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ORIGINAL CONTRIBUTION

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Micellization of triblock copoly(ethyleneoxide/tetrahydrofuran/ethylene oxide)

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Abstract The association behaviour of triblock copoly(ethylene oxide/tetrahydrofuran/ethylene oxide), in particular $E_{100}T_{27}E_{100}$, in aqueous solutions has been investigated by means of static and dynamic light scattering, nuclear magnetic resonance (NMR) and surface tension techniques. On raising the polymer concentration at room temperature, the copolymer aggregates to form micelles with an aggregation number of about 105 ($R_{G,\,\mathrm{mic}} \approx 15$ nm and $R_{H,\,\mathrm{mic}} \approx 13$ nm, as revealed by light scattering and FT-PGSE NMR measurements, respectively). The micelles are kinetically quite stable, the micellar lifetime is shown to be more than 1 h. The residence time of a single unimer in a micelle is more than 140 ms. The apparent radius of gyration $R_{G,\,\mathrm{mic}}$ is fairly independent of concentration, but large effects are observed on varying the temperature. Raising the temperature initially results in an increase of the apparent micellar size, followed by a maximum at an intermediate temperature ($\approx 45\,°\mathrm{C}$). At higher temperatures a contraction of the micelles is observed. The shape of the micelles also appear to vary in this temperature interval. The interactions responsible for these phenomena are discussed in terms of, e.g., the temperature-dependent solubility of the alkylene oxide segments in water and polydispersity effects.

Key words Block copolymers – micelle – temperature

Introduction

The association behaviour of copolymers is of industrial as well as scientific interest. The latter has during the past years resulted in numerous publications on the subject (cf. Refs. [1–4]. A substantial part of the work in the area concerns the micellisation and mesophase formation of amphiphilic alkylene oxide block copolymers of the copoly(ethylene oxide/propylene oxide) type in aqueous solution. Interesting phenomena exhibited by these systems include a strongly temperature-dependent micellisation and a thermally reversible "pseudo" gelation at higher concentrations involving mesophase formation of copolymer micelles rather than of unimers [5–7]. The present work is primarily centred on the study of the influence of concentration, temperature and salt on the micellar properties of triblock copoly(ethylene oxide/tetrahydrofuran/ethylene oxide) in water. This association behaviour of this copolymer has to our knowledge not been investigated previously. The molar mass and size of the micelles are determined by a combination of gel chromatography and light scattering, referred to as GPC-LS. Micellar characterisation was also performed by diffusion measurements with dynamic light scattering (DLS) and a self-diffusion nuclear magnetic resonance technique (FTPGSE-NMR). The copolymer system discussed in this paper displays some intriguing variation of the micellar properties, especially on changing the temperature. Part of this behaviour is similar to that displayed by block copoly(ethylene oxide/propylene oxide/ethylene oxide), often referred to by the trade name Pluronic, while other aspects differ substantially.

Experimental

A triblock copoly(ethylene oxide/tetrahydrofuran/ethylene oxide), denoted $E_{100}T_{27}E_{100}$, was synthesized by Akzo Nobel Surface Chemistry; Stenungsund, Sweden. Before use, the polymer was dialysed against a Millipore water, recrystallised in acetone and finally freeze-dried. As dialysing membrane, Ultrasette from Filtron Technology Corp. with a molecular weight cut-off of 6000 was used. The molecular weight (given by the manufacturer) is about $12\,500\ \mathrm{g\,mol^{-1}}$. The block ratio was obtained from the NMR spectra.

Self-diffusion NMR measurements were performed by means of the FTPGSE technique [8], with a JEOL FX-60 spectrometer operating at 60 MHz. The 90°-τ-180°-τ-is a echo pulse sequence with two additional rectangular magnetic field gradients pulses of magnitude G, separation Δ and duration δ. The echo amplitude at 2τ, $A(2\tau)$, is given by

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

where γ is the gyro magnetic ratio and T_2 the transverse relaxation time [8].

