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Preparation and Self-Assembled Toroids of Amphiphilic Polystyrene-C_{60}-Poly(*N*-isopropylacrylamide) Block Copolymers

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ABSTRACT: An amphiphilic polystyrene-C_{60}-poly(*N*-isopropylacrylamide) (PS-C_{60}-PNIPAAm) block copolymer was successfully prepared through atom transfer radical polymerization, demonstrating the facile approach to obtain two-armed polymer-C_{60} nanohybrids, in which the C_{60} molecules bond to two different polymeric arms. The chemical structures were characterized with Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The PS-C_{60}-PNIPAAm block copolymer exhibited self-assembly in chloroform into toroids. The self-assembly of PS-C_{60}-PNIPAAm, which is usually not observed with diblock copolymers and polymer-C_{60} nanohybrids, could be attributed to the selective solubility and the strong interaction between C_{60} molecules.

Introduction

Polymer-bound buckminsterfullerene (C_{60}), which provides a combination of the advantages and attractive properties of C_{60} and polymers, has been widely studied.[1−20] One approach to prepare this kind of hybrid is end-capping C_{60} to polymer chains through addition reactions.[2,3,15] Polymer chains possessing C_{60} were also obtained by means of copolymerization using a C_{60}-containing monomer[4] or polymer modification.[8] The reactive species of controlled free radical polymerization were reactive toward C_{60}.[5,6] These reactions have been widely applied to preparation of C_{60} end-bonded polymer hybrids.[5−8,10,11,13] C_{60} was also bound to the end of an amphiphilic block copolymer to introduce amphiphilic character to the polymer-C_{60} hybrids.[13] In addition, multiarmed polymer-C_{60} hybrids with C_{60} as a core were reported.[12,16,17] C_{60} with two well-defined polymer arms, including polystyrene (PS), poly(*p*-vinylphenol) (PVP), and PS-PVP diblock copolymer, was prepared through nitroxide-controlled free radical polymerization.[5] Wang and coworkers[12] reported C_{60}-anchored two-armed poly(*tert*-butylacrylate). Four-armed poly(vinyl alcohol)-C_{60} hybrids[16] and star polyfluorene-C_{60} hybrids[17] were also prepared. However, the arms attached on C_{60} molecules are the same, which limits the diversity of molecular design and functions of the hybrid materials. Therefore, this work reports the first approach to incorporate different arms onto one C_{60} molecule to bring new architecture and properties to the polymer-C_{60} hybrid materials. Two different polymeric arms, PS and poly(*N*-isopropylacrylamide) (PNIPAAm) were attached to C_{60} to produce PS-C_{60}-PNIPAAm block copolymer. The presence of PS and PNIPAAm arms leads to amphiphilic PS-C_{60}-PNIPAAm.

In selective solvents, amphiphilic block copolymers self-assemble to different kinds of supramolecular nanostructures, including micelles, vesicles, and helices.[21−25] Most of the systems were based on diblock copolymers. Recently, the aggregates of triblock copolymers, which are more complex than diblock copolymers, received more attention. Jiang and coworkers[26] reported the formation of ring-shaped morphology from an ABA amphiphilic triblock copolymer in a dilute solution. Wooley et al.[27] then demonstrated that a toroidal morphology could be the dominant assembly in an amphiphilic triblock copolymer possessing anionic segments. Addition of a divalent cation of 2,2′-(ethylenedioxy)diethylamine into the dilute solution of the triblock copolymer enhanced the formation of toroidal assembly. Formation of hollow micelles was reported by Lee et al.[28] with a rod−coil−rod triblock copolymer solution in a selective solvent for the coil segments. Transitions between toroids and other assemblies were observed with dumbbell-shaped rod amphiphiles possessing different lengths of hydrophobic alkyl chains.[29] Other toroidal nanostructures were observed with stereocomplexation of block copolymers.[30] Biohybrid triblock copolymers were also reported to exhibit self-assembled toroidal architectures.[31] In addition, studies focused on the relationships between toroidal structures and phase diagrams.[32] The effect of composition controls of polymers on the supramoelcular structures was also examined,[33] extending the understanding about the formation of toroidal nanostructures.

