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Thermoresponsive Supramolecular Dendronized Polymers

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Abstract: Combining the concepts of supramolecular polymers and dendronized polymers provides the opportunity to create bulky polymers with easy structural modification and tunable properties. In the present work, a novel class of side-chain supramolecular dendronized polymethacrylates is prepared through the host–guest interaction. The host is a linear polymethacrylate (as the backbone) attached in each repeat unit with a β-cyclodextrin (β-CD) moiety, and the guest is constituted with three-fold branched oligoethylene glycol (OEG)-based first- (G1) and second-generation (G2) dendrons with an adamantyl group core. The host and guest interaction in aqueous solution leads to the formation of the supramolecular polymers, which is supported with ^{1}H NMR spectroscopy and dynamic light scattering measurements. The supramolecular formation was also examined at different host/guest ratios. The water solubility of hosts and guests increases upon supramolecular formation. The supramolecular polymers show good solubility in water at room temperature, but exhibit thermoresponsive behavior at elevated temperatures. Their thermoresponsiveness is thus investigated with UV/Vis and ^{1}H NMR spectroscopy, and compared with their counterparts formed from individual β-CD and the OEG dendritic guest. The effect of polymer concentration and molar ratio of host/guest was examined. It is found that the polar interior of the supramolecules contribute significantly to the thermally-induced phase transitions for the G1 polymer, but this effect is negligible for the G2 polymer. Based on the temperature-varied proton NMR spectra, it is found that the host–guest complex starts to decompose during the aggregation process upon heating to its dehydration temperature, and this decomposition is enhanced with an increase of solution temperature.

Keywords: cyclodextrins · dendrimers · host–guest systems · polymers · supramolecular chemistry

Introduction

Supramolecular polymers have received considerable interest during recent decades in areas such as chemistry and materials science.[1] Different types of supramolecular polymers, including main-chain[2] and side-chain supramolecular polymers,[3] have been reported, and these polymers possess dynamic and living characteristics, thus providing an alternative and easier route to tune the polymer structures compared with their covalent counterparts. Up to now, much emphasis has been put on the control of supramolecular morphologies through structural design. Recently, there has been increasing interest in developing supramolecular polymers with functions,[4] such as self-healable plastics,[5] photovoltaic materials,[6] and hydrogels for drug delivery.[7,8] Supramolecular polymers are constituted from monomeric units by means of highly directional non-covalent forces, such as metal coordination,[6] hydrogen-bonding,[9] as well as π–π,[10] ionic,[11] or hydrophobic interactions.[12] Among these, one prominent example, which is based on the princi-

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ple of hydrophobic interactions, is the inclusion complexation between the host cyclodextrins (CDs) and the guest hydrophobic moieties of appropriate size.[13] CDs are cyclic oligosaccharides composed of six, seven, or eight D(+)-glucose units (named α-, β-, or γ-CD, respectively), and the molecular geometry affords to them a hydrophobic inner cavity of different sizes.[14] Various molecules, fitted into the cavity size of CDs, can form supramolecular inclusion complexes with different binding constants,[15] and this binding difference is especially interesting in tuning the assembly by competition inclusion between CDs and guest molecules.[16] Threading of CDs by a linear polymer chain to form polyrotaxanes or polypseudorotaxanes has been intensively studied[13b] for supramolecular hydrogels[17] or bio-related applications.[18] Supramolecular inclusion polymers for stimuli-responsiveness, mainly based on a linear polymer architecture, have also been brought to attention recently.[19]

Dendronized polymers are a novel class of cylindrical polymers with branched dendrons pendent at each repeating unit of a linear polymer main-chain.[20] The structural characteristics of these polymers include high rigidity, easy functionalization, and more importantly, bulkiness of individual molecules having dimensions in the range of 3–7 nm.[21] Based on these attributes, dendronized polymers have drawn significant interest and have been utilized for DNA wrapping,[22] helix formation,[23] self-assembly,[24] catalytic supports,[25] nanomaterials,[26] and so on. These polymers are typically constructed through a covalent linkage between the polymer main-chain and the pendent dendrons, and are prepared using either the macromonomer[27] or attach-to route.[28] Despite the significant progress in the synthetic strategies, the tedious synthetic procedure remains a major drawback for this promising class of polymers. In contrast to the covalent congeners, supramolecular dendronized polymers (SDPs) combine the structural characteristics of covalent dendronized polymers and the structure variability of supramolecular polymers, thus forming a promising class of bulky supramolecular polymers. Recently, SDPs have received much attention though most are based on weak interactions, such as metal coordination[29] and acid–base interactions.[30]

Thermoresponsive polymers[31] are one of the most attractive stimuli-responsive polymers, and have shown promising applications in various areas.[32] These polymers possess a lower critical solution temperature (LCST) in aqueous solutions, and their chains start to dehydrate below this temperature, followed by chain collapse and then formation of mesoglobules or aggregates, which is a an entropy-driven association process of the polymer solute.[33] Up to now, most thermoresponsive polymers have had a linear architecture and are constructed through covalent linkages. To avoid the slow phase transition in cooling and the significant hysteresis caused by strong hydrogen bonding in polyacrylamides, oligoethylene glycol (OEG)-based comb-like (co)polymers[34] and dendrimers[35] were developed. These OEG-derivatives do not possess sites for strong hydrogen-bonding formation, and thus show small hysteresis. However, to achieve sharp and fast phase transitions in both heating and cooling processes with small hysteresis remains a challenge.

We recently reported a series of OEG-based first- (G1) to third-generation (G3) dendronized polymethacrylates, which show fast and sharp transitions upon heating and cooling with small hysteresis.[36] Their phase-transition temperatures are easily tunable in the range of 32–65 °C, and mostly dependent on polymer peripheral groups.[37] Furthermore, the dendronization architecture results in these polymers exhibiting dehydration of the interior part at a much higher temperature than that of the peripheral units,[38] and this heterogeneous dehydration may offer the possibility to fabricate molecular devices on the individual molecule level. To combine the structural advantages from both covalent dendronized polymers and supramolecular polymers, the present contribution describes a novel construction of thermoresponsive polymers through the supramolecular strategy using host and guest interactions (Figure 1). The host is a linear polymethacrylate (as the backbone) attached in each repeat unit with a β-cyclodextrin (β-CD) moiety, and the guest is three-fold branched oligoethylene glycol (OEG)-based G1 and G2 dendrons with an adamantyl (Ada) core. β-CD and adamantane are selected as both can form inclusion complexes in water with a high binding constant in the range of $1\times10^{5}\,\mathrm{M}^{-1}$. The inclusion complexation was investigated by ^{1}H NMR spectroscopy and dynamic light scattering measurements. The supramolecular polymers show good solubility in water at room temperature, but exhibit characteristic thermoresponsive behavior at elevated temperature. Their thermoresponsiveness is thus investigated using UV/Vis and ^{1}H NMR spectroscopy. The effect of polymer concentration and molar ratio of host/guest was examined. Temperature-varied ^{1}H NMR spectroscopy was utilized to investigate the thermally induced dehydration and dissociation process.

