

Characterization of Interactions in Aqueous Solutions of Hydroxyethylcellulose and Its Hydrophobically Modified Analogue in the Presence of a Cyclodextrin Derivative

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The formation of associative networks in semidilute aqueous solutions of hydrophobically modified hydroxyethylcellulose (HM-HEC) is dependent on intermolecular hydrophobic interactions. Addition of hydroxypropyl- β -cyclodextrin (HP- β -CD) monomers to the system provides decoupling of these associations via inclusion complex formation with the polymer hydrophobic tails. Results from viscosity, polymer NMR self-diffusion, and dynamic light scattering (DLS) measurements show that the hydrophobic interactions in HM-HEC solutions are effectively suppressed when the level of HP- β -CD addition increases. Small-angle neutron scattering (SANS) results reveal that the large-scale association complexes in HM-HEC solutions are strongly diminished when the concentration of HP- β -CD rises. The time correlation data obtained from the DLS experiments unveiled the existence of two relaxation modes: one single exponential at short times followed by a stretched exponential at longer times. The fast mode is always diffusive, whereas the slow mode exhibits progressively stronger wavevector dependence as the intensity of the hydrophobic interactions increases. This feature, as well as the accompanying drop of the stretched exponential β as the HP- β -CD concentration decreases, is attributed to enhanced hydrophobic interactions and can be well rationalized in the framework of the coupling model of Ngai.

Introduction

Hydrophobically modified (HM) polymers or water-soluble associative polymers form supramolecular structures in aqueous media mainly because of hydrophobic interactions. These polymers are currently used in a range of applications, including paint formulations and paper coatings, and they have potential for use in personal care products, as well as in pharmaceutical formulations.^{1,2} HM polymers are usually equipped with a water-soluble backbone onto which a low number of hydrophobic groups have been chemically attached. Despite the fact that the substitution degree of hydrophobic groups is low, aqueous solutions of these polymers usually exhibit interesting rheological behaviors such as a much stronger viscosity enhancement with increasing polymer concentration as compared with the corresponding system with the unmodified parent polymer. A usual way to modulate the strength of the hydrophobic interactions is to add a surfactant, which at high concentration decouples hydrophobic polymer–polymer associations by encapsulating each hydrophobic tail in a micelle.^{1,2} Another efficient approach that will be utilized in this work is to decouple the hydrophobic associations by addition of cyclodextrin (CD). This compound is a cyclic oligomer of glucose with the shape of a truncated cone, and it can consist of 6, 7, or 8 glucose units (corresponding to α -, β -, and γ -CD) joined by α -1,4-glucosidic linkages.³ The truncated cone has a hydrophobic inner core and a hydrophilic outer shell, making it possible for the

hydrophobic segments of the polymer to reside inside them and form a complex, referred to as an inclusion compound.

The interaction between CD and hydrophobically modified polymers has been studied from the early 1990s and it has been established^{4,5} that CD molecules form complexes with the hydrophobic moieties through a process where the polymer hydrophobic tails are hidden within the CD cavities and only the outer shell of the CD molecules is exposed to the aqueous medium. Because of this deactivation of the hydrophobic groups, the strength of the association is diminished and this gives rise, e.g., to a decrease in the solution viscosity. The previous investigations have shown that the strength of the hydrophobic interactions can be tuned by CD addition. Quite recently,⁶ we reported the effects of β -CD addition and temperature on the rheological features of semidilute solutions of the anionic copolymer alginate and its hydrophobically modified analogue (HM-alginate). The viscosity results revealed cross-linking of the alginate chains at high β -CD concentration and low temperatures, whereas the rheological data for the HM-alginate solutions demonstrated that high levels of β -CD addition and elevated temperatures promoted decoupling of the hydrophobic associations. The cross-linking effect of the alginate chains was ascribed to the formation of crystallites of β -CD monomers.

In the present work, to avoid complications due to aggregation and crystallization of β -CD, we have instead made use of hydroxypropyl- β -cyclodextrin (HP- β -CD). It is shown that HP- β -CD can be used to decouple associations in aqueous solutions of nonionic hydroxyethyl cellulose that has hexadecyl C16 groups (HM-HEC) attached to the polymer backbone. This HP- β -CD derivative does not form aggregates or crystallites in aqueous solution. To evaluate the effect of hydrophobic interac-

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tions, the hydrophilic hydroxyethyl cellulose (HEC) precursor has been employed as a reference.

The interactions in the polymer/HP- β -CD mixtures have been characterized with the aid of rheology, spin-echo NMR, small angle neutron scattering (SANS), and dynamic light scattering (DLS). The aim of this study is to gain a better understanding of how deactivation of hydrophobic associations influences the structural and dynamical features of these fairly simple polymer systems. This work will provide us with important information of how a controlled modulation of the association strength will affect the characteristic properties of the system. To the best of our knowledge, a systematic examination of the effect of deactivation of hydrophobic tails on structural and dynamical features has not been reported before.

Experimental Section

Materials. The cyclodextrin derivative HP- β -CD was supplied by Aldrich and used as received. In this work, a HEC sample with the commercial name Natrosol 250 GR (Lot. No. A-0382), obtained from Hercules, Aqualon Division, was utilized as a reference and as the precursor for the synthesis of the hydrophobically modified analogue (HM-HEC). The degree of substitution of hydroxyethyl groups per repeating anhydroglucose unit of this polymer is 2.5 (given by the manufacturer). The molecular weight ($M_w = 400\,000$) of this sample in dilute aqueous solution was determined by intensity light scattering⁷ at 25 °C.

Dilute HEC solutions were dialyzed against Millipore water for several days to remove low-molecular-weight impurities and were thereafter isolated by freeze-drying. Regenerated cellulose with a molecular-weight cutoff of about 8000 (Spectrum Medical Industries) was used as the dialyzing membrane.

