Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Azide-based heterobifunctional poly(ethylene oxide)s: NaN_3-initiated “living” polymerization of ethylene oxide and chain end functionalizations

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Experimental details

Materials.

α-Azide-*ω*-thiol PEO ($M_{n,AzPEO}$ = 4,700 g/mol, 2 g) was dissolved in methanol 200 ml and heated to 40°C under an inert gas for 30 min. The gold(III) chloride trihydrate (tetrachloroauric(III) acid ($HAuCl_4$) : Sigma-Aldrich Chem. Co., reagent) solution (0.5 g in methanol 20 ml) was delivered into the reactor using a syringe. The reaction system was kept at 40°C under an inert gas for 30 min, followed by introducing sodium borohydrate (0.5 g) dissolved dropwise in methanol 60 ml with stirring. After a complete reaction (24 h), the gold solution was precipitated in excess ether and the precipitate was dried in a vacuum oven. In addition, the nano-sized gold particles using *α*-thiol-*ω*-azide PEO (HS-PEO-N_3) as the stabilizer were prepared by following the same procedures as those described in the case of *α*-thiol-*ω*-amine PEO.

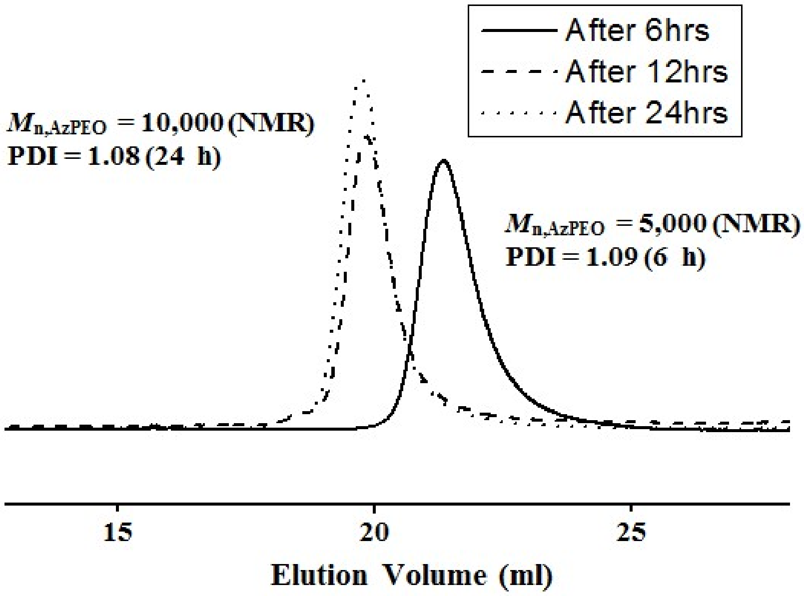
Synthesis of α-azide-ω-amine PEO

New α-azide PEO ($M_{n,SEC}$ = 4,800) was reacted with TsCl (tosyl chloride) in the presence of triethylamine in dichloromethane (DCM) at 40°C for 24 h. The resulting α-azide-ω-tosyl PEO was further reacted with potassium thioacetate in DMF at 85^{o}C for 24h. All products were precipitated in excess diethyl ether. α-Azide-ω-thioacetate PEO was deacetylated using excess hydrazine, followed by addition of HCl (1.0 N) until the pH value reached to ~7. The precipitate was re-dissolved in methanol, followed by precipitation in excess diethyl ether and drying in vacuum oven at room temperature prior to analysis. The resulting α-azide-ω-thio1 PEO was reacted with triphenyl phosphine in methanol under refluxing for 24 h, followed by precipitation in diethyl ether and drying it.

Supporting Data

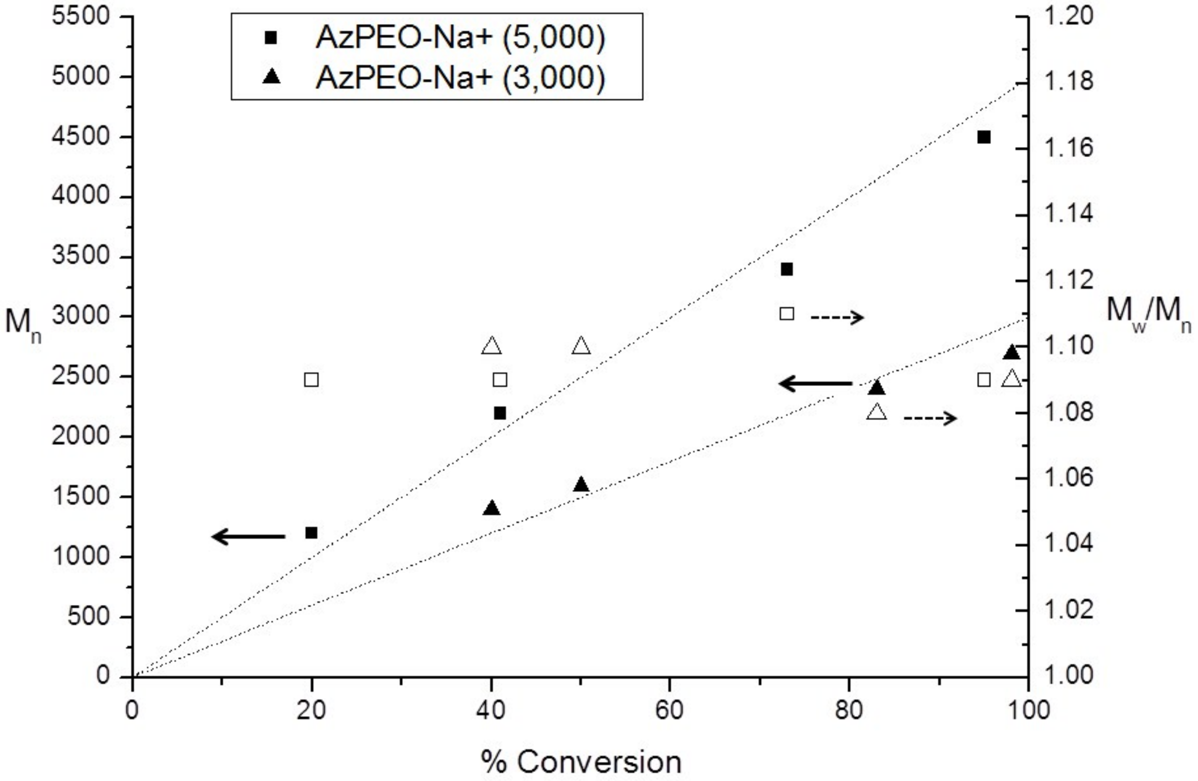
Synthesis of α-azide PEO and chain-end functionalizations.

The complete reaction was investigated through the examination of %conversion of monomer with time.



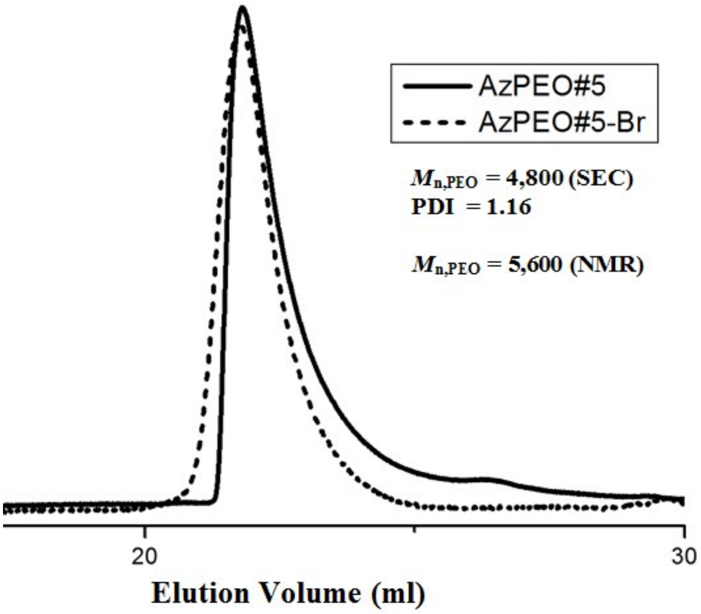
SI Figure 1. Size exclusion chromatograms of the formed polymers with the reaction time in NaN_3-initiated polymerization of EO in DMF at 50°C.

