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Synthesis of Fullerene-Containing Poly(ethylene oxide)-*block*-Polystyrene as Model Shape Amphiphiles with Variable Composition, Diverse Architecture, and High Fullerene Functionality

Xue-Hui Dong, Wen-Bin Zhang, Yiwen Li, Mingjun Huang, Shuo Zhang, Roderic P. Quirk, and Stephen Z. D. Cheng**

Department of Polymer Science, College of Polymer Science and Polymer Engineering,

The University of Akron, Akron, OH 44325-3909, U.S.A.

E-mail: wz8@uakron.edu; scheng@uakron.edu

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Experimental Section

Chemicals and Solvents. *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), 4-Methoxybenzyl chloride (Aldrich, 98%), potassium *tert*-butoxide (*t*BuOK, Aldrich, sublimed grade, 99.99% trace metals basis), *p*-toluenesulfonic acid monohydrate (*p*TsOH, Aldrich, ACS reagent, > 98.5%), ethylene Oxide (EO, Aldrich, > 99.5%) was transferred through the high vacuum line to an evacuated flask cooled to -78 °C and containing freshly-ground calcium hydride (Acros Organics, 93%, 0-20 mm grain size). It was stirred and degassed periodically over a period of 4 hours. It was then transferred through the vacuum line to another flask containing neat dibutylmagnesium and a small amount of 1,10-phenanthroline (Aldrich, > 99%) as the indicator. The mixture became purple if the oxygen and moisture have been completely excluded. It was further stirred for 30 min at -78 °C before being transferred into a calibrated ampoule, diluted with an equal amount of THF, and flame-sealed off from the vacuum line. Toluene (EMD, ACS grade) was first stirred over freshly-ground calcium hydride in a flask on the vacuum line with intermittent degassing by cooling to -78 ^{o}C in an isopropyl alcohol (IPA)/dry ice bath, pumping, and warming up to 25 ^{o}C to remove air and hydrogen gas generated during the drying process. This should be sufficient for most purposes after re-distillation. For further drying, toluene was vacuum transferred into a second flask containing sodium dispersion (Hodgson Chemicals Inc., 40% sodium dispersion in paraffin). The toluene was again subjected to several freeze-pump-thaw cycles before final distillation into flasks containing poly(styryl)lithium and equipped with Rotaflo® stopcocks. The orange color of the poly(styryl)lithium was used as an indication of purity. Toluene was distilled directly from these flasks, as needed, through the high vacuum line. Methanol (MeOH, Fisher Scientific, reagent grade) was purified by degassing intermittently on high vacuum line using

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repeated freeze-pump-thaw cycles with liquid nitrogen cooling and transferred to pre-calibrated ampoules. 1-Chloronaphthalene (Acros, technical grade) was purified by stirring over freshly-ground calcium hydride for 24 h with frequent degassing on the high vacuum line. It was then distilled on the high vacuum line into a flask that was subsequently sealed from the line. The flask was opened in the dry box and the solvent was transferred to a crimp bottle and stored over activated 4Å molecular sieves under argon. Tetrahydrofuran (THF, EMD, ACS grade) was stirred over freshly-ground calcium hydride for 24 h with frequent degassing on the high vacuum line using a dry ice/ isopropyl alcohol bath for cooling. It was vacuum transferred onto a sodium mirror in a 2-L flask equipped with a Rotaflo® stopcock. This step was repeated until the sodium mirror maintained its integrity. The purified THF was distilled directly from the sodium mirror into ampoules and reactors, as needed.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector.

Synthetic Procedure. *PEO-OH*. The reactor as shown in Figure S20 was equipped with an ampoule of ethylene oxide in THF, an ampoule of *t*-BuOK in THF, and a methanol ampoule. After connecting to the high vacuum line, the reactor was thoroughly dried by using a soft yellow flame. Anhydrous THF was transferred into the reactor by using a dry ice/isopropanol bath of – 78 ^{o}C. The reactor was sealed off the line under vacuum using a hand torch. The initiator was added by breaking the initiator ampoule. The cooled EO ampoule was then broken by a magnetic hammer to add the monomer into the reactor. The reaction mixture was left to stir for 12-24 h. A sample was

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taken at this time by sealing off the ampoule and it could be functionalized with different functional groups by using various quenching reagents. When quenched by the addition of excess methanol, it gave hydroxyl-end functionalized PEO (PEO-OH). The material was precipitated into cold ethyl ether to give PEO-OH as a white powder (or wax depending on molecular weight). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm, δ): 3.64 (br, 272H, -CH_2CH_2O-), 1.20 (s, 9H, (CH_3)$_3$C-O-). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm, *δ*): 71.1 (-OCH_2CH_2-), 61.1 ((CH$_3$)$_3$*C*-O-), 27.5 ((*C*H$_3$)$_3$C-O-). FT-IR (cm^{-1}): 2882, 1464, 1342, 1280, 1240, 1107, 958, 842. SEC (THF, RI detector): (Table S1).

PEO-C_{60}. PEO-(N$_3$)-OH (M_n=2.5 kg/mol, 0.2 g, 0.08 mmol), Fulleryne01 (84.4 mg, 0.10 mmol), CuBr (11 mg, 0.10 mol) and anhydrous toluene (30 mL) were added into a reaction flask with a magnetic stirrer. After three freeze-pump-thaw cycles, PMDETA (17 mg, 0.10 mmol) was introduced into the mixture under nitrogen protection. The flask was degassed for three extra freeze-vacuum-thaw cycles, and 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. Further elution with chloroform/methanol (v:v = 90:10) gave a colored fraction, which was collected, concentrated, and recrystallized in amyl acetate. PEO-C_{60} was obtained as brown powder after drying *in vacuo* for 24 h (158 mg, 72 %). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm, δ): 8.43 (s, 1H, triazole), 6.45 (m, 1H, (-CH$_2$)$_2$C*H*OCO-Ar-), 4.67, 4.55 (m, 2H, -NCH_2CH-), 3.91-4.04 (m, 2H, -CH_2CH(-OCO-)CH$_2$-), 3.64 (br, 272H, -CH_2CH_2O-), 3.35 (m, 1H, -CH$_2$CH_2CH(-OCO-)CH$_2$-), 2.90 (m, 1H, -CH$_2$CH_2CH(-OCO-)CH$_2$-), 1.20 (s, 9H, (CH_3)$_3$C-O-). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm, *δ*): (Figure S9). FT-IR (cm^{-1}): 2882, 1725 (C=O), 1464, 1342, 1280, 1240, 1107, 958, 842, 524.

4-Methoxybenzyl azide. 4-Methoxybenzyl chloride (1.0 g, 6.4 mmol), and NaN_3 (830 mg, 12.8

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mmol) was dissolved in anhydrous DMF (10 mL) in a 50 mL round bottle flask with a magnetic stirrer. The mixture was stirred at 90 °C for 24 hours. The mixture was diluted with 200 mL hexanes and washed with water three times. The organic layer was collected and dried under anhydrous Na_2SO_4 overnight. 4-Methoxybenzyl azide was obtained after solvent removal. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm, δ): 5.70-5.80 (m, 2H, phenyl ring), 5.15-5.25 (m, 2H, phenyl ring), 4.20 (s, 2H, -ArCH_2N_3), 3.75 (s, 3H, -ArOCH_3).

