Angewandte
Eine Zeitschrift der Gesellschaft Deutscher Chemiker
Chemie

Supporting Information

69451 Weinheim, Germany

Controlling Polymer Architecture based on Host-Guest Interactions

Liang Chen, Xinyuan Zhu[*], Deyue Yan[*], Yan Chen, Qun Chen, and Yefeng Yao

S1. β-CD's Chemical Inactivity in this System

Natural β-CD has hydroxyls located at 2-position, 3-position and 6-position. These hydroxyls might participate in chemical reactions in certain circumstance. However, according to our observation, they are inactive in our system.

In Figure S1.1, 1-H of β-CD (4.82 ppm in Figure S1.1a and c) and methenes directly bonded to tertiary nitrogen atom in AP (2.25 ppm in Figure S1.1b and c) are chosen as the internal reference. Since there are seven 1-H in one β-CD molecule and six hydrogen atoms in selected methenes in one AP molecule, if β-CD forms 1:1 inclusion compound with AP, the ratio of integral areas should be 7:6; the result shown in Figure S1.1c is 7:5.9, which agrees quite well with the result from Elementary Analysis (EA)

---

[*] xyzhu@sjtu.edu.cn; dyyan@sjtu.edu.cn

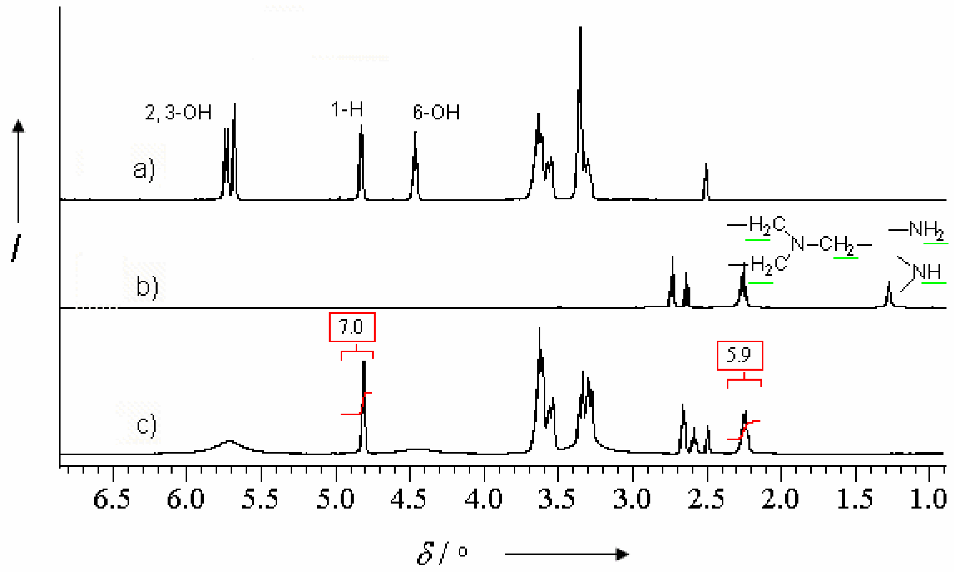


Figure S1.1 ^1H NMR spectra of a) β-CD; b) AP; and c) their inclusion compound. a and c were performed in DMSO-d_6, while sample b was dissolved in $CDCl_3$.

