Chemical Polymerization of 2-Pentadecylaniline Confined to a Planar Liquid/Liquid Interface

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ABSTRACT: The monomer 2-pentadecylaniline was spread at a planar aqueous/cyclohexane interface. Its behavior was studied at different subphase sulfuric acid concentrations by monitoring the interfacial pressure with a Wilhelmy balance. The isotherms obtained are discussed. It was found that the monomer was best trapped at the interface at high sulfuric acid concentrations. Polymerization of a monolayer of 2-pentadecylaniline using an acidic ferric chloride solution in the aqueous subphase was possible, yielding a poly(2-pentadecylaniline) film. The polymer formed was characterized by GPC, UV-vis, and ^{1}H NMR.

Introduction

Many investigations have been published to date on monolayers at a planar gaseous/liquid interface.[1-5] Such monolayers are interesting in that the average intermolecular distance and orientation can be controlled in a systematic manner with a Langmuir trough.[6] Furthermore, molecules assembled in a Langmuir film can generally reorient as they are compressed because they are constrained to a surface which is fluid, in contrast to self-assembly and epitaxial monolayer formation where molecules are essentially bound to fixed sites on a solid substrate.[7] Many investigators have taken advantage of these features by using the Langmuir–Blodgett (LB) trough as a means to polymerize monolayer films, for multilayer deposition and subsequent studies.[8-11]

We have recently shown that the Langmuir trough can be used for real-time investigations of the polymerization behavior of monolayers of functionalized anilines and pyrroles at an air/aqueous interface.[12] The effects of confining the polymerization reaction to this fluid surface can be compared with reactions in the bulk.[13] Additionally, the effects of variables such as intermolecular distance, applied surface pressure, temperature, and subphase environmental conditions can be compared in a systematic and convenient manner, and useful thermodynamic parameters such as activation energies and areas can be determined.[14]

Monolayers at the planar liquid/liquid interface are much less investigated, although this is a fluid interface as well. Most of the previous research has dealt with monolayers of phospholipids[15-20] or crown ethers at an oil/aqueous interface.[21,22] To date little work has been found in the literature dealing with chemical reactions in monolayers at a planar liquid/liquid interface.[23] Compared to an air/liquid interface, however, more control can be gained by restricting chemical reactions to monolayers at a liquid/liquid interface. The molecules can be oriented both by mechanically restricting the interfacial area with a barrier through the use of a modified Langmuir[24] trough and by altering the polarities of the two phases. Molecules in a monolayer at a liquid/liquid interface are also less susceptible to oxidation through the air.

Furthermore, investigating the behavior of monomers and their chemistry at a planar liquid/liquid interface will help in understanding the reactions at curved interfaces such as emulsions and micelles. A planar surface can be compared to an opened micelle, and the factors that contribute to the orientation of the molecules can be investigated more easily.[4]

Numerous experimental difficulties must be considered to investigate molecular monolayers and their chemistry at liquid/liquid interfaces. To use modified interfacial Langmuir troughs, the interfacially-investigated compound should be completely insoluble in the aqueous and organic phases and should be prevented from creeping around the barrier and outside surfaces of the trough. Additionally, considerable complications arise with spreading solutions of amphiphiles, including the potential for the spreading solvent itself to act as a surfactant or to remain at the interface and change the interfacial tension or plasticize the spread amphiphile. The liquid/liquid interface is also more sensitive to impurities than the air/water interface since impurities from both phases tend to accumulate at the interface.[4,5]

This paper will describe an approach to deal with the above-described problems and the behavior of 2-pentadecylaniline at an aqueous/cyclohexane interface and its polymerization. The chemical structure of the monomer and polymer are shown in Figure 1. We are not aware of previous attempts to polymerize monolayers confined to a planar liquid/liquid interface, though a significant amount of work has been done on interfacial nonmonolayer polymerization[25] and polymerization of micelles.[26,27]

Experimental Part

The monomer, 2-pentadecylaniline, was synthesized using a procedure described elsewhere.[28] HPLC-grade cyclohexane (Fisher) was used without further purification. Subphase solutions were made with ACS reagent-grade chemicals and Milli-Q water.

The experiments were run in crystallizing dishes that were cleaned with chromic sulfuric acid, chloroform, and Milli-Q water before use. For each experiment 80 mL of cyclohexane and 80 mL of aqueous sulfuric acid were used, and a constant interfacial area of 7000 mm^2 was maintained in the crystallizing dish.

