Effects of PEO−PPO Diblock Impurities on the Cubic Structure of Aqueous PEO−PPO−PEO Pluronics Micelles: fcc and bcc Ordered Structures in F127

Kell Mortensen,*,† Walther Batsberg,‡ and Søren Hvidt§

Department of Natural Sciences, University of Copenhagen, DK-1871 Frederiksberg, Denmark; Risø National Laboratory, Danish Technical University, DK-4000 Roskilde, Denmark; and Department of Chemistry-NSM, Roskilde University, DK-4000 Roskilde, Denmark

Received October 11, 2007; Revised Manuscript Received January 2, 2008

ABSTRACT: We report on structural properties of PEO−PPO−PEO type of triblock block copolymers (Pluronics F127) with special emphasis on the effect of diblock PEO−PPO impurities on the ordered gel phase. Commercial F127 polymers contain as received roughly 20% PEO−PPO diblock and 80% PEO−PPO−PEO triblock copolymers. Aqueous solutions of F127 copolymers used as received form fcc ordered micellar structure. Copolymers depleted with respect to the diblock impurity, resulting in a pure PEO−PPO−PEO triblock copolymer system, form bcc ordered micelles within the major parts of the gel phase. However, close to the disorder-to-order transition, the purified F127 copolymer system also forms fcc structure, thus giving rise to a novel sequence of micellar phases: disorder−fcc−bcc. This is the phase sequence predicted theoretically for pure block copolymer melts.

I. Introduction

A large variety of di- and triblock copolymer systems form cubic ordered systems of micelles when mixed in solvents that selectively dissolve one of the blocks. While the disorder−order transition and the given ordered structure dependence of polymer architecture have been the subject for a large number of experimental and theoretical studies, the effect of detailed molecular compositions and the influence of impurities in the polymer have only been addressed in a few studies.

Several investigations have concerned the physical origin of stabilizing a specific cubic ordered structure like body-centered cubic (bcc), face-centered cubic (fcc), or hexagonal close packed (hcp). In soft matter systems the energy difference between fcc and hcp is normally relatively small, and one may expect close-packed systems (cps) of mixed fcc and hcp type of structures, i.e., mixed ABC and ABAB type of layering, rather than pure phases.

The stability of bcc and fcc (or hcp) and the transition between these phases have been studied in both atomic systems, in colloids and in block copolymer micelles.[1−8] A number of theoretical papers have treated the bcc−fcc transition relevant for polymeric systems.[9−11]

Both bcc and fcc phases have been observed in block copolymer micellar systems, as based on diblock as well as triblock copolymers. Examples are solutions of polystyrene−polyisoprene (PS−PI) diblock copolymers which, for example, in decane form spherical micelles. McConnell and Gast showed experimentally that bcc and fcc/hcp structures were formed below the order−disorder transition depending on the micellar corona thickness.[7] It was argued that a thick corona leads to soft interaction potential and thereby bcc ordering, whereas thinner coronas cause greater short-range intermicellar repulsions favoring the fcc structure.

A large variety of amphiphilic block copolymers based on the hydrophilic poly(ethylene oxide), PEO, covalently bound to for example hydrophobic poly(propylene oxide), PPO, or poly(butylene oxide), PBO, self-assemble in aqueous solutions into spherical micelles that order in cubic structures at concentrations typically above roughly 20 wt % polymers. Also in these systems, both bcc and fcc types of structures are documented. The thermal changes in degree of hydrophilicity of both PEO and PPO and PBO lead in these systems to temperature-induced order−order transition, reflecting changes in micellar aggregation number and/or in the swelling of the PEO−corona. Hamley et al. used SAXS to identify the regions of ordered phases.[1] They reported a low-temperature bcc phase for concentrations greater than 30 wt % copolymer, while elsewhere in the diagram the fcc structure seemed favored. The observation of a bcc phase at high copolymer concentrations was ascribed to increasing softness of the interactions between spheres as the copolymer content increases. It may seem surprising that a bcc structure is favored at higher concentrations given the fact that the volume fraction for a bcc phase, $\phi_{\mathrm{bcc}} = 0.68$, is lower than for a fcc structure, $\phi_{\mathrm{fcc}} = 0.74$. The authors noted, however, that in the limit of a pure diblock copolymer melts only the bcc structure has been observed experimentally.

In the literature there are, however, disagreements as to the reported ordered phase for such PEO−copolymer systems. This is in particular the case for the commercially available PEO−PPO−PEO triblock copolymers (trade name Pluronics from BASF). We have recently shown that Pluronics typically contain between 10 and 25 wt % lower size contaminants.[12,13] With this rather large dispersity in molecular characteristics, one may speculate whether the different assignments of the ordered phases may reflect different degrees of impurities and/or molar size distribution in the specific samples studied. We have therefore made extended studies of the properties of one of the most studied Pluronics triblock copolymer systems, F127, with nominal molecular characteristics $EO_{99}PO_{69}EO_{99}$, using interaction chromatography for purification.

---

* Corresponding author. E-mail: kell@life.ku.dk.
† University of Copenhagen.
‡ Danish Technical University.
§ Roskilde University.

10.1021/ma702269c CCC: $40.75

Different cubic structures have been assigned to the F127 micellar systems. On the basis of the two-dimensional neutron scattering pattern of a shear-aligned sample of cubic ordered F127 micelles, we reported bcc-ordered micellar phase in 20 wt % F127 solution.[14] The argument for bcc order was based on an identical scattering pattern to that observed in the related P85 and F88 copolymer micelles where the bcc structures were proven from more extended crystallographic studies.[15] Further one- and two-dimensional SANS studies by Prud'homme et al.[16] were in agreement with the bcc assignment, but Prud'homme also discussed the possibility of ordering in a simple cubic lattice (sc). The fcc structure was clearly excluded. Wu et al.,[17] on the other hand, reported X-ray scattering data that were interpreted according to formation of a fcc lattice. According to the results given below, these published discrepancies may very well all be true identifications resulting from samples of different degrees of purity.

