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Comicellization of binary mixtures of block copolymers with different block lengths in a selective solvent

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Comicellizations of poly(α-methylstyrene)-*block*-poly(p-vinylphenethyl alcohol)s (KT-326 and KT-327) with slightly different block lengths in benzyl alcohol are investigated by means of static and dynamic light scattering. The critical micellization temperature (T_1) of KT-326 is lower than that (T_2) of KT-327. The apparent molecular weight, radius of gyration and hydrodynamic radius have been measured for micellar solutions with different KT-326/KT-327 compositions after single-step and double-step temperature jumps (T-jumps) from the unimer region. The following conclusions were deduced. In a single-step T-jump from unimer region I ($T > T_2$) to region III ($T < T_1$), where both copolymers form micelles in their respective pure solutions, comicellization takes place to form micelles having a copolymer composition close to the composition of the solution. In a jump from region I to region II ($T_1 < T < T_2$), where only KT-327 can form micelles in its pure solution, some fraction of KT-326 is incorporated with KT-327 to form comicelles, but the extent of the incorporation is limited even in a solution with a high KT-326 content. In a double-step T-jump from region I to region II, and subsequently to region III after the second jump, some fraction of KT-326 forms comicelles with existing micelles formed in the first jump, while another fraction of KT-326 forms micelles of pure KT-326. Copyright © 1996 Elsevier Science Ltd.

(Keywords: comicellization; micelle; block copolymer; light scattering)

INTRODUCTION

Extensive studies of micellization in multicomponent aqueous solutions have been made, and have demonstrated the formation of mixed micelles, i.e. comicellization, between surfactants with different lengths of alkyl chains and between ionic and non-ionic surfactants[1–13]. It is also expected that diblock copolymers with different chain lengths and/or compositions will form comicelles in a selective solvent. Tian *et al.*[14] discovered the comicellization of polystyrene-*block*-poly(methyl methacrylate) in a mixture of water and dioxane by use of an ultracentrifuge. Shim *et al.*[15] studied the theory of comicellization between diblock copolymers with different chain lengths and block compositions, and determined that the concentration–composition regime of the comicellization depends upon the segment interaction strength between unlike blocks. In connection with polydispersity effects on the critical micelle concentration (c.m.c.) of diblock copolymers in a selective solvent, Gao and Eisenberg[16] and Linse[17] demonstrated theoretically that the presence of polydispersity in the chain length and/or block composition reduced the c.m.c. and changes the critical micelle temperature (c.m.t.). More extensive and systematic studies, particularly experimental ones, are needed for a better understanding of comicellization in polymeric systems.

In this study, comicellization between diblock copolymers with different block lengths in a selective solvent has been studied by means of static and dynamic light scattering (LS). In our previous study[18], we investigated the micellization kinetics for two poly(α-methylstyrene)-*block*-poly(p-vinylphenethyl alcohol)s with slightly different block lengths in benzyl alcohol, and found that both of them have a c.m.t. a little above room temperature, but different c.m.t. values T_1 and T_2. In the present study, for mixtures of this pair of copolymers, the comicellization behaviour has been observed at a temperature T where only one of the copolymers forms micelles in its pure solution, i.e. $T_1 < T < T_2$, and at a temperature T where both form micelles i.e. $T < T_1, T_2$. The polymer composition in the comicelles and the fraction of comicellized copolymers were estimated as a function of the polymer composition in solution by analysis of the LS results. The method of the LS analysis adopted here was developed in a previous paper[18] and based on the fact that the molecular weight, radius of gyration and hydrodynamic radius observed by LS are

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Table 1 Molecular weights and compositions of the block copolymers

Copolymer	$10^{-4}M_{\mathrm{P\alpha MS}}$	$10^{-4}M_{\mathrm{PVPA}}$	$10^{-4}M_{\mathrm{total}}$	ϕ^{a}_{PVPA}	$\partial n/\partial c$ (ml g^{-1})
KT-326	7.0	1.1	8.1	0.11	0.0653
KT-327	11.3	1.23	12.5	0.08	0.0671

[a] The fractional degree of polymerization of the PVPA block

differently weighted averages for polydisperse particles in solution.

EXPERIMENTAL

Materials

The poly(α-methylstyrene)-*block*-poly(p-vinylphenethyl alcohol)s (PαMS-*b*-PVPA)s were prepared by anionic polymerization[19]. The molecular weights and block compositions with sample codes are listed in *Table 1.* The molecular weight distribution indices M_w/M_n were around 1.1. The PαMS block of KT-327 is larger than that of KT-326, while the PVPA block lengths are almost the same in both materials.

Benzyl alcohol (BA) was used as supplied commercially. BA is a thermodynamically good solvent for PVPA and a non-solvent for PαMS, so that PαMS-*b*-PVPA may form crew-cut, star-shaped micelles with PαMS cores and PVPA corona[20].

Preparation of sample solutions

Stock solutions were prepared by dissolving the respective block copolymers in BA and keeping the solutions at 55–60°C for 2–3 h. The stock solutions were mixed and/or diluted by adding optically purified solvent in a dust-free optical cell to make a sample solution with the desired concentration and polymer composition. Details of the preparation of solutions for light scattering were described in a previous paper[18]. The total polymer concentrations of mixed solutions were fixed at about 1.6×10^{-3} g (g solution)$^{-1}$. Solutions of the pure copolymers were also prepared. The concentrations and compositions for the samples prepared are listed in *Table 2.*

Light-scattering measurements

Light-scattering measurements were carried out by using an Ohtsuka Electronic DLS-700 spectrometer with an argon ion laser operating at 488 nm as the light source.

The excess Rayleigh ration $\Delta R(\theta)$ as a function of the scattering angle θ was calculated from the measured excess scattered intensity using the Rayleigh ratio of benzene ($3.40_5 \times 10^{-5}$ cm^{-1} at 25°C) as standard[21].

Since a conventional analysis using extrapolation to the dilute limit is not applicable to micellization, we evaluated the apparent molecular weight M_{app} and the apparent radius of gyration R_{gapp} at finite experimental concentrations c without extrapolation. M_{app} and R_{gapp} are defined as

$$M_{\mathrm{app}} = \frac{\Delta R(0)}{Kc} \tag{1}$$

$$R_{\mathrm{gapp}} = \frac{(\text{initial slope})3\lambda_0^2 M_{\mathrm{app}}}{16\pi^2 n^2} \tag{2}$$

where K is the optical constant given by $K = 4\pi^2 n^2 (\partial n/\partial c)^2/\lambda_0^4 N_A$, with n, λ_0 and N_A being the refractive index, the wavelength of the incident beam and the Avogadro constant, respectively. The refractive index increments (dn/dc) used were 0.0653 ml g^{-1} and 0.0671 ml g^{-1} for KT-326 and KT-327, respectively[18]. The $(\partial n/\partial c)$ for the mixtures were calculated by assuming additivity for the composition. The temperature dependence of $(\partial n/\partial c)$ was negligible. Because of the small content and the small $(\partial n/\partial c)$ of PVPA in BA, the obtained R_{gapp} can be regarded as that of the PαMS part of the micelle.

