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Clickable Stars by Combination of AROP and Aqueous AGET ATRP

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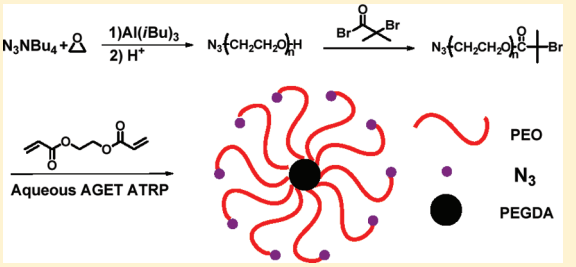
ABSTRACT: A series of star-shaped poly(ethylene oxide) (PEO) with azide groups at the end of each arm were synthesized by combination of anionic ring-opening polymerization (AROP) and aqueous activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP). First, α-azido, ω-hydroxy heterofunctional PEOs were prepared by AROP of ethylene oxide (EO) using tetrabutylammonium azide as initiator and triisobutylaluminum as catalyst. Then, a clickable PEO ATRP macroinitiator, α-azido, ω-bromoisobutyryl heterofunctional PEO, was synthesized by an esterification of the ω-hydroxy end group with 2-bromoisobutyryl bromide. Finally, an AGET ATRP of ethylene glycol diacrylate (EGDA) was carried out in water using the α-azido, ω-bromoisobutyryl heterofunctional PEOs as macroinitiator and surfactant. The absolute molecular weights of the products were characterized by static laser light scattering in water. Azide PEO stars with $M_w = 6.58 \times 10^6$ and average 309 arms were obtained using azide PEO macroinitiators with $M_n = 9800$ and [EGDA]/[MI] = 58. However, control over topology was lost for [EGDA]/[MI] > 100, resulting in irregular aggregates. The core−shell morphology of the functional star PEOs was observed by transmission electron microscopy. Fluorescent PEO stars were obtained by "clicking" dansyl probes onto the star shell, as verified by fluorescence spectra.



INTRODUCTION

Poly(ethylene oxide) (PEO), also referred to as poly(ethylene glycol), is a Food and Drug Administration (FDA) approved polymer that has been widely investigated in materials science and biotechnology due to its stability, biocompatibility, water solubility, nontoxicity, rapid clearance from the body, and lack of immunogenicity.[1−6] Recently, nonlinear PEOs with highly branched architectures (star,[7−14] hyperbranched,[15−19] and dendrimer-like[20−25]) have attracted the interest of chemist and biologist because of their unique properties such as low viscosity, high solubility, versatile functionality in comparison with their linear analogues, and the intriguing potential for biomedical and pharmaceutical applications. Because of the facile synthetic routes, star-shaped PEOs have been widely studied.[12] There are three major strategies for the preparation of star PEO. One is the so-called "core-first" method, which involves the anionic ring-opening polymerization (AROP) of ethylene oxide (EO) from a multifunctional initiator.[26,27] Second is the "coupling-onto" method which requires attaching living or active linear PEO arms onto a multifunctional core.[28−30] The last is the "arm-first" procedure, in which living or active linear PEO arms are cross-linked by reaction with a cross-linker to form the core of the star.[31−33] The "arm-first" method is considered to be an efficient method for the preparation of star polymers with a high number of arms and high molecular weight due to the larger size of the cross-linked core and less steric hindrance as compared to the other two strategies. Atom transfer radical polymerization (ATRP),[34−38] one of the most robust controlled/living radical polymerization (CRP) techniques, has been employed to prepare star polymers by the "arm-first" method using either a linear macroinitiator or macromonomer as arm precursors in the reaction with a divinyl cross-linker.[7,39−49] It is worth noticing that the uniform star PEOs can be prepared in a heterogeneous system via ATRP in aqueous dispersed media using linear PEO macroinitiator or macromonomer without any additional surfactant.[50−52] In this case, PEO macroinitiator or macromonomer acts not only as the reactant but also as the surfactant.

