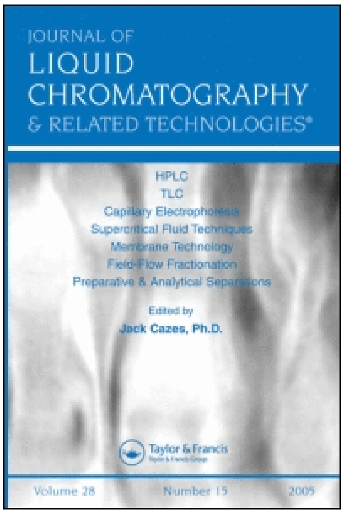

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STUDY OF POLYSTYRENE-BLOCK-POLY(METHYL METHACRYLATE) MICELLES BY SIZE EXCLUSION CHROMATOGRAPHY/ LOW ANGLE LASER LIGHT SCATTERING ANOMALOUS MICELLIZATION

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ABSTRACT

Anomalous micellization behaviour consisting in the simultaneous presence of two kinds of micelles was observed in the micellar system polystyrene-*block*-poly(methyl methacrylate) in 1,4-dioxane/cyclohexane. This anomaly already known, particularly from static light scattering studies of various micellar systems, was now observed by size exclusion chromatography/low-angle laser light scattering technique. For the solvent mixture 1,4-dioxane/70 vol. % cyclohexane, this method enabled a partial size exclusion chromatography separation of the regular and anomalous micelles and allowed to

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estimate the weight-average molecular weight of both. Anomalous micellization was reliably detected by size exclusion chromatography although the static light scattering data provided only weak confirmation of this phenomenon.

INTRODUCTION

The association of block copolymers to micelles in dilute solutions in selective solvents (i.e. good solvents for one block which are precipitants for the other block) is well known. In most cases, the process of micellization follows the simple closed association model which assumes a dynamic equilibrium between micelles (monodisperse in size and molecular weight) and molecularly dissolved copolymer - unimer.[1,2]

The application of size exclusion chromatography (SEC) to the study of micellar systems is accompanied by two phenomena that take place in the column during the SEC separation: (i) the dissociation of micelles and (ii) the loss of a certain amount of the solute. For the former phenomenon, the dynamics of the unimer ⇄ micelles equilibrium is responsible. Micelles separated from the unimer in the SEC column tend to dissociate into the unimer to re-establish the equilibrium concentration of the unimer in the micellar zone.[3,4] This complicates the SEC analysis of micellar systems since the resulting chromatograms reflect two simultaneous processes: SEC separation and unimer ⇄ micelles re-equilibration. However, the obtained chromatograms provide indirect information on the dynamics of unimer ⇄ micelles equilibrium. The partial loss of the solute in the column is, in general, ascribed to the thermodynamically poor quality of solvent for the copolymer.

Two different mechanisms have been proposed for this phenomenon: (i) adsorption of the unimer on the column packing[5,7] and (ii) steric trapping of micelles formed from the unimer inside the pores of the column packing gel.[8,9] As evident, in both cases the unimer form of copolymer (i.e. unimer present in the injected sample and/or formed by dissociation of micelles in the column) is assumed to be "active" in the process of "solute losing".

Polystyrene-block-poly(methyl methacrylate) (PS-PMMA) in a mixed 1,4-dioxane/cyclohexane solvent of high cyclohexane contents forms micelles with PMMA core and PS shell. In our previous articles, results of the SEC study of micellar systems based on PS-PMMA samples of different molecular weight and composition have been reported.[6,7] Coupling SEC with low-angle laser light scattering detector (LALLS) allowed for a better interpretation of elution curves and for the direct determination of molecular weight characteristics of micelles for many micellar systems. Values of weight-average molecular weight of micelles obtained by SEC/LALLS agreed with those determined independently by static light scattering (SLS) and did not depend on the concentration of the injected sample (in accordance with the closed association model of micelles formation). The dissociation of PS-PMMA micelles and the loss of a certain amount of unimer during the SEC separation were evident. Both effects were more pronounced for micellar systems of lower molecular weight PS-PMMA samples. The loss of unimer in the column was studied in details and this phenomenon was ascribed to the adsorption of the unimer on the column packing.[7]

In this article we report on the phenomenon of anomalous micellization observed for a particular PS-PMMA/1,4-dioxane/cyclohexane system. SEC/LALLS and the standard SLS were applied again.

