). The white solid melted at 36.4−38.6 °C. ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (t, 3H), 1.28 (bs, 24H), 1.45 (m, 2H), 1.63 (m, 2H), 2.39 (t, 2H), 3.64 (bs, 2H), 6.61 (d, 1H), 6.74 (s, 1H), 6.81 (d, 1H), 7.08 (t, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 14.15$, 19.42, 22.73, 28.82, 28.96, 29.21, 29.40, 29.59, 29.73, 31.95, 80.70, 89.89, 114.57, 117.93, 122.02, 124.80, 129.11, 146.15. FTIR (KBr): 3425, 3307, 3189, 2919, 2848, 1610, 1600, 1470, 1314, 1196, 1161, 861, 782, 714, 685 cm^{-1}. MS (FAB) exact mass calcd: $(m + 1)$ 342.3161. Found: 342.3205. Anal. Calcd for $C_{24}H_{39}N$: C, 84.39; H, 11.51; N, 4.10. Found: C, 84.48; H, 11.41; N, 4.08.

Monolayer Characterization. All of the monolayer and polymerization studies were conducted on KSV LB5000 equipment. The surface pressure (π) measurements were obtained using the Wilhelmy plate technique. Paper plates hung from a Pt wire were used for the Wilhelmy balance measurements. Each plate was cut from P5 Fisherbrand filter paper. The surface potential (ΔV) measurements were conducted using the vibrating plate method. This method uses a vibrating plate ca. 3 mm above the surface of the interface and a platinum plate, 3 cm^2, just below the surface of the air−aqueous interface. The π and ΔV vs mean molecular area (A) isotherms were measured while compressing the films at a constant speed of ca. 4−6 $Å^2$ $molecule^{-1}$ min^{-1}. The trough and barriers were made of Teflon.

The monomer solutions in chloroform were prepared (0.5−1.0 mg mL^{-1}) and deposited on the interface by carefully adding the solution to the surface with a microsyringe and then allowing the solvent to evaporate. The water used for the subphase was purified by a Millipore system (≥ 18 MΩ resistance). The subphase temperature was maintained with water jacket just below the Teflon trough connected to a circulating bath. The subphase temperature (±0.1 °C) was determined by placing a thermometer just below the surface of the interface.

The polymerizations were carried out at constant applied surface pressure and subphase temperature. The aniline monomers were oxidatively polymerized on a subphase solution of 0.10 M sulfuric acid and 0.03 M ammonium peroxydisulfate. The film was compressed at ca. 45 $Å^2$ $molecule^{-1}$ min^{-1} until the surface pressure was within 5 mN m^{-1} of the desired surface pressure, it was then compressed at ca. 15 $Å^2$ $molecule^{-1}$ min^{-1}. It has been previously shown that such aniline containing surfactants do not polymerize under these conditions when the film is in the expanded state.[2] Once the target surface pressure was reached, there was a brief induction period, 15−60 s, when the change in A was considerably slower. The end of this period was designated as the beginning of the reaction, and the mean molecular area at this time is A_0. The polymerization was monitored by the change in the mean molecular area of the surfactant at a constant applied surface pressure. The polymerization was deemed complete when the change in mean molecular area, within experimental error, was zero.

The cyclic voltammetry measurements were performed on an EG&G Princeton Applied Research model 273 potentiostat/galvanostat. The potentiostat/galvanostat was controlled by a model 270/250 Research Electrochemistry Software package, version 4.30, that was loaded on a PC computer. The working electrode was a 0.006 cm^2 platinum button, the counter electrode was a platinum plate, and the reference electrode was Ag/Ag^+ (Ag wire in 0.1 M $AgNO_3$). The Ag/Ag^+ had a potential of +0.33 V vs the SCE.[7] The scan rate was 50 mV s^{-1}. The acetonitrile used in these experiments was refluxed and distilled over calcium hydride. The electrolyte compound used for all experiments was 0.10 M lithium perchlorate which was not dried before use. The concentrations of the surfactant solutions were ca. 0.05−0.10 M. The platinum working electrode was cleaned between each scan, and the voltammetry measurements were repeated a minimum of two times to ensure reproducibility. The anodic peak potential, E_{pa}, was determined to be at the point of maximum current flow.