Control experiment. 4-Methoxybenzyl azide (10 mg, 0.06 mmol), styrene (10 mg), CuBr (2 mg), and $CDCl_3$ (1 mL) was added into an 8 inch NMR tube. The mixture was degassed for three freeze-vacuum-thaw cycles before adding PMDETA (4 mg). The NMR tube then was sealed with flame under vacuum, and placed into a thermal bath at 45 °C. The integrity of azide group was monitored by ^{1}H NMR spectrometry based on the integration ratio between protons of the methylene group adjacent to azide (4.20 ppm, S^A), and those of the methoxy group (3.75 ppm, S^B). The normalized integration area, *I*, was calculated according to the follow equation.

$$I = \frac{S^A \times S_0^B}{S^B \times S_0^A}$$

where S and S_0 are integration area at the beginning (t = 0 hour) and predetermined reaction time, respectively.

Results and Discussions

The anionic polymerization of ethylene oxide was performed in THF under a high vacuum atmosphere. The polymerization was usually allowed to proceed for 24 hours to ensure a high conversion (~ 80%) for a targeted molecular weight. The hydroxyl-functionalized PEO was then obtained by quenching the living PEO^-K^+ polymer with methanol (Scheme S2) and precipitation into cold ethyl ether. After drying *in vacuo* for 24 hour, the PEO was characterized by ^{1}H NMR

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spectroscopy and SEC to determine its molecular weight and polydispersity. ~~Since THF is not a good solvent for PEO in which PEO would adopt a more compact conformation, the molecular weights determined by SEC using the standard calibration curve were overestimated~~. The molecular weights determined by SEC are overestimated when a PS calibration is applied because PS and PEO exhibit different hydrodynamic properties in THF. More accurate molecular weight measurement was obtained by ^{1}H NMR analysis. A representative ^{1}H NMR spectrum is shown in Figure S20. The singlet peak at 1.20 ppm (integration area = S_A) can be assigned to the nine protons at the initiating chain-end [–C(CH_3)$_3$] and the peaks at 3.65 ppm (integration area = S_B) to the methylene protons (-OCH_2CH_2-) on the PEO backbone (4 × N; N = degree of polymerization). The integration ratio between these peaks (S_B/S_A) was then used to calculate the number average molecular weight by the following equation (Eq. S1).

$$M_n^{PEO} = \frac{9 \times S_B}{4 \times S_A} \times 44 \qquad \text{(Eq. S1)}$$

The hydroxyl-functionalized PEOs (PEO-OH) were obtained with several different molecular weights, ranging from M_n = 2.5k to 11.0k g/mol. The characterizations of these PEOs are summarized in Table S1. Representative SEC traces are shown in Figure S22 in SI, indicating that they exhibit monomodal, symmetric distributions with narrow polydispersities.

The "click" reaction at room temperature between PEO-(N_3)-OH (1 equivalent) and excess Fulleryne01 (1.2 equivalents) yielded the desired chain-end-functionalized PEO, PEO-C_{60} (Scheme S1). The successful covalent linkage is first evidenced by the FT-IR spectra (Figure S7 in SI). The characteristic azide absorption band near 2100 cm^{-1} disappears, suggesting a complete reaction since side reactions such as nitrene formation and thermo-promoted cycloaddition to C_{60} have been shown to be absent under these reaction conditions. This conclusion is also supported by the ^{1}H

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NMR spectrum where the characteristic chemical shifts owing to Fulleryne01 (6.45 ppm (*e*), 4.00 ppm (*h*+*i*), 3.35 ppm (*f*), 2.90 ppm (*g*)) and the triazole formation (8.43 ppm (*d*)) are observed (Figure S8). The integration ratios among proton *e*, proton *g* and proton *a* are 1.02:0.83:9.00, and they are very closed to 1:1:9 as predicted for the structure within the range of measurement errors, confirming a high degree of functionality. The integrations of other protons, such as *h* and *f*, are too close to the proton *b* in chemical shifts and therefore, cannot provide accurate values. In the ^{13}C NMR spectrum (Figure S9 in SI), it also shows the sp^3 carbons (60.8, 63.6 ppm) as well as sp^2 carbons (135-155 ppm) of the C_{60} unit.

The SEC chromatogram of PEO-C_{60} is shown in Figure S6. Unexpectedly, the retention volume of PEO-C_{60} is slight larger than its precursor PEO-(N_3)-OH, which apparently indicates a decrease of molecular weight. ~~This abnormal phenomenon might due to some specific interactions between SEC column and fullerene moieties.~~ This abnormal phenomenon might be due to some specific interactions between SEC column and fullerene moieties and/or interactions between PEO and fullerene, which would result in a more compact conformation. Shoulder peaks are observed for PEO-C_{60} in the SEC trace on the high molecular weight side. Since higher additions have been proven to not occur under these reaction conditions, these high molecular shoulders are unlikely due to the formation of multi-addition products. Considering the fact that THF is a non-solvent for C_{60} and a theta solvent for PEO and that PEO is not miscible with C_{60}, the shoulder peaks are due probably to aggregation of PEO-C_{60} in THF. Similar observations were also reported for C_{60} end-capped PEO stars[1] and C_{60} end-capped poly(ε-caprolactone).[2]

To further unambiguously confirm the molecular structure and explain the shoulder peaks in SEC chromatogram, MALDI-TOF mass spectra were utilized to characterize the product. PEO-C_{60}

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with a low molecular weight PEO (M_n^{PEO}=2.5 kg/mol) was used to be a model compound. Figure S4 shows MALDI-TOF mass spectra on this PEO-C_{60}. A narrow distribution with molecular weight in accordance to the proposed structure is observed, confirming the cleanliness of the reaction and the stability of the resulting fullerene polymer. The spectra don't show a perfect Gaussian distribution but shift a little towards small molecular weight fractions. It is due to the fact that small molecules prefer to be ionized and therefore, give rise to a stronger signal which shifts the distribution to the left of spectra. No other signals are observed. Considering the fact that MALDI-TOF mass spectroscopy can detect impurities to a level as low as 1%, the results prove that the samples are free of homo-polymer and multi-addition impurities. The polymer is thus clearly identified the structure, uniformity, and purity.

A quantitative estimation of fullerene functionality can be achieved by using Beer-Lambert law[3] according to Eq. 3-Eq. 5 (Figure S5). For the measurement to be reliable, the absorbance should be kept in a reliable range of spectrometer scale, preferably between 0.2 and 0.8. At A = 0.50, this corresponds to $c_{\text{Fulleryne01}}$ = 1.353×10^{-5} M and c_{polymer} = 1.361×10^{-5} M; hence C_{60}% = 100.6%. Therefore, the C_{60}% functionality was determined to be quantitative within the range of measurement errors. Consider that the structure was precisely confirmed previously, the UV-Vis spectrum provides an effective way to characterize the functionality of fullerene-containing polymers. The power of "click" chemistry has indeed provided a solid ground for optimal results, as expected with the high efficiency as demonstrated in the model reactions. In this way, both the molecular weight and molecular weight distribution of the PEO segments remain the same after functionalization. Based on this procedure, the C_{60} content in the polymer, C_{60} wt % is estimated using Eq. 4 and Eq. 5. The results are listed in the first two rows of Table 1.

