Alternating Stereospecific Copolymerization of Ethylene and Propylene with Metallocene Catalysts

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Abstract: The copolymerization of ethylene and propylene with bridged metallocenes $Me_2E(3\text{-}RCp)(Flu)X_2$/MAO (E = C, X = Me; E = Si, X = Cl; R = H or alkyl) was investigated. Ethylene/propylene copolymerization with metallocenes having heterotopic active sites (R =Me, i-Pr) yield alternating, isotactic ethylene/propylene copolymers with percentages of alternating EPE+PEP triads in the range of 61−76% at 50% ethylene incorporation. Both the nature of the substituent R and the bridge E influence the copolymerization behavior including the copolymerization activity, copolymer sequence distribution, molecular weight, and stereochemistry. Silicon-bridged metallocenes produce copolymers with higher activity and molecular weight but lower propylene incorporation at similar feeds than the carbon-bridged analogues. Isotactic PEPEP sequences were observed for all metallocenes, while the tacticities of the EPPE sequences varied with the bridge and the substituent on the metallocene ligand. Isotactic PEPEP sequences and atactic EPPE sequence errors in the alternating copolymers are consistent with a mechanism where the comonomers are enchained alternately at the heterotopic coordination sites of the metallocenes. Isotactic EPPE sequences are indicative of occasional multiple insertions at the stereospecific site, caused by an isomerization of the chain prior to monomer insertion (backskip).

Introduction

The development of well-defined polymerization catalysts from coordination compounds has created new opportunities for the synthesis of polymers with tailored structures and properties.[1−3] Correlations of the coordination geometry with the catalytic behavior of these compounds have revealed new insights into the details of catalytic olefin insertions into metal carbon bonds. The analysis of the stereochemistry of α-olefin polymerization has proven a powerful mechanistic probe; the preparation of syndiotactic polypropylene from C_s-symmetric $R_2C(Cp)(9\text{-}Flu)MX_2$ metallocenes[4] and of hemiisotactic polypropylene from the C_l-symmetric $R_2C(3\text{-}RCp)(9\text{-}Flu)MX_2$ metallocenes[5−7] provides some of the most convincing evidence for Cossee's alternating site mechanism for olefin insertion proposed in 1960.[8,9]

Many transition metal catalysts possess multiple coordination sites for activation and conversion of substrates. For stereoselective and enantioselective catalysis, the widespread application of C_2-symmetric catalysts is largely a consequence of our inability to control the locus of the catalytic chemistry at coordination sites with different steric environments. C_2-symmetric ligands are often employed to limit the number of reaction pathways. Recently, we[10] and others[11−13] have sought to exploit the dual coordination sites of C_1-symmetric metallocenes to control the kinetic selectivities and thus the sequence specificities in olefin copolymerization. Bridged metallocenes with heterotopic coordination sites, such as $Me_2C(CpR)(9\text{-}Flu)ZrCl_2$,[10,13] $CH_2CH_2(Ind)(9\text{-}Flu)ZrCl_2$,[11] and *meso*-$Me_2Si(Ind)_2ZrCl_2$,[12] have been shown to yield highly alternating copolymers of ethylene and α-olefins. These results were interpreted in terms of a mechanism involving the alternating insertion of olefins at the two heterotopic coordination sites exhibiting different kinetic selectivities for the two comonomers (Figure 1). The $Me_2C(CpR)(9\text{-}Flu)ZrCl_2$ and $CH_2CH_2(lnd)(9\text{-}Flu)ZrCl_2$ metallocenes[10,11] were reported to yield isotactic, alternating ethylene/propylene copolymers, suggesting that the coordination site for propylene insertion is isospecific.

For the cyclopentadienyl-fluorenyl metallocenes $Me_2C(3\text{-}RCp)(9\text{-}Flu)ZrCl_2$, the sequence distributions could be simulated with a kinetic model employing different kinetic selectivities at the two coordination sites. This "switching-site" kinetic model was developed simultaneously by Kaminsky and Leclerc.[10,13] Support for the alternating site copolymerization mechanism was provided by comparing the derived copolymerization parameters for the unsymmetrical catalysts with those for symmetrical model catalysts whose structures were designed to mimic the coordination sites of the unsymmetrical catalyst.[10]

These preliminary results reveal that with appropriate ligand design, it is possible to prepare ethylene/α-olefin copolymers

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(1) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170.

(2) *Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, 2000; Vol. 1, p 2.

(3) Soga, K.; Shiono, T. *Prog. Polym. Sci.* **1997**, *22*, 1503−1546.

(4) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256.

(5) Spaleck, W.; Antberg, M.; Dolle, V.; Klein, R.; Rohrmann, J.; Winter, A. *New J. Chem.* **1990**, 14, 499−503.

(6) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1995**, *497*, 105−111.

(7) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Rapid Commun.* **1991**, *48/49*, 253−295.

(8) Cossee, P. *Tetrahedron Lett.* **1960**, 12.

(9) Cossee, P. *Tetrahedron Lett.* **1960**, 17.

(10) Leclerc, M. K.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 922−925.

(11) Jin, J. H.; Uozumi, T.; Sano, T.; Teranishi, T.; Soga, K.; Shiono, T. *Macromol. Rapid Commun.* **1998**, *19*, 337−339.

(12) Uozumi, T.; Miyazawa, K.; Sano, T.; Soga, K. *Macromol. Rapid Commun.* **1997**, *18*, 883−889.

(13) Arndt, M.; Kaminsky, W.; Schauwienold, A. M.; Weingarten, U. *Macromol. Chem. Phys.* **1998**, *199*, 1135−1152.

10.1021/ja0100773 CCC: $20.00

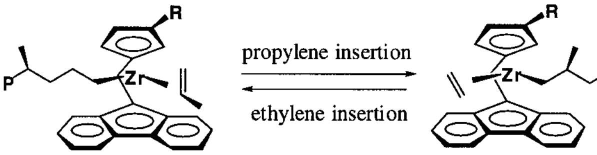
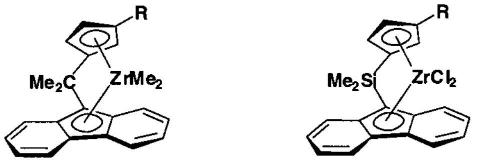


Figure 1. Proposed two-site switching insertion mechanism.



R = H (**1a**), Me (**2a**), i-Pr (**3a**)   R = H (**1b**), Me (**2b**), i-Pr (**3b**)

Figure 2. Metallocenes under investigation.

Table 1. Ethylene/Propylene Copolymerizationsa: Productivity and Molecular Weight

metallocenes	Zr ($\times 10^{-7}$ mol)	Al:Zr	E:P	% E[b]	*A*[c]	Mn × 10^3 (Mw/Mn)[d]
1a	20	2000:1	0.148	33.5	2,082	28.1 (2.0)
lb	2.4	4167:1	0.079	49.1	18,488	152 (2.3)
2a	17.5	809:1	0.108	49.4	7,130	17.6 (2.0)
2b	3.2	3933:1	0.043	49.8	29,100	232 (2.5)
3a	7.1	1408:1	0.096	50.1	4,960	63.4 (2.0)
3b	1.0	10000:1	0.033	46.1	51,280	539 (2.2)

[a] MAO as cocatalyst, 0 °C, ethylene is fed through constant pressure over liquid propylene. [b] Calculated by Kakugo's method. [c] *A* is expressed in kg EP/mol Zr/h. [d] Measured by GPC at 135 °C.

with an alternating sequence distribution. However, the catalysts investigated to date exhibit modest productivities and yield low molecular weight polymers with significant amounts of both sequence errors and stereoerrors in the alternating EP copolymers. In an effort to improve the sequence specificity and stereospecificity of alternating copolymerization, we have carried out a series of investigations on the stereospecific alternating copolymerization of ethylene and propylene as well as the influence of coordination geometry on the polymerization behavior of *ansa*-cyclopentadienyl-fluorenyl metallocenes. The stereochemistry of ethylene/propylene copolymers is compared with that of propylene homopolymers in an attempt to assess the origins of stereoerrors and sequence errors originating in the EP copolymers.

