2672 *Macromolecules* **2010**, *43*, 2672–2675
DOI: 10.1021/ma100021a

Macromolecules
COMMUNICATION TO THE EDITOR

Formation of Polymeric Yolk/Shell Nanomaterial by Polymerization-Induced Self-Assembly and Reorganization

Wen-Ming Wan and Cai-Yuan Pan*

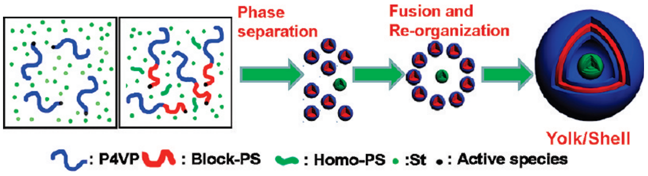
Department of Polymer Science and Engineering,
CAS Key Laboratory of Soft Matter Chemistry,
University of Science and Technology of China, Hefei,
Anhui 230026, P. R. China

Received January 5, 2010
Revised Manuscript Received February 11, 2010

In the past decade, the hollow particles with a mobile functional core have gained great attention because they displayed potential applications in drug delivery, catalysis, and artificial cell.[1] These particles are of a pseudo-triple-layer structure which is called yolk/shell nanoparticles. A general and efficient method for preparing this type of material is based on removing the intermediate layer of the trilayer nanoparticles by chemical dissolution or thermal decomposition.[2] However, the removing methods displayed some problems, such as destruction of the encapsulated agents and multistep and complicated synthetic procedure. For keeping away from the removal step, a microemulsion method has been developed, which was performed by polycondensation of tetraethoxysilane on the surface of a water droplet with functional nanoparticles, such as Fe_3O_4 inside, or by encapsulation of nanoparticles with SiO_2 shell in aqueous mixtures of surfactants.[3] However, all these methods are based on the template-assisted approach, the available templates are limited, and so the yolk/shell nanoparticles reported are mainly prepared from inorganic materials. Hitherto, the preparation of yolk/shell nanoparticles with the polymer yolk and the polymer shell is not successful, and investigation on their synthesis should be valuable in polymer chemistry.

Generally, self-assembly is a common strategy to prepare nanostructural materials; self-assembling of the block copolymer, polystyrene-*b*-poly(acrylic acid), and homopolystyrene (homo-PS) may form a trilayer structure. Unfortunately, the yolk/shell nanoparticles were not formed.[4] Thus, a strategy for preparation of polymer yolk/shell nanomaterials needs to be developed. On the basis of our previous results, the spherical micelles could be prepared by polymerization-induced self-assembling,[5] and by tuning feed molar ratio and reaction conditions, the vesicles can be achieved via polymerization-induced self-assembly and reorganization (PISR) because continuous propagation of the core polymer chains can alter the force balance involving stretching of the core chains, the surface tension between the core and outside solvent, and repulsion among the corona chains.[6] We can imagine, during the formation process of vesicles via fusion and reorganization of the spherical micelles, the nanoparticles existed in the reaction media may be encapsulated in the vesicles, forming yolk/shell nanomaterials (Scheme 1). Based on the type and the properties of nanoparticles in the polymerization system, various yolk/shell nanoparticles can be prepared. So, we raised an idea for preparation of the polymeric yolk/shell nanomaterials via PISR.

Scheme 1. Formation of Polymeric Yolk/Shell Nanomaterials via PISR



To test the above idea, we designed a polymerization system, where the reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene (St) was carried out in methanol using *S*-1-dodecyl-*S*-(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate-terminated poly(4-vinylpyridine) (P4VP-TC) as chain transfer agent and stabilizer.[7] In addition, P4VP is a functional polymer; for example, after being treated with fluorescent dyes or quantum dots, the resulting yolk/shell nanoparticles display fluorescence properties. RAFT polymerization was selected in this study because the nanoparticle cores can be formed *in situ*, and so previous preparation of the mobile particles is not needed. On the basis of the mechanism of RAFT polymerization, when feed molar ratio of 2,2′-azobis(isobutyronitrile) (AIBN)/RAFT agent is higher than 1, the homopolymer must be formed at initial polymerization,[8] because high concentration of AIBN decomposed rapidly to produce high concentration of the initial radicals, and the irreversible termination of homo-PS and PS-*b*-P4VP chains cannot be avoided owing to high concentration of the chain radicals, so the homo-PS should be yielded. Because of instability of homo-PS in methanol, the PS nanospheres stabilized by the block copolymer chains, P4VP-*b*-PSs with short PS chain length, are first formed. Successively, as the chain length of the PS blocks in the free block copolymer chains increases past a critical value, the phase separation occurs to form spherical micelles.[5] Afterward, the homo-PS will no longer be produced due to significant decrease of the AIBN concentration. Continuous polymerization of the core PS in the micelles will alter force balance and transition of the spherical micelles to other morphologies is taken place via reorganization, which is called as polymerization-induced reorganization. Thus, we studied the ratio effect of AIBN/RAFT agent on the morphologies.

