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

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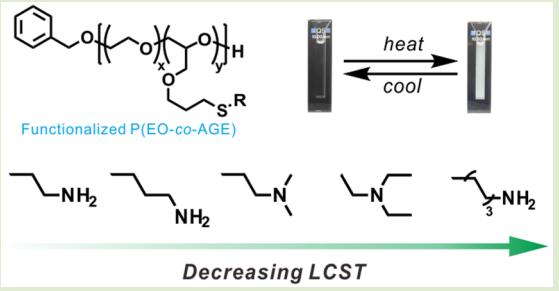
Supporting Information

ABSTRACT: Thermoresponsive polymers exhibiting lower critical solution temperatures (LCSTs) in aqueous solution have garnered considerable attention for the development of smart materials. Herein, we report the synthesis and properties of pH-tunable thermoresponsive poly(ethylene oxide) (PEO)-based functional polymers bearing pendant amine groups with varying cloud points. Well-defined poly(ethylene oxide-*co*-allyl glycidyl ether) (P(EO-*co*-AGE)) copolymers were prepared via controlled anionic ring-opening copolymerization of ethylene oxide (EO) with 10 mol % of a functional allyl glycidyl ether (AGE) comonomer. Facile, modular thiol−ene click chemistry was then employed to introduce a library of different aminothiols as side chains to the initial P(EO-*co*-AGE) copolymer. Depending on the nature of the pendant amine groups (primary amine, dimethylamine, and diethylamine) and the hydrophobicity of the side chains (ethyl, propyl, and hexyl), the cloud points could be tuned from 44−100 °C under different pH conditions. This is the first systematic investigation into the effect of PEO copolymer side chains on cloud point, which opens up the opportunity to make new thermoresponsive polymers for a variety of smart material applications.



Polymers capable of responding to various environmental stimuli such as temperature,[1−3] pH,[4] light,[5] and mechanical force[6] have attracted significant attention, with applications ranging from environmental materials to biomedical devices. Thermoresponsive polymers, in particular, have been investigated for the development of smart materials due to their unique phase transition properties in aqueous solution, including lower critical solution temperature (LCST) and upper critical solution temperature (UCST).[7−10] In particular, the lower critical solution temperature (LCST) is the temperature above which phase separation is observed, which coincides with decreasing polymer solubility.[11,12] At low temperatures, LCST-type thermoresponsive polymers are soluble, owing to hydrogen bonding with the surrounding water molecules, resulting in restricted intra/intermolecular interactions between polymer chains. Upon heating, the hydrogen bonds are disrupted, and the polymer chains exhibit a phase transition, with solubility decreasing due to the disruption of the interactions between the polymer and the solvating water molecules. It has been suggested that the LCST is dependent on many external parameters, including monomer composition, the hydrophilic/hydrophobic balance, molecular weight, concentration, and the ionic species present.[13−16] The ability to develop thermoresponsive polymers with a wide range of LCSTs that can be tuned depending on external stimuli is therefore of significant interest.[17−20]

The most studied thermoresponsive polymer, poly(*N*-isopropylacrylamide) (PNIPAM), exhibits a clear phase transition at a LCST of 32 °C, close to body temperature.[13] Water-soluble, nontoxic, and nonimmunogenic poly(ethylene oxide) (PEO) is another biologically important synthetic polymer that is widely used in biomedical applications.[21−23] However, PEO's LCST (nearly 100 °C)[24] is too high for most biomedical applications, prompting studies on the LCST behavior of PEO-based polymers. These studies have tailored the LCST of PEO by introducing hydrophobic side chains to the PEO backbone or by the integration of new functional monomers.[25] As notable examples, a range of monomers containing hydrophobic side chains have been copolymerized with ethylene oxide (EO) to yield functional PEO derivatives exhibiting varying LCST values, including glycidyl methyl ether,[26] ethoxyl vinyl glycidyl ether,[27,28] *N*,*N*-diisopropyl ethanol amine glycidyl ether,[4] allyl glycidyl ether (AGE),[28] and *N*,*N*-dibenzyl amino glycidyl.[28,29] Although the aforementioned functional monomers lead to modulation of the LCST, a major drawback of their use is the requirement of separate syntheses for each functional copolymer with varying comonomer contents. As a result, there is a significant time

