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Deuterium-NMR study of microscopic effects in collapsing polyacrylamide gels

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Deuterium-NMR spectra and relaxation measurements for selectively deuterated acrylamide units in polyacrylamide (PA) gels exhibiting collapse transitions are presented. The main aim of the present study is to investigate the microscopic dynamics of the segmental units of the polymer network while the entire gel is approaching the collapse transition accompanied by the critical long-wavelength diffusivelike excitations. The D nucleus, with the electric quadrupole interaction, is directly sensitive to the chain dynamics because of the random modulations of the electric-field-gradient components in the frame of reference of the external field, induced by the motion of the monomer axes. From the analysis of the spectra and of the relaxation rates, it is shown how, while the macroscopic motions exhibit critical slowing down, the dynamics of the segmental units is described by practically isotropic local modes, weakly coupled to the density fluctuations of the PA network. Quantitative estimates of the effective correlation times are given.

I. INTRODUCTION

The polyacrylamide (PA) gels consist of a cross-linked polymer network (obtained through polymerization of acrylamide) with water trapped among the chains. The early studies by Tanaka and collaborators[1] pointed out the remarkable properties of these gels, particularly their collapse transition. By changing external conditions such as temperature, electric field, or acetone concentration in the medium, the PA gels undergo a volume phase transition with sizable, continuous, and reversible changes in volume, associated with swelling or shrinking processes. The collapse transition corresponds to the kinetics of the phase separation in binary mixtures or to the spinodal decomposition; PA gels appear to be the prototype of other systems, such as synthetic polyvinyl gels or DNA, polysaccharide, polypeptide gels showing analogous phenomena. Universality concepts, formerly developed for simple fluids or magnets at phase transitions and then extended to long-chain polymer solutions,[2] appear suited to describe PA gels at the collapse transition. In particular, dynamic light-scattering experiments[3-7] indicated critical divergence and slowing down of the concentration fluctuations of the polymer network, which are rather successfully described by hydrodynamic-type approaches.

The studies of phase transition in crystals and in magnetic systems have shown how the thermodynamical effects are accompanied by microscopic critical dynamics. In the case of PA gels, the light-scattering (LS) experiments investigate the long-wave length ($q \approx 0$) excitations and can hardly probe the microscopic dynamics of the polymer network. Inelastic neutron scattering (NS), in principle, can study the dynamical response of the system for selected wave vectors q, so as to span from the $q \approx 0$ region of LS up to q values corresponding to a few monomer units along the polymer chains. However, energy resolution down to the MHz region of the fluctuations cannot be achieved in conventional triple-axes NS spectrometers. High-resolution experiments have been carried out at the quasielastic high-resolution inelastic spectrometer (IRIS) inverse backscattering spectrometer in polysaccharide gels.[8] The effective correlation times for the water have been obtained at different temperatures, yielding values from 5×10^{-11} to 10^{-11} s (for q in the range 0.5–1.5 Å^{-1}), higher by a factor of 10–40 than the corresponding correlation time for pure H_2O. A direct study of the polymer chains was not possible, in view of the limited contribution from the network to the dynamical structure factor.

A successful experimental approach to the study of the microscopic local dynamics at the phase transitions in crystals or in magnetic systems has been nuclear magnetic relaxation (NMR).[9] In gels one can expect that the segmental motions of the monomer units of the network be reflected in the relaxation rate. A few NMR experiments in noncollapsing gels have been carried out up to now, in agarose gels for different water contents[10] or at the sol-gel transition in gelatin[11] that is most used in the study of the properties of the fluid. In particular, the ratio T_2/T_1 for the water has been considered in terms of possible fractal-like effects.[12] Proton spin-lattice relaxation and NMR diffusion constant measurements in PA gels undergoing collapse transitions have been also reported.[13]

In this paper we present the results of a D-NMR study of the polymer chains dynamics, carried out in deuterated PA gels, at various resonant frequencies. The selective deuteration of the CH_2-CH groups of the acrylamide units yields a local probe (the D nucleus with the electric quadrupole interaction) that is directly sensitive to the segmental chain dynamics. In fact the D quadrupole relaxation is driven by the random modulations of the electric-field-gradient (EFG) components V_{jk} (in the frame of reference of the external magnetic field H) when the monomer unit of the chain locally rotates or reorients the frame of reference of the principal axis of the static EFG tensor. Substituting the protons of the PA chain with deuterons also has the technical advantages of improving the resolution conditions, avoiding the superposition of signals arising from protons being exchanged or from residual protons in the deuterated liquids (water or acetone) of the medium. The only problem associated with such an experimental approach is the weakness of the signal: this could be circumvented by integration techniques, under conditions of high stability for the phase of the receiver and of the magnetic field.

