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Gravity in the segregation phenomenon observed near the gelation threshold

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We investigate the phase diagram of sols and gels formed by copolymerization of acrylamide and bisacrylamide. In the vicinity of the sol-gel transition, we observe segregated samples with a viscous zone lying above an elastic part. A detailed rheological study has been done in the different domains of concentrations. The interpretation of the data in terms of critical behavior demonstrates that the samples where segregation occurs are gel phases. We also report calculations of the deformation and of the sedimentation kinetics of a tenuous polymer network under its own weight and experimental measurements in the segregated samples of the variations with height of the total monomer concentration and of the mobility of Brownian probes. This set of results shows that the gravitational field is at the origin of this segregation phenomenon.

Gravity effects in fluids near gas-liquid or liquid-liquid critical points are now well known.[1,2] On the contrary, only few works[3,4] have been devoted to the influence of gravity in the vicinity of the connectivity transitions in spite of the relevance of these transitions in practical applications such as fluid invasion in porous medium or heterogeneous material technology. In the present paper, we report the first study of the effect of the gravity in polymer gels near the sol-gel transition.

The phase diagram of the sols and the gels formed by copolymerization of bifunctional monomers (A) and plurifunctional monomers (B) is easy to understand. If either the total concentration in monomers, $c=c_A+c_B$, or the percentage of plurifunctional monomers, $\chi=c_B/c$, is too low, only finite-size macromolecules are formed at the end of the chemical reaction and a sol phase exhibiting a viscous behavior is obtained. On the contrary, if c and χ are large enough, an infinite polymer network extends in the sample and a gel phase with an elastic behavior is formed. In disagreement with this simple description, we have observed that between the two domains where sols and gels are obtained there is a narrow domain in which the samples segregate exhibiting a viscous zone above an elastic part. In order to elucidate the origin of this phenomenon, we have performed various experiments and calculations which are reported in the present paper. In Sec. I, we describe the materials used in this study and we characterize the nature of the different phases which are obtained; we also report rheological investigations done in the sol, the gel, and the intermediate domains. In Sec. II, we discuss the results in terms of a gelation critical point and we study the influence of the gravitational field on tenuous polymer networks.

I. EXPERIMENTAL STUDY

A. Materials and nature of the phases

The experiments are performed on samples synthesized by radicalar copolymerization of acrylamide (A) and N,N'-methylene bisacrylamide (B) in aqueous solution. The initiator is ammonium persulfate at a concentration of 1.7×10^{-4} g/g; oxygen, which is an inhibitor of the reaction, has been carefully eliminated. In all the experiments, the ratio χ is kept constant and equal to 1.22×10^{-2} in the molar fraction. The nature of the phases formed 8 days after the sample preparation is determined from the fall of millimetric particles of zircone (density 3.76) and of resin (density 1.09). We observe that for $c<0.8\times10^{-2}$ g/g the particles fall to the bottom of the tube indicating that the sample is a sol, and that for $c>1.1\times10^{-2}$ g/g the particles remain at the top of the tube indicating that the sample is a gel. In all these experiments the concentration in N,N'-methylene bisacrylamide is lower than 5×10^{-4} g/g. In these conditions the inhomogeneities which are encountered at large concentration and which are related to the low solubility of N,N'-methylene bisacrylamide do not occur.[5,6]

Between the domains where sols and gels are observed, i.e., for c ranging between 0.8×10^{-2} and 1.1×10^{-2} g/g, the particles begin to fall and then stop at an intermediate level revealing that the samples exhibit a viscous part lying above an elastic part. Moreover, the height at which the particles stop depends on the concentration: it increases regularly from zero for $c=0.8\times10^{-2}$ g/g up to the height of the sample for $c=1.1\times10^{-2}$ g/g.

