Micellization of Model Graft Copolymers in Dilute Solution

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ABSTRACT: The micellization behaviors of graft copolymers consisting of polystyrene, PSt, backbones and poly(*tert*-butyl methacrylate), PtBuMA, or poly(methacrylic acid), PMAA, branches were studied in dilute solutions by low angle laser light scattering, LALLS, viscometry, and dynamic light scattering, DLS. *tert*-Amyl alcohol, a selective solvent for the PtBuMA branches, and tetrahydrofuran, THF, a selective solvent for the PSt backbones, were used to promote the formation of micelles from the PSt-*g*-PtBuMA and PSt-*g*-PMAA graft copolymers, respectively. Low aggregation numbers were obtained in all cases due to the specific architectural characteristics of the samples. Aggregation numbers were dependent on the type of the component (backbone or branches) that was insoluble in the selective solvent. The formation of micelles from the PSt-*g*-PtBuMA graft copolymers in *tert*-amyl alcohol is evidenced by the appearance of large and rather loose aggregates at a certain concentration range. This kind of behavior was not observed for the micelles formed from the graft copolymers with PMAA branches in THF. Stable and compact structures were obtained in this case, with their hydrodynamic behavior resembling that of hard spheres.

Introduction

Self-assembling macromolecules have been the subject of numerous studies during the last decade, due to their academic interest and their industrial applications.[1−4] One of the most common examples of such self-assembly is the formation of polymeric micelles. When block copolymers are dissolved in a selective solvent (thermodynamically a good solvent for one of the blocks and a precipitant for the other block), they associate to form micelles having cores that consist predominanttly of the insoluble block, with coronas of the solvated block.

Systematic work from both experimental and theoretical points of view[5−10] has been devoted to the study of micelles formed by diblock copolymers. Similar studies have been extended to triblock copolymers, mainly for solvents selective for the outer blocks.[11−17] Relatively few studies on the formation of micelles composed of graft copolymers or more complex structures have appeared in the literature.[18−26] Most of this work, with some exceptions, deals with rather ill-defined copolymers, characterized by chemical and compositional heterogeneity, broad molecular weight distributions, and poor control over the number and the placement of the branches along the backbone. The change of architecture imposes constraints that affect the properties of the micelles, i.e., degree of aggregation, shape and density of micelles, etc. Other parameters, like the selective solvent quality, the temperature, the composition of the copolymer, etc., play an important role in the determination of the micellar properties.

Graft copolymers consisting of polystyrene, PSt, backbones and poly(*tert*-butyl methacrylate), PtBuMA, branches were prepared recently using the “grafting onto” technique.[27] The backbone was bromomethylated by following the procedure of Itsuno et al.[28] and was added to a solution containing living PtBuMA chains for the preparation of PSt-*g*-PtBuMA copolymers. Hydrolysis of the *tert*-butyl groups with HCl provided copolymers with ionic branches, PSt-*g*-PMAA. Spherical and relatively monodisperse (in size) micelles were prepared in a water−tetrahydrofuran (THF) 80/20 (v/v) mixed solvent.[29]

In this paper, we report the micellar properties of the PSt-*g*-PtBuMA graft copolymers in *tert*-amyl alcohol, which is a selective solvent for the PtBuMA branches. Micellar properties are also reported for the PSt-*g*-PMAA copolymers in THF, a solvent selective for the PSt backbone. Static and dynamic light scattering and viscometry were used in our study.

Experimental Section

The graft copolymers were prepared by anionic polymerization, employing high vacuum techniques, in all glass reactors.[30] Linear PSt chains were bromomethylated with trioxane and trimethylbromosilane, $(CH_3)_3SiBr$, using tin tetrabromide, $SnBr_4$, as the catalyst, to incorporate the functional bromomethyl, $-CH_2Br$, groups randomly along the backbone. One of the PSt backbones was made by polymerizing styrene-d_8 (Cambridge Isotopes, Halogen free), to allow for neutron scattering contrast in other experiments.[29] *tert*-BuMA was polymerized at −78 °C under high vacuum using (diphenylhexyl)lithium as initiator and THF as solvent. The bromomethylated PSt backbone was added to the living polymer solution to perform the grafting reaction. The reaction proceeded for 5 days at −78 °C, and finally, the excess of the living PtBuMA solution was quenched with MeOH. The graft copolymer was precipitated in cold MeOH and was purified from the excess PtBuMA arm by extraction with hot MeOH in a Soxhlet apparatus. The *tert*-butyl groups were hydrolyzed using aqueous HCl (6 N) in 1,4-dioxane at 85 °C for about 5 h. The reactions describing the synthesis of the graft copolymers are given in Scheme 1.

