Interfacial Tension of a Polystyrene−Poly(ethylene oxide) Diblock Copolymer at the Water−Toluene Interface

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ABSTRACT: This paper investigates the interfacial properties of a polystyrene−poly(ethylene oxide) (PS−PEO) diblock copolymer adsorbed at the water−toluene interface using axisymmetric drop shape analysis-profile (ADSA-P). The molecular weight of the PS block was 231 400 while the PEO block had a molecular weight of 20 670. The diblock copolymer was dissolved in toluene to form a 0.131 mg/mL solution and was allowed to adsorb onto a pendant drop of water at 20 °C. The variation in interfacial tension with time during the equilibration process was similar to that of a surfactant, beginning at the water−toluene interfacial tension and decreasing to an equilibrium value of 27.8 mJ/m^2 after a period of 2 h. The interface was then compressed by decreasing the volume of the drop in a linear manner. The shape of the resulting interfacial tension−area isotherm can be rationalized by a schematic model of the interfacial molecular conformation. According to the proposed model, the average molecular spacing is determined by the PS block at the start of compression and by a combination of the PEO block and the PS brush at the end of compression. These results show that the use of ADSA-P to measure interfacial tensions is a useful way to obtain indirect evidence of the interfacial molecular conformation.

Introduction

The surface activity of polymers is of industrial importance, and the adsorption of these materials at liquid−air and liquid−liquid interfaces has interested scientists for many years. In the early 1970s, Glass[1] reported a series of experiments in which he extended the pendant drop technique to study the adsorption of a series of water-soluble polymers at a liquid−liquid interface. The interfacial tensions were computed from the shapes of pendant drops of water immersed in either hexane or benzene. Poly(ethylene oxide) (PEO) was among the water-soluble polymers studied at that time. It is a unique material since it is soluble in both water and aromatic solvents, and so the interfacial activity was studied by adsorption from both benzene and aqueous solution.[1] In both types of experiments, the equilibrium interfacial tension was about 19 mJ/m^2 and there was little effect of molecular weight of the polymer.[1]

More recently, electrocapillary wave diffraction techniques have been applied to polymers adsorbed at various liquid−liquid interfaces using Langmuir film techniques. Both PEO and polystyrene (PS) were investigated in various interfacial configurations: toluene/PEO in water; PEO in toluene/water; spread films of PEO at toluene/water; PS and PEO in toluene/water; and PS in toluene/PEO in water. Among other data, these measurements confirmed that PEO is highly surface active, that the limiting interfacial tension was about 19 mJ/m^2, and that the final adsorbed state was independent of the path by which equilibrium was reached.[2] For the case of PS adsorbing from toluene at the toluene−water interface, the interfacial tension was shown to be the same as that of pure toluene−water (i.e., 36 mJ/m^2), which indicates the likelihood of a depletion layer of PS at the interface[2] similar to the PS depletion layer at the air−toluene interface.[3−5]

Over the past decade, the adsorption of diblock copolymers at interfaces has attracted attention both theoretically and experimentally. The theoretical predictions derived from scaling theories[6,7] and mean field approximations[8] have been examined using techniques such as direct force measurements,[9−12] neutron reflectivity,[13−15] and ellipsometry.[16] In all of these cases, the adsorption has been on to a solid surface, and the interpretations were based on the relative sizes of the two polymer components of the diblocks. However, there now appears to be some disagreement between theoretical predictions and experimental measurements. For example, recent work[17] on the adsorption of diblock copolymers of poly(dimethylsiloxane)−polystyrene (PDMS−PS) at the air−ethyl benzoate interface (using a Langmuir trough) concluded that current theories appear to underestimate the amount of energy required to stretch the diblock copolymer chains for this system.

To determine the behavior of a diblock copolymer at a liquid−liquid interface, the interfacial tension of the toluene−water interface was investigated in the presence of a PS−PEO diblock copolymer. A modern derivative of the pendant drop technique, axisymmetric drop shape analysis-profile (ADSA-P), was used to measure the interfacial tension during the adsorption process and also during compression of the interface after equilibrium had been reached. These results can be interpreted through the use of a schematic model of the interfacial molecular conformation.

Experimental Section

Materials. The PS−PEO diblock copolymer (Polymer Laboratories, Church Stretton, UK) selected for this study contains PS with a molecular weight of 231 400 and PEO with a molecular weight of 20 670. The number of segments, N, associated with these molecular weights are 2225 and 470, respectively. A solution was obtained by dissolving 3.28 mg of the copolymer in 25 mL of toluene.

