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Current Opinion in Colloid & Interface Science 6 (2001) 471–478

Current Opinion in
Colloid & Interface
Science

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Block copolymer assembly to control fluid rheology

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Abstract

Recent experimental studies on the rheology of block copolymer micelles are reviewed. Where appropriate, we draw analogies between the viscoelastic properties of polymeric micelles and those of colloidal dispersions. We also present some important differences between these two classes of complex fluids, namely the ability to tune self-assembly through solvent–polymer interactions. Finally, new experimental results for attractive micellar solutions of polyelectrolytes are presented. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Rheology; Diblock copolymers; Polymeric micelles; Associative polymers; Adhesive hard spheres; Strain hardening

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1. Introduction

Self-assembling block copolymers exhibit a wide range of morphologies and rheological behavior. Their unique properties have been exploited in a wide range of applications, including paints, coatings, adhesives, cosmetics, eye care products, fracturing fluids, and drug delivery agents [1–7]. An extensive literature, both theoretical and experimental, exists on the interesting rheology exhibited by block copolymers in selective solvents. Recent reviews have been published on the morphology [8,9•] and shear-induced microstructure [10,11] of block copolymer solutions and on the relationship between structure and viscoelasticity [12•]. Excellent reviews on several aspects of block copolymer solution behavior can also be found in the text edited by Alexandridis and Lindman [13••].

In this paper, we discuss recent work on the rheology of block copolymers in selective solvents, drawing analogies between colloidal systems and polymeric micelles where appropriate. We refer to a solvent as ‘selective’ for one block if it is a good solvent for that block, leading to a self-assembled structure with this block exposed to the solvent. Our review will concentrate on diblock copolymers in dilute and semidilute solutions, although some relevant results from stars, triblock, and telechelic systems are also described. Finally, we limit our discussion to polymers in small-molecule solvents such as water or decane; this is in contrast to the series of papers on diblocks dissolved in short homopolymers that has been recently reviewed by Watanabe [14]. Abbreviations used throughout the text are listed in Table 1.

2. Close-packed micelles: the formation of cubic gels

Diblocks and triblocks containing water-soluble PEO blocks are among the most widely studied in the literature. The first systems to be investigated systematically were PEO–PPO–PEO and PEO–PPO

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PII: S1359-0294(01)00122-4

Table 1
Abbreviations for polymers used in the text

PS	Polystyrene
P4VP	Poly(4-vinylpyridine)
PI	Polyisoprene
PB	Polybutadiene
PtBS	Poly(*tert*-butylstyrene)
PNaMA	Poly(sodium methacrylate)
PNaA	Poly(sodium acrylate)
PAA	Poly(acrylic acid)
PEtA	Poly(ethyl acrylate)
PEO	Poly(ethylene oxide)
PPO	Poly(propylene oxide)
PBO	Poly(butylene oxide)

copolymers. More recently, PEO–PBO–PEO and PEO–PBO systems have also been investigated. The solution morphology of these copolymers has been well-characterized using small-angle X-ray and neutron scattering (SAXS and SANS). As concentration is increased, so-called 'symmetric' diblocks (with a roughly equal number of hydrophobic and hydrophilic groups) show a progression of isotropic micellar–cubic micellar–hexagonal–lamellar structure, which is analogous to the phase behavior seen in surfactant solutions [12•,15,16•]. Hexagonal-to-gyroid transitions have also been observed in ternary water/oil/copolymer systems [17•]. As the copolymer asymmetry increases, the tendency to form lamellar and hexagonal phases decreases due to packing constraints. Morphological transitions can also be triggered by varying temperature. Polyalkylene oxides exhibit decreased solubility in water as temperature is increased; this anomalous behavior leads to a critical gelation temperature for the block copolymers.

The morphology of the cubic phase depends strongly on the nature of intermicellar repulsions. Hamley et al. [18••,19] and Pople et al. [20] showed that sharp, short-range interactions, typical of hard spheres, favor a face-centered cubic (FCC) structure, while softer repulsive interactions favor a body-centered cubic (BCC) structure. Schematics of the hard-sphere and soft-sphere potentials are shown in Fig. 1. The FCC structure is favored at high temperatures, due to contraction of the PEO corona [21]. The FCC-to-BCC transition can also be observed as the block length of the corona is decreased [18••], which agrees with the classic series of experiments performed by McConnell et al. [22,23] on PS–PI diblocks in decane. Ordered cubic crystals have also been observed in micelles with long-range electrostatic repulsions; for example, PtBS–PNaMA diblocks in water exhibit strong intermicellar repulsions due to the polyelectrolyte nature of the water-soluble block [24•].

