Cyclodextrin-Based Hyperbranched Polymers: Molecule Design, Synthesis, and Characterization

Wei Tian, Xiaodong Fan,* Jie Kong, Tao Liu, Yuyang Liu, Yi Huang, Shengjie Wang, and Guobin Zhang

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, P. R. of China

Received October 23, 2008; Revised Manuscript Received December 5, 2008

ABSTRACT: The cyclodextrin (CD) molecule, a host for a variety of smaller molecular guests, and hyperbranched polymers both possess molecule cavities in their molecular architectures. If the hyperbranched poly(β-cyclodextrin)s are established using modified β-CD molecules as monomers, their molecular inclusion capabilities for smaller molecular guests may be enhanced due to the combination of two different molecule cavities from both their hyperbranched topography architecture and CD molecule chain segments. Herein, three types of hyperbranched poly(β-cyclodextrin)s, i.e., HBP-AB_x from AB_x-type β-CD monomers, HBP-(B_y + AB_x) from B_y core molecules and AB_x-type β-CD monomers, and water-soluble HBP-AB_2 from AB_2-type β-CD monomers, were synthesized via hydrosilylation reaction under the thermal or ultraviolet activated polymerization. The hyperbranched structures of resultant poly(β-cyclodextrin)s were characterized using ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, ^{1}H−^{29}Si heteronuclear multiple bond correlation, and size exclusion chromatography/multiangle laser light scattering (SEC/MALLS). The molecule inclusion and recognition behaviors of the novel hyperbranched poly(β-cyclodextrin)s as well as their macromolecular structures, degree of branching, and thermal properties were investigated in detail. UV−vis spectroscopy results show that HBP-AB_2 has molecular inclusion capabilities and also can form inclusion complexation with single or double guests, including phenolphthalein (PP) and methyl orange (MO). Compared with AB_2-type β-CD monomer, the molecular inclusion capability of the hyperbranched polymer was enhanced. Furthermore, HBP-AB_2 presents molecular recognition behavior when MO solution is added into their PP solution.

Introduction

Since hyperbranched polyphenylene was synthesized for the first time by Kim and Webster in 1988,[1a] a variety of hyperbranched polymers were prepared by the single monomer methodology (SMM) or the double monomer methodology (DMM), such as hyperbranched polyethers,[1b] polyesters,[1c] polyamides,[1d] poly(ester−amide)s,[1e] polyacrylates,[1f] poly(ether−ketone)s,[1g] polycarbonates,[1h] polyurethanes,[1i] polycarbosiloxanes,[1j] polysulfones,[1k] and polyarylenes.[1l] To date, hyperbranched polysaccharides have attracted attention due to their unique structures accompanied by specific properties, such as the multivalent or cluster effect on carbohydrate−protein interactions and encapsulation-release properties of unimolecular reversed micelles.[2] Kadokawa et al. reported the synthesis of a hyperbranched polyaminosaccharide by the acid-catalyzed polymerization of an oxazoline sugar with two hydroxyl groups.[2a,b] Satoh et al. presented that the ring-opening multibranching polymerization of latent AB_m-type monomers could be employed to synthesize hyperbranched D-mannan,[2c] hyperbranched poly(2,5-anhydro-D-glucitol),[2d] hyperbranched polytetritols,[2e] hyperbranched D-glucan, and D-galactan.[2g] Furthermore, amphiphilic hyperbranched polysaccharides based on these polymers and their controlled-release property of the encapsulated guest molecules were demonstrated by them.[2i−k]

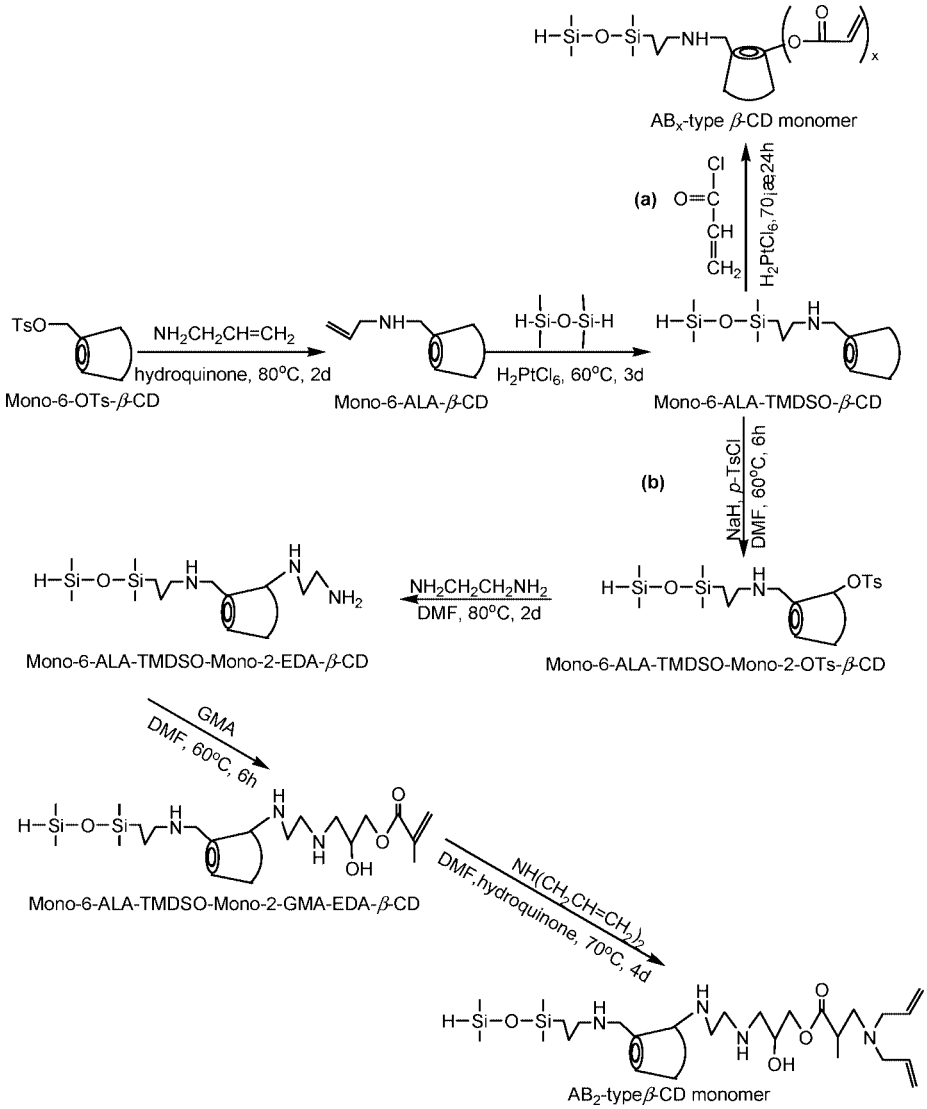
As an important cyclic oligosaccharide composed of glucose units linked by 1,4-R-glycosidic bonds,[3a,b] cyclodextrin (CD) was usually not considered as a candidate monomer for hyperbranched polymer due to the complicated synthetic process.[3c] However, CD-based hyperbranched polymer will possess specific structures and properties merits if it is successfully designed and obtained. (i) Hyperbranched polymers possess special properties such as low viscosities, good solubility, and multifunctional end groups. Especially the molecule cavities of them can form inclusion complexations with guest molecules in their molecular architectures.[4] (ii) CD molecule with a hydrophilic surface with numerous hydroxyl groups and a hydrophobic internal cavity lined with alkyl groups and glycosidic oxygen atoms can act as a host for a variety of smaller molecule guests through noncovalent interactions.[5] (iii) When the combination of two molecular cavities from the hyperbranched polymer and CD molecule is obtained in one polymer chain, molecular inclusion and recognition behaviors of this polymer may be enhanced compared with either CD or hyperbranched polymer depending on their cooperative interaction.[6] (iv) CD-based hyperbranched polymer may possess polysaccharide-like bioactivities due to the introduction of oligosaccharides units. Correlation of structure to bioactivities of polysaccharides is one of the most intriguing and challenging scientific endeavors.[7] If the hyperbranched poly(β-cyclodextrin)s are established using modified β-CD molecules as monomers, their molecular inclusion and recognition capabilities for smaller molecular guests may be enhanced due to the combination of two different molecule cavities from both their hyperbranched topography architecture and CD molecule chain segments. This polymer structure not only possesses some interesting characters in the research of relationship between properties and structure but also may endow some important applications in inclusion technologies and the complex drugs delivery system.

Herein, the novel hyperbranched poly(β-cyclodextrin)s using modified β-CD molecule as monomers are designed for establishing a novel hyperbranched polymer based on our previous studies on hyperbranched polymer,[8] linear β-CD (one of CDs[3a,b]) polymers,[9] and β-CD polymer brushes.[6] Three types of hyperbranched poly(β-cyclodextrin)s, i.e., HBP-AB_x from AB_x-type β-CD monomer, HBP-(B_y + AB_x) from a B_y core molecule and AB_x-type β-CD monomer, and water-soluble HBP-AB_2 from AB_2-type β-CD monomer, were synthesized via hydrosilylation reaction under the thermal or ultraviolet (UV)-

* Corresponding author: e-mail happytw_3000@163.com, Tel +86-29-88431655, Fax +86-29-88431655.

10.1021/ma8023848 CCC: $40.75
Published on Web 01/13/2009

Scheme 1. Synthetic Routes for AB_x-Type (a) and AB_2-Type (b) β-CD Monomers



activated polymerization. The molecule inclusion and recognition behaviors of the novel hyperbranched poly(β-cyclodextrin)s as well as their macromolecular structures, degree of branching (DB), and thermal properties were investigated in detail.

Experimental Section

Materials. Mono-6-OTs-β-CD was synthesized according to the method reported in the literature.[10a] Monovinyl β-CD (GMA-EDA-β-CD) was synthesized according to our previous work.[9a] Allylamine (>99.7%) and diallylamine (>99.5%) were supplied by Zouping Mingxing Chemical Ltd. (Shandong Province, China) and were distilled before use. 1,1,3,3-Tetramethyldisiloxane (>99.0%) was obtained from Zhejiang Sanmen Qianhong Ltd. (Sanmen City, Zhejiang Province, China). Glycidyl methacrylate (GMA) was acquired from Heng Guang Chemical Plant (Luo-Yang, China). Acryloyl chloride (AC) was purchased from Haimen Best Fine Chemical Ltd. (Haimen, China). Chloroplatinic acid (H_2PtCl_6) (39%, platinum) was provided by Shaanxi Kaida Chemical Ltd. (Xi'an City, Shaanxi Province, China). Bis(acetylacetonato)platinum(II) [$Pt(acac)_2$] were purchased from Alfa Aesar Co. *p*-Toluenesulfonyl chloride (*p*-TsCl), ethylenediamine (EDA), and other reagents were analytic grade and were all purchased from Tianjiin Kermel Chemical Reagents Development Center (Tianjin City, China). They were dried with 4 Å grade molecular sieves before use without further purification.