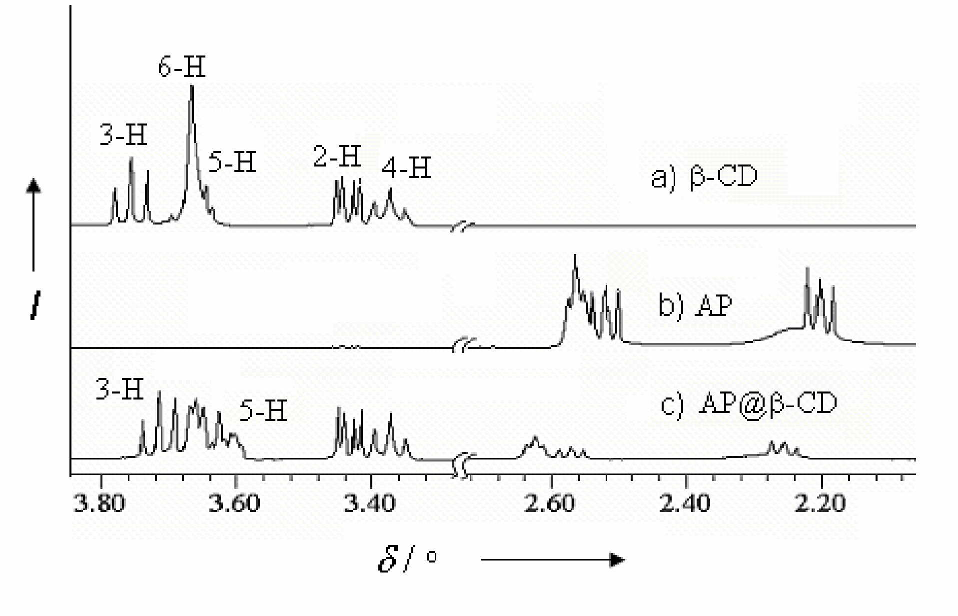


Figure S1.2 ^1H NMR spectra of β-CD, AP and their inclusion compound in D_2O (sectional).

Figure S1.2 gives clear evidence that AP has been encapsulated in the cavity of β-CD, rather than simply forming a complex via hydrogen bonds: Hydrogen atoms locate inside the cavity (3-H, 5-H) show obvious shifts in the spectrum of the inclusion compound due to the intermolecular interaction between β-CD and AP, while those hydrogen atoms outside the cavity (2-H, 4-H and 6-H) remain unchanged.

Furthermore, hydrogen atoms in AP also reveal noticeable changes.

If the vinyl groups reacted with hydroxyls and transformed into ethylene groups, new peaks would appear in the 2.0 - 4.0 ppm range. However, Figure S1.3 shows that, even after 24 hours at 40 °C, the ^{1}H NMR spectrum remains unchanged. Therefore, it can be concluded that, although greatly activated by the sulfone group, the DV vinyl groups would still not react with the β-CD's hydroxyl groups at this temperature.

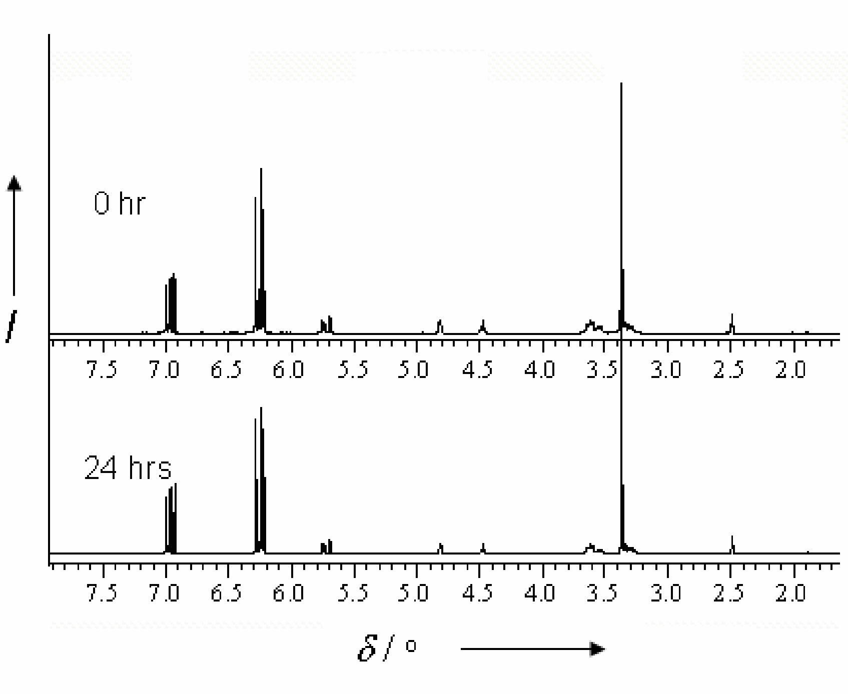


Figure S1.3 ^{1}H NMR spectra of β-CD and DV recorded at various time (DMSO-d_6).

In the ^{1}H NMR spectra of polymerized samples (Figure S2.1), the ratio of integrals of the primary hydroxyl (6-OH), anomeric proton (1-H), and secondary hydroxyl (2-OH, 3-OH) peaks remain constant at 1:1:2. Since 1-H would not take part in the chemical reaction (if cyclic structure is retained), this invariant ratio further confirms that hydroxyls don't participate in the reaction.

S2. Characterization of Poly(Sulfone-Amine) (PSA)

In Figure S2.1, the vinyl signals at 6.3 and 7.0 ppm have disappeared (ref to Figure S1.3), indicating that the reaction between vinyl and amino groups is complete and polymerization proceeds smoothly at the presence of β-CD. Moreover, the disappearance of vinyl groups suggests the addition between AP and DV is rather stable and the retro-Michael addition can be negligible.

