*Macromolecules* **2000,** *33,* 7693−7699

# Hyperbranched Polymers Made from $A_2$ and $BB'_2$ Type Monomers. 1. Polyaddition of 1-(2-Aminoethyl)piperazine to Divinyl Sulfone

**Deyue Yan* and Chao Gao**

*College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, The People's Republic of China*

*Received March 10, 2000; Revised Manuscript Received July 6, 2000*

ABSTRACT: A new strategy for synthesis of hyperbranched polymers from commercially available $A_2$ type and $BB'_2$ type monomers has been developed. In the first part of this series, hyperbranched polysulfone−amine with multiamino groups is prepared by polyaddition of 1-(2-aminoethyl)piperazine ($BB'_2$) to divinyl sulfone ($A_2$) without any catalysts. The products are soluble in water and organic solvents such as *N*,*N*-dimethylformamide, chloroform, and *N*-methyl-2-pyrrolidone. The polymerization mechanism has been investigated with FTIR, HPLC, and MS. During the reaction, secondary amino groups of 1-(2-aminoethyl)piperazine react rapidly with vinyl groups of divinyl sulfone within 15 s, forming dominant dimers and some other species. The dimer can be considered as a new $AB'_2$ type of monomer. Further reactions among $AB'_2$ molecules and $AB'_2$ with other species result in the formation of hyperbranched polymers. The degree of branching of the resulting polymer is higher than 50%. No gelation occurs in solution polymerization when the $A_2$ to $BB'_2$ ratio equals 1. Similarly, there is no gelation in solution polymerization if the feed ratio of $A_2$ to $BB'_2$ is 3/2; however, gelation does occur when the resulting polymer is separated from the solution. There are both terminal amino groups and vinyl groups in the hyperbranched polysulfone−amine if the feed $A_2$ to $BB'_2$ ratio is 3/2, which further react with each other in bulk state resulting in a cross-linked material. If the terminal amino groups are protected by hydrochloride acid in advance in the solution, then no gelation can be observed after the product is separated from the solution.

## Introduction

The interest in hyperbranched polymers increased rapidly over the past decade due to their unique physical and chemical properties as compared to their linear analogues.[1−13] Hyperbranched polymers were prepared mainly by polycondensation of an $AB_x$ type monomer which has one "A" functional group and $x$ "B" functional groups.[14] This approach has been widely used to synthesize a variety of hyperbranched polymers such as polyethers,[15,16] polyesters,[17−19] polyamides,[20] polyurethanes,[21] poly(siloxysilanes),[22] polycarbonates,[23] poly(ether ketones),[24] and so forth. Most of $AB_x$ type monomers are unavailable commercially. It is cumbersome to synthesize a new $AB_x$ monomer. Recently, Kakimoto and co-workers[25] successfully performed the polycondensation of diamines ($A_2$) with trimesic acid ($B_3$) in the presence of triphenyl phosphite and pyridine as condensation agents, resulting in the hyperbranched aromatic polyamide. The authors[25] pointed out that gel formation was observed when the total monomer concentration was increased to 0.31 mol/L or 4.9 wt %. So the allowed concentration of the raw materials for the preparation of hyperbranched polymers is limited. Furthermore, the polycondensation of diamines and tricarboxylic acids leads to gelation within 10−20 min when the feed ratio of amino groups to carboxylic acid groups is equal to 1 ($A_2/B_3 = 3/2$).[25,26]

In this work, we present a novel approach for the synthesis of hyperbranched polymers from a $BB'_2$ type of trifunctional monomer and an $A_2$ type of difunctional monomer. Both the $BB'_2$ type monomer and the $A_2$ type monomer are commercially available. In the $BB'_2$ monomer there are one B functional group and two B′ functional groups. Both B and B′ groups can react with A group, and the reactivities of B and B′ groups are different from each other. The difference in reactivities may be attributed to the distinct in chemical environment or chemical structures of the two functional groups. Through this approach, hyperbranched polysulfone−amine was successfully prepared by the polymerization of 1-(2-aminoethyl)piperazine ($BB'_2$) and divinyl sulfone ($A_2$) without any catalysts.

## Experimental Section

**Characterization.** The $^1$H NMR studies were conducted on a Bruker 500 MHz NMR spectrometer with $CDCl_3$ as solvent. FTIR measurements were performed on a Bruker Equinox 55 spectrometer using a Barnes analytical FTIR sealed cell (KBr 0.5 mm). HPLC chromatograms were obtained on a Waters 515 HPLC with C-18 column as immobile phase and water and acetonitrile (25:75) as mobile phase. HP 1100 LC/MSD was used to obtain the mass spectrum. The molecular weight was measured in chloroform solution on VPO K-7000 with polystyrene standards ($M_n = 7000$). TGA was implemented in nitrogen on a PE Pyris-7 thermal analyzer. All the samples were heated at 20 °C/min heating rate from 25 to 700 °C. DSC was carried out with a PE Pyris-1 thermal analyzer. All the samples were heated at 10 °C/min heating rate from 25 to 200 °C under nitrogen for the first scan, then cooled at 10 °C/min cooling rate to −50 °C, and immediately heated at 10 °C/min heating rate from −50 to 200 °C for the second scan.

