Polymer Architectures

DOI: 10.1002/ange.200502306

Controlling Polymer Architecture through Host–Guest Interactions**

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Structure and performance are two fundamental characteristics of a polymeric material. Therefore, controlling the structure to get a desired property remains one of the main goals of polymer chemistry.[1] Nowadays, supramolecular principles are also commonly utilized in the design and synthesis of polymer structures, with cyclodextrin (CD) being one of the most widely used hosts. However, most of these works concern the construction of novel supramolecular systems[2–4] rather than controlling the molecular structure of the guest polymer.[5] Herein we report a supramolecular method to control the architecture of polymers. The branched structure of a polymer can be adjusted conveniently using such a method. Moreover, this supramolecular approach is versatile and can be used for the design and preparation of materials with special topological structures, functionalities, and properties.

The polycondensation–addition of 1-(2-aminoethyl)piperazine (AP), a BB'_2 monomer, and divinylsulfone (DV), an A_2 monomer, is a typical reaction for preparing hyperbranched polymers[6] by monomer-coupling methods.[7] The difference in reactivity between primary amino and secondary amino groups makes it possible to form an $AabB'_2$-type intermediate rapidly; further polymerization gives hyperbranched poly(sulfone–amine) (PSA).

A ^{1}H NMR experiment in situ revealed that neither AP nor DV react with β-CD, despite its many active hydroxy groups (see Supporting Information). Interestingly, the similarities in the size and polarity of the AP molecule and the β-CD cavity induce complexation, and intermolecular hydrogen bonds between the amino and hydroxy groups also help to stabilize the inclusion compound (IC). ^{1}H NMR and elemental analysis confirmed that AP is located in the cavity of β-CD[8] and forms a 1:1 IC. The equilibrium constant between AP and β-CD was measured by two NMR methods, namely conventional NMR binding titration and NMR diffusion measurements.[9] Both experiments gave a value for K_a in the range of $(100 \pm 10)\,\text{M}^{-1}$. This value is similar to those for ICs between β-CD and various small organic molecules.[9d]

A series of PSA samples were then prepared by adjusting the amount of β-CD. The optical rotations of these samples (see Supporting Information) suggest the presence of β-CD in the final products. A comparison of the wide-angle X-ray diffraction (WAXD) and NMR spectra before and after polymerization reveals that reaction between AP and DV can be carried out successfully in the presence of β-CD: the diffractogram of the IC formed by AP and β-CD in a 1:1 ratio (Figure 1 a) shows strong crystalline peaks and corresponds to a typical crystalline IC formed by β-CD and small guest molecules. It is different from the diffractograms of pure β-CD (Figure 1 b) and polymerized samples (Figure 1 c–f). Furthermore, in the ^{1}H NMR spectra of the polymerized samples the peaks at $\delta = 6.3$ and 7.0 ppm, assigned to the vinyl moiety, are no longer observed, which means that all of the vinyl groups have been transformed into dimethylenes ($-CH_2-CH_2-$) by polymerization and that the retro-Michael addition is negligible. A DEPT-135 experiment revealed that there are only secondary carbon atoms in the guest polymer chains, thereby further suggesting the complete conversion of the vinyl groups. These results confirm that the reaction between the vinyl and amino groups can take place even in the presence of an equimolar amount of β-CD.

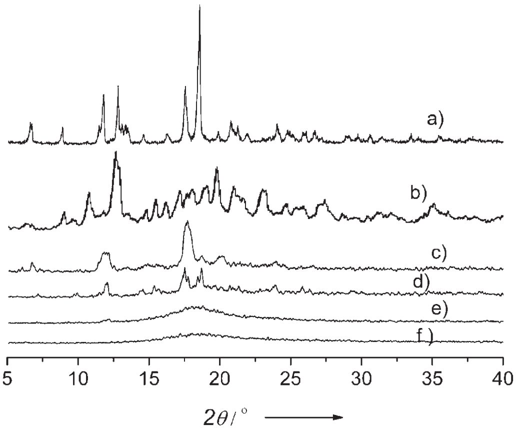

Figure 1. Diffractograms of a) IC formed by AP and β-CD; b) pure β-CD, and PSA samples with a β-CD to AP molar ratio of c) 1:1, d) 0.5:1, e) 0.14:1, and f) 0.02:1.

