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Letters

Gelation of Micellar Block Polyelectrolytes: Evidence of Glassy Behavior in an Attractive System

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We present small-angle neutron scattering and rheology for micellar solutions of polystyrene−poly(acrylic acid) block copolymers that can be regarded as attractive colloids. These systems form gels at high effective micellar volume fractions ($\phi > 0.64$) that are suggestive of disordered colloidal glasses. At the gel point, the solution rheology follows the scaling predicted by classical percolation theory, with $G' \sim G'' \sim \omega^{\Delta}$. We argue that this scaling could be due either to formation of a percolated network or to a pretransitional glassy phase.

The mechanism of gel formation in complex fluids remains a subject of intense study. The appearance of a structurally disordered elastic phase occurs in physically and chemically cross-linked polymeric systems[1−3] as well as colloidal dispersions,[4−6] emulsions,[7] and block copolymer solutions.[8,9] Often, gelation is described in terms of percolation theory[10] or classical mean-field theory,[11,12] whereby systems are characterized by the extent of reaction or concentration, p, with gelation occurring at some critical value, p_c. The equilibrium modulus, G_o, and the low shear viscosity, η_o, are then given by

$$G_o \sim \left(\frac{|p - p_c|}{p_c}\right)^t \quad \text{for} \quad p > p_c \tag{1}$$

$$\eta_o \sim \left(\frac{|p - p_c|}{p}\right)^{-s} \quad \text{for} \quad p < p_c \tag{2}$$

where t and s are critical exponents that characterize the system above and below the gel point, respectively. Near p_c, the storage and loss moduli, G' and G'', have a power-law dependence on frequency:[1,13]

$$G' \sim G'' \sim \omega^{\Delta} \tag{3}$$

It can be shown that $\Delta = t/(t + s)$,[13,14] leading to a value of 1 from classical mean-field considerations,[11,12] 0.72 from the electrical network analogy,[15] and $0.67 \le \Delta \le 1.0$ from percolation theory, depending on hydrodynamic interactions.[16,17] Results from percolation theory have been

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modified to include the effects of elasticity of the network backbone[18,19] and also to account for screening of excluded volume in polymeric networks,[20] the latter leading to predictions for Δ in the range $0 \leq \Delta \leq 1.0$.

A wide variety of systems exhibit critical behavior that is in good agreement with eq 3, albeit with exponents that sometimes differ significantly from the predictions of percolation theory. These include chemically cross-linked poly(dimethylsiloxane),[1,21,22] model polyurethanes,[23] poly(ethylene oxide),[24] epoxies,[14,25,26] and tetraethylsiloxane gels.[27] Several physical gels also follow this scaling, including alginate[28] and pectin,[3] as well as gelled clays.[6] Many of these systems yield $\Delta \sim 0.5-0.7$, although exponents in the range $0.2 \leq \Delta \leq 0.9$ have been reported.[21,22]

The formation of a "gel phase" has also been observed in colloidal dispersions and is typically interpreted in terms of a disordered glass, as first observed by Pusey and van Megen.[4,29] For monodisperse hard spheres, experiments and computer simulations have shown that a liquid−glass transition occurs at a volume fraction, ϕ, of 0.56−0.60.[29,30] Polydisperse hard spheres also exhibit a liquid−glass transition at higher ϕ. For example, Bartsch et al.[31] demonstrated that polystyrene spheres with moderate polydispersity (16%) form glasses at $\phi \sim 0.64$. Mason and Weitz[32] were the first to experimentally characterize the rheological behavior of such colloidal hard sphere glasses. Above the glass transition, G' starts to dominate over the G'' and becomes independent of frequency, while G'' versus frequency exhibits a minimum.[32]

Models for the dynamics of soft glassy materials have been developed by Sollich and co-workers,[33,34] who characterize such systems by a mean-field "noise temperature," x, that is equal to 1 at the glass transition. The authors find that the storage and loss moduli scale as[33]

$$G' \sim \begin{cases} \omega^2 & \text{for } 3 < x \\ \omega^{x-1} & \text{for } 1 < x < 3 \end{cases} \tag{4}$$

$$G \sim \begin{cases} \omega & \text{for } 2 < x \\ \omega^{x-1} & \text{for } 1 < x < 2 \end{cases} \tag{5}$$

For $x > 3$, the systems are liquid and the scaling follows that of the classic Maxell model. As x approaches 1 at the glass transition, both moduli become nearly flat with frequency. At intermediate values below the glass transition ($1 < x < 2$), both moduli scale with the same exponent; in other words, the behavior is exactly that predicted by eq 3.[33] Thus, the model predicts that the power-law scaling of G' and G'' at the gel point, typically taken to be characteristic of a percolation transition, may also be observed in soft crowded systems below the glass transition.

