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Modifying the rheological behavior of associative triblock copolymers in aqueous media through surfactant additives

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Abstract

The rheological behavior of aqueous micellar solutions of a triblock copolymer, bearing two small hydrophobic end-blocks of polybutadiene and a large hydrophilic middle block of poly(sodium methacrylate), was studied in the presence of a cationic (dodecyl trimethyl ammonium bromide) or an anionic (sodium dodecyl sulfate) surfactant. Depending on the concentration and the charges of the interacting (with the water soluble middle block) surfactants, the rheological behavior of the triblock copolymer micelles (which resemble compact spheres, based on scattering studies) can be altered dramatically. The surfactant additives can either solidify a liquid-like system (low triblock concentration, dominated by loops) or alternatively liquefy a gel (high triblock concentration, dominated by bridges). Apparently, the hydrophobic tails of the surfactants prefer to join the hydrophobic polybutadiene cores of the triblocks, whereas by increasing the surfactant concentration the core functionality can be changed. In addition interactions between the oppositely charged hydrophilic surfactant heads and middle blocks can yield complexes producing new hydrophobic domains. These findings suggest possibilities for controlling complex fluid rheology.

Keywords: Rheology; Poly(butadiene-*b*-sodium methacrylate-*b*-butadiene); Micelles in water

1. Introduction

Solutions of triblock copolymers in selective solvents for the middle block have been the subject of many studies due to their interesting self-assembling behavior (flower-like and bridged micelles, physical gels, etc.) and dynamics, as well as the resulting potential to control fluid rheology [1–10]. Among them associative triblock copolymers in aqueous media have attracted considerable interest (experimental as well as theoretical) as a consequence of their potential use in rheology control of aqueous fluids, super-absorbents, controlled drug-release systems, paints, coatings, adhesives, actuators and sensors, etc. [1,3,6–16]. In all cases the chemical nature of the blocks plays the major role in affecting the microscopic and macroscopic properties (hydrophilic to hydrophobic content, ionic or neutral character of the water soluble block, interactions with the solvent media, etc.). Thus, a great deal of effort has been directed in understanding the behavior and structure of such systems as well as in finding ways of controlling their rheological properties.

Apart from parameters like polymer concentration, temperature, salt valency and concentration and pH, that have been found to affect the properties of associative triblock copolymer aqueous solutions and physical gels, the interactions with low molecular weight surfactant molecules have been investigated

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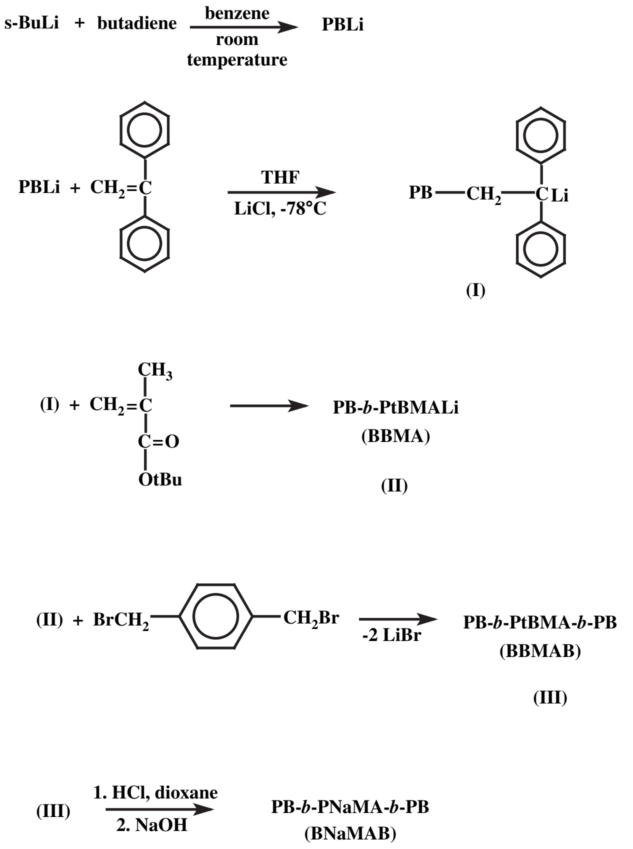
to some extent [14–17]. It has been found that the surfactants influence the rheological properties of the solutions profoundly, in a manner that depends primarily on the polymer concentration; typically, the plateau modulus exhibits a non-monotonic dependence on surfactant concentration for low polymer concentrations and a monotonic decrease for higher polymer concentrations. The study of associative polymer/surfactant systems has emerged as an attractive field of research recently, as in addition to their potential applications these complexes exhibit many similarities with biological systems (for example, those involving interactions between proteins and lipids) [18]. Therefore, the study of this category of self-organized systems will not only lead to useful knowledge from the practical point of view but can also shed some light on biological mechanisms and organization processes in soft matter. The interaction of aqueous chemical gels with surfactants is a closely related field [16,19]. Consequently, associative polymer aqueous solutions have a close resemblance to natural systems and offer a great variety of parameters by which the systems can be affected and therefore be controlled. Despite these important developments, however, a consistent set of experimental information about the effects of surfactants on the rheology and structure of well-defined micellar systems (based on triblock copolymers, which can form both loops and bridges, as discussed below) over a wide set of parameters as outlined above is still missing. Yet, this is necessary if one is to tailor the flow properties of this type of responsive systems, and in particular to exert a dramatic change on their rheology, say from liquid-like to solid-like and vise versa. To accomplish such a formidable task it is necessary to work with model systems, starting from well-characterized triblock copolymers; this approach has not been frequently followed in the past.

In this work we present a rheological investigation of model triblock copolymer aqueous micellar systems interacting with surfactants at different concentrations. With the support of a few selected scattering experiments, we demonstrate that the addition of surfactants provides an efficient means for the molecular control of the structure and rheological properties of the triblock copolymer solutions (or gels). As such, these systems are proposed as good models for studying in further detail the rheological response in the presence of additives. We describe the material's synthesis and characterization, as well as the experimental methods in Section 2. Then, in Section 3 we present the experimental results and discuss them in view of the data analysis and literature information. The main results and conclusions are put together in Section 4.

2. Experimental

2.1. Materials preparation

The triblock copolymer precursor containing polybutadiene (PB) end-blocks with high 1,4 microstructure (85%, ^{1}H NMR) and a poly(*tert*-butylmethacrylate) (P^{t}BMA) middle block (rr: 2%, rm: 46%, mm: 52%) [20] was synthesized (Scheme 1) by anionic polymerization high vacuum techniques [21].



Scheme 1. General reactions for the synthesis of the poly(butadiene-*b*-sodium methacrylate-*b*-butadiene) triblock copolymer.

