Temperature-Induced Fractionation of a Quasi-Binary Self-Associating Polymer Solution. A Phase Behavior and Polymer Self-Diffusion Investigation

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Received October 25, 1999; Revised Manuscript Received June 15, 2000

ABSTRACT: Dynamic properties of quasi-binary aqueous solutions of ethyl(hydroxyethyl)cellulose (EHEC) and the hydrophobically modified analogue (HM-EHEC) have been investigated with the PFG-SE NMR technique. By taking advantage of the phase behavior of the (HM-)EHEC solutions, different polymer fractions could be obtained by simply adjusting the temperature within the two-phase region and collecting the coexisting phases. We discuss the connection between phase behavior, microphase structure, polymer structure, and polymer dynamics by following the self-diffusion of polymers in these fractions as a function of concentration and temperature. By extrapolating the diffusion coefficient to infinite dilution, we observe a significant difference in hydrodynamic radius between the separated fractions. The width of the distribution of diffusion coefficients is used to recognize differences in associative behavior of the different polymer fractions. The echo decays of highly associative fractions show, in addition to the characteristic curved echo decay commonly observed in solutions of associative polymers, a single diffusing component with a very slow diffusion coefficient ($D \sim 10^{-14}$ m^2 s^{-1}).

Introduction

Often when phase behavior of an aqueous polymer solution is considered, the discussions imply that the solution is binary; i.e., the solution contains only a single polymer component dissolved in a solvent. Strictly, this is never the case, because regardless of how careful the polymer material is synthesized and purified, there is always a distribution of molecular weights present. Thus, all polymer solutions are multicomponent systems, and depending on the distribution of molecular weights the phase behavior may be complex. Koningsveld and Staverman discussed the influence of a distribution of molecular weights on the phase behavior, and in particular, they found that in a quasi-binary representation the cloud point curve cannot be expected to coincide with the coexistence curve.[1] This is because the tie lines are generally not located in the plane of the diagram. In the present investigation we have used a cellulose derivative, ethyl(hydroxyethyl)cellulose, EHEC, which in aqueous solution has a lower critical consolute temperature, LCST.[2,3] Thus, phase separation is induced by increasing the temperature, and in this way cloud point curves and coexistence curves can be determined. As a consequence of the chemical structure of EHEC (Figure 1), the phase behavior of aqueous solutions is expected to be complex. In addition to a molecular weight distribution, there is also a distribution in chemical composition that is expected to further increase the complexity of the phase behavior.

In recent publications it has been found that the dynamics of the EHEC chains is complicated.[4,5] The distribution of diffusion coefficients, as given by pulsed field gradient spin echo NMR (PFG-SE NMR), was found to be substantially wider than can be accounted for by polymer polydispersity effects alone. The phenomenon was suggested to arise from association and cluster formation due to the heterogeneous EHEC structure, and it was argued that the interchain associations are long-lived on the time scale of the NMR experiment (on the order of 1 s). In this context it is valuable to note that this behavior has also been observed in solutions of hydrophobically modified model compounds with a low molecular weight polydispersity and a less complicated chemical structure in terms of chain grafting.[6]

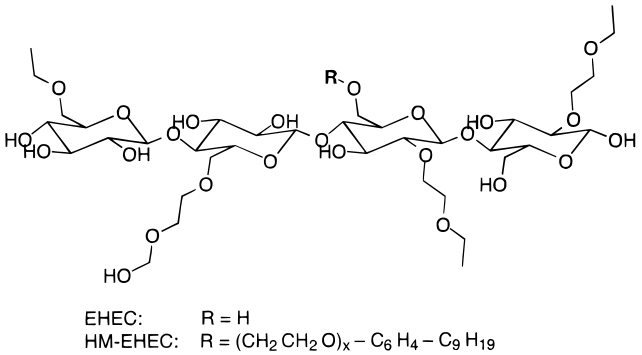

Figure 1. Schematic chemical structure of EHEC and HM-EHEC. The figure is drawn to illustrate the average chemical composition, and it should be noted that certain glucose residues may have a considerable different substitution. Thus, deviations from the average composition along one certain polymer chain or among different polymer chains are expected.

To further elucidate structure and dynamics in EHEC solutions, diffusion of a noninteracting probe polymer in an EHEC matrix was followed.[7] It was found that already at an EHEC concentration corresponding to 1 wt % the diffusion of the probe molecule was severely obstructed, and an unexpectedly strong dependence on

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10.1021/ma991783f CCC: $19.00

the probe molecular weight was found. The latter effect was even more pronounced when the concentration of the matrix increased to 6 wt %. The observations were suggested to be due to a spatially inhomogeneous distribution of EHEC polymers. In one investigation, the dynamics of HM-EHEC was followed as a function of temperature.[4] When phase separation was approached, the measured diffusion coefficient increased, while the distribution width decreased. This was interpreted as a “microfractionation”, where nonassociating species diffuses freely and more hydrophobic molecules associates.

To summarize, the translational dynamics in EHEC solutions is likely to be influenced by the polymer structure, and this is a parameter which also has been shown to influence thermodynamics and phase behavior of EHEC solutions. The present investigation take advantage of this behavior. The aim is to gain improved knowledge about correlation between polymer structure, phase behavior, and dynamics by following the polymer diffusion in different EHEC fractions, which were obtained by separating coexisting phases in the two-phase area.

Experimental Section

Materials. EHEC and HM-EHEC (Figure 1) were supplied by Akzo Nobel Surface Chemistry AB, Stenungsund, Sweden. The two different polymers have approximately the same molecular weight ($M_w \approx 100\,000$) and degrees of ethyl and hydroxyethyl substitution: $DS_{ethyl} = 0.6-0.7$ and $MS_{EO} = 1.8$, respectively. The numbers were given by the manufacturer, and they refer to the average substitution per glucose unit of the cellulose of the unpurified (HM-)EHEC samples. Before use, the polymers were purified as described elsewhere. A recent investigation found that the purification procedure changed the average substitution degrees slightly, and after purification they were determined to be $DS_{ethyl} = 0.8$ and $MS_{EO} = 2.1$.[8] The only structural difference between EHEC and HM-EHEC is a low amount of covalently attached branched nonylphenol onto the latter. The hydrophobic modification was determined to 1.7 mol %, relative to the number of glucose units, by using UV absorbance at 275 nm with phenol in aqueous solution as reference.

