Test of the Assumption of the Scaling Law for Polymer Monolayers

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The assumption of the scaling law, that the monomer structure remains constant as the polymer concentration changes from the dilute to semidilute regime, has been tested by use of optical second-harmonic generation. The monomer orientation does not change as the polymer concentration is increased. This observation is the first confirmation of the basic assumption of the scaling law which describes polymer behavior in two-dimensional space.

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Many types of polymers are spreadable on an aqueous solution under suitable conditions.[1] In general, the polymer film reduces the surface tension of the aqueous solution. The reduction of surface tension due to the presence of the polymer monolayer is easily measurable and is also known as the surface pressure of the polymer film. The surface pressure has been extensively studied by numerous people[2,3] to understand the polymer film behavior at an interface. One recent development in the understanding of the surface pressure of a polymer monolayer is a description in terms of scaling theory,[4] which successfully describes the polymer solution properties. Recently Vilanove and Rondelez[5] have used a scaling theory to describe the isotherms of polymer films. Unlike a three-dimensional system, there is no obvious reason in a two-dimensional system for the occupied area per monomer to be constant, because of the orientational freedom at the interface. For example, it is now well known that a surfactant molecule[6,7] changes its orientation as the surface concentration is increased. The radius of the polymer (R_f) in a dilute polymer concentration regime is expressed in terms of the monomer size a, the number of monomers N, and the characteristic scaling exponent ν as

$$R_f \sim aN^{\nu}. \tag{1}$$

Furthermore, the correlation length[4] and osmotic compressibility[4] also can be expressed in terms of the scaling exponents in d-dimensional space as functions of polymer concentration c in the semidilute polymer concentration regime where the individual polymer behavior is no longer applicable:

$$\xi \sim R_f(C^*/C)^M \sim aC^{-\nu/(d\nu-1)}, \tag{2a}$$

$$\pi \sim kT/\xi^d \sim kTC^{\kappa}/a^d, \tag{2b}$$

where k is the Boltzmann constant, T is the absolute temperature, and C^* is the overlap concentration.

In Eq. (2) the monomer size is assumed to be constant as the polymer concentration is increased. In three-dimensional systems, it is obvious that the volume of the monomer is constant, but it is not clear that the occupied area per monomer in a two-dimensional system is constant because of its orientational freedom.

In this Letter, we have tested the basic assumption of the scaling theory in a two-dimensional system, in which the structure of the monomer in the semidilute concentration regime is the same as in a dilute polymer concentration. The structure of the monomer is monitored by measurement of the orientation of the monomer molecules.

Optical second-harmonic generation (SHG) has been used to measure the orientation of monomers at the air-water interface. SHG[8] is an effective surface probe because it is forbidden in centrosymmetric media but allowed at interfaces where inversion symmetry is necessarily broken. The surface nonlinear susceptibility $\boldsymbol{\chi}_s^{(2)}$ arising from a monolayer of adsorbates can be written as

$$\chi_{s,ijk}^{(2)} = N_s \langle T_{ijk}^{\lambda\mu\nu} \rangle \alpha_{\lambda\mu\nu}^{(2)}, \tag{3}$$

where N_s is the surface density of molecules, $\boldsymbol{\alpha}^{(2)}$ is the molecular nonlinear polarizability, $\langle T_{ijk}^{\lambda\mu\nu} \rangle$ is the coordinate transformation connecting the laboratory (x,y,z) and molecular (ξ,η,ζ) axes, and the angular brackets denote an average over the molecular orientation. If $\boldsymbol{\chi}_s^{(2)}$ is dominated by a single component $\chi_{s,\xi\xi\xi}^{(2)}$ along a molecular ξ axis and the latter is randomly distributed in the azimuthal plane, the nonvanishing components[9] of $\chi_s^{(2)}$ can be written as

$$\chi_{s,\perp\perp\perp}^{(2)} = N_s \langle \cos^3\theta_m \rangle \alpha_{\xi\xi\xi}^{(2)}, \tag{4a}$$

