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Synthesis of HBPE-b-PS Copolymers with Controlled Molecular Weights and Low Polydispersities via *in situ* ATRP

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Abstract: The functionalized polyolefins are important in both fundamental research and industrial practice. However, the direct processes have been greatly limited by some fundamental chemical difficulties, such as catalyst poisoning. Also there is no facile reaction site on most polyolefins by chemical modification. We report here in an *in situ* ATRP method for the synthesis of hyperbranched polyethylene block polystyrene copolymers with controlled molecular weights and low polydispersities. First we introduced reactive terminal groups to hyperbranched polyethylene branches as macroinitiators by end-quenching reaction with injected styrene derivatives in the Pd-catalyzed ethylene polymerization system. And then hyperbranched polyethylene-based block polystyrene copolymers were directly synthesized via *in situ* ATRP method by using the macroinitiators. The resulting hyperbranched polyethylene block polystyrene copolymers have narrow distribution (from 1.01 to 1.44) of molecular weights, controllable molecular weights, and good compatibilities.

Keywords: Polyolefin, Hyperbranched, Polyethylene, *In situ* ATRP, Block copolymer

Introduction

In despite of important commercial applications of polyolefins, the lack functionality and poor compatibility with other materials has limited the application of polyolefins in many areas, like polymer alloy and polymer blends. To solve these problems, some methods have been developed to obtain functionalized polyolefins, and to broaden their applications scope [1-6]. The functionalized polyolefins are important in both fundamental research and industrial practice.

These various methods can be divided into three kinds, include (1) direct copolymerization of α-olefin with functional monomer, (2) chemical modification of the performed polyolefin, and (3) reactive copolymer approach by incorporating reactive monomers that can be selectively and effectively interconverted to functional groups [7-9].

Although, the direct processes have been greatly limited by some fundamental chemical difficulties by using the traditional olefin catalysts, such as catalyst poisoning. Great advances have been achieved in the copolymerization of olefins with polar monomers, by the use of new made less oxophilic late transition metal catalysts, such as Fe, Ni, Co and Pd complexes [10-12].

For the chemical modification, there is no facile reaction site on some polyolefins, like polyethylene and polypropylene. The only way is to activate these polyolefins by breaking some stable C-H bonds and forming free radicals along the polymer chain. However, this process is always accompanied with many undesirable side reactions, like degradation and crosslink.

In view of these methods, the third approach is a relatively new one. Several new reactive comonomers can be effectively incorporated into polyolefins in the side chains or at the chain end [13,14]. So far, there are only a few reports describing the introduction of a reactive terminal group to polyolefin through a chain transfer reaction during polymerization with chain transfer agents [14-16]. The basic idea of this is to circumvent the chemical difficulties in the processes by designing a reactive copolymer "intermediate" that can be effectively synthesized and be subsequently interconverted to functional polymer especially in synthesizing functional polyolefins.

In some scientists' work, polyolefin with all end capped with functional groups, have been prepared by first synthesis of a chelate version of a Pd (II) α-diimine catalyst derived from the single insertion of reactive groups into a palladium-methyl bond [17-21]. The "living" polymerization of ethylene with such a catalyst system leads to polyethylene with a narrow molecular weight distribution containing functionalized groups. And the *in situ* chain transfer reaction during the metallocene polymerization process reported by Chung group provides an interesting and convenient route to obtain a terminal functional polymer [22].

The polyolefin containing a terminal functional group as a very promising material possesses almost the same physical properties (melting temperature, glass transition temperature, etc.) and almost the same polyolefin chain structures as those of the pure polyolefin. The terminal reactive group at the chain end has good mobility and can provide a reactive site for various applications, such as producing of block or graft copolymers, reactive blending to improve the com-

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patibility of two dissimilar polymer blends and adhesion to the substrates [23].

