

Synthesis of fullerene-containing poly(ethylene oxide)-*block*-polystyrene as model shape amphiphiles with variable composition, diverse architecture, and high fullerene functionality†

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A series of [60]fullerene (C₆₀)-containing poly(ethylene oxide)-*block*-polystyrene (PEO-*b*-PS) with various numbers and different locations of C₆₀ along the polymer chains were designed and synthesized *via* a combination of “click” chemistry and living/controlled polymerization techniques such as anionic polymerization, atom transfer radical polymerization, and reversible addition–fragmentation chain transfer polymerization. One C₆₀ was tethered either to the end of a PS block (PEO-*b*-PS-C₆₀) or at the junction point between PS and PEO blocks [PEO-(C₆₀)-PS]; while multiple C₆₀s could be attached randomly along the PS block (PEO-*b*-PS/C₆₀). The reaction conditions were carefully controlled to ensure a quantitative C₆₀ functionality at precise locations in the case of PEO-*b*-PS-C₆₀ and PEO-(C₆₀)-PS and to avoid crosslinking in the synthesis of PEO-*b*-PS/C₆₀. The results have implications in the precision synthesis of fullerene polymers in general. These C₆₀-containing diblock copolymers possess different composition, diverse architecture, and high fullerene functionality. They can serve as model “shape amphiphiles” for the construction of complex hierarchical structures *via* the interplay between C₆₀–C₆₀ aggregation and block copolymer self-assembly/micro-phase separation.

Introduction

Recognition of the importance of anisotropic shape and interactions has led to an exciting field of “shape amphiphiles” for the construction of novel functional hierarchical structures in the past few decades. Shape amphiphiles usually refer to the hybrids of molecular segments of distinct shapes and competing interactions¹ and have been predicted by computer simulation to exhibit rich phase behaviours and various unusual structures due to packing constraints and amphiphilic interactions.^{2,3} Typical shape amphiphiles include polymer tethered nanoparticles,^{4–8} disc–rod mesogenic hybrids,¹ sphere–cube or disc–cube conjugates,⁹ where [60]fullerene (C₆₀) is a frequent spherical building block.

Fullerene is an intriguing class of carbon-based molecular nanoparticles with wide-ranging applications due to its outstanding electronic properties and the possibility to perform precise chemical modification.^{10–12} Self-assembly of C₆₀-based

shape amphiphiles is an important approach to control their electronic properties *via* manipulating their ordered structure formation of C₆₀ in multi-dimensions across different length scales.^{1,3,4,13–16} To achieve tailor-made hierarchical structures, the precise control of important molecular parameters, such as surface chemistry, chain composition, and polymer architecture, is a prerequisite. Although living/controlled polymerization techniques developed in the past few decades have furnished the chemists with sufficient control over the composition, molecular weight, and polydispersity of polymers, the coupling between polymer chains and functional materials such as C₆₀ (so-called “grafting-to” approach) is often plagued by the difficulty in purification as a result of incomplete functionalization and possible multi-addition and chain degradation.^{17–20} On the other hand, the “growing-from” approach in the synthesis of fullerene polymers is usually problematic due to C₆₀’s reactive nature toward common reactive intermediates.^{17–21} Challenges in the synthesis of fullerene polymers thus lie in the precise control of C₆₀ locations on a polymer chain while ensuring a quantitative functionality and a well-defined stable structure. This is particularly true for C₆₀-functionalized block copolymers, where different sites for functionalization are available.

Block copolymers have been extensively studied in the past three decades due to their versatile self-assembly behaviours and diverse supramolecular structures.^{22,23} For example, most of the amorphous–semicrystalline block copolymers can grow single

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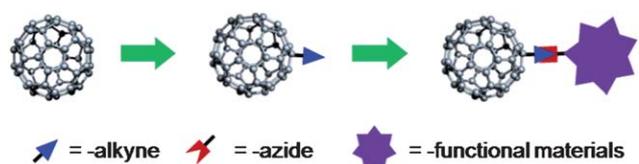
† Electronic supplementary information (ESI) available: Synthesis and characterization of PEO-C₆₀; additional results and discussions; and detailed characterization data of new compounds. See DOI: 10.1039/c1py00435b

crystals in dilute solutions using the self-seeding techniques,²⁴ in which the amorphous blocks are tethered on both of the folded surfaces of the single crystal lamellae.^{24–26} Amphiphilic block copolymers are known to form various micellar morphologies in selective solvents^{27,28} or phase-separate into different nanostructures in the bulk or thin films.^{29,30} A typical block copolymer that has been studied in great detail is poly(ethylene oxide)-*block*-polystyrene (PEO-*b*-PS).^{24,26,28} The combination of this block copolymer and C₆₀ hence gives shape amphiphiles of distinct structures (Fig. 1), including surfactant-like block copolymers with C₆₀ at the chain end (PEO-*b*-PS-C₆₀), lipid-like block copolymers with C₆₀ at the junction point [PEO-(C₆₀)-PS], and block copolymers with multiple C₆₀s randomly tethered at the PS block (PEO-*b*-PS/C₆₀). Driven by the interplay between the C₆₀-C₆₀ aggregation and the block copolymer self-assembly, they provide a versatile platform to achieve hierarchically ordered arrangement of C₆₀s. Some pioneering works have already been carried out in this direction with certain successes. Amphiphilic block polymers with C₆₀ at the junction point, such as PS-(C₆₀)-poly(*N*-isopropylacrylamide) (PNIPAM) and PS-(C₆₀)-PEO, were reported though a quantitative functionality was not shown.^{31,32} Later on, improved synthesis by “click” chemistry was reported in the synthesis of a series of C₆₀-functionalized thermo-responsive diblock copolymers with controlled numbers of C₆₀ at designated positions.³³ Functionalizing polymers with multiple C₆₀s was reported extensively with different fullerene loadings, especially in combination with conjugated polymers to form so-called “double-cable” polymers as promising organic photovoltaic materials.^{34–41} However, the lack of control over the primary structure of such polymers in terms of grafting position, grafting density, *etc.*, and their propensity to undergo crosslinking lead to an unsuccessful finding of well-defined “double-cable” structures.⁴¹ It is, therefore, essential to control precise locations of C₆₀s while ensuring a high degree of functionality during synthesizing polymers.

Recently, we have demonstrated a “click” chemistry approach as a general method to incorporate fullerenes into functional materials under mild conditions (Scheme 1) by the model synthesis of C₆₀-endcapped PS and poly(ϵ -caprolactone) with a quantitative fullerene functionality.^{6,7} The highly reactive prototype alkyne-functionalized fullerene, Fulleryne01, can be



Fig. 1 Model shape amphiphiles based on the combination of C₆₀ and block copolymers with different C₆₀ locations [orange: polystyrene; green: poly(ethylene oxide)].



Scheme 1 General functionalization methodology to Fullerene materials *via* “Click” chemistry.

synthesized in three steps in high yields, facilitating the modular and efficient synthesis of fullerene polymers.⁷ Complicated purification procedures, such as fractionation, can be avoided. Similar methods have also been reported by other groups in the synthesis of fullerene-based hybrid materials, such as porphyrin-C₆₀ conjugate,⁴² fullerene sugar ball,⁴³ C₆₀-PNIPAM,³³ C₆₀-viral nanoparticle conjugates⁴⁴ among others.^{45–47} It is thus quite advantageous for a variety of applications, particularly in heterogeneous systems, biological environments, and multiple functionalizations.

In this publication, we report our recent efforts in the synthesis of shape amphiphiles based on PEO-*b*-PS and C₆₀ using combined techniques of living/controlled polymerization and “click” chemistry. Specifically, C₆₀ is located at the end of the PS block (PEO-*b*-PS-C₆₀), or at the junction point between PS and PEO blocks [PEO-(C₆₀)-PS], or randomly tethered along the PS block (PEO-*b*-PS/C₆₀) (Fig. 1). The “click” reaction ensures a quantitative C₆₀ functionality at precise locations in the cases of PEO-*b*-PS-C₆₀ and PEO-(C₆₀)-PS and avoids cross-linking in the synthesis of PEO-*b*-PS/C₆₀.

Experimental section

Chemicals and solvents

The following chemicals were used as received: [60]fullerene (MTR Ltd, >99.5%), sodium azide (NaN₃, Aldrich, Reagent-Plus®, >99.5%), epichlorohydrin (Acros, 99%), *N,N*-dimethylformamide (DMF, Aldrich, 99.9%), methanol (MeOH, Fisher Scientific, reagent grade), deuterated chloroform (CDCl₃, Aldrich, 99.8 atom% D), *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), triethylamine (TEA, Aldrich, 99%), 2-bromoisobutyryl bromide (Aldrich, 98%), oxalyl chloride (Aldrich, ReagentPlus®, >99%), ammonium chloride (NH₄Cl, Aldrich, >99.5%), and sodium hydroxide (NaOH, Aldrich, >97.0%). 2,2'-Azobisisobutyronitrile (AIBN, Aldrich, 98%) was purified by recrystallization from ethanol. Cuprous bromide (CuBr, Aldrich, 98%) was freshly purified by stirring in acetic acid overnight, washed with acetone, and dried in vacuum. Dichloromethane (CH₂Cl₂, Fisher Scientific, reagent grade), styrene (Aldrich, 99%), and vinyl benzyl chloride (VBC, Aldrich, >90%) were purified by stirring over freshly ground calcium hydride for 12 hours and redistilled under vacuum before use. Fulleryne01 and *S*-1-dodecyl-*S'*-(*r,r'*-dimethyl-*r''*-acetic acid)trithiocarbonate (TC) were prepared according to reported procedures.^{7,48} Preparation of poly(ethylene oxide) (PEO-OH) and C₆₀-endcapped poly(ethylene oxide) (PEO-C₆₀) is described in the ESI†.

