A Novel Linear−Hyperbranched Multiblock Polyethylene Produced from Ethylene Monomer Alone via Chain Walking and Chain Shuttling Polymerization

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ABSTRACT: A novel linear−hyperbranched multiblock polyethylene was prepared from ethylene monomer alone via chain walking and chain shuttling polymerization in the presence of chain transfer agent ($ZnEt_2$). In the binary catalyst system, α-diimine nickel(II) bromide complex (CatA) produced chain segments with hyperbranched architecture via chain walking, and *ansa*-ethylenebis(1-η^5-indenyl)zirconium dichloride (CatB) yielded linear chain segments, while $ZnEt_2$ facilitated chain exchanges between two active metal centers. The resultant multiblock polyethylene featured a narrow weight distribution and useful combining properties of linear and branched polyethylene. Further, polymers were expediently prepared in an effective and economical polymerization process from ethylene monomer alone.

Introduction

Obtaining polymers with novel architectures and outstanding performances attracted significant attention in polymer chemistry[1,2] from commercially abundant and cheap monomers. Ethylene is the simplest and most inexpensive olefin monomer, and linear polyethylene is capable of predominant tensile strength and high melt-fracture resistance, but relatively poor toughness. Usually in order to improve polyethylene properties, it is desirable to introduce a second monomer such as 1-hexene, 1-octene, 1-decene, and other 1-alkenes into the backbone of polyethylene for preparing ethylene-based block polyolefin.[3,4] Because of the amorphous "soft" branched segment and "hard" linear segment, ethylene-based block polyolefin is readily amenable for applications as thermoplastic elastomers, compatibilizers, and high-impact plastics.[5,6] Living olefin polymerization (LOP) is an important candidate for preparing block polyolefin via sequential monomers addition, in which a number of catalysts such as diamine bisphenolate zirconium catalysts, fluorinated bis(phenoxyimine)titanium complexes, palladium, and nickel α-diimine catalysts have been employed.[7,8] Dow Co. effectively produced polyethylene-*b*-poly(ethylene-*co*-octene) via chain shuttling polymerization (CSP) and coordination chain transfer polymerization (CCTP). The resultant block architecture furnished materials with useful combining properties of linear and branched polyolefin.[9,10] However, in all aforementioned strategies, expensive comonomers such as 1-hexene, 1-octene, and 1-decene were used, leading to high costs for commercial utility.

Recently, there have been tremendous advances in polymerization technology and transition metal catalyst, such as metal-catalyzed coordination polymerization for linear polyethylene,[11−14] chain walking olefin polymerization with Ni,Pd−diimine catalysts for hyperbranched polyolefin,[15−19] and chain shuttling polymerization for block polyolefin.[9] In this paper, we synthesized a novel linear−hyperbranched multiblock polyethylene that featured alternating "hard" block (linear polyethylene) and "soft" block (hyperbranched polyethylene) only from ethylene monomer via chain walking and chain shuttling polymerization. This strategy stands out from LOP, CSP, and CCTP for just using ethylene, carrying out under moderate polymerization conditions and obtaining the resultant polymer with novel microstructure.

Results and Discussion

Toward the goal of preparing linear−hyperbranched multiblock polyethylene, homogeneous single site α-diimine nickel(II) bromide complex (CatA) and *ansa*-ethylenebis(1-η^5-indenyl)zirconium dichloride (CatB) were employed for ethylene polymerization with diethylzinc ($ZnEt_2$) as chain transfer agent. CatA is a chain walking catalyst and can yield completely amorphous polyethylene with very low glass transition temperatures (T_g).[15] By contrast, CatB is of high activity for ethylene polymerization and generates linear materials with melting temperatures (T_m) over 130 °C at certain conditions[20−22] (Figure 1). Both catalyst precursors are activated by methylaluminoxane (MAO), which make it possible that the binary catalysts operate in ethylene polymerization together. Many literatures[23−26] have reported main group metal alkyls such as ZnR_2, AlR_3, GaR_3, SnR_4, and PbR_4 were applied as chain transfer agents in olefin polymerization. Among these agents, $ZnEt_2$ is one of most effective agents, which allows us to utilize it as chain transfer agent (CTA).

