Macromolecules **1992,** *25,* 5440-5445

Self-Assembly in Aqueous Block Copolymer Solutions

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Received March 26, 1992; Revised Manuscript Received June 12, 1992

ABSTRACT: The aggregation of EO_{99}–PO_{65}–EO_{99} (EO and PO being ethylene oxide and propylene oxide, respectively) in water has been studied. By gel permeation chromatography (GPC) and self-diffusion studies, it was found that micelles are formed in dilute solutions, but only at higher temperatures. The micelles formed have a hydrodynamic radius of approximately 10 nm over a wide temperature range. The residence time of the polymer molecules in the micelles is extremely long (~hours). At higher polymer concentrations, a clear isotropic gel is formed at intermediate temperatures. The extension of the gel region depends strongly on the presence of cosolutes, such as inorganic salts and hydrocarbons; detailed phase diagrams are presented and discussed. Furthermore, the self-diffusion of the polymer and of solubilized oil was studied. The diffusion of the polymer molecules is slow ($D_p \approx 10^{-11}$–10^{-12} m^2/s), decreasing with increasing polymer concentration (roughly as $D_p \approx c^{-1}$) up to 20 wt %. In the gel region, the echo-amplitude decay curves reveal a distribution of diffusion coefficients, precluding detailed analyses. The self-diffusion of the oil is comparable to that of the polymer ($D_{oil} \approx D_p$), and several orders of magnitude slower than the diffusion of water ($D_w \approx 10^{-9}$ m^2/s).

Introduction

In analogy with low molecular weight surfactants,[1] block copolymers form aggregates of different kinds, depending on the molecular weight, the block sizes, the solvent composition, and the temperature. At low concentrations, it is generally observed that micelles are formed,[2,3] whereas at higher concentrations, liquid crystalline phases may occur.[4] This applies to block copolymers of the EO_a–PO_b–EO_c type as well (EO and PO being ethylene oxide and propylene oxide, respectively). Thus, these generally form micelles in dilute aqueous solutions, provided that the temperature is sufficiently high.[5-14] Moreover, for certain PEO–PPO–PEO block copolymers, a "gel" region appears at high concentrations (typically >20 wt %).[12-16] Due to the possibility of solubilizing both water-soluble and water-insoluble cosolutes in these gels, much effort has been directed toward their application as delivery systems for pharmaceutically active substances.[17,18] Much less effort, however, has been directed toward an understanding of the structure of the gels and the mechanisms of their formation.

One of the few exceptions from this is a study by Wanka et al.,[13] where both micellization and gelation phenomena were investigated for several PEO–PPO–PEO block copolymers. These researchers found evidence for long-range order in the gels, by using small-angle neutron scattering (SANS). From these findings, it was inferred that the gels consist of large domains of cubic liquid crystalline regions. The SANS data furthermore were interpreted to suggest that the mizellar size in the gels is roughly the same as in dilute solutions. Conclusions similar to those of Wanka et al. have later been reached by Mortensen et al.[12] Furthermore, Rassing et al. studied the gelation of EO_{99}–PO_{65}–EO_{99} by means of ^{13}C NMR.[15] These researchers found indications of conformational changes in the PPO block at higher temperatures, which was interpreted as a dehydration of the micellar core. A similar conclusion was drawn by Wanka et al., based on DSC measurements.[13]

In a separate investigation, we studied the temperature-dependent micellization in aqueous EO_{99}–PO_{65}–EO_{99} solutions.[11] It was found that micelles are formed in this system, provided that the temperature is sufficiently high. With increasing temperature, the critical micellization concentration (cmc) decreases. Model calculations, using an extended mean-field theory, agree well with the experimental findings. However, although the behavior in dilute solutions is fairly well understood, little is still known about the temperature-dependent gel formation. Thus, the behavior of concentrated EO_{99}–PO_{65}–EO_{99} solutions is the subject of the present investigation. The self-diffusion of water in this system will be treated in a separate paper.[19]