Instrumentation and characterizations

All ¹H and ¹³C NMR spectra were acquired in CDCl₃ using a Varian Mercury 300 or Varian 500 NMR spectrometer. The ¹H NMR spectra were referenced to the residual proton impurities in CDCl₃ at δ 7.27 ppm. The ¹³C NMR spectra were referenced to ¹³CDCl₃ at δ 77.00 ppm. The molecular weight of the PEO homopolymer was calculated based on the integration ratio between the peaks at 1.20 ppm [–C(CH₃)₃] and 3.64 ppm (–OCH₂CH₂–) in ¹H NMR spectra (see ESI for details, eqn (S1)†). The molecular weight of the PS blocks in the block

copolymer was calculated based on the integration ratio between the peak at 3.64 ppm ($-\text{OCH}_2\text{CH}_2-$, S_A) and broad peaks between 7.40 and 6.30 ppm (the protons on the phenyl rings on PS blocks, S_B) in ^1H NMR spectra using eqn (1):

$$M_n^{\text{PS}} = M_n^{\text{PEO}} \times \left(\frac{S_B}{S_A}\right) \times \left(\frac{104 \times 4}{44 \times 5}\right) \quad (1)$$

The degree of polymerization (N) and number average molecular weight (M_n) of poly(vinyl benzyl chloride) (PVBC) segments and PS segments of PEO-*b*-PS/Cl can be calculated based on eqn (2):

$$\begin{aligned} N_{\text{PVBC}} &= \frac{M_n^{\text{PEO}}}{44 \times S_A} \times 4 \times S_C \times \frac{1}{2} \\ M_n^{\text{PVBC}} &= \frac{M_n^{\text{PEO}}}{44 \times S_A} \times 4 \times S_C \times \frac{152}{2} \\ N_{\text{PS}} &= \frac{M_n^{\text{PEO}}}{44 \times S_A} \times 4 \times S_B \times \frac{1}{5} - N_{\text{PVBC}} \\ M_n^{\text{PS}} &= \left(\frac{M_n^{\text{PEO}}}{44 \times S_A} \times 4 \times S_B \times \frac{1}{5} - N_{\text{PVBC}}\right) \times 104 \end{aligned} \quad (2)$$

where S_C is the integration area of hydrogen on the ethylene group adjacent to the chloride (4.51 ppm).

Fourier transform infrared (FTIR) spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films onto KBr plates from polymer solutions or by making a KBr pellet from a mixture with the sample. The data were processed using Win-IR software.

Ultraviolet-visible light (UV-Vis) spectra were recorded on a HP 8453 UV-Vis Spectrometer System. Concentration dependent UV spectra were used to measure the degree of fullerene functionality based on the Beer-Lambert Law⁴⁹ because the chromospheres in Fulleryne01 and the fullerene polymers are identical. A calibration curve is then obtained using Fulleryne01 dilute solution in toluene (Fig. S1 in ESI†). The linear relationship is fitted to the following equation:

$$A = kc + b \quad (3)$$

where A is the absorbance of the UV light at 330 nm, c is the molar concentration of the C_{60} derivative, k is the slope, and b is the intercept. For Fulleryne01, the slope k was determined to be $3.5872 \times 10^4 \text{ M}^{-1}$, and the intercept b was determined to be 1.26×10^{-2} . The square of correlation coefficient (r^2) is calculated to be 0.998, indicating a very good linearity. There is no attempt to force the fitting line passing through the origin ($b = 0$). Fullerene polymer solutions with a series of concentrations were prepared in toluene and their absorbance was measured at 330 nm where the homo-PEO and PEO-*b*-PS are essentially transparent (absorbance $\approx 10^{-4}$). A standard curve was obtained for the fullerene polymer and fitted to eqn (3). At a specific absorbance, the ratio between the corresponding $c_{\text{Fulleryne01}}$ and c_{polymer} determines the degree of C_{60} functionality, $f_{\text{C}_{60}}$ (eqn (4)):

$$f_{\text{C}_{60}} = c_{\text{Fulleryne01}}/c_{\text{polymer}} \times 100\% \quad (4)$$

The C_{60} content in these polymers, C_{60} wt%, is estimated using the following equation:

$$\text{C}_{60}\text{wt}\% = \frac{M_{\text{C}_{60}} \times n}{M_{\text{Polymer}} + M_{\text{Fulleryne01}} \times n} \times 100\% \quad (5)$$

where n is the number of C_{60} per chain of block copolymer, $M_{\text{C}_{60}}$, M_{polymer} , and $M_{\text{Fulleryne01}}$ are the molecular weights of C_{60} , azide-functionalized polymer, and Fulleryne01, respectively.

Size-exclusion chromatographic analyses (SEC) were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10³/10⁴ Å), mixed bed (10³/10⁴/10⁶ Å)] and a double detector system with THF as eluent at a flow rate of 1.0 mL min⁻¹ at 30 °C; the detector system consisted of a differential refractometer (Waters 410) and a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm). Regular SEC calibrations were conducted with PS standards (Polymer Laboratories).

General synthetic procedures

PEO-Br. PEO-OH ($M_n = 8.8 \text{ kg mol}^{-1}$, 2.2 g, 0.25 mmol) and 25 mL anhydrous CH_2Cl_2 were added into a 50 mL round-bottom flask equipped with a magnetic stirrer. After dissolving completely, TEA (0.378 g, 3.75 mmol) was added. The solution was cooled to 0 °C in an ice bath and 2-bromoisobutryl bromide (0.85 g, 3.75 mmol) in 5 mL of anhydrous CH_2Cl_2 was added dropwise within 20 min. The solution was stirred at room temperature for 24 h. The mixture was then diluted with 200 mL CH_2Cl_2 and washed three times with water to remove salt. The organic layer was dried over anhydrous Na_2SO_4 overnight. After removal of the solvent, the polymer was precipitated into excess cold ethyl ether and collected by filtration. The resultant white powder was dried *in vacuo* for 24 hours to give PEO-Br (1.93 g, 88%). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 4.33 (m, 2H, $-\text{CH}_2\text{CH}_2\text{O}(\text{C}=\text{O})-$), 3.64 (br, 770H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.93 (s, 6H, $-(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{Br}$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 71.1 ($-\text{OCH}_2\text{CH}_2-$), 61.1 ($(\text{CH}_3)_3\text{C}-\text{O}-$), 55.6 ($-(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{Br}$), 30.7 ($-(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{Br}$), 27.5 ($(\text{CH}_3)_3\text{C}-\text{O}-$). FT-IR (cm^{-1}): 2882, 1730 ($\text{C}=\text{O}$), 1464, 1342, 1280, 1240, 1107, 958, 842. SEC (THF, RI detector): $M_n = 11.1 \text{ g mol}^{-1}$, $M_w = 12.0 \text{ g mol}^{-1}$, PDI = 1.07.

PEO-*b*-PS. PEO-Br ($M_n = 8.8 \text{ kg mol}^{-1}$, 0.5 g, 0.06 mmol), styrene (3 mL), CuBr (7 mg, 0.06 mmol) and 5 mL anhydrous toluene were added into a reaction flask equipped with a magnetic stirrer. The mixture was degassed by three freeze-vacuum-thaw cycles. PMDETA (11 mg, 0.06 mmol) was introduced into the mixture under nitrogen protection and the mixture became light green. After three extra freeze-vacuum-thaw cycles, the flask was immersed into a 90 °C oil bath. After the reaction was carried out for the prescribed time, the flask was quenched by liquid nitrogen. The resultant solution was passed through a short column of silica gel for removal of the metal salt. By adding the polymer solution into an excess mixture of cold ethyl ether and hexanes ($v : v = 50 : 50$), the PEO-*b*-PS block copolymer was precipitated and collected by vacuum filtration. The block copolymer (0.93 g) was obtained after drying *in vacuo* for 24 h. ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 6.30–7.40 (br, 430H, phenyl rings), 3.64 (br, 770H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.67–2.15 (br, 87H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20–1.67 (br, 174H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93

(m, 6H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 144.8–146.6, 127.0–128.5, 125.4, 71.1, 64.6, 61.1, 41.0–47.8, 44.0, 27.5. FT-IR (cm^{-1}): 3082, 3059, 3026, 2920, 2882, 1943, 1884, 1807, 1728, 1643, 1601, 1493, 1452, 1350, 1298, 1250, 1107, 1029, 951, 844, 758, 699, 542. SEC (THF, RI detector): $M_n = 21.8$ kg mol $^{-1}$, $M_w = 23.6$ kg mol $^{-1}$, PDI = 1.08.

