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Synthesis and Characterization of Homopolymers and Copolymers Containing *closo*-$[B_{12}H_{12}]^{2-}$ Boron Cage Derivatives

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Abstract: New $[B_{12}H_{12}]^{2-}$ boron cage functionalized neutral and ionic methacrylate and styrene monomers (**1**, **2**, **3**) were synthesized and these monomers were used to prepare homopolymers (**4**, **5**, **6**) and copolymers with methylmethacrylate (MMA) (**7**, **8**), 2-hydroxyethylmethacrylate (HEMA) (**11**, **12**, **13**, **17**), 2-hydroxyethylacrylate (HEA) (**14**, **15**, **18**), acrylamide (AA) (**16**), and styrene (**9**, **10, 19**) with different monomer ratios. Free-radical initiated bulk and solution polymerization methods were used to synthesize these polymers and they were characterized by ^{1}H NMR, ^{11}B NMR, and IR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). Generally, the polymers show broad ^{1}H NMR and ^{11}B NMR peaks compared to their respective monomers. The copolymers have high molecular weights with higher $[B_{12}H_{12}]^{2-}$ boron cage mole ratios. All the polymers on which DSC experiments were conducted (**4b**, **5b**, **6b**, **7**, **8**, **9**, **10**, **17**, **18**, and **19**) are non-glassy amorphous solids, except styrene copolymers (**9**, **19**) and homopolymer (**6b**) which show T_g values of 100, 117, and 162 °C, respectively. Copolymers **9** and **10** have higher thermal stability (320 °C) than polymers **5b**, **4b**, and **8**, which are stable up to 244, 250, and 260 °C, respectively. The homopolymers retained more weight than the copolymers when they were heated to 400 °C.

Keywords: boron · dodecahydroborate · inorganic polymers · polymers

Introduction

Interest in polymers containing boron cage compounds ($C_2B_{10}H_{12}$ (carboranes), $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$) derives from their stability towards acids/bases and their very high thermal stability.[1] These polymers have potential applications as neutron shields,[2] pre-ceramic materials (heat shield),[3] microwave-absorbing materials,[4] cation exchangers,[5] and in boron neutron capture therapy (BNCT).[6] A carborane carboxylic acid copolymer was used in extreme UV lithography (EUV) to improve oxygen etch resistance to the EUV material.[7] A number of siloxane-based carborane-containing polymers have been studied[15] because the polymers maintain elastomeric properties while gaining thermal stability from the carborane. Keller and co-workers[3c,16b,c] have prepared a series of these polymers (siloxane-acetylene-carborane) in different ratios. It was found that a siloxyl-diacetylene-ferrocenylene-carboranyl polymer is converted to a thermoset at 350 °C, and it converts to a ferromagnetic ceramic material upon heating to 1000 °C.[16k] The same group have reported that a cured siloxane-diacetylene-carborane polymer showed a very high oxidative stability up to 1000 °C. Most of the boron-cage containing polymers reported so far are derived from a carborane unit.

For economic reasons, carborane-containing polymers have not been widely applicable. Different polymerization methods have been used to make these carborane-containing polymers. Condensation, anionic, cationic, radical, grafting,[4b] plasma[8] polymerizations methods have been applied. Carborane-cage-containing polyesters,[9] polyamides,[10] polyacrylates,[11] polyepoxides,[12] polyetherketones,[13] polystyrenes,[14] polysiloxanes,[15] polyurethanes,[16] polyureas,[17] polyhydrazides,[18] polyoxadiazoles,[19] polyalkenes,[20] and polyalkynes[21] have been reported. These polymers were

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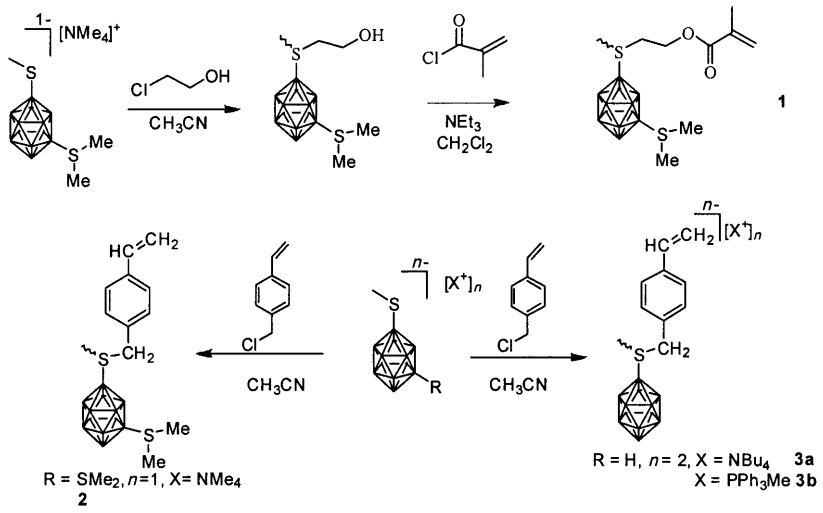
prepared by homopolymerization of the carborane monomer or copolymerization of carborane with non-carborane monomers or copolymerization of different functional groups of carborane monomers. Recently, oligomers of carborane made by gaseous ionization of *o*-carborane to form four *o*-carborane-containing clusters have been reported.[22]

Herein, we present a new form of boron-cage-containing polymers prepared from a dimethyl sulfide derivative of the *closo*-$[B_{12}H_{12}]^{2-}$ cage.[23] An advantage of dimethyl sulfide derivatives of *closo*-$[B_{12}H_{12}]^{2-}$ over carboranes is that the cage compound *closo*-$[1,7\text{-}\{(CH_3)_2S\}_2B_{12}H_{10}]$ is prepared from the borane dimethyl sulfide complex (BH_3Me_2S) in one step and in good yield. Preparation of carboranes involves multistep procedures and their commercially available precursor (decaborane) is expensive. We have prepared one new *closo*-$[B_{12}H_{12}]^{2-}$ cage containing methacrylate ($[(1\text{-}MeSCH_2CH_2OC(O)C(Me)=CH_2)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$) and two new styrene ($[(1\text{-}(MeS\text{-}CH_2\text{-}Ph\text{-}CH=CH_2)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ and $[NBu_4][1\text{-}(MeS\text{-}CH_2\text{-}Ph\text{-}CH=CH_2)B_{12}H_{11}]$ (**3**)) derivatives of the *closo*-$[B_{12}H_{12}]^{2-}$ cage. We employed these monomers to synthesize homopolymers and copolymers. The copolymerization was carried out with methylmethacrylate (MMA), 2-hydroxyethylmethacrylate (HEMA), 2-hydroxyethylacrylate (HEA), acrylamide (AA), and styrene (St).

Results and Discussion

Alkylation of prochiral methylthioethers $[NMe_4]_2[1\text{-}MeSB_{12}H_{11}]$ and $[NMe_4][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ yields a racemic mixture.[24] The precursor to monomer **1** ($[1\text{-}MeSCH_2CH_2OH)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$) (Scheme 1) was synthesized by the nucleophilic substitution reaction of $[NMe_4][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ and 2-chloroethanol according to the method of Shore and co-workers.[25] Methacrylate monomer **1** was prepared by the esterification of the alcohol ($[1\text{-}(MeSCH_2\text{-}CH_2OH)\text{-}7\text{-}(Me_2S)\text{-}B_{12}H_{10}]$) with methacryolylchloride in dichloromethane in the presence of triethylamine (Scheme 1). The white powder was unstable at room temperature. In fact, after chromatographic separation (after the polymerization inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added), the white powder turned to yellow when it was left at room temperature overnight. The color change is most likely due to air oxidation of the fine powder instead of polymerization. This color change was prevented by crystallizing the white powder right after chromatography and storing it in a refrigerator at 4 °C. Styrene monomer **2** and ionic styrene monomers **3a/3b** were prepared by the nucleophilic substitution reaction of $[NMe_4][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ and $[(NBu_4]_2[1\text{-}(MeS)B_{12}H_{11}]/[(PPh_3Me)]_2[1\text{-}(MeS)B_{12}H_{11}]$ with 4-vinylbenzyl chloride, respectively (Scheme 1). Monomers **1** and **2** were characterized by ^1H NMR, ^{11}B NMR, ^{13}C NMR, and IR spectroscopy, as well as MS-EI and single-crystal X-ray crystallography. Monomer **3a** was characterized by ^1H NMR, ^{11}B NMR, and IR spectroscopy, as well as MS-ESI, and **3b** was characterized by single-crystal X-ray crystallography in addition to ^1H NMR, ^{11}B NMR, and IR spectroscopy as well as MS-ESI. The methylene protons next to the sulfur are diastereotopic as evidenced from the ^1H NMR spectrum, which shows two separate multiplets at $\delta = 3.10/3.43$ ppm (for **1**) and $\delta = 3.83/4.34$ ppm (for **2** and **3**). A single crystal of **1** suitable for X-ray crystallography was obtained by diffusion of hexane solvent into dichloromethane solutions of **1.** The crystal is triclinic, space group $P\bar{1}$. In **1**, there is only one type of independent molecule (one enantiomer) in the unit cell. Thus the two enantiomers crystallized in different unit cells giving a mixture of racemates of **1**. The two methyl groups on S2 are disordered and their geometry as shown in the molecular structure is approximate (Figure 1).

