Macromolecules **2004,** *37,* 2930−2937

Hydrophobically Modified Associating Polyacrylamide Solutions: Relaxation Processes and Dilational Properties at the Oil−Water Interface

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Received January 11, 2004; Revised Manuscript Received February 23, 2004

ABSTRACT: The interfacial dilational viscoelastic properties of hydrophobically associating block copolymer composed of acrylamide (AM) and a low amount of 2-phenoxylethyl acrylate (POEA) (<1.0 mol %) at the octane−water interfaces were investigated by means of two methods: the interfacial tension response to sinusoidal area variations and the relaxation of an applied stress. The dependencies of interfacial dilational modulus and phase angle on the polymer concentration were explored. The influence of sodium dodecyl sulfate (SDS) on the dilational viscoelastic properties of polymer solutions was studied. The results obtained by oscillating barriers method showed that the dilational modulus passed through a maximum value with increasing polymer concentration, while the phase angle decreased with increasing concentration below 200 ppm, then showed very low concentration dependence up to 3000 ppm, and increased dramatically above it. When SDS was added to the aqueous phase, the dilational modulus passed through a maximum with increasing SDS concentration, while the change of phase angle depended on the polymer bulk concentration. The results obtained by the relaxation of an applied stress show that two main relaxation processes exist in the interface at low bulk concentration below the critical aggregation concentration: one is the fast process involving the exchange of hydrophobic microdomains between the proximal region and distal region in the interface with a characteristic time value from several tens of seconds to several seconds at different bulk concentration; the other is the slow relaxation process involving conformational changes of polymer chain in the interface with characteristic time value from 1000 s to several tens of seconds, depending on the bulk concentration. However, there is only one main relaxation process controlling the dilational properties above c^*: a fast relaxation process with the characteristic relaxation time of less than 1 s, which is believed to be related to the associations formed by hydrophobic microdomains. Anionic surfactant SDS can influence the dilational properties of polymer solutions by the following ways: first, SDS can absorb onto the interface and bind to the hydrophobic microdomains to change the characteristic times and contributions of the existed relaxation processes of polymer chains; second, SDS can provide a new fast relaxation process involving the exchange of SDS molecules between monomers and mixed micelles in interface. The information on relaxation processes obtained from interfacial tension relaxation measurements can explain the results from dilational viscoelasticity measurements very well. The negative phase angles have been obtained in some case. It is believed that the in-interface slow relaxation process, which sometimes dominates the dilational viscoelasticity of polymer film, is responsible for this phenomenon in our employed experimental method.

1. Introduction

Water-soluble polymers modified with relatively low amounts of a hydrophobic comonomer (a few percent) have recently become the subject of extensively research due to their interesting solution behavior.[1−2] In aqueous solution, above the overlap concentration of the polymer chains, the hydrophobic groups form intermolecular hydrophobic associations, resulting in a strong increase in solution viscosity.

Many uses for polymers of this type have been suggested, including in environmentally friendly formulations of paints and in medical formulations, although the main area of interest remains their use as aqueous viscosity modifiers in tertiary oil recovery system.[1−5] The increase in viscosity can improve sweep efficiency during enhanced oil recovery processes. The nonionic water-soluble copolymers of acrylamide prepared with hydrophobic comonomers have attracted a great deal of interest. They were extensively developed in the 1980s and their applications for enhanced oil recovery were pursued because of the large market potential that existed.

The interaction of hydrophobically associating water-soluble copolymers with small molecule surfactants is of fundamental importance for many industrial applications such as enhanced oil recovery and latex paint technology.[1,6] This interest stems from the need to accurately control the solution viscosity under a variety of shear conditions. When added to an aqueous solution of hydrophobically associating water-soluble copolymer, a small molecule anionic surfactant such as sodium dodecyl sulfate binds to the copolymeric regions in a noncooperative process causing a shift from intra- to interchain liaisons. This is evidenced by a peak in the apparent viscosity at surfactant concentrations below that of the cmc. Above the surfactant cmc, intra- and interchain interactions are destroyed, each hydrophobic region of each copolymer chain being solubilized in a single micelle.[7]

The bulk solution properties of different types of hydrophobically associating water-soluble copolymers have been widely studied in the absence of and in the

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10.1021/ma049923v CCC: $27.50

presence of different types of surfactants, and wide range of experimental methods including surface tension, viscosity, dialysis equilibrium, NMR, ESR, fluorescence, and different scattering techniques have been applied.[8−23] It is well-known that solution rheological properties of hydrophobically associating water-soluble copolymers are affected by hydrophobe type and content, molecular weight, degree of hydrolysis, temperature, salinity and the presence of different types of surfactants.[5] The added surfactant affects both the lifetime and the structure of the transient associating polymer−surfactant network, due to mixed micellization between surfactant molecules and the hydrophobic microdomain of polymer. The viscosity maximum appeared with increasing surfactant concentration is the result of two opposing effects: an increase in the lifetime of mixed micellar cross-links and a decrease in the number of cross-links. Experimental results indicate that the viscosity enhancement is not due to the formation of additional mixed plurifunctional aggregates but to an increase in the lifetime of the preexisting cross-links resulting from surfactant binding.[16,22] The structure of the network and the compositions of the mixed micellar cross-links are quite similar for the various surfactants, when the mixtures are compared at their respective viscosity maxima, and the differences in viscosifying efficiency between the different surfactants are due to differences in the lifetimes of the mixed micellar junctions.

Although the interfacial properties of hydrophobically associating water-soluble copolymers are very important for understanding the nature of associating polymers and their interactions with surfactants, the progress in this field was rather slow for many years mainly due to lack of suitable experimental techniques. Traditional methods such as surface tension measurement has been employed to detect the surfactant−polymer complexes at the air−water interface through the observation of a strong synergistic lowering of the surface tension,[24−27] but the application of the Gibbs adsorption equation usually leads to large errors when used to determine the polymer adsorption. Even more, recent studies have shown that surface tension can be insensitive to the state of the surface layer and is not a good predictor of the total amount of polymer in surface layer.[28] Fortunately, our knowledge about the structure of adsorbed polymer films has increased significantly mainly because of the application of neutron reflection,[29−33] which allows one to determine not only the adsorption but also the distribution of monomers normal to the liquid surface. However, on the other hand, any information on the dynamics of polymer chains at liquid interface is still quite limited.

