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Surface gelation

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Résumé. — Les conditions de formation d'un gel polymérique superficiel sont discutées et comparées à des mesures préliminaires de tension interfaciale obtenues avec des ionomères. On montre en particulier qu'une solution semi-diluée de polymères *associés* adsorbés sur une interface peut avoir un profil de concentration qui satisfasse les conditions de gélification. Les propriétés élastiques peuvent être estimées pour un bon solvant et aussi dans la région de pré-mouillage. On montre enfin que des solutions de polystyrène (légèrement) sulfoné dans le sulfure de di-méthyle présentent un comportement de gel superficiel au-delà d'un certain niveau de substitution.

Abstract. — We discuss the conditions required for surface polymer gelation and present some preliminary experimental evidence from surface tension studies on an ionomer system. In particular, a semi-dilute solution of *associating* polymers which adsorb onto an interface may have a profile that exceeds the gelation threshold sufficiently near the surface. We estimate the gel film elastic properties in both good solvents and the prewetting region. Lightly sulfonated polystyrene ionomers are shown to exhibit gel-like surface rheology in dimethylsulfoxide (DMSO) for sufficient levels of substitution.

1. Introduction.

Polymer gels which have the property of supporting weak shears (with a concentration dependent shear modulus) have many industrial applications, e.g. adhesives, rubbers, etc. Microphase separation [1], or syneresis, and spinodal decomposition [2] of binary mixtures supported in a gel are currently investigated phase transitions in preformed networks. Polymer gelation itself, i.e. the transition from a semi-dilute polymer solution to a macroscopically connected network which was originally modelled by Flory [3] and Stockmayer [4] as a percolation process, has received considerable elaboration in terms of scaling corrections to mean field exponents [5] and the inclusion of both solvent effects [6] and enthalpic association [7, 8] contributions to crosslinking. The purpose of this study is to suggest that polymer solutions in contact with an adsorbing interface (solid or fluid) may experience a surface gelation, i.e. the adsorbed layer may be crosslinked while the bulk solution maintains a vanishing shear modulus. We predict the conditions required for this phenomenon, estimate the thickness of the gel film for both good and poor solvents, present some surface tension evidence with associating polymer solutions, and suggest further experimental methods of observation. There is a certain similarity between the theoretical aspects of this investigation and the demonstration [9, 10] that, in a half-space, surface bond percolation may be enhanced if the surface concentration of active sites exceeds the bulk percolation threshold.

Reversible physical gels are often constructed from polymers which are chemically partially substituted with associating groups. Examples of such systems are provided by the sulfonated ethylene-propylene diene monomer terpolymers [11] (elastomeric ionomers) and polystyrene based thermoplastic ionomers [11] where in both polymeric materials a fraction of the monomer units are modified by metal-sulfonate groups. Joanny [8] has discussed the global phase diagram to be expected in this case. In nonpolar solvents, the polar sulfonate groups tend to mutually associate, leading to a reduced second virial coefficient. In dilute solution, the radius of gyration of an isolated chain will then be expected to decrease with increasing degree of substitution, leading to an eventual collapse and phase separation. In semi-dilute solutions, where the polymer chains are overlapping and entangled, there will exist a competition between intra- and inter-chain associations. Thus, in semi-dilute solution chain crosslinking and eventual gelation will compete with phase separation. This behaviour leads to the schematic phase diagram sketched in figure 1a, where it is assumed that increasing temperature weakens the associations. The sol and gel regions of the phase diagram are distinguished by *connectivity*, not concentration. The sol is a more or less viscous fluid while the gel is an elastic network.

In section 2, we show some preliminary surface tension data on the sodium salt of polystyrene sulfonate ionomers in dimethyl sulfoxide (DMSO). Section 3 is devoted to a discussion of the relevant theoretical ideas.

2. Experimental.

2.1 POLYMER PREPARATION. — Anionically polymerized styrene was purchased from Polymer Laboratories, Ltd. The molecular weight of the polystyrene was 115,000 with $M_w/M_n < 1.05$. The preparation of sulfonated polystyrene ionomers was similar to that described previously [12]. The following procedure was generally utilized : 6 g of polystyrene were dissolved in 80 mls of 1, 2 dichloroethane. The solution was heated to 50 °C, and the appropriate amount of acetyl-sulfate was added, in this instance, 6.8 mmoles of acetic anhydride and 4.4 mmoles of concentrated sulfuric acid. The solution was stirred for 60 min at 50 °C, and the reaction was terminated by the addition of 5.4 mls of methanol. Then, 11.0 meq of sodium acetate (diluted with water and methanol) was added with vigorous agitation to completely neutralize all sulfonic acids present. The solution was subsequently filtered and the polymer was isolated as the sodium salt by steam stripping. The sulfonated polymer was vacuum dried for 24 hours at 80 °C. Sulfur content of the polymers was determined by Dietert sulfur analysis and was used to calculate the sulfonate