Single crystals for **2** were obtained in the same way as those of **1** (diffusion of hexane solvent into dichloromethane solutions of **2**). The crystal is triclinic, space group $P\bar{1}$. The unit cell of **2** contains two independent racemic enantiomers. Unlike **1**, the racemates of **2** crystallize in the same unit cell (Figure 2). Crystallization was unsuccessful when using tetrabutylammonium as the cation of **3a**. To obtain a single crystal, the tetrabutylammonium cation was replaced by triphenylmethylphosphonium cation. Monomer **3b** was obtained from the reaction of $[(PPh_3Me)]_2[1\text{-}(MeS))B_{12}H_{11}]$ with 4-vinylbenzyl chloride, which initially formed the triphenylmethylphosphonium salt of **3a** (Figure 3). Colorless crystals of **3b** were obtained by diffusion of toluene into a dichloromethane solution of **3b**. There is only one type of inde-



Scheme 1. Synthesis of monomers **1**, **2**, and **3**.

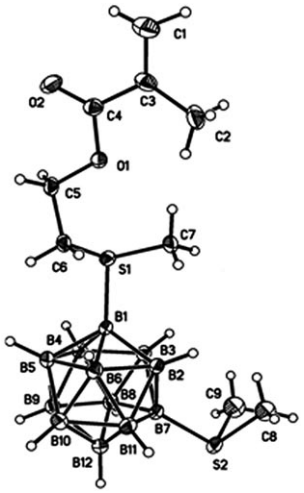


Figure 1. ORTEP plot of the molecular structure of **1** (25% thermal ellipsoids).

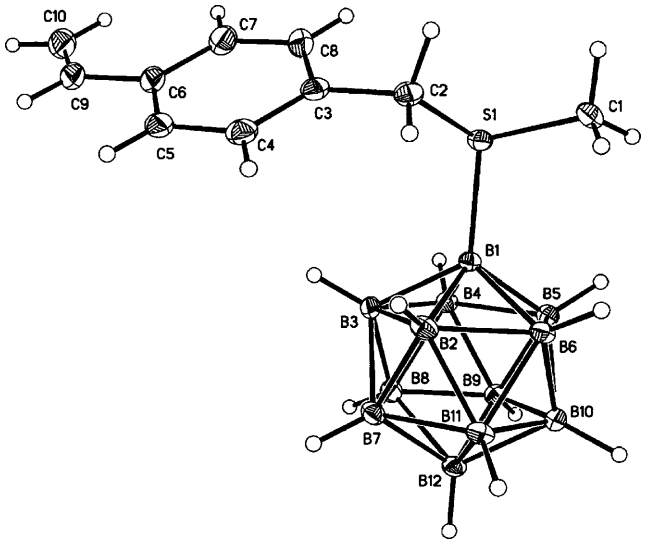


Figure 3. ORTEP plot of the molecular structure of the anionic part **3** (25% thermal ellipsoids).

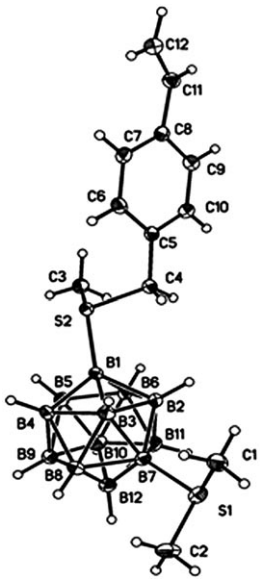


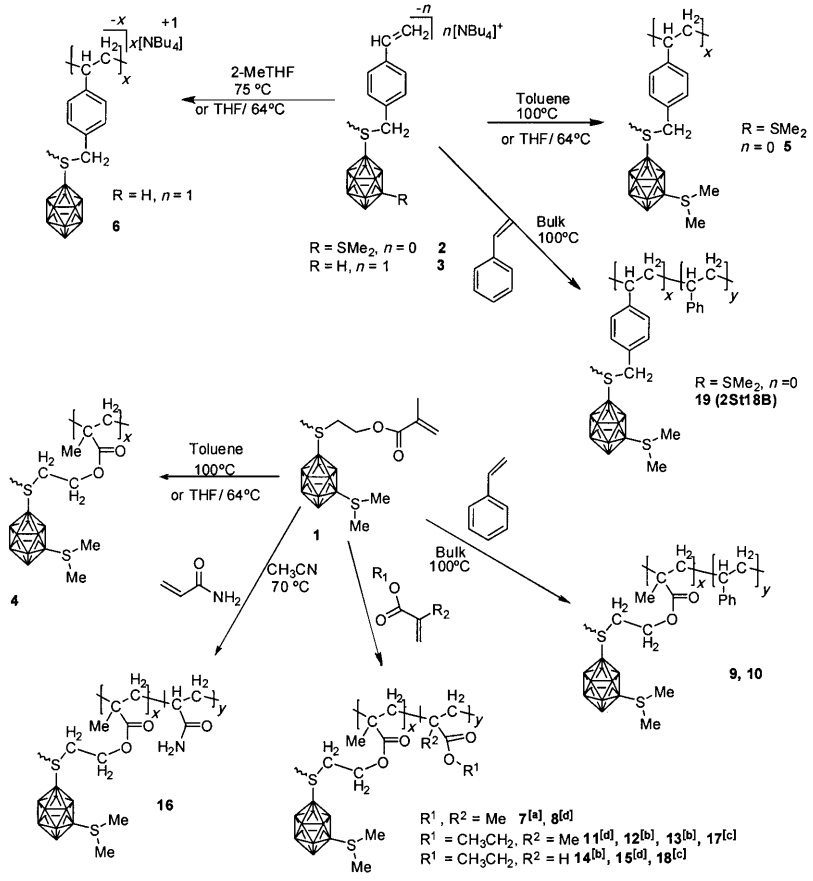
Figure 2. ORTEP plot of the molecular structure of **2** (25% thermal ellipsoids).

pendent molecule (enantiomer) in the unit cell of **3b** and like monomer **1**, **3b** crystallizes as a mixture of racemates. The methacrylate unit on **1** forms approximately 3/4 of a circle parallel to B1–B12 axis starting from C7 (on S1) to C2 (Figure 1). The B–B bond lengths in **1** range from 1.753(5) to 1.816(5) Å. The vinyl bond (CH_2=C) of **1** was differentiated from the single bond (CH_3–C) by its shorter bond length (1.325(5) Å ((CH_3–C)= 1.472 Å)). The X-ray crystal structure (Figure 2) of **2** shows the vinyl benzyl group pointing away from the B_{12} cage (parallel to B1–B12 axis). Selected bond lengths and angles for **1**, **2**, and **3b** are given in Table S2 in the Supporting Information.

