Dynamic and Viscoelastic Properties during the Thermal Gelation Process of a Nonionic Cellulose Ether Dissolved in Water in the Presence of Ionic Surfactants

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ABSTRACT: Dynamic light scattering (DLS) and shear relaxation experiments have been performed at various temperatures on the thermoreversible gelling aqueous systems ethyl(hydroxyethyl) cellulose (EHEC)/sodium dodecyl sulfate (SDS) and EHEC/cetyltrimethylammonium bromide (CTAB). Both the shear relaxation modulus and the decay of the time correlation function are slowed down as the gel is formed. The DLS results indicate initially an exponential decay followed by a stretched exponential at longer times. The relaxation time of the fast mode decreases with increasing temperature, whereas the characteristic time of the stretched exponential increases as the gel evolves. The fast relaxation mode is found to be diffusive at all temperatures, while the slow mode exhibits a complex wave vector dependence. The characteristic features are the same for both systems, but the shear relaxation modulus measurements as well as the DLS experiments suggest that the level of chain association or entanglement is higher for the EHEC/SDS system than for the EHEC/CTAB system.

Introduction

Systems of nonionic water-soluble polymers in the presence of ionic surfactants have attracted increasing attention during the last years because of their interesting properties and their importance in various applications. The behavior of these systems is governed by a subtle balance between hydrophobic, hydrophilic, and ionic interactions. Aqueous solutions of ethyl(hydroxyethyl) cellulose (EHEC) in the presence of an ionic surfactant constitute a system of this class.[1,2] This system has been studied by various experimental techniques,[3–9] and a number of characteristic features have been recognized. It is well established[1,5,10] that EHEC in the presence of an ionic surfactant forms a physically cross-linked gel in the semidilute concentration regime at elevated temperatures. It has recently been argued[1,7,10] that the driving force in the process of forming physical junction zones is the enhanced binding of surfactant to the polymer chains as the temperature increases. Quite recently the interaction of EHEC (the same sample was used as in the present work) with the anionic surfactant sodium dodecyl sulfate (SDS) and with the cationic surfactant cetyltrimethylammonium bromide (CTAB) was investigated[11] over a broad temperature range with the aid of surfactant and polymer NMR self-diffusion measurements. Most of these NMR experiments were conducted at a constant surfactant concentration of 4 m*m* (the same concentration as that employed in this investigation), where these semidilute EHEC (1 wt %)/surfactant solutions evolve gels at higher temperatures. During the sol–gel transition it was found that the amount of surfactant bound to the polymer was practically independent of temperature for both polymer/surfactant systems. On the basis of this finding and some other indications, the gelling of these systems could be rationalized in the framework of a model where the gelation process is governed by a delicate interplay between surfactant induced associations and enhanced polymer–polymer interactions at elevated temperatures due to gradually deteriorated thermodynamic conditions. At higher temperatures, approaching phase separation, the conjecture is that strong intermolecular association or entanglement gives rise to the formation of dense "lumps" of chains.[12] The polymer NMR self-diffusion results indicate that the strength of the chain association effect is higher for the EHEC/SDS system than that of the corresponding EHEC/CTAB system.

In order to further elucidate the difference in the interaction situation between these systems we have carried out dynamic light scattering (DLS) and shear stress relaxation measurements over an extended temperature range on the semidilute aqueous systems EHEC/DS and EHEC/CTAB, both with a constant surfactant concentration of 4 m*m*. It is well established[13] that the shear relaxation modulus $G(t)$ and the time correlation function of the electric field $g^{(1)}(t)$ in DLS are connected via the longitudinal bulk modulus and the cooperative diffusion coefficient. Moreover, a number of theoretical models[14–22] suggest that when the coupling of the concentration fluctuation to the viscoelasticity is strong, the time correlation function of the concentration fluctuation is bimodal, consisting of a single exponential decay and a nonexponential mode characterizing the structural changes or the viscoelastic response of the system. In the semidilute regime, in the long wavelength limit, the initial decay of the correlation function yields the cooperative diffusion coefficient (fast mode), followed at longer times by the wave vector, q, independent viscoelastic relaxation mode (slow mode), associated with chain disengagement relaxation. In addition, viscoelastic and DLS studies[23] on incipient chemical gels have shown that both the time correlation functions of concentration fluctuations as well as the shear relaxation modulus are described

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by power-law time decays with different power-law exponents.

The principal aim of this study is to survey how the interplay between hydrodynamic and viscoelastic effects of these systems affects the dynamic features extracted from time correlation functions. In this context the q dependences of the fast and the slow modes of these systems at different temperatures will be scrutinized. Furthermore, the results from the viscoelastic and DLS measurements will show that the level of polymer chain association or entanglement is different depending on the type of surfactant present.

