Gelation of polymers adsorbed at a water-air interface

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GELATION OF POLYMERS ADSORBED AT A WATER–AIR INTERFACE

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ABSTRACT

Rheological data on air–water interfaces with adsorbed water-soluble polymer layers are presented which prove the existence of a surface gel. The gel is found to behave thixotropically and its yield stress is determined under various conditions. The gelation seems to be related to the lack of relaxation of the surface upon compression on a Langmuir trough. A tentative gelation mechanism is proposed and the gelation phase diagram is discussed qualitatively.

INTRODUCTION

Polymers are often surface active, and their behaviour at water–air interfaces (mainly as spread monolayers) has already been studied a few decades ago [1]. Most of these early studies were entirely concerned with static properties, i.e. surface tension. Dynamic aspects (e.g., surface rheology) require more subtle experimental techniques which were, along with some theory, developed in the sixties and seventies [2]. Experimental data, however, on the dynamic state of adsorbed polymers are still quite scarce. In contrast, there is a vast literature on experimental results for polymer layers under static conditions [3], and some elegant theories have been developed to describe the adsorption equilibrium of flexible chain molecules [4–6].

Again and again, however, the question arises whether the static properties represent a true equilibrium or a frozen non-equilibrium state. Several observations, such as hysteresis effects in isotherms and the failure of the simple Gibbs' law for the surface tension of polymer solutions, were taken as evidence that the adsorption of polymers is irreversible. Some years ago, however, it was shown [7] that polydispersity in the polymer sample could also account for such observations, while maintaining the equilibrium idea. This strengthened the belief in reversible adsorption. More recent measurements by Furusawa and Yamamoto [8] on the exchange between bulk and adsorbed polymers provided evidence of true irreversibility.

In this paper we consider the dynamic state of adsorbed oligomers and

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polymers at a water—air interface, in order to decide whether long-living non-equilibrium states do or do not occur. In some of the early studies the suggestion was made that a polymer on a liquid surface may form a two-dimensional gel if sufficiently concentrated [9]. Recently, the idea of surface gelation reappeared in a paper by Kim et al. [10] and some, though rather indirect, evidence was presented. We will report rheological results at sufficiently low shear which definitely show that various polymers do form a surface gel. Moreover, this surface gel behaves thixotropically. In connection with this result we will discuss the time dependence of the surface tension, i.e. relaxation effects.

EXPERIMENTAL

Surface rheological measurements under constant shear stress were carried out in a low-shear plate viscometer designed by Van Vliet et al. [11]. The apparatus consists of a circular, double-walled and thermostated vessel (inner diameter 14.3 cm) containing the solution, with a shallow dish, usually a plastic Petri dish (diameter 2.85 cm), containing a circular iron plate floating in the middle of the vessel. A rapidly rotating bar magnet, positioned under the vessel, exerts a weak torque on the iron plate and, hence, on the dish so that a shear stress builds up, both on the bulk fluid under the dish and on the surface surrounding the rim of the dish. By varying the distance between the rotating magnet and the iron disc the torque can easily be varied over four orders of magnitude. Surface shear stresses in the range $5 \cdot 10^{-8}$ – 10^{-3} N m⁻¹ can thus be exerted on the surface.

Surface tensions were measured on an automated Langmuir trough. The trough itself is made of Teflon and has a Teflon barrier with which one can carry out compressions and decompressions with a wide range of speeds. A sensitive Cahn-Ventron compensating balance was used to measure the force on a platinum Wilhelmy plate suspended in the surface. The solution level in the trough was carefully controlled by means of an optical device, in order to measure surface tensions reproducible to within $2 \cdot 10^{-2}$ mN m⁻¹ over long time periods. The apparatus was enclosed in a box to minimize the effects of surface contamination, evaporation and mechanical disturbance. Experiments were usually carried out as follows. A polymer solution was poured into the trough and allowed to equilibrate until the surface balance recorded a constant value within the accuracy limits of the experiment. Subsequently, a compression was carried out and the surface pressure was recorded during and after the compression. Various rates of compression were used ranging between 5 and 10^2 mm² s⁻¹.

A few experiments were performed in a different trough with a barrier capable of carrying out sinusoidal displacements. By recording both the phase and the amplitude of the sinusoidal variations in the force on the Wilhelmy plate one can obtain both viscous and elastic components of the surface response to deformation [12].