Experimental Section

Methods. For the GPC experiments, a Superose 6 column was used, with a LKB 2142 differential refractometer as the detector. The flow rate was 0.30 or 0.20 mL/min, and the initial polymer concentration was 1 wt %. All solutions were filtered through a Millipore filter (5.0 μm) before injection. The ^{1}H FTPGSE technique was used to obtain self-diffusion coefficients.[20] In this technique, one uses a 90°–τ–180°–τ–echo pulse sequence, with two added rectangular magnetic field gradient pulses of magnitude G, separation Δ, and duration δ. The echo amplitude (A) at $t = 2\tau$ is given by[21]

$$A(2\tau) = A(0) \exp[-2\tau/T_2 - \gamma^2 G^2 D \delta^2 (\Delta - \delta/3)] \quad (1)$$

where T_2 is the transverse relaxation time and γ the magnetogyric ratio. In this work, the diffusion coefficients D were obtained by measuring the echo amplitude as a function of δ, keeping the other parameters fixed. The NMR spectrometer used as a JEOL FX-60, operating at 60 MHz.

Material. In the experiments we used a specially purified sample of Pluronic F127, which was kindly supplied by BASF Wyandotte, USA. The polymer has a total molecular weight of 12 500, and consists of approximately 70% PEO; i.e., the approximate formula is EO_{99}–PO_{65}–EO_{99}. D_2O was obtained from Norsk Hydro, Norway, and was of 99.8% purity. NaCl and NaSCN were from Merck, Germany, and Mallinckrodt, USA, respectively. *tert*-Butylbenzene and *p*-xylene were from Aldrich, Germany, and BDH, England, respectively. All additives were of analytical grade and were used without further purification.

Results

Dilute Solutions. At low temperatures, the GPC experiments result in chromatograms like that shown in Figure 1a. As can be seen, the sample consists of two fractions. The slowest peak is probably due to some impurity (presumably of a block copolymer nature), since its intensity is independent of temperature (see Figure 1) and since a similar chromatogram was obtained in toluene

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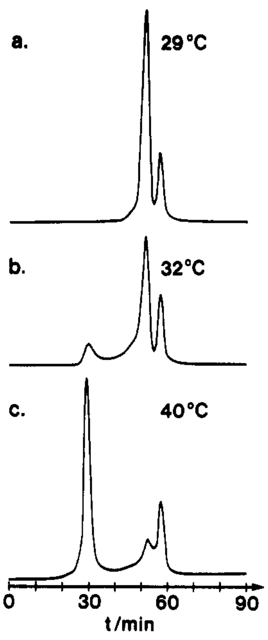

Figure 1. GPC chromatograms at some different temperatures. The initial polymer concentration was 1.0 wt %.

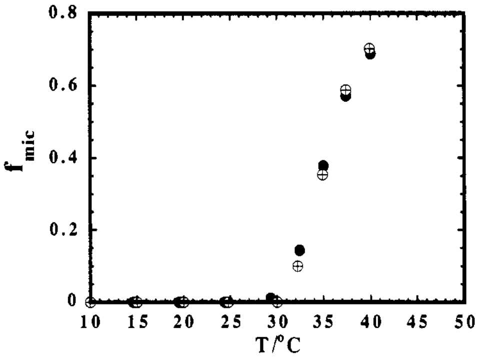

Figure 2. Temperature dependence of the relative intensity of the peak corresponding to aggregates (micelles) at a flow rate of 0.30 mL/min (crossed circles) and 0.20 mL/min (filled circles).

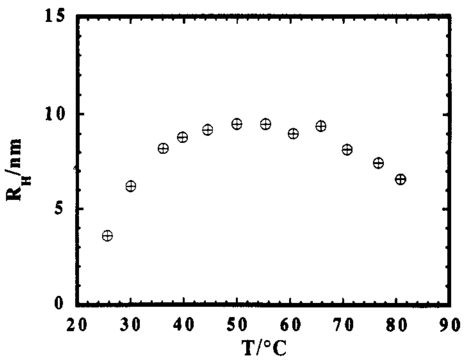

Figure 3. Temperature dependence of the effective average polymer hydrodynamic radius (R_H) in a 1 wt % solution.

