

# Preparation of Hyperbranched Polymers Through ATRP of In Situ Formed AB\* Monomer

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**ABSTRACT:** The self-condensing vinyl polymerization of an AB\* monomer formed in situ by atom transfer radical addition from divinylbenzene (DVB) and (1-bromoethyl)benzene (BEB) using atom transfer radical polymerization technique was studied. The catalyst concentration has a dramatic effect on polymerization. To study the polymerization mechanism and to achieve high molecular weight polymer, the polymerization was carried out in bulk with a catalyst to monomer ratio, 2,2'-bipyridine to DVB, of 0.2 at 90°C. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy and size-exclusion chromatography coupled with multiangle laser light scattering were used to analyze the polymerization aliquots and the obtained polymer. The intrinsic viscosities of the prepared polymers were also measured. Experimental results, from the comparison of the apparent molecular weights measured by size-exclusion

chromatography with the absolute values measured by multiangle laser light scattering as well as viscosity measurements, indicate the existence of hyperbranched structures in the prepared polymers. In sharp contrast to hyperbranched polymers from AB\* monomer preprepared, hyperbranched ploy(divinylbenzene) prepared at equimolar amount of DVB and BEB has numerous residual pendant vinyl groups rather than only one double bond at its focal point. The hyperbranched polymers show relatively narrow molecular weight distribution (2.13–3.77) and exhibit excellent solubility in common organic solvents such as acetone. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 850–856, 2006

**Key words:** hyperbranched polymer; self-condensing vinyl polymerization; atom transfer radical polymerization; divinylbenzene; AB\* monomer

## INTRODUCTION

The synthesis of polymers with well-controlled and novel structures has received much attention during the past two decades.<sup>1,2</sup> In particular, dendrimers are among the most well-defined synthetic polymer structures. However, the preparation of these perfectly branched macromolecules requires a multistep reaction and the intermediate purification steps; they are often long and tedious, which actually limits their commercial development. As a result of searching for simpler methods to prepare dendritic macromolecules, hyperbranched polymers have been developed as an alternative to dendrimers, since they can be prepared in only one-pot reaction.<sup>3–5</sup> In 1953, Flory pointed out that the polycondensation of AB<sub>x</sub> ( $x \geq 2$ ) monomer would lead to the formation of branched, but not crosslinked, structures.<sup>6</sup> This proposal was first applied in the step-growth synthesis of hyper-

branched polyphenylenes by Webster and Kim.<sup>7–9</sup> Subsequently, it was extended to other step-growth polymerizations such as aromatic and aliphatic esters,<sup>10–12</sup> siloxanes,<sup>13</sup> and amines.<sup>14,15</sup> In addition to the step-growth polymerization used in the preparation of hyperbranched polymers, an original idea and pioneer work is that proposed by Frechet and coworkers; they have demonstrated a new method, named self-condensing vinyl polymerization (SCVP), to prepare hyperbranched polymers by carbocationic systems.<sup>16</sup> Shortly afterwards, SCVP was extended by Hawker et al. and Matyjaszewski and coworkers to living radical polymerization, and hyperbranched polystyrenes and polyacrylates have been prepared from functionalized styrene and acrylate monomers.<sup>17–29</sup> Generally, the functionalized monomers used in SCVP to prepare hyperbranched polymers are described as AB\*,<sup>23–26,30,31</sup> A represents the double bond and B\* is the functional group that can be activated to form an active center and initiate the polymerization of the double bond A. Although SCVP exhibits some advantages over step-growth polymerization in the preparation of hyperbranched polymers with different structures or high molecular weight, the AB\* monomers satisfying the mechanism of SCVP are either much too expensive or tedious to prepare. Recently, Baskaran has demonstrated the preparation of

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hyperbranched poly(divinylbenzene) from divinylbenzene (DVB) and 1,3-di-isopropenylbenzene by anionic SCVP.<sup>32,33</sup> Atom transfer radical polymerization (ATRP), reported by Matyjaszewski and coworkers in 1995, is a living radical polymerization that has been demonstrated to successfully polymerize a series of vinyl monomers such as styrenes, methacrylates, and acrylonitrile.<sup>34–37</sup> It is proved that the application of ATRP has resulted in the synthesis of polymers with very narrow molecular weight distribution ( $M_w/M_n < 1.1$ ).<sup>37</sup> Irrespective of the number and types of monomers, which can be successfully polymerized, ATRP has also been shown to be more versatile with respect to the novel polymer architectures such as graft copolymer, block copolymer, and (hyper-)branched polymers.<sup>18–29</sup> Most importantly, ATRP can be carried out under moderate polymerization conditions and at relatively low cost in comparison with ionic polymerization.

