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Synthesis of Neutral, Water-Soluble Oligo−Ethylene Glycol-Containing Dendronized Homo- and Copolymers of Generations 1, 1.5, 2, and 3

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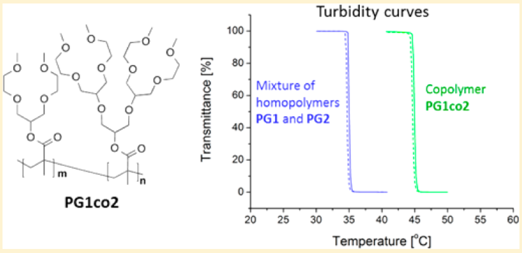
S *Supporting Information*

ABSTRACT: Oligo-ethylene glycol-containing dendronized monomers **MG1**, **MG1.5**, **MG2**, and **MG3** were synthesized in a particularly easy fashion on the gram scale involving only few steps. Their corresponding homopolymers (**PG1**, **PG1.5**, **PG2**, and **PG3**) and copolymers (**PG1*co*2**, **PG1*co*3**, and **PG2*co*3**) were synthesized via free radical polymerization. All the polymers are soluble in water and also in organic solvents such as DCM, $CHCl_3$, 1,4-dioxolane, DMF, and DMSO. Their glass transition temperatures (T_g) are in the range -68 °C $< T_g < -48$ °C and thus rather low. All polymers show thermoresponsive behavior which was investigated by turbidity measurements. Interestingly, a 1:1 mixture of homopolymers **PG1** and **PG2** behaves identical with **PG1** alone, while the collapse curve of copolymer **PG1*co*2** is almost superimposable with that of **PG2** alone. Thus, in the former case **PG1** dominates the thermoresponsive behavior while in the latter this is done by the G2-dendrons in the copolymer. Finally, the polymer chains were visualized by AFM, confirming the rod-like behavior of these rigidified polymers.



INTRODUCTION

Dendronized polymers[1] (DPs) carry dendritic units (dendrons) at every repeat unit and by this have a tunable main chain cross-sectional radius.[2] This variable thickness is the key feature that makes them differ from common linear polymers. The dense substitution with dendrons not only increases the persistence length of the main chain[3] but also turns the main chain into an object with an "interior" and a "surface" including countless lateral functional groups on this "surface".[4] The reversibly swellable interior of low generation DPs provides these unusual macromolecules with a mode of responsivity that is absent in conventional polymers.[5] It potentially opens the way into applications based upon persistence lengths, which are tunable by the degree of swelling, but also offers novel transport options by translocation[6] of guest-loaded DPs through nanopores. The numerous functional groups, which are the terminal functional groups of the dendrons, have a radial probability distribution and do therefore not all reside on the "surface".[7] Those that happen to connect the macromolecule to the outside world determine the solubility behavior but also, e.g., the adhesion of DPs to solid substrates. This was used to immobilize enzymes on simple glass slide with the help of DPs.[8]

Most DPs are neutral and soluble in organic solvents. The working horses from our laboratory carry Boc-protected amine groups as the peripheral functional groups which can be easily converted into charged ammonium groups or carboxylates. In both cases the resulting DPs are water-soluble; thus, the charges shield the hydrophobic interior of the thick macromolecules against the aqueous environment, very much as it is known for micelles. Water-soluble polymers are attractive for many fields of application including construction, agriculture, and pharmaceuticals.[9] There is a growing demand for nontoxic and biocompatible water-soluble polymers which needs to be served by providing cheap, robust and synthetically scalable solutions. Noncharged polymers are preferred because they do not cause problems with cell lysis and also do not normally have a complex aggregation behavior. Oligoethylene glycol (OEG) and its variants proved to be valuable in this regard. Attachment of OEG groups of different compositions is an often used strategy to render otherwise hydrophobic polymers water-soluble.[10] There are even a few DPs, whose entire branch work or part of it is based on OEG units.[11] Also these polymers are water-soluble and furthermore show thermoresponsivity.[12] Most DPs are homopolymers even though an increasing number of blockcopolymers[13] and particularly alternating

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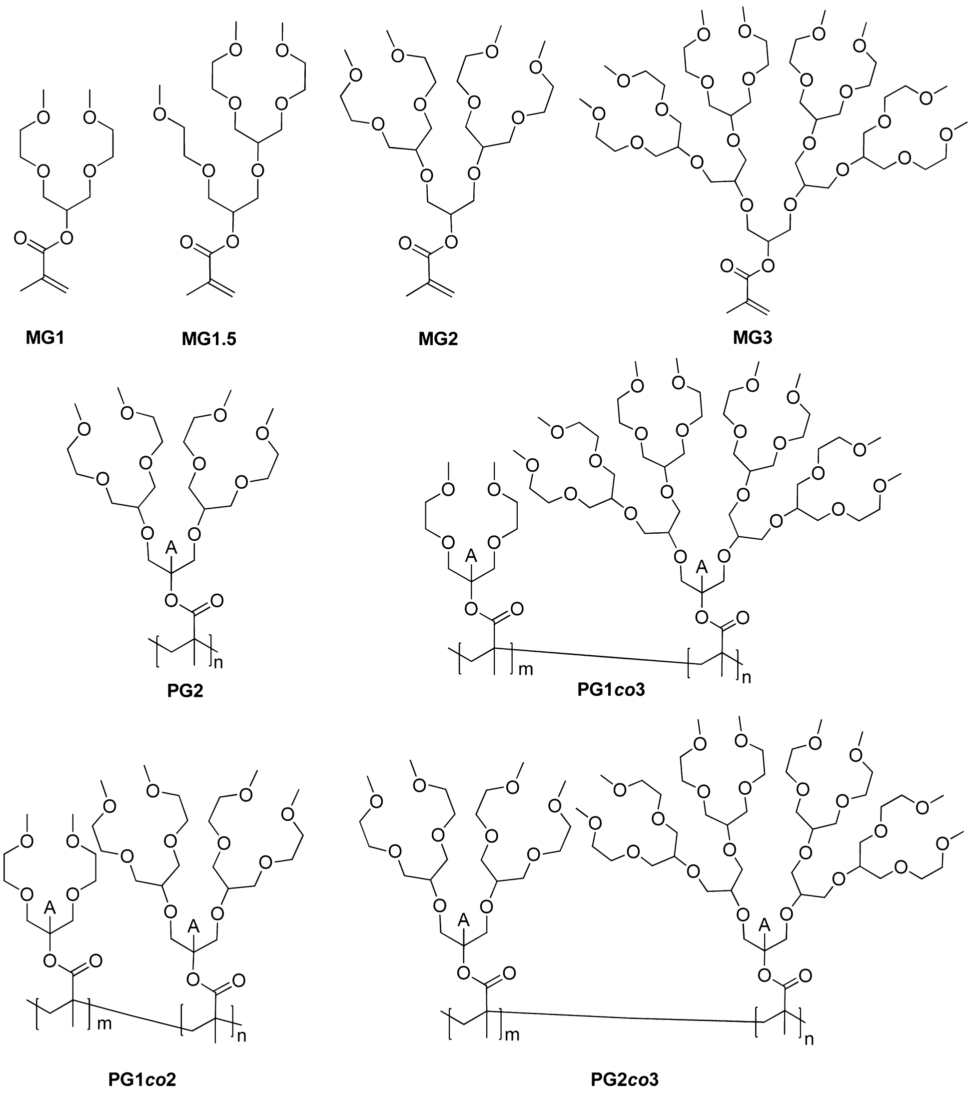


Figure 1. Chemical structures of all synthesized macromonomers and some of the new homo- and copolymers. The hydrogen atoms nearest to the main chains are denoted as A.

