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Preparation of hyperbranched copolymers of maleimide inimer and styrene by ATRP

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Abstract

Novel hyperbranched copolymers were prepared by the atom transfer radical copolymerization of *N*-(4-α-bromobutyryloxy phenyl) maleimide (BBPMI) with styrene in 1-methyl-2-pyrrolidone (NMP) using the complex of CuBr/2,2′-bipyridine as catalyst. The copolymerization behavior was investigated by comparison of the conversion of double bond of BBPMI determined by ^{1}H NMR with that of styrene. The hyperbranched structure of resulting copolymers was verified by gel permeation chromatography (GPC) coupled with multi-angle laser light scattering (MALLS). The influences of dosage of catalyst and monomer ratio on the polymerization rate and structure of the resulting polymers were also investigated. The glass transition temperature of the resulting hyperbranched copolymer increases with increasing mole fraction of BBPMI, f_{BBPMI}. The resulting copolymers exhibit improved solubility in organic solvents; however, they show lower thermal stabilities than their linear analogues.

Keywords: Atom transfer radical polymerization; Self-condensing vinyl polymerization; Hyperbranched polymer

1. Introduction

Application of hyperbranched polymers and dendrimers as melt modifiers for plastics has attracted much attention because of their low melt viscosity [1–6], which is derived from their globe-like structure with less chain entanglement compared with linear polymers. Generally, there are two main approaches to hyperbranched polymers: Flory method and Fréchet method. Flory method involves the polycondensation of AB$_x$ ($x \geq 2$) type monomers, where A and B are reactive functional groups. Each resulting macromolecule possesses one unreacted A functional group and $(x-1)(n+1)$ unreacted B functional groups, where n is the degree of the polymerization [7–10]. Fréchet method employs the self-condensing vinyl polymerization (SCVP) of **AB*** monomers, in which **A** is a vinyl group and **B*** is a functional group that can be transformed into an active center, such as cationic [11], radical [12–16], or anionic [17,18], to initiate the polymerization of vinyl group, **A**. The **AB*** monomer is called inimer (initiator monomer). Based on the mechanism of atom transfer radical polymerization (ATRP), if **B*** is an alkyl halide, it can be transformed into a radical under the catalysis of transition-metal complexes, such as CuX/2, 2′-bipyridine (X = Cl or Br), to initiate SCVP of the inimer to produce hyperbranched polymer [12–16]. In addition to the above-mentioned two main routes, there are also some notable variants have been reported [19,20], such as multi-branching ring-opening polymerization of latent AB$_x$ monomers and A$_2$ + B$_3$ methodology, etc.

The synthesis of hyperbranched polymer by ATRP has received much attention because of the variability of vinyl monomers and mild polymerization conditions [21–26]. However, most of the hyperbranched polymers employed as melt modifiers are prepared by Flory method [2–5]. Our group has reported the use of highly branched polystyrene prepared by ATRP as melt modifier for polycarbonates [6]. When hyperbranched polymers are blended with engineering plastics with high processing temperatures, they must be sufficiently thermally stable. On the other hand, *N*-substituted maleimide has been attached much importance in the synthesis of polymers with high thermal stability [27–31]. Jiang et al. [31] synthesized copolymers of 4-(chloromethyl) styrene and *N*-cyclohexyl maleimide via ATRP. However, the heat-resistant units maleimide moieties are not in the main chains of the resulting polymers, which will lower the heat-resistant efficiency somewhat. Chen et al. [32] synthesized star polymers in one pot by ATRP of *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide and

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styrene. In this work, a novel maleimide inimer, *N*-(4-α-bromobutyryloxy phenyl) maleimide (BBPMI), was devised and hyperbranched polymers with maleimide moieties and phenyls in their main chains were prepared by the atom transfer radical copolymerization of BBPMI with styrene.

2. Experimental

2.1. Reagents

2,2′-Bipyridine (Bipy), 1-methyl-2-pyrrolidone (NMP), acetone, butanone, ethanol, tetrahydrofuran (THF), acetic acid, methanol, anisole and petroleum ether (30–60 °C) are analytical reagents from Shanghai Chemical Reagent Corporation and used as received. Copper(I) bromide (CuBr, AR grade, from Shanghai Chemical Reagent Corporation) was purified by stirring in acetic acid, washing with methanol, and then dried under vacuum. Styrene (St) was distilled under reduced pressure before use. Azodiisobutyronitrile (AIBN), AR grade, was recrystallized from ethanol. BBPMI was synthesized according to our previous report [33]. Purity of BBPMI determined by HPLC is 99.4%.

2.2. Preparation of poly(BBPMI)

Bipy (0.78 g, 5 mmol), CuBr (0.359 g, 2.5 mmol), BBPMI (3.38 g, 10 mmol), anisole (3.24 g, 30 mmol) and a magnetic stir bar were added to a 100 mL dry round bottom flask. The flask was cycled between vacuum and nitrogen (×10 times) to remove the oxygen. Then the flask was sealed and placed in a preheated, thermally regulated oil bath at 80±1 °C. After stirring for 18 h and cooling, 25 mL of acetone was added to dissolve the product. The solution was filtrated to remove the salt from catalyst. Petroleum ether (five times the acetone in volume) was added to the filtrate to precipitate the resulting polymer. After repeating the dissolution and precipitation processes another round, the polymer was dried under vacuum at 40 °C for 24 h. The ^{1}H NMR was shown in Fig. 5(A).