Polymer Characterization. The polymerized Langmuir film was removed from the air−aqueous interface by passing the solution at the interface through a small glass frit, which collects the polymeric material. The polymer was washed with deionized water and dried under vacuum for a minimum of 2 h. Size exclusion chromatography (SEC) molecular weight analysis was performed at room temperature using a Waters Associates liquid chromatography apparatus equipped with Phenomenex columns and a Kratos Analytical Spectroflow 757 absorbance detector set at 254 nm. The mobile phase was THF, and the instrument was calibrated with polystyrene standards.

The infrared measurements were performed on a Fourier transform infrared spectrometer (Bio-Rad FTS-40A) with a diffuse reflectance spectrometer accessory. The base forms of the polymer samples were prepared by dissolving a polymer sample in a small amount of chloroform, extracting several times with 0.10 M ammonium hydroxide and deionized water, and then mixing the polymer solution with a small amount of KBr powder. Once the chloroform had evaporated, the sample was dried under vacuum for 2 h. The sample mixture was placed in the top half of the sample cup that was already filled with KBr powder. UV−vis data were collected on a Varian-Cary 5E UV−vis−NIR spectrophotometer. The solvent used for the measurements was Fisher spectrograde chloroform.

Results and Discussion

Monolayer Characterization. The $\pi-A$ isotherms of 2ODA, 3ODA, 2PDA, and 3PDA on a 0.10 M H_2SO_4 subphase at 25 °C are shown in Figure 2. The $\pi-A$ isotherms of 2PDA and 3PDA under these conditions were previously reported.[3,8] The degree of ionization of the anilinium group is assumed to be close to unity for all four molecules. This is a good assumption as the pK_a value of 2-pentadecylaniline at the air−aqueous interface was previously estimated[9] at 4.6. Isobaric creep measurements[2] showed that the monomers were stable over the time frame of the polymerization reactions performed. The isotherms show that 2ODA and 3ODA formed more condensed monolayer films than their alkyl counterparts. For 2ODA, the pressure onset area was at 60 A^2 $molecule^{-1}$, and its collapse pressure at 24 mN m^{-1} was near 34 A^2 $molecule^{-1}$. Though this collapse pressure was 16 mN m^{-1} lower than that recorded for 2PDA, both ortho isomers had similar collapse areas at ca. 36 A^2 $molecule^{-1}$. In contrast, 3ODA had a pressure

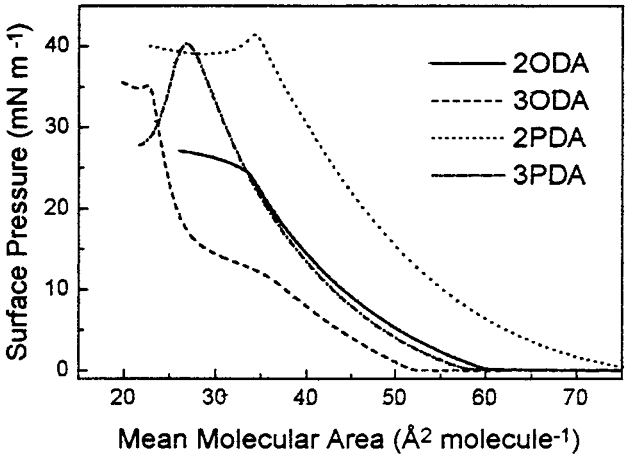

Figure 2. Surface pressure (π) vs mean molecular area (A) isotherms of 2ODA, 3ODA, 2PDA, and 3PDA on 0.10 M H_2SO_4 at 25 °C.

