

## Surface Rheology of a Polymer Monolayer: Effects of Polymer Chain Length and Compression Rate

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We study surface layers of a simple homopolymer poly(vinyl acetate) on the air–water interface as a function of the concentration and the polymer molecular weight. Our results suggest that there is an effect of the compression rate on both the structure of the layers and their rheological behavior, while the length of the chain influences only the rheology. At very low compression speeds, the surface layer of short chains does not exhibit the classical semi-dilute regime behavior, forming instead a solid phase. For fluid layers, we report on the dependence of surface viscosity upon the concentration, showing a first crossover, which happens close to the semi-dilute-concentrated regime boundary, from a scaling behavior with the concentration to an Eyring-like liquid. A second rheological transition happens at very high concentrations, near close packing, where the Newtonian liquid phase gives way to a soft solid phase.

## Introduction

In multiphase systems, surface films serve to stabilize interfaces and often contribute significantly to the material mechanical properties. The primary classes of surface-active molecules are small surfactants, lipids, proteins, and bio- or synthetic polymers. Recent research is also focusing on the use of solid colloidal particles.<sup>1</sup> Controlling liquid surface properties is an area of significant interest in diverse areas ranging from designing personal care products and detergents to oil recovery and wastewater management. The rheology of interfaces can play an important role in the rheology of the bulk system.<sup>2,3</sup> Long-chain polymer molecules can adsorb to liquid interfaces (air–water or oil–water) in a variety of ways. For example, block co-polymers can be designed with hydrophilic and hydrophobic groups, which partition on either side of the interface. At high surface densities, these co-polymer layers can form brushes, with at least part of the molecules extending out of the interface plane.<sup>4</sup> At low densities, many synthetic polymers can lie on the interface plane, with their conformation quite strictly confined to two dimensions.<sup>5</sup> Biopolymers such as proteins often denature at interfaces, and many proteins are known to unfold, so that most monomers lie on the interface.<sup>6,7</sup> We focus here, on a simpler case, that of a homopolymer, which is known to form a flat conformation, lying on the air–water interface plane.<sup>8</sup> Looking at the simple homopolymer, we aim to understand not just the effect of surface confinement on the equilibrium chain conformation, which has been the object of previous work, but also to address the rheology of the polymer film. In particular, we want to consider how polymer chain length

influences the shear properties of the film and to understand processing parameters, such as how the rate of compression affects the film.

The chain conformation, fluctuation behavior, and rheology of homopolymers in bulk polymer solutions have been studied extensively, leading to a set of sophisticated theories and models.<sup>9,10</sup> In polymer solutions, there are typically four regions as a function of the increasing concentration: gas, semi-dilute, concentrated, and melt. The boundaries between these regions as well as the equilibrium thermodynamic functions and linear response moduli can be obtained from the scaling theory. They are functions simply of the molecular weight  $M_w$  and the monomer concentration  $\phi$ . The equilibrium scaling also manifests itself in the bulk properties; for example, it is well-known that the shear viscosity in an entangled polymer solution scales with the molecular weight as  $\eta_{3d} \sim M_w^{3.4}$ . Polymers confined to two dimensions (2D) are generally less well-understood. The scaling arguments by de Gennes and others make predictions for the equilibrium chain conformation of polymers in two dimensions,<sup>9</sup> and these have been very successful in explaining the statistical properties of chains at least in some regimes of concentration. For example, the dependence of the radius of gyration upon the concentration in the semi-dilute regime was verified early on using poly(vinyl acetate) (PVAc) as a model system.<sup>8</sup> On the other hand, the *dynamics* of polymers in two dimensions is rather unexplored and less well-understood compared to polymer dynamics in bulk solutions. In part, this is due to the fact that there is less control on the behavior of polymers on interfaces than in the bulk. For example, confinement to an interface leads many organic polymers to aggregate and form brittle layers. Other polymers do not spread at all onto interfaces and dissolve into the subphase. There are actually only few known systems for which the “universal” behavior expected for two-dimensional “good solvent” or “ $\theta$  solvent” conditions is found! This is not to say that the ideal polymer behavior is only of academic interest. On the contrary,

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even relatively complex molecules, such as proteins and copolymers, have semi-dilute regimes that are well-described as semi-dilute polymer regimes.<sup>4,7</sup> Some bulk behavior has a direct correspondence in two dimensions, in particular, the existence of a semi-dilute concentration regime and the excluded volume effect. Recent experiments indicate that, on the contrary, there are other properties that are unique to two dimensions. For example, the compressional dynamics (i.e., concentration fluctuations) in the semi-dilute regime is described by a time scale that is not related to the classical bulk mechanisms of Rouse modes or reptation.<sup>11</sup>

PVAc was the first polymer described as having a “good-solvent” configuration at the air–water interface,<sup>8</sup> and it has been studied extensively since then as a model system.<sup>11–18</sup> This has enabled various fundamental properties to be explored. While PVAc is a “model” system of choice, it was already clear from the work of Monroy et al.<sup>19</sup> and ourselves<sup>18</sup> that, as the surface layer becomes denser, even this “simple” system displays complex properties. Monroy et al.<sup>19</sup> discussed the presence of a glass transition as a function of the temperature at the high concentration limit of the semi-dilute regime. In previous work, we investigated the onset of a shear modulus, indicating a solidification of the polymer layer, i.e., “jamming”, at very high concentrations, where the monomers are packed together.<sup>18</sup> In the present work, we investigate more deeply the mechanical properties of PVAc layers, aiming to understand the factors that control viscosity and the liquid–solid transition in the monolayer. We perform experiments on PVAc chains with a range of molecular weights, measuring the response to shear deformation as well as the compression modulus. We use a very sensitive surface shear rheometer, a modified Langmuir trough that enables large compression ratios, and a second surface shear rheometer, which is capable of measuring the frequency dependence of the surface shear modulus. We find several new results: (a) layers compressed continuously at extremely low strain rate do not exhibit the classic semi-dilute polymer phase; (b) throughout the semi-dilute regime, the compression strain rate has a stronger effect on the dynamical properties than the polymer chain length; (c) in the concentrated regime, the shear viscosity increases as the exponential of the pressure, in a 2D analogue of Eyring’s theory for pressure dependence of bulk viscosities. The onset point for this behavior depends upon both the compression strain rate and the molecular weight.

