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Synthesis of hyperbranched polymethacrylates in the presence of a tetrafunctional initiator

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Abstract

A series of hyperbranched polymers were synthesized in high yield by self-condensing vinyl polymerization (SCVP) of 2-[(2-bromobutyryl)oxy]ethyl methacrylate (BBEM) in the presence of an ATRP initiator: THABP (a tetrafunctional initiator)/CuBr/bpy. The structure and properties of the polymers obtained were characterized by NMR and SEC/RALLS/DV/RI. The effect of the tetrafunctional initiator on degree of branching (DB), molecular weight and molecular weight distribution of polymers was studied. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched polymers; Tetrafunctional initiator; Self-condensing vinyl polymerization

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1. Introduction

Highly branched polymers, such as dendrimers and hyperbranched polymers have received great attention in recent years [1,2], because they have a special structure, large number of terminal groups and physical properties different from their linear analogs, such as high solubility and low melt viscosity. They can be potentially used as macroinitiators [3] and cross-linking agents [4] in coating materials.

Dendrimers are monodisperse molecules with well-defined and perfectly branched structure. But they are prepared by multiple steps, isolations and purifications are generally required. The tedious syntheses of dendrimers preclude their industrial applications on a large scale.

Hyperbranched polymers are less regular than dendrimers, but they show properties similar to dendrimers [5], and they can be prepared by one-step polymerization, so hyperbranched polymers are considered to be alternatives to dendrimers for practical use.

The first hyperbranched polymer was prepared by Kim and Webster [6] in 1988. Since then, various hyperbranched polymers have been synthesized, e.g. hyperbranched polyphenylenes [7], polyethers [8], polyesters [9], poly(ether ketones) [5] and polyurethanes [10]. Two main methods have been used to synthesize hyperbranched polymers. The most common method proposed by Flory [11] is self-condensation polymerization of AB_n ($n \geq 2$) type monomers. The second method described recently by Fréchet et al. [12] is called self-condensing vinyl polymerization (SCVP), using a vinyl monomer AB^*, in which A is a double bond, B^* is an initiation group. When B^* initiates A to polymerize, a new propagating center A^* is formed (see Scheme 1). Both A^* and B^* can reinitiate the polymerization of A with rate constants k_A and k_B, respectively. Successive additions of monomers produce branched polymers. 'Living' polymerization techniques, such as group transfer polymerization [13], nitroxide mediated radical polymerization [14], cationic polymerization [11,15] and atom transfer radical polymerization (ATRP) [16–19] have been applied to the syntheses of hyperbranched polymers by SCVP.

The main drawback of hyperbranched polymers is their broad molecular weight distributions (MWDs) [12]. Müller et al. [20] suggested that by adding a small amount of multifunctional initiator into the reaction system, the MWD of hyperbranched polymers could become narrower. Yan et al. [21] gave theoretical prediction of hyperbranched polymers produced by SCVP in the presence of a multifunctional initiator. A few reports about the effect of multi-functional initiator on MWD and DB of hyperbranched polymers prepared by self-condensation polymerization of AB_n type monomers have been published [22,23], but little experimental result in SCVP has been reported.

In our experiment, we synthesized hyperbranched polymers by ATRP in the presence of a tetrafunctional initiator

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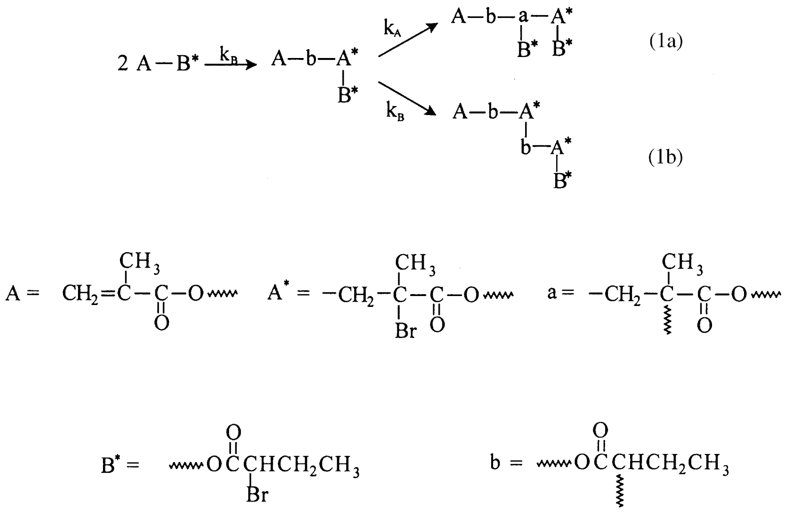


Scheme 1.

