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Synthesis and characterization of hyperbranched polyacrylates in the presence of a tetrafunctional initiator with higher reactivity than monomer by self-condensing vinyl polymerization

Chun-Yan Hong, Cai-Yuan Pan*

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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Abstract

A series of hyperbranched polyacrylates were synthesized by self-condensing vinyl polymerization (SCVP) of 2-[(2-bromobutyryl)oxy]-ethyl acrylate (BBEA). A tetrafunctional atom transfer radical polymerization (ATRP) initiator (THABI) capped with bromoisobutyrate, which has higher reactivity than the initiating site of monomer, was used as core-forming molecules. The structure and properties of the obtained polymers were characterized by NMR and SEC/RALLS/DV/RI. The effect of the tetrafunctional initiator on 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

1. Introduction

Recently, there has been increasing interest in dendritic polymers, i.e. dendrimers and hyperbranched polymers [1–3]. These two kinds of macromolecules have some similarities, for example, both of them have branched structures, large number of functional groups and globular shape; they show higher solubility and lower melt viscosity compared to their linear analogues [4].

Nevertheless, there are also many differences between dendrimers and hyperbranched polymers. Dendrimers are monodisperse and perfectly branched, the terminal groups are located on the surface of molecule. They are synthesized by multi-step reactions requiring time-consuming purification, which generally precludes their commercial development. Hyperbranched polymers have less regular structure, broad molecular weight distribution, and the functional groups are distributed throughout the molecule. One of the common methods of preparation of hyperbranched polymers is polycondensation of AB_m-type monomers [5]. Ring-opening polymerizations have also been used for synthesizing hyperbranched polymers [6–9].

Another method to prepare hyperbranched polymers is self-condensing vinyl polymerization (SCVP) developed by Fréchet et al. [10]. This approach involves a monomer of AB^* type, where A is a vinyl group and B^* is an initiation group capable of initiating the polymerization of vinyl monomers. When initiation occurs by addition of B^* group to a double bond of another monomer, a dimer with two initiating sites, A^* and B^*, and one double bond was formed. Both B^* and A^* can initiate the vinyl group of another molecule in the same way with rate constants k_B and k_A, respectively (see Scheme 1). Repeating this reaction affords a hyperbranched polymer. SCVP has been applied to various types of living polymerization, such as living cationic polymerization [10], group transfer polymerization [11], nitroxide-mediated polymerization [12] and atom transfer radical polymerization (ATRP) [13–15].

Since hyperbranched polymers are easier to be produced, they are more attractive than dendrimers for application on a large scale. Major drawbacks of hyperbranched polymers are the lack of controlling molecular weight and broad molecular weight distribution. Recently, theoretical work by Müller et al. [16] and Yan et al. [17,18] as well as computer simulation work by Frey et al. [19] have shown that the introduction of multifunctional initiator into the hyperbranched polymerization system can narrow the molecular weight distribution.

Hult et al. [20] reported the synthesis of hyperbranched aliphatic polyesters by polycondensation of 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) as core-forming molecule. Successive addition of the monomer led to

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* Corresponding author. Fax: +86-551-3631760.
E-mail address: pcy@ustc.edu.cn (C.-Y. Pan).

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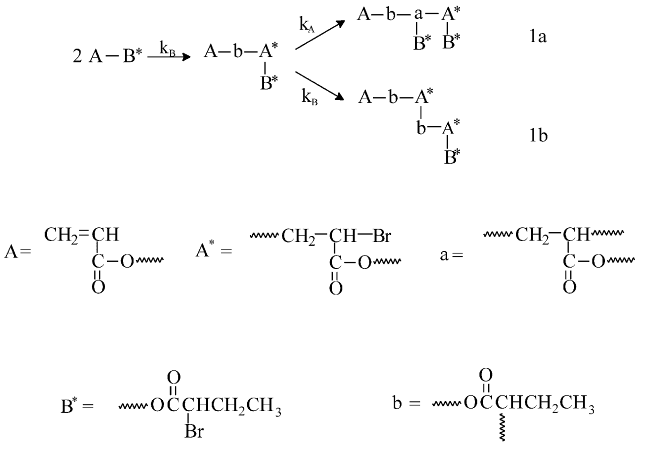