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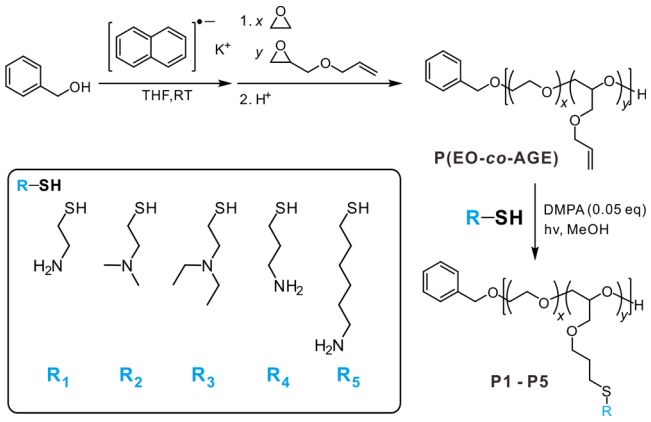
and materials investment for the preparation of a library of materials with a range of LCST values.

As an alternative strategy, postpolymerization functionalization of a single PEO-based starting copolymer with a defined molecular weight, architecture, and polydispersity can be used to furnish a library of copolymers with varying LCSTs. In particular, PEO-based copolymers with functional allyl side chains offer a unique handle that is amenable to quantitative thiol−ene click chemistry, with prior work showing the successful controlled copolymerization of EO and AGE, followed by conjugation with multifunctional peptide units.[30] In addition to lowering the LCST, controlling the LCST behavior of PEO-based polymers with an external stimuli such as pH can offer new application opportunities.

Herein, we describe the synthesis of a series of thermoresponsive, functional PEO-based polymers bearing pendant amine groups via postpolymerization modification of P(EO-*co*-AGE) copolymers through thiol−ene coupling chemistry using five different aminothiols (R-SH, see Scheme 1),

Scheme 1. Synthesis of Amine-Functionalized PEO-Based Polymers, P1−P5, with Different Pendant Amine Groups (R_1−R_5)



including cysteamine (R_1), *N*,*N*-dimethylaminoethanethiol (R_2), *N*,*N*-diethylaminoethanethiol (R_3), 3-amino-1-propanethiol (R_4), and 6-amino-1-hexanethiol (R_5). This allowed a systematic investigation into the effect of PEO copolymer side chains on LCST behavior through varying the nature of the amine groups (primary R_1 vs tertiary R_2 and R_3), the length of the side chains (R_1, R_4, and R_5), and the pH. Generally, LCST behavior is determined qualitatively by measuring the cloud point temperature; this is the temperature that corresponds to the polymer solution optically changing from transparent to turbid.[31] The modified functional copolymers, **P1**−**P5**, were successfully characterized by ^{1}H NMR and GPC analysis, with the resulting copolymers exhibiting significantly different, yet tunable LCST behavior under varying pH conditions. Lee and co-workers previously reported that the LCST of amine-functionalized poly(2-hydroxyethyl methacrylate) (PHEMA) was significantly affected by the pH of the solution.[32] However, to the best of our knowledge, there have been no reports on thermoresponsive PEO-based polymers that have cloud points that can be tuned by varying the nature of the amino group or side-chain length.

As illustrated in Scheme 1, the copolymer precursor used for thiol−ene addition was synthesized via anionic ring-opening copolymerization of EO and AGE, following the procedure reported by Lynd and co-workers.[33] Polymerization was initiated with benzyl alkoxide, which was generated by treatment of benzyl alcohol with a dilute solution of potassium naphthalenide. This method is known to be a convenient and effective method for initiating anionic ring-opening polymerization of glycidyl ethers.[34] The molecular weight and PDI of P(EO-*co*-AGE) were characterized by ^{1}H NMR spectroscopy and GPC (Figure 1 and Figure S1, S2). The number average molecular weight (M_n) was found to be ~6400 g·mol^{-1} by ^{1}H NMR using the methylene protons of the terminal benzyl group as an internal reference (4.55 ppm). In addition, the ratio of the comonomers in the polymer backbone was determined using the characteristic allyl peaks at 5.13 and 5.22 ppm (peak *f* in Figure 1a) and 5.85 ppm (peak *e* in Figure 1a), with the results being in good agreement with the targeted value (10 mol % AGE units). The GPC of P(EO-*co*-AGE) showed a similar molecular weight to that obtained via ^{1}H NMR and a narrow molecular weight distribution for P(EO-*co*-AGE) (PDI = 1.10, Figure S2).

