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Slow dynamics in transient polyelectrolyte hydrogels formed by self-assembly of block copolymers

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Transient polyelectrolyte hydrogels were formed by self-assembly of triblock copolyelectrolytes with a central hydrophilic block, poly(acrylic acid) (PAA), and two hydrophobic end blocks, poly(n-butyl acrylate$_{50\%}$-*stat*-acrylic acid$_{50\%}$) [P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)]. The relaxation of the concentration fluctuations was investigated by dynamic light scattering as a function of the concentration, the pH, the temperature, and the ionic strength. A relatively fast mode was observed at all polymer concentrations caused by cooperative diffusion of the polymers. Above the critical percolation concentration a second slow relaxation mode was observed caused by a linear displacement of small heterogeneities in the network with constant velocity. The relative amplitude of the slow mode was determined by the strength of the electrostatic repulsion. The velocity of the displacement in the transient network is shown to be directly correlated to the terminal relaxation time of the shear modulus and has the same Arrhenius temperature dependence. Both the velocity of the displacement and the mechanical relaxation strongly slow down with decreasing degree of ionization below 0.7 and increasing ionic strength above 0.5 M. A ballistic relaxation process has been reported earlier for colloidal gels, and the present study shows that it can also occur in polymeric networks.

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I. INTRODUCTION

Triblock (BAB) copolymers self-assemble when dissolved in a selective solvent for the A blocks above the critical aggregation concentration (CAC). In dilute solution flower-like micelles are formed consisting of solvophobic cores of B blocks surrounded by a solvated corona of A blocks. A further increase of the concentration leads to bridging of flower-like micelles into larger aggregates [1–6]. The aggregates grow in size with increasing concentration until at the critical percolation concentration (C_p) a system spanning transient network is formed [7–9]; see Fig. 1.

The viscosity (η) increases strongly close to C_p and is controlled by the lifetime of the bridges that form the network, which depends on the exchange rate of the B blocks between multiplets. Fast exchange rates were found when the B blocks are very short [5,10–16] or not very solvophobic [17–20]. However, the majority of self-assembled block copolymers have extremely slow exchange rates and are in practice kinetically frozen [13,21–27].

One way to render these systems dynamic is to incorporate hydrophilic units within the hydrophobic blocks [28–35]. We have studied the effect of incorporating acrylic acid (AA) within the poly(n-butyl acrylate) B block of the triblock P(nBA-*stat*-AA)-*b*-PAA-*b*-P(nBA-*stat*-AA) [36–39]. We have found that incorporation of 50 mol % of AA in the B block led to the formation of dynamic transient networks with a characteristic relaxation time that could be tuned between 10^{-3} and 10^{8} s by varying the average degree of ionization (α) of all AA units between 0.90 and 0.10, corresponding to a change of the pH between 8 and 4 [37]. The extremely slow relaxation time at $\alpha = 0.20$ means that the systems behaved as covalently bound hydrogels. Nevertheless the systems reached thermodynamic equilibrium, because freezing-in of the exchange occurred progressively over a period of hours [37].

We used static light scattering to investigate the structure of self-assemblies formed by these triblock copolyelectrolytes as a function of C, α, and ionic strength and compared it to that formed by the equivalent diblock copolyelectrolyte [38]. At very low concentrations we observed the formation of star- or flower-like micelles, respectively for diblocks or triblocks. With increasing concentration, bridging of the flower-like micelles led to aggregation and consequently to an increase of the scattering intensity until, above about 10 g/L, repulsive interactions between the coronas dominated the effect of bridging leading to a decrease of the intensity when the concentration was further increased. In the case of diblock copolymers only repulsive interactions between the star-like micelles were observed. Increasing the ionic strength or decreasing α caused an increase of the effective attraction for triblocks and at high ionic strengths macroscopic phase separation was observed. The results could be quantitatively described by modelling the flower-like micelles as sticky hard spheres, which was earlier done successfully for neutral triblock copolymers [2,5].

The relaxation of concentration fluctuations can be investigated by dynamic light scattering (DLS) [40] through the measurement of the intensity autocorrelation function. In binary solutions the relaxation is caused by cooperative diffusion that is driven by the osmotic modulus. However, for viscoelastic solutions such as entangled polymers or transient networks, one also needs to consider the elastic modulus [41–44]. If the relaxation of the latter is much slower than the cooperative diffusion, then a second slow relaxation mode is expected independent of scattering wave vector (q) and directly related to the mechanical relaxation. The relative amplitude of the slow mode is determined by the relative strength of the osmotic and the elastic modulus. A q-independent slow mode has indeed been observed for transient gels formed by entangled semidilute polymer solutions [45,46], self-assembled triblock

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FIG. 1. Schematic representation of the aggregation for amphiphilic triblock BAB copolymers. The associating blocks B are represented in black, and the solvophilic block A in gray.

copolymers [4,47–51], and emulsions of small droplets connected by triblock copolymers [52–54]. However, slow modes with relaxation times inversely proportional to q^2 have also been observed and have been attributed to the diffusion of clusters or large scale heterogeneities [4,49,50].

