

Effects of Temperature and Chemical Modification on Polymer Langmuir Films[†]

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We previously reported on a rheological study of Langmuir films of poly(*tert*-butyl methacrylate) (PtBMA), and this work describes further studies on this system. Here, surface pressure–area (Π – A) isotherms and interfacial shear rheology experiments are performed to better understand the effects of two modifications: varying the temperature between 5 and 40 °C and introducing small amounts of carboxylic acid groups by partially hydrolyzing the polymer. Increased temperature produced isotherms with lower plateau surface pressures, Π_p , and Π values shifted to lower areas above Π_p . Film properties transition from being primarily viscous to being dominated by elasticity as Π_p is crossed for all temperatures studied, even as the value of Π_p changes. Increasing the hydrolysis fraction leads to isotherms shifted to lower areas throughout the curve and higher Π_p values. Both temperature variation and chemical modification are believed to affect the relative importance of polymer–polymer and polymer–subphase interactions.

1. Introduction

Interfacial polymer films are industrially important for their ability to stabilize systems such as emulsions and foams, and they have been studied for decades.¹ Previously, we reported on a rheological study of poly(*tert*-butyl methacrylate) (PtBMA) Langmuir films, and those results revealed important information about the monolayer-to-multilayer transition.² To extend that study, this work focuses on studying the surface pressure–area (Π – A) isotherms and rheological properties of Langmuir systems involving the same polymer subjected to two key alterations: temperature variation and minor chemical modification. These changes affect both polymer–polymer and polymer–subphase interactions.

Temperature is an important parameter in the study of monolayer systems. By changing the amount of thermal energy available, interactions between molecules and with the subphase can be changed, and this variation can often be observed in the shape of the Π – A isotherm and in the rheological properties. In the study of Langmuir monolayers, the general trend is for isotherms to shift to larger areas and higher transition pressures as the temperature increases. This is the case for systems such as myristic acid and *n*-octadecylamine.¹ For polymer monolayers, however, this is not the case. A variety of effects have been observed in response to temperature changes, and various explanations have been put forth to address them. Isotherms of poly(vinyl acetate) films are seen to shift to higher area and surface pressures with increasing temperature.^{3,4} However, films of acrylate polymers have been observed to shift in either direction, with poly(methyl acrylate) and poly(*n*-butyl methacrylate) exhibiting expansion at elevated temperature, while poly(methyl methacrylate) and poly(*iso*-butyl methacrylate) exhibit the opposite trend.^{3,5} Brinkhuis and co-workers have

suggested that these systems may be extremely sensitive to polymer tacticity.⁵ It is also possible that the cohesive interactions between polymers are temperature dependent. Another factor that should be considered is entropy. For a fixed molecular area, the surface pressure dependence on temperature can provide information about the disorder of the system. A negative value for $d\Pi/dT$ during a phase change suggests an increase in entropy.⁶

Previous studies on the temperature dependence of the surface rheology of polymer systems are rare. Ogarev et al. report a decrease in surface viscosity by approximately 1 order of magnitude for a 30 °C increase in temperature for poly(dimethyl siloxane) films.⁷ More recent work has examined interfacial viscoelasticity for poly(vinyl acetate) systems and found a slight shift in the maximum dynamic moduli to lower surface pressures at higher temperature.⁸

Another method of varying the interactions between polymer molecules and the subphase is to chemically modify the structure of the polymer. To test the effect of this approach on this system, PtBMA molecules were partially hydrolyzed to the corresponding carboxylic acids. This results in a poly(*tert*-butyl methacrylate) polymer with a small number of carboxylic acids distributed throughout the chain. The result of this chemical modification is a polymer with slightly increased hydrophilicity. In fact, complete hydrolysis of PtBMA produces poly(methacrylic acid), which is completely soluble in water. Thus, by slightly adjusting the hydrophilic character of these polymers, the partially hydrolyzed chains should exhibit enhanced attraction to the subphase as compared with unmodified PtBMA, and this change may be apparent in the Π – A isotherms for these materials. We are not aware of any similar approaches to studying Langmuir films of modified polymers being reported previously.

