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Formation of rodlike block copolymer micelles in aqueous salt solutions

V K Aswal¹, A G Wagh¹ and M Kammel²

¹ Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India

² Hahn-Meitner-Institut, Glienickestrasse 100, D-14109 Berlin, Germany

E-mail: vkaswal@barc.gov.in

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Abstract

SANS measurements have been performed on the water-soluble PEO–PPO–PEO triblock copolymer P85 [(EO)₂₆(PO)₃₉(EO)₂₆] in the presence of salts KCl, KF and K₂CO₃ in aqueous solution. Addition of these salts entropically favours dehydration from the micelles (similar to that of increasing temperature) and this leads to the formation of rodlike block copolymer micelles at ambient temperature. The rodlike micelles coexist with spherical micelles at higher salt concentrations or temperatures in these systems even up to the onset of phase separation. The hydration properties of the salt anions determine the population of the rodlike micelles.

Block copolymers consist of two different types of polymer chains, which are covalently bonded together. In a liquid which is a good solvent for one block and a poor solvent for the other, such block copolymers self-associate to form micelles. There is a lot of current interest in PEO–PPO–PEO (polyethylene oxide–polypropylene oxide–polyethylene oxide) triblock copolymers as they are widely used for various applications in the nanotechnology, pharmaceutical, textile and detergent industries [1–4]. In an aqueous solution these block copolymers form micelles composed of a core of PPO blocks and an outer shell consisting of PEO end blocks and water. The micelles can be formed by increasing temperature and/or copolymer concentration beyond a specific concentration (critical micelle concentration) or temperature (critical micellization temperature). The micelle structure depends strongly on the temperature as well as the chemical composition of the copolymer. A large number of studies on such PEO–PPO–PEO triblock copolymers have been published, including extended reviews [5–10].

The dehydration from PPO blocks due to temperature rise transforms unimers to micelles. However, once the micelles are formed, their structure depends on the dehydration behaviour of PEO blocks. This makes temperature an important parameter to control the properties of micellar solutions of block copolymers [11–15]. The most common result for the unimers is to

form spherical micelles whose aggregation number increases with temperature. As the radius of the core increases, there is a growing entropic contribution from the stretched PPO blocks to the free energy per micelle. Hence the radius of the spherical micelle cannot increase indefinitely and a sphere-to-rod shape transition of the micelles can be expected if the size of the PEO blocks is not too large compared to that of the PPO block. The formation of rodlike micelles is of great interest in applications such as modifying the flow properties of a solution, nanocarriers for drug delivery, synthesis of nanorods and generating liquid crystals. It may not always be possible to maintain or vary the temperature in these applications. In this paper, we show that selective salts can be used to induce the sphere-to-rod transition of block copolymer micelles at ambient temperature. The small-angle neutron scattering (SANS) technique has been used to characterize the shape transition in these block copolymer solutions. SANS covers a length scale (1–500 nm) where most of the micelle structures changing from spherical to rodlike or disclike shapes are formed [16–19].

The block copolymer P85 [(EO)₂₆(PO)₃₉(EO)₂₆] was obtained from BASF and used as supplied. All the salts used (KCl, KF and K₂CO₃) were purchased from Fluka. The samples for SANS experiments were prepared by dissolving known amounts of block copolymer and salts in D₂O. The use of D₂O as solvent instead of H₂O provides better contrast in neutron experiments. Small-angle neutron scattering experiments were carried out using the V4 SANS instrument at the BER II reactor at the Hahn-Meitner-Institut in Berlin, Germany [20]. The wavelength of the neutron beam was 0.6 nm and the experiments were performed at three different sample-to-detector distances of 1, 6 and 16 m to cover a scattering vector Q range of 0.03–3.5 nm⁻¹. The scattered neutrons were detected using a ³He two-dimensional 64 cm × 64 cm detector. The measurements were made for 0.5 wt% of block copolymer with several concentrations of each salt. The salts were added up to the maximum concentrations till the phase separation (clouding) in these systems occurred. The concentrations of salts at which the clouding occurs are 3.8, 1.42 and 0.61 M for KCl, KF and K₂CO₃, respectively. The temperature was kept fixed at 30 °C for all the measurements in the presence of salts. The temperature dependence of the rodlike micelle formation was investigated with one of these samples (0.5 wt% + 0.35 M KF) and compared with its dependence on the salt concentration. The data were corrected and normalized to an absolute scale using BerSANS-PC data processing software [21].