Furthermore, we have determined the total concentration in monomers as a function of the height in the samples by means of refractive-index measurements. The method which is used consists of measuring the horizontal deviation of a laser beam which crosses the sample (the cells have a square horizontal section; the angle of incidence of the beam on the vertical side of the cells is 45°).[7] With this setup, we can measure variations of 10^{-4} in the refractive index. From the deviation at different heights in the sample, we deduce the variations of the total monomer concentration γ as a function of the distance z from the bottom of the cell. Typical results obtained on a sample prepared with $c=0.93\times10^{-2}$ g/g are

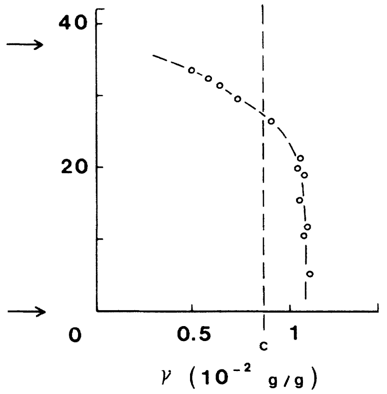

FIG. 1. Variation of the total monomer concentration (horizontal scales) for different values of the height in the sample (vertical scales). The arrows on the left correspond to the bottom and the top. The measurements have been done 8 days after the preparation of the sample of 0.93×10^{-2} g/g in concentration.

given in Fig. 1. We observe a smooth variation of the concentration over about 1 cm. This shows that the segregated samples do not exhibit a sharp interface. In conclusion, the phenomenon which is observed is different from a phase separation.

B. Rheological measurements

First, we are going to investigate the variations of the viscosity and of the elastic modulus as a function of the time during the copolymerization reaction. We use a magnetic levitation sphere rheometer[8,9] which permits the measurement of the steady-state zero-shear viscosity and the steady-state linear elastic modulus even in the vicinity of the gelation critical point. Typical results are reported in Fig. 2. For a concentration in the sol domain [$c=0.75\times10^{-2}$ g/g in Fig. 2(a)], the viscosity increases continuously and approaches an equilibrium value after 50 h (the time is measured from the moment when the reactives are mixed). At this time, we can consider that the copolymerization reaction is nearly achieved since more than 95% of the monomers have reacted.[10,11] For concentrations in the gel domain [$c=1.1\times10^{-2}$ g/g in Fig. 2(b)], we observe a quick increase of the viscosity which is followed by the appearance of an elastic modulus which increases and stabilizes after 50 h. Such behaviors are exactly those expected and they have been observed on a different kind of gelling system.[12] At a concentration for which a segration process is observed in the final state [$c=0.93\times10^{-2}$ g/g in Fig. 2(c)], the elastic modulus does not reach a steady value after the characteristic chemical time, i.e., 50 h and goes on increasing markedly (about a factor of 3 within 80 h). Since the reaction kinetics slightly depends on c in the range of concentrations which is concerned here (rate $\sim c^{1.25}$), this increase of the elastic modulus after 50 h cannot be attributed to a chemical effect.

From these measurements we deduce the viscosity η and the elastic modulus G at equilibrium as a function of c. The variations of η and G are shown in Fig. 3. No