The active PBLi solution, resulting from the polymerization of butadiene with *s*-BuLi in benzene, was ampulized and attached to a second polymerization reactor, washed with diphenylhexyllithium (DPHL) and rinsed with THF, which was the solvent for the polymerization of *tert*-butylmethacrylate (^{t}BMA). To this reactor, immersed into a dry ice/isopropanol bath at −78 °C, diphenylethylene (DPE), LiCl and the living PBLi were introduced in that order under stirring. Then purified ^{t}BMA was introduced by distillation and polymerized. In this way a diblock copolymer having half the molecular weight of the desired triblock was synthesized. The living diblock chains were coupled with an appropriate amount of *p*-dibromomethylbenzene in THF [22]. Excess of living diblock (with respect to the stoichiometric amount) over the linking agent was used in order to ensure complete coupling. The reaction was left to proceed at −78 °C for 5 h and for an additional four days at −20 °C. After this period the mixture was deactivated with degassed methanol. The desired triblock was isolated from the final crude product by solvent/non-solvent fractionation using toluene as the solvent and methanol as the non-solvent. The sample was thoroughly dried (above the glass transition temperature of P^{t}BMA) in a vacuum oven for a period of one week or more (code name BBMAB).

The poly(butadiene-*b*-sodium methacrylate-*b*-butadiene) triblock copolymer was prepared by the hydrolysis of the P^{t}BMA blocks and subsequent neutralization of the COOH groups with NaOH [23,24]. Block copolymer samples were dissolved in distilled dioxane to which a stoichiometric excess of HCl over the ester groups was added. The reaction was allowed to proceed for 6 h at 85 °C, under a continuous stream of argon or N_2 flow to prevent side reactions on the PB block. After hydrolysis the poly(butadiene-*b*-methacrylic acid-*b*-butadiene) triblock copolymer was dissolved in THF (about 2 wt% solution) and the calculated stoichiometric amount of NaOH as an ethanolic solution was added drop-wise through a volumetric pipette under vigorous stirring. The solid copolymer was recovered from acetone and dried under vacuum.

2.2. Characterization of precursor and final triblock copolymer

Analysis of intermediate and final products in the course of the synthesis of the PB-*b*-P^{t}BMA-*b*-PB precursor was conducted by size exclusion chromatography (SEC) in terms of molecular weight distribution and compositional homogeneity at 30 °C in THF (or $CHCl_3$) at a flow rate of 1 mL/min. A Waters system composed of a Waters 600 Pump Controller, a set of four Styragel columns (continuous porosity range 10^3–10^6 Å), a Waters 410 differential refractometer and a Waters 996 photodiode array UV detector interfaced with a computer were used. Number average molecular weights were determined by membrane osmometry (MO) in toluene, refluxed over CaH_2 and distilled prior to use, at 37 °C, using a Jupiter Instruments Company Model 231 membrane osmometer. Weight-average molecular weights were obtained by low angle laser light scattering (LALLS) using a Chromatix KMX-6 low angle laser light scattering photometer equipped with a He–Ne laser operating at 633 nm. THF, refluxed over sodium metal and distilled just prior to use, was the solvent used at 25 °C. The required specific refractive index increments, d*n*/d*c*, were determined with a Chromatix KMX-16 laser differential refractometer operating at the same wavelength/temperature as the LALLS and calibrated with aqueous NaCl solutions. The microstructure of the PB blocks and the average composition of the precursor copolymers as well as the extent of transformation reactions were determined by ^{1}H NMR (Varian 200 MHz instrument in $CDCl_3$ at 30 °C) or ^{13}C NMR (Bruker MSL 400 spectrometer capable of high-power ^{1}H-decoupling and equipped with magic angle spinning unit, at 30 °C) spectroscopy. More details on the synthesis and characterization of the polymer used are given elsewhere [24]. The molecular characteristics of relevance to this work are listed in Table 1.

2.3. Samples preparation

The triblock was dissolved in de-ionized water at different concentrations. Due to the strong incompatibility of sodium methacrylate and butadiene blocks, the critical micelle concentration (cmc) for formation of triblock copolymer micelles in water is expected to be very low [25]. In fact, some indirect fragmental evidence from dynamic light scattering measurements suggests that the cmc value is below 100 ppm [26]; such low cmc values are typical of associative triblock copolymers with hydrophilic/hydrophobic blocks [3a]. At a relatively low concentration (0.5 wt%) flower-like micelles are predominantly formed, with the hydrophobic butadiene tails comprising the core and the methacrylic middle blocks the shell, but some micelles are already bridged together forming a few microgel-like clusters [26,14]; the solution exhibits a liquid response (as discussed below) and this indicates that the individual micelles constitute the majority of species [26]. On the other hand, at higher concentrations (above 1.5 wt%) the micelles are predominantly interconnected via bridges, thus producing a solid-like network [1,3,10,14,26]. To ensure that the systems are well-characterized, the dilute solution properties were investigated in some detail (see Section 3.1 below).

Table 1
Molecular characteristics of the poly(butadiene-*b*-methacrylic acid-*b*-butadiene) (BNaMAB) triblock copolymer used in this study and the poly(butadiene-*b*-*tert*-butyl methacrylate-*b*-butadiene) (BBMAB) precursor

Sample	M_w [a] ($\times10^{-4}$)	M_n [b] ($\times10^{-4}$)	$M_{n,PBd}$ [b] ($\times10^{-4}$)	M_w/M_n [c]	wt% PBd [d]
BBMAB	10.1	9.54	0.32 [e]	1.09	7
BNaMAB [f]	7.41	6.77	0.32	1.09	9.5

[a] By LALLS in THF at 25 °C. All molecular weights units are in g/mol.

[b] By membrane osmometry in toluene at 37 °C.

[c] By SEC in THF at 30 °C.

[d] By ^{1}H NMR in $CDCl_3$ at 30 °C.

[e] By LALLS and SEC.

[f] Molecular characteristics calculated based on complete hydrolysis and neutralization of the precursor.

Two types of triblock micelle–surfactant complexes were investigated. One using a cationic surfactant, dodecyl trimethyl ammonium bromide (DTMAB), and the other using an anionic surfactant, sodium dodecyl sulfate (SDS). Both surfactants have the same hydrophobic tail, a hydrocarbon consisting of 12 carbon atoms, but different polar hydrophilic heads. As will be discussed below, the different charges of the surfactant play an important role in their interactions with poly(sodium methacrylate) middle block. As these interactions depend, among other factors, on the surfactant's critical micelle concentration (cmc), we note that for DTMAB cmc = 0.54 wt% (or 15 mM) and for SDS cmc = 0.23 wt% (or 8 mM), in water [27].

