Structural Properties of Bulk and Aqueous Systems of PEO−PIB−PEO Triblock Copolymers As Studied by Small-Angle Neutron Scattering and Cryo-Transmission Electron Microscopy

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Received February 25, 1997; Revised Manuscript Received August 11, 1997[⊗]

ABSTRACT: The phase behavior of a low molecular weight (M_w = 6000) symmetric triblock copolymer of poly(ethylene oxide) and poly(isobutylene), PEO−PIB−PEO, in the bulk as well in aqueous, D_2O, solutions has been studied using small-angle neutron scattering and cryo-transmission electron microscopy. In aqueous solutions PEO−PIB−PEO self-associates into micelles. At low polymer concentration, the micelles predominantly have threadlike form, with lengths of typically 1−2000 Å. Those coexist, however, with spheroidal micelles of similar diameter. For a polymer concentration above roughly 20% the aggregates probably have a more disclike shape, as the micelles organize in lamellar structure. The 30% solution forms a bulk lamellar structure which, upon shear, organizes in a monodomain crystal. The bulk, PEO−PIB−PEO block copolymer forms at low temperatures a lamellar ordered phase induced by the PEO crystallization into lamellar sheets of PEO chains, presumably in helical form with a single fold. In a temperature regime near the transition temperature of $T_c \approx 45$ °C, the PEO chains unfold, giving rise to significant swelling of the lamellar. Above $T_c \approx 45$ °C, a strong correlation peak is observed corresponding to that observed in amorphous block copolymer systems, but it is still not clear whether this peak reflects strong concentration fluctuations of a disordered phase or the Bragg scattering of an ordered mesophase of amorphous blocks.

1. Introduction

The dynamics of diblock copolymer melts and solutions have recently attracted extensive interest on account of the diversity of phase morphologies and the resulting phase transitions. As for the well-studied low molecular weight surfactants, self-association of block copolymers is observed on dissolution in a selective solvent which is a good solvent for one block but a poor or nonsolvent for the other. Such materials typically associate into micellar aggregates which may, for example, be spherical, rodlike, or discs, depending on the molecular makeup and the location in the phase diagram. In aqueous systems, block copolymers with poly(ethylene oxide) as the water soluble part have recently attracted great interest both within application and in basic research.[1−4]

While many block copolymers in their bulk state undergo order−disorder transitions as a consequence of enthalpy-driven phase separation on the length scale of the polymer size,[5,6] ordering on the mesoscopic length scale may also occur when one of the blocks crystallizes. Block copolymers of poly(ethylene oxide) typically show the latter type of ordering at low temperature,[7−12] but may in addition form fluctuation-induced ordering, as observed in the poly(ethylene propylene)−poly(ethylene oxide), PEP−PEO, type of block copolymers.[10]

The thermodynamics and the structural characteristics have been studied extensively in a few aqueous block copolymer systems, where the poly(propylene oxide)−poly(ethylene oxide), PPO−PEO, type of block copolymers are probably the most studied system. There is, however, still rather limited information and understanding available on the aqueous as well as the bulk phases of other PEO−related block copolymers. It is the aim of the present paper to present such new information on a new triblock copolymer system composed of poly(ethylene oxide), PEO, and poly(isobutylene), PIB.

The paper describes small-angle neutron scattering and cryo-transmission electron microscopy (TEM) studies which are used to elucidate the structural features of the bulk as well as D_2O solutions of a triblock copolymer of poly(ethylene oxide), PEO, and poly(isobutylene), PIB. The study concerns a relatively low molecular weight PEO−PIB−PEO triblock copolymer with molecular weight M_w = 6000 g/mol, 2000 g/mol for both of the two PEO blocks and for the PIB block. With reference to these molecular sizes, we use in the following the abbreviation EIBE-222 for the block copolymer. The measurements cover a broad range of temperature and encompass a wide span of concentration in the D_2O solutions.

In the bulk, the EIBE-222 triblock copolymer form at low temperature an ordered lamellar phase induced by PEO crystallization. At $T \sim 45$ °C the PEO micro-

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S0024-9297(97)00249-0 CCC: $14.00

domains melt, resulting in a major change in the scattering function. Close to the melting point of PEO, the lamellar phase changes character as a result of unfolding the PEO chain. Well above T_c, concentration fluctuations dominate the scattering pattern.

In aqueous solutions the EIBE-222 block copolymers self-associate at low polymer concentrations into a complex dispersion of coexisting threadlike and spheroid micelles. For a copolymer concentration on the order of 5−20%, threadlike micelles dominate, forming an entangled network structure. Above 20% the polymers associate presumably in disc-shaped micelles, forming lamellar structures.

2. Experimental Section

A. Material. The triblock copolymer, poly(ethylene oxide)−poly(isobutylene)−poly(ethylene oxide), PEO−PIB−PEO or EIBE, was synthesized using a two-step process in which poly(isobutylene), PIB, was functionalized with phenol at both ends, using boron triflouride etherate (BF_3·OEt_2) as catalyst, and then coupled with tosylated monomethoxy poly(ethylene oxide), PEO.[13]

The molecular weight of all three blocks was close to 2000 g/mol, giving a total mass of 6000 g/mol. With reference to the size of each of the three blocks we will denote the polymer EIBE-222.