SI Figure 2 represents a typical plot of the molecular weight against %conversion in the ring-opening polymerization of EO using NaN_3 as a functional anionic initiator.



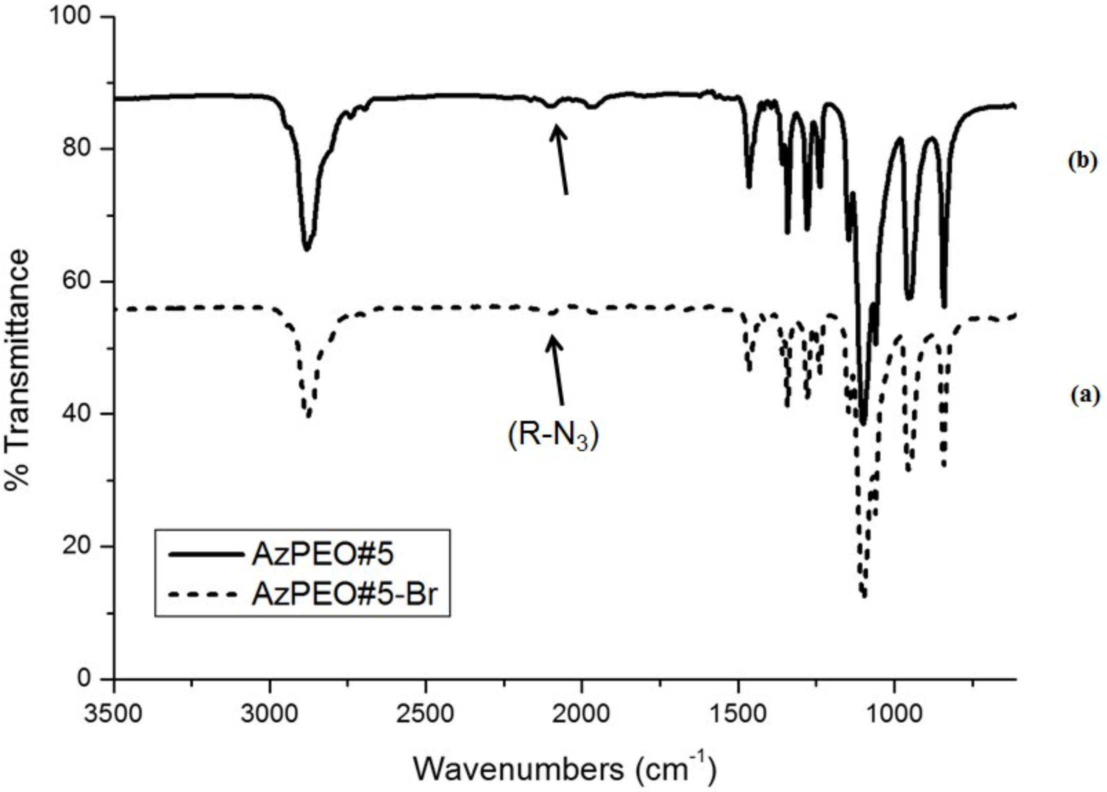
SI Figure 2. A typical plot of the change of molecular weight against %conversion in NaN_3-initated polymerization of EO in DMF at 50°C.

The molecular weights and the molecular weight distributions of α-azide PEO and the corresponding α-azide-ω-bromo PEO mentioned in Figure 3 of the main text are shown in SI Figure 3.



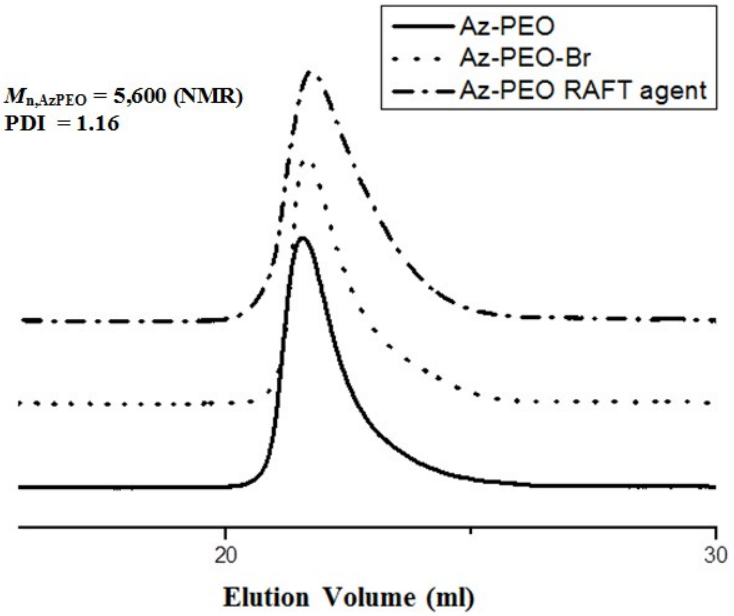
SI Figure 3. Size exclusion chromatograms of α-azide PEO and corresponding α-azido-ω-bromo PEO mentioned in Figure 2 of the main text.

In addition, the FT-IR spectra of *α*-azide PEO (Az PEO 3) and corresponding *α*-azide-*ω*-bromo PEO are shown in Figure 3 in the main text are shown in SI Figure 4.

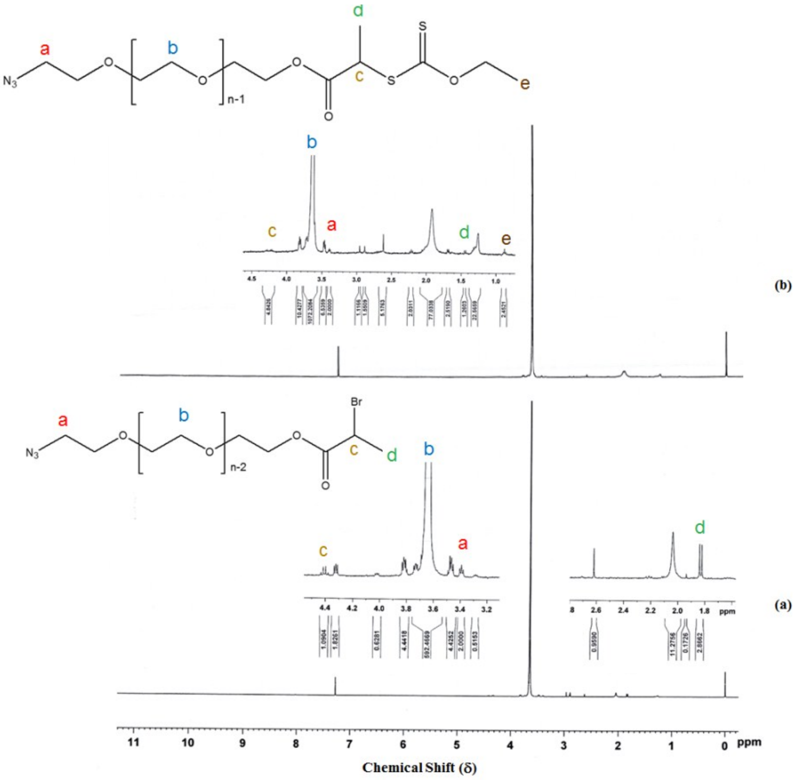


SI Figure 4. FT-IR spectra of *α*-azide PEO and corresponding *α*-azide-*ω*-bromo PEO.

