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Synthesis and Performance of *ansa*-Metallocene Catalysts with Substituted Heterocyclic and Indenyl Ligands[1]

M. J. Elder[a], Y. Okumura[b], R. L. Jones[c], B. Richter[c], and N. Seidel[d]

[a] *W.R. Grace/Davison Corp., Columbia, Maryland, USA*
[b] *Showa Denko Corp., Tokyo, Japan*
[c] *Basell Polyolefins, Frankfurt am Main, Germany*
[d] *Procter & Gamble Corp., Germany*
e-mail: Michael.Elder@grace.com

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Abstract—Synthesis of new *ansa*-metallocene catalysts incorporating branched alkyl groups *alpha* to the bridgehead carbon of indenyl and thiapentalenyl ligands is reported. Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$ and Me_2Si(2,5-Me_2-3-Ph-Thiapentalenyl)$_2ZrCl_2$ type metallocenes with one and two isopropyl groups substituted for 2-methyl substitutents were prepared and used as procatalysts in propylene polymerizations and E/P copolymerizations. The 2-isopropyl groups influenced catalyst activity, molecular weight, and the relative amounts of microstructure errors. In contrast to procatalysts with only 2-methyl groups, polymer molecular weights increased in E/P copolymerizations with 2-isopropyl substituted complexes.

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Group 4 *ansa*-metallocene catalysts with C_2-symmetry have received considerable attention due to their high polymerization activity and ability to produce isotactic polypropylene of homogeneous composition when activated with MAO and other cocatalysts [1–4]. Me_2Si(2-Me-Benz[e]Indenyl)$_2ZrCl_2$ and Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$ are two industrially relevant examples of this class of metallocene procatalyst [5, 6]. Catalysts of similar structure with high polymerization rates have been developed using thiapentalene instead of indenyl ligands [7]. Methyl substitutents *alpha* to the bridgehead carbon and bulky groups in the frontier region of the metal complex are established ligand features for obtaining high molecular weight polymer and stereoselectivity control with these types of metallocenes. The complexes however have found limited use in ethylene/propylene copolymerizations due to a significant decrease in polymer molecular weight when ethylene is added to the polymerization system. As a consequence, some recent research efforts have focused on developing new types of *ansa*-metallocenes that combine high isospecificity with the capability of producing high molecular weight E/P copolymers [8–11]. Here we report on the synthesis of several *ansa*-metallocene catalysts incorporating branched alkyl groups *alpha* to the bridgehead carbon and their behavior in propylene polymerizations and E/P copolymerizations.

[1] The text was submitted by the authors in English.

EXPERIMENTAL

Ligands and metallocene synthesis. The substituted indenyl ligands and corresponding bis-indenyl zirconocenes were synthesized according references [12–14]. Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$ was synthesized as described in reference [6]. 2,5-dimethyl-3-phenyl-cyclopenta-4H-cyclopenta[b]thiophene was prepared as described in reference [7]. 5-Isopropyl-2-methyl-3-phenyl-4H-cyclopenta[b]thiophene and the bisheterocenyl, and mixed carbocenyl-heterocenyl ligands and metallocenes were prepared according to [15].

Polymerizations. The polymerization method used with homogeneous catalysts activated with $[Ph_3C][B(C_6F_5)_4]$ is described in [13]. Polymerization with MAO activated homogeneous catalysts was conducted as follows: A 1 l stainless steel Büchi reactor equipped with an oil circulating temperature control bath was swept with dry nitrogen at 110°C for 1 h prior to polymerization. At room temperature, 2 ml of a 1 M solution of Al(*i*-Bu)$_3$ in toluene was added by syringe, followed by 250 g of liquid propylene. Stirring was initiated and the reactor was heated to 40°C. For E/P copolymerizations, ethylene overpressure was added to the reactor at this point. A toluene solution of the zirconocene (0.5 mg/ml solution) was reacted with 30 wt % MAO in toluene from Albemarle (Al/Zr mol ratio = 4.100) for 10 min and polymerization was initiated by charging the catalyst solution to the reactor with 50 g of propylene under pressure and raising the temperature to 65°C. For E/P copolymerizations, constant

