Observation of Gelation Process in Two Dimensions

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The gelation process in a monolayer adsorbed at the oil/water interface has been monitored by measurement of the shear mechanical properties. A clear sol-gel transition has been observed for the first time in a two-dimensional system.

The sol-gel transition is of current interest because it can be seen as an experimentally realizable model of percolation theory[1] and also because it may show a fractal character.[2] We would like to report, in this Letter, the first observation of a sol to gel transition in a two-dimensional (2D) system. Experiments done in samples other than three-dimensional ones are of particular interest because the dimensionality is one of the most important parameters.

The experimental setup is schematically shown in Fig. 1. A diacrylic ester, whose molecular formula is shown in the inset of Fig. 2, was dissolved in hexadecane. The solution was then carefully poured over triple-distilled water held in a glass container with a flat quartz bottom. The solute molecules were subsequently adsorbed at the hexadecane-water interface because of their amphipathic nature and formed a monolayer.[3] The double bond, $CH_2 = CH-$, at the end of the molecule is unstable against the formation of single bonds with other molecules, $-(CH_2-CH)-$, and hence these molecules can form polymers, although an energy barrier has to be overcome for this process to occur. Note that each double bond can be connected to two neighbors. Therefore, each molecule can be connected to four molecules, i.e., four bonds per site in the bond percolation model. At a high density, the polymerization can proceed slowly by thermal activation, but the process is accelerated greatly by uv irradiation. The preparation of the monomer, the conditions for the uv irradiation, and the identification of the final product have been reported elsewhere.[4]

In order to study the polymerization process, the in-plane shear mechanical properties were monitored. The technique was essentially the same as that previously employed for the monolayer study at the air/water interface.[5] Before the solution was poured in, a Teflon disk was placed on the water. The perimeter of the disk was shaped into a knife edge. The sharp edge provided a line of singularity for the oil-water-Teflon intersection. Therefore, the meniscus was locked at the edge and a slight mismatch of the relative height of the water surface and the disk perimeter did not cause any serious trouble. A step-function torque was applied to the film by passing a current through a galvanometer coil attached to the disk. The deflection of the disk was then monitored and analyzed with a standard calculation.[6]

In a typical experiment, the monomer concentration was $c = 0.19$ mol/L. After the solution was poured in (at time τ_0), the monolayer formation did not occur instantaneously because some molecules had to diffuse through the solvent to reach the interface. Thus, a period of time had to elapse before the uv irradiation could commence. However, the process during this initial period was
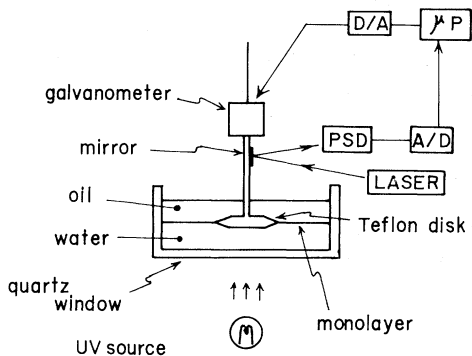

FIG. 1. Experimental setup for the measurement of shear mechanical properties of adsorbed monolayers at the oil/water interface.

complicated by the spontaneous polymerization. Because the density of monomer at the interface was extremely high, thermally activated polymerization could occur at a nonnegligible rate. It was observed that, within a relatively short time (~ 10 min) after τ_0, a finite shear modulus both at the resonant frequency (μ_ω, $\omega/2\pi \sim 0.5$ Hz) and at zero frequency (μ_0) started appearing. The shear modulus increased very slowly and reached a constant value of about 0.2 dyn/cm 70 min after τ_0. The saturation may be due to a competing slow degradation (breakup of the bonds) or the depletion of active centers (impurities) where the spontaneous polymerization can occur easily. The film was subsequently irradiated with uv for a period of time and measurements were made after each irradiation. The irradiation-measurement cycle was repeated to study the cumulative effect. The calculated shear modulus (μ) is shown in Fig. 2. The rate of increase of μ with the uv irradiation time was orders of magnitude faster than that of the initial period. Moreover, once the irradiation was stopped, no further change of μ was observed in 1 h. From this and the previous observations,[4] it is reasonable to assume that the degree of polymerization depends only on the cumulative uv irradiation time, the abscissa in Fig. 2.
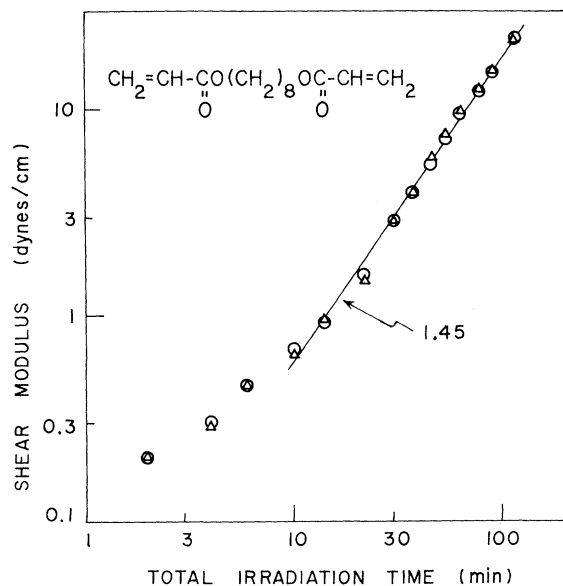
In order to show that the shear modulus measured was not due to the bulk polymerization effect, the upper phase (hexadecane solution) was carefully removed at the end of the experiment and was replaced with an aliquot of pure hexadecane. This procedure was repeated four times, but no change of μ was seen. Then the temperature was varied from 28 to 18 °C (the freezing point of hexadecane). As the temperature was lowered, the shear modulus *decreased* from $\mu_\omega = 22.0$ dyn/cm and $\mu_0 = 22.6$ dyn/cm at 28 °C to $\mu_\omega = 19.9$ dyn/cm and $\mu_0 = 19.5$ dyn/cm just above 18 °C. This suggests that the elasticity observed is indeed due to the gel formation rather than due to crystallization or a glass transition.