$$\chi_{s,\perp\parallel\parallel}^{(2)} = \chi_{s,\parallel\perp\parallel}^{(2)} = \chi_{s,\parallel\parallel\perp}^{(2)} = \tfrac{1}{2} N_s \langle \sin^2\theta_m \cos\theta_m \rangle \chi_{\xi\xi\xi}^{(2)}, \tag{4b}$$

where the subscripts $\perp$ and $\parallel$ refer to directions perpendicular and parallel to the surface, respectively, and θ_m is the polar angle between the ξ axis and the surface normal z. It follows from Eqs. (4a) and (4b) that a measurement of the ratio of any two linear combinations of $\chi_{s,\perp\perp\perp}^{(2)}$ and $\chi_{s,\perp\parallel\parallel}^{(2)}$ can yield a weighted average of θ_m. Furthermore, the test of the equality of Eq. (4b) can determine whether $\boldsymbol{\alpha}^{(2)}$ is dominated by a single component.

An alternative way to measure the polar angle is to determine the output polarizer angle for a null SHG signal with a specific input polarizer angle. The details of the null-angle technique can be found in the work of Heinz.[10]

A polybutyl alcohol[11,12] (PBA) monolayer was spread with use of a solution of the polymer dissolved in methanol and delivered onto the water surface by a microliter syringe. Evaporation of the methanol left the PBA molecules uniformly distributed on the water surface. The surface pressure was monitored throughout the experiments by a Wilhelmy plate. In most cases it required several hours for the monolayers to stabilize. The trough was made of glass with its edges coated with paraffin to help contain the water with a hydrophobic barrier. The area per molecule was varied by squeezing of the water surface area by a movable hydrophobic sweeping bar. The molecular structure of PBA is shown in the inset in Fig. 1. The PBA was functionized from polybutadiene by hydroboration and oxidation processes.[11] The molecular-weight distribution of the polymer was very narrow, and M_w/M_n was 1.07.

For the SHG experiments we used the frequency-doubled output of a Q-switched Nd-doped yttrium aluminum garnet laser at 532 nm as the pump beam with an energy of 24–30 mJ per 10-ns pulse and 30 Hz pulse frequency in a cross-sectional area of 0.5 cm^2.

There was a small amount of signal from the water surface proportional to $|\chi_w|^2$. The surface with polymer monolayers gave a signal proportional to $|\chi_w+\chi_s|^2$. To deduce the value of χ_s, we have measured the phase difference between water and the system by an interference technique.[10] It was found to be negligible.

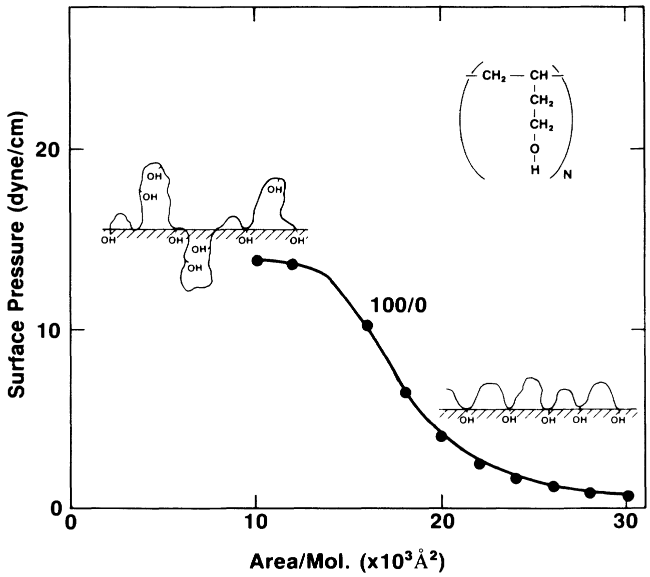

FIG. 1. Surface pressure vs specific surface area per polymer. Insets: Conceptual drawing of monolayer structure and the chemical structure of PBA.