All experiments were carried out at $\sim 20^\circ\text{C}$.

MATERIALS

Carefully deionized and ultrafiltrated water was used throughout. Polymers were used as provided by the manufacturer (see Table 1). Other chemicals were of analytical grade. A few experiments were carried out with deaggregated, defatted and globuline-free bovine serum albumine (BSA). An extensive investigation of surface properties of BSA solution will appear soon [13].

TABLE 1

Molecular weight and origin of polymers used in this study

Name	Code	M.W.	Manufacturer
Poly(vinyl pyrrolidone)	PVP K12	3,200	BASF
	PVP K90	930,000	BASF
Poly(vinyl alcohol)(12% acetate)	PVA 217 EE	143,000	Kurashiki
Polyacrylamide	PAAm	75,000	Cyanamid
Polystyrenesulphonate	PSS	354,000	Pressure Chem. Corp.
Polyethylene oxide	PEO-100,000	100,000	Aldrich
	PEO-1500	1,500	Baker
	PEO-600	600	Baker

RESULTS AND DISCUSSION

Figure 1 shows examples of a rheological experiment for two PVP samples of different molecular mass (PVP K12 and PVP K90, respectively). Similar results were obtained with the PVA, PSS, PAAm and PEO-100,000 samples. The plots give the rate of deformation as a function of shear stress. In contrast to the conclusions of Vocel and Ryan [14], these results definitely show a yield value. Since, for all the samples, the bulk solutions were far too dilute (~ 1 ppm) to have gel-like properties, it must be the surface layer which behaves as a gel. Consequently, the shear stress is given as a surface shear stress (N m^{-1}). All yield values at concentrations of ~ 1 ppm were of the order of $5 \cdot 10^{-7} \text{ N m}^{-1}$. Given the geometry of the viscometer, this corresponds to an absolute force of the order of 10^{-7} N , which is indeed so low that it may have escaped detection in earlier experiments. A much stronger gel is formed by BSA. A 100 ppm solution of this globular protein was found to have a surface yield value of $5 \cdot 10^{-4} \text{ N m}^{-1}$, which is close to the detection limit of earlier studies. For example, Graham [15] reports no yield values for the surface of a BSA solution, and Vocel and Ryan [14] concluded that there was no yield value for various flexible polymers. In both studies, the minimum shear stress was probably between 10^{-4} and $5 \cdot 10^{-4} \text{ N m}^{-1}$.

The surface gel built up from flexible polymers thus appears extremely

Fig. 1. Rate of deformation $\dot{\gamma}$ of two PVP samples (K12 and K90) in 1 ppm solution as a function of surface shear stress σ . ($\circ$), PVP K90; ($\square$), PVP K12.

fragile. However, if we take into account that the surface layer is, typically, 1 nm thick, it is by no means weak. If we consider a slice, 1 nm thick, of a bulk gel with a bulk yield stress of 10^3 Pa, we arrive at a surface yield stress of 10^{-6} N m $^{-1}$, which is close to our result.

Below the yield value, we observe purely elastic deformation. Above the yield value, the rate of deformation increases roughly linearly with the applied stress. Under conditions of flow, one may expect that the gel is fragmented into small clusters by breakage of the weakest bonds. If, then, the shear stress is removed or sufficiently reduced the gel gradually reforms and in time a yield stress builds up again. This is the typical behaviour of a thixotropic system, and means that the bonds in the gel are reversible. An example is given in Fig. 2, where the rate of deformation is plotted against the applied stress for increasing and decreasing stress, as indicated by the arrows. The two branches of the curve do not coincide, because the gel needs time and quiescent conditions to form.