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Scheme 1

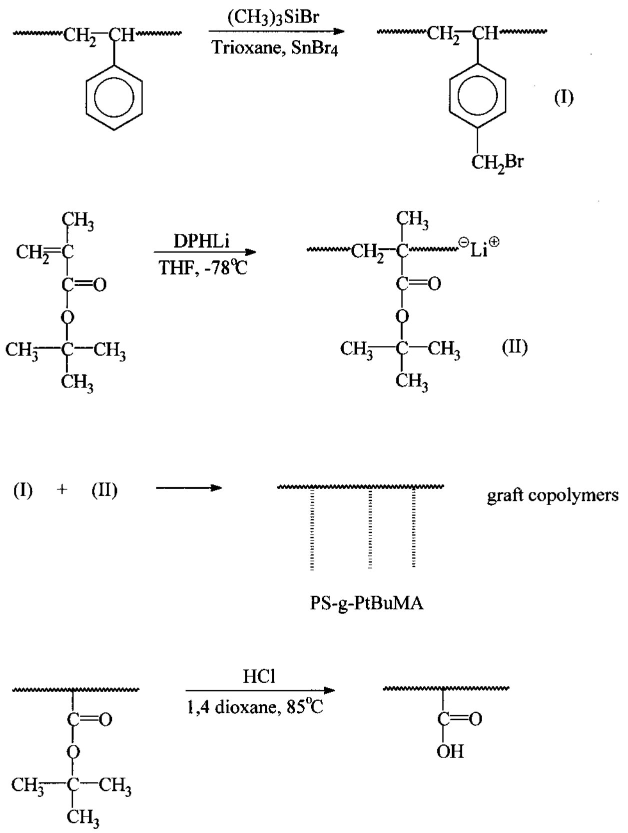

Table 1. Molecular Properties of the Graft Copolymers in THF at 25 °C

sample	PSt-*g*-PtBuMA #3[a]	dPSt-*g*-PtBuMA[b]
$M_w \times 10^{-4}$ [c]	32.6	26.9
$M_{nPSt} \times 10^{-4}$ [d]	7.98	7.32
$M_{nPtBuMA} \times 10^{-4}$ [d]	3.36	2.50[e]
$A_2 \times 10^4$ [c]	2.6	2.99
N [f]	6.8	5.7
$[\eta]$ (mL/g) [g]	64.7	55.4
K_H [g]	0.38	0.36
R_v (nm) [g]	14.9	13.3
$D_0 \times 10^7$ (cm^2/s) [h]	3.27	3.72
K_D [h]	59.8	43.8
R_h (nm) [h]	14.5	12.8
R_v/R_h [i]	1.03	1.04

[a] wt % PS = 21.8. [b] wt % d-PS = 36. [c] By LALLS. [d] By membrane osmometry in toluene at 38 °C. [e] By size exclusion chromatography in THF. [f] Number of branches calculated from the molecular weights of the graft copolymers, the backbone, and the branch. [g] By viscometry. [h] By DLS. [i] By viscometry and DLS.

The molecular characteristics of the samples are reported in Table 1. More details regarding the synthesis of the graft copolymers are given elsewhere.[29]

THF and *tert*-amyl alcohol were purified by refluxing for at least 24 h over Na and CaH_2, respectively, and were fractionally distilled just prior to use. Graft copolymers with MAA branches were easily dissolved at room temperature in THF. As a precaution and in order to achieve equilibrium structures, the solutions were heated at 50 °C for 1 h before measurements were performed. Graft copolymers having PtBuMA branches formed macroscopic dispersions of swollen particles in *tert*-amyl alcohol. Complete dissolution was achieved after treating the solutions at 50 °C for at least 1 h. The characteristic bluish tint due to the presence of micelles was developed in this case. No precipitation was observed at room temperature after the thermal treatment of the solutions.

Apparent weight-average molecular weights, $M_{w,app}$, and second virial coefficients, A_2, were obtained by static light scattering measurements at 25 °C using a Chromatix KMX-6 low angle laser light scattering (LALLS) photometer operating at wavelength λ = 633 nm. The equation describing the concentration dependence of the reduced intensity is

$$Kc/\Delta R_\theta = 1/M_{w,app} + 2A_2c + ... \qquad (1)$$

where K is a combination of optical and physical constants, including the refractive index increment dn/dc, c is the concentration, and ΔR_θ is the excess Rayleigh ratio of the solution over that of the solvent. Stock solutions were prepared, followed by dilution with solvent to obtain solutions with lower concentrations. All solutions were optically clarified by filtering through 0.22 μm pore size nylon filters directly into the scattering cell. In certain cases, where large micelles were formed, 0.45 μm pore size filters were used. The specific refractive index increment (dn/dc) values, required for the determination of the optical constant K, were measured by a Brice-Phoenix differential refractometer (model BP-2000−V) at 25 °C for λ = 633 nm or by an Otsuka differential refractometer (model DRM-1020) under the same conditions. Aqueous NaCl solutions were used for the calibration of the instruments.