**Materials.** Divinyl sulfone (DV) was purchased from Aldrich and purified by vacuum distillation before use. 1-(2-Aminoethyl)piperazine (AP, Aldrich) was used as received.

**Polymerization.** When the feed ratio of DV to AP is 1/1, a typical experimental procedure is as follows (PA-1 in Table 1): a three-necked flask was charged with 2.363 g (20 mmol) of DV, 2.584 g (20 mmol) of AP, and 15 mL of chloroform. The mixture was heated at 40 °C for 5 days under stirring and poured into 500 mL of methanol. The precipitated product was collected by filtration and purified by reprecipitation from chloroform solution into methanol. The product was washed with methanol and acetone and dried under vacuum at 80 °C

10.1021/ma000438j CCC: $19.00

**Table 1. Reaction Conditions and Results of the Polymerization of Divinyl Sulfone and 1-(2-Aminoethyl)piperazine**

| code | ratio[a] | solvent | concn[b] | time (days) | yield (%) | $DB_{NMR}$ (%) | $DB_{tit}$ (%) | $\eta_{inh}$[c] (dL/g) |
|---|---|---|---|---|---|---|---|---|
| PA-1 | 1:1 | $CHCl_3$ | 1:7.5 | 5 | 93.0 | 53.2 | 54.6 | 0.25 |
| PA-2 | 1:1 | $H_2O$ | 1:7.5 | 5 | 85.8 | 50.6 | 51.2 | 0.28 |
| PA-3 | 3:2 | $CHCl_3$ | 1:5 | 7 | 95.5 | 52.5 |  | 0.31 |
| PA-4 | 3:2 | $H_2O$ | 1:5 | 7 | 87.3 | 57.1 |  | 0.18 |
| PA-5 | 1:1 | $CHCl_3$ | 1:2.5 | 4 | 96.4 | 53.4 | 54.7 | 0.42 |
| PA-6 | 3:2 | $CHCl_3$ | 1:2.5 | 6 | 97.8 | 54.3 |  | 0.35 |
| PA-7 | 1:1 | DMF | 1:1.5 | 1 | 89.3 | 55.7 | 58.4 | 0.23 |
| PA-8 | 3:2 | DMF | 1:1.5 | 1 | 90.1 | 58.2 |  | 0.21 |

[a] The initial mole ratio of divinyl sulfone to 1-(2-aminoethyl)piperazine. [b] The volume ratio of divinyl sulfone to solvent. [c] The inherent viscosity of the hydrochloride measured at the concentration of 0.5 g/dL in water at 25 °C.

for 24 h. Yield: 4.6 g (93%) of snow-white powder. $^1H$ NMR ($CDCl_3$): $\delta$ 3.3, 3.2 ($-CH_2SO_2CH_2-$), 2.1 ($-NH-$, secondary amino proton), 1.25 ($-NH_2$, primary amino proton). IR (KBr): $\nu$ 3450−3250 (amino groups), 1314.9, 1130.1 $cm^{-1}$ ($SO_2$). Anal. Calcd for $C_{10}H_{21}N_3O_2S$: C, 48.51%; H, 8.49%; N, 16.98%; S, 12.94%. Found: C, 48.45%; H, 8.61%; N, 16.91%; S, 12.99%. If the precipitant was 500 mL of methanol and 20 mL of 10 N aqueous HCl, the product obtained was hydrochloride of the polysulfone−amine. IR (KBr): 2750−2150 (tertiary amino group), 1315, 1133 $cm^{-1}$ ($SO_2$).

For the polymerization of DV and AP with the ratio 3/2, DV (3.545 g, 30 mmol) was reacted with AP (2.584 g, 20 mmol) under reaction conditions similar to those aforementioned. After the mixture was heated at 40 °C for 7 days, the reaction solution was then poured into 500 mL of methanol containing 30 mL of 10 N aqueous HCl with stirring. The product was collected by filtration and purified by reprecipitation from water solution into methanol and then dried under vacuum at 70 °C for 24 h. Yield: 7.8 g of snow-white powder. IR (KBr): 3450−3250 (primary or secondary amino group), 2520 (tertiary amino group), 1613 (C═C), 1332 and 1133 $cm^{-1}$ ($SO_2$). $^1H$ NMR ($D_2O$): $\delta$ 2.08 (secondary amino proton), 6.4 and 6.8 (vinyl protons).

**End-Capping Reaction.** End-capping of amino groups: In a three-neck flask, 2.3 g of polymer PA-1 was dissolved in 30 mL of chloroform, and then 1.2 g of benzoyl chloride and 2 mL of triethylamine in 15 mL of chloroform solution were added to the mixture. The reaction was conducted at room temperature for 10 h with stirring. Then the reaction mixture was poured into 500 mL of tetrohydrofuran (THF); the precipitate was collected by filtration. The crude product was purified by reprecipitation from chloroform solution into THF. The product was filtered, washed with THF, and dried overnight in a vacuum at about 100 °C to give the end-capped polymer. This polymer was used to measure the molecular weight.