In a small-angle neutron scattering experiment, one measures the differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector magnitude Q , and for a monodisperse system of micelles it can be expressed as [22]

$$\frac{d\Sigma}{d\Omega}(Q) = nF(Q)S(Q) + B \quad (1)$$

where n is the number density of the micelles and B is a constant term that represents the incoherent scattering background mainly from the hydrogen atoms present in the sample. The block copolymer micelles can be considered as a core-shell composite with distinct scattering length densities of the core and the shell. The structure of these micelles is described by following a model proposed by Pedersen [23]. In this model the shell is described as consisting of non-interacting Gaussian polymer chains and these chains are assumed to be displaced from the core (else the mathematical approximations will not work as the chains overlap each other and the core), i.e. a mushroom polymer configuration is assumed. Non-penetration of the chains into the core region is mimicked by moving the centre of mass of the chains a distance R_g away from the surface of the core, where R_g is the radius of the gyration of the chains. The form factor $F(Q)$ comprises four terms: the self-correlation of the core, the self-correlation of the chains, the cross term between core and chains, and the cross term between different chains. The structure factor $S(Q)$ has a value of about unity for dilute systems.

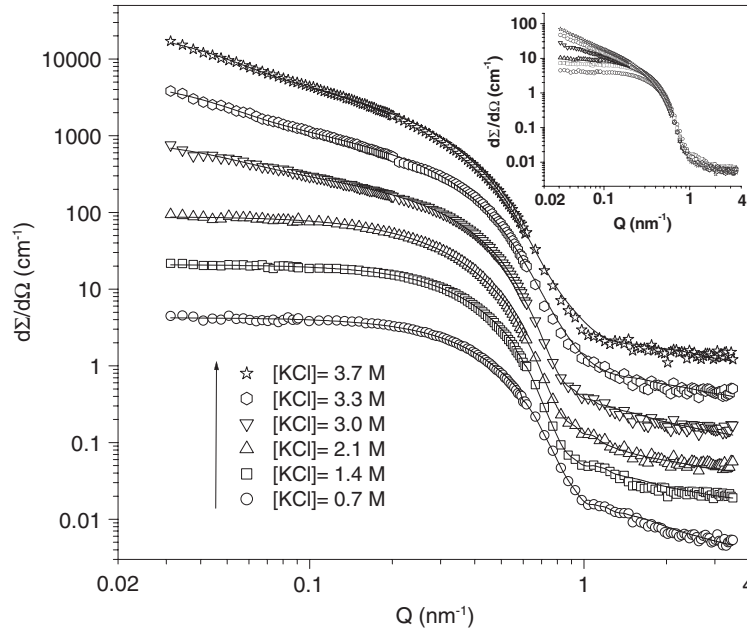


Figure 1. SANS data from 0.5 wt% P85 block copolymer solution at 30°C with varying KCl concentration. To show the clarity of the fits the data for increasing KCl concentrations are shifted vertically. The inset shows the data without any shifting.

In the case of polydisperse micelles, equation (1) can be written as

$$\frac{d\Sigma}{d\Omega}(Q) = \int \frac{d\Sigma}{d\Omega}(Q, R) f(R) dR + B. \quad (2)$$

The polydispersity in the micellar size (R) has been accounted for by a Schultz distribution as given by

$$f(R) = \left(\frac{Z+1}{R_m}\right)^{Z+1} R^Z \exp\left[-\left(\frac{Z+1}{R_m}\right)R\right] \frac{1}{\Gamma(Z+1)} \quad (3)$$

where R_m is the mean value of the distribution and Z is the dimensionless width parameter. The polydispersity of this distribution is given by $\Delta R/R_m = 1/(Z+1)^{1/2}$.