Dynamic light scattering (DLS) measurements were performed using a Brookhaven BI 2000 SM goniometer, a BI 2030 AT correlator with 72 channels and a ca. 28 mW Ar^+ laser operating at λ = 488 nm. The temperature was controlled to 25 ± 0.1 °C. Correlation functions were analyzed to second order by the method of cumulants. Measurements were obtained at 45, 90, and 105°. The angular dependence of the ratio Γ/q^2, where Γ is the decay rate of the correlation function and q is the scattering vector, was not very important due to the large sizes of the micelles. Apparent translational diffusion coefficients at zero concentration $D_{o,app}$, were measured using

$$D_{app} = D_{o,app}(1 + K_Dc + ...) \qquad (2)$$

where K_D is the coefficient of the concentration dependence of the diffusion coefficient including both themodynamic and frictional components ($K_D = 2A_2M - k_f - u_2$, where A_2 is the second virial coefficient, M is the molecular weight, k_f is the coefficient of the concentration dependence of the friction coefficient, and u_2 is the partial specific volume of the polymer).

Apparent hydrodynamic radii at infinite dilution, R_h, were calculated by aid of the equation

$$R_h = kT/6\pi\eta_sD_{o,app} \qquad (3)$$

where η_s is the viscosity of the solvent, k is Boltzmann's constant, and T is absolute temperature. Viscometry experiments were performed using Cannon-Ubbelohde dilution viscometers in a water bath at 25 ± 0.01 °C. Intrinsic viscosities, $[\eta]$, were obtained using both the Huggins

$$\eta_{sp}/c = [\eta] + K_H\,[\eta]^2c + ... \qquad (4)$$

and the Kraemer equations

$$\ln \eta_r/c = [\eta] - K_K[\eta]^2c + ... \qquad (5)$$

where K_H and K_K are the Huggins and Kraemer coefficients, respectively, η_{sp} (=η_r − 1) is the specific viscosity, and η_r, the ratio of the solution to solvent flow times, is the relative viscosity. The solvent flow time was greater than 200 s in all cases, so no kinetic energy corrections were made. Viscometric radii, R_v, were calculated using

$$R_v = (3/10\pi N_A)^{1/3}([\eta]M_{app})^{1/3} \qquad (6)$$

where N_A is the Avogadro number and M_{app} is the apparent

Table 2. Micellar Properties of the Graft Copolymers in *tert*-Amyl Alcohol at 25 °C

	PSt-*g*-PtBuMA #3[a]	dPSt-*g*-PtBuMA[b]
$(M_w)_{mic} \times 10^{-6}$ [c]	3.46	2.93
$A_2 \times 10^5$ [c]	−2.58	1.17
N[d]	6.8	5.7
N_w[e]	10.6	10.9
$[\eta]$ (mL/g)[f]	31.2 (50.8)[g]	35.0 (43.2)[g]
K_H[f]	0.82 (−0.79)[g]	0.28 (−0.67)[g]
R_v (nm)[f]	25.7 (30.3)[g]	25.3 (27.2)[g]
$D_0 \times 10^6$ (cm^2/s)[h]	2.63	2.94
K_D[h]	39.4	79.6
R_h (nm)[h]	23.3	20.9
R_v/R_H[i]	1.10 (1.30)[g]	1.22 (1.31)[g]

[a] wt % PS = 21.8. [b] wt % d-PS = 36.0. [c] By LALLS. [d] Number of branches calculated from the molecular weights of the graft copolymers, the backbone, and the branch. [e] Degree of aggregation. [f] By viscometry. [g] Data obtained by extrapolation from the lower concentration regime. [h] By DLS. [i] By DLS and viscometry.

weight average molecular weight obtained by light scattering measurements.

Results and Discussion

a. Hydrodynamic Properties of the PS-*g*-PtBuMA Graft Copolymers in THF. The hydrodynamic properties of the non-hydrolyzed graft copolymers were measured in THF, a common good solvent for both components. The results are reported in Table 1. Behavior typical of flexible (nonaggregated) polymers in dilute solution is indicated by the data. Specifically, linear plots were obtained in all cases, the K_H values are ~1/3 (the limit corresponding to flexible homopolymers in good solvents), and the ratios of the viscometric to hydrodynamic radii, R_v/R_h, are close to unity, the limit predicted for rigid spheres.[31] In addition the R_T/R_v ratio, where R_T is the thermodynamic radius, defined as $R_T = (3/16\pi N_A)^{1/3}(A_2M^2)^{1/3}$ varies between 0.94 and 0.97, values which are close to the hard sphere limit. Similar values were obtained for star polymers with five and six arms,[32] indicating that the behavior of graft copolymers with small numbers of branches resembles that of star polymers with the same number of branches.