The individual catalyst system and binary catalyst system were typically activated with MAO in the presence of varying contents of $ZnEt_2$, and ethylene polymerization was conducted under 1 atm ethylene pressure for 30 min and 20 °C. Then the resultant polyethylene was analyzed by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) (Table 1). Data from run 1 and run 2 recorded a slight decrease in molecular weight of the resultant polyolefin, indicating that chains transferred from nickel to zinc in the ethylene polymerization with CatA/MAO/$ZnEt_2$. 100 equiv of diethylzinc resulted in a sharp drop of molecular weight from 2.77×10^4 to 3.0×10^3 (run 3 versus run 4), which suggested that quantitative chain transfer occurred with $ZnEt_2$.[27] In addition, the resultant polymers obtained by binary catalyst system in

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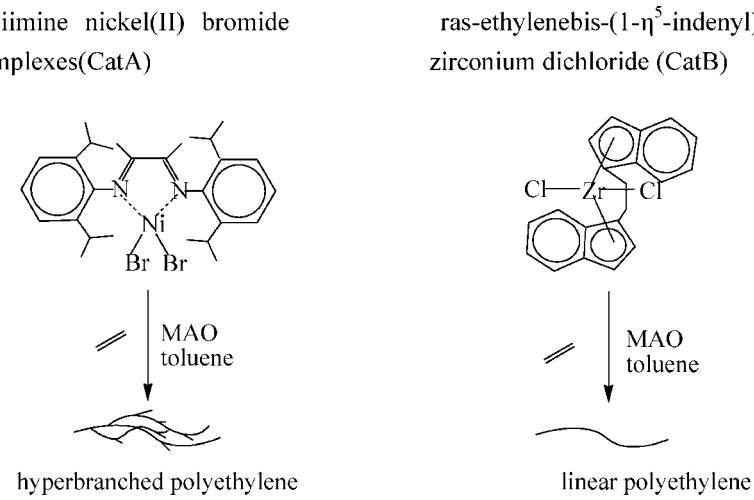


Figure 1. Architecture of polyethylene produced via Ni- and Zr-based catalysts.

Table 1. Ethylene Polymerization Catalyzed by Individual and Binary Catalyst System in the Absence and Presence of $ZnEt_2$[a]

run	CatA/ CatB (μmol/μmol)	[$ZnEt_2$]/[CatA + CatB] (mol/mol)	activity (10^{-6}g/(mol h atm))	M_n[b] (g/mol)	M_w/M_n	T_m[c]	ΔH_f[c]
1	1/0	0	0.72	97 300	1.87	−[d]	−
2	1/0	100	1.6	92 900	2.38	−[d]	−
3	0/1	0	0.68	27 700	2.86	131	173
4	0/1	100	0.42	3 000	2.73	130	176
5	0.5/0.5	0	0.7	80 100	3.77	124	9.6
6	0.5/0.5	100	0.84	134 500	1.94	122	6.0
7	0.5/0.5	150	0.97	95 600	2.21	121	2.5
8	0.5/0.5	50	0.91	135 200	2.23	122	7.5
9	0.5/0.5	25	0.78	115 000	2.54	123	8.6
10	0.25/0.75	100	0.68	138 300	1.91	120	15.2

[a] Polymerization conditions: t_p = 30 min, 50 mL of toluene solvent, T_p = 20 °C, 1 atm of ethylene gas, MAO as cocatalyst and Al/(CatA + CatB) = 1000. [b] Determined by GPC at 150 °C versus polystyrene standard. [c] From DSC measurements. [d] Completely amorphous.

the presence of $ZnEt_2$ had higher molecular weight than that with only one catalyst system, and it was up to 1.3×10^5 g/mol (run 6). We presumed that active linear chain transferring to nickel largely increased relative rate of propagation due to less steric hindrance of linear chain as compared to branched chain. Meanwhile, active branched chain on zirconium led to decrease relative rate. Because of the contrary and complicated influence of chain microstructure on relative rate, polyethylene achieved higher molecular weight via chain transfer.

The molecular weight distribution of polyethylene prepared in binary catalyst system was also enumerated in Table 1. Synthesis of linear−hyperbranched block polyethylene was pursued in runs 6−10, and the polymerization was carried out in the presence of varying molar equivalents of $ZnEt_2$ at constant temperature. In run 5, polyethylene was produced with a broad and bimodal molecular weight distribution (M_w/M_n = 3.77) which highlighted that each catalyst operated independently in polymerization process, so the resultant polyethylene produced in run 5 was similar to the mixture of hyperbranched and linear polymer, which could obtain in runs 1 and 3, respectively. Surprisingly, the GPC curves of the resultant polymers prepared using the binary catalyst system with various molar equivalents of $ZnEt_2$ were unimodal. Especially, the resultant polymer with 100 mol equiv of $ZnEt_2$ had narrowest molecular weight distribution (M_w/M_n = 1.91, run 10). The results of runs 6−10 were in contrast to run 5, which suggested that CatA/CatB/MAO/$ZnEt_2$ system was capable of catalytically preparing linear−hybranched block polyethylene (Figure 2).

