Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

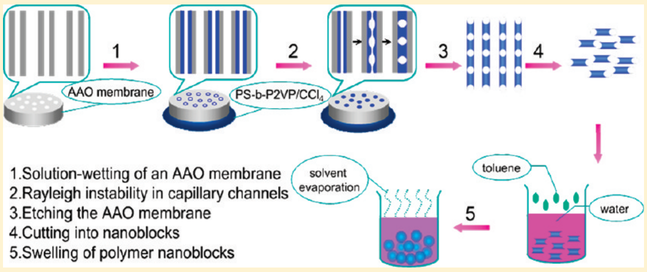
Fabrication of Polymer Nanospheres Based on Rayleigh Instability in Capillary Channels

Shilin Mei, Xunda Feng,[†] and Zhaoxia Jin*

Department of Chemistry, Renmin University of China, Beijing 100872, China

Supporting Information

ABSTRACT: We report a simple method to produce block copolymer nanospheres by swelling the short rodlike entities generated from Rayleigh instability of polymer nanotubes within the cylindrical nanopores of an anodic aluminum oxide (AAO) membrane. Poly(styrene-*b*-2-vinylpyridine) (PS-*b*-P2VP) nanotubes were first allowed to form inside the cylindrical nanopores through solution-wetting of an AAO membrane followed by solvent evaporation. Upon thermal annealing, undulations in the nanotube wall occurred due to Rayleigh instability and finally led to the formation of nanorods containing regular encapsulated holes. The structures were susceptible to ultrasonication and could be cut into short rodlike blocks with uniform size. These PS-*b*-P2VP entities were suspended in water with the help of a nonionic surfactant and then swollen by a good solvent for both PS and P2VP. The swollen PS-*b*-P2VP entities were deformable and spontaneously evolved into nanospheres so as to minimize the interfacial energy. The characterization of the nanospheres by transmission electron microscopy confirmed that the swollen PS-*b*-P2VP could microphase-separate into an ordered structure under three-dimensional confinement. Furthermore, the selective swelling of P2VP within the PS-*b*-P2VP nanospheres by ethanol/HCl mixture yielded the internal structural reconstruction and the formation of mesoporous nanospheres. The obtained mesoporous nanospheres of PS-*b*-P2VP may be useful as nanocontainers in the application of supporting catalyst.



INTRODUCTION

Nanocontainers with multilevel interior structures are expected to show remarkable performance in the application of catalysis, sensors, and biomedicine.[1,2] In these nanocontainers, the nanomaterials from block copolymers (BCPs) are of great importance due to their numerous chemical compositions and complex nanostructures that can meet various requirements in the applications.[1] These complicated hybrid microstructures of BCP nanocontainers can be obtained through a phase separation process.[1] However, the ordered and controllable microstructure from phase separation requires BCP with a narrow distribution of its molecular weight, which brings more difficulties in the fabrication of specific BCP nanostructures, for example, nanospheres of BCPs. Miniemulsion polymerization is a widely used method to fabricate polymeric nanoparticles and nanocapsules.[3] But most of these BCP particles with ordered pattern from phase separation obtained through emulsion-based approaches are in micrometer size.[4−6] Yabu et al. developed a controlled precipitation method to produce onionlike BCP nanoparticles.[7,8] In addition, these polymer nanoparticles from their droplets inside microfluidics devices[9−11] or from inkjet printer[12] were successfully obtained recently. Commercially available BCP samples with narrow polydispersity index (PDI) value can be used to produce the corresponding BCP nanospheres. Such simple approaches based on physical process demonstrate their powerful applications in the fabrication of polymer nanospheres.

We have found another interesting physical phenomenon which is useful in the fabrication of polymer nanospheres. Rayleigh instability is a general phenomenon of liquid cylinders to limit their surface energy.[13] There were some reports on the fabrication of nanoparticles based on this phenomenon, but all these studies were limited to metal nanoparticles.[14−18] It is observed that the average diameter of metal nanoparticles and spacing between adjacent particles are related to the size of original nanowires, and thus they are easily adjustable.[15] The well-established template wetting of polymer solution or melt can be used to produce polymer nanotubes or nanorods.[19,20] The Rayleigh instability of polymer nanotubes in AAO capillary channels was studied by Chen et al.[21] Unlike the Rayleigh instability of metal nanowires which creates nanospheres, the instability of polymer nanotubes in AAO membrane generates polymer nanorods with periodic encapsulated holes.[21]

