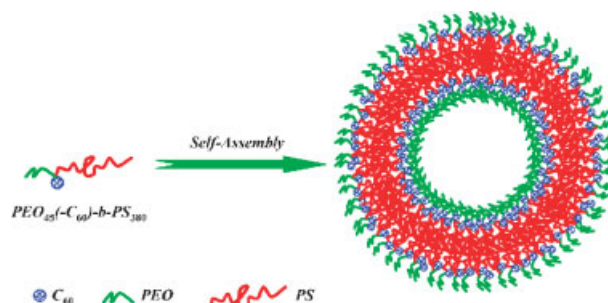


Fabrication of Fullerene-Containing Hybrid Vesicles via Supramolecular Self-Assembly of a Well-Defined Amphiphilic Block Copolymer Incorporated with a Single C₆₀ Moiety at the Diblock Junction Point^a

Xiaofeng Wang, Yanfeng Zhang, Zhiyuan Zhu, Shiyong Liu*

A well-defined amphiphilic block copolymer bearing a reactive azide group at the interface of two blocks, poly(ethylene oxide)(-azido)-*block*-polystyrene (PEO(-N₃)-*b*-PS), has been successfully synthesized via a combination of end group transformation and atom transfer radical polymerization (ATRP). The subsequent [3 + 2] cycloaddition reaction between PEO(-N₃)-*b*-PS and C₆₀ led to the facile preparation of PEO(-C₆₀)-*b*-PS, in which a single C₆₀ moiety was located at the diblock junction point. Fullerene-containing hybrid vesicles were then fabricated for the first time via the supramolecular self-assembly of PEO₄₅(-C₆₀)-*b*-PS₃₈₀ in aqueous solution using 1,4-dioxane as the cosolvent. The current example augurs well for tunable spatial ordering of desired moieties (fullerene or other functional nanoparticles) by employing block copolymers as self-organizing templates.



Introduction

C₆₀, a representative member of the fullerene family, has attracted ever-increasing attention since its discovery due

to the unique physical and chemical properties, endowing fullerene-containing materials with broad and promising applications in superconductors, ferromagnets, lubrications, photoconductors, catalysts, molecular medicines.^[1,2] However, the poor solubility and processibility of fullerenes greatly limit their practical applications. To solve this problem, the approach of incorporation of fullerenes into polymeric materials has been proposed.^[3–6]

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Among various fullerene-containing polymeric materials, fullerene-terminated telechelic polymers,^[7–9] i.e., polymers possessing one or two fullerene end groups have been extensively explored such that the location of fullerene moieties can be precisely known.^[10,11] Previous investigations in this respect focused on their aggregation behavior in solution^[12] and the bulk miscibility^[13] or

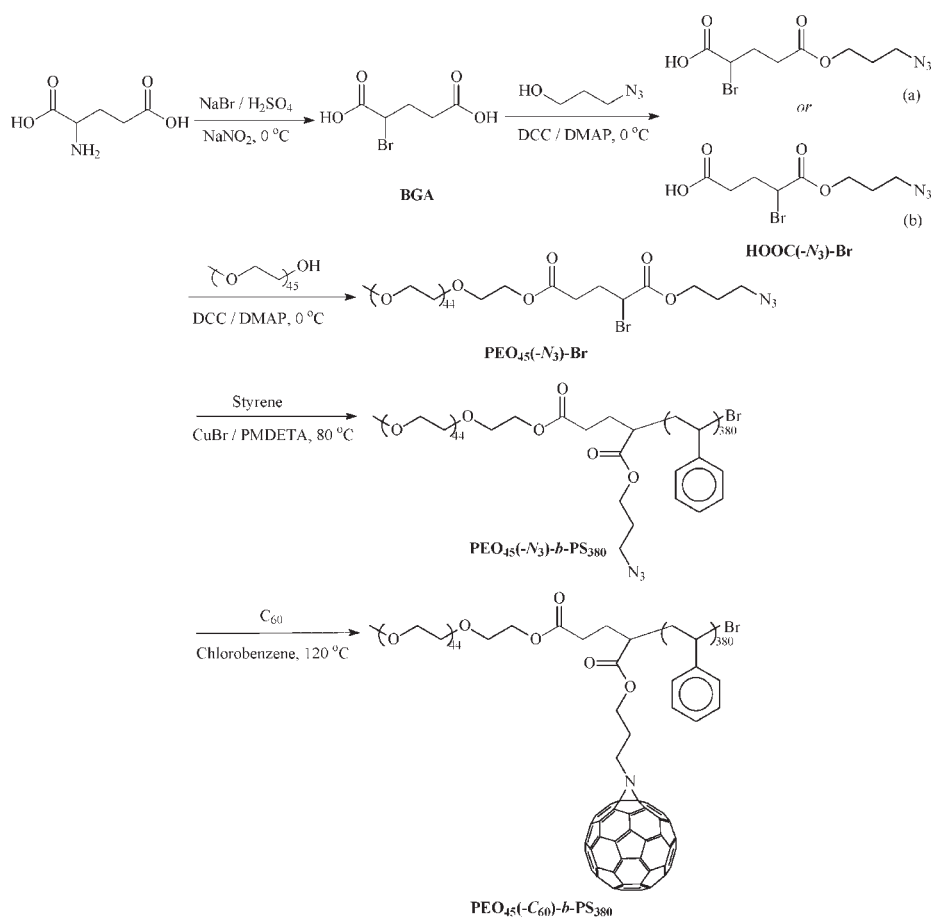
^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