Composition of linear segment and hyperbranched segment in resultant polymer is a key parameter. Calculated from the comparison of catalyst activity in run 1 and run 3, run 5 contained about 48.6 wt % linear and 51.4 wt % hyperbranched

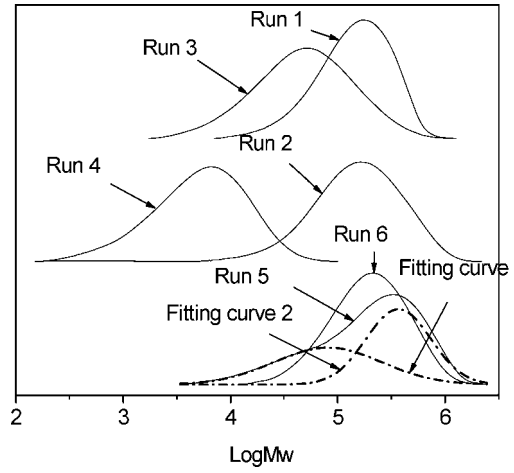


Figure 2. Effect of $ZnEt_2$ on molecular weight distribution of resultant polyethylene. The product prepared in CatA/CatB possesses bimodal molecular weight distribution, while the product prepared in CatA/CatB/$ZnEt_2$ possesses narrow molecular weight distribution, and the curve of run 5 was viewed as similar summation of fitting curve 1 and fitting curve 2.

polyethylene, since the resultant polyethylene of run 5 was similar to the mixture of that of run 1 and run 3 on the basis of the above analysis. According to the activity of CatA and CatB in the presence of $ZnEt_2$ (run 2 and run 4), linear polymer weight percent of run 6 was about 21 wt %. When the ratio of CatA/CatB was 0.25/0.75 in the presence of 100 mol equiv of $ZnEt_2$, the resultant polymer with 44% linear segment was produced (run 10). Therefore, linear−hyperbranched multiblock polyethylene with different contents of linear and hyperbranched

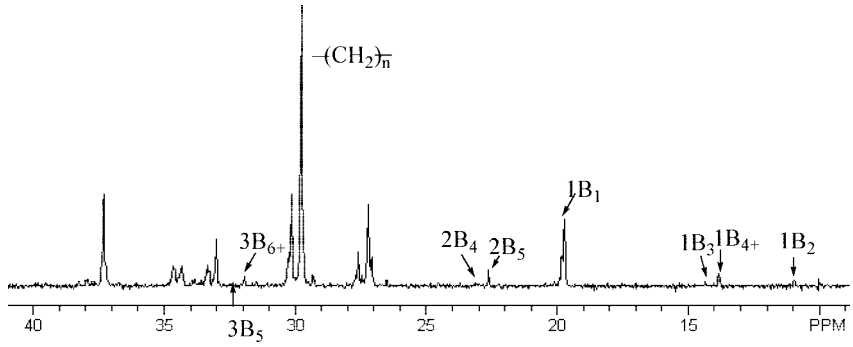


Figure 3. ^{13}C NMR (o-$C_6D_4Cl_2$, 300 MHz, 120 °C) of branched polyethylene formed by CatA/ MAO at 20 °C (run 1).[28,29]

Table 2. Short Chain Branching Distribution Determined Approximatively from ^{13}C Nuclear Magnetic Resonance Spectroscopy for Linear−Hyperbranched Polyethylene[a] [28,29] (See Supporting Information)

run	methyl	ethyl	propyl	butyl	amyl	long	total branch[b]
1	91.2	3.4	2.5	2.6	1.8	9.3	110.8
2	84.4	2.8	1.5	1.5	1.4	8.8	100.4
5	56.4	3.2	2.8	1.5	1.4	9.1	74.4
6	57.8	2.8	2.5	1.2	1.3	7.2	72.8
10	52.6	4.5	1.1	1.0	1.1	4.4	64.7

[a] ^{13}C nuclear magnetic resonance (300 MHz) spectra were obtained with o-$C_6H_4Cl_2$ as the solvent at 120 °C. [b] Number of branches per 1000 carbons.

segments were effectively produced via the binary catalyst system in the presence of $ZnEt_2$.