EXPERIMENTAL

Copolymer

Polystyrene-block-poly(methyl methacrylate) (PS-PMMA) was synthesized by anionic polymerization. The details on the synthesis are described elsewhere.[6] A copolymer with 52.6 wt. % of PS according to elemental analysis was prepared. The molecular weight characteristics determined by size exclusion chromatography/low-angle laser light scattering were: weight-average molecular weight $\overline{M}_w = 91000$, number-average molecular-weight $\overline{M}_n = 87500$. This analysis (done in THF) showed a concentration record with a single, narrow and symmetrical peak.

Size Exclusion Chromatography (SEC)

Waters 150 C apparatus with two detectors coupled on line: a low-angle laser light scattering (LALLS) photometer (Chromatix CMX-100) (wavelength λ=632.8 nm) and a standard Waters differential refractometer (DR) was applied. For the characterization of the copolymer sample five column in series (PL gel) having upper permeability limits of 10^6, 10^5, 10^4, 10^3, and $5x10^2$, respectively, and THF as eluent with a flow rate of 1 mL/min were used. The SEC study of the micellar systems was carried out with one column packed with μ-styragel (10^5). Different 1,4-dioxane/cyclohexane mixtures were employed as the mobile phase at a temperature of 25°C. Both, 1,4-dioxane and cyclohexane (both Rhone Poulenc, for analysis) were distilled over sodium wire before use.

The copolymer was always dissolved in a given solvent mixture for 24 h at a temperature of 25°C prior to analysis. The SEC experiments were carried out at a flow rate of 1 mL/min, the concentration of injected solutions (100μL) ranged from 5 to 50 mg/mL.

Static Light Scattering (SLS)

SEM-633 apparatus from SEMATECH (wavelength $\lambda = 632.8$ nm) was used. The weight-average molecular weight of all scattering particles in the solution, $\overline{M}_w^{(p)}$ was obtained at 25°C using the relation:

$$Kc/R_0 = 1/\overline{M}_w^{(p)} + 2A_2c \qquad (1)$$

where K is the optical constant, R_0 is the Rayleigh ratio extrapolated to zero angle, c is the copolymer concentration and A_2 is the second viral coefficient. $\overline{M}_w^{(p)}$ can be given by:

$$\overline{M}_w^{(p)} = \sum_{i=1}^{p} w_i (\overline{M}_w)_i \qquad (2)$$

where w_i and $(\overline{M}_w)_i$ are the mass fraction and weight-average molecular weight of individual kinds of scattering particles (micelles, unimer) in the solution, respectively.

The estimates of the critical micelle concentration (CMC) were obtained from the shape of the dependencies Kc/R_0 vs c. The details on $\overline{M}_w^{(p)}$ and CMC determination from the SLS data are available elsewhere.[1,2]

RESULTS AND DISCUSSION

The results of static light scattering (SLS) measurements are shown in Fig. 1 where the dependencies of Kc/R_0 (extrapolated to zero angle) on overall concentration of copolymer c are given for different solvent mixtures. It can be concluded from Fig. 1 that in the solvent mixtures 1,4-dioxane/(0-50) vol. % cyclohexane copolymer is dissolved molecularly (unimer) while in mixtures with a higher content of cyclohexane, the presence of micelles in the solutions is evident. Except for curve 5, where a slight decrease in Kc/R_0 was detected for very low values of c, Fig. 1 represents typical results for associating block copolymers in selective solvents, i.e., for regular micelles formed by closed

