## pH-Tunable Thermoresponsive PEO-Based Functional Polymers with Pendant Amine Groups

Joonhee Lee,<sup>1</sup> Alaina J. McGrath,<sup>2</sup> Craig J. Hawker,<sup>2</sup>\* and Byeong-Su Kim<sup>1</sup>\*

<sup>1</sup>Department of Chemistry, School of Natural Science, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea

<sup>2</sup>Materials Research Laboratory, University of California Santa Barbara, Santa Barbara, California 93106, United States

E-mail: bskim19@unist.ac.kr, hawker@mrl.ucsb.edu

**Materials**. All chemicals were used as received from Sigma-Aldrich unless otherwise specified. THF was collected from a dry solvent system and used immediately thereafter. Allyl glycidyl ether was degassed via several freeze-pump-thaw cycles, and was distilled from butyl magnesium chloride to a flask for storage. Ethylene oxide (EO) was condensed into a Schlenk flask and degassed via several freeze-pump-thaw cycles, then distilled to a flame-dried burette immediately before use. Potassium naphthalenide was prepared from potassium metal and recrystallized naphthalene in dry THF and stirred with a glass-coated stirrer bar for 24 h at room temperature before use.

**Characterization.** <sup>1</sup>H NMR spectra were recorded on a Varian VNMRS 600 MHz spectrometer at room temperature using CDCl<sub>3</sub> as a solvent. Gel permeation chromatography (GPC) analysis was carried out using a Waters 2695 separation module with a Waters 2414 refractive index (RI) detector and a Waters Alliance HPLC system (2695 separation module) using chloroform containing 0.25 wt% triethylamine as a mobile phase. Linear poly(ethylene oxide) (PEO) standards were applied as calibration samples. Thiol-ene reactions were irradiated with a UVP Black ray UV Bench Lamp XX-15L, which emits 365 nm light at 15 W. The transmittances of the aqueous polymer solutions were measured using a Shimadzu UV3600 UV-vis spectrometer equipped with a temperature controller. A 500 nm wavelength was used to determine the LCST, which was defined as a temperature at which the transmittance had decreased by 10%.<sup>S1,S2</sup>

Synthesis of P(EO-co-AGE)



Scheme S1. Synthesis of P(EO-*co*-AGE).

This procedure is based upon the synthesis of P(EO-*co*-AGE) described by Lee et al.<sup>S3</sup> Polymerizations were performed in a custom-made five-armed thick-walled glass reactor fitted with ACE-threads under an inert argon atmosphere. The reactors were fitted with Teflon stoppers, a burette containing anhydrous tetrahydrofuran (THF), a flexible connector attached to a burette containing ethylene oxide (EO) (stored in an ice bath), and a glass arm connector sealed with a 6 mm Puresep septum and attached to a Schlenk line via a flexible connector. The reactor was flame-dried under vacuum and refilled with argon five times. Under a positive pressure of argon, anhydrous THF was added by opening the threaded stopcock on the attached burette. Benzyl alcohol initiator was added via a gastight syringe through a 6 mm Puresep septum. Potassium naphthalenide (0.30 M in THF) was added dropwise via gastight syringe until a light green color persisted in the solution, indicating complete deprotonation of the benzyl alcohol initiator. Condensed EO was added by lifting the cold burette and allowing the EO to drain into THF solution while AGE was simultaneously added via gastight syringe. The addition of the monomers immediately quenched the green color, and the polymerization was carried out at room temperature for 2 days. The reaction was guenched with degassed acidic methanol and precipitated from hexane. The resulting polymer was purified using a short pad of silica gel (10% MeOH/dichloromethane as eluent).  $M_n$  and PDI ( $M_w/M_n$ ) were determined by <sup>1</sup>H NMR and GPC analysis, respectively.



Figure S1. <sup>1</sup>H NMR spectrum of P(EO-*co*-AGE) polymer precursor (600 MHz, CDCl<sub>3</sub>, 298 K).



Figure S2. GPC traces of P(EO-co-AGE), P2, and P3. CHCl<sub>3</sub> was used as an eluent.

## General procedure for thiol-ene coupling



Scheme S2. Thiol-ene coupling reactions of P(EO-*co*-AGE) to afford P1–P5.

This procedure is based upon the synthesis of P(EO-*co*-AGE) described by Kang et al. <sup>84</sup> The thiol-ene reactions between P(EO-*co*-AGE) and the aminoethanethiol hydrochlorides (3.0 equivalents for each "ene" moiety) were carried out using 2,2-dimethoxy-2-phenylacetophenone (0.05 equivalents for each "ene" moiety) as a photoinitiator in methanol. The reaction mixture was degassed via three freeze-pump-thaw cycles, backfilled with argon, and irradiated with UV light ( $\lambda = 365$  nm) for 2 h until complete disappearance of the alkene peaks as indicated by <sup>1</sup>H NMR analysis. Triethylamine and water were then added to the reaction mixtures to neutralize the hydrochloride salt and obtain the free amines. Methanol and excess triethylamine were then removed under reduced pressure. The aqueous layers were extracted with dichloromethane three times and washed with brine. The organic fractions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The concentrated mixtures were precipitated twice into hexane. The resulting viscous polymers were obtained and dried under high vacuum for one day (typical isolated yield of 80–90%).



**Figure S3.** Transmittance curves of **P5** in aqueous solution at pH 13 during heating (red circle) and cooling (blue square) scans.

## References

- (S1) Koda, Y.; Terashima, T.; Sawamoto, M. ACS Macro Lett. 2015, 4, 1366.
- (S2) Kawaguchi, T.; Kojima, Y.; Osa, M.; Yoshizaki, T. Polym. J. 2008, 40, 455.
- (S3) Lee, A.; Lundberg, P.; Klinger, D.; Lee, B. F.; Hawker, C. J.; Lynd, N. A. *Polym. Chem.* **2013**, *4*, 5735.
- (S4) Kang, T.; Amir, R. J.; Khan, A.; Ohshimizu, K.; Hunt, J. N.; Sivanandan, K.; Montañez,
- M. I.; Malkoch, M.; Ueda, M.; Hawker, C. J. Chem. Commun. 2010, 46, 1556.