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Preparation and Toroid Formation of Multiblock Polystyrene/C_{60} Nanohybrids

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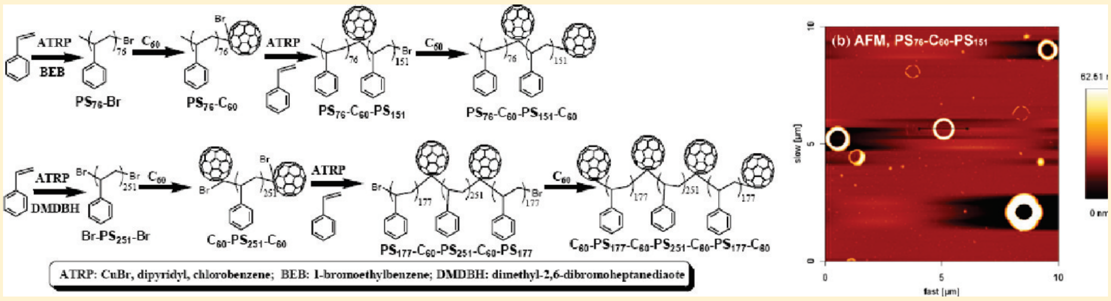
ABSTRACT:



Multiblock polystyrene/C_{60} nanohybrid block copolymers have been prepared with sequential atom transfer radical polymerization using 1-bromoethylbenzene and dimethyl-2,6-dibromoheptanediaote as monofunctional and difunctional initiators, respectively. The polystyrene/C_{60} nanohybrids have been characterized with gel permeation chromatography and UV−vis spectrometry. The self-assembly behaviors of the polystyrene/C_{60} nanohybrids have been studied. The multiblock polystyrene/C_{60} nanohybrids tend to form toroids in chloroform and to form spherical aggregates in the mixture of chloroform and methanol. Moreover, selective polystyrene/C_{60} nanohybrids also form toroids in cyclohexane. The toroids shapes and formation mechanism in cyclohexane are different from those in chloroform. The polystyrene/C_{60} nanohybrids are a new group of materials for toroids preparation and application.

■ INTRODUCTION

Creation and control of the curvature and topology is important and interesting for the preparation of novel and functional soft materials. In contrast to the low-molecular-weight surfactants, macromolecular amphiphiles received much research attention of morphological assemblies.[1] The chain structures of the amphiphilic polymers play an important role in their self-assembly behaviors.[2] As a result, triblock copolymers, compared to diblock copolymers, are expected to demonstrate assembled aggregates having novel morphologies and properties. Some theoretical and simulated studies revealed the formation of ring-shaped aggregates in wormlike micellar systems[3−5] and opened the window to the scope of toroidal structures from amphiphilic block copolymers. Nevertheless, the theoretical prediction told that the presence of toroidal structures might be very difficult as their regime of formation was very narrow.[5] Jiang's group found that increases in the annealing time help the transformation of the amphiphilic polystyrene (PS)/poly(4-vinylpyridine) (PVP) ABA triblock copolymer from a rod-shaped structure to a ring-shaped structure in a dioxane/water mixture solution.[6] The effect of shear flow rate on the formation of ring-shaped micelles of the same triblock copolymer was also examined.[7] Formation of the ring-shaped micelles at different flow rates performed via different pathways. Wang and Jiang further demonstrated the temperature-induced reversible transformation between toroidal and cylindrical micelles of the polystyrene poly(4-vinylpyridine) triblock copolymer.[8] Pochan and co-workers[9] reported the toroidal micelles of poly(acrylic acid-*b*-methyl acrylate-*b*-styrene) by mimicking the self-assembly behavior of DNA induced by multivalent counterions. Dilute polymer solutions and slow evaporation of tetrahydrofuran in the aqueous solutions are essential for eventual toroid formation. The research group also studied the effect of block copolymer compositions and sequence on the formation of toroidal morphology of triblock copolymers.[10] Formation of toroids could be only observed with specific copolymers. A successive paper reported with the same group demonstrated the mechanisms for formation of toroidal micelles from two different morphological precursors, i.e., mixture of cylindrical and spherical micelles and disklike micelles.[11] Lee and co-workers[12] observed the formation of toroidal micelles of dumbbell-shaped rod amphiphiles in aqueous solution. The lengths of hydrophobic alkyl chains of the amphiphiles significantly affect the self-assembled morphologies transforming from closed spheres to toroids.[13] Reynhout et al.[14] prepared biohybrid triblock copolymers and found the copolymers possessing certain block lengths of