mechanical properties.^[14] It should be noted for C₆₀-terminated polymers such as poly(ethylene oxide) (PEO),^[15] poly(acrylic acid) (PAA),^[16] poly(methyl methacrylate) (PMMA),^[17] and poly[methacrylic acid]-*block*-poly[2-(dimethylamino)ethyl methacrylate] (PMAA-*b*-PDMAEMA),^[18] they typically form nanoparticles with aggregated (i.e., less well-defined) C₆₀ cores in selective solvents of polymer chains.

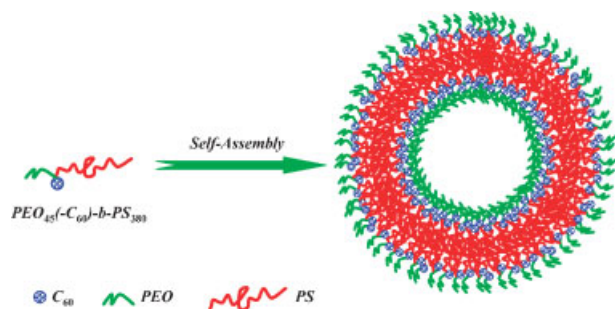
In certain circumstances, it is highly desirable to tune the spatial ordering of fullerene moieties within a polymer matrix in a more elaborate fashion (e.g., fullerene nanowires, nanotubes, and nanofilms), which can further broaden its practical applications in the fields of solar cells, molecular medicines, and superconductors. Using polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP), Ikkala and coworkers^[19] fabricated C₆₀-containing nanostructures via the combination of block copolymer self-assembly and charge-transfer complexation between fullerenes and P4VP segments.

Eisenberg and coworkers^[20] and Park and coworkers^[21] investigated the assembly of CdS or CdSe/ZnS quantum dots in vesicles or nanorods of PAA-based block copolymers. Just recently, Zubarev et al.^[22] reported a stimulating approach for controlling the interfacial assembly of nanoparticles (e.g., gold nanoparticles) in self-assembled nanostructures of block copolymers, starting from gold nanoparticles covalently multi-attached with V-shaped heteroarm chains. The supramolecular self-assembly of heteroarm star polymers leads to the precise location of gold nanoparticles at the core-shell interfaces of rod-like micelles or vesicles.

In this communication, we synthesized well-defined amphiphilic block copolymers incorporated with a single C₆₀ moiety at the diblock junction point, PEO₄₅(-C₆₀)-*b*-PS₃₈₀, via the combination of atom transfer radical polymerization (ATRP) and [3 + 2] cycloaddition between reactive azide residue and C₆₀ (Scheme 1). We demonstrated that PEO₄₅(-C₆₀)-*b*-PS₃₈₀ can self-assemble into



Scheme 1. Reaction schemes employed for the preparation of well-defined amphiphilic block copolymer incorporated with a single C₆₀ moiety at the diblock junction point, PEO₄₅(-C₆₀)-*b*-PS₃₈₀.



Scheme 2. Schematic illustration of the fabrication of fullerene-containing hybrid vesicles via the self-assembly of PEO₄₅(-C₆₀)-b-PS₃₈₀ in water.

fullerene-containing hybrid vesicles in aqueous solution, with C₆₀ presumably locating at the inner and outer PEO/PS interface within vesicle bilayers (Scheme 2).