Water of Millipore quality was used to prepare samples for phase studies, while heavy water (99.8% D_2O) from Dr. Glaser AG was used to prepare samples to NMR measurements.

Methods. For the phase separation studies, polymer stock solutions with a concentration of 3 wt % were prepared. The stock solutions were dissolved and equilibrated at room temperature for 5 days while stirring with a magnetic bar. Six double samples were made by transferring 8−10 g of each stock solution to 10 mL glass tubes, which were closed with Teflon tightened screw caps. Each of the 12 samples was equilibrated at the desired temperature by tilting end over end for 2 h and later separated into two coexisting phases by centrifugation (1500*g*) for an additional 2 h at the same temperature. Three different phase separation temperatures, T_p’s, located above the cloud point curves for both HM-EHEC and EHEC (Figure 2) were selected for investigations (67, 79.5, and 91 °C). The two phases were separated by decanting the low-viscous transparent supernatant from the dense high-viscous slightly turbid bottom phase, which was concentrated in polymer. The bottom phase became clear after being exposed to room temperature for less than a minute. The weight fraction of the concentrated bottom phase was determined by weighing and subtracting the glass tube tara. From here on, the top phase and the polymer material originating from a top phase will be denoted ϕ', while the bottom phase and the polymer material extracted from this phase will be referred to as ϕ''.

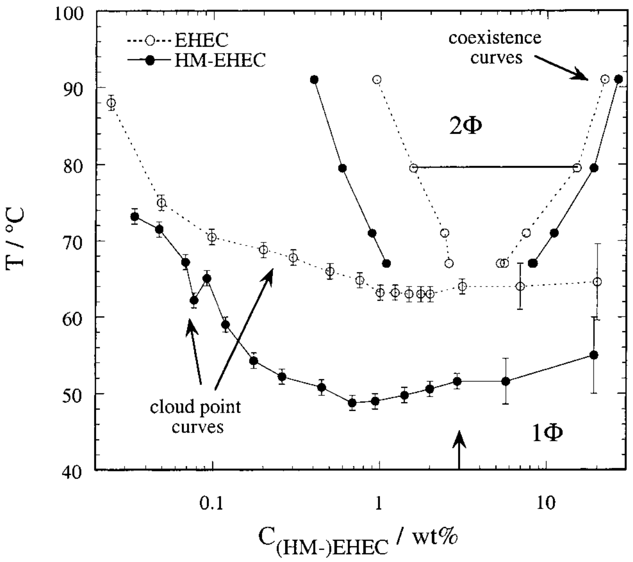

Figure 2. Quasi-binary phase diagram of aqueous solutions of (HM-)EHEC. Above the lines, the systems have a two-phase behavior (2ϕ), while below they have one-phase behavior (1ϕ). The cloud point curves refer to the temperature at which the solution becomes cloudy, while the coexisting curves are obtained by analyzing the two phases in equilibrium. One tie line is indicated (EHEC at 79.5 °C). The arrow located at 3 wt % shows the polymer concentration of the mother solution used to obtain the coexisting curves. The cloud point curves for (HM)-EHEC are reproduced from ref 3.

The phase compositions were analyzed by weighing the solid residue after freeze-drying a known amount of each phase. For samples prepared with HM-EHEC, the content of hydrophobic grafts in each phase (and the distribution of hydrophobic tails in between the phases) was calculated as an average from independent UV absorption measurements at five different polymer concentrations. These solutions were prepared from the solid dry content obtained from each phase. The background absorption was compensated for by subtracting the corresponding EHEC absorption curve.

The 12 different freeze-dried polymer fractions, originating from the two phases in equilibrium at the three different T_p’s, were dissolved in D_2O to obtain stock solutions with a concentration of ca. 3 wt %. These stock solutions were diluted to 12 different concentration series, each containing 10 concentrations ranging from ca. 0.05 to 3 wt %.

The PFG-SE NMR Experiment. In polydisperse polymer systems, the echo decay obtained from a PFG-SE NMR experiment can be evaluated according to

$$E(q) = \frac{\int P(D)\exp(-4\pi^2 q^2 D\Delta)\,\mathrm{d}D}{\int P(D)\,\mathrm{d}D} \tag{1}$$

where $P(D)$ is the normalized distribution of diffusion coefficients, D, and Δ is the effective diffusion time. Furthermore, $q = \gamma\delta g/2\pi$, where γ is the magnetogyric ratio for protons and δ and g are the length and the strength of the field gradient pulse, respectively. One distribution function that may be used for the evaluation is the log-normal distribution function,[4]

$$P(D) = \frac{1}{D\sigma\sqrt{2\pi}}\exp\left[\left(\frac{\log(D) - \log(D_m)}{\sqrt{2}\sigma}\right)^2\right] \tag{2}$$

where D_m is the mass weighted median diffusion coefficient and σ is a measure of the width of the distribution. In self-associating polymer systems the use of eqs 1 and 2 sometimes fails to describe the echo decay. However, modifying eq 1 to include a “second” diffusing component, as in eq 3, has shown

