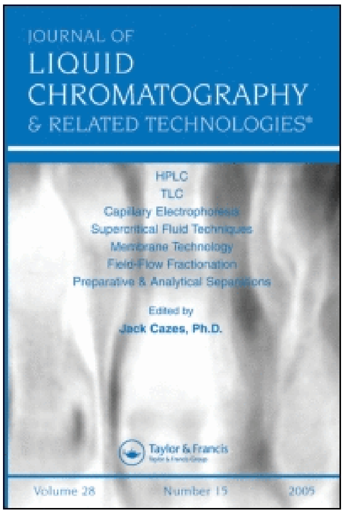

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Study of Polystyrene-Block-Poly(Methyl Methacrylate) Micelles by Size Exclusion Chromatography/Low Angle Laser Light Scattering. Influence of Copolymer Composition and Molecular Weight

Zlatka GrubiŠIc-Gallot[a]; Yves Gallot[a]; Jan Sedláček[b]
[a] Institut Charles Sadron, (CRM-EAHP)(CNRS-ULP), Strasbourg, Cedex, France [b] Dept. of Physical and Macromolecular Chemistry Faculty of Science, Charles University Albertov, Prague, Czech Republic

To cite this Article GrubiŠIc-Gallot, Zlatka , Gallot, Yves and Sedláček, Jan(1995) 'Study of Polystyrene-Block-Poly(Methyl Methacrylate) Micelles by Size Exclusion Chromatography/Low Angle Laser Light Scattering. Influence of Copolymer Composition and Molecular Weight', Journal of Liquid Chromatography & Related Technologies, 18: 12, 2291 — 2307

To link to this Article: DOI: 10.1080/10826079508013964

URL: http://dx.doi.org/10.1080/10826079508013964

JOURNAL OF LIQUID CHROMATOGRAPHY, 18(12), 2291-2307 (1995)

STUDY OF POLYSTYRENE-BLOCK-POLY(METHYL METHACRYLATE) MICELLES BY SIZE EXCLUSION CHROMATOGRAPHY/LOW ANGLE LASER LIGHT SCATTERING. INFLUENCE OF COPOLYMER COMPOSITION AND MOLECULAR WEIGHT

ZLATKA GRUBIŠIC-GALLOT[1], YVES GALLOT[1], AND JAN SEDLÁČEK[2]
[1]Institut Charles Sadron, (CRM-EAHP)(CNRS-ULP)
6, rue Boussingault
67083 Strasbourg, Cedex, France
[2]Dept. of Physical and Macromolecular Chemistry
Faculty of Science, Charles University
Albertov 2030, Prague, Czech Republic

ABSTRACT

Results of size exclusion chromatography study of the micellar systems polystyrene-*block*-poly(methyl methacrylate) in the mixed solvent 1,4-dioxane/cyclohexane are reported and the behaviour of copolymers with different overall molecular weight and chemical composition is compared. At higher content of cyclohexane, the effect of the solute trapping in the column due to the adsorption of the unimer on the packing was observed. This effect was more pronounced for the lower molecular-weight copolymers as compared with the higher molecular-weight ones and was found to depend significantly on the thermodynamic quality of solvent (eluent). Experiments in 1,4-dioxane/70 vol.% cyclohexane showed strong influence of unimer - micelles re-equilibration in the column on the resulting chromatograms, especially for the micellar systems of the lower molecular-weight copolymers. For the copolymers of higher molecular-weight, the micelles dissociation in the column was reduced probably due to the more entangled and compact cores of micelles.

INTRODUCTION

The formation of copolymer associates - micelles in dilute solutions of block copolymers in selective solvents (i.e. thermodynamically good solvent for one block and at the same time poor solvent for the other block) is well-known. The formation of these micelles is described by the "closed association" model. This model is characterized by an equilibrium between the micelles (M), with a narrow molecular-weight and size distribution, and the molecularly dissolved copolymer - unimer (U).

$$n\,U \rightleftarrows M \qquad (1)$$

where n is the association number. The equilibrium, (i.e. the association number and concentrations of unimer and micelles) and the dynamics of its achievement depend upon several parameters such as the nature of the copolymer and the selectivity of solvent (usually controlled by the composition of a solvent mixture or/and by the temperature) [1,2].

