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Hyperbranched polymers made from A_2, B_2 and BB'_2 type monomers, 2. Preparation of hyperbranched copoly(sulfone-amine)s by polyaddition of *N*-ethylethylenediamine and piperazine to divinylsulfone

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Abstract

The new approach for preparation of hyperbranched polymers from commercially available A_2 and BB'_2 type monomers was further extended to synthesize hyperbranched copolymers. In this work, hyperbranched copoly(sulfone-amine)s were prepared by polyaddition of piperazine (B_2) and *N*-ethylethylenediamine (BB'_2) to divinylsulfone (A_2). The polymerization mechanism was investigated with FTIR and LC-MSD. During the copolymerization, secondary-amino groups of piperazine and *N*-ethylethylenediamine react rapidly with vinyl groups of divinylsulfone within 50 s, and then the residual vinyl groups react with primary-amino groups resulting in hyperbranched copoly(sulfone-amine)s. The crystallization behaviors of the resulting polymers were characterized with DSC and X-ray diffraction. When the initial mole ratio of B_2 to BB'_2 is equal to or higher than three, $r \geq 3$, resulting copolymers are semi-crystalline, while those with $r < 3$ are amorphous. Interestingly, the resulting polymers with $r = 3$ exhibit the highest melting temperature comparing with other semi-crystalline samples. The degree of branching of hyperbranched copolymers was determined by ^{1}H NMR. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched copoly(sulfone-amine)s; *N*-ethylethylenediamine; Degree of branching

1. Introduction

Hyperbranched polymers [1–5] have drawn more and more attention since a decade before, and large amounts of hyperbranched polymers have been prepared [6–18]. However, few reports have been published concerning the preparation of hyperbranched copolymers. In previous parts of this series, the approach for synthesis of hyperbranched polymers from A_2 and BB'_2 type monomers has been presented [19,20]. As mentioned previously, A_2 has two functional groups and BB'_2 has one B functional group and two B' functional groups. Both B and B' can react with A, but B is much more active than B'. Therefore, during the reaction, B groups of BB'_2 react much faster with A groups of A_2 generating dominant dimers. The dimers can be regarded as new AB'_2 monomers. Further polymerization of AB'_2 leads to hyperbranched polymers. Now this method is utilized to prepare hyperbranched copolymers. Copolymerization of divinylsulfone (A_2) with piperazine (B_2) and *N*-ethylethylenediamine (BB'_2) has been conducted without any catalysts. The inherent viscosity of copolymers approaches 0.87 dl/g, so the molecular weight of the hyperbranched copoly(sulfone amine)s is rather high. The crystallization of resulting copolymers was observed when the fed mole ratio of piperazine to *N*-ethylethylenediamine is equal to or higher than three, $r \geq 3$.

2. Experimental

2.1. Materials and instrumentation

Divinylsulfone (DV, Aldrich) was purified by vacuum distillation before use. Piperazine (PZ, Aldrich) and *N*-ethylethylenediamine (NDA, Aldrich) were used as received. Organic solvents such as chloroform, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), and *N*-methyl pyrrolidone (NMP) are analytical pure reagents and purified by distillation before use.

Fourier-transform infrared (FTIR) measurements were performed on a Bruker Equinox 55 spectrometer with Barnes Analytical FTIR Sealed Cell (KBr 0.5 mm). Mass

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Table 1
Copolymerization of divinylsulfone with *N*-ethylethylenediamine and piperazine

No.	PZ/NDA	Solvent	Yield (%)	η_{inh} (dl/g)	DB (%)	T_g (K)	T_m[a] (K)	T_d (K)
PA-1	1:1	H_2O	93.5	0.33	33.7	253.1	–	525
PA-2	1:1	DMF	87.5	0.38			–	
PA-3	1:1	NMP	92.4	0.43			–	
PA-4	1:1	DMA	90.6	0.51			–	
PA-5	1:1	$CHCl_3$	94.5	0.55	31.8	253.2	–	527
PA-6	1:5	$CHCl_3$	91.3	0.72	58.3	251.5	–	523
PA-7	1:2	$CHCl_3$	93.8	0.52	43.2	252.4	–	530
PA-8	2:1	$CHCl_3$	97.3	0.89	25.4	254.8	–	543
PA-9	3:1	$CHCl_3$	95.4	0.86	20.6	256.5	444.9	561
PA-10	4:1	$CHCl_3$	95.8	0.75	14.3	257.9	441.9	560
PA-11	5:1	$CHCl_3$	96.9	0.84	11.7	258.3	438.6	562