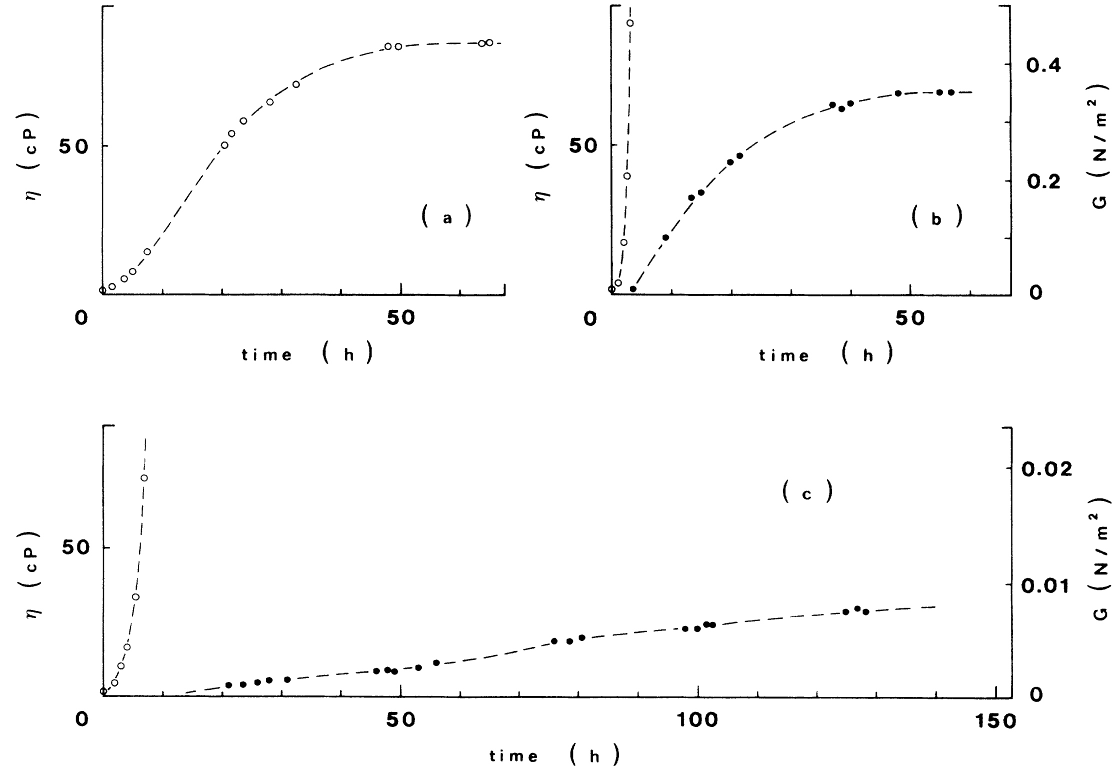

FIG. 2. Variations of the viscosity (○) and of the elastic modulus (●) vs time for different monomer concentrations. (a) $c=0.75\times10^{-2}$ g/g, (b) $c=1.10\times10^{-2}$ g/g, (c) $c=0.93\times10^{-2}$ g/g.

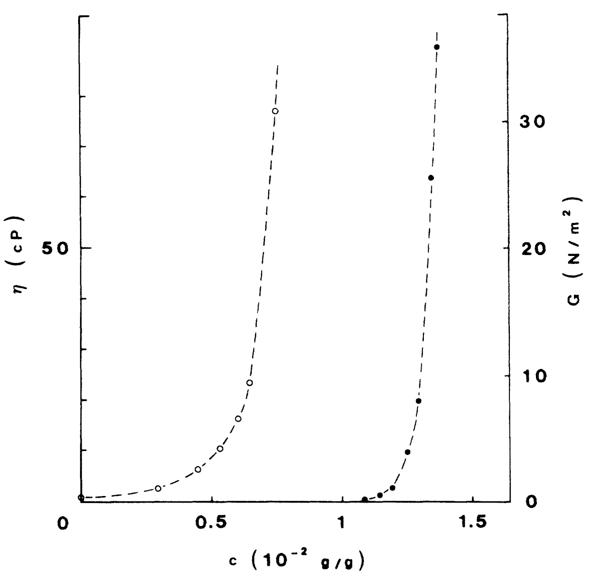

FIG. 3. Variations of the viscosity (○) and of the elastic modulus (●) vs the monomer concentration.

point is reported between $c = 0.75\times10^{-2}$ g/g and 1.1×10^{-2} g/g where the rheological quantities do not reach steady values after 50 h and where a phase segregation is observed a few days latter.