## Polymer Monolayers

**Conformation and Equilibrium Properties in Two Dimensions.** The separation of concentration into four regions, dilute, semi-dilute, concentrated, and melt, has been proposed before. At very low surface densities, the surface pressure increases linearly with the increasing surface concentration. The 2D polymer layer can be thought of as a two-dimensional gas. The surface pressure is typically so low that there are no systematic experi-

ments in this regime. For isolated polymer chains, it is well-known that the mean end–end distance,  $R$ , scales as a power of the polymerization number  $N$ :  $R = aN^\nu$ , where  $a$  is the Kuhn length (of the order of one or two monomers for a flexible polymer, such as PVAc) and  $\nu$  is the Flory exponent.<sup>9</sup> The theoretical prediction for a flexible polymer in a 2D good solvent is that the chain conformation obeys a self-avoiding random walk statistics, and the scaling exponent is  $\nu = 0.75$ .<sup>9</sup>

There are two useful quantities to describe the concentration of polymer in the surface layer. One is the (dimensionless) surface area fraction occupied by monomers, which is labeled in this paper as  $\phi$ . The other is the mass density (mass of polymer per unit area), which is labeled as  $\Gamma$ . The two are of course proportional to each other:  $\phi = \Gamma \times a^2/w$ , with  $w$  being the monomer mass and  $a^2$  being the area occupied per monomer. The reason for keeping both quantities is that  $\Gamma$  is the experimentally controlled variable (by spreading and compressing), whereas  $\phi$  is the natural variable for the theory. In general,  $w$  is well-known, but  $a^2$  is not; therefore, in practice, the effective value of  $a^2$  is determined experimentally from the regimes in isotherms, as performed in this work.

When the concentration is increased above a value  $\phi^*$ , defined as the overlap packing fraction, the chains can no longer be regarded as isolated. At  $\phi^*$ , the area corresponding to the radii of gyration  $R_g$  covers the available area and the chains have a significant mutual contact. The overall surface concentration is the same as that within each unperturbed chain. The dependence of  $\phi^*$  on  $N$  follows from scaling arguments.<sup>9</sup>

$$\phi^* = N^{1-2\nu} \quad (1)$$

Above  $\phi^*$  is the semi-dilute regime, in which the dependence of the osmotic pressure  $\Pi$  on  $\phi$  is stronger than linear, following a power law

$$\Pi = \Pi^* \left( \frac{\phi}{\phi^*} \right)^y \quad (2)$$

where  $\Pi^*$  is the pressure at  $\phi^*$  and the exponent  $y$  is a function of Flory’s exponent  $\nu$ :  $y = 2\nu/(2\nu - 1)$ . For good solvent conditions,  $y = 3$ . The density–density correlation length  $\xi$  falls as a power law of the concentration, starting from a value  $\xi \sim R_g$  at  $\phi^*$ .<sup>9</sup>  $\xi$  is known as the blob size. It is expected from entropic reasons that the individual chains should remain relatively segregated throughout the semi-dilute regime rather than extensively intertangled.<sup>9</sup>

The semi-dilute power law scaling regime lasts up to a surface concentration of  $\phi^{**}$ . The theoretical argument setting the upper bound of the semi-dilute regime, i.e.,  $\phi^{**}$ , is that the blob size has dropped to a length comparable to the persistence length of the chain. In previous work on PVAc, we showed that the surface layer can still be compressed considerably above  $\phi^{**}$ , by a factor greater than 4.<sup>18</sup> This means that there is a substantial fraction of free surface area still available at  $\phi^{**}$ . Above  $\phi^{**}$ , the pressure increases very slowly with the concentration. It was shown in ref 18 that a final upturn of the pressure can be seen at a concentration  $\phi^{***}$ , which was described as a close packing of the monomers. Around  $\phi^{***}$ , the monolayer is a 2D polymer melt. The regime between  $\phi^{**}$  and  $\phi^{***}$  is called concentrated.

**Dynamics in Polymer Monolayers.** The dilatational modulus  $\varepsilon$  and the shear modulus  $G$  characterize the linear response to a deformation for an isotropic material in 2D. The former gives the stress response as proportional to a change in area, and an equilibrium dilatational modulus  $\varepsilon_{\text{eq}}$  can be determined from

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quasi-static measurements of the surface pressure as a function of the area

$$\varepsilon_{\text{eq}} = -A_0 \left. \frac{d\Pi}{dA} \right|_{A_0} \quad (3)$$

When the area of the monolayer is made to oscillate sinusoidally around  $A_0$  at a frequency  $\omega$ , the complex dilational modulus  $\varepsilon^*(\omega)$  is measured. As usual in linear viscoelasticity, the real part of the modulus  $\varepsilon'(\omega)$  is the elastic in-phase response, and the imaginary part  $\varepsilon''(\omega)$  is the response  $90^\circ$  out of phase with the strain and is proportional to the dissipation.

Analogously, the complex shear modulus  $G^*$  is defined as the ratio of the shear stress response to an induced strain (shape change at constant area). Similarly, as described above for the complex dilational modulus, the complex shear modulus has a real component (in-phase, elastic) response and an imaginary component (out of phase, dissipative) response:  $G^*(\omega) = G'(\omega) + iG''(\omega)$ . A liquid-like monolayer is expected to have  $G' = 0$ , whereas it is possible that  $G''$ ,  $\varepsilon'$ , and  $\varepsilon'' \neq 0$ .

The compressional dynamics involves the motion that polymers need to undergo when the concentration is changed. In the semi-dilute regime, this involves reconfiguration of the chain at all length scales from the polymer size downward, because the area available per chain changes but so does the statistical correlation of monomer pair distances, i.e., the “blob size”  $\xi$ . There does not need to be rearrangement of the centers of mass of different polymers relative to each other. It is well-known and follows from eqs 2 and 3 that the equilibrium compressional modulus has the same scaling with the concentration as the osmotic pressure. The elastic component of the complex compressional modulus is seen experimentally to have the same scaling with concentration,<sup>11</sup> although it can have a higher value than the equilibrium modulus. In other words, there are several cases where it has been shown that  $\varepsilon'$  has a frequency-dependent component in the semi-dilute regime. The compressional viscosity describes the dissipation that arises in the polymer chain rearrangement. There have been few attempts to model this theoretically. In previous work, we have shown that, while  $\varepsilon'$  scales the same way as the surface pressure,  $\varepsilon' \sim \Gamma^y$  as in eq 2,  $\varepsilon''$  scales as  $\varepsilon'' \sim \Gamma^{2y}$ . This suggested the origin of  $\varepsilon$  as a “friction between blobs”.<sup>11</sup> For a good solvent chain ( $y = 3$ ), we expect  $\varepsilon'' \sim \Gamma^6$ . Up to now there has been no measurement of the shear viscosity (which is very small), but it would be plausible to expect the same scaling form.