The best fit to the data is obtained for block copolymer solutions in the presence of salts by assuming a mixture of spherical and rodlike micelles. The mean core radius R_m and total volume fraction of the micelles ϕ along with the length L and fraction of rodlike micelles ϕ_r on their formation were the fitting parameters in the analysis. Throughout the data analysis, corrections were made for instrumental smearing [24]. The parameters in the analysis were derived by means of a nonlinear least-square fitting program [25]. The radius of gyration R_g of the polymer segment in the shell region of the micelle has been kept fixed (1.2 nm), as it does not show any significant change with varying the salt concentration or temperature.

Figure 1 shows the variation in SANS data from 0.5 wt% P85 block copolymer solution with increasing concentration of KCl. The scattering intensity in the low Q region at lower KCl concentrations increases with an increase in KCl concentration but remains flat. This is an indication of spherical micelles present in the system and their concentration increasing with the increase in KCl concentration. At higher KCl concentrations, there is a dramatic change in the scattering intensity in the low Q region. The scattering intensity as a function of Q on a log-log

Table 1. Fitted structural parameters of P85 block copolymer micelles in the presence of varying concentrations of KCl at fixed temperature (30 °C).

KCl concentration (M)	Structure	Core radius R_m (nm)	Length L (nm)	Total micelle vol. fraction ϕ (%)	Rodlike micelle fraction ϕ_r (%)
0.7	Spherical	3.44 ± 0.06	—	0.94 ± 0.08	0
1.4	Spherical	3.79 ± 0.08	—	1.05 ± 0.10	0
2.1	Spherical	3.90 ± 0.08	—	1.22 ± 0.10	0
3.0	Spherical + rodlike	3.90 ± 0.08	220 ± 15	0.85 ± 0.06	9 ± 1
3.3	Spherical + rodlike	3.90 ± 0.08	350 ± 25	0.72 ± 0.04	20 ± 2
3.7	Spherical + rodlike	3.90 ± 0.08	400 ± 35	0.57 ± 0.04	42 ± 4

scale shows a straight line with the slope approaching -1 with increasing KCl concentration; this suggests the formation of rodlike micelles at higher KCl concentrations [26, 27]. The solid curves in figure 1 are the fitted data. The structure of the micelles and their parameters as obtained from the analysis using equation (2) are given in table 1.

Table 1 shows that at low KCl concentrations (up to 2.1 M) the block copolymer solution consists of spherical micelles. The data are fitted for spherical micelles coexisting with unimers. It is expected that most of the block copolymers dissolved in the present systems for different salt concentrations and temperatures form micelles. However, a small fraction of block copolymers may be present as unimers at low salt concentrations or temperatures. The scattering from such unimers has been used to adjust the fitting in these systems. The radius of gyration of the unimers is assumed to be 1.8 nm as reported in the literature [28]. The core radius as well as the volume fraction of the spherical micelles increase with the KCl concentration. The polydispersity in the core radius of the micelles remains almost the same ($15 \pm 2\%$) in these systems. Once all unimers have been converted into spherical micelles and the hydrophobic chains inside the micelles stretched to the maximum, this leads to the spherical to rodlike transition of micelles. The block copolymer solution at and beyond the KCl concentration of 3.0 M consists of rodlike micelles coexisting with spherical micelles. The rodlike micelle fraction increases from 9 to 42% on increasing the salt concentration from 3.0 to 3.7 M. On the other hand, the total volume fraction of micelles decreases as expected because hydrated water to micelles is reduced on the formation of rodlike micelles [29]. The length of the micelles increases with an increase in the KCl concentration.