2.4. Methods

The linear rheological properties of the micelles were measured with a Rheometric Scientific ARES-HR sensitive strain-controlled rheometer with a dual range force rebalance transducer 100FRTN1. A cone- and plate geometry (25 mm diameter, 0.04 rad cone angle) was used along with a home-made PDMS (5 cp) solvent trap system to eliminate water evaporation during measurements. Temperature control (at 20 ± 0.1 °C) was achieved via re-circulation of water/

ethylene glycol mixture. Three types of oscillatory measurements were performed: (i) dynamic frequency sweeps at constant strain amplitude in the linear regime, in order to assess the viscoelastic character of the test samples; (ii) dynamic time sweeps at constant frequency and strain amplitude, in order to ensure the time stability of the samples and (iii) dynamic strain sweeps at constant frequency (or alternatively, frequency sweeps under constant large nonlinear strains) in order to determine the range of linear viscoelasticity and examine the nonlinear response of the test samples.

Experimental information on the dynamic structure of the micelles was obtained via dynamic light scattering (photon correlation spectroscopy). The intermediate scattering function $C(q,t) = [(G(q,t)-1)/f^*]^{1/2}$ ($f^* \le 1$ is an instrument coherence factor) of the micellar solutions at a given scattering wavevector q, was computed from the experimental normalized light scattering intensity autocorrelation function $G(q,t) \equiv \langle I(q,t)I(q)\rangle/|\langle I(q)\rangle|^2$ [28]. $G(q,t)$ was measured over a broad time range (10^{-7}–10^3 s) with an ALV-5000 goniometer/correlator set-up using a Nd:YAG laser at $\lambda = 532$ nm and at different wavevectors $q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the medium and θ the scattering angle. For the higher concentrations studied, the presence of multiple relaxation processes in $S(q,t)$ requires broad dynamic range and the analysis by inverse Laplace transformation (ILT), $C(q,t) = \int L(\ln\tau)\exp(-t/\tau)\mathrm{d}\ln\tau$. The distribution of relaxation times $L(\ln\tau)$ can be decomposed as a sum of distributions $L(\ln\tau) = \sum_i L_i(\ln\tau)$. The intensity of the i-th process can be obtained from the area of the corresponding distribution $L_i(\ln\tau)$, $I_i(q) = I(q)\int_{\ln\tau} L_i(\ln\tau)\mathrm{d}\ln\tau$, with $I(q)$ being the total scattering intensity; the relaxation rate Γ_i is obtained from the peak position of $L_i(\ln\tau)$ [29].

Small angle X-ray scattering (SAXS) measurements were carried out with a line collimation spectrometer consisting of a three slit-collimation system and a 10 cm linear detector situated 40 cm from the sample attached to a Rigaku 12 kW rotating anode with Cu target as an X-ray source. The wavevector q ranged from 0.15 to 3 nm^{-1}, with $q = (4\pi n/\lambda)\sin(\theta/2)$, $\lambda = 0.154$ nm is the wavelength and θ is the scattering angle. Due to collimation the measured intensity can be considered as infinite smeared intensity.

3. Results and discussion

3.1. Dilute solution characterization

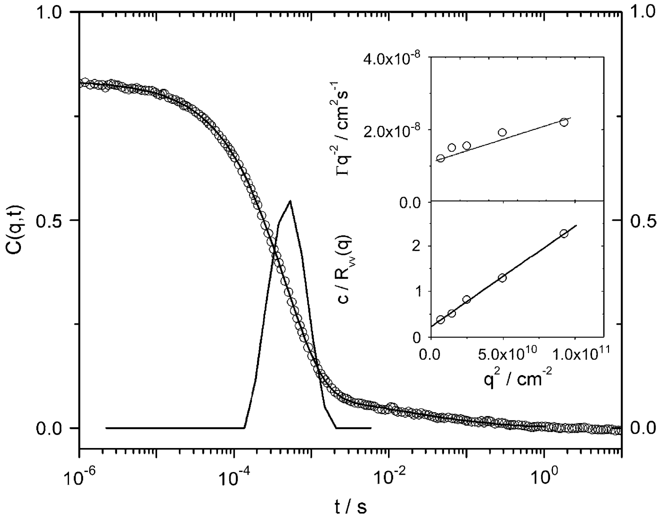


Fig. 1. The relaxation function $C(q,t)$ describing the diffusion of the micellar structures in 1.1×10^{-3} wt% BNaMAB in water at $q = 0.0303$ nm^{-1} along with the unimodal distribution function $L(\ln\tau)$. The variation of the effective diffusion coefficient Γ/q^2 and the associated light scattering intensity with q is shown in the inset.

A solution of 1.1×10^{-3} wt% BNaMAB polymer was dissolved under stirring and heating at 40 °C for 24 h and then filtered through 1 μm into the light scattering cell (20 mm diameter). To examine the presence of different structures even at very dilute solutions, we employed PCS to record the $C(q,t)$ at different scattering angles and hence q. Fig. 1 displays the $C(q,t)$ at $q = 0.0303$ nm^{-1} ($\theta = 150°$) for high resolution and contribution of small moieties in the light scattering intensity. Nevertheless, $C(q,t)$ is a single decay function as also revealed by the unimodal $L(\ln\tau)$. The diffusion $D = \Gamma/q^2$ and the absolute Rayleigh intensity $R_{\mathrm{vv}}(q) = (I(q)/I_{\mathrm{T}})R_{\mathrm{T}}$ (with I_{T} and R_{T} being the polarized intensity and Rayleigh ratio for the neat toluene) are shown in the inset of Fig. 1. Both the positive slope of $D(q)$ and the q-dependent $R_{\mathrm{vv}}(q)$ indicate large structures with $D_0(q \to 0) = 1.3 \times 10^{-8}$ cm^2/s and a radius of gyration $R_{\mathrm{g}} = 170$ nm obtained from the slope and intercept of c/R_{vv} vs q^2. Using the measured value of the refractive index increment $\mathrm{d}n/\mathrm{d}c = 0.145$ cm^3/g, the $R_{\mathrm{vv}}(q \to 0)/cH$, where $H = (2\pi n(\mathrm{d}n/\mathrm{d}c))^2/\lambda^4 N)$ leads to a weight-average molecular weight $M_{\mathrm{w}} = 15 \times 10^6$ g/mol, i.e., an aggregation of about 200 BNaMAB chains. Moreover, the hydrodynamic radius $R_{\mathrm{h}} = k_{\mathrm{B}}T/6\pi\eta_{\mathrm{s}}D_0$, with η_{s} being the solvent viscosity assumes a value of 172 nm, which is very close to R_{g}. This closeness of R_{g} to R_{h} suggests a rather compact micellar structure, also supported by the large aggregation number. We thus envisage spherical micelles consisting of a large core and a very dense corona, or alternatively spherical microgel-like micellar particles with many small cores interconnected via the dense grafted chains [30].