Scheme 1.

hyperbranched polyesters with polydispersity below two and degree of branching >80%. Frey et al. [21] reported the preparation of hyperbranched polyglycerols by ring-opening polymerization, using partially deprotonated TMP as core initiator under slow addition of monomer. The M_n of the polymers was in the range of 1250–6500, polydispersities ranged from 1.13 to 1.47. Recently, Moore et al. [22] synthesized hyperbranched phenylacetylene polymers by slow addition of AB_2 monomer 3,5-diiodophenylacetylene to a solution of a multifunctional core. The molecular weight ($M_w = 8$–90 kDa) was controlled by varying the monomer: core ratio and low polydispersity indexes were achieved.

Most of these efforts have been focused on polycondensation of AB_2 type monomer or ring-opening polymerization by slow monomer addition, but until now, little experimental study about the effect of multifunctional initiator on SCVP has been reported.

In a previous paper [23], we described hyperbranched polyesters prepared by 2-[(2-bromobutyryl)oxy]ethyl methacrylate (BBEM) in the presence of a tetrafunctional initiator THABP, the reactivity of THABP is similar to that of B^* in the monomer. In this paper, we synthesized hyperbranched polymers by ATRP in the presence of a tetrafunctional initiator with reactivity higher than that of monomer. To our knowledge, it is the first attempt to investigate the effect of different reactivities of multifunctional ATRP initiator and monomer on SCVP.

2. Experimental

2.1. Materials

Copper (I) bromide (AR, Shanghai Chemical Reagent Plant) was purified by stirring in glacial acetic acid, washing with ethanol, and then drying in vacuum oven at 70°C. 2,2′-Bipyridine(bpy) (Aldrich, 99%) was recrystallized from *n*-hexane. Methylene chloride was dried with calcium hydride and distilled before use. Triethylamine was dried with potassium hydroxide and distilled. 2-Hydroxylethyl α-bromobutyrate (HEBrB) and 6,6-bis(5-hydroxyl-2-oxapentyl)-4,8-dioxaundecanediol-1,11(THA) $C(CH_2OCH_2CH_2CH_2OH)_4$ were prepared according to Refs. [24,25].

For HEBrB: ^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 1.01 (t, 3H, $-CH_2CH_3$), 2.01 (m, 2H, $-CH_2CH_3$), 3.68 (t, 2H, $-OCH_2CH_2OH$), 4.09 (t, 1H, $-CH(Br)CH_2CH_3$), 4.26(t, 2H, $COOCH_2CH_2$).

For THA: ^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 1.82 (m, 8H, 4-$CH_2CH_2CH_2$–), 3.39 (s, 8H, 4-C–CH_2OCH_2), 3.56 (t, 8H, 4-O–CH_2), 3.73 (t, 8H, 4-CH_2OH).

All other chemicals were of analytical grade and were used as-received.

2.2. Synthesis of 2-((α-bromobutyryl)oxy)ethyl acrylate (BBEA)

To a 150 ml three-necked flask equipped with a magnetic stirrer, were added HEBrB (10.6 g, 0.05 mol), triethylamine (5.6 g, 0.055 mol), and CH_2Cl_2 (60 ml). After cooling to 0°C in an ice bath, a solution of 2-acryloyl chloride (5.0 g, 0.055 mol) in 10 ml CH_2Cl_2 was added dropwise for 1 h under nitrogen while stirring. The reaction mixture was then stirred at room temperature for additional 24 h. After removal of the precipitate formed during evaporation of CH_2Cl_2 by filtration, a yellow oil was obtained, washed with water five times (20 ml each) and dried over anhydrous magnesium sulfate overnight. The volatiles were evaporated under reduced pressure to afford a crude product. Pure BBEA (10.3 g, 78% yield) was obtained by passing a solution of crude product in CH_2Cl_2 through silica gel column.