The fitting of data for systems consisting of mixtures of rodlike and spherical micelles in figure 1 is based on a linear dependence on the varying slope of the scattering cross-section on a log-log scale in the low Q region. The rodlike micelles show a straight-line behaviour with slope -1 in the Q range $1/l < Q < 1/R$, where R is the radius and $L (=2l)$ is the length of the micelle [30]. The data in figure 1 show slopes of -0.71 , -0.90 and -0.98 for KCl concentrations of 3.0, 3.3 and 3.7 M, respectively. This varying slope of scattering data can only be obtained using the system consisting of rodlike as well as spherical micelles. We compare the calculated curves in figure 2 where (a) all the micelles are rodlike and (b) both rodlike and spherical micelles coexist. In the case when all the spherical micelles convert to rodlike (figure 2(a)), the significant linear dependence similar to that of scattering data is only seen when the length of the rodlike micelles is higher than 100 nm. However, all the data show

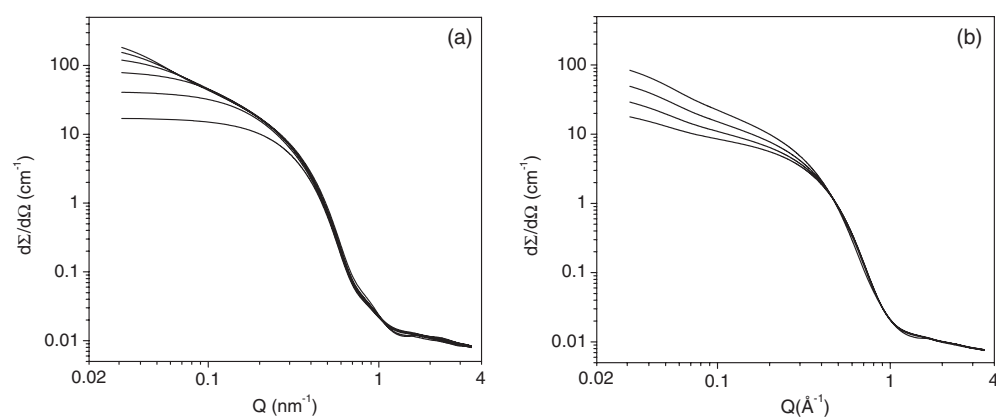


Figure 2. Calculated scattering profiles for block copolymer solution consisting of (a) only rodlike micelles and (b) both rodlike and spherical micelles. The curves in (a) from bottom to top correspond to the rodlike micelles with fixed core radius $R = 3.9$ nm and varying lengths $L = 10, 25, 50, 100, 200$ and 400 nm, respectively. The curves in (b) from bottom to top correspond to the mixtures of rodlike ($R = 3.9$ nm, $L = 400$ nm) and spherical micelles ($R = 3.9$ nm) with increasing rodlike micelle fraction $\phi_r = 5, 10, 20$ and 40% , respectively.

similar slopes in their respective Q range $1/l < Q < 1/R$ and the difference between different data exists below the Q range of $1/l$ of different length micelles. These data (figure 2(a)) show a very different behaviour than those observed in figure 1, and thus rule out the possibility of formation of all rodlike micelles. It was therefore fitted that the system consists of both rodlike and spherical micelles, where the slope of the scattering pattern can be tuned with varying fraction of rodlike micelles present in the system (figure 2(b)).

Figures 3 and 4 show the SANS data of 0.5 wt% P85 in the presence of salts KF and K_2CO_3 , respectively. These data follow a similar trend as has been observed in the case of KCl (figure 1). However, the concentration scales of salts needed to produce similar results are different in the three cases. Thus the phase separation of micelles in the presence of KCl, KF and K_2CO_3 occurs at very different concentrations of 3.8, 1.42 and 0.61 M, respectively. The micellar parameters on additions of KF and K_2CO_3 are given in tables 2 and 3, respectively. The addition of KF shows the formation of rodlike micelles at a concentration of 1.23 M and only 6% of spherical micelles at this concentration convert to rodlike micelles. The fraction of rodlike micelles increases from 6 to 35% on increasing the KF concentration from 1.23 to 1.4 M. In the case of addition of K_2CO_3 , the rodlike micelles are not formed up to the concentration of 0.57 M and the rodlike micelle fraction is only 6% at 0.6 M before the phase separation (0.61 M) occurs.