Synthesis of HM-HEC and Solution Preparation. The HM-HEC polymer was synthesized according to a procedure described elsewhere.⁸ A 1000-mL glass separable reactor equipped with a mechanical stirrer, thermometer, and a condenser tube was charged with 50 g of HEC and 400 g of 88% isopropyl alcohol (ARCUS), and 3.5 g of a 48% aqueous solution of sodium hydroxide was added to prepare a slurry. The slurry was stirred at ambient temperature for 30 min in a nitrogen atmosphere. To this mixture, 9.7 g of glycidyl hexadecyl ether (Sigma-Aldrich) was added to conduct a reaction at 80 °C for 8 h and thereby accomplish hydrophobization of the polymer. After completion of the hydrophobization reaction, adding acetic acid neutralized the liquid reaction mixture and the product was collected by filtration. The product was washed twice with 500 g of 80% acetone and then twice with 500 g of acetone and dried at 70 °C for 24 h under reduced pressure to remove remaining acetone. By this procedure, 44.8 g of the HM-HEC was obtained. To remove low-molecular-weight impurities, the polymer was thoroughly dialyzed against water (7 days) and isolated by freeze-drying as described above. The NMR analysis of the freeze-dried sample did not reveal the presence of unreacted species.

The chemical structure (see Figure 1) and purity of the HM-HEC was ascertained by ¹H NMR (deuteron-DMSO as a solvent) with a Bruker AVANCE DPX300 NMR spectrometer (Bruker Biospin, Fällanden, Switzerland) operating at 300.13 MHz at 298.2 K. The ¹H chemical shift in DMSO-*d*₆ is referred to the residual C₂HD₅-SO proton (2.50 ppm) of C₂D₆SO. The hydrophobic modification degree (glycidyl hexadecyl ether groups) was determined from the peak ratios between the anisomeric protons and the methyl protons of the glycidyl hexadecyl chain. The degree of substitution of the hydrophobic groups determined from NMR analysis was 1 mol %.

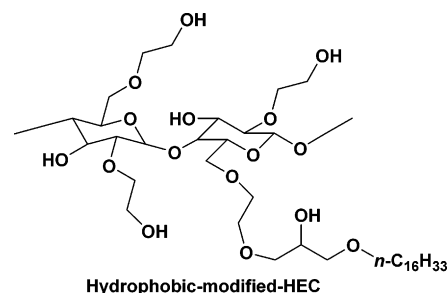


Figure 1. Schematic illustration of the chemical structure of the hydrophobically modified hydroxyethylcellulose (HM-HEC).

All the solutions were prepared in heavy water (D₂O) by weighing the components, and the solutions were homogenized by stirring at room temperature for 1 day. Most of the measurements were conducted in the semidilute range at a fixed polymer concentration of HEC and HM-HEC of 2.0 wt %, and some measurements were also performed on a dilute (0.2 wt %) polymer solution. All experiments were carried out at a temperature of 25 °C.

Viscosity. The steady shear viscosity measurements were performed in a Paar-Physica MCR 300 rheometer using a cone-and-plate geometry, with a cone angle of 1° and a diameter of 75 mm. To prevent evaporation of the solvent, the free surface of the sample was always covered with a thin layer of low-viscosity silicone oil (the value of the viscosity is virtually not affected by this layer).

NMR Self-Diffusion Measurements. All NMR experiments were carried out in 5 mm NMR tubes with the aid of the pulsed gradient spin-echo (PGSE) NMR technique⁹ on a Bruker DMX-200 AVANCE NMR spectrometer, and the polymer self-diffusion coefficients were determined.

The polymer self-diffusion experiments for HM-HEC solutions with and without added HP- β -CD were all executed in exactly the same manner by keeping all experimental parameters at fixed values. The gradient pulse duration (δ) and the experimental observation time (Δ) were kept constant at 3 and 100 ms, respectively, while the gradient strength (g) was increased in 32 steps from 0–4.5 T m⁻¹. All measurements were performed in the narrow pulse width approximation, i.e., with $\delta \ll \Delta$. The self-diffusion coefficients (D_s) of the HM-HEC were evaluated by following the attenuation of the intensities of the signals of methylene (1.25 ppm, $-(CH_2)_{14}-$).

In complex polymer systems, the spin-echo attenuation (R) is frequently found to be nonexponential and the echo decays can be described by using a stretched exponential^{10,11}

$$R = \frac{I(g)}{I(0)} = \exp[-(k^2 D_s t_{\text{eff}})^\epsilon] \quad (1)$$

where $I(g)$ and $I(0)$ denote the echo amplitudes with and without the field gradient pulses, respectively, $k \equiv \gamma g \delta$, where γ is the magnetogyric ratio of the proton ($\gamma = 2.6752 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$), and $t_{\text{eff}} = \Delta - \delta/3$ is the effective experimental observation time. The stretched exponential ϵ ($0 < \epsilon \leq 1$) is a measure of the width of the distribution of self-diffusion coefficients. This distribution is usually ascribed to some kind of heterogeneity of the sample. A candidate for such heterogeneity is the polydispersity in size of the observed species.