2.3. Preparation of hyperbranched poly(BBPMI-co-St)

Typically, Bipy (0.375 g, 2.4 mmol), CuBr (0.172 g, 1.2 mmol), BBPMI (2.03 g, 6 mmol), styrene (1.25 g, 12 mmol), NMP (1.2 g, 12 mmol) and a magnetic stir bar were added to a 100 mL dry round bottom flask. The flask was sealed with a rubber septum and then cycled between vacuum and nitrogen (×10 times) to remove the oxygen. Then the mixture was stirred at 80 °C under N_2 atmosphere. Samples were taken periodically to monitor the conversion of double bonds by ^{1}H NMR using NMP as internal standard. After reaction, the polymerization product was dissolved in butanone and filtrated to remove the salt from catalyst, then precipitated in ethanol. After repeating these dissolution and precipitation processes another round, the polymer was dried under vacuum at 40 °C for 24 h. In the following discussions, when conversion is mentioned, it will be understood that conversion of the double bonds is implied, unless stated otherwise. When yield is used, it means yield of solid polymers determined gravimetrically.

2.4. Preparation of linear poly(BBPMI-co-St)

BBPMI (2.03 g, 6 mmol), styrene (0.625 g, 6 mmol), anisole (10 mL), AIBN (0.0203 g, 1 wt% of BBPMI) and a magnetic stir bar were added into a 100 mL dry round bottom flask and the flask was placed into an oil bath at 80 °C. After polymerization for 1.5 h, the polymerization mixture was diluted by 50 mL butanone and precipitated in excessive ethanol. The resulting solid polymer was dried under vacuum at 40 °C for 24 h to yield 82%. The ^{1}H NMR spectrum of the resulting linear copolymer is shown in Fig. 5(B). Mole fraction of BBPMI, F_{BBPMI}, calculated based on ^{1}H NMR spectrum is 0.5 and $M_{\mathrm{n,GPC}}$ is 8400.

