Hollow Spheres from Shell Cross-Linked, Noncovalently Connected Micelles of Carboxyl-Terminated Polybutadiene and Poly(vinyl alcohol) in Water

Youwei Zhang,[†,‡] Ming Jiang,*[,†] Jiongxin Zhao,[‡] Jin Zhou,[‡] and Daoyong Chen[†]

Department of Macromolecular Science and The Key Laboratory of Molecular Engineering of Polymers (Ministry of Education), Fudan University, Shanghai 200433, China, and College of Material Science and Engineering, Donghua University, Shanghai 200051, China

Received July 27, 2003; Revised Manuscript Received December 17, 2003

ABSTRACT: Noncovalently connected micelles (NCCM) with carboxyl-ended polybutadiene (CPB) as the core and poly(vinyl alcohol) (PVA) as the shell were formed in aqueous solutions, driven by hydrogen bonding between the component polymers. Shell cross-linked micelles and hollow spheres were obtained successively on the basis of NCCM: The shell structure was locked in by the cross-linking reaction of PVA with glutaraldehyde. Cavitation of the cross-linked micelles was realized by switching the aqueous medium to the THF-rich mixture. The cavitation process was monitored by dynamic light scattering, which indicated a substantial mass decrease and size expansion. The resultant hollow spheres are stable in aqueous solutions, and their shell thickness could be adjusted by changing the core/shell ratio of the micelle precursors. SEM observations proved that the mechanical stability of the hollow spheres depended on both the cross-linking degree and the thickness of the shell.

Introduction

Self-assembled polymeric materials with well-defined structures such as micelles or vesicles have been attracting increasing interest for their great potential applications.[1−4] In recent years, among these new materials on submicron or nanometer scales, polymeric hollow spheres have received special attention because compared to the ordinary micelles, as nanocontainers or nanoreactors, they are expected to have much higher efficiency of encapsulation, particularly for large-size molecules. The self-assembly method,[5−8] template polymerization,[9−12] and micro- or miniemulsion polymerization[13,14] have been used to prepare polymeric hollow spheres. In the traditional self-assembly method, several sequential steps are needed: synthesis of a block copolymer composed of a cross-linkable block and a degradable block, micellization, cross-linking the shell block, and finally removing the core block by degradation chemically or biologically.[5−8]

In recent years, we have developed several approaches to obtain noncovalently connected micelles (NCCM), which are different from the above traditional micelles in that the core chains and the shell chains are connected through noncovalent interactions, mainly hydrogen bonding.[15−17] Quite recently, Pispas et al. reported the solution properties of MCCM composed of poly(2-vinylpyridine) and end-sulfonic acid polystyrene and polyisoprene.[18] Using NCCM as precursors, we can easily obtain hollow spheres by simple cross-linking the shell chains and subsequent dissolution of the core chains.[19] This procedure could avoid the possible difficulties in the synthesis of the block copolymers and the subsequent degradation of the core chains. Thus, a broad range of common polymers can be used. In addition, the size and thickness of the hollow spheres can be adjusted easily in a certain range through changing preparation conditions such as the weight ratio of shell to core. Using this method, we have obtained hollow spheres of cross-linked poly(4-vinylpyridine) in chloroform/nitromethane/DMF.[19]

This work aims at obtaining hydrophilic hollow spheres in aqueous media. For this purpose, we prepared NCCM with carboxyl-terminated polybutadiene (CPB) as the core and hydrophilic poly(vinyl alcohol) (PVA) as the shell first. By cross-linking PVA shell and dissolving CPB core, we were able to produce nanocages[8a] of PVA in aqueous media. Having hydrophilic, nontoxic, and biocompatible PVA shell and large central space, these hollow spheres are expected to have great application prospects in various biomedicine fields.

Surfactant-Free Particles of CPB in Water

In our previous studies,[20] it was found that ionomers, in which the backbone carried a few molar percent of ionic or polar groups, could form stable nanoparticles in water when adding the ionomer solution in an organic solvent dropwise to an excess of water. In this solvent mixture, the insoluble hydrophobic chains undergo an intrachain contraction and interchain association forming nanometer aggregates, which are stabilized by the ionic or polar groups on the periphery.

In this study, we examined the formation of nanoparticles of CPB first. CPB is a low molecular weight ($M_n = 3565$) polybutadiene with carboxyl groups at both ends. Narrowly distributed nanoparticles of CPB (P1) were formed when 1 volume of its dilute solution in THF was added dropwise into a 20-fold volume of water under stirring. In a typical case, the average hydrodynamic diameter $\langle D_h \rangle$ of the particles is 194 nm (Figure 1). Obviously, these surfactant-free CPB particles are stabilized by the carboxyl groups enriched on their surface. However, this particle size is much larger than that of the ionomers in which the carboxyl is in its salt state[21] because in the present case the carboxyl groups

† Fudan University.
‡ Donghua University.
* Corresponding author. E-mail: mjiang@fudan.edu.cn.

10.1021/ma035085d CCC: $27.50
Published on Web 01/29/2004

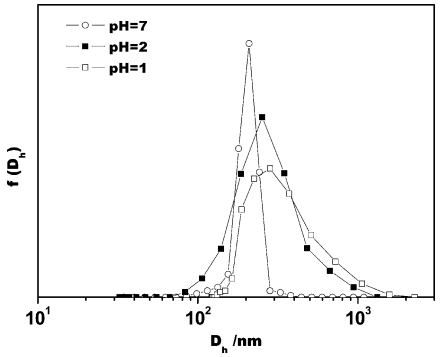

Figure 1. Hydrodynamic diameter distribution ($f(D_h)$) of CPB particle P1 in THF/water (v/v, 1/20) at different pH values.

