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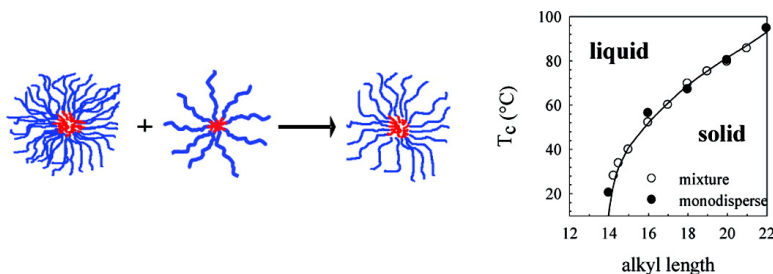
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Structure and Viscoelasticity of Mixed Micelles Formed by Poly(ethylene oxide) End Capped with Alkyl Groups of Different Length

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Poly(ethylene oxide) (PEO) end capped with an alkyl group is a highly asymmetric diblock copolymer that forms spherical micelles in aqueous solution resembling multiarm star polymers. The effect of varying the length of the alkyl end group on the structure and viscoelasticity was investigated for pure and mixed micelle suspensions. The aggregation number (p) of the micelles increased and the critical association concentration (CAC) decreased with increasing the length of the end group. At high concentrations a discontinuous reversible liquid–solid transition was observed below a critical temperature (T_c) that increased with increasing length of the end group. Mixing end-capped PEO with different alkyl lengths led first to formation of the micelles by polymers with the lowest CAC into which the other polymers were incorporated when the concentration was increased. The viscoelastic properties at high concentrations are the same for pure systems and mixtures with the same average length of the alkyl end group.

Introduction

Hydrophobically end-capped poly(ethylene oxide) (PEO) is an asymmetric amphiphilic block copolymer that aggregates in water into spherical star-like micelles above a critical association concentration (CAC).¹ The aggregation number (p) and CAC depend on the relative length of the soluble and insoluble block. For a given soluble block length, p increases and the CAC decreases with increasing length of the insoluble block.^{2–4}

At high volume fractions solutions of polymeric micelles^{1,5} or star polymers⁶ jam and a liquid–solid (glass) transition occurs. The effective thermodynamic volume fraction of the micelles or star polymers is the parameter that determines the transition, which means that the transition can be induced by either increasing the concentration or varying the temperature in the case of a marginal solvent. For polymeric micelles the transition is accompanied by the appearance of crystalline order. For PEO end capped with an alkyl group it was demonstrated that the transition is discontinuous by which we mean that in equilibrium solutions either have a relatively low viscosity or do not flow at all when tilted.⁷ If the transition is induced by a temperature quench, a disordered solid (glass) is formed first and crystalline order appears more slowly.⁷ In the case of multiarm star polymers theory⁸ predicts crystallization at concentrations close to the glass transition, but a distinct crystalline order has not been observed experimentally.⁹

Here we report a study of the liquid–solid transition of PEO end capped with an alkyl group in which the number of PEO segments is kept constant at 100 and the number of carbons in the alkyl group is varied between 12 and 22. Amari et al.¹⁰ studied the effect of the length of the alkyl group between 11 and 17 for PEO chains with a constant length of 40 segments. They determined the liquid–solid transition using the tube inversion method and found that it shifted to larger concentrations and lower temperatures when the alkyl length was reduced. In the solid state the micelles formed a body-centered crystal (bcc) phase.^{11,12} Notice that these authors used the expression “hard gel”, but since there is no cross-linking between the micelles we prefer to use the term solid. We stress, however, that at the conditions studied here the PEO segments are fully mobile. The PEO segments were reported to crystallize only at very high concentrations and low temperatures.^{11,12} The largest alkyl chains partially crystallize within the micellar cores at low temperatures,¹³ but this had no effect on the measurements reported in the present study.

Experimental work has been reported on binary mixtures of different block copolymers in organic solvents^{14,15} and on mixtures of block copolymers of PEO-poly(butylene oxide) or PEO-poly(propylene oxide) in water; see ref 16 and references cited therein. These experiments showed that generally mixed micelles are formed at conditions where both individual polymers formed micelles. With increasing concentration the polymer with the lowest critical association concentration forms micelles first into which the other polymers are progressively incorporated. An analogous situation occurs if micellization is induced by

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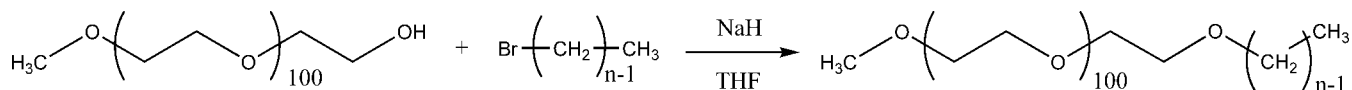


Figure 1. Reaction scheme of the synthesis of poly(ethylene oxide)-*b*-alkyl copolymer with $n = 12$ –22.

changing the temperature. A few theoretical studies^{17,18} have been reported on micellization of two block copolymers with the same chemical structure and different composition.