Results

Six metallocenes were investigated to probe both the influence of the bridging group (Me_2C vs Me_2Si) and the nature of the cyclopentadienyl substituents R (= H, Me, i-Pr) on propylene homopolymerization and ethylene−propylene copolymerization (Figure 2). The syntheses of these compounds were carried out as described in the literature.[6,14−16]

Ethylene−Propylene Copolymerization. Ethylene/propylene copolymerizations were conducted at 0 °C in liquid propylene with a constant overpressure of ethylene and kept to less than 5% conversion in propylene. Ethylene/propylene feed ratios were calculated from tabulated fugacities and the partial pressures of ethylene and propylene.[17,18] Table 1 summarizes the copolymerization productivity and copolymer molecular weight of representative copolymer samples. A large range of Al:Zr ratios was employed due to the large differences in activities of different metallocenes and an experimental requirement to provide a minimum of 1 mmol of MAO to scavenge impurities.

As previously reported, the isopropylidene-bridged metallocenes **la** and **2a** exhibit modest activities for EP copolymerization and yield copolymers of low molecular weight (Table 1). The productivities and molecular weights of the copolymers increased approximately 10-fold upon substitution of the carbon bridge by the silicon bridge. The magnitude of this effect seems to increase with increasing size of the cyclopentadienyl substituent.[19]

The nature of the cyclopentadienyl substituent has a modest influence on the productivities: productivities increase slightly from the unsubstituted to the substituted, but are generally within the same order of magnitude. Within the silicon-bridged series, molecular weight varied with the substituent in the order H < Me < i-Pr, at similar Al:Zr ratio and ethylene incorporation. A similar trend is observed for the carbon-bridged series, suggesting that increased steric demands at the β-position of the cyclopentadienyl ring may inhibit chain transfer.

The nature of the bridging group has an influence on the copolymerization behavior as the carbon-bridged metallocenes incorporate propylene more readily. As can be seen in Table 2, the silicon-bridged metallocenes consistently incorporate more ethylene at a given feed ratio (compare % E/(E:P), **2a**: 49.4/0.108 = 457; **2b**: 49.8/0.043 = 1158) and thus exhibit a lower selectivity for propylene incorporation. The nature of the cyclopentadienyl group has a modest influence on the tendency to incorporate propylene, with the unsubstituted catalyst **1a** exhibiting the highest incorporation.

Copolymer Sequence Distribution. The sequence distributions of EP copolymers derived from metallocenes **2a**, **3a**, **2b**, and **3b** are highly alternating (Table 2 and Figure 3). The copolymer composition was investigated by ^{13}C NMR as described by Randall;[20] the sequence distribution at the triad level can be conveniently analyzed and described in terms of the first-order Markov copolymerization parameters. Reactivity ratios r_e and r_p were calculated from the copolymer sequence by using a nonlinear least-squares optimization routine in Matlab with use of at least four sets of triad data for each optimization. A relatively narrow range of E:P feed ratios (0.016−0.23) was investigated to yield copolymers with compositions close to 50% ethylene. The average values for r_e and r_p are reported in Table 2. The 90% confidence level reported in Table 2 was estimated by using the Bootstrap program in Matlab.

As previously reported[10,13] for *ansa*-cyclopentadienyl-fluorenyl metallocenes, the nature of the β-substituent on the cyclopentadienyl ring has a dramatic effect on the copolymer sequence distribution. Shown in Figure 3 are triad distributions for a series of 50:50 EP copolymers prepared with metallocenes **lb−3b.** From this figure, it can be seen that the most highly alternating sequence is obtained from the methyl-substituted **2b**, followed by the isopropyl-substituted **3b.**

Further insight into the sequence distributions can be obtained from the sequence-derived copolymerization parameters r_e and r_p. The product of the reactivity ratios $r_e r_p$ provides a useful

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(14) Chen, Y. X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1995**, *497*, 1−9.

(15) Razavi, A.; Ferrara, J. *J. Organomet. Chem.* **1992**, *435*, 299−310.

(16) Spaleck, W.; Antberg, M.; Aulbach, B.; Bachmann, B.; Dolle, V.; Haftka, S.; Kuber, F.; Rohrmann, J.; Winter, A. In *Ziegler Catalysts*; Fink, G., Mulhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; pp 83−98.

(17) Maxwell, J. B. *Databook on Hydrocarbons;* D. Van Nostrand Company: New York, 1950.

(18) Kravchenko, R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 1−6.

(19) It is known that the Al:Zr ratio influences both the activity and molecular weight; however, the magnitude of the increase observed suggests that it cannot be accounted for by the different AI:Zr ratios employed.

(20) Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 1402−1406.

Table 2. Reactivity Ratios[a] (0 °C) of Ethylene/Propylene Copolymers

	1a[b]	**1b**	**2a**	**2b**	**3a**	**3b**
$r_e \pm \delta r_e$	2.43	5.00 ± 0.41	1.80 ± 0.18	4.08 ± 0.60	2.28 ± 0.04	5.10 ± 0.54
$r_p \pm \delta r_p$	0.192	0.032 ± 0.008	0.013 ± 0.005	0.006 ± 0.003	0.016 ± 0.003	0.016 ± 0.004
$r_e r_p$	0.46	0.16	0.02	0.03	0.04	0.08

[a] Calculated from dyad distributions based on Kakugo's method.[63] [b] Only one polymerization to compare to Herfert et al.[46]

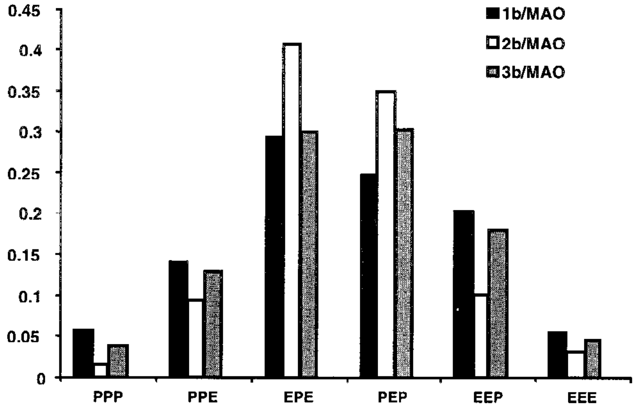

Figure 3. Triad distribution of the copolymers produced by **lb**/MAO, **2b**/MAO, and **3b**/MAO at 0 °C, 50% ethylene incorporation.

Table 3. Triad Distributions of 50/50 Copolymers by Metallocenes **1**−**3**/MAO[a]

metallocene	EEE	EEP+PEE	PEP	EPE	PPE+EPP	PPP
la[b]						
lb	5.5	20.6	24.6	29.5	14	5.7
2a	1.9	11.3	37.4	35.9	11.6	1.9
2b	3.1	10.1	35.0	40.8	9.4	1.6
3a	3.2	15.1	31.8	35.4	11.9	2.6
3b	4.6	18.2	30.5	30.2	12.6	3.9

[a] All polymerization were conducted at 0 °C, in liquid propylene with constant ethylene overpressure. [b] Not enough 50/50 copolymer sample could be obtained at 0 °C.