In this study, we demonstrated a novel method to fabricate polymer nanospheres based on these polymer nanorods with periodic encapsulated holes generated from Rayleigh instability of polymer nanotube within AAO channels. The hole-containing polymer nanorods from Rayleigh instability have controllable size that is related to the diameter of capillary channels and the concentration of polymer solution.[21] We then cut these polymer

Received: November 11, 2010
Revised: December 30, 2010
Published: February 22, 2011

dx.doi.org/10.1021/ma102573p | *Macromolecules* 2011, 44, 1615–1620

nanorods to isolated blocks, and the sizes of these short blocks are narrowly distributed. These isolated blocks can be suspended in water with the addition of a nonionic surfactant. Upon the addition of a good solvent for polymer blocks in aqueous suspension, these swollen blocks will deform to polymer nanospheres with controllable size. Here we used a diblock copolymer poly(styrene-*b*-2-vinylpyridine) (PS-*b*-P2VP) as a model to demonstrate this fabrication method. Because the phase separation of PS-*b*-P2VP accompanies its swelling process, the produced BCP nanospheres will have ordered microstructure. We further studied the BCP nanospheres with hollow interior structures by selective swelling. Because the surface chemistry of PS-*b*-P2VP nanospheres has ordered patterned based on their phase separation, during the selective swelling in ethanol/acid aqueous solution, P2VP phase can be dissolved and drawn from nanospheres, leaving voids in nanospheres after deswelling. By using TEM to characterize the PS-*b*-P2VP nanosphere, we observed that the solid spheres of PS-*b*-P2VP gradually transformed to perforated spheres with complicated multilevel interior structure. The microstructure revolution of PS-*b*-P2VP demonstrated a coherent result of topological and curvature confinement. Compared with the morphology reconstruction of BCP nanorods,[22] the transformation of BCP nanospheres happens under a mild condition. These porous spheres with interior structures are good candidates as BCP nanocontainers. Since many BCPs with narrow distribution of molecular weights are commercially available, our study provides not only a general path to create BCP nanospheres with patterned phase separation microstructure but also a platform to study the BCP nanospheres with multilevel interior structures.

EXPERIMENTAL SECTION

Poly(styrene-*b*-2-vinylpyridine) (M_n(PS) = 23 600 g/mol; M_n(P2VP) = 10 400 g/mol; M_w/M_n(PS-*b*-P2VP) = 1.04) was obtained from Polymer Source Inc. Poly(ethylene glycol) monododecyl ether ($C_{12}E_6$) was the product of Tokyo Chemical Industry Co., Ltd. Analytical grade toluene, carbon tetrachloride, ethanol, sodium hydroxide, and hydrochloric acid (37%) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., and used as received. Deionized water (Millipore Q; >18 MΩ cm) was used for all aqueous solutions. Anodic aluminum oxide (AAO) membranes (Anodisc 13, 0.2 μm) were purchased from Whatman Ltd. The membranes were rinsed thoroughly with tetrachloromethane, tetrahydrofuran, and deionized water (Millipore Q; >18 MΩ cm) in sequence and then annealed at 150 °C for 1 h in vacuum before use. Its pore size is about 270 nm based on our SEM characterization.

In the fabrication of polymer nanotube by template wetting of polymer solution, a clean AAO membrane was immersed in a PS-*b*-P2VP/CCl_4 (80 mg/mL) solution for 12 h. Subsequently, the membrane was picked up from the solution and dried at ambient conditions and then in vacuo. Residual polymer layer on AAO membrane was scrapped off by a sharp blade before further manipulation. The obtained PS-*b*-P2VP nanotubes with AAO membrane were annealed at 180 °C for 20 min to produce polymer nanorods with periodic encapsulated holes based on the Rayleigh instability. Then the AAO membrane was dissolved in 5 wt % sodium hydroxide aqueous solution to release these polymer nanorods. After thoroughly washed by DI water, these polymer nanorods were redispersed in water to perform ultrasonication. Thirty minutes ultrasonication is enough to cut these polymer nanorods to our desired PS-*b*-P2VP nanoblocks.