Again, α-azide-ω-bromo PEO ($M_{n,AZPEO}$ = 5,600 g/mol) was synthesized by following the same procedures as shown in Scheme 2 in the main text, followed by reaction with potassium ethyl xanthogenate in DMF because of its solubility. The SECs of all products are shown in SI Figure 5. In addition, the ^{1}H NMR spectra of α-azide-ω-bromo PEO and the corresponding RAFT agent are shown in SI Figure 6.

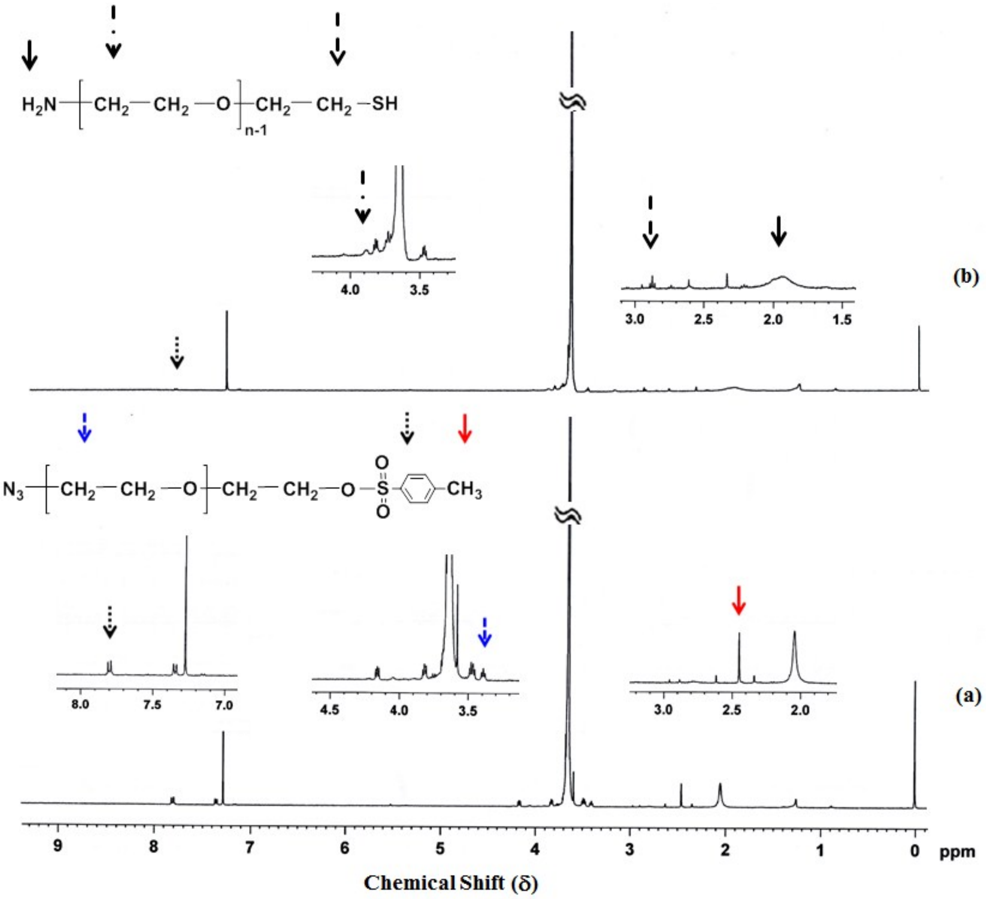


SI Figure 5. Size exclusion chromatograms of α-azide PEO, corresponding α-azide-ω-bromo PEO, and the corresponding α-azide PEO-based RAFT agent.

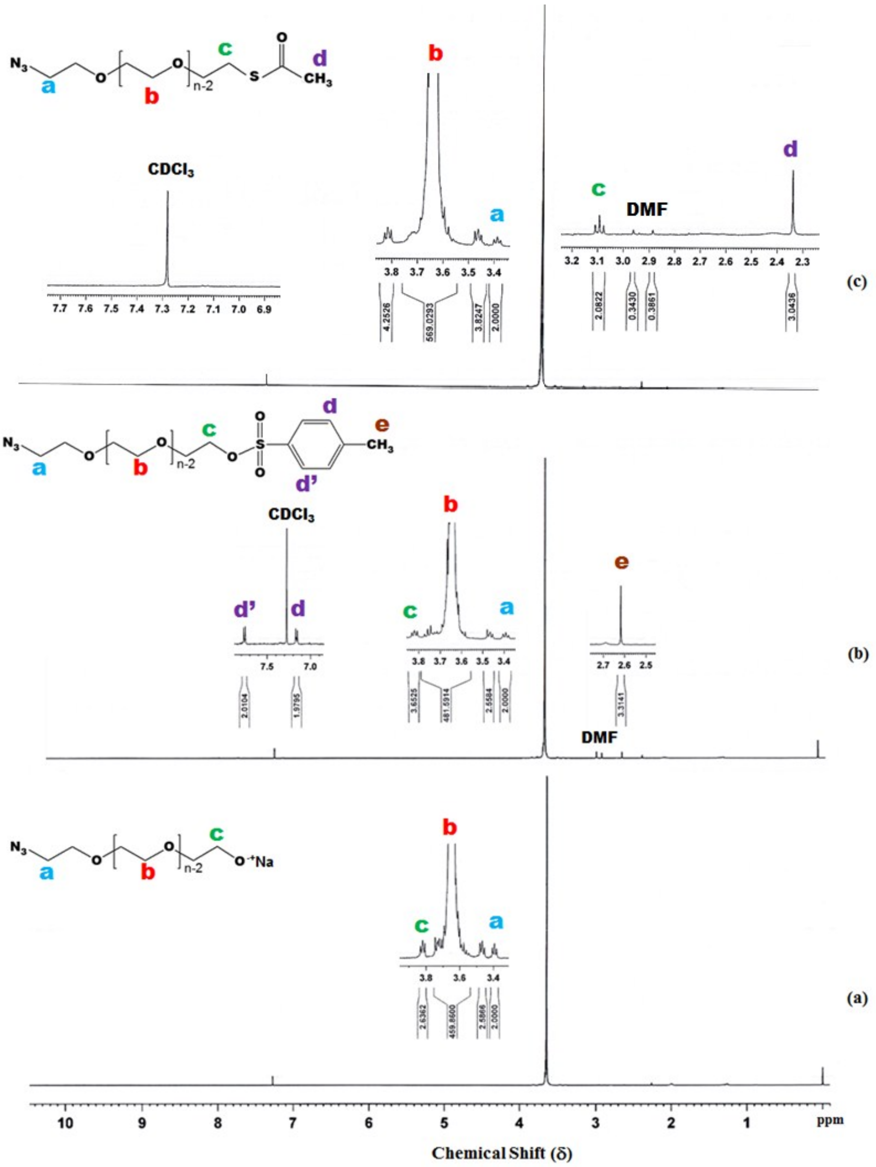


SI Figure 6. ^{1}H NMR spectra of α-azide-ω-bromo PEO and the corresponding α-azide PEO-based RAFT agent.

In addition, SI Figure 7 shows ^{1}H spectra of α-azide-ω-tosyl PEO and corresponding α-azide-ω-thiol PEO obtained from the reaction of α-azide-ω-tosyl PEO with sodium hydrosulfide (NaSH) in . However, not only the thiolation yield was not quantitative but also most fractions of the azide groups were converted to the amine groups shown in SI Figure 7b.



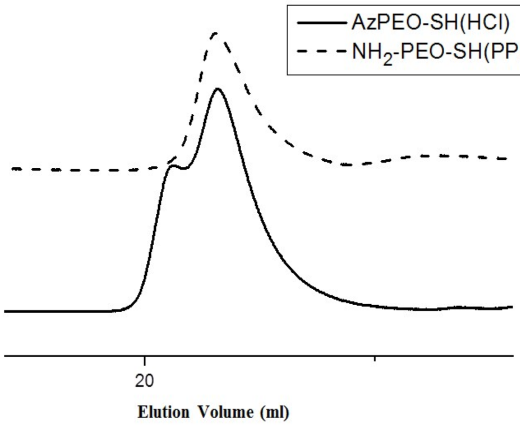
SI Figure 7. The ^{1}H NMR spectra of (a) α-azide-ω-tosyl PEO and (b) α-amine-ω-thiol PEO obtained from the reaction using NaSH from the in $CDCl_3$.