In this work, we report on the preparation of hyperbranched poly(divinylbenzene) by ATRP of AB\* monomer formed in situ from commercially available DVB and an ATRP initiator, (1-bromoethyl)benzene (BEB).

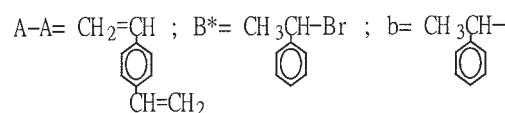
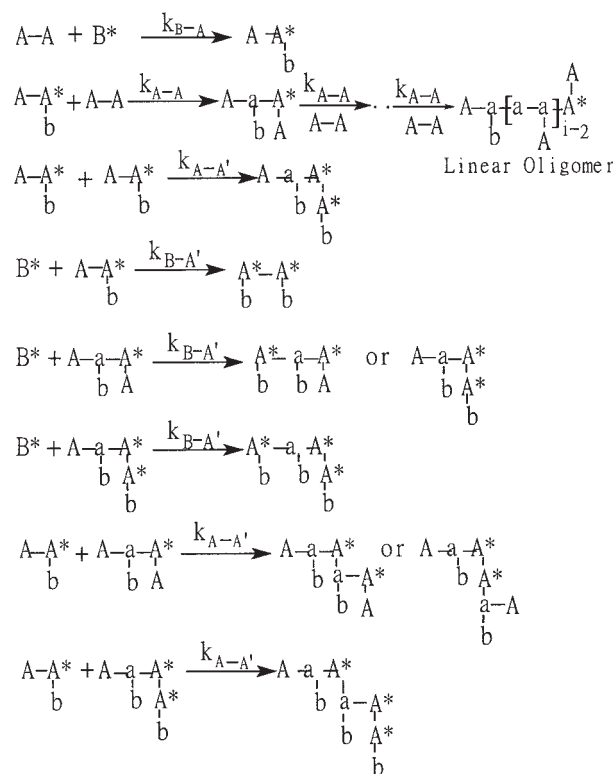
## EXPERIMENTAL

### Material

DVB (mixture of 1,3- and 1,4-isomers and 20% ethylstyrene, DVB, Fluka), BEB ( $\geq 95\%$ , BEB, Fluka, Switzerland), and 2,2'-bipyridine (BPY, analytical agent from Shanghai Chemical Corporation) were used as received. Copper (I) bromide (analytical agent from Shanghai Chemical Corporation) was purified by stirring in glacial acetic acid, washing with methanol, and then drying under vacuum at 60°C. The other reagents and solvents were analytical agents from Shanghai Chemical Corporation and used without further purification.

### Synthesis of hyperbranched polymer from divinylbenzene and (1-bromoethyl)benzene

DVB (1.3 g, 10 mmol, 1.0 equiv), BEB (1.85 g, 10 mmol, 1.0 equiv), BPY (0.312 g, 2 mmol, 0.2 equiv), and copper (I) bromide (0.144, 1 mmol, 0.1 equiv) were added into a 100-mL dry round-bottom flask with a magnetic stir bar. The flask was cycled with nitrogen more than 10 times to eliminate the moisture and oxygen, then sealed and placed into an oil bath at (90  $\pm$  1)°C. Polymerization aliquots were taken to monitor the conversion (<sup>1</sup>H NMR double bonds and initiator, GC measurements were also carried out for selected polymerization aliquots) and the molecular weight growth with polymerization time (size-exclusion chromatography (SEC)). For obtaining solid polymer sam-



Scheme 1

ples, the reaction mixture was dissolved with acetone and the solution was filtered and poured into excess petroleum ether under rapid stirring, the precipitated polymers were recovered and dried in vacuum at 50°C.

