Study of polystyrene monolayers in two dimensions

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The surface pressure of a series of monodisperse polystyrene monolayers covering a wide range of molecular weights was measured as a function of surface concentration and polymer molecular weight on an aqueous, i.e. hydrophilic, substrate. The determined experimental surface pressure–polymer surface concentration relationship corresponds closely to the theoretical scaling concepts. Interestingly, these relationships are dependent on the delivery solvent used in the formation of a polymer monolayer. An important implication of these studies is that the properties of the chains as observed in a particular solvent system (a three dimensional system) is retained, to a large extent, when the chains are placed onto an aqueous substrate and the solvent is evaporated. The solvent quality of the surface, in this particular instance, is poor. Therefore, it appears that the solvent qualith of the delivery solvent has a profound influence on the chain properties at the interfacial region.

(Keywords: monolayer; air–water interface; surface pressure; scaling concepts; solvent quality)

INTRODUCTION

Dilute and semidilute polymer solutions in the bulk and/or at an interface (and thin polymer films) are becoming increasingly useful in a large number of practical applications, such as in viscosification of aqueous and nonaqueous liquids, colloidal stability, coatings and membranes. Therefore, an understanding of polymer properties in these systems is important not only for these practical applications, but because a deeper understanding is required to extend the range of applicability of these materials. At present, the polymer solution properties in a three-dimensional space have been extensively studied both from a theoretical and experimental viewpoint[1,2]. Due to the complexity of these solution properties (especially above the chain overlap concentration), scaling theories are extensively used for an understanding of the static and dynamic properties of these solutions[1]. In this particular concentration regime, the correlation length, osmotic compressibility and shear viscosity are expressed as a function of the reduced polymer concentration with the appropriate scaling exponents. Techniques such as neutron scattering, light scattering and viscometry have confirmed the predicted functional dependence of the reduced polymer concentration on the relevant fundamental properties of polymer solutions in a three-dimensional space[2].

In contrast with these studies, relatively few experimental[3–5] studies have been performed in a two-dimensional space. Daoud and Jannink have predicted[7] that the overlap polymer concentration (c^*) depends on the polymer molecular weight with the exponent (ν), and that the surface pressure can be expressed in a general form with a reduced concentration (c/c^*). In our measurements, the surface pressure of a series of monodispersed polystyrenes has been measured as a function of surface concentration and polymer molecular weight on a nondissolving and nonabsorbing liquid substrate, pure water. These measurements are quantitatively compared to the predictions of Daoud and Jannink[7]. Two different delivery solvents (cyclohexanone, a non-polar solvent, and DMF, a polar solvent) were used to spread the polymer at the appropriate concentration to form a monolayer on the aqueous surface.

EXPERIMENTAL

Polymer preparation

The polystyrenes used throughout this study were purchased from Pressure Chemical Company (Pittsburgh, Pennsylvania). The specific monodispersed molecular weights ($M_w/M_n < 1.1$) of these anionically polymerized polymers are 4000, 35 000, 115 000, 900 000 and 1 800 000 gm mol^{-1}. The spreading solvents, cyclohexanone and dimethylformamide, DMF, (Aldrich Chemical Company, Gold Label) were used as received.

Surface balance

The surface pressures of a polymer monolayer were measured by the Wilhelmy technique using a platinum plate attached to a torsion wire[8]. A Teflon coated stainless steel trough was used. The accuracy of the pressure determination was ± 0.5 dynes cm^{-1}. Double distilled water was used as the substrate. As noted previously, cyclohexanone and dimethylformamide were used as the spreading solvents. A measured amount of the polymer solution was dissolved in the spreading solvent, and the polymer was delivered onto the substrate using a micrometer pipette (accuracy $\pm 1\%$). The spreading solvent was evaporated and/or dissolved in the substrate, so that the polymer molecules formed a monolayer. The monolayer was compressed with a Teflon coated stainless

