

EFFECT OF TOPOLOGY ON THE AQUEOUS SOLUTION BEHAVIOR OF AMPHIPHILIC BLOCK AND GRAFT COPOLYMERS OF n-BUTYL ACRYLATE AND ACRYLIC ACID

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Introduction

Amphiphilic block copolymers with ionizable hydrophilic blocks have structural features of polyelectrolytes, microphase-separated copolymers, and surfactants. In dilute aqueous solutions, they self-assemble into micelles consisting of a dense hydrophobic core and an extended charged corona. These micelles are of interest due to their various potential applications as stabilizers, thickening agents, drug carriers etc. For these applications, an understanding of fundamental parameters such as the critical micelle concentration (cmc), the aggregation number, the micellar shape and stability is required.

Whereas much work has focused on the effect of external conditions on the micellization behavior of amphiphilic ionic block copolymers, such as solvent-polymer interactions, concentration, pH, ionic strength and temperature etc.^{1,2} only few experiments have been reported on study of the effect of the copolymer topology on micellization behavior.² Recent research has revealed that the polymer topology plays an important role in determining micellar properties; even only one graft chain per macromolecule can change considerably the micellar characteristics of complex block copolymers.³ In contrast to block copolymers, amphiphilic graft copolymers with water-soluble side-chains should be able to form unimolecular micelles, where the backbone of one copolymer molecules is stabilized by a corona formed by the hydrophilic side-chains.

Selb and Gallot⁴ studied solutions of polystyrene-*graft*-poly(4-N-ethyl vinylpyridinium bromide), PS-g-P4VPQ, and compared the data to those obtained with the corresponding block copolymers. With increasing water content the authors found micelle formation of the block copolymers whereas only unimers were observed for the graft copolymers. The authors assumed that the side-chains efficiently screen the collapsed backbone and thus keep it in solution in unimeric form. However, since polystyrene forms glassy, "frozen" micellar cores it is not clear whether these unimers are the thermodynamically stable forms in water.

In order to gain a deeper understanding of the parameters that control aggregation in dynamic copolymer micelles, we synthesized a series of graft copolymers with a low T_g , nonpolar backbone, poly(n-butyl acrylate) (PnBA) and a range of poly(acrylic acid) (weak polyacid, PAA) side-chains with different chain length and compositions. As comparison, a series of block copolymers, PnBA-*b*-PAA, with different block lengths and compositions were synthesized. We describe the aggregation behavior of these amphiphilic copolymers in aqueous solution. Our aim is a better understanding of the influences of chain length, topology and pH as well as ionic strength on micelle formation and micellar stability of these copolymers.

Experimental

Materials. The graft copolymers were synthesized via atom transfer radical copolymerization (ATRP) of nBA with PtBA macromonomers.⁵ The block copolymers were made by ATRP of tBA, initiated with PnBA macroinitiators.⁶ CuBr/PMDEATA was used as catalyst in acetone at 40-60 °C. The *tert*-butyl groups of the PtBA segments were hydrolyzed by HCl in dioxane at 80 °C to form poly(acrylic acid). The graft copolymers are designated as nBA_x-g-(AA_y)_z, where x and y are number-average degrees of polymerization and z is the average number of grafts per backbone.

Methods and Instrumentation. Steady-state fluorescence spectra of the air-equilibrated solutions were recorded with a Hitachi F-4000 fluorescence spectrophotometer. Small-angle neutron scattering (SANS) measurements were performed with the instrument D11 of the ILL (Grenoble, France) with a neutron wavelength $\lambda = 6 \text{ \AA}$ at sample-to-detector distances of 1.1, 4, and 16 m. For the unimolecular micelles or unimers, the Debye scattering function for Gaussian coils was used for fitting the scattering curves. For micellar aggrega-

tes, a model of polydisperse spheres was employed, assuming that the scattering intensity is mainly coming from the core.⁶ Dynamic light scattering (DLS) measurements were carried out with an ALV DLS/SLS-SP 5022F equipment which consists of an ALV-SP 125 laser goniometer, an ALV 500/E correlator, and a He-Ne laser with wavelength $\lambda = 632.8 \text{ nm}$.

Results and Discussion

Critical Micelle Concentration, cmc. A study of the cmc of the block and graft copolymers was carried out using tensiometry and fluorescence spectroscopy. The aggregation behavior as a function of the architecture of the copolymers and external conditions, e.g. pH and ionic strength, was investigated by dynamic light scattering (DLS) and small angle neutron scattering (SANS).

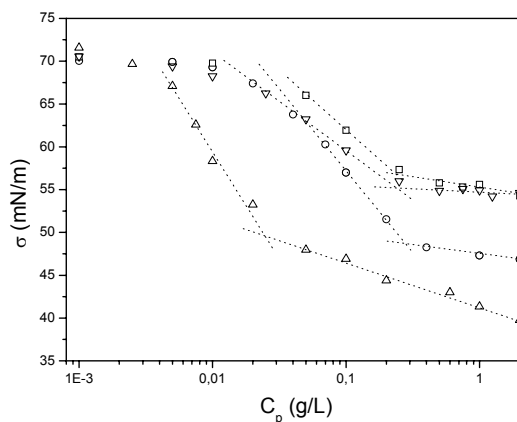


Figure 1. Concentration dependence of the surface tension of aqueous solutions of nBA₁₃₈-g-(AA₈₅)_{2.0} graft copolymer at (Δ) pH 5, cmc = 0.024 g/L; (○) pH 7, (▽) pH 8, (□) pH 10, cmc = 0.24-0.28 g/L.