To study the effect of temperature on Langmuir films of PtBMA, both surface pressure–area isotherms and interfacial rheology measurements were made. For the chemically modified polymer experiments, hydrolysis percentages less than 10% were used so as not to drastically alter the original molecular

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character, and only Π -A isotherms were recorded for these cases. Partially hydrolyzed PtBMA samples were also studied at two different subphase acidities.

2. Materials and Methods

The polymer used for these experiments is poly(*tert*-butyl methacrylate) rich in syndiotactic microstructure, with approximately 52% *rr* triads as measured by ^{13}C NMR. The samples have a molecular weight of either $M_n = 81.5$ kg/mol or $M_n = 211.5$ kg/mol and a polydispersity index of $\text{PDI} \approx 1.3$ (Polymer Source). For the temperature studies, the polymer was used as received. The partially hydrolyzed samples were prepared by the authors using one of the two methods described below.

The quantitative hydrolysis of *tert*-butyl ester groups in the PtBMA was carried out under mild conditions using iodotrimethylsilane (TMSI).^{9,10} The amount of hydrolysis was controlled by the treatment of the polymers with the desired quantity of TMSI, followed by aqueous hydrolysis. All reactions were performed with Schlenk techniques under nitrogen. Iodotrimethylsilane (TMSI) was purchased from Aldrich and distilled from calcium hydride. Tetrabutylammonium fluoride solution (TBAF) was purchased from Aldrich (1.0 M in tetrahydrofuran) and used as received. Deuterated chloroform was purchased from Acros and distilled from calcium hydride. Dichloromethane was passed through columns of activated alumina. Methanol was purchased from Fisher Chemicals and used as received. ^1H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a 400 MHz spectrometer.

2.1. Direct Preparation of Hydrolyzed PtBMA. The required amount of TMSI was added dropwise to a stirred solution of PtBMA in CH_2Cl_2 (~ 0.1 M), and the reaction mixture was stirred at room temperature for 2 h. The amount of hydrolysis was estimated by ^1H NMR spectroscopy by comparing the *tert*-butyl hydrogen peaks of *tert*-butyl iodide, *tert*-butyl ester (on the polymer), and trimethylsilyl ester (on the polymer). After the volatiles were removed in vacuo, the polymer was dissolved in CH_2Cl_2 and precipitated from a methanol/water mixture (2:1 by volume). The precipitation was repeated to hydrolyze the silyl ester, and the polymer was dried to a constant weight at room temperature under reduced pressure.

2.2. Incremental Preparation of Hydrolyzed PtBMA. The required amount of TMSI was added dropwise to a stirred solution of PtBMA in CDCl_3 (~ 0.1 M), and the reaction mixture was stirred at room temperature for 2 h. An aliquot was removed and analyzed by ^1H NMR spectroscopy. The amount of dealkylation was estimated by comparing the *tert*-butyl hydrogen peaks of *tert*-butyl iodide and the polymer. The aliquot was then treated with TBAF, and the mixture was stirred at room temperature for 30 min. After removal of the volatiles in vacuo, the polymer was dissolved in CH_2Cl_2 and precipitated from a methanol/water (2:1 by volume) mixture three times. The polymer was dried to a constant weight at room temperature under reduced pressure. To obtain more hydrolyzed PtBMA, more TMSI was added to the reaction mixture, and the entire procedure was repeated. The successive aliquots afforded a series of hydrolyzed PtBMAs with various hydrolysis fractions.

2.3. Interfacial Experiments. All interfacial experiments were performed in a Teflon Langmuir trough (40 cm \times 5.5 cm) equipped with movable Delrin barriers (KSV). The subphase used for most of this work was purified water (Millipore Milli-Q) with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ and $\text{pH} \approx 5$. For some experiments, a 10 mM citric acid buffer solution was used as the subphase to maintain a pH of 3.2. Using coils in the

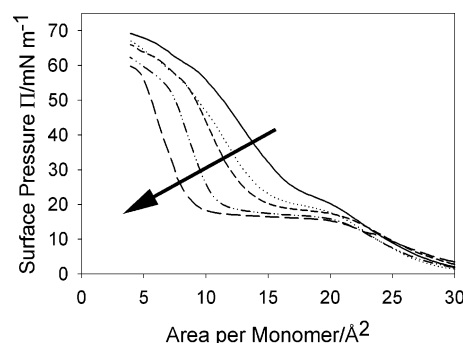


Figure 1. Π -A isotherms for Langmuir films of PtBMA ($M_n = 211$ kg/mol) at temperatures of $T = 5$ (—), 15 (\cdots), 23 ($- - -$), 30 ($\cdot \cdot \cdot$), and 40 $^\circ\text{C}$ (—). The isotherms are all coincident at low surface pressures; however, the plateau occurs at lower surface pressures at higher temperature. Above the plateau, the high-temperature isotherms are shifted toward lower areas.

