Dynamics of Block Copolymer Micelles in Aqueous Solution

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ABSTRACT: The dynamics of aqueous micelles of triblock $E_nP_mE_n$ copolymers (E_n = poly(ethylene oxide); P_m = poly(propylene oxide)) is investigated. It is shown on a theoretical basis that the amplitude of the relaxation process associated with the $E_nP_mE_n$ micelle formation−breakup must go from negative to positive upon increasing temperature in relaxation experiments using the temperature-jump (T-jump) method with light scattering detection. New experimental T-jump results for solutions of two different $E_nP_mE_n$ copolymers clearly confirm this prediction. These results do not support the claim made by Kositza et al. [*Langmuir* **1999**, *15*, 322; *Macromolecules* **1999**, *32*, 5539] that the temperature at which the amplitude of the slow process observed in T-jump experiments goes through zero corresponds to a change in the nature of this process, from micelle formation−breakup below this temperature to micelle clustering above this temperature.

Introduction

The dynamics of aqueous micelles of triblock $E_nP_mE_n$ copolymers (E_n = poly(ethylene oxide); P_m = poly(propylene oxide)) has been much investigated since 1995.[1−7] Most investigations were performed using the temperature-jump (T-jump) relaxation method, with light scattering detection of the relaxation processes[1−6] and concerned the copolymer $E_{13}P_{30}E_{13}$ (abbreviated L64).[2−7] The stopped-flow method has also been used to investigate L64 solutions, but to a lesser extent.[6,7]

The T-jump investigation of $E_nP_mE_n$ micellar solutions at temperatures well below the cloud temperature T_C revealed the existence of two relaxation processes.[2−6] These processes were assigned to the exchange of $E_nP_mE_n$ copolymers between micelles and intermicellar solution (fast process) and to the formation−breakup of the copolymer micelles (slow process). This assignment is the same as for solutions of conventional surfactants, and it has been dealt with in the theories of micelle kinetics of Aniansson and Wall,[8] Kahlweit,[9] and Waton.[10]

The fast relaxation process associated with the copolymer exchange is characterized by a positive relaxation amplitude (corresponding to an *increase* of the intensity of scattered light with time) and by a relaxation time τ_1 ranging between 10 μs and 10 ms, depending on the copolymer nature and the temperature. In some studies the values of τ_1 in the microsecond range (corresponding to high copolymer concentrations and copolymers of low molecular weight) were found to be dependent on the angle of observation (angle between the incident and scattered beams).[2,3] This behavior was explained on the basis of a coupling of the surfactant exchange process to the fluctuations of the micelle concentration. The increase of intensity of scattered light with time is due to the incorporation of some free copolymers into the micelles following the jump of temperature.

The slow relaxation associated with the micelle formation−breakup is characterized by a negative amplitude, i.e., a *decrease* of the intensity of scattered light with time.[2−6] The corresponding relaxation time τ_2 has values that range between 0.2 and 100 ms and that depend on concentration.[2,3,5,6] This suggested that for $E_nP_mE_n$ copolymer micelles the formation−breakup proceeds via the so-called coagulation−fragmentation reactions.[2,3,6] An important observation about the micelle formation−breakup relaxation is that its amplitude decreased rapidly and vanished upon increasing temperature. Owing to this fact, the measurements reported in refs 2 and 3 were restricted to relatively low temperatures where the relaxation amplitude was always negative. The measurements on L64 solutions reported in refs 5 and 6 extended to higher temperatures, well beyond the range where the relaxation amplitude for the micelle formation−breakup relaxation vanished. These measurements revealed a relaxation process with a positive amplitude (corresponding to an *increase* of the scattered light intensity with time) that increased with temperature. This process, with the relaxation time τ_3, was considered as a third relaxation characterizing $E_nP_mE_n$ solutions. It was assigned to micelle clustering because the investigated L64 solutions were closer to the cloud temperature T_C of the system. Note however that this third process became detectable at 45 °C, which is some 15 °C below T_C, in the experimental conditions used.[6] Stopped-flow experiments[6,7] were claimed to confirm the existence of this third relaxation process.

