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AGGREGATION BEHAVIOR AND MULTIPLE MORPHOLOGIES OF HIGHLY ASYMMETRIC BLOCK COPOLYMERS OF STYRENE AND 5-(N, N-DIETHYLAMINO)ISOPRENE.



Izabel Cristina Riegel^{1,2*}, *Cesar Liberato Petzhold*¹, *Dimitrios Samios*¹ and *Adi Eisenberg*².

(1) Institute of Chemistry, Federal University of Rio Grande do Sul,
Av. Bento Gonçalves, 9500 CP 15003, Porto Alegre, RS, 91501-970, Brazil (2) Department of Chemistry, McGill
University
801 Sherbrooke Street West, Montreal, QC, H3A 2K6, Canada
e-mail: iriegel@bravo436.chem.mcgill.ca

The aggregation behavior of highly asymmetric aminofunctionalized di and triblock copolymers consisting of styrene and 5-(N,N-diethylamino)isoprene was studied. Copolymers having approximately the same composition, but of two different molecular weights were investigated in solutions of 1,4-dioxane, as the common solvent, and water. The critical water concentration (cwc), i.e., the water content at which the aggregation starts, was monitored via turbidity measurements. The cwc depends on many factors: the initial copolymer concentration, the copolymer molecular weight and the copolymers structural properties (di or triblock). It increases with decreasing initial concentration and molecular weight of the copolymer. The resulting morphologies are also influenced by these factors. So far, spheres, compound micelles, vesicles and a new morphology, consisting of bowl-shaped structures, were identified by transmission electron microscopy.

Introduction

A new class of polar monomers containing aliphatic tertiary amino groups was developed, known as 5-(N,N-dialkylamino)isoprenes¹. As a diene they can be polymerized anionically.

The polymerization behavior of these aminofunctionalized monomers as well as the structure and properties of the resulting homopolymers have been investigated², however few studies on their copolymerization were reported.

Through anionic copolymerization of 5-(N,N-diethylamino)isoprene and a non polar monomer as styrene, amphiphilic block copolymers with special architectures and defined molecular weight distribution can be obtained. Moreover, a positive charged ionic block is obtained by quaternization of the tertiary amino group. These quaternized species show interesting solution behavior suggesting applications in catalysis and as drug delivery systems.

It is widely known that amphiphiles can self-assemble into a large variety of microstructures in selective solvents that are good for one and poor for the other block.

Crew-cut micelle-like aggregates³ represent a new type of aggregate formed in solution by the self-assembly of

highly asymmetric amphiphilic block copolymers. The aggregates are termed crew-cut because the dimensions of the core are bigger than those of the corona. They are prepared by first dissolving the copolymer in a common solvent for both blocks and then adding water (precipitant) to the solution to induce aggregation of the hydrophobic segments. As the addition of water progresses, the quality of the solvent for the long block (polystyrene) gradually decreases. The micelization of the hydrophobic segments starts when the water content reaches a critical point (cwc). The common solvent is removed from the aggregates by dialyzing the colloidal solution against water.

One of the noteworthy phenomena seen in the crew cut aggregate system is the existence of multiple morphologies. These include spheres, rods, vesicles, lamellae and several other structures⁴.

Crew-cut micelle-like aggregates of polystyrene-*b*-poly(acrylic acid) diblock copolymers (PS-*b*-PAA), which in aqueous solution form anionic micelles, have been extensively studied by Eisenberg and co-workers⁵. It has been found that the morphologies are influenced by many variables, i.e., the composition of the block copolymer, the copolymer concentration, the type of the common solvent, the type and concentration of added ions, and others.

This study focuses on the investigation of the aggregation behavior of quaternized diblock (PS-b-PAI) and triblock (PAI-b-PS-b-PAI) copolymers of styrene and 5-(N,N-diethylamino)isoprene by turbidity measurements. The resulting morphologies were identified by transmission electron microscopy. Since these studies have started only recently, the cationic copolymers have not been investigated as extensively as the anionic PS-b-PAA systems⁶.

Experimental

Polymer Samples

The synthesis of the copolymers was described elsewhere⁶. Two sets of copolymers with different molecular weights but with approximately the same composition were investigated. The materials are summarized in Table 1. After synthesis they were quaternized according to recommended procedures² in order to obtain positively charged block copolymers.

Table 1. Molecular characteristics of diblock (PAI-b-PS) and triblock (PAI-b-PS-b-PAI) copolymers of styrene and 5-(N,N-diethylamino)isoprene.

| Copolymers ^a | PAI ^b (mol%) | Mn (g/mol) ^c | Mw/Mn ^c |
|---|----------------------------|----------------------------|--------------------|
| PAI ₁₀ -b-PS ₂₆₇ | 4.4 | 26,800 | 1.39 |
| PAI ₁₀ -b-PS ₂₆₇ -b-PAI ₁₀ | 8.8 | 20,900 | 1.19 |
| PAI ₆ -b-PS ₁₂₀ | 4.9 | 13,900 | 1.20 |
| PAI ₆ -b-PS ₁₂₀ -b-PAI ₄ | 8.3 | 13,600 | 1.18 |

^a The numbers indicate the number average degrees of polymerization of each block;

^b The PAI content was determined by NMR relative to that of the PS block;

^c Parameters determined by SEC.