Abstract in Chinese:

集超分子聚合物与树枝化聚合物两概念于一体, 本工作报道以带有β-环糊精的线性聚合物为主体、核点带有金刚烷的烷氧醚树枝化基元为客体，通过主客体作用在水相中形成的超分子树枝化聚合物。对超分子形成过程及其结构采用核磁共振及激光光散射手段进行分析。这种超分子聚合物于室温下在水中有很好的溶解性，但随温度的升高，聚合物表现出优异的温度敏感行为。通过紫外/可见光谱等手段对其水溶液的温度诱导相转变过程进行了研究。结果表明超分子聚合物内核的高亲水性对侧基元尺寸较小的一代聚合物的温敏性有贡献，但对侧基元尺寸较大的二代聚合物基本没有贡献。同时发现温敏过程中的链段脱水会导致超分子聚合物的解缔合，而且解缔合程度随溶液温度的升高而进一步加强。但这种解缔合现象并没有对超分子聚合物的温度敏感行为产生明显影响。

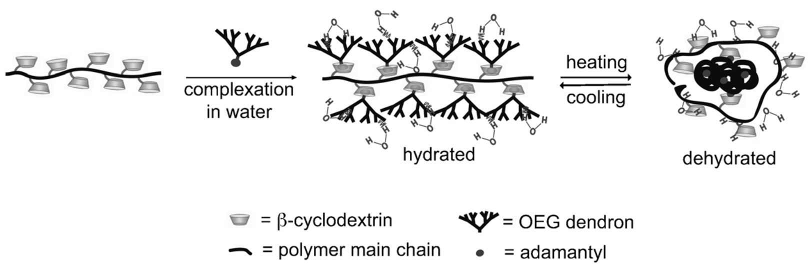


Figure 1. Illustration of side-chain supramolecular dendronized polymers (SDPs) prepared through host–guest inclusion and their collapse in water.

Results and Discussion

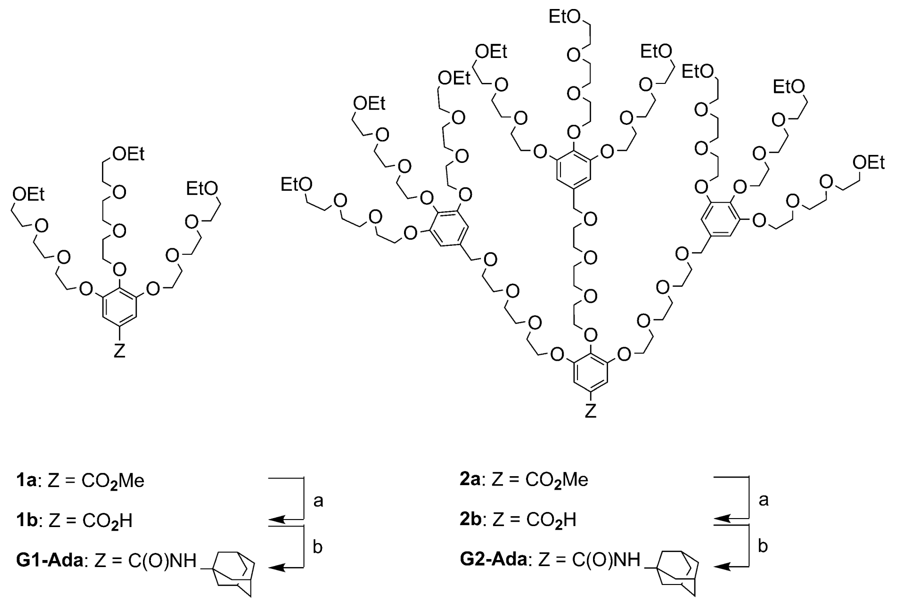
Host and Guest Synthesis

The OEG-based dendritic guests **G1-Ada** and **G2-Ada** were effectively synthesized in two steps, starting from their corresponding dendron methyl ester **1a** and **2a** (Scheme 1).[39] These esters were first saponified in the presence of LiOH into the corresponding dendritic acid **1b** and **2b**, which were then coupled with 1-adamantaneamine by EDC/HOBt strategy[40] to form the corresponding dendritic guests. The host polymer with the β-cyclodextrin (β-CD) moiety appended was obtained by directly polymerizing the CD-based monomer, similar to literature methods (Scheme 2).[41] Here, mono-6-deoxy-6-amino-β-CD (**3**) was treated with active ester **4** in a mixed solvent of *N*,*N*-dimethylformamide (DMF) and methanol to form the macromonomer **5**, which was subjected to free radical polymerization in highly concentrated DMF solutions and afforded linear CD polymer poly(**5**) with a well-defined structure. The high CD monomer concentration in polymerization media is a prerequisite for obtaining a high-molar-mass polymer.

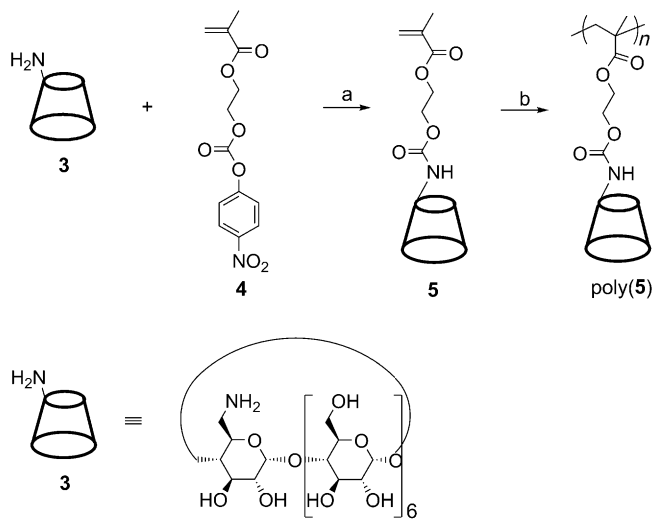
Supramolecular Dendronized Polymers (SDPs) by Host–Guest Inclusion Complexation

Mixing OEG-based dendron guests (**G1-Ada** or **G2-Ada**) with host polymer poly(**5**) in aqueous solution at room temperature formed clear solutions, where the strong host–guest inclusion complexation between β-CD and adamantane moieties is supposed to induce dendritic guests anchoring to the CD polymer, thus forming the side-chain SDPs (Figure 1, step one).