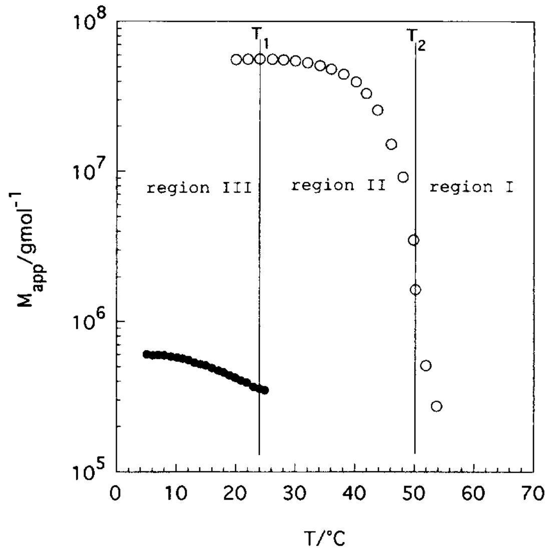

Figure 1 Change in M_{app} with temperature T for pure KT-326 (●) and KT-327 (○) under cooling at a rate of 2°C/30 min

The autocorrelation function $g^{(2)}(\tau)$ of the scattered light intensity was transformed to the correlation function $g^{(1)}(\tau)$ of the electric field using the following equation for the homodyne

$$g^{(2)}(\tau) = A(1 + B|g^{(1)}(\tau)|^2) \tag{3}$$

where A and B are constants. Using a non-linear least squares fitting to the cumulant expansion[22]

$$|g^{(1)}(\tau)| = \exp\left(-\bar{\Gamma}\tau + \frac{\mu_2}{2}\tau^2 - \ldots\right) \tag{4}$$

we evaluated the average decay late $\bar{\Gamma}$ and the second cumulant μ_2. The obtained $\bar{\Gamma}$ followed a q^2 dependence, i.e. $\bar{\Gamma} = Dq^2$. From the diffusion coefficient D so calculated, the hydrodynamic radius R_h was calculated using the Stokes–Einstein equation.

$$R_h = \frac{k_B T}{6\pi\eta D}$$

where k_B and T are the Boltzmann constant and the absolute temperature, respectively. The solvent viscosity η was measured as a function of temperature using an Ubbelohde-type viscometer. Since the extrapolation to zero concentration could not be made, the hydrodynamic radius thus calculated was the apparent hydrodynamic radius R_{happ}.

KT-326 and KT-327 start to form micelles around $T_1 = 24$°C and $T_2 = 50$°C, respectively, under cooling at a rate of 2°C/30 min, as shown in *Figure 1.* Three temperature regions are supposed, as illustrated in *Figure 1*: in region I above T_2, KT-326 and KT-327 are both in the unimer state; region II ranges from T_1 to T_2, where KT-327 forms micelles in its pure solution while KT-326 does not; and in region III below T_1, both KT-326 and

Table 2 Characteristics of the sample solutions

Sample code	Total polymer concentration (10^{-4} g (g solution)$^{-1}$)	KT-326 concentration (10^{-4} g (g solution)$^{-1}$)	KT-327 concentration (10^{-4} g (g solution)$^{-1}$)	Fractional content of KT-326 in total polymers
KT6/7-00	8.14	0	8.14	0
KT6/7-52	16.0	8.38	7.61	0.524
KT6/7-77	16.1	12.4	3.67	0.772
KT6/7-87	16.0	13.9	2.13	0.867
KT6/7-100	15.2	15.2	0	1

KT-327 form micelles in their respective pure solutions. We first let each solution stay at 60°C in region I to decompose micelles completely into unimers, and then quenched to the desired temperatures to make light-scattering measurements as a function of time. Three types of temperature jump (*T*-jump) experiment were performed: (1) *T*-jump A, a single-step jump, from region I (60°C) to region III (15°C); (2) *T*-jump B, a single-step jump, from region I (60°C) to region II (35°C); and (3) *T*-jump C, a double-step jump, from region I (60°C) to region II (35°C) to region III (15°C).

It took about 4 min to measure a set of data for static light scattering, which was much shorter than the time-scale of micellization, so no correction for time lag was needed. As for the dynamic measurements, the accumulation time was about 10 min, so the data were taken more than 30 min after quenching, when micellization during data acquisition could be ignored.

RESULTS AND DISCUSSION

Micelle formation in pure copolymers KT-326 and KT-327

Figure 2 shows the variations with time for M_{app} and R_{gapp} for KT-326 (KT6/7-100) at 15°C, and *Figure 3* shows those for KT-327 (KT-6/7-00) at 15°C and 35°C. As was discussed in detail in our previous study[18], the micellization proceeds stepwise by two processes. The change in micellization from the first to the second process was observed around $t = 20$ h in KT-327 at 35°C, while only the fast first process was observed in KT-326 and KT-327 at 15°C, because the process slowed down with decreasing temperature. The rate of the first process depends strongly on the polymer concentration, as shown in our previous paper[18]. However, the second process has almost no concentration dependence of the growth rate[18], so that after reaching a quasi-equilibrium state at the end of the first process, the micellization behaviour, and therefore M_{app}, R_{gapp} and R_{happ}, depends very weakly on the concentration. It was demonstrated in our previous paper that an increase in micelle fraction with rapid growth in size is the dominant observable process in the first step, while the growth in micelle size primarily takes place by decomposition and formation of micelles with exchange of unimers.

The results of the double-step jump (*T*-jump C) (the second *T*-jump after *T*-jump B shown above) for pure KT-327 (KT6/7-00) are also illustrated in *Figure 3*. No substantial change in M_{app} or R_{gapp} after the second quench was observed. The second quench appears to depress the slight increase in M_{app} observed before the second quench, but the effect, if any, of the second quench was apparently minor.