3.2. BNaMAB–DTMAB complexes

Fig. 2 depicts the linear viscoelastic spectra of an aqueous BNaMAB solution at a concentration of 0.5 wt% and different amounts of added cationic surfactant DMTAB. Whereas the pure micellar solution exhibits liquid-like response with very low moduli (G' is barely resolved at low frequencies), addition of a small amount of surfactant alters its behavior drastically. In particular, with 0.055 wt% DMTAB (this amounts to 5% surfactant with respect to the COO$^-$ groups of the copolymer) the solution turns into a gel with nearly frequency independent storage modulus G' over four decades and almost parallel loss modulus G'' for more than two decades (at high frequencies there is a weak dependence of G'' on frequency with slope of about 0.4, suggesting some local energy dissipation within the gel network) [31,32]. This type of behavior is reminiscent

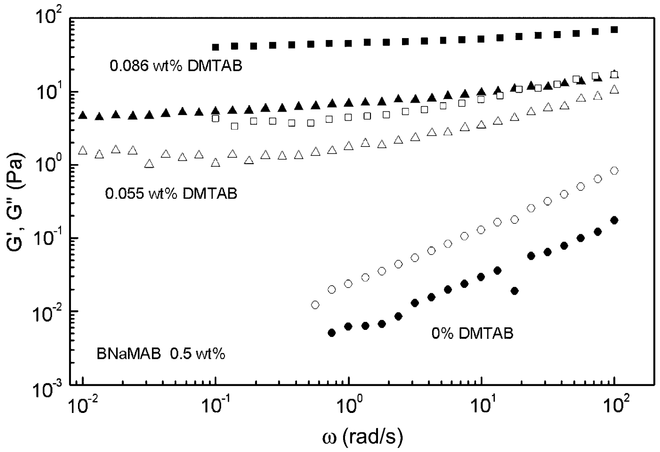


Fig. 2. Dynamic frequency sweeps of BNaMAB 0.5 wt% aqueous solutions in the linear viscoelastic regime, with different amounts of added cationic surfactant DMTAB: 0 wt% (●); 0.055 wt% (▲) and 0.086 wt% (■). Open symbols refer to G'' and closed symbols to G'.

of a (physical) network, and a typical average mesh size in such a case can be roughly estimated from the plateau modulus G' according to $\xi = (k_BT/G')^{1/3}$, yielding $\xi \simeq 44$ nm. At higher DMTAB concentration, namely 0.086 wt% (or 10% over the COO^- groups of the copolymer), the gel becomes stronger as its storage modulus nearly doubles in magnitude, the frequency dependence of both G' and G'' being unchanged, and the corresponding mesh size becomes $\xi \simeq 22$ nm.

Alternatively, in associating systems the plateau modulus G' typically scales with the number density of elastically active chains, ν, through the relation $G' = \nu k_BT$; one can then estimate the proportion of bridging hydrophilic chains between hydrophobic cores (an indication of the strength of the network) as $x \equiv \nu/n = G'/(nk_BT)$, where n is the number density of total chains in the solution [10]. In this case, x takes the values of 0.03 and 0.24 for the 0.055% and 0.086% DMTAB addition, respectively; this in fact implies that in the former case one chain out of 33 participates in the network acting as bridge between hydrophobic clusters (resulting in weak gel), whereas in the latter case one over four chains acts as bridge (stronger gel). It should be emphasized that the present simplified analysis is based under the assumption of nearly the same micelles, and as such it only serves as a guide for obtaining indicative trends for the effects of surfactant addition. A more thorough analysis accounts for the different probabilities of micelles and bridges' formation and predicts an increase of plateau modulus with surfactant concentration, followed by a peak and a gradual decrease [14]. However, in the system at hand it cannot be applied presently as several parameters (such as for example the number of micelles and the aggregation number per micelle) are unknown; their investigation is the subject of future work.

With reference to Fig. 2 an additional remark is in order. We actually identified the pure 0.5 wt% aqueous BNaMAB solution as a liquid-like system. It is important to note, however, that its dynamic rheological response suggests that it is very close to the percolation limit. In fact, as seen in this figure, G' and G'' are nearly parallel over the entire frequency range studied, with $G'' > G'$; the least-square fits through the data indicate slopes of $\Delta = 0.72$ and 0.76 for G' and G'', respectively. In a percolation limit, $G' \sim G'' \sim \omega^{\Delta}$ and the phase angle $\delta = \tan^{-1}(G''/G') = (\pi/2)\Delta$ with typical values around 0.7 for weak gel and 0.5 for strong gel, the latter bearing analogies to a disordered colloidal glass [32]. The experimental value of Δ from the loss angle is 0.82 (small deviation from the moduli slopes), thus it is roughly consistent with the literature. At much lower frequencies (beyond the instrumental resolution) the system should flow ($G' \sim \omega^2$ and $G'' \sim \omega$). Similar results were reported in the past for triblock copolymer micelles at different concentrations and temperatures [2a,4c,32a]. Note that a pure 0.1 wt% aqueous BNaMAB solution exhibits truly Newtonian flow behavior.

In Fig. 3 we observe that the strong gels (here 0.5 wt% BNaMAB with 0.086 wt% DTMAB) exhibit a maximum in G'' during dynamic strain sweeps. This feature, which is typical of several systems exhibiting solid-like response [33] (such as block copolymer gels [3b,34], hard sphere glasses [35], dense emulsions [36], soft sphere glasses [37]) suggests some enhanced local relaxations and enhanced dissipation of energy with strain, and of course an onset of nonlinear response before the G'–G'' crossover that corresponds to the liquid behavior. Phenomenologically, this type of behavior can be considered as a weak strain overshoot, according to a recently proposed classification of the large amplitude oscillatory shear response of complex fluids, by Hyun et al. [33]; it can be described by the soft glassy rheology model or other simple models resembling a generalized Maxwell model with a strain-dependent structural relaxation time [38].

