Macromolecules 1990, 23, 981-987

mation of the Y-branches[5-7] though the amount is very small in our samples as shown in Table V. The term $(1 - f)N_S$ indicates the number of the fragments to form the Y-branches by the recombination with other polymeric molecules. Therefore, the number N_Y of the Y-branches is expressed as

$$N_Y = 2(1 - f)N_S + N_V \tag{2}$$

Then from eqs 1 and 2, f is given by

$$f = 1 - \frac{1}{2}\frac{N_Y}{N - N_0 + N_Y + N_H} \tag{3}$$

When the numbers of the respective structural units are expressed per 10 000 carbon atoms, eq 3 reduces to

$$f = 1 - \frac{1}{2}\frac{N_Y}{10^4 m(M^{-1} - M_0^{-1}) + N_Y + N_H} \tag{4}$$

where M_0 and M are the molecular weights of the unirradiated and irradiated polymers, respectively, and m is the molecular weight of the CH_2 groups. When the M_n's shown in Table IV are used together with the N_H and N_Y values given in Table III, f has been determined to be about 0.9 for the polyethylene fractions. Therefore, most of the fragments appear to be stabilized without the formation of the Y-branches. The N_S value can be also calculated for each irradiation using eq 2 and then the G-value for the chain scission is estimated to be 1.8. This value is somewhat large compared to the G-values of 0.50 and 0.52 obtained for n-$C_{16}H_{34}$ and n-$C_{17}H_{36}$ in liquids.[8,9] However, such an extent of discordance should be allowable in the case of the complicated polyethylene samples.

On the other hand, the methyl, ethyl, and butyl branches have almost no influence of the irradiation, whereas trans and cis double bonds significantly increase in concentration with increasing radiation dose. In particular, the amount of the trans double bonds increases to the level of the cis double bonds, although the trans double bonds are not included in the unirradiated fractions. Almost similar results were also obtained in the irradiation of the low molecular weight polyethylene (HW). These results are in good accord with those previously reported by Randal et al.[5-7] Further discussion will be given somewhere together with the results of the irradiation in the solid state.[10]

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Gelation of Semidilute Polymer Solutions by Ion Complexation: Critical Behavior of the Rheological Properties versus Cross-Link Concentration

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ABSTRACT: The gelation of hydrolyzed polyacrylamide solutions by addition of chromium(III) has been investigated by using physicochemical and rheological approaches. First, we have studied the formation of cross-links by complexation using UV–visible spectroscopy and dialysis. Comparison with a low molecular weight model of the polymer has allowed us to understand the influence of specific polymer effects and to delimit the range of HPAM and Cr(III) concentrations within which the link concentration can be determined. Second, we have investigated the steady-state viscosity and the steady-state elastic modulus of samples of constant polymer concentration and various Cr(III) concentrations. In the vicinity of the gelation threshold, the variations of the rheological quantities versus the cross-link concentration have been interpreted in terms of critical behavior. The exponents have been found in good agreement with the scalar percolation predictions; the prefactors and the width of the critical region have been described in terms of the gelation of semidilute polymer solutions.

1. Introduction

Several works have been recently devoted to the study of gelation and, in particular, of the critical behavior of the rheological properties near the sol–gel transition.[1-5] In such studies, comparison of the experimental results with the models of the transition, classical theory, or percolation model requires a good knowledge of the number of cross-links formed in the medium, which is difficult to achieve for many gelling processes (copolymerization or polycondensation processes). In the present work,

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we have investigated the gelation of a water soluble synthetic polymer (hydrolyzed polyacrylamide) in the presence of a transition-metal ion (chromium(III)). The advantage of this system is the possibility of following the polymer–ion interaction by UV–visible spectroscopy and the very slow kinetics of the quasi-irreversible cross-link formation. Relating our studies on the complexation of Cr(III) with hydrolyzed polyacrylamide to the rheological properties we have been able to determine the variations of the viscosity and the elastic modulus as a function of the link concentration upon gelation, allowing a direct comparison with theoretical predictions.

The complexation of metal ions with polymer chains containing ligand groups leads to modifications of the macroscopic behavior of the solutions. These changes are due to the formation of complexes liganded with more than one polymer group, which creates intramolecular and/or intermolecular cross-links, the percentage of them depending on the polymer concentration. The case of dilute polymer solutions has been widely investigated;[6] in particular, it has been observed that the complexation exhibits specific effects that are not encountered with low molecular weight molecules. Thus the determination of the cross-link concentration requires a complete physicochemical study. In order to characterize the hydrolyzed polyacrylamide–Cr(III) interaction, we have investigated the nature of the phases formed over a wide range of concentrations and compared the UV–visible absorbances measured with the polymer to those observed with a low molecular weight model of the polymer.[7] These results, presented in part 3, allow us to delimit a range of concentrations within which the link concentration can be determined.