The bond lengths of the vinyl double bond in **2** and **3b** are 1.312(4) and 1.305(7) Å, respectively, which are shorter than the vinyl bond length in the methacrylate monomer **1** (1.325(5) Å). The B–B bond lengths range from 1.744(4) to 1.812(4) Å in **2** and from 1.754(6) to 1.802(6) in **3**. Unlike **2**, the molecular structure of **3b** (Figure 3) reveals that the vinylstyrene group is bent (perpendicular to the B1–B12 axis). Structural data including bond length and bond angle tables are available in the Supporting Information. The unit cell of **3** contains two disordered toluene molecules (see the Supporting Information).

All polymerizations employed AIBN (2,2′-azo-bis(isobutyronitrile) as a radical initiator. Copolymerization of the B_{12} cage containing monomers (**1** or **2**) with MMA, HEMA, AA, and styrene monomers were performed by bulk (whenever the B_{12} monomer can dissolve in the low molecular weight monomers) or solution polymerization (where both B_{12} and small molecular weight monomers can dissolve in a suitable solvent; Scheme 2). The molecular weights of the polymers are given in Table 1.

Homopolymers **4a**, **5a**, and **6a** were synthesized by radical-initiated polymerization of **1** and **2** in toluene, and **3** in 2-methyl-THF, respectively. Polymers **4a** and **5a** formed solid materials and were isolated by filtration, whereas **6a** stuck to the glass vessel as a gel. After the solvent was evaporated, it was scraped from the glass. The ^{1}H NMR or ^{1}H{^{11}B} NMR spectra are provided in the Results and Discussion section of the Supporting Information. The ^{11}B NMR resonances of **4a**/**4b** at $\delta = -10.5$ ppm (B1 and B7) and the three boron resonances that are centered at −15 ppm (B2–B6, B8–B12) (Figure 4) for monomer **1** are not observed for polymer **4a**/**4b** due to signal broadening. The same types of homopolymers (**4b**, **5b**, **6b**) were synthesized at 64 °C in THF, and resulted in smaller molecular weight distributions (PDI 1.27, 2.69, 2.45, respectively). An oily polymer material started to come out of the solution after 1 h for **4b** and **5b**, whereas the polymer **6b** comes out of the solution after 3 h. The proton NMR spectra of **4b**, **5b**, and **6b** are the same as **4a**, **5a**, and **6a** except for a slight change in the chemical shifts attributed to NMR solvent differences. From the GPC chromatograms, **4b** and **6b** show a bimodal distribution (see the Supporting Information), and homopolymer **5b** shows two peaks clustered together. The reason **5b** shows closely clustered peaks in the light scattering peak compared to **4b** and **6b** might be due to the fact that it is less polar than **4b** and **6b** (**4b** has polar methacrylic groups and **6b** has a polar cationic tetrabutylammonium group).



Scheme 2. Synthesis of polymers. [a] Bulk polymerization at 100 °C. [b] Bulk polymerization at 80 °C. [c] Polymerization in toluene at 100 °C. [d] Polymerization in toluene at 80 °C.

Methacrylate monomer **1** and various mole ratios of MMA (1:18), MMA (1:2), HEMA (1:3), HEA (1:3) were polymerized in toluene to form the respective copolymers **8**, **17**, and **18**. After polymerization, the mole ratio of the monomers in the polymer was found to be 1:18 (**7**), 1:1 (**8**), 1:2 (**17**), and 1:3 (**18**) (from ^{1}H NMR integration ratios). Copolymer **7** is soluble in chloroform and THF. In the proton NMR spectra of **17** and **18** (Figure 5), the hydroxyl group shifted downfield (4.83 ppm) due to hydrogen bonding with the polar NMR solvents (DMF or DMSO). The GPC plot of **17** (Figure 6) shows a bimodal distribution. The IR spectra of these copolymers show the absence of a vinyl stretching frequency of the acrylate unit and strong bands at 1726 and 2520 cm^{-1}, which were assigned to carbonyl and B–H stretches, respectively.

Three B_{12}-cage-containing styrene copolymers were prepared by bulk polymerization of **1** with styrene (**9**, **10**) or **2** with styrene (**19**). All three polymer products **9**, **10**, and **19** form transparent polymer solids. The ^{1}H NMR spectra (Figure 7) of **9** and **10** show polymerized styrene polymer peaks (δ = 6.3–7.5 ppm, Ar^{CH} and δ = 1–1.9 ppm, CH), B–H protons and thiomethyl protons of **1**. The proton signals that belong to the S-CH_2CH_2O unit of copolymers **9** and **10** are not observed. These proton signals were observed when MMA, HEMA or HEA were used as a co-monomer with **1**. The reason why the S-CH_2CH_2O proton signals in **9** and **10** were not observed might be due to the formation of micelles. But when **1** is replaced with **2** as shown in the ^{1}H NMR spectrum (Figure 7) of polymer **19**, the diastereotopic S-CH_2 peaks are visible (δ = 4.19 and 3.68 ppm).

Copolymers **11**, **12**, **13**, **14**, and **15** were prepared by bulk and/or solution polymerization of **1** and non-B_{12} boron cage monomers (HEMA, HEA). Polymer **16** was prepared by solution polymerization of **1** and acrylamide. Results and Discussion for these copolymers are provided in the Supporting Information.

Differential scanning calorimetry (DSC) of the polymers (**4b**, **5b**, **6b**, **7**, **8**, **10**, **9**, **19**, and **18**) was carried out. From the DSC experiment, polymers **4b**, **5b**, **7**, **8**, **10**, and **18** were found not to melt or undergo a glass transition up to 200 °C. Polymers **5b**, **4b**, and **8** are stable

Table 1. Summary of monomers used, solvent, and polymer molecular weights.

Monomer(s), Ratio (mol)	Solvent	Polymer, Ratio[a]	M_N, M_W, PDI (GPC solvent)
1	THF	**4b**	90750, 116000, 1.27 (DMF[b])
2	THF	**5b**	4260, 11470, 2.69 (DMF[b])
3	THF	**6b**	9600, 23600, 2.45 (DMF[b])
1+MMA, 1:18	bulk	**7**, 1:18	45000, 89000, 1.98 (THF)
1+MMA, 1:2	toluene	**8**, 1:1	85300, 346000, 4.06 (DMF[b])
1+styrene, 1:17	bulk	**9**, 1:17	12000, 33000, 2.72 (THF)
1+styrene, 1:7	bulk	**10**, 1:7	165000, 723000, 4.4 (DMF[b])
1+HEMA, 1:14	toluene	**11**	partially soluble
1+HEMA, 1:14	bulk	**12**	insoluble
1+HEMA, 1:28	bulk	**13**	partially soluble
1+HEA, 1:16	bulk	**14**	partially soluble
1+HEA, 1:16	toluene	**15**	partially soluble
1+AA, 1:25	acetonitrile	**16**	partially soluble
1+HEMA, 1:3	toluene	**17**, 1:2	19050, 48100, 2.52 (DMF[b])
1+HEA, 1:3	toluene	**18**, 1:3	67720, 561000, 8.3 (DMF[b])
2+styrene, 1:18	bulk	**19**, 1:18	9342, 34500, 3.69 (THF)

[a] Ratio of monomers in the polymer (mol). [b] 10 mM LiCl in DMF.

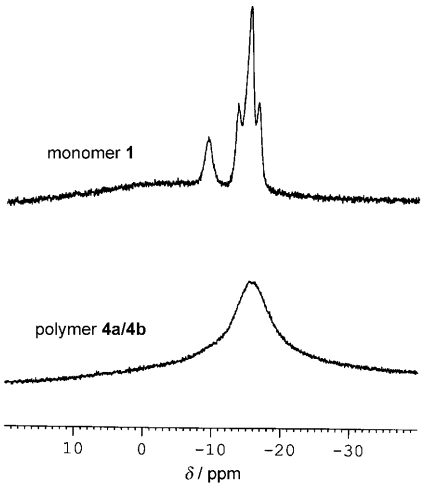


Figure 4. $^{11}B\{^1H\}$ NMR spectra of monomer **1** and polymer **4a**/**4b**.