### Characterization

<sup>1</sup>H NMR spectra were taken on a Bruker ARX-300 spectrometer at room temperature in CDCl<sub>3</sub>. SEC was carried out on an SEC line consisting of a Waters 1515 isocratic HPLC pump and a Waters 2414 refractive index detector at room temperature in tetrahydrofuran. The apparent molecular weights were calculated based on linear polystyrene standards. The absolute molecular weights of the solid polymers were obtained by SEC coupled with a multiangle laser light scattering (MALLS) detector. The polymer intrinsic viscosity was measured in THF at 25°C.

## RESULTS AND DISCUSSION

The polymerization process may be quite complex in comparison with that of AB\* monomer preprepared. Scheme 1 illustrates the hypothetical polymerization

route.

Upon the activation of the B\* group of BEB, the atom transfer radical addition starts through one of the double bonds of DVB resulting in the formation of AB\* monomer, A-A\*(b), with an initiating site (A\*) and one double bond (A). Subsequently, the A\* group of A-A\*(b) will initiate the double bond of the other molecule A-A\*(b) to start the SCVP. Meanwhile, B\* group of BEB can also initiate the double bonds of DVB and A-A\*(b) to form A-A\*(b) and intermediate, (b)-A\*-A\*(b), with two A\* groups but no double bond, the A\* group of A-A\*(b) initiates the double bond of DVB and will result in the formation of intermediate with two double bonds and one A\* group. Regardless of the complexity, assuming there are no side reactions, such as termination by coupling or intramolecular cyclization, every molecule, including DVB, BEB, A-A\*(b), intermediates, oligomers, and macromolecules of different molecular weights formed in the polymerization should have one double bond on average at the equimolar amounts of DVB and BEB. The \* indicates that at this structural group monomer or double bond can be added; it can be either an active center or in its dormant form. A indicates that the (macro)molecule contains double bond. The lower case letters, a and b, describe how the site has been consumed and can no longer participate in the polymerization.

As shown in Scheme 1, DVB and BEB may be present throughout the polymerization process. The structures of the intermediates are quite complex: intermediates containing more than one double bond or no double bond coexist in the polymerization solution. It is commonly accepted that the degree of branching is directly related to the rate constants of the reaction at either A\* or B\* when an AB\* monomer preprepared is used in SCVP to prepare hyperbranched polymers.<sup>30,31</sup> Should  $k_A$  or  $k_B$  dominate, mostly a linear chain would result. Polymer from 4-(chloromethyl)styrene at low catalyst concentration is the typical example of this case.<sup>19</sup> However, the rate constants of reaction at A\* or B\* should be almost the same due to their similarity in structures as shown in Scheme 1. The determinant governing the degree of branching may be the reactivities of the double bonds of the unreacted monomer (DVB) and the pendant vinyl groups of the polymer chains.

### Polymerization behavior of the system of DVB and BEB

Preliminary experiments on the polymerization of equimolar DVB and BEB showed that the reaction was extremely sensitive to catalyst concentration. As shown in Table I, rapid onset of crosslinking was observed at relatively high catalyst concentration, though high molecular weight polymers could readily

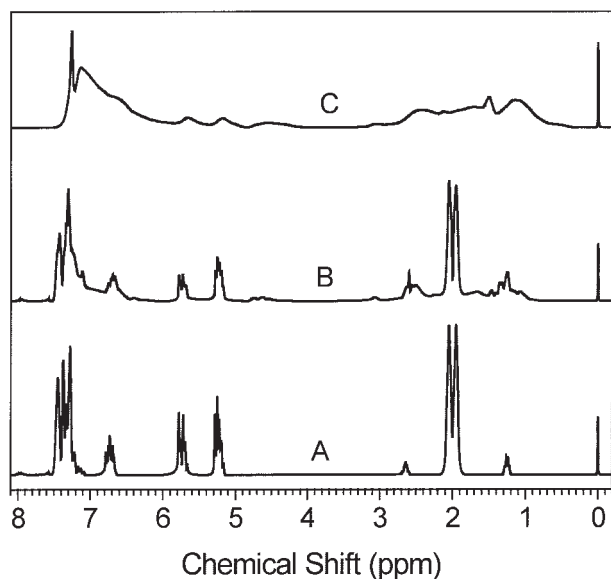
TABLE I  
Dependence of Crosslinking Reaction Time on Catalyst Concentration

[DVB]	[BEB]	[BPY]	[CuBr]	Gelation Time
1	1	0.1	0.05	>45 h
1	1	0.2	0.1	3 h
1	1	0.3	0.15	30 min
1	1	0.4	0.2	20 min

be prepared by careful control of the polymerization. For appropriate polymerization rate and experimental reduplication, the feed ratio, [DVB]/[BEB]/[BPY]/[CuBr] = 1/1/0.2/0.1, was employed in the subsequent experiments, unless stated otherwise.