Recent work¹⁹ on mixtures of PEO with different chain lengths end capped with the same alkyl showed that mixed micelles were formed and that this led to melting of the solid. To our knowledge, no systematic investigation of mixtures of PEO end capped with different sizes of the alkyl group has been reported so far. Here we will show that mixing PEO with the same molar mass end capped with different alkyl groups leads to formation of mixed micelles at high concentrations. Remarkably, the viscoelastic properties of these mixed micelle suspensions were found to be identical to that of pure micelle suspensions with the same average length of the alkyl end groups. An implication that is useful for practical applications is that one can simply mix two polymers to obtain an average system with the desired properties instead of synthesizing polymers with different alkyl lengths.

Materials and Methods

Materials. Poly(ethylene oxide) monomethyl ether was purchased from Aldrich. The weight-average molar mass (M_w) determined by MALDI-TOF and light scattering was 4.5 ± 0.2 kg/mol, and the polydispersity index (M_w/M_n) estimated by size exclusion chromatography (SEC) was 1.05. The SEC results showed also that the polymer contained 5% w/w of dihydroxy telechelic chains with a molar mass twice as large. Alkyl bromide with different alkyl lengths were also purchased from Aldrich and had a purity grade of 96%.

Synthesis of the copolymers for the present investigation was done following the method used by Nicol et al.²⁰ PEO monomethyl ether was hydrophobically modified by reacting the corresponding PEO-sodium alcoholate with alkyl bromide in THF (Williamson reaction), see Figure 1. Size exclusion chromatography in THF showed that the functionalization had no influence on the molar mass distribution. ¹H NMR showed that quantitative functionalization was attained within the experimental error of 5%. The chemical shifts of PEO- C_{14} in CDCl_3 were, δ (ppm), 0.88 (t, 3H, alkyl terminal CH_3), 1.25 (m, 22H, CH_2 alkyl), 1.57 (qt, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{alk}$), 3.38 (s, 3H, $\text{CH}_3-\text{O}-\text{PEO}$), 3.56 (t, 2H, $\text{PEO}-\text{O}-\text{CH}_2-\text{alk}$), and 3.5–3.9 (m, ~ 430 H, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$).

Clear solutions of functionalized PEO (PEO- C_n) were obtained in deionized water (Millipore) at pH 7 after stirring for 1 h at 90 °C. The total PEO concentration (C) was calculated using a density of 1.15 kg/L.²¹ The small temperature dependence of the density was neglected. Functionalized PEO was soluble up to $C = 750$ g/L.

Rheology. Rheology measurements were done using a stress-controlled rheometer (AR2000, TA Instruments) with a cone and plate geometry (diameter 6 cm and angle 0.58° or 4 cm and 2°). The temperature was controlled by a Peltier system. Solvent evaporation was avoided by covering the geometry with mineral oil. Oscillatory measurements were done at 1 Hz with an imposed stress of 10 Pa or imposed deformation of 0.5% to determine the storage (G') and loss moduli (G''). In both cases the measurements were in the linear response regime for the solids and liquids. For the liquids the dynamic

viscosity obtained from G'' was the same as the viscosity obtained from flow measurements with an imposed stress of 10 Pa.

Light Scattering. Light scattering measurements were made using an ALV-5000 multibit, multitau, full digital correlator in combination with a Spectra-Physics laser emitting vertically polarized light at $\lambda = 532$ nm. The temperature was controlled by a thermostat bath to within ± 0.1 °C. The relative excess scattering intensity (I_r) was determined as the total intensity minus the solvent scattering divided by the scattering of toluene at 20 °C. I_r is related to the osmotic compressibility ($(d\pi/dC)^{-1}$) and z -average structure factor ($S(q)$)^{22,23}

$$I_r = KCRT(d\pi/dC)^{-1}S(q) \quad (1)$$

where R is the gas constant and T the absolute temperature.

$$K = \frac{4\pi^2 n^2}{\lambda^4 N_a} \left(\frac{dn}{dC} \right)^2 \left(\frac{n_s}{n} \right)^2 \frac{1}{R_s} \quad (2)$$

where N_a is Avogadro's number, dn/dC is the refractive index increment, and R_s is the Rayleigh ratio of toluene. $(n_s/n)^2$ corrects for the difference in scattering volume of the solution with refractive index n and toluene with refractive index n_s , $R_s = 2.79 \times 10^{-5} \text{ cm}^{-1}$ at $\lambda = 532$ nm and 20 °C. The refractive index increment of PEO in water is $0.135 \text{ cm}^3/\text{g}$,^{24,25} and we assumed that the value for functionalized PEO is the same since the functional group is small. $S(q)$ describes the dependence of I_r on the scattering wave vector: $q = (4\pi/\lambda) \sin(\theta/2)$, with θ being the angle of observation. For the systems studied here $S(q)$ was unity in the q range covered by light scattering.