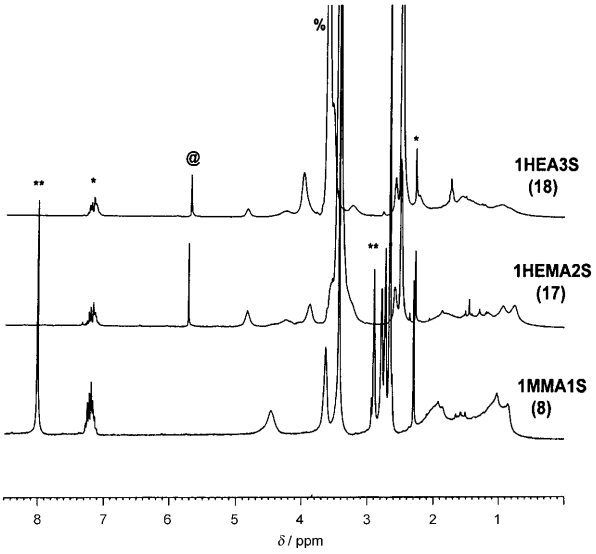


Figure 5. Top: ^1H NMR spectrum of **18** in $[D_6]$DMSO; middle: ^1H NMR spectrum of **17** in $[D_6]$DMSO; bottom: ^1H NMR spectrum of **8** in $[D_7]$DMF. * = toluene, @ = CH_2Cl_2, ** = DMF, % = H_2O.

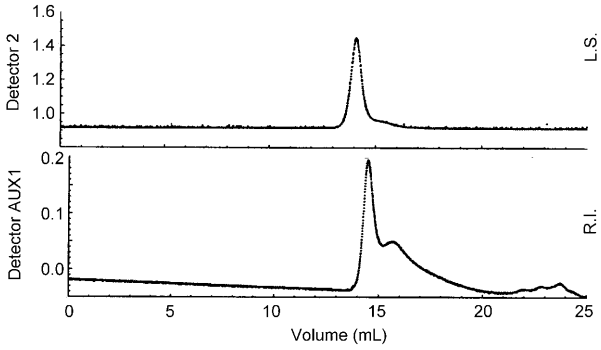


Figure 6. GPC curve of **17** showing bimodal distribution (V_0 = 13.5 mL, V_t = 27.6 mL). There is a 0.5 mL difference in elution volume for the two detectors.

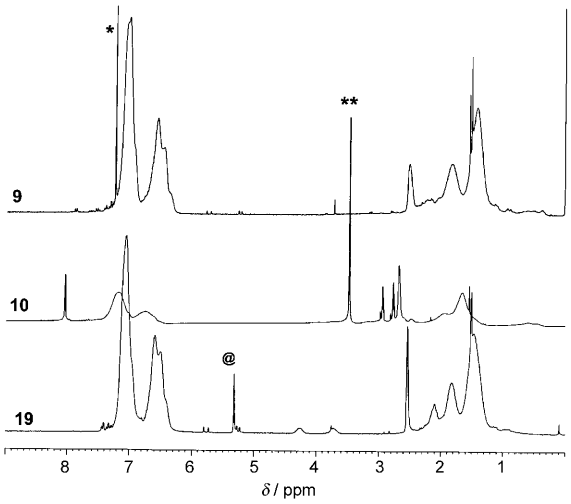


Figure 7. Top: ^1H NMR spectrum of **9** in $CDCl_3$; middle ^1H NMR spectrum of **10** in $[D_7]$DMF; bottom: ^1H NMR spectrum of **19** in CD_2Cl_2. * = $[D_7]$DMF, ** = H_2O, @ = CD_2Cl_2.

up to 244, 250, and 260 °C, respectively (see Supporting Information for the DSC thermograms). Polymers **9**, **19**, and **6b** show a glass transition at 100, 117, and 162 °C, respectively (Figure 8 and Table 2). The reason the glass transition increased for **19** and **6b** compared with polystyrene or **9** is that the copolymer is random and the bulky B_{12} cages stiffen the polymer chains making it more difficult for the chain to undergo conformational changes, that is, increased T_g. A detailed discussion on the DSC is provided in the Results and Discussion section in the Supporting Information.

Thermogravimetric analyses of the polymers were carried out under an argon atmosphere at a rate of 5 °C per minute from room temperature to 400 °C. The TGA thermograms are shown in Figures 9 and 10, and in the Supporting Information. The color of the polymers changed from white to black after the heating phase. Generally, the copolymers retain less weight percentage than the homopolymers. Even

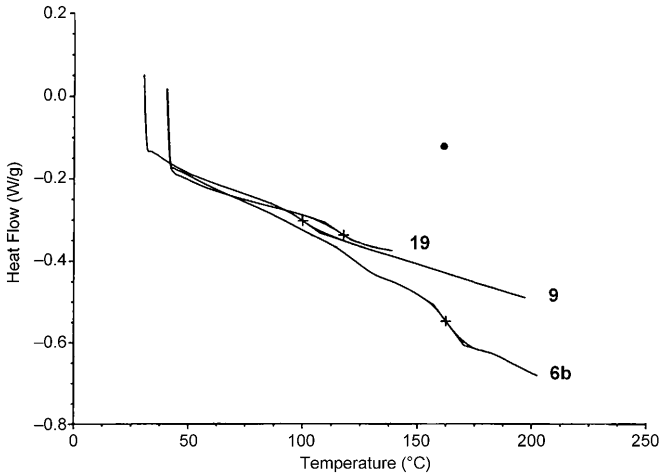


Figure 8. DSC showing glass transition temperatures for **6b**, **19**, and **9**.

Table 2. Summary of data for DSC and TGA experiments.

Polymer	Monomer, D[a]	Ratio[b]	T_g [°C]	$T_{D,I}$ [°C][c]	wt %[d]	T_{MD} [°C][e]
4b	**1**, MMA	1:0	–[f]	275	78	275
5b	**2**, St	1:0	–[f]	260	91	230
6b	**3**, St	1:0	162	–	–	–
7	**1**+MMA	1:18	–[f]	–	36	297
8	**1**+ MA	1:1	–	285	69	275
9	**1**+St	1:17	100	–	45	321
10	**1**+St	1:7	–[f]	–	67	323
19	**2**+St	1:18	117	–	51	300

[a] Homopolymer derivatives (styrene or MMA). [b] B_{12} to non-B_{12} ratio in the polymer. [c] Temperature of decomposition isotherm. [d] % weight retention. [e] Temperature of main chain degradation. [f] No glass transition observed.

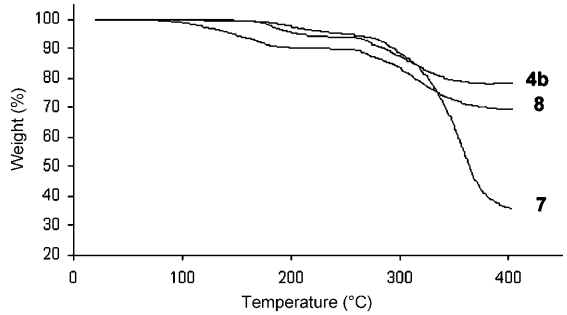


Figure 9. TGA curves for **4b**, **8**, and **7**.

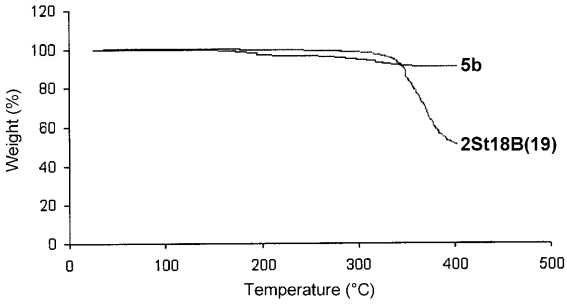


Figure 10. TGA curves for **5b** and **19**.

though the methacrylate homopolymers retain more weight than the copolymers after heating to 400 °C, their main chain starts to degrade at lower temperature than the copolymers with a higher percentage of non-B_{12} cage (MMA) monomer units. The TGA data for the polymers is given in Table 2 and more discussion is provided in the Supporting Information.