Then the PS-*b*-P2VP nanoblocks collected by centrifugation were dispersed in 4.5 mL $C_{12}E_6$ aqueous solution (the concentration of $C_{12}E_6$ is 1.4 mg/mL) under stirring and light ultrasonication. A small amount of toluene (0.5 mL) was dropped into this aqueous suspension under light sonication. When these toluene microdroplets were dispersed in aqueous solution, the original clear suspension gradually became opaque. This opaque emulsion was kept at room temperature for 48 h under stirring to swell the PS-*b*-P2VP nanoblocks by adsorbing toluene. Subsequently, the suspension was heated to 70 °C to evaporate toluene. After removing toluene, the suspension containing PS-*b*-P2VP nanospheres was centrifuged at 10 000 rpm for 10 min, and its supernatant containing free $C_{12}E_6$ was discarded. To thoroughly remove $C_{12}E_6$ adsorbed on PS-*b*-P2VP nanospheres, fresh DI water was added to wash these nanospheres. After three circles of washing and centrifugation, the obtained PS-*b*-P2VP nanospheres were used in further morphology characterizations. To observe the multilevel interior structure of BCP nanospheres produced by selective swelling, PS-*b*-P2VP nanospheres were dispersed in ethanol:0.01 M HCl (1:4 v/v) mixture solution and then heated for 1.5 h at 50 or 80 °C. These BCP nanospheres, of which P2VP blocks were selectively swollen in acid environment, were characterized by transmission electron microscopy (TEM).

The dynamic light scattering (DLS) of polymer nanospheres suspension was characterized using a laser light scattering spectrometer (632.8 nm, ALV/DLS/SLS-5022F, by ALV/Laser Vertriebs gesellschaft m.b. H., Langen, Germany). Signals at 45° scattering angle were recorded and analyzed with associated software. Before the characterization of DLS, PS-*b*-P2VP nanospheres samples were filtered by a polycarbonate membrane (pore size of 0.8 μm) to remove dust.

Scanning electron microscopy (SEM, JEOL 7401) was performed at an accelerating voltage of 5 kV. Prior to SEM characterization, the samples were coated with a thin layer of gold. The size distributions of polymer nanoblocks and nanospheres were measured using Image J software based on their SEM images. More than 100 units were counted in the statistic.

TEM studies were performed with a Hitachi TEM (TEM, H-7650B) at an accelerating voltage of 100 kV. A droplet of PS-*b*-P2VP suspension in water was placed onto copper grids for TEM analysis. To investigate the phase separation of PS-*b*-P2VP nanospheres and nanocontainers, the sample was stained by I_2 vapor at 60 °C for 30 min before observation.

RESULTS AND DISCUSSION

The instability of liquid cylinders has been studied over 100 years.[13] To reduce surface energy, liquid cylinders will break into droplets with uniform size and regular spacing between adjacent droplets. This phenomenon paves a special way for researchers to fabricate metal nanoparticles.[14−17] In particular, compared with other fabrication methods of metal nanoparticles, the preparation based on Rayleigh instability has its special advantage that all nanoparticles are assembled to a long chain with a steady spacing between adjacent particles.[16] Such assembled metal nanoparticles may have potential applications in some plasmonic devices. Rayleigh instability of polymer thin film has been extensively studied from theoretical and experimental aspects.[23−26] Because Rayleigh instability usually induces unwanted undulation of polymer thin films[25] or deformation of polymer nanofibers in the electrospinning fabrication,[26] most studies concentrated on controlling or suppressing its happening.[27,28] Although there are many successful fabrications of metal nanoparticles based on the Rayleigh instability phenomenon, the preparation of polymer nanoparticles through Rayleigh instability is still not reported yet. Chen et al. have investigated the instability of polymer nanotube confined within AAO membrane.[21,29] In AAO membrane, the resulting structures after Rayleigh instability are polymer nanorods with periodical encapsulated holes. This is different from the product of the instability of metal nanowires. However, it is observed that these polymer nanorods have a very weak connection in their annular films surrounding the encapsulated holes. Chen et al. have found that the film is very thin and easily broken during sample preparations or morphology characterizations.[21] That inspires us to cut these nanorods at this weak part. We prepared PS-*b*-P2VP nanotubes (see Supporting Information Figure S1) and then annealed PS-*b*-P2VP nanotube/AAO at 180 °C for 20 min. Figure 1 shows the SEM and TEM characterizations of PS-*b*-P2VP nanorods with periodical encapsulated holes. These nanorods were dispersed in water and then sonicated for 30 min in a sonication bath. By collecting these polymer nanostructures in suspension and characterizing their morphology, we found that most of these polymer nanorods were cut to isolated blocks with nearly uniform size (Figure 2a).

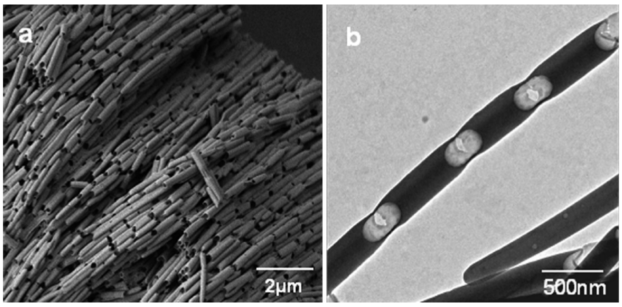


Figure 1. PS-*b*-P2VP nanorods with periodical encapsulated holes: (a) SEM image and (b) TEM image.