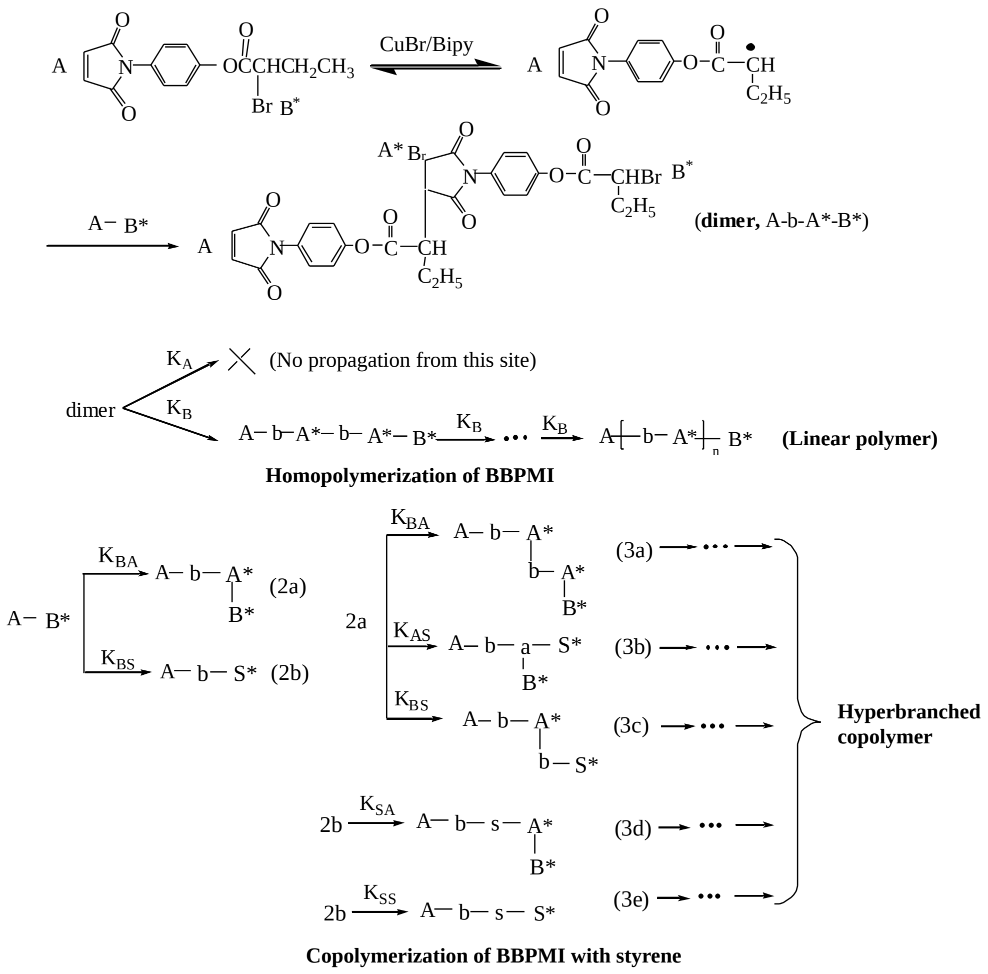
2.5. Characterization methods

The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker ARX-300 NMR spectrometer at room temperature in $CDCl_3$. Gel permeation chromatography (GPC) was performed on a GPC line consisting of a Waters 1515 isocratic HPLC pump and Waters styrage HR 4e, HR 1 and HR 0.5 column, and a Waters 2414 refractive index detector at room temperature. The eluent was tetrahydrofuran with a flow rate of 1 mL/min and the data were obtained with linear polystyrene standards. Multi-angle laser light scattering (MALLS) was conducted on 703-T mini DAWN tristar light scattering photometer. Thermal gravimetry analysis (TG) was carried out on SDTQ-600 thermalgravimetric analyzer under N_2 atmosphere in the temperature range of 50–600 °C, at a heating rate of 10 °C/min. DSC was performed on a PE-7 thermal analysis system under N_2 atmosphere with a temperature range of 50–250 °C, at a heating rate of 20 °C/min.

3. Results and discussion

3.1. Atom transfer radical copolymerization of BBPMI with styrene

As reported previously [33], the homopolymerization of BBPMI only resulted in linear polymer because of the poor activity of maleimide radicals to initiate the maleimide double bonds due to steric hindrance. On the other hand, styrene can be copolymerized with maleimide monomer to produce alternating copolymers via the formation of charge transfer complex (CTC). It is expected that the addition of styrene into the ATRP system of BBPMI can introduce chain propagation from **A***, k_{AS}, and finally results in the formation of hyperbranched copolymers, as shown in Scheme 1. In Scheme 1, all the chain propagation possibility, including k_{BA}, k_{BS}, k_{AS}, k_{SA} and k_{SS}, are included. In fact, k_{BA}, k_{BS}, k_{AS}, k_{SA} and k_{SS} are not equivalent to each other. So some of these chain propagations will occur predominantly and others may be insignificant. And the differences of these propagation rate constants will affect



Scheme 1. Homopolymerization of BBPMI and hypothetic copolymerization of BBPMI with styrene using the complex of CuBr/Bipy as catalyst. * An active site in which the bromine atom can transfer under catalysis of the complex of CuBr/Bipy, forming a radical. **A** denotes the double bond of BBPMI. **a**, **b** and **s** indicate the sites that have been consumed. k_{BA}, k_{BS}, k_{AS}, k_{SA} and k_{SS} denote the propagation rate constants of **B*** to BBPMI, **B*** to St, **A*** to St, **S*** to BBPMI and **S*** to St, respectively.

the consumption rates of BBPMI and styrene and thus the final structure of the resulting copolymers.

3.2. Kinetics of the atom transfer radical copolymerization

Fig. 1 is the ^{1}H NMR spectra of the liquid polymerization samples at various polymerization time. The peak at 6.73 ppm marked with **2** is related to the protons of double bonds of BBPMI. The peaks at 5.22–6.67 ppm marked with **3** and **4** correspond to the protons of double bonds of styrene. The strong peak at 2.85 ppm marked with **7** corresponds to the protons of methyl group attached to nitrogen atom of NMP. The conversions of double bonds are determined by comparing the peaks area of **2** and **4** with **7**. Firstly, mole ratio of BBPMI to St 1:2, is employed in copolymerization. As shown in Fig. 2(A), in the first 10 min, the conversion of BBPMI has reached 55.7%, while that of styrene is only 19.2%. To investigate the copolymerization mechanism further, mole ratio of 1:1 is employed, as shown in Fig. 2(B). In the first 15 min, the conversion of BBPMI and styrene is 66.3 and 21.4%, respectively. So it can be concluded that in the initial stage of the ATRP in NMP, the α-butyryloxy radical from **B*** initiate the double bonds of BBPMI prior to those of styrene. That is to say, $k_{BA} \gg k_{BS}$. At least two BBPMI inimers were incorporated in every resulting oligomer. So the conversion of BBPMI has been above 50% in the first 10 min.

In general, the propagation rate constant of alternating copolymerization is much faster by far than that of vinyl polymerization [34]. On the assumption that k_{BA}, k_{AS}, and k_{SA}, occur predominantly in the copolymerization, the chain propagation style in the early stage can be expressed in Scheme 2. Only k_{AS} consumes styrene, thus the conversion of styrene is lower than that of BBPMI in the early stage. As the polymerization proceeds, more and more **B*** will convert into **A*** because radical from **B*** can initiate **A** to form **A***. The active sites in polymerization system will be present mainly as **A*** and **S***.