However, in the latter T-jump relaxation studies[5,6] the micelle formation−breakup and the micelle clustering relaxation processes were never observed simultaneously, that is, with a given solution under given experimental conditions. From the results it appears that the amplitude of the micelle formation−breakup was too small for detection or reliable measurements at above a certain temperature T_1. Likewise, the amplitude of the micelle clustering became detectable, and the relaxation time measurable only at a temperature about 4 °C above T_1.[5,6] This is illustrated in Figures 1 and 2 which reproduce results from refs 5 and 6. It is seen that continuous curves can be drawn through the experimental points (τ_2 and τ_3 values and the corresponding relaxation amplitudes, located below T_1 for the micelle formation−breakup and above $T_1 + 4$ for the

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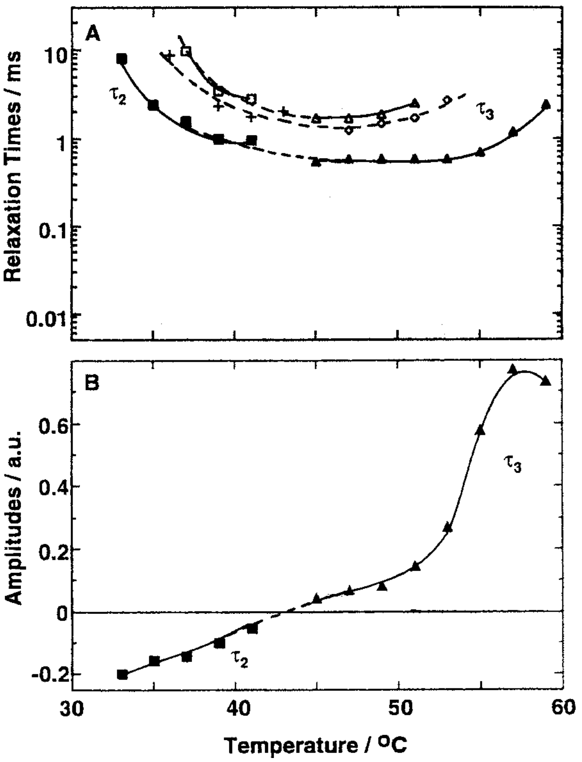

Figure 1. (A) Temperature dependence of the relaxation times τ_2 and τ_3 for aqueous solutions of 2.5% (w/v) purified L64 (■, ▲), 2.5% (w/v) industrial L64 (□, △) and a mixture of 2.5% w/v purified L64 and 0.25% w/v L61 (+, ◇). (B). Temperature dependence of the amplitudes associated with the relaxation times τ_2 and τ_3 for an aqueous solutions of 2.5% (w/v) purified L64. Adapted from Figure 3 in ref 5. Lines in full: as drawn by the authors. Broken lines: drawn by us.

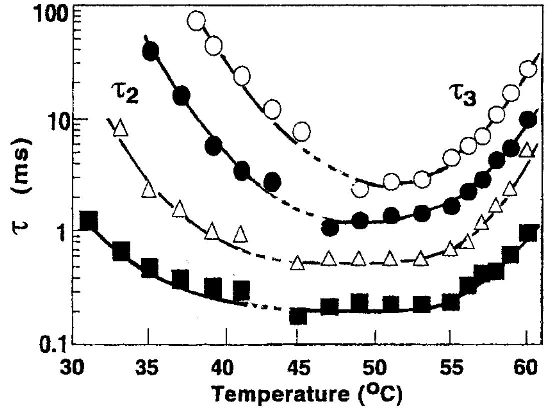

Figure 2. Temperature dependence of the relaxation times τ_2 and τ_3 for aqueous solutions of purified L64 of concentration 0.625% (○), 1.25% (●), 2.5% (△), and 5% (■). Adapted from Figure 3 in ref 6. The solid lines going through the data points were drawn by us to emphasize the continuity in the variation of the values of τ_2 and τ_3 with temperature.