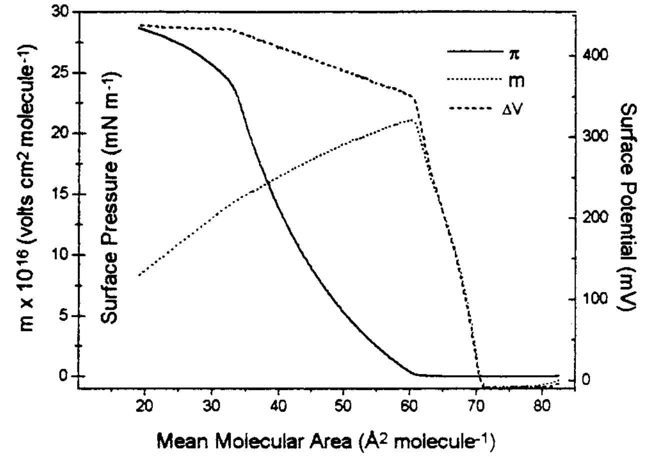

Figure 3. Surface pressure (π), potential (ΔV), and normalized surface potential (m) vs mean molecular area (A) for 2ODA on 0.10 M H_2SO_4 at 25 °C.

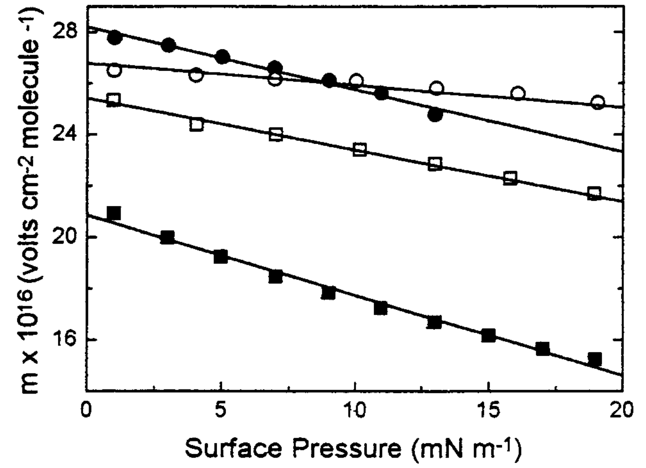

Figure 4. Plot of m for 2ODA (■), 3ODA (●), 2PDA(□), and 3PDA (○) at their corresponding surface pressures (π). The line slopes are −3.1 (2ODA), −2.4 (30DA), −2.0 (2PDA), and −0.87 (3PDA) × 10^{-17} m π^{-1}.

onset area of 52 A^2 molecule^{-1} and a collapse pressure of 35 mN m^{-1} at 23 A^2 molecule^{-1}. Between the onset and collapse areas, there appears to be a phase transition which occurred at ca. 37 A^2 molecule^{-1} and at a surface pressure of ca. 14 mN m^{-1}.

The surfactants in this study are structurally similar, making a comparison of their electronic properties important. Surface potential measurements provide insight into the effect that mean molecular area has on the relative orientation of the headgroup. A monolayer film at the air−aqueous interface can be treated as an assembly of molecular dipoles which can shift the potential across an interface.[10,11] This potential shift, relative to a clean aqueous surface, is referred to as the surface potential of the monolayer, ΔV. Since ΔV is dependent on the concentration of molecules, a more convenient way of expressing the surface potential results is the surface potential per molecule (m), which is determined from ΔV divided by the number of molecules per cm^2 (n):[12]

$$m = \Delta V/n \quad (1)$$

The surface potential per molecule is a reflection of the dipole moment of a surfactant normal to the interface and the surface potential due to the double layer caused by the ionized surfactants.

Figure 3 shows the π, m, and ΔV vs A isotherms of 2ODA on a 0.10 M H_2SO_4 subphase at 25 °C. For all four molecules, the value of m increased dramatically prior to and reached a maximum value near the pressure onset area. As the film was compressed further, m slowly decreased. These results indicate that the molecule was reorienting at the interface. Figure 4 shows the change in the value of m at different surface pressures for the surfactants. The slopes of the lines are an indication of the susceptibility of the molecule to orientational change at the interface. When comparing the slopes of the two sets of isomers, 2ODA with 3ODA and 2PDA with 3PDA, the two ortho isomers had more negative values than the two meta isomers. Also, m was smaller at all surface pressures for the ortho isomers than the meta isomers, an indication that the anilinium headgroup of these two monomers contributes less to the overall value ΔV. Since contribution of the anilinium headgroup to the value of m is predicted to be positive and largest when the C−N bond is approximately perpendicular to the interface, it is believed that the two ortho isomers have C−N bonds closer to a parallel orientation at the interface than the two meta isomers.[3] As the anilinium ion is rotated away from a perpendicular orientation, the value of m should decrease as the headgroup's dipole becomes closer to a parallel orientation at the interface.