^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 1.04 (t, 3H, –C–CH_3), 2.02 (m, 2H, –CH_2–C–), 4.09 (t, 1H, –CH(Br)–), 4.30 (s, 4H, –OCH_2CH_2O–), 5.88 (d, 1H, CH_2=CH–), 6.18 (dd, 1H, CH_2=CH–), 6.50 (d, 1H, CH_2=CH–).

2.3. Synthesis of tetrafunctional initiator, THABI

Tetrafunctional initiator $C[CH_2OCH_2CH_2CH_2OOCC(Br)-(CH_3)_2]_4$ (THABI) was prepared by the reaction of $C(CH_2OCH_2CH_2CH_2OH)_4$ with α-bromoisobutyryl chloride in quantitative yield according to the method described in Ref. [23].

^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 1.93 (m, 32H, 4-$CH_2CH_2CH_2$, 4-C(Br)$(CH_3)_2$), 3.38 (s, 8H, 4-C–CH_2OCH_2), 3.48 (t, 8H, 4-O–CH_2), 4.25 (t, 8H, 4-CH_2–OCO)

2.4. Polymerization

General procedure of polymerization is as follows. A glass tube was charged with BBEA, Cu(I)Br, bpy and THABI, degassed by three freeze–evacuate–thaw cycles, sealed under vacuum, and placed in an oil-bath thermostated at 100°C for 18 h while stirring. Feed ratios are listed in Table 1. The reaction mixture was then dissolved in

Table 1
Conditions and results of the polymerization of BBEA (Conditions: BBEA, 1.00 g (3.77 mmol); CuBr, 5.4 mg (0.0377 mmol); bpy, 0.018 g (0.113 mmol); temperature, 100°C; time, 18 h)

No.	THABI:BBEA (molar ratio)	Yield (%)	DP_n (th)[a]	DP_n (NMR)[b]	E_I[c]
A1	0	94		183	
A2	1:115	95	105	140	0.79
A3	1:40	93	37	51	0.78
A4	1:30	94	28	37	0.81

[a] Number-average degree of polymerization DP_n (th) was calculated based on the molar ratio of BBEA consumed to the THABI added.

[b] DP are calculated according to Eqs. (1) and (2).

[c] E_I is the percentage of THABI in the polymer to THABI added.

tetrahydrofuran (THF). The resultant polymer was obtained by precipitation in excess hexane, and dried under vacuum at 30°C for 48 h.

2.5. Characterization

^1H NMR spectra were recorded on a Bruker DMX-500 NMR instrument using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Size exclusion chromatography (SEC^3) measurements were performed as follows: A dual SEC detector (Model T60, Viscotek Corp.), 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 Corp.) coupled to a programmable HPLC pump (Model 590, Waters Corp.). Two chromatographic columns (American Polymer Standards Corp., Mentor, Ohio), 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 is described in Ref. [26].

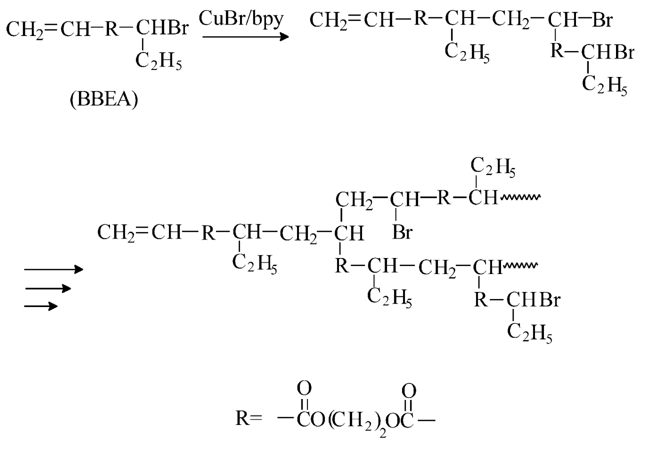
3. Results and discussion

As pointed out by Müller et al. [16] and Yan et al. [17,18], in SCVP system, growing polymer chains can react with each other and the reaction rate of a given polymer chain with other ones is proportional to the number of its functional groups. Thus, large molecules with more functional groups grow faster than small ones. As conversion increases, this rate difference becomes larger, resulting in broad molecular weight distribution of the hyperbranched polymers.