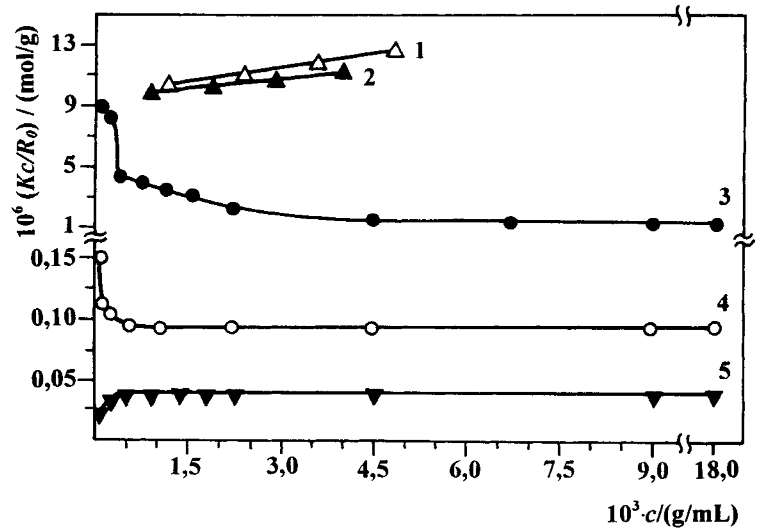

Figure 1. Concentration dependence of Kc/R_0 from static light scattering for solutions of PS-PMMA in mixtures 1,4-dioxane/cyclohexane at 25 °C. Vol.% of cyclohexane: 0 (1); 50 (2); 60 (3); 70 (4); 80 (5).

Table 1

Critical Micelle Concentration (CMC) and Weight-Average Molecular Weight of all Scattering Particles in the Solution, $\overline{M}_w^{(M)}$ *

Content of Cyclohexane	SLS		SEC/LALLS
in vol. %	CMCin g/mL	$10^{-6} \times \overline{M}_w^{(p)}$	$10^{-6} \times \overline{M}_w^{(M)}$
60	1×10^{-4}	0.67	12
70	$<1 \times 10^{-5}$	11	26
80	$<5 \times 10^{-6}$	26	36

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* Determined by static light scattering (SLS) and weight-average molecular weight of micelles, $\overline{M}_w^{(M)}$, determined for concentration of injected solution c = 10 mg/mL by size exclusion chromatography/low-angle laser light scattering (SEC/LALLAS), for PS-PMMA micellar system in 1,4-dioxane/cyclohexane of various contents of cyclohexane.

association. The detailed interpretation is available, e.g., in ref. 2. Values of critical micelle concentrations (CMC) and weight-average molecular weight of all scattering particles in the solution, $\overline{M}_w^{(p)}$, were determined for different solvent mixtures (see Table 1). The latter were obtained by extrapolating the Kc/R_0 values from the horizontal parts of Kc/R_0 vs. c dependencies (Fig. 1 Curves 3, 4, 5) to c = 0 (Eq. 1). For solvent mixtures containing 70 and 80 vol. % cyclohexane, only upper estimates of CMC were available since they were shifted to very low copolymer concentrations. Both CMC and $\overline{M}_w^{(p)}$ values exhibit the trends typical for block copolymer micellar systems: the decrease in thermodynamic quality of solvent (i.e. the increase in cyclohexane content in the mixture) results in (i) decrease in CMC and (ii) increase in $\overline{M}_w^{(p)}$ values. From the closed association model, the value of CMC is very close to the equilibrium concentration of unimer in the regular micellar system. According to the standard procedure, the low CMC value usually allows to omit the unimer contribution to the value of $\overline{M}_w^{(p)}$ in Eq. 2 and to consider $\overline{M}_w^{(p)}$ as the weight-average molecular weight of micelles, $\overline{M}_w^{(M)}$. According to this approximation the values of $\overline{M}_w^{(p)}$ given in Table 1 should represent values of $\overline{M}_w^{(M)}$ for the studied system.

