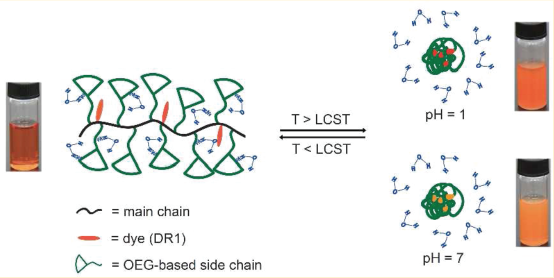
Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

Comblike Thermoresponsive Polymers with Sharp Transitions: Synthesis, Characterization, and Their Use as Sensitive Colorimetric Sensors

Lianxiao Liu, Wen Li,* Kun Liu, Jiatao Yan, Guixia Hu, and Afang Zhang*

Department of Polymer Materials, College of Materials Science and Engineering, Shanghai University, Chengzhong Street 20, Shanghai 201800, China

S *Supporting Information*



ABSTRACT: The synthesis and thermoresponsive behavior of two structural novel comblike polymers are presented, which are constituted by polymethacrylates main chain with dendritic oligoethylene glycol (OEG) side groups spaced with a linear hydrophobic alkyl [PG1(A)] or hydrophilic OEG unit [PG1(G)]. The design of this comblike architecture is to retain the unique thermoresponsive behavior of OEG-based dendritic polymers and, on the other side, to eliminate the tremendous synthesis effort for the dendronized polymer analogues. Their thermoresponsive behavior was investigated with UV/vis and temperature-varied ^{1}H NMR spectroscopy to determine their apparent LCSTs and follow chain dehydration process, respectively. These polymers show sharp and fast transitions with small hystereses. The phase transition temperatures are located in between 27 and 34 °C, which is in the vicinity of physiological temperature, and these transition temperatures are independent of polymer concentration. The thermoresponsiveness of these polymers is also compared with the corresponding macromonomers as well as the densely packed dendronized polymer analogues reported previously, focusing on chemical structure and architecture effects. It was found that the more hydrophobic polymer PG1(A) could form denser aggregates than that of the more hydrophilic polymer PG1(G). On the basis of the exceptional thermoresponsive behavior of these comblike polymers, this architecture is utilized for fabricating polymer sensors. Random copolymerization of the macromonomers with the monomer bearing solvatochromic dye moiety (Disperse Red 1) affords the thermoresponsive copolymers which act as sensitive dual-sensors for both temperature and pH value.

INTRODUCTION

Polyethylene glycols (PEGs) and their analogues oligoethylene glycols (OEGs) have been well investigated for various material applications due to their unique properties, including biocompatibility, low toxicity, and good water solubility.[1] They were incorporated into different part of polymers to enhance the functionality.[2] Especially, polymers carrying short OEG side chains endeavor phase transitions when heating their aqueous solutions to their lower critical solution temperatures (LCSTs), which makes them one of interesting thermoresponsive polymers.[3] In contrast to the intriguing thermoresponsive polymer poly(*N*-isopropylacrylamide) (PNiPAM), which shows sharp phase transition but exhibits unavoidable large hysteresis upon cooling due to the strong intermolecular hydrogen bonding,[4] OEG-based thermoresponsive polymers are superior in several aspects: (1) they are nontoxic; (2) thermally induced phase transitions normally exhibit small hysteresis; (3) the LCST of these polymers can be tuned easily by various routes, including modification of the terminal groups,[5] the length of the OEG chains,[6] or the copolymer compositions.[7] Thus, OEG-based thermoresponsive polymers attract more and more attention recently, and they are considered to be good candidates in many applications, such as drug delivery,[8] smart surface,[9] and water dispersants.[10]

One of the most active research directions recently is to construct OEG-based thermoresponsive polymers of different architectures. Comblike homo- and copolymers with polymethacrylate as the backbone and short OEG as the side chains were synthesized by Ishizone et al. first via anionic polymerization[6a] or later by Lutz et al. via atom transfer radical polymerization (ATRP) strategy.[7b,11] Zhao and co-workers reported the synthesis of polyacrylates and polystyrenes with OEG pendent groups through nitroxide-mediated radical polymerization (NMRP).[6b,12] These work discovered that polymer composition and molecular weight, terminal groups of the side chains, and polymer end-groups all show influence on the polymers' LCSTs. Because of the simple structure of these polymers, the architecture effects[13] on their LCSTs were not brought into much attention. Recently, hyperbranched copolymers from OEG-based polymethacrylates were synthesized by Davis and co-workers.[14] They pointed out

Received: August 17, 2011
Revised: September 29, 2011
Published: October 10, 2011