The rich phase behavior of PEO-containing copolymers corresponds to fascinating rheological properties; the most notable is formation of a gel from low viscosity solutions as the temperature is increased [16•,25–27]. For example, the block lengths and concentration can be adjusted to obtain a system that exhibits a liquid-to-gel transition at a temperature of roughly 35°C [16•,25], which can be useful for drug delivery applications [28]. Rheological 'phase boundaries' have been measured for several copolymers that show transitions between sols, 'soft gels,' and 'hard gels' [26,27,29•,30,31•,32••]. Data for copolymers of differing molecular weights can be scaled using the critical micelle concentration and temperature; in general, increasing the PEO block length shifts the phase boundaries to lower concentrations [29•,32••]. The sol–hard gel transition corresponds to the formation of a close-packed micellar gel, described above. The soft gels, on the other hand, show a fractal structure consistent with the idea of a percolated network of micelles [27]. The soft gel transition has also been ascribed to a spherical-to-cylindrical micelle transition [26,33] or the occurrence of defects in the cubic phase [20,30].

From a rheological point of view, the only drawback of many of these studies is that they report only sol–gel boundaries as determined by tube inversion, and not values for rheological parameters over the range of measurable frequencies and shear rates. The latter measurements would be beneficial if a prescribed viscosity or elastic modulus is required for a particular application. Values of the high frequency modulus vs. concentration would also be useful for comparison with available theories and experimental data for polymerically stabilized colloids [34–36]. We

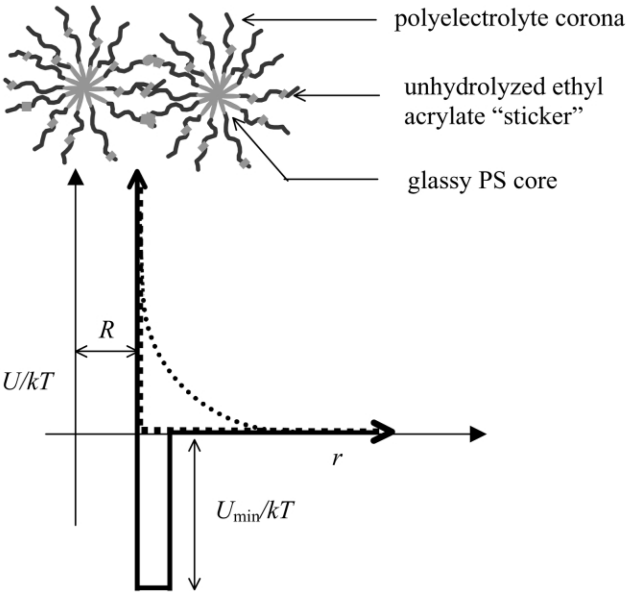

Fig. 1. Interparticle potential for adhesive hard spheres, and possible corresponding lengths in 'sticky' polymeric micelles. For comparison, the potential for hard spheres (heavy dashed line) and soft spheres (dotted line) is also shown.

note that some comparisons between tube-inversion studies and detailed rheometric measurements have been performed; for example, Li et al. [27] demonstrated that the sol–gel boundaries for a PEO–PBO copolymer determined by tube inversion corresponded to the crossover point between G' and G'' measured at a frequency of 1.0 Hz. Kelarakis et al. [32••] also recently quantified earlier measurements by defining a 'hard gel' as a solution with a yield stress exceeding 40 Pa. These solutions do not flow upon tube inversion and have an elastic modulus, G', that is higher than their loss modulus, G''. Systems with $G' > G''$ and a small but measurable yield stress are defined as 'soft gels', and solutions with $G'' > G'$ that flow are defined as sols [32••].

One interesting extension of this idea is to create block copolymer aggregates with anisotropic morphologies, such as hard cylinders and hard platelets rather than hard spheres, and study the resulting structure and rheology. Bendejacq and Ponsinet [37,38] have recently shown that it is possible to create well-defined cylindrical and platelet-like aggregates from PS–PAA copolymers via a solvent-casting process. The resulting films can then be swollen to form solutions of anisotropic polymeric aggregates. Like the non-equilibrium morphologies discovered by Eisenberg and co-workers [8], these aggregates are 'frozen' due to the glassy nature of the PS block. Work is ongoing to characterize the viscoelasticity of these solutions.