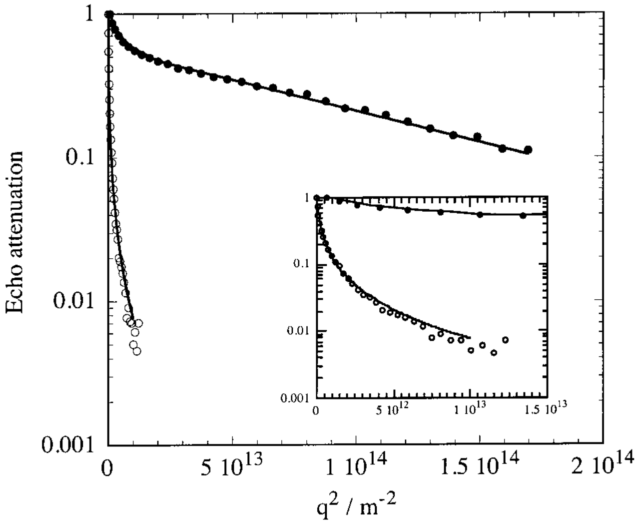

Figure 3. Echo decays for EHEC ϕ' and HM-EHEC ϕ'' fraction, both at 3 wt %. For clarity, an enlargement of the echo decays at lower q values is also shown. The solid lines correspond to the best fits of eq 1 (EHEC) and eq 3 (HM-EHEC) to the data.

to provide an adequate description of the data[4]

$$E(q) = f\frac{\int P(D)\exp(-4\pi^2q^2D\Delta)\,\mathrm{d}D}{\int P(D)\,\mathrm{d}D} + (1-f)\exp(-4\pi^2q^2D_{\mathrm{net}}\Delta) \quad (3)$$

In eq 3, f is the fraction of polymers that belongs to the distribution, $P(D)$, and $(1 - f)$ is the fraction that diffuses with the diffusion coefficient D_{net}. D_{net} has been interpreted in terms of a slowly diffusing "static" network, which shows up as a straight line at high q values when the logarithm of the echo decay is plotted vs q^2. The contribution to the echo decay by the aggregated polymers is still accounted for by the log-normal distribution of diffusion coefficients.[4]

To illustrate the different functional forms of the echo decays, Figure 3 shows data for EHEC and HM-EHEC, both at a polymer concentration of 3 wt %. Note the much higher q values needed in the case of HM-EHEC, where the maximum gradient strength, as allowed by the PFG hardware, was used. In the case of EHEC, the echo decay could in all but a few cases be described by using eqs 1 and 2. On the other hand, for the majority of the HM-EHEC samples this was not possible, and consequently eq 3 had to be used.

A 200 MHz Bruker DMX spectrometer, equipped with a gradient probe capable of providing 9 T/m at 40 A, was used in the diffusion experiments. Because of the relatively fast T_2 relaxation of the polymers, the stimulated spin echo sequence was used in all experiments. Depending on the measured diffusion coefficient, δ was chosen to a value between 1 and 15 ms, and depending on the concentration of the polymer, Δ was chosen so as to obtain an acceptable echo attenuation (smaller than 0.1) with a good signal-to-noise. In all experiments, g was varied between 0.2 and 6.4 T/m in 32 steps.

Most of the NMR experiments were performed at room temperature (22 °C), but for temperature scan measurements on concentrated HM-EHEC samples the temperature of the NMR diffusion probe was controlled within ±0.1 °C.

The experimental NMR data were analyzed by nonlinear least-squares regression of eq 1 in combination with eq 2 or eq 3 using the Levenberg–Marquardt algorithm. In the fitting procedure, D_{m}, σ, and f are treated as adjustable parameters.

It has been argued that a universal scaling law can describe the concentration and molecular weight dependence of transport properties in polymer solutions.[9] The concentration dependence of the polymer self-diffusion coefficient, D_{m}, can be described by the following hydrodynamic scaling law[9]

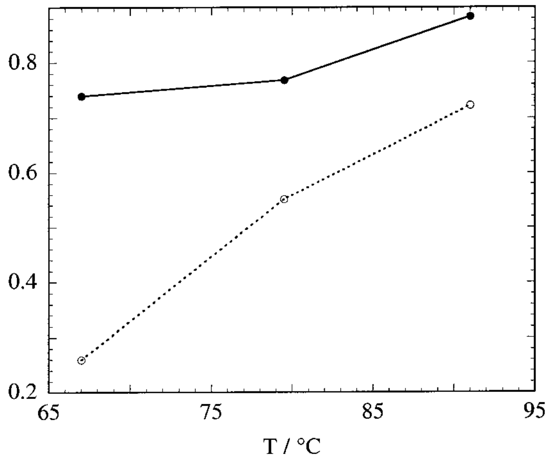

Figure 4. Distribution of polymer material between the two phases in equilibrium presented as the fraction of polymer mass in the bottom phase vs the phase separation temperature: EHEC (○) and HM-EHEC (●).

$$D_{\mathrm{s}}(c) = D_0\exp(-\alpha c^{\mu}) \quad (4)$$

where D_0 is the self-diffusion coefficient in the limit of infinite dilution and μ ($0.5 \le \mu \le 1$) and α are a scaling exponent and prefactor, respectively. Equation 4 ascribes to D_{m} a stretched-exponential dependence on polymer concentration c. Phenomenologically, the scaling coefficients α and μ both depend on polymer molecular weight and solvent quality.[9] The obtained D_0 may be used in combination with the Stokes–Einstein relation

$$R_{\mathrm{h}} = \frac{kT}{6\pi\eta(T)D_0} \quad (5)$$

to calculate the hydrodynamic radius of the polymer coils.

Results

Phase Behavior. Previous investigations of the phase behavior of aqueous solutions of (HM-)EHEC have shown a remarkably flat cloud point minimum,[3,10] and the corresponding coexistence curves appear very different from the full cloud point curves.[3] This result is reproduced in Figure 2 and shows the coexistence curves obtained from 3 wt % (HM-)EHEC mother solutions and the cloud point curves of the same systems. Comparing the coexistence curves of the two polymers, the HM-EHEC system shows a more concentrated ϕ'' phase but, on the other hand, a more dilute ϕ' phase than the corresponding EHEC system at all temperatures. These results are compiled in Figure 4 and presented as the fraction of polymer mass in the ϕ'' phase vs T_{p}.