Measurements. The ^{1}H NMR spectrum was conducted on a Bruker Avance 300 spectrometer (Bruker BioSpin, Switzerland) operating at 300 MHz (^{1}H) in d_6-DMSO. ^{13}C NMR and ^{29}Si NMR were recorded on a Bruker Avance 500 spectrometer (Bruker BioSpin, Switzerland) operating at 125.7 MHz (^{13}C) and 50.7 MHz (^{29}Si) in d_6-DMF or d_6-DMSO. The ^{29}Si spectrum was measured in d_6-DMSO solutions at 78 mg/mL concentration in standard NMR tubes (5 mm o.d.) at 298 K. Chemical shifts are referenced to external liquid ammonia. ^{29}Si long-range gHMBC spectra were acquired with pulse field gradients in absolute value mode. The spectral windows for ^{1}H and ^{29}Si domains were 14 and 200 ppm, respectively. The multiple-bond delay was adjusted to a coupling constant of 5 Hz. The data were collected in a 8192 × 256 matrix with 8 transients per t_1 increment. The recycle period was 1.5 s. Sine-bell window functions were applied before Fourier transformation in a 2048 × 1024 matrix. Standard procedures of the spectrometer software (Topspin ver. 2.0) were used.

Separation of samples performed on preparative high-performance liquid chromatography (HPLC) was performed on LC-8A (all parts from Shimadzu, Japan). The chromatographic system consisted of a model LC-8A pump for analytical separation, a model LC-20AD pump for preparative separation, a SPD-20A UV detector, a RID-10A differential refractometer detector, and CS-light software. The analytical column was C18 ODS (5 μm, 150 mm × 4.6 mm). The preparative column was C18 ODS (5 μm, 250 mm × 20 mm).

A matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF MS) was performed on a Kratos CFRplus (Krato Analytical Co. of Shimadzu Biotech, Britain). 1

Table 1. Main Characterization Data for AB_x-Type and AB_2-Type β-CD Monomers

characterization method	AB_x-type β-CD monomer	AB_2-type β-CD monomer
^{1}H NMR (DMSO, δ, ppm)	3.38−3.77 (β-CD protons); 4.90 [7H, C(1)−H]; 4.35 [(6 − x)H, C(6)−O−H]; 5.58−5.75 [14H, C(2, 3)−O−H)]; 2.75, 2.94 (2H, β-CD−CH_2−NH−); 1.31, 1.54 (protons from β addition); protons from α addition is overlapped; 0.08 [6H, −$SiO(CH_3)_2$−]; 0.13 [6H, −$OSi(CH_3)_2$ −H]; 5.86−5.89, 6.23−6.27, (2H, −CH═CH_2); 6.05−6.11, (1H, −CH═CH_2)	3.10−3.84 (β-CD protons); 4.82 [7H, C(1)−H]; 4.48 [6H, C(6)−O−H)]; 5.5.78 [13H, C(2, 3)−O−H)]; 1.03, 1.71, 2.60 (protons from β addition); 0.93, 1.77 (protons from α addition); 0.06 [6H, −$SiO(CH_3)_2$−]; 0.10 [6H, −$OSi(CH_3)_2$−H]; 2.64−2.66 (4H, β-CD−NH−CH_2−CH_2−NH−); 2.08−2.13 (protons from −NH− and −OH); 1.23, 2.67, 2.73, 2.89 4.08, 4.15 (protons from GMA); 3.01, 5.02−5.16, 5.65 (protons from diallylamine)
^{13}C NMR (DMSO for AB_x-type and DMF for AB_2-type, δ, ppm)	102.4 (C-1); 82.6 (C-4); 73.4, 72.7, 72.0 (C-3, 5, 2); 70.6 (C-3′); 69.5 (C-5′); 63.9 (C-6′); 60.6 (C-6); 52.59, 31.2 (carbon atoms from β addition); 47.9, 20.7 (carbon atoms from α addition); 0.7 [−$SiO(CH_3)_2$−]; 0.03 [−$OSi(CH_3)_2$−H]; 125.4 (−*C*H═CH_2); 128.9 (−CH═*C*H_2); 162.2 (−COO−)	102.7 (C-1); 101.9 (C-1′); 82.5 (C-4); 84.5, 80.7 (C-4′); 78.5 (C-2′); 74.7, 73.6, 72.9 (C-3, 5, 2); 71.9 (C-5′); 71.3 (C-3′); 61.9 (C-6′); 61.1 (C-6); 30.7 (carbon atoms from β addition); 23.5, 11.3 (carbon atoms from α addition); 0.1 [−$SiO(CH_3)_2$−]; 0.8 [−$OSi(CH_3)_2$−H]; 51.4 (−CH_2−NH−GMA); 175.9, 70.1, 52.3, 38.8, 15.5 (carbon atoms from GMA); 137.6, 117.3, 57.6 (carbon atoms from diallylamine)
^{29}Si NMR (DMSO, δ, ppm)	−18.7 [−$SiO(CH_3)_2$−] −22.6 [−$OSi(CH_3)_2$−H]	− −
MALDI-TOF MS (DMF, m/z)	Found: 1429 (average value)	Calcd for $C_{64}H_{116}O_{37}N_4Si_2$: 1589; Found: 1590
Anal. (%)	Found: C 46.82, H 6.71, N 0.95 (average value)	Calcd for $C_{64}H_{116}O_{37}N_4Si_2 \cdot 4H_2O$: C 46.25, H 7.50, N 3.37; Found: C 46.36, H 7.63, N 3.53

μL of the mixture (1:1, v/v) of the sample solution and the matrix was spotted onto the wells of the MALDI sample plate and air-dried. The sample was analyzed in the linear ion-mode with CHCA as matrix. External calibration was achieved using a standard peptide mixture and protein mixture from Sigma.

Elemental analysis was conducted on a VARIO ELIII elemental analyses meter (VARIO, Germany).

The molecular structure parameters of hyperbranched polymers were determined on a DAWN EOS size exclusion chromatography/multiangle laser light scattering (SEC/MALLS) instrument equipped with a viscometer (Wyatt Technology); HPLC grade DMF containing LiCl (0.01 mol/L) (at 40 °C) was used as eluent at a flow rate of 0.5 mL/min. The chromatographic system consisted of a Waters 515 pump, differential refractometer (Optilab rEX), and one column, MZ 10^3 Å 300 × 8.0 mm. A MALLS detector (DAWN EOS), quasi-elastic light scattering (QELS), and a differential viscosity meter (ViscoStar) were placed between the SEC and the refractive index detector. The molecular weight (M_w) and molecular weight distribution (MWD) were determined by a SEC/DAWN EOS/Optilab rEX/QELS model. The intrinsic viscosity (η_n) and hydrodynamic radius ($R_{h(n)}$) were determined by a SEC/DAWN EOS/Optilab rEX/ViscoStar model. The refractive index increment (dn/dc) value of sample in THF solution was determined by an Optilab rEX detector at 25 °C through batch model. ASTRA software (Version 5.1.3.0) was utilized for acquisition and analysis of data.

Thermogravimetric analyzer (TGA) measurement was performed on a TQ-50 (TA). An ≈10.0 mg sample was put in an alumina crucible and heated from ambient temperature to 600 °C with a heating rate of 20 K/min (nitrogen atmosphere, flow rate of 150 mL/min).

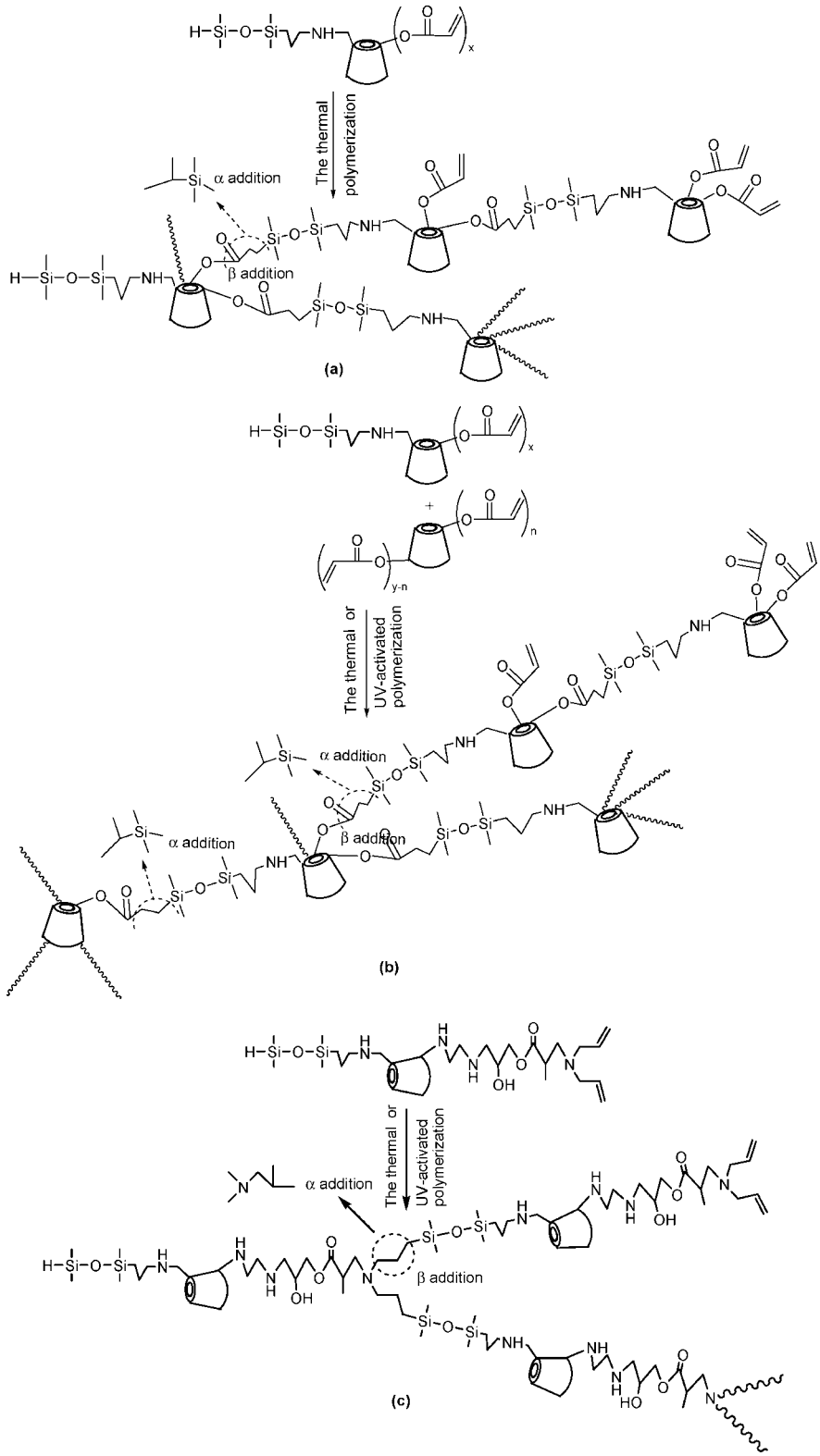
UV−vis spectroscopy measurement was preformed on a Shimadzu UV-2550 model spectroscopy (Shimadzu, Japan).

