

Preparation of hyperbranched polymers by self-condensing vinyl radical polymerization

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Abstract

A novel acrylic AB* monomer, 2-(2-chloroacetoxy)-ethyl acrylate (CAEA), was prepared from 2-hydroxyethyl acrylate with chloroacetyl chloride in the presence of triethylamine. The self-condensing vinyl polymerization of CAEA and CAEA with styrene catalyzed by the complex of CuCl/2,2'-bipyridyl has been studied. Hyperbranched polymers and copolymers containing ester groups in the main chain were prepared from radical polymerization. All the polymerization products were characterized by ¹H-NMR. It has been proved that CAEA exhibits distinctive polymerization behavior. During the initial stage of the polymerization, molecular weight of the polymer formed increases exponentially with polymerization time, and then the increase rate slows down. However, a significant amount of monomer remains present throughout the polymerization consistent with typical chain polymerization. Also, if a much longer polymerization time was used, the polymerization system became gel. As a result of the unequal reactivity of the primary ester halide and the secondary ester halide, 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 CAEA. Hyperbranched polymers and copolymers exhibit improved solubility in organic solvent. However, they have some lower thermal stability compared with their linear analogs. © 2001 Elsevier Science Ltd. All rights reserved.

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1. 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 as expected [1,2]. A method commonly used to achieve these goals is the introduction of branching into polymer structure. Dendritic polymers provide dramatic examples of the effect of branching on polymer

structure and properties, as they have been shown to exhibit a number of physical properties distinctly different from linear polymers [3,4]. 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 and one-pot reactions [5–8]. These polymers are usually obtained by the reaction of AB₂ 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 AB₂ monomer, reaction between two monomers results in the formation of a dimer with one A group and

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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. Besides 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 (SCVP), by which functionalized vinyl monomers can be used to synthesize hyperbranched polymers with a whole carbon backbone from a cationic polymerization [9]. In the method described by Frechet, 3-[(1-chloroethyl)ethenyl]benzene was used as the monomer and was cationically polymerized in the presence of SnCl_4 . This monomer satisfies the AB_2 requirements for formation of hyperbranched polymers as the vinyl group acts as the difunctional group and an additional alkyl halide functional group acts as the A group. By activation of the A group, by the Lewis acid, polymerization through the double bond occurred cationically. After this original idea and pioneer work, Hawker, Scott, Weimer, Matyjaszewski and Frechet have extended this method into living radical polymerization field, the monomers employed were 4-(chloromethyl) styrene and self-made styrene type monomers [10–12]. However, because the cost of the monomers used is very expensive, or the preparation of the monomer is too trivial to process [10–13]. The related works in the preparation, properties and application of hyperbranched polymers by SCVP are relatively few. The goal of this paper is to prepare a new functional acrylate monomer capable of occurring self-condensing vinyl living radical polymerization through classical and simple organic synthesis reaction in very low cost. It has been proved that new hyperbranched polymers and copolymers containing ester groups in their backbone can be synthesized from this new monomer prepared.

2. Experiment

2.1. Reagents

2-hydroxyethyl acrylate, a commercial product from Wuxi Huayi chemicals factory, was used as received. 2,2'-bipyridyl (Bipy) is analytical reagent and 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°C and 107°C was collected and used. Copper(I) chloride (CuCl , A.R. grade) was purified by stirring in acetic acid, washing with methanol, and then drying under

reduced pressure. AIBN, A.R grade, was recrystallized from ethanol. Acetone, tetrahydrofuran (THF), ethanol, acetic acid, methanol, petroleum ether (30–60°C), ether, triethylamine, activated charcoal, H_2SO_4 and NaHCO_3 , A.R grade, were used without further purification.