In some strongly associating or gelling polymer systems,^{12–14} it is necessary to add a second term (slow mode) that describes slow polymer self-diffusivities. In the present work, the decay of the spin-echo attenuation data for the associating HM-HEC

solutions can be well described by the following expression

$$R = A \exp[-(k^2 t_{\text{eff}} D_{\text{fe}})^\epsilon] + (1 - A) \exp[-(k^2 t_{\text{eff}} D_{\text{se}})^\kappa] \quad (2)$$

Here, $0 \leq A \leq 1$ describes the contribution of the fast decay to the attenuation. The first term on the right-hand side of eq 2 denotes the fast decay (D_{fe} is some effective fast diffusion coefficient), which is portrayed by a stretched exponent, and the second term describes the nonexponential behavior of the slow self-diffusion mode (D_{se}). The slow mode likely arises from the diffusion of long-lived associations¹⁴ that are formed in solutions of the HM-HEC polymer, and this effect is accommodated by the second stretched exponential function. In the analysis of the echo-attenuation data, a nonlinear fitting algorithm (a modified Levenberg–Marquardt method) was employed to obtain best-fit values of the parameters A , D_{fe} , ϵ , D_{se} , and κ appearing on the right-hand side of eq 2. We have found that the values of the stretched exponents ϵ and κ are both typically around 0.7. The profile of the echo attenuation is usually complex in strongly associating polymer systems.^{12,13} In this case, it is difficult to obtain a well-resolved NMR spectrum because of overlapping signals due to broad profiles (i.e., fast T_2 relaxation), which occur as a consequence of association or specific interactions. Furthermore, polydisperse polymers and/or long-lived (on the NMR time window) polymer clusters give rise to nonexponential signal decay because of a broad distribution of self-diffusion coefficients. In this work, the progressive addition of HP- β -CD to the solution makes it difficult to unambiguously extract values of the fast diffusion coefficient D_{fe} (values around $10^{-11} \text{ m}^2 \text{ s}^{-1}$), whereas the values of the slow self-diffusion coefficient are more easy to determine in a systematic way (see the discussion below). Because of this problem with the resolution of the fast mode, the change of the association situation in HM-HEC solutions with increasing levels of HP- β -CD addition will be monitored in terms of the slow mode. The parameter D_{se} is related to the mean polymer self-diffusion coefficient D_s via the gamma function Γ through the expression $\langle 1/D_s \rangle = (1/\kappa)(1/D_{\text{se}})\Gamma(1/\kappa)$.

Small-Angle Neutron Scattering (SANS). Small-angle neutron scattering measurements were performed on 2 wt % solutions of HEC and HM-HEC in the presence of various amounts of HP- β -CD at the SANS installation at the IFE reactor at Kjeller, Norway. The details of the spectrometer and the experimental procedure have been described elsewhere.¹⁵ The scattering length density calculated for the HP- β -CD monomers ($\rho_{\text{HP-}\beta\text{-CD}} \approx 0.8 \times 10^{10} \text{ cm}^{-2}$) is quite close to that of HM-HEC ($\rho_{\text{HM-HEC}} \approx 1.4 \times 10^{10} \text{ cm}^{-2}$). However, due to the small size of the individual HP- β -CD molecules, the scattering from HP- β -CD in the solutions is negligible in comparison with that of HEC or HM-HEC.

Standard reductions of the scattering data, including transmission corrections, were conducted by incorporating data collected from empty cell, beam without cell, and blocked-beam background to obtain the scattered intensities in absolute scale (cm^{-1}). Subtraction of the solvent scattering was then carried out to determine the coherent macroscopic scattering cross section $d\Sigma/d\Omega(\mathbf{q})$ of the system.

Dynamic Light Scattering. The beam from an argon ion laser (Lexel laser, model 95), operating at 514.5 nm with vertically polarized light, was focused onto the sample cell through a temperature-controlled chamber filled with refractive index matching silicone oil.

In the present study, the full homodyne intensity autocorrelation function $g^2(\mathbf{q}, t)$ was measured at different scattering angles in the range 30° – 90° with an ALV-5000 multiple τ digital

correlator. The correlation functions were recorded in the real-time “multiple τ ” mode of the correlator, in which 256 time channels were logarithmically spaced over an interval ranging from 0.2 μs to almost 1 h.

If the scattered field obeys Gaussian statistics (as for all solutions considered in this work), the measured correlation function $g^2(\mathbf{q}, t)$ can be related to the theoretically amenable first-order electric field correlation function $g^1(\mathbf{q}, t)$ by the Siegert relationship¹⁶ $g^2(\mathbf{q}, t) = 1 + B|g^1(\mathbf{q}, t)|^2$, where B is usually treated as an empirical factor.

For light-scattering experiments, the solutions were filtered in an atmosphere of filtered air through 0.8 μm filters or 5 μm filters for the most viscous solutions directly into precleaned 10 mm NMR tubes (Wilma Glass Company) of the highest quality.

In DLS studies on associating polymer systems,^{10,15,17} it has frequently been observed that the decay of the correlation function can initially be described by a single exponential, followed at longer times by a stretched exponential

$$g^1(t) = A_f \exp(-t/\tau_f) + A_s \exp[-(t/\tau_{\text{se}})^\beta] \quad (3)$$

with $A_f + A_s = 1$. The parameters A_f and A_s are the amplitudes for the fast and the slow relaxation modes, respectively. Analyses of time correlation functions of concentration fluctuations in the domain $\mathbf{q}L < 1$, where L is a characteristic length (the dynamic screening length in the semidilute regime), have demonstrated that the first term (short-time behavior) on the right-hand side of eq 3 is related to the cooperative diffusion coefficient D_c ($\tau_f^{-1} = D_c \mathbf{q}^2$). As will be discussed below, the fast mode in this work was always found to be \mathbf{q}^2 -dependent. This quantity reflects a concerted motion of polymer chains relative to the solvent. The second term (long-time feature) is ascribed to disengagement relaxation of individual chains^{18,19} or cluster relaxation.²⁰ The variable τ_{se} is an effective relaxation time that depends on the stretched exponent β ($0 < \beta \leq 1$), which is a measure of the width of the distribution of relaxation times. The mean relaxation time is given by

$$\tau_s = \int_0^\infty \exp[-(t/\tau_{\text{se}})^\beta] dt = (\tau_{\text{se}}/\beta)\Gamma(1/\beta) \quad (4)$$

where $\Gamma(\beta^{-1})$ is the gamma function of β^{-1} .