The paper is organized as follows. In Sec. II the experimental results are presented for the quadrupole-perturbed D-NMR spectrum of solid acrylamide (from which the estimate of the EFG tensor at the deuteron sites is obtained) and for D spectra and relaxation times for gels along the collapse curve, by adding acetone up to about 70% in the fluid, at constant temperature. For the sake of completeness a few other results obtained for ordinary (nondeuterated) gels with deuterated water and acetone are also recalled. In Sec. III we discuss the motional averaging of the spectra and the D relaxation rates, as resulting from some possible descriptions for the segmental motions, and by considering the expected changeover along the collapse curve. Summarizing remarks and conclusions are briefly presented in Sec. IV.

II. EXPERIMENTAL DETAILS AND RESULTS

A. Experiment

D3-acrylamide CD_2-CD-$CONH_2$ (Cambridge Isotope Laboratories), with a deuteration degree of 98%, was used. After removal of the inhibitor, the PA gels, with ordinary water, were prepared by following standard procedures.[5] Some gels were left swollen as resulting from the formation (R gels), while others were dried for about 2 days at 30 °C and then swollen by addition of H_2O. The gels can be considered zero hydrolyzed (ZH) when only a limited degree of spontaneous ionization, due to preparation and thermal effects, is present. After several months from the preparation it was noticed that the R gels could be further swollen; thus some spontaneous hydrolysis had occurred and this can affect the degree of the collapse transition[3-6] (from second order for ZH to a marked first order in the case of strong hydrolysis). Other ZH gels were prepared with ordinary acrylamide, with D_2O and eventually deuterated acetone, and used to study the condition of the liquid medium.

The D-NMR measurements were carried out by means of a Bruker MSL 200 pulse spectrometer. The constant field H_0, provided by the Oxford Superconducting Magnet, was set to about 5.86 T, corresponding to the measuring D-NMR frequency of about 38 330 kHz. For the measurements at lower frequency a standard Jeol electromagnet was used. The strength of the rf field H_1 could be increased up to about 100 G.

For the D-NMR spectrum in solid acrylamide the quadrupolar echo technique[14] $[(90)_x\text{-}\tau\text{-}(90)_y]$ was used. After acquisition of the echo signal at 2τ (τ was set at 60 μs, while the pulse length used was typically 3 μs) Fourier transform (FT) yielded the quadrupole-broadened powder spectrum of deuterons in acrylamide. From this spectrum an order-of-magnitude estimate for the electric-field gradient component V_{ZZ} in the frame of reference of the principal axes of the tensor was obtained, as explained below.

In gels the free-induction decay (FID) can directly be detected, the recovery time of the spectrometer being around 5–10 μs (for a 90° pulse width around 5 μs). The FT directly gives the D spectra in the gels.

The T_1 relaxation measurements have been carried out by monitoring the recovery of the D nuclear magnetization from the height of the FID following the 90° pulse, after a saturating pulse. The recovery of the magnetization was occasionally also detected by measuring the height of the Zeeman echo signal,[14] which in the case of the narrow lines is mostly related to the inhomogeneity of the constant magnetic field. The T_1's measured in the two cases were practically the same. Above the collapse, where the D-NMR signals are broader, the Zeeman echo was no longer detected (the decay of the transverse magnetization being irreversible), and the recovery of the FID signal was used to measure T_1.

The T_2 measurements were obtained from the decay of the Zeeman echo in the R gel and for concentrations of acetone up to about 50%. For broader lines, where the Zeeman echo was hardly detectable, T_2 was estimated from the dephasing time of the FID signal, which is directly related to the relaxation function for the transverse D magnetization.

All the measurements were performed at room temperature, without thermal stabilization (this could be responsible for some differences observed in the relaxation rates, in different runs, around the collapse condition).