2.2. Preparation of 2-(2-chloroacetyloxy)-ethyl acrylate

2-hydroxyethyl acrylate (8 ml; 0.125 mol), triethylamine (21 ml; 0.15 mol), 100 ml ether and a little CuCl were added into a three-neck flask equipped with thermometer and stirrer. Chloroacetyl chloride (10 ml, 0.125 mol) dissolved in 25 ml ether was added dropwise into the flask under stirring in a period of 1 h at 0–4°C. After the addition of chloroacetyl chloride, the reaction was carried out at 35°C for 6 h. The reaction mixture was washed with diluted H_2SO_4 (10% in weight) three times at first, then concentrated NaHCO_3 solution and distilled water three times respectively. An orange transparent ether solution was obtained after these above 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 slightly yellow transparent oil liquid in a yield of 63%.

2.3. Typical polymerization procedure of CAEA

In a typical polymerization, Bipy (0.624 g; 4.0 mmol; 0.4 equiv), CuCl (0.2 g; 2.0 mmol; 0.2 equiv), CAEA (1.92 g; 10 mmol; 1.0 equiv) and a stirrer bar made of PTFE were added into a dry flask. The flask was cycled between vacuum and nitrogen more than 10 times to remove the oxygen. Then the flask was sealed and placed in a preheated, thermally regulated oil bath at $125 \pm 1^\circ\text{C}$. After a certain period of polymerization, the flask was removed from the oil bath and allowed to cool for a few minutes. 12 ml acetone was added into the flask, and the mixture was stirred at room temperature to complete the dissolution of the polymer, then petroleum ether (five times to acetone in volume) was added to precipitate the resulting polymer. After repeating the above dissolution and precipitation processes another time, the resulting polymer was dried at 50°C under reduced pressure and the monomer conversion or polymer yield was calculated gravimetrically. Finally, excess acetone was added into 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 with the mixture of petroleum ether and acetone (volume in 5:1) three times. After completely drying under reduced

pressure at 50°C for at least 24 h, an orange transparent polymer was obtained.

2.4. Typical copolymerization procedure of CAEA 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), CAEA (1.44 g; 7.5 mmol; 1.0 equiv), styrene (3.12 g; 30 mmol; 4 equiv), and a stirrer bar made of PTFE, were added into a dry flask. The following pretreatment and polymerization process were the same as that stated in Section 2.3. After polymerization, about 25 ml 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 with methanol three times, then purified by reprecipitation from the acetone solution into excess petroleum ether. Drying at room temperature for several hours allowed volatilization of the solvent, 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.

2.5. Preparation of linear polymer of CAEA and copolymer of CAEA with styrene

Linear poly(CAEA) was prepared as follows: CAEA (7.68 g, 0.04 mol) and AIBN (0.0384 g, 0.5% of CAEA in weight) were added into a round bottom flask, the flask was placed into an oil bath at 50°C. After a certain period of polymerization, tetrahydrofuran 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. Yield was 13%.

Linear poly(CAEA-co-styrene) was prepared as follows: CAEA (7.68 g, 0.04 mol), styrene (4.56 g, 0.04 mol) and AIBN (0.0612 g, 0.5% of monomer in wt.) were added into a round bottom flask, the flask was placed into an oil bath at 50°C. After a certain period of polymerization, tetrahydrofuran 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, yield was 25%. The ¹H-NMR is illustrated in Fig. 5A, F_{CAEA} was calculated and is equal to 0.47.

2.6. Characterization methods

NMR: NMR spectra were taken on a Bruker ARX-300 type NMR spectrometer at room temperature in CDCl₃.

SEC: Size exclusion chromatography was processed at room temperature in tetrahydrofuran. The data were obtained with linear polystyrene standards.

FTIR: FTIR was carried out on a Nicolet FTIR 20 SX/B spectrometer.

Thermal analysis: Thermal analysis was performed on a PE-7 thermal analysis system. DSC was carried out under N₂ atmosphere with a temperature range 50–150°C heated at 20°C/min. TG was carried out under air atmosphere, in a temperature range of 25–310°C, with a heating rate of 10°C/min.