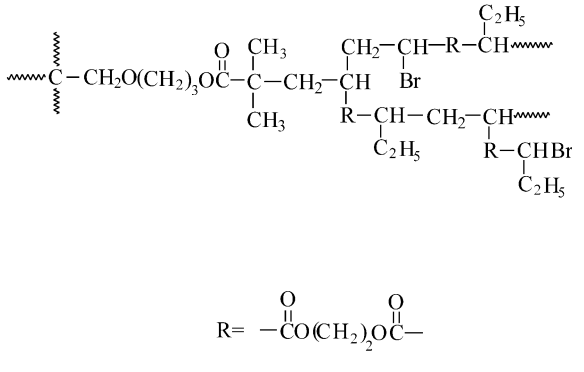
Müller et al. [16] and Frey et al. [19] suggest that addition of a core molecule with structure B_f (representing a polyfunctional initiator in the case of SCVP and a poly-B-functional molecule for AB_m-type polycondensation) into the polymerization system can lower the polydispersity index of the target hyperbranched polymer.

In our previous report [23], we synthesized hyperbranched polyesters by SCVP of BBEM in the presence of a tetrafunctional initiator THABP capped with α-bromopropionyl group, the reactivity of THABP being similar to that of 2-bromobutyryl group in monomer. The polydispersity index of the hyperbranched polymers was still high ($M_w/M_n = 2.16$–5.69). A question is, if we use a multifunctional initiator with initiating reactivity higher than that of monomer, can the polydispersity of the polymer obtained be improved? For solving this question, we synthesized a tetrafunctional initiator, $C[CH_2OCH_2CH_2CH_2OOCC(Br)(CH_3)_2]_4$ (THABI). It has been reported that for ATRP, tertiary alkyl halides have higher reactivity than secondary sites [27], so THABI has higher reactivity than the monomer BBEA.

Polymerization of BBEA and polymerization of BBEA with different feed ratios of THABI/BBEA were carried out in bulk by ATRP; CuBr and bpy were used as catalyst and ligand. The conditions and results are listed in Table 1. The theoretical structure of hyperbranched polymers prepared without and with THABI are shown in Schemes 2 and 3, respectively.



Scheme 2.



Scheme 3.

3.1. NMR result

The ^{1}H NMR spectra are shown in Fig. 1. With respect to the assignments of polymers with similar structure [14,15], ^{1}H NMR data of BBEA and THABI, the signals in Fig. 1 can be divided into five regions. Region 1: the signals from 5.8 to 6.5 ppm are ascribed to the methine and methylene protons of the double bond at the end of polymer. Region 2: the signals from 4.0 to 4.6 ppm correspond to the ethylene glycol group, the methine proton germinal to bromine in both A* and B* groups, and methylene protons adjacent to ester oxygen of THABI units. Region 3: signals at 3.38 and 3.48 ppm are representative of two methylene groups linked to ether oxygen of THABI unit. Region 4: signals from 1.3 to 2.9 ppm are assigned to methine and methylene protons of BBEA unit in the polymer backbone, methylene protons in both A* and B* groups, methylene protons in the middle of trimethylene of THABI unit. Region 5: signals from 0.8 to 1.3 ppm belong to methyl group in B*, polymer backbone, and methyl protons of the bromoisobutyrate group of THABI unit after initiation. (see Table 2).

