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Preparation of water-soluble hyperbranched poly(sulfone-amine)s by polyaddition of *N*-ethylethylenediamine to divinyl sulfone

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Abstract

The new approach for synthesis of hyperbranched polymers from commercially available A_2 and BB'_2 type monomers has been further developed. Water-soluble hyperbranched poly(sulfone-amine)s with multiple amino end groups were prepared by direct polyaddition of divinyl sulfone (DV, A_2) to *N*-ethylethylenediamine (NDA, BB'_2). Effects of reaction conditions such as the feed ratio and solvents on the polymerization have been investigated. When the feed ratio of DV to NDA was equal to 1, no gelation occurred during the polymerization in water or organic solvents. Similarly, when the feed ratio of DV to AP was equal to 3/2, no insoluble or cross-linked material was observed in chloroform or other organic solvents such as *N*,*N*-dimethylforamide, *N*,*N*-dimethylacetamide and *N*-methyl-2-pyrrolidone. Interestingly, when water was used as solvent, the reaction mixture got turbid within 15–20 min and gelation occurred within 12–15 h. The turbid mixture formed during initial stage becomes a transparent solution in aqueous acid, which was coined as 'pseudo-gelation'. The solubility of the resulting polymer in water is as high as 1.68 g/ml. The degree of branching (DB) of all the resulting hyperbranched polymers is higher than 50% and the highest one is 70.9%. The reaction mechanism is presented and demonstrated with FTIR, HPLC and MS. During polymerization, secondary amino groups of NDA react rapidly with vinyl groups of DV within 12 s dominantly generating dimers which can be regarded as a new AB'_2 type monomer. Further polymerization of the new monomers leads to hyperbranched poly(sulfone-amine)s. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched polysulfone-amine; *N*-ethylethylenediamine; Divinyl sulfone

1. Introduction

Dendritic polymers, dendrimers or hyperbranched polymers, have received much attention over the last decade. The stepwise synthetic schemes required for the preparation of dendrimers limit their broad range of applications [1]. Therefore, hyperbranched polymers that can be prepared by one-step polycondensation of AB_x type monomers are more attractive in large-scale manufacture and industrial utilization. Except the method of polymerization of AB_x monomer [2], other approaches to hyperbranched polymers like self-condensation vinyl polymerization [3] and ring-opening polymerization [4–8] have been reported.

Recently, Kakimoto [9], Russo [10] and Fréchet [11] explored the new strategy for preparation of hyperbranched polymers by polymerization of A_2 type difunctional monomers and B_3 type trifunctional monomers in the presence of catalysts or condensing agents. More recently, the authors of this paper [12] reported a novel approach for synthesis of hyperbranched polymers from A_2 monomers and BB'_2 type trifunctional monomers. During the reaction, B groups of the BB'_2 react fast with A groups of A_2 generating dominant dimers that is now a new type of AB'_2 monomers. Further polymerization of the AB'_2 leads to hyperbranched polymers. In this work, a new approach has been developed, and a new kind of water-soluble hyperbranched poly(sulfone-amine)s was successfully prepared by one-step polyaddition of *N*-ethylethylenediamine (NDA, BB'_2) to divinyl sulfone (DV, A_2) without any catalysts.

2. Experimental

2.1. Materials and instrumentation

DV and NDA were purchased from Aldrich. DV was purified by vacuum distillation before use. NDA was used as supplied. Chloroform, *N*,*N*-dimethylforamide (DMF), *N*-methyl-2-pyrrolidone (NMP) and other organic solvents

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Table 1
Reaction conditions and results of polymerization of DV and NDA

Polymer No.	Ratio[a]	Solvent	Concentration[b]	Time	Yield (%)	DB (%)	η_{inh} (dl/g)
P-1	1:1	$CHCl_3$	1:6	5 day	95	70.9	0.12
P-2	1:1	H_2O	1:5	6 day	87	65.8	0.10
P-3	1:1	DMA	1:4	8 day	98	56.4	0.13
P-4	3:2	$CHCl_3$	1:7	6 day	94	60.1	0.13
P-5	3:2	DMA	1:4	5 day	96	57.5	0.11
P-6	3:2	NMP	1:4	5 day	95	58.9	0.12
P-7	3:2	DMF	1:4	5 day	93	62.7	0.14
P-8	3:2	H_2O	1:5	12 h	–	–	Gel
P-9	3:2	H_2O	1:10	15 h	–	–	Gel

[a] The initial mole ratio of DV to NDA.
[b] The volume ratio of DV to solvent.

were commercially purchased and purified by distillation before use.