Experimental Part

Materials

Styrene (99%, Sinopharm Chemical Reagent Co. Ltd.) was distilled under reduced pressure just prior to use. 3-Azidopropanol was prepared from 3-chloropropanol following literature procedures.^[23] Poly(ethylene glycol) mono-methyl ether (PEO₄₅-OH, $\bar{M}_{n,GPC} \approx 2000$, Aldrich), copper(I) bromide (CuBr, 98%, Aldrich), C₆₀ (99.5%, Aldrich), *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA, 98%, Aldrich), L-glutamic acid (99%, Sinopharm Chemical Reagent Co. Ltd.), sodium azide (NaN₃, 99%, Alfa Aesar), *N,N*-dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) were used as received.

Synthesis of 2-Bromoglutaric Acid (BGA)

To a solution of L-glutamic acid (50 g, 0.34 mol) and sodium bromide (188 g, 1.83 mol) in 1.0 M H₂SO₄ (0.5 L) cooled to 0 °C was added portionwise an aqueous solution of sodium nitrite (28 g, 0.406 mol). After stirring for 2 h at 0 °C, urea (4.5 g, 0.037 mol) was added to terminate the reaction. The aqueous phase was extracted by diethyl ether (3 × 100 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and then evaporated to dryness (27.5 g, yield: 36%).

¹H NMR (CDCl₃): δ = 10.10 (2H, COOH), 4.48 (1H, CHBrCOO), 2.70 (2H, CH₂COO), 2.56–2.28 (2H, CH₂CHBrCOO) (Figure S1, a).

Synthesis of HOOC(-N₃)-Br

BGA (16 g, 75.8 mmol), anhydrous diethyl ether (200 mL), and DCC (10.3 g, 50.0 mmol) were added into a dry 500 mL round-bottomed flask, the reaction mixture was cooled to 0 °C in an ice-water bath. A solution of 3-azidopropanol (5 g, 49.5 mmol) and DMAP (0.6 g, 4.9 mmol) in anhydrous diethyl ether (50 mL) was added dropwise over a period of 30 min under magnetic stirring. After the addition was completed, the reaction mixture was stirred at 0 °C for 1 h and

then at room temperature for 12 h. After removing insoluble *N,N'*-dicyclohexylurea via suction filtration, the solvent was removed under reduced pressure to afford the crude product. It was further dissolved in saturated aqueous solution of NaHCO₃ (100 mL) and filtered. The filtrate was extracted with dichloromethane (3 × 30 mL). The aqueous phase was adjusted to pH 1 and thoroughly extracted with dichloromethane. The combined organic phase was dried over anhydrous MgSO₄ and then evaporated to dryness, affording slightly yellow liquid (2.6 g, yield: 15%).

¹H NMR (CDCl₃): δ = 5.85 (1H, COOH), 4.48 (1H, CHBrCOO), 4.26 (2H, COOCH₂), 3.47 (2H, N₃CH₂), 2.63 (2H, CH₂COO), 2.56–2.28 (2H, CH₂CHBrCOO), 1.99 (2H, N₃CH₂CH₂) (Figure S1, b).

Synthesis of PEO₄₅(-N₃)-Br

PEO₄₅(-N₃)-Br macroinitiator was prepared via the esterification of PEO₄₅-OH with an excess of HOOC(-N₃)-Br in the presence of DCC and DMAP. A typical procedure was as follows: PEO₄₅-OH (3.4 g, 1.7 mmol) and HOOC(-N₃)-Br (1 g, 3.4 mmol) were dissolved in anhydrous dichloromethane (50 mL), and the reaction mixture was cooled to 0 °C, DCC (1.4 g, 6.8 mmol) and DMAP (0.16 g, 1.3 mmol) were added under magnetic stirring. The mixture was stirred at 0 °C for 1 h and then at room temperature for 12 h. After removing insoluble *N,N'*-dicyclohexylurea by filtration, PEO₄₅(-N₃)-Br was obtained as white powders by precipitation