The variations of the zero-frequency rheological properties in the vicinity of the gel point are typical of the sol–gel transition: when the cross-link concentration is increased, the viscosity, in the sol phase, exhibits a divergence and the elastic modulus, in the gel phase, increases from zero.[8,9] The exponents κ and θ, which characterize the variations of the rheological properties, have been determined for various systems during the reaction leading to the gel formation. Contrary to the universality expected in the frame of classical or percolation theories, these experimental values differ from one another. In the present study, the rheological measurements have been performed as a function of the cross-link concentration and we have determined, in addition to the exponents κ and θ, the prefactors of the power laws and the width of the critical region. The results presented in part 4 have been compared to the predictions concerning the gelation of cross-linked semidilute polymer solutions.[10] The measurements performed during the complexation kinetics are also discussed.

2. Experimental Section

Reagents. The polymer used in this study is a high molecular weight partially hydrolyzed polyacrylamide, $-[CH_2CHCOONa]_X-[CH_2CHCONH_2]_Y-$ (HPAM, $M_w = 6 \times 10^6$, Rhône Poulenc Rhodoflood AD37), obtained by copolymerization of acrylamide and sodium acrylate. The degree of hydrolysis $X/(X + Y)$ is 24% and the acrylate monomers follow a statistical distribution along the chains.[11]

The transition-metal ion chromium(III) is obtained from the $CrCl_3(OH_2)_6$ salt (Merck quality ultrapure). In aqueous solutions, Cr(III) is surrounded by six ligands (atoms or molecules) arranged in an octahedron: the substitution of one or two of these ligands by the ^-OOC functions of the acrylate monomers leads to the formation of strong and quasipermanent monosubstituted or disubstituted complexes.

Preparation of the Samples. The samples are prepared by mixing equal volumes of an initial polymer solution and an initial Cr(III) solution. The solvent is highly purified water (Millipore quality Milli-Q) containing 20 g/L NaCl ($\simeq$0.34 M) in order to keep a constant ionic strength. Furthermore, we can consider it a good solvent of the polymer.[12]

The polymer solutions are prepared at room temperature: the polymer in its powder form is dissolved in the solvent (without addition of any bactericide agent) with gentle magnetic stirring for 24 h. The solutions are then kept in the refrigerator and used within a few months. The solutions prepared in this way at a concentration above 6000 ppm were inhomogeneous, but in the present work we were only interested in lower concentrations.

The chromium solutions prepared in the same solvent were kept in the dark at room temperature. They were used at least for 1 day but no more than 1 month after the dissolution of the $CrCl_3(OH_2)_6$ salt. We have verified that under these conditions equilibrium with respect to the chloride complexes is reached and that the solutions do not contain polynuclear species (i.e., complexes containing more than one metallic ion).

Rheological Measurements. The viscosity and the elastic modulus of the samples were measured during the complexation kinetics with a magnetic levitation sphere rheometer. The principle of this device has already been described[13,14] and we shall only describe its performance. The shear rate can be chosen as small as 10^{-4} s^{-1}, the deformation can be decreased to 10^{-2}, and the stability of the electronic device allows us to extend the duration of a measurement to 2000 s. This enables us to accurately determine the steady-state zero shear viscosity and steady-state linear elastic modulus even in the vicinity of the sol–gel transition where long relaxation times occur, provided that the kinetics of the reaction is slow enough. The temperature of the sample is regulated by a circulation of water coming from a thermostated bath. All measurements were performed at 25.0 ± 0.1 °C.

UV–Visible Spectroscopy. The spectra were recorded with a Kontron spectrometer (Model Uvikon 860), which allows automatic acquisition of spectra at various time intervals. Thermostated cells have been used only for the study of the kinetics.

Dialysis. Polymer–Cr(III) mixtures, 5 cm^3, were poured in dialysis bags (Spectra/Por no. 3, mw cutoff = 3500), which were immersed in a sample tube containing 10 cm^3 of either the solvent or Cr(III) solutions. The cellulose membranes were carefully washed in order to eliminate their glycerol content, and we have checked in the absence of polymer that they do not modify the pH or interact with Cr(III) ions. The free Cr(III) was titrated outside the membranes by inductively coupled plasma emission.

3. Characterization of the HPAM/Cr(III) Interaction

Phase Diagram. Depending on HPAM and Cr(III) concentrations, the nature of the phase formed varies. The diagram shown in Figure 1 has been established by visual observation of the samples and of their behavior on tilting the tube. Observations were made between 1 and 3 days after the preparation, on mixtures maintained at 30 °C. For low polymer concentrations ($c_{poly} < 1250$ ppm), only viscous phases, i.e., sols, are obtained, which are either homogeneous or inhomogeneous. As expected, the limiting polymer concentration is found to be on the same order as the overlapping concentration c^*_{poly}, which has been determined by plotting the low shear rate viscosity against the polymer concentration ($c^*_{poly} \cong 1250$ ppm). For polymer concentrations greater than 1250 ppm, at low Cr(III) concentrations viscous homogeneous sols are observed while at high Cr(III) concentrations elastic phases, i.e., gels, are obtained, which are either homogeneous or turbid and expulse the solvent.

