

# Preparation of Hyperbranched Polymers by Atom Transfer Radical Polymerization

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**ABSTRACT:** A cheap acrylic AB\* monomer, 2-(2-chloroacetyloxy)-isopropyl acrylate (CAIPA), was prepared from 2-hydroxyisopropyl acrylate with chloroacetyl chloride in the presence of triethylamine. The self-condensing vinyl polymerization by atom transfer radical polymerization (ATRP), a “living”/controlled radical polymerization, has yielded hyperbranched polymers. All the polymerization products were characterized by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR). CAIPA exhibited distinctive polymerization behavior that is similar to a classical step-growth polymerization in the relationship of molecular weight to polymerization time, especially during the initial stage of the polymerization. However, a significant amount of monomer remained present throughout the polymerization, which is consistent with typical chain polymerization. Also, if a much longer polymerization time was used, the polymer became gel. As a result of the unequal reactivity of group A\* and B\*, the polymerization is different from an ideal self-condensing vinyl polymerization: the branch structures of polymers prepared depend dramatically on the ratio of 2,2'-bipyridyl to CAIPA. Hyperbranched polymers exhibit improved solubility in organic solvent, however, they have lower thermal stability than their linear analogs. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2114–2123, 2002

**Key words:** hyperbranched polymers; atom transfer radical polymerization; NMR; thermogravimetric analysis; self-condensing vinyl polymerization

## INTRODUCTION

The accurate control of macromolecular architecture is an important theme in modern polymer science, with many advanced materials that possess new or improved properties.<sup>1,2</sup> A method commonly used to achieve these goals is the introduction of branching into the polymer struc-

ture. Dendritic polymers provide dramatic examples of the effect of branching on polymer structure and properties because they have been shown to exhibit physical properties distinctly different from linear polymers.<sup>3,4</sup> However, because the synthesis of regularly branched dendrimers is not trivial and requires multistep synthesis, their commercial development has been limited to only a few structures. The synthesis of hyperbranched polymers, polymers that possess less perfect branched structures, has been explored to develop dendritic molecules in single

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and one-pot reactions.<sup>5–8</sup> These polymers are usually obtained by the reaction of AB<sub>2</sub> monomer, in which A and B are functional groups capable of reacting with each other to form stable bonds. Because of the unusual structure of the AB<sub>2</sub> monomer, reaction between two monomers results in the formation of a dimer with one A group and three B groups. This process repeats itself by reaction with monomer, dimer, trimer, etc., as in classical step-growth polymerization. The resulting macromolecules have one A group and  $n + 1$  B groups, where  $n$  is the number of repeat units. In addition to the step-growth polymerization used in the preparation of hyperbranched polymers, the original idea and pioneer work should be that proposed and carried out by Frechet and co-workers; they have described a new method, named self-condensing vinyl polymerization, by which AB\* monomers can be used to synthesize hyperbranched polymers with a whole carbon backbone by cationic polymerization.<sup>9</sup> This monomer satisfies the AB\* requirements for formation of hyperbranched polymers because the vinyl group acts as the difunctional group A and an additional alkyl halide functional group acts as the B\* group. By activation of the B\* group with a Lewis acid, polymerization through the double bond occurs cationically. After this original idea and pioneer work, Hawker, Scott, Weimer, Matyjaszewski, and Frechet have extended this method into the living radical polymerization field; the monomers employed were 4-(chloromethyl) styrene, self-made styrene type and acrylic AB\* monomers.<sup>10–15</sup> However, the cost of the monomers used is very expensive and preparation of the monomers is difficult.<sup>10–16</sup> Matyjaszewski and co-workers have reported on the polymerization of AB\* monomer with mismatched reactivities.<sup>17</sup> In summary, the commercial development of polymers from these AB\* monomers may be limited. We report here studies on the preparation of hyperbranched polymer from a very inexpensive acrylic AB\* monomer by atom transfer radical polymerization (ATRP), a “living”/controlled radical polymerization system that has been demonstrated to successfully polymerize styrene,<sup>18–22</sup> (meth)acrylates,<sup>18,223–26</sup> and acrylonitrile.<sup>27</sup> There are some comprehensive reviews in the literature on ATRP.<sup>28–30</sup> As will be later demonstrated, hyperbranched polymers can be prepared from this inexpensive acrylic AB\* monomer when a high concentration of catalyst is employed.

## EXPERIMENTAL

### Reagents

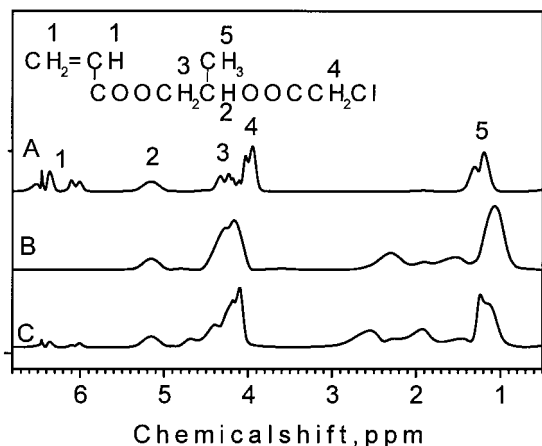
2-Hydroxyisopropyl acrylate, a commercial product from Wuxi Huayi Chemicals, was used as received. 2,2'-Bipyridyl (Bipy), an analytical reagent, was used as obtained from Shanghai No.1 chemical reagent factory. Chloroacetyl chloride, a chemical reagent from Shanghai No.1 chemical reagent factory, was distilled under atmospheric pressure; the distillate between 105 and 107 °C was collected and used. Copper (I) chloride (CuCl, AR grade) was purified by stirring in acetic acid, washing with methanol, and then drying under reduced pressure. AIBN, AR grade, was recrystallized from ethanol. Acetone, tetrahydrofuran (THF), ethanol, acetic acid, methanol, petroleum ether (30–60 °C), ether, triethylamine, activated charcoal, H<sub>2</sub>SO<sub>4</sub>, and NaHCO<sub>3</sub> (AR grade) were used without further purification.