b. Micellar Properties of the PS-*g*-PtBuMA Graft Copolymers in *tert*-Amyl Alcohol. The experimental results concerning the solution properties of the graft copolymers in *tert*-amyl alcohol are listed in Table 2. *tert*-Amyl alcohol is a relatively good solvent for PtBuMA but is a nonsolvent for PSt. LALLS data (e.g., in Figure 1) clearly indicate the formation of micelles in this solvent. With increasing concentration, the $Kc/\Delta R_\theta$ values initially decrease sharply and then show an upturn with a small but positive slope. This behavior corresponds to a gradual micellization until stable structures are formed. An equilibrium between unimers and micelles is established in the transition area. This equilibrium is shifted gradually in favor of the micelles by the increasing concentration until the linear dependence is obtained. Here the micelles dominate the solution properties. In both cases no cmc (critical micelle concentration) was observed, meaning that the micelles are formed at concentrations lower than the 3×10^{-5} or 7×10^{-5} g/mL concentrations used for the two samples. The apparent molecular weights were obtained by extrapolation of the linear part of the plot (higher concentration regime) to infinite dilution. Much higher molecular weights were measured in *tert*-amyl alcohol, compared with those found in THF, due to the existence of micelles in the solution. The degree of association, N_w, defined as the ratio of the micelle to the unimer molecular weight is rather low and is almost the same for both samples, despite the fact that the deuterated sample has a higher PSt content than the other one. This result can be explained by considering that the degree of micellization is more sensitive to the specific architecture than to the PSt content. The insoluble component is the backbone, which is well protected by the soluble component. In other words, the PtBuMA branches act as a solubilizing agent for the PSt backbones, thus preventing the formation of large micelles. This behavior is in agreement with previous studies that showed that micelles formed by graft copolymers have relatively low degrees of association or do not associate at all, as in the case of multigrafted backbones.[19−20,33−36]

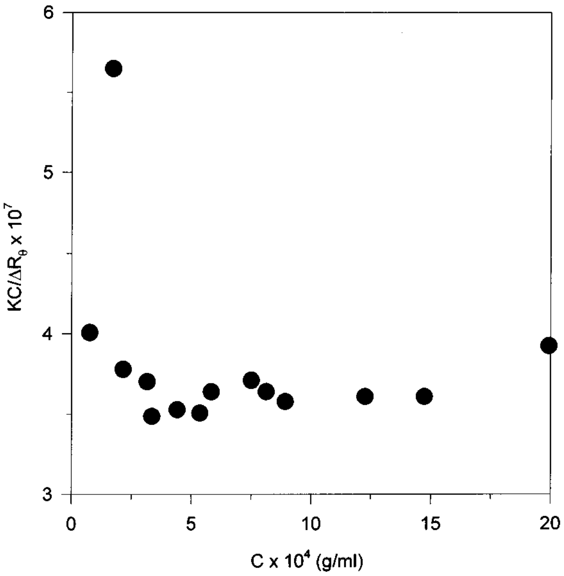

Figure 1. LALLS plot for dPSt-*g*-PtBuMA in tert-amyl alcohol at 25 °C.

The second virial coefficients measured by LALLS were near zero for both samples. This is explained by the higher apparent molecular weight of the micelles, as compared with the unimers, and by the rejection of the solvent from the core of the micelles, leading to more favorable interactions, such as those between the solvent with the PtBuMA branches.

Characteristic viscosity plots were obtained in *tert*-amyl alcohol (e.g., in Figure 2). The Huggins plots show an initial decrease of the η_{sp}/c values upon increasing concentration, followed by a change of the slope, which becomes positive at a concentration of ~$(7-8) \times 10^{-3}$ g/mL. Keeping in mind the results from LALLS, where the equilibrium was shifted in favor of the micelles at much lower concentrations $(2-4) \times 10^{-4}$ g/mL), we can reach the following conclusions: In the lowest concentration regime ($c < 10^{-4}$ g/mL), single chains are almost exclusively present, and upon increasing concentration, an equilibrium between single chains and micelles is established. This equilibrium is shifted toward the micelles at $c > 10^{-4}$ g/mL, but the structures initially formed can be considered as large and loose aggregates, leading to higher solution viscosities. At concentrations higher than $(7-8) \times 10^{-3}$ g/mL more compact and stable micelles were obtained, as indicated by the positive K_H values and by their $[\eta]$ values, which are much lower than those measured for the single chains in THF, a common good solvent. Raspaud et al. observed the existence of rather loose aggregates instead of classical micelles for PSt-*b*-PI-*b*-PSt triblocks in *n*-heptane, a

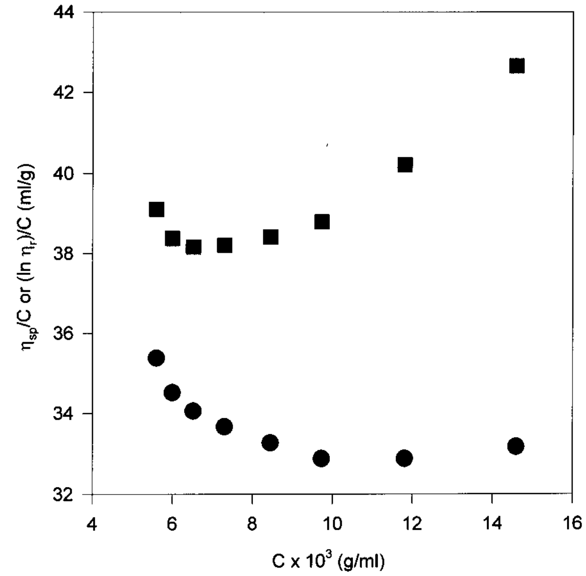

Figure 2. Viscosity plot for PSt-*g*-PtBuMA #3 in tert-amyl alcohol at 25 °C: (■) = η_{sp}/c; (●) = $(\ln \eta_r)/c$.