PEO-*b*-PS- N_3 . PEO-*b*-PS ($M_n^{\text{PEO}} = 8.8$ kg mol $^{-1}$, $M_n^{\text{PS}} = 9.0$ kg mol $^{-1}$, 0.8 g, 0.045 mmol), sodium azide (29 mg, 0.45 mmol) and anhydrous DMF (10 mL) were added into a 50 mL round-bottom flask. The mixture was stirred at room temperature for 24 hours. The resultant mixture was diluted with 200 mL of chloroform and washed with water three times to remove excess sodium azide. After removal of the majority of the solvent, the polymer was precipitated into an excess mixture of ethyl ether and hexanes ($v : v = 50 : 50$), and a white solid was collected by filtration. The PEO-*b*-PS- N_3 was obtained in 87% yield (0.69 g) after drying under vacuum for 24 hours. ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 6.30–7.40 (br, 430H, phenyl rings), 3.64 (br, 770H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.67–2.15 (br, 87H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20–1.67 (br, 174H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93 (m, 6H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 144.9–146.4, 127.1–128.6, 125.5, 71.1, 64.6, 61.1, 41.1–47.9, 44.1, 27.5. FT-IR (given in Fig. S2†, cm^{-1}): 3082, 3060, 3027, 2920, 2869, 2098 (N_3), 1943, 1884, 1807, 1730, 1641, 1601, 1493, 1452, 1349, 1300, 1249, 1110, 1029, 950, 844, 758, 699, 542. SEC (THF, RI detector): $M_n = 22.2$ kg mol $^{-1}$, $M_w = 23.4$ kg mol $^{-1}$, PDI = 1.06.

PEO-*b*-PS- C_{60} . PEO-*b*-PS- N_3 ($M_n^{\text{PEO}} = 8.8$ kg mol $^{-1}$, $M_n^{\text{PS}} = 9.0$ kg mol $^{-1}$, 0.4 g, 0.022 mmol), Fulleryne01 (23 mg, 0.027 mmol), CuBr (3 mg, 0.022 mmol) and anhydrous toluene (30 mL) were added into a reaction flask with a magnetic stirrer. The mixture was degassed by three freeze–vacuum–thaw cycles. PMDETA (4 mg, 0.022 mmol) was introduced into the mixture under nitrogen protection. The flask was stirred at room temperature for 24 hours. The reaction mixture was concentrated and applied to the top of a short column of silica gel. The column was eluted with toluene first to remove the excess Fulleryne01. It was then further eluted with chloroform/methanol ($v : v = 90 : 10$) to give a colored fraction, which was collected, concentrated, and recrystallized in amyl acetate to give PEO-*b*-PS- C_{60} as a brown powder (310 mg, 77%). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 7.80 (m, 1H), 6.30–7.40 (br, 430H, phenyl rings), 5.20 (br, 1H, $-\text{CH}_2\text{CH}(\text{Ar})-\text{N}-$), 3.64 (br, 770H, $-\text{CH}_2\text{CH}_2\text{O}-$), 2.90 (br, 1H, $-\text{CH}_2\text{CH}_2\text{CH}(\text{OCO})-\text{CH}_2-$), 1.67–2.15 (br, 87H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20–1.67 (br, 174H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93 (m, 6H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): (given in Fig. S3†). FT-IR (given in Fig. S2†, cm^{-1}): 3082, 3059, 3026, 2918, 2867, 1945, 1871, 1801, 1724 (C=O), 1601, 1493, 1452, 1349, 1299, 1249, 1107, 1030, 949, 842, 758, 699, 540.

PEO-Epoxy. PEO-OH ($M_n = 9.0$ kg mol $^{-1}$, 3.5 g, 0.39 mmol), epichlorohydrin (15 mL), and NaOH (5 g, 125 mmol) were added into a 50 mL round-bottom flask equipped with a magnetic stirrer. After stirring for 36 h at room temperature, the resultant mixture was filtered to remove the undissolved solid. By precipitating the filtrate into excess cold ethyl ether three times,

the product was collected as white powder (3.15 g, 90% yield). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 3.64 (br, 820H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.16 (m, 1H, $-\text{CH}(\text{O})\text{CH}_2-$), 2.79 (m, 1H, $-\text{CH}(\text{O})\text{CH}_2-$), 2.61 (m, 1H, $-\text{CH}(\text{O})\text{CH}_2-$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 71.1 ($-\text{OCH}_2\text{CH}_2-$), 61.1 ($(\text{CH}_3)_3\text{C}-\text{O}-$), 50.8 ($-\text{CH}(\text{O})\text{CH}_2-$), 44.2 ($-\text{CH}(\text{O})\text{CH}_2-$), 27.5 ($(\text{CH}_3)_3\text{C}-\text{O}-$). FT-IR (cm^{-1}): 2885, 1467, 1342, 1280, 1240, 1147, 1107, 1061, 963, 842. SEC (THF, RI detector): $M_n = 10.0$ kg mol $^{-1}$, $M_w = 11.0$ kg mol $^{-1}$, PDI = 1.10.

PEO- (N_3) -OH. PEO-Epoxy ($M_n = 9.0$ kg mol $^{-1}$, 2.2 g, 0.24 mmol) was dissolved in 15 mL of DMF. NaN_3 (0.33 g, 5 mmol) and ammonium chloride (0.27 g, 5 mmol) were then added. After stirring at 50 °C for 24 h, the mixture was dissolved in 200 mL of CH_2Cl_2 and washed with water for 3 times to remove inorganic salts. The organic layer was collected and dried over anhydrous Na_2SO_4 overnight. After removal of the solvent by rotary evaporation, the product was obtained as a white powder by precipitation into excess cold ethyl ether with a yield of 76% (1.67 g). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 3.64 (br, 820H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 71.1 ($-\text{OCH}_2\text{CH}_2-$), 61.1 ($(\text{CH}_3)_3\text{C}-\text{O}-$), 53.4 ($-\text{CH}_2\text{CH}(\text{CH}_2\text{N}_3)\text{OH}$), 27.5 ($(\text{CH}_3)_3\text{C}-\text{O}-$). FT-IR (given in Fig. S7†, cm^{-1}): 2882, 2098 (N_3), 1467, 1360, 1280, 1147, 1109, 1061, 946, 842. SEC (THF, RI detector): $M_n = 10.3$ kg mol $^{-1}$, $M_w = 11.0$ kg mol $^{-1}$, PDI = 1.07.

PEO- (N_3) -Br. The esterification was carried out by a similar procedure to that of PEO-Br in 87% from PEO- (N_3) -OH. ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 5.12 (m, 1H, $-\text{CH}_2\text{CH}(\text{CH}_2\text{N}_3)\text{OCO}-$), 3.64 (br, 820H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.93 (s, 6H, $-\text{C}(\text{O})\text{C}(\text{CH}_3)_2\text{Br}$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 171.5 ($-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{Br}$), 71.1 ($-\text{OCH}_2\text{CH}_2-$), 61.1 ($(\text{CH}_3)_3\text{C}-\text{O}-$), 55.6 ($-\text{C}(\text{O})\text{C}(\text{CH}_3)_2\text{Br}$), 50.9 ($-\text{CH}_2\text{CH}(\text{CH}_2\text{N}_3)\text{O}-$), 30.7 ($-\text{C}(\text{O})\text{C}(\text{CH}_3)_2\text{Br}$), 27.5 ($(\text{CH}_3)_3\text{C}-\text{O}-$). FT-IR (cm^{-1}): 2881, 2100 (N_3), 1737 (C=O), 1467, 1359, 1280, 1240, 1147, 1107, 1061, 946, 842. SEC (THF, RI detector): $M_n = 9.5$ kg mol $^{-1}$, $M_w = 10.4$ kg mol $^{-1}$, PDI = 1.10.

PEO- (N_3) -PS. The polymerization was carried out by a similar procedure to that of PEO-*b*-PS from PEO- (N_3) -Br except that the polymerization was performed at 45 °C over an extended time. ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 6.30–7.40 (br, 440H, phenyl rings), 3.64 (br, 820H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.67–2.15 (br, 88H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20–1.67 (br, 176H, $-\text{CH}_2\text{CH}(\text{Ar})-$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93 (m, 6H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 144.6–146.6, 127.0–128.5, 125.4, 71.1, 61.1, 41.0–47.7, 44.0, 27.5. FT-IR (given in Fig. S12†, cm^{-1}): 3082, 3059, 3026, 2922, 2101 (N_3), 1945, 1873, 1804, 1729 (C=O), 1601, 1493, 1452, 1349, 1298, 1110, 1029, 946, 844, 696, 540. SEC (THF, RI detector): $M_n = 21.2$ kg mol $^{-1}$, $M_w = 23.5$ kg mol $^{-1}$, PDI = 1.10.