The triblock copolymer was characterized by NMR and GPC in a THF solvent.[13] The GPC traces for the individual components before coupling gave M_w/M_n ratios of less than 1.2. The block copolymer sample contains no unreacted PIB or PEO, but around 10% of diblock PEO−PIB as determined from the composition by NMR with a GPC trace indicating a small shoulder corresponding to the diblock, however, with M_w/M_n ratios still less than 1.2.

The triblock copolymer was dissolved in water (D_2O) at room temperature. Deuterium oxide, D_2O, was used in order to obtain good contrast and low background in the neutron-scattering experiments. The solutions discussed below are all given in weight percent.

B. Small-Angle Neutron Scattering. Small-angle neutron-scattering experiments were performed using the Risø-SANS facility. The dilute samples were mounted in sealed quartz containers (Suprasil from Hellma, FRG), with a 2 mm flight path.

The results presented below were obtained using the combination of two or more of the scattering patterns obtained with different instrumental settings, using 3, 6, and 14 Å-wavelength neutrons and a sample-to-detector distance of 1, 3, and 6 m, respectively, giving scattering vectors within the range of 0.002−0.5 $Å^{-1}$, where the scattering vector $\bar{q}$ is given by the scattering angle θ and the neutron wavelength λ:

$$|\bar{q}| = q = 4\pi/\lambda \sin(\theta/2)$$

The neutron wavelength resolution was $\Delta\lambda/\lambda = 0.18$, and the neutron beam collimation was determined by the pinhole sizes of 16 and 7 mm diameters at the source and sample positions, respectively, and the collimation length which was equal to the sample-to-detector distance. The smearing induced by the wavelength spread, the collimation, and the detector resolution was included in the data analysis discussed below, using Gaussian approximations for the different terms.[14]

The scattering data were corrected for the background arising from the quartz cell, from D_2O, and from other sources, as measured with the neutron beam blocked by a plastic containing boron at the sample position. The incoherent scattering from an H_2O sample was used to determine deviations from a uniform detector response and to convert the data into absolute units.

The scattering patterns discussed in the present paper are all, except for the shear-aligned 30% specimen, azimuthally isotropic. The data have been reduced by azimuthal averaging to the one-dimensional $I(q)$ scattering functions which depend only on the absolute value of $\bar{q}$. The scattering pattern of the shear-aligned 30% polymer sample is presented in its two-dimensional form.

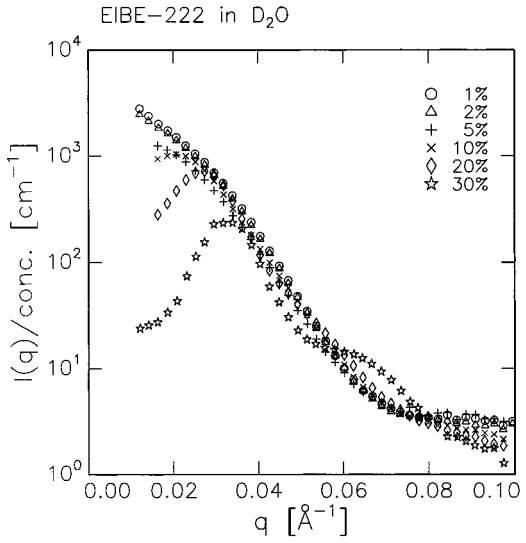

Figure 1. Small-angle neutron scattering data of aqueous D_2O solutions of PEO−PIB−PEO, EIBE-222, as obtained with a polymer concentration ranging from 1−30% and measured at ambient temperature.

C. Cryo-Transmission Electron Microscopy. Specimens for electron microscopy were prepared in a controlled enviroment vitrification system, to ensure fixed temperature and to avoid water loss from the solution during sample preparation. The specimens were prepared as thin liquid films, less than 0.25 μm thick, on perforated polymer/carbon films and quenched into liquid ethane at its freezing point. The technique leads to vitrified specimens; i.e., the water does not undergo crystallization during thermal fixation. In this way, component segregation and rearrangement are prevented, and the original fluid microstructure is preserved. The vitrified specimens were transferred to a JEOL 2000FX or 1210 transmission electron microscopes, where imaging was carried out in a Gatan 626 cooling holder at a temperature of about −170 °C, using a 100 kV acceleration voltage. We used Kodak SO-163 film developed to the maximum electron speed. Low-electron exposures of less than 10 electrons/$Å^2$ were used for imaging.

D. Rheological Measurements. Rheological measurements were carried out on 5% aqueous solutions on a Stress-Tech rheometer (Rheological Instruments). The viscosity was recorded over a shear rate range of 1−10 s^{-1}.

3. Results and Discussion: Dilute Solutions

A. Small-Angle Neutron Scattering. Figure 1 shows the scattering function of aqueous solutions of the EIBE-222 triblock copolymer in the concentration range of 1−30%, as obtained at ambient temperature. By the polymer concentration being increased up to about 10%, the only effect on the scattering function is the formation of a "correlation hole" due to intermicellar correlations. The 20 and 30% polymer concentrations give a somewhat more structured scattering function, indicating a different micellar form as discussed below.