### Preparation of 2-(2-Chloroacetyloxy)-isopropyl Acrylate

2-Hydroxyisopropyl acrylate (8 mL; 0.125 mol), triethylamine (21 mL; 0.15 mol), 100 mL ether, and a little CuCl were added into a three-necked flask equipped with a thermometer and a stirrer. Chloroacetyl chloride (10 mL, 0.125 mol) dissolved in 25 mL of ether was added in a dropwise manner into the flask and the solution was stirred for 1 h at 0–4 °C. After the addition of chloroacetyl chloride, the reaction was continued at 35 °C for 6 h. The reaction mixture was washed three times with diluted H<sub>2</sub>SO<sub>4</sub> (10% by weight) at first, and then three times each with concentrated NaHCO<sub>3</sub> solution and distilled water. An orange transparent ether solution was obtained following these purification processes. Anhydrous sodium sulfate and activated charcoal were added into the solution, and the solution was allowed to stand overnight. The solution was filtered. Volatilization of ether left a slightly yellow transparent oil liquid in a yield of 72% and with the proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectrum shown in Figure 1A.

### Typical Polymerization Procedure of CAIPA

In a typical polymerization, Bipy (0.624 g; 4.0 mmol; 0.4 equiv), CuCl (0.2 g; 2.0 mmol; 0.2 equiv), CAIPA (2.06 g; 10 mmol; 1.0 equiv), and a stirrer bar made of PTFE were added to a dry flask. The flask was cycled between vacuum and



**Figure 1** (A)  $^1\text{H}$  NMR spectrum of CAIPA. (B)  $^1\text{H}$  NMR spectrum of linear poly(CAIPA). (C)  $^1\text{H}$  NMR spectrum of hyperbranched polymer sample 15 from CAIPA.

nitrogen >10 times to remove the oxygen. Then, the flask was sealed and placed in a preheated, thermally regulated oil bath at  $125 \pm 1$  °C. After a certain period of polymerization, the flask was removed from the oil bath and allowed to cool for a few minutes. Then, 12 mL of acetone was added to the flask, and the mixture was stirred at room temperature to complete the dissolution of the polymer. Then, petroleum ether (5 times the acetone in volume) was added to precipitate the resulting polymer. After repeating these dissolution and precipitation processes another time, the polymer was dried at 50 °C under reduced pressure, and the monomer conversion or polymer yield was calculated gravimetrically. Finally, excess acetone was added to the flask to dissolve the resulting polymer, and the solution was filtered to remove the insoluble salts and most of the Bipy. The resulting slightly orange solution was concentrated and washed three times with a mixture of petroleum ether and acetone (5:1, v/v). After complete drying under reduced pressure at 50 °C for at least 24 h, an orange transparent polymer was obtained.

#### Typical Copolymerization Procedure of CAIPA with Styrene

In a typical copolymerization, Bipy (0.468 g; 3.0 mmol; 0.4 equiv), CuCl (0.15 g; 1.5 mmol; 0.2 equiv), CAIPA (1.55 g; 7.5 mmol; 1.0 equiv), styrene (3.12 g; 30 mmol; 4 equiv), and a stirrer bar made of PTFE were added to a dry flask. The ensuing pretreatment and polymerization process

were the same as that stated in the polymerization of CAEA. After polymerization, ~25 mL of acetone was added, and the mixture was stirred to complete the dissolution of the polymer. Then, the solution was poured into a large amount of petroleum ether with rapid stirring to precipitate the products. The precipitated polymer was collected and washed three times with methanol, then purified by reprecipitation from the acetone solution into excess petroleum ether. Drying at room temperature for several hours allowed volatilization of the solvent, and then the sample was heated in a vacuum oven at 50 °C for at least 24 h. The monomer conversion or polymer yield was calculated gravimetrically.

#### Preparation of Linear Polymer of CAIPA and Copolymer of CAIPA with Styrene

Linear poly(CAIPA) was prepared as follows: CAIPA (7.68 g, 0.04 mol) and AIBN (0.0384 g, 0.5% CAIPA by wt) were added into a round-bottomed flask and the flask was placed into an oil bath at 50 °C. After 45 min of polymerization, THF was added to dilute the polymerization mixture. The solid polymer was precipitated into methanol twice and dried at 40 °C for 24 h in vacuo to yield 17%.