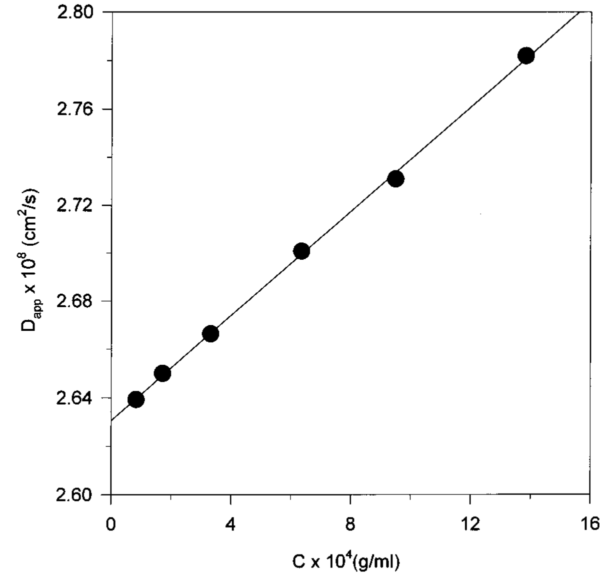

Figure 3. DLS plot for PSt-*g*-PtBuMA #3 in tert-amyl alcohol at 25 °C ($\theta = 45°$).

Table 3. Micellar Properties of the Hydrolyzed Graft Copolymers in THF at 25 °C

sample	PSt-*g*-PMAA	dPSt-*g*-PMAA
$M_w \times 10^{-4}$ [a]	23.0	19.0
% wt PSt	36.4	39.8
$(M_w)_{mic} \times 10^{-5}$ [b]	25.6	7.34
$A_2 \times 10^5$ [b]	0.34	1.39
N [c]	6.8	5.7
N_w [d]	11.1	3.8
$[\eta]$ (mL/g) [e]	31.1	36.5
K_H [e]	2.43	0.83
R_v (nm) [e]	23.3	16.2
$D_0 \times 10^7$ (cm^2/s) [f]	1.96	3.13
K_D [f]	−197	−117
R_h (nm) [f]	24.2	15.1
R_v/R_H [g]	0.96	1.07

[a] Calculated from the M_w of the original copolymer by taking into account that the degree of hydrolysis is 100% (by ^{1}H-NMR). [b] By LALLS. [c] Number of branches calculated from the molecular weights of the graft copolymers, the backbone, and the branch. [d] Degree of aggregation. [e] Viscometry. [f] By DLS. [g] By DLS and viscometry.

selective solvent for the polyisoprene, PI, chains.[13] This behavior was explained by considering the entropy loss associated with central block back-folding, which is necessary to produce stable structures. A similar behavior was observed in our system, but only within a certain concentration regime, due to the different topologies of the two structures (triblock versus graft copolymers).

Dynamic light scattering data confirm the results obtained by LALLS and viscometry. A typical plot of D_{app} versus c is shown in Figure 3. The plot is linear and the angular dependence was negligible. The $D_{o,app}$ values are lower by almost 1 order of magnitude compared to those obtained in THF. This is indicative of the decreased mobility of the aggregates as compared to the single chains. The linearity of such plots reflects the existence of stable structures in the concentration regime used for the DLS measurements. The K_d values were positive but lower than those measured in THF, indicating that the reduced polymer−solvent interactions (known from the low A_2 values) are more important than the increased molecular weights of the micelles in determining the K_d values. The second moment values μ_2/Γ^2 were lower than 0.1 for all concentrations, with the values decreasing even more upon increasing concentration. This is an indication that the micelles have low polydispersities. The hydrodynamic radius, R_h, calculated using the Stokes−Einstein equation (eq 3) is generally lower than the corresponding R_v values. For both samples the ratio R_v/R_h is higher than unity, the value which is expected for spherical particles. The result can be rationalized by considering that the loose aggregates initially obtained are susceptible to deformation during the flow in the capillary viscometry tube, leading to deviations from the spherical shape. It is known that the intrinsic viscosity reflects both static and dynamic contributions[37] ($[\eta] \sim R_G{}^2R_h$) and since the radius of gyration, R_G, is more sensitive to the larger dimension of nonspherical particles, it is reasonable to obtain R_v/R_h values greater than unity. This observation, in addition to the fact that R_h is a purely hydrodynamic parameter and consequently is not seriously affected by small shape deformations, leads to the conclusion that R_v/R_h values larger than unity indicate the presence of elliptical species. Generally, the more loose and larger the aggregates, the more susceptible they are to possible deformations.