Figure 2 shows the scattering function of 2% EIBE-222 as observed at temperatures $T = 7$ and 70 °C. We observe only a weak temperature dependence for the low-concentration samples ($c \leq$ approximately 5%). The high-temperature data show a small decrease in intensity at the smallest q values, and a slightly less steep slope at intermediate q values.

The $I(q)$-scattering functions have been Fourier-transformed using the indirect method of Glatter,[15,16] giving the distance distribution function $p(R)$, which is

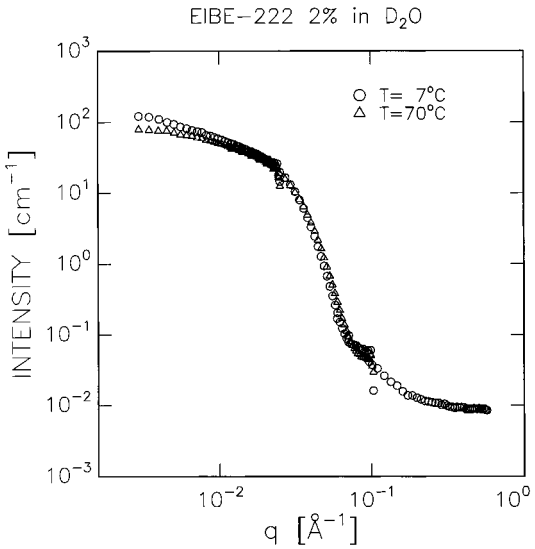

Figure 2. Small-angle neutron scattering data of aqueous solutions of 2% EIBE-222 in D_2O, as obtained at 7 and 70 °C.

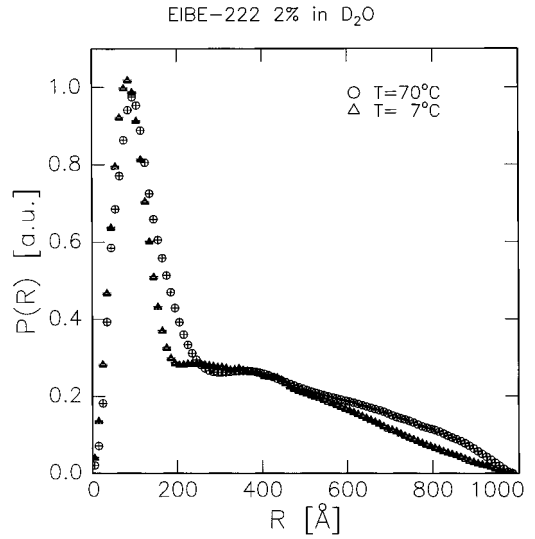

Figure 3. Pair correlation function of aqueous solutions of 2% EIBE-222 in D_2O, at 7 and 70 °C, as obtained from indirect Fourier transform of the scattering data shown in Figure 2.

the scattering density correlation function multiplied by the distance squared. In the indirect Fourier transformation method, $p(R)$ is parameterized into cubic-spline functions, B_n, with coefficients a_n: $p(R) = \sum a_n B_n(R)$. The a_n parameters are determined by a constrained least-square analysis. In addition, an independent uniform background, describing the incoherent scattering, has been included in the data analysis.

Figure 3 shows the resulting distance distribution function $p(R)$ of the 2% EIBE-222 copolymer solution, corresponding to the T = 7 and 70 °C scattering functions shown in Figure 2. The $p(R)$ function shows correlation up to distances of the order of at least 1000 Å, which is the resolution of the scattering data. A major peak appear in $p(R)$ centered around 90 Å. Such a $p(R)$ function is typical for cylindrical or threadlike micelles, but the intense 90 Å peak may as well reflect the additional presence of some spherical micelles, as discussed below.

The $p(R)$ functions for T = 7 and 70 °C given in the same figure show qualitative similar behavior, both with a correlation up to 1000 Å or more. The peak around 90 Å appears, however, in the fit broader at T = 70 °C.

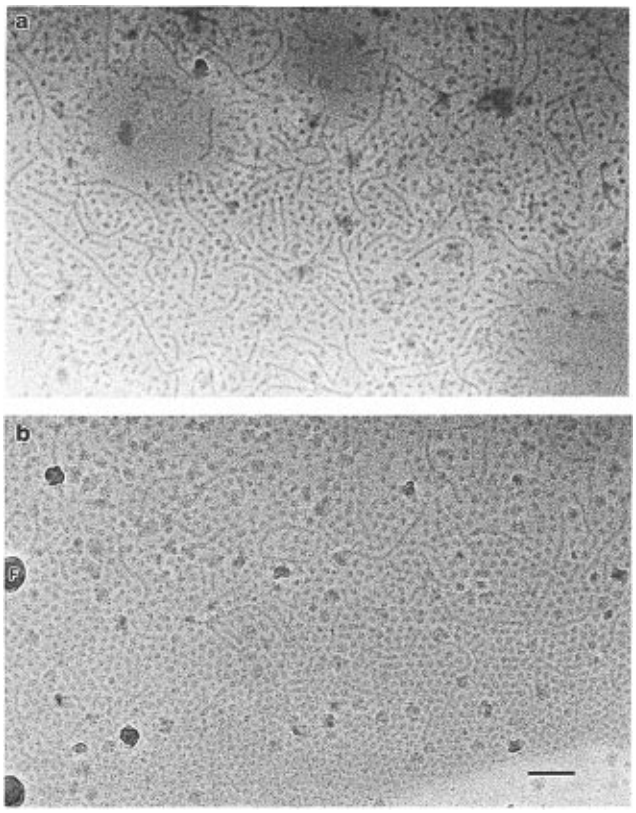

Figure 4. Cryo-TEM pictures of vitrified specimens of a 1% EIBE-222 block copolymer in D_2O as observed at two different sites of the same sample (a and b). (a) Coexistense of wormlike and spherical micelles. (b) Dominating spherical micelles.