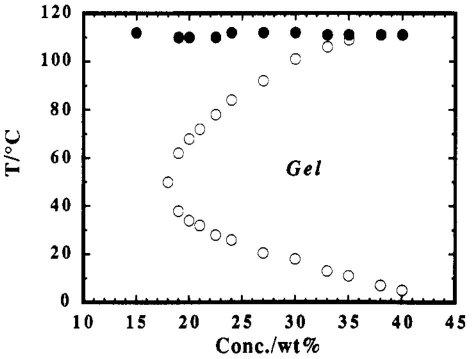

Figure 4. Phase behavior of the EO_{99}–PO_{65}–EO_{99}–water system. The solid circles refer to the CP.

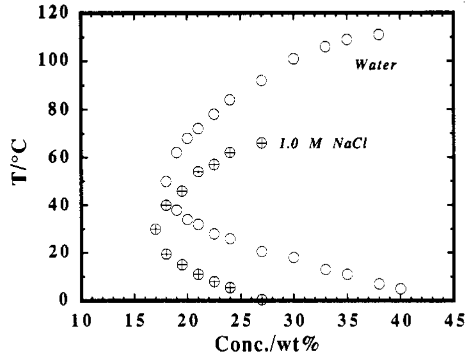

Figure 5. Phase behavior of the EO_{99}–PO_{65}–EO_{99}–water system in the presence of 1.0 M NaCl (crossed circles). Shown also is the phase diagram for the polymer–water system (open circles). CP in the presence and absence of 1.0 M NaCl is 75 and 110 °C, respectively.

(results not shown). At approximately 30 °C, a new peak, corresponding to a higher molecular weight, appears (see Figure 1b). As the temperature is increased further, the relative intensities of the peaks are shifted so that an increasing fraction of the polymer contributes to the peak corresponding to the larger aggregates (Figure 1). By varying the temperature, it is possible to follow the whole aggregation process (Figure 2). It should be noted that this behavior is independent of the flow rate. Unfortunately, since GPC requires calibration, it was not possible to obtain the molecular weight of the aggregates.

With the FTPGSE-NMR technique, the self-diffusion coefficient of the polymer is obtained by measuring the rms displacement of the molecules under study.[20] Since the measuring time is of the order of 100 ms, the rms displacement corresponds to several hundred times R_G. The interpretation of the self-diffusion data is thus relatively simple. As can be seen in Figure 3, the hydrodynamic radius (R_H; obtained by using the Stokes–Einstein equation) increases with temperature, to a broad maximum. At all temperatures, however, R_H is quite small.

Phase Diagrams. Shown in Figure 4 is the phase diagram for the polymer–water system. As can be seen, a large gel region exists at high polymer concentrations and intermediate temperatures. The existence region for the gel is well below the cloud point (CP $\approx$ 110 °C). The lower concentration and temperature boundaries of the gel region are very sharp, as shown previously,[13,14] and are easily determined with good accuracy (±1 wt % and ±1–2 °C, respectively). The upper temperature boundaries are somewhat more difficult to determine accurately, and some hysteresis (±3–4 °C) exists. The upper boundaries were obtained on heating.

The stability range of the gel phase is strongly dependent on the presence of cosolutes. Thus, NaCl, which is often referred to as a typical "salting-out" cosolute, displaces the whole gel region, as well as CP, to lower temperatures (Figures 5 and 6). NaSCN, a typical "salting-in" cosolute, on the other hand, displaces the gel region, as well as CP, to higher temperatures (Figures 7 and 8).

Since the polymer solution contains hydrophobic regions, it is capable of solubilizing hydrophobic substances. While the solubility of moderately hydrophobic substances, like aromatic hydrocarbons, is dramatically enhanced in the polymer solution, the solubility of more hydrophobic substances, like aliphatic hydrocarbons, remains quite low. In Figure 9, we show the phase diagram in the presence and absence of 10 *p*-xylene molecules for every polymer

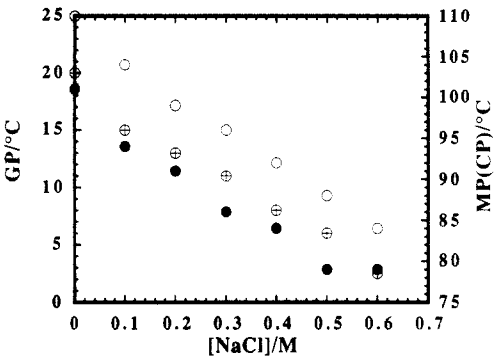

Figure 6. Gelation point (GP, crossed circles), melting point (MP, filled circles), and cloud point (CP, open circles) of a 30 wt % solution as a function of NaCl concentration.