In the analysis of correlation function data, a nonlinear fitting (a modified Levenberg–Marquardt method) was employed to obtain the best-fit values of the parameters A_f , τ_f , τ_{se} , and β appearing on the right-hand side of eq 3.

Results and Discussion

Rheological Properties. Figure 2 shows the shear rate dependence of the viscosity for 2 wt % solutions of HEC and HM-HEC in the presence of different amounts of HP- β -CD. At low shear rates, a Newtonian behavior is observed for all systems. The very small change of the viscosity observed for the HEC/HP- β -CD system at different levels of HP- β -CD addition suggests only weak interactions between the cosolute and the unmodified polymer. In contrast, strong effects of HP- β -CD addition are evident in solutions of HM-HEC, where a pronounced decline of the viscosity at low shear rates is detected as the concentration of HP- β -CD is increased. The most marked shear-thinning effect at higher shear rates is found for the HM-HEC solution without HP- β -CD, i.e., the system that exhibits the strongest association network and viscosity enhancement. The progressive decrease in viscosity as the shear rate rises indicates that the intermolecular junctions are disrupted at a rate

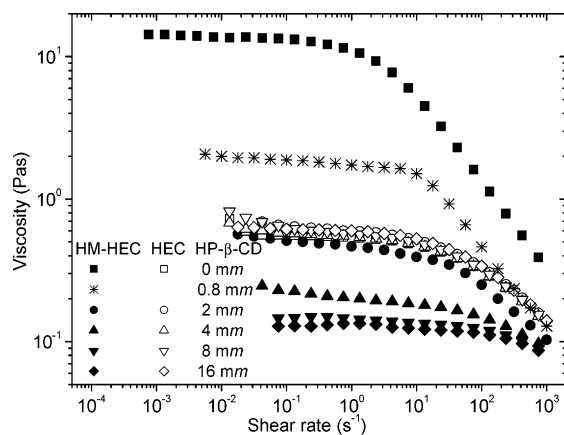


Figure 2. Effect of HP- β -CD concentration on the shear rate dependence of the viscosity (every 2nd point is shown) for aqueous 2 wt % solutions of HEC and HM-HEC.

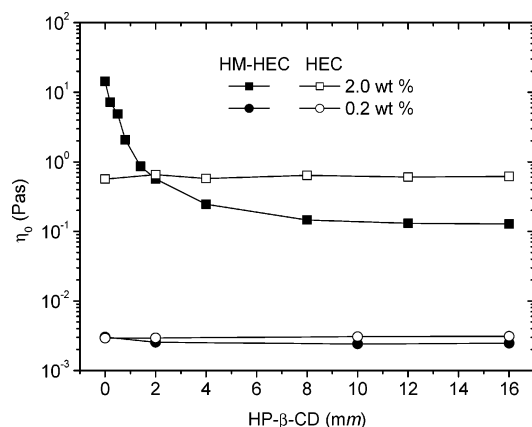


Figure 3. Effect of HP- β -CD addition on the zero-shear viscosity for dilute (0.2 wt %) and semidilute (2 wt %) solutions of HEC and HM-HEC.

faster than their rate of reformation, resulting in a decrease in the junction density and hence a drop in the viscosity. To check possible hysteresis effects, the shear rate dependence of the viscosity for some solutions with high intensity of hydrophobic associations was registered as a function of increasing shear rate (up-ramp curve) and the subsequent decline in shear rate (down-ramp curve) was probed. No significant hysteresis effects were detected under the considered experimental conditions, and the up-ramp curve and the down-ramp curve virtually coincided.

Effects of the addition of HP- β -CD on the zero-shear viscosity for 2 wt % solutions of HEC and HM-HEC are illustrated in Figure 3. The value of η_0 for HM-HEC exhibits a strong decrease initially, but at a HP- β -CD concentration of approximately 8 mm, the zero-shear viscosity levels out. This indicates that the HP- β -CD molecules encapsulate the hydrophobic tails of the polymer, and at a sufficiently high HP- β -CD concentration, most of the hydrophobic moieties are deactivated. The reason that most of the hydrophobic effect is inhibited already at a low level of HP- β -CD addition is probably because the hydrophobicity of the polymer is quite low (1 mol % of hydrophobic groups). In the case of the HEC/HP- β -CD system, no effect of HP- β -CD addition is visible and the values of η_0 at HP- β -CD concentrations above 2 mm are significantly higher than the corresponding ones for the HM-HEC/HP- β -CD system. This can probably be ascribed to a difference in the intensity of the entanglement couplings of the HEC/HP- β -CD and HM-HEC/HP- β -CD systems. The conjecture is that the bulky inclusion complexes that are formed with the hydrophobic

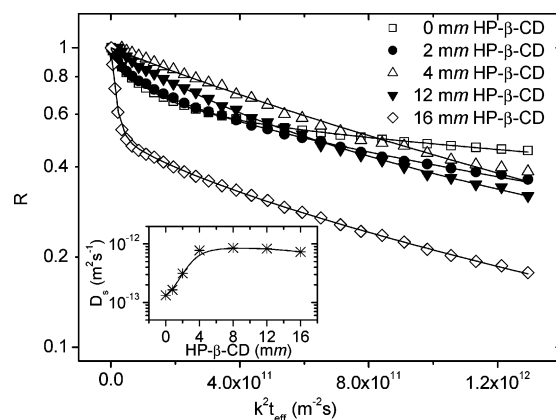


Figure 4. Plot of the proton spin-echo attenuation as a function of $k^2 t_{\text{eff}}$ for aqueous HM-HEC solutions of 2 wt % in the presence of different amounts of HP- β -CD. The curves are fitted with the aid of eq 2 (see text). The inset shows the effect of HP- β -CD addition on the slow polymer self-diffusion coefficient.

tails on the HM-HEC chains constitute a steric hindrance for the development of efficient entanglements in the semidilute HM-HEC/HP- β -CD solutions, whereas the evolution of entanglements in the corresponding HEC solutions is more effective. In the dilute (0.2 wt %) polymer concentration regime, a close inspection of the viscosity data reveals a weak initial decrease of η_0 for the HM-HEC/HP- β -CD system (decoupling of hydrophobic interactions), and only a slight difference in the values of η_0 between the systems can be discerned.