In a previous light scattering study of P(nBA-*stat*-AA)-*b*-PAA-*b*-P(nBA-*stat*-AA) in aqueous solutions we focused on the fast relaxation mode due to cooperative diffusion (D_c) [38]. We showed that at low concentrations D_c was equal to the self-diffusion coefficient of individual flower-like micelles. With increasing concentration, D_c first increased due to bridging, before decreasing at higher concentrations due to repulsion between the coronas. The concentration dependence of D_c was found to be compatible with the model of sticky hard spheres. Measurements on solutions of equivalent diblock copolyelectrolytes that form star-like micelles showed only the effect of repulsion.

It was noted that a second slow relaxation mode appeared for the transient gels formed by triblocks above the percolation threshold that was absent for the solutions of star-like micelles. The objective of the present study was to investigate the slow dynamics in these transient hydrogels and relate it to the mechanical relaxation. The effect of the concentration, the pH, the temperature, and the ionic strength has been studied in the range where the system was monophasic. We will show that the slow relaxation time in these systems increases linearly with q^{-1} suggesting that the slow mode is caused by linear displacements of small heterogeneities in the network. It may be attributed to a ballistic process after the release of elastic constraints in the network. This kind of slow dynamics has been observed in colloidal gels [55,56], but to our knowledge it has not yet been reported for polymeric networks.

II. MATERIALS AND METHODS

A. Materials

The synthesis of P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)$_{100}$-*b*-PAA$_{200}$-*b*-P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)$_{100}$ has been described in detail in Ref. [36]. The sample used for the present investigation was the same as that used in earlier studies [36–39], and is noted as TH50. Sodium hydroxide 1 M (Labonline), D-glucono-δ-lactone (GDL) (Fluka, ~99%), and sodium chloride (Labonline, >99%) were used as received.

B. Sample preparation

The polymer was dissolved in pure water containing sufficient NaOH so that all acrylic acid groups were ionized [57]; i.e., the degree of ionization (α) was unity. The solutions were filtered through 0.2 μm pore size GHP Acrodisc filters. Subsequently, small aliquots of a NaCl solution were added to set the ionic strength and α was reduced gradually to the desired value by adding the required amount of GDL as reported elsewhere [37]. The total molar concentration of Na$^+$ incorporated in the system, [Na$^+$], is the sum of the amount of NaOH added to reach $\alpha = 1$ and the amount of added NaCl:

$$[\mathrm{Na}^+] = \frac{x_{\mathrm{AA}} C}{x_{\mathrm{AA}} M_{\mathrm{AA}} + x_{n\mathrm{BA}} M_{n\mathrm{BA}}} + [\mathrm{NaCl}]. \quad (1)$$

Here C is the weight concentration of polymer, $x_{\mathrm{AA}} = 0.75$ and $x_{n\mathrm{BA}} = 0.25$ are the molar fractions of AA and nBA units, respectively, and $M_{\mathrm{AA}} = 72$ g/mol and $M_{n\mathrm{BA}} = 128$ g/mol are their molar masses.

C. Methods

1. Light scattering measurements

Light scattering measurements were done using an ALV-CGS3 system operating with a vertically polarized laser with wavelength $\lambda = 632$ nm. The measurements were done at 20 °C over a wide range of scattering wave vectors [$q = 4\pi\ n\ \sin(\theta/2)/\lambda$, with θ the angle of observation and n the refractive index of the solvent].

With dynamic light scattering measurements, the normalized intensity autocorrelation function [$g_2(t)$] is measured, which is related to the electric field autocorrelation function [$g_1(t)$]: $g_2(t) = 1 + g_1^2(t)$ [58]. $g_1(t)$ was analyzed in terms of a relaxation time (τ) distribution [$A(\tau)$] using the REPES routine [40]:

$$g_1(t) = \int A(\log_{10}\tau)\exp(-t/\tau)d\log_{10}\tau. \quad (2)$$

Unfortunately, this method has a tendency to describe an asymmetric broad relaxation time distribution by multiple modes or a broad symmetric distribution. Therefore we also analyzed $g_1(t)$ in terms of the sum of a relatively narrow log-normal distribution to describe the fast mode and a generalized exponential (GEX) distribution to describe the slow mode:

$$A(\log_{10}\tau) = k\tau^p \exp[-(\tau/\tau^*)^s],$$

where k is a normalization constant. The two shape parameters p and s allow for a wide range of monomodal relaxation time distributions [59].