C_{60}-anchored polymers also exhibit self-assembly behavior. Two-armed C_{60}-$(PS)_2$, C_{60}-$(PVP)_2$, and C_{60}-$(PS\text{-}PVP)_2$ formed stable micelles in dilute tetrahydrofuran (THF) solutions.[5] C_{60}-poly(*tert*-butylmethacrylate) formed a self-induced large compound vesicle in mixed solvents composing a good solvent for both C_{60} and poly(*tert*-butylmethacrylate) and a poor solvent for C_{60}.[7] Tam and co-workers[10] also reported similar results with C_{60}-poly(methyl methacrylate) in ethyl acetate/decalin mixed solvent. Another example is micelles from double C_{60}-capped triblock copolymer.[13] The above reports suggested that C_{60} itself could be considered as a "block" unit in the C_{60}-polymer hybrid because of solubility difference, to enhance the induction of their self-assembly. Moreover, the strong interaction between C_{60} molecules might also contribute to induce the microphase separation of C_{60}-polymer hybrids in solutions. In addition to the preparation and characterization of amphiphilic PS-C_{60}-PNIPAAm, we also report the first demonstration that the prepared PS-C_{60}-PNIPAAm hybrid self-assembles into toroidal nanostructures.

Experimental Section

Materials. Styrene (99%, Acros) was purified by distillation under reduced pressure before use. *N*-Isopropylacrylamide (NIPAAm, 99%, Acros), C_{60} (Aldrich), copper(I) bromide (CuBr, Strem), 2,2-dipyridyl (Acros), and 1-bromoethylbenzene (BEB, Tokyo Chem. Ind.) of reagent grade were used as received. Reagent-grade solvents were purchased from Tedia Chem. Co. THF was dried with sodium by refluxing and distilled out before use. Purification on chlorobenzene was dried with calcium chloride and distillation. Chloroform was refluxed with calcium chloride and distilled out before use.

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Characterization. FTIR spectra were obtained with a Perkin-Elmer Spectrum One FTIR. The molecular weights of polymers were measured with a gel permeation chromatography (GPC) composed of a Laboratory Alliance series III pump, an RI 2000 refractive index detector, and a PLgel Mixed D column with polystyrene gel particles of 5 μm in diameter as stationary phase. The linear range of molecular weights for PLgel Mixed D column in measurement is 200−400 000 g/mol. The elution was performed using THF with a flow rate of 1.0 mL/min at 40 °C. Monodispersed styrene samples were used as standards for molecular weight calibration. An X-ray photoelectron spectroscopy (XPS) analysis was conducted using a VG Microtech MT-500 ESCA (British) using a Mg Kα line as a radiation source. The background pressure in the analytical chamber was 1.0×10^{-5} Pa. Scanning and transmission electron microscopy (SEM and TEM) observations were performed with a Hitachi 4800N SEM and a Hitachi H-7500 TEM, respectively. The samples in solutions were placed on 200-mesh copper grids for TEM observation. Atomic force microscopy (AFM) was observed with a Seiko SPI3800N AFM.

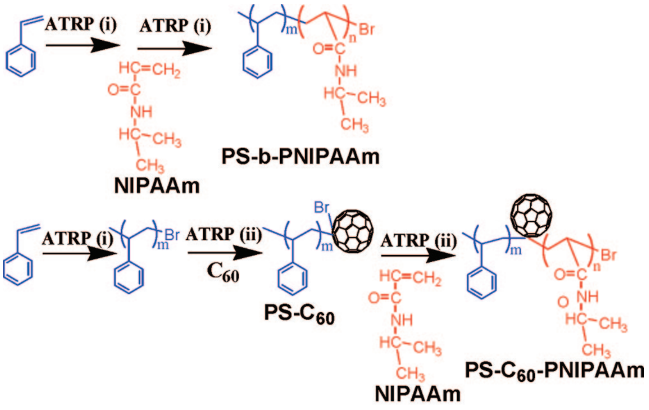
Preparation of PS-C_{60}-PNIPAAm Nanohybrid Copolymer. Bromine end-capped polystyrene (PS-Br) was prepared by atom transfer radical polymerization (ATRP) using BEB as an initiator.[34] Styrene (10.4 g, 100 mmol), CuBr (0.14 g, 1.0 mmol), and 2,2′-dipyridyl (0.468 g, 3 mmol) were charged in a 20-mL round-bottom flask. After being purged with dry argon for 15 min, BEB (0.185 g, 1.0 mmol) was added to the reaction system. The reaction system was frozen with liquid nitrogen, degassed with vacuum, and filled with dried nitrogen The process was repeated three times. The system was then reacted at 80 °C for 24 h. The reaction mixture was diluted with THF (20 mL). PS-Br was obtained with precipitation from excess methanol and purified by repeated dissolution−precipitation process three times. The product yield was 80%. The number-average molecular weight (M_n) and the polydispersity index (PDI = M_w/M_n) of PS-Br measured with GPC were 9100 g/mol and 1.25, respectively.