Conclusions

Monomers containing functionalized *closo*-$[B_{12}H_{12}]^{2-}$ cages were synthesized and used to synthesize various homopolymers and copolymers. In general, the molecular weight of the copolymers increases as the proportion of B_{12} cages increases. The polymers for which DSC experiments were carried out (**4b**, **5b**, **6b**, **7**, **8**, **9**, **10**, **19**, **17**, and **18**) are amorphous. The T_g value of the styrene chain polymers (**9**, **19**, **6b**) increases as the proportion of B_{12} cages (**1** or **2**) increases. The presence of a methacrylate-containing B_{12} cage monomer unit (**1**) in styrene copolymers (**10** and **9**) increased the thermal stability compared to that obtained for a styrene-containing B_{12} cage copolymer (**19**) and homopolymer **5b**. However, the thermal stability decreased as the ratio of methacrylate-containing B_{12} cage monomer (**1**) increased in MMA chain polymers (**7**, **8**, and **4b**). When heated to 400 °C, the styrenic homopolymer (**5b**) retains more weight than the methacrylic homopolymer (**4b**), and the copolymers retain less weight than the homopolymers.

Experimental Section

General methods: All reagents were purchased from Aldrich unless noted otherwise. 2-Chloroethanol, 4-vinylbenzyl chloride, 2,2′-azo-bis(isobutyronitrile) (AIBN), Na_2SO_4, and acrylamide were used without further purification. Monomers methylmethacrylate (MMA), 2-hydroxyethylmethacrylate (HEMA), 2-hydroxyethylacrylate (HEA), and styrene were distilled just before use. DMF was dried from 4 Å molecular sieves, and acetonitrile and dichloromethane were dried over P_2O_5. The solvents toluene, THF, and 2-methyl-THF were dried over sodium/benzophenone ketyl and transferred over a high vacuum line before use. $[NMe_4][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$, and $[(NBu_4)]_2[1\text{-}(MeS)B_{12}H_{11}]$/$[(PPh_3Me_4)]_2[(1\text{-}(MeS)B_{12}H_{11}]$ were prepared by reduction of $[1\text{-}(Me_2S)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ and $[(SMe_3)][1\text{-}(Me_2S)B_{12}H_{11}]$ by potassium phthalimide in refluxing DMF, respectively.[24] TLC was done on a silica gel thin layer plate, and a methanol solution of palladium chloride or iodine vapor was used as stain. All chromatographic separations were performed on a Selecto silica gel (230–430 mesh), which was purchased from Fisher Scientific. ^1H, ^{13}C, and ^{11}B NMR spectra were obtained on a Bruker DPX-250 or DPX-400 spectrometers at 250.1/400.1 MHz, 62.9/100.6 MHz, and 80.25 MHz for DPX-250, respectively. Boron spectra were externally referenced to $BF_3{\cdot}OEt_2$ in C_6D_6 ($\delta = 0$ ppm). Molecular weights were determined by using a Shimadzu 10, a GPC (gel permeation chromatography) system with a refractive index and light scattering detectors. The molecular weights and polydispersity indices were determined by importing the text files of the chromatograms into ASTRA software. First the autobaseline was done on the chromatograms from both detectors and the respective peaks were selected. After the amount of sample injected was entered into the ASTRA software, a report of molecular weights and polydispersity indices was generated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. Mass spectra were recorded on Micromass QTOF electrospray (ESI) or Micromass VG-70 EI spectrometers. Differential scanning calorimetry measurements were performed on DSC Q100 TA instrument (Wilmington, DE). Thermogravimetric analyses were performed with a Perkin–Elmer TGA 7 analyzer with a TAC 7/DS thermal analysis instrument controller, and samples were loaded on a platinum crucible. Elemental analyses were obtained from Galbraith Laboratories.

Single-crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffraction system by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A single crystal of **1**, **2**, and **3b** was mounted on the tip of a glass fiber coated with Fomblin oil (a pentafluoropolyether). Unit cell parameters were obtained by indexing the peaks in the first ten frames and were refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO-SMN package (Nonius BV, 1999).[26] Absorption correction for the structures was accounted for by using SCALEPACK. All non-hydrogen atoms were located and refined anisotropically. All hydrogen atoms connected to boron were located on difference maps and their positional and isotropic thermal parameters were refined. All other hydrogen atom positions were calculated by assuming standard geometries. A

satisfactory disorder model was not obtained for structure **2** due to a large peak close to the S1 atom. In structure **3**, two seriously disordered toluene solvent molecules are present in the unit cell (detailed information is provided in the Supporting Information). CCDC-696969 (**1**), CCDC-696970 (**2**), and CCDC-696971 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Monomer synthesis

Synthesis of [1-MeSCH$_2$CH$_2$OC(O)C(Me)=CH$_2$)-7-(Me$_2$S)B$_{12}$H$_{10}$] (1)

Synthesis of monomer precursor [1-MeSCH$_2$CH$_2$OH)-7-(Me$_2$S)B$_{12}$H$_{10}$]: 2-Chloroethanol (0.54 g, 6.7 mmol) was added to a solution of [NMe$_4$][1-(MeS)-7-(Me$_2$S)B$_{12}$H$_{10}$] (0.95 g, 2.94 mmol) in acetonitrile (30 mL). The reaction mixture was stirred at 60 °C for five days, and the acetonitrile was evaporated to give a yellow residue. The yellow residue was partitioned between dichloromethane and water (30 mL, 1:1) and the dichloromethane layer was separated. The remaining aqueous layer was extracted once more with dichloromethane (30 mL). The dichloromethane layers were combined and dried over anhydrous Na_2SO_4, filtered, and dichloromethane evaporated to give a yellow oil. The pure product was isolated as a white solid by column chromatography on a silica gel column. The pure product was a white solid (yield, 0.56 g, 65 %). M.p. 104–105 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 4.11 (m, 2H, CH_2O), 3.37 (dt, 1H, J = 13.9, 4.58 Hz, CH_2S), 3.04 (m, 1H, CH_2S), 2.67 (s, 3H, MeS), 2.57 (s, 6H, Me_2S), 2.24 ppm (t, J = 4.7 Hz, 1H, OH); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): δ = 59.04 (CH_2OH), 45.49 (CH_2S), 25.69 (Me_2S), 24.76 ppm (MeS); MS (ESI): m/z calcd ($C_5H_{24}S_2O_1B_{12}Na_1$) 317.2361 [$M$+Na]$^+$, found (317.2364).

[(1-MeSCH$_2$CH$_2$OC(O)C(Me)=CH$_2$)-7-(Me$_2$S)B$_{12}$H$_{10}$] (1): Triethylamine (0.35 g, 3.46 mmol) was added to a solution of [(1-MeSCH$_2$CH$_2$-OH)-7-(Me$_2$S)B$_{12}$H$_{10}$] (0.62 g, 2.11 mmol) in dichloromethane (30 mL). To the mixture was added methacryolylchloride (0.26 g, 2.49 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for 5 h in the dark. After 5 h, the reaction mixture was extracted with water (25 mL), HCl (0.048 M), water (20 mL), saturated $NaHCO_3$ (20 mL), and brine (20 mL). The dichloromethane layer was separated, and the aqueous layer extracted once more with dichloromethane. The dichloromethane layer was dried over anhydrous Na_2SO_4, filtered, and then the dichloromethane evaporated to give a thick oil (yield, 0.76 g, 82 %). It was purified by chromatography on a silica gel column. M.p. 115–116 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 6.12 (q, J = 1.27 Hz, 1H, C=CH_2), 5.66 (quintet, J = 1.58 Hz, 1H, C=CH_2), 4.50 (m, 2H, CH_2O), 3.43 (m, 1H, CH_2S), 3.10 (m, 1H, CH_2S), 2.61 (s, 3H, MeS), 2.52 ppm (s, 6H, Me_2S), 1.94 dd, J = 1.58, 1.1 Hz, 3H, MeC=); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): δ = 166.84 (C=O), 135.89 (C=), 126.06 (CH_2=), 59.92 (CH_2O), 42.54 (CH_2S), 25.96 (MeS), 24.45 (Me_2S), 18.33 ppm (CH_3); ^{11}B NMR (80 MHz, $CDCl_3$, 25 °C) δ = −8.2 (s), −12.8 (s), −15.3 (d), −16.6 ppm (d); MS (EI): m/z calcd ($C_9H_{28}S_2O_2B_{12}$) 362.2714, found 362.2717.