base of the trough, the subphase temperature could be accurately controlled by an external water bath over the range $T = 5$ – 40 $^\circ\text{C}$. The lower limit of this temperature range was imposed by the freezing point of the subphase, and the upper bound was limited by subphase evaporation over the time scale of the experiments. To form the Langmuir films, the polymer of interest was dissolved in chloroform (1 mg/mL), and this solution was gently added to the interface using a glass microsyringe (Hamilton). Surface pressure was measured using a platinum Wilhelmy plate and a force transducer with a reported resolution of $4 \mu\text{N/m}$ (KSV), and the barriers were compressed at a rate of 1 mm/min to allow the system to remain close to equilibrium.¹

The interfacial stress rheometer (ISR) developed by Brooks et al. was used to measure the viscoelastic properties of these films.¹¹ This device has been described previously, but in short, it utilizes Helmholtz coils surrounding a standard Langmuir trough to provide a magnetic field gradient that can move a magnetic rod situated at the interface of interest. As the rod moves, it creates a 2-D shear flow profile in a narrow channel. Using a photodiode array, the position of the rod can be measured. To ensure the usefulness of this approach, the Boussinesq number was determined to be greater than 1000, indicating the dominance of interfacial drag over subphase drag. Additionally, only small-amplitude oscillations were used so that the system remained in the linear viscoelastic regime.

3. Results and Discussion

3.1. Temperature Dependence. Isotherms and rheological measurements were investigated over a range of temperatures. Figure 1 presents the Π -A isotherms for Langmuir films of PtBMA at five different temperatures from 5 to 40 $^\circ\text{C}$. At low surface pressures, the curves are all coincident. However, there is a significant change in the height of the plateau surface pressure, Π_p , as the temperature is varied. For the highest temperatures studied, the plateau transition occurs at a markedly lower surface pressure, and the opposite is true for reduced temperature. Over this range of temperatures, the plateau surface pressures vary by almost 6 mN/m. The Π_p values for these isotherms, as determined by the inflection point, are shown in Figure 2. Additionally, at high temperature, the plateau is much broader and more well-defined. Above Π_p , the surface pressure begins to increase again for all cases, but the curves are now separated, with the high-temperature isotherms shifted toward lower areas. All isotherms also show a second transition marked by a bend at surface pressures between 50 and 60 mN/m. This

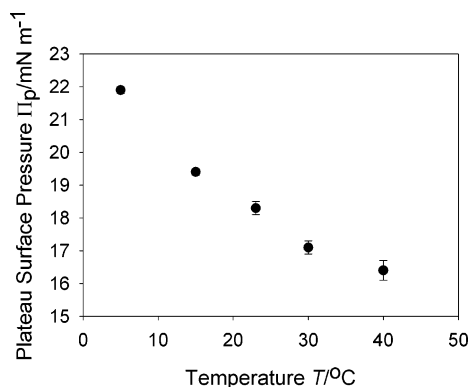


Figure 2. Plateau surface pressure values for the P – A isotherms shown in Figure 1 for Langmuir films of PtBMA ($M_n = 211$ kg/mol) at temperatures of $T = 5$ – 40 °C. The Π_p values decrease with increasing temperature, and the values change by almost 6 mN/m over the range of temperatures studied.

bend seems to be slightly sharper at high temperature and more rounded at low temperature. Due to the offset between the isotherms at high surface pressure, the upper portions of the isotherms do not all extrapolate to intersect the surface pressure axis near 72.8 mN/m, as was the case at room temperature.² This is most noticeable for the isotherms measured at the highest two temperatures, where the curves will have extrapolated intercepts substantially lower than this value. However, the values the isotherms approach can be explained by the decreasing surface tension for the pure air–water interface in response to increased temperature. In fact, the surface tension at 5 °C is 74.9 mN/m, and the value at 40 °C is 69.6 mN/m.¹² As before, these represent the maximum obtainable surface pressures for Langmuir systems, so it is understandable that the isotherms approach this limit for small available surface area. Finally, the observed shifts for these syndiotactic-rich PtBMA films in response to temperature are qualitatively similar to the results reported by Brinkhuis for other syndiotactic methacrylate polymers.⁵