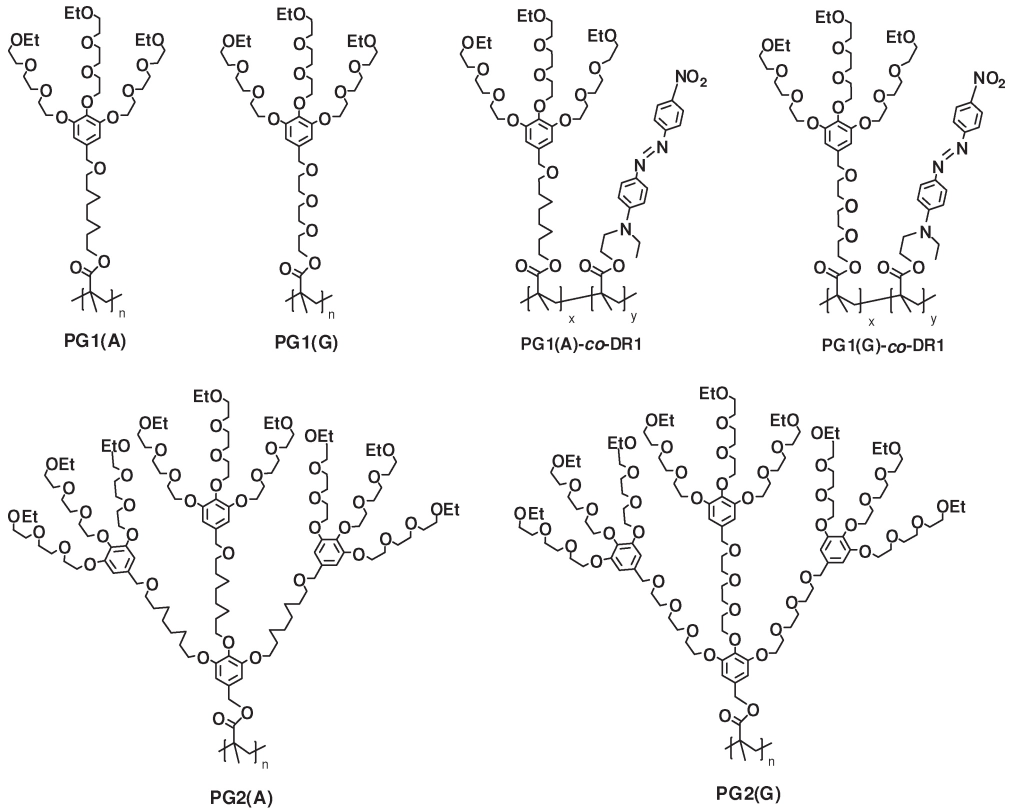


Figure 1. Chemical structures of the ethoxyl-terminated comblike homopolymers PG1(A) and PG1(G) and copolymers PG1(A)-*co*-DR1 and PG1(G)-*co*-DR1 from present work as well as the ethoxyl-terminated dendronized polymethacrylates PG2(A) and PG2(G) reported in previous work.[5b,16a] Nomenclature: A and G represent interior with alkyl (A) and oligoethylene glycol (G) linkage, respectively; PG1 and PG2 represent the polymers carrying the first (G1) and second generation (G2) of dendrons, respectively.

the polymer architecture shows big influence on their phase transitions, as the LCSTs of the hyperbranched polymers are normally 5−10 deg lower than that of the linear counterparts. Alternatively, we reported recently a series of thermoresponsive polymers with OEG linkages based on dendronized polymer concept (from PG1 to PG3).[5b,15] These polymers combine the structural characteristics from dendronized polymers, including the bulkiness, cylindrical molecular shape, and high rigidity with a more or less stretched backbone in the interior, together with the unique properties of OEG units. They were prepared via conventional radical polymerization in bulk and could be achieved with high molar masses. These polymers show unprecedented thermoresponsive properties with sharp phase transitions in both heating and cooling processes as well as small hysteresis. Their phase transition temperatures can be tuned in the range of 32−65 °C, depending mostly on the peripheral units (either methoxyl or ethoxyl). Furthermore, the dendritic architecture takes great effects on their thermoresponsiveness and features these polymers with heterogeneous dehydration of the peripheral units at a lower temperature than that of the interior parts.[16] This behavior affords a possibility to fabricate a molecular nanocapsule. But the tedious multiple step synthesis remains the major disadvantage to these polymers, which limit their widely applications to different research areas.

In the past two decades, it has seen renaissance of interest in developing polymer sensors based on thermoresponsive polymers.[17] The principle is to make use of the microenvironmental changes from the phase transitions of the thermoresponsive polymers: below LCST, the polymers are water-soluble and polar, while upon heated to elevated temperature, the polymers are dehydrated and become hydrophobic and, in most cases, forming aggregates by entropy-driving collapse. By incorporating solvatochromic dyes[18] into the polymers covalently, temperature-induced minor environmental polarity changes can initiate the specific change of optical or emissive properties of the dyes. Thus, sharpness and reversibility of the phase transitions of the thermoresponsive polymers make them extremely suitable for loading the solvatochromic dyes to have a reliable and accurate sensing. By choosing different chromophores, polymer-based sensors can be classified into fluorescent and visible sensors. The majority of such polymer sensors are based on PNiPAM[19] and, more recently, on OEG-based polymers.[20] Up to now, it still remain a challenge to develop a better thermoresponsive polymer for loading sensor that its LCST shows minor or negligible influence after loading dye, and it can efficiently prevent fluorescent dye from self-quenching.

In present report, we present the synthesis of OEG-based polymers PG1(A) and PG1(G) with comblike architecture which contain first generation (G1) dendrons spaced with a linear hydrophobic alkyl or hydrophilic OEG units in the side chain (Figure 1). Their structures and compositions are similar to the second generation (G2) dendronized polymer analogues PG2(A) and PG2(G), except the lower density of the OEG dendritic side units. These polymers show similar thermoresponsive behaviors as their dendronized polymer counterparts, but their synthesis is greatly simplified. Their thermoresponsiveness was thus investigated with UV/vis and temperature-varied proton NMR spectroscopy and compared with the macromonomers and dendronized counterparts, and the structure and architecture effects were examined in details. Based on the characteristic thermoresponsive behavior of these comb-like polymers, copolymers PG1(A)-*co*-DR1 and PG1(G)-*co*-DR1 containing 5 mol % of the solvatochromic dye (Disperse Red 1, DR1) were synthesized to fabricate novel dual sensors which can show sensitive response to both temperature and pH value.

■ EXPERIMENTAL SECTION

Materials. Compounds **1** and **2** were synthesized according to the previous report.[15b] Dichloromethane (DCM) was distilled from CaH_2 for drying. Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. 0.1 M HCl was used for making the pH 1 solution. Other reagents and solvents were purchased at reagent grade and used without further purification. All reactions were run under a nitrogen atmosphere. Macherey-Nagel precoated TLC plates (silica gel 60 G/UV254, 0.25 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel 60 M (Macherey-Nagel, 0.04−0.063 mm, 200−300 mesh) was used as the stationary phase for column chromatography.

Instrumentation and Measurements. ^{1}H NMR spectra were recorded on a Bruker AV 500 (500 MHz) spectrometer. Gel permeation chromatography (GPC) measurements were carried out on a Waters GPC e2695 instrument with 3 column set (Styragel HR3 + HR4 + HR5) equipped with refractive index detector (Waters 2414), and DMF (containing 1 g L^{-1} LiBr) as eluent at 45 °C. The calibration was performed with poly(methyl methacrylate) standards in the range of M_p = 2540−936 000 (Polymer Standards Service-USA, Inc.). UV/vis turbidity measurements were carried out on a PE UV/vis spectrophotometer (Lambda 35) equipped with a thermostatically regulated bath. Aqueous polymer solutions were placed in the spectrophotometer (path length 1 cm) and heated or cooled at a rate of 0.2 °C min^{-1}. The absorptions of the solution at λ = 500 nm were recorded every 5 s. The LCST is determined the one at which the transmittance at λ = 500 nm had reached 50% of its initial value.