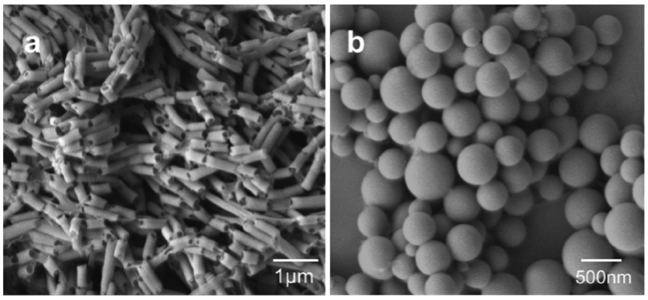
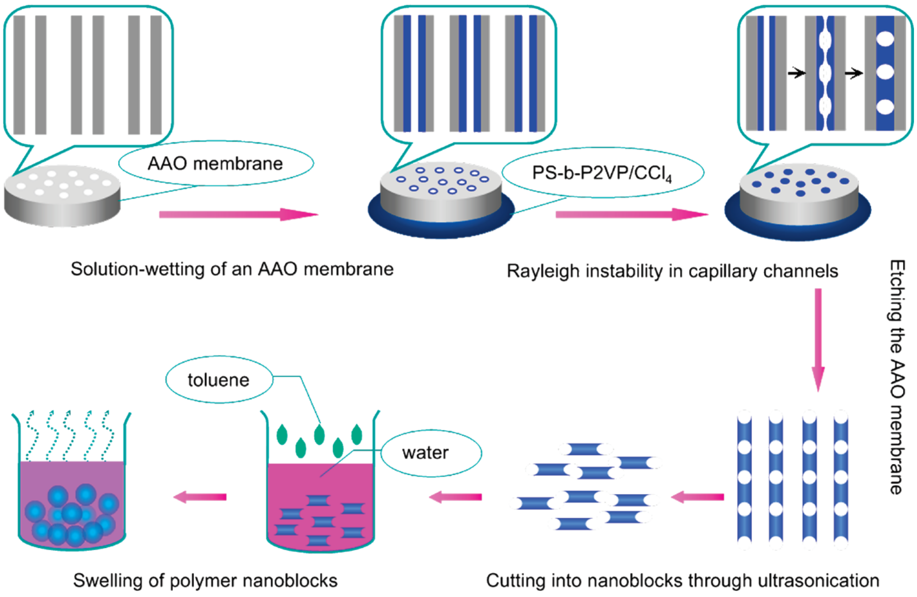


Figure 2. SEM images of PS-*b*-P2VP nanoblocks obtained by ultrasonication (a) and PS-*b*-P2VP nanospheres produced by swelling their nanoblocks (b).

We dispersed the PS-*b*-P2VP nanoblocks in $C_{12}E_6$ aqueous solution under stirring. Nonionic surfactant $C_{12}E_6$ was added to improve the stability of PS-*b*-P2VP nanoblocks in aqueous solution. Subsequently, toluene was added into this suspension drop-by-drop under ultrasonication, and the original clear suspension became an opaque emulsion. Because toluene is a good solvent for PS-*b*-P2VP, and it is immiscible with water, thus these small toluene microdroplets were adsorbed by BCP blocks, inducing the swelling of BCP blocks.[30] It is known that oil will form droplets in water to lower its surface tension. Swollen BCP blocks adjust their morphology to lower their surface energy in aqueous solution as oil in water. After 48 h swelling, the transformation of BCP nanoblocks to nanospheres finished. The adsorbed toluene in swollen BCP nanospheres was removed by evaporation at 70 °C. These obtained deswelling polymer nanostructures were characterized by SEM and TEM after washing. We observed that most of polymer nanoblocks change to nanospheres (Figure 2b). Thus, we obtained polymer nanospheres through a combination of Rayleigh instability of polymer nanotube inside capillary channels and swelling process. Scheme 1 shows the experimental process we used. To test the applicability of this experiment procedure to homopolymers, we also fabricated PS nanospheres based on the same process (Figure S2). Because the size of polymer nanospheres is controlled by the size of polymer nanoblocks, we measured and counted these polymer nanospheres and nanoblocks by using Image J software based on SEM images (Figure 2a and Figure S3). For a comparison, the size of polymer nanospheres was also measured by dynamic light scattering. Figure 3a is the histogram of the size distribution of polymer nanospheres obtained from SEM images. The size distribution from dynamic light scattering (Figure 3b) is compared with the result obtained from