The first evidence for the complexation between OEG-based dendritic guests and the CD polymer was the change in the water solubility at room temperature. CD polymer poly(**5**) itself dissolves very slowly in water owing to its strong intermolecular hydrogen bonds, but dissolves quickly in the presence of **G1-Ada** or **G2-Ada**. This may be explained by the inclusion between the adamantane moiety from the guest and the CD moiety in the host polymer, leading to the CD polymer covered with water-soluble OEG dendrons thus, retarding intermolecular interactions of the CD polymer. Alternatively, the guest **G1-Ada** becomes more water-soluble in the presence of poly(**5**), which can be understood by the hydrophobic adamantane moiety being included inside the CD cavity with the hydrophilic OEG dendron remaining in the aqueous environment. The complexation of **G2-Ada** and poly(**5**) in aqueous solution to form supramolecular dendronized polymers was therefore examined by ^{1}H NMR spectroscopy, and the spectra are shown in Figure 2. For comparison, the proton NMR spectrum from the complexation of the same guest dendron (**G2-Ada**) with individual β-CD is also included. Upon addition of one equivalent of poly(**5**) (based on CD moieties) to the **G2-Ada** aqueous solution, all the proton signals from **G2-Ada** become broader and the corresponding signal heights decrease, with the methylene and methine proton signals from the adamantyl group more pronounced. The proton signals from the adamantyl group also



Scheme 1. Synthesis procedures for OEG-based dendritic guests **G1-Ada** and **G2-Ada**. Reagents and conditions: a) **1a** or **2a**, LiOH·H_2O, MeOH/H_2O, −5 to 25 °C, 12 h, (97 % and 75 % for **1b** and **2b**, respectively); b) **1b** or **2b**, 1-adamantaneamine, EDC, HOBt, TEA, DCM, −15–25 °C, overnight (56 % and 71 % for **G1-Ada** and **G2-Ada**, respectively).[39]



Scheme 2. Synthesis procedures for the host polymer poly(**5**). Reagents and conditions: a) **3**, **4**, DiPEA, DMF/MeOH, −15–25 °C, overnight, 53 %; b) **5**, AIBN, DMF, 60 °C, 12 h, 40 %.

shift downfield. These demonstrate that the adamantane moiety was included inside the CD cavity[42] and the dendrons were attached onto the host polymer to form SDPs. In contrast, for the complex formed from the guest dendron **G2-Ada** with individual β-CD, all the proton signals from both **G2-Ada** and β-CD were clearly shown and in sharp resolution, and only chemical shifts of the protons from adamantyl moieties shifted downfield (compare (c) with (a) in Figure 2). For example, the characteristic adamantyl proton signals at about $\delta = 1.50$ and 1.80–1.90 ppm were shifted downfield to $\delta = 1.69$ and 2.08–2.20 ppm, respectively. The signal broadness in spectrum (b) in comparison with (c) in Figure 2 is assigned to the macromolecular effect.

^1H NMR titration measurements were carried out to investigate the supramolecular formation in detail. The molar ratio of CD to adamantane moieties is between 0.2 and 1.5, and the typical spectra are summarized in Figure 3. When 0.2 equivalents of poly(**5**) (based on CD moiety) were initially added to the **G2-Ada** solution, the proton signals from the adamantyl group became broader and their intensity decreased, and proton signals from the OEG dendron also changed slightly. With successive addition of poly(**5**), all proton signals from **G2-Ada** gradually became broader, and the intensities decreased. When 0.8 equivalents of poly(**5**) were introduced, the signals from the aromatic ring (at $\delta =$ 6.98 ppm) and from the adamantyl group (at $\delta = 1.50$ and 1.90 ppm) almost disappeared. The signal intensity from other protons also decreased significantly. Further addition of poly(**5**) caused the ^1H NMR spectrum to change only slightly and tended to remain unchanged once the guest/host molar ratio reached 1. This phenomenon demonstrated that, with the addition of host polymer poly(**5**) to the **G2-Ada** aqueous solution, more and more guest molecules change from the free state to the polymeric state owing to the inclusion. When the guest/host molar ratio reaches 1, nearly all the guest molecules were complexed with CD polymer. One thing is necessary to address here: the signal at $\delta =$ 1.9 ppm from the adamantyl group is monomodal in all these cases, irrespective of the ratio of host and guest units, which suggests that the complexation is in a fast dynamic.[43]

Dynamic light scattering measurements were carried out to investigate the supramolecular formation from **G2-Ada** and poly(**5**). The hydrodynamic radius (Rh) value of free poly(**5**) in water was determined to be approximately 7 nm, while upon complexation with **G2-Ada**, it increased to approximately 12 nm (see Figure S2 in the Supporting Information for details). This indicates that the size of the polymer increased significantly after the attachment of dendrons onto its side chains.