Experimental Section

Materials and Solutions Preparation. The EHEC sample used is designated DVT 89017 and was manufactured by Berol Nobel AB (Stenungsund, Sweden). The degree of substitution of ethyl groups was $DS_{ethyl} = 1.9$ per anhydroglucose unit, and the molar substitution of ethylene oxide groups was $MS_{EO} = 1.3$ per anhydroglucose unit. The number average molecular weight M_n for this polydisperse sample ($M_w/M_n \approx 2$) is about 100 000 and for a 1 wt % EHEC solution in pure water the cloud point cp = 34 °C. All these data have been given by the manufacturer. The cationic CTAB and anionic SDS were both obtained from Fluka and were used without further purification.

The dilute EHEC solution was dialyzed against pure water for at least 1 week to remove salt (impurity from the manufacturer) and was then freeze-dried. As-dialyzing membrane-regenerated cellulose with a molecular weight cutoff of 8000 (Spectrum Medical Industries) was used. After freeze-drying, the polymer was redissolved in water. Samples were prepared by weighing the components and the solutions were homogenized by stirring at room temperature for several days. Solutions prepared in this way did not exhibit any time-dependent effects.[24] All the measurements were performed on semidilute EHEC/SDS and EHEC/CTAB systems with an EHEC concentration of 1.0 wt % and a surfactant concentration of 4.0 m*m*, well above the critical concentration for formation of polymer bound micelles.

Stress Relaxation Measurements. In a stress relaxation experiment a constant strain is applied to the system, and the time-dependent stress needed for maintaining the deformation is recorded. The results are reported in terms of the shear relaxation modulus $G(t) = \sigma(t)/\gamma_0$, the ratio of stress to the (constant) strain. The relaxation spectrum $H(\tau)$ (τ is the relaxation time) is related to $G(t)$ via the equation[25] $G(t) = G_e + \int_{-\infty}^{\infty} H(\tau) \exp(-t/\tau) \, d \ln \tau$, where the constant G_e is added to allow for a discrete contribution to the spectrum. In the present work the function $H(\tau)$ was evaluated from $G(t)$ with the first approximation scheme of Alfrey[26]

$$H(\tau) \cong - \left. \frac{dG(t)}{d \ln t} \right|_{t=\tau}$$

The stress relaxation experiments were performed in a Bohlin VOR rheometer system in the temperature range 22–40 °C with a cone-and-plate geometry. The cone angle was 5° and its diameter 30 mm. Special devices were used to avoid evaporation. The temperature in the measuring cell of the rheometer was maintained with the aid of a computer-controlled water bath. Temperature calibration of the sample chamber was carried out with a temperature probe because the bath temperature was a few degrees higher than that of the sample chamber. However, at a preset temperature, the temperature variation of the sample chamber was small (±0.1 °C) over the investigated range. In all experiments the decay of stress at a constant strain was monitored as a function of time. Special care was exercized to ensure that all measurements were performed within the linear viscoelastic regime. In order to fulfill this criterion all experiments were conducted at a constant strain amplitude of 10%. From these measurements $G(t)$ was determined. At a given temperature the sample was allowed to equilibrate for 2 h before measurements were commenced. The reproducibility of an experimental run without changing the sample was usually better than ±2%.

Dynamic Light Scattering. The beam from an argon ion laser (Spectra Physics Model 2020), operating at the wavelength 488 nm with vertically polarized light, was focused on the sample cell. This cell was held in a thermostat block filled with refractive index matching silicone oil, the temperature constancy being controlled to within ±0.05 °C at all temperatures studied. The sample solutions were filtered at room temperature in an atmosphere of filtered air through a 0.45 μm filter (Gelman Sciences) directly into precleaned 10-mm NMR tubes (Wilmad Glass Company) of highest quality.

The light scattering process defines a wave vector $q = (4\pi n/\lambda) \sin(\Theta/2)$, where λ is the wavelength of the incident light in a vacuum, Θ is the scattering angle, and n is the refractive index of the medium. The value of n was determined at each temperature of measurement at $\lambda = 488$ nm by using an Abbe' refractometer.

In the present study the full homodyne intensity autocorrelation function $g^{(2)}(q,t)$ was measured at six different scattering angles (30, 45, 52, 60, 75, and 90°) and at temperatures from 22 to about 40 °C with an ALV-5000 multiple τ digital correlator. The measurements were started at the lowest temperature, and the temperature was slowly increased. However, it should be noted that the sol–gel transition was found to be reversible, and no disturbing hysteresis effects were observed. At each temperature of measurement the sample was allowed to equilibrate for at least 2 h, before experiments were carried out. The correlation functions were recorded in the real time "multiple τ" mode of the correlator, in which 256 time channels are logarithmically spaced over an interval ranging from 0.2 μs to almost 1 h. In the analysis of correlation function data a nonlinear fitting algorithm (a modified Levenberg–Marquardt method) was employed to obtain best-fit values for the parameters appearing on the right hand side of eq 2 (see below).