In all solutions we observed a fast q^2-dependent relaxation mode, which was caused by cooperative diffusion of the solute. The cooperative diffusion coefficient was calculated from the average relaxation rate as $D_c = \langle\tau^{-1}\rangle/q^2$. In dilute solutions D_c is related to the z average hydrodynamic radius of the solute:

$$R_h = \frac{kT}{6\pi\eta D_c} \quad (3)$$

with k Boltzmann's constant and η the viscosity of the solvent. At higher concentrations, interactions cannot be neglected anymore and an apparent R_h or, equivalently, a dynamic correlation length (ξ_d) is measured.

At higher polymer concentrations, we observed an additional slow relaxation mode. At large α or low ionic strength this mode was also q^2 dependent and was caused by the presence of a small amount of spurious scatterers that could not be fully removed by filtration. The relative amplitude of this mode decreased with decreasing concentration, decreasing α, and increasing ionic strength. In the following we will only consider situations where the contribution of these spurious scatterers could be neglected. In transient gels formed at lower values of α and larger ionic strengths a broad q-dependent slow mode appeared, which was the object of the present investigation.

2. *Oscillatory shear measurements*

Oscillatory shear measurements were done in the linear response regime with a controlled-strain rheometer (ARES, Rheometric Scientific) equipped with a plate-plate geometry (gap = 0.20 mm, diameter = 25 mm). To prevent water evaporation, the geometry was covered with silicon oil. The temperature was controlled with a thermostatic bath.

III. RESULTS AND DISCUSSION

In the following we will first show that the slow mode appears only in the transient network above the percolation concentration and investigate its q dependence. Then we will look at the dependence of the slow mode on the degree of ionization, the ionic strength, and the temperature. Finally, we will compare the slow relaxation of the concentration fluctuations with the relaxation of the shear modulus and discuss its origin.

A. Dynamic light scattering

Figures 2(a) and 2(b) show normalized intensity autocorrelation functions and the corresponding relaxation time distributions for solutions of TH50 at different concentrations for $\alpha = 0.50$ and [Na$^+$] = 0.5 M. At $C \leqslant 8$ g/L, a single fast relaxation mode was observed with a relaxation time that decreased with decreasing concentration until $C = 1$ g/L, below which it became independent of the concentration. The relaxation at low concentrations corresponds to the diffusion of flower-like micelles. The formation of aggregates due to bridging of flowers led to an increase of the relaxation time at higher concentrations. At $C \geqslant 15$ g/L, a second slow relaxation mode appeared. This mode was not present in the case of diblock copolymers which only showed the fast mode even at high concentrations; see [60]. The viscosity started to increase strongly at this concentration indicating that a transient system spanning network was formed [36].

As was mentioned in the introduction, the fast relaxation mode at higher concentrations ($C \geqslant 15$ g/L) represents the cooperative diffusion of the network (breathing mode). The concentration dependence of the fast relaxation was discussed elsewhere [38] in terms of the dynamic correlation length of the system (ξ_d). Its relaxation time decreased with increasing concentration because the system became more homogeneous with increasing polymer concentration. The origin of the slow mode is less obvious. Its relative amplitude increased with increasing C between 15 and 20 g/L and decreased at higher C, while its relaxation time became almost independent of C after increasing strongly between 15 g/L and 20 g/L [see Figs. 2(a) and 2(b)].