Figure 1 shows the measured surface pressure π as a function of the surface area per molecule for PBA on a water substrate. To understand the surface isotherm of PBA monolayers in terms of scaling theory, Fig. 1 was replotted in a log-log graph of π vs C as shown in Fig. 2. The slope of the isotherm gives the characteristic scaling power (κ) which is 5. The scaling isotherm, which is independent of molecular weight of the polymer, fits reasonably to the experimental data up to the area per polymer of 1.75×10^4 Å^2 (surface density $=5.7\times10^{-5}$/Å^2).

We have estimated the value of ν, which is equal to 0.65, with the assumption that the monomer size a remained constant. In comparison, $\nu=0.75$ for a good solvent and 0.50 for a poor solvent. In addition, the inset in Fig. 2 shows σ_p as a function of number of monomers, where σ_p is the occupied area per polymer at which the ideal-gas isotherm from a dilute concentration region is equal to the scaling isotherm from a semidilute concentration regime. Since $\sigma_p \sim R_f^2 \sim a^2N^{2\nu}$ [Eq. (1)], ν can be calculated from the slope of the log-log plot of σ_p vs N, with $\nu=0.65$, which is consistent with the value obtained from the pressure measurements. The question of

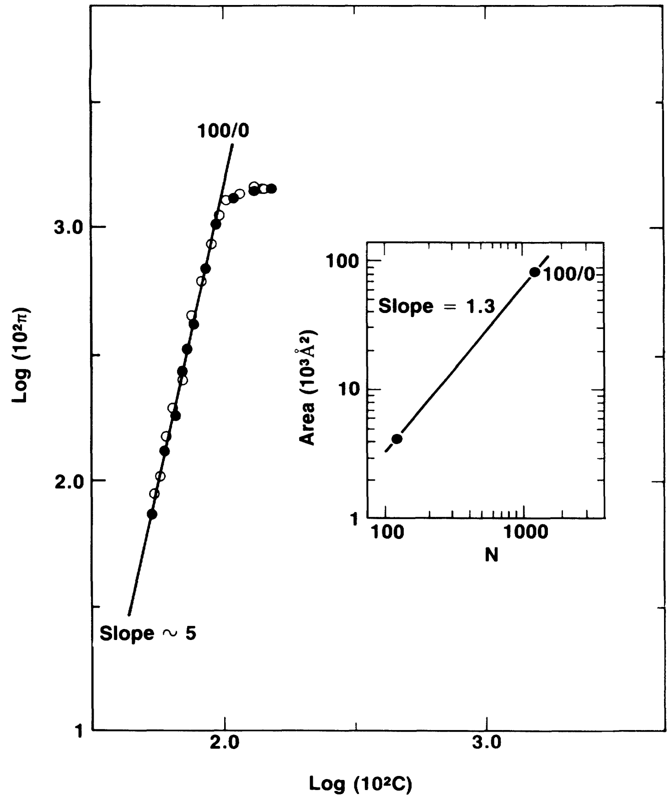

FIG. 2. Surface pressure vs surface concentration in log-log representation. Filled- and open-circle data represent number of monomers: $N=1300$ and 120, respectively. C is the polymer concentration in units of milligrams per square meter, and π is the surface pressure (dynes per centimeter).

why $\nu = 0.65$ rather than 0.75 or 0.5 can be addressed by investigation of the chemical structure of the monomer in terms of the hydrophilic and hydrophobic balance. The hypothesis that the water/air interface acts as a marginal solvent for the four-carbon-per-OH monomer can be checked by the systematic reduction of the amounts of OH moiety on the polybutadiene backbone. The value of ν was observed to decrease toward 0.5, the value expected for a poor solvent.[12] Therefore, we have found that the scaling exponent with a constant monomer size is consistent and reasonable with the polymer behavior in terms of surface pressure versus concentration and σ_p vs N. The next question to consider, therefore, is whether a is indeed constant, and this question is answered via the SHG technique.