Various techniques are currently used for the study of micellar systems e.g. light scattering [2,3], sedimentation [4], size exclusion chromatography (SEC) [5]. The application of SEC to the separation and characterization of individual components for a micellar system is usually complicated by the unimer $\rightleftarrows$ micelles association and dissociation which takes place in the SEC column. Chromatograms obtained with micellar systems reflect two competing processes: (i) the separation of the solute in the column; and (ii) the disturbing and subsequent re-establishment of the unimer $\rightleftarrows$ micelles equilibrium (Eq. 1). The shape of the corresponding chromatograms depends on the relative rates of these two processes as proposed theoretically [6] and confirmed by SEC studies on various block copolymer micellar systems [5,7,8]. Additional complications in the use of SEC to study of micellar systems often arise due to the loss of the solute in the column during the SEC separation. The adsorption of the unimer form of the copolymer is most frequently given as the reason for this phenomenon [7-9].

These effects, the strong influence of the unimer $\rightleftarrows$ micelles re-equilibration on the shape of chromatograms and the significant loss of the solute in the course of the SEC separation were observed in previous work [10]. This latter study used SEC coupled with a low-angle laser light scattering (LALLS) detector applied to a polystyrene-*block*-poly(methyl methacrylate) (PS-PMMA) in a mixed 1,4-dioxane/cyclohexane solvent. In this solvent, micelles with PMMA core and PS shell are formed at higher contents of cyclohexane. Use of the LALLS detector was found to be very advantageous for the subsequent interpretation of the elution curves and for the determination of the molecular weight characteristics of the micelles; molecular weights of micelles determined by this detector were found to be in agreement with those determined independently by static light scattering.

This article focuses on the influence of the composition and overall molecular weight of PS-PMMA on the behaviour of the micellar system in 1,4-dioxane/cyclohexane. The same techniques, i.e. SEC/LALLS and the static light scattering, were applied.

EXPERIMENTAL

Copolymers

Samples of polystyrene-*block*-poly(methyl methacrylate) (PS-PMMA) having different overall molecular-weight and composition were synthesized by anionic polymerization using phenylisopropylpotassium as initiator. The details of syntheses are described elsewhere [10]. The chemical composition of copolymers was determined by elemental analysis. For the determination of weight-average molecular weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$), size exclusion chromatography/low angle laser light scattering was used.

Size exclusion chromatography

Waters 150 C apparatus with two detectors coupled on line: a low-angle laser light scattering (LALLS) photometer (Chromatix CMX-100) and a standard Waters differential refractometer (DR) was applied [11]. For the characterization of the copolymer samples five column in series (PL gel) having upper permeability limits of 10^6, 10^5, 10^4, 10^3 and 5×10^2, respectively, and tetrahydrofuran (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. The copolymers were always dissolved in a given solvent mixture for 24 h at a temperature of 25°C prior to analysis. All the SEC experiments were carried out at a flow rate of 1 mL/min, using the concentration of the injected sample (100μL) of 10 mg/mL.

Static light scattering

SEM-633 apparatus from SEMATECH (wavelength λ = 632.8 nm) was used. The weight-average molecular weights of micelles, $\bar{M}_w^{(M)}$ were obtained at 25°C using the relation:

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

where K is the optical constant, R_o is the Rayleigh ratio extrapolated to zero angle, c is the copolymer concentration and A_2 is the second virial coefficient. $\bar{M}_w^{(p)}$ is the weight-average molecular weight of all scattering particles in solution, which can be considered as the value of $\bar{M}_w^{(M)}$ provided that the equilibrium concentration of unimer is small in comparison with the concentration of micelles [2]. The estimates of the critical micelle concentration (CMC) were obtained from the shape of the dependencies Kc/R_o vs c. The details on $\bar{M}_w^{(M)}$ and CMC determination from the static light scattering data are available elsewhere [2,10].