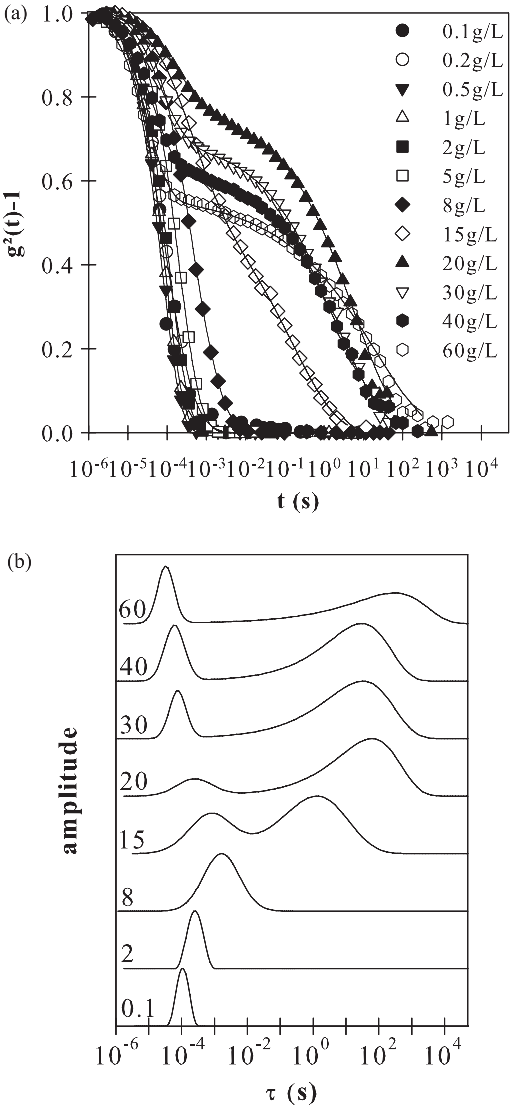

FIG. 2. Correlation functions at $q = 1.9 \times 10^7$ m^{-1} (a) [the solid lines correspond to nonlinear fits of the autocorrelation function (see materials and methods section)] and the corresponding relaxation time distributions (b) for TH50 at α = 0.50, [Na$^+$] = 0.5 M at different polymer concentrations.

The q dependence of the correlation functions is shown in Fig. 3(a) for a transient network formed at $C = 40$ g/L, $\alpha = 0.57$, and [Na$^+$] = 0.5 M. The relative amplitude of the slow mode was independent of q, but both fast and slow modes shifted to longer times with decreasing q. The fast mode superimposed after normalization of the time axis by $(q_\theta/q_{90^\circ})^2$, see Fig. 3(b), as expected for cooperative diffusion. However, the slow mode did not superimpose indicating that it was not caused by translational diffusion.

The characteristic relaxation time of the slow mode (τ_s), taken at the maximum of the distribution, was found to be proportional to q^{-1}, which suggests that it was caused by a ballistic motion. The characteristic speed of this ballistic motion may be calculated as $v = 1/(q\,\tau_s)$. Figure 4 shows for a few examples that v was independent of q over the whole angular range investigated implying that the displacement extended over at least a few hundred nanometers. This result

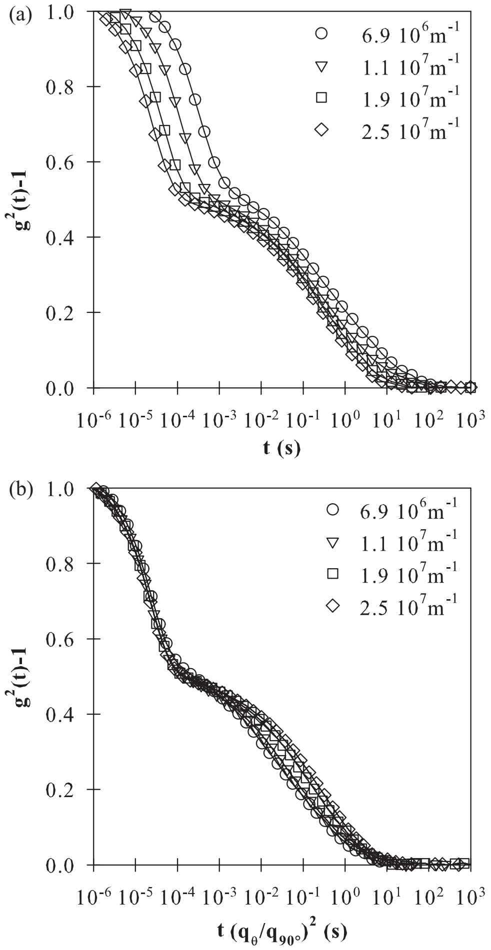

FIG. 3. (a) q dependence of the correlation functions for TH50 at $C = 40$ g/L, $\alpha = 0.57$, and $[\mathrm{Na}^+] = 0.5$ M. (b) Same data as in (a) after normalization by $(q_\theta/q_{90°})^2$. The solid lines are guides to the eye.

was unexpected since, as mentioned in the introduction, in previous DLS studies of transient polymeric networks the relaxation time of the slow mode was either q independent or q^{-2} dependent. However, slow dynamics with a q^{-1}-dependent relaxation time have been reported in the literature for colloidal gels [55,56] where it was suggested that it was caused by a ballistic process after intermittent release of elastic constraints within the network. However, the molecular mechanism is still unclear.

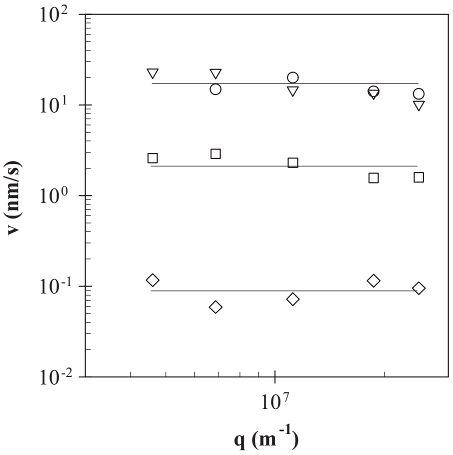

FIG. 4. q dependence of the velocity of the ballistic motion observed in TH50 solutions at $C = 40$ g/L, $\alpha = 0.57$ and $[\mathrm{Na}^+] = 0.5$ M (○), 0.7 M (▽), 0.85 M (□), and 1 M (◇).The solid lines are guides to the eye.