Polymer Self-Diffusion Measurements. As we can see from Figure 4, there is a curvature when the attenuation decays are plotted in a Stejskal–Tanner representation.²¹ This suggests that the sample contains a distribution of species with significantly different self-diffusion coefficients. The fitted curves reveal that the signal decays under all conditions are well described by eq 2. To characterize the change of mobility of the polymer chains when the hydrophobic interactions are decoupled by adding HP- β -CD to the semidilute HM-HEC solution that forms a transient network, the effect of HP- β -CD concentration on the slow polymer self-diffusion coefficient D_s is depicted in the inset plot. It is obvious that the diffusivity increases considerably upon addition of HP- β -CD, and D_s levels out at concentrations above 4 mm. The surmise is that the slow self-diffusion mode originates from the long-lived associations that are formed in solutions of the hydrophobically modified polymer, and the gradual disruption of these association complexes with increasing HP- β -CD concentration promotes a faster average migration of the polymer chains. This clearly demonstrates that the polymer dynamics is largely influenced by the intensity of the hydrophobic associations.

SANS Results. SANS experiments allow us to disclose structural changes in the system on a mesoscopic length scale. Figure 5 illustrates SANS spectra for 2 wt % HEC and HM-HEC solutions with different levels of HP- β -CD addition. The most conspicuous feature of the q dependence of the scattered intensity is the behavior in the low q range. However, we should note that with this SANS spectrometer a restricted part of the low q region is probed; hence, detailed information in the Guinier regime is not accessible. The q dependence of the scattered intensity in the low q region can be described by a power law $I(q) \sim q^{-\gamma}$, and the values of γ are displayed in the inset plot. The results reveal a strong upturn of the scattered intensity at low q values for the HM-HEC solution without HP- β -CD, and the upturn is reduced to that observed for the HEC systems as the concentration of HP- β -CD in the solution is raised

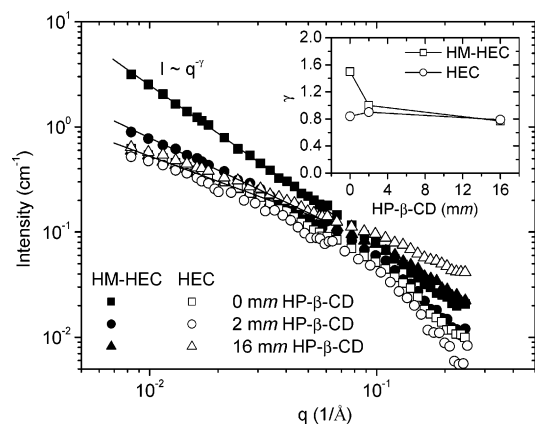


Figure 5. SANS intensity (every 2nd point is shown) plotted versus the scattering vector q at three different HP- β -CD concentrations for 2 wt % solutions of HEC and HM-HEC.

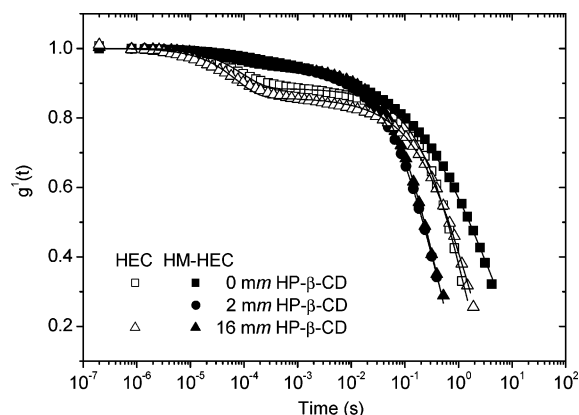


Figure 6. Plot of the first-order field correlation function versus time (every 3rd point is shown) for 2 wt % solutions of HEC and HM-HEC at the indicated HP- β -CD concentrations and a scattering angle of 90° .

(see the inset). It is generally argued²² that the low- q features depict the scattering from large structural inhomogeneities or multichain domains,²³ resulting either from hydrophobic interactions or from molecular associations. These results show that, in solutions of HM-HEC without HP- β -CD, large-scale structures are formed via hydrophobic interactions, whereas the tendency to form association structures is inhibited in the presence of HP- β -CD through the deactivation of the hydrophobic moieties. We note that the degree of association is not influenced by the addition of HP- β -CD in the semidilute HEC solution. The difference at high q between HEC and HM-HEC at high HP- β -CD concentrations is caused by the contribution of a large amount of free HP- β -CD molecules in the HEC solution to the scattered intensity, whereas in the HM-HEC sample most of the HP- β -CD is attached to the polymer as inclusion complexes.