(THABP) and studied the effect of THABP on DB, molecular weight (MW) and MWD of the polymers obtained.

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA) was distilled under reduced pressure. Methylene chloride was dried with calcium hydride and distilled before use. Triethylamine was dried with potassium hydroxide and distilled. Copper (I) bromide was stirred in glacial acetic acid, washed with ethanol, then dried under vacuum. All other chemicals were used as received.

2.2. Synthesis of 2-((α-bromobutyryl)oxy)ethyl methacrylate (BBEM)

HEMA (6.3 g, 0.04 mol), CH_2Cl_2 (50 ml), triethylamine (4.45 g, 0.044 mol) were added into a 150 ml three-neck flask equipped with a magnetic stirrer. A solution of 2-bromobutyryl chloride (8.2 g, 0.044 mol) in 10 ml CH_2Cl_2 was added dropwise into the flask in an ice-bath under nitrogen while stirring. After complete addition, the reaction mixture was stirred at room temperature for additional 4 h. The precipitate formed was filtered off. When CH_2Cl_2 in filtrate was evaporated, additional precipitate and a yellow oil were obtained. The precipitate was filtered off, and then washed with CH_2Cl_2. The oil and CH_2Cl_2 wash were combined and washed with water five times (20 ml each), then dried over anhydrous magnesium sulfate overnight. The crude product was obtained by evaporation of CH_2Cl_2, and then purified by passing the residue through silica gel column, 6.2 g of pure BBEM was obtained in 56% of yield.

^{1}H NMR ($CDCl_3$) δ: 1.04 (t, 3H, –C–CH_3), 1.89 (s, 3H, =C–CH_3), 2.02 (m, 2H, –CH_2–C–), 4.09 (t, 1H, –CH(Br)–), 4.30 (m, 4H, –OCH_2CH_2O–), 5.50, 6.12 (m, CH_2=C–).

2.3. Synthesis of tetrafunctional initiator

6,6-Bis(5-hydroxyl-2-oxapentyl)-4,8-dioxaundecanediol-1,11(THA) $C(CH_2OCH_2CH_2CH_2OH)_4$ was prepared according to the method described in Ref. [24]. Tetrafunctional initiator $C(CH_2OCH_2CH_2CH_2OCOCH(Br)CH_3)_4$ (THABP) was prepared by the reaction of THA with α-bromopropionyl chloride in quantitative yield.

^{1}H NMR ($CDCl_3$) δ: 1.83 (d, 12H, 4-CH_3), 1.91 (m, 8H,

Table 1
Conditions and results of the polymerization of BBEM (conditions: BBEM, 3.58 mmol; CuBr, 0.0358 mmol; bpy, 0.122 mmol; temperature, 100°C; time, 12 h)

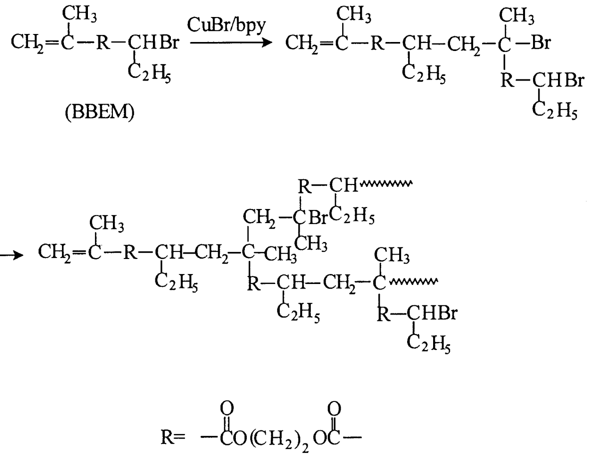
No.	THABP (mmol)	Yield (%)	$M_n{}^a \times 10^{-4}$	$M_w{}^a \times 10^{-4}$	$M_w/M_n{}^a$	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$	b (%)^c	B^*/A^{*d}
H1	0	93	10.7	30.8	2.88	2.65	3.91	26	2.86
H2	0.031	94	17.8	55.4	3.11	2.58	5.69	28	2.80
H3	0.066	94	18.3	76.9	4.21	3.26	5.39	31	2.22
H4	0.127	93	27.3	71.9	2.63	4.73	2.16	36	1.79

[a] Measured by SEC^3.

[b] Measured by SEC/RI.

