

Two-Dimensional Properties of Surfactant-like Polymer Monolayers

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Received July 7, 1987; accepted September 8, 1987

A functional polymer monolayer at an air/water interface has been studied systematically by substituting a hydrophobic backbone with a hydrophilic moiety (OH) by measuring the surface pressure as a function of surface concentration for different molecular weight polymers. The characteristic scaling exponent (ν) estimated from the isotherms and the overlap surface concentration suggests that the air/water interface becomes a better solvent as the amount of hydrophilic functional groups is increased. Also, the isotherms show that the area per polymer molecule increases with increasing amounts of OH groups. However, the water surface tension is most effectively reduced at the 50% substitution level, not at 100%. This optimum amount of OH group on the hydrophobic polymer is equivalent to the hydrophic/lipophilic balance of a surfactant in the formation of microemulsions. Furthermore, the surface occupied area per OH group (σ_o) is estimated with the ideal gas law at a dilute surface concentration. The results show that the σ_o is a minimum at the same substitution level at which the reduction of water surface tension is a maximum. © 1988 Academic Press, Inc.

INTRODUCTION

Many proteins and some types of polymers are spreadable on an aqueous solution under suitable conditions (1). The presence of the polymer film, in general, reduces the surface tension of aqueous solutions. The surface pressure of a monolayer (the reduction of surface tension due to the presence of a monolayer) is easily measurable with various experimental techniques (2). The surface pressure-concentration (π - C) isotherms for surfactants and polymer monolayers have been extensively studied by numerous workers because of their importance to many scientific disciplines. Most isotherms for polymer monolayers do not show the characteristics of phase transitions as shown in surfactant monolayers (3). Studies of isotherms have been conducted to find the characteristics of the thermodynamic states of polymer monolayers and interactions in the low surface concentration regime (4). Recently, Vilanove and Rondelez (5) discussed the behavior at low and high surface pressure of polymer monolayers in terms of a scaling theory. From the

monolayer isotherms, they measured for the first time, the characteristic scaling exponent ν for the radius of gyration of isolated coils constrained to a surface. Their results also show that the air-water interface can be a different quality solvent for polymers depending on the chemical structure of their respective monomers.

We have studied systematically the effects of chemical structure on π - C isotherms of polymer monolayers by partially functionalizing the hydrophobic polymer backbone rather than completely changing the monomer structure. Part of the hydrophobic polymer (poly-1,2-butadiene) is systematically substituted with a hydrophilic group ($-\text{OH}$). The amount of the $-\text{OH}$ group on the backbone controls the affinity of the functional polymer molecules for the water surface. For example, nonfunctional poly-1,2-butadiene does not form a monolayer at an air/water interface, but the 10% substituted functional polymer forms a very stable monolayer at the interface.

In this paper, the scaling theory (6) for the π - C isotherms in a semidilute concentration regime will be tested in terms of the molecular

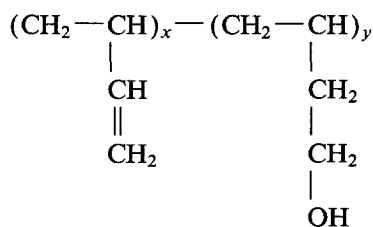
weight (M_w) and surface concentration (c) dependence at a fixed substitution. The isotherm can be expressed as $\pi \sim (c/c^*)^\kappa$ with $\kappa = 2\nu/(2\nu - 1)$ and should be independent of M_w in the semidilute concentration regime. Furthermore, with an ideal gas isotherm in the dilute concentration regime, the overlap surface concentration, c^* can be estimated. As a consequence, the specific surface area per molecule is determined to be dependent on M_w in the form of $\sigma \sim R^2 \sim aN_m^{2\nu}$ with $N_m = M_w/M_a$. a and M_a are the monomer size and molecular weight, respectively. Values of ν from the isotherms and the overlapping concentration are consistent and are 0.62 and 0.55 for $X = 1.0$ and 0.5, respectively, where X is the ratio of the number of substituted monomers and total number of monomers in a polymer molecule. This indicates that the air/water interface changes from a poor solvent to a good solvent as the amount of hydrophilic substitution increases. This finding is in good agreement with the results of Vilanove and Rondelez.

The second part of this paper is devoted to the dependence of surface properties on the amount of hydrophilic substitution for polymers of constant molecular weight. As mentioned previously, the value of ν increases as X increases. The specific area per molecule also becomes larger as expected. However, the area per OH group is minimum at 50% substitution, i.e., where the collapsed pressure (defined later) is at a maximum. This indicates that the most effective coverage, the maximum reduction of the surface tension of the aqueous phase, is not achieved at 100% substitution but at an optimum hydrophilic substitution. In this case, 50% hydrophilic replacement of the hydrophobic polybutadiene with the —OH group performs the largest surface tension reduction at the air/water interface.