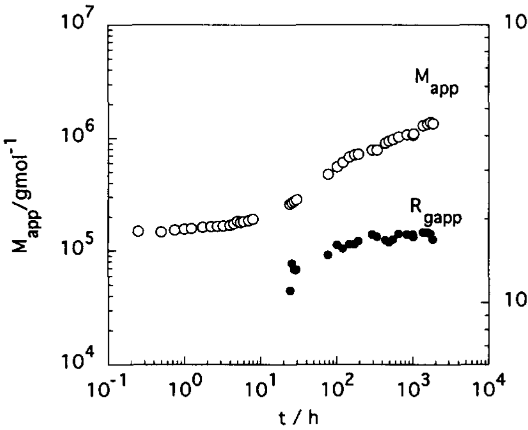

Figure 2 Variations with time for M_{app} (○) and R_{gapp} (●) for pure KT-326 (KT6/7-100) with a single-step *T*-jump from 60°C to 15°C (*T*-jump A)

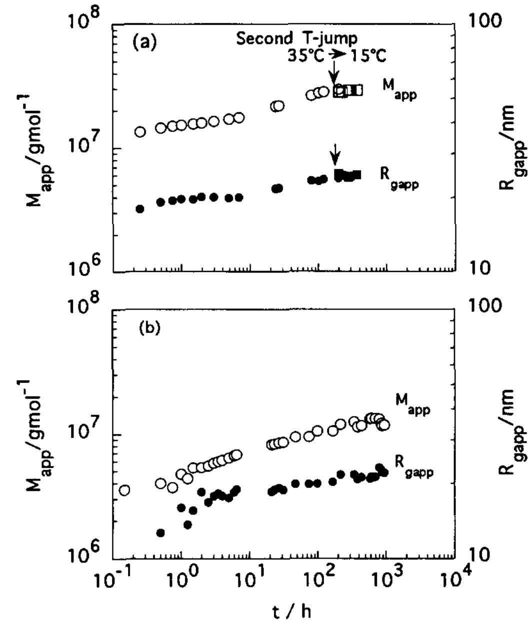

Figure 3 Variations with time for M_{app} and R_{gapp} for pure KT-327 (KT6/7-00) with single-step and double-step *T*-jumps. (a) Plots of M_{app} for *T*-jump B with *T*-jump C: (○) first jump to 35°C; (□) second jump to 15°C. Plots of R_{gapp} for *T*-jump B with *T*-jump C: (●) first jump to 35°C; (■) second jump to 15°C. (b) Plots of M_{app} for *T*-jump A to 15°C (○) and R_{gapp} for *T*-jump A to 15°C (●)

Micelle formation in mixed solutions of KT-326 and KT-327

In *Figure 4* are presented the variations with time for M_{app} and R_{gapp} for mixed solutions with different polymer compositions. As in the pure solutions (see

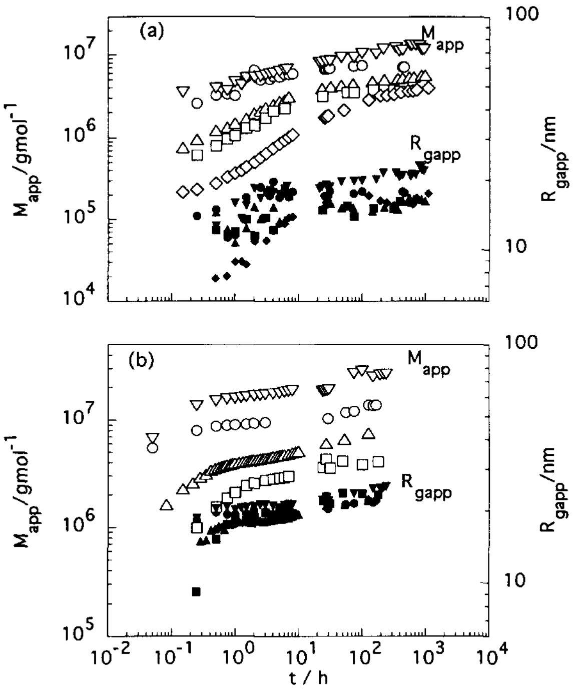

Figure 4 Variations with time for M_{app} and R_{gapp} for the single-step T-jumps of KT-326/KT-327 mixed solutions, along with those of the pure copolymers: (a) T-jump A to 15°C; (b) T-jump B to 35°C. M_{app}: (▽) KT6/7-00; (○) KT6/7-52; (△) KT6/7-77; (□) KT6/7-87; (◇) KT6/7-100. R_{gapp}: (▼) KT6/7-00; (●) KT6/7-52; (▲) KT6/7-77; (■) KT6/7-87; (◆) KT6/7-100

Figure 2), stepwise micellization was observed at 35°C in mixed solutions with T-jump B, whereas monotonic micellization was found at 15°C in mixed solutions with T-jump A, which may involve only the first process because R_{gapp} was almost constant while M_{app} still increased after 10 h.

Figure 5 shows the results for the double-step jump (T-jump C) in mixed solutions. An abrupt increase in M_{app} after the second jump was observed*, with the gap between the log–log plots increasing with increasing KT-326 content. On the other hand, one can see no appreciable change in R_{gapp} with the second quench. In the following, we will be concerned with the comicelles formed by the first process with the single-step T-jumps A and B, and the second jump of double-step T-jump C. The kinetics of the comicellizations will be discussed in detail elsewhere.

Comicellization in single-step T*-jumps*

In *Tables 3* and *4* are summarized the values of M_{app}, R_{gapp} and R_{happ} for pure and mixed solutions with T-jump A at about 24 h and T-jump B at about 10 h, respectively. In the respective pure solutions, some fraction of KT-326 formed micelles in T-jump A at around 24 h and no micelles in T-jump B at around 10 h, while almost the whole fraction of KT-327 formed micelles under both conditions.

T*-jump A (single-step jump to region III).* In region III, KT-326 and KT-327 can form micelles in their respective pure solutions, so both the copolymers must be involved in micellization. However, it remains to be seen whether there occurs comicellization or independent micellization. We can find no theoretical reason for each block copolymer to form its own micelles independently, because between the two polymers there is only a slight difference in the block length of the PαMS forming the cores of the micelles. We therefore calculated the values of M_{app0}, R_{gapp0} and R_{happ0} that would have been observed if the micellization had taken place independently. The results are shown in *Table 3* for comparison with the experimental values. The values for independent micellization were calculated from the values for micelles formed in the respective pure solutions on the basis of the approximation of additivity for the scattered light intensity, the details of which are described in the Appendix. The calculated values are different from the observed values. In particular, the observed M_{app} is larger than the calculated value for independent micellization, and as the KT-326 content increases, the observed R_{gapp} decreases in parallel with the decreasing M_{app}, while the calculated R_{gapp0} decreases more gently. Note that if the micelles had formed independently, there would have remained much free KT-326, and the observations of a large M_{app} and a parallel decrease in R_{gapp} suggest induced micellization of KT-326 to give comicelles with KT-327. Comicellization is also supported by the polydispersity index (μ_2/Γ^2) of particle size obtained

