Polyaddition of B_2 and BB'_2 Type Monomers to A_2 Type Monomer. 1. Synthesis of Highly Branched Copoly(sulfone−amine)s

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ABSTRACT: A new approach for preparation of highly branched copolymers from A_2, B_2, and BB'_2 type monomers was reported in this work. Highly branched copoly(sulfone−amine)s were synthesized by polyaddition of piperazine (B_2) and 1-(2-aminoethyl)piperazine (BB'_2) to divinyl sulfone (A_2). The polymerization mechanism was investigated with FTIR and LC-MSD. During the polymerization, secondary amino groups of B_2 and BB'_2 monomers react rapidly with vinyl groups of A_2 monomers within 40 s, and then the residual A groups react with B′ groups resulting in highly branched copoly(sulfone−amine)s. Thermal properties and the aggregation structure of resulting polymers were characterized with DSC and X-ray diffraction, respectively. When the initial mole ratio of B_2 to BB'_2 (r) is equal to or higher than three ($r \geq 3$ or $B/B' \geq 3.5$), resulting branched copolymers are semicrystalline, while copolymers in the case of $r < 3$ are amorphous. The degree of branching (DB) of the highly branched copoly(sulfone−amine)s was defined and determined by ^1H NMR. The degree of branching of the products increased with decreasing the fed ratio of piperazine to 1-(2-aminoethyl)piperazine. The ratio of the inherent viscosity to the molecular weight decreased with increasing the degree of branching.

Introduction

Highly branched or hyperbranched polymers have drawn much attention of various research groups for 10 years,[1−7] and a variety of hyperbranched polymers have been prepared.[8−13] Most of hyperbranched polymers are obtained by polycondensation of AB_2 type monomers. However, few papers have been published concerning the preparation of hyperbranched copolymers through the copolymerization method. In this work, a novel approach for synthesis of hyperbranched or highly branched copolymers from commercially available A_2, B_2, and BB'_2 type monomers has been described. Highly branched copoly(sulfone−amine)s with various degree of branching were prepared by one step copolymerization of divinyl sulfone (A_2) with piperazine (B_2) and 1-(2-aminoethyl)piperazine (BB'_2).

In our previous work,[14] the new strategy for synthesis of hyperbranched polymers from A_2 and BB'_2 type monomers has been presented. Now this strategy is extended to prepare highly branched or branched copolymers from A_2, B_2, and BB'_2 type monomers in order to control the degree of branching (DB) of resulting polymers and to investigate physical properties of the products. Copolymerization of divinyl sulfone (DV) with piperazine (PZ) and 1-(2-aminoethyl)piperazine (AP) has been conducted without any catalysts. Increasing the fed ratio of PZ to AP led to the decrease of the degree of branching. Semicrystalline of resulting branched polymers was observed when the fed mole ratio of PZ to AP was equal to or higher than 3 ($r \geq 3$).

Experimental Section

Characterization. ^1H nuclear magnetic resonance (NMR) measurements were carried out on a 500 MHz Bruker NMR spectrometer with D_2O as solvent. Fourier transform infrared (FTIR) measurements were performed on a Bruker Equinox 55 spectrometer with a Barnes analytical FTIR sealed cell (KBr 0.5 mm). X-ray powder diffraction was taken by using Cu Kα radiation with a Rigaku III Dmax 2500.

Mass spectra were obtained on a HP 1100 mass spectrograph detector (MSD). The conditions of the spray chamber were as follows: polarity, positive; ionization mode, APCI; fragmentor, 70 V; nebulizer pressure, 60 psig; drying gas flow, 7.0 mL/min; drying gas temperature, 325 °C. The tested sample taken from the reaction system during initial reaction period was protected by aqueous 2 N hydrochloric acid as soon as it was taken from the reaction mixture.

Thermogravimetric analysis (TGA) was performed under nitrogen on a PE Pyris-7 thermal analyzer. All samples were heated at 20 °C/min heating rate from 25 to 650 °C. Differential scanning calorimetric studies were conducted under nitrogen on a PE Pyris-1 DSC thermal analyzer. All samples were heated at 20 °C/min heating rate from 35 to 200 °C for the first scan, then cooled at 20 °C/min to −80 °C, and immediately heated at 20 °C/min from −80 to 200 °C for the second scan.

The molecular weight of the product was obtained on the HP 1100 gel permeation chromatograph (GPC) with water as solvent and PEO as standards, and the column used was G6000 PW (XL). The inherent viscosity (η_{inh}) of the resulting polymer was measured at a concentration of 1.0 g/dL in water at 25 °C.