After successful polymerization of P(EO-*co*-AGE), we performed photochemical-mediated thiol−ene additions with five different aminothiols (R_1−R_5) to give the copolymers **P1**−**P5**, as shown in Scheme 1. ^{1}H NMR spectroscopy clearly confirmed the successful functionalization of P(EO-*co*-AGE) with different pendant amine groups that are sensitive to external pH (Figure 1). The quantitative addition of aminothiols to the P(EO-*co*-AGE) allyl groups was indicated by the disappearance of the allylic peaks from the functional AGE comonomer. The concomitant appearance of peaks corresponding to aminoalkyl groups also supported the successful conversion. GPC analyses showed narrow single peaks for **P2** and **P3**, verifying the purity of the resulting polymers and the lack of interchain coupling (Figure S2). It should be noted that **P1**, **P4**, and **P5** could not be analyzed by GPC due to the strong interactions between the pendant primary amine groups and the GPC column. Table 1 summarizes the characterization data for the PEO-based copolymers with pendant amine groups prepared through anionic ring-opening polymerization and thiol−ene addition.

The resulting polymers formed transparent aqueous solutions at room temperature due to the high aqueous solubility of the PEO backbone. Significantly, raising the temperature induced abrupt increase in turbidity, demonstrating thermally induced phase transition behavior. This allowed the thermoresponsive phase transition behaviors of the polymers to be investigated by UV−vis spectroscopy. Transmittance changes in 0.10 wt % aqueous polymer solutions as a function of temperature were measured by UV−vis spectroscopy at 500 nm, with the cloud points being defined as the temperature at which a 10% decrease in transmittance was recorded (Figure 2).[37,38] The cloud points of **P1** were 70 and 91 °C at pH 13.0 and 12.5, respectively (Figure 2a). When the pH was below 12.5, no phase transitions were observed below 100 °C, suggesting that the primary amine groups on the side chains were protonated under more acidic conditions. Consequently, **P1** consists of both a hydrophilic PEO backbone and protonated amine groups below pH 12, resulting in increased solubility in water at higher temperatures. This observation was in accordance with previous reports showing the effect of hydrophobic/hydrophilic side chains on the nature of the ionizable groups.[19,39] As shown in Figure 2b, the behavior of **P2** showed significant variation, with the cloud point being 91 °C at pH 9.0 and 50 °C at pH 13.0. The LCST

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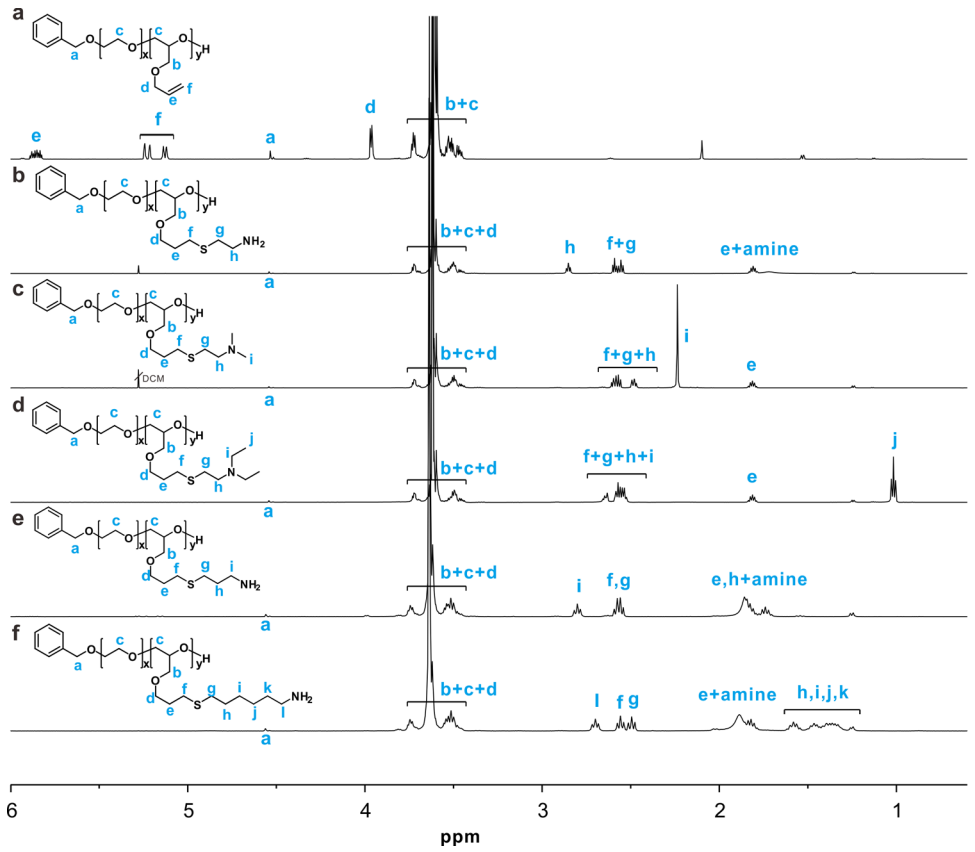