The surface behavior of the alkynyl isomers can be attributed to structural differences that affect their arrangement at the interface. As illustrated in Figure 1, 2ODA is predicted to be more favorably oriented for polymerization than its alkyl counterpart, even at low surface pressures. From the surface pressure and potential measurements, it is proposed that the alkynyl isomers underwent an orientational change as the film was compressed, which is similar to that proposed for 2PDA and 3PDA.[3] However, the relative orientation of the two alkynyl isomers appears to be influenced to a greater degree by film compression.

Polymer Characterization. According to SEC data, the product of the monolayer polymerization of 2ODA had a M_w of 16 000 and a M_n of 2800. Only low molecular weight oligomer was recovered from the polymerization of 3ODA, which had a M_w of 2800 (5−6 repeat units) and a polydispersity of 1.4.

The materials produced were violet and dark brown for poly(2ODA) and poly(3ODA), respectively. Poly-

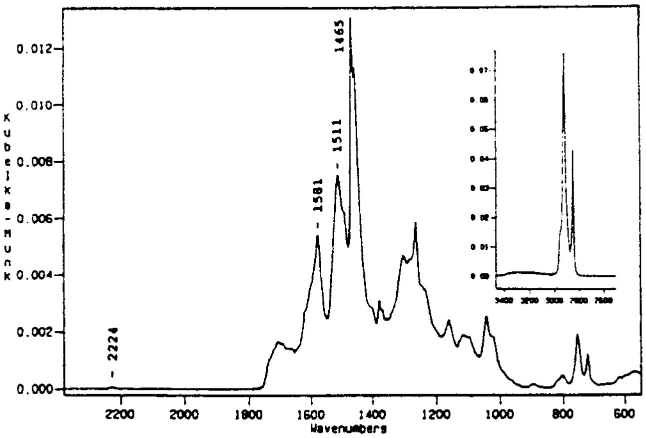

Figure 5. Infrared spectrum of poly(2ODA) base.

(2ODA) had absorption maxima at 300, 410, and 595 nm. The spectrum was similar to that of polyaniline in the pernigraniline base form that was reported by Lee et al.,[12] indicating that poly(2ODA) was in this oxidative state.

Figure 5 shows the infrared spectrum of poly(2ODA) in its base form. The vibrational bands at 2923 and 2852 cm^{-1} correspond to the asymmetric and symmetric C–H stretching, and the band at 1465 cm^{-1} is assigned to the C–H bending of the long hydrophobic chain. The vibrational band at 1581 cm^{-1} is assigned to the C=N and C=C stretching of the quinoid diimine unit, while the band at 1511 cm^{-1} is attributed to the C–C aromatic ring stretching of the benzenoid diamine unit of the polymer backbone.[14] The very weak band at 2224 cm^{-1} is assigned to the C≡C stretch of the acetylene on the alkyl chain. This band is similar in intensity and position to that of the monomer (2221 cm^{-1}), indicating that the acetylene group remains intact after polymerization.

Polymerization Kinetics. The concentrations of monomer, [ANI], and polymer repeat units, [PANI] were determined from the following expressions:[3]

$$[\mathrm{ANI}] = (1/A)(A - A_\infty)/(A_0 - A_\infty) \tag{2}$$

$$[\mathrm{PANI}] = (1/A)(A_0 - A)/(A_0 - A_\infty) \tag{3}$$

The polymerization rate of the aniline surfactants at the interface can then be determined as[3]

$$-\frac{[\mathrm{ANI}]}{\mathrm{d}t} = \frac{1}{A}\left[\frac{\mathrm{d}(A_0 - A)/(A_0 - A_\infty)}{\mathrm{d}t}\right] \tag{4}$$