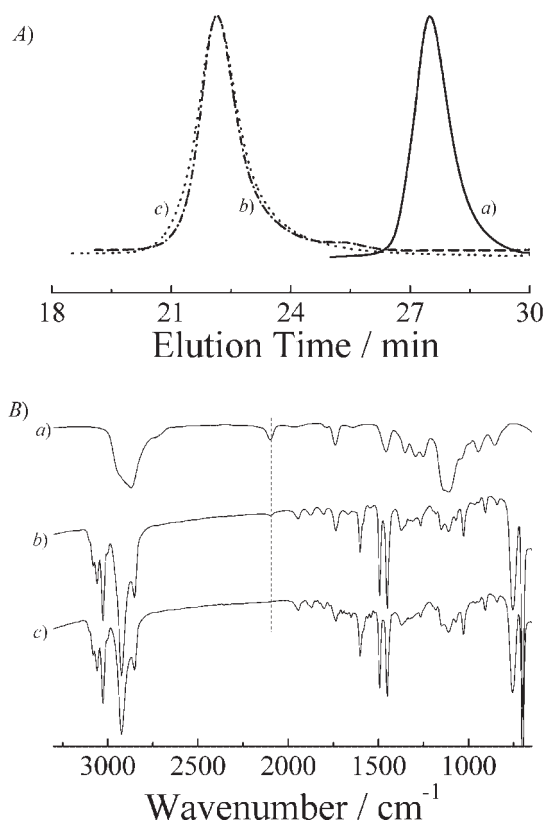


Figure 1. (A) THF GPC traces of (a) PEO₄₅(-N₃)-Br, (b) PEO₄₅(-N₃)-b-PS₃₈₀, and (c) PEO₄₅(-C₆₀)-b-PS₃₈₀; (B) FT-IR spectra of (a) PEO₄₅(-N₃)-Br, (b) PEO₄₅(-N₃)-b-PS₃₈₀, and (c) PEO₄₅(-C₆₀)-b-PS₃₈₀.

of the filtrate into excess diethyl ether (three times) and subsequent drying in a vacuum oven overnight at room temperature (3.3 g, yield: 85%).

^1H NMR (CDCl_3): $\delta = 4.48$ (1H, CHBrCOO), 4.40 (2H, $\text{COOCH}_2\text{-CH}_2\text{O}$), 4.26 (2H, $\text{COOCH}_2\text{CH}_2\text{CH}_2\text{N}_3$), 3.95 (2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.71 (4H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.47 (2H, N_3CH_2), 3.45 (3H, OCH_3), 2.63 (2H, CH_2COO), 2.56–2.28 (2H, $\text{CH}_2\text{CHBrCOO}$), 1.99 (2H, $\text{N}_3\text{CH}_2\text{CH}_2$) (Figure S1, c).

$\overline{M}_{n,\text{GPC}} = 1700$, $\overline{M}_w/\overline{M}_n = 1.10$ (Figure 1A, a).

Synthesis of $\text{PEO}_{45}(-\text{N}_3)\text{-}b\text{-PS}_{380}$

$\text{PEO}_{45}(-\text{N}_3)\text{-}b\text{-PS}_{380}$ was prepared via the ATRP of styrene in bulk at 80°C for 4 h using $\text{PEO}_{45}(-\text{N}_3)\text{-Br}$ as the macroinitiator. To a Schlenk flask equipped with a magnetic stirring bar, styrene (4.69 g, 45.0 mmol), $\text{PEO}_{45}(-\text{N}_3)\text{-Br}$ (0.228 g, 0.1 mmol), PMDETA (34 mg, 0.2 mmol), and CuBr_2 (2 mg, 0.01 mmol) were added. The flask was carefully degassed by three freeze-pump-thaw cycles, and then CuBr (27 mg, 0.19 mmol) was introduced under the protection of nitrogen flow. The flask was sealed under vacuum and placed in an oil bath thermostated at 80°C . After 4 h, the flask was quenched into liquid nitrogen to terminate the polymerization. The reaction mixture was diluted with THF and passed through a silica gel column to remove copper catalyst. After removing most of the solvent, the solution was precipitated into an excess of methanol. The precipitate was collected by filtration, and finally dried in a vacuum oven at room temperature for 24 h (3.7 g, yield: 74%).

^1H NMR (CDCl_3) $\delta = 7.24\text{--}6.28$ (5H, C_6H_5), 3.68 (4H, $\text{OCH}_2\text{CH}_2\text{O}$), 1.85 (1H, $\text{C}_6\text{H}_5\text{CH}$), 1.43 (2H, $\text{C}_6\text{H}_5\text{CHCH}_2$) (Figure S2).