The interfacial pressure was monitored by suspending a platinum plate through the interface and applying the Wilhelmy method[5] with on-line data acquisition through a modified KSV 5000 surface balance. The balance was zeroed before addition of monomer; therefore, the measured interfacial pressure reflects the change in interfacial tension relative to the "clean" interface.

The interface was checked for purity by suction of the interface and observance of the interfacial pressure. If no pressure change with time occurred, except that due to displacement of the Wilhelmy plate in the aqueous phase, the solvents and chemicals were regarded as pure.

Isotherms were run by injecting a 2-pentadecylaniline cyclohexane solution (0.15 mg/mL) beneath the interface. Cyclohexane was chosen because the monomer was easily dispersed in it, and when spread the cyclohexane would not perturb the

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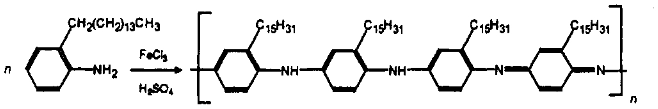

Figure 1. Reaction scheme for the polymerization of 2-pentadecylaniline.

interfacial tension. It should be noted that this spreading procedure only works for amphiphiles which spread spontaneously at the interface and was chosen as a convenient manner in which to deliver a known amount of 2-pentadecylaniline to the interface; i.e., the solvent is only used for introducing the compound. The compound must spread by itself.

The mean molecular area was changed by adding different amounts of the monomer solution, ranging from 20 μL per injection to 100 μL, e.g., 1.2 mL of added solution for the smallest theoretical mean molecular areas being studied.

Polymerization was studied by varying the mean molecular area, the acid concentration, and the ferric chloride concentration.

The polymer was collected by suction of the cyclohexane and the subphase until only a small volume of both was left. Clean water was then injected into the subphase to wash the polymer, and most of the subphase was suctioned again. This was repeated twice. After a few hours the cyclohexane evaporated and the polymer was collected on the surface of a fine-fritted glass disk by suction.

UV-vis-near-IR spectra were recorded in a chloroform solution with a Varian Cary-5 instrument. ^{1}H-NMR 200-MHz spectra were obtained with a Varian XL-Series NMR spectrometer system. The polymer was dissolved in a mixture of $CDCl_3$, DMSO-d_6, and a small amount of N_2D_4 in D_2O solution as a reducing agent before the measurements were started. Gel permeation chromatography (GPC) data were collected using a Waters Associates liquid chromatograph apparatus equipped with a U6K injector and a UV spectrophotometric detector from Perkin-Elmer. Two phenomenex 7.8 mm × 30 cm Phenogel 5 consecutive linear gel columns were used, a 500 Å followed by a 1000 Å type. The eluting solvent was HPLC-grade THF at a flow rate of 1.0 mL/min. Retention times were calibrated using polystyrene standards.

Results and Discussion

Interfacial Spreading Behavior of 2-Pentadecylaniline. 2-Pentadecylaniline can be spread at the aqueous/cyclohexane interface as the solid monomer itself or as a solution in cyclohexane. The solid monomer is slightly soluble in cyclohexane. When a small amount is dropped into cyclohexane, it dissolves very slowly. However, the moment it contacts the aqueous/cyclohexane interface it immediately spreads, shaking the entire interface. Cyclohexane itself, of course, does not spread at the cyclohexane/aqueous interface. Therefore, it is the monomer with its amphiphilic structure that gives the driving force for spreading. Similar behavior has been reported for proteins.[29]

The spreading of a solution of 2-pentadecylaniline in cyclohexane is preferred to that of the solid, because small amounts can be more accurately delivered at the interface. This is experimentally important in that the amount of monomer spread in the isotherm experiments reported here is less than 10 μg. The same interfacial pressures, however, were obtained upon equilibration, whether the monomer was spread as a solid, in small cyclohexane solution droplets floated from beneath the interface, or spread directly into the interface. The latter was accomplished by lifting the tip of the syringe at the interface, resulting in a meniscus of the aqueous subphase at the hydrophilic metal tip.

Though common in classical Langmuir–Blodgett studies, chloroform and methylene chloride cannot be used as spreading solvents though both spread well at the aqueous/cyclohexane interface. They tend to be adsorbed at the aqueous/cyclohexane interface with the monomer, giving a contribution to the interfacial pressure and disturbing the observed system, especially at low interfacial pressures.

