Polymerization of conducting polymers confined to free surfaces: a comparison of the Langmuir–Blodgett polymerizations of 3-alkyl pyrroles and 2-alkyl anilines*

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The Langmuir–Blodgett (LB) polymerization of two monomers, 2-pentadecyl aniline and 3-hexadecyl pyrrole, is compared. Both monomers reacted to form polymers at air–aqueous interfaces. The aniline monomer showed autoacceleration upon polymerization and polymerized much faster as the applied surface pressure increased. The pyrrole monomer polymerized faster than the aniline, but showed little dependence on applied surface pressure. A new LB polymerization experiment where the monomers were pre-oriented in a double compartment trough before chemical polymerization is introduced. The differences in the polymerization behaviour of the two monomers are discussed in terms of their conformation.

(Keywords: conducting polymers; monolayers; polymerization; oxidative coupling; polyaniline; polypyrrole; Langmuir–Blodgett)

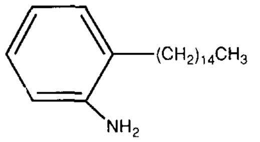
INTRODUCTION

The Langmuir–Blodgett (LB) technique has been known for a long while as a method for obtaining oriented polymeric monolayers by polymerizing monomers at an air–water interface[1,2]. The interest in the technique has been almost exclusively in preparing polymer layers which are subsequently analysed by other techniques[3–6]. Recently, interest in conducting polymers has led to the development of several new electroactive polymers which can be spread as preformed polymers or polymerized on the LB trough[7–10].

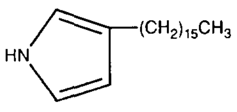
Polymerization reactions within an insoluble monolayer can be studied on the LB trough by observing changes in variables such as the surface potential, u.v.-visible spectra or mean molecular area of a monolayer in real time. Our laboratory has developed experiments that use the LB trough to study polymerization kinetics in real time by monitoring changes in the mean molecular area and barrier speed[11–13]. Under conditions of constant applied surface pressure this is analogous to volume dilatometry in two dimensions[14], where the mean molecular area takes the place of the specific volume.

One important difference between LB polymerizations and their bulk analogues is that the monomers are essentially 'pre-oriented' by the surface and through the use of different applied surface pressures, the distance between reacting monomers can be varied.

This paper compares the LB polymerization of two conducting polymers which are thought to polymerize by an oxidative coupling mechanism. Some similarities and several important differences between the two LB polymerizations are outlined. The chemical structures of the monomers used in this study are:



2-pentadecyl aniline



3-hexadecyl pyrrole

EXPERIMENTAL

The monomers, 2-pentadecyl aniline[7,15], and 3-hexadecyl pyrrole[16], were synthesized using procedures described elsewhere and were used in solution (~1 mg ml^{-1} in spectro grade chloroform). Subphase solutions were made with ACS reagent grade chemicals and Milli-Q® water.

Unless otherwise stated, LB experiments were performed at 27°C on a KSV 5000 LB system equipped with both Wilhelmy balance and floating barrier pressure sensors. Isotherms were carried out at ambient temperature and using compression and expansion speeds of 7.5×10^{17} Å^2 min^{-1}. Aniline polymerizations were carried out on a subphase of aqueous sulphuric acid and ammonium peroxydisulphate solution added to the trough. Pyrrole polymerizations were carried out on a subphase of aqueous ferric chloride.

Single compartment polymerization experiments were carried out by spreading the monomer on the initiator solution subphase and quickly compressing to a given surface pressure which was maintained constant during the reaction by changing the barrier position.

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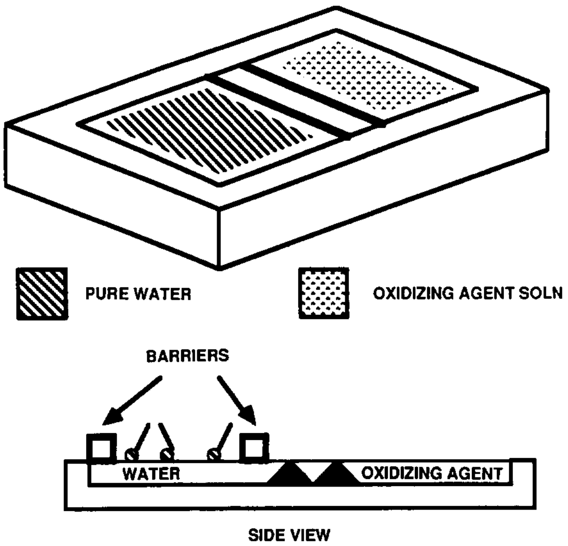