B. Quadrupole-perturbed D-NMR spectrum in acrylamide

In Fig. 1(a) the D-NMR spectrum of solid acrylamide, obtained from a FT of half of the quadrupolar echo signal, is shown. The spectrum evidences the static perturbative effects of the quadrupole interaction on the Zeeman levels. A quantitative analysis of these effects in acrylamide is out of the scope of the present work. We only observe that the spectrum is qualitatively in agreement with the quadrupole effects expected for the deuterons in the CD_2 and CD groups. In fact the D spectrum results from the distributions of two symmetric satellites, corresponding to the $\pm 1 \leftrightarrow 0$ transitions. For deuterons in the CD_2 groups, from the results in malonic acid[15] and in solid glycine[16] one expects $e^2 q \Omega / h \approx 166$ kHz and asymmetry parameter of the EFG close to zero, while for the CD one should have values around 180 kHz and 0.1, respectively, as indicated by a series of measurements for ring deuterons in benzene derivatives.

In light of the spectrum in Fig. 1(a) and of the above considerations, one can assume for an order-of-magnitude estimate of the EFG at the deuteron site in the

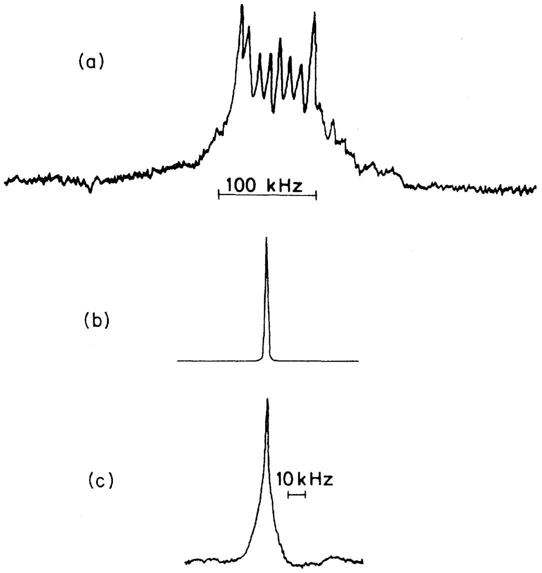

FIG. 1. (a) D-NMR spectrum for solid acrylamide, obtained through FT of the quadrupolar echo, at $\nu_L \cong 9700$ kHz. (b) D-NMR line in the reference PA gel (left swollen as obtained) at $\nu_L \cong 38\,330$ kHz, showing practically only the linewidth due to the inhomogeneity of the field. (c) D-NMR spectrum, obtained for an almost totally collapsed PA gel (concentration of acetone in the fluid $c_A \geq 60\%$), from FT of the FID signal, again at $\nu_L = 38\,330$ kHz.

chains of the PA gels an average value of the quadrupole coupling constant $\omega_Q = e^2qQ/h \approx 2\pi \times 170$ kHz and asymmetry parameter close to zero.

C. D-NMR spectra in PA gels

In the presence of complicated and possibly anisotropic motions of the segmental units of the PA chains in the gels, the analysis of the D-NMR line shape is expected to yield information on the mechanisms and the rates of such motions.[17] Anisotropic motions should cause an only partial average of the EFG components V_{JK} of the static tensor in its frame of reference, leading to a residual EFG tensor $(V_{JK})_{\text{res}}$. The distribution with respect to the magnetic field H_0 of the axes of $(V_{JK})_{\text{res}}$ gives broadening and structure of the D-NMR line.

As appears from Fig. 1(b), the NMR spectrum for the deuterons of the CD_2 and CD groups in the PA chains, in the *R* gel, shows a single, very narrow line. No residual, staticlike quadrupole effects are observable. This remarkable observation points out that, in spite of the restrictions related to the cross linking of the PA chains (due to the bis-acrylamide), in times shorter than about 10^{-6} s the monomer axes can take a practically isotropic distribution, leading to the zero-order parameter. Only for a gel well above the critical concentration of acetone for the collapse (about 42%), is a significant broadening of the D-NMR line observed [see Fig. 1(c)]: the spectrum appears to be a superposition of a narrow line and a broad one. The narrow line can be attributed to the deuterons of the CD_2 group, where fast reorientations about the twofold axis should still occur.