The conjugation of active molecules such as drugs, peptide sequences, and ligands of biological interest onto end-functionalized PEG, called "PEGylation", is extensively utilized for biomedical applications.[53−64] There is a need for a simple procedure to prepare heterofunctional PEOs (i.e., X-PEO-Y, where X is employed for architecture design and Y for functionality).[65−67] "Click" reactions, a term introduced by Sharpless, are widely used in polymer chemistry during the past few years due to their high specificity, quantitative yields, and near-perfect fidelity of the linking reaction conducted in the presence of most functional groups.[68] The use of click chemistry for PEGylation is extremely attractive since the cyclic triazole linking unit can be viewed as a biocompatible linkage.[69,70] Recently, the direct syntheses of clickable α-azido, ω-hydroxy heterofunctional PEO by controlled/living AROP of EO using functional initiators were reported.[71−73]

In this article, a series of α-azido, ω-hydroxy heterofunctional PEOs with different molecular weights were prepared according to procedures in the previous report.[71] After converting the hydroxyl group to 2-bromoisobutyryl group by esterification, the α-azido, ω-bromoisobutyryl heterofunctional PEOs were used as

Received: November 27, 2010
Revised: January 27, 2011
Published: March 04, 2011

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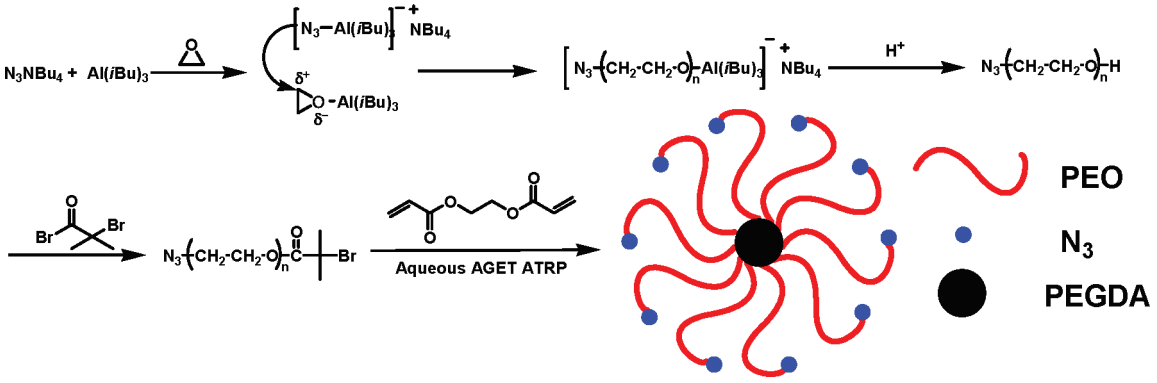
Scheme 1. Synthetic Route to Clickable Star PEOs



a dual macroinitiator and a surfactant to prepare clickable star PEOs employing ethylene glycol diacrylate (EGDA) as cross-linker via an AGET (activators generated by electron transfer) ATRP in aqueous dispersed media[74−77] (Scheme 1). The influence of PEO macroinitiator chain length and amount of added cross-linker on the polymerization were investigated in detail. A model "click" reaction between azide star PEO and a dansyl probe containing alkyne group, which was further verified by the fluorescence spectra, was carried out under mild conditions to illustrate the ease of shell functionalization.

EXPERIMENTAL SECTION

Materials. Tetrabutylammonium azide and triisobutylaluminum (1.0 mol/L in toluene) were purchased from Aldrich and used as received. Ethylene oxide (EO, Aldrich, 99.5%) was dried with calcium hydride (CaH_2) for 48 h and then distilled before use. Toluene and tetrahydrofuran (THF) were distilled from flasks containing sodium and benzophenone. Ethylene glycol diacrylate (EGDA, Aldrich, 90%, technical grade) was purified by passing through a basic alumina column to remove the inhibitor. Bis(2-pyridylmethyl)octadecylamine (BPMODA)[78] and 5-(dimethylamino)-*N*-(2-propynyl)-1-naphthalenesulfonamide[79] were synthesized according to the previously published procedures. All other reagents and solvents were purchased from Aldrich and used without further purification.