For the SHG measurements, we first tested and found the equality of Eq. (4b). From this we conclude that the polarizability tensor $\alpha^2_{\xi\xi\xi}$ is indeed dominated by a single component ξ and that Eqs. (4a) and (4b) can be applied in order to deduce its orientation. Also, it has been shown that χ_s arises mainly from nonlinearity along the C$-$OH bond from previous measurements; therefore, our measurements refer to the orientation of this functional group (vinyl group) which is the main component that resides on the water surface. We have, in addition, measured the polar angle by the null-angle technique with the resulting angular difference of less than 1° from the two different techniques. After the molecular orientation is determined, Eq. (3) can also be tested. In other words, the signal of the SHG from the monolayer is proportional to the square of the concentration if the monomer indeed maintains its structure as the concentration increases.

Figure 3 shows the results of the square root of SHG intensity and the polar angle as functions of the polymer surface concentration. The polar angle stays at 24° from the normal of the water surface as the surface concentration is increased. Since this is the angle for C-OH, the chain is likely normal to the surface because of the carbon chain hindrance. However, the square root of the SHG intensity is linearly proportional to the surface density up to the critical concentration at which the surface pressure no longer follows the scaling isotherm. Above this critical density, some monomers no longer stay on the water surface, but may form a multilayer or loops. This phenomenon, manifest in the cancellation of the SHG contribution from the double layer, is the cause for the small reduction of the SHG intensity above the critical concentration. These results indicate that the monomer structure of a polymer monolayer at the air/water interface remains constant as the polymer surface concentration increases from dilute to semidilute concentration. Above the critical polymer concentration, the polymer film is no longer a single monolayer.

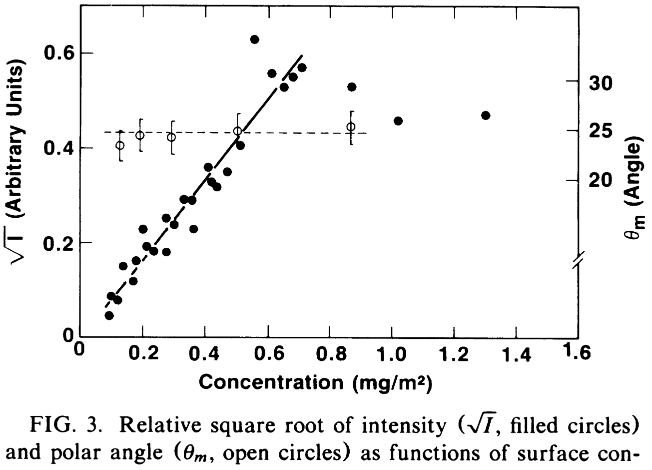

FIG. 3. Relative square root of intensity ($\sqrt{I}$, filled circles) and polar angle (θ_m, open circles) as functions of surface concentration.

In conclusion, by use of the technique of optical SHG, we have been able to study for the first time the monomer structure of a polymer monolayer from a dilute-concentration regime to a high-concentration regime. By measuring the molecular orientation of the monomer and SHG signal, we have tested the basic assumption of the scaling theory in a two-dimensional system. The results indicate that the monomer structure of the polymer remains constant as the polymer concentration increases from a dilute to a semidilute concentration regime. The polar angle is 24° which is equivalent to our having the carbon chain standing normal to the water surface. This also indicates that the monomer is always in a condensed state regardless of the total polymer surface concentration; therefore, the assumption of the scaling theory, that the area per monomer is constant, is reasonable and confirmed by this experiment. Above the critical surface concentration, the polymer film is no longer a monolayer but either in multiple layers or in loops. The next question is whether this finding is general or depends on the quality of the solvent (interface). This problem is addressed, and the results show that this is general for the different amounts of OH moiety on the polybutadiene backbone, which changes the quality of the solvent character of the interfaces for the polymers. The detailed results will be reported later.

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