Scheme 1. Fabrication Process of Polymer Nanospheres Based on Rayleigh Instability Phenomenon of Polymer Nanotubes in AAO Capillary Channels



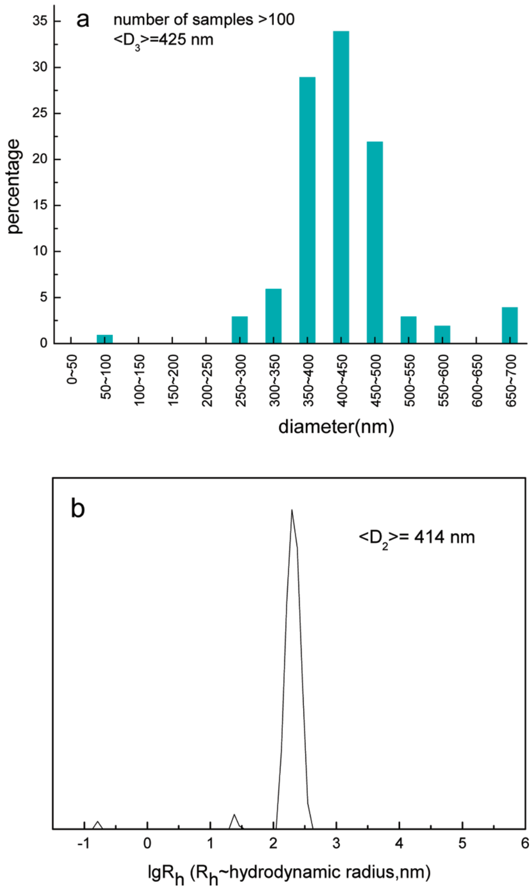


Figure 3. (a) Histogram of the size distribution of polymer nanospheres obtained from morphology characterization. (b) Hydrodynamic radius (R_h) distribution of polymer nanospheres from dynamic light scattering characterization.

Table 1. Diameter Data of Polymer Nanospheres Obtained from Calculation (D_1), DLS (D_2), and SEM Image (D_3)

D_1	D_2	D_3
418 nm	414 nm	425 nm

morphology characterization. The average diameters from these two characterizations namely D_2 (From DLS characterization) and D_3 (From SEM images) are listed in Table 1. For a comparison, the D_1, which was calculated from the average size of polymer nanoblocks based on the constant of polymer volume during the transition from nanoblocks to nanospheres (the detailed calculation is given in the Supporting Information), is also listed in Table 1. It is clear that the size of polymer nanospheres we obtained is close to that from calculation. The findings indicate that the size of polymer nanospheres can be controlled through adjusting the size of hole-containing polymer nanorods. On the basis of theoretical studies, the main factors determining the size of polymer nanorods are the wall thickness of polymer nanotube in AAO membrane and the diameter of AAO pore size. By manipulating these experimental parameters, our fabrication method of polymer nanospheres based on Rayleigh instability and swelling can produce size-controllable polymer nanospheres. Using an AAO membrane with smaller pore size (~180 nm), we obtained smaller polymer nanospheres (~310 nm) using the same experimental procedure (see Supporting Information Figure S4).

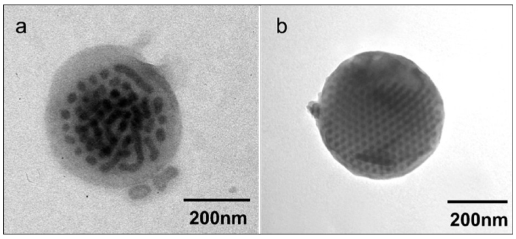


Figure 4. TEM images of a PS-*b*-P2VP nanosphere after 24 h swelling (a) and 48 h swelling (b) in toluene. P2VP is darker than PS due to I_2 staining.