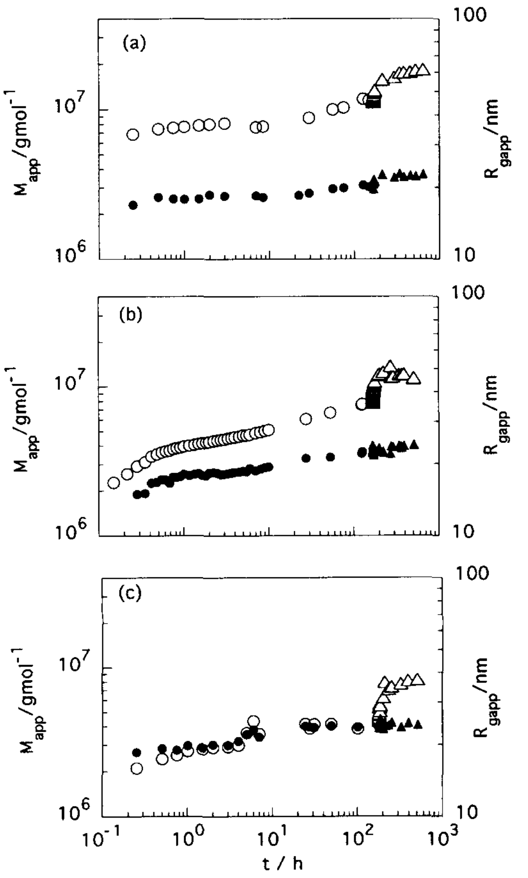

Figure 5 Variations with time for M_{app} and R_{gapp} for the double-step T-jumps (T-jump C) of KT-326/KT-327 mixed solutions: (a) KT6/7-52; (b) KT6/7-77; (c) KT6/7-87. At 35°C: (○) M_{app}; (●) R_{gapp}. 15°C: (△) M_{app}; (▲) R_{gapp}

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*The abrupt change can be seen in the logarithmic time scale with the time counted from the first jump. If we look at the change in the time scale $\log(t - t_0)$ with the time $(t - t_0)$ measured from the second jump (t_0), the change with time is seen not as abrupt but as a gradual increase

Table 3 Numerical results for *T*-jump A (60°C to 15°C) at about 24 h

Sample code	$10^{-6}M_{app}$	R_{gapp} (nm)	R_{happ} (nm)	$10^{-6}M_{app0}$	R_{gapp0} (nm)	R_{happ0} (nm)	σ^a (%)
KT6/7-00[b]	8.47	19.1	27.5				
KT6/7-52	6.69	17.1	25.0	4.92	18.4	25.9	16.0
KT6/7-77	4.14	15.8	24.4	3.21	17.6	24.1	14.6
KT6/7-87	3.18	14.8	23.6	2.55	16.9	22.9	14.2
KT6/7-100[c]	1.61	14.8	20.3				

[a] The deviation defined by $\sigma^2 = [(\Delta M_{app}/M_{app})^2 + (\Delta R_{gapp}/R_{gapp})^2 + (\Delta R_{happ}/R_{happ})^2]/3$

[b] At 27 h

[c] For a *T*-jump of 40°C to 15°C at 24 h

Table 4 Numerical results for *T*-jump B (60°C to 35°C) at about 10 h

Sample code	$10^{-6}M_{app}$	R_{gapp} (nm)	R_{happ} (nm)	$10^{-6}M_{app0}$	R_{gapp0} (nm)	R_{happ0} (nm)	σ (%)
KT6/7-00	17.9	22.1	33.7				
KT6/7-52	8.98	19.5	34.8	8.68	22.1	33.1	8.4
KT6/7-77	5.10	19.3	31.8	4.23	22.0	31.8	
KT6/7-87	2.98	20.0	30.0	2.51	21.8	30.3	10.5
KT6/7-100	(0.08)						

Table 5 Numerical results for a single-step *T*-jump from 60°C to 24°C at about 8 h

Sample code	$10^{-6}M_{app}$	R_{gapp} (nm)	R_{happ} (nm)	$10^{-6}M_{app0}$	R_{gapp0} (nm)	R_{happ0} (nm)	σ^a (%)
KT6/7-00	12.7	18.4	29.1				
KT6/7-52	8.64	17.5	27.6	6.26	18.2	28.0	16.1
KT6/7-100[a]	0.26						

[a] At a concentration of 12.0×10^{-4} g (g solution)$^{-1}$

Table 6 Numerical results for *T*-jump C (60°C to 35°C to 15°C)[a]

Sample code	$10^{-6}M_{appA}$	$10^{-6}M_{appB}$	$10^{-6}\Delta M^b_{app}$	R_{gappA} (nm)	R_{gappB} (nm)	R_{happA} (nm)	R_{happB} (nm)
KT6/7-00	29.2	29.5	−0.3	24.6	23.8	37.7	39.4
KT6/7-52	21.2	13.7	7.5	24.0	22.1	37.8	37.2
KT6/7-77	12.1	7.49	4.6	23.7	22.0	36.6	35.4
KT6/7-87	8.24	4.09	4.15	24.1	23.4	34.1	37.8
KT6/7-100	3.36		(3.36)	15.6		25.0	

[a] Times (h) from the top (M_{appA} at 35°C/M_{appB} at 15°C after quenching): 199/173, 168/361, 125/226, 179/336 and 0/317

[b] $\Delta M_{app} = M_{appA} - M_{appB}$

from dynamic light scattering. The values of $\mu_2/\bar{\Gamma}^2$ ranged from 0.012 to 0.086, and these are comparable to the values for micellar solutions of the pure polymers.

T*-jump B (single-step jump to region II).* For *T*-jump B in region II, KT-326 does not form micelles in its pure solution. The apparent quantities calculated for the independent micellization are compared with the observed values in *Table 4*. As in the results for *T*-jump A, the observed M_{app} is larger than the calculated one, while the observed R_{gapp} is smaller. These results indicate induced comicellization of KT-326. In *T*-jump B, the observed M_{app} decreases more rapidly with increasing KT-326 content than in *T*-jump A. This implies that in solutions of higher KT-326 content, there remains a greater amount of free KT-326 that is not involved in any micelles. In other words, this may suggest a saturation of the KT-326 content in the comicelles in the composition range of the present experimental mixtures.

When the micellization temperature was set at 24°C around the boundary between regions II and III, where a pure KT-326 solution substantially showed no micellization, similar light-scattering results were obtained, as shown in *Table 5*, again suggesting induced comicellization. The features of comicellization detailed here are presented schematically in *Figure 6*, along with the features of micellization in pure copolymer solutions.