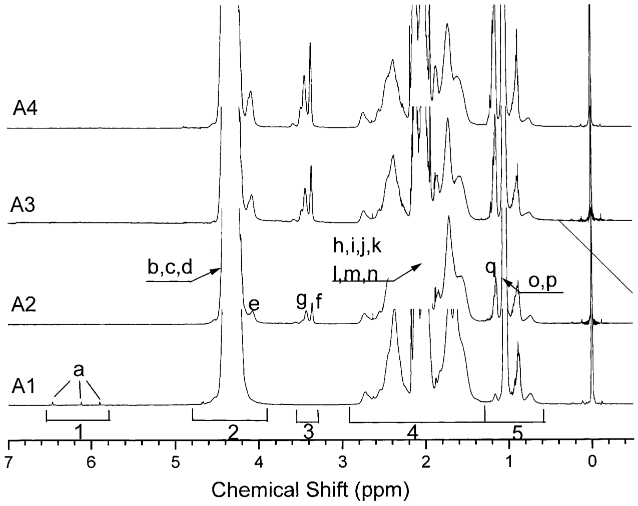


Fig. 1. ^{1}H NMR spectra of homopolymer of BBEA (A1) and hyperbranched polymers prepared in the feed ratio of THABP:BBEA 1/115 (A2), 1/40 (A3) and 1/30. (A4) (The composition and conditions of the polymerizations are the same as that listed in Table 1).

From Fig. 1, we can see that for A1, obtained from the homopolymerization of BBEA, the signals of double bond still exist. For the samples A2 to A4, the signals of double bond disappeared, and the signals at 3.38 and 3.48 ppm of the tetrafunctional initiator, THABI, can be seen clearly. As discussed before, BBEA reacts with each other to form hyperbranched polyester with vinyl group at one end of the polymer (see Scheme 2). THABI initiates the polymerization of BBEA to afford a polymer without end-standing vinyl group (see Scheme 3). Since the equilibrium between tertiary bromine of THABI and CuBr is faster than that between secondary bromine of BBEA and CuBr, the initiation reactivity of THABI is higher than that of BBEA. It is reasonable that at the initial stage of polymerization, more tetrafunctional initiators initiate the polymerization of BBEA than BBEA reacting with each other. Even though BBEA initiates another BBEA to polymerize, the formed oligomer with the end-standing vinyl group will also react with THABI or oligomers capped with THABI. Thus, the vinyl signals are not observed in ^{1}H NMR spectra of A2 to A4 in Fig. 1.

In order to estimate how many tetrafunctional initiators participate in the initiation, the degree of polymerization (DP) would be calculated based on proton NMR data. Assuming that there is no side reaction, such as intramolecular cyclization, each macromolecule should contain one double bond or a THABI unit. When B* of AB* monomer initiates the polymerization of A, one active site A* and one branch point b are formed (see Scheme 1), hence the sum of A* and B* is a constant. Therefore, in region 2, the number of methine next to bromine in both A* and B* groups remains constant. The number-average degree of polymerization (DP$_n$) could be calculated from the integration ratio of the signals of ethylene glycol group and methine proton adjacent to bromine in BBEA unit to methylene protons next to ether oxygen in THABI or vinyl group.

For sample A1, DP$_n$ can be calculated using Eq. (1):

$$\mathrm{DP_n} = (I_2/5)/(I_1/3) \tag{1}$$

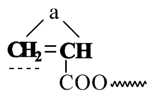
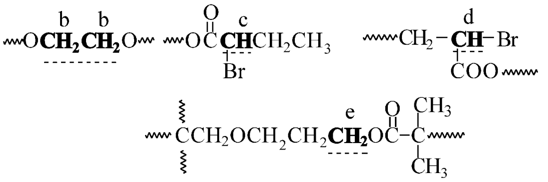
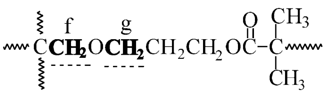
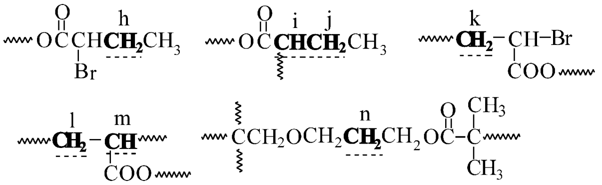
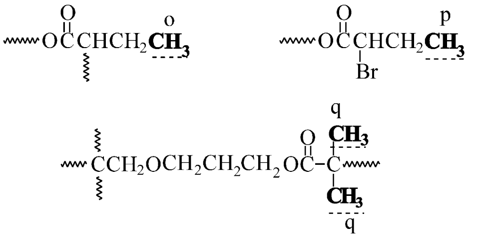
For sample A2, A3 and A4, DP$_n$ can be calculated using Eq. (2):

