VIP Toroidal Micelles

DOI: 10.1002/anie.200900533

Toroidal Micelles of Uniform Size from Diblock Copolymers**

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Block copolymers can spontaneously self-assemble in a selective solvent to form micelles of various morphologies, such as spherical micelles, cylindrical micelles, and vesicles.[1–3] Recent studies have expanded the variety of micellar shapes to unconventional forms that include toroids,[4–11] tubes,[12] disks,[13] helices,[14] Janus micelles,[15] and other complex forms.[16,17] The toroid (donut or ring-shaped) structure is the focus herein because of the difficulty in achieving uniformity in size despite the simplicity in shape. Practically all the ring-shaped micelles reported to date are the ring-closure products of rod-shaped micelles, which coexist with the precursor micelles, and thus a broad size distribution cannot be avoided. For example, Pochan, Wooley, and co-workers observed a dominant toroidal morphology in an amphiphilic poly(acrylic acid)-*block*-poly(methyl acrylate)-*block*-polystyrene ABC triblock copolymer upon addition of a divalent organic counterion.[4] Zhu et al. reported the slow evolution of ring-shaped micelles from rod-shaped micelles in an aqueous solution of a poly(4-vinyl pyridine)-*block*-polystyrene-*block*-poly(4-vinyl pyridine) ABA triblock copolymer.[5] Owing to the bending energy penalty, the ring-closure assembly of rods is in general energetically less favorable. Therefore, the formation of the toroidal micelles is restricted to a few specific systems, and a pure toroidal micelle of uniform size has not been realized.

Recently, He and Schmid reported that micelles of unique shape could be formed by a different pathway from the conventional route.[18] In contrast to the conventional micelle coalescence pathway, they suggested a growth pathway by computer simulation to form toroidal micelles. Herein, we report on the first observation to our knowledge of pure toroidal micelles of highly uniform in shape and size.

The ring-shaped micelles were derived from polyisoprene-*block*-poly(2-vinylpyridine) (PI-*b*-P2VP) diblock copolymer in a THF/ethanol solvent mixture. The PI_{1100}-*b*-$P2VP_{220}$ copolymer, where the number in subscripts stands for the number average degree of polymerization of each block, has a narrow molecular-weight distribution, as shown by a polydispersity index of 1.04. The block copolymer was first dissolved in THF, which is a good solvent for both blocks. Ethanol, a selective solvent for P2VP block, was then added slowly to the solution under mild stirring until the desired volume ratio of THF to ethanol was reached (see Supporting Information for details). As the ethanol was added, the solvent quality for the PI block gradually becomes poor, and PI blocks aggregate to form crew-cut micelles with a core of PI block and a corona of P2VP block. The structure characterization of the micelles was carried out by atomic force microscopy (AFM), transmission electron microscopy (TEM), and light-scattering experiments.

Figure 1 shows the AFM and TEM images of the micelles spin-coated on carbon-coated mica from 20:80 v/v THF/ethanol mixed solvent. The initial block copolymer concentration in THF was 1 $mg\,mL^{-1}$ and the final concentration was 0.2 $mg\,mL^{-1}$ after the addition of ethanol. As shown in Figure 1 a–d, both the TEM and AFM height images show exclusively ring-shaped micelles that are highly uniform in shape and size. The average diameter $2R$ of the toroid determined from the peak-to-peak distance in Figure 1 e is (70 ± 3) nm, and the ring width $2r$ is (27 ± 3) nm. The height of the toroidal ring (2–3 nm, Figure 1 e) is much smaller than the ring width from the TEM or AFM images. This discrepancy between the apparent height and the ring width would in part arise from the deformation of the soft PI core. Such low-modulus materials are known to not reflect the correct height in the AFM measurements.[19] This structure is clearly different from the collapsed vesicle structure, which usually appears to have a lighter center and a darker periphery in the AFM or TEM image.[1] Both AFM and TEM results for the toroidal micelles show that the inside and outside of the rings have the same contrast.