3,4,5-Tris{2-[2-(2-ethoxyethoxy)ethoxy]ethoxy}benzyloxyoctyl Methacrylate [MG1(A)]. MAC (0.41 g, 3.92 mmol) was added dropwise to a mixture of **1** (2.00 g, 2.61 mmol), TEA (1.32 g, 13.05 mmol), and DMAP (0.20 g) in dry DCM (40 mL) at 0 °C over 5 min. The mixture was stirred for 4 h at rt and then quenched with MeOH. After washing successively with aqueous $NaHCO_3$ solution and brine, the organic phase was dried over $MgSO_4$. Purification by column chromatography with DCM/MeOH (30:1, v/v) afforded MG1(A) (2.20 g, 95%) as colorless oil. ^{1}H NMR ($CDCl_3$): δ = 1.17−1.20 (m, 9H, CH_3), 1.32−1.37 (m, 8H, CH_2), 1.56−1.68 (m, 4H, CH_2), 1.92−1.93 (m, 3H, CH_3), 3.40−3.43 (m, 2H, CH_2), 3.48−3.73 (m, 30H, CH_2), 3.77 (t, 2H, CH_2), 3.83 (t, 4H, CH_2), 4.10−4.15 (m, 8H, CH_2), 4.36 (s, 2H, CH_2), 5.52−5.53 (m, 1H, CH_2^a), 6.07−6.08 (m, 1H, CH_2^b), 6.55 (s, 2H, CH).

2-{2-[2-(3,4,5-Tris{2-[2-(2-ethoxyethoxy)ethoxy]ethoxy}benzyloxy)-ethoxy]ethoxy}ethyl Methacrylate [MG1(G)]. MAC (0.48 g, 4.55 mmol) was added dropwise to a mixture of **2** (2.33 g, 3.03 mmol), TEA (1.53 g, 15.15 mmol), and DMAP (0.20 g) in dry DCM (40 mL) at 0 °C over 5 min. The mixture was stirred for 4 h at rt and then quenched with MeOH. After washing successively with aqueous $NaHCO_3$ solution and brine, the organic phase was dried over $MgSO_4$. Purification by column chromatography with DCM/MeOH (30:1, v/v) afforded MG1(G) (2.30 g, 92%) as colorless oil. ^{1}H NMR ($CDCl_3$): δ = 1.20−1.23 (m, 9H, CH_3), 1.95−1.96 (m, 3H, CH_3), 3.51−3.56 (m, 6H, CH_2), 3.59−3.77 (m, 34H, CH_2), 3.80 (t, 2H, CH_2), 3.86 (t, 4H, CH_2), 4.12−4.17 (m, 6H, CH_2), 4.30−4.32 (m, 2H, CH_2), 4.46 (s, 2H, CH_2), 5.57−5.58 (m, 1H, CH_2^a), 6.13−6.14 (m, 1H, CH_2^b), 6.58 (s, 2H, CH).

Polymerization of MG1(A) in Bulk. Monomer MG1(A) (0.50 g, 0.60 mmol) and AIBN (2.50 mg) were added into a Schlenk tube. The mixture was thoroughly deoxygenated by several freeze−pump−thaw cycles and then stirred at 65 °C for 4 h. After cooling to rt, the polymer was dissolved in DCM and purified by silica gel column chromatography with DCM as an eluent. PG1(A) was yielded (0.35 g, 70%) as a highly viscous oil. ^{1}H NMR ($CDCl_3$): δ = 0.80−1.10 (m, 3H, CH_3), 1.19−1.23 (m, 9H, CH_3), 1.27−1.34 (m, 10H, CH_2), 1.62 (br, 4H, CH_2), 3.45−3.74 (m, 32H, CH_2), 3.79−3.98 (m, 8H, CH_2), 4.11−4.15 (m, 6H, CH_2), 4.37 (br, 2H, CH_2), 6.56 (br, 2H, CH).

Polymerization of MG1(G) in Bulk. Monomer MG1(G) (0.30 g, 0.36 mmol) and AIBN (1.50 mg) were added into a Schlenk tube. The mixture was thoroughly deoxygenated by several freeze−pump−thaw cycles and then stirred at 65 °C for 3 h. After cooling to rt, the polymer was dissolved in DCM and purified by silica gel column chromatography with DCM as an eluent. PG1(G) was yielded (0.18 g, 60%) as a highly viscous oil. ^{1}H NMR ($CDCl_3$): δ = 0.85−1.08 (m, 3H, CH_3), 1.18−1.22 (m, 9H, CH_3), 1.27−1.33 (m, 2H, CH_2), 3.49−3.74 (m, 40H, CH_2), 3.78−3.85 (m, 6H, CH_2), 4.10−4.14 (m, 8H, CH_2), 4.43 (br, 2H, CH_2), 6.56 (br, 2H, CH).

Synthesis of Copolymer PG1(A)-co-DR1. Monomer MG1(A) (0.60 g, 0.72 mmol), MDR1 (14.40 mg, 0.04 mmol), and AIBN (3 mg) were dissolved in dry DMF (0.10 mL) inside a Schlenk tube. The solution was thoroughly deoxygenated by several freeze−pump−thaw cycles and then stirred at 65 °C for 8 h. After cooling to rt, the polymer was dissolved in little DCM and purified by silica gel column chromatography with DCM/hexane (1:3, v/v) as an eluent. PG1(A)-*co*-DR1 was yielded (0.33 g, 46%) as a highly viscous red color oil. ^{1}H NMR ($CDCl_3$): δ = 0.86−1.09 (m, CH_3), 1.18−1.22 (m, CH_3), 1.27−1.34 (m, CH_2), 1.62 (br, CH_2), 3.33−3.92 (m, CH_2), 4.11−4.14 (m, CH_2), 4.36 (br, CH_2), 6.55 (br, CH), 6.87 (br, CH), 7.92 (br, CH), 8.30 (br, CH).

Synthesis of Copolymer PG1(G)-co-DR1. Monomer MG1(G) (0.60 g, 0.72 mmol), MDR1 (14.40 mg, 0.04 mmol), and AIBN (3 mg) were dissolved in dry DMF (0.1 mL) inside a Schlenk tube. The solution was thoroughly deoxygenated by several freeze−pump−thaw cycles and then stirred at 65 °C for 6 h. After cooling to rt, the polymer was dissolved in little DCM and purified by silica gel column chromatography with DCM/hexane (1:3, v/v) as an eluent. PG1(G)-*co*-DR1 was yielded (0.49 g, 82%) as a highly viscous red color oil. ^{1}H NMR ($CDCl_3$): δ = 0.86−1.09 (m, CH_3), 1.18−1.22 (m, CH_3), 1.27−1.34 (m, CH_2), 3.49−3.85 (m, CH_2), 4.10−4.12 (m, CH_2), 4.43 (br, CH_2), 6.55 (br, CH), 6.87 (br, CH), 7.92 (br, CH), 8.30 (br, CH).