SANS data on 0.5 wt% P85 in the presence of 0.35 M KF at different temperatures are shown in figure 5. It is observed that the effect of increasing temperature is similar to that of adding salt. This system shows the spherical micelles up to $50^\circ C$ (table 4). The core radius of the micelles increases with temperature. At higher temperatures rodlike micelles coexist with the spherical micelles and the fraction of spherical micelles converting to rodlike micelles at $58^\circ C$ prior to the cloud point ($60^\circ C$) has been found to be 35%. We have found no systemic studies in the literature similar to that presented here on low P85 concentration as a function of temperature or any salt concentrations. The results reported by Mortensen [31] for 1 wt% P85 at fixed temperature of $80^\circ C$ suggest the existence of only rodlike micelles. However, the data and the fit shown are over a very limited Q range. For higher concentration samples the inter-particle structure factor still dominates the scattering function, and detailed information

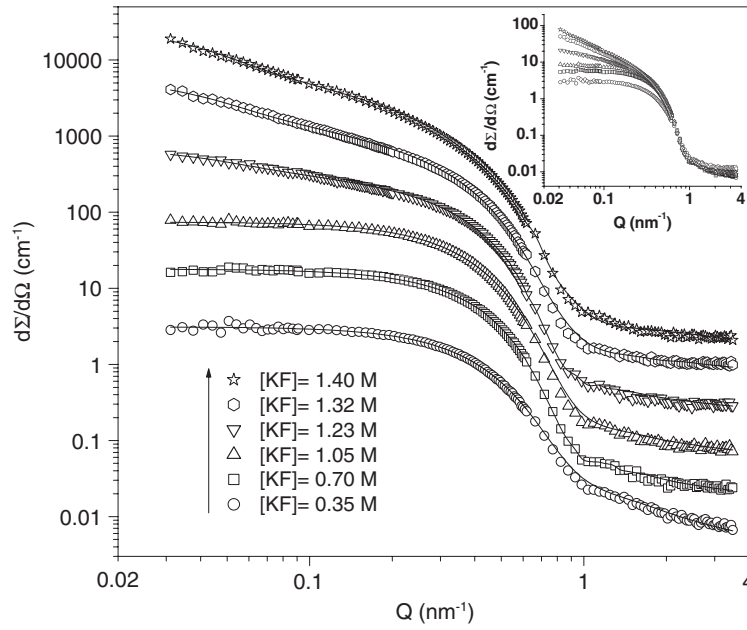


Figure 3. SANS data from 0.5 wt% P85 block copolymer solution at 30 °C with varying KF concentration. To show the clarity of the fits the data for increasing KF concentrations are shifted vertically. The inset shows the data without any shifting.

Table 2. Fitted structural parameters of P85 block copolymer micelles in the presence of varying concentration of KF at fixed temperature (30 °C).

KF concentration (M)	Structure	Core radius R_m (nm)	Length L (nm)	Total micelle vol. fraction ϕ (%)	Rodlike micelle fraction ϕ_r (%)
0.35	Spherical	3.50 ± 0.08	—	0.67 ± 0.06	0
0.70	Spherical	3.56 ± 0.08	—	1.23 ± 0.10	0
1.05	Spherical	3.90 ± 0.08	—	1.03 ± 0.10	0
1.23	+ rodlike	3.90 ± 0.08	180 ± 10	0.98 ± 0.08	6 ± 1
1.32	+ rodlike	3.90 ± 0.08	300 ± 20	0.82 ± 0.06	19 ± 2
1.40	+ rodlike	3.90 ± 0.08	390 ± 35	0.64 ± 0.04	35 ± 4

on the form of micelles has not been obtained due to complications in the calculation of $S(Q)$ for non-spherical micelles [19, 32, 33]. Most of the results on the formation of rodlike micelles are qualitative, based on the large increase in the scattering cross-section and the scattering profile, showing a slope of about -1 in the log-log plot.

