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Synthesis of Hydroxy-Terminated Polyethylene via Controlled Chain Transfer Reaction and Poly(ethylene-*b*-caprolactone) Block Copolymer

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Recent progress in homogeneous transition metal catalysts for olefin polymerization provides a synthetic route to functionalized polyolefins that have been a challenging subject since the discovery of Ziegler−Natta catalysts in the 1950s.[1] In general, functionalized polyolefins can be prepared by (1) modification of preformed polyolefins,[2] (2) direct copolymerization of olefins with a functional monomer (protected or nonprotected),[3] and (3) in-situ chain transfer to chain transfer agent during polymerization.[4] Among these methods, the in-situ chain transfer method is a convenient way to make terminally functionalized polyolefins which can be further utilized in making the polymers with diverse structure such as block and graft copolymers. The block copolymers consisting of two immiscible polymer chains have been known as a very effective compatibilizer in a polymer blend of two immiscible homopolymers.[5] Especially, the block copolymers of polyolefin and vinyl monomers are particularly useful for blending of polyolefins that are not compatible with many other polymers.[6] Alkyl zinc,[4a] borane,[4b] and silanes[4c] compounds were used as a chain transfer agent in conventional $TiCl_3/Al(C_2H_5)_3$ or homogeneous metallocene-catalyzed olefin polymerization. However, these methods need extra chain transfer agents during the polymerization. In our previous study,[7] we found that the chain transfer reaction of ethylene copolymerization with metallocene/methylaluminoxane (MAO) catalysts could be controlled through proper combination of metallocene catalysts and comonomer like allylbenzene and, in some cases, chain transfer to aluminum became dominant chain transfer reaction of ethylene copolymerization. Among several factors that affect the mode of chain transfer reactions, controlling steric bulkiness of the ligand in metallocene catalyst is critical in homogeneous metallocene-catalyzed polymerization. As steric bulkiness of the ligand increases, β-hydride elimination tends to decrease. The reason for suppression of β-H elimination with the steric bulkiness suggested by Bercaw[8] is that the β-agostic interaction, which is a key step for β-H elimination, is difficult to achieve due to the steric repulsion between the bulky ligand and the axial polymer chain. Consequently, the aluminum transfer reaction becomes the predominant chain transfer reaction in this case. In this study, we report the facile synthesis of hydroxy-terminated polyethylene (PE-OH) through controlled chain transfer reaction and its transformation to poly(ethylene-*b*-caprolactone) block copolymer.

Scheme 1. Synthesis of Hydroxy-Terminated Polyethylene and Poly(ethylene-*b*-caprolactone) Block Copolymer

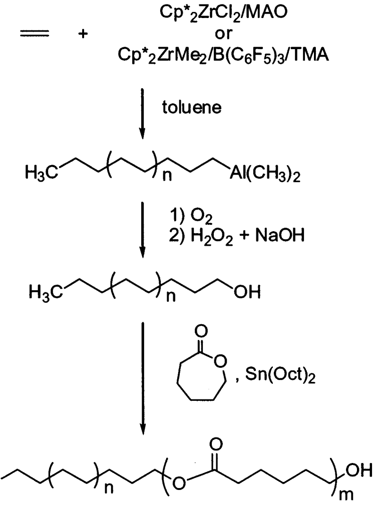

Table 1. Results of Ethylene Polymerization at Various Temperatures[a]

run no.	temp (°C)	yield (mg)	activity[b]	β-H elim/ Al-tr[c]	M_n[d]	PDI[d]
1	30	288	364		12750	2.08
2	50	373	471		8150	1.70
3	70	678	857	0.35	4140	1.81
4	90	439	555	1.28	1900	2.74

[a] Polymerization conditions: catalyst = $Cp^*{}_2ZrCl_2$/MAO, [Zr] = 1.9 μmol, [Al]/[Zr] = 2000, ethylene pressure = 1.25 atm, solvent = 30 mL of toluene, t = 20 min. [b] Activity = kg/(mol of cat atm h). [c] Ratio of β-H elim/Al-tr calculated by ^{1}H NMR. [d] M_n and PDI determined by GPC using 1,2,4-TCB as solvent at 135 °C.