The kinetic plots of $\ln([A_0]/[A])$ vs time for monomer ratio of 1:2 are shown in Fig. 2(A). It can be seen that the slope of the plot decreases with time. This phenomenon can be explained as follows. In the first 10 min, the consumption rate of double bonds of BBPMI, **A**, is very high, due to the SCVP of BBPMI

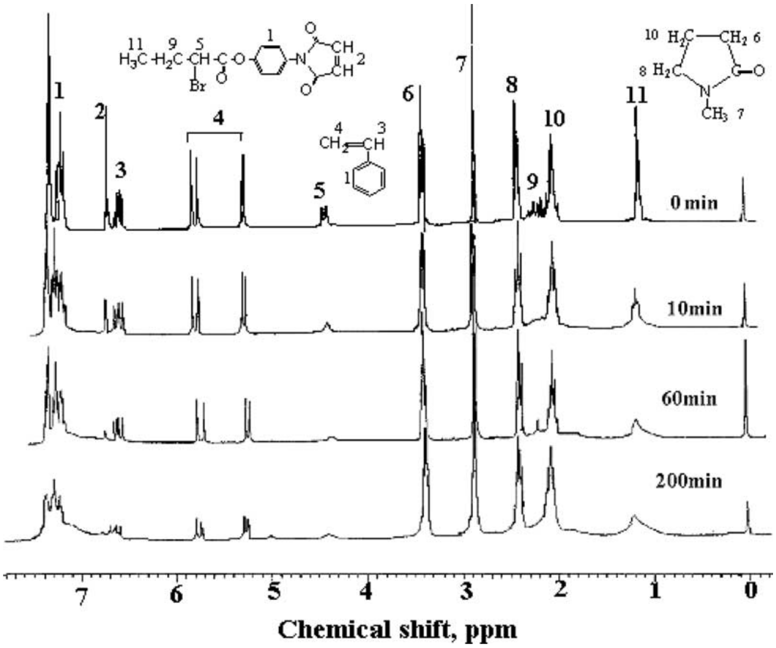


Fig. 1. ^{1}H NMR spectra of liquid samples at various polymerization time, [BBPMI]/[St]/[CuBr]/[Bipy]/[NMP] = 1/2/0.2/0.4/2, 80 °C.

to form oligomers. In the next 10–80 min, the consumption rate of **A** decreases. In this period, the chain propagation includes lots of alternating copolymerization of **A** with styrene. After polymerization for 80 min, the consumption rate of **A** decreases a little further, in which alternating propagation should be few because of the very lower concentration of **A**.

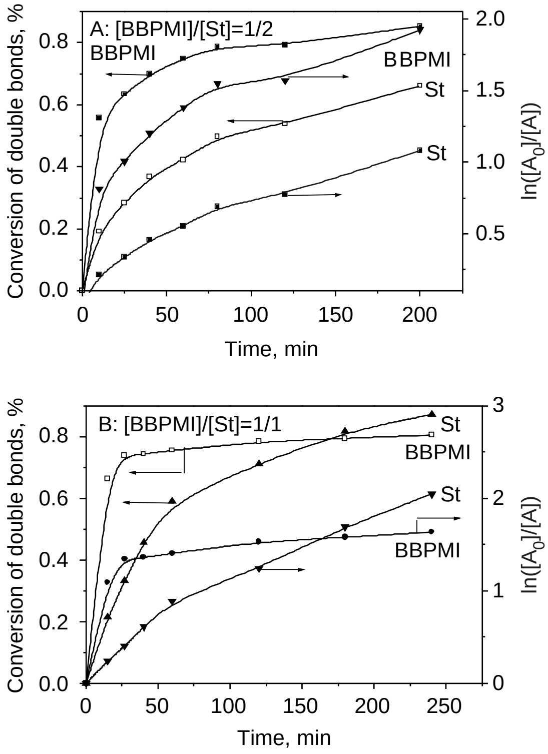
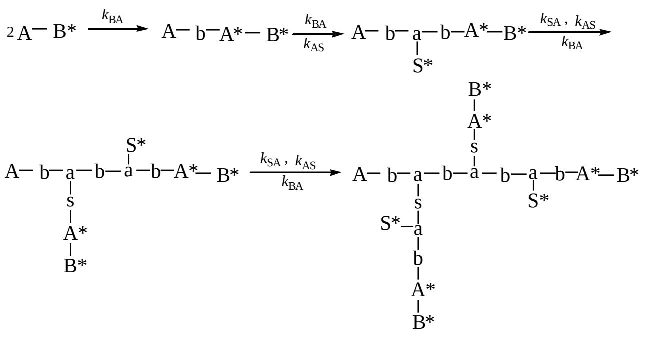


Fig. 2. Conversion of double bonds and ln($[A_0]/[A]$) plots in atom transfer radical copolymerization, [BBPMI]/[CuBr]/[Bipy]/[NMP] = 1/0.2/0.4/2, 80 °C, $[A_0]$ and $[A]$ means the initial concentration and temporal concentration of double bounds.

Because of the presence of alternating propagation, the consumption rate of St in the first 80 min is also faster than that in the next polymerization time. As shown in Fig. 2(B), when ratio of [BBPMI]/[St], 1:1, is employed, the consumption rates of double bonds of styrene and BBPMI in the early stage are also faster than that in the next polymerization time because of the same cause mentioned above.

3.3. Molecular weights of the resulting copolymers

The smaller hydrodynamic volume of hyperbranched polymer will lead to longer retention time in GPC, the molecular weight of hyperbranched polymer obtained by GPC, which is apparent value based on linear polystyrene standards, is lower than that determined by other methods, such as ^{1}H NMR and MALLS [13]. The molecular weights of the resulting copolymers determined by MALLS and GPC are showed in Tables 1 and 2 and Fig. 3. The significant discrepancies observed in the M_w determined by GPC and MALLS indicate the hyperbranched structure of the



Scheme 2. The possible chain propagation style in the early stage of the atom transfer radical copolymerization of BBPMI with styrene catalyzed by the complex of CuBr/Bipy in NMP.