The broad line, mostly from the CD group, reflects the occurrence of a residual $(V_{JK})_{\text{res}}$ and/or a slowing down of the rate of the motions towards the rigid-lattice condition. For the moment we only remark that in the assumption of a Gaussian line shape, from the width of the broad component of the line in Fig. 1(c), one estimates a spin-spin relaxation rate of the order of $T_2^{-1} \approx 3 \times 10^4$ s^{-1}.

D. D relaxation rates

The spin-lattice recovery plots in the *R* gels can be fitted as the superposition of two exponentials, with coefficients 2/3 and 1/3, yielding two effective time constants $(T_1)_{2/3}$ and $(T_1)_{1/3}$. Correspondingly the echo signal following a $(\pi/2,\pi)$ sequence of rf pulses exhibits a fast decaying component and a slowly decaying one.

On the basis of the coefficients of the two exponentials in the recovery plot one should consider $(T_1)_{2/3}$ as the average relaxation time of the deuterons of the CD_2 groups, while $(T_1)_{1/3}$ pertains to the CD groups. Then, for the *R* gel at room temperature, $(T_1)_{CD_2} = 3.6 \times 10^{-3}$ s and $(T_1)_{CD} = 1.4 \times 10^{-1}$ s, while from the decay of the echo $(T_2)_{CD_2} = 2.6 \times 10^{-3}$ s and $(T_2)_{CD} = 0.7 \times 10^{-1}$ s.

One should remark that the detectability of separate time constants in the recovery plots indicates that a common spin temperature does not occur. This is consistent with the small dipolar interaction between the deuterons of the two groups. The relaxation rates of the CD_2 deuterons should be due mostly to the 180° flipping motion around the twofold axis. From the value of $(T_1)_{CD_2}$, by using for the relaxation rate the expression for liquids[18] $T_1^{-1} = T_2^{-1} = \frac{3}{8}\omega_Q^2\tau_c$ from the experimental values given above, by taking for ω_Q the value estimated in Sec. II B, one derives a correlation time for the flipping motion around $\tau_c = 6.5 \times 10^{-10}$ s.

The relaxation rate of the CD deuteron reflects the time dependence of the V_{JK}^H components induced by the motion of the segmental units of the chains, as will be discussed in Sec. III. In Fig. 2 we report the behaviors of the deuterons' relaxation along the collapse curve. The CD_2 relaxation rates appear slightly affected by the collapse. Only for concentration of acetone c_A much larger than the critical one, is a decrease of T_1^{-1} by a factor around 2 observed, as a possible consequence of the modification of the potential barrier for the flipping motion under strong shrinking of the gel. One can mention that the behavior of the D relaxation rates as a function of c_A is similar to the one detected in high-resolution proton NMR for the CH_2 group at 300 MHz.[19] Also the order of magnitude of the proton relaxation rate measured in the *R* gel[19] can consistently be justified if one uses for the correlation time the value $\tau_c = 6.5 \times 10^{-10}$ s derived from the results for deuterons. In fact one can write,[18] in that case,

$$T_1^{-1} = \omega_d^2[J(\omega_L) + 4J(2\omega_L)]\ ,$$

and by using for the spectral density the simple expression $J(\omega)=2\tau_c/(1+\omega^2\tau_c^2)$ and for the strength of the dipolar interaction $H_d=\omega_d/\gamma$, a value $H_d=\mu_H/d^3\cong 2G$ (d, H-H distance), one expects for the proton relaxation rate, as due to the flipping motion, at $\omega_L=2\pi\times$ 300 MHz, the value $T_1^{-1}=3.5\ \mathrm{s}^{-1}$, in satisfactory agreement with the experimental value[19] $T_1^{-1}\cong 3\ \mathrm{s}^{-1}$. We will no longer discuss the data pertaining to the CD_2 deuterons, while we discuss extensively in Sec. III the relaxation mechanism due to the reorientation of the axis of the segmental unit of the PA chain with respect to $\mathbf{H}_0$, which is effective for the CD deuteron.

E. Other miscellaneous results

A few measurements of other NMR quantities in the PA gels that are useful for the discussion are briefly mentioned in the following.