Materials. Divinyl sulfone (DV, Aldrich) was purified by vacuum distillation. Piperazine (PZ, Aldrich)) and 1-(2-aminoethyl)piperazine (AP, Aldrich) were used as received. Organic solvents such as chloroform, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and *N*-methyl-2-pyrrolidone (NMP) are analytical pure reagents and purified by distillation before using.

Polymerization. A typical example is given as follows: in a flask were placed 0.8614 g (10 mmol) of PZ, 1.2921 g (10 mmol) of AP, and 15 mL of chloroform. When the mixture was totally dissolved, 2.363 g (20 mmol) of DV was added. The mixture was heated to 40 °C and then kept for 60 h and poured into 500 mL of methanol. The precipitate was collected and purified by reprecipitation from chloroform solution into methanol. The product was washed with hot methanol and acetone and dried under vacuum at 80 °C for 24 h. Yield: 4.1 g of white powdery product (91.1%). IR (KBr): 1290, 1130 cm^{-1} (SO_2), 3450−3250 cm^{-1} ($-NH_2$ or $-NH-$). Calcd for $C_{18}H_{37}N_5O_4S_2$: C, 47.82%; H, 8.19; N, 15.50%; S, 14.17%. Found: C, 47.75%; H, 8.23%, N, 15.46%; S, 14.21%.

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Table 1. Copolymerization of Divinyl Sulfone (A_2) with Piperazine (B_2) and 1-(2-Aminoethyl)piperazine (BB'_2)[a]

sample	B_2/BB'_2	A/B/B′	solvent	yield (%)	η_{inh} (dL/g)	DB[b] (%)	M_w	D[c]	T_d (K)
PA-1	1:5	12:7:10	DMA	91.3	0.57	48.3	37 469	1.31	543
PA-2	1:2	3:2:2	DMA	92.5	0.73	42.6	42 697	1.28	540
PA-3	1:1	4:3:2	$CHCl_3$	91.1	0.56	35.2			545
PA-4	1:1	4:3:2	DMF	92.7	0.68				
PA-5	1:1	4:3:2	NMP	93.6	0.52				
PA-6	1:1	4:3:2	DMA	95.1	0.83	34.5	37 997	1.22	546
PA-7	1:1	4:3:2	H_2O	90.4	0.41	36.8			546
PA-8	2:1	6:5:2	DMA	94.7	1.15	26.7	46 105	1.35	567
PA-9	3:1	8:7:2	DMA	95.8	0.95	21.4	37 579	1.24	568
PA-10	4:1	10:9:2	DMA	97.6	1.05	16.1	40 965	1.33	572
PA-11	5:1	12:11:2	DMA	96.5	0.87	11.9	33 218	1.29	578
PLSA[d]			H_2O	98.2	1.54		17 431	1.35	584
PHSA[e]		2:1:2	$CHCl_3$	87.3	0.396	54.1	32 234	1.33	540

[a] The fed ratio of divinyl sulfone to piperazine and 1-(2-aminoethyl)piperazine is equal to 1, and the initial concentration of divinyl sulfone is 1.98−2.2 mol/L. [b] Degree of branching determined by ^{1}H NMR. [c] Molecular weight distribution (M_w/M_n) measured by GPC. [d] Linear poly(sulfone−amine) made by polymerization of divinyl sulfone with piperazine. [e] Hyperbranched poly(sulfone−amine) made by polyaddition of 1-(2-aminoethyl)piperazine to divinyl sulfone.

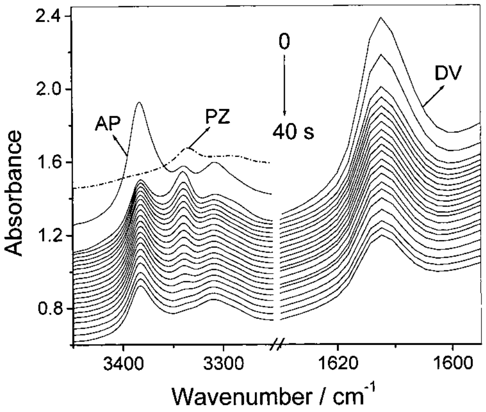


Figure 1. In situ FTIR spectra of the reaction system of DV, PZ, and AP in chloroform within initial 40 s, $r = 1$.

