



## Synthetic of Polydivinylbenzene Block Hyperbranched Polyethylene Copolymers via Atom Transfer Radical Polymerization

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The blocked copolymers of polydivinylbenzene block hyperbranched polyethylene were successfully synthesized via in situ copolymerization by Atom Transfer Radical Polymerization (ATRP) method, in which hyperbranched polyethylene capping reactive functional terminal groups were used as macro-comonomers. Hyperbranched polyethylene branches capping functional terminal groups are obtained by injecting divinylbenzene in ethylene “living” polymerization system via end-quenching reaction. The various macro-comonomers have terminal reactive groups on hyperbranched polyethylene branches obtained by varying temperature, pressure, co-monomer type or structure and feed processing duration in chain walking ethylene “living” polymerization processes. It may provide a new way for directly preparing polyolefin-based functionalized block copolymers by various polyolefin-based macro-comonomers. The resulting polydivinylbenzene block hyperbranched polyethylene copolymers have still relatively narrow distribution of molecular weights (around 1.18), predetermined molecular weights, and good compatibilities with polar and nonpolar polymers.

**Keywords:** Polyolefin; Hyperbranched; Polyethylene; Atom Transfer Radical Polymerization

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### 1. Introduction

Polyolefins, including polyethylene (PE) and polypropylene (PP), are most used important materials employed in a wide range of areas, such as commercial commodities, industrial applications and agricultural applications.<sup>1, 2</sup> And these polyolefins materials are still increasing with a continuous growth of their application. However, the poor functional ability and compatible ability with other materials due to lacking facile reactive point on polyolefins has limited the application of polyolefins in many areas, even in polymer alloy, polymer composites/nanocomposites<sup>3-7</sup> and polymer blends.<sup>8, 9</sup> One direct way to active these polyolefin materials with functional groups is breaking some stable C–H bonds and forming free radicals along the polyolefin chain. In these direct processes, there are always accompanied with many undesirable side reactions, like degradation or crosslinking.

And also to satisfy the need to reduce environmental impact of polyolefins, usages of recycled polyolefins in functionations have received particular attention and consideration, with results applied to the market. To active these unreactive polyolefins in recent years, technological functions of polyolefins, including novel polymerization processes by high-performance catalyst systems and the novel polyolefin-based specialty materials, are fundamental keys to their continuous successful market expansion.<sup>7, 10-20</sup> Hyperbranched polyolefins obtained by late transition metal catalysts with end functional groups, are one of the main successes products of these new technologies and

are able to develop hyperbranched polyolefins-based polymer materials.<sup>12-16, 21-30</sup> These end functional hyperbranched polyolefins, could polymerize with other polar monomer by some copolymerization methods.<sup>6-10, 14-19</sup> These functionalized polyolefins, containing polar groups, have continued to witness increased applications. In these methods, ATRP process offering an effective approach can incorporate specific properties into a material while retaining properties of the parent polyolefins.

In the polyolefin hyperbranching process, the occurrence of hyperbranching reactions can be controlled in relation to the structure of the starting polyolefins by varying reaction parameters like temperature, pressure, co-monomer type and feed process. The hyperbranched polyolefins, with the end polar reagents, are able to be soluble in the normal solution such as THF. In addition, the after grafting reaction occurs mainly at the interface of the end functional hyperbranched polyolefins and is affected by the content of end functional groups.

In this work, we introduced macro-comonomers through end-quenching reaction by injecting divinylbenzene (DVB) into the ethylene “living” polymerization system. The various macro-comonomers are the ones which have terminal reactive groups on hyperbranched polyethylene branches obtained by varying temperature, pressure, co-monomer type or structure and feed processing duration in chain walking ethylene “living” polymerization processes. Thus the final series blocked copolymers materials of polydivinylbenzene block hyperbranched polyethylene were successfully synthesized via in situ copolymerization by Atom Transfer Radical Polymerization (ATRP) method.

