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Catalytic Regioselective Introduction of Allyl Alcohol into the Nonpolar Polyolefins: Development of One-Pot Synthesis of Hydroxyl-Capped Polyolefins Mediated by a New Metallocene IF Catalyst

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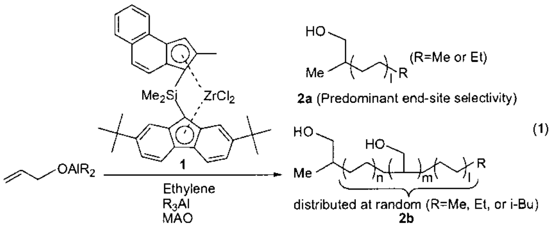
Received October 30, 2001

Research and development of high-performance olefin polymerization catalysts, especially well-defined transition-metal complexes, has contributed significantly to the advancement of polymer chemistry. This is due to the subtle control that ligands exert on the metal center to which they are coordinated, and these specifically designed catalysts are powerful tools for creating precisely controlled polymers such as functionalized polymers, branched polymers, and block copolymers.[1] Of particular importance among the functionalized polymers is the controlled copolymerization of simple olefins with polar monomers, because the incorporation of functional groups into an otherwise nonpolar material is a substantial way to modify the properties of a polymer. The constraint in this approach is the poisoning of catalyst components by polar groups.[1m] Promising catalysts containing group 10 transition metals[2] or organolanthanides[3] have recently been described. Although Ziegler−Natta catalysts containing group 4 transition metals are known for their highly oxophilic nature,[4] zirconocene/methylaluminoxane (MAO) catalysts were successful in copolymerizing ethylene with 10-undecen-1-ol[5] or other polar monomers[6] having long CH_2 spacers between polar and vinyl groups. Recently, we discovered, as a result of ligand-oriented catalyst design research, a new stereorigid bridged metallocene having an indenyl and a fluorenyl ligand named IF catalyst **1**, exhibiting high catalytic performance for olefin polymerization[7] and ethylene/10-undecen-1-ol copolymerization.[8] We paid particular attention to the uptake of allyl alcohol having only one CH_2 chain spacer. The copolymerization of propylene and allyl alcohol has only been reported using $TiCl_3$/ethyl aluminum sesquichloride solid catalyst.[9] The catalyst activities or polar monomer uptake, however, were very low, and M_w/M_n values of the obtained copolymers were broader. In our polymerization systems, the copolymerization of ethylene with allyl alcohol using IF catalyst **1**/MAO cocatalyst was conducted as follows: Subjecting the toluene solution of IF catalyst **1** and MAO to the solution of allyl alcohol masked by alkylaluminum and ethylene led to the predominant production of polyolefin **2a** or **2b** (eq 1).



The results are shown in Table 1. On the other hand, another representative metallocene catalyst, η^5-tetramethylcyclopentadienyl-dimethylsilylene-(η^1-*N*-*tert*-butylamido)titanium dichloride, or *rac*-dimethylsilylene-bis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride, was employed in this polymerization system and exhibited no polymerization.

Table 1. Ethylene/Allyl Alcohol Polymerization Using Metallocene IF Catalyst **1**/MAO Catalyst System[a]

entry	R_3Al[b]	yield (g)	M_w/M_n[c]	mol %[d]	M_w[e] (kg/mol)	number of OH groups[f]	
						end	in
1	Et_3Al	5.05	2.38	0.33	10 700	1	nd
2	Me_3Al	1.67	2.42	0.17	31 800	1	nd
3	$(i\text{-}Bu)_3Al$	3.80	2.59	1.20	60 600	1	10
4	$(n\text{-}Oct)_3Al$	3.50	2.54	0.22	32 600	1	0.1

[a] Conditions: 0.1 MPa pressure, 50 °C, toluene, 900 mL, time 100−105 min. IF catalyst **1**, 0.025 mmol; MAO, 1.57 mmol. [b] Allyl alcohol, 40 mmol; R_3Al, 48 mmol. [c] GPC analysis. [d] Comonomer content was determined by ^1H NMR. [e] GPC analysis. [f] See Supporting Information.

In our previous report, olefins having an alcohol group containing long CH_2 spacers such as 10-undecen-1-ol were introduced into the inner site of the polymer chain, and the chain transfer to triethylaluminum occurred at the activated bond between Zr and ethylene units and gave rise to *n*-alkyl groups at both polymer chain ends.[8] Quite interestingly, the use of allyl alcohol, on the other hand, gave rise to **2a** with complete switch of the regioselectivity (entry 1). Analysis by ^{13}C NMR revealed signals of end groups due to hydroxymethyl and Et (Me) groups only, and there were no peaks which were attributable to the carbon of vinyl or vinylidene (114.4, 39.1 ppm) derived from the chain-transfer reaction caused by monomer and/or β-hydride elimination, which implies that the chain termination predominantly occurred at the incorporated masked allyl alcohol unit by triethylaluminum (Figure 1a). To the best of our knowledge, such a regioselectivity has never been reported in the literature. This chain end regioselectivity was also found for trimethylaluminum (entry 2) (Scheme 1). The use of triisobutylaluminum or tri-*n*-octylaluminum, however, led to incorporation of allyl alcohol into the chain end and the inner site (entries 3, 4). Analysis of a copolymer (entry 3) by ^{13}C NMR revealed the following two points: (1) one chain end group was hydroxymethyl (97%) and the other end group was alkyl (methyl 65% and isobutyl 38%) due to the predominant chain termination by alkylaluminum and (2) the additional existence of an inner hydroxymethyl group, which implies that the propagation reaction of ethylene easily proceeded compared to the polymerization using triethylaluminum or trimethylaluminum (Figure 1b).