In this paper we show that the given crystalline structure actually depends critically on the purity of the triblock copolymer. Commercial block copolymers of PEO−PPO−PEO typically include a relatively large amount of diblock copolymers PPO−PEO with one full PEO block length, but rather small PPO segments.[12] This is the case also for F127, where about 20% of the materials as received is such diblock copolymers. In aqueous solutions of F127-polymers used as received, i.e., with the 20% diblocks, we find a dominating fcc-ordered structure within the gel phase. In F127 samples purified for the diblock content the bcc phase dominates the gel phase, and only in the near vicinity of the ordering temperature is fcc order observed. The role of the diblock is, however, rather complex, as seen in the systematic temperature variation studies where we compare samples of either similar total copolymer concentration (20 wt % F127 as received relative to 20 wt % F127 purified) or with similar concentrations of the pure triblocks (25 wt % F127 as received relative to 20 wt % F127 purified). Here, we also report rheological data of the as-received sample when dissolved in either H_2O or D_2O, in order to investigate differences in characteristic temperatures in the two solvents. We will report on the detailed unimer-to-micelle transition regime of samples fractionated into relatively narrow molecular characteristics in a forthcoming paper.[18]

II. Experimental Section

A. Sample Preparation. The F127 Pluronics polymers were obtained from BASF (Parsippany, NJ) as a gift. Interaction chromatography (IC) was used for preparative fractionation of F127, where the fractionation was performed according to PPO block lengths. Details are given below.

Aqueous solutions of either F127 as received or purified F127 were prepared for neutron scattering experiments. Deuterated water, D_2O, was used as solvent in the attempt to obtain good scattering contrast and low background in the small-angle neutron scattering experiments. The concentrations are all given in terms of weight concentration. Samples of given concentrations were for the SANS studies mixed into 2 mm thick quartz cuvettes (QZ-type from Helma). The F127 solutions were cycled between 4 and 80 °C a few times and finally stored at 4 °C for about 24 h to ensure that the polymers were fully dissolved. All samples appeared after this preparation procedure liquid-like and transparent at 4 °C.

Three samples were made for these studies, as given in Table 1. To distinguish between purified F127 and polymers as received, we abbreviate the purified system F127main, while the as received material is abbreviated F127AR. In the purified 20 wt % F127main sample and in the 20 wt % F127AR the total polymer concentrations are the same, while in the 20 wt % purified F127main and in the 25 wt % F127AR sample there are the same concentrations of triblock copolymers.

Table 1. Sample Characteristics

F127 in D_2O sample abbreviation	total polymer concn (wt %)	triblock copolymer concn (wt %)
20 wt % F127main	20.0	20.0
20 wt % F127AR	19.7	15.8
25 wt % F127AR	25.7	20.5

For comparative analysis, we also prepared 20 and 25 wt % F127AR samples for rheology studies. Here we used both normal water, H_2O, and deuterated water, D_2O, as solvent, in order to determine changes in characteristic temperatures between the two aqueous solvents. A Bohlin VOR rheometer with a C14 Couette geometry was used for oscillatory measurements of the temperature-dependent mechanical properties at 1 rad/s, as described elsewhere.[19]

B. Liquid Chromatography. A Shimadzu high-performance liquid chromatography (HPLC) system consisting of a LC-10AD pump, a SPD-M10A photodiode-array detector, and a RID 10A differential refractive index (RI) detector was used for interaction chromatography. The RI signal is proportional to the weight concentration of polymer, since PEO and PPO have very similar differential refractive index increments. In interaction chromatography enthalpic interactions with the column packing material are used to separate a mixture of polymers. The column for the present characterization was a Nucleosil CN 120 Å from Macherey-Nagel. The eluent was a 55 wt % methanol in water mixture, and 100 μL of a 10 mg/mL F127AR solution was injected. The chromatograms were obtained with a temperature gradient from 30 to 60 °C and a flow rate of 0.5 mL/min. Under these chromatographic conditions, separation occurs according to PPO block length.

Eluent gel permeation chromatography (EGPC) was performed using a Superose 6HR column with an eluent containing 2 mg/mL F127AR, as described in ref 13.

F127main and F127front were obtained after semipreparative fractionation of F127AR using a Nucleosil 120 Å CN column.

C. Scanning Calorimetry. Differential scanning calorimetry was performed using a Nanocal scanning calorimeter from CSC (Calorimetry Science Corp., Provo, UT) with a cell volume of 0.322 mL. Scans were performed with a scan rate of 20 °C/h. The thermal lag was negligible at this and lower scan rates.

D. Scattering Experiments. The structural investigations were done using small-angle neutron scattering (SANS) with temperature-controlled environment in the 5−80 °C temperature range. D_2O was used for the aqueous media to enhance contrast between polymers and water and ensure the lowest level of incoherent background. The neutron scattering experiments were performed using the SANS-2 instrument at the Paul Scherrer Institute in Switzerland,[20] using standard data treatment. The spectra were

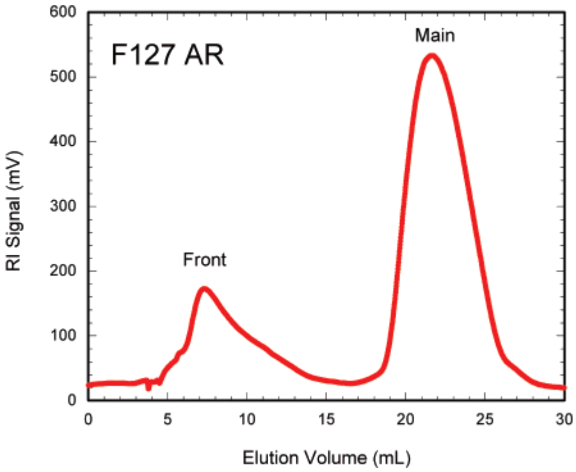

Figure 1. Interaction chromatography on a CN column in 55 wt % methanol−water mixture with a temperature gradient from 30 to 60 °C. The relative areas of the peaks marked Front and Main are 23 and 77%, respectively.