where A, A_0, and A_∞ are the mean molecular areas at specified time during the reaction, at the reaction beginning, and at the end of the reaction, respectively. Figure 6 shows the rate of polymer formation of 2ODA and 2PDA. In the case of 2ODA, the rate was at a maximum early in the reaction and then decreased with time, but for 2PDA, the rate was slower at the beginning of the polymerization and increased as the reaction proceeded. The rate behavior of 2PDA was typical of what is observed in the 3-dimensional chemical and electrochemical polymerization of aniline. Once the polymerization is initiated, normally the polyaniline formation rate autoaccelerates.[15–17] It was suggested by Shim and Park that autoacceleration is due to the newly formed polymer or oligomers assisting the monomeric aniline oxidation; therefore, the propagation accelerates.[16] However, autoacceleration was not apparent in the polymerization of 2ODA. The polymer formation rates of the two meta isomers, 3ODA and 3PDA, are shown in Figure 7 and appear to be similar for the two compounds under these conditions.

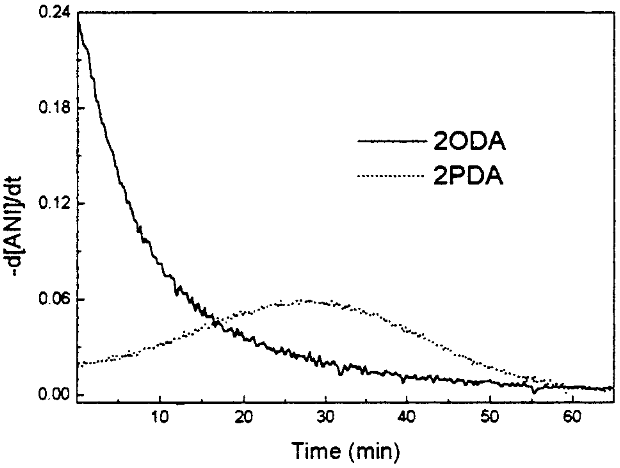

Figure 6. Rate of reaction vs time for 2ODA and 2PDA at an applied surface pressure of 5 mN m^{-1}. Temperature held constant at 25 °C.

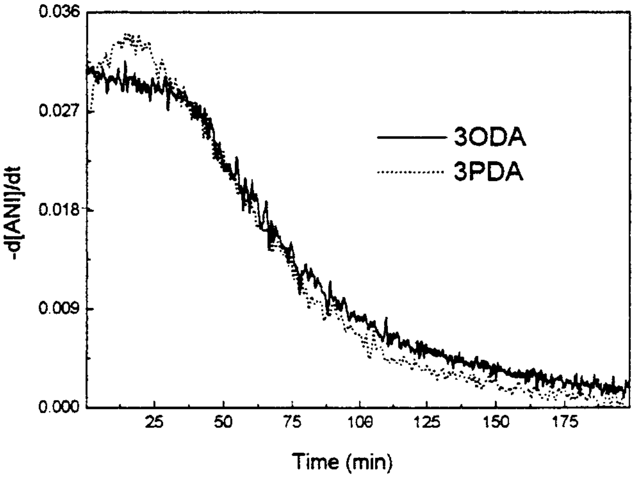

Figure 7. Rate of reaction vs time for 3ODA and 3PDA at an applied surface pressure of 5 mN m^{-1}. Temperature held constant at 25 °C.

Previous studies have shown that the polymerization rate of aniline is first order in monomer concentration prior to the formation of polymer and can be expressed by the following rate expression:

$$-\frac{\mathrm{d}[\mathrm{ANI}]}{\mathrm{d}t} = k^{\mathrm{app}}[\mathrm{ANI}] \tag{5}$$

where k^{app} is an apparent rate constant for this polymerization.[17] Once polymer has formed, the polymerization autoaccelerates, and the rate expression for the formation of substituted polyaniline in a Langmuir film, which is oxidized by a chemical oxidant, was found to be as follows:[3]

$$-\frac{\mathrm{d}[\mathrm{ANI}]}{\mathrm{d}t} = k[\mathrm{ANI}][\mathrm{PANI}] + k'[\mathrm{ANI}] \tag{6}$$

where k' is the true rate constant and is determined at the beginning of the reaction when no polymer is present and k is the rate constant that accounts for the

Table 1. Rate Constant Data for 2ODA and 3ODA at 25 °C

surface press. ($\mathrm{mN\ m^{-1}}$)	2ODA k' ($\mathrm{min^{-1}}$)	3ODA k' ($\mathrm{min^{-1}}$)	k (molecules $\mathrm{nm^{-2}\ min^{-1}}$)
5	0.119	0.0158	0.005 38
10	0.173	0.0213	0.005 70
15	0.182		

autoacceleration and is first order in polymer and monomer concentration.