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Table S1. Molecular Weight Characterization of PEO-OH.

Label	$M_{n,target}$ *(kg/mol)*	$M_{n,SEC}$ *(kg/mol)*	$M_{n,NMR}$ *(kg/mol)*	PDI^a
PEO3k-OH	3.0	3.0	2.5	1.06
PEO5k-OH	5.0	6.2	5.1	1.10
PEO8k-OH	10.0	12.0	8.4	1.10
PEO9k-OH	10.0	12.8	9.0	1.10
PEO12k-OH	10.0	13.5	11.0	1.07

(a) polydispersity was measured using SEC.

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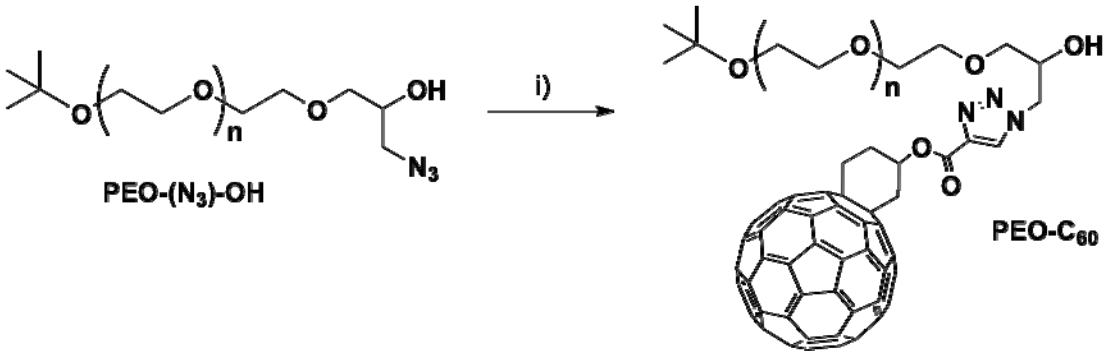
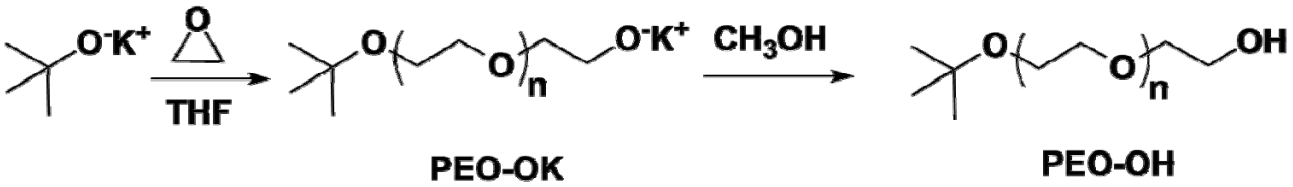
Scheme S1. Synthesis of Chain-end-functionalized PEO (PEO-C_{60}) [a]



[a] (i) Fulleryne01, CuBr, PMDETA, toluene, r.t., 72%.

Scheme S2. Synthesis of PEO-OH by Living Anionic Polymerization of Ethylene Oxide



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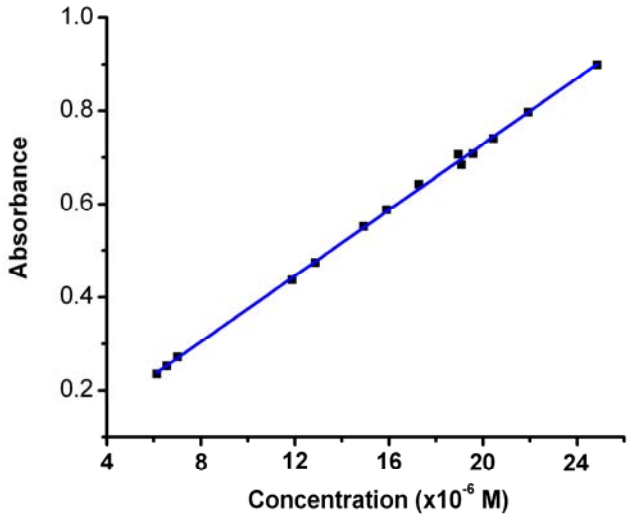

Figure S1. Calibration curve for Fulleryne01.

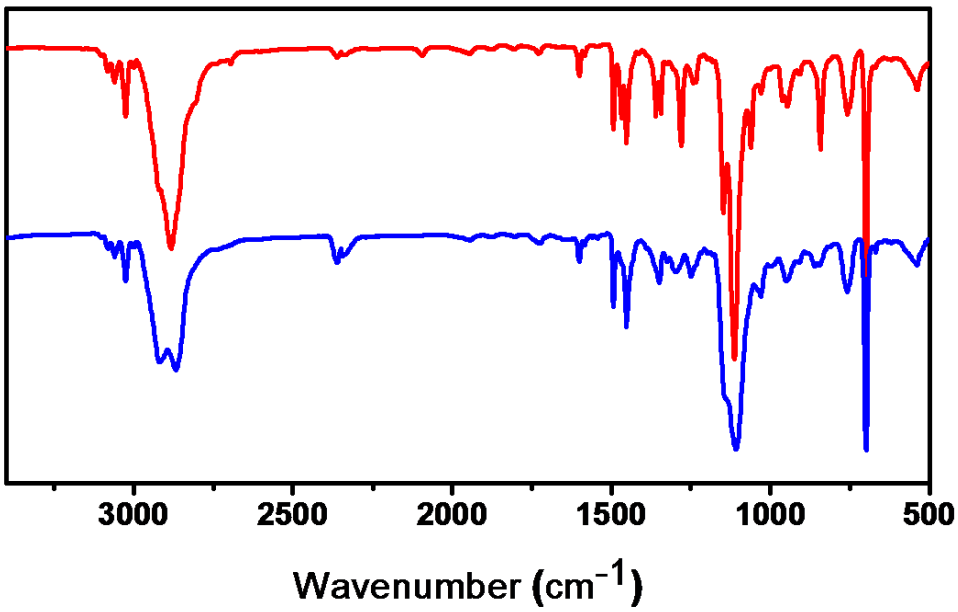

Figure S2. FT-IR spectra of PEO-*b*-PS-N_3 (red) and PEO-*b*-PS-C_{60} (blue). The results were based on the samples with M_n^{PEO} = 8.4 kg/mol and M_n^{PS} = 9.0 kg/mol.