Measurements. Nuclear magnetic resonance (NMR) spectra were examined in $CDCl_3$ at 30 °C using a Bruker Advance 300 MHz spectrometer. The apparent molecular weights and dispersity (M_w/M_n) were determined by gel permeation chromatography (GPC; Polymer Standards Services (PSS); columns (guard, 10^5, 10^3, and 10^2 Å), with *N*,*N*-dimethylformamide (DMF) eluent at 35 °C, flow rate = 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410)) calibrated with linear PEO standards using WinGPC 6.0 software from PSS. The weight fraction of the star PEOs was also determined using GPC by monitoring the decrease of the macroinitiator peak area relative to the increase in the star polymer peak area. The absolute molecular weight of azide star PEOs was measured on a Brookhaven Instruments Corp. BI-200SM (Brookhaven Instruments, Holtsville, NY) goniometer. The instrument laser provided vertically polarized light of wavelength 532 nm. Samples in aqueous solution were placed in borosilicate scintillation vials for measurements and were referenced against scattering from a toluene standard. The typical scattering angle range used was 70°−130°. The instrument bath was filled with decahydronaphthalene, and measurements were typically made at 25 °C. Particle size and size distribution of star polymers were measured by dynamic light scattering (DLS) at 25 °C using 1.0 mg/mL aqueous solution of polymer on a high performance particle sizer, Model HP5001 from Malvern Instruments, Ltd. Transmission electron microscopy (TEM) analysis was conducted using an Hitachi H-7100 TEM (Hitachi High Technologies America) operating at 50 kV. A drop of 3 mg/mL star PEO aqueous solution was placed onto the surface of Formvar-carbon film-coated copper grids. Excess solution was quickly wicked away with a filter paper. All grids were finally negatively stained by 2 wt % phosphotungstic acid. Fluorescence excitation spectra were recorded on Varian Cary 50 fluorescence spectrometer at 339 nm emission.

Synthesis of α-Azido, ω-Hydroxy Heterofunctional PEO. α-Azido, ω-hydroxy heterofunctional PEOs were prepared by AROP of EO with tetrabutylammonium azide in the presence of triisobutylaluminum, according to the literature procedure.[71] Initially, 0.285 g (1.0 mmol) of tetrabutylammonium azide, 5.9 g of EO (134 mmol), and 100 mL of anhydrous toluene were charged to a 200 mL glass reactor equipped with a magnetic stirrer, under nitrogen atmosphere, and then 2.0 mL of triisobutylaluminum (1.0 mol/L in toluene) was added via a syringe at −90 °C to start the polymerization. The temperature of the polymerization system was slowly raised to room temperature. After 12 h polymerization, the reaction was terminated by addition of a few drops of hydrochloric acid. The solution was purified by filtration to remove the salt, and then the filtrate was concentrated before pouring into a large amount of cold diethyl ether to precipitate the product. The final product was obtained after drying the precipitate under vacuum at room temperature for 24 h.

Synthesis of α-Azido, ω-Bromoisobutyryl Heterofunctional PEO. α-Azido, ω-bromoisobutyryl heterofunctional PEOs were synthesized by the esterification of α-azido, ω-hydroxy heterofunctional PEOs with 2-bromoisobutyryl bromide in the presence of triethylamine in THF. Typically, the α-azido, ω-hydroxy heterofunctional PEO (4.4 g, 1.0 mmol, M_n = 4400) was dissolved in 100 mL of anhydrous THF, followed by the introduction of triethylamine (TEA) (0.20 g, 2 mmol, 0.28 mL) via a syringe. Then 2-bromoisobutyryl bromide (0.46 g, 2 mmol, 0.25 mL) in 5 mL of anhydrous THF was added dropwise to the vigorously stirred solution at 0 °C over 30 min. The reaction mixture was stirred at room temperature overnight. The precipitate was removed by filtration, and the solution was evaporated to dryness. The crude product was dissolved in 40 mL of methylene chloride, then washed successively with 1.0 M $NaHCO_3$ aqueous solution and water, and finally dried over anhydrous $MgSO_4$, filtered, and concentrated before pouring into large amount of cold ethyl ether to precipitate the product. The resulting white solid was dried under vacuum at room temperature for 24 h.

Synthesis of Azide Star PEOs by Aqueous AGET ATRP. Azide star PEOs were synthesized by AGET ATRP of EGDA in aqueous dispersed media using α-azido, ω-bromoisobutyryl heterofunctional PEOs as macroinitiator and surfactant. The general procedure was as follows: α-azido, ω-bromoisobutyryl heterofunctional PEO (0.1 g,