When the feed ratio of DV to AP is 3/2, there are many vinyl groups in the resultant polymer. End-capping of vinyl groups is as follows: after the polymerization was carried out for a given time, a sufficient amount of 2-aminopropane was added to the reaction system and heated at 60 °C for 48 h. The mixture was poured into 800 mL of methanol, and the precipitate was collected and purified by reprecipitation from water solution into methanol. The product was dried under vacuum at 80 °C for 24 h, and snow-white powder polymer was obtained. $^1H$ NMR ($CDCl_3$): $\delta$ 3.3, 3.2 ($-CH_2SO_2CH_2-$), 3.12 (CH), 1.8 ($-NH-$), 1.25 ($-NH_2$), 1.08 ($CH_3$).

## Results and Discussion

The new strategy for preparation of hyperbranched polymers from $A_2$ type monomers and $BB'_2$ type monomers is described below.

**Polymer Synthesis.** Polyaddition of divinyl sulfone (DV) to 1-(2-aminoethyl)piperazine (AP) with the ratio of 1/1 or 3/2 was carried out in water or organic solvents such as chloroform, *N*,*N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP). Reaction conditions and results are summarized in Table 1.

When the ratio of DV to AP is equal to 1, the resulting polymer is soluble in water, acid aqueous solution, and organic solvents such as chloroform, DMF, NMP, and their mixture. The solubility of the hydrochloride of the hyperbranched polymer is as high as 1.5 g/mL in water. In the IR spectrum of the resulting polymer, a broad absorption band from 3450 to 3250 $cm^{-1}$ ($\nu_{N-H}$) was still observed, while the absorption peak at 1613 $cm^{-1}$ ($\nu_{C=C}$) disappeared, which indicated vinyl groups had completely reacted with amino groups. In the IR spectrum of the hydrochloride, a new strong absorption band attributed to tertiary amino appeared at 2529 $cm^{-1}$, which implied there were large amount of tertiary amino groups in the polymer chains. In the $^1H$ NMR spectrum, the peaks for the protons of secondary amino groups and primary amino groups were observed at 2.08 and 1.25 ppm, respectively, while the peak of vinyl groups was absent. These data further confirmed that the vinyl groups totally reacted with the amino groups, and a branched polymer had been obtained since there were a lot of primary amino groups in terminal units of the polymer.

For the polycondensation of $A_2$ and $B_3$ monomers with 3/2 feed ratio, successful examples without gelation have been seldom reported since the critical conversion of gelation is lower compared with the polymerization of 1/1 monomer ratio.[25,27] Aharoni[26] has reported that gelation occurred within 10−20 min during the polymerization of $A_2$ and $B_3$. In this work, no gelation was observed with the polyaddition of $A_2$ and $BB'_2$ in solvent. The hydrochloride of the resulting polymer, i.e., the amino groups of the hyperbranched polymer have been converted into the ammonium hydrochloride and cannot further react with vinyl groups, can dissolve in water, and the solubility is as high as 1.45 g/mL. The sample can be deprotected from the ammonium hydrochloride at 150 °C, which results in cross-linking. The end-capped polymer with benzoyl chloride is soluble in chloroform, DMF, and NMP. The polymer end-capped with 2-aminopropane is still soluble in water and chloroform. The hyperbranched polymer separated from the solution by precipitation with methanol becomes a cross-linked material. The existence of solvent seems important for the reservation of the resulting hyperbranched polymer. In addition, the product is a reactive polymeric cross-linking agent, which is probably useful for the preparation of interpenetrating polymer networks (IPN).[28] In the IR spectrum of the polymeric hydrochloride, the absorption of carbon−carbon double bonds from 1620 to 1605 $cm^{-1}$ and that of amino groups from 3450 to 3250 $cm^{-1}$ were still present. In the $^1H$ NMR spectrum of the same polymer, the protons of the vinyl groups were observed at peaks of 6.4 and 6.8 ppm, and those of amino groups were detected at the peak of 2.08 ppm. These examinations confirmed that there are

**Table 2. End-Capping Reaction of the Resulting Polysulfone−Amine**

| code | ratio[a] | $M_n$ | $\eta_{inh}$[b] (dL/g) | $\eta_{inh}$[c] (dL/g) |
|---|---|---|---|---|
| PEA-1 | 1:1 | 19 500 | 0.15 | 0.24 |
| PEA-2 | 3:2 | 21 300 | 0.18 | 0.27 |

[a] The initial mole ratio of divinyl sulfone to 1-(2-aminoethyl)piperazine. [b] The inherent viscosity of the end-capped polymer measured at a concentration of 0.5 g/dL in chloroform at 25 °C. [c] The inherent viscosity of the hydrochloride of the end-capped polymer measured at a concentration of 0.5 g/dL in water at 25 °C.

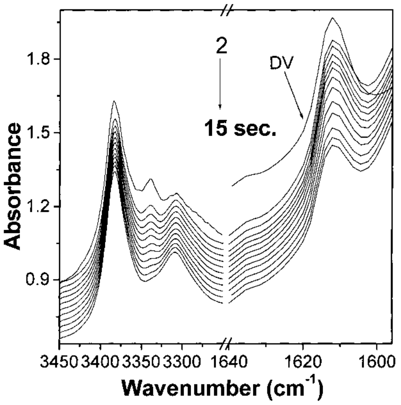


**Figure 1.** FTIR spectra for the reaction system of DV and AP with the feed ratio of 1:1 in chloroform within initial 15 s.