^1H nuclear magnetic resonance (^1H NMR) measurements were carried out on a 500 MHz Bruker NMR spectrometer with D_2O as solvent. FTIR measurements were performed on a Bruker Equinox 55 spectrometer using Barnes Analytical FTIR Sealed Cell (KBr 0.5 mm) with $CHCl_3$ as solvent. High-pressure liquid chromatograms were obtained on a Waters 515 HPLC with C-18 column as immobile phase and water and acetonitrile (25:75) as mobile phase. The sample was terminated with 2N aqueous HCl as soon as it was taken from the reaction system to avoid further reaction. HP 1100 liquid chromatograph and mass spectrum detector (LC/MSD) was used to obtain the mass spectrum and the sample was terminated with 2N aqueous HCl as soon as it was taken from the reaction system to avoid further reaction. The molecular weight of the product was measured on the HP 1100 gel permeation chromatograph (GPC) with water as solvent and PEO as standards and the column used was G6000 PW (XL). TGA was performed 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 to −50°C and immediately heated at 10°C/min heating rate from −50 to 200°C for the second scan. The inherent viscosity (η_{inh}) of the resulting polymer was measured at a concentration of 0.5 g/dl in water at 25°C.

2.2. Polymerization

One typical polymerization is as follows (P-1 in Table 1): a flask was charged with 4.726 g (40 mmol) of DV, 3.526 g (40 mmol) of NDA and 15 ml of chloroform. The mixture was heated at 45°C for 5 days under stirring, and then poured into 800 ml of methanol containing 20 ml of 12N aqueous HCl. The precipitated product (hydrochloride of the polymer) was collected by filtration and washed with hot methanol and acetone, and dried under vacuum at 70°C for 24 h, then, a snow-white powdery product was obtained.

2.3. End-capping reaction

When the polymerization was carried out for a given time, 3 ml of triethylamine and 2.2 g of benzoyl chloride in 15 ml of chloroform solution was added to the mixture. The reaction was conducted at room temperature for 10 h with stirring. Then, the reaction mixture was poured into 600 ml of tetrohydrofuran (THF) and 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 in a vacuum at about 100°C overnight to give the end-capped polymer.

3. Results and discussion

3.1. Polymer synthesis

Hyperbranched polysulfone-amine was prepared by direct polymerization of DV and NDA in a suitable solvent without any catalysts. The reaction conditions and results of the polymerization are summarized in Table 1.

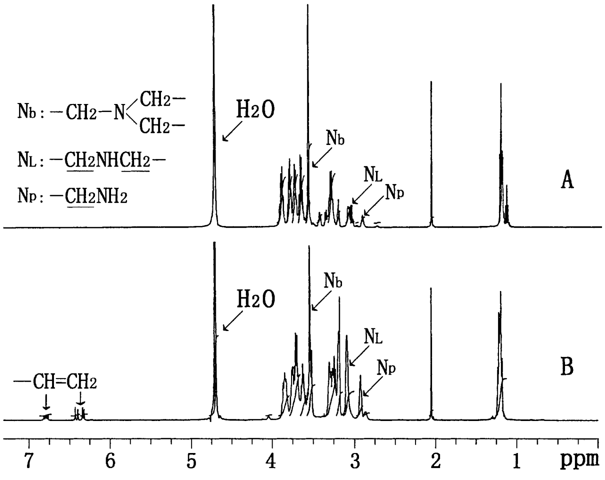


Fig. 1. ^1H NMR spectra of hyperbranched poly(sulfone amine)s: (A) $r = 1$; (B) $r = 3/2$.

Table 2
End-capping reaction of the resulting polymer

Code	Ratio[a]	Solvent	T_1[b] (day)	T_2[c] (h)	η_{inh1}[d] (dl/g)	η_{inh2}[e] (dl/g)	M_w	D[f]
PE-1	1:1	$CHCl_3$	8	15	0.098	0.12	35,810	1.32
PE-2	1:1	DMA	10	15	0.10	0.13	28,470	1.34
PE-3	3:2	$CHCl_3$	10	20	0.12	0.15	35,510	1.25
PE-4	3:2	NMP	8	20	0.11	0.14	32,640	1.28

[a] The initial mole ratio of DV to NDA.
[b] Polymerization time.
[c] Reaction time of end-capping.
[d] The inherent viscosity of the end-capped polymer measured at a concentration of 0.5 g/dl in chloroform at 25°C.
[e] The inherent viscosity of the polymer without end-capping measured at a concentration of 0.5 g/dl in water at 25°C.
[f] Molecular weight distribution (M_w/M_n) of the resulting hyperbranched polymer.