3. Temperature-induced transitions

Since self-assembly of polymeric micelles is governed by polymer–solvent interactions, the thermotropic rheological behavior of polymeric micelles can be much richer than expected for colloidal dispersions. Examples include the PEO-containing block copolymers mentioned above. However, these systems are by no means the only solutions where temperature can be used to induce a structural change and alter the rheological response. The thermotropic behavior displayed by alkylene oxide copolymers is atypical; in fact, most diblock solutions show the opposite behavior, with an increase in temperature leading to decreased selectivity of the solvent and an eventual breakdown of the structure. This behavior is exemplified by the rheology of PS–PI and PS–PI–PS copolymers in di-*n*-butylphthalate (DBP), investigated by Lodge et al. [39]. Di-*n*-butylphthalate is selective for PS, and both the diblocks and triblocks form ellipsoidal micelles with PI cores at low temperatures. However, above 10°C, DBP begins to swell the micelle cores, corresponding to an elongation of the micelles. This increase in the effective size leads to a dramatic increase in G', roughly two orders of magnitude [39]. However, at temperatures above 40°C the micelles begin to disintegrate due to increasing solubility of PI in DBP, leading to a sharp drop in the moduli. Finally, at $T > 60$°C, the observed microstructure and rheology is similar to that of a disordered, entangled polymeric solution.

Another important class of systems in which the rheology is highly temperature-dependent are those where the less-soluble block is below its glass transition temperature, T_g, and the micellar core is 'frozen'. These solutions typically show a rubbery-to-viscous transition as temperature is increased [40,41••]. Sato et al. [41••] examined PS–PI–PS and PS–PI copolymers in tetradecane, a selective solvent for PI. At $T < T_g$, the PS blocks form glassy domains, and the rheological response is solid-like, with an elastic modulus that is independent of frequency. At higher temperatures, the PS domains become fluid, allowing for bulk fluid flow, and at high enough temperatures, the response is that of a viscoelastic fluid, with $G' \sim \omega^2$ and $G'' \sim \omega$. At the transition between these two extremes, a power-law dependence of the moduli is observed at high frequencies. However, the moduli deviate from this dependence at low frequencies, suggesting that any self-similarity of the solution structure at the gel point disappears at large length scales.

4. Transitions between semidilute polymers, soft colloids, and hard spheres

Rheological measurements on dilute diblock micelles also demonstrate that the intermicellar potential can be varied to produce hard-sphere or soft-sphere behavior. Physically, this can be achieved in some cases by varying the ratio between blocks, which will in turn affect the aggregation number. Higher aggregation numbers typically lead to denser brushes that have a sharper repulsive potential, characteristic of hard spheres. An example is the concentration dependence of the low shear viscosity, η_o, for spherical PS–P4VP micelles in toluene, a selective solvent for PS [42•]. Depending on the total molecular weight and ratio between blocks, the samples exhibited either polymeric ($\eta_o \sim c^{2.5}$), soft sphere, or hard sphere ($\eta_o/\eta_s = [1 - c/c^*]^{-2}$) behavior. The concentration at which the viscosity was observed to diverge, c^*, was found to increase with increasing particle softness. Above c^*, data from hard sphere and soft sphere systems show the scaling $G' \sim N_{agg}^{1.48} r^{-2.46}$, similar to the theoretical prediction of $G' \sim N_{agg}^{3/2} r^{-2}$ for polymerically stabilized colloidal particles [42•]. Similar results were obtained by Vlassopoulus et al. [43••], who studied PS–PI and 1,4-PB stars in decane, a selective solvent for PI. Increasing the number of star arms sharpens the potential in much the same way that increasing the aggregation number does. The viscosity of stars with 32 arms was found to follow the same scaling as semidilute polymer solutions, while spherical micelles and higher functionality stars exhibited behavior reminiscent of soft spheres and stars with 128 arms showed hard-sphere behavior. A master curve can be obtained when these data are scaled using an effective volume fraction, calculated based on the measured hydrodynamic size [43••]. Previously published data [44,45] on colloidal hard spheres was found to follow the same scaling. Spherical micelles of PS–PEO copolymers in water also exhibit a divergence in the viscosity at $c \sim 10.0$ wt.%, which is just above the overlap concentration [46]. However, in this case the divergence in the viscosity appears to coincide with the formation of large worm-like micelles [46].