Rheological properties are the main characteristics of the dynamic properties of a film. There are two rheological properties of the interfacial films−interfacial shear and dilational viscoelasticity. The interfacial shear property has been the most investigated viscoelastic property of liquid−liquid interface film in the past. However, it seems that the shear deformations are connected mainly with the processes of the structural reorganization characterized by a broad and almost continuous spectrum of relaxation times. On the contrary, the measurements of dynamic dilational viscoelasticity can be used to study the every single chemical and physical progress in the system and provide more information on the dynamics of polymer chains and their interaction with surfactant molecules at interface.[34]

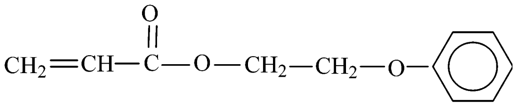

Figure 1. Chemical structure of the hydrophobic monomer 2-phenoxylethyl acrylate (POEA).

The dilational viscoelasticity of both insoluble polymer monolayer[35−42] and adsorbed polymer film,[28,43−57] unlike solution properties, has been studied by rather few researchers. Some of the results for adsorbed polymer films correspond to a frequency range during which the viscoelastic behavior of adsorbed polymer films is analogous to that of insoluble monolayers.[52−57] Although the application of low-frequency experimental techniques will give more information on the relaxation processes in adsorbed polymer films, only recently was the dynamic surface viscoelasticity of adsorbed nonionic homopolymer films measured at the liquid−gas interface in broad frequency and concentration ranges using a combination of three different methods of relaxation spectrometry of the surface layer.[28,45,47,50]

In this paper, we have investigated the interfacial dilational properties of hydrophobically associating water-soluble copolymer adsorbed at oil−water interface and studied the interfacial interaction between polymer and anionic surfactant by using oscillating barriers method and interfacial tension relaxation method over the frequency range from 0.0033 to 0.1 Hz.

2. Experimental Section

2.1. Materials and Sample Preparation. The structure of the hydrophobe monomer is shown in Figure 1. The sample was polyacrylamide hydrophobically modified with 2-phenoxylethyl acrylate (POEA) prepared by a micellar copolymerization technique. The synthesis and characterization of the copolymers are reported elsewhere.[58] It was dissolved in deionized water (resistivity > 18 MΩ·cm^{-1}) to a certain concentration and used as water phase. Octane, A. P., was obtained from Bodi chemical reagent Ltd., Tianjin, China, and used as the oil phase without further treatment. Sodium dodecyl sulfate (SDS) was obtained from Engineering Factory of Tianjin, China, and recrystallized by acetone. The critical micelle concentration (cmc) was found by conductivity to be 8×10^{-3} mol/L.

2.2. Interfacial Dilational Viscoelasticity Measurements.[59] The dilational rheology gives a measure of the interfacial resistance to changes in area. The interfacial dilational modulus ϵ at a particular frequency is characterized by its absolute value $|\epsilon|$ and by a phase angle θ describing the phase difference between dynamic interfacial tension variation and interfacial area variation:

$$\epsilon \equiv \frac{d\gamma}{d(\ln A)} = |\epsilon|\exp(i\theta) \qquad (1)$$

where ϵ is the dilational modulus, γ is the interfacial tension, θ is the phase angle, and A is the area of the interface. When a relaxation process takes place in or near the interface as a result of a disturbance, the interface will exhibit viscoelastic rather than pure elastic behavior. Dilational modulus can also be expressed as the summation of elastic and viscosity contributions:

$$\epsilon = \epsilon_d + i\omega\eta_d \qquad (2)$$

where the real part (storage modulus) represents the elastic energy stored in the interface and is known as the dilational elasticity ϵ_d, and the imaginary part (loss modulus) may be expressed in terms of the interfacial dilatonal viscosity η_d because it accounts for the energy dissipated in the relaxation process.

To probe the dilational viscoelasticity of the interfacial film, the Langmuir trough−Wilhelmy plate technique, which is most convenient and suitable for working at liquid−liquid interface, was employed. The interface area can be changed in sine oscillation (0.0033−0.1 Hz) mode by the horizontal slide of the barriers. The dynamic interfacial tension was measured by the Wilhelmy plate method, using a PTFE plate suspended in the middle of the trough area from a sensitive force transducer.

2.3. Interfacial Tension Relaxation Measurement.[60,61] Moving barriers can be used to produce a little change in interfacial area in a short period of time. The film is able to come to equilibrium before any disturbance was applied. The method allows one to convert any kind of interfacial tension change into the interfacial dilational modulus and its component parts, provided that the form of the area change applied is known.

For an instantaneous area change rising from $\Delta A(t) = 0$ for $t \leq 0$ to $\Delta A(t) = \Delta A$ for $t > 0$, the values of ϵ are obtained as a function of the frequency by Fourier transformation (FT) of the interfacial tension decay obtained from the experiment by the following relationship:

$$\epsilon(\omega) = \frac{FT\Delta\gamma(t)}{FT(\Delta A/A)(t)} = \frac{\int_0^\infty \Delta\gamma(t)\exp(-i\omega t)\,\mathrm{d}t}{\int_0^\infty [\Delta A(t)/A]\exp(-i\omega t)\,\mathrm{d}t} \qquad (3)$$

Here ω is the angular frequency. In an ideal system which is not diffusion-controlled and in which only one relaxation mechanism occurs, the decay curve of γ vs t can be represented by an exponential equation.

For a real system a number of relaxation processes may occur and the decay curve would be expressed by the summation of a number of exponential functions:

$$\Delta\gamma(t) = \sum_{i=1}^{n} A_i \exp(-B_i t) \qquad (4)$$

Here B_i is the characteristic frequency of the ith process; A_i is the fractional contribution which that relaxation process makes to restore the equilibrium; n is the total number of the relaxation processes.

For an instantaneous change in area

$$\int_0^\infty \frac{\Delta A}{A}\exp(-i\omega t)\,\mathrm{d}t = \frac{\Delta A/A}{i\omega} \qquad (5)$$

With this, Eq 3 becomes

$$\epsilon = \frac{i\omega}{\Delta A/A}\int_0^\infty \Delta\gamma(t)[\cos\omega t - \sin\omega t]\,\mathrm{d}t \qquad (6)$$

The real part of eq 6 is the dilational elasticity ϵ_d and the imaginary part is the interfacial dilatonal viscosity η_d: i.e.,

$$\epsilon_d(\omega) = \frac{\omega}{\Delta A/A}\int_0^\infty \Delta\gamma(t)\sin(\omega t)\,\mathrm{d}t \qquad (7)$$

$$\omega\eta_d(\omega) = \frac{\omega}{\Delta A/A}\int_0^\infty \Delta\gamma(t)\cos(\omega t)\,\mathrm{d}t \qquad (8)$$

Other parameters such as the tangent of phase angle, dilational modulus etc can all be obtained from these two parameters.