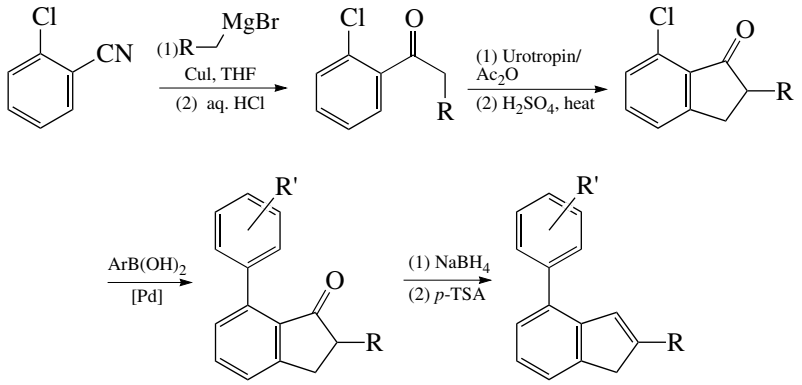


Fig. 1. Synthetic method for 2-R-4-Aryl-Indenes.

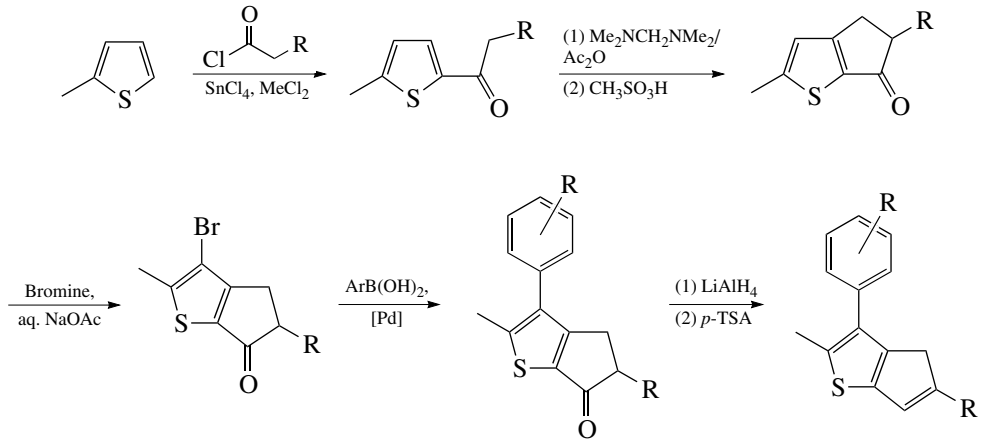


Fig. 2. General route for 2-Me-3-Aryl-5-R-Thiapentalenes.

reactor overpressure was maintained throughout the run by feeding ethylene on demand via a pressure regulator. At the end of the run, stirring was stopped and all residual monomers were vented while cooling the reactor to room temperature. After purging with nitrogen for 10 min, the reactor was opened and the polymer removed. The polymer was dried in a vacuum oven at 50°C for 2 h under nitrogen sweep. Reported activities were calculated from the polymer and zirconocene weights. MAO/Si supported catalysts were prepared as outlined in reference [15]. E/P copolymerizations with supported catalysts were conducted in the same manner as described above for polymerizations with homogeneous catalysts except that the polymerizations were conducted in a 10 l autoclave (t_{pol} = 1 h). The polymer analyses followed the standard procedures detailed in references [13, 15].

RESULTS AND DISCUSSION

Synthesis of ligands and metallocenes. A general method, outlined in Fig. 1, was used to prepare 2-alkyl-4-aryl-indenes [12]. Alkyl groups at the 2-position were introduced by reacting Grignard reagents with 2-chlorobenzonitrile. Olefin functionality was then added using urotropin/acetic anhydride reagents and the ring was closed under acidic conditions. The resulting substituted indanone was Suzuki coupled with phenylboronic acid and the indanone converted to the indene in the usual fashion.

5-Isopropyl and other 5-substituted thiapentalenes were synthesized as outlined in Fig. 2 [15]. A Friedel-Crafts acylation reaction with 2-methylthiophene gave the desired carbonyl side chain. The product was reacted with tetramethydiaminomethane/acetic anhydride to build in the olefin functionality and the ring closed with methanesulfonic acid. The substituted cyclopenta[b]thiophenone was brominated cleanly at the 3-position using standard conditions and Suzuki coupling gave 3-phenyl substitution in high yield that was then transformed into the thiapentalene. The substituted indenes and thiapentalenes were converted into bridged ligands and *ansa*-zirconocenes in the usual manner, as outlined in Fig. 3. All other permutations of