Clearly, the HM-EHEC prefers the concentrated phase to the dilute phase, while it is not until above ca. 80 °C that the greater part of EHEC is found in the ϕ'' phase. However, even though the mass distribution of HM-EHEC is only weakly influenced by T_{p}, the distribution of hydrophobic group density between the phases, $K_{\mathrm{f,hfob}}$, changes significantly (Figure 5).

At 67 °C, the dilute phase holds 25 wt % of the HM-EHEC material, but this fraction carries only about four hydrophobic grafts per chain on average, compared to seven for the nonfractionated HM-EHEC. On the other hand, at 91 °C, when the dilute phase contains only 10

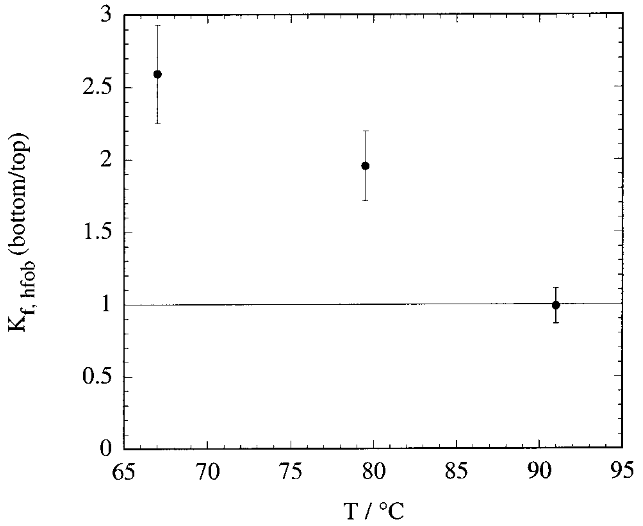

Figure 5. Fractionation of HM-EHEC chains with respect to hydrophobic graft density as a function of phase separation temperature. $K_{\rm f,\,hfob}$ is defined as the hydrophobic graft density ratio between the ϕ'' and the ϕ' phase. The bars indicate the estimated error in the numerical values obtained from independent measurements of the hydrophobic tail concentration.

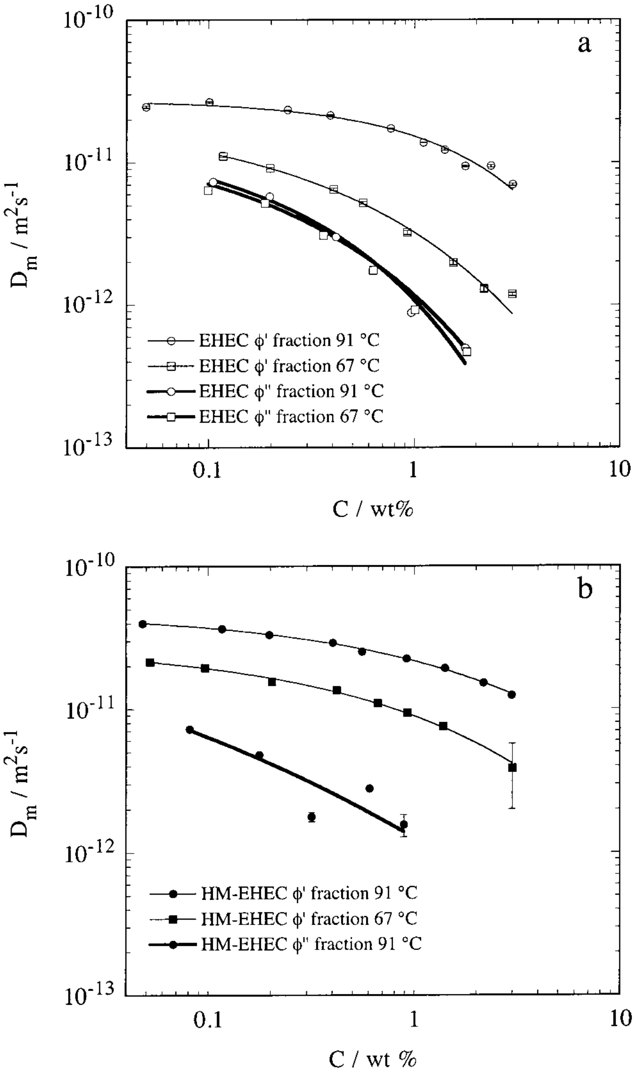

Figure 6. $D_{\rm m}$ (obtained from eq 3) as a function of polymer concentration for EHEC (a) and HM-EHEC (b). The lines correspond to the best nonlinear fit of eq 4 to the data. Thin lines refer to samples prepared from polymer material originating from the dilute top phase, ϕ', while thick lines refer to samples prepared from polymer material originating from the concentrated bottom phase, ϕ'', at the indicated temperature. Data from samples prepared from polymer material obtained at a phase separation temperature of 79.5 °C are omitted for clarity.

wt % of the polymer material, no significant fractionation with respect to the hydrophobic graft density was observed.

Concentration Dependence of $D_{\rm m}$. In Figure 6, the concentration dependence of $D_{\rm m}$ for the ϕ' and ϕ'' fractions of EHEC (a) and HM-EHEC (b) is shown.

For clarity, the data obtained from polymer material originating from the fractionation at $T_{\rm p} = 79.5$ °C are omitted. The full lines in Figure 6a,b represents the best nonlinear fit of eq 4 to the data, which gives the diffusion coefficient at infinite dilution (D_0) for each (HM-)EHEC fraction. The D_0's obtained for (HM-)EHEC fractionated at different $T_{\rm p}$'s are shown in Figure 7.