Notwithstanding the visual evidence of the ring structure of the micelles, there remains a concern as to whether this structure indeed exists in solution or it is formed during the spin-coating and drying process. To resolve the issue, the micelles in 20:80 v/v THF/ethanol solution were characterized by dynamic and static light scattering experiments. The time autocorrelation function obtained from the dynamic light-scattering experiments was analyzed by fitting to the second-order cumulant decay function.[20] Figure 2 a shows the plot of the first cumulant (average decay time constant Γ) of the autocorrelation function versus the square of the scattering vector q^2. A high degree of linearity in the Γ vs. q^2 plot confirms that the fluctuation of the scattered light was caused by the translational diffusion of the micelles. The diffusion constant was determined according to the relationship $D = \Gamma/q^2$. The hydrodynamic radius was obtained by the Stokes–Einstein equation, namely $R_h = kT/6\pi\eta D$, as 36.5 nm. The ratio of the second cumulant to the square of the first cumulant, μ_2/Γ^2, represents the polydispersity of the system. For a monodisperse system, $\mu_2 = 0$, and the autocorrelation

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[**] *Published on the occasion of the 25th anniversary of the Max Planck Institute for Polymer Research, Mainz.*
This work was supported by NRL (R0A-2007-000-20125-0), SRC (R11-2008-052-03002-0), and WCU (R31-2008-000-10059-0) programs.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900533.

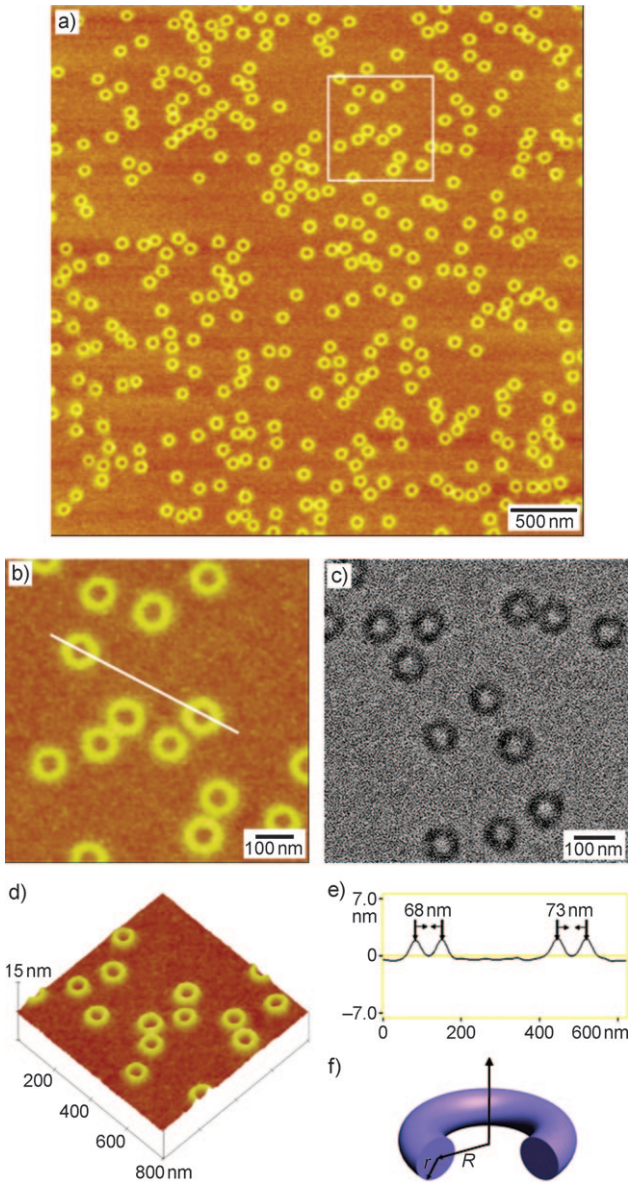

Figure 1. a) AFM height image of the ring-shaped micelles spin-coated on carbon-coated mica from the 20:80 v/v THF/ethanol solvent mixture. The diblock polymer concentration is 0.2 mg mL^{-1}. b) Magnified image of the boxed area in (a). c) Corresponding TEM image after staining by O_5O_4. d) 3D height image of (b). e) Cross-sectional height profile along the white line in (b). f) Geometric parameters of a toroid.