[c] Molar percentage of branch unit to total BBEM units in the polymer.

[d] Molar ratio of active sites B^* and A^*.



Scheme 2.

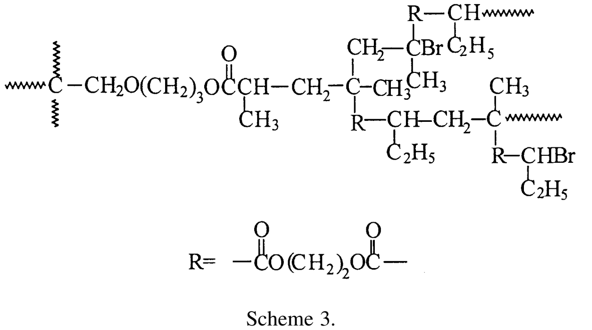
4-C–CH_2–C–), 3.36 (s, 8H, 4-C–CH_2–O–), 3.47 (t, 8H, 4-O–CH_2–), 4.26 (t, 8H, 4-CH_2–OCO–), 4.36 (q, 4H, 4-CH(Br)–).

2.4. Polymerization

Monomer, Cu(I)Br, bipyridine (bpy), THABP were added into a polymerization tube. Feed ratios are listed in Table 1. The mixture in the tube was degassed by three freeze-evacuate-thaw cycles, then the tube was sealed under vacuum, and placed in an oil bath kept at 100°C for 12 h while stirring. The reaction mixture was then dissolved in tetrahydrofuran (THF). The precipitate was obtained by pouring the solution into excess methanol. The polymer was filtered off and dried under vacuum at 30°C.

2.5. Characterization

^{1}H NMR spectra were measured on a Bruker DMX-500 NMR instrument with $CDCl_3$ as solvent and tetramethylsilane as standard. Size exclusion chromatography (SEC^3) measurements were as follows: A dual SEC detector (Model T60, Viscotek), with right angle laser light scattering (RALLS) and differential viscometer (DV) detectors in series, was combined on-line with a differential refractometer (RI, Model 410, Waters) coupled to a programmable HPLC pump (Model 590, Waters). Two chromatographic columns (American Polymer Standards, Mentor, OH), measuring 30 cm in length and packed with 5 μm diameter PS gel, were used in series. THF was degassed ultrasonically and used as the mobile phase at a flow rate of 1.0 ml/min. The samples were dissolved in THF and filtered through 0.2 μm pore size membrane filters. Measurements were performed at 25°C, and injection volumes of the sample solutions were 100 μl. TriSEC software (Viscotek) was used to treat the data obtained. The setup of the SEC^3 system was described in our previous paper [25].



Scheme 3.

3. Results and discussion

3.1. Structures of polymers

Polymerizations of BBEM with or without the tetrafunctional initiator, THABP, were carried out in bulk using CuBr and bpy as catalyst and ligand. The conditions and results of the polymerizations are listed in Table 1. High yields of the soluble polymers (>93%) were obtained in 12 h.

In order to study the effects of tetrafunctional initiator on MW, MWD and structures of the polymers obtained, the polymerizations at various molar ratios of BBEM/THABP were performed. The structures of the hyperbranched polymers prepared by polymerization of BBEM without and with THABP are shown in Schemes 2 and 3, respectively.

Fig. 1 shows the ^{1}H NMR spectra of the samples. In spite of the complicated structures, based on ^{1}H NMR data of BBEM, THABP and poly(methyl methacrylate) (PMMA) prepared by the polymerization of MMA using ethyl α-bromobutyrate/CuBr/bpy as initiation system [26], we can divide the signals in Fig. 1 into five regions. Take H2 in Fig. 1 as an example, Region 1: the signals from 5.5 to 6.2 ppm correspond to the protons of the double bond at one end of the hyperbranched polymers obtained. Region 2: the signals from 4.0 to 4.6 ppm are ascribed to the ethylene group of BBEM unit, the methine proton next to bromine at the end of the polymer chain, and methylene protons adjacent ester oxygen of THABP units. Region 3: the signals at 3.36 and 3.47 ppm are representative of two methylene groups linked to ether oxygen of THABP unit, the former is next to quaternary carbon. Region 4: signals from $\delta = 1.6$ to 2.7 ppm belong to methine and methylene protons of BBEM units in the backbone of polymer, methyl and methylene protons of BBEM unit at the end of polymer chain, and methylene protons in the middle of trimethylene of THABP unit. Region 5: signals from 0.6 to 1.6 ppm correspond to methyl group in butyrate and in polymer backbone. The small peaks in Regions 4 and 5 are attributed to the main chain stereo-isomerism (see Table 2).