In this Letter, we present results for aqueous micellar gels of polystyrene−poly(acrylic acid) diblock copolymers (PS−PAA). Although the micelles are attractive, the rheology and effective volume fraction above the gel point are characteristic of a jammed glassy system. However, these systems exhibit power-law behavior at the gel point, reminiscent of a percolated network. As we will discuss further below, the occurrence of a percolated network at low to moderate concentrations does not necessarily preclude formation of a glass at higher ϕ, and there are several attractive systems that exhibit characteristics of both phenomena. The variety of solution morphologies exhibited by block polyelectrolytes has been widely studied;[35−38] however, little has been published on the interesting rheology displayed by these copolymers. Our results are among the first rheological studies presented on block polyelectrolyte assemblies in water.[39]

The block copolymers selected for this study were prepared from polystyrene−poly(ethyl acrylate) diblocks (PS−PEA). A partial hydrolysis reaction leads to a PS−PAA diblock with unhydrolyzed ethyl acrylate groups along the water-soluble block. These diblocks self-assemble in water to form spherical micelles with a PS core and a corona of PAA and unhydrolyzed ethyl acrylate groups.[40] Since the hydrophobic ethyl acrylate groups can potentially act as "stickers" between micelles, we can consider these assemblies to be attractive colloids. We reported previously[9,40] that these solutions undergo a liquid−gel transition at concentrations of 1−2 wt % in water and that the gel phase boundary depends on the extent of the hydrolysis reaction; that is, the concentration for gel formation decreases with an increase in the number of ethyl acrylate groups, with the highest concentration required for fully hydrolyzed PS−PAA diblocks.[9,40] Moreover, the elastic modulus of these systems increases with the number of ethyl acrylate groups,[9,40] supporting the idea of intermicellar attractions.

Polystyrene−poly(ethyl acrylate) copolymers with a molecular weight of 5300/8100 g/mol were obtained from Rhodia (Cranbury, NJ) in the form of a 40 wt % aqueous solution. The hydrolysis reaction was performed at 90 °C and a polymer concentration of 10 wt %. The reaction mixture was stirred while 1.0 equiv of 2 M NaOH was added dropwise. The mixture was then held at 90 °C and stirred overnight, resulting in a transparent gel.

After hydrolysis, the copolymers were dialyzed against deionized, filtered water (ultrapure Milli-Q) for approximately 1 week and against water at pH 10 for 2−3 days. SpectraPor membranes with a molecular weight cutoff of 6000−8000 g/mol were used for the dialysis. Characterization using ^{1}H NMR was performed on solutions of the purified sample in deuterated pyridine, and it was found that approximately 85% of the ethyl acrylate groups were hydrolyzed, leading to a final molecular weight of 5300/6170 g/mol.

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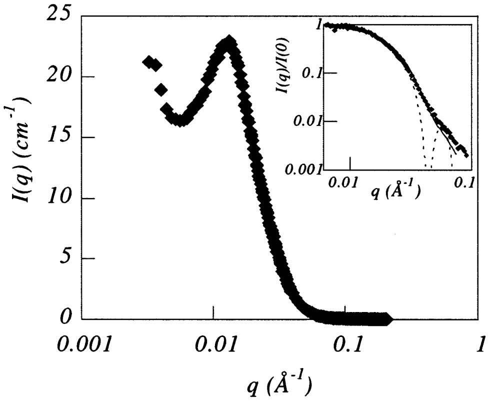

Figure 1. SANS data on a sample at 2.0 wt %, showing increase in intensity at low q, indicating aggregation or intermicellar attraction. Inset: SANS data on a sample at 0.58 wt % polymer, normalized to unity at low q. The dotted line is a fit to the form factor for monodisperse spheres with a radius of 10.1 nm, and the solid line is a fit to the form factor for polydisperse spheres with a mean radius of 10.1 nm and a polydispersity of 19%.

Samples for rheology were prepared at the desired concentration, heated to 80 °C, and stirred overnight. This temperature was determined to be high enough to allow movement of the short PS chains and equilibration of the solution structure.[37] Samples were allowed to rest for 24 h before rheological measurements were performed. Samples for small-angle neutron scattering (SANS) measurements were prepared by dissolving freeze-dried polymer in D_2O and stirring at 80 °C for several days. In pure D_2O, it can be shown that the majority of the scattered intensity arises from the PS core.

Rheological studies were performed at 20 °C using a strain-controlled Rheometrics ARES rheometer with either a cone-and-plate geometry (cone angle = 0.04 rad, diameter = 40 mm) or a couette geometry (cup diameter = 28.5 mm, bob diameter = 26 mm, bob length = 36 mm). Oscillatory experiments were typically performed at strains of 1−2%, well within the linear viscoelastic regime for our systems. Samples were allowed to equilibrate after loading for 2−3 h, and evaporation was prevented either using a solvent trap or by applying paraffin oil to the sample edges.