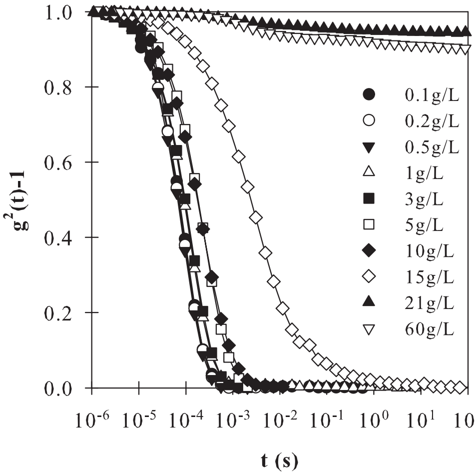

FIG. 5. Evolution of the correlation functions at $q = 1.9 \times 10^7$ m^{-1} for TH50 at different concentrations for $\alpha = 0.20$ and $[\mathrm{Na}^+] = 0.5$ M.

1. Effect of the ionization degree

Figure 5 shows correlation functions for TH50 solutions at different concentrations for $\alpha = 0.20$ and $[\mathrm{Na}^+] = 0.5$ M. As for $\alpha = 0.50$ we observed a single fast mode due to cooperative diffusion of individual and aggregated micelles. However, in this case the formation of a system spanning network rendered the system nonergodic, because the exchange time of the bridges was extremely slow as was shown by dynamic mechanical measurements [37]. The contribution of the slow mode to the scattering intensity was much higher at $\alpha = 0.20$ than at $\alpha = 0.50$.

2. Effect of $[\mathrm{Na}^+]$

The effect of the ionic strength for $[\mathrm{Na}^+] \geqslant 0.5$ M was investigated in detail for systems at $C = 40$ g/L and $\alpha = 0.57$. For $[\mathrm{Na}^+] < 0.5$ M the contribution of spurious scatterers leading to a q^2-dependent slow mode could not be neglected. The total scattering intensity increased sharply with increasing ionic strength and for $[\mathrm{Na}^+] > 1$ M the solution became turbid; see Fig. 6(a). As mentioned in the introduction and discussed in [38], adding more than 1 M salt to these systems induces phase separation. Macroscopic phase separation was very slow, as it was observed visually only after one month at $[\mathrm{Na}^+] = 1.2$ M. The relative amplitude of the slow mode increased strongly with increasing ionic strength; see Fig. 6(b). The increase of the scattering intensity was mostly caused by the increase of the slow mode, see Fig. 6(a), while the contribution of the fast mode to the scattering intensity increased only weakly. We stress that the scattering intensity was independent of q in the range covered by light scattering up to $[\mathrm{Na}^+] = 1$ M, implying that the heterogeneities that cause the slow mode were smaller than about 15 nm, i.e., much smaller than the ballistic displacement.

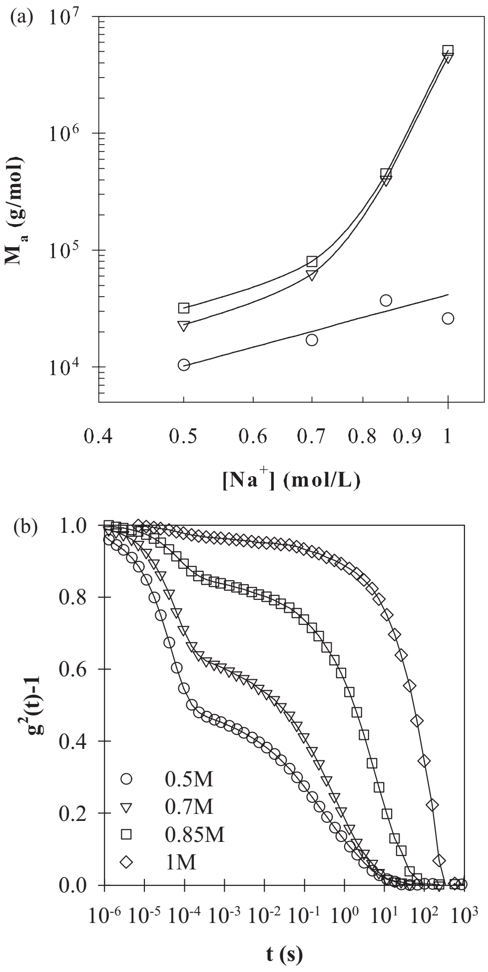

FIG. 6. (a) Evolution of the total scattering intensity (□) and the contribution of the fast (○) and the slow (∇) modes as a function of $[\mathrm{Na}^+]$ for TH50 at $C = 40$ g/L and $\alpha = 0.57$. (b) Correlation functions of these systems at $q = 1.9 \times 10^7\ \mathrm{m}^{-1}$.