Comparison with the amount of BBEM units in the polymer, methyl group on the double bond and THABP unit in the polymers obtained could be neglected, this will lead to less than 1% of error. The integral value of each proton of ethylene group in BBEM unit should be equal to that of

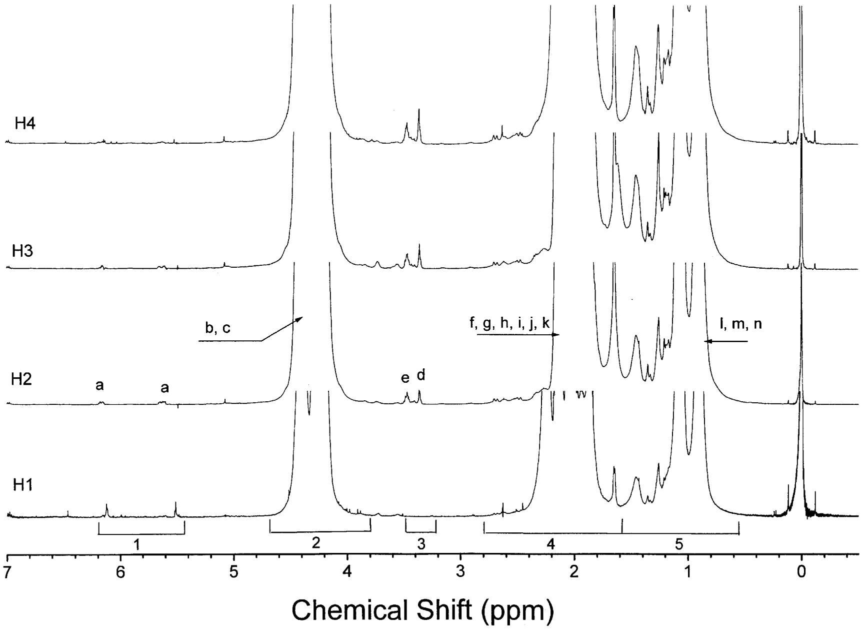
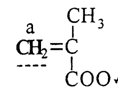
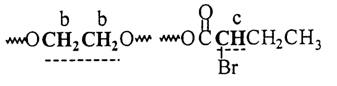
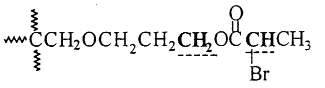
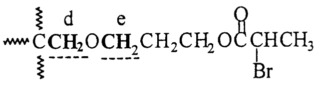
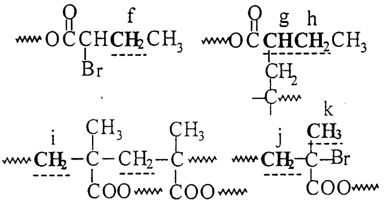
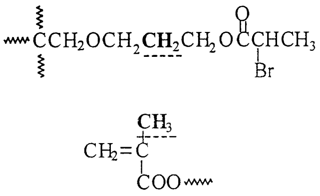
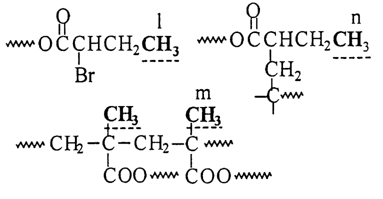
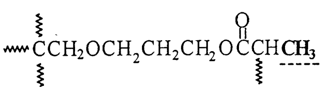


Fig. 1. ^{1}H NMR spectra of homopolymer of BBEM (H1) and hyperbranched polymers prepared in the presence of 0.031 (H2), 0.066 (H3) and 0.127 mmol (H4) of THABP. (The composition and conditions of the polymerizations are the same as those listed in Table 1.)

Table 2
Assignment of structures to the corresponding regions of the ^{1}H NMR spectra in Fig. 1[a]

