Synthesis and Properties of Carborane-Containing Dendronized Polymers

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ABSTRACT: Carborane-containing dendronized polymers were successfully synthesized using two different approaches up to the fourth generation. Nitroxide-mediated polymerization (NMP) was effective for the polymerization of carborane-functionalized styrenic monomers, leading to well-defined polymers with high boron content and narrow molecular weight distributions (PDI < 1.1). The resulting carborane-functionalized polymers could then be dendronized using a divergent approach to introduce aliphatic polyester dendrons of generation 1−4 grafted from the polymer backbone. This first approach afforded a maximum degree of dendronization of 70%. To increase the degree of dendronization, a first-generation macromonomer was polymerized using NMP to yield a fully functionalized first-generation dendronized polymer. This material was also dendronized up to the fourth generation. Both approaches produced water-soluble dendronized polymers (1 mg/mL in pure water) with high molecular weights (in excess of 70 kDa). It was found that the solubility of the polymer produced from the second approach, where dendronization occurred at every monomer unit, exceeded that of the first approach.

Introduction

Carborane-containing macromolecules have attracted attention due to the unique properties of the icosahedral boron-rich carborane clusters. As a result of their high thermodynamic stability, these compounds have been postulated as potential flame-retardant materials.[1] In addition, the extremely high neutron capture cross section of ^{10}B atoms, the highest of all light elements,[2] not only makes them ideal for radiation shielding coatings[3] but also enables their use in medicinal applications.[4] Specifically, one type of chemotherapy, dubbed boron neutron capture therapy (BNCT), is an extensively studied experimental approach for tumor treatment[5] and has been the focus of extensive research since first proposed by Locher and co-workers in 1936.[4] This method relies on the cytotoxic effect produced as a result of the nuclear reaction between ^{10}B and thermal neutrons.[2] In this binary procedure, upon irradiation of ^{10}B nuclei with thermal neutrons, a radiation dose composed of high linear energy transfer (LET) lithium ions and alpha particles (^{7}Li and α) is produced and has a penetration path length of about 10 μm in biological tissues, which is approximately equivalent to one cell diameter.[6] Therefore, it is theoretically possible to destroy cancer cells without affecting adjacent healthy cells if a significantly high ^{10}B concentration is selectively accumulated within a tumor. However, one of the main challenges to BNCT therapy has been achieving the selective delivery of high ^{10}B concentrations to cancer cells, where a minimum of 10^{9} ^{10}B atoms per cell, or ~30 μg of ^{10}B per gram of tumor tissue, is needed.[7,8]

To address this issue, carborane cages have received significant attention due to their boron-rich nature, high stability, charge neutrality, and ease of chemical modification.[9] Unfortunately, the lipophilic nature of carboranes prohibits their direct intravenous delivery to target tissues. To overcome this difficulty, conjugation of carborane cages with various hydrophilic biological molecules, including sugars,[10] nucleic acids,[10] liposomes,[11] and DNA binding units such as trimethoxyindole (TMI),[12] has been investigated, but very limited success has been achieved. Recently, the incorporation of carborane cages within dendrimers has begun to attract attention. In the early 1990s, Newkome and co-workers synthesized a completely water-soluble hydrocarbon dendrimer internally functionalized with multiple carborane cages.[13] Subsequently, Qualmann et al. also reported a water-soluble poly(lysine) dendrimer functionalized with carborane units, where the carboranes were introduced at the dendrimer periphery.[14] In addition, other carborane-containing dendritic structures have been reported,[15−17] but none of these have simultaneously exhibited water solubility, biocompatibility, biodegradability, and low toxicity, which are key properties required for BNCT.

In our group, we have recently extended this approach to the incorporation of carborane cages within aliphatic polyester dendrimers to produce water-soluble conjugates using the divergent dendrimer growth approach.[18−20] These carborane-functionalized aliphatic polyester dendrimers were prepared up to the fifth generation, and because of their numerous peripheral hydroxyl groups, they exhibited water solubility. Additionally, on the basis of previous studies, it is known that the aliphatic polyester dendrimer structure is nontoxic and biocompatible.[21] However, the tedious stepwise synthesis of these macromolecules limited the achievable molecular weights (MWs) to ~20 kDa, which is well below the MW cutoff for renal filtration, known to be in the range of 30−50 kDa.[22] To overcome this limitation, we decided to investigate the synthesis of a similar class of branched macromolecules that can reach MWs greater than 50 kDa using an easier synthetic approach. This can be achieved by combining a classic polymerization method with the divergent dendrimer synthesis to make carborane-containing dendronized polymers, as depicted in Figure 1.

Dendronized polymers[23] represent an interesting new class of macromolecules that have a unique cylindrical shape and can exhibit a large number of functionalizable groups at their

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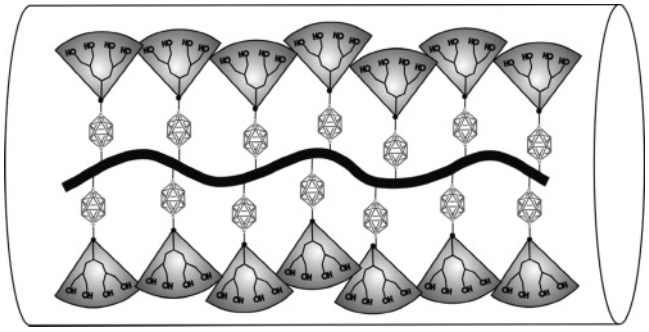


Figure 1. Schematic representation of carborane-loaded dendronized polymer.

periphery.[24] The growth of aliphatic polyester dendrons from linear polymer backbones to produce water-soluble dendronized polymers has recently been reported.[24−27]

Here, we present the synthesis and characterization of carborane-containing dendronized polymers based on the same aliphatic polyester dendritic units, as a new addition to the family of macromolecules with promising properties for BNCT applications. As far as the authors know, this is the first report on carborane-containing dendronized polymers, combining high MW (>50 kDa), water solubility, high boron content, and a low polydispersity index (PDI).

Results and Discussion

Synthesis and Polymerization of Carborane-Functionalized Monomers. The preparation of dendronized polymers can be carried out in a number of ways, including (a) polymerization of dendron-functionalized macromonomers, (b) grafting of dendrons to a linear polymer backbone, or (c) the divergent dendronization of appropriately functionalized linear polymers. We initially chose to use a combination of methods (a) and (c), where a low-generation dendritic monomer is first polymerized and then dendronized to higher generations. To accomplish this, we treated *p*-carborane with 2 equiv of *n*-butyllithium (*n*-BuLi) in THF, followed by treatment with 2 equiv of trimethylene oxide to give *p*-dihydroxypropyl carborane (**1**) in 90% yield after acidic workup and crystallization of the crude product from chloroform (Scheme 1).[20] The resulting diol (**1**) was treated with 1 equiv of the highly reactive benzylidene-protected anhydride of bisMPA (**2**), which was synthesized in two steps following a literature procedure.[28] The resulting monofunctionalized hydroxylcarborane (**3**) was isolated in 50% yield after purification by column chromatography. Further treatment of (**3**) with 1 equiv of acryloyl chloride gave the [G1]-(Bn) acrylate monomer (**4**) in 98% yield after purification by column chromatography (Scheme 1).

With monomer **4** in hand, polymerization was attempted using the nitroxide-mediated polymerization (NMP) strategy. This was done by heating the universal alkoxyamine initiator (**5**), initially reported by Hawker and co-workers,[29] to 125 °C in the presence of monomer **4**, using chlorobenzene as the solvent. Unfortunately, the polymers obtained using this methodology were bimodal in nature, with size exclusion chromatography (SEC) data indicating the presence of high MW (M_w > 280 kDa) main peaks and low MW (M_w < 7 kDa) shoulders. Attempts to optimize the polymerization conditions by varying the reaction time and monomer concentration all failed to give a well-defined polymer with low PDI (Table 1).

Having been unsuccessful in the production of well-defined polymers from the acrylate monomer **4**, we turned our attention to the preparation of an analogous styrene functionalized *p*-carborane monomer (**7**) (Scheme 2). From previous studies, we have already shown that NMP of a styrene-functionalized *o*-carborane gave a well-defined polymer with PDI < 1.1,[18] and we reasoned that similar results could be obtained with the *p*-carborane analogue.

The synthesis of monomer (**7**) was again accomplished by deprotonating *p*-carborane with *n*-BuLi (1.0 equiv) in THF to give a statistical mixture of three components, including a monoanion, a dianion, and the starting material.[30] This mixture was then treated with 1 equiv of 4-vinylbenzyl chloride to give the *p*-carborane-functionalized monomer (**7**) in 50% yield after purification by column chromatography using hexanes as the eluent.

Contrary to the results with monomer **4**, this styrenic monomer was successfully polymerized by NMP to give a well-defined polymer (**9**) that could be subsequently dendronized (Scheme 3). The polymerization involved 80 equiv of monomer **7** in the presence of 1 equiv of the alkoxyamine initiator **5**, a catalytic amount of the free nitroxyl radical **8** (0.05 equiv), and acetic anhydride (1.8 equiv). After degassing under N_2 for 1 h, the polymerization was carried out for different time periods at 125 °C. We have found that high MWs (>16 kDa) and low PDIs (<1.1) were afforded with a monomer concentration of 5.0 M and a polymerization time of 7 h, producing polymers in greater than 90% yield (Table 2, bold entry). Other conditions, where the monomer concentration was decreased or the monomer-to-initiator ratio was varied, resulted in either lower molecular weights or broader molecular weight distributions (Table 2). We refer to the polymerization of monomer **7** by NMP as *route A*. After this successful polymerization, dendronization of carborane-loaded poly(styrene) (CPS, **9**) to higher generations was achieved using the divergent dendrimer growth, as detailed below.

Dendronization of the Preformed Linear Carborane-Functionalized Polymer. The [G1]-(Bn) dendronized polymer was prepared utilizing the "grafting from" approach. The carborane-loaded polymer **9** was first treated with a stoichiometric quantity of *n*-BuLi, relative to the number of carborane units in the polymer. The resulting polyanion was subsequently reacted with excess benzylidene-protected anhydride **2** to afford the [G1]-(Bn) dendronized polymer with ∼70% functionalization. The key to this dendronization step was optimization of the polymer concentration prior to reaction with *n*-BuLi to give the polyanion. It was found that when the reaction was carried out at polymer concentrations greater than 0.6 mM, the high anion concentration resulted in precipitation of the polymer and a final product having a bimodal MW distribution. However, at lower concentrations, precipitation of the polyanion was not observed, and the isolated product remained well-defined. The degree of dendronization was determined by comparison of the ^{1}H NMR of the polymer prior to and after reaction with anhydride **2**. The ratio of the aromatic (styrene) protons (δ = 6.2−6.6 ppm) from the polymer backbone to the aliphatic protons in the benzylidene protecting groups of the dendron (δ = 5.4 ppm) gave the percentage of carborane units functionalized with the [G1]-(Bn) group, which was found to be ∼70% (Figure 2).