RESULTS AND DISSCUSION

Four samples of polystyrene-*block*-poly(methyl methacrylate) (PS-PMMA) with different molecular-weights and contents of PS and PMMA were synthesized. Their characteristics are given in Tab. 1. Applying solvent mixture 1,4-dioxane/cyclohexane at various compositions as the eluent, SEC analyses of these copolymers were carried out. The region of solvent composition where PS-PMMA micelles were detected by SEC/LALLS was determined for each copolymer (Tab. 1). For all solvent mixtures where micelles were detected, good unimer-micelle resolution was achieved in the chromatograms of all copolymer samples. The peaks of micelles (detected by DR) were found to increase in intensity with the decrease in thermodynamic quality of solvent, i.e. with the increasing cyclohexane content. Just the opposite trend was observed for the peaks of unimer. The loss of some of the solute in the SEC column was observed for all copolymers at higher contents of cyclohexane. This trapped solute was always completely eluted by a zone of good solvent (an injection of 100 μl of 1,4-dioxane). In the previous article [10] an explanation of this phenomenon was proposed based on the adsorption of the unimer form of the PS-PMMA copolymer on the column packing. The amount of solute lost on the column was found to depend significantly on the thermodynamic quality of the solvent (eluent) and on the molecular weight and composition of the copolymer as shown in Fig. 1. This figure shows the mass fraction of copolymer, w, which passed through the column as a function of the solvent composition. Values of w represent the mass of the copolymer detected by DR (both forms: unimer and micelles) divided by the mass of copolymer injected into the column. All dependencies in Fig. 1 pass through a minimum and the following explanation can be proposed. There are at least two important aspects of the solute loss in the column affected by the solvent composition: (i) the affinity of the unimer to the adsorption on the column packing, which would be expected to increase with the decrease in the thermodynamic

TABLE 1

Weight-average molecular weight ($\bar{M}_w$), polydispersity index ($\bar{M}_w/\bar{M}_n$) and chemical composition in wt.% of polystyrene (PS) of polystyrene-*block*-poly(methyl methacrylate) copolymers (PS-PMMA). Composition range of 1,4-dioxane/cyclohexane mixed solvent (in vol.% of cyclohexane) where micelles of PS-PMMA were detected by size exclusion chromatography/low angle laser light scattering (SEC/LALLS). Weight-average molecular weight of micelles ($\bar{M}_w^{(M)}$) determined by SEC/LALLS and by static light scattering (SLS), polydispersity index of micelles ($\bar{M}_w^{(M)}/\bar{M}_n^{(M)}$) by SEC/LALLS and critical micelle concentration (CMC) by SLS in 1,4-dioxane/70 vol.% cyclohexane.

No.	Characteristics of copolymers			Selective solvent composition[a]	Characteristics of micelles in 1,4-dioxane/70vol.% cyclohexane			
			composition		SEC/LALLS		SLS	
	$10^{-3}\times\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	wt.% of PS	vol.% of cyclohexane	$10^{-6}\times\bar{M}_w^{(M)}$	$\bar{M}_w^{(M)}/\bar{M}_n^{(M)}$	$10^{-6}\times\bar{M}_w^{(M)}$	CMC in g/mL
I	96	1.04	64.0	80 - 85	--	--	1.8	1×10^{-4}
II	162	1.03	66.5	65 - 80	20	1.08	18	$<1\times10^{-5}$
III	91	1.04	52.6	60 - 80	26	1.11	11	$<1\times10^{-5}$
IV	172	1.05	51.2	60 - 75	71	1.13	77	$<5\times10^{-6}$

[a] Composition range of 1,4-dioxane/cyclohexane mixed solvent where micelles were detected by SEC/LALLS.

