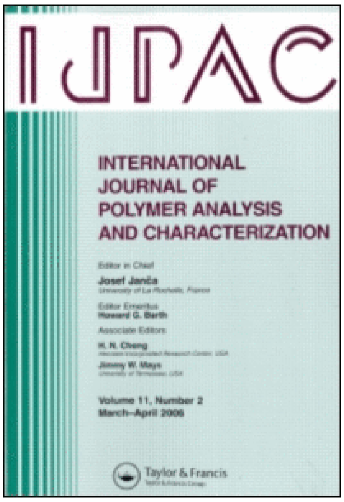

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# A New Technique of Solubilization of Nanosized Hydrophobic Materials in Aqueous Media

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# *A New Technique of Solubilization of Nanosized Hydrophobic Materials in Aqueous Media*

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*Injection of solutions containing molecularly dissolved copolymer polystyrene*-block-*poly(methacrylic acid) (SA) in dioxane produced block copolymer micelles of this hydrophobic/hydrophilic copolymer in water. When the SA solution in dioxane also contained block copolymer micelles of polystyrene*-block-*hydrogenated polybutadiene* block-*polystyrene (Kraton), the product was three-layered (onion) micelles with polystyrene forming the middle layer. The molecular solutions of SA and homopolystyrene in dioxane led to micelle-like particles in which the solubilized polystyrene was kept in water solution by the shell-forming SA molecules. Mechanisms of the processes involved were discussed.*

*Keywords*: Block copolymers; Copolymer micelles; Solubilization into micelles; Static and dynamic light scattering

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Hydrophilic/hydrophobic block copolymers in aqueous media form micelles with hydrophobic cores and hydrophilic shells that are, as a rule, of spherical shape[1]. Appropriate block copolymers usually cannot be dissolved in aqueous media directly. Desired micelles must be prepared first in a mixture of water with some organic cosolvent, and then they can be transferred into water by stepwise dialysis[2]. During this process, micelles became more compact, but are believed to retain their molecular weight, i.e., aggregation number. Only some highly asymmetric hydrophilic/hydrophobic block copolymers were reported to provide other morphologies (rods, lamellae, etc.) when transferred into water[3,4].

Block copolymers may also form so-called onion-type micelles that have three concentric layers[5,6]. A technique has been developed for their preparation from two block copolymers that had one common block, i.e., AB and BC copolymers. First, micelles of the AB copolymer were prepared in a solvent selective for the B blocks. If necessary, they were transferred (often by dialysis) into another solvent (still selective for B blocks) that was a good solvent for both blocks of the BC copolymer. Then, the solvent properties of that particular solvent were suddenly changed in such a way that the solvent became a poor one not only for the A block, but also for the B block. The shell of the AB micelles collapsed, but the collapsing B blocks entrapped the B blocks of the BC copolymer and the soluble C blocks kept the resulting onion micelles in solution.

Specifically, this approach was used for two systems in which the B block was poly(2-vinylpyridine). The AB copolymer was either poly(*t*-butyl acrylate)-*block*-poly(2-vinylpyridine)[5] or polystyrene-*block*-poly(2-vinylpyridine)[6]. The BC copolymer was poly(2-vinylpyridine)-*block*-poly(ethylene oxide). In acidic aqueous solvents poly(2-vinylpyridine) is protonized and soluble, while in basic aqueous solvents it is insoluble. In these systems, the sudden change of the solvent properties consisted in alkalizing the solution. The resulting onion micelles had polystyrene or poly(*t*-butyl acrylate) inner core poly(2-vinylpyridine) outer core and poly(ethylene oxide) shell.

The change of pH is a very effective change of solvent properties but, unfortunately, it is applicable only for polymer blocks that can exist in ionized and neutral forms. For B blocks that cannot exist in an ionic form (e.g., polystyrene) a more substantial change of solvent composition seems to be called for. Our preliminary experiments with such systems showed that the change had to be quite fast; otherwise, the system had a strong tendency to precipitate. The dialysis procedure proved to be unsuccessful.