Since both blocks are soluble in toluene, we can define the asymmetry of the polymer (β) in terms of the Flory radii (R_F) of the equivalent polymers in solution:[18]

$$\beta = R_{F,PS}/R_{F,PEO} \tag{1}$$

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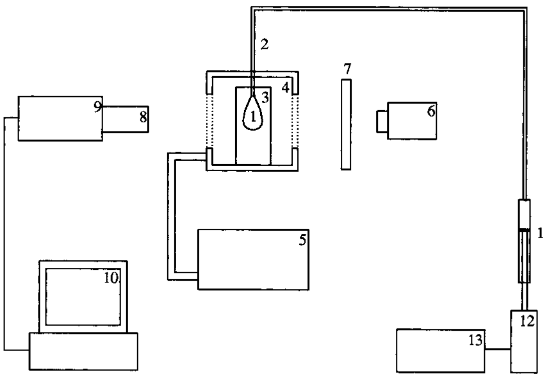

Figure 1. Schematic drawing of the ADSA-P apparatus: (1) pendant drop of water; (2) Teflon capillary; (3) quartz cuvette; (4) environmental chamber; (5) water bath; (6) light source; (7) diffuser; (8) microscope; (9) CCD camera; (10) computer workstation; (11) syringe; (12) stepper motor; (13) stepper motor controller.

The Flory radius is obtained from the relation

$$R_F = aN^{3/5} \qquad (2)$$

where a is the size of the individual polymer segments and N is the number of segments. The ratio a_{PS}/a_{PEO} is known from light scattering measurements to be 0.87[19] so that the asymmetry of the copolymer used in this investigation is 2.21.

Measurement of the Interfacial Tension. A schematic diagram of the ADSA-P apparatus is shown in Figure 1. A pendant drop of doubly distilled water was formed on the end of a vertical Teflon capillary of circular cross-section. The volume of the drop was controlled by the stepper motor which was attached to the plunger of a syringe connected to the other end of the capillary. The drop was then lowered into a quartz cuvette that had been filled with the copolymer solution, and the cuvette was enclosed in an environmental chamber controlled to 20.0 ± 0.1 °C by a thermostated water bath. The pendant drop was illuminated by a white light source shining through a heavily frosted diffuser. Using a microscope and a charge-coupled device (CCD) video camera, images of the pendant drop were digitized to an image of 640 × 480 pixels with 256 gray levels. The images were acquired from the digitization board by a Sun SPARCstation 10 workstation. The entire setup was mounted on a vibration table to minimize the effects of external vibrations.

The determination of the interfacial tension from the images of the pendant drops has been described in detail previously.[10−22] Briefly, ADSA-P software determines the experimental drop profile coordinates to subpixel resolution. Theoretical drop profiles are computed from the Laplace equation of capillarity, and nonlinear regression techniques are used to minimize the deviation of the theoretical drop profiles from the experimental coordinates to calculate the interfacial tension, as well as the area, volume, and apex radius of curvature of the pendant drop.

It has been shown recently that ADSA-P can be used in a manner analogous to that of the classical film balance.[23] By using the stepper motor and syringe to remove liquid from the drop, the surface area of the drop is decreased, and the change in interfacial tension can be plotted as a function of either time or drop surface area. For an insoluble film of octadecanol, there was excellent agreement between the results obtained by this new technique and those obtained with a traditional Langmuir trough.[23] However, ADSA-P requires much smaller sample volumes than the Langmuir trough (the size of the drops used in this study was about 0.05 cm^3). Furthermore, since the current configuration of ADSA-P can acquire up to two images per second, it is much better suited for studying kinetic processes than the slowly responding Langmuir trough.

In the present set of experiments, the change in interfacial tension between the pendant drop of water and the toluene containing the PS−PEO diblock copolymer was monitored as a function of time during adsorption. The volume of the pendant drop was held constant during this process. Once equilibrium had been attained, the volume of the drop was reduced in a linear manner with time to attain a maximum area compression ratio $A_{final}/A_{initial}$ of 0.20.

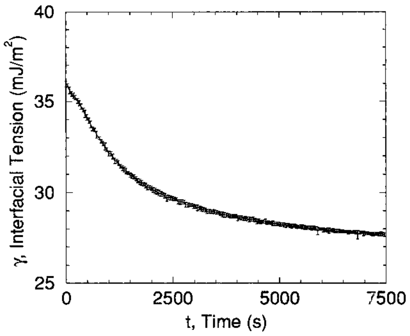

Figure 2. Variation in the water−toluene interfacial tension during the adsorption of the PS−PEO copolymer. Measurements were made every 15 s, but for clarity in the figure, only every fourth data point is plotted. The error bars correspond to the 95% confidence intervals from ten calculations of the interfacial tension with twenty arbitrarily selected points along the drop profile. The interfacial tension at the end of this period was taken to be the equilibrium value.

