Notes

One-Pot Synthesis of Hyperbranched Polyethylenes Tethered with Polymerizable Methacryloyl Groups via Selective Ethylene Copolymerization with Heterobifunctional Comonomers by Chain Walking Pd−Diimine Catalysis

Jianli Wang, Kejian Zhang, and Zhibin Ye*

School of Engineering, Laurentian University, Sudbury, Ontario, Canada P3E 2C6

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Distinct from linear analogues, hyperbranched polymers have structures and topologies similar to dendrimers and possess some outstanding materials properties, such as low solution/melt viscosity, enhanced solubility, abundance in reactive terminal group, etc.[1] Unlike dendrimers that often require tedious synthetic procedures,[2] hyperbranched polymers are more easily produced in a large scale,[1] which encourages their use in a variety of potential applications, including rheological additives,[3] toughening agents,[4] drug delivery,[5] etc. In particular, hyperbranched polymers containing a large number of terminal polymerizable double bonds, such as methacryloyl and acryloyl groups, have great potential as new high-performance UV/radical curable cross-linkers for thermoset applications.[6−11] Several hyperbranched polymers functionalized with methacryloyl/acryloyl groups have been reported in the literature.[6−11] However, multistep reactions, along with specially designed monomers, are generally required for synthesis of these uniquely functionalized hyperbranched polymers. Developing one-step synthetic procedures using commercially abundant monomers is thus highly desired for commercial applications.

Chain walking ethylene polymerization with Pd−diimine catalysts represents a new concept for synthesis of hyperbranched polyethylenes.[12] In this strategy, the control of chain topology is achieved uniquely through the chain walking mechanism of the late transition metal catalysts while with simple and commercially abundant ethylene as monomer. This is in sharp contrast to the conventional synthetic approaches for hyperbranched polymers, where the hyperbranched topology is usually introduced by using specifically designed functional monomers.[12] Moreover, this strategy allows a convenient tuning of polymer chain topology from linear to moderately branched to hyperbranched structure by simple adjustment of polymerization conditions, such as ethylene pressure and reaction temperature.[12,13] Owing to their reduced oxophilicity, Pd−diimine catalysts also possess high tolerance toward polar functional groups, like ester and halide groups, and thus allow the unprecedent copolymerization of ethylene with polar monomers, typically acrylates and functionalized 1-alkenes bearing polar groups, to prepare hyperbranched polyethylenes tethered with various functionalities.[14−17]

Utilizing the unique features of chain walking polymerization, we report here a one-pot approach for the synthesis of novel hyperbranched polyethylenes tethered with methacryloyl groups by selective ethylene copolymerization with two heterobifunctional comonomers, acryloyloxyethyl methacrylate (AEM) and 2,2-dimethyl-4-pentenyl methacrylate (DMPM) (Scheme 1). A typical Pd−diimine catalyst, $[(\mathrm{ArN{=}C(Me){-}(Me)C{=}NAr})\mathrm{Pd}(\mathrm{CH_3})(\mathrm{N{\equiv}CMe})]^+\mathrm{SbF_6}^-$ (Ar = 2,6-$(i\mathrm{Pr})_2\mathrm{C_6H_3}$), was used for the chain walking polymerization in this work. This unique one-step synthetic chemistry is based on our finding that Pd−diimine catalysts cannot copolymerize methacrylate type comonomers though they are successful in copolymerizing acrylates and 1-alkenes. To demonstrate this, one ethylene polymerization run in the presence of the simplest methacrylate monomer, methyl methacrylate (MMA) at a concentration of 0.6 M in the polymerization system, was carried out at 25 °C and ethylene pressure of 1 atm using the Pd−diimine catalyst (run 2 in Table 1). One control homopolymerization run without the addition of MMA was also conducted (run 1 in Table 1). The polymerization results are summarized in Table 1.