Measurements of the dynamics under shear have, thus far, proven elusive for the “model” polymer monolayers, in which chains lie flat on the liquid interface. This is because the shear moduli of these systems are very low, except at concentrations near close packing.<sup>18</sup> There have been studies of shear rheology of polymer layers, for example,<sup>20</sup> where the shear response became significant but only at a conformational transition involving out-of-plane rearrangement of the chains. It could be expected that, in the semi-dilute regime (where the absolute concentration is very low), the surface layer would behave as a fluid dilute suspension, with the polymers contributing to the viscosity, a term linear with the concentration.

## Methods

**Langmuir Trough.** PVAc can be spread on the surface of water to form an insoluble Langmuir film. Relatively dilute ( $M_w = 17\,000$ ,  $0.051$  mg/mL;  $M_w = 45\,500$ ,  $0.167$  mg/mL;  $M_w = 170\,000$ ,  $0.189$  mg/mL;  $M_w = 275\,000$ ,  $0.147$  mg/mL) solutions

are prepared in tetrahydrofuran (THF, Fischer Scientific), and then a series of small ( $\sim 1$   $\mu\text{L}$ ) droplets is delivered in succession to the surface with a microsyringe (Hamilton 710RN), typically depositing up to  $100$   $\mu\text{L}$ . The THF evaporates rapidly, leaving a dilute layer of PVAc. In this work, we spread less than  $0.2$  mg/m<sup>2</sup> of PVAc and rely on continuous compression via the Langmuir trough barriers to increase the concentration. Other work had shown that the surface pressure as a function of the concentration is the same whether the concentration is increased by the addition of aliquots or continuous compression.<sup>15</sup> Our own experiments showed that there were systematic differences between the isotherms, especially in the shear viscosity at high concentrations, depending upon the spreading method. This is not so surprising given that the aliquot method can lead, in principle, to polymer overlap if drops are added on a layer with a pre-existing finite concentration. We choose instead to work with continuously spread layers and actually explore the finer point of the effect of the compression strain rate on the polymer layer.

In previous work,<sup>18</sup> we had shown that the first compression was slightly different from other subsequent compressions performed after expansion. In this work, we have focused on the first compression only.

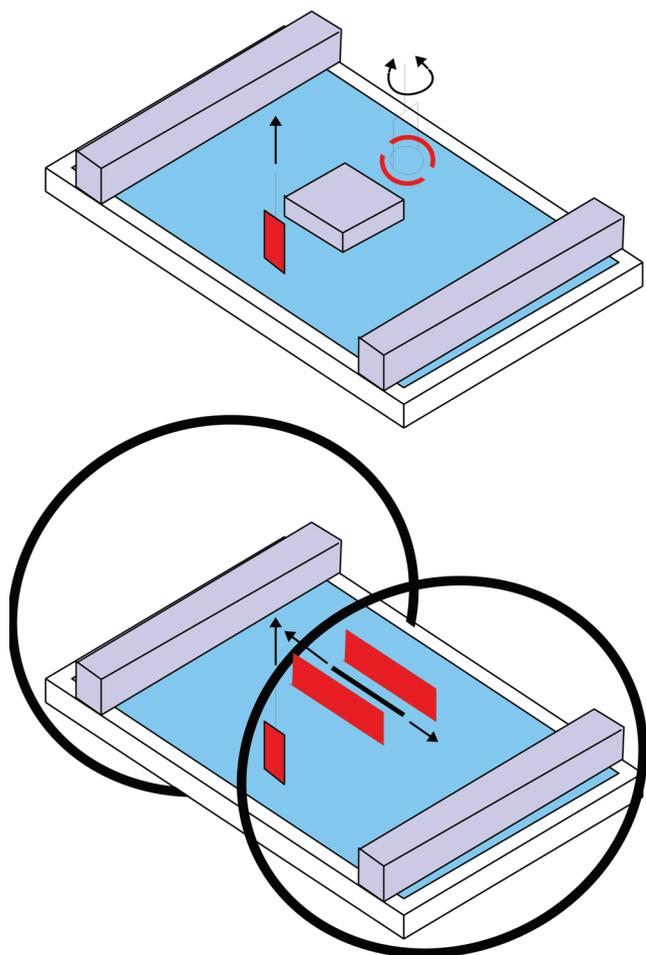
The measurable surface tension of the liquid surface,  $\gamma$ , decreases compared to the value for pure water,  $\gamma_0$ , because the film exerts a certain surface pressure  $\Pi$ , with  $\Pi = \gamma_0 - \gamma$ . Using a Langmuir trough, an insoluble monolayer can be compressed at different speeds, reducing the available area and, consequently, increasing the surface concentration. The surface pressure  $\Pi$  is recorded, giving a  $\Pi$ - $A$  isotherm. If a monolayer has long relaxation times, then the measured surface pressure  $\Pi$  can be affected by the compression rate, and  $\Pi$  is best thought of as a surface stress.

For the isotherm experiments, we use a trough (model 600, Nima, U.K.) that has a surface area of  $20 \times 30$  cm. Two barriers sweep the surface of the liquid, compressing the surface layer symmetrically, as sketched in Figure 1. With this trough, it is normally possible to compress a surface layer by a factor of around 6. We have included a block in the center of the trough that acts as an “island”, leaving enough free space for the Wilhelmy plates but removing  $42$  cm<sup>2</sup> of the surface area. This is a large fraction of the area when the barriers are closed and increases the compression factor to 10.5. The trough was maintained at  $23$  °C. Plates (1 cm wide) made of filter paper are used as Wilhelmy pressure sensors. We showed in previous work how it is possible to measure the shear modulus of the surface layer by using two Wilhelmy sensor plates positioned parallel and perpendicular to the axis of compression.<sup>21,22</sup> However, that method is not sensitive enough for the phenomena investigated here; therefore, pressure was measured with a single sensor, leaving enough space to fit the du Nuoy ring for surface rheology, as described below. Unless stated otherwise, we report results on the first compression, starting from dilute conditions ( $\Pi \lesssim 10^{-3}$  N/m).