PEO- (C_{60}) -PS. The “click” reaction was carried out by a similar procedure to that of PEO-*b*-PS- C_{60} in 71% from PEO- (N_3) -PS. ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 7.80 (m, 1H), 6.30–7.40 (br, 440H, phenyl rings), 4.35 (br, 4H), 3.64 (br, 820H, $-\text{CH}_2\text{CH}_2\text{O}-$), 2.90 (m, 1H, $-\text{CH}_2\text{CH}_2\text{CHO}(\text{C}=\text{O})\text{CH}_2-$),

1.67–2.15 (br, 88H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.20–1.67 (br, 176H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93 (m, 6H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): Fig. S13†. FT-IR (given in Fig. S12†, cm^{-1}): 3082, 3059, 3026, 2882, 1724, 1601, 1491, 1449, 1352, 1273, 1109, 842, 696, 544.

PEO-TC. *S*-1-Dodecyl-*S'*-(*r,r'*-dimethyl-*r''*-acetic acid)-tri-thiocarbonate (TC, 3.65 g, 0.01 mol) was dissolved in 20 mL of CH_2Cl_2 in a 100 mL flask and 2 droplets of anhydrous DMF were added as catalyst. A solution of oxalyl dichloride (3.81 g, 0.03 mol) in 10 mL of CH_2Cl_2 was added dropwise into the solution at 0 °C. After stirring for 12 h at room temperature, the solvent and excess oxalyl chloride were removed using a rotary evaporator to give *S*-1-dodecyl-*S'*-(*r,r'*-dimethyl-*r''*-carbonyl chloride)trithio carbonate. PEO-OH ($M_n = 9.0 \text{ kg mol}^{-1}$, 1.0 g, 0.11 mmol) and TEA (224.4 mg, 2.22 mmol) were dissolved in 20 mL of CH_2Cl_2 in a 50 mL round-bottom flask equipped with a magnetic stirrer. *S*-1-Dodecyl-*S'*-(*r,r'*-dimethyl-*r''*-carbonyl chloride)trithiocarbonate (855 mg, 2.22 mmol) in 10 mL of CH_2Cl_2 was added dropwise at 0 °C. After stirring for another 36 h at room temperature, the resultant mixture was filtered to remove the undissolved solid. By precipitating the filtrate into excess cold ethyl ether three times and recrystallizing in amyl acetate, the product, PEO-TC, was collected in 85% yield (0.85 g). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 4.24 (t, 2H, $-\text{CH}_2\text{O}(\text{C}=\text{O})-$), 3.64 (br, 836H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.27 (t, 2H, $-\text{SCH}_2\text{CH}_2-$), 1.69 (s, 6H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{S}-$), 1.65 (m, 2H, $-\text{SCH}_2\text{CH}_2-$), 1.2–1.4 (m, 18H, $-\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.9 (t, 3H, $-\text{SC}_{11}\text{H}_{22}\text{CH}_3$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 71.1 ($-\text{OCH}_2\text{CH}_2-$), 61.1 ($(\text{CH}_3)_3\text{C}-\text{O}-$), 36.8 ($-\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 31.8 ($-\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 28.8–29.5 ($-\text{SCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_3$), 27.5 ($(\text{CH}_3)_3\text{C}-\text{O}-$), 25.2 ($-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{S}-$), 22.6 ($-\text{SCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_3$), 14.0 ($-\text{SCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_3$). FT-IR (cm^{-1}): 2889, 1966, 1733, 1695, 1643, 1467, 1342, 1280, 1242, 1147, 1107, 1061, 963, 842. SEC (THF, RI detector): $M_n = 13.4 \text{ kg mol}^{-1}$, $M_w = 14.4 \text{ kg mol}^{-1}$, PDI = 1.06.

PEO-*b*-PS/Cl. PEO-TC ($M_n = 9.0 \text{ kg mol}^{-1}$, 0.4 g, 0.045 mmol), styrene (1.5 mL), vinyl benzyl chloride (0.1 mL), AIBN (0.75 mg, 0.0045 mmol) and 5 mL anhydrous toluene were added into a reaction flask equipped with a magnetic stirrer. The flask was degassed by three freeze–vacuum–thaw cycles and immersed into a 110 °C oil bath. After a prescribed time, the flask was quenched by liquid nitrogen. By adding the polymer solution into an excess mixture of cold ethyl ether and hexanes ($v : v = 50 : 50$), the PEO-*b*-PS/Cl was precipitated and collected by vacuum filtration. The block copolymer was obtained after drying *in vacuo* for 24 h as a white powder (0.69 g). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 6.30–7.40 (br, 340H, phenyl rings), 4.52 (br, 9H, $-\text{CH}_2\text{Cl}$), 3.64 (br, 836H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.67–2.15 (br, 70H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.20–1.67 (br, 140H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.27 (m, 18H, $-\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93 (m, 9H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$, $-\text{SC}_{11}\text{H}_{22}\text{CH}_3$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 145.1–150.0, 127.3–128.0, 125.5, 71.1, 63.0, 61.1, 41.1–47.9, 40.4, 31.9, 29.5, 27.5, 22.6, 14.0. FT-IR (cm^{-1}): 3082, 3059, 3026, 2922, 2875, 1945, 1872, 1803, 1724, 1643, 1601, 1493, 1452, 1351, 1298, 1250, 1107, 1029, 951, 909, 843, 758, 699, 540. SEC (THF, RI detector): $M_n = 15.8 \text{ kg mol}^{-1}$, $M_w = 18.0 \text{ kg mol}^{-1}$, PDI = 1.17.

PEO-*b*-PS/ N_3 . PEO-*b*-PS/Cl ($M_n^{\text{PEO}} = 9.0 \text{ kg mol}^{-1}$, $M_n^{\text{PS}} = 7.0 \text{ kg mol}^{-1}$, $N_{\text{Cl}} = 4.5$, 0.50 g, 0.024 mmol), NaN_3 (32.5 mg, 0.5 mmol), and anhydrous DMF (5 mL) were added into a round-bottom flask with a magnetic stirrer. After stirring for 24 hours, the mixture was diluted with 100 mL chloroform and washed with water for three times. The organic layer was collected and dried under anhydrous Na_2SO_4 . After removal of the excess solvent, the product was repeatedly precipitated into a mixture of ethyl ether and hexanes ($v : v = 50 : 50$). PEO-*b*-PS/ N_3 was obtained as white powder after drying *in vacuo* for 24 h (440 mg, 88%). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 6.30–7.40 (br, 340H, phenyl rings), 4.23 (br, 9H, $-\text{Ar}-\text{CH}_2\text{N}_3$), 3.64 (br, 836H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.67–2.15 (br, 70H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.20–1.67 (br, 140H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.27 (m, 18H, $-\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93 (m, 9H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$, $-\text{SC}_{11}\text{H}_{22}\text{CH}_3$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): 145.0–150.1, 127.5–128.0, 125.4, 71.1, 63.0, 61.1, 41.1–48.0, 40.4, 31.9, 29.5, 27.5, 22.6, 14.0. FT-IR (given in Fig. S16†, cm^{-1}): 3082, 3060, 3026, 3026, 2883, 2098 ($-\text{N}_3$), 1945, 1872, 1803, 1724, 1643, 1601, 1493, 1467, 1453, 1360, 1344, 1280, 1148, 1109, 1061, 945, 842, 757, 696, 544. SEC (THF, RI detector): $M_n = 16.0 \text{ kg mol}^{-1}$, $M_w = 18.1 \text{ kg mol}^{-1}$, PDI = 1.13.

PEO-*b*-PS/ C_{60} . The “click” reaction was carried out by a similar procedure to that of PEO-*b*-PS- C_{60} with PEO-*b*-PS/ N_3 ($M_n^{\text{PEO}} = 9.0 \text{ kg mol}^{-1}$, $M_n^{\text{PS}} = 7.0 \text{ kg mol}^{-1}$, $N_{\text{N}_3} = 4.5$, 200 mg, 0.0125 mmol), Fulleryne01 (100 mg, 0.125 mmol), CuBr (18 mg, 0.125 mmol), PMDETA (21.6 mg, 0.125 mmol), and 40 mL of anhydrous toluene. The product was recrystallized in amyl acetate to give PEO-*b*-PS/ C_{60} as a brown powder (146 mg, 73%). ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 7.98 (br, 4.5H), 6.30–7.40 (br, 340H, phenyl rings), 5.45 (br, 9H, $-\text{Ar}-\text{CH}_2\text{N}-$), 3.97 (m, 2H, $-\text{CH}_2\text{CH}(\text{OCO})\text{CH}_2-$), 3.64 (br, 836H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.35 (m, 1H, $-\text{CH}_2\text{CH}_2\text{CH}(\text{OCO})\text{CH}_2-$), 2.90 (m, 1H, $-\text{CH}_2\text{CH}_2\text{CH}(\text{OCO})\text{CH}_2-$), 1.67–2.15 (br, 70H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.20–1.67 (br, 140H, $-\text{CH}_2\text{CH}(-\text{Ar})-$), 1.27 (m, 18H, $-\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{O}-$), 0.93 (m, 9H, $-\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)_2\text{CH}_2-$, $-\text{SC}_{11}\text{H}_{22}\text{CH}_3$). ^{13}C NMR (CDCl_3 , 500 MHz, ppm, δ): Fig. S17†. FT-IR (given in Fig. S16†, cm^{-1}): 3082, 3060, 3026, 3026, 2882, 1945, 1872, 1803, 1728 ($\text{C}=\text{O}$), 1601, 1491, 1449, 1352, 1273, 1109, 842, 696, 544, 528.