2.4. Experimental Procedure. The interfacial dilational viscoelasticity meter JMP2000A (Powereach Ltd., Shanghai, China), which had been described elsewhere,[62−63] was employed. The working principle is similar to that of Lucassen and Giles.[59] To probe the dilational viscoelasticity of the interfacial film, a Langmuir trough with a pair of PTFE barriers was used. In the interfacial dilational viscoelasticity measurements, the interface area can be changed in sine oscillation (0.0033−0.1 Hz) mode by the horizontal slide of the barriers. The dynamic interfacial tension was measured by the Wilhelmy plate method, using a PTFE plate suspended in the middle of the trough area from a sensitive force transducer. The water phase (90 mL) and oil phase (50 mL) was poured into the trough successively and carefully. The Wilhelmy plate should be completely submerged under the surface of the oil phase. The dilational viscoelasticity experiment began after 12 h of preequilibrium of the oil−water system. In the interfacial tension relaxation measurements, the film was expanded about 15% in area by a sudden and simultaneous movement of two parallel barriers, situated in the interface over 2 s, and then the film relaxes spontaneously. All experiments were performed at the temperature 30 °C.

3. Results and Discussion

3.1. Influence of Polymer Concentration on the Interfacial Dilational Viscoelasticity. The typical dependence of the interfacial dilational viscoelasticity of the hydrophobically associating water-soluble copolymer P(AM/POEA) on the polymer concentration is shown in Figure 2. The figure shows a plot of dilational modulus and phase angle vs concentration for different frequencies (from 0.0033 to 0.1 Hz). It can be seen that the dilational modulus appeared a maximum value at 3000 ppm. The dilational modulus showed very low concentration dependence below 200 ppm, then increased with increasing polymer concentration up to 3000 ppm and decreased dramatically above it. On the other hand, the phase angle decreased with increasing concentration below 200 ppm and then showed very low concentration dependence up to 3000 ppm and increased dramatically above it.

The interfacial dilational viscoelasticity is generally believed to be caused by the microscopic relaxation processes at the interface and near the interface. So the data of dilational viscoelasticity can provide the information about molecular interaction and structure at the interface. For low molecular weight surfactant systems, the two types of relaxation processes usually considered are the exchange of molecule between the bulk solution and the interface and conformational changes in the interface.[49] However, for macromolecules, the characteristic diffusional time is too large and one can consider only rapid interface strains corresponding to the homogeneous polymer concentration outside the interface layer.

According to the model provided by Noskov et al.,[28,45,47,50] although the exchange of macromolecules between the surface layer and the bulk phase can be neglected, the exchange of monomers between different regions of the surface layer has to be taken into account. Two main parts of the surface film are considered by them: a relatively narrow concentrated region contiguous to the gas phase (the proximal region), and region of “tails” and “loops” protruding into the bulk of the liquid where the global concentration of monomers is essentially lower (the distal region). It is essential that the width of the distal region exceeds that of the proximal region and the monomer concentration in the proximal region is essentially higher. The surface tension depends first of all on the concentration in the proximal region, and the relaxation of surface stresses at a surface dilation proceeds at the expense of drawing chains up to the surface (transition of monomers from the distal region to the proximal region) or squeezing chains out of the surface (the reverse transition), which

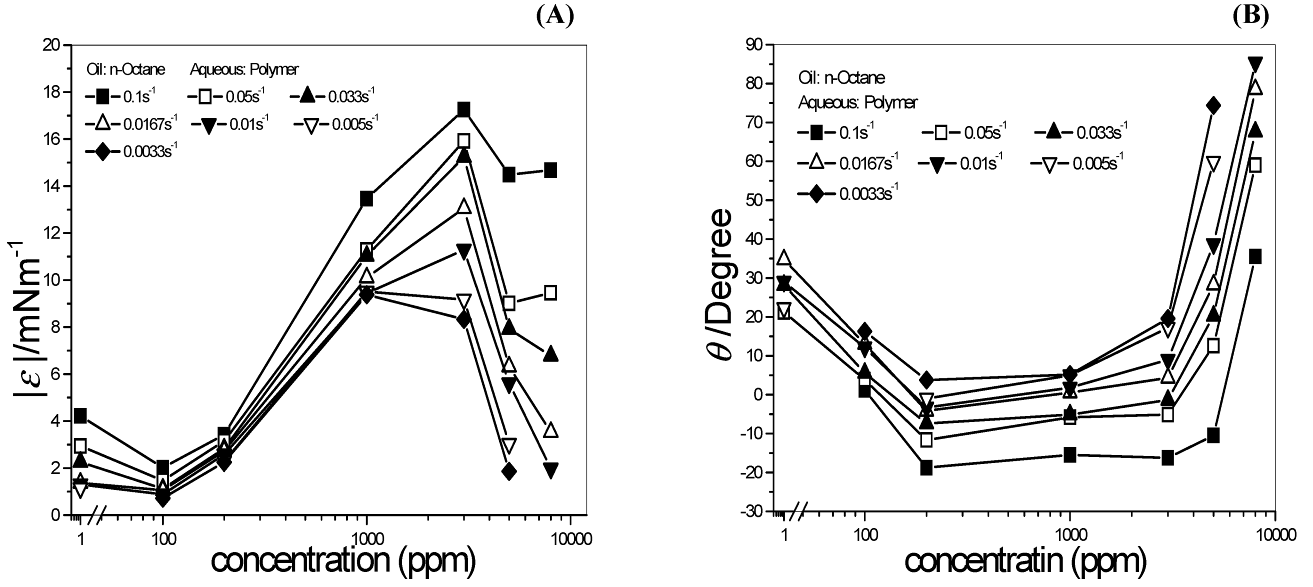

Figure 2. Interfacial dilational viscoelasticity as a function of polymer concentration at different dilational frequencies: (A) dilational modulus; (B) phase angle.

can take place as a result of two processes: the slow relaxation process of inner strains of a polymer chain or the fast relaxation process of the exchange of the chain as a whole.