Synthesis of B_y Core Molecule. B_y core molecule was prepared via acyl reaction between β-CD and AC in KOH solution according to our previous work.[9b] Conversion: 87%. ^{1}H NMR (DMSO, δ, ppm): 3.13−3.87 (β-CD protons); 4.92 [7H, C(1)−H]; 4.47 [C(6)−O−H]; 5.69−5.79 [C(2, 3)−O−H]]; 5.82−5.95, 6.32 (2H, −CH═CH_2); 6.20 (1H, −CH═CH_2). ^{13}C NMR (DMSO, δ, ppm): 100.5 (C-1); 97.5 (C-1′); 80.1 (C-4); 71.5 (C-2′); 72.5, 71.3, 70.3 (C-3, 5, 2); 69.5 (C-3′); 68.7 (C-5′); 62.3 (C-6′); 58.8 (C-6); 130.0 (−*C*H═CH_2); 127.1 (−CH═*C*H_2); 164.3 (−COO−). MALDI-TOF MS (DMF, m/z): Found: 1375.7 for $[M + Na]^+$ (average value). Anal. (%): Found: C 45.60, H 6.61, N 0.35 (average value). The average acyl degree determined by MALDI-TOF MS is 4.07, and the y index of B_y may be equal to 4.

The synthesis of AB_x-type and AB_2-type β-CD monomers can be found in the Supporting Information.

General Procedures of Polymerizations. (a) *Thermal polymerizations*. The operations were carried out in an inert nitrogen atmosphere. Modified β-CD monomers [including AB_x-type (0.5 g), (B_y + AB_x)-type (0.5 g, AB_x/B_y = 100/1), and AB_2-type (0.5 g)] and DMF were mixed, and H_2PtCl_6−divinyltetramethyldisiloxane solution was used as catalyst on hydrosilylation addition of monomers. The reaction was kept at 100 °C for 4 days. After the reaction was completed, the mixture was allowed to cool to room temperature, and then a large amount of cold acetone was added. The precipitate was repeatedly dissolved in DMF and poured into a large amount of cold acetone several times. Resulting polymers obtained including HBP-AB_x, HBP-(B_y + AB_x), and HBP-AB_2 were dried at ambient temperature for 5 days in a vacuum oven. (b) *UV-activated polymerizations*. Modified β-CD monomers [including (B_y + AB_x)-type (0.5 g, AB_x/B_y = 100/1), and AB_2-type (0.5 g)] and DMF were mixed, and $Pt(acac)_2$ was used as a photocatalyst on hydrosilylation addition of monomers. The reaction system cooled in water bath was packed with aluminum foil and was irradiated at 471.4 mW/cm^2 of UV light intensity. The polymerization was finished at about 10 h. The purification procedure was similar to the previous one. Resulting polymers obtained HBP-(B_y + AB_x) and HBP-AB_2 were dried at ambient temperature for 5 days in a vacuum oven.

Scheme 2. Synthetic Routes for HBP-AB_x (a), HBP-(B_y + AB_x) (b), and HBP-AB_2 (c)



Investigation on Molecular Inclusion and Recognition Behaviors of HBP-AB_2. Molecular inclusion behaviors of HBP-AB_2 were measured by UV−vis spectroscopy, using phenolphthalein (PP) (5×10^{-5} mol/L) and methyl orange (MO) (5×10^{-5} mol/L) as guest molecules in a buffer solution with ionic strength equal to 0.1 mol/L and pH = 11. In contrast, the concentration of HBP-AB_2 is 0.7×10^{-5} mol/L and AB_2-type β-CD monomer is 1.6×10^{-4} mol/L to ensure the same concentration of β-CD units between them. Molecular recognition behaviors were measured by the same measurement. MO (5×10^{-5} mol/L) as a guest molecule was added into a buffer solution of HBP-AB_2 (0.25 mg/mL) including PP with pH = 11, and ionic strength of the solution is 0.1 mol/L.

Results and Discussion

Molecule Design and Preparation of Modified β-CD Monomers. It is well-known that a wide variety of chemically modified β-CD have been synthesized.[9a,10] To obtain hyper-

Table 2. Main Polymerization Results of Hyperbranched Poly(*β*-cyclodextrin)s

no.	monomer/core	polymerization method[a]	time	temp, °C	M_n, g/mol	M_w, g/mol	MWD	d*n*/d*c*	η_n, mL/g	$R_{h(n)}$, nm
1	AB_x	1	3 days	80	17 520	34 680	1.98	0.087[b]	4.5	2.2
2	AB_x	1	4 days	80	27 500	38 190	1.39	0.087[b]	5.0	2.7
3	AB_x	1	4 days	100	41 850	83 290	1.99	0.087[b]	5.0	3.1
4	AB_x/B_y	1	4 days	100	64 710	112 200	1.74	0.018	0.7	1.8
5	AB_x/B_y	2	10 h	20	47 700	61 770	1.30	0.019	2.9	1.5
6	AB_2	1	4 days	100	36 690	69 220	1.89	0.093	15.8	3.9
7	AB_2	2	10 h	20	16 700	34 590	2.10	0.048	2.1	1.7

[a] 1: Thermal polymerization and H_2PtCl_6 as the catalyst; 2; UV-activated polymerization and $Pt(acac)_2$ as the catalyst. [b] The d*n*/d*c* value is an average one of samples 1, 2, and 3 for comparing with their molecular structure parameters under the same standard. This method should be reasonable for the polymers possessing the similar structure, the same polymerization method and the high molecular weight according to the literature.[15]

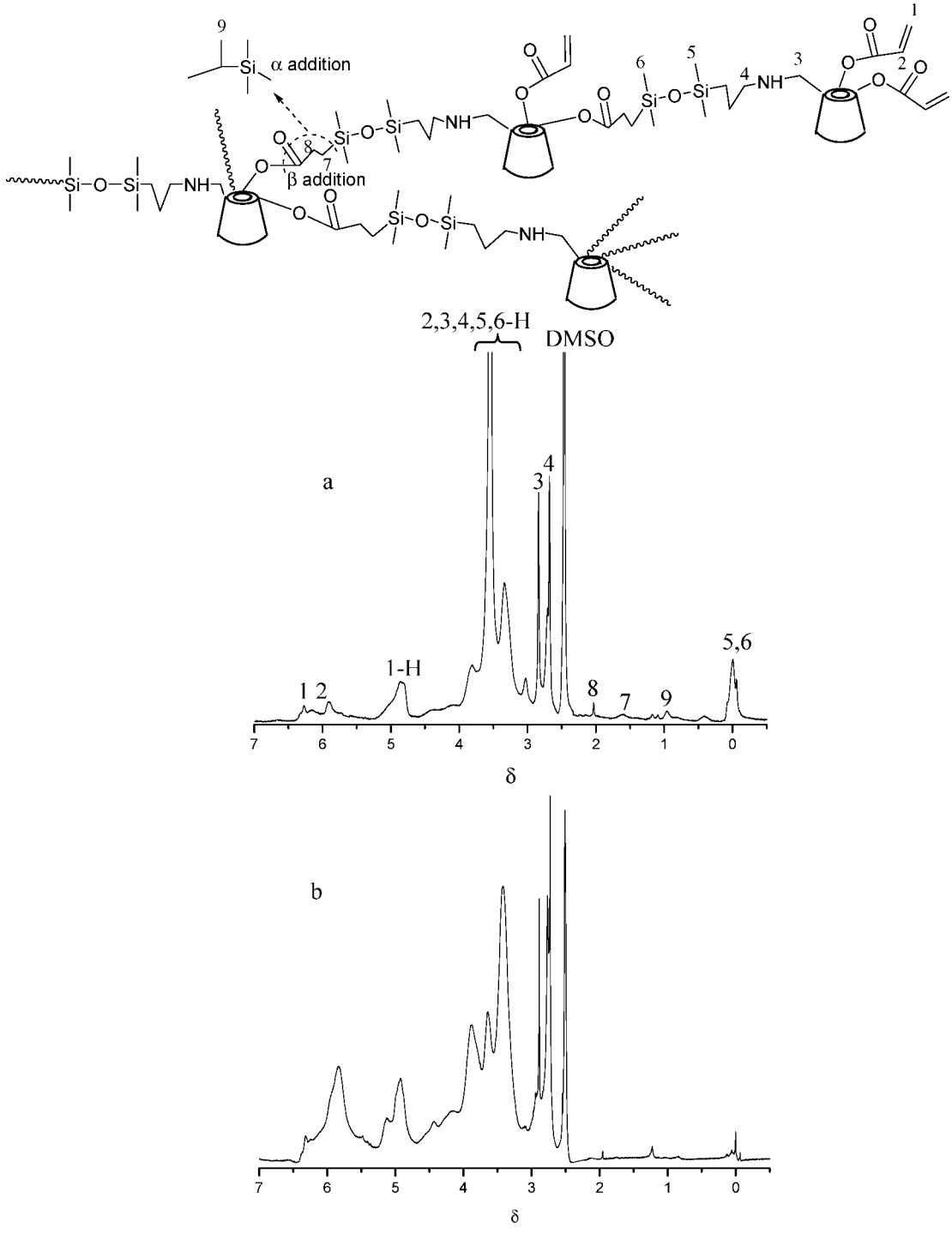


Figure 1. ^{1}H NMR spectra of HBP-AB_x (no. 3) (a) and HBP-(B_y + AB_x) (no. 4) (b).