Because of a complex diffusion behavior (high degree of self-association) of HM-EHEC in the concentrated phase, the echo decay could not be well described by eqs 1 and 2 (see Experimental Section), and we have chosen not to determine D_0 for these fractions. It is clear that for EHEC D_0 is independent of $T_{\rm p}$ (within experimental errors), while for the HM-EHEC ϕ' fraction, D_0 increases with increasing $T_{\rm p}$.

The distribution width of diffusion coefficients, σ, for the ϕ' and ϕ'' fractions of EHEC and HM-EHEC are shown in parts a and b of Figure 8, respectively.

Starting with Figure 8a, we note that the concentration dependence of σ is similar for most EHEC fractions. In addition, all curves approach the same σ value (σ about 0.7−0.9) in the limit of infinite dilution. However, the ϕ' fraction ($T_{\rm p} = 91$ °C) displays a significantly different behavior, as seen as a less steep increase in σ with concentration. For HM-EHEC, the evolution of σ in the ϕ' fraction ($T_{\rm p} = 67$ °C) is close to that found in the EHEC case, but for the ϕ' fraction ($T_{\rm p} = 91$ °C) σ is much smaller, indicating less associative properties. Data from the HM-EHEC ϕ'' fractions are limited to a small concentration range (0−1 wt %) because the echo decays at higher concentrations could not be described with eqs 1 and 2 in combination. However, already in this range, σ takes on large values, indicating very strong associative properties.

Figure 9 shows the distribution of diffusion for ϕ' and ϕ'' fractions obtained at $T_{\rm p} = 91$ °C. For EHEC (Figure 9a), a pronounced difference in $D_{\rm m}$ between the ϕ' and ϕ'' fractions (with $D_{\rm m}$ for the unfractionated sample located in between) can be observed (cf. Figure 6a). At this concentration (0.1 wt %), the width of diffusion coefficients is similar for the three samples (cf. Figure 8a). $D_{\rm m}$ for different fractions of HM-EHEC follows the same trend as for EHEC, while a wider distribution in the ϕ'' fraction and a smaller distribution in the ϕ' fraction is noted as compared to the unfractionated sample (Figure 9b).

Next, we consider in some detail the echo decays obtained for HM-EHEC samples at high concentrations. As mentioned in the Experimental Section, these samples typically have a large fraction $(1 - f)$ which appears as a straight line at high q values, giving a very slowly diffusing component with diffusion coefficient $D_{\rm net}$ (cf. Figure 3). Since this study deals with the diffusion behavior of polymer material obtained from fractionation at different $T_{\rm p}$'s, it is also of interest to investigate the diffusion behavior of these fractions as a function

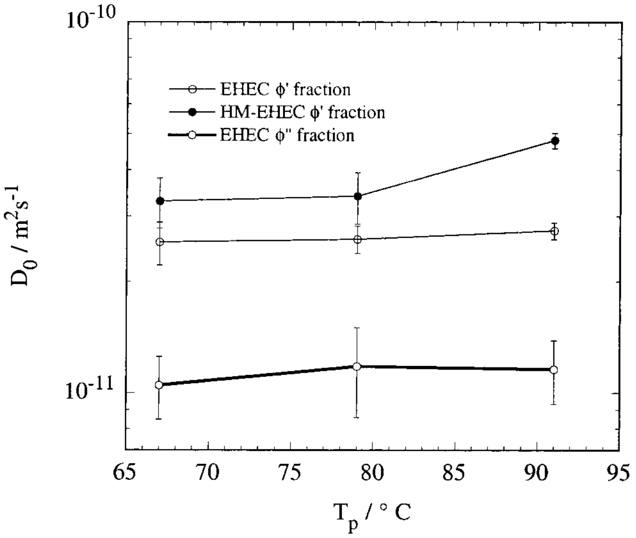

Figure 7. D_0(22 °C) (from eq 4) as a function of the phase separation temperature. Thin lines refer to samples prepared from polymer material originating from the dilute top phase, ϕ', while thick lines refer to samples prepared from polymer material originating from the concentrated bottom phase, ϕ'' EHEC (○) and HM-EHEC (●). The arrow in the lower left corner marks D_0 of the unfractionated (HM)-EHEC's at 19 °C.

of temperature. In particular, we are interested in whether the fraction of the slowly diffusing component changes as the experimental temperature is varied. In Figure 10, the echo decays for samples at 3% are measured at different temperatures. Starting with the ϕ' fractions in Figure 10a, it is clear that a rather low degree of self-association is observed for the samples obtained from fractionation at $T_p = 91$ °C (observed as a moderate curvature). In particular, there is no (or a very small) contribution from a "static" network, and the echo decays rapidly for these samples. On the other hand, for the ϕ' fraction obtained at $T_p = 67$ °C, a straight line at high q values can be seen, which indicates the presence of a slowly diffusing component (with diffusion coefficient D_{net}). Also noted is that the fraction of the slow component appears to decrease slightly when the temperature is increased from 25 to 45 °C. In Figure 10b, the temperature dependence in the echo decays for the ϕ'' fractions, obtained at different T_p's, is shown. In this case, all fractions display a significant contribution from the slowly diffusing component. For the ϕ'' sample obtained at $T_p = 67$ °C, the fraction of the slowly diffusing species is rather large, while for $T_p = 91$ °C it is somewhat smaller. Furthermore, the fraction appears to be independent of the experimental temperature. Although $(1 - f)$ differs between the samples obtained at different T_p's, we note that fairly the same (within experimental errors) diffusion coefficient is obtained, $D_{net} \approx 1 \times 10^{-14}$ m^2 s^{-1}.

Figure 11 shows the echo-decay data originating from the 3 wt % sample of HM-EHEC ϕ'' phase, at $T_p = 91$ °C. At this stage we would like to stress that the q value used, to reach a significant echo attenuation, is very large. More specifically, we note that $q^{-1} \approx 40$ nm. Although the signal-to-noise ratio is quite poor at the larger echo attenuations, it appears that the echo decay is more or less a straight line, from the slope of which we obtain $D_{net} = 1 \times 10^{-14}$ m^2 s^{-1}, which gives a rms displacement, $\langle z^2\rangle^{1/2}$, of approximately 100 nm.