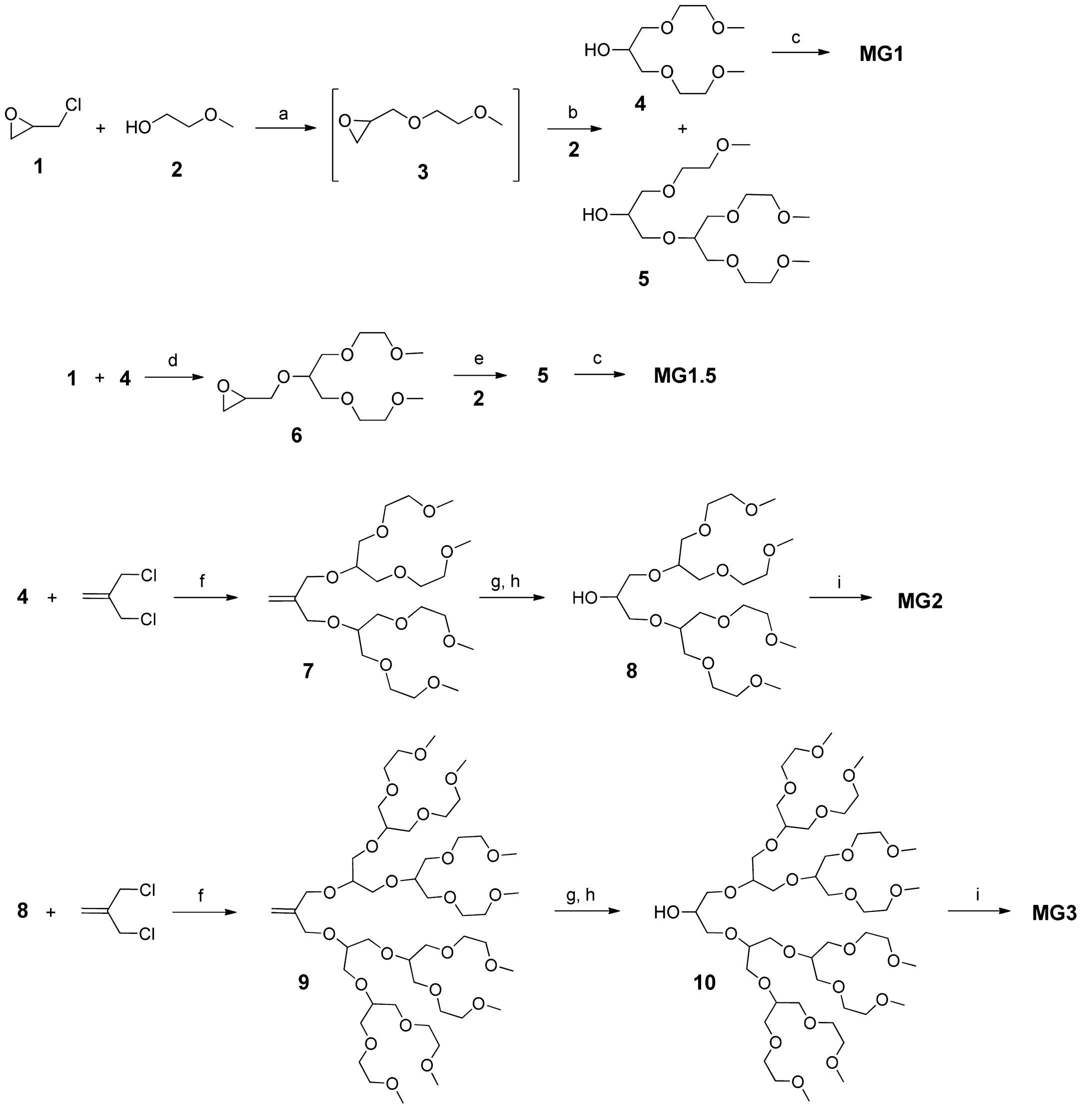
copolymers[14] have been reported. Recently there was also a report on a copolymer for which the authors claim a gradient structure.[14g] Furthermore, our laboratory has recently reported copolymerization parameters of the first generation OEG-based macromonomer **MG1** (Figure 1) with styrene and different acrylates.[15a]

We here report the syntheses of monomers **MG1**, **MG1.5**, **MG2**, and **MG3**, which are either modified to known procedures[15] under efficiency aspects (**MG1**, **MG1.5**) or new (**MG2** and **MG3**). These monomers were converted into their homopolymers through free radical polymerization and also used to create the random copolymers **PG1*co*2**, **PG1*co*3**, and **PG2*co*3**. Besides the more general motivation given above, there were two further concrete aspects that made us synthesizing these novel polymers. First, the rheological behavior of our prototype DPs points toward an interaction between these polymers in the melt that could be the result of interchain hydrogen bond formation and/or π,π-stacking.[16] To prevent this from happening, DPs of the kind **PG1**, **PG1.5**, **PG2**, and **PG3** are ideal candidates because they can obviously not undergo such interaction. Thus, these novel DPs are expected to provide us with a more comprehensive picture of the intrinsic nature of DPs as exemplified, e.g. by their behavior in melt. Second, DPs are "thick" and can be viewed as molecular cylinders. While the homopolymers typically have a smooth cylindrical "surface", copolymers using monomers with dendrons of different generation may open the possibility to create "corrugated cylinders" (Figure 1). We consider this an attractive option for expanding topology reminiscent of colloidal molecules.[17] Further, we report the lower critical solution temperatures (LCSTs) of both homo- and copolymers and address the question which dendron in a copolymer determines the turbidity behavior. Finally, we provide AFM tapping mode images of some of the polymers synthesized while adsorbed as single chain entities on mica substrate.

■ RESULTS AND DISCUSSION

The synthetic routes to the dendrons **4**, **5**, **8**, and **10** and the corresponding macromonomers **MG1**, **MG1.5**, **MG2**, and **MG3** are delineated in Scheme 1. All procedures are based on the cheap commercial starting materials epichlorohydrin **1** and ethylene glycol monomethylester **2**. **MG1** had been published earlier but was then synthesized in a one-pot procedure from **1** and **2** which—given the manifold possibilities for nucleophilic

Scheme 1. Reagents and Conditions[a]



[a]Key: (a) **1**:**2** = 1:1, NaH, THF, room temperature 16 h, then 65 °C, 4 h; (b) **3**:**1** = 1:2, NaOH/H_2O, 55 °C, overnight, **4** (53%), **5** (30%); (c) MAC, DMAP, TEA, DCM, 0−25 °C, overnight, 86%; (d) **1**:**4** = 1:1, NaH, THF, room temperature 16 h, then 65 °C, 4 h; (e) **6**:**2** = 1:2, NaOH/H_2O, 50 °C, overnight, 85%; (f) NaH, [15]-crown-6, KI, THF (yields for **7** and **9**, respectively: 84% and 85%); (g) O_3, DCM/MeOH, −78 °C; (h) $NaBH_4$, DCM/MeOH, −78 °C to room temperature (yields for **8** and **10**, respectively: 95% and 91%); (i) MAA, DMAP, DIEA, DCM, 0−40°C, overnight (yields for **MG2** and **MG3**, respectively: 82% and 85%).