[a] The symbol '–' represents no melting temperature measured with DSC.

spectra were obtained on a HP 1100 liquid chromatography-mass spectrograph detector (LC-MSD). ^{1}H nuclear magnetic resonance (NMR) measurements were carried out on a 500 MHz Bruker NMR spectrometer with D_2O as solvent. Tetramethylsilane (TMS) was used as the internal standard in all cases. X-ray powder diffraction was taken by using CuK_α radiation with a Rigaku III Dmax 2500.

Thermo-gravimetric 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 inherent viscosity (η_{inh}) of the resulting polymer was measured with a Ubbelohde viscometer at a concentration of 0.5 g/dl in 1 N hydrochloric acid aqueous at 25°C.

2.2. Synthesis

A typical experimental example is given as follows (PA-1 in Table 1): Mixtures of 0.8614 g (10 mmol) of PZ, 0.8815 g (10 mmol) of NDA, 2.363 g (20 mmol) of DV, and 15 ml of water was heated at 45°C with stirring for 72 h. The reaction mixture was then poured into 500 ml of methanol. The precipitate was collected by filtration and reprecipitated from water solution into methanol, and dried under vacuum at 80°C for 24 h. Yield 3.8 g (93.5%). IR (KBr): 1311, 1135 cm^{-1} (SO_2), 3450–3250 cm^{-1} (–NH_2 or –NH–). Calcd for $C_{16}H_{34}N_4O_4S_2$: C, 46.76%; H, 8.28%; N, 13.64%; S, 15.58%. Found: C, 46.71%, H, 8.35%, N, 13.60%, S, 15.64%.

3. Results and discussion

The fed mole ratio of DV to PZ and NDA was equal to 1, while the ratio of PZ to NDA was ranging from 0.2 to 5. The reaction mechanism and thermal properties of resulting polymers were carefully investigated.

3.1. Polymer synthesis

The polymerization was implemented at 35–45°C in a variety of solvents including water, chloroform, DMF, DMA and NMP. The results are summarized in Table 1. It can be found that chloroform is the most effective solvent, in which the polymer with the highest inherent viscosity ($\eta_{inh} = 0.89$ dl/g) can be prepared. It is not necessary to use any catalysts for the polymerization. No cross-linking was observed throughout the polymerization in water and in organic solvents. In the IR spectrum of the resulting polymer, the absorption peaks of sulfone groups (SO_2) were observed at 1311 and 1135 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 spectrum. In the ^{1}H NMR spectrum, the peak for the protons of amino groups was found at 2.08 ppm, while the peaks for the protons of vinyl groups were not observed. These data indicate the vinyl groups of DV have completely reacted

