

A New Method for Synthesizing Hyperbranched Polymers with Reductive Groups Using Redox/RAFT/SCVP*

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Abstract The novel hyperbranched polymers containing reductive groups were successfully prepared and characterized using redox/reversible addition fragmentation chain transfer (RAFT)/self-condensing vinyl polymerization (SCVP) method. Several redox initiating chemicals such as Cu(III)/—CONH₂, Ce(IV)/—CONH₂ and Ce(IV)/—OH were chosen to increase the free radical generating rate, and the chain transfer agent (CTA) was used to reduce the molecular chain propagating rate, in order to obtain polymers with high degree of branching. Detailed analyses based on the molecular weight, α value and the degree of branching of polymers (DB) obtained from ¹H-NMR spectra and multi detector size exclusion chromatography (MDSEC) suggested the acquiring of hyperbranched polyacrylamides with Cu(III)/—CONH₂ and Ce(IV)/—CONH₂ as initiator in the presence of the CTA. Meanwhile, the as-prepared poly(*N*-hydroxymethyl acrylamide) (PNHAM) with higher DB value (0.48) proved that using Ce(IV)/—OH as the initiator could increase the free radical generating rate and diminish the gap between the propagating rate and the initiation rate during the reaction procedure. In addition, the effect of oxidant concentration on the Mark-Houwink index (α) value and the DB was also studied.

Keywords: Hyperbranched polymers; Redox; RAFT; SCVP; Free radical polymerization.

INTRODUCTION

Hyperbranched polymers have attracted immerse attention because of their special three-dimensional (3D) structures and interesting properties^[1–3]. The last two decades has witnessed the significant development of synthesizing techniques and methods for hyperbranched polymers^[4–8]. For example, Fréchet and co-workers reported a promising and facile method, the self-condensing vinyl polymerization (SCVP), that did not generate any gels even at high monomer conversion^[9]. Later, many other polymerization techniques such as nitroxide-mediated radical polymerization, atom transfer radical polymerization (ATRP), reversible addition fragmentation polymerization (RAFT), cationic polymerization, and anionic polymerization were reported successively^[10–12].

Using classic free radical polymerization, Zhang and co-workers prepared branched polyacrylamides^[13]. In comparison, the acrylamide monomer having the reductive amide group could be initiated by Cu(III) to form a linear polymer, while the as-formed initiating centers based on the pendant reductive amide groups of the polymer might result in the branched polymers. Clearly, the formation of polyacrylamide with an 8% degree of branching could allow the researchers to prepare these polymers from commercially available chemicals in large

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quantity and thereby study their properties in detail. In addition, this method will also expand the scope of inimers and increase the structural diversity of hyperbranched polymers.

In theory, the mechanism of this approach is in agreement with the idea of Fréchet. Several inimers could be polymerized to form hyperbranched structures with high degree of branching (DB) in SCVP. However, the DB of this polymerization only reaches 8%, which may be ascribed to the non-equal active rates between the generation and propagation of the free radicals^[14]. For radical polymerization, the propagation rate of the free radical is much higher than the initiation rate, leading to the formation of branched polymers with low DB. Reducing the gap between the propagating rate and the initiation rate is the key to improve the DB of the polymers to form hyperbranched polymers. In other word, it is important to either raise the initiation rate or reduce the polymerization rate. Initiation rate can be increased by selecting oxidizing and reducing agents with high active rate constant; however, for given polymers, the selection is very limited because its monomers are usually fixed. The propagation rates can be decreased by adding some inhibitors or applying controlled free radical polymerization. It is more effective when the two approaches are combined to reduce the gap between the propagating rate and the initiation rate.

In this work, we selected Cu(III) and Ce(IV) as oxidants, and amide groups and hydroxyl groups as reducing agents. The effects of the redox reaction on the DB, conversion and molecular weight were investigated in details. As Cu(III) and Ce(IV) may interfere ATRP reactions, RAFT was used to control the propagation rates of free radicals.

EXPERIMENTAL

Materials

All the chemicals were directly utilized without further purification unless otherwise specified. The Cu(III) solution was prepared with determined concentration according to reported method^[15]. S,S'-Bis(α,α -dimethyl- α' -acetic acid)-trithiocarbonate (BDAAT) was obtained following a literature procedure^[16]. Distilled deionized water was produced by Millipore Filtration System (Millipore, simplicity, US).

Preparation of Branched PAM by Redox/SCVP

All polymerizations were carried out in a glass tube sealed with a rubber cap under nitrogen. A representative example (S1 or S3) of the polymerization is described as follows. Acrylamide (AM) (568 mg, 8 mmol), Ce(IV) (82 mg, 0.15 mmol) or Cu(III) (0.5 mL 0.15 mmol) and water (5 mL) were added to a glass tube. Oxygen was removed through repeated vacuum-nitrogen cycles. The polymerization was performed at 45 °C in an oil bath for a predetermined reaction time. The obtained polymers were then precipitated by dropping the solution into a large excess of acetone to remove monomer and oxidant. The precipitated polymer was separated by centrifugation, redissolved in a small amount of water, and reprecipitated from acetone. Finally the polymer was obtained by vacuum drying.