The aim of this work is to synthesize hyperbranched polyethylene-based block polystyrene copolymers via *in situ* Atom Transfer Radical Polymerization (ATRP) polymerization. This has to be achieved via a two-step process. The first step is to introduce reactive terminal groups to hyperbranched polyethylene branches as called macroinitiators by directly end-quenching of Pd-catalyzed ethylene "living" polymerization with styrene derivatives. The ethylene "living" polymerization was completely quenched at the very beginning of adding the styrene derivatives. There is no dormant propagating species after 2,1-insertion of a styrene-functional unit. Then the hypebranched based macroinitiators, with controlled molecular weights and narrow polydispersities, have been synthensized by the first step. The second step is to synthesize block copolymers via *in situ* ATRP method by using the hyperbranched polyethylene-based macroinitiators. This *in situ* ATRP approach can be used to directly synthesize polyolefin-based block copolymers with various functional monomers such as lactones, acrylates, and styrene. It offers an opportunity for the direct synthesis of polyolefin based copolymers with good compatibilities.

Experimental

Materials

The Pd-diimine CWP catalyst ([(ArN≡C(Me)-(Me) CdNAr)Pd(CH_3)(N≡CMe)]$^+$ SbF_6^- (Ar=2,6-(*i*Pr)$_2C_6H_3$)), was synthesized according to the literature procedure [7]. Ultrahigh purity N_2 and polymer-grade ethylene (both obtained from Praxair) were purified by passing through 3 Å/5 Å molecular sieve and oxiclear columns to remove moisture and oxygen, respectively, before used. Styrene (99 %) (from Aldrich) were distilled under reduced pressure before use. Copper (I) bromide(CuBr) (99.999 %) was purified by stirring in glacial acetic acid, then, washing with methanol and finally drying under vacuum, was purified by acetic acid and methanol, before used. Anhydrous dichloromethane (99.8 %), anhydrous diethyl ether (g99 %), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (99 %), St-CH_3, St-CH_2Cl, St-CH=CH_2 etc., were obtained from Aldrich and were used as received. toluene (g99.5 %), methanol (g99.8 %), tetrahydrofuran (THF) (>99 %) were received from Fisher. All manipulations involving air- and/or moisturesensitive compounds were carried out in a N_2-filled drybox or using Schlenk techniques.

End-quenched Ethylene "living" Polymerization with Styrene Derivatives at 1 atm and 15 °C

Chain walking ethylene "living" polymerizations were carried out at 15 °C, under ethylene pressure of 1 atm in a 500 m*l* jacketed glass reactor equipped with a magnetic stirrer. The reactor temperature was maintained by passing water through the jacket using a temperature controlled circulating water bath. The typical polymerization procedure was as follows. The glass reactor was dried over night at about 150 °C in an oven, followed by cooling to room temperature under a vacuum. The reactor further underwent a vacuum-ethylene process for three cycles, and was then pressurized with ethylene. The ethylene pressure was maintained at 1 atm during the polymerization by a continuous feed from the supply cylinder. The reactor temperature was then maintained at 15 °C by using the circulating bath. Subsequently, anhydrous CH_2Cl_2 (35 m*l*) was injected into the reactor. After thermal equilibration for about 10 min, the Pd-diimine catalyst (0.1 mmol) dissolved in anhydrous CH_2Cl_2 (15 m*l*) was injected into the reactor to start the polymerization. After a prescribed polymerization time, the polymerizations were mixed with styrene derivates, separately. The mixture were stirred for 1 h at the same condition, and then precipitated in acidic methanol. In order to remove the catalyst residue remaining in the polymer, the oily polymer precipitate was redissolved in THF, and then precipitated in the acetone. The purified polymers were dried for about 24 h under a vacuum at room temperature.

Synthesis of Hyperbranched Polyethylene Block Polystylene Copolymers by *in situ* ATRP

The following is a typical ATRP procedure. The hyperbranched polyethylene-VBC (HBPE-Cl) macroinitiator (0.12 g), toluene (4.2 m*l*), styrene (3.4 g), CuBr (9.4 mg), PMDETA (13.7 mg) and a PTFE stirrer were added into a 50 m*l* Schlenk reactor sealed with a rubber stopper. The reaction mixture was then subject to three freeze-pump-thaw cycles and finally filled with nitrogen. After stirring the reaction mixture for 10 min at room temperature, the reactor was placed in a thermostated oil bath at 100 °C and protected with dry N_2 throughout the polymerization. Samples were took out at different time intervals during polymerization to monitor monomer conversion (calculated based on the molar ratio between styrene and ethylene units from ^{1}H NMR spectroscopy) and molecular weight of the block copolymers using gel permeation chromatography. The block copolymers precipitated in acidic methanol were washed with a large amount of methanol three times and dried under vacuum at 60 °C overnight. The monomer conversion or polymer yield was calculated gravimetrically.