Region	Structure	
	Major	Minor
1	 $\overset{a}{\underline{CH_2}}=C(CH_3)COO\sim$	
2	 $\sim O\overset{b}{\underline{CH_2}}\overset{b}{\underline{CH_2}}O\sim$ $\sim OC(=O)\overset{c}{\underline{CH}}(Br)CH_2CH_3$	 $\sim C(\sim)(\sim)CH_2OCH_2CH_2\underline{CH_2}OC(=O)\underline{CH}(Br)CH_3$
3	 $\sim C(\sim)(\sim)\overset{d}{\underline{CH_2}}O\overset{e}{\underline{CH_2}}CH_2CH_2OC(=O)CHCH_3(Br)$	
4	 $\sim OC(=O)CH(Br)\overset{f}{\underline{CH_2}}CH_3$ $\sim OC(=O)\overset{g}{\underline{CH}}(CH_2-C\sim)\overset{h}{\underline{CH_2}}CH_3$ $\sim\overset{i}{\underline{CH_2}}-C(CH_3)(COO\sim)-\underline{CH_2}-C(CH_3)(COO\sim)\sim$ $\sim\overset{j}{\underline{CH_2}}-C(\overset{k}{\underline{CH_3}})(COO\sim)-Br$	 $\sim C(\sim)(\sim)CH_2OCH_2\underline{CH_2}CH_2OC(=O)CH(Br)CH_3$ $CH_2=C(\underline{CH_3})COO\sim$
5	 $\sim OC(=O)CH(Br)CH_2\overset{l}{\underline{CH_3}}$ $\sim OC(=O)CH(CH_2-C\sim)CH_2\overset{n}{\underline{CH_3}}$ $\sim CH_2-C(\overset{m}{\underline{CH_3}})(COO\sim)-CH_2-C(\underline{CH_3})(COO\sim)\sim$	 $\sim C(\sim)(\sim)CH_2OCH_2CH_2CH_2OC(=O)CH(\sim)\underline{CH_3}$

[a] Major means the major part of structure in this region. Minor means the minor part of structure that could be neglected in calculation in this region.

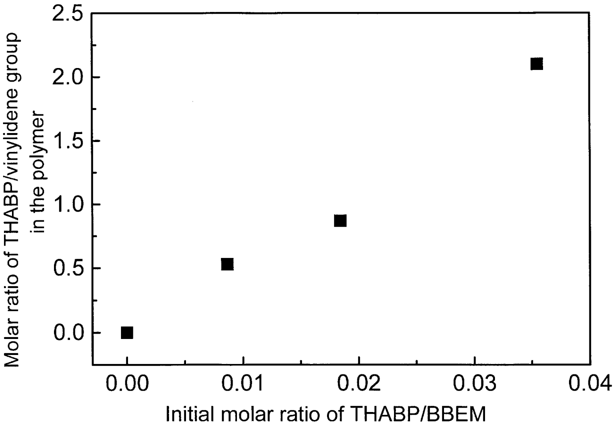


Fig. 2. Influence of the initial ratio of THABP/BBEM on the molar ratio of THABP unit/vinylidene group in hyperbranched polymer. (The composition and conditions are the same as those listed in Table 1.)

other groups in BBEM. Therefore, the integral value of methine proton next to bromine at the end of polymer chain, x, can be calculated according to Eq. (1):

$$x = \frac{11I_2 - 4(I_4 + I_5)}{15} \tag{1}$$

where I_2, I_4 and I_5 are relative integral values of the peaks at Regions 2, 4 and 5, respectively. When secondary bromine of BBEM participates in initiation reaction, branch point is formed. Thus, the percentage (b) of branch points to total BBEM units in the polymer, that is, the percentage of methine of branched units to total methine of BBEM units, can be estimated by Eq. (2).

$$b = \frac{I_2 - 5x}{I_2 - x} \times 100\% \tag{2}$$

The results calculated are listed in Table 1. If the polymer was perfectly dendritic, $b = 50\%$. If the polymer is linear, $b = 0$. The results listed in Table 1 show that b values are between 26 and 36%, indicating that these polymers are not perfect dendrimer, which is resulted from the different reactivities of A^* and B^*. In the present case, A^* and B^* are tertiary and secondary bromide, respectively, thus A^* is more active than B^* [27], that is, $k_A > k_B$ (see Scheme 1). The initiation of A by A^* resulted in increase of one B^* on a new polymer chain (see reaction (1a)). Thus

Table 3
Characterization data of PS and hyperbranched polymers via SEC/RI/RALLS/DV

Sample	Retention volume (ml)	$M_p{}^a \times 10^{-4}$	$[\eta]_p{}^a$ (dl/g)	$R_{gp}{}^a$ (nm)
PS-C	14.91	4.90	0.275	8.07
H1	14.95	14.46	0.114	8.35
H2	15.00	21.63	0.116	9.59
H3	14.91	21.65	0.106	9.32
H4	15.04	30.22	0.089	9.83

[a] The subscript p means that the data are at peak position.