Preparation of Hyperbranched PAM and PNHAM by Redox/RAFT/SCVP

All polymerizations were carried out in a glass tube sealed with a rubber cap under nitrogen. A representative example (S5 or S7) of the polymerization is described as follows. AM (213 mg, 3 mmol) or *N*-hydroxymethylacrylamide (NHAM) (202 mg, 2 mmol), Ce(IV) (274 mg, 0.5 mmol or 109 mg, 0.2 mmol), BDAAT (169 mg, 0.6 mmol or 113 mg, 0.4 mol) and water (5 mL) were added to a glass tube. Oxygen was removed through repeated vacuum-nitrogen cycles. The polymerization was performed at 85 °C in an oil bath for a desired reaction time. The obtained polymers were then precipitated by dropping the solution into a large excess of acetone to remove monomer and oxidant. The precipitated polymer was separated by centrifugation, redissolved in a small amount of water, and reprecipitated from acetone. Finally the polymer was obtained by vacuum freeze drying.

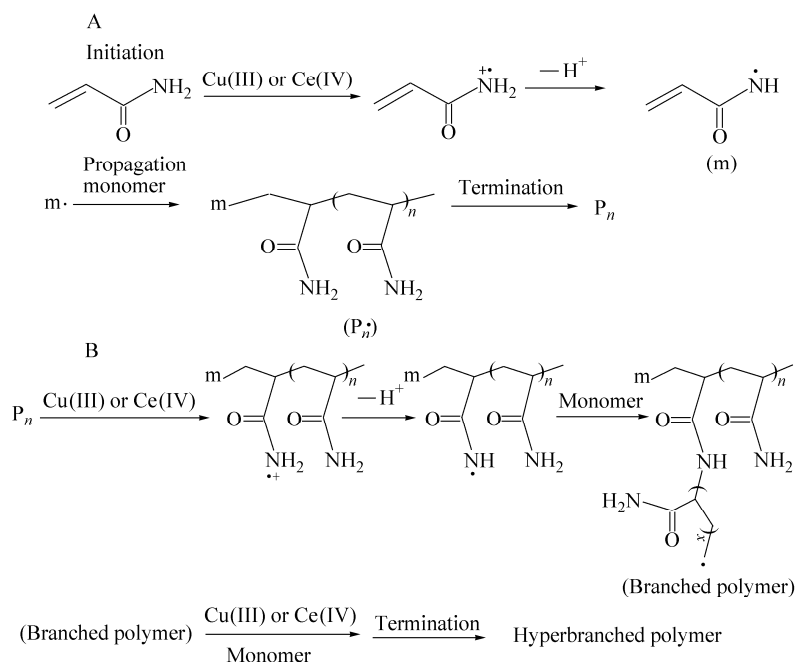
Analysis

$^1\text{H-NMR}$ spectra were recorded on a Bruker AVIII 600 MHz. PAM S1: signal 1 ($-\text{CHH}-$, δ): (1.55, 1.66, 2 H), signal 2 ($-\text{CH}-$, δ): (2.15, 2.17, 1 H). PAM S3: signal 1 (δ = 1.56, 1.68, 2 H), signal 2 (δ = 2.16, 2.18, 1 H) and signal 3 ($\text{NH}-\text{CHH}-$ and $\text{N}-(\text{CHH})_2-$, δ): (3.31, 0.06 H). S5, signal 1 (δ = 1.56, 1.68, 2 H), signal 2 (δ = 2.16, 2.18, 1 H) and signal 3 (δ = 3.31, 0.22 H). PNHAM, S8: signal 1' ($-\text{CHH}-$, δ): (1.55, 1.66, 2 H), signal 2' ($-\text{C}(\text{CO})\text{H}-$, δ): (2.15, 2.17, 1 H), signal 3' ($\text{NH}-\text{CHH}-\text{OH}$ and $\text{NH}-\text{C}(\text{CH}_2)\text{H}-\text{OH}$, δ): (4.58, 1.82 H), PNHAM S9: signal 1' (δ = 1.55, 1.66, 2 H), signal 2' (δ = 2.15, 2.17, 1 H), signal 3' (δ = 4.58, 1.65 H), PNHAM S10: signal 1' (δ = 1.55, 1.66, 2 H), signal 2' (δ = 2.15, 2.17, 1 H, $-\text{C}(\text{CO})\text{H}-$), signal 3' (δ = 4.58, 1.52 H), linear PNHMA, signal 1' (δ = 1.55, 1.66, 2 H), signal 2' (δ = 2.15, 2.17, 1 H), signal 3' (δ = 4.58, 1.98 H).