If we assume that, close to the sol-gel transition, the number of connected bonds is proportional to the total irradiation time τ, then, from the scaling argument of percolation theory,[7] we would expect

$$\mu \sim (\tau - \tau_c)^{t'}, \tag{1}$$

where τ_c is the transition time. However, as we have mentioned earlier, the gelation has already started before the initiation of the irradiation. Therefore, τ_c must be negative in our time scale. Because an accurate estimation of τ_c is not possible, we plot, in Fig. 2, μ vs τ and draw a line through the points for $\tau \geq 10$ min. The slope is about 1.45. Using an argument similar to the one given by de Gennes,[1,8] one may say that t' is equal to the conductivity exponent, t; in 2D, $t = \sim 1.2$–1.3.[9] The discrepancy, however, should not be taken too seriously because of the uncertainty in τ_c.
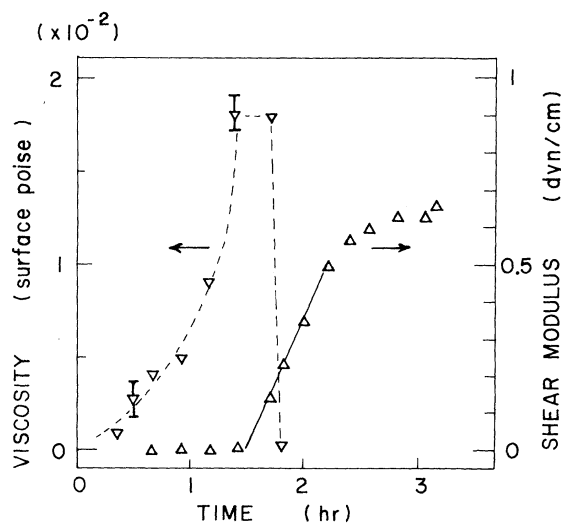
FIG. 2. Shear modulus of a diacrylic ester polymerized at the hexadecane-water interface vs the total uv irradiation time. Triangles represent μ_ω and circles μ_0. Dispersion is negligible and the viscosity (η_ω) is zero within the uncertainty of the measurement.

FIG. 3. Shear modulus (μ_ω) and viscosity (η_ω) of a diacrylic ester vs total elapsed time without uv irradiation. Lines are only a guide for the eye.

It is then interesting to see if there is indeed a clear sol-gel transition in these monolayers. Since one measurement took a relatively long time ($\sim$ 3–5 min), the spontaneous polymerization rate and hence the density of monolayer should be low enough to allow such measurement. This could be achieved by lowering the concentration (slower adsorption). In Fig. 3 are shown the shear viscosity (η_ω) and μ_ω measured as a function of time: There was no uv irradiation and hence the polymerization was spontaneous. The concentration was $c = 3.2 \times 10^{-2}$ mol/L. As one would expect, the viscosity increased initially as the polymer size grew. However, after 1.5 h, a nonzero modulus started appearing, indicating the formation of an infinite size cluster, and from this point on $\eta_\omega \sim 0$. This implies that the polymer clusters that contribute to η_ω are the largest ones which later become part of the infinite cluster, and the contribution of smaller clusters to the mechanical properties is negligible. Although the data thus seem to be quite reasonable from the point of view of the percolation theory, unfortunately they are not very useful in determining the exponent, t', because of the saturation discussed earlier. Nonetheless, the initial growth of μ appears to be nearly linear, i.e., $t' \sim 1$.

As a counterexample of a monolayer polymer which should not have a sol-gel transition, a monolayer of a monomer which has only one double bond (monoacrylic ester, $C_{18}H_{37}-OCO-CH=CH_2$) was polymerized. Because each molecule can be connected to only two others, they form linear chains. The viscosity steadily increased as a function of irradiation time and the film became extremely viscoelastic while μ_0 remained zero. The behavior was reminiscent of the glass transition, but no sol-gel transition was seen as expected.[10]

In summary, we have shown that it is feasible to observe a sol-gel transition in monolayer polymers. Further improvements of the experiment are clearly needed to allow quantitative studies. Our future research includes the determination of the exponent, the frequency dependence, and the critical bond number (the average completed bond number per site at the threshold).

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[10]The analysis of these data will be published elsewhere.