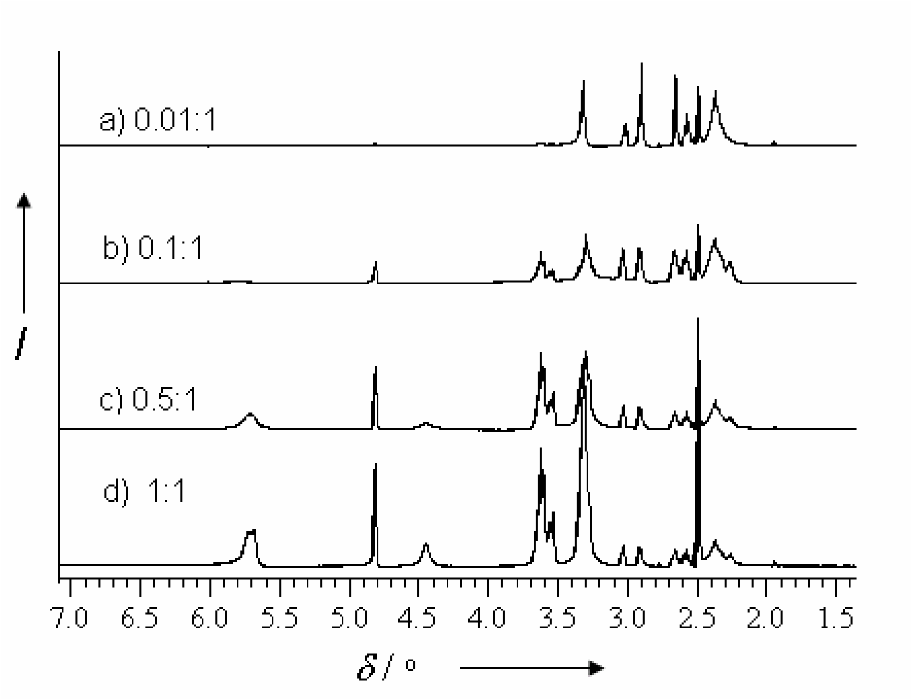


Figure S2.1 ^{1}H NMR spectra of PSAs (in DMSO-d_6).

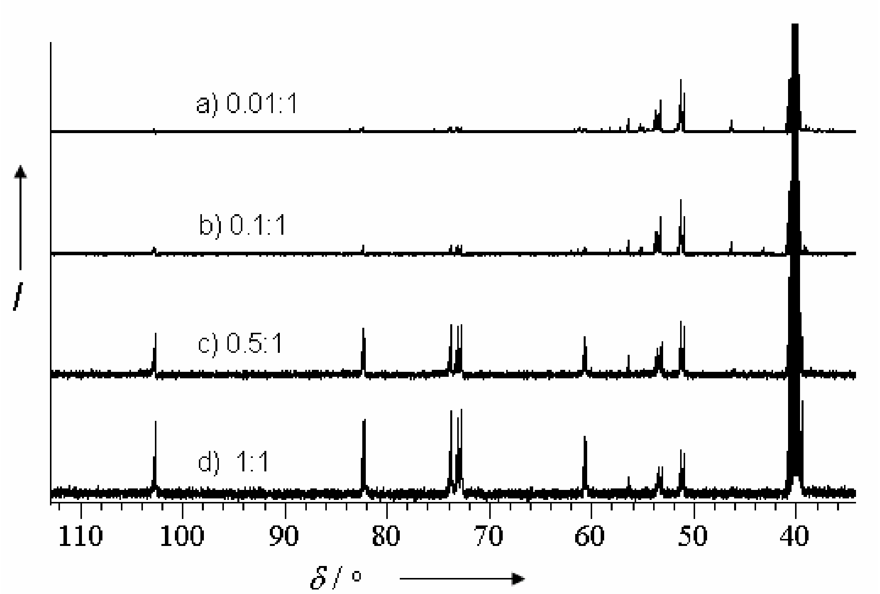


Figure S2.2 ^{13}C NMR spectra of PSAs (in DMSO-d_6).

The ^{13}C NMR spectra are shown in Figure S2.2, and they are rather hard to interpret. Signals of the β-CD's carbons are well separated, but the signals in the range of 40~50 ppm are severely overlapped, making it unrealistic to determine the structure of polymer based merely on these 1D NMR spectra.