micelle clustering) through the gap between T_1 and $T_1 + 4$. The continuity of the results through the gap is particularly striking for the relaxation amplitude (Figure 1B). The results in Figures 1 and 2 suggest that the second and third T-jump relaxation processes may in fact be associated with a single and same equilibrium, i.e., the micelle formation–breakup. The amplitude of this process would simply go from negative to positive at a temperature corresponding to that at about midrange of the gap between T_1 and $T_1 + 4$, as is suggested by the results in Figure 1B. At this stage we recall that the relaxation amplitude for the micelle formation–breakup process has been reported to change sign for several micellar systems based on conventional surfactants.[11–13]

It may be argued that the processes characterized by τ_2 and τ_3 were also detected by stopped-flow.[6,7] However, these experiments were performed in conditions very different from those by T-jump. As noted by the authors,[7] the stopped-flow experiments involved very large perturbation of the micellar equilibria. Then, the results cannot be directly compared to those from T-jump experiments where the perturbation is much smaller. Indeed the rate equations governing the evolution of the system toward the new state of equilibrium are nonlinear in the case of large perturbations. This by itself results in nonexponential relaxation signals. The stopped-flow relaxation signals were analyzed in terms of three discrete relaxation processes, but only the results for the intermediate process agreed with the τ_2 values from T-jump.[6,7]

The purpose of the work described in this paper was to check whether a third relaxation process does characterize micelle clustering in aqueous $E_nP_mE_n$ solutions. New T-jump relaxation studies of these systems were therefore undertaken. Special care was taken in exploring the temperature range between T_1 and $T_1 + 4$ (see above) where the relaxation amplitude is very small and which is supposed to separate the range where the relaxation is due to micelle formation–breakup from that where it is due to micelle clustering. The high sensitivity of the detection of our setup permitted us to obtain reliable values of the relaxation times and amplitudes even at temperatures very close to that where the amplitude goes through a zero value. Two types of results are presented below. First in a theoretical section we show that the relaxation amplitude for the micelle formation–breakup process can change sign in the case of $E_nP_mE_n$ solutions. Next, in an Experimental Section, we present T-jump results for the formation–breakup of the micelles in two different $E_nP_mE_n$ solutions: a 5 wt % solution of L64 and a 10 wt % solution of P84 ($E_{19}P_{43}E_{19}$). The last solution was selected in the present study because its critical micellization temperature (cmT) is about 30 °C lower than the temperature T_{MG} at which the micelles start to grow rapidly and become elongated. Moreover, T_{MG} is some 20 °C lower than the cloud temperature.[14] Such a very large separation of the three characteristic temperatures helps in the interpretation of the results.

The results show that indeed the second and third relaxation processes discussed by Kositza et al.[5,6] are a single and same process, the micelle formation-breakup, and that the relaxation amplitude associated with this process goes from negative to positive as the temperature is increased.

Experimental Section

The samples of L64 and P84 where the same as in previous studies.[2,3]

The T-jump relaxation setup with light scattering detection has been described.[2] The relaxation processes were monitored by following the time dependence of the intensity of the light scattered by the investigated solutions. The jump of temperature was of 1 ± 0.1 °C. The sensitivity of the detection allowed the determination of the relaxation time to better than ±10% when the T-jump induced a relative change of the intensity of scattered light of about 1%. At around the temperature where the relaxation amplitude changed sign the error on the measured relaxation time was about ±15%. The copolymer solutions for T-jump measurements contained 50 mM KCl.

Theoretical Section: Effect of Temperature on the Amplitude of the Relaxation Associated with the Micelle Formation−Breakup

The possibility that the amplitude of the slow process may change sign upon increasing temperature for the investigated block copolymer systems can be readily shown. The T-jump investigations of $E_nP_mE_n$ copolymer solutions were generally performed at constant copolymer concentration, C, and increasing temperature, T. Indeed, in these systems the critical micelle concentration (cmc) decreases very rapidly as T is increased, and micelles form upon heating of $E_nP_mE_n$ solutions.[15]