The dynamic light scattering apparatus used is a Photon Correlation spectrometer, PCS-100 model 164, from Malvern equipped with an argon ion laser ($\lambda = 501.7$ nm) positioned at a measuring angle of 120°. A Multi-8 Correlator, series 7032 from Malvern, is connected to the laser. The autocorrelation function of the scattered light is an exponential function of the time t, $f(t) \sim \exp(-t/\tau_c)$, where τ_c is the characteristic decay time. The characteristic decay time is related to the diffusion coefficient (D) as described in Eqs. (2) and (3) [9, 10]:

$$\tau_c = \frac{1}{q^2D}\ , \quad (2)$$

$$q = \frac{4\pi n}{\lambda}\sin(\theta/2)\ . \quad (3)$$

Here, q is the wave vector, n the refractive index, λ the wavelength and θ the angle of observation. R_H was calculated using the Stokes–Einstein equation, $R_H = k_BT/(6\pi\eta D)$, where T is the temperature, k_B the Boltzmann's constant and η the solvent viscosity.

The static light scattering apparatus was a Dawn FHC from Wyatt Technology, which simultaneously measures 15 different angles between 45° and 135° ($\lambda = 632.8$ nm). A pump from Pharmacia, type P-500, and a Superose 6 GPC column (Pharmacia) are connected to the Dawn FHC. A differential refractometer (from LKB, type 214) working at 950 nm, was placed after the light scattering equipment. This was used for on-line mass detection (see Fig. 1). The light scattered from a dilute polymer solution

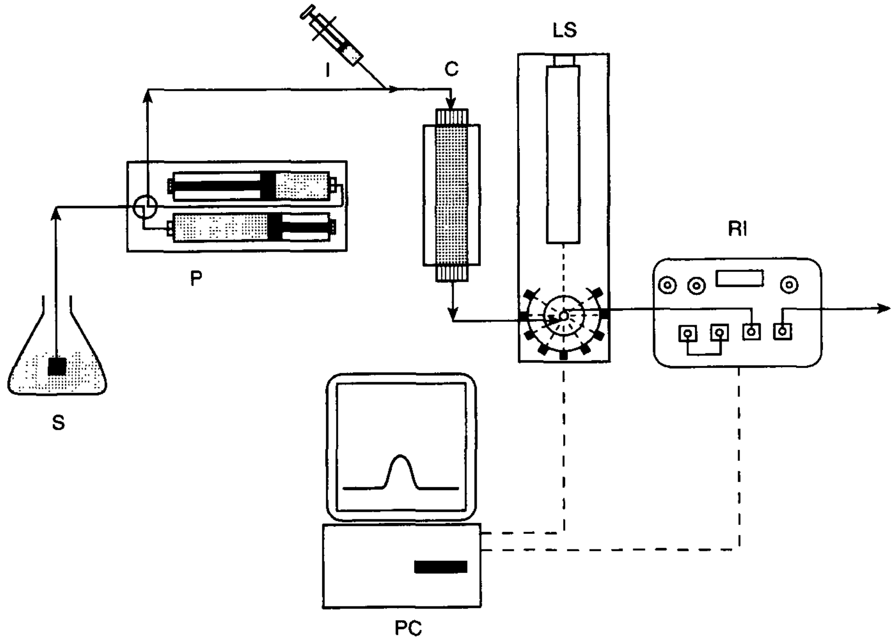


Fig. 1 Schematic representation of the GPC-LC apparatus. **S** solvent (mobile phase 0.05 M $NaNO_3$), **P** pump, **I** injection, **C** column, **LS** light scatter, **RI** refractometer, **PC** personal computer

can be expressed as

$$\frac{KC}{\Delta R(\theta)} = \frac{1}{M_W}\left(1 + \frac{16\pi^2 n_0^2 R_G^2}{3\lambda_0^2}\sin^2(\theta/2) + \cdots\right) + 2A_2C + \cdots, \qquad (4)$$