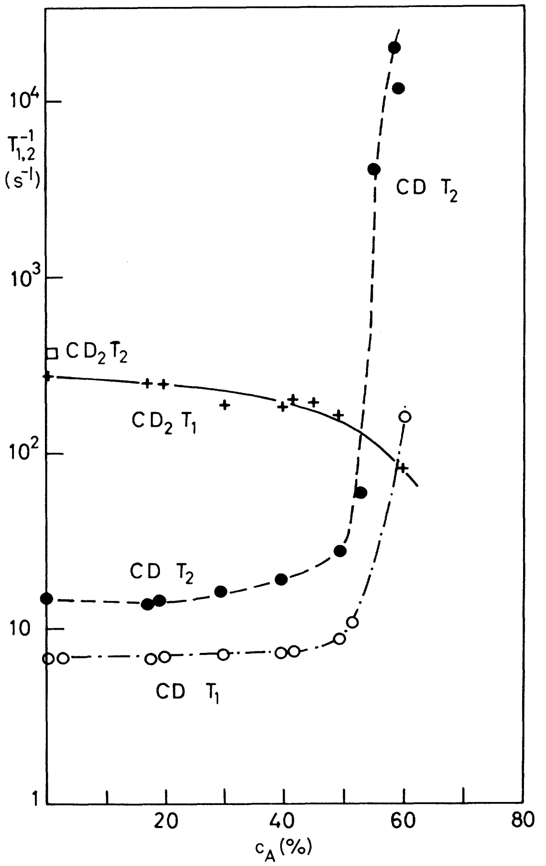

FIG. 2. Relaxation rate of the deuterons of the PA chains as a function of the acetone concentration. The lines are guides for the eye and refer to —·—·—·, T_1^{-1} for the CD group; — — —, T_2^{-1} for the CD group; ——, T_1^{-1} for the CD_2 group. The critical concentration is expected around 42% , the gel being almost zero hydrolyzed (Refs. 4 and 13). The data reported in the figure refer to the measuring frequency $\nu_L\cong 38$ MHz. For $c_A\cong 0\%$ and $c_A\cong 50\%$, the measurements performed at $\nu_L\cong 11$ MHz show no sizable frequency dependence, within experimental error.

The deuteron spin-lattice relaxation of D_2O in ordinary PA gel (with CH_2-CH units in the chain) was measured $T_1\cong 0.4$ s, close to the value $T_1\cong 0.45$ s in pure D_2O and in mixtures D_2O-H_2O.[20] The diffusion constant of the water in the gel, measured from the NMR echo attenuation in the presence of the gradient of the magnetic field, is $D\cong 2.25\times 10^{-5}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$, also close to the value for pure D_2O.

Thus one is led to the conclusion that the dynamical status of the large part of the water trapped among the PA chains in the R gel is practically the same as the free liquid. Only a thin layer of water bound to the "surface" of the gel can exhibit different NMR behavior, as has been shown from the ratio T_2/T_1 for protons in blood plasma gels, evidencing fractal-like effects.[12] Furthermore one should stress that the D relaxation rates for D_2O did not show large variations up to concentrations of acetone above the critical one, evidencing that the microscopic motions of the fluid are largely independent by the dynamics and the progressive shrinking of the polymer chains.

III. ANALYSIS OF THE D RELAXATION RATES ALONG THE COLLAPSE CURVE

In Fig. 2 one notes the following relevant features: (i) T_1^{-1} and T_2^{-1} do not show a strong variation on approaching the critical concentation c_A^{crit}; (ii) the ratio T_2/T_1 is almost constant for $c_A\le c_A^{\text{crit}}$; (iii) only well above the collapse a dramatic divergence in T_2^{-1} and, to a less extent, in T_1^{-1} occurs and then the ratio T_2/T_1 changes significantly.

The relaxation process of the CD deuteron is mostly driven by the time dependence of the V_{JK}^H components in the frame of reference of the magnetic field induced by the motions of the Σ^P frame of reference of V_{JK}^P.