Dendron growth was carried out to the fourth generation using an iterative deprotection and esterification approach. Removal of the benzylidene protecting groups in the dendronized polymers was carried out using a Pd-catalyzed hydrogenolysis with PdOH/C (20 wt %) in a 1:1 solution of CH_2Cl_2/methanol with typical yields greater than 95%. Although deprotection of low-MW dendronized polymers can be achieved in quantitative

Scheme 1. Synthesis of [G1]-(Bn)-Dendronized Acrylate Polymer (DMAP = 4-(Dimethylamino)pyridine)

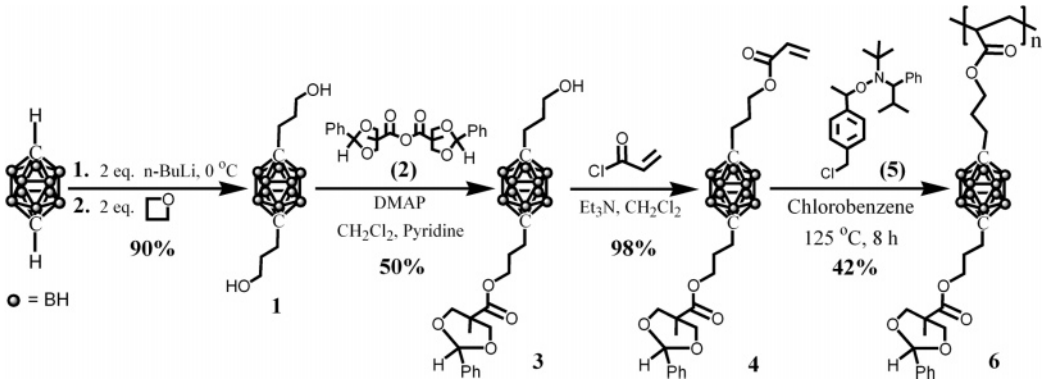
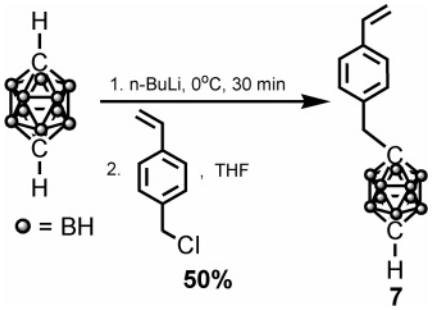


Table 1. Results from Polymerization of Monomer 4 by Nitroxide-Mediated Polymerization (NMP) Using Various Conditions

monomer:initiator ratio	[monomer] (M)	reaction time (h)	temp[a] (°C)	polymer nature	M_w[b] (g/mol)	PDI
40:1	0.4	1	125	broad	27 000	2.4
40:1	0.4	8	125	broad	28 000	2.0
40:1	0.4	12	125	multimodal	54 000	3.4
40:1	0.9	1	125	multimodal	14 000	1.4
40:1	0.9	8	125	multimodal	45 000	2.6
40:1	1.5	1	125	broad	54 000	1.6
40:1	1.5	8	125	broad	280 000	2.5

[a] All polymerizations were conducted in chlorobenzene. [b] Weight-average molecular weight (M_w) from size exclusion chromatography (SEC) using polystyrene standards.

Scheme 2. Synthesis of Carborane-Functionalized Styrene Monomer (THF = Tetrahydrofuran)



yields, it was found that this reaction leads to a bimodal MW distribution and significant MW broadening at higher generations. Similar results were reported by Yoshida et al. in the divergent synthesis of dendronized poly(hydroxystyrene) with very high MW.[24] It was reported that trans acetalization byproducts were responsible for this effect, and they could be removed by carrying out the deprotection under homogeneous acid-catalyzed conditions instead of hydrogenolysis. However, several iterations to achieve quantitative yields were required.[24,30] In our study, we found it more efficient to carry out a near-quantitative Pd-catalyzed deprotection first, followed by the acid-catalyzed deprotection using H_2SO_4 (2% v/v) in THF/MeOH (4:3 v/v), as this allowed for a total reaction time of less than 24 h. This treatment was followed by neutralization of the excess acid with ammonia, and the products were isolated in nearly quantitative yields after several washings with THF/MeOH (9:1) to remove all the ammonium sulfate salt that was generated. The deprotection reaction was followed by NMR (^{1}H, ^{13}C, 600 MHz) and SEC analysis to verify the completion of the reaction. This was indicated by the absence of proton signals from the benzylidene protecting group in the ^{1}H NMR as well as the absence of any high-MW shoulder in the SEC analysis, which is a result of intermolecular coupling of polymer chains.

Achieving complete deprotection is a key step to the successful synthesis of well-defined high generation dendronized polymers. This is clearly shown in Figure 3, which depicts the major difference between the dendronized polymers obtained following an incomplete deprotection using hydrogenolysis alone and the polymers obtained when the deprotection was driven to completion using the acid-catalyzed conditions described above. In the former case, SEC analysis indicated that, beyond the second generation, significant shoulders at high MW (corresponding to double, triple, and quadruple the MWs of the major peak) were formed (Figure 3a). However, as illustrated in Figure 3b, the polymers obtained following complete deprotection using the acid-catalyzed second step were well-defined, with no presence of shoulders at higher MWs. These results confirm that the origin of the aforementioned byproducts was the incomplete removal of benzylidene groups prior to dendron growth.

Molecular Weight Determination by SEC. In this study, SEC was used to evaluate the molecular weight of the carborane-containing dendronized polymers. The observed weight-average molecular weight (M_w, PS standard) and PDIs obtained by SEC are summarized in Table 3. The underestimation of the M_w by SEC, leading to a large discrepancy between the theoretical MW values and SEC derived values, is caused by the significant difference in the hydrodynamic radii of the dendronized polymers, with their compact rodlike architecture, as compared to the linear poly(styrene) (PS) standards used to calibrate the instrument. As has been previously observed, this effect becomes more pronounced for the higher generation dendronized polymers, where the observed MWs were significantly lower than the theoretical values (Table 3).[24] These results show the limitations of SEC for the characterization of these materials, requiring the utilization of NMR analysis to obtain a more accurate estimation of the MW. The MW evaluation from ^{1}H NMR was achieved by comparing the integration of the two chloromethyl protons (δ = 4.5 ppm), initially part of the alkoxyamine initiator (**5**), to the aromatic proton signals (δ = 6.0−6.8 ppm) originating from the polymer backbone or to the proton signal of the benzylidene protecting group (δ = 5.4 ppm). The MWs estimated by NMR analysis were found to be in good agreement with the theoretical MWs (Table 3).

Scheme 3. Synthesis of [G-1]-$(OH)_2$ to [G-4]-$(OH)_{16}$-Dendronized Polymers

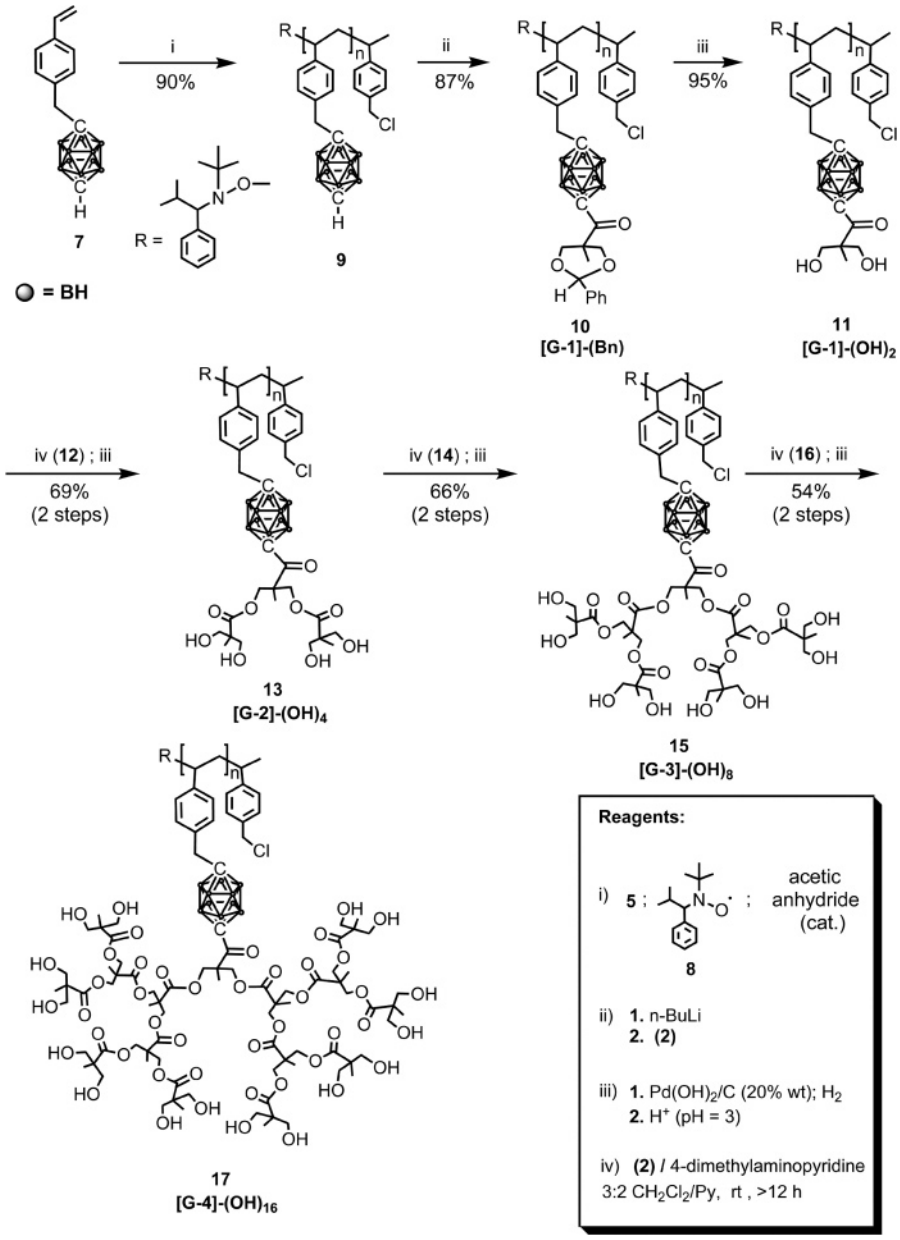


Table 2. Results from Polymerization of Monomer 7 by Nitroxide-Mediated Polymerization (NMP) Using Various Conditions

monomer:initiator ratio	[monomer] (M)	reaction time (h)	temp[a] (°C)	polymer nature	M_w[b] (g/mol)	PDI
40:1	1.5	3	125	monomodal	3000	1.08
40:1	1.5	5	125	monomodal	4500	1.10
40:1	1.5	7	125	monomodal	6000	1.12
40:1	1.5	9	125	monomodal	7000	1.11
40:1	1.5	24	125	monomodal	8500	1.23
100:1	3.8	8	125	monomodal	16 000	1.25
100:1	3.8	10	125	broad	17 000	1.30
100:1	3.8	12	125	broad	21 500	1.45
80:1	3.8	7	125	monomodal	12 000	1.08
80:1	**5.0**	**7**	**125**	**monomodal**	**15 000**	**1.10**
80:1	5.0	10	125	monomodal	16 000	1.25
80:1	5.0	12	125	broad	22 000	1.40

[a] All polymerizations were conducted in chlorobenzene. [b] Weight-average molecular weight (M_w) from size exclusion chromatography (SEC) using polystyrene standards.