where C is the polymer concentration, K, an optical constant and $\Delta R(\theta)$, the difference between the Rayleigh ratio of the solution and that of the pure solvent [11]. M_W is the average molecular weight molar mass, R_G^2 the mean square radius of gyration, λ_0 the wavelength in vacuum, n_0 the solvent refractive index and A_2 the second viral coefficient. Note that, in general, the application of light scattering theory to block copolymer solutions leads to the determination of an apparent average molecular weight molar mass and mean square radius gyration [11]. However, Eq. (4) will also apply for a block copolymer, giving the true molecular weights and radius, if the different types of blocks in the polymer gives the same contribution to the differential refractive index increment (dn/dc) [11]. The above explained static light scattering arrangement is using Eq. [4] for each slice (0.01 ml) on the GPC spectra to calculate both the M_W and R_G^2. The presented result in this paper is the weighted-average molecular weight and the z-average mean square radius of the results of the slice results in each peak. The refractive index increment (dn/dc) was determined by means of a Wyatt Optilab 903 Interferometric Refractometer ($\lambda = 633$ nm). Measurements were performed at concentrations between 0.05 and 0.3 wt%. The dn/dc value for the copolymer, $E_{100}T_{27}E_{100}$, obtained from these measurements is 0.1485 ml g^{-1}. This was shown to be almost independent of the copolymer composition. The corresponding value for $E_{38}T_{15}E_{38}$ (the same type of copolymer with a different relation between the E and T block) was 0.1487 ml g^{-1}, indeed indicating that the E and T blocks have very similar dn/dc values. We can therefore evaluate with confidence the light scattering data with the same principles as for homopolymers. The temperature dependence of the dn/dc parameters was evaluated at 25 °C and 50 °C for $E_{100}T_{27}E_{100}$ and these data show that the dn/dc value increases with 0.00016 per degree (Table 1).

Surface tension measurements were performed at 23 ± 1 °C by means of the drop volume technique. A thorough description of the apparatus used and the measurement procedure is given in ref. [12].

Table 1 Refractive index increment measurement at 633 nm

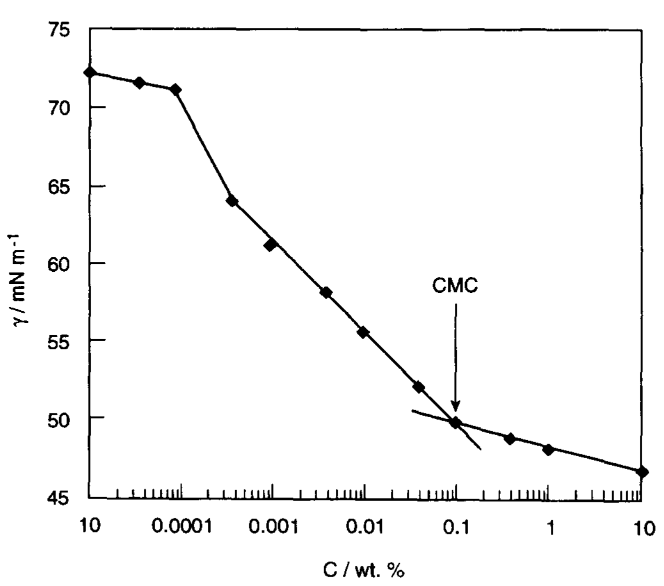
Polymer	Temp [°C]	(dn/dc) [ml/g]
$E_{100}T_{27}E_{100}$	25	0.1485
$E_{100}T_{27}E_{100}$	50	0.1497
$E_{38}T_{15}E_{38}$	25	0.1487

Results and discussion

Surface tension

The surface tension (γ) versus the logarithm of the bulk concentration, log C, measured at 25 °C by the drop volume technique for $E_{100}T_{27}E_{100}$ is shown in Fig. 2. The plot shows after a small drop in γ with log C a linear decrease γ with log C with a slope ≈ -5.8. Then, the decrease of γ with C slows down substantially, but no stable plateau is reached in the concentration interval studied. It is interesting to note that the breakpoint between the two linear regimes is quite clear-cut. This behaviour differs somewhat from the observations in copoly(ethylene oxide/propylene oxide/ethylene oxide systems), where an intermediate regime often is found in the region just prior to the cmc and the breakpoint prior to this regime is proposed to correspond to the formation of unimolecular micelles [13, 14]. This region is not present in the surface tension curve for the $E_{100}T_{27}E_{100}$ studied in this work. The cmc of this polymer is ≈ 0.1 wt%, identified by the hollow arrow at the breakpoint between the two linear regimes shown in Fig. 2. However, as evident from the GPC-LS data (vide infra), a limited amount of micelles seems to be present in the system also below this concentration. The surface tension at the cmc is relatively