The normalized electric field autocorrelation function, $g_1(t)$, was calculated from the measured intensity correlation function using the so-called Siegert relation.²⁶ $g_1(t)$ was analyzed in terms of a relaxation time (τ) distribution using the REPES routine²⁷

$$g_1(t) = \int A(\tau) \exp(-t/\tau) d\tau \quad (3)$$

For all systems a fast q^2 -dependent relaxation mode was observed caused by relaxation of the concentration fluctuations of the micelles. The cooperative diffusion coefficient was calculated from the average relaxation rate as $D_c = \langle \tau^{-1} \rangle / q^2$. In addition, a slow diffusional mode was observed at higher PEO concentrations. Slow modes are expected for semidilute solutions of star polymers,²⁸ but in the present case they are mainly caused by a very small weight fraction of large spurious scatterers, probably PEO aggregates.^{29–31} The aggregates cannot be removed completely from the viscous solutions at high concentrations. Here we discuss only the contribution of the fast mode. The light scattering intensity of the fast mode was obtained

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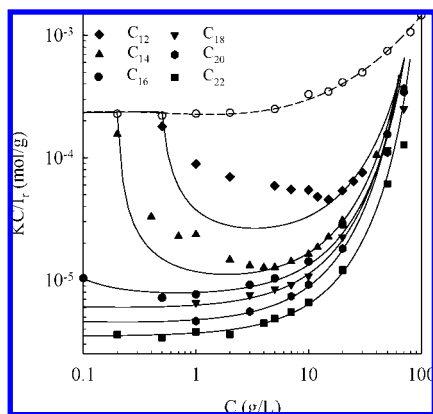


Figure 2. Concentration dependence of KC/I_r for PEO end capped with different alkyl end groups at 20 °C. Results obtained for nonfunctionalized PEO are shown as open symbols. The solid lines represent the model predictions, see text.

by multiplying the total intensity with the relative amplitude of the fast mode obtained from dynamic light scattering.

Fluorescence. Fluorescence measurements were done on solutions containing 2×10^{-7} M pyrene with a Horiba-Jobin (Yvon France) fluorescence spectrophotometer in the right-angle geometry. Excitation spectra were recorded corresponding to the emission wavelength at 371 nm. The widths of the slits were set at 2 nm. We determined the ratio of the amplitudes of pyrene excitation peaks situated at 337.5 and 333 nm ($I_{337.5}/I_{333}$).

Results and Discussion

Monodisperse Micelles. *Light Scattering.* Static and dynamic light scattering measurements were done at 20 °C on solutions of PEO end capped with an alkyl group over a range of concentrations. Figure 2 shows the concentration dependence of KC/I_r for PEO- C_n with n between 12 and 22. For comparison, results for nonfunctionalized precursor PEO were also plotted. For PEO- C_{12} and PEO- C_{14} , we observed at low concentrations a decrease of KC/I_r starting from the value of nonfunctionalized PEO caused by formation of micelles at the CAC. For larger alkyl end groups the CAC was smaller than the lowest concentration covered in the experiment. KC/I_r decreased with increasing alkyl length because the aggregation number of the micelles increased. At higher concentrations KC/I_r increased for all systems because repulsive excluded volume interaction between micelles became significant. At $C > 50$ g/L, the values of KC/I_r were comparable for all systems and approached that of nonfunctionalized PEO. The reason is that, at high concentration, the scattering is mainly due to the concentration fluctuations of PEO segments of strongly overlapping chains.³²

For monodisperse hard spheres, the osmotic compressibility can be described by the so-called Carnahan–Starling equation.³³ In the case of soft micelles we can use the same equation using an effective volume fraction (ϕ_e)

$$\frac{KC}{I_r} = \frac{1}{M_w} \left[\frac{1 + 4\phi_e + 4\phi_e^2 - 4\phi_e^3 + \phi_e^4}{(1 - \phi_e)^4} \right] \quad (4)$$

where M_w is the weight-average molar mass of the micelles. $\phi_e = C/C^*$, with C^* being the so-called overlap concentration, where $\phi_e = 1$. Of course, eq 4 can only be expected to describe the initial increase of the KC/I_r before interpenetration of the micelles

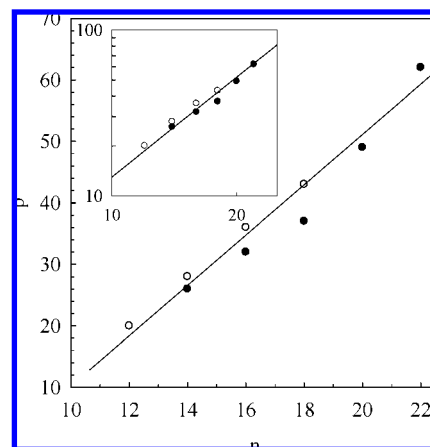


Figure 3. Aggregation number of PEO micelles as a function of the length of the alkyl end group (filled symbols). Open symbols represent data from Laffèche et al.³⁵ The insert shows the same data in a double-logarithmic representation. The solid line in the insert has slope = 2.

becomes significant. At higher concentrations a weaker increase is observed both for star polymers and polymeric micelles.^{32,34} Excluded volume interaction between PEO segments increases with decreasing temperature, which means that for a given concentration ϕ_e increases with decreasing temperature.³²

At low concentrations one has to consider the contribution of free chains. Laffèche et al.³⁵ showed that the polymers started to form micelles at a critical association concentration (CAC) that increased with decreasing alkyl length. If micelle formation is a fully cooperative process and only free chains with molar mass M_a or micelles with aggregation number p are formed, then M_w is given by

$$M_w = M_a \frac{CAC + p(C - CAC)}{C} \quad C > CAC \quad (5)$$

$$M_w = M_a \quad C < CAC$$

The solid lines in Figure 2 represent eq 4 using eq 5 for M_w . The overlap concentrations varied between 120 and 130 g/L without a significant dependence on the alkyl length. In the concentration range studied here the effect of residual free chains was significant only for PEO- C_{14} and PEO- C_{12} . For these systems KC/I_r started to decrease at a concentration close to the CAC determined with fluorescence, but the predicted decrease of KC/I_r was too abrupt, indicating that micellization was not strictly cooperative. In addition, for these systems interaction between the polymers was not negligible at concentrations where the molar mass of the micelles became constant. This means that p could not be obtained accurately, especially for PEO- C_{12} . For PEO with the larger alkyl groups, eq 4 describes the data reasonably well in the concentration range covered here.