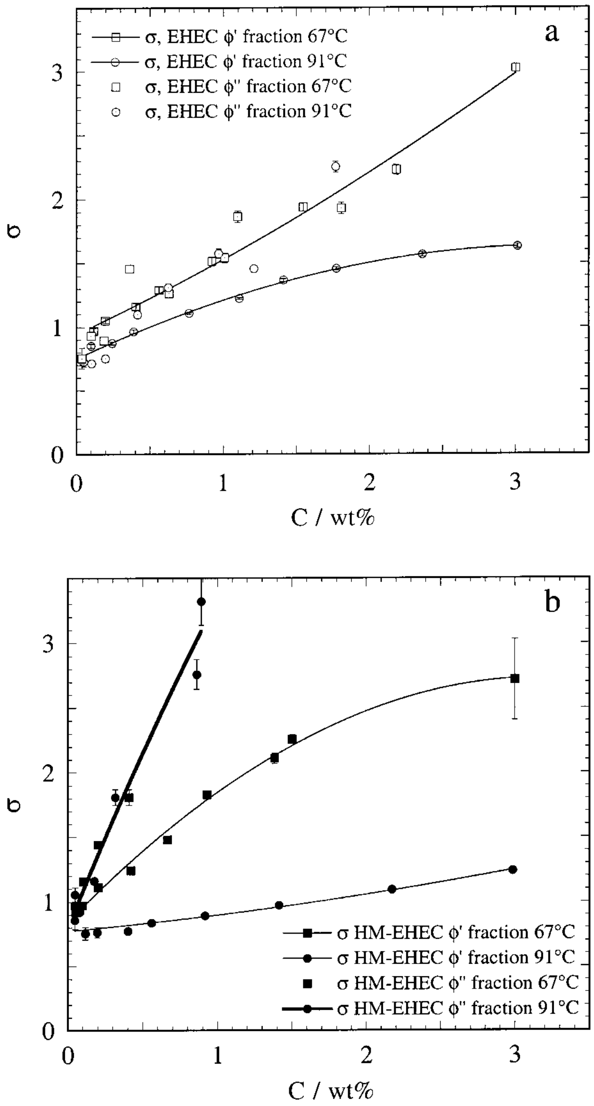

Figure 8. Width of distribution of diffusion coefficients, σ, as a function of EHEC (a) and HM-EHEC (b) concentration. The lines are only drawn as a guide for the eye.

Discussion

As mentioned in the Introduction, the complex phase behavior of multicomponent polymer systems may have various origins. For systems with either a distribution in chain length or a distribution of substitution patterns, a separation of the system into two phases is expected to cause a fractionation of the polymer material.

The HM-EHEC distribution between the phases is less influenced by changing T_p (Figure 4). Here, most of the polymer material resides in the ϕ'' phase already at temperatures slightly above the cloud point temperature. This is suggested to be partly be due to the more hydrophobic nature of HM-EHEC compared to EHEC, but also due to the network forming properties of HM-EHEC. In a concentrated phase, an infinite network via the hydrophobic grafts is more avourably established than in a dilute phase.[11]

In light of the weak T_p dependence of the HM-EHEC mass distribution, the hydrophobe distribution (Figure 5) appears more sensitive to changes in T_p. Let us assume that HM-EHEC polymers in the ϕ' fraction obtained at $T_p = 91$ °C (at this T_p the ϕ' phase contains only ca. 10 wt % of the total HM-EHEC material) is found also in the ϕ' phase at lower T_p's. Then, apart from

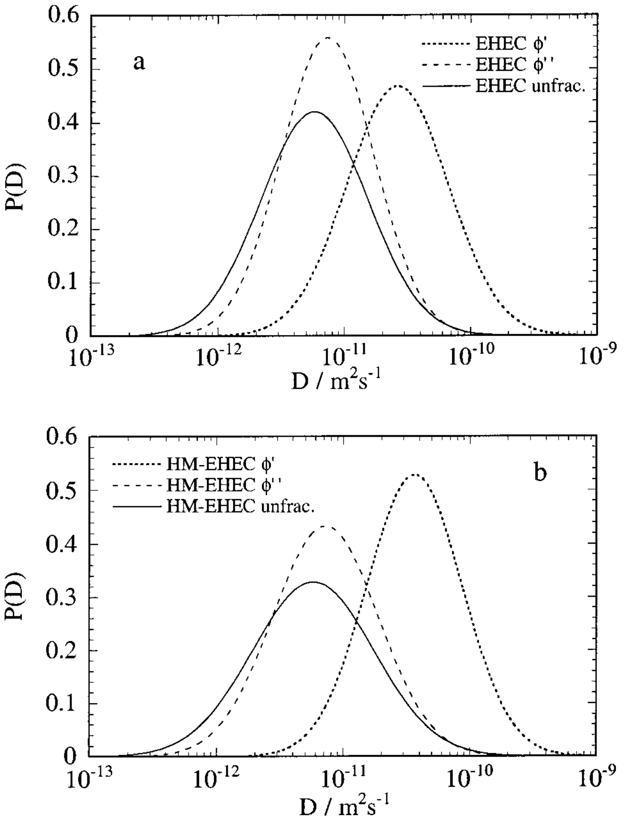

Figure 9. Distribution of diffusion coefficients, $P(D)$, for polymer material originating from top, ϕ'', and bottom, ϕ'', phases after fractionation at T_p = 91 °C compared to the distribution of diffusion coefficients in the unfractionated polymer sample. All curves are obtained at a polymer concentration corresponding to 0.1 wt %. EHEC (a) and HM-EHEC (b).

these HM-EHEC chains, the rest of the ϕ' fraction at T_p = 67 °C, which is ca. 15 wt % of the HM-EHEC material, must have a *very* low degree of hydrophobic modification. As a rough estimate, which takes into account the differences in $K_{f,hfob}$ between T_p = 91 and 67 °C (Figure 5), this additional HM-EHEC material has a substitution degree corresponding to only $^1/_3$ of the average substitution.