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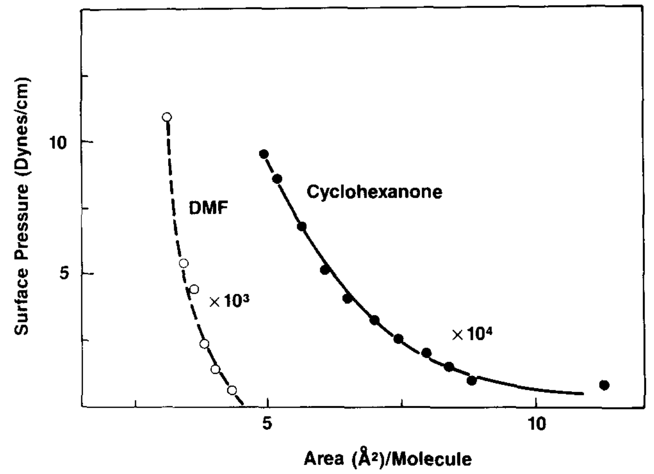

Figure 1 Typical surface pressure–polymer concentration isotherm profiles of a monodispersed polystyrene (molecular weight: 900000 gm mol^{-1}) on an aqueous surface. The delivery solvent is (●), cyclohexanone and (○), dimethylformamide

steel sweeping bar after the surface pressure became constant. This equilibrium time was one or two hours. The maximum compression ratio was 2.5 (750 cm^2→300 cm^2 for an active surface), and the compression took about one hour. The substrate temperature was controlled within ±0.1°C of room temperature (~25°C).

A typical surface isotherm profile (surface pressure, π *versus* specific area per molecule, A) is shown in *Figure 1*. All surface pressure measurements were performed in the range 1~20 dyne cm^{-1}. The ideal two-dimensional gas behaviour was not observed in this pressure regime. In order to observe this behaviour, the sensitivity of surface balance has to be improved approximately $\times 10^2$ to monitor the anticipated 10^{-2} dynes cm^{-1} change in a surface pressure at a large specific area per molecule. Therefore, in this paper, the only concentration regime which is examined is the semidilute concentration regime in which the surface pressure is high enough to monitor the scaling behaviour of a polymer monolayer. For this particular objective, the experimental pressure sensitivity in this work is adequate to test scaling exponents above the chain overlap concentration.

DISCUSSION AND RESULTS

The static and dynamic properties of polymer solutions have been described reasonably well in terms of scaling exponents. Theoretically[1] the polymer molecule radius (R) in a d-dimensional space for a good solvent is expressed with its molecular weight (N) to an exponent ν:

$$R \approx aN^{\nu} \qquad \nu = 3/(d+2) \tag{1}$$

a is the monomer size.

This equation indicates that ν is 0.75 and 0.6 for $d=2$ and 3, respectively. However, for a poor solvent, ν is independent of a dimensional space, and is 0.5.

Also, the surface or osmotic pressure (π) of the polymer solution[7] in a d-dimension is

$$\pi/T \approx c^{\kappa} \quad \text{with} \quad \kappa = \nu d/(\nu d - 1) \tag{2}$$

Equation (2) gives $\kappa = 3$ and ∞ for a good solvent and a poor solvent, respectively, in a two-dimensional space.

It is also important to recognize that an alternative approach in understanding a polymer monolayer is to consider the polymer molecules as behaving as surfactant-like molecules. In other words, the polymer molecules do not lie on the interface to make a true two-dimensional monolayer, but essentially form a globule on the interface. In this approach, the phase diagram (i.e. the surface pressure *versus* the specific area per molecule) strongly depends on the molecular weight not only in the dilute region, but also in the high concentration regime. In the high concentration regime, the polymer monolayer can be considered as in the two-dimensional liquid state. In this case, the surface pressure can be expressed[8] in an empirical relationship based on the consideration that the isothermal compressibility is reasonably constant.

$$\kappa_T = -\frac{1}{\sigma}\frac{d\sigma}{d\pi} = -\frac{d\ln\sigma}{d\pi} = \text{constant} \tag{3}$$

then

$$\sigma = \sigma(0)e^{-\kappa_T \pi} \tag{4}$$

Equation (4) indicates that $\sigma(0)$ is an extrapolated area per molecule at the condition of $\pi = 0$. Roughly, this area per molecule is the cross-sectional area of the polymer molecule at an air–liquid interface. Therefore, if the polymer molecule behaves as described previously, then this cross-section may depend on the solvent quality of either the spreading solvent and/or the air–water interface. Furthermore, the quantity $\sigma(0)$ may be related to the specific area (σ^*) of the polymer molecule at which entanglements (in the scaling sense) begin to dominate polymer properties.