The dependence of p on the number of carbon atoms in the alkyl end group (n) is represented in Figure 3 and shows that p increased approximately linearly with n . Extrapolation gives $p = 0$ for $n \approx 7$. For comparison, data from Laffèche et al.³⁵ for similar systems are also shown. The present results for p were systematically somewhat lower, which is perhaps caused by the

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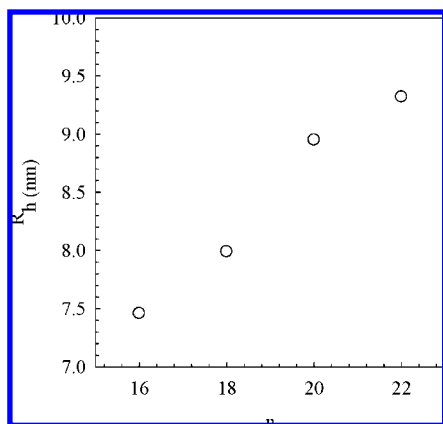


Figure 4. Hydrodynamic radius of PEO micelles as a function of the length of the alkyl end group.

fact that the alkyl group was connected to the PEO chain via an ester in ref 35 while here we used an ether group. The increase of p with increasing length of the hydrophobic group has been observed before.^{36,37} Pham et al.³⁷ reported $p = 66$ for PEO with $M_w = 35$ kg/mol end capped on both ends with C_{18} via a urethane link and $p = 40$ when end capped with C_{16} . For very asymmetric diblock copolymers, p is predicted to increase almost linearly with the length of the hydrophobic block.¹ Recently, Meng et al.³⁸ calculated quantitatively the association number for PEO end capped with alkyl groups, i.e., the system studied here. They predicted for the system studied here (about 100 EO segments) $p = 24$ for C_{16} and $p = 26$ for C_{18} , i.e., somewhat smaller than the experimental values.

Ameri et al.¹⁰ studied the effect of the alkyl chain length end capped on PEO chains with about one-half the molar mass as those studied here. They reported a linear increase of p with about the same absolute values at 20 °C and $p = 0$ for $n = 7$. However, they observed a significant increase of p with increasing temperature, whereas we found no significant temperature dependence. Booth et al.³⁹ plotted the same data in a double-logarithmic representation and found a power law dependence with an exponent close to 2 which was predicted for block copolymers in the so-called super segregation limit.⁴⁰ The insert of Figure 3 shows that the present results can also be interpreted as power law dependence on C with exponent 2. Clearly the range of n is too limited for an unambiguous interpretation.

Dynamic light scattering was used to determine the cooperative diffusion coefficient of these systems as described in the Materials and Methods section. The values at low concentrations tend to the self-diffusion coefficient (D_0) that is related to the z -averaged hydrodynamic radius (R_h) through the so-called Stokes–Einstein equation⁴¹

$$D_0 = \frac{kT}{6\pi\eta R_h} \quad (6)$$

In Figure 4 hydrodynamic radii are plotted as a function of the length of the alkyl end group. Unfortunately, the combined effect of high CAC and interaction renders determination of R_h for PEO- C_{12} and PEO- C_{14} uncertain. For PEO- C_{16} to PEO- C_{22} the increase of R_h was close to the increase predicted by the model

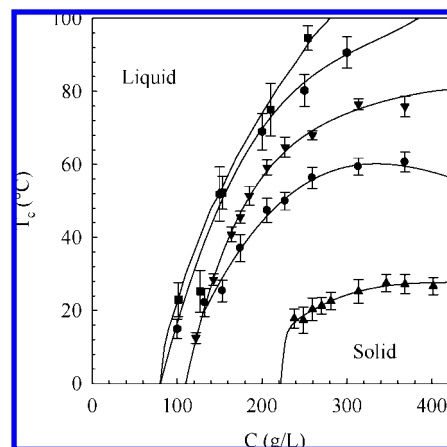


Figure 5. Concentration dependence of T_c for solutions of PEO- C_n with different n . The symbols are the same as in Figure 2. Error bars indicate the difference between the temperature where G' of the solid starts to decrease and where the viscosity becomes equal to that of the liquid during heating at a rate of 5 °C/min. Solid lines are guides to the eye.

of Daoud and Cotton for star polymers without swelling:⁴² $R_h \propto p^{0.25}$. The overlap concentration of the micelles can be estimated as $C^* = 3M_w/(4\pi R_h^3 N_a)$. Using the values of M_w obtained from static light scattering and R_h from dynamic light scattering we find that C^* is close to the values deduced from the concentration dependence of KC/I_r . Ameri et al.¹⁰ observed an approximately linear increase of the hydrodynamic volume with p , implying $R_h \propto p^{1/3}$, but neither their data nor the present data are sufficiently precise to judge whether the different scaling is significant. In order to properly test scaling laws a much broader range of n is needed.