Fig. 2 The surface tension for $E_{100}T_{27}E_{100}$ as a function of concentration at 25 °C

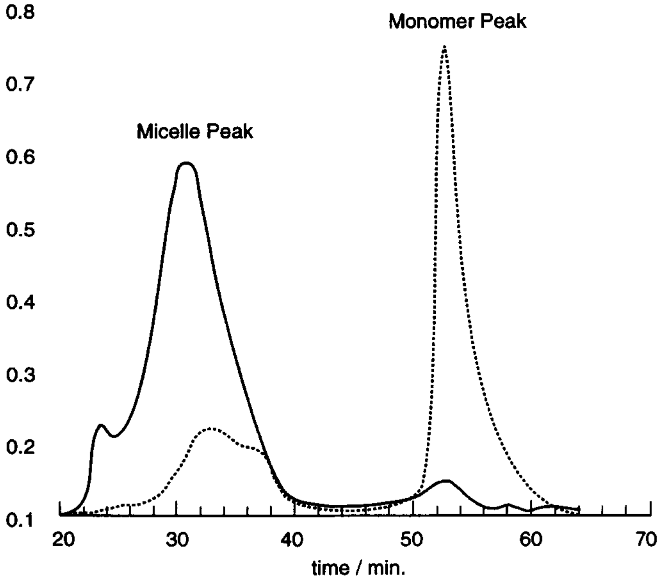


high $\gamma_{\mathrm{cmc}} = 50\ \mathrm{mN\,m^{-1}}$. However, as mentioned previously, the surface tension continues to decrease slightly with the polymer concentration also above the cmc, atleast until $C = 10$ wt%, where $\gamma = 47\ \mathrm{mN\,m^{-1}}$. The reason for this is probably polydispersity of the copolymer sample. The surface tension versus concentration curve indicates that the monomers activity increases up to at least 10%.

Light scattering

The effects of concentration on the radius of gyration (R_G) and the molecular weight (M_W) of the copolymer micelles was first investigated by GPC-LS. The micelles could be separated from the unimers by the GPC-column in the same way as for $E_{100}P_{70}E_{100}$ (Pluronic F127) [5], see Fig. 3. It should be noted that the measurements were found independent of the flow rate between 0.15 ml min^{-1} and 0.30 ml min^{-1} (results not shown), which corresponds to residence times in the column between 30 and 60 min respectively. Since the micelles are separated from the unimers in the column, the micelles are no longer in equilibrium with the surroundings and may be expected to dissociate. However, the absence of a flow rate dependence indicates that the micelles are stable at least during 60 min. Moreover, there is also a clear baseline separation between the monomer and micelle peaks as is shown in Fig. 3. The light scattering intensity from the first peak, corresponding to the micelles, is much higher than that of the second, while the signal from the refractive index detector is larger for the second peak. An approximate molecular weight of $(2 \pm 1) \times 10^4\ \mathrm{g\,mol^{-1}}$ was estimated for the second peak (in qualitative agreement with the molecular weight of the $E_{100}T_{27}E_{100}$ unimers which is $\approx 1.1 \times 10^4\ \mathrm{g\,mol^{-1}}$). The corresponding value for the first peak is $(1 \pm 0.05) \times 10^6\ \mathrm{g\,mol^{-1}}$, indicating that this represents the micellar fraction of the copolymer sample. The values of M_W and R_G for the unimers will not be discussed further in this work, since the signal/noise ratios for the light scattering data for the unimers were too small.

