

New Metallocene Catalyst Having an Indenyl Group and a Fluorenyl Group for Ethylene–Polar Monomer Copolymerization

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New stereorigid bridged zirconocene having an indenyl group and a fluorenyl group as ligand was synthesized and investigated as an ethylene/1-hydroxy-10-undecene copolymerization catalyst. This catalyst using MAO as a cocatalyst promoted polymerization to produce copolymers having high molecular weight (M_w :121000) and high polar monomer content (36.7 mol%), displaying higher polymerization activities at higher temperature.

The development of high performance olefin polymerization catalysts has been the subject of extensive studies over the last 45 years since specifically designed catalysts are powerful tools for creating precisely-controlled polymers such as functionalized polymers, branched polymers, and block copolymers.¹ Paramount and challenging among these targets is the controlled copolymerization of simple olefins with polar monomers, because the constraint with the poisoning of catalyst components is still unsolved. Polar groups exercise control over important properties such as toughness, adhesion, barrier properties, solvent resistance, miscibility with other polymers, and rheological properties. Promising catalysts containing group 10 transition metals² or organolanthanide³ have recently been described. Although Ziegler–Natta catalysts containing group 4 transition metals are known for their highly oxophilic nature,⁴ zirconocene/MAO catalysts were successful in copolymerizing ethylene with 1-hydroxy-10-undecene,⁵ 1-chloro-10-undecene,⁶ *N,N*-bis(trimethylsilyl)-1-amino-10-undecene,⁷ 1-hydroxy-5-hexene⁸ and an *o*-heptenylphenol derivative.⁹ However, higher polar monomer uptake with high molar mass copolymer produced at high polymerization temperature have been unsuccessful. Additionally microstructure of produced copolymer, especially the analysis of chain end group has not been investigated.

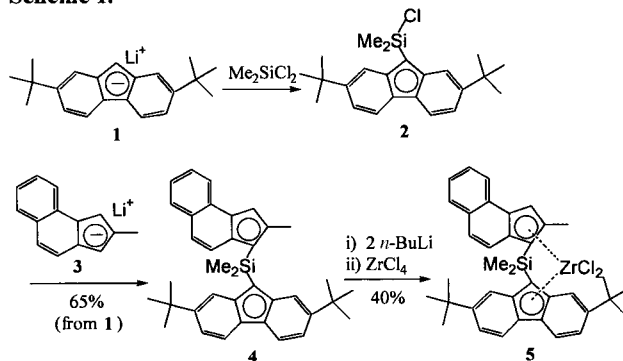
Recently, we have found, as a result of ligand-oriented catalyst design research, that new stereorigid bridged zirconocenes having an indenyl and a fluorenyl ligands exhibit high catalytic performance for olefin polymerization.¹⁰ These results prompted us to conduct further study on metallocene catalysts as potentially viable ethylene–polar monomer polymerization catalysts.

In this paper, (1)we introduced dimethylsilylene-bridged zirconocene wherein a specific substituent is introduced at the specific position of the indenyl and fluorenyl ligands, which promote an ethylene/1-hydroxy-10-undecene copolymerization at high temperature, and produced copolymers having high molecular weight and high polar monomer content with higher polymerization activities. (2)We characterized the structure of chain end groups and monomer sequences of this copolymer, and investigated the mechanism of the chain transfer reaction in this copolymerization.

A general synthetic route for new zirconocene employed in this study is shown in Scheme 1. The indenyl–fluorenyl ligand **4**

was prepared in high yield (65% starting from material **1**) by the coupling reaction with **2** and **3**. The dimethylsilylene-bridged zirconocene possessing the indenyl and fluorenyl ligand, namely dimethylsilylene (2-methylbenzo[e]inden-3-yl) (2,7-di-*tert*-butyl-9-fluorenyl) zirconium dichloride **5**, was obtained as bright orange powder in moderate yields (40%) by treatment of $ZrCl_4$ with the same equiv of the lithium salt of the dimethylsilylene-bridged substituted indenyl and fluorenyl ligand.¹¹

Scheme 1.



Zirconocene **5** was investigated as ethylene/1-hydroxy-10-undecene polymerization catalysts using MAO as a cocatalyst in the presence or absence of trialkylaluminum at the atmospheric pressure. The representative results are summarized in Table 1. The polymerization activities obtained were in the range of 0.1–43 kg / mmol-Zr·h·atm. In all cases, amorphous or solid copolymers were obtained having narrow molecular weight distributions (M_w/M_n : 1.63–2.45). The melting temperature (T_m) of the copolymers lies in the range of n.d.–130.4 °C, suggesting that the polar monomer was certainly introduced to a polyethylene backbone. ¹H NMR analysis revealed that the polar monomer introduced into polyethylene backbone was estimated to be up to 36.7 mol%. Interestingly, the addition of tri-*iso*-butylaluminum (TIBA) to the reaction medium containing polar monomer was effective to display higher catalytic activity (42.3 kg / mmol-Zr·h·atm) having a comonomer content of 0.25 mol% (entry 2) in comparison with low catalytic activity (0.73 kg / mmol-Zr·h·atm) having similar comonomer content (0.20 mol%) in the absence of TIBA (entry 1). This success may be due to the reduced Lewis basicity of the polar monomer by masking with TIBA.

