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Determination of the ν Exponent for Soluble Polymeric Monolayers at an Air/Water Interface

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ABSTRACT: The scaling theory predicts that the surface pressure Π of polymer monolayers in the semidilute region varies with the surface concentration Γ according to the power law $\Pi \sim \Gamma^y$, where $y = 2\nu/(2\nu - 1)$. For spread polymeric films, it has been established that experiments were indeed in good agreement with the theory. We proposed a test of the scaling theory for adsorbed polymeric monolayers by measuring the high-frequency limit of the surface modulus ϵ_0 as a function of the surface pressure Π (it is shown that $\epsilon_0 = y\Pi$). The exponent ν for soluble polymer samples of poly(ethylene oxide), Pluronic F127, Pluronic F68, and poly(vinyl alcohol) are found to be ca. 0.77, in agreement with the scaling theory for the good solvent condition. The experimental value for methylcellulose is $\nu = 0.64$, which suggests that the air/water interface behaves as a poor solvent for the polymer.

1. Introduction

It has been shown that polymer chains at air/water interfaces partially interpenetrate each other in the semidilute region.[1,2] Like the osmotic pressure of bulk polymer solutions,[3] the surface pressure varies with the surface concentration Γ according to the power law

$$\Pi \sim \Gamma^y \qquad (1)$$

and is independent of the molecular weight. Here, the exponent $y = 2\nu/(2\nu - 1)$ and ν is the critical exponent of the excluded volume. Several theoretical calculations have been carried out to estimate the value of the exponent ν for two-dimensional (2D) polymers in a good solvent. A value of 0.77 is predicted by ϵ-expansion calculations.[1] Monte Carlo simulations give a value around 0.75.[19] In the case of 2D systems under Θ conditions, the value of ν predicted by theoretical calculations and computer simulations is in the ranges $0.51 < \nu < 0.59$.[4,20,21]

Studies involving spread polymeric layers of poly(vinyl acetate),[2] poly(methyl acrylate),[5,12] and poly(ethylene oxide)[6] showed that the surface pressures of these polymeric films are in good agreement with the above scaling law, and the exponent ν was experimentally found to be ca. 0.77. This indicates that the air/water interface is a good solvent for the polymers. Vilanove et al.[12] found the exponent y in eq 1 for poly(methyl methacrylate) films to be ca. 16.5, irrespective of the molecular weight at 25 °C. The corresponding excluded volume exponent, $\nu = 0.53$, implies that the air/water interface is a poor solvent for PMMA.

To the best of our knowledge, this power law behavior has not been verified for adsorbed (soluble) polymeric monolayers. This is probably due to the fact that the adsorption Γ cannot be easily measured accurately.

In this work, we determine the exponent y, and therefore the exponent ν, for soluble polymer chains through measurements of the high-frequency limit surface dilational modulus ϵ_0 as a function of surface pressure Π (it is shown that $\epsilon_0 = y\Pi$). It permits the determination of the exponent ν without having to measure the surface concentration Γ. Surface dilational viscoelasticity ϵ can be studied in a wide range of frequency through various techniques such as surface light scattering,[13-15] capillary waves,[8,10,16] longitudinal waves,[17,18] and the modified Langmuir trough.[9] In this study, we used the modified Langmuir trough to measure ϵ at frequencies about 0.1 Hz; this corresponds to the high-frequency limit for the polymer samples studied.

Our objective is to determine the value of the exponent ν for polymers possessing different chain topologies (by examining homopolymers and block copolymers) at different temperatures and molecular weights. Especially, the exponent ν is obtained for adsorbed layers of poly(ethylene oxide), triblock poly(ethylene oxide/propylene oxide/ethylene oxide) copolymers of different block lengths, poly(vinyl alcohol), and methylcellulose.