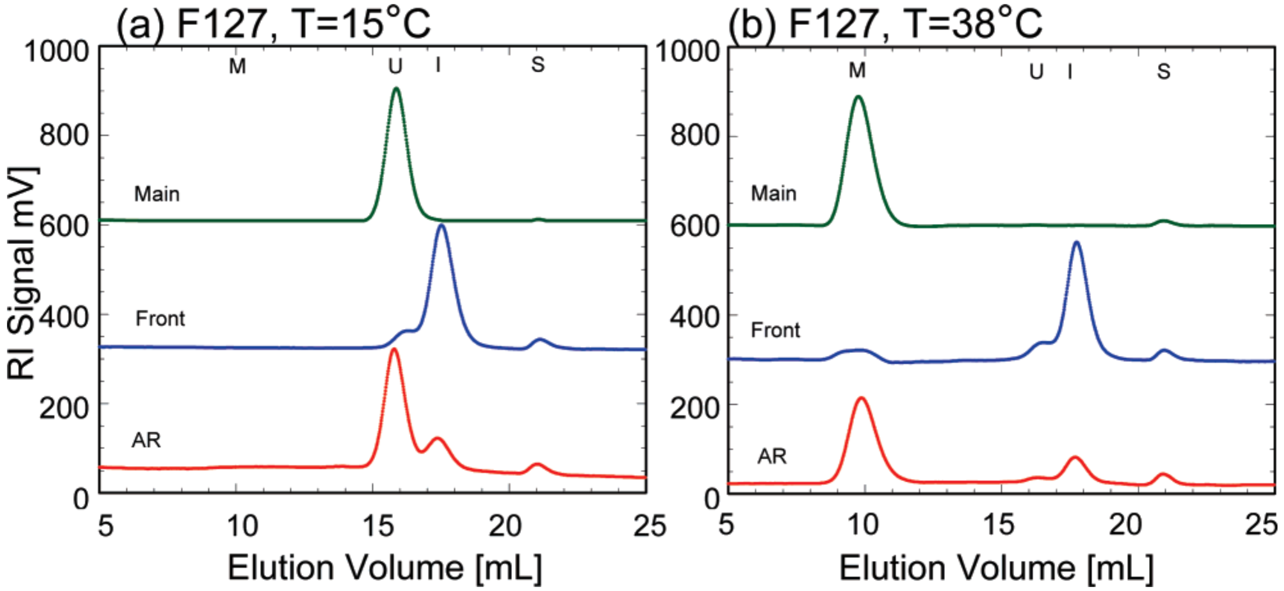

Figure 2. Eluent gel permeation chromatography (EGPC) of F127 measured as received and fractionated. The measurements we done at 15 °C (a) and 38 °C (b), respectively. Eluting peaks are marked M, U, and I for micelles, unimers, and impurities, respectively. All injected samples contained sucrose as internal standard, giving rise to the peak marked S on chromatograms.

normalized to absolute intensity using the incoherent scattering of pure water H_2O.

We did not find significant texture in the samples at any temperatures measured. The azimuthally isotropic scattering pattern were averaged to form the $I(q)$ scattering function which only depends on the numerical value of the scattering momentum

$$q = \frac{4\pi}{\lambda}\sin\theta$$

where 2θ is the scattering angle and λ is the nominal neutron wavelength. The data reported below were all made using 5.6 Å neutrons with 9% wavelength resolution. The collimation length and the sample-to-detector distances were both 3 m.

III. Results and Discussion

A. Chromatography. Figure 1 shows the interaction chromatography results of F127 polymers used as received. The chromatogram shows two distinct peaks, which has previously been characterized in detail for another Pluronics copolymer.[12] The *main peak* represent polydisperse PEO−PPO−PEO triblock copolymers while the *front peak* represents impurities dominated by PEO−PPO diblock copolymers with full block size of PEO, but only small sized PPO. The relative areas of the peaks marked Front and Main are 23 and 77 wt %, respectively.

Figure 2 shows eluent gel permeation chromatography (EGPC) results of F127AR and fractionated F127 (F127front and F127main according to Figure 1) using a Superose 6HR column with an eluent containing 2 mg/mL F127AR polymers. Eluting peaks marked as U, M, and I represent unimers, micelles, and impurities, respectively. The eluent peak marked S is an internal standard (sucrose) added to the solutions.

Parts a and b of Figure 2 show the chromatography obtained at 15 and 38 °C, respectively. It appears from the peak areas at $T = 15$ °C that the F127AR solutions consist of 22% PEO−PPO diblock impurities and 78% triblock PEO−PPO−PEO copolymer which are all dissolved as unimers. At $T = 38$ °C all triblock unimers have aggregated into micelles, while the diblock impurities remain unchanged as unimers. This is further supported by the EGPC data of the two fractions: F127main and F127front. The F127main fraction of triblock copolymers shows unimers equal to the F127AR at 15 °C and only micellar aggregates at 38 °C, both with characteristics similar to the unimers and the micelles of F127AR. The diblocks of the F127front, on the other hand, show basically no temperature dependence; i.e., these polymers do not form micelles on their own and do not contribute to the micellar aggregates of F127AR present in the eluent.

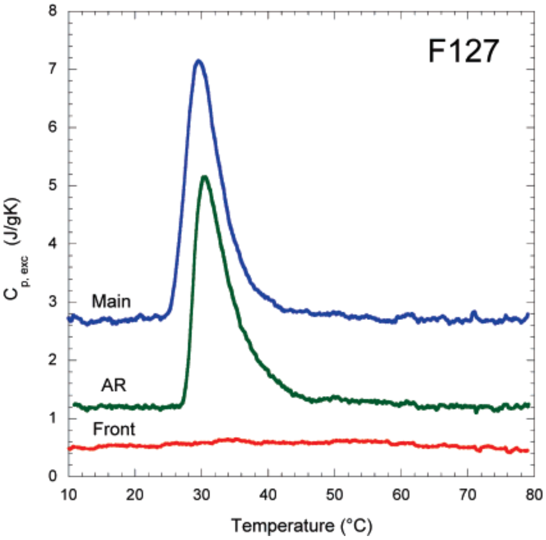

Figure 3. Differential scanning calorimetry thermograms of F127AR and fractions F127main and F127front. Concentrations are 2 mg/mL. The excess heat capacity per gram of polymer is shown.

These conclusions are further supported by the calorimetric measurements.