This observation may be used to rationalize the change in the fraction $(1 - f)$ of D_{net}, which was observed to decrease with increasing T_p. We note that since D_{net} is observed mainly for HM-EHEC samples, the introduction of hydrophobic grafts on the EHEC chains, which enhances the network forming properties, increases the relative fraction of this slowly diffusing component. Following the discussion above, on increasing T_p from 67 to 91 °C, the concentration of HM-EHEC molecules with a low $MS_{hydrophobe}$ will increase in the ϕ'' fraction. This may increase the fraction of polymer molecules that can be described with the log-normal distribution of diffusion coefficients and thereby decrease the fraction of polymers that are strongly associated, i.e., those described by D_{net}.

For all samples, it is found that σ increases when the polymer concentration increases. The opposite is usually found for nonassociative polymers in solution, and an averaging process between fast and slowly diffusing species is argued to give a more narrow distribution of diffusion coefficients than can be expected from molecular weight distributions.[12] In line with ideas put forward by Ngai, we interpret our observations as being due to the associative character of the EHEC chains which results in increased dynamical/topological constraints when the concentration is increased.[13,14] In this view, the polymer chains have a more associative behavior the larger the slope of the curves (σ vs concentration). Thus, HM-EHEC ϕ'' fractions are con-

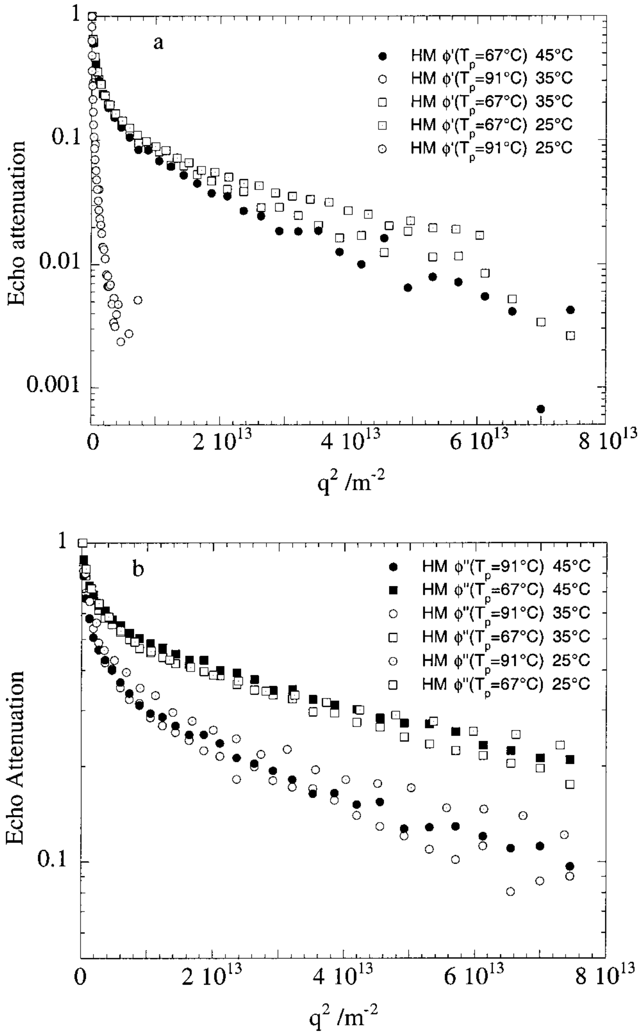

Figure 10. Temperature dependence of the echo decays for 3 wt % HM-EHEC ϕ' fractions (a) and ϕ'' fractions (b), obtained at different T_p's.

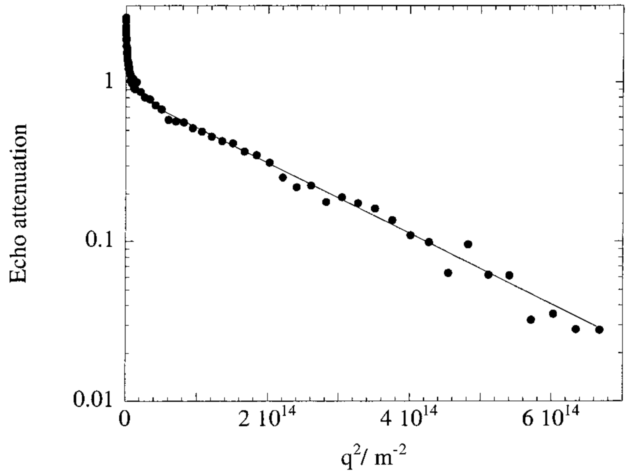

Figure 11. Echo decay for the 3 wt % HM-EHEC ϕ'' fraction, obtained at T_p = 91 °C. The line is fit to the data at high q values and gives $D = 1 \times 10^{-14}$ m² s⁻¹.

sequently more associative than the corresponding EHEC fractions, which is in line with the stronger network forming properties of the HM-EHEC system.[5]

The evolution of σ as a function of concentration for the EHEC ϕ' fraction obtained at $T_p = 91$ °C shows a less pronounced increase than the other EHEC fractions. This may be anticipated since this fraction has a more hydrophilic character and therefore is expected to have a smaller tendency to self-associate. On the other hand—and this is somewhat unexpected—there is a striking similarity between the other fractions. This would suggest that there are only small differences in associative character in these fractions. Analysis of the substitution degree (MS_{EO} and DS_{ethyl}, see Experimental Section) in the ϕ' and the ϕ'' fractions has not shown a significant difference in average substitution between the fractions. We have chosen not to present these data in more detail, since the analysis was restricted to some fractions that were in abundant quantity, only.