Table 4. Copolymer Stereochemistry: PEPEP and EPPE Tacticities

metallocene	% E	PP	EP	EE	PEPEP	EPPE(m:r)
2a	44.7	13.5	83.8	2.7	60:30:10[a]	1:1
2b	43.0	17.1	79.8	3.2	75:20:5[a]	3:2
3a	45.3	11.9	82.7	5.4	75:25[b]	1:1
3b	39.6	23.6	73.4	2.9	80:20[b]	4:1

[a] Ratio of mm:(mr+rm):rr. [b] Ratio of mm:(mr+rm+rr).

metric to describe the sequence distribution in olefin copolymers: values approaching zero are indicative of alternating sequences while a value of $r_e r_p = 1$ is indicative of a statistical (Bernoullian) distribution of comonomers. Copolymers derived from the unsubstituted complexes **la** and **lb** yield values for the product $r_e r_p$ that range from 0.46 to 0.16 (0 °C), revealing a tendency to alternation, which is common to many metallocene copolymers.[1,18,21] Copolymers derived from metallocenes **2**−**3** with β-substituents on the cyclopentadienyl ring yield lower values of $r_e r_p$ (Table 2). The magnitude of the product of $r_e r_p$ and thus the degree of alternation depends on both the nature of the substituent and to a lesser degree the nature of the bridging group (Me_2C vs Me_2Si). For instance, among the silicon-bridged metallocenes, the degree of alternation decreased in the order Me > i-Pr, as shown in Figure 3 for representative polymers containing close to 50% ethylene. This is reflected in the increase of $r_e r_p$: 0.03 (R = Me) and 0.08 (R = i-Pr). At 50% ethylene incorporation, the sequence distribution of the copolymer produced by **3b** is less alternating than the ones by **2b** and approaches that of **lb** (Figure 3).

The nature of the bridging group has a less dramatic influence on the copolymer sequences. The product of reactivity ratios $r_e r_p$ and sequences for the methyl-substituted metallocenes **2a**,**b** are very similar (Table 2). For the isopropyl-substituted metallocenes **3a** and **3b**, the carbon-bridged **3a** generated more alternating copolymer structure than the silicon-bridged **3b.** Thus the influence of the bridging group appears to depend on the Cp substituent. Table 3 lists the triad distributions of the 50/50 copolymers by all metallocenes except **la.**

Copolymer Microstructure. Analysis of the PEPEP sequences of the alternating copolymers by ^{13}C NMR reveals an isotactic microstructure (Table 4, Figure 4). The ^{13}C NMR of the copolymers yields information on the relative stereochemistry of both the PEPEP and EPPE sequences. The chemical shift of the methyl peaks (the underlined propylene unit) in the three isomeric pentads PE^mPE^mP, PE^mPE^rP, and PE^rPE^rP have been assigned[22] and appear at 20.12, 20.08, and 20.04 ppm, respectively (using benzene-d_6 as standard). Two other pentads PEPEE and EEPEE are observed in the same region, and appear 0.02 ppm downfield from PE^mPE^rP and PE^rPE^rP, respectively. Because of the interference of the PE^mPE^rP, PEPEE and PE^rPE^rP, EEPEE resonances, the stereochemistry of PEPEP was analyzed for copolymers containing <50% ethylene (Table 4). At these ethylene incorporations, contributions from EEPEE and PEPEE sequences are less than 10% of the total area under examination and are assumed to be negligible for the estimation of the ratios of the PEPEP diastereosequences. As shown in Table 4, the PEPEP sequences of ethylene/propylene copolymers obtained from metallocenes **2**−**3** are predominantly isotactic. Given in Figure 4 is a ^{13}C NMR of a PEPEP sequence derived from metallocene **2a** which leads to an estimate for mm/mr/rr of 60/30/10. This estimate is likely a lower limit on the stereospecificity if the contributions from the PEPEE and EEPEE sequences are factored into the measured areas.

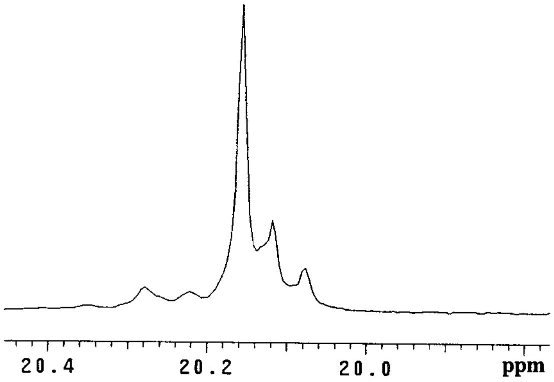

Figure 4. ^{13}C spectra of methyl group resonances in the PEPEP sequence of copolymer made by **2a**/MAO (44.7% ethylene).

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(21) Galimberti, M.; Piemontesi, F.; Fusco, O. In *Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, 2000; Vol. 1, pp 309−343.

(22) Zetta, L.; Gatti, G.; Audisio, G. *Macromolecules* **1978**, *11*, 763−766.

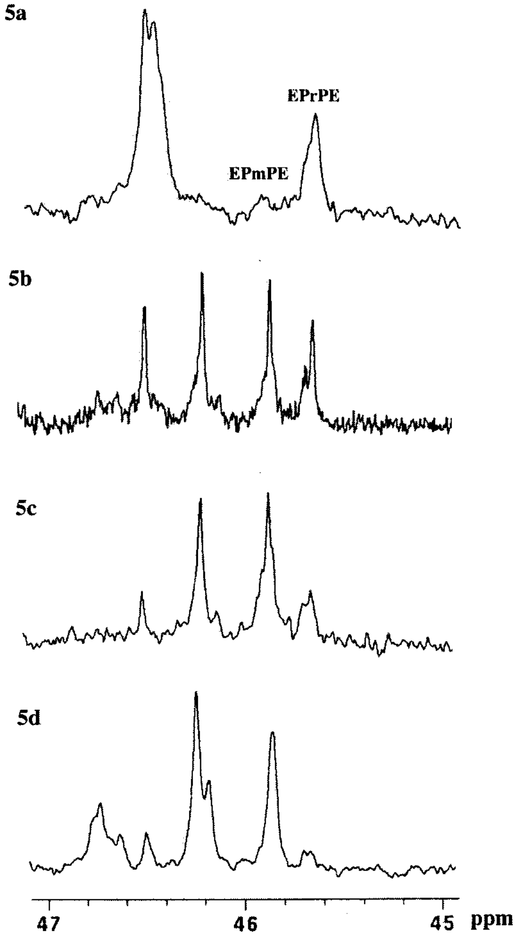

Figure 5. (a−d) ^{13}C chemical shift of $S_{\alpha\alpha}$ in EPPE: **lb**/MAO (a), **2a**−**3a**/MAO (b), **2b**/MAO (c), and **3b**/MAO (d).

Copolymers obtained from metallocenes **la** and **lb** also yield isotactic PEPEP sequences, but quantitative analyses are further complicated by contributions from syndiotactic PP sequences. Nevertheless, a qualitative analysis indicates that isotactic PEPEP sequences predominate for metallocenes **1**−**3**.

