Supramolecular Control of the Branched Topology of Poly(sulfone-amine) from Divinylsulfone and Hexamethylenediamine

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ABSTRACT: A supramolecular method to control the branched topology of polymerized product from the $A_2 + B_4$ reaction system has been developed. Depending on the feed ratio, the polycondensation-addition of divinylsulfone (DV, an A_2 monomer) and hexamethylenediamine (HDA, a B_4 monomer) gives a highly branched polymer (DV/HDA = 1:1) or chemical cross-linking gel (DV/HDA = 2:1). By introduction of β-cyclodextrin (β-CD) into this reaction system, the HDA molecule is selectively encapsulated into the cavity of β-CD. Interestingly, one hydrogen atom of each primary amino group in HDA molecule is physically protected by the CD cavity, so the dendritic unit (HDA molecule) is transformed into a linear unit through the inclusion complexation. Therefore, by merely adjusting the amount of β-CD, a cross-linking gel, hyperbranched polymer, highly branched polymer, slightly branched polymer, or linear polymer can be obtained, respectively. In short, the branched topology of the polymerized product from the $A_2 + B_4$ reaction system can be easily controlled by using this supramolecular approach.

Introduction

Supramolecular systems have captured increasing attention over the past few years in polymer science, and cyclodextrin (CD) is one of the most widely used supramolecular hosts.[1−11] Because of its unique molecular structure of a hydrophobic cavity and a hydrophilic outer surface, CD tends to form inclusion complexes with many guest molecules via noncovalent interactions. Importantly, the inclusion complexation changes the physical and chemical properties of the included guest molecules, such as the solubility and reactivity. Therefore, various CDs (α-CD, β-CD, and γ-CD) and their derivatives are frequently introduced into different polymerization reactions for designing the structure and properties of final products.[5,6c,7a,8−11]

In the 1970s, Ogata[8] and Maciejewski[9] reported the inclusion polymerization of polyamides, organosilicon oligomers, and poly(vinylidene chloride)s in a CD matrix. Monomers, like diamine and vinylidene chloride, were first complexed with CDs, and then inclusion polymerization of pseudo-rotaxane monomers was carried out in aqueous or organic solvents. After that, Wenz et al.[10] synthesized the water-soluble nylon based on the solid-state polymerization of an inclusion compound between α,ω-amino acid and α-CD. α-CD molecules threaded onto the nylon chains prevent the strong hydrogen bonds between the linear nylon chains, which makes great contribution to the melioration of solubility. Recently, free radical polymerization of styrene in the γ-CD channel was performed by Tonelli et al.[6c] Because of the fact that the conformation of the styrene molecule was restricted within the γ-CD cavity, the obtained polystyrene was found to be syndiotactic-rich. Except for the inclusion polymerization in the hydrophobic channel, the amphiphilic nature of CD having a hydrophobic cavity and a hydrophilic outer surface makes it an excellent candidate for a phase transfer agent. For instance, Ritter et al.[5c−e] have done extensive research on the aqueous homopolymerization and copolymerization of various hydrophobic monomers solubilized by complexation with CDs or their derivatives. Compared with traditional organic-solvent polymerization of hydrophobic monomers, the CD-mediated polymerization in aqueous media is a green way to prepare the macromolecular compounds. Furthermore, CD can be used as a noncovalent protective agent for specific functional groups in some reaction systems. One typical example was reported by Kulkarni,[11a] who complexed β-CDs with divinyl monomers, such as ethylene glycol dimethacrylate or ethylene glycol methacrylate 4-vinyl benzoate. It was found that one methacrylate unit of the guest molecule lost its reactivity when encapsulated in the β-CD ring and the other methacrylate unit outside the β-CD could be reacted; therefore, the free radical polymerization of inclusion complexes gave a linear polymer with pendant vinyl groups.