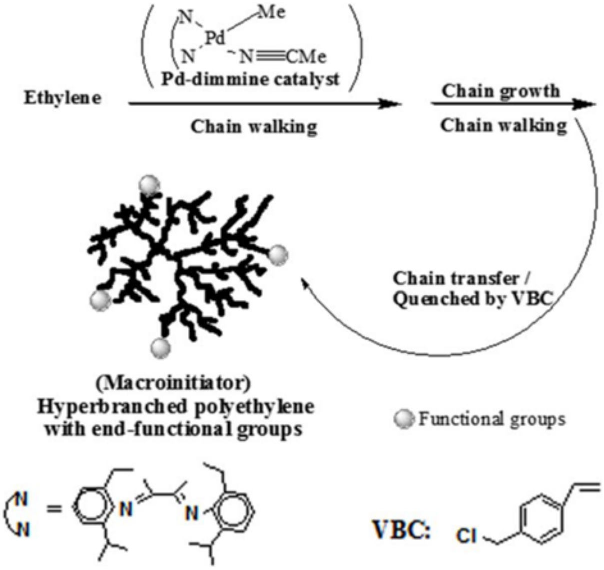
Characterizations

^{1}H NMR spectra (200 MHz) of the polymer samples were all obtained on a Varian Gemini 2000 spectrometer at ambient temperature. $CDCl_3$ was used as the solvent for polyethylene-*b*-polystyrene block copolymers.

Hydrogen atoms were placed in calculated positions Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratory PL-GPC220 system equipped with a differential refractive index detector, one guard column (PL 1110-1120), and three Polymer Laboratory 30 m mixed columns. The system operated at 30 °C, and THF was used as the eluent at a flow rate of 1.0 m*l*/min. Polystyrene standards (PL EasiVials) covering molecular weights from 580 to 6,035,000 g/mol were used for the column calibration.

Results and Discussion

Hyperbranched polyethylenes with end-capping functional agents are able to be fabricated via various styrene derivatives added to the Pd-diimine catalyzed "living" polymerization. In this study, chloromethyl styrene (VBC) was employed in the quenched reaction during the process of ethylene "living" polymerization (in Scheme 1). And no external protection agents were needed for the functional groups of these styrene derivatives in the process, which are benefited greatly from their less oxiphic and characteristic of chain walking mechanism. The ethylene "living" polymerization was carried out with a typical cationic Pd-catalyst at the condition of ethylene pressure of 1 atm and 15 °C. When VBC were added in the system of ethylene "living" polymerization, the propagating Pd$^+$-C site immediately form a functional styrene structure-capped propagating site with metal cation with a VBC unit as shown in Scheme 1. Pd-diimine catalyst underwent β-H elimination, leading to end-capping hyperbranched polyethylene chains with benzyl chloride functional groups. Furthermore, there was no further reinsertion after end-quenching by VBC.



Scheme 1. Process in synthesis of macroinitiator.

Table 1. Hyperbranched polyethylenes by ethylene "living" polymerization with different polymerization time

Run	"Living" polymerization time (h)	Polymer before quenching		
		$\overline{Mn}$ (kg·mol^{-1})	PDI	η_w (m*l*·g^{-1})
1	0.5	9.1	1.00	8.5
2	1.0	17.0	1.00	10.1
3	2.0	28.9	1.04	12.8
4	4.0	53.4	1.05	16.1

The obtained hyperbranched polyethylenes with benzyl chloride functional end groups and their corresponding hyperbranched polyethylenes are all in the narrow PDI range from 1 to 1.05 shown in Table 1 and 2. The molecular weights ($\overline{Mn}$) of hyperbranched polyethylenes before quenching are significantly improved from 9.1 kg·mol^{-1} to 53.4 kg·mol^{-1}, with the polymerization time increasing from 0.5 h to 4 h in Table 1.

To investigate the end-quenching process, an excessive amount of VBC were employed in the quenching reaction during different ethylene "living" polymerization time within various quenching time as 0.3 h, 0.5 h and 1 h shown in Table 2 (Run 5-Run 10). The GPC results of before and after quenching reaction, are all shown in Table 1 and Table 2. And NMR results of the molecular weights and branch densities in all cases are all shown in Table 2 and Figure 1.