Recently we developed a procedure (we will call it ‘‘injection procedure’’) that allowed solubilization of insoluble polymer materials in aqueous media. In our previous study[7], we employed this procedure for solubilization of Kraton (block copolymer polystyrene-*block*-hydrogenated polybutadiene *block*-polystyrene) in water using Pluronics (block copolymers of ethylene oxide and propylene oxide) as solubilizing agents. We prepared Kraton micelles in dioxane (in this solvent, micelles are formed with hydrogenated polybutadiene core and polystyrene shell), added a solution of a Pluronic in dioxane and injected this mixture into excess water. As a result, the polystyrene shells of Kraton micelles collapsed, and a substantial number of these micelles formed large agglomerates with a fairly narrow size distribution that were kept in solution by an adsorbed layer of the Pluronic molecules. Both blocks of the Pluronics are incompatible with polystyrene. Consequently, the solubilization was a result of surface adsorption and not of any interpenetration of polystyrene and poly(propylene oxide) blocks.

The aim of the present study is to explore the utility of the injecting procedure for preparation of various types of nanosized dispersions and to obtain a picture of processes taking place during the procedure. We studied the injection of a molecular solution of polystyrene-*block*-poly (methacrylic acid) (SA) in dioxane into water or a mixed solvent (dioxane/water mixtures) known as selective solvents for micelle formation of polystyrene-*block*-poly(methacrylic acid). After we established that SA micelles were actually formed, we proceeded to our next goal: preparation of onion-type micelles with polystyrene outer core (middle layer). We started with Kraton micelles in dioxane, added a molecular solution of polystyrene-*block*-poly(methacrylic acid) in the same solvent and injected the mixture into water or into dioxane/water. In a third set of experiments we injected mixtures of SA and various samples of polystyrene and poly(methyl methacrylate) into water and studied solubilization of these polymers into the micelles.

## EXPERIMENTAL SECTION

### Polymers

Polystyrene samples with molecular weights $9 \times 10^3$ (PS9), $20.4 \times 10^3$ (PS20), $98 \times 10^3$ (PS100), $498 \times 10^3$ (PS500) and $1.8 \times 10^6$ (PS1800) were standards from the Pressure Chemical Co. (U.S.A.). Poly(methyl methacrylate) $M_w = 110 \times 10^3$ (PMMA110) was prepared by standard radical polymerization. Kraton was a previously studied[8] block copolymer polystyrene-*block*-hydrogenated polybutadiene-*block*-polystyrene, $M_w = 60 \times 10^3$, 29 wt% polystyrene (Shell Co., Houston, Texas). In dioxane it forms micelles with aliphatic cores and polystyrene shells,[7] $M_w = 4.6 \times 10^6$, hydrodynamic radius $R_H = 18.4$ nm. Diblock copolymer of styrene and methacrylic acid (SA) ($M_w = 44.2 \times 10^3$, 58 wt%

polystyrene) was prepared by anionic polymerization, as described in ref. [3].

## Static Light Scattering (SLS)

Measurements were performed on a Sofica instrument equipped with a He-Ne laser. Data were treated by the standard Zimm method. Refractive index increments, d*n*/d*c*, were measured on a Brice-Phoenix differential refractometer. When mixed solvents were employed, effective values of d*n*/d*c* were measured under the condition of osmotic equilibrium between the solution and the mixed solvent, using a fixed-volume dialysis cell[10]. When the polymer solution could not be prepared by direct dissolution, d*n*/d*c* values were calculated from a simplified Gladston-Dale rule, i.e., from the difference between the refractive indices of the polymer and the solvent, assuming the specific polymer density equal to 1.0 g/mL (Table I).

## Dynamic Light Scattering (DLS)

Measurements were performed with solutions of the lowest concentration 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 the standard cumulant method. Hydrodynamic radius $R_H$ was evaluated from the diffusion coefficient using the Stokes–Einstein formula.

## Preparation of Stabilized Dispersions

0.5 mL of a dioxane (D) solution of SA with either Kraton micelles, or PS, or PMMA was injected into 19.5 mL of either water (W) or a mixture of 80 vol% of dioxane and 20 vol% of water (further 80D/20W), both solvents being precipitants for PS and PMMA. The concentration of Kraton, or PS, or PMMA in the injected dioxane solution was constant in a given series of experiments ($1 \times 10^{-3}$ or $4 \times 10^{-4}$ g/mL) and the amount of SA was varied. The solution of SA alone in dioxane was injected into both solvents as well.