Figure 2 shows $\ln \pi$ *versus* $\ln c$ plots for monolayers containing a variety of polymer molecular weights. These monolayers were spread from cyclohexanone. By analogy

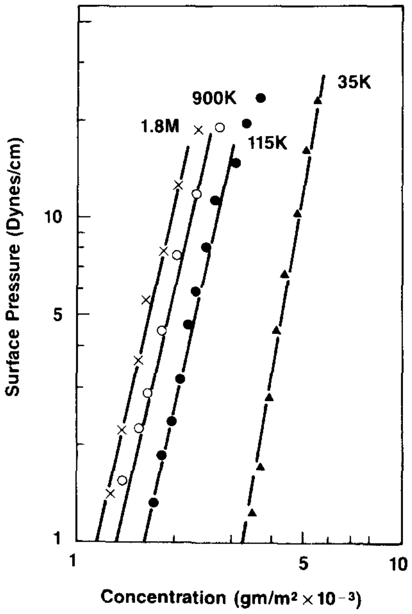

Figure 2 Surface pressure–polymer concentration profiles of monodispersed polystyrene monolayers spanning a broad molecular weight range on an aqueous surface. The delivery solvent is cyclohexanone

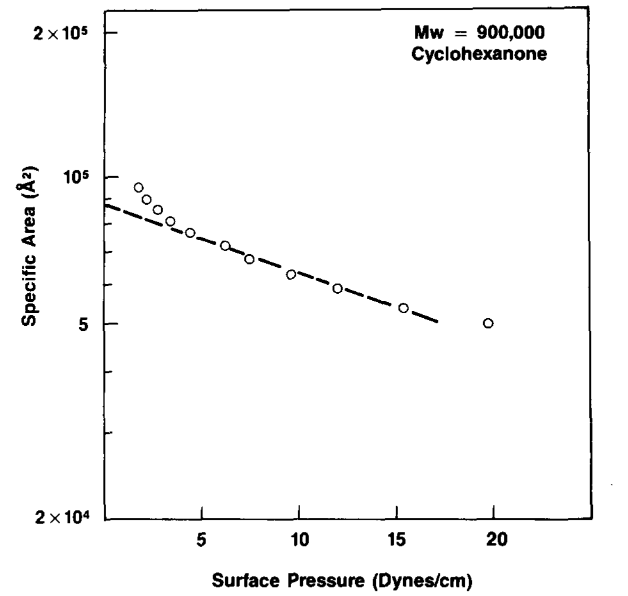

Figure 3 A typical semilog plot of surface pressure *versus* specific area

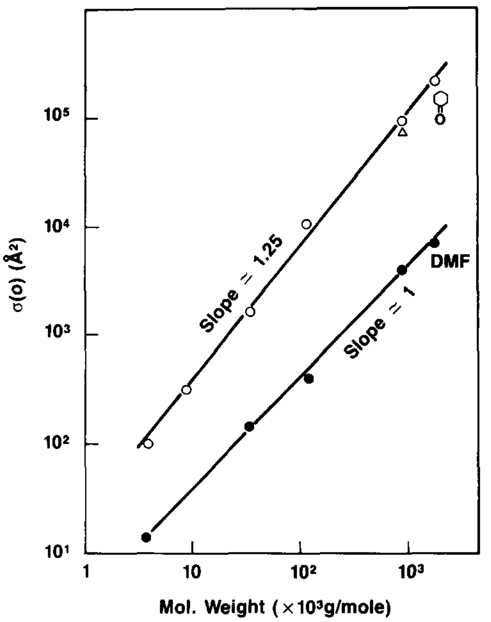

Figure 4 Graph of the constant $\sigma(0)$ (defined in the text) as a function of the molecular weight of the monodisperse polystyrene. The delivery solvent is (○), cyclohexanone; (●) dimethylformamide. △ is the square of the measured hydrodynamic radius[11] in cyclohexanone by dynamic light scattering