The WAXD spectra of polymerized samples are illustrated in Figures 1 c–f. Figure 1 c corresponds to the sample polymerized in the presence of an equimolar amount of β-CD. To our surprise, its diffractogram is identical to those of polyrotaxanes/pseudopolyrotaxanes formed by β-CD and

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[**] This work was supported by the National Natural Science Foundation of China (grant nos. 20574044, 20104004, and 50233030). X. Z. thanks Prof. Reiko Saito for her helpful suggestion and Dr. Daniel Schmidt for his assistance in proofreading the manuscript.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

linear polymers, and the characteristic reflections at $2\theta = 11.66°$ and $18.00°$ indicate that the β-CD molecules are threaded onto the polymer chain to form a channel-like structure.[10] It can be inferred from this result that linear PSA is obtained by polymerization in the presence of large amounts of β-CD. The intensities of the characteristic diffraction peaks reduce gradually with decreasing amounts of β-CD, and when the ratio of β-CD to AP is below 0.14:1 only a diffuse peak, which is close to that of pure, amorphous, hyperbranched PSA synthesized from AP and DV in the absence of β-CD, is observed (Figures 1 c–f).

Standard solid-state CP/MAS ^{13}C NMR spectra are shown in Figure 2. Split signals at $\delta = 94.6$ and 96.6 ppm assigned to the conformationally strained α-1,4-glycosidic linkage are noticeable in the spectrum of natural β-CD (Figure 2 a); however, they are no longer observed in the spectra of polymerized samples (Figures 2 b and 2 c). This result reveals that the β-CD molecules in the polymerized samples have a more symmetric conformation than in pure β-CD. In other words, the β-CD host molecules are still threaded by the polymer chains after polymerization.[11]

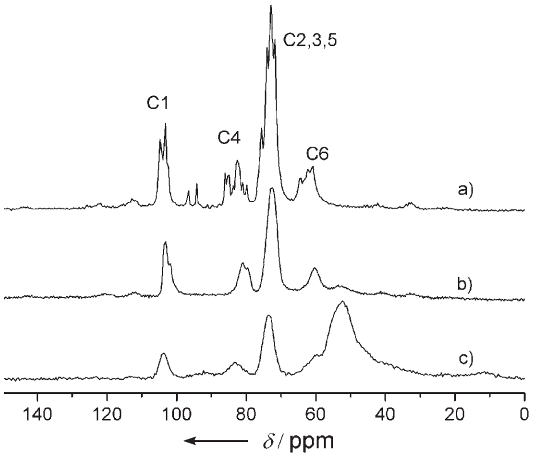


Figure 2. Solid-state CP/MAS ^{13}C NMR spectra of pure β-CD (a) and PSA samples with a β-CD to AP molar ratio of 1:1 (b) and 0.1:1 (c).

The structural units of PSA can be distinguished completely with the help of ^{1}H,^{1}H-COSY, and ^{13}C,^{1}H-HSQC techniques. Consequently, the degree of branching (DB) of various products can be determined. Details of DB determination can be found in the Supporting Information. The relation between the DB and the β-CD:AP ratio is illustrated in Figure 3. From these results, it can be seen that the DB of the PSAs decreases with increasing β-CD.

The final products are very stable. The polymerized samples with CD have a higher decomposition temperature than pure PSA, which means that the polymer chains are stabilized by inclusion complexation with β-CD (see Supporting Information).

Now we have a clear image of how to control the branched structure of PSA by adjusting the amount of β-CD. Thus, 1) changing the amount of β-CD gives samples with various architectures, 2) the β-CD does not take part in the chemical reaction itself, although it binds with guest molecules through host–guest interactions, and 3) β-CD remains threaded onto the polymer chains after polymerization. A diagram illustrating these concepts is given in Scheme 1.