The P4VP-TC used in this study had a M_n = 10 400 g/mol and M_w/M_n = 1.08. Using the conditions and recipe of preparing vesicles,[6] the molar ratio of St/P4VP-TC = $10^5/10$ was fixed, but the ratios of AIBN/P4VP-TC were varied from 1/10 to 40/10, the GPC was used to trace the RAFT polymerization, and the results are shown in Figure 1A. When the ratio of AIBN/P4VP-TC was 1/10, a unimodal GPC curve was obtained (not shown). For the RAFT polymerizations with the molar ratios of AIBN/P4VP-TC = 10/15, 10/10, 20/10, and 40/10, all the traces show two curves: one at low elution time is the PS-*b*-P4VP, and another is the homo-PS that might be formed at initial polymerization. By comparison of these GPC traces, we can see that the lower molecular weight curves shifted toward higher elution time with increasing ratio of AIBN/P4VP-TC because irreversible termination of the chain radicals in high concentration occurred easily, forming homo-PS chains with low molecular weight.

The molar ratio of AIBN/P4VP-TC also influences the morphologies formed in the RAFT polymerization. When the molar ratio of AIBN/P4VP-TC = 1/10, the RAFT polymerization of St produced the vesicles without any nanospheres inside, as shown in Figure 2A. When the AIBN usage increased to the molar ratio of AIBN/P4VP-TC = 1/1.5, we could see some vesicles with a nanosphere inside, which might be formed via encapsulation of

---

*Corresponding author. E-mail: pcy@ustc.edu.cn.

Published on Web 02/18/2010
© 2010 American Chemical Society

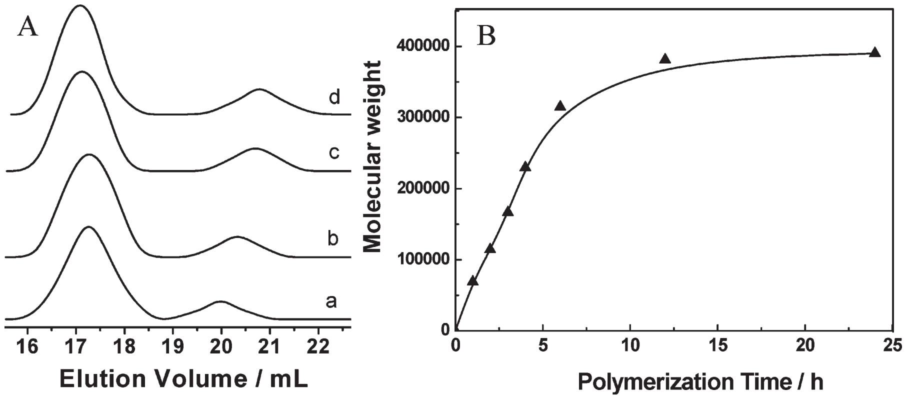


Figure 1. (A) GPC traces of the products prepared by RAFT polymerization with various molar ratios of AIBN/P4VP-TC = 1/1.5 (a), 1/1 (b), 2/1 (c), and 4/1 (d). Styrene (St): 2 g; methanol: 1 g. Feed molar ratio of P4VP-TC/St = 10:100000; 80 °C; 24 h. (B) Relationship of molecular weights with polymerization time. RAFT polymerization with a feed molar ratio: St/P4VP-TC/AIBN = 100000:10:10 was carried out in methanol (St: 2 g; methanol: 1 g) at 80 °C.