Figure 1a shows the proton nuclear magnetic resonance (^{1}H NMR) spectrum of the polymer produced in the presence of MMA. The spectrum is identical to that of homopolyethylene with only methyl, methylene, and methine resonances from the hyperbranched polyethylene sequences in the narrow region from 0.6 to 1.5 ppm.[16,17] No resonance peak due to the incorporation of MMA is found, suggesting that MMA was not copolymerized even at a high concentration of 0.6 M. From the polymer productivity data shown in Table 1, the presence of MMA did not seem to inhibit the polymerization with a similar quantity of polymer produced compared to the control run. This is drastically different from the copolymerization of ethylene with copolymerizable acrylate and 1-alkene comonomers, where comonomer incorporation often leads to significant reduction in polymerization activity as well as the polymer molecular weight.[14b,15a] From Table 1, the two polymers have almost identical number-average molecular weight (M_n) and polydispersity index (PDI) data determined by using gel permeation chromatography with on-line viscometry (GPC-VIS). All these results suggest that the polymer synthesized in the presence of MMA is essentially an ethylene homopolymer and methacrylate comonomers cannot be copolymerized with ethylene by chain walking polymerization with Pd−diimine catalysts. The exact reason for the inaccessibility of methacrylates to copolymerization with ethylene by Pd−diimine catalysts is not known, possibly due to the sterically bulkier structure of the 1,1-disubstituted monomers.

This finding led us to synthesize and utilize the two heterobifunctional monomers (AEM and DMPM), possessing two different double bonds at each of the two ends, as comonomers for chain walking ethylene copolymerization. Both of these two monomers contain one copolymerizable group

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* Corresponding author: e-mail zye@laurentian.ca; Fax 1(705) 675-4862.

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Scheme 1. Structures of Heterobifunctional Comonomers and Synthesis of Hyperbranched Polyethylene Tethered with Terminal Methacryloyl Groups