EXPERIMENTAL

The surface pressure was measured by the usual Langmuir surface balance technique, which measures the actual surface force between a clean surface and a monolayer covered

surface using a force-string gauge. The surface balance we have used is made by Laude. The overall sensitivity is ± 0.05 dyn/cm. Polybutadiene was synthesized by anionic polymerization and the M_w/M_n was about 1.07. Poly-1,2-butadiene was then functionalized with a hydrophilic moiety (—OH) by hydroboration and an oxidation process. The resulting functional polymers have the molecule structure



where $y = 0.1, 0.2, 0.3, 0.5, 0.7$, and 1.0 and $x + y = 1$. During the modification reactions, the molecule weight distribution was retained with no side reactions. The details of the functionalization method will be described in a later publication (7). The polymer was first dissolved in a good solvent, either tetrahydrofuran (THF) or methanol depending on the amount of the —OH group. For the 50% substituted polymer, the methanol and THF were used to see whether the spreading solvent affected the polymer monolayers, and the result showed that there were very minor differences within experimental error. The pure spreading solvents were also tested by measuring the residual pressure after spreading the solvent. The solvent independence of the isotherms indicates that the effects of the spreading solvent are minimal for this experiment. By compressing and expanding the monolayers at least two times, the stability and reversibility of the isotherms were examined. The isotherms are extremely stable and reversible.

RESULTS AND DISCUSSION

Figure 1 shows the isotherms of $X = 0.5$ and 1.0 for two different molecular weight polymers. The open circles and triangles represent data for $N_m = 120$, and the closed circles

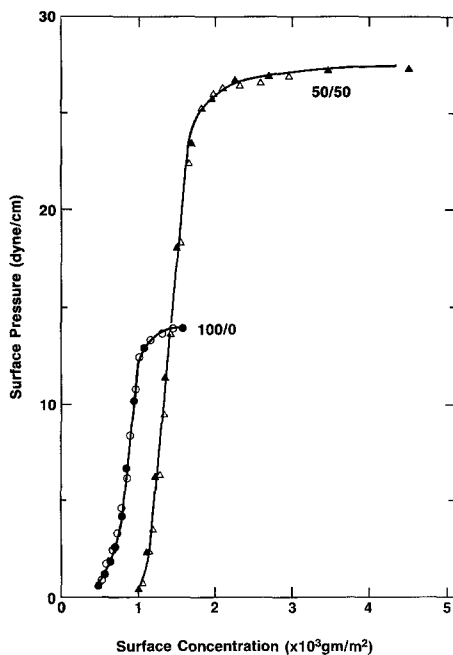


FIG. 1. Surface pressure vs surface concentration of 100% (circles) and 50% (triangles) substituted poly-1,2-butadiene. Solid and open represent $N_m = 1300$ and 120, respectively.

and triangles are for $N_m = 1300$. There is no difference between the isotherms of the low and high molecular weight polymers in the experimental pressure range. The same isotherms are replotted in log-log scale to find the values of κ in Fig. 2. Clearly, there is no molecular weight dependence in these isotherms as expected in the scaling theory. The values of κ (the slope of the isotherms) are 13 and 5 for $X = 0.50$ and 1.00, respectively. Consequently, the scaling exponent values of ν for $X = 0.5$ and 1.0 are 0.55 and 0.62, respectively. Furthermore, the specific area per molecule was estimated from the crossover surface concentration obtained from the intersection of the surface pressure of the monolayer in the ideal gas law $\pi = \rho k_B T$ (with ρ density of molecules, k_B = Boltzmann constant, and T is absolute temperature) and the scaling isotherm in the semidilute concentration $\pi \sim \pi_0 (c/c^*)^\kappa$. The results are shown in the inset in Fig. 2. Even though there are only

two data points, it shows the consistency of the values of ν as indicated in the figure. It is interesting to compare these results with those of Vilanove and Rondelez. The PVAC is much more hydrophilic than even the 100% substituted poly-1,2-butadiene due to the number of carbons from the polymer backbone to the hydrophilic moiety. The carbon number for the 100% substituted poly-1,2-butadiene is 2 from the backbone. Therefore, it is not surprising to see that the air/water interface is a relatively poor solvent. This is again understandable from the limited solubility of butanol in water. This is the reason that the polymer monolayer is stable at the air/water interface. When the hydrophilic substitution is decreased, the effective carbon number (C_{eff}) is increased. As a consequence, the air/water interface becomes a poorer solvent for this polymer layer, which is shown in the 50% substituted poly-1,2-butadiene. This tendency is more noticeable in the less hydrophilic polymers as shown in the Fig. 3.