B. Calorimetry. Figure 3 shows differential scanning calorimetry (DSC) measurements of F127 as received (AR) as well as the main and front fractionated parts. Both the F127AR and the F127main fraction show the enthalpic peak characterizing the triblock copolymer micellization process. The impurities represented by the F127front fraction, on the other hand, show no corresponding DSC peak, in agreement with the previous conclusion from EGPC that there is no aggregation in this diblock copolymer system. The heat transfer of F127main exceeds that of F127AR per gram of polymers, and its transition

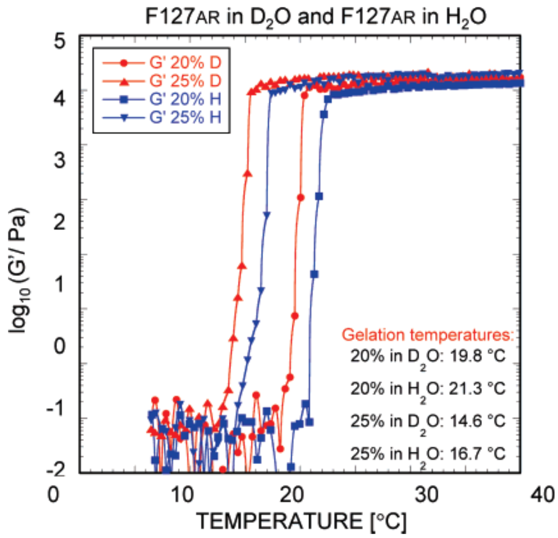

Figure 4. Oscillatory rheology measurements of F127/D_2O and F127/H_2O solutions, both with 20 and 25 wt % polymers used as received (F127AR), respectively.

temperature is slightly lower, both consistent with removal of impurities, which do not contribute to micellization.

C. Rheology. Rheological studies were made on the polymers as received in an attempt to document the disorder-to-order transition temperature independently and investigate the effect the substitution of H_2O with D_2O has on this value.

Figure 4 shows the elastic storage modulus of F127AR polymer solutions measured at 1 rad/s and dissolved in either D_2O or H_2O, both with concentrations of 20 and 25 wt %. The elastic data show in all four cases a roughly 6 order of magnitude change in modulus from the noise level, typical for the micellar ordering properties of Pluronics systems.[19,21] The temperature-induced disorder-to-order transition is according to these rheology data equal to 19.8 and 14.6 °C for 20 and 25 wt % D_2O solutions, respectively. The shift by substituting normal water with deuterated water is about −2 deg, which to some extent reflects the higher molar concentration in D_2O but which also may reflect differences in the dynamics of the water molecules association to the polymer backbone.

D. Structural Results. The scattering patterns are all dominated by a pronounced first-order correlation peak as has been documented previously for these block copolymers, revealing the correlations between spherical micellar aggregates (see for example ref 15). In the ordered domains, we observed further Bragg peaks giving details on the ordered lattice structure.

Figures 5 and 6 show examples of the scattering results. In Figure 5 we show corresponding $S(q)$ data for the 20 wt % F127main, 20 wt % F127AR, and 25 wt % F127AR samples, as obtained at different temperatures near the ordering temperature. Figure 6 shows the temperature-dependent evolution of the scattering functions, clearly showing the abrupt changes reflecting the two types of phase transitions: disorder-to-fcc and fcc-to-bcc.

A large number of scattering experiments have been made on Pluronics type of block copolymers. The typical result is a solution of independent unimers at low temperature and low concentration and a wide temperature/concentration range where micelles are formed and are in equilibrium with the unimer phase. For polymer concentrations typically above ∼20 wt %, the micelles form cubic ordered structures at a given temperature where the micelle concentration has reached a critical value.

The scattering patterns shown in Figure 5 are in agreement with such reported results. At 9 °C the scattering patterns of 20 wt % F127main and 20 wt % F127AR reveal both solutions dominated by liquid systems of spherical micelles, while the 25 wt % F127AR data are clearly different, indicating that this system is close to the transition temperature to a high-temperature ordered state.

The rather broad temperature range of micellization observed in these and other Pluronics is a result of relative large dispersity in molecular parameters; when commercial PEO−PPO−PEO block copolymers are fractionated into narrow molar size