ring-opening of **1** and the other epoxides involved—resulted in complex mixtures of products requiring nontrivial purifications leading to a low yield (22%).[15a] This is why we aimed at first performing the nucleophilic substitution of **2** selectively at the chlorinated carbon of **1**, before then reacting the obtained epoxide **3** further with **2**. Intermediate **3** was in fact obtained as the sole product when **1** and **2** were reacted with one another in a 1:1 ratio in THF using NaH as the base. Compound **3** could either be used as obtained or after distillation. Further reaction with **2** in a ratio **3**:**2** = 1:2 afforded a mixture of dendrons **4** and **5** whereby **4** was the main product (yields: **4**, 53%, **5**, 30%). The compounds were easily separated by distilling off the lighter product and subjecting the remainder to a simple chromatography. Both dendrons were converted with MAC into the monomers **MG1** and **MG1.5**, respectively, in high yields (>85%).

The incomplete dendron **5** used for the synthesis of **MG1.5** can either be obtained as the side product of the synthesis of **4** or be made selectively by the reaction of **1** with dendron **4** to furnish epoxide **6** which is then ring-opened with **2**.

With sufficient dendron **4** in hand, we started synthesis of **MG2** and **MG3** following a previously reported procedure which was developed for structurally related non-OEG-dendrons and proved to be very potent in our case.[18,19] First the commercially available methallyl dichloride (MDC) was etherified with **4**[20] at both chloromethyl groups to give the geminally disubstituted olefin **7**. This proved to be an efficient process when performed with NaH (1.5 equiv per OH) and catalytic amounts of KI, [15]crown-5, and [18]-crown-6 in dry THF. Flash chromatography afforded pure **7** in 84% on the 12.5 g scale. Ozonolysis with subsequent reductive work-up ($NaBH_4$) gave the second generation dendron **8** in excellent yield (95%). This dendron was either directly converted into

Table 1. Homo- and Copolymerizations: Conditions and Results

	polymerization conditions[a]						GPC[c]		
entry	monomer, amt (mmol)	[AIBN] (mol %)	solvent, amt (mL)	[monomer] (mol L^{-1})	time (h)	yield[b] (%)	M_n (kDa)	PDI	DP_n[d]
1	**MG1**, 0.60	0.1	toluene, 0.5	1.2	17	90	210	4.3	760
2	**MG1**, 0.60	0.1	toluene, 0.1	6.0	5, 17 (gel)	18	639	7.3	2310
3	**MG1**, 0.60	0.1	DMF, 0.1	6.0	17	97	118	4.1	425
4	**MG1**, 3.60	0.1	toluene, 3	1.2	17	80	280	2.8	1016
5	**MG1.5**, 0.40	0.2	toluene, 0.2	2.0	17	86	646	5.0	1584
6	**MG2**, 0.30	0.1	toluene, 0.05	6.0	5	86	144	3.4	266
7	**MG2**, 0.20	0.2	toluene, 0.1	2.0	17	93	219	3.5	406
8	**MG3**, 0.084	0.5	toluene, 0.05	1.68	17	44	66	2.6	62
9	**MG3**, 0.10	0.5	toluene, 0.05	2.0	17	37	57	2.3	54
10	**MG1**, 0.10 **MG2**, 0.10	0.2	toluene, 0.1	2.0	3	46	446	3.4	RUG1,[e] 751 RUG2, 442 (1.7:1)
11	**MG1**, 0.15 **MG2**, 0.15	0.1	toluene, 0.05	6.0	5	73	168	34	RUG1, 206 RUG2, 206 (1:1)
12	**MG1**, 0.10 **MG2**, 0.10	0.2	toluene, 0.1	2.0	17	86	133	8.1	RUG1, 163 RUG2, 163 (1:1)
13	**MG1**, 0.05 **MG3**, 0.05	0.2	toluene, 0.05	2.0	3	27	323	3.0	RUG1, 371 RUG3, 206 (1.8:1)
14	**MG1**, 0.10 **MG3**, 0.10	0.2	toluene, 0.1	2.0	17	75	147	4.1	RUG1, 182 RUG3, 91 (2:1)
15	**MG2**, 0.05 **MG3**, 0.05	0.2	toluene, 0.05	2.0	2	42	316	2.5	RUG2, 343 RUG3, 122 (2.8:1)
16	**MG2**, 0.10 **MG3**, 0.10	0.2	toluene, 0.1	2.0	17	75	317	4.9	RUG2, 295 RUG3, 147 (2:1)

[a] All polymerizations were carried out at 60 °C. [b] Yield: isolated by precipitation. [c] All GPC measurements were done with DMF (1% LiBr) as eluent at 45 °C. [d] DP_n = number-average degree of polymerization. [e] RUG1 stands for repeat unit with first generation dendron.

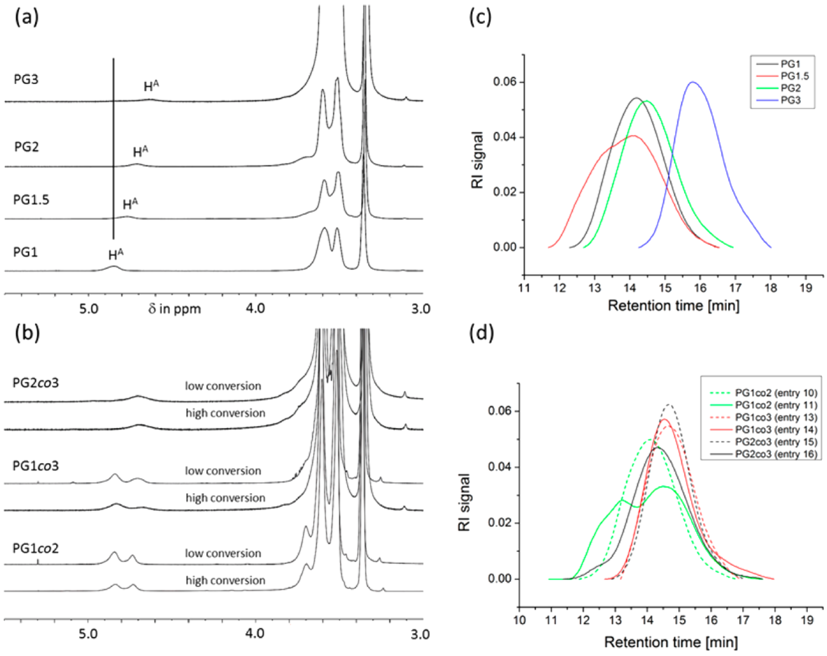


Figure 2. ^1H NMR spectra of the synthesized homo- (a) and copolymers (b) in $CDCl_3$ at 25 °C. The signals of the protons, HA, absorb between δ = 4.62 and 4.85 ppm and can be differentiated for the different generations except for **PG2*co*3**. GPC elution curves (DMF; at 45 °C) of the homo- (c) and copolymers (d) synthesized in this study. In part d for each copolymer, the curves at low (dashed line) and high conversion (full line) are given. The curves are largely monomodal except for **PG1.5** (red line in part c) and for **PG1*co*2** at high conversion. For a discussion, see text.

monomer **MG2** or subjected to the same etherification/ozonolysis procedure to first furnish the olefin **9** and then the third generation dendron **10**. Reaction of **10** with MAA gave monomer **MG3**. Monomers **MG2** and **MG3** were synthesized both on the 0.9 g-scale. The new monomers were obtained in high purity (see Supporting Information for spectra).