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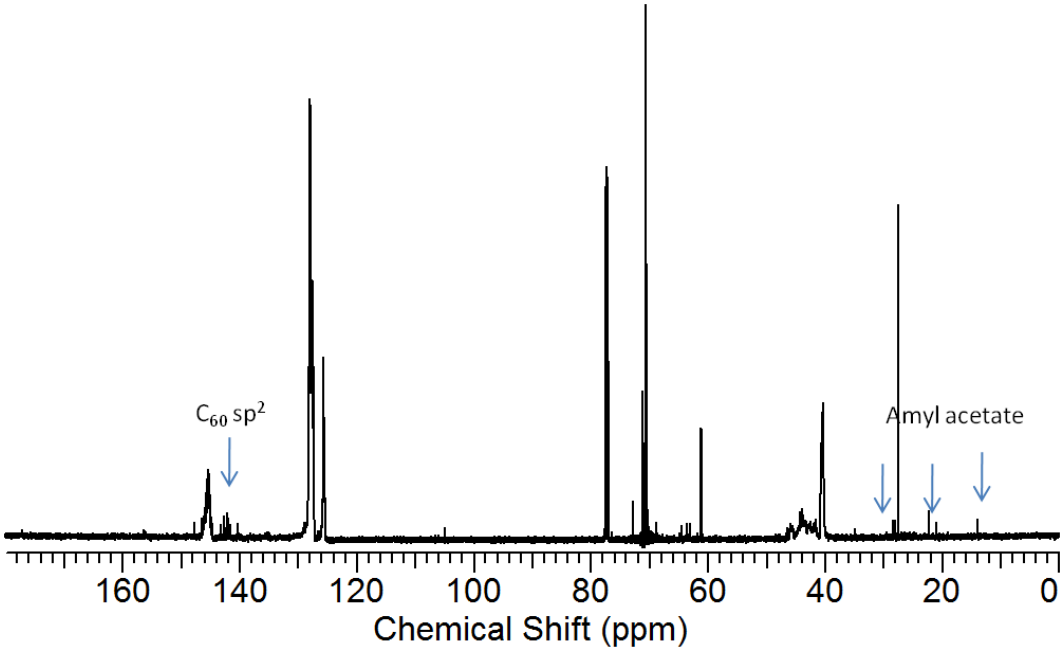

Figure S3. ^{13}C NMR spectrum of PEO-*b*-PS-C_{60}. The results were based on the samples with M_n^{PEO} = 8.4 kg/mol and M_n^{PS} = 9.0 kg/mol.

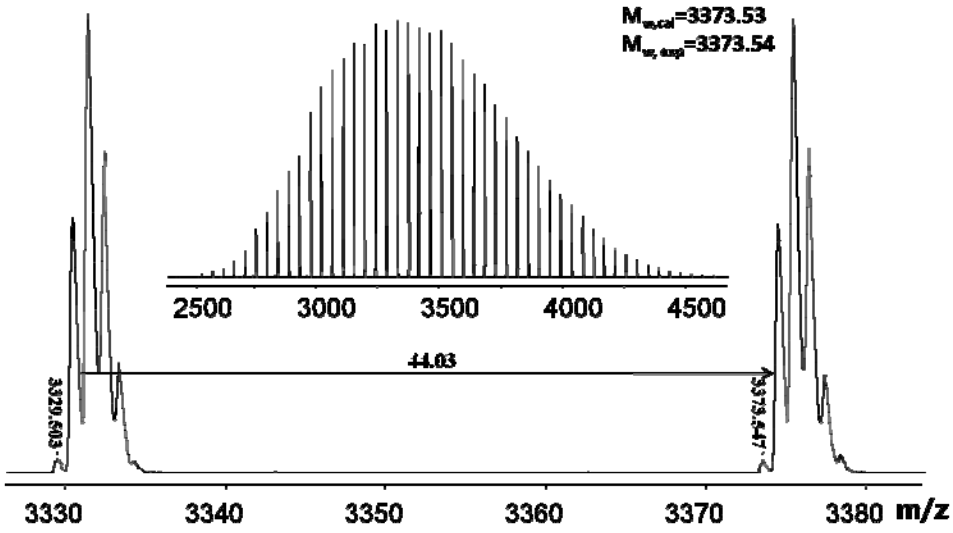

Figure S4. MALDI-TOF mass spectrum of PEO-C_{60}. The results were based on samples with PEO molecular weight of 2.5 kg/mol.

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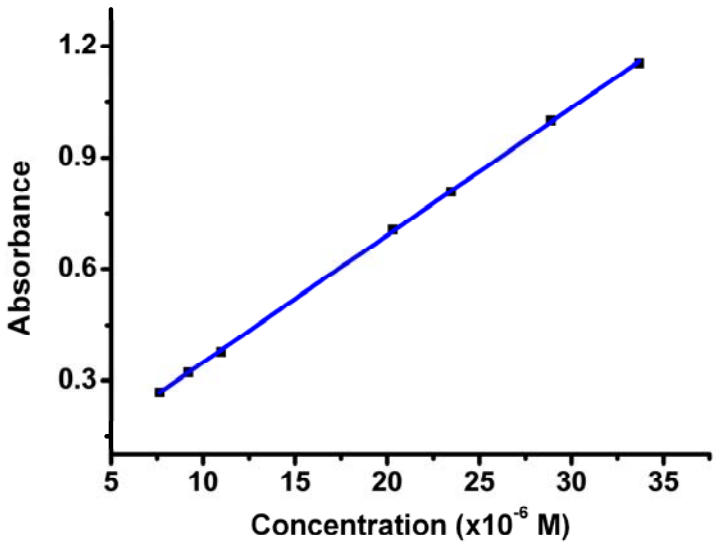

Figure S5. Plots of absorbance vs concentration for PEO-C_{60}. The samples were based on PEO4-OH with PEO molecular weight of 2.5 kg/mol.

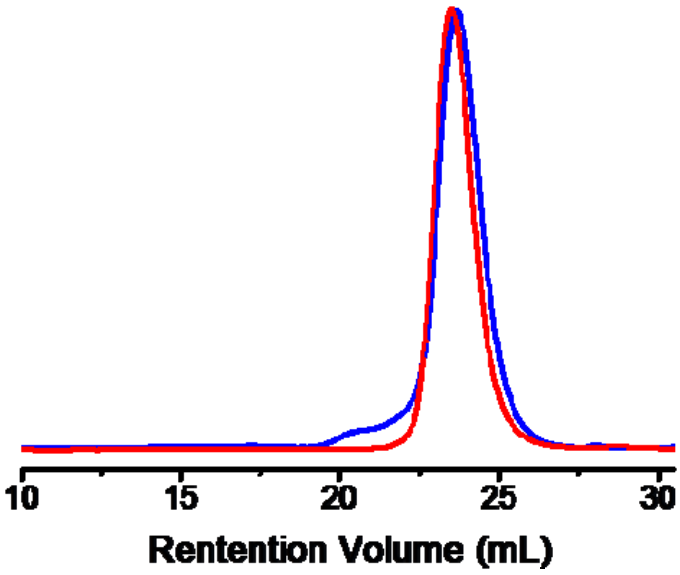

Figure S6. SEC overlay of PEO-OH (red); and PEO-C_{60} (blue) chromatograms. The results were based on samples with PEO molecular weight of 2.5 kg/mol.