For a system containing free copolymer with a concentration $X_1 \approx$ cmc and micelles of aggregation number m and molar concentration Z, the mass conservation equation writes

$$C = X_1 + mZ \tag{1}$$

When a T-jump of amplitude ΔT (difference between the final temperature, T_f, and the initial temperature, T_i) is applied to the system, $dC/dT = 0$. Besides, since the number of micelles per unit volume, i.e., Z, is nearly constant during the fast exchange process,[8−10] it results that at the end of this process:

$$\Delta m_1 = -(1/Z)(dX_1/dT)\Delta T \tag{2}$$

In T-jump experiments ΔT is always positive. Since the cmc of $E_nP_mE_n$ copolymers decreases upon increasing temperature,[15] dX_1/dT is negative and Δm_1 is positive (see eq 2). Thus, the fast process results in an increase of m, and the closer to the cmc the experiments are performed, the smaller Z and the larger Δm_1. The increase of m gives rise to an increase of the intensity of scattered light, and the relaxation signal corresponding to the fast T-jump process (copolymer exchange) must therefore have a positive amplitude. This predicted behavior was consistently observed in all T-jump studies of $E_nP_mE_n$ copolymers.[1−6]

When the system reaches its final state of equilibrium at the end of the slow relaxation associated with the micelle formation−breakup, the final value of m depends on temperature but only little on concentration as the micelles are fairly monodisperse.[16] The increase of m between the initial and final temperatures is given by

$$\Delta m = (dm/dT)\Delta T \tag{3}$$

Equations 2 and 3 assume the value of ΔT to be small, as was the case in T-jump studies.[1−6]

The type of time dependence of the amplitude of the relaxation associated with the slow micelle formation−breakup (increase or decrease of the intensity of scattered light with time) is then easily predicted by comparing the values of Δm_1 and Δm. Three situations can arise:

(i) If $\Delta m_1 > \Delta m$, the slow micelle formation−breakup relaxation step brings the system to its state of final equilibrium with a decrease of the size reached by the micelles at the end of the fast exchange process. Thus, the intensity of scattered light decreases with time during this slow relaxation; that is, the relaxation amplitude associated with the micelle formation−breakup is negative.

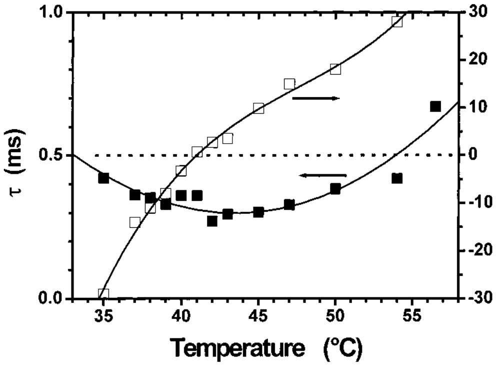

Figure 3. Temperature dependence of the relaxation time and relaxation amplitude (expressed as the relative change of the intensity I of the scattered light, $\Delta I/I$) of the slow T-jump relaxation process for a 5 wt % L64 aqueous solution in the presence of 50 mM KCl.

(ii) If $\Delta m_1 < \Delta m$, the micelle size increases during the slow relaxation. Thus, the intensity of scattered light increases with time, and the relaxation amplitude associated with the micelle formation−breakup is negative.

(iii) If $\Delta m_1 = \Delta m$, the relaxation amplitude associated with the micelle formation−breakup is zero.

One must now check whether the values of Δm_1 and Δm for $E_nP_mE_n$ copolymers change upon increasing temperature in such a way that one goes situation (i) (negative relaxation amplitude) to situation (ii) (positive relaxation amplitude), as the results in Figure 1B suggest. The results reported for $E_nP_mE_n$ copolymers show that log cmc $\approx$ log X_1 decreases nearly linearly upon increasing T,[15] and thus $|dX_1/dT|$ decreases rapidly upon increasing T. During the fast exchange process, Z remains nearly constant (independent of T).[8−10] It results from eq 2 that Δm_1 decreases rapidly upon increasing T. On the contrary, since m increases relatively slowly with temperature,[15] Δm as given by eq 3 varies slowly with T. Close to the critical micellization temperature Δm_1 is larger than Δm, and the slow relaxation process has a negative amplitude, as observed in all studies.[2−6] At higher temperature Δm_1 decreases and can become smaller than Δm, resulting in a positive amplitude. In between these two regimes, the relaxation amplitude of the slow process goes through a zero value. This simple reasoning explains the results in Figure 1B without the need to invoke a third relaxation process associated with micelle clustering.