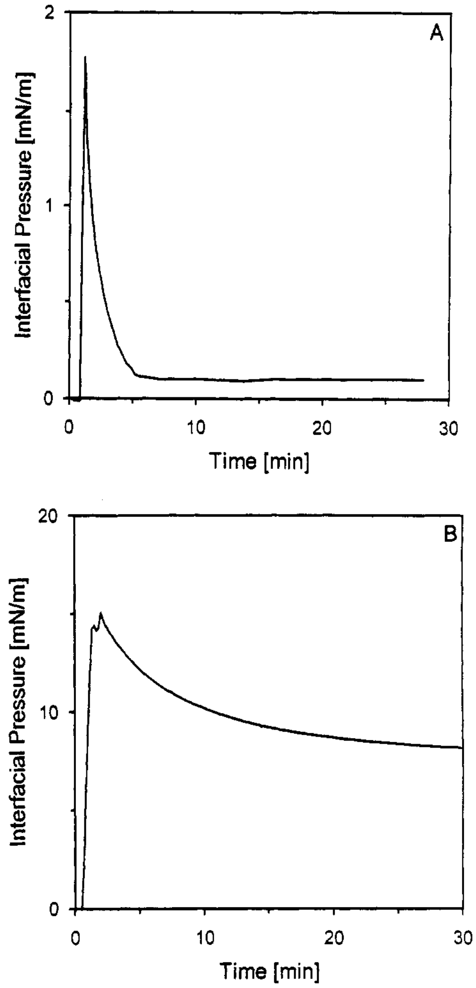

Figure 2. Interfacial pressure of 2-pentadecylaniline upon spreading. The amount spread corresponds to a theoretical mean molecular area of 50 Å^2/molecule. (A) Spreading at a 0.4 M sulfuric acid/cyclohexane interface. (B) Spreading at a 4.0 M sulfuric acid/cyclohexane interface.

In this initial study, many of these experimental difficulties related to working at the liquid/liquid interface (mentioned in the Introduction) were avoided by using crystallizing dishes and not a modified Langmuir trough. This eliminates the problem of barrier creep due to the possible solubility of the monomer in one of the phases. Isotherms, however, were only obtainable by applying the technique of repeated spreading of small amounts of monomer and not by compression of a barrier. The crystallizing dishes offer the additional advantages of easy cleaning and a convenient visible check for purity. Spreading can also be easily controlled by visibly keeping the tip of the syringe at the interface while spreading.

Figure 2 shows the measured interfacial pressure vs time upon spreading of a cyclohexane solution of 2-pentadecylaniline at the 0.4 M sulfuric acid/cyclohexane interface. The interfacial pressure rises almost instantaneously and then levels off to a significantly lower value. The peak signal of the interfacial pressure measured immediately after spreading is influenced by the spreading conditions. As the solution was spread at locations closer to the Wilhelmy plate, the maximum interfacial pressure observed increased. This implies that it takes some seconds until the molecules in the monolayer diffuse sufficiently over the whole interface to equalize the pressure. Upon equilibration, the interfacial pressure was independent of the location where the solution was spread.

On contact with the sulfuric acid subphase at the interface 2-pentadecylaniline is protonated. This monomer salt should be less soluble in cyclohexane and thus have increased interfacial activity. Therefore protonated molecules would have a higher tendency to stay at the interface while those that are not protonated could more easily dissolve into the organic phase. Figure 2A shows that at low subphase acid concentrations the equilibrium interfacial pressure is low; therefore, less monomer is trapped at the interface. Previous studies have shown that significantly higher surface pressures can be attained for monolayers of this monomer at the air/aqueous interface. These studies have also shown that the monomer is practically insoluble in acidic aqueous phases.[30] This implies that little monomer is trapped at the interface with a 0.4 M sulfuric acid subphase. As a result, the interfacial pressure equilibration shown in Figure 2A reflects the exchange of protonated and nonprotonated monomer between the interface and the cyclohexane phase, as well as lateral diffusion within the interface. The low value of the measured interfacial pressure upon equilibration then reflects that most aniline molecules are in solution rather than trapped at the interface.

Figure 2B shows the spreading behavior of the monomer for a 4.0 M sulfuric acid subphase. Again, a rapid rise in the interfacial pressure is observed, followed by relaxation to a significantly higher interfacial pressure. This implies more monomer molecules are trapped at the interface.

Though the peak interfacial pressure was influenced by the spreading technique, the equilibrium value depended only upon the chemical nature of the interface and the temperature. Therefore, isotherms of the monomer could be measured by repeatedly spreading additional small amounts of the solution. The results for different subphase acid concentrations are reported in Figure 3. The interfacial pressure is shown as a function of the theoretical mean molecular area, assuming all aniline molecules stayed at the interface. While this is obviously not the case, it provides a convenient manner of comparing the isotherms relative to each other and to experimental data from monolayers at the air/aqueous interface.