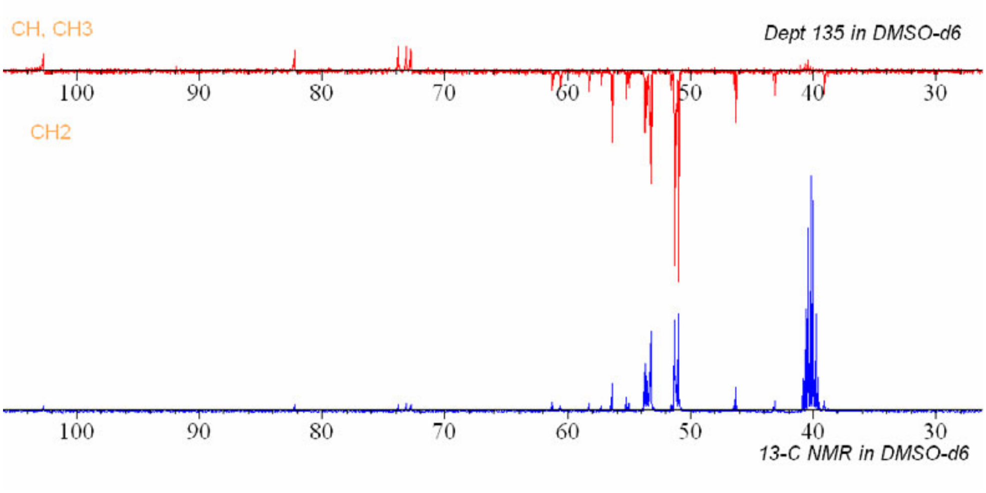


Figure S2.3 DEPT 135° and ^{13}C NMR spectura of PSA in DMSO-d_6

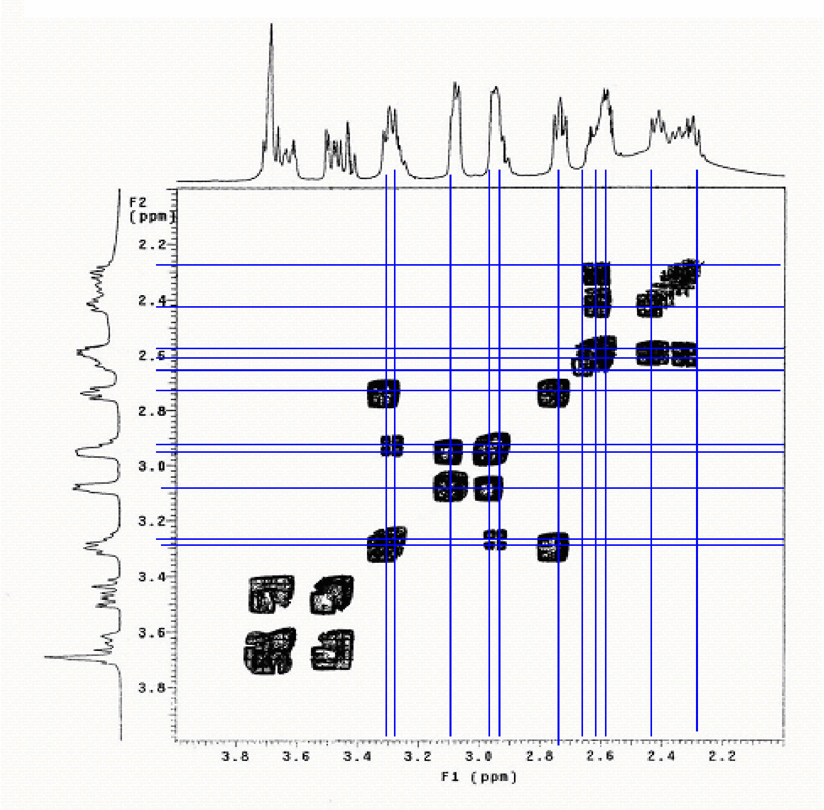


Figure S2.4 ^{1}H-^{1}H COSY of PSA in D_2O (β-CD:AP = 0.1:1)

In Scheme S3.1, it can be found that the final product has very interesting characteristics: (1) All carbon atoms in the final polymerized products exist in the form of methylene units (DEPT experiment was performed and illustrated in Figure S2.3, it can be found that all carbon atoms except for those from the host cyclodextrins are secondary carbon atoms); (2) Each spin system consists of two adjacent methylenes (Linear unit B is a much more complex spin system; however, if the ^1H-^1H COSY was measured in D_2O, the rapid exchange between various active hydrogens would transform this spin system into two isolated simple systems again, each of them consisting of two methylenes. Ref to Scheme S3.1).