Experimental Section: Relaxation Time and Relaxation Amplitude for the Micelle Formation−Breakup in Solutions of $E_nP_mE_n$ Copolymers

Figures 3 and 4 show the temperature dependence of the relaxation time and relaxation amplitude measured for the slow process for the investigated solutions of L64 and P84. In both instances the relaxation amplitude changes from negative at low T to positive at high T. No evidence of an additional relaxation process was found for either system in the whole T range. The results for the L64 system are particularly relevant. Thus, the variations of the relaxation time and relaxation amplitude with temperature have shapes very similar to those reported by Kositza et al.[5,6] (see continuous lines in Figures 1A and 2) with a minimum

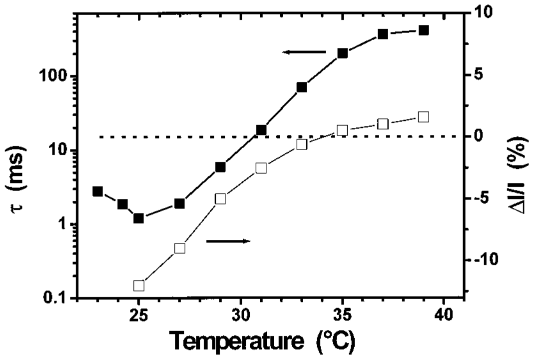

Figure 4. Temperature dependence of the relaxation time and relaxation amplitude (expressed as the relative change of the intensity I of the scattered light, $\Delta I/I$) of the slow T-jump relaxation process L64 for a 10 wt % P84 aqueous solution in the presence of 50 mM KCl.

in the variation of the relaxation time and a passage through zero for the relaxation amplitude. The results in Figure 2 for the 5 wt % L64 solution show a gap between 45 and 49 °C which, according to the authors,[6] separates the ranges of observation of the micelle formation–breakup and the micelle clustering equilibria (low T range and high T range, respectively). Such a gap is nearly absent in our measurements (see Figure 3) as the high sensitivity of our detection allowed measurements of relaxation times even in the case of very small relaxation amplitudes. Our results clearly show the continuity of the data around the temperature at which the relaxation amplitude goes from negative to positive. This temperature is lower than in Figure 2, owing to the presence of the 50 mM KCl in our system. This small amount of salt shifts the cloud temperature downward.[17] It apparently also shifts downward the temperature at which the amplitude vanishes. Note that the data points in Figure 3 extend to a temperature that is at least as close to T_C as in ref 6.

For the 10 wt % P84 solution in the presence of 50 mM KCl the results in Figure 4 show that the temperature T_0 at which the relaxation amplitude changes sign is 34 °C. This temperature is well below that for rapid micelle growth ($T_{MG} = 53 \pm 1$ °C).[14] It is also well below the cloud temperature of the system ($T_C = 72$ °C).[14] Thus, the change of sign of the amplitude is not related to rapid micellar growth or clouding. Besides, T_0 being well below T_{MG}, one can reasonably infer that the micelle aggregation number N increases fairly slowly with temperature in the range corresponding to the data in Figure 4. A slow change of N with T was assumed in the theoretical section to explain how the relaxation amplitude can change sign upon increasing temperature. This assumption thus receives a posteriori support.

It may be argued that the temperature T_0 at which the relaxation amplitude is zero is also that where the relaxation process changes of nature, being due to micelle formation–breakup below T_0 and to micelle clustering above T_0. However, for the solutions investigated in the present study, the relaxation time was measured even at temperatures within 0.5 °C from T_0. The results showed no evidence of a third relaxation process, and the variations of the measured relaxation time and amplitude with temperature showed no discontinuity (see Figures 3 and 4). Besides, it is not easily understood why one would only monitor the micelle formation–breakup just below T_0 and why this process would cease being detectable just above T_0, where only the micelle clustering would then be monitored.