**Surface Rheology.** The method of measuring perpendicular pressures in a Langmuir trough has the advantage of relying simply on the conventional Langmuir trough hardware, but it is not the most sensitive technique available to probe shear response.<sup>21</sup> In this work, we wanted to investigate the onset of the shear response. An extremely sensitive rheometer was developed commercially by Camtel (CIR-100, Camtel, U.K.) and is based on a du Nuoy ring maintained in oscillation on the interface plane. The CIR-100 is stress-controlled, maintaining a set amplitude and frequency through feedback. It relies on the “normalized resonance” technique, which (in combination with a sensitive transducer) makes it particularly sensitive. We use a modified CIR-100 instrument, where the rheometer head is attached to an optical rail and mounted, so that it can be freely positioned over a Langmuir trough. The ring is lowered onto the liquid surface by turning a

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**Figure 1.** Diagrams of experimental setup for measurement of surface pressure and surface shear rheology. Two instruments were used. The Camtel CIR-100 is sketched on top, together with our trough setup to increase the compression ratio. The du Nuoy ring is held by a sensitive mechanical transducer to measure the torque on the ring. The ISR developed in Stanford is sketched below. The magnetic coils are positioned in anti-Helmholtz configuration, generating a magnetic field gradient that moves the magnetized needle in the open channel. A linear array sensor measures the needle displacement. Both instruments are stress-controlled.

precision micrometer movement. An aluminum ring with two openings for the layer to flow inside defines the shear deformation geometry, as sketched in Figure 1. This external ring is 3.5 cm in diameter. The du Nuoy ring is 1.2 cm in diameter. The du Nuoy ring is set in oscillation in the surface plane. In this work, the oscillation frequency was set to 3 Hz and the angular amplitude was  $5 \mu\text{rad}$ . The strain is therefore very small,  $2.6 \times 10^{-4} \%$ . This setup allows the study of the onset of shear viscoelasticity as a function of the concentration, in particular the detection of very small surface viscosities in the polymer layers in the semi-dilute regime.

A powerful surface shear rheometer (ISR) was developed by Brooks et al. and is described fully in refs 23 and 24. It generates simple shear deformations in the monolayer by inducing oscillations along the axis of a needle that floats on the surface at the midpoint of a linear canal. This instrument is built around a commercial trough (Minitrough, KSV, Finland). We have used it here to investigate the frequency dependence of the shear modulus, for relatively high packing and high modulus, which are

conditions where the instrument is very precise.<sup>24</sup> Frequency sweeps were acquired at a fixed strain amplitude of 3%.

## Results

**Pressure Isotherms.** Pressure isotherms taken in continuous compression at several compression speeds and for different molecular weights are shown in Figure 2. These equilibrium isotherms show a strong dependence upon the compression speed. In particular, at the lowest compression speed of  $1 \text{ cm}^2/\text{min}$ , which corresponds to a compression strain rate of around  $10^{-4} \text{ s}^{-1}$ , it is clear that the polymer layers of the molecular weights 45 000 and 170 000 exert a significantly reduced osmotic pressure. For the higher compression speeds (2, 5, 20, 100, and  $300 \text{ cm}^2/\text{min}$ ), the isotherms are more similar to each other, but it can still be seen that, for 45 000 and 170 000, the compression speed affects the surface pressure. For the highest molecular weight, 275 000, there is little dependence of surface pressure upon the strain rate and similarly for the lowest molecular weight, 17 000. For this polymer, it is safe to assume that all of the molecules spread at the interface remain in the surface layer and that desorption and diffusion into the bulk can be excluded. We found that the isotherms of the shortest molecular-weight polymer were particularly sensitive to the initial spreading concentration and, particularly, at slow compression speeds, the upturn concentration and the shape of the pressure isotherms could vary widely. There is clearly some additional complexity in the short-chain molecules, which we do not explore in further detail here.

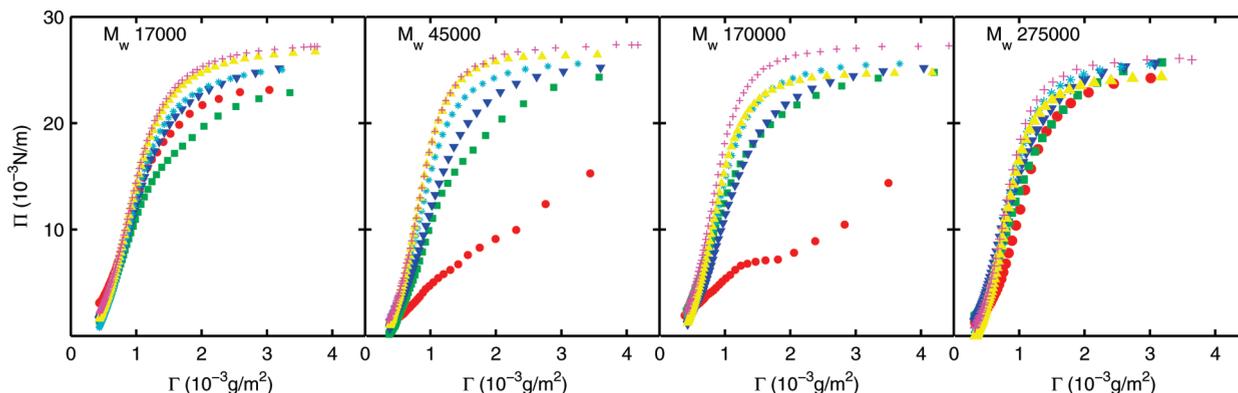
To investigate further the effect of the molecular weight and the speed compression on the structure of the monolayer, it is useful to derive the compression modulus  $\epsilon$  from the isotherms, using eq 3 (values of  $\epsilon$  are obtained by fitting the isotherm data with a high-grade polynomial. This polynomial function is drawn as a solid line in Figure 3). For  $\Gamma \lesssim 0.8 \times 10^{-3} \text{ g/m}^2$  or  $\Pi \lesssim 10 \times 10^{-3} \text{ N/m}$ , the layer is in the semi-dilute regime. In this regime, the film can be thought as a 2D network made of segregated polymer chains and the pressure and compressibility are power laws of the concentration. We do not study it here but confirm that the Flory exponent found is close to the good solvent value ( $\nu \sim 3/4$ ). The compression moduli increase as the layer is compressed. We label  $\epsilon^{**}$  the maximum of  $\epsilon$  and  $\Gamma^{**}$  and  $\Pi^{**}$  the corresponding surface concentration and pressure. We present the dependence of  $\Gamma^{**}$ ,  $\Pi^{**}$ , and  $\epsilon^{**}$  obtained from Figure 3 in Figures 4, 5 and 6. Note that, for clarity in Figures 3 and 4, we have not included the slowest compression speed reported in Figure 2. The packing fraction at the peak is often taken to be equal to the surface fraction  $\phi^{**}$ , introduced above as the boundary between semi-dilute and concentrated regimes.