to the three dimensional studies, data in *Figure 2* show the same slope for all the molecular weights examined. However, the isotherms do not overlap each other, which is not identical with earlier measurements[3]. That is, the only variable quantity is the polymer concentration (inverse of the specific area) for each different molecular weight. To understand this result, the surface pressure of the polymer monolayer was analysed as if surfactant behaviour[8] is occurring. A typical example of results is shown in *Figure 3*, where ln σ *versus* π plots are used to estimate $\sigma(0)$ for $M_w = 900\,000$ polymer. As anticipated $\sigma(0)$ shows a very strong dependence on molecular weight. The results of the analysis are presented in *Figure 4*.

Therefore, all of the isotherms can be presently superimposed by a constant factor, i.e. a constant $\sigma(0)$, which is directly related to $(c^*)^{-1}$ as defined in the three dimensional semidilute polymer concentration regime. The results of the superposition process are presented in *Figure 5* which shows that a universal fitting curve is produced possessing a slope of 5.0.

As described previously, the overlap polymer concentration in three dimensions is a direct function of the polymer molecular weight. Similarly, *Figure 4* shows the molecular weight dependence of $\sigma(0)$. As anticipated, $\sigma(0)$ increases with the molecular weight in a form of $N^{1.25}$. This result indicates that R increases with molecular weight, that is,

$$R \approx \sqrt{\sigma(0)} \approx N^{0.63} \tag{5}$$

This result is remarkable because it is known that in an aqueous environment, these polymers are completely insoluble. Therefore, it is apparent from these measurements that the delivery solvent is an important factor in the behaviour of polymers on a two-dimensional aqueous surface.

Finally, it should be noted that combining the results of *Figures 3* and *5*, it is easily shown that

$$\pi \approx [\sigma(0)c]^{\kappa} \tag{6}$$

with $\kappa = 5.0$.

We now turn our attention to the more polar spreading solvent, dimethylformamide, in order to more fully explore the effect of solvent quality on the properties of the polymer monolayers. *Figure 6* shows $\sigma(0)$ *versus* molecular weight for DMF as a spreading solvent. It should be noted that $\sigma(0)$ for DMF is at least 10 times smaller than for cyclohexanone. *Figure 7* shows the $\pi - \sigma(0)$ interrelationship. In this instance, κ is found to be 16.7 which is significantly larger than that observed with the relatively nonpolar solvent cyclohexanone.

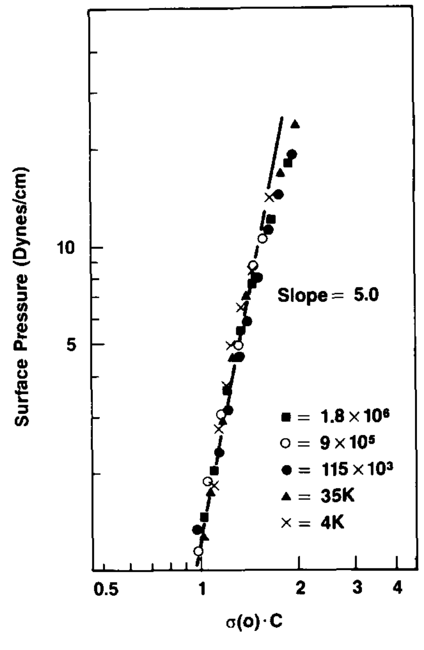

Figure 5 Superposition of the surface pressure–polymer concentration curves from *Figure 2*. The constant $\sigma(0)$ is taken from *Figure 4*