The relative stereochemistry of the EPPE sequences (Figure 5) is also illuminating. Due to the low intensity of $S_{\alpha\alpha}$ resonances in the EPPE sequences, only qualitative estimates of the relative stereochemistry can be obtained from the ratio of resonances at 45.85 and 45.65 ppm; these resonances have been assigned as the $\mathrm{EP^{m}PE}$ and $\mathrm{EP^{r}PE}$ diastereosequences, respectively.[23] The EPPE sequences from copolymers derived from **la** and **lb** were almost 100% syndiotactic (Figure 5a) whereas copolymers from both **2a** and **3a** exhibit an equal amount of m and r diads, indicative of atactic EPPE diastereosequences (Figure 5b). Copolymers derived from the silicon-bridged metallocene **2b** were slightly enriched in EPmPE diads (Figure 5c), whereas the ones from metallocene **3b** were highly enriched in EPmPE diads (Figure 5d).

Propylene Homopolymerization. The homopolymerization of propylene was conducted by using MAO-activated metallocenes **la**−**3a, lb**−**3b** at 0 °C in liquid propylene. Results are tabulated in Table 5.[24] In contrast to those reported for EP copolymerization, the productivities for propylene homopolymerization of the carbon-bridged metallocenes are 1−2-fold higher than those of the silicon-bridged metallocenes. Within both sets of bridged metallocenes, no significant differences in productivities were observed as a function of the cyclopentadienyl substituent.

As previously observed,[6,7,14,25] the nature of the bridging group has a significant influence on the stereoselectivity of this class of catalysts. The C_s-symmetric metallocenes **la** and **lb** both produced syndiotactic polypropylene, with percentages of syndiotactic pentads [rrrr] = 90% and 78%, respectively. The carbon-bridged metallocenes **2a** and **3a** produced hemiisotactic polypropylene (Figure 6a), while the silicon-bridged **2b**/MAO and **3b**/MAO produced poorly isotactic polypropylene (described by Spaleck as an isotactic/syndiotactic stereoblock copolymer)[25] with isotactic pentads ranging from 28 to 36%. For metallocene **3b**/MAO the ratio of mmmr:mmrr:mrrm pentads is close to 2:2:1 (Figure 6c), suggesting that isolated rr stereoerrors predominate over isolated r stereochemical defects in these polymers. It is intriguing to note that **2b**/MAO exhibited an intermediate situation (Figure 6b).

To test for the influence of monomer concentration on the stereoselectivity, propylene polymerization with **2b**/MAO was conducted at six different propylene concentrations ranging from 1.05 to 11.11 M at 20 °C. Figure 7 shows that [mmmm] and [m] decrease with increasing propylene concentrations, conversely, [rrrr] and [r] increased.

Discussion

Metallocene catalysts have proven highly effective copolymerization catalysts due to their well-defined kinetic behavior, ease of incorporation of comonomer, and tendency to produce statistical copolymers with homogeneous composition distributions.[1,21] Recently, we and others have shown that it is possible to manipulate the sequence distribution in olefin copolymers with appropriate choice of either comonomers or ligand design.[10−13,21,26−29] It has long been known in both radical[30] and coordination polymerization[31,32] that alternating copolymers can be produced from mixtures of comonomers where one of the comonomer pairs will not readily homopolymerize ($r_2 = 0$, thus $r_1r_2 = 0$). Recently this strategy has been used with considerable success to prepare new classes of crystalline polymers based on alternating ethylene/norbornene,[33−37] ethylene/styrene,[38−40] and ethylene/isobutylene[41] copolymers. This strategy provides access to new classes of crystalline polymers by

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[23] Tritto, I.; Fan, Z.; Locatelli, P.; Sacchi M. C. *Macromolecules* **1995**, *28,* 3342−3350.

[24] For peaks with area over 20% of the total, the error from measurement is within ±5%; for peaks of lower intensity we estimate a relative error of ±20%.

[25] Spaleck, W.; Aulbach, M.; Bachmann, B.; Kuber, F.; Winter, A. *Macromol. Symp.* **1995**, *89*, 237−247.

[26] Uozumi, T.; Ahn, C. H.; Tomisaka, M.; Jin, J.; Tian, G.; Sano, T.; Soga, K. *Macromol. Chem. Phys.* **2000**, *201*, 1748−1752.

[27] Galimberti, M.; Resconi, L.; Albizzati, E. European Patent Application 632066, 1995.

[28] Galimberti, M.; Piemontesi, F.; Mascellani, N.; Camurati, I.; Fusco, O.; Destro, M. *Macromolecules* **1999**, *32*, 7968−7976.

[29] Galimberti, M.; Piemontesi, F.; Fusco, O.; Camurati, I.; Destro, M. *Macromolecules* **1998**, *31*, 3409−3416.

[30] Odian, G. *Principles of Polymerizations*, 3rd ed.; Wiley-Interscience: New York, 1991; pp 455−457.

[31] Natta, G. *J. Polym. Sci.* **1959**, 531−549.

[32] *Alternating Copolymers*; Cowie, J. M. G., Ed.; Plenum Press: New York, 1985.

[33] Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4674−4680.

[34] Harrington, B. A.; Crowther, D. J. *J. Mol. Catal. A., Chem.* **1998**, *128*, 79−84.

[35] Arndt, M.; Kaminsky, W. *Macromol. Symp.* **1995**, *97*, 225−246.

[36] Kaminsky, W.; Noll, A. *Polym. Bull.* **1993**, *31*, 175−182.

[37] Montag, P.; Ruchatz, D.; Fink, G. *Kautschuk Gummi Kunststoffe* **1996**, *49*, 582.

[38] Venditto, V.; De Tullio, G.; Izzo, L.; Oliva, L. *Macromolecules* **1998**, *31*, 4027−4029.

[39] Oliva, L.; Immirzi,. A.; Tedesco, C.; Venditto, V.; Proto, A. *Macromolecules* **1999**, *32*, 2675−2678.

[40] Xu, G. X. *Macromolecules* **1998**, *31*, 2395−2402.

Table 5. Propylene Homopolymerization:[a] at 0 °C, Liquid Propylene

metallocene	A^b	mmmm	mmmr	rmmr	mmrr	xmrx	mrmr	rrrr	rrrm	mrrm
la	3207	0.0	0.0	1.2	2.1	0.0	1.2	90	4.4	1.3
lb	1428	0.5	0.5	1.6	2.9	1.3	2.1	78.9	8.2	4.0
2a	5466	1.	11.5	7.7	23.T	0.0	0.0	19.9	14.	9.7
2b	1970	28.5	16.4	4.9	12.8	16.0	6.8	6.3	4.3	4.0
3a	3648	16.2	12.0	8.0	1	0.0	0.0	17.4	13.1	9.2
3b	1500	36.5	16.0	4.5	15.7	5.1	1.6	4.7	4.9	7.4

[a] [Zr] = l × 10^{-5} M, Al:Zr = 2000:1. [b] *A* is expressed in kg PP/mol Zr/h.