Figure 1. Representative ^{1}H NMR spectra of the synthesized polymers (600 MHz in $CDCl_3$). (a) P(EO-*co*-AGE), (b) **P1**, (c) **P2**, (d) **P3**, (e) **P4**, and (f) **P5**.

Table 1. Molecular Weight Data and Cloud Points of Polymers Prepared in This Study

				cloud point (°C)			
entry	thiols	M_n[a] (g/mol)/NMR	PDI[b]	pH 11	pH 12	pH 13	log *P*[c]
$P(EO_{117}$-*co*-$AGE_{11})$		6400	1.10				
P1	cysteamine	6900	N/A	100	100	70	0.01
P2	*N*,*N*-dimethylaminoethanethiol	7800	1.10	72	63	50	1.19
P3	*N*,*N*-diethylaminoethanethiol	8000	1.12	65	58	45	2.34
P4	3-amino-1-propanethiol	7500	N/A	85	79	66	0.53
P5	6-amino-1-hexanethiol	7800	N/A	61	51	44	2.07

[a]Molecular weight (M_n), as determined from ^{1}H NMR spectra of resulting polymer. [b]PDI was measured by GPC using $CHCl_3$ as an eluent. [c]Log *P* values for thiols were obtained using ALOGPS 2.1.[35,36]

decreased with increasing pH as the balance of hydrophilicity and hydrophobicity was changed by the protonation state of the *N*,*N*-dimethylamino group. Figure 2c also clearly shows that the cloud point of **P3** decreased as the pH was increased from 9.0 to 13.0. The results from these three polymers show that as the amine group is changed from primary to tertiary, the cloud point of the polymer at pH 13 decreased. Although a phase transition below 100 °C was not observed for **P1** at pH 12.0, **P2** and **P3** showed clear decreases in transmittance at pH 12.0 and 11.0, suggesting that the alkyl groups on the tertiary amines enhanced their hydrophobicity, inhibiting the hydration of the protonated amine moieties. As a result, the polymers retained a hydrophobicity/hydrophilicity balance and exhibited LCST behavior at lower pH values. These observations indicate that the LCST transition is primarily affected by the hydrophobicity of the amine groups, in accordance with previous findings for other materials.[40] As further evidence, the phase transition behavior of **P3** in Figure 2c shows that the cloud points of **P3** were lower than those of **P1** and **P2** at high pH, and that the transmittance dropped more drastically upon heating. This was likely due to the increased hydrophobicity of the diethylamino group in **P3**, which resulted in this polymer showing the lowest cloud points under basic conditions.

In order to investigate the effect of side chain hydrophobicity further, polymers with primary amine groups but different side chain lengths were examined. In this series, the cloud point of **P1**, **P4**, and **P5** were compared and analyzed according to the length of the pendant chains. Again, **P1**, **P4**, and **P5** showed pH-responsive LCST behavior due to the primary amine groups. By comparing the transmittance curves shown in Figure 2, it can be seen that the polymer with the longest side chain (**P5**) exhibited the lowest cloud point at a given pH. As the side chain length was increased from ethyl (**P1**) to propyl (**P4**) to hexyl (**P5**), the cloud point at pH 13 decreased from 70 to 66

