4548 *Macromolecules* **2005,** *38,* 4548−4550

Polymerization of Spherical Poly(styrene-*b*-4-vinylpyridine) Vesicles to Giant Tubes

Lichao Gao, Linqi Shi,* Wangqing Zhang, Yingli An, Zhen Liu, Guiying Li, and Qingbin Meng

Institute of Polymer Chemistry, N&T Joint Academy, Nankai University, Tianjin 300071, China

Received January 25, 2005

Revised Manuscript Received April 7, 2005

Bilayer-structured vesicles have attracted much attention because of their unique ability to encapsulate a selected solution volume and the potential applications of this phenomenon in pharmacology.[1] Additionally, vesicles are considered as good models for understanding properties of cell and organelle membranes with closed bilayer structures.[2] Most interesting is the recent discovery of the structure transition between vesicles and micelles; the transition affects rheological properities of surfactant solutions, although the mechanism of the transition has not been depicted by any theory. Mendes et al.[3] showed the flow-induced transition of vesicles to threadlike micelles of the surfactant cetyltrimethylammonium 3-hydroxynaphthalene-2-carboxylate using small-angle neutron scattering. Danino et al.[4] imaged the structural transition from micelles to bilayers induced by flow as samples of hexadecylpyridinium chlorate and sodium chlorate solutions were being prepared for direct imaging cyrogenic-temperature transmission electron microscopy. The vesicular morphology has also been successfully modified by a cosurfactant,[5] by pH,[6] and by light.[7] Each of these transitions has been achieved by spontaneously varying the curvature or by modifying the area/volume ratio of the thin and soft membrane.[8]

The studies mentioned above centered on the transition between the vesicles and micelles. The transition from spherical vesicles to giant tubular vesicles has not been reported. In this communication, we report the transition from vesicle to giant tubes by heating the deposited PS_{80}-*b*-$P4VP_{110}$ vesicles on substrate. To the best of our knowledge, this is the first report that discusses the transition from vesicles to giant tubes, bringing further insight into the behavior of polymeric vesicles.

The amphiphilic block copolymer PS_{80}-*b*-$P4VP_{110}$ (PDI = 1.27) was synthesized via atom transfer radical polymerization (ATRP).[9] The block copolymer was first dissolved in CH_2Cl_2 to prepare a 2.0 mg/mL solution. Subsequently, 50 mL of 2-propanol was slowly added to 5.0 mL of the block copolymer solution with stirring. The formation of vesicles, as indicated by the appearance of turbidity in the polymer solution, typically occurred when the content of 2-propanol in the solution reached 5 vol %. The vesicular solution was allowed to sit overnight and then heated in a thermostatically controlled bath at 42 °C for 9 h to remove the CH_2Cl_2 (some of the 2-propanol evaporated during this time). The appropriate volume of 2-propanol was added to the vesicular solution to bring the polymer concentration to 0.20 mg/mL.

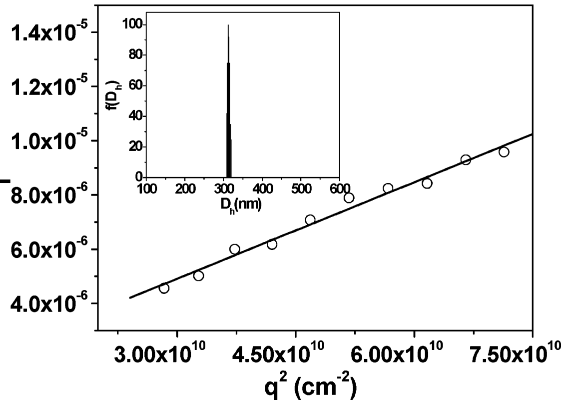

Figure 1. Zimm plot of the vesicular solution at 25 °C, where the polymer concentration is 0.20 mg/mL. The inserted figure shows the hydrodynamic diameter distribution $f(D_h)$ of the vesicles, and D_h is about 312 nm.