The introduction of hydrophobic group POEA into PAM modifies the flow behavior of the precursor polymer. This is mainly due to intramolecular association, intermolecular association, or both. For associating polymer, there is a critical concentration above which the polymer solution shows enhanced viscosity. This critical concentration is also known as the overlap concentration, or the critical aggregation concentration. The viscosity at c^* is mainly due to intermolecular association. The interaction and association of polymer molecules at interface reflects those in the bulk solution. So the relaxation process corresponding to associations must be taken into account.

P(AM/POEA) has high surface activity due to its hydrophobic modification and can absorb at the interface. The surface tension value has been found to be about 45 mN/m for 6000 ppm polymer at 30 °C. The c^* of P(AM/POEA) is about 5000 ppm at 25 °C. Similar to Noskov's model, when P(AM/POEA) molecules absorb onto the interface, the hydrophobic microdomain stays in the proximal region contiguous to the oil phase and determines the interfacial tension while the AM part protruding into the distal region by the form of "tails" and "loops" . When the bulk concentration is higher than c^*, the microdomains absorbed at the interface will form associations, which will result in a fast relaxation process at dilational measurements.

At very low bulk concentrations (below 200 ppm), the absorbed macromolecules have an almost flat two-dimensional conformation and do not form long loops and tails. The dilational viscous component is close to zero, while dilational elasticity increases slightly with increasing polymer concentration. This results in the obvious decrease of phase angle at an almost constant dilational modulus value.

At further increase of the bulk concentration (from 200 to 3000 ppm), the interfacial polymer concentration increases and hinders complete unfolding of some of the adsorbing polymer coils in the interfacial layer. Gradually some loops and tails appear in the distal region of the interfacial layer. This leads to a relaxation of exchange of hydrophobic microdomain between the proximal and distal regions of the interfacial layer and the dilational viscous component increases. At the same time, the interaction among hydrophobic microdomains increases and results in the increase of dilational elasticity. Our experimental results show that the influence of the above relaxation process on the dilational viscous component is similar to that of dilational elasticity, so the dilational phase angle keeps almost constant until 3000 ppm with the dramatical increase of dilational modulus.

Table 1. Characteristics of the Copolymer P(AM/POEA)

sample	MA (mol %)	POEA (mol %)	[η] (mL/g)	$M_w \times 10^6$	K_H
P(AM/POEA)	99.44	0.56	656	9.9	0.48

Table 2. Interfacial Relaxation Processes and Their Characteristic Times Derived for Polymer Solutions

	process 1		process 2	
concn (ppm)	A_1/mN m^{-1}	τ_1/s	A_2/mN m^{-1}	τ_2/s
1	0.40	28.6	1.14	1075.3
10	0.12	10.0	0.73	416.7
100	0.34	3.8	0.20	263.2
200	0.19	3.4	0.49	58.8
3000	1.63	7.7	1.17	76.8
5000	3.64	4.8	0.67	76.9
6000	3.10	0.6		
8000	4.28	0.8		

Subsequent increase of bulk concentration (above 5000 ppm) leads to the faster exchange of hydrophobic microdomains between the proximal and distal regions and consequently results in a decrease of dilational modulus and increase of phase angle. It is also worth noting that the associations formed by hydrophobic microdomain in interfacial layer may lead to a faster exchange between monomers and them, which has a shorter characteristic relaxation time than that of hydrophobic microdomain exchange between the proximal and distal regions as seen in Table 2. The faster exchange between hydrophobic microdomains and their associations will decrease the dilational modulus dramatically, similar to that of surfactant solutions above their critical micelle concentration.

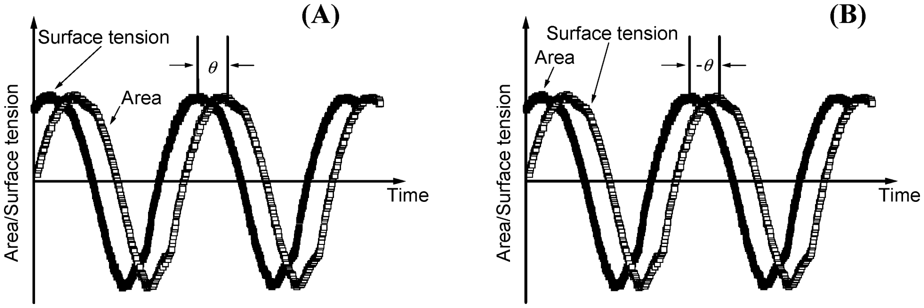

Figure 3. Definition of phase angle: (A) positive phase angle; (B) negative phase angle.

The characteristic relaxation times can provide the most important information about relaxation processes. But nowadays, even reliable estimations of the main relaxation times in adsorbed films of the most important polymers are still lacking.[28] For example, Noskov has obtained a value of 0.06 s for PEG solution at a concentration of 0.001 wt % by fitting to the experimental viscoelasticity data, though there should exist at least two main relaxation processes at the surface according to his model.[47]

To confirm our explanation above, the method of interfacial tension relaxation measurement has been employed to detect the microscopic relaxation processes in the interfacial layer. We can determine the characteristic relaxation time (τ) and contribution of different relaxation process (A), which are connected with the dynamic characteristics of macromolecules, by this method (Table 2).

We can see clearly from Table 2 that there exist two main relaxation processes below c^*: the fast relaxation process involving the exchange of hydrophobic microdomain between different regions in interfacial layer and the slow relaxation process involving conformational changes of polymer chain in the interface. Both processes become faster with increasing bulk concentration below 200 ppm then change little until 5000 ppm, with the characteristic times of several seconds and several tens of seconds, respectively. At the same time, the contribution of the fast process (A_1) becomes more and more important with increasing bulk concentration. However, there is only one main relaxation process controlling the dynamic dilational properties above c^*: a fast relaxation process with the characteristic relaxation time of less than 1 s, which is believed to be related to the associations formed by hydrophobic microdomains. The results from interfacial tension relaxation measurements are in good agreement with those from dilational viscoelasticity measurements.