C_{60} (0.1 g, 0.14 mmol), CuBr (0.025 g, 0.175 mmol), 2,2′-dipyridyl (0.08 g, 0.52 mmol), and 5 mL of chlorobenzene were charged into a 20-mL reactor. After being purged with dry argon for 15 min, PS-Br (0.55 g, 0.06 mmol) was added to the reaction system. The reaction system was frozen with liquid nitrogen, degassed with vacuum, and filled with dried nitrogen. The process was repeated three times and then reacted at 120 °C for 24 h. The reaction mixture was poured into excess methanol, purified by repeated dissolution−precipitation process three times, and then dried under vacuum. Unreacted C_{60} was taken out by dissolving the polymers in tetrahydrofuran and filtrating. PS-Br was separated from PS-C_{60} by its different solubility in benzene/methanol.[5] The final product of PS-C_{60} was obtained (0.57 g, yield: 92%). The M_n and PDI of PS-C_{60} measured with GPC were 10 300 g/mol and 1.33, respectively.

PS-C_{60} was then used as a macroinitiator for ATRP of NIPAAm. NIPAAm (2.0 g, 19.8 mmol), CuBr (0.025 g, 0.175 mmol), and 2,2′-dipyridyl (0.08 g, 0.52 mmol) were dissolved in chlorobenzene (5 mL), and the solution was charged into a 20-mL round-bottom flask. After being purged with dry argon for 15 min, PS-C_{60} (0.15 g, 0.015 mmol) was added to the reaction system. The reaction system was frozen with liquid nitrogen, degassed with vacuum, and filled with dried nitrogen. The process was repeated three times and then reacted at 120 °C for 24 h. The reaction mixture was poured into excess methanol, purified by repeated dissolution−precipitation process three times, and then dried under vacuum to give the product PS-C_{60}-PNIPAAm (0.16 g, yield: 50%). The M_n and PDI of PS-C_{60}-PNIPAAm measured with GPC were 22 200 g/mol and 1.66, respectively.

Results and Discussion

Scheme 1. Synthesis of Amphiphilic Polystyrene-*b*-Poly(*N*-isopropylacrylamide) (PS-*b*-PNIPAAm) and PS-C_{60}-PNIPAAm Hybrid Materials



Atom transfer radical polymerization (ATRP) (i) tetrahydrofuran, CuBr, 2,2-dipyridyl, 25 °C, 48 h

Atom transfer radical polymerization (ATRP) (ii) Chlorobenzene, CuBr, 2,2-dipyridyl, 120 °C, 24 h

In this work, we report the first preparation of C_{60}-polymer hybrids possessing two different arms via ATRP. The active species of the growing chain ends of ATRP are reactive toward C_{60} readily.[6] This reaction has been demonstrated to be an effective approach to prepare C_{60}-capped polymer chains.[7−14] First, PS-Br prepared from ATRP was reacted with C_{60} molecules to result in PS-C_{60} nanohybrid under an ATRP condition (using CuBr as a catalyst and 2,2′-dipyridyl as a ligand). In this reaction, C_{60} abstracted a bromine atom from the PS-Br chain end to form a new C−Br group on C_{60}. The formed C−Br group could serve as an initiating site for further ATRP.[34] That is to say, PS-C_{60} is a kind of macroinitiator for ATRP. Using NIPAAm as a monomer, we grew a PNIPAAm chain to PS-C_{60} through ATRP. The resulting product was coded as PS-C_{60}-PNIPAAm. The synthesis routes and the chemical structures of the polymer-C_{60} nanohybrids are shown in Scheme 1. The M_n and PDI of PS-C_{60} were 10 300 g/mol and 1.33, respectively (Figure 1). The molecular weight of PS-C_{60} is similar to that measured for PS-Br, indicating that the presence of C_{60} groups does not attribute to the hydrodynamic radius of PS-C_{60} in THF.[5] The M_n of PS-C_{60}-PNIPAAm is 22 200 g/mol, which is larger than that of PS-C_{60}, demonstrating the formation of PNIPAAm chain bonded to PS-C_{60}. However, the PDI value found with of PS-C_{60}-PNIPAAm is 1.66. The relatively large PDI value of PS-C_{60}-PNIPAAm suggests the portion of large molecular weight detected in GPC analysis could be contributed from molecular aggregation of PS-C_{60}-PNIPAAm. Although C_{60}-anchored two-armed polymers have been reported,[5,12] PS-C_{60}-PNIPAAm is the first example of a polymer-C_{60} hybrid possessing two different polymer arms sharing a C_{60} unit.