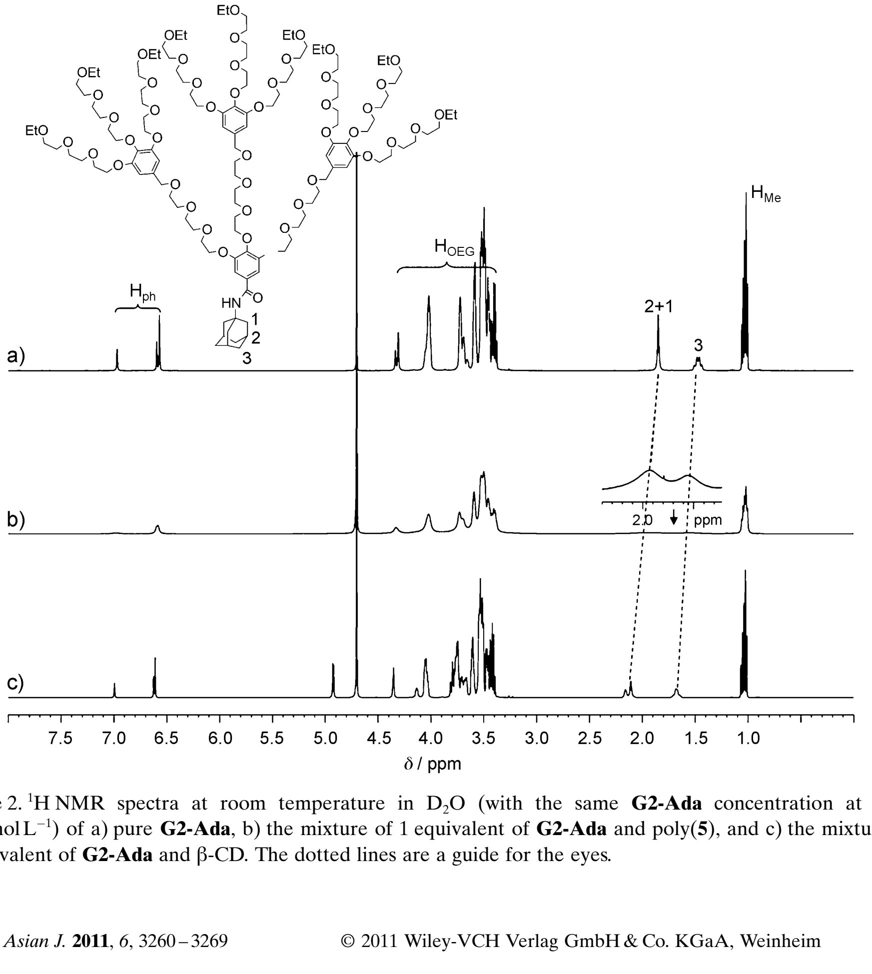


Figure 2. ^1H NMR spectra at room temperature in D_2O (with the same **G2-Ada** concentration at 1.6×10^{-2} mol L^{-1}) of a) pure **G2-Ada**, b) the mixture of 1 equivalent of **G2-Ada** and poly(**5**), and c) the mixture of 1 equivalent of **G2-Ada** and β-CD. The dotted lines are a guide for the eyes.

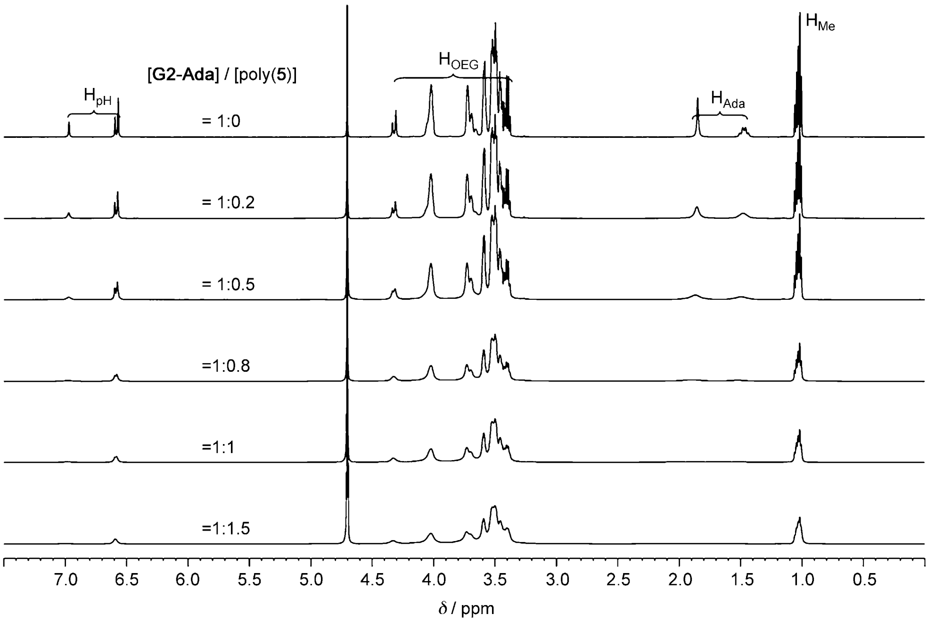


Figure 3. ^{1}H NMR spectra of complex from **G2-Ada** (at the same concentration of 1.6×10^{-2} mol L $^{-1}$) and poly(**5**) with different molar ratio (based on CD moieties).

Thermoresponsive Behavior of Supramolecular Dendronized Polymers

First- (**SPG1**) and second-generation (**SPG2**) supramolecular dendronized polymers formed from the CD polymer poly(**5**) with the corresponding **G1-Ada** and **G2-Ada** are water-soluble at room temperature, but show interesting thermoresponsive behavior at elevated temperature owing to the dehydration of the OEG units.[37] Interestingly, dendritic guests **G1-Ada** and **G2-Ada** themselves also show thermoresponsiveness. The thermoresponsive behavior of these dendritic guests and their corresponding supramolecular polymers was thus investigated by turbidity measurements using UV/Vis spectroscopy, and the typical turbidity curves are shown in Figure 4. From these curves the apparent LCST of **G1-Ada**, **G2-Ada**, **SPG1**, and **SPG2** were determined to be 28.2, 38.1, 52.7, and 34.4 °C, respectively. The phase transition temperature of **SPG2** is especially attractive as it is close to the body's temperature. The phase transition curves demonstrate that the phase transitions are quite fast and sharp, and the hysteresis is very small (around 1 °C). These thermoresponsive behaviors are quite similar to the corresponding OEG-based first- (PG1) and second-generation (PG2) dendronized polymers formed through covalent linkages.[36] Interestingly, the LCST of **SPG1** is much higher than that of the corresponding dendritic guest, while the LCST of **SPG2** is a little lower than that of the corresponding dendritic guest. Furthermore, the phase transitions of **SPG1** and **SPG2** are sharper than their corresponding dendritic guests alone. These results demonstrate that: (1) the hydrophobic adamantyl moiety within **G1-Ada** contributes more significantly to its thermally-induced phase transitions (both heating and cooling) than the case for **G2-Ada**. The reason arises from the smaller dendron size of **G1-Ada** than that of **G2-Ada**, thus the hydrophobic adamantyl moiety occupies a higher percentage in the dendron, which leads to the decrease of the overall hydrophobicity of the guest molecule; (2) the polar interior (CD moieties) of the supramolecular polymers contributes significantly to the thermally-induced phase transitions for **SPG1**, but for **SPG2**, this effect is negligible. As proven in our previous report, the interior part of dendronized polymers shows less contribution to the polymer's thermoresponsiveness when OEG outer units are dense enough to cover the polymer periphery.[37] The result here suggests that the size of the second generation OEG dendron is big enough to cover the surface of the individual supramolecular polymer, which shields the hydrophilic CD moieties; (3) the sharper phase transitions of supramolecular polymers than that of their corresponding guest molecules should arise from the macromolecular crowding effect, which facilitates the dehydration and aggregation kinetics of OEG units. Another factor for the fast phase transitions is the absence of strong hydrogen bonding in these OEG-based polymer systems when compared to the conventional thermoresponsive polymer poly(*N*-isopropylacrylamide). These have also been demonstrated in the covalent **PG1** and **PG2**.[44]