It is important to note that the dilational phase angle has a negative value, which means a negative viscosity, during the concentration range from 200 to 3000 ppm at the frequency range above 0.01 Hz. The surface dilational viscosity has been obtained negative by the method of surface quasielastic light scattering (SQELS) for both solutions of conventional surfactants[64−66] and polymer films,[41,54,57,67−68] and there is no exact mechanism responsible for it.[65,28]

In our experimental method, the homogeneous deformations of the liquid interface are created by a pair of barriers oscillating in sinusoidal mode in a Langmuir trough and the corresponding changes of the interfacial tension are measured by using a Wilhelmy plate. The dilational modulus can be determined from the amplitude ratio of the oscillations of the interfacial tension and interface area, while the phase shift between the oscillations of the interfacial tension and interface area determines he phase angle of the interfacial dilational viscoelasticity. According to the general definition of dilational phase angle, the phase angle has a positive value when the phase of interfacial tension oscillation is ahead of that of interfacial area oscillation, while the negative one will appear when the phase of interfacial area oscillation is ahead of that of interfacial tension oscillation.

In our previous studies the negative phase angles have been obtained for the absorbed interfacial film at which the in-interface slow relaxation process dominates the dilational viscoelasticity, such as films containing HPAM molecules, crude oil fractions with high molecular weights and aggregations. On the other hand, the positive phase angles appears for the absorbed film at which the fast exchange of molecules between interface and bulk solution dominates the dilational viscoelasticity. For a certain area change, the negative phase angle will appear when the oscillation frequency becomes high enough that the fast exchange of molecules cannot compensate the interfacial concentration change caused by area change. So the higher the oscillation frequency is, the larger possibility the film has to show a negative phase angle. Our experimental results here can be explained by the reason discussed above and in good agreement with our previous results.

3.2. Influence of Anionic Surfactant on the Interfacial Dilational Viscoelasticity for Polymer Solutions.

It is well-known that surfactant concentration greatly affects viscosity of associating polymer systems. For anionic surfactant a viscosity maximum occurred at a surfactant concentration close to or lower than the critical micelle concentration (cmc). Viscosity increases of up to 5 orders of magnitude were observed, which were caused by the formation of mixed micelles containing surfactant molecules and hydrophobic microdomains.[69−70] The viscosity maximum occurred at a SDS concentration of 7.5×10^{-4} mol/L for 5000 ppm P(AM/POEA) used in this article.

The dependence of the interfacial dilational viscoelasticity for the 5000 ppm associating polymer on the dilational frequency at different SDS concentration is shown in Figure 4. Two important features may be extracted from these data. First, we see that the dilational modulus passed through a maximum with increasing SDS concentration, while the phase angle decreased monotonically. Second, the dilational modulus decreased dramatically and was almost not frequency dependent at SDS concentration above 4×10^{-4} mol/L.

The presence of hydrophobic groups along the copolymer backbone may allow, dependent upon the chain flexibility, both inter- and intrachain associations which

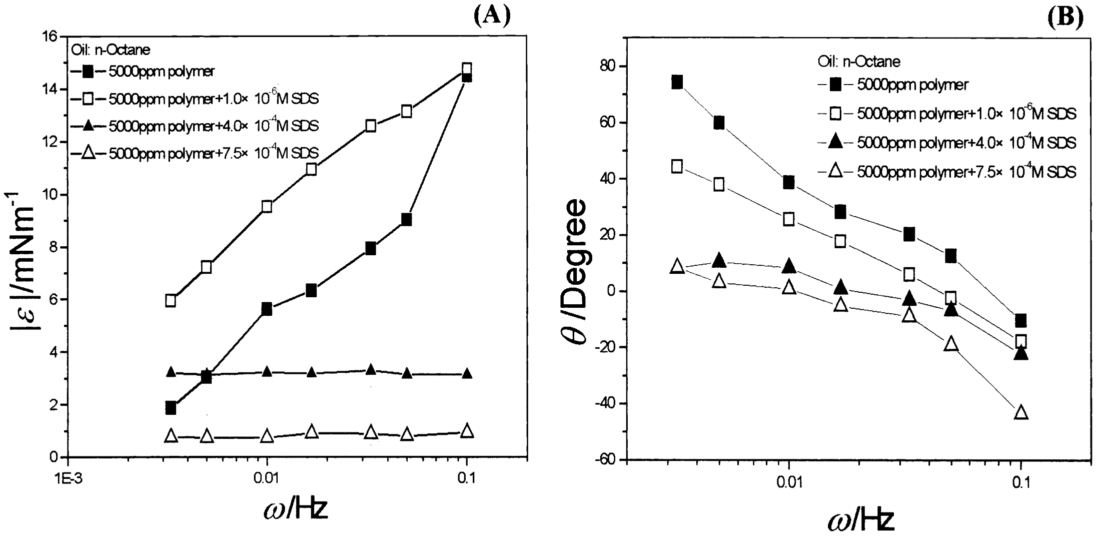

Figure 4. Interfacial dilational viscoelasticity for 5000 ppm polymer as a function of dilational frequency at different SDS concentration: (A) dilational modulus; (B) phase angle.

Table 3. Change of Interfacial Tension ($\Delta\gamma$) after the Area Change for 5000 ppm Polymer at Different SDS Concentrations

SDS concn (mol/L)	$\Delta\gamma$ (mN/m)
no SDS	3.78
1×10^{-6}	2.53
1×10^{-5}	1.00
4×10^{-4}	0.06

are in many ways analogous to micellar aggregates. Small molecule surfactants, when added to such a system, can interact with these hydrophobic groups leading to the formation of mixed micellelike aggregates.[7] These mixed micelles exist both in solution and at interface. The mixed micelles in solution either may promote chain linking by acting as a bridge between two polymer chains or may disrupt such linkages by solubilizing each hydrophobic group of a polymer chain into a single micelle. The mixed micelles at the interface may lead to a very fast exchange of SDS molecules between surfactant monomers and interfacial mixed micelles, and at the same time influence the characteristic relaxation times of the other processes mentioned above. When the interface is compressed, the SDS molecules can bind to the hydrophobic groups, while when the interface is expanded, the micellelike aggregates in turn liberate the SDS molecules.

The added surfactants will also influence the interfacial polymer concentration through two ways:[31] one is to adsorb competitively with polymer molecules at interface; the other is to decrease the hydrophobic ability of polymer molecules by forming mixed micelles. Both ways will decrease the interfacial polymer concentration.