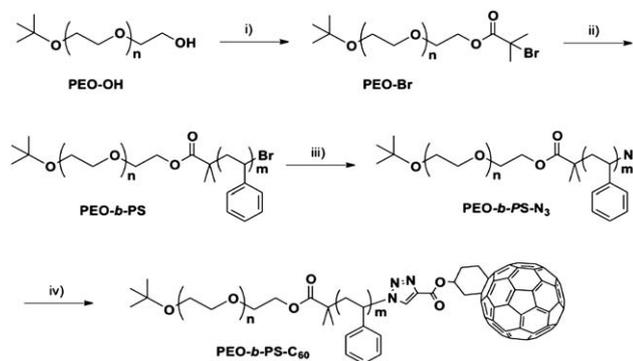
Results and discussions

Giant surfactant with a diblock copolymer tail (PEO-*b*-PS- C_{60})

A nanoparticle tethered with a polymer chain resembles the structure of a small-molecule surfactant in that they both possess a compact head and a long tail, though their sizes are very different. Hence, it is a type of “giant surfactant”.⁸ An important molecular parameter in their self-assembly is the composition of the single polymer tail (*e.g.* homopolymer *vs.* block copolymer). The synthesis of a giant surfactant with a single block copolymer tail is thus the first target. The synthesis began with hydroxyl-functionalized PEOs (PEO-OH), which could be synthesized by anionic polymerization with controlled molecular weights and low polydispersity (see ESI† for details). Combined with ATRP and RAFT polymerization techniques, the PS block can be synthesized in a controlled fashion with exact locations of

reactive azide groups. The synthetic scheme for PEO-*b*-PS- C_{60} is outlined in Scheme 2, which is similar to the synthesis of PS- C_{60} as reported previously,⁷ except that a macroinitiator (PEO-Br) is used in place of the ethyl α -bromoisobutyrate. The macroinitiator was obtained by esterification of PEO-OH with α -bromoisobutyryl bromide in 88% yield. Following ATRP at 90 °C and subsequent nucleophilic substitution with NaN₃, the PEO-*b*-PS- N_3 is “clicked” with Fulleryne01 to give the target C_{60} -end-capped block copolymer (PEO-*b*-PS- C_{60}) in a straightforward way.

The chemical structures, molecular weights, and polydispersities were characterized by ¹H NMR, ¹³C NMR, FT-IR spectrometry, and SEC chromatography. After esterification, new chemical shifts appear in the ¹H NMR spectrum at 1.92 and 4.30 ppm, which can be assigned to protons on $-(CH_2)_2Br$ and adjacent to the ester linkage $[-(C=O)OCH_2-]$, respectively (Fig. 2a). The degree of functionalization can be determined by the integration ratio among the chemical shifts at 4.30, 1.92, and 1.20 ppm. The ratio of 1.78 : 6.34 : 9.00 is close to the expected 2 : 6 : 9 and suggests a high degree of α -bromoisobutyrate functionality. The block copolymer formation was evidenced by new chemical shifts appearing in the ¹H NMR spectrum at the aromatic region (Fig. 2b). An apparently complete shift of the SEC trace to a lower elution volume further confirms the success of polymerization (Fig. 3). The block copolymer was obtained as a white powder. After the “click” reaction, it turned into a brown powder. The typical absorption band of azide (2100 cm⁻¹) on the FT-IR spectrum disappears completely (Fig. S2†). In the ¹H NMR spectrum of PEO-*b*-PS- C_{60} , the signals, though weak, can be identified and assigned to the Fulleryne01 component at δ 2.9 ppm (proton *i*), to the one near triazole at δ 5.2 ppm (proton *g*), and to the one on the triazole at δ 7.8 ppm (proton *h*), respectively as indicated in Fig. 2c. The existence of C_{60} was confirmed by ¹³C NMR, in which the sp³ carbons as well as sp² carbons of the C_{60} moiety (60.8, 63.6, and 135–155 ppm overlapping with aromatic carbons) can be clearly observed (Fig. S3 in the ESI†). In the SEC chromatogram, after C_{60} functionalization, the retention volume essentially remained the same, yet a high molecular weight shoulder peak appears (Fig. 3). The question then arises concerning the explanation of this high molecular weight shoulder and the degree of fullerene



Scheme 2 Synthesis of chain-end-functionalized PEO-*b*-PS (PEO-*b*-PS- C_{60}): (i) 2-bromoisobutyryl bromide, TEA, CH₂Cl₂, rt, 88%; (ii) styrene, CuBr, PMDETA, toluene, 90 °C, 38%; (iii) NaN₃, DMF, rt, 87%; and (iv) Fulleryne01, CuBr, PMDETA, toluene, rt, 77%.

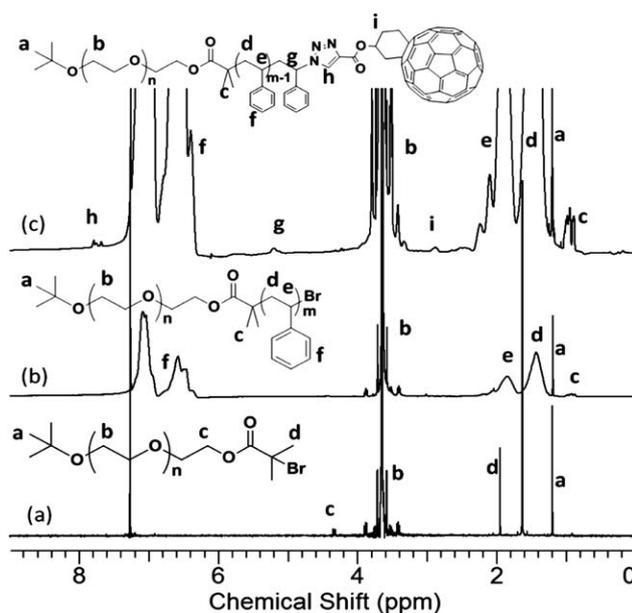


Fig. 2 ¹H NMR spectra of (a) PEO-Br; (b) PEO-*b*-PS; and (c) PEO-*b*-PS- C_{60} . The results were based on the samples with $M_n^{PEO} = 8.4 \text{ kg mol}^{-1}$ and $M_n^{PS} = 9.0 \text{ kg mol}^{-1}$.

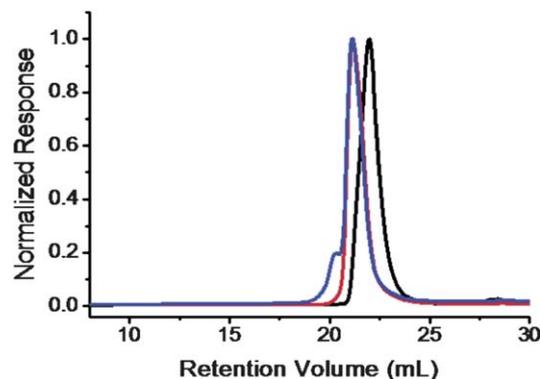


Fig. 3 SEC overlay of PEO-Br (black); PEO-*b*-PS (red); and PEO-*b*-PS- C_{60} (blue) chromatograms. The results were based on the samples with $M_n^{PEO} = 8.4 \text{ kg mol}^{-1}$ and $M_n^{PS} = 9.0 \text{ kg mol}^{-1}$.

functionality. However, due to the high molecular weight, it was difficult to measure the degree of C_{60} functionality either by MALDI-TOF mass spectra or by comparing the integration ratio in ¹H NMR spectra accurately.

Previously, the “click” chemistry approach to fullerene polymers was demonstrated by the synthesis of PS- C_{60} in which such a high molecular weight shoulder was not observed in SEC and the possibility of high addition was thus excluded.⁷ In the case of PCL- C_{60} , a shoulder peak was indeed observed, but MALDI-TOF mass spectrometry suggested that the formation of multi-addition products is very unlikely.⁶ The C_{60} -containing block copolymers in this paper are very difficult to characterize by MALDI-TOF mass spectrometry due to their high molecular weights and the presence of two repeating units of different ionization efficiencies. As a reference for comparison, PEO- C_{60} with a low PEO molecular weight ($M_n^{PEO} = 2.5 \text{ kg mol}^{-1}$) was synthesized as a model compound. The detailed procedure and