2. Theory

The surface dilational viscoelasticity ϵ is a measure of the response of the surface to dynamic surface deformations. In the case of sinusoidal dilation/compressional area changes, the viscoelascity ϵ depends not only on the polymer surface concentration Γ but also on ω, the frequency of surface deformation. It is conveniently represented by a complex function

$$\epsilon = -\left(\frac{\partial \Pi}{\partial \ln A}\right)_T = \epsilon_d + i\omega\eta_d = |\epsilon|e^{i\theta} \qquad (2)$$

where ϵ_d and η_d are the dilational elasticity and viscosity, respectively. The real and imaginary parts of ϵ can also be represented by the dilational elastic modulus $|\epsilon|$ and the loss angle θ, as shown in eq 2. In the limit of high frequencies of area dilation/compression, where $\omega \gg \omega_{\text{diff}}$, the characteristic frequency for diffusion, the interchange of polymer molecules between the surface and the bulk becomes negligible. Hence, the soluble polymeric monolayers act like "insoluble" ones (i.e., the product ΓA = constant) and the surface viscoelasticity ϵ in eq 2 may be written as[8]

$$\epsilon(\omega \rightarrow \infty) = \epsilon_0 = (d\Pi/d \ln \Gamma)_T \qquad (3)$$

Note that the quantity ϵ_0, that is, the high-frequency limit of the surface modulus, may be identified as the thermodynamic surface elastic modulus and can be measured experimentally.

Combining eqs 1 and 3 gives

$$\epsilon_0 = y\Pi \qquad (4)$$

Equation 4 can be used to determine the exponent y for

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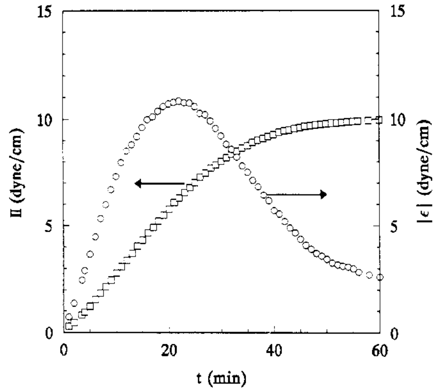

Figure 1. Surface pressure Π (□) and surface modulus |ε| (○) of PEO as a function of time at a bulk concentration of 1.2×10^{-4} wt %.

soluble polymer chains at air/water interfaces. Evidently, this has the advantage that measurement of the surface adsorption Γ is avoided.

3. Experimental Section

The exponents for polymer samples of poly(ethylene oxide) (PEO), poly(ethylene oxide/poly(propylene oxide) triblock copolymers of Pluronic F68 ($(EO)_{79}(PO)_{30}(EO)_{79}$) and F127 ($(EO)_{106}(PO)_{69}(EO)_{106}$), poly(vinyl alcohol) (PVA), and methylcellulose (MC) were obtained. PEO with M_w = 31K and $M_w/M_n < 1.03$ was purchased from Scientific Products, Inc. F68 (M_w = 13,900, M_n = 9400) was purchased from Fluka, and F127 (M_w = 17500, M_n = 11600) was received as a gift from BASF. Methylcellulose (MC) with M_w = 41000 and PVA (87–89% hydrolyzed) with M_w = 18000 and 115500 were purchased from Aldrich. All samples were used as received without further purification.

Surface tensions are measured by means of the Wilhelmy plate technique using platinum film. The apparatus employed to measure surface dilational modulus is similar to the one designed by Lucassen and Giles[9] with minor modifications. Four Teflon bars form a rectangular enclosed area in a Teflon-coated aluminum trough. The two upper bars were driven to sinusoidally sweep the surface by two computer-controlled microstep motors. Surface tension variations $\Delta\sigma$ resulting from the area variations ΔA were measured once again by the Wilhelmy plate method.

The surface modulus ε is obtained as

$$|\epsilon| = \frac{|\Delta\sigma|}{|\Delta A/A|} \tag{5}$$

The relative area variation in the present study has an amplitude of 0.058. The loss angle θ is obtained by comparing the surface tension variation curves with the area variation curves. Loss angles were reproducible to within ±2°, except at rather low values of modulus (≈3 dyn/cm).

The apparatus was tested extensively against possible leakage prior to the experiment by spreading a small amount of insoluble surfactant onto the enclosed rectangular area and then monitoring the surface tension of this area. The background loss angles—i.e., the recorded surface tension variations lag behind the actual values caused by the slow response time to the electrobalance—were obtained by studying insoluble monolayers for which the loss angles ought to be zero at low frequencies. At 10 cycles per minute, this correction was 27°.