Linear poly(CAIPA-co-styrene) was prepared as follows: CAIPA (7.68 g, 0.04 mol), styrene (4.56 g, 0.04 mol), and AIBN (0.0612 g, 0.5% of monomer by wt) were added to a round-bottomed flask and the flask was placed in an oil bath set at 50 °C. After 45 min of polymerization, THF was added to dilute the polymerization mixture. The solid polymer was precipitated into methanol twice and dried at 40 °C for 24 h in vacuo to yield 20%. The  $^1\text{H}$  NMR spectrum is illustrated in Figure 2A, (mole fraction of monomer unit CAIPA in the increment of polymer formed from monomer mixture having the composition  $f_1 [F_{\text{CAIPA}}] = 0.43$ ).

#### Characterization Methods

The  $^1\text{H}$  NMR spectra were taken on a Bruker ARX-300 type NMR spectrometer at room temperature in  $\text{CDCl}_3$ . Size exclusion chromatography (SEC) was conducted at room temperature in THF. The data were obtained with linear polystyrene standards. Fourier transform infrared spectroscopy (FTIR) was carried out on a Nicolet FTIR 20 SX/B spectrometer. Thermal analysis was performed on a PE-7 thermal analysis system. Dif-

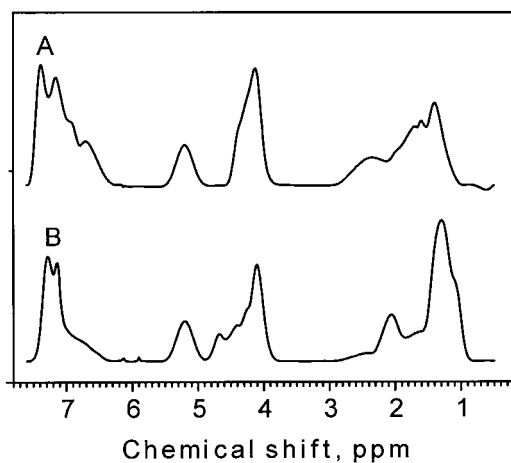
ferential scanning calorimetry (DSC) was carried out under  $N_2$  atmosphere in the temperature range 50–150 °C at a heating rate of 20 °C/min. Thermogravimetric analysis (TG) was carried out under air atmosphere, in the temperature range 25–480 °C, at a heating rate of 10 °C/min.

## RESULTS AND DISCUSSION

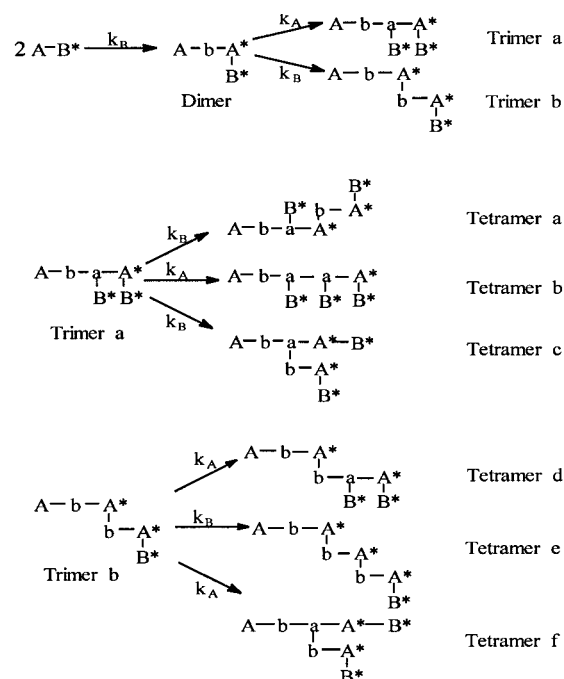
### The Self-Condensing Vinyl Polymerization of CAIPA

The idealized case of the polymerization is shown in Scheme 1. On activation of the  $B^*$  group (the primary ester halide), the polymerization begins by propagation through the double bond of the monomer, resulting in the formation of the dimer with the  $Ab$ ,  $A^*$  (the secondary ester halide) and  $B^*$ . The  $*$  indicates that monomer can be added at this structural group; it can be either an active site or dormant.  $Ab$  indicates that the double bond is a part of the macromolecule. The lower case letter,  $b$ , describes how the site has been consumed and can no longer participate in the polymerization. It is obvious that the degree of branching will be directly related to the rate constant  $k_A$  and  $k_B$ .<sup>31,32</sup>

The  $^1H$  NMR spectrum of CAIPA, shown in Figure 1A, is marked 1, 2, 3, 4, and 5 corresponding to the three protons of the double bond and the protons of  $-COOCH<$ ,  $-COOCH_2-$ ,  $-CH_2Cl$ , and  $-CH_3$ , respectively. This spectrum



**Figure 2** (A)  $^1H$  NMR spectrum of linear poly(CAIPA-co-styrene). (B)  $^1H$  NMR spectrum of hyperbranched polymer of CAIPA with styrene (polymerization at 125 °C for 15 h;  $[CAIPA]/[St]/[Bipy]/[CuCl] = 1:1:0.4:0.2$ ).