$$\frac{d[B^*]}{dt} = k_A[A][A^*] \tag{3}$$

When A is initiated by B^*, one active site A^* increased on the polymer chain newly formed and branch point is formed (see reaction (1b)).

$$\frac{d[A^*]}{dt} = k_B[A][B^*] \tag{4}$$

The molar percentage of B^* to the total active species is equal to that of methine group next to bromine standing at the end of polymer chain to the total BBEM units in the polymer, thus

$$B^* = \frac{4x}{I_2 - x} \times 100\% \tag{5}$$

As already discussed, a branch point is the result of A initiated by B^*, the molar percentage of A^* to the total BBEM units equals to b. Therefore, the ratio of B^*/A^* can be calculated based on the values of b and B^*.

$$\frac{B^*}{A^*} = \frac{4x}{I_2 - 5x} \tag{6}$$

When A^* and B^* have the same reactivity, $B^*/A^* = 1$. The values of B^*/A^* listed in Table 1 demonstrate that A^* has higher reactivity than B^* does, and the values of B^*/A^* decreased as the increase of THABP used, which was the result of the increase of secondary bromide initiating rate as the increase of its concentration.

In our experiment, the tetrafunctional initiator and monomer are mixed together before polymerization (batch polymerization). Fig. 2 shows that the ratio of THABP to vinylidene group in polymer increased with the increase of the initial ratio of THABP to monomer ($[THABP]_0/[M]_0$). The possible explanation is: at low ratio of THABP/BBEM, since the amount of THABP is much smaller than that of monomer, the monomer molecules have more chances to react each other than reacted with THABP. As a result, the polymers without core are predominant. When the ratio of THABP/BBEM is higher, the incorporation of monomer and vinylidene-terminated macromolecules with THABP or polymer with THABP as core becomes statistically more frequent, resulting in higher content of THABP in the polymer.

3.2. Molecular weight and molecular weight distribution

The data of PS standard sample and hyperbranched polymers characterized via SEC/RI/RALLS/DV are shown in Tables 1 and 3. The MWs obtained via conventional SEC/RI are all less than those obtained via SEC^3 as indicated in Table 1. The former values were calibrated by PS standard samples and there exists the difference in solution behavior between PS samples and the hyperbranched polymers, therefore, we only obtained relative MWs with this

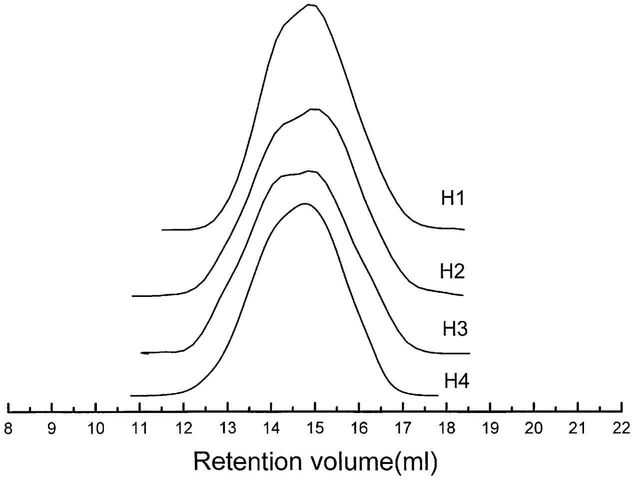


Fig. 3. SEC/RI curves of hyperbranched polymers H1, H2, H3 and H4 (see Table 1).

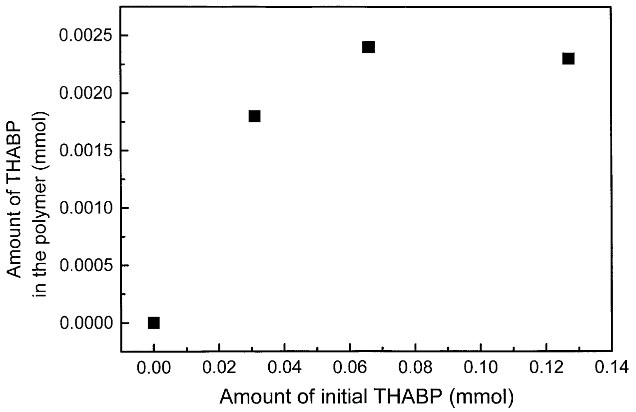


Fig. 4. The effect of the initial amount of THABP on the amount of THABP in the hyperbranched polymer obtained. (The composition and conditions of the polymerizations are the same as those listed in Table 1.)

technique. The compact architecture of hyperbranched polymers leads to a retention volume larger than that of PS with the same MW, and the MW M_p larger than that of PS sample with the same retention volume as inferred from Table 3. Those results further support the fact that these polymers have branched structure.