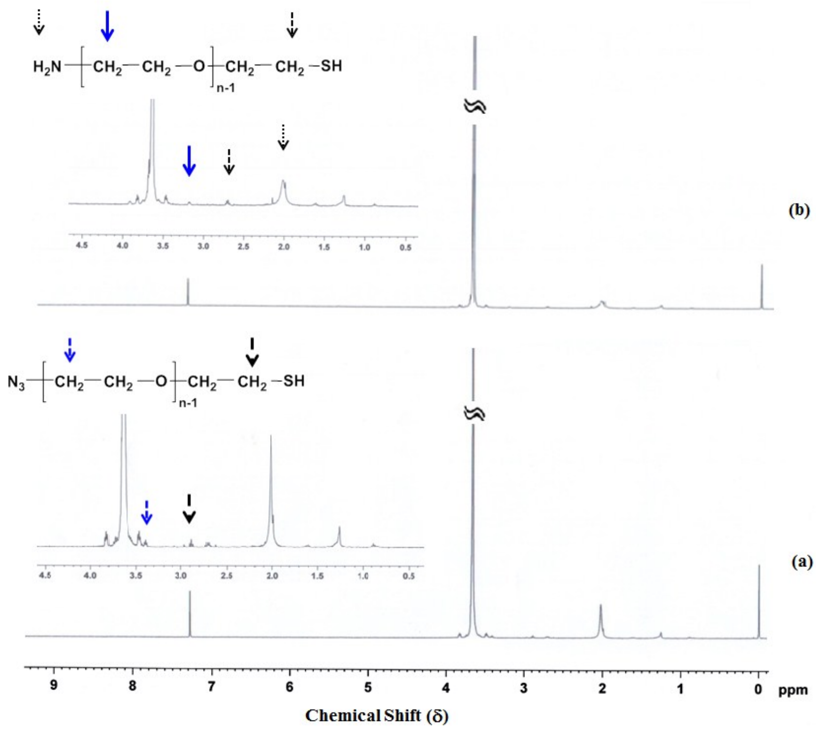
SI Figure 8. ^{1}H NMR spectra of (a) α-azide PEO, (b) corresponding α-azide-ω-tosyl PEO, and (c) corresponding α-azide-ω-thioacetate PEO in $CDCl_3$.

SI Figure 9 shows a comparison of size exclusion chromatograms of the deacetylated compound of α-azide-ω-thioacetate PEO ($M_{n,AzPEO}$ = 4,800 g/mol) using hydrazine after the treatment with HCl (1.0 N) and corresponding α-amine-ω-thiol PEO obtained from the reaction of deacetylated product with triphenyl phosphine (PPh_3). In particular, α-amine-ω-thiol PEO exhibits a polyelectrolyte behavior in THF. In particular, all disulfide fractions had to be reduced to the thiol groups. SI

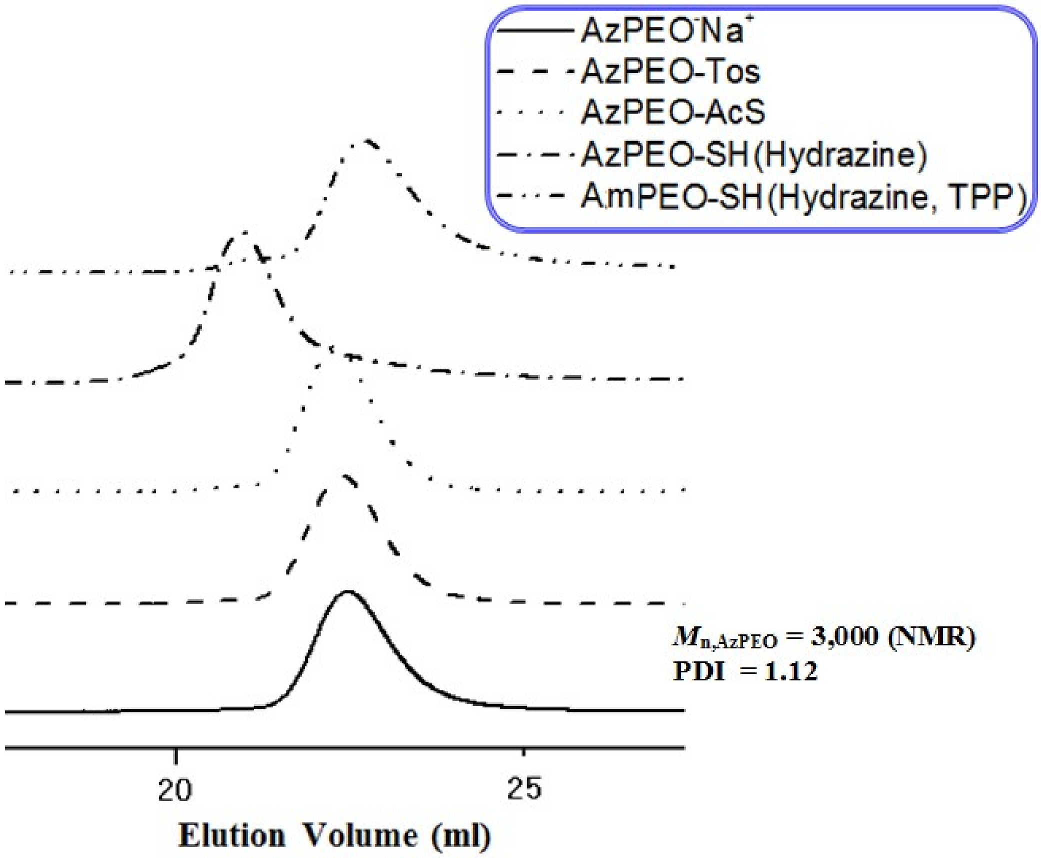
Figure 10 represents the ^{1}H NMR spectra of the corresponding products. The chemical shift at δ = 3.38 ppm in SI Figure 10a disappeared after its reduction as shown in SI Figure 10b.