According to the evaluation of the static EFG tensor given in Sec. III B one can assume $V_{ZZ}^P=eq=\hbar\omega_Q/eQ$ and $V_{XX}^P=V_{YY}^P=-\hbar\omega_Q/2eQ$ with $\omega_Q=2\pi\times 170$ kHz. The D relaxation rates can be written[18]

$$1/T_1=\tfrac{1}{8}(e^2Q^2/\hbar^2)[J_1(\omega_L)+4J_2(2\omega_L)] \tag{1a}$$

and

$$1/T_2=\tfrac{1}{32}(e^2Q^2/\hbar^2)[9J_0(0)+10J_1(\omega_L)+4J_2(2\omega_L)]\ , \tag{1b}$$

where J_α are the spectral densities for the correlation functions of V_0, V_1, and V_2, these latter ones being the EFG functions $V_0=V_{zz}^H$, $V_1=(V_{xz}^H-iV_{yz}^H)$, and $V_2=\frac{1}{2}(V_{xx}^H-V_{yy}^H)-iV_{xy}^H$. One obtains

$$J_\alpha(\omega)=\langle |V_\alpha|^2\rangle \int e^{-i\omega t}g_\alpha(t)dt\ ,$$

where $g_\alpha(t)$ are the normalized correlation functions for V_α ($\alpha=0,1,2$) and $\langle |V_\alpha|^2\rangle$ the ensemble averages. By writing the V_{jk}^H components as a function of V_{JK}^P through the Euler angles specifying the orientation of Σ^P with respect to Σ^H, for our case one obtains[18,20] $\langle |V_1|^2\rangle=\langle |V_2^2|\rangle=3V_{ZZ}^2/10$ and $\langle |V_0|^2\rangle=\frac{3}{15}V_{ZZ}^2$. Then, Eqs. (1) can be rewritten

$$1/T_1=\tfrac{3}{80}\omega_Q^2[J(\omega_L)+4J(2\omega_L)]\ , \qquad (2a)$$

$$1/T_2=\tfrac{3}{160}\omega_Q^2[3J(0)+5J(\omega_L)+2J(2\omega_L)]\ , \qquad (2b)$$

where, in view of the isotropic distribution of the chains with respect to $\mathbf{H}_0$ we have introduced a single spectral density $J(\omega)$, which can be thought to involve the correlation function $\langle \mathbf{n}(0)\mathbf{n}(t)\rangle$ of a unit vector $\mathbf{n}$ describing the random motions of a segmental unit.

One can remark that the condition of fast motions compared to ω_L, yielding the usual simplifications $J(\omega_L)\cong J(2\omega_L)\cong J(0)$ in nonviscous liquids,[18] does not necessarily hold in PA gels. In fact, for the long-wavelength components of the collective excitations, the hydrodynamic result for the decay rate of the fluctuations, namely $\Gamma_q \cong Dq^2$, can be used, with D collective diffusivity of the gel. By considering for the minimum wave vector, a value around $q_{\min}\cong 2\pi/(2dn)\cong 3\times 10^6$ cm^{-1} (d is the length of the segmental unit, n is the average number of monomers between links), and for D values[21] around 10^{-7} cm^2 s^{-1}, one estimates $\Gamma_{\min}$ in the MHz range. Therefore in the evaluation of the spectral densities in Eqs. (2), in principle one has to retain the full frequency dependence.

In view of the complex features of the segmental dynamics one can specialize $J(\omega)$ only through rather drastic assumptions and by extending models of motions that have been proven suitable for similar circumstances or systems. In particular, one can try to extend the picture[2] for concentration fluctuations of macroscopic character, as used in the interpretations of light-scattering experiments. Thus one can tentatively assume for $J(\omega)$ a superposition of Lorentzian-like functions, each with a characteristic frequency Γ_q, describing the density fluctuations in the PA network in the form of overdamped phonons. The frequencies Γ_q should go[2] as

$$\Gamma_q=\begin{cases} Dq^2 & \text{for } 0\le q\le q_F\ ,\\ Dq^3/q_F & \text{for } q\ge q_F\ ,\end{cases} \qquad (3)$$

where $q_F\cong R_F^{-1}$ (R_F is the Flory radius) and D is the cooperative diffusion constant. In this way, by integrating over $\mathbf{q}$ the spectral densities in Eqs. (2), one obtains