It has been suggested that increasing the temperature of Langmuir films leads to a decrease in the strength of interaction between polymers and subphase in systems that exhibit negative values of $d\Pi/dT$, such as this one. Also, an increased strength of attraction between polymer molecules at high temperature may play a role in such systems.⁵ In either case, a relative increase in the importance of cohesive attraction between polymers compared to the attraction between polymer and subphase may help explain the isotherm shifts observed here. If cohesion is dominant at high temperature, it should require less surface pressure to force polymer out of the first monolayer, which is directly in contact with the subphase. During this transition, there would now be less of an energetic penalty if the intermolecular attraction played a larger role. Further, for more strongly cohesive systems, the shift to lower areas above the plateau could be the result of closer packing.

Analysis of the surface pressure as a function of the surface concentration, Γ , (Figure 3) enables the determination of the scaling exponent, ν . For 2-D polymer systems in the semidilute regime, the predicted scaling between surface pressure and surface concentration is $\Pi \sim \Gamma^{2\nu/(2\nu-1)}$.¹³ Using this relation, the slope of a power law fit to the semidilute regime of the Π – Γ isotherm corresponds to scaling exponents of $\nu = 0.54$ – 0.57 . These values are similar, and there does not appear to be a trend in the scaling exponent as a function of temperature. As was the case for the room temperature isotherm, this suggests that PtBMA molecules exist in collapsed coils under nearly theta

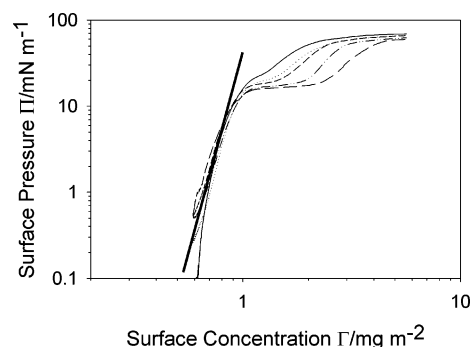


Figure 3. Π – Γ isotherms for Langmuir films of PtBMA ($M_n = 211$ kg/mol) at temperatures of $T = 5$ (—), 15 ($\cdot\cdot\cdot$), 23 (---), 30 ($-\cdot-\cdot-$), and 40 °C (—). A power law fit to the portion of each curve corresponding to the semidilute regime suggests scaling exponent values of $\nu \approx 0.54$ – 0.57 .

conditions at the air–water interface. Interestingly, while the strength of the polymer–subphase interaction seems to be altered on the basis of the Π – A isotherms during and above the plateau transition, there seems to be almost no change for the low-surface-pressure portions of the curve. The quality of the air–water interface as a solvent remains unchanged.

The rheological properties of PtBMA films were also studied as functions of temperature. Both small-amplitude oscillation and creep compliance methods were used. Figure 4 presents the surface shear storage and loss moduli, G'_s and G''_s , for PtBMA systems at three temperatures and a range of surface pressures near the plateau. Although data were collected over a wider temperature range, this figure presents viscoelastic properties at 15, 23, and 30 °C which represent the general observations. In all cases, at low surface pressure, the films display viscoelastic character, but the surface shear loss modulus is greater in magnitude than the storage modulus. The primary feature of these plots is the value of the surface pressure when G'_s becomes greater than G''_s , indicating a shift in the relative character of the PtBMA film. In Figure 4a, which presents data measured at 15 °C, this transition occurs between $\Pi = 18$ and 19 mN/m. At 23 °C, the changeover takes place in the range $\Pi = 17$ – 18 mN/m, and at 30 °C, the transition is between $\Pi = 16$ and 17 mN/m.