Unfortunately, our interfacial relaxation measurement cannot catch the possible fast relaxation process of exchange of SDS molecules between monomers and mixed micelles we discussed above, which may have a characteristic time of less than 0.1 s. But the low values of dilational modulus, which are close to zero, combined with their being almost independent of frequency mean strongly that there exist fast relaxation processes far faster than our highest dilational frequency. In addition, the change of interfacial tension ($\Delta\gamma$) after the area change, which is listed in Table 3, decreased dramatically with increasing SDS concentration and was close to zero at 4×10^{-4} mol/L, while the $\Delta\gamma$ of SDS solution was 0.58 mN/m at the same concentration. This result can be explained only by the existence of a relaxation process of exchange of SDS molecules in interface, which is faster than the SDS monomers exchange between the interface and bulk solution.

Table 4. Interfacial Relaxation Processes and Their Characteristic Times for 5000 ppm Polymer at Different SDS Concentrations

	process 1		process 2	
SDS concn (mol/L)	A_1/mN m^{-1}	τ_1/s	A_2/mN m^{-1}	τ_2/s
no SDS	3.64	4.8	0.67	76.9
1×10^{-6}	1.47	10	1.31	55.6
1×10^{-5}	0.44	11.8	0.34	90.9
4×10^{-4}	0.032	7.7	0.079	33.3

The characteristic relaxation times and contributions of the other two relaxation processes are listed in Table 4. The characteristic time of both the fast and the slow processes passed through a maximum with increasing SDS concentration. The contribution of the fast process to dilational modulus decreased monotonically with increasing SDS concentration, while that of the slow process passed through a maximum. Both the contributions of two processes became very small at 4×10^{-4} mol/L SDS. It seems that the influence of SDS on the characteristic times of existed process plays the important role in controlling dilational properties of polymer film at low SDS concentration and may increase the dilational modulus, while the exchange of SDS molecules between monomers and mixed micelles in the interface dominates the film dilational properties at relative high SDS concentration and caused the very low value of dilational modulus.

The phase angle data in Figure 4 showed that the polymer film became more elastic with increasing SDS concentration. This may be explained by the reason that the ratio of contribution of the fast process to that of the slow process, which is responsible for the ratio of viscosity to elasticity, decreased monotonically with increasing SDS concentration.

The dependence of the interfacial dilational viscoelasticity for the 200 ppm associating polymer on the dilational frequency at different SDS concentration is shown in Figure 5. The characteristic relaxation times and contributions of different relaxation processes are

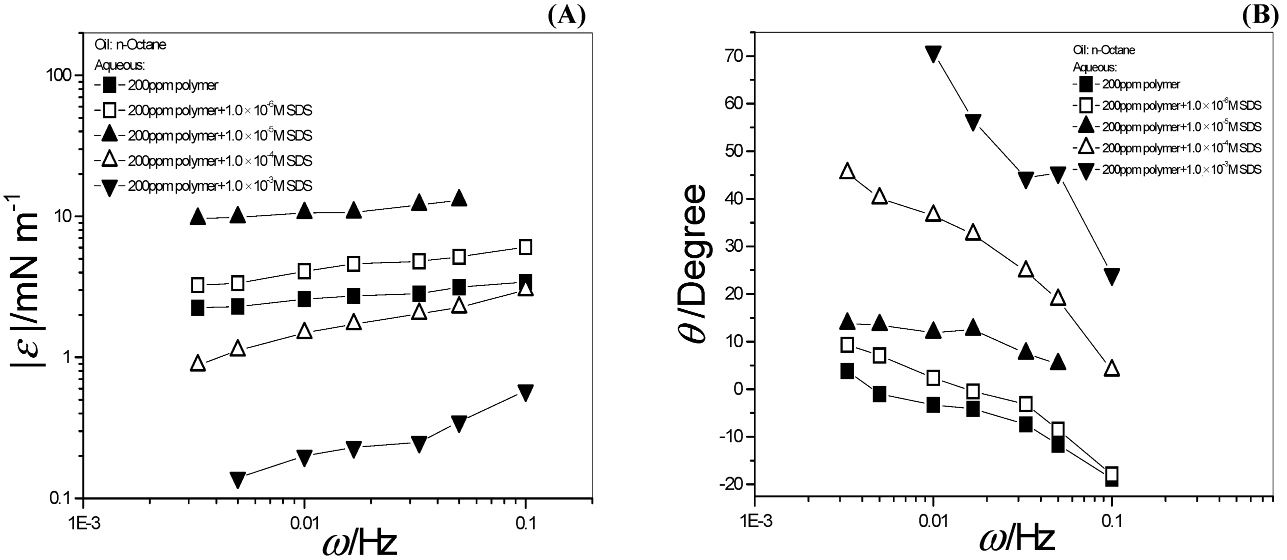

Figure 5. Interfacial dilational viscoelasticity for 200 ppm polymer as a function of dilational frequency at different SDS concentration: (A) dilational modulus; (B) phase angle.

Table 5. Interfacial Relaxation Processes and Their Characteristic Times for 200 ppm Polymer at Different SDS Concentrations

	process 1		process 2	
SDS concn (mol/L)	A_1/mN m^{-1}	τ_1/s	A_2/mN m^{-1}	τ_2/s
no SDS	0.19	3.4	0.49	58.8
1×10^{-6}	0.26	22.7	0.55	178.6
1×10^{-5}	1.40	5.9	1.08	192.3
1×10^{-4}	0.26	5	0.15	66.7
1×10^{-3}	0.21	0.9	0.039	14.5

Table 6. Change of Interfacial Tension ($\Delta\gamma$) after the Area Change for 200 ppm Polymer at Different SDS Concentrations

SDS concn (mol/L)	$\Delta\gamma$ (mN/m)
no SDS	2.71
1×10^{-6}	0.81
1×10^{-4}	0.46
1×10^{-3}	0.20

listed in Table 5. The changes of interfacial tension ($\Delta\gamma$) after the area change are listed in Table 6. Similar trends to the 5000 ppm solution in dilational modulus, characteristic relaxation times, and $\Delta\gamma$ were observed, which have been discussed above. However, the phase angle increased monotonically with increasing SDS concentration. This may be explained by the fact that the interfacial polymer concentration is so low that the SDS molecules absorbed in the interface dominate the film dilational properties even at very low SDS concentration such as 10^{-4} mol/L. So the film became more viscous with increasing SDS concentration, which increased the exchange of SDS molecules between the interface and bulk solution. It is interesting to note that the ratio of contribution of the fast process to that of the slow process increased monotonically with increasing SDS concentration in this case, which is in good agreement with the phase angle data.