Although CD has been widely used in polymer synthesis, to the best of our knowledge, no attention has been focused on controlling the branching structure of the guest polymer. In a recent communication,[7a] our research group has developed a method to control the polymeric architecture by introducing β-CD into an $A_2 + BB'_2$ reaction system. As reported,[12,13] the polycondensation-addition of divinylsulfone (an A_2 monomer) and 1-(2-aminoethyl)piperazine (a BB'_2 monomer) is a typical reaction for preparing hyperbranched polymers via the $A_2 + BB'_2$ strategy. Adding β-CD into this system, inclusion com-

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plexation is induced by the similarities of the size and polarity between the 1-(2-aminoethyl)piperazine and the β-CD cavity. Interestingly, one hydrogen atom of the primary amino group in the 1-(2-aminoethyl)piperazine molecule is physically protected by the CD cavity, so the inclusion complex behaves as a bifunctional monomer during the polymerization. Therefore, the branching structure of the polymer chains can be easily controlled by merely adjusting the amount of β-CD. In the present study, we extend this supramolecular synthetic approach into an $A_2 + B_4$ system (divinylsulfone + hexamethylenediamine). It has been found that structure and performance of the final products can be controlled by changing the amount of supramolecular host.

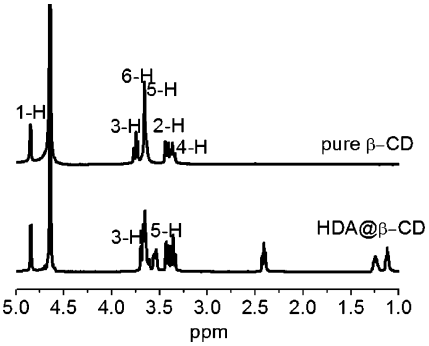


Figure 1. ^{1}H NMR spectra of β-CD and its inclusion compound with HDA in D_2O.

Experimental Section

Materials. Divinylsulfone (DV, 97%), benzoyl chloride (99%), and 4-dimethylamino pyridine (DMAP, 98%) were purchased from Aldrich. Hexamethylenediamine (HDA, 99%), urea (99%), magnesium sulfate ($MgSO_4$, 98%), hydrochloric acid (HCl, 37%), and sodium bicarbonate ($NaHCO_3$, 99%) were purchased from a local commercial company SCRC without any purification. β-CD was also purchased from SCRC and recrystallized three times from distilled water, followed by drying under vacuum at 100 °C. *N*,*N*-dimethylformamide (DMF) was purified by the standard purifying procedure. Other solvents were used without further purification.

Preparation of Inclusion Complex between β-CD and HDA. A clear solution was obtained by putting β-CD (1.135 g, 1 mmol) into 50 mL of distilled water. Then, HDA (1.162 g, 10 mmol) was added. The solution was heated to 70 °C and stirred for 5 h. Subsequently, the solution was cooled and kept in a refrigerator at 4 °C for recrystallization. The filtered precipitate was washed with cold distilled water three times to remove free HDA and β-CD. Finally, the white precipitate was dried under vacuum at 70 °C for 24 h.

Copolymerization of DV and HDA. The following copolymerization procedure (β-CD/DV/HDA = 0.1:1:1) is typical: β-CD (454.0 mg, 0.4 mmol) and HDA (464.8 mg, 4 mmol) were dissolved in 20 mL of distilled water, and then the solution was kept at 70 °C for 5 h. After the solution was cooled to room temperature, DV (472.6 mg, 4 mmol) was added and nitrogen was bubbled in. The system was stirred at 40 °C under nitrogen for 120 h, and then the mixture was kept in a refrigerator at 4 °C for recrystallization for at least 48 h. The filtered precipitate was washed with cold distilled water three times to remove free monomers and β-CD. Finally, the white precipitate was dried under vacuum at 70 °C for 24 h.

Remove β-CD from Linear Poly(sulfone-amine) Sample. An amount of 3.2 g of poly(sulfone-amine) sample synthesized from DV and HDA in the presence of an equivalent amount of β-CD was dispersed in 20 mL of distilled water, and then 0.5 g urea was added. After the solution was stirred at 60 °C for 10 h, 20 mL of CH_2Cl_2 was added and stirred for another 2 h at 40 °C with reflux. Subsequently, the organic solution was collected. The extraction step was repeated three times. Then 2 g of anhydrous $MgSO_4$ was added to the CH_2Cl_2 solution to remove residual water. The solution was concentrated after filtration and then kept in a refrigerator at 4 °C for recrystallization. The filtered precipitate was washed with ether. Finally, the white precipitate was dried under vacuum at 70 °C for 24 h.