Interestingly, the trend in the crossover surface pressure in response to temperature closely parallels the observed shift in the plateau surface pressures. These results are summarized in Table 1. This correspondence signifies an important connection between a conformation change in the Langmuir film reflected by the plateau in the Π – A isotherm and the rheological properties of the film. In the previous discussion of the room temperature case, the changeover to the PtBMA film having a dominant elastic character above Π_p was attributed to the formation of a multilayered system.² This is likely still the case at the other temperatures studied. The fact that the rheology tracks the conformational change is a significant observation because it helps isolate the source of the elastic transition. Even as the surface pressure at which chain pile-up occurs changes, the signature of this process can be clearly seen in the rheology.

Creep compliance experiments were also performed at different temperatures using the procedure described previously.² The data were fit to a three-element mechanical model consisting of a Voigt–Kelvin element connected in series with an additional dashpot. The primary property of interest is the long-time, limiting viscosity of the PtBMA film that corresponds to this final dashpot. Measured values of surface shear viscosity, η_s , at several surface pressures are shown as functions of

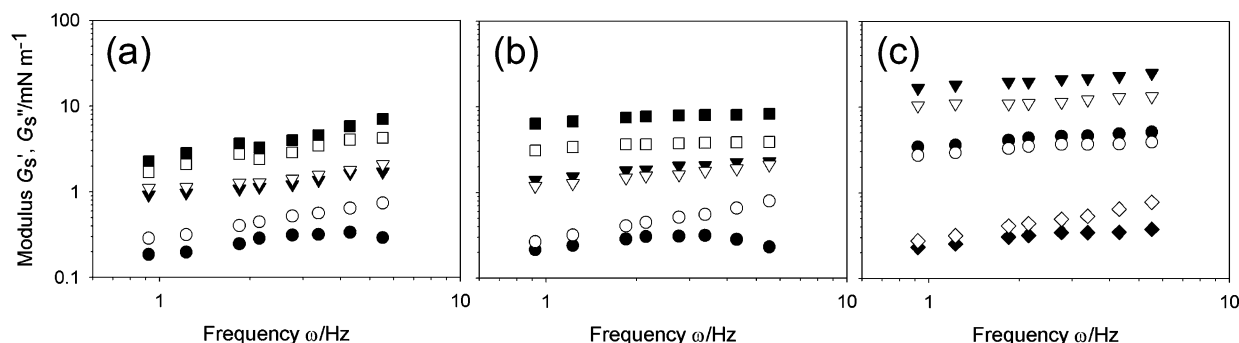


Figure 4. PtBMA ($M_n = 211$ kg/mol) surface shear storage and loss moduli near the plateau surface pressure for $T = 15$ (a), 23 (b), and 30 °C (c). The surface pressures included are $\Pi = 16$ (\diamond), 17 (\circ), 18 (∇), and 19 mN/m (\square). In each case, G'_s is greater than G''_s at low surface pressure, but the opposite is true at higher values of Π . The value at which this crossover occurs decreases as the temperature is increased.

TABLE 1: Summary of the Temperature Dependence of the Plateau Surface Pressure and $G'_s - G''_s$ Crossover Surface Pressure for Langmuir Films of PtBMA ($M_n = 211$ kg/mol)^a

temperature (°C)	plateau surface pressure (mN/m)	$G'_s - G''_s$ crossover surface pressure (mN/m)
15	19.4	18–19
23	18.3	17–18
30	17.1	16–17
40	16.4	15–16

^a The surface pressure values track each other well over this range of temperatures.

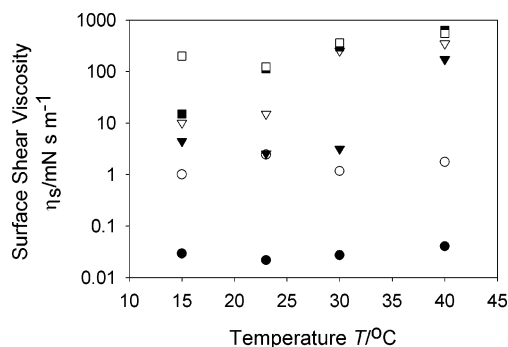


Figure 5. Surface shear viscosity of PtBMA ($M_n = 211$ kg/mol) films as a function of temperature for surface pressures of $\Pi = 5$ (\bullet), 15 (\circ), 16 (\blacktriangledown), 18 (∇), 19 (\blacksquare), and 20 mN/m (\square). There is a marked increase in η_s for each surface pressure series at the temperature where the plateau surface pressure occurs for that system.