c. Micellar Properties of the Hydrolyzed Graft Copolymers in THF. Hydrolysis of the *tert*-butyl groups with aqueous HCl leads to the formation of graft copolymers with poly(methacrylic acid) branches. Their micellar properties were studied in THF, which is a very good solvent for the backbone and a poor solvent for the PMAA branches, due to its low polarity. The experimental results are listed in Table 3. It is obvious from the increased molecular weights that micelles are formed in THF. As in the case of the nonhydrolyzed samples in *tert*-amyl alcohol, the LALLS plots (e.g., in Figure 4) show a steep decrease of the reduced scattering intensity with increasing concentration. This is a characteristic indicator of the existence of micelles in the solution. The micellar molecular weights were obtained by extrapolation of the higher concentration regime plot, where the equilibrium is shifted toward the micelles, to infinite dilution. Also, in this case no cmc could be detected for either sample, indicating that the cmc is lower than 8.7×10^{-5} and 1×10^{-4} g/mL for dPSt-*g*-PMAA and PSt-*g*-PMAA, respectively.

The second virial coefficients showed very small but positive values in both cases, suggesting that the solvent

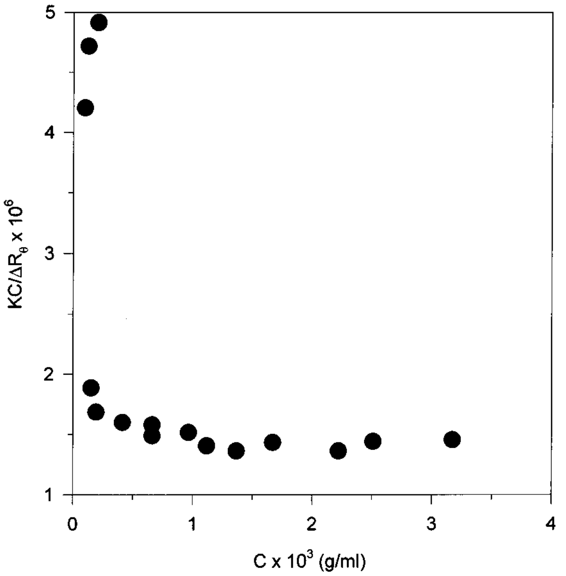

Figure 4. LALLS plot for d-PSt-*g*-PMAA in THF at 25 °C.

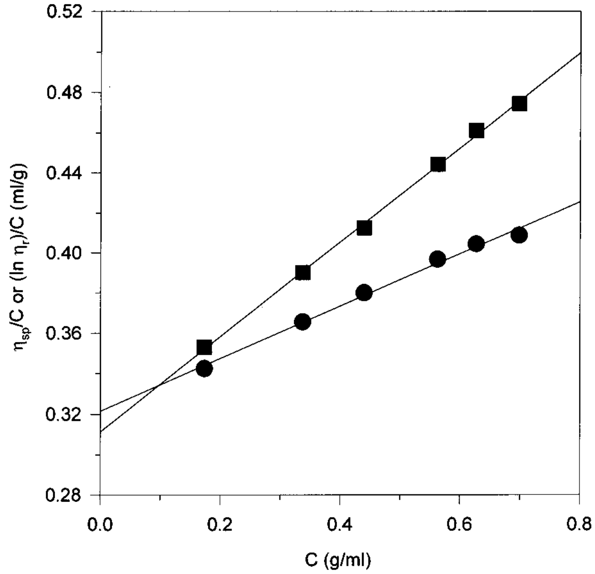

Figure 5. Viscosity plot for PSt-*g*-PMAA in THF at 25 °C: (■) = η_{sp}/c; (●) = (ln η_r)/c.

is rejected from the micellar core in order to avoid the unfavorable PMAA–solvent interactions. On the other hand, the solvated PSt corona hinders the long-range PMAA segment–PMAA segment interactions.

The degree of micellization, N_w, was determined as the ratio of the micellar weight-average molecular weight, measured by LALLS, divided by the weight-average molecular weight of the unimer, which was calculated from the M_w of the nonhydrolyzed copolymers considering that the degree of hydrolysis is 100%. This assumption was verified experimentally by measuring the degree of hydrolysis by ^{1}H-NMR spectroscopy.[29,38] The degree of micellization is larger for the sample with the higher PMAA content, as is normally expected, since THF is a selective solvent for PSt. Nevertheless, the difference in the N_w values for the two copolymers (3.8 and 11.1) is so large that it cannot be explained by the former assumption only. It seems that the number of branches also plays an important role for this behavior in the following sense: the higher the number of grafts, the greater is the tendency to form large micelles. Specifically, the protonated sample has 6.8 PMAA branches per backbone compared to 5.7 branches of the deuterated sample, making the formation of large micelles easier in the former case. The N_w values are generally lower, but of the same order of magnitude, as compared with the micelles formed from the nonhydrolyzed graft copolymers in *tert*-amyl alcohol. Nevertheless, the content of the insoluble component is much higher in the former case. In other words, we need a much higher PMAA content to reach a degree of micellization in THF similar to the one observed in *tert*-amyl alcohol for the nonhydrolyzed samples. This behavior can be explained by the thermodynamic quality of the two solvents for both components. THF is a very good solvent for PSt but not a strong nonsolvent for PMAA, since its dielectric constant ($\epsilon = 7.4$) is not so low as to eliminate polymer–THF interactions. This is an indication that we must have higher PMAA contents to reach the same aggregation numbers, N_w, as with the nonhydrolyzed samples in *tert*-amyl alcohol. This latter solvent seems to be a very bad solvent for the backbone and a very good solvent for the branches.