The existence of inhomogeneous phases, sols or gels observed at a given value of the ratio $c_{poly}/c_{Cr(III)}$, is related to the formation of a large number of intramolecular links

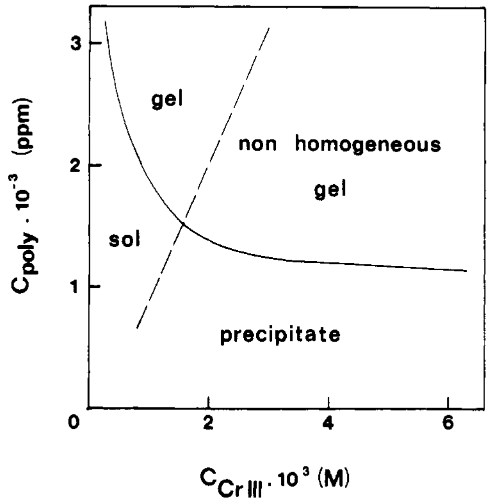

Figure 1. Nature of the phases formed as a function of Cr(III) and polymer concentrations.

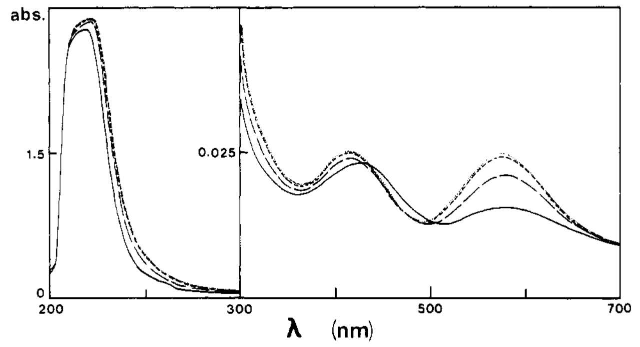

Figure 2. UV–visible spectra of a 4.5 × 10^{-4} M Cr(III) and 2500 ppm HPAM solution recorded 2 min (—), 62 min (– –), 542 min (- - -), and 962 min (· · ·) after the mixing of the reagents.

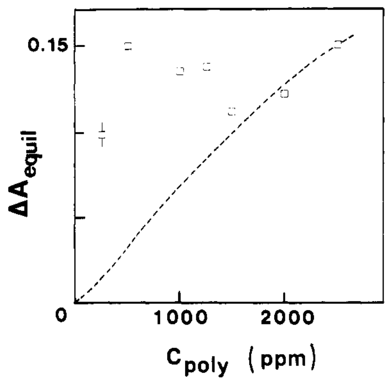

Figure 3. Experimental (□) and calculated (- - -) variations of ΔA_{equil} at 250 nm for solutions of 4 × 10^{-4} M Cr(III) and increasing HPAM concentrations. For the lowest polymer concentrations (c_{poly} < 1500 ppm) the large uncertainties on ΔA_{equil} (represented by a vertical bar) are due to the nonexponential slow kinetics.

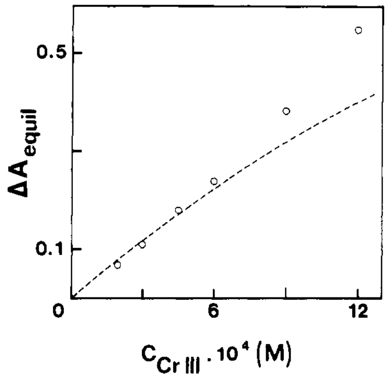

Figure 4. Experimental (○) and calculated (- - -) variations of ΔA_{equil} at 250 nm for solutions of 2500 ppm HPAM and increasing Cr(III) concentrations.

which causes the contraction of the chains. Similar behavior has been observed in other systems such as ionic gels[15] or polymer solutions in the presence of ions forming labile complexes.[16] Furthermore, the line that separates the domains where sols or gels are observed has been predicted.[10,16,17] However, a comparison of the results of Figure 1 with these predictions is only possible if for each HPAM and Cr(III) concentration the number of intermolecular cross-links is known. Unfortunately, as we shall see later, this is possible for certain ranges of concentrations but not for all.

Spectroscopic Investigations. The interaction between HPAM and Cr(III) proceeds by ligand substitution; one or more of the six initial ligands of the Cr(III) ion, which are OH_2, OH^-, or Cl^-, can be substituted by the ^-OOC groups of the acrylate monomers. Such a substitution modifies the UV–visible spectrum of Cr(III): a variation of the absorbance and a shift of the peaks in the visible range are observed (Figure 2).