SEC/LALLS experiments on PS-PMMA sample were performed for all 1,4-dioxane/cyclohexane mixtures studied by SLS. Copolymer was always dissolved in the same solvent mixture as that used for SEC mobile phase. To study the effect of solvent composition, the concentration of injected sample (100μL) of 10 mg/mL and a flow rate of 1 mL/min were applied. The shapes of resulting chromatograms are shown in Fig. 2. In the concentration profiles (DR response), the peaks at a lower elution volume (V_e = 9.2 mL Fig. 2b, V_e = 9.1 mL Fig. 2c, V_e = 9.2 mL Fig. 2d) for which significant LALLS detector responses were obtained, were ascribed to micelles. The peaks at higher elution volume (V_e= 11.4 -12.0 mL) correspond to the unimer in the case of all solvent mixtures studied. The small peaks at V_e = 13.9-14.5 mL (at the permeation limit of the column) correspond to the SEC system peaks and probably reflect the selective solvation of the solute.[10] It is seen from Fig. 2 that the region of solvent composition where micelles were detected by SEC/LALLS corresponds to that resulting from SLS measurements. The phenomenon of solute loss, which is evident from the areas below the DR records, was observed from 60 vol .% cyclohexane content and was most pronounced for 1,4-dioxane/70 vol. % cyclohexane (Fig. 2 c). The trapped solute was always completely eluted by a zone of good solvent (100 μL of 1,4-dioxane).[6,7] According to the SLS results, the unimer $\rightleftarrows$ micelles equilibrium should be shifted strongly in favour of micelles in all micellizing solutions injected (c = 10 mg/mL) (see CMC values in Table 1). The decrease in the fraction of micelles detected after the passage

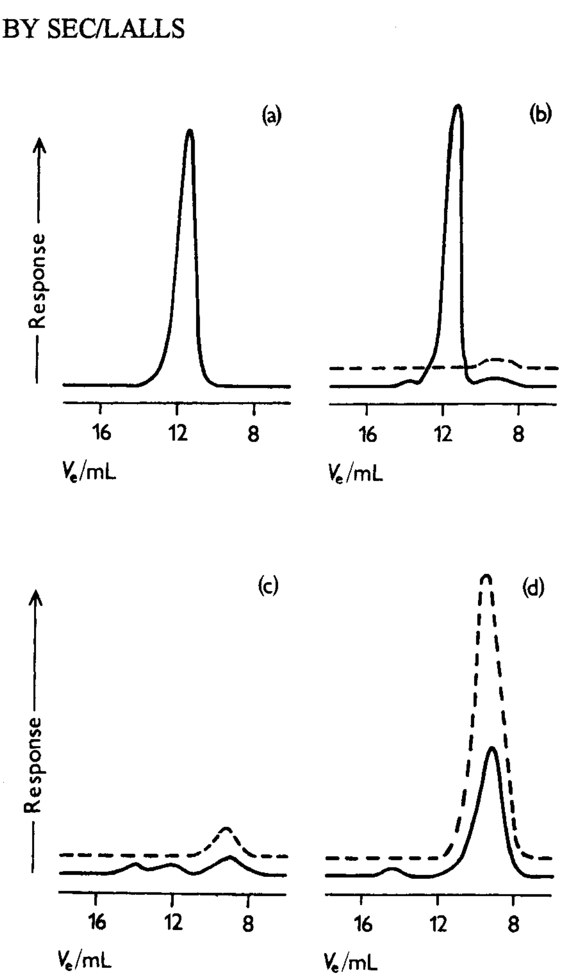

Figure 2. SEC curves of PS-PMMA in mixtures 1,4-dioxane/cyclohexane at 25 °C. Vol.% of cyclohexane: 0-50 (a); 60 (b); 70 (c); 80 (d). Concentration 10 mg/mL; injection volume 100 μL; flow rate 1 mL/min. Full line -DR response; dashed line - LALLS response.

through the column reflects the unimer $\rightleftarrows$ micelles re-equilibration (dissociation of micelles) in the course of separation. Unimer resulting from this process is partly trapped (adsorbed) on the column packing and partly detected as the unimer peak (Fig. 2 b, c).