It may also be argued that a difference of composition between the L64 samples used in the present study and in refs 5–7 may be in part responsible for differences between the two studies. Indeed, $E_nP_mE_n$ copolymers are known to be heterogeneous in composition, and different samples can have slightly differing compositions.[18,19] However, Figure 1A shows that the purification affects only the numerical values of the measured quantities (relaxation time and amplitude) and not the shape of their variations with temperature.

At this stage of the investigation of the relaxation behavior of $E_nP_mE_n$ copolymer micelles the possibility that future T-jump relaxation studies performed at temperatures very close to T_C may reveal the existence of a relaxation associated with micelle clustering cannot be excluded. Our results however indicate the absence of such a process in the range of temperatures investigated here and in the Kositza et al. studies.[5,6]

Conclusions

This paper reports an investigation of the temperature-jump relaxation behavior of triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) copolymer micelles. It is shown theoretically and experimentally that the amplitude of the relaxation process associated with the copolymer micelle formation–breakup goes from negative to positive upon increasing temperature, when monitoring this process by means of the time dependence of the intensity of the scattered light. The experimental results relative to solutions of two different copolymers showed no evidence of the existence of a third relaxation process associated with micelle clustering, contrary to what has been advanced by others.

References and Notes

(1) Hecht, E.; Hoffmann, H. *Colloids Surf. A* **1995**, *96*, 181.
(2) Michels, B.; Waton, G.; Zana, R. *Langmuir* **1997**, *13*, 3111.
(3) Waton, G.; Michels, B.; Zana, R. *J. Colloid Interface Sci.* **1999**, *212*, 593.
(4) Goldmints, I.; Holzwarth, J. F.; Smith, K. A.; Hatton, T. A. *Langmuir* **1997**, *13*, 6130.
(5) Kositza, M. J.; Bohne, C.; Alexandridis, P.; Hatton, T. A.; Holzwarth, J. F. *Langmuir* **1999**, *15*, 322.
(6) Kositza, M. J.; Bohne, C.; Alexandridis, P.; Hatton, T. A.; Holzwarth, J. F. *Macromolecules* **1999**, *32*, 5539.
(7) Kositza, M. J.; Bohne, C.; Hatton, T. A.; Holzwarth, J. F. *Prog. Colloid Polym. Sci.* **1999**, *112*, 146.
(8) Aniansson, E. A. G.; Wall, S *J. Phys. Chem.* **1974**, *78*, 1024; **1975**, *79*, 857. Aniansson, E. A. G.; Wall, S.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, *80*, 905.
(9) Kahlweit, M. *J. Colloid Interface Sci.* **1981**, *90*, 92; *Pure Appl. Chem.* **1981**, *53*, 2069.
(10) Waton, G. *J. Phys. Chem. B* **1997**, *101*, 9727.
(11) Teubner, M.; Diekmann, S.; Kahlweit, M. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 1278.
(12) Baumgardt, K.; Klar, G.; Strey, R. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 1222.
(13) Herrmann, C. U.; Kahlweit, M. *J. Phys. Chem.* **1980**, *84*, 1536.
(14) Waton, G.; Michels, B.; Zana, R., manuscript in preparation.
(15) Alexandridis, P.; Hatton, T. A. *Colloid Surf. A.* **1995**, *96*, 1, and references therein.
(16) Al-Saden, A. A.; Whateley, T. L.; Florence, A. T. *J. Colloid Interface Sci.* **1982**, *90*, 303.
(17) Bahadur, P.; Pandya, K.; Almgren, M.; Li, P.; Stilbs, P. *Colloid Polym. Sci.* **1993**, *271*, 657.
(18) Yu, G.-E.; Altinok, H.; Nixon, S. K.; Booth, C.; Alexandridis, P.; Hatton, T. A. *Eur. Polym. J.* **1997**, *33*, 673.
(19) Zhou, Z.; Chu, B. *Macromolecules* **1987**, *20*, 3089; **1988**, *21*, 2548.

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