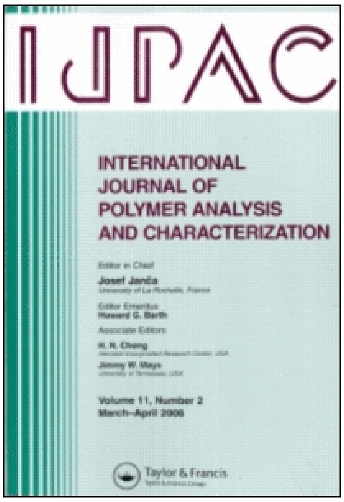

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Nanosize Aggregates of Block Copolymers of Styrene and Hydrogenated Butadiene in Water

Petr Munk[a]; Stanislav Rangelov[b]; Zdenek Tuzar[c]
[a] Department of Chemistry and Biochemistry and Center for Polymer Research, The University of Texas at Austin, Austin, TX, USA [b] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria [c] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

To cite this Article Munk, Petr , Rangelov, Stanislav and Tuzar, Zdenek(1998) 'Nanosize Aggregates of Block Copolymers of Styrene and Hydrogenated Butadiene in Water', International Journal of Polymer Analysis and Characterization, 4: 5, 435 — 446

To link to this Article: DOI: 10.1080/10236669808009727

URL: http://dx.doi.org/10.1080/10236669808009727

Int. J. Polym. Anal. Charact.,
1998 Vol. 4, pp. 435–446
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in India.

Nanosize Aggregates of Block Copolymers of Styrene and Hydrogenated Butadiene in Water

PETR MUNK[a], STANISLAV RANGELOV[b] and ZDENEK TUZAR[c,*]

[a] *Department of Chemistry and Biochemistry and Center for Polymer Research, The University of Texas at Austin, Austin, TX 78712, USA;* [b] *Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria;* [c] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 16206 Prague 6, Czech Republic*

(Received 30 October 1997; In final form 20 March 1998)

Three-block copolymer polystyrene-*block*-hydrogenated polybutadiene-*block*-polystyrene forms micelles with aliphatic cores and polystyrene shells in dioxane. When a solution of these micelles with an appropriate stabilizer (e.g., a block copolymer of ethylene oxide and propylene oxide) is injected into excess water, a stable dispersion results. The resulting particles have a hydrodynamic radius around 55 nm and particle molecular weight is hundreds of millions. The mechanism of the particle formation and their structures are discussed.

Keywords: Block copolymer micelles; Micellar aggregates; Pluronic®; Kraton®; Static and dynamic light scattering

INTRODUCTION

Block copolymers in selective solvents associate forming micelles which, with a few exceptions, assume a spherical shape and a simple core/shell structure.[1] Recently, Zhang and Eisenberg[2] reported on some other morphologies (rods, lamelae, vesicles, etc.) of aggregates in water formed by highly asymmetric hydrophilic/hydrophobic

---

[*] Corresponding author.

block copolymers. Procházka *et al.*[3] have shown that a judicious coprecipitation of properly chosen copolymer solutions may lead to another kind of supermolecular structure. In their experiments they started with a solution of poly(*t*-butyl methacrylate)-*block*-poly(2-vinylpyridine) and poly(ethylene oxide)-*block*-poly(2-vinylpyridine) in acidified water. The former copolymer forms in this solvent copolymer micelles with soluble protonized poly(2-vinylpyridine) shells. The latter copolymer is dissolved molecularly. When alkali is slowly added to this mixture, around pH 5, poly(2-vinylpyridine) is deprotonized and becomes insoluble in water. The micellar shell collapses and in the collapsing process captures the poly(2-vinylpyridine) blocks of the other copolymer. The result are onion-type micelles with poly(*t*-butyl methacrylate) inner core, poly(2-vinylpyridine) outer core, and poly(ethylene oxide) shell.