The rate of the reaction was fit to eq 6, and the autoacceleration rate constant, k, and the true rate constant, k', were determined from the plot of [PANI] vs k^{app}, where k' was the y-intercept of the line and k was the slope of the line.[3] Table 1 shows the calculated rate constants of 2ODA and 3ODA. The values of k' and k for 2PDA and 3PDA were previously reported.[3] The values of k' for 2PDA were an order of magnitude less than those of 2ODA, while the values of k' for 3PDA were only slightly larger than those of 3ODA. It should be noted here that for polymerizations that are initially very fast, like 2ODA, there is some uncertainty in determining the value of k', which is due to significant monolayer polymerization during the initial compression. If polymerization occurs prior to the recorded beginning of the polymerization, the recorded values of A_0 and k' may be slightly lower than its true value.

If autoacceleration is significant, then a plot of k^{app} vs [PANI] would have a positive slope. However, in the case of 2ODA this plot has a negative slope, indicating that autoacceleration was not detected during polymerization. This result may be explained by the large value of k' and the low molecular weight material obtained from this polymerization. The rate constant, k', of 2ODA was ca. 6−10 times greater than that of 2PDA at surface pressures between 5 and 15 mN m^{-1}, and as in the case 2PDA, k' increased with increasing surface pressure.[3] To illustrate this observation, the half-lives of the reactions at 10 mN m^{-1} were calculated, and it was determined that 2ODA and 2PDA had half-lives of ca. 3.5 and 17 min, respectively. Therefore, because k' was so large, autoaccleration was not detected. Further, high molecular weight polymer was produced early in the reaction of 2PDA, indicating a chain type polymerization and kinetics.[2] When high molecular weight material is produced during a chain type polymerization, the rate of the polymerization is assumed to be nearly equal to the propagation rate since there are relatively few monomers participating in the initiation step (the formation of 4-aminodiphenylamine (ADPA)).[18] This assumption is valid for the polymerization of 2PDA and 3PDA as high molecular weight material was produced. However, low molecular weight material was produced in the reaction of 2ODA, so a more accurate expression for the polymerization is

$$-\mathrm{d[ANI]}/\mathrm{d}t = R_{\mathrm{p}} + R_{\mathrm{ADPA}} \tag{7}$$

where R_{ADPA} is formation rate of ADPA, which is a function of the monomer and oxidant concentrations. The oxidant concentration is constant during the reaction and does not need to be included in the rate expression. Therefore, the expression for R_{ADPA} can be written as

$$R_{\mathrm{ADPA}} = 2k''[\mathrm{ANI}]^2 \tag{8}$$

where k'' is the rate constant for the formation of ADPA. The rate expression and k^{app} can now be rewritten as

$$-\mathrm{d[ANI]}/\mathrm{d}t \cong R_{\mathrm{p}} + R_{\mathrm{ADPA}} = k[\mathrm{PANI}][\mathrm{ANI}] + k'[\mathrm{ANI}] + 2k''[\mathrm{ANI}]^2 \tag{9}$$

and

$$k^{\mathrm{app}} = k[\mathrm{PANI}] + k' + 2k''[\mathrm{ANI}] \tag{10}$$

The results suggest that values of k' and k'' are significantly larger than k for the polymerization of 2ODA and account for the decrease in k^{app} at low monomer concentrations. Therefore, the slope of the plot of k^{app} vs [PANI] is slightly negative because the rate of disappearance of monomer is attributed not only to propagation but also to ADPA formation. It is believed that the low molecular weight material produced in the reaction of 2ODA can be attributed to a high initiation rate, R_{ADPA}, which leads a high number of polymer chains with few repeat units per chain. Because of the complexity of the polymerization kinetics, precise determination of k'' for this reaction is beyond the scope of the Langmuir film technique.