branched poly(*β*-cyclodextrin)s with well-defined branched structures, herein, a series of modified *β*-CD monomers were designed and prepared via functionalized reactions of C-2 or C-6 hydroxyl groups in *β*-CD molecule. Then Si−H as "A"

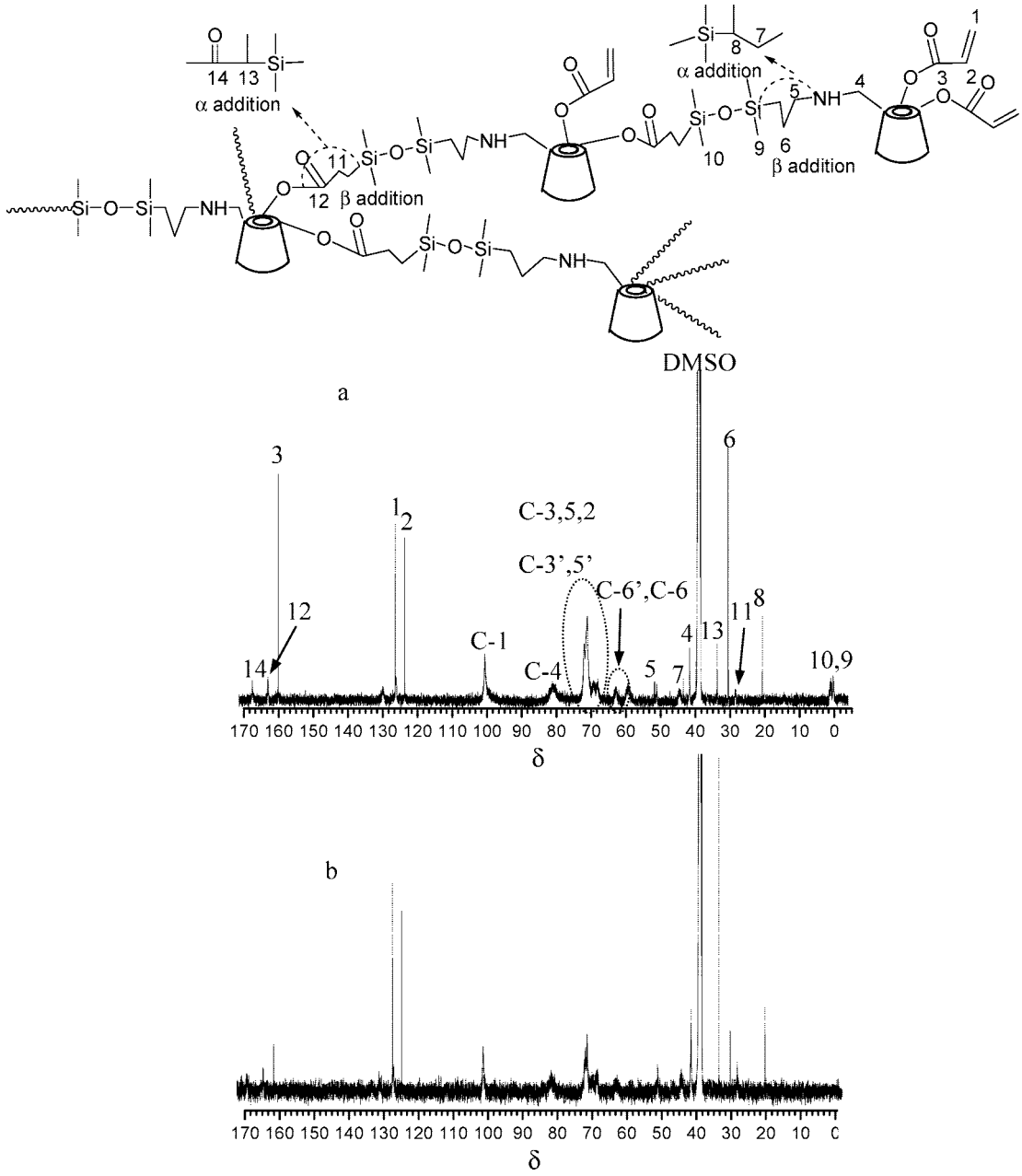


Figure 2. ^{13}C NMR spectra of HBP-AB_x (no. 3) (a) and HBP-(B_y + AB_x) (no. 4) (b).

group and −CH═CH_2 as "B" group in monomers were employed to conduct hydrosilylation reaction in polymerization. Synthetic routes of the modification are shown in Scheme 1.

At first, the reaction of Mono-6-OTs-β-CD with allylamine yielded Mono-6-ALA-β-CD with alkene groups. Subsequently, Mono-6-ALA-TMDSO-β-CD with Si−H as "A" group was obtained by hydrosilylation reaction using 1,1,3,3-tetramethyldisiloxane as the reactant. Mono-6-ALA-β-CD was purified by preparative HPLC because it was difficult to remove unreacted Mono-6-OTs-β-CD from the crude product. As can been seen from the analytical chromatogram of Mono-6-ALA-β-CD (Figure S1a in the Supporting Information), two peaks with different retention time demonstrate the crude product has two compounds. After being preparative separation, their structures are confirmed by ^1H NMR spectra (Figure S2). The first peak is referring to Mono-6-OTs-β-CD, and the second one is referring to Mono-6-ALA-β-CD. Therefore, the pure product of Mono-6-ALA-β-CD can be obtained by this method (Figure S1b). However, for Mono-6-ALA-TMDSO-β-CD, its purification procedure can be facilitated by dissolve−precipitation using DMF and acetone as solvent instead of preparative HPLC. The reason is that Mono-6-ALA-TMDSO-β-CD is soluble in acetone, but Mono-6-ALA-β-CD is extremely insoluble due to the existence of allyl groups.

Modified β-CD monomers with "B" group of −CH═CH_2 can be obtained via two routes. The first one is that the AB_x-type β-CD monomer is obtained from Mono-6-ALA-TMDSO-β-CD and acryloyl chloride (Scheme 1a) where acyl reaction occurs at the C-6 position in β-CD molecule. It can be confirmed by the ^{13}C NMR spectrum, and the data are shown in Table 1. The chemical shift of C-6′ compared with the original C-6 indicates a downshift. The enhanced chemical shift of neighboring C-5′ shows that C-6 hydroxyl groups are substituted. In addition, the unchanged chemical shift of C-1 and C-4 tells us that the reaction is not occurring at the C-2 or C-3 position. Furthermore, the data of the ^{29}Si NMR spectrum as shown in Table 1 confirm that there exist two different silicon atoms in AB_x-type β-CD monomer. The average acyl degree of monomer determined by MALDI-TOF MS (Figure S3a) is 2.29. The result means that AB_x-type β-CD monomer is a mixed monomer in

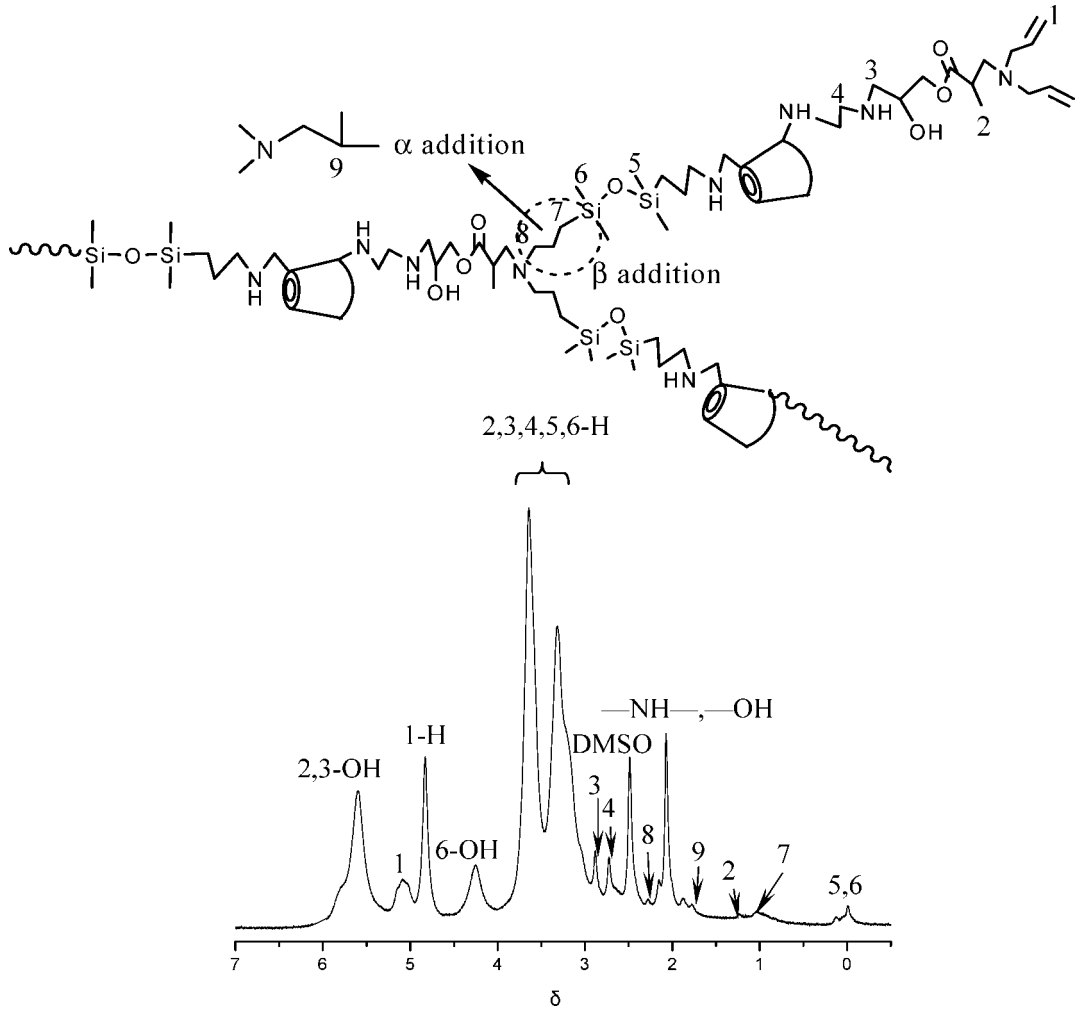


Figure 3. ^{1}H NMR spectrum of HBP-AB_2 (no. 6).

which the index "*x*" is equal to 2, 3, or others. Unfortunately, so far, these mixed monomers have not been separated by preparative HPLC due to the extreme similar structure difference among them. However, it has little effect on the subsequent polymerization reaction and resulting polymer structures.