3.3. BNaMAB–SDS complexes

As the concentration of pure BNaMAB in water increases, its behavior changes from liquid to solid, due to the formation

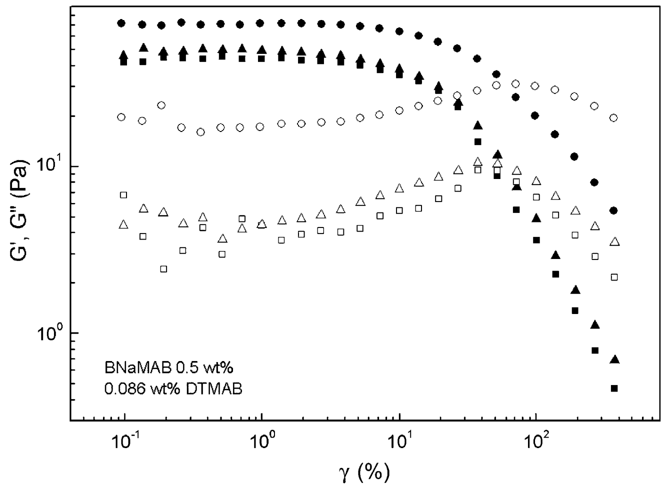


Fig. 3. Dynamic strain sweeps of a BNaMAB 0.5 wt% aqueous solution with 0.086 wt% added DMTAB at different frequencies (0.1 rad/s, ■; 1 rad/s, ▲; 100 rad/s, ●). Open symbols refer to G'' and closed symbols to G'.

of bridges among the flower-like micelles. In this particular example of 1.7 wt% concentration, the dynamic frequency sweeps of Fig. 4 indicate the formation of a gel with a characteristic average correlation length of $\xi \simeq 52$ nm. Upon adding anionic surfactant SDS (0.1 wt% or 10% over the COO^- groups of the copolymer) we observe strengthening of the gel with a corresponding reduction of mesh size to about 38 nm. However, a striking change occurs when the SDS concentration is further increased to about 0.3% (or 30% over the COO^- groups of the copolymer): the gel breaks-up and a liquid results. These findings are qualitatively similar to those reported for a hydrophobic ethoxylated urethane (HEUR)/SDS system [14a]. A percolation type analysis as in the case of the 0.5 wt% aqueous BNaMAB solution (Fig. 1) is clearly not applicable in this situation, as the G' curve indicates the existence of slow relaxation mode [39]. Therefore, in this case, which is clearly different from that of Fig. 2 (0.5 wt% BNaMAB), the lack of real power-law behavior is attributed to the slow mode, suggesting that the self-similarity in the structure of this complex polymer/surfactant system vanishes at large length scales. As already discussed in previous works [2a,b], this mode is related to some kind of dynamically heterogeneous structure resulting from strong composition fluctuations in the system. A practical aspect of this is that the fractal nature of the system is lost, and fewer chains participate in bridges.

As discussed, with reference to Fig. 2, one can again assess the network strength by estimating the proportion of hydrophilic chains forming bridges. For the pure BNaMAB 1.7 wt%, one finds $x = 0.07$ (one chain over 14 acts as bridge), whereas for the 0.1% SDS addition one finds $x = 0.125$ (one chain over eight). As there is not much difference between these two cases, and given the uncertainty of this approximate procedure, one can state that under the same surfactant concentration in the range 0.055–0.22 wt%, the effect of DMTAB on the aqueous micellar solution is more remarkable than that of SDS on the aqueous gel.

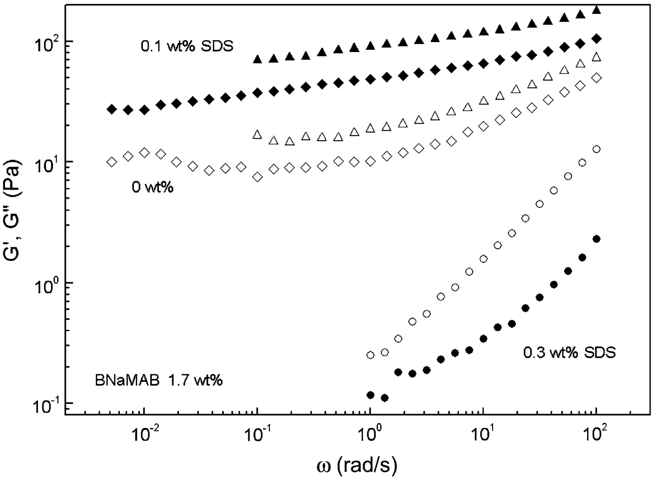


Fig. 4. Dynamic frequency sweeps of BNaMAB 1.7 wt% aqueous solutions in the linear viscoelastic regime, with different amounts of added anionic surfactant SDS: 0 wt% (◆); 0.1 wt% (▲) and 0.3 wt% (●). Open symbols refer to G'' and closed symbols to G'.

The above picture is corroborated by scattering experiments. In particular, the dynamics of the (pure) BNaMAB aqueous solutions at high concentrations (1.6 wt%) become slower compared to the dilute solutions (Fig. 1) and more complex as the relaxation function of the concentration fluctuations $C(q,t)$ of Fig. 5 displays a bimodal shape. Two diffusive processes were detected (see also inset of Fig. 5), a fast process with a diffusion coefficient $D_f = 2.3 \times 10^{-9}$ cm^2/s and a slow one with a diffusion coefficient $D_s = 2 \times 10^{-9}$ cm^2/s. We note that this solution is at a slightly different concentration than the one used for the rheological studies, and has underwent different treatments for the light scattering experiments. It does exhibit, however, typical features of a weak gel, i.e., an ergodic intermediate scattering function accompanied by a slow relaxation mode, the latter being the signature of the gel. This macroscopic immobilization (rheological response) and parallel ergodic $C(q,t)$ with a slow mode are known to characterize very soft gels and glasses [40]. Upon addition of a small amount of surfactant SDS (about 0.30 wt%), a speed-up of the micelle dynamics is clearly observed in Fig. 5. What is more spectacular, however, is the fact that the slow gel-like mode disappears and only one mode is detected with a diffusion coefficient $D = 2 \times 10^{-9}$ cm^2/s, very close to the fast diffusion coefficient of the pure BNaMAB micellar system. This is in harmony with the respective rheological results, demonstrating the SDS-mediated breaking of the gel. Note that the slow modes are common in polyelectrolyte systems and still not fully understood [41].