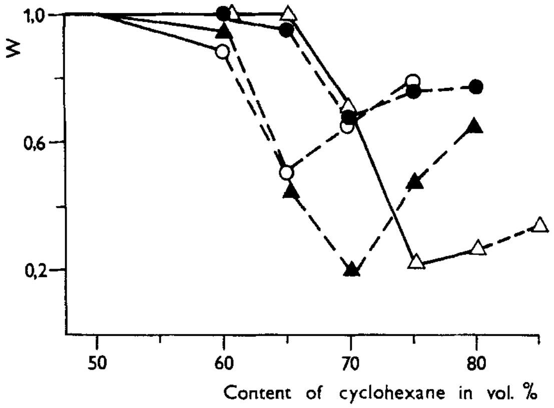

FIGURE 1. Weight fraction, *w*, of PS-PMMA samples which passed through SEC column as function of the content of cyclohexane in the 1,4-dioxane/cyclohexane mixed solvent used as the eluent. Concentration of the injected solution c = 10 mg/mL; injection volume: 100 μL; flow rate: 1 mL/min. Overall weight-average molecular weight of copolymers and content of PS block in the copolymers, respectively: 96 000; 64.0 wt.% (sample *I*) (△), 162 000 66.5 wt.% (sample *II*) (●), 91 000; 52.6 wt.% (sample *III*) (▲), 172 000; 51.2 wt.% (sample *IV*) (○). Dashed line: solvent compositions where micelles were detected by SEC.

quality of the solvent for a given copolymer, i.e. with the increase in content of cyclohexane; and (ii) the equilibrium concentration of the unimer in the column and the rate of the re-establishment of this equilibrium concentration (i.e. the rate of the dissociation of micelles) in the course of unimer-micelles separation. The equilibrium concentration of unimer is generally reported as decreasing with the decrease in the thermodynamic quality of solvent. A similar decrease might be assumed for the rate of dissociation of micelles in the column because more compact micelle cores may be expected in the thermodynamically worse solvent, which hinders a release of the unimer from the micelles. Considering (i) and (ii) the position of minima in Fig. 1 may represent a solvent composition (the quality of solvent) for which the combined effect of both the adsorption affinity of the unimer and its equilibrium concentration are the highest. Although a further drop in the thermodynamic quality of the solvent should cause an increase in the affinity of the unimer to the adsorption, it is simultaneously accompanied by a drop in the concentration of unimer and the latter effect seems to predominate leading, in fact, to the rise in *w* as shown in Fig. 1. A similar observation was reported by Price et. al. in the SEC study of the micellar solutions of polystyrene-*block*-poly(ethylene-*co*-propylene). The authors observed negligible adsorption for the thermodynamically bad solvents but the complete loss of the solute on the column in the thermodynamically better solvents where less stable micelles were present [8].

If we compare the behaviour of copolymers having similar molecular weight but differing in chemical composition (sample *I* vs. *III*, sample *II* vs. *IV*) we observe that the position of the minimum is shifted towards the thermodynamically worse solvent (i.e. higher cyclohexane content) for copolymers with a shorter insoluble (PMMA) block. A similar phenomenon is observed if the solvent composition corresponding to the last point in the dependencies in Fig. 1 is considered. This composition represents the highest content of cyclohexane in 1,4-dioxane/cyclohexane mixed solvent in which a given copolymer was found to be still soluble (solvent composition was changed in steps of five vol.%).

Fig. 1 also offers a comparison between copolymers having similar composition but differing in molecular weight (sample *I* vs. *II* and sample *III* vs. *IV*). Both the position of the minima and the position of the last points in the dependencies in Fig. 1 are shifted towards thermodynamically better solvent for the copolymers with the higher molecular weight. This seems to be ascribable to the longer insoluble blocks (PMMA) in the copolymers having the higher molecular weight (sample *II* and *IV*).

It is also seen from Fig. 1 that the highest losses of the solute in the column were detected for the lower molecular-weight copolymers (compare the depth of the minima in Fig. 1). This finding can be easily explained if we take into account the conformation of the unimer form of copolymer chains in a selective solvent mixture. It may be assumed that this conformation is similar to that known as unimolecular micelles [12] i.e. the insoluble PMMA block slightly collapsed and partially protected by a better soluble PS block which is forming a shell. From this point of view the longer soluble PS block of the higher molecular-weight samples should provide a better protection of the collapsed insoluble PMMA block and thus the unimer adsortion affinity could be reduced to some extent. The effect of the equilibrium concentration of unimer and the rate of its re-establishment must also be considered. The re-equilibration process might be expected to be slowed down for the higher molecular weight copolymers in comparison with the lower molecular-weight ones because of the more difficult disentanglement processes in cores of micelles of the former. All of the above effects probably contribute to the observed dependence of w on the molecular-weight of copolymers (Fig. 1).