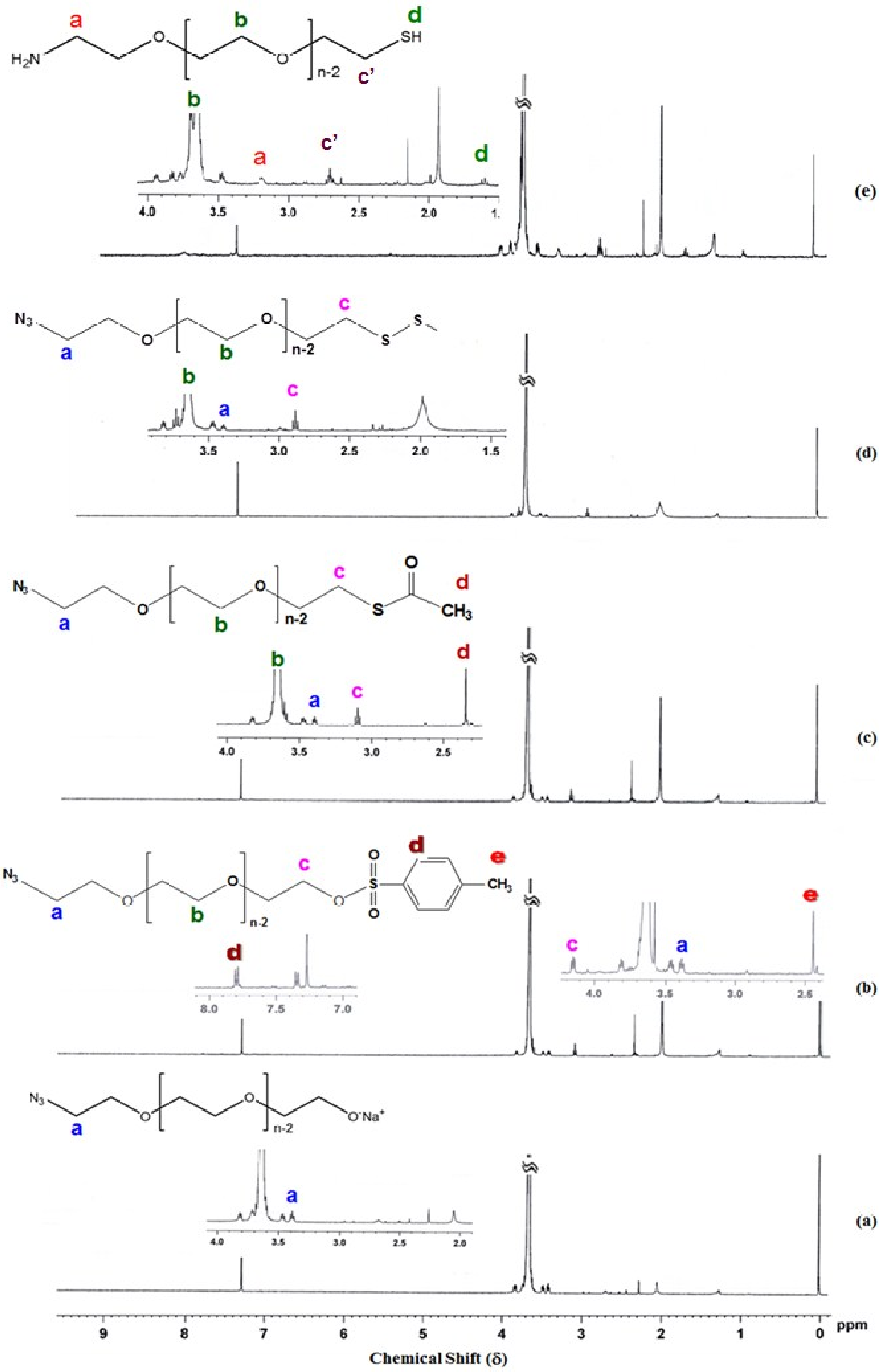
SI Figure 9. Size exclusion chromatograms of α-azide-ω-thiol PEO and corresponding α-amine-ω-thiol PEO in THF as an eluent at 30^{o}C.



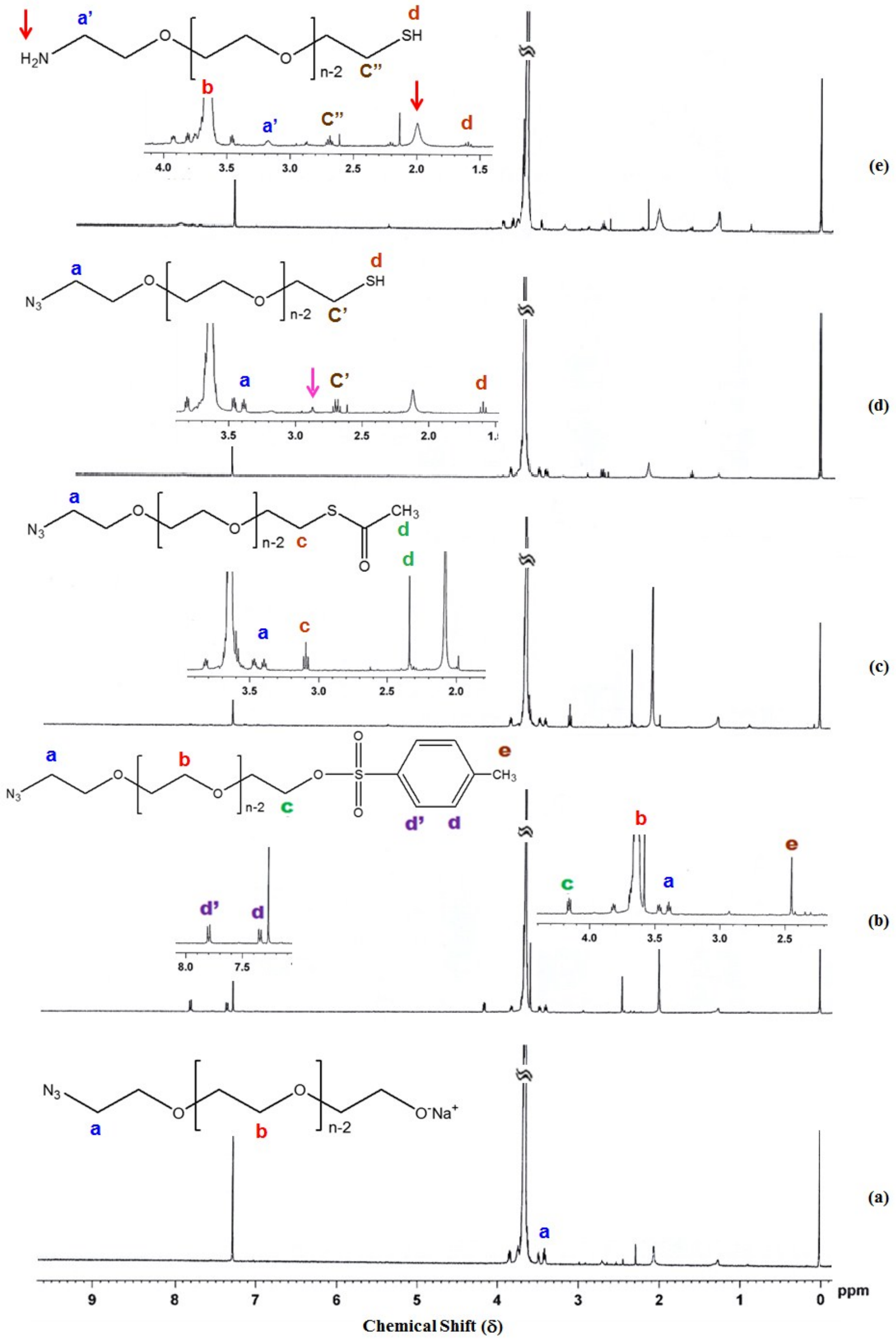
SI Figure 10. A comparison of the ^{1}H NMR spectra of (a) deacetylated product, α-azide-ω-thiol PEO in the main text and (b) corresponding α-amine-ω-thiol PEO obtained from the reaction with triphenyl phosphine.