$$\mathrm{DP_n} = (16/5)\{[I_2 - (I_3/2)]/I_3\} \tag{2}$$

where I_1, I_2 and I_3 represent the integral values of the signals at regions 1, 2 and 3, respectively. The results are listed in Table 1.

When all tetrafunctional initiators participate in the initiation, the number-average degree of polymerization DP$_n$ (th) can be calculated based on the initial molar ratio of BBEA consumed to THABI added. The results are listed in Table 1. All DP$_n$ (th)s are lower than that calculated from proton NMR data, indicating that not all THABI initiates the polymerization of BBEA. The percentage of THABI in the polymer to all THABI added can be calculated based on the initial ratio of THABI to BBEA and DP$_n$ (NMR). Around 80% of THABI added participated in the initiation.

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

Region	Structure
1	
2	
3	
4	
5	

Considering that once the macromolecule with THABI is formed, its DP increases fast because of the larger amount of active sites in this molecule. When difference between the number of active sites in hyperbranched polymer and in THABI becomes large, the possibility of THABI initiating BBEA will be too small. Thus, around 20% of the tetrafunctional initiator added remained in the polymerization system. It can be expected that higher the reactivity of multifunctional initiator, or lower the reactivity of monomer, higher is the efficiency of multifunctional initiator used.

The data listed in Table 1 indicate that the DPs of the samples decrease with increasing initial molar ratio of THABI to the monomer. This is reasonable at similar conversion, less monomer is polymerized by each tetrafunctional initiator for higher molar ratio of THABI/BBEA. Thus, the molecular weight can be controlled by the feed ratio of THABI to monomer.

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

Sample	M_n[a]	M_w[a]	M_w/M_n[a]	M_n[b]	M_w/M_n[b]	M_p[a]	$[\eta]_p$[a] (dl/g)	R_{gp}[a] (nm)
A1	18,100	34,600	1.91	6950	2.92	34,900	0.0539	4.18
A2	17,400	32,400	1.86	7900	2.22	23,100	0.0416	3.10
A3	13,600	16,100	1.18	6210	1.49	15,000	0.0353	2.46
A4	11,100	12,200	1.10	4240	1.80	12,000	0.0285	2.20

[a] Measured by SEC^3 (SEC/RI/RALLS/DV), the subscript p means that the data are at peak position.

[b] Measured by SEC^1 (SEC/RI).

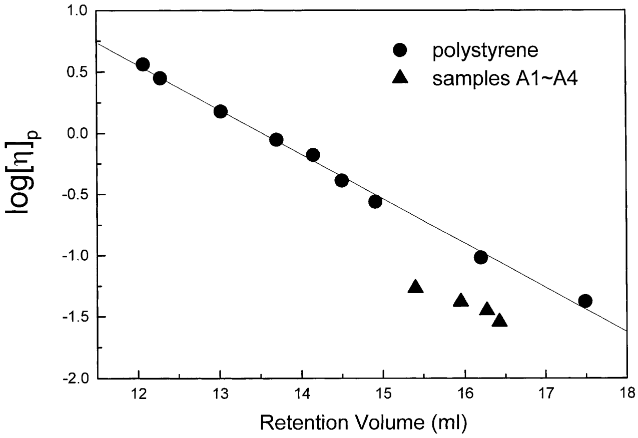


Fig. 2. Plot of $\log[\eta]_p$ vs retention volume (see Table 3).