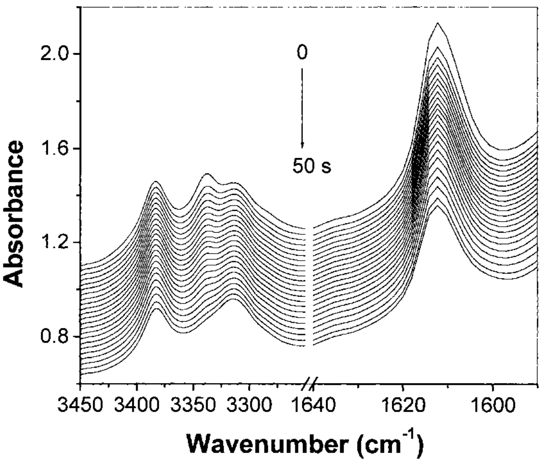
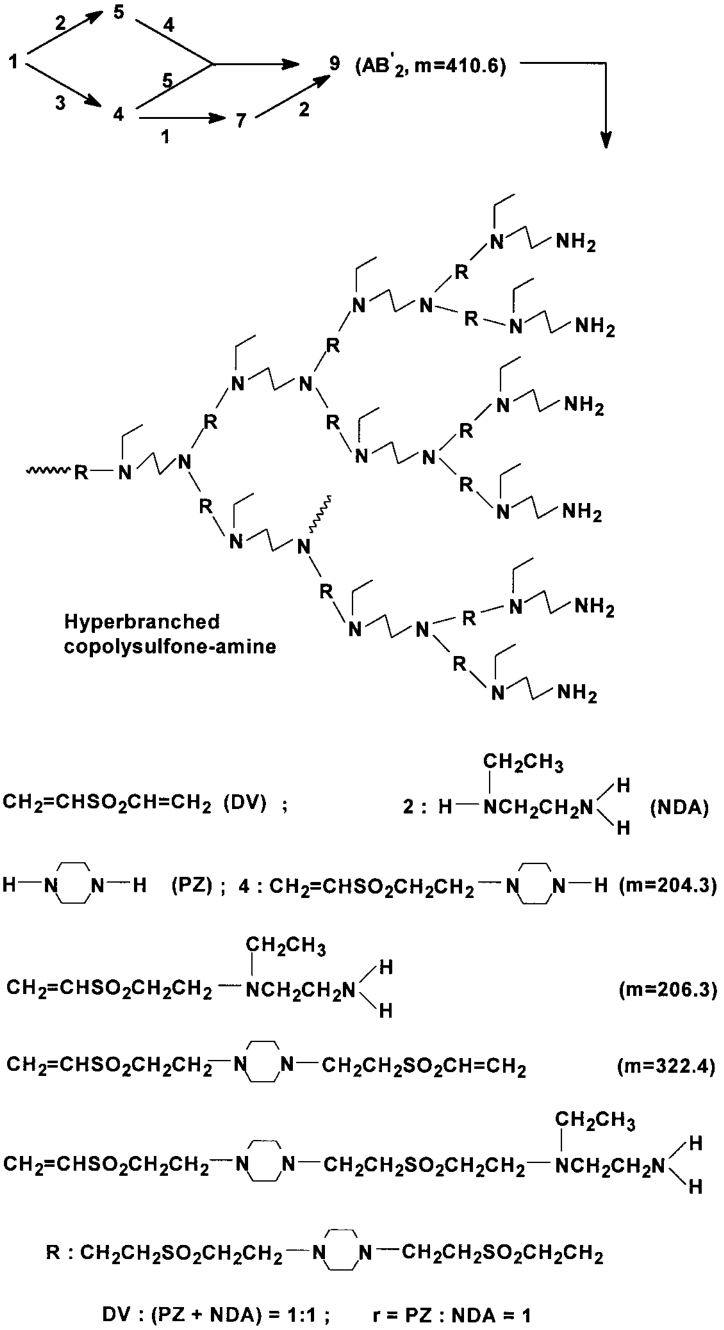


Fig. 1. In situ FTIR spectra of the reaction system of DV, PZ and NDA with $r = 1$ in chloroform within initial 50 s.



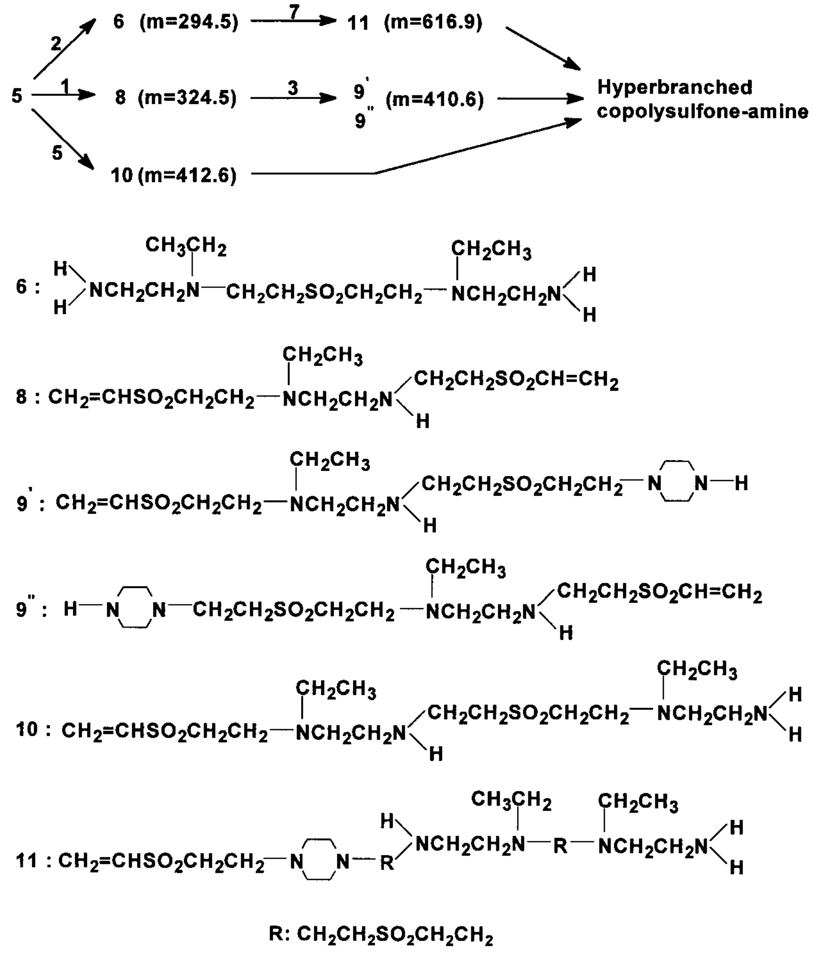
Scheme 1.