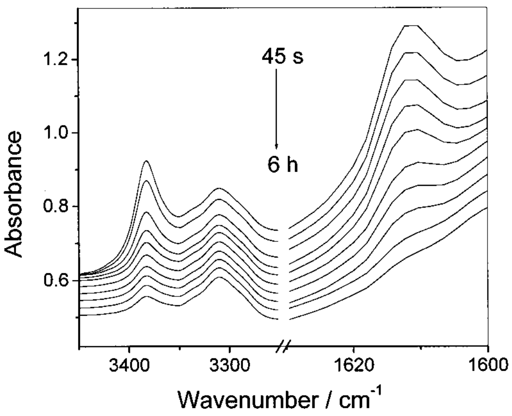


Figure 2. In situ FTIR spectra of the reaction system of DV, PZ, and AP in chloroform from 45 s to 6 h, $r = 1$.

Hydrocholorination of Polymer. The resulting copolymer (2 g) was added to aqueous 6 N hydrochloric acid (30 mL) with stirring. After dissolving perfectly, the solution was poured into 300 mL of acetone. The precipitate was collected and reprecipitation from water solution into acetone. Yield: 2.4 g of product. The hydrochloride of the branched copoly(sulfone−amine) was well soluble in water, so it was used as the sample in the measurement of ^{1}H NMR, GPC, and viscosity. IR (KBr): 1290, 1130 cm^{-1} (SO_2), 2750−2250 cm^{-1} (hydrochloride of tertiary amino groups). ^{1}H NMR (D_2O): δ 3.7 ($CH_2SO_2CH_2$), 3.5 ($CH_2N(CH_2)_2$), 3.35 (methylene attached to piperazine ring), 3.2 (piperazine ring), 3.0 (methylene attached to primary amino group, CH_2NH_2), 2.8 (methylene attached to secondary amino group, CH_2NHCH_2), 2.08 ($-NH_2$ or $-NH-$).