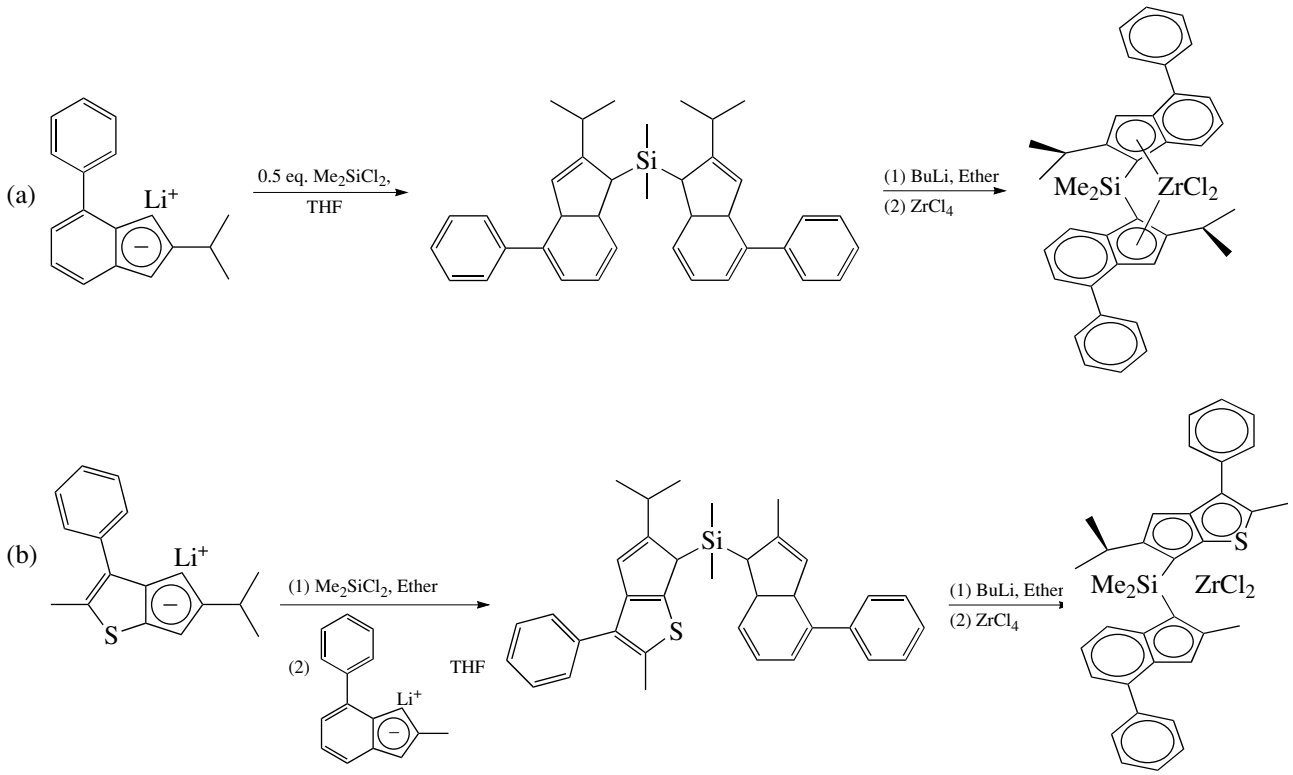


Fig. 3. Preparation methods for metallocenes with the same (a) and different (b) Cp ligands.

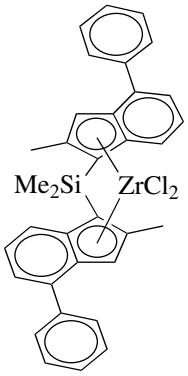
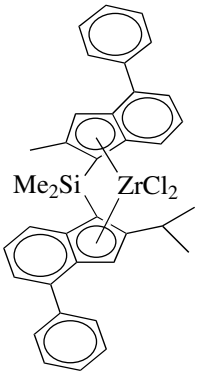
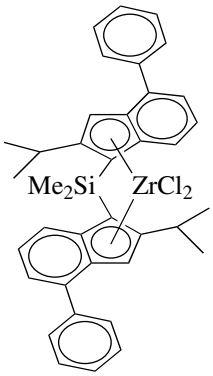
biscarbocenyl, bisheterocenyl, and mixed carbocenyl-heterocenyl ligands could be synthesized following similar routes.