In order to get information about the rheological properties at different heights in the segregated samples, we have studied the diffusion coefficient of Brownian probes (polystyrene lattices of 91 nm in diameter), using the quasielastic light-scattering technics. First, we have measured the diffusion coefficient D in homogeneous samples in order to establish a correlation between the values of D and the rheological properties.[13] In the sol domain, D is found to be related to the viscosity η by the Stokes-Einstein's law as long as c is $<0.6\times10^{-2}$ g/g. For c between 0.6×10^{-2} and 0.75×10^{-2} g/g, D decreases less rapidly than the value deduced from η. For instance, a discrepancy of a factor of 2 is observed between these two values when $c = 0.75\times10^{-2}$ g/g; D is then of the order of 6×10^{-10} cm²/s. In the homogeneous gels prepared for $c > 1.1\times10^{-2}$ g/g, the autocorrelation function exhibits a slow decrease corresponding to values of $D \leq 3\times10^{-10}$ cm²/s. These results indicate that we can characterize the local mechanical properties in the medium from the measurement of the diffusion coefficient.

In the samples where a segregation phenomenon occurs, we find that the diffusion coefficient varies greatly with the height of the point of measurement. Figure 4 presents the results obtained on the same sample as that of Fig. 1. In the lower part ($z \leq 20$ mm), the values of D indicate that the medium has the characteristic behavior of a gel. In the upper part ($z \geq 20$ mm), the diffusion coefficient increases and the values show that the medium is a sol. It should be noted that the characteristic level above which a viscous behavior is observed, $Z \cong 20$ mm, is of the same order as the level found in the concentration variations (Fig. 1).

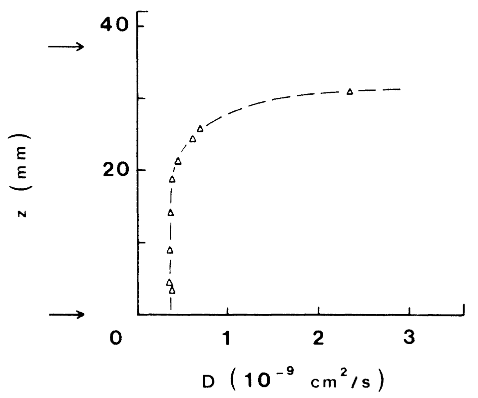

FIG. 4. Variation of the diffusion coefficient of latex probes (horizontal scales) for different values of the height in the sample (vertical scales). The experimental conditions are the same as in Fig. 1.

II. DISCUSSION

A. Gelation critical point

In order to determine whether the segregated samples belong to the sol or the gel domains of the phase diagram or whether they belong to a new domain, we have determined the critical concentrations from the variations of the viscosity and of the elastic modulus in the homogeneous samples. In that respect, we have related the behaviors of η and G (see Fig. 3) to the critical properties of the sol-gel transition which are now well established.[14,15,16,12] Power laws are expected for the rheological quantities:

$$\eta = \eta_0 \left[\frac{p_c - p}{p_c} \right]^{-\kappa}, \quad G = G_0 \left[\frac{p - p_c}{p_c} \right]^{\theta},$$

where κ and θ are the exponents which characterize the critical behaviors of the viscosity and of the elastic modulus and where η_0 and G_0 are the prefactors. The parameter p represents the fraction of links in the medium and p_c its value at the critical point. In our case, p is related to c but from the experimental variations it is not clear whether the behaviors of the viscosity and of the elastic modulus lead to a single value of the critical concentration, c_c. In practice, we fit the variations of η and G in the following manner. The experimental points are plotted as $\eta^{-1/X}$ (or $G^{1/Y}$) versus c in linear scales. When X (or Y) is equal to the exponent of the critical behavior of η (or G), the points fall on a straight line crossing the c-scale at c_c. Figure 5 illustrates the results of this procedure when applied independently to η and G. The values determined for κ and θ, which are equal to 1.5 and 7.5, respectively, cannot be compared directly with the predictions of the percolation models since the relation between p and c is unknown. The critical concentrations deduced separately from the viscosity and from the elastic modulus variations are the same. The value found for c_c, which is equal to 0.8×10^{-2} g/g, is the lowest limit of the range where segregation is observed. This establishes that there only exist sol and gel domains and that the samples with segregation all belong to the gel domain.