Munk et al.[39] studied the micelles formed by PSt-*b*-PMAA diblock and PMAA-*b*-PSt-*b*-PMMA triblock copolymers in a mixed solvent composed of 80 vol % dioxane and 20 vol % water. The aggregation numbers found in all cases, including those for samples with compositions similar to the samples used for the present study, were much higher than those determined for the graft copolymers. This is a result of the different topologies of linear and graft copolymers, as has been frequently reported in the literature.

Linear plots were obtained from viscometric measurements (e.g., in Figure 5), reflecting the absence of any possible deformation or dissociation due to the shear forces employed in the viscometry tube and, consequently, the existence of stable micelles, at least for the concentration and shear rate ranges used for the measurements. No indication of the existence of single chains was observed due to the higher concentrations used for viscometric measurements as compared with light scattering measurements. The intrinsic viscosities of the micellar systems were lower than those of the single chains in a good solvent and the Huggins coefficients had very large values. These results, in combination with the increased molecular weights of the micelles, indicate the existence of compact structures with strong hydrodynamic interactions.

Dynamic light scattering was also employed to study the hydrodynamic properties of the micelles. A characteristic plot is given in Figure 6. The plots were linear with negative slopes, meaning that $K_d < 0$. Similar results were also obtained in other studies of micellization or aggregation phenomena[40–42] and are associated with the low A_2 values observed for these systems. The existence of negative K_d values implies the presence of strong intermicellar attractive forces, resulting in small excluded volumes and, consequently, in low A_2 values. The polydispersities of the micelles were rather high, as was indicated by the large μ_2/Γ^2 values (larger than 0.1). Nevertheless, with increasing concentration, lower μ_2/Γ^2 values were obtained. The R_h values were very close to the corresponding R_v values, the ratio R_v/R_h being near unity. Small deviations from unity can be explained either by random experimental errors or by polydispersity of the micelles. This result, in combination with the low [η] values and the increased K_H values, implies that the micelles formed by the hydrolyzed graft copolymers in THF are very compact and behave similarly to hard spheres.

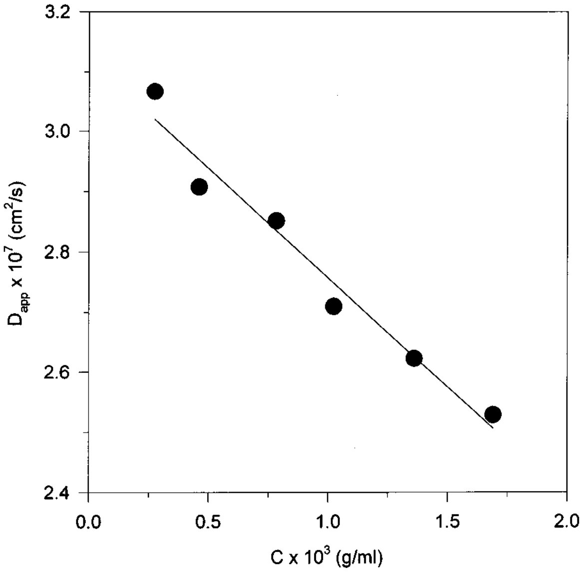

Figure 6. DLS plot for dPSt-*g*-PMAA in THF at 25 °C (θ = 45°).

Conclusions

Graft copolymers having PSt backbones and PtBuMa branches form multimolecular micelles in *tert*-amyl alcohol, which is a selective solvent for the PtBuMA branches. The aggregation numbers were very low for both samples, in comparison with linear diblocks, due to the architectural constraints imposed by the graft architecture and were almost the same despite the fact that the two samples have different contents of the insoluble component. The solubilization of the backbone (core of the micelles) from the branches is responsible for this behavior. The formation of stable micelles is accomplished through the intermediate formation of large and loosely bound aggregates, which can be deformed in the viscometry tube due to the shear forces employed therein, giving rise to the appearance of rather elliptical structures. Graft copolymers with PMAA branches, prepared by the hydrolysis of the *tert*-butyl groups, form micelles in THF, which is a selective solvent for the PSt backbone. The aggregation numbers are also low in this case and depend strongly on the number of the PMAA branches (insoluble component) rather than the PMAA content. Compact structures with strong intermicellar attractive forces exist in THF. They behave hydrodynamically as hard spheres.