End-Capping to Poly(sulfone-amine)s by Benzoyl Chloride. The typical end-capping procedure for the sample (β-CD/DV/HDA = 0.1:1:1) is as follows: Amounts of 2 g of samples and 2 g of DMAP were dissolved in 20 mL of dry DMF solution. Nitrogen was bubbled in. Then 2 mL of benzoyl chloride was added within 30 min and stirred for 24 h at room temperature. The reaction solution was pour into 200 mL of ethane. The filtered precipitate was washed with HCl to remove superfluous DMAP and washed with $NaHCO_3$ solution to remove superfluous HCl. Finally, the precipitate was dried under vacuum at 70 °C for 24 h. The other samples were end-capped by the same way.

Methods. The molecular weights of the synthesized samples were evaluated by GPC-MALLS (multi-angle laser light scattering) after benzylated end-capped. The GPC-MALLS system consisted of a Waters 2690D Alliance liquid chromatography system, a Wyatt Optilab DSP differential refractometer detector, and a Wyatt DAWN EOS MALLS detector. Two chromatographic columns (Styragel HR3, HR4) with a precolumn were used in series. DMF containing 10 mM LiBr was used as the mobile phase at a flow rate of 0.3 mL/min at 30 °C. Eighteen angles were utilized for the determination of M_w. The experimental results show that the intensity of the scattered light has no obvious angular dependence. The data were processed with Astra software (Wyatt Technology). Here, the refractive index increment (d*n*/d*c*) of polymer samples in DMF was measured by using a novel differential refractometer[14] at 25 °C and 633 nm.

^{1}H NMR, ^{13}C NMR, COSY, HSQC, and solid-state CP/MAS ^{13}C NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. Quantitative ^{13}C NMR spectra were measured by the method of inverse gated ^{1}H decoupling.

Wide-angle X-ray diffraction (WAXD) patterns were measured by a Rigaku III Dmax 2500 diffractometer, using Cu Kα radiation. Scans were collected in the 2θ range from 4 to 40°, with a step of 0.02° and a scan rate of 0.1°/min.

Thermal gravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 instrument with a heating rate of 20 °C/min under a dry nitrogen atmosphere (flow rate 20 mL/min). The calorimetric measurements were carried out on a Perkin-Elmer Pyris-1 series differential scanning calorimeter (DSC) under a flowing nitrogen atmosphere. Here, the heating rate was 10 °C/min.

Results and Discussion

It is well-known that when divinylsulfone (DV, an A_2 monomer) mixes with hexamethylenediamine (HDA, a B_4 monomer), Michael Addition takes place.[7a,15] With dependence on different experimental conditions, highly branched polymer or chemical cross-linking gel might be obtained. Noting that amine compounds can readily form inclusion complexes with cyclodextrins (CDs), we introduced CDs into the reaction system of DV and HDA and then investigated the influence of supramolecular interaction on polymerization.

With the addition of HDA into a saturated β-CD aqueous solution, a white precipitate appeared, indicating the formation of an inclusion complex between β-CD and HDA. Figure 1 gives the ^{1}H NMR spectra of pure β-CD and its inclusion complex with HDA. It can be found that hydrogen atoms located inside the cavity of β-CD (3-H, 5-H) show obvious shifts in the spectrum of the inclusion complex due to the intermolecular interaction between HDA and β-CD, while the hydrogen atoms outside the cavity (1-H, 2-H, 4-H, 6-H) remain unchanged. It

Table 1. Molecular Weight (M_w and M_n), Polydispersity (PDI), Yield, and the Degree of Branching (DB) of Poly(sulfone-amine)s

entry	ratio[a]	yield (%)	M_w[b] ($\times 10^4$)	M_n[b] ($\times 10^4$)	PDI	d*n*/d*c*	DB[c]
1	0	85.7	2.81	2.60	1.08	0.094	0.25
2	0.05	73.8	1.94	1.17	1.65	0.093	0.20
3	0.10	75.7	1.54	1.29	1.19	0.095	0.17
4	0.15	73.4	1.80	1.50	1.20	0.094	0.14
5	0.20	81.5	1.40	1.03	1.36	0.095	0.13
6	0.25	75.6	1.82	1.65	1.10	0.100	0.09
7	0.50	83.6	1.79	1.70	1.05	0.097	0.03
8	1	79.4	1.94	1.80	1.08	0.094	0.01

