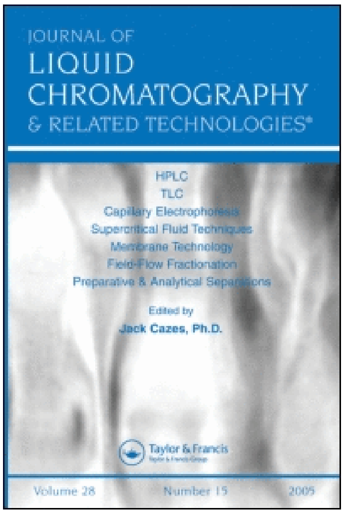


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

STUDY OF POLYSTYRENE-*BLOCK*-POLY(METHYLMETHACRYLATE) MICELLES BY SEC/MALS. DETERMINATION OF MOLECULAR WEIGHTS AND SIZE DISTRIBUTION

Z. Grubišic-Gallot[a]; M. Žigon[b]; J. Sedláček[c]; Yves Gallot[a]
[a] Institut Charles Sadron (CRM-EAHP) (CNRS-ULP), Strasbourg-Cedex, France [b] National Institute of Chemistry, Ljubljana, Slovenia [c] Charles University, Prague 2, Czech Republic

To cite this Article Grubišic-Gallot, Z. , Žigon, M. , Sedláček, J. and Gallot, Yves(1999) 'STUDY OF POLYSTYRENE-*BLOCK*-POLY(METHYLMETHACRYLATE) MICELLES BY SEC/MALS. DETERMINATION OF MOLECULAR WEIGHTS AND SIZE DISTRIBUTION', Journal of Liquid Chromatography & Related Technologies, 22: 14, 2109 — 2124
To link to this Article: DOI: 10.1081/JLC-100101788
URL: http://dx.doi.org/10.1081/JLC-100101788

J. LIQ. CHROM. & REL. TECHNOL., 22(14), 2109–2124 (1999)

STUDY OF POLYSTYRENE-*BLOCK*-POLY(METHYLMETHACRYLATE) MICELLES BY SEC/MALS. DETERMINATION OF MOLECULAR WEIGHTS AND SIZE DISTRIBUTION

Z. Grubišic-Gallot,[1] M. Žigon,[2] J. Sedláček,[3] Yves Gallot[1]

[1] Institut Charles Sadron (CRM-EAHP) (CNRS-ULP)
6, rue Boussingault,
F-67083 Strasbourg-Cedex, France

[2] National Institute of Chemistry
Hajdrihova 19
SI-1000, Ljubljana, Slovenia

[3] Dept. of Physical and Macromolecular Chemistry
Laboratory of Specialty Polymers, Faculty of Science
Charles University
Albertov 2030
CZ-12840 Prague 2, Czech Republic

ABSTRACT

Polystyrene-*block*-poly(methyl methacrylate) micelles in 1,4-dioxane/cyclohexane were studied by size exclusion chromatography coupled with multi angle light scattering (SEC/MALS). A sufficient unimer - micelles resolution achieved by SEC made it possible to use MALS detector for the direct determination of distributions and corresponding averages of molecular weights and gyration radii of micelles.

www.dekker.com

Contrary to the standard static light scattering approach, the SEC/MALS technique provided these averages in one analytic run with a minimum amount of copolymer sample. In most systems, very narrow molecular weights and size distributions of micelles were obtained. For a given copolymer, the micellar association number increased with decreasing thermodynamic quality of solvent. Under given thermodynamic conditions, it increased with increasing length of insoluble poly(methyl methacrylate) block and with decreasing length of soluble polystyrene block. The micellar radius of gyration was predominantly controlled by the molecular weight of the copolymer.

INTRODUCTION

Block copolymer micellar systems are a unique subject of increasing interest from both academic and practical points of view. Potential applications of block copolymer micelles in the fields of pharmacology (drug delivery systems), ecology, agriculture, etc. are very promising. Block copolymer micelles, i.e. multimolecular copolymer associates with a core formed by a block of low solubility and a protective shell formed by a block of high solubility, are known to be formed when a block copolymer is dissolved in a selective solvent (i.e., a good solvent for one block and precipitant for the other).