■ RESULTS AND DISCUSSION

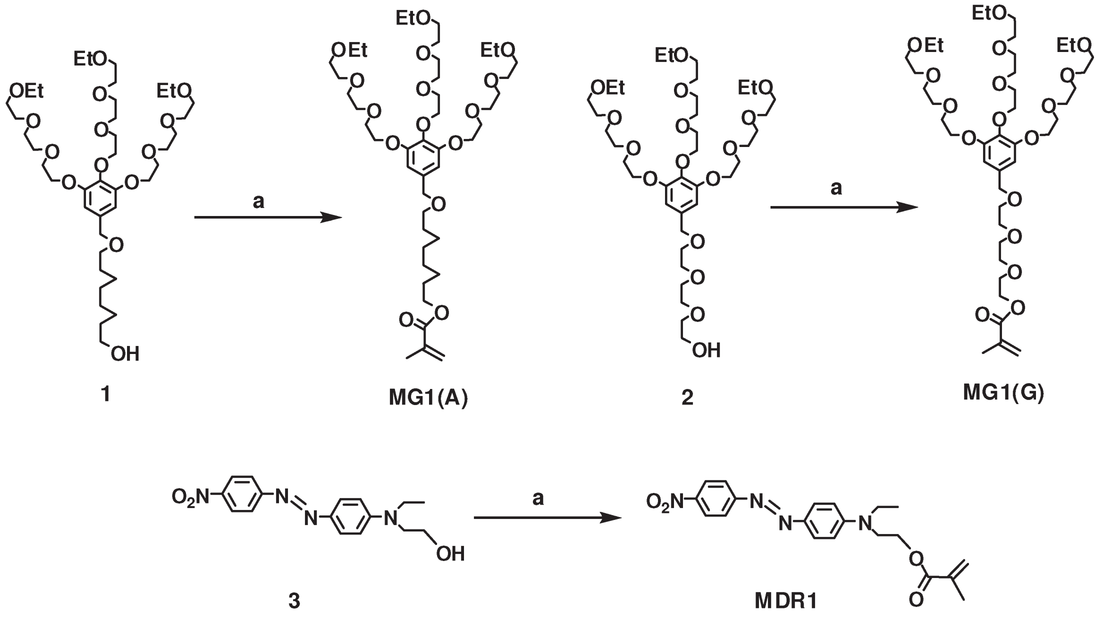
Synthesis. The ethoxyl-terminated dendritic structure is selected as the corresponding dendritic polymers show LCSTs in the vicinity of physiological temperature. The macromonomer route is applied here for the synthesis of these polymers in order to achieve well-defined structures. Starting from two ethoxyl-terminated dendron alcohols **1** and **2** with alkyl and OEG tails, respectively,[15b] the reaction with MAC in the presence of TEA as base and DMAP as catalyst afforded directly their corresponding macromonomers MG1(A) or MG1(G) in high yields (92 or 95%) and on gram scales. Both macromonomers are colorless viscous liquid at room temperature; thus, their free radical polymerization was able to be carried out in bulk with AIBN as the initiator. The polymerization media became solidified in less than 30 min for both cases, indicating the fast polymerization kinetics. The polymerizations were then stopped after 3−4 h to avoid the possible gelation. After purification by column chromatography with DCM as eluent, PG1(A) and PG1(G) were

Table 1. Conditions for and Results from the Polymerization of the Macromonomers MG1(A) and MG1(G) as Well as the Copolymerization of MG1(A) and MG1(G) with MDR1

				GPC results			
entries	monomers	time (h)	yield (%)	$M_n \times 10^{-5}$	DP_n[a,b]	PDI	LCST (°C)[c]
PG1(A)	MG1(A)	4	70	1.7	204	2.0	27.4
PG1(G)	MG1(G)	3	60	3.0	358	2.2	33.7
PG1(A)-*co*-DR1	MG1(A)/MDR1[d]	8	46	1.1	133/7	3.2	25.5
PG1(G)-*co*-DR1	MG1(G)/MDR1[d]	6	82	2.0	240/12	2.3	32.8

[a] DP_n = apparent number-average degree of polymerization, which is calculated from the relative molar masses M_n (and the ratio of OEG unit and DR1 for the copolymers). [b] The copolymer composition ratios were analyzed with ^{1}H NMR spectroscopy (Figures S9 and S10) by counting the proton integrations (I) at 6.55 ppm (signal a) from OEG dendrons and at 7.92 ppm (signal c) from DR1 moieties, and calculated according to [OEG unit]:[DR1] = $[I_{6.55}]/2$:$[I_{7.92}]/4$. [c] The apparent LCST of the polymers were determined as the temperature at 50% of the initial transmittance. [d] The feed molar ratio of the macromonomers to MDR1 is 95:5.

Scheme 1. Synthesis of the Macromonomers[a]



[a] Reagents and conditions: (a) MAC, DMAP, TEA, DCM, −5 to 25 °C, 4 h [92%, 95%, and 65% for MG1(A), MG1(G), and MDR1, respectively]. DCM = dichloromethane, DMAP = *N*,*N*-dimethylaminopyridine, MAC = methacryloyl chloride, TEA = triethylamine.

achieved in yields of 60−70%. All the macromonomers and polymers were characterized by ^{1}H NMR spectroscopy (see Supporting Information for the spectra). The molar masses of the polymers were determined by GPC with DMF as eluent, and the results are summarized in Table 1. Both PG1(A) and PG1(G) with high molar masses were obtained.

Thermoresponsive Behavior. Both PG1(A) and PG1(G) show thermoresponsive behavior: their aqueous solutions are transparent below 25 °C but turn into turbid when heated to elevated temperatures. Interestingly, the corresponding macromonomers MG1(G) and MG1(A) also exhibit thermoresponsiveness. UV/vis spectroscopy was thus applied to investigate the thermoresponsive behavior of all the monomers and polymers and to determine their apparent LCSTs[21] and examine the architecture effects. The turbidity curves measured at 500 nm were plotted in Figure 2a, which leads to the following conclusions: (1) comblike polymers PG1(A) and PG1(G) show unique thermoresponsive behavior with sharp phase transitions ($\Delta < 1.2°$) and small hysteresis ($\Delta < 1°$) during heating and cooling processes, resembling to the dendronized counterparts PG2(A) and PG2(G), which should come from the simultaneous dehydration of dense OEG branching units.[22] (2) The apparent LCSTs of these comblike polymers are dependent slightly on their interior structures: the LCST of PG1(A) with a hydrophobic tail is 27.4 °C, about 6 deg lower than that of PG1(G) which possesses a hydrophilic tail. The low density of grafted dendrons here affords the side units high mobility which facilitates interior part evolved in the dehydration. (3) Although all these polymers possess the same dendron in the periphery as their dendronized counterparts, their apparent LCSTs are 2−4 deg lower than these of the latter. This can be understood that back-folding of peripheral ethoxyl units for the case of dendronized polymers PG2(A) and PG2(G) enhanced by the high dense peripheral dendritic units[23] leads to the more hydrophilic OEG units exposed onto the molecular surface, thus causing the increase of LCST. (4) The apparent LCSTs of macromonomers are quite different from those of their corresponding comblike polymers. MG1(A) shows a LCST at 15.5 °C, which is 12 deg