Good separation of peaks of micelles in chromatograms in Fig. 2 enabled direct determination of $\overline{M}_w^{(M)}$ from LALLS and DR detectors responses; the results are summarized in Table 1. As evident from Table 1, there is a great difference between the values of $\overline{M}_w^{(M)}$ determined by SEC/LALLS and values of $\overline{M}_w^{(p)}$ (that should represent the weight-average molecular weight of micelles given by SLS - see above). For all solvent mixtures where micelles were detected, the $\overline{M}_w^{(p)}$ values provided by SLS were significantly lower as compared to $\overline{M}_w^{(M)}$ values from SEC/LALLS. The difference is most pronounced for 1,4-dioxane/60 vol. % cyclohexane and decreases with increasing cyclohexane content. Both methods provided reproducible values and no changes were observed if the period of copolymer solution aging (see Experimental) was prolonged from one day to one week. The SLS method in micellar studies has been known for a long time as a powerful and reliable tool for $\overline{M}_w^{(M)}$ determination.[1,2] The method of SEC/LALLS was tested for various PS-PMMA/1,4-dioxane/cyclohexane micellar systems in our previous studies and was found to provide $\overline{M}_w^{(M)}$ values which are in a good agreement with those obtained by independent SLS measurements.[6,7] Thus, the discrepancy found for the reported micellar system (Table 1) cannot be explained by the errors associated with the methods used. For the more reliable explanation, the possible effect of the anomalous micellization should be taken into consideration. This phenomenon has been reported in connection with the studies of micellization of various block copolymers in different selective solvents.[2,11-13] In these systems two kinds of micelles differing in size and molecular weight were observed: (i) the expected compact spherical "regular micelles" with a lower size and molecular weight and (ii) particles with a higher size and often also higher molecular weight: "the anomalous micelles." The formation of anomalous micelles was often detected under the conditions relatively close to the "onset" of micellization, i.e. if the overall copolymer concentration only slightly exceeded the CMC value (for a given thermodynamic quality of solvent) or if the thermodynamic quality of solvent dropped down just so that the micelles began to be detected (for a given copolymer concentration and for systems where thermodynamic quality of solvent is controlled by temperature). The presence of anomalous micelles in the studied PS-PMMA/1,4-dioxane/cyclohexane system can be deduced from the slight decrease in Kc/R_0 for $c \rightarrow 0$ found in 1,4-dioxane/80 vol. % cyclohexane (see Fig. 1 Curve 5). In order to find a more reliable confirmation of the anomalous behaviour, the influence of the copolymer concentration in the injected sample on the SEC/LALLS results was studied. A flow rate of 1 mL/min and injection volume of 100 μL were applied and concentrations c = 5, 10, 20, 30, 40, and 50 mg/mL were tested. The most interesting results were obtained for the micellar system in 1,4-dioxane/70 vol. % cyclohexane. The shapes of resulting chromatograms are given in Fig. 3. The strong concentration dependence of the shape of chromatograms is evident from this Figure. For the lower concentrations (c = 5 and 10 mg/mL), only unimer and symmetrical micellar peaks were detected. However, for the higher concentrations (c = from