$\overline{M}_{n,\text{GPC}} = 30\,800$, $\overline{M}_w/\overline{M}_n = 1.13$ (Figure 1A, b).

The actual degree of polymerization (DP) of PS block was calculated to be 380 according to the equation, $\text{DP} = [I_d \times 4 \times 45] / 5I_a$, where I_d and I_a were the integral areas of peaks d and a (^1H NMR spectrum, Figure S2), respectively. Thus, the obtained diblock copolymer bearing a reactive azide group was denoted as $\text{PEO}_{45}(-\text{N}_3)\text{-}b\text{-PS}_{380}$.

Synthesis of $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$

A 100 mL Schlenk flask was charged with $\text{PEO}_{45}(-\text{N}_3)\text{-}b\text{-PS}_{380}$ (0.418 g, 0.01 mmol), C_{60} (21.6 mg, 0.03 mmol), and chlorobenzene (40 mL). The reaction mixture was stirred at 120°C under N_2 atmosphere for 48 h. After removing the solvent, the crude product was dissolved in dichloromethane and filtered. The product was purified by repeated precipitation into n -hexane to remove unreacted C_{60} . $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ was dried in a vacuum oven at room temperature for 24 h, affording 0.377 g slightly brown powders (yield: 88.7%).

$\overline{M}_{n,\text{GPC}} = 31\,000$, $\overline{M}_w/\overline{M}_n = 1.17$ (Figure 1A, c).

Preparation of Fullerene-Containing Hybrid Vesicles

$\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ (5 mg) was dissolved in 1,4-dioxane (1 mL) by stirring for ≈ 4 h. To induce the supramolecular self-assembly of $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$, de-ionized water (6 mL) was slowly added via

a syringe pump ($0.2\text{ mL}\cdot\text{min}^{-1}$) to the polymer solution under vigorous stirring. After being slowly stirred at room temperature for 12 h, the dispersion was transferred to dialysis tubing (molecular weight cutoff, 14 kDa), and then dialyzed against de-ionized water for about 2 d to remove 1,4-dioxane.

Characterization

All ^1H NMR spectra were recorded on a Bruker AV300 NMR spectrometer (resonance frequency of 300 MHz for ^1H) operated in the Fourier transform mode. CDCl_3 was used as the solvent. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30°C). It used a series of three linear Styragel columns HT2, HT4, and HT5 at an oven temperature of 45°C . The eluent was THF at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$. A series of low polydispersity polystyrene standards were employed for calibration. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The spectra were collected over 64 scans with a spectral resolution of 4 cm^{-1} . Transmission electron microscopy (TEM) observations were conducted on a Philips CM 120 electron microscope at an acceleration voltage of 100 kV. High resolution transmission electron microscopy (HRTEM) observations were conducted on a JEOL-2010 electron microscope at an acceleration voltage of 200 kV. All samples for TEM and HRTEM observations were prepared by placing $10\ \mu\text{m}$ solution on copper grids coated successively with thin films of Formvar and carbon. Scanning electron microscopy (SEM) was carried out on a JSM-6700F electron microscope. A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632\text{ nm}$) as the light source was employed for dynamic and static laser light scattering (LLS) measurements. UV-Vis absorption spectra were recorded with a computer-controlled UNICO UV/VIS 2802 PCS spectrophotometer.

Results and Discussion

Synthesis of C_{60} -Containing Amphiphilic Diblock Copolymer

The general synthetic routes employed for the preparation of well-defined amphiphilic block copolymer incorporated with a single C_{60} moiety at the diblock junction point, $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$, is displayed in Scheme 1. The first step involved is the preparation of $\text{PEO}_{45}(-\text{N}_3)\text{-Br}$ macroinitiator via esterification reaction of $\text{PEO}_{45}\text{-OH}$ with a trifunctional core molecule, $\text{HOOC}(-\text{N}_3)\text{-Br}$. The ATRP of styrene using $\text{PEO}_{45}(-\text{N}_3)\text{-Br}$ as macroinitiator leads to the formation of $\text{PEO}_{45}(-\text{N}_3)\text{-}b\text{-PS}_{380}$ bearing a reactive azide group at the interface of PEO and PS blocks. Finally, the $[3 + 2]$ cycloaddition reaction between $\text{PEO}_{45}(-\text{N}_3)\text{-}b\text{-PS}_{380}$ and C_{60} leads to the facile preparation of well-defined $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$, in which a single C_{60} moiety was incorporated at the diblock junction point.