Results and Discussion

Shear Stress Relaxation. In Figures 1a and b the relative shear relaxation modulus $G(t)/G(0)$, where $G(0)$ is the initially measured relaxation modulus, is depicted for the systems EHEC/SDS and EHEC/CTAB, respectively. The general trend is similar for both systems, namely that the relaxation functions exhibit a pronounced shift in the decay time toward higher values as the temperature increases. This finding, which bears a resemblance to that observed[8] for the time correlation functions obtained from DLS on EHEC/surfactant systems (see Figures 4a and b), suggests that the relaxation process is slowed down as the gel zone is approached. A similar time dependence of G has recently been observed in a study[27] on a thermoreversible gelling polysaccharide system.

Figure 2 shows log–log representations of G as a function of time at different temperatures for the systems EHEC/SDS (a) and EHEC/CTAB (b). The characteristic feature observed for both systems is that the time dependence of G gradually declines as the gel evolves, indicating enhanced elastic response. This trend is consistent with a previous rheological study[6,10] on the EHEC/CTAB system, where the shear storage modulus G' was observed to become strongly dominating over the shear loss modulus G'' at higher temperatures. Another interesting feature of Figure 2 is that the values of G, especially at elevated temperatures, are significantly higher for the system EHEC/SDS than the corresponding ones for the EHEC/CTAB system. This suggests that, to disentangle a cluster association or an entanglement coupling during the gel forming process, more energy is required for the former system than that of the latter one. It has been established from a number of studies[25,28–36] that the shear relaxation modulus of

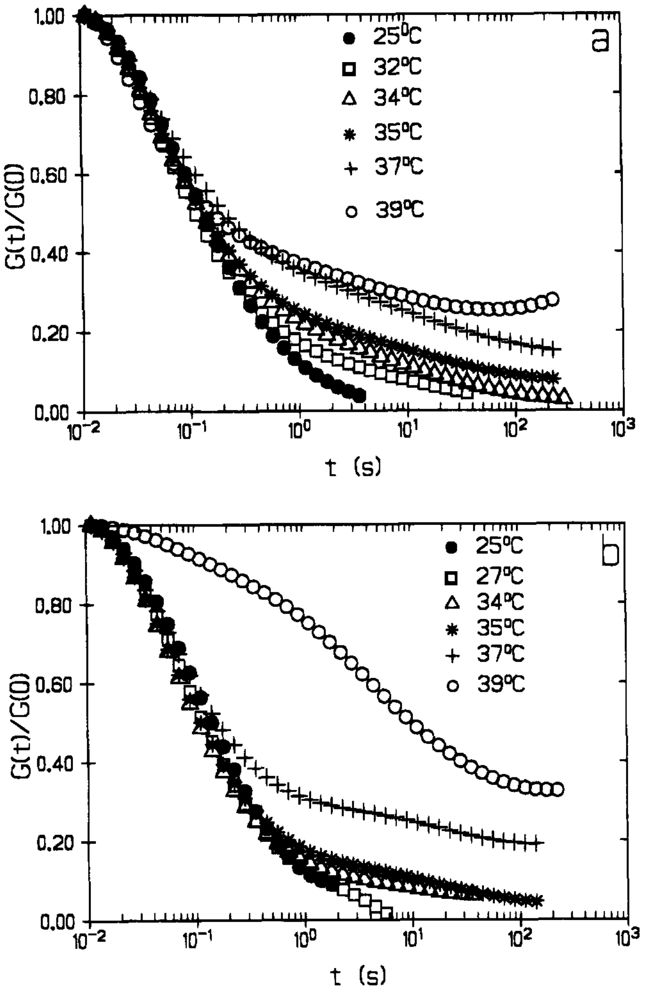

Figure 1. Plot of the relative shear relaxation modulus as a function of time for the systems EHEC/SDS (a) and EHEC/CTAB (b) at the temperatures indicated.