$$T_1^{-1}=\frac{3}{80}\frac{\omega_Q^2}{Dq_m^3}\left[30q_F-12\sqrt{2}K\left\{\frac{1}{16}\ln\frac{q_F^2+\sqrt{2}Kq_F+K^2}{q_F^2-\sqrt{2}Kq_F+K^2}+\frac{1}{2\sqrt{2}}\ln\frac{q_F^2+2Kq_F+2K^2}{q_F^2-2Kq_F+2K^2}+\frac{1}{8}\arctan\frac{\sqrt{2}Kq_F}{K^2-q_F^2}\right.\right.$$
$$\left.\left.+\frac{1}{\sqrt{2}}\arctan\frac{Kq_F}{2K^2-q_F^2}\right\}+q_F\ln\frac{(q_m^6+q_F^2K^4)(q_m^6+4q_F^2K^4)}{(q_F^6+q_F^2K^4)(q_F^6+4q_F^2K^4)}\right]\ , \qquad (4a)$$

with $K=(\omega_L/D)^{1/2}$ and

$$T_2^{-1}=\frac{3}{160}\frac{\omega_Q^2}{Dq_m^3}\left[30q_F-4\sqrt{2}K\left\{\frac{5}{16}\ln\frac{q_F^2+\sqrt{2}Kq_F+K^2}{q_F^2-\sqrt{2}Kq_F+K^2}+\frac{1}{4\sqrt{2}}\ln\frac{q_F^2+2Kq_F+2K^2}{q_F^2-2Kq_F+2K^2}+\frac{1}{16}\arctan\frac{\sqrt{2}Kq_F}{K^2-q_F^2}\right.\right.$$
$$\left.+\frac{5}{\sqrt{2}}\arctan\frac{Kq_F}{2K^2-q_F^2}\right\}+q_F\left[5\ln\frac{q_m^6+q_F^2K^4}{q_F^6+q_F^2K^4}+2\ln\frac{q_m^6+4q_F^2K^4}{q_F^6+4q_F^2K^4}\right]$$
$$\left.+6q_F\left[1+\ln\frac{q_m}{q_F}\right]\right]\ . \qquad (4b)$$

In the limit $\omega_L\rightarrow 0$, Eqs. (4) reduce to the ones already considered for the dipolar relaxation mechanism.[13] The frequency dependence of the relaxation rate expected on the basis of Eqs. (4) is rather steep for $\omega_L\le 2\pi\times 10$ MHz, for $D\cong 10^{-7}$ cm^2 s^{-1} corresponding to K less than the maximum wave vector $q_{\max}\cong \pi/2d$. However, for $\omega_L\ge 2\pi\times 10$ MHz the ω_L dependence of the relaxation rate is weak, roughly of the form $T_1^{-1}\propto \omega_L^{-1/2}$. This is the result of the broad distribution of the effective correlation frequencies Γ_q.

A test of the applicability of Eqs. (4) on the basis of the measurements at various frequencies is hard to carry out for practical reasons: for deuterium ν_L cannot be increased above ≈ 40 MHz, while at low frequencies the signal-to-noise ratio becomes severe, even for a large number of acquisitions. Measurements carried out at $\nu_L\approx 11$ MHz, for $c_A\approx 0\%$ and $c_A\approx 50\%$ do not show appreciable variations with respect to the data $\nu_L=38$ MHz (see Fig. 2). A more realistic test is based on the concentration dependence along the collapse curve. On approaching c_A^{crit} one expects[4] the diffusion constant D $[D]$ to decrease roughly as $[D]\propto |c_A-c_A^{\text{crit}}|$ as a result of the critical slowing down of the density fluctuations in the gel network. No evidence of a sizeable dependence of the relaxation rates on approaching c_A^{crit} from below is observed (see Fig. 2). For T_1 the lack of this dependence could be due to a compensation of effects of the modes having $\Gamma_q\ge\omega_L$ and these with $\Gamma_q\le\omega_L$. T_2 should reflect the slowing down of the decay rate. In fact, from Eqs. 2(b) and 4(b), by considering only the term in $J(0)$ that should dominate around the collapse, one can write

$$T_2^{-1}\cong\tfrac{3}{160}\omega_Q^2J(0)\cong\tfrac{9}{16}(q_F/Dq_m^3)\omega_Q^2\ . \qquad (5)$$