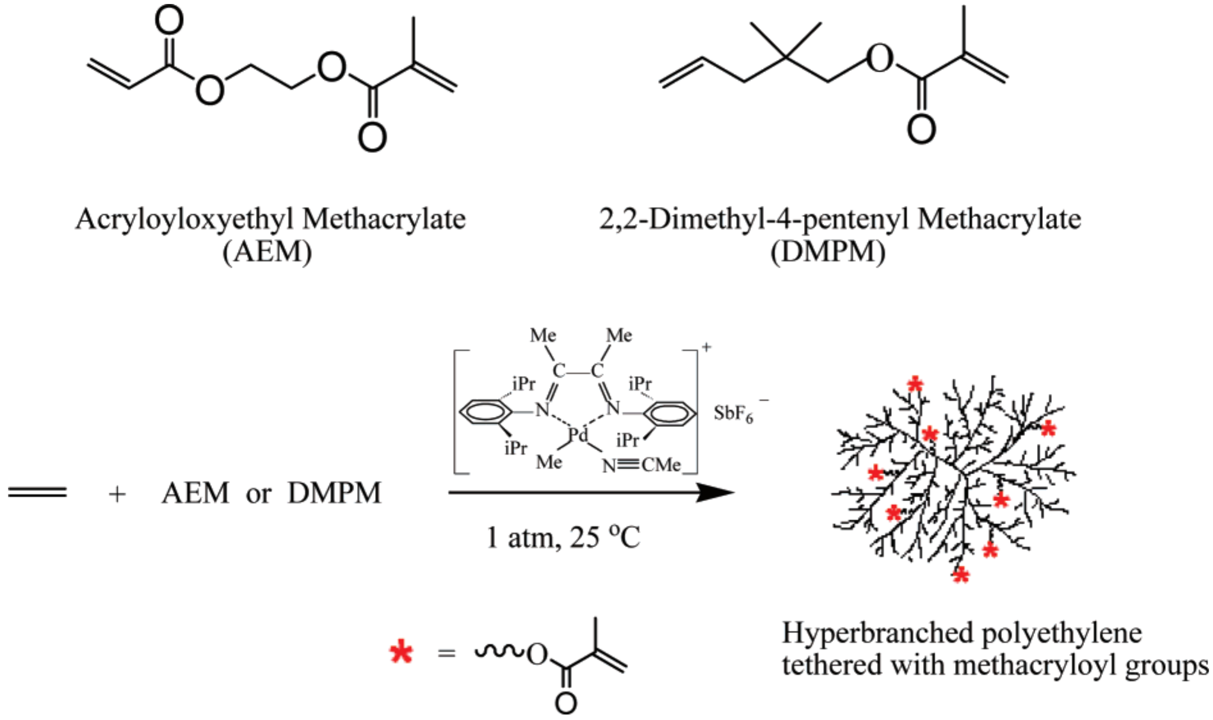

Table 1. Polymerization Conditions and Results and Polymer Properties

run	comonomer and concn (mL)[a]	polymer amount (g)	comonomer incorporation[b] (mol %)	GPC-VIS[c] M_n (kg/mol)	GPC-VIS[c] PDI	branching density[d] (per 1000 C)	thermal transitions [e]
1		9.8		118	1.70	102	−67.5 °C (T_g)
2	MMA, 0.6 M	11.2	0	118	1.66	100	−67.5 °C (T_g)
3	AEM, 0.1 M	3.3	0.2	63	1.74	102	−68.6 °C (T_g)
4	AEM, 1.0 M	2.2	3.6	62	1.47	90	−64.3 °C (T_g)
5	DMPM, 0.15 M	6.0	0.6	5.2	3.47	106	−71.2 °C (T_g)

[a] Other conditions: Pd−diimine catalyst, 0.1 mmol; solvent, CH_2Cl_2; total volume, 50 mL; temperature, 25 °C; ethylene, 1 atm; polymerization time, 24 h. [b] Comonomer percentage in the copolymers determined using ^{1}H NMR spectroscopy in $CDCl_3$ at room temperature. [c] Number-average molecular weight (M_n) and polydispersity index (PDI) determined using gel permeation chromatography with on-line viscometry (GPC-VIS). [d] Branching density determined using ^{1}H NMR spectroscopy. [e] Thermal transition temperatures determined using differential scanning calorimetry in the second heating scan at 10 °C/min.

(acryloyl and 1-alkenyl, respectively) and one incopolymerizable methacryloyl moiety. Owing to the complete selectivity of the Pd−diimine catalyst toward the acryloyl or 1-alkenyl groups in the two heterobifunctional comonomers, hyperbranched polyethylenes tethered with methacryloyl end groups will be resulted via the sole enchainment of the acryloyl or 1-alkenyl groups (Scheme 1). In these functionalized hyperbranched polymers produced, intra- or intermolecular cross-linking should be absent owing to the complete incopolymerizability of the methacryloyl groups in chain walking copolymerization. However, cross-linking might occur due to thermally initiated radical polymerization among the pendant methacryloyl groups. In designing the 1-alkenyl type heterobifunctional monomer, DMPM, a quaternary blocking carbon was introduced between the 1-alkenyl and the methacryloyl groups to block the Pd catalyst from walking to the carbon next to the methacryloyl group during chain growth, which can possibly deactivate the catalyst.[15a]

Chain walking ethylene copolymerizations with the two heterobifunctional monomers were carried out at an ethylene pressure of 1 atm and polymerization temperature of 25 °C. The reduced ethylene pressure was chosen with the purpose of generating hyperbranched chain topology,[13] and the temperature of 25 °C was selected to minimize the possible thermal initiated radical cross-linking among the methacryloyl groups at elevated temperatures. For AEM, two levels of comonomer concentration were chosen. Table 1 summarizes the polymerization conditions and results.