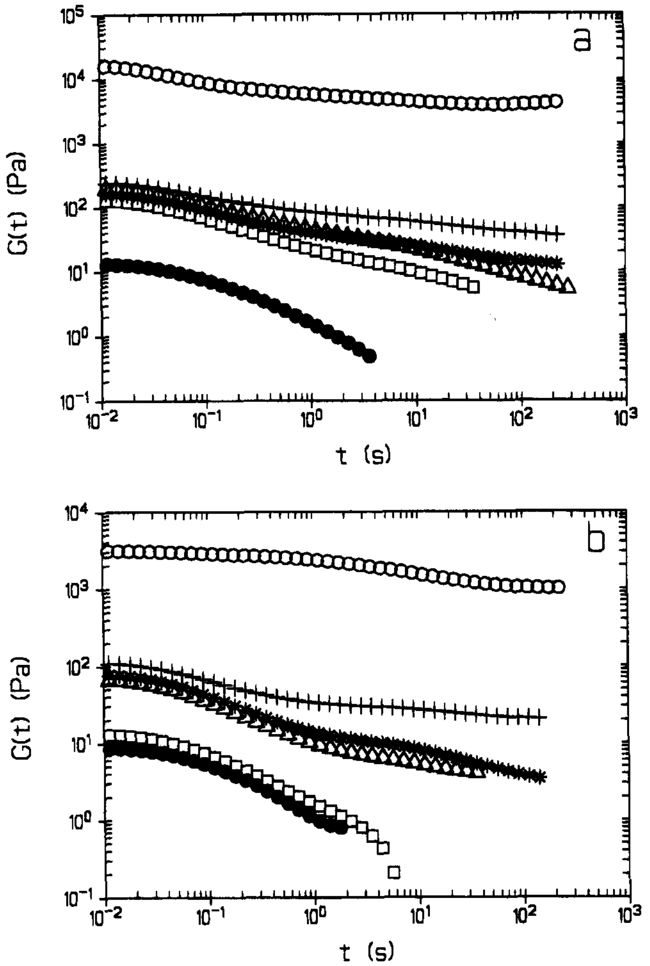

Figure 2. Plot of the shear relaxation modulus versus time for the systems EHEC/SDS (a) and EHEC/CTAB (b) at different temperatures (°C): 25 (●), 32 (□), 34 (Δ), 35 (*), 37 (+), 30 (○).

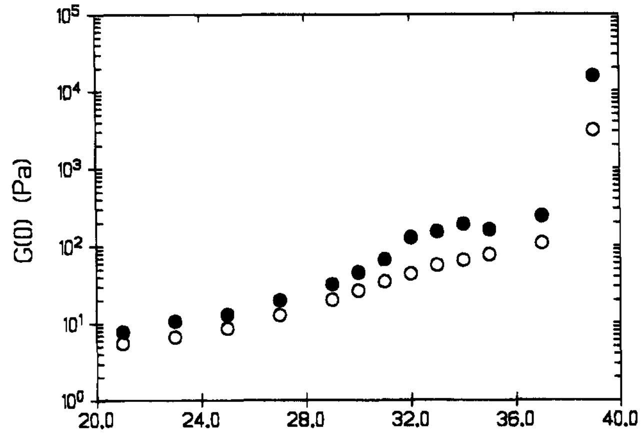

Figure 3. Temperature dependence of the initial shear relaxation modulus for the systems EHEC/SDS (●) and EHEC/CTAB (○).

the incipient gel decays as a power law $G(t) \sim t^{-\Delta}$. This led to the realization that in the linear response domain, G' and G'' will both follow similar power laws in frequency $G' \sim G'' \sim \omega^{\Delta}$. Oscillatory shear measurements on incipient gels from various systems of chemically and physically cross-linked networks have yielded values of Δ covering the whole physically accessible range ($0 < \Delta < 1$) of Δ. For example, in the case of the thermoreversible gelling system gelatin the values of the power-law exponent in the incipient gelation zone are generally located in the range 0.6–0.8,[37–39] but values as low as 0.2–0.3 have been observed[39] under certain experimental conditions. Values of Δ in the range $0 < \Delta < 1$ can be rationalized in the framework of the theoretical model of Muthukumar.[34] In this model, where screening of excluded volume interactions was taken into account, all values of the relaxation exponent for $0 < \Delta < 1$ are possible for a fractal dimension d_f in the physically acceptable range $1 \le d_f \le 3$. Low values of the exponent could be explained in terms of screening of excluded volume effects.

In the present investigation (see Figures 2a and b) we have, in the long time limit, estimated a Δ value of 0.2 at 37 °C (close to the gel point) for both systems. However, this estimation is probably rather crude and we will therefore defer a more detailed discussion of the values of Δ to a forthcoming paper.[40] In that work, dealing with oscillatory shear experiments on the same EHEC/surfactant systems as utilized in this study, we will report values of Δ in the range from 0.2 to 0.4, depending on polymer concentration and type of surfactant.

In Figure 3 the temperature dependence of the initial shear relaxation modulus is illustrated for the systems EHEC/SDS and EHEC/CTAB. A conspicuous feature is the drastic rise of $G(0)$ for both systems at about 37 °C, the incipient gel zone. At all temperatures the value of $G(0)$ is higher for the EHEC/SDS system than that of the other system, and this trend is strengthened at higher temperatures. This may indicate that a "stronger" physical gel evolves in the presence of SDS than with CTAB of the same concentration. This conjecture is supported by a recent oscillatory shear study,[40] where the gel strength parameter, evaluated at the gel point, was found to be much higher for the EHEC (1 wt %)/SDS (4 m*m*) system than the corresponding EHEC (1 wt %)/CTAB (4 m*m*) system. A close inspection of the data in Figure 3, reveals a "bump" at higher temperatures for the EHEC/SDS system (solid circles). However, we do not believe that this effect announces any significant difference in behavior between the systems.