### 2. Experimental Section

#### 2.1 Materials

The Pd-diimine CWP catalyst system,  $[(ArN=C(Me)-(Me)CdNAr)Pd(CH_3)(N=CMe)]^+ SbF_6^-$  ( $Ar = 2,6-(iPr)_2C_6H_3$ ), was synthesized according to

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the procedure in the previous literatures.<sup>10, 12, 21</sup> The ultrahigh purity  $N_2$  and the polymer-grade ethylene used in this report both are obtained from Praxair. Copper (I) bromide (CuBr) (99.999%) was purified by glacial acetic acid and methanol before used, and was finally dried under vacuum. The materials of anhydrous diethyl ether (99%), anhydrous dichloromethane (99.8%), *N, N, N', N'', N'''*-pentamethyldiethylenetriamine (PMDETA) (99%), and divinylbenzene (DVB) etc., were purchased from Aldrich and were used as received. Tetrahydrofuran (THF) (>99%), methanol (99.8%) and toluene (99.5%), were obtained from Fisher. All operations in experiment processes, involving air- and/or moisture-sensitive compounds, were carried out in a  $N_2$ -filled dry glove box or using standard Schlenk techniques under dry  $N_2$ .

## 2.2 Preparation of DVB capping hyperbranched polyethylene (HYPE-DVB)

The typical ethylene “living” polymerization procedure was as follows. Ethylene “living” polymerizations were first carried out at 15 °C, in a 500 mL jacketed glass reactor with a magnetic stirrer, under ethylene pressure of 1 atm. The reactor temperature using the circulating bath was maintained at 15 °C. Subsequently,  $CH_2Cl_2$  (35 mL) was injected into the reactor. After thermal equilibration for about 30 mins, the Pd-diimine catalyst (0.1mmol) dissolved in  $CH_2Cl_2$  (15 mL) was injected into the reactor to start the polymerization. After a prescribed polymerization time the polymerizations were mixture with styrene derivatives (200 times than Pd-diimine catalyst), separately (Run 1-Run 4). After 1h, the productions were precipitated in methanol. To remove the catalyst residue in the polymerization process, the obtained oily polymers were redissolved in THF, and precipitated in the acetone. The purified polymers were dried for about 24 h under a vacuum at room temperature.

## 2.3 Synthesis of HYPE-b-PDVB block copolymers by ATRP

The following is a typical ATRP procedure (Run 5 –Run 8). The HYPE ended with DVB groups as macroinitiator (HYPE-DVB, 0.01mmol), toluene (4.2mL), styrene (30mmol), CuBr (0.06mmol), PMDETA (0.08mmol) and a PTFE stirrer were added into a 50 mL sealed Schlenk reactor filled with nitrogen. The reactor was placed in a oil bath at 100

°C with dry  $N_2$  throughout the whole polymerization. Samples were took out at different time intervals during polymerization to monitor monomer conversion (calculated based on  $^1H$  NMR spectroscopy) and molecular weight of the block copolymers using gel permeation chromatography. The block copolymers were washed with a large amount of methanol three times and dried under vacuum at 60 °C overnight.

## 2.4 Characterization

$^1H$  NMR spectra of the macro-comonomers based on hyperbranched polyethylenes were measured at room temperature from a Varian Gemini 2000 spectrometer.  $CDCl_3$  was used as the solvent in the NMR measurement. Hydrogen atoms were calculated by NMR results. 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 30m mixed columns. The GPC system was operated at 30 °C, and THF was used as the eluent at a flow rate of 1.0 mL/min. The column calibration used are polystyrene standards (PL EasiVials) with molecular weights range from 580 to 6 035 000 g/mol.

## 3. Results and discussions

As mentioned above, hyperbranched polyethylenes with end functional groups are successfully synthesized by injecting DVB to the Pd-diimine catalyzed “living” ethylene polymerization system. No external protection agents are needed to protect the functional groups of these styrene derivatives in the “living” ethylene polymerization process, which are benefited greatly from their less oxiphic and characteristic of chain walking mechanism in the Pd-diimine catalyst system. The preparation process of PDVB-b-HYPE copolymers was shown in Fig 1.

When DVB monomer was added into the ethylene “living” polymerization system, the  $\beta$ -H elimination underwent through Pd-diimine catalyst, leading to cap hyperbranched polyethylene branched chains with vinyl benzyl end groups. It showed that the propagating  $Pd^I-C$  site in Pd-diimine catalyst system could immediately form a functional vinyl benzyl structure-capped propagating site, as the same time DVB added.