In order to obtain information on structural features at smaller length scale, small angle X-ray scattering measurements were carried out. The measured SAXS intensity depicted in Fig. 6 is typical of scattering from particles with a sharp interface. The lower q part can be well fitted by a Guinier type of behavior [42] leading to a value of gyration

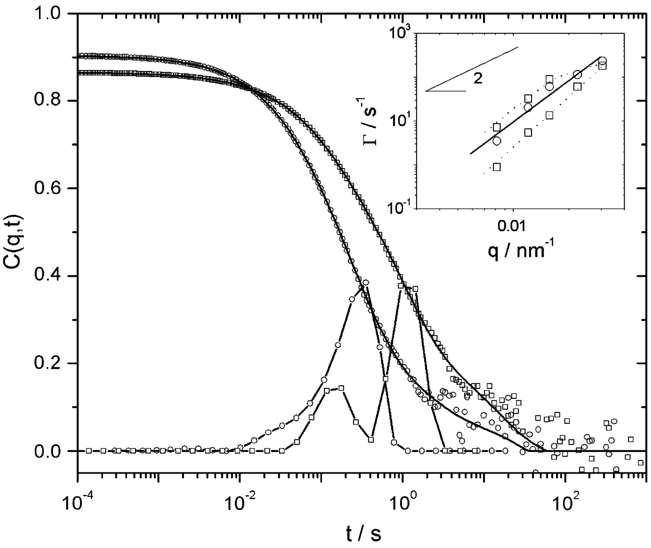


Fig. 5. Relaxation functions for 1.7 wt% BNaMAB aqueous solution with 0.3 wt% SDS (open circles) and without (open squares) at 0.008 nm^{-1} along with the distribution functions $L(\ln \tau)$. The relaxation rates for the single (with SDS) and the double (without SDS) relaxation processes of $C(q,t)$ are shown in the inset.

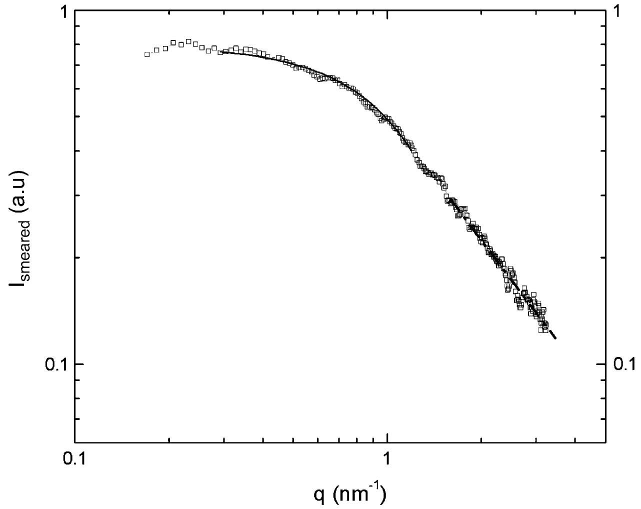


Fig. 6. SAXS spectrum of the BNaMAB 1.7 wt% aqueous solution with 0.1 wt% added SDS (gel-like solution). The lower q continuous line represents a Guinier fit with $R_g = 1.2$ nm and the higher q dotted line is q^{-3} power law, corresponding to the Porod limit with infinite slit collimation.

radius of 1.2 nm, which for a sphere will lead to a 1.5 nm radius; this is the typical value for a spherical SDS micelle at similar concentrations [27]. At larger q, the intensity appears to follow a power law, $I \sim q^{-3}$, which is typical of sharp interface scattering in the case of infinite slit collimation, i.e., Porod scattering (corresponding to $I \sim q^{-4}$ in the case of point collimation) [42]. Such scattering is typical from micelles scattering, i.e., SAXS is mostly sensitive to the presence of SDS micelles.

In contrast to the BNaMAB–DTMAB case, there is no G'' thickening and pronounced maximum when the BNaMAB–SDS gels are sheared at different frequencies with increasing amplitude (Fig. 7). Instead, G'' remains insensitive to strain and thins weakly only beyond the G'–G'' crossover in the liquid region. Note that the strength on the gels in both cases is comparable, and thus the difference should relate to the gel structure itself.

Motivated by the strain sweeps of Figs. 3 and 7 we performed some large amplitude oscillatory shear measurements in the two types of gels. Fig. 8 indicates that the gel of 0.5 wt% BNaMAB with 0.055 wt% DTMAB is liquefied when the strain amplitude increases from 1% (linear regime) to 30% (nonlinear regime). Similarly, the gel of 1.7% BNaMAB with 0.25 wt% SDS (or 20% over the COO$^-$ groups of the copolymer) liquefies when the strain amplitude increases from 1% to 10%, and exhibits faster relaxation modes (apparently, further breaking of bridges) as the amplitude progressively increases further to 100% (Fig. 9).

3.4. A tentative interpretation: surfactant-mediated micellar changes

The above results can be summarized as follows: the micellar system 0.5 wt% BNaMAB in water is a liquid; upon addition of cationic surfactant DTMAB (0.055 wt%) it becomes a gel. Increasing surfactant concentration yields stronger gel,

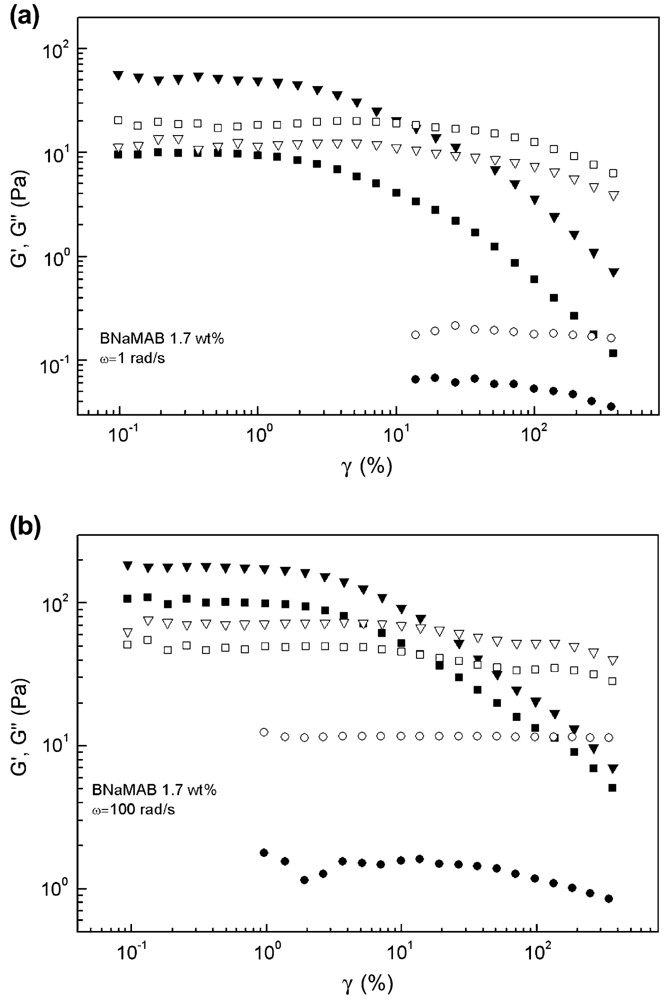


Fig. 7. Dynamic strain sweeps of BNaMAB 1.7 wt% aqueous solutions at a frequency of 1 rad/s (a) and 100 rad/s (b), with different amounts of added SDS (0 wt%, ■; 0.1 wt%, ▼; 0.3 wt%, ●). Open symbols refer to G'' and closed symbols to G'.