In the present paper, we report an application of a similar procedure aimed at solubilization of polystyrene-*block*-hydrogenated polybutadiene-*block*-polystyrene (Shell Co., commercial name Kraton®) in water. We started with solutions of Kraton in dioxane. In this solvent Kraton forms micelles with an aliphatic core and polystyrene shells. Our intention was to add to this micellar solution a molecularly soluble copolymer that, upon some appropriate change of the solvent, would coprecipitate with polystyrene producing again onion-type micelles. Obvious choice for this additional copolymer were block copolymers with a polystyrene block, e.g., polystyrene-*block*-poly(methacrylic acid) or polystyrene-*block*-poly(ethylene oxide). Such experiments are in progress and the results will be published later.

The procedure described above could be understood also in different terms: upon the change of the solvent and the collapse of the micellar shell, the micelles will tend to fuse and the copolymer will precipitate out of solution. Such a precipitation could be prevented by addition of a substance that will adhere to the collapsed micelles and protect them from precipitation. Such a substance must adhere to polystyrene (it is not necessary that it is compatible with it) and simultaneously form a hydrophilic protective layer. For this purpose we have selected in this study block copolymers of ethylene oxide and propylene oxide (PEO-PPO copolymers). Some three-block copolymers poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) are available as commercial products, Pluronics®. These copolymers are known to stabilize suspensions and emulsions[4,5] and to adsorb on solid surfaces.[6,7] Hydrophobic interactions between PPO and the surface are the driving force for the above processes. It is anticipated that PPO moiety anchors the macromolecule to the surface while PEO segments extend into aqueous phase.

The crucial part of the research consisted of finding conditions under which the Kraton particles would remain in solution. In the preferred procedure we prepared a mixture of the Kraton micelles and a PEO–PPO copolymer in dioxane and injected it into excess water. The resulting solution was quite turbid, but did not precipitate and was stable with respect to time, sonication, dilution, etc. We have studied these solutions by both static and dynamic light scattering techniques.

EXPERIMENTAL SECTION

Materials

For the Kraton® sample we used a commercially available product G1652 (Shell Co., Houston, Texas) (hereinafter Kraton) that we studied previously.[8] Its molecular weight is 60×10^3 with the central aliphatic block of 42×10^3 and the two polystyrene blocks of 9×10^3 each. For the Pluronic® sample we employed a commercial sample L-64 from Fluka Co. (hereinafter Pluronic). Some other block copolymers of ethylene oxide and propylene oxide studied were synthesized in the Institute of Polymers, Bulgarian Academy of Sciences according to a known method.[9] The following samples have been studied (E and P represent the poly(ethylene oxide) and poly(propylene oxide) blocks, respectively; subscripts designate the average number of monomer units):

(1) $E_xP_yE_x$ (a) $x = 13$, $y = 30$ (Pluronic); (b) $x = 30$, $y = 16$; (c) $x = 24$, $y = 11$;
(2) $P_yE_xP_y$ (a) $x = 26$, $y = 4$; (b) $x = 26$, $y = 11$; (c) $x = 26$, $y = 15$;
(3) $E_xP_yE_zP_yE_x$ $x = 8$, $y = 15$, $z = 10$.

Dioxane was a product of Fluka and was used as received. Water was double distilled.

Sample Preparation

Kraton was dissolved in dioxane in a sealed ampoule at 100°C to form a 10 mg/mL molecular solution. Upon cooling, the Kraton molecules reorganized themselves and formed micelles. This micellar solution was mixed with the copolymer solution of ethylene oxide and propylene oxide in dioxane. For each of PEO–PPO copolymers, a set of mixtures differing in its concentration was prepared. An aliquot of each mixture was injected into excess water. The resulting solution was further diluted with water at a 1 : 64 ratio. The final mixtures had identical concentration of Kraton (3.8×10^{-6} g/mL), a concentration of PEO–PPO copolymer varying between 0.125 and 6 multiples of the Kraton concentration, and concentration of dioxane less than 0.3 vol%. For a successful preparation of nanosized particles it was necessary to use for injection a thin needle and to inject as quickly as possible under the surface of water. Otherwise, a visible amount of a macroscopic precipitate would form. The samples that did not form a precipitate were studied by static and dynamic light scattering.