The second one is that AB_2-type β-CD monomer is obtained from Mono-6-ALA-TMDSO-β-CD with *p*-TsCl, EDA, GMA, or diallylamine where reaction occurs at the C-2 position in β-CD molecule (Scheme 1b). The synthetic procedure of Mono-6-ALA-TMDSO-Mono-2-OTs-β-CD, as a monosubstituent product at the C-2 position, was similar to Mono-2-OTs-β-CD according to the literature.[10b] Acetone was still used instead of gel chromatography and ultrafiltration. Mono-6-ALA-TMDSO-Mono-2-EDA-β-CD and Mono-6-ALA-TMDSO-Mono-2-GMA-EDA-β-CD were synthesized and purified being similar to our reported method.[9a] Finally, the monomer was obtained via Michael addition reaction. The value and single peak of MALDI-TOF MS (Figure S3b) demonstrate that the monomer is high in purity. The data of NMR and elemental analysis results shown in Table 1 further confirm AB_2-type β-CD monomer possesses the designed molecular structures.

Synthesis of Hyperbranched Poly(β-cyclodextrin)s. Using modified β-CD as monomers, hyperbranched poly(β-cyclodextrin)s including HBP-AB_x, HBP-(B_y + AB_x), and HBP-AB_2 were synthesized via one-pot hydrosilylation reaction under thermal or UV conditions. Synthetic routes and molecular structure parameters of hyperbranched polymers are shown in Scheme 2 and Table 2, respectively. HBP-AB_x was prepared using AB_x-type β-CD monomer and H_2PtCl_6 at 80 °C for 3 days (Scheme 2a and no. 1 in Table 2). The increased polymerization time and temperature lead to an increase of M_n and $R_{h(n)}$ (no. 2 and no. 3). For example, the polymerization was carried out at 100 °C for 4 days to give the highest M_n and $R_{h(n)}$ values, i.e., the M_n of 41 850 and the $R_{h(n)}$ of 3.1 (no. 3). However, the η_n value is from 4.5 to 5.0 for nos. 1−3 and do not change evidently. According to our previous work,[8b] the η_n value tends to increase with the increase of M_n and $R_{h(n)}$ for hyperbranched polymer. In this paper, the unusual phenomenon may be ascribed to the difference in DB value and chemical structures.

When a core molecule is added, hyperbranched polymers may possess the more perfect macromolecular configuration with higher DB value and narrower molecular weight distributions.[4] Hence, HBP-(B_y + AB_x) with a B_y core molecule was synthesized under the same polymerization conditions with HBP-AB_x (Scheme 2b and no. 4). Compared with the hyperbranched polymer without core (no. 3), the increase of M_n for no. 4 indicates that the polymerization occurred for several, while not limited to only one, −CH═CH_2 groups in the B_y core molecule group. At the same time, the decreased MWD of no. 4 demonstrates that hyperbranched polymer with the core possesses more regular structure.

It should be pointed out that the polymerizations from no. 1 to no. 4 were carried out under rigorous conditions such as high temperature, long time, and nitrogen atmosphere due to steric hindrance of modified β-CD monomers. In this case, UV-activated polymerization is a facile approach for rapidly initiating hydrosilylation between Si−H and carbon−carbon unsaturated groups.[11] Therefore, HBP-(B_y + AB_x) (no. 5) was

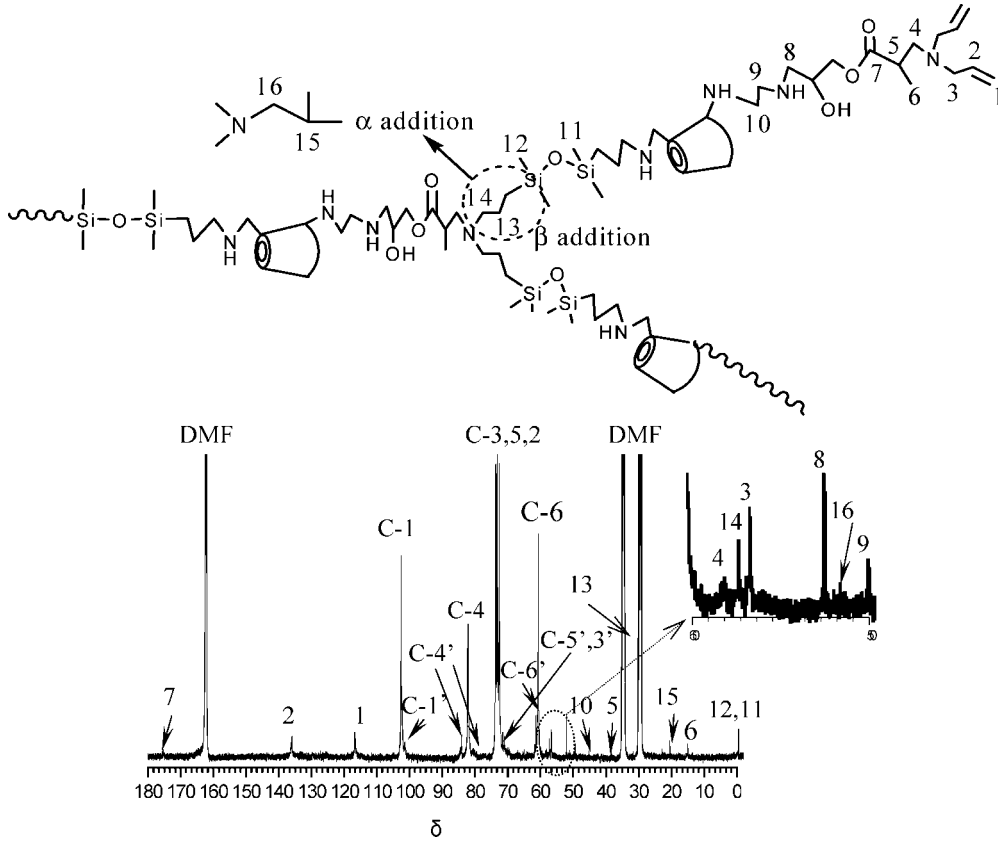
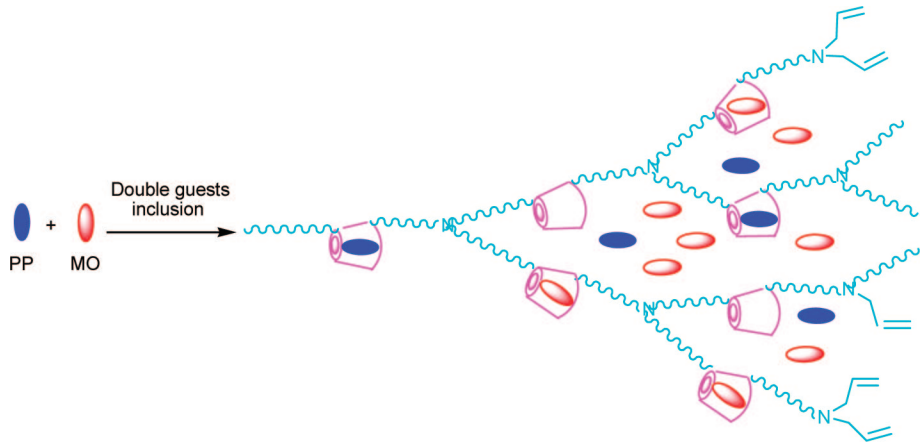


Figure 4. ^{13}C NMR spectrum of HBP-AB$_2$ (no. 6).

Scheme 3. Schematic Representation for Possible Inclusion Mechanism of HBP-AB$_2$ with Double Guests



prepared under UV-activated polymerization at the low temperature though the M_n value was lower than no. 4. In addition, Pt(acac)$_2$ was also employed as the UV-activated hydrosilylation catalyst according to our previous work.[11f] Here, HBP-AB$_2$ was synthesized with AB$_2$-type β-CD monomer via hydrosilylation reaction under the thermal (no. 6) or UV-activated polymerization (no. 7) (Scheme 2c). It should be noted that the η_n values between no. 6 and no. 7 are much different besides the differences in molecular weights and $R_{h(n)}$ values. The molecular weight and the $R_{h(n)}$ value of no. 6 are ca. double of those of no. 7. This large difference in η_n values may be caused by the different polymerization methods. HBP-AB$_2$ possesses more well-defined macromolecular structures than that of HBP-AB$_x$ or HBP-(B$_y$ + AB$_x$) due to the difference between AB$_2$-type and AB$_x$-type β-CD monomers. The former is a pure monomer, but the latter is a mixed monomer.

Characterization of Hyperbranched Poly(β-cyclodextrin)s. To investigate hyperbranched structures of poly(β-cyclodextrin)s, ^{1}H NMR and ^{13}C NMR were employed. ^{1}H NMR spectra for HBP-AB$_x$ and HBP-(B$_y$ + AB$_x$) are shown in Figure 1. In comparison with AB$_x$-type β-CD monomer (Table 1), it is clear that the new chemical shifts at δ 0.98, δ 1.60, and δ 2.03 can be attributed to protons from α and β additions. The hydrosilylation reaction can be classified into two categories: α addition to form methyl groups as the side chain and β addition to form the linear chain.[8a−c] The signals from −CH=CH$_2$ groups at around δ 6 seem to be too large for the terminal groups compared with the other signals in Figure 1. A possible explanation is that the signals may be overlapped by the hydroxyl signals from β-CD. At the same time, the appearance of new chemical shifts in ^{13}C NMR spectra (Figure 2a) at δ 169.07, δ 164.51, δ 34.23, and δ 28.78 indicates that