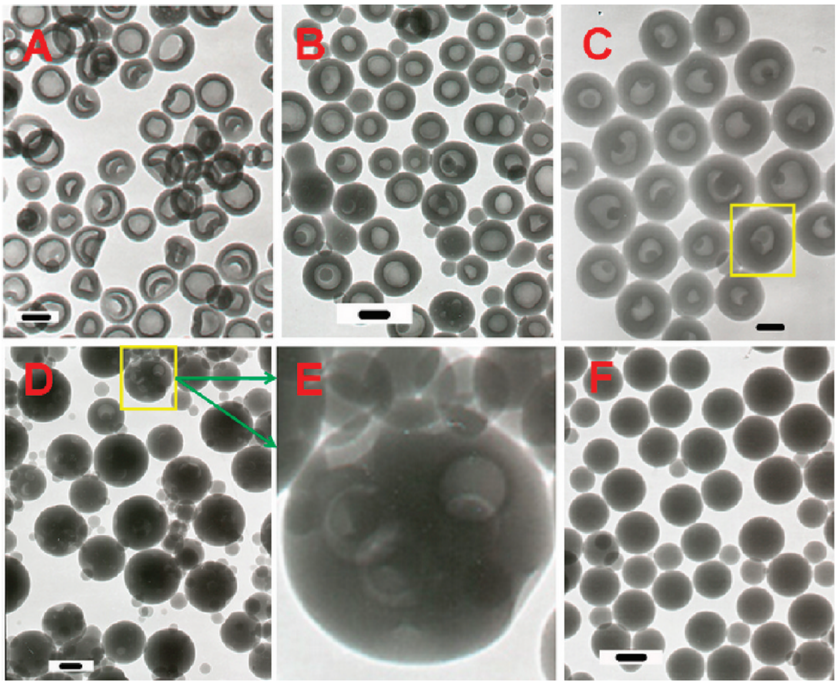


Figure 2. TEM images of the morphologies formed in RAFT polymerization with various molar ratios of AIBN/P4VP from 1/10 (A) to 1/1.5 (B), 1/1 (C), and 2/1 (D); magnification of one particle in D image (E) and 4/1 (F). Feed molar ratio: P4VP-TC/St = 10:100000; St: 2 g; CH_3OH: 1 g; 80 °C; 24 h. The scale bars are 200 nm for (A−C) and 1000 nm for (D, F).

the PS spheres by the vesicles during their formation process, as shown in Scheme 1. Figure 2B shows yolk/shell nanoparticles coexisted with the vesicles without a sphere inside, and so the preparation of yolk/shell via RAFT polymerization is feasible.

For preparation of the yolk/shell nanomaterials, we continued to increase the molar ratio of AIBN/P4VP to 1:1, and the TEM image of the resulting particles in Figure 2C demonstrates that almost all vesicles contained a mobile nanosphere; by statistic estimation, ~95% of the particles are the yolk/shell nanoparticles and around 5% are the nanospheres. This result is different from the self-assembling of PS-*b*-PAA and PS.[4] In the copolymerization, the chain length of the PS block grew step by step, which induced transition of the spherical micelles, and complete transition of the spherical micelles into vesicles took 5−8 h generally,[6] while the nanospheres were formed at initial polymerization as aforementioned. Therefore, in the fusion and reorganization process of the spherical micelles, the PS nanospheres were encapsulated by the vesicles.

Further increase of AIBN content in the feed did not improve the quality of yolk/shell nanoparticles. For example, the RAFT polymerization with AIBN/P4VP-TC = 2/1 yielded microscale spheres with some cavities containing a nanosphere as shown in Figure 2D,E. The polymerization with high concentration of AIBN produced more inactive chains, homo-PS and P4VP-*b*-PS with short PS block (Figure 1A), forming more inactive PS nanospheres. At the same time, the P4VP-TC consumed in the formation of inactive chains increased also. With further increase of PS chain length, the formed yolk/shell nanoparticles became unstable, inducing the aggregation of yolk/shell nanoparticles and nanospheres. The aggregates have smooth surface with many spheres on their surface (Figure S2), indicating fusion of the different nanospheres and the yolk/shell nanoparticles. When the AIBN increased continuously to the ratio of AIBN/P4VP = 4/1, the polymerization produced more homo-PS chains, leading to formation of more PS nanospheres. They needed more PS-*b*-P4VP chains as stabilizer, which prevented the formation of