Molecular weight, polydispersity and intrinsic viscosity ($[\eta]$) were measured by Viscotek 270-MDSEC equipped with the differential refractive index (RI), viscometer, and two-angle light scattering (LS) triplet detectors. For LS, the laser wavelength was 650 nm. A set of two columns of Viscotek G2500PWxl and Waters Wat011545 was equipped in the SEC. 0.1 mol/L NaNO_3 aqueous solution was used as the eluent at a flow rate of 1 mL/min, and the polyethylene oxide std-PEO22K was used for calibration at 35 °C. OmniSEC software was used to process the data using the exact sample concentration, and 100% recovery of the hyperbranched polymer where dn/dc value was 0.170. The product was dissolved in 0.1 mol/L NaNO_3 solution and passed through 0.2 μm filter before injection. Because the SEC equipped with detectors of light scattering and viscometer, the results not only gave the molecular weight, molecular weight distribution but also gave the intrinsic viscosity, mean square radius of gyration (R_g) and α of polymers. In the same test conditions, the α value can reflect the polymer's topology structure. Wang *et al.*^[8] and Dong *et al.*^[17] confirmed the hyperbranched structure of polymers they synthesized through the α value decreased to 0.39 or 0.16 in the same test conditions^[8, 17].

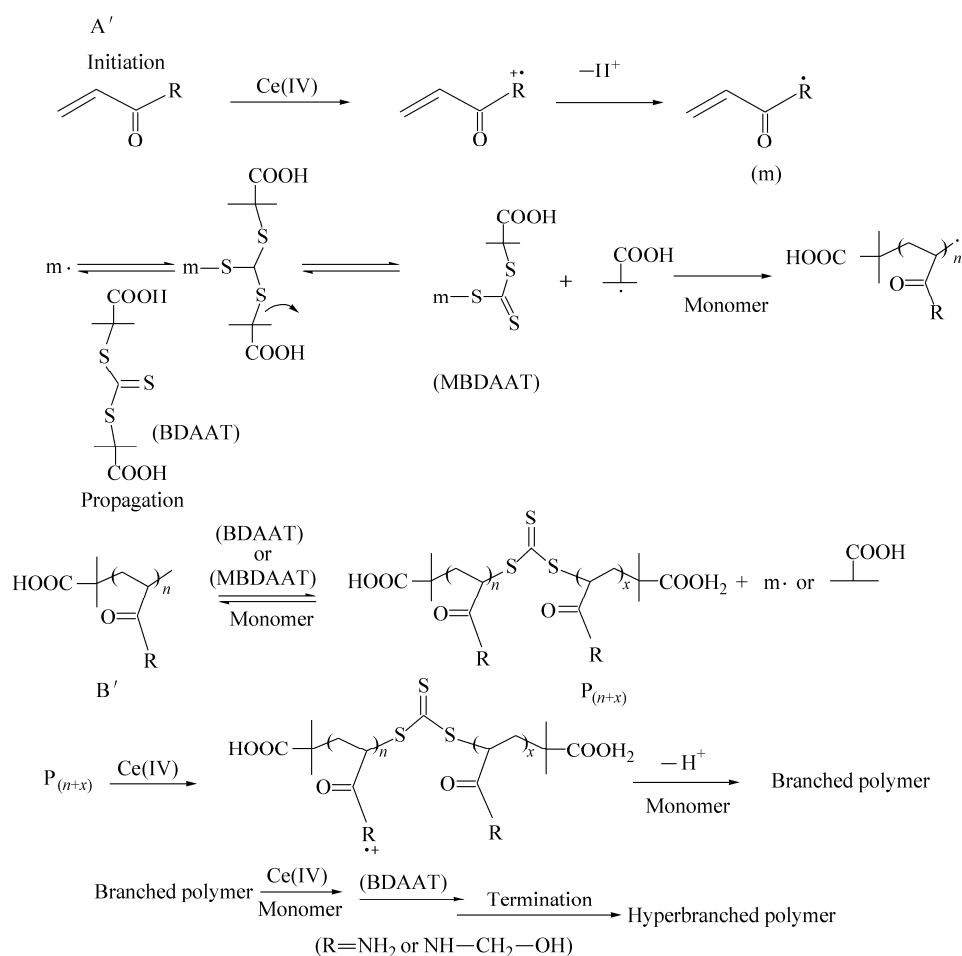
RESULTS AND DISCUSSION

The Redox/RAFT/SCVP reaction mechanisms are shown in Scheme 1 and Scheme 2. As the concentration of BDAAT is a trace in the mixture, the reaction mechanism is in agreement with the idea of Zhang and coworkers as shown in Scheme 1, in which AM monomer is selected with an oxidant Cu(III) or Ce(IV) ^[13]. In the A stages,