**TABLE I** Refractive index increments d*n*/d*c* (in mL/g) of polymers in $H_2O$ and a mixture dioxane/water, 80/20 by volume (80D/20W).

| Polymer | Kraton | | SA | | PS | | PMMA |
|---|---|---|---|---|---|---|---|
| Solvent | $H_2O$ | 80D/20W | $H_2O$ | 80D/20W | $H_2O$ | 80D/20W | $H_2O$ |
| d*n*/d*c* | 0.186 | 0.112 | 0.188 | 0.132 | 0.260 | 0.210 | 0.160 |

# RESULTS AND DISCUSSION

In all our experiments, the visual appearance of the solution after injection was typical for micelle solutions. In most instances, the resulting solutions were stable with time. The exceptions were experiments aimed at solubilization of homopolystyrene. These solutions were stable long enough to allow for a measurement of SLS, but precipitated before we were able to perform the measurement of DLS. (DLS measurements were done on the solutions that were used in the SLS measurement and had the lowest concentration.) The results of both types of measurements suggested that the suspended particles were not very polydisperse. We therefore attempted a more detailed analysis of the properties of these particles using an evaluation procedure described previously[6].

## Evaluation Techniques for Multicomponent Solutions

When two different polymers are present in a solution and possibly form composed particles, it is often convenient to select one polymer as the reference material onto which the other one is adsorbed (see our previous paper[6]). When studying the Kraton micelles solubilized by the SA copolymer, we will consider Kraton as the reference material. For solubilization of PS or PMMA into SA micelles, the reference material will be SA. It is further convenient to define $\delta$, the coefficient of preferential sorption of the solvating copolymer BC (SA in the Kraton/SA case), as

$$\delta = c_{\mathrm{BC,ad}}/c_{\mathrm{AB}} \tag{1}$$

where $c_{\mathrm{AB}}$ is the total concentration of the AB copolymer in the solution and $c_{\mathrm{BC,ad}}$ is the concentration of the BC copolymer that is adsorbed onto the collapsed AB micelles. The convenient representation of the SLS data then reads

$$R(0)/K_{\mathrm{AB}}c_{\mathrm{AB}} = M_{\mathrm{app}} = M_{\mathrm{AB}}[1 + \delta(\mathrm{d}n/\mathrm{d}c)_{\mathrm{BC}}/(\mathrm{d}n/\mathrm{d}c)_{\mathrm{AB}}]^2 \tag{2}$$

Here, $R(0)$ is the Rayleigh ratio of the scattering system extrapolated to vanishing concentration and scattering angle, $K_{\mathrm{AB}}$ is the well-known light scattering constant calculated with the refractive increment of the AB copolymer, $M_{\mathrm{app}}$ is the resulting apparent molecular weight, $M_{\mathrm{AB}}$ is the molecular weight of the AB material in the micelles, $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{BC}}$ and $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{AB}}$ are the refractive increments of the copolymers studied.

In the first step of our analysis of the Kraton/SA case, we assume that $M_{\mathrm{AB}}$ is known and corresponds to the original AB micelles. Then, we evaluate the sorption parameter $\delta$ (it is included in the Tables as $\delta_1$) and compare it with the known ratio of the concentrations of the two copolymers $\varDelta = c_{\mathrm{BC}}/c_{\mathrm{AB}}$. The case when $\delta_1 = \varDelta$ can be interpreted as formation of onion micelles with all BC copolymer present being incorporated into them.

However, a result of $\delta_1$ being substantially larger than $\varDelta$ is physically meaningless. This situation means that our original assumption of each particle containing just one original AB micelle is not fulfilled. In this case, we have to change our model. We assume that all BC unimers are incorporated into the micelles or their agglomerates. Thus, equation (2) is again applicable, but $\delta$ must be set equal to $\varDelta$, and $M_{\mathrm{AB}}$ must be evaluated as the unknown. The ratio $N_{\mathrm{Kr}} = M_{\mathrm{AB}}/M_{\mathrm{AB,orig}}$, where $M_{\mathrm{AB,orig}}$ is the molecular weight of the original AB micelles, now represents the weight average number of the original AB micelles in the agglomerates of the micelles.