with the amino groups of NDA and PZ, and the resulting copoly(sulfone-amine)s with end amino groups were prepared.

When the initial mole ratio of PZ to NDA was equal to or less than 2, $r \leq 2$, the reaction mixture was a homogeneous solution throughout the polymerization. When the ratio of PZ to NDA was equal to or larger than 3, $r \geq 3$, precipitation occurred during the reaction in water, while no precipitation was observed when the reaction was carried out in strong polar organic solvents such as DMA, DMF and NMP.

3.2. Polymerization mechanism

The polymerization process was investigated with FTIR and LC-MSD. Fig. 1 shows the FTIR spectra for the reaction of DV with PZ and NDA at initial stage. The absorption peak at 3334 cm^{-1} (secondary-amino group) rapidly decreased with the reaction, and totally disappeared at about 50 s, while the peaks at 3383 and 3313 cm^{-1} (primary-amino groups) changed little. During this period, the absorption band from 1622 to 1600 cm^{-1} (C=C) also rapidly decreased. Then, the absorption peaks at 3383 and



Scheme 2.

1613 cm^{-1} gradually decreased with the reaction. When the absorption peak at 1613 cm^{-1} totally disappeared at about 6 h, the peak from 3450 to 3250 cm^{-1} was still observed. These data suggest that the reaction of secondary-amino groups with vinyl groups is significantly faster than that of primary-amino groups with vinyl groups, therefore intermediates 9 that now can be regarded as a new kind of AB$'_2$ type monomers may be the dominant species formed during the initial reaction period. Further polymerization of 9 leads to hyperbranched copoly(sulfone-amine)s.

In accordance with the characteristic outcomes given above, the reaction mechanism is shown in Scheme 1.

Secondary-amino groups of NDA (BB$'_2$) and PZ (B_2) react rapidly with vinyl groups of DV (A_2), and generates 4, 5, 7, and then 9. Now 9 is a new type of AB$'_2$ monomer. Further polyaddition of 9 gives hyperbranched copoly(sulfone-amine)s. Since there are so many reaction species in the system, other competitive reactions may exist (Scheme 2).

The reaction mechanism was further demonstrated with the mass spectrum of the reaction mixture at initial stage. Fig. 2 shows the mass spectrum for the reaction mixture of PZ, NDA and DV with $r = 1$. The peak of AB$'_2$ monomer (9) was found at $m/z = 411.2$, and the peaks of 4, 5 and 7 were observed at $m/z = 205.1$, 207.1 and 323.1, respectively. The peaks of the fed monomers DV, NDA, and PZ were not found in the corresponding mass spectrum, which further indicated the monomers had been completely reacted and formed oligomers at the initial stage.

3.3. Degree of branching

Degree of branching (DB) is one of the most important parameters for the structure of hyperbranched polymers [21–28]. For hyperbranched copolymers made of A_2, B_2 and BB$'_2$ type monomers, DB can be expressed by [20]:

$$DB = (N_b + N_t)/(N_b + N_t + N_l + N_L) \quad (1)$$

Wherein 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.