The isotherms in Figure 3 show a clear relation between the interfacial pressure and the aqueous phase sulfuric acid concentration. The higher the acid concentration, the higher the interfacial pressure that can be reached at the same mean molecular area. For the case of the pure water subphase, the isotherm shows no measurable increase in interfacial pressure with decreasing mean molecular area. The largest interfacial pressure was found for the 4.0 M sulfuric acid subphase. At this concentration the monomer is trapped at the interface, yielding changes in interfacial pressure at theoretical mean molecular areas of 400–600 Å^2/molecule where at an air/aqueous interface there is no change observed.[8]

Results qualitatively analogous to those seen in Figure 3 have been observed for surface pressures measured with monolayers of 2-pentadecylaniline at the air/aqueous interface.[31] Several important differences are observed between isotherms of the monomer at the cyclohexane/aqueous and air/aqueous interfaces. First, with pure water aqueous phases no significant interfacial pressure change is seen, while a significant surface pressure change is measured. Second, high values of the interfacial pressure are only measured at significantly higher acid concentrations and lower surface areas than corresponding surface pressure values. Third, at high acid concentration, changes in interfacial pressure are observed at very high surface areas where no measurable surface pressure change is observed. While quantitative interpretion may not be possible, the above results do indicate that the monomer forms a less stable monolayer at the cyclohexane/aqueous interface than the air/aqueous interface.

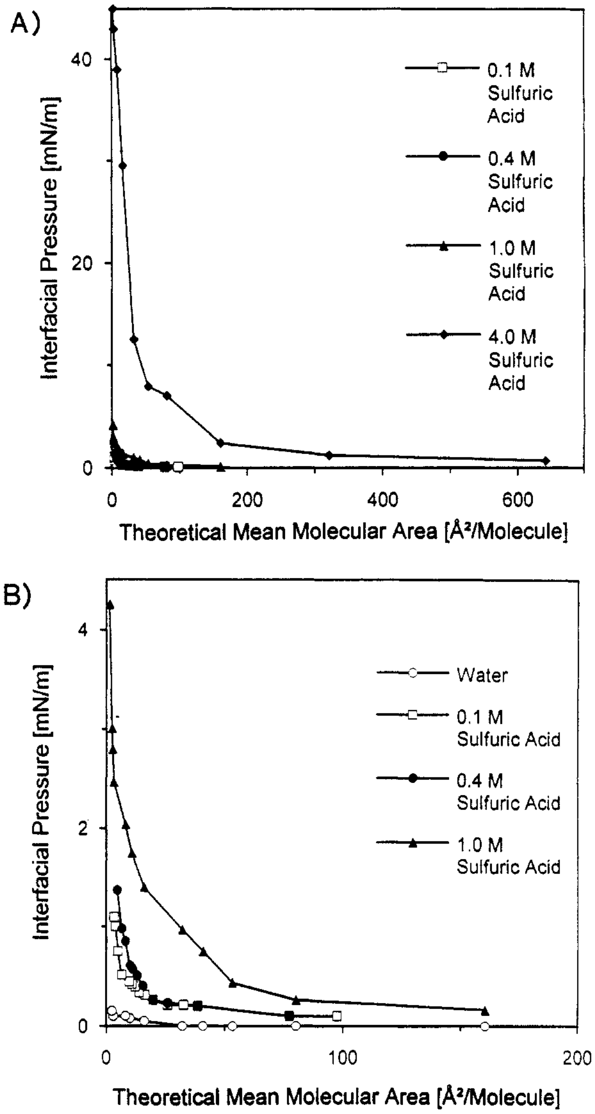

Figure 3. Interfacial pressure of 2-pentadecylaniline at equilibrium (T = 23.5 °C): (A) full scale; (B) enlarged scale.

The change in interfacial pressure with acid concentration (shown in Figure 2) may arise for two different reasons. First, increasing the acid concentration will increase the interfacial tension of the cyclohexane/aqueous interface, which may enhance the amphiphilic character of 2-pentadecylaniline at this interface. Second, increasing the acid concentration may increase the relative concentration of protonated monomer at the interface. In order to distinguish whether the trapping of the monomer is caused by the increase in interfacial tension or the increase in protonated species due to the higher acid concentration, experiments were run with an aqueous 4.0 M solution of sodium chloride and 0.1 M sulfuric acid in the subphase. The results obtained were comparable to those yielded with 4.0 M sulfuric acid only. The primary effect of increasing the sulfuric acid concentration is thus an increase in the interfacial tension between the two phases that increases the tendency of the monomer to remain at the interface. The expected increase in protonation might enhance the interfacial activity of the monomer as well, though this appears to be a minor effect.