^{1}H NMR elucidation of the copolymer microstructures confirms the selective incorporation of both AEM and DMPM in the hyperbranched copolymers through the sole enchainment of the acryloyl and 1-alkenyl groups, respectively. Figure 1b shows the ^{1}H NMR spectrum of the copolymer synthesized in run 4 (with AEM at 1.0 M), and Figure 1c shows the spectrum of AEM for comparison. In Figure 1b, the incorporation of AEM and the presence of methacrylate groups in the copolymer can be evidenced from the signals of the double bond protons (e* at 6.12 and 5.58 ppm), the signal of the methyl protons on the methacryloyl group (f* at 1.94 ppm), and the signals of the methylene groups between the two ester functionalities (c*, d*

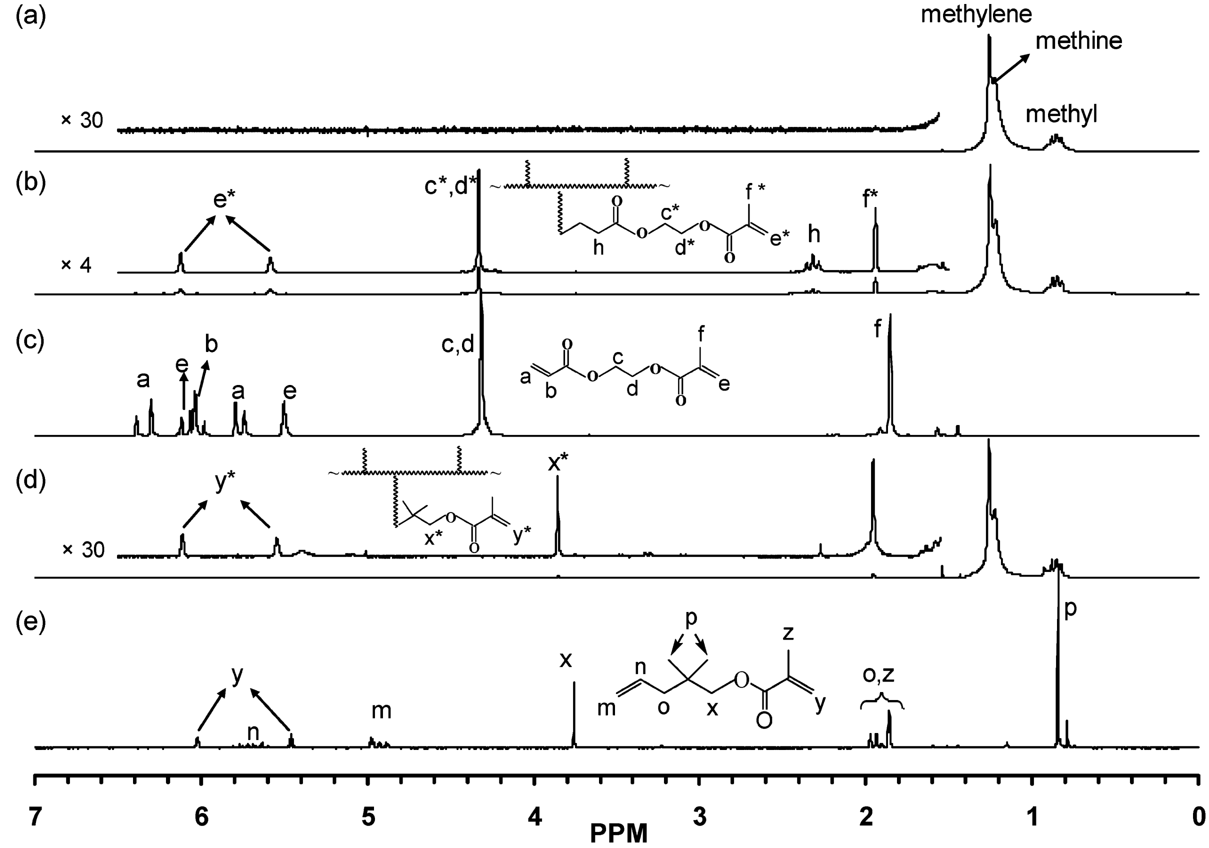

Figure 1. ^{1}H NMR spectrum of (a) polymer synthesized in run 2, (b) copolymer of ethylene and acryloyloxyethyl methacrylate synthesized in run 4, (c) acryloyloxyethyl methacrylate, (d) copolymer of ethylene and 2,2-dimethyl-4-pentenyl methacrylate synthesized in run 5, and (e) 2,2-dimethyl-4-pentenyl methacrylate.

at 4.31 ppm). On the contrary, the signals attributable to the acrylate groups are not found. This corroborates that AEM is incorporated through enchainment of acryloyl groups and methacryloyl functionalities are intact. In addition, a new triplet signal (h) located at 2.31 ppm, not found in the comonomer, is observed in Figure 1b. This triplet resonance is assigned to the methylene protons of the incorporated acryloyl group, whose structure is shown in Figure 1b. Such a unique microstructure has been typically observed in olefin−acrylate copolymers prepared using Pd−diimine catalysts.[14a,b,16,17] The mechanism leading to this microstructure has been elucidated clearly in the reports by Brookhart et al.[14a,b] It is a consequence of the 2,1-insertion of acrylate comonomer into the Pd−polymer bond followed by rearrangement, leading to the formation of a six-member stable chelate structure available for subsequent ethylene insertion.[14a,b]