Water Solubility and Boron Content. The main goal of the present work was to synthesize water-soluble carborane-functionalized dendronized polymers with high boron content as potential candidates for BNCT. At low generations (G1−G2), the dendronized polymers were insoluble in water. This lack of water solubility is mainly caused by the highly lipophilic carborane cages and polymer backbone. This effect can be overcome by introducing a large number of hydrophilic groups around each carborane cage to impart an overall water solubility. It was found that solubility in water, at a concentration of 0.5 mg/mL, was achieved at the third generation, with 8 hydroxyl groups per carborane cage. Dendronization to the fourth

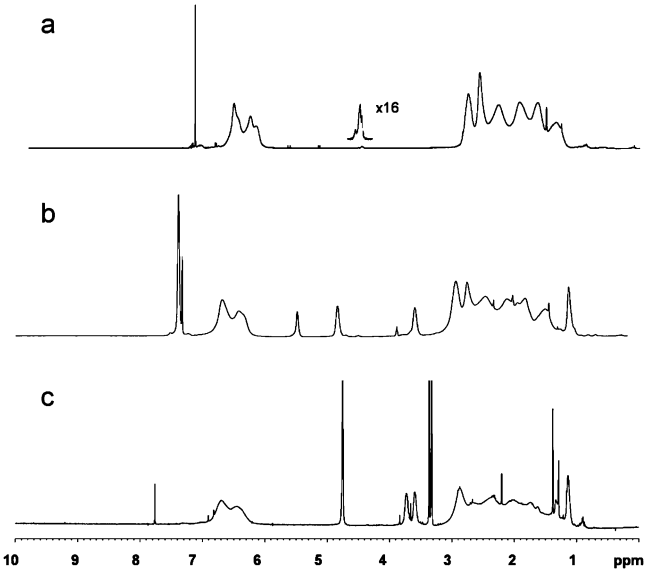


Figure 2. ^{1}H NMR of (a) polymer **9**, (b) [G-1]-(Bn)-dendronized polymer **10**, and (c) [G-1]-$(OH)_2$-dendronized polymer **11**.

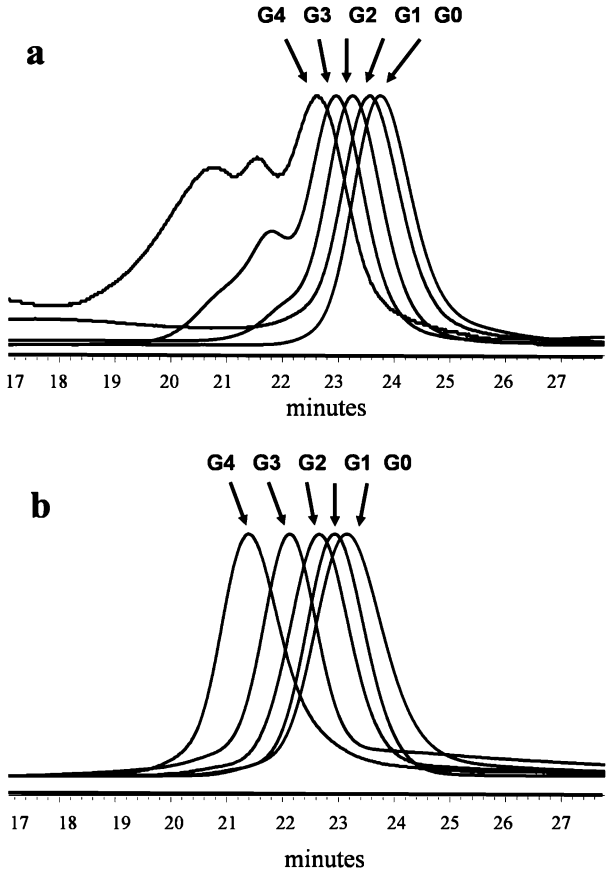


Figure 3. Size exclusion chromatography (SEC) analysis of [G0]−[G4]-benzylidene protected polymers having performed generation growth after Pd-catalyzed deprotection only (a) and Pd-catalyzed deprotection followed by acid-catalyzed deprotection (b).

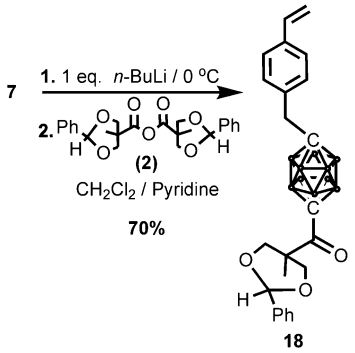
generation, where 16 hydroxyl groups were appended to each carborane cage, resulted in a solubility of 1 mg/mL in water. This was consistent with our previously reported results on carborane loaded dendrimers, where water solubility (1 mg/mL) was achieved with the same carborane:OH-group ratio of 1:16.[30] At the fourth generation, the deprotected dendronized polymer ([G4]-$(OH)_{16}$-CPS) had a boron content of 12% and a MW exceeding 100 kDa, as determined from ^{1}H NMR data.

Table 3. Comparison of Molecular Weights (MWs) Determined by Size Exclusion Chromatography (SEC) to the Theoretical and NMR Calculated MWs

		SEC (THF)[b]		NMR
compound	theor MW[a]	M_w	PDI	calcd MW
CPS (**9**)	21 000	15 000	1.06	21 000
[G1]-(Bn)-CPS (**10**)	37 000	18 000	1.15	32 000
[G1]-$(OH)_2$-CPS (**11**)	27 000	13 000	1.09	29 000
[G2]-$(Bn)_2$-CPS (**12**)	49 000	20 000	1.14	54 000
[G2]-$(OH)_4$-CPS (**13**)	40 000	16 000	1.18	33 000
[G3]-$(Bn)_4$-CPS (**14**)	84 000	23 000	1.15	92 000
[G3]-$(OH)_8$-CPS (**15**)	65 000	19 000	1.15	74 000
[G4]-$(Bn)_8$-CPS (**16**)	153 000	30 000	1.18	164 000
[G4]-$(OH)_{16}$-CPS (**17**)	115 000	25 000	1.16	114 000

[a] Based on the SEC data of **9**. [b] Relative to polystyrene standards, THF = tetrahydrofuran.

Scheme 4. Synthesis of [G1]-(Bn) Macromonomer



This approach, although successful in making high-MW carborane-containing polymers, was still limited by the incomplete functionalization of the premade polymer with the [G1]-(Bn) dendron, which left some of the carborane cages unfunctionalized. In order to solve this issue, a different route to making a fully functionalized carborane containing polymer was adopted. This was accomplished by first synthesizing a G1-dendron-containing macromonomer and then polymerizing it by NMP to obtain a polymer having the [G1]-(Bn) dendron at every repeat unit. This approach is termed *route B*. Dendronization of the fully [G1]-(Bn)-functionalized polymer was carried out using the same iterative deprotection and coupling steps described previously in route A.[24,25] Preparation of the [G1]-(Bn)-macromonomer **18** was accomplished by treating monomer **7** with 1 equiv of *n*-BuLi in THF to deprotonate the remaining acidic proton on the carbon vertex (Scheme 4). This was followed by reaction of the resulting carbanion with the benzylidene protected anhydride **2** to yield macromonomer **18** in nearly quantitative yield after purification by column chromatography using CH_2Cl_2/hexanes (1:1) as the eluent.

Polymerization of macromonomer **18** (80 equiv) by NMP in the presence of 1 equiv of the alkoxyamine initiator (**5**), a catalytic amount of the free nitroxide radical (**8**) (0.05 equiv), and acetic anhydride (1.8 equiv) resulted in the formation of well-defined, low PDI (<1.1) polymers having high MWs (>10 kDa). Best results were achieved with a macromonomer concentration in the range of 0.5−0.7 M and a polymerization time of 7 h. This carborane-loaded linear polymer was subsequently dendronized up to the fourth generation using the iterative deprotection and coupling approach described above.

Molecular Weight Determination. The MWs of the dendronized polymers prepared by route B were determined by SEC and ^{1}H NMR (Table 4 and Figure 4). Similarly to the previous samples, the measured SEC values grossly underestimated the polymer MWs, again due to the difference in hydrodynamic

Table 4. Comparison of Molecular Weights (MWs) Determined by Size Exclusion Chromatography (SEC) to the Theoretical and NMR Calculated MWs

		SEC (THF)[b]		NMR
compound	theor MW[a]	M_w	PDI	calcd MW
[G1]-(Bn)-CPS (**19**)	21 000	13 000	1.07	21 000
[G1]-$(OH)_2$-CPS (**20**)	17 000	9 500	1.10	17 000
[G2]-$(Bn)_2$-CPS (**21**)	35 000	16 000	1.10	36 000
[G2]-$(OH)_4$-CPS (**22**)	27 000	13 500	1.20	28 000
[G3]-$(Bn)_4$-CPS (**23**)	64 000	20 000	1.18	61 000
[G3]-$(OH)_8$-CPS (**24**)	48 000	17 000	1.23	46 000
[G4]-$(Bn)_8$-CPS (**25**)	122 000	29 000	1.23	101 000
[G4]-$(OH)_{16}$-CPS (**26**)	90 000	N/A	N/A	75 000

[a] Based on the SEC data of **19**. [b] Relative to polystyrene standards, THF = tetrahydrofuran.

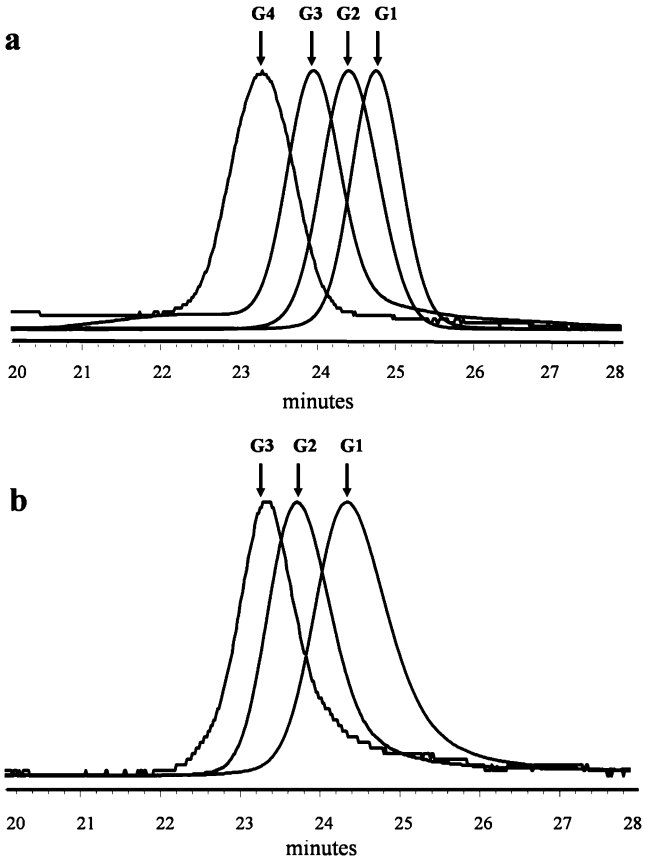


Figure 4. Size exclusion chromatography (SEC) analysis of the benzylidene protected G1−G4 series (top) and the deprotected G1−G3 series (bottom) of dendronized polymers.

volume between the dendronized polymers and the linear PS standards used to calibrate the instrument. Fortunately, ^{1}H NMR measurements, based on the relative integration of the ^{1}H signal corresponding to the two chloromethyl protons ($\delta = 4.5$ ppm), originally part of the alkoxyamine initiator **5**, to the ^{1}H signal corresponding to the benzylidene protecting group proton ($\delta =$ 5.4 ppm) again provided closer agreement with the theoretical values (Table 4). It should be noted that, due to its lack of solubility in THF, the [G4]-$(OH)_{16}$-CPS could not be characterized by SEC.