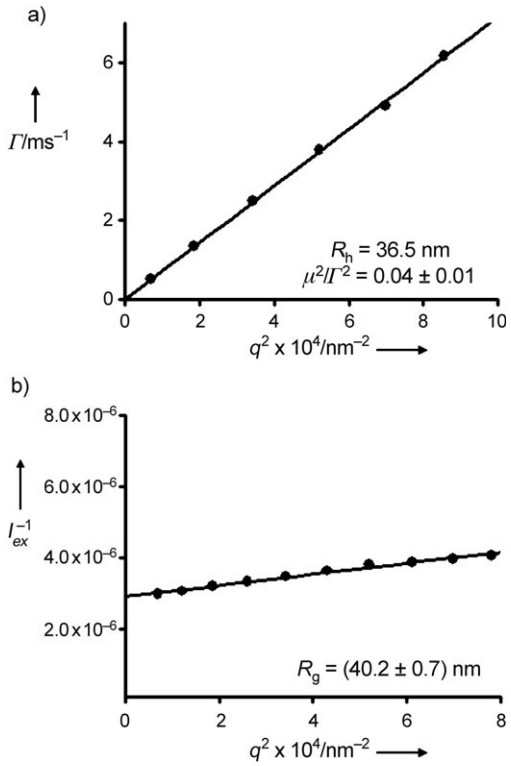

Figure 2. a) Dependence of the decay rate Γ of the autocorrelation function on the square of scattering vector q^2, as measured by dynamic light scattering. b) Partial Zimm plot for the toroidal micelles.

function becomes a single-exponential decay. The small value of μ_2/Γ^2, namely 0.04 ± 0.01, reflects the high uniformity of the micelles.

Figure 2b shows the angular dependency of the excess scattering intensity I_{ex} measured by static light scattering. The plot of $1/I_{ex}$ versus q^2 also shows a good linear relationship, and the radius of gyration (R_g) of the micelles was calculated from the slope of the partial Zimm plot, [21] namely $1/I_{ex}(q) \approx (1 + R_g^2 q^2/3)$, as (40.2 ± 0.7) nm. The parameter R_g of a toroid (Figure 1 f) is a function of the radius (R) and the ring width ($2r$), namely $R_g = R(1+3/4Z^2)^{1/2}$, where $Z = R/r$. Taking R as 35 nm and $2r$ as 27 nm from the AFM measurements, $Z = 2.6$, which gives a value for R_g of 37 nm. The discrepancy from the measured R_g value could be attributed in part to the fact that the ring-shaped micelle does not have the simple toroidal structure illustrated in Figure 1 f, but rather a core–shell-like ring structure with a PI core and a P2VP corona. Furthermore, the micelle dimension in the dried state as measured by AFM may deviate a little from the value in the solution.

Another parameter that is sensitive to the structure of the micelles is the ratio R_g/R_h ($R_g/R_h = 0.77$ for a sphere, and 1.00 for a spherical shell). As there have been few reports on the R_g/R_h value of toroids, we tried to calculate the R_g/R_h value for toroidal objects. The friction constant $f = 6\pi\eta R\theta(Z)$ of a toroidal structure is also a function of R and Z. The parameter $\theta(Z)$ is a complex geometric function of Z, which can be calculated numerically.[22] Again, taking $Z = 2.6$ from the AFM data, the following can be obtained: $\theta(Z) = 1.05$, and the R_g/R_h value of the toroidal object, $(1 + 3/4Z^2)^{1/2}/\theta(Z) = 1.06$, which is favorably compared with the experimentally measured value, $R_g/R_h = 40.2$ nm/36.5 nm $= 1.1$. If we use the R_g value calculated from the AFM measurement (37 nm), the R_g/R_h value becomes 1. Considering the limitations in the precise determination of the micelle dimension, the agreement between the measured and calculated R_g and R_g/R_h values appears to be satisfactory and can be taken as further evidence for the toroidal shape of the micelles.