The relaxation of the fast mode shifted slightly with increasing $[\mathrm{Na}^+]$ because ξ_d increased from 3.5 to 4.5 nm between $[\mathrm{Na}^+] = 0.5$ M and 1 M. This evolution is consistent with the weak increase of the scattering intensity of the fast mode; see Fig. 6(a). The relaxation of the slow mode was ballistic at each ionic strength, but the velocity decreased for $[\mathrm{Na}^+] = 0.85$ M and 1 M; see Fig. 4. We will show below that the velocity is correlated to the viscoelastic relaxation of the transient networks.

3. Effect of the temperature

The effect of the temperature was studied for a transient network formed at $C = 40$ g/L, $\alpha = 0.57$, and $[\mathrm{Na}^+] = 0.5$ M. Figure 7 shows the correlation functions measured at different temperatures with the time axis normalized by the viscosity of the solvent. In this representation the fast mode superimposed indicating that the correlation length of the network was independent of the temperature ($\xi = 3.5$ nm). The relaxation time of the slow mode decreased with increasing temperature and is clearly not controlled by the solvent viscosity. The relative amplitude of the slow mode was independent of the temperature indicating that the heterogeneities in the network causing the slow modes do not depend on the temperature.

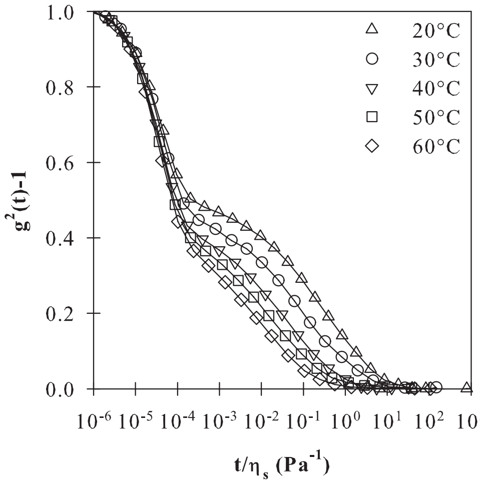

FIG. 7. Temperature dependence of the correlation functions at $q = 1.9 \times 10^7\ \mathrm{m}^{-1}$ normalized by the viscosity of the solvent (η_s) for TH50 at $C = 40$ g/L, $\alpha = 0.57$, and $[\mathrm{Na}^+] = 0.5$ M.

B. Dynamic mechanical relaxation

As mentioned in the introduction, we have already reported in detail the effect of C, α, and the temperature on the dynamic mechanical properties of the network [36,37]. Here we extend these measurements to study the effect of the ionic strength.

The effect of $[\mathrm{Na}^+]$ on the frequency-dependent loss (G'') and storage (G') shear moduli were investigated over a range of temperatures (20–60 °C) for networks formed at $\alpha = 0.57$ and three polymer concentrations: 20, 40, and 90 g/L. The range of $[\mathrm{Na}^+]$ that could be studied was restricted by the effects of phase separation, which was faster and occurred at lower $[\mathrm{Na}^+]$ for $C = 20$ g/L. For all results shown here shear measurements were done before any signs of macroscopic phase separation appeared. Moreover, we observed that the dynamic mechanical properties of the networks were practically independent of time as long as there were no signs of phase separation. For each system, master curves could be constructed by time-temperature superposition; see Fig. 8(a). For $[\mathrm{Na}^+] < 1$ M the temperature dependence could be described in terms of an activated process with an activation energy that was close to the value that we reported elsewhere for other values of α: $E_a = 120$ kJ/mol [36]. However, E_a increased strongly at higher $[\mathrm{Na}^+]$; see [60]. The master curves obtained at each ionic strength could in turn be superimposed by horizontal and vertical shifts indicating that the relaxation process was similar for each $[\mathrm{Na}^+]$; see Fig. 8(b). Elsewhere we reported that the results obtained for transient networks formed at different α could also be superimposed [36].