Moreover, we found that the morphology change was accompanied by microphase separation of PS-*b*-P2VP in BCP nanospheres. Figure 4 is the TEM image of a PS-*b*-P2VP nanosphere we obtained. P2VP blocks are darker than PS blocks due to the I_2 staining. After 24 h swelling in toluene, the phase separation of PS-*b*-P2VP is still not complete as observed in Figure 4a. After a longer swelling time (48 h), most of these PS-*b*-P2VP nanospheres presented a pattern of P2VP cylinders in PS matrix which is similar the equilibrium pattern for our BCP (Figure 4b). The BCP nanoparticles with ordered pattern have produced by Yabu et al. through the self-organized precipitation method.[31,32] They obtained polystyrene-*b*-polyisoprene nanoparticles with well-developed lamellar structure[31] or frustrated phase.[8] Because nanosphere is a three-dimensional (3D) confinement to BCP microphase separation, some special structure features will be present due to the synergy of surface field, commensurability, and curvature based on theoretical simulations.[1,33,34] Recently, Li et al. reported an experimental study of the morphology evolution of BCP nanoparticles in 3D confinement driven by solvents.[32] Starting from concentric lamellae poly(styrene-*b*-isoprene), the morphology change to PI cylinders in PS matrix and further to PS-core−PI-shell spherical structures in PS matrix was observed by transmission electron microtomography during the solvent annealing process. Their study demonstrated that the novel microstructures from BCP phase separation may exist in 3D confinement. Such a highly complex microphase structure is a good template for the fabrication of metal or metal alloy nanomaterials.[35,36] Our preparation method provides another unique way to obtain BCP nanospheres with well-developed microstructure. A further detailed investigation of the phase separation of BCP nanospheres is in progress.

Since we are concerned about BCP nanocontainers, to this end, we chose to selectively swell BCP nanospheres. Selective swelling is a unique method to create special nanostructure in BCP nanomaterials.[37,38] The morphology reconstruction of BCP nanomaterials is reversible in the swelling−deswelling process under moderate swelling ratio. However, at high swelling ratio, the significant volume change during swelling−deswelling may lead to mesoporous nanostructure.[22,39,40] There are some interesting studies based on the morphology reconstruction of BCP nanorods.[22,40] We expected that special features could be achieved in the selective swelling of BCP nanospheres. So we dispersed these PS-*b*-P2VP nanospheres in 0.01 M HCl(aq)/ethanol (4:1 v/v) mixture for 1.5 h at 50 or 80 °C under stirring. Figure 5 is the TEM images of the swollen PS-*b*-P2VP nanosphere. It is clear that swollen BCP nanosphere becomes a nonsolid particle. Because P2VP domains are soluble in acid

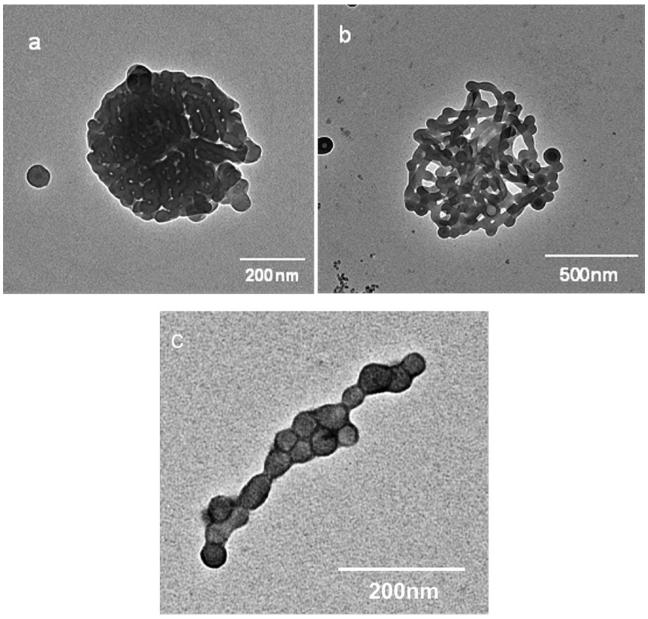


Figure 5. TEM images of PS-*b*-P2VP nanosphere suspended in ethanol:0.01 M HCl(aq) mixture (v/v: 1:4) for 1.5 h (a) at 50 °C and (b) at 80 °C. (c) A destructed part of PS-*b*-P2VP nanosphere. The sample was stained by I_2. P2VP corona shows darker than PS core.

mixed solution, they were drawn to outside during the swelling process. In the deswelling step they formed corona surrounding the PS strands, leaving voids inside BCP spheres. The PS-*b*-P2VP nanospheres look like loosely twinned strand balls. Under a higher temperature condition (80 °C), the PS domains take a severe reconstruction to accommodate the highly swollen P2VP domains, inducing a nearly hollow sphere (Figure 5b). Similar with that in BCP nanorods, a transformation of the strands into strings of spheres happens.[22] However, the temperature in our experiment is lower than that in PS-*b*-P2VP nanorods reconstruction,[22] which may be the result of small size and high curvature of our PS-*b*-P2VP nanospheres compared with their nanorods. Such a size dependence of the rate of structure transition was also observed in Li's experiments.[32] Figure 5c showed a destructed part of the BCP sphere which demonstrated the core (PS)−corona (P2VP) morphology.