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synthetic polymers might form toroidal structures in solutions. Nevertheless, the toroidal micelles in the reported systems are not pure and coexist with micelles in other structures. Chang and co-workers prepared pure toroidal micelles of highly uniform in shape and size from polyisoprene-*b*- poly(2-vinylpyridine) copolymer in a tetrahydrofuran (THF)/ethanol solvent mixture.[15]

In addition to the amphiphilic block copolymers, C_{60}-anchored polymers also exhibit self-assembly behavior. For examples, C_{60} hybrids having two polymer arms, C_{60}-(PS)$_2$, C_{60}-(PVP)$_2$, and C_{60}-(PS-PVP)$_2$, formed stable micelles in dilute THF solutions.[16] C_{60}-poly(*tert*-butyl methacrylate) and C_{60}-poly(methyl methacrylate) formed self-induced large compound vesicle in mixed solvents composing a good solvent for both C_{60} and polymeric arms and a poor solvent for C_{60}.[17,18] Another example is micelles from double-C_{60}-capped triblock copolymer.[19] C_{60} moieties act as a "block" unit in the C_{60}-polymer hybrid. The strong interaction between C_{60} molecules also induces the microphase separation of C_{60}-polymer hybrids in solutions. Hence, C_{60}-polymer hybrids are reasonably expected to form self-assembled toroidal micelles. In the previous paper,[20] we prepared amphiphilic polystyrene-C_{60}-poly(*N*-isopropylacryamide) (PS-C_{60}-PNPAAm) hybrids and reported the first example of toroidal micelles from C_{60}-polymer hybrids. As PS-C_{60}-PNIPAAm hybrids formed toroids in chloroform (1 mg/mL), the amphiphilic feature of the nanohybrid could not be the key factor to induce the formation of toroidal micelles. Hence, the contribution of C_{60} to the formation of toroids is intersting and worthy of study. In this work, various multiblock C_{60}-PS hybrid materials and their self-assembly behaviors have been studied. We have found that toroids are the general and dominant morphological strctures for the multiblock C_{60}-PS hybrids in chloform. This result is surprsingly different from what reported to amphiphilic block copolymers, as the formation of toroidal micelles has been restricted to specific polymer solution systems.[2−15]

■ EXPERIMENTAL SECTION

Materials. Styrene (99%) was purchased from Acros Chem. Co. and was purified by distillation under reduced pressure prior to use. C_{60} was purchased from Aldrich Chem. Co. and used as received. Copper(I) bromide (CuBr, Strem), 2,2-dipyridyl (Acros), 1-bromoethylbenzene (BEB, Tokyo Chem. Ind.), and dimethyl-2,6-dibromoheptanediaote (DMDBH, Aldrich) in reagent grade were used as received. Reagent grade solvents were purchased form from Tedia Chem. Co. Tetrahydrofuran (THF) was dried with sodium by refluxing and distilled out prior to use. Purification on chlorobenzene was drying with calcium chloride and distillation. Chloroform was refluxed with calcium chloride and distilled out prior to use.

Characterization. Fourier transform infrared (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 LAB-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. UV−vis absorption spectra were recorded with a Perkin-Elmer Lamda 25 UV−vis spectrophotometer. 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} Nanohybrids Using a Monofunctional ATRP Initiator. Bromine end-capped polystyrene (PS-Br) was prepared through atom transfer radical polymerization (ATRP) using a monofunctional initiator BEB.[20] The number-average molecular weight (M_n) and the polydispersity index (PDI = M_w/M_n) of PS-Br measured with GPC were 8000 g/mol (PS$_{76}$-Br) and 1.21, 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 purging with dry argon for 15 min, PS$_{76}$-Br (0.55 g, 0.06 mmol) was added into the reaction system. The reaction system was frozen with liquid nitrogen, degassed with vacuum, and filled up with dried nitrogen The process was repeated for three times and then reacted at 120 °C for 24 h. The reaction mixture was poured into excess methanol and purified by repeated dissolution−precipitation process for three times and then dried under vacuum. Unreacted C_{60} was taken out by dissolving the polymers in tetrahydrofuran and filtration. PS$_{76}$-Br was separated from PS-C_{60} by their different solubility in benzene/methanol. The final product of PS$_{76}$-C_{60} was obtained (0.48 g, yield 86%).

The bromine atom of PS$_{76}$-Br transferred to C_{60} of PS$_{76}$-C_{60} after the C_{60} end-capping reaction. Hence, PS$_{76}$-C_{60} was used as a macroinitiator for further ATRP of styrene. The product of PS$_{76}$-C_{60}-PS$_{151}$ was obtained.