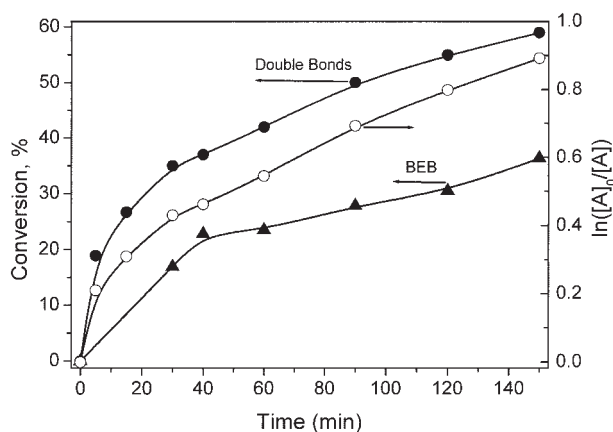
Figure 1(A,B) shows the respective <sup>1</sup>H NMR spectra of the polymerization aliquots at different polymerization time. The signals at chemical shifts of 7.2–7.5 ppm correspond to the protons of the benzene ring, and the area of these peaks is expressed as  $S_1$ . The signals at chemical shifts of 6.75, 5.75, and 5.25 ppm are attributed to the protons of the double bond. The signals of the proton to bromine in B\* (BEB) overlap with the signals of one proton of the double bond at chemical shift of 5.25 ppm, and the area of the peaks at chemical shift of 5.75 ppm is expressed as  $S_2$ . The signals at chemical shifts of 2.65 and 1.25 ppm are assigned to the protons of —CH<sub>2</sub>— and —CH<sub>3</sub> of 3- or 4-ethylstyrene mixed in DVB. The signals at chemical shift of 2.0 ppm are associated with the methyl protons geminal to bromine in the initiator (B\*), and the area of these peaks is expressed as  $S_3$ . Upon the conversion of the B\* group and the double bonds to A\* group and polymer backbone, two broad sets of peaks at chemical shifts of 4.4–4.8 ppm and 0.8–3.1 ppm appear. The methyl protons geminal to bromine in BEB (B\*), at chemical shift of 2.0 ppm, are shifted upfield, at chemical shift of 1.3 ppm, as the bromine is removed and monomer added, forming b. Conversions of the double bond and BEB were calculated by comparison of  $S_1$ ,  $S_2$ , and  $S_3$ .

Figure 2 illustrates the dependence of the conversions of the double bond and BEB on the polymerization time. The conversion of the double bond increases rapidly in the initial stage of polymerization and reaches about 35% after 30 min polymerization. However, the conversion of BEB is only about 17%, indicating that the consumption of vinyl groups to BEB in molar ratio is above 4 : 1 and one consumed BEB has initiated more than four vinyl groups. The polymerization aliquots with a polymerization time of 0 and 30 min were also analyzed by gas chromatography to investigate the ratio of the residue DVB to BEB. The GC results also suggest strongly that the consumed double bonds are mainly from DVB rather than the pendant vinyl groups. Consequently, a reasonable de-