**Scheme 1** Polymerization procedure of CAIPA catalyzed by the complex of Bipy and  $CuCl$ .

is in agreement with its expected structure. The  $^1H$  NMR spectra of the linear poly(CAIPA) and the hyperbranched polymer sample no. 15 from CAIPA are shown in Figures 1B and 1C, respectively. The spectrum in Figure 1C is fully consistent with the expected branched structure. The peaks for chemical shift at  $\delta = 6.4$ , 6.1, and 5.9 ppm correspond to protons of the double bond, group A. From the total area of these peaks, the unit peak area of one proton in hyperbranched polymers can be calculated and expressed as  $S_i$ . The peak for chemical shift at  $\delta = 5.2$  ppm is related to the proton of  $>CHOOC-$ , and the area of this peak is expressed as  $S_1$ . The overlapping peaks around chemical shifts from 4.0 to 4.7 ppm are derived from the protons of group  $A^*$ ,  $B^*$ , and  $-COOCH_2-$ ; the area of these peaks is expressed as  $S_2$ . The area of these peaks around chemical shift from 1.0 to 2.8 ppm is expressed as  $S_3$ . Assuming that there are no side reactions, such as termination by coupling or intramolecular cyclization, each hyperbranched polymer should have only one double bond. So the number average polymerization degree  $X_n$  or number average molecular weight  $M_n$ , and the number of group  $A^*$  and  $B^*$  as well as their percentage of the hyperbranched polymers, can be calculated according to eqs. 1–5:

$$X_n = (3S_i + S_1 + S_2 + S_3)/11S_i \quad (1)$$

$$M_n = 206X_n \quad (2)$$

$$N_{-\text{CH}_2\text{Cl}} + N_{>\text{CHCl}} = X_n \quad (3)$$

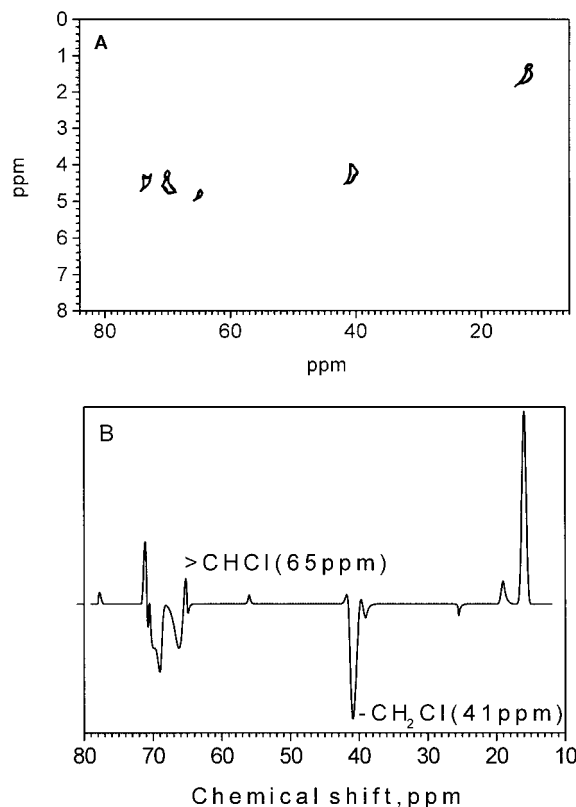
$$(2N_{-\text{CH}_2\text{Cl}} + N_{>\text{CHCl}} + 2X_n)S_i = S_2 \quad (4)$$

$$>\text{CHCl}\% = [(N_{>\text{CHCl}})/X_n] \times 100\% \quad (5)$$

In this work, the total proton number of one molecule of CAIPA is 11, the molecular weight of CAIPA is 206, and  $N_{-\text{CH}_2\text{Cl}}$  and  $N_{>\text{CHCl}}$  are the numbers of group B\* and A\*, respectively.

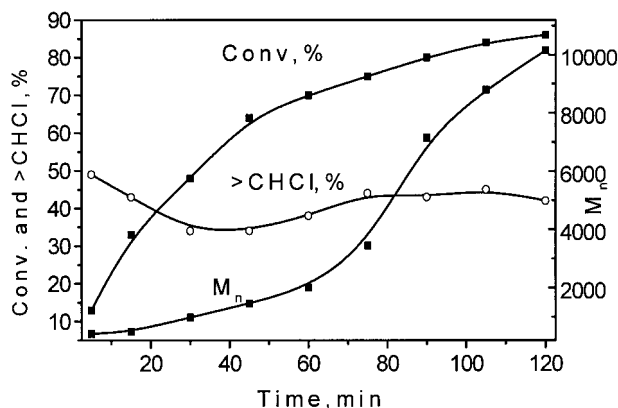
Further support for the assignment of ester halide signals can be obtained from gradient heteronuclear multiple quantum correlation (gHMQC), and distortionless enhancement can be determined by polarization transfer (DEPT) NMR experiments. The results in Figure 3A, which shows the gHMQC spectrum of the same polymer sample as in Figure 1C, clearly demonstrates that the proton near 4.2 ppm is attached to a C-atom near 41 ppm (a methylene,  $-\text{CH}_2-$  group, according to the DEPT spectrum, Figure 3B) and the proton near 4.7 ppm is connected to a C-atom near 65 ppm (a methane  $-\text{CH}-$  group, Figures 3A and 3B).