Turbidity Experiments

The experiments were performed on a Varian-Cary 50 UV spectrophotometer, at a wavelength of 700 nm. The solvents used were dried according to recommended procedures. Samples were prepared by first dissolving the quaternized copolymers in dioxane. The solutions were stirred overnight. Deionized water (Milli Q) was added to the solutions with a microsyringe at a rate of one drop every 10s until the desired concentration. The turbidity values were followed during 15 to 30 min after each water addition and mixing of the solutions. Measurements were performed until the water content reached ca. 30 wt %, i.e. well after aggregation occurred.

Transmission Electron Microscopy

The experiments were carried out on a JEM2000-FX microscope operating at 80 kV. Following the turbidity experiments the resulting colloidal solutions (ca. 30 wt % water) were dialyzed against deionized water for 3 days to remove the organic solvent. Aqueous aggregate solutions free of organic solvents were used to prepare the TEM samples. A drop of the dilute solution was placed onto copper grids pre-coated with Formvar and carbon.

Results and conclusions

As water is added to the initial solution, the quality of the solvent decreases for the polystyrene block. When the water content reaches a critical value the hydrophobic segments aggregate and the solution undergoes microphase separation. This critical value is defined as the critical water content (cwc). The start of the micelization can be observed by an increase in the turbidity of the solution. Figure 1 shows a plot of cwc versus the logarithm of the initial copolymer concentration for the different copolymers.

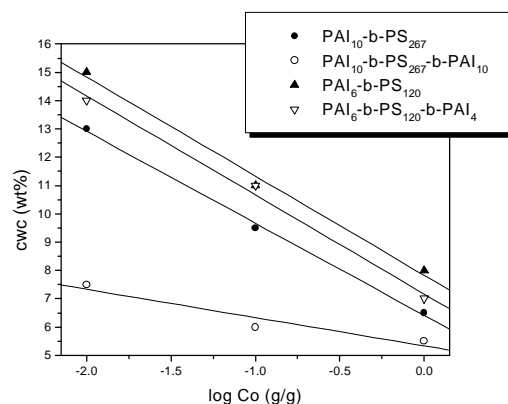


Figure 1. Critical water concentration as a function of the logarithmic of the initial copolymer concentration for solutions in 1,4-dioxane.

The cwc decreases with the increasing molecular weight and initial concentration. It can also be observed that it is dependent on structural properties of the copolymer (di or triblock). After each water jump, the increase in the turbidity of the solution was monitored as a function of time in order to follow the process of aggregation, and as a guarantee that the morphology changes have stopped before the next water addition (Figures 2 and 3).

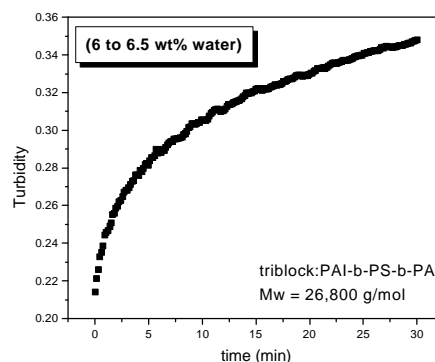


Figure 2. Turbidity versus time for 0.1 wt% copolymer/1,4-dioxane solutions. PAI₁₀-b-PS₂₆₇-b-PAI₁₀

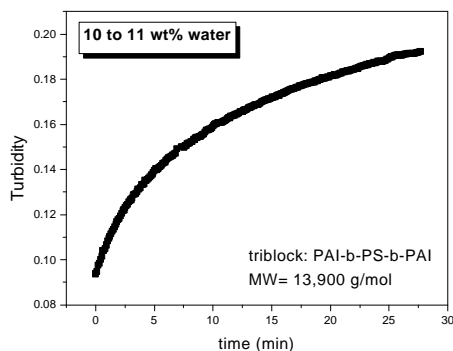


Figure 3. Turbidity versus time for 0.1 wt% copolymer/1,4-dioxane solutions. PAI₅-b-PS₁₂₀-b-PAI₄

At the cwc and in a range from 2 to 3 wt% water above this value, the increase in the turbidity proceeded for about 30 min. After that, i.e., at water contents of cwc+3 wt% water and higher, the morphological changes took c.a. 10 min to be completed for both di and triblock copolymers.

The morphologies of the aggregates were also studied as a function of the initial copolymer concentration and the copolymers molecular weigh; it was found that they are influenced by these factors, as is exemplified in Figures 4 and 5. Spheres, compound micelles, vesicles and a new morphology, consisting of bowl-shaped

structures, were identified by transmission electron microscopy. It is important to mention that the new morphology was found only in the triblock copolymers systems (Figure 5a).