Results

The first step in our procedure was to determine the value of the water−toluene interfacial tension. The water−toluene interfacial tension was measured every 10 s for a period of 5 min for each of two runs. The error of each measurement was approximately 0.1 mJ/m^2 and the mean value and 95% confidence limits for the resulting 60 measurements was 35.300 ± 0.009 mJ/m^2.

Figure 2 shows the interfacial tension between water and the copolymer−toluene solution as a function of time during the adsorption process onto a pendant drop of constant volume. Measurements were made every 15 s for a period of 2 h. For each measurement, ten sets of twenty randomly selected profile points were used to compute the 95% confidence intervals of each data point. Note that the confidence intervals were generally of the order of 0.1 mJ/m^2. During the last minute of the experiment, the interfacial tension was changing at an average rate of only -4.06×10^{-4} (mJ/m^2)/s. Therefore, the average interfacial tension of the last four data points, 27.80 ± 0.02 mJ/m^2, was taken to be the equilibrium value.

Once equilibrium had been reached, the volume of the pendant drop was decreased linearly over a period of 10 min to compress the interface. Strictly speaking, this should result in a nonlinear variation in area with time. However, for the range of drop sizes used in this study, the area compression rate was essentially linear: a linear regression on the data has a slope of -7.75×10^{-4} cm^2/s with a linear correlation coefficient $r = 0.997$. After a compression to 20% of the initial area, the surface area was re-expanded by increasing the volume of the pendant drop. The resulting variations in volume and interfacial tension are shown as functions of time in Figure 3; the results are also plotted as interfacial tension versus area in Figure 4. On compression, the interfacial tension changes almost linearly from the initial value to about 25 mJ/m^2. There is then a rapid decrease to about 18 mJ/m^2, and finally the isotherm becomes almost vertical as the interfacial tension decreases to a final measured value of about 15 mJ/m^2. Since the accuracy of ADSA-P decreases with drop size, the lowest interfacial tensions are the least accurate.

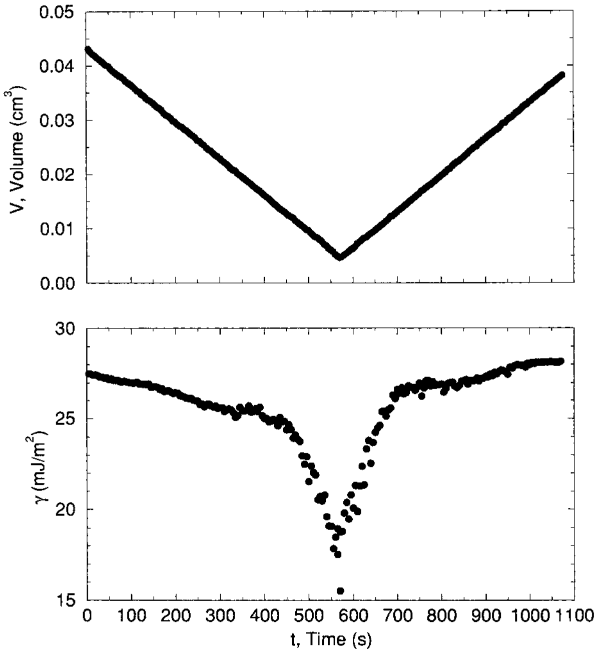

Figure 3. Variation in drop volume and interfacial tension with time as the volume of the pendant drop is changed in a linear manner. The pendant drop was initially at equilibrium. The average compression rate was -7.75×10^{-4} cm^2/s.

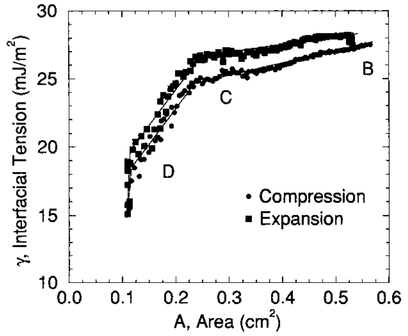

Figure 4. Change in interfacial tension with area during compression and expansion. The letters B, C, and D correspond to different conformations of the interfacial molecules (see Figure 7).

It can also be seen that the process appears to be almost reversible when the drop is re-expanded: Although hysteresis of about 1 mJ/m^2 is evident, the breaks in the γ−A isotherm occur at similar areas for compression and re-expansion.