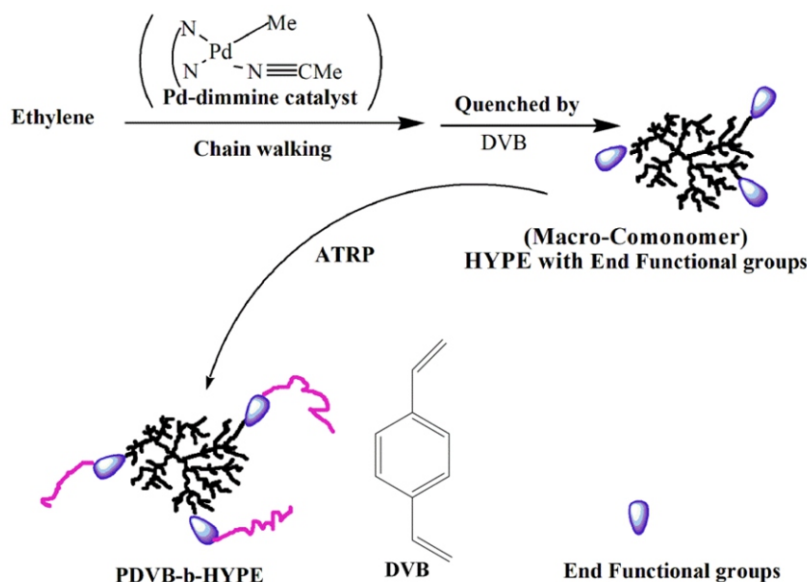


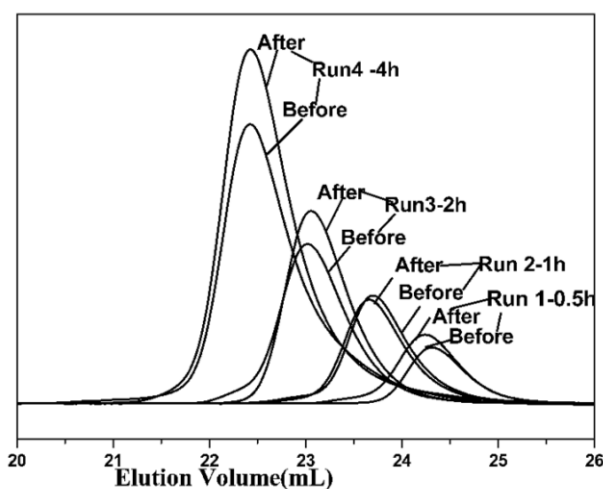
Fig. 1 Schematic illustrations depicting the preparation of PDVB-b-HYPE copolymers.

The polydispersity (PDI) of the obtained hyperbranched polyethylenes functionalized with vinyl benzyl end groups and their corresponding hyperbranched polyethylenes, are shown in Table 1 with a narrow range from 1 to 1.04. The details of GPC results have been shown in Table 1 and Fig 2. The molecular weights ( $\overline{M}_n$ ) of hyperbranched polyethylenes (before quenching with DVB monomer) are significantly increased from 9.1 Kg.mol<sup>-1</sup> to 53.0 Kg.mol<sup>-1</sup> in Table 1 with polymerization time increasing from 0.5 h to 4 h. After quenching reaction by DVB monomer, the  $\overline{M}_n$ s measured by GPC are almost the same as before quenching, comparing the values shown in Table 1 and Fig 2. These results furthermore indicate that there was no further chain walking reaction in the ethylene “living” polymerization after quenching with DVB monomer.

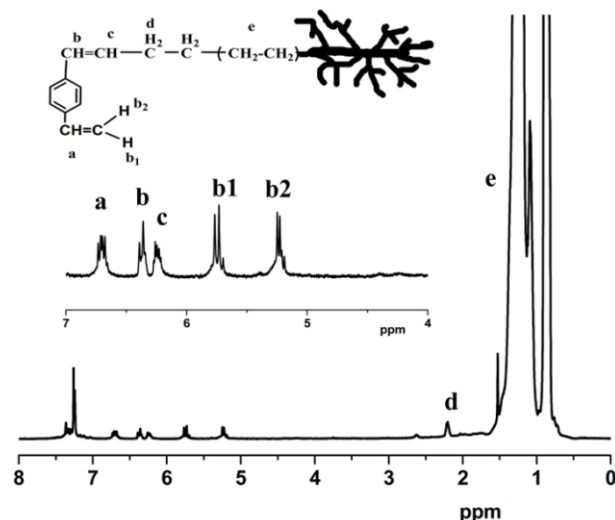
The typical results of NMR measurement have been shown in Fig 3. It shows the <sup>1</sup>H NMR spectrum of the representative vinyl benzyl end groups functionalizing hyperbranched polyethylene (Run 1). The pendant phenyl vinyl groups are clearly present from double bond chemical shifts at 6.58–6.83ppm (–CH=CH<sub>2</sub>), 5.61–5.91ppm(–CH=CH<sub>2</sub>)