Scheme 1 Branched PAM reaction mechanism

the radicals are generated *via* an amide group/Cu(III) redox process, which rapidly initiated the monomer to form polymers. If the concentration of the oxidizing agent was sufficient, the as-formed linear polymers should be further oxidized to produce the branched polymers in the *B* stages. When the concentration of BDAAT is abundant in the reaction mixture, the reaction mechanism should adapt to what is shown in Scheme 2. AM and NHAM monomers are selected with an oxidant, Ce(IV). In the *A'* stages, the radicals $m^{\bullet}$ are generated through a hydroxyl/Ce(IV) or amide/Ce(IV) redox process, reacting with the initial BDAAT to form the monomer BDAAT and the free radical of leaving group. Along with the RAFT polymerization being carried out gradually, the linear polymers were formed. At the same time, the Ce(IV) could react with the hydroxyl or amide units of these linear polymers, which produces new propagating radicals, and BDAAT would be consumed again. Through several redox reactions, the hyperbranched polymers were obtained. In Scheme 2, the concentration of free radicals and branching points were proportional to the concentration of oxidizing agents. Therefore, it was necessary for BDAATs to be present in the reaction solution in high concentration.



Scheme 2 Hyperbranched PNHAM reaction mechanism

According to the definition by Frey, the value of DB can be calculated from equation (1), where *D* denotes the number of branching units and *L* denotes number of linear units, and thereby *D* + *L* was the total number of units^[18]. Based on Scheme 1 and Scheme 2, the structures of branched units for PAM and PNHAM are shown in Fig. 1. For PAM, a branching unit was formed as one of the amide group in the molecular chain was redoxed to initiate a branched chain, thus the peak 3 (CONH-CHH and CONH-(CHH)₂) can represent the branching unit as shown in Fig. 2. The other repeat units were the linear units which can be represented by the peak 1

($-\text{CHH}-\text{CH}-$). The total number of units is represented by the area of ($1 + 3$). Therefore, the DB can be calculated by using the area ratio of $3/(1 + 3)$. For PNHAM, the ^1H -NMR spectrum is shown in Fig. 3. There are two kinds of probability to form branching points, the first is the branching points from the OH groups, and the second is the branching points generated at the $\text{NH}-\text{CHH}-\text{OH}$ group. In the first case, the area of OH group will decrease, and no matter the linear PNHAM or the branched PNHAM, the area ratio of $3'$ ($\text{NH}-\text{CHH}-\text{OH}$ group), $2'$ ($\text{CO}-\text{C}(\text{CO})\text{H}-$ group) and $1'$ ($-\text{CHH}-$ group) should be 2:1:2. In addition, because the hydroxyl groups may react with carbonyl groups forming the acetal groups, which can also decrease the area of hydroxyl group, and it has no effect on the area ratio of other groups. In the second case, the peak contributing to branching points ($\text{NH}-\text{CHH}-\text{OH}$ group) does not separate with that of the repeat units ($\text{NH}-\text{CHH}-\text{OH}$); however, the area ratio of each group in molecular chain will not be consistent with the result of 2:1:2. Thus, the decrease of ($\text{NH}-\text{CHH}-\text{OH}$) group area equal to D which can be got by the area of ($1'-3'$) and the area of $2'$ represents the total number of units. The equation is rewritten as $\text{DB} = (1'-3')/2'$.