All polymerizations were performed on the 100 mg to 1 g scale of the respective monomers and with AIBN as initiator at 60 °C whereby all initial solutions were fully clear and transparent. The results are compiled in Table 1. Relevant NMR spectra and GPC elution curves are shown in Figure 2. Entries 1−9 of Table 1 refer to homopolymerizations and entries 10−16 to copolymerizations. The best conditions regarding achievable molar mass and prevention of gel formation were first explored with **MG1**. Concentration had a strong effect. As the comparison of entries 1 and 2 shows, polymerizations at 6 mol/L of monomer in toluene had to be quenched already after 5 h to prevent gel formation, while at 1.2 mol/L the polymerization could be run for 17 h without problems. When quenched after 5 h (at 6 mol/L) yields were poor and the material had an unattractively broad PDI = 7.3 (entry 2). This broad dispersity is likely due to branching, the onset of cross-linking. While there are no unequivocal results available yet, we consider it reasonable to assume that the α-CH positions (to oxygen) in the macromonomers and the corresponding polymers can undergo chain transfer and therefore can cause cross-linking. When switching to DMF as solvent, gel formation could be suppressed even at high conversion but the molar masses were relatively low. The largest scale polymerization of **MG1** (1 g) was therefore performed in toluene and at low monomer concentration (entry 4). Low monomer concentrations proved advantageous also in the other hompolymerizations (entries 5−9). Yields referring to precipitated and high vacuum-dried products were 80% and above except for **MG3**. At initiator concentrations of 0.1−0.2 mol % this monomer did not polymerize at all and at a concentration of 0.5 mol % yields could not be pushed beyond around 40%. As is known from other macromonomer polymerizations,[21] chain lengths decreases with increasing monomer mass, so also here. While for **MG1** and **MG1.5** chain lengths were about 1000 and higher (DP_n), for **MG2** they dropped to a few hundred to arrive at a few tens for **MG3**. The GPC elution curves of all polymers are monomodal (Figure 2c) except for **PG1.5**. The reason for the broadening in this case is not known. The proton NMR spectra of all homopolymers can be easily differentiated by the chemical shift of the proton nearest to the backbone, H^A (Figure 2a). The shifts gradually move upfield with increasing dendron generation (δ in ppm for **PG1**, 4.85; **PG1.5**, 4.77; **PG2**, 4.70; **PG3**, 4.64) (Figure 2a). This feature proved useful in case of the copolymers where the comonomer composition could be determined in two of the three cases by NMR integration.[22] All homopolymers gave satisfactory data from combustion analysis.

The copolymerizations were performed for the three possible combinations between **MG1**, **MG2** and **MG3** at molar feed ratios of 1:1. They were run to relatively low and high conversion in order to obtain qualitative information about the initial and the overall monomer incorporation. Co-monomer composition was determined by NMR integration for **PG1*co*2** and **PG1*co*3** and by weighing back recovered monomer for **PG2*co*3**. In the former case the chemical shift differences of the protons H^A of the homopolymers also showed in the copolymers, which allowed an easy analysis (Figure 2b). For **PG1*co*2**, the ratio of G1 to G2 repeat units was RUG1: RUG2 = 1.7:1 for the low conversion case (entry 10). Prolonging reaction time to 17 h (entry 12) or performing copolymerization at high concentration for 5 h (entry 11), resulted in high conversions and a ratio RUG1: RUG2 = 1:1 indicating that **MG1** has the higher reactivity than **MG2**. This is what one would expect based on the considerably lower molecular weight of **MG1** compared to **MG2**.[15a] For entry 11 these high conversions also resulted in a reproducible bimodal distribution (Figure 2d) and the very high PDI = 34. This bimodality and extreme distribution are likely due to **MG2** homopolymerization competing with regular copolymerization at high conversion. Additionally, because of the high concentration applied, chain transfer effects may compete with linear polymerization. For the monomer combination **MG1** and **MG3** the differences in incorporation rate do not seem to depend much on conversion which, given the even larger molecular weight differences between these monomers and **MG1** and **MG2** is unexpected. For the combination **MG2** and **MG3** the situation is back to "normal". While at lower conversion RUG2:RUG3 = 2.8:1 (entry 15) at higher conversion RUG2:RUG3 = 2:1 was found (entry 16). Despite the uncertainty with regard to the monomer combination **MG1** and **MG3**, taking all homo- and copolymerizations together, it is safe to conclude the reactivity relation: **MG1**> **MG2** > **MG3**.

All the polymers are soluble in water and in organic solvents such as DCM, $CHCl_3$, 1,4-dioxolane, DMF and DMSO. They are insoluble in *n*-hexane which provided an opportunity for purification by precipitation. All polymers are sticky solids in line with their rather low glass transition temperatures (T_g) which range from -68 °C < T_g < -48 °C (Table 2). For comparison, the T_g's of tri(oxyethylene) glycol-based polymethacrylates **PG1(OH)** and **PG2(OH)** are $T_g = -45$ °C and $T_g = -40$ °C, respectively, and of their methoxy-terminated counterparts $T_g < -80$ °C.[11a,d]

Table 2. Number Average Molecular Weight and Glass Transition Temperatures (T_g) of all Synthesized Homo- and Copolymers

polymer	M_n (kDa)	T_g (°C)
PG1	280	−48.5
PG1.5	200	−55.6
PG2	219	−68.5
PG3	67	−68.4
PG1*co*2	168	−57.3
PG1*co*3	147	−65.9
PG2*co*3	317	−68.4

Furthermore, the thermoresponsive behavior of the homo- and copolymers was investigated by turbidity measurements using a $\lambda = 500$ nm light source. In general the transitions are sharp and have negligible hysteresis (Figure 3; Δ(**PG1**) = 0.2, Δ(**PG2**) = 0.4) as is commonly observed for OEG-based DPs. Also the LCSTs increase with generation indicating the increasing hydrophilicity of the higher generation DPs. This increase is even more pronounced than in other DP cases. The fact that **PG3** does not follow this expectation (Figure 3a) is due to the rather short main chain of the sample (Table 1, entry 8), rendering its LCST to still be molar mass dependent. The turbidity curves of the copolymers deserve a few more comments. It was of interest to see whether the thermoresponsive behavior of a copolymer would be dominated by either of its two different dendrons. This investigation was started by measuring a 1:1 mixture of the homopolymers **PG1** and **PG2**. These mixtures turned out to behave identical with **PG1** alone, proving that both polymers act independently from one another. In contrast, the heating and cooling curves of **PG1*co*2** (Table 1, entry 10; Figure 3b) are almost superimposable with that of **PG2** (Figure 3a). Thus, the G2 dendrons of **PG1*co*2** are the ones that determine the behavior, suggesting in a first approximation that the G1 dendrons are