The formation of micelles (micellization) mostly follows the simple closed association model (Eq. 1) which assumes a dynamic equilibrium between micelles, M (with a strict value of association number n) and molecularly dissolved copolymer-unimer, U.[1,2]

$$nU \rightleftarrows M \qquad (1)$$

A great number of techniques are used for the study of a broad spectrum of problems concerning micellar systems: from standard viscometry, sedimentation velocity, and static light scattering to advanced methods such as quasielastic light scattering, small- angle X-ray, or neutron scattering and fluorescence methods.[2-4] In our previous papers, we reported in detail on the application of size exclusion chromatography/low angle laser light scattering (SEC/LALLS) technique in the study of polystyrene-*block*-poly(methyl methacrylate) (PS-PMMA) micellar systems in a mixed 1,4-dioxane/cyclohexane solvent.[5-7] In such systems, micelles with PMMA core and PS shell are formed at higher contents of cyclohexane. We demonstrated advantages of the SEC/LALLS technique in: (i) determination of molecular weight (MW) averages of micelles; (ii) qualitative evaluation of the dynamics of unimer - micelles re-equilibration and (iii) elucidation of the mode of micelles formation (standard closed association or anomalous micellization).[7] The coupling of SEC with a MW-sensitive detector (light scattering photometer) was found essential in these studies.

In this article, the application of SEC coupled with advanced multi-angle light scattering (MALS) detection in the analysis of the above type of micellar systems is reported. The easy determinations of the distribution and corresponding averages of (i) MW and (ii) apparent radius of gyration (R_g) of micelles are demonstrated.

Dependencies of MW and R_g averages on both variables, copolymer characteristics (MW and chemical composition), and thermodynamic quality of the solvent are discussed.

EXPERIMENTAL

Copolymer

All the polystyrene-*block*-poly(methyl methacrylate) (PS-PMMA) samples were synthesized by living anionic polymerization. The details of the synthesis are described elsewhere.[5,8]

Size Exclusion Chromatography (SEC)

Two different SEC sets were employed. For characterization of copolymers, a Waters 150 C apparatus coupled with an LALLS photometer (Chromatix CMX-100, wavelength λ = 633 nm) and a standard Waters differential refractometer (DR) was used. For this purpose, five columns in a series (PLgel) having upper permeability limits of 10^6, 10^5, 10^4, 10^3, and $5x10^2$ and tetrahydrofuran as eluent with a flow rate of 1 mL/min were used.

For the study of micellar systems, a Perkin Elmer liquid chromatograph coupled with an MALS Dawn-DSP laser photometer (Wyatt Technology Corporation, WTC) operating at 17 angles (19.3°, 25.0°, 32.6°, 39.7°, 46.6°, 54.4°, 62.1°, 70.7°, 80.4°, 90.0°, 99.6°, 109.3°, 119.0°, 128.9°, 138.0°, 146.2°, and 153.7°), equipped with a He-Ne laser (λ=633 nm), and Optilab-DSP differential refractometer (DR) was used.

One μ-Styragel (10^5) column was used. The data were acquired and evaluated by WTC software Astra 4.50 directly giving the number-, weight-, and z-averages of MW and R_g and corresponding MW and R_g distributions.

Various 1,4-dioxane/cyclohexane mixtures (D/C; composition given in vol.%) were employed as the mobile phase at a temperature of 25°C. Both 1,4-dioxane and cyclohexane (Fluka, analytical grade) were distilled over sodium

Table 1

Molecular Weights and Chemical Composition of Block Copolymers PS-PPMA

Sample No.	$10^{-3}\cdot M_{w,COP}$	PS Content (wt. -%)	$10^{-3}\cdot M_{w,PS}$	$10^{-3}\cdot M_{w,PMMA}$
1	57	46.2	26	31
2	96	64.0	61	35
3	92	52.6	48	44
4	162	66.5	108	54
5	182	51.2	93	89
6	334	46.4	155	179

wire before use. The copolymer was always being 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 (100 μL) being 10 mg/mL. For the majority of analyzed micellar systems, an effect of partial adsorption of the unimer form of copolymer on column packing was observed (details on this phenomenon are described in Ref. 6). The adsorbed unimer was completely washed out of the column by successive injections of 1,4-dioxane (100 μL, 2-4 times) after each analysis of a micellar system.

RESULTS AND DISCUSSION

A series of six PS-PMMA block copolymers of low polydispersities ($M_w/M_n < 1.05$) differing in molecular weight and chemical composition were used for this study. Their weight-average molecular weights ($M_{w,\ COP}$) determined by SEC/LALLS and M_w of the soluble PS block and insoluble PMMA block obtained from $M_{w,\ COP}$ and chemical composition (elemental analysis) are given in Table 1. 1,4-Dioxane/cyclohexane (D/C) solvent mixtures of five different compositions have been used as eluents for SEC/MALS analyses (D45/C55, D40/C60, D35/C65, D30/C70, and D20/C80).

The range of solvent composition where micelles were detected using this technique is evident from Table 2: it seems to be governed predominantly by the length of the PMMA block: with increasing length of this block, it is shifted towards thermodynamically better solvents (solvents with lower cyclohexane contents). In solvent mixture D45/C55, no micelles were detected for any copolymer sample.