Oxidation potential may also explain the differences in reactivities of the two ortho monomers as it affects the ease of formation of the cation radical intermediates that lead to polymer. The oxidation potentials of the 2ODA and 2PDA were 0.75 and 0.72 mV, respectively, suggesting that the alkylaniline was more easily oxidized. Since 2ODA reacts faster than its alkyl counterpart, it is unlikely that the slight difference in oxidation potential is the reason for the difference in k'.

The reactivities of 3PDA and 3ODA were similar at the beginning of the polymerization, and both monomers had similar k' values at a surface pressure of 5 mN m^{-1}. However, the k values for 3ODA were about a third of those calculated for 3PDA. As in the case of 2ODA polymerization, the low k value can be explained by the low molecular weight material that was produced in this reaction and the effect that R_{ADPA} had on the reaction.

Conclusions

The surface behavior of 2ODA and 3ODA on acidic subphases was characterized using surface pressure and potential measurements. It was determined that the triple bond affected the conformation of the surfactants at the interface compared to that of 2PDA and 3PDA.

A Langmuir polymerization study of the two alkynyl isomers at the aqueous interface was presented. Low molecular weight oligomers were produced in the reaction of 3ODA, while slightly higher molecular weight material was produced in the polymerization of 2ODA. The polymerization rates of the alkynyl isomers were determined and compared to the rates of 2PDA and 3PDA polymerization. It was found that 2ODA polymerized at a faster rate than 2PDA and that autoacceleration was not observed. The rate differences can be attributed to the relative orientation of the monomers at the air−aqueous interface. We speculate that the initiation rate increased in the case of 2ODA because of an improved headgroup alignment. Further, both monomers were found to be sensitive to surface pressure. The rate constant, k', was similar for the two meta isomers.

The polymerization of aniline surfactants at the aqueous interface behaved like a chain polymerization in which the molecular weight of the polymer was affected by the rate of the initiation step. If the initiation rate is relatively large, the molecular weight of the polymer will decrease. The low molecular weight material produced in the polymerization of 2ODA suggests that the formation rate of the propagating dimer is faster than in the case of 2PDA.

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References and Notes

(1) Gaines, G. L. *Insoluble Monolayers at Liquid−Gas Interfaces;* Interscience: New York, 1966.
(2) Bodalia, R. R.; Duran, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 11467.
(3) Kloeppner, L. J.; Duran, R. S. *Langmuir* **1998**, *14*, 6734.
(4) Zhou, H.; Duran, R. S. In *Macromolecular Assemblies in Polymeric Systems*; Stroeve, P., Balazs, A. C., Eds.; American Chemical Society: Washington, DC, 1992; Chapter 4.
(5) Kloeppner, L. J.; Nguyen, C. K.; Duran, R. S. *Polym. Prepr., Am. Chem. Soc. Div Polym. Chem.* **1995**, *36* (1), 580.
(6) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.
(7) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969.
(8) Zhou, H.; Stern, R.; Batich, C.; Duran, R. S. *Makromol. Chem., Rapid Commun.* **1990** *11*, 409.
(9) See ref 8.
(10) Davies, J. T.; Rideal, E. K. *Can. J. Chem.* **1955**, *33*, 947.
(11) Davies, J. T.; Rideal, E. K. *Interfacial Phenomena,* 2nd ed.; Academic Press: New York, 1963.
(12) Harkins, W. D.; Fischer, E. K. *J. Chem. Phys.* **1933**, *1*, 852.
(13) Lee, J. Y.; Ong, L. H.; Chuah, G. K. *J. Appl. Electrochem.* **1993**, *23*, 1031.
(14) Wudl, F.; Angus, R. O.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677.
(15) Wei, Y.; Sun, Y.; Tang, X. *J. Phys. Chem.* **1989**, *93*, 4878.
(16) Shim, Y. B.; Park, S. M. *Synth. Met.* **1989**, *29*, E169.
(17) Tzou, K.; Gregory, R. V. *Synth. Met.* **1992**, *47*, 267.
(18) Bacon, J.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 6596.

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