4. Results and Discussion

The surface pressure Π, the surface modulus |ε|, and the loss angle θ at a frequency of 10 cycles per minute (cpm) are measured simultaneously as a function of time for a newly created interface by sweeping it with a Teflon barrier. An example of such a measurement for PEO is shown in Figure 1. At a deformation frequency of 10 cpm, the loss angles θ for all polymer samples at low bulk concentrations (ca. 1×10^{-4} wt %) are observed to be zero within experimental accuracy (ca. 2–3°), and therefore the measured values of |ε| correspond to the high frequency moduli $\epsilon_0 = d\Pi/d \ln \Gamma$.

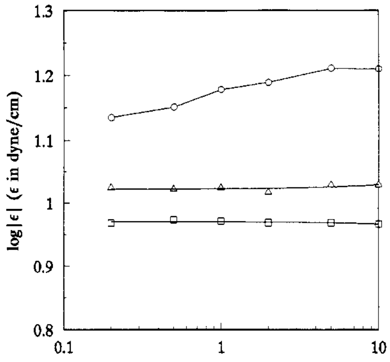

Figure 2. Surface modulus |ε| as a function of surface deformation frequency for PVA: (○) 5×10^{-4} wt % of PVA(M_w=18K); (△) 5×10^{-4} wt % of PVA(M_w=115.5K); (□) 1.2×10^{-4} wt % of PVA(M_w=18K).

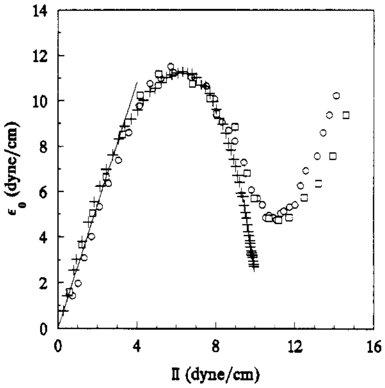

Figure 3. Measured high-frequency surface moduli ϵ_0 plotted as a function of surface pressure Π: (□) F68; (○) F127; (+) PEO. The solid line represents $\epsilon_0 = 2.7\Pi$.

To ensure that a frequency of 10 cpm is sufficiently high to reach the high-frequency limit, we performed the measurement of modulus at different frequencies ranging from 0.2 to 10 cpm for all polymer samples. As expected, we found that this limit is a strong function of polymer molecular weight and bulk concentration. For example, Figure 2 shows the measured surface modulus |ε| plotted as a function of surface deformation frequency for PVA at different bulk concentrations and different molecular weights. At the same bulk concentration of 5×10^{-4} wt %, a frequency dependence is observed for the lower molecular weight (M_w = 18K) PVA but not for the higher molecular weight (M_w = 115.5 K) sample. Also, it is noted that the modulus is independent of frequency at lower bulk concentration ($C = 1.2 \times 10^{-4}$ wt %), even though the molecular weight is low (M_w = 18K). All polymer samples were studied at low bulk concentrations, and the frequency dependence was examined.

Displayed in Figure 3 are the $\epsilon_0 \sim \Pi$ data for PEO, F127, and F68. The curves of ϵ_0 vs Π were obtained from the $\epsilon_0 \sim t$ and $\Pi \sim t$ curves at the same t. It should be noted that, in the case of PEO, which also forms stable spread films at the air/water interface, the ϵ_0 vs Π data obtained in our adsorption experiments are identical to those from spread layers.[11] An examination of Figure 3 reveals that, for the three polymers studied here, and in the range $0.5 < \Pi < 3$ dyn/cm, ϵ_0 varies linearly with Π according to eq 4. The exponents y were obtained by linearly fitting the data and are given in Table I. The exponent y was found to be ca. 2.7. These results imply that the pressure of adsorbed films formed by the PEO,

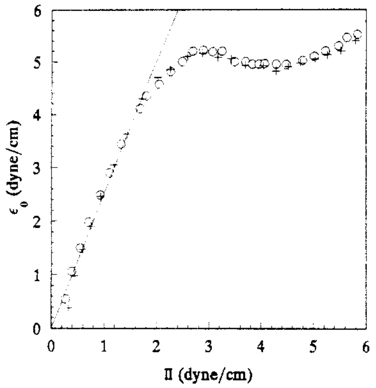

Figure 4. Surface modulus ϵ_0 as a function of surface pressure Π for PVA: (○) M_w = 18K; (+) M_w = 115.5K.