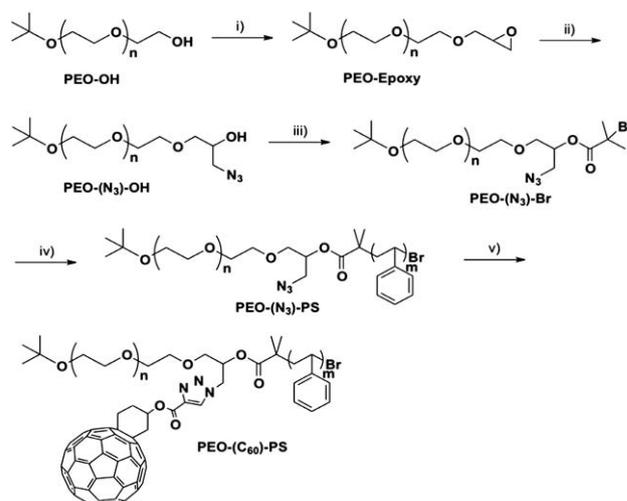
characterization are described in the ESI (Scheme S1, and Fig. S4–S9†). Fig. S4† shows the MALDI-TOF mass spectrum of the product. A narrow distribution with the molecular weights in accordance with the proposed structure is observed, confirming the cleanness of the reaction and the stability of the resulting fullerene polymer. The reason that a perfect Gaussian distribution was not observed but slightly shifts towards the smaller molecular weight fraction side is due probably to the fact that small molecules are easier to be ionized and thus give rise to stronger signal. Nevertheless, no higher addition product signal was observed. Considering the low molecular weight and high ionization efficiency of PEO, any higher addition product, if present, shall be observed by MALDI-TOF mass spectroscopy that are known to be sensitive to impurities of 1% or less. The result indicates that PEO- C_{60} is free of homo-polymer and multi-addition impurities, which is consistent with the previous finding. This is further confirmed by the quantitative fullerene functionality (100.6%) for PEO- C_{60} as determined by the Beer–Lambert law within the range of error (Fig. S5 in the ESI†). Despite this evidence, the SEC trace of PEO- C_{60} (Fig. S6†) still shows a shoulder peak, which can only be invoked by the aggregation of PEO- C_{60} in THF caused by the poor solubility of C_{60} in THF and the amphiphilic feature of the molecule.

Similar results were also obtained in the case of PEO-*b*-PS- C_{60} . The degree of fullerene functionality was measured to be 100.4% (Fig. S10†), again a quantitative functionalization though a shoulder peak is still observed in the SEC trace (Fig. 3). It is consistent with the above explanation for PEO- C_{60} since multi-addition would significantly decrease the degree of C_{60} functionality. The “click” chemistry has indeed provided a powerful means to assure a high degree of functionalization and least influence on the molecular weight and polydispersity of the parent polymer after functionalization. Several PEO-*b*-PS- C_{60} polymers have been synthesized and their molecular characterizations are summarized in Table 1.

Giant lipids with asymmetric composition [PEO-(C_{60})-PS]: achieving quantitative in-chain functionality

Compared to small-molecule surfactants, lipids in nature are much more versatile in their structures and self-assemblies. Typical lipids include fatty acids, waxes, sterols, phospholipids, and cholesterol, composed of a polar head with various numbers

of tails of different composition.⁵⁰ In analogy to such lipids, the “giant lipids” refer to nanoparticles tethered with two or more polymer tails of different composition. A block copolymer with a nanoparticle at the junction point, such as PEO-(C_{60})-PS, can thus be viewed as a prototype giant lipid. The synthetic scheme is shown in Scheme 3. To tether an azide group at the junction point of two blocks, hetero-functional groups need to be attached to the PEO chain-end to allow orthogonal chain growth and “click” functionalization. The epoxy group was thus introduced by treating PEO-OH with epichlorohydrin under basic conditions in 90% yield followed by a quantitative ring opening reaction to give an azide and a hydroxyl group [PEO-(N_3)-OH].⁵¹ The synthesis of the macroinitiator [PEO-(N_3)-Br] is similar to that of PEO-Br by esterification. ATRP was performed at a much lower temperature of 45 °C over an extended time. This is critical to obtain a high functionality of azide which is known to decompose to reactive intermediates such as nitrene at elevated temperatures, leading to the partial loss of the azide functionality.^{33,52} To avoid thermal decomposition, a low-temperature



Scheme 3 Synthesis of PEO-*b*-PS with C_{60} tethered at the junction point [PEO-(C_{60})-PS]: (i) epichlorohydrin, NaOH, rt, 90%; (ii) NaN_3 , NH_4Cl , DMF, 50 °C, 76%; (iii) 2-bromoisobutyryl bromide, TEA, CH_2Cl_2 , rt, 87%; (iv) styrene, CuBr, PMDETA, toluene, 45 °C, 35%; and (v) Fullerene C_{60} , CuBr, PMDETA, toluene, rt, 71%.

Table 1 Molecular characterization of fullerene polymers

Label	$M_n^{all} / \text{kg mol}^{-1}$	$M_n^{PEO} / \text{kg mol}^{-1}$	$M_n^{PS} / \text{kg mol}^{-1}$	$M_n^{PVBC} / \text{kg mol}^{-1}$	PDI ^b	$f_{C_{60}}^c$		C_{60}^d (wt%)
						¹ H NMR	UV-Vis	
PEO- <i>b</i> -PS- C_{60} -1	14.7	8.4	5.5	—	1.07	—	1	5.7
PEO- <i>b</i> -PS- C_{60} -2	18.2	8.4	9.0	—	1.06	—	1	4.3
PEO- <i>b</i> -PS- C_{60} -3	25.4	11.0	13.6	—	1.06	—	1	3.3
PEO-(C_{60})-PS-1	19.5	8.4	10.3	—	1.09	—	1	4.3
PEO-(C_{60})-PS-2	19.0	9.0	9.2	—	1.08	—	1	4.4
PEO-(C_{60})-PS-3	31.8	11.0	20.0	—	1.10	—	1	2.6
PEO- <i>b</i> -PS/ C_{60} -1	19.8	9.0	6.3	0.7	1.17	4.5	5.8	19.0
PEO- <i>b</i> -PS/ C_{60} -2	24.8	9.0	7.2	1.3	1.15	8.7	8.2	29.7

^a Molecular weight was calculated by ¹H NMR. ^b Polydispersity of the precursors, measured by SEC. ^c Degree of C_{60} functionality as determined by ¹H NMR and UV-Vis spectrometry. ^d C_{60} weight content in the polymer, calculated according to eqn (5).

polymerization was executed at 45 °C. A control experiment was performed to confirm the integrity of the azide group by using ^1H NMR spectrometry to monitor the change of 4-methoxybenzyl azide under identical reaction conditions, *i.e.* in the presence of styrene, CuBr, and PMDETA at 45 °C. The azide functionality was followed based on the integration ratio of protons on the ethylene group adjacent to azide (4.20 ppm), and those on the methoxy group (3.75 ppm). The normalized integration area does not decrease over time even after 36 hours, indicating that no side reaction takes place between the azide and vinyl group under these conditions (see the description in the ESI and Fig. S11†). Although it requires 2–3 days for polymerization of styrene to a reasonable molecular weight, it affords a quantitative azide functionality which is important in obtaining a well-defined “clicked” product with high degree of C_{60} functionality. The “click” reaction was then performed in a similar manner as in the case of PEO-*b*-PS- C_{60} , again exemplifying the modular feature of this approach.

In the ^1H NMR spectra, the successful installment of epoxy group is evidenced by the signals at δ 3.16, 2.79, and 2.61 ppm (Fig. 4a). The degree of chain-end functionality is determined by the integration ratio between the peaks at δ 3.16, 2.79, 2.61, and 1.20 ppm, which is 0.99 : 0.91 : 0.96 : 9.04, very close to 1 : 1 : 1 : 9 and consistent with a quasi-quantitative conversion. After ring opening with NaN_3 , the signals at δ 3.17, 2.79, and 2.61 ppm in the ^1H NMR spectra completely disappeared (Fig. 4b) and a strong band near 2100 cm^{-1} characteristic of the azide appeared in the FT-IR spectrum (Fig. S7†). Since the new signals from methylene near the azide and hydroxyl group have

very similar shifts to the methylene protons on the PEO backbone, no new peaks can be observed (Fig. 4b).⁵¹ The PEO-(N_3)-OH was also used to synthesize PEO- C_{60} as discussed earlier and described in the ESI†. After esterification, the protons (*d* and *c*) of PEO-(N_3)-Br can be seen at δ 1.92 and 5.15 ppm, respectively (Fig. 4c). The SEC overlay of these polymers shows that their elution volumes and polydispersities are essentially unchanged, since the small chain-end functional groups exert little influence on the overall hydrodynamic radius of the polymers. With the macro-initiator PEO-(N_3)-Br, ATRP was performed (Scheme 3) and the conversion was kept less than 40% by controlling the polymerization time so as to control the molecular weight of the PS block while maintaining a low polydispersity. The polymerization was carried out at a low temperature of 45 °C to avoid thermal degradation of the azide functionality.^{33,52} After the polymerization, the FT-IR spectrum of PEO-(N_3)-PS shows an absorption band at 2100 cm^{-1} , characteristic of the azide functionality (Fig. S12†). Therefore, the azide functionalities should be intact during the polymerization, though the degree of azide functionality is still difficult to determine due to the low signal intensity of chain-end groups in the ^1H NMR spectrum (Fig. 4d). Nevertheless, the UV-Vis spectrometry provides an effective way to measure the C_{60} functionality of PEO-(C_{60})-PS after C_{60} was attached, which is indirect evidence of the degree of azide functionality on the precursor polymer.