The dependence of monomer conversion, number average molecular weight, and the percentage of the secondary ester halide, group A\*, on polymerization time of CAIPA at 125 °C catalyzed by the complex of CuCl and Bipy is shown in Figure 4. During the early stage of polymerization, the number average molecular weight of the polymers formed grows exponentially with polymerization time, as expected for a step-growth polymerization. This result is the same as that reported by Frechet and co-workers for a cationic self-condensing vinyl polymerization.<sup>9</sup> However, the rate of increase of molecular weight slows down after ~90 min of polymerization. In view of monomer conversion, a significant amount of CAIPA remains present throughout the polymerization, which is consistent with a chain growth polymerization mechanism. From these results of molecular weight and monomer conversion increase tendencies, it can be concluded that the self-condensing vinyl polymerization behavior of CAIPA is very distinctive. In the case of monomer conversion, especially the presence of CAIPA in the polymerization system throughout the polymerization process, the polymerization behavior



**Figure 3** (A) Gradient heteronuclear multiple quantum correlation NMR spectrum of hyperbranched polymer sample 15. Proton signals on the y-axis are related to the carbon to which they are attached, x-axis. (B) Distortionless enhancement by polarization transfer NMR spectrum of the sample as in A.  $^{13}\text{C}$  NMR of carbons with one or three protons attached yield positive signals, whereas carbons with two protons attached yield negative signals.

is similar to a classical chain polymerization. The dependence of molecular weight on polymerization time contrasts to a classical chain polymerization but is similar to a typical step-growth polymerization. According to the ideal procedure of self-condensing vinyl polymerization proposed by Frechet et al.,<sup>9</sup> the number of groups A\* should be equal to the number of groups B\*, so the percentage of them should be the same and equal to 50%. However, the experiment results are not as expected. As shown in Figure 4, the percentage of group A\* is nearly equal to 50% at the initial stage of polymerization because most of the products are dimer, then the percentage decreases and remains relatively stable at ~43% at the end. The unexpected experimental results imply that there is an apparent difference in the activation energy required to form radical  $-\text{CH}_2\cdot$  from group B\*



**Figure 4** The dependence of monomer conversion, number average molecular weight and the percentage of the secondary ester halide on polymerization time of CAIPA at 125 °C ([CAIPA]/[Bipy]/[CuCl] = 1:0.4:0.2).

and to form radical  $>CH\cdot$  from group A\*; the reactivity of these two radicals formed is also different because of their different structures. These results mean that  $k_A$  is much bigger than  $k_B$ .<sup>31,32</sup> It has been proved that initiation of MMA from primary haloesters is slow.<sup>33,34</sup>

#### Influences of Polymerization Conditions on Polymerization Rate and the Structures of the Polymers Formed

Although CAIPA exhibits very distinct polymerization behavior, the chain propagation mecha-

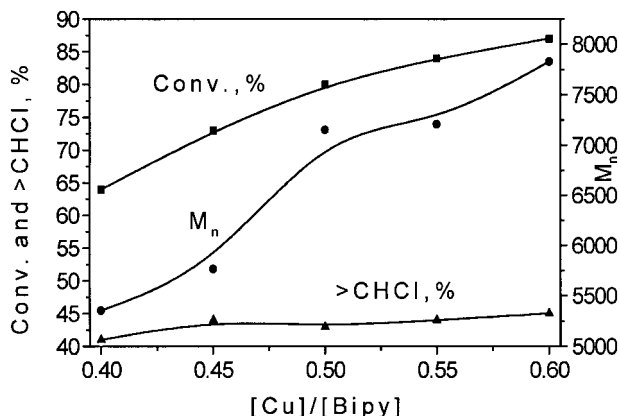
nism should be still radical polymerization. So polymerization temperature will affect not only the radical concentration in the polymerization system but also the chain propagation reaction rate constant  $k_p$ . So, the polymerization temperature should be a very vital factor in the self-condensing vinyl polymerization of CAIPA. Unfortunately, the polymerization rate is extremely slow at low temperature, and there will be apparent side reactions, such as the elimination of HCl at 130 °C. This elimination reaction will make the <sup>1</sup>H NMR spectrum so irregular and complex that it is impossible to calculate the molecular weight or the branch parameters of the polymers formed. In this paper, the polymerization temperature was selected at 125 °C, and mainly the influences of the Bipy/CAIPA ratio on polymerization rate and polymer structures were investigated. It has been recently noted that the Cu/Bipy ratio can be increased up to 1:1,<sup>35,36</sup> so the influence of the CuCl/CAEA ratio was also studied. The experimental results are listed in Table I and Figure 5. Polymerization accelerates when the Bipy/CAIPA ratio increases; at the same ratio of Bipy to CAIPA, the polymerization accelerates also when more CuCl is used.

When the molecular weight of the polymers formed increases along with polymerization time, the numbers of groups A\* and B\* in a selected macromolecule also increase, so it is reasonable to consider that the number of radicals formed in

**Table I** Influences of Polymerization Time and the Ratios of [M]/[Bipy]/[CuCl] on the Polymerization of CAIPA at 125 °C

No.	[M]/[Bipy]/[CuCl]	Time (h)	Conv (%)	$M_n$	>CHCl (%)
01	1/0.05/0.025	24	30	9610	6
02	1/0.1/0.03	12	20	6559	14
03	1/0.1/0.05	12	36	13880	24
04	1/0.15/0.05	12	49	32659	31
05	1/0.15/0.075	12	50	35057	33
06	1/0.2/0.07	9	64	18950	38
07	1/0.2/0.1	9	74	2886 <sup>a</sup>	41
08	1/0.2/0.1	6	67	9925	38
09	1/0.25/0.08	9	72	20279	39
10	1/0.25/0.125	6	73	22530	39
11	1/0.25/0.125	9	79	6003 <sup>a</sup>	40
12	1/0.3/0.1	4	70	13748	42
13	1/0.3/0.15	4	79	5997 <sup>a</sup>	39
14	1/0.4/0.2	1.5	80	7152	43
15	1/0.4/0.2	2	86	10148	42
16	1/0.5/0.25	2	89	6258 <sup>a</sup>	43
17	1/0.5/0.25	1	76	7671	44

<sup>a</sup>  $M_n$  of the soluble part.