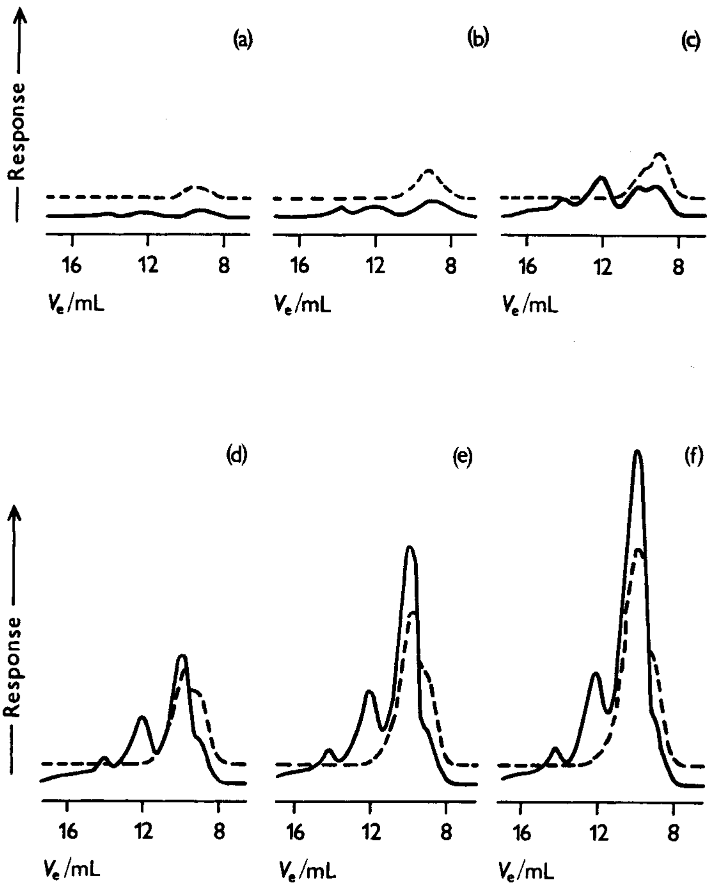

Figure 3. SEC curves of PS-PMMA in 1,4-dioxane/70vol.% cyclohexane at 25 °C. Flow rate 1 mL/min; injection volume 100 μL. Concentration of samples injected (in mg/mL): 5 (a); 10 (b); 20 (c); 30 (d); 40 (e); 50 (f). Full line -DR response; dashed line -LALLS response.

20 to 50 mg/mL) both DR and LALLS profiles of micelles are deformed and evidently consist of two strongly overlapped peaks. For c = 20 mg/mL two distinct maxima at V_e = 9.1 mL and V_e = 10.1 mL are apparent (Fig. 3 c). The resolution of these maxima is decreasing with the further increase in c (Figs 3 d -f), evidently due to the increase in intensity of the micellar peak of the higher elution volume. On the basis of LALLS and DR detectors responses, mass fractions of micelles detected after the passage through the column, w, and corresponding values of $\overline{M}_w^{(M)}$ were determined from the overall SEC profiles of

micelles. Values of w represent the mass of detected micelles divided by the mass of copolymer injected into the column. These values are listed in Table 2 for the different concentrations. Unfortunately, due to the strong overlapping, neither w nor $\overline{M}_w^{(M)}$ values corresponding to the individual peaks of the overall SEC micelles profiles were accessible. The deformation of the micellar peaks in Figs 3 c -f is evidently caused by the simultaneous presence of two kinds of particles (differing in molecular weight) in the micellar zone eluted out from the column. The particles with the slightly lower elution volume and with the higher molecular weight represent anomalous micelles, those with the higher elution volume and the lower molecular weight represent regular micelles. We assume that, regardless of the concentration applied, these two kinds of micelles were present in all injected samples and that they were present in approximately the same mass ratio. This may be deduced from the SLS results for 1,4-dioxane/70 vol. % cyclohexane (Fig. 1, Curve 4) where the Kc/R_0 values do not change in the region of higher c.