Table 2

Properties of Copolymer Samples[a]

	PS-PMMA Copolymer Sample			Composition of Selective Solvent (1,4-dioxane/cyclohexane, vol%)											
		PMMA		D40/C60			D35/C65			D30/C70			D20/C80		
No.	**10^{-3} $M_{w,COP}$**	**Cont.[b]**	**$10^{-3}\cdot M_w$**	**$10^{-6}\cdot M_w$**	**$R_{g(z)}$**	**n**	**$10^{-6}\cdot M_w$**	**$R_{g(z)}$**	**n**	**$10^{-6}\cdot M_w$**	**$R_{g(z)}$**	**n**	**$10^{-6}\cdot M_w$**	**$R_{g(z)}$**	**n**
1	57	53.8	31	Unimer			Unimer			Not determined[c]			11	21	200
2	96	36.0	35	Unimer			Unimer			Unimer			10	27	107
3	92	47.4	44	14	35	155	13	30	144	20	32	226	24	35	269
4	162	33.5	54	Not determined[c]			6	35	37	19	41	121	180	120	1110
5	182	48.8	89	5	30	27	17	34	98	39	43	220	Insoluble		
6	334	53.6	179	45	53	135	110	69	330	Insoluble			Insoluble		

---

[a] Weight-average molecular weight, M_w, of PS-PMMA, copolymers, content and M_w of insoluble PMMA block; M_w, z-average radius of gyration $R_{g(z)}$ (nm) and association number n for micelles as determined by SEC/MALS in 1,4-dioxane/cyclohexane solvent mixtures of various compositions. [b] Wt. - %. [c] Micelle characteristics could not be reliably determined due to their low concentration.

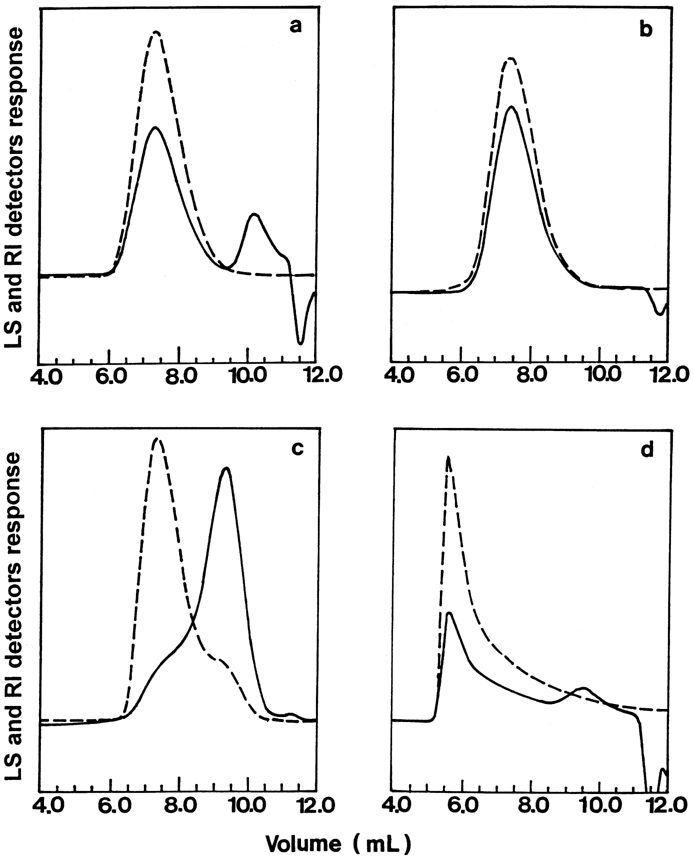


Figure 1. SEC curves for PS-PMMA in mixtures 1,4-dioxane/cyclohexane. PS-PMMA sample code (Table 1), vol.% of cyclohexane: (a) 3, 70; (b) 3, 80; (c) 5, 60; (d) 4, 80; ---- LS response at angle 90°, — DR response.

Efficiency in Unimer-Micelles SEC Separation

For a majority of the reported micellar systems, SEC concentration records (DR responses) consist of sufficiently separated peaks, a symmetrical peak of micelles and a peak of unimer. An example of these chromatograms is given in Figure 1a, where the peak with a lower elution volume and higher intensity corresponds to micelles, while the peak at a higher elution volume corresponds to unimer. For a given copolymer, the ratio of intensities of the micellar to unimer peak was increasing with decreasing quality of solvent. For samples No. 1 and 3 (lower MW samples with an important PMMA content, Table 1), only the micellar peak was detected in the thermodynamically worst solvent D20/C80 (for a representative chromatogram, see Figure 1b). However, for these two samples, the unimer adsorption on the column packing was observed as well (see Experimental). Two micellar systems (sample No. 4 in D35/C65 and sample No. 5 in D40/C60, at the onset of micellization for both samples), showed exceptional concentration records with a poor unimer - micelles resolution (an example is given in Figure 1c). For sample No. 4 in D20/C80 (the system producing the largest micelles - see Table 2), the concentration record with a non-symmetrical micellar peak accompanied by a large tailing was obtained (see Figure 1d).