The frequency dependence of the shear moduli is typical for transient networks with an almost frequency independent elastic modulus (G_{el}) at high frequencies and a liquid-like behavior at low frequencies. G_{el} was independent of the ionic strength for $[\mathrm{Na}^+] \leqslant 0.7$ M, but decreased at higher $[\mathrm{Na}^+]$; see [60]. The relaxation of the shear modulus was characterized

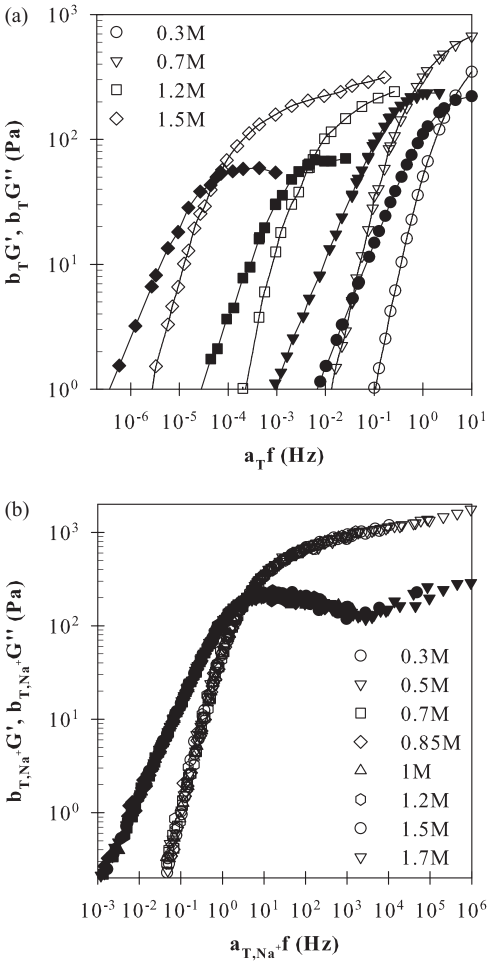

FIG. 8. (a) Master curves of the frequency dependence of the storage (open symbol) and loss (filled symbol) shear modulus at different [Na$^+$] obtained by frequency-temperature superposition at $T_{\mathrm{ref}} = 20\,^\circ$C for TH50 at $C = 40$ g/L and $\alpha = 0.57$. The solid lines are guides to the eye. (b) Same data as in (a) after frequency-[Na$^+$] superposition at $[\mathrm{Na}^+]_{\mathrm{ref}} = 0.3$ M.

by a broad relaxation time distribution. Here we define a characteristic relaxation time (τ_{el}) as the inverse of the angular frequency where G' and G'' cross. The dependence of τ_{el} on [Na$^+$] at 20 °C is plotted in the inset of Fig. 9 showing a small systematic dependence on the polymer concentration. As explained in the materials and methods section, [Na$^+$] contains contributions of the counterions and of excess ions. Remarkably, the polymer concentration dependence of τ_{el} disappeared if the data were plotted as a function of the excess concentration of sodium ions ($[\mathrm{Na}^+]_{\mathrm{ex}}$); see Fig. 9. τ_{el} depended weakly on the ionic strength for $[\mathrm{Na}^+]_{\mathrm{ex}} < 0.4$ M, but increased exponentially at higher $[\mathrm{Na}^+]_{\mathrm{ex}}$.

The weak dependence of τ_{el} on the ionic strength for $[\mathrm{Na}^+]_{\mathrm{ex}} < 0.4$ shows that screening of electrostatic interactions does not influence much the exchange rate of the hydrophobic blocks between micellar cores. The exponential increase of τ_{el} with $[\mathrm{Na}^+]_{\mathrm{ex}}$ at larger values mirrors the exponential increase of τ_{el} with decreasing α for $\alpha < 0.6$ at $[\mathrm{Na}^+] = 0.5$ [37]. We speculate that it is caused by the effect of high salt concentrations on hydration of the AA units.

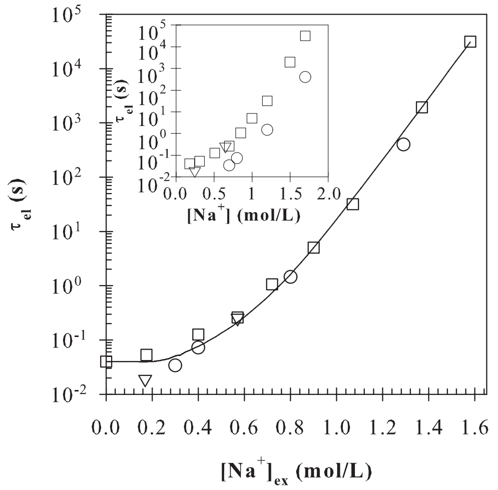

FIG. 9. Evolution of the characteristic relaxation time as a function of the excess of Na$^+$ concentration for TH50 solutions for $\alpha = 0.57$ at different polymer concentrations (20 g/L (triangles), 40 g/L (squares), 90 g/L (circles). The solid line is a guide to the eye. The inset shows the same data as a function of the total Na$^+$ concentration.