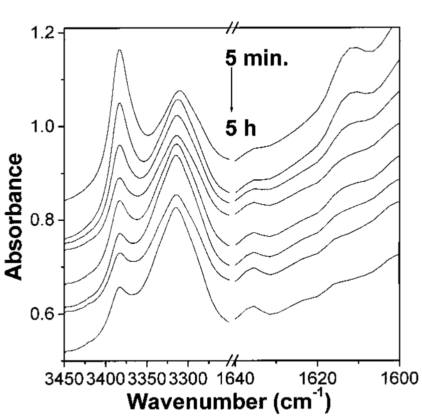


**Figure 2.** FTIR spectra for the reaction system of DV and AP with the feed ratio of 1:1 in chloroform from 5 min to 5 h.

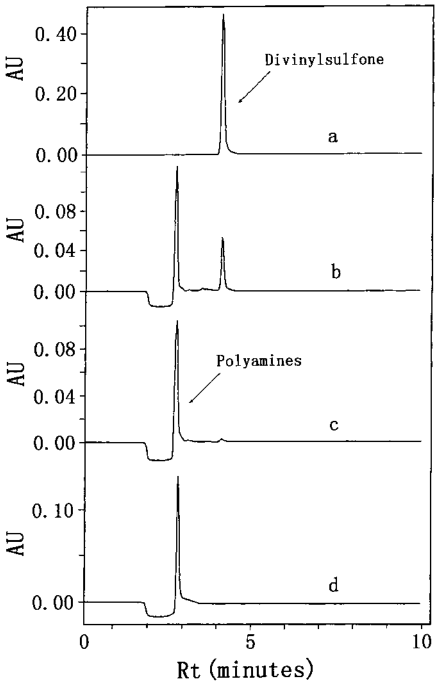


**Figure 3.** HPLC chromatogram for the reaction system of DV and AP with the feed ratio of 1:1 in water: (a) pure divinyl sulfone; (b) 2 s; (c) 8 s; (d) 12 s. The sample was hydrochlorinated with 1 N aqueous HCl as soon as it was taken from the reaction system to avoid further reaction.

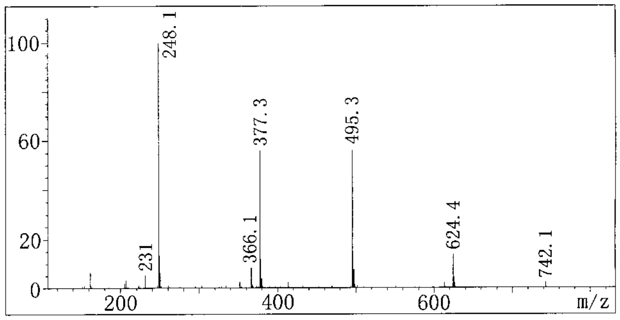


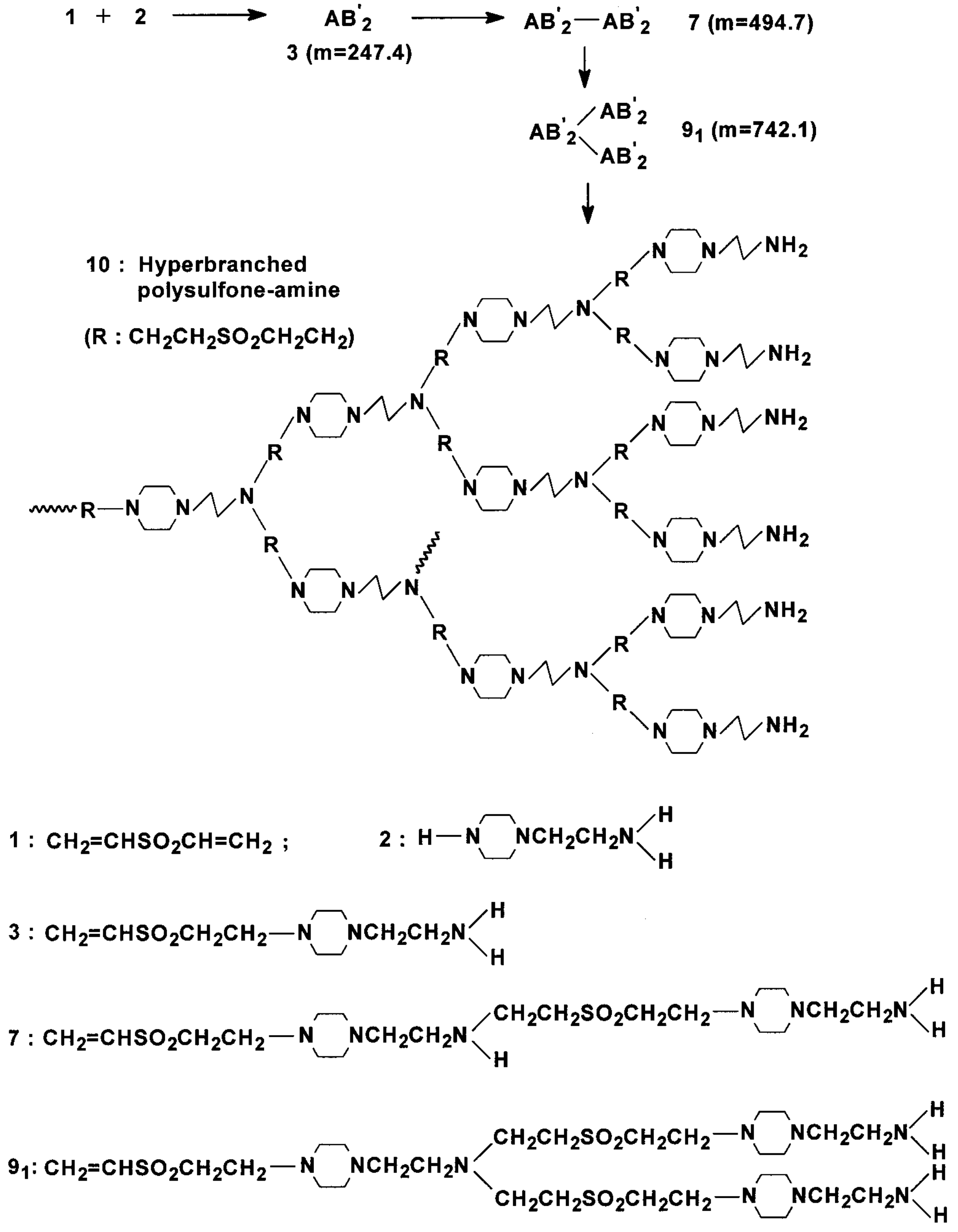
**Figure 4.** Mass spectrum of the sample taken from the reaction system of DV and AP in water with the feed ratio of 1:1 at 40 s.