Static Light Scattering

Measurements were performed on a Fica at 546 nm. The starting solution was diluted to obtain a solution with adequate turbidity, and filtered using a 0.8-μm filter. The angular dependence of light scattering was measured in a routine way usually at four concentrations and the Zimm plots (not presented) were constructed and evaluated.

Dynamic Light Scattering

Measurements were performed with solutions of the lowest concentrations used in static light scattering. An ALV 5000 multibit, multitau autocorrelator (Langen, Germany) and an argon ion laser ($\lambda =$ 514 nm) were employed. Data were processed using REPES[10] method.

RESULTS

In the first series of experiments, we determined conditions under which the block copolymers of ethylene oxide and propylene oxide were capable of stabilizing the Kraton particles. Only three samples proved to act as good stabilizers: $E_{13}P_{30}E_{13}$ (Pluronic), $P_{15}E_{26}P_{15}$, and the $E_8P_{15}E_{10}P_{15}E_8$. While the Pluronic copolymer produced nanosized particles at all Pluronic to Kraton concentration ratios larger than 0.125, these ratios for the $P_{15}E_{26}P_{15}$ copolymer needed to be at least 4, and for the $E_8P_{15}E_{10}P_{15}E_8$ copolymer at least 6. The remaining copolymers did not stabilize Kraton particles at any concentration because of the unfavorable length of either PPO or PEO blocks. In the next series of experiments, we prepared a set of samples from the mixtures of Kraton with various concentrations of the Pluronic copolymer, as well as with the high concentrations of the $P_{15}E_{26}P_{15}$, and $E_8P_{15}E_{10}P_{15}E_8$ copolymers, filtered through 0.8-μm filters, and measured by dynamic and static light scattering.

The analysis of the correlation functions from the dynamic light scattering yielded a spectrum of correlation times that was converted into a spectrum of the hydrodynamic radii of the suspended particles. A typical spectrum is in Figure 1. Since in this plot the horizontal axis is displayed in a logarithmic scale, the equal area representation $R_HA(R_H)$ vs. $\log R_H$ ($A(R_H)$ is the distribution function of intensities corresponding to R_H) is used to ensure that peaks of equal intensities

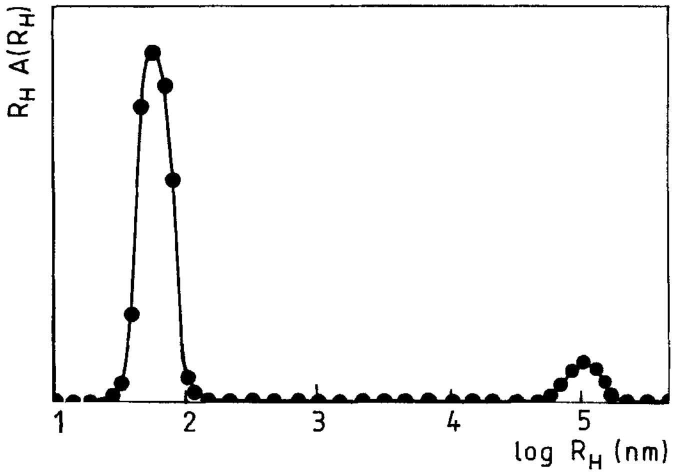

FIGURE 1 Distribution of hydrodynamic radii of the suspended particles obtained by dynamic light scattering for Kraton® G1652 stabilized by Pluronic® L-64 with a 1/4 ratio Kraton/Pluronic.

appear with the same areas. While the form of the spectrum varied slightly with the details of the applied computational procedure, all the spectra had several common features. Most of them had a dominant peak at a hydrodynamic radius between 50 and 60 nm, the width of the peak was relatively narrow and the peak accounted for 90–99% of the scattered intensity. There was always another peak corresponding to very large particles. Its intensity was between 1–10% and its position varied in size from thousands to tens of thousands of nm. The positions of the dominant peak are reported in Table I.