We observe that the concentration  $\Gamma^{**}$  is insensitive to the speed of compression, as shown in Figure 6. Note however that the slowest compressions are anomalous, and we do not report them on this Figure 6, because the state of the polymer does not appear to be a semi-dilute liquid phase. For the fixed compression rate, it is seen, in Figure 5, that the peak value of the compressibility is also independent of the molecular weight.

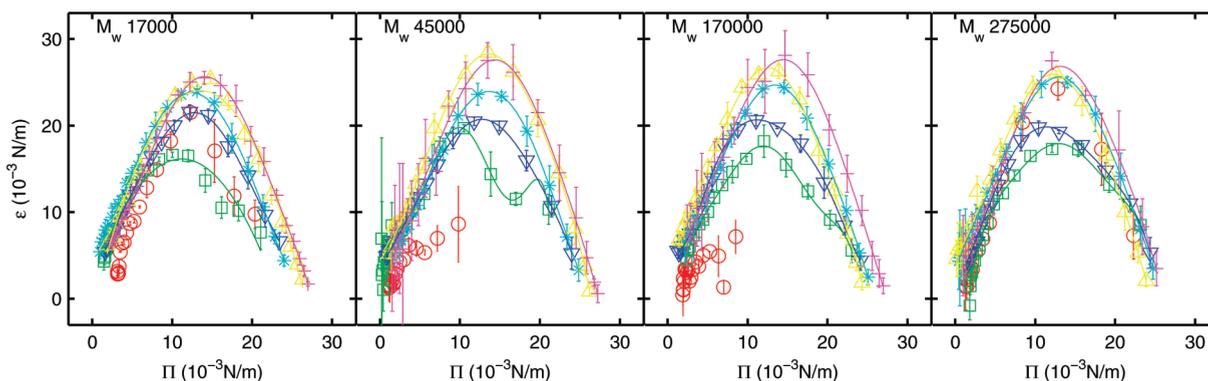
Despite having the same concentration, the layers at  $\phi^{**}$  are actually not all the same to each other, because they differ in compressibility and rheological properties. The peak value of the compression modulus is greatest for the layers being compressed fastest. The strain rate can be obtained by dividing the compression speed by the surface area. In our compressions, the speed is maintained constant, and this results in an isotherm that covers a (small) range of strain rates. At any given point, we can however determine the compression strain rate, and in particular, this is interesting at the peak position of  $\epsilon$ .

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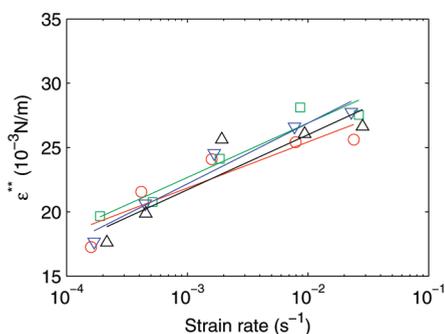
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**Figure 2.**  $\Pi$ – $A$  curves of PVAc monolayer for four different molecular weights and six different compression speeds: (red ●) 1  $\text{cm}^2/\text{min}$ , (green ■) 2  $\text{cm}^2/\text{min}$ , (blue ▼) 5  $\text{cm}^2/\text{min}$ , (cyan \*) 20  $\text{cm}^2/\text{min}$ , (yellow ▲) 100  $\text{cm}^2/\text{min}$ , and (magenta +) 300  $\text{cm}^2/\text{min}$ . The slowest isotherms (red ●, 1  $\text{cm}^2/\text{min}$ ) show a very characteristic shape, distinct from the “classical” semi-dilute regime behavior. We found the  $M_w = 17\,000$  polymer isotherms to be very sensitive on the initial spreading concentration.



**Figure 3.** Compression modulus obtained for different molecular weights as marked and continuous compression at different speeds: (red ○) 1  $\text{cm}^2/\text{min}$ , (green □) 2  $\text{cm}^2/\text{min}$ , (blue ▼) 5  $\text{cm}^2/\text{min}$ , (cyan \*) 20  $\text{cm}^2/\text{min}$ , (yellow Δ) 100  $\text{cm}^2/\text{min}$ , and (magenta +) 300  $\text{cm}^2/\text{min}$ .



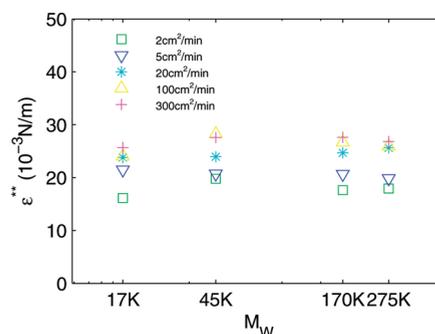
**Figure 4.** Peak value of compression modulus plotted against the strain rate for all of the molecular weights: (red ○) 17 000, (green □) 45 500, (blue ▼) 170 000, and (black Δ) 275 000.