vinyl groups and amino groups in the resulting hyperbranched polymer, which is consistent with the phenomena aforementioned. When the DV concentration in the reaction mixture approaches 3.5 mol/L, gelation appears at approximately 50 min under the same reaction conditions. So all of the polymerization was carried out at a suitable concentration of monomers (Table 1). The respective molecular weights of the end-capped polymers are shown in Table 2.

**Reaction Mechanism.** For the polymerization of 1/1 feed ratio, the reaction process was investigated in situ with FTIR. As shown in Figure 1, the absorption peak at 3334 cm$^{-1}$ (assigned to secondary amino groups) rapidly decreases with reaction and totally disappears at about 15 s, while the peaks at 3383 and 3311 cm$^{-1}$ (assigned to primary amino groups) change a little. During this period, the area of the absorption band from 1620 to 1605 cm$^{-1}$ (assigned to carbon−carbon double bonds) decreases to about a half of the feed DV. Then, the absorption peaks at 3383 and 1613 cm$^{-1}$ gradually decrease with reaction time. When the peak at 1613 cm$^{-1}$ totally disappears at about 5 h, the peaks of primary amino groups at 3383 and 3311 cm$^{-1}$ still exist (Figure 2). These data indicate the reaction of secondary amino groups with vinyl groups is much faster than that of primary amino groups with vinyl groups; therefore, the dimers that can be regarded as a new kind of $AB'_2$ type monomers may be the dominant intermediate at the beginning of the reaction. Further polyaddition of $AB'_2$ monomers results in hyperbranched polysulfone−amine.

The outcomes obtained from FTIR spectra are in agreement with those found from HPLC and MS. For the reaction system of DV and AP at the ratio of 1/1, the peak in the chromatogram of HPLC at the retention time (Rt) for DV (4.018 min) rapidly decreases with reaction and totally disappears at about 12 s from the HPLC chromatogram (Figure 3). These data further confirm that the reaction of DV and AP during the initial period is very fast indeed. Furthermore, the sample obtained from the reaction system was measured with MSD (Figure 4). The major molecular ion peak for $AB'_2$ molecules ($m$ = 247.4) is observed from