[a] β-CD/HDA. [b] Determined by GPC-MALLS, after benzylated end-capped. [c] Determined by ^{1}H NMR.

can be deduced that the HDA molecule is embraced in the cavity of the β-CD.[16] On the basis of the integral areas of 1-H of the β-CD and the methylenes in HDA, it can be calculated that a 1:1 stoichiometric complex between HDA and β-CD is formed. NMR titration results in the Supporting Information confirm the formation of an inclusion complex with the stoichiometric ratio. On the other hand, when DV is added into a β-CD solution, the ^{1}H NMR spectrum of β-CD is almost unchanged. These facts demonstrate that β-CD keeps inactive in the DV + HDA reaction system and only selectively complexes with the HDA monomer.

Molecular simulations in the Supporting Information reveal that the HDA molecule perfectly matches for the β-CD cavity. The primary amino group in the HDA molecule has two hydrogen atoms: one in the equatorial position and the other in the axial position. Importantly, the former can form a hydrogen bond with adjacent 6-OHs of the β-CD to lose its reactivity, while the latter keeps its activity. Moreover, the steric effect also prevents the equatorial hydrogen in the CD cavity from reacting. Therefore, the HDA monomer encapsulated by β-CD behaves as a bifunctional monomer during polymerization. It implies that the branched topology of poly(sulfone-amine) from DV and HDA might be tuned by adjusting the amount of β-CD.

By changing the amount of β-CD, different polymerization samples were synthesized via the polycondensation-addition of DV to HDA with the ratio of 1/1 in water. Reaction conditions and results are summarized in Table 1. In the absence of β-CD, the vinyl groups of the DV molecule react with primary amines of HDA immediately, forming the secondary amino groups. Although the activity of the secondary amines decreases greatly owing to the high steric hindrance, some secondary amines still take part in the polymerization at a suitable reaction temperature (such as 40 °C).[15] Therefore, highly branched polymers might be obtained. Careful examination of the structure of obtained polymers shows that four different types of subunits may be present. Scheme 1 displays the structural units of poly(sulfone-amine) synthesized from DV and HDA, and the branched topology of polymerized products can be verified by nuclear magnetic resonance (NMR) analysis.

^{1}H, ^{1}H-COSY, and ^{13}C, ^{1}H-HSQC spectra in Figure 2a,b were performed for assignment of the molecular structure.[7a,17] Scheme 1 reveals that 1-H/2-H, 2-H/3-H, 2-H/6-H, 2-H/9-H, 4-H/5-H, and 7-H/8-H are in different spin systems. On the basis of the cross-peaks in the 2D-NMR spectra, the assignment of each structural unit for poly(sulfone-amine) is performed, and the corresponding details are given in Figure 2. Thus, the degree of branching (DB) for branched poly(sulfone-amine) can be calculated according to the following equation:[18]

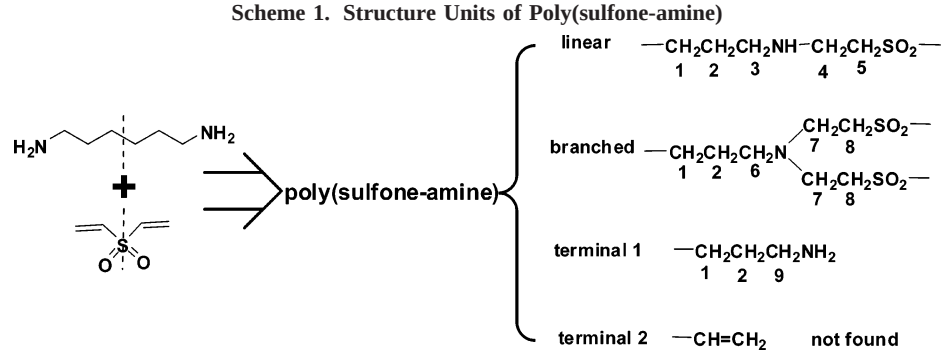
$$\mathrm{DB} = (\mathrm{D} + \mathrm{T})/(\mathrm{D} + \mathrm{T} + \mathrm{L}) \quad (1)$$