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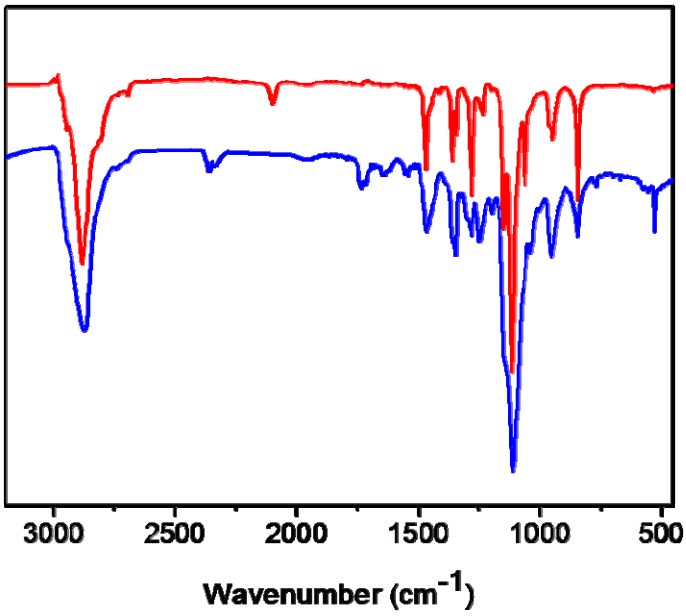

Figure S7. FT-IR spectra of PEO-(N_3)-OH (red) and PEO-C_{60} (blue). The samples were based on PEO4-OH with PEO molecular weight of 2.5 kg/mol.

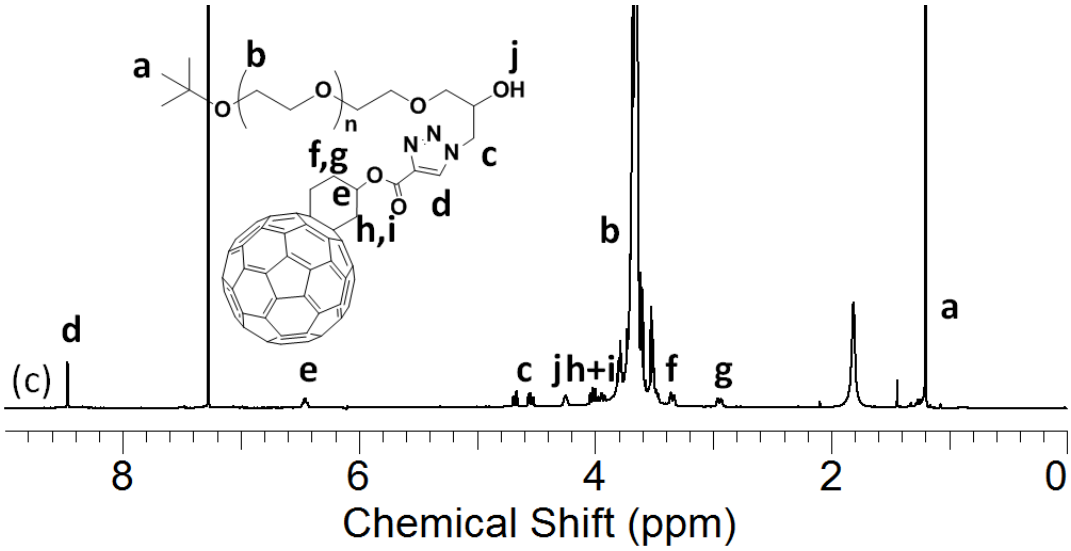

Figure S8. ^{1}H NMR spectrum of PEO-C_{60}. The results were based on samples with PEO molecular weight of 2.5 kg/mol.

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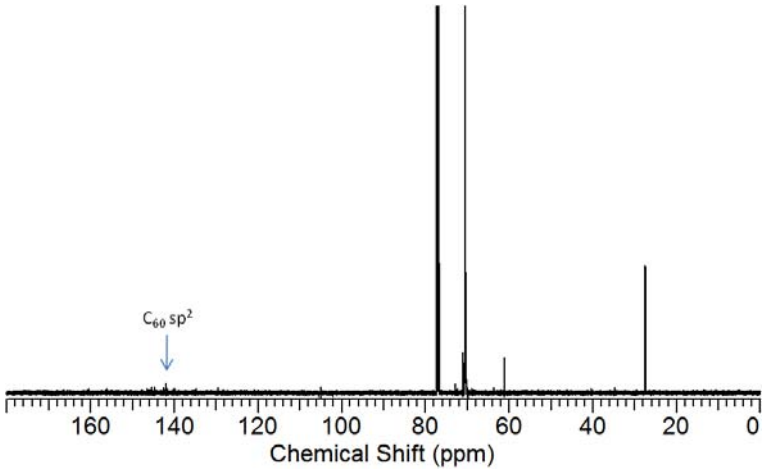

Figure S9. ^{13}C NMR spectrum of PEO-C_{60}. The sample has a PEO molecular weight of 2.5 kg/mol.

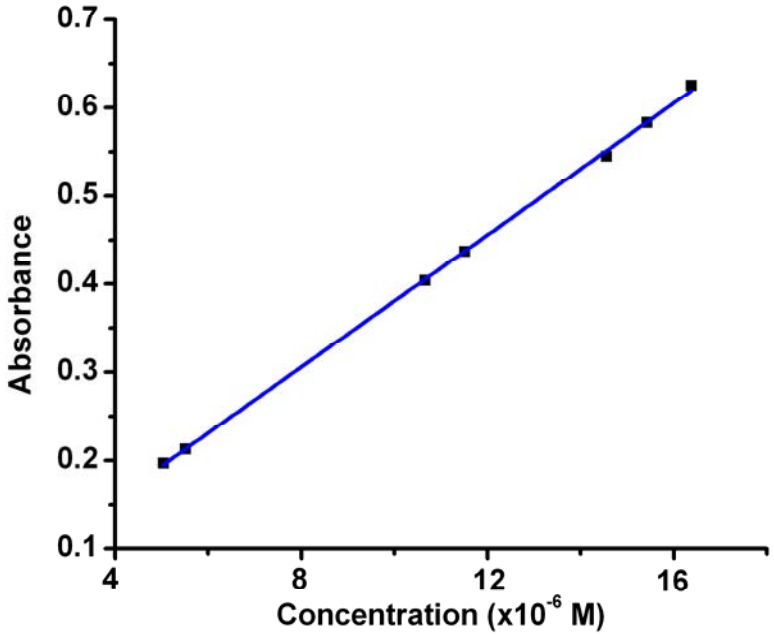

Figure S10. Plots of absorbance vs concentration for PEO-*b*-PS-C_{60}. The results were based on the samples with M_n^{PEO} = 8.4 kg/mol and M_n^{PS} = 9.0 kg/mol.

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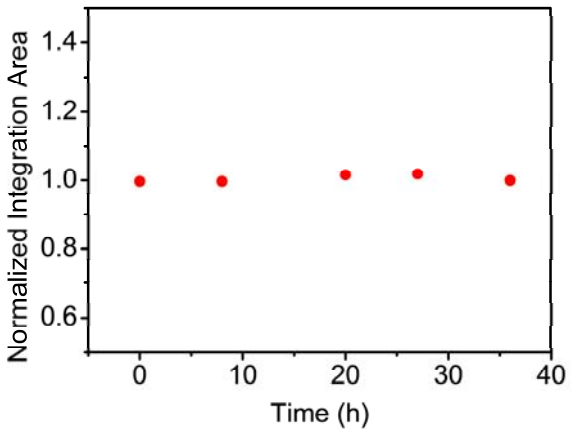

Figure S11. Plots of normalized integration area of the protons on the ethylene group adjacent to azide group vs time for 4-methoxybenzyl azide at 45 ^{o}C.