When the ratio of DV to NDA is equal to 1, no gelation occurred during the polymerization in water or organic solvents such as DMF, *N*,*N*-dimethylacetamide (DMA) and NMP. In the IR spectrum of the resulting polymer, a broad absorption band from 3450 to 3250 cm^{-1} (ν_{N-H}) was still observed, while the absorption peak at 1613 cm^{-1} ($\nu_{C=C}$) totally disappeared. In the ^1H NMR spectrum, the proton of amino group was observed as a peak at 2.07, while that of vinyl group was not observed (Fig. 1). These data indicate that vinyl groups of DV have completely reacted with the amino groups and the resulting polymer is a branched one.

In Aharoni [13,14] and Kakimoto's [9] work, the direct polymerization of A_2 and B_3 results in gelation within 10–20 min when the feed ratio is 3/2. In our work, no gelation occurred in chloroform or other organic solvents even the reaction had been preformed for 30 days when the ratio of DV to NDA is equal to 3/2. The hydrochloride of the resulting polymer is well soluble in water, and the end-capped hyperbranched polymer with benzoyl chloride is soluble in chloroform, NMP, DMF and the mixture of them. In the IR spectrum of the hydrochloride of the polymer, the absorption band from 3450 to 3250 cm^{-1} and the absorption peak at 1613 cm^{-1} were still observed. In the ^1H NMR spectrum, the proton of amino group was observed as a peak at 2.07, and that of vinyl group observed at 6.3 and 6.8 (Fig. 1). These data suggest that the resulting hyperbranched polymer still possesses vinyl groups and amino groups. In these cases, the possible reason for the absence of gelation is the non-equal reactivity of secondary amino and primary amino groups. In a suitable solvent, reaction between a primary amino group and a vinyl one generates a secondary amino group that can react rather fast with a vinyl group forming a branched unit. On the other hand, cross-linking occurred quickly for the bulk polymerization with 3/2 ratio. These phenomena showed that a suitable concentration of solution is very important for the formation of hyperbranched structures. When the reaction was carried out in water, the mixture got turbid within 15–20 min. Interestingly, the turbid mixture formed during the initial stage got transparent in aqueous HCl. So the turbidity may be caused by the intermolecular aggregation through hydrogen bonds. We coined this phenomenon as 'pseudo-gelation'. Further reaction of the mixture for 12–15 h leads to gelation, which may result from the extremely high micro-concentration of the hyperbranched poly(sulfone-amine)s.

To determine the molecular weight of the hyperbranched polymers, the resulting polymers were end-capped with benzoyl chloride in the presence of triethylamine. The molecular weight (M_w) of the end-capped polymer with the feed ratio of 1/1 or 3/2 is given in Table 2. The molecular weights of the resulting polymers measured by GPC are rather high (>25,000), and the molecular weight distributions are rather

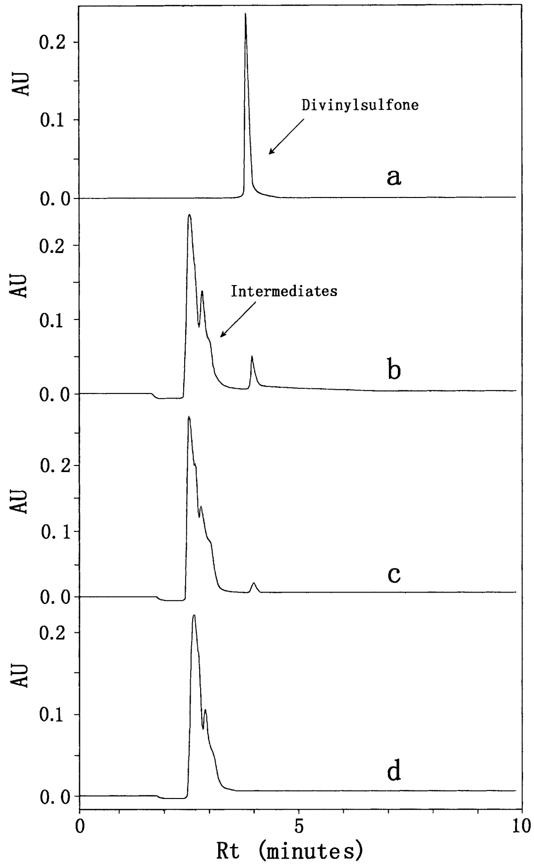


Fig. 2. HPLC chromatograms of the reaction mixture of DV and NDA ($r = 1$) in water: (a) pure DV; (b) 3 s; (c) 8 s; (d) 12 s.

narrow ($M_w/M_n < 1.35$). The inherent viscosity of sample PE-1 is the lowest one, while its molecular weight is higher than the others, which may be attributed to its higher degree of branching (DB).