Dynamic Light Scattering. Light scattering spectroscopy is a common method[41-43] for studying the dynamics in polymer solutions and gels. If the scattered field obeys Gaussian statistics the measured homodyne intensity autocorrelation function $g^{(2)}(q,t)$ can be related to the theoretically amenable first-order electric field correlation function $g^{(1)}(q,t)$ by the Siegert relationship

$$g^{(2)}(q,t) = 1 + B|g^{(1)}(q,t)|^2 \qquad (1)$$

where B is usually treated as an empirical factor. Dynamic light scattering experiments allow concentration fluctuations with well-defined wave vectors to be observed and the time dependence of $g^{(1)}(q,t)$ may be expressed as $g^{(1)}(q,t) = \langle \delta c_q(t) \cdot \delta c_{-q}(0)\rangle / \langle |\delta c_q|^2\rangle$, where $\delta c_q(t)$ is the concentration fluctuation of wave vector q. This type of experiment monitors how concentration fluctuations relax toward equilibrium at a length scale of $1/q$.

A number of DLS studies[8,16,17,23,27,37,44-58] on *complex* polymer systems have revealed the existence of a long-time tail of the correlation function, which consists of a distribution of relaxation times. A relaxation process, which exhibits a spectrum of relaxation times, has traditionally[59-62] been described by adopting the empirical Williams–Watts exponential relaxation function.[63] In a recent theoretical study[64] on entangled polymer systems the fractional exponential of the Williams–Watts type has been predicted by using an integral equation approach in which physical arguments are introduced to estimate the memory kernel. In this semiempirical relaxation model of Douglas and Hubbard the nonexponential decay (spectrum of relaxation times) of a relaxation function is attributed to memory effects which arise from inhomogeneities of the system. We may also note that heterogeneities in cross-link density of the network can alter the chain dynamics strongly.[65]

In the present DLS study, as well as in other DLS investigations[8,20,49,57] on complex polymer systems, the decay of the time correlation function can initially be described by a single exponential followed at longer times by a stretched exponential

$$g^{(1)}(t) = A_f \exp(-t/\tau_f) + A_s \exp[-(t/\tau_{se})^\beta] \qquad (2)$$

with $A_f + A_s = 1$. The parameters A_f and A_s are the amplitudes for the fast and the slow relaxation mode, respectively. The variable τ_{se} is some effective relaxation time, and β $(0 < \beta \leq 1)$ is a measure of the width of the distribution of relaxation times. In the above cited approach of Douglas and Hubbard β is interpreted as a measure of inhomogeneity or disorder effects and the specific value of β depends on the topological dimension of the modeled cluster. The mean relaxation time is given by

$$\tau_s \equiv \int_0^\infty \exp[-(t/\tau_{se})^\beta]\mathrm{d}t = (\tau_{se}/\beta)\Gamma(1/\beta) \qquad (3)$$

where $\Gamma(1/\beta)$ is the gamma function.

In the analysis of time correlation functions from DLS at long wavelengths in the semidilute regime, the first term (short-time behavior) on the right-hand side of eq 2 yields the cooperative diffusion coefficient D_c ($\tau_f^{-1} = D_c q^2$), which reflects a concerted motion of polymer chains relative to the solvent. The conjecture is that the slow relaxation time τ_s is associated with chain disengagement relaxation.

In Figures 4a and b, the normalized time correlation function data at various temperatures for the systems EHEC/SDS and EHEC/CTAB, respectively, are depicted in the form of semilogarithmic plots. We note that for both systems there is a progressive slowing down of the long time relaxation process as the temperature increases. A close comparison of the correlation functions at a given temperature reveals that the shift toward longer times is stronger for the EHEC/SDS system than for the EHEC/CTAB system. These results probably indicate a situation of enhanced dynamical constraints as the gel evolves.

In this study the value of $\beta = 0.45 \pm 0.05$ is found to hold for both systems, and β is observed to be independent of q and of temperature, except for the two highest temperatures where slightly lower values ($\beta \approx 0.35$) are obtained. The value of 0.45 is practically the same as found[8] for a thermoreversibly gelling system of a similar EHEC sample in the presence of 9 m*m* CTAB. Values of β in the range 0.2–0.7 have been reported[8,45,46,49,50,52] for gelling systems of a different nature.

It should be mentioned that the DLS measurements on the system EHEC/SDS cover only temperatures up to 36 °C, because at higher temperatures an incipient turbidity of the system became visible and the system displayed nonergodic features,[66-68] implying that the time-averaged intensity correlation function is not equal to the ensemble-averaged intensity correlation function. However, by checking the dependence of the decay curves of the time correlation function on the scattering position of the incident light in the sample, the nonergodic problem could not be recognized for any of the systems at the temperatures reported in this work, and the samples of both systems were optically clear. This indicates that the scattering elements, although localized, exhibit quite large displacements so that the scattered field can be considered as a zero-mean complex Gaussian variable.