Both tensiometric (Fig. 1) and fluorometric data show the graft copolymers have a rather high cmc, which depends on pH, it strongly decreases for pH < 6, when the ionization of the acrylic acid side chains decreases. This points to the fact that the micelles are dynamic rather than static in nature.

Dynamic Light Scattering, DLS. The DLS data in Fig. 2 confirm the cmc results: polymolecular micelles are only formed for pH < 7. The hydrodynamic radius of the micelles strongly depends on pH and on the fraction of acrylic acid in the copolymer. Table 1 shows that aggregation increases as the ionic strength is increased. Due to the shielding of the ionic charges the micelles can accommodate more polymer chains. However, even at 1 M NaCl there is no micelle formation at pH 8.

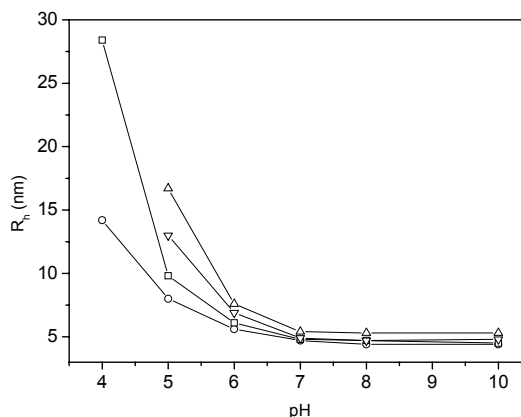


Figure 2. pH dependence of the hydrodynamic radius for 1.0 g/L of (○) nBA₁₃₈-g-(AA₈₅)_{2.0}; (□) nBA₁₁₈-g-(AA₂₀)_{4.3}; (▽) nBA₂₂₄-g-(AA₂₀)_{4.1} (precipitates at pH 4) (Δ) nBA₁₆₇-g-(AA₂₀)_{1.7} (precipitates at pH 4) in 0.1 M NaCl aqueous solutions at 25 °C. The fraction of AA segments increases in this order.

Table 1. Effect of Ionic Strength on the Hydrodynamic Radius and its Distribution of a 1 g/L Aqueous Solution of nBA₂₂₄-g-(AA₂₀)_{4,1}.

c _{NaCl} (mol/L)	0.0	0.1	0.2	0.5	1.0
R _h (nm), pH 5	8.6	11.6	12.8	23.5	precipitate
PDI (μ ₂ /Γ ²)	0.07	0.05	0.05	0.07	precipitate
R _h (nm), pH 8	-	4.2	4.1	4.5	4.8
PDI (μ ₂ /Γ ²)	-	0.63	0.55	0.66	0.58

Small-Angle Neutron Scattering (SANS). First, we investigated the graft copolymers in aqueous solutions at concentration higher than cmc in the presence of 0.17 M NaCl. As an example, the SANS curves for nBA₁₁₁-g-(AA₃₇)₁₀ are given in Fig. 3. For the solutions at pH = 8 or 10 the scattering intensity is very low and can only be explained by the presence of unimers. Some increase of the scattering intensity for $q < 0.02 \text{ \AA}^{-1}$ is observed. It is presumably due to the presence of much larger species, which were also observed by DLS and FF-TEM, as seen further below. For pH = 6 a higher scattering intensity is observed, indicating the onset of aggregation. However, only at pH = 4 a much larger scattering from compact micellar aggregates is observed.

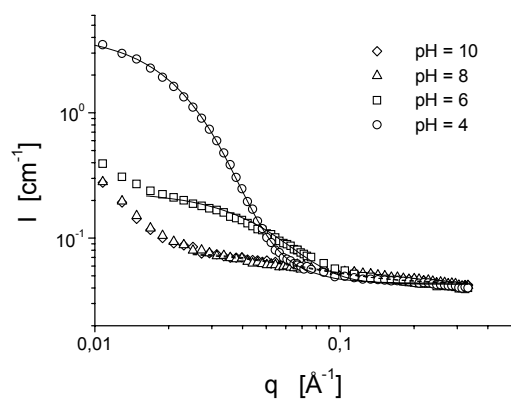


Figure 3. SANS intensity as a function of the scattering vector q for 2 g/L solutions of nBA₁₁₁-g-(AA₃₇)₁₀ in 0.17 M NaCl/D₂O and at different solution pH. Fitted curves for the Gaussian coil (□) and the model of polydisperse spheres (○) are given.