3.2. Polymerization mechanism

For the reaction system of DV and NDA at a feed ratio of 1/1, the polymerization process was investigated with HPLC, MS and FTIR. In the chromatogram of HPLC, the peak for DV rapidly decreases with the reaction, and totally disappears at about 12 s (Fig. 2), which implies that the reaction between two monomers is extremely fast. McDowell and co-workers [15,16] had investigated the reaction rate for the addition of amines to *p*-polyvinyl sulfone. In their experiments, the rate of secondary amines is 3–75 times higher than that of primary amines. In our case, the reaction rate of the secondary amino group in NDA is 50–70 times higher than that of its primary amino group determined from the integration data of in situ FTIR. From mass spectrum of the reaction mixture at initial stage, the molecular ion peak of the dimer AB'_2 ($m = 206.3$) is observed at the $m/z = 207.1$ ($m + 1$). The fragment ion peak of AB'_2 losing its primary amino group ($m = 190$) and that of AB'_2 losing its ethyleneamino ($-CH_2CH_2NH_2$) group ($m = 161.3$) are observed at $m/z = 190.1$ and 162.1, respectively (Fig. 3). These data significantly suggest secondary amino groups of NDA react rapidly with the vinyl groups of DV, and form the dimer AB'_2. Furthermore, the peaks of $(AB'_2)_2$ ($m = 412.6$) and $(AB'_2)_3$ ($m = 618.9$) are observed at $m/z = 413.2$ and 619.3, respectively, which implies that the polymerization of AB'_2 monomers begins in the meantime.

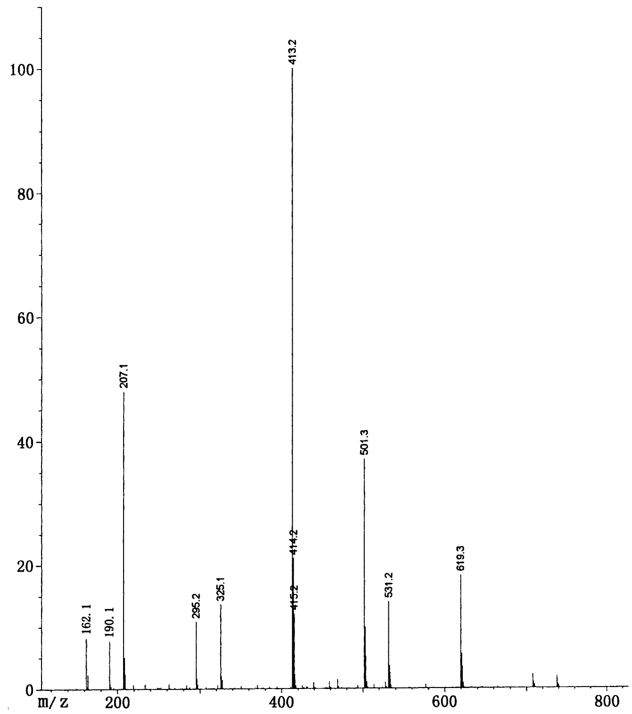


Fig. 3. Mass spectrum of the sample taken from the reaction system of DV and NDA in water with $r = 1$ at 50 s.

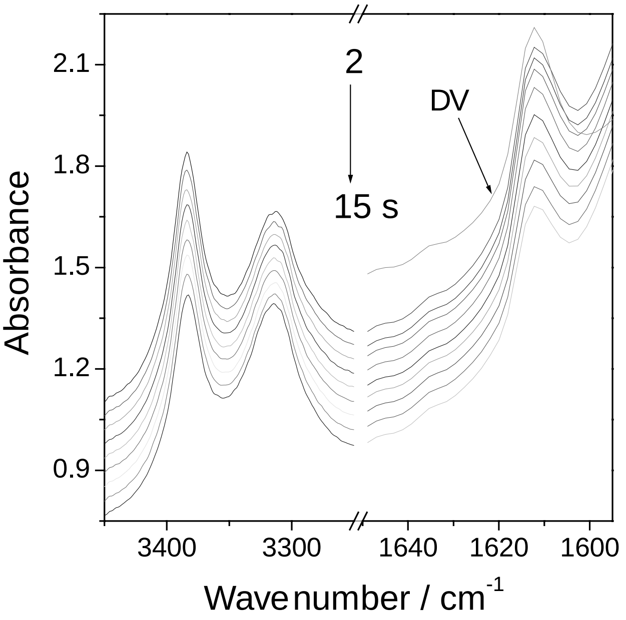


Fig. 4. In situ FTIR spectra for the reaction system of DV and NDA with $r = 1$ in chloroform within initial 15 s.