temperature in Figure 5. The general trend of viscosity increasing as surface pressure rises can be clearly seen. Additionally, for surface pressures far above or below the plateau surface pressure, η_s does not seem to be a strong function of temperature. However, near Π_p , there is a large jump in the value of the surface shear viscosity. The magnitude of this sudden change is approximately 1 order of magnitude. As was the case with the surface storage and loss moduli, this increase in viscosity also tracks the position of the plateau surface pressure as the temperature is varied. This can be easily seen by examining the data collected at specific surface pressures. For instance, for $\Pi = 16$ mN/m, the surface viscosity is fairly constant for $T = 15$, 23 , and 30 °C; however, there is a marked increase in the value when $T = 40$ °C. Other surface pressure series can be analyzed in the same way.

3.2. Chemical Modification. Representative isotherms for a series of modifications on the same material, PtBMA with $M_n = 81.5$ kg/mol, measured at $T = 22.5$ °C are shown in Figure 6. As the fraction of carboxylic acids increases, the isotherms shift to lower average areas and the plateau surface pressures increase. In contrast to the effect of changing the temperature

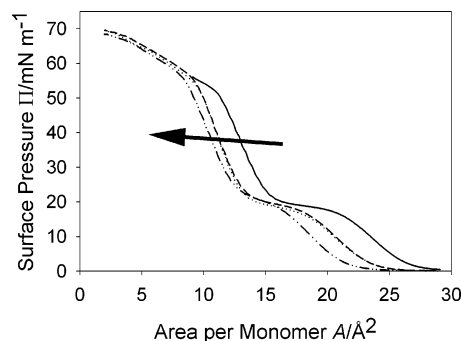


Figure 6. Π – A isotherms measured at $T = 22.5$ °C of PtBMA ($M_n = 81.5$ kg/mol) films with different hydrolysis percentages: 0 (—), 3.1 (···), 4.9 (---), and 9.3% (- · - ·). As the hydrolysis fraction is increased, the isotherms shift to lower average areas and higher plateau surface pressures. At high surface pressure, the isotherms still extrapolate to intersect the axis near 72.8 mN/m.

of the system, these isotherms are separated over the entire range of areas, whereas the systems at different temperatures showed isotherms that were coincident at large areas and then began to separate near the plateau. Additionally, the isotherms for the partially hydrolyzed samples still extrapolate to intersect the surface pressure axis near 72.8 mN/m, the maximum attainable surface pressure for a system at the air–water interface at this temperature. It should be noted that, in determining the mean monomer area, the values are corrected for the decreasing molar mass of the repeating unit of the polymer due to chemical modification.

The isotherms for the partially hydrolyzed PtBMA molecules revealed some general trends that are illustrated in Figure 7. This figure presents the height of the plateau, Π_p , as determined by the inflection point of the curve as well as the mean monomer area at lift-off, A_{lo} , which is determined by extrapolating the low- Π region of the isotherm back to its intersection with the area axis. Since the main aspect of interest is how these values are changed relative to the isotherm of unmodified PtBMA, only the differences are shown in this plot. The data in this figure reflect experiments on PtBMA with $M_n = 211$ kg/mol. Each point in this figure corresponds to a separate attempt at chemical modification and reflects the average of several repeated measurements of the isotherm for each compound. One point in Figure 7b does not fit well with the trend, but the remaining data points show a linear relation between the amount of isotherm shift and hydrolysis fraction. The outlying point may result from error in determining the concentration during the preparation of the spreading solution. Measurements were made three times on this sample; however, due to the limited quantity of material synthesized, further data could not be collected.