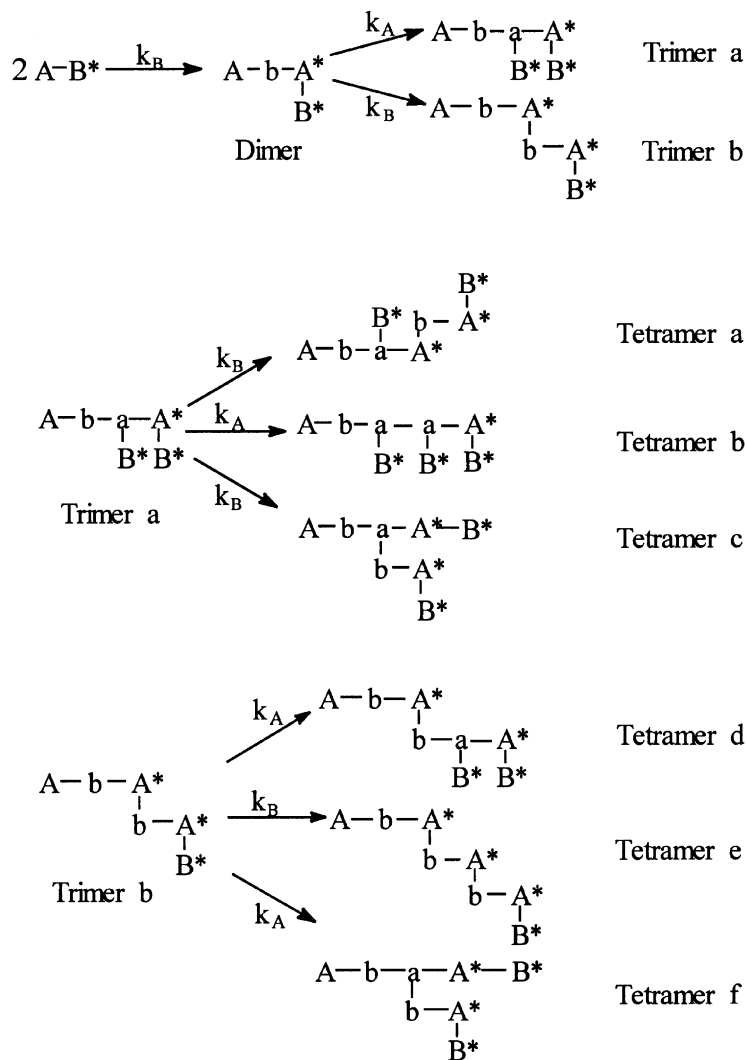
3. Results and discussion

3.1. The self-condensing vinyl polymerization of CAEA

Scheme 1 shows the idealized case of the polymerization. Upon 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 at this structural group monomer can be added; it can be either an active site or in its 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 obviously that the degree of branching will be directly related to the rate constant k_A and k_B [14,15].

For comparison purpose, Fig. 1A and B illustrates the ¹H-NMR spectrum of CAEA with the assignment of the peaks and the ¹H-NMR spectrum of linear poly(CAEA). Fig. 1A is in conformity with its expected structure. Fig. 1C is the ¹H-NMR spectrum of the hyperbranched polymer sample no. 13 from CAEA; it 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 carbon-carbon double bond, group A, at the focal point of the hyperbranched polymers. From the total area of these three peaks, the unite peak area of one proton in hyperbranched polymers can be determined and expressed as S_i . The peaks for chemical shift at $\delta = 4.7, 4.4$ and 4.2 ppm are related to the protons of the secondary ester halide, group A*, -COOCH₂CH₂OOC- and the primary ester halide, group B*, respectively, the area of these peaks is expressed as S_1, S_2 and S_3 . The area of the others peaks around chemical shift from $\delta = 1.0$ –2.8 ppm is expressed as S_4 . Assuming that there are no side reactions, such as termination by coupling or intramolecular cyclization, each hyperbranched polymers should have only one double bond. So the number average polymerization degree X_n or number average molecular weight M_n , the number of group A* or group B* as well as their percentage of the hyperbranched polymers can be calculated according to Eqs. (1)–(5)

$$X_n = (3S_i + S_1 + S_2 + S_3 + S_4)/9S_i \quad (1)$$



Scheme 1. Polymerization procedure of CAEA catalyzed by the complex of Bipy and CuCl.