While the dehydration from blocks of copolymer decides the structure of micelles, the stability of these structures is still decided by the delicate balance of hydrophilic repulsion to the hydrophobic attraction between the copolymer molecules. The dehydration beyond a limit

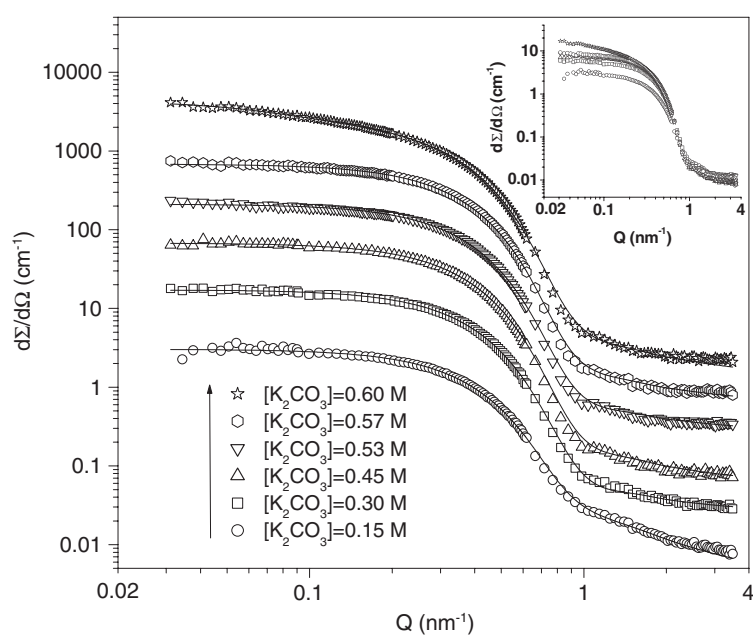


Figure 4. SANS data from 0.5 wt% P85 block copolymer solution at 30 °C with varying K_2CO_3 concentration. To show the clarity of the fits the data for increasing K_2CO_3 concentrations are shifted vertically. The inset shows the data without any shifting.

Table 3. Fitted structural parameters of P85 block copolymer micelles in the presence of varying concentration of K_2CO_3 at fixed temperature (30 °C).

K_2CO_3 concentration (M)	Structure	Core radius R_m (nm)	Length L (nm)	Total micelle vol. fraction ϕ (%)	Rodlike micelle fraction ϕ_r (%)
0.15	Spherical	3.65 ± 0.8	—	0.65 ± 0.04	0
0.30	Spherical	3.67 ± 0.8	—	1.12 ± 0.10	0
0.45	Spherical	3.82 ± 0.8	—	1.15 ± 0.10	0
0.53	Spherical	3.90 ± 0.8	—	1.02 ± 0.08	0
0.57	Spherical	3.90 ± 0.8	—	0.94 ± 0.08	0
0.60	+ rodlike	3.90 ± 0.8	85 ± 5	0.88 ± 0.08	6 ± 1

makes the hydrophobic attraction dominating and the phase separation, which is surfactant rich in concentration, occurs at the cloud point [34]. The conformation of the PPO block in spherical micelles depends on the hydrated water associated with the PEO blocks, which can be controlled with the addition of salts or varying the temperature. Once these blocks have been stretched to the maximum as the hydration to micelles decreases, the entropic contribution from the stretched PPO blocks to the free energy per micelle gives rise to the formation of rodlike micelles [7]. The effect of addition of salt has been found to be similar to that of increasing temperature. The hydration of salt ions is entropically favoured by the dehydration of the micelles. The propensity of salt to induce micellization depends on the hydration properties of their ions [35–38]. Hydration of anions Cl^- , F^- and CO_3^{2-} follows the order $Cl^- < F^- < CO_3^{2-}$ [39]; the concentrations of corresponding salts needed to induce