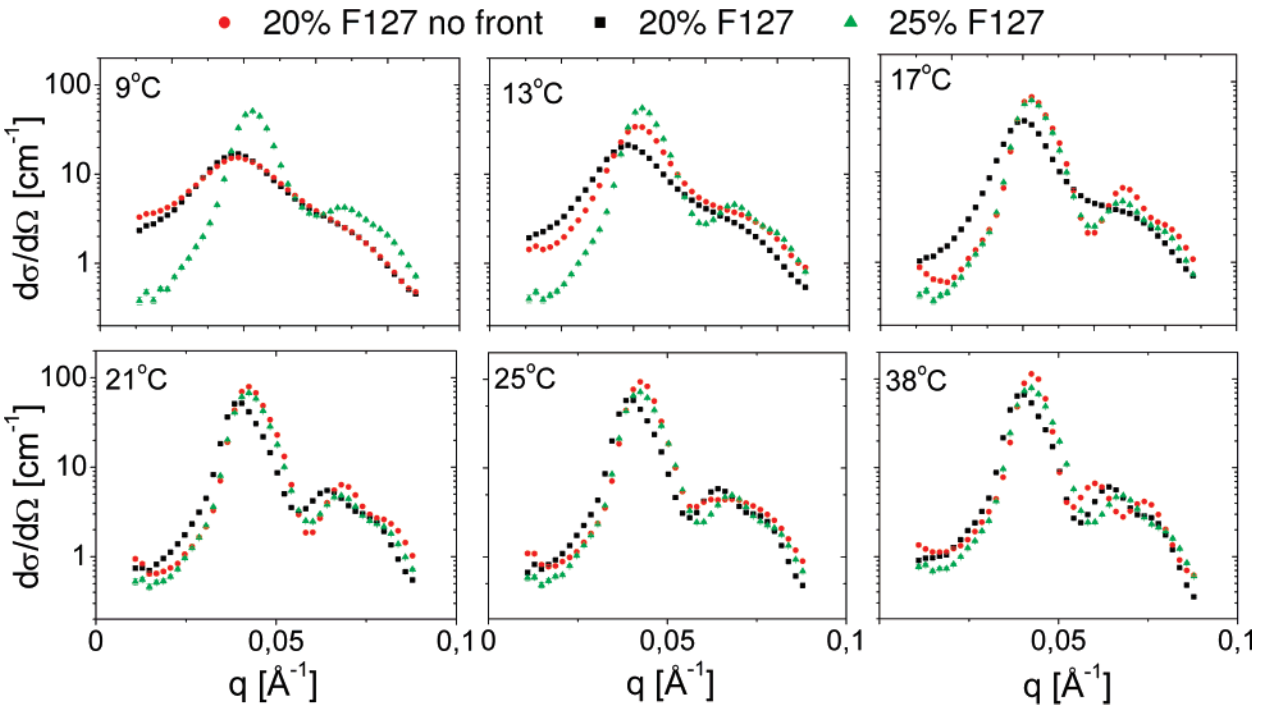

Figure 5. Figures comparing the scattering functions of F127 micelles as formed from 20 wt % F127main (purified) and 20 and 25 wt % F127 as received. Panels a−f give the three sets of data for temperatures in the regime 9 to 38 °C.

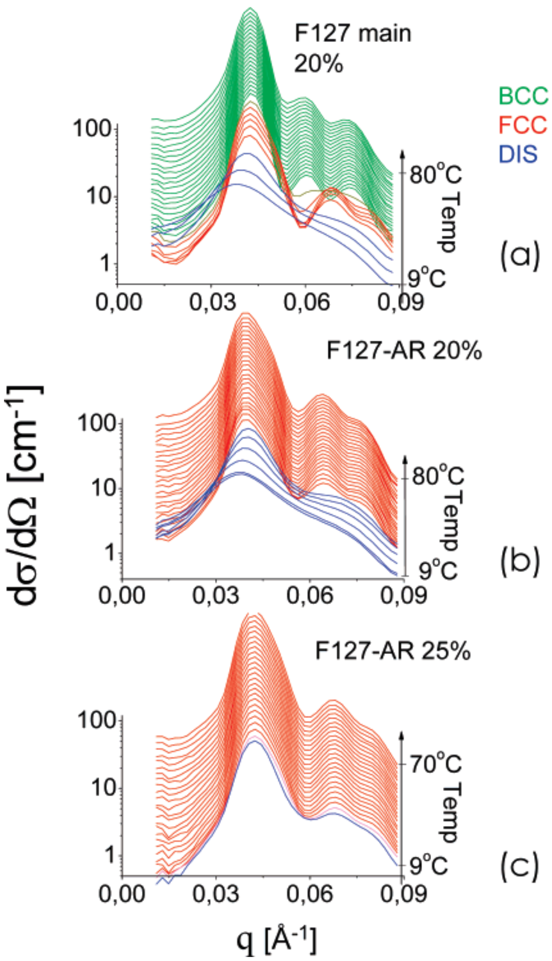

Figure 6. Temperature dependence of the scattering function of three aqueous F127 solutions: (a) 20 wt % F127main (purified) and (b) 20 and (c) 25 wt % F127 as received. The scattering functions are obtained in the temperature regime 9−80 °C with ∼2.5 °C increment. The individual scattering curves are artificially displaced proportional with temperature. The curves are colored to highlight the different phases: blue, disordered; red, fcc; green, bcc.

distribution, the temperature range of micellization is effectively narrowed.[12,18] The given micellization temperature is determined primarily by the PPO component of the triblock PEO−PPO−PEO copolymer, which has a solubility in water that is markedly dependent on molar mass.[12,22]

It is on this basis surprising to find that, within experimental accuracy, the 20 wt % F127main and the 20 wt % F127AR scattering data are identical, suggesting that both the number and the size of the micelles are the same in these two systems. On the basis of the chromatography studies given above, one would argue that the parameters of the 20 wt % F127main should rather be identical to the 25 wt % F127AR system having the same concentration of pure triblock copolymers, and one should expect that the rather hydrophilic PPO−PEO impurity in the F127AR samples should only affect the initial micellization rather vaguely. But this is certainly not the result. The SANS data presented here, showing identical 9 °C structural characteristics of the 20 wt % F127AR and the 20 wt % F127main solutions, suggest that the initial micellization is actually governed by the total amount of polymers in the solution and not just the amount of given triblock copolymer.

At $T \approx 13$ °C the scattering function of the purified 20 wt % F127main system evolves from that of the solution with similar total concentration, 20 wt % F127AR, toward the characteristics of the 25 wt % F127AR sample of similar triblock copolymer concentration. In the 15 and 20 °C patterns of Figure 5 the scattering functions of the 20 wt % F127main is almost indistinguishable from that of the 25 wt % F127AR, while that of the 20 wt % F127AR now is significantly different. These characteristics are summarized in Table 2.

The 25 wt % F127AR sample shows fcc characteristics within most of the temperature regime where this sample was measured, 9−70 °C. Only at the lowest temperatures (9 °C) does the scattering function indicate disordered structure. From the SANS data we estimate that the disorder-to-order transition to be at roughly $T \approx 12$ °C. This is slightly lower than the transition observed by rheology data, which we associate with combination of minor difference in exact polymer concentration (SANS samples 25.7 wt %) and absolute calibration of the SANS temperature measurements.

Both the 20 wt % F127main and the 20 wt % F127AR samples show changes in scattering function that clearly reveal transformation from disordered system of block copolymer micelles into an ordered structure. The ordering temperature is $T_c = 14$ and 20 °C for 20 wt % solutions of F127main and F127AR, respectively. The transition temperature of 20 wt % F127AR is in excellent agreement with that obtained from rheology.

All materials form fcc structures upon increasing the temperature above T_c, as revealed by the observed Bragg reflections that can be associated with respectively {111}, {200}, {220}, {311}, and {222} type of reflections (see Figure 6).

While the F127AR micelles remain having fcc symmetry to the highest temperatures studied (70−80 °C), the purified F127main system has fcc ordered structure in only a narrow temperature regime near T_c. At $T = 25$ °C the F127main system shows a first-order order−order phase transition from fcc to bcc symmetry. The Bragg peaks in the bcc phase are identified as {110}, {200}, and {211} reflections (Figure 6).