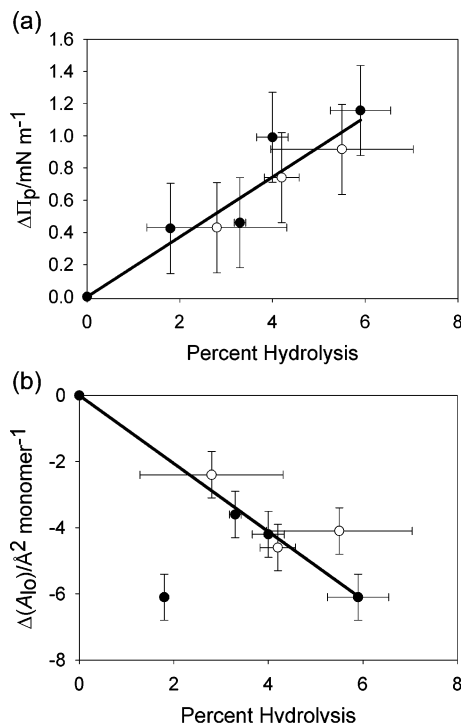


Figure 7. Quantification of the amount of shift in the plateau surface pressure, Π_p (a), and the mean monomer lift-off area, A_{10} (b), as functions of percent hydrolysis for PtBMA films with $M_n = 211$ kg/mol for both direct (white) and incremental (black) synthesis. The general trends are increasing values of Π_p and decreasing values of A_{10} as the hydrolysis fraction is increased.

An examination of the changing interactions that result from partially hydrolyzing these chains may explain the observed behavior. As mentioned previously, an increase in the fraction of carboxylic acid groups should increase the hydrophilicity of the chain, leading to a stronger attraction to the subphase. If the polymers are bound more strongly to the interface, it should require higher surface pressures to force chains out of the first layer. This describes the observed increasing values of Π_p as the hydrolysis fraction is increased. However, this effect is much weaker than that observed by varying the subphase temperature. Additionally, the hydrolyzed monomers should slightly increase the solubility of the chains. While this may only have an effect on a very local level around the modified group, it may lead to sections of the new polymers sitting lower in the water compared to residing at the interface, as the unmodified chains seem to do. This would allow slightly more interfacial area to be free for the remaining interfacial segments to pack, resulting in a shift in the isotherm to lower areas, as observed.

Another interesting feature of these partially hydrolyzed PtBMA isotherms is that the scaling exponent, ν , does not vary with the hydrolysis fraction. The Π – Γ isotherms corresponding to the data presented in Figure 6 are shown in Figure 8. Again, the slope of the power law fit is related to ν , and since slopes are nearly constant for these isotherms, the scaling exponent is always $\nu \approx 0.54$. Therefore, the polymers are still under nearly theta solvent conditions. It is reasonable to expect that increasing the hydrolysis fraction would lead to chains adopting slightly more expanded conformations at the air–water interface due to increased solubility; however, these results do not suggest that this occurs.

To further probe the partially hydrolyzed PtBMA molecules, experiments were also performed on a more acidic subphase. For pyvalic acid, the small molecule analogue of the hydrolyzed PtBMA repeat unit, $pK_a \approx 5$ in water, a citric acid buffer was

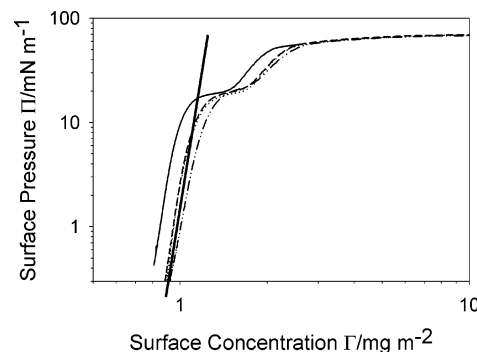


Figure 8. Π – Γ isotherms of PtBMA ($M_n = 81.5$ kg/mol) films with different hydrolysis percentages: 0 (—), 3.1 (· · ·), 4.9 (---), and 9.3% (- · - ·). The slope of each curve in the semidilute regime is nearly identical and corresponds to a scaling exponent value of $\nu \approx 0.54$.

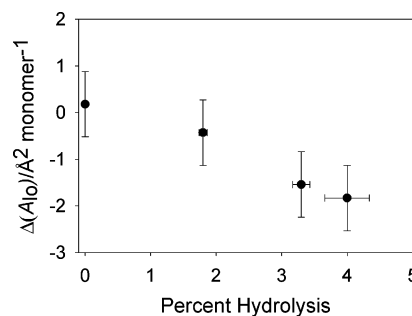


Figure 9. Quantification of the amount of shift in the mean monomer lift-off area, A_{10} , as a function of percent hydrolysis for PtBMA films with $M_n = 211$ kg/mol on a subphase with pH 3.2 compared to pH 5. Negative values indicate a lower lift-off area on the more acidic subphase. The amount of the shift increases with the hydrolysis percentage.

used to maintain a value of pH 3.2 for the subphase. Working at this pH value should ensure that the vast majority of hydrolyzed PtBMA groups remain protonated. By contrast, for the purified water subphase used in our previous experiments, $pH \approx 5$, only half of the hydrolyzed groups are expected to be protonated. This could lead to some electrostatic repulsion between negatively charged groups, but this repulsion should be minimized by working at low pH.