$$M_n = 192X_n \quad (2)$$

$$N_{-CH_2Cl} + N_{>CHCl} = X_n \quad (3)$$

$$(2N_{-CH_2Cl} + N_{>CHCl} + 4X_n)S_i = S_1 + S_2 + S_3 \quad (4)$$

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

Here 9 is the total proton number of one molecule of CAEA, 192 is the molecular weight of CAEA, N_{-CH_2Cl} and $N_{>CHCl}$ are the number of group B^* and group A^* .

Further support for the assignment of ester halide signals can be obtained from pulse field gradient heteronuclear multiple quantum correlation (HMQC) and distortionless enhancement by polarization transfer

(DEPT) NMR experiments. Fig. 2A, which shows the HMQC spectrum of the same polymer sample as in Fig. 1C, clearly demonstrates that the proton near 4.2 ppm is attached to a C-atom near 42 ppm (a methylene, $-CH_2-$ group, according to the DEPT spectrum, Fig. 1B) and the proton near 4.7 ppm connected to a C-atom near 56 ppm (a methane $-CH-$ group, Fig. 2A and B).

Fig. 3 shows the dependence of monomer conversion, number average molecular weight and the percentage of the secondary ester halide, group A^* , on polymerization time of CAEA at 125°C catalyzed by the complex of CuCl and Bipy. 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. It is

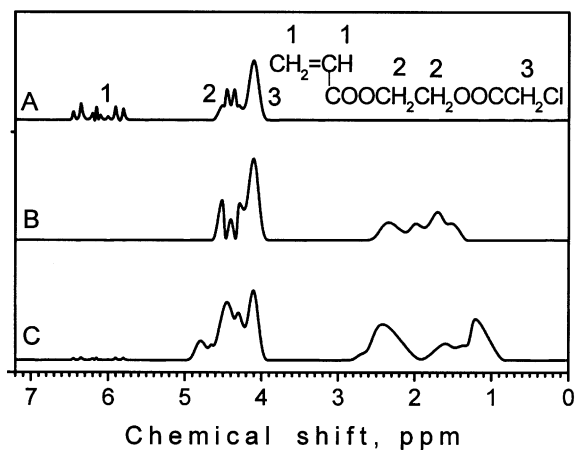


Fig. 1. (A) ¹H-NMR spectrum of CAEA. (B) ¹H-NMR spectrum of linear poly(CAEA). (C) ¹H-NMR spectrum of hyperbranched polymer sample 13.

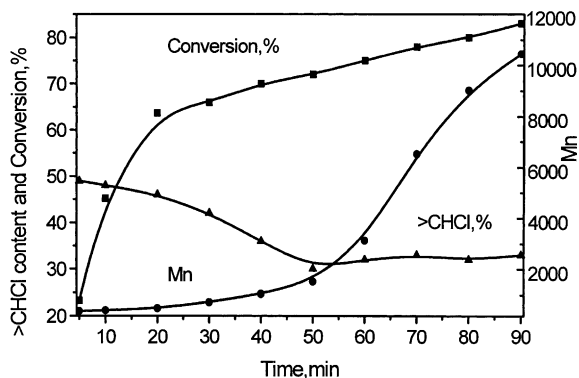


Fig. 3. The dependence of monomer conversion, number average molecular weight and the percentage of the secondary ester halide on polymerization time of CAEA at 125°C, [CAEA]/[Bipy]/[CuCl] = 1:0.4:0.2.