For the evaluation of molecular masses in this complex system, we used the Zimm version of static light scattering. We will use the term *agglomerate* for the fused clusters of Kraton micelles, and the term *aggregate* for the complexes having these agglomerates as a core and solubilized by the shell of a copolymer of ethylene oxide and propylene oxide. The term *particle* will be used when a more general situation is described.

The evaluation of Zimm plots of solutions of large particles (monodisperse or polydisperse) is usually straightforward. All information is obtained from the dependence of the quantity $Kc/R(\theta)$ on the concentration of the particles c and the scattering angle θ. Here, $K = [4\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2]/(\lambda_0^4 N_{\mathrm{Av}})$, where $\mathrm{d}n/\mathrm{d}c$ is the refractive index increment of the particles, n_0 is the refractive index of the solvent, λ_0 is the wavelength *in vacuo*, N_{Av} is the Avogadro constant and $R(\theta)$ is the Rayleigh factor at angle θ. In a multicomponent system, a judicious choice of the values of c and $\mathrm{d}n/\mathrm{d}c$ must be made. In the present case, it is reasonable to make the following choice: the concentration and the

TABLE I Characteristics of Kraton particles stabilized in water by block copolymers of ethylene oxide and propylene oxide

EP sample	*Kr/EP**	$M_{\mathrm{app}} \times 10^{-6}$	$M_{\mathrm{A},\gamma} \times 10^{-6}$	$M_{\mathrm{agg}} \times 10^{-6}$	R_{G} (nm)	R_{H} (nm)	ρ
$E_{13}P_{30}E_{13}$	1/0.125	993	829	933	137	75	0.9
	1/0.2	585	442	530	85	50	1.8
	1/0.5	454	239	359	77	52	1.2
	1/1	324	105	210	66	42	1.7
	1/2	517	82	247	76	56	1.2
	1/4	675	42	210	119	60	1.3
	1/6	687	23	161	130	55	1.6
$P_{15}E_{26}P_{15}$	1/4	650	40	200	108	62	1.1
$E_8P_{15}E_{10}P_{15}E_8$	1/6	530	18	126	88	55	1.3

*The ratio of weights of Kraton® G1652 and PEO–PPO (w/w).

refractive index increment refer to Kraton only ($dn/dc = 0.186\,\mathrm{mL/g}$). With this choice, the system is treated as a polymer in a mixed solvent, where the PEO–PPO copolymer is considered to be a solvent component. The resulting molecular weight M_{app} is an apparent one. It is related to the molecular weight M_{A} of the Kraton agglomerate as

$$M_{\mathrm{app}} = M_{\mathrm{A}}[1 + \gamma(dn/dc)_{\mathrm{B}}/(dn/dc)_{\mathrm{A}}]^2. \qquad (1)$$

This relation is derived in the appendix. In Equation (1), γ is the mass of the sorbate B (PEO–PPO) per unit mass of the polymer A (Kraton).

The true molecular weight of the Kraton agglomerate as well as of the whole solvated aggregate, M_{agg}, may be obtained when γ is known (or assumed). There are two limiting possibilities. (a) When γ is vanishingly small (the amount of PEO–PPO solubilizing the particles is negligible compared to the amount of Kraton in the aggregate) $M_{\mathrm{app}} = M_{\mathrm{A}}$. (b) When γ is given by the overall stoichiometry of the mixture (all PEO–PPO is attached to the particles) then M_{A} (we will now denote it as $M_{\mathrm{A},\gamma}$) is evaluated from Equation (1). M_{agg} is then calculated as $M_{\mathrm{agg}} = M_{\mathrm{A},\gamma}(1 + \gamma)$. All relevant values are included in Table I.