Dynamic Light Scattering. The decay of the time correlation function can be well-described by eq 3 (see the fitted curves in Figure 6) for all the solutions in this study. The change in behavior as illustrated in Figure 6 shows time correlation function data (at a scattering angle of 90°) for 2 wt % solutions of HEC and for HM-HEC at different levels of HP- β -CD addition. The results divulge that the slow relaxation process is shifted toward shorter times with the addition of HP- β -CD in the HM-HEC solution. This indicates that the association effect becomes weaker. In the case of the HEC solutions, the correlation functions virtually collapse onto each other and no effect of HP- β -CD addition can be traced. It is expected that strong association structures should favor the growth of the slow

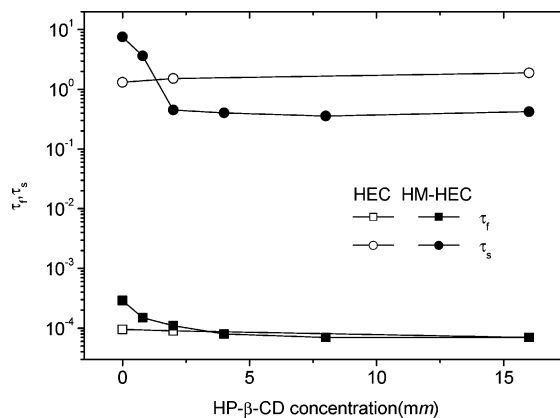


Figure 7. Effect of HP- β -CD addition on the fast and the slow relaxation time (see eqs 3 and 4) for dilute (0.2 wt %) and semidilute (2 wt %) solutions of HEC and HM-HEC at a scattering angle of 90° .

mode in the relaxation process. The analysis of the correlation functions, with the aid of eq 3, for the HM-HEC/HP- β -CD solutions shows that as the level of HP- β -CD addition increases the influence of the slow mode is reduced. The slow mode seems to be related to long-lived chain associations.

In Figure 7, the HP- β -CD concentration dependencies of the fast and the slow relaxation times (calculated by means of eq 3) in 2 wt % solutions of HEC and HM-HEC are shown. The value of τ_s is virtually unaffected by the addition of HP- β -CD in the HEC solution, whereas a significant drop of τ_s at low HP- β -CD concentrations is found for the hydrophobically modified polymer. We may note that these features are reminiscent of those presented above from the viscosity study (cf. Figure 3). This finding supports our conjecture that the slow mode reflects the disengagement of chains. Again, we can argue that the addition of HP- β -CD decouples the hydrophobic associations and thereby hastens the slow relaxation process in HM-HEC/HP- β -CD solutions. In the case of the HEC/HP- β -CD system, the relatively more efficient entanglement couplings yield longer relaxation times than for the HM-HEC/HP- β -CD system at moderate HP- β -CD concentrations.

The fast relaxation time at long wavelengths in semidilute solutions is linked with the cooperative diffusion process, where the collective motion of the chains (all chains move together) or the network respiration,²⁴ i.e., the pulsating motion of the chains within the mesh-units of the network, governs the behavior of τ_f . This type of process should not be very sensitive to changes in the entanglement and/or association situation, which is supported by the results displayed in Figure 7. The initial decrease of τ_f or the increase of the cooperative diffusion coefficient for the HM-HEC solution with the addition of HP- β -CD can probably be rationalized in terms of decreasing nonuniformities of the network.²⁵ It has been reported²⁵ that the degree of nonuniformity of the network structure can play a role in the diffusion properties. This approach predicts an increase of the value of the diffusion coefficient with decreasing nonuniformity. It is reasonable to assume that a more homogeneous network is developed when the hydrophobic associations are decoupled in the presence of HP- β -CD. This hypothesis is consistent with the SANS results.

Figure 8 shows the angular dependence of the time correlation functions for 2 wt % solutions of HM-HEC without HP- β -CD and with 16 mm HP- β -CD. A close comparison of the time correlation functions, at a given scattering angle, reveals that the shift in the relaxation time toward longer times is stronger for the solution without HP- β -CD. A characteristic feature of the decays is that the slow mode becomes more dominant as

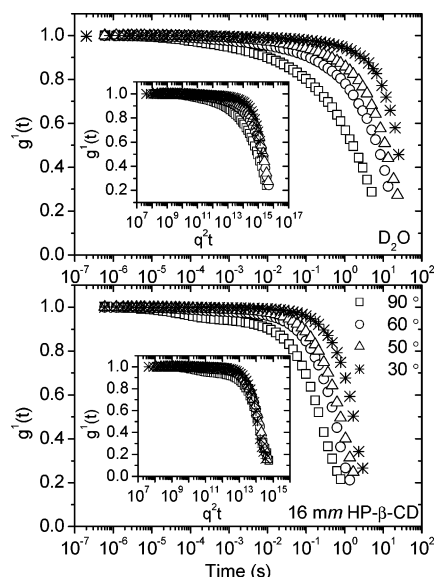


Figure 8. First-order electric field correlation function versus time (every 3rd data point is shown) for 2 wt % solutions of HM-HEC at the HP- β -CD concentrations and scattering angles indicated. The inset plots show the same correlation functions versus the reduced quantity $q^2 t$.

the scattering angle decreases. The inset plots illustrate the q dependences of the correlation functions in a reduced form (i.e., vs $q^2 t$). We can see that the correlation function data at different scattering angles practically collapse onto a single curve at short and long times for the HM-HEC/HP- β -CD (16 mm) system, reflecting the diffusive character of the relaxation modes. However, for the HM-HEC solution without HP- β -CD, a separation of the curves at longer times can be traced, showing stronger q dependence than that of a diffusive mode for the slow relaxation process. This indicates that there are associations caused by hydrophobic interactions in the HM-HEC solutions without HP- β -CD and that these interactions are mostly absent in the presence of high amounts of HP- β -CD where most of the hydrophobic groups have been encapsulated by the HP- β -CD molecules.