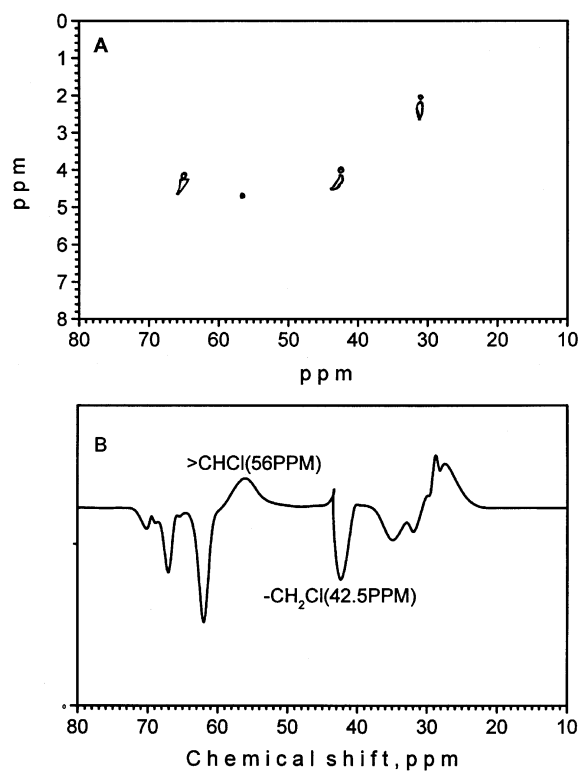


Fig. 2. (A) Gradient field heteronuclear multiple quantum correlation NMR spectrum of hyperbranched polymer sample 13. Proton signals on the *y*-axis are related to the carbon to which they are attached, *x*-axis. (B) Distortionless enhancement by polarization transfer NMR spectrum of the sample as in A. ¹³C-NMR of carbons with only one proton attached yield positive signals, while carbons with two protons attached yield negative signals.

the same as that reported by Frechet and coworkers previously for a cationic self-condensing vinyl polymerization [9]. However, the rate of increase of molecular weight slows down after about 80 min polymerization. In view of monomer conversion, it increases rapidly at first, then increases some slowly and linearly 20 min later. A significant amount of CAEA remains present throughout the polymerization, consistent with a chain growth polymerization mechanism. From the above results of molecular weight and monomer conversion increase tendencies, it can be concluded that the self-condensing vinyl polymerization behavior of CAEA is very distinctive. In the case of monomer conversion, especially the presence of CAEA in the polymerization system throughout the polymerization process, the polymerization behavior 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 [9], the number of group A* should be equal to the number of group 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 Fig. 3, 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 about 32% 1 h later. The unexpected experimental results imply that there is an apparent difference in the activation energy required to form radical $-\dot{\text{C}}\text{H}^*$ from group B* and to form radical $>\dot{\text{C}}\text{H}^*$ from group B*, the reactivity of these two radicals formed is also different, due to their different structures. It means that k_A is much bigger than k_B [14,15].

Table 1

Influences of polymerization times and the ratios of [M]/[Bipy]/[CuCl] on the polymerization of CAEA at 125°C

	[M]/[Bipy]/[CuCl]	Time	Conversion (%)	M_n^{1H-NMR}	>CHCl (%)	M_n^{SEC}	M_w/M_n
01	1/0.05/0.025	24 h	84	5900	6	6100	4.5
02	1/0.1/0.03	12 h	48	2300	12		
03	1/0.1/0.05	12 h	95	7500	16	6400	3.7
04	1/0.15/0.05	12 h	74	8500	13		
05	1/0.15/0.075	12 h	90	16 000	21	11 000	3.6
06	1/0.2/0.07	9 h	91	32 000	22	21 000	4.1
07	1/0.2/0.1	6 h	93	6200 ^a	23		
08	1/0.25/0.08	6 h	82	4000 ^a	28		
09	1/0.25/0.125	6 h	72	3000 ^a	27		
10	1/0.3/0.15	1 h	69	2600	28	1700	3.8
11	1/0.3/0.15	70 min	73	4600	30		
12	1/0.4/0.2	30 min	66	720	42		
13	1/0.4/0.2	1 h	75	3100	32	1200	5.4
14	1/0.4/0.2	70 min	78	6500	33		
15	1/0.4/0.2	1.5 h	83	10 000	33		
16	1/0.5/0.25	1 h	80	16 000	39	5400	4.5
17	1/0.5/0.25	1.5 h	83	4700 ^a	40		

^a Mn of the soluble part.