**Scheme 1. Reaction Mechanism of Divinyl Sulfone and 1-(2-Aminoethyl)piperazine**

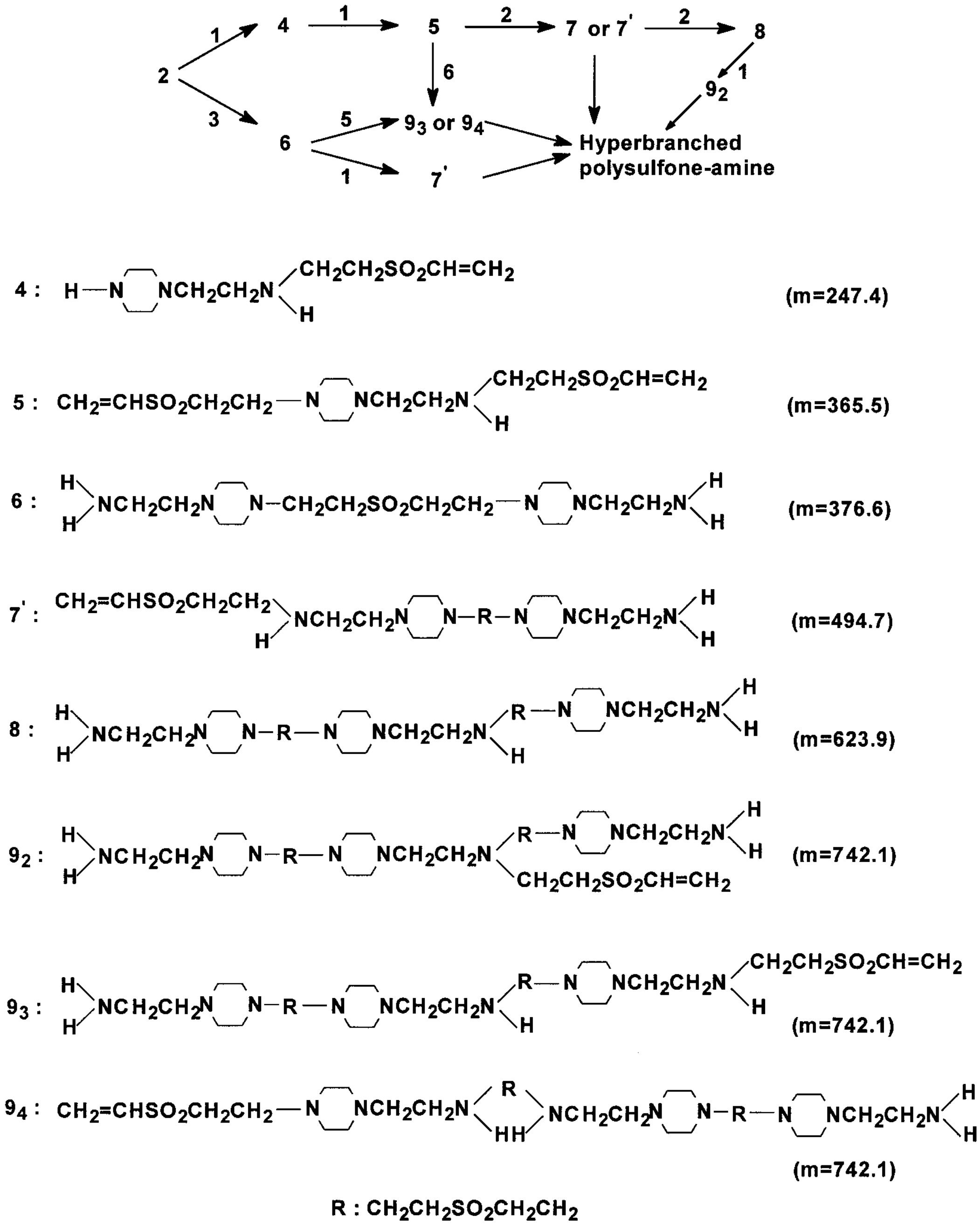


the mass spectrum of the reaction mixture at $m/z$ = 248.1 ($m$ + 1). The peak of $AB'_2$ fragment ion (the residual moiety of $AB'_2$ without its primary amino group, $m$ = 231.4) is also observed at $m/z$ = 231. These data suggest the secondary amino groups react with the vinyl groups, generating $AB'_2$ type dimers. Moreover, the peaks of $(AB'_2)_2$ ($m$ = 494.7) and $(AB'_2)_3$ ($m$ = 742.1) are found at $m/z$ = 495.3 and 742.1, respectively, which indicates that the self-condensing polyaddition of $AB'_2$ monomers begins in the meantime. On the other hand, the peaks of $m/z$ = 366.1, 377.3, and 624.4 in the mass spectrum indicate the existence of the other species. The relative intensity of the peak at 366.1 is much lower than that at 377.3, which further identifies the result of FTIR; i.e., the reaction between secondary amino groups and vinyl groups is much faster than that between primary amino groups and vinyl groups. Among the all species exhibited in the mass spectrum, only species for $m/z$ = 366.1 with two vinyl groups may lead to gel formation during further reaction. However, the amount of this species is too small to reach the critical condition of gelation. So no cross-linking was observed in the polymerization.

In accordance with the experimental data given above, the reaction mechanism probably reads as Scheme 1. In the reaction system there are vinyl groups (A), active hydrogen atoms of secondary amino groups (B), and active hydrogen atoms (B′) of primary amino groups. The reaction of B and A is much faster than that of B′ and A due to the stronger electron-donating (or nucleophlicity) of secondary amino groups.[29] The dimers, $AB'_2$ (3), formed dominantly in the initial period act as a new monomer. Further polymerization of 3 results in higher oligomers (7 or $9_1$) and finally hyperbranched polymer. Scheme 2 shows other reactions in the reaction system of DV and AP.