**Figure 5** The effect of  $[\text{CuCl}]/[\text{Bipy}]$  on monomer conversion, number average molecular weight, and the percentage of the secondary ester halide polymerization at 125 °C for 70 min ( $[\text{CAIPA}]/[\text{Bipy}] = 1:0.4$ ).

the macromolecule increases too. As a result of the increased radical number in one macromolecule, the probability of the coupling reaction between two macromolecules derived from radical-radical recombination will increase gradually. Finally, the polymerization system will become gel because of the coupling reaction. In other words, macromolecules of higher molecular weight will more easily undergo a crosslinking reaction and become gel because they have more radicals in their molecules; therefore, the soluble part left after the crosslinking reaction must have a relatively low molecular weight. Furthermore, it is also reasonable to deduce that the appearance of insoluble material will be somewhat earlier when more Bipy or CuCl is used. Results listed in Table I coincide well with these deductions. The determined molecular weights of samples 07, 11, 13, and 16 are lower than expected, because these samples should have been derived from the crosslinking reaction of fractions of higher molecular weight over a long polymerization time. Indeed, the polymerization system will become gel after 9 h of polymerization when the ratio of Bipy to CAIPA is 0.2, whereas the crosslinking reaction will occur after only 4 or 2 h of polymerization at the Bipy-to-CAIPA ratio of 0.3 or 0.5.

Degree of branching is a very important parameter in characterizing hyperbranched polymers. As indicated by the results just presented, polymers obtained from CAIPA do not possess perfect dendritic architecture because of the structure difference between groups B\* and A\*. In this paper, the percentage of group A\*, the secondary ester halide, is selected as the param-

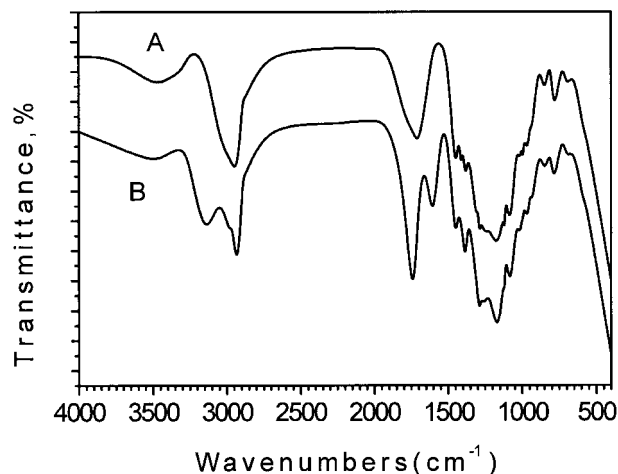
eter to characterize the branched structure of the polymers prepared. As shown in Table I and Figure 4, and similar to the dependence of monomer conversion or molecular weight on the catalyst-to-CAIPA ratios, the percentage of the secondary ester halide shifts to 50% when more Bipy is used. Also, increasing the dosage of CuCl aids the formation of branch structures at a low ratio of Bipy to CAIPA.

In summary, it can be concluded that both the polymerization rate and polymer structures depend dramatically on the ratios of Bipy to CAIPA. Increasing the ratio of Bipy to CAIPA not only accelerates the polymerization but also favors the formation of branched structures. However, the molecular weight of the hyperbranched polymers will be relatively lower when a higher ratio of Bipy to CAIPA is used because of the crosslinking reaction derived from radical-radical recombination. Therefore, this crosslinking reaction must be the key to solving the contradiction concerning polymerization rate, especially the branch structure and molecular weight in the preparation of hyperbranched polymers from the self-condensing vinyl radical polymerization catalyzed by the complex of Bipy and CuCl.

In general, hyperbranched polymers exhibit improved solubility in organic solvents compared with their linear analogs of similar molecular weight, as also observed in our experiment. The solubility improvement of the polymers obtained is dramatically dependent on the ratio of Bipy to CAIPA. Sample 01 has similar molecular weight to sample 15, but the difference between their solubility in acetone is very apparent. Sample 15 can dissolve completely in acetone, with a solid content >50%, and the polymer solution is transparent because of the hyperbranched structure. Sample 01 can only partial dissolve in acetone, even though the solid content is <10%, and the polymer solution remains semitransparent because of its almost linear structure. Sample 12, with a molecular weight of 13748, can also dissolve in acetone completely and form a transparent polymer solution. These experimental results provide more proof of the presence of branch structure in the polymers prepared and the dependence of branch degree on the ratio of Bipy to CAIPA.