Scattering experiments were performed at 25 °C on the PAXY small angle diffractometer at the Laboratoire Léon Brillouin (LLB) in Saclay, France, and on the NG3 line at the NIST Center for Neutron Research in Gaithersburg, MD. D_2O was used to quantify solvent scattering, which was subsequently subtracted off. The incoherent scattering from each sample was estimated from the signal at high q and was subtracted from the data. Data were obtained for 0.003 Å$^{-1} > q > 0.2$ Å^{-1}.

The SANS spectra for representative samples in the liquid and gel regimes are shown in Figure 1. The data at low concentrations were fit to the form factor for polydisperse spheres[41] to yield an estimate for the core radius, R_{core}, of 10.1 nm and a polydispersity of 19%. This moderate polydispersity prevents formation of a colloidal crystal. Indeed, integrated spectra from gel samples, as well as 2-D detector images, show no evidence of long-range order or the close-packed cubic gel structure observed in several well-studied poly(ethylene oxide)−poly(propylene oxide) and poly(ethylene oxide)−poly(butylene oxide) gels.[42,43] Interestingly, the data on gel samples show an increase at low q, indicating intermicellar attraction or formation of larger aggregates at moderate concentrations. The spectra for dilute solutions do not exhibit this increase, remaining relatively constant in the range 0.003 Å$^{-1} > q > 0.1$ Å^{-1}, and thus shows no evidence of aggregate formation under dilute conditions. Similar characteristics have been seen in systems of telechelic associative polymers,[44] although the increase at low q for concentrated systems is not as dramatic.

These data, along with an estimate of the micelle size, can be used to compute the effective volume fraction of our gels. The micelle aggregation number, N_{agg}, is given by

$$N_{\mathrm{agg}} = \frac{4\pi R_{\mathrm{core}}^{\ 3}}{3V_{\mathrm{PS}}} \tag{6}$$

where V_{PS} is the volume of the styrene block, calculated as 8.36 nm^3, yielding $N_{\mathrm{agg}} = 516$. The effective volume fraction ϕ is then

$$\phi = \frac{4\pi R_{\mathrm{mic}}^{\ 3}}{3}\frac{cN}{N_{\mathrm{agg}}} \tag{7}$$

where N is Avogadro's number, c is the molar concentration of polymer, and R_{mic} is the effective radius of the micelle, which is difficult to evaluate. The stretch length of the PS−PAA chain, which is the maximum possible micelle radius, can be calculated as 41.3 nm. Estimates of the micelle hydrodynamic radius from dynamic light scattering are somewhat larger, in the range 50−88 nm, depending on concentration. However, this is not unexpected, as the hydrodynamic radius is larger than the true radius in general. Other methods of determining either R_{mic} or ϕ were attempted, including dilute viscometry and modeling of the SANS data with an adhesive hard sphere structure factor. Both of these methods resulted in a micellar radius that was larger than the maximum size given above, perhaps due to polydispersity effects. Thus, we chose to scale ϕ using the measured hydrodynamic size at the lowest concentration; $R_{\mathrm{mic}} = 50$ nm. It is worth noting that this type of scaling for ϕ, rather than a scaling based on the static size, has been suggested as the most appropriate for polymeric micelles.[45]

The viscoelastic moduli are shown for samples at varying polymer concentrations in Figure 2. As the polymer concentration is increased, the samples show a transition from a viscoelastic fluid to an elastic gel, with G' nearly flat with frequency and greater than G''. The transition appears over a small range of concentrations, between 1.13 and 1.40 wt %, which correspond to $\phi = 0.60-0.74$, indicating highly crowded systems. Effective volume fractions greater than 1.0 suggest that the micellar corona is compressed at concentrations above 1.60 wt %. The concentrations corresponding to crowded systems exhibit a minimum in G'' with frequency, similar to that observed by Mason and Weitz[7] for colloidal glasses.

At a concentration of 1.22 wt % ($\phi = 0.64$), the rheology obeys a power law in frequency, with the data following the scaling $G' \sim G'' \sim \omega^{\Delta}$ beautifully, as shown in Figure 3. We find the critical exponent $\Delta = 0.51 \pm 0.01$. Although