Table 1
Molecular weights and characteristics of poly(BBPMI-*co*-St) prepared by ATRP with various dosage of catalyst (at 80 °C for 2 h)

Entry	[BBPMI]/[St]/ [CuBr]/[Bipy]/[NMP]	Yield (%)	$M_{\mathrm{w,GPC}}$	$M_{\mathrm{w,MALLS}}$	$M_{\mathrm{w,GPC}}/M_{\mathrm{n,GPC}}$	$M_{\mathrm{w,MALLS}}/M_{\mathrm{w,GPC}}$	$[S^*]/([A^*]+[B^*])$
1	1/2/0.05/0.1/2	59	1810	4080	1.6	2.3	–
2	1/2/0.1/0.2/2	65	3300	6200	2.0	1.9	–
3	1/2/0.15/0.3/2	69	5830	11,000	2.4	1.9	0.069
4	1/2/0.2/0.4/2	79	17,800	47,600	2.6	2.4	0.268
5	1/2/0.25/0.5/2	83	19,000	58,950	2.5	3.1	0.368
6	1/2/0.5/1/3	Gel					

Molecular weights of solid samples obtained after precipitation in ethanol.

Table 2
The characterization results of hyperbranched poly(BBPMI-*co*-St) with different monomer ratio (at 80 °C for 2 h)

Entry	[BBPMI]/[St]	f_{BBPMI}[a]	Yield (%)	F_{BBPMI}[b]	T_g (°C)	$M_{\mathrm{w,GPC}}$	$M_{\mathrm{w,MALLS}}$
1	1/4	0.20	70	0.250	150	25,100	60,000
2	1/2	0.33	79	0.358	151	17,800	47,600
3	1/1	0.50	79	0.550	152	15,800	42,300
4	1/0.5	0.67	85	0.678	158	14,500	35,500
5	1/0.25	0.80	90	0.818	160	13,500	30,100

[BBPMI]/[CuBr]/[Bipy]/[NMP] = 1/0.2/0.4/2.

[a] f_{BBPMI} means mole fraction of BBPMI monomer in the feed of styrene and BBPMI.

[b] F_{BBPMI} means mole fraction of BBPMI unit in poly(BBPMI-*co*-St) determined by ^{1}H NMR.

copolymers prepared by ATRP. The copolymers prepared by ATRP also exhibit enhanced solubility in organic solvents, such as butanone and THF, in comparison to their linear analogues.

Furthermore, as shown in Fig. 3, there are no discrepancy between $M_{\mathrm{w,GPC}}$ and $\mathrm{M}_{\mathrm{w,MALLS}}$ in first 10 min, then some discrepancies can be observed and the discrepancy increase with polymerization time, suggesting an increase of extent of branching [35]. The phenomenon reveals that the branching mainly takes place after the first hour; which is in agreement with the chain propagation behavior discussed before. In the corresponding GPC chromatograms of the resulting copolymers in Fig. 4, there are two-modal peaks can be observed. As revealed by the kinetics study using ^{1}H NMR, in the initial stage of the polymerization less than 10 min, most of BBPMI monomers and a little styrene monomers have been consumed to form oligomers. Then most styrene monomers were grafted from the oligomers with multi-active centers. Meanwhile, the oligomers coupled with each other to form branched copolymers. The two-modal peaks should correspond the polymers before and after the grafting and coupling. In the hompolymerization of BBPMI by ATRP, several oligomers can be detected throughout the polymerization in GPC [33].

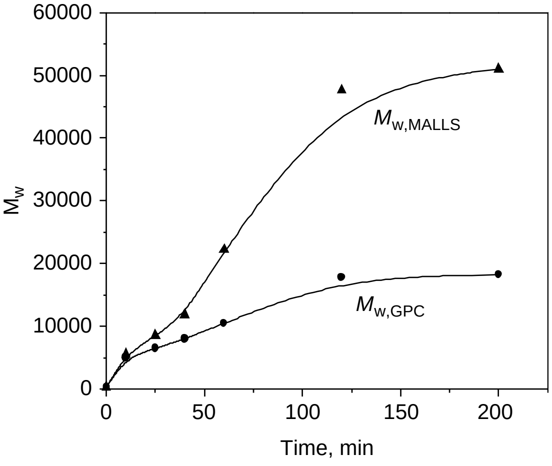


Fig. 3. Dependence of molecular weights of resulting solid copolymers after precipitation on polymerization time, [BBPMI]/[St]/[CuBr]/[Bipy]/[NMP] = 1/2/0.2/0.4/2, 80 °C.