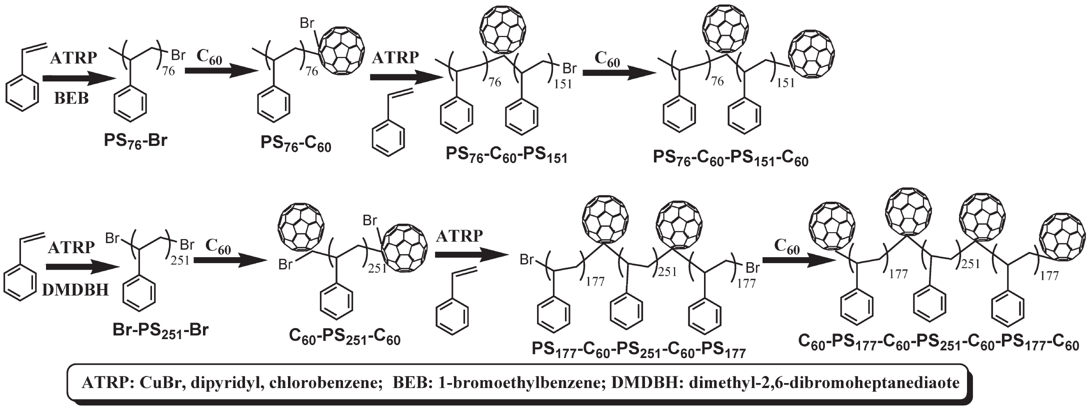
End-capping PS$_{76}$-C_{60}-PS$_{151}$ with C_{60} was performed with the same manner of preparation of PS$_{76}$-C_{60} from PS$_{76}$-Br. The product was coded as PS$_{76}$-C_{60}-PS$_{151}$-C_{60}.

Preparation of PS/C_{60} Nanohybrids Using a Difunctional ATRP Initiator. Telechelic bromine end-capped polystyrene (Br-PS-Br) was prepared through ATRP using a difunctional initiator DMDBH. The obtained PS has a M_n of about 26 200 g mol^{-1}, and a PDI of 1.19, and is coded as Br-PS$_{251}$-Br. With the method mentioned above, end-capping Br-PS$_{251}$-Br with C_{60} resulted in the product of C_{60}-PS$_{251}$-C_{60}; a PS chain has C_{60} at two ends. C_{60}-PS$_{251}$-C_{60} was utilized as a macroinitiator for ATRP of styrene to result in the product of PS$_{177}$-C_{60}-PS$_{251}$-C_{60}-PS$_{177}$ and the C_{60} end-capped analogue of C_{60}-PS$_{177}$-C_{60}-PS$_{251}$-C_{60}-PS$_{177}$-C_{60}.

■ RESULTS AND DISCUSSION

C_{60}-polymer nanohybrids have been prepared through atom transfer radical polymerization (ATRP).[20] The synthetic methodology has been utilized in this work to prepare multiblock PS/C_{60} nanohybrids. As shown in Scheme 1, PS chains possessing one and two end-capped bromine groups have been prepared through ATRP of styrene using BEB and DMDBH as the initiators, respectively. The bromine end-capped polystyrenes (PS$_{76}$-Br and Br-PS$_{251}$-Br) were reacted with C_{60} molecules under an ATRP condition to incorporate C_{60} moieties to the PS chain ends. In the previous work,[20] we have demonstrated that the bromine atom of the PS chain ends would transfer to C_{60} in the reaction. The transferred bromines could serve as the initiating cites of ATRP from the C_{60} moieties. Hence, the PS/C_{60} nanohybrids could be used as macroinitiators for ATRP of styrene. As a result, another PS chains grown from the C_{60} moieties has been incorporated to the PS/C_{60} nanohybrids. Some multiblock PS/C_{60} nanohybrids have been prepared in this work through repeating the ATRP of styrene and the end-capping reaction of C_{60} (Scheme 1). Generally, the chain lengths of polymers prepared with ATRP are controllable by the relationships between reaction conversions and reaction time. However, different initiating/catalytic systems would result in different reaction rates. Hence, in this work we only demonstrate the

Scheme 1. Preparation of Multiblock Polystyrene/C_{60} Nanohybrids through Sequential Atom Transfer Radical Polymerization Using Monofunctional (BEB) and Difunctional (DMDBH) Initiators