where D, T, and L represent the fractions of the dendritic, terminal, and linear units, respectively. The DB of the sample synthesized from DV and HDA without β-CD is 0.25 when calculated from ^{1}H NMR or quantitative ^{13}C NMR spectra.

Adding β-CD into the reaction system, an HDA molecule is embraced into the cavity of the β-CD to form an inclusion complex so that some dendritic units are transformed into linear units. With an increase of the β-CD amount, the topological structure of polymerized products changes greatly. Table 1 gives the DB of all samples. It is clear that the topological structure of poly(sulfone-amine) can be tuned from branched (DB = 0.25) to linear by simply increasing the β-CD amount.

The supramolecular control of β-CD on the branched topology can be corroborated by the WAXD spectra. Figure 3 shows that when the amount of β-CD is low, the polymerized samples are crystalline and the diffraction patterns are similar to that of pure branched poly(sulfone-amine) synthesized without β-CD. It has been well reported[19] that the branched polymers can crystallize when DB < 0.3, which agrees with our observation very well. Interestingly, as soon as the ratio of β-CD/HDA approaches 0.25 or higher, the diffractograms are totally different. The WAXD patterns of samples with large β-CD amount are identical to those of polyrotaxanes/pseudopolyrotaxanes formed by β-CD and linear polymers. Two characteristic reflections at $2\theta = 11.66°$ and 18.00° indicate that β-CD molecules are threaded onto the polymer chains to form a channel-like structure.[20] With the increase of the β-CD amount, the intensity of characteristic diffractions is strengthened greatly, implying the transition of polymer architecture from branched to linear. The linear polymer can be extracted from the β-CD channels into the CH_2Cl_2 solution at high temperature, which has been described in the experimental part. Figure 3 shows that the WAXD pattern of the extracted linear polymer is similar to that of branched poly(sulfone-amine) without β-CD; however, the characteristic diffractions of the former is much stronger and sharper than those of the latter. The existence of the polyrotaxane/pseudopolyrotaxane structure can be confirmed by solid-state CP/MAS ^{13}C NMR experiments. Figure 4 shows that although the resonance frequencies are similar for β-CD and its crystalline inclusion complex with poly(sulfone-amine), the

Scheme 1. Structure Units of Poly(sulfone-amine)



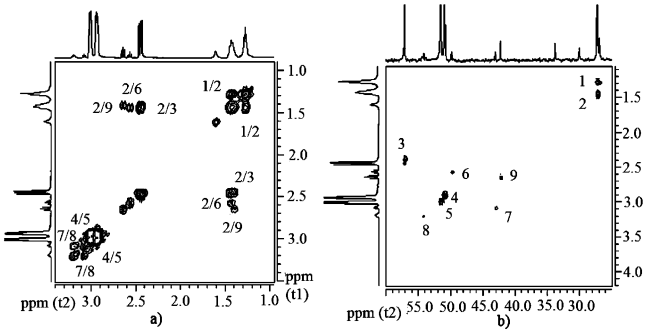


Figure 2. 2D NMR spectrum of poly(sulfone-amine) synthesized by DV and HDA without β-CD in $CDCl_3$: (a) ^1H, ^1H-COSY spectrum, (b) ^{13}C, ^1H-HSQC spectrum.

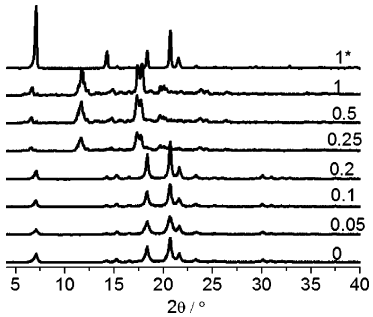


Figure 3. X-ray diffractograms of poly(sulfone-amine)s from DV and HDA at the ratio of 1:1 in the presence of different β-CD amounts. The number corresponds to the molar ratio of β-CD:HDA. 1*: the extracted linear polymer.