Figure 2 shows the UV−vis spectra of PS-C_{60}-PNIPAAm and PS-*b*-PNIPAAm in cyclohexane. Both samples exhibited similar absorption spectra in the wavelength lower than 300 nm. The characteristic absorption peaks of C_{60} at 272 nm could not be distinguished because of overlapping with the absorption peaks of PS-*b*-PNIPAAm. However, the presence of C_{60} in PS-C_{60} and PS-C_{60}-PNIPAAm nanohybrid copolymers could be demonstrated with the absorption peak at 330 nm in the UV−vis absorption spectra of PS-C_{60}-PNIPAAm, as PS-*b*-PNIPAAm block copolymer did not show absorption at around 330 nm.[6] The absorption intensity of C_{60} in PS-C_{60}-PNIPAAm was somewhat less than that observed for PS-C_{60}, indicating the decrease in the C_{60} concentration of the polymer-C_{60} nanohybrids because of the incorporation of some PNIPAAM portion after NIPAAm copolymerization. On the other hand, no absorption peaks were observed with PS-C_{60}-PNIPAAm in the wavelength of about 430 nm. This result might suggest that PS-C_{60}-PNIPAAm is a 1,2-substituted derivative, rather than a

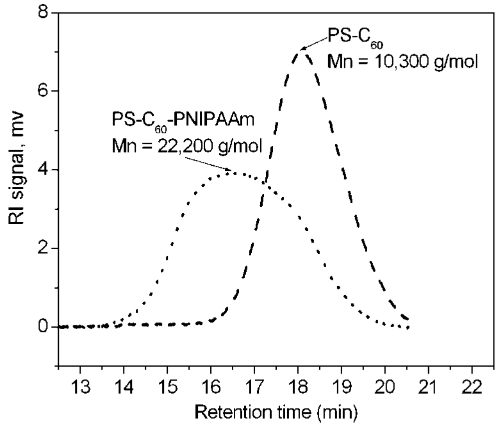


Figure 1. Gel permeation chromatograms of PS-C$_{60}$ and PS-C$_{60}$-PNIPAAm.

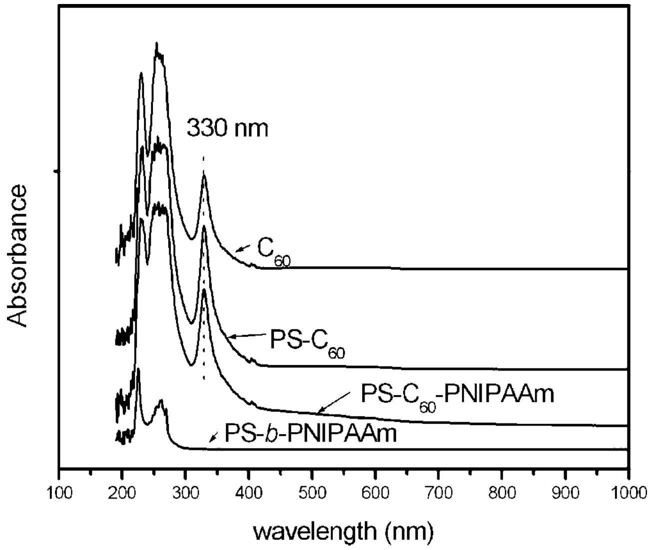


Figure 2. UV−visible spectra of C$_{60}$, PS-C$_{60}$-PNIPAAm, and PS-*b*-PNIPAAm. The absorption at about 330 nm indicates the presence of C$_{60}$ of PS-C$_{60}$-PNIPAAm.