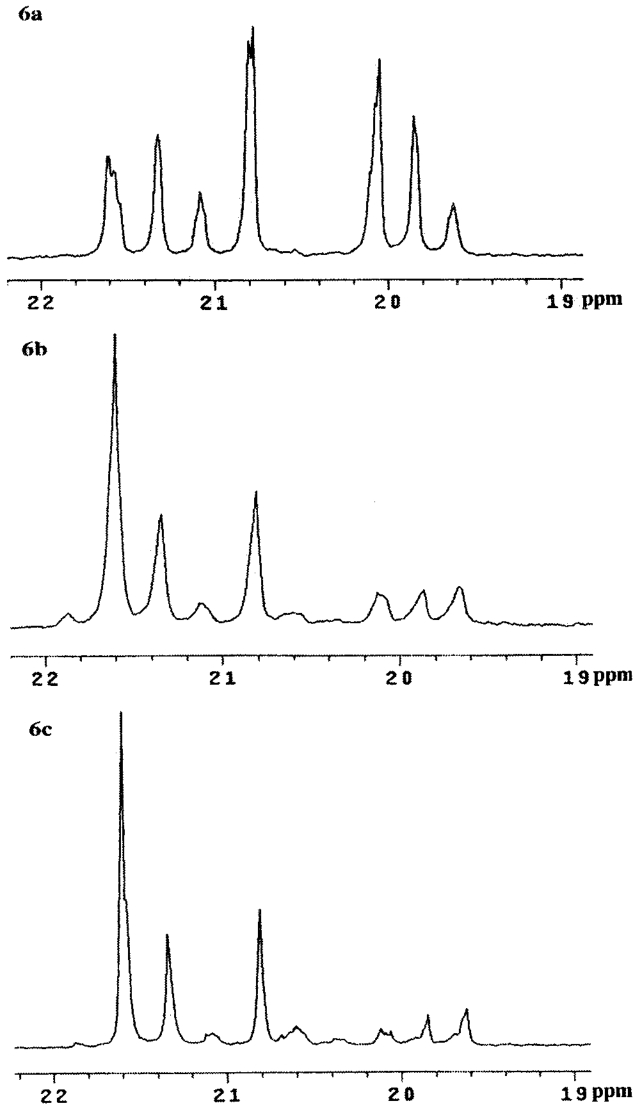

Figure 6. Pentad distributions of polypropylene: **2a**/MAO (a), **2b**/MAO (b), and **3b**/MAO (c).

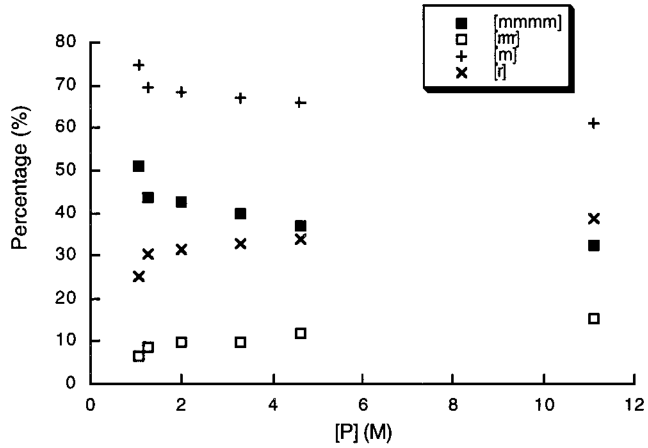

Figure 7. Dependence of dyad [m] ([r]) and pentad [mmmm]([rrrr]) on propylene concentration (**2b**, 20 °C, toluene).

the appropriate combination of comonomers, but is limited by the necessity to choose comonomers that are sluggish to homopolymerize; this restriction often leads to modest productivities due to the slow insertion of the comonomer (norbornene/styrene/isobutylene).

Only recently have alternating copolymers of ethylene and α-olefins been produced by metallocenes exhibiting substantial activity for α-olefin homopolymerization (i.e. $r_2 \neq 0$).[10-12,42-44] While this research is in its very early stages, two general strategies have emerged. One approach relies on specifically substituted C_s-symmetric *ansa*-metallocenes derived from either bis-fluorenyl or fluoreny/3,4-dimethyl cyclopentadienyl complexes.[10,21,43,44] The role of the ligand structure on the alternating sequence selectivity for this class of catalysts is still poorly understood, but as noted by Galimberti all of these catalysts have at least one fluorenyl ligand.[21] The second approach takes advantage of the alternating insertion of olefins at heterotopic coordination sites of C_1-symmetric catalysts. To produce alternating copolymers with this class of catalysts, the kinetic selectivities toward the two comonomers need to be sufficiently different to select one of the comonomers at a given site. Moreover, to produce stereoregular alternating copolymers, the site selective for the α-olefin must also be stereospecific.

While the "alternating-site" copolymerization strategy remains to be fully tested as a mechanistic hypothesis, it provides a useful strategy to guide the design of new metallocenes for the synthesis of alternating ethylene/α-olefin copolymers. Investigations by the late Professor Soga showed that C_1-symmetric *ansa*-metallocenes derived from metallocenes such as *meso*-Me_2Si(indenyl)$ZrCl_2$[12] and Me_2Si(fluorenyl)(indenyl)$ZrCl_2$[11] can yield alternating copolymers; we and Kaminsky's group have shown that highly alternating copolymers are obtained from C_1-symmetric *ansa-metallocenes* $Me_2C(RCp)$(Fluorenyl)$ZrCl_2$.[10,13] The sequences of the latter copolymers could be adequately modeled by using a kinetic mechanism based on the alternate insertion of olefins at two sites with differing kinetic selectivities for ethylene and propylene. Nevertheless, the modest activities, molecular weights, sequence selectivity, and stereospecificity of this first generation of catalysts stimulated us to investigate the influence of metallocene structure on the polymerization behavior and in particular the factors which influence the sequence and stereoselectivity. In this contribution, we report the alternating copolymerization of ethylene and propylene with

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(41) Shaffer, T. D.; Canich, J. A. M.; Squire, K. R. *Macromolecules* **1998**, *31*, 5145−5147.

(42) Arndt, M.; Beulich, I. *Macromol. Chem. Phys.* **1998**, *199*, 1221−1232.

(43) Resconi, L.; Jones, R. L. European Patent Application 729968, 1996.

(44) Yu, Z.; Marques, M.; Rausch, M. D.; Chien, J.-C. W. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2795−801.

a series of C_1-symmetric catalysts and report the influence of ligand structure on the productivity, molecular weight, sequence selectivity, and stereoselectivity. As previously reported,[10] the isopropylidene-bridged metallocenes **la** and **2a** are moderately active for the copolymerization of ethylene and propylene at 0 °C in liquid propylene to give EP copolymers of modest molecular weight (Table 1). Replacement of the isopropylidene bridge by a dimethylsilyl bridge results in a dramatic increase in activities and molecular weights of the EP copolymers (Table 1):[25] the productivities of the carbon-bridged metallocenes were less than 7000 kg of polymer/mol of Zr/h, whereas those for the silicon-bridged metallocenes were greater than 18000 kg of polymer/mol of Zr/h. Similarly, the molecular weights of copolymers derived from the carbon-bridged metallocenes were less than 65000, whereas those from the silicon-bridged congeners were greater than 230000 under similar copolymerization conditions (Table 1). Similar effects have been observed in propylene homopolymerization and have been attributed to the 10° difference in the metal centroid angles[7] leading to a larger coordination-gap aperture for the carbon-bridged congeners.