*Comicellization in a double-step jump (*T*-jump C, region I to region II to region III)*

The abrupt micellization induced by the second jump

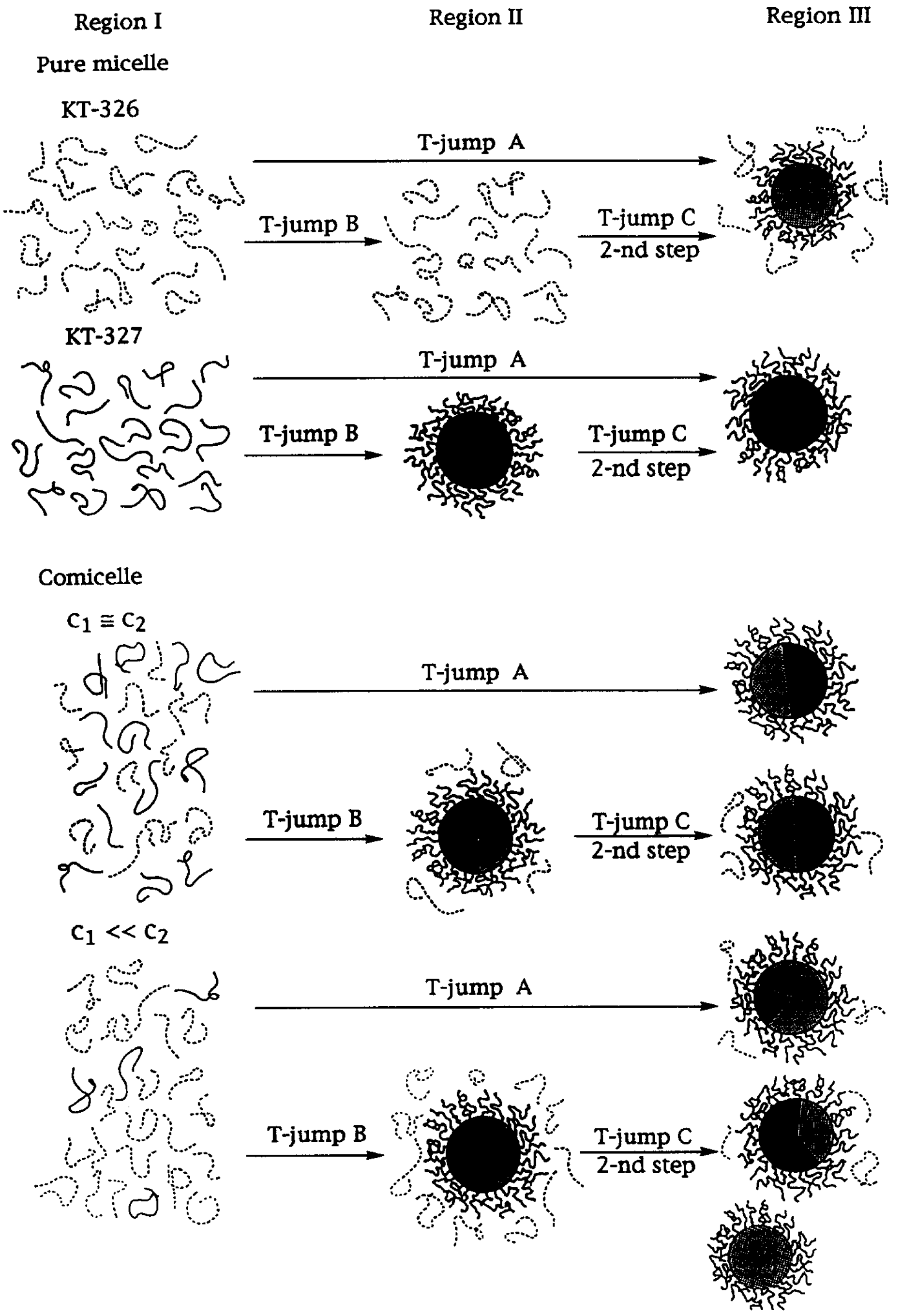

Figure 6 Schematic representation of the micellization features for pure and mixed copolymer solutions with single-step and double step T-jumps: (▨) KT-326 in micelles; (■) KT-327 in micelles. Here T-jump C stands for T-jump B with the second step of T-jump C (see the text)

stabilizes after about 200 h, and the growth of M_{app} becomes very slow. At this stage, the first process may finish, and possibly the second process can begin simultaneously. The differences in M_{app} between just before the second jump and just after stabilization of micellization are listed in *Table 6*. The difference in M_{app} decreases with increasing KT-326 content in the mixed solution. This seems to conflict with the fact that the amount of free KT-326 in the solution before the second jump is expected to be larger for a larger initial KT-326 content. If the free KT-326 had formed its own new micelles independently, irrespective of the presence of the already-formed micelles, the difference in M_{app} would have increased with increasing KT-326 content. In quantitative terms, if this were the case, then the ΔM_{app} expected for independent micellization would be given by the product of the fractional concentration c_2 of KT-326 and the M_{app} of pure KT-326; with the M_{app} of pure KT-326 being 3.36×10^6, ΔM_{app} would be 1.76×10^6, 2.59×10^6 and 2.91×10^6 for KT6/7-52, KT6/7-77 and KT6/7-87, respectively. The values of ΔM_{app} could also be lower because of the involvement of some KT-326 in micelles. The observed ΔM_{app} are much larger than expected. Therefore, the free KT-326 copolymers, at least some of them, must be incorporated into the existing comicelles and/or involved in forming new comicelles of KT-326 and KT-327 after the second quench. The features of comicellization detailed here for

Table 7 Calculated characteristic quantities of micellar solutions for T-jump A (60°C to 15°C) at about 24 h[a]

Sample code	ϕ_1	ϕ_2	w_a	θ_{1a}/θ_{2a} (%)	$10^{-6}M_a$	σ (%)
KT6/7-00	1		(1)	100/0	8.47	(0.26)
KT6/7-52	1	1.19	1.10	43/57	6.10	0.35
KT6/7-77	1	0.72	0.78	29/71	5.26	2.9
KT6/7-87	1	0.65	0.70	19/81	4.54	4.4
KT6/7-100		0.39	(0.39)	0/100	4.01	0.61

[a] $R_{gmi} = 0.094M^{1/3}$ nm; $R_{hmi} = 0.136M^{1/3}$ nm for both KT-326 and KT-327. R_{gmi} and R_{hmi} are defined in the Appendix

Table 8 Calculated characteristic quantities of micellar solutions for T-jump B (60°C to 35°C) at about 10 h[a]

Sample code	ϕ_1	ϕ_2	w_a	θ_{1a}/θ_{2a} (%)	$10^{-6}M_a$	σ (%)
KT6/7-00	1		(1)	100/0	17.9	(1.1)
KT6/7-52	1	0.234	0.60	79/21	14.9	6.7
KT6/7-77	1	0.186	0.37	61/39	13.5	4.1
KT6/7-87	1	0.081	0.20	66/34	14.2	1.6

[a] $R_{gmi} = 0.085M^{1/3}$ nm; $R_{hmi} = 0.13M^{1/3}$ nm for both KT-326 and KT-327

a double-step jump are also presented schematically in *Figure 6*.