We have first investigated the interaction of Cr(III) with sodium acetate used as a low molecular weight model of the polymer.[7] In this case, all the equilibrium constants of complexation are known. Taking into account the interaction of the Cr(III) with the Cl^- from the solvent (water containing 0.34 M of NaCl), the acid–base equilibria, and the substitution by acetate ions, we have calculated the concentrations of the various species present at equilibrium in the mixtures. The results have been compared with the absorbances observed at 250 nm. The difference between the absorbance measured at equilibrium and that measured just after the mixing of the components, ΔA_{equil}, has been found to be proportional to the calculated concentration of the monosubstituted Cr(III). This agreement has been observed over a very large range of concentrations (more than two decades in sodium acetate).

In the case of the HPAM, depending on the polymer and Cr(III) concentrations, agreement or difference is observed between the spectroscopic results and the calculated concentrations (Figures 3 and 4). The results of Figure 3 have been obtained at a fixed Cr(III) concentration and for the same range of polymer concentration as investigated in the phase diagram. The discrepancies observed are due to effects specific to macromolecules. We have verified that they are neither due to an interaction of the Cr(III) with the acrylate monomers nor to a substitution by two neighboring carboxylic groups on the chain nor to turbidity.

In the *dilute regime* ($c_{poly} < c^*_{poly}$), similar differences between the complexation with the low molecular weight model and with the polymer chain have already been observed.[6] Three different effects can be evoked to interpret them.

First, in a dilute solution the ligands are not homogeneously distributed, since a polymer solution can be viewed as a solution of droplets containing a polymer solution of concentration equal to c^*_{poly}. We have introduced such a ligand distribution in our calculations. The concentration of the monosubstituted complexes and that of the bisubstituted ones are found very close to the concentrations calculated with an homogeneous distribution (relative differences less than 10%).

Second, the distribution of the ions can also be inhomogeneous. Indeed, due to the presence of charges on

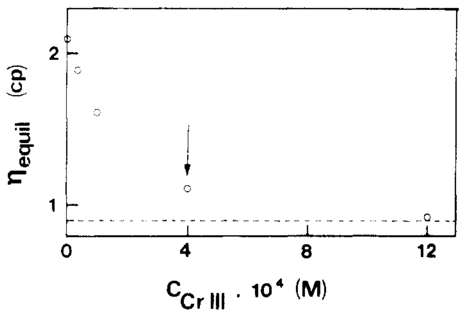

Figure 5. Viscosity of solutions of 250 ppm HPAM and increasing Cr(III) concentrations; the dashed line represents the solvent viscosity. The point indicated by an arrow corresponds to the same concentrations as those of the point marked by a vertical bar in Figure 3.

Table I
Comparison of the Concentrations of Free Cr(III) Ions Measured by Dialysis and Calculated for Samples of Different HPAM and Cr(III) Concentrations

initial concens			
c_{poly}, ppm	$c_{Cr(III)}$, M	$c_{Cr(III)}$, M, dialysis	$c_{Cr(III)}$, calcd
250	4×10^{-4}	2.8×10^{-4}	3.97×10^{-4}
250	1.2×10^{-3}	9.6×10^{-4}	1.19×10^{-3}
500	4×10^{-4}	2.4×10^{-4}	3.96×10^{-4}
500	1.2×10^{-3}	9.0×10^{-4}	1.19×10^{-3}

the polymer chain, which are either initial charges in the case of a polyelectrolyte or charges formed by the complexation in the case of a neutral polymer,[18] the condition of the Donnan equilibrium leads to an inhomogeneous distribution of the free ions. Under our experimental conditions, as a high concentration of a passive salt is added, the electrostatic interactions are always completely screened.

Third, the conformation of the chain can be modified by the complexation. At low rates of cross-linking, theoretical calculations have shown that intramolecular cross-linking leads to the formation of small loops[19,20] whose size, in the case where all the monomers can react, is determined by the stiffness of the chain. As a result, a slight decrease in the viscosity is expected. In the range of concentrations where large differences between the spectroscopic measurements and the calculations are observed (Figure 3), the viscosity of the mixtures (for instance, the point indicated by an arrow on Figure 5) has been found very low in comparison with the viscosity of the polymer solution in the absence of Cr(III) and is on the order of the solvent viscosity. This observation shows that the polymer chain is then completely collapsed. Therefore, the spectroscopic measurements are not reliable due to the presence of a large number of multisubstituted complexes and a modification of the molar extinction coefficients. We have performed dialysis experiments in the same range of concentrations. The results summarized in Table I clearly confirm that the number of free Cr(III)'s is lower than that predicted by the calculations.