Water Solubility and Boron Content. The aqueous solubility of the series of polymers prepared by route B was evaluated and compared to the polymer series from route A. It was found that higher solubilities occurred with the polymers synthesized via route B (Table 5). Here, a solubility of 1 mg/mL was achieved with the third-generation dendronized polymer ([G3]-$(OH)_8$-CPS, **24**), and higher concentrations (>1 mg/mL) were achieved at the fourth-generation ([G4]-$(OH)_{16}$-CPS, **26**). These results show that when the carborane-loaded polymer is functionalized with dendrons at each repeat unit, the water solubility is enhanced. The boron content of the fourth-generation deprotected dendronized polymer [G4]-$(OH)_{16}$-CPS, prepared using route B, was estimated from ^{1}H NMR to be ~8%.

Table 5. Solubility in Water

dendron generation	route A (mg/mL)	route B (mg/mL)
1	0	0
2	0	0.5
3	0.5	>1.0
4	>1.0	>2.0

Conclusions

High-molecular-weight carborane-containing dendronized polymers were successfully prepared up to the fourth generation by two different approaches. Using the first approach (route A), we were able to achieve ~70% functionalization of the carborane-loaded polymer with the first-generation dendrons. In the second approach (route B), a fully functionalized dendronized polymer was synthesized by introducing the dendron unit within a macromonomer, followed by polymerization using NMP. Both sets of dendronized polymers were characterized by NMR (^{1}H and ^{13}C) and SEC. It was found that SEC data underestimated polymer MWs, but ^{1}H NMR data closely matched theoretical values. The resulting polymers, having MWs in excess of 50 kDa, exhibited water solubility when the OH:carborane ratio exceeded 8:1. Additionally, the fully dendronized polymers, prepared by route B, exhibited greater solubility than those prepared by route A. However, higher boron content is achieved via route A, where dendronization does not occur at every carborane unit. To our knowledge, this is the first report of the synthesis of well-defined carborane-containing dendronized polymers that exhibit high MW and aqueous solubility. Because of these characteristics, the synthesized polymers may serve as potential agents for BNCT applications, which will be the focus of our future studies.

Experimental Section

Materials. 4-Vinylbenzyl chloride (≥90%), 4-(dimethylamino)-pyridine (DMAP, 99%), 2,2-bis(hydroxymethyl)propionic acid (bisMPA, 98%), benzaldehyde dimethylacetal (99%), *p*-toluenesulfonic acid monohydride (*p*-TSAOH, 98%), *n*-butyllithium (2.5 M), and palladium hydroxide (20 wt % Pd/C) were purchased from Sigma-Aldrich. Benzylidene-2,2-bis(oxymethyl)propionic acid and its anhydride were prepared following literature procedures.[31] Dichloromethane (DCM) was distilled under nitrogen from calcium hydride immediately prior to use. Tetrahydrofuran (THF) was passed through two columns of activated molecular sieves using a solvent drying system supplied by MBraun, immediately prior to use. All other reagents were commercially obtained and used without further purification.

Characterization. NMR spectra were measured on Bruker DRX 500 MHz and Avance 600 MHz spectrometers. ^{1}H spectra were recorded at 600 MHz, ^{11}B spectra were recorded at 190 MHz, and ^{13}C NMR spectra were recorded at 150 MHz in $CDCl_3$ or methanol-d_4. The nondeuterated solvent signal was used as the internal standard for both ^{1}H and ^{13}C spectra. Where aliphatic ^{1}H NMR signals from the dendrimer overlap with signals form the B−H in the carborane cage or with the broad polymer signals, an accurate integration could not be assigned. In these cases, theoretical values are provided in parentheses. High-resolution mass spectrometry using electrospray ionization (HRMS (EI+)) was conducted for the synthesized monomers on a Micromass Quattro Ultima triple quadrupole mass spectrometer using positive ion mode. Elemental analyses were also conducted for the synthesized monomers using

a Thermo Flash EA1112 elemental analyzer equipped with a CHN reactor and O reactor. The samples were weighed out on a Mettler-Toledo MX5 balance prior to elemental analysis. Polymer molecular weight and polydispersity index (PDI) were estimated by size exclusion chromatography (SEC) using a Waters 2695 separations module equipped with a Waters 2414 refractive index detector and four Polymer Labs PLgel individual pore size columns, with 5 μm bead size and pore sizes of 100, 500, 10^3, and 10^5 Å, kept at 40 °C. Polystyrene standards were used for calibration, and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min.

General Procedure for Polymer Synthesis Using Nitroxide-Mediated Polymerization (NMP). A flame-dried round-bottom flask was charged with *p*-carborane styrene monomer (**7**) (1.03 g, 3.95×10^{-3} mol) in chlorobenzene (1.2 mL) under argon. Alkoxyamine initiator (**5**) (0.018 g, 4.8×10^{-5} mol), along with a catalytic amounts of the free nitroxide radical (**8**) (0.3 mL of a 9 mM solution in chlorobenzene, 2.4×10^{-6} mol), and acetic anhydride (8.2 μL, 8.6×10^{-5} mol) were added to the flask charged with monomer **7**. The solution was degassed under N_2 for 1 h and heated to 125 °C for 7 h. The polymer was precipitated from methanol as a white solid and recovered by filtration through a glass fritted funnel. The collected solid was dried in a vacuum oven overnight to give **9** as a white powder: 0.9 g (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.2−1.5 (br, ∼364 H, $-CH_2CHPh$), 2.1−2.5 (br, ∼274 H, $-CHCH_2$), 2.5−2.7 (br, ∼228 H, $-CH_2C(BH)_{10}$), 2.7−2.9 (br, ∼180 H, $-CH(BH)_{10}$), 4.5 (m, 2 H, $-CH_2PhCl$), 6.3−6.6 (br, ∼320 H, −Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 40.2 ($-CH_2CHPh$), 44.6 ($-CH_2CHPh$), 58.3 ($-CH_2C(BH)_{10}$), 127.4 ($-CH{=}CCHCH_2$), 129.3 ($-CH{=}CCH_2C(BH)_{10}$), 134.03 ($-CCHCH_2$ and $-CCH_2C(BH)_{10}$). SEC (THF eluent), $M_w = 1.5 \times 10^4$ Da, PDI = 1.06.

General Procedure for Dendronization of Premade Carborane-Loaded Polymer. In a flame-dried round-bottom flask, under an argon atmosphere, [G0]-polymer (**9**) (0.506 g, 3.37×10^{-5} mol) was introduced as a solution in THF (52 mL). The solution was cooled to 0 °C, followed by a slow addition of *n*-BuLi (0.9 mL, 2.2×10^{-3} mol) via a syringe. After 30 min at 0 °C, the solution was warmed up to room temperature, the benzylidene-protected anhydride (**2**) (1.2 g, 2.8×10^{-3} mol) was added, and the reaction mixture was stirred for an extra 8 h at room temperature. The polymer was precipitated from methanol and recovered by filtration through a glass fritted funnel. After drying in a vacuum oven overnight, the [G1]-(Bn)-dendronized polymer (**10**) was obtained as a white powder (0.6 g, 87% yield, and ∼70% functionalization). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.8−1.0 (br, ∼176 H, $-CH_3C$), 2.5−2.7 (br, ∼344 H, $-CH_2CH$), 2.7−3.0 (br, ∼385 H, $-CH_2C(BH)_{10}$), 3.5 (br, ∼108 H, $-CH_2OCHPh$), 4.4 (m, 2 H, $-CH_2PhCl$), 4.7 (br, ∼92 H, $-CH_2OCHPh$), 5.4 (br, ∼54 H, $-CHO_2Ph$), 6.1−6.8 (br, ∼320 H, $-PhCH_2C(BH)_{10}$), 7.3 (br, ∼245 H, $-PhCHO_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.5 ($-CH_3C$), 40.2 ($-CH_2CHPh$), 44.6 ($-CH_2CHPh$), 49.7 ($-CH_2C(BH)_{10}$), 73.5 ($-CH_2OCHPh$), 81.8 ($-CH_2CHPh$), 84.7 ($-CCH_3$), 102.2 ($-CHO_2Ph$), 126.4 ($-CH{=}CCH_2C(BH)_{10}$ and $-CH{=}CH-CCHO_2$), 128.2 ($-CH{=}CH-CCH_2C(BH)_{10}$ and $-CH{=}CCHO_2$), 129.0 ($-CH{=}C-CH_2C(BH)_{10}$ and $-CH{=}CH-CH{=}CCHO_2$), 137.7 ($-CCHCH_2$ and $-CCHO_2$), 193.6 ($-COC(OCH_2)_2CH_3$). SEC (THF eluent), $M_w = 1.8 \times 10^4$ Da, PDI = 1.15.

General Procedure for the Pd-Catalyzed Deprotection of the Benzylidene Protecting Group. A round-bottom flask was charged with the first-generation protected carborane polymer, [G1]-(Bn)-CPS (**10**) (0.505 g, 2.81×10^{-5} mol), and dissolved in a 1:1 mixture of CH_2Cl_2:methanol. Subsequently, PdOH/C (20%) was added, and the flask was evacuated and backfilled with H_2 three times. The flask was fitted with a H_2-filled balloon, and the reaction mixture was stirred vigorously overnight at room temperature. The catalyst was removed by filtration through a plug of celite and washed with methanol. The filtrate was evaporated to dryness on a rotary evaporator in vacuo, yielding the desired product as a white foam in quantitative yield (0.47 g, 99%).