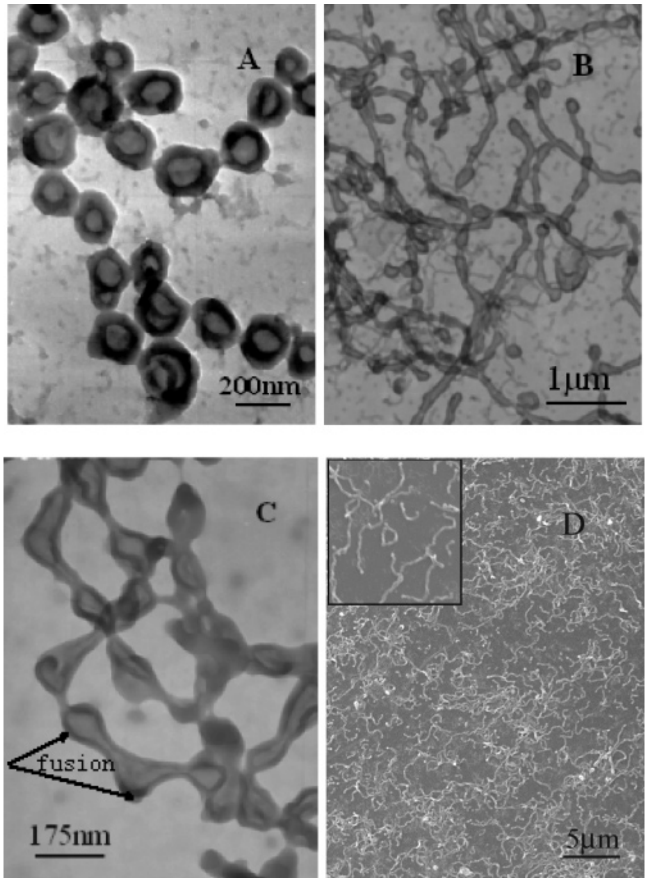

Figure 2. TEM images of the spherical PS_{80}-*b*-$P4VP_{110}$ vesicles (A), the resultant tubular vesicles formed on a carbon surface (B), an enlarged TEM image of the tubular vesicles shown in B (C), and an SEM image of the tubular vesicles formed on a piece of glass slide (D).

The structure of the vesicles was first characterized by a combination of static laser scattering (SLS) and dynamic laser scattering (DLS) measurement. Figure 1 shows the Zimm plot of I^{-1} of the vesicles vs q^2 at 25 °C, where I is the scattering intensity of the sample at a scattering angle θ.[10] From the line fitted in Figure 1,

---

* To whom correspondence should be addressed.

10.1021/ma050162l CCC: $30.25

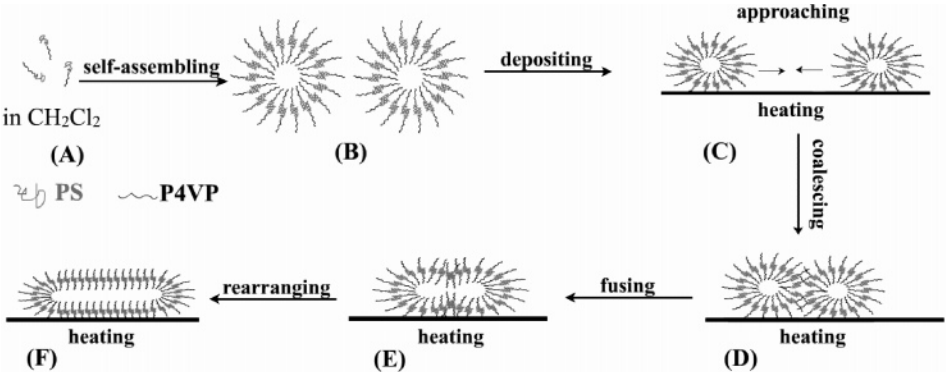

Figure 3. Schematic illustration of the transition from vesicles to giant tubular vesicles.

the apparent gyration radius R_g^0 of the vesicles is calculated as $R_g^0 = (3S/T)^{0.5}$,[10] where S is the slope and T is the intercept of the line fitted in Figure 1. The calculated value is 162.3 nm. The hydrodynamic diameter of the vesicles measured at a scattering angle of 90° is about 312 nm, or the hydrodynamic radius R_h^0 is about 156 nm, which is inset in the figure. The values of Γ/q^2 of the vesicles measured at scattering angles ranging from 30° to 150° are essentially independent of q^2, which suggests that the vesicles are uniformly spherical.[11] The R_g^0/R_h^0 value can reveal the morphology of particles dispersed in solution.[12] The R_g^0/R_h^0 value of the vesicles is about 1.04, which is very consistent with that of typical vesicles in solution;[12] this confirms the structure of the vesicles in 2-propanol.

The morphology of the vesicles was also confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Samples for TEM and SEM were prepared by placing a drop of the vesicular solution onto a carbon-coated copper grid or onto a clean glass slide and then dried at a given temperature. A TEM image of the vesicles formed at room temperature is shown in Figure 2A. Clearly, the size of the vesicles is uniform with a diameter of ~200 nm. We note that the hydrodynamic diameter D_h of the vesicles measured by DLS is a bit larger than that observed by TEM. It is likely that the vesicles are swollen in 2-propanol, while TEM observation shows the dried aggregates.