When the feed ratio is equal to 3/2, the reaction is more complex, which was investigated in situ with FTIR, too. Similar to the reaction with 1/1 feed ratio, secondary amino groups of $BB'_2$ monomer rapidly

**Scheme 2. Other Reactions in the System of Divinyl Sulfone and 1-(2-Aminoethyl)piperazine**



decrease with reaction and totally disappear at about 12 s (Figure 5). Then, the amino and vinyl groups slowly decrease with reaction, and the two sorts of groups are still present at 6 h (Figure 6). These data further prove the reaction scheme given above is correct; otherwise, the primary amino peaks would have vanished. Figure 7 shows the chromatogram of HPLC for the reaction system of the 3/2 feed ratio. The peak of DV is still observed after 1 h reaction. The experimental data are fully in agreement with each other. After the formation of $AB'_2$ intermediate the polymerization proceeds smoothly. Therefore, there are a certain amount of free amino groups and vinyl groups in the resulting polymer, which might be able to form the three-dimensional network in much more concentrated solution or bulk. To obtain stable solid product, the hyperbranched polymer should be end-capped before precipitation.

**Degree of Branching.** The degree of branching (DB) is one of the most important parameters for the structural characterization of hyperbranched polymers.[30-34] When the monomer ratio is equal to 1, the resulting polymer contains the following units: (1) branched units ($N_b$, tertiary amino groups except the piperazine groups, $-CH_2N(CH_2-)_2$); (2) linear units ($N_l$, secondary amino groups, $-CH_2NHCH_2-$); (3) terminal groups ($N_t$, primary amino groups, $-CH_2NH_2$). The DB of a hyperbranched polymer is defined[30] as the number of branched and terminal units divided by the total units. Since every unit contains a sulfone group ($-CH_2SO_2CH_2-$, $N_s$), so DB can be calculated from the ratio of $(N_b + N_t)/N_s$. The relative percentages of the units aforementioned can be calculated by the respective integration of the $^1$H NMR peaks. The peaks attributed to the protons of branched units, terminal units, and sulfone units were found at 2.7, 3.04, and 3.25 ppm, respectively. The values of DB for various polymer samples calculated from the integration of $^1$H NMR peaks ($DB_{NMR}$) are summarized in Table 1. Since the resulting polymer

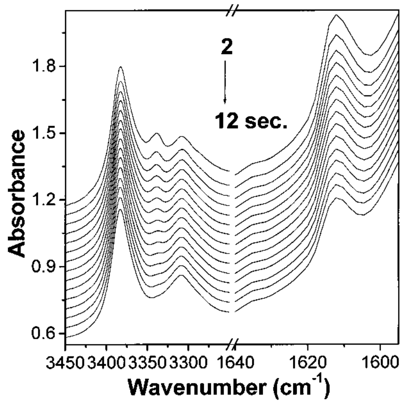


**Figure 5.** FTIR spectra for the reaction system of DV and AP with the feed ratio of 3:2 in chloroform within initial 12 s.

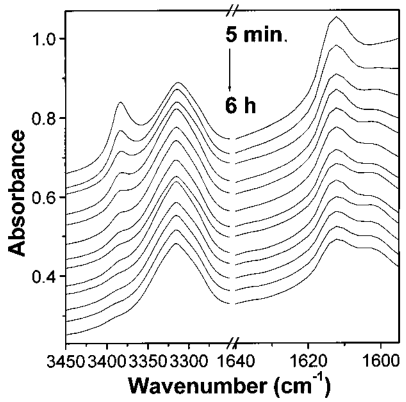


**Figure 6.** FTIR spectra for the reaction system of DV and AP with the feed ratio of 3:2 in chloroform from 5 min to 6 h.

contains primary, secondary, and tertiary amino groups, it is possible to determine its DB by using the double-titration method ($DB_{tit}$).[35,36] The values of $DB_{tit}$ are also given in Table 1.

When the monomer ratio is equal to 3/2, terminal units consist of vinyl groups ($N_v$) and primary amino groups ($-CH_2NH_2$, $N_p$). The $DB_{NMR}$ is defined as the ratio of $(N_b + N_v + N_p)/(N_b + N_v + N_p + N_l)$. In our work, the vinyl group is end-capped with 2-aminopropane, so either the integration of its methyl groups ($CH_3$) or that of tertiary carbon groups (CH) can be used to estimate the $DB_{NMR}$. The peaks attributed to the protons of branched units, linear units, primary amino groups, and methyl groups were located at 2.68, 3.08, 2.92, and 1.08 ppm, respectively. The values of $DB_{NMR}$ are also summarized in Table 1.

**Thermal Properties.** The glass transition temperature ($T_g$) is observed at −18.6 and −12.6 °C for the polymer samples PA-4 and PA-1, respectively. There are no melting and crystallization peaks in the DSC curve, which indicates the hyperbranched polysulfone−amine is amorphous. In TGA curve, the temperatures for 5% weight loss of PA-4 and PA-1 samples are 290 and 280 °C, respectively.

## Conclusions

The polymerization of divinyl sulfone ($A_2$) and 1-(2-aminoethyl)piperazine ($BB'_2$) without any catalysts has been investigated as a novel approach to prepare hyperbranched polysulfone−amines. During polymerization, secondary amino groups of 1-(2-aminoethyl)piperazine react fast with vinyl groups of divinyl sulfone forming dominant dimers, which can be regarded as a new $AB'_2$ type of monomers. Further polymerization of this monomer results in hyperbranched polysulfone−amine. When the feed ratio of $A_2$ to $BB'_2$ is equal to 1, no gelation was observed in water or organic solvent. The hyperbranched polymer with large amount of amino groups is well soluble in water, chloroform, and polar organic solvents such as *N*,*N*-dimethylformamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone. When the feed ratio of $A_2/BB'_2$ is 3/2, the hyperbranched polymer containing amino and vinyl end functional groups has been successfully obtained through hydrochlorination of the resulting polymer. Furthermore, since functional groups of monomers exhibit different reactivity, the degree of branching for the hyperbranched polymer is high than 50%. The direct polymerization of other $A_2$ and $BB'_2$ monomers has been successfully investigated and will be published elsewhere.