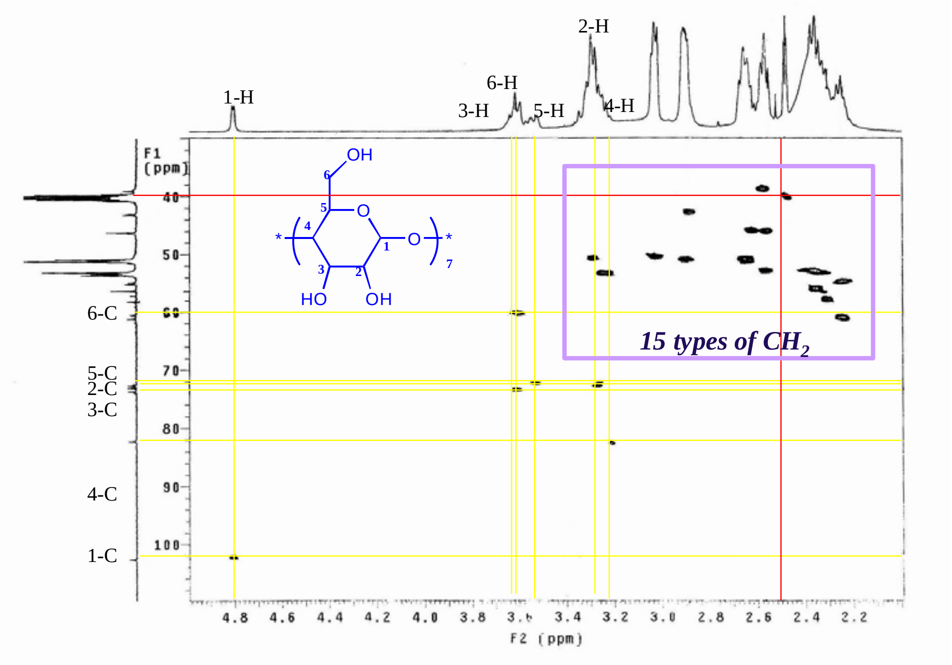


Figure S2.5 ^{13}C-^1H HSQC of a polymerized sample in DMSO-d_6 (β-CD:AP = 0.04:1).

In terms of the features mentioned above, two conclusions can be made: 1) Each cross peak in the ^1H-^1H COSY spectrum represents a spin system (Figure S2.4); 2) Every carbon atom in the polymer chain appears in the ^{13}C-^1H HSQC spectrum (Figure S2.5). Taking signals from β-CD (crossing points of the yellow lines in Figure S2.5) and the DMSO-d_6 (crossing point of the red line) away, the spectrum indicates that there are 15 kinds of methylenes in the polymer chains, which agrees well with Scheme S3.1.

Table S2.1 Molecular weight & Optical Rotation of PSAs

Ratio/β-CD:AP	0:1	0.14:1	0.5:1	1: 1	Natural β-CD
M_n[a]	8050	7630	8010	10040	1135
M_w[a]	10111	9440	9310	11260	1135
PI[a]	1.256	1.237	1.162	1.122	1
[α][b]/ °	0	49.859	90.266	-[c]	127.49

[a] M_n, M_w and PI were determined by GPC analysis with Polystyrene standards. 0.05 M $NaNO_3$ aqueous solution was used as eluent.

[b] Optical rotation is measured at 27 °C in distilled water, the wavelength is 589 nm. Mass percentages of these solutions are 1%.

[c] Poly(sulfone-amine) with the feed ratio of β-CD:AP=1:1 can be dissolved upon heating, but it turned to turbid again as the temperature decreased.

The molecular weight and optical rotation data are shown in Table S2.1. As can be seen, optical rotation increases with the feed ratio. If the feed ratio is high enough, the polymers encapsulated by β-CD will aggregate together, which results in turbidity because of the formation of crystalline inclusion complex.