This may be interpreted as an increased number of spherical micelles at elevated temperatures, and/or thicker threadlike micelles. It should be noted, however, that the main difference between the 7 and 70 °C data seems to be in the interparticle structure factor and any detailed interpretation of the $p(R)$ function should be limited.

Figure 4 shows cryo-TEM images of the 1% solution of the EIBE-222 copolymer vitrified from ambient temperature. Figure 4a clearly shows dominating threadlike micelles, in agreement with the interpretation of the SANS scattering data. From the TEM pictures the typical micellar length appears to be on the order of 1000−2000 Å, with relative large variation in size, however. The persistent length of the micelles, as observed from the cryo-TEM, is on the order of 500 Å. The cryo-micrographs also show, however, many spheroidal micelles with diameters close to or equal to that of the threadlike micelles. The TEM picture does not allow detailed characterization of the diameter, since appearance on the photo is highly sensitive to experimental conditions.[17] In some regimes of the sample, as shown in Figure 4b, spheroidal micelles seem to be the dominating structure. This may be a result of the segregation of dispersed particles in the liquid during specimen preparation.[18]

The SANS-scattering data are clearly dominated by the threadlike micelles. This is partly because these micelles are the dominating form, and partly because these aggregates are much larger and thereby dominate the scattering pattern. The pronounced peak in the pair-correlation function $p(R)$ at R = 90 Å may partly reflect the spherical micelles, and partly the cross section of the wormlike micelles. The limited resolution of the SANS data does not allow a more detailed

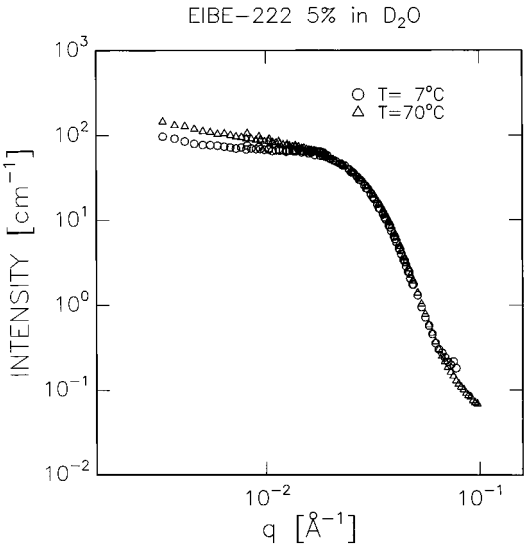

Figure 5. Small-angle neutron scattering data of aqueous solutions of 5% EIBE-222 in D_2O, as obtained at 7 and 70 °C.

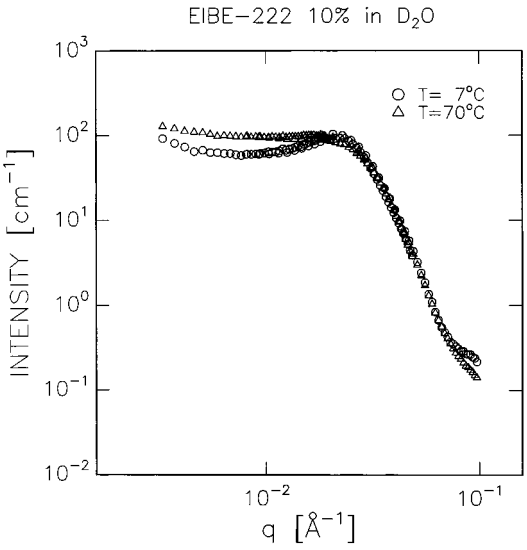

Figure 6. Small-angle neutron scattering data of aqueous solutions of 10% EIBE-222 in D_2O, as obtained at 7 and 70 °C.

interpretation of the relations between threadlike and spherical micelles, and the polydispersity in length of the elongated micelles. The combined information from the cryo-TEM and scattering technique gives, however, detailed information on the micellar form and sizes.

One may speculate that the coexistence of threadlike and spheroidal micelles is related to the presence of around 10% PEO-PIB diblock copolymers, as revealed by NMR. The diblock copolymers may act as "co-surfactants" or "co-amphiphile" and may thus contribute to the coexistence.

B. Concentrated Aqueous Suspensions. Solutions of higher polymer concentrations, e.g., the 5, 10, and 20% solution shown in respectively Figures 5, 6, and 9, also show only little, but still some, temperature dependence. At low scattering angles the main effect on concentration is a pronounced "correlation hole", revealing important virial effects. The general feature with relation to temperature is that at high T values, the low-q scattering increases slightly, whereas for $q >$ 0.03 $Å^{-1}$ the scattering roughly remains unchanged, as seen in Figure 5 and 6.