1,4-substituted derivative.[2] The result is coincident to the proposed reaction mechanism between PS-Br and C$_{60}$. The chemical structures of the organic parts of the PS-C$_{60}$-PNIPAAm nanohybrid copolymers were characterized with FTIR and XPS. As shown in Figure 3, the phenyl groups of PS chains in PS-C$_{60}$ exhibit the absorption peaks at 1492 and 1600 cm^{-1} in their FTIR spectrum. These two absorption peaks also appear in the FTIR spectrum of PS-C$_{60}$-PNIPAAm. In addition, the appearance of the absorption peaks at 1646 (−C=O) and 1256 cm^{-1} (C−N) in the FTIR spectrum of PS-C$_{60}$-PNIPAAm demonstrates the success of incorporation of PNIPAAm chains to the nanohybrid copolymer. Figure 4 shows the XPS spectra of the nanohybrid copolymers. The chemical structure of PS-C$_{60}$ was characterized with the absorption peaks at 284.6 (C=C) and 285.0 eV (C−H, C−C) in the C$_{1s}$ core spectrum. The appearance of the Br$_{3d}$ signal at 71 eV demonstrates that the bromine atoms transfer to C$_{60}$ in the reaction between PS-Br and C$_{60}$. In addition, the acryamide groups of PS-C$_{60}$-PNIPAAm exhibit the absorption peaks at 286.3 (C−O) and 287.1 eV (C(=O)−N) in its C$_{1s}$ core spectrum. Moreover, the presence of PNIPAAm chains is also demonstrated with the appearance of the N$_{1s}$ absorption peak at 402 eV, as this N$_{1s}$ signal is not observed with PS-C$_{60}$.

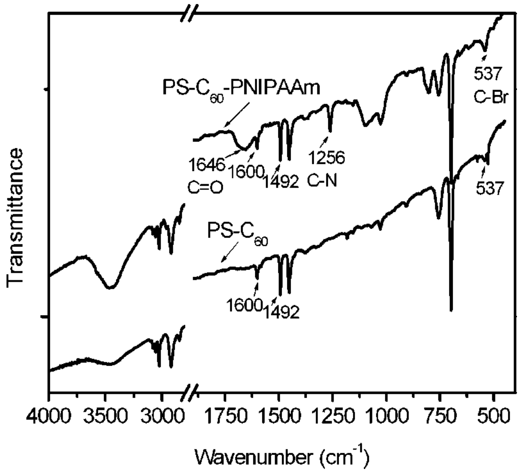


Figure 3. FTIR spectra of PS-C$_{60}$ and PS-C$_{60}$-PNIPAAm.

PS-C$_{60}$-PNIPAAm nanohybrids were dissolved in chloroform, which is a good solvent for PS but a poor solvent for C$_{60}$ and PNIPAAm. The morphologies of the PS-C$_{60}$-PNIPAAm in the chloroform solutions at various concentrations were observed with TEM (Figure 5). PS-C$_{60}$-PNIPAAm gathers together in the solution with a concentration of 0.1 mg/mL. Some bubblelike structure formed in the solution, just like what can be seen with soap in water. Some ringlike structures appeared in the solution with a concentration of 0.5 mg/mL. The shapes and sizes of the ring structures were not uniform. Well-isolated, self-assembled toroids were observed with the solution at a concentration of 1 mg/mL. The toroids merged with each other in high-concentration solutions, as observed with the PS-C$_{60}$-PNIPAAm solutions in concentrations of 1.5−2.0 mg/mL. The sizes of the toroids formed in the 1.0 mg/mL solution were in a range from about 200 to 1000 nm. The ring figuration could be attributed to the self-assembly of C$_{60}$, appearing as the relatively dark drawing in the TEM micrograph. The corona at the outer ring figuration might represent the presence of a polymer region. The structures of toroids suggest that the self-assembly of PS-C$_{60}$-PNIPAAm might be contributed from the interaction between C$_{60}$ molecules. Moreover, PS-*b*-PNIPAAm block copolymer in chloroform formed a homogeneous solution. No toroids could be observed with the PS-*b*-PNIPAAm/chloroform solution. The above facts further support the contribution of C$_{60}$ to the formation of toroids.