^{13}C NMR measurements were performed to elucidate the branching structures of linear−hyperbranched multiblock polyethylene, short branches from methyl, ethyl, butyl, to amyl, and the longer were identified approximatively by the unique carbon resonances (Figure 3), which allowed the calculation of the density of each branching type per 1000 carbons in polymers.[28,29] As shown in Table 2, such hyperbranched architectures owed to the chain walking mechanism of CatA. Moreover, among branches were predominately methyl, the number of total branch strictly depended on the molar ratio of CatA/CatB, which indicated that the weight percent of linear segment in block polyolefin increased with the decrease of the molar ratio of CatA/CatB.

In random copolymer, the melting temperature (T_m) of linear−branched block polyolefin always maintains a linear relationship with branch density in backbone.[30] In run 1 and run 2, the melting temperature (T_m) of the resultant polyethylene was more than 130 °C, which evidenced that CatB produced linear polyolefin. The T_m of the polyethylene obtained by using binary catalyst system in the presence of $ZnEt_2$ were equal to or higher than120 °C, which was the typically characteristic of linear polyethylene (Figure 4). On the basis of above analysis, high T_m enabled an unambiguous identification of the microstructure of linear−hybranched polyethylene.

To avoid continuous process and expensive comonomer, only one monomer, ethylene, was introduced into one batch for polymerization in this work. CatA produced segments of hyperbranched polyethylene, and then the segment were exchanged with chain shutting agent bearing linear segments produced by CatB, so chain shuttling occurred. After that, the linear segments on metal active center of CatA "outgrew" new hyperbranched segments. And then the multiblock segments were obtained for chain shuttling occurred repeatedly. Simultaneously, the metal active center of CatB was also involved in chain shuttling. The resultant block polyethylene featured alternating hard (linear and high glass transition temperature)

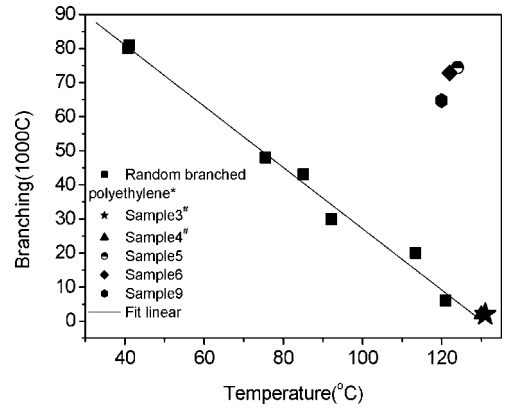


Figure 4. Temperature of the melting point of polyethylenes as a function of branching: (*) ref 30; (#) based on the assumption that the CatB/MAO and CatB/MAO/$ZnEt_2$ system produced polyethylenes bearing no branch, except for two methyl on chain ends. The melting temperature of random copolymer maintained a linear relationship with branching number; by contrast, T_m of block polymer was equal to or higher than 120 °C.

and soft (hyperbranched and low glass transition temperature) blocks, represented combining properties of hyperbranched and linear polyethylene.[9,10]

We continued a fundamental investigation of catalyst system via electron paramagnetic resonance (EPR) at 20 °C. CatA/CatB in toluene did not show any measurable EPR signal (Figure 5a), indicating that Ni(II) had no paramagnetism while CatB did not appear signal due to the absence of single electron. However, when CatA/CatB were activated by MAO, a striking signal with in $g = 2.12$ was detected (Figure 5b,c), indicating the formation of Ni(II) complex. As reported in related literatures,[15,31] only the Ni(II) complex (Scheme 1, species **3**) was capable of catalyzing ethylene polymerization, but a small amount of Ni(II) complex was reduced into Ni(I) complex (Scheme 2, species **4**) by MAO.[32,33] To our best knowledge, it was first reported that α-diimine nickel(II) bromide complex was reduced to Ni(I) complex. Then the signal intensity decreased dramatically by introducing 1 atm of ethylene into catalyst system for 5 min; it was possible Ni(I) was continuously reduced by ethylene into finely nickel metal without observation of EPR signal.[32]

Addition of $ZnEt_2$ into the CatA/CatB/Al system enhanced not only EPR signal strength before and after introducing ethylene for 5 min (Figure 6) but also the activity in ethylene polymerization (Figure 6 and Table 1). The possible reason was that besides chain transfer agent, $ZnEt_2$ acted as a scavenger, so the degree of alkylation CatA can be increased effectively with same amount of MAO. On the basis of these influence, the polymerization rate in the presence of $ZnEt_2$ maintained very stable during polymerization process (see Supporting Informa-