Table 1. Changes in $\langle D_h \rangle$ and PDI of CPB Particles P1 and Micelles M4 in THF/Water (v/v, 1/20) with pH of the Medium

sample code	pH of the solution	$\langle D_h \rangle$ (nm)	polydispersity index (PDI)
P1	7.0	194	0.07
	2.0	296	0.35
	1.0	584	0.56
M4	7.0	284	0.17
	2.0	266	0.19
	1.0	263	0.17

are only partially ionized in water. It was found that both the particle size and its polydispersity increased significantly when the pH value of P1 solution was adjusted to acidic conditions (Table 1). The results are understandable as in the acidic medium the carboxyl groups are fully protonated, which, of cause, suppresses the stabilization of the particles. In addition, it was found that the CPB particle size increased with increasing the initial concentration of CPB in THF: the size (nm) was 155, 194, 205, and 228 when the concentration (mg/mL) was 0.6, 1.0, 1.2, and 1.5, respectively.

Formation of (CPB)−PVA Micelles and the Stabilization Mechanism

When 1 volume of CPB/THF dilute solution was added dropwise into 20 volumes of PVA aqueous solution under stirring, a bluish tinge appeared. DLS studies found that in an appropriate range of CPB/PVA compositions particles with a size around 100−200 nm appeared, and the peak associated with PVA chains disappeared. This indicates that the two polymers probably formed micelles with CPB as the core and PVA as the shell, which was denoted as (CPB)−PVA. The gathering of the PVA chains around the CPB aggregates is believed to be driven by hydrogen-bonding interactions between the carboxyl groups in CPB and the hydroxyl groups in PVA. Although THF is a poor solvent for PVA, subsidiary measurements showed that the chain sizes of PVA in water and in THF/water (v/v, 1/20) were 27.6 and 28.3 nm, respectively. This means that in the solvent mixture the PVA chains keep solvated.

A series of micelles M1−M6 were obtained by adding 1 mL of CPB solution at a concentration of 1.0 mg/mL in THF into 20 mL of PVA solutions in water with concentrations ranging from 0.1 to 4.0 mg/mL, corresponding to the weight composition of CPB/PVA from 1/2 to 1/80 (Table 2, Figure 2). The resultant (CPB)−PVA micelles in THF/water (v/v, 1/20) were very stable as the average hydrodynamic diameter $\langle D_h \rangle$ almost did not change in an interval of 4 months: for micelles of M3 and M4, $\langle D_h \rangle$ varied from 263 to 264 nm and from 284 to 287 nm, respectively.

Table 2. Preparation Conditions and Compositions of CPB Particle and (CPB)−PVA Micelles[a]

micelle code	*c*/PVA (mg/mL)	CPB/PVA (w/w)	CPB/PVA (chain no., calcd)	$\langle D_h \rangle$ (nm)
P1	0	1/0		194
M1	0.1	1/2	14.8	244
M2	0.5	1/10	2.96	255
M3	1.0	1/20	1.48	263
M4	2.0	1/40	0.74	284
M5	2.2	1/44	0.67	308
M6	4.0	1/80	0.37	350

[a] The concentration of CPB/THF solution is 1.0 mg/mL. There was about 10% decrease in the size of the micelles after THF in the solution was removed by dialyzing against water for 3 days. Typically, the $\langle D_h \rangle$ of M4 decreased from 284 to 264 nm after dialysis. The data listed here are for the micelle solutions prepared without subsequent removal of THF.

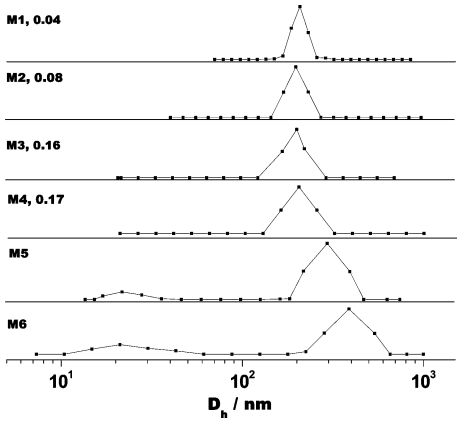

Figure 2. Hydrodynamic diameter distribution curves of micelles solution M1−M6 in THF/water (v/v, 1/20). The numerals in legend refer to PDI.

Figure 2 displays the dependence of D_h of (CPB)−PVA micelles on composition. The main features of the micelles shown in Table 2 and Figure 2 are as follows. First, $\langle D_h \rangle$ of the micelles increases with increasing of the initial concentration of PVA solution. This trend is in agreement with that reported previously for the NCCMs of slightly sulfonated polystyrene and poly(vinylpyridine) in organic medium[16a] and poly(styrene-*co*-methacrylic acid) and poly(vinylpyrrolidone) in water.[16d] Obviously, the extent of gathering of PVA chains around the CPB core due to the favorable enthalpy of forming hydrogen bonding depends on PVA concentration. The higher concentration leads to more chains moving to and concentrating around the CPB core and consequently larger particles.