Figure 1d shows the ^{1}H NMR spectrum of the copolymer synthesized in run 5 (with DMPM at 0.15 M), and Figure 1e shows that of DMPM comonomer. The incorporation of DMPM and the tethering of methacryloyl groups in the copolymer were evidenced on the basis of signals x* and y* shown in Figure 1d. Similarly, the 1-alkenyl groups were not observed, showing the comonomer incorporation occurred through sole enchainment of the 1-alkenyl groups. The comonomer molar percentages in the three copolymers were calculated on the basis of their ^{1}H NMR spectra. Table 1 lists the calculation results. Comparing runs 3 and 4, increasing AEM concentration from 0.1 to 1.0 M during polymerization led to an increase in comonomer molar percentage from 0.2 to 3.6% and a decrease in both polymer productivity and polymer molecular weight, which are consistent with the literature results on ethylene copolymerization with methyl acrylate.[14a,b] The branching densities of these hyperbranched polymers (listed in Table 1), resulting from chain walking of the Pd−diimine catalyst, were determined on the basis of the methyl, methine, and methylene signals of the ethylene sequences in the ^{1}H NMR spectra.

Like the homopolymers synthesized in runs 1 and 2, the copolymers obtained in runs 3−5 are completely amorphous oil-like materials at room temperature. Differential scanning calorimetry (DSC) measurements showed that they exhibit similar thermal behaviors with a glass transition temperature (T_g) at about −67 °C and a very weak endotherm centered at about −35 °C (Table 1).[16,17] The comonomer incorporation does not introduce other thermal transitions. However, the incorporation of AEM slightly increases the value of T_g (copolymer in run 4), while DMPM incorporation seems to slightly reduce the value of T_g. In the first heating scan during DSC measurement, a broad exothermic peak centered at about 130 °C was observed with the AEM copolymer synthesized in run 4, indicating the exothermic polymerization of the pendant methacryloyl groups in this polymer having the highest content of methacryloyl groups. In the subsequent (second and third) heating scans, no exotherm was found, indicating the polymerization was complete in the first heating scan. Such an exothermic peak was not detected with other two copolymers due to the low contents of methacryloyl groups.