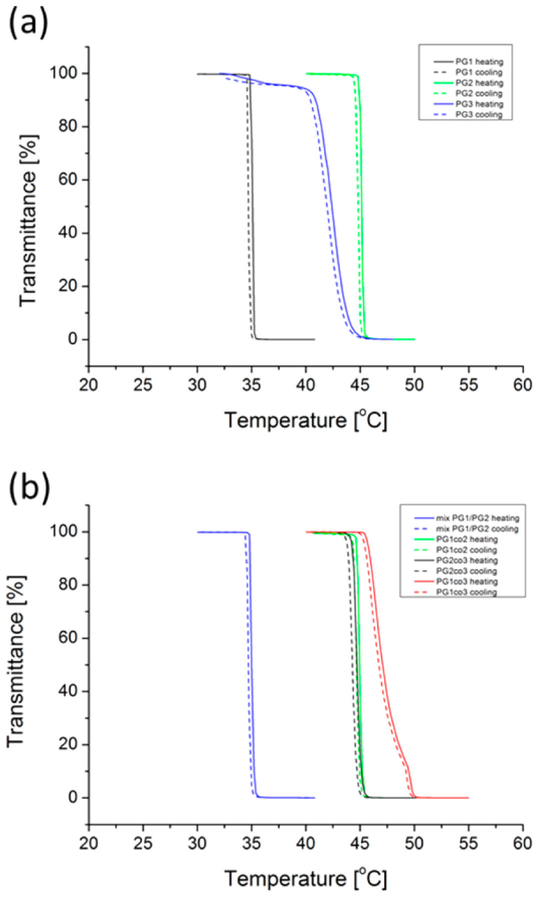


Figure 3. Determination of lower critical solution temperatures (LCST): Plots of transmittance vs temperature for 0.25 wt % aqueous solutions of (a) **PG1** (Table 1, entry 4), **PG2** (entry 7), and **PG3** (entry 9). (b) **PG1*co*2** (entry 10), **PG1*co*3** (entry 13), **PG2*co*3** (entry 15) and a 1:1 mixture of **PG1** (entry 4) and **PG2** (entry 7). Heating and cooling rate: 0.2 °C/min.

basically buried within the molecular structure. Looking into the other two copolymers, however, it becomes evident that the effect is not of general validity. The matter is further complicated by the fact that the **PG3** samples have short main chains only. On the basis of the observation with other thermoresponsive DPs we tentatively assume that $\mathrm{LCST}_{\mathbf{PG3}} > \mathrm{LCST}_{\mathbf{PG2}}$ in contrast to what Figure 3a suggests. This assumption is further supported by the transmittance curve of **PG1*co*3** which lies above 45 °C and thus well above $\mathrm{LCST}_{\mathbf{PG1}}$. Thus, also in this copolymer the larger dendron controls the thermoresponsive behavior. This is contrasted, however, by copolymer **PG2*co*3** which exhibits heating and cooling curves very similar to **PG2** suggesting that in this case, and contrary to the other two cases, the lower generation dendron largely controls the behavior. It seems that we have discovered a peculiar effect of molecular structure on thermoresponsivity, which requires more in depth studies on sequence and copolymer composition before a full understanding can be gained.

Finally, the DPs were adsorbed on mica and directly imaged by tapping mode AFM (Figures 4a–c). Single "well-behaved" chains are clearly visible for **PG2** (Figure 4a) and the coprepared chains of **PG1**, **PG2** and **PG3** (Figure 4b). **PG1** coils up into islands, while **PG2** chains are more extended. **PG3** chains appear as dots because of their short chain length. The image in Figure 4b can be used to determine height differences between the three samples which amount to roughly 0.5 nm between **PG1** and **PG2** and 0.7 nm between **PG2** and **PG3**. These height differences are smaller than those observed for our working horse DP series.[2] We refrain from providing h_{AFM} values for the different DPs because they strongly depend on exogenic factors such as humidity and, thus, vary from measurement to measurement. This can nicely be seen by comparing Figures 4a and 4b which both contain **PG2** chains. Interestingly, while the heights along the contours of the homopolymers were essentially constant, those of the copolymer **PG1*co*3** varies quite a bit. This can already be seen from the height profile provided in Figure 4c, where the

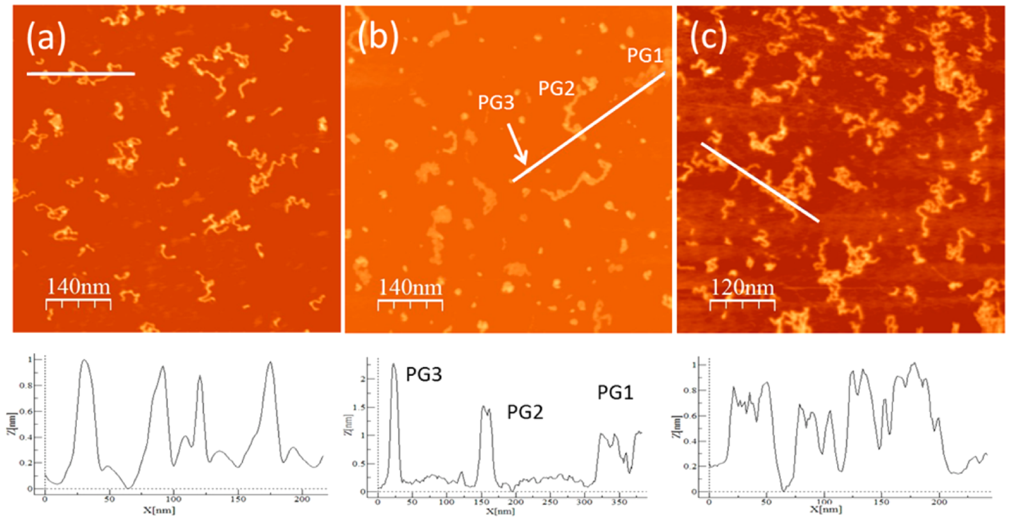


Figure 4. AFM height images of (a) **PG2** (Table 1, entry 7), (b) a mixture of **PG1** (Table 1, entry 4), **PG2** (Table 1, entry 7), and **PG3** (Table 1, entry 8), and (c)**PG1*co*3** (Table 1, entry 13) . Samples were prepared from DCM solution [2 mg/L (a and c) and (0.6 mg **PG1** + 0.6 mg **PG2** + 0.6 mg **PG3**)/L (b)] by spin coating (2000 rpm) on mica, and air-dried for 4 h before AFM imaging. The height scale of these images is not the same in order to obtain good contrast, and therefore, the color of the images cannot be directly compared. The *Z* scale is 10 nm for parts a and b and 6 nm for part c.

h_{AFM} values vary strongly depending on where the analysis is performed. This is a first indication of a corrugated surface of these objects. Higher resolution images are required to establish this point more convincingly.