For the resultant copolysulfone-amine in this work, N_t is the primary-amino groups, N_L the secondary-amino groups, N_l a half of the tertiary-amino groups from PZ units, and N_b the branched tertiary-amino groups. In the ^{1}H NMR

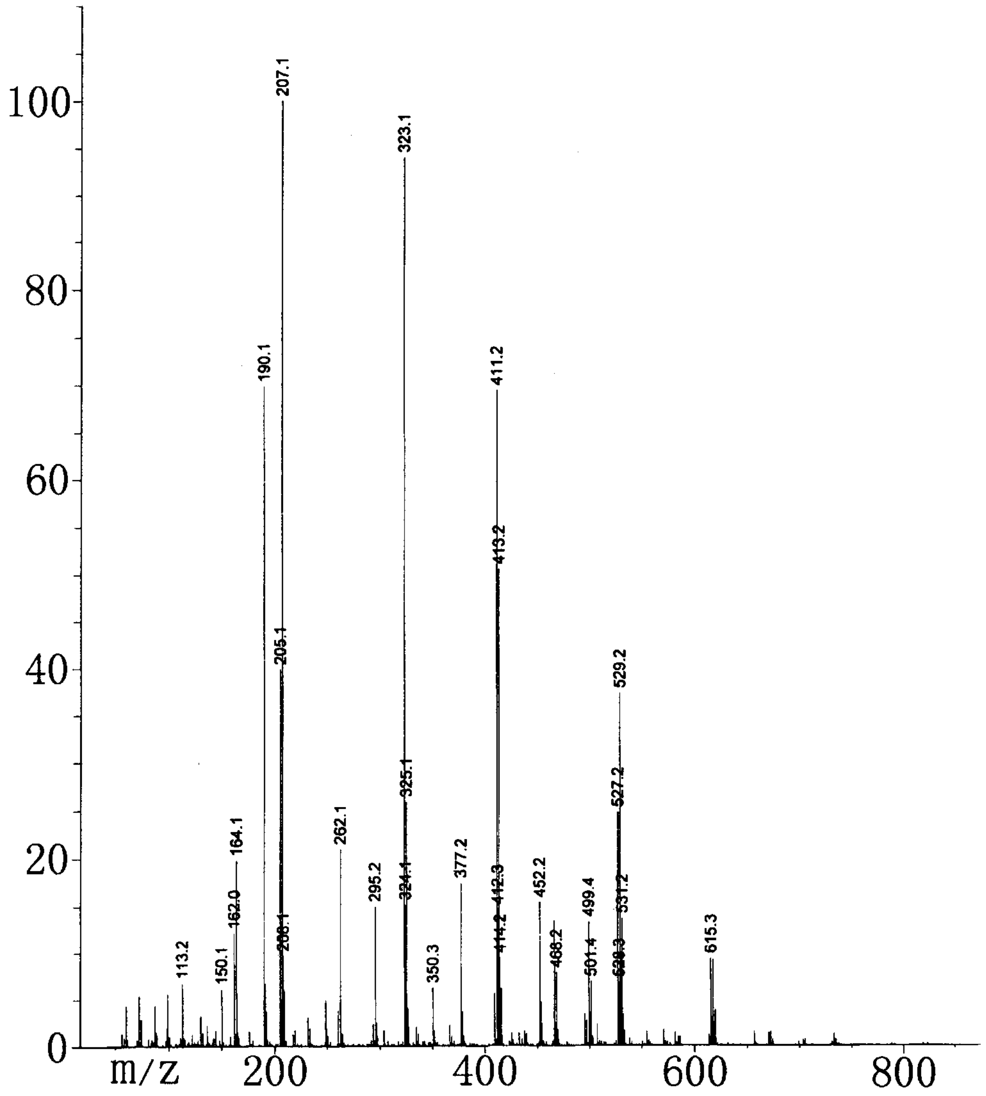


Fig. 2. Mass spectrum of the reaction mixture of PZ, NDA and DV with $r = 1$ in water at 92 s.