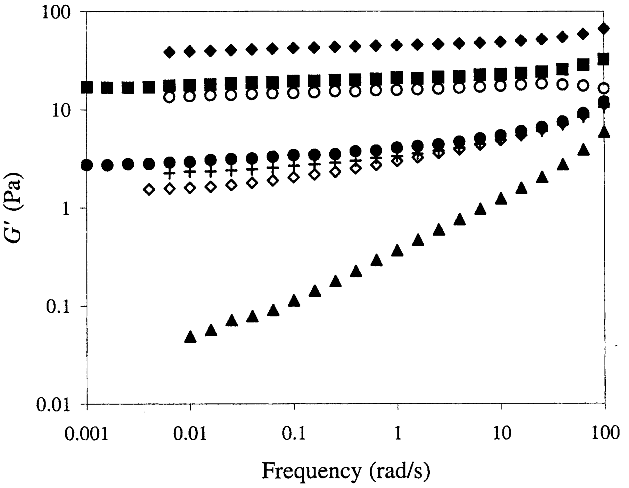

Fig. 2. Storage modulus vs. frequency for several concentrations of PS–PNaA in water. Symbols represent the following concentrations: 2.86 wt.% (filled diamonds), 2.65 wt.% (filled squares), 2.33 wt.% (open circles), 2.10 wt.% (filled circles), 1.60 wt.% (crosses), 1.40 wt.% (open diamonds), and 1.22 wt.% (filled diamonds).

5. Associating micelles: analogies to 'sticky' spheres

The idea of using colloidal scaling laws to describe the behavior of polymeric micelles has recently been extended to associative micellar solutions [47•,48•,49••]. These include telechelic associative polymers [48•,49••], ABA triblocks in microemulsion solvents [50,51], and end-functionalized diblock copolymers [52,53]. Typically, the intermicellar potential is described in terms of an adhesive hard sphere model [54], where the strength of attraction $U_{\min}/kT$ is expressed in terms of a 'stickiness parameter', $1/\tau$. More detailed interaction potentials for micelles of telechelics have also been calculated [47•,55•].

The parameters for the adhesive hard sphere model can be determined experimentally using dilute viscometry or dynamic light scattering [48•,56], or by fitting SANS spectra on concentrated solutions. One of the most extensive experimental studies was performed by Russel and co-workers [48•,49••], who examined the rheology and phase behavior of telechelic hydrophobically-modified PEO in aqueous solutions. These solutions exhibit a phase separation due to intermicellar attractions, as was first predicted by Semenov et al. [47•]. The phase boundaries observed for samples with different sticker lengths were found to be in agreement with the bimodal curve for adhesive hard spheres [48•]. Moreover, the estimated value for $1/\tau$ can be used to scale the high frequency modulus through the dependence of the intermicellar attraction on aggregation number [49••].

A bridge between the behavior of associative telechelics and adhesive hard spheres can be provided by micelles with a number of 'sticky' groups on the corona arms. In our group, we have realized this physically through the use of micellar solutions of block polyelectrolytes with glassy cores. Due to the fixed hydrophobic core, these micelles can be thought of a model for 'sticky' spheres (Fig. 1). The polymers are prepared from PS–PEtA diblocks that are subjected to a partial hydrolysis reaction, leading to a