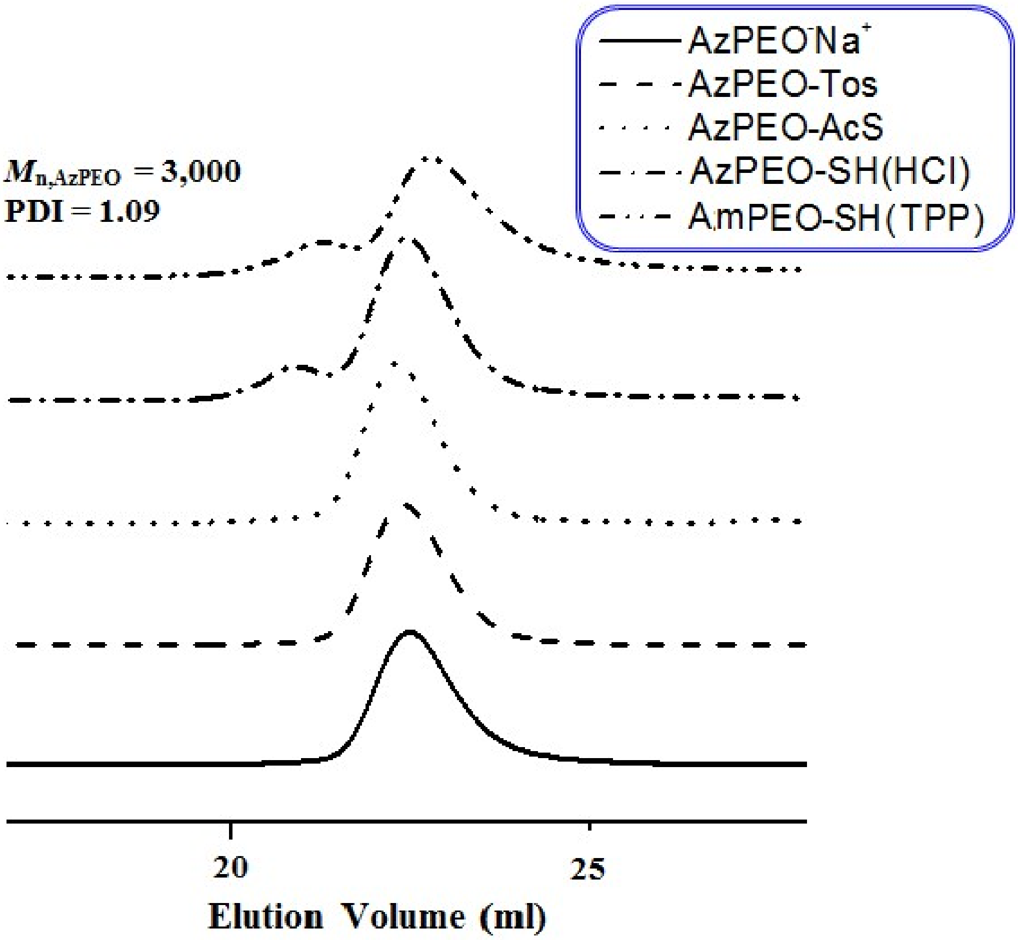
SI Figure 11. Size exclusion chromatograms of α-azide PEO (Az PEO 4), corresponding α-azide-ω-tosyl PEO, corresponding α -azide-ω-thioacetate PEO, corresponding α-azide-ω-thiol PEO after the treatment of hydrazine in acetonitrile, and corresponding α-amine-ω-thiol PEO after reduction using triphenyl phosphine (TPP) in THF as an eluent at 30°C.



SI Figure 12. ^{1}H NMR spectra of (a) α-azide PEO (Az PEO 4), (b) corresponding α-azide-ω-tosyl PEO, (c) corresponding α-azide-ω-thioacetate PEO, (d) corresponding α-azide-ω-thiol, and (e) corresponding α-amine-ω-thiol PEO after reduction using triphenyl phosphine (TPP) in $CDCl_3$.



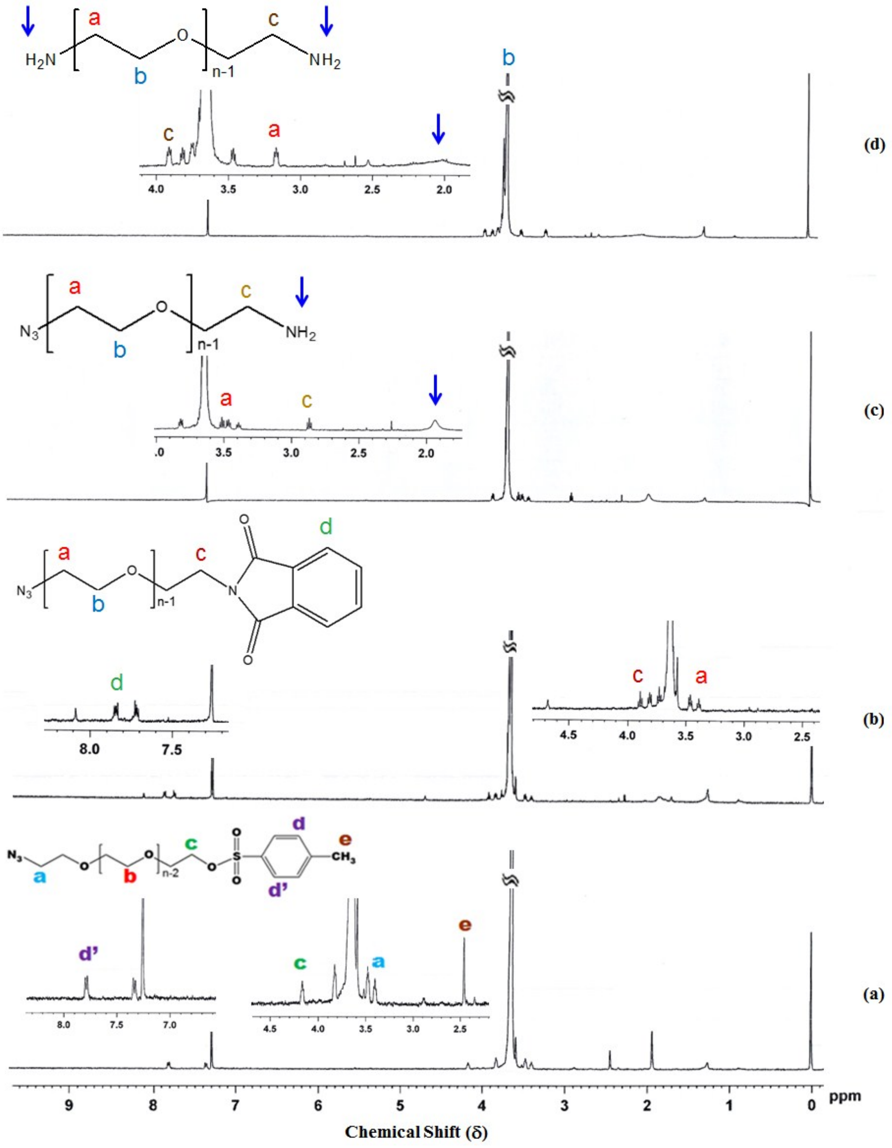
SI Figure 13. Comparison of the ^{1}H NMR spectra of (a) α-azide PEO, (b) corresponding α-azide-ω-tosyl PEO, (c) corresponding α-azide-ω-thioacetate PEO, (d) corresponding α-azide-ω-thiol PEO, and (e) corresponding α-amine-ω-thiol PEO in $CDCl_3$.