The consideration of efficiency of micelles - unimer separation in SEC analysis of any micellar system is not straightforward since the dissociation of micelles during the SEC separation process should be always taken into account. This phenomenon arises from the dynamics of the unimer ⇄ micelles equilibrium. Micelles separated from the unimer in the SEC column tend to dissociate to re-establish the equilibrium concentration of the unimer in the micellar zone. SEC concentration records thus reflect two simultaneous processes: SEC separation and unimer ⇄ micelles re-equilibration. A simple theoretical modeling of these processes predicts complication with a unimer-micelles resolution for each system with a non-negligible rate of micelles dissociation.[9,10]

Our previous studies of micellar systems PS-PMMA/1,4-dioxane/ cyclohexane showed very low values of critical micelle concentrations (CMC < 0.1 mg/mL).[5,6] Since the CMC values roughly correspond to the equilibrium concentration of unimer in a micellar system,[2] the unimer ⇄ micelles equilibrium is strongly shifted in favor of micelles in the solutions used for the SEC analyses (concentration 10 mg/mL). Regardless of the characteristics of both the copolymer and solvent mixture, the equilibrium weight concentration of unimer in these solutions was estimated to be at least two orders of magnitude smaller than the weight concentration of micelles.

For all the micellar systems, the amount of unimer observed after the sample passed through the column (detected as the unimer peak in a regular run and/or after washing out of the column) evidently exceeds that in the injected sample. This finding confirms that the rate of the micelles dissociation during the SEC analysis is not negligibly small in comparison with the rate of the SEC separation process.

From this point of view, the good unimer - micelles resolution achieved for majority of micellar systems might be surprising. We propose two effects that most probably simultaneously contribute to this finding. (i) Concentration dependence of the rate of micelles dissociation: a continuous decrease in the concentration of micelles in the micellar zone along the column due to their dissociation simultaneously decreases the rate of this process.

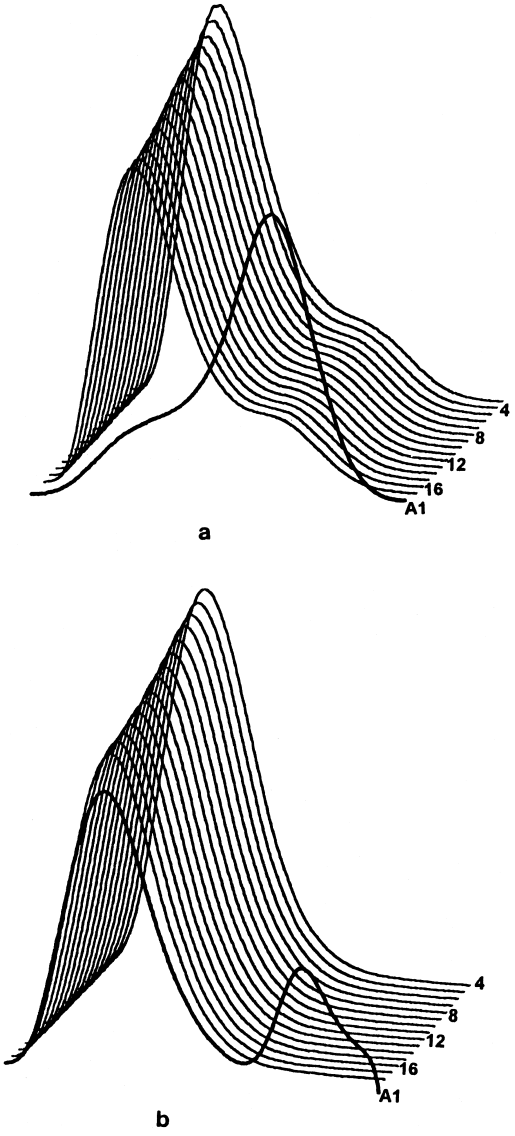


Figure 2. 3D plots: (a) sample No. 5 in mixture 1,4-dioxane/cyclohexane D40/C60 and (b) sample No. 5 in mixture 1,4-dioxane/cyclohexane D30/C70; LS responses at different angles (see the text, marked as 2-18), DR response (marked as A1).

Thus, the dissociation may prevail in the early stages of the SEC analysis and the unimer formed in this dissociation may still be efficiently separated. (ii) Partial adsorption of the unimer on the column packing: the adsorption effect, which is usually very undesirable in SEC practice, may, in the reported case, contribute to the separation of unimer from micelles. Nevertheless, these two effects were evidently insufficient to achieve a good unimer-micelles resolution in the case of samples No. 4 and 5 at the onset of micellization (see above and Figure 1c).