[(1-(MeS-CH$_2$-Ph-CH=CH$_2$))-7-(Me$_2$S)B$_{12}$H$_{10}$] (2): 4-Vinylbenzylchloride (0.16 g, 1.05 mmol) was added to a solution of [NMe$_4$][1-(MeS)-7-(Me$_2$S)B$_{12}$H$_{10}$] (0.3 g, 0.93 mmol) in acetonitrile (15 mL). A white solid (NMe$_4$Cl) precipitated after 30 min of stirring. It was further stirred for 16 h, the acetonitrile was evaporated under vacuum, and the residue was extracted from dichloromethane/water (1:1). The dichloromethane layer was dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated to give a light yellow oil (yield, 0.29 g, 86 %). It was purified by column chromatography on a silica gel column. M.p. 104–105 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.42 (d, J = 8.21 Hz, 2H, CH^{Ar}), 7.24 (d, J = 8.21 Hz, 2H, CH^{Ar}), 6.74 (dd, J = 16.11, 10.51 Hz, 1H, CH), 5.77 (d, 1H, J = 17.22 Hz, CH_2), 5.31 (d, 1H, J = 10.91 Hz, CH_2), 4.34 (d, J = 13.58 Hz, 1H, CH_2S), 3.82 (d, J = 13.43 Hz, 1H, CH_2S), 2.54 (s, 6H, Me_2S), 2.30 ppm (s, 3H, MeS); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): δ = 22.16 (MeS), 25.73 (Me_2S), 47.46 (CH_2S), 115.58 (CH_2=), 127.18, 129.95 (CH^{Ar}), 129.73 (C^{Ar}), 135.71 (CH=), 138.75 ppm (C^{Ar}); ^{11}B NMR (80 MHz, $CDCl_3$, 25 °C): δ = −9.14 (s), −13.49 (s), −15.15 (d), −16.36 ppm (d); MS (EI): m/z calcd ($C_{12}H_{28}S_2B_{12}$) 366.2816, found 366.2744.

Synthesis of [NBu$_4$][1-(MeS-CH$_2$-Ph-CH=CH$_2$) B$_{12}$H$_{11}$] (3a): 4-Vinylbenzyl chloride (0.33 g, 2.16 mmol) was added to a solution of [NBu$_4$]$_2$[1-(MeS)B$_{12}$H$_{11}$] (1.31 g,1.95 mmol) in acetonitrile (35 mL). It was further stirred for 20 h and the acetonitrile was evaporated. The residue was extracted from dichloromethane/water (1:1). The dichloromethane layer was separated and dried over anhydrous sodium sulfate. The solvent (CH_2Cl_2) was filtered and evaporated to give a light yellow semi-solid (yield, 0.94 g, 88 %). It was purified by column chromatography on a silica gel column. M.p. 157–158 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.39 (d, 2H, J = 8.22 Hz, CH^{Ar}), 7.24 (d, 2H, J = 8.21 Hz , CH^{Ar}), 6.6 (dd, 1H, J = 17.7, 10.55 Hz, CH), 5.66 (d, J = 17.7 Hz, 1H, CH_2), 5.27 (d, J = 10.9 Hz, 1H, CH_2), 4.29 (d, J = 13.59 Hz, 1H, CH_2S), 3.76 (d, J = 13.58 Hz, 1H, CH_2S), 3.12 (m, 8H, CH_2N), 2.29 (s, 3H, MeS), 1.6 (m, 8H, CH_2), 1.5 (m, 8H, CH_2), 1.01 ppm (t, J = 7.27 Hz, 12H, CH_3); ^{11}B NMR (80 MHz, $CDCl_3$, 25 °C): δ = −14.2 (d), −15.9 ppm (d); MS (ESI): m/z calcd ($C_{10}H_{23}SB_{12}$) 305.2733, found 305.2717.

Synthesis of [PPh$_3$Me][1-(MeS-CH$_2$-Ph-CH=CH$_2$)B$_{12}$H$_{11}$] (3b): 4-Vinylbenzyl chloride (0.42 g, 2.75 mmol) was added to a solution of [PPh$_3$Me]$_2$[1-(MeS)B$_{12}$H$_{11}$] (1.94 g, 2.62 mmol) in acetonitrile (35 mL). It was further stirred overnight and the acetonitrile was evaporated. The residue was extracted from dichloromethane/water (1:1). The dichloromethane layer was separated and dried over anhydrous sodium sulfate. The solvent (CH_2Cl_2) was filtered and evaporated to give a light yellow semi-solid (yield, 1.4 g, 93 %). It was purified by column chromatography on silica gel column. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.66–7.91 (m, 15H, CH$^{Ar(PPh_3Me)}$), 7.39 (d, 2H, J = 8.22 Hz, CH^{Ar}), 7.24 (d, 2H, J = 8.21 Hz, CH^{Ar}), 6.6 (dd, 1H, J = 17.7, 10.55 Hz, CH), 5.66 (d, J = 17.7 Hz, 1H, CH_2), 5.27 (d, J = 10.9 Hz, 1H, CH_2), 4.29 (d, J = 13.59 Hz, 1H, CH_2S), 3.76 (d, J = 13.58 Hz, 1H, CH_2S), 2.87 (d, 3H, J_{H-P} 14 Hz, Me-P), 2.18 ppm (s, 3H, MeS); ^{11}B NMR (80 MHz, $CDCl_3$, 25 °C): δ = −14.2 (d), −15.9 ppm (d).

Polymer synthesis

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethyl-methacrylate) (4a): AIBN (0.000251 g) was added to a solution of **1** (0.025 g, (0.069 mmol) in toluene (1 mL). The solution was heated at 100 °C for 16 h. The white solid formed was isolated by vacuum filtration and was washed with toluene and dichloromethane to give **4a**. ^{1}H-{^{11}B} NMR (250 MHz, [D$_7$]DMF, 25 °C): δ = 4.55 (brs, 2H, CH_2O), 3.43 (brs, 2H, CH_2S), 2 (v br) (brs, CH_2), 2.72 (brs, 6H, Me_2S), 2.63 (brs, 3H, MeS), 1.45 (brs, 10H, BH), 1.05, 1.21 ppm (brs, CH_3); ^{11}B NMR (80 MHz, [D$_7$]DMF, 25 °C): δ = −10.5 (sh), −15.2 (brs), −16.8 (d), −17.9 ppm (d); GPC (DMF, 40 °C): M_N = 97010 g mol^{-1}, polydispersity index (PDI) 3.55.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethyl-methacrylate) (4b): THF (2 mL) was added to a mixture of (0.1 g, 0.276 mmol) of **1** and AIBN (0.0028 g). The reaction mixture was stirred at 64 °C. An oily substance separated after 1 h. The solution was stirred for 20 h at 64 °C, cooled, and the THF was decanted. The oily residue was washed with THF (2×5 mL) and the THF evaporated under vacuum to give **4b** as a white solid. ^{1}H{^{11}B} NMR (250 MHz, [D$_6$]DMSO, 25 °C): δ = 4.33 (brs, 2H, CH_2O), 3.31 (brs, 2H, CH_2S), 2.65 (brs, 6H, Me_2S), 2.54 (brs, 3H, Me_2S), 1.47 (brs, 10H, BH), 1.03, 0.85 ppm (brs, CH_3); GPC (DMF, 10 mM LiCl, 70 °C): M_N = 90750 g mol^{-1}, PDI = 1.23.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfido-4′-methylstyrene) (5a): The synthetic procedure for **4a** was used for the synthesis of **5a** (see Supporting Information). ^{1}H NMR (250 MHz, [D$_7$]DMF, 25 °C): δ = 7.1–7.5 (brs, 2H, CH^{Ar}), 6.5–6.9 (brs, 2H, CH^{Ar}), 4.25–4.5 (brs, 1H, CH_2S), 3.85–4.2 (brs, 1H, CH_2S), 2.71 (brs, 6H, Me_2S), 2.25–2.5 ppm (br, CH_2 + MeS); ^{1}H{^{11}B} NMR (250 MHz, [D$_7$]DMF, 25 °C, TMS): δ = 1.6 ppm (brs, 10H, BH); ^{11}B NMR (80 MHz, [D$_7$]DMF, 25 °C): δ = −9.2 (brs), −15.8 ppm (brs); GPC (DMF, 10 mM LiCl, 40 °C): M_N = 1.98 x10^3 g mol^{-1}, PDI = 11.4.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfido-4′-methylstyrene) (5b): The synthetic procedure for **4b** was used for the synthesis of **5b** (see Supporting Information). ^{1}H {^{11}B} NMR (250 MHz, [D$_6$]DMSO, 25 °C): δ = 7.5 (brs, 2H, CH^{Ar}), 6.6 (brs, 2H, CH^{Ar}), 4.27 (brs, 1H, CH_2S), 4.01 (brs, 1H, CH_2S), 2.54 (brs, 6H, Me_2S), 2.32 (brs,