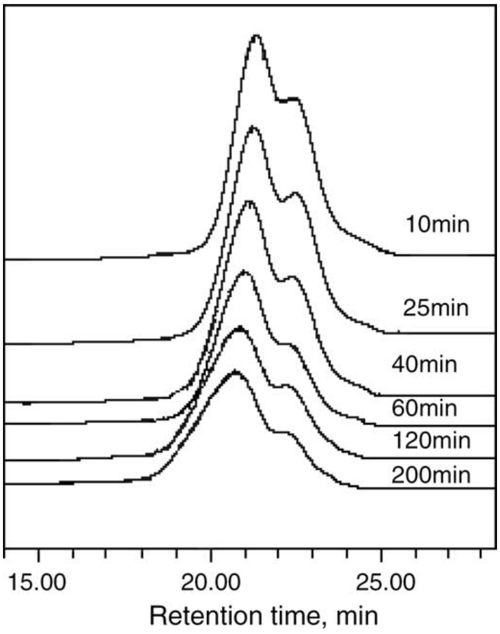


Fig. 4. GPC chromatograms of the resulting solid copolymers after precipitation at various polymerization time, [BBPMI]/[St]/[CuBr]/[Bipy]/[NMP] = 1/2/0.2/0.4/2, 80 °C.

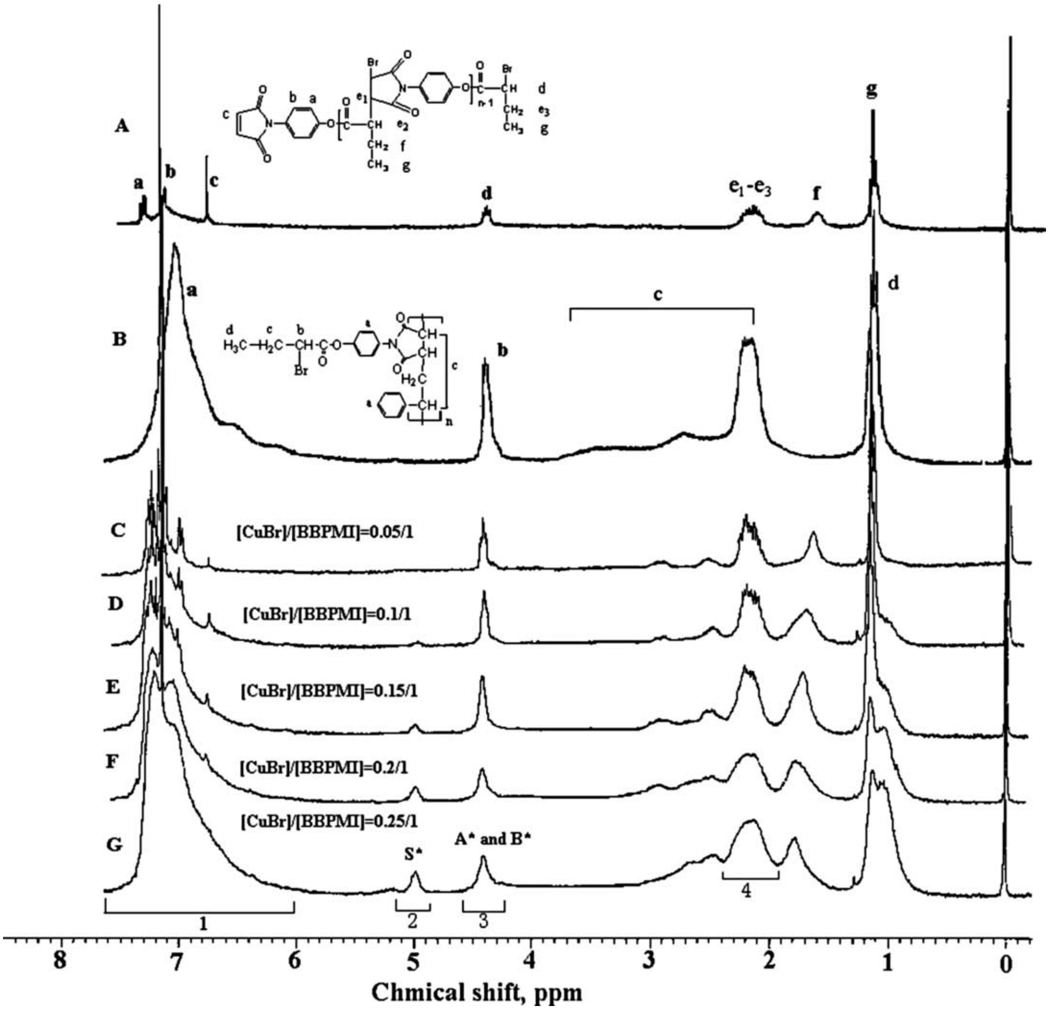


Fig. 5. (A) ^{1}H NMR spectrum of poly(BBPMI) prepared by ATRP; (B) ^{1}H NMR spectrum of linear poly(BBPMI-*co*-St); (C)–(G) ^{1}H NMR spectra of poly(BBPMI-*co*-St) prepared by ATRP with various ratio of [CuBr]/[BBPMI], [BBPMI]/[St]/[NMP] = 1/2/2, [CuBr]/[Bipy] = 1/2, at 80 °C for 2 h.

Obviously, the addition of styrene not only can lead to the formation of hyperbranched structure but also accelerate the polymerization to prepare products with much higher molecular weights.