The molecular weights ($\overline{Mn}$) of the end-capped hyperbranched polyethylenes are increased from 9.7 kg·mol^{-1} to 53.4 kg·mol^{-1} with the ethylene "living" polymerization time increasing. The molecular weights ($\overline{Mn}$) of the resulting end-capped hyperbranched polyethylenes have no significant change in all the quenched cases (shown in Figure 2 and Table 2) compared with their corresponding hyperbranched polyethylenes before quenched (in Table 1).

As for example in Figure 2, the $\overline{Mn}$ of the Run 2 is 17.1 kg·mol^{-1} before quenched at polymerization time of 1 h and after quenched about 17.7 kg·mol^{-1} even under various

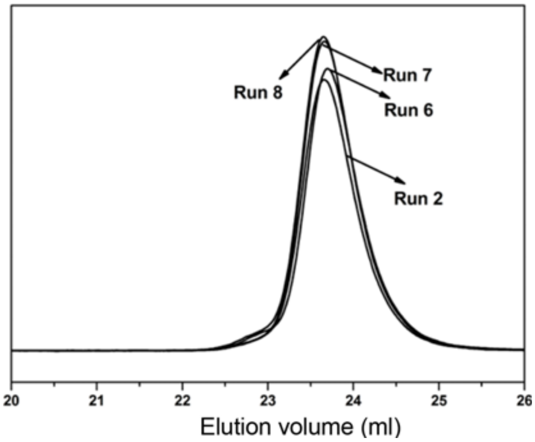


Figure 1. GPC results for hyperbranched polyethylene (Run 2 polymerization time 1 h) immediately before quenched and for hyperbranched polyethylene with end-functional groups after quenching at different VBC quenching time: 10 mins (Run 6), 30 mins (Run 7) and 60 mins (Run 8).

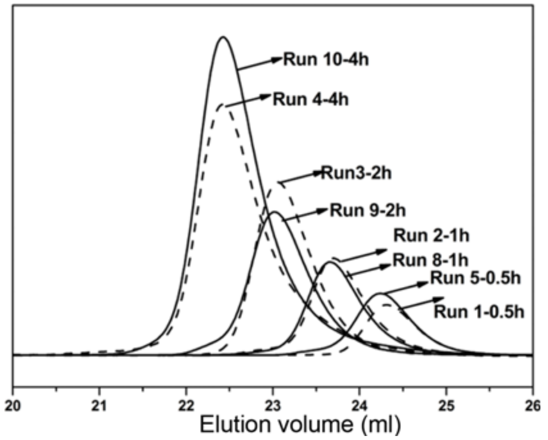


Figure 2. GPC results for the end-capped hyperbranched polyethylenes (in solid lines) and their corresponding hyperbranched polyethylenes (in dotted lines) obtained immediately before quenching reaction.

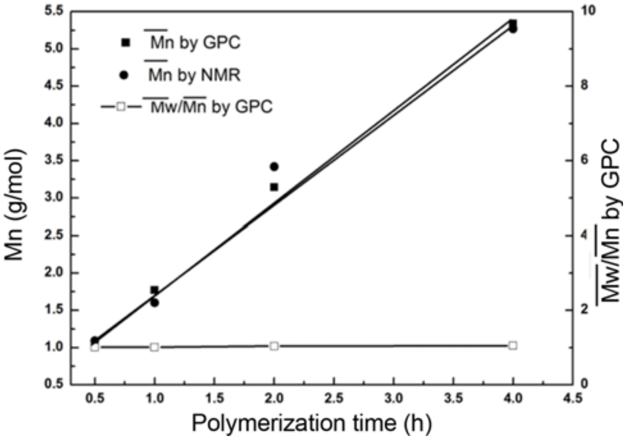


Figure 3. Plot of end functional polyethylene number-average molecular weight ($\overline{Mn}$) and molecular weight distribution ($\overline{Mw}/\overline{Mn}$) obtained at end-quenching different ethylene living polymerization time by VBC.