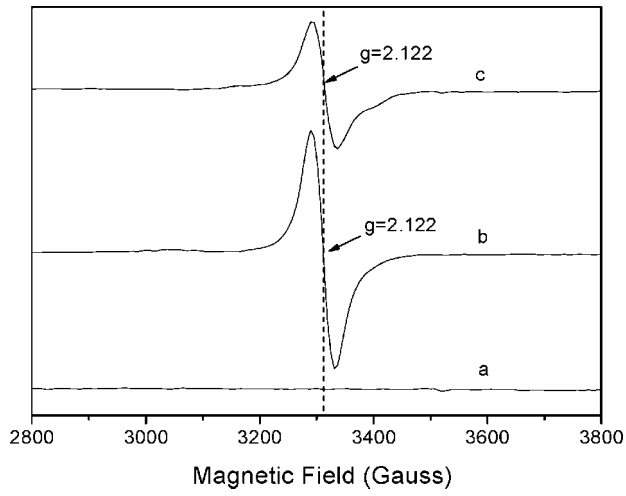


Figure 5. Monitoring catalyst system at different polymerization time via EPR at 293 K: (a) EPR spectra of catalyst system (CatA/CatB = 0.5/0.5); (b, c) EPR spectra of catalyst system (CatA/CatB/Al = 1/1/1000) before and after introducing ethylene for 5 min under atmosphere pressure.

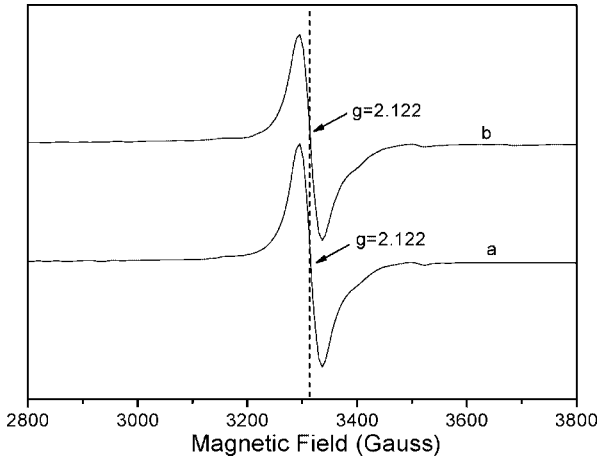
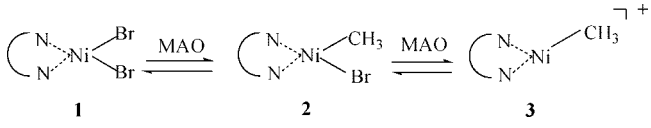
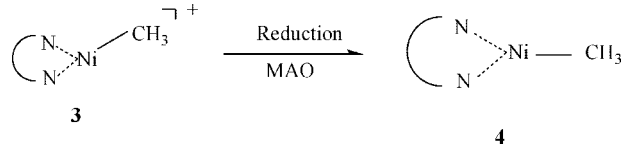


Figure 6. Monitoring of binary catalyst system at different polymerization time via EPR at 293 K: binary catalyst system (CatA/CatB/Al/$ZnEt_2$ = 0.5/0.5/1000/ 100) (a) before and (b) after introducing ethylene for 5 min under atmosphere pressure.

Scheme 1



Scheme 2



tion), which favored the synthesis of multiblock polymer.

In summary, a novel linear−hyperbranched multiblock polyethylene was synthesized via chain walking and chain shuttling polymerization in one pot. In binary catalyst system, homogeneous single site α-diimine nickel(II) bromide complexes (CatA) produced chain with hyperbranched architecture via chain walking while *ansa*-ethylenebis(1-η^5-indenyl)zirconium dichloride (CatB) afforded linear chain. Then chain transfer agent ($ZnEt_2$) facilitated chain shuttling between two active metal centers. Because of combining properties of linear and branched polyethylene, the synthesized material was excellent elastomer with high melting temperature and narrow molecular weight distribution. Moreover, the material was expediently produced in effective and economical polymerization processes from ethylene monomer alone.

Supporting Information Available: Polymerization details, GPC and ^{13}CNMR spectra of polymers, and kinetic curves of ethylene polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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