Figure 1 Double compartment trough for LB polymerization experiments. The top of the figure illustrates two different subphases separated by double submerged barriers. The lower part is a side view of the trough: bold squares represent barriers which compress and move monolayer; triangles represent double submerged barriers to keep subphases separate (the liquid between the submerged barriers is pure water)

Double compartment LB polymerization experiments were carried out on a double compartment LB trough as schematically shown in *Figure 1*. The monomer was spread on pure water in one compartment of the trough for the pyrrole or 0.5 M H_2SO_4 for the aniline. The second trough compartment contained the oxidizing agent dissolved in the subphase. The monolayer was then compressed to a given pressure and moved to the other subphase by translating two barriers confining the monolayer. After transfer to the second compartment, the pressure was maintained constant by displacing one barrier. The film transfer speed was $50\,\mathrm{mm\,min^{-1}}$.

The polymerization reaction was followed by monitoring the barrier displacement (as reflected by the mean molecular area) or the change in barrier speed needed to maintain constant surface pressure as a function of reaction time[11]. Polystyrene equivalent molecular weights as measured by g.p.c. in tetrahydrofuran were ~4000–6000 for poly(2-pentadecyl aniline)s polymerized under the conditions of this study and ~8000–15 000 for the poly(3-hexadecyl pyrrole)s. More complete polymer characterization data are available elsewhere[11,15,16,18].

RESULTS

Both monomers studied could be spread at the air–water interface to form stable monolayers. *Figure 2* shows compression isotherms of both materials. Both monomers also showed little hysteresis between compression and expansion isotherms and negligible changes in surface area during isobaric creep measurements below the collapse pressure. The isotherms of the monomers are considerably different from each other. The aniline shows a surface pressure onset at an area of ~49 Å^2 and collapse of the monolayer at an applied surface pressure of $\sim 20\,\mathrm{mN\,m^{-1}}$ and a surface area of 33 Å^2. The pyrrole is seen to have a significantly smaller onset area and higher collapse pressure.

The differences in the monolayer behaviour between the two monomers likely arises from the placement of the side chain substitution. In the aniline, the non-polar alkyl side chain is substituted adjacent to the polar amine moiety. In the pyrrole, however, the side chain is somewhat farther away from the polarizable nitrogen. *Figure 3* shows the two monomers at the air–water interface. We suppose that the 2-alkyl aniline side chain has to assume *gauche* conformations near the phenyl ring to effectively leave the water surface. In contrast, the pyrrole side chain can easily adopt more *trans* conformations as it leaves the water surface.

Previous studies from our group have shown that both 2-pentadecyl aniline[11–13] and 3-hexadecyl pyrrole[16] can be polymerized with the LB trough at air–aqueous interfaces. It is therefore interesting to look at these polymerization reactions in more detail and to compare them. To do this, the polymerization reactions were run under two conditions. In the first case, each monomer was polymerized by spreading it on a subphase containing the oxidizing agent in a single compartment LB trough. In the second case, the monomer was spread on a pure water subphase (or in the case of the aniline monomer 0.5 M H_2SO_4), compressed to a constant pressure in one compartment of a double compartment LB trough, and transferred to the second subphase containing the oxidizing agent solution for polymerization.

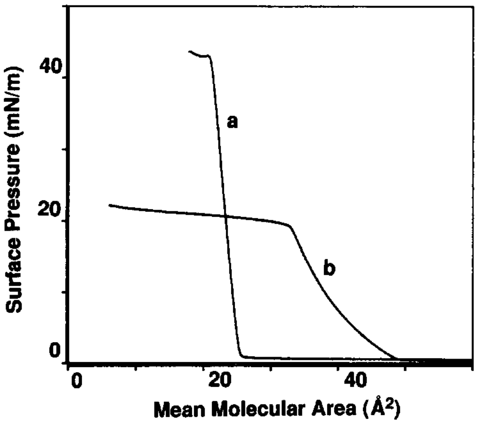

Figure 2 Surface pressure *versus* mean molecular area isotherms of the two monomers on a pure water subphase at 23°C with a barrier speed of $50\,\mathrm{mm\,min^{-1}}$: (a) 3-hexadecyl pyrrole; (b) 2-pentadecyl aniline