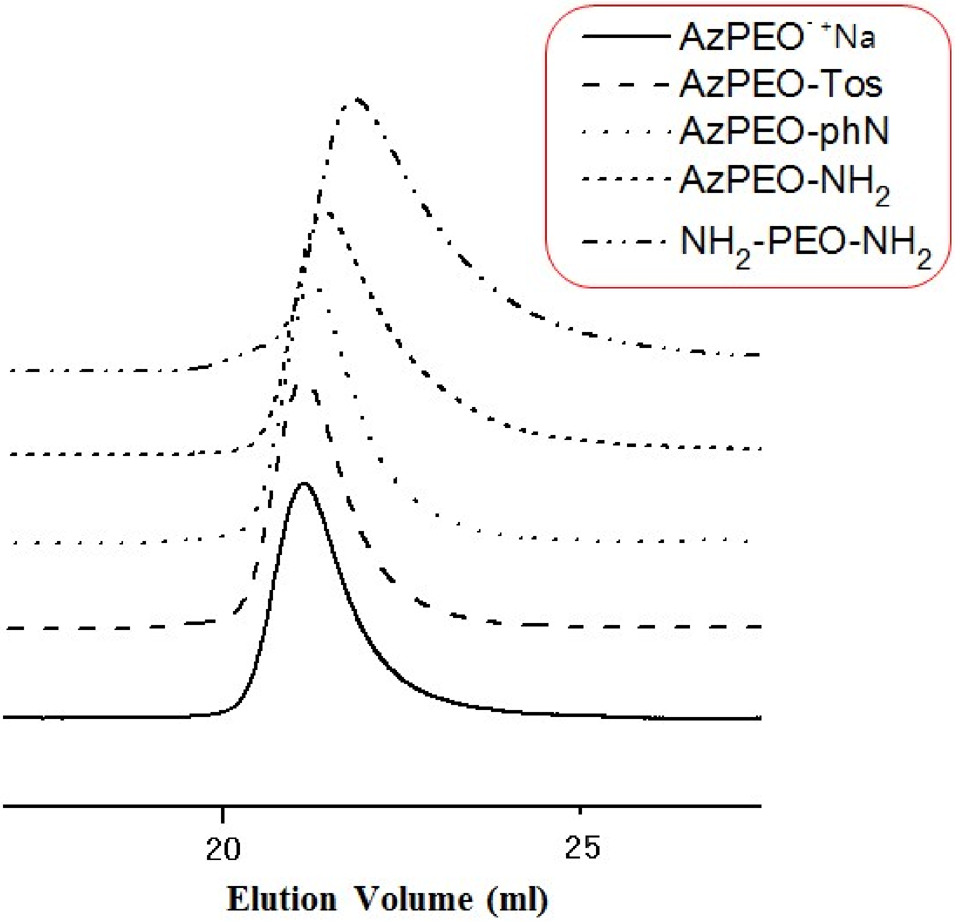
SI Figure 14. SECs of α-azide PEO (Az PEO 4), corresponding α-azide-ω-tosyl PEO, corresponding α-azide-ω-thioacetate PEO, corresponding α-azide-ω-thiol PEO, and corresponding α-amine-ω-thiol PEO in THF at 30°C.

Originally, concerning the coupled product having the disulphide bond, a monomial product was expected to be generated through the reduction of α-azide-ω-thiol PEO using triphenyl phosphine. Unfortunately, in spite of the performance of the reductive process of α-azide-ω-thiol PEO using triphenyl phosphine, there was still coupled product arising from coupling of the nitrenes generated from the azide group as shown in SI Figure 14.[S3] This coupled product having no disulphide bond could not be reduced by triphenyl phosphine leading to a monomodal distribution.

SI Figure 15 shows the ^{1}H NMR spectra of typical α-azide PEO, corresponding α-azide-ω-tosyl PEO, corresponding α-azide-ω-phthalimide PEO, and corresponding α-azide-ω-amine PEO in CDCl$_3$. The chemical shift (singlet) at $\delta = 3.38$ ppm is assigned to the protons on the methylene group adjacent to the azide group in SI Figure 8a. The chemical shifts at $\delta = 7.15$ ppm and $\delta = 7.75$ ppm shown in SI Figure 8b completely disappeared in SI Figure 8c. Based on this result, the thioacetylation yield was over 98 mol%.

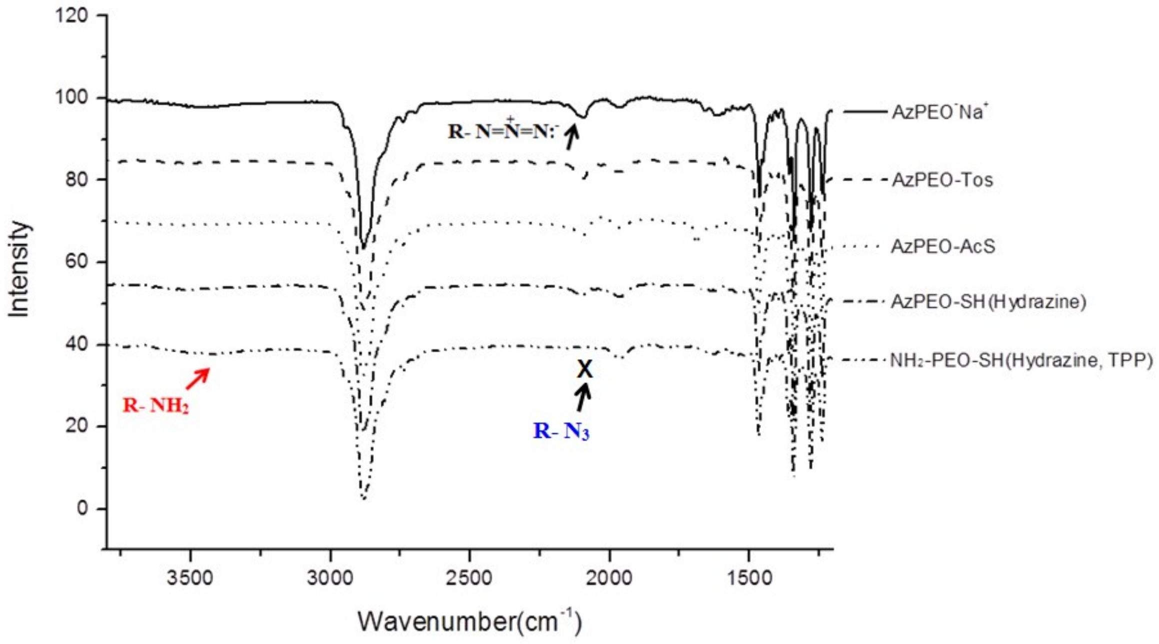


SI Figure 15. Comparison of ^{1}H NMR spectra of α-azide-ω-tosyl PEO, corresponding α-azide-ω-phthalimide PEO, corresponding α-azide-ω-amine PEO, and corresponding α,ω-diamine PEO in CDCl$_3$.

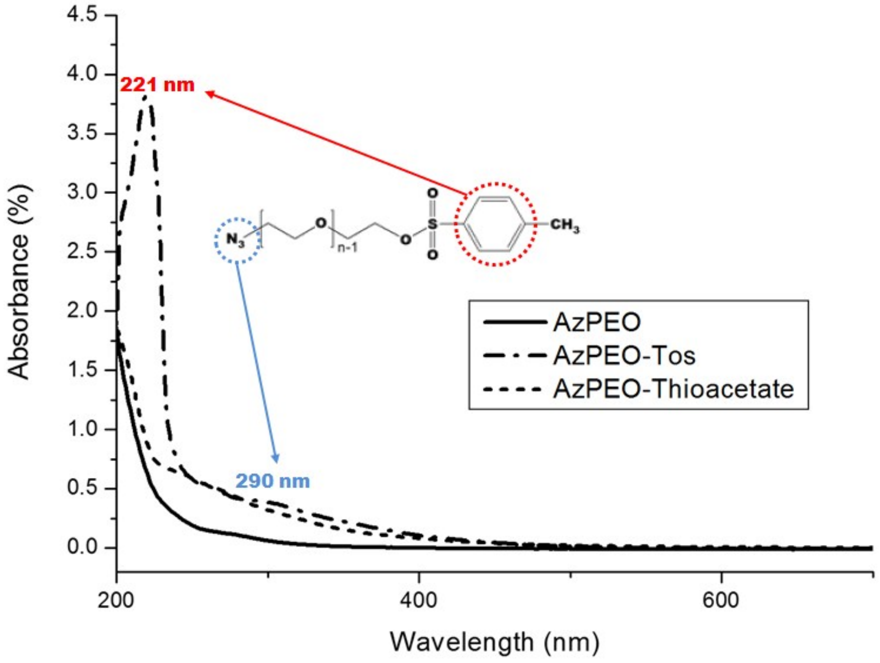


SI Figure 16. SECs of α-azide-ω-tosyl PEO, corresponding α-azide-ω-phthalimide PEO, corresponding α-azide-ω-amine PEO, and corresponding α,ω-diamine PEO in THF.

In addition, tosylation of α-azide PEO was carried out in DCM at 40°C for 24 h, followed by thioacetylation using potassium thioacetate. The FT-IR spectra of the resulting products exhibit no any difference shown in SI Figure 17. In particular, the asymmetric S=O stretching frequency of α-azide-ω-tosyl PEO could not be distinguished in the ranges of 1372-1335 cm^{-1}. However, UV visible spectrum of the chain end-tosylated product shows a great difference due to the existence of the phenyl group shown in SI Figure 18.