The results obtained from the MS and HPLC are conformed to that observed from FTIR spectra. Although the absorption band of secondary amino group is not observed directly in FTIR spectra, the change of primary amino groups and vinyl groups provides further evidence for the reaction process described above. During the initial 15 s, the absorption band of primary amino groups only changes a little, while the area of the vinyl group band

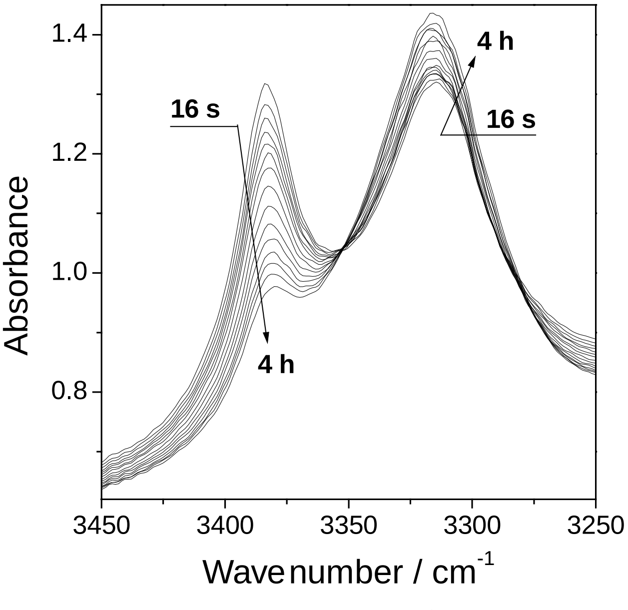
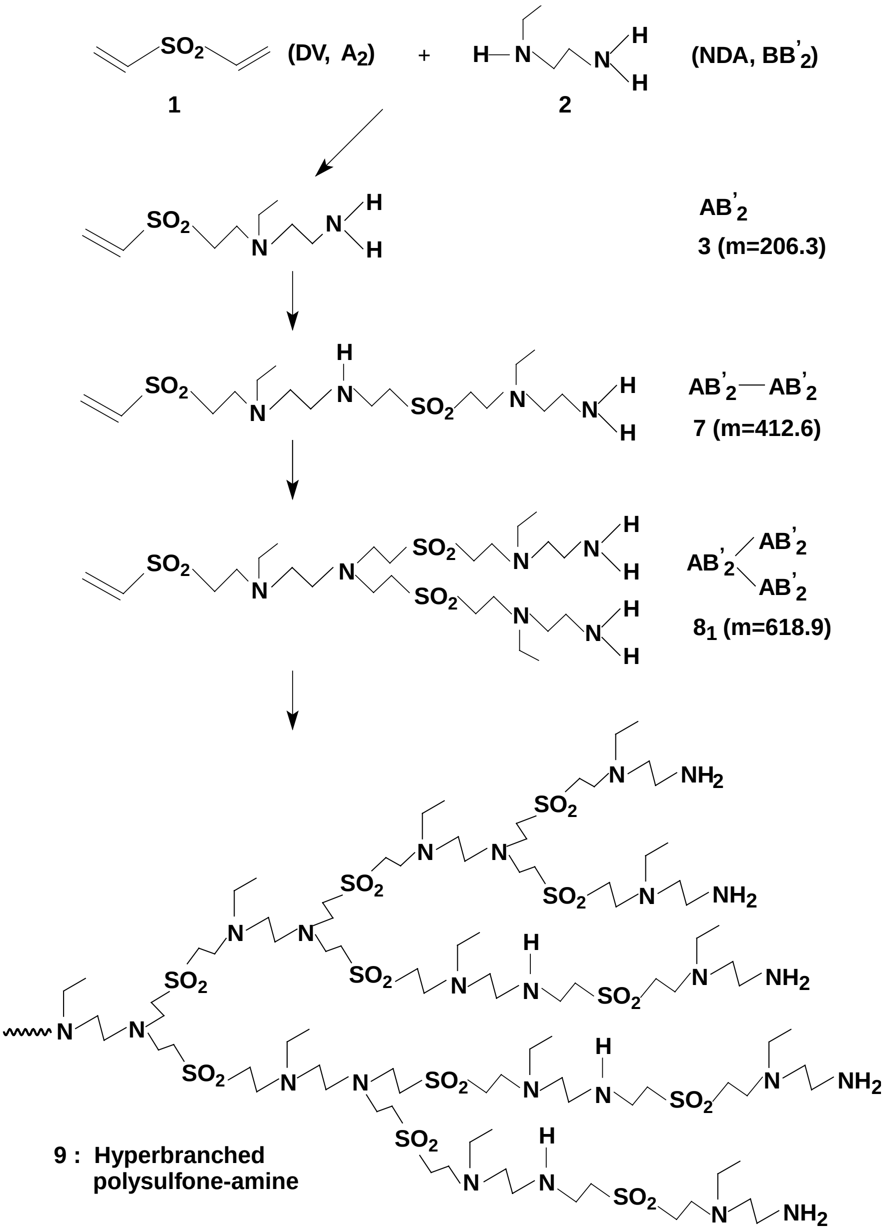