Rheology. As mentioned above, at high concentrations the micelles jammed below a critical temperature where a discontinuous liquid–solid transition occurred. This transition was determined by measuring the shear modulus during heating with a rate of 5 °C/min from 5 to 95 °C with an imposed stress of 10 Pa. The transition was easily observed by the strong decrease of G' and G'' at T_c .³²

The liquid–solid state diagram as a function of concentration and temperature was determined for PEO- C_n with different n , Figure 5. T_c increased with increasing concentration up to 300 g/L and for a fixed concentration with increasing length of the alkyl end group. T_c was relatively independent of the concentration between 300 and 400 g/L and decreased at higher concentrations (not shown). This decrease occurred at about the same concentration for all systems studied here and is tentatively attributed to incomplete hydration of the PEO chains.⁴³ For PEO- C_{12} , no liquid–solid transition was observed for C up to 500 g/L and T down to 5 °C, perhaps because the aggregation number was too low. It has been predicted⁴⁴ that star polymers do not jam below a critical number of arms of 34. The observation that PEO- C_{14} jammed even if the aggregation number at low concentrations was less than this value could be due to the fact that p increased with increasing concentration when the micelles started to overlap.⁴⁵

Ameri et al.¹⁰ also found that the liquid–solid transition, measured by tube inversion, shifted to higher temperatures and lower concentrations when the alkyl group was longer. A similar

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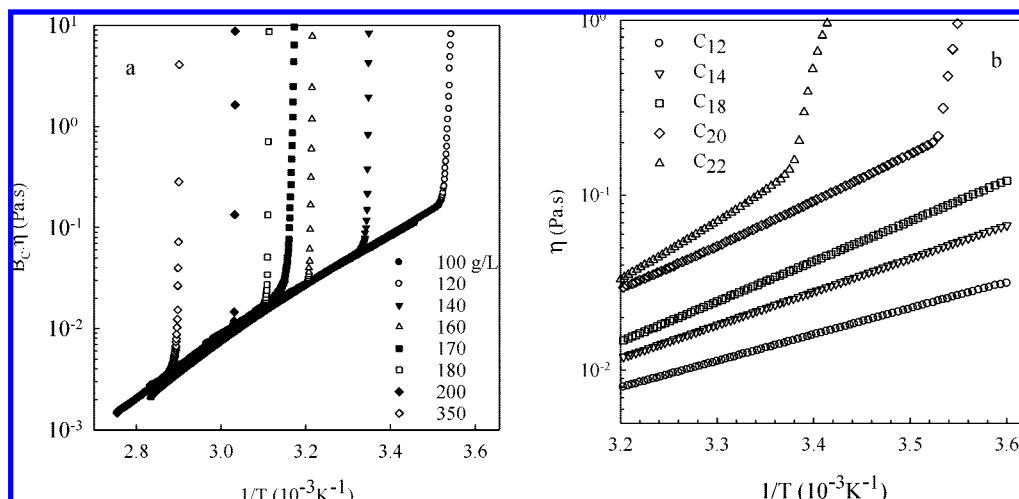


Figure 6. (a) Master curve of the relative viscosity as a function of the inverse of the absolute temperature for PEO- C_{18} at different concentrations with $C_{\text{ref}} = 120$ g/L. (b) Viscosity as a function of T^{-1} for PEO- C_n with different n at $C = 100$ g/L.

state diagram was observed with a sharp increase of T_c at low concentrations followed by a flattening off at higher concentrations. The increase occurred at higher concentrations because smaller PEO chains were used in that study. For the smaller PEO chains they found that a solid was formed even for C_{11} , whereas for the larger PEO studied here no solid was observed for C_{12} .

A temperature-induced reversible liquid–solid transition was also observed for polybutadiene star polymers in a marginal solvent.⁶ By suitable mapping unto the equivalent hard-sphere system it could be shown that the liquid–solid transition can be understood as a glass transition of effective hard-sphere particles.⁴⁶ The softness of micelles increases with decreasing aggregation number. This explains why the liquid–solid transition occurs at lower temperatures when p is decreased, because the increased softness after decreasing p needs to be compensated by increased excluded volume interactions between the PEO segments.

The viscosity of solutions of PEO- C_n with varying n was studied over a wide range of concentrations and temperatures. The solutions were presheared at 90 °C (5 min at 300 s^{-1}) in order to fully homogenize the systems. Subsequently, the temperature was reduced at a rate of 5 °C/min down to 5 °C, during which the viscosity was measured using continuous shear with an imposed stress of 10 Pa. The results were almost the same if a slower rate or lower stress was used.

Figure 6a shows the relative viscosity (η_r) as a function of the inverse absolute temperature for PEO- C_{18} at different concentrations. η_r increased exponentially with T^{-1} until at T_c it diverged abruptly. We stress that the measured viscosity below T_c was not stable and that the data in the sharp upturn represent only transient values while the system is solidifying. At a given temperature above T_c η_r increased strongly with increasing concentration, see Figure 7, and we used vertical shift factors B_c to superimpose the data.