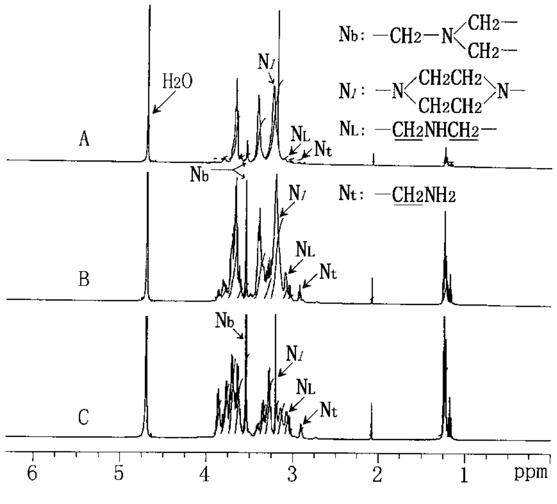


Fig. 3. ^{1}H NMR spectra of copoly(sulfone-amine)s: (A) $r = 5$; (B) $r = 2$; and (C) $r = 1/5$.

spectrum (Fig. 3), the protons of N_t, N_L, N_l and N_b were found as peaks at δ 2.85, 3.08, 3.18 and 3.57 ppm, respectively. The values of DB, which were determined from the integration of the corresponding peaks in ^{1}H NMR spectrum, are summarized in Table 1. Evidently, DB decreases with increasing the ratio of PZ to NDA, *r*. Therefore the DB of hyperbranched copoly(sulfone-amine)s can be well controlled by the ratio of PZ to NDA.

3.4. Thermal behaviors

In hyperbranched copolymers made from A_2 and $(B_2 + BB'_2)$ monomers, the average length of the segment between two branched points increases with increasing the amount of linear monomer (B_2). Therefore, the copoly(sulfone-amine) with different ratio of PZ to NDA may exhibits different thermal properties. Figs. 4 and 5 show

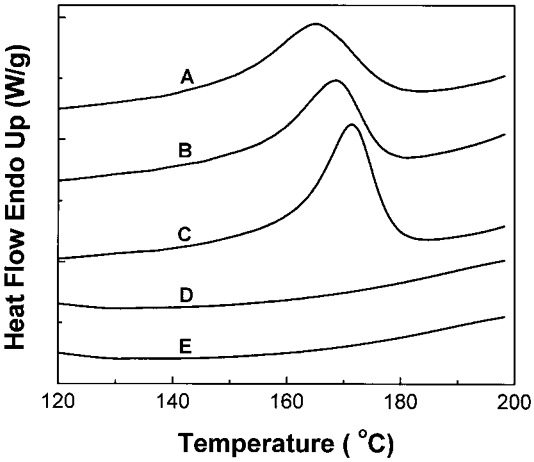


Fig. 4. DSC endothermic curves of the samples made from PZ, NDA and DV: (A) $r = 5$; (B) $r = 4$; (C) $r = 3$; (D) $r = 2$; and (E) $r = 1$.

DSC curves of resulting copolymers. When the ratio of PZ to NDA was equal to or larger than 3, $r \geq 3$, the broad melting and crystallization peaks of the copolymers were observed, and when the value of r was equal to 2 or less than 2, no melting and crystallization peaks could be found. Obviously, if the ratio of PZ to NDA is less than 2, the DB of the polymer is higher than 25%, then the regularity of the highly branched copoly(sulfone-amine)s is too poor to fit the copolymer chains into a lamella. However, as far as we know, the reason for the decrease of crystallinity with increasing r is not clear. The details will be further studied. Interestingly, the melting temperature (T_m) of the copolymer decreased with the increase of r, which may be attributed to the hydrogen bonds in the polymers. The number of hydrogen bonds increases with decreasing r. When the linear units of the branched copolymer reach a specific number, the structure of the polymers may be optimized for the formation of hydrogen bonds and crystals.

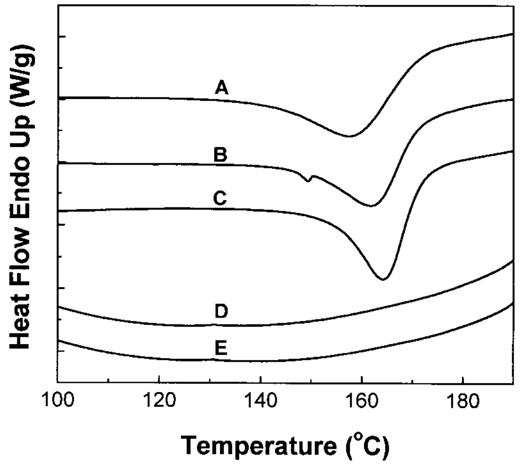


Fig. 5. DSC exothermal curves of the samples made from PZ, NDA and DV: (A) $r = 5$; (B) $r = 4$; (C) $r = 3$; (D) $r = 2$; and (E) $r = 1$.