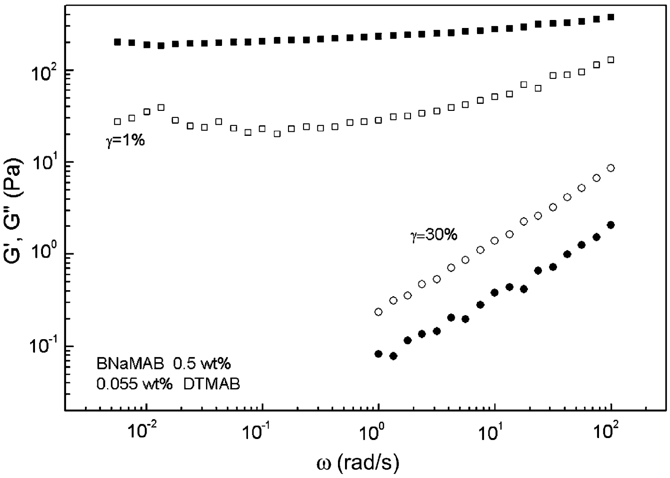


Fig. 8. Dynamic frequency sweeps of BNaMAB 0.5 wt% aqueous solutions with 0.055 wt% added cationic surfactant DMTAB at different strain amplitudes: 1% (■) and 30% (●). Open symbols refer to G'' and closed symbols to G'.

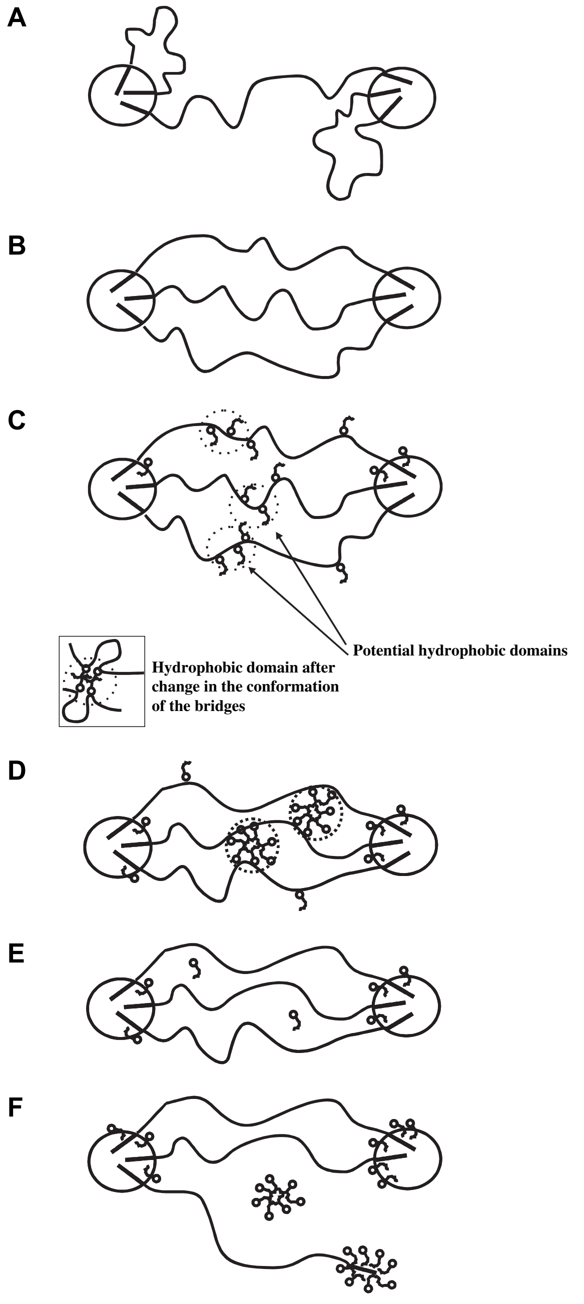


Chart 1. Cartoon representing different possible situations with the associative triblock copolymer solutions in water (neat copolymer and in the presence of surfactant) with ionic solvated blocks. (A) Neat triblock copolymer solution at relatively low concentration: end-associating hydrophobic blocks (butadiene, which forms the cores) of the same polymer chain can belong to the same micelle (looped conformation) or different micelles (bridging conformation). The middle hydrophilic blocks of poly(sodium methacrylate) form the loops or bridges. At this concentration several single micelles (no bridges) might exist. (B) Neat triblock copolymer solution at higher concentration: the bridging conformation is preferred and a physical gel is formed. Looped conformations and free dangling ends may also be present, but are outnumbered by the bridges. (C) Addition of surfactant (at a concentration below its cmc) having different head charge that the repeating units of the bridging hydrophilic blocks, can lead to polymer/surfactant complexation (attraction). Some surfactant molecules may be situated at the core corona interface of the micelles, as the hydrophobic tails prefer the core. Complexation sites can form hydrophobic domains after changes in the middle block conformation due to electrostatic interactions (inset). (D) Surfactant concentration of case C increases above cmc. Surfactant micelles are formed and complexed to the bridging blocks, forming additional hydrophobic domains. This case was not accessible experimentally due to gel collapse. (E) Addition of surfactant (at concentration below its cmc) having the same head charge as the bridging blocks. Here, complexation is not possible (repulsions). However, surfactant molecules can be situated in the core/corona interface of polymeric micelles (enthalpy). This situation is not considered in this work. (F) Surfactant concentration increases further above its cmc. Surfactant micelles are formed. Changes in the functionality of the micellar cores and formation of free dangling ends are possible (similarly to case E), weakening the gel. Eventually, the gel will liquefy (not shown here).