The trifunctional core molecule, $\text{HOOC}(-N_3)\text{-Br}$, was synthesized via the esterification of 3-azidopropanol with an excess of 2-bromoglutamic acid (BGA), which was prepared from L-glutamic acid. Figure S1 (a) in the supporting information shows the ^1H NMR spectrum of $\text{PEO}_{45}(-N_3)\text{-Br}$, together with the peak assignments. The integral ratio of peak *c* ($\delta = 4.3$ ppm, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{N}_3$) to that of peak *h* ($\delta = 3.7$ ppm, methylene protons of PEO) was calculated to be $\approx 1:90$, indicating that the degree of end-group transformation is nearly 100%. Moreover, FT-IR spectrum (Figure 1B, a) of $\text{PEO}_{45}(-N_3)\text{-Br}$ clearly revealed the appearance of two absorbance peaks at 2100 and 1739 cm^{-1} , which is characteristic of the terminal azido and carbonyl groups, respectively.

The ATRP of styrene in bulk using $\text{PEO}_{45}(-N_3)\text{-Br}$ as the macroinitiator led to the preparation of $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}$ bearing a reactive azide group at the diblock junction point (Scheme 1). In the first series of experiments, PEO-based macroinitiator prepared from $\text{PEO}_{45}\text{-OH}$ and 2-bromo-succinic acid was used. However, we found that it exhibited quite low initiating efficiency (less than 10%) during the bulk ATRP of styrene, which should be ascribed to bromine elimination reactions due to the presence of two neighboring α -carbons. In this communication, 2-bromoglutamic acid was employed for the esterification reaction of $\text{PEO}_{45}\text{-OH}$ (Scheme 1). GPC traces in Figure 1A clearly showed that the elution peak shifts to higher molecular weight after block copolymerization of styrene. The diblock copolymer elution peak is mono-modal and symmetric, confirming the complete consumption of $\text{PEO}_{45}(-N_3)\text{-Br}$ macroinitiator. The DP of the PS block was determined to be 380 by ^1H NMR (Figure S2). The obtained diblock copolymer was thus denoted as $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}_{380}$. The molecular weight and molecular weight distribution were characterized by GPC analysis in THF: $\overline{M}_{n,\text{GPC}} = 30\,800$, $\overline{M}_w/\overline{M}_n = 1.13$ (Figure 1A). FT-IR spectrum of $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}_{380}$ clearly reveals the presence of absorption peaks of PS block. Most importantly, the signal characteristic of azide group at 2100 cm^{-1} is clearly evident, indicating the presence of reactive azide group (Figure 1B).

The [3 + 2] cycloaddition reaction between organic azide and C_{60} has been extensively employed to prepare C_{60} -containing polymers. The reaction proceeds mainly through mono-addition, with little or no multi-addition products.^[6] Thus, reacting $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}_{380}$ with a two-fold excess of C_{60} leads to the facile preparation of well-defined $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$, with a single C_{60} moiety incorporated at the junction point. The reaction was conducted in chlorobenzene at 120°C . Figure 1B also shows the FT-IR spectrum of $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$. Compared to that of $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}_{380}$, we can clearly observe the complete disappearance of absorption peak characteristic of azide group at 2100 cm^{-1} . This suggests the successful

covalent attachment of C_{60} at the diblock junction point. GPC analysis (RI detector, THF eluent, Figure 1A) of $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ ($\overline{M}_{n,\text{GPC}} = 31\,000$, $\overline{M}_w/\overline{M}_n = 1.17$) reveals insignificant difference compared to the $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}_{380}$ precursor, implying that the fullerene moiety contributes little to the hydrodynamic volume of the diblock copolymer chains after covalent incorporation.

Figure S3 shows the UV spectra of pristine C_{60} (hexane), $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}_{380}$, and $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ in 1,4-dioxane. $\text{PEO}_{45}(-N_3)\text{-}b\text{-PS}_{380}$ exhibits an absorption maximum at 268 nm and is essentially transparent at wavelengths longer than 300 nm. On the other hand, pristine C_{60} in hexane exhibits three characteristic absorptions at 212, 256, and 330 nm. $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ in 1,4-dioxane exhibits two absorption maxima at 283 and 328 nm. Moreover, when an UV detector (330 nm) was used in GPC analysis in THF, a mono-modal and relatively symmetric elution peak at almost the same position as that from the RI detector was obtained. Thus, the above results further confirmed the successful covalent attachment of C_{60} to the diblock junction point.