Radius of gyration R_{G} of scattering particles is routinely evaluated from the initial slope of the angular dependence of the intensity of scattered light. When the particle is composed of two materials having different refractive increments and different sterical arrangements, the value of R_{G} is distorted. In the present case, in which PEO–PPO may be presumed to be located more towards the periphery of the particles and has refractive index increment equal to $0.140\,\mathrm{mL/g}$ for EPE and PEP, and $0.137\,\mathrm{mL/g}$ for the pentablock, that is, lower than Kraton, the R_{G} values could be underestimated, but probably only slightly. R_{G} values may also be influenced by erroneous extrapolation to vanishing scattering angle. Even this error usually leads to underestimation of R_{G}. It should be noted that the observed values of R_{G} are not influenced by possibly erroneous values of concentration or refractive index increments. Observed R_{G} values represent the z-average and, as such, are grossly affected by the presence of even small numbers of very big particles. The observed values of R_{G} are also included in Table I.

Neither sonication nor the removal of the remaining dioxane by dialysis, noticeably changed the particle mass and size.

DISCUSSION

Molecular weights reported in Table I are in tens to hundreds of millions. As the molecular weight of Kraton G1652 micelles in dioxane is 4.6×10^6 (Ref. [8]), it is obvious that the observed particles are aggregates of tens to hundreds of the original micelles. Further, both blocks of Kraton are strongly hydrophobic; thus, in water the Kraton part of the aggregates must form rather compact domains. The first question to be answered is how much PEO–PPO is attached to the particles and where is it located. Poly(ethylene oxide) blocks are hydrophilic. Poly(propylene oxide) blocks are mildly hydrophobic but their hydrophobicity is not sufficient to induce micelle formation in PEO–PPO copolymers at our experimental conditions (cmc values are orders of magnitude higher than the actual concentrations). Neither of these blocks is compatible with either block of Kraton. It follows that neither block of PEO–PPO can interpenetrate any block of Kraton. The interaction between our two copolymers can occur only as a surface interaction. It is known that Pluronics can form interacting layers on polystyrene surfaces.[11,12]

From the above facts we may construct a plausible model of the particle structure. When the micellar solution of Kraton is injected into water, the dioxane diffuses from the micellar shells, the shells collapse but for some period of time remain swollen enough to allow interpenetration with shells of the neighboring micelles, This process, of course, leads to the formation of large agglomerates. The PEO–PPO molecules then stabilize the agglomerates.

Using the above model, we may now return to the question about the amount of PEO–PPO in the aggregates. Only those molecules may be part of the aggregate that can be accommodated on the available polystyrene surface. The maximum available surface per one original micelle is its surface in the collapsed form. In dioxane, Kraton micelles contain about 70 vol% dioxane and their radius is 18.4 nm.[8] We assume that the radius of a dioxane-free Kraton micelle is *ca* 10 nm and thus its surface is 1200 nm^2. The actual available surface of the agglomerate per micelle must be less. The necessary surface area per one molecule of PEO–PPO is determined by the sterical demands of the poly(ethylene oxide) blocks that extend into water. Based on Ref. [11], we assume that one molecule of Pluronic needs about 10 nm^2

of polystyrene surface. Thus, one collapsed Kraton micelle can accommodate about 120 molecules of L-64. Their collective molecular weight is about 0.4×10^6. This is less than 10% of the mass of the Kraton micelle (4.6×10^6). Moreover, due to the agglomeration of the Kraton micelles, the available polystyrene surface was overestimated in the above calculation. Consequently, in the following considerations we will utilize the values of molecular weight obtained assuming that the amount of PEO–PPO in the aggregates is negligible (values reported in M_{app} column of Table I).