Figure 5 shows the temperature dependences of the relaxation times, calculated with the aid of eq 2 in combination with eq 3, for the systems EHEC/SDS and EHEC/CTAB. It is obvious that the fast relaxation time τ_f decreases significantly with increasing temperature, even when the change of the solvent viscosity with temperature is accounted for (the dashed curve in Figure 5) the value of τ_f falls off by a factor of 3. Practically the same type of behavior is observed for both systems. The observed tendency of τ_f suggests that the diffusion coefficient increases as the gel zone is approached. In a recent study[69] the diffusion behavior in gels and the corresponding solutions was analyzed and it was found that nonuniformities in the network structure play a major role in the dynamic response of the system. This model predicts that for a gelling system with increasing nonuniformity of the network a reduction of the relaxation rate, i.e., an increase of the cooperative diffusion coefficient is anticipated. In view

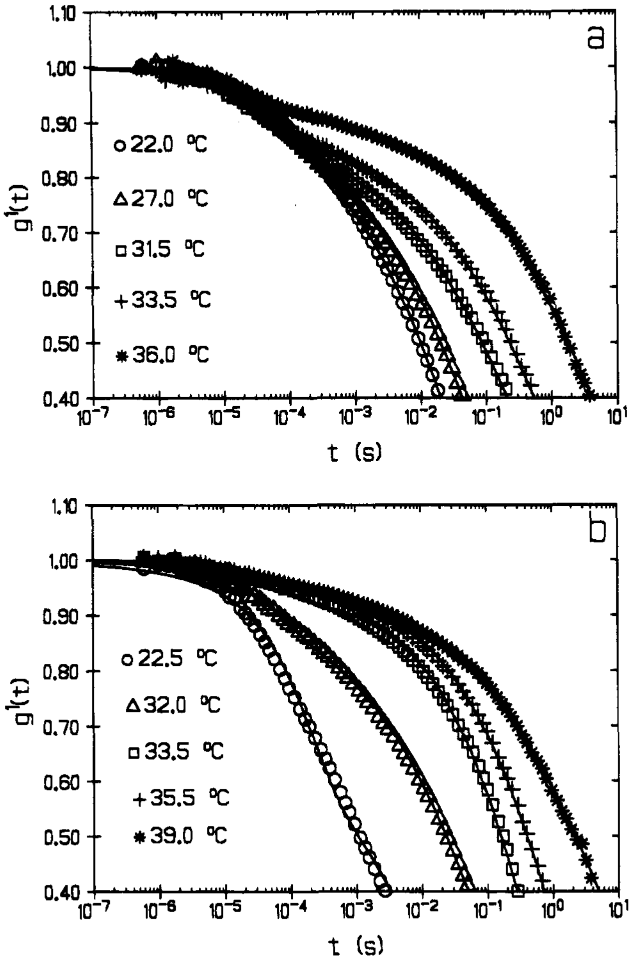

Figure 4. Plot of the first-order electric field correlation function versus time (every second data point is shown) for the systems EHEC/SDS (a) and EHEC/CTAB (b) at the temperatures indicated. The curves are fitted with the aid of eq 2 (see text). The scattering angle $\Theta = 90°$.

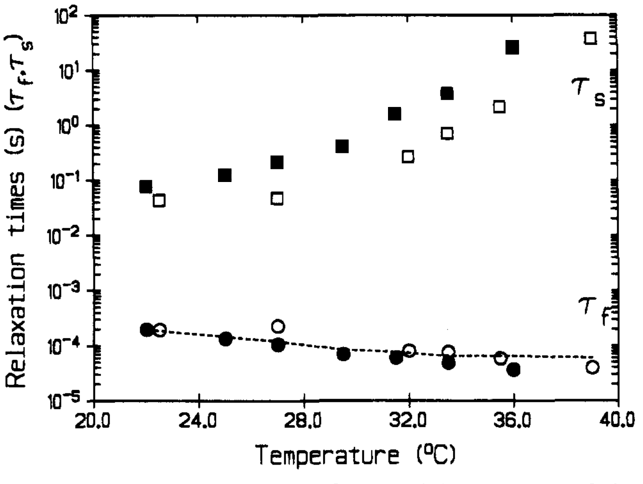

Figure 5. Temperature dependences of the fast (τ_f) and the slow (τ_s) relaxation times for the systems EHEC/SDS (●, ■) and EHEC/CTAB (○, □). The vlaues of τ_f and τ_s have been obtained from a fitting procedure of eq 2, together with eq 3 (see text). The dashed curve indicates the behavior when the change of the viscosity of the solvent with temperature is accounted for (see text for details).

of this prediction, the trend of τ_f in the present EHEC/surfactant systems suggests that the nonuniformity of the network increases as the gel evolves. This type of behavior is not unreasonable, because enhanced chain associations at elevated temperature, due to deteriorated thermodynamic conditions, may contribute to building up heterogeneities in the gel structure.

The slow relaxation time increases strongly as the temperature increases and the values of τ_s are consistently higher for the EHEC/SDS system than for the EHEC/CTAB system. This tendency seems to become more accentuated at higher temperatures. The observed rise of τ_s with increasing temperature is consistent with the surmise of enhanced chain associations and possible entanglements as the gel zone is approached. The observed difference in the behavior of τ_s for the two systems, probably reflects that the strength of chain association is stronger for the EHEC/SDS system.