SEC-MALS Characterization of Micelles

The application of an MALS detector made it possible to monitor the intensity of the scattered light at 17 different angles (Figure 2) and to calculate the values of MW and apparent radius of gyration (R_g) for each slice of the micellar peak from the dependence of $K \cdot c/R_\theta$ on scattering angle θ (Figure 3, K being optical constant, c solution concentration, R_θ the Rayleigh ratio at angle θ.[11] On the basis of these values, the distribution and averages of MW and R_g were obtained (Figure 4, Table 2).

For a majority of micellar systems with a sufficient unimer - micelles resolution, the micelles exhibited a very low non-uniformity in MW (M_w/M_n <1.04, M_z/M_w < 1.04), and R_g ($R_{g(z)}/R_{g(w)}$ < 1.02). These results confirm the closed association model of micelles formation which assumes micelles monodisperse in MW and size under given thermodynamic conditions. Broad MW and R_g distributions were obtained only for sample No. 4 in D20/C80 (Figure 4d) which produces extremely large and high-MW micelles. The high average values of association number and radius of gyration obtained from the part of chromatogram close to the apex of micellar peak (n = 1110 and $R_{g(z)}$ = 120 nm, Table 2) can be explained by the formation of micellar "clusters" which are known to appear in micellar systems close to the onset of precipitation and which do not follow the closed association model.[12]

In Table 2, the most important characteristics of micelles, association number n, values of M_w and $R_{g(z),}$ are summarized. For two micellar systems with a poor unimer - micelles resolution (sample No. 4 in D35/C65 and sample No. 5 in D40/C60), these values correspond to the lower elution volume part of micellar peak, approximately up to the apex, where both MW and R_g distributions are narrow. For all the micellar systems, the association number was calculated from number-average molecular weights of micelles and PS-PMMA sample. The data given in Table 2 show that in the studied systems, micelles of a large variety in n and M_w are formed (n ranging from 27 to 330, M_w from $5 \cdot 10^6$ to $110 \cdot 10^6$) depending on the parameters of both copolymer composition and solvent mixture.

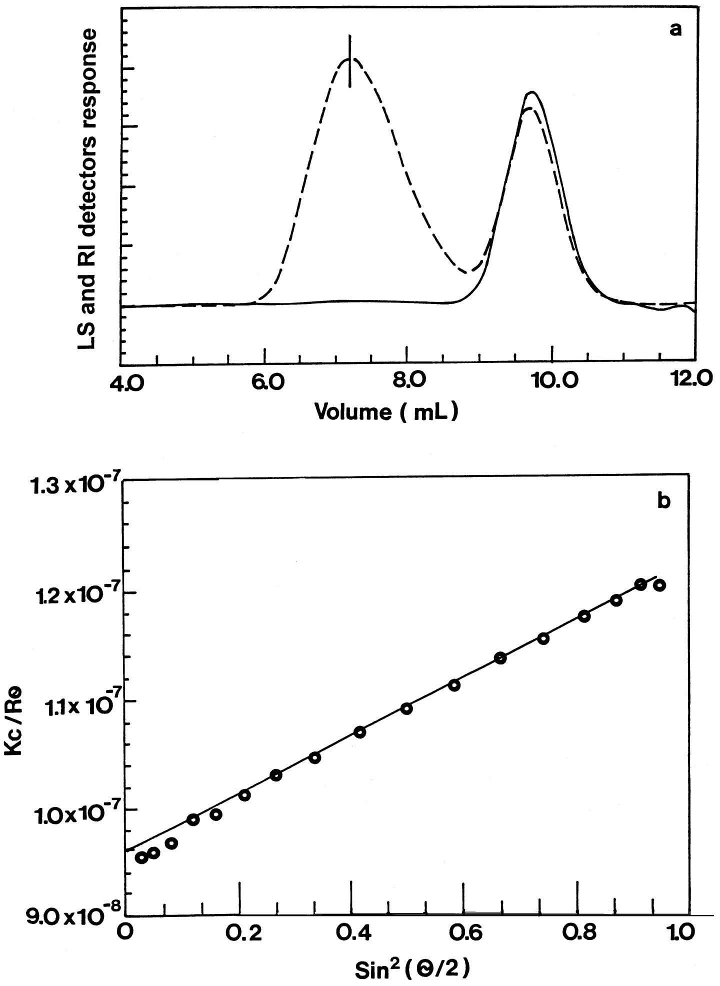


Figure 3. (a) SEC curves of sample No. 2 in mixture 1,4-dioxane/cyclohexane D40/C60, ------- LS response at angle 90°, — DR response, and (b) dependence of $K \cdot c/R_\theta$ on the scattering angle θ for the slice at the apex of the micellar peak.