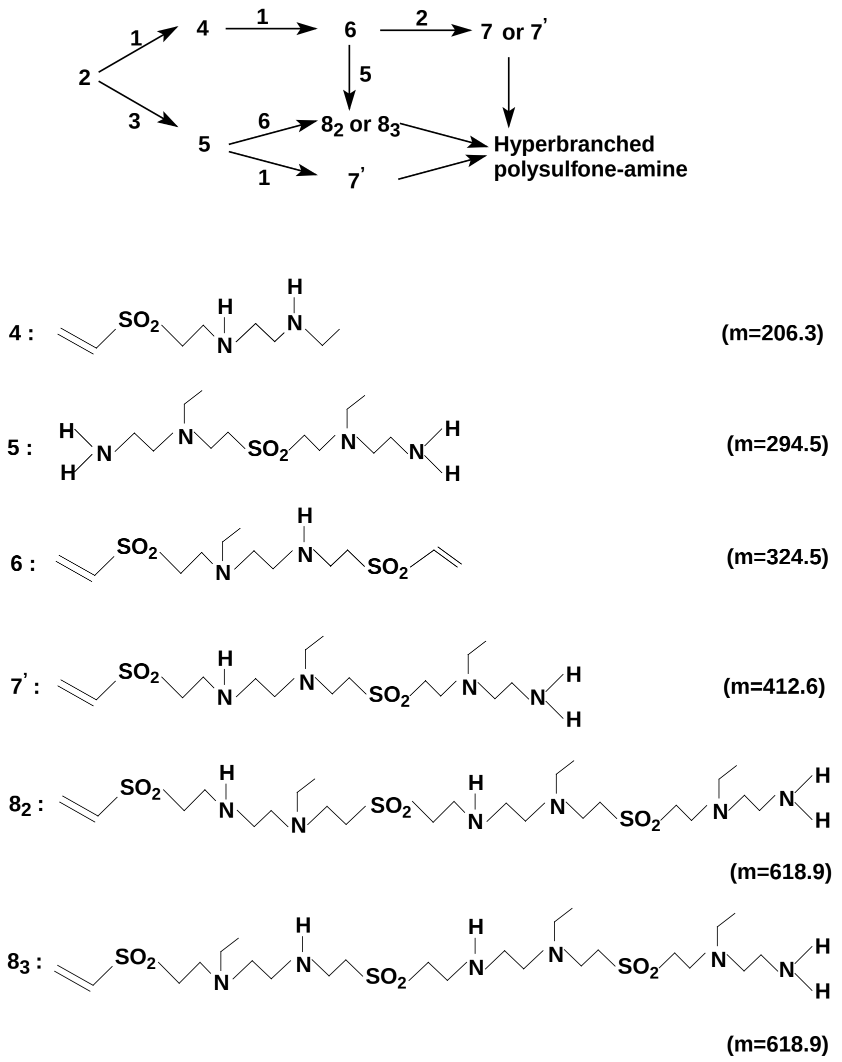
Fig. 5. In situ FTIR spectra from 3450 to 3250 cm^{-1} for the reaction system of DV and NDA with $r = 1$ in chloroform from 16 s to 4 h.



Scheme 1.

decreases nearly one half (Fig. 4). Then, the absorption bands of amino groups and vinyl groups decrease gradually with the reaction time. The band of vinyl groups vanishes completely after about 4 h, while the band of amino groups is still present in the IR spectra. These data indicate that the reaction of the secondary amino groups and vinyl groups is much faster than that of primary amino groups and vinyl groups at the initial stage of the reaction, generating the dominant dimers that now are a new kind of AB'_2 type monomers. Further polymerization of AB'_2 results in hyperbranched polymers. Interestingly, one of the primary amino absorption peaks from 3250 to 3335 cm^{-1} enlarges gradually with the reaction, and the peak at 3313 cm^{-1} shifts about 2 cm^{-1} toward lower wavenumber (Fig. 5), which may be due to the formation of hydrogen bonds between amino groups and sulfone groups.