The first-order peak position q^* (equal to q_{111} of the fcc phase and to q_{110} of the bcc phase) decreases smoothly with increasing temperature T. In particular, we notice that q^* varies smoothly across the fcc-to-bcc transition of F127main, demonstrating that the transition is epitaxial. There is at most a ∼1% change in q^* at the order-to-order transition temperature. With the intermicellar distance R_{hs} given by q^* (and the lattice parameters, a_{fcc} or a_{bcc}) according to

$$R_{hs} = \frac{\sqrt{6}}{4}\frac{2\pi}{q^*} = \left\{\frac{\sqrt{2}}{4}a_{fcc} \text{ or } \frac{\sqrt{3}}{4}a_{bcc}\right\} \qquad (1)$$

this further indicates that the number of micelles is fixed during the transition, in perfect agreement with the conclusion made by Lodge et al. studying the exitaxial fcc−bcc transition in PS−PI type of micelles.[4,5] In the micellar case, one could have envisioned changes in the number of particles, for example, by micellar fusion, fission, or dissolution.

Table 2. Structural Characteristics *S*(*q*)

temperature range (°C)	state	purified F127main		as-received F127AR
<13	disordered	*S*(20.0 wt % F127main)	=	*S*(20.0 wt % F127AR)
13−22	ordered	*S*(20.0 wt % F127main)	≈	*S*(25.0 wt % F127AR)
22	ordered	*S*(20.0 wt % F127main)	≠	*S*(20.0 wt % F127AR) and *S*(25.0 wt % F127AR)

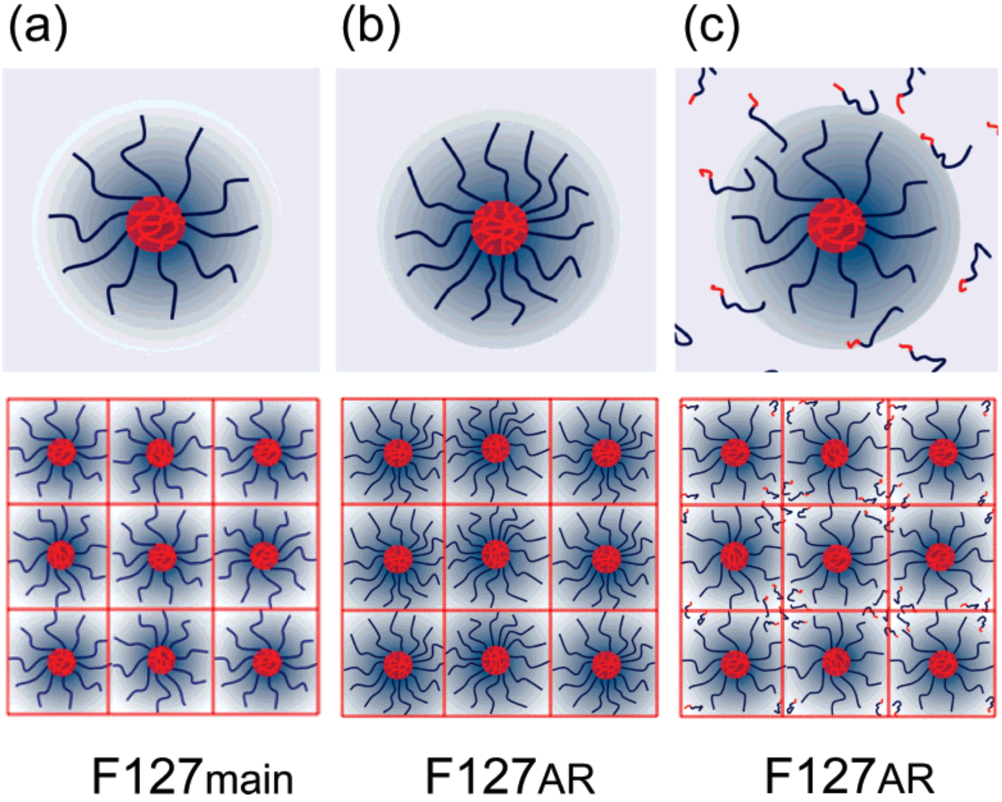

Figure 7. Sketch of the micellar structure of the F127 systems. (a) F127main consisting of pure PEO−PPO−PEO triblock copolymers, where all polymers are incorporated into micelles with relatively soft corona. (b) and (c) give two possibly organization of F127AR solutions containing both PEO−PPO−PEO triblock and PEO−PPO diblock copolymers: the diblocks incorporated into the micelles (b) and the diblocks dissolved in the water phase (c).

The experimental result that the fcc micellar phase is energetically favored in F127AR, while bcc phase is favored in the majority of the F127main system could be explained in a simple picture describing the micellar structure and in particular in the corona properties. In the micellar structures sketched in Figure 7, the overall sizes of the F127AR and F127main micelles are all assumed similar. In the F127AR micelle sketched in Figure 7b both tri- and diblock copolymers are incorporated in the micelle, resulting in corona properties that are distinctly different from that of the pure triblock copolymer (F127main) micelle sketched in Figure 7a. In the F127main system of pure PEO−PPO−PEO triblock copolymers, the corona is relatively dilute, resulting in a rather soft intermicellar interaction potential, which stabilizes the bcc phase. With F127AR micelles looking like that sketched in Figure 7b, on the other hand, the addition of PEO−PPO diblock copolymers with PEO block lengths similar to that of the triblock copolymers, and PPO sizes up to half of the corresponding PPO middle block, cause a significant denser corona while the small PPO units only affect the micellar core properties slightly. The dense corona will result is a harder repulsion potential which could account for the fcc structure.

This picture is, however, in contradiction to the chromatography data shown in Figures 1 and 2, showing unambiguously that the diblock impurities of the F127front are not incorporated in the copolymer micelles. If this is true also for the high-concentration samples studied by SANS, the dissolved PEO−PPO diblock impurities should, in analogy with a related system of star polymer systems discussed by Stiakakis et al.,[23] contradictory cause softening of the interaction potential stabilizing the bcc phase. Other related studies have shown that solvated polymers can induce a depletion interaction that results in an attractive force between the micelles. This situation is schematically shown in Figure 7c. Such effect of depletion interaction induced by solvated polymers have been shown both theoretically[24] and experimentally for colloids, polymer stars, and micelles.[25−27] In a related picture one may speculate that the diblock chains effectively occupying the “empty” space between the spherical close-packed micelles, thereby resulting in the harder repulsion.