CONCLUSIONS

As judged by number of steps, overall yields, and total experimental effort, we have presented the arguably easiest synthetic access to a variety of water-soluble, neutral DPs with generations up to three based on the corresponding macromonomers **MG1**, **MG1.5**, **MG2**, and **MG3**. These monomers were prepared as analytically pure materials on the several gram scale. This variety of DPs comprises both homo- and (presumably random) copolymers. Copolymer compositions were determined by NMR spectroscopy and weighing of unconsumed monomers, respectively. The copolymers differ from dendronized homopolymers because their "surface" should not be smooth and near cylindrical but rather corrugated. A first indication for the correctness of this expectation was obtained from the AFM image of copolymer **PG1*co*3**. All polymers described are thermoresponsive, whereby the generation dependence of LCST is stronger than in other OEG-based DPs. While the thermoresponsivity of the copolymers is fully reproducible, there does not seem to be a straightforward interpretation of where the transition is to be expected solely based on the two different dendrons involved in each of the three cases.

EXPERIMENTAL SECTION

Materials. Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. Tetrahydrofuran (THF) was refluxed over lithium aluminum hydride (LAH) and dichloromethane (DCM) distilled from CaH_2 for drying. 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 60G/UV_{254}, 0.25 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel 60 M (Macherey-Nagel, 0.04−0.063 mm, 230−400 mesh) was used as the stationary phase for column chromatography. Further abbreviations: DIEA, *N*,*N*-diisopropylethylamine; DMAP, 4-dimethylaminopyridine; MAA, methacrylic anhydride; MAC, methacryloyl chloride; TEA, triethylamine.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 (^1H, 300 MHz; ^{13}C, 75 MHz) spectrometer. Chemical shifts are reported as δ values (ppm) and were calibrated according to internal standard CHCl3 (7.26 ppm). High-resolution ESI-Q-TOF-MS analyses (solvent, DCM/MeOH; ion polarity, positive; set capillary, 4500 V) were performed on Bruker Daltonics maXis by the MS service of the Laboratorium für Organische Chemie, ETH Zürich. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. Gel permeation chromatography (GPC) measurements were carried out by using a PL-GPC 220 instrument equipped with refractive index (RI), viscosity, and light scattering (LS; 15° and 90° angles) detectors and a 2 × PL-Gel Mix-B LS column set (2 × 30 cm) using DMF with LiBr (1 g L^{-1}) as the eluent at 45 °C. Universal calibration was performed with poly(methyl methacrylate) standards in the range of M_p = 2680−3 900 000 (Polymer Laboratories Ltd., U.K.). Differential scanning calorimetry (DSC) measurements were performed using the DSC Q1000 differential scanning calorimeter from TA Instruments in a temperature range of −95 ∼ +100 °C with a heating rate of 10 °C min^{-1}. Samples of a total weight ranging between 3 and 10 mg were closed into aluminum pans of 40 μL, covered by a holed cap, and analyzed under a nitrogen atmosphere. The glass transition temperature (T_g) was taken in the second heating run. The AFM measurements were carried out on a Nanoscope IIIa Multi Mode Scanning probe microscope (from Digital Instruments, San Diego, CA) operated in the tapping mode with an "E" scanner (scan range 10 μm × 10 μm) and operated in the tapping mode at room temperature in air. Olympus silicon OMCL-AC160TS cantilevers (from Atomic Force F&E GmbH, Mannheim, Germany) were used with a resonance frequency between 200 and 400 kHz and a spring constant around 42 N/m. The samples were prepared by spin-coating (2000 rpm) the polymer solution onto freshly cleaved mica (from PLANO W. Plannet GmbH, Wetzlar, Germany). UV/visturbidity measurements were carried out for the lower critical solution temperature (LCST) determination on a Varian Cary 100 Bio UV/vis spectrophotometer equipped with a thermostatically regulated bath. Solutions of the polymers in deionized water were filtered with a 0.45 μm filter before adding into a cuvette (path length 1 cm), which was placed in the spectrophotometer 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 minute.

Syntheses. ***2,5,9,12-Tetraoxatridecan-7-ol (4).*** NaH (60% in mineral oil) (40.00 g, 1.00 mol) was rinsed with toluene and added as dry powder to dry THF (850.0 mL) under N_2 atmosphere. Ethylene glycol monomethyl ether (78.85 mL, 1.00 mol) was then added and stirred for 2 h. Thereafter epichlorohydrine (0.96 mol) was added, and the reaction mixture was stirred for 16 h at room temperature, then heated to 65 °C for 4 h. The reaction mixture was filtered through Celite and concentrated under reduced pressure to afford the desired crude intermediate **3**, which was used without further purification. Ethylene glycol monomethyl ether (151.4 mL, 1.92 mol) was added to an aqueous solution of NaOH (19 mol/L; 1.0 equiv), then heated to 55 °C and **3** was added. The reaction mixture was stirred overnight at this temperature and then extracted with DCM (3 × 200 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to afford the crude products. Distillation under vacuum afforded the desired **4** as colorless oil (106.0 g, 53%). The residue in the flask was purified by flash chromatography with hexane/ethyl acetate (2:1 to 1:2) to give alcohol **5** as pale yellow oil (24.62 g, 30%). ^1H NMR (300 MHz, $CDCl_3$): data of **4**, 4.03−3.94 (m, 1H), 3.67−3.46 (m, 12H), 3.37 (s, 6H); data of **5**, 3.92−3.88 (m, 1H), 3.71−3.66 (m, 2H), 3.60−3.46 (m, 20H), 3.32 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): data of **4** were reported in ref 19; data of **5**, 78.8, 72.4, 71.8, 71.5, 71.4, 70.7, 69.6, 58.9. HRMS (ESI): m/z = 341.2171 ($[M + H]^+$, $C_{15}H_{33}O_8^+$; calcd, 341.2170).

*2,5,9,12-Tetraoxatridecan-7-yl Methacrylate (**MG1**). Esterification Procedure (A) According to Reference 15a.* Dendron **4** (5.00 g, 24.02 mmol), triethylamine (10.00 mL, 3.0 equiv), and DMAP (293 mg, 0.1 equiv) were dissolved in DCM (150.00 mL). Methacryloyl chloride (6.92 mL, 3 equiv) was slowly added at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. The mixture was then quenched with saturated aqueous $NaHCO_3$ and extracted with DCM. The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to afford the crude product. Purification by flash chromatography with hexane/ethyl acetate (2:1) as eluent afforded **MG1** as colorless oil (5.71 g, 86%). ^1H NMR (200 MHz, $CDCl_3$): 6.12 (s, 1H); 5.57 (t, 1.6 Hz, 1H); 5.23−5.18 (m, 1H); 3.71−3.49 (m, 12H); 3.36 (s, 6H); 1.94 (s, 3H).

*2-((2,5,9,12-Tetraoxatridecan-7-yloxy)methyl)oxirane (**6**).* To a three-necked flask charged with NaH (60% in mineral oil, 0.40 g, 10 mmol, 1.0 equiv) and freshly distilled, dry THF (10.00 mL) under N_2 atmosphere was added a solution of dendron **4** (2.08 g, 10.00 mmol) in THF (2.00 mL). After the mixture had been stirred for 2 h at room temperature, epichlorohydrine (1.00 g, 10.50 mmol, 1.05 equiv.,) was added to the solution via syringe. The resulting mixture was stirred for 16 h at room temperature and then heated to 65 °C for 4 h. After cooling to room temperature the reaction was quenched with aqueous NH_4Cl followed by extraction with DCM (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated. The crude material was then purified by flash chromatography with hexane/ethyl acetate (2:1) to give the desired product **6** as colorless oil (2.30 g, 88%).