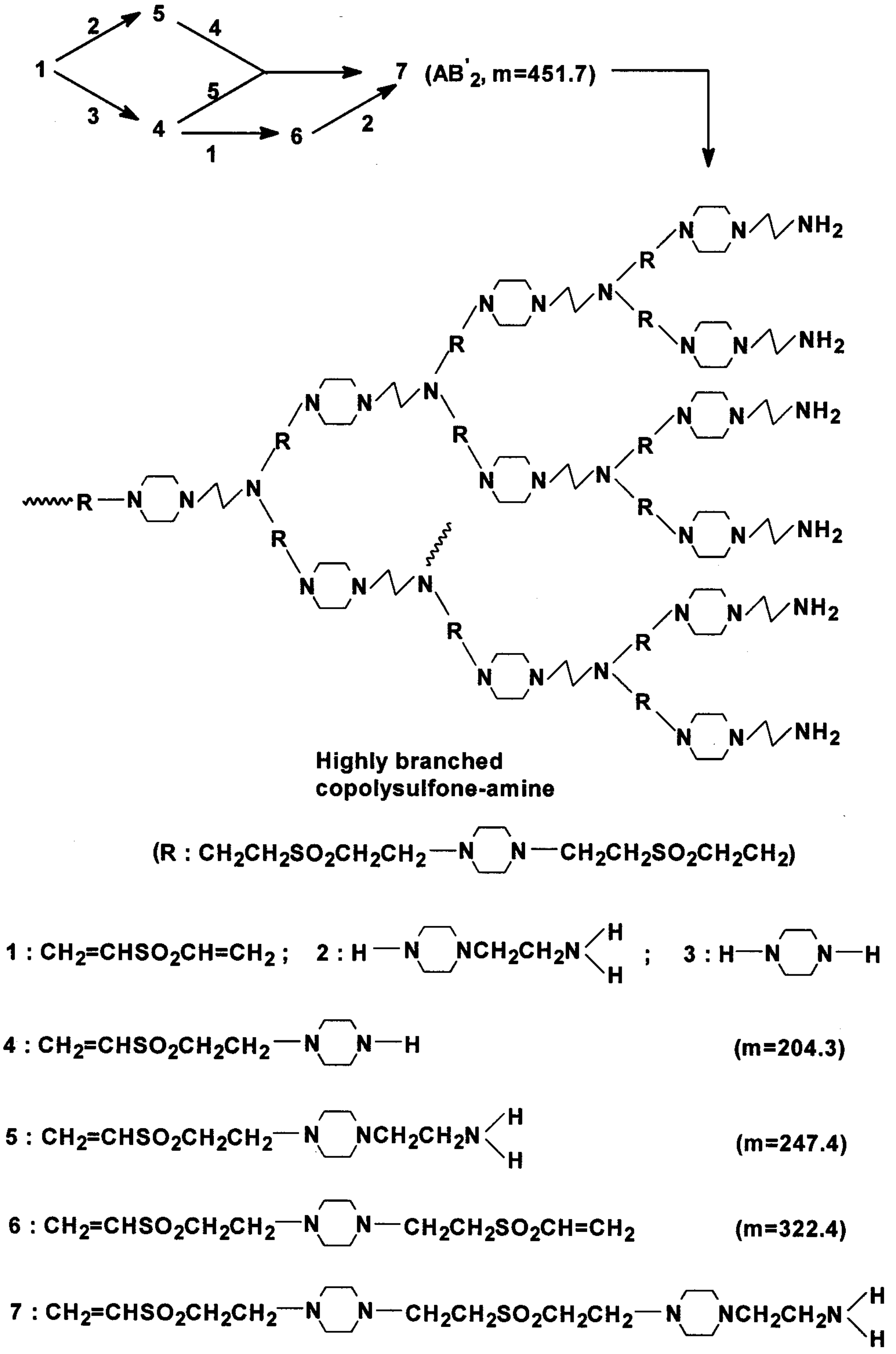
Results and Discussion

Polymer Synthesis. The fed mole ratio of DV to PZ and AP was equal to 1, while the ratio of PZ to AP (r) was ranging from 0.2 to 5. The polymerization was implemented at 35−45 °C in a variety of solvents including chloroform, DMF, DMA, NMP, and water. No gelation has been observed. The results are summarized in Table 1. From Table 1 we can find that DMA is the most effective solvent, in which the polymer with the highest molecular weight ($M_w = 46\ 105$) can be prepared. It is not necessary to use any catalysts for the polymerization. In IR spectra of resulting polymers, the absorption peaks of sulfone groups (SO_2) were observed at 1290 and 1130 cm^{-1}. The absorption band of amino groups still appeared at 3450−3250 cm^{-1}, while that of vinyl groups ($CH_2{=}CH$) disappeared from the IR spectra. In ^{1}H NMR spectra, the peak of protons of amino groups was found at 2.08 ppm, while the peaks of protons of vinyl groups were not observed. These data indicate vinyl groups of DV have completely reacted with amino groups of AP and PZ.

In water and chloroform, when $r \leq 2$ (or B/B′ $\leq 5/2$), the reaction mixture is a homogeneous solution throughout the polymerization, while when $r \geq 3$ (or B/B′ $\geq 7/2$), precipitation was observed during the reaction. The precipitates were well soluble in strong polar organic solvents such as DMA, DMF, and NMP and aqueous protonic acid such as aqueous HCl and H_2SO_4, so no cross-linking occurred in the polymerization. The precipitation may have resulted from the crystallization of polymers. In strong polar organic solvents, such as DMF, DMA, and NMP, etc., no precipitation occurred throughout the reaction. When $r \geq 2$ (or B/B′ $\geq 5/2$), the tough film can be obtained from the resulting solution, and the study of the influence of relatively low degree of branching on the film behavior is in progress.

Polymerization Mechanism. FTIR and LC-MSD were used to investigate the polymerization process. Figure 1 shows FTIR spectra taken during the reaction of DV with PZ and AP at initial stage. The absorption peak at 3334 cm^{-1} (secondary amino group) rapidly decreases with the reaction and totally disappears at 40 s, while peaks at 3383 and 3313 cm^{-1} (primary amino groups) almost remain constant. During this period, the area of the absorption band from 1620 to 1603 cm^{-1} (C=C) decreases to about one-fourth of that of the divinyl sulfone material. Then, absorption peaks at 3383 and 1613 cm^{-1} gradually decrease with reaction time.