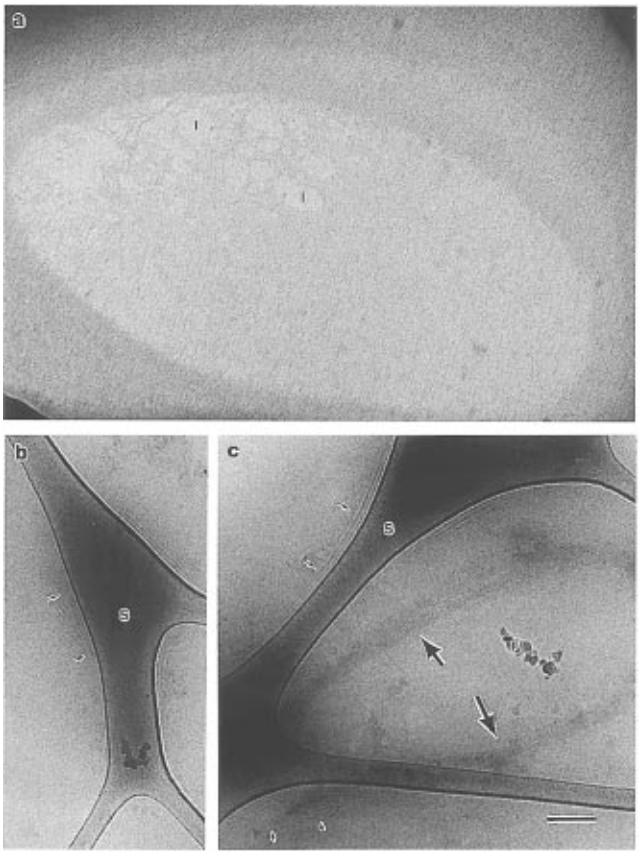

Figure 7. Three different fields of the same vitrified specimen of a 10% EIBE-222 aqueous (D_2O) solution: (a) a network of threadlike micelles partially oriented by shear during specimen preparation; note areas of empty vitreous ice (I) surrounded by thorn network; (b and c) bundles of threadlike micelles in ice (large arrows) and apparent lamellar structures (small arrowheads) formed at the edges of the supporting film (S). F is a frost particle. Bar = 100 nm.

Because of the relatively high concentration of the polymer, the 10% EIBE-222 solution is quite difficult to be made into cryo-specimens, and the interpretation of the micrographs is not straightforward. The high shear needed to produce thin liquid films may affect the structures observed, and segregation of dispersed material is another difficulty.[18] However, cryo-TEM images give some useful information about the microstructure of the system. Figure 7 shows three different fields taken from the same cryo-specimen. In Figure 7a we see quite clearly the network formed by threadlike micelles. In thin areas of the specimen, we observe "thorn" parts of that network with some empty vitreous ice areas (I). Note also that the network has been sheared in one direction, roughly from the lower left corner to the upper right one, during the thinning of the liquid film prior to vitrification. In Figure 7b and 7c we see areas of the vitreous sample close to the edges of the perforated support film (S). Near those edges we quite often find higher concentrations of the dispersed phase, the polymer in our case. This may lead to formation of new phases, locally, as observed here. Interfaces, in general, may induce local order.[21] Small arrowheads point to lamellae formed near the edges. Large arrows indicate bundles of threadlike micelles away from the edges. Dynamic mechanical experiments have shown a markedly increased shear modulus at a shear rate of the order of 2−5 s^{-1}, as shown in Figure 8.[19] One may speculate that this frequency dependent modulus may reflect the characteristic time for the