ATRP: CuBr, dipyridyl, chlorobenzene; BEB: 1-bromoethylbenzene; DMDBH: dimethyl-2,6-dibromoheptanediaote

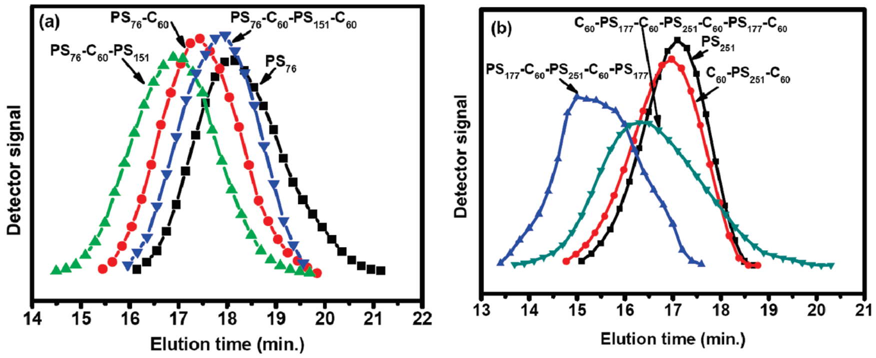


Figure 1. Gel permeation chromatograms of multiblock polystyrene/C_{60} nanohybrids prepared with (a) monofunctional and (b) difunctional initiators.

sequential ATRPs but not control the chain lengths of polystyrenes. The PS/C_{60} nanohybrids have been preliminarily characterized with FTIR. They all show spectra similar to the spectrum recorded with PS, which exhibits the absorption peaks of the phenyl groups at 1492 and 1600 cm^{-1}.

Figure 1 shows the GPC chromatograms of the multiblock PS-C_{60} nanohybrids. With use of BEB as the monofunctional initiator for styrene ATRP, PS chains having a number-averaged molecular weight (M_n) of about 8000 g mol^{-1} (PS_{76}-Br) has been obtained. Incorporation of C_{60} to PS_{76} slightly increases the molecular weight to about 9300 g mol^{-1} (PS_{76}-C_{60}). The molecular weight of C_{60} is 720 g mol^{-1}, which is smaller than the molecular weight difference between PS_{76}-C_{60} and PS_{76}. The deviation could be attributed to the globularity morphology of C_{60}. Sequential ATRP of styrene using PS_{76}-C_{60} as a macroinitiator grows another PS chains to PS_{76}-C_{60}, consequently increasing the molecular weight of PS_{76}-C_{60}-P_{151} to 21 300 g mol^{-1}. The increase in the molecular weight provides direct evidence supporting to the growth of another PS chain to PS-C_{60} through the sequential ATRP of styrene. End-capping PS_{76}-C_{60}-PS_{151} with C_{60} results in PS chains (PS_{76}-C_{60}-PS_{151}-C_{60}) possessing two C_{60} moieties. Nevertheless, the molecular weight of PS_{76}-C_{60}-PS_{151}-C_{60} measured with GPC is about 11 800 g mol^{-1}. The measured molecular weight is much lower than the expected value. As the PS chains should not break down in the end-capping reaction of C_{60}, the molecular weight deviation of GPC analysis could be attributed to the conformational change of PS_{76}-C_{60}-PS_{151}-C_{60} in the elution solvent (THF). The strong interaction between the two C_{60} moieties of PS_{76}-C_{60}-PS_{151}-C_{60} collapses the polymer chains and makes the nanohybrid form aggregates like unimolecular micelles in THF, consequently to reduce the retention time in GPC measurements. The molecular weights of the other series of PS/C_{60} nanohybrids are also obtained with GPC analysis. With use of the difunctional initiator of DMDBH, the obtained polymer (Br-PS_{251}-Br) has a number-averaged molecular weight of about 26 200 g mol^{-1}, which is higher than the molecular weight of PS_{76}-Br prepared with the monofunctional initiator of BEB. After end-capped with C_{60}, sequential ATRP of styrene using C_{60}-PS_{251}-C_{60} as a macroinitiator extends the polymer chain length. The obtained PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177} nanohybrid has a molecular weight up to 60 600 g mol^{-1}. Moreover, the C_{60}-capped PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177} still exhibit a relatively lower molecular weights in GPC analysis, as the nanohybrid chains collapse in THF due to the strong interaction between C_{60} moieties. Table 1 collects the ATRP reaction conditions for the preparation of the PS/C_{60} nanohybrids and their molecular weights. Except for PS_{76}-C_{60}-PS_{151}-C_{60} and C_{60}-PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177}-C_{60}, the GPC data for most samples could be still reliable.[7,17] For the samples showing curious elution time in GPC measurements, the weight-averaged molecular weights of the sample might be obtained with a static light scattering measurement. Nevertheless, the