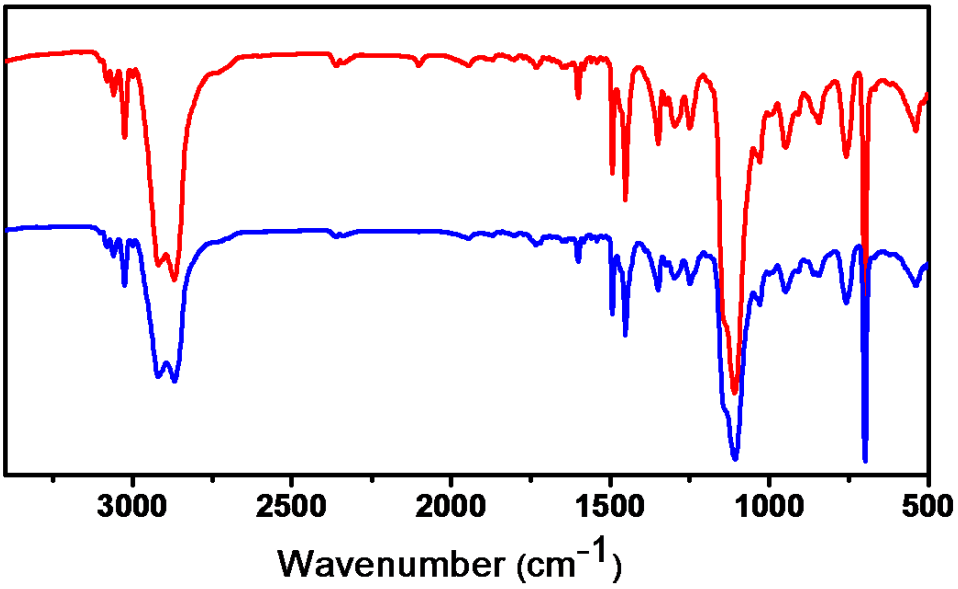

Figure S12. FT-IR spectra of PEO-(N_3)-PS (red) and PEO-(C_{60})-PS (blue). The results were based on the samples with M_n^{PEO} = 9.0 kg/mol and M_n^{PS} = 9.2 kg/mol.

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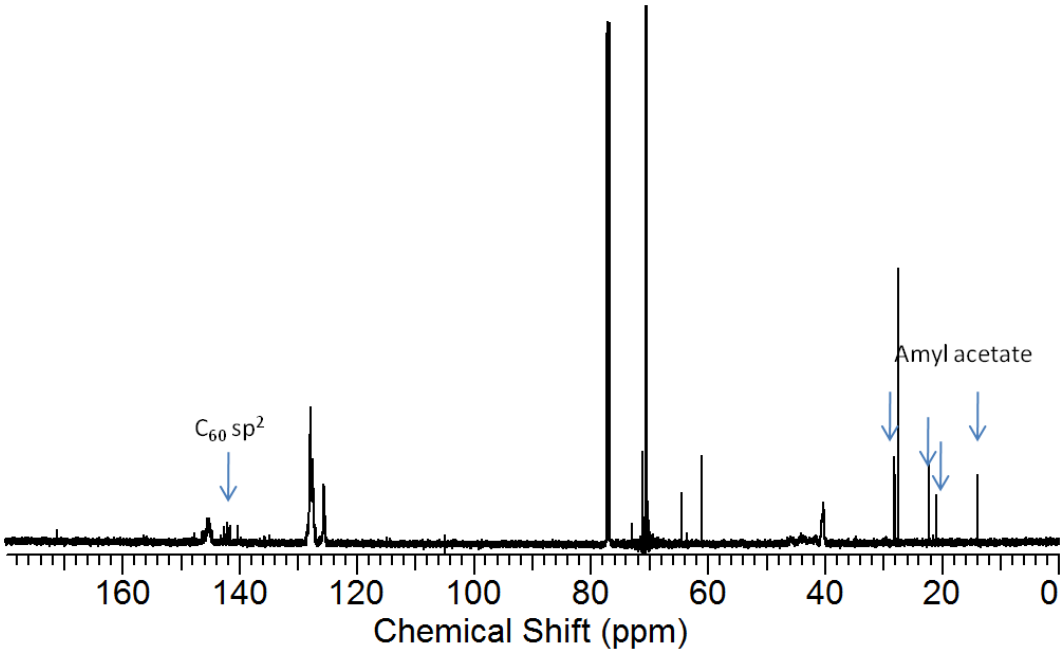

Figure S13. ^{13}C NMR spectrum of PEO-(C_{60})-PS. The results were based on the samples with M_n^{PEO} = 9.0 kg/mol and M_n^{PS} = 9.2 kg/mol.

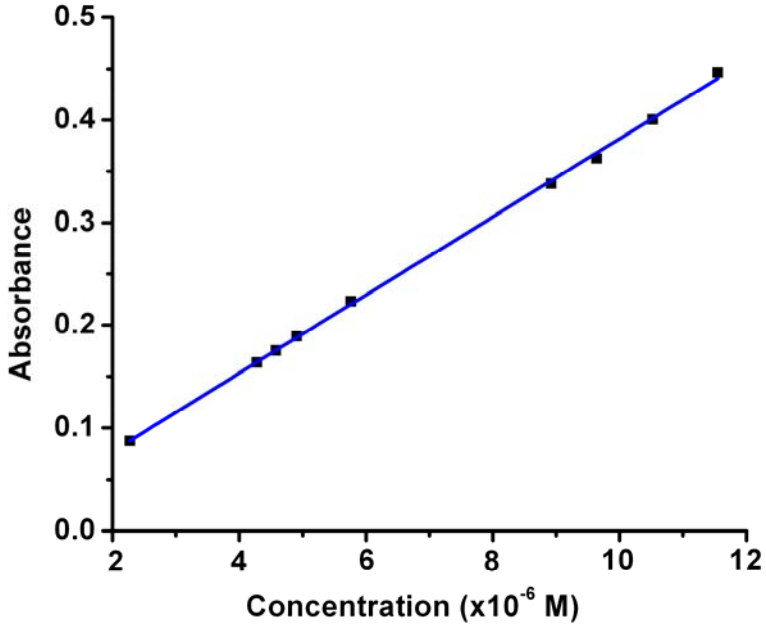

Figure S14. Plots of absorbance vs concentration for PEO-(C_{60})-PS. The results were based on the samples with M_n^{PEO} = 9.0 kg/mol and M_n^{PS} = 9.2 kg/mol.

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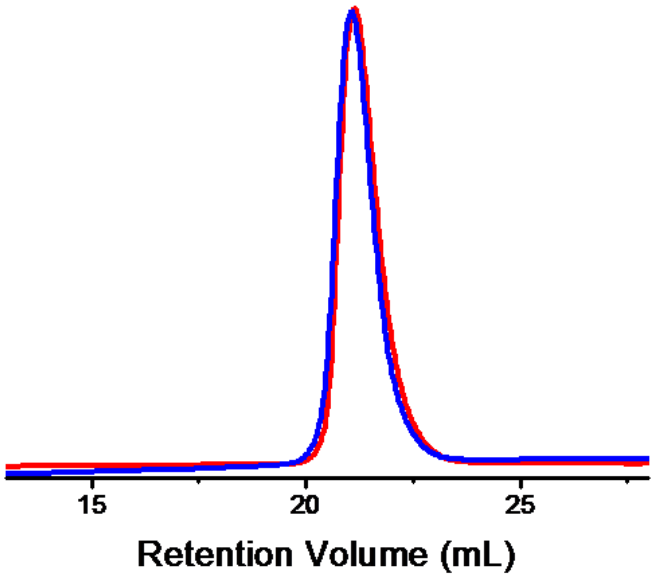

Figure S15. SEC chromatogram of PEO-*b*-PS/Cl with different molecular weights (red: PEO-*b*-PS/Cl-1; blue: PEO-*b*-PS/Cl-2, see Table 1).