No evidence of such a divergent term is observed in the experimental data, the ratio T_2/T_1 remaining practically the same for $c_A \approx c_A^{\text{crit}}$. One is led to the conclusion that the picture of overdamped modes cannot be extended to include the high wave-vector excitations, even though the proper modification in the dispersion relation $\Gamma_q = \Gamma_q(q)$ is taken into account [see eq. (3)]. In other words, the motions of a subunit of the PA chains cannot be considered the integrated effect of all the q modes, which for $q \cong 0$ exhibit critical slowing down. This conclusion, joined to the observation of a D-NMR line indicating isotropic motions, suggests that local modes, weakly coupled to the density fluctuations of the PA network, describe the dynamics of the segmental units. In terms of wave vectors the local modes can be thought of as having q of the order of the inverse monomer length and this causes the most effective variations in the EFG functions. Therefore for the analysis of the behavior of the relaxation rate along the collapse we turn to a local model, suggested by an analogous description for the relaxation mechanism in polymer solutions[22,23] and corresponding to the diffusion of bond orientations along the PA chain. The spectral density involves correlation times for three-bond jumps and for isotropic subchain motions[22,23] and from the optimization of the parameters in polymer solutions, a single effective correlation time τ_e can be introduced.[23,19] Then

$$J(\omega) = \tau_e\{[\sqrt{5}(p+1)^{1/2}(9+p)/10p] - 1\}/10 , \qquad (6)$$

with $p^2 = 1 + \omega^2\tau_e^2$. In view of the slight, if any, frequency dependence observed for $\nu_L \leq 38$ MHz one deduces $p \approx 1$. Therefore in Eqs. (2) one can assume $J(\omega) = J(0) \approx 0.2\tau_e$ and $T_1^{-1} \approx \frac{3}{80}\omega_Q^2\tau_e$, which fits the experimental data in Fig. 2 for $\tau_e \approx 2\times10^{-10}$ s, a value consistent with the ones measured in polymer solutions.

In this simple picture of local conformational motions, unaffected by the critical density fluctuations, one can justify the insensitivity of the relaxation rates on approaching c_A^{crit}. For $c_A > c_A^{\text{crit}}$, possibly as a consequence of the shrinking, the effective correlation time τ_e becomes longer, the relaxation rates increase, and the ratio T_1/T_2 changes strongly, in view of the presence of $J(0) > J(\omega_L)$ in Eq. (2b). In particular the maximum value of T_1^{-1} is obtained for $\tau_e \approx 1.73/\omega_L$ yielding $(T_1^{-1})_{\max} \approx 200\ \text{s}^{-1}$, in substantial agreement with the experimental findings. T_2^{-1} continues to diverge until τ_e reaches the value ω_Q^{-1}, namely in the slow-motion regime where motional narrowing occurs and Eq. 2(b), based on the weak-collisions approach, would lose its validity; for $\tau_e \geq \omega_Q^{-1}$ the linewidth reaches the rigid-lattice condition. The maximum value of T_2^{-1} is expected around $T_2^{-1} \cong 9\omega_Q/160 \cong 6\times10^4\ \text{s}^{-1}$. The sizeable, but not total, broadening of the linewidth observed for $c_A \cong 60\%$ [see Fig. 1(c)], where $T_2^{-1} \cong 2\times10^{-4}\ \text{s}^{-1}$, also supports the above estimates.

IV. SUMMARIZING REMARKS AND CONCLUSIONS

In the PA gels the medium is essentially in the condition of a free liquid, the relaxation times and the diffusion constant being practically equal to the ones in ordinary water. This is true up to concentrations of acetone of around 55%.

While the macroscopiclike motions of the gel, corresponding to diffusional $q \cong 0$ excitations of hydrodynamical character, exhibit slowing down and critical behavior on approaching the collapse, the microscopic motions of the segmental units of the PA chains do not show critical effects. The relaxation rates (an average of a possible distribution) are at relatively high frequency and stay practically constant along the collapse. The dynamics of the segmental units is described by practically isotropic local modes weakly coupled to the density fluctuations of the PA network.

Above the collapse, possibly as a consequence of the shrinking, the effective correlation time of the local conformational modes becomes longer and the components of the spectral density at low frequency dominate.

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