For the detailed interpretation of the results in Fig. 3, the process of the micelle dissociation during the SEC separation of micelles from the unimer is important. For any micellar system this dissociation is driven by the tendency to re-establish the equilibrium concentration of unimer in the micellar zone. Since this equilibrium unimer concentration is almost constant above the CMC, the same amount of micelles still tends to dissociate regardless of the concentration of micelles in the micellar zone. For a higher concentration of micelles in a column zone, this dissociation causes a less significant decrease in the resulting peak of micelles and vice versa. This seems to be qualitatively confirmed for the reported system by the concentration dependence of the values of w evident from Table 2. It is clear that for the exact interpretation the other effects complicating the process described should be taken into account, e.g. the spreading of micelles zone and mainly the concentration dependence of the rate of dissociation of micelles. Anomalous micelles are considered as more complex and more difficult to be disentangled in a comparison with the regular ones, moreover they often behave as non-equilibrium species. It can be assumed that the anomalous micelles either do not dissociate in the column or that the rate of their dissociation is lower in comparison with the rate of dissociation of the regular ones. In the course of the SEC separation of sample containing both the anomalous and regular micelles the relative fraction of the former in the micellar zone should therefore increase continuously as a result of a more rapid dissociation of the latter. Resulting micellar peak should thus be enriched with the anomalous micelles.

This complex process seems to be responsible for the concentration dependence of the shape of SEC chromatograms in Fig. 3. With decreasing concentration of the injected sample, the fraction of regular micelles detected decreases more rapidly as compared to the fraction of anomalous ones. (See

Table 2

Mass Fraction, w, of PS-PMMA sample, which passed through SEC Column in the Form of Micelles and Weight-Average Molecular Weight of These Micelles, $\overline{M}_w^{(M)}$ *

c	70 Vol. % Cyclohexane		80 Vol. % Cyclohexane	
In mg/mL	w in %	$10^{-6} \times \overline{M}_w^{(M)}$	w in %	$10^{-6} \times \overline{M}_w^{(M)}$
5	10	27	48	40
10	12	26	58	36
20	16	21	68	33
30	29	16	70	32
40	38	14	73	32
50	49	14	75	30

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* Determined by size exclusion chromatography/low-angle laser light scattering for various concentraiton of injected sample, c, and various content of cyclohexane in 1,4-dioxane/cyclohexane solvent mixtures.

Figs 3f-d). The single symmetrical peak of micelles detected for c = 5 and 10 mg/mL (Figs 3 a, b) appears at a lower elution volume (V_e = 9.1 mL) than that corresponding to the regular micelles observed at higher concentrations. This indicates that in these cases the process of the micelles dissociation during the SEC separation has led to a big decrease in the concentration of the regular micelles in the system or very probably even to their total disappearance. Thus, micellar peaks in Figs 3 a, b can be assumed to be formed predominantly, or even exclusively, by the anomalous micelles. Then, the values of $\overline{M}_w^{(M)}$ resulting from the chromatograms in Figs 3 a, b can be regarded as the lower estimate of weight-average molecular weight of the anomalous micelles that should be close to the real value. The estimate of the weight-average molecular weight of the regular micelles can be roughly derived from the value of $\overline{M}_w^{(p)}$ obtained for 1,4-dioxane/70 vol. % cyclohexane by SLS (Table 1). This value represents the weight-average molecular weight of regular and anomalous micelles (provided that the contribution of unimer to this value is negligible). For evaluating the mass fraction of anomalous micelles in the solution used for SLS, the value of w determined by SEC for c = 10 mg/mL (Table 2) can be taken as lower estimate (some amount of anomalous micelles may have dissociated in the column). If the above mentioned estimates of mass fraction and weight-average molecular weight of anomalous micelles are used, the upper estimate of weight-average molecular weight of regular micelles can be easily calculated from Eq. 2 to be 9×10^6.