Quantitative analysis

Here, by a detailed analysis of the LS data, we will try to estimate the polymer composition in a micelle and the comicelle-forming fractions in mixed solutions under various conditions. The method of the LS analysis is essentially the same as that developed in our previous paper[18], and is here extended to apply for mixed solutions. The analysis is based on the fact that M_{app}, R_{gapp} and R_{happ} observed by LS are differently weighted averages for polydisperse particles in solution, of which the details are described in the Appendix. Consider a solution containing two types (a and b) of micelles and unimers of block copolymers 1 and 2. M_{app} is expressed as an average with weights of the weight fraction and the refractive index increment

$$M_{app} = M_a w_a r_a^2 + M_b w_b r_b^2 + M_1 w_1 r_1^2 + M_2 w_2 r_2^2$$

where the subscripts a, b, 1 and 2 denote the components, and M, w and r are the molecular weight, the weight fraction in the total solute and the relative refractive index increment, respectively. R_{gapp}^2 is the z-average R_g^2; therefore, one has

$$R_{gapp}^2 = R_{ga}^2 z_a + R_{gb}^2 z_b + R_{g1}^2 z_1 + R_{g2}^2 z_2$$

with

$$z_k = M_k w_k r_k^2 / M_{app} \quad \text{for } k = \text{a and b}$$

$$z_i = M_i w_i r_i^2 / M_{app} \quad \text{for } i = 1 \text{ and } 2$$

R_{happ} obtained by the cumulant method from the correlation function measured at wavenumber q is given by

$$R_{happ}^{-1} = R_{ha}^{-1} s_a + R_{hb}^{-1} s_b + R_{h1}^{-1} s_1 + R_{h2}^{-1} s_2$$

Here, the weights s_k and s_i are proportional to the intensities of scattered light at q from the components k and i, respectively, and are given by equations (A13) and (A14). If the weight fractions w_k and w_i can be estimated from M_{app}, R_{gapp} and R_{happ} by these equations, then it is simple to calculate the composition θ_{ik} of copolymer i in micelle k, the fraction ϕ_i of copolymer i that forms micelles and/or the weight fraction f_{ik} of copolymer i in micelle k. To make the estimation, we must determine the exponent ν and the prefactors L_{gi} and L_{hi} for pure micelles of KT-326 and KT-327 to connect the molecular weight M with the radii R_g and R_h through equations (A17) and (A18). In the present calculations, assuming micellar shapes to be spherical, we set the exponent ν equal to 1/3 for both of R_g and R_h, and the prefactors were determined such that the experimental data were reproduced well, as mentioned later. Since the difference in M_w and block composition between the copolymers KT-326 and KT-327 is so small, the same prefactor was used for micelles of both polymers. As a consequence, only the amount of micelles of type a, i.e. $c_1\phi_1 f_{1a} + c_2\phi_2 f_{2a} (= w_a)$, is determinable, but not each term of $\phi_1 f_{1a}$ and $\phi_2 f_{2a}$ separately (see equations (A15)–(A18)). Hence, we assumed that all of KT-327 formed micelles of type a at 35°C and 15°C under the present conditions, i.e. it was assumed that $\phi_1 = f_{1a} = 1$.

T-*jump A.* *In Table 7* are listed the values of ϕ_2, w_a, θ_{1a}/θ_{2a} and M_a for T-jump A at about 24 h. These values were estimated by a least squares fitting of the equations to reproduce the experimental values (*Table 3*) for M_{app}, R_{gapp} and R_{happ}, with ϕ_2 and M_a being the parameters. One type of micelle only, i.e. $w_b = 0$, was assumed, and the prefactors were determined such that they reproduced R_{gapp} and R_{happ} for pure KT-327 (KT6/7-00) for the observed M_{app}, i.e. $L_g = 0.094$ nm and $L_h = 0.136$ nm. The deviations σ of the calculated values from the observaed values were reasonably small, as shown in *Table 7*, where the devaition σ is defined as

$$\sigma^2 = [(\Delta M_{app}/M_{app})^2 + (\Delta R_{gapp}/R_{gapp})^2 + (\Delta R_{happ}/R_{happ})^2]/3$$

with Δ denoting the difference between observed and calculated values. In the pure KT-326 solution, about 40% of the copolymers form micelles, while more than 40% of the KT-326 fraction in mixed solutions forms comicelles with KT-327. The KT-326 contents in the comicelles are lower than but close to the contents in solution, since some of the KT-326 is still free as unimers.

T-*jump B.* In *Table 8* are listed the values of ϕ_2, w_a θ_{1a}/θ_{2a} and M_a for T-jump B at about 10 h; these values were estimated in the same way as for T-jump A, but with the prefactors being $L_g = 0.085$ nm and $L_h = 0.13$ nm. KT-326 is induced to form comicelles with KT-327, but the composition levels off with increasing KT-326 content to about 40% at the highest KT-326 concentration. A large portion of the KT-326, ranging from 77% to 92% is still present as free unimers. This result is quite understandable because micelles of type a with a larger θ_{2a} must be unstable in region II, since pure KT-326 is unable to form micelles in region II. This contrasts with the comicellization behaviour seen for T-jump A in region III.

T-*jump C.* As pointed out before, the light-scattering data suggest that in the double-step T-jump, some of the remaining KT-326 unimers are incorporated into existing

Table 9 Calculated characteristic quantities of micellar solutions for *T*-jump C (35°C to 15°C) (data from *Table 6*)[a]

Sample code	ϕ_1	ϕ_2	f_{2a}	$\phi_2 f_{2a}$	w_a	θ_{1a}/θ_{2a} (%)	w_b	$10^{-6}M_a$	$10^{-6}M_b$	σ (%)
KT6/7-52	1	1.06	1.06	1.12	1.06	45/55	−0.03	20.0	5.87	0.43
KT6/7-77	1	0.59	0.70	0.41	0.54	42/58	0.32	20.6	5.87	0.15
KT6/7-87	1	0.54	0.16	0.086	0.21	63/37	0.39	27.8	5.87	0.45
KT6/7-100		0.57			0	0/100	0.57		5.87	1.06

[a] $R_{\mathrm{gm}i} = 0.088M^{1/3}$ nm; $R_{\mathrm{hm}i} = 0.14M^{1/3}$ nm for both KT-326 and KT-327. The pure-micelle-forming fraction w_f of free KT-326 not involved in comicelles with KT-327 was taken as 0.5 for KT6/7-52 and KT6/7-87; $W_f = 0.3$ for KT6/7-77

Table 10 Calculated characteristic quantities of micellar solutions for *T*-jump C (60°C to 35°C) (data from *Table 6*)[a]