Fig. 1. — (a) Typical phase diagram for a polymer solution which exhibits a sol-gel transition. A prewetting line is also sketched. (b) Sketch of the polymer volume fraction profile near an adsorbing interface. Note the plateau-like structure when the bulk volume fraction is in the prewetting domain.

content. In this specific example, the sulfonated polystyrene contained 9.2 mole percent sulfonate moieties. Table I shows the specific characterization data for the sulfonate ionomers used in this study.

Table I. — *Specific characterization data for sulfonated polystyrene ionomers (sodium salt).*

Designation	Weight % sulfur	Sulfonation level (mole %)
126A	0.34	1.1
126B	1.07	3.6
126C	2.59	9.2

The polymer solutions were prepared in stoppered volumetric flasks utilizing conventional magnetic stirrers for agitation. The polymer was weighed into the flask to an accuracy of 0.001 g. The polymer concentration in DMSO (Aldrich Chemical Company-spectrophotometric grade) for the surface tension measurements was 5 wt %.

2.2 SURFACE TENSION MEASUREMENT. — The surface tension was measured with a Fisher Model 215 Autotensiomat surface tension analyser, which is based on the de Nuoy ring principle. The surface tension analyser employs a strain-sensitive wire which is fixed at one end to a balance beam and the other end to a transducer, which provides a force that is proportional to the surface tension as the ring is pulled out of the liquid. The typical output of the analyser is shown in figure 2a and b, where the ordinate on the figure corresponds to the pulling force on the ring. The absolute surface tension is the maximum output with a small correction [13] which depends on the size of the ring, the diameter of the wire, the densities of the phases, and the curvature of the detached liquid interface. The abscissa in figure 2 is the ring displacement from the surface. If the solution is not *elastic*, the detachment of the solution from the ring is abrupt, and the output pulling force on the ring is as shown in figure 2a. However, if the solution is *elastic*, the surface may be deformable as shown in figure 3. In this case, the typical trace is shown in

Fig. 2. — Typical surface tensiometer traces : (a) for a solution ; (b) for an elastic gel.

Fig. 3. — Sketch of the assumed form of the meniscus for a « pulled » gel film.

figure 2b. The accuracy and the reproducibility of the experiment are about 0.1 dyne/cm and 0.5 dyne/cm, respectively.

Figure 4 shows the output for the DMSO, 126A, 126B, and 126C solutions. The corrected absolute surface tensions are tabulated with viscosity data in table II. The interesting aspect is the non-monotonic behaviour of the change in surface tension ($\Delta\gamma$) with increasing sulfonate level. Furthermore, the 126C solution trace exhibits the characteristic elastomer shape while the bulk remains fluid. These properties are consistent with surface gelation as discussed in the next section.

3. Theory.

Consider a polymer solution in contact with a sharp interface : a free surface, a solid surface, or an immiscible fluid. For an adsorbing surface, there will be an increased (over the bulk) polymer concentration in proximity to the interface with a profile [14, 15] decaying to the bulk value in a correlation length [16, 17] ξ_b . In both good and theta solvents, an interpolation formula which describes the profile near the surface ($x \ll \xi_b$, where x is the distance to the surface) and takes into account the proximal exponent discovered by Eisenriegler, Binder, and Kremer [18] is given by

$$\phi = \phi_s(a/x)^m [1 + (x/D)]^{-1} \tag{1}$$

Table II.

Solution	Surface tension	Δ (dyne/cm)	Viscosity (c.p. at 11 s ⁻¹)
DMSO	38.5		2.00
126A	35.4	3.1	3.25
126B	33.6	4.9	8.87
126C	36.2	2.3	12.17

Fig. 4. — Tensiometer traces for the four samples : (a) is DMSO ; (b) is 126A ; (c) is 126B ; (d) is 126C.