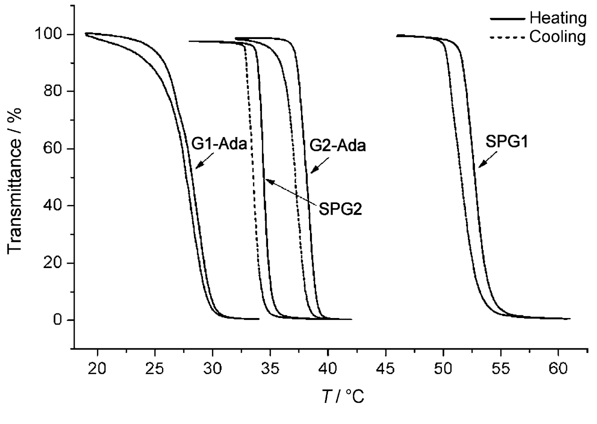


Figure 4. Plots of transmittance versus temperature for 0.25 wt % aqueous solution **G1-Ada**, **G2-Ada**, **SPG1**, and **SPG2**.

The effects of concentration and molar ratio of host/guest on the thermoresponsiveness of SDPs were further examined. For comparison, supramolecular complex (**SM2**), formed from **G2-Ada** and individual β-CD, was also investigated. The LCSTs from one equivalent of **G2-Ada** with poly(**5**) or β-CD at different concentrations were measured, and the results are plotted in Figure 5a. With a concentration decrease from 1 wt% to 0.05 wt%, the LCST for **SPG2** increases from 33.3 °C to 36.6 °C ($\Delta = 3.3$ °C), while the LCST for **SM2** increased from 40.7 °C to 51.2 °C ($\Delta = 10.5$ °C), hence the latter case shows a much higher concentration dependence. This result suggests that the LCST of supramolecular polymers is less sensitive to the solution concentration when compared with the corresponding supramolecular monomers or derivatives. This observation is also in good agreement with thermoresponsive dendronized polymers formed through covalent linkages.[36] The effect of the host/guest molar ratio (at the same concentration of **G2-Ada**) on the LCST was investigated, and the results are shown in Figure 5b. For **SPG2**, with an increase of host/guest molar ratio, the LCST decreased first, and then tended to remain unchanged at about 34 °C when the host/guest molar ratio reached 1. Even when the host/guest molar ratio exceeded 1, existence of uncomplexed hydrophilic CD units showed negligible influence on the LCST. However, for **SM2**, the values of LCST increased with the host/guest molar ratio, and this tendency was kept when the host/guest molar ratio exceeded 1. This result demonstrates that the supramolecular polymer shows a different entropy-driven association process than its dendritic guest.

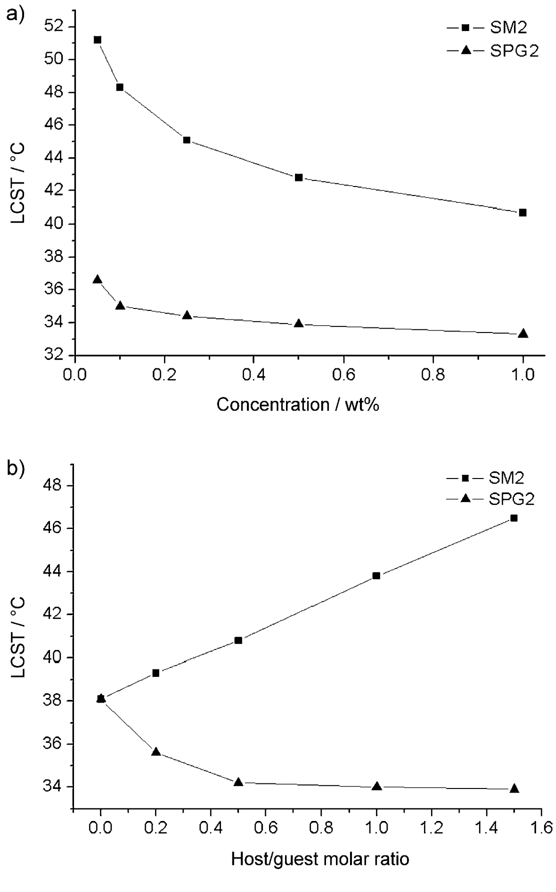


Figure 5. LCST dependence of **SPG2** and **SM2** on concentrations a) and host/guest molar ratio b) ([**G2-Ada**] $= 9.7 \times 10^{-4}$ mol L $^{-1}$).

Temperature dependent ^{1}H NMR spectroscopy was utilized to investigate the thermally induced dehydration process of the supramolecular dendronized polymers in aqueous solution. ^{1}H NMR spectra of **SPG2**, formed from equal equivalents of **G2-Ada** and poly(**5**), were recorded at 21 °C, 36 °C, and 45 °C (Figure 6). As expected, when the solution temperature was increased to 36 °C, which is slightly above the phase transition temperature (34.4 °C), proton signals from OEG units ($\delta = 3.2$–4.5 ppm) became broader and their intensities decreased because of the dehydration. With a further increase of temperature (such as for 45 °C), these signal intensities decreased even more. The exception is that the signal intensities from the adamantyl group slightly increased (see inset within Figure 6); this indicates the increase in mobility of the adamantane moieties with solution temperature. This mobility increase suggests adamantane moieties may (partially) escape from the cavity of CD in the supramolecular polymer when the solution temperature increases, thus causing decomplexation.[45]