When $\delta_1$ is smaller than $\varDelta$, it is safe to assume that not all BC unimers are incorporated into the onion micelles and that the excess unimers form micelles of their own. We assume further that these micelles are virtually the same as micelles formed in the absence of the AB "core" micelles. In this situation, equation (2) has to be modified to

$$\begin{aligned} R(0)/K_{\mathrm{AB}}c_{\mathrm{AB}} = M_{\mathrm{app}} = M_{\mathrm{AB}}[1 + \delta(\mathrm{d}n/\mathrm{d}c)_{\mathrm{BC}}/(\mathrm{d}n/\mathrm{d}c)_{\mathrm{AB}}]^2 \\ + M_{\mathrm{BC}}(\varDelta - \delta)[(\mathrm{d}n/\mathrm{d}c)_{\mathrm{BC}}/(\mathrm{d}n/\mathrm{d}c)_{\mathrm{AB}}]^2 \end{aligned} \tag{3}$$

Here, the second term accounts for the scattering of the BC micelles; their molecular weight is $M_{\mathrm{BC}}$. The only unknown in this relation is $\delta$ that could be evaluated from it as

$$\delta = a/2 - b + [b^2M' + a^2/4 - ab - ac]^{1/2} \tag{4}$$

where $M' = M_{\mathrm{app}}/M_{\mathrm{AB}}, a = M_{\mathrm{BC}}/M_{\mathrm{AB}}, b = (\mathrm{d}n/\mathrm{d}c)_{\mathrm{AB}}/(\mathrm{d}n/\mathrm{d}c)_{\mathrm{BC}}$ and $c = c_{\mathrm{BC}}/c_{\mathrm{AB}}$. The values resulting from equation (4) are included in the tables as $\delta_2$.

## Micelles of SA Copolymer

SA solution in dioxane when injected (at concentrations employed in our present study) into either the 80D/20W or into pure water produces micelles. Resulting values of $M_w$ and $R_H$ were in water $1.9 \times 10^6$ and 14 nm, respectively, and in 80D/20W $3.2 \times 10^6$ and 16 nm, respectively. Both values in both solvents were lower than the values of SA solution prepared by direct dissolution in 80D/20W ($6.9 \times 10^6$ and 21 nm, respectively). This difference is most probably caused by the fact that the system after injection is not at equilibrium. (Micelles prepared by direct dissolution are not necessarily at equilibrium either, as we have shown in our previous publication[11].) We assume that during our injection procedure the micelle-forming process acquires a nucleation character. A typical nucleation process begins when randomly formed molecular clusters are sufficiently large to become thermodynamically more stable than individual molecules (unimers in our case). The nuclei grow by incorporating other unimers, but the growth stops when the unimer is exhausted. At this moment the size of the micelles may still be distinctly smaller than the size of equilibrium micelles. Further equilibration would require exchange of unimers among micelles, but this may be blocked kinetically.

## Kraton Micelles Stabilized by SA

When a mixture of Kraton micelles and SA is used for injection, the solution has a typical micellar appearance. The SLS data were evaluated using Zimm plots with the light scattering constant $K_{AB}$ based on the refractive index increment of Kraton; the concentration referred to Kraton as well. The apparent molecular weights $M_{app}$, radii of gyration $R_G$ of the aggregates, the adsorption parameters $\delta_1$, $\delta_2$ and the agglomeration numbers $N_{Kr}$ are collected in Tables II–IV together with the hydrodynamic radii $R_H$ from DLS. The DLS method implies that the distribution of particle sizes is narrow.

In table II we are reporting two series of injections of Kraton/SA mixtures into water. It is apparent that the reproducibility of the results is not good. This is a result of the nonequilibrium kinetics-controlled nature of the preparative technique. Nevertheless, it can be seen from Tables II–IV that for most experiments the model of particles containing a low multiple of Kraton micelles is the most convenient. Moreover, the ratio

**TABLE II** Properties of particles formed by injection of mixtures of SA and Kraton copolymers into water. $\Delta = \mathrm{SA/Kraton}$; $c$ of injected Kraton is $1 \times 10^{-3}$ g/mL.

| $\Delta$ | $M_{app} \times 10^{-6}$ | $R_G$, nm | $R_H$, nm | $\delta_1$ | $\delta_2$ | $N_{Kr}$ |
|---|---|---|---|---|---|---|
| 0.25 | 76.0 | 37 | 40 | 3.03 | | 10.53 |
| 0.5 | 30.5 | 29 | 32 | 1.56 | | 2.93 |
| 1.0 | 39.5 | 22 | 35 | 1.93 | | 2.14 |
| 1.5 | 38.0 | 24 | 32 | 1.87 | | 1.32 |
| 2.5 | 94.0 | 32 | 32 | 3.52 | | 1.67 |
| 1.0[a] | 18.6 | 19 | 21 | 1.00 | 1.00 | 1.00 |
| 3.0[a] | 28.1 | — | 23 | 1.46 | 1.35 | 0.38 |
| 4.0[a] | 42.7 | 18 | 24 | 2.02 | 1.93 | 0.37 |

[a] Second series of experiments.