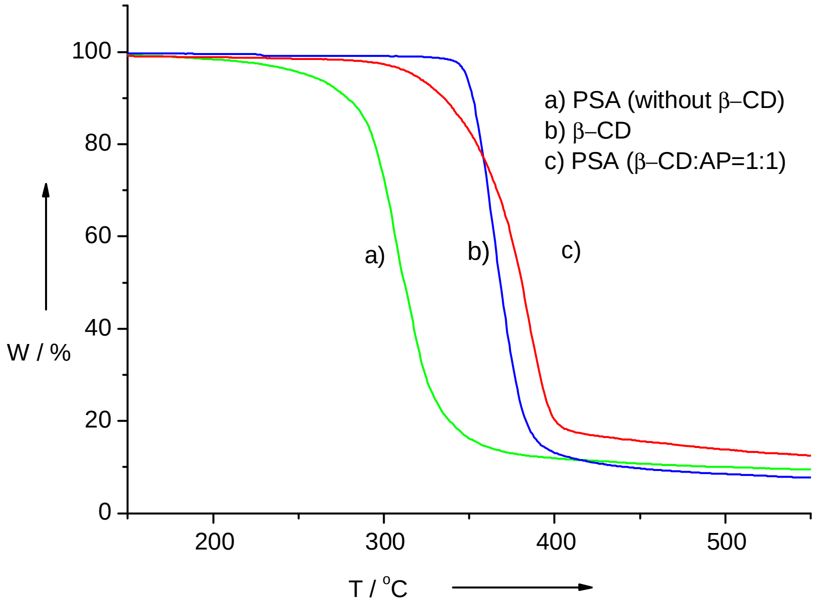


Figure S2.6 TGA traces of pure β-CD and PSAs

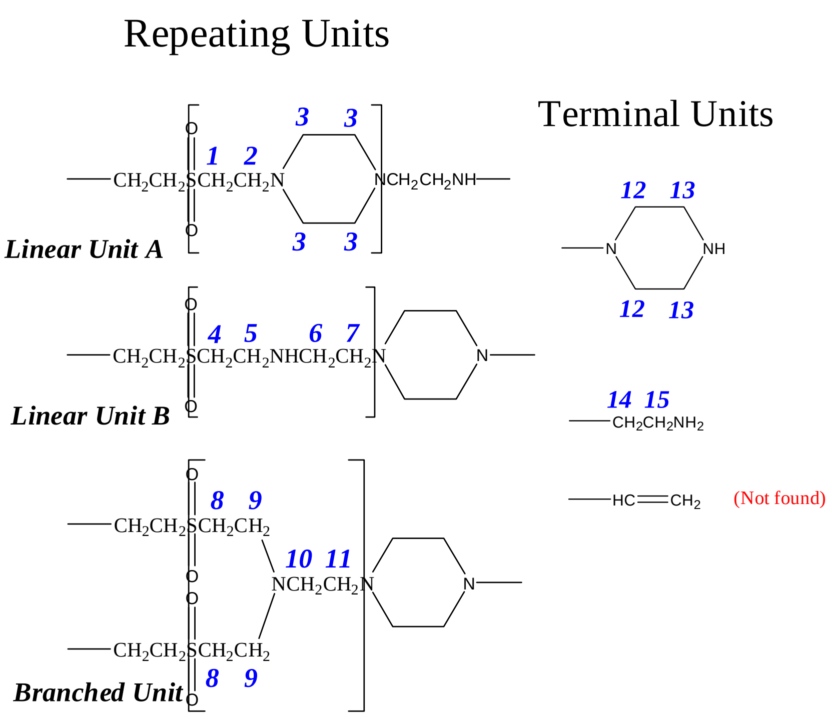
Figure S2.6 reveals that PSA polymerized in the presence of β-CD has a much higher decomposition temperature than hyperbranched poly(sulfone-amine) without β-CD, because the polymer chains are protected by inclusion complexation with β-CD. Besides, TGA traces further prove the Michael addition reaction between AP and DV is rather stable, which agrees well with the result from NMR.

S3. Determination of Degree of Branching

S3.1 Linear unit, branching unit and terminal unit

Here we adopted a new method involving 2D NMR techniques to calculate the degree of branching. Scheme S3.1 lists all possible units in poly(sulfone-amine). These units can be divided into two groups: repeating units and terminal units.

Scheme S3.1 Structural units of poly(sulfone-amine).



Labeled substructures inside square brackets represent all methylenes in the repeating units. Terminal units come from AP or DV. Identification of these structures in the spectra is assisted by NMR spectra of the monomers. Combined with the 2D NMR spectra in Figure S2.4 and Figure S2.5, the 15 kinds of methylenes can be distinguished completely.