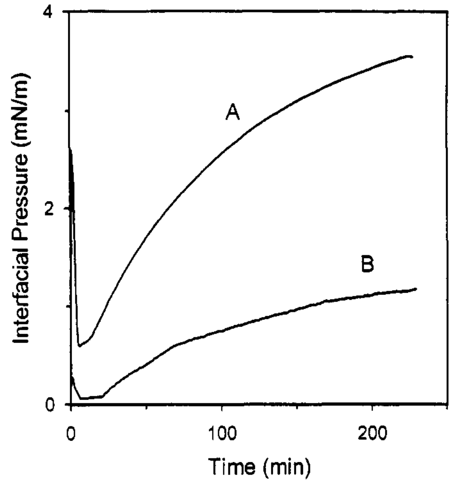

Figure 4. Interfacial pressure vs time plot showing the influence of sulfuric acid subphase concentration on the polymerization of 2-pentadecylaniline at the liquid/liquid interface (cyclohexane/aqueous H_2SO_4, 0.03 M $FeCl_3$, $T = 25$ °C, initial theoretical mean molecular area 25.5 Å^2/repeat unit): (A) 0.4 M sulfuric acid; (B) 0.1 M sulfuric acid.

As described above there is, of course, the question of how much monomer is dissolved in the organic phase. As the spread amount is increased, the theoretical mean molecular area becomes smaller than the cross-sectional area of the molecule. This indicates that incomplete spreading is observed, as has been reported by Hutchinson et al., for chemically different low molecular weight compounds.[32]

Interfacial Polymerization of 2-Pentadecylaniline. Polymerization of 2-pentadecylaniline is thought to follow an oxidative coupling mechanism;[33] therefore, interfacial polymerization of a monolayer of the monomer was tried with an aqueous solution of ferric chloride as the oxidizing agent. No reaction occurred with neutral aqueous subphases. With acidic subphases, however, polymer was formed. The change in interfacial pressure during polymerization at the 0.1 and 0.4 M sulfuric acid/cyclohexane interface is shown in Figure 4. The interfacial pressure is seen to increase monotonically with reaction time in all cases where polymer was formed. The effect of increasing the acid concentration, as shown in Figure 4, was to increase the measured interfacial pressure and apparently the degree of conversion. This can be explained by the change in the surface area occupied per monomer unit during polymerization that is also observed at the air/aqueous interface.[12]

Due to the higher density of a polymer compared to its monomer, the mean molecular area per molecule decreases, thus leading to empty sites at the interface,[30] so that additional monomer dissolved in the organic phase can diffuse to the interface and thus increase the interfacial pressure. In addition, the oligomers and polymers that will be formed during the reaction are less soluble in cyclohexane and preferentially stay at the interface as well.

There is no influence of the $FeCl_3$ concentration on the molecular weight of the polymer formed in the investigated concentration range from 0.01 to 0.05 mol/L. As shown in Figure 5, there is also no influence of the amount spread at the interface, on the time required for the interfacial pressure to reach a constant value; i.e., different initial monomer surface concentrations appear to react in the same manner. It should be noted that no change in interfacial pressure was observed for monomer surface concentrations corresponding to surface areas larger than about 50 Å^2.

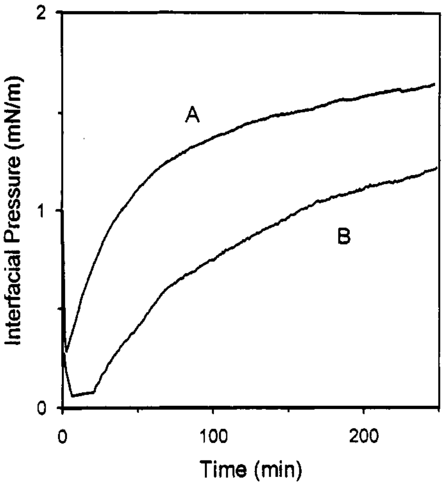

Figure 5. Interfacial pressure vs time for the polymerization of 2-pentadecylaniline at the cyclohexane/0.1 M sulfuric acid interface ($T = 25$ °C, 0.03 M $FeCl_3$). (A) Initial theoretical mean molecular area 14.1 Å^2/repeat unit. (B) Initial theoretical mean molecular area 25.5 Å^2/repeat unit.