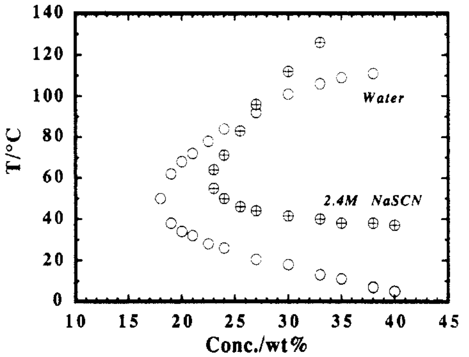

Figure 7. Phase behavior of the EO$_{99}$–PO$_{65}$–EO$_{99}$–water system in the presence of 2.4 M NaSCN (crossed circles). Shown also is the phase diagram for the polymer–water system (open circles). CP in the presence and absence of 2.4 M NaSCN is 129 and 110 °C, respectively.

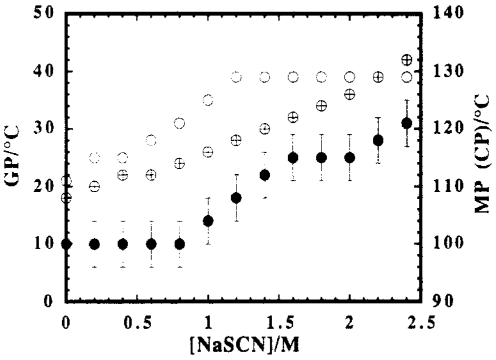

Figure 8. Gelation point (GP, crossed circles), melting point (MP, filled circles), and cloud point (CP, open circles) of a 30 wt % solution as a function of NaSCN concentration. Error bars given for the melting point apply to CP as well.

molecule. As can be seen, the lower temperature gel boundary is displaced to lower temperatures in the presence of oil, whereas a small increase in the upper gel boundary and a small decrease in the phase separation temperature are observed. A similar behavior was obtained for *tert*-butylbenzene (results not shown).

Polymer and Oil Self-Diffusion. In Figure 10, we show the concentration dependence of the polymer self-diffusion coefficient, D_p. We see that the polymer self-diffusion is several orders of magnitude slower than the water self-diffusion ($D_w \approx 10^{-9}$ m^2/s)[19]. At low concentrations D_p decreases with increasing polymer concentration (roughly as $D_p \approx c^{-1}$). Furthermore, at low polymer concentrations, the echo-amplitude decay is roughly monoexponential. On entering the gel region, D_p increases. However, an increasing divergence from monoexponential amplitude decay is observed (Figure 11) as well. The strict meaning of a well-defined diffusion coefficient thus vanishes in the gel region, and D_p depends on the diffusion time. The values of D_p reported from the gel phase are thus to be considered as effective average values. Note that the echo-amplitude decay is monoexponential once more, at temperatures above the gel region (Figure 11).

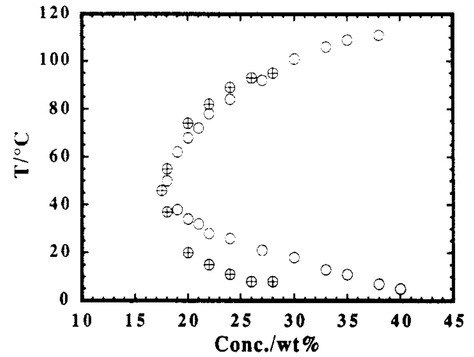

Figure 9. Phase behavior of the EO$_{99}$–PO$_{65}$–EO$_{99}$–water system in the presence of solubilized *p*-xylene at an oil-to-polymer ratio of 10/1 (crossed circles). Shown also is the phase diagram for the polymer–water system (open circles). CP in the presence and absence of *p*-xylene is 105 and 110 °C, respectively.