When the vesicular aggregates deposited on the TEM grids are heated at 50 °C and for 30 min, giant tubes are obtained, as shown in Figure 2B. The tubes have a width of about 100 nm and lengths in excess of 10 μm. We infer from these micrographs that the giant tubes are formed by aggregation of the vesicles. Figure 2C shows an enlarged image of the tubes containing a prominent coalescence of deformed vesicles indicated by arrows, which is very similar to the prolate structure reported by Kas and Sackmann et al.[13] We conclude that the formation of the giant tubes results from coalescence and fusion of the vesicles. "Polymerization" of vesicles may be an accurate description. The tubes can also be obtained on glass substrates when the vesicles are treated under the same conditions. Figure 2D shows an SEM image of the tubes formed on a piece of glass slide. The glass-supported giant tubes are very similar to those in Figure 2B.

As discussed above, it is believed that the formation of the giant tubes is due to the coalescence and the fusion of the vesicles. To further understand the temperature effect on the morphological transition, the spherical vesicles were heated at temperatures ranging from 25 to 60 °C after deposition on TEM grids. The results indicate that tubes can be formed at lower temperatures between 40 and 50 °C, although the morphology of tubes are not as perfect as that shown in Figure 2B (for a sample heated at 50 °C). Light scattering results indicate that the size of vesicles dispersed in 2-propanol remains essentially constant as a function of temperature, even at a temperature as high as 60 °C. This suggests that the coalescence and fusion (polymerization) of the spherical PS_{80}-*b*-$P4VP_{110}$ micelles only occur in the heating process after the vesicles are deposited onto a suitable substrate such as glass or TEM copper grid and cannot be achieved in solution. This may be related to the glass transition temperature T_g of PS block in PS_{80}-*b*-$P4VP_{110}$ (the calculated T_g of the PS_{80} block is close to 50 °C[14]), above which the "polymerization" takes place.

Our findings are schematically summarized in Figure 3. The block copolymer PS_{80}-*b*-$P4VP_{110}$ first self-assembles into spherical vesicles in 2-propanol. Upon heating the deposited vesicles, coalescence and fusion take place and dumbbell-like aggregates form. After the rearrangement of the resultant dumbbell-like aggregates, the giant tubular vesicles are obtained.

Acknowledgment. The financial support by National Natural Science Foundation of China (No. 50273015, 20328407, and 20474032), Chinese Education Ministry Foundation for Nankai University, and Tianjin University Joint Academy is gratefully acknowledged.

References and Notes

(1) (a) Yang, P.; Zhao, D.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1998**, *10*, 2033. (b) Huang, H.; Remsen, E. E.; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1999**, *121*, 3805.
(2) Lipowsky, R.; Sackmann, E. *Structure and Dynamics of Membranes*; Elsevier: Amsterdam, 1995; Vol. 1.
(3) Mendes, E.; Narayanan, J.; Oda, R.; Kern, F.; Candau, S. J. *J. Phys. Chem. B* **1997**, *101*, 2256.
(4) Danino, D.; Talmon, Y.; Zana, R. *Colloids Surf. A* **2000**, *169*, 67.
(5) Oda, R.; Bourdieu, L.; Schmutz, M. *J. Phys. Chem. B* **1997**, *101*, 5913.
(6) Pinazo, A.; Perez, L.; Infante, M. R.; Pons, R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1475.
(7) Bruckner, E.; Sonntag, P.; Rehage, H. *Langmuir* **2001**, *17*, 2308.
(8) (a) Dobereiner, H. G.; Selchow, O.; Lipowsky, R. *Eur. Biophys. J.* **1999**, *28*, 174. (b) Petrov, P. G.; Lee, J. B.; Dobereiner, H. G. *Europhys. Lett.* **1999**, *48*, 435.
(9) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 3531.
(10) (a) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1991. (b) Bantle, S.; Schmidt, M.; Burchard, W. *Macromolecules* **1982**, *15*, 1604.

(11) Xu, R.; Winnik, M. A.; Hallett, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 87.
(12) (a) Wu, C.; Zuo, J.; Chu, B. *Macromolecules* **1989**, *22*, 633. (b) Antonietti, M.; Heinz, S.; Schimidt, M. *Macromolecules* **1990**, *23*, 3796. (c) Huber, K.; Bantle, S.; Lutz, P.; Burchard, W. *Macromolecules* **1985**, *18*, 1461. (d) Burchard, W.; Schmidt, M.; Stockmayer, W. *Macromolecules* **1980**, *13*, 1265.
(13) Kas, J.; Sackmann, E. *Biophys. J.* **1991**, *60*, 825.
(14) O'Driscoll, K.; Sanayei, R. A. *Macromolecules* **1991**, *24*, 4479.

MA050162L