Two facts are evident from Table 2: (i) For a given copolymer sample, the n and M_w values significantly increase with decreasing thermodynamic quality of solvent while increase in $R_{g(z)}$ is only weak. The exception is evident only for sample No. 3 for which both n and $R_{g(z)}$ values were slightly higher in D40/C60 compared with D35/C65. This may be ascribed to the effect of anomalous micellization in D40/C60.

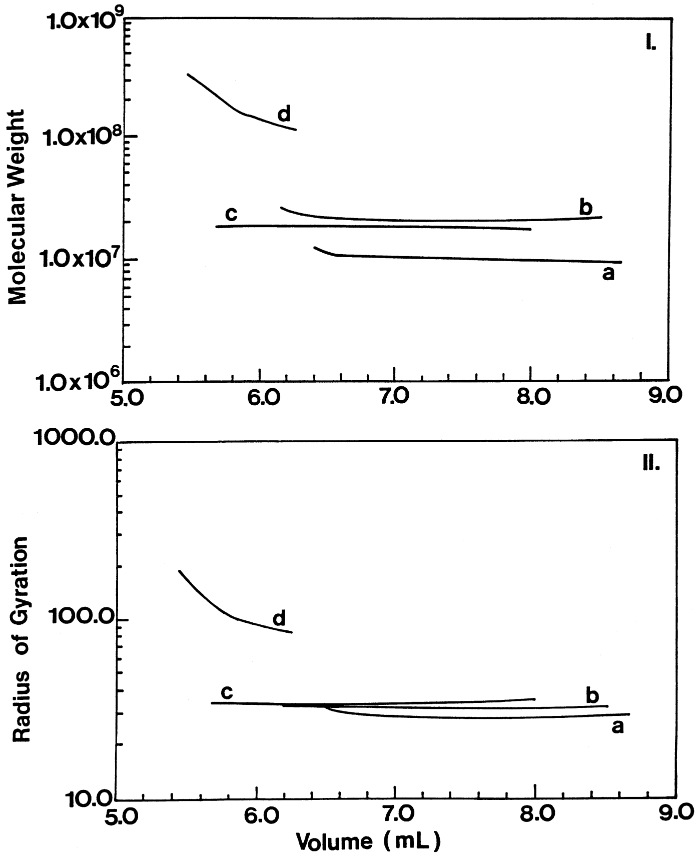


Figure 4. MW (I) and R_g (in nm) (II) vs. elution volume for PS-PMMA micelles in mixtures 1,4-dioxane/cyclohexane. PS-PMMA sample code (Table 1), vol.% of cyclohexane: (a) 2, 80; (b) 3, 70; (c) 5, 65; (d) 4, 80.

This phenomenon has been reported in the studies of micellization of various block copolymers in different selective solvents.[2,7,13-15] In such systems, the formation of so called anomalous micelles was observed mostly at the onset of micellization, *i.e.* when the thermodynamic quality of the solvent decreased to the level at which micelles began to be detected. These micelles exhibited a higher MW and size than regular ones formed subsequently in thermodynamically worse solvents. (ii) For samples having similar length of the PMMA block but differing in the PS block, a significant increase in association number is evident with a decrease in the PS block length (cf. samples No. 1 and 2 in D20/C80 and samples No.3 and 4 in both D35/65 and D30/C70). On the other hand, for samples having a similar length of the PS block and differing in the PMMA block, the association number decreases with decreasing PMMA block length (cf. samples No. 4 and 5). This is in a qualitative agreement with theoretical thermodynamic predictions according to which the association number should increase with the length of the core-forming block but decrease with the length of the shell-forming block.[16]

Dependence of Radius of Gyration of Micelles on the Copolymer Molecular Weight

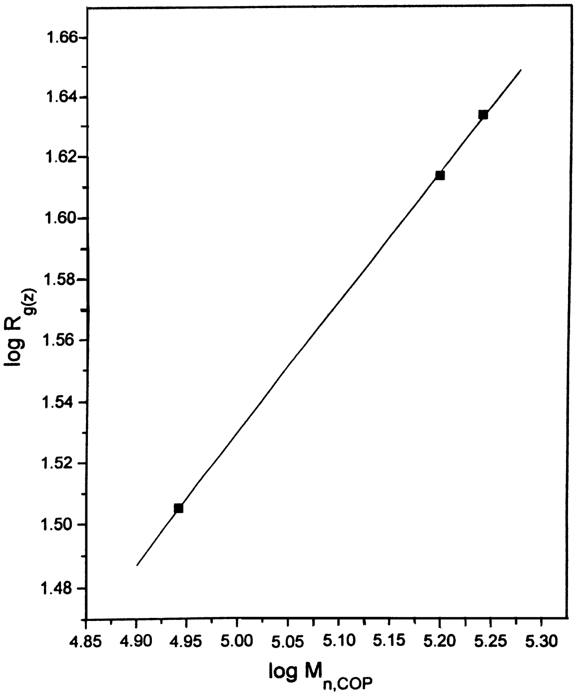
Theoretical considerations of the micellar structure based on so-called scaling approach[17] result in various power equations which predict the trends in relations between structural parameters of micelles (mainly the core, shell and micelle dimensions) and characteristics of block copolymers.[2] For the dependence of radius of gyration of a micelle on the number-average molecular weight of the copolymer, the following scaling relation has been derived:

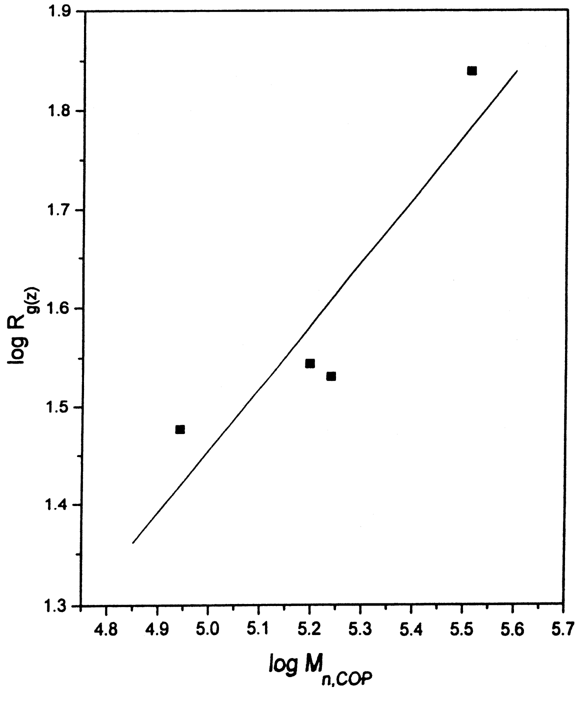
$$R_g \sim (M_{n,\,COP})^a \qquad (2)$$

where exponent a = 0.44.[18] This dependence predicts R_g of micelles to be governed by copolymer molecular weight only, irrespective of the copolymer composition. Light scattering techniques (including SEC/MALS) are well known to provide R_g often as apparent values only (due to a possible different contrast of micellar core and shell)[2] which may differ from the real R_g values by up to 15-20%.[19] Nevertheless, assuming a systematic deviation between apparent and real values for a given type of copolymers, the apparent R_g values can be well applied to the verification of the above dependence. Generally, a more serious complication is that a reliable verification always requires a set of copolymers of a sufficient range of composition and molecular weights which, however, form regular micelles under the same thermodynamic conditions.[18,20] In the case of the studied set of PS-PMMA, this was partly fulfilled in D35/C65 and D30/C70, *i.e.* in selective solvents of "medium quality".

In Figure 5, the double-logarithmic plots of $R_{g(z)}$ vs. $M_{n,\,COP}$ are given for these two solvent mixtures. For D30/C70, the plot is satisfactorily linear with a slope a = 0.43, which is in a very good accordance with theoretical prediction (Figure 5a). However, for D35/C65, a worse agreement with theory was achieved: the $R_{g(z)}$ values are evidently more dispersed and the linear representation of the plot leads to a value of a = 0.63 (Figure 5b). This discrepancy between experimental results and theory was ascribed to a great scatter of experimental results.

Figure 5 (right). Radius of gyration ($R_{g(z)}$) of PS-PMMA micelles formed in 1,4-dioxane/cyclohexane vs. number-average molecular weight of PS-PMMA copolymer ($M_{n,COP}$). Vol.% of cyclohexane: (a) 70 and (b) 65.


log $R_{g(z)}$
1.66
1.64
1.62
1.60
1.58
1.56
1.54
1.52
1.50
1.48
4.85
4.90
4.95
5.00
5.05
5.10
5.15
5.20
5.25
5.30
log $M_{n,COP}$


log $R_{g(z)}$
1.9
1.8
1.7
1.6
1.5
1.4
1.3
4.8
4.9
5.0
5.1
5.2
5.3
5.4
5.5
5.6
5.7
log $M_{n,COP}$

CONCLUSION

A series of PMMA-PS/1,4-dioxane/cyclohexane micellar systems differing in copolymer characteristics and selective solvent composition have been analyzed by the SEC/MALLS technique. Despite unimer-micelles re-equilibration during the SEC analysis, a sufficient unimer-micelles separation was achieved for majority of micellar systems. This enabled us to apply the SEC/MALS technique as an appropriate tool for a rapid and easy determination of the distributions and corresponding averages of MW and R_g of micelles. All these data were obtained in single "analytic run" with a minimum amount of copolymer sample.