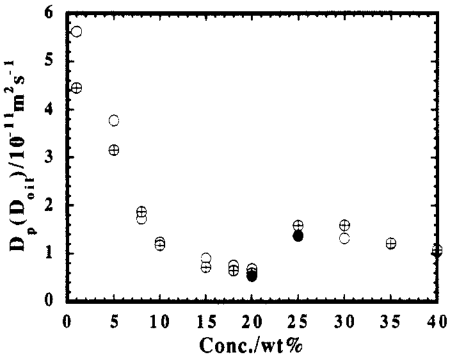

Figure 10. Concentration dependence of the polymer self-diffusion coefficient (D_p) at 27 °C (open circles) and 54 °C (crossed circles). Shown also is the diffusion coefficient (at 27 °C) of *tert*-butylbenzene (D_{oil}), solubilized at a molecular ratio of oil/polymer of 8/1 (filled circles). The gel boundary in the presence of oil is 16 wt %, whereas the boundaries at 27 and 54 °C in the absence of oil are 22 and 19 wt %, respectively.

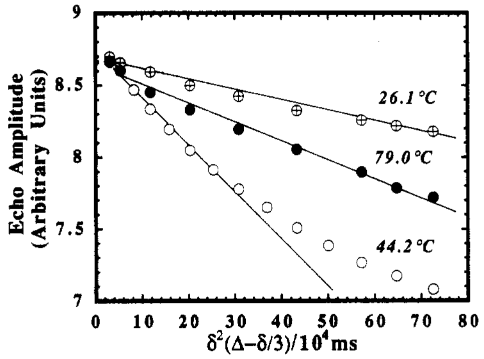

Figure 11. Echo amplitude versus $\delta^2(\Delta - \delta/3)$ for a 20 wt % solution at some different temperatures. The gel boundaries at 20 wt % are 34 and 68 °C.

In addition, the diffusion of solubilized *tert*-butylbenzene in the gel was investigated. This substance is sufficiently hydrophobic for its solubility in water to be negligible, at the same time as it is sufficiently polar to allow solubilization. The results of these measurements are shown in Figure 10. As we can see, the oil self-diffusion coincides quite closely with that of the polymer, whereas it is several orders of magnitude slower than the water self-diffusion ($D_w \approx 10^{-9}$ m^2/s).[19]

Discussion

Dilute Solutions. From both self-diffusion and GPC experiments (see Figures 1–3), it is clear that the block copolymers investigated here *do* form aggregates (micelles), provided that the temperature is sufficiently high. This has been found in several previous investigations as well.[5-14] It is likely that the micelles consist of a compact PPO core, surrounded by protecting PEO chains, since PPO in itself is not extensively soluble in water.[22] This is further suggested by the high CP (CP $\approx$ 110 °C), which is about the same as that of PEO of a comparable total molecular weight.[23] Although the hydrodynamic radius of the micelles is fairly small at all temperatures, this should not be taken as an indication of the micelles being "hard spheres". Taking the aggregation number obtained by Attwood et al. ($N \approx 10$ at 40 °C),[7] we obtain a hard-sphere radius of about 36 Å, which (not unexpectedly) is considerably smaller than the hydrodynamic radius obtained. Thus, the PEO chains in the corona are highly swollen at this temperature.

The reason that a higher temperature is needed to form micelles is that the effective EO–EO, PO–PO, and EO–PO interactions are temperature dependent. With increasing temperature, both PO and EO blocks will repell each other progressively less. At some temperature, the effective PO–PO attraction will dominate over the PEO–PEO repulsion, and micelles will form. This effect was nicely demonstrated by Brown et al., who showed that the (effective) second virial coefficient of Pluronic P85 decreases dramatically with increasing temperature.[14] Analogous findings have been reached by direct surface force measurements in similar systems.[24] This temperature dependence is of a quite general nature, and not limited to the PEO (PPO)–water system. Instead, the same temperature dependence has been observed also for many nonionic low molecular weight surfactants,[1,25] as well as for several polysaccharides.[25] Moreover, the solvent does not need to be water. Instead, qualitatively the same behavior occurs in several other polar solvents.[23,26]