MeS), 1.53 ppm (brs, 10H, BH); GPC (DMF, 10 mM LiCl, 70°C): M_N = 4260 g mol^{-1}, PDI = 2.69.

Poly(tetrabutylammonium)(undecahydrododecaborane-1-methylsulfido-4′-methylstyrene (6a): AIBN (0.0002 g) was added to a solution of **3** (0.018 g, 0.033 mmol) in 2-methyl-THF (1 mL), and the solution was heated slowly to 75°C. It was heated for 6 h at 75°C. An oily substance stuck to the wall of the glassware. The 2-methyl-THF was decanted and the oily substance was washed with more 2-methylTHF. The oily substance was dried at 80°C and a white solid was isolated (**6a**). ^{1}H NMR (250 MHz, CD_3CN, 25°C): δ = 6.7–7.2 (brs, 2H, CH^{Ar}), 6.15–6.7 (brs, 2H, CH^{Ar}), 3.95–4.4.45 (brs, 1H, CH_2S), 3.5–3.9 (brs, 1H, CH_2S), 3.03 (m, 8H, CH_2N), 2–2.25 (br m, 3H, MeS), 1.51 (m, 8H, CH_2), 1.25 (q, 8H, CH_2), 0.96 ppm (t, 12H, CH_3); ^{11}B NMR (80 MHz, $CDCl_3$, 25°C): δ = −14.2 (d), −15.9 ppm (d); GPC (DMF, 10 mM LiCl, 70°C): M_N = 3.98 x10^4 g mol^{-1}, PDI = 15.54.

Poly(tetrabutylammonium)(undecahydrododecaborane-1-methylsulfido-4′-methylstyrene (6b): The synthetic procedure of **4b** was used for the synthesis of **6b** (see Supporting Information). ^{1}H{^{11}B} NMR (250 MHz, $[D_6]$DMSO, 25°C): δ = 7.48 (brs, 2H, CH^{Ar}), 6.46 (brs, 2H, CH^{Ar}), 4.21 (brs, 1H, CH_2S), 3.82 (brs, 1H, CH_2S), 3.17 (brs, 8H, CH_2N), 2.22 (br m, 3H, MeS), 1.58 (brs, 8H, CH_2), 1.32 (brs, 8H, CH_2), 1.16 (s, 11H, BH), 0.95 ppm (brs, 12H, CH_3); GPC (10 mM LiCl in DMF, 70°C) M_N = 9600 g mol^{-1}, PDI = 2.45.

Poly(7-dimethylsulfido)decahydrodecaborane-1-methylsulfidoethylmethacrylate-co-methylmethaylacrylate) (7): Monomer **1** (0.0762 g, 0.21 m mol) was dissolved in MMA (0.38 g, 3.8 mmol) and AIBN (0.005 g) was added. The solution was heated at 100°C for 17 h to form a transparent solid (**7**). ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ = 4.34 (brs, 2H/18, CH_2O), 3.62 (brs, 3H, CH_3O), 3.15 (brs, 1H/18, CH_2S), 3.4 (brs,, 1H/18, CH_2S), 2.65 (brs, 3H/18, MeS), 2.57 (brs, 6H/17.5, Me_2S), 1.6–2.1 (br, 2H, CH_2), 0.87, 1.043 ppm (brs, 3H, CH_3); ^{11}B NMR (80 MHz, $CDCl_3$, 25°C): δ = −9.8 (br), −16 ppm (br); IR (KBr): $\tilde{\nu}$ = 2997.9, 2952.16 ((C–H)aliphatic), 2523.2 (B–H), 1734.30 cm^{-1} (C=O); GPC (THF, 40°C): M_N = 45 000 g mol^{-1}, PDI = 1.98.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-methylmethacrylate) (8): Monomer **1** (0.042 g, 0.112 mmol) and MMA (0.025 g, 0.25 mmol) were dissolved in toluene (1 mL) and the solution was heated at 80°C in the presence of AIBN (0.0008 g) for 16 h. The white solid that precipitated was washed with toluene and dried under vacuum (**8**). ^{1}H NMR (250 MHz, $[D_7]$DMF, 25°C): δ = 4.39 (brs, 2H, CH_2O, 3.55 (brs, 3H, CH_3O), 3.35 (brs, 2H, CH_2S), 2.70 (brs, 3H, MeS), 2.65 (brs, 6H, Me_2S), 1.7–2.2 (br, 4H, CH_2), 0.78, 0.94 ppm (brs, 6H, CH_3); ^{11}B NMR (80 MHz, $[D_7]$DMF, 25°C): δ = −9.3 (sh), −14.9 ppm (brs); IR (KBr): $\tilde{\nu}$ = 2994, 2949 (CH_2, CH_3), 2519.8 (s, B–H), 1731 cm^{-1} (s, C=O); GPC (DMF, 10 mM LiCl, 70°C): M_N = 8.53 × 10^4 g mol^{-1}, PDI = 4.06.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-styrene) (9): Monomer **1** (0.05 g, 0.14 mmol) was added to styrene (0.25 g, 2.4 mmol) followed by AIBN (0.003 g). The solution was heated at 100°C for 16 h to give a transparent solid (**9**). ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ = 6.6–7.1 (brs, CH^{Ar}), 6.15–6.6 (br, CH^{Ar}), 2.40 (brs, Me_2S + MeS), 1.5–1.9 (brs, CH), 1.1–1.5 ppm (brs, CH_2); ^{11}B NMR (80 MHz, $CDCl_3$, 25°C): δ = −9.8 (sh), −15.3 ppm (brs); IR (KBr): $\tilde{\nu}$ = 3082, 3059, 3025 cm^{-1} (C–H, aromatic), 2921, 2849 (CH_2, CH, aliphatic), 2517.3 (B–H), 1734.1 cm^{-1} (C=O), 1600.77 cm^{-1} (C=C, aromatic); GPC (THF, DMF, 40°C): M_N = 12 000 g mol^{-1}, PDI = 2.72.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-styrene) (10): The synthetic procedure for **9** was used for the synthesis of **10** (see Supporting Information). ^{1}H NMR (250 MHz, $[D_6]$DMSO, 25°C, TMS): δ = 6.8–7.2 (brs, CH^{Ar}), 6.3–6.7 (br, CH^{Ar}), 2.55 (brs, Me_2S + MeS), 1.7–1.2 (brs, CH), 1.1–1.65 ppm (brs, CH_2); IR (KBr): $\tilde{\nu}$ = 3082, 3059, 3025 (C–H, aromatic), 2925, 2849 (CH_2, CH)), 2517.7 (B–H), 1729 (C=O), 1600 cm^{-1} (C=C, aromatic); GPC (DMF, 10 mM LiCl, 70°C): M_N = 1.65 × 10^5 g mol^{-1}, PDI = 4.38.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-hydroxyethylmethylmethacrylate) (11): HEMA (0.125 g, 0.96 mmol), **1** (0.025 g, 0.069 mmol), and AIBN (0.002 g) were added to toluene (0.5 mL) and the solution was heated at 80°C for 6 h resulting in the formation of a white solid. The white solid was filtered and washed with toluene (**11**). ^{1}H NMR (250 MHz, $[D_6]$DMSO, 25°C, TMS): δ = 4.71 (brs, 1H, OH), 1.78 (brs, 2H, CH_2O), 3.47 (brs, 2H, CH_2C=O), 2.58 (brs, MeS + Me_2S), 1.6–2.1 (brs, 2H, CH_2), 0.66, 0.83 ppm (brs, 3H, CH_3).