General Procedure for Acid-Catalyzed Deprotection of the Benzylidene Protecting Group. Because of the equilibrium between the benzaldehyde (or benzaldehyde dimethylacetal) generated as a deprotection byproduct and the benzylidene protected dendrons, a small percentage (<10%) of benzylidene groups usually remained after Pd-catalyzed hydrogenolysis. Therefore, the product was subjected to an acid-catalyzed deprotection to achieve complete removal of the benzylidene group. The partially protected polymer, recovered after the Pd-catalyzed hydrogenolysis (**10**) (0.47 g, 2.61×10^{-5} mol), was dissolved in THF/methanol (4:3 v/v, 100 mL) and transferred to a round-bottom flask. Concentrated sulfuric acid (2% v/v, pH 3) was added to the flask, and the solution was allowed to stir overnight (8−12 h) at room temperature. The excess sulfuric acid was neutralized with a 7 N solution of ammonia in methanol to precipitate ammonium sulfate as a white solid. The precipitate was removed by filtration, and the filtrate was concentrated in vacuo. The viscous liquid was taken up in THF (G1−G2) or in THF/MeOH (9:1) (G3−G4) and filtered to remove any remaining undissolved ammonium sulfate. This was repeated several times until no further salt was observed. Upon evaporation of solvent, the resulting viscous oil was dried under vacuum to give the deprotected dendronized polymer as a white foam in quantitative yield.

General Procedure for the Divergent Growth of Dendrons. A flame-dried round-bottom flask equipped with a magnetic stir bar (under argon atmosphere) was charged with the hydroxyl-terminated dendronized polymer (generations 1−3) in a mixture of CH_2Cl_2/pyridine (3:2). The benzylidene-protected anhydride of bisMPA (**2**) was introduced along with a catalytic amount of 4-(dimethylamino)pyridine (DMAP), and the solution was stirred for 12−72 h at room temperature. Then, 2 mL of water was added, and the reaction was stirred for an extra 18 h to quench the excess unreacted anhydride. The product was isolated by diluting the mixture with CH_2Cl_2 (100 mL) and washing with 1 M $NaHSO_4$ (3 × 100 mL), 10% Na_2CO_3 (3 × 100 mL), and brine (100 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered through a glass fritted funnel. The filtrate was evaporated to dryness on a rotary evaporator in vacuo. The polymer was isolated by precipitation from methanol as a white powder in good yields.

Synthesis of Compound 3. *p*-Dihydroxypropylcarborane (**1**)[20] (2.05 g, 7.7×10^{-3} mol) was introduced to a flame-dried round-bottom flask, equipped with a magnetic stir bar (under an argon atmosphere) and dissolved in CH_2Cl_2:pyridine (5:1, 50 mL). Benzylidene-protected anhydride (**2**) (3.32 g, 7.7×10^{-3} mol) was added, along with a catalytic amount of DMAP (9.40 g, 7.7×10^{-4} mol), and the reaction mixture was stirred overnight at room temperature under argon. The product of the reaction was a statistical mixture of three components, including a monoester, a diester, and the starting material. The crude product was separated by column chromatography (CH_2Cl_2:EtOAc, 9:1) to give **3** as a white powder: 1.78 g (50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.02 (s, 3 H, $-CH_3C$), 1.41 (m, 2 H, $-CH_2CH_2OH$), 1.55 (m, 2 H, $-CH_2CH_2OCO$), 1.75 (m, 4 H, $-CH_2(CH_2)_2OCOC$ and $-CH_2(CH_2)_2OH$), 3.48 (t, 2 H, J = 6.21, $-CH_2OH$), 3.65 (d, 2 H, J = 11.37, $-CH_2OCHPh$), 4.08 (t, 2 H, J = 6.10, $-CH_2OCO$), 4.60 (d, 2 H, J = 11.38, $-CH_2OCHPh$), 5.48 (s, 1H, −CHPh), 7.39 (m, 3H, Ph), 7.42 (m, 2H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.81 ($-CH_3C$), 28.72 ($-CH_2(CH_2)_2OH$ and $-CH_2(CH_2)_2OCO$), 32.47 ($-CH_2CH_2OCO$), 34.18 ($-CH_2CH_2OH$), 42.41 ($-CCH_3$), 61.84 ($-CH_2OH$), 63.80 ($-CH_2OCO$), 73.56 ($-CH_2OCHPh$), 78.22 ($-C(CH_2)_3OH$), 78.86 ($-C(CH_2)_3OCO$), 101.73 ($-CHO_2Ph$), 126.21 ($-CH{=}C-CHO_2$), 128.20 ($-C{=}CH-CH{=}CH$), 128.97 ($-CH{=}(CH)_2$), 137.78 ($CH{=}C\text{-}CHO_2$), 173.78 ($C-CO_2\text{-}(CH_2)_3$). Anal. Calcd C 51.70%; H 7.81%. Found: C 51.98%, H 7.69%. HRMS (EI+) *m/z* calcd for $C_{20}H_{36}B_{10}O_5$ [M+]: 464.6068; found: 464.6105.

[G1]-(Bn)-Dendronized Acrylate Monomer (4). Acryloyl chloride (0.268 mL, 3.30×10^{-3} mol) and Et_3N (0.920 mL, 6.60×10^{-3} mol) were added to a flame-dried round-bottom flask, charged with compound **3** (1.54 g, 3.30×10^{-3} mol) in 10 mL of CH_2Cl_2 under argon. The reaction mixture was stirred for 2 h at

room temperature under argon and monitored by TLC. After completion, the solvent was evaporated in vacuo to give the crude product as a yellow viscous liquid, which was purified by column chromatography (100% DCM) to give the desired acrylate carborane monomer **4** as a colorless oil: 0.827 g (98%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) = 1.0 (s, 3 H, $-CH_3C$), 1.5 (m (br), 4 H, $-CH_2(CH_2)_2OCOCH{=}CH_2$ and $-CH_2(CH_2)_2OCOC$), 1.6 (m (br), 4 H, $-CH_2CH_2OCOCH{=}CH_2$ and $-CH_2CH_2OCOC$), 3.6 (d, 2 H, J = 5.54, $-CH_2OCHPh$), 4.0 (m, 4 H, $-CH_2OCOCH{=}CH_2$ and $-CH_2OCOC$), 4.6 (d, 2 H, J = 5.57, $-CH_2OCHPh$), 5.4 (s, 1 H, $-CHPh$), 5.8 (d, 1 H, J = 5.12, $-CH_2{=}CHCO_2$), 6.1 (dd, 1 H, J = 5.17, $-CH{=}CH_2$), 6.3 (d, 1 H, J = 8.61, $-CH_2{=}CHCO_2$), 7.3 (m, 5 H, $-Ph$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ (ppm) = 17.8 (CH_3-C), 28.5 ($-CH_2(CH_2)_2OCOCH{=}CH_2$ and $-CH_2(CH_2)_2$-OCOC), 34.0 ($-CH_2CH_2OCOCH{=}CH_2$ and $-CH_2CH_2OCOC$), 42.4 ($-CCH_3$), 63.4 ($-CH_2OCOCH{=}CH_2$), 63.8 ($-CH_2OCOC$), 73.5 ($-CH_2OCHPh$), 101.7 ($-CHO_2Ph$), 125.5 ($-CH{=}CH-CH{=}C-CHO_2$), 126.1 ($-C{=}CH-CH{=}CH$), 128.2 ($-CH{=}C-CHO_2$), 128.9 ($-CH{=}C-CHO_2$), 136.1 ($-CH_2{=}CHCO_2$), 137.7 ($-CH_2{=}CHCO_2$), 167.1 ($-CH_2{=}CHCO_2$), 173.7 ($-CH_3CCO_2(CH_2)_3$). Anal. Calcd C 53.26%, H 7.38%. Found: C 53.36%, H 7.54%. LRMS (EI+) m/z calcd for $C_{23}H_{38}B_{10}O_6$ [M+]: 518.65; found: 518.72.

[G1]-(Bn)-Dendronized Acrylate Polymer (6). The alkoxyamine initiator **5** (0.007 g, 1.93×10^{-5} mol), along with catalytic amounts of the free nitroxide radical **8** (0.1 mL of a 9.08 mM solution in chlorobenzene, 9.6×10^{-7} mol), and acetic anhydride (3.30 μL, 3.5×10^{-5} mol) were added to a flame-dried round-bottom flask charged with macromonomer **4** (0.407 g, 7.85×10^{-4} mol) in chlorobenzene (0.4 mL). The solution was degassed under N_2 for 1 h and heated at 125 °C under N_2 for 8 h. The polymer was precipitated from methanol, filtered, and dried in a vacuum oven overnight to give **6** as a white powder: 0.17 g (42%). SEC (THF eluent), $M_w = 2.8 \times 10^5$ Da, PDI (broad) = 2.5.

[G0]-Styrene Monomer (7). *p*-Carborane (3.02 g, 2.1×10^{-2} mol) dissolved in dry THF (150 mL) was introduced in a flame-dried round-bottom flask (under argon atmosphere) equipped with a magnetic stir bar, and the flask was cooled to 0 °C. To this solution, *n*-BuLi (2.5 M) (1.95 mL, 2.1×10^{-2} mol) was added dropwise, and the solution was stirred for 30 min at 0 °C. The solution was allowed to warm to room temperature, followed by a very slow addition of 4-vinylbenzyl chloride (2.93 mL, 2.1×10^{-2} mol) via a syringe. The solution was stirred for 8 h at room temperature and was monitored by TLC analysis. The solvent was subsequently removed by rotary evaporation, and the crude product was purified by silica-packed column chromatography in straight hexanes to yield the monosubstituted *p*-carborane monomer **7** as a white solid (2.70 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.6 (s, {1 H}, $-CH(BH)_{10}$), 2.9 (s, {2 H}, $-CH_2C(BH)_{10}$), 5.25 (d, 1 H, J = 10.81, $-CH_2{=}CHPh$), 5.75 (d, 1 H, J = 17.48, $-CH_2{=}CHPh$), 6.7 (dd, 1 H, J = 17.56, $-CH{=}CH_2$), 6.9 (d, 2 H, J = 8.11, $-CH{=}C-CH{=}CH_2$), 7.3 (d, 2 H, J = 7.95, $-CH{=}C-CH_2C(BH)_{10}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 44.5 ($-CH_2C(BH)_{10}$), 58.4 ($-CH_2{=}CPh$), 113.9 ($-CH_2{=}CPh$), 126.0 ($-CH{=}CCH_2C(BH)_{10}$), 130.0 ($-CH{=}C-CH{=}CH_2$), 136.3 ($-C-CH{=}CH_2$). Anal. Calcd C 50.74%; H 7.74%. Found: C 49.95%, H 7.88%. HRMS (EI+) m/z calcd for $C_{11}H_{20}B_{10}$ [M+]: 260.2568; found: 260.2545.