Figure 6b shows the effect of varying n on the temperature dependence of the viscosity at a given PEO concentration ($C = 100$ g/L). For each value of n the temperature dependence of η_r for $T > T_c$ can be written as $\eta_r \propto \exp(E_a/RT)$, where E_a is the activation energy. E_a increased approximately linearly with increasing n from 28 kJ/mol for PEO- C_{12} to 60 kJ/mol for PEO- C_{22} . PEO- C_{16} was an exception to this behavior and showed an activation energy that was even slightly larger than for PEO- C_{22} (not shown). The

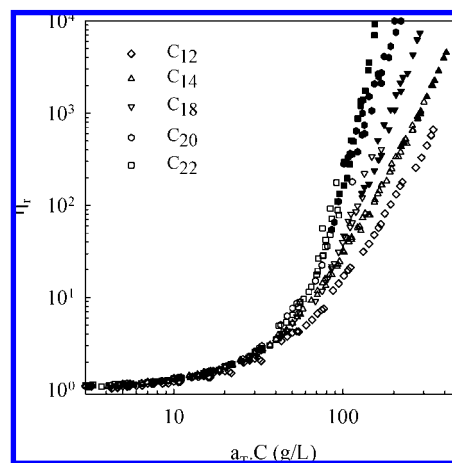


Figure 7. Master curves of the concentration dependence of the relative viscosity for PEO- C_n with different n with $T_{\text{ref}} = 20$ °C. The filled symbols represent values obtained by extrapolation from higher temperatures.

deviant behavior of PEO- C_{16} was observed for two separately synthesized samples. We believe that it was caused by an unknown pollution of the hexadecyl bromide used in this study.

Master curves of the concentration dependence of η_r obtained at different temperatures could be obtained using horizontal shift factors (a_T). The temperature dependence of the shift factors was consistent with the activation energies obtained for the different alkyl end groups. At conditions where the systems were solid ($T < T_c$), η_r was obtained by extrapolation from the values at higher temperatures. The master curves are plotted in Figure 7, showing that the concentration dependence of the viscosity is stronger if PEO is functionalized with larger alkyl groups. The results for PEO- C_{16} were very close to that of PEO- C_{18} and are not shown for clarity.

Roovers et al.³⁴ reported viscosity results for solutions of polybutadiene star polymers with three different aggregation numbers ($p = 32, 64$, and 128). The authors showed that the increase of the viscosity became stronger with increasing p in agreement with the present results on polymeric micelles.

Mixed Micelles. We mixed PEO- C_{12} and PEO- C_{22} in different ratios, yielding a range of average functionalities (PEO- $C_{(\bar{n})}$). For example PEO- C_{16} was obtained by mixing 60% PEO- C_{12} and 40% PEO- C_{22} . The effect of mixing on the CAC was

(46) Foffi, G.; Sciortino, F.; Tartaglia, P.; Zaccarelli, E.; Verso, F. L.; Reatto, L.; Dawson, K. A.; Likos, C. N. *Phys. Rev. Lett.* **2003**, *90*, 238301.

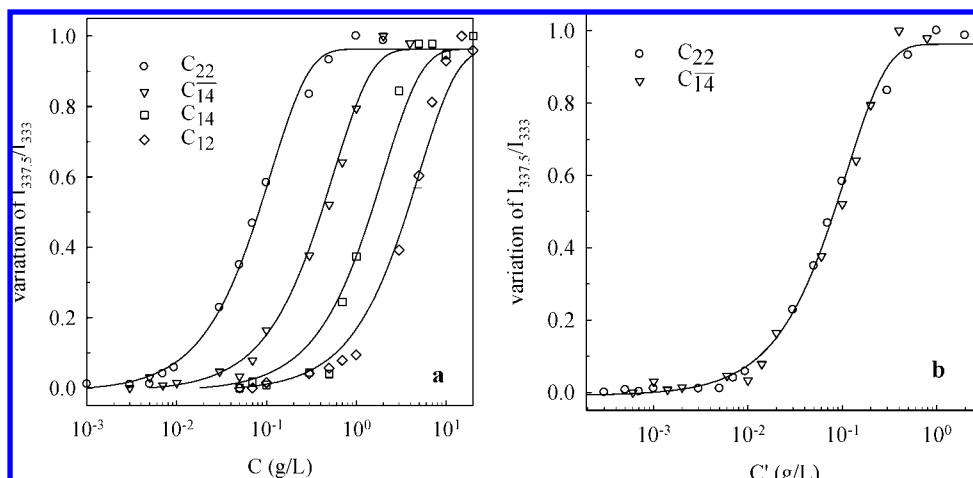


Figure 8. Variation of $I_{337.5}/I_{333}$ as a function of the total PEO concentration (C) (a) or the PEO- C_{22} concentration (C') (b) for PEO micelles with different alkyl lengths indicated in the figures. The lines are guides to the eye.