A similar set of experiments was performed in which the average compression rate was -1.14×10^{-2} cm^2/s ($r = 0.995$), which was 15 times faster than the previous set of experiments. The resulting interfacial tension−area isotherm is shown in Figure 5, while Figure 6 shows the effect of varying the compression ratio at a fixed compression rate. Four different compression ratios are shown. The overlap is remarkable, but once again it should be noted that the accuracy of the measurements decreases at very small areas. The general shapes of these isotherms are the same as Figure 4, but the break at 19 mJ/m^2 is no longer obvious. The small amount of hysteresis for all the curves implies that there is no irreversible desorption from the interface.

Discussion

During the equilibration process, the adsorption of the diblock copolymer at the toluene−water interface results in a behavior that is similar to that of a surfactant. Both the PS and the PEO components are soluble in toluene, but as noted earlier, PS does not adsorb at the water−toluene interface and in fact probably forms a depletion layer.[2] Therefore, any changes in the interfacial tension must be the result of the adsorption of the PEO into the interface.

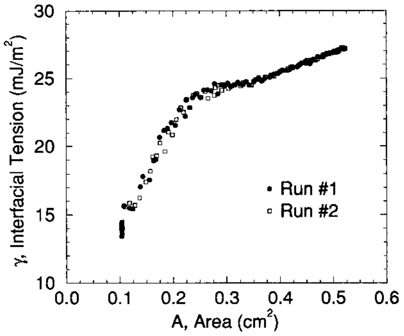

Figure 5. Interfacial tension as a function of area for a compression rate of -1.14×10^{-2} cm^2/s for each of two experimental runs. For clarity, only the compression portion of the isotherm is shown.

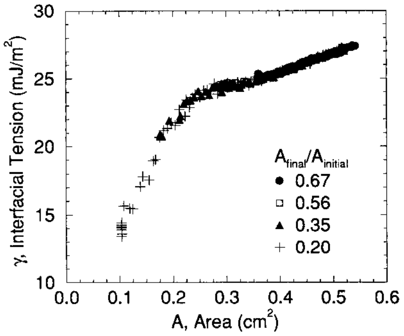

Figure 6. Interfacial tension as a function of area for four different compression ratios $A_{final}/A_{initial}$. The compression rate was -1.14×10^{-2} cm^2/s. For clarity, only the compression portion of the isotherm is shown.

During compression of the equilibrated interface, Figures 4−6 show that there is a decrease in interfacial tension with area. These results can be at least partially explained by considering the relative sizes of the two components of the diblock copolymer. The areas occupied by the PS and PEO blocks can be calculated from the Flory relationships:

$$\frac{A_{PEO}}{A_{PS}} = \frac{R_{F,PEO}^2}{R_{F,PS}^2} = \left(\frac{a_{PEO}}{a_{PS}}\right)^2\left(\frac{N_{PEO}}{N_{PS}}\right)^{6/5} = \left(\frac{1}{0.87}\right)^2\left(\frac{470}{2225}\right)^{6/5} = 0.204 \quad (3)$$

Here A represents area and the subscripts denote the type of block. Note that this is almost identical to the maximum compression ratios which were possible to apply in the experiments, namely $A_{final}/A_{initial} = 0.20$.

To account for this result and to explain the shapes of the γ−A isotherm, a model of the conformational changes of the interfacial molecules is shown in schematic form in Figure 7. During adsorption (structure A in Figure 7), the diblock copolymer molecules move to the interface from the toluene. The PEO block adsorbs to the interface, while the PS block remains in the bulk toluene.

At the end of the equilibration process, there is a densely packed arrangement of the PS−PEO copolymer

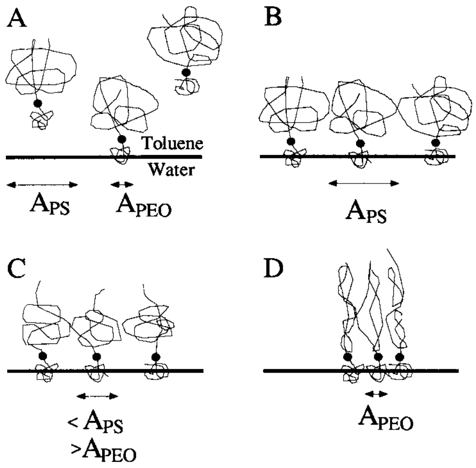

Figure 7. Schematic diagram of the conformation of the PS−PEO copolymer at the water−toluene interface: (A) adsorption; (B) equilibrium; (C) during compression; (D) final state after full compression. A_{PS} and A_{PEO} denote the cross-sectional areas of PS and PEO, respectively.

at the interface (structure B in Figure 7). Because the PS block is much larger than the PEO block, it can be assumed that the average spacing is equal to the Flory area of the PS block. As there is no room at the interface for more diblock copolymer molecules to adsorb, the interfacial tension reaches a steady equilibrium value of 27.8 mJ/m^2. Note that this value is between that of the water−toluene interface (35.3 mJ/m^2 as measured in these experiments) and that of an adsorbed monolayer of PEO (19 mJ/m^2 as measured previously[1,2]) and is due to the concentration of PEO segments at the interface.