Theoretical and experimental studies [13,28] show that hyperbranched polymers obtained via SCVP have broad MWDs. The reason is that each growing chain can couple with another chain, the rate of which is proportional to the number of its functional groups. Müller et al. [17] suggested that the polydispersity can be decreased by adding multifunctional initiator, G_f, into the reaction system to prevent coupling of the growing chains. If monomer molecules are added slowly enough to the initiator solution so they can only react with G_f, or the already formed macromolecules, but cannot react each other, the polydispersity index (P_w/P_n) decreases with the increase of f: $P_w/P_n \approx 1 + 1/f$. If initiator and monomer are mixed together (batch process), $P_w/P_n \approx 1 + P_n/f^2$.

Batch process was used in our study. The polymer without a THABP unit (P_0) and polymer with a THABP unit: one-armed (P_1), two-armed (P_2), three-armed (P_3), four-armed (P_4) polymers would be formed.

The SEC/RI curves of the hyperbranched polymers obtained are shown in Fig. 3. For polymers H2 and H3, two peaks could be clearly seen. As the initial concentration of THABP increased, the curves approached symmetry, indicating that the MWD of macromolecules tends to homogeneity. At low ratio of THABP/BBEM, large amount of the hyperbranched polymer chains were not connected to THABP. THABP initiated mainly vinylidene-terminated hyperbranched polymer chain except that growing chains reacted each other and with the monomer during the polymerization. The macromolecules with a THABP unit grew to form high MW polymer comparison with the polymer obtained from homopolymerization of BBEM. As a result, higher polydispersity indices of the polymers H2 and H3, even higher than that of the polymer H1 were obtained (see Table 1 and Fig. 3). When much THABP (such as the molar ratio of $[\text{THABP}]_0/[\text{BBEM}]_0 = 1/28$) was added into the polymerization system, the reaction of growing chains each other will be prevented by addition of THABP to the terminal vinylidene groups of preformed polymer chains. Therefore, M_w/M_n decreased. Based on initial amount of BBEM ($[\text{BBEM}]_0$), yield (y), and DP obtained via SEC[3], the number of hyperbranched macromolecules produced (N_p) can be calculated by Eq. (7).

$$N_p = \frac{[\text{BBEM}]_0 \times y}{\overline{\text{DP}}} \tag{7}$$

Among the N_p macromolecules, some of them have THABP as their core, the others end with vinylidene group. The molar ratio of the polymer capped with THABP to that with the ending vinylidene group (P_{GV}) can be estimated based on integral values of the peaks at $\delta = 3.36$ ($I_{3.36}$) and $\delta = 5.5$–6.2 ppm ($I_{6.0}$).

$$P_{GV} = \frac{I_{3.36}}{4I_{6.0}} \tag{8}$$

The results listed in Table 1 show that M_n increased with the increasing ratio of $[\text{THABP}]_0/[\text{BBEM}]_0$. As already discussed, the effect of THABP on M_n becomes significant only when the ratio of THABP to monomer is high enough. The higher the ratio of $[\text{THABP}]_0/[\text{BBEM}]_0$, the higher the proportion of THABP-core polymer, so the MW of the polymer obtained from higher ratio of $[\text{THABP}]_0/[\text{BBEM}]_0$ is also larger (see Table 1 and Fig. 2).

The molar amount of hyperbranched polymer with THABP unit as core can be calculated from the N_p and P_{GV}.

$$P_{\text{THABP}} = N_p \frac{P_{GV}}{P_{GV} + 1} \tag{9}$$

The results in Fig. 4 demonstrate that as initial amount of

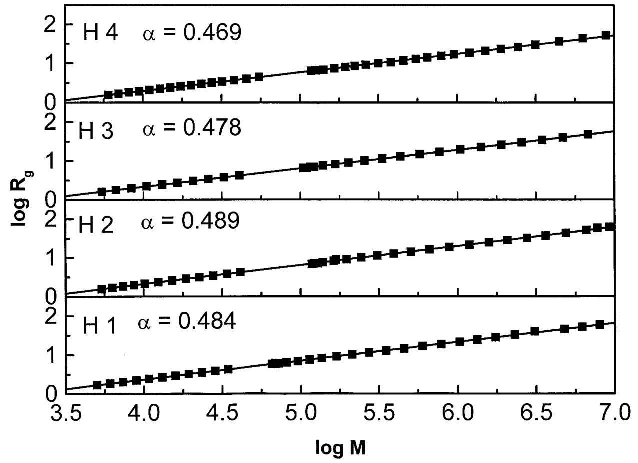


Fig. 5. Exponential α values of the hyperbranched polymer H1, H2, H3 and H4 (see Table 1).