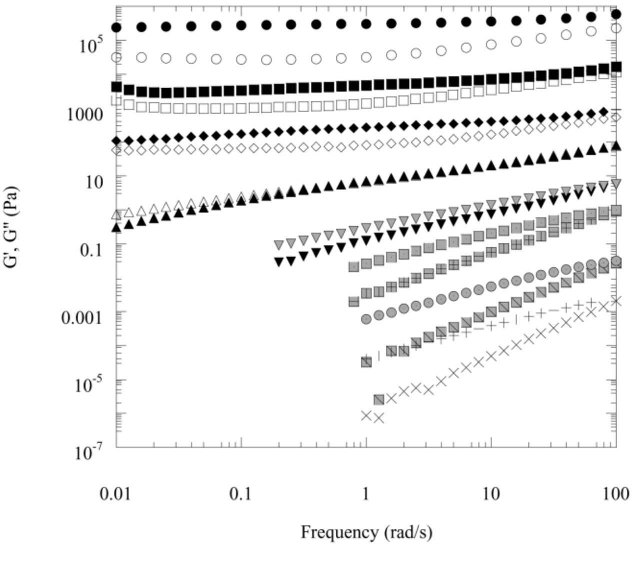

Fig. 3. Storage and loss modulus for samples with 2.0 wt.% PS–PNaA with differing concentrations of surfactant: 0.0 wt.% (filled and open circles), 0.1 wt.% (filled and open squares), 0.2 wt.% (filled and open diamonds), 0.3 wt.% (filled and open triangles), 0.4 wt.% (filled and open inverted triangles), 0.6 wt.% (hatched and dotted squares), 0.8 wt.% (diagonal squares and dotted circles), and 1.0 wt.% (x's and crosses). Note the transition from an elastic gel, with G' nearly flat with frequency, to a viscoelastic liquid, with $G' \sim \omega^2$, as surfactant is added. The moduli have been multiplied by the following scale factors to allow for easier comparison: 0.0 wt.%, 20 000; 0.1 wt.%, 1000; 0.2 wt.%, 50; 0.3 wt.%, 10; 0.4 wt.%, 1; 0.6 wt.%, 0.25; 0.8 wt.%, 0.001; 1.0 wt.%, 0.001.

diblock polymer consisting of PS–PAA with unhydrolyzed ethyl acrylate 'stickers' along the PAA chain. The extent of hydrolysis, and hence the number of ethyl acrylate groups, is directly related to the amount of base added in the hydrolysis reaction. In aqueous solutions, these systems form clear gels at a polymer concentration of 1–2 wt.% [53]. We have shown that the hydrophobic ethyl acrylate groups lead to intermicellar associations, with a greater number of stickers corresponding to a more elastic gel. SANS spectra on concentrated solutions [52] can be fit to the adhesive hard sphere model and demonstrate that the stickiness parameter increases monotonically with the number of ethyl acrylate stickers. Thus, the intermicellar attraction and solution rheology can be tuned via the hydrolysis reaction.

The gel-to-liquid transition can be triggered by either decreasing polymer concentration, increasing the extent of the hydrolysis reaction, or by adding an anionic surfactant [53]. In the case of added surfactant, SANS has demonstrated that the micellar structure is preserved and the surfactant only acts to screen the hydrophobic stickers. Examples of the gel-to-liquid transition are shown in Figs. 2 and 3. These systems display critical gelation behavior, with $G' \sim G'' \sim \omega^{0.49-0.51}$ at $c = c_c$ and the equilibrium modulus varying as $G_0 \sim (c/c_c - 1)^{2.81}$ above the gel point [53]. The dependence of the gel point on the extent of hydrolysis is summarized in Fig. 4, which shows that the critical gel concentration decreases with increasing intermicellar attraction. Analogous behavior has been observed for attractive colloidal particles [57] in which the interparticle attraction was modified through an added dispersant.

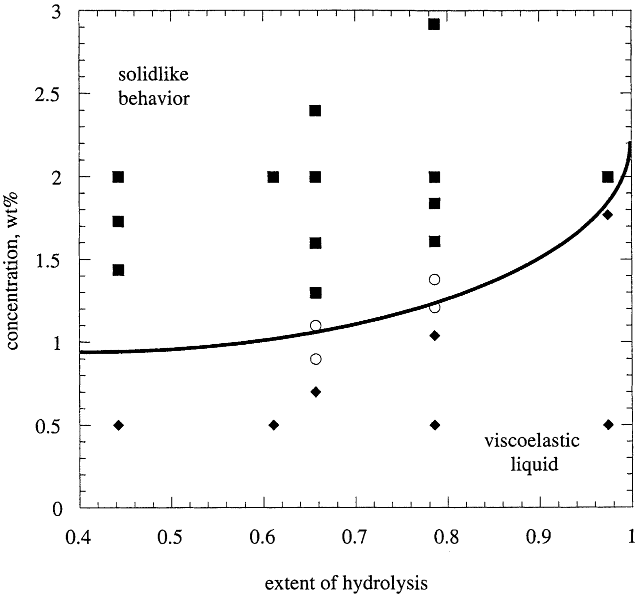

Fig. 4. Liquid-to-gel phase boundary for a PS–PNaA diblock in water, showing the dependence of the critical gel concentration on extent of hydrolysis.