The first stage of compression results in the "squeezing" of the PS polymer (structure C in Figure 7). The applied forces are balanced by osmotic and elastic forces caused by lateral interaction of the adsorbed polymer. This repulsion is gentle at first and proceeds until an area compression of about 57% is obtained (i.e., the area has been reduced from 0.56 to 0.24 cm^2 in Figure 4). During this time, the interfacial tension decreases slowly due to a slow increase in the surface concentration of PEO segments on the surface but also due to a contribution from the stretching of the PS brush.[6] There is still no overlap of the PEO units; the interfacial tension in this portion of the isotherm decreases to about 25 mJ/m^2.

As the compression continues and the segment density increases, the osmotic stress assumes greater importance than the elastic stress[24] and the interfacial tension now decreases more rapidly with increased compression (the portion of the isotherm from point C to point D in Figure 4). At point D, the interfacial tension is about 19 mJ/m^2. This is the same value that has been reported for a complete PEO monolayer at the toluene−water interface.[1,2] It is tempting to assign this to the structure D in Figure 7, where the PEO molecules are just touching and the PS molecules have formed an extended brush, similar to the model proposed by Alexander[25] and extended by Marques and Joanny.[18] In this model, a small change in the area results in a large change in the interfacial tension (i.e., the surface compressibility is very large). It is noted in Figure 4 that a dramatic but reversible decrease in the interfacial tension results on compression past this point.

However, it is shown in Figure 6 that the sudden change in slope at 19 mJ/m^2 is not readily discernible.

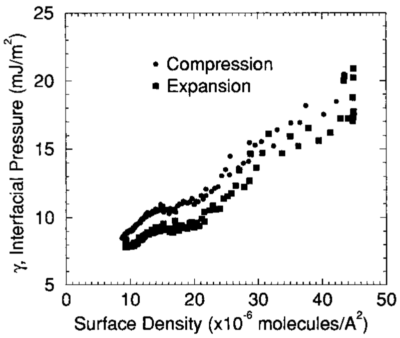

Figure 8. Data of Figure 4 replotted as surface density versus interfacial pressure. The surface density cannot be directly measured but was calculated by assuming that the molecules were just touching at the start of compression and that there was no desorption from the interface.

An intriguing paper by Kent et al.[6] has addressed the energetics associated with the compression of the monolayer films of PS−PDMS block copolymers. Although their experiments were performed on monolayers at the air−liquid interface, their results are pertinent to the system described in this paper. They point out that the interfacial tension must include a term related to the stretching energy of the polymer brush (i.e., PS) and a conclusion from their arguments must be that when the PEO blocks just touch in the schematic of Figure 7, the interfacial tension must be lower than 19 mJ/m^2 by an amount equal to the stretching energy.

Using the ADSA-P methodology, we can confirm a value of the interfacial tension of homopolymer PEO at the water−toluene interface as being 18.4 mJ/m^2. In order to apply the comparative method employed by Kent et al.,[6] polymer adsorption would have to assessed quanitatively. Some reasonable approximations of the surface density can be made by assuming that the PS blocks are just touching at the first equilibrium point (i.e., point B). Using the formulation[6] that $R_g = 0.117M^{0.595}$, then the area occupied by one PS molecule (and therefore one copolymer molecule) is 11.51×10^4 A^2, which corresponds to a surface density σ of 8.7×10^{-4} molecules/A^2. Assuming that the number of molecules at the interface is fixed, the data in Figure 4 were redrawn in Figure 8 to show the interfacial pressure generated as the polymer is stretched. It can be seen that the plot is almost linear. Unfortunately, interpretation and separation of the interfacial pressure components are not justified at this time and must await quantitative development of the adsorption isotherm of PEO at the same interface. Results from such experiments are nontrivial and will be discussed in a future publication.

Summary and Conclusions

The results obtained in this paper demonstrate that a PS−PEO diblock copolymer at the water−toluene interface behaves like a surfactant. Compression of the interface after equilibrium has been reached results in an interfacial tension−area isotherm that can be explained by considering the rearrangement of the diblock copolymer molecules at the interface. These results demonstrate that the interfacial tension measurements can be a useful way to provide indirect evidence of the conformation of the PS−PEO copolymer at the interface.

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