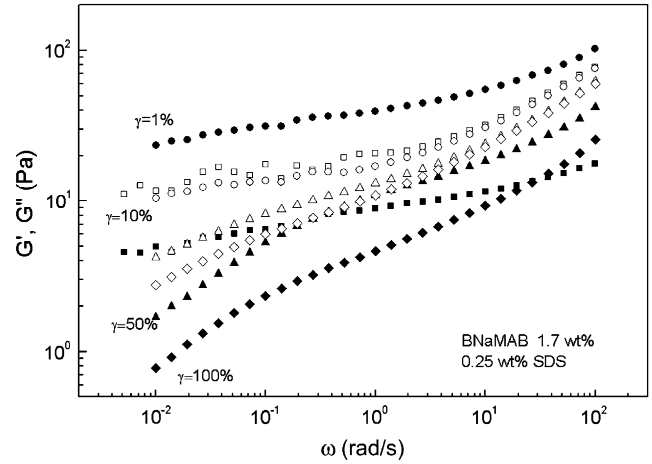


Fig. 9. Dynamic frequency sweeps of BNaMAB 1.7 wt% aqueous solutions with 0.25 wt% added anionic surfactant SDS at different strain amplitudes: 1% (●); 10% (■); 50% (▲) and 100% (◆). Open symbols refer to G'' and closed symbols to G'.

but beyond a concentration of 0.22 wt% in DTMAB, phase separation takes place, as evidenced visually; the system is macroscopically separated into a top clear water-rich phase and a bottom opaque polymer-rich phase. On the other hand, the micellar system 1.7 wt% BNaMAB in water is a gel; upon addition of anionic surfactant SDS up to a concentration of 0.25 wt%, the system remains a gel, stronger than the pure micellar gel. For SDS concentration above 0.28 wt%, the gel liquefies.

An assessment of these phenomena is based on the interactions of the hydrophobic and hydrophilic parts of both copolymer micelle and surfactant. Before proceeding with a rational interpretation of the findings, it is important to note that all DTMAB concentrations used here are below the cmc, whereas SDS concentrations $c \geq 0.25$ wt% lie above the cmc [43]; in the latter case we deal with the interactions of the copolymer micelles with small nearly spherical surfactant micelles (which are in equilibrium with free surfactant molecules).

Starting with the pure BNaMAB triblock in aqueous solution, we consider two situations, a relatively low concentration (Chart 1A), and a higher concentration (Chart 1B). In the former case, the hydrophobic end-blocks of the same polymer chain can belong to the same micelle (looped conformation, which may be preferred) or different micelle (bridging conformation); loops and bridges will coexist [14b]. The middle hydrophilic blocks form the loops or the bridges. On the other hand, in the latter case, the bridging conformation is most probable and a physical gel is formed [26], as the data also indicate. Looped conformations and free dangling ends may also be present, but to a limited degree [14a].

The cationic DTMAB surfactant has a long hydrocarbon tail that likes to be in the environment of the polybutadiene core of the micelle (Chart 1C). It is thus expected that these tails will be incorporated into the micellar cores (enthalpic reasons); this may reduce the number of polybutadiene blocks participating in a core, primarily for entropic reasons (the core size cannot increase forever). The DTMAB head has opposite charge than the hydrophilic methacrylic water soluble block of the micelle (or bridge); this will result in a DTMAB–PMAA complexation and charge compensation (Chart 1C). The characteristic of this complexation is the formation of hydrophobic domains after the electrostatic interaction of the surfactant heads with the middle copolymer block; these domains (illustrated in detail in the inset of Chart 1C) should become more pronounced as the surfactant concentration increases. In such a case, the bridges become less hydrophilic (because of the charge neutralization), and more hydrophobic regions (the domain complexes) form instead, rendering the gel stiffer (larger modulus); this can be visualized as a network with more junctions and bridges (therefore, smaller mesh size). Eventually, as the amount of added DTMAB increases above the cmc, the complexation (now involving surfactant micelles) becomes stronger (Chart 1D), the solubility of the PMAA block is reduced much, and finally phase separation will take place, accompanied by a destruction of the network (gel collapse).

Turning now to the anionic SDS surfactant, it has the same charge as the PMAA hydrophilic block, providing strong repulsions. The latter, along with the hydrophobicity of the SDS tails, tend to preferentially accommodate the SDS into the hydrophobic micellar core (Chart 1E for $c < \mathrm{cmc}$). The surfactant effects are much stronger when $c > \mathrm{cmc}$ (Chart 1F) and yield a reduced number of polybutadiene chains per gel network junction. This claim is supported by recent dynamic light scattering experiments on similar complexes formed by diblock copolymer micelles and SDS [26]; they indicate that increasing the concentration of SDS yields smaller micelles with less mass (less number of chains per micelle). Therefore, the net effect of the surfactant is to increase the 'functionality' of the gel network, creating more and smaller junctions, leading to gel of similar or slightly larger modulus (not a large effect). As SDS micelles are present in this high concentration case (Chart 1F), the dangling ends (from polybutadiene not participating in cores) will be incorporated into the SDS micelles. As the concentration of SDS increases further, the balance between electrostatic repulsions and entropic attractions of its micelles might result in an eventual destruction of most junctions, and thus the gel, yields eventually a liquid behavior.

These results are qualitatively consistent with earlier studies on the complexation of cationic surfactants and anionic hydrophobically modified polyelectrolytes, where the picture of mixed micelles was discussed [44]; they are further corroborated to the estimated ratio of Debye to Bjerum lengths (about 2), indicating reduced counterion screening and enhanced complexation (e.g., resulting in precipitation as in the DTMAB case at high concentrations). In this respect, the current findings suggest a universality of behavior in these polymer/surfactant systems, which is certainly advantageous for controlling the phase behavior and in particular the rheology of such soft systems in a variety of applications.

4. Conclusions

The present investigation on the interaction of cationic (dodecyl trimethyl ammonium bromide, DTMAB) and anionic (sodium dodecyl sulfate, SDS) surfactants with a triblock copolymer (BNaMAB), bearing two hydrophobic small end-blocks of polybutadiene and a large hydrophilic middle block of poly(sodium methacrylate), in aqueous solutions revealed the following results: in the very dilute regime (0.0011 wt%) spherical compact micelles are formed. Then, at a concentration of 0.5 wt%, the aqueous BNaMAB solution exhibits liquid-like behavior, close to the percolation threshold; upon addition of cationic surfactant DTMAB (0.055–0.22 wt%) it becomes a gel (stronger the more the surfactant added). Eventually, further addition of DTMAB results in gel collapse and phase separation. In the case of neat BNaMAB, when triblock concentration reaches 1.7 wt%, a weak gel is formed. The situation remains so even after adding anionic surfactant SDS (up to a concentration of 0.25 wt%). Finally, for SDS concentration above 0.28 wt%, the gel breaks down and a liquid-like system is recovered. These phenomena are interpreted in view of the surfactant/polymer interactions, which have two important features: (a) the hydrophobic tails prefer (enthalpically) to join the hydrophobic cores of the triblocks, and depending on their concentration they may change the core functionality in polymer chains (entropic reasons); (b) the hydrophilic heads will interact with the middle blocks, and in the case of opposite groups they will form complexes, which reduce the system's mobility. These findings seem to be universal, characterizing a variety of amphiphilic polymer/surfactant systems, and provide a route for controlling complex fluid rheology.

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