The mechanism behind this temperature dependence is still a matter of some controversy. In principle, models in the literature focus on the solvent–solvent, the solute–solvent, or the solute–solute interactions. Ourselves, we have focused on the latter of these models. From quantum mechanical calculations, but also from ^{13}C NMR chemical shift measurements, the conformation of the –OCCO– segment is divided into two classes, one being polar, having a low energy and a low statistical weight, and one being less polar, or nonpolar, having a higher energy and a higher statistical weight. At low temperatures, the former class of states dominates, and the solute–solvent interaction is favorable, whereas at higher temperature, the latter class of states becomes increasingly populated, rendering the solute–solvent interaction less favorable. For a more comprehensive discussion of the mechanisms of the temperature dependence, and clouding in particular, see ref 25.

Although we here use the term micelle, which is well-established and has a clear meaning for simple surfactants, we should note that there are many differences between micelles formed by low molecular weight surfactants and the aggregates (micelles) formed by block copolymers. One of these striking differences is clearly shown in Figure 1b,c. The fact that it is possible to separate the unaggregated polymer molecules (unimers) from the aggregates on the time scale of these experiments (1–2 h) indicates that the residence time of a polymer molecule in an aggregate is *extremely* long. This should be compared to the residence time of a monomer in a micelle, formed by a low molecular weight surfactant, which is of the order of milliseconds, or even less, although it increases strongly with the surfactant chain length.[27] It should be mentioned here that other researchers have found extremely long micellar lifetimes in aggregated block copolymer solutions as well. Thus, Booth et al.[28] and Tuzar et al.[29] both obtained separate peaks for the unimers and the aggregates, using GPC and ultracentrifugation, respectively. Similar observations have recently been made by Desjardin et al.[37] Our results are thus in line with these earlier findings.

From the self-diffusion experiments on the dilute polymer solutions, it should, in principle, be possible to obtain the hydrodynamic radii of both populations, since there is slow exchange, especially on the NMR time scale, between the populations. In practice, however, it is difficult to fit biexponential curves unambiguously if the two exponential decay rates differ by less than a factor of 2 or 3, as in our case. The hydrodynamic radius reported should therefore be regarded as an effective average parameter.

At low temperatures, the average hydrodynamic radius increases with increasing temperature (Figure 3). The increase corresponds to the aggregation process observed in the GPC experiment. The transition temperature is slightly lower than in the GPC experiment, which is due to the concentration in the self-diffusion experiment (1 wt %) being higher than the *real* concentration in the GPC experiment (due to the dilution in the latter). Since the cmc of nonionic low molecular weight surfactants and PEO–PPO–PEO block copolymers is a decreasing function of the temperature[1,5,11] (cf. the GPC experiments), we would expect the transition to take place at higher temperature, the lower the polymer concentration.[11]

Several other researchers have studied the micellization of PEO–PPO–PEO block copolymers in water.[5-14] It is generally found that these block copolymers *do* form micelles, provided that none of the blocks is too abundant. Furthermore, the cmc decreases[5,11] with increasing temperature, whereas the hydrodynamic radius of the micelles increases.[5-14] Thus, our GPC and self-diffusion data are in line with these earlier findings. For T = 50 °C, we obtain $R_H \approx 10$ nm, in good agreement with the findings of other researchers.[7,13] The same result was found with photon correlation spectroscopy (PCS; results not shown). Note that the hydrodynamic radius of the micelles is rather insensitive to temperature. Thus, $R_H \approx 10$ nm, essentially independent of temperature in the temperature range 40–70 °C. A similar finding was obtained from GPC, which shows that the elution volume of the micelles is constant in the temperature range 30–45 °C. Furthermore, the weak variation of R_H with temperature above critical micellization temperature (cmt) has been predicted from model calculations.[11]