$$\text{DB} = \frac{D}{D+L} \quad (1)$$

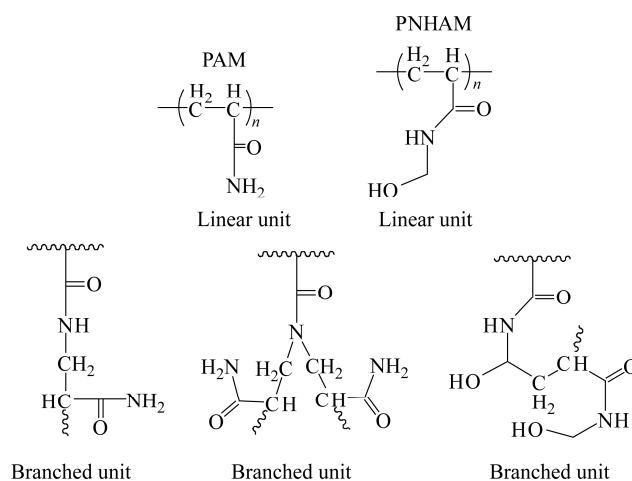


Fig. 1 The scheme of the branched units for PAM and PNHAM

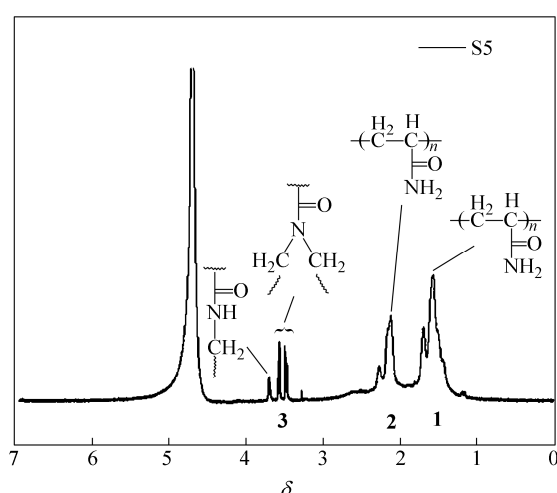


Fig. 2 ^1H -NMR of hyperbranched PAM

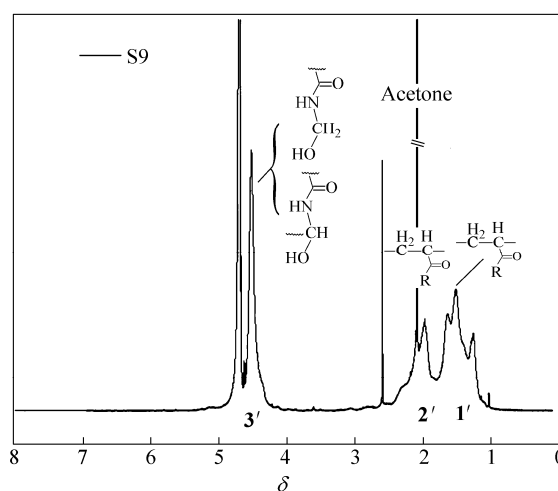


Fig. 3 ^1H -NMR of hyperbranched PNHAM

In order to test which one is the major mechanism, we characterized the PNHAM by ^1H -NMR, ^{13}C -NMR and IR. The structures of NHAM and PNHAM were analysis by IR as shown in Fig. 4. The peak of 3300 cm^{-1} is contributing to the bending vibration absorption of $\text{N}-\text{H}$ and $\text{O}-\text{H}$ groups. The stretch vibration absorption of $\text{C}=\text{O}$ group is located at 1750 cm^{-1} . The difference between the NHAM and PNHAM is the double band, the peaks of 3050 , 1630 and 620 cm^{-1} disappeared from the IR spectrum of PNHAM, which confirmed that polymerization was successfully carried out. On the other hand, the IR spectrum also shows that the residual monomers are not contained in the PNHAM.

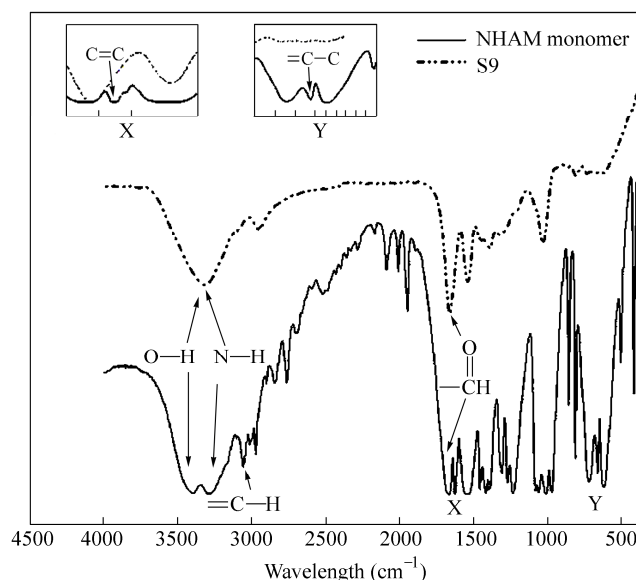


Fig. 4 IR spectrum of hyperbranched PNHAM and NHAM monomer

Figure 5 is the ^1H -NMR spectrum of S9 which was also assayed using dimethyl sulfoxide- d_6 and D_2O . The corresponding groups for signals **f'** ($\text{NH}-\text{CH}_2-\text{OH}$), ($\delta = 8.2, 0.34\text{ H}$), **e'** ($\text{NH}-\text{C}(\text{CH}_2)\text{H}-\text{OH}$), ($\delta = 6.8, 0.20\text{ H}$), **c'** ($\text{NH}-\text{CHH}-\text{OH}$ and $\text{NH}-\text{C}(\text{CH}_2)\text{H}-\text{OH}$), ($\delta = 4.7, 0.65\text{ H}$), **b'** ($-\text{C}(\text{CO})\text{H}-$, δ : (2.0, 0.68 H) **a'** ($-\text{CHH}-$, δ : (1.5, 1.00H) are displayed in Fig. 5. According to the integration ratio among the hydroxyl,