One may wonder what the nature of the intermolecular bonds is. In an early paper by Hotta [16] it is suggested that molecules at a water–air interface experience rather strong, unscreened Van der Waals forces between parts projecting from the water. This would suggest that gelation cannot occur at water–oil interfaces. We checked this conjecture by measuring the shear rate–shear stress curve for PVP at a water–n-octane interface. This was carried out as follows. A layer of n-octane, 1 mm thick, was formed by

pouring the *n*-octane over a PVP solution. As PVP is insoluble in *n*-octane, no polymer can reach the *n*-octane–air interface. We found that *n*-octane has no effect at all: a gel is still formed (Fig. 3). Hence, more specific forces seem to be needed for gelation. We suggest that water molecules tend to form bridges between proton-accepting moieties of the polymer. Such a mechanism has already been invoked for association phenomena in solutions of water-soluble polymers [17] and is likely to be important in the phase boundary where the local monomer concentration is high, so that there are many possibilities for the formation of water-controlled intermolecular bonds. Our suggestion would imply that surface gels always form when polymers with proton-accepting groups are at a water surface.

The formation of a gel-like structure with the ability to withstand a shear has important consequences for the behaviour of the adsorbed film under compression. Upon displacement of the barrier, shear stresses build up in the surface and the surface tension becomes inhomogeneous. This is convincingly illustrated in Fig. 4, where a series of photographs shows the displacement of small pieces of paper (black dots) placed on the surface. Initially, the pieces lie in a straight line parallel to the barrier. As the barrier moves and stresses build up, the dots in the middle move away from the barrier, while the dots on the side move only slightly; a parabola appears. Apparently, the gel sticks to the wall of the trough and, under the stresses, part of the polymer accumulates in the centre of the surface. Very similar results were recently reported by Malcolm [18] for (spread) polypeptides at the air–water interface. That the surface tension becomes inhomogeneous under these conditions was also verified by means of the Wilhelmy plate.

Given the gel-like nature of the surface layer one might conclude that adsorbed chain molecules never occur as kinetically free entities. They are not only strongly entangled (especially at high molecular weight), but also tied to other molecules by physical bonds. It follows that the molecules are separated from the bulk phase by a huge kinetic barrier. If this is indeed the case then it should be expected that an adsorbed polymer layer cannot, after compression, relax to its equilibrium surface pressure, since this would involve detachment of chains from the network. Low-molecular-weight surfactants such as CTAB do desorb rapidly, and oligomers of ethylene oxide (PEO-1500 and PEO-600, respectively) relax on a timescale of hours (Fig. 5). Also, the yield value of the PEO-1500 solution is about half the value of the PEO-100,000 solution, whereas PEO-600 has no detectable yield value. All the high-molecular-weight polymers ($M.W. > 3000$) show very little relaxation. An illustrative example is given in Fig. 6, where $\Delta\pi/\Delta\pi_0$ for PVP K90 is plotted versus time. It is seen that the surface pressure may drop initially 10–20%, and no further decrease is observed even after several days. Even the polyelectrolyte PSS showed this pattern, and for this polymer the addition of salt did not detectably change this behaviour. It seems that the tendency to form surface gels is a rather general one, at least for aqueous systems.

Fig. 4.

Fig. 5. Relaxation of the surface pressure. Surface pressure increment ($\Delta\pi$) relative to the surface pressure increment immediately after compression ($\Delta\pi_0$) as a function of time for 1 ppm solution of a polymer (PEO-100,000) and two oligomers (PEO-1500 and PEO-600, respectively) and for a $5 \cdot 10^{-3}$ M solution of a cationic surfactant (CTAB).

Figure 7 gives the results for the yield stress as a function of the polymer concentration in the bulk solution, for PVP K12 and PVP K90. The remarkable fact is that, contrary to expectation, the yield value decreases with increasing concentration. Since bulk gels always become stronger on increasing the density, this result is further proof of a true surface effect. We can envisage the following explanation.

From theoretical work [6] it is known that, at low concentration, molecules arriving at the surface unfold completely to a largely two-dimensional structure, whereas at higher concentrations loops and tails occur. As the formation of bonds presumably only occurs at the very surface, the number of effective bonds per molecule, and hence the gel strength, is higher for the unfolded structures. That flat structures occur as a result of adsorption from a dilute solution was also concluded in Ref. [8].

For the theoretical study of gels, percolation models have proven to be suitable [19,20]. Gels consisting of chains with reversible interchain bonds

Fig. 4. Photographs showing the position of surface markers (black dots) at various positions of the barrier during a full compression-decompression cycle; a, b, c, d: compression; e, f, g, h: decompression.

Fig. 6. Relaxation of the surface pressure, plotted as $\Delta\pi/\Delta\pi_0$ versus time, for a 1 ppm PVP K90 solution.