Propylene and ethylene/propylene polymerizations. Polymerization results for analogs of Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$ replacing one and both of the 2-methyl groups with isopropyl groups are collected in Table 1 [13]. Catalyst activities and molecular weights decreased with increasing number of 2-isopropyl substitutents. Both the C_2-symmetric and C_1-symmetric zirconocenes with pseudo-C_2-symmetry produced primarily two types of microstructure errors: steric inversion from insertion of a 1,2-propylene with the "wrong" π-face coordinated to the metal, and regioerrors from insertion of a 2,1-erythro (**E**) coordinated propylene. Replacing both α-methyls with isopropyl groups resulted in a highly regioselective catalyst with increased stereoerrors while replacing one α-methyl for isopropyl gave intermediate levels of regio and stereoerrors. Conversion via a 180° olefin rotation of a 1,2-propylene unit coordinated to the "wrong" π-face into a 2,1-E preinsertion configuration was shown to be an energetically favorable process for Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$ type metallocenes [16]. While the α-isopropyl group had a significant effect on the type of errors the overall enantioselectivity trend was: Me_2Si(2-Me-4-Ph-Indenyl)(2-*i*-Pr-4-Ph-Indenyl)$ZrCl_2$ ~ Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$ > Me_2Si(2-*i*-Pr-4-Ph-Indenyl)$_2ZrCl_2$.

Thiapentalene-based metallocenes are more open structures than similarly substituted bis-indenyl complexes due to a smaller 5-member heterocyclic fused ring and different spacial orientation of the pendent phenyl group at the thiapentalene 3-position. Three types of thiapentalene-containing C_1-symmetric complexes were prepared: a bisthiapentalene complex with one α-*i*-Pr group, a mixed thiapentalenyl/indenyl zirconocene with a α-*i*-Pr group on the thiapentalene, and a mixed Thia/Ind complex with the α-*i*-Pr group on indene. Bulk propylene polymerization results at 65°C with MAO activated catalysts are collected in Table 2. Catalyst activities were similar for the three zirconocenes in polymerizations without hydrogen. Hydrogen had an activating effect and larger differences in catalyst activities were observed for these runs. Polymer melting points and total microstructure errors decreased moving from left to right in the table as the ligand structures became more closed. Structure (Me-Indenyl)(*i*-Pr-Thiapentalenyl), combining the most highly substituted coordination site with the least sterically congested site, produced significantly higher molecular weight polymer than the others in this series.

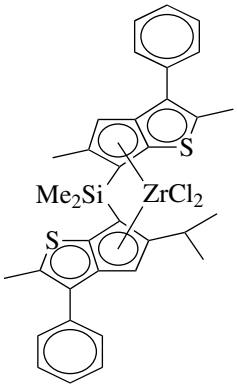
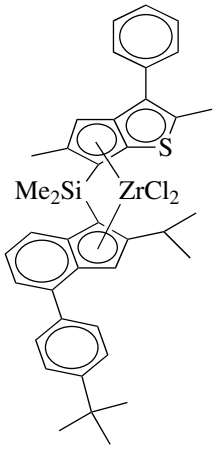
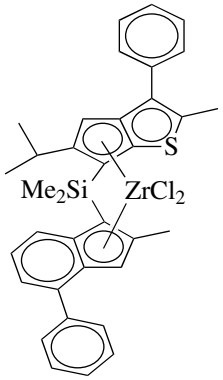
The incorporation of branched alkyl groups *alpha* to the bridgehead carbon of bisindenyl metallocenes as a way to limit chain termination by transfer to ethylene was initiated based on molecular modeling studies [14, 17]. Figure 4 compares the molecular weights of *i*-PP

Table 1. Homopolymerization behavior of bisindenyl metallocenes with α-isopropyl substitutents ($[Ph_3C][B(C_6F_5)_4$ activator)

Catalyst	 (Me-Indenyl)$_2$	 (Me-Indenyl)(*i*-Pr-Indenyl)	 (*i*-Pr-Indenyl)$_2$
kg PP (mmol Zr)$^{-1}$ h^{-1}	1300	334	72
$M_w \times 10^{-3}$, g/mol	2300	950	280
T_m, °C	159	160	157
mrrm, %	<0.01	0.10	0.33
regio-errors, %	0.25	0.12	0.04

Note: 50°C, bulk propylene, 1 h, B/Zr m.r. = 1.5. Regioerrors = 2,1- + 3,1-uints.