In order to rationalize the enhanced interaction at elevated temperatures and the different interaction strength of the systems, a scenario was suggested where the gelation process is governed by a delicate interplay between surfactant induced associations and enhanced chain associations generated by deteriorated thermodynamic conditions at elevated temperatures. Gradually, stronger polymer–polymer interactions are expected to come into play as phase separation is approached. The conjecture is that at this stage, strong intermolecular interactions give rise to the formation of dense "lumps" of polymer chains.[12] Since the phase separation curve for the EHEC (1 wt %)/SDS system is located at lower[3] temperatures than that of the corresponding EHEC (1 wt %)/CTAB system, it is not surprising that the level of chain association or entanglement is, at a given temperature, higher for the former system (higher values of τ_s). The intricate interplay between thermoreversible gelation and macroscopic phase separation has recently been discussed[70] theoretically. In this work, the influence of factors such as polymer molecular weight, functionality, and the multiplicity of the network junctions were discussed.

The q dependences of the inverse fast and slow relaxation times may be expressed as $\tau_f^{-1} \sim q^{\alpha_f}$ and $\tau_s^{-1} \sim q^{\alpha_s}$, respectively. The value of α_f is practically independent of temperature ($\alpha_f \approx 2$) (see Figure 6a) and suggests that the fast mode is diffusive for both systems. When it comes to the q dependence of the slow relaxation time (see Figure 6b) a more intricate behavior arises. In this case the value of α_s decrases with increasing temperature for both systems, but the values of α_s are consistently lower for the EHEC/SDS system than the corresponding ones for the other system. In this context it is interesting that, based on a vast number of DLS studies on other complex systems of various nature, no consensus seems to exist concerning the q dependence of the slow mode. In some DLS investigations on semidilute polymer solutions and gelling systems, τ_s^{-1} was found to be q^2 dependent,[44,71–74] whereas in other papers[15,75,76] τ_s^{-1} was reported to be independent of q. Furthermore, a number of studies on associating[57] polymer systems and gelling systems[45,46,49,50,55] (both physical and chemical gels) have revealed that the q dependence of the slow mode is significantly stronger than that of the fast mode. In addition, it should be mentioned that in some publications on chemically gelled systems,[58,77,78] it has been observed that the slow mode disappears when the gel is formed, leaving only the diffusive mode. In the theoretical analysis of time correlation functions of complex systems, essentially two different pictures emerge.

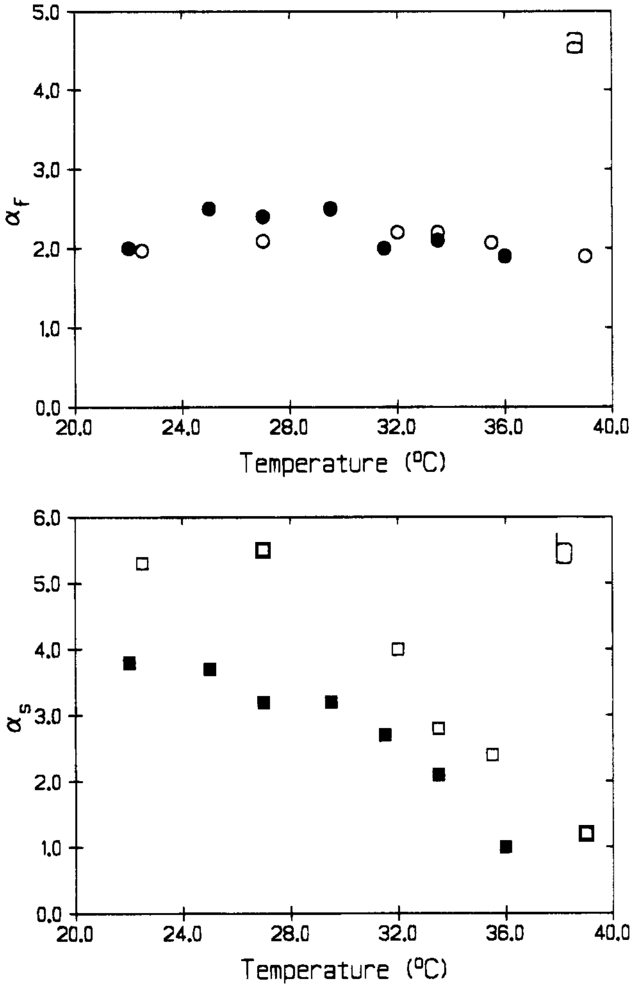

Figure 6. Power law exponents α_f and α_s (see text), illustrating the q dependences of the fast (a) and the slow (b) inverse relaxation times, respectively, for the systems EHEC/SDS (●, ■) and EHEC/CTAB (○, □).

