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Sol–Gel Transition of Hydrolyzed Polyacrylamide + Chromium III: Rheological Behavior versus Cross-Link Concentration

Sol–gel transition investigations usually proceed by measuring the time evolution of the relevant quantities[1] during the chemical reaction leading to gelation and the results are compared to the predictions of the theoretical models assuming that the experimental parameter (the time) and the theoretical one (the number of cross-links) are linearly related in the vicinity of the transition. This assumption is not obvious and we have studied a system polymer + cross-linker in which we have been able to determine the number of cross-links formed as a function of the concentrations of polymer and cross-linkers.[2] This system consists of high molecular weight hydrolyzed polyacrylamide ($M_w \cong 6 \times 10^6$, degree of hydrolysis ≅24%[3]) and chromium(III) salt in an aqueous solution containing 20 g/L of NaCl, which is a good solvent for the polymer.[4] In addition, it is a good example of the various systems of practical interest.

Rheological measurements have been performed by using a magnetic sphere rheometer[5,6] whose ranges of shear rates and deformations and times of measurements as long as 2000 s allow the determination of the steady-state zero-shear viscosity and the steady-state linear elastic modulus up to the vicinity of the transition. Since the cross-link formation proceeds through a ligand substitution reaction on chromium(III), the kinetics are very slow. We have been able to follow the evolution of the rheological quantities and to determine accurately the equilibrium values which are reached about 50 h after the preparation of the samples achieved by mixing equal volumes of polymer and chromium solutions. The equilibrium concentration of cross-links has been determined by a UV–visible spectrophotometric study of the chromium complexes. We have made a comparison with a low molecular weight model of the polymer to ensure that no complexation enhancement occurs in the range of concentrations where the rheological measurements are performed.[2] Figure 1a presents the results of a systematic study done with 2500 ppm in polymer (about 2 times the chain overlapping concentration) as a function of the concentration in cross-links (c_l). The divergence of the viscosity and the smooth increase from zero of the elastic modulus are characteristic of critical behavior.

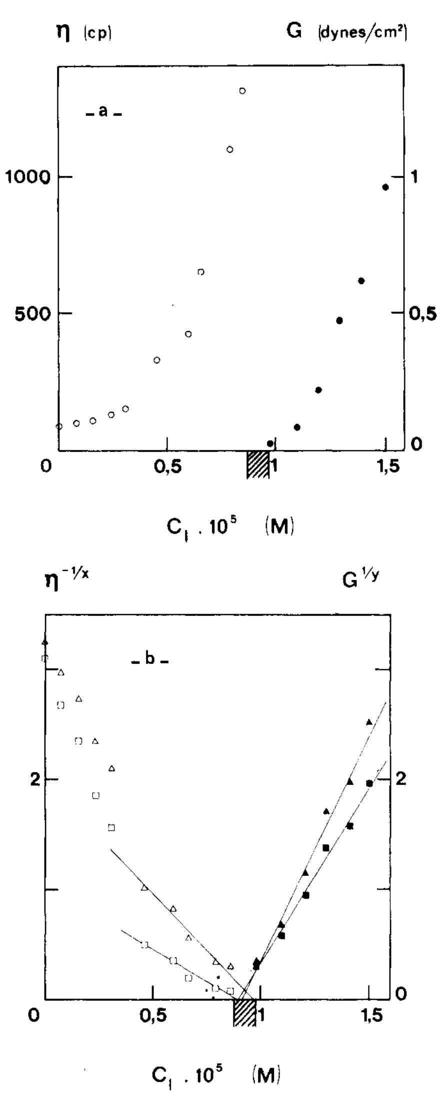

Figure 1. (a) Variations of the viscosity (○) and of the elastic modulus (●) versus concentration in cross-links. (b) Variations of $\eta^{-1/X}$ and $G^{1/Y}$, in arbitrary units, for different values of X and Y: (□) $X = 0.7$; (△) $X = 1.1$; (▲) $Y = 1.8$; (■) $Y = 2$. The chosen values of κ and θ are those for which the experimental points lie on a straight line intersecting the c_l-scale within the interval in which $c_{l,c}$ is located (shaded range).

The gel point, $c_{l,c}$, is unambiguously located between the last point in the viscous regime (8.7×10^{-6} M) and the first one in the elastic regime (9.7×10^{-6} M). If the molecular weight of the polymer is taken into account, the number of cross-links per chain at the threshold is found to be of the order of 11. This value is much larger than the value predicted by the classical theory which is one per chain[7] (it corresponds to c_l equal to 0.8×10^{-6} M). We have attributed this large discrepancy to the formation of small intrablob loops: indeed, the binding probability between the monomers of the same chain in a good solvent falls off quickly with the chemical distance.[8] Assuming that the sizes of the loops are related to the persistence length, the number of monomers in the loops is only 1% of the total number of monomers. Therefore, the contour length of the chain and consequently its mechanical properties are negligibly affected by the loops. This result has been corroborated by viscometric measurements performed in the dilute regime.[9] Moreover, at a constant polymer

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concentration, the percentage of intrablob links is constant. It must be noted that the small intrablob loops involved here differ from the loops found in the cyclizations investigated by Dušek, K., Gordon, M., and Ross-Murphy, S. B.,[10] in the sense that they only occur on a short scale and thus do not affect the critical properties of the transition. In conclusion, the results presented in Figure 1a can be compared without any assumption to the classical and percolation models of gelation.