Fig. 3 GPC chromatogram for $E_{100}T_{27}E_{100}$ at 25 °C and a concentration at 0.5 wt%. The **dotted line** is the **RI** signal and the **full line** is the **light scatter** signal



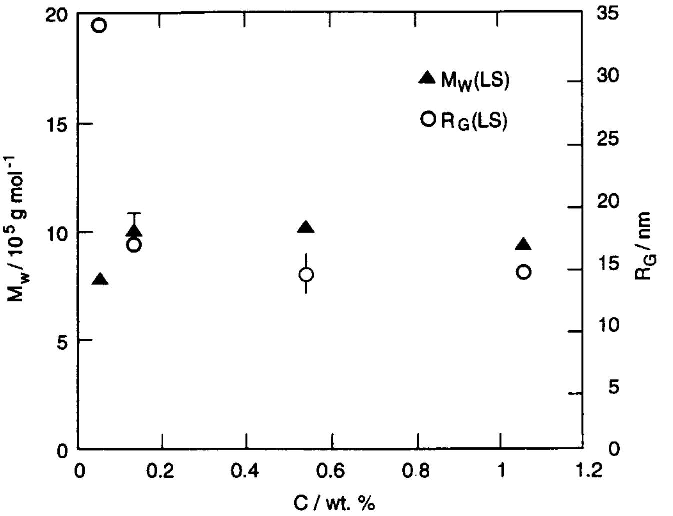


Fig. 4 Concentration dependence of M_W and R_G for $E_{100}T_{27}E_{100}$ micelles at 25 °C

Measurements of M_W and R_G of the copolymer micelles versus the polymer concentration (C) were performed between 0.5 and 1 wt%. The polymer solution was first allowed to equilibrate at a given concentration before being injected into the GPC-column and analysed by the GPC-LS instrument. We chose not to go to higher concentrations, because of problems with the column due to saturation. It is clear from Fig. 4, that both $R_{G,\mathrm{mic}}$ and $M_{W,\mathrm{mic}}$ for $E_{100}T_{27}E_{100}$ are quite constant in this interval ($M_{W,\mathrm{mic}} \approx 1 \times 10^6\ \mathrm{g\,mol^{-1}}$ and $R_{G,\mathrm{mic}} \approx 15$ nm), indicating that the micellar properties are insensitive to concentration in this region. Note that the somewhat higher $R_{G,\mathrm{mic}}$ value observed at 0.052 wt% is most likely due to the rather high experimental noise level at this rather low concentration. The molecular weight of the micelles corresponds to an aggregation number of ≈ 105. An interesting observation was that the fraction of $E_{100}T_{27}E_{100}$ micelles only increases from 24 to 32 wt% over the interval studied while the aggregation number was constant. The reason for this observation was, however, not investigated further. The GPC-LS data were also checked by batch

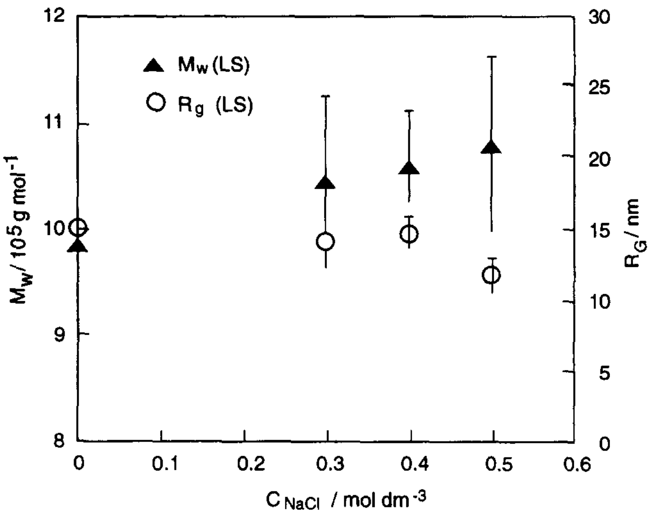


Fig. 5 Salt dependence of M_w and R_G for $E_{100}T_{27}E_{100}$ micelles at 25 °C and a polymer concentration of 0.5 wt%