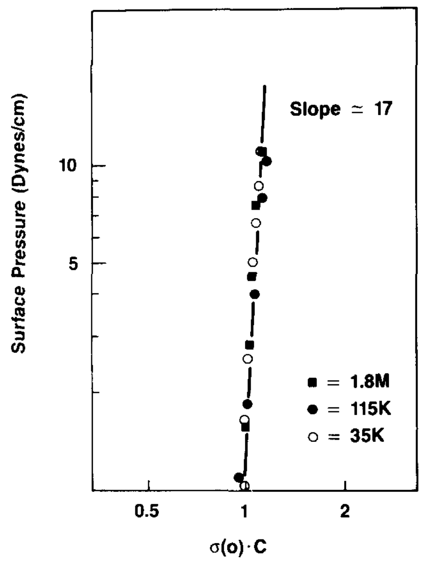

Figure 6 The results of the superposition of the surface pressure–polymer concentration profiles of monodispersed polystyrene monolayers spanning a broad molecular weight range on an aqueous surface. The delivery solvent is dimethylformamide

Furthermore, a linear relationship is found between $\sigma(0)$ and N as shown in *Figure 6*; the slope ν is 0.50 ± 0.03. This value is very close to $\nu = 0.5$, i.e. theta solvent conditions.

The experimental values ν and κ are related (equation 2) with each other systematically, i.e. $\kappa = 5.0$ when $\nu = 0.63$ for cyclohexanone, and $\kappa = 16.7$ when $\nu = 0.5$ for DMF. Furthermore, the experimental value ν for cyclohexanone is very similar with the theoretical value ($\nu = 0.6$) in three dimensions and κ is consistent with the expected value ($\kappa = \nu d/(\nu d - 1) = 4.85$) for a good solvent. These exponents show that the properties of the polymer monolayer, spread with a good solvent cyclohexanone on a poor solvent (water), are not only determined by the substrate (water), but also by the delivery solvent. That is, the polymer conformation established in the three dimensional solvent system is retained, to a large degree, when the chain is placed onto a poor, nonabsorbing substrate and the solvent is evaporated off. Therefore, it is established that the experimentally determined scaling exponents are closer to the theoretical values for a good solvent, rather than for a poor solvent when the delivery solvent is a relatively good solvent and vice versa.

CONCLUSIONS

Polystyrene monolayers were studied on a water substrate with two differing spreading solvents in the semidilute concentration regime. A direct comparison was made between the experimentally determined and the theoretical two dimensional scaling exponents for the radius of gyration as a function of molecular weight ($R \approx M^{\nu}$), and the surface pressure as a function of the polymer concentration, $\pi \approx [\sigma(0)c]^{\kappa}$. It is found that ν and κ strongly depend on the quality of the spreading solvents. A good solvent, such as cyclohexanone, exhibits $\nu = 0.63 \pm 0.05$ and $\kappa = 5.0 \pm 0.5$. The value ν is closer to the theoretical value $\nu = 0.6$ in three dimensions, and κ is consistent with the expected value (4.85). However, a more polar solvent such as DMF, shows that $\nu = 0.5 \pm 0.03$ and $\kappa = 16.7 \pm 0.5$. Both of these latter values are close to the predicted values for a poor solvent or theta solvent conditions, i.e. $\nu = 0.5$ and $\kappa = \infty$ as described in scaling arguments.

Even though the exponents (ν,κ) are somewhat consistent with the scaling arguments, the striking observation in this study is that the surface pressure in the semidilute concentration regime strongly depends on the polymer molecular weight. This may be due to the ability of the polymer molecules to retain a minute amount of the delivery solvent within the polymer coil itself by forming a microgel, which preserves the three dimensional behaviour. Because of this, the solvent quality of the delivery solvent has a profound influence on forming the polymer monolayer on the nonadsorbing substrate. Experiments are proceeding in order to establish if it is possible for a coil to retain enough solvent to significantly influence its conformational properties. The extension of these studies from the purely nonionic polymers described above (nonadsorbing conditions) to lightly charged ionically associating polymers (adsorbing conditions) will be reported on in the near future.

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