Further research will systematically study the relation between experimental parameters and BCP nanostructures. Under a well-controlled experimental condition, the BCP nanospheres with multilevel interior nanostructure could be achieved, and that will deepen our knowledge about BCP nanocontainers. On the other hand, this fabrication method also provides us a chance to experimentally investigate the radial morphology revolution with the increase of curvature in BCP nanospheres that is only illustrated by theoretical simulations[1] and confirmed by several experiments.[4,31,32]

CONCLUSION

In this study, we demonstrated a facile fabrication method to produce polymer nanospheres based on a combination of Rayleigh instability and swelling process. Polymer nanorods with periodic encapsulated holes were generated by Rayleigh instability of polymer nanotubes in capillary channels of AAO membranes. After cutting these nanorods into individual polymer nanoblocks and swelling them in a mixture of toluene/water, we obtained polymer nanospheres with narrow size distribution. The size of polymer nanospheres is related to experimental parameters which can be adjusted and easily controllable. In our demonstrated model, the nanoparticles of diblock copolymer polystyrene-*b*-poly(2-vinylpyridene), due to the synergy of microphase separation of BCP with swelling process, showed ordered pattern on their surface. A further selective swelling in ethanol/acid mixture induced a dramatically structure reconstruction to accommodate the increased volume of P2VP domains in swelling process, leaving mesoporous PS-*b*-P2VP nanospheres after deswelling. Such BCP nanospheres with complicated interior structure have potential applications in biosensors, drug delivery, and supporting materials for catalyst, and they are also the good template to generate complex metal nanostructure.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed calculation of the size of polymer nanospheres and extensive figures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jinzx@ruc.edu.cn.

Present Address

†Max Plank Institute for Dynamics and Self-Organization, Gottingen, Germany.

ACKNOWLEDGMENT

The authors gratefully acknowledge the National Nature Science Foundation of China (Grant 21074149), the Fundamental Research Funds for the Central Universities, and the Research Funds of Renmin University of China for financial support. We also thank Prof. Goh Suat Hong at the National University of Singapore for his helpful suggestions.

REFERENCES

(1) Pinna, M.; Hiltl, S.; Guo, X.; Boker, A.; Zvelindovsky, A. V. *ACS Nano* **2010**, *4* (5), 2845–2855.

(2) Zhao, Y.; Jiang, L. *Adv. Mater.* **2009**, *21* (36), 3621–3638.

(3) Katharina, L. *Angew. Chem., Int. Ed.* **2009**, *48* (25), 4488–4507.

(4) Okubo, M.; Saito, N.; Takekoh, R.; Kobayashi, H. *Polymer* **2005**, *46* (4), 1151–1156.

(5) Jeon, S. J.; Yi, G. R.; Koo, C. M.; Yang, S. M. *Macromolecules* **2007**, *40*, 8430–8439.

(6) Kitayama, Y.; Kagawa, Y.; Minami, H.; Okubo, M. *Langmuir* **2010**, *26* (10), 7029–7034.

(7) Yabu, H.; Higuchi, T.; Ijiro, K.; Shimomura, M. *Chaos* **2005**, *15* (4), 047505–7.

(8) Higuchi, T.; Tajima, A.; Motoyoshi, K.; Yabu, H.; Shimomura, M. *Angew. Chem., Int. Ed.* **2008**, *47* (42), 8044–8046.

(9) Karnik, R.; Gu, F.; Basto, P.; Cannizzaro, C.; Dean, L.; Kyei-Manu, W.; Langer, R.; Farokhzad, O. C. *Nano Lett.* **2008**, *8* (9), 2906–2912.

(10) Chen, C. H.; Shah, R. K.; Abate, A. R.; Weitz, D. A. *Langmuir* **2009**, *25* (8), 4320–4323.

(11) Choi, S. W.; Cheong, I. W.; Kim, J. H.; Xia, Y. N. *Small* **2009**, *5* (4), 454–459.

(12) Bohmer, M. R.; Steenbakkers, J. A. M.; Chlon, C. *Colloids Surf., B* **2010**, *79* (1), 47–52.

(13) Rayleigh, L. *Proc. London Math. Soc.* **1878**, *10*, 4–13.

(14) Qin, Y.; Lee, S. M.; Pan, A.; Gosele, U.; Knez, M. *Nano Lett.* **2008**, *8* (1), 114–118.

(15) Shin, H. S.; Yu, J.; Song, J. Y. *Appl. Phys. Lett.* **2007**, *91* (17), 173106.