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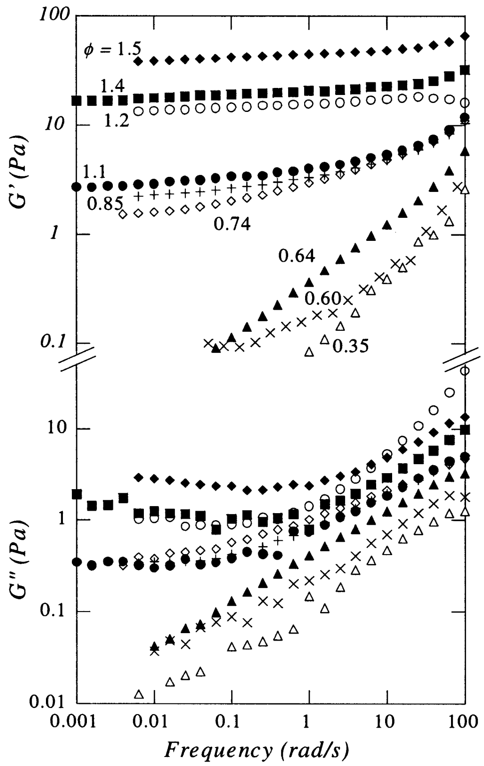

Figure 2. Storage modulus, G', and loss modulus, G'', versus frequency for several polymer concentrations. Volume fractions are calculated based on eq 7. Symbols represent the following concentrations: 2.86 wt % (filled diamonds, $\phi = 1.5$), 2.65 wt % (filled squares, $\phi = 1.4$), 2.33 wt % (open circles, $\phi = 1.2$), 2.10 wt % (filled circles, $\phi = 1.1$), 1.60 wt % (pluses, $\phi = 0.85$), 1.40 wt % (open diamonds, 0.74), 1.22 wt % (filled triangles, $\phi = 0.64$), 1.13 wt % (crosses, $\phi = 0.60$), and 0.65 wt % (open triangles, $\phi = 0.35$).

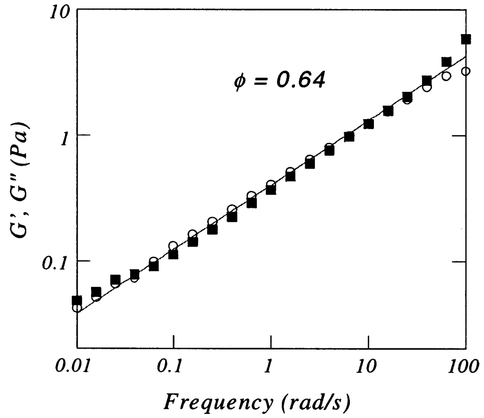

Figure 3. Storage modulus (filled squares) and loss modulus (open circles) at a polymer concentration of 1.22 wt % ($\phi = 0.64$). The solid line is a fit to the data, yielding the exponent $\Delta = 0.51 \pm 0.01$.

some authors have interpreted this scaling behavior itself as indicative of a self-similar structure,[6] this behavior could be exhibited by either a percolated gel or a pretransitional glass phase, as discussed above.

Both the high value of ϕ and the rheology of the gel phase suggest that the system is a disordered glass. However, the structure at the gel point and the mechanism for gelation remain unclear, due in part to the difficulty in accurately defining ϕ for soft spheres, as mentioned above. There are two possibilities. The first is that the scaling of G' and G'' at the gel point is due to the formation of a percolated network, which we might expect given the attractive nature of our system. In this case, percolation and the glass transition would be separate phenomena, with percolation preceding the structural arrest associated with a liquid−glass transition. This argument was developed by Mallamace and co-workers[46] for short-range attractive polymeric micelles. However, these authors showed that critical rheology and structural arrest occurred in two very different regions of the phase diagram. Simulations on associative polymers have also shown that geometrical percolation can precede a “clustering transition”.[47] Gel formation is associated with this second transition, and the resulting phase exhibits several glasslike characteristics.[47] In our case, if percolation is responsible for the scaling at the gel point, the glass transition must occur almost simultaneously. The second possibility is that the power-law behavior at the gel point is due solely to a liquid−glass transition, with the nature of the transition modified by intermicellar attractions. Structural arrest of attractive spheres has been studied theoretically using mode-coupling theory[48,49] and is related to a low-temperature extension of the liquid−glass transition line;[48] however, attractive glasses show stronger localization of particles and have a higher modulus than glasses formed from purely repulsive colloids.[48] Molecular dynamics simulations on attractive spheres have also shown that a glass transition can be driven by either attractive or repulsion interactions, depending on the strength of interparticle attraction and the volume fraction.[50] The differences between these two types of glassy states appear to be subtle, although both display a different nonexponential decay of the correlation function,[50] which could be observed experimentally.

In summary, we have presented rheological results for attractive micellar gels of block polyelectrolytes that exhibit power-law behavior at the gel point ($\phi \sim 0.64$). The rheology of the gel phase and high value of ϕ are suggestive of a crowded colloidal glass; however, the mechanism of gelation could be either percolation or a liquid−glass transition. More theoretical descriptions of the rheological behavior near the glass transition are needed to resolve this issue, despite recent developments.

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