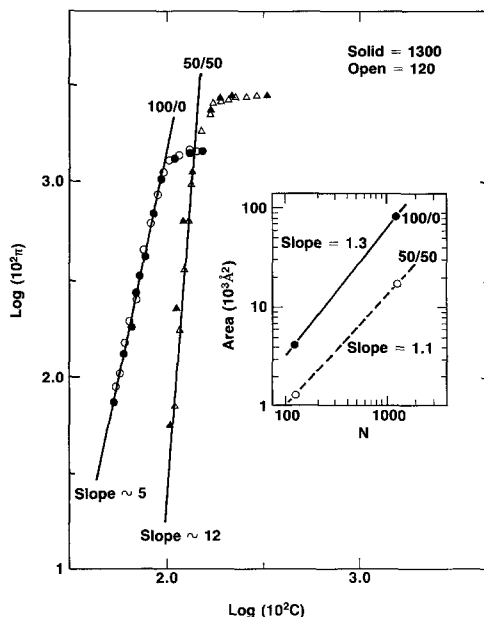


FIG. 2. Log-log representation of Fig. 1. Insert is a plot of area per molecule as a function of number of monomers for the 100% substituted (●) and 50% substituted (○) polymers.

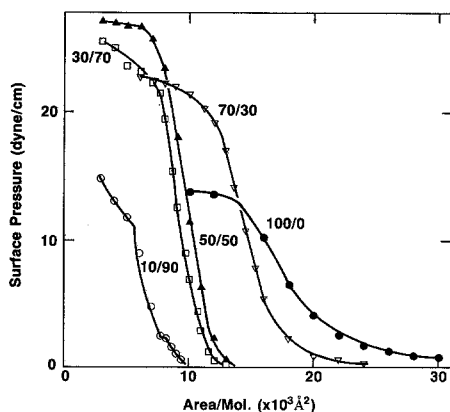


FIG. 3. Surface pressure isotherms for 10% (○), 30% (□), 50% (▲), 70% (▽), and 100% (●) substituted polymers.

Figure 3 shows the surface pressure vs the specific area per molecule for the various substitutions ($X = 0.1, 0.3, 0.5, 0.7$, and 1.0) with $N_m = 1300$. There are several interesting findings in the Fig. 3. First, the specific area per molecule at a fixed surface pressure is decreased as X becomes smaller. Second, the collapsed pressure (which is defined later) is increased initially and then decreased as the substitution is increased. Finally, the isotherm for the $X = 0.1$ shows a flat portion near $\pi \simeq 2.5$ dyn/cm, which is indicative of a two-dimensional phase transition. This phase transition is because the air/water interface is so poor that a tail-tail interaction is attractive enough to cause a phase transition. This attractive interaction could be the response of the nonspreadability of the pure polybutadiene. Since this paper focuses upon the X dependence of the surface properties, the phase transition of the 10% substituted polybutadiene will be discussed a later publication.

To examine the first observation (the decrease of specific area per molecule as X is lowered), we estimated the overlap concentration as described earlier. From the overlap concentration, the specific area per molecule (σ_p) is calculated. The results are shown in Fig. 4. As expected, σ_p monotonically increased as the value of X increased because of

the expansion of polymer molecules due to the addition of hydrophilic —OH groups. The increase was slow at low X values, but fast for X greater than 0.5. We have estimated the occupied area per OH group (σ_o) to understand the rate of increase of σ_p . Since we know the number of functional groups in an individual polymer, the σ_o is equivalent to $\sigma_p/(N_m^*X)$. The result is shown in the Fig. 4. Interestingly, σ_o decreases initially and then increases as X is increased. This finding is consistent with the previous result that the backbone of the polymer is in a relatively poor solvent, so that the segments between the functional group are collapsed. Therefore, the total area per polymer molecule is roughly linear with N_m (i.e., $\sigma_p \sim aN_m^{2\nu} \sim aN_m$). As a consequence, σ_o is proportional to $N_m/(N_m^*X) \sim 1/X$.

However, in the high substitution regime, the air/water interface is a good enough solvent for the polymer backbone to be self-avoiding (i.e., $\nu \sim 0.62$ for $X = 1.0$). The surface area per polymer molecule is propor-