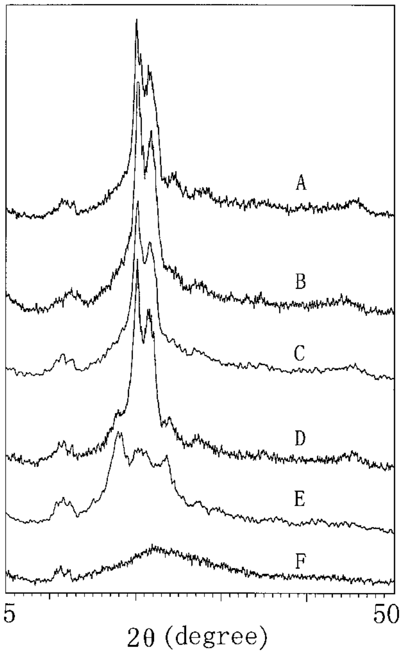


Fig. 6. X-ray powder patterns of poly(sulfone-amine)s: (A) linear polymer prepared from PZ and DV (PLSA); (B) $r = 5$; (C) $r = 4$; (D) $r = 3$; (E) $r = 2$; and (F) $r = 1$.

The analysis of X-ray diffraction gives further evidence for the semi-crystallization of the copolymers. Similar to the result of DSC, crystallization peaks were hardly observed in the X-ray powder pattern of the copolymer with $r = 1$. When the value of r was equal to 2, a small crystallization peak appeared, and the obvious semi-crystallization peaks existed in the patterns of the samples with $r \geq 3$ (Fig. 6).

TGA measurements have been performed for the copolymers with various values of r (Fig. 7). The decomposition temperatures (T_d, 5% weight loss) are summarized in Table 1. T_d of semi-crystalline samples is about 15–30°C higher than that of amorphous sample.

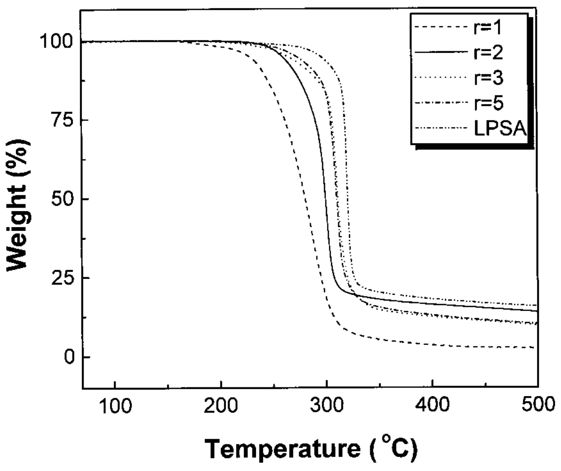


Fig. 7. TGA curves of the samples with different values of r.

The direct copolymerization of other A_2, B_2, and BB'_2 monomers has been investigated, and will be published later.

4. Conclusion

Hyperbranched copoly(sulfone-amine)s with various lengths of linear segments between two branching points were prepared by copolymerization of DV with PZ and NDA. No gelation occurred throughout the polymerization process. The DB of hyperbranched copolymers can be well controlled by adjusting the ratio of PZ to NDA. The reaction of secondary-amino groups of PZ and NDA with vinyl groups of DV is significantly faster than that of primary-amino groups of NDA with vinyl groups of DV. Therefore, the dominant intermediate that can be regarded as a new AB'_2 type monomer forms rapidly in the initial reaction stage. Further polymerization of AB'_2 results in hyperbranched copolysulfone-amines. When the fed ratio of PZ to NDA reaches 3, the resulting copolymers are semi-crystalline. The melting temperature of the copolymer with $r = 3$ is higher than that of the copolymers with higher values of r (4 and 5). The decomposition temperatures of the semi-crystal samples are higher than those of amorphous samples by 15–30°C.

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