Sample code	ϕ_1	ϕ_2 $(= \phi_2 f_{2a})^b$	w_a	θ_{1a}/θ_{2a} (%)	$10^{-6}M_a$	σ (%)
KT6/7-52	1	0.43	0.70	68/32	19.4	0.31
KT6/7-77	1	0.218	0.40	58/42	18.5	1.44
KT6/7-87	1	0.035	0.16	81/19	24.1	0.60

[a] $R_{\mathrm{gm}i} = 0.082M^{1/3}$ nm; $R_{\mathrm{hm}i} = 0.14M^{1/3}$ nm for both KT-326 and KT-327

[b] In this case, $f_{2a} = 1 - f_{2b} = 1$, since micelles of type b are assumed not to be formed

comicelles formed in the first jump, while other residual KT-326 unimers may form new micelles of pure KT-326 (see *Figure 6*). So, the fractions of comicelle-forming KT-326 and pure-micelle-forming KT-326 were estimated by fitting the data in *Table 6* to the equations for a fixed M_b of pure micelles and a fixed fraction w_f of pure-micelle-forming KT-326 in the residual KT-326 not involved in comicelles of type a. First, the micelle-forming fraction f_{2b} and the micellar molecular weight M_b were determined for the pure solution of KT-326 (KT6/7-100) in the same way as before, putting the prefactors here as $L_g = 0.088$ nm and $L_h = 0.14$ nm. The results are shown in *Table 9*. Around 320 h after quenching to 15°C, about 60% of KT-326 forms micelles of $M_b \approx 6 \times 10^6$. The fraction f_{2b} corresponds to w_f in this case. Then, taking ϕ_2 and f_{2a} as the fitting parameters, the estimations for mixed solutions were made, where the fixed M_b was taken to be the value obtained above and the values of w_f were 0.5, 0.3 and 0.5 for KT6/7-52, KT6/7-77 and KT6/7-87, respectively[*]. The results are shown in *Table 9*. The deviations σ are small enough, showing that the model reproduces the experimental data reasonably well. The values of ϕ_2, w_a, θ_{1a}/θ_{2a} and M_a for the micellar solution just before the second *T*-jump were also evaluated and are shown in *Table 10*[†].

The obtained values of $\phi_2 f_{2a}$ and θ_{2a} are larger than those of micelles formed in region II in the first *T*-jump[†]. Note that the quantity $\phi_2 f_{2a}$ represents the fraction of KT-326 that forms comicelles of type a, and that $\phi_2 f_{2a} = \phi_2$ for a single-step *T*-jump such as the first *T*-jump. This indicates incorporation of KT-326 into existing comicelles in the second quench. However, the KT-326 content of the comicelles here is not as large as that of the comicelles formed in the direct *T*-jump to region III (*T*-jump-A). In the double-step *T*-jump, after the second jump a large number of the remaining KT-326 unimers are competitively involved in both comicellization and new micelle formation. This results in a difference in θ_{2a} relative to the single-step *T*-jump. In the first micellization process occurring after the second quench, the already-formed micelles do not completely decompose but become smaller in association number, with no change in the number of micelles. In the second process, comicellization may occur involving comicelles, unimers produced by decomposition and KT-326 unimers that have not formed micelles in the first *T*-jump, along with an increase in the number of micelles. This sort of micellization process is much slower than the first process, so that most of the KT-326 remaining after the first *T*-jump has a chance to form new pure micelles by the fast first process, especially in high KT-326 content solutions.

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[*] The values of w_f were taken to be less than the value for KT6/7-100 (0.57) since the micelle-forming fraction decreases with decreasing concentration in pure KT-326 at 15°C. In the case of KT6/7-52, the value of w_f had almost no effect on the result because $f_{2a} = 1$ and $f_{2b} = 0$; the values of 0.3 and 0.5 for w_f minimize the deviations σ for KT6/7-77 and KT6/7-87, respectively. The value of w_f has no large effect on the calculated values of $\phi_2 f_a$ and θ_{1a}/θ_{2a}

[†] Compared with the micelles formed at around 10 h in *T*-jump B (see *Table 8*), the micelles formed in the first *T*-jump at a time just before the second jump have a much larger M_w since the time is much longer, but they have a similar θ_{1a}/θ_{2a} and the micelle-forming fraction ϕ_2 is also almost unchanged. These results arise from the fact that in the second process, the growth in micelle size dominates over the increase in micelle fraction that primarily occurs in the first process by micellization from unimers

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APPENDIX

Estimation of comicelle composition and fraction by data analysis of static and dynamic light scattering

We will here propose a method of estimating comicelle composition, molecular weight and micelle-forming fraction for block copolymer mixtures in solution from M_{app}, R_{gapp} and R_{happ} measured by light scattering. The idea of the estimation is based on the fact that M_{app} is primarily determined by the molecular weight and the micelle-forming fraction, while R_{gapp} and R_{happ} are determined by the micelle size; in other words, each of these three quantities reflects the structure and composition of the micelles in solution in a different way from the others.

Consider a mixture of block copolymers 1 and 2 in a selective solvent, and that these copolymers form micelles of types a and b with different compositions of copolymers. The system we are then concerned with is considered generally to consist of two types of micelles and two kinds of unimers in the solvent. In characterizing the micellization, we try to estimate the molecular weights of the micelles, the copolymer compositions in the micelles and the fraction of micelle-forming copolymers in the total polymer content. Let us now define some terms. M_k denotes the molecular weight of micelle k (= a and b). The block copolymers i of weight fraction ϕ_i form the micelles, and the weight fraction f_{ik} of the micelle-forming copolymer i is incorporated into micelles k. Extreme cases are described with these quantities, for instance, as follows. If $\phi_i = 0$, then copolymer i forms no micelles at all and is not incorporated into comicelles. If $f_{i\text{b}} = 0$ ($i = 1$ and 2), then only one type of comicelle forms. If $f_{2\text{a}} \approx 0$, then copolymer 1 forms no comicelles, only micelles of type a with almost pure copolymers. From these definitions, we obtain

$$f_{i\text{a}} + f_{i\text{b}} = 1 \quad \text{for } i = 1 \text{ and } 2 \qquad \text{(A1)}$$

If we let the total concentration of copolymer i in the solution be C_i in weight, then the concentrations of comicelles W_k and unimers W_i are given by

$$\begin{aligned} W_k &= C_1\phi_1 f_{1k} + C_2\phi_2 f_{2k} && \text{for } k = \text{a and b} \\ W_i &= C_i(1 - \phi_i) && \text{for } i = 1 \text{ and } 2 \end{aligned} \qquad \text{(A2)}$$