In the *semidilute regime* ($c_{poly} > c^*_{poly}$), the first two effects do not take place and only the third is involved. When the rate of cross-linking is low, the disubstituted complexes form either intermolecular links, which lead to junction points, or intramolecular links, which give rise to small loops since the conformation of the chain between two entanglements is the same as that of the chain in dilute solution.[21] The relative proportion of the two types of links is independent of the Cr(III) concentration at fixed polymer concentration but depends on the polymer concentration. Its variation with c_{poly} can be calculated; thus, in the frame of the Daoud model[10] we can interpret the line of the phase diagram that separates sol and gel phases.[22] At a large rate of cross-linking, important modifications of the chain conformation occur, leading to the expulsion of the solvent and gel syneresis.

From the spectroscopic results (Figures 3 and 4), we can determine the range of concentrations where the complexation with the polymer behaves similary to that with the molecular weight model. For instance, for a polymer concentration equal to 2500 ppm, calculations and measured absorbances are in agreement up to a Cr(III) concentration equal to 6×10^{-4} M.

4. Sol–Gel Transition

Experimental Results. The range of concentrations chosen for the rheological measurements is that in which the calculation of the cross-link concentration has been shown to be reliable. We have performed a systematic study of the rheological properties for different samples with a fixed polymer concentration (c_{poly} = 2500 ppm) and various Cr(III) concentrations ($c_{Cr(III)} \leq 6 \times 10^{-4}$ M). As the kinetics of the complexation is very slow, typically equilibrium is reached 50 h after mixing of the components (see Figure 2), we have been able to follow the evolution of the rheological properties, for each sample, during the entire cross-linking reaction. This slow kinetics allows us, for each measurement, to reach the end of the viscoelastic relaxations and thus to determine the steady-state quantities. It also enables us to check that each point corresponds to the zero shear limit for the viscosity and to the linear regime for the elastic modulus by repeating the measurements with different shear rates and displacements, respectively.

The results are presented in Figure 6a for the samples whose final state is a sol and in Figure 6b for the samples that are gels at equilibrium. From these measurements, it is possible to study the time dependence of the rheological quantities or to investigate the variation of their equilibrium values as a function of the concentration and, in particular, as a function of the calculated cross-link concentration. Finally, one can note that large differences in the rheological behaviors are observed for nearly equal Cr(III) concentrations.

Equilibrium Viscosities and Elastic Moduli. The values of the viscosity and of the elastic modulus determined at the end of the complexation reaction, η_{equil} and G_{equil}, respectively, are plotted in Figure 7 as a function of the calculated cross-link concentration, c_{links}. In the following paragraphs, we discuss the value of the cross-link concentration at the gel point, the critical behavior of η_{equil} and G_{equil}, and, finally, the variation of η_{equil} in the vicinity of $c_{links} = 0$.

The *concentration of the cross-links at the gelation threshold*, located in the dashed region on Figure 7 (8.7×10^{-6} M $\leq c_{links} \leq 9.7 \times 10^{-6}$ M), corresponds to a number of links per chain on the order of 10. This value differs from the prediction of the classical theory, which is one link per chain at the gel point. This discrepancy is due to the existence of a percentage of disubstituted complexes forming intrablob[23] links (see part 3), which do not contribute to the gelation. If we assume that the number of monomers participating in a small loop is determined by the persistence length of the polymer, we can estimate the number of monomers "lost" in the loops per chain. The value found, 3×10^2, is very small compared to the total number of monomers in a chain, 7.8×10^4. As a consequence, the properties of the chains and, in

