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Organic/Inorganic Hybrid Vesicles Based on A Reactive Block Copolymer

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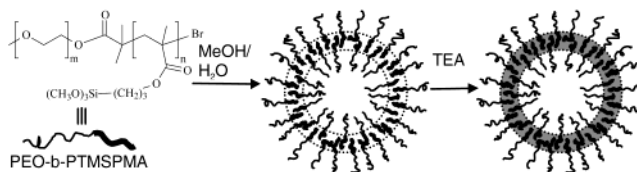
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In a selective solvent, block copolymers may form micelles by self-assembly.¹ Recently, a variety of different morphologies such as vesicles, rods, and tubules have been discovered and have drawn much attention.^{2–13} Particularly, vesicles are of major importance due to their potential applications for the encapsulation and release of guest species.^{3b,5b} Typical coil–coil block copolymers, which may produce vesicles in a solution, include polystyrene-*b*-poly(acrylic acid),^{2a–e} polystyrene-*b*-poly(ethylene oxide)^{2f} and polybutadiene (or polyethylethylene)-*b*-poly(ethylene oxide)⁴ etc.^{3,5–7} In certain cases, rod–coil,^{8,11} multiblock⁹ and also linear–dendritic hybrid copolymers¹⁰ may also form polymeric vesicles. If some repeat units in one of block copolymer segments bear reactive groups, the vesicle may be fixed by chemical cross-linking. Such hollow nanoparticles are shape-persistent due to their stability against environmental change. Thus far, only a few successful cross-linking reactions within the vesicle wall have been reported, such as photodimerization³ and polymerization.^{11–13} In addition, silica or polyorganosiloxane hollow nanoparticles have attracted some attention recently due to their stable inorganic structures. This kind of hollow particle was made mainly by sol–gel reaction on the surface of a colloid¹⁴ or of a micelle^{15,16} which acts as a template. An organic/inorganic hybrid vesicle was prepared by sol–gel of the micelle given by a lipid with alkoxyisilyl head, and its larger-scale aggregation was made through layer-by-layer self-assembly.¹⁷

In this communication, we present a simple approach to organic/inorganic hybrid hollow particles based on hydrolysis and polycondensation reactions within the polymeric vesicles preformed in a selective solvent. A novel amphiphilic diblock copolymer which bears reactive trimethoxysilane groups in one segment was used as the precursor of the hybrid vesicle (Scheme 1).

The diblock copolymer, poly(ethylene oxide)-*block*-poly(3-(trimethoxysilyl) propyl methacrylate) (PEO-*b*-PTMSPMA), was prepared by solution atom transfer radical polymerization (ATRP) of TMSPMA with CuBr/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine as catalyst and bromoisobutyryl monomethyl PEO₄₅ ester as a macroinitiator (PEO–Br) in anisole. The efficiency of macroinitiator was also confirmed by chain extension reactions with *n*-butyl methacrylate by ATRP. Size exclusion chromatography trace showed a monomodal peak with low polydispersity (Figure S1). Molecular weights obtained by ¹H NMR in CDCl₃ and monomer conversion agree well (Table S1). ²⁹Si NMR (Figure S2) of the copolymers gave one peak at δ –40.9 ppm, which was assigned to Si of the trimethoxysilyl group. The results reveal the successful preparation of the block copolymer.

The ¹H NMR spectrum in CD₃OD of a block copolymer, PEO₄₅-*b*-PTMSPMA₅₉, M_w/M_n 1.28, showed broad peaks assigned to the protons of PTMSPMA block (Figure S3A). Comparing to the one

Scheme 1. Approach to Hollow Hybrid Polymer Particles

obtained in CDCl₃, this broadening indicates that the block copolymer forms weak aggregates in methanol. When water was added into the solution, ¹H NMR analysis (Figure S3B) showed that the peaks corresponding to the protons of the PTMSPMA segments disappeared, while the peak of the PEO protons remained unchanged. Then a micelle solution was made by adding water dropwise into a block copolymer solution in methanol (1.0 g/l) until water content reached 55 wt %. A drop of such solution was taken out and freeze-dried for transmission electron microscopy (TEM) analysis. As shown in Figure S4, it revealed a vesicular morphology, and the diameter of vesicle is nearly 100 nm. The above results proved that PTMSPMA forms the wall of vesicles and PEO forms the corona. However, the vesicles at this time were easily deformed at dryness.

With a base catalyst, R–Si(OCH₃)₃ groups may be hydrolyzed easily into –Si(OH)₃, which are subsequently transferred into cross-linked polysilsesquioxane by polycondensation. Therefore a small amount of triethylamine (TEA) was added into the vesicle solution. The clear solution was stirred for several days, and then a drop of solution was taken for TEM analysis. As shown in Figure 1A, a hollow structure is clearly recognized. The contrast became much higher as compared with that without addition of TEA. Energy-dispersive X-ray (EDX) spectra in the field of TEM windows (Figure S5) gave signals of the expected elements, i.e., Si and O, which were from the vesicles. The plot of the statistical size distribution (Figure S6) of the particles obtained from TEM images gave a mean outer radius of 45.6 ± 12.1 nm. This dimension agrees with that of vesicles before addition of TEA (Figure S4). The wall thickness of the particles is 16.9 ± 2.5 nm and is highly uniform. A scanning electron microscopy (SEM) image (Figure 1B) of this sample shows mainly donut particles, which are believed to be collapsed vesicles due to very high vacuum during analysis. It also demonstrates there are solvent pools included inside vesicles.