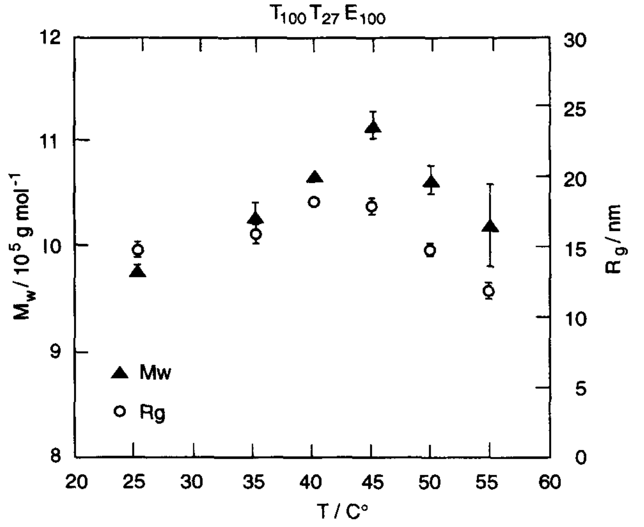


Fig. 6 Temperature dependence of M_w and R_G for $E_{100}T_{27}E_{100}$ micelles. The polymer concentration is 1 wt%

measurements performed at the same temperature (25 °C). These measurements resulted in a molecular weight of 1.2×10^6 g mol^{-1} and 19 nm radius of gyration, which both are in relatively good agreement with the values obtained by means of GPC-LS (see Fig. 4).

The effect of added salt, NaCl, was also investigated. Measurements were made at salt concentrations up to 0.5 M NaCl. A small increase of $M_{W,\text{mic}}$ and a concomitant decrease of $R_{G,\text{mic}}$ was observed on increasing the NaCl content from 0 to 0.5 M (Fig. 5). The same behaviour is observed in micellar systems of non-ionic surfactants upon additions of most inorganic salts [15, 16]. This salting-out effect is due to the fact that adding salt makes water a poorer solvent for ethylene oxide based surfactant and block copolymers [17, 18]. The salting-out effect, consequently lowers the two-phase boundary for non-ionic and copolymer systems. It also results in denser micelles with an increasing molecular weight of the micelles like observed for the $E_{100}T_{27}E_{100}$ copolymer micelles when adding NaCl.

The temperature dependence of the $E_{100}T_{27}E_{100}$ micelles was investigated at temperatures ranging from 25 °C to 55 °C. Measurements were not possible above the latter temperature, due to stability problems of the Superose 6 GPC column. The measurements were performed at 1 wt% and the data from these measurements are shown in Fig. 6. A rather remarkable temperature dependence is observed for the micellar radius of gyration ($R_{G,\text{mic}}$). This involves an increase of R_G at low temperatures, followed by a maximum at $T \approx 45$ °C, and then, on further increasing the temperature, a pronounced decrease is observed. Only a small increase was observed in the molecular weight of the micelles ($M_{W,\text{mic}}$) in the same temperature interval. This is in strong contrast to the observations for the Pluronic F 127 copolymer. Here a temperature increase results in an increase of both $M_{W,\text{mic}}$ and $R_{G,\text{mic}}$ from 5×10^5 to 1.4×10^6 g mol^{-1} and 5.7 to 8.1 nm, respectively [1].

The temperature dependence of the micellar size was also studied by FTPGSE-NMR. Typical plots of the logarithms of the echo amplitude ($A(2\tau)$) as a function of the pulse duration, δ, are displayed in Fig. 7. The data can, due to the difference between the self-diffusion coefficient of the monomers and the micelles, not be fitted by a single-exponential. This shows that the residence times of the copolymers in the micelles are larger than 140 ms, which is the separation between the gradient pulses. It should be mentioned that the measurements were also performed in CD_3COCD_3, in which copolymer association into micelles is avoided. These measurements resulted in a nice single-exponential relation between $A(2\tau)$ and $\delta(\Delta - \delta/3)$ proving that the curve shape in D_2O is not due to the polydispersity of the unimers. The single-exponential fit yielded a value of the diffusion coefficient, $D = 9.9 \times 10^{-11}$ m^2 s^{-1}. Biexponential fits were used to fit FTPGSE-NMR data obtained in D_2O [19, 20]. The measurements were performed at 1 and 10 wt%, respectively. $A(2\tau)$ versus $\delta^2(\Delta - \delta/3)$ curves were at all temperatures nicely biexponential at 10 wt%. However, for the lower concentration, $C = 1$ wt%, a rather strange behaviour was observed. Here, the biexponential character of the curve decreased with increasing temperature (see Fig. 8). The curve at $T = 49.5$ °C is finally nicely fitted by a single exponential, with a resulting diffusion coefficient of