4. Conclusion

The dilational modulus of hydrophobically associating water-soluble copolymer AM/POEA at the octane−water interface passed through a maximum with increasing bulk concentration under dilational frequency range from 0.0033 to 0.1 Hz, while the phase angle decreased with increasing concentration below 200 ppm, then showed very low concentration dependence up to 3000 ppm and increased dramatically above it.

The results from interfacial tension relaxation measurements show that two main relaxation processes exist in the interface at low bulk concentration below *c**: one is the fast process involving the exchange of hydrophobic microdomains between the proximal region and distal region in the interface with characteristic time value from several tens of seconds to several seconds at different bulk concentration; the other is the slow relaxation process involving conformational changes of polymer chain in the interface with characteristic time value from 1000 to several tens of seconds, depending on the bulk concentration. However, there is only one main relaxation process controlling the dilational properties above *c**: a fast relaxation process with a characteristic relaxation time of less than 1 s, which is believed to be related to the associations formed by hydrophobic microdomains. The information on relaxation processes from interfacial tension relaxation measurements can explain the results from dilational viscoelasticity measurements very well.

Anionic surfactant SDS can influence the dilational properties of polymer solutions in the following ways: first, SDS can decrease the interfacial polymer concentration; second, SDS can absorbed onto the interface and bind to the hydrophobic microdomains to change the characteristic times and contributions of the existed relaxation processes of polymer chains; third, SDS can provide a new fast relaxation process involving the exchange of SDS molecules between monomers and mixed micelles in interface. The influence of SDS on the characteristic times of existed process of polymer chains plays an important role in controlling the dilational properties of polymer film at low SDS concentration and may increase the dilational modulus, while the exchange of SDS molecules between monomers and mixed micelles in the interface dominates the film dilational properties at relatively high SDS concentrations and caused the very low value of dilational modulus.

The negative phase angles have been obtained in the concentration range from 200 to 3000 ppm at a frequency range above 0.01 Hz. It is believed that the in-interface slow relaxation process, which dominates the dilational viscoelasticity of polymer film, is responsible for this phenomenon.

Acknowledgment. Financial support by the Chinese National Key Basic Research Development Program "Fundamental Studies of the Extensively Enhanced Petroleum Recovery" (Project Grant G19990225) is greatly acknowledged.

Note Added after Print Publication. A transcription error resulted in an erroneous Figure 4 when this Article was published on the Web 3/26/2004 (ASAP) and in the April 20 issue (Vol. 37, No. 8, p 2935). The electronic version of the Article was corrected on 8/18/2004 and an Addition and Correction appears in the September 7, 2004, issue (Vol. 37, No. 18).

References and Notes

(1) Glass, J. E. *Polymers in Aqueous Media*; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1989.

(2) McCormick, C. L.; Block, J.; Schulz, D. N. Water-soluble Polymers. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1989; Vol. 17, p 730.

(3) Shaw, K. G.; Leipold, D. P. *J. Coat. Technol.* **1985**, *57*, 63.

(4) *Polymers as Rheology Modifiers*; Schulz, D. N., Glass, J. E., Eds.; American Chemical Society: Washington, DC, 1991.

(5) Taylor, K. C.; Nasr-El-Din, H. A. *J. Pet. Sci. Eng.* **1998**, *19*, 265.

(6) Goddard, E. D.; Ananthapadmanabhan, K. P. Applications of Polymer-Surfactant Systems. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Marcel Dekker: New York, 1998.

(7) Biggs, S.; Selb, J.; Candau, F. *Langmuir* **1992**, *8*, 838.

(8) Piculell, L.; Guillemet, F.; Thuresson, K.; Shubin, V.; Ericsson, O. *Adv. Colloid Interface Sci.* **1996**, *63*, 1.

(9) Kevelam, J.; van Breemen, J. F. L.; Blokzijl, W.; Engberts, J. B. F. N. *Langmuir* **1996**, *12*, 4709.

(10) Wang, Y. L.; Han, B. X.; Yan, H. K. *Langmuir* **1997**, *13*, 3119.

(11) Wang, Y. L.; Lu, D. H.; Long, C. F.; Han, B. X.; Yan, H. K. *Langmuir* **1998**, *14*, 2050.

(12) Nilsson, S.; Thuresson, K.; Hansson, P.; Lingdman, B. *J. Phys. Chem. B* **1998**, *102*, 7099.

(13) Seng, W. P.; Tam, K. C.; Jenkins, R. D. *Colloids Surf. A* **1999**, *154*, 365.

(14) Bromberg, L.; Temchenko, M.; Colby, R. H. *Langmuir* **2000**, *16*, 2609.

(15) Folmer, B. M.; Kronberg, B. *Langmuir* **2000**, *16*, 5987.

(16) Jimenez-Regalado, E.; Selb, J.; Candau, F. *Langmuir* **2000**, *16*, 8611.

(17) Jean, B.; Lee, L. T.; Cabane, B. *Colloid Polym. Sci.* **2000**, *278*, 764.

(18) Sukul, D.; Pal, S. K.; Mandal, D.; Sen, S.; Bhattacharyya, K. *J. Phys. Chem. B* **2000**, *104*, 6128.

(19) Petit-Agnely, F.; Iliopoulos, I.; Zana, R. *Langmuir* **2000**, *16*, 9921.

(20) Smith, G. L.; McCormick, C. L. *Langmuir* **2001**, *17*, 1719.

(21) English, R. J.; Laurer, J. H.; Spontak, R. J.; Khan, S. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 6425.

(22) Piculell, L.; Egermayer, M.; Sjostrom, J. *Langmuir* **2003**, *19*, 3643.

(23) *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Marcel Dekker: New York, 1998.

(24) Asnacios, A.; Langevin, D.; Argillier, J.-F. *Macromolecules* **1996**, *29*, 7412.

(25) Babak, V. G.; Skotnikova, E. A.; Lukina, I. G.; Pelletier, S.; Hubert, P.; Dellacherie, E. *J. Colloid Interface Sci.* **2000**, *225*, 505.

(26) Stubenrauch, C.; Albouy, P.-A.; Klitzing, R.v.; Langevin, D. *Langmuir* **2000**, *16*, 3206.