Second, the micelles of M1−M4 display a unimodal distribution. However, from M5 and M6 in which the initial concentrations of PVA solution are 2.2 and 4.0 mg/mL, respectively, in addition to the main peak, a weak one appears at a low diameter region. This small peak around 20 nm is quite close to that for pure PVA solutions. In addition, this small peak becomes broader and larger with further increasing of PVA concentration. The results clearly indicate that as the weight ratio of CPB/PVA decreases to 1/44 and accordingly the chain number ratio to 0.67, the CPB core surface is "saturated" by PVA chains, and therefore, some PVA chains remain free in the solution. As the PVA chains are much smaller than that of the particles, the presence of a

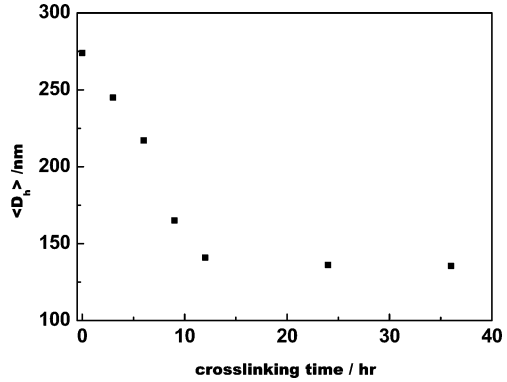

Figure 3. Dependence of $\langle D_h \rangle$ of M4 in water on the cross-linking reaction time. GA/HCl/VA = 0.2/1.0/1.0 (mol), room temperature.

small amount of free PVA chains in the solutions of M1−M4 could not be completely excluded.

It is interesting to compare the stabilization mechanisms between the surfactant-free particles and NCCM. As mentioned above, the particle size of P1 increases significantly from 194 to 584 nm as the pH of the medium decreases from 7 to 1. This could obviously be attributed to the suppression of the electrostatic stabilization due to protonation of the carboxyl groups. However, the same measurements for the micelle M4 showed completely different results; namely, the pH decrease caused only a minor size change from 284 to 263 nm (Table 1). As increasing protonation of the carboxyl groups of CPB obviously favors their hydrogen-bonding interaction with PVA and the consequent decrease of the particle size, it is reasonable to think that, in the acidic media, in the presence of PVA, the CPB aggregates are stabilized mainly by the solvated PVA chains. Thus, we are able to do the subsequent structural locking of the micelles by shell cross-linking, which has to be preformed in low-pH media.

Shell Cross-Linking of (CPB)−PVA Micelles

As hydroxyl groups can react easily with aldehyde groups by aldehyde condensation in acidic media, formaldehyde and glutaradehyde have been widely used to react with hydroxyl groups of PVA to produce Vinylon fibers, PVA membranes, PVA hydrogels, etc.[22,23] Here, glutaradehyde (GA) was selected to cross-link the shell of (CPB)−PVA micelles in acidic media. Typically, 13 mol % of GA based on the repeating units of PVA, corresponding to an aimed cross-linking degree of 52% as one GA molecule can react with four hydroxyl groups, was added dropwise into the stirred solution of M4. Then, the mixture was kept stirred at room temperature for 24 h, followed by dialysis against water for 3 days to remove impurities including chlorhydric acid, unreacted GA, and THF; thus, an aqueous solution of cross-linked micelles C4 was obtained. The IR results showed that the fractions of the reacted hydroxyl groups for C4 were 8.3, 14.6, 20.1, 27.0, 33.6, and 37.0% at the reaction time of 3, 6, 9, 12, 24, and 36 h, respectively.

DLS was used to monitor the process of the shell cross-linking. Figure 3 shows the results for M4 in THF/water (1/20) displaying a slow but substantial change of $\langle D_h \rangle$; i.e., after about 10 h reaction, $\langle D_h \rangle$ decreased from 274 to 141 nm. This result shows that the reaction was completed in about 12 h. Figure 3 tells us that the degree of cross-linking of PVA shell can in fact be controlled simply by changing reaction time. Using higher concentrations of GA and chlorhydric acid caused more pronounced decrease of $\langle D_h \rangle$ (data not shown).

Generally, the decrease of $\langle D_h \rangle$ by shell cross-linking here is much more pronounced than that reported for the micelles of partially quaternized DMAEMA−MEMA diblock copolymer[24] and of PAMA−PCEMA−PGMA triblock copolymer[25] reported in the literature. However, a similar large decrease of the size for PI-*b*-PAA micelles was reported.[8a] In our case, this apparent size change probably reflects a decrease of the swelling degree of the micelle shell in water caused by the replacement of the hydroxyl groups by the ether groups in the cross-linking reaction.

The success of locking the structure of the micelles was proved by the following facts. First, dilution with water has almost no effect on the $\langle D_h \rangle$ of the GA-treated micelle solution. For NCCM, due to no chemical bonds connecting the core and shell, $\langle D_h \rangle$ of the micelles often varies with dilution.[17] In the present case, the GA-treated micelles C4 showed little change of $\langle D_h \rangle$ from 136 to 139 nm when it was diluted to a quarter of its ordinary concentration, while the original micelles M4 displayed a pronounced decrease from 284 to 224 nm. It was also found that only the GA-treated micelles with an aimed degree of cross-linking larger than 24% could keep its size against dilution. Considering the incompleteness of the cross-linking reaction and the existence of intramolecular interactions, the effective cross-linkage contributed by intermolecular reactions is much lower than that of the aimed one. Thus, the minimum real degree of shell cross-linking needed for locking the structure of (CPB)−PVA micelles is small, similar to that reported by the groups of Armes[24] and Liu.[26]

Second, switching the medium for the micelles from water to THF/water (v/v, 9/1) resulted in macroscopic precipitation for the original micelle M4, indicating that CPB was dissolved, the micelles disintegrated, and PVA precipitated. However, no substantial change except a slight deepening of the bluish tinge for C4 solutions occurred. In fact, only the micelles with an aimed degree of shell cross-linking above 50% remained stable in THF/water (v/v, 9/1), while those with a lower cross-linking degree precipitated gradually. This can be rationalized by the fact that the cross-linking reaction between the hydroxyl groups of PVA and aldehyde groups of GA improved the solubility of PVA shell in the THF-rich solvent. As for the micelles with a low degree of shell cross-linking, swelling property of the cross-linked shell in THF/water (v/v, 9/1) is still not good enough to prevent the reaggregation of the micelles.