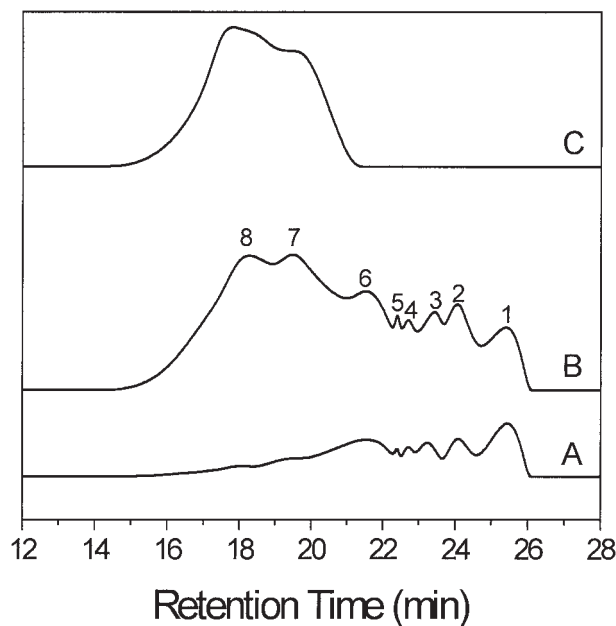


**Figure 1** (A) <sup>1</sup>H NMR spectrum of polymerization aliquot before polymerization. (B) <sup>1</sup>H NMR spectrum of polymerization aliquot of 90 min polymerization. (C) <sup>1</sup>H NMR spectrum of the solid polymer of 90 min polymerization.

duction may be proposed that one molecule of intermediates formed in this stage contains more than four double bonds on average. The most probable structure may be linear oligomers bearing several pendant vinyl groups and one halogen end group as shown in Scheme 1. As the polymerization proceeds, the residual DVB decreases and the pendant vinyl groups increase gradually regardless of the decreased total concentration of vinyl groups. Not only the double bonds of DVB but also the pendant vinyl groups should be involved in polymerization. The pendant vinyl groups participate in polymerization giving rise to the coupling of oligomers. This results in the formation of branched structures and high molecular weight poly-



**Figure 2** Dependence of the conversion of the double bond and BEB on the polymerization time.



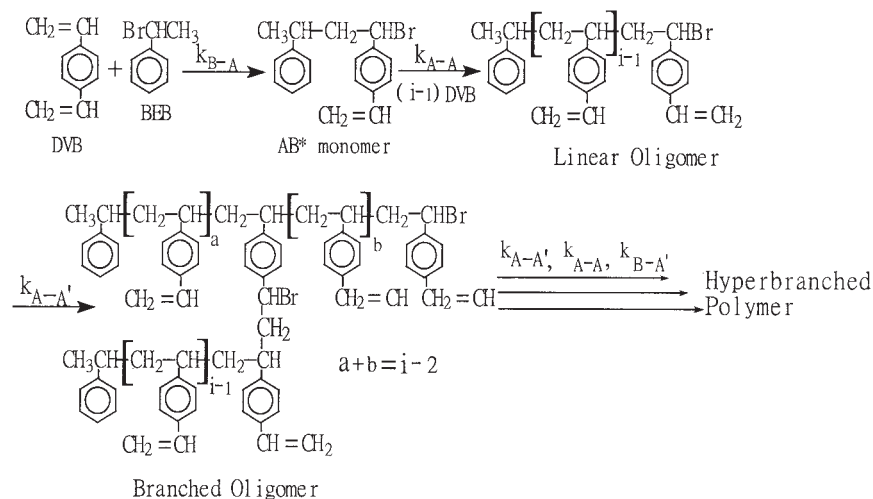
**Figure 3** (A and B) SEC traces of polymerization aliquots of 15 and 90 min polymerization. (C) SEC trace of the solid polymer of 90 min polymerization.

mers rapidly and crosslinking material finally. As a result of decrease in the total concentration of double bonds and limited reactivity of the pendant vinyl groups, the increase rate of double bond conversion slows down apparently.

For more information to probe the polymerization behavior, the polymerization aliquots were also analyzed by SEC. Although SEC does not yield quantitative information, it is still helpful to analyze qualitatively the molecular weight growth and the percent content of different fraction. Figures 3(A) and 3(B) illustrate the results. The presence of high molecular weight polymers, besides several fractions of lower molecular weights, was observed at the initial stages of the polymerization. It must be emphasized here that the signals of DVB and BEB overlapping with those of the mobile phase at retention time of 28–31 min, are present throughout the polymerization, indicating the presence of DVB and BEB in the whole polymerization processes. All these experimental results are similar to those of ordinary SCVP of AB\* monomer prepared.<sup>16,19,24</sup> Surprisingly, the amount of fractions 4–6 is much lower compared with their higher or lower analogs, suggesting that the coupling of growing oligomers is the major reaction pathway and the coupling of oligomers will proceed rapidly regardless of the limited reactivity of pendant vinyl groups.