The scattering curves at pH = 8 and pH = 10 are for all graft copolymers very similar and are well described by the Gaussian coil model with radii of gyration $R_g = 2.1\text{-}3.2 \text{ nm}$. This and especially the scattering intensity indicate that under these conditions the copolymer is present as single molecule, i. e. unimer. In contrast to that, the scattering curves for pH 4 and 6 are fitted well by the model of polydisperse spheres and the results are summarized in Table 7. The q -range above 0.02 \AA^{-1} is largely dominated by the scattering from the core of the micelles, thus the size and the molecular weight of the core were extracted from these data. We observed good agreement between the values for the aggregation numbers obtained via the intensity extrapolated to $q = 0$, $N_{agg}(I_0)$, and fitting the core radius and calculation of $N_{agg}(R_{core})$ assuming the bulk density of PnBA.

Investigation of a series where we systematically varied the number and the length of the hydrophilic PAA side chains as well as the composition of the copolymers again confirm the cmc and DLS results. In general, relatively large micellar aggregates are observed only in acidic solution, while unimers are observed in basic solution. Moreover, the onset of aggregation shifts towards lower pH with increasing relative content of the hydrophilic PAA block, as to be expected.

SANS results of the block copolymer solutions show that the onset of aggregation of the block copolymers occurred at a pH approximately 1 to 1.5 units higher than that of the corresponding graft copolymers with similar fraction of hydrophilic segments. This indicates that the architecture of the copolymer molecules has a significant influence on its aggregation properties in aqueous solution and the block copolymers have a stronger tendency for aggregation than the corresponding graft copolymers. Moreover, block copolymers show significantly higher aggregation numbers, N_{agg} , than graft copolymers of similar acrylic acid content, as is seen in Fig. 4. The reason for

that is twofold. Firstly the block copolymers due to their more pronounced amphiphilic structure have a more pronounced tendency for aggregation, which results in micelle formation at relatively higher pH. Secondly they are structurally less constrained than their graft copolymer counterparts, and thus are able to form much larger micellar cores, which explains the significantly larger aggregation numbers.

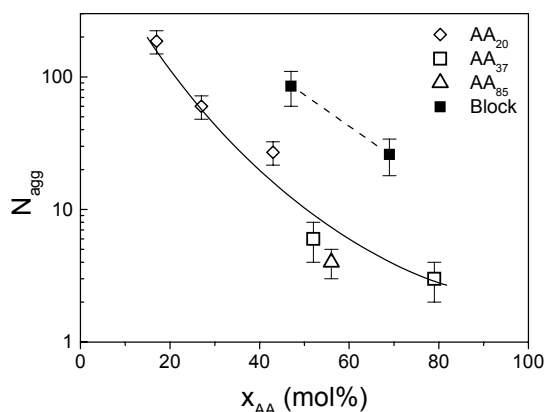


Figure 4. Aggregation number as a function of the fraction of AA units in the copolymers at pH = 5 for various graft and diblock copolymers at $c = 2 \text{ g/L}$ in 0.1 M NaCl/D₂O solutions at 25°C.

Conclusions

The combined results of tensiometry, fluorometry, DLS, and SANS give information on the aqueous solution properties of a wide range of amphiphilic block and graft copolymers of nBA and AA. The critical micelle concentration (cmc), the micellar size as well as the aggregation number strongly depend on the fraction of AA units, pH, and topology. At $\text{pH} > 6$ the polymers have high cmc values ($> 0.1 \text{ g/L}$) and predominantly form unimolecular micelles with PnBA core and PAA corona. With decreasing pH, cmc values decrease and micelles are formed with the aggregation number and the hydrodynamic radii increasing with decreasing pH and AA content. Above cmc, graft copolymers form micelles with significantly lower aggregation numbers than block copolymers of the same composition. A more detailed study of these systems can be found elsewhere.⁶

Acknowledgements. This research was supported by the Marie Curie Research Training Network POLYAMPHI, the Deutsche Forschungsgemeinschaft, and Rohm and Haas Co., Philadelphia, PA. We thank O. Borisov (CEA Grenoble) for discussions and J. Zipfel and P. Lindner (ILL, Grenoble, France) for the help with the SANS measurements and J. Liu for help with the surface tension measurements.

References

- (1) Förster, S.; Plantenberg, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 688; Zhang, L.; Barlow, R. J.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6055;
- (2) Förster, S.; Abetz, V.; Müller, A.H.E. *Adv. Polym. Sci.* **2004**, *166*, 173
- (3) Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. *Macromolecules* **2000**, *33*, 1741; Yun, J.; Faust, R.; Szilágyi, L. S.; Kéki, S.; Zsuga, M. *Macromolecules*, **2003**, *36*, 1717; Cai, Y.; Burguiere, C.; Armes, S. P. *Chem. Commun.* **2004**, 802-803
- (4) Selb, J.; Gallot, Y. *Polymer* **1979** *20*, 1273; Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 1775
- (5) Schön, F.; Hartenstein, M.; Müller, A. H. E. *Macromolecules* **2001**, *34*, 5394; Hartenstein, M.; Cai, Y.; Müller, A. H. E. submitted to *Macromolecules*
- (6) Cai, Y.; Hartenstein, M.; Gradzielski, M.; Zhang, M.; Mori, H.; Pergushov, D. V.; Zipfel, J.; Lindner, P.; Borisov, O.; Müller, A. H. E. submitted to *Macromolecules*