where a is a typical monomer dimension, ϕ is the polymer volume fraction and ϕ_s is its value at the surface ; the proximal exponent $m \approx 1/3$ in good solvent and $m = 0$ in theta solvents [14, 18] ; D is the extrapolation length [14], i.e. the thickness of an adsorbed isolated chain and depends on the nature of the polymer-surface interaction in the given solvent — typically for intermediate adsorption ($a \leq D \leq \xi_b$) ; $\phi_s \approx (a/D)$ assuring in the central region ($D < x < \xi_b$) self-similar scaling behaviour [12], $x \propto \xi$. If $\phi_b \leq \phi_g \leq \phi_s$, [ϕ_g is the polymer volume fraction on the gelation curve (Fig. 1a)] the bulk is fluid but there is a surface gel film of thickness $\Lambda = \xi(\phi_g)$, where $\xi \simeq a\phi^{-1/(m+1)}$. The surface elastic modulus $G_s \approx \int_0^\Lambda T\xi^{-3} dx$ where (T/ξ^3) is the bulk elastic modulus of a network [16, 19]. Assuming $\Lambda \gg D$, and using equation (1), G_s becomes

$$G_s \approx TD^{-2}[1 - (D/\Lambda)^2] \quad (2)$$

for both good and theta solvents. The surface tension (in the absence of gelation) of a polymer solution may be expressed as [14, 15, 20]

$$\gamma - \gamma_0 = -kTD^{-2} - \mu\Gamma \quad (3)$$

where γ_0 is the solvent surface tension ; k is a constant of order unity, $\Gamma = \int_0^\infty (\phi - \phi_b) dx$ is the surface excess, μ is the monomer exchange chemical potential [16] and is proportional to ϕ_b^p (p is 3 and 9/4 for theta and good solvents, respectively). For dilute and semidilute solutions, the first (concentration independent) term usually dominates. For a rectangular macroscopic interface of dimensions L_y and L_z , a virtual displacement, δL_y , in the y direction leads to an increase in the interfacial energy, U

$$U = \gamma L_z(\delta L_y) + (1/2) G_s(\delta L_y)^2 \quad (4)$$

or a retraction force per unit length Π given by

$$\Pi = \gamma + G_s(\delta L_y)/L_z. \quad (5)$$

Note that for $(\delta L_y)/L_z$ of order unity, the adsorptive reduction in the surface tension (relative to the pure solvent value) tends to be cancelled by the surface elasticity. This is consistent with the non-monotonic dependence of the retraction force observed on Π as a function of sulfonate level.

In poor solvents ($T < T_c$) and in dilute solution [to the left of the coexistence curve (Fig. 1a)], the system may be either in the weak or strong adsorption regime as delineated by the prewetting line [21, 22]. For weak adsorption (to the left of the prewetting line), the surface volume fraction ϕ_s remains less than its value on the coexistence curve [22] and thus no gel film is formed. For strong adsorption, ϕ_s lies in the semi-dilute single phase region (to the right of the denser branch of the coexistence curve). The concentration profile is predicted [20] to have a plateau (Fig. 1b) as it passes through the bulk biphasic region. For the schematic phase diagram (Fig. 1), the plateau is in the gel phase and hence the film thickness coincides approximately to the plateau width [22]

$$A \cong (R_g/4) [\ln \beta^{-1}/(\ln \phi_b^{-1})^{1/2}], \quad (6)$$

where β describes the separation between the bulk concentration and the coexistence curve

$$\beta = 1 - (\phi_b/\phi_1); \quad (7)$$

and ϕ_1 is the volume fraction on the coexistence curve. The gel modulus maintains the form (Eq. (2)), but in the prewetting region the film may become significantly thicker than R_g .

The distinction between a reversible, physical gel and a semi-dilute polymer solution is essentially a matter of time scales, similar to the difference between a glass and a fluid. An entangled, semi-dilute solution behaves as a transient gel with a characteristic lifetime, T_{rep} , the reptation time [16] which is proportional N^3 . Hence, in order to distinguish a surface gel from a simple entangled polymer solution, experiments must be performed at frequencies, ω , low compared to the reptation rate, $\omega \ll T_{rep}^{-1}$. Quasistatic measurements such as surface tension or interfacial pressure should exhibit the gel elasticity (Eq. (2)). Direct observation of the slow-down of the chain diffusion near gelation could, in principle, be obtained by forced Rayleigh scattering [23].

4. Final comments.

We have discussed the conditions for the formation of a surface gel film created by adsorption across the sol-gel coexistence curve of a solution of associating polymers. Preliminary surface tension measurements on ionomer solutions yield qualitative systematics which agree with our predictions. First, at high sulfonation levels the force profiles have the characteristic elastomer shape. Second, in the same range of substitution, the surface force begins to increase suggesting an additional (elastic) contribution to the interface deformation energy. Further experiments are required to confirm our conjecture of surface gelation.

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