Table 2. Homopolymerization results for MAO-activated thiapentalene/indenyl metallocenes with α-isopropyl groups

Catalyst	 (Me-Thiapentalenyl)(*i*-Pr-Thiapentalenyl)		 (Me-Thiapentalenyl)(*i*-Pr-Indenyl)		 (Me-Indenyl)(*i*-Pr-Thiapentalenyl)	
H_2, mmol	0	100	0	100	0	100
kg PP (mmol Zr)$^{-1}$ h^{-1}	276	1807	337	1240	444	683
$M_w \times 10^{-3}$, g/mol	316	176	302	228	883	340
T_m, °C	157	155	158	158	160	161
Total errors*, %	0.84	–	0.53	–	0.41	–

Note: 1 l reactor, 300 ml propylene, 65°C, 0.5 h, MAO (Al/Zr = 4100), 2 mmol Al (*i*-Bu)$_3$.
* *mrrm* + 2,1- + 3,1-units.

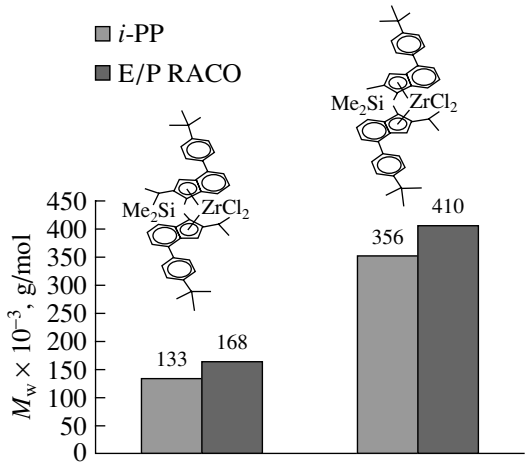


Fig. 4. Molecular weights of *i*-PP and E/P random copolymers produced with 2-*i*-Pr substituted bisindenyl metallocenes supported on MAO/Si. (Bulk propylene, 65°C, 1 h. C_2H_4—Raco produced at fixed C_2H_4 overpressure).

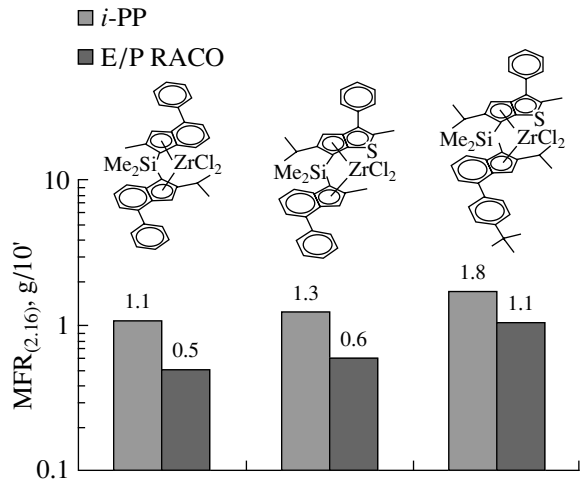


Fig. 5. Melt Index values for *i*-PP and E/P random copolymers produced with C_1-symmetric metallocenes supported on MAO/Si (Bulk propylene, 65°C, 1 h. C_2H_4—Raco produced at fixed C_2H_4 overpressure).

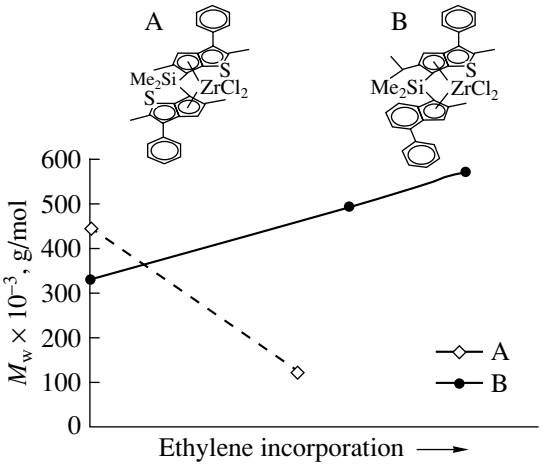


Fig. 6. Polymer molecular weight with increasing ethylene incorporation for two *ansa*-metallocenes, with and without a branched α-group. (MAO/Si supported catalysts, bulk propylene + C_2H_4, 65°C, 1 h.)

and E/P random copolymers produced at 65°C with 2-*i*-Pr substituted bisindenyl zirconocenes on MAO/Si support. In both cases, the molecular weight of the copolymer was increased relative to the homopolymer.