The peak value of the compression modulus,  $\epsilon^{**}$ , is plotted in Figure 4 as a function of the strain rate. As we present it in Figure 4,  $\epsilon^{**}$  appears to have a linear dependence upon the logarithm of the strain rate:

$$\epsilon^{**} \sim c \ln \frac{dA}{dt} \quad (4)$$

with  $c$  being a constant independent of the molecular weight (except for  $M_w = 17\,000$ ). We stress that the weak dependence of  $\epsilon$  upon the strain rate means that we cannot distinguish just on the basis of the data with respect to a power law dependence, such as

$$\epsilon^{**} \sim c \left[ \frac{dA}{dt} \right]^{1/n} \quad (5)$$

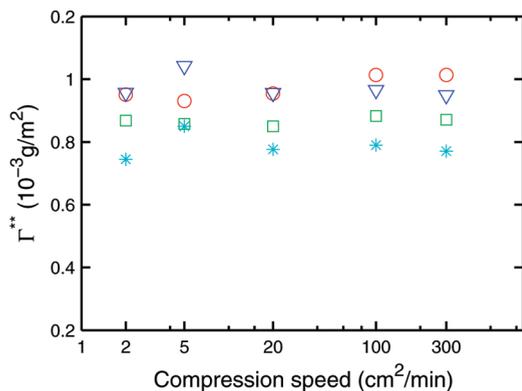


**Figure 5.** Dependence of the maximum compressibility value  $\epsilon^{**}$  upon the molecular weight, as labeled in the figure.

Equation 5 is defined in this form in analogy to the work of Kampf<sup>25</sup> on the collapse of dendritic monolayers. Fitting with eq 5 gives  $n = 11 \pm 1.5$ , which is remarkably similar to the dependence of collapse pressure upon strain rate found in ref 25. However, in the present case, it does not seem appropriate to consider the “event” at the peak in  $\epsilon$  as a failure of the material. In the absence of a convincing model, an exponent value of  $1/n \approx 0.1$  appears very small and hard to justify on scaling grounds.

The phenomenological law of eq 4 seems more appropriate. The error (from fitting and reproducibility) on the data in Figure 4 is of the order of the symbols used in the Figure 4. It can be noted that there is a systematic deviation of the data from

(25) Kampf, J. P.; Frank, C. W.; Malmström, E. E.; Hawker, C. J. *Science* **1999**, *283*, 1730–1733.



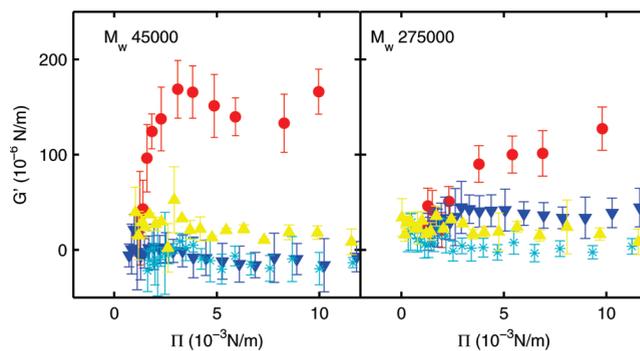
**Figure 6.** Surface concentration  $\Gamma^{**}$  at the maximum compressibility as a function of the compression speed for different molecular weights: (red  $\circ$ ) 17 000, (green  $\square$ ) 45 500, (blue  $\nabla$ ) 170 000, and (cyan  $*$ ) 275 000.

the form of eq 4, with the high strain rate peak values appearing to level off. More fitting parameters would be needed to describe this, and at present, we are not aware of a model that would justify this. We would just remark that the deviation of the high strain rate data to the alternative scaling of eq 5 is more severe.

**Surface Rheological Measurements at Low Density.** Additional information on the  $M_w$  and speed compression dependencies of the layer structure can be obtained from experiments of surface rheology. In these experiments, the  $M_w = 17\,000$  is not shown because of the anomalous behavior observed in the pressure isotherms. Figure 7 shows the surface elastic shear modulus  $G'$  as a function of the surface pressure, for two molecular weights. The elastic component of the shear modulus is almost negligible for the all compression speeds, except the slowest rate, where it is clear that the layer has a finite elasticity (i.e., it is solid-like) starting from very low concentrations and pressures. These are the same conditions where the surface pressure has anomalously low values in the isotherms. This is an indication that the monolayer during very slow compressions is able to restructure into a solid-like structure. This happens only for very slow compression speeds and the shortest chains. When we increase the length of the chains ( $M_w = 275\,000$ ), we find that  $G'$  is zero within our precision and is smaller than  $G''$  for almost all of the compression speeds. Only for the slowest compression,  $G'$  is not zero but still smaller for the  $M_w = 275\,000$  than for the shorter polymers. Clearly, in this solidification process, which occurs for the very slow compression speeds, the chain length plays an important part. It is likely that, if the solid-like phase requires a degree of chain orientation or deviation of conformation from the liquid-like structure, this would be more difficult for the longer chains.

In Figure 8, the surface loss modulus  $G''$  is presented as a function of the surface pressure for each molecular weight and three different speeds of compression. This shows that  $G''$ , which is proportional to the shear viscosity, depends upon the molecular weight and the speed of compression. At slow compression speeds, the dependence upon the molecular weight is much less pronounced.

When the monolayer enters the semi-dilute regime, monomers are forced to be in contact with other monomers belonging to their own and other chains. In this regime, we see  $G''$  deviating from zero. Figure 9a shows a very steep increase as a power of the concentration, up to values around  $100\ \mu\text{N/m}$ . The resolution of the CIR-100 is around  $G'' \sim 10\ \mu\text{N/m}$ ; thus, there is not a wide range of concentrations for which the power law can be measured accurately. A solid line showing  $G'' \sim \Gamma^6$ , the scaling expected for



**Figure 7.** Surface elastic shear modulus  $G'$  as a function of the surface pressure for two molecular weights, as marked, and for (red  $\bullet$ )  $1\ \text{cm}^2/\text{min}$ , (blue  $\blacktriangledown$ )  $5\ \text{cm}^2/\text{min}$ , (cyan  $*$ )  $20\ \text{cm}^2/\text{min}$ , and (yellow  $\blacktriangle$ )  $100\ \text{cm}^2/\text{min}$ .

viscosity in the semi-dilute regime, is shown in Figure 9a, but this is not a fit to the data.