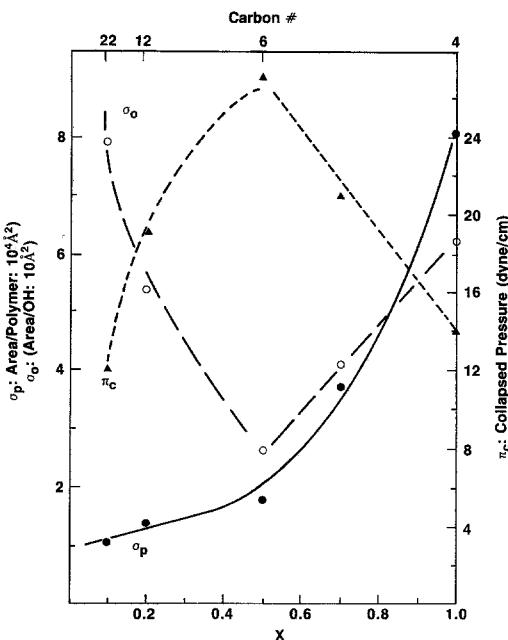


FIG. 4. Area/polymer (σ_p , ●), area/OH (σ_o , ○), and the collapsed pressure (π_c , ▲) vs the fraction of OH substitution (X).

tional to $N_m^{2\nu}$ with $2\nu > 1.0$, and ν also depends on the value of X . Therefore, σ_o is no longer inversely proportional to X , but has a more complicated dependence: $N_m^{(2\nu-1)}/X$. The solid line in Fig. 4 is the numerical calculation of σ_o with the surface area per monomer = 9\AA^2 . This shows that the numerical calculation is in reasonable agreement with the experimental values. Because of the excluded area and the quality of solvent the packing area per OH shows the minimum at 50%. Furthermore, it is interesting to note that the smallest σ_o is slightly larger than the cross section of the corresponding long chain single alcohol (e.g., stearic alcohol). This may be due to the steric hindrance of the backbone.

The collapsed pressure is determined by the area per molecule where an isotherm changes sharply. The results are shown in Fig. 4. It shows that the collapsed pressure depends strongly on the value of X . The collapsed pressure is increased and then decreased as the amount of substitution is increased. The maximum collapsed pressure is shown at 50% substituted polybutadiene. In other words, the 50% substituted polymer monolayer can reduce the surface tension of the water most effectively. It is interesting that this substituted amount is the same value shown for the minimum area per —OH group. This finding is not surprising from our understanding of the isotherm of a long chain alcohol monolayer: the surface pressure of the long chain alcohol monolayer is increased as the area per molecule is decreased. However, in this functional polymer case, the change of the area per —OH group is not only the response to the reduction of the surface tension, but also the effective carbon number between the —OH group is important as well. In general, decreasing one carbon is almost equivalent to raising by 10 K the isotherm of a simple chain surfactant so that the surface pressure is increasing. Since increasing the amount of the —OH group on a polymer backbone is the same as reducing the hydrophobic chain length, the surface pressure is increased as X increases. This may be the reason for the ob-

servation of low X values. However, for high X values, the increasing area per —OH group for increasing X is the response to reducing the collapsed pressure.

The balancing of the effective carbon number and the specific surface area per —OH group provides the maximum reduction of the surface tension of the water surface, i.e., the maximum surface pressure of the functional polymer. This kind of a balancing effect can be found in the formation of microemulsions or micellar solutions with a surfactant of different carbon chain length (i.e., optimum hydrophilic/lipophilic balance). The average carbon number between the —OH groups is calculated and shown in Fig. 4. The average carbon number decreases as the value of X is increased.

SUMMARY

The chemical structural effect on the properties of a functional polymer monolayer has been studied systematically by substituting the hydrophilic moiety (—OH) on the hydrophobic backbone (poly-1,2-butadiene). In the semidilute concentration regime, the surface pressure is independent of the molecular weight, and can be expressed in terms of the scaling exponents (κ). With the ideal gas law, the overlapping concentration is determined from the scaling isotherms. Then the area per polymer molecule is estimated and the characteristic scaling exponent ν for the radius of the polymer is evaluated and is consistent with the finding from the isotherms. The value of ν indicates that the air/water interface becomes a poorer solvent as the amount of hydrophilic moiety is reduced.

Furthermore, the area per polymer molecule is increased as the amount of the hydrophilic component is added because of the extension of the carbon backbone by excluded volume effects. The area per hydrophilic component (OH) is at a minimum 50% substituted polymer. At the same substitution, the collapsed pressure shows a maximum. This in-

icates that there is an optimum degree of hydrophilic substitution for the hydrophobic polymer to be effective at the interface, which is equivalent to the hydrophilic/lipophilic balance of a surfactant system. In other words, the carbon number between the hydrophilic components and the solvent quality of the air/water interface for the functionalized polymer are the balancing parameters.

The 10% hydrophilic substituted polymer shows a two-dimensional phase transition, and this phase transition is due to the attractive interaction between the tails. In the future, this phase transition will be examined in detail. We also feel that the distinction between the functional polymer and a single chain surfactant should be based on their rheological properties at interfaces, which is a challenging problem for the future.

ACKNOWLEDGMENTS

We are grateful to P. Pincus, T. A. Witten, and W. Dozier for helpful discussions and criticisms prior to publication.

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