Table 2. Hyperbranched polyethylenes with functional end groups

Run	"Living" polymerization time (h)	Quenching time (h)	End-capped hyperbranched polyethylene after quenching				
			$\overline{Mn}$ (kg·mol^{-1})	PDI	η_w (m*l*·g^{-1})	$\overline{Mn}$ (NMR) (kg·mol^{-1})	Branch density per 1000C
5	0.5	1	9.7	1.00	8.6	9.5	97
6	1	0.3	17.7	1.01	10.0	16.0	98
7	1	0.5	17.7	1.01	10.0	15.9	97
8	1	1	17.7	1.01	10.0	16.0	98
9	2	1	31.3	1.04	13.0	34.2	100
10	4	1	53.4	1.05	16.1	52.7	101

quenching time. Obviously, there is a negligible increase of $\overline{Mn}$ in the end functional hyperbranched polyethylenes compared with that in the same ethylene polymerization time before quenched, due to the artificial delay in process of injecting VBC to the "living" polymerization system. These results indicate that the end-quenching happens immediately and no further reinsertion in ethylene "living" polymerization after end-quenching with VBC.

The molecular weights ($\overline{Mn}$) and the branching density of end-capping hyperbranched polyethylenes at different polymerization time, calculated by NMR, have also been listed in Table 2. The branching densities in the polyethylene backbone of the functional end-capping hyperbranched polyethylenes are about 100 branches per 1000 carbons, calculated by results of ^{1}H NMR measurements on the basis of the resonances of methylene, methine, and methyl protons of the polyethylene sequences. The results of molecular weights ($\overline{Mn}$) calculated by ^{1}H NMR are in good agreement with the $\overline{Mn}$ measured by GPC as shown in Table 2 and Figure 3.

^{1}H NMR spectra of obtained functional end-capping hyperbranched polyethylenes are shown in the Figure 4(a) an 4(b). The concentration of the incorporated terminal VBC units was determined by the integrated intensity ratio between the chemical shift at 4.60 ppm (-CH_2Cl), corresponding to 0.5-1.5 ppm (-CH_2-) in ethylene units, and the chemical shifts between 7.20 and 7.30 ppm, corresponding to -C_6H_4-. The peaks at about 6.26-6.41 ppm respond to protons in -C*H*=C*H*-Ph-(formed by β-H elimination), respectively (seen in Figure 4(a)). The *p*-methyl styrene (MS) also be used in the end quenching process. The ^{1}H NMR spectra of HBPE with active end MS groups was shown in Figure 4(b), determining the successful end functional HBPE by MS quenching. There is no detectable direct chain propagating process after adding VBC or MS. In Figure 4(a), the ethylene "living" polymerization was completely quenched at the very beginning of adding VBC or MS. The present of the vinylene group (6.26 and 6.41 ppm) next to the benzyl chloride (-CH=CH-Ph-)end functionality suggests that VBC is enchained through a 2,1-insertion to form an intermediate with the cationic Pd center and a subsequent benzyl transfer reaction occurs in the presence of the excessive VBC to