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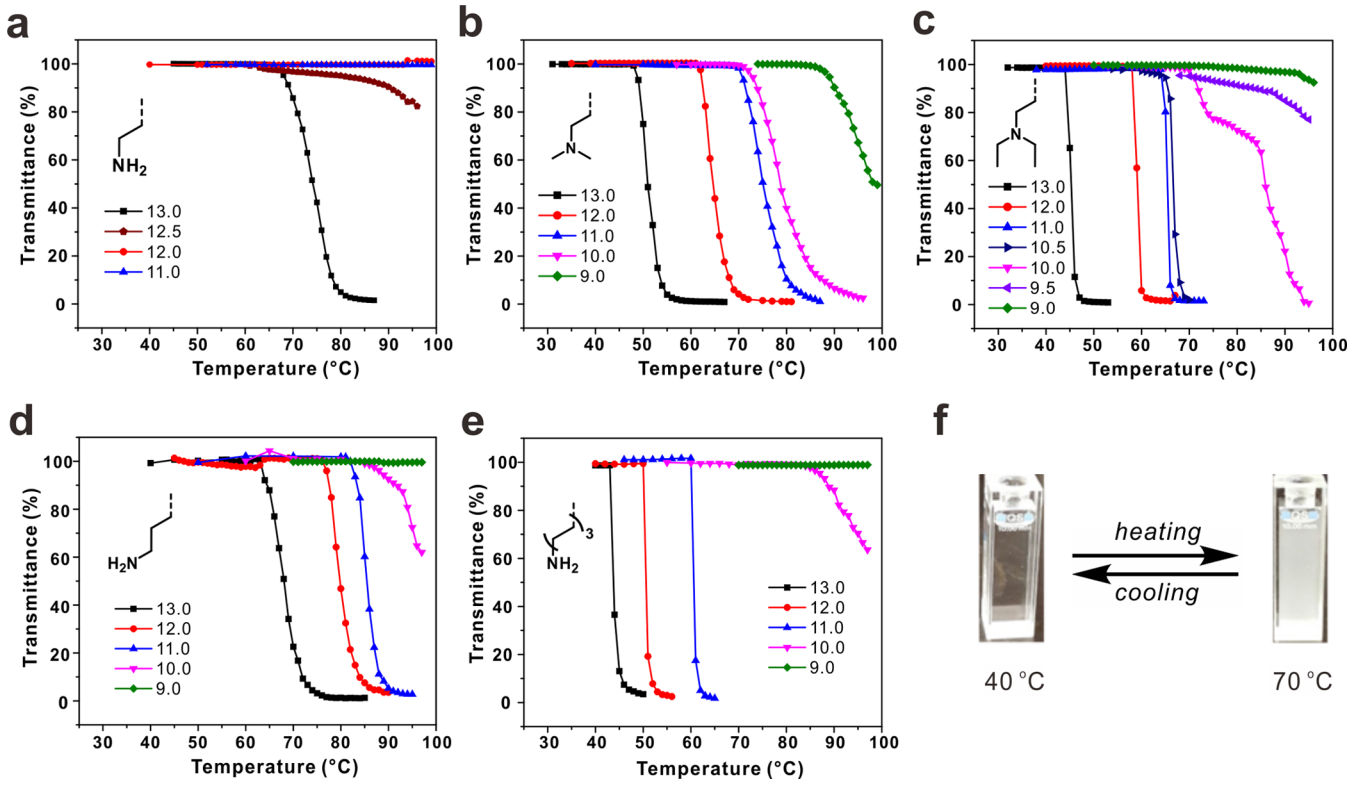

Figure 2. (a–e) Temperature-dependent transmittance curves for (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, and (e) **P5** in solutions with different pH values. (f) Turbidity change of **P2** at pH 13 when cycling the temperature. All polymers were tested at a concentration of 0.10 wt %.