0.022 mmol, M_n = 4500), EGDA (0.1 g, 0.59 mmol), $CuBr_2$ (0.005 g, 0.022 mmol), BPMODA (0.012 g, 0.027 mmol), and hexadecane (0.004 g) were dissolved in 1.0 mL of methylene chloride (CH_2Cl_2) in a round-bottom flask by stirring at 30 °C for 1 h. The resulting homogeneous organic solution was then cooled to room temperature, and 10 mL of water was added. The mixture was subjected to sonication in an ice bath (Misonix sonicator S-4000 duty cycle at 50%, amplitude set at 70% for 10 min). The aqueous dispersion was transferred to a Schlenk flask and purged with nitrogen for 30 min to remove oxygen and CH_2Cl_2. After injecting 0.2 mL of a deoxygenated aqueous solution of ascorbic acid, containing 0.011 mmol of ascorbic acid into the aqueous dispersion, the flask was immersed in an oil bath thermostated at 70 °C to activate the catalyst and start the polymerization. Samples were taken at timed intervals to determine the molecular weight by GPC and to measure the diameter by DLS. The polymerization was terminated by bubbling air into the mixture. After filtration, the azide star PEO was purified using centrifugal filter units (Millipore) to remove any unreacted monomer and PEO macroinitiator.

Synthesis of Dansyl Star PEO by "Click" Reaction. A typical procedure was as follows: azide star PEO (0.10 g, 0.0065 mmol of azide group approximately), 5-(dimethylamino)-*N*-(2-propynyl)-1-naphthalenesulfonamide (29 mg, 0.10 mmol), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 18 mg, 0.10 mmol) were dissolved in DMF (2.0 mL). The reaction mixture was degassed by three freeze−pump−thaw cycles before adding CuBr (14 mg, 0.1 mmol) to the frozen mixture under nitrogen flow. The mixture was left under nitrogen and stirred at 40 °C for 24 h. Then, the solution was exposed to air and passed through an alumina column to remove the copper salt. The unreacted dansyl probe was removed by dialysis against DMF.

RESULTS AND DISCUSSION

Synthesis of α-Azido, ω-Hydroxy Heterofunctional PEO. α-Azido, ω-hydroxy heterofunctional PEO was prepared by AROP of EO with tetrabutylammonium azide in the presence of triisobutylaluminum. As previously reported, the polymerization involves a complexation of the propagating active species with 1 equiv of triisobutylaluminum and a strong nucleophilic activation of the EO via complexation with the remaining triisobutylaluminum. After insertion of the activated monomer in the growing chain, the triisobutylaluminum is released to activate another EO molecule, making the controlled chain propagation possible.[71] The results and polymerization conditions are shown in Table 1 as well as the GPC traces in Figure 1. The catalytic system shows very high activity for EO polymerization, providing high yield under mild conditions. The molecular weight of the product increased with the increasing molar ratio of EO to tetrabutylammonium azide, and the theoretical molecular weight matches the GPC value, which indicates that essentially every tetrabutylammonium azide molecule initiated only one living PEO chain and the polymerizations were well controlled. The dispersity (M_w/M_n) decreased as the $[EO]/[N_3NBu_4]$ ratio increased. This illustrates that the chain propagation could be faster than the initiating reaction leading to better control for higher targeted DP.

The chain-end functionality of azide group and hydroxyl group is important for the subsequent star synthesis and "click" reaction and was determined by ^{13}C NMR. As Figure 2 shows, the signals of the methylene carbons next to azide group and hydroxyl group could be clearly detected at around 51 ppm (C^1) and 62 ppm (C^5), respectively, indicating the existence of the two end groups. In addition, the chain-end functionality of the azide group was quantified by analysis of the ^1H NMR spectra as shown in Figure 3. The results summarized in Table 1 are in good agreement with the theoretical and GPC values.

Table 1. Synthesis of α-Azido, ω-Hydroxy Heterofunctional PEOs[a]

sample	$[EO]/[N_3NBu_4]$	yield (%)	$M_{n,theo}$[b]	$M_{n,NMR}$[c]	$M_{n,GPC}$[d]	M_w/M_n[d]
MI-1	101	99.9	4500	4100	4400	1.53
MI-2	134	99.9	6000	6500	7400	1.39
MI-3	240	93.0	9900	10500	9700	1.34

[a] Polymerization conditions: $[Al(iBu)_3]/[N_3NBu_4]$ = 2, [EO] = 1.0 mol/L, rt, in toluene, 12 h. [b] Calculated by conversion: $M_{n,theo} = ([EO]_0)/([N_3NBu_4]_0) \times$ conversion $\times$ 44 + 43, where 43 is the molecular weight of end groups. [c] Calculated by ^1H NMR: $M_{n,NMR} = (I^s/((I^{a+s} - I^s) \times 0.55\%) \times 0.5 + 0.5) \times 44 + 43$. [d] Measured by GPC, DMF as solvent, calibrated with PEO standards.