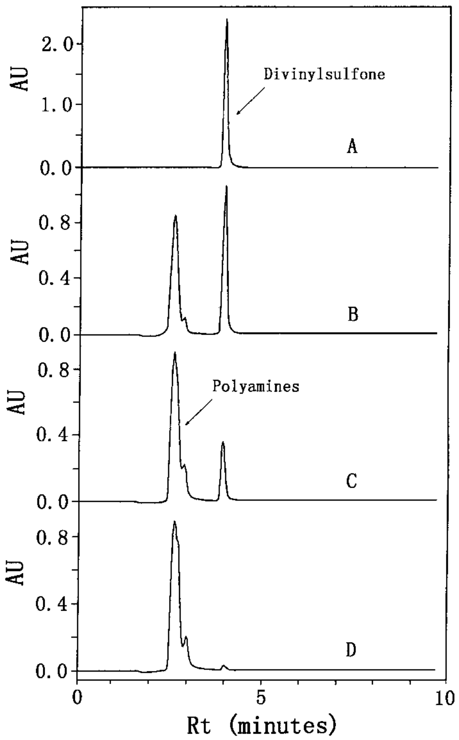


**Figure 7.** HPLC chromatogram for the reaction system of DV and AP with the feed ratio of 3:2 in water: (A) divinyl sulfone; (B) 2.4 min; (C) 30 min; (D) 60 min. The sample was hydrochlorinated with 1 N aqueous HCl as soon as it was taken from the reaction system to avoid further reaction

**Acknowledgment.** This work was sponsored by the National Natural Science Foundation of China (No. 29974017) and W. L. Gore & Associates, Inc., USA. The measurements of FTIR and LC/MS were carried out at the Instrumental Analytical Center of Shanghai Jiao Tong University, and we thank Mrs. Pinfang Zhu and Ping Tao for their generous permission to use the EQUNIOX-55 FTIR spectroscopy and HP 1100 LC/MSD.

## References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.
(2) Kim, Y. H.; Webster, O. W. *Polym. Prepr.* **1988**, *29* (2), 310.
(3) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1992**, *114*, 4947.
(4) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561.
(5) Fréchet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 1399.

(6) Malmströn, E.; Hult, A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555.
(7) Kim, Y. H. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, *36*, 1685.
(8) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(9) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Grubbs, L. R. B. *Science* **1995**, *269*, 1080.
(10) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.
(11) Simon, P. F. W.; Radke, W.; Müller, A. H. E. *Macromol. Rapid Commun.* **1997**, *18*, 865.
(12) De Brabander-van der Berg, E.; Meijer, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308.
(13) Emrick, T.; Chang, H. T.; Fréchet, J. M. J. *Macromolecules* **1999**, *32*, 6380.
(14) Gaynor, S. G.; Edelman, S.; K. Matyjaszewsky, K. *Macromolecules* **1996**, *29*, 1079.
(15) Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843.
(16) Urich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Macromolecules* **1992**, *25*, 4583.
(17) Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, *26*, 4617.
(18) Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, *27*, 1611.
(19) Kumar, A.; Ramakrishnan, S. *Macromolecules* **1996**, *29*, 2524.
(20) Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1999**, *32*, 2215.
(21) Spindler, R.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 4809.
(22) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.
(23) Bolton, D. H.; Wooley, K. L. *Macromolecules* **1997**, *30*, 1890.
(24) Hawker, C. J.; Chu, F. *Macromolecules* **1996**, *29*, 4370.
(25) Jikei, M.; Chon, S. H.; Kakimoto, M.; Kawauchi, S.; et al. *Macromolecules* **1999**, *32*, 2061.
(26) Aharoni, S. M.; Edwards, S. F. *Macromolecules* **1989**, *22*, 3361.
(27) Odian, G. *Principles of Polymerization*; John & Sons: New York, 1991; p 108.
(28) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981; Chapter 3.
(29) Knipe, A. C.; Watts, W. E. *Organic Reaction Mechnisms*; John Wiley & Sons: Chichester, 1990; Chapter 13.
(30) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
(31) Yan, D. Y.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7024.
(32) Müller, A. H. E.; Yan, D. E.; Wulkow, M. *Macromolecules* **1997**, *30*, 7015.
(33) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.
(34) Hölter, D.; Frey, H. *Acta Polym.* **1997**, *48*, 298.
(35) Critchfield, F. E.; Johnson, J. B. *Anal. Chem.* **1957**, *29*, 957.
(36) Critchfield, F. E.; Johnson, J. B. *Anal. Chem.* **1956**, *28*, 430.

MA000438J