Phase Diagrams. In Figures 4–9, we show the phase diagram of the polymer–water system, and the effects of different cosolutes on the phase behavior. As can be seen in Figure 4, a gel region appears in the phase diagram at high polymer concentrations and at intermediate temperatures. [It should be noted that no two-phase region was observed in this system. Whether this is due to the two-phase region being extremely narrow, or to some other reason, is uncertain at present.] It has been inferred from SANS data that the gel consists of a close-packed (cubic) array of micelles.[12,13] Since we know from experiments in the dilute regime that polymer molecules start to aggregate at a temperature which is slightly higher than the temperature for gelation, and since the cmt decreases with increasing polymer concentration,[1,5,11] it does not seem far-fetched to infer from these experiments that the lower temperature gel boundary is actually coincident with or close to the cmt line. If the concentration is high enough ($\sim c^*$ for the solvated micelles), the aggregates will order in a regular way, and a lattice is formed. For concentrations above the critical gelation concentration, but at low temperatures, the viscosity of the polymer solution is low, which is due to the lack of aggregation and the low molecular weight of the polymer. At high temperatures, on the other hand, the lattice is disrupted by the contraction of the micelles (Figure 3) and the viscosity of the polymer solution is low once more.

Wanka et al. at least partly studied the occurrence of the gel region of, inter alia, Pluronic F127.[13] Qualitatively, but not quantitatively, their results concerning the lower temperature gel boundary agree with our findings. Since the experiments are very simple, this discrepancy may be a result of batch differences, which we have observed as well. Our findings are quantitatively in better agreement with the limited data reported by Schmolka.[16]

The presence of cosolutes influences both the aggregation process and the conformation of the polymer molecules. These effects can often be explained in terms of their distribution in the solution.[30-32] Large polarizable anions like SCN^- have a slight tendency to accumulate at an interface (broadly speaking), and thus also close to the polymer investigated here. This increases the solubility of the polymer, and thus moves the stability region of the gel and the CP to higher temperatures (Figures 7 and 8). Other ions, e.g., Na^+ and SO_4^{2-}, are depleted close to the polymer, inter alia due to image charge effects, i.e., the effective repulsion acting between ions and low-dielectric interfaces. As the depletion close to the polymer can be viewed as an increase in the interfacial tension between the polymer and water (broadly speaking), we expect a decrease in the solubility of the polymer. This results in a decrease in CP at the same time as the gel region is displaced to lower temperatures (Figures 5 and 6).

The effects of hydrocarbons have to be discussed in a completely different way, since their solubility in water is extremely low. Thus, these substances tend to accumulate in the comparably hydrophobic PPO cores of the micelles. It is interesting to note that while the solubility of moderately hydrophobic substances, like aromatic hydrocarbons, is dramatically enhanced in the presence of the polymer, the effect on the solubility of more hydrophobic substances, like aliphatic hydrocarbons, is remarkably small.[33] The latter effect seems to reflect the finite polarity of the PPO core. The presence of the solubilized hydrocarbon is expected to expell water from the micellar core, thus promoting micellization. Furthermore, solubilized oil affects the hydrophilic–hydrophobic balance, so that the attraction between the PO segments may dominate over the repulsions between the PEO palisades at a lower temperature. Therefore, a decrease in the lower temperature gel boundary is expected (Figure 9).

Our results are in agreement with earlier studies on the effects of different cosolutes on the gelation behavior of aqueous PEO–PPO–PEO block copolymer solutions. Schmolka found that some inorganic salts (e.g., NaCl) lower the temperature where "liquefication" occurs, whereas some sparingly water soluble cosolutes (e.g., *m*-toluidine) enhance the "gel strength".[16]

Polymer and Oil Self-Diffusion. One approach to determine the structure of a colloidal system is to use X-ray diffraction. However, despite a relatively long sampling time, in order to overcome the low contrast, and a thorough equilibration procedure, we observed no diffraction patterns. This might be due to the lack of any long-range order in the gel, but it is also possible that the equilibration time (several weeks) is too short to obtain equilibrium. However, recent SANS data by Wanka et al.[13] and by Mortensen et al.[12] indicate that the gels consist of a close-packed array of micelles of roughly the same size as those outside the gel region.