In majority of micellar systems, very narrow MW and R_g distributions of micelles were obtained (in agreement with the closed association model of micelles formation) except for one sample forming, most probably, micellar clusters in a thermodynamically very bad solvent.

The length of the insoluble PMMA block was found to be the most important parameter in determining the selective solvent composition where micelles are formed. The micellar association number was controlled mainly by the thermodynamic quality of the solvent.

In a solvent mixture of a given thermodynamic quality, it was increasing with increasing length of the PMMA block and with decreasing length of the PS block. Depending on these parameters, micelles with association numbers ranging from 27 to 330 (M_w from $5 \cdot 10^6$ to $110 \cdot 10^6$) were formed.

Values of micellar $R_{g(z)}$ (varying from 21 to 69 nm) were found to be governed predominantly by the overall molecular weight of the copolymer. The $R_{g(z)}$ vs. $M_{n,\,COP}$ dependence corresponded very well with the theory for D30/C70, while for D35/C65, a certain deviation from the theoretical prediction was observed. However, in the latter case, a discrepancy between experiment and theory could be ascribed to a great scatter of experimental results.

ACKNOWLEDGMENTS

Financial support from the Grant Agency of the Czech Republic (contract No. 203/97/0249) and Czech-Slovenian support (Kontakt 98ME0248) are gratefully acknowledged.

The financing of the bilateral French-Slovenian project No. 4688 by CNRS, France, and the Ministry of Science and Technology of the Republic of Slovenia is also acknowledged. The authors thank Mrs. Mira Mikuz for her valuable technical assistance.

REFERENCES

1. Z. Tuzar, P. Kratochvíl, Adv. Colloid Interface Sci., **6**, 201-232 (1976).
2. Z. Tuzar, P. Kratochvil, "Micelles of Block and Graft Copolymers in Solutions," in **Surface and Colloid Science Series**, Vol. 15, M. Matijevic, Ed., Plenum Press, New York, 1993, pp. 1-83.
3. M. Pacovská, K. Procházka, Z. Tuzar, P. Munk, Polymer, **34**, 4585-4588 (1993).
4. K. Procházka, D. J. Kiserow, S. E. Webber, Acta Polym., **46**, 277-290 (1995).
5. Z. Grubišic-Gallot, Y. Gallot, J. Sedláček, Macromol. Chem. Phys., **195**, 781-791 (1994).
6. Z. Grubišic-Gallot, Y. Gallot, J. Sedláček, J. Liq. Chromatogr., **18**, 2291-2307 (1995).
7. Z. Grubišic-Gallot, Y. Gallot, J. Sedlčèk, J. Liq. Chromatogr. & Rel. Technol., **21**, 2459-2472 (1998).
8. D. Freyss, M. Leng, P. Rempp, Bull. Soc. Chim. Fr., **1964**, 221-224 (1964).
9. K. Procházka, T. Mandák, M. Kočiřik, B. Bednář, Z. Tuzar, J. Chem. Soc., Faraday Trans., **89**, 1103-1108 (1990).
10. K. Procházka, T. Mandák, B. Bednář, J. Trněná, Z. Tuzar, J. Liq. Chromatogr., **13**, 1765-1783 (1990).
11. P. Wyatt, Anal. Chim. Acta, **272**, 1 (1993).
12. A. Qin, M. Tian, C. Ramireddy, S. E. Webber, P. Munk, Z. Tuzar, Macromolecules, **27**, 120-126 (1994).
13. Z. Tuzar, J. Stehlícek, Č. Koňák, F. Lednický, Makromol. Chem., **189**, 221-226 (1988).
14. T. P. Lally, C. Price, Polymer, **15**, 325-326 (1974).
15. P. A. Canham, T. P. Lally, C. Price, R. B. Stubbersfield, J. Chem. Soc., Faraday Trans. I, **76**, 1857-1867 (1980).

16. A. Halperin, A. Alexander, Macromolecules, **22**, 2403-2412 (1989).

17. P. G. de Gennes, **Scaling Concepts in Polymer Physics**, Cornell University Press, Ithaca, 1979.

18. T. L. Bluhm, M. D. Whitmore, Can. J. Chem., **63**, 249-252 (1985).

19. Z. Tuzar: Private communication.

20. T. L. Bluhm, S. L. Malhotra, Eur. Polym. J., **22**, 249-251 (1986).

Received September 8, 1998
Accepted January 24, 1999
Manuscript 4880

Downloaded At: 10:21 24 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081JLC100101788