3.2. Influences of polymerization conditions on polymerization rate and the structures of the polymers formed

Although CAEA exhibits very distinctive polymerization behaviors, the chain propagation mechanism 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 CAEA. Unfortunately, the polymerization rate is extremely slow at some low temperature on one hand. On the other hand, there will be apparent side reactions such as the elimination of HCl at 130°C. This elimination reaction will make the ¹H-NMR spectrum so irregular and complex that it is impossible to calculate the molecular weight as well as the branch parameters of the polymers formed. In this paper, the polymerization temperature was selected at 125°C, and mainly the influence of Bipy and CuCl ratios to CAEA on polymerization rate and polymer structures were investigated. The experimental results are listed in Table 1 and Fig. 4 respectively. Polymerization accelerates when the ratio of Bipy to CAEA increases, at the same ratio of Bipy to CAEA; the increase of CuCl dosage can also accelerate the polymerization.

When the molecular weight of the polymers formed increases along with polymerization time, the number of group B* and group A* in a selected macromolecule also increases, so it is reasonable to consider that the number of radicals formed in the macromolecule increases too. As a result of the increased radical number in one macromolecule, the probability of the coupling reaction

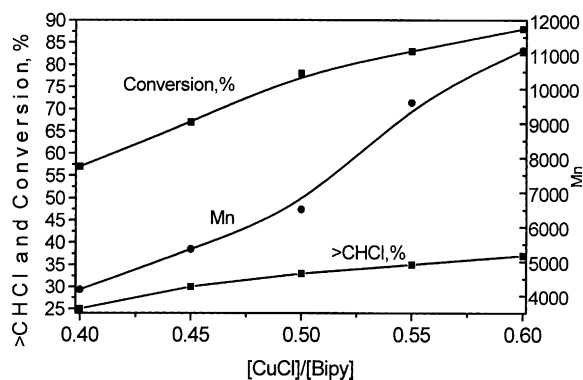


Fig. 4. The effect of [CuCl]/[Bipy] on monomer conversion, number average molecular weight and the percentage of the secondary ester halide, polymerization at 125°C for 70 min, [CAEA]/[Bipy] = 1:0.4.

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 some higher molecular weight more easily undergo crosslinking reaction and become gel because they have more radicals in their molecules, so the soluble part left after crosslinking reaction must have 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 1 coincide well with these deductions. The determined molecular weights of samples 07, 08, 09 and 17 are lower than expected, it should be derived from the crosslinking reaction of these fractions

with high molecular weight over a long polymerization time. Indeed, the polymerization system will become gel after 6 h polymerization when the ratio of Bipy to CAEA is 0.2, while the crosslinking reaction will occur after only 1.5 h polymerization at the Bipy to CAEA ratio of 0.5.

Branch degree is a very important parameter in characterizing hyperbranched polymers. As the results described in Section 3.1, polymers obtained from CAEA do not possess perfect dendritic architectures because of the structure difference between group B* and group A*. In this paper, the percentage of group A* is selected as the parameter to characterize the branched structure of the polymers prepared. As shown in Table 1 and Fig. 3, similar to the dependence of monomer conversion or molecular weight on the catalyst to CAEA ratios, the percentage of the secondary ester halide shifts to 50% when more Bipy is used. Also, increasing the dosage of CuCl at the same ratio of Bipy to CAEA is profitable to the formation of branched structures.

In a summary, it can be concluded that both the polymerization rate and polymer structures depend dramatically on the ratios of Bipy and CuCl to CAEA. Increasing the ratio of Bipy or CuCl to CAEA 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 or CuCl to CAEA is used due to the crosslinking reaction derived from radical–radical recombination. So it must be the key to solve the contradiction between 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 CAEA. Sample 01 has similar molecular weight to sample 14, but the difference between their solubility in acetone is very apparent. Sample 14 can dissolve completely in acetone with a solid content higher than 50%; the polymer solution is also transparent because of the hyperbranched structure. Sample 01 can only partially dissolve in acetone even though the solid content is lower than 10%, and the polymer solution is still semi-transparent due to its almost linear structure. The molecular weights of sample 06 and 16 are 32 000 and 16 000 respectively; they can still dissolve in acetone completely and form transparent polymer solution. These experimental results prove again the presence of branch structures in the polymers prepared and the dependence of branch degree on the ratio of Bipy to CAEA.