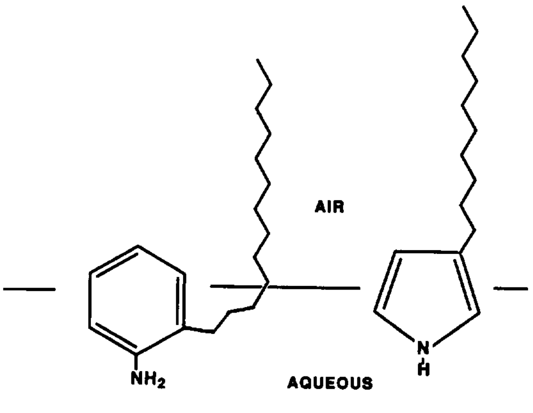

Figure 3 Diagram of the conformation of the substituted pyrrole and aniline at the air–aqueous interface: (a) 2-pentadecyl aniline; (b) 3-hexadecyl pyrrole

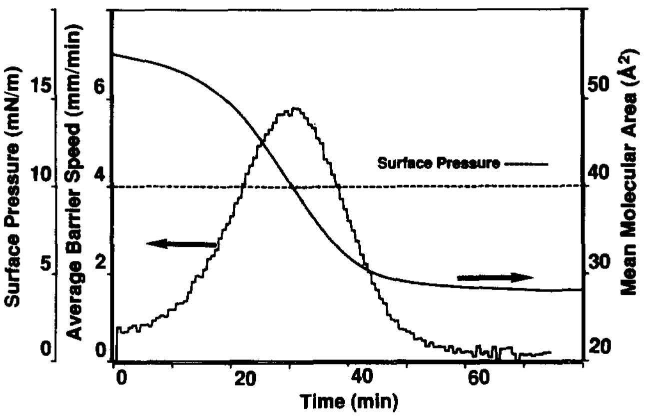

Figure 4 Surface pressure, mean molecular area and average barrier speed *versus* reaction time during the LB polymerization of 2-pentadecyl aniline at ambient temperature and with a subphase of 0.5 M H_2SO_4 with 0.05 M ammonium peroxydisulphate

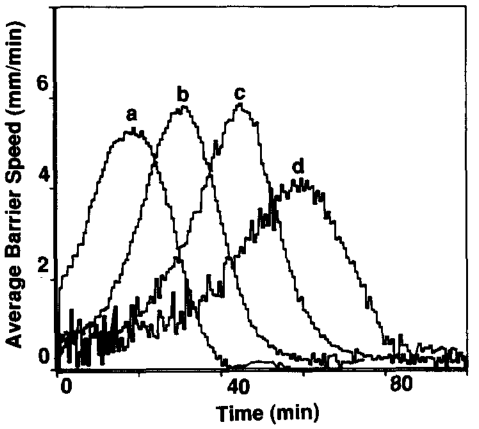

Figure 5 Barrier speed *versus* time at different applied surface pressures during the polymerization of 2-pentadecyl aniline at ambient temperature and with a subphase of 0.5 M H_2SO_4 with 0.05 M ammonium peroxydisulphate: (a) 20; (b) 10; (c) 5; (d) 3 mN m^{-1}

Polymerization in the single compartment LB trough

Figure 4 shows results from the LB polymerization of 2-pentadecyl aniline in a single compartment trough. In this case, the applied surface pressure was maintained constant at 10 mN m^{-1}. During the reaction, the mean molecular area is seen to decrease, coming to a constant value of 28 Å^2 after ~60 min. The barrier speed is observed to increase at the beginning of the reaction, come to a peak value and decrease to about zero at the end of the polymerization. This is similar to an autoacceleration effect seen in conventional electrochemical polymerizations of aniline[17]. At very low (< 1 mN m^{-1}) applied surface pressures, negligible polymerization is observed with 2-pentadecyl aniline. It should also be noted that no polymerization is seen when the monomer is compressed on a pure water subphase. The polymer formed is also not highly oxidized[11] but appears to be air stable over periods of ⩾10 h. The polymer exhibits little hysteresis upon compression–decompression cycles below the collapse pressure and little surface area change in isobaric creep measurements.

An interesting aspect of the LB polymerization of 2-pentadecyl aniline is the effect of applied surface pressure upon the reaction. The effect of different applied surface pressures on this polymerization are shown in *Figure 5*. There is a marked increase in the polymerization rate as the surface pressure increases[12]. At a given surface pressure the polymerization results are very reproducible however.

Figure 6 shows results from the polymerization of 3-hexadecyl pyrrole in a single compartment trough at an applied surface pressure of 15 mN m^{-1}. The mean molecular area also decreases during this polymerization, coming to a value of 16 Å^2 after 25 min. Unlike the aniline polymerization, the barrier speed decreases monotonically throughout the reaction. Like the aniline monomer, no polymerization occurs if the monomer is compressed on a pure water subphase. Unlike aniline however, the pyrrole monomer does polymerize with extremely low or no applied surface pressures. In general, the pyrrole also polymerized more rapidly than the aniline. The LB polymerized polymer also shows properties consistent with a stable monolayer film, i.e. little hysteresis upon compression–decompression cycles and little isobaric creep.