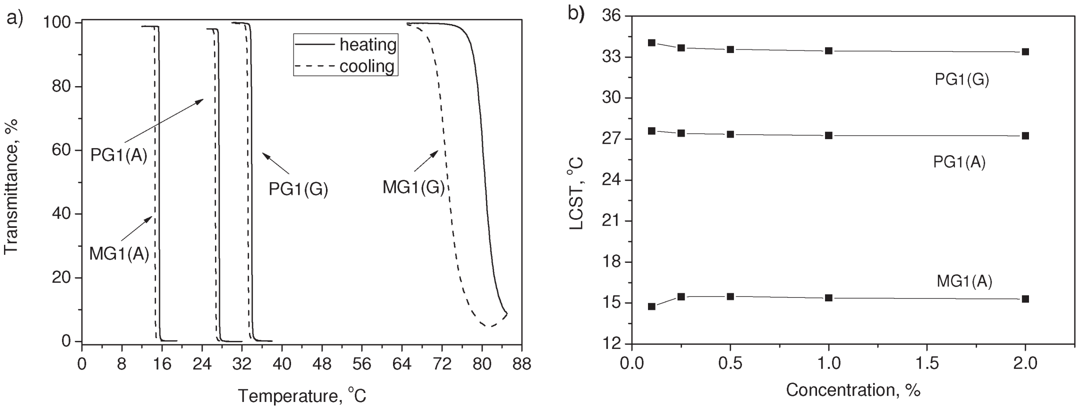


Figure 2. (a) Plots of transmittance vs temperature for 0.25 wt % aqueous solutions of MG1(A), MG1(G), PG1(A), and PG1(G). Heating and cooling rate = 0.2 °C/min. (b) Dependence of LCST on the concentration of MG1(A), PG1(A), and PG1(G). For turbidity curves, see Figures S1 and S2a in the Supporting Information.

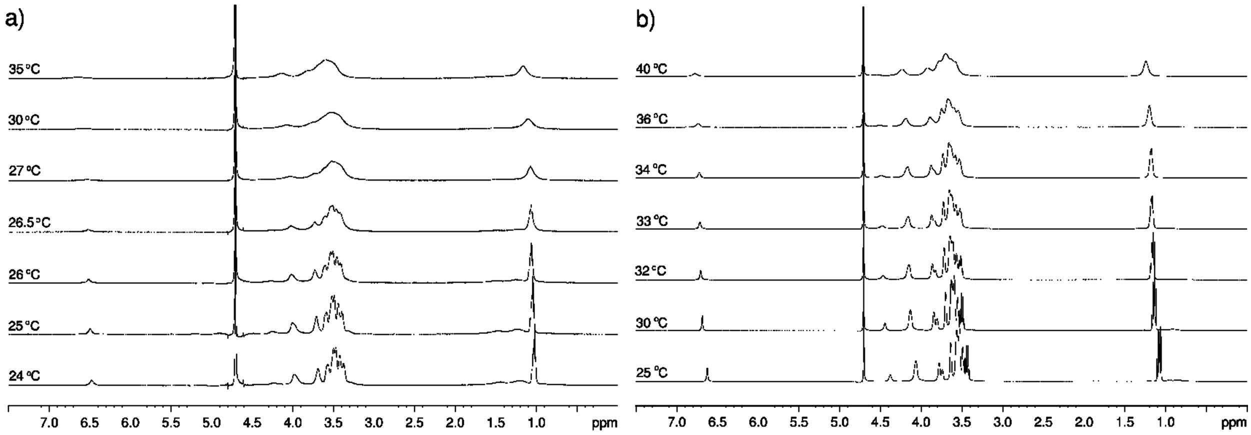


Figure 3. Temperature-dependent ^{1}H NMR spectra of PG1(A) (LCST = 27.2 °C) (a, 1.0 wt %) and PG1(G) (LCST = 33.4 °C) (b, 1.0 wt %) in D_2O.

lower than its corresponding polymer PG1(A), while the LCST of MG1(G) is above 80 °C, which is about 46 deg higher than that of its corresponding polymer PG1(G). Furthermore, MG1(A) exhibits sharp phase transitions; in contrast, the phase transitions of MG1(G) are less sharp and show a larger hysteresis. Comparing the macromonomer to its corresponding polymer, their overall hydrophilicities are nearly the same. By polymerization, the OEG dendrons are aligned alone the polymer main chain, which shades the linkage [either alkyl tail inside PG1(A) or OEG tail inside PG1(G)] to a certain degree and thus leads the polymer's thermoresponsiveness dependent more on the peripheral dendrons. Therefore, the LCSTs of PG1(A) and PG1(G) are similar as they possess the same periphery dendron. In sharp contrast, the tails in the macromonomers MG1(A) and MG1(G) are exposed equally outside, which will join the dehydration altogether; therefore, MG1(A) with a hydrophobic tail starts dehydration at much lower temperature than its polymer, while MG1(G) with a hydrophilic tail starts dehydration at much higher temperature than its polymer. So, the architecture shows significant influence on their thermoresponsiveness.

The influence of the concentration (from 0.1% to 2%) of PG1(A) and PG1(G) on their LCSTs was also studied, and the results are plotted in Figure 2b. Overall, the LCST of the polymer decrease slightly with the increase of concentration, though the decrease is less than 1 deg when polymer concentration increased from 0.1 to 2%, proving the polymer concentration shows negligible influence on their LCST. For comparison, the concentration influence on the LCST of the macromonomer MG1(A) was also investigated. Though the molecule is small, its LCST show only minor concentration dependence (from 0.1 to 2%). This is quite different from the OEG-based dendrimers, where LCST shows obvious concentration dependence.[24] The most unusual phenomenon for MG1(A) is that at a diluted concentration (from 0.1 to 0.25%) the LCST increases first from 14.8 to 15.5 °C, but with concentration from 0.5% to 2% the LCST decreases. For the phase transitions curves, see Figure S2a. All these suggest the macromonomer and the polymer adopt a different thermoresponsive mechanism: the dehydration of neighboring OEG units along main chain for the polymers facilitates the aggregation, while the dehydrated macromonomers need to diffuse to meet each other in order to form aggregates.