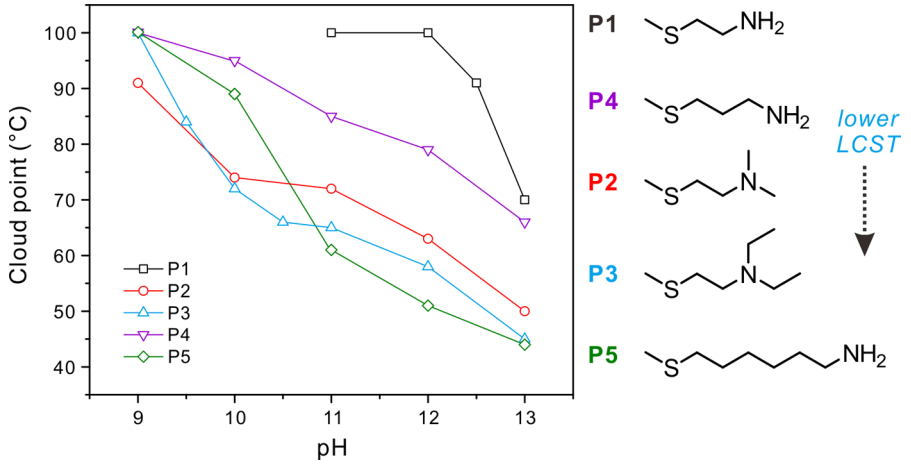

Figure 3. Summary of all cloud points for **P1**–**P5** as a function of pH.

to and 44 °C for **P1**, **P4**, and **P5**, respectively. These observations indicate that the LCST transition is significantly affected by the length of the side chain. It was observed that the phase transition of **P5** was reversible with a clear hysteresis occurring during the cooling process (Figure S3).

A comparison of the cloud points of the different polymers as a function of pH is shown in Figure 3, which clearly shows that the cloud point at a given pH decreased as the hydrophobicity of the amine group or length of the side chain was increased. To quantitatively investigate the effect of side chain hydrophobicity, the octanol/water coefficients (log *P*) of the thiols (R_1–R_5) were calculated using the software ALOGPS 2.1, based on a well-known computational model (Table 1).[35,36] Comparing the log *P* values of the side chain of **P1**, **P2**, and **P3**, it can be seen that the hydrophobicity increased as the number of carbons on the N atom increased. Increasing the hydrophobicity of the amine moiety significantly lowered the cloud points at all pH values. As expected, the side chain length was also highly correlated with hydrophobicity, as can be seen by comparing the log *P* values of **P1**, **P4**, and **P5**.

Despite these relationships, comparing the log *P* values of **P3** and **P5** shows there was not an exact correlation between cloud point and hydrophobicity. It should be noted that **P3** and **P5** have the same number of carbons on their side chains. Nevertheless, the log *P* values of **P3** and **P5** are 2.34 and 2.07, respectively, indicating that **P3** was more hydrophobic than **P5**. However, the cloud point of **P3** was higher than **P5** between pH 11.0 and 13.0, suggesting that the primary amine group on

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P5 can collapse into a globule state at lower temperatures due to intra/interchain hydrogen bonds.[41] As shown in Figure S3, the hysteresis is observed clearly in a heating-and-cooling cycle, attributed to the formation of additional hydrogen bonds of each primary amine groups that inhibits hydration in the cooling process. The LCST trends of **P3** and **P5** reversed below pH 11.0, as protonated primary amines can be hydrated much more easily than the protonated tertiary amines due to the hydrophobic diethyl groups that inhibit interaction with water. It can therefore be concluded that LCST-type phase transition is affected by a complicated interaction of the hydrophilicity/hydrophobicity balance with hydrogen bonding ability.

In summary, the pH-responsive LCST behavior of PEO-based functional polymers with different pendant amine groups and varying side chain lengths has been investigated. Five different aminothiols, including cysteamine, *N*,*N*-dimethylaminoethanethiol, *N*,*N*-diethyl aminoethanethiol, 3-amino-1-propanethiol, and 6-amino-1-hexanethiol could be quantitatively introduced to a single, well-defined P(EO-*co*-AGE) copolymer starting material via facile and modular thiol−ene chemistry. The transmission spectra for aqueous solutions of these copolymers revealed that cloud point was not only tuned by the pH of the solution but also by the hydrophobicity of the pendant amine moieties. The polymer library also exhibited different thermoresponsive phase transition behavior depending on the side chain length with the hydrophilicity/hydrophobicity balance being the dominant factor in controlling LCST behavior. By designing pH-tunable, thermoresponsive PEO-based polymers with multiple types of amine and different chain lengths, an effective and facile method of controlling LCST behavior has been developed. This fundamental and systematic investigation provides a platform to understand a wide range of LCST behaviors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00830.

Detailed experimental procedures and additional ^{1}H NMR and GPC data (PDF).

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Notes

The authors declare no competing financial interest.

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