From eq 5, it follows that the hydrodynamic radius R_H of a polymer coil is inversely proportional to the diffusion coefficient at infinite dilution D_0. This can be used to translate the data given in Figure 7. For EHEC it follows that R_H both in ϕ' and in ϕ'' fractions are independent of T_p and is significantly smaller in the ϕ' fraction (ca. a factor of 2). If we recall that these fractions have a similar associative behavior (as judged from σ vs concentration), this suggests a fractionation with respect to chain length. At first sight this is in contrast to an earlier investigation in which it was reported that the cloud point temperature was independent of a degradation of the EHEC chain (to a lower molecular weight).[15] However, by considering the multicomponent character of these systems, it is no surprise that the cloud point temperature fails to report that one parameter of the system has been changed. In fact, the determination of a cloud point curve must be seen as a very crude way to characterize a polymer system, which is disperse both with respect to molecular weight and substitution pattern. On the other hand, one should be careful and not make final conclusions. At this stage, we cannot rule out the possibility that the decrease in R_H is an effect arising from intrapolymer chain association. (cf. the discussion about HM-EHEC below).

Turning to HM-EHEC, even though D_0 (and R_H as given by eq 5) only could be determined in the ϕ' fractions, a comparison with values obtained in the nonfractionated HM-EHEC sample gives at hand that also here a fractionation with respect to chain length seems to occur.[4] While R_H determined in the EHEC system seems insensitive to T_p, a significant decrease is observed when increasing T_p for the HM-EHEC ϕ' fraction (see Figure 7). As discussed in connection with the EHEC data, a small R_H may turn the thoughts to a short polymer chain, but considering Figure 5 the explanation may partly be hidden behind the increased hydrophobic graft density compared to that in the ϕ' fractions at lower T_p's. The degree of intra-aggregation is frequently suggested to correlate with $MS_{hydrophobe}$ and hence will influence the R_H of the polymer coil.[16,17]

Another peculiarity is that at $T_p = 91$ °C, where there is no difference in graft density of HM-EHEC in between the two coexisting phases, there is a pronounced difference in associative character as shown in Figure 8b. Despite a similar substitution degree, the polymer material from the ϕ' phase shows a much smaller increase of σ with concentration. Indeed, this is in agreement with that the individual HM-EHEC chains form intra-aggregates (and inter-aggregation is suppressed).

One novel result pertains to the slowly diffusing component in the solution, the presence of which we ascribe to a network formed by associating polymers (cf. Figures 10 and 11). This network influences the overall measured diffusion behavior of the total polymer matrix. Regarding the polymers associated with the network, this fraction appears to be relatively invariant when changing the experimental temperature for ϕ'' fractions obtained at different T_p's. However, for ϕ' fractions at different T_p's a slight decrease in the network fraction is observed as the temperature is increased.

We note that the presence of a static network (on the time scale of the experiment) can severely change the diffusion behavior of the rest of the polymers diffusing freely in solution. In particular, it has been shown by computer simulations that the diffusion coefficient of freely diffusing polymers depends more strongly on the molar mass when a static, heterogeneous matrix is present.[18] Moreover, considering the evaluation of the PFG-SE NMR, the presence of a static network complicates the evaluation of the freely diffusing polymer since the NMR peaks arising from the network overlaps with the peaks from the rest of the polymers.

We note, however, that the presence of a slow component in polymer systems appears to be quite general. It has been observed in concentrated polymer solutions[19] but also, as is the case in this work, in more dilute solutions.[4] Recently, it has been reported by Appel et al. that, in a melt, polymers display a very large rms displacement (100 nm).[20] The motion of individual chains (attached in cross-links) cannot account for this value, but rather the authors argue that the observation depends on a cooperative motion of the whole gel-like network.

Conclusions

In this paper we have used a combination of dynamic and thermodynamic investigations to obtain detailed information about systems of complex associating polymers. For HM-EHEC it was observed that polymer chains with a high hydrophobic substitution degree is biased toward the concentrated phase at phase separation temperatures, T_p's, slightly above the cloud point temperature. When T_p was increased, this fractionation disappeared and the hydrophobic modification degree was the same in the two phases. The character of the polymer material influences the diffusion behavior, and in particular it was found that the HM-EHEC chains that are soluble at a high temperature but has a hydrophobic substitution degree similar to the original HM-EHEC sample (obtained as the ϕ' fractionation at a high T_p) have much less accentuated associative properties. The polymer chains in this fraction also have a smaller hydrodynamic radius, R_H, than the polymer chains in the original HM-EHEC sample. This suggests that in this specific HM-EHEC fraction inter-aggregation is suppressed, and due to an intramolecular segregation, the HM-EHEC chains rather form individual entities with a structure resembling micelles comprising a hydrophobic core covered with a hydrophilic corona. Apart from the specific detailed knowledge, this shows that fractionation by use of phase separation is a powerful technique to single out polymer fractions with highly specific properties from polymer material of a technical grade.

For HM-EHEC, we observe the presence of a slowly diffusing component, the fraction of which depends on the temperature of phase separation (and fractionation). Although the fraction of this component differs between different samples, the measured diffusion coefficient appears to be relatively invariant, and we note that $\langle z^2 \rangle^{1/2} \approx 100$ nm, i.e., a similar value that was found in a melt of poly(propylene glycol).[20] In that paper the authors pointed out that the time scale of the PFG-SE was chosen so that the polymer diffusion was restricted to the tube as set by the interaction with neighboring polymers (i.e., the idea of reptation). On the basis of differences in concentrations between melt and a dilute solution of polymers as used in this work, the measured mean-square displacements are unexpectedly small, and at present we cannot account for these results in a quantitative way.

Acknowledgment. The NUTEK- and Industry Sponsored Centre for Amphiphilic Polymers (CAP) are gratefully acknowledged for financial support.

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MA991783F