Sequence Distribution. Analysis of the copolymerization parameters and sequence distribution for copolymers having mole fractions of propylene close to Xp = 0.5 reveals that the copolymers prepared by metallocenes **2a**,**b** and **3a**,**b** are predominantly alternating (Table 2). Estimates of the degree of alternation of the copolymers can be obtained by analysis of the sequence distributions of copolymers at various feed ratios using the first-order Markov copolymerization model according to the method of Randall.[20,45] The first-order Markov analysis is derived from a kinetic model that assumes a single type of polymerization site for monomer enchainment.[30] The selectivity of this site for olefin insertion is represented by the copolymerization parameters $r_e = k_{ee}/k_{ep}$ and $r_p = k_{pp}/k_{pe}$. The product of these parameters r_er_p is a useful metric to describe the sequence distribution: values of r_er_p that approach zero are indicative of alternating copolymers whereas large values of r_er_p are indicative of blocky copolymers. Since the first-order Markov analysis assumes a single type of polymerization site, it is nominally an inappropriate model to interpret the behavior of catalysts that are proposed to alternate sites for each olefin insertion. We do not wish to imply that conformance of the sequence distribution to the first-order Markov model necessarily implies anything about the polymerization mechanism; for the purposes of this paper, we use this model simply as a convenient metric to describe the copolymer sequence distribution. The advantage of this method of analysis is that the copolymerization parameters r_e and r_p can be readily derived from the experimental data and the product r_er_p, indicative of the sequence distribution, can be compared for copolymers containing a range of comonomer contents.

The copolymerization parameters for a series of EP copolymers prepared from metallocenes **la−3a and lb−3b** are presented in Table 2. It is known that many metallocenes tend to exhibit a slight tendency for alternation with values for r_er_p ranging from 0. 16 to 1.4; this alternating tendency seems to be most pronounced for the C_s-symmetric metallocenes of the type **la**,**b**.[46] The low values for r_er_p for polymers derived from the C_1-symmetric metallocenes **2a**, **2b**, **3a**, and **3b** (r_er_p = 0.02−0.08) are indicative of a high degree of sequence alternation; by way of contrast values for r_er_p for the C_s-symmetric metallocenes are higher (r_er_p = 0.16 **(lb),** 0.46(**la**)). A direct comparison of the sequence distributions for 50/50 copolymers derived from **lb−3b** is presented in Figure 3; from this figure it can be seen that the methyl-substituted metallocene **2b** exhibits the highest tendency toward alternation with the EPE/PEP triads constitituting approximately 75% of the triads in the copolymer (Table 3). Comparison of the sequence-derived copolymerization parameters reveals that the nature of the bridge has only a slight influence on the sequence distribution: for the methyl-substituted derivatives **2a** and **2b**, the sequence distributions are indistinguishable, whereas for the isopropyl-substituted metallocenes, the lower value of r_er_p for **3a** indicates that copolymers derived from this metallocene are slightly more alternating than those from **3b.** The nature of the cyclopentadienyl substituent has a much larger influence on the sequence: as evidenced for the silicon-bridged metallocenes, introduction of an alkyl substituent in the 3-position of the cyclopentadienyl ring results in a dramatic increase in the degree of alternation (compare $r_er_p = 0.16$ for **lb** vs $r_er_p = 0.03-0.08$ for **2b−3b).** For the 3-alkyl-substituted metallocenes, the degree of alternation appears to vary inversely with the size of the 3-alkyl substituent. For the silicon-bridged complexes, the most highly alternating polymers were obtained from the methyl-substituted metallocene **2b** ($r_er_p = 0.03$).

Stereochemistry. Analysis of the microstructure of the alternating copolymers prepared from metallocenes **2a**, **3a**, **2b**, and **3b** by ^{13}C NMR reveal that the PEPEP sequences are predominantly *isotactic.* This is illustrated in Figure 4 for the EP copolymer (44.7% ethylene) obtained from **2a** where the ^{13}C NMR spectrum of the methyl region exhibits a 60:30:10 ratio of the mm:(mr + rm):rr triads. Soga reported that indenyl-fluorenyl metallocenes yield isotactic EP copolymers;[11] the only other known examples of an isotactic alternating EP copolymer are those prepared by Elgert and Audisio, who obtained this material in low yield by hydrogenating isotactic *trans*-1,4-polypentadiene.[22,47] As a tactic regular structure, this material could in principle be crystalline,[48] but the properties of this material are unknown. We have observed no evidence of crystallinity in the samples prepared in this study. The glass transition temperatures for all the copolymers range from −54 to −56 °C, as determined by DSC. Presumably a higher degree of alternation and higher tacticities will be required for this material to crystallize from the melt. From a mechanistic perspective, the fact that the PEPEP sequences in these copolymers are isotactic indicates that propylene inserts in a stereoselective coordination site.[49] There are two limiting interpretations to account for the stereospecific alternating copolymerization. The first limiting mechanism is that these metallocenes, despite their C_1-symmetry, behave as single site catalysts and that both ethylene and propylene insert at the isospecific site. In the context of the Cossee hypothesis[8,9] where olefin insertion involves a migration of the chain from one coordination site to another, this would require that the polymer chain would isomerize back to its original coordination site prior to coordination and insertion of either ethylene or propylene.[50] In this case, the first-order Markov mechanism would be a valid model for interpreting the copolymerization behavior of the catalysts and the reactivity ratios derived from the sequence

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(45) Randall, J. C.; Hsieh, E. T. *Macromolecules* **1982**, *15*, 1584−1586.

(46) Herfert, N.; Montag, P.; Fink, *G. Macromol. Chem. Phys.* **1993**, *194*, 3167−3182.

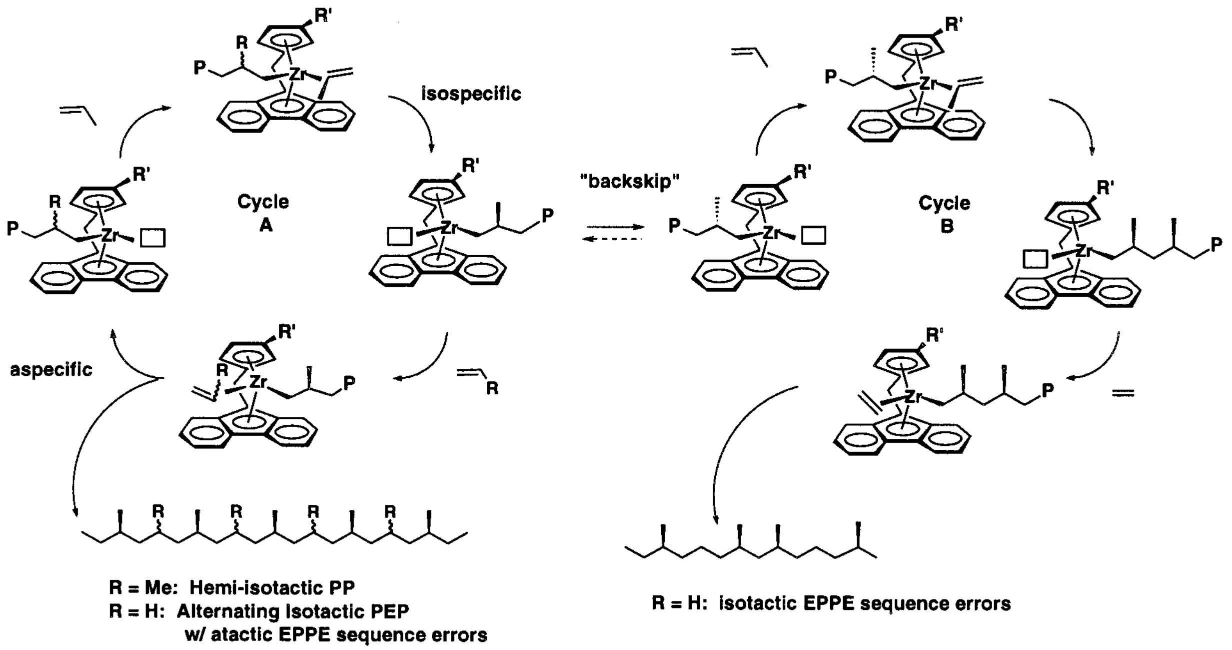
(47) Elgert, K.-F.; Ritter, W. *Makromol. Chem.* **1976**, *177*, 2781.