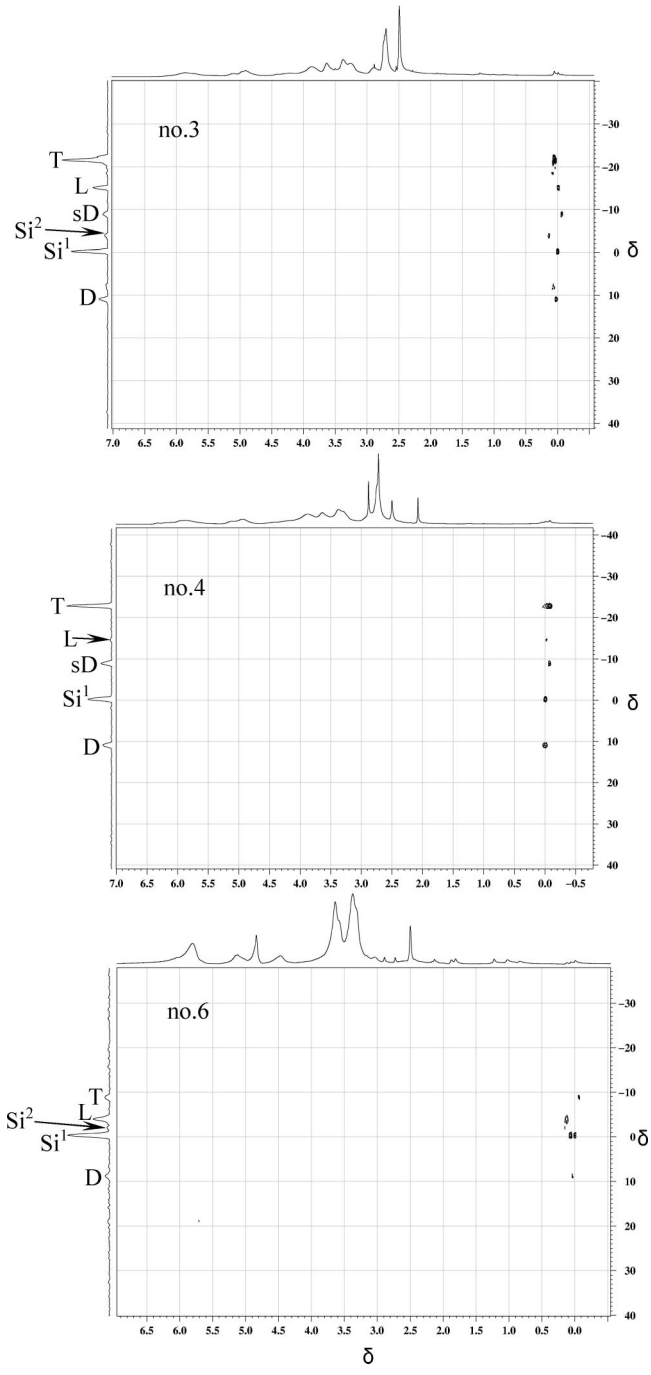


Figure 5. $^{1}H-^{29}Si$ HMBC spectra of hyperbranched poly(β-cyclodextrin)s.

Table 3. Assignments for Si Atoms in Hyperbranched Poly(β-cyclodextrin)s

sample	Si^1	Si^2	D	sD	L	T	DB
no. 3	−0.5	−4.3	10.6	−9.2	−16.5	−20.2 to −23.4	0.55
no. 4	−0.3	−	11.2	−8.8	−14.7	−23.1	0.83
no. 6	−0.1	−1.5	8.6	−	−3.8	−8.8	0.40

the polymerization was also carried out containing α and β additions. The ^{1}H NMR spectrum (Figure 1b) and ^{13}C NMR spectrum (Figure 2b) for HBP-(B_y + AB_x) are similar to HBP-AB_x because of their similar structures.

^{1}H NMR and ^{13}C NMR spectra of HBP-AB_2 are presented in Figure 3 and Figure 4, respectively. Compared with the data of AB_2-type β-CD monomer listed in Table 1, the appearance of new chemical shifts at δ 1.88, δ 2.28 in Figure 3 and δ 57.7, δ 51.8 in Figure 4 can also be attributed to the α and β additions

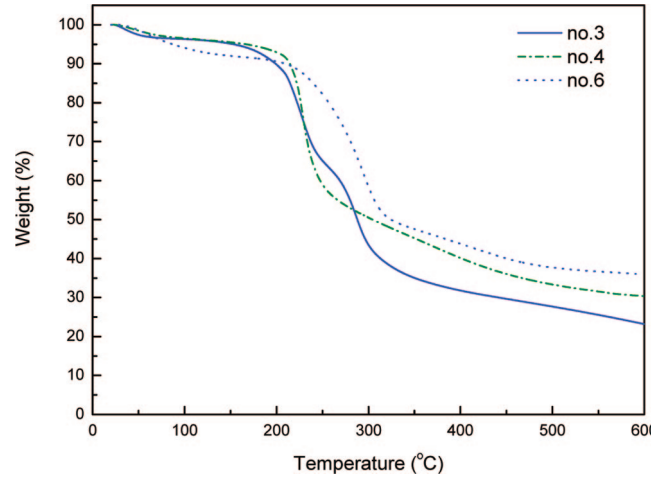


Figure 6. TGA thermograms for hyperbranched poly(β-cyclodextrin)s.

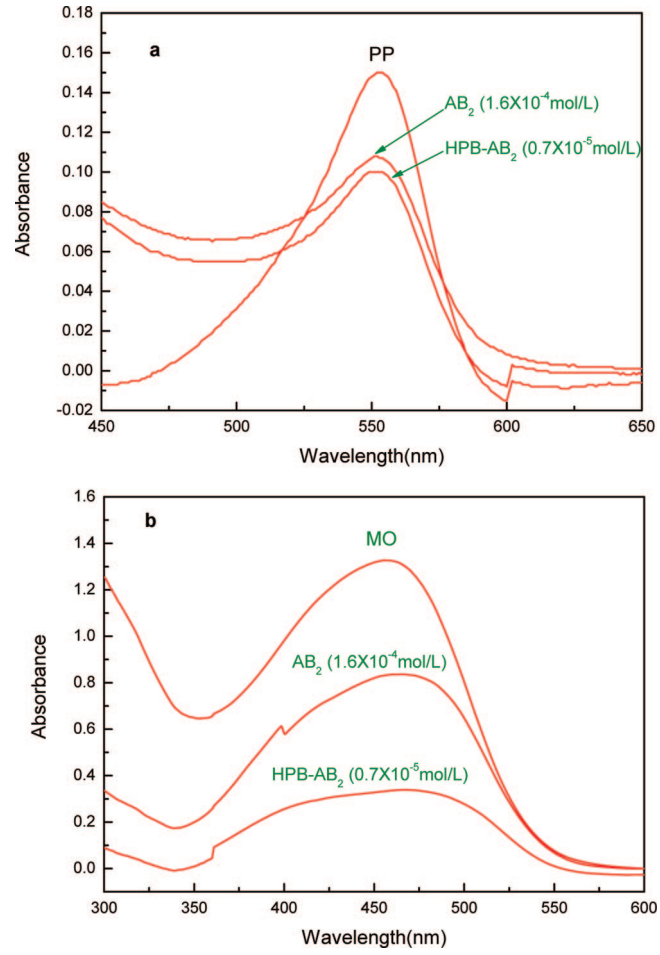


Figure 7. UV spectra of PP (a) and MO (b) solution in the presence of AB_2-type β-CD monomer and HBP-AB_2.

in polymerization. In addition, the proton peak of methylene from α addition can be overlapped by solvent peak in Figure 3. In a word, NMR results demonstrate that HBP-AB_x, HBP-(B_y + AB_x), and HBP-AB_2 have been successfully synthesized.

DB is a key parameter to describe the branching structures of hyperbranched polymers, which can finely distinguish the difference of branching units.[12] As for silicon-based hyperbranched polymers, DB is usually calculated by quantitative ^{29}Si NMR data.[13] However, in this paper, one-dimensional (1D) ^{29}Si NMR spectra of hyperbranched poly(β-cyclodextrin)s with

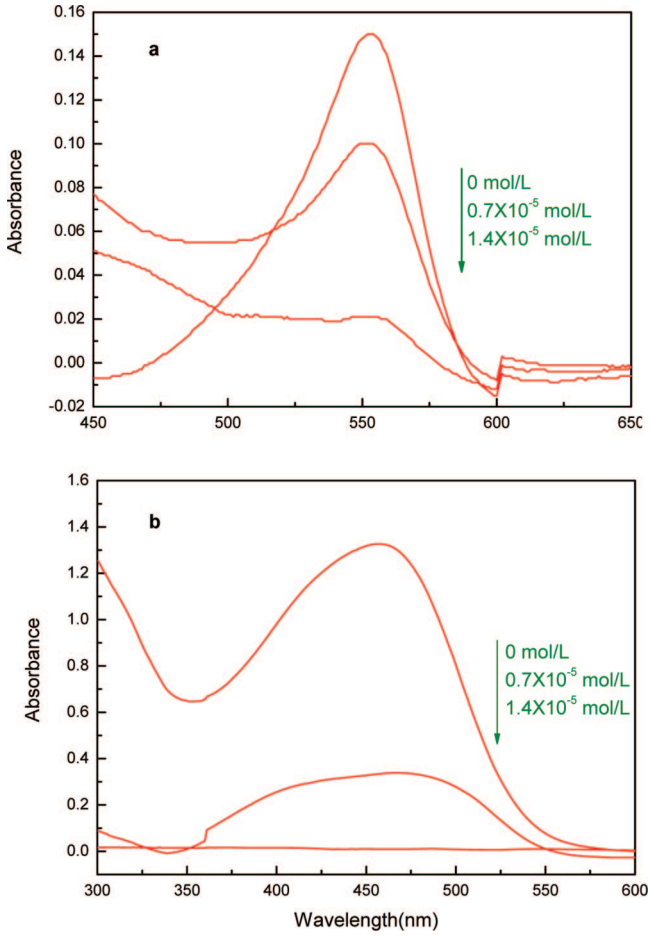


Figure 8. UV spectra of PP (a) and MO (b) solution in the presence of different concentration HBP-AB_2.

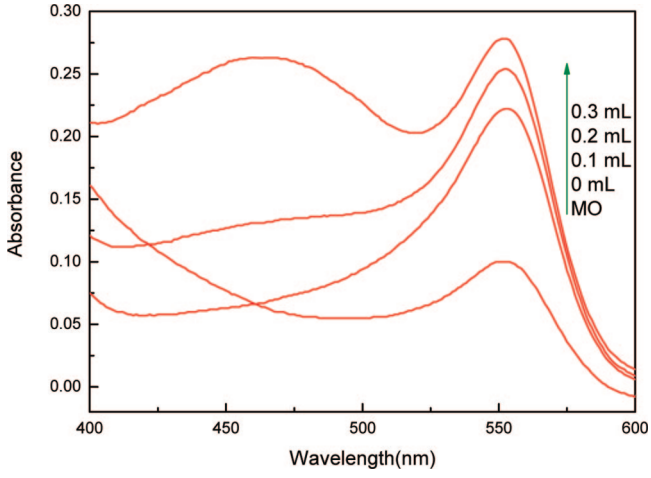


Figure 9. UV spectra of PP + HBP-AB_2 solution in the presence of different concentration MO solution.

weak signal and dominated noise result in the difficulty in confirming silicon atoms. So $^1H-^{29}Si$ heteronuclear multiple bond correlation[14] ($^1H-^{29}Si$ HMBC) was for the first time employed to calculate DB of the silicon-based hyperbranched polymers.