(27) Avranas, A.; Iliou, P. *J. Colloid Interface Sci.* **2003**, *258*, 102.

(28) Noskov, B. A.; Akentiev, A. V.; Bilibin, A. Yu.; Zorin, I. M.; Miller, R. *Adv. Colloid Interface Sci.* **2003**, *104*, 245.

(29) Lee, L. T.; Mann, E. K.; Guiselin, O.; Langevin, D.; Farnoux, B.; Penfold, J. *Macromolecules* **1993**, *26*, 7046.

(30) Purcell, I. P.; Lu, J. R.; Thomas, R. K.; Howe, A. M.; Penfold, J. *Langmuir* **1998**, *14*, 1637.

(31) Jean, B.; Lee, L.-T.; Cabane, B. *Langmuir* **1999**, *15*, 7585.

(32) Taylor, D. J. F.; Thomas, R. K.; Hines, J. D.; Humphreys, K.; Penfold, J. *Langmuir* **2002**, *18*, 9783.

(33) Taylor, D. J. F.; Thomas, R. K.; Li, P. X.; Penfold, J. *Langmuir* **2003**, *19*, 3712.

(34) Noskov. B. A. *Colloid Polym. Sci.* **1995**, *273*, 263.

(35) Lee, W.; Esker, A. R.; Yu, H. *Colloids Surf. A* **1995**, *102*, 191.

(36) Richards, R. W.; Rochford, B. R.; Taylor, M. R. *Macromolecules* **1996**, *29*, 1980.

(37) Baumberger, S.; Aguie-Beghin, V.; Douillard, R.; Lapierre, C.; Monties, B. *Ind. Crops Prod.* **1997**, *6*, 259.

(38) Booth, C.; Richards, R. W.; Taylor, M. R.; Yu, G.-E. *J. Phys. Chem. B* **1998**, *102*, 2001.

(39) Cathala, B.; Aguie-Beghin, V.; Douillard, R.; Monties, B. *Polym. Degrad. Stab.* **1998**, *59*, 77.

(40) Milling, A. J.; Richards, R. W.;; Hiorns, R. C.; Jones, R. G. *Macromolecules* **2000**, *33*, 2651.

(41) Milling, A. J.; Hutchings, L. R.; Richards, R. W. *Langmuir* **2001**, *17*, 5297.

(42) Milling, A. J.; Hutchings, L. R.; Richards, R. W. *Langmuir* **2001**, *17*, 5305.

(43) Regismond, S. T. A.; Gracie, K. D.; Winnik, F. M.; Goddard, E. D. *Langmuir* **1997**, *13*, 5558.

(44) Myrvold, R.; Hansen, F. K. *J. Colloid Interface Sci.* **1998**, *207*, 97.

(45) Noskov, B. A.; Alexandrov, D. A.; Loglio, G.; Miller, R. *Colloids Surf. A* **1999**, *156*, 307.

(46) Zhang, J.; Pelton, R. *Colloids Surf. A* **1999**, *156*, 111.

(47) Noskov, B. A.; Akentiev, A. V.; Loglio, G.; Miller, R. *J. Phys. Chem. B* **2000**, *104*, 7923.

(48) Fromyr, T.; Hansen, F. K.; Kotzev, A.; Laschewsky, A. *Langmuir* **2001**, *17*, 5256.

(49) Kopperud, H. B. M.; Hansen, F. K. *Macromolecules* **2001**, *34*, 5635.

(50) Noskov, B. A.; Akentiev, A. V.; Miller, R. *J. Colloid Interface Sci.* **2002**, *255*, 417.

(51) Jain, N. J.; Albouy, P.-A.; Langevin, D. *Langmuir* **2003**, *19*, 8371.

(52) Richards, R. W.; Taylor, M. R. *Macromolecules* **1997**, *30*, 3892.

(53) Huang, Q. R.; Wang, C. H. *J. Non-Cryst. Solids* **1998**, 235−237, 464.

(54) Peace, S. K.; Richards, R. W.; Williams, N. *Langmuir* **1998**, *14*, 667.

(55) Huang, Q. R.; Wang, C. H. *Langmuir* **1999**, *15*, 634.

(56) Esker, A. R.; Zhang, L. H.; Sauer, B. B.; Lee, W.; Yu, H. *Colloids Surf. A* **2000**, *171*, 131.

(57) Milling, A. J.; Richards, R. W.; Baines, F. L.; Armes, S. P.; Billingham, N. C. *Macromolecules* **2001**, *34*, 4173.

(58) Dai, Y. H.; Wu, F. P.; Li, M. Z.; Wang, E. J. *Acta Polym. Sinica* **2003**, No.4, 525.

(59) Lucassen, J.; Giles, D. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 217.

(60) Cárdenas-Valere, A. E.; Bailey, A. I. *Colloids Surf. A* **1993**, *79*, 115.

(61) Murry, B. S.; Ventura, A.; Lallemant, C. *Colloids Surf. A* **1998**, *143*, 211.

(62) Sun, T. L.; Zhang, L.; Wang, Y. Y.; Zhao, S.; Peng, B.; Li, M. Y.; Yu, J. Y. *J. Colloid Interface Sci.* **2002**, *255*, 241.

(63) Wang, Y. Y.; Zhang, L.; Sun, T. L.; Zhao, S.; Yu, J. Y. *J. Colloid Interface Sci.* **2003**, *270*, 163.

(64) Earnshaw, J. C.; McCoo, E. *Langmuir* **1995**, *11*, 1087.

(65) Monroy, F.; Kahn, J. G.; Langevin, D. *Colloids Surf. A* **1998**, *143*, 251.

(66) Monroy, F.; Munoz, M. G.; Rubio, J. E. F.; Ortega, F.; Rubio, R. G. *J. Phys. Chem. B* **2002**, *106*, 5636.

(67) Huang, Q. R.; Wang, C. H. *Langmuir* **1996**, *12*, 2679.

(68) Buzza, D. M. A.; Jones, J. L. McLeish, T. C. B.; Richards, R. W. *J. Chem. Phys.* **1998**, *109*, 5008.

(69) Iliopoulos, I.; Wang, T. K.; Audebert, R. *Langmuir* **1991**, *7*, 617.

(70) Magny, B.; Iliopoulos, I.; Audebert, R.; Riculell, L.; Lindman, B. *Prog. Colloid Polym. Sci.* **1992**, *89*, 118.

MA049923V