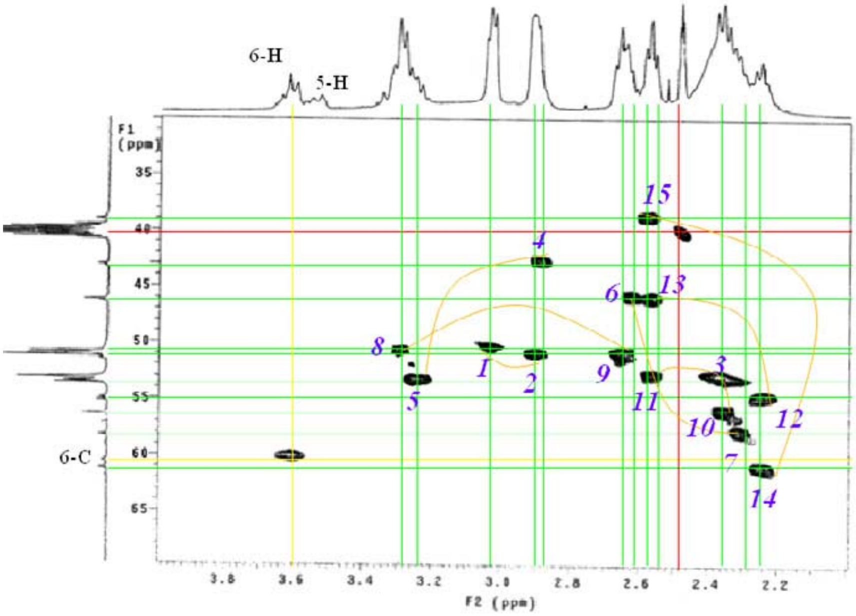


Figure S3.1 Assignment of the cross peaks in the ^{13}C-^{1}H HSQC spectrum.

In Figure S3.1, assignments of the 15 distinct types of methylenes are shown. The crossing points of yellow lines and red lines show cross peaks from C-6, H-6 of β-CD and from DMSO-d_6 respectively. Brown curves link methylenes from the same spin system (refer to cross peaks in Figure S2.4). Now the assignments are made, integrals of each unit can be used to calculate the degree of branching.

S3.2 Determination of the degree of branching (DB)

The formula put forward by Yan and Müller (listed below) is adopted to determine the DBs of the polymerized samples:

$$DB = (N_{branched} + N_{terminal} - 1) / (N_{branched} + N_{terminal} + N_{linear} - 1)$$

The calculated DBs are shown in Table S3.1, and their relation with the molar ratio of β-CD to AP is illustrated in Figure S3.2.

Table S3.1 Degree of branching of polymerized samples with various molar ratios of β-CD to AP.

Ratio/β-CD:AP	0.01:1	0.02:1	0.04:1	0.1:1	0.2:1	0.5:1	1:1
DB	0.42	0.27	0.24	0.22	0.16	0.06	0.03

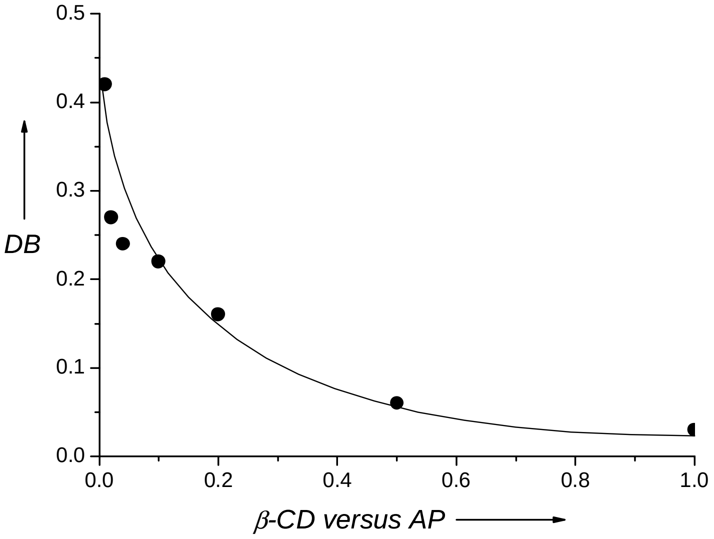
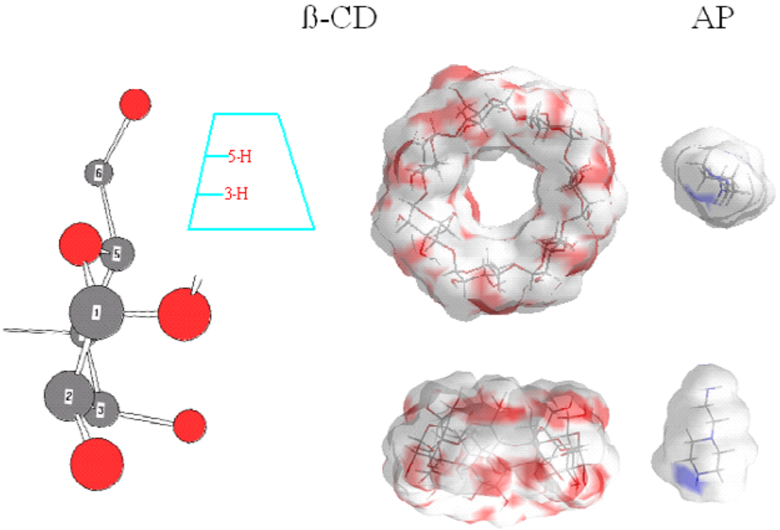