Table 1. Preparation Conditions and Molecular Weights of Polystyrene/C_{60} Nanohybrids

sample	polymerization conditions for ATRP of styrene (molar ratio)	M_n[a] (g mol^{-1})	M_w/M_n[a]
PS_{76}	styrene (100); BEB (1); CuBr (1); 2,2′-dipyridyl (3) 80 °C, 17 h	8 000	1.21
PS_{76}-C_{60}		9 300	1.34
PS_{76}-C_{60}-PS_{151}	styrene (100); PS_{76}-C_{60} (1); CuBr (1); 2,2′-dipyridyl (3) 80 °C, 24 h	21 300	1.39
PS_{76}-C_{60}-PS_{151}-C_{60}		11 800[b]	1.28
PS_{251}	styrene (100); DMDBH (1); CuBr (1); 2,2′-dipyridyl (3) 80 °C, 20 h	26 200	1.19
C_{60}-PS_{251}-C_{60}		23 600	1.27
PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177}	styrene (1000); C_{60}-PS_{251}-C_{60} (1); CuBr(1); 2,2′-dipyridyl (3) 80 °C, 24 h	60 600	1.37
C_{60}-PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177}-C_{60}		50 000[b]	1.48

[a] Data from GPC measurements. [b] Molecular aggregation into unimolecular micelles to reduce the elution time in GPC measurements.

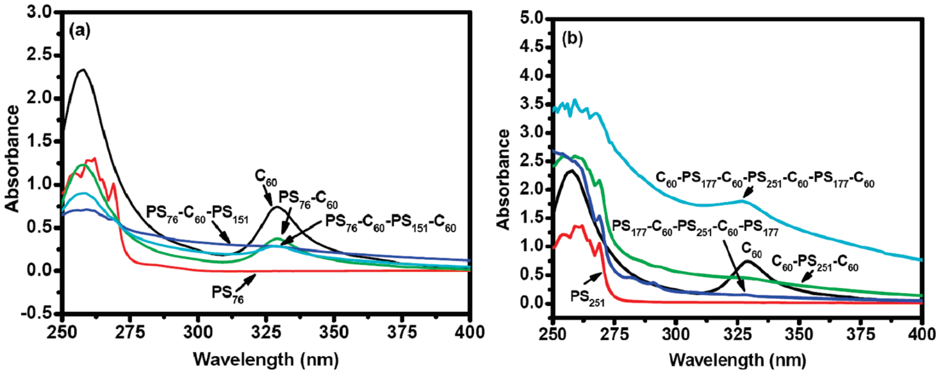


Figure 2. UV−vis spectra of multiblock polystyrene/C_{60} nanohybrids prepared with (a) monofunctional and (b) difunctional initiators.

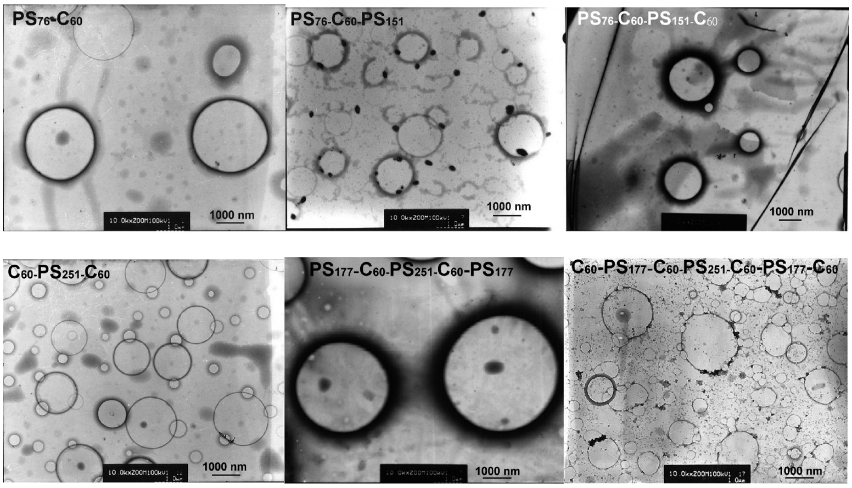


Figure 3. Transmission electron micrographs of selective PS/C_{60} nanohybrids in chloroform (1.0 mg mL^{-1}).