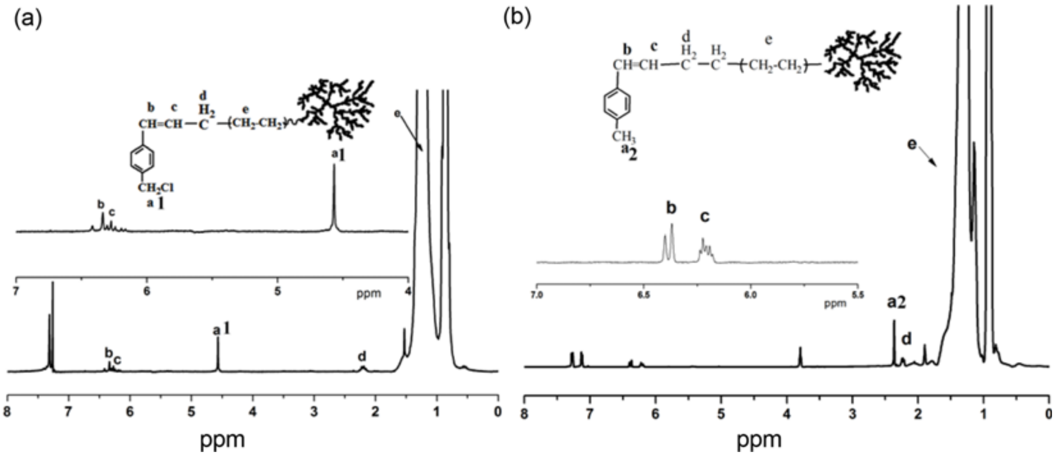
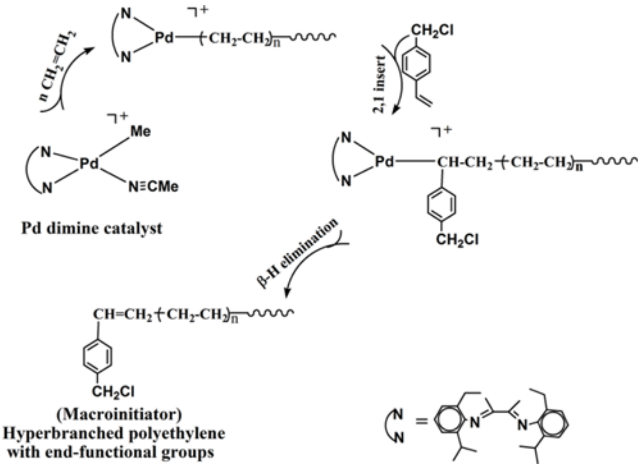


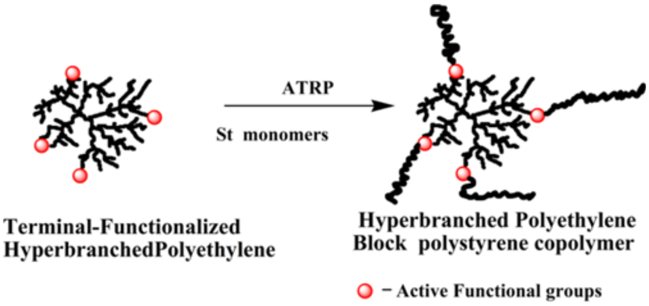
Figure 4. ^{1}H NMR spectra of the end-capped polymer synthesized in (a) Run 8 with VBC quenching, and (b) MS quenching (both with same "living" polymerization time 1 h).



Scheme 2. The suggested mechanism of VBC quenching.

synthesize the hyperbrachened polyethylene with end-functional groups. The suggested mechanism of VBC quenching can be seen in Scheme 2.

The end functionalities (VBC units) density of in the functional end-capping hyperbranched polyethylenes are about 1 VBC end unit per 100 branches (combined with results of Table 1), calculated by results of ^{1}H NMR measurements on the basis of the resonances of methylene and methyl protons of the polyethylene sequences, and phenyl and benzyl chloride protons of the VBC parts. These results suggested that functional hyperbranched polyethylenes with benzyl chloride end functional groups (VBC units) were successfully prepared.



Scheme 3. Process of systhesis of hyperbranched polyethylene block polystyrene copolymer.

Table 3. Synthesis of hyperbranched polyethylene block polystylene copolymers via *in situ* ATRP

Run	"ATRP" polymerization time (h)	$\overline{Mn}$ (kg·mol^{-1})	PDI	η_w (ml·g^{-1})
11	0	9.7	1.01	8.6
12	3	11.4	1.04	8.7
13	6	17.4	1.26	10.0
14	10	22.8	1.34	12.1
15	13	30.1	1.36	16.0
16	15	37.7	1.44	23.4
17	18	48.4	1.44	24.6
18	22	52.6	1.42	23.9

Synthesis of Hyperbranched Polyethylene Block Polystyrene (HYPE-*b*-PS) Copolymer via *in situ* ATRP (in Scheme 3)

The end groups of these functional hyperbranched polyethylenes are all active ones and can be used in various cases as macroinitiators for subsequent polyolefins modifications or for polyolefins of many architectures synthesis. The topology and chain length of these hyperbranched polyethylene-based macroinitiators can be conveniently controlled by adjusting the conditions in ethylene "living" polymerization process, such as polymerization time and temperature. These hyperbranched polyethylene-based macroinitiators are completely amorphous at room temperature and have good solubility in toluene even at room temperature.