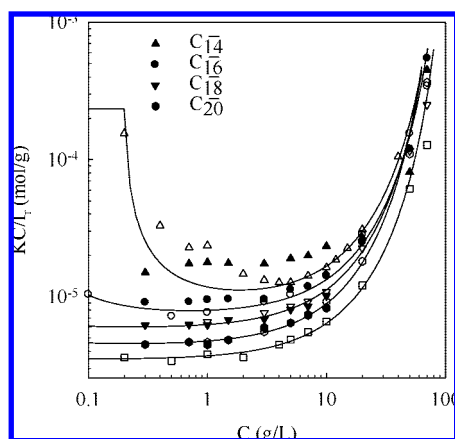


Figure 9. Concentration dependence of KC/I_r for mixtures of PEO- C_{12} and PEO- C_{22} with different ratios at 20 °C (closed symbols). The open symbols and lines represent data and fits to eq 4 for monodisperse systems as in Figure 2.

investigated using fluorescence spectroscopy. Figure 8a compares the relative variation of $I_{337.5}/I_{333}$ as a function of the PEO concentration for pure PEO- C_{12} , PEO- C_{14} , and PEO- C_{22} with that of the mixture PEO- C_{14} . The increase of $I_{337.5}/I_{333}$ is caused by a change in the environment of the pyrene probe and indicates micelle formation. The pure systems show the expected decrease of the CAC with increasing alkyl length, but the concentration dependence for PEO- C_{14} is different from that of PEO- C_{14} . In Figure 8b the data for PEO- C_{22} and PEO- C_{14} are plotted as a function of the PEO- C_{22} concentration (C'). In this representation the data superimpose, which demonstrates that in the mixture the initial micelle formation is the same as for pure PEO- C_{22} .

Light Scattering. Static and dynamic light scattering measurements were done for a range of concentrations at 20 °C, and in Figure 9 the results are compared with those obtained for monodisperse systems. For $\bar{n} > 16$ the results obtained for mixtures were very close to that of the equivalent monodisperse systems. However, the results for PEO- C_{14} and PEO- C_{16} were significantly different, especially for PEO- C_{14} . The latter showed no signs of a CAC at low concentrations, contrary to pure PEO- C_{14} . This is consistent with the observation that the PEO- C_{22} that is present in the mixtures forms micelles at very low concentrations.

The contribution of free PEO- C_{12} to I_r is negligible compared to that of PEO- C_{22} micelles, so that I_r represents the scattering

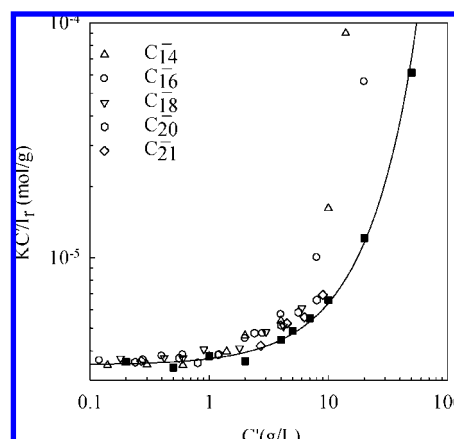


Figure 10. KC'/I_r of PEO- C_{22} as a function of the concentration of PEO- C_{22} for mixtures of PEO- C_{12} and PEO- C_{22} with different ratios. The filled symbols and line represent data and the fit to eq 4, respectively, for pure PEO- C_{22} .

from the latter at low concentrations when all PEO- C_{12} is present as free polymers. We verified that this is indeed the case by plotting KC'/I_r as a function of the concentration of

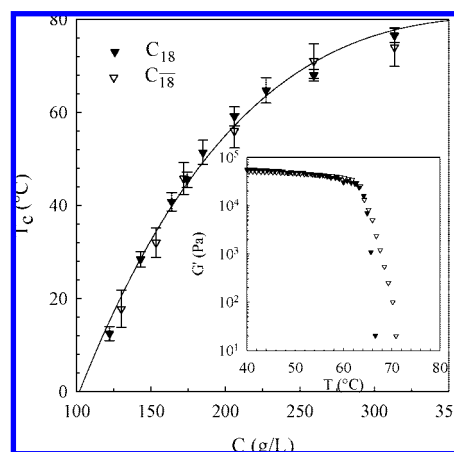


Figure 11. Comparison of the concentration dependence of T_c for mixed micelles formed by 40% PEO- C_{12} and 60% PEO- C_{22} yielding PEO- C_{18} and monodisperse micelles formed by PEO- C_{18} . The line is a guide to the eye. The inset shows the temperature dependence of G' as a function of temperature during heating for PEO- C_{18} and PEO- C_{18} at 250 g/L.

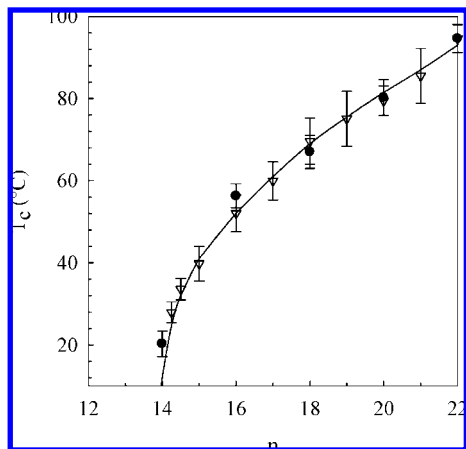


Figure 12. Comparison of the dependence of T_c on the average length of the alkyl end groups for mixtures of PEO- C_{12} and PEO- C_{22} (open symbols) and monodisperse systems (filled symbols) at $C = 250$ g/L. The solid line is a guide to the eye.