Swelling and Cavitation of Shell Cross-Linked (CPB)−PVA Micelles[27]

Taking advantage of (CPB)−PVA micelles without chemical bonds connecting the core and shell, we tried to produce hollow spheres of hydrophilic PVA in water by removing the CPB core from the cross-linked micelles in THF-dominated mixtures. For this purpose, an excess of THF, a good solvent for CPB, was added into the aqueous solution of the cross-linked micelles to make the final solvent composition of THF/water (v/v, 9/1). The DLS technique was used to trace the process of core dissolution and the formation of the hollow spheres. As shown in Figure 4, changes in intensity of scattering light I_s and average hydrodynamic diameter $\langle D_h \rangle$ with time apparently follow different ways. The intensity

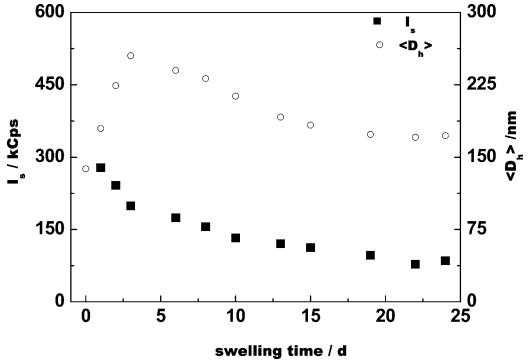

Figure 4. $\langle D_h \rangle$ and scattering intensity I_s of shell cross-linked micelles C4 vs swelling time in THF/water (v/v, 9/1).

Table 3. $\langle D_h \rangle$ and PDI of Original Micelle M4, Cross-Linked Micelle C4, "Semihollow Sphere" SH4, and Hollow Sphere H4 in Different Media

sample code	in THF/water (v/v, 9/1)		in water	
	$\langle D_h \rangle$ (nm)	PDI	$\langle D_h \rangle$ (nm)	PDI
M4[a]			284	0.17
C4			136	0.21
SH4[b]	192	0.02	220	0.20
H4[c]	171	0.01	251	0.19

[a] M4 in THF (v/v, 1/20). [b] SH4 was obtained by swelling C4 in THF/water (v/v, 9/1) for 13 days. [c] H4 was obtained by swelling C4 in THF/water (v/v, 9/1) for 22 days.

monotonically decreases while the size increases first and then decreases after reaching the maximum. Obviously, the continuous decrease of the intensity reflects the gradual decrease in the weight of the micelles due to the removal of CPB from the core.

When the medium of the micelles was switched from water to the THF-dominated mixture, the micelle size changes were governed by two processes, that is, core swelling and core extracting. The former was much quicker than the later. Therefore, the swelling of the CPB core dominated in the first period and accordingly forced the PVA shell to expand though THF was not a good solvent for the cross-linked PVA. Thus, the size of the micelles reached its maximum at 2.5 days. As the extracting process continued, more and more CPB chains diffused out, and the process gradually turned to be the dominant one; thus, the expanded PVA shell shrank accordingly. After about 18 days, both the size and the weight of the micelle no longer changed substantially, which meant that the cavitation of the micelle was completed. This was obviously longer than that by biodegradation.[28]

Using this fairly long cavitation process of the micelles, we can readily attain hollow spheres with different degrees of cavitaion by simply controlling the swelling time. Thus, the "semihollow sphere" SH4 and the hollow sphere H4 in THF/water (v/v, 9/1) were obtained by 13 and 22 days swelling of C4, respectively. For separating the extracted CPB chains from the hollow sphere solutions, the solution pH was adjusted to about 1.0, causing CPB to be precipitated. After centrifugation, the supernatant liquid was dialyzed against water for 3 days; thus, stable aqueous solutions of SH4 and H4 were obtained. Table 3 lists the size and its polydispersity of micelle M4, cross-linked micelle C4, "semihollow sphere" SH4, and hollow sphere H4 in the different media. The main features of the results are as follows. First, both the sizes and the