**TABLE III** Properties of particles formed by injection of mixtures of SA and Kraton copolymers into water. $\Delta = \mathrm{SA/Kraton}$; $c$ of injected Kraton is $4 \times 10^{-3}$ g/mL.

| $\Delta$ | $M_{\mathrm{app}} \times 10^{-6}$ | $R_G$, nm | $R_H$, nm | $\delta_1$ | $N_{\mathrm{Kr}}$ |
|---|---|---|---|---|---|
| 1.0 | 42.5 | 28 | 19 | 2.0 | 2.29 |
| 3.0 | 127.0 | 45 |  | 4.2 | 1.70 |
| 4.0 | 191.0 | 55 | 18 | 5.4 | 1.63 |

**TABLE IV** Properties of particles formed by injection of mixtures of SA and Kraton copolymers into 80D/20W. $\Delta = \mathrm{SA/Kraton}$; $c$ of injected Kraton is $1 \times 10^{-3}$ g/mL.

| $\Delta$ | $M_{\mathrm{app}} \times 10^{-6}$ | $R_G$, nm | $R_H$, nm | $\delta_1$ | $N_{\mathrm{Kr}}$ |
|---|---|---|---|---|---|
| 0.25 | 60.0 | 40 | 72 | 2.21 | 7.78 |
| 0.5 | 20.3 | 23 | 35 | 0.93 | 1.75 |
| 1.0 | 28.6 | 23 | 30 | 1.27 | 1.31 |
| 1.33 | 39.0 | 28 | 30 | 1.62 | 1.27 |
| 2.5 | 73.0 | 37 | 39 | 2.53 | 1.02 |

$R_G/R_H$ is rather small. This suggests that the prevailing number of particles in the solution have a symmetry that is more or less spherical.

Despite the poor reproducibility of the results, several trends are seen clearly. When there is a too low ratio of the mass of the stabilizing SA copolymer, the average number of Kraton micelles in the aggregate goes up. When there is an excess of the SA copolymer, the model of onion micelles containing only one core Kraton micelle is appropriate; the onion micelles are in this case accompanied by SA micelles formed by the excess SA copolymer. When the original concentration of the mixture used for the injection is increased, the formation of clusters is enhanced, but the number of the core micelles contained in them remains rather low.

We will now explore the processes in our system after injection. The collapsing polymer, polystyrene blocks in the present case, in water represents a system in a strong segregation limit. After completion of the process, the polystyrene chains are essentially frozen in whatever structure they are embedded in: the final system is not at equilibrium and its state is strongly dependent on kinetic factors. Thus from the properties of the final system it should be possible to infer the nature and role of the kinetic factors. In the following paragraphs we will develop a plausible molecular model of the injection procedure.

What phenomena are at play when the solvent suddenly becomes a poor one for polystyrene? Formation of contacts between polystyrene segments becomes thermodynamically advantageous; it is the driving force of the process. The contacts are formed fastest in regions of highest segment concentration. In dilute solutions, the regions of highest segment concentrations are the shells of the Kraton micelles; their collapse is fast. Other regions of large segment concentration are the polystyrene blocks of the SA molecules that are at this moment in a coiled form. They partially collapse (a full collapse is prevented by the molecular rigidity of their relatively short blocks) and most probably form so-called unimer micelles: structures with a relatively dense polystyrene cluster and a loose poly(methacrylic acid) coil. During the next stage, these particles collide and form the final particles. Three processes compete with each other:

1. Collisions of collapsed Kraton micelles may lead to interpenetration of their polystyrene outer layers and to agglomerates of the original Kraton micelles. This process is governed by a relatively slow diffusion of the collapsed micelles. It becomes less important as the total concentration of the system decreases.
2. Collisions of the unimer micelles with the collapsed micelles lead to their incorporation and to a gradual buildup of the onion micelles. As the buildup proceeds, the newly formed poly(methacrylic acid) shell prevents the agglomeration process. The unimer micelles are also incorporated into the previously existing agglomerates and stabilize them by the same mechanism. This process is governed by much faster diffusion of the unimers and at low concentrations becomes the prevailing mechanism.
3. Finally, a number of unimer micelles may come together and produce SA micelles. This is a typical nucleation process: clusters of too few unimers are not thermodynamically stable. Only clusters that are large enough may survive and become the precursors of the micelles. At low concentrations, this process is slower than the formation of onion micelles and takes place mainly after the onion micelles are saturated by the unimers.