Figure 2a compares the Mark−Houwink plot (intrinsic viscosity vs molecular weight) of the four polymers synthesized in runs 1−4, obtained from GPC-VIS measurements.[13,18] A very similar and weak dependency of intrinsic viscosity on polymer molecular weight was observed, indicating the similar hyperbranched chain topology possessed in these polymers. The incorporation of small sized comonomer does not seem to significantly affect the chain topology of the copolymers.[17] This

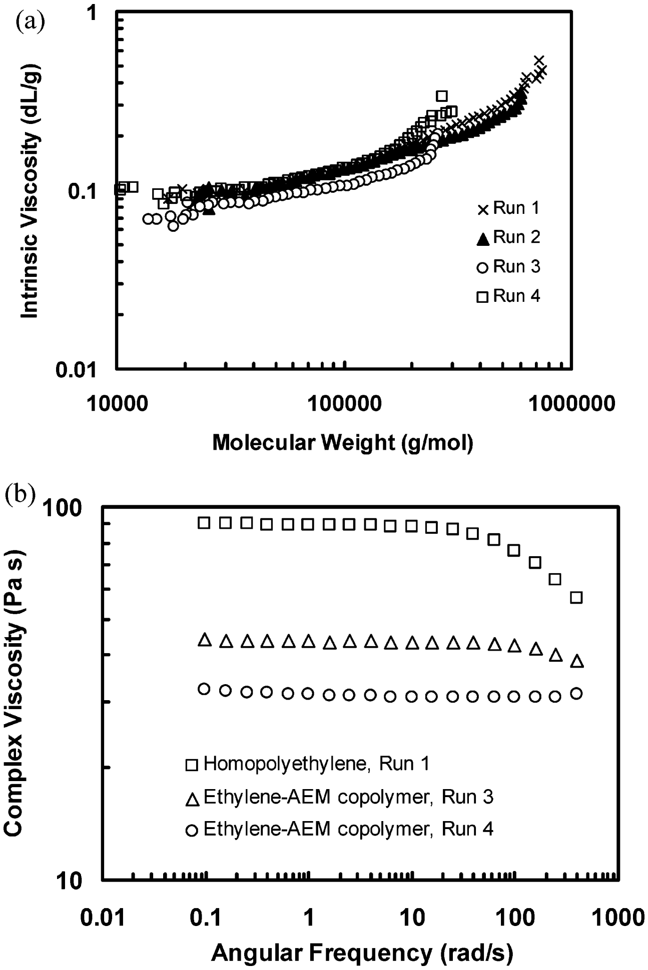

Figure 2. (a) Intrinsic viscosity vs molecular weight plot from gel permeation chromatography−viscometry measurements in tetrahydrofuran at 30 °C. (b) Polymer melt complex viscosity spectra obtained at 25 °C from small-amplitude dynamic oscillatory measurements.

is different from the copolymers of ethylene with acryloyl−POSS (polyhedral oligomeric silsesquioxane) macromonomer, where significant reductions in the intrinsic viscosity of the copolymers occurs owing to the covalent tethering of highly compact POSS nanospheres of high mass density.[16] Figure 2b compares the complex viscosity spectra obtained at 25 °C for the three polymers synthesized in runs 1, 3, and 4, respectively. The homopolyethylene synthesized in run 1 possesses a low Newtonian viscosity of 89 Pa s at 25 °C and exhibits shear thinning at the high-frequency end. The two ethylene−AEM copolymers possess even reduced Newtonian viscosity (43 and 31 Pa s, respectively) and do not show obvious shear thinning behavior due to their reduced molecular weight.

In summary, we synthesized hyperbranched polyethylenes tethered with polymerizable methacryloyl groups, utilizing the unique selective copolymerization of ethylene with two heterobifunctional comonomers, AEM and DMPM. These functionalized hyperbranched polymers exhibit low glass transition temperature and low melt viscosity and have great potential for applications like inkjet printable UV-curable macro-cross-linker.

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Supporting Information Available: Experimental part and themograms of the polymers obtained from DSC measurements. This information is available free of charge via the Internet at http://pubs.acs.org.

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