The effect of applied surface pressure on the polymerization of 3-hexadecyl pyrrole is shown in *Figure 7*. Unlike the aniline monomer, the time of complete reaction of 3-hexadecyl pyrrole is not greatly affected by the applied surface pressure. Measurements performed on different $FeCl_3$ subphases indicated that $FeCl_3$ concentrations of > ~0.005 M were necessary to obtain polymer. Furthermore, at low pressures additional features appear in the initial time region of the curve.

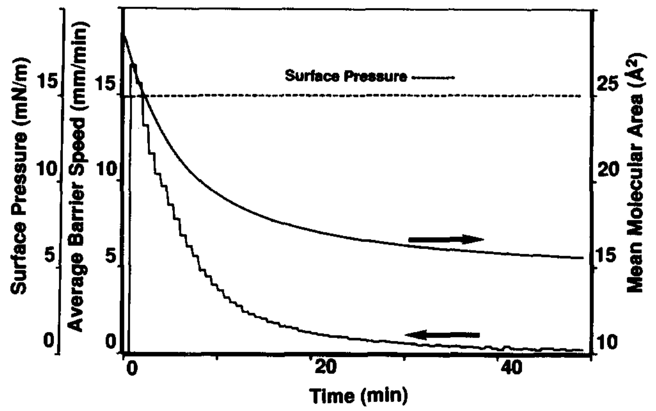

Figure 6 Surface pressure, mean molecular area and average barrier speed *versus* reaction time during the LB polymerization of 3-hexadecyl pyrrole at 25°C and with a subphase of 0.1 M $FeCl_3$

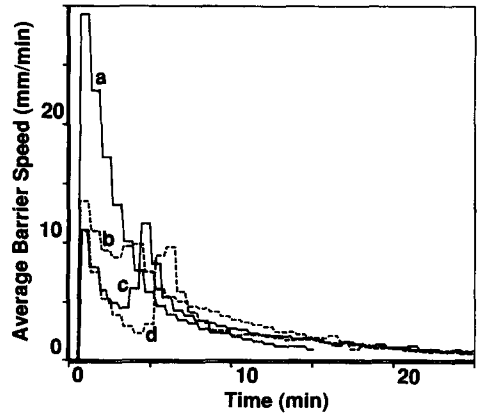

Figure 7 Barrier speed *versus* time at different applied surface pressures during the polymerization of 3-hexadecyl pyrrole at 23°C and with a subphase of 0.05 M $FeCl_3$: (a) 20; (b) 10; (c) 5; (d) 3 mN m^{-1}

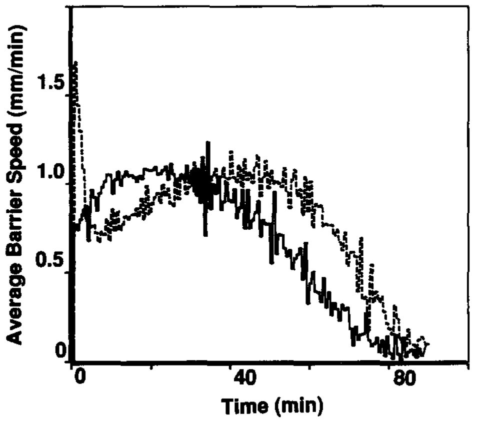

Figure 8 Barrier speed *versus* time during the polymerization of 2-pentadecyl aniline at 25°C with a subphase of 0.5 M H_2SO_4 with 0.02 M ammonium peroxydisulphate and applied surface pressure of 30 mN m^{-1}: (——) single compartment; (– – –) double compartment

This behaviour may reflect rate-limiting steps in the initial reaction mechanism and is discussed further below.

Polymerization in the double compartment LB trough

The 2-pentadecyl aniline was polymerized in the double compartment trough by shifting a precompressed monolayer from a pure water subphase to one with initiator solution. *Figure 8* compares the barrier speed *versus* time data for the single and double compartment polymerization experiments. Within experimental accuracy both polymerization reactions were the same.

Similar double compartment polymerization experiments were also performed with the pyrrole monomer. In these experiments, the precompressed film behaved differently from single compartment pyrrole polymerizations. In all cases polymer formed but the precompressed monomer appeared to give a lower yield. It should be noted that polypyrrole formed in either the single or double compartment experiments is not highly oxidized[16] and is therefore slightly unstable in the air atmospheres used in these experiments; rapid characterization was necessary to obtain reproducible and meaningful results.