The q dependences of the inverse fast and slow relaxation times can be expressed as $\tau_f^{-1} \propto q^{\alpha_f}$ and $\tau_s^{-1} \propto q^{\alpha_s}$, respectively. To quantitatively determine the q dependences of the relaxation times, plots of the relaxation times as functions of q have been carried out and some illustrations for the fast and the slow mode are displayed in Figure 9a and b, respectively. The fast mode is always diffusive ($\alpha_f \approx 2$), while the slow mode exhibits a stronger q dependence at low levels of HP- β -CD addition. The value of the stretched exponent β is, under all conditions, practically independent of q , but the numerical value of β increases strongly as the strength of the hydrophobic interactions declines (see Figure 9c and d).

To interpret and understand relaxation phenomena in complex systems, Ngai and co-workers^{20,26,27} have devised a scheme that provides a general description of the dynamics in constrained and associating systems. The present DLS results can be rationalized in the framework of this model. This approach addresses the problem of how the relaxation of a specific chain or cluster is “slowed down” because of its coupling to complex surroundings. In the coupling model of Ngai,²⁰ the value of the stretched exponent β , or the value of the coupling parameter n ($\beta = 1 - n$), is a direct measure of the coupling strength of the relaxation mode to its complex environments. A high value of

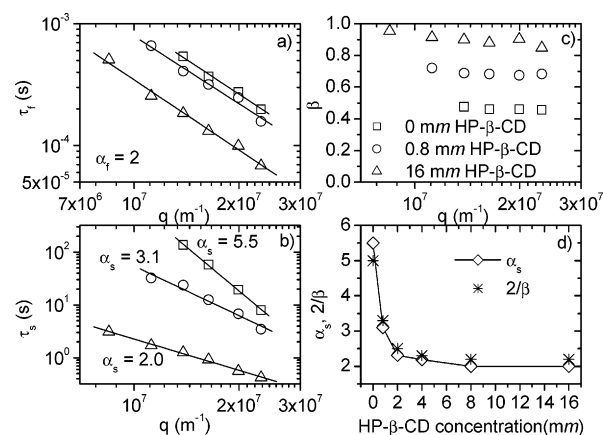


Figure 9. Illustration of the wavevector dependences of (a) the fast and (b) the slow relaxation times and (c) the stretched exponent β for 2 wt % HM-HEC solutions at the HP- β -CD concentrations indicated. (d) Effect of the level of HP- β -CD addition on the quantities $2/\beta$ (see the text for explanation) and α_s , illustrating the q dependence of the slow relaxation time.

n or a low value of β indicates strong coupling effects. This model yields an expression of the form given by eq 3, and it recognizes the existence of short and long time domains that are separated by a crossover time t_c beyond which coupling effects influence the dynamics. In this framework, the system under consideration is said to be composed of “basic units”, which interact nonlinearly and more or less strongly with each other. At short times ($t \leq t_c$), the relaxation of the temporal correlation function (e.g., the field autocorrelation function as in the present case) is not affected by coupling effects between the basic units and can be expressed by the general form

$$\phi(t) = \exp(-t/\tau_0) \quad t < t_c \quad (5)$$

where τ_0 is the characteristic time for unconstrained relaxation and this quantity exhibits a q^2 dependence that is the hallmark of a diffusive mode. At $t > t_c$, cooperative constraints between the basic units come into play and the relaxation function $\phi(t)$ depends on the coupling strength ($0 \leq n < 1$) between these units. In this stage, the relaxation process is described by a stretched exponential function

$$\phi(t) = \exp[-(t/\tau_s^*)^{1-n}] \quad t > t_c \quad (6)$$

The basic prediction of this model is that n rises (or β decreases) as the strength of the interaction between the basic units is increased. Continuity of the fast and slow processes of the correlation function at $t = t_c$ leads immediately to the important relationship

$$\tau_s^* = [t_c^{-n} \tau_0]^{1/(1-n)} \quad (7)$$

This equation links, through the coupling parameter n , the effective relaxation time τ_s^* to the independent relaxation time τ_0 and the crossover time t_c . By considering the relaxation of the system over the whole time window accessible in the DLS experiments, this approach yields an expression of the form (eq 3) employed in the analyses of the present correlation functions. In view of eq 7, the marked upturn of the slow relaxation time at low levels of HP- β -CD addition (cf. Figure 7) can readily be ascribed to the enhanced coupling effects with low values of β .

Another inherent aspect of the coupling model is the prediction²⁰ of the anomalous q dependence of the slow

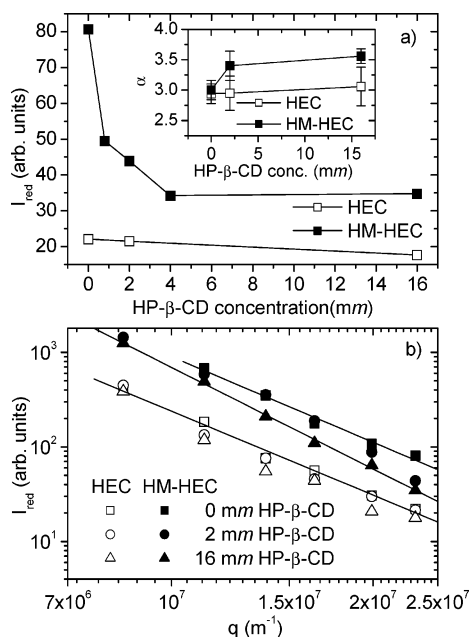


Figure 10. (a) Effect of HP- β -CD concentration on the reduced scattered intensity (at a scattering angle of 90°) for 2 wt % solutions of HEC and HM-HEC. (b) Illustration of the wavevector dependences of the reduced scattered intensity for HEC and HM-HEC solutions at the HP- β -CD concentrations indicated. The inset in part a shows the effect of HP- β -CD addition on the parameter α , expressing the q dependence of the reduced scattered intensity.

relaxation time through the relationship

$$\tau_s^*(q) = [t_c^{-n} \tau_0(q)]^{1/(1-n)} \propto q^{-2/(1-n)} \propto q^{-2/\beta} \quad (8)$$

It is evident from the above expression that as the coupling or interaction in the solution is enhanced, there is a concomitant increase in the coupling parameter n , or a decrease of β , and the q dependence of τ_s becomes stronger than that of a diffusive process. A comparison between the experimental results and the values determined with the aid of eq 8 is depicted in Figure 9d. The agreement between the experimental and the calculated values is good. The results show that an augmented q dependence of the slow mode emerges as the strength of the hydrophobic interactions increases, whereas a diffusive character of the slow mode appears when the hydrophobic interactions are decoupled.