^{1}H NMR spectroscopy was used to follow the dehydration process of the polymers, and the spectra from 24 to 35 °C for PG1(A) and from 25 to 40 °C for PG1(G) were recorded (Figure 3). The proton signals of OEG moieties, which appears at δ = 3.2–4.5, are resolved at lower temperatures but broaden increasingly with the increase of solution temperature, simultaneously their intensities decrease, indicating the dehydration of

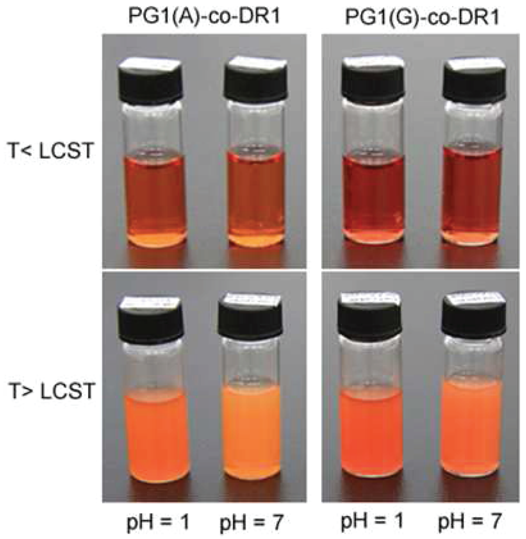


Figure 4. Photographs of the copolymer solutions below and above the phase transition temperature at pH 1 and 7. Copolymer concentrations: 0.60 mg mL^{-1}.

OEG units. The temperatures to initiate the chain dehydration for PG1(A) and PG1(G) are 26.5 and 33 °C, respectively, which are slightly lower than their corresponding LCST. This is understandable as the former is an indication for the dehydration of OEG units, while the latter is an indication for aggregation of the dehydrated or collapsed OEG units. Comparison of the NMR spectra from both PG1(A) and PG1(G) leads to another interesting point. The spectra from PG1(A) change dramatically when solution temperature increased above the dehydration temperature, and the signals from aromatic ring ($\delta = 6.5$) and alkyl tail ($\delta = 1.1-1.6$) almost disappeared. But the spectra from PG1(G) are always much resolved than these from PG1(A) at the same temperature. Even at elevated temperature, for example 40 °C, which is much higher than the initial dehydration temperature, the spectra from PG1(G) are still less broader, and the signal from aromatic ring ($\delta = 6.5$) can still be visualized. Since the signals' sharpness and intensities are indication of the proton mobility under the circumstance, we thus can preliminarily conclude that the aggregates formed from PG1(A) are denser than those from PG1(G).

Synthesis of Dual Sensors for Temperature and pH Value. The unique thermoresponsive behaviors of these comblike polymers make them attractive candidates for fabricating various responsive materials. It is known that Disperse Red 1 (DR1) is a solvatochromic dye which can change its color with the solvent polarity.[25] We thus consider covalently incorporating this dye into the comblike polymers may fabricate sensitive colorimetric sensors. Furthermore, the sizable dimension of these dendritic polymers may afford the polymer sensors special characteristics. Herein, DR1 with polymerizable unit (MDR1) (Figure 1) was prepared from compound **3** and was radically copolymerized with MG1(A) and MG1(G) to afford random copolymers PG1(A)-*co*-DR1 and PG1(G)-*co*-DR1, respectively. The feed molar ratio of the macromonomer to MDR1 is 95:5. The copolymer compositions were analyzed with ^{1}H NMR spectroscopy (Figures S9 and S10) by counting the proton integrations at 6.55 ppm (signal a) from OEG dendrons and at 7.92 ppm (signal c) from DR1 moieties, and the results are summarized in Table 1. Coincidently, the molar ratios of the dye moiety within the copolymers are nearly the same as these fed in the monomer mixtures. These copolymers also show thermoresponsive behavior as their homopolymer counterparts, but their LCSTs are slightly lower (Δ = 1°−2°) due to the introduction of the hydrophobic dye DR1 moieties (see Figure S2b for the turbidity curves). It is interesting to point out that incorporation of the dye moieties inside the comblike copolymers only shows minor influence on their LCSTs, and this is in sharp contrast to the conventional OEG-based polymers where LCST decreased more than 10 deg after introduction of the same dye at 5 mol %.[20a]

Dissolving the copolymers in water at pH 1 or 7 at room temperature yielded the solutions with red color (Figure 4). Visually, all copolymer solution color at both pH conditions is quite different from the purple color of aqueous solution from free DR1 (at pH = 1), indicating the obvious interaction of DR1 moieties with the OEG polymer. The red color from PG1(A)-*co*-DR1 solutions is less intensive than that from PG1(G)-*co*-DR1, which suggests the more hydrophobic environment enhanced the interaction. The pH value shows weak influence on the solution color below the LCSTs since the color at pH 1 is nearly the same as that at pH 7 for both polymers. Upon increasing solution temperature above their LCSTs, different solvatochromic shift happened for copolymer solutions at different pH values. The turbid solutions all changed their color, which is a direct evidence for the sensing ability of these copolymers. It is necessary to mention that light scattering of the colloidal above LCST may also contribute partially to the color difference of the solutions below and above the LCST.

The visual inspection is further confirmed by UV/vis spectroscopy and investigated in more detail. The temperature-dependent UV/vis spectra of these copolymers at different pH values were recorded (Figures S3 and S4), and typical spectra below and above their LCSTs are shown in Figure 5a. The plots of the wavelength with maximum absorbance (λ_{max}) versus temperature are shown in Figure 5b. Below LCST (20 °C), the aqueous solutions of copolymers PG1(G)-*co*-DR1 at either pH 1 or pH 7 show λ_{max} at about 500 nm, which is blue shift when comparing to that from free DR1 in water at pH 1 (λ_{max} = 515 nm).[20a] For the more hydrophobic copolymer PG1(A)-*co*-DR1 the blue shift is even enhanced, and the aqueous solutions at either pH 1 or pH 7 show λ_{max} at about 488 nm. Interestingly, the solution pH show negligible influence on the blue shift below LCST since the aqueous solutions for either PG1(G)-*co*-DR1 or PG1(A)-*co*-DR1 give nearly the same λ_{max} at both pH 1 and pH 7, similar to previous report.[20a] These results indicate the interaction of the OEG polymer with DR1 moieties dominates the state of dye in the solution at low temperature, and this interaction enhances with the increase of polymer hydrophobicity. With increase of solution temperature to above their LCSTs, the λ_{max} for the copolymer solutions at both pH 1 and 7 all shows obvious shifts. At solution pH 1, the λ_{max} for both copolymer PG1(G)-*co*-DR1 (at 40 °C) and PG1(A)-*co*-DR1 (at 32 °C) red shifts to 526 nm. While at solution pH 7, the λ_{max} for copolymer PG1(G)-*co*-DR1 and PG1(A)-*co*-DR1 blue shifts to 483 and 478 nm, respectively. The more hydrophobic copolymer PG1(A)-*co*-DR1 always shifts more strongly than the more hydrophilic one at both pH conditions. The results here are partially different from the report from Hoogenboom et al.,[20a] where no λ_{max} shift happened for the OEG-based polymer sensors when solution pH is 7. On the basis of above observation, we can conclude that either polymer dehydration or acidic condition