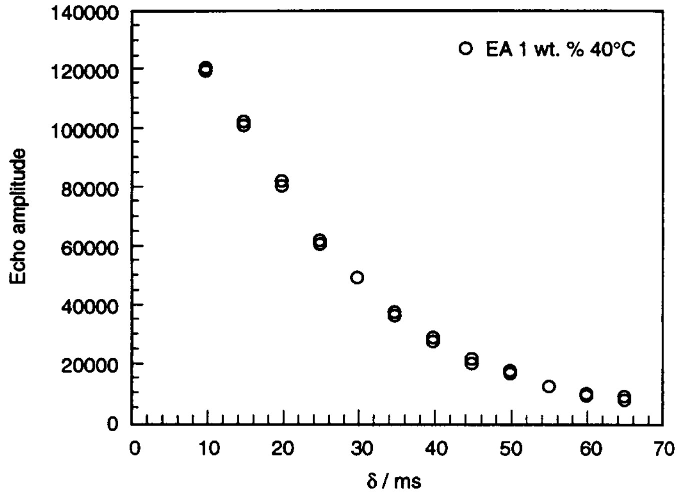


Fig. 7 Self diffusion measurement of $E_{100}T_{27}E_{100}$ at 1 wt% and 40 °C. Here the echo amplitude is plotted against δ

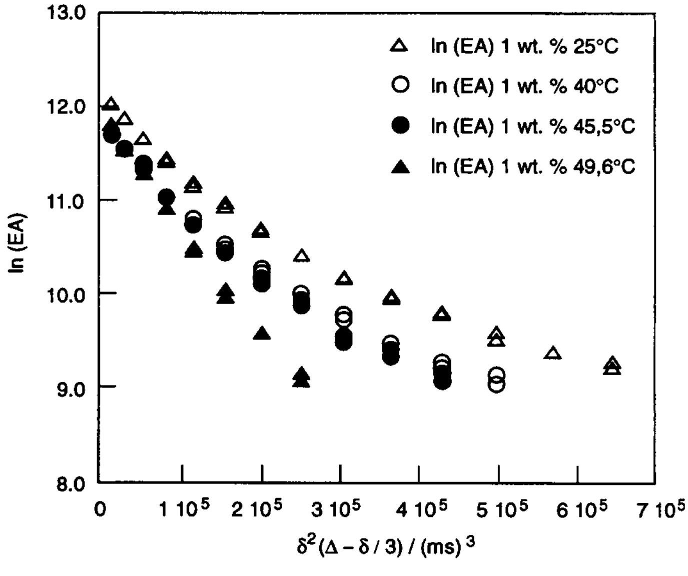


Fig. 8 The biexponential character of the echo amplitude in a 1 wt% solution of $E_{100}T_{27}E_{100}$ at four different temperatures

1.0×10^{-10} $m^2 s^{-1}$, which is similar to the diffusion coefficient found for $E_{100}T_{27}E_{100}$ in acetone. This implies that only free copolymer molecules contribute to the detected signals at this concentration and temperature. The behaviour arises from a broadening of the micellar peak with increasing temperature. Upon raising the temperature the micellar contribution will vanish for the low concentration samples, while for those with a higher concentration, the micellar concentration is large enough to give a contribution even as the peak gets broader.