[G1]-$(OH)_2$-CPS (11). Deprotection of **10** (0.505 g, 2.81×10^{-5} mol) in 20 mL of (1:1) CH_2Cl_2:methanol was carried out, as described in general procedures, for 12 h at room temperature under a H_2 atmosphere, followed by acid-catalyzed deprotection using sulfuric acid in THF/methanol for an extra 12 h at room temperature. For the acid-catalyzed deprotection, to a round-bottom flask charged with **10** (0.500 g, 2.8×10^{-5} mol) in a solution of THF/methanol (4:3 v/v, 100 mL), concentrated sulfuric acid (2% v/v, pH 3) was added, and the solution was stirred overnight at room temperature. The excess sulfuric acid was neutralized with a solution of 7 N ammonia in methanol, and the resulting ammonium sulfate salt was removed following the same method described in general procedures. Upon evaporation of solvent, the resulting viscous oil was dried under vacuum to give polymer **11** as a white foam (0.45 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.1 (br, ~174 H, $-CH_3C$), 2.6−2.7 (br, ~433 H, $-CH_2CHPh$ and $-CHPhCH_2$), 2.7−2.8 (br, ~385 H, $-CH_2C(BH)_{10}$), 3.6 (br, ~115 H, $-CH_2$-OH), 3.96 (br, ~119 H, $-CH_2OH$), 6.0−6.8 (br, ~320 H, $-Ph$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.1 ($-CH_3C$), 29.7 ($-CH_2CHPh$), 40.1 ($-CH_2CHPh$), 44.5 ($-CH_2C(BH)_{10}$), 53.3 ($-CCH_3$), 58.3 ($-CCH_2OH$), 126.3 ($-CH{=}CH-CCH_2(BH)_{10}$), 129.5 ($-CH{=}CH-CCH_2(BH)_{10}$), 134.0 ($-CH{=}CH-CCH_2(BH)_{10}$), 194.1 ($-COCCH_3$). SEC (THF, eluent), $M_w = 1.3 \times 10^4$ Da, PDI = 1.09.

[G2]-$(Bn)_2$-CPS (12). The coupling was carried out, as described in general procedures, using [G1]-$(OH)_2$-CPS (**11**) (0.407 g, 3.13×10^{-5} mol), benzylidene-protected anhydride (**2**) (0.851 g, 1.99×10^{-3} mol), and DMAP (0.25 mL of a 10 mM solution in CH_2Cl_2, 2.5×10^{-6} mol) in a solution of 3:2 CH_2Cl_2/pyridine (25 mL) and stirring for 24 h at room temperature. After quenching, washing, precipitation, and drying, polymer **12** was isolated as a white powder (0.6 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.9 (br, ~403 H, $-CH_3C$, peripheral), 1.2 (br, ~264 H, $-CH_3C$, internal), 2.5−2.7 (br, ~405 H, $-CH_2CH$), 2.7−3.0 (br, ~385 H, $-CH_2C$-$(BH)_{10}$), 3.6 (br, ~264 H, $-CH_2OCHPh$), 4.3 (br, ~116 H, $-CH_2$-$OCHPh$), 4.4 (br, ~136 H, $-CH_2OCHPh$), 4.5 (br, ~242 H, $-CH_2OCHPh$), 5.4 (br, ~120 H, $-CHO_2Ph$), 6.0−6.8 (br, ~320 H, $-PhCH_2C(BH)_{10}$), 7.3 (br, ~190 H, $-PhCHO_2$), 7.4 (br, ~110 H, $-PhCHO_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.6 ($-CH_3C$, peripheral), 23.46 (CH_3C, internal), 42.5 ($-CH_2CHPh$), 53.9 ($-CH_2CHPh$), 58.3 ($-CH_2C(BH)_{10}$), 64.5 ($-CH_2OCHPh$), 73.3 ($-CH_2OCHPh$), 81.8 ($-CH_2CHPh$), 84.54 ($-CCH_3$), 86.35 ($-CCH_3$), 101.7 ($-CHO_2Ph$), 126.2 ($-CH{=}CCH_2C(BH)_{10}$ and $-CH{=}CH-CCHO_2$), 128.1 ($-CH{=}CH-CCH_2C(BH)_{10}$ and $-CH{=}CCHO_2$), 128.8 ($-CH{=}C-CH_2C(BH)_{10}$ and $-CH{=}CH-CH{=}CCHO_2$), 129.3 ($-CH{=}C-CH_2C(BH)_{10}$), 134.1 ($-CH{=}CH-CH{=}CCHO_2$), 137.8 ($-CCHCH_2$ and $-CCHO_2$), 172.9 ($-COC(OCH_2)_2CH_3$, internal), 193.7 ($-COC(OCH_2)_2CH_3$, peripheral). SEC (THF, eluent), $M_w = 2.0 \times 10^4$ Da, PDI = 1.14.

[G2]-$(OH)_4$-CPS (13). Deprotection of **12** (0.510 g, 2.55×10^{-5} mol) in 20 mL of (1:1) CH_2Cl_2:methanol was carried out, as described in general procedures, using both hydrogenolysis and acid-catalyzed deprotection. Polymer **13** was recovered as a white foam (0.3 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.1 (br, ~430 H, $-CH_3C$), 2.6−2.7 (br, ~392 H, $-CH_2CHPh$ and $-CHPhCH_2$), 2.7−3.0 (br, ~385 H, $-CH_2C(BH)_{10}$), 3.5−3.7 (br, ~502 H, $-CH_2OH$), 4.2−4.3 (br, ~198 H, $-CH_2OH$), 6.0−6.8 (br, ~320 H, $-Ph$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 ($-CH_3C$), 17.0 ($-CH_3C$), 29.0 ($-CH_2CHPh$), 40.1 ($-CH_2CHPh$), 44.5 ($-CH_2C(BH)_{10}$), 50.2 ($-CCH_3$), 53.8 ($-CCH_3$), 58.8 ($-CCH_2$-OH), 64.4 ($-CCH_2OH$), 126.5 ($-CH{=}CH-CCH_2(BH)_{10}$), 129.3 ($-CH{=}CH-CCH_2(BH)_{10}$), 134.0 ($-CH{=}CH-CCH_2(BH)_{10}$), 175.4 ($-COCCH_3$), 194.1 ($-COCCH_3$). SEC (THF, eluent), $M_w = 1.6 \times 10^4$ Da, PDI = 1.18.

[G3]-$(Bn)_4$-CPS (14). The coupling was carried out as described in general procedures, using [G2]-$(OH)_4$-CPS (**13**) (0.208 g, 1.30×10^{-5} mol), benzylidene-protected anhydride (**2**) (0.600 g, 1.41×10^{-3} mol), and DMAP (8.2 μL of a solution of 10 mM in CH_2Cl_2, 8.1×10^{-7} mol) in a solution of 3:2 CH_2Cl_2/pyridine (30 mL) and stirring at room temperature for 48 h. Upon quenching, washing, precipitation, and drying, polymer **14** was isolated as a white powder (0.3 g, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.9 (br, ~976 H, $-CH_3C$, peripheral), 1.1 (br, ~486 H, $-CH_3C$, internal), 1.5 (br, ~422 H, $-CH_3C$, internal), 2.7−3.0 (br, ~138 H, $-CH_2C(BH)_{10}$), 3.6 (br, ~521 H, $-CH_2OCHPh$), 3.7 (br, 117 H, $-CH_2OCHPh$), 3.8−4.1 (br, 182 H, $-CH_2OCHPh$), 4.4 (br, ~501 H, $-CH_2OCHPh$), 4.6 (br, ~516 H, $-CH_2OCHPh$), 5.4 (br, ~261 H, $-CHO_2Ph$), 6.0−6.8 (br, ~320 H, $-PhCH_2C(BH)_{10}$), 7.3 (br, ~1008 H, $-PhCHO_2$), 7.4 (br, ~612 H, $-PhCHO_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 ($-CH_3C$, peripheral), 17.0 (CH_3C, internal), 19.0 (CH_3C, internal), 29.0 ($-CH_2CHPh$), 50.8 ($-CH_2CHPh$), 53.8 ($-CH_2CHPh$), 58.0 ($-CH_2C(BH)_{10}$), 64.4 ($-CH_2OCHPh$), 75.0 ($-CH_2OCHPh$), 101.7 ($-CHO_2Ph$), 126.0 ($-CH{=}CCH_2C(BH)_{10}$ and $-CH{=}CH-CCHO_2$), 128.2 ($-CH{=}CH-CCH_2C(BH)_{10}$ and $-CH{=}CCHO_2$), 129.0 ($-CH{=}C-CH_2C$-

$(BH)_{10}$ and $-CH{=}CH-CH{=}CCHO_2$), 134.0 ($-CH{=}CH-CH{=}CCHO_2$), 137.8 ($-CCHCH_2$ and $-CCHO_2$), 172.9 ($-COC(OCH_2)_2CH_3$, internal), 193.7 ($-COC(OCH_2)_2CH_3$, peripheral). SEC (THF, eluent), $M_w = 2.3 \times 10^4$ Da, PDI = 1.15.

[G3]-$(OH)_8$-CPS (15). Deprotection of **14** (0.210 g, 9.13×10^{-6} mol) was carried out, as described in general procedures, using both hydrogenolysis and acid-catalyzed deprotection. For hydrogenolysis, 20 mL of (1:1) CH_2Cl_2:methanol was used with a reaction time of 12 h. After acid-catalyzed deprotection in THF/methanol (4:3 v/v), polymer **15** was recovered as a white foam (0.10 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.1 (br, ~886 H, $-CH_3C$), 1.2 (br, ~764 H, $-CH_3C$), 2.7−2.9 (br, ~325 H, $-CH_2C(BH)_{10}$), 3.6 (br, ~ 1054 H, $-CH_2OH$), 4.1−4.3 (br, ~500 H, $-CH_2OH$), 6.0−6.8 (br, ~320 H, −Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 ($-CH_3C$), 17.0 ($-CH_3C$), 19.0 ($-CH_3C$), 29.0 ($-CH_2$-CHPh), 50.2 ($-CH_2C(BH)_{10}$), 54.0 ($-CCH_3$), 58.0 ($-CCH_2OH$), 64.2 ($-CCH_2OH$), 75.0 ($-CCH_2OH$), 126.2 ($-CH{=}CH-CCH_2$-$(BH)_{10}$), 128.8 ($-CH{=}CH-CCH_2(BH)_{10}$), 129.3 ($-C{=}CH-CH{=}CCH_2(BH)_{10}$), 137.8 ($-CH{=}CH-CCH_2(BH)_{10}$), 172.9 ($-COC$-$CH_3$), 193.7 ($-COCCH_3$). SEC (THF, eluent), $M_w = 1.9 \times 10^4$ Da, PDI = 1.15.