Beyond the semi-dilute regime, crossing the semi-dilute-concentrated transition, the scaling with concentration starts to fail. Here, the values of  $G''$  are large; therefore, it is clear that there is no scaling. To begin to justify the form of the viscosity at high concentration, we recall the very basic classical model of Eyring<sup>26</sup>

$$\eta = \phi e^{\epsilon/k_B T} \quad (6)$$

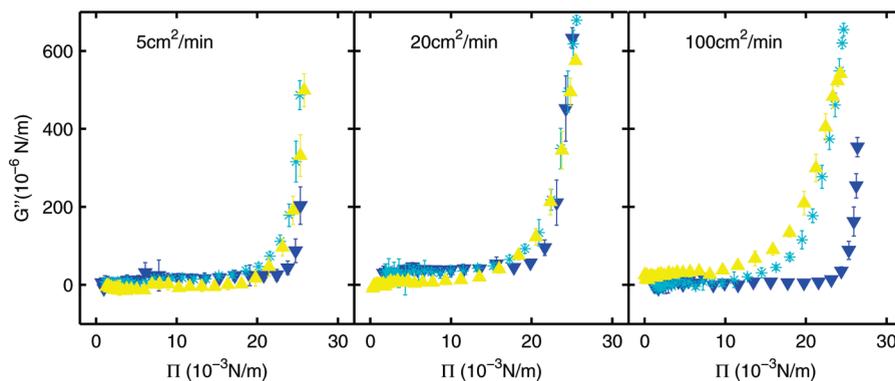
which is modified, to account for an externally applied pressure, to the form

$$\eta = \phi e^{(\epsilon + PV)/k_B T} = \eta_0 e^{PV/k_B T} \quad (7)$$

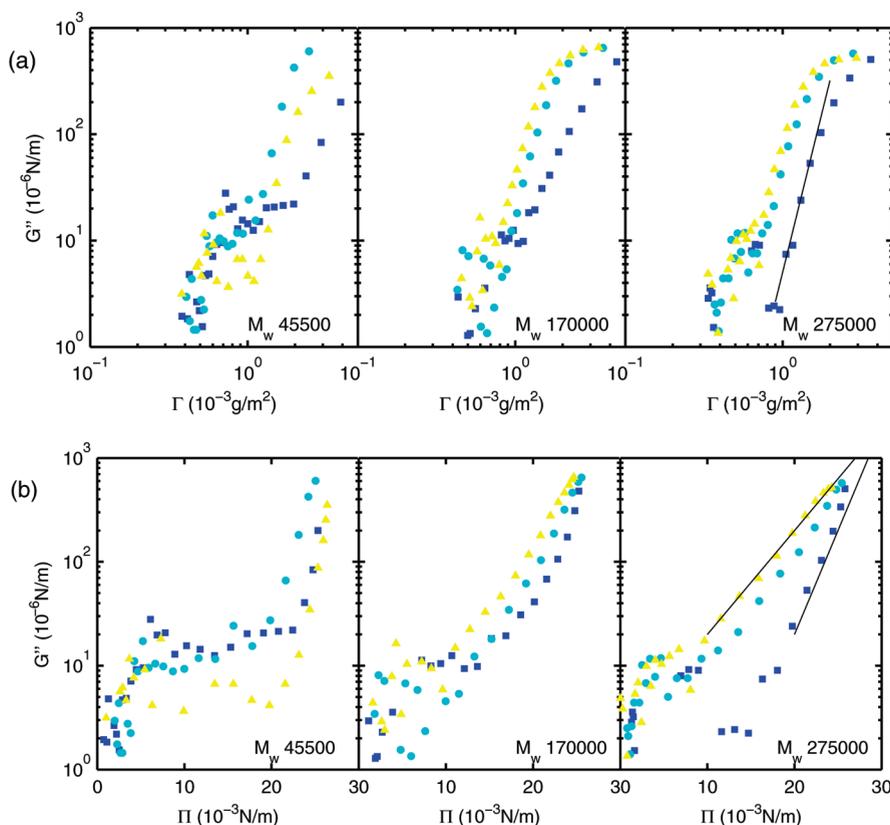
where  $\epsilon$  is the height of an energy barrier that molecules need to overcome to flow past each other,  $P$  is the pressure, and  $V$  is the molecular volume. In the case of 2D layers,  $\Pi$  and  $A_m$  (a molecular area) would replace  $P$  and  $V$  in eq 7. We plot in Figure 9b the logarithm of  $G''$  as a function of  $\Pi$ . This seems to support the form of Eyring's equation quite well at high pressures. The solid lines drawn on the  $M_w = 275\,500$  data correspond to  $A_m = 40$  and  $80A^2$ . The square root of these values (i.e.,  $\sim 6$  and  $9A$ ) can be compared to the molecular bond length between PVAc monomers, which is  $2.3A$ . The fact that the length obtained from Eyring's equation is at the monomer rather than the polymer scale (keeping in mind that the  $M_w = 275\,500$  has around 3000 monomers in the chain, which is a clear distinction) indicates that the result of deformation under shear is a mechanism of monomers hopping rather than the polymer moving as a whole. This is a clear result that can be understood in the conditions of this experiment, in which the strain amplitude is very small ( $< 10^{-3}\%$ ). For larger strain amplitudes, we would expect the polymer "disk" diameter to be a relevant length scale.

Within the picture supported by our data, we are suggesting that, in the semi-dilute regime, there is a completely negligible barrier and a scaling of viscosity with concentration, possibly  $\eta \sim \phi^6$ , as seen in compressional experiments.<sup>11</sup> Into the concentrated regime, the motion becomes limited by a barrier hopping mechanism, with the surface pressure acting to make hopping more difficult. We would hope that a simple hypothesis, such as this, could be tested in the future by computer simulation. We have not explained the effect of the compression rate on the measured viscosity. A higher compression speed leads to a monolayer with a higher value of viscosity and a weaker

(26) Tabor, D. *Gases, Liquids and Solids and Other States of Matter*; Cambridge University Press: Cambridge, U.K., 1990.



**Figure 8.** Surface loss modulus  $G''$  as a function of the surface pressure for three different compression speeds, as marked in each panel, and for molecular weights: (blue  $\nabla$ ) 45 000, (cyan  $*$ ) 170 000, and (yellow  $\Delta$ ) 275 000.