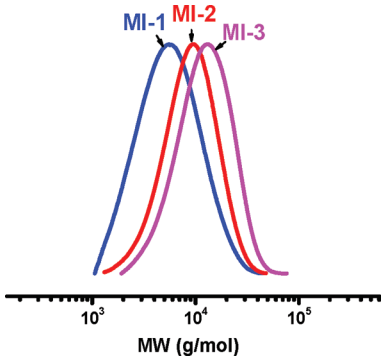


Figure 1. GPC traces of α-azido, ω-hydroxy heterofunctional PEOs.

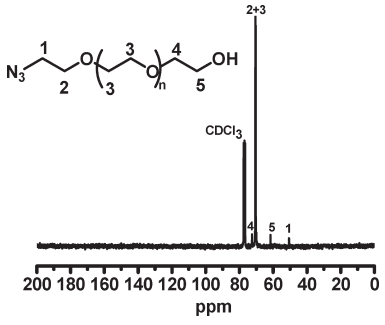


Figure 2. ^{13}C NMR spectrum of α-azido, ω-hydroxy PEO (MI-1 in Table 1).

Synthesis of α-Azido, ω-Bromoisobutyryl Heterofunctional PEO. The α-azido, ω-hydroxy heterofunctional PEOs were converted into azide PEO macroinitiators for ATRP by a simple esterification reaction. A typical ^1H NMR spectrum of one such product is shown in Figure 4. After esterification, new signals corresponding to methyl protons (H^d) and methylene protons (H^c) of 2-bromoisobutyrate at 1.95 and 4.34 ppm are present in the spectra, indicating that the terminal hydroxyl groups were esterified. The molecular weight of α-azido, ω-bromoisobutyryl heterofunctional PEOs was calculated according to the following equation:

$$M'_{n,NMR} = \left(\frac{I^s}{I^d \times 0.55\%} \times 1.5 + 1\right) \times 44 + 192$$

(192 is the molecular weight of end groups), which closely match the values in Table 1 indicating good functionality on each chain end.

Synthesis of Azide Star PEOs by Aqueous AGET ATRP. The ATRP technique was employed for synthesis of star PEOs using the α-functional PEO macroinitiator in homogeneous systems.[7] However, for PEO macroinitiator with high molecular weight, the low concentration of initiating sites decreases the polymerization efficiency. In order to increase efficiency, a large amount of divinyl cross-linker was used, which could lead to gelation. Thus, the stars with high molecular weight PEO macroinitiator should be prepared more efficiently in a heterogeneous or dispersed medium. The key aspects of this concept is that the concentration of initiating sites is still high enough in the hydrophobic part of the dispersed medium to provide efficient initiation while the PEO macroinitiator with higher molecular weight is a better surfactant to stabilize the polymeric system. Azide PEO macroinitiators with different molecular weights were used to prepare azide PEO stars by aqueous AGET ATRP. The AGET ATRP allows easy operation with reagents that are not sensitive to oxygen, before the reducing agent is added. The results and polymerization conditions are summarized in Table 2. The ratio of PEO macroinitiator to EGDA was fixed at 1:1 by weight. Star PEOs with molecular weight of several millions (by SLLS) and hundreds of arms were successfully prepared by AGET ATRP in aqueous dispersed media via the "arm-first" method. As expected, the GPC curves indicate that the PEO macroinitiator with higher molecular weight shows higher polymerization efficiency, resulting in larger area fraction of star polymers (A_{star}).

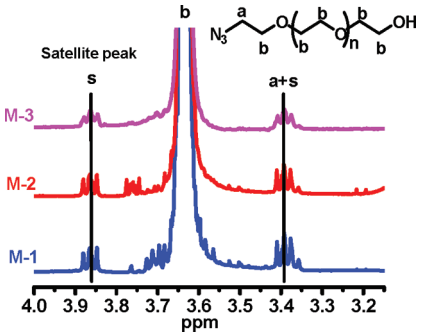


Figure 3. End-group analysis of α-azido, ω-hydroxy PEOs by ^{1}H NMR.

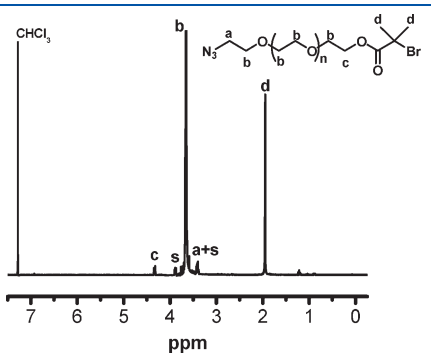


Figure 4. ^{1}H NMR spectrum of α-azido, ω-bromoisobutyryl heterofunctional PEO (from MI-1).