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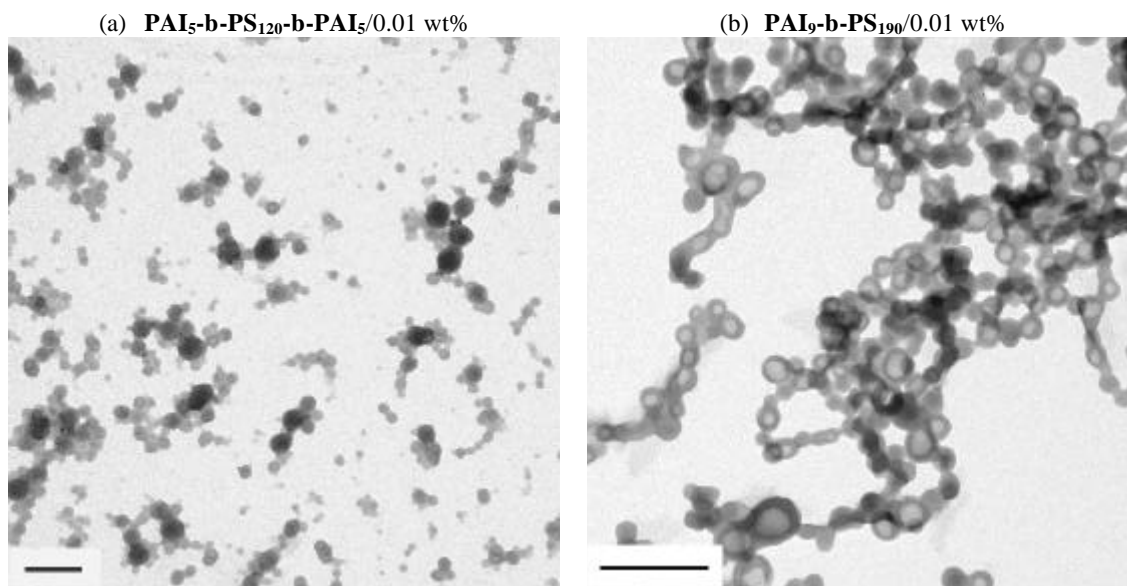


Figure 4. Morphologies for the indicated copolymers in solution. The scale bars are equivalent to (a) 200 nm and (b) 500 nm. The initial copolymer concentration is 0.01 wt%.

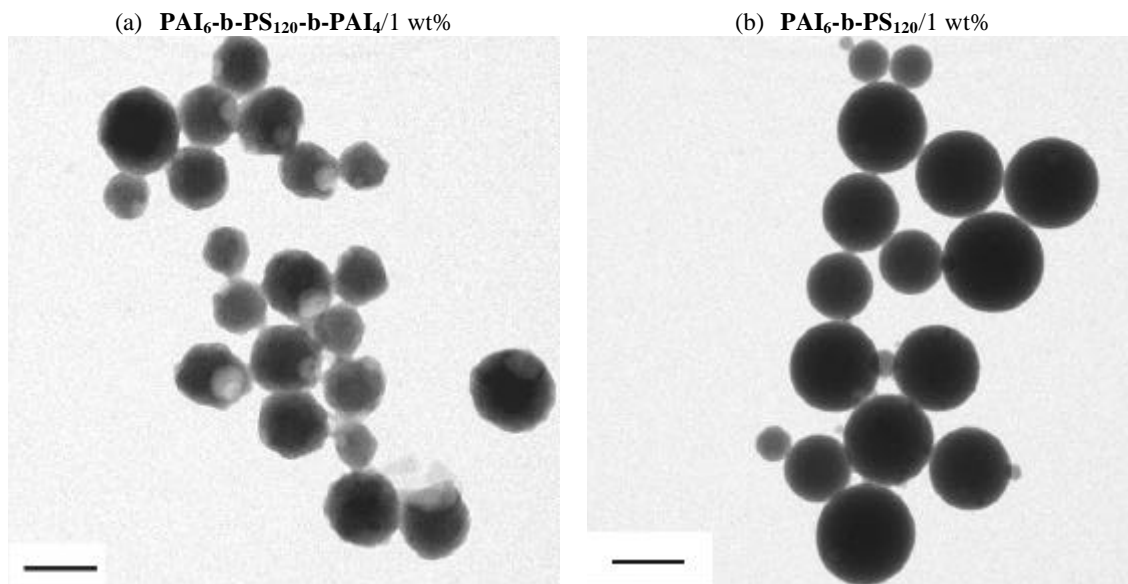


Figure 5. Morphologies for the indicated copolymers in aqueous solution solution after dialysis. The scale bars are equivalent to (a) 200 nm and (b) 500 nm. The initial copolymer concentration is 1 wt%.