As mentioned above, and as seen in Figure 10, the polymer self-diffusion is slower than the water diffusion by several orders of magnitude ($D_w \approx 10^{-9}$ m^2/s)[19]. With increasing polymer concentration, D_p decreases, roughly as $D_p \approx c^{-1}$, up to a polymer concentration of approximately 20 wt %. This behavior is well-known from experimental studies[34] and from theoretical analyses of the polymer self-diffusion in dilute solutions,[35] and is due to obstruction effects. Considering this, it seems likely that solutions up to approximately 20 wt % are dilute with respect to the polymer. This is of the same order of magnitude as what was obtained from intrisic viscosity ($c^* \approx 10$ wt %, results not shown), although the significance of the latter parameter in a self-assembling system may be disputed.

On entering the semidilute regime, we expect from scaling theory that D_p should have another functional form ($D_p \approx \Phi^{-1.75}$ in good solvents, Φ being the polymer volume fraction)[36]. In our case, the situation is complicated by the aggregation process, although we would still expect D_p to decrease with increasing polymer concentration. Instead, we find that D_p is *higher* in the gel region. However, since the echo-amplitude decay for the polymer is not monoexponential in the gel (Figure 11), it is not meaningful to discuss a unique diffusion coefficient. Instead, there exists a *distribution* of diffusion coefficients, of which the values of D_p reported constitute effective averages. Thus, D_p depends on the diffusion time, since we effectively average over different parts of the distribution at different diffusion times (results not shown).

These findings show that polydisperse aggregates form in the gel. Note that the echo-amplitude decay is monoexponential in dilute solutions as well as in concentrated solutions at low and high temperatures (Figure 11), which indicates that the polymer molecules, as well as the micelles, are not polydisperse themselves. Furthermore, the oil diffusion is comparable to that of the polymer, but several orders of magnitude slower than that of water. Thus, the gel is not bicontinuous, but consists of discrete polymer aggregates. These results are in line with previous SANS data, indicating that the gel contains crystalline regions, embedded in material of short-range order.[13]

Although D_p is less well-defined in the gel region, it seems clear from Figure 11 that the echo amplitude decays faster in the gel region than in the low-viscous regions, which is equivalent to a higher effective diffusion coefficient (eq 1). One of the reasons for this could be that we "lose" the signal from slowly diffusing polymer molecules, due to line broadening. D_p should then be an average only over the faster components, and should therefore increase in the gel region. However, no anomalous intensity losses were observed (results not shown). Furthermore, conformational effects could, in principle, give rise to the anomalous behavior. In the case of associating polymers, however, these are likely to be dampened, particularly for low molecular weight polymers. Furthermore, SANS data suggest that the gel consists of a close-packed array of micelles of roughly the same size as those in dilute solutions. Little therefore suggests that conformational effects are significant in the present system. Whether the increase in D_p is real, originating from some change in the diffusion mechanism on entering the gel region, or due to some artifact unaccounted for is difficult to say at present. Further studies, including NMR relaxation measurements, are necessary.

Summary

EO_{99}–PO_{65}–EO_{99} forms micelles in dilute aqueous solutions, provided that the temperature is sufficiently high. The cmc decreases with increasing temperature, in analogy with low molecular weight nonionic surfactants and other PEO–PPO–PEO block copolymers. The average residence time of a single polymer molecule in the aggregates is extremely long (~hours). The micelles formed are relatively small ($R_H \approx 10$ nm), in good agreement with earlier findings. At higher polymer concentrations, and at intermediate temperatures, a gel region exists. This is found to consist of discrete polymer aggregates. For the gels to form, the temperature must be higher than the critical micellization temperature (cmt). Moreover, the polymer concentration must be higher than the overlap concentration of the hydrated aggregates. Therefore, the occurrence of the gel is markedly affected by the presence of cosolutes that influence either the micellization or the "size" of the aggregates.

Acknowledgment. Carina Göransson and Ingegerd Lind are acknowledged for experimental help. Dr. Mikael Jonströmer is thanked for introducing M.M. to the FTPGSE technique. This work was financed by Berol Nobel AB and the Swedish National Board for Technical Development.

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Registry No. NaCl, 7647-14-5; NaSCN, 540-72-7; $CH_3C_6H_4$-*p*-CH_3, 106-42-3; $C_6H_5CHMe_3$, 98-06-6; Pluronic F127 (block copolymer), 106392-12-5.