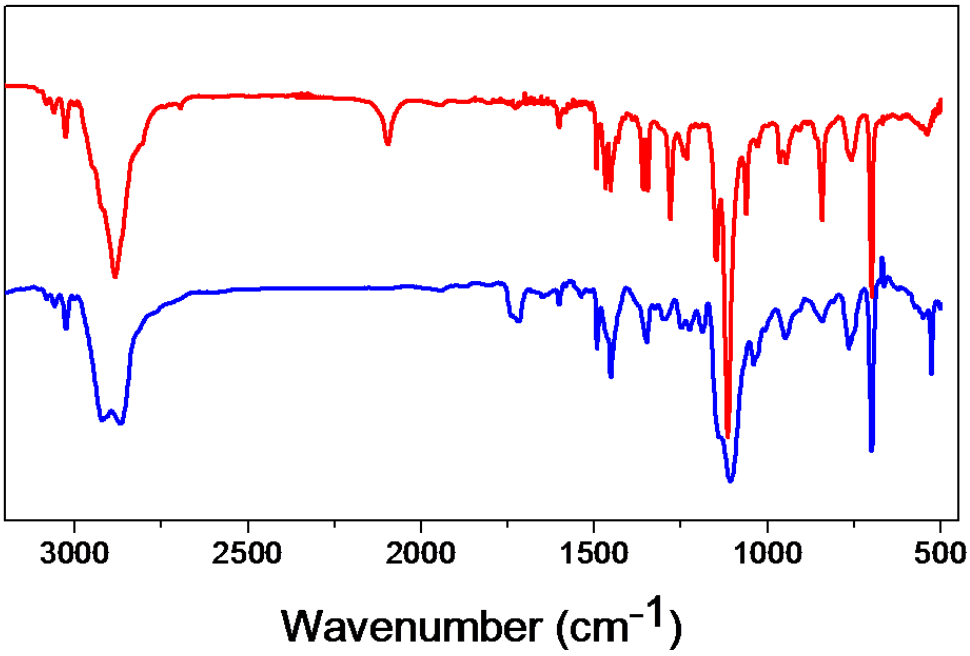

Figure 16. The FT-IR spectra of PEO-*b*-PS/N_3 (red), and PEO-*b*-PS/C_{60} (blue). The results were based on the samples with M_n^{PEO} = 9.0 kg/mol and M_n^{PS} = 7.0 kg/mol.

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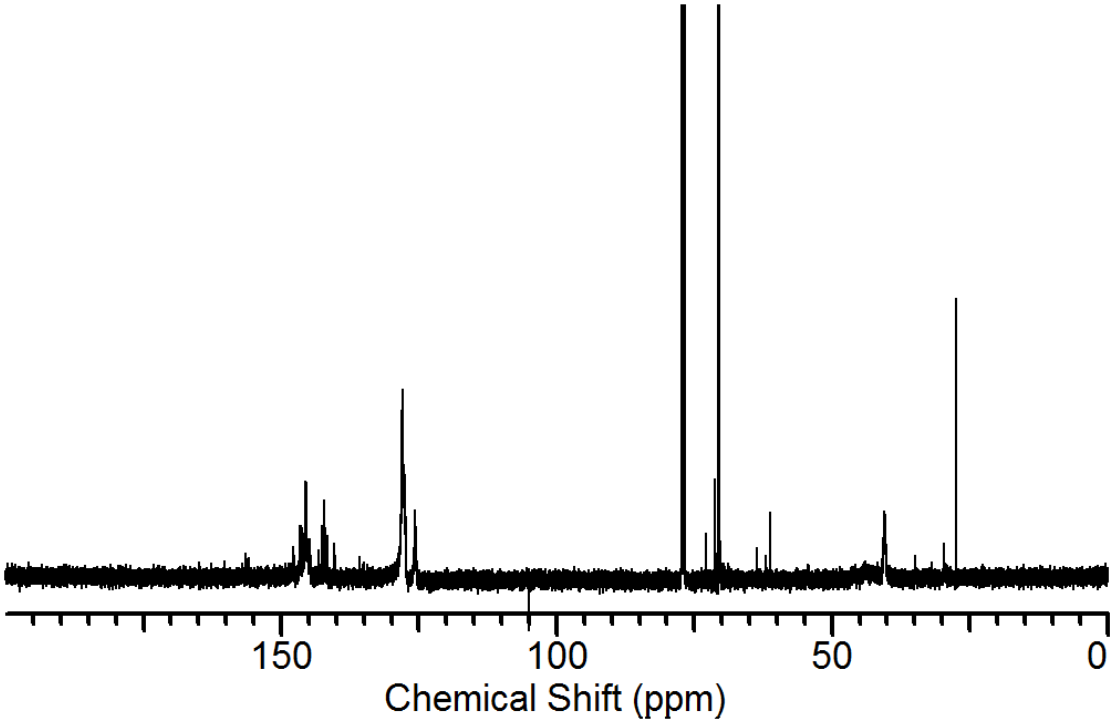

Figure S17. ^{13}C NMR spectrum of PEO-*b*-PS/C_{60}. The results were based on the samples with M_n^{PEO} = 9.0 kg/mol and M_n^{PS} = 7.0 kg/mol.

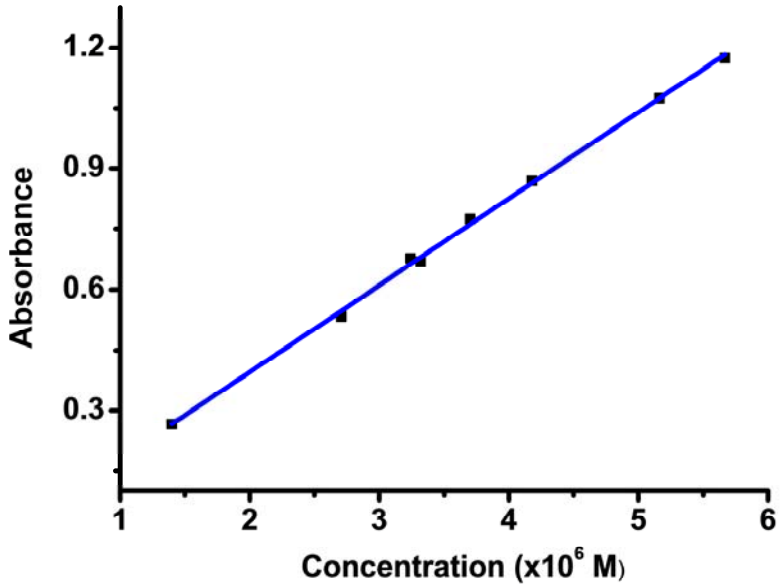

Figure S18. Calibration curve for PEO-*b*-PS/C_{60}-1, Table 1.