E. fcc-to-bcc Transition. Fits to the fcc and bcc scattering functions using spherical form factor for the micelles give quite perfect agreements. The resulting parameters include the micellar diameter (as seen by the neutrons), the cubic lattice parameter, and the correlation length of the ordered system. Figure 8 shows representative experimental data and the respective fitted curves. The model function was smeared by the instrumental resolution parameters using Gaussian approximations.[28] We noticed already from the raw data that the q^* value of the 20 wt % F127main micellar system resembles that of the 25 wt % F127AR system, while the 20 wt % F127AR value of q^* is distinctly different. Similarly, the fits give resulting core size of the 20 wt % F127main micellar system ($R_c = 45.9$ Å) close to that of 25 wt % F127AR system ($R_c = 46.1$ Å), while the 20 wt % F127AR system results in a slightly smaller value ($R_c = 45.4$ Å).

The origin of the fcc-to-bcc transformation is related to the mutual micellar interaction potential, as discussed above. In previous systems of cubic ordered micellar systems showing both bcc and fcc close-packed structure, the bcc phase is close to the disordered phase where the micellar corona properties are expected to be more soft, while the fcc phase is observed further into the ordered phase. Our system shows the opposite.

Hamley and co-workers described thermoreversible fcc/bcc transitions in amphiphilic PEO−PBO block copolymers.[1−3] In the PEO−PBO system fcc was obtained upon heating, as the solvent quality of water for the PEO corona blocks decreased,

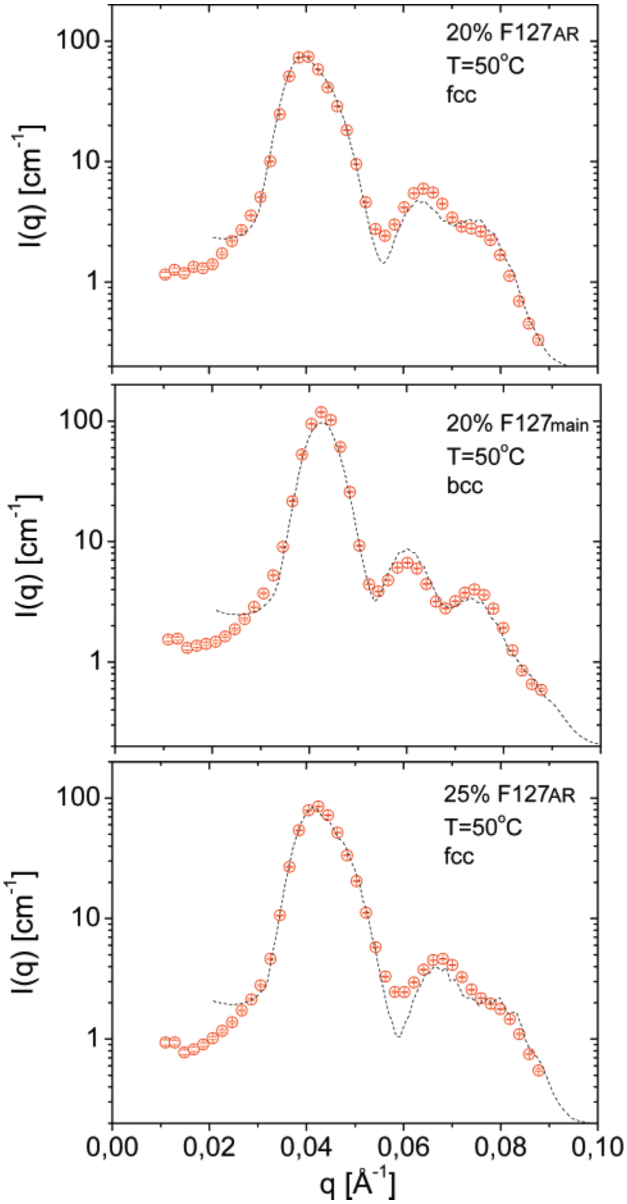

Figure 8. Experimental scattering function (circles) of 20 wt % F127AR, 20 wt % F127main, and 25 wt % F127AR and corresponding fits (broken lines) using fcc for the F127AR systems and bcc structure factors for the F127main system, respectively, and solid sphere form factors.

leading to shrinkage of the corona. The resulting more dense corona causes a steeper interaction potential favoring the fcc lattice structure. Lodge et al.[5] argued that in a system of PS−PI micelles the fcc-to-bcc transition is driven primarily by decreasing aggregation number, which dilutes the corona brush and thereby softens the intermicellar potential. None of these explanations seem applicable for the fcc-to-bcc transformation observed in F127main.

Semenov has, on the basis of an analytical mean-field treatment, predicted a disordered−cps−bcc sequence of micellar phases similar to that observed here, except for the fact that he in the more accurate calculations finds both closed-packed fcc and closed-packed hcp phases: disordered−fcc−hcp−bcc.[10] Semenov's calculation was based on a block copolymer melt system with χN as the parameter and where the resulting nearest-neighbor distance is a main parameter governing the ordered phase (χ is the Flory−Huggins inteaction parameter and N the number of Kuhn segments). The energy difference between fcc and hcp is most likely very small and could be difficult to verify experimentally.[29] At the hcp/fcc-to-bcc transition, Semenov predicts a small, 3%, discontinuity in the nearest-neighbor distance and thereby in the lattice parameter. We may identify a small discontinuity also in our data, but with a value only of the order of 1%, i.e., hardly visible in the resolution of our experiment. Theoretical self-consistent-field theory studies of pure block copolymers by Matsen and Bates[29] have confirmed the disordered−cps−bcc sequence, cps being fcc or hcp close-packed structure, but have, to our knowledge, not previously been observed experimentally.