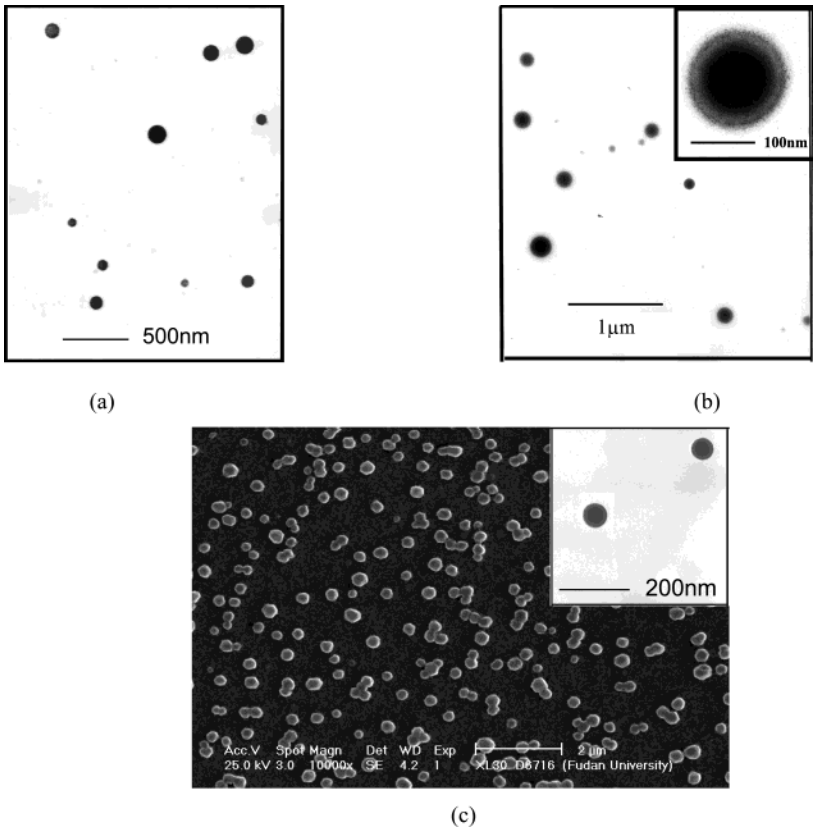

Figure 5. (a) TEM micrograph of micelles M4 without staining. The specimen was prepared from the micellar solution in THF/water (v/v, 1/20). (b) TEM micrograph of micelles M4 stained by I_2 solution; the inset is for a typical micelle at a large magnification. The specimen was prepared from the micellar solutions in water. (c) SEM micrograph of cross-linked micelles C4; the inset is the typical TEM micrograph of C4 without staining. The specimens were prepared from the micellar solutions in water.

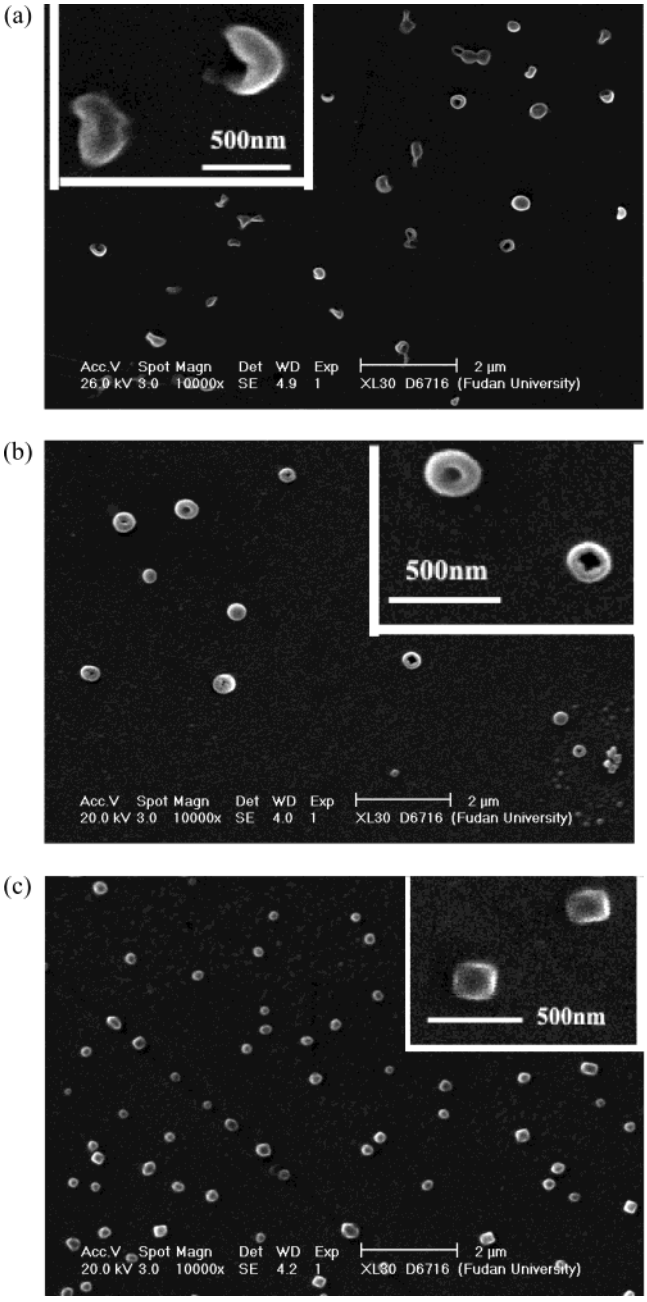

Figure 6. SEM micrographs of hollow spheres H1 with different shell cross-linking degree (the molar ratio of GA/VA is 0.5 (a), 1.25 (b), and 2.5 (c)). The specimens were prepared from H1 in THF/water (9/1).

size distributions of H4 and SH4 in THF/water (v/v, 9/1) are smaller than their corresponding sizes in water, indicating that the cross-linked PVA shell has much less swelling ability in THF than in water. Second, in THF/water (v/v, 9/1), hollow sphere H4 has a smaller size than that of "semihollow sphere" SH4, while in water, it is the opposite case. This demonstrates again that the PVA shell of SH4 is forced to expand in THF/water (v/v, 9/1) due to the swelling of the remaining CPB chains. Third, after full cavitation, the size of the micelles in water increases more than 100 nm.

The shell cross-linking and subsequent cavitation of the micelles described above were employed to M1 and M3, producing the corresponding hollow spheres of H1 and H3. By UV measurements, on the basis of the absorbance of the double bonds in CPB around 237 nm, it was found that about 93% of CPB was extracted in H3.