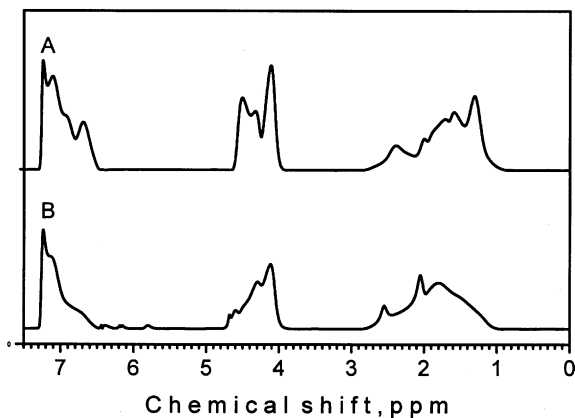


Fig. 5. (A) $^1\text{H-NMR}$ spectrum of linear poly(CAEA-co-styrene), (B) $^1\text{H-NMR}$ spectrum of hyperbranched copolymer of CAEA and styrene, polymerization at 125°C for 18 h, $[\text{CAEA}]/[\text{St}]/[\text{Bipy}]/[\text{CuCl}] = 1:1:0.4:0.2$.

3.3. Copolymerization of CAEA with styrene

Based on the investigation of the self-condensing vinyl polymerization of CAEA, styrene was introduced as a comonomer to synthesize novel hyperbranched polymer containing not only ester groups but also styrene units in the polymer backbone through radical copolymerization. Fig. 5B is the $^1\text{H-NMR}$ spectrum of the hyperbranched copolymer from CAEA and styrene with $f_{\text{CAEA}} = 0.5$. The other copolymers have similar spectra to Fig. 5B. The peaks for chemical shift at about 7 ppm, from the benzene ring, prove the existence of styrene unit in the copolymers. The weight percent of CAEA or styrene in copolymer was calculated according to the peak area in the spectrum. The apparent peaks for chemical shift at $\delta = 4.7$ ppm, corresponding to the secondary ester halide, group A*, prove the branch structures in the copolymers obtained. The other more direct proof supporting the branched structures should be 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. Fig. 6B is the FTIR spectrum of the same copolymer sample as in Fig. 5B. For comparison purpose, the FTIR spectrum of linear poly(CAEA) is also plotted as curve A. The peak at 1600 cm^{-1} in curve B proves again the existence of styrene unit in the hyperbranched copolymer backbone. So it can be concluded that CAEA can copolymerize with styrene successfully to prepare hyperbranched copolymer. Table 2 lists the detailed polymerization and DSC determination results. It shows that the glass transition temperature increases when the weight percentage of styrene unit in the copolymer increases. The direct and main reason for this increase of T_g should be

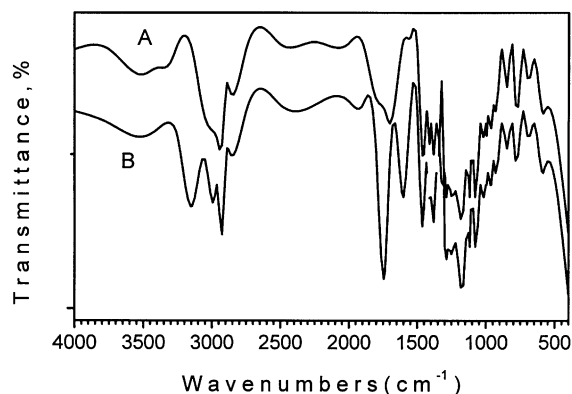


Fig. 6. (A) FTIR spectrum of linear poly(CAEA). (B) FTIR spectrum of the same hyperbranched copolymer as in Fig. 5B.

that styrene is a relatively rigid structural unit compared with CAEA, the decrease of the free volume of the copolymer because of the decrease of the degree of branching may be also a reason. However, it must be pointed out that CAEA will introduce an ester group into the copolymer main chain when it acts as a branch unit. In addition, there is not any insoluble material formed throughout the copolymerization processes, although the monomer conversion is relatively higher than that of the polymerization discussed in Section 2.2. In fact, it can be simply explained by the decrease of the concentration of CAEA and catalyst because of the introduction of styrene.