This unusual regioselectivity observed for allyl alcohol was caused by the combination of IF catalyst **1** and alkylaluminums having different steric hindrance. This may be attributed to the interaction between the Zr cation and the oxygen atom of masked

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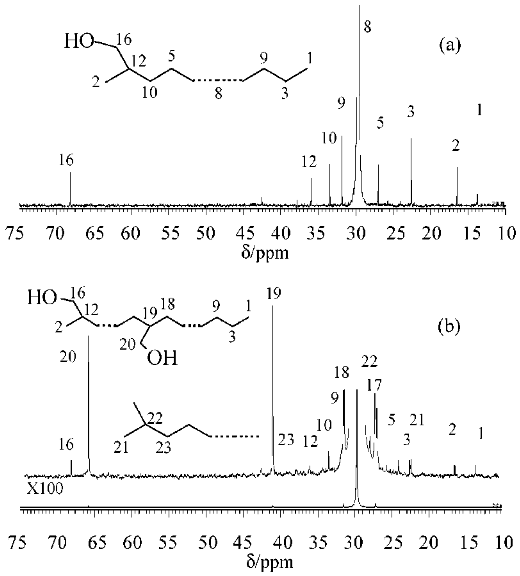
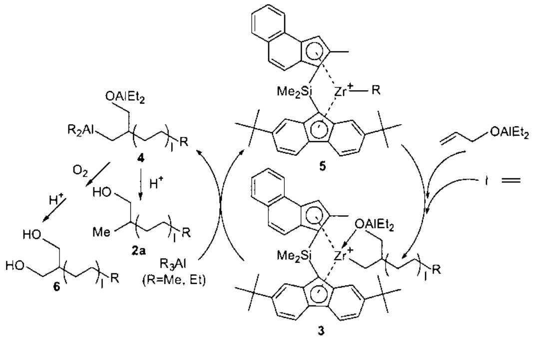


Figure 1. ^{13}C NMR spectra (270 MHz) of a copolymer. (a) Entry 1 in Table 1. (b) Entry 3 in Table 1.

Scheme 1



allyl alcohol adjacent to Zr, which determines whether the reaction goes to the chain transfer (small steric hindrance: Me, Et) or to the successive monomer insertion into the activated bond between Zr and the polymer chain (large steric hindrance: i-Bu). Considering the information that substitution of the hydrogen atom in the hydroxyl group with larger methyl or trimethylsilyl groups does not prevent the polar monomer from coordinating to the active site,[5d,10] aluminum offers an advantage for protecting groups because of its ubiquitous existence in polymerization formulations.[11]

To gain a mechanistic insight into this unusual regioselectivity, we postulated the tentative intermediate **3** (Scheme 1). The oxygen atom of the inserted masked allyl alcohol is located near the Zr cation and resulted in stable tentative intermediate **3**, to which the nucleophilic attack from triethylaluminum occurred quickly at the chain end bonded to Zr to produce the intermediate **4**, which is the precursor of **2a**. We tried to detect the tentative intermediate **3** by direct observation using NMR technique, but it was unsuccessful.

To seek more detailed information, we trapped intermediate **4** generated from tentative intermediate **3**. Thus, the aerobic oxidation of **4** was conducted in toluene. We found that aerobic oxidation of **4** followed by acid hydrolysis produced diol **6**. The assignment of diol **6** was characterized by ^{13}C NMR analysis (Figure 2). The chemical yield of diol **6** from **4** was estimated at 72% from the intensity of hydroxymethyl group of **6** (65.6 ppm, peak no. 15) and **2a** (68.1 ppm, peak no. 16). This aerobic oxidation efficiency is reasonable.[12,13] Additionally, another hydroxymethyl group (62.7 ppm, peak no. 14) was found. This result shows that the chain transfer to triethylaluminum also occurred at the activated bond between Zr and ethylene units, which was estimated at 23%.

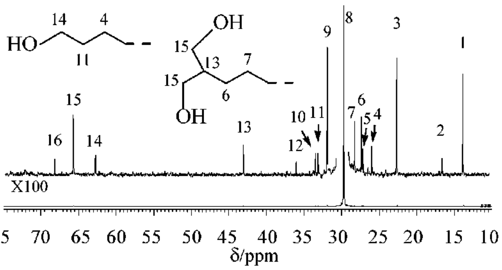


Figure 2. ^{13}C NMR spectra (270 MHz) of a copolymer obtained by the aerobic oxidation of the reaction medium of entry 1 in Table 1.

In summary, we have established the end-site-selective introduction of an alcohol group into the polyolefins by the combination of new metallocene IF catalyst **1** and alkylaluminums. The observation of diol **6** suggested the existence of intermediate **4**, which might be produced from tentative intermediate **3** by the chain-transfer reaction to alkylaluminum. We believe that this study should provide the strategic basis for controlling the regioselectivity in the one-pot synthesis of hydroxyl-capped polyolefins. Additionally, it is expected that diol **6** may be highly useful as a starting material for polymer syntheses and graft copolymerization.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0174377