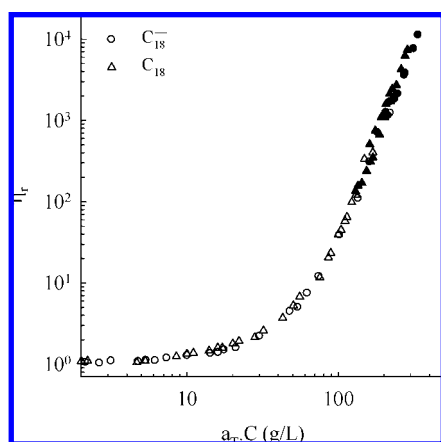


Figure 13. Master curves of the concentration dependence of the relative viscosity at $T_{ref} = 20$ °C for pure PEO- C_{18} and for mixtures of 40% PEO- C_{12} and 60% PEO- C_{22} (PEO- C_{18}). The filled symbols represent values obtained by extrapolation from higher temperatures.

PEO- C_{22} , Figure 10. At low concentrations the results are the same for the different mixtures within experimental error, which demonstrates that KC'/η_r represents the contribution of just the PEO- C_{22} micelles. At higher concentrations the contribution of PEO- C_{12} leads to stronger interactions and thus a stronger increase of KC'/η_r compared to pure PEO- C_{22} . These results show that only PEO- C_{22} micelles are formed at low concentrations and that PEO- C_{12} is incorporated at higher concentrations. In addition, dynamic light scattering measurements showed that the hydrodynamic radii of mixtures measured at low concentrations were close to that obtained for pure PEO- C_{22} . Relaxation due to diffusion of free PEO- C_{12} chains could not be seen in the relaxation time distribution because the relative amplitude of the scattered light intensity was too small.

Rheology. The liquid–solid state diagram was obtained for mixtures of 40% PEO- C_{12} and 60% PEO- C_{22} yielding PEO- C_{18} , using the same procedure as described above for monodisperse micelles. The results were the same as that of pure PEO- C_{18} within the experimental error, Figure 11. The inset of Figure 11 shows an example of the temperature dependence of G' as a function of the temperature during cooling for PEO- C_{18} and PEO- C_{18} at the same concentration.

The liquid–solid transition was also studied at a fixed polymer concentration ($C = 250$ g/L) for different ratios of PEO- C_{12} and

PEO- C_{22} yielding varying \bar{n} . The dependence of T_c on \bar{n} is compared with the dependence of T_c on n for pure systems in Figure 12. Within the experimental error, the value of T_c for the mixtures was the same as that of the monodisperse systems with the same average length of the alkyl end group. The sharp decrease of T_c at $\bar{n} = 14$ is consistent with the observation that PEO- C_{12} did not jam at least down to 5 °C. It appears that dense suspensions of mixed systems are equivalent to monodisperse systems with the same average length of hydrophobic group, which is a strong indication that mixed micelles are formed at higher concentrations.

The viscosity of the mixed micelles PEO- C_{18} was studied over a wide range of concentrations and temperatures. A master curve of the concentration dependence of η_r was obtained using the same shift factors as for the equivalent monodisperse system (PEO- C_{18}). Figure 13 shows that the concentration dependence of PEO- C_{18} and PEO- C_{18} is the same, confirming that mixtures behave as monodisperse systems with the same average length of the hydrophobic group.

The most likely interpretation of the rheology results is that at high concentrations monodisperse mixed micelles are formed with the same aggregation number as pure micelles with the same average length of the alkyl groups. On the other hand, light scattering and fluorescence measurements showed that with increasing concentration, first, micelles of the most hydrophobic polymer formed at its CAC and that the less hydrophobic polymer was progressively incorporated into these micelles. As mentioned in the Introduction, the latter feature was also found for mixtures of other block copolymers. The observed behavior agrees with the theoretical model of Brovinskii et al.,¹⁷ while Sens et al.¹⁸ predicted that each copolymer formed separate pure micelles if the hydrophilic block was the same and the hydrophobic block was different. However, these theoretical models assume very large hydrophobic and hydrophilic blocks, which is not the case for the systems studied here.

Conclusion

The aggregation number of spherical micelles formed by hydrophobically end-capped PEO increases approximately linearly with the length of the hydrophobic block. When the alkyl end group was C_{14} or larger a discontinuous liquid–solid transition occurred at a critical temperature. For a given polymer concentration, T_c increased with increasing length of the alkyl end group.

In binary mixtures of functionalized PEO with the same chain length and different alkyl groups first the polymers with the lowest CAC, i.e., with the longest alkyl group, associate to form micelles. The other polymers are incorporated into the micelles at higher concentrations. The rheology of dense suspensions of mixed micelles is the same as that of pure systems with the same average alkyl length. This means that a continuous range of intermediate functionalities can be obtained by mixing two polymers with extreme functionalities at different ratios.

The effect on the rheology is different for mixtures of PEO with the same chain length end capped with different alkyl groups and mixtures of PEO with different chain lengths and end capped with the same alkyl group. In both cases mixed micelles are formed. However, in the former case the mixture gives an average rheological response, while in the latter case both the viscosity and T_c are reduced compared to the pure systems.¹⁹ The interaction between micelles with polydisperse coronas and monodisperse cores is weaker than between micelles with monodisperse coronas and polydisperse cores.