(48) Chien, H. Y.; McIntyre, D.; Cheng, J. L.; Fone, M. *Polymer* **1995**, *36*, 2559−2565.

(49) We feel a chain-end control mechanism would be unlikely for these alternating copolymerizations since the stereogenic center of the chain-end is four carbons removed from the metal center.

(50) Corradini, P.; Cavallo, L.; Guerra, G. In *Metallocene-Based Polyolefins*; Wiley Series in Polymer Science; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, 2000; Vol. 2, pp 3−36.

Scheme 1. Proposed Mechanism for Alternating Polymerization and Copolymerization of Olefins



distributions in Table 2 would thus represent the kinetic selectivities at this single coordination site. An alternative interpretation is that olefin insertion occurs alternately at the two different heterotopic coordination sites and that the two sites exhibit different kinetic selectivities toward the two comonomers. While we cannot rule out the single-site mechanism at this time, indirect evidence for the alternating site hypothesis is provided by the stereochemistry of the copolymers and a comparison of the copolymer stereochemistry with that of the corresponding propylene homopolymers. In propylene homopolymerization, metallocene **2a** produces hemiisotactic polypropylene[5−7]—an alternating mictrostructure of propylene where the stereocenters alternate between isotactic and random configurations. The fact that these metallocenes yield hemiisotactic polypropylenes suggests that one coordination site is stereoselective and one coordination site is nonstereoselective. The observation that metallocenes **2a** and **3a** yield hemiisotactic polypropylenes and isotactic alternating EP copolymers is consistent with the alternating site mechanism where ethylene inserts at the nonstereoselective site and propylene inserts at the stereoselective site (Figure 1, Scheme 1, cycle A). While we have no direct evidence to establish which site is which, the theoretical models of Guerra and Corradini would predict that propylene preferentially binds and inserts at the coordination site on the same side as the 3-R substituent of the cyclopentadienyl ligand (Scheme 1).[50]

Further support for the alternating site hypothesis comes from analysis of the stereoerrors of the EPPE sequences and their relationship to stereosequences of the alternating copolymers and the corresponding homopolypropylenes. The ratio of EPPE dyads in copolymers derived from metallocenes **2a** and **3a** is approximately stereorandom, while dyads derived from metallocenes **2b** and **3b** are enriched in isotactic m dyads (Table 4, Figure 5). Stereorandom EPPE sequences are inconsistent with a single site mechanism since if olefin insertion occurs only at the stereoselective site to give isotactic PEPEP sequences, then the occasional EPPE sequence errors should be isotactic.

The alternating-site hypothesis would predict two possible mechanistic origins of sequence errors, which of course could operate simultaneously: (1) the kinetic selectivity at one or both of the two insertion sites may be insufficient to fully discriminate between the comonomers at a given feed ratio and/or (2) loss of fidelity in the alternation of olefin insertion at the two heterotopic sites might lead to multiple insertions at one site and a consequent diminuition in the sequence selectivity. Both of these effects have been fully discussed as sources of stereoerrors in propylene homopolymerization.[7,51,52] In the first case, EPPE sequence errors resulting from poor kinetic selectivities could result from the following insertion sequence: a normal isospecific propylene insertion followed by a stereorandom propylene insertion at the ethylene site. To generate the EPPE sequence, this stereorandom propylene insertion would have to be followed by an ethylene insertion at the propylene site. This situation involves two insertion errors and would result in stereorandom EPPE sequences since the second propylene would insert at the nonstereoselective ethylene site (Scheme 1, cycle A). In the latter case, backskip of the polymer chain to the stereoselective propylene site would result in an isotactic EPPE placement (represented as $EP^{m}PE$, Scheme 1, cycle B).

The observation that the syndiospecific propylene polymerization catalysts derived from **la** and **lb** yield isotactic PEPEP sequences and syndiospecific EPPE sequences is consistent with an alternating site insertion mechanism for these two catalysts (Figure 5, Scheme 1, cycle A). The fact that metallocenes **2a** and **3a** yield hemiisotactic polypropylene, isotactic PEPEP sequences, and stereorandom EPPE sequences is also consistent with an alternating site mechanism where the major source of sequence errors comes from poor kinetic selectivity rather than chain backskip (Scheme 1, cycle A).

The microstructural analysis of polymers derived from **2b**−**3b** is more complicated. Homopolymers of propylene derived from these metallocenes are predominantly isotactic, but contain some syndiotactic sequences. This "isotactic/syndiotactic" stereoblock structure has been previously interpreted in terms of the alternating insertion of propylene at non- and stereoselective sites with frequent isomerization of the chain ("backskip") from the nonstereoselective site to the stereoselective site (Scheme 1, cycle B).[25] The rate of inversion (or "backskip") in this case could even be competitive with insertion as proposed by Collins for other C_l-symmetric catalysts.[53,54] Nevertheless, these metallocenes produce highly alternating EP copolymers, implicating an alternating site mechanism where the frequency of backskip for EP copolymerization is less frequent than that for propylene homopolymerization.

An unusual trend is the diminuition of the sequence selectivity with increasing size of the cyclopentadienyl substituent (Figure 3, Table 2). Within the context of the alternating site mechanism, one might expect a greater difference in kinetic selectivity and thus greater discrimination between the two comonomers at the two sites as the size of the 3-cyclopentadienyl substituent increases, opposite of the observed trends. Another interpretation is that the increasing size of the 3-Cp substituent leads to more frequent "backskip" of the polymer chain prior to monomer insertion, leading to multiple insertions at one site and more frequent sequence errors. This is supported by the analysis of the tacticity of the EPPE sequences: they are predominantly isotactic for EP copolymers derived from **2b** and **3b**. These results suggest that a substantial fraction of the EPPE sequence errors derived from metallocenes **2b** and **3b** are derived from site isomerization (Scheme 1, cycle B). Although the quantitation of the EPPE tacticity is difficult due to the low signal to noise, there appears to be correlation between the number of sequence errors for metallocenes **2b** and **3b** and the degree of tacticity of the EPPE sequences, consistent with increasing frequency of chain backskip as the size of the 3-Cp substituent increases.