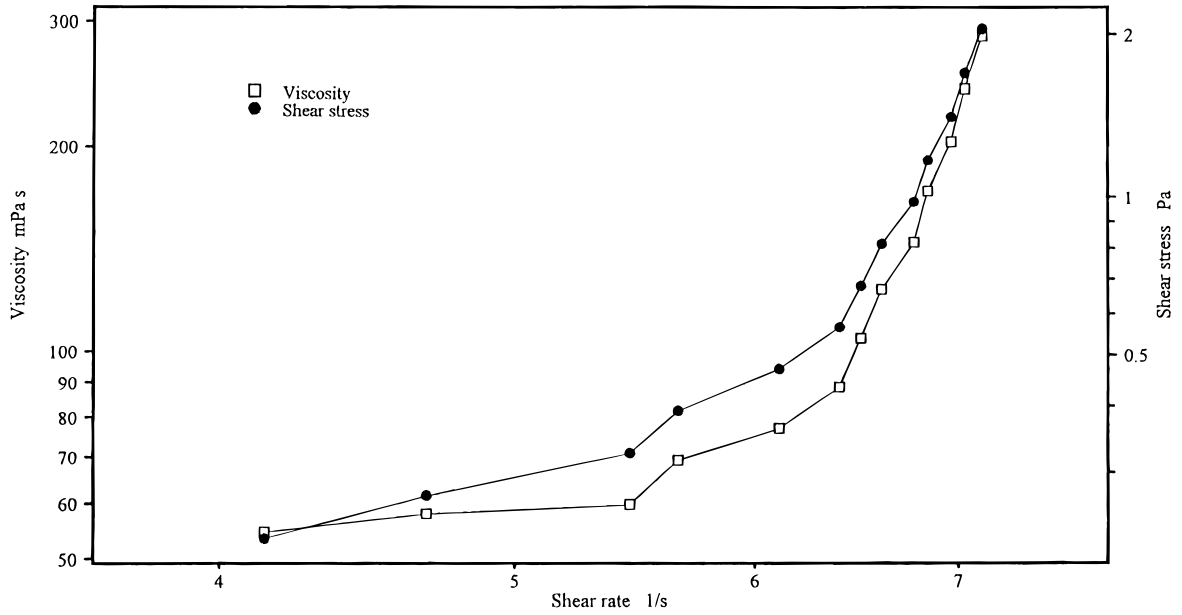

Figure 8. Viscosity and shear stress of a solution of 5% EIBE-222 block copolymer in D_2O.

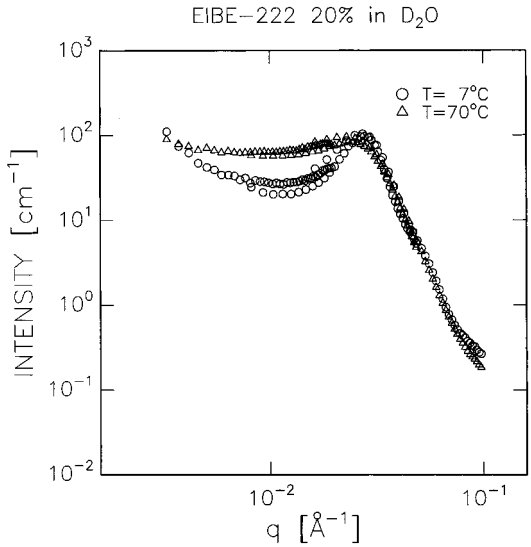

Figure 9. Small-angle neutron scattering data of aqueous solutions of 20% EIBE-222 in D_2O, as obtained at 7 and 70 °C.

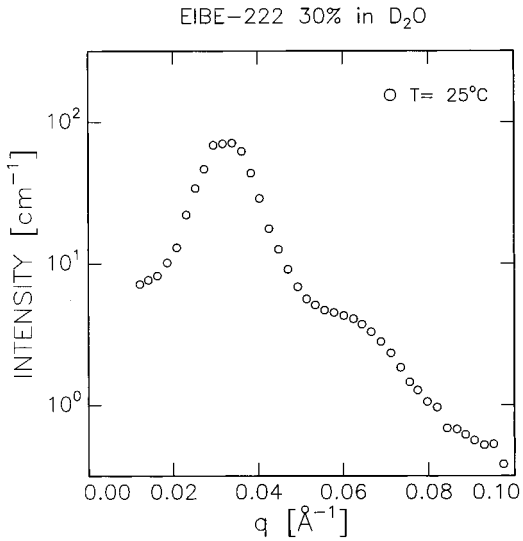

Figure 10. Small-angle neutron scattering data of aqueous solutions of 30% EIBE-222 in D_2O, as obtained at 7 and 70 °C.

micelles to disentangle from the network, or the micelles to break up. In SANS experiments utilizing a Couette type of shear cell for the sample[20] we were not able to resolve any shear dependent scattering, neither within the range of the onset of the increasing shear modulus nor at higher shear rates, indicating that the rheological behavior is not governed by the local micellar structure, but likely by connectivity of the micellar network.

The scattering pattern of aqueous suspensions of 20% or more EIBE-222 block copolymers shows a scattering function with significant higher order peaks, as seen in Figures 9 and 10. Such scattering functions reflect relatively highly ordered liquids, and/or paracrystalline properties. The suspensions tend to form lamellar structures at these high concentrations, as discussed below, thus suggesting that the copolymer aggregates have the shape of extended discs.

While the 20% sample still is a low-viscosity liquid, the 30% sample appears as a pastelike solid. Figure 11 shows the observed scattering pattern as obtained in a shear field with the velocity direction horizontal, the neutral direction vertical, and the shear gradient perpendicular to the figure, i.e., parallel to the neutron beam. The scattering pattern reveals lamellar structures with periodicity of $d = 100$ Å. In the shear field the polycrystalline sample is transferred into a single domain structure, equivalent to other ordered micellar suspensions.[4]

4. Bulk Copolymer

The scattering function of pure EIBE-222 shows an intense scattering peak at $q = 0.044$ Å^{-1} which disappears upon heating (Figure 12a), indicating an ordered low-temperature structure.