and 5.12–5.34ppm(–CH=CH<sub>2</sub>). Meanwhile, the vinyl groups, connecting with polyethylene units, next to the phenyl groups (from DVB) are also evident with chemical shifts at 6.30–6.43 ppm (–Ph-CH=CH–) and 6.15–6.30ppm(–Ph-CH=CH–). The peaks at 0.5-1.5ppm chemical shift are corresponding to –CH<sub>2</sub>– from the polyethylene units in the materials, and the chemical shifts between 7.20 ppm and 7.30 ppm, corresponding to –C<sub>6</sub>H<sub>6</sub>– units. The other vinyl benzyl end groups capping hyperbranched polyethylenes prepared from Run 2 to Run 4 have the same signals with <sup>1</sup>H NMR spectrums in Run 1 as shown in Fig 1. With these NMR results, it shows that the hyperbranched polyethylene-macro-comonomers have been successfully synthesized. The end DVB units density of in HYPE-DVB are about 1 DVB unit per 1000 carbon, calculated by results of <sup>1</sup>H NMR measurements on the basis of the resonances of methylene and methyl protons of the HYPE sequences, and phenyl and vinyl benzyl protons of the DVB parts.

As we mentioned, these hyperbranched polyolefins with functional end groups, could be polymerized with other polar co-monomer (such as styrene or divinylbenzene monomers) by ATRP methods. The results



**Fig. 2** GPC results of Run1-Run 4 before and after capping DVB at various polymerization times.



**Fig. 3** Typical <sup>1</sup>H NMR spectrum for HYPE-DVB (macro-comonomer) in Run 1.

**Table 1** Run1-Run 4 before and after capping DVB at various polymerization times.

Run	Time h	Before quenched			End functional HYPE after quenched by DVB ( quenching time is 1h)		
		$\overline{M}_n$	$\eta_w$	PDI	$\overline{M}_n$	$\eta_w$	PDI
		Kg.mol <sup>-1</sup>	mL.g <sup>-1</sup>		Kg.mol <sup>-1</sup>	mL.g <sup>-1</sup>	
1	0.5	9.1	8.5	1.00	9.7	8.6	1.00
2	1.0	17.0	10.1	1.00	17.7	10.3	1.01
3	2.0	28.9	12.8	1.04	31.2	13.0	1.04
4	4.0	53.4	16.1	1.05	53.0	16.2	1.04

of in situ grafting copolymerization by ATRP method have been listed in Table 2. The  $\overline{M}_n$  and PDI results of copolymers from Run 5-8 are used to investigate the effect of copolymerization reaction time (t) on copolymer structure. A good linear relationship between  $\overline{M}_n$  and t can be seen from Table 1 shown in Fig 4(a). This relationship suggests that the molecular weights obtained by in situ graft copolymerization are proportional to reaction time. It means that the concentration of the polymeric growing species in the copolymerization process remained constant within a very short time. This phenomenon is because ATRP reaction relied on establishing equilibrium between macro-comonomer concentration and free radical concentration before adding DVB comonomers, which made the free-radicals at a lower concentration and greatly inhibited the radical termination reactions. The reaction of radical coupling could not be observed by GPC results with the absence of signal higher-molecular-weight in Fig 4(b). In addition, the PDI results of the polymeric comonomers from GPC measurements are still narrow around 1.1, which could be seen in Table 2. These results further suggest that PDVB-block-HYPE materials have been successfully prepared by ATRP reaction method.

The functional active end groups, capping on the hyperbranched polyethylenes, can be used in various cases like macro-comonomers for polyolefins subsequent modifications or for architectures synthesis of many materials based on polyolefins. The microstructure of chain length and topology from these hyperbranched polyethylene-based macro-comonomers can be controlled conveniently by adjusting the conditions

in their polymerization process as we mentioned before, such as polymerization time and polymerization temperature. These hyperbranched polyethylene-base macro-comonomers are completely amorphous as transparent viscous liquid at room temperature and have good solubility in normal solvents like toluene or tetrahydrofuran solvent, even at room temperature.