DISCUSSION

The isotherms of the two monomers studied indicate clear differences in their behaviour at air–aqueous interfaces. These differences are borne out in the polymerization behaviour as well and are discussed below.

The surface area change observed in the polymerization of 2-pentadecyl aniline is reasonable if a predominantly 1,4-linked polymer is formed. In this case, the monomeric conformation shown in *Figure 3* would have to change in such a way that the side chain could leave the water surface closer to an all-*trans* conformation. This picture is consistent with the fact that no polymerization is measurable at very low surface pressures. The mean molecular area of the polymer formed (~23 Å^2 at 20 nN m^{-1} surface pressure) and the pressure dependence of the polymerization rate also support this interpretation. The effect of applied surface pressure might be to change the conformation of the monomer in such a way as to favour this 1,4 linkage.

The polymerization behaviour of the 3-hexadecyl pyrrole reflects a large difference in this polymerization compared to the aniline monomer. The surface area change upon polymerization was similar to the aniline monomer (~20 Å^2 for pyrrole compared to 25 Å^2 for aniline, both at 20 mN m^{-1}) yet the final surface areas were quite different (~15 Å^2 for pyrrole compared to 23 Å^2 for aniline at 20 mN m^{-1}). A 15 Å^2 mean molecular area for poly(3-hexadecyl pyrrole) is far too small for a monolayer of molecules packed in the same sense as its monomer. Furthermore ^{1}H n.m.r. measurements of the polymer formed on the LB trough have shown a very regular 2,5-linked polymer is formed[16]. It is sterically impossible for 2,5-linked polymer to pack in monolayers with the same conformation as the monomer. The area change observed in the LB polymerization must therefore reflect a large conformation change of the monomer upon polymerization. One possibility is the formation of the helical conformation at the surface; helical conformations have been proposed for bulk polypyrroles[19].

In single compartment polymerization studies however, there is little evidence that the time for the polymerization to be completed is significantly affected by the applied surface pressure. Also the pyrrole does not show the auto-acceleration effect seen in the aniline monomer. This may be understandable given the nature of the polymerization experiment. The monomer was spread directly upon the oxidizing agent solution where it remained at low pressure until compressed (minutes). During this time it could easily have started reacting.

From *Figure 7* it can be seen that in single compartment polymerization experiments the barrier speeds are essentially independent of the applied surface pressure after reaction times of ~10 min. At shorter reaction times however, the barrier speed is obviously affected by the pressure. The initial barrier speed at 20 mN m^{-1} is indeed higher than those at the other pressures, but the decrease with lower applied pressures is not as large as seen in the aniline data of *Figure 5*. Furthermore, a peak obviously appears in the data at the lower pressures and this peak shifts to shorter times as the pressure increases. This indicates that the higher initial barrier speeds at higher pressure may result from the peak superimposed on another reaction. These data imply that at low pressures, two reactions may be competing. Further kinetics runs and g.p.c. data taken as a function of reaction time lead us to believe that the peak may correspond to the formation of the 3-alkyl-substituted 2,5-bis(2-pyrrolyl)pyrrolidine (or another similar trimer-like structure). Further experiments to confirm this are in progress in our laboratory. If this were the case, it would imply that the rate-limiting step at the beginning of the polymerization reaction is independent of the applied surface pressure and does not involve two or more monomer molecules. This is unlike what is observed for 2-pentadecyl aniline[12]. This step may be, for instance, the formation of a radical cation. However the rate-limiting step of the second reaction does depend on the surface pressure and should involve two or three monomer molecules.

The double compartment LB polymerization is a useful means to further compare the reactions of these two monomers. Under these conditions the monomer should be pre-oriented *before* the polymerization process starts. In the cases of the aniline monomer, the results are consistent with the above-mentioned picture. In the case of the pyrrole monomer, one might have suspected that increased applied surface pressure in the double compartment experiment would slow down or even stop the reaction. While the observed results are not in disagreement with this, they are far from conclusive. Experiments to understand the polymer conformation at a monolayer in more detail are being continued in our laboratory.

The double compartment LB polymerization experiment described here may also prove valuable for studying other chemical reactions. It has the advantage of being relatively fast and simple to perform and requires only micrograms of monomer per experiment. It is also one of few methods whereby it is possible to pre-orient all monomer molecules prior to reacting them. Furthermore by varying the surface pressure one can vary the average distance between monomers over a wide range. In this manner it may be possible to study a wide variety of chemical reactions that normally occur in bulk phases by confining the reactants to a free surface.

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