Now we need to determine the structure of the aggregates. As is apparent from Table I, the observed radii of gyration are much larger than the hydrodynamic radii. This is not possible for any compact particles. Obviously, this is the result of the polydispersity of the system. The values derived from the Zimm plot are distorted by the presence of the very large particles even when they are present in a small amount. The distortion is especially severe for the radius of gyration (z-average). Consequently, we will consider the observed values of R_{G} as spurious and leave them out from further analysis. We will be concerned only with the dominant aggregates.

The analysis of the dynamic light scattering led to the conclusion that only a small fraction of the scattered light could be assigned to very large particles. It follows that the molecular weights determined from static light scattering represent primarily dominant particles. In our opinion, the molecular weights are overestimated (due to the large particles) by a factor of less than two. If we model our particles as spheres, we can calculate their volume V from their hydrodynamic radius. Then the ratio $\rho = M/V$ represents the density of the polymer material within the particle. The resulting values are included in Table I (values of M were taken from the M_{app} column). For virtually all our samples the M/V values are between one and two. This is physically impossible, but it becomes plausible when it is considered that the apparent molecular weights were exaggerated by a similar factor due to the presence of very large particles. We may conclude that the dominant particles are rather compact.

What is the mechanism leading to such particles? In our opinion, the process consists of two phases. In the first phase, the dioxane diffuses from the original micelles, they become sticky and form agglomerates. This agglomeration proceeds as a nucleation: micelles in some volume element of the solution come together and are fused by interpenetration of the polystyrene blocks. The nuclei are formed throughout the solution which explains the narrow distribution of the particle sizes. PEO–PPO plays no or a minor role in this phase. In the second phase, in the absence or an insufficient amount of PEO–PPO, the primary agglomerates aggregate further and the polymer precipitates. However, when a sufficient amount of PEO–PPO is present, it adsorbs itself on to the surface of the primary agglomerates and stabilizes them against further aggregation. Because the PEO–PPO attaches itself to the primary particles after they are formed, the size of the particles is essentially independent of the amount of PEO–PPO present. The PEO–PPO molecules may be strongly or loosely attached to the Kraton surface. If their attachment is loose and reversible, a perpetuous exchange of the molecules occurs. Even in this case, when a molecule of PEO–PPO leaves the surface, the poly(ethylene oxide) chains of the neighboring attached molecules still provide sufficient protection against aggregation of the primary aggregates.

The capability of PEO–PPO to protect Kraton particles against further aggregation depends strongly on their structure. Probably several factors are at play simultaneously. The poly(propylene oxide) blocks must be long enough to be attached sufficiently strongly, but short enough in order not to inhibit the protective power of the poly(ethylene oxide) blocks. The latter blocks should be long enough to have sufficient protective power and preferably should be the terminal blocks of the copolymers to extend far enough from the polystyrene surface.

CONCLUSIONS

Stable dispersions of Kraton particles with a particle weight of hundreds of millions can be prepared by injecting a solution of Kraton micelles and PEO–PPO molecules in dioxane into excess water. The particles are rather compact with a hydrodynamic radius about 50–60 nm. The agglomerates of collapsed Kraton micelles are stabilized by a protective layer of PEO–PPO. This layer forms only a minor fraction of the particle mass. Since both copolymers are available in commercial quantities, aqueous dispersions of these nanosized particles can be obtained readily.

APPENDIX

Let us consider light scattering of a particle that is composed of two parts, A and B, their molecular weights being M_A and M_B, respectively. In the limit of vanishing concentration, the scattered intensity is an algebraic sum of intensities scattered by individual particles. Consequently, the Rayleigh factor of scattered light at zero angle, $R(0)$, by such a dilute solution is given by the relation

$$R(0) = 16\pi^4(\Delta\alpha)^2 N/\lambda_0^4. \qquad \text{(A1)}$$

Here, N is the number of particles in unit volume, $\Delta\alpha$ is the excess polarizability of the particle, and λ_0 is the wavelength of light *in vacuo*. The excess polarizability is related to the dielectric constant ε and the refractive index n (the subscript zero refers to pure solvent) as

$$\varepsilon - \varepsilon_0 = n^2 - n_0^2 = 4\pi\Delta\alpha N. \qquad \text{(A2)}$$