Decomplexation Related to Thermally Induced Chain Collapse

Based on the temperature dependent ^{1}H NMR spectra discussed above, supramolecular dendronized polymers start to decompose as the temperature approaches their LCSTs. Several factors may be responsible for this dissociation: (1) the inclusion constant of adamantane into β-CD decreases with an increase in the solution temperature,[19f] therefore, the inclusion complex becomes less stable at high temperature; (2) the hydrophobic domains formed from dehydration of OEG chains compete with the hydrophobic adamantane to form an inclusion complex with CD; (3) the hydrophobic domains formed from dehydration of OEG chains compete against the hydrophobic cavity within CD to take the hydrophobic adamantane; (4) aggregation of the hydrophobic do-

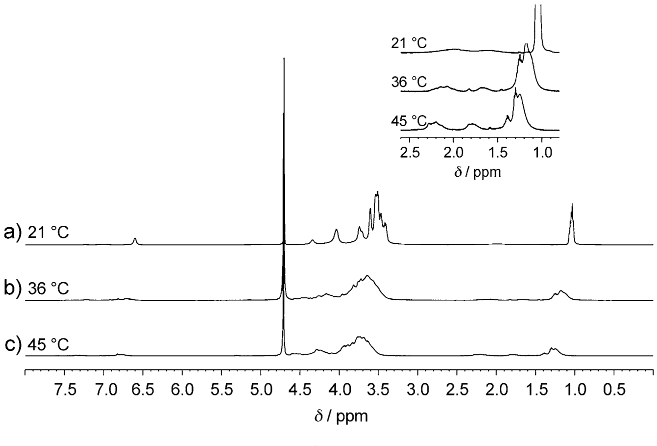


Figure 6. Temperature-dependent ^{1}H NMR spectra of **SPG2**: a) 21 °C, b) 36 °C, c) 45 °C. The inset shows partial spectrum in the range of $\delta = 1.0$–2.5 ppm.

mains formed from the dehydrated OEG units causes steric hindrance, which prevent the guests from inclusion.[45a] In order to examine whether any or all of these possibilities really contribute to the dissociation, proton NMR spectroscopy is a convenient tool. However, owing to the inherent broad NMR signals from supramolecular polymers, it is not easy to accurately monitor and investigate the decomplexation process involved in thermally-induced phase transitions on the polymer level. Instead, we choose the supramolecular complex (**SM2**) from **G2-Ada** and β-CD as the model system, and the typical spectra in the range of 1.0–2.7 ppm are shown in Figure 7a (for full spectra see Figure S3 in the Supporting Information). At room temperature (21 °C), proton signals from the supramolecular complex are time-averaged and well-resolved, because the complexation kinetics are a rapid exchange process relative to the NMR time scale. However, as the solution temperature is increased to 36 °C, which correlates to the temperature for the OEG chain collapse[44] and is just below the phase transition temperature of the inclusion complex (39 °C), a series of new split proton signals appeared. For example, characteristic proton signals from adamantane, peripheral methyl, and the aromatic ring split into two groups, respectively. This tendency is enhanced when the solution temperature is further increased. The proton signal splitting suggests the complexation kinetics become a slow exchange process relative to the NMR timescale once dehydration occurs. By comparison with the spectra from native **G2-Ada** solution at the same temperature (Figure S4 in the Supporting Information), these new split proton signals come from the decomplexed (free) **G2-Ada**. By comparing the signal intensities, the percentage of decomplexed species can be roughly calculated, and the results are plotted in Figure 7b.[46] For the case of 1 wt % aqueous solution of **SM2**, the decomplexation starts around 36 °C with a percentage of decomplexed species around 6 %, which increased to 87 % at 50 °C. As increasing the concentration of the inclusion complex reduces its phase transition temperature slightly, a high concentration solution (6 wt %) of **SM2** is used for comparison (Figure 7b). It shows a similar decomplexation tendency as the 1 wt % case, but the dissociation starts slightly earlier (34 °C) as expected. In conclusion, the supramolecular complex between **G2-Ada** and β-CD decomplexes when the solution temperature increases to the point at which OEG units just start to dehydrate, forming the hydrophobic micro-domains. The percentage of decomplexed species increases linearly with temperature, and at a high temperature such as 50 °C, the majority of **G2-Ada** in the system becomes uncomplexed. This linear increase surprisingly suggests the phase transition following the aggregation does not contribute significantly to the dissociation. As for the case reported by Yamaguchi and co-workers,[45a] the decrease of binding constant between the host and the guest, together with the steric hindrance formed from the dehydrated hydrophobic domains are main factors responsible for the dissociation. Based on the above observation, we can conclude that increase of SDP solution temperature shows a dual effect of favoring the dissociation of dendrons and inducing the aggregation of free dendrons within loops of the main chains (Figure 1, step two). Similar observations have also been reported extensively for the supramolecular polymers formed by electrostatic interactions.[11]

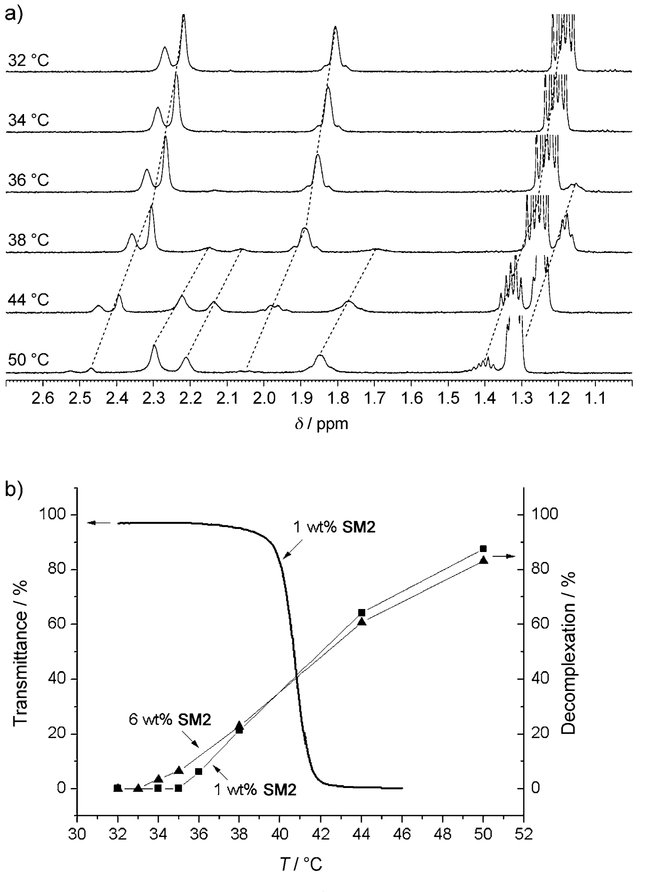


Figure 7. a) Temperature-dependent ^{1}H NMR spectra of 1 wt % aqueous solution of **SM2**. The dotted lines are a guide for the eyes. b) Plots of transmittance and dissociation percentage versus temperature for 1 wt % and 6 wt % aqueous solutions of **SM2** (the solid lines between the plots are a guide for the eyes).