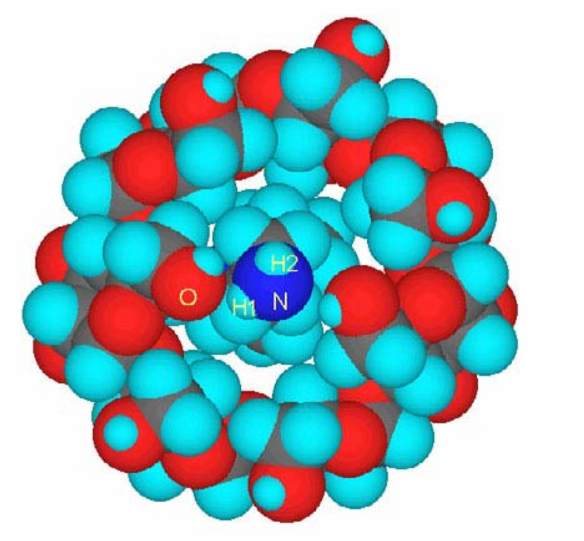
Figure S3.2 Molar ratios of β-CD to AP versus DB in polymerized samples.

S4. Possible Mechanisms and Potential Applications

S4.1 Mechanism for architectural control



(a) Size matching



(b) Hydrogen bonding (Site recognition)

Figure S4.1 Molecular models of β-CD and AP molecules

Molecular simulations give a clear picture of how β-CD controls the structure of the final products. In Figure S4.1, it is observed that the AP molecule perfectly matches for the β-CD cavity. In addition, the primary amino group in AP molecule has two hydrogen atoms: one in equatorial position and the other in axial position. The former can form hydrogen bond with adjacent 6-OHs in β-CD to stabilize the inclusion compound, and the latter, together with the secondary amine, can react with vinyl groups in DV during polymerization. Moreover, if an AP is included in the CD cavity, steric effects also favor the formation of linear units.

Those AP units encapsulated by β-CDs will therefore behave as bifunctional monomers in the polymerization, explaining why the products' DBs decrease with increasing amounts of β-CD.

S4.2 Potential applications

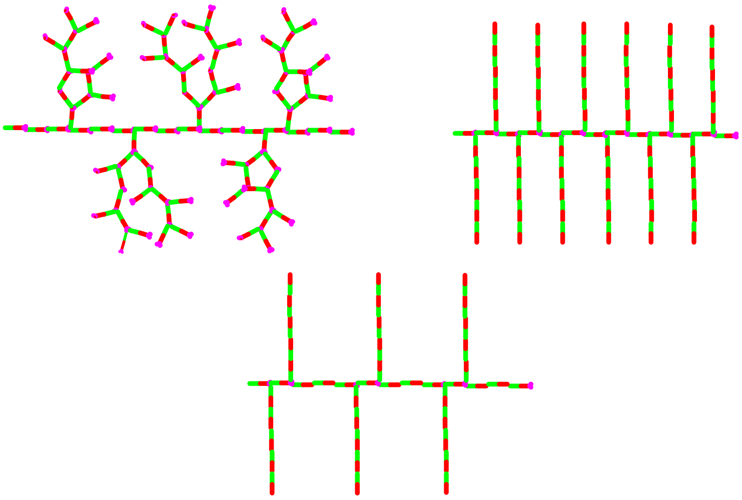


Figure S4.2 Topological structures originating from a linear stem.

In this work, we use β-CD to control polymer architecture via host-guest interaction. This represents a simple new approach to control the degree of branching of a hyperbranched polymer only by adjusting the amount of β-CD. Moreover, this architecture-controlling method has at least two other merits: (1) Compared with ordinary products from step-polymerization, the final product (e.g. ratio of β-CD:AP = 1:1) has plenty of active groups protected by the cavity of β-CD, which may serve as sites for further reactions. After further modification, polymers with new topological structures such as those in Figure S4.2 can be obtained. Although these structures have already been prepared by various living polymerizations (cationic, anionic and radical polymerizations), in our method, they can be synthesized solely by condensation polymerization. (2) This method has wide applicability: Here we report its application in the copolymerization of A_2 +BB’$_2$ or A_2+B_4. Actually, it is also feasible for AB_2, AB_3 and other A_n+B_m or A_nB_m polymerization.