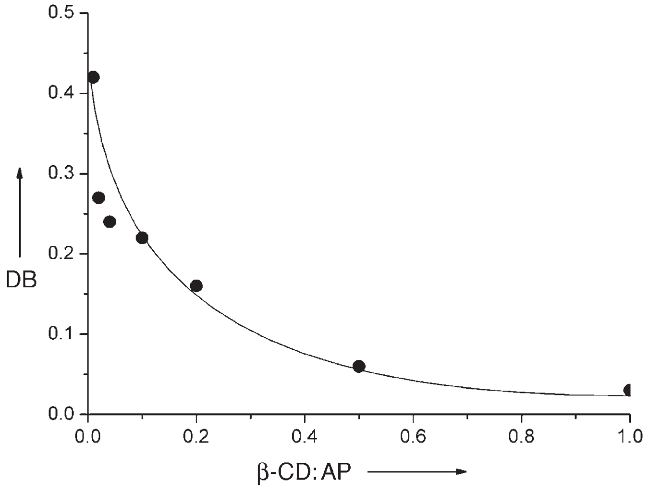
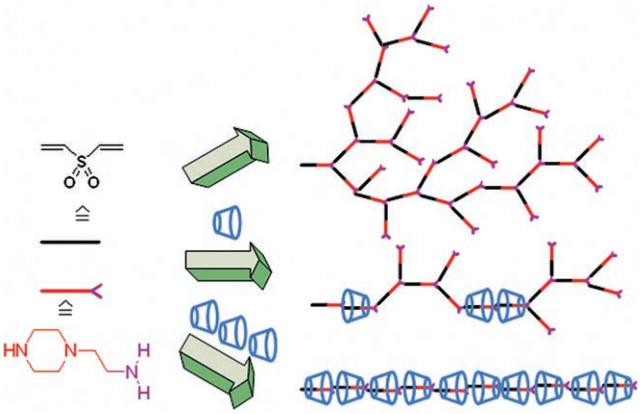


Figure 3. Relation between the molar ratio of β-CD and AP and the DB of the obtained PSA.



Scheme 1. Proposed mechanism for an architecturally controlled polymerization.

Molecular simulations gave a possible explanation as to how β-CD controls the structure of the final products. They showed that an AP molecule matches the β-CD cavity perfectly. The primary amino group in the AP molecule has two hydrogen atoms, one in an equatorial position and the other in an axial position. The former can form a hydrogen bond with adjacent 6-OH groups in β-CD to stabilize the inclusion compound, and the latter, together with the secondary amine, can react with the vinyl groups of DV. Moreover, if an AP molecule is present in the CD cavity, steric effects also favor the formation of linear units. It seems that AP units encapsulated by β-CD molecules behave as bifunctional monomers during polymerization, and this explains why the DB of the PSAs decreases with increasing amounts of β-CD.

Copolymerization of AP and DV is a typical $(A_2+BB'_2)$-type reaction. In fact, this physical protection approach is also feasible for AB_2, AB_3, and other A_n+B_m or A_nB_m polymerizations. For instance, CD can be used to control the cross-linking in a polymerization system. It is well known that if an A_2 monomer (DV) and a B_4 monomer (hexamethylenediamine; HDA) are mixed together, chemical cross-linking takes place. However, adding β-CD to such a system means that β-CD will form an inclusion complex with HDA, and this complex will behave as bifunctional monomer in the polymerization. Thus, upon adding a small amount of β-CD the product changes from a gel to a water-soluble polymer. Figure 4 shows that further increasing the amount of β-CD reduces the area of the amorphous halo and that the characteristic reflections at $2\theta=11.66°$ and 18.00°, which correspond to channel-like structures,[10] become stronger and stronger, thus indicating the formation of a linear polymer in the presence of large amounts of β-CD. Similarly, the solid-state CP/MAS ^{13}C NMR spectra (Figure 5) confirm that the β-CD molecules are threaded onto the polymer chains.[11] Therefore, the cross-linking of a polymerization system can be well controlled by adjusting the amount of β-CD.

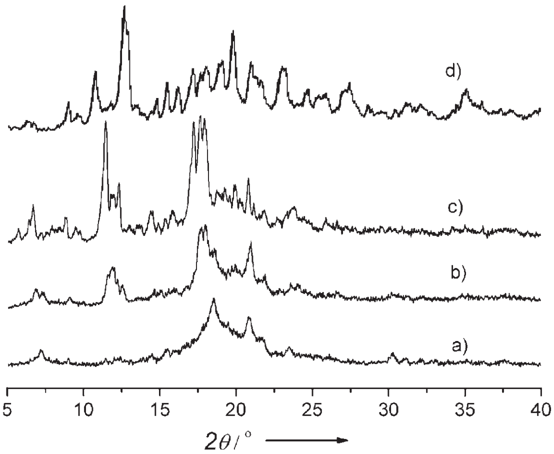


Figure 4. Diffractograms of copolymers of HDA and DV for different β-CD/HDA ratios: a) 0.2:1; b) 0.5:1; c) 1:1; d) 1:0.