experimental values are not associating to the molecular weight of the PS/C_{60} chains due to molecular aggregation. A similar result was previously reported by Okamura et al.[16] and Ravi et al.[18]

The organic structures of the PS/C_{60} nanohybrids have been characterized with FTIR. The presence of C_{60} moieties of the PS/C_{60} nanohybrids is characterized with UV−vis spectroscopy. Figure 2 shows the UV−vis spectra of the PS-C_{60} nanohybrids. C_{60} exhibits absorption peaks at about 260 and 330 nm. The absorption at about 260 nm overlaps with the absorptions of PS. As PS does not show absorption at around 330 nm, the absorption peak of C_{60} at 330 nm could be used for identical characterization of the presence of C_{60} in the PS/C_{60} nanohybrids. As a result, obvious absorptions at about 330 nm appear in the spectra of PS_{76}-C_{60} and C_{60}-PS_{251}-C_{60}, compared to the spectra of PS_{76} and PS_{251} which do not show absorption in the wavelength region. Moreover, the intensities of the peaks at 330 nm of the PS/C_{60} nanohybrids vary with their mass fractions of C_{60}. As it can be seen, PS_{76}-C_{60}-PS_{151} has a relatively low intensity of absorption at 330 nm compared to PS_{76}-C_{60}.

Meanwhile, the absorption intensity of PS_{76}-C_{60}-PS_{151}-C_{60} increases with the C_{60} attachment, as C_{60} moiety has been incorporated to the chain end of PS_{76}-C_{60}-PS_{151} nanohybrid.

Figure 3 shows the TEM micrographs of some PS/C_{60} nanohybrids in chloroform at a concentration of 1.0 mg mL^{-1}. The PS/C_{60} nanohybrids surprisingly tend to form toroidal structures in chloroform solutions. Formation of toroids in solution has been reported to amphiphilic block copolymers.[2−15] The solution selectivity of the hydrophobic and hydrophilic segments of the block copolymers in the utilized solvent plays a critical role on the formation of toroids. Similarly, PS-C_{60}-PNIPAAm amphiphilic nanohybrid reported in our previous paper formed toroids in chloroform.[20] Nevertheless, the PS/C_{60} nanohybrids are not amphiphilic. Their trends of toroids formation could be attributed to the strong interaction of C_{60} molecules. As a result, chloroform is a selective solvent of C_{60} and PS chains. In the previous work we did not observe toroids of PS-C_{60} in SEM micrographs.[20] It is noticeable that PS_{76}-C_{60} also forms toroidal structure in chloroform in TEM observation. Nevertheless, we still do not see toroids in the SEM micrographs of PS_{76}-C_{60}. As SEM observation involves dry-state samples, the toroidal structure of PS-C_{60} in solution (seen in TEM) might be destroyed in the drying process. Compared to PS_{76}-C_{60}, PS_{76}-C_{60}-PS_{151} forms relatively fewer and nonuniform toroids due to its relatively low C_{60} content. On the other hand, the uncompleted and open toroids suggest that the formation of toroids of PC/C_{60} nanohybrids could undergo through the mechanism of end-to-end cylinder connection.[7] Furthermore, PS_{76}-C_{60}-PS_{151}-C_{60} forms the most beautiful toroidal structures with relatively thick rings. The inner sides of the rings are sharp and clear. The corona appearing at the outer sides of the rings indicate the PS chains assemble toward the outer side of the rings. The PS/C_{60} nanohybrids prepared with the difunctional initiator also form toroidal structures in chloroform. Among the three samples, the toroids of PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177} are the most beautiful. The C_{60} contents of the PS/C_{60} nanohybrids might be critical to the toroid formation. On the other hand, the location of C_{60} might also affect the formation of toroids. Figure 4 shows the TEM micrographs of PS_{76}-C_{60}-PS_{151}-C_{60} and C_{60}-PS_{251}-C_{60} in different concentration in chloroform, as these two samples have similar C_{60} contents but different C_{60} locations. Both PS_{76}-C_{60}-PS_{151}-C_{60} and C_{60}-PS_{251}-C_{60} form toroid in chloroform at a concentration of 1.0 mg mL^{-1}. Nevertheless, the toroidal structure of PS_{76}-C_{60}-PS_{151}-C_{60} is more beautiful (Figure 3). As shown in Figure 4, C_{60}-PS_{251}-C_{60} forms particle aggregates in chloroform at concentrations of 0.5 and 1.5 mg mL^{-1}. Meanwhile, toroidal structures still appear in the TEM micrograph of the 0.5 mg mL^{-1} solution of PS_{76}-C_{60}-PS_{151}-C_{60}. As a result, PS_{76}-C_{60}-PS_{151}-C_{60} shows relatively high ability to form toroids in chloroform. Moreover, addition of methanol, which is a poor solvent for both PS chains and C_{60}, to chloroform reduces the salvation ability of chloroform for the nanohybrids. All PS/C_{60} nanohybrids form particle aggregates in the mixture of chloroform and methanol (v/v = 1/1), as shown in Figure 5. The particle sizes vary from 100 to 1000 nm, depending on the structures of the nanohybrids. Increases in the C_{60} contents reduce the particle sizes. However, it remains to be studied further.