In accordance with the experimental data aforementioned, the reaction mechanism may be as shown in Scheme 1. During polymerization, vinyl groups of 1 react fast with secondary amino groups of 2 forming 3. Intermediate 3 can be regarded as a new AB'_2 type of monomer. Further polyaddition of AB'_2 leads to hyperbranched polysulfone-amine. Since there are competing reactions between vinyl groups with secondary amino groups and vinyl groups with primary amino groups, other minor reactions as shown in Scheme 2 are also present. The reaction of BB'_2 and AB'_2 formed in



Scheme 2.

the initial stage leads to the species 5 with two primary amino groups, which may act as the cores of hyperbranched poly(sulfone-amine)s. Species 6 containing two vinyl groups might act as a cross-linking agent. However, no gelation was observed in the reaction with 1/1 feed ratio. The reason may attribute to the minor amount of this species.

For the system of DV and NDA at the ratio of 3/2, the reaction is more complex. In the chromatogram of HPLC, the peak of DV is still observed after reacting for 1 h (Fig. 6). In FTIR spectra, the absorption peaks of primary amino groups vary only a little during initial 20 s (Fig. 7), and are still observed after 4 h (Fig. 8). All of these data give further identification for the polymerization mechanism given above, i.e. the reaction of secondary amino groups and vinyl groups is much faster than that of primary amino groups and vinyl groups, otherwise, the primary amino peaks would vanish more rapidly in the IR spectra.

3.3. Degree of branching

The DB is very important for hyperbranched polymers [17–22]. When the feed ratio is equal to 1, the resulting polymer contains the following units: (1) branched units (N_b), (2) linear units (N_L) and (3) terminal units (N_t). The DB is the ratio of branched and terminal units to the total units, i.e.

$$\mathrm{DB} = \frac{N_b + N_t}{N_b + N_t + N_L} \tag{1}$$

The fractions of the branched, terminal and linear units can be calculated from the integration of corresponding peaks of the ^{1}H NMR spectrum. The peaks attributed to the protons of branched, linear and terminal groups were observed at 3.57, 3.08 and 2.85 ppm, respectively (Fig. 1). The values of DB calculated with this method are summarized in Table 1.

When the feed ratio is equal to 3/2, terminal groups

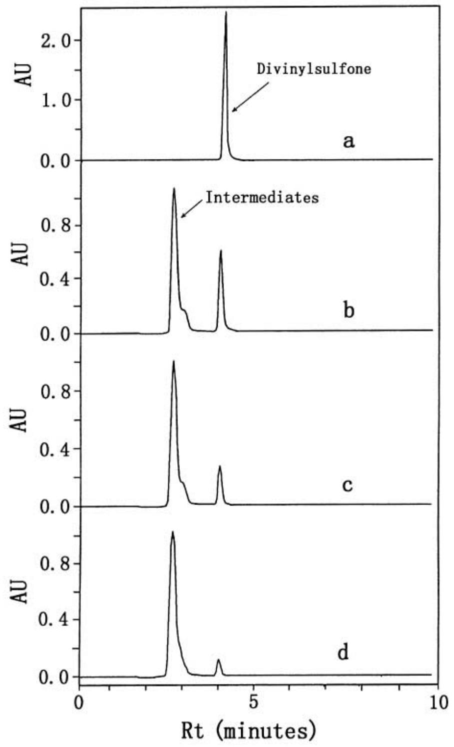


Fig. 6. HPLC chromatograms of the reaction mixture of DV and NDA with $r = 3/2$ in water: (a) pure DV; (b) 5 min; (c) 30 min; (d) 1 h.

contain vinyl groups (CH_2=CH, N_v) and primary amino groups (CH_2NH_2, N_p). The DB is defined as

$$\mathrm{DB} = \frac{N_b + N_v + N_p}{N_b + N_v + N_p + N_L} \tag{2}$$

The peaks of vinyl groups locate at 6.8 and 6.4 ppm, and peaks of branched units, primary amino groups and secondary amino groups were found at 3.57, 2.83 and 3.08 ppm, respectively (Fig. 1). The values of DB are also summarized in Table 1.