The molecular weights of the prepared PDVB-b-HYPE copolymers under various ATRP time are shown in Fig 4(b), and were investigated by the GPC traces. It shows that the molecular weights of the PDVB-b-HYPE copolymers have consistent increase from 16.8 Kg.mol<sup>-1</sup> to 64.3 Kg.mol<sup>-1</sup> in Table 2 and Fig 4(b), which demonstrates the successful chain extension in the resulting polydivinylbenzene blocked hyperbranched polyethylene copolymers. These results show that obtained PDVB-b-HYPE copolymers with controlled molecular weight and still relatively narrow polydispersities have been successfully synthesized via in situ ATRP method.

#### 4. Conclusions

The functionalization of hyperbranched polyethylenes can be prepared through injecting composites with double or more functional groups like divinylbenzene in the ethylene “living” polymerization process. Hyperbranched polyethylene introducing with reactive end groups on branches, can be used as macromonomers for further directly synthesis of block copolymers. Polydivinylbenzene block hyperbranched polyethylene copolymers have been successfully synthesized via in situ

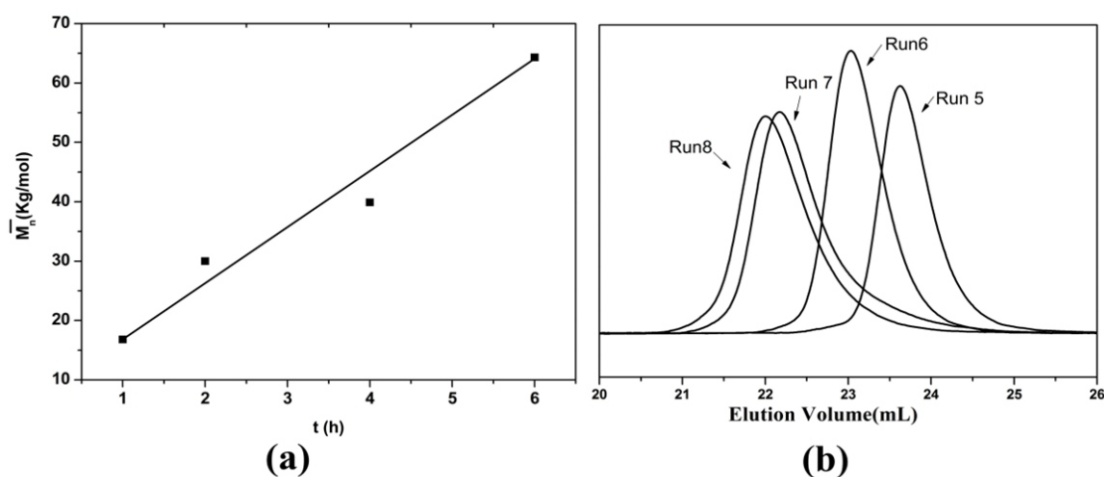


Fig. 4 (a) Dependence of  $\overline{M}_n$  on time; (b) GPC results of block copolymers at various polymerization time.

Table 2 Synthesis of PDVB-b-HYPE copolymers via ATRP method.

Run	“ATRP” polymerization time	Mn	PDI	$\eta_w$
	h	Kg.mol <sup>-1</sup>		mL.g <sup>-1</sup>
5	1	16.8	1.01	10.2
6	2	30.0	1.03	12.6
7	4	39.9	1.42	16.5
8	6	64.3	1.18	18.7

The hyperbranched polyethylene-based macro-comonomers used here were synthesized in Run 1, in Table 1

ATRP process. The resulting polystyrene-block-hyperbranched polyethylene materials have controllable structure and molecular weights, which also have good compatibilities with each constituting block parts. The structure of the block copolymers can be changed by altering the polymerization conditions. The molecular weights of the prepared block copolymers increase as the polymerization time increases (from 16.8 to 64.3 Kg.mol<sup>-1</sup>). The obtained HYPE-b-PDVB materials have better compatibility, and mechanical processing performance, compared with nonpolar polyolefin. The new improvements, as mentioned above in chain walking ethylene “living” polymerizations, provide a new technique of preparing controllable modifying polyolefins based polymer materials.

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