For the detailed study of the PS-PMMA micellar systems the selective solvent mixture 1,4-dioxane/70 vol.% cyclohexane was chosen. Solutions of the copolymers in this solvent mixture were studied by means of static light scattering; the results are shown in Fig. 2 where the dependencies of Kc/R_0 (extrapolated to zero angle) on the overall concentration of copolymer in solution, c, are given. The dependencies exhibit a shape typical of associating systems and suggest that all the copolymers form micelles from low copolymer concentrations. The estimates of values of critical micelle concentration (CMC) (the copolymer concentration at which micelles are just detected by a given method) are given in Tab. 1. In this table the values of weight-average molecular weight of micelles $\bar{M}_w^{(M)}$ obtained from the static light scattering measurements are also given. Values of $\bar{M}_w^{(M)}$ were obtained extrapolating the Kc/R_0 values from the horizontal parts of

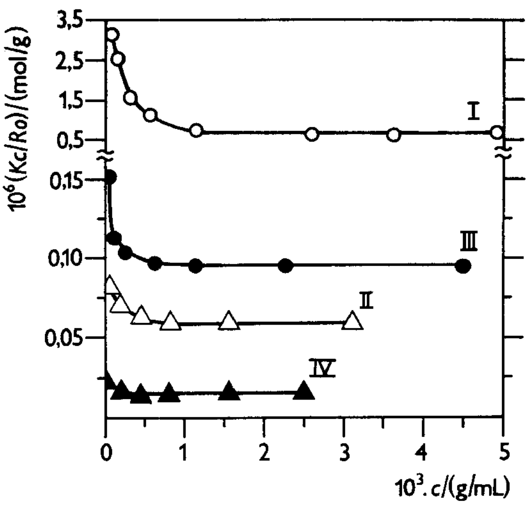

FIGURE 2. Concentration dependence of Kc/R_0 from static light scattering measurements for solutions of samples of PS-PMMA in the mixture 1,4-dioxane/70vol.% cyclohexane at 25°C. Overall weight-average molecular weight of copolymers and content of PS block in the copolymers, respectively: 96 000; 64.0 wt.% (sample *I*), 162 000; 66.5 wt.% (sample *II*), 91 000; 52.6 wt.% (sample *III*), 172 000; 51.2 wt.% (sample *IV*)

dependencies in Fig. 2 to c=0 (Eq. 2). Although this process leads to the weight-average molecular weight of all scattering particles (i.e. so-called particles molecular weight $\bar{M}_w^{(p)}$) this value can be considered as $\bar{M}_w^{(M)}$ in the case of all copolymers because the unimer contribution to the measured value $\bar{M}_w^{(p)}$ is negligible. This is a result of the very low values of CMC (Tab. 1) (CMC is close to the equilibrium concentration of unimer in a micellar system) as already discussed in the previous article [10].

In Fig. 3 the chromatograms resulting from SEC experiments carried out with the copolymers in 1,4-dioxane/70 vol% cyclohexane are shown. In the concentration profiles (DR response) the peaks with a lower elution volume (V_e= 9.1 mL Fig. 3b, V_e= 8.9 mL Fig. 3c, V_e= 8.6 mL Fig. 3d) for which high LALLS detector responses