#### Copolymerization of CAIPA with Styrene

Because the hyperbranched polymer from CAIPA is a viscous solid with a subambient  $T_g$ , styrene



**Figure 6** (A) FTIR spectrum of linear poly(CAIPA). (B) FTIR spectrum of the same hyperbranched copolymer as in Figure 2B.

was introduced as a comonomer to synthesize hyperbranched polymers of higher  $T_g$ . The  $^1\text{H}$  NMR spectrum of the hyperbranched copolymer from CAIPA and styrene, with mole fraction of monomer CAIPA in the monomer mixture during copolymerization [ $f_{\text{CAIPA}}$ ] = 0.5, is shown in Figure 2. The others copolymers have similar spectra to those in Figure 2B. The peaks for chemical shift at  $\sim 7.0$  ppm, from the benzene ring, prove the existence of the styrene unit in the copolymers. The weight percent of CAIPA or styrene in the copolymer was calculated according to the peak area in the spectrum. The apparent peaks at chemical shift  $\delta = 4.7$  ppm, corresponding to the proton of the secondary ester halide, indicate the branch structures in the copolymers formed. Other more direct proof supporting the branched structures is provided by the following experimental phenomena: when the copolymers obtained were purified by reprecipitation from the

acetone solution into excess petroleum ether, the copolymers precipitated very slowly. The FTIR spectrum of the same copolymer sample as in Figure 2B is shown in Figure 6B. For comparison purposes, the FTIR spectrum of linear poly(CAIPA) is also plotted as curve A in Figure 6. The peak at  $1600\text{ cm}^{-1}$  in curve B proves again the existence of a styrene unit in the hyperbranched copolymer backbone. Therefore, it can be concluded that CAIPA can successfully copolymerize with styrene to form a hyperbranched copolymer. The detailed polymerization and DSC determination results are listed in Table II. These results indicate that the  $T_g$  increases when the weight percentage of styrene unit in the copolymer increases. The direct and main reason for the increase of  $T_g$  should be that styrene is a relatively rigid structural unit compared with CAIPA. The decreases of the free volume of the copolymer derived from the decrease of the degree of branching may be also a reason; however, it should be pointed out that CAIPA will introduce an ester group into the polymer main chain when it acts as a branch unit. It must be emphasized here that there isn't any insoluble material formed throughout the copolymerization processes, although the monomer conversion is relatively high. This result can be simply explained by the decrease of the concentration of CAIPA and catalyst because of the introduction of styrene.

### Thermal Gravimetry Analysis

Because of structural differences, including especially the presence of the secondary ester halide structure in the branched polymers, significant differences in thermal stability are expected. As shown in Figure 7, both the linear poly(CAIPA) and linear poly(CAIPA-co-styrene) exhibit higher thermal stability than their branched analogs.

**Table II** Copolymerization Data of CAIPA with Styrene in Bulk at  $125^\circ\text{C}^a$

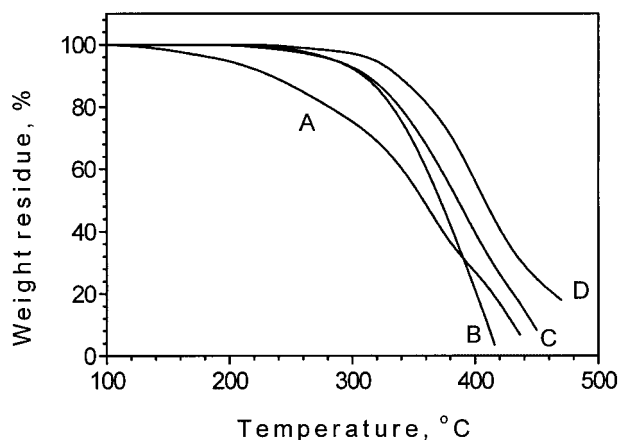
No	$f_{\text{CAIPA}}$	Time (h)	Conv. (%)	$F_{\text{CAIPA}}$	$T_g$ ( $^\circ\text{C}$ ) <sup>b</sup>	$M_{n,\text{SEC}}$	$M_w/M_n$
01	0.1	15	92	0.13	96	8365	2.7
02	0.2	15	85	0.24	85	6848	2.3
03	0.3	15	88	0.35	77	5983	2.7
04	0.4	15	81	0.40	70	5295	3.1
05	0.5	15	90	0.46	— <sup>c</sup>	4834	3.4

<sup>a</sup> [CAIPA]/[Bipy]/[CuCl] = 1/0.4/0.2.

<sup>b</sup> In  $\text{N}_2$  at  $20^\circ\text{C}/\text{min}$ ,  $T_g$  of linear polystyrene determined is  $105^\circ\text{C}$ .

<sup>c</sup> Glass transition has not been observed in the temperature range employed.





**Figure 7** TG curves of linear and hyperbranched polymers of CAIPA and CAIPA with styrene (in air at 10 °C/min): (A) sample 15; (B) linear poly(CAIPA); (C) hyperbranched polymer 05 from CAIPA with styrene; (D) linear poly(CAIPA-co-styrene).

The initial weight loss temperatures of linear polymer and copolymer are 226 and 245 °C, respectively; however, these temperatures are only 134 and 232 °C, respectively, for the hyperbranched polymer of CAIPA and CAIPA with styrene.