3.4. Dosage of catalyst and monomer ratio on the structure and molecular weights of the resulting copolymers

Generally, the dosage of catalyst has very noticeable effect on polymerization rate and the degree of branching of the resulting polymer in SCVP of **AB*** inimer based on ATRP [13,35]. The ^{1}H NMR spectra of poly(BBPMI-*co*-St) prepared by ATRP with various ratios of [CuBr]/[BBPMI] are shown in Fig. 5. For comparison, the ^{1}H NMR spectra of poly(BBPMI) prepared by ATRP, linear poly(BBPMI-*co*-St) prepared by traditional free radical polymerization were also shown in Fig. 5. Because poly(BBPMI) prepared by ATRP is oligomer ($M_{n,GPC} = 2000$) [33], the signal corresponding to double bond of BBPMI inimer at 6.73 ppm is strong, and the signals at 2.1 ppm partly derived from –CH_2– in CH_3–CH_2–CHBr– still keep the multi-peak characteristics of that of BBPMI inimer since many **B*** still be present as terminal groups [33]. Generally, the linear poly(BBPMI-*co*-St) has an alternating structure due to the formation of charge transfer complex (CTC) and the alternating structure of similar copolymer has been verified [32]. In Fig. 5(B), the signals derived from protons of –CH_2– in CH_3–$\mathbf{CH_2}$–CHBr– group in region **4** also keep the multi-peak characteristics since **B*** is only present as a pendant group. The signal at 6.73 ppm is very weak in the spectrum of poly(BBPMI-*co*-St) prepared by ATRP, indicating the formation of polymers with high molecular weights. Appearance of new peaks at 1.7 and 5.0 ppm in the spectrum of poly(BBPMI-*co*-St) prepared by ATRP compared with that of alternating linear copolymer suggests that the copolymers prepared by ATRP is not of a linear structure. Furthermore, the signal in region **4** of Fig. 5(C)–(E) corresponding to the copolymers with lower ratios of [CuBr]/[BBPMI] still partly keep the multi-peaks characteristics, suggesting the presence of CH_3–CH_2–CHBr–COO– group. That is to say, quite a few of **B*** are still present in the resulting copolymers and do not initiate chain propagation to form branching chains. As mentioned previously, most **B*** should be converted into **A*** and **S*** in the final structure of the resulting copolymers. After polymerization for a period of time, quite a few of **S*** has been present in the polymerization system. The activation energy required to form radical from **B*** may be higher than that required to form radical from **A*** or **S***. So some **B*** are retained in the obtained polymer when dosage of catalyst is low. Fig. 5(F) and (G) correspond to the copolymers with higher ratios of [CuBr]/[BBPMI], in which the multi-peaks characteristics of the signal in region **4** gradually disappear, suggesting more and more **B*** have been converted into **A*** or **S***. Furthermore, it can be seen in Table 1 that more and more **A*** or **B*** have been converted into **S***.

In the ^{1}H NMR spectra of the resulting poly(BBPMI-*co*-St) prepared by ATRP, the peaks in region **1** are related to the protons of phenyls and double bonds of BBPMI. The peak marked with **2** derives from protons of –C**H**BrPh–, i.e. **S***. The peak marked with **3** corresponds to the protons of **A*** and **B***. On the whole, the bromine atoms of the resulting hyperbranched copolymers are derived from BBPMI inimers and the number of protons geminal to bromine atoms remains constant. S_1, S_2 and S_3 denote the area of region **1** except for that of double bonds, region **2** and **3**, respectively. The area of peak due to $CHCl_3$ in region **1** has been calculated by comparing the height of this peak with that of the peak attached to inner standard TMS (tetramethylsilane) and has been deducted from S_1. The mole faction of BBPMI in hyperbranched copolymers, F_{BBPMI}, and the ratio of **S*** to **A*** and **B*** can be calculated according to Eqs. (1) and (2)

$$F_{\mathrm{BBPMI}} = \frac{S_2 + S_3}{\frac{S_1 - 4(S_2+S_3)}{5} + S_2 + S_3} \tag{1}$$

$$\frac{[S^*]}{[A^*] + [B^*]} = \frac{S_2}{S_3} \tag{2}$$

here 4 is the number of protons of –Ar– in BBPMI inimer and 5 is the number of protons of Ar– in styrene monomer.

The molecular weights determined by GPC and MALLS of the resulting copolymers with various ratios of [CuBr]/[BBMPI] are listed in Table 1. Obviously, the higher ratio of [CuBr]/[BBPMI] favors preparation of copolymers with high molecular weights. According to ATRP mechanism, the increase of ratio of [CuBr]/[BBPMI] results in an increase of polymerization rate and consequently increase the degree of branching since branching mainly occurs in the end stage. But too high ratio of [CuBr]/[BBPMI] leads formation of insoluble gel (Table 1, entry 6), which results from the coupling of macromolecular radical. Unfortunately, the degree of branching cannot be obtained explicitly because there is no method to differentiate between the microstructures of **A***, **B*** and **a**, **b**.