The solutions (1 mg/mL) of polymers and polymer-C$_{60}$ nanohybrids were spin-coated on silicon surface (3000 rpm) and dried under ambient condition to examine their morphologies in dry state. PS-C$_{60}$ formed a smooth dense film on silicon surface. A microphase separation appeared with the film due to C$_{60}$ aggregation (Figure 6a). Similarly, a condensed film with a microphase-separated sea−island structure was observed with PS-*b*-PNIPAAm block copolymer (Figure 6b). PS-C$_{60}$-PNIPAAm exhibited different morphology with formation of self-assembled toroidal structures on silicon surface (Figure 6c). The diameters of the rings were still not unique and in a range from about 200 to 1000 nm. The ring widths of the toroids were about 30 nm, no matter how big the toroids, indicating that the toroids in different diameters composed similar molecular assembly in the rings. The arrows in Figure 6c indicate that some rings formed from fusions of two or three toroids, suggesting that the large toroids might form ring fusions of some smaller toroids. Figure 6d shows the AFM image of the PS-C$_{60}$-PNIPAAm toroids. The heights of the rings measured with AFM were about 37 nm, which is similar to the ring widths of the toroids. Therefore, the toroids were like a bangle rather than a hollow cylinder.

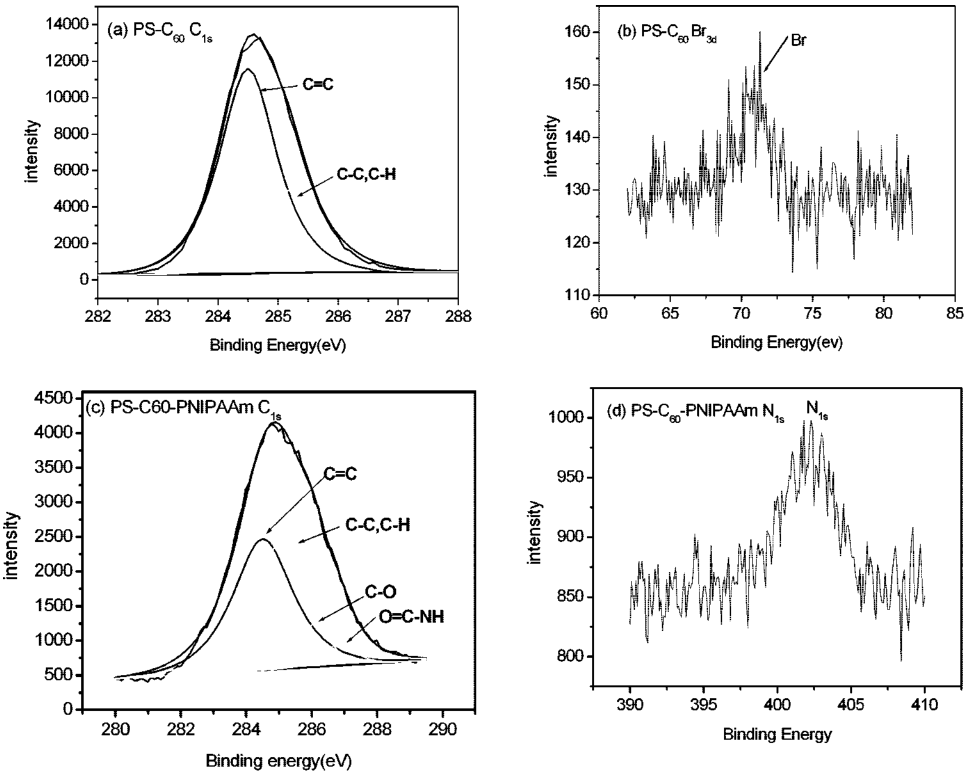


Figure 4. XPS analysis on the polymer-C_{60} nanohybrids. (a) C_{1s} core spectrum of PS-C_{60}, (b) Br_{3d} core spectrum of PS-C_{60}, (c) C_{1s} core spectrum of PS-C_{60}-PNIPAAm, and (d) N_{1s} core spectrum of PS-C_{60}-PNIPAAm.