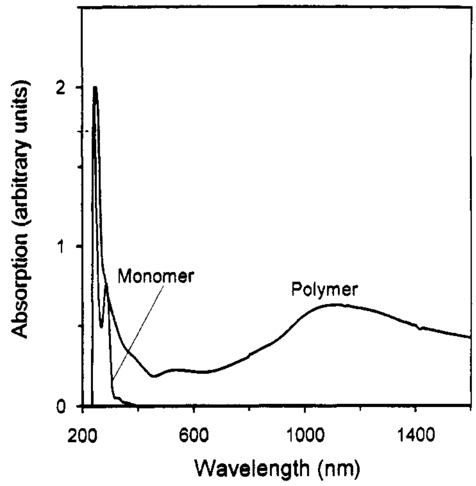

Figure 6. UV–vis–near-IR of 2-pentadecylaniline and poly(2-pentadecylaniline) in chloroform.

Characterization of Polymer

In the polymerization of the monolayers, the highest molecular weight (50 000) and the lowest conversions were observed with the lowest acid concentration in the subphase (0.1 M). For 0.4, 1.0, or 4.0 M subphase sulfuric acid concentrations, a polymer with a molecular weight of 3000–4000 was yielded with high conversion relative to the 0.1 M subphase. All polymers formed under these conditions were monomodal with a polydispersity of about 2.

Polymerization with excess monomer in the organic phase yielded trimodal polymer with peak molecular weights of 118 000, 20 000, and 4000. It should be noted that all molecular weights are relative to polystyrene and as such are only indicative.

The UV–vis–near-IR spectra were recorded in chloroform solution (Figure 6). The spectra for the polymers synthesized under different conditions show the same peaks. They are independent of molecular weight. Three peaks are observed: 290, 530, and 1100 nm. During the reaction the peak at 320 nm for the monomer disappears. The polymer solution is violet; i.e., its oxidation state is comparable to pernigraniline.[34]

Further characterization of the formed polymer was done by NMR. The polymer is soluble in chloroform and insoluble in dimethyl sulfoxide. To prevent interference of the paramagnetic conducting polymer main chain with the rest of the NMR signals, the polymer was reduced before spectra were run. For reduction, a mixture of D_2O and hydrazine-d_4 was used. To achieve complete conversion, DMSO-d_6 had to be added to the $CDCl_3$ for better mixing of the solvents. Upon reduction the solution changes its color from violet to yellow.

The ^1H NMR showed the signals for the 1,4-polymerized aniline consistent with leucoemeraldine. The protons of the aromatic ring give broadened multiplets in the range 6.85–6.40 ppm. No protons belonging to the amino group can be detected, probably due to fast proton–deuterium exchange with D_2O. The C-15 side chain gives peaks as a triplet at 2.3 ppm for the methylene group attached to the ring; a multiplet at 1.50 ppm is observed for the methylenes next to the first one. At 1.10 ppm the methylenes of the long alkyl chain give the strongest signal, and the terminal methyl group shows a triplet at 0.7 ppm. Unfortunately, due to the small amount of polymer sample which could be reasonably collected over several experiments (hundreds of micrograms) and the intrinsic difficulties involved in interpreting polyaniline spectra,[35] a more detailed interpretation of the NMR was not possible.

Given that the monomer is oriented at the interface and the polymerization reaction is confined to the interface and that one of the two possible monomer side-reaction positions is blocked with an alkyl chain, it is probable that the polymer formed is highly configurationally regular.

Conclusions

It has been shown that it is possible to introduce the monomer 2-pentadecylaniline to a planar liquid/liquid interface from cyclohexane solution. At the interface it is protonated upon contact with the sulfuric acid subphase. The salt formed spreads well at the interface and is poorly soluble in both phases. Unprotonated monomer is thought to preferentially dissolve from the interface into the organic phase. The higher the interfacial tension of the interface, the more monomer is bound to it.

The preoriented monomer could be polymerized at the planar interface with acidic ferric chloride subphase solutions, yielding a polymer that is in a pernigraniline-like oxidation state.

Given that the monomer is oriented at the interface and the polymerization reaction is confined to the interface and that one of the two possible monomer side-reaction positions is blocked with an alkyl chain, it is probable that the polymer formed is highly configurationally regular. Further investigations at the liquid/liquid interface are underway.

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