$^1H-^{29}Si$ HMBC spectra of hyperbranched poly(β-cyclodextrin)s are shown in Figure 5. The ^{29}Si NMR spectra are projective ones determined by the long-range correlation between ^1H signal and ^{29}Si signal. Assignment results of the chemical shifts in ^{29}Si NMR spectra are presented in Table 3 according to the literature,[13] our previous work,[6,8d,e] and the

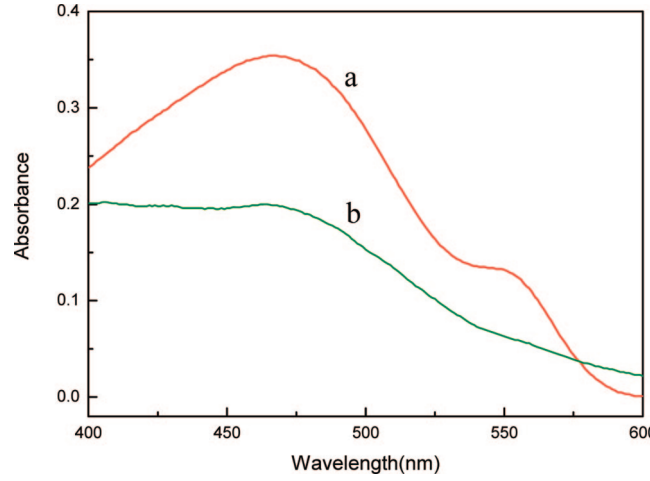


Figure 10. UV spectra of PP + MO solution (a) and PP + MO solution in the presence of HBP-AB_2 (b).

effect of substitute groups on chemical shifts of silicon atoms. The detailed segment structures of polymers containing silicon atoms in different environments are listed in Chart 1. Silicon atom labeled as Si^1 represents the first one of Si−O−Si linkage in the linear chain, and Si^2 represents the silicon atom of original Si−H linkage. Obviously, the Si^2 peak cannot be found in Figure 5b, which conforms that the B_y core molecule is effective in the regulation of molecular structures.

T, L, sD, and D represent terminal units with two linkages, linear units with two linkages, semi-dendritic units, and perfect dendritic units with two linkages, respectively. The relative area integration ratio of D, sD, and L represents their number ratio in Figure 5. The ratio is 1:2/3:3 for HBP-AB_x, 1:4/3:1/3 for HBP-(B_y + AB_x), and D:L is 1:3 for HBP-AB_2, respectively. The DB value of HBP-AB_x and HBP-(B_y + AB_x) can be calculated from the number of D, sD, and L using Frey's equation (eq 1).[12b] It should be noted that only one sD peak appears in Figure 5a,b, although the linkage way of sD is more than one. On the other hand, the DB value of HBP-AB_2 can be calculated by eq 2[12b] since the polymer is from the well-defined AB_2-type β-CD monomer. All the DB values are listed in Table 3. Obviously, the sequence of DB value is as follows: HBP-(B_y + AB_x) > HBP-AB_x > HBP-AB_2. The results indicate that the macromolecular configuration of HBP-(B_y + AB_x) is more regular than those of other two polymers. The low DB value of HBP-AB_2 can be attributed to the few "B" groups in monomer and the steric hindrance in polymerization.

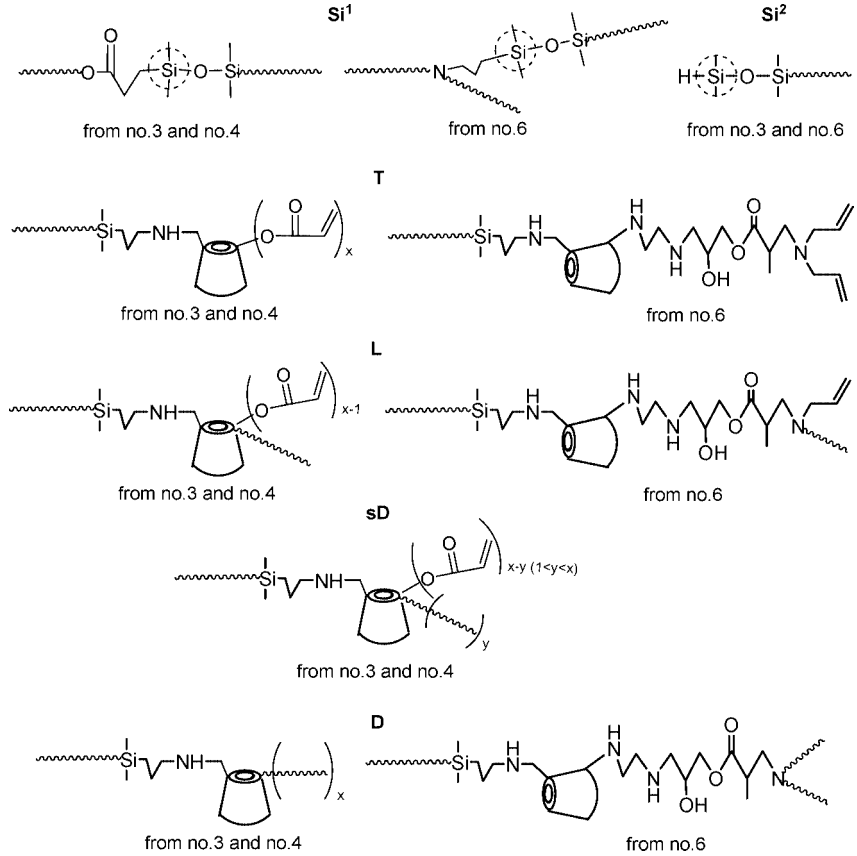
$$\mathrm{DB} = \frac{2D + sD}{\frac{2}{3}(3D + 2sD + L)} \quad (1)$$

$$\mathrm{DB} = \frac{2D}{2D + L} \quad (2)$$

The TGA weight loss curves of HBP-AB_x, HBP-(B_y + AB_x), and HBP-AB_2 are presented in Figure 6. Decomposition temperature at 5% mass loss and residual weight of of HBP-AB_x are about 151 °C and 22%, respectively, while decomposition temperature and residual weight of HBP-(B_y + AB_x) are about 164 °C and 30%, which indicates that the thermal stability is obviously increased as the result of the incorporation of the B_y core molecule into its polymer structures.

Molecular Inclusion and Recognition Behaviors of Hyperbranched Poly(β-cyclodextrin)s. UV−vis spectroscopy was employed to study the molecular inclusion behaviors of hyperbranched poly(β-cyclodextrin)s, such as HBP-AB_2. Phe-

Chart 1. Six Possible Environments for Silicon Atoms in Hyperbranched Poly(β-cyclodextrin)s



nolphthalein (PP) and methyl orange (MO) were used as guest molecules in a buffer solution of pH 11 with ionic strength of 0.1 mol/L. The intensity of UV absorption at 550 and 465 nm reflects the inclusion effects for PP and MO, respectively. In contrast, the concentration of HBP-AB_2 is set as 0.7×10^{-5} mol/L and AB_2-type β-CD monomer is set as 1.6×10^{-4} mol/L to ensure the same concentration of β-CD units between them.

Compared with AB_2-type β-CD monomer, the peak intensity decreases of PP or MO (at 550 and 465 nm) in the hyperbranched polymer solution (HBP-AB_2) indicates the enhanced molecular inclusion ability of the polymer as shown in Figure 7. Considering that the hyperbranched polymer solution employed possesses the same concentration of β-CD units with that in AB_2-type β-CD monomer, so the cooperative effects of two different hydrophobic cavities from hyperbranched topography structure and β-CD linkage lead to the enhancement of molecular inclusion ability of hyperbranched poly(β-cyclodextrin)s. With the increase of concentration of HBP-AB_2, the peak intensity of PP and MO solution decreases more obviously (Figure 8), further indicating that HBP-AB_2 can totally form inclusion complexes with guest molecules due to their two types of molecule cavities from β-CD and branched architecture in HBP-AB_2.[6]

On the other hand, as shown in Figure 9, the original peak intensity of PP in the presence of HBP-AB_2 decreases after the addition of MO. HBP-AB_2 possesses a capability of molecular recognition from both β-CD and hyperbranched polymer cavities. So PP was displaced by MO and went into the bulk buffer solution again. It is interesting that HBP-AB_2 can also form inclusion complexes with double guests including PP and MO as shown in Figure 10. However, the molecular number of PP should be less than that of MO in two different cavities due to molecular recognition behavior of HBP-AB_2. Therefore, the inclusion mechanism of HBP-AB_2 with double guests is suggested in Scheme 3.

Conclusion

The novel hyperbranched poly(β-cyclodextrin)s were designed and synthesized from modified β-CD monomers via one-pot hydrosilylation reaction under the thermal or UV-activated conditions. DB values of HBP-AB_x, HBP-(B_y + AB_x), and HBP-AB_2 determined by $^1H-^{29}Si$ HMBC are 0.55, 0.83, and 0.40, respectively. TGA analysis indicates that the thermostability of HBP-(B_y + AB_x) is higher than that of HBP-AB_x but is lower than that of HBP-AB_2. The B_y core molecule is effective in the regulation of molecular structures. UV−vis spectroscopy results show that HBP-AB_2 has molecular inclusion capabilities and also can form inclusion complexation with single or double guests, including PP and MO. Compared with AB_2-type β-CD monomer, the molecular inclusion ability of the hyperbranched polymer was enhanced due to the cooperative effect of two different hydrophobic cavities from hyperbranched topography architecture and β-CD linkage. Furthermore, HBP-AB_2 presents molecular recognition behavior when MO solution is added drop by drop into PP and hyperbranched polymers solution. Hyperbranched poly(β-cyclodextrin)s will endow some important potential applications in inclusion technologies and the complex drugs delivery system.

Acknowledgment. The authors are grateful to the National Natural Science Foundation of China (No. 20674060) and Shaanxi Province Natural Science Foundation (No. 2007B16) for financial support.