Conclusions

In summary, supramolecular dendronized polymers were prepared by host–guest inclusion complexation in aqueous solutions between OEG-based dendritic guests and β-CD decorated polymers. Both these dendritic guests and the corresponding supramolecular polymers are water-soluble at room temperature, but show thermoresponsive behavior in water. The supramolecular polymers show much sharper phase transitions with smaller hysteresis than the dendritic guests alone; the phase transition temperatures from the former show less dependence on the guest/host ratios and the concentrations than those from the latter. All these arise from a positive macromolecular effect. Temperature varied ^{1}H NMR spectroscopy shows that the supramolecular polymers start to decompose upon their chain dehydration (just below the phase transition temperature), and this tendency enhances with an increase of solution temperature. Thus, increase of SDP solution temperature can show a dual effect of favoring the dissociation of dendrons and inducing the aggregation of free dendrons within loops of the main chains. With the supramolecular complex (**SM2**), formed from **G2-Ada** and β-CD as the model, the decomplexation process is followed and surprisingly, it is observed that this dissociation process is independent of the aggregation induced by the dehydration. Interestingly, this dissociation does not contribute significantly to the thermoresponsive behavior. This work provides a novel strategy to fabricate thermoresponsive bulky polymers with easy structural variability but with less synthetic effort, which would find applications in developing stimuli-responsive biomaterials and sensors.

Experimental Section

Materials

OEG-based dendrons **1a** and **2a** were synthesized according to the previous reports.[37] Mono-6-deoxy-6-amino-β-CD (**3**) was prepared according to the literature method.[47] 2-(4-Nitro-phenoxycarbonyloxy) ethyl methacrylate (**4**) was synthesized directly from 2-hydroxyethyl methacrylate and 4-nitrophenyl chloroformate in the presence of triethylamine (TEA).[48] Azobisisobutyronitrile (AIBN) was recrystallized from methanol. TEA was dried over NaOH pellets. Tetrahydrofuran (THF) was refluxed over lithium aluminium hydride (LAH) and dichloromethane (DCM) was distilled from CaH_2 for drying. Pure water was redistilled. Other reagents and solvents were purchased at reagent grade and used without further purification.

Instrumentation and Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 500 (^{1}H: 500 MHz; ^{13}C: 125 MHz) spectrometer. High resolution MALDI-TOF-MS analyses were performed on IonSpec Ultra instruments. Gel permeation chromatography (GPC) measurements were carried out on a Water GPC e2695 instrument with 3 column set (Styragel HR3+HR4+HR5) equipped with refractive index detector (Waters 2414) and DMF (containing 1 gL^{-1} LiBr) as eluent at 45°C. UV/Vis turbidity measurements were carried out for the lower critical solution temperature (LCST) determination on a PE UV/Vis spectrophotometer Lambda 35 equipped with a thermostatically regulated bath. Aqueous polymer solutions were placed in the spectrophotometer (pathlength: 1 cm) and heated or cooled at a rate of 0.2 °C min^{-1}. The absorptions of the solution at $\lambda = 500$ nm were recorded every five seconds. The LCST is determined as the temperature at which the transmittance at $\lambda = 500$ nm had reached 50% of its initial value. Dynamic light scattering (DLS) measurements were performed on an ALV/DLS/SLS-5022F spectrometer equipped with a multi-τ digital time correlation (ALV5000) and a cylindrical 22 mW He–Ne laser ($\lambda_0 = 632$ nm, UNIPHASE) as the light source.

General Procedure for Saponification of Methyl Ester by LiOH (A)

$LiOH{\cdot}H_2O$ was added into a solution of methyl ester in a mixed solvent of methanol and water (5:1, v/v) at −5°C with stirring, and then the reaction temperature was allowed to rise to room temperature. After stirring for 6 h, the solvents were evaporated in vacuo at room temperature, and the residue was dissolved with DCM. The pH value of the solution was adjusted carefully to around 5–6 with 10% $KHSO_4$ aqueous solution. The organic phase was washed with brine. All aqueous phase was triply extracted with DCM. The combined organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated in vacuo. Purification by column chromatography afforded the corresponding acid.

General Procedure for Amide Coupling with EDC/HOBt (B)

EDC was added into a solution of the acid, TEA, and HOBt in dry DCM at −15°C. After the mixture became a clear solution, 1-adamantaneamine in DCM was dropped into the solution at −15°C, and the mixture was allowed to rise to room temperature and stirred overnight. The mixture was washed successively with $NaHCO_3$ and brine, and all aqueous phases were triply extracted with DCM. The combined organic phases were dried over $MgSO_4$. After filtration, the solvent was evaporated under vacuum. Purification with column chromatography afforded the product.

3,4,5-Tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzoic acid (1b)

According to general procedure A, from $LiOH{\cdot}H_2O$ (1.30 g, 30.98 mmol) and compound **1a** (2.0 g, 3.01 mmol) in MeOH (40 mL) and H_2O (10 mL), **1b** was yielded as a colorless oil (1.9 g, 97%). ^{1}H NMR (CD_2Cl_2): $\delta = 1.13$–1.16 (m, 9H; CH_3), 3.46–3.48 (m, 6H; CH_2), 3.53–3.68 (m, 24H; CH_2), 3.71–3.79 (t, 2H; CH_2), 3.85–3.87 (m, 4H, CH_2), 4.16–4.21 (m, 6H; CH2), 7.32 ppm (s, 2H; CH). ^{13}C NMR (CD_2Cl_2): $\delta = 15.04$, 15.10, 61.71, 66.55, 68.99, 69.74, 69.96, 70.42, 70.62, 70.68, 70.75, 70.88, 72.60, 109.23, 124.59, 143.05, 152.47, 169.81 ppm. HR-MS: m/z calcd. for $C_{32}H_{56}O_{14}$ $[M+Na]^+$ 687.37; found 687.3572.