For the thermodynamically worse solvent mixture i.e., for 1,4-dioxane/ 80 vol. % cyclohexane, no concentration dependence of the shape of SEC chromatograms was found. For all concentrations of the injected sample, both DR and LALLS records corresponded to that given in Fig. 2 d for c = 10 mg/mL exhibiting only single micellar peak with no detectable deformation. The determination of $\overline{M}_w^{(M)}$ and w values from LALLS and DR detectors responses led to the results given for different concentrations in Table 2. For these results, a similar interpretation as given above for the mixture containing 70 vol. % cyclohexane can be given. Again, the simultaneous presence of regular and anomalous micelles (differing in the molecular weight and the rate of dissociation) can cause an increase in $\overline{M}_w^{(M)}$ with decreasing concentration of the injected sample (Table 2). However, the increase in $\overline{M}_w^{(M)}$ is lower than for the solvent with 70 vol. % cyclohexane. The fact that no SEC separation of the regular and anomalous micelles was observed in this case could be explained by too small a difference in hydrodynamic volumes of these particles in a thermodynamically very bad solvent. In the 1,4-dioxane/80 vol. % cyclohexane mixture, only very approximate estimates of molecular weight of individual micelles are possible. It may roughly be said that the value of $\overline{M}_w^{(M)}$ resulting for c = 5 mg/mL from SEC/LALLS (Table 2) represents a lower limit for weight-average molecular weight of anomalous micelles, the value of $\overline{M}_w^{(p)}$ resulting from SLS (Table 1) an upper limit for weight-average molecular weight of regular micelles.

In a 1,4-dioxane/60 vol. % cyclohexane mixture, no measurable influence of the concentration of injected sample on the SEC results was detected. The shape of SEC concentration records corresponded to that given in Fig. 2 b: micelles were always well separated from unimer and their mass fraction w was from 5 to 6% regardless of the concentration of the injected sample. Values of $\overline{M}_w^{(M)}$ resulting from SEC/LALLS were found to be unchanged with the concentration of the injected sample, being within the limits of experimental errors equal to the value given by this method for 1,4-dioxane/60 vol. % cyclohexane solvent mixture in Table 1. Both, the high value of $\overline{M}_w^{(M)}$ compared to $\overline{M}_w^{(p)}$ from SLS and no systematic influence of concentration of injected sample on the value of w indicate that the micelles peak detected for all concentrations represents the anomalous micelles.

The obtained results suggest that regular micelles either dissociated always completely during the SEC separation or that they were not present at all in the injected samples. The second possibility is more reliable from the subsequent consideration. If the product $\overline{M}_w^{(M)}$ w is compared with the value of $\overline{M}_w^{(p)}$ determined in 1,4-dioxane/60 vol. % cyclohexane by SLS (Table 1) it is evident that $\overline{M}_w^{(p)}$ is contributed predominantly by anomalous micelles. A contribution of the remaining scattering particles is considerably smaller (ca one order of magnitude) and seems to correspond to the contribution of unassociated copolymer - unimer. For a more precise conclusion to be drawn from Eq. 2, a considerably higher accuracy in determination of $\overline{M}_w^{(M)}$ and w values for anomalous micelles than that offered by SEC/LALLS is needed. These results indicate that in 1,4-dioxane/60 vol. % cyclohexane, only a small mass fraction of copolymer is associated into the relatively high molecular weight (anomalous) micelles while the remaining majority of copolymer is present in the form of unimer.

This finding differs from that obtained by the standard interpretation of SLS results (Fig. 1, Curve 3; Table 1). According to SLS, the unimer $\rightleftarrows$ micelles equilibrium should be shifted strongly in favour of relatively low molecular weight micelles (formed by association of only 7 or 8 unimer chains) in PS-PMMA/1,4-dioxane/60 vol. % cyclohexane system. Evidently, in this anomalous case the standard SLS applied as the only method is not sensitive enough to characterize reliably the composition of the micellar system studied.

CONCLUSION

The method of SEC/LALLS was shown to be a powerful tool (especially in combination with standard SLS) for the confirmation and study of anomalous micellization phenomenon. Two points can be insinuated for an anomalous behaviour of the studied system: (i) a significant difference in values of $\overline{M}_w^{(M)}$ resulting from independent SEC/LALLS and SLS measurements and (ii) a strong dependence of the values of $\overline{M}_w^{(M)}$ resulting from SEC/LALLS on the concentration for some solvent compositions.

As it was demonstrated, the phenomenon of anomalous micellization may remain undiscovered if only the SLS method is applied and in such a case SLS can provide less or more distort information on the composition of micellar system.

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