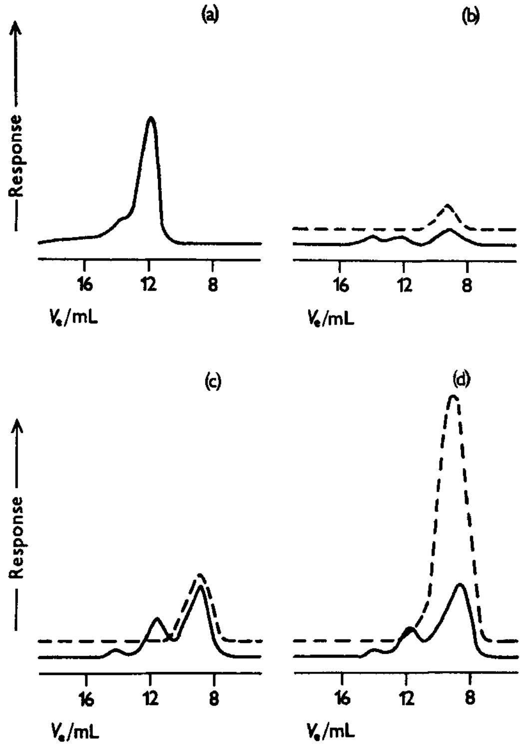

FIGURE 3. SEC curves of PS-PMMA samples in mixture 1,4-dioxane/ 70 vol.% cyclohexane at 25°C. Overall weight average molecular-weight of copolymers and content of PS block in the copolymers, respectively: 96 000; 64.0 wt.% (sample *I*)(a), 91 000; 52.6 wt.% (sample *III*)(b), 162 000; 66.5 wt.% (sample *II*)(c), 172 000; 51.2 wt.% (sample *IV*)(d). Concentration c= 10 mg/mL; injection volume: 100 µL; flow rate: 1 mL/min. Full line: DR response; dashed line: LALLS response. (V_e: elution volume)

were obtained were ascribed to micelles. The peaks at higher elution volume (V_e= 11.6-12.0 mL) correspond to the unimer in the case of all copolymers studied. The small peaks at V_e=13.8-14.2 mL (at the permeation limit of the column) correspond to the SEC system peaks and probably reflect the selective solvation of the solute [10,13].

As mentioned previously, the values of CMC (see above and Tab. 1) are, according to the closed association model (Eq. 1), very close to the equilibrium concentration of the unimer in the micellar system. It can therefore be deduced that for all copolymer samples in the 1,4-dioxane/70 vol.% cyclohexane the unimer $\rightleftarrows$ micelles equilibrium was significantly shifted in favour of the micelles in the solutions injected on the SEC column (c = 10 mg/mL). For example, in the injected solution of sample No. *I*, ca 99 wt.% of copolymer was in the form of micelles. This fraction was even higher for the samples *II*, *III* and *IV*. Considering the values of $(1.0 - w)$ for the 1,4-dioxane/70 vol.% cyclohexane solvent mixture from Fig. 1 (which represent the fraction of unimer trapped in the column) and the intensities of unimer peaks in Fig. 3 as well, it is clear that the amount of micelles detected after the passage through the column does not reflect the micellar equilibrium concentration in the injected sample for any copolymer investigated. This is due to the dissociation of micelles in the course of the SEC experiment, as already described in ref [10]. As soon as the micelles are separated from the unimer in the column (as a result of different hydrodynamic volumes) the equilibrium (Eq. 1) is disturbed in the zone of micelles and a certain amount of the micelles tends to dissociate to re-establish the unimer $\rightleftarrows$ micelles equilibrium. As seen in Fig. 3 this process is in 1,4-dioxane/70 vol.% cyclohexane more pronounced for the micellar systems of the lower molecular-weight copolymers and in case of sample No. *I* it even leads to the total disappearance of the micelles from the system (Fig. 3a). The fact that the fraction of the micelles which dissociate in the column is reduced in the case of the higher molecular-weight copolymers (Fig. 3c, d) might be explained by a lower rate of dissociation of these micelles due to the more entangled and compact micelles cores as already proposed above. Also the values of CMC (Tab. 1) seem to suggest that the equilibrium concentration of unimer is lower in the micellar systems of higher molecular-weight copolymers. Unfortunately the exact comparison is not possible since only upper estimates of CMC were available for the samples *II, III* and *IV* due to the shift of the onset of micellization to very low copolymer concentrations.