Supporting Information Available: Detailed synthetic procedures and the characterizations of AB_x-type and AB_2-type β-CD

monomers. The material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kim, Y. H.; Webster, O. W. *Polym. Prepr.* **1988**, *29*, 310–311. (b) Pastor-Pérez, L.; Barriau, E.; Frey, H.; Pérez-Prieto, J.; Stiriba, S.-E. *J. Org. Chem.* **2008**, *73*, 4680–4683. (c) Jena, K. K.; Raju, K. V. S. N.; Prathab, B.; Aminabhavi, T. M. *J. Phys. Chem. B* **2007**, *111*, 8801–8811. (d) Chao, D. M.; Ma, X. D.; Lu, X. F.; Cui, L. L.; Mao, H.; Zhang, W. J.; Wei, Y. *Macromol. Chem. Phys.* **2007**, *208*, 658–664. (e) Gelade, E. T. F.; Goderis, B.; de Koster, C. G.; Meijerink, N.; van Benthem, R. A. T. M.; Fokkens, R.; Nibbering, N. M. M.; Mortensen, K. *Macromolecules* **2001**, *34*, 3552–3558. (f) Yoo, S. H.; Lee, J. H.; Lee, J.-C.; Jho, J. Y. *Macromolecules* **2002**, *35*, 1146–1148. (g) Choi, J.-Y.; Tan, L.-S.; Baek, J.-B. *Macromolecules* **2006**, *39*, 9057–9063. (h) Parzuchowski, P. G.; Jaroch, M.; Tryznowski, M.; Rokicki, G. *Macromolecules* **2008**, *41*, 3859–3865. (i) Vanjinathan, M.; Shanavas, A.; Raghavan, A.; Sultan Nasar, A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3877–3893. (j) Zhu, X.; Jaumann, M.; Peter, K.; Möller, M.; Melian, C.; Adams-Buda, A.; Demco, D. E.; Blumich, B. *Macromolecules* **2006**, *39*, 1701–1708. (k) Grunzinger, S. J.; Hayakawa, T.; Kakimoto, M.-A. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 4785–4793. (l) Shi, J.; Tong, B.; Zhao, W.; Shen, J.; Zhi, J.; Dong, Y.; Haussler, M.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **2007**, *40*, 5612–5617.

(2) (a) Kadokawa, J.; Sato, M.; Karasu, M.; Tagaya, H.; Chiba, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 373–2376. (b) Kadokawa, J.; Tagaya, H. *Polym. Adv. Technol.* **2000**, *11*, 122–126. (c) Satoh, T.; Imai, T.; Ishihara, H.; Maeda, T.; Kitajyo, Y.; Narumi, A.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromolecules* **2003**, *36*, 6364–6370. (d) Imai, T.; Satoh, T.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromolecules* **2003**, *36*, 6359–6363. (e) Imai, T.; Satoh, T.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromolecules* **2004**, *37*, 3113–3119. (f) Satoh, T.; Imai, T.; Kitajyo, Y.; Maeda, T.; Narumi, A.; Kaga, H.; Kaneko, N.; Kakuchi, T. *Macromol. Symp.* **2004**, *217*, 36–46. (g) Satoh, T.; Imai, T.; Ishihara, H.; Maeda, T.; Kitajyo, Y.; Sakai, Y.; Kaga, H.; Kaneko, N.; Ishii, F.; Kakuchi, T. *Macromolecules* **2005**, *38*, 4202–4210. (h) Tao, Y. Z.; Zhang, L. N. *Biopolymers* **2006**, *83*, 414–423. (i) Satoh, T.; Tamaki, M.; Kitajyo, Y.; Maeda, T.; Ishihara, H.; Imai, T.; Kaga, H.; Kakuchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 406–413. (j) Kitajyo, Y.; Imai, T.; Sakai, Y.; Tamaki, M.; Tani, H.; Takahashi, K.; Narumi, A.; Kaga, H.; Kaneko, N.; Satoh, T.; Kakuchi, T. *Polymer* **2007**, *48*, 1237–1244. (k) Kitajyo, Y.; Nawa, Y.; Tamaki, M.; Tani, H.; Takahashi, K.; Kaga, H.; Satoh, T.; Kakuchi, T. *Polymer* **2007**, *48*, 4683–4690.

(3) (a) D'Souza, V. T.; Lipkowitz, K. B. *Chem. Rev.* **1998**, *98*, 1741–1742. (b) Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743–1754. (c) Miyawaki, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *Tetrahedron* **2008**, *64*, 8355–8361.

(4) (a) Gao, C.; Yan, D. Y. *Prog. Polym. Sci.* **2004**, *29*, 183–275. (b) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2679–2669. (c) Bartels, J. W.; Cheng, C.; Powell, K. T.; Xu, J. G.; Wooley, K. L. *Macromol. Chem. Phys.* **2007**, *208*, 1676–1687. (d) Hirao, A.; Sugiyama, K.; Matsuo, A.; Tsunoda, Y.; Watanabe, T. *Polym. Int.* **2008**, *57*, 554–570.

(5) (a) Reineccius, T. A.; Reineccius, G. A.; Peppard, T. L. *J. Agric. Food Chem.* **2005**, *53*, 388–392. (b) Hapiot, F.; Tilloy, S.; Monflier, E. *Chem. Rev.* **2006**, *106*, 767–781. (c) Villalonga, R.; Cao, R.; Fragoso, A. *Chem. Rev.* **2007**, *107*, 3088–3116.

(6) Tian, W.; Fan, X. D.; Liu, Y. Y.; Jiang, M.; Huang, Y.; Kong, J. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5036–5052.

(7) (a) Zhang, L.; Zhang, M.; Dong, J.; Guo, J.; Song, Y.; Cheung, P. C. *Biopolymers* **2001**, *59*, 457–464. (b) Zhang, M.; Cheung, P. C. K.; Ooi, V. E. C.; Zhang, L. *Carbohydr. Res.* **2004**, *339*, 2297–2301.

(8) (a) Si, Q. F.; Wang, X.; Fan, X. D.; Wang, S. J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1883–1894. (b) Kong, J.; Fan, X. D.; Si, Q. F.; Wang, S. J.; Wang, X.; Zhang, G. B. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3930–3941. (c) Zhang, G. B.; Fan, X. D.; Kong, J.; Liu, Y. Y.; Wang, M. C.; Qi, Z. C. *Macromol. Chem. Phys.* **2007**, *208*, 541–548. (d) Wang, S. J.; Fan, X. D.; Kong, J.; Wang, X.; Liu, Y. Y.; Zhang, G. B. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2708–2720. (e) Wang, S. J.; Fan, X. D.; Kong, J.; Liu, Y. Y. *J. Appl. Polym. Sci.* **2008**, *107*, 3812–3822.

(9) (a) Liu, Y. Y.; Fan, X. D.; Gao, L. *Macromol. Biosci.* **2003**, *3*, 715–719. (b) Huang, Y.; Fan, X. D. *Acta Polym. Sin.* **2006**, *3*, 505–509.

(10) (a) Petter, R. C.; Salek, J. S.; Sikorski, C. T.; Kumaravel, G.; Lin, F. T. *J. Am. Chem. Soc.* **1990**, *112*, 3860–3868. (b) Breslow, R.; Yang, Z.; Ching, R.; Trojandt, G.; Odobel, F. *J. Am. Chem. Soc.* **1998**, *120*, 3536–3537. (c) Kikuzawa, A.; Kida, T.; Nakatsuji, Y.; Akashi, M. *J. Org. Chem.* **2005**, *70*, 1253–1261. (d) Wang, H.; Chen, Y.; Li, X.-Y.; Liu, Y. *Mol. Pharmaceutics* **2007**, *4*, 189–198. (e) Liu, Y.; Zhang, Q.; Chen, Y. *J. Phys. Chem. B* **2007**, *111*, 12211–12218.

(11) (a) Fry, B. E.; Neckers, D. C. *Macromolecules* **1996**, *29*, 5306–5312. (b) Wang, F.; Kaafarani, B. R.; Neckers, D. C. *Macromolecules* **2003**, *36*, 8225–8230. (c) Wang, F.; Neckers, D. C. *J. Organomet. Chem.* **2003**, *665*, 1–6. (d) Buchgraber, C.; Spanring, J.; Pogantsch, A.; Turner, M.; Kern, W. *Synth. Met.* **2004**, *147*, 91–95. (e) Spanring, J.; Buchgraber, C.; Ebel, M.; Svagera, R.; Kern, W. *Polymer* **2006**, *47*, 156–165. (f) Zhang, G. B.; Fan, X. D.; Kong, J.; Liu, Y. Y. *J. Chem. Chinese Univ.* **2007**, *28*, 2403–2407.

(12) (a) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583–4588. (b) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30–35. (c) Lach, C.; Frey, H. *Macromolecules* **1997**, *30*, 7024–7033. (d) Frey, H.; Hölter, D. *Acta Polym.* **1999**, *50*, 67–76.

(13) (a) Lach, C.; Müller, P.; Frey, H.; Mülhaupt, R. *Macromol. Rapid Commun.* **1997**, *18*, 253–260. (b) Yoon, K.; Son, Y. D. *Macromolecules* **1999**, *32*, 5210–5216. (c) Chojnowski, J.; Cypryk, M.; Fortuniak, W.; Scibiorek, M.; Rózga-Wijas, K. *Macromolecules* **2003**, *36*, 3890–3897. (d) Jaumann, M.; Rebrov, E. A.; Kazakova, V. V.; Muzafarov, A. M.; Goedel, W. A.; Möller, M. *Macromol. Chem. Phys.* **2003**, *204*, 1014–1026. (e) Zhu, X. M.; Jaumann, M.; Peter, K.; Mö1ller, M.; Melian, C.; Adams-Buda, A.; Demco, D. E.; Blü1mich, B. *Macromolecules* **2006**, *39*, 1701–1708.

(14) (a) Furihata, K.; Seto, H. *Tetrahedron Lett.* **1999**, *40*, 6271–6275. (b) Biesemans, M.; Martins, J. C.; Willem, R.; Lycka, A.; Ruzicka, A.; Holecek, J. *Magn. Reson. Chem.* **2002**, *40*, 65–69. (c) Edden, R. A. E.; Keeler, J. *J. Magn. Reson.* **2004**, *166*, 54–68. (d) Delso, I.; Tejero, T. *Tetrahedron Lett.* **2007**, *48*, 4101–4104.

(15) Xie, T.; Penelle, J.; Verraver, M. *Polymer* **2002**, *43*, 3973–3977.

MA8023848