[G4]-$(Bn)_8$-CPS (16). The coupling was carried out, as described in general procedures, using [G3]-$(OH)_8$-CPS (**15**) (0.102 g, 5.37×10^{-6} mol), benzylidene-protected anhydride (**2**) (1.70 g, 3.99×10^{-3} mol), and DMAP (8.1 μL of a 10 mM solution in CH_2Cl_2, 8.1×10^{-7} mol) in a solution of 3:2 CH_2Cl_2/pyridine (50 mL) and stirring for 72 h at room temperature. Upon quenching, washing, precipitation, and drying, polymer **16** was isolated as a white powder (0.16 g, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.9 (br, ~776 H, $-CH_3C$, peripheral), 1.1 (br, ~704 H, $-CH_3C$, internal), 2.7−3.0 (br, ~184 H, $-CH_2C(BH)_{10}$), 3.6 (br, ~800 H, $-CH_2OCHPh$), 4.3 (br, ~873 H, $-CH_2OCHPh$), 4.6 (br, ~679 H, $-CH_2OCHPh$), 5.4 (br, ~464 H, $-CHO_2Ph$), 6.0−6.8 (br, ~320 H, $-PhCH_2C(BH)_{10}$), 7.3 (br, ~1672 H, $-PhCHO_2$), 7.4 (br, ~772 H, $-PhCHO_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 ($-CH_3C$, peripheral), 17.0 (CH_3C, internal), 19.0 (CH_3C, internal), 29.0 ($-CH_2CHPh$), 50.8 ($-CH_2CHPh$), 53.8 ($-CH_2CHPh$), 58.0 ($-CH_2C(BH)_{10}$), 64.4 ($-CH_2OCHPh$), 75.0 ($-CH_2OCHPh$), 101.7 ($-CHO_2Ph$), 126.0 ($-CH{=}CCH_2C(BH)_{10}$ and $-CH{=}CH-CCHO_2$), 128.2 ($-CH{=}CH-CCH_2C(BH)_{10}$ and $-CH{=}CCHO_2$), 129.0 ($-CH{=}C-CH_2C(BH)_{10}$ and $-CH{=}CH-CH{=}CCHO_2$), 134.0 ($-CH{=}CH-CH{=}CCHO_2$), 137.8 ($-CCHCH_2$ and $-CCHO_2$), 172.9 ($-COC(OCH_2)_2CH_3$, internal), 193.7 ($-COC(OCH_2)_2CH_3$, peripheral). SEC (THF, eluent), $M_w = 3.0 \times 10^4$ Da, PDI = 1.18.

[G4]-$(OH)_{16}$-CPS (17). Deprotection was carried out, as described in general procedures, including both hydrogenolysis and acid-catalyzed deprotection, with **16** (0.153 g, 5.10×10^{-6} mol) dissolved in 20 mL of 1:1 CH_2Cl_2:methanol. Polymer **17** was isolated as a white foam (0.12 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.1 (br, ~902 H, $-CH_3C$), 1.2 (br, ~376 H, $-CH_3C$), 1.3 (br, ~294 H, $-CH_3C$), 2.7−2.9 (br, ~326 H, $-CH_2C$-$(BH)_{10}$), 3.6 (br, ~1057 H, $-CH_2OH$), 4.1−4.3 (br, ~656 H, $-CH_2$-OH), 6.0−6.8 (br, ~320 H, −Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 ($-CH_3C$), 17.0 ($-CH_3C$), 19.0 ($-CH_3C$), 29.0 ($-CH_2CHPh$), 50.2 ($-CH_2C(BH)_{10}$), 54.0 ($-CCH_3$), 58.0 ($-CCH_2$-OH), 64.2 ($-CCH_2OH$), 75.0 ($-CCH_2OH$), 101.7 ($-CHO_2Ph$), 126.2 ($-CH{=}CH-CCH_2(BH)_{10}$), 128.8 ($-CH{=}CH-CCH_2(BH)_{10}$), 129.3 ($-C{=}CH-CH{=}CCH_2(BH)_{10}$), 137.8 ($-CH{=}CH-CCH_2$-$(BH)_{10}$), 172.9 ($-COCCH_3$), 193.7 ($-COCCH_3$). SEC (THF, eluent), $M_w = 2.5 \times 10^4$ Da, PDI = 1.16.

[G1]-(Bn)-Functionalized Monomer (18). A solution of monomer **7** (1.51 g, 5.79×10^{-3} mol) in THF (150 mL) was added to a flame-dried round-bottom flask (under argon atmosphere) equipped with a magnetic stir bar, and the flask was cooled to 0 °C. To this solution, *n*-BuLi (2.5 M) (0.54 mL, 5.76×10^{-3} mol) was added dropwise, and the solution was stirred for 1 h at 0 °C. The solution was warmed to room temperature and benzylidene anhydride (**2**) (2.45 g, 5.76×10^{-3} mol) was added. The solution was stirred for an extra 8 h at room temperature. Once TLC analysis showed no further change in the reaction product, the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica (CH_2Cl_2:hexanes, 1:1) to yield the [G1]-(Bn)-functionalized macromonomer **18** as a white solid (1.85 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.9 (s, 3 H, $-CH_3C$), 2.9 (s, 2 H, $-CH_2C(BH)_{10}$), 3.4 (d, 2 H, $J = 5.78$, $-CH_2$-OCHPh), 4.7 (d, 2 H, $J = 5.78$, $-CH_2OCHPh$), 5.2 (d, 1 H, $J = 5.47$, $-cis$-$CH_2{=}CHPh$), 5.4 (s, 1 H, $-CHO_2Ph$), 5.7 (d, 1 H, $J = 8.77$, $-trans$-$CH_2{=}CHPh$), 6.7 (dd, 1 H, $J = 5.44$, $-CH{=}CH_2$), 6.9 (d, 2 H, $J = 4.04$, $-CH{=}C-CH{=}CH_2$), 7.3 (m (br), 7 H, $-PhCH_2C(BH)_{10}$ and $-PhCHO_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.4 ($-CH_3C$), 43.9 ($-CH_2C(BH)_{10}$), 49.7 ($-CCH_3$), 73.5 ($-CH_2OCHPh$), 102.2 ($-CHO_2Ph$), 114.0 ($-CH_2{=}CPh$), 126.3 ($-CH{=}CCH{=}CH_2$), 128.2 ($-CH{=}CCH_2C(BH)_{10}$), 129.9 ($-CH{=}C-CH{=}CH_2$), 136.3 ($-CH_2{=}CPh$), 194.8 ($-COC(OCH_2)_2CH_3$). Anal. Calcd C 59.46%; H 6.94%. Found: C 58.61%, H 7.07%. LRMS (EI+) *m*/*z* calcd for $C_{23}H_{32}B_{10}O_3$ [M+]: 464.33; found: 464.34.

[G1]-(Bn)-CPS (19). The alkoxyamine initiator **5** (0.005 g, 1.35×10^{-5} mol) along with catalytic amounts of the free nitroxide radical **8** (0.1 mL of a 9.08 mM solution in chlorobenzene, 6.7×10^{-7} mol) and acetic anhydride (2.3 μL, 2.4×10^{-5} mol) were added to a flame-dried round-bottom flask charged with macromonomer **18** (0.504 g, 1.21×10^{-3} mol) in chlorobenzene (2.0 mL). The solution was degassed under N_2 for 1 h and heated at 125 °C under N_2 for 7 h. The polymer was precipitated from methanol, filtered, and dried in a vacuum oven overnight to give **19** as a white powder: 0.4 g (80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.8−1.0 (br, ~160 H, $-CH_3C$), 2.5−2.7 (br, ~240 H, $-CH_2CHPh$), 2.7−3.0 (br, ~265 H, $-CH_2C(BH)_{10}$), 3.5 (br, ~112 H, $-CH_2OCHPh$), 4.4 (m, 2 H, $-CH_2OCHPh$), 4.7 (br, ~102 H, $-CH_2OCHPh$), 5.4 (br, ~50 H, $-CHO_2Ph$), 6.1−6.8 (br, ~220 H, $-PhCH_2C(BH)_{10}$), 7.3 (br, ~245 H, $-PhCHO_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.5 ($-CH_3C$), 40.2 ($-CH_2CHPh$), 44.6 ($-CH_2CHPh$), 49.7 ($-CH_2C(BH)_{10}$), 58.4 ($-CH_2CHPh$), 73.5 ($-CH_2OCHPh$), 81.8 ($-CH_2CHPh$), 84.7 ($-CCH_3$), 102.2 ($-CHO_2$-Ph), 126.4 ($-CH{=}CCH_2C(BH)_{10}$ and $-CH{=}CH-CCHO_2$), 128.2 ($-CH{=}CH-CCH_2C(BH)_{10}$ and $-CH{=}CCHO_2$), 129.0 ($-CH{=}C-CH_2C(BH)_{10}$ and $-CH{=}CH-CH{=}CCHO_2$), 137.7 ($-CCHCH_2$ and $-CCHO_2$), 193.6 ($-COC(OCH_2)_2CH_3$). SEC (THF eluent), $M_w = 1.3 \times 10^4$ Da, PDI = 1.08.

[G1]-$(OH)_2$-CPS (20). Deprotection of **19** (0.303 g, 2.3×10^{-5} mol) in 30 mL of (1:1) CH_2Cl_2:methanol was accomplished by hydrogenolysis and acid-catalyzed deprotection as described in general procedures. Polymer **20** was recovered as a white foam (0.26 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.1 (br, ~145 H, $-CH_3C$), 2.7−3.0 (br, ~255 H, $-CH_2C(BH)_{10}$), 3.6 (br, ~108 H, $-CH_2OH$), 3.7 (br, ~98 H, $-CH_2OH$), 6.0−6.8 (br, ~220 H, −Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.1 ($-CH_3C$), 29.7 ($-CH_2CHPh$), 40.1 ($-CH_2CHPh$), 44.5 ($-CH_2C(BH)_{10}$), 53.3 ($-CCH_3$), 58.3 ($-CCH_2OH$), 126.3 ($-CH{=}CH-CCH_2(BH)_{10}$), 129.5 ($-CH{=}CH-CCH_2(BH)_{10}$), 134.0 ($-CH{=}CH-CCH_2(BH)_{10}$). SEC (THF, eluent), $M_w = 9.5 \times 10^3$ Da, PDI = 1.1.

[G2]-$(Bn)_2$-CPS (21). The coupling was carried out, as described in general procedures, using [G1]-$(OH)_2$-CPS (**20**) (0.240 g, 2.53×10^{-5} mol), benzylidene-protected anhydride (**2**) (0.85 g, 1.99×10^{-3} mol), and DMAP (0.23 mL of a 10 mM solution in CH_2Cl_2, 2.25×10^{-6} mol) in a solution of 3:2 CH_2Cl_2/pyridine (25 mL) and stirring at room temperature for 24 h. Upon quenching, washing, precipitation, and drying, polymer **21** was isolated as a white powder (0.33 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.9 (br, ~285 H, $-CH_3C$, peripheral), 1.2 (br, ~128 H, $-CH_3C$, internal), 2.5−2.7 (br, ~235 H, $-CH_2C(BH)_{10}$), 3.6 (br, ~176 H, $-CH_2$-OCHPh), 4.3 (br, ~94 H, $-CH_2OCHPh$), 4.4 (br, ~190 H, $-CH_2$-OCHPh), 4.5 (br, ~102 H, $-CH_2OCHPh$), 5.4 (br, ~88 H, $-CHO_2Ph$), 6.0−6.8 (br, ~220 H, $-PhCH_2C(BH)_{10}$), 7.3 (br, ~280 H, $-PhCHO_2$), 7.4 (br, ~150 H, $-PhCHO_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.6 ($-CH_3C$), 42.5 ($-CH_2CHPh$), 53.9 ($-CH_2CHPh$), 58.3 ($-CH_2C(BH)_{10}$), 64.5 ($-CH_2OCHPh$), 73.3 ($-CH_2OCHPh$), 101.7 ($-CHO_2Ph$), 126.2 ($-CH{=}CCH_2C(BH)_{10}$ and $-CH{=}CH-CCHO_2$), 128.1 ($-CH{=}CH-CCH_2C(BH)_{10}$ and $-CH{=}CCHO_2$), 128.8 ($-CH{=}C-CH_2C(BH)_{10}$ and $-CH{=}CH-CH{=}CCHO_2$), 129.3 ($-CH{=}CH-CH{=}CCHO_2$), 137.8 ($-CH{=}$

CH−CH═CCHO$_2$), 172.9 (−*C*OC(OCH$_2$)$_2$CH$_3$, internal), 193.7 (−*C*OC(OCH$_2$)$_2$CH$_3$, peripheral). SEC (THF, eluent), M_w = 1.6 × 10^4 Da, PDI = 1.1.