^1H NMR (300 MHz, $CDCl_3$): 3.88 (dd, 3.3 11.7 Hz, 1H); 3.76−3.72 (m, 2H); 3.63−3.53 (m, 12H); 3.37 (s, 6 H); 3.17−3.14 (m, 1H); 2.78 (dd, 3.9, 4.8 Hz, 1H); 2.62 (dd, 2.7, 5.1 Hz, 1H). ^{13}C NMR

(75 MHz, $CDCl_3$): 78.6; 72.0; 71.6; 71.5; 71.4; 70.9; 59.1; 51.1; 44.6. HRMS (ESI): 265.1648 ([M + H]$^+$, $C_{12}H_{25}O_6^+$; calcd, 265.1646 (error, 0.7 ppm)).

*7-((2-Methoxyethoxy)methyl)-2,5,8,12,15-pentaoxahexadecan-10-ol (**5**).* Ethylene glycol monomethyl ether (0.79 mL, 2.0 equiv., 10.00 mmol) was added to an aqueous solution of NaOH (19 mol/L; 2.0 equiv) which was then heated to 55 °C before compound **6** (1.32 g, 5.00 mmol) was added. The reaction mixture was stirred overnight at 55 °C and then extracted with DCM (3 × 40 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to yield crude material, which was purified by flash chromatography with hexane/ethyl acetate (2:1) to give dendron **5** as colorless oil (1.45 g, 85%).

*7-((2-Methoxyethoxy)methyl)-2,5,8,12,15-pentaoxahexadecan-10-yl Methacrylate (**MG1.5**).* According to the esterification procedure A, **MG1.5** (0.90 g) was prepared from dendron **5** (0.85 g, 2.5 mmol) in 90% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): 6.11 (s, 1H); 5.55 (t, 1.2 Hz, 1H); 5.18−5.14 (m, 1H); 3.80−3.48 (m, 21H); 3.35 (s, 9H); 1.93 (s, 3H).

*7,13-Bis((2-methoxyethoxy)methyl)-10-methylene-2,5,8,12,15,18-hexaoxanonadecane (**7**). Etherification Procedure (B).* To a suspension of NaH (60% in mineral oil, 3.78 g, 1.5 equiv. per OH) and [15]-crown-5 (694 mg, 10 mol %) in freshly distilled, dry THF (40.0 mL) under N_2 atmosphere a solution of dendron **4** (13.1 g, 2.0 equiv., 63.0 mmol) in THF (20.0 mL) was added. After the mixture had been stirred for 2 h at 40 °C, KI (523 mg, 10 mol %), [18]-crown-6 (833 mg, 10 mol %) and MDC (3.94 g, 31.5 mmol) dissolved in THF (10.00 mL) were added to the solution. The reaction mixture was stirred under reflux for 4 d, then cooled to room temperature and quenched with saturated aqueous NH_4Cl. Extraction with DCM (3 × 200 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to afford a crude material which was further purified by flash chromatography with hexane/ethyl acetate (2:1 to 1:1) to give the desired compound **7** as a pale yellow oil (12.5 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): 5.16 (s, 2H); 4.13 (s, 4H); 3.66−3.49 (m, 26H); 3.35 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 143.4; 114.0; 77.20; 72.0; 71.3; 70.8; 59.1. HRMS (ESI): 491.2819([M + Na]$^+$, $C_{22}H_{44}NaO_{10}^+$; calc. 491.2827 (err., −1.5 ppm)).

*7,13-Bis((2-methoxyethoxy)methyl)-2,5,8,12,15,18-hexaoxanonadecan-10-ol (**8**). Ozonolysis/Reduction procedure (C).* To a chilled solution of **7** (10.00 g, 21.35 mmol) in DCM (150.0 mL)/ MeOH (22.0 mL) (−78 °C) was bubbled O_3. After the mixture had turned light blue, ozonolysis was stopped and the ozone removed by letting O_2 or N_2 pass through the solution. $NaBH_4$ (1.21 g, 1.5 equiv., 32.0 mmol) was added to the reaction mixture at −78 °C and the mixture was then allowed to slowly warm to room temperature before being stirred overnight. The reaction was quenched with 3 mL saturated aqueous NH_4Cl solution and diluted with DCM, dried over $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by flash chromatography with hexane/ethyl acetate (1:2) to afford compound **8** as a colorless oil (9.58 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.94−3.86 (m, 1H); 3.72−3.48 (m, 31H); 3.36 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): 78.8; 72.2; 72.0; 71.9; 70.8; 69.8; 59.1. HRMS (ESI): 473.2955([M + H]$^+$, $C_{22}H_{45}NaO_{11}^+$; calcd, 473.2956 (error, 0.2 ppm)).

*7,13-Bis((2-methoxyethoxy)methyl)-10-((3-methylbuta-1,3-dien-2-yl)oxy)-2,5,8,12,15,18-hexaoxanonadecane (**MG2**). Esterification procedure (D).* To a solution of **8** (1.00 g, 1.0 equiv, 2.12 mmol) in DCM (10.0 mL) were added DIEA (0.77 mL, 2.1 equiv, 4.45 mmol) and DMAP (26 mg, 0.1 equiv) under N_2 atmosphere. The mixture was cooled to 0 °C and methacryloyl anhydride (0.63 mL, 2.0 equiv., 4.24 mmol) was slowly added neat. Thereafter the reaction mixture was warmed to room temperature, then heated to 40 °C and stirred overnight. The obtained solution was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography with ethyl acetate/acetone (1:1, v/v) to afford **MG2** as a pale yellow oil (0.94 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.11 (s, 1H); 5.55 (t, 1.5 Hz, 1H); 5.16−5.08 (m, 1H); 3.84−3.49 (m, 30H); 3.36 (s, 12H); 1.93 (s, 3H).

*10,16-Bis((2,5,9,12-tetraoxatridecan-7-yloxy)methyl)-7,19-bis((2-methoxyethoxy)methyl)-13-methylene-2,5,8,11,15,18,21,24-octaoxapentacosane (**9**).* This was prepared according to the etherification procedure (B) from **8** (9.04 g, 19.2 mmol) and MDC (1.20 g, 9.60 mmol). After 4 d, the reaction was quenched and purified by flash chromatography with ethyl acetate/acetone (2:1−1:1, v/v) as eluent to give compound **9** as pale yellow oil (8.14 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): 5.14 (s, 2H); 4.07 (s, 4H); 3.70−3.47 (m, 62H); 3.34 (s, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): 143.5; 113.3; 78.6; 77.6; 71.9; 71.3; 71.2; 70.8; 70.7; 70.2; 59.0. HRMS (ESI): 1014.6403 ([M + NH$_4$]$^+$, $C_{46}H_{96}NO_{22}^+$; calcd, 1014.6419 (error, −1.5 ppm)).