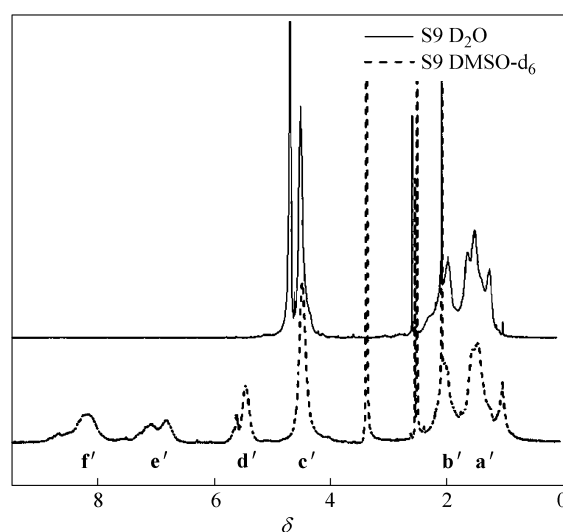


Fig. 5 ^1H -NMR spectrum of hyperbranched PNHAM

methylene and CH₂ of molecular chain, we confirmed that the branched point initiated from the methylene, and the DB value was equal to 35% which coincided with the result of Fig. 6. In addition, since the conformation and the chemical environment of the hydroxyl groups were different, leading to two different signals (**e'** and **f'**). The area of signal **e'** was 0.20 and 37% of the overall hydroxyls area which also suggests the branched point initiating from the methylene units. In addition, the result of ¹³C-NMR spectrum for PNHAM also supported the second reaction mechanism, *i.e.* the branched point was generated at the methylene group. The peak of **l** represents the NH—C(CH₂)H—OH group, and the peak of **m** is the methylene coming from the double band, which is adjacent to the NH—C(CH₂)H—OH group. These two peaks are the direct evidence for the branched point. Other peaks of ¹³C-NMR spectrum are assigned to the carbon atom of molecular chain, which are shown in Fig. 6. In addition, in the δ range of 150–100, no peak was found suggested that the monomers were completely removed from the polymers. These results confirmed that the branching points were generated at the NH—CHH—OH group.

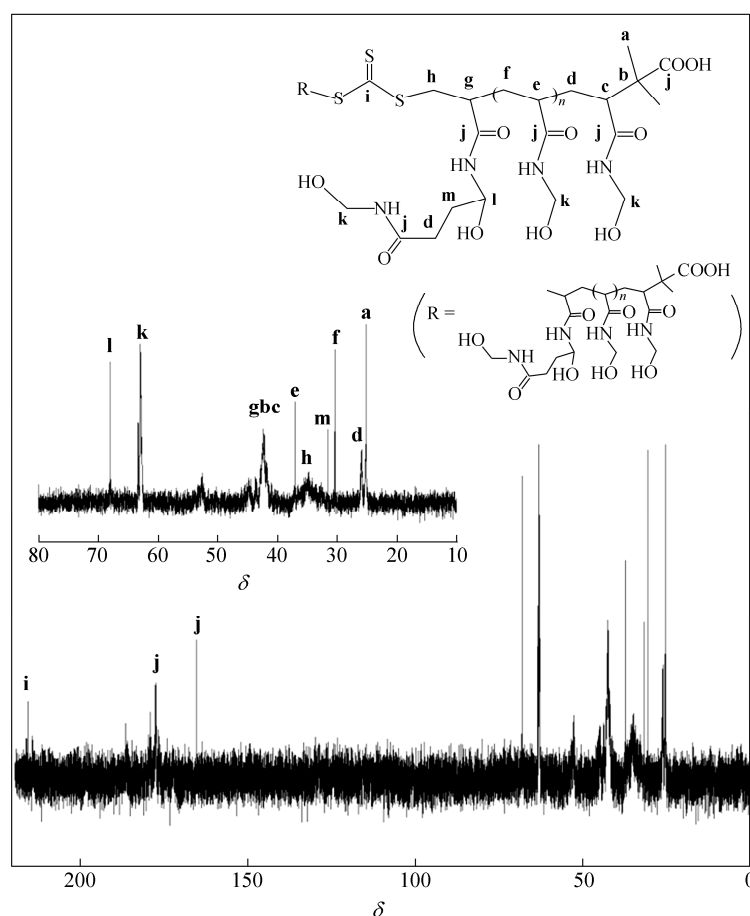


Fig. 6 ¹³C-NMR spectrum of hyperbranched PNHAM

To investigate whether there is positive correlation between the reactivity of the oxidant and the degree of branching for the polymers, we performed several parallel experiments S1, S2, S3, and S4. From the experimental results displayed in Table 1, it can be concluded that the addition of an oxidizing agent would lead to much higher conversion and lower M_w , which was in agreement with the rules for free radical polymerization. With further increase in the concentration of oxidation agents, significantly more free radicals were produced, which raised the polymerization rate and the conversion at the same time. The decrease in M_w could be attributed

to that more polymeric molecules were formed. Meanwhile, the addition of an oxidizing agent or increasing the oxidizing ability of the oxidant did not significantly improve the DB of the polymers, and the α value only decreased from 0.75 to 0.66, which is the characteristics of low DB polymers. These results suggest that raising the concentration or ability of the oxidizing agent is insufficient to eliminate the difference between the generating and propagating rates of the free radicals.