Table I. Measured Values of Exponents y and ν

polymer	M_w (K)	T (°C)	y	ν	Π (dyn/cm)
PEO	31	25	2.75 ± 0.1	0.79 ± 0.02	0.5–3
F127	17.5	25	2.60 ± 0.1	0.81 ± 0.02	0.5–4
F68	13.9	25	2.60 ± 0.1	0.81 ± 0.02	0.5–4
PVA	18	25	2.6 ± 0.2	0.81 ± 0.03	0.3–1.8
PVA	115.5	25	2.6 ± 0.2	0.81 ± 0.03	0.3–1.8
MC	41	25	4.7 ± 0.1	0.65 ± 0.02	0.2–5
MC	41	35	4.7 ± 0.1	0.65 ± 0.02	0.2–5
MC	41	45	4.7 ± 0.2	0.65 ± 0.03	0.2–5

F127, and F68 samples follow the scaling theory in the semidilute region. For pressures above 3 dyn/cm, the modulus ϵ_0 does not vary linearly with Π. This is an indication that the simple scaling relationship given by eq 1 is no longer valid for the systems.

We also considered poly(vinyl alcohol) of different molecular weights (18 000 and 115 000). Results of $\epsilon_0 \sim \Pi$ for these polymers are given in Figure 4. The exponent y was determined to be $y = 2.6$ ($\nu = 0.81$) for both samples. This observation is in agreement with the scaling theory which predicts that the exponent is independent of the polymer molecular weight.

Shown in Figure 5 are the data of ϵ_0 vs Π for methylcellulose, which were obtained at different temperatures. At 25 °C, experiments were performed at different bulk concentrations, and ϵ_0 was observed to be only a function of surface pressure Π and independent of bulk concentration. The same conclusion can also be drawn for all other polymers investigated. The exponent y was determined in the pressure range 0.2–5 dyn/cm. The experimental value of y is $y = 4.7$ and $\nu = 0.65$, which suggests the air/water interface is not a good solvent for polymeric MC at 25 °C. Data obtained at higher temperatures (35 (Δ) and 45 °C (□)) yield the same value for the exponent ν and suggest the interface remains as a poor solvent at these temperatures. All the experimental results are given in Table I.

In conclusion, the scaling exponent y and therefore the exponent ν of the excluded volume were determined for five different soluble polymers through surface modulus measurements. The experimental values of exponent ν for poly(ethylene oxide), Pluronic F127, Pluronic F68, and poly(vinyl alcohol) are ca. 0.8, which implies that the air/water interface behaves as a good solvent for the four polymers. In contrast, ν is 0.65 for methylcellulose in the temperature range 25–45 °C, suggesting the interface is not a good solvent for methylcellulose.

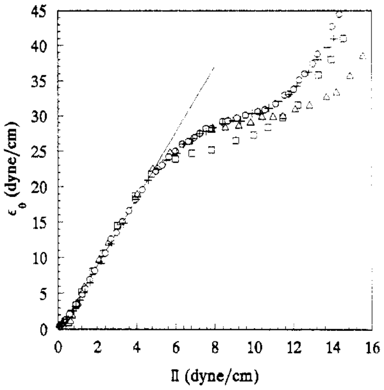

Figure 5. Surface modulus ϵ_0 as a function of surface pressure Π for methylcellulose: (○) 2.0×10^{-4} wt % of MC at 25 °C; (+) 1.0×10^{-4} wt % of MC at 25 °C; (Δ) 1.0×10^{-4} wt % of MC at 35 °C; (□) 1.0×10^{-4} wt % of MC at 45°C

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