Self-Assembly of $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ in Aqueous Solution

In aqueous solution, amphiphilic block copolymers can self-assemble into aggregates with morphologies from spheres, rods, lamellae, and vesicles, to large compound micelles. Among them, the self-assembly of asymmetric $\text{PEO}\text{-}b\text{-PS}$ block copolymers with relatively long PS blocks has been extensively studied, which can form complex nanostructures as described above.^[24] If C_{60} was covalently attached to the diblock copolymer, then the self-assembly of the block copolymer can lead to the ordered spatial arrangement of C_{60} molecules.

Fukuda coworkers^[25] studied the micellization behavior of C_{60} molecules covalently attached with double arms of PS, PVPh, and $\text{PS}\text{-}b\text{-PVPh}$, where PVPh is poly(4-vinylphenol). They found that in THF, $\text{C}_{60}\text{-}(\text{PS})_2$ can unimolecularly dissolve, whereas $\text{C}_{60}\text{-}(\text{PVPh})_2$ and $\text{C}_{60}\text{-}(\text{PS}\text{-}b\text{-PVPh})_2$ form multi-molecular micelles. In the current study, $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ bears a single C_{60} moiety at the diblock junction point; thus, block copolymer self-assembly in aqueous solution can be utilized to tune the ordering of C_{60} molecules.

As the DP of PS block is quite high compared to that of PEO block, $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ cannot directly dissolve in water. Thus, a cosolvent approach was employed to actuate the self-assembly process in aqueous solution. Water was slowly added into the $\text{PEO}_{45}(-\text{C}_{60})\text{-}b\text{-PS}_{380}$ solution in 1,4-dioxane under vigorous stirring, and a slightly turbid dispersion was obtained. After dialyzing out 1,4-dioxane, the morphologies of self-assembled

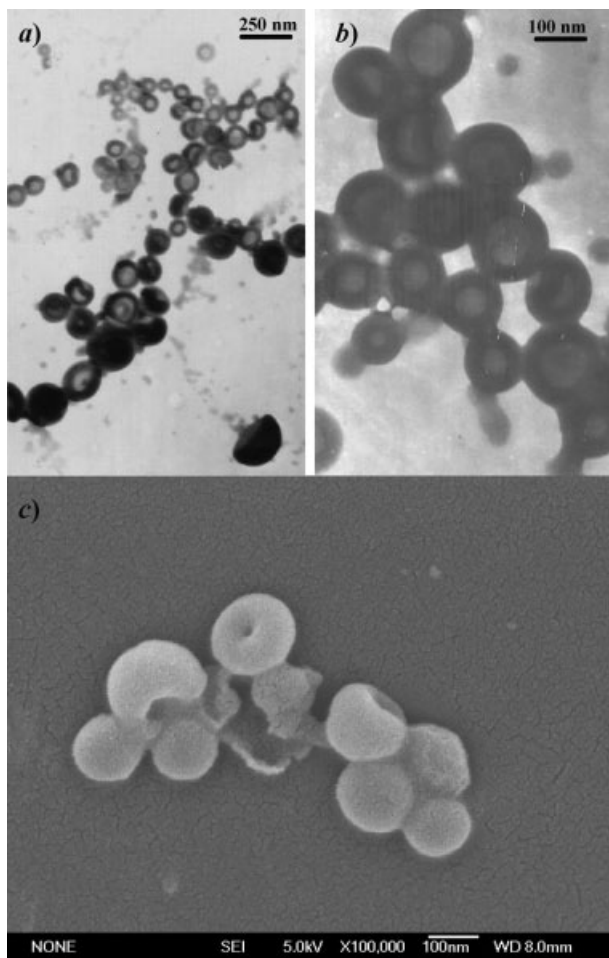


Figure 2. Typical TEM (a, b) and SEM (c) images of fullerene-containing hybrid vesicles self-assembled from PEO₄₅(-C₆₀)-*b*-PS₃₈₀ in aqueous solution using 1,4-dioxane as the cosolvent.