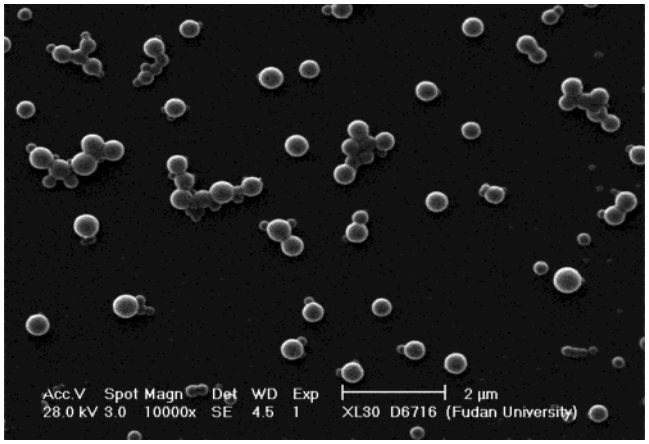

Figure 7. SEM micrograph of hollow spheres H3. (the molar ratio of GA/VA is 0.5). The specimen was prepared from H3 in THF/water (9/1).

Morphology of Micelles, Shell Cross-Linked Micelles, and Hollow Spheres

TEM and SEM were used to study the morphologies of the micelles and hollow spheres. For M4 without staining, TEM micrograph shows dark spheres with a sharp boundary (Figure 5a). The expected core−shell structure could not be seen, probably due to the poor contrast between the PVA shell and the background as a result of the loose chain packing of PVA. Therefore, the I_2 staining technique was used to improve the contrast. Figure 5b is a typical TEM micrograph of micelle M4 treated by I_2, which could selectively stain PVA chains as the hydroxyl groups of PVA form complex with I_2.[29] Now we can see that the micelles M4 have a perfect spherical shape showing a distinct core−shell structure. The size of the micelles in the picture ranges from about 80 to 240 nm and is smaller than that measured by DLS (160−400 nm, $\langle D_h \rangle = 284$ nm), which may be caused by the chain contraction of PVA shell during water evaporation in the sample preparation.

Figure 5c shows a SEM micrograph of the cross-linked micelles of M4, namely, C4. It can be seen that after shell cross-linking the spherical shape of the micelle was generally retained. Comparing Figure 5c with its inset, we can see that there is a large discrepancy in the particle size of C4 in the SEM (300−400 nm) and TEM micrographs (65−80 nm), which can be attributed to the effect of the substrate. In the TEM observations, copper grids coated successively with thin films of Formvar and carbon were used, which was hydrophobic, while in the SEM observations, relatively hydrophilic glass substrates were used. The hydrophilic PVA shell of C4 tends to contract on the carbon-coated grid while spread on the glass leading to the large size difference.

Differing from the solid spherical particles, spheres with a central cavity are readily deformed or even broken in the sample preparation or SEM observation under high vacuum. Thus, for hollow spheres, what one observes in SEM is often broken bodies or dented pieces instead of perfect spheres. However, this damage of the external shape of the examined objects favors the identification of the hollow interior and even estimation of the shell thickness.[12,30,31] Figure 6 presents the SEM

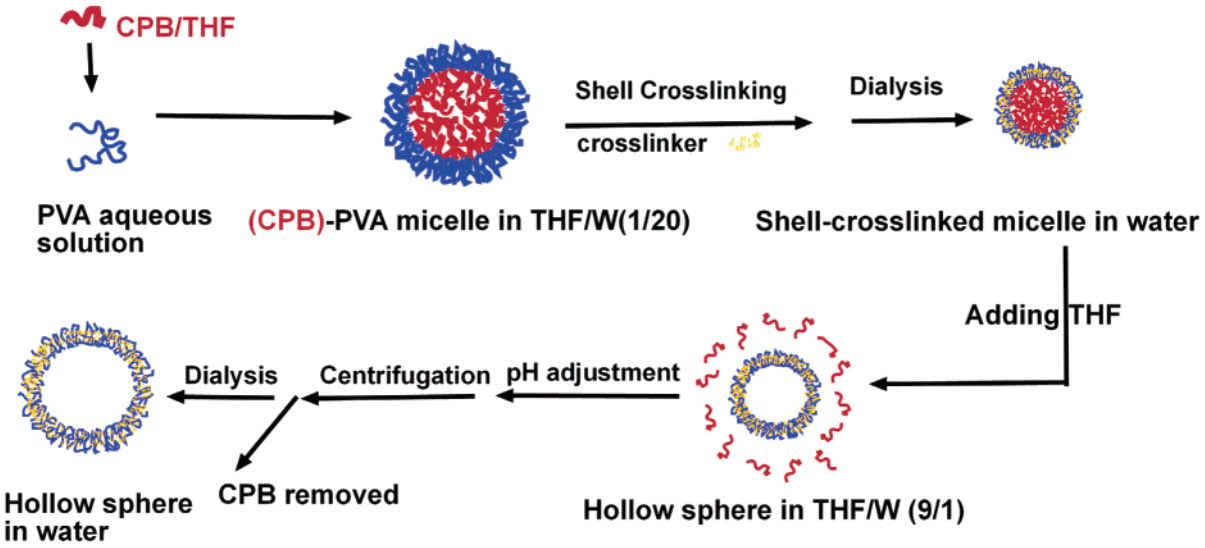

Figure 8. Schematic illustration for preparing hollow spheres in water.

micrograph of hollow spheres H1 with different targeted cross-linking degree. H1 was obtained from micelles M1 with the thinnest shell of PVA, i.e., composition of CPB/PVA was 1/2, among all the micelles listed in Table 2. As the shell is thin, substantial deformation of the hollow spheres was expected. As shown in Figure 6a, no perfect spheres were found as the particles could no longer keep their integrity. Instead, various badly deformed particles appeared. This indicates the damage of the external shape and the shrinkage of the shell due to the flexibility of the cross-linked PVA. However, this external shape deformation can be suppressed or even avoided by improving the stiffness of the shell through increasing the shell cross-linking degree. As the molar ratio of GA/VA increased from 0.5 to 1.25, the particles kept their lateral round contour but the central part was badly collapsed (Figure 6b). Furthermore, when the molar ratio of GA/VA increased to 2.5, the spherical integrity of the particles was basically retained, but all the particles possess a faintly sunk center (Figure 6C).