In conclusion, a supramolecular method to control polymer architecture by merely adjusting the amount of host molecules present has been developed. Using this method, polymers with a large number of unreacted functional groups "inhibited" by β-CD have been obtained. These groups can be "re-activated" after removal of β-CD, thus allowing further modifications. For example, linear PSA can react with the intermediate $AabB'_2$ formed by AP and DV to form a dendronized polymer. Similarly, polymer brushes can be produced from the reaction of linear PSA with piperazine and DV. All the polymerizations described herein were carried out in aqueous solution, although the reactions can also be performed in organic solvents such as DMF and DMSO. However, we found that an aqueous solution is the most efficient system, thus illustrating that hydrophobic interactions have an important influence on the polymerization. Although the scope of suitable monomers is limited by the aqueous medium, this is a green way to synthesize polymers, which is important for both science and industry.[4a,5a] Other compounds besides CD, such as crown ethers and calixarenes, can also be used as hosts. Therefore, this approach can be extended to organic solvents for some systems.

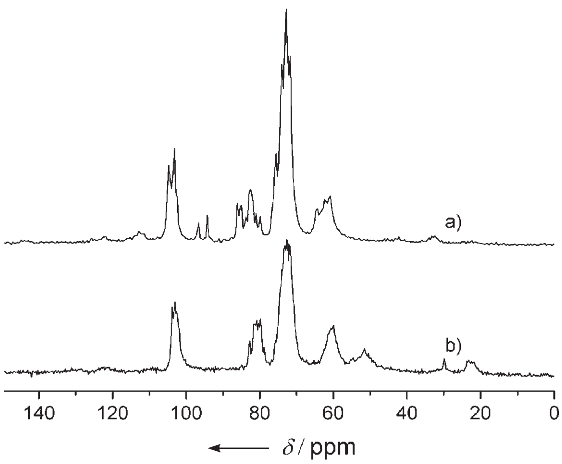


Figure 5. Solid-state CP/MAS ^{13}C NMR spectra of a) pure β-CD and b) a copolymer of HDA and DV (β-CD/HDA = 1:1).

Experimental Section

Inclusion between AP and β-CD: Purified β-CD (5.675 g, 5 mmol) was added to 100 mL of distilled water. The mixture was heated to 50 °C to get a clear solution, and then AP (5.168 g, 40 mmol) was added. After stirring at this temperature for 30 min, the solution was further heated to 70 °C and stirred for another 5 h. The solution was then kept in a refrigerator at 5 °C for recrystallization. The filtered precipitate was washed with cold distilled water to remove free AP. Finally, the white precipitate was dried under vacuum at 100 °C for 24 h. Element analysis for one AP molecule encapsulated by one β-CD molecule ($C_{48}H_{85}N_3O_{35}$): calcd. C 44.98, H 6.91, N 3.48; found C 45.27, H 6.78, N 3.32.

Copolymerization of AP and DV: A typical copolymerization procedure (where the feed ratio of β-CD to AP is 0.1:1) is as follows. β-CD (113.5 mg, 0.1 mmol) was dissolved in 20 mL of distilled water and then AP (129.21 mg, 1 mmol) was added. This mixture was stirred at 70 °C for 5 h. After cooling the solution to room temperature, DV (118.15 mg, 1 mmol) was added. The reaction bulb was then sealed and filled with nitrogen to avoid oxidation. After stirring for 120 h at 40 °C, the reaction mixture was freeze-dried to remove the solvent. Dialysis was performed with a Cellu·Sep H1 membrane, with a nominal molecular weight cut-off of 2000 $g\,mol^{-1}$ (MFPI Inc.), in order to remove free β-CD and unreacted monomers. The dialysis procedure was carried out in distilled water for 48 h. β-CD can be removed by dialysis for linear polymers, whereas for those polymers with a high degree of branching an enzyme degradation method can be used.[5c] Further details of the experiments and analysis can be found in the Supporting Information.

Copolymerization of HDA and DV: A typical copolymerization procedure (β-CD:HDA = 0.1:1) is as follows. β-CD (113.5 mg, 0.1 mmol) and HDA (116.2 mg, 1 mmol) were dissolved in 20 mL of distilled water and the solution was kept at 70 °C for 5 h. After cooling the solution to room temperature, DV (118.15 mg, 1 mmol) was added. After stirring for 120 h at 50 °C, the mixture was dialyzed and freeze-dried to remove solvent and unreacted monomers.

Received: July 1, 2005
Revised: September 30, 2005

Keywords: cyclodextrins · polymers · supramolecular chemistry · synthesis design

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