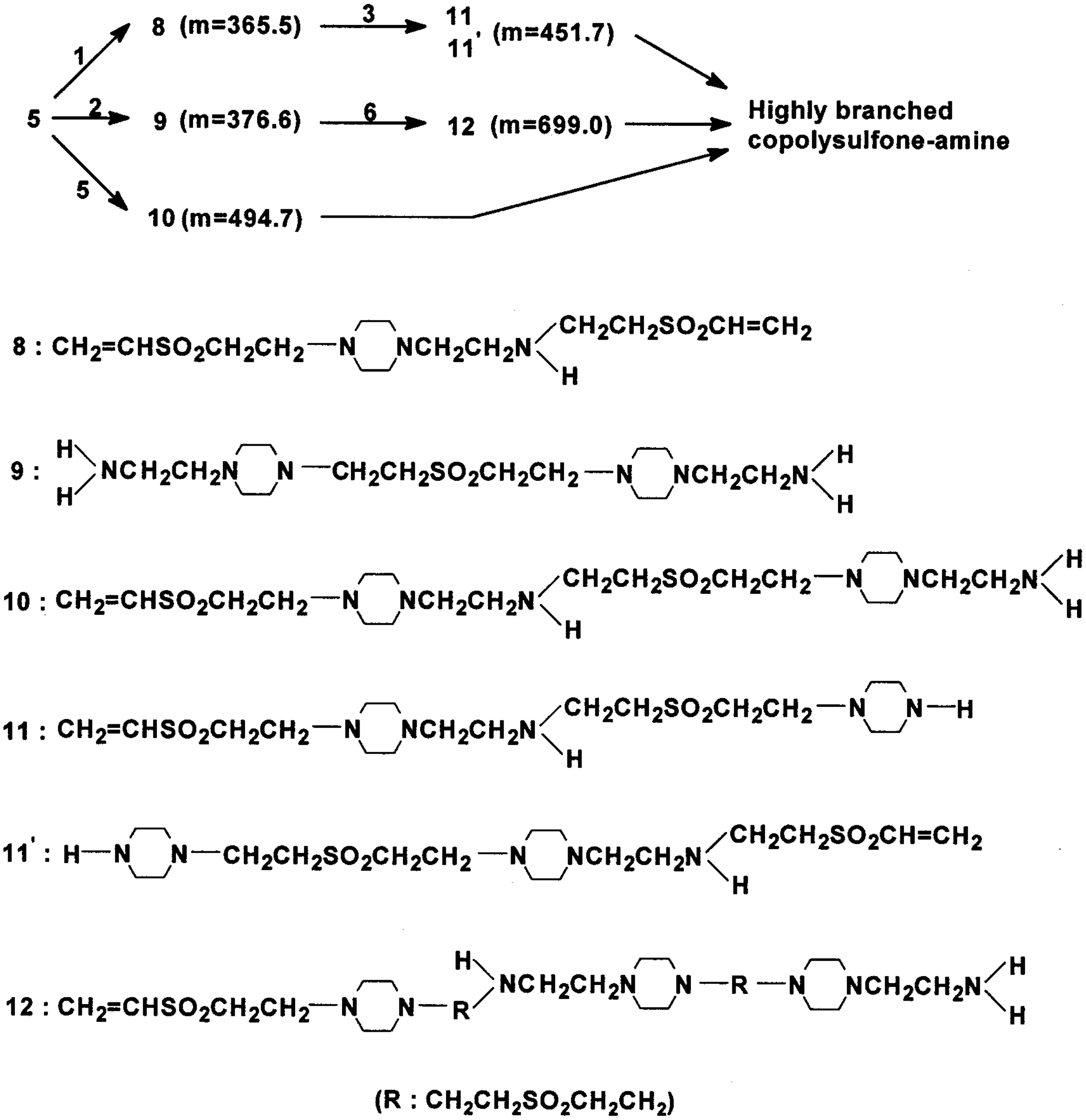
Scheme 1. Reaction Mechanism for Polyaddition of PZ and AP to DV



When the absorption peak at 1613 cm^{-1} totally disappears at about 6 h, the peak at 3383 cm^{-1} is still observed (Figure 2). These data further indicate that the reaction of secondary amino groups with vinyl groups is significantly faster than that of primary amino groups with vinyl groups;[15–18] therefore, the intermediate **7** that now can be regarded as a new kind of AB$'_2$ type monomers may be formed during the initial reaction period. Further polymerization of AB$'_2$ leads to highly branched copoly(sulfone–amine)s. Furthermore, the area of the absorption band from 3250 to 3330 cm^{-1} almost remains unchanged throughout the polymerization, and the peak at 3313 cm^{-1} shifts about 2 cm^{-1} toward lower wavenumber, which may be partially due to the generation of secondary amino groups by reaction of vinyl groups with primary amino groups and partially due to the formation of hydrogen bonds between amino groups and sulfone groups.