And then the hyperbranched polyethylene-based macroinitiators were introuduced in the Atom Transfer Radical Polymerization (ATRP) system. A common challenge in the system is to minimize both radical coupling and incomplete chain initiation in order to obtain block copolymers with low polydispersity. We optimized to use low macroinitiator concentrations in this work. Meanwhile, high ratios of $[Cu]_0/[I]_0$ was used in our polymerization system to the purpose of enhancing initiation efficiency. CuBr/PMDETA was used as the catalyst system for all ATRP runs (in Table 3) along with the choice of toluene as the solvent. Meanwhile, monomer conversion was restricted to minimize chain transfer/coupling reactions. In designing this ATRP system, we have used a low macroinitiator concentration of 2.6×10^{-3} M and a CuBr/PMDETA catalyst system (molar ratio of 1:1.2) with a high [CuBr]/[macroinitiator] molar ratio of 6 to maximize the initiator efficiency. The polymerization was carried out at 100 °C with a styrene concentration of 7.8 M.

The hyperbranched polyethylene block polystylene copolymers with designed structures, controlled molecular weights and low polydispersities can be finally synthesized via *in situ* ATRP with the hyperbranched polyethylene-based macroinitiators and styrene as monomer. Molecular weight and chemical structure of each block copolymer have been characterized by gel permeation chromatography (GPC) and ^{1}H NMR, respectively.

Table 3 summarizes the details and results of hyperbranched polyethylene block polystyrene copolymers under various ATRP time. In these cases, Atom Transfer Radical Polymerization was carried out by using hyperbranched polyethylene-based macrointiators prepared in Run 11 (Table 3).

The molecular weights of the obtained block copolymer under various ATRP time can be investigated by the GPC traces shown in Figure 5. Radical coupling is not observed from the absence of signal high-molecular-weight in Table 3 and Figure 5. With increasing polymerization time, there is a slight broadening in distribution of molecular weights from 1.01 to 1.44 in the hyperbranched polyethylene block polystylene copolymers. With polymerization time increased, the molecular weights ($\overline{Mn}$) of the block copolymers show consistent increase from 9.7 kg·mol^{-1} to 52.6 kg·mol^{-1} in Table 3 and Figure 6, demonstrating the successful chain extension in the resulting hyperbranched polyethylene block polystylene copolymers. The structures of these hyperbranched polyethylene block polystylene copolymers were analyzed by ^{1}H NMR measurement in Figure 7.

As shown in Figure 7, the hyperbranched PE fingerprint was also evident in the thermal responses (shielding effect) of block copolymers. The peaks at 0.5-1.5 ppm were due to the protons of -CH_2- groups at the backbone of hyperbranched PE blocks. The ^{1}H NMR spectra of hyperbranched polyethylene block polystylene copolymers demonstrated that the peaks at 4.50-4.91 ppm were due to the protons of the phenmethyl groups at the chains of polystylene blocks in the block copolymer. The quantitative analysis of these block copolymer composition were calculated through the ratio of two integrated intensities between the aromatic protons in the polystylene blocks (at 6.4-6.9 ppm) and the methylene protons in hyperbranched polyethylene parts (at 0.5-1.5 ppm) by the number of protons in both chemical shifts represent.

Each chain of the block copolymer contains hyperbranched polyethylene segments and polystyrene segments. The peaks at 4.50-4.91 ppm, attributable to the protons in PS blocks, compared to protons in hyperbranched polyethylene phenmethyl blocks at 0.5-1.5 ppm, are increased with increasing polymerization time, which means that more and more PS blocks dissolved in the solvent. The presence of both blocks derived from hyperbranched polyethylenes and polystylenes

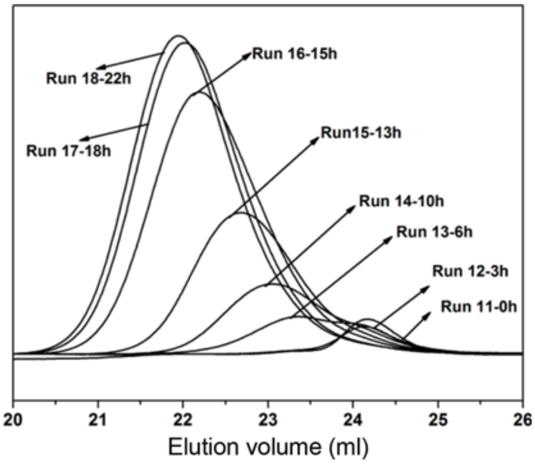


Figure 5. GPC results of the polymer sampled after different polymerization time in ATRP of styrene with VBC-quenched hyperbranched polyethylenes synthesized as the macroinitiator in Run 11.