It is clear that for the exact interpretation of chromatograms in Fig. 3 other effects should also be considered - in particular the unimer - micelle SEC separation efficiency for each micellar system and the unimer trapping on the column packing. In our case the SEC process deals with the separation of particles (unimer and micelles) for which a significant difference in hydrodynamic volume is expected. This difference is probably not the same for all of the micellar systems studied. We suppose however that this fact has only little influence on the results in Fig. 3. The trapping of the unimer on the column packing is probably more important. The overall influence of this phenomenon is however difficult to evaluate. On the one hand, it might promote the separation of micelles from unimer (a certain amount of unimer which is being formed by the dissociation of micelles in the SEC column is continuously drawn off by adsorption, which can be thus regarded as an additional separation mechanism to SEC process). On the other hand, the trapping of unimer contributes to the reduction of the concentration of the unimer in the micellar zone and thus supports the dissociation of the micelles.

Good separation of peaks of micelles in chromatograms in Fig. 3 b-d enabled direct determination of $\bar{M}_w^{(M)}$ and polydispersity index $\bar{M}_w^{(M)}/\bar{M}_n^{(M)}$ of micelles from LALLS and DR detectors responses; the results are summarized in Tab. 1. As already stated in the previous article [10], in the case of copolymer sample No. *I* 80 vol.% of cyclohexane in 1,4-dioxane/cyclohexane mixed solvent was necessary for the micelles to be detected by SEC. For the micelles of this copolymer, the value of $\bar{M}_w^{(M)}$ was determined to be 7.9×10^6 by SEC/LALLS and 8.5×10^6 by static light scattering in 1,4-dioxane/80 vol.% cyclohexane [10].

There seems to be satisfactory agreement between the values of $\bar{M}_w^{(M)}$ determined by SEC/LALLS and by static light scattering for all copolymers except for the sample No. *III* (Tab. 1). For this sample the static light scattering provided a significantly lower value of $\bar{M}_w^{(M)}$ as compared with SEC/LALLS. Both values were reproducible and the differences between them cannot be explained by errors associated with the methods used. We suppose that this discrepancy might be caused by the effect of anomalous micellization. This phenomenon has been reported in connection with the study of micellization of various block copolymers in different selective solvents [14-16]. In these systems two kinds of micelles differing in size and molecular weight were observed: (i) the expected spherical regular micelles with a lower size and molecular weight and (ii) particles with a higher size and molecular weight: the anomalous micelles. Often only a small fraction of copolymer was found to be in the form of anomalous micelles. The formation of anomalous micelles by equilibrium association of regular ones was proposed for the systems studied by Price et. al. [15] and by Tuzar et. al. [14]. Provided that there exist two kinds of micelle in our micellar system of copolymer No. *III* in 1,4-dioxane/70 vol.% cyclohexane, the anomalous ones might be assumed to be more difficult to disentangle (due to their complexity), i.e. their rate of dissociation into the unimer may be lower compared with the rate of the dissociation of the regular ones. In the course of the SEC separation of this sample the relative fraction of anomalous micelles in the micellar zone should therefore increase continuously as a result of a more rapid dissociation of the regular micelles. The micellar peak in Fig. 3 b should thus be enriched with the anomalous micelles. Since this peak (DR response) seems to be symmetrical and since a certain SEC separation between regular and anomalous micelles should be expected (leading at least to the deformation of the shape of this peak) it might be even assumed that this peak is formed predominantly or even exclusively by the anomalous micelles. It might be concluded therefore, that the value of $\bar{M}_w^{(M)}$ resulting from SEC/LALLS is significantly affected by the presence of anomalous micelles. It is even possible that this value is very close to the weight average molecular-weight of anomalous micelles, provided that a major part of regular micelles had dissociated during the SEC separation process. The value of $\bar{M}_w^{(M)}$ resulting from the static light scattering represents the weight-average molecular weight of all scattering particles in solution, i.e. the weight-average molecular weight of regular and anomalous micelles, since the contribution of unimer to this value is negligible (see above). If the fraction of anomalous micelles in the solution is small compared to the fraction of regular ones, $\bar{M}_w^{(M)}$ should be close to the weight-average molecular weight of regular micelles.

Further research is in progress aimed at the SEC separation of regular and anomalous micelles. It should be noticed that the SEC results confirmed the anomalous behaviour of the copolymer No. *III* in 1,4-dioxane/cyclohexane over a wide range of solvent composition investigated; however no clear evidence of anomalous micellization was found by the static light scattering so far (see also Fig. 2). Results will be published in a forthcoming article devoted exclusively to this phenomenon.