The success of this “click” reaction is supported by NMR, FT-IR spectroscopy, SEC, and quantitative UV analysis. The signals from the Fulleryne01 component at δ 2.9 ppm (proton *k*), 3.2 ppm (proton *j*), 4.0 ppm (proton *l*), the hydrogen atom at the junction carbon at δ 4.35 ppm (proton *c*, and *h*), and the triazole ring at δ 7.8 ppm (proton *i*) were observed as indicated in Fig. 4e. Due to the high molecular weight of the diblock copolymer and the low intensity of the characteristic peaks, it is difficult to measure their integration ratio quantitatively and accurately. In the ^{13}C NMR spectra (Fig. S13†), the sp^2 carbons of the C_{60} moiety (135–155 ppm overlapping with aromatic carbons) can be clearly observed. The FT-IR spectrum of PEO-(C_{60})-PS exhibits the complete disappearance of azide vibration at 2100 cm^{-1} , suggesting a complete transformation (Fig. S12†). Similar to that observed in PEO- C_{60} and PEO-*b*-PS- C_{60} , the retention volume essentially remains the same after C_{60} functionalization while a shoulder appears at the high molecular weight side (Fig. 5), which can also be attributed to the aggregation of C_{60} in THF. Again, a quantitative functionality of 100.3% was determined for PEO-(C_{60})-PS (Fig. S14†), confirming that only mono-addition takes place under the reaction conditions.

Crosslinking-free attachment of multiple C_{60} s onto PS block (PEO-*b*-PS/ C_{60})

One drawback in functionalizing polymers with fullerene is the limited content of C_{60} in the final materials, compromising the electronic properties. This can be partially compensated by attaching multiple C_{60} s onto a polymer. The so-called “double-cable” polymer is a typical example.⁴¹ Traditionally, it is composed of a conjugated polymer backbone as the donor and C_{60} s tethered as acceptors.^{53,54} Such polymers were expected to show a great promise in improving organic solar cell’s performance by forming two separate channels to transport holes and

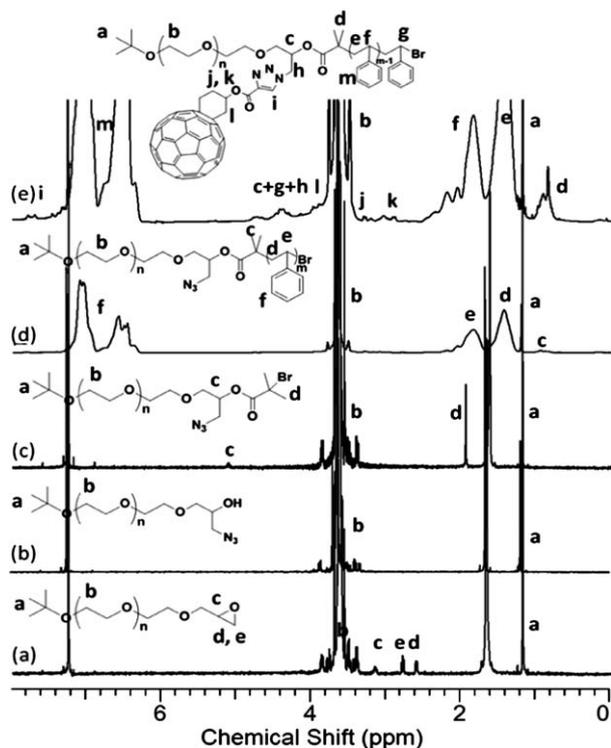


Fig. 4 ^1H NMR spectra of (a) PEO-Epoxy; (b) PEO-(N_3)-OH; (c) PEO-(N_3)-Br; (d) PEO-(N_3)-PS; and (e) PEO-(C_{60})-PS. The results were based on the samples with $M_n^{\text{PEO}} = 9.0 \text{ kg mol}^{-1}$ and $M_n^{\text{PS}} = 9.2 \text{ kg mol}^{-1}$.

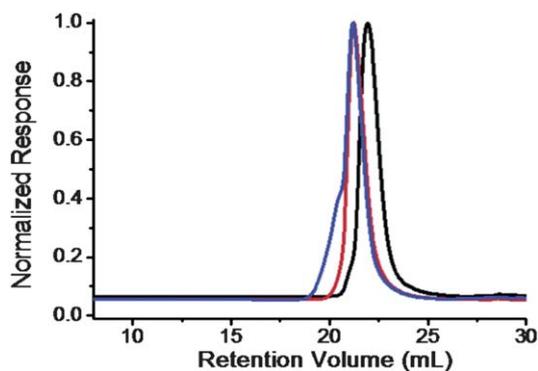
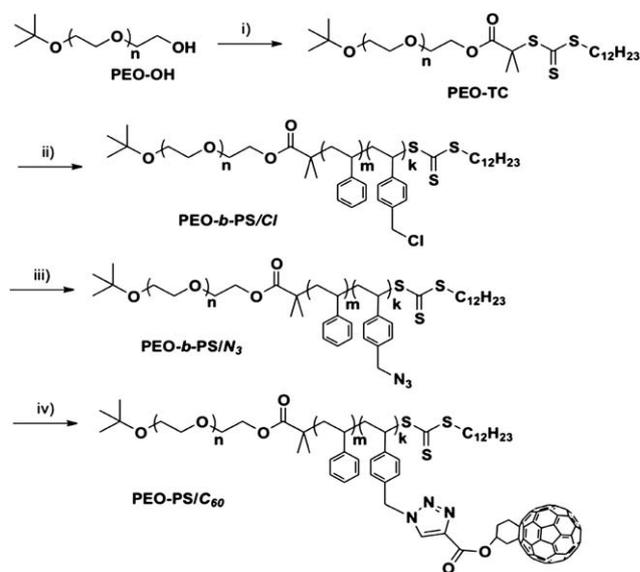


Fig. 5 SEC overlay of PEO-(N₃)-Br (black); PEO-(N₃)-PS (red); and PEO-(C₆₀)-PS (blue) chromatograms. The results were based on the samples with $M_n^{\text{PEO}} = 9.0 \text{ kg mol}^{-1}$ and $M_n^{\text{PS}} = 9.2 \text{ kg mol}^{-1}$.

electrons, respectively.⁴¹ However, most of the “double cable” polymers developed so far failed the expectation, showing low efficiencies in the organic photovoltaic devices. Attaching many fullerenes to one block will surely affect the self-assembled phase behaviors, since not only does it add significant C₆₀-C₆₀ interactions into the system, but also it increases the volume fraction of C₆₀ significantly. To gain insight into such systems, PEO-*b*-PS/C₆₀ was chosen as the model system to study the synthesis and self-assembled phase behaviors, in the hope of elucidating the basic underlying physics using well-defined samples of high purity prepared by the “click” chemistry. Majority of the works reported so far is based on the reaction between pristine C₆₀ and functional polymers.^{35,37-40} The biggest challenge in attaching multiple C₆₀s onto polymers lies in the efficiency and the potential crosslinking due to multi-addition, which makes it difficult to achieve high fullerene loading. Esterification has been used to attach carboxylic acid functionalized C₆₀s onto polymer, yet the efficiency is relatively low.⁵⁵ Here, we demonstrate a crosslinking-free attachment of C₆₀s onto the PS blocks of PEO-*b*-PS utilizing “click” chemistry, which provides a viable solution through precise functionalization.

To prepare PEO-*b*-PS with multiple reactive azide functionalities on the PS block, vinyl benzyl chloride (VBC) was chosen as a comonomer with styrene. Hence, it is no longer suitable to use ATRP because benzyl chloride is also a good initiator for ATRP. Instead, RAFT-mediated polymerization is compatible with the monomer and was chosen as the method to prepare PEO-*b*-PS/Cl. The synthetic scheme is shown in Scheme 4. The diblock copolymer, PEO-*b*-PS/Cl, was first polymerized by RAFT with PEO-TC as the macro-chain transfer agent. The azide group was readily introduced by reacting PEO-*b*-PS/Cl with NaN₃ in DMF. “Click” reaction was then applied to link fullerene moieties onto the PS blocks with a controllable loading in the absence of crosslinking. By continuously increasing the C₆₀ loading on the PS block, the PS coils may become more and more stretched due to the increasing bulky volume of C₆₀.⁵⁶

PEO-OH was converted to a macro-chain transfer agent, PEO-TC, a light yellow powder in 85% yield. Fig. 6a shows the ¹H NMR spectrum of this product. The characteristic signal of PEO at 3.64 ppm (proton *b*) and the signals from TC at 1.69 (*d*), 1.65 (*f*), 1.26 (*h*), and 0.90 (*i*) ppm are apparent. A chemical shift at 4.24 ppm can be assigned to the protons on the methylene



Scheme 4 Synthesis of multiple-C₆₀S-functionalized PEO-*b*-PS (PEO-*b*-PS/C₆₀): (i) *S*-1-dodecyl-*S'*-(*r,r'*-dimethyl-*r''*-carbonyl chloride)trithio carbonate, TEA, CH₂Cl₂, rt, 85%; (ii) styrene, vinyl benzyl chloride, AIBN, toluene, 110 °C, 38%; (iii) NaN₃, DMF, rt, 88%; and (iv) Fullerene01, CuBr, PMDETA, toluene, rt, 73%.