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-hydroxyethylmethylmethacrylate) (12): Monomer **1** (0.05 g, 0.134 mmol) and AIBN (0.003 g) were added to HEMA (0.25 g, 1.92 mmol). The solution was heated at 80°C for 18 h to give a white polymer (insoluble polymer) (**12**). IR (KBr): $\tilde{\nu}$ = 3448.6 (br, OH), 2950.6 (C–H), 2524.4 (B–H), 1719.1 cm^{-1} (C=O).

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-hydroxyethylmethylmethacrylate) (13): The synthetic procedure for **12** was used for the synthesis of **13** (see Supporting Information). ^{1}H NMR (250 MHz, $[D_7]$DMF, 25°C, TMS): δ = 4.96 (brs, 1H, OH), 4.45 (brs, 2/15H, CH_2O), 4.07 (brs, 2H, CH_2O), 3.77 (brs, 2H, CH_2C=O), 2.77 (brs, 3H/15, MeS), 2.68 (brs, 6H/15, Me_2S), 2.95–2.2, 1.55–1.7, 1.2–1.35 (br m, CH_2), 0.95, 1.06 ppm (brs, 3H, CH_3); ^{11}B NMR (80 MHz, $[D_7]$DMF, 25°C, $BF_3{\cdot}OEt_2$): δ = −16 ppm (brs); IR (KBr): $\tilde{\nu}$ = 3437 (OH), 2950 (C–H, aliphatic), 2526 (B–H), 1725.8 cm^{-1} (C=O).

Poly(7-(dimethylsulfido)decahydrododecaborane-methylsulfidoethylmethacrylate-co-hydroxyethylmethacrylate) (14): The synthetic procedure for **12** was used for the synthesis of **14** (see Supporting Information). ^{1}H NMR (250 MHz, $[D_7]$DMF, 25°C, TMS): δ = 4.86 (brs, 1H, OH, 4.46 (brs, 2H/15, CH_2O), 4.18 (brs, 2H, CH_2O), 3.74 (brs, 2H, CH_2C=O), 2.785 (brs, 3H/15, MeS), 2.67 (brs, 6H/15, Me_2S), 2.456, 1.959, 1.752 ppm (brs, 2H, CH_2); ^{11}B NMR (80 MHz, $[D_7]$DMF, 25°C): δ = −15.6 ppm (br); IR (KBr): $\tilde{\nu}$ = 3435 (OH), 2954 (C–H) aliphatic), 2523 (B–H)), 1735 cm^{-1} (C=O).

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-hydroxyethylmethacrylate) (15): The synthetic procedure for **11** was used for the synthesis of **15** (see Supporting Information). ^{1}H NMR (250 MHz, $[D_6]$DMSO, 25°C, TMS): δ = 4.75 (brs, 1H, OH), 4.15–4.55 (brs, 2H/15, CH_2O), 3.99 (brs, 2H, CH_2O), 2.66 (brs, MeS + Me_2S), 1.78, 1.57 ppm (brs, 2H, CH_2).

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-acrylamide) (16): Monomer **1** (0.035 g, 0.096 mmol), acrylamide (0.175 g, 2.46 mmol), and AIBN (0.002 g) were added to acetonitrile (1 mL). The solution was heated at 70°C for 4 h. The white solid formed was filtered and washed with acetonitrile (**16**). ^{1}H NMR (250 MHz, $[D_6]$DMSO, 25°C, TMS): δ = 7.07, 6.69 (brs, 2H, NH_2), 4.15 (brs, 2H/15, CH_2O), 2.51 (brs, 6H/15, Me_2S), 1.97, 1.36 ppm (brs, 2H, CH_2); ^{11}B NMR (80 MHz, $[D_6]$DMSO, 25°C): δ = −16.9 ppm (br); IR (KBr): $\tilde{\nu}$ = 3342, 3196 (N–H), 2934 (C–H, aliphatic), 2523 (B–H), 1663 cm^{-1} (br, C=O).

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-hydroxyethylmethylmethacrylate) (17): HEMA (0.0306 g, 0.24 mmol) and **1** (0.0305 g, 0.084 mmol) were dissolved in toluene (0.5 mL) to form a clear solution. AIBN (0.0007 g) was added and the reaction mixture was heated at 100°C for 2 h. A white solid stuck to the surface of the reaction glass. The toluene was decanted, and the white solid was washed with more toluene and dichloromethane and then dried. The white solid was isolated by scraping it from the glass (**17**). ^{1}H NMR (250 MHz, $[D_6]$DMSO, 25°C, TMS): δ = 4.83 (brs, 1H, OH), 4.15–4.5 (brs, 2H/2, CH_2O), 3.91 (brs, 2H, CH_2O), 3.59 (brs, 2H, CH_2O), 3.27 (brs, 2H/2, CH_2S), 2.62 (brs, 3H/2, MeS), 2.52 (brs, 6H/2, Me_2S), 1.65–2.1 (brs, 3H, CH_2a), 0.78, 0.955 ppm (brs, 4.5H, CH_3); ^{11}B NMR (80 MHz, $[D_6]$DMSO, 25°C): δ = −15.2 ppm (brs); IR (KBr): $\tilde{\nu}$ = 3429 (brs, OH), 2938 (CH_2, CH_3), 2520 (B–H), 1726 cm^{-1} (C=O); GPC (DMF, 10 mM LiCl, 70°C): M_N = 19 050 g mol^{-1}, PDI = 2.52.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfidoethylmethacrylate-co-hydroxyethylmethacrylate) (18): The synthetic procedure for **17** was used for the synthesis of **18** (see Supporting Information). ^{1}H NMR (250 MHz, $[D_6]$DMSO, 25°C, TMS): δ = 4.82 (brs, 0.18H, OH), 4.1–4.5 (brs, 2H/3, CH_2O), 4.00 (brs, 2H, CH_2O), 3.59 (brs, 2H, CH_2O), 3.25 (brs, 2H/3, CH_2S), 2.59 (brs, 3H/3, MeS), 2.52 (brs, 6H/3, Me_2S), 1.65–2.1 (brs, 2.67H, CH_2 aliphatic), 0.78, 0.955 ppm (brs, 1H, CH_3); IR (KBr): $\tilde{\nu}$ = 3448 (brs, OH), 2952 (CH_2, CH_3), 2520 (B–H),

1734 cm^{-1} (C=O); ^{11}B NMR (80 MHz, [D_6]DMSO, 25 °C): $\delta = -15.6$ ppm; GPC (DMF, 10 mM LiCl, 70 °C): $M_N = 67720\ g\,mol^{-1}$, PDI = 8.3.

Poly(7-(dimethylsulfido)decahydrododecaborane-1-methylsulfido-4′-methylstyrene-co-styrene (19): The synthetic procedure for **9** was used for the synthesis of **19** (see Supporting Information). ^1H NMR (250 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 6.2$–6.7, 6.8–7.2 (br, 5.3H, CH^{Ar}), 4.19 (br s, 1/18, CH_2S), 3.68 (br s, 1/18, CH_2S), 2.46 (br s, 9/18, Me_2S + MeS), 1.9–2.2, 1.6–1.9, 1.1–1.6 ppm 3H, CH aliphatic); ^{11}B NMR (80 MHz, CD_2Cl_2, 25 °C): $\delta = -9.2$ (sh), -15.2 ppm (t); IR (KBr): $\tilde{\nu} = 3082$, 3058, 3024 (C-H-Ar), 2921, 2848 (C–H, aliphatic), 2517 (B–H), 1601 cm^{-1} ($C–C^{Ar}$); GPC (THF, 40 °C): $M_N = 9342\ g\,mol^{-1}$, PDI = 3.69.

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