*10,16-Bis((2,5,9,12-tetraoxatridecan-7-yloxy)methyl)-7,19-bis((2-methoxyethoxy)methyl)-2,5,8,11,15,18,21,24-octaoxapentacosan-13-ol (**10**).* According to the ozonolysis/reduction procedure (C), dendron **10** (8.01 g) was prepared from **9** (8.73 g, 8.76 mmol) as a pale yellow oil (91%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.90−3.82 (m, 1H); 3.75−3.50 (m, 67H); 3.36 (*s*, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): 79.2; 78.7; 72.2; 72.0; 71.3; 71.2; 70.8; 70.5; 69.8; 59.1. HRMS (ESI): 1018.6349 ([M + NH$_4$]$^+$, $C_{45}H_{96}NO_{23}^+$; calcd, 1018.6368 (error, 1.8 ppm)).

*10,16-Bis((2,5,9,12-tetraoxatridecan-7-yloxy)methyl)-7,19-bis((2-methoxyethoxy)methyl)-2,5,8,11,15,18,21,24-octaoxapentacosan-13-yl methacrylate (**MG3**).* According to the esterification procedure (D) **MG3** (0.91 g) was prepared from dendron **10** (1.00 g, 1.0 mmol) as a pale yellow oil (85%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.10 (s, 1H); 5.54 (t, 1.5 Hz, 1H); 5.10−5.07 (m, 1H); 3.76−3.49 (m, 67H); 3.36 (s, 24H); 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.7; 136.5; 125.5; 79.0; 78.6; 72.9; 71.9; 71.2; 70.8; 70.3; 69.1; 59.0; 18.4. HRMS (ESI): 1086.6614 ([M + NH$_4$]$^+$, $C_{49}H_{100}NO_{24}^+$; calcd, 1086.6630 (error, −1.5 ppm)).

General Procedure for Polymerization (E). AIBN solution of toluene or DMF with the concentration specified in Table 1 was freshly prepared in advance. The required amount of the monomer was added into a Schlenk tube, then the required AIBN solution was added via a syringe. The reaction mixture was thoroughly deoxygenated by several freeze-pump-thaw cycles and then stirred at 60 °C for the desired time. After cooling to room temperature, the polymer was dissolved in DCM and purified by precipitation from *n*-hexane.

According to general procedure for polymerization (E) from **MG1** (1.00 g, 3.6 mmol), AIBN (0.1 mol %) and toluene (3.00 mL), polymerization for 17 h afforded **PG1** as a colorless sticky solid (0.80 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): 4.85 (br., 1H); 3.59−3.51 (m, $_{12H}$); 3.36 (s, 6H); 1.82 (br., 1.6H); 1.05−0.93 (m, 2.6H). ^{13}C NMR (75 MHz, $CDCl_3$): 71.9; 70.7; 68.8; 59.0. Anal. Calcd (%) for $(C_{13}H_{24}O_6)_n$ $(276.33)_n$: C, 56.51; H, 8.75. Found: C, 56.32; H, 8.97.PG1.5

According to general procedure for polymerization (E) from **MG1.5** (163.3 mg, 0.40 mmol), AIBN (0.2 mol %) and toluene (0.20 mL), polymerization for 17 h afforded **PG1.5** as a colorless sticky solid (140 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): 4.77 (br., 1H); 3.84−3.43 (m, 21H); 3.35 (s, 9H); 1.83 (br., 1.5H); 1.00−0.89 (m, 2.6H). ^{13}C NMR (75 MHz, $CDCl_3$): 78.6; 72.0; 71.0; 70.7; 70.6; 59.0. Anal. Calcd (%) for $(C_{19}H_{36}O_9)_n$ $(408.49)_n$: C, 55.87; H, 8.88. Found: C, 55.71; H, 8.93.PG2

According to general procedure for polymerization (E) from **MG2** (108 mg, 0.20 mmol), AIBN (0.2 mol %) and toluene (0.10 mL), polymerization for 17 h afforded **PG2** as a colorless sticky solid (100 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): 4.70 (br., 1H); 3.60−3.51 (m, 30H); 3.34 (s, 12H); 2.11 (br., 1.2H); 0.89 (br., 2.6H). ^{13}C NMR (75 MHz, $CDCl_3$): 78.5; 71.9; 70.9; 70.8; 70.7; 58.9. Anal. Calcd (%) for $(C_{25}H_{48}O_{12})_n$ $(540.65)_n$: C, 55.54; H, 8.95. Found: C, 55.65; H, 9.02.PG3

According to general procedure for polymerization (E) from **MG3** (107 mg, 0.10 mmol), AIBN (0.5 mol %) and toluene (0.05 mL), polymerization for 17 h afforded **PG3** as a colorless sticky solid (40 mg, 37%). ^{1}H NMR (300 MHz, $CDCl_3$): 4.64 (br., 0.8H); 3.60−3.50 (m, 61H); 3.33 (s, 24H); 1.94 (br., 0.9H); 0.82 (br., 2.4H). ^{13}C NMR

(75 MHz, CDCl$_3$): 78.5; 72.0; 70.7; 58.9. Anal. Calcd (%) for $(C_{49}H_{96}O_{24})_n$ $(1069.28)_n$: C, 55.04; H, 9.05. Found: C, 54.84; H, 9.04.PG1*co*2

According to general procedure for polymerization (E) from **MG1** (41 mg, 0.15 mmol), **MG2** (81 mg, 0.15 mmol), AIBN (0.1 mol %) and toluene (0.10 mL), polymerization for 17 h afforded **PG1*co*2** (1:1) as a colorless sticky solid (89 mg, 73%). ^{1}H NMR (600 MHz, CDCl$_3$): 4.84 (br., 1H); 4.73 (br., 1H); 3.70–3.52 (m, 42H); 3.36 (s, 18H); 1.82 (br., 2.4H); 1.01–0.89 (m, 5.7H). ^{13}C NMR (75 MHz, CDCl$_3$): 78.6; 72.0; 71.0; 70.8; 59.0.PG1*co*3

According to general procedure for polymerization (E) from **MG1** (28 mg, 0.10 mmol), **MG3** (107 mg, 0.10 mmol), AIBN (0.2 mol %) and toluene (0.10 mL), polymerization for 17 h afforded **PG1*co*3** (2:1) as a colorless sticky solid (81 mg, 75%). ^{1}H NMR (300 MHz, CDCl$_3$): 4.83 (br., 0.91H); 4.67 (br., 0.46H); 3.60–3.50 (m, 47H); 3.35 (s, 18H); 1.86 (br., 2.4H); 0.92 (br., 4.1H). ^{13}C NMR (75 MHz, CDCl$_3$): 78.5; 72.0; 71.0; 70.8; 59.0.PG2*co*3

According to general procedure for polymerization (E) from **MG2** (54 mg, 0.10 mmol), **MG3** (107 mg, 0.10 mmol), AIBN (0.2 mol %) and toluene (0.10 mL), polymerization for 17 h afforded **PG2*co*3** (2:1) as a colorless sticky solid (107 mg, 75%). ^{1}H NMR (300 MHz, CDCl$_3$): 4.70 (br., 1H); 3.60–3.50 (m, 60H); 3.34 (s, 24H); 1.93 (br., 1.4H); 0.88 (br., 2.7H). ^{13}C NMR (75 MHz, CDCl$_3$): 78.5; 72.0; 70.8; 70.7; 58.9.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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