## CONCLUSION

The self-condensing vinyl polymerizations of CAIPA and CAIPA with styrene were studied. Hyperbranched polymers were prepared by atom transfer radical polymerization. CAIPA exhibits very distinctive polymerization behavior. In view of monomer conversion, the polymerization is similar to classical chain polymerization. However, the molecular weight of the polymers formed increases exponentially with polymerization time during the initial stage of polymerization, and then the rate of increase slows down. Because CAIPA is a typical asymmetric monomer, the polymerization is different from an ideal self-condensing vinyl polymerization due to the unequal reactivity of groups A\* and B\*. Both the polymerization rate and the branch structure of the polymers prepared depend dramatically on the ratio of catalyst to monomer. At a low catalyst-to-CAIPA ratio, the polymers prepared do not have a high degree of branching, and the polymerization rate is also relatively slow. However, there will be a significant tendency to crosslink during polymerization when the catalyst-to-monomer ratio is

increased. As a result of radical-radical recombination, there is a contradiction between preparing polymers with a high degree of branching and preparing polymers with high molecular weight. When styrene was introduced as a comonomer, polymerization could occur smoothly without a crosslinking reaction because of the decreased concentration of catalyst and radical. The glass transition temperature of the hyperbranched polymers of CAIPA with styrene rises when the content of styrene is increased. Because the secondary ester halide is more labile to heat than the primary one, the hyperbranched polymer of CAIPA and copolymer of CAIPA with styrene show lower thermal stability than their linear analogs. It is reasonable to expect that hyperbranched polymers prepared from CAIPA, a very cheap AB\* monomer, will find application in the fields of coating and adhesive of high solid content.

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## REFERENCES

1. Webster, O.W. *Science* 1991, 251, 887.
2. Frechet, J.M.J. *Science* 1994, 263, 1710.
3. Leduc, M.R.; Hawker, C.J.; Dao, J.; Frechet, J.M.J. *J Am Chem Soc* 1996, 118, 11111.
4. Jasen, J.F.; De Brabander vanden Berg, E.M.; Meijer, E.W. *Science* 1994, 26, 1226.
5. Malmstroem, E.; Johansson, M.; Hult, A. *Macromolecules* 1995, 28, 1698.
6. Kim, Y.H. *J Polym Sci Polym Chem* 1998, 36, 1685.
7. Desimone, J.M. *Science* 1995, 269, 1060.
8. Yan, D.; Zou, Z. *Macromolecules* 1999, 32, 819.
9. Frechet, J.M.J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M.R.; Grubbs, R.B. *Science* 1995, 263, 1080.
10. Scott, G.G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* 1996, 29, 1079.
11. Weimer, M.W.; Frechet, J.M.J.; Gitsov, I. *J Polym Sci Polym Chem* 1998, 36, 955.
12. Hawker, C.J.; Frechet, J.M.J.; Grubbs, R.B.; Dao, J. *J Am Chem Soc* 1995, 117, 10763.
13. Matyjaszewski, K.; Scott, G.G.; Kulfan, A.; Podwika, M. *Macromolecules* 1997, 30, 5192.
14. Matyjaszewski, K.; Scott, G.G. *Macromolecules* 1997, 30, 7034.
15. Matyjaszewski, K.; Scott, G.G. *Macromolecules* 1997, 30, 7042.
16. Hawker, C.J.; Barclay, G.G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* 1996, 29, 5245.

17. Matyjaszewski, K.; Pyun, J.; Gaynor, S.G. *Macromol Rapid Commun* 1998, 19, 665.
18. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
19. Matyjaszewski, K.; Patten, T. E.; Xia, J. *J Am Chem Soc* 1997, 119, 674.
20. Matyjaszewski, K.; Patten, T. E.; Xia, J. *Science* 1996, 272, 866.
21. Percec, V.; Barboiu, B.; Newmann, A.; Ronda, J. C.; Zhao, H. *Macromolecules* 1996, 29, 3665.
22. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
23. Grimaud, T.; Matyjaszewski, K. *Macromolecules* 1997, 30, 2216.
24. Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* 1996, 29, 8576.
25. Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1997, 30, 2244.
26. Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1997, 30, 2249.
27. Jo, S. M.; Paik, h. J.; Matyjaszewski, K. *Polym Prepr* 1997, 38, 697.
28. Matyjaszewski, K. *Chem Eur J* 1999, 5, 3095.
29. Patten, T.E.; Matyjaszewski, K. *Adv Mater* 1998, 10, 901.
30. Patten, T.E.; Matyjaszewski, K. *Acc Chem Res* 1999, 32, 895.
31. Yan, D.; Muller, A. H. E.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7024.
32. Muller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* 1997, 30, 7015.
33. Matyjaszewski, K.; Wang, J.L.; Grimaud, T.; Shipp, D.A. *Macromolecules* 1998, 31, 1527.
34. Wang, J.L.; Grimaud, T.; Matyjaszewski, K. *Macromolecules* 1997, 30, 6507.
35. Levy, A.T.; Olmstead, M.M.; Patten, T.E. *Inorg Chem* 2000, 39, 1628.
36. Kickelbick, G.; Reinohl, U.; Ertel, T.S.; Weber, A.; Bertagnolli, H.; Matyjaszewski, K. *Inorg Chem* 2001, 40, 6.