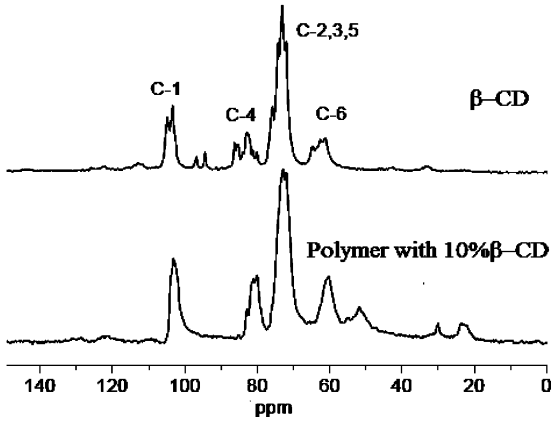


Figure 4. CP/MAS ^{13}C NMR spectra of pure β-CD and poly(sulfone-amine) synthesized from DV and HDA in the presence of 10% β-CD.

multiple resonances for each carbon type in pure β-CD become a single resonance for the crystalline inclusion complex. In the spectrum of natural β-CD, split signals at 94.6 and 96.6 ppm assigned to the conformationally strained α-1,4-glycosidic linkage are noticeable; however, they are no longer observed in the spectrum of the polymerized sample. All of these results demonstrate that β-CD molecules in the polymerized samples have a more symmetric conformation than natural β-CD molecules. In other words, the β-CD host molecules are threaded on the polymer chains after polymerization.[21] Further evidence for the polyrotaxane/pseudopolyrotaxane structure comes from the thermal decomposition analysis. Figure 5 presents the thermal decomposition curves of polymerized samples with different amounts of β-CD. With the increase of the amount of β-CD, more and more chain segments are protected by inclusion complexation with β-CD, which improves the thermal stability of poly(sulfone-amine) samples.

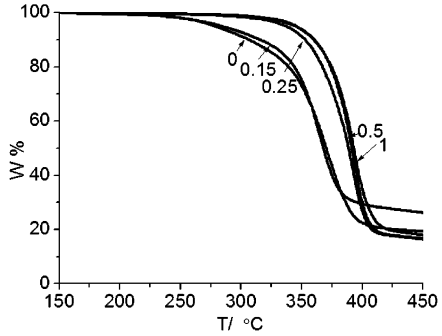


Figure 5. TGA curves of samples with different amounts of β-CD. The number corresponds to the molar ratio of β-CD/HDA.

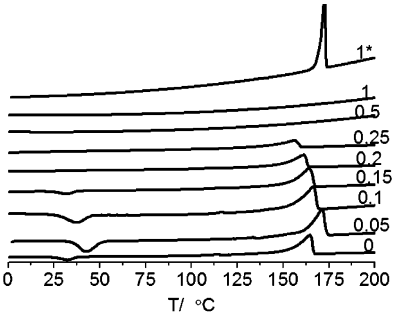


Figure 6. DSC thermograms for poly(sulfone-amine)s with different β-CD amounts. The number corresponds to the molar ratio of β-CD:HDA. 1*: the extracted linear polymer.

Figure 6 shows the DSC curves of the synthesized samples with different amounts of β-CD. For pure, branched poly(sulfone-amine) without any β-CD, the peak temperatures of cold crystallization and the melting endotherm are 29.9 and 158.4 °C, respectively. With the addition of a small amount of β-CD into the reaction system, both the crystallization peak and the melting endotherm shift to high temperature, and the corresponding enthalpies become large. Apparently, the decrease of DB facilitates the crystallization of poly(sulfone-amine) chains. However, owing to the inclusion complexation between β-CD and the polymeric guest, further increasing the β-CD amount destroys the regular stacking of the poly(sulfone-amine) chains. Correspondingly, both the cold crystallization peak and the melting endotherm shift to low temperature, and the enthalpies reduce gradually. Finally, when the ratio of β-CD to HDA reaches to 0.5 or higher, the cold crystallization and melting peaks disappear completely because of the formation of many polyrotaxanes/pseudopolyrotaxanes. When β-CD/HDA is 1:1, the pseudopolyrotaxane appears, indicating the formation of linear poly(sulfone-amine). For comparison, Figure 6 also gives the melting behavior of poly(sulfone-amine) after extraction by CH_2Cl_2. Both temperature and enthalpy of the melting peak are the highest among all samples, and the crystallinity of extracted linear poly(sulfone-amine) is high enough to prevent cold crystallization upon heating. These experimental results support the existence of linear poly(sulfone-amine).