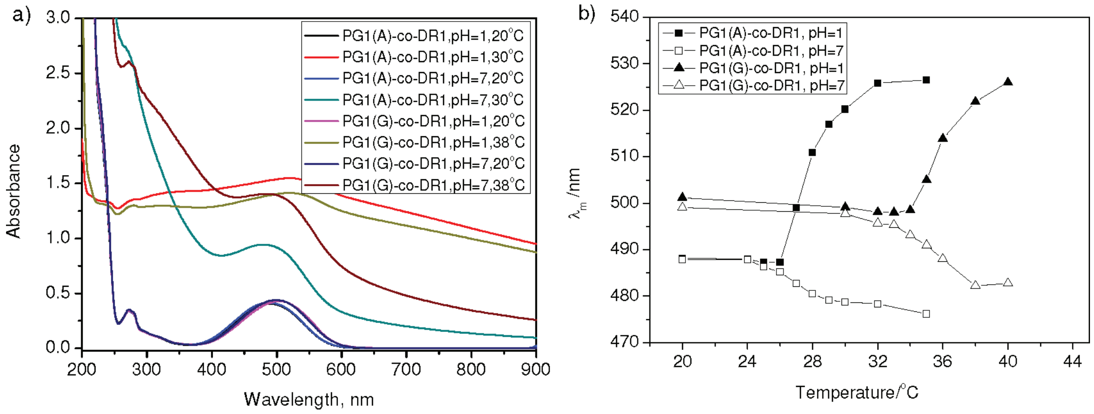


Figure 5. (a) UV/vis spectra of PG1(A)-*co*-DR1 and PG1(G)-*co*-DR1 at solution pH 1 and 7 below and above their LCSTs. (b) Plots of λ_{max} vs temperature for copolymer sensor solutions at solution pH 1 and 7. For more temperature varied UV spectra, see Figures S3 and S4 in the Supporting Information. Copolymer concentrations: 0.20 mg mL^{-1}.

cannot lead to λ_{max} red shift, and this can happen only in polymer dehydrated state at acidic solutions. Since the red shift of λ_{max} is an indication of the protonation of the dye moieties, it is clear that DR1 moieties can only be protonated at β-nitrogen atom in the dehydrated polymer media, and the more hydrophobic polymer facilitates the protonation at a lower temperature. In contrast, at pH 7 where no driving force for the protonation of β-nitrogen exists due to the pK_a of DR1,[20a] dehydration of copolymers leads to the formation of more hydrophobic phase, which induces further blue shift of λ_{max}.

Furthermore, the sharp transitions of these comblike copolymers carrying OEG dendrons afford the polymer sensors higher sensitivity than the copolymers carrying short OEG chains reported previously.[20a] The λ_{max} of the solutions at pH 1 all moved to much higher wavelength in a fast fashion with the increase of the solution temperature above their LCST. For example, 2 deg temperature difference (from 27 to 29 °C) causes the λ_{max} to shift 18 nm (from 499 to 517 nm) for PG1(A)-*co*-DR1. While for previously reported OEG-based polymer sensors, the same red shift ($\Delta\lambda_{max}$ = 18 nm) can only be realized in about 5 deg. This interesting property may afford this kind of polymer sensors promising applications.

■ CONCLUSIONS

Two structurally novel comblike polymers were efficiently synthesized via free radical polymerization through macromonomer strategy. These polymers carrying OEG dendron in the side chains spaced with either hydrophobic alkyl chain or hydrophilic OEG chain are all thermoresponsive and show sharp phase transitions with small hysteresis. In contrast to conventional linear thermoresponsive polymers, the concentration shows negligible influence on their phase transition temperature. Comparing with the corresponding macromonomers as well as the densely packed dendronized polymer analogues, both chemical structure and architecture show significant effects on their thermoresponsiveness. The more hydrophobic polymer PG1(A) could form denser aggregates than that from the more hydrophilic polymer PG1(G) due to the enhanced hydrophobic interaction. On the basis of the characteristic thermoresponsive behavior of these comblike polymers, the architecture is utilized to fabricate polymer sensors by covalently incorporating solvatochromic dye (Disperse Red 1). It is interesting to find that incorporating 5 mol % of hydrophobic dye unit shows a minor influence on the phase transition temperature of the polymers. These polymer sensors are responsive to both pH value and temperature. At pH 7 where no driving force for the protonation of β-nitrogen exists, more hydrophobic dehydrated copolymers facilitate further blue shift of λ_{max}, while at pH 1 the dye moieties can be protonated at the β-nitrogen atom in the dehydrated polymer media, and the more hydrophobic polymer enhances the protonation at a lower temperature. The copolymer solutions exhibit big red λ_{max} shift upon minor increase of solution temperature at acidic conditions, which makes them highly sensitive sensors. These findings galantine these comblike polymers ideal candidates as polymer-based sensors, which may find broad interest in various material applications.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Plots of concentration-dependent transmittance vs temperature for PG1(A), PG1(G) and MG1(A), temperature-varied UV spectra of PG1(A)-*co*-DR1 and PG1(G)-*co*-DR1 at pH 1 and 7, as well as proton NMR spectra of macromonomers and (co)polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86-21-69982829. Fax: +86-21-69982827. E-mail: wli@shu.edu.cn (W.L.), azhang@shu.edu.cn (A.Z.).

■ ACKNOWLEDGMENT

We thank Dr. Hongmei Deng from the Instrumental Analysis of Research Center (Shanghai University) for her assistance in NMR measurements. This work is financially supported by National Natural Science Foundation of China (Nos. 21034004, 21104043, and 20974020) and the Science and Technology Commission of Shanghai (No. 10520500300).

■ REFERENCES

(1) (a) Knop, K.; Hoogenboom, R.; Fischer, D.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 6288–6308. (b) Thompson, M. S.; Vadala, T. P.; Vadala, M. L.; Lin, Y.; Riffle, J. S. *Polymer* **2008**, *49*, 345–373.