In accordance with experimental data given above, the reaction mechanism is probably as shown in Scheme 1. During polymerization, secondary amino groups of **2** (BB$'_2$) and **3** (B$_2$) react rapidly with vinyl groups of **1** (A$_2$), generating **4**, **5**, **6**, and then **7**. Intermediate **7** is now a new type of AB$'_2$ monomer. Further polyaddition

Scheme 2. Other Reactions in the Reaction System of PZ, AP, and DV



of the new monomer gives higher oligomers and finally results in highly branched copoly(sulfone−amine)s. Naturally, there may be other minor competing reactions as shown in Scheme 2.

The measurement of GPC showed that the molecular weight of the resulting highly branched or branched copoly(sulfone−amine)s was relatively large (>20 000) and the molecular weight distribution was very narrow ($M_w/M_n < 1.35$). Therefore, the competing cyclization reaction was negligible.

The mass spectrum of the reaction mixture at initial stage provides further identification for the reaction mechanism presented. Figure 3 shows the mass spectrum of the reaction mixture of PZ, AP, and DV with $r = 1$, which was taken after a very short reaction time (78 s). The peak of **7** (AB'_2) is found at $m/z = 452.2$, and peaks of **4**, **5**, and **6** are observed at $m/z = 205.1$, 248.1, and 323.1, respectively. Peaks of fed monomers **1**, **2**, and **3** are not found in the corresponding mass spectrum, which further indicates the monomers have been completely reacted with each other at initial stage and formed oligomers. The result obtained from the mass spectrum is in agreement with that observed from the FTIR spectrum.

Degree of Branching. The degree of branching (DB) is one of the most important parameters for the structure of hyperbranched or highly branched polymers.[19−25] Here, we have to coin a definition of DB for branched polymers made of A_2, B_2, and BB'_2 type monomers. If N_b represents the number of branched units, N_t symbolizes that of terminal units, and N_l and N_L denote those of linear units from B_2 monomers and BB'_2 monomers, respectively; DB can be expressed by

$$\mathrm{DB} = (N_b + N_t)/(N_b + N_t + N_l + N_L) \qquad (1)$$

In the case of the copolymerization of DV with PZ and AP (Scheme 3), N_b is the tertiary-amino groups except those from piperazine units, N_t the primary amino groups, N_L the secondary amino groups, and N_l is half of the tertiary-amino groups from piperazine since every unit from piperazine has two tertiary-amino groups. Let N_p be the total number of tertiary-amino groups of piperazine rings in the copolymer; N_l can be calculated in terms of eq 2:

$$N_l = (N_p/2) - (N_b + N_t + N_L) \qquad (2)$$

On the other hand, since every unit of the highly

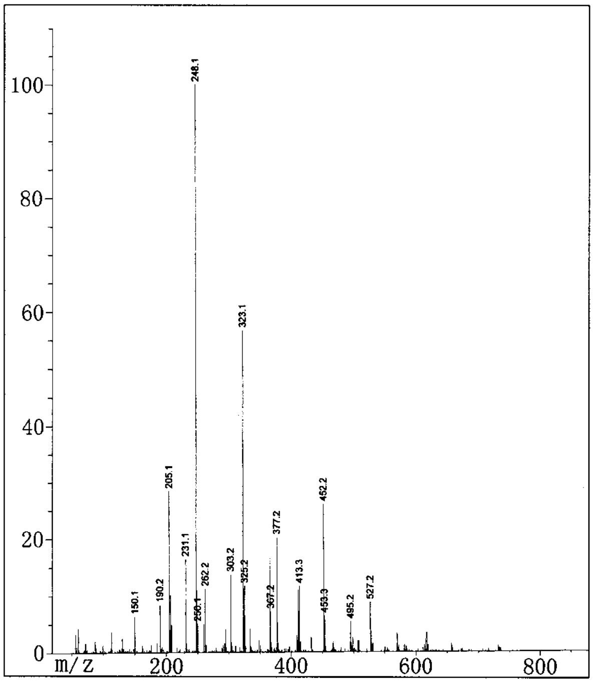
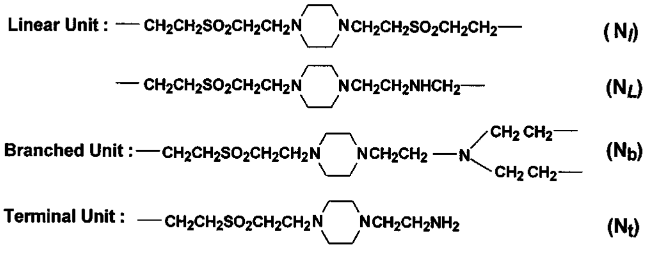


Figure 3. Mass spectrum of the reaction mixture of PZ, AP, and DV at 78 s, $r = 1$.