As expected, the monomer ratio has very obvious effect on the final composition and structure of the resulting copolymers. The molecular weights and F_{BBPMI} of the resulting copolymers with various monomer ratios are shown in Table 2. The molecular weight increases with decreasing dosage of inimer, BBPMI. While the higher mole ratio of St to BBPMI leads to lower degree of branching. If ratio of [St]/[BBPMI] increases, as shown in Fig. 6, more and more **A*** or **B*** converts into **S***, suggesting the formation of linear polystyrene chains. If very high mole ratio of St to BBPMI, such as 50:1, is employed, it is imaginable that star polymers can be obtained due to the grafting of the residual styrene monomers from the outer surface of the hyperbranched cores [32].

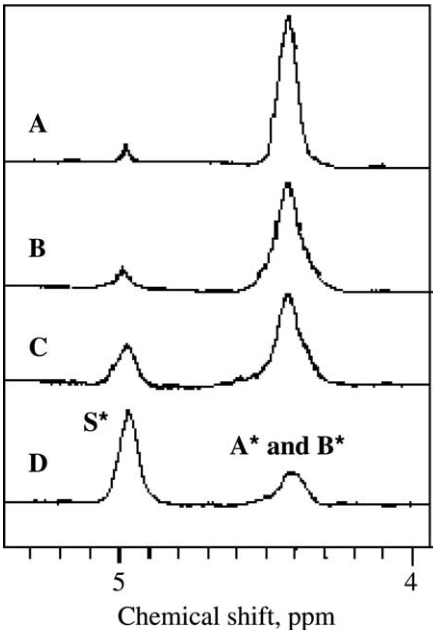


Fig. 6. Effect of changing the ratio of [St]/[BBPMI] on the ratio of $[S^*]/[A^*+B^*]$ in the ^{1}H NMR spectra: (A) sample 4 in Table 2, [St]/[BBPMI] = 0.5/1, $[S^*]/[A^*+B^*] = 0.089$, (B) sample 3 in Table 2, [St]/[BBPMI] = 1/1, $[S^*]/[A^*+B^*] = 0.159$, (C) sample 2 in Table 2, [St]/[BBPMI] = 2/1, $[S^*]/[A^*+B^*] = 0.314$, (D) sample 1 in Table 2, [St]/[BBPMI] = 4/1, $[S^*]/[A^*+B^*] = 1.887$.

3.5. DSC and TG analysis

The T_g data of hyperbranched poly(BBPMI-*co*-St) with various F_{BBPMI} are also listed in Table 2. It can be seen that T_g increases with increasing F_{BBPMI}. The reason for the increase of T_g should be that the maleimide moieties and phenyls of BBPMI are in the main chains of the resulting polymers while the phenyls of styrene units are only present as pendant groups.

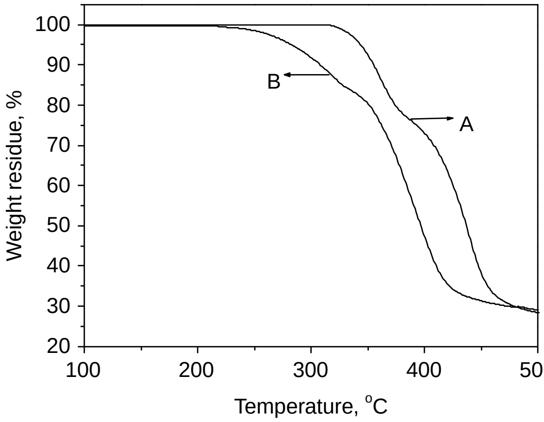


Fig. 7. (A) TG curve of linear poly(BBPMI-*co*-St); (B) TG curve of hyperbranched poly(BBPMI-*co*-St), sample 3 in Table 2.

From the TG curves shown in Fig. 7, it can be observed that the initial weight loss temperature of hyperbranched copolymer sample, 219 °C, is lower than that of its linear analogue, 313 °C. Generally, because of structural differences, including especially the presence of secondary benzylic or ester halide structures, hyperbranched polymers show lower thermal stabilities compared with their linear analogues [22,35]. In the structure of hyperbranched poly(BBPMI-*co*-St), the presence of halide structures in **S*** and **A***, which may be more prone to elimination than that in **B***, should be responsible for the relative lower thermal stability. In addition, **S*** and **A*** in the hyperbranched copolymer are in the backbone of the macromolecular chains, while **B*** in the linear copolymer are only present as pendant groups. The cleavage of carbon bromine bonds in the hyperbranched copolymer has more serious effect on the thermolysis of polymer than that in the linear copolymer.

4. Conclusion

Novel hyperbranched poly(BBPMI-*co*-St) was successfully prepared by the atom transfer radical copolymerization of BBPMI with St using the complex of CuBr/Bipy as catalyst. The hyperbranched structure was verified by GPC coupled with MALLS and branching mainly takes places at the end stage. It was observed that higher ratio of [CuBr]/[BBPMI] can accelerate the polymerization and consequently favors the formation of polymer with higher molecular weight and extent of branching since branching mainly occurs in the end stage. The glass transition temperature of the resulting hyperbranched poly(BBPMI-*co*-St) increases with increasing F_{BBPMI}. The resulting hyperbranched copolymers exhibit much better solubility in organic solvents, such as butanone and THF, than their linear analogues. However, the initial weight loss temperatures of a hyperbranched sample and that of its linear analogue are 219 and 313 °C, respectively, suggesting the lower thermal stabilities of the resulting hyperbranched copolymers.

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