The structure is most likely a result of crystallization of the PEO blocks into lamellae of helical PEO chains, as observed in related PEO systems.[7−12] The scattering data do not, however, show higher order reflections to prove the lamellar phase. The absence of second order reflections may partly be due to significant reduction in this intensity due to the relatively close to symmetric system (volume fraction of PIB is $f = 0.37$ as discussed

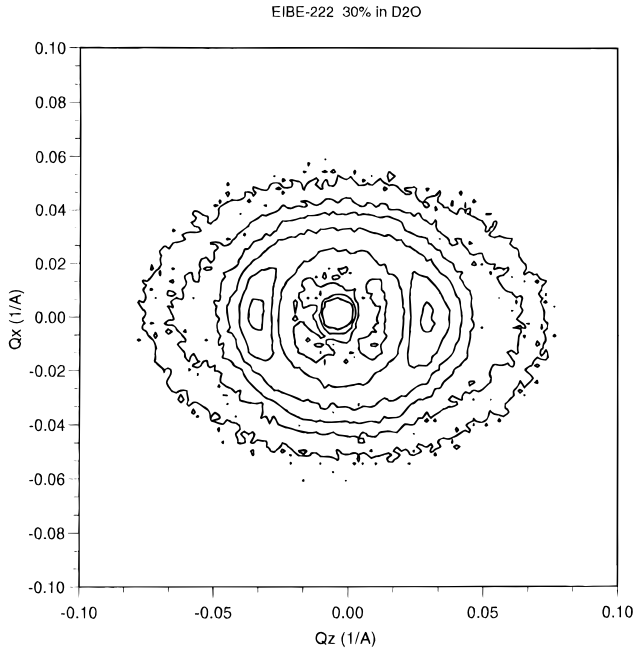

Figure 11. Small-angle neutron scattering data of a shear-aligned mesophase of aqueous solutions of 20% EIBE-222 in D_2O, as obtained at 25 °C.

below). The periodicity of EIBE-222 is

$$d = 2\pi/q_{10} = 140 \text{ Å}$$

where $q_{10} = 0.044$ Å^{-1} is the scattering momentum of the first-order Bragg peak. Wide-angle scattering remains also to be performed on the EIBE-222 block copolymer to verify the lamellar organization and the crystalline PEO structure. The thickness d_{PIB} and d_{PEO} of respectively the PIB and PEO lamellae must fulfill

$$d_{PIB} = fd_{10} \quad \text{and} \quad d_{PEO} = (1 - f)d_{10}$$

where f is the volume fraction of PIB. With the mass density 0.918 and 1.01 g/cm^3 of respectively PIB and PEO, the molecular configuration of EIBE-222 gives $f = 0.37$, and thus a PEO-lamellae thickness of $d_{PEO} = 88$ Å.

This experimentally observed value, $d_{PEO} = 88$ Å, is significantly less than the value expected for an unfolded PEO chain of $M_w = 2000$ g/mol, corresponding to 45 EO units, irrespective of helical or zigzag polymorph PEO. In the helical form, the chain length is 2.78 Å/repeat unit (19.48 Å/pitch of 7 units[22]). In the zigzag form, the chain length is 3.56 Å/unit (7.12/repeat of 2 units[22]). In unfolded configuration the PEO block thus should have the length $d_1^{helix} = 125$ Å and $d_1^{zz} = 161$ Å for respectively helical and zigzag configuration. Related PEO-block copolymers have been shown to be in the helical conformation, with the number of chain folds depending on both molecular architecture, crystallization temperature, and thermal history.[11] It is most likely that the PEO block in the EIBE-222 material behave similarly. With the values given above, we find that the ratio between the thickness of the PEO lamellae and the length of the unfolded chain is close to 2, thus indicating a single fold in the PEO chain assuming that each PEO block makes up the lamellae thickness. If anchoring between PEO chains of neighboring lamellae take place inside the lamellae, on the other hand, the PEO chains will have three folds.