Scheme 3. Various Units of Highly Branched Copoly(sulfone−amine)s Prepared from DV, PZ, and AP



branched copoly(sulfone−amine)s contains one sulfone group ($-CH_2SO_2CH_2-$), the sulfone groups is equal to the total units. Let N_s represents the sulfone groups, and then DB can be calculated from eq 3:

$$\mathrm{DB} = (N_b + N_t)/N_S \tag{3}$$

In the ^{1}H NMR spectrum (Figure 4), the peaks of N_b, N_t, and N_s are observed at 3.5, 3.0, and 3.7 ppm, respectively,[26] and the percentage of every corresponding peak can be determined from the integration of the related peak. The DB values calculated are summarized in Table 1.

Table 1 shows that DB decreases with increasing the ratio of B_2/BB'_2. Therefore, DB of the branched polymers can be well controlled by the fed ratio of B_2 to BB'_2 in this approach. Through the copolymerization method, a series of polymers with various DB can be easily designed and prepared.

Interestingly, the inherent viscosity of the branched copoly(sulfone−amine)s is dependent on the degree of branching (Figure 5). Since the viscosity is related to degree of branching and molecular weight, the y-axis is defined as the ratio of inherent viscosity to molecular weight of the product. The ratio of inherent viscosity to molecular weight decreased with the degree of branching. In other words, the higher the degree of branching, the lower the viscosity for highly branched polymers with the same molecular weight. This conclusion is amenable to the general observation reported.[27]

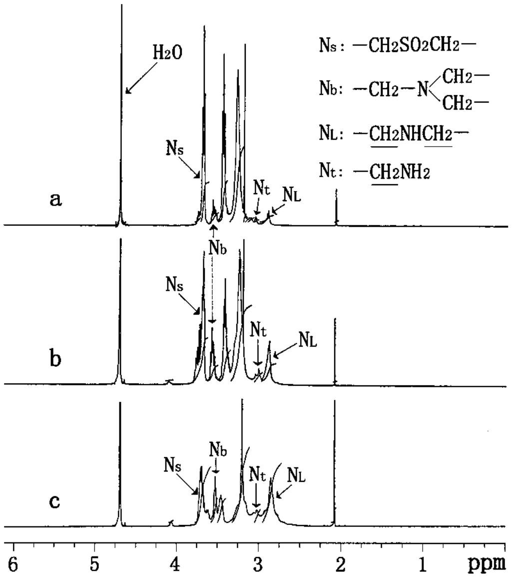


Figure 4. ^{1}H NMR spectra of copoly(sulfone−amine)s: (a) $r = 5$, (b) $r = 2$, (c) $r = 1/5$.

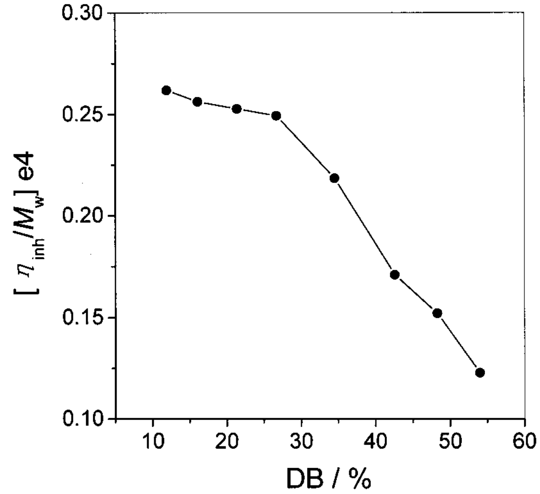


Figure 5. Relationship between the degree of branching and the ratio of inherent viscosity to molecular weight of the branched copoly(sulfone−amine)s.

Thermal Behaviors. The average length of the segment between two branched units increases with increasing the ratio of B_2 to BB'_2. Thermal properties of the polymers depend on its composition. Figures 6 and 7 show DSC curves of the resulting branched copolymers with different values of r. When $r \geq 3$ (or $B/B' \geq 7/2$), the melting and crystallization peaks are observed, and when the value of r is equal to 2 or less than 2 (or $B/B' \leq 5/2$), no melting and crystallization peaks can be found. The melting temperature (T_m) of linear poly(sulfone−amine) (PLSA) made from PZ and DV is higher than that of branched polymers. Conventionally, T_m of the copolymer would have decreased if r had decreased. However, the T_m of the sample with $r = 3$ ($A/B/B' = 8/7/2$) is slightly higher than those of the samples with $r = 4$ ($A/B/B' = 10/9/2$) and 5 ($A/B/B' = 12/11/2$).