(2) (a) Gasteier, P.; Reska, A.; Petra, S.; Salber, J.; Offenhäusser, A.; Möller, M.; Groll, J. *Macromol. Biosci.* **2007**, *7*, 1010–1023. (b) Lapienis, G. *Prog. Polym. Sci.* **2009**, *34*, 852–892. (c) Osada, K.; Kataoka, K. *Adv. Polym. Sci.* **2006**, *202*, 113–153. (d) Joralemon, M. J.; McRae, S.; Emrick., T. *Chem. Commun.* **2010**, *46*, 1377–1393.

(3) Lutz, J. F. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3459–3470.

(4) (a) Cheng, H.; Shen, L.; Wu., C. *Macromolecules* **2006**, *39*, 2325–2329. (b) Keerl, M.; Smirnovas, V.; Winter, R.; Richtering, W. *Angew. Chem., Int. Ed.* **2008**, *47*, 338–341.

(5) (a) Ishizone, T.; Seki, A.; Hagiwara, M.; Han, S. *Macromolecules* **2008**, *41*, 2963–2967. (b) Li, W.; Zhang, A.; Schlüter, A. D. *Chem. Commun.* **2008**, 5523–5525.

(6) (a) Han, S.; Hagiwara, M.; Ishizone, T. *Macromolecules* **2003**, *36*, 8312–8319. (b) Hua, F.; Jiang, X.; Li, D.; Zhao, B. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2454–2467.

(7) (a) Jones, J. A.; Novo, N.; Flagler, K.; Pagnucco, C. D.; Carew, S.; Cheong, C.; Kong, X. Z.; Burke, N. A. D.; Stöver, H. D. H. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6095–6140. (b) Lutz, J. F.; Hoth, A. *Macromolecules* **2006**, *39*, 893–896. (c) Qiao, Z.-Y.; Du, F.-S.; Zhang, R.; Liang, D.-H.; Li, Z.-C. *Macromolecules* **2010**, *43*, 6485–6494.

(8) (a) Hu, Z.; Cai, T.; Chi, C. *Soft Matter* **2010**, *6*, 2115–2123. (b) Lutz, J.-F. *Adv. Mater.* **2011**, *23*, 2237–2243.

(9) Gillich, T.; Benetti, E. M.; Rakhmatullina, E.; Konradi, R.; Li, W.; Zhang, A.; Schlüter, A. D.; Textor, M. *J. Am. Chem. Soc.* **2011**, *133*, 10940–10950.

(10) Chen, G.; Wright, P. M.; Geng, J.; Mantovani, G.; Haddleton, D. M. *Chem. Commun.* **2008**, 1097–1099.

(11) Lutz, J. F.; Akdemir, Ö.; Hoth, A. *J. Am. Chem. Soc.* **2006**, *128*, 13046–13047.

(12) Jiang, X.; Zhao, B. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3707–3721.

(13) (a) Jia, Z.; Chen, H.; Zhu, X.; Yan, D. *J. Am. Chem. Soc.* **2006**, *128*, 8144–8145. (b) Gao, M.; Jia, X.; Kuang, G.; Li, Y.; Liang, D.; Wei, Y. *Macromolecules* **2009**, *42*, 4273–4281. (c) Gao, M.; Jia, X.; Li, Y.; Liang, D.; Wei, Y. *Macromolecules* **2010**, *43*, 4314–4323.

(14) Luzon, M.; Boyer, C.; Peinado, C.; Corrales, T.; Whittaker, M.; Tal, L.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2783–2792.

(15) (a) Li, W.; Zhang, A.; Feldman, K.; Walde, P.; Schlüter, A. D. *Macromolecules* **2008**, *41*, 3659–3667. (b) Li, W.; Wu, D.; Schlüter, A. D.; Zhang, A. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4530–4534. (c) Li, W.; Zhang, A. *Sci. China Chem.* **2010**, *53*, 2509–2519.

(16) (a) Junk, M. J. N.; Li, W.; Schlüter, A. D.; Wegner, G.; Spiess, H. W.; Zhang, A.; Hinderberger, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 5683–5687. (b) Junk, M. J. N.; Li, W.; Schlüter, A. D.; Wegner, G.; Spiess, H. W.; Zhang, A.; Hinderberger, D. *J. Am. Chem. Soc.* **2011**, *133*, 10832–10838.

(17) (a) Hu, J.; Liu, S. *Macromolecules* **2010**, *43*, 8315–8330. (b) Liu, X.-Y.; Cheng, F.; Liu, Y.; Li, W.-G.; Chen, Y.; Pan, H.; Liu, H.-J. *J. Mater. Chem.* **2010**, *20*, 278–284. (c) Pietsch, C.; Schubert, U. S.; Hoogenboom, R. *Chem. Commun.* **2011**, *47*, 8750–8765.

(18) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319–2358.

(19) (a) Iwai, K.; Matsumura, Y.; Uchiyama, S.; de Silva, A. P. *J. Mater. Chem.* **2005**, *15*, 2796–2800. (b) Koopmans, C.; Ritter, H. *J. Am. Chem. Soc.* **2007**, *129*, 3502–3503. (c) Gota, C.; Okabe, K.; Funatsu, T.; Harada, Y.; Uchiyama, S. *J. Am. Chem. Soc.* **2009**, *131*, 2766–2767.

(20) (a) Pietsch, C.; Hoogenboom, R.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 5653–5656. (b) Pietsch, C.; Vollrath, A.; Hoogenboom, R.; Schubert, U. S. *Sensors* **2010**, *10*, 7979–7990.

(21) Precisely speaking, this transition temperature should be referred to as lower critical aggregation temperature (LCAT) because this term describes more precisely the effect observed by turbidity measurements (cloud point determinations). Though strictly speaking the term LCST is not proper in the present connection, it is nevertheless much more often used than LCAT; thus, we stick to it throughout the article.

(22) Bolisetty, S.; Schneider, C.; Polzer, F.; Ballauff, M.; Li, W.; Zhang, A.; Schlüter., A. D. *Macromolecules* **2009**, *42*, 7122–7128.

(23) Ballauff, M.; Likos, C. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 2998–3020.

(24) Li, W.; Zhang, A.; Chen, Y.; Feldman, K.; Wu, H.; Schluter, A. D. *Chem. Commun.* **2008**, 5948–5950.

(25) Lacroix, P. G.; Malfant, I.; Iftime, G.; Razus, A. C.; Nakatani, K.; Delaire, J. A. *Chem.—Eur. J.* **2000**, *6*, 2599–2608.