C. Comparison between DLS and dynamic mechanical relaxation

The appearance of the slow mode in DLS is clearly related to the formation of a transient network. That τ_s obtained from DLS is correlated to τ_{el} obtained from rheology can be seen most clearly in Fig. 10, which shows that the slow mode at different temperatures superimposes if the correlation functions are plotted as a function of t/τ_{el}. The relaxation is characterized by a broad distribution of relaxation times both for DLS and rheology and the width of the distribution is independent of the temperature; see inset of Fig. 10.

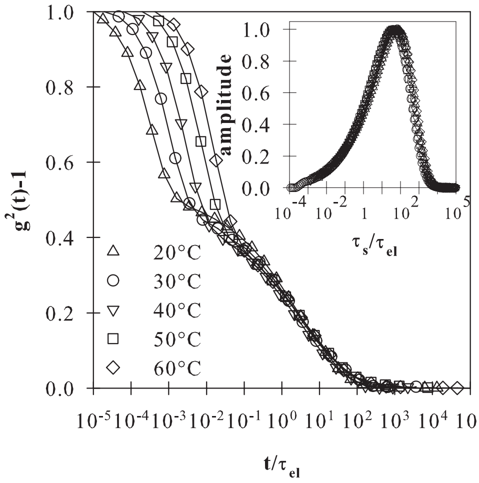

FIG. 10. Evolution of the correlation functions normalized by the relaxation time obtained by rheology (τ_{el}) at different temperatures for a system at $C = 40$ g/L, $\alpha = 0.57$, and $[\mathrm{Na}^+] = 0.5$ M. The inset represents the relaxation time distributions of the slow mode normalized by τ_{el} at different temperatures. The solid lines are guides to the eye.

The correlation between τ_s and τ_{el} is confirmed by their dependence on C, α, and [Na$^+$]. The strong increase of τ_s between $C = 15$ and 20 g/L followed by a weak dependence at higher C, see Fig. 2, is similar to the concentration dependence of τ_{el} [36]. The strong increase of τ_{el} with decreasing α up to 10^8 s at $\alpha = 0.20$ [37] explains why the system was nonergodic at $\alpha = 0.20$ as the relaxation time was longer than the measurement time. The dependence of τ_{el} with [Na$^+$] shown in Fig. 8 is the same as that of the velocity of the ballistic motion shown in Fig. 4.

These observations show the close relationship between the velocity of the ballistic motion observed by DLS and the relaxation of the shear modulus. However, we can equally well relate the velocity to the viscosity of the system (η), because its variation is close to that of τ_{el} as G_{el} is only weakly dependent on T, [Na$^+$], and α. Therefore we suggest two possible explanations for the correlation between τ_{el} and v. The first is that the velocity is controlled by the macroscopic viscosity η, which would be the case if an object of constant size was propelled with constant force through the network after constraint release. The second possibility is that the velocity is controlled by the lifetime of the transient bonds of the network, i.e., τ_{el}.

The clear relationship between the slow dynamics of the concentration fluctuations and the mechanical relaxation leaves open the question of the origin of the slow mode. As mentioned above, it has been suggested that it is caused in colloidal gels by the release of elastic constraints [55,56]. The constraints are supposed to be spontaneously created by restructuring of the gel, which implies that the system evolves with time. We have observed aging for the transient gels formed at higher ionic strengths, but if it happens also at lower ionic strengths it was too slow to be noticeable. For the colloidal gels, the relaxation of the slow mode could be described by a compressed exponential, i.e., faster than exponential, while here we find a broad distribution of relaxation times. This suggests that a broad range of elastic constraints causes relaxation with a broad range of velocities. However, in the absence of detailed knowledge about the molecular origin of the ballistic processes we cannot elaborate these suggestions further.

IV. CONCLUSION

Transient hydrogels formed by self-assembly of triblock copolyelectrolytes TH50 contained small (<20 nm) heterogeneities that contributed significantly to the intensity of the light that was scattered by these systems. Their contribution increased with decreasing degree of ionization and increasing ionic strength. They cause a slow relaxation mode in dynamic light scattering in addition to the relatively fast breathing mode of the transient network. The characteristic relaxation time of the slow mode increased inversely proportional to the scattering wave vector implying a linear displacement with constant velocity that was possibly caused by a ballistic process after the release of elastic constraints. A ballistic relaxation process has so far only been reported for colloidal gels. The observation of this type of dynamics in polymeric networks extents its occurrence to a new class of materials, which may help in elucidating its origin.

The velocity was strongly correlated to the mechanical relaxation of the gels indicating that it is controlled either by the viscosity of the system or by the lifetime of the bridges that form the polymeric network. The velocity has the same Arrhenius temperature dependence as the mechanical relaxation and both strongly slow down with increasing ionic strength and decreasing degree of ionization.

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