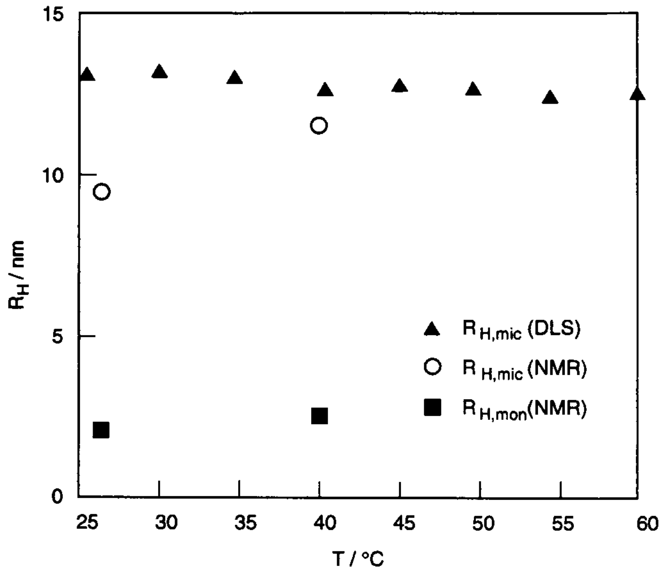


Fig. 9 Hydrodynamic radius of the micelle and the monomer of $E_{100}T_{27}E_{100}$ measured with FT-PGSE NMR (filled squares monomers, circles micelles) and dynamic light scattering (filled triangles)

The micellar and unimer size obtained from the biexponential fits at 1 wt%, turned out to be in good accord with the LS data presented above. The diffusion coefficients for the 10 wt% solution were approximately 50% slower than for the 1 wt%. This is due to the increasing obstruction between polymer molecules micelles at higher concentrations.

The corresponding dynamic light scattering data only reflects the micellar diffusion. This is because the micellar aggregates gives a much stronger light scattering signal than the unimers. As a result the autocorrelation function exhibits monoexponential decay. The signal/noise ratio in the determination of the micellar hyrodynamic radius by light scattering is much better than that obtained by NMR diffusion measurement, since no biexponential fitting is involved. The hydrodynamic radius obtained from dynamic light scattering (Fig. 9) agrees reasonably well with the micellar hydrodynamic radius obtained by the biexponential fitting to the NMR diffusion data (Fig. 9). Nevertheless, both sets of data show that the micellar hydrodynamic radius is temperature-independent, in contrast to the temperature dependence of the radius of gyration. The R_H values were in both cases also found to be smaller than R_G. We also compared the $E_{100}T_{27}E_{100}$ with the more commonly investigated $E_{100}P_{27}E_{100}$, which has approximately the same molecular weight and number of ethylene oxide segments. Both block copolymers form micelles in water. $E_{100}T_{27}E_{100}$ forms micelles in the whole temperature interval 25–55 °C with a very small change of the cmc values with temperature. $E_{100}P_{70}E_{100}$, on the other hand, does not form micelles until 30 °C and the cmc decreases rather strongly with increasing temperature. The aggregation number of the $E_{100}T_{27}E_{100}$ micelles do not vary with the temperature, while the $E_{100}P_{70}E_{100}$ micelles increases in size when raising the temperature. Water is a poor solvent for the polytetrahydrofuran (PT) already at 25 °C. Therefore, the PT segments associate into a close packed core in the $E_{100}T_{27}E_{100}$ micelles. The size and shape of these micelles will, hence, only be determined by the interaction between polyethylene oxide (PEO) and water. This will not differ much in the temperature interval investigated. For $E_{100}P_{70}E_{100}$, the solubility of polypropylene oxide (PPO) in water is also reduced upon raising the temperature. This induces relatively large effects at the cmc as well as changes in the size and shape of the micelles.

The association dynamics for the two block copolymers is similar. Both $E_{100}T_{27}E_{100}$ and $E_{100}P_{70}E_{100}$ form micelles very rapidly, if the conditions are right, it is nevertheless possible to separate the micelles from the unimers by means of a GPC-column, even though the experimental time is up to 1 h. By this, we can conclude that the micelles of this block copolymers are kinetically rather stable. The lifetime of a block copolymer micelle should be measured in minutes or hours, whereas that of a non-ionic surfactant micelle is often less than a second. The residence time of a unimer in a micelle must be longer than 140 ms, which is the longest time used in the FT-PGSE NMR measurement.

Conclusion

We observed that the $E_{100}T_{27}E_{100}$ micelles at low copolymer concentration, between 0.1 and 1 wt%, are rather independent of both temperature and concentration with respect to the aggregation number. They are further kinetically stable with a micellar lifetime of more than 1 h. The lifetime of a single unimer in the micellar aggregates is more than 140 ms. A micellar solution can therefore be diluted to concentrations less than the CMC without extensive disruption of the micelles for at least 1 h.

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