Figure 6 shows the representative SEM and AFM micrographs of the toroids of PS_{76}-C_{60}-PS_{151}. The samples were obtained with spin-coating the chloroform solution of PS_{76}-C_{60}-PS_{151} silicon wafer surfaces. Ring-shaped assemblies in various diameters form on silicon wafer surfaces. The sizes of the toroids in dry state are comparable to the toroids in chloroform.

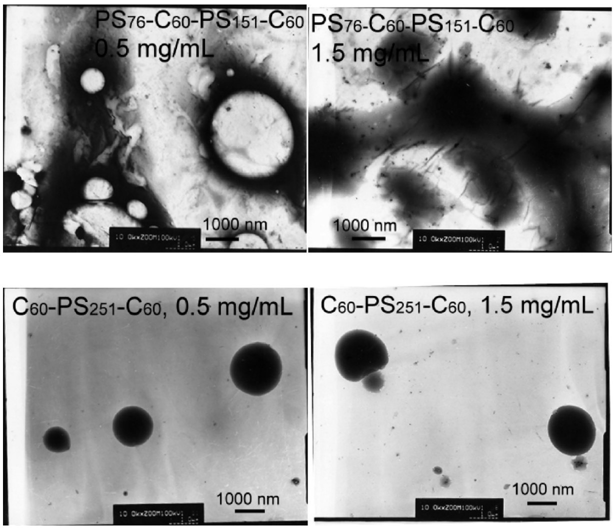


Figure 4. Transmission electron micrographs of PS_{76}-C_{60}-PS_{151}-C_{60} and C_{60}-PS_{251}-C_{60} in different concentration in chloroform.

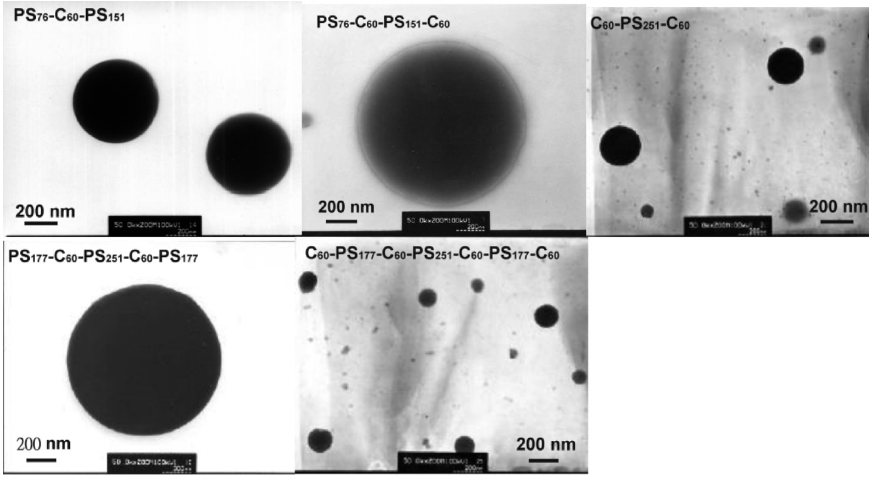


Figure 5. Transmission electron micrographs of selective PS/C_{60} nanohybrids in mixture of chloroform and methanol (v/v = 1/1, 1.0 mg mL^{-1}).