aggregates were observed by TEM and SEM (Figure 2). From Figure 2a and b, we can clearly observe typical vesicular nanostructures with diameters in the range of 60–150 nm, and most of the vesicles were unilamellar ones. We can also see from Figure 1b that the wall thickness is quite uniform (≈ 30 nm), and it is almost independent of vesicle sizes. Figure 2c shows a typical SEM image of the self-assembled aggregates, revealing relatively uniform spherical nanoparticles. Most importantly, we can also observe some broken and collapsed shells. This again confirms the presence of hollow spheres. A schematic illustration of the self-assembly of PEO₄₅(-C₆₀)-*b*-PS₃₈₀ in aqueous solution was shown in Scheme 2. As PEO is hydrophilic and PS is highly hydrophobic, the observed fullerene-containing hybrid vesicle shells should consist of hydrophobic PS and well-solvated PEO chains, with the latter attaching to vesicle walls at the outer and inner region. As a single C₆₀ moiety is located at the diblock junction point, we tentatively speculate that C₆₀ should spatially arrange

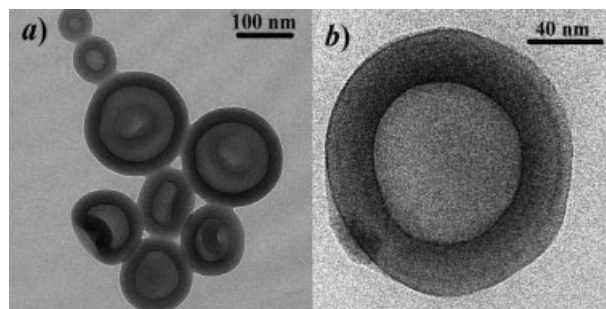


Figure 3. Typical HRTEM images of fullerene-containing hybrid vesicles self-assembled from PEO₄₅(-C₆₀)-*b*-PS₃₈₀ in aqueous solution using 1,4-dioxane as the cosolvent.

into double corona shapes within self-assembled vesicles (Scheme 2).

HRTEM was further employed to observe the actual morphologies of hybrid vesicles (Figure 3). Again we can clearly observe hollow nanostructures and most of them are unimolecular ones. A magnified image (Figure 3b) clearly shows that the outer and inner interface of vesicle walls exhibit much higher contrast compared to other regions, possibly reflecting the spatial ordering of C₆₀ molecules as shown in Scheme 2. However, as the size of spherical C₆₀ is so small (≈ 0.7 nm), we cannot directly observe the exact locations C₆₀ molecules within self-assembled vesicles.

Dynamic and static LLS were then used to characterize the C₆₀-containing hybrid vesicles. Figure S4 shows typical hydrodynamic radius distributions, $f(R_h)$, of vesicles self-assembled from PEO₄₅(-C₆₀)-*b*-PS₃₈₀. R_h is in the range of 50–240 nm, with an average hydrodynamic radius, $\langle R_h \rangle$, of ≈ 100 nm and a vesicles size distributions (μ_2/Γ^2) of 0.12, respectively. Static LLS revealed an apparent molar mass ($\bar{M}_{w,app}$) of 2.1×10^8 g · mol⁻¹ and an average radius of gyration, $\langle R_g \rangle$, of 97 nm. The average aggregation number, N_{agg} , of PEO₄₅(-C₆₀)-*b*-PS₃₈₀ chains inside each hybrid vesicles is then calculated to be ≈ 4 300. As one block copolymer chain contains only one C₆₀ moiety, the number of C₆₀ molecules per hybrid vesicle can thus be obtained (≈ 4 300).

Conclusion

We demonstrated that well-defined amphiphilic block copolymer incorporated with a single C₆₀ moiety at the diblock junction point, PEO(-C₆₀)-*b*-PS, can be prepared via a combination of ATRP and cycloaddition reaction between azide and fullerenes. The obtained C₆₀-containing amphiphilic diblock copolymer can self-assemble in aqueous solution into fullerene-containing hybrid vesicles, which were preliminarily characterized by TEM, HRTEM, and LLS. Block copolymer self-assembly has been success-

fully utilized to tune the spatial ordering of C₆₀, which might further broaden the application scopes of fullerenes. By changing the relative block lengths of PEO and PS blocks, we expect that nanostructures with more complex morphologies embedded with orderly arranged C₆₀ can be obtained, and further studies are currently undergoing in our laboratory.

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