(16) Toimil-Molares, M. E.; Balogh, A. G.; Cornelius, T. W.; Neumann, R.; Trautmann, C. *Appl. Phys. Lett.* **2004**, *85* (22), 5337–5339.

(17) Karim, S.; Toimil-Molares, M. E.; Balogh, A. G.; Ensinger, W.; Cornelius, T. W.; Khan, E. U.; Neumann, R. *Nanotechnology* **2006**, *17* (24), 5954.

(18) Wu, Y.; Fowlkes, J. D.; Rack, P. D.; Diez, J. A.; Kondic, L. *Langmuir* **2010**, *26* (14), 11972–11979.

(19) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Gosele, U. *Science* **2002**, *296* (5575), 1997.

(20) Feng, X.; Jin, Z. *Macromolecules* **2009**, *42* (3), 569–572.

(21) Chen, J. T.; Zhang, M.; Russell, T. P. *Nano Lett.* **2007**, *7* (1), 183–187.

(22) Wang, Y.; Gosele, U.; Steinhart, M. *Nano Lett.* **2008**, *8* (10), 3548–3553.

(23) Callegari, G.; Calvo, A.; Hulin, J. P.; Brochard-Wyart, F. *Langmuir* **2002**, *18* (12), 4795–4798.

(24) McGraw, J. D.; Li, J. F.; Tran, D. L.; Shi, A. C.; Dalnoki-Veress, K. *Soft Matter* **2010**, *6*, 1258–1262.

(25) Park, J.; Suh, K. Y.; Seo, S.; Lee, H. H. *J. Chem. Phys.* **2006**, *124* (21), 214710.

(26) Haupt, B. J.; Senden, T. J.; Sevick, E. M. *Langmuir* **2002**, *18* (6), 2174–2182.

(27) Hohman, M. M.; Shin, M.; Rutledge, G.; Brenner, M. P. *Phys. Fluids* **2001**, *13* (8), 2201–2220.

(28) Son, Y.; Martys, N. S.; Hagedorn, J. G.; Migler, K. B. *Macromolecules* **2003**, *36* (15), 5825–5833.

(29) Chen, D.; Chen, J. T.; Glogowski, E.; Emrick, T.; Russell, T. P. *Macromol. Rapid Commun.* **2009**, *30* (4−5), 377–383.

(30) Im, S. H.; Jeong, U. Y.; Xia, Y. N. *Nature Mater.* **2005**, *4* (9), 671–675.

(31) Yabu, H.; Higuchi, T.; Shimomura, M. *Adv. Mater.* **2005**, *17* (17), 2062–2065.

(32) Li, L.; Matsunaga, K.; Zhu, J.; Higuchi, T.; Yabu, H.; Shimomura, M.; Jinnai, H.; Hayward, R. C.; Russell, T. P. *Macromolecules* **2010**, *43* (18), 7807–7812.

(33) Tang, P.; Qiu, F.; Zhang, H.; Yang, Y. *Phys. Rev. E* **2005**, *72*, 016710.

(34) Chantawansri, T. L.; Bosse, A. W.; Hexemer, A.; Ceniceros, H. D.; Garcia-Cervera, C. J.; Kramer, E. J.; Fredrickson, G. H. *Phys. Rev. E* **2007**, *75* (3), 031802.

(35) Peterca, M.; Percec, V. *Science* **2010**, *330* (6002), 333–334.

(36) Arora, H.; Du, P.; Tan, K. W.; Hyun, J. K.; Grazul, J.; Xin, H. L.; Muller, D. A.; Thompson, M. O.; Wiesner, U. *Science* **2010**, *330* (6001), 214–219.

(37) Xu, T.; Goldbach, J. T.; Misner, M. J.; Kim, S.; Gibaud, A.; Gang, O.; Ocko, B.; Guarini, K. W.; Black, C. T.; Hawker, C. J.; Russell, T. P. *Macromolecules* **2004**, *37* (8), 2972–2977.

(38) Xu, T.; Misner, M. J.; Kim, S.; Sievert, J. D.; Gang, O.; Ocko, B.; Russell, T. P. *New Polym. Mater.* **2005**, *916*, 158–170.

(39) Chen, J. T.; Zhang, M. F.; Yang, L.; Collins, M.; Parks, J.; Avallone, A.; Russell, T. P. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45* (20), 2912–2917.

(40) Chen, D.; Park, S.; Chen, J. T.; Redston, E.; Russell, T. P. *ACS Nano* **2009**, *3* (9), 2827–2833.