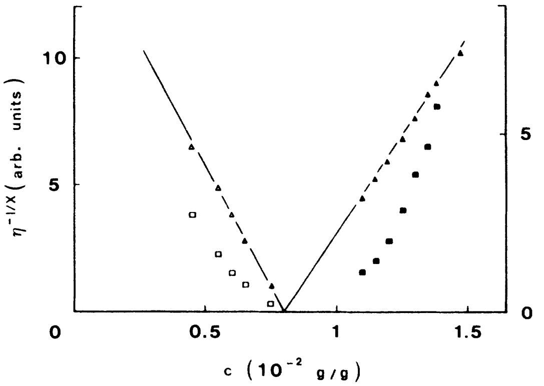

FIG. 5. Variations of $\eta^{-1/X}$ and $G^{1/Y}$ vs c for different values of X and Y. (△) $X=1.5$, (□) $X=1.0$, (▲) $Y=7.5$, (■) $Y=3.0$.

B. Kinetics of sedimentation

Gravity can influence the formation of segregated phases by different ways depending on the relative values of the characteristic sedimentation time τ_s and of the characteristic chemical time τ_c.

If $\tau_s \ll \tau_c$, the sedimentation equilibrium is reached at any time and the chemical reaction takes place in a medium where the concentration is not uniform (the monomers and the copolymers are heavier than the solvent). Since the mechanical properties depend greatly on the concentration, one expects that there exists a range of the initial concentration in monomers where the samples exhibit a viscous zone lying above an elastic part. In this scheme, the critical gelation point would be located within this range of c. This is in disagreement with our experiments which show that the segregated phases all belong to the gel domain.

Now, let us estimate τ_s and compare its value to τ_c which has been found of the order of 2×10^5 s. The sedimentation equation results form the conservation law of the solute

$$\frac{\partial\gamma}{\partial t}=-sg\frac{\partial\gamma}{\partial z}+D\frac{\partial^2\gamma}{\partial z^2}\ . \tag{1}$$

g is the gravitational acceleration, s the sedimentation coefficient, and D the cooperative diffusion coefficient. γ, the total monomer concentration at the height z, is expressed in g/g. s and D are

$$s=\frac{(1-x)m}{f},\quad D=\frac{kT}{f}\ .$$

m represents the molecular weight of the sedimenting elements and f their friction. x is the ratio of the mass density of the solvent ρ_0 to the polymer mass density ρ_p which is supposedly independent of m; x is of the order of 0.7 for the materials used here. Assuming small variations of γ, the value of f is kept independent of z. At equilibrium, the profile described by (1) involves the characteristic length Λ:

$$\Lambda=\frac{kT}{(1-x)gm}\ ,$$

and out of equilibrium the equation is governed by τ_s:

$$\tau_s=\frac{\Lambda}{sg}=\frac{kTf}{(1-x)^2g^2m^2}\ .$$

This expression can be used to calculate τ_s in various cases. First, we consider that the medium is a dilute solution of macromolecules. This is the case at the beginning of the copolymerization reaction; in addition, we find from chemical considerations[11] that $m=10^7$ g/mol. Then τ_s is approximately 10^{10} s and thus it is much larger than τ_c. For a semidilute solution, taking as a sedimenting element a blob of size 100 Å, which is the value expected for a 10^{-2} g/g polyacrylamide solution, τ_s is found to be of the order of 10^{15} s. Finally, let us consider the case of weakly concentrated gels. From permeability measurements on the same system,[15] we know that the characteristic length of the sedimenting unit is much larger than the blob size in a semidilute solution at the same concentration (by a factor of 100). Then τ_s is found to be approximately 10^5 s. In conclusion, the sedimentation process mostly occurs after the end of the chemical reaction.