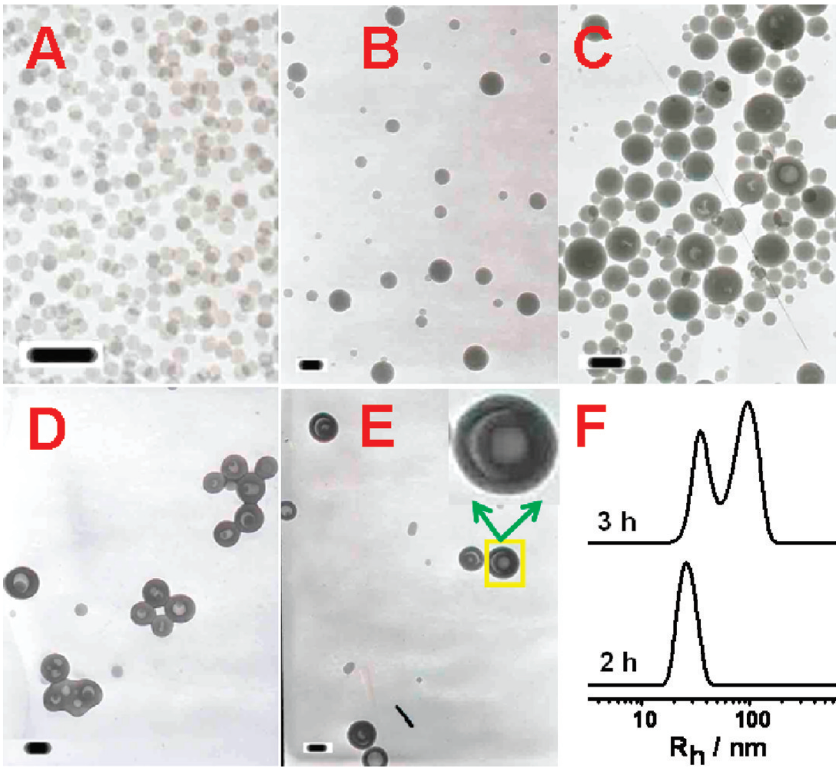


Figure 3. TEM images of the yolk/shell nanoparticles formed at different polymerization times: 2 (A), 3 (B), 4 (C), 6 (D), and 24 h (E). Laser light scattering curves of the particles formed at 2 and 3 h (F). Feed molar ratio: St/P4VP-TC/AIBN = 100000:10:10; CH_3OH: 1 g; St: 2 g; 80 °C. Scale bars are 200 nm.

active spherical micelles, and so no vesicles were formed, but the microscale spherical particles were produced (Figure 2F). Thus, the ratio of AIBN/P4VP is important for formation of yolk/shell structures.

In order to clarify the formation mechanism, TEM was used to follow the formation of yolk/shell nanoparticles. Figure 3A shows formation of the uniform spherical micelles with a diameter of ~30 nm, but their D_h measured by LLS was ~50 nm (Figure 3F). When the polymerization lasted to 3 h, two kinds of nanoparticles were formed: one has a diameter of ~60 nm, and the diameter of the others is ~160 nm, as shown in Figure 3F. The two different size particles are clearly seen in their TEM image of Figure 3B. The small size was the spherical micelle, and the large size was the vesicle with a nanosphere inside. In comparison with the RAFT polymerization with AIBN/P4VP-TC = 1/10, in which reorganization of the spherical micelles started at 4 h of polymerization,[6] the reorganization for the polymerization with molar ratio of AIBN/P4VP-TC = 1/1 started much earlier (Figure 3F) because the propagation rate of the polymer chains was much faster (23 100 g/mol in 3 h, Figure 1B) than that (12 200 g/mol in 3 h)[6] of polymerization with AIBN/P4VP-TC = 1/10. This is ascribed to more AIBN accelerating the polymerization rate, which is a general phenomenon for RAFT polymerization.[8] When the polymerization continued, the growth of core PS blocks led to instability of the spherical micelles, which induced their fusion and reorganization, so more and more vesicles were formed. We can see increase of the big size vesicles with a mobile nanosphere inside and relative decrease of the small size micelles with evolution of the polymerization (Figure 3C,D). We said that encapsulation of the nanospheres by the vesicles occurred in the fusion and reorganization of the spherical micelles because we can see two, occasionally three spheres in one vesicle (as pointed by square frame in Figure 2C), and we also observed very few of the coaxial two vesicles (Figure 3E), probably they are formed by encapsulation of an active spherical micelle with a vesicle in the fusion and reorganization process of the spherical micelles. With growth of the PS block chains, the inner micelles became a small vesicle and the outer vesicle became bigger. In principle, when the inactive PS nanospheres were stabilized by active block chains, P4VP-*b*-PS-TC, the yolk/shell nanoparticles can be formed also, but by this formation mechanism, we cannot explain formation of the vesicles with two or three spheres; also, it is difficult to interpret the formation of coaxial vesicles in Figure 3E. In addition, Figure 3F shows that the size of some spherical micelles increased from ~50 to ~160 nm in 1 h of polymerization, which cannot be fulfilled by gradual propagation of the core PS blocks (Figure 1B), and so it is a reasonable explanation that the yolk/shell nanoparticles were formed via encapsulation of the PS nanospheres by the vesicles in the reorganization. Thus, this strategy is a more versatile approach for preparation of the yolk/shell nanomaterials. When copolymerization of the St with a functional monomer, such as vinyl monomer having fluorescent group or metal complex, is performed, the yolk/shell nanoparticles with a mobile functional core inside could be prepared.