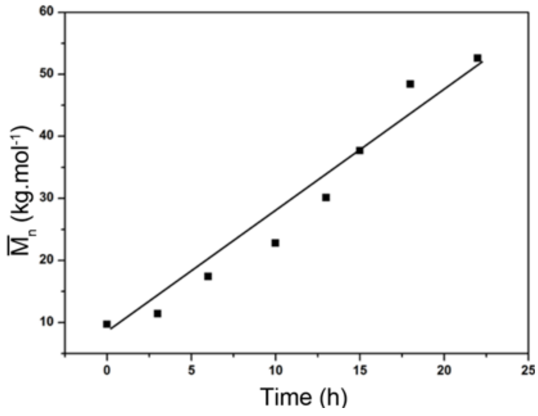


Figure 6. The molecular weights ($\overline{Mn}$) of the block copolymers are increased with the increasing polymerization time.

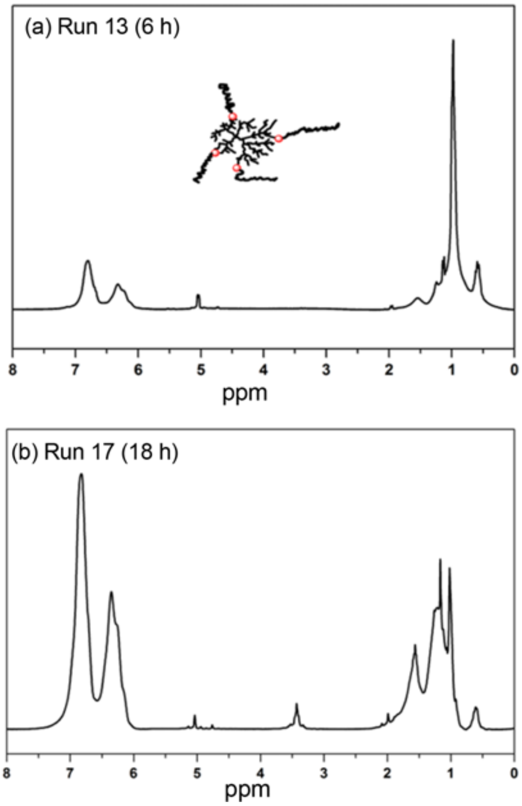


Figure 7. ^{1}H NMR spectra for block copolymers (a) of Run 13 at 6 h polymerization time ($\overline{Mn}$=17.4 kg·mol^{-1}) and (b) of Run 17 at 18 h polymerization time ($\overline{Mn}$=48.4 kg·mol^{-1}).

in the block copolymers were clearly demonstrated by ^{1}H NMR results. These results showed that hyperbranched polyethylene block polystyrene copolymers with controlled molecular weight and low polydispersities have been successful synthesized via *in situ* ATRP.

Conclusion

A series of hyperbranched polyethylene-based block polystyrene copolymers have been successfully synthesized via *in situ* ATRP. The hyperbranched polyethylenes with functionalized end groups were prepared through introducing reactive terminal groups to hyperbranched polyethylene branches by the quenching reaction with injected styrene derivatives in the Pd-catalyzed ethylene polymerization system. Due to the presence of the end functionalities, these hyperbranched polyethylenes can be used as macroinitiators or macromonomers for further directly synthesis of block copolymers and polymers of other complex chain architectures. Thus hyperbranched polyethylene block polystyrene copolymers were synthesized by using the hyperbranched polyethylene-based macroinitiators via *in situ* ATRP. The resulting hyperbranched polyethylene block polystyrene copolymers have narrow distribution (from 1.01 to 1.44) of molecular weights and controllable molecular weights, and good compatibilities in each constituting block. The molecular weights of these copolymers are increased with increasing time of polymerization (from 9.7 kg·mol^{-1} to 52.6 kg·mol^{-1}).

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