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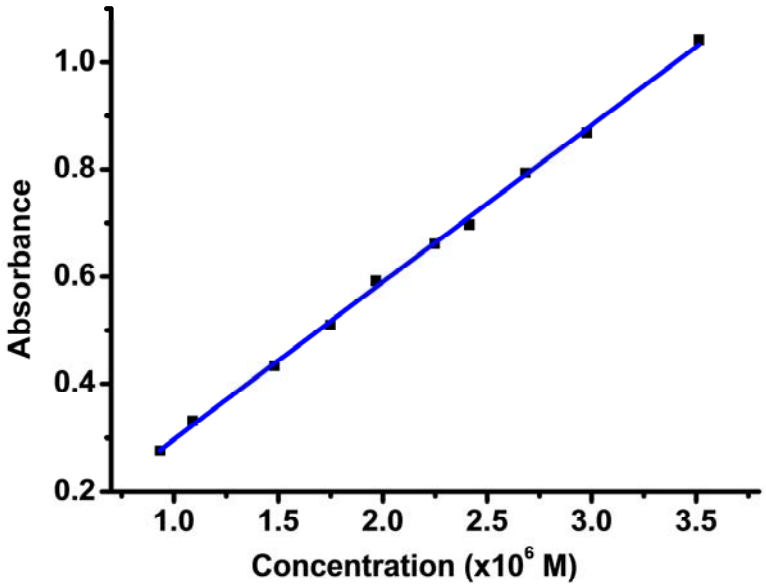

Figure S19. Calibration curve for PEO-*b*-PS/C_{60}-2, Table 1

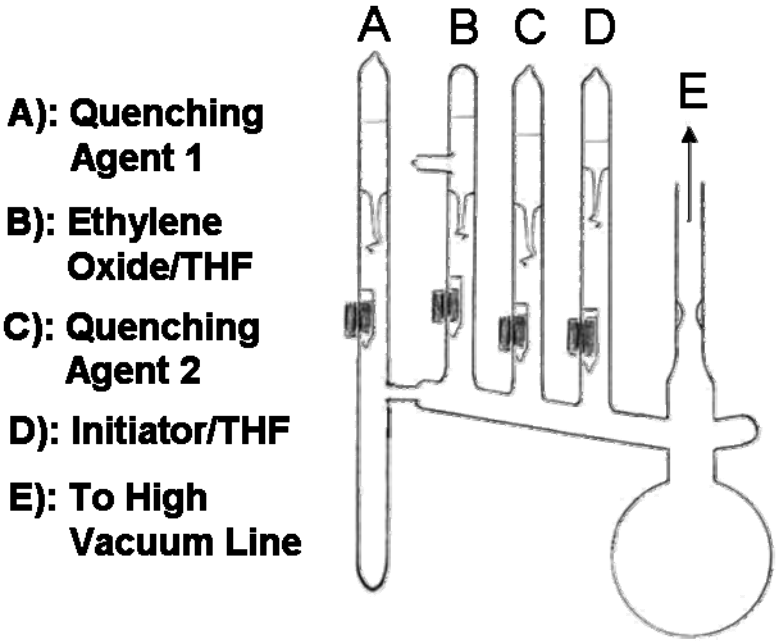

Figure S20. Reactor for the synthesis of PEO by anionic polymerization.

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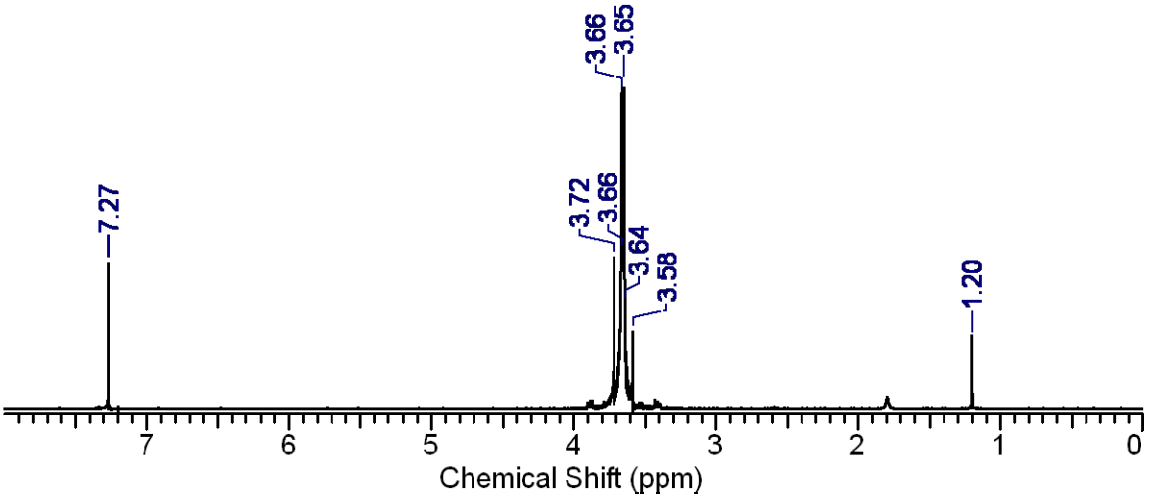

Figure S21. Representative ^{1}H NMR spectrum of PEO-OH.

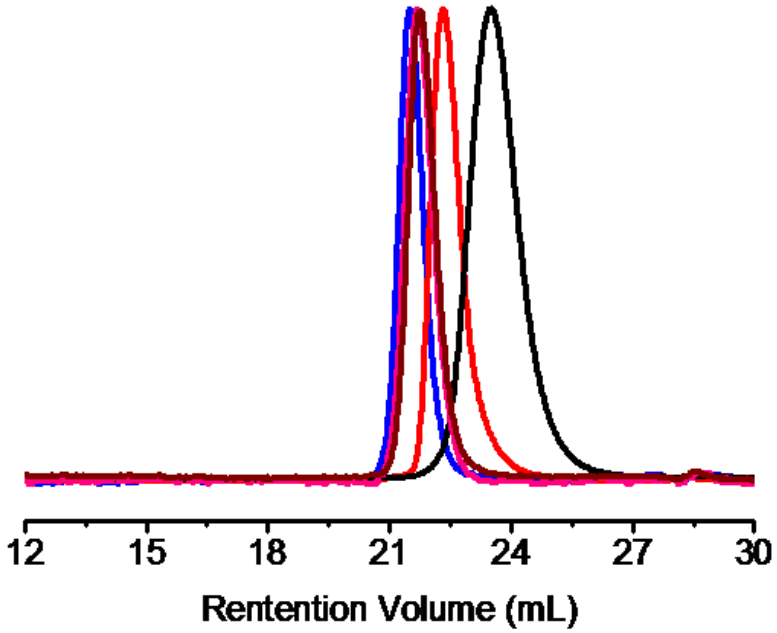

Figure S22. SEC chromatogram of PEO-OH with different molecular weights (From right to left: PEO3k-OH; PEO5k-OH; PEO8k-OH; PEO9k-OH; PEO11k-OH, see Table S1).

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