In summary, we have developed a facile and feasible approach for preparation of polymeric yolk/shell nanomaterials in one-pot RAFT polymerization via PISR. The yolk/shell morphologies could be created by RAFT polymerization of St with a feed molar ratio of AIBN/P4VP-TC = ~1/1, and the different morphologies from vesicles to yolk shell, to microscale spheres with some cavities, and to microscale spheres can be prepared just by varying the ratio of AIBN/P4VP-TC.

Acknowledgment. We thank the National Natural Science Foundation of China for financial support under Contracts 50673086 and 50633010.

Supporting Information Available: Text giving general experimental procedures. This material is available free of charge via Internet at http://pubs.acs.org.

References and Notes

(1) (a) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111. (b) Marinakos, S. M.; Novak, J. P.; Brousseau, L. C., III; House, A. B.; Edeki, E. M.; Feldhaus, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 8518. (c) Lou, X. W.; Yuan, C.; Rhoades, E.; Zhang, Q.; Archer, L. A. *Adv. Funct. Mater.* **2006**, *16*, 1679. (d) Jiang, P.; Bertone, J. F.; Colvin, V. L. *Science* **2001**, *291*, 453.

(2) (a) Kamata, K.; Lu, Y.; Xia, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2384–2385. (b) Lee, K. T.; Jung, Y. S.; Oh, S. M. *J. Am. Chem. Soc.* **2003**, *125*, 5652–5653. (c) Zhang, K.; Zhang, X.; Chen, H.; Chen, X.; Zheng, L.; Zhang, J.; Yang, B. *Langmuir* **2004**, *20*, 11312–11314. (d) Xing, S. X.; Tan, L. H.; Chen, T.; Yang, Y. H.; Chen., H. Y. *Chem. Commun.* **2009**, 1653–1654.

(3) (a) Wu, X. J.; Xu, D. S. *J. Am. Chem. Soc.* **2009**, *131*, 2774–2775. (b) Lin, Y.-S.; Wu, S.-H.; Tseng, C.-T.; Hung, Y.; Chang, C.; Mo, C.-Y. *Chem. Commun.* **2009**, 3542–3544.

(4) (a) Zhang, L.; Eisenberg, A. *Polym. Adv. Technol.* **1998**, *9*, 677–699. (b) Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1996**, *118*, 3168–3181.

(5) (a) Zheng, G. H.; Pan, C. Y. *Macromolecules* **2006**, *39*, 95–102. (b) Wan, W. M.; Pan, C. Y. *Macromolecules* **2007**, *40*, 8897–8905. (c) Zheng, Q.; Zheng, G. H.; Pan, C. Y. *Polym. Int.* **2006**, *55*, 1114–1123.

(6) (a) Wan, W. M.; Sun, X. L.; Pan, C. Y. *Macromolecules* **2009**, *42*, 4950–4952. (b) Wan, W. M.; Hong, C. Y.; Pan, C. Y. *Chem. Commun.* **2009**, *39*, 5883–5885. (c) Wan, W. M.; Sun, X. L.; Pan, C. Y. *Macromol. Rapid Commun.*, DOI: 10.1002/marc.200900640.

(7) (a) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754–6756. (b) Wan, W. M.; Pan, C. Y. *Macromolecules* **2008**, *41*, 5085–5088. (c) Wan, W. M.; Pan, C. Y. *Chem. Commun.* **2008**, *43*, 5639–5641.

(8) Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079–1131.