During the polymerization process, an appropriate amount of a sample was withdrawn from the Schlenk flask under nitrogen protection for GPC and DLS measurement. Figure 5 shows the evolution of the GPC and DLS traces of the star synthesis. The polymerization reached the highest conversion within 6 h. The aggregates in the initial system have a diameter of more than 100 nm. As the polymerization proceeded, the PEO arms were chain extended with EGDA forming an amphiphilic block structure, which efficiently micellized in water with the organic components trapped inside the micelle, leading to smaller diameter particles. Further incorporation of more PEO arms to the cross-linked micellular structures resulted in uniform star polymers. The diameters of the final star products ranged from 15 to 50 nm, depending on the star molecular weight and chain length of PEO arms.

The aqueous AGET ATRP was carried out with different amounts of EGDA to investigate its influence on star structure. The α-azido, ω-bromoisobutyryl heterofunctional PEO prepared from MI-3, with M_n = 9800, was chosen as the macroinitiator for this study, and the feeding molar ratio of EGDA to PEO macroinitiator was changed from 7.5 to 180. The results are summarized in Table 3. The polymerization with the molar ratio of [EGDA]/[MI] as low as 7.5 was successful, leading to a star PEO in high yield (S-4). Samples S-1 and S-5 have exactly the same feeding molar ratio of [EGDA]/[MI] = 26.5. However, the higher yield of star PEO was obtained with the PEO

Table 2. Influence of PEO Macroinitiator Chain Length on Star Synthesis by Aqueous AGET ATRP[a]

sample	MI	[EGDA]/[MI]	A_{star}[b] (%)	diameter[c] (nm)	$M_{n,GPC}$[d]	M_w/M_n[d]	$M_{w,SLLS}$[e] ($\times 10^6$)	N_{arm}[f]
S-1	MI-1	26.5	60.1	15.7	100 900	1.34	1.99 ± 0.36	173
S-2	MI-2	44.1	65.8	24.4	154 000	1.35	4.40 ± 0.21	246
S-3	MI-3	57.6	77.7	43.8	382 500	1.37	6.58 ± 0.36	309

[a] Polymerization conditions: [MI]/[$CuBr_2$]/[BPMODA]/[ascorbic acid] = 1/1/1/0.5, weight ratio of MI:EGDA = 1:1, 70 °C. [b] The area fraction of star polymers, determined by the multipeak splitting of the GPC curve using Gaussian function. [c] Measured by DLS (highest volume %), 1.0 mg/mL, water as solvent. [d] Measured by GPC, DMF as solvent, calibrated with PEO standards. [e] Measured by static laser light scattering (SLLS), the dn/dc of each sample are 0.1537 mL/g (S-1), 0.1342 mL/g (S-2) and 0.1203 mL/g (S-3) in water, measured on Brice-Phoenix, Model BP-2000-V, differential refrectometer photometer using vertically polarized light 532 nm wavelength. [f] Number-average value of the number of arms per star molecule (N_{arm}) was estimated based on the following equation:

$$N_{arm} = \frac{M_{w,SLLS}}{M_w/M_n \times M_{n,MI}} \frac{A_{star}(1 + Conv_{EGDA}) - Conv_{EGDA}}{A_{star}(1 + Conv_{EGDA})}$$

where $M_{n,MI}$ is the molecular weight of macroinitiator and $Conv_{EGDA}$ is the conversion of EGDA cross-linker measured by ^{1}H NMR, assuming that PEO macroinitiator and star PEO have similar dn/dc in DMF.