Table 1. Effect of temperature on conversion, M_w and PDI

Sample	AM (mmol)	Oxidant (mmol)	CTA (mmol)	Conversion (%)	M_n (10^3)	M_w (10^3)	PDI	M_{th}	α	DB
S1 ^a	8.00	0.15	–	66	4.55	9.10	2.1	–	0.75	0
S2 ^a	3.00	0.50	–	83	1.39	3.05	2.2	–	0.74	0
S3 ^b	8.00	0.15	–	85	3.72	8.92	2.4	–	0.66	3%
S4 ^b	3.00	0.50	–	88	1.95	4.10	2.1	–	0.61	5%
S5 ^c	3.00	0.50	0.60	55	0.028	0.048	1.7	495	0.52	10%
S6 ^c	3.00	1.00	1.20	52	0.014	0.021	1.5	424	0.45	18%
S7 ^d	2.00	0.20	0.40	52	0.050	0.110	2.2	585	0.48	11%
S8 ^d	2.00	0.40	0.40	78	0.079	0.174	2.2	686	0.46	18%
S9 ^d	2.00	0.80	0.40	84	0.241	0.602	2.5	–	0.39	35%
S10 ^d	2.00	1.20	0.40	85	0.284	0.769	2.7	–	0.30	48%

^a Cu(III), AM, Temperature = 45 °C, Time = 3 h; ^b Ce(IV), AM, Temperature = 45 °C, Time = 3 h;

^c Ce(IV), AM, BDAAT, Temperature = 80 °C, Time = 5 h; ^d Ce(IV), NHAM, BDAAT, Temperature = 80 °C, Time = 5 h

When the BDAAT was introduced (S5, S6), conversion, M_w and PDI all decreased significantly compared with S3 and S4, since the propagating radicals could be quickly converted to dormant species, which led to the decrease in propagating rate. However, the measured M_n of S5 or S6 far exceeded the molecular weight theoretically calculated (M_{th}) according to the reported equation for linear polymers^[19]. Because the reducing groups of macromolecules can be initiated repeatedly, the large gap between the M_n and M_{th} was expected. On the other hand, this phenomenon confirmed that branched polymers were formed. Furthermore, the α value and DB proved that polymers were in the characteristics of branched state, and the variation trends of α value and DB were also consistent with our purpose.

Increasing the reactivity of the reducing groups might further improve the initiation rate. With the oxidizing agent remaining the same, *N*-hydroxymethyl acrylamide was selected as the monomer. It turned out that the conversion, M_w and PDI of S7, S8, S9 and S10 all increased significantly compared with S5 and S6. The same phenomenon that M_n was far larger than linear M_{th} was observed again, which is the characteristics of branched state. Along with the addition of oxidant, the variation trends of α and DB were similar to the results of AM. The α value of the hyperbranched polymer reached 0.30 and the DB reached 48%, which suggested a more compact hyperbranched structure of the products.

The plots of $\lg[\eta]$ versus $\lg M_w$ of the hyperbranched polyacrylamide and poly(*N*-hydroxymethyl acrylamide) are shown as Fig. 7 and Fig. 8. After the plot was linearly fitted, α value could be obtained as listed in the Table 1. The variation of the α value reflected the trend of their degree of branching of the polymers. In addition, for S2, S3, S4, the part of high molecular weight with lower slope led to the conclusion that long branched chains were formed. Due to the large propagating rate of free radicals, the long branched chains would be formed right after the generation of the free radicals by the redox reaction. On the other hand, for samples S5 and S6, the slope of the part of low molecular weight was lower than the part of high molecular weight. As the BDAAT was introduced to the system, propagating radicals were quickly converted to the dormant species, therefore the polymerization rate was controlled and it is evitable for the scale of branched chains to be reduced. Figure 8 clearly shows the plot of $\lg[\eta]$ versus $\lg M_w$ of S8, S9 and S10 and the minimum α value could reach 0.30. These results definitively proved that a hyperbranched structure was successfully formed during redox/RAFT/SCVP.