The analysis of X-ray diffraction gives further evidence for the crystallization of the branched copoly(sulfone−amine)s. Crystallization peaks are hardly

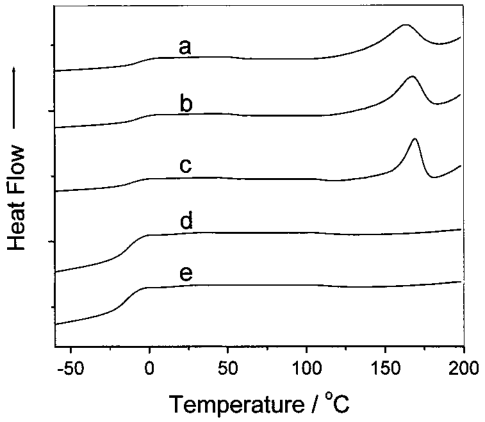


Figure 6. DSC endothermic curves of branched copoly(sulfone−amine)s: (a) $r = 5$, (b) $r = 4$, (c) $r = 3$, (d) $r = 2$, (e) $r = 1$.

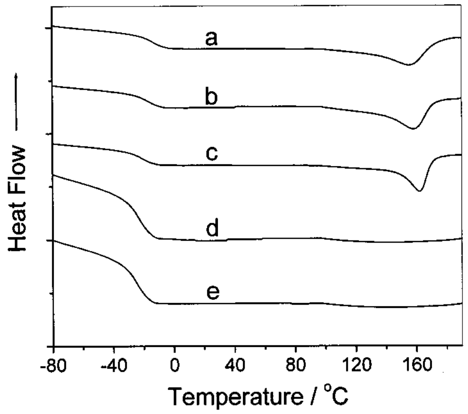


Figure 7. DSC exothermal curves of branched copoly(sulfone−amine)s: (a) $r = 5$, (b) $r = 4$, (c) $r = 3$, (d) $r = 2$, (e) $r = 1$.

observed in the X-ray powder patterns for polymers with $r \leq 2$ (or $B/B' \geq 5/2$). When $r \geq 3$ (or $B/B' \geq 7/2$), the obvious crystallization peaks appear at $2\theta = 20°$. When the value of r gets to 5 ($A/B/B' = 12/11/2$), the crystallization peak of the branched copolymer is very similar to that of linear poly(sulfone−piperazine) (PLSA).

From DSC curves of the resulting copolymers, it can be found that the melting temperature (T_g) of the highly branched copoly(sulfone−amine)s is ranging from −12.5 to −3.2 °C.

TGA measurements have been performed in order to investigate the heat resistance of the resulting branched copolymers. The temperatures for 5% weight loss (T_d) are summarized in Table 1. The T_d of the samples is ranging from 250 to 315 °C. The T_d of crystalline samples is about 5−20 °C higher than that of amorphous samples. This kind of highly branched copoly(sulfone−amine)s may be used as a new antioxidant.

Conclusions

A series of highly branched or branched copoly(sulfone−amine)s were prepared by direct copolymerization of divinyl sulfone with piperazine and 1-(2-aminoethyl)piperazine. The degree of branching of resulting branched copolymers can be controlled by the fed ratio of piperazine to 1-(2-aminoethyl)piperazine. The reaction between secondary amino groups and vinyl groups is significantly faster than that between primary amino groups and vinyl groups, which ensures the successful synthesis of branched copolymers without gelation. When the fed ratio of piperazine to 1-(2-aminoethyl)piperazine is equal to or higher than 3 (or $B/B' \geq 7/2$), resulting branched copolymers are semicrystalline. The melting temperature of the branched copolymer with $r = 3$ (or $A/B/B' = 8/7/2$) is slightly higher than that of the copolymers with $r = 4$ (or $A/B/B' = 10/9/2$) and 5 (or $A/B/B' = 12/11/2$). The decomposition temperature, T_d, of the branched copoly(sulfone−amine)s ranges from 250 to 315 °C,and the T_d of semicrystalline samples is higher than that of amorphous samples by 5−20 °C.

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