To check the validity of this result, we have studied the elastic modulus at time τ_c, $G(\tau_c)$, in the samples where a segregation occurs [see Fig. 2(c)]. If the sedimentation process has no time to take place during τ_c, $G(\tau_c)$ would be independent of the height of the measurement point in the sample and would be described by the power-law variation found for G in the range of $c>1.1\times10^{-2}$ g/g. Several experiments have been performed for three different concentrations belonging to the range where a segregation occurs. In Fig. 6, we report the values of $G(\tau_c)$ for these three concentrations and the values of the

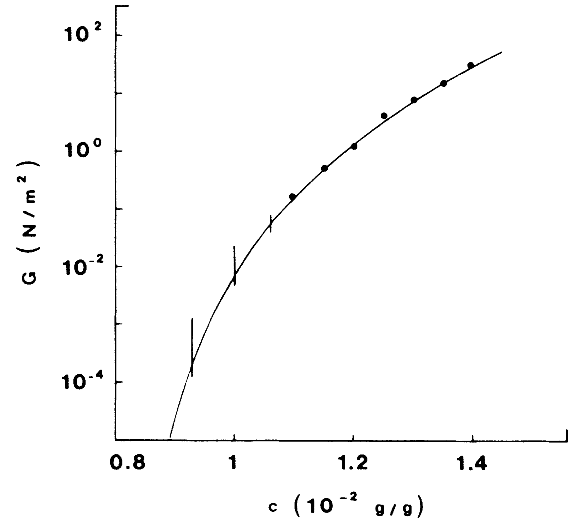

FIG. 6. Variation of the elastic modulus $G(\tau_c)$ in the domain where a segregation occurs (vertical bars), and G in the domain where homogeneous gels are formed (●) as a function of the concentration. The curve drawn as a solid line gives the power-law variation calculated from the parameters $c_c=0.8\times10^{-2}$ g/g, $Y=7.5$, and $G_0=246N/m^2$ corresponding to the best fit in Fig. 5.

elastic modulus measured in homogeneous samples. We also have indicated the power law calculated from the parameters corresponding to the best fit in Fig. 5. The large error bars observed for the samples where a segregation occurs are due to the irreproducibilities which are to be related to the difficulty of controlling very slow kinetics and to the proximity of the critical point; indeed, this greatly enhances the effect of the uncertainties on the parameters which govern the chemical reaction. We have also encountered irreproducibilities in the determination of the characteristic level Z which have the same origin. Finally, in spite of the large errors bars, we observe a good agreement between the experimental points and the power-law variation over the entire range of c; G varies over 6 decades. This result confirms the interpretation in terms of critical behavior and the fact that the segregated samples belong to the gel domain—the sedimentation taking place essentially at the end of the chemical reaction. Thus, the influence of the gravity occurs after the formation of an infinite polymer network.

C. Gravity collapse of the polymer network

Let us now determine the conditions under which a collapse of a tenuous polymer network under the gravitational field may occur. In principle, the calculation of the concentration profile can be done from the variation of the chemical potential versus the height as it was performed in the cases of gas-liquid and liquid-liquid critical points.[1,2] However, in the case of polymer gelling systems, the thermodynamic based calculations are tricky and we develop here a mechanical description.[17] At equilibrium, an element of the polymer network is submitted to three forces: its weight, the Archimedes' force, and a restoring force. For a network which does not adhere to the sides of the vessel, the vertical displacement u of an element is given by

$$(K+\tfrac{4}{3}G)\frac{\partial^2 u}{\partial z^2}-(1-x)\rho_p g=0\ , \qquad (2)$$

where K is the bulk osmotic modulus. It should be noted that contrary to the case of a global deformation of the whole medium (polymer + solvent) which would involve the elastic modulii, the deformation considered here is a relative displacement of the network with respect to the solvent and to the macromolecules of finite size—the medium keeping the same shape. From (2), we deduce that the concentration in monomers belonging to the polymer network at a height z, γ_{net}, is given by

$$\left[K+\frac{4}{3}G\right]\frac{1}{\gamma_{\text{net}}}\frac{\partial\gamma_{\text{net}}}{\partial z}+(1-x)\rho_p g\gamma_{\text{net}}=0\ . \qquad (3)$$