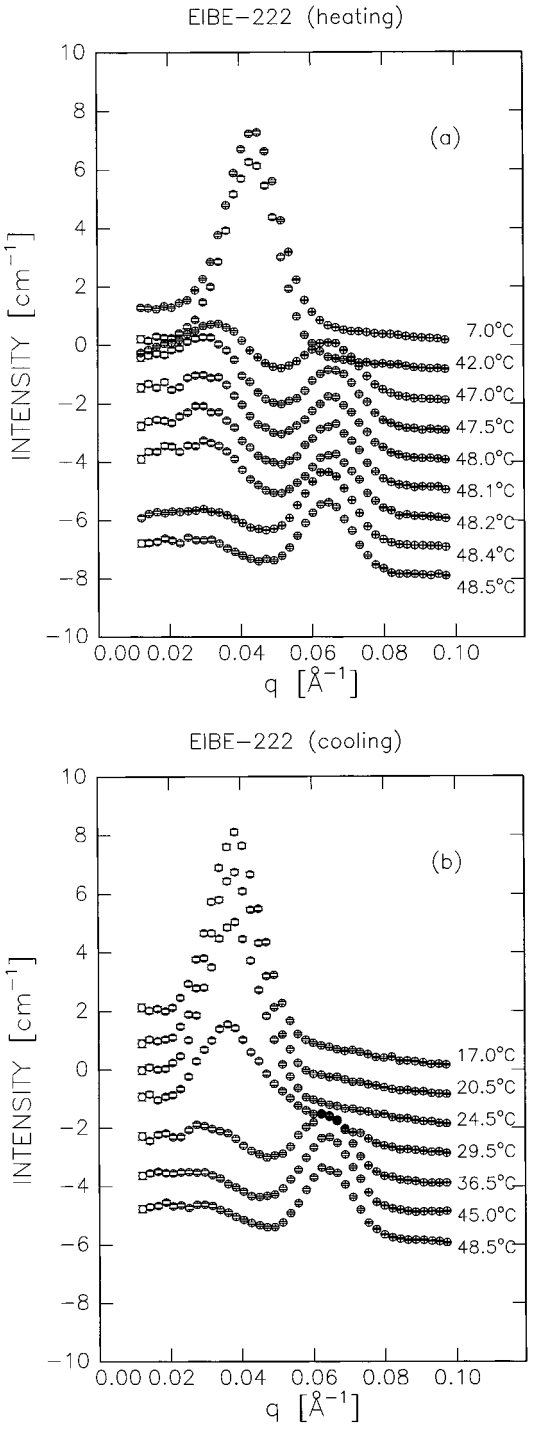

Figure 12. Small-angle neutron scattering data of bulk EIBE-222, as obtained in the temperature range 7−50 °C during heating (a) and during cooling (b). The scattering pattern has been shifted relative to each other in order to make the results more clear. At high q, the $I(q)$ values are the same, independent of temperature.

Upon heating, the lamellar structure remains basically unaffected up to the temperature $T_c = 45$ °C, above which the intensity of the $q = 0.044$ Å^{-1} peak decreases to zero within a few degrees. Above this $T_c = 45$ °C transition, a new structure develops. In the vicinity of the transition temperature two peaks appear in the scattering pattern, one at $q = 0.032$ Å^{-1} and another at $q = 0.065$ Å^{-1}, i.e., with a ratio close to 2. The ratio 2 between the two correlation peaks points to a new swollen lamellar structure with a lamellar spacing of $d = 200$ Å. This finding indicates that the PEO chains tend to unfold near the transition temperature of 45 °C.

Equivalent results have recently been observed in a diblock copolymer of polystyrene and PEO, PS−PEO.[12] Using the same analysis as above, we find that the PEO-lamellae thickness in this regime is $d_{PEO} = (1-0.37) \times 200$ Å $= 126$ Å, in perfect agreement with the expected length of the 2000-molecular weight PEO chain in helical crystal form, as discussed above.

Upon further heating, the intensity of the $q \sim 0.032$ Å^{-1} peak vanishes, whereas the intensity near the $q \sim 0.065$ Å^{-1} peak only changes little (Figure 12a). It is likely that the latter correlation peak in this temperature range reflects scattering of amorphous block copolymers, either concentration fluctuations in the disordered phase or Bragg reflections of an ordered mesophase.[6] Further studies are needed to clarify this and should be done when new material is available.

Upon cooling, the $q \sim 0.032$ Å^{-1} peak reflecting unfolded PEO lamellae regains some of its intensity (Figure 12b), but not to the level observed in the heating process. For heating and cooling rates of approximately 0.2 °C/min, the ordering and disordering temperatures of the lamellar structure have a hysteresis of the order of 10 °C. Such hysteresis is commonly observed in the PEO type of block copolymers and is resulting from the fact that the lamellar block copolymer formation is a consequence of the strong first-order amorphous to crystalline phase transition of pure PEO domains.

It is not possible, on the basis of our present data, to resolve the structure of the EIBE-222 above the melting point of PEO. More studies are in progress, including those of PEO−PIB−PEO block copolymers of different molecular architecture and investigations of possible time dependence of the two peaks observed.

5. Conclusions

In aqueous solutions, EIBE-222 forms at low concentrations (up to roughly 10% polymer concentration) threadlike micelles coexisting with spherical micelles. The micelles are only slightly sensitive to temperature. It is a speculation that the presence of PEO−PIB diblock copolymers (10%) act as "co-surfactants" or "co-amphiphile", and thus contribute to the coexistence of threadlike and spherical micelles. At higher polymer concentrations, disclike micelles are presumably formed, which for concentrations above 20−30% order in form of bulk lamellar structures. Near interfaces, the lamellar structure may be formed at significant lower concentrations. The study of the aqueous micellar solutions have proven that a combination of techniques are essential to really extract the structural properties of complex materials. The combined study using both scattering methods (SANS) and direct imaging (cryo-TEM) has given detailed information on the coexistence of micellar aggregates in different forms: spherical and threadlike. Such coexistence could not have been concluded on the basis of the small-angle scattering technique only. EIBE-222 forms in the bulk a low-temperature lamellar ordered phase induced by the PEO crystallization into lamellar sheets of PEO chains, presumably in helical form with a single fold. In a temperature regime near the transition temperature of $T_c \approx 45$ °C, the PEO chains unfold, giving rise to significant swelling of the lamellar to 200 Å periodicity. Above $T_c \approx 45$ °C, a strong correlation peak is observed, corresponding to that observed in amorphous block copolymer systems. It is not at present clear, however, whether this peak reflects strong concentration fluctuations of the Leibler type in a disordered phase or the Flory−Huggins interaction has induced an ordered mesophase of amorphous blocks.

Acknowledgment. This work has been supported by the Danish Polymer Centre. Electron microscopy was performed at the Chemical Centre of the Lund University, where Y.T. was a summer visitor at the Physical Chemistry 1 Department. We thank Dr. Xiangbing Li for producing the images of Figure 7 at the center for Interfacial Engineering, the University of Minnesota.

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MA970249+