For a selected radical derived from A\* or B\*, it can initiate not only the double bond of DVB but also the pendant vinyl group undergoing polymerization. The polymerization reactivity ratio can be expressed as





Scheme 2

$k_{A-A}[M][R\cdot]/k_{A-A'}[M][R\cdot] = k_{A-A}/k_{A-A'}$  or  $k_{B-A}[M][R\cdot] = k_{B-A'}[M][R\cdot] = k_{B-A}/k_{B-A'}$ : it is similar to the monomer reactivity ratio defined in classical radical copolymerization. Apparently, radicals formed will tend to initiate double bonds of DVB rather than the pendant vinyl groups due to their relatively lower reactivities. However, this in fact is not the case; the actual expression should include the number of vinyl groups in the selected molecules when which type of double bond will take advantage to participate in polymerization is considered. It means that the real expression should be  $2k_{A-A}/i \times k_{A-A'}$  or  $2k_{B-A}/i \times k_{B-A'}$ . Here, 2 and  $i$  represent one molecular DVB and oligomer contain two and  $i$  double bonds.

Although the polymerization rate is finally affected by the total concentration of DVB and pendant vinyl groups, it is undoubted that oligomers bearing several double bonds have advantage in taking part in polymerization. The relatively high amount of fractions 1 and 2 throughout the whole polymerization support strongly these statement and explanation, since these two fractions correspond to components of low molecular weights, such as A-A\*(b), bearing only one or two double bonds. Based on the above statement and explanation, it should be easy to understand and accept the presence of high molecular weight polymers after only 15 min polymerization and the very low amount of fractions 4–6 derived from the rapid coupling reaction of oligomers bearing several pendant vinyl groups.

After the polymerization, solid polymers were recovered by separation in excess petroleum ether. The typical  $^1\text{H}$  NMR spectrum, as shown in Figure 1(C), is quite different from those of hyperbranched polymers from AB\* monomers prepared, in which the signals corresponding to A\* and B\* groups at chemical shift of 4.0–5.0 ppm are much stronger than those

attributed to the double bonds. Because one macromolecule bears only one double bond but  $n$  ( $A^* + B^*$ ) groups, here,  $n$  is the number average degree of polymerization.<sup>18,19,23,24</sup> However, NMR results of the solid polymers, as shown in Figure 1(C), indicate that the number of double bonds is about five times that of the A\* groups. It can be concluded that one macromolecule of the solid polymers bears numerous pendant vinyl groups rather than only one double bond. It has been proved by the following simple experiment. The polymerization system of styrene, dissolving the obtained solid polymer using AIBN as initiator at 70°C, will become a gel after only 5 min polymerization. Furthermore, the signals associate with the protons of the double bonds and the bromine end groups are blunt rather than sharp peaks, which implies the chemical environment is quite complex. Linking the results obtained by  $^1\text{H}$  NMR and GPC analysis of the polymerization aliquots, an outline of the polymerization procedure may be expressed as Scheme 2. It shows that the polymerization proceeds by a modified SCVP mechanism that involves incorporation of the linear bromine-terminated fragments bearing several pendant vinyl groups into the other fragments, resulting in an irregularly branched structure.

#### Evidence for the branched structure from light scattering and viscosity measurements

For more evidences to verify branching structure, light scattering and viscosity measurements have been carried out. Table II lists the dependence of molecular weights on the polymerization time and the comparison of molecular weights measured by SEC and MALLS. In terms of the molecular weight, it increases gradually during the first hour, then molecular weight increases rapidly and reaches its highest value after

TABLE II  
Dependence of Molecular Weight on Polymerization Time and Comparison of Molecular Weight from SEC and MALLS

No.	Polymerization time (min)	$M_{n,SEC}$	$M_{w,SEC}$	$M_{w,MALLS}$	$M_{w,SEC}/M_{n,SEC}$	$M_{w,MALLS}/M_{w,SEC}$
1	30	4815	10233		2.13	
2	30	5031	11746	27380	2.33	2.33
3	60	4881	12641		2.59	
4	60	4924	12628	33169	2.56	2.63
5	90	5843	16980	51250	2.91	3.02
6	120	6217	17972		2.89	
7	150	7018	26483	109600	3.77	4.14
8	150	7677	21330	97290	2.78	4.56
9	180	4959	13593	82950	2.74	6.10 <sup>a</sup>

<sup>a</sup> Molecular weight of the soluble part.