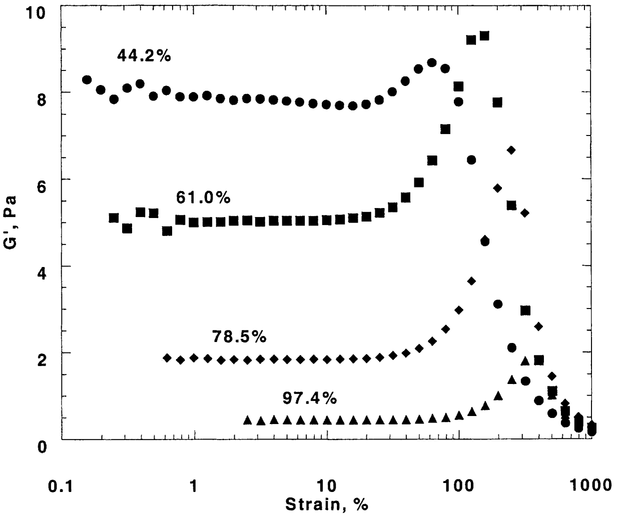

Fig. 5. Strain hardening behavior for a PS–PNaA diblock as a function of extent of hydrolysis, or decreasing U_{min}/kT.

We have also shown that these block copolymer micelles exhibit some of the same non-linear rheology as attractive colloids. One of the most notable rheological features is the appearance of strain-hardening. The elastic modulus, G', shows an upturn at high strains, rather than displaying the monotonic decrease typically seen in polymer solutions. The critical strain and degree of strain hardening decrease with increasing concentration and U_{min}/kT (Figs. 5 and 6). Similar behavior has been observed in colloidal gels of adhesive hard spheres [58] and fumed silica [59,60], and a variety of biopolymers [61–64]. Theories have been developed that attribute this behavior to the fractal nature of the colloidal gel [58] or biopolymer network [61].

It is possible to use the partial hydrolysis technique, together with the preparation technique developed by Bendejacq and Ponsinet [37,38], to create attractive anisotropic aggregates. This provides an exciting new direction for investigation of the viscoelasticity of 'sticky' platelets, and we are currently studying the rheology and shear-induced microstructure of these solutions.

6. Conclusions

Diblock copolymer solutions exhibit a range of viscoelastic behavior that can be tuned using a variety of techniques. The versatility of these systems is due in part to the fact that they provide a bridge between semidilute polymer solutions and colloidal dispersions. The theoretical framework developed for colloidal solutions has been useful in describing the

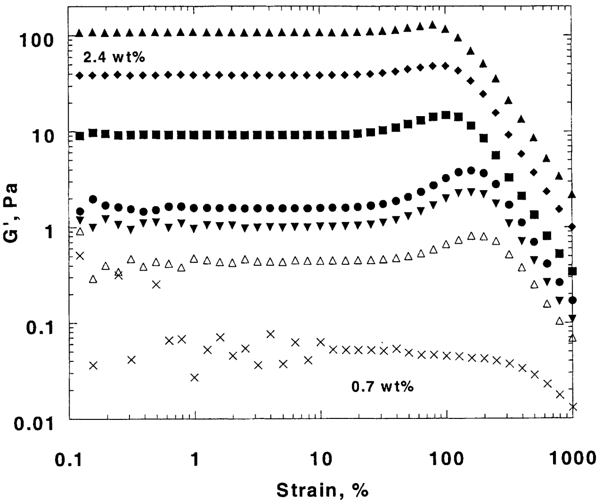

Fig. 6. Strain hardening behavior for a partially hydrolyzed PS–PNaA diblock in water as a function of polymer concentration.

structure of concentrated micellar gels and the low shear viscosity of certain dilute diblock systems. The viscoelasticity and non-linear behavior of attractive diblock micelles also display some similarities to data taken on adhesive hard sphere systems. A robust means of measuring and controlling the intermicellar attraction must be developed in order to fully interpret data from attractive systems. Future directions include the investigation of attractive anisotropic aggregates formed from block copolymers.

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• of special interest
•• of outstanding interest

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