Thickening the shell of the hollow spheres also improved their shape stability. Figure 7 presents the morphology of hollow spheres H3 from micelles M3. Compared with the thin shell spheres H1 shown in Figure 6a, we can clear see the effect of the weight ratio of shell to core of the micelle precursor on the observed morphologies. As the weight ratio of PVA shell to CPB core increases from 2:1 to 20:1, hollow spheres H3 displayed the perfect spheres with smooth surface. Therefore, for such cross-linked thick shell, SEM could not tell us the presence of the central cavity.

Conclusions

Our findings can be summarized as follows (Figure 8). When a dilute CPB/THF solution was added dropwise into PVA solution, micellization took place: the aggregates of CPB with carboxyl groups enriched on their surface were stabilized by the solvated PVA chains which gathered around the aggregates, driven by hydrogen bonding between the carboxyl of CPB and hydroxyl of PVA. The structure of PVA shell could be successfully locked in by reaction with glutaraldehyde. Furthermore, cavitation of the resultant shell cross-linked micelles was realized by switching the medium from water to THF/water (v/v, 9/1). The process was monitored by DLS, which showed a substantial mass decrease and size expansion. After dialysis against water, stable hydrophilic hollow spheres of cross-linked PVA in water were attained. The mechanical stability of the hollow spheres depended on the cross-linking degree and thickness of the shell, both of which are controllable in practice. Such kind of nontoxic, hydrophilic, biocompatible hollow spheres have application potentials, particularly in biomedical fields.

Experimental Section

Sample. Poly(vinyl alcohol) (PVA,124) was the commercial product of Kaurary Co. Japan, with a degree of saponification of 99% and a degree of polymerization of 2400. Carboxyl-terminated polybutadiene (CPB) was synthesized as described in ref 17. The carboxyl content was determined to be 0.561 mmol/g, and hence the calculated number-average molecular weight was 3565.

Micelle Preparation. Micellar solutions were typically prepared by adding 1 mL of CPB/THF solution (1 mg/mL) dropwise into 20 mL of stirred PVA/water solution with a desired concentration. The mixture was stirred for about 20 h at room temperature and then kept for 7 days before measurements.

Shell Cross-Linking of Micelles. A typical shell cross-linking process was as follows: 0.9 mL of 1 M HCl (100 mol % catalyst HCl based on hydroxyl of PVA) was added dropwise into 20 mL of stirred solution of micelle M4, and the mixture was continued to be stirred for about 15 min, followed by adding 0.39 mL of 0.3 M glutaradehyde aqueous solution (13 mol % cross-linker GA based on hydroxyl of PVA), and the reaction mixture was kept stirring for 24 h at room temperature. After reaction completion, the reaction solution was dialyzed against water for 3 days to remove impurities including catalyst, unreacted cross-linker, and THF.

The fraction of the reacted hydroxyl groups with GA was determined by IR. This was based on the measurements of the intensity ratio of the peak around 854 nm to that at 1150 nm, which are associated with the CH bonds connected to hydroxyl and the ether group, respectively. The calibration curve was obtained from the corresponding measurements of a series of PVA fibers with known fraction of the reacted hydroxyl groups.

Measurements. Malvern Autosizer 4700 laser light scattering (LLS) spectrometers were used. The $\langle D_h \rangle$ and polydispersity index (PDI, i.e., $\langle \mu_2 \rangle / \Gamma^2$) were obtained by a CONTIN analysis. TEM observations were performed on a Philips CM 120 electron microscope at an accelerating voltage of 80 kV.

The samples were prepared by placing 5 μL micelle solutions on copper grids, which were coated with thin films of Formvar and carbon, and allowing them to dry in a desiccator. The micelle solution is stained as follows. 1 mL of iodine aqueous solution (10 mg/mL) was added into 10 mL of micelle solution, and the mixture was stirred for 3 days followed by dialysis against water for 3 days. SEM observations were conducted with a Philips XL30. The samples preparation for SEM observations was similar to that for TEM, except that glass substrate was used.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (NNSFC No. 50173006, 50333010). The CPB sample was kindly supplied by Prof. X. Z. Han, the Changchun Institute of Applied Chemistry, China.