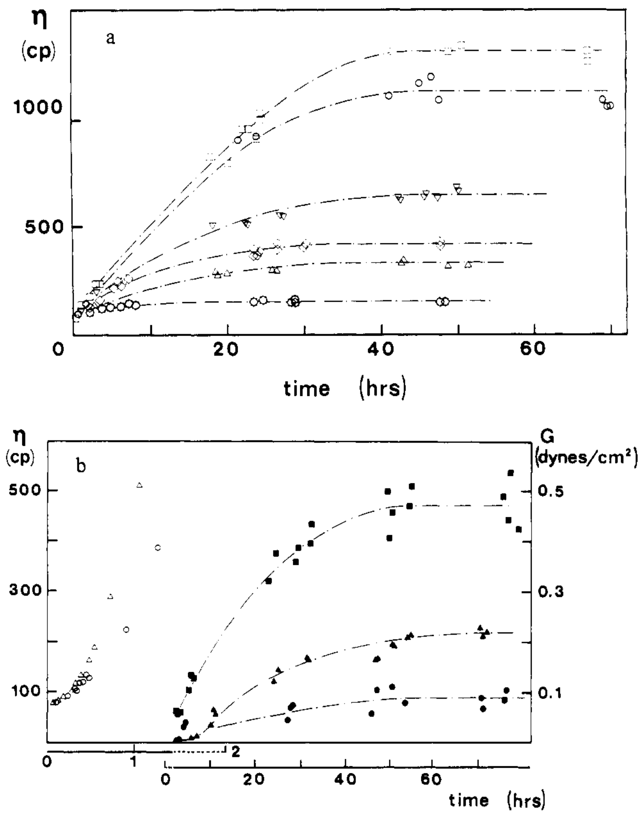

Figure 6. Variations of the viscosity (empty symbols) and of the elastic modulus (full symbols) versus time observed for a fixed polymer concentration, 2500 ppm, and Cr(III) concentrations increasing up to 5 × 10^{-4} M. (a) Samples whose final state is a sol obtained from Cr(III) concentrations of (○) 10^{-4} M, (△) 1.5 × 10^{-4} M, (◇) 2 × 10^{-4} M, (▽) 2.5 × 10^{-4} M, (○) 2.75 × 10^{-4} M, and (□) 3 × 10^{-4} M. (b) Samples whose final state is a gel obtained for Cr(III) concentrations of (●) 4 × 10^{-4} M, (▲) 4.5 × 10^{-4} M, and (■) 5 × 10^{-4} M.

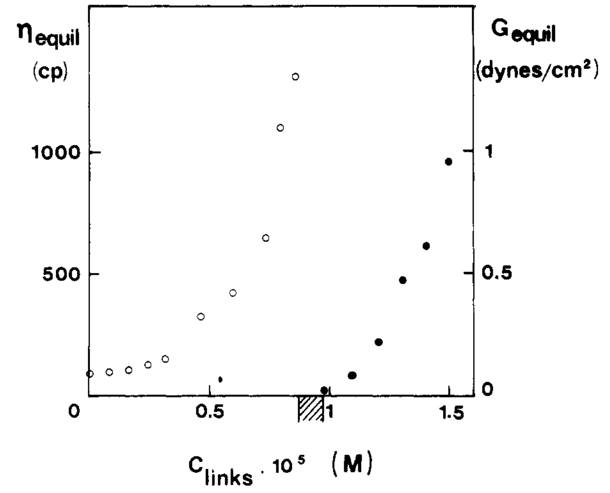

Figure 7. Variations of the viscosity (○) of the elastic modulus (●) versus the cross-link concentration.

particular, their entropic elasticity are negligibly affected.

The *description of the sol–gel transition* in terms of critical phenomena provides power law behavior for the viscosity before the gel point and for the elastic modulus beyond it:

$$\eta_{\text{equil}} = \eta_{\text{equil},0}\left(\frac{p_c - p}{p_c}\right)^{-\kappa} \quad \text{and} \quad G_{\text{equil}} = G_{\text{equil},0}\left(\frac{p - p_c}{p_c}\right)^{\theta}$$

p in the classical theory represents the advancement of the reaction and in a percolation model is the fraction of cross-links formed. p_c corresponds to the value of p at the gelation threshold. In contrast to previous studies,[1-5] which used time as the experimental parameter, in the present study the experimental parameter c_{links} is directly related to the theoretical one p since we have

$$\frac{p - p_c}{p_c} = \frac{c_{\text{links}} - c_{\text{links,c}}}{c_{\text{links,c}}}$$

Table II
Critical Parameters Obtained by Fitting the Points of Figure 7

	viscosity	elastic modulus
exponent	0.9 ± 0.2	1.9 ± 0.1
prefactor	215 ± 35[a]	2.0 ± 0.1[b]
width of the critical domain	55 ± 10%	≥60%

[a] cP. [b] dyn/cm².

It may be noted that the existence of intrablob cross-links does not modify this expression, since their proportion is constant because the experiments are done at a fixed polymer concentration. The determination of the critical exponents is simply done by plotting $\eta^{-1/X}$ and $G^{1/Y}$ versus c_{links} for different values of X and Y. The values retained for κ and θ correspond to the values of X and Y for which the experimental points fall on a straight line intercepting the c_{links} axis in the region where the gel point is located.[24] From such a plot, it is also possible to determine the values of the prefactors $\eta_{\text{equil},0}$ and $G_{\text{equil},0}$ and the extent of the critical domain, which can be characterized by the relative width, $\Delta c_{\text{links}}/c_{\text{links,c}}$, of the domain where the experimental points are well fitted by power laws. The results found by fitting the points of Figure 7 are given in Table II.

The values of the exponents of the viscosity and of the elastic modulus are in good agreement with those predicted by the scalar percolation model, 0.75 and 1.9, respectively. In this model, the determination of κ and θ lies on an analogy suggested by de Gennes[25] between the elasticity of an incomplete network of springs, which describes the elasticity of a gel, and the conductivity of a conductor–insulator mixture and the viscosity and the conductivity of a supernormal conductor mixture. Recent theoretical works[26,27] have shown that the exponents characterizing the mechanical properties are not universal but depend on the model chosen to describe the mechanical properties of a link. However, in the case of flexible polymer gels, the entropic origin of the elasticity supports the assumption of a scalar description.[28,29]

The width of the critical domain has been investigated theoretically by Daoud[10] for the gelation of a semidilute solution in a good solvent. He has shown that the width of the region where percolation exponents are expected varies drastically with the polymer concentration. For c_{poly} near c^*_{poly} the relative width is very large and varies as $(c_{\text{poly}}/c^*_{\text{poly}})^{-5/4}$. In the case of a melt, the width of the critical region is very small and only mean-field exponents can be observed. In the present work, the polymer concentration is equal to $2c^*_{\text{poly}}$, so the relative width of the percolation domain is expected to be very large, on the order of 75%. A good agreement is therefore found with our experimental determination (Table II).