150 min polymerization, 26,483 and 109,600 measured by SEC and MALLS, respectively. Based on the increase in tendencies of double bond conversion and molecular weight, it may be concluded that the polymerization of DVB mainly forming linear oligomers bearing numerous pendant vinyl groups and the polymerization of linear oligomers resulting in high molecular weight polymers should be dominant at different stages of the polymerization. When the molecular weight of polymers formed increases along with polymerization time, the number of A\* groups, especially the number of the pendant vinyl groups in a selected macromolecule, also increases as shown in Schemes 1 and 2. Finally, the polymer will become gel. Undoubtedly, macromolecules of some higher molecular weight will more easily to undergo a crosslinking reaction and become gel because they bear more pendant double bonds and A\* groups. In other words, the soluble part left after crosslinking reaction must have a relatively lower molecular weight as shown in Table II (run 9).

It is generally accepted that light scattering measurements are highly effective in the characterization of polymers containing branched structures. The  $M_w$  values obtained by light scattering will differ from those obtained by standard SEC analysis. Results listed in Table II confirm the existence of branched structures. The intrinsic viscosity was measured and plotted against molecular weight as shown in Figure 4. The slope of  $\log[\eta]$  versus  $\log[M]$  is much lower than that for the linear polystyrene (MHS exponent  $\alpha = 0.7$  for linear polystyrene versus 0.48 for the polymers obtained here), which indicates a decreased level of interaction between solvent and polymer as is typically encountered in densely branched macromolecules. This result again confirms that the polymers prepared are of hyperbranched structures.

## CONCLUSIONS

The preparation of hyperbranched polymers from commercially available DVB and BEB by ATRP has

been studied. Hyperbranched poly(divinylbenzene)s, with absolute molecular weights between 27,380 and 109,600 were prepared as measured by SEC coupled with MALLS analysis. At an equimolar amount of DVB and BEB, the polymerization is dramatically affected by the catalyst concentration, the ratio of DVB to BPY. The polymerization system will become gel after only 20 min reaction at a ratio of DVB to BPY of 0.4. The polymerization proceeds by a modified SCVP mechanism. At first, BEB initiates the polymerization of DVB resulting in the formation of linear oligomers or intermediates bearing several pendant vinyl groups, then the incorporation of the linear oligomers into the other oligomers gives rise to rapid increase of molecular weight and an irregularly branched structure. Numerous pendant vinyl groups in the linear oligomer lead to the crosslinking. In a sharp contrast to hyperbranched polymers from AB\* monomers prepared, one macromolecule prepared here contains numerous residual pendant vinyl groups rather than only one double bond at its focal point, as evidenced by <sup>1</sup>H NMR. Comparison of the apparent molecular weights from SEC with the absolute values

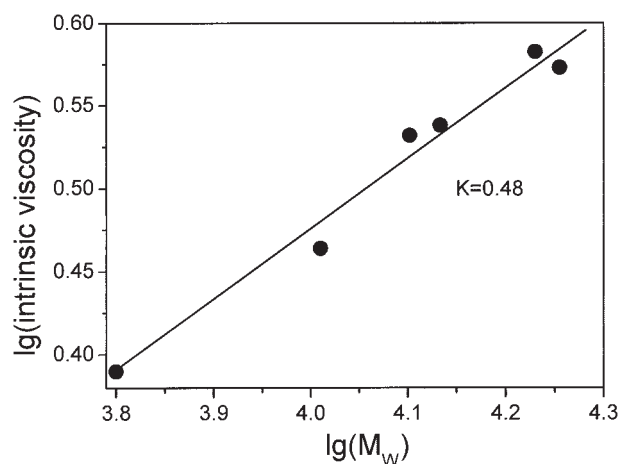


Figure 4 Mark-Houwink-Sakurada plot for polymers in THF at 25°C.

from MALLS as well as viscosity measurements confirm the presence of hyperbranched structures. Most importantly, it is reasonable to expect that some other types of hyperbranched polymers can be prepared from divinyl monomers, such as (meth)acrylate, by living radical polymerization based on this research.

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