Polymerization of ethylene was carried out in toluene with a catalyst having sterically hindered pentamethylcyclopentadienyl ligand, $Cp^*{}_2ZrCl_2$/MAO, and all the polymerization mixtures were subjected to oxidative workup to convert the aluminum-terminated end groups to hydroxy groups. Oxidation of aluminum-terminated polyethylene was accomplished by bubbling dry oxygen into the polymerization solution followed by addition of hydrogen peroxide and NaOH solution (Scheme 1). The polymerization results are summarized in Table 1.

Ethylene polymerization with $Cp^*{}_2ZrCl_2$/MAO in toluene at 50 °C affords polyethylene with an average molecular weight (M_n) of 8150 (Table 1, run 2). After oxidative workup of the polymer, ^{1}H and ^{13}C NMR spectra (Figure 1) of the polymer show the peaks corresponding to hydroxyl methyl end groups, but there is no peaks of olefin end groups formed by β-H elimination. The resonances at 3.65 ppm in the ^{1}H NMR and at 62.97 ppm in the ^{13}C NMR are a clear indication of the presence of a hydroxy methyl end group. The ratio of the hydroxy-terminated end group to the methyl end group was estimated by integration of ^{1}H NMR spectrum.

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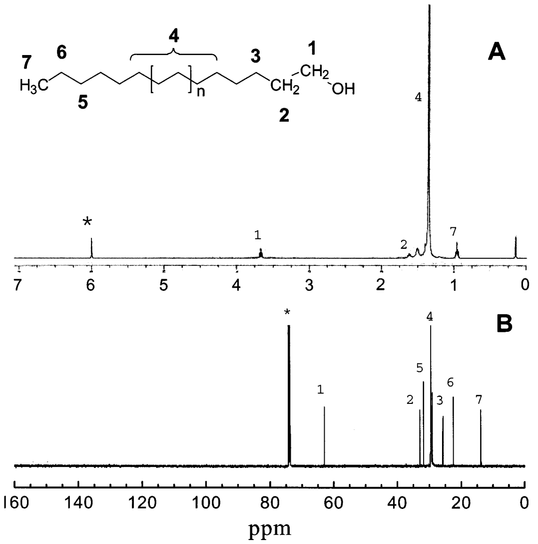

Figure 1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of hydroxy-terminated polyethylene (run 2 in Table 1) using 1,1,2,2-tetrachloroethane solvent at 100 °C (* solvent peak).

It was found, however, that the ^{1}H NMR technique had some limitation to quantify the content of hydroxy methylene (triplet, 3.61 ppm) and methyl end group (triplet, 0.90 ppm) groups presumably due to the formation of micellar aggregation of hydrophilic $-$OH group in hydrophobic tetrachloroethane-d_2 solvent. The aggregation phenomenon was supported by a variable temperature ^{1}H NMR experiment that showed the change of integration value of the hydroxy methyl group. As temperature increased, the integration ratio of $-CH_2-$OH/$-$CH$_2-CH_3$ increased. The ^{1}H NMR measurement at 120 °C reveals that at least more than 85% of the polymer chain has a hydroxy methyl end group.

The polymerization temperature was also an important factor in chain transfer mode of the polymerization. Generally, the β-H elimination of transition metal catalyzed polymerization increases as temperature increases. The ^{1}H NMR spectrum of the polyethylene obtained at 70 °C shows small but clear peaks of the olefinic double bond, indicating that β-H elimination also occurred during the polymerization.

If chain transfer to aluminum was the only chain transfer reaction of the polymerization, controlling aluminum transfer rate enables the molecular weight control of polyethylene. To investigate the effect of trimethylaluminum (TMA) concentration, the $Cp*_2ZrMe_2/B(C_6F_5)_3$ catalyst system, instead of $Cp*_2ZrCl_2$/MAO, was used, and a prescribed amount of TMA was added into the polymerization reactor. To avoid the conversion of $B(C_6F_5)_3$ to $Al(C_6F_5)_3$ by $AlMe_3$,[9] $Cp*_2ZrMe_2$ and $B(C_6F_5)_3$ were placed in the reactor first, and $AlMe_3$ was added into the reactor right after the polymerization started. As expected, the molecular weight of the polyethylene decreased linearly as the concentration of TMA increased (Table 2).