Provided that the molar ratio of DV to HDA is enhanced from 1:1 to 2:1, the average functionality of the reaction system is much larger than 2. According to Carothers gel theory, the chemical cross-linking gel will form. Actually, we did observe the formation of a chemical cross-linking gel exactly in this feed ratio. To adjust the critical gel point, β-CD was added into such a reaction system. On addition of a small amount of β-CD (β-CD/DV/HDA = 0.1:2:1), a clear and homogeneous solution was produced and gelation was no longer observed. On the basis of the aforementioned discussion, it can be imagined that some

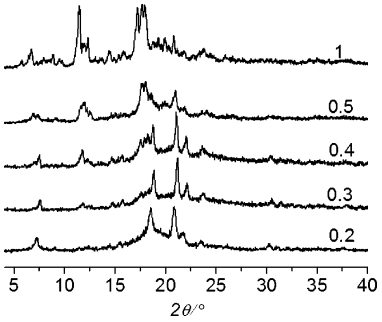


Figure 7. X-ray diffractograms of poly(sulfone-amine)s from DV and HDA at the ratio of 2:1 in the presence of different β-CD amounts. The number corresponds to the molar ratio of β-CD/HDA.

dendritic units are transformed into linear units due to the complexation of β-CD with HDA, which leads to the formation of highly branched polymers instead of the cross-linking gel. Figure 7 shows that further increasing the β-CD amount to 40%, the area of the amorphous halo related to the branched topology reduces and the characteristic reflections at $2\theta = 11.66°$ and 18.00° corresponding to channel-like structures appear. It suggests the formation of some long linear segments within the polymer backbone in the presence of many β-CD molecules.[20] Moreover, the solid-state CP/MAS ^{13}C NMR spectra in the Supporting Information also confirm that β-CD molecules are threaded onto the polymer chains. With the increase of the β-CD amount, the intensities of channel-like characteristic reflections improve greatly, illustrating the transition of resultant polymer from branched into linear topology. Therefore, it can be concluded that the cross-linking of a polymerization system can be well controlled by adjusting the amount of β-CD.

Conclusions

Supramolecular control of the branched topology of poly(sulfone-amine) from divinylsulfone (DV, an A_2 monomer) and hexamethylenediamine (HDA, a B_4 monomer) has been carefully investigated. When the feed ratio is 1:1, the polycondensation-addition of DV to HDA gives the branched poly(sulfone-amine). With the help of the 2D-NMR technique, it is found that the degree of branching (DB) of the polymerized sample is 0.25. Adding β-CD into this reaction system, HDA monomer is selectively encapsulated into the cavity of the β-CD, which behaves as a bifunctional monomer in polymerization. Increasing the β-CD amount, more and more dendritic units are transformed into linear units. Correspondingly, the DB of poly(sulfone-amine) is decreased. Finally, in the presence of a large amount of β-CD, linear poly(sulfone-amine) is formed in the β-CD channel.

If the feed ratio of DV to HDA reaches 2:1, a chemical cross-linking gel appears. Similarly, by introducing a small amount of β-CD into the reaction system, the chemical cross-linking gel can be avoided and a highly branched poly(sulfone-amine) is formed. Further increasing the β-CD amount, the architecture of the resultant polymer changes from branched to linear. It means that the cross-linking of a polymerization system can be well controlled by adjusting the amount of β-CD.

In conclusion, the branched topology of the polymerized product from the $A_2 + B_4$ reaction system can be easily controlled using the host−guest interaction between CDs and guest molecules.

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Supporting Information Available: Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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