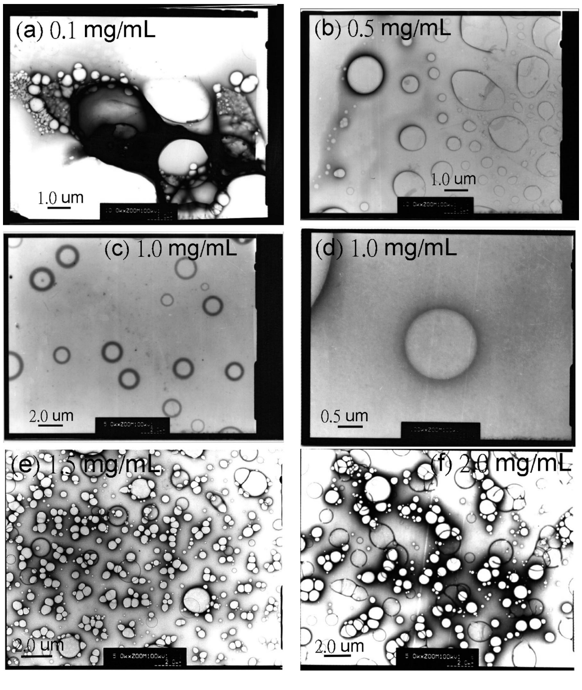


Figure 5. TEM images of PS-C_{60}-PNIPAAm in chloroform solutions at concentrations of (a) 0.1 mg/mL, (b) 0.5 mg/mL, (c) 1.0 mg/mL, (d) 1.0 mg/mL in high amplification, (e) 1.5 mg/mL, and (f) 2.0 mg/mL.

Self-assembly of C_{60}-poly(*tert*-butyl methacrylate) (C_{60}-*b*-P*t*BMA) in mixed solvents has been reported.[7] C_{60}-*b*-P*t*BMA formed core−shell micelles, which further assembled to large compound vesicles (LCVs). However, self-stand LCVs in dry states were not obtained. The formation of toroids in dilute solutions of triblock copolymers in a mixture of selective solvents was proposed through an end-to-end/end-to-midpoint connection mechanism of linear cylinders.[27] However, mixed selective solvents were not employed in this work. Intermediates of the transition between cylinders-to-toroids were also not observed for PS-C_{60}-PNIPAAm in chloroform. Therefore, the toroidal structures of PS-C_{60}-PNIPAAm should form from their self-assemblies. PS-C_{60}-PNIPAAm could be considered as a rod−coil block copolymer. In chloroform, PNIPAAm blocks associate by the hydrophilic interaction as cores, and the PS blocks form the corona layer.[28] In addition, the strong interaction between C_{60} molecules prevents the aggregation of PNIPAAm chains and stablizes the ring structures under solvent evaporation. The role of C_{60} in the formation of toroidal structures of PS-C_{60}-PNIPAAm is also demonstrated as the solution of PS-PNIPAAm diblock copolymer in chloroform only formed sea−island phase separation on silicon surface.

Formation of toroidal structures of PS-C_{60}-PNIPAAm is solvent-dependent, as they were found in chloroform but not in chlorobenzene (Figure 7a). Chlorobenzene is a good solvent for C_{60} but a poor solvent for the polymers. PS-C_{60}-PNIPAAm molecules therefore aggregate together in chlorobenzene. In addition, while a mixture of chloroform/methanol (v/v 1/1) was utilized as a solvent, PS-C_{60}-PNIPAAm formed particles rather than toroids in the solutions (Figure 7b). As methanol is a good solvent for PNIPAAm, the presence of methanol disturbs the amphiphilic characteristic of PS-C_{60}-PNIPAAm in the mixed solvent. Therefore, the morphology of PS-C_{60}-PNIPAAm in the chloroform/methanol mixture is similar to what observed with PS-C_{60} (Figure 6a). In addition, Wooley and co-workers[33] demonstrated that the formation of toroidal morphology with triblock copolymers is dependent on polymer composition and sequence. The chain length effect of PS-C_{60}-PNIPAAm on the toroids formation was preliminarily examined with another PS-C_{60}-PNIPAAm sample, which has a relatively low molecular weight of 10 600 g/mol and was prepared from a PS-Br sample having a molecular weight of 7200 g/mol. SEM image of this