Poly(ethylene-*b*-caprolactone) block copolymer was synthesized from PE-OH and ϵ-caprolactone by using stannous octoate as a catalyst for ring-opening polymerization of ϵ-caprolactone. Despite that the every procedure was carefully taken to avoid residual water in the polymerization system, a small amount of caprolactone homopolymer was generated, but poly(ϵ-caprolactone) homopolymer was easily removed by extraction with acetone (Scheme 1).

Table 2. Effect of Trimethylaluminum Concentration on Ethylene Polymerization with $Cp*_2ZrMe_2/B(C_6F_5)_3$[a]

run no.	Al/Zr ratio	TMA[d] (mmol/L)	yield (mg)	activity[b]	M_n[c]	PDI[c]
5	50	3.16	204	258	9600	1.73
6	200	12.66	351	444	4550	2.35
7	500	31.66	384	485	3460	3.23
8	1000	63.33	796	1006	2520	2.41

[a] Polymerization condition: [Zr] = 1.9 μmol, $B(C_6F_5)_3$ = 1.5 equiv, ethylene pressure = 1.25 atm, temperature = 50 °C, solvent = 30 mL of toluene, t = 20 min. [b] Activity = kg/mol of cat atm h. [c] M_n and PDI determined by GPC using 1,2,4-TCB as solvent at 135 °C. [d] TMA = trimethylaluminum.

To remove any polyethylene homopolymer formed by incomplete oxidation of the terminal aluminum$-$carbon bond, the remaining polymer was further extracted with *n*-heptane, but the extracted solution did not contain any polymeric products. To confirm the purity of the block copolymer, the remaining polymer was extracted again by chloroform, because polyethylene homopolymer is not extractable by chloroform while the poly(ethylene-*b*-caprolactone) block copolymer is soluble in hot chloroform. All the polymeric product was extracted with chloroform, indicating that oxidative workup of aluminum-terminated polyethylene was quantitative.

GPC analysis of PE-OH and poly(ethylene-*b*-caprolactone) block copolymer also supports that all of the PE-OH was used as an initiator in ring-opening polymerization of ϵ-caprolactone.

Structural analysis of the poly(ethylene-*b*-caprolactone) block copolymer with ^{1}H and ^{13}C NMR spectroscopy confirmed the formation of the block copolymer. In ^{13}C NMR spectrum, the carbonyl carbon of caprolactone unit appeared at 173.16 ppm. The ^{1}H NMR spectrum also shows the methylene peaks of PE at 1.3 ppm as well as the peaks from the caprolactone unit at 4.1 [$-CH_2-O-$], 2.3 [$-C(O)-CH_2-$], 1.7, and 1.4 ppm [$-CH_2-CH_2-CH_2-$]. DSC analysis of the block copolymer shows double melting points at 57.5 and 125.7 °C, which is typical in crystalline diblock copolymer. Melting point of polyethylene block, however, decreased compared to that of PE-OH presumably due to the hindered crystalline packing.

In summary, chain transfer to aluminum occurred selectively during the ethylene polymerization with $Cp*_2ZrCl_2$/MAO catalyst below 50 °C, resulting in the aluminum-terminated polyethylene. The hydroxy-terminated polyethylene was obtained quantitatively by oxidative workup and successfully transformed to poly(ethylene-*b*-caprolactone) block copolymer by using stannous octoate as a catalyst for ring-opening polymerization of ϵ-caprolactone.

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Supporting Information Available: Experimental procedure, figures showing ^{1}H NMR, ^{13}C NMR spectra, GPC profile, and DSC curves of poly(ethylene-*b*-caprolactone) block copolymers, plot of M_n as a function of 1/[TMA], and variable temperature ^{1}H NMR results of PE-OH. This material is available free of charge via the Internet at http://pubs.acs.org.

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