In terms of the fractional concentrations $c_i = C_i/(C_1 + C_2)$, $w_k = W_k/(C_1 + C_2)$ and $w_i = W_i/(C_1 + C_2)$

$$\begin{aligned} w_k &= c_1\phi_1 f_{1k} + c_2\phi_2 f_{2k} && \text{for } k = \text{a and b} \\ w_i &= c_i(1 - \phi_i) && \text{for } i = 1 \text{ and } 2 \end{aligned} \qquad \text{(A3)}$$

Then, the weight fraction θ_{ik} of copolymer i in comicelle k is given by

$$\theta_{ik} = c_i\phi_i f_{ik}/w_k \qquad \text{(A4)}$$

and the specific refractive index increment r_k of comicelles k is given by

$$r_k = (c_1\phi_1 f_{1k} r_1 + c_2\phi_2 f_{2k} r_2)/w_k \qquad \text{(A5)}$$

where r_1 and r_2 are the refractive index increments of block copolymers 1 and 2, respectively, to the $(\mathrm{d}n/\mathrm{d}c)_\text{s}$ used for the calculation of M_{app}, i.e. $r_i = (\mathrm{d}n/\mathrm{d}c)_i/(\mathrm{d}n/\mathrm{d}c)_\text{s}$.

In treating the quantities measured by light scattering, we have to approximate the solution as infinitely dilute. This may be a serious approximation, but there is no way to avoid it under the experimental conditions employed. If the discrepancy from the true dilute limit is almost the same in all cases, then the approximation is not so bad as long as we are concerned with the relative sizes of the micelles. Under the dilute limit approximation, M_{app} is the weight average molecular weight of the system, with the refractive index increment of each component being taken into account. So, M_{app} is given by

$$M_{\text{app}} = M_\text{a} w_\text{a} r_\text{a}^2 + M_\text{b} w_\text{b} r_\text{b}^2 + M_1 w_1 r_1^2 + M_2 w_2 r_2^2 \qquad \text{(A6)}$$

where M_1 and M_2 are the molecular weights of block copolymers 1 and 2, respectively. R_{gapp}^2 is the z-average R_g^2; therefore, one has

$$R_{\text{gapp}}^2 = R_{\text{ga}}^2 z_\text{a} + R_{\text{gb}}^2 z_\text{b} + R_{\text{g1}}^2 z_1 + R_{\text{g2}}^2 z_2 \qquad \text{(A7)}$$

with

$$z_k = M_k w_k r_k^2/M_{\text{app}} \quad \text{for } k = \text{a and b} \qquad \text{(A8)}$$

$$z_i = M_i w_i r_i^2/M_{\text{app}} \quad \text{for } i = 1 \text{ and } 2 \qquad \text{(A9)}$$

R_{happ} obtained by the cumulant method from the correlation function measured at wavenumber q is given by.

$$R_{\text{happ}}^{-1} = R_{\text{ha}}^{-1} s_\text{a} + R_{\text{hb}}^{-1} s_\text{b} + R_{\text{h1}}^{-1} s_1 + R_{\text{h2}}^{-1} s_2 \qquad \text{(A10)}$$

Here, the weights s_k and s_i are proportional to the intensities of scattered light q from the components k and i, respectively. The weights can be calculated from the following approximate expressions of scattered light intensity R for each component

$$R_k(q) = w_k n_k^2/(1 + q^2 R_{\text{g}k}^2) \qquad \text{(A11)}$$

$$R_i(q) = w_i n_i^2/(1 + q^2 R_{\text{g}i}^2) \qquad \text{(A12)}$$

Then

$$s_k = R_k(q)/\sum_{i=k,i} R_j(q) \qquad \text{(A13)}$$

$$s_i = R_i(q)/\sum_{i=k,i} R_j(q) \qquad \text{(A14)}$$

In the present study, since the block lengths of KT-326 and KT-327 are very close to each other, 'phase separation' during micelle formation may not occur. Hence, the most likely case for a single-step T-jump is single comicelle formation, i.e. the case where only micelles of type a are formed. This case is described by

$$f_{1\text{b}} = f_{2\text{b}} = 0$$

$$f_{1\text{a}} = f_{2\text{a}} = 1$$

This case includes the extreme case where only micelles consisting of pure copolymer 1 are formed, while copolymer 2 does not form any micelles ($\phi_2 = 0$).

Evaluation of $R_{\text{g}k}$, R_{hk}, $R_{\text{g}i}$ *and* R_{hi}

We now have the very important issue that $R_{\text{g}k}$ and $R_{\text{h}k}$ from equations (A7) and (A10) should be evaluated from M_k and θ_{ik}. For pure copolymer micelles, $R_{\text{g}k}(M_k)$ and $R_{\text{h}k}(M_k)$ can readily be obtained experimentally, while those of the unimers may be approximated by those of the linear polymers. This approximation is valid because the contributions to R_{gapp} and R_{happ} from the unimers are usually very small owing to the low intensity of scattered light from these species.

Here, we adopt the assumption of simple additivity for $R_{\mathrm{g}k}$ and $R_{\mathrm{h}k}$, since the structure of the comicelle may be similar to the structure of the pure micelle for copolymers with only a slight difference in block length. In other words, $R_{\mathrm{g}k}$ and $R_{\mathrm{h}k}$ are assumed to be approximated by

$$R_{\mathrm{g}k} = R_{\mathrm{gm1}}(M_k)\theta_{1k} + R_{\mathrm{gm2}}(M_k)\theta_{2k} \tag{A15}$$

$$R_{\mathrm{h}k} = R_{\mathrm{hm1}}(M_k)\theta_{1k} + R_{\mathrm{hm2}}(M_k)\theta_{2k} \tag{A16}$$

with

$$R_{\mathrm{gm}i}(M) = L_{\mathrm{g}i}M^{\nu} \tag{A17}$$

$$R_{\mathrm{hm}i}(M) = L_{\mathrm{h}i}M^{\nu} \tag{A18}$$

where $R_{\mathrm{gm}i}(M)$ and $R_{\mathrm{hm}i}(M)$ are, respectively, the R_{g} and R_{h} for a pure micelle of copolymer i as a function of the micellar molecular weight M. In the present calculations, ν was taken as 1/3 for spherical micelles, and $L_{\mathrm{g}i}$ and $L_{\mathrm{h}i}$ were chosen according to the micellization conditions in view of the fact that M_{app}, R_{gapp} and R_{happ} depend on the temperature history of the solution. Both $R_{\mathrm{g}i}$ and $R_{\mathrm{h}i}$ for the unimers can be taken as 8 nm for KT-326 and KT-327.

Eventually, we can estimate some of the quantities M_k, ϕ_i and f_{ik} (or θ_{ik}), three of them at the maximum, from the observed values of M_{app}, R_{gapp} and R_{happ} by minimizing the deviation of the calculated values from the experimental values.