The exponent of the viscosity (κ) and that of the elastic modulus (θ) have been calculated by plotting $\eta^{-1/X}$ and $G^{1/Y}$ versus c_1. We retain the values of X and Y for which the experimental points fall on straight lines intercepting the c_1 scale inside the range where $c_{1,c}$ is located. From such plots (see Figure 1b), we have deduced

$$\kappa = 0.9 \pm 0.2$$

$$\theta = 1.9 \pm 0.1$$

These values are quite different from the predictions of the classical theory (0 and 3, respectively) but are in good agreement with those of the percolation model (0.75 and 1.9, respectively). Investigations on various systems (radical copolymerization,[11] vulcanization in semidilute solutions,[12] and thermoreversible gelation[13]) also showed good agreement with the percolation predictions for θ. But, in some cases, discrepancies have been observed which may be attributed to the influence of chain rigidity[14] or to the failure of the assumption of linearity between the experimental parameter and the theoretical one.

The width of the critical region which corresponds to the range of the cross-link concentration where power laws are observed is found to be very large, greater than 60% of the relative distance from the critical point. In contrast to time-dependent studies for which the width of the critical range can be drastically reduced because of the nonlinear variation of the cross-link concentration versus time, the value which is determined here is perfectly reliable. Moreover, it is in good agreement with the Daoud's predictions concerning vulcanization in semidilute solutions.[15]

In conclusion, our study of the sol–gel transition as a function of the concentration in cross-links shows that a large number of intrablob links exist at the threshold but that the mechanical properties are well described by the percolation model. A more detailed study of chromium(III) cross-linking in hydrolyzed polyacrylamide solutions is in progress and will be reported later.

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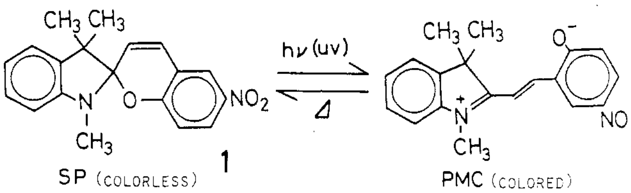
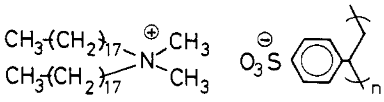
Rate Control of Thermal Isomerization of a Spirobenzopyran Embedded in Bilayer-Immobilized Cast Film by the Phase Transition

It is widely known that photochromism of spirobenzopyran derivatives is largely influenced by the physical state of the surrounding matrices due to a large steric requirement during the isomerization. A typical example is the effect of the glass transition of polymer matrices on the thermal decoloration (isomerization of UV-induced merocyanine (PMC) to starting spiropyran (SP)).[1-5] Our recent work revealed that when spirobenzopyrans were incorporated into an aqueous bilayer membrane, the decoloration kinetics was strongly dependent on the membrane fluidity which is altered by the crystal to liquid crystal phase transition.[6] In light of the development of photoresponsive materials and devices, photochromic phenomena taking place in the solid phase would be of considerable interest. It has been shown by Kunitake and his co-workers that bilayer-immobilized solid films are obtainable by simple casting methods.[7-9] A noteworthy feature of these films is that the immobilized bilayers maintain considerably well the characteristics of bilayers dispersed in water and show clearly the crystal to liquid crystal phase transition.[7-9] In this paper we report the thermal decoloration of a spirobenzopyran compound 1 embedded in a bilayer cast film which consists of an ion complex between dioctadecyldimethylammonium and poly(styrene sulfonate) (M_w = 500000) ($2C_{18}N^+2C_1$–PSS^-). It is found that the crystal to liquid crystal phase transition of the bilayer cast film brings about an abrupt increase in the reaction rate.





$2C_{18}\overset{+}{N}2C_1-PSS^-$

The bilayer-immobilized cast film was prepared in a similar method described by Kunitake et al.[8] The polyion complex, $2C_{18}N^+2C_1$–PSS^-, was dissolved in chloroform together with 0.5 mol % of 1 and cast onto a quartz plate (film thickness, 10 μm). The cast film was then allowed to stand for 1 h at 60 °C at relative humidity of 100% and dried under vacuum before kinetic measurements. This