1-Adamantyl 3,4,5-tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzamide (G1-Ada)

According to general procedure B, from **1b** (0.50 g, 0.77 mmol), 1-adamantaneamine (0.24 g, 1.59 mmol), TEA (0.39 g, 3.85 mmol), EDC (0.22 g, 1.15 mmol), and HOBt (0.16 g, 1.18 mmol) in DCM (20 mL), **G1-Ada** was yielded as a colorless oil (0.35 g, 56%). ^{1}H NMR ($CDCl_3$): $\delta =$ 1.19–1.22 (m, 9H, CH_3), 1.68–1.73 (m, 6H, 3CH_2 in adamantane), 2.11 (br, 9H, 3CH_2 and 3CH in adamantane), 3.50–3.54 (m, 6H, CH_2), 3.57–3.73 (m, 24H, CH_2), 3.78–3.86 (m, 6H, CH_2), 4.17–4.21 (m, 6H, CH_2), 5.80 (s, 1H, NH), 6.98 ppm (s, 2H, CH). ^{13}C NMR ($CDCl_3$): $\delta = 15.14$, 29.48, 36.38, 41.58, 52.33, 66.62, 69.09, 69.72, 69.79, 70.49, 70.59, 70.62, 70.64, 70.73, 72.34, 107.08, 131.32, 141.16, 152.37, 166.17 ppm. HR-MS: m/z calcd. for $C_{41}H_{69}NO_{13}$ $[M+Na]^+$ 806.48; found 806.5306.

3,4,5-Tris(2-(2-(2-(3,4,5-tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyloxy)ethoxy) ethoxy)ethoxy)benzoic acid (2b)

According to general procedure A, from $LiOH{\cdot}H_2O$ (0.70 g, 16.68 mmol) and compound **2a** (2.0 g, 0.82 mmol) in MeOH (40 mL) and H_2O (10 mL), **2b** was yielded as colorless oil (1.5 g, 75%). ^{1}H and ^{13}C NMR spectra and HR-MS data are the same as previously reported.[37]

1-Adamantyl 3,4,5-tris(2-(2-(2-(3,4,5-tris(2-(2-(2-ethoxyethoxy)ethoxy) ethoxy) benzyloxy)ethoxy)ethoxy)ethoxy)benzamide (G2-Ada)

According to general procedure B, from **2b** (0.40 g, 0.17 mmol), 1-adamantaneamine (0.05 g, 0.33 mmol), TEA (0.10 g, 1.00 mmol), EDC (0.06 g, 0.31 mmol), and HOBt (0.03 g, 0.22 mmol) in DCM (10 mL), **G2-Ada** was yielded as a colorless oil (0.30 g, 71%). ^{1}H NMR ($CDCl_3$): $\delta =$ 1.21–1.24 (m, 27H, CH_3), 1.68–1.74 (m, 6H, 3CH_2 in adamantane), 2.11 (br, 9H, 3CH_2 and 3CH in adamantane), 3.51–3.87 (m, 138H, CH_2), 4.12–4.22 (m, 24H, CH_2), 4.45 (s, 6H, CH_2), 5.81 (s, 1H, NH), 6.58 (s, 6H, CH), 7.00 ppm (s, 2H, CH). ^{13}C NMR ($CDCl_3$): $\delta = 15.15$, 29.48, 36.38, 41.57, 52.34, 66.62, 68.75, 69.04, 69.30, 69.71, 69.80, 70.47, 70.50, 70.63, 70.66, 70.71, 70.78, 72.27, 72.34, 73.22, 107.10, 131.37, 133.72, 137.69, 141.12, 152.37, 152.58, 166.12 ppm. HR-MS: m/z calcd. for $C_{128}H_{219}NO_{49}$ $[M+Na]^+$ 2577.47; found 2577.5908.

Compound 5

Compound **4** (0.26 g, 0.88 mmol) in DMF was dropped into the solution of **3** (0.5 g, 0.44 mmol) and diisopropylethylamine (DiPEA; 0.3 g, 2.32 mmol) in DMF (5 mL) and MeOH (0.5 mL) at −15°C. After stirring for 1 h, the mixture was allowed to rise to room temperature and stirred overnight. Precipitation in diethyl ether three times yielded β-CD monomer **5** as a slightly yellow powder (0.3 g, 53%). ^{1}H NMR (D_2O): $\delta = 1.95$ (s, 3H, CH_3), 2.80–2.85 (m, CH_2, 1H), 3.22–3.27 (m, CH_2, 1H), 3.45–3.96 (m, CH+CH_2, 40H), 4.09–4.43 (m, 4H, partly overlapped with β-CD protons), 4.96–4.98 (m, CH, 7H), 5.84 (s, 1H, CH), 6.11 ppm (s, 1H, CH). ^{13}C NMR ([D$_6$]DMSO): $\delta = 18.41$, 60.37, 62.17, 63.67, 72.50, 72.62, 72.87, 73.43, 73.51, 81.98, 102.40, 126.42, 136.12, 156.54, 166.92 ppm. HR-MS: m/z calcd. for $C_{49}H_{79}NO_{38}$ $[M+Na]^+$ 1312.43; found 1312.4956.

Poly(5)

Monomer **5** (0.5 g) and AIBN (2.5 mg) were dissolved in DMF (0.4 mL) in a Schlenk tube. The solution was thoroughly deoxygenated by several freeze—pump–thaw cycles and then stirred at 60 °C for 16 h. After cooling to RT, the polymer was dissolved in water and dialyzed against deionized water (MWCO: 8000–10000) for three days. After evaporation of water in vacuo, the title polymer was yielded as a colorless solid (0.2 g, 40%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 3.28$–3.95 (m), 4.85 (br, CH_2), 4.48 (br, CH_2), 5.73 (br).

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[39] Abbreviations: Ada = adamantyl, AIBN = azobis(isobutyronitrile), CD = cyclodextrin, DCM = dichloromethane, DiPEA = diisopropylethylamine, DMF = *N*,*N*-dimethylformamide, EDC = 1-(3-dimethylaminopropyl)-3-ethylcarbo-diimide hydrochloride, G1 = first generation, G2 = second generation, HOBt = N-hydroxybenzotriazole, LAH = lithium aluminum hydride, LCST = lower critical solution temperature, OEG = oligoethylene glycol, SDP = supramolecular dendronized polymers, TEA = triethylamine.

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