## Solubilization of Polystyrene and Poly(methyl methacrylate) in SA Micelles

When a molecular solution of polystyrene and the SA copolymer is injected into a solvent that is a precipitant for polystyrene, a solution is obtained that exhibits typical micellar properties: bluish opalescence and DLS behavior suggesting particles with a narrow distribution of sizes. For the calculation of the apparent molecular weights from the SLS measurements, we used the light scattering constant *K* based on the SA copolymer as well as its concentration. This allowed us to treat the results again using equation (2) in which the quantity $M_{AB}$ referred to the content of copolymer SA in the particles, and $\delta = \Delta$ represented the amount of polystyrene solubilized in the particles. The molecular weight of the whole particles (presumably micelles) was $M_{mic} = M_{AB}(1 + \Delta)$. The experimental data are collected in Tables V–VII.

In several instances we were able to perform the DLS measurements only after several hours or the day after their preparation. Some samples that yielded well-behaved Zimm plots when measured by SLS immediately after preparation partially precipitated before the DLS measurement could be done.

**TABLE V** Properties of particles formed by injection of mixtures of SA copolymer and polystyrene (PS) into water. $\Delta = SA/PS$; $c$ of injected PS is $1 \times 10^{-3}$ g/mL.

| PS | $\Delta$ | $M_{app} \times 10^{-6}$ | $R_G$, nm | $R_H$, nm | $M_{SA} \times 10^{-6}$ | $M_{mic} \times 10^{-6}$ |
|---|---|---|---|---|---|---|
| PS9 | 1.5 | 9.10 | | 19 | 2.46 | 4.11 |
| PS9 | 3.0 | 6.86 | | 19 | 3.21 | 4.29 |
| PS9 | 4.0 | 6.66 | | 20 | 3.68 | 4.60 |
| PS20 | 1.5 | 46.5 | 48 | * | 12.6 | 21.0 |
| PS100 | 0.25 | 75.0 | 92 | * | 1.76 | 8.79 |
| PS100 | 0.5 | 47.0 | 75 | * | 3.31 | 9.94 |
| PS100 | 1.5 | 29.0 | 54 | * | 7.85 | 13.1 |
| PS100 | 2.5 | 46.0 | 50 | | 19.1 | 26.7 |
| PS500 | 1.5 | 38.2 | 40 | * | 10.3 | 17.2 |
| PS500 | 3.0 | 21.45 | 47 | 28 | 10.0 | 13.4 |
| PS500 | 4.0 | 21.4 | 43 | 36 | 11.8 | 14.8 |
| PS1800 | 1.5 | * | | | | |
| PMMA100 | 1.5 | 5.5 | | 20 | 2.2 | 3.7 |

*Sample precipitated.

**TABLE VI** Properties of particles formed by injection of mixtures of SA copolymer and polystyrene (PS) into water. $\Delta = SA/PS$; $c$ of injected PS is $4 \times 10^{-3}$ g/mL.

| PS | $\Delta$ | $M_{app} \times 10^{-6}$ | $R_G$, nm | $R_H$, nm | $M_{SA} \times 10^{-6}$ | $M_{mic} \times 10^{-6}$ |
|---|---|---|---|---|---|---|
| PS9 | 3.0 | 54.9 | 76 | * | 25.8 | 33.4 |
| PS9 | 4.0 | 53.7 | 86 | * | 29.7 | 37.1 |

*Sample precipitated.