That site isomerization occurs and that it appears to be more probable for the silicon-bridged metallocenes relative to the carbon-bridged metallocenes is further supported by analysis of the homopolypropylene microstructures. At 0 °C in liquid propylene, the carbon-bridged metallocenes **2a** and **3a** produce hemiisotactic polypropylene, consistent with a strict migratory insertion mechanism. However, as discussed above, isotactic/syndiotactic stereoblock polypropylene is formed by the silicon-bridged metallocenes **2b**−**3b**, which strongly suggests that site isomerization is competitive with insertion in this case.[16]

Further evidence for site isomerization in propylene polymerization with **2b** was obtained by investigating the influence of monomer concentration on the microstructure.[7,53−60] Since site-isomerization is a unimolecular process and olefin insertion a bimolecular process dependent on olefin concentration, the ratio of the processes should depend on monomer concentration. As shown in Figure 7, the polypropylene microstructure is quite sensitive to propylene concentration with the [mmmm] pentad decreasing and the [rrrr] pentad increasing with increasing monomer concentration. For metallocenes with the general structure of Me$_2$Si(RCp)(Flu)ZrCl$_2$ (Scheme 1, cycle A), strict migratory insertion produces hemiisotactic polypropylene with equal amounts of [mmmm] and [rrrr] diastereosequences. A backskip of the polymer chain that converts the insertion site from the nonstereoselective to the stereoselective site will convert some fraction of rr diads to mm diads. Thus, the frequency of chain backskip can be crudely estimated from the relative number of pairs ([mmmm], [rrrr]) and ([m], [r]). Note from Figure 7 that as propylene concentration (propylene pressure) decreases the fraction of [mmmm] and [mm] diastereosequences increases and that of the [rrrr] and [r] stereosequences decreases. This is consistent with the general observation that lower monomer concentration leads to more polymer chain backskips.[4,25,51,53,58,61,62]

Competition from site-isomerization (or backskip) appears to be more significant for the silicon-bridged complexes than for the carbon-bridged species. This is consistent with the lower syndiospecificity of **lb** relative to **la**,[6,7,14,25] the fact that **2b**, **3b** yield more tactic polypropylene microstructures than **2a**, **3a**, and the observation that the EPPE stereoerrors for **2b**, **3b** are isotactic while those of **2a**, **3a** are atactic. The silicon bridge appears to enhance the steric influence posed by the 3-Cp substitutent and the two might work cooperatively to create the steric congestion around the catalytic sites, resulting in more frequent skipped insertions in polymerizations by **2b**−**3b,** consistent with early predictions by Ewen.[7]

Conclusion

In summary, silicon-bridged metallocenes of the series Me$_2$Si(RCp)(Flu)ZrCl$_2$ (R = Me, i-Pr) are capable of producing high molecular weight isotactic, alternating ethylene/propylene copolymers with high productivities. Analysis of the microstructure and sequence distribution of the homo- and copolymers are consistent with a Cossee-type alternating site mechanism where olefin inserts alternately at heterotopic coordination sites. Occasional multiple insertions at a given site, caused by isomerization (or backskip) of the chain prior to monomer insertion, have been identified as a possible origin of stereoerrors as well as sequence errors in both propylene co- and homopolymerization. The difference in the copolymerization behavior between different metallocenes in all aspects such as sequence distributions, stereochemistry, activity, and molecular weight can be rationalized by the cooperative influence of the bridging atom and 3-Cp substituent. These results demonstrated that synthesis of ethylene/α-olefin copolymers with defined microstructures such as controlled sequence distribution, nonrandom stereochemistry, and desirable Mw is possible by systematic variations of the metallocene ligand frame.

Experimental Section

General Consideration. All manipulation with organometallic compounds were conducted by using standard Schlenk and drybox techniques. Complexes Me$_2$C(Cp)(Flu)ZrCl$_2$ **(la),** Me$_2$C(3-MeCp)(Flu)ZrCl$_2$ (**2a**), Me$_2$C(3-^{i}PrCp)(Flu)ZrCl$_2$ (**3a**), Me$_2$Si(Cp)(Flu)ZrCl$_2$ **(lb),** Me$_2$Si(3-MeCp)(Flu)ZrCl$_2$ (**2b**), and Me$_2$Si(3-^{i}PrCp)(Flu)ZrCl$_2$ (**3b**) were synthesized according to literature procedures.[6,14−16]

Toluene was passed through two purification columns packed with activated alumina and supported copper catalysts. Polymerization grade ethylene and propylene gases were purchased from Matheson. Liquid propylene was either obtained from Amoco or purchased from Scott Specialty gases. Both monomers were further purified by passage through two columns packed with activated alumina and supported

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(51) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564−573.

(52) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskela, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348−4355.

(53) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771−3778.

(54) Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000−1009.

(55) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667−76.

(56) Fait, A.; Resconi, L.; Guerra, G.; Corradini, P. *Macromolecules* **1999**, *32*, 2104−2109.

(57) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329−9330.

(58) Kukral, J.; Lehmus, P.; Feifel, T.; Troll, C.; Rieger, B. *Organometallics* **2000**, *19*, 3767−3775.

(59) Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971−3977.

(60) Nele, M.; Collins, S.; Dias, M. L.; Pinto, J. C.; Lin, S.; Waymouth, R. M. *Macromolecules* **2000**, *33*, 7249−7260.

(61) Rieger, B.; Jany, G.; Fawzi, R.; Steimann, M. *Organometallics* **1994**, *13*, 647−653.

(62) Miyake, S.; Bercaw, J. E. *J. Mol. Catal. A: Chem.* **1998**, *128*, 29−39.

(63) Kakugo, M.; Naito, Y.; Mizunuma, K.; Miyatake, T. *Macromolecules* **1982**, *15*, 1150.

copper catalyst. Methylaluminoxane (MAO), type 3A, purchased from Akzo Nobel, was dried in vacuo prior to use.

Propylene Homopolymerization. A 300-mL stainless steel reactor equipped with a mechanical stirrer was evacuated, purged three times with Ar and three times with gaseous propylene by pressurizing and venting, and charged with 100 mL of liquid propylene. Propylene was cooled to 0 °C and an injection tube containing 20 mL of toluene solution of metallocene and MAO (metallocene and MAO were mixed and stirred for 5 s before being poured into the injection tube) was taken out of the drybox. The injection tube was pressurized with 250 psig of Ar and injected to the reactor and polymerization proceeded for 20 min. The reaction was quenched by injection of 5 mL of methanol solution and the reactor was slowly vented and opened. The polymer was stirred in 300 mL of methanol containing 5% concentrated hydrochloric acid, rinsed with methanol, and dried at 40 °C in vacuo overnight.

Ethylene−Propylene Copolymerization. A 300-mL stainess steel reactor equipped with a mechanical stirrer was evacuated, purged three times with Ar and three times with gaseous propylene by pressurizing and venting, and charged with 100 mL of liquid propylene. Propylene was cooled to the reaction temperature and overpressurized with ethylene to the desired total pressure. After 30 min of equilibration, an injection tube containing 20 mL of a toluene solution of metallocene and MAO (metallocene and MAO were mixed and stirred for 5 s before being poured into the injection tube) was taken out of the drybox. The injection tube was pressurized with 250 psig of Ar and injected into the reactor and polymerization proceeded for 20 min. Polymerization temperature was maintained by a water/ethylene glycol cooling bath (internal cooling loop), and an external water/ice bath if necessary. The reaction was quenched by injection of a 5-mL methanol solution and the reactor was slowly vented and opened. The polymer was stirred in 300 mL of methanol containing 5% concentrated hydrochloric acid, rinsed with methanol, and dried at 40 °C in vacuo overnight.

Polymer Characterization. Polymer molecular weights and molecular weight distributions were determined by 135 °C gel permeation chromatography. ^{13}C NMR measurements were carried out on a Varian UI300 spectrometer. A 150−300 mg sample of each sample was dissolved in 2.5 mL of *o*-dichlorobenzene/10 vol % benzene-d_6 in a 10-mm-diameter tube. The spectra were acquired at 100 °C using a delay time of 0 s for polypropylene and 5 s for ethylene/propylene copolymers. A 2−3 mg sample pf chromium(lIm) triacetylacetonate was added as a paramagnetic substance to reduce the relaxation times. The tacticity of the PEPEP triad was analyzed by deconvolution of the three overlapped peaks (chemical shifts of the underlined primary methyl in PEPEP) using Varian-400 MHz NMR software.

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