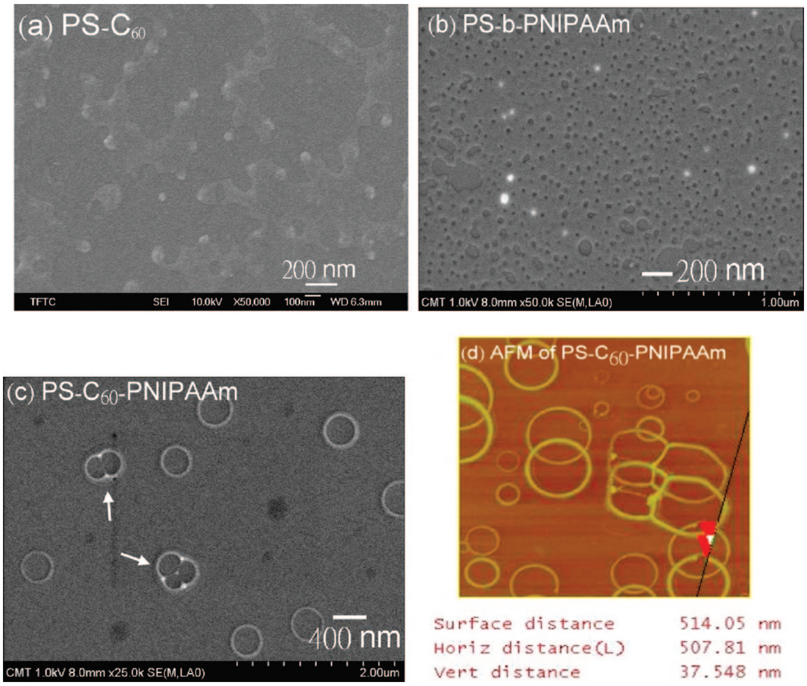


Figure 6. SEM images of (a) PS-C_{60}, (b) PS-b-PNIPAAm, and (c) PS-C_{60}-PNIPAAm morphologies from their solutions in chloroform (1 mg/mL) spin-coating on silicon surface. (d) AFM image of PS-C_{60}-PNIPAAm toroids. The heights of the rings are about 37.5 nm.

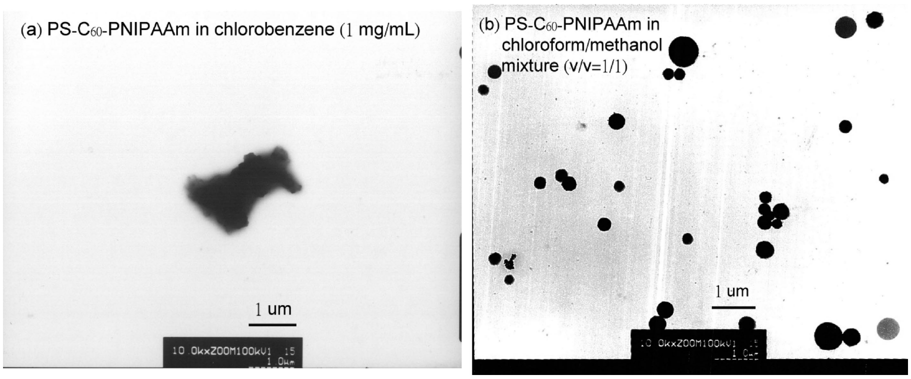


Figure 7. TEM images of PS-C_{60}-PNIPAAm in (a) chlorobenzene and (b) chloroform/methanol (v/v: 1/1) solutions of 1 mg/mL.

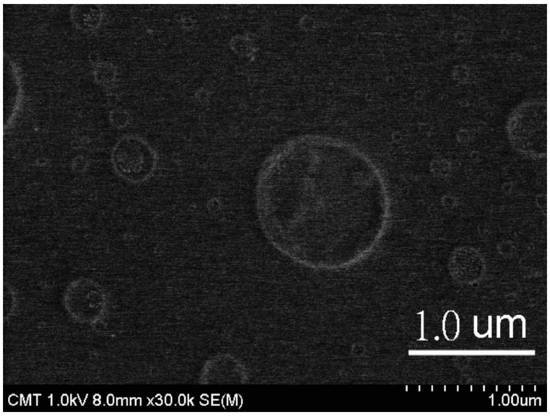


Figure 8. SEM image of low molecular weight sample (10 600 g/mol) of PS-C_{60}-PNIPAAm.

low molecular weight sample is show in Figure 8, in which the torodial structure is still observed. The result indicates that the formation of torodial morphology could be found with PS-C_{60}-PNIPAAm copolymers in wide range compositions. However, further investigation is required.

Conclusions

In conclusion, we reported the facile approach to prepare two-armed polymer-C_{60} nanohybrids, in which the C_{60} molecule bonds to two different polymeric arms. The synthesis route was demonstrated with the preparation of the amphiphilic organic/inorganic PS-C_{60}-PNIPAAm block copolymer through ATRP. The nanohybrid exhibits self-assembly into toroidal structure in chloroform and in dried state. The strong interaction between C_{60} molecules is believed to attribute the prevention of PNIPAAm chain aggregation and stablization of the ring structures under solvent evaporation. Self-assembly behaviors of C_{60}-polymer nanohybrids by means of the interaction between C_{60} molecules are worthy for further studies.

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