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References and Notes

(1) Elias, H.-G. *Int. J. Polym. Mater.* **1976**, *4*, 209.
(2) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 30.
(3) Zhao, J.; Pearce, E. M.; Kwei, T. K.; Jeon, H. S.; Kesani, P. K.; Balsara, N. P. *Macromolecules* **1995**, 28, 1972.
(4) Tuzar, Z.; Kratochvil, P. *Surf. Colloid Sci.* **1993**, *15*, 1.
(5) Mandema, W.; Zeldenrust, H.; Emeis, C. A. *Makromol. Chem.* **1979**, *180*, 1521.
(6) Stejkal, J.; Hlavata, D.; Sikora, A.; Konak, C.; Plestil, J.; Kratochvil, P. *Polymer* **1992**, *33*, 3675.
(7) Liu, G.; Smith, C. K.; Hu, N.; Tao, J. *Macromolecules* **1996**, *29*, 220.
(8) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3276.
(9) Price, C.; McAdam, J. D. G.; Lally, T. P.; Woods, T. P. *Polymer* **1974**, *15*, 228.
(10) Halperin, A. *Macromolecules* **1987**, *20*, 2943.
(11) Bednar, B.; Devaty, J.; Koupalova, B.; Kralicek, J.; Tuzar, Z. *Polymer* **1984**, *25*, 1178.
(12) Yang, Y.-W.; Yang, Z.; Zhou, Z.-K.; Attwood, D.; Booth, C. *Macromolecules* **1996**, *29*, 670.
(13) Raspaud, E.; Lairez, D.; Adam, M.; Carton, J.-P. *Macromolecules* **1994**, *27*, 2956.
(14) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1991**, *24*, 1975.
(15) Canham, P. A.; Lally, T. P.; Price, C.; Stubberfield, R. B. *J. Chem. Soc., Faraday Trans. 1* **1980**, *70*, 1857.
(16) Tuzar, Z.; Stepanek, P.; Konac, C.; Kratochvil, P. J *Colloid Interface Sci.* **1985**, *105*, 372.
(17) ten Brike, G.; Hadziioannou, G. *Macromolecules* **1987**, *20*, 486.
(18) Tuzar, Z.; Kratochvil, P.; Prohazka, K.; Contractor, K.; Hadjichristidis, N. *Macromol. Chem.* **1989**, *190*, 2967.
(19) Price, C.; Woods, D. *Polymer* **1974**, *15*, 389.
(20) Selb, J.; Gallot, Y. *Macromol. Chem.* **1981**, *182*, 1775.
(21) Candau, S.; Guenet, J.-M.; Boutillier, J.; Picot, C. *Polymer* **1979**, *20*, 1227. Candau, S.; Boutillier, J.; Candau, F. *Polymer* **1979**, *20*, 1237.
(22) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 7378.
(23) Prochazka, K.; Glockner, G.; Hoff, M.; Tuzar, Z. *Macromol. Chem.* **1984**, *185*, 1187.
(24) Tsitsilianis, C.; Papanagopoulos, D.; Lutz, P. *Polymer* **1995**, *36*, 3745.
(25) Bayer, U.; Stadler, R. *Macromol. Chem. Phys.* **1994**, *195*, 2709.
(26) Iatrou, H.; Willner, L.; Hadjichristidis, N.; Halperin, A.; Richter, D. *Macromolecules* **1996**, *29*, 581.
(27) Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. Nonlinear Block Copolymers. *Adv. Polym. Sci.*, in press.
(28) Itsuno, S.; Uchikoshi, K.; Ito, K. *J. Am. Chem. Soc.* **1990**, *112*, 8187.
(29) Gettinger, L. C.; Jackson, L. C.; Han, C. C.; Pitsikalis, M.; Mays, J. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (1), 406. Gettinger, C. L.; Chanzy, H.; Jackson, C. L.; Han, C. C.; Pitsikalis, M.; Mays, J. W. *Macromolecules*, submitted for publication.
(30) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(31) Roovers, J.; Martin, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2513.
(32) Bauer, B. J.; Fetters, L. J.; Graessley, W. W.; Hadjichristidis, N.; Quack, G. F. *Macromolecules* **1989**, *22*, 2337.
(33) Dondos, A.; Rempp, P.; Benoit, H. *J. Chem. Phys.* **1965**, *62*, 821.
(34) Dondos, A.; Rempp, P.; Benoit, H. *J. Polym. Sci., Polym Lett. Ed.* **1966**, *4*, 293.
(35) Ulbrich, K.; Konac, C.; Tuzar, Z.; Kepecek, *J. Makromol. Chem.* **1987**, *188*, 1261.
(36) Gallot, Y.; Leng, M.; Benoit, H.; Rempp, P. *J. Chem. Phys.* **1962**, *59*, 1093.
(37) Weill, G.; des Cloizeaux, J. *J. Phys.* **1979**, *40*, 99.
(38) Ramireddy, C.; Tuzar, Z.; Prochazka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992**, *25*, 2541.
(39) Qin, A.; Tian, M.; Ramireddy, C.; Webber, S. E.; Munk, P. *Macromolecules* **1994**, *27*, 120.
(40) Pitsikalis, M.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 179.
(41) Zhou, Z.; Pieffer, D. G.; Chu, B. *Macromolecules* **1994**, *27*, 1428.
(42) Pispas, S.; Allorio, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 2903.

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