Both dynamic light scattering (DLS) and static light scattering (SLS) analyses were performed during the process of vesicle formation as showed in Figure 1C, Figure S7, and S8, respectively. When water was added into the methanol solution, vesicles formed spontaneously as indicated by the measured hydrodynamic radius, $R_h = 42.2$ nm. Upon addition of TEA, essentially no change of the vesicle dimension was observed, i.e. $R_h = 42.6$ nm was found. The apparent diffusion coefficients (D_{app}) of both, the particles before and after addition of TEA, did not exhibit a significant dependence

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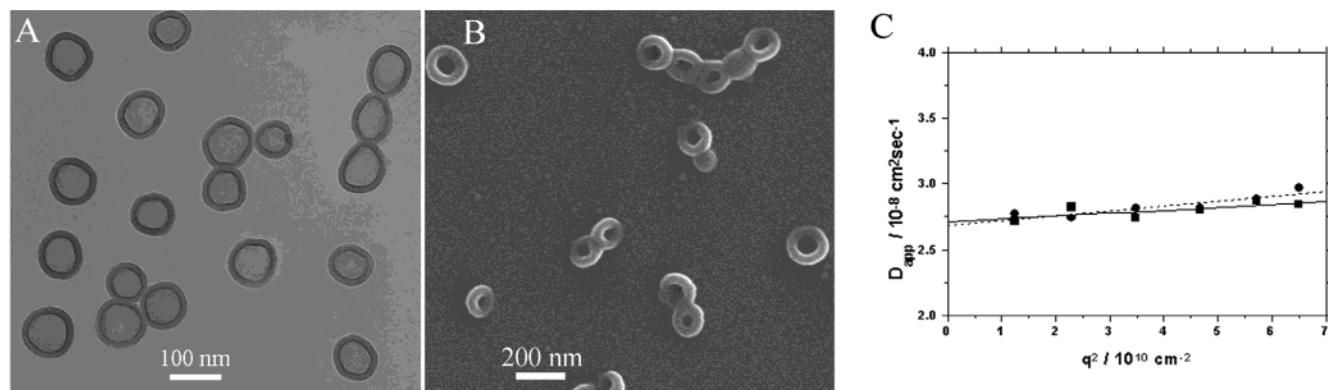


Figure 1. (A) TEM images of the vesicles after addition of 1.3 wt % TEA in methanol/water 45:55 (w/w) at a polymer concentration of 0.45 g/L and (B) SEM image of the particles. (C) The apparent diffusion coefficient D_{app} as a function of the scattering vector q^2 before (■, —, $R_{h,app} = 42.2$ nm) and after addition (●, ---, $R_{h,app} = 42.6$ nm) of TEA in the condition.

on the scattering vector. This demonstrates the low polydispersity and the spherical symmetry of the uncross-linked and cross-linked vesicles. Only the molar mass of the vesicles decreased upon cross-linking from 7.95×10^7 to 6.29×10^7 . This decrease of the molar mass is believed to originate from the loss of $-\text{O}_{0.5}\text{CH}_3$ groups during hydrolysis and cross-linking reactions. Assuming 100% hydrolysis and cross-linking reactions the theoretical molar mass is 5.99×10^7 , in good agreement with the experimentally observed value. With the molar mass of block copolymer obtained by ^1H NMR (16 700 Da), the aggregation number of uncross-linked vesicles is calculated to be $N_{agg} = 4760$. The light-scattering results strongly suggest that the aggregation number does not change during the cross-linking reaction, which is quite remarkable. From the radius, the area per block copolymer is estimated to be 7.7 nm^2 , which is a reasonable value for a polymeric vesicle.

The wall thickness (16.9 nm, Figure 1A) of the vesicles is slightly larger than the contour length of PTMSPMA₅₉ (14.8 nm) in qualitative agreement to the expected bilayer formation within the vesicle wall.^{18,19} The uniform wall thickness, no matter the size of the particle, also reveals the self-assembly nature of the vesicles. Since it is a bilayer structure, the wall thickness may be controlled by changing the length of PTMSPMA segments during polymer synthesis. Ongoing research studies also reveal that the hybrid vesicles could be produced under different conditions, such as different initial polymer concentration, 0.1–10 g/L, and different water content, 34–90 wt %. Other morphologies such rod, lamellae, sphere, and tubule were also observed and will be reported in forthcoming papers.

In summary, based on a new reactive block copolymer, vesicles were produced by adding water into a methanol solution of the block copolymer. With the introduction of a small amount of base as catalyst, organic/inorganic hybrid polymer vesicles with a polysilsesquioxane wall were synthesized. Thus, we have developed a new scaffold for preparing the novel hybrid vesicles which are easily extended to other particle morphologies. Owing to the reactivity of the precursor block copolymers and the convenient preparation of the robust hollow particles, this type of hybrid vesicle with a cross-linked wall may find applications for the encapsulation of dyes, catalysts, and other functional species as well as covalently binding guest molecules or other functional segments to be introduced to the vesicle wall.

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Supporting Information Available: Table S1, Figures S1–S8, and experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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