Recognizing that, at vanishing concentration, n equals essentially to n_0, that N could be written as $N = c_A N_{Av}/M_A$, and that

$$n - n_0 = (\mathrm{d}n/\mathrm{d}c_A)c_A + (\mathrm{d}n/\mathrm{d}c_B)c_B. \qquad \text{(A3)}$$

We may combine Equations (A1), (A2), and (A3) (eliminating $\Delta\alpha$ and $n - n_0$) into

$$\begin{aligned} R(0) &= [(4\pi^2 n_0^2/\lambda_0^4 N_{Av})(\mathrm{d}n/\mathrm{d}c_A)^2] \\ &\quad \times [1 + (c_B/c_A)(\mathrm{d}n/\mathrm{d}c_B)/(\mathrm{d}n/\mathrm{d}c_A)]^2 c_A M_A. \qquad \text{(A4)} \end{aligned}$$

The first bracket of Equation (A4) is the well-known light scattering constant K_A calculated with the refractive index increment of component A, $\mathrm{d}n/\mathrm{d}c_A$. The ratio c_B/c_A is the ratio of concentrations of components A and B within the particles, it is equal to γ, which is the ratio of masses of components M_B/M_A within the particle. Equation (A4) is now changed to

$$R(0)/K_A c_A \equiv M_{app} = M_A[1 + \gamma(\mathrm{d}n/\mathrm{d}c)_B/(\mathrm{d}n/\mathrm{d}c)_A]^2. \qquad \text{(A5)}$$

This equation is, of course, identical with the equation for the light scattering of a polymer in a mixed solvent, where part B is considered to be a second component of the solvent mixture, concentration of which in solution is vanishingly small. In that case, γ is the coefficient of preferential adsorption. A similar reasoning has been already used in our previous paper.[13]

Acknowledgments

This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/96/1381) and by the US–Czech Science and Technology Joint Fund No. 95010. S.R. thanks UNESCO for the funding provided.

References

[1] Tuzar, Z. and Kratochvíl, P. (1993). *Surf. Colloid Sci.*, **15**, 1.
[2] Zhang, L. and Eisenberg, A. (1995). *Science*, **268**, 1728.
[3] Procházka, K., Martin, T.J., Webber, S.E. and Munk, P. (1996). *Macromolecules*, **29**, 6526.
[4] Killmann, E., Maier, H. and Baker, J.A. (1998). *Colloids and Surfaces*, **31**, 51.
[5] Fears, M.A. and Luckham, P.F. (1994). *Colloids and Surfaces A. Physicochem. Eng. Aspects*, **86**, 317.
[6] Amii, M.M. and Park, J. (1994). *J. Appl. Polym. Sci.*, **52**, 539.
[7] Rangelov, S. and Mircheva, V. (1997). *J. Materials Sci., Letters*, **16**, 209.
[8] Tuzar, Z., Pleštil, J., Koňák, Č., Hlavatá, D. and Sikora, A. (1983). *Makromol. Chem.*, **184**, 2111.
[9] Newton, R.A. (1982). In: *Kirk–Othmer Encyclopedia of Chemical Technology*, M. Grayson and D. Eckroth, eds., 3rd ed. (Wiley: New York), Vol. 18, pp. 633–45.
[10] Jakeš, J. (1998). *Czech. J. Phys.*, **180**, 201.
[11] Li, J.-T., Caldwell, K.D. and Rapaport, N. (1994). *Langmuir*, **10**, 4475.
[12] Fears, M.A. and Luckham, P.F. (1997). *Langmuir*, **13**, 2922.
[13] Tian, M., Arca, E., Tuzar, Z., Webber, S.E. and Munk, P. (1995). *J. Polym. Sci., Polym. Phys.*, **33**, 1713.