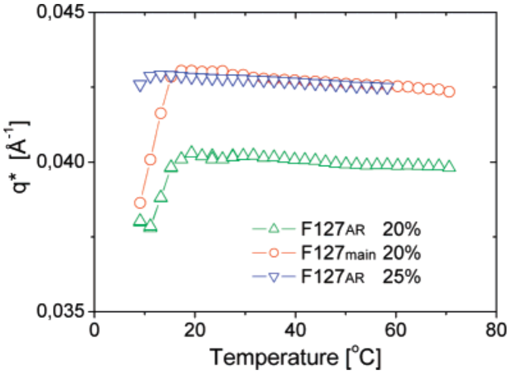

Figure 9. Temperature dependence of the first-order peak-position, q^*, of three aqueous F127 solutions: (a) 20 wt % F127main (purified triblock), and (b) 20 and (c) 25 wt % F127AR. The peak values are obtained from Lorentzian fits to the SANS data.

It thus appears that the purified F127main micellar system is the first experimental system in agreement with the theoretical studies. Certainly, the system is different from other soft polymer and colloidal systems showing bcc-to-fcc transitions, which all show the disorder-bcc-fcc phase sequence governed by changes in interaction potential as a result of changes in the corona properties.

IV. Conclusion

In conclusion, we have studied the effect of PEO−PPO diblock copolymer impurities in aqueous systems of PEO−PPO−PEO triblock copolymers. We have shown that the diblocks in low concentration solutions are not incorporated into the micelles. At higher concentration, the effect of the diblocks seems rather complex. The intermicellar correlation peak of the 25 wt % F127AR and the 20 wt % F127main is almost exactly the same, in agreement with the conclusion that the diblocks do not incorporate into the micelles. But the more detailed structure function shows that while the 20 wt % F127main function is almost identical to that of the 25 wt % just above the disorder-to-order transition, it is similar to that of the 20 wt % system below the disorder-to-order transition. The position of the diblock copolymers relative to the micelles and their exact role in the micellar ordering thus remains unanswered.

Purified F127 systems containing only the main PEO−PPO−PEO triblock copolymers show novel phase properties, with phase sequence with a narrow range of fcc close packed structure between the micellar disordered phase and the bcc cubic ordered micellar phase. Such phase sequence is similar to that predicted for pure diblock copolymer melts.

Acknowledgment. We are grateful to the Danish Natural Science Council for financial support in the DANSCATT grant and to the Paul Scherrer Institut for use of their neutron beam facility and the SoftComp EU-Networks of Excellence.

References and Notes

(1) Hamley, I. W.; Pople, J. A.; Fairclough, J. P. A.; Terrill, N. J.; Ryan, A. J.; Booth, C.; Yu, G.-E.; O. Diat; O.; Almdal, K.; Mortensen, K.; Vigild, M. *J. Chem. Phys.* **1998**, *108*, 6929.
(2) Hamley, I. W.; Pople, J. A.; Diat, O. *Colloid Polym. Sci.* **1998**, *276*, 446.
(3) Hamley, I. W.; Daniel, C.; Mingvanish, W.; Mai, S. M.; Booth, C.; Messe, L.; Ryan, A. J. *Langmuir* **2000**, *16*, 2508.
(4) Bang, J.; Lodge, T. P.; PWang, X.; Brinker, K. L.; Burghardt, W. R. *Phys. Rev. Lett.* **2002**, *89*, 215505.
(5) Lodge, T. P.; Bang, J.; Park, M. J.; Char, K. *Phys. Rev. Lett.* **2004**, *92*, 145501.
(6) Park, M. J.; Bang, J.; Harada, T.; Char, K.; Lodge, T. P. *Macromolecules* **2004**, *37*, 9064.
(7) McConnell, G. A.; Gast, A. P.; Huang, J. S.; Smith, S. D. *Phys. Rev. Lett.* **1993**, *71*, 2102.
(8) McConnell, G. A.; Gast, A. P. *Macromolecules* **1997**, *30*, 435.
(9) Robbins, M. O.; Kramer, K.; Grest, G. S. *J. Chem. Phys.* **1988**, *88*, 3286.
(10) Seminov, A. N. *Macromolecules* **1989**, *22*, 2849.
(11) Watzlawek, M.; Likos, C. N.; Löwen, H. *Phys. Rev. Lett.* **1999**, *82*, 5289.
(12) Batsberg, W.; Ndoni, S.; Trandum, C.; Hvidt, S. *Macromolecules* **2004**, *37*, 2965.
(13) Hvidt, S.; Batsberg, W. *Int. J. Polym. Anal. Charact.* **2007**, *12*, 13.
(14) Mortensen, K.; Talmon, Y. *Macromolecules* **1995**, *28*, 8829.
(15) Mortensen, K. *J. Phys.: Condens. Matter* **1996**, *8*, A103.
(16) Prudhomme, R. K.; Wu, G.; Schneider, D. K. *Langmuir* **1996**, *12*, 4651.
(17) Wu, C.; Liu, T.; Chu, B.; Schneider, D. K.; Graziano, V. *Macromolecules* **1997**, *30*, 4574.
(18) Batsberg, W.; Hvidt, S.; Mortensen, K., to be published.
(19) Hvidt, S.; Jørgensen, E. B.; Brown, W.; Schillen, K. *J. Phys. Chem.* **1994**, *98*, 12320.
(20) Strunz, P.; Mortensen, K.; Janssen, S. *Physica* **2004**, *B 350*, e783.
(21) Brown, W.; Schillen, K.; Almgren, M.; Hvidt, S.; Bahadur, P. *J. Phys. Chem.* **1991**, *95*, 1850.
(22) Mortensen, K.; Brown, W. *Macromolecules* **1993**, *26*, 4128.
(23) Stiakakis, E.; Vlassopoulos, D.; Likos, C. N.; Roovers, J.; Meier, G. *Phys. Rev. Lett.* **2002**, *89*, 208302.
(24) Lipos, C. N. *Phys. Rep.* **2001**, *348*, 267.
(25) Tuinier, R.; Rieger, J.; de Kruif, C. G. *Adv. Colloid Interface Sci.* **2003**, *103*, 1.
(26) Stiakakis, E.; Vlassopoulos, D.; Roovers, L. *Langmuir* **2003**, *19*, 6645.
(27) Abbas, S.; Lodge, T. P. *Phys. Rev. Lett.* **2007**, *99*, 137802.
(28) Pedersen, J. S.; Posselt, D.; Mortensen, K. *J. Appl. Crystallogr.* **1990**, *23*, 321.
(29) Matsen, M.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091.

MA702269C