3.2. SEC result

The data of the samples characterized via SEC/RI/RALLS/DV (SEC^3) and conventional SEC/RI (SEC^1) are shown in Table 3. It can be seen that the molecular weights obtained via SEC^1 are all less than those obtained via SEC^3. For conventional SEC^1, the molecular weight is calibrated with polystyrene standards, giving relative molecular weights to the standards. SEC^3 utilizing a combination of refractive index (RI), right angle light scattering (RALLS), and differential viscosity (DV) detectors, this technique can generally obtain absolute weight-average molecular weight (M_w), and is a useful tool for characterizing branched polymers.

Fig. 2 shows that all intrinsic viscosities $[\eta]_p$ of the samples A1 to A4 fall below the straight line obtained by plotting $\log[\eta]_p$ of PSt standard against retention volume, supporting the formation of branched polymers. Generally, hyperbranched polymer has lower intrinsic viscosity ($[\eta]_p$) than linear PSt at the same retention volume of GPC, due to compact structure of hyperbranched polymers in comparison with linear PSt. The data listed in Table 3 indicate that the molecular weight decreases with increasing the feed ratio of THABI to BBEA, which is consistent with that observed by ^{1}H NMR data. The intrinsic viscosity and radii of gyration of polymers have the same trend with molecular weight.

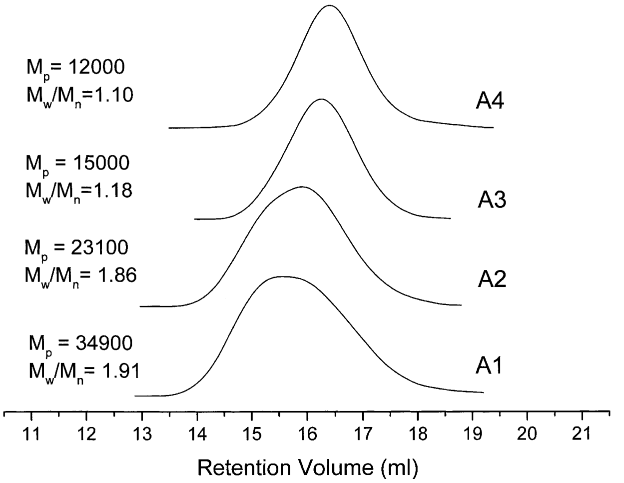


Fig. 3. SEC/RI curves of hyperbranched polymers A1, A2, A3 and A4 (see Table 1).

The SEC/RI curves of the samples are shown in Fig. 3. As the initial concentration of THABI increased, the curves approached symmetry, indicating homogeneous trend of macromolecules. It is observed from Table 3 and Fig. 3 that the molecular weight distribution becomes narrow with increasing initial molar ratio of THABI to BBEA. This further verifies that increasing the initiation reactivity of multifunctional initiator can narrow the molecular weight distribution.

In our previous paper [23], the tetrafunctional initiator THABP has similar reactivity with the monomer (BBEM). At low feed ratio of THABP/BBEM, bimodal molecular weight distributions were observed, because both polymers obtained via reactions between monomers, and from THABP initiation exist in the polymerization system. Molecular weight distribution improved at a high feed ratio of THABP/BBEM, but only 7% of THABP added participated in the initiation of AB^* monomer. Comparing with the present result, it is reasonable to conclude that adding multifunctional initiator with higher initiating reactivity into SCVP system can improve the molecular weight distribution.

4. Conclusion

Hyperbranched polymers can be prepared by ATRP of BBEA in the presence of tetrafunctional initiator THABI, CuBr and bpy. More than 78% of THABI added participates in the initiation, and narrower molecular weight distribution of hyperbranched polyesters were obtained due to THABI with higher initiation reactivity than that of initiation sites in the AB^* monomer. At conversion higher than 90%, increasing the initial molar ratio of THABI/BBEA will lower the DP of hyperbranched polyester, and molecular weight can be essentially controlled by the feed ratio of THABI/BBEA. Enlarged difference of initiating reactivity between multifunctional initiator and initiating site of monomer would lower the polydispersity of the polymer. The molecular weight distribution becomes narrower on increasing the feed ratio of THABI/BBEA.

Acknowledgements

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