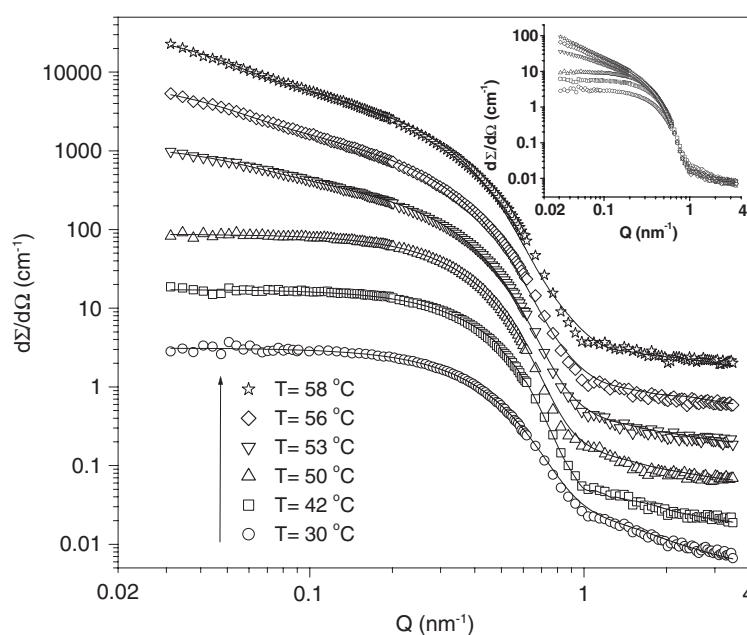


Figure 5. SANS data from 0.5 wt% P85 + 0.35 M KF block copolymer solution with varying temperature. To show the clarity of the fits the data for increasing temperature are shifted vertically. The inset shows the data without any shifting.

Table 4. Fitted structural parameters of P85 block copolymer micelles at different temperatures.

Temperature (°C)	Structure	Core radius R_m (nm)	Length L (nm)	Total micelle vol. fraction ϕ (%)	Rodlike micelle fraction ϕ_r (%)
30	Spherical	3.55 ± 0.8	—	0.66 ± 0.06	0
42	Spherical	3.66 ± 0.8	—	1.28 ± 0.10	0
45	Spherical	3.86 ± 0.8	—	1.10 ± 0.10	0
50	Spherical	4.12 ± 0.8	—	0.85 ± 0.06	0
53	Spherical + rodlike	4.12 ± 0.8	150 ± 10	0.72 ± 0.04	17 ± 2
56	Spherical + rodlike	4.12 ± 0.8	280 ± 20	0.65 ± 0.04	27 ± 3
58	Spherical + rodlike	4.12 ± 0.8	480 ± 40	0.57 ± 0.04	35 ± 4

rodlike micelles have also been observed in the same order. To the best of our knowledge this is the first report suggesting that rodlike micelles coexist with spherical micelles even up to onset of the clouding in these systems.

In summary, the effect of addition of salts has been compared with the effect of increasing temperature on the formation of rodlike micelles in aqueous block copolymer solutions. These studies show that an entropy-induced salting-out effect in the presence of salts can be used to induce rodlike micelles at ambient temperature. Rodlike micelles coexist with spherical

micelles at higher salt concentrations or temperature, even up to onset of the phase separation. The choice of salt can be used to control the population of the rodlike micelles in these systems.