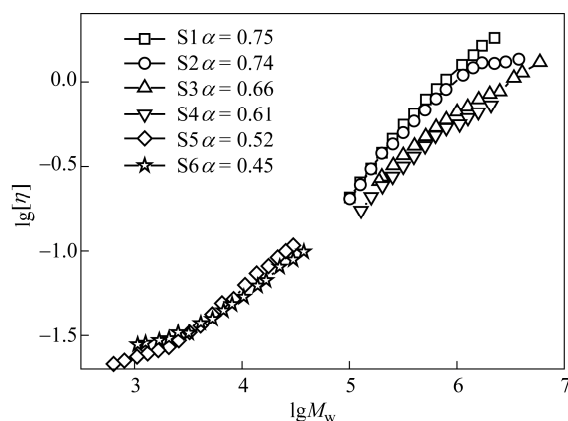


Fig. 7 Mark-Houwink plot of branched PAM

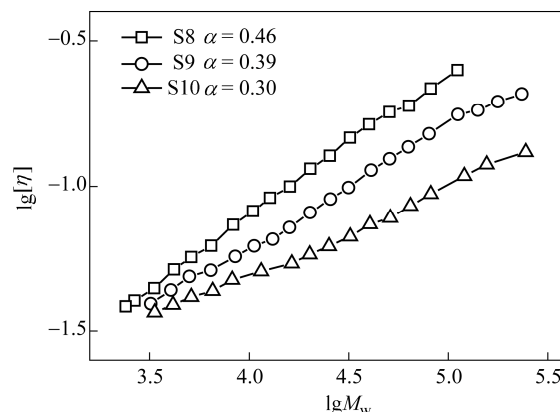
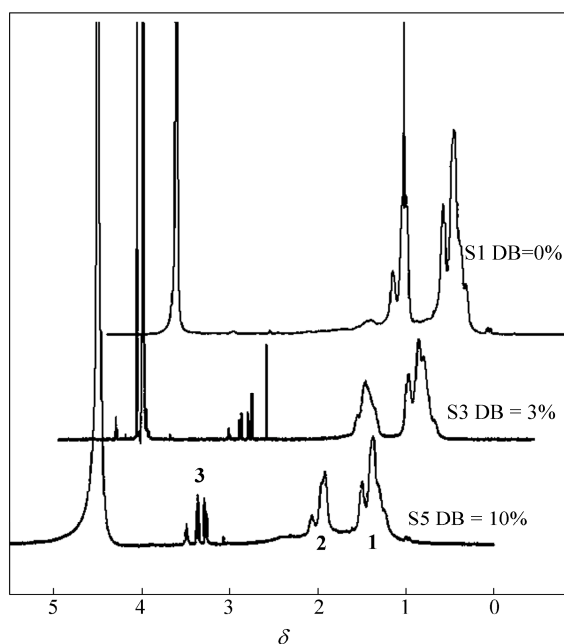
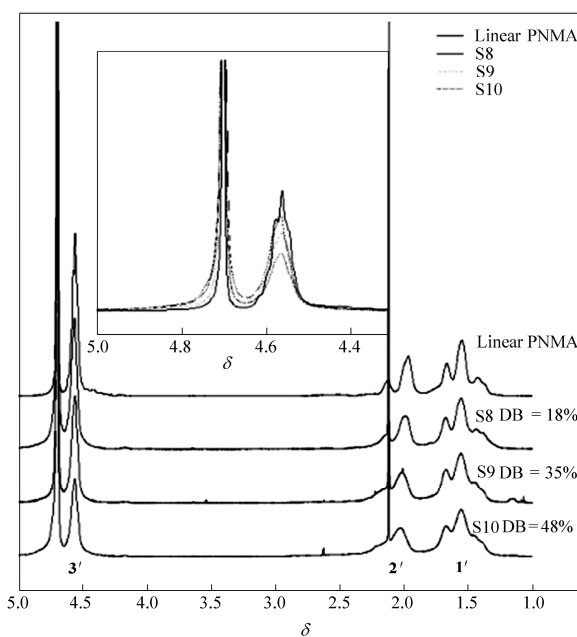


Fig. 8 Mark-Houwink plot of hyperbranched PNHAM

The structural information including the DB was also obtained from the ^1H -NMR spectra. Figures 9 and 10 show the ^1H -NMR spectra of PAM and PNHAM. According to the calculation equation, the DB of S3 is 3% and the DB of S5 is 10%. For PNHAM, the DB of S8, S9 and S10 were determined to be 18%, 35% and 48%, respectively. The result from analyzing ^1H -NMR spectra is consistent with the result of SEC.

Fig. 9 ^1H -NMR spectrum of branched PAMFig. 10 ^1H -NMR spectrum of hyperbranched PNHAM

CONCLUSIONS

In summary, a new method for synthesizing hyperbranched polyacrylamides was presented using the monomer having a reductive group as the starting material through redox/RAFT/SCVP in the presence of Cu(III) and Ce(IV). The ^1H -NMR spectra and MDSEC analysis confirmed the formation of hyperbranched polymers. The increase of initiator concentration and active rate constant effects did not enhance the degree of branching. In addition, the propagation rate was suppressed when the BDAAT was introduced, and the gap between initiation and propagation rates decreased significantly.

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