THABP increased, the amount of THABP in the polymer increased, then was leveled off. It is interesting to note that the amount of THABP in the polymer is only less than 6.1% of initial THABP added. The possible reason is that once hyperbranched polymer with THABP unit is formed, its degree of polymerization increased very fast because of large amount of active sites A^* and B^* in this hyperbranched macromolecule. The possibility of THABP initiating monomer to polymerize becomes very low. Therefore, most of THABP did not participated the initiation reaction.

3.3. Characterization of branching

The data listed in Table 3 shows that the retention volumes of H1–H4 samples are equal to or larger than that of PS-C sample (14.91 ml) and that the intrinsic viscosity ($[\eta]_p$) of the former samples are much less than that of PS standard, while the MWs (M_p) of the hyperbranched polymers are all several times larger than that of PS-C standard sample. This indicates that hyperbranched polymers display more compact molecular architecture than linear PS standards. The higher the degree of branching (DB) of a polymer is, the greater the size reduction will be. The value of M_p for H4 sample is the highest in the hyperbranched polymers prepared, while its $[\eta]_p$ value is the smallest, indicating H4 sample has the highest DB. The value of M_p for H3 sample is slightly larger than that of H2 sample, while $[\eta]_p$ of the former polymer are less than that of the latter one, indicating that H3 sample has more branched structure than that of H2. H1 has similar $[\eta]_p$ as H2, while the M_p of H1 is smaller than that of H2, so H1 has the lowest DB.

The DB of the samples increases slightly with the increasing ratio of $[\text{THABP}]_0/[\text{BBEM}]_0$, which is consistent with the results obtained from ^{1}H NMR data (see Table 1). The possible explanation is: DB of the polymer obtained is lower than that of polymer prepared from monomer with $k_A = k_B$, because the higher reactivity of A^* than that of B^* ($k_A > k_B$) will reduce DB of the polymer. The rate constant k_G of the tetrafunctional initiator is similar to k_B, as the ratio of $[\text{THABP}]_0/[\text{BBEM}]_0$ increased, higher concentration of B^* in BBEM/THABP system enhanced the possibility of B^* to initiate A, resulting in higher DB (see Table 1). All the results show that we can check the reasonability of the synthetic methods for the hyperbranched polymers via SEC^3 technique.

The information concerning conformation of polymer chain can be inferred from the exponential α values obtained from the plot of $\log R_g$ vs. $\log M$. According to Ref. [29], a value of 0.5–0.6 corresponds to the linear polymer chain in random coil, a value of less than 0.5 indicates the presence of branched molecular architecture, a value of 1 means the presence of rod-like polymer chain and a value of 0.33 stands for the presence of sphere structure. We concluded that the samples obtained are all branched polymers from the data shown in Fig. 5. The exponential α of samples has the following order: H4 $<$ H3 $<$ H2 $\approx$ H1. The order of DB is opposite to this order. All these results further support the fact derived qualitatively from Table 3, and are consistent with the results obtained via NMR data (see Table 1).

4. Conclusion

Hyperbranched polymers could be prepared by ATRP of BBEM using CuBr/bpy as catalyst and ligand, respectively. The addition of tetrafunctional initiator, THABP can decrease the polydispersity index only at high molar ratio of $[\text{THABP}]_0/[\text{BBEM}]_0$. When this ratio was lower than 1/55, M_w/M_n was increased, even higher than that of the polymer prepared from homopolymerization of BBEM. The formation of hyperbranched polymer with a THABP core increases greatly the possibility of its reaction with vinylidene group. It was found that only less than 7% of initial THABP participated the polymerization. The amount of THABP unit in the polymer increased, then leveled off as the increase of initial molar ratio of THABP/BBEM. For BBEM, active site A^* has higher activity than B^* does, and only initiation of A by B^* produces branch point, thus the contents of branch points to the total BBEM units in the polymers are 26–36%. As the initial molar ratio of THABP/BBEM increased, the concentration of B^* increased comparison with the concentration of A group. The degree of branching has the following order: H4 $>$ H3 $>$ H2 $\approx$ H1, while the order of the intrinsic viscosity ($[\eta]_p$) is opposite.

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