**TABLE VII** Properties of particles formed by injection of mixtures of SA copolymer and polystyrene (PS) into 80D/20W. $\Delta = \text{SA}/\text{PS}$; $c$ of injected PS is $1 \times 10^{-3}$ g/mL.

| PS | $\Delta$ | $M_{\text{app}} \times 10^{-6}$ | $R_G$, nm | $R_H$, nm | $M_{\text{SA}} \times 10^{-6}$ | $M_{\text{mic}} \times 10^{-6}$ |
|---|---|---|---|---|---|---|
| PS9 | 1.5 | 123.0 | 159 | 85 | 29.0 | 48.3 |
| PS20 | 1.5 | 26.5 | 42 | 72 | 6.24 | 10.4 |
| PS100 | 0.25 | 34 | 30 | 54 | 0.62 | 3.14 |
| PS100 | 0.5 | 17 | 25 | 36 | 0.97 | 2.92 |
| PS100 | 1.5 | 19 | 31 | 40 | 4.47 | 7.45 |
| PS100 | 2.5 | 36 | 32 | 45 | 13.4 | 18.8 |
| PS100 | 1.5 | 32.1 |  | 51 | 7.56 | 12.6 |
| PS500 | 1.5 | 101.5 | 57 | 45 | 23.9 | 39.8 |
| PS1800 | 1.5 | 212.1 | 107 | 48 | 50.0 | 83.3 |
| PMMA100 | 1.5 | 6.2 | 29 | 25 | 2.9 | 4.9 |

The experimental results are quite scattered. It is difficult to establish any clear-cut dependence on the experimental variables. However, several patterns can be observed. The masses of the micelles are two to ten times larger than the mass of pure SA micelle. Polystyrenes with higher molecular weights tend to produce larger micelles. Particles prepared by injection into water have quite large radii of gyration that are even larger than the hydrodynamic radii and they have a tendency to precipitate. Injection into the 80D/20W mixture produces more stable and more micelle-like particles. Surprisingly, poly(methyl methacrylate), which is in most experimental situations incompatible with polystyrene, is apparently solubilized into polystyrene micelle cores quite easily.

What information can we obtain from these observations about the processes that occur after the injection? Both polystyrene and SA are soluble in dioxane. During the initial molecular collapse the polystyrene molecules become irregular globules. During the next phase, they participate in the nucleation process and together with the semi-collapsed unimer SA micelles form the final SA micelles, in which the polystyrene molecules are solubilized.

It is plausible to assume that the collapsed polystyrene globules have a more expressed tendency to aggregate (i.e., to form the nuclei) than the partially protected polystyrene blocks of SA. The extent of this aggregation may then determine the size of the particles (which are mostly much larger than micelles of pure SA). The internal reorganization of the particles may affect their stability and size. In water the original aggregates reorganize slowly (polystyrene is presumably in a glassy state), have an irregular shape (high $R_G/R_H$ ratios) and a tendency to aggregate further through exposed PS domains on the particle surface. In 80D/20W the PS microphase is swollen; it reorganizes faster, producing particles that are closer in their properties to classical micelle systems (i.e., have slightly lower free energy).

It is interesting to note that micelles prepared by the present method do not obey the rules deduced in previous studies of solubilization of homopolymers in micelle cores.[12,13] Specifically, polystyrene molecules that have much larger mass than the PS blocks of the stabilizing SA copolymer may be incorporated in the micelles.

## CONCLUSIONS

Our experiments have shown that the new injection procedure is very flexible and can produce micellar systems with only moderate polydispersity of the resulting particles. It was used for the preparation of several types of self-assembling nanosized particles.

1. Molecular solutions of polystyrene-*b*-poly(methacrylic acid) (SA) solutions in dioxane when injected into water yield micelles that are smaller than similar micelles produced by a direct dissolution of the copolymer in a selective solvent.
2. Mixed solution of Kraton micelles and SA in dioxane when injected into water or into a water/dioxane mixture that is a selective solvent for SA yields three-layered (onion) micelles with poly(hydrogenated butadiene) inner core, polystyrene middle layer and poly(methacrylic acid) shell. In addition to these micelles a moderate amount of clusters containing a very small number of Kraton micelles is also present.
3. Molecular solution of polystyrene and SA in dioxane when injected in water yields micelle-like particles containing solubilized polystyrene. These particles are somewhat irregular and may precipitate upon long standing. The same solution injected into water/dioxane mixture produces similar particles that are more regular and more stable.

A plausible mechanism was proposed that determined the nature of the various products. The mechanism involved a combination of the nucleation of semicollapsed unimer micelles and accretion of unimers on a pre-formed nucleus—a Kraton micelle.

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