In a first approximation, i.e., for small variations of γ_{net} Eq. 3 involves the characteristic length Λ':

$$\Lambda'=\frac{K+4G/3}{(1-x)\rho_0 g c_{\text{net}}}\ ,$$

which is similar to the length Λ introduced previously (Sec. II B). c_{net} is the value of γ_{net} in the absence of the gravitational field.

In order to determine the importance of the gravity effects, Λ' has to be compared to the height of the sample H. If $\Lambda' \gg H$, no concentration profile occurs and the mechanical properties of the medium are independent of z. On the contrary, if $\Lambda' \leq H$ the polymer network collapses and a gravitational-induced profile of the mechanical behavior takes place. Unfortunately, the value of Λ' is difficult to calculate since the evaluation of the factors K and c_{net} is tricky. In the case of our experimental study, the bulk osmotic modulus K is lower than G or of the same order as G because there exists only few entanglements in the medium (the values of c are low). Thus Λ' varies in the same way as G/c_{net}. For a tenuous ramified structure of a given size the elastic modulus increases more slowly than its mass. For instance, the exponent which characterizes the increase of the elastic modulus of a percolation network is larger than the mass exponent.[18] Thus Λ' approaches zero as the samples are prepared nearer and nearer to the phase diagram limit. Thus, there exists a range of c where Λ' is smaller than H or of the same order as H: in that range of the gel domain a profile of the mechanical properties induced by the gravity occurs.

The measurement of the variation of γ_{net} versus z and the determination of Λ' for various concentrations would be very interesting. Unfortunatly, these measurements are difficult to achieve since we must distinguish monomers belonging to the polymer network from those belonging to the finite-size macromolecules. The refractive-index method described in Sec. I A (see Fig. 1) permits the characterization of the total monomer concentration γ. We have found a smooth variation for γ; however, it may differ from the variation of γ_{net}. Furthermore, because of the gravity-induced profile of γ_{net} we expect a variation of the mechanical properties with the height in the samples. This corresponds well to the results obtained from the diffusion coefficient of Brownian probes (see Fig. 4). In addition, although Z and Λ' are not simply related, the ways they vary are expected to be the same. Now, in all the domain of concentration where segregated samples are formed, we observe a continuous increase of Z. For instance, for samples of 60 mm in height, we find that Z is about 20 mm for $c=0.93\times10^{-2}$ g/g and the Z is about 50 mm for $c=1.0\times10^{-2}$ g/g (the irreproducibilities discussed previously lead to uncertainties of 1 cm on Z). In conclusion, all the results observed on samples in which segregation has taken place are consistent with a description in terms of gravity-induced collapse of the polymer network.

The existence of an intermediate domain of concentration within which the properties vary with the height in the sample is not universal in the sense that it depends on the nature of the gel. For instance, in the case of gels formed by addition of a crosslinking agent to a semidilute polymer solution, the bulk osmotic modulus is always larger than the elastic modulus. Then, Λ' is larger than H and the gravity has no effect on the samples near the phase diagram limit.

III. CONCLUSION

The segregated phases that we have observed in samples prepared by copolymerization of bifunctional monomers and plurifunctional monomers have been found to be gel phases in which the gravitational field induces a collapse. Furthermore, we have shown that in the case of our experiments, the sedimentation essentially occurs at the end of the chemical process. Theoretical and experimental studies of situations where growth and sedimentation are coupled would be of great interest. The influence of the gravitational field is not universal since it depends on the gelling system: the action of the gravity forces on the network is counterbalanced not only by the elastic modulus but also by the bulk osmotic modulus, the value of which can be drastically different depending on the physicochemical system. Such gravity effects are expected in many systems involving weakly connected networks.

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