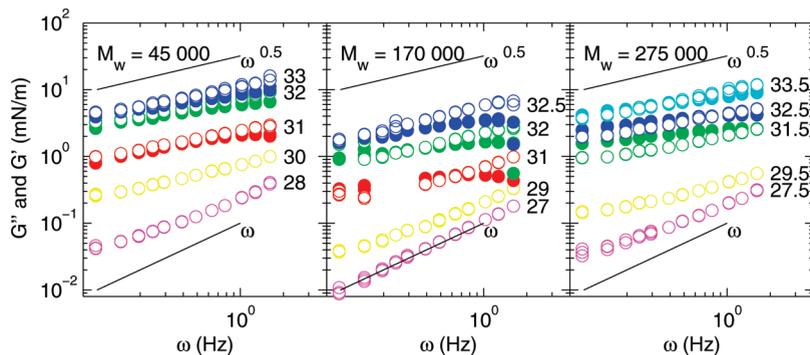
**Figure 9.** Values of  $G''$  as a function of (a) concentration and (b) surface pressure for molecular weights, as marked on the panels. Compression speeds are (blue  $\blacksquare$ )  $5 \text{ cm}^2/\text{min}$ , (cyan  $\bullet$ )  $20 \text{ cm}^2/\text{min}$ , and (yellow  $\blacktriangle$ )  $100 \text{ cm}^2/\text{min}$ . Solid lines are (a) theoretical predictions from scaling arguments and (b) from Eyring's theory of viscosity.

dependence upon  $\Pi$ , which results in a smaller molecular area in Eyring's theory. A detailed investigation of the crossover point between scaling and Eyring's liquid theory is beyond the scope of this paper, but the data show that the polymer molecular weight and compression strain rate are both important parameters.

An increase of the viscous dissipation in a polymer network could have been expected when the length of the chain increases, but the compression rate result is unexpected. Because little is known of the chain conformation at or around  $\Gamma^{**}$ , it is difficult to present a definitive view. We suggest that the compression strain rate could influence the rheological behavior of the monolayer by forcing the average chain conformation into different structures. For example, compression in the trough (which is a uniaxial compression) could lead to chain anisotropy and alignment. However, it should also be considered that the same compression process, happening over a very large range of strain,

is also forcing the polymers to rearrange both intra- and inter-molecularly. Therefore, the external compression can also be seen as a process that provides a dense monolayer with the energy to randomize its configurations, thereby maintaining a system in equilibrium in a condition where it would otherwise jam or crystallize. To try and distinguish between these general ideas, a control experiment was carried out where shear was first measured during fast compression. Then, compression was halted, and shear viscosity was monitored as a function of time. There was no drop in the shear viscosity, which implies that the high shear dissipation is a property of the structure of the monolayer (acquired at high compression speed) but not the fact that the monolayer is being compressed quickly.

**Surface Rheological Measurements at High Density.** All of the data presented above are obtained with the CIR-100 instrument showing  $G'' > G'$ . From previous work, we know



**Figure 10.** (●)  $G'$  and (○)  $G''$  measured as a function of the frequency with the ISR, for different molecular weights. These measurements are at very high packing, performed at constant pressure (as marked in the figure), and show a transition from Newtonian fluid to soft solid behavior.

that increasing the concentration even further should lead to an increase of  $G'$ , which we had explained as the complete close packing of monomers on the surface.<sup>18</sup> Figure 10 shows the frequency dependence of  $G'$  and  $G''$  obtained with the ISR. Because, in a frequency sweep, the monolayer needs to be held at constant pressure for a long time (tens of minutes for each of the low-frequency points), it was not feasible to acquire this data during a single continuous compression. The Langmuir trough was therefore operated in feedback mode to maintain fixed pressure. It was also not possible to attain the very high concentration starting from dilute conditions and during a single compression. Therefore, these data correspond to layers that have been compressed by the addition of further polymer in nondilute conditions. Despite these differences [which may make a direct quantitative comparison to the cylindrical internal reflection (CIR) data on first and continuous compressions inappropriate], we believe that the results shed light on the process of polymer close packing.

The ISR data confirms that, below  $\Pi \approx 29 \times 10^{-3}$  N/m, the shear response is dominated by  $G''$  and  $G'' \sim \omega$ , as expected for a Newtonian fluid. This is in agreement with the CIR-100 measurements above, which showed  $G'' \gg G'$ . An interesting transition happens at around  $\Pi \approx 31 \times 10^{-3}$  N/m, with  $G''$  exhibiting a weaker dependence upon the frequency  $G'' \sim \omega^{0.5}$  and the elastic modulus having a similar magnitude to the viscous modulus. These factors combined indicate that the layer at this stage is in a soft solid state, possibly a two-dimensional analogue of a paste. Remarkably, the behavior at very high packing is almost independent of the molecular weight, something that is in contrast to bulk polymer melts, where the molecular weight plays a major role  $\eta_{3d} \sim M_w^{3.4}$ . This is an indication that reptation-like mechanisms are not responsible for the shear response observed here.

### Conclusions

We have found that the mechanical and rheological properties of PVAc monolayers depend upon not only the polymer chain

length but also how the layer is created and compressed; in particular, the shear response depends upon the compression rate.

Very slow compressions also gave rise to unexpected and novel behavior, leading to a solid-like monolayer at low densities, which is most evident for the shorter chains. We described this as a process of polymer chain rearrangement into a solid state, which has time to develop during slow compressions and for moderate length polymers. For the highest polymer weight, the osmotic pressure in the semi-dilute regime is almost independent of compression speed and even the slowest compression does not lead to a solid phase. It would be interesting to explore further the structural properties of the solid phase and, in particular, the morphology at the molecular scale.

As expected, the transition from a semi-dilute to concentrated regime observed in the isotherms is not affected by the polymer chain length; physically, this transition concentration should only depend upon the number of monomers on the surface. The speed of compression is found to affect the magnitude of the elasticity  $\epsilon^{**}$ , a result which is not described by the equilibrium scaling theory.

The rheological measurements have provided further evidence that the structure of these monolayers depends upon the pathway of formation. The surface pressure and the concentration at which  $G''$  starts to increase quickly are related to the molecular weight and the compression speed.

Isotherms of compression and surface rheology of PVAc monolayers have revealed that the rheological properties of a simple two-dimensional polymer system depend upon the molecular weight and the compression speed. Vice versa, the changes in elastic modulus and surface loss shear modulus under different compression regimes indicate that the underlying structure of the monolayer is affected by the compression, and it is likely that the polymer chains are being forced to change their average equilibrium configurations under compression.

**Acknowledgment.** We thank Kevin Peters for help with CIR measurements.