Most of the theoretical advances[18-22] are concerned with the coupling of the concentration fluctuation and the viscoelastic effect in the form of longitudinal stress relaxation modes. These models predict that the slow mode, characterizing the structural or viscoelastic mode, consists of a distribution of relaxation times that are all *independent* of q because the viscoelastic response is not of hydrodynamic origin. In the theoretical approach elaborated by Wang[18-20] the coupling of the concentration fluctuation to the viscoelastic effect is considered. The model predicts a bimodal time autocorrelation function of concentration consisting of one single exponential decay associated with cooperative diffusion and a group of broadly distributed q independent modes, characterizing the viscoelastic relaxation. The analysis of Wang yields a relationship of a form[20] similar to that given in eq 2.

Some years ago Ngai and co-workers[59,79] devised a scheme to treat relaxations in complex systems. This approach addresses the problem of how the relaxation of a specific chain or cluster is "slowed down" due to the coupling to complex surroundings. Recently, Ngai[80] developed a modified version of this coupling model to analyze the relaxation of time correlation functions in solutions of clusters with a mass distribution. The surmise is that in solutions of this type the interaction between the clusters as well as cluster interpenetration give rise to dynamical constraints or couplings between the clusters that will slow down the slow relaxation process. This coupling model also yields, in conformity with the above cited coupling model of Wang, an expression of the form displayed in eq 2, but in this case a q dependence of τ_s stronger than that of τ_f can be rationalized. The coupling model of Ngai[80] predicts that $\alpha_s = \alpha_f/(1 - n)$, where the coupling parameter n ($0 < n < 1$) is a measure of the coupling strength of the relaxation mode to its surroundings and the quantity $1 - n$ is proportional to β in eq 2. This model suggests a q dependence of the slow mode stronger than that of the fast mode. In a recent work[57] on aqueous solutions of a hydrophobically end-capped poly(oxyethylene)-urethane, the observation of higher values of α_s as compared with the corresponding ones of α_f could successfully be described in the framework of the coupling model of Ngai. This hydrophobically associating system is characterized by a gradually stronger q dependence of τ_s^{-1} as the concentration increases, and it has been found,[81] even at a high concentration, that the relaxation of the shear modulus is practically instantaneous, indicating that the clusters are not entangled. Another illustration of this behavior is the studies of Delsanti et al.[45,46] on polyurethane systems, which are composed of polymer clusters formed by chemical gelation near the gel point, where a stronger q dependence of the slow mode was observed. On the basis of rheological experiments, they argued[82] that although clusters are imbricated they are not entangled.

In the light of these considerations, together with the theoretical predictions, the decrease of α_s with increasing temperature depicted in Figure 6b may be rationalized in the following way. At low temperatures, the polymer network is composed of interpenetrating but nonentangled clusters, leading to a rapidly relaxing shear modulus. However, at elevated temperature, when the gel evolves, the feature of strong chain association or entanglement gradually becomes more important and the lifetime of the tie points increases as well as the viscoelastic response (see Figure 1–3). Our conjecture is that the coupling of the concentration fluctuation to the viscoelasticity is strengthened as the gel zone is approached, giving rise to the strong reduction of the q dependence of the slow mode. Since the viscoelastic effect is, at all considered temperatures, stronger for the EHEC/SDS system than for the EHEC/CTAB system (see Figures 2 and 3), it is not surprising to note that the values α_s of the former system are lower than the corresponding ones of the latter system. Incidentally, we may note that in a previous light scattering study[8] on aqueous solutions of EHEC (1 wt %) in the presence of CTAB, the q dependence of the normalized inverse scattered intensity function was found to decline as the gel zone was approached. At the gel point this quantity was practically independent of q.

Summary and Conclusions

The combined measurements of viscoelasticity and DLS on the thermoreversible gelling systems EHEC/SDS and EHEC/CTAB have shown that the relaxation processes are slowed down as the gel evolves. This effect is more pronounced for the former system.

The results from the DLS experiments indicate two relaxation modes: an exponential at short times followed by a stretched exponential at longer times. The fast relaxation mode is diffusive at all temperatures and the corresponding relaxation time τ_f falls off with increasing temperature in the same way for both systems. This trend may suggest that the nonuniformity of the polymer network increases as the gel is formed. The slow mode is characterized by a mean relaxation time τ_s, which increases with increasing temperature, probably due to enhanced polymer chain associations. The slow mode exhibits a complex q dependence. At low temperatures, the q dependence of τ_s^{-1} is considerably stronger than that of τ_f^{-1}, whereas as the gel evolves the q dependence of the slow mode gradually ceases. This peculiar behavior is attributed to an intricate interplay between hydrodynamic and viscoelastic effects.

The picture that emerges from this study is that at low temperatures the solution consists of overlapping but nonentangled clusters, while as the gel forms, strong chain associations or entanglements give rise to a network of long-lived junction zones and with an enhanced viscoelastic response. Both the rheological and the DLS measurements reveal that the interaction situation of the two investigated systems is quantitatively different and the results suggest that the level of chain association or entanglement is significantly higher for the EHEC/SDS system than for the EHEC/CTAB system.

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