Fig. 7. Yield stress σ_y of the surface gel as a function of polymer concentration in the bulk solution. ($\circ$), PVP K12; ($\square$), PVP K90.

have been considered by Coniglio et al. [21]. For our rheological data we need to consider such a gel under mechanical stress. Clearly, the yield point corresponds to the loss of connectivity, i.e. to the percolation threshold P_c of a gel under a stress. If the process of bond formation is indeed reversible, the effect of external stress is to shift the association/dissociation equilibrium of the bonds towards a reduced number of bonds. In order to calculate this effect, one needs the number of bonds over which the stress effectively distributes, i.e. the number of independent connective paths through the gel from one side to the other. The analogous property in percolation models is the conductivity. Hence, by combining two-dimensional chain percolation with a simple bond formation equilibrium it should be possible to predict yield stresses for the kind of surface gels studied here. In Fig. 8 we reproduce the phase diagram proposed by Coniglio et al. [21] and we include gelation curves for gels under stress. With increasing stress the gelation curve moves downwards, so that the gel will fall apart at a lower temperature than the gel which experiences no external forces.

Finally, we want to note that there is as yet no reason to assume that the occurrence of surface gelation is restricted to fluid interfaces. The idea of surface gelation may also help to understand the dynamic state of adsorbed polymers at solid-liquid interfaces, and provide an explanation for some of the more troublesome experimental data.

Fig. 8. Phase diagram of a polymer gel under mechanical stress (schematic).

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REFERENCES

- 1 G.L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces*, Wiley, New York, NY, 1966.
- 2 M. Joly, *Rheological Properties of Monomolecular Films*, Part I and II, in E. Matijević (Ed.), *Surface and Colloid Science*, Vol 5, Wiley-Interscience, New York, NY, 1972, pp. 1-193.
- 3 M.A. Cohen Stuart, T. Cosgrove and B. Vincent, *Adv. Colloid Interface Sci.*, in press.
- 4 A. Silberberg, *J. Chem. Phys.*, 48 (1968) 2835.
- 5 P.G. De Gennes, *Macromolecules*, 15 (1982) 492.
- 6 J.M.H.M. Scheutjens and G.J. Fleer, *J. Chem. Phys.*, 83 (1979) 1619.
- 7 M.A. Cohen Stuart, J.M.H.M. Scheutjens and G.J. Fleer, *J. Polym. Sci., Polym. Phys. Ed.*, 18 (1980) 559.
- 8 K. Furusawa and K. Yamamoto, *J. Colloid Interface Sci.*, 96 (1983) 268.
- 9 D.J. Crisp, in J.F. Danielli, K.G.A. Pankhurst and A.C. Riddiford (Eds), *Surface Phenomena in Chemistry and Biology*, Pergamon, New York, NY, 1958, p. 23.
- 10 M.W. Kim, P.G. Peiffer and P. Pincus, *J. Phys. Paris Lett.*, 45 (1984) 953.
- 11 T. van Vliet, A.E.A. de Groot-Mostert and A. Prins, *J. Phys. E*, 14 (1981) 745.
- 12 J. Lucassen and M. van den Tempel, *Chem. Eng. Sci.*, 27 (1972) 1283-1291.
- 13 J.G.E.M. Fraaye, in preparation.
- 14 J. Vocel and J.T. Ryan, *Can. J. Chem. Eng.*, 49 (1971) 425.
- 15 D.E. Graham, *Structure of Adsorbed Protein Films and Stability of Foams and Emulsions*. Thesis, Unilever Res. Lab., Colworth, U.K., 1976.
- 16 H. Hotta, *J. Colloid Sci.*, 9 (1954) 504.
- 17 W. Burchard, *Habilitationsschrift*, Freiburg, 1966.
- 18 B.R. Malcolm, *J. Colloid Interface Sci.*, 104 (1984) 520.
- 19 P.G. De Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca, NY, 1979, Ch. V.
- 20 D. Stauffer, *Scaling Theory of Percolation Clusters*, *Phys. Rep.*, 54 (1979) 1-74.
- 21 A. Coniglio, H.E. Stanley and W. Klein, *Phys. Rev. B*, 25 (1982) 6805.