Figure 5 shows a similar comparison of *i*-PP and E/P copolymer molecular weights (melt flow measurements) for biscarbocenyl and mixed carbocenyl-heterocenyl type structures. Random copolymer molecular weights increased relative to homopolymer in all cases and fractional melt-flow E/P copolymers were possible with two of these complexes. Increasing the ethylene concentration gave additional increases in polymer molecular weight for complexes with the α-*i*-Pr sunstitutent as shown in Fig. 6. By contrast, molecular weight was significantly reduced for the complex with only α-methyl groups.

The substitution of branched alkyl groups at the 2-position of Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$/MAO type catalysts effectively limited chain termination by transfer to ethylene in E/P copolymerizations. Analogs with 2-isopropyl groups were also more regio-selective with high overall enantioselectivity in the case of complexes with one α-methyl and one α-isopropyl substitutent. Jüngling and his coworkers have shown that low molecular weight polypropylenes produced with Me_2Si(Benz[e]Indenyl)$_2ZrCl_2$/MAO resulted from chain transfer to propylene following a 2,1-misinsertion [18]. Lower molecular weight E/P copolymers produced with Me_2Si(2-Me-Benz[e]Indenyl)$_2ZrCl_2$ or Me_2Si(2-Me-4-Ph-Indenyl)$_2ZrCl_2$ type metallocenes may similarly be the result of chain transfer to ethylene following a propylene 2,1-misinsertion. If this were the case, one would expect to find 2-butenyl end groups in low molecular weight E/P copolymers produced with this type of catalyst.

REFERENCES

1. Ewen, J.A., *J. Am. Chem. Soc.*, 1984, vol. 106, p. 6355.
2. Kaminsky, W., Külper, K., Brintzinger, H.H., and Wild, F.R.W.P., *Angew. Chem., Int. Ed. Engl.*, 1985, vol. 24, p. 507.
3. Brintzinger, H.H., Fischer, D., Mülhaupt, R., Rieger, B., and Waymouth, R.M., *Angew. Chem., Int. Ed. Engl.*, 1995, vol. 34, p. 1143.
4. Resconi, L., Cavallo, L., Fait, A., and Piemontesi, F., *Chem. Rev.*, 2000, vol. 100, p. 1253.
5. Stehling, U., Diebold, J., Kirsten, R., Roll, W., Brintzinger, H.H., Jüngling, S., Mülhaupt, R., and Langhauser, F., *Organometallics*, 1994, vol. 13, p. 964.
6. Spaleck, W., Küber, F., Winter, A., Rohrmann, J., Bachmann, B., Amberg, M., Dolle, V., and Paulus, E.F., *Organometallics*, 1994, vol. 13, p. 954.
7. Ewen, J.A., Elder, M.J., Jones, R.L., Rheingold, A.L., Liable-Sands, L.M., and Sommer, R.D., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 4763.
8. Fischer, D., *EUPOC Conf.*, 2003.
9. Sugano, T., *SPO Conf.*, 1999.

10. Iwama, N., Uchino, H., Osano, T.Y., and Sugano, T., *Organometallics*, 2004, vol. 23, p. 3267.
11. Richter, B., *German–Chinese Bilateral Symp. on Organometallic Catalysts & Olefin Polymerizations*, Mülheim, Germany, 2003.
12. Int. Patent WO 98/40331, 1998.
13. US Patent 6121182, 2000; Int. Patent WO 97/40075, 1997.
14. Int. Patent WO 01/48034, 2001.
15. Int. Patent WO 03/045964, 2003.
16. Guerra, G., Longo, P., Cavallo, L., and Resconi, L., *J. Am. Chem. Soc.*, 1997, vol. 119, p. 4394.
17. Weiss, H., Fischer, D., and Steiger, S., BASF/Basell internal communication.
18. Jüngling, S., Mülhaupt, R., Stehling, U., Brintzinger, H.H., Fischer, D., and Langhauser, F.J., *J. Polym. Sci., Part A: Polym. Chem.*, 1995, vol. 33, p. 1305.