In the scalar description, the prefactor of the elastic modulus is the analogue of the prefactor of the conductivity, σ_0. The only available determination of σ_0 has been obtained by numerical simulation on a cubic resistor network[30] and is expressed as a function of the conductivity of the network for $p = 1$: $\sigma_0 = 0.1\sigma(p{=}1)$. The analogue of $\sigma(p=1)$ in the case of gels formed in a good solvent is the osmotic modulus of a semidilute polymer solution of identical concentration. Its value can be deduced from the expression of the osmotic pressure:

$$E = \frac{k_B T N_A c^*_{\text{poly}} \Pi_0}{M} \left(\frac{c_{\text{poly}}}{c^*_{\text{poly}}} \right)^{3\nu/(3\nu-1)}$$

where k_B is the Boltzmann constant, T the temperature, N_A the Avogadro number, and Π_0 the prefactor of the osmotic pressure, which has been calculated theoretically by des Cloizeaux et al.:[31] $\Pi_0 = 1.51$. The exponent ν, which relates the radius of gyration to the molecular weight, has been found equal to 0.6 for HPAM in salt water.[32] Consequently, the value expected for $G_{\text{equil},0}$ is equal to 3 dyn/cm^2, which, taking into account the influence of the network geometry chosen to calculate σ_0 and the uncertainty on the determination of c^*_{poly} (about 15%), is in good agreement with our measurement (see Table II). There is no result allowing us to determine the value of the prefactor of the viscosity. Nevertheless, the overall results show that the scalar percolation model gives a good description of the sol–gel transition.

In the limit $c_{\text{links}} = 0$, the viscosity can be assumed to increase as $\eta_{\text{equil}} = \eta_{\text{poly}}(1 + \alpha c_{\text{links}})$ where η_{poly} is the viscosity of the polymer solution in the absence of Cr(III). For the values of the viscosity measured in the range $c_{\text{links}} \leq 10^{-6}$ M, we found $\alpha^{-1} \cong 8 \times 10^{-6}$ M. This value is on the order of $c_{\text{links,c}}$ as is expected in an effective medium description of the variation of the viscosity.[33]

Time-Dependent Results. We have proceeded to analyze the variations of the viscosity and of the elastic modulus with the time (Figure 6) two different ways. First, as is usually done in sol–gel investigations, we have assumed that the percentage of links is linearly related to time in the vicinity of the gelation threshold and we have determined the critical parameters of the rheological quantities for a sample whose final state is a gel. Second, for the whole $c_{\text{Cr(III)}}$ range, we have compared the time dependences deduced from the rheology to those observed by spectroscopy.

The *critical behavior* of the evolution of the viscosity and of the elastic modulus has been studied for $c_{\text{Cr(III)}} = 4.5 \times 10^{-4}$ M for which large enough variations are observed. Following the same fitting procedure as previously we found for the critical exponents $\kappa = 0.9 \pm 0.2$ and $\theta = 1.9 \pm 0.2$, for the prefactors $\eta_0 = 100 \pm 5$ cP and $G_0 = (2.7 \pm 0.2) \times 10^{-3}$ dyn/cm^2, and for the width of the critical region $\Delta t/t_c \cong 65\%$ in the sol phase and $\Delta t/t_c \cong 250\%$ in the gel phase. It is particularly interesting to compare these results with those found by analyzing the variations of the viscosity and of the elastic modulus with cross-link concentration (see Table II). If the error bars are taken into account, the exponents are identical but the prefactors and the widths of the critical domain differ considerably. In particular, in the gel phase a finite extent of the critical region is observed in the time-dependent study, while as the link concentration at the end of the kinetics is 1.2×10^{-5} M, all the points (i.e., up to $\Delta t/t_c \cong 4000\%$) are expected to belong to the critical region. As shown in the following paragraph, these discrepancies come from the nonlinear dependence of the cross-link concentration on time, showing the failure, in the case of our gels, of the assumption usually made.