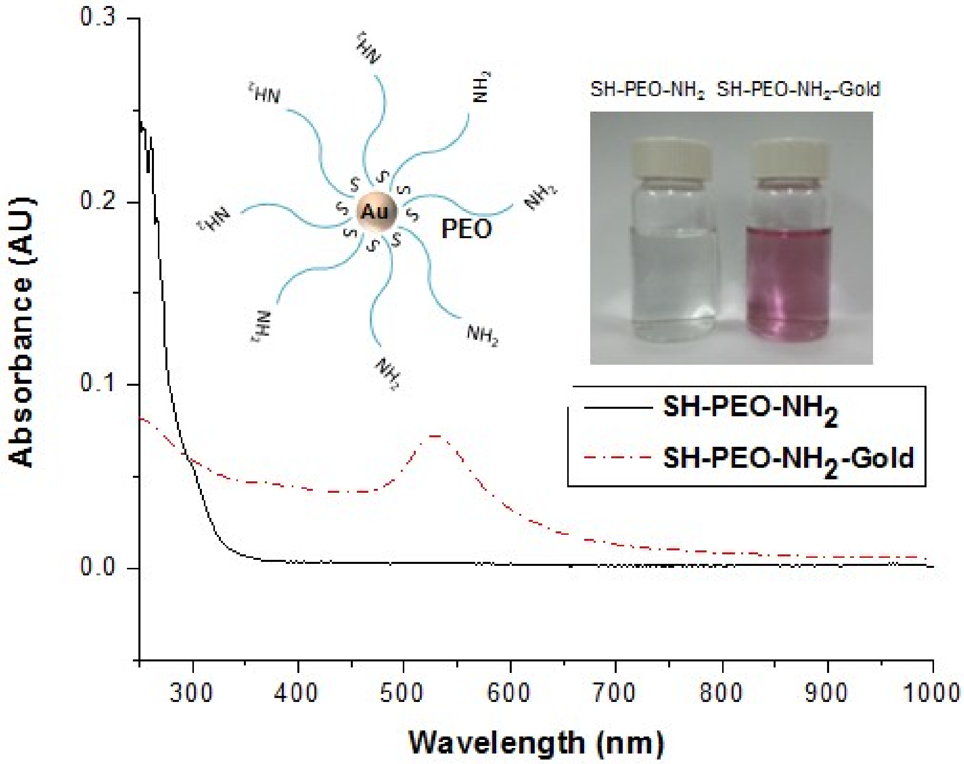
SI Figure 17. A comparison of the FT-IR spectra of α-azide PEO (Az PEO 4), corresponding α-azide-ω-tosyl PEO, corresponding α-azide-ω-thioacetate PEO, corresponding α-azide-ω-thio1 PEO, and corresponding α-amine-ω-thio1 PEO.



SI Figure 18. UV visible spectra of α-azide PEO, corresponding α-azide-ω-tosyl PEO, and corresponding α-azido-ω-thioacetate PEO.

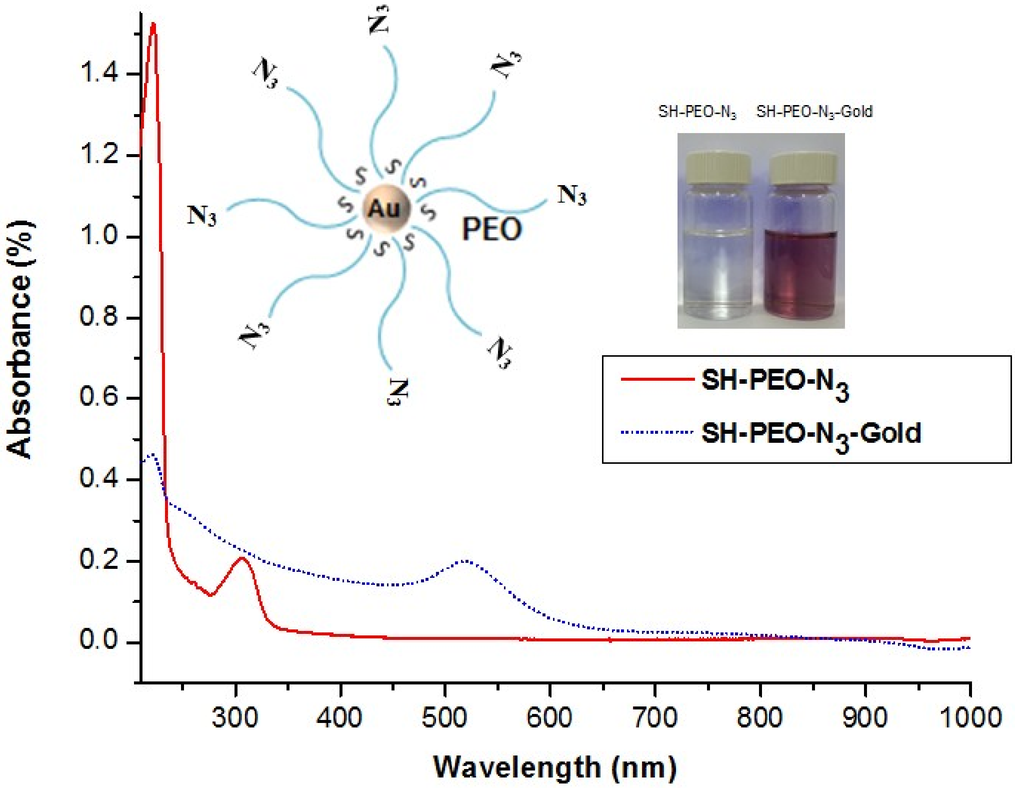
Synthesis of gold nanoparticles

Both α-amine-ω-thiol PEO and α-azide-ω-thiol PEO were used as polymeric stabilizers for synthesizing nano-sized gold particles in methanol, their preparative procedures were described in the Experimental section in the Supporting Information. In practice, SI Figure 19 show a photo image of α-amine-ω-thiol PEO-coated gold nanoparticle and UV/Visible spectra of the gold solution. The absorption maximum at δ = 535 nm indicates a simple generation of typical gold nanoparticles.



SI Figure 19. UV/Visible spectra of α-amine-ω-thiol PEO (Az PEO 3) in methanol and α-amine-ω-thiol PEO-coated gold nanoparticle solution and their photo images.

In addition, SI Figure 20 shows UV/Visible spectra of α-azide-ω-thiol PEO, α-azide-ω-thiol PEO-coated gold nanoparticle in methanol and their photo images. Presumably, the appearance of the absorption maximum of α-azide-ω-thiol PEO at δ = 310 nm informs the existence of the azide group and the absorption maximum of α-azide-ω-thiol PEO-coated gold nanoparticle appears at δ = 535 nm like α-amine-ω-thiol PEO-coated gold nanoparticle. The important aspect in this study is to show clearly different UV/Visible spectra of α-amine-ω-thiol PEO and α-azide-ω-thiol PEO.



SI Figure 20. UV/Visible spectra of α-azide-ω-thiol PEO (Az PEO 4) in methanol and α-azide-ω-thiol PEO-coated gold nanoparticle solution and their photo images.

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(S2) J. Kim, S. Lee, J. H. Nam, Y. J. Cho, J. Kim, J. Y. Lee, H.-J. Kang, S. Kim, H. T. Kim, H. M. Park and J. Kim, *Macromol. Res.,* 2011, **19(7),** 716-721.

(S3) P. N. D. Singh, S. M. Mandel, R. M. Robinson, Z. Zhu, R. Franz, B. S. Ault and A. D. Gudmundsdottir, *J. Org. Chem.,* 2003, **68,** 7951-7960.