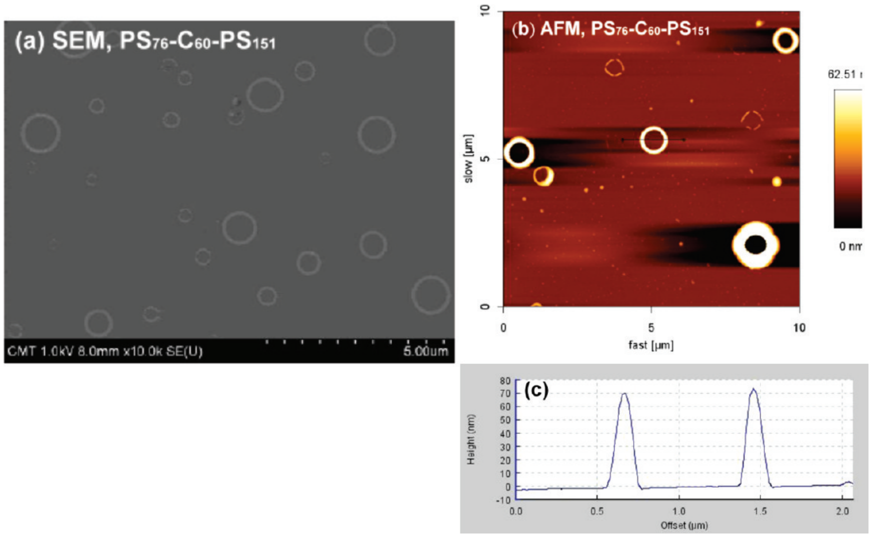


Figure 6. (a) Scanning electron and (b) atomic force micrographs of PS_{76}-C_{60}-PS_{151}. (c) Height profile corresponding to the lined region in (b).

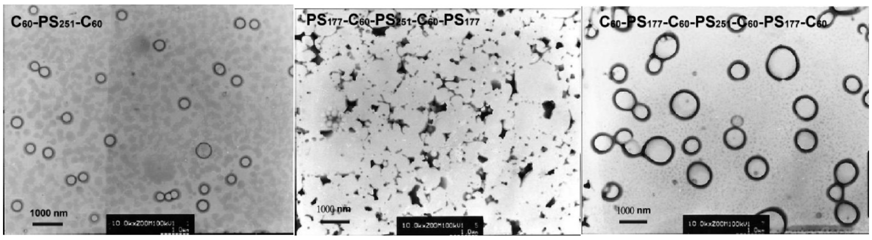


Figure 7. Transmission electron micrographs of selective PS/C_{60} nanohybrids in cyclohexane (1.0 mg mL^{-1}).

The relatively small but broken rings suggest the small toroids are relatively unstable in spin-coating and drying process. The widths of the toroidal rings are quite uniform (about 200 nm). Nevertheless, the thicknesses of the toroidal rings are about 70 nm read from AFM measurement. The difference between width and thickness indicates the cross section of the ring is an ellipse rather than a circle. The toroids might shrink in the drying process. The gravity could be another factor to result in the deformation of the toroids.

Figure 7 shows the TEM micrographs of C_{60}-PS_{251}-C_{60}, PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177} and C_{60}-PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177}-C_{60} in cyclohexane (1.0 mg mL^{-1}). Toroidal structures appear with C_{60}-PS_{251}-C_{60} and C_{60}-PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177}-C_{60}. In contrast, PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177} only forms disorder aggregates. The morphological structures of the samples in cyclohexane are different from the structures formed in chloroform. Cyclohexane is a relatively poor solvent for C_{60} compared to chloroform. The poor solubility of C_{60} in cyclohexane leads the nanohybrids tend to form short rods or spherical micelles. Hence, the formation of toroids of C_{60}-PS_{251}-C_{60} should not be conducted with the mechanism of end-to-end connection[7] and could be illustrated with the nucleation and growth mechanism proposed by He and Schmid.[21] The spherical micelles transform into disks. Afterward, the center of the disk generates a hole and evolves into rings. The toroids formed according to this mechanism usually have small sizes,[15] as shown in Figure 7. The relatively uniform and small toroids of C_{60}-PS_{251}-C_{60} could be potentially utilized in some practical applications. On the other hand, the long PS end chains of PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177} depress the nucleation of holes in the micelle disks. As a result, PS_{177}-C_{60}-PS_{251}-C_{60}-PS_{177} only displays aggregates in cyclohexane.

CONCLUSION

In conclusion, multiblock polystyrene/C_{60} nanohybrids have been prepared through ATRP using monofunctional and difunctional initiators. The synthetic route demonstrates a new scope of design and synthesis of polymer/C_{60} nanohybrids. Compared to other block copolymers for toroids formation, the polystyrene/C_{60} nanohybrids tend to form toroidal structures in chloroform in wide ranges of polymer structures and chains lengths. Some of the prepared polystyrene/C_{60} nanohybrids also form toroids in cyclohexane. The toroids shapes and formation mechanism in cyclohexane are different from what in chloroform. Here we have provided a new group of materials for toroids preparation and application.

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