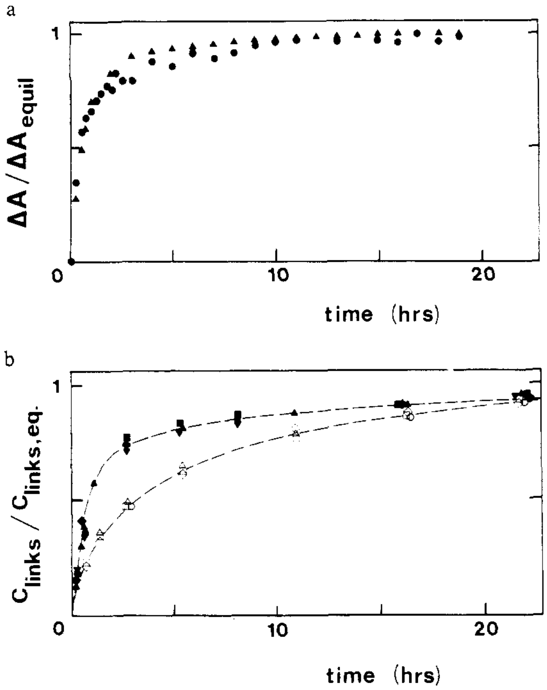

Figure 8. (a) Variations of $\Delta A/\Delta A_{\text{equil}}$ versus time for solutions of 2500 ppm HPAM and Cr(III) concentrations equal to 2×10^{-4} M (●) and 4×10^{-4} M (▲). (b) Variations of $c_{\text{links}}/c_{\text{links,equil}}$ versus time deduced from the rheological measurements. The empty symbols correspond to the samples whose final state is a sol: (○) 1.5×10^{-4} M; (△) 2×10^{-4} M; (□) 2.5×10^{-4} M; (◇) 3×10^{-4} M. The full symbols correspond to the samples whose final state is a gel: (●) 4×10^{-4} M; (▲) 4.5×10^{-4} M; (■) 5×10^{-4} M; (◆) 5.5×10^{-4} M; (▼) 6×10^{-4} M.

Let us now compare the *time dependences observed in rheology and in spectroscopy*. From the spectra in Figure 2, we can calculate the difference ΔA between the absorbance measured at time t and that measured just after mixing of the components. In the range of polymer and Cr(III) concentrations used, we have shown in section 3 that no effect specific to polymer complexation occurs. Thus, ΔA at 250 nm is proportional to the concentration of the monosubstituted complexes and, as the reaction of bisubstitution is instantaneous,[34] to the concentration of links. The results obtained for two of the Cr(III) concentrations used in the rheological study are reported on Figure 8a. As expected the kinetics of cross-linking in the range investigated is independent of $c_{\text{Cr(III)}}$.[34] Let us now analyze the rheological results and compare them to the spectroscopic ones. We have studied the evolution of the concentration of links deduced from the rheological measurements. For each value of time, the experimental value of the viscosity or of the elastic modulus is converted to a link concentration by using the equilibrium variation η_{equil} and G_{equil} versus c_{links} (see Figure 7). The results obtained for the various $c_{\text{Cr(III)}}$ investigated are reported in Figure 8b. It is noteworthy that all the points deduced from the measurements performed on the samples whose final phase is a gel lie on the same curve, close to the curve of the real kinetics observed in spectroscopy, whereas all the points derived from the variation of the viscosity for the samples whose final state is a sol lie on a different curve. The difference between the two curves (more than a factor 2 for t close to 5 h) is clearly larger than the uncertainty due to the data treatment. Two phenomena can contribute to the origin of these unexpected results. First, a "chemical" effect involving the transformation of intermolecular cross-links into intramolecular cross-links can occur. As a matter of fact, chelates are known to be more stable than other complexes. Such a mechanism has already been evoked to explain the time decrease of the viscosity of a polymer + reticulant agent solution from an initial value larger than the viscosity of the polymer solution.[35] Second, we think that the rheological quantities can be affected by the competition between the rate of growth of the macromolecules and the rate of their relaxations. Indeed at the beginning of the growth process only macromolecules of small size are formed and their conformation has time to relax before a new link is formed. On the other hand, when gelation occurs there exist large macromolecules whose characteristic times of relaxation are so long that their configuration remains frozen during the growth. These distinct regimes of growth can lead to different rheological behavior. Further experiments comparing the evolution of the rheological quantities for various kinetics are needed to check this hypothesis.

5. Conclusion

In this work, we have studied the sol–gel transition taking the link concentration as the control parameter. We have found that not only for the exponents but also the gelation threshold the prefactors and the width of the critical domain can be reliably interpreted. Over a wide range of link concentration, the experimental values of the viscosity and of the elastic modulus exhibit critical behavior characterized by exponents and prefactors well described by an analogy with the scalar percolation model. The link concentration at the threshold differs from the classical prediction due to the large percentage of intrablob cross-links that are involved in the low concentration samples investigated here. Comparison with measurements performed during complexation shows the limitations of the usual assumption of the existence of a linear relation near the threshold between the link concentration and time. In conclusion, comparison with studies of the critical behavior of other polymer–cross-linker systems will be of interest in order to check the universality of this global understanding of the gelation of semidilute solutions, which has been found reliable in the case of the hydrolyzed polyacrylamide–Cr(III) system.

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