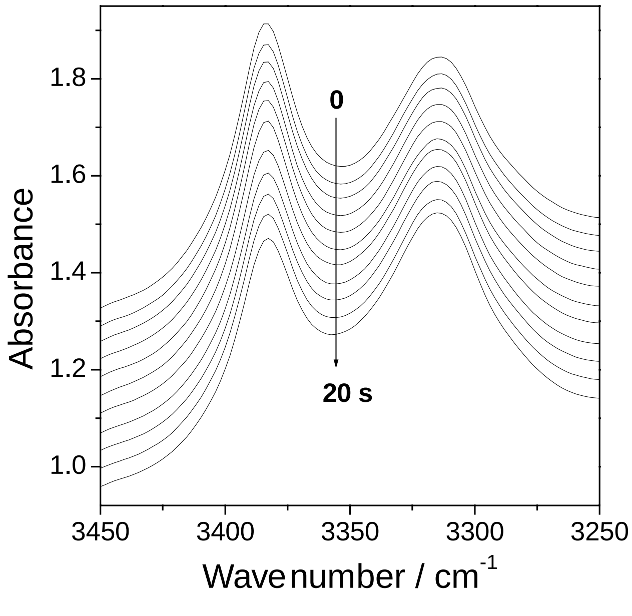


Fig. 7. In situ FTIR spectra from 3450 to 3250 cm^{-1} for the reaction system of DV and NDA with $r = 3/2$ in chloroform within initial 20 s.

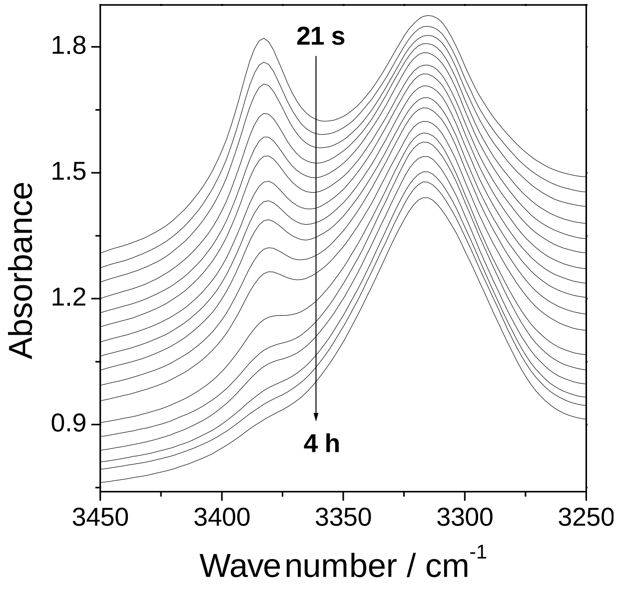


Fig. 8. In situ FTIR spectra from 3450 to 3250 cm^{-1} for the reaction system of DV and NDA with $r = 3/2$ in chloroform from 21 s to 4 h.

If an AB'_2 type monomer, in which two B groups have the equal reactivity, is used to synthesize hyperbranched polymers, the theoretical maximum of DB is equal to 50% [23–27]. However, in this work, the reactivity of secondary amino groups is much higher than that of primary amino groups. Reaction between a primary amino group and a vinyl group results in a secondary amino group, which reacts faster with a vinyl group forming a branched unit. Therefore, the DB in this work is higher than 50%.

3.4. Thermal properties

The absence of melting and crystallization peaks in DSC curves of resulting polymers demonstrates that the hyperbranched polymers obtained in this work are amorphous. The glass transition temperature (T_g) of P-1 and P-3 is −23.5 and −20.4°C, respectively. In TGA curves of samples P-1 and P-3, the temperatures for 5% weight loss are 280 and 290°C, respectively.

4. Conclusions

The stepwise polymerization of A_2 and BB'_2 type monomers can be successfully used to synthesize hyperbranched polymers. Through this new approach, hyperbranched poly(sulfone-amine)s were prepared from DV and NDA without any catalysts. FTIR, HPLC and MS measurements confirm that the reaction of secondary amino groups and vinyl groups is the major reaction during the initial stage, which results in dimers. Further polymerization of dimers and other species leads to hyperbranched poly(sulfone-amine)s. The structure and different units of resulting polymers can be identified in terms of ^{1}H NMR spectra, and the value of the DB is higher than 50%. Gelation can be avoided in organic solvents no matter what the mole ratio of A_2 to BB'_2 is 1/1 or 3/2. When water is used as the solvent, a new phenomenon coined as 'pseudo-gelation' is found in this work. The resulting hyperbranched polymers show good solubility in water and organic polar solvents but limited solubility in cyclohexane or hexanes.

Acknowledgements

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