The anomalous behaviour of copolymer No. *III* complicates the correlation between the molecular weight of micelles and the type of the copolymer tested. If however, the value of $\bar{M}_w^{(M)}$ determined by static light scattering for the micelles of copolymer No. *III* is considered as an upper estimate for the weight-average molecular weight of the regular micelles, and provided that this estimate is not very far from the real value, the increase in the weight-average molecular weight of the regular micelles with increasing length of the insoluble PMMA block in the copolymers may be deduced for the mixed solvent 1,4-dioxane/70 vol.% cyclohexane (Tab. 1).

CONCLUSION

For all PS-PMMA copolymers solute trapping due to the adsorption of unimer in the column packing was observed in 1,4-dioxane/cyclohexane solvent mixture for higher contents of cyclohexane. This effect was more pronounced for copolymers with lower overall molecular weights. The SEC results obtained in 1,4-dioxane/70 vol.% cyclohexane showed that the rate of the re-establishment of the unimer $\rightleftarrows$ micelles equilibrium in the zone of micelles (leading to the decrease in the amount of the micelles detected after the passage though the column) was certainly not negligible in comparison with the rate of the SEC separation process. A higher fraction of micelles was detected in the case of copolymers having higher overall molecular weights. This is probably due to the higher stability of these micelles and the lower values of CMC. The molecular weight of micelles formed in 1,4-dioxane/70 vol.% cyclohexane was found to increase with the increasing length of the insoluble (PMMA) block.

ACKNOWLEDGEMENTS

The authors are grateful to J.P. Lingelser from I.C.S. for his valuable assistance in the synthesis of the copolymer samples. One of the authors (J.S.) is grateful to the French Ministry for Research and Technology for granting the post-doctoral fellowship at the Institut Charles Sadron.

REFERENCES

1. Z. Tuzar, P. Kratochvíl, Adv. Colloid Interface Sci., 6: 201 (1979).

2. Z. Tuzar, P. Kratochvíl, Surface and Colloid Science Series Vol. 15, M. Matijevic, Ed., Plenum Press, 1993, p. 1-83.

3. J. Selb, Y. Gallot, Makromol. Chem., 181: 2605 (1980).

4. M. Pacovská, K. Procházka, Z. Tuzar, P. Munk, Polymer, 34: 4585 (1993).

5. P. Špaček, M. Kubín, J. Applied Polym. Sci., 30: 143 (1985).

6. K. Procházka, T. Mandák, M. Kočiřík, B. Bednář, Z. Tuzar, J. Chem. Soc., Faraday Trans., 86: 1103 (1990).

7. C. Booth, T. D. Naylor, C. Price, N. S. Rajab, R. B. Stubbersfield, J. Chem. Soc., Faraday Trans. I, 74: 2352 (1978).

8. C. Price, A. L. Hudd, C. Booth, B. Wright, Polymer, 23: 651 (1982).

9. P. Špaček, J. Appl. Polym. Sci., 32: 4281 (1986).

10. Z. Grubišic-Gallot, Y. Gallot, J. Sedláček, Macromol. Chem. Phys., 195: 781 (1994).

11. A. Halbwachs, Z. Grubišic-Gallot, Makromol. Chem., Rapid Commun., 7: 709 (1986).

12. C. Sadron, Pure Appl. Chem., 4: 347 (1962).

13. D. Berek, T. Macko, C. H. Fischer, 34th IUPAC International Symposium on Macromolecules, Prague, July 13-18, 1992, Proceedings p. 6-7 (1992).

14. Z. Tuzar, J. Stehlíček, Č. Koňák, F. Lednický, Makromol. Chem., 189: 221(1988).

15. T. P. Lally, C. Price, Polymer, 15: 325 (1974).

16. P. A. Canham, T. P. Lally, C. Price, R. B. Stubbersfield, J. Chem. Soc., Faraday Trans. I, 76: 1857 (1980).

Received: February 24, 1995
Accepted: March 7, 1995