3.4. 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 Fig. 7, both the linear poly(CAEA) and linear poly(CAEA-co-styrene) exhibit higher thermal stability than their branched analogs. The initial weight loss temperature of linear polymer and copolymer is 165°C and 244°C; however, it is only 153°C

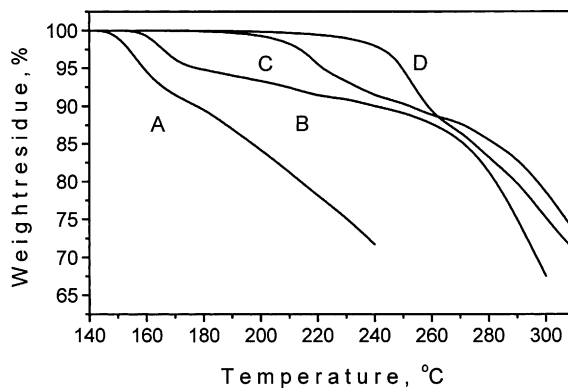


Fig. 7. TG curves of linear and hyperbranched polymers and copolymers of CAEA and CAEA with styrene (in air at 10°C/min): (A) sample 15, (B) linear poly(CAEA), (C) hyperbranched copolymer 05, (D) linear poly(CAEA-co-styrene).

and 212°C for the hyperbranched polymer and copolymer.

4. Conclusion

The self-condensing vinyl polymerization of CAEA and CAEA with styrene was studied. Novel hyperbranched polymers containing ester groups in their backbone were prepared by living free radical polymerization. It is shown that CAEA exhibits very distinctive polymerization behavior. In view of monomer conversion, the polymerization is similar to classical chain polymerization. However, molecular weight of the polymers formed increases exponentially with polymerization time during the initial stage of polymerization, and then the increase rate slows down. The polymerization is different from an ideal self-condensing vinyl polymerization because of the unequal reactivity of the primary ester halide and the secondary one. 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 CAEA ratio, the polymers prepared do not have high degree of

Table 2
Copolymerization dates of CAEA and styrene in bulk at 125°C^a

f_{CAEA}	Time (h)	Conversion (%)	F_{CAEA}	T_g (°C) ^b	$M_{n\text{SEC}}$	M_w/M_n
0.1	18	91	0.13	100	9300	2.4
0.2	15	88	0.29	92	7200	3.0
0.3	15	89	0.36	84	5900	2.9
0.4	15	85	0.40	77	5300	3.1
0.5	18	92	0.47	— ^c	4600	4.0

^a [CAEA]/[Bipy]/[CuCl] = 1/0.4/0.2.

^b In N₂ at 20°C/min, the T_g of linear polystyrene determined is 105°C.

^c Glass transition has not been observed in the temperature range employed.

branching; the polymerization rate is also relatively slow. However, the polymerization will suffer a significant tendency to crosslink when the catalyst to monomer ratio is increased. As a result of radical–radical recombination, there is a contrary between preparing polymers with a high degree of branching and preparing polymers with high molecular weight. When styrene was introduced as a comonomer, the polymerization can occur smoothly without a crosslinking reaction because of the decreased concentration of catalyst and radical. The glass transition temperature of the hyperbranched copolymers of CAEA with styrene rises when the content of styrene increased. Because the secondary ester halide is more labile to heat than the primary one, the hyperbranched polymer of CAEA and copolymer of CAEA with styrene show lower thermal stability than their linear analogs.

Acknowledgements

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