[G2]-(OH)$_4$-CPS (22). Deprotection of **21** (0.305 g, 1.91 × 10^{-5} mol) in 30 mL of (1:1) CH_2Cl_2:methanol was carried out by both hydrogenolysis and acid-catalyzed deprotection. Polymer **22** was recovered as a white foam (0.28 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.1 (br, ∼258 H, −CH$_3$C), 2.7−3.0 (br, ∼248 H, −CH$_2$C(BH)$_{10}$), 3.5−3.7 (br, ∼356 H, −CH$_2$OH), 4.2−4.3 (br, ∼188 H, −CH$_2$OH), 6.1−6.8 (br, ∼220 H, −Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 (−*C*H$_3$C), 17.0 (−*C*H$_3$C), 29.0 (−*C*H$_2$CHPh), 50.2 (−*C*H$_2$C(BH)$_{10}$), 53.8 (−*C*CH$_3$), 58.8 (−C*C*H$_2$-OH), 64.4 (−C*C*H$_2$OH), 75.0 (−C*C*H$_2$OH), 129.3 (−*C*═CH−CH═CCH$_2$(BH)$_{10}$), 134.0 (−CH═CH−*C*CH$_2$(BH)$_{10}$). SEC (THF, eluent), M_w = 1.4 × 10^4 Da, PDI = 1.2.

[G3]-(Bn)$_4$-CPS (23). The coupling was carried out, as described in general procedures, using [G2]-(OH)$_4$-CPS (**22**) (0.201 g, 1.44 × 10^{-5} mol), benzylidene-protected anhydride (**2**) (1.0 g, 2.7 × 10^{-3} mol), and DMAP (0.15 mL of a 10 mM solution in CH_2Cl_2, 1.5 × 10^{-6} mol) in a solution of 3:2 CH_2Cl_2/pyridine (25 mL) and stirring at room temperature for 48 h. Upon quenching, washing, precipitation, and drying, polymer **23** was isolated as a white powder (0.30 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.9 (br, ∼508 H, −CH$_3$C, peripheral), 1.1 (br, ∼244 H, −CH$_3$C, internal), 1.5 (br, ∼118 H, −CH$_3$C, internal), 2.7−3.0 (br, ∼242 H, −CH$_2$C(BH)$_{10}$), 3.6 (br, ∼330 H, −CH$_2$OCHPh), 3.7 (br, ∼174 H, −CH$_2$OCHPh), 3.8−4.1 (br, ∼180 H, −CH$_2$OCHPh), 4.4 (br, ∼322 H, −CH$_2$OCHPh), 4.6 (br, ∼180 H, −CH$_2$OCHPh), 5.4 (br, ∼170 H, −CHO$_2$Ph), 6.0−6.8 (br, ∼220 H, −CHO$_2$Ph), 7.3 (br, ∼945 H, −PhCHO$_2$), 7.4 (br, ∼472 H, −PhCHO$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 (−*C*H$_3$C, peripheral), 17.0 (*C*H$_3$C, internal), 19.0 (*C*H$_3$C, internal), 29.0 (−*C*H$_2$CHPh), 50.8 (−CH$_2$*C*HPh), 53.8 (−CH$_2$*C*HPh), 58.0 (−*C*H$_2$C(BH)$_{10}$), 64.4 (−*C*H$_2$OCHPh), 75.0 (−*C*H$_2$OCHPh), 101.7 (−*C*HO$_2$Ph), 126.0 (−*C*H═CCH$_2$C-(BH)$_{10}$ and −*C*H═CH−CCHO$_2$), 128.2 (−*C*H═CH−CCH$_2$C-(BH)$_{10}$ and −*C*H═CCHO$_2$), 129.0 (−CH═*C*−CH$_2$C(BH)$_{10}$ and −*C*H═CH−CH═CCHO$_2$), 134.0 (−*C*H═CH−CH═CCHO$_2$), 137.8 (−*C*CHCH$_2$ and −*C*CHO$_2$), 172.9 (−*C*OC(OCH$_2$)$_2$CH$_3$, internal), 193.7 (−*C*OC(OCH$_2$)$_2$CH$_3$, peripheral). SEC (THF, eluent), M_w = 2.0 × 10^4 Da, PDI = 1.18.

[G3]-(OH)$_8$-CPS (24). Deprotection of **23** (0.203 g, 1.02 × 10^{-5} mol) in 30 mL of (1:1) CH_2Cl_2:methanol was carried out using both hydrogenolysis and acid-catalyzed deprotection as detailed in general procedures. Polymer **24** was recovered as a white foam (0.15 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.1 (br, ∼768 H, −CH$_3$C), 1.2 (br, ∼118 H, −CH$_3$C), 2.7−2.9 (br, ∼238 H, −CH$_2$C(BH)$_{10}$), 3.6 (br, ∼692 H, −CH$_2$OH), 4.1−4.3 (br, ∼522 H, −CH$_2$OH), 6.0−6.8 (br, ∼220 H, −Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 (−*C*H$_3$C), 17.0 (−*C*H$_3$C), 19.0 (−*C*H$_3$C), 29.0 (−*C*H$_2$CHPh), 50.2 (−*C*H$_2$C(BH)$_{10}$), 54.0 (−*C*CH$_3$), 58.0 (−C*C*H$_2$OH), 64.2 (−C*C*H$_2$OH), 75.0 (−C*C*H$_2$OH), 101.7 (−*C*HO$_2$-Ph), 126.2 (−*C*H═CH−CCH$_2$(BH)$_{10}$), 128.8 (−CH═*C*H−CCH$_2$-(BH)$_{10}$), 129.3 (−*C*═CH−CH═CCH$_2$(BH)$_{10}$), 137.8 (−CH═CH−*C*CH$_2$(BH)$_{10}$), 172.9 (−*C*OCCH$_3$), 193.7 (−*C*OCCH$_3$). SEC (THF, eluent), M_w = 1.7 × 10^4 Da, PDI = 1.23.

[G4]-(Bn)$_8$-CPS (25). The coupling was carried out, as described in general procedures, using [G3]-(OH)$_8$-CPS (**24**) (0.150 g, 8.82 × 10^{-6} mol), benzylidene-protected anhydride (**2**) (1.7 g, 3.97 × 10^{-3} mol), and DMAP (88.0 μL of a 10 mM solution in CH_2Cl_2, 8.8 × 10^{-7} mol) in a solution of 3:2 CH_2Cl_2/pyridine (30 mL) and stirring at room temperature for 72 h. Upon quenching, washing, precipitation, and drying, polymer **25** was isolated as a white powder (0.18 g, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.9 (br, ∼1025 H, −CH$_3$C, peripheral), 1.1 (br, ∼455 H, −CH$_3$C, internal), 1.5 (br, ∼105 H, −CH$_3$C, internal), 2.7−3.0 (br, ∼245 H, −CH$_2$C(BH)$_{10}$), 3.6 (br, ∼612 H, −CH$_2$OCHPh), 4.3 (br, ∼625 H, −CH$_2$OCHPh), 4.4 (br, ∼598 H, −CH$_2$OCHPh), 4.6 (br, ∼438 H, −CH$_2$OCHPh), 5.4 (br, ∼298 H, −CHO$_2$Ph), 6.0−6.8 (br, ∼220 H, −PhCH$_2$C(BH)$_{10}$), 7.3 (br, ∼1640 H, −PhCHO$_2$), 7.4 (br, ∼1298 H, −PhCHO$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 (−*C*H$_3$C, peripheral), 17.0 (*C*H$_3$C, internal), 19.0 (*C*H$_3$C, internal), 29.0 (−*C*H$_2$CHPh), 50.8 (−CH$_2$*C*HPh), 53.8 (−CH$_2$*C*HPh), 58.0 (−*C*H$_2$C(BH)$_{10}$), 64.4 (−*C*H$_2$OCHPh), 75.0 (−*C*H$_2$OCHPh), 101.7 (−*C*HO$_2$Ph), 126.0 (−*C*H═CCH$_2$C(BH)$_{10}$ and −*C*H═CH−CCHO$_2$), 128.2 (−*C*H═CH−CCH$_2$C(BH)$_{10}$ and −*C*H═CCHO$_2$), 129.0 (−CH═*C*−CH$_2$C(BH)$_{10}$ and −*C*H═CH−CH═CCHO$_2$), 134.0 (−*C*H═CH−CH═CCHO$_2$), 137.8 (−*C*CHCH$_2$ and −*C*CHO$_2$), 172.9 (−*C*OC(OCH$_2$)$_2$CH$_3$, internal), 193.7 (−*C*OC(OCH$_2$)$_2$CH$_3$, peripheral). SEC (THF, eluent), M_w = 2.9 × 10^4 Da, PDI = 1.23.

[G4]-(OH)$_{16}$-PSC (26). Deprotection was carried out, as described in general procedures, using both hydrogenolysis and acid-catalyzed deprotection, with **25** (0.151 g, 5.21 × 10^{-6} mol) in 30 mL of (1:1) CH_2Cl_2:methanol. Polymer **26** was recovered as a white foam (0.10 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.1 (br, ∼895 H, −CH$_3$C), 1.2 (br, ∼674 H. −CH$_3$C), 1.3 (br, ∼90 H, −CH$_3$C), 2.7−2.9 (br, ∼218 H, −CH$_2$C(BH)$_{10}$), 3.6 (br, ∼1200 H, −CH$_2$OH), 4.1−4.3 (br, ∼895 H, −CH$_2$OH), 6.0−6.8 (br, ∼220 H, −Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 16.0 (−*C*H$_3$C), 17.0 (−*C*H$_3$C), 19.0 (−*C*H$_3$C), 29.0 (−*C*H$_2$CHPh), 50.2 (−*C*H$_2$C-(BH)$_{10}$), 54.0 (−*C*CH$_3$), 58.0 (−C*C*H$_2$OH), 64.2 (−C*C*H$_2$OH), 75.0 (−C*C*H$_2$OH), 101.7 (−*C*HO$_2$Ph), 126.2 (−*C*H═CH−CCH$_2$(BH)$_{10}$), 128.8 (−CH═*C*H−CCH$_2$(BH)$_{10}$), 129.3 (−*C*═CH−CH═CCH$_2$-(BH)$_{10}$), 137.8 (−CH═CH−*C*CH$_2$(BH)$_{10}$), 172.9 (−*C*OCCH$_3$), 193.7 (−*C*OCCH$_3$).

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