References and Notes

(1) Meier, W. *Chem. Soc. Rev.* **2000**, *29*, 295−303.
(2) Chiu, D. T.; Wilson, C. F.; Karlsson, A.; Danielsson, A. *Chem. Phys.* **1999**, *247*, 133−139.
(3) Caruso, F. *Adv. Mater.* **2001**, *13*, 11−22.
(4) Lasic, D. D. *Liposomes: From Physics to Applications*; Elsevier: Amsterdam, 1992.
(5) (a) Ding, J. F.; Liu, G. J. *Chem. Mater.* **1998**, *10*, 537−542. (b) Ding, J. F.; Liu, G. J. *J. Phys. Chem. B* **1998**, *102*, 6107−6113. (c) Steward, S.; Liu, G. J. *Chem. Mater.* **1999**, *11*, 1048−1054. (d) Maskos, M.; Harris, J. R. *Macromol. Rapid Commun.* **2001**, *22*, 271−273.
(6) Sanji, T.; Nakatsuka, Y.; Ohnishi, S.; Sakurai, H. *Macromolecules* **2000**, *33*, 8524−8526.
(7) Nardin, C.; Hirt, T.; Leukel, J.; Meier, W. *Langmuir* **2000**, *16*, 1035−1041.
(8) (a) Huang, H. Y.; Remsen, E. E.; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1999**, *121*, 3805−3806. (b) Zhang, Q.; Remesen, E. E.; Wooley, K. L. *J. Am. Chem. Soc.* **2000**, *122*, 3642−3651.
(9) (a) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 111−114. (b) Caruso, F.; Lichtenfeld, H.; Donath, E.; Mohwald, H. *Macromolecules* **1999**, *32*, 2317−2328. (c) Caruso, F.; Mohwald, H. *J. Am. Chem. Soc.* **1999**, *121*, 6039−6046.
(10) (a) Hotz, J.; Meier, W. *Langmuir* **1998**, *14*, 1031−1036. (b) Meier, W. *Chimia* **1999**, *53*, 214−215. (c) Sauer, M.; Streich, D.; Meier, W. *Adv. Mater.* **2001**, *13*, 1649−1651.
(11) Sun, L.; Crooks, R. M.; Chechik, V. *Chem. Commun.* **2001**, *4*, 359−360.
(12) Zha, L. S.; Zhang, Y.; Yang, W. L.; Fu, S. K. *Adv. Mater.* **2002**, *14*, 1090−1092.
(13) Okubo, M.; Konishi, Y.; Minami, H. *Colloid Polym. Sci.* **1998**, *276*, 638−642.
(14) Jang, J.; Ha, H. *Langmuir* **2002**, *18*, 5613−5618.
(15) (a) Liu, S. Y.; Zhang, G. Z.; Jiang, M. *Polymer* **1999**, *40*, 5499−5453. (b) Liu, S. Y.; Jiang, M.; Liang, H. J.; Wu, C. *Polymer* **2000**, *41*, 8697−8702.
(16) (a) Zhao, H. Y.; Gong, J.; Jiang, M.; An, Y. L. *Polymer* **1999**, *40*, 4521−4525. (b) Zhao, H. Y.; Liu, S. Y.; Jiang, M.; Yuan, X. F. *Polymer* **2000**, *41*, 2705−2709. (c) Yuan, X. F.; Zhao, H. Y.; Jiang, M.; An, Y. L. *Acta Chim. Sin.* **2000**, *58*, 118−121 (Chinese). (d) Yuan, X. F.; Jiang, M.; Zhao, H. Y.; Wang, M. *Langmuir* **2001**, *17*, 6122−6126.
(17) Wang, M.; Zhang, G. Z.; Jiang, M.; Chen, D. Y. *Macromolecules* **2001**, *34*, 7172−7178.
(18) Orfanou, K.; Topouza, D.; Sakellarion, G.; Pispas, S. *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 2454.
(19) Wang, M.; Jiang, M.; Ning, F. L.; Chen, D. Y. *Macromolecules* **2002**, *35*, 5980−5989.
(20) (a) Zhang, G. Z.; Niu, A. Z.; Peng, S. F.; Jiang, M. *Acc. Chem. Res.* **2001**, *34*, 249−256. (b) Liu, S. Y.; Hu, T. J.; Liang, H. J.; Jiang, M. *Macromolecules* **2000**, *33*, 8640−8643.
(21) (a) Li, M.; Jiang, M.; Zhu, L.; Wu, C. *Macromolecules* **1997**, *30*, 2201−2203. (b) Li, M.; Zhang, Y. B.; Jiang, M.; Zhu, L. *Macromolecules* **1998**, *31*, 6841−6844.
(22) Dan, Y.; Chen, S. Y.; Zhang, Y. F.; Xiang, F. R. *J. Polym. Sci., Polym. Phys.* **2000**, *38*, 1069−1077.
(23) (a) Yeom, C. K.; Lee, K. H. *J. Membr. Sci.* **1996**, *109*, 257−265. (b) Park, J. S.; Park, J. W.; Ruckenstein, E. J. *Appl. Polym. Sci.* **2001**, *82*, 1816−1823.
(24) Butun, V.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 12315−12316.
(25) Liu, F. T.; Liu, G. J. *Macromolecules* **2001**, *34*, 1302−1307.
(26) Ding, J. F.; Liu, G. J. *Macromolecules* **1998**, *31*, 6554−6558.
(27) Murthy, K. S.; Ma, Q. G.; Clark, C. G.; Remsen, E. E.; Wooley, K. L. *Chem. Commun.* **2001**, 773−774.
(28) Liu, X. Y.; Jiang, M.; Yang, S. L.; Chen, M. Q. *Angew. Chem.* **2002**, *41*, 2950−2953.
(29) (a) Noguchi, H.; Jodai, H.; Yamaura, K.; Matsuzawa, S. *Polym. Int.* **1998**, *47*, 428−432. (b) Lyoo, W. S.; Yeum, J. H.; Ghim, H. D.; Park, J. M. *Colloid Polym. Sci.* **2003**, *281*, 416−422.
(30) Kuang, M.; Duan, H. W.; Wang, J.; Chen, D. Y. *Chem. Commun.* **2003**, 496−497.
(31) Virezema, D. M.; Hoogboom, J.; Velonia, K.; Rowan, A. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 772−776.

MA035085D