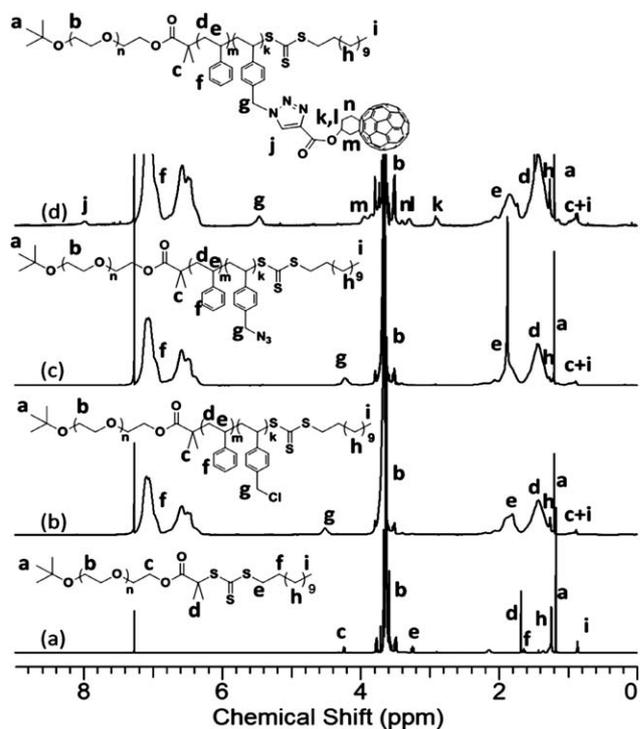


Fig. 6 ¹H NMR spectra of (a) PEO-TC; (b) PEO-*b*-PS/Cl; (c) PEO-*b*-PS/N₃; and (d) PEO-*b*-PS/C₆₀. The samples were based on the samples with $M_n^{\text{PEO}} = 9.0 \text{ kg mol}^{-1}$ and $M_n^{\text{PS}} = 7.0 \text{ kg mol}^{-1}$.

adjacent to the as-formed ester group (proton *c*), further confirming the structure of the product. A SEC trace of PEO-TC is identical to its precursor, indicating the integrity of the backbone (data not shown). Copolymerization was carried out with PEO-TC ($M_w = 9.0 \text{ kg mol}^{-1}$) as the macro-chain transfer agent, and

AIBN as the initiator. The conversion was controlled below 40% so as to keep a narrow polydispersity. The overall molecular weight was controlled by polymerization time while the ratio between styrene segments and VBC segments on the polymer chain was controlled by their feed ratio. This molar fraction of VBC incorporation can be determined from ^1H NMR spectra (Fig. 6b) by the integration ratio between the broad chemical shifts between 7.40 and 6.30 ppm (phenyl rings on the PS blocks) and the chemical shift at 4.51 ppm (hydrogen on the ethylene group adjacent to the chloride, proton *g*) (eqn (2)). The degree of polymerization and number average molecular weight of the PVBC segments and the PS segments can also be calculated accordingly. The SEC diagrams (Fig. S15†) show narrow polydispersity with different molecular weights and segment ratios.

PEO-*b*-PS/ N_3 can then be readily obtained by reacting with NaN_3 in DMF.^{35,38} The azide group was characterized by FT-IR and ^1H NMR. In the IR spectrum, a typical azide absorption band at 2100 cm^{-1} is observed with relatively strong intensity (Fig. S16†). The signal of the azide group in a high molecular weight polymer is usually weak (Fig. S2 and S12†). A relatively strong absorption indicates the existence of multiple azide groups on the PS block. A complete shift from 4.51 ppm to 4.25 ppm, corresponding to the protons on the methylene proton close to the chloride group (proton *g*), is observed, which indicates full conversion with no chloride residual.

“Click” chemistry was utilized here to connect Fulleryne01 onto the PS block to avoid multi-addition which may result in crosslinking. The product was collected in 73% yield as a dark brown powder. The loss is mainly due to residual adsorption onto column during purification to remove the copper catalyst and excess Fulleryne01. After “click” reaction, the absorption band of the azide group around 2100 cm^{-1} on the FT-IR spectrum disappears completely, indicating the success of the reaction (Fig. S16†). A new strong band appears at 1728 cm^{-1} due to the existence of a carbonyl group on Fulleryne01. The characteristic absorption of fullerene is also found at 525 cm^{-1} . The ^1H NMR spectrum (Fig. 6d) exhibited broad chemical shifts at δ 2.90 ppm (*k*), 3.35 ppm (*l*), 3.40 ppm (*n*), and 3.97 ppm (*m*) assignable to the protons on the Fulleryne01 moiety. The signal from protons near the triazole (proton *g*) and the one on the triazole (proton *j*) appears at δ 5.45 ppm and 7.98 ppm, respectively. It also clearly shows the sp^3 carbons (60.8, 63.6 ppm) and sp^2 carbons (135–155 ppm) of the C_{60} unit in the ^{13}C NMR spectrum (Fig. S17†). Fig. 7 is a SEC trace overlay of the final product and its precursors. After polymerization, a symmetric peak with lower retention volume is observed. After the “click” reaction, large shoulder peaks appear on the high molecular weight side, which is much more significant than in previous cases. This may in part be due to the increase of overall molecular volume as a result of multiple- C_{60} attachment and/or the aggregation of C_{60} s, since the molecules possess much higher C_{60} loading. Since it was carried out under mild conditions where the thermal [3 + 2] cycloaddition between the azide and pristine C_{60} core should not take place, the reaction only occurred between the azide and the alkyne under the copper catalyst, which rules out the possibility of multi-addition and crosslinking. Therefore, the product can now be reversibly dissolved in most common organic solvents such as toluene, THF, CHCl_3 , CH_2Cl_2 , and others, even after long-term storage. The degree of C_{60}

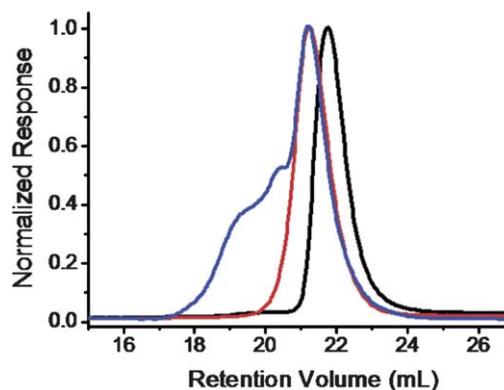


Fig. 7 SEC overlay of PEO-OH (black), PEO-*b*-PS/Cl (red), and PEO-*b*-PS/ C_{60} (blue) chromatograms. The samples were based on the PEO molecular weight of 9.0 kg mol^{-1} and the PS/PVBC molecular weight of 7.0 kg mol^{-1} .

functionality was also measured by UV-Vis spectrometry. Solutions in toluene with a series of concentrations were prepared and their absorbance was measured at 330 nm to get a standard curve which is fitted to eqn (1). The linear fitting curves for PEO-*b*-PS/ C_{60} -1 ($M_n^{\text{PEO}} = 9.0\text{ kg mol}^{-1}$, $M_n^{\text{PS}} = 6.3\text{ kg mol}^{-1}$) and PEO-*b*-PS/ C_{60} -2 ($M_n^{\text{PEO}} = 9.0\text{ kg mol}^{-1}$, $M_n^{\text{PS}} = 7.2\text{ kg mol}^{-1}$) yield the average number of C_{60} per chain ($N_{\text{C}_{60}}$) to be 5.8 and 8.2, respectively (Fig. S18 and S19†). This is similar to the C_{60} loading per chain (4.5 and 8.7, respectively) obtained from the ^1H NMR spectra using eqn (2). The C_{60} content in the polymer, $\text{C}_{60}\text{ wt}\%$, can then be estimated using eqn (5). The $\text{C}_{60}\text{ wt}\%$ in this case can be as high as $\sim 30\%$. The characterizations are summarized in Table 1.

Conclusions

In summary, “click” chemistry provides an efficient and modular approach to construct fullerene-containing polymers and highlights a quantitative functionality, mild reaction condition, and crosslinking-free process. This is demonstrated by the synthesis of C_{60} -containing diblock copolymers with different compositions and architectures, such as chain-end-functionalized PEO-*b*-PS (PEO-*b*-PS- C_{60}), junction-point-functionalized PEO-*b*-PS [PEO-(C_{60})-PS], and multiple- C_{60} s-functionalized PEO-*b*-PS (PEO-*b*-PS/ C_{60}). These fullerene polymers resemble the structure of giant surfactants and giant lipids and may serve as model compounds for shape amphiphiles. The method can also be applied to the synthesis of “double-cable” polymers to improve the control of their primary chemical structure and avoid crosslinking to facilitate processing. The work currently ongoing in our group involves using the self-assembly of these polymers, such as single crystal growth, micellization, and block copolymer phase separation in the bulk solution and thin film, as templates to manipulate the ordered structure formation of C_{60} in multi-dimensions across different length scales.

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