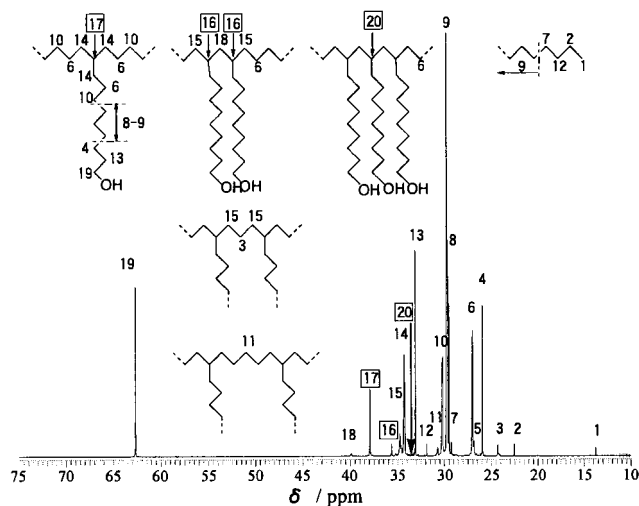
Next, polymerization using zirconocene **5** / MAO in conjunction with highly excess 1-hydroxy-10-undecene and TIBA was investigated, and was found to give the copolymer having a higher comonomer content (36.7 mol%), and a higher M_w : 121000 despite moderate activities (entry 3). An attempt to determine the microstructure of this copolymer was unsuccessful.

Table 1. Ethylene / 1-hydroxy-10-undecene polymerization using zirconocene **5** / MAO catalyst system

Entry	5 μmol	R ₃ Al mmol	Ethylene L/hr	Alcohol ^a mmol	Time min	Temperature °C	Yield g	Activity ^b mol% ^c	M _w ^d kg/mol	T _m ^e °C
1	2.3	-	100	0.48	50	80	1.40	0.73	289,500	130.4
2	1.7	TIBA(0.75)	100	0.48	3	80	3.00	42.3	388,100	128.5
3	25	TIBA(48)	2	40	12	50	0.97	0.20	121,000	n.d
4	25	TEA(96)	2	80	60	80	2.50	0.10	7,700	65.9

Conditions: 0.1 MPa pressure, toluene; 500 mL, MAO 1.57 mmol (Albemarle). ^a1-Hydroxy-10-undecene was treated with R₃Al before adding toluene solution of MAO and **5**. ^bkg-polymer·mmol-Zr⁻¹·h⁻¹·atm⁻¹. ^cComonomer content in polymer determined by ¹H NMR. ^dGPC analysis. ^eT_m: DSC measurement.

ful because of its higher M_w . However, the addition of triethylaluminum (TEA) instead of TIBA resulted in an decrease of M_w (7700) of the copolymer having very narrow M_w/M_n : 1.63. This result suggests that TEA plays as chain transfer reagent. Then, we investigated the microstructure of the copolymer, and found following three facts with the help of ¹³C NMR analysis. (1) Both the chain end groups in the copolymer were almost *n*-alkyl groups, such as methyl, ethyl, *n*-Pr, or *n*-Bu group etc., and there were no peaks that were attributable to the carbon of vinyl (114.4 ppm) or vinylidene (39.1 ppm) group derived from the chain transfer reaction caused by monomer and/or hydride β-elimination. (2) The peak attributable to the methyl carbon of the undecenol group (19.7 ppm) was hardly found at the polymer chain end. (3) A sequence analysis of the copolymer revealed that the incorporated alcohol in a polyethylene backbone was almost isolated type: EUE (91%), and the others were EUU (8%) and UUU (1%). The results (1) and (2), and the fact that the copolymer of lower M_w was obtained by adding TEA confirm that TEA acts as the chain transfer agent at the activated bond between Zr and ethylene unit, and give rise to *n*-alkyl groups at the both polymer chain ends.

**Figure 1.** ¹³C NMR spectra of a copolymer (270 MHz) of poly(ethylene-co-10-undecen-1-ol) (entry 4).

In summary, new zirconocene **5** was prepared and investigated as an ethylene/1-hydroxy-10-undecene copolymerization catalyst. This catalyst produced copolymers having high molecular weight and high polar monomer content with higher polymerization activities at higher temperature. A ¹³C NMR investigation of a copolymer showed that UU and UUU sequences existed in a polyethylene backbone, and that the

chain transfer reaction in this copolymerization almost exclusively occurred at the activated bond between Zr and ethylene unit by TEA. The influence of substitution groups of the ligands and cocatalysts as well as potential applications of the catalysts are under active investigation.

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- Zirconocene **5**: ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS); δ 1.26 (s, 9H), 1.35 (s, 9H), 1.44 (s, 3H), 1.54 (s, 3H), 2.37 (s, 3H), 7.0–8.02 (m, 13H). Anal. Found: C, 65.66; H, 6.06; Zr, 13.40%. Calcd for C₃₇H₄₀SiCl₂Zr: C, 65.84; H, 5.97; Zr, 13.52%. FD-mass: *m/z*: 675(M⁺).