References

- [1] Alexandridis P and Lindman B 2000 *Amphiphilic Block Copolymers* (Amsterdam: Elsevier Science)
- [2] Kataoka K, Harata A and Nagasaki Y 2001 *Adv. Drug Deliv. Rev.* **47** 113
- [3] Forster S and Konard M 2003 *J. Mater. Chem.* **13** 2671
- [4] Hamely I W 2005 *Block Copolymers in Solution: Fundamentals and Applications* (New York: Wiley)
- [5] Chu B 1995 *Langmuir* **11** 414
- [6] Alexandridis P and Hatton T A 1995 *Colloids Surf. A* **96** 1
- [7] Mortensen K 1996 *J. Phys.: Condens. Matter* **8** A103
- [8] Hamely I W 2001 *J. Phys.: Condens. Matter* **13** R643
- [9] Riess G 2003 *Prog. Polym. Sci.* **28** 1107
- [10] Nakashima K and Bahadur P 2006 *Adv. Colloid Interface Sci.* **123–126** 75
- [11] Malmsten M and Lindman B 1992 *Macromolecules* **25** 5440
- [12] Mortensen K and Brown W 1993 *Macromolecules* **26** 1128
- [13] Alexandridis P, Nivaggioli T and Hatton T A 1995 *Langmuir* **11** 1468
- [14] Jain N J, Aswal V K, Goyal P S and Bahadur P 1998 *J. Phys. Chem. B* **102** 8452
- [15] Ganguly R, Aswal V K, Hassan P A, Gopalakrishnan I K and Yakhmi J V 2005 *J. Phys. Chem. B* **109** 5653
- [16] Mortensen K 1998 *Curr. Opin. Colloid Interface Sci.* **3** 12
- [17] Pedersen J S and Svaneborg C 2002 *Curr. Opin. Colloid Interface Sci.* **7** 158
- [18] Aswal V K and Goyal P S 2004 *Pramana: J. Phys.* **63** 65
- [19] Hamely I W and Castelletto V 2004 *Prog. Polym. Sci.* **29** 909
- [20] Keiderling U and Wiedenmann A 1995 *Physica B* **213/214** 895
- [21] Keiderling U 2002 *Appl. Phys. A* **74** S1455
- [22] Chen S H and Lin T L 1987 *Methods of Experimental Physics* vol 23B, ed D L Price and K Skold (New York: Academic) p 489
- [23] Pedersen J S 2000 *J. Appl. Crystallogr.* **33** 637
- [24] Pedersen J S, Posselt D and Mortensen K 1990 *J. Appl. Crystallogr.* **23** 321
- [25] Bevington P R 1969 *Data Reduction and Error Analysis for Physical Sciences* (New York: McGraw-Hill)
- [26] Aswal V K, De S, Goyal P S, Bhattacharya S and Heenan R K 1998 *Phys. Rev. E* **57** 776
- [27] Duval M, Waton G and Schosseler F 2005 *Langmuir* **21** 4904
- [28] Aswal V K and Kohlbrecher J 2006 *Chem. Phys. Lett.* **425** 118
- [29] Mortensen K and Talmon Y 1995 *Macromolecules* **28** 8829
- [30] Glatter O and Kratky O 1982 *Small-Angle X-Ray Scattering* (London: Academic)
- [31] Mortensen K 2001 *Polym. Adv. Technol.* **12** 2
- [32] Mortensen K and Pedersen J S 1993 *Macromolecules* **26** 805
- [33] Mao G M, Sukumaran S, Beaucage G, Saboungi M L and Thiyagarajan P 2001 *Macromolecules* **34** 552
- [34] Degiorgio V 1987 *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions* ed V Degiorgio and M Corti (Amsterdam: North-Holland) p 303
- [35] Alexandridis P and Holzwarth J F 1997 *Langmuir* **13** 6074
- [36] Aswal V K, Goyal P S, Kohlbrecher J and Bahadur P 2001 *Chem. Phys. Lett.* **349** 458
- [37] Su Y L, Liu H Z, Wang J and Chen J Y 2002 *Langmuir* **18** 865
- [38] Mata J P, Majhi P R, Guo C, Liu H Z and Bahadur P 2005 *J. Colloid Interface Sci.* **292** 548
- [39] Israelachvili J N 1992 *Intermolecular and Surface Forces* (New York: Academic)