Another possible structure which has $R_g/R_h \approx 1$ is the vesicle. Although the AFM and TEM images (Figure 1 a–d) indicate convincingly that the micelles are toroids not vesicles, it was further confirmed by growing gold nanoparticles using

the micelles as a template. In ethanol-rich solvents, P2VP blocks constitute the corona decorating the outer surface of the micelle, which can complex with various metal precursors. If the donut-shaped structure observed in the dried state is a collapsed vesicle, the gold particles should be distributed evenly at the centre of the circle, whereas the toroidal micelles would host the gold particles exclusively along the periphery of the circle. For this purpose, the micelles in a 20:80 v/v THF/ethanol solvent mixture (the initial polymer concentration in THF is $1\,mg\,mL^{-1}$) were first dialyzed against pure ethanol to remove THF. This procedure was used to match the solvent with the other chemical reagents used for the formation of gold nanoparticles. The dialysis process does not affect the structure of the donut-shaped micelles, and the micelle size remains unchanged (see the Supporting Information, Figure S1). $HAuCl_4$ (0.2 equiv relative to the 2-vinylpyridine moiety) in ethanol was added to the dialyzed micelle solution, and after 24 h incubation, the gold ions bound to the micelles were reduced with $NaBH_4$.[23] As seen in Figure 3 and the insets showing a enlarged view of single micelles, the gold nanoparticles are exclusively located along the toroidal ring, thus maintaining the structural integrity of the micellar shape. The gold nanoparticles are uniform, with a diameter of (10 ± 2) nm, as determined from the TEM measurement (left inset in Figure 3 right).

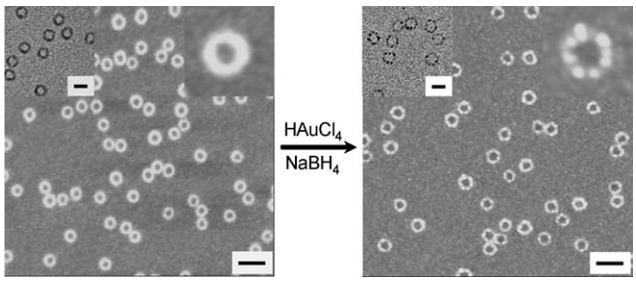

Figure 3. AFM height images of toroidal micelles before (left) and after (right) the preparation of gold nanoparticles. Left insets: TEM image stained by O_5O_4; right insets: enlarged AFM height image of a toroidal micelle. Scale bars: large images, 200 nm; insets, 100 nm.

The exclusive accumulation of gold nanoparticles along the ring is unequivocal evidence of the toroidal shape of the micelles. Furthermore, these donut-shaped micelles are very stable and the micellization process is reproducible. They can retain their structure in solution over several months and appear to be a thermodynamically stable structure. Although nanoring formation has been carried out on a diverse set of materials[24] and by various methods,[25] such a highly uniform ring-shaped object has, to the best of our knowledge, never been realized by a self-assembly process.

The mechanism of formation of ring-like micelles has been understood to date as a process of intra- or intermicellar coalescence.[26] In this system, however, only ring-shaped micelles were found during the addition of ethanol (see the Supporting Information, Figure S2), which indicates that the formation of the toroidal micelles follows a totally different path from the conventional one. We believe that the ring-shaped micelles might have formed according to the pathway suggested by He and Schmid.[18] In this new mechanism, toroidal micelles can spontaneously form in the homogeneous solution by the nucleation and growth mechanism in which the spherical micelles first grow into small disks, a hole then nucleates at the center of the disks, and they then eventually evolve into rings. The authors predicted that the minimization of bending energy favors a uniform size distribution of ring micelles, which is consistent with the very narrow size distribution of the toroidal micelles found herein. Although it remains to be elucidated further, we suspect that the low glass transition temperature of the core-forming PI block would allow the micelles to reorganize readily in response to the environmental changes and enable the unique micellar structure to be attained. We have attempted using polystyrene-*b*-poly(2-vinylpyridine), which has a similar composition, but it did not form toroidal micelles.

In summary, we have successfully obtained donut-shaped micelles of highly uniform shape and size from PI_{1100}-*b*-$P2VP_{220}$ diblock copolymer in a selective solvent for P2VP. The micelles are stable enough to be used as a template to grow gold nanoparticles along the ring. Apart from the scientific interest, the nanosized toroidal objects have great potential for practical applications.[27] By virtue of the stable and well-defined structure, the donut-shaped micelles reported herein would be able to serve as a model system to study their properties, as well as being a promising candidate for a nanotemplate in the evolving field of nanoscience and nanotechnology.

Received: January 28, 2009
Published online: April 28, 2009

Keywords: block copolymers · micelles · nanoparticles · self-assembly · toroids

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