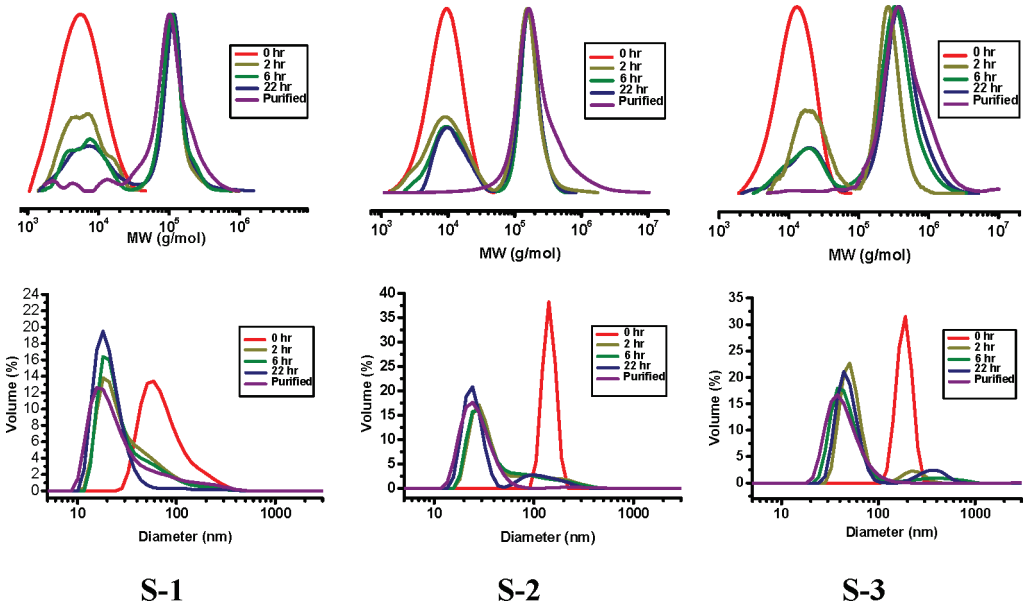


Figure 5. Evolution of the GPC and DLS traces during the star synthesis in aqueous AGET ATRP process.

Table 3. Influence of EGDA Amount on Star Synthesis in Aqueous AGET ATRP[a]

sample	[EGDA]/[MI]	A_{star} (%)[b]	diameter (nm)[c]	$M_{n,GPC}$[d]	M_w/M_n[d]
S-4	7.5	73.7	32.7	161 800	1.26
S-5	26.5	75.6	37.2	318 700	1.28
S-1[e]	26.5	60.1	15.7	100 900	1.34
S-3[f]	59.0	77.7	43.8	382 500	1.37
S-6	90.0	83.4	50.7	433 500	1.37
G-1[g]	125		220.2		
G-2[g]	180		458.8		

[a] Polymerization conditions: [MI]/[$CuBr_2$]/[BPMODA]/[ascorbic acid] = 1/1/0.5, molecular weight of MI: 9800, 70 °C. [b] The area fraction of star polymers, determined by the multipeak splitting of the GPC curve using Gaussian function. [c] Measured by DLS, water as solvent (highest vol %). [d] Measured by GPC, DMF as solvent, calibrated with PEO standards. [e] The same data in Table 2; molecular weight of MI: 4500. [f] The same data in Table 2. [g] Irregular aggregates.

macroinitiator with longer chains, which strongly confirms that the PEO macroinitiator with higher molecular weight has higher activity in an aqueous ATRP. The diameters of the final products were not significantly changed when [EGDA]/[MI] was increased from 7.5 to 90. This indicates that the diameter of star PEO is controlled by the length of PEO arm rather than the size of PEGDA core. When the ratio of [EGDA]/[MI] was higher than 100, irregular aggregates with diameter of several hundred nanometers were obtained.

The morphology and diameter of the products were studied by TEM (Figure 6). All the samples were negatively stained by phosphotungstic acid. The star PEOs show uniform spherelike morphologies with core−shell microstructure in TEM images, and the trend of diameter change agrees quite well with the DLS data. In addition, the TEM image of G-1 shows large irregular morphology, indicating that the star synthesis is uncontrolled when [EGDA]/[MI] is higher than 100.

Synthesis of Dansyl Star PEO by "Click" Reaction. The azide groups are stable during the aqueous AGET ATRP process, meaning that the star PEOs prepared can be further modified by "click" reactions. In this study, 5-(dimethylamino)-*N*-(2-propynyl)-1-naphthalenesulfonamide, a dansyl probe modified by alkyne group, was chosen as a model molecule to "click" onto the shell of azide star PEO (S-3).[79−82] The extra dansyl probe was removed by dialysis. The final fluorescent dansyl star PEO was characterized by fluorescence spectroscopy by comparison with the model molecule and the unmodified star PEO. Figure 7 shows the synthetic route and the fluorescence spectra, in which the modified star PEO displays a strong emission peak at 541 nm when excited at 339 nm, similar to the pure dansyl probe. The unmodified star PEO did not show any emission. On the basis of the emission intensities and the concentrations of fluorescent dansyl star PEO and pure dansyl probe, it could be concluded that the "click" efficiency exceeded 90%. The results confirm that the α-azido groups on PEO chain end were well-preserved and still accessible for subsequent modification after star synthesis.