The Π – A isotherms for PtBMA with hydrolysis percentages up to 4.9% were measured on both purified water and citric acid buffer subphases. Although the isotherms all had the same general shape, there were slight variations between the two conditions. For the hydrolyzed samples, the lift-off areas were lower on the low-pH subphase than on water. There was almost no shift for the unmodified PtBMA sample. The amount by which A_{10} changed in response to the acidic subphase is shown as a function of hydrolysis fraction in Figure 9. A negative value of ΔA_{10} indicates a lower value for the lift-off area on the citric acid buffer.

The change to the subphase acidity did not have a large impact on the plateau surface pressure. The values for Π_p follow the trend observed on the purified water subphase of increasing as the hydrolysis fraction was increased. The difference between experiments on the water and buffer subphases was typically within 0.3 mN/m.

Additionally, the scaling exponent values were determined from the hydrolyzed PtBMA isotherms on the pH 3.2 subphase, and these are all in agreement with those observed on the purified water subphase. In all cases, the value was found to be $\nu \approx 0.54$. Thus, the polymer coils remain under nearly theta solvent conditions at the air–water interface for all cases.

4. Conclusions

In this work, we have reported on two extensions to our previous work studying interfacial polymer systems: changes in temperature and chemical modification. Both of these alterations can change the interactions that govern the shape of the surface pressure–area isotherm and interfacial rheological properties.

By changing the temperature of PtBMA films, the strength of interaction between polymer molecules and the subphase can be varied, and these changes lead to observable differences in the shapes of the Π – A isotherms. Most notably, the plateau surface pressure shifts to lower values and the isotherms tend to lower average areas above the plateau as the temperature is increased. This is interpreted as an increase in the relative importance of cohesive attraction between polymer molecules compared to the polymer–subphase interaction. Also, a rheological transition is seen as G'_s overtakes G''_s as the surface pressure is increased, indicating a fundamental transition to the PtBMA film being predominantly elastic in character. This changeover occurs at a surface pressure that closely tracks the plateau surface pressure, even as Π_p changes in response to temperature. Finally, the surface shear viscosity is seen to be independent of temperature for surface pressures far from the plateau; however, near this transition, the viscosity jumps by approximately an order of magnitude at the temperature–surface pressure combination that corresponds to the isotherm plateau.

Additionally, partial hydrolysis of PtBMA results in a higher strength of attraction between polymer and subphase. This effect is apparent in the changes in the shape and position of the Π – A isotherms, which generally have higher plateau surface pressures and lower lift-off areas as the hydrolysis fraction is increased. Despite having a stronger attraction to the subphase, the scaling exponent does not change for these molecules, and the polymers exist as collapsed coils in the semidilute concentration regime.

By changing the acidity of the subphase, the effect of protonating the hydrolyzed PtBMA groups was addressed. While the introduction of hydrolyzed groups led to slightly increased solubility and lower values of A_{10} compared to the unmodified polymer, the use of a more acidic subphase resulted in even

further reduced lift-off areas. This difference is attributed to a reduction in the amount of electrostatic repulsion between carboxylate anions. No significant changes in the plateau surface pressure or scaling exponent were observed in response to the subphase pH change.

Hopefully, an increased understanding of the intermolecular forces that govern Langmuir polymer films will further the knowledge of polymer conformation in such thin film systems. This would be particularly valuable in understanding the mechanisms that make polymer-stabilized emulsions and foams possible. Furthermore, this could also be beneficial in grasping the sources of viscoelasticity in two-dimensional polymer systems. In the future, additional experiments could be performed to better understand any effects surface pressure gradients, such as those observed by Peng and Barnes,¹⁴ may have on the rheological behavior of these polymer films.

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