The reduced intensity (I_{red}) is a powerful parameter to detect large association complexes in solutions. Figure 10a shows that the reduced intensity for the HM-HEC polymer falls off strongly at concentrations of HP- β -CD up to about 4 mm, demonstrating that the effect of the hydrophobic associations is strongly diminished at high levels of HP- β -CD addition. This is a further support of the surmise that hydrophobic interactions in this system lead to the evolution of large-scale structures. For the

HEC system, the value of the reduced intensity is lower and practically unaffected by the level of HP- β -CD addition. This difference between the systems may announce that, even at high concentrations of HP- β -CD, there exist some remaining association complexes in the HM-HEC solutions that give rise to this excess scattering. It has been observed²⁸ for aqueous solutions of other hydrophobically modified polymers that due to steric hindrance some of the hydrophobic tails of the polymer may not be accessible to the HP- β -CD molecules.

In Figure 10b, the q dependences of the reduced intensity for 2 wt % solutions of HEC and HM-HEC are illustrated at different levels of HP- β -CD addition. In the limited q range covered in these measurements, the wave vector dependence of the reduced intensity I_{red} can be portrayed by a power law $I_{\text{red}} \propto q^{-\alpha}$, where the values of α are displayed in the inset of Figure 10a. The value of α is close to 3 for the HEC/HP- β -CD system under all conditions, indicating a rather homogeneous network structure.²⁹ The increasing value of α for the HM-HEC/HP- β -CD system may be a harbinger of the evolution of a more homogeneous network at higher concentrations of HP- β -CD, where the hydrophobic associations are disrupted.

Conclusions

The use of HP- β -cyclodextrin monomers provides an efficient way of deactivating the hexadecyl groups attached onto the HEC backbone, and thereby, the hydrophobic associations in the HM-HEC solutions are suppressed. The overall results from viscosity, NMR-self-diffusion, and DLS analyses clearly suggest that the hydrophobic tails are deactivated by the addition of HP- β -CD. The SANS data presented in this work reveal that the decoupling of hydrophobic moieties gives rise to inhibition of the formation of large-scale association structures. The general picture that emerges is that the truncated cone structures from HP- β -CD encapsulate hydrophobic tails on the HM-HEC chains and thereby reduce the intensity of the hydrophobic associations. A schematic illustration of the main effect of HP- β -CD addition on the hydrophobic groups in semidilute HM-HEC solutions is depicted in Figure 11. This picture illustrates the progressive decoupling of the hydrophobic tails as the concentration of HP- β -CD increases.

The results from the DLS experiments indicate the existence of two relaxation modes, which are well-described under all conditions by eq 3, where the initial decay of the correlation function has an exponential profile followed by a stretched exponential at longer times. The fast mode is always diffusive (q^2 -dependent) for both the unmodified and modified polymer. The marked rise of the slow relaxation time, characterizing cluster disengagement relaxation, and the pronounced increase in the zero-shear viscosity as well as the noticeable drop in the value of the polymer self-diffusion coefficient from PGSE-NMR suggest that enhanced associations are formed in the HM-HEC solutions at low levels of HP- β -CD addition. At high HP- β -

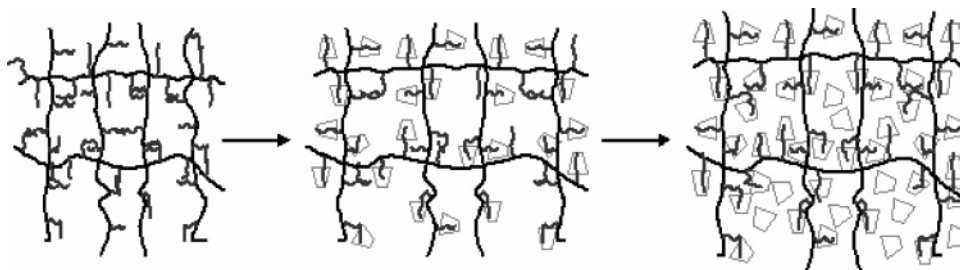


Figure 11. Schematic illustration of the gradual deactivation the hydrophobic moieties of the hydrophobically modified polymer as the HP- β -CD concentration increases.

CD concentrations, the hydrophobic interactions are suppressed but the higher values of the zero-shear viscosity and the slow relaxation time for the semidilute solutions of HEC indicate that entanglements that are more efficient are formed in the HEC solutions than in the corresponding HM-HEC solutions.

By tuning the intensity of the hydrophobic associations via addition of various amounts of HP- β -CD, these DLS results have shown that the q dependence of the slow relaxation mode decreases gradually and approaches that of a diffusive process when most of the hydrophobic moieties have been deactivated. This finding strongly suggests that the augmented q dependence of the slow relaxation time is directly related to enhanced hydrophobic associations. This feature, as well as the accompanying drop of the stretched exponential β and the rise of the slow relaxation time, can be attributed to augmented intermolecular interactions, and they can be rationalized within the framework of the coupling model of Ngai.

This work has demonstrated that a controlled modulation of the stickiness can constitute an important basis in the examination of the impact of hydrophobic associations on different physical quantities.

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