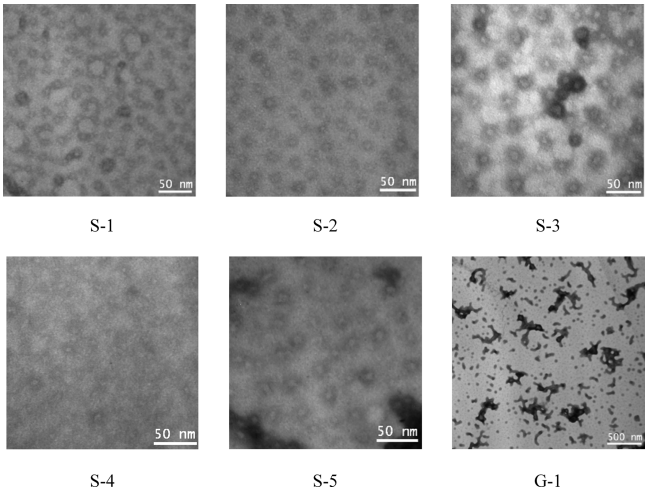


Figure 6. TEM images of azide star PEOs.

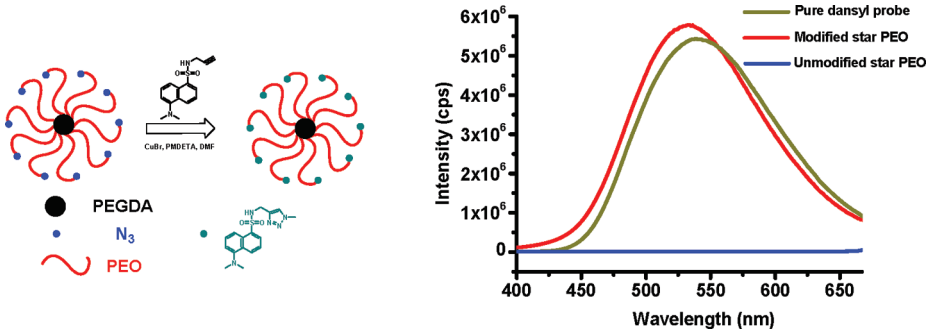


Figure 7. Synthetic route and fluorescence spectra of dansyl star PEO. Concentrations for fluorescence analysis: dansyl probe, 8.7×10^{-5} mol/L; modified and unmodified star PEOs, 1.5 mg/mL, 9.1×10^{-5} mol/L functional group.

CONCLUSIONS

In summary, α-azido, ω-bromoisobutyryl heterofunctional PEOs were synthesized by controlled/living AROP of EO with tetrabutylammonium azide as initiator in the presence of triisobutylaluminum as catalyst and a subsequent esterification reaction. Then clickable star PEOs with peripheral azide groups were prepared via "arm-first" method by aqueous AGET ATRP using α-azido, ω-bromoisobutyryl heterofunctional PEOs as dual macroinitiator and surfactant in a chain extension cross-linking reaction with EGDA. The polymerization was studied by tuning the length of PEO macroinitiator and the amount of EGDA cross-linker. The PEO macroinitiator with higher molecular weight exhibits higher activity during the aqueous AGET ATRP process, which contrasts the activity in homogeneous systems. This phenomenon can be attributed to the separated hydrophobic part in the aqueous dispersed medium and the better surfactant activity of longer PEO chains. Star polymers were obtained while varying the [EGDA]/[MI] ratio from 7.5 to 90 using azide PEO macroinitiator with M_n = 9800. However, control over topology was lost for [EGDA]/[MI] > 100, resulting in irregular aggregates. The azide groups were preserved on the star arm terminal units, as confirmed by "clicking" dansyl probes onto the PEO star and characterized by fluorescence spectra.

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ACKNOWLEDGMENT

The authors thank Shengpeng Liu, Viet Lam, Dr. Annette Jacobson, and Dr. Linda A. Peteanu for the technical assistance. The financial support from NSF (DMR-09-69301) and by WCU (World Class University) program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology (R33-10035-0) is gratefully appreciated.

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