single-crystal X-ray structure analysis. With the same combination of ligand and metal, the generation of optically pure left- or right-handed helices by using chiral anions is currently under investigation. Furthermore, the formation of linear coordination polymers (Figure 1a) with ligands such as **3** and **5** and silver or copper is also being studied.

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[15] Suitable crystals were obtained from acetonitrile/toluene/hexane. Reflections were measured on an area detector. Crystal dimensions: $0.12 \times 0.10 \times 0.05$ mm (mounted in a capillary). $C_{48}H_{36}AgF_6N_4P \cdot 11/4\,CH_3CN$, $M_r = 1034.6$, monoclinic, space group $C2/c$, $a = 17.7806(8)$, $b = 34.529(2)$, $c = 38.715(2)$ Å, $\beta = 91.915(5)^\circ$, $V = 23756$ Å^3, $Z = 16$, $\rho_{calcd} = 1.15\ \mathrm{g\,cm^{-3}}$, $F(000) = 8456$, $T = 295$ K, monochromatized $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ cm; 27682 measured reflections ($R_{int} = 0.10$, $2\theta_{max} = 52.6^\circ$), of which 19624 were unique and were corrected for absorption. Final conventional $R = 0.11$ and $Rw = 0.11$ (statistically weighted) for 5092 observed reflections ($I > 3\sigma(I)$). $T_{min}/T_{max} = 0.35/0.86$ (SADABS), Xtal3.4 program system. Phenyl and pyridine rings were refined as rigid bodies, and the geometries of the anions and solvent molecules were constrained to "idealized" values, with isotropic thermal parameters. Ring 24n was modeled as disordered over two sets of sites of equal occupancy. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100747. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Alternating Ethene/Propene Copolymerization with a Metallocene Catalyst**

Margarete K. Leclerc and Robert M. Waymouth*

Metallocene catalysts have introduced an element of design into the construction of polyolefins of defined architecture.[1] Correlation of the catalyst structure with the structure of the resulting polymers has provided considerable insight into the mechanism of polymerization. For example, the syndiospecific polymerization of propene with [{(Cp)(Me$_2$C)(Flu)}ZrCl$_2$]-based catalysts strongly implicates a Cossee-type mechanism[2] in which the olefin inserts at alternating enantiotopic coordination sites with each insertion (Cp = cyclopentadienyl, Flu = fluorenyl).[3] Differentiation of the coordination sites by methyl substitution on the Cp ring in these systems yields hemiisotactic polypropene,[4–6] in which olefin insertion occurs alternately at an aspecific and isospecific coordination site; substitution of the Cp ring with the larger *tert*-butyl substituent yields isotactic polypropylene.[7,8] The latter result has been interpreted by invoking a "chain-skipping" mechanism in which the polymer chain "skips" out of the more sterically hindered site prior to olefin insertion, resulting in polyinsertions at only one isospecific coordination site.[9]

Metallocene catalysts have also proven useful for olefin copolymerization as copolymers produced with metallocene catalysts tend to have more random comonomer distributions and better compositional homogeneity than copolymers produced with heterogeneous catalysts.[1] However, metallocene catalysts also offer the possibility to design catalyst

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systems for *nonrandom* olefin copolymers. In particular, we sought to exploit the alternating-site insertion behavior proposed for bridged-fluorenyl complexes[3–8] to design catalysts for the alternating copolymerization of olefins. Herein we report the copolymerization of ethene and propene with catalysts derived from **2**/MAO and **3**/MAO (Figure 1; MAO = metylaluminoxane) to produce highly alternating ethene/propene copolymers (alt-EP), which, until recently,[10, 11] could be obtained only by hydrogenation of polyisoprene or 1,4-poly(pentadiene).[12,13] Soga et al. have recently reported that *meso*-[{(Me$_2$Si)(1-MeInd)}ZrCl$_2$]/MAO systems (Ind = indenyl) give alternating ethene/octene copolymers.[14]

[{(3-*t*BuCp)(Me$_2$C)(Flu)}ZrMe$_2$] **1**

[{(3-MeCp)(Me$_2$C)(Flu)}ZrMe$_2$] **2**

[{(3,4-Me$_2$Cp)(Me$_2$C)(Flu)}ZrMe$_2$] **3**

[{(Cp)(Me$_2$C)(Flu)}ZrMe$_2$] **4**

Copolymerizations of ethene and propene with **1**/MAO, **2**/MAO, and **3**/MAO were carried out using a variety of monomer feed compositions. The sequence distributions of the polymers obtained were estimated by ^{13}C NMR spectroscopy. The experimental results are summarized in Table 1.

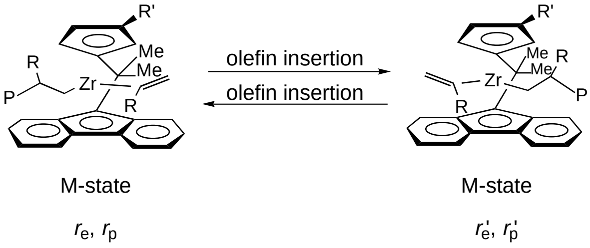

Figure 1. Olefin polymerization with **1**/MAO and **2**/MAO (R' = *t*Bu and Me, respectively). R = H, Me.

Copolymers produced from **1**/MAO with ethene contents of 44–51% exhibit random sequence distributions with no preferential formation of EPE and PEP triads even at equal E/P contents.[15] The copolymerization parameters r_1 and r_2 and their product $r_1r_2 = 0.51–0.57$ are comparable to those obtained with other metallocenes.[16, 17] For these copolymers, satisfactory fits for the triad distributions were obtained only by the second-order Markovian model (Table 2); first-order Markovian statistics yielded poor fits. The second-order Markovian copolymerization parameters r_{11} and r_{21} show little variation for copolymers made under a variety of conditions. Moreover, the monomer distributions are very similar to those obtained with the unsubstituted system **4**/MAO.[18] These results, coupled with the observation that the

Table 1. E/P Copolymerization, reactivity ratios, and triad distribution.

Cat.[a] (*T*[°C])	% E in the Comonomer	% E in the Polymer	r_1[b]	r_2[b]	EEE	PEE + EEP	PEP	EPE	EPP + PPE	PPP
1/MAO (0)	14.7	51	3.94	0.144	8.6	24.8	18.0	19.6	19.9	9.1
1/MAO (20)	9.7	44	4.62	0.111	5.5	19.3	19.2	16.8	23.6	15.6
2/MAO (0)	9.7	49	1.56	0.022	1.9	11.3	37.4	35.9	11.6	1.9
2/MAO (20)	7.2	48	2.07	0.022	2.0	10.4	35.4	35.8	13.0	3.4
3/MAO (0)	7.1	48	1.59	0.017	0.9	10.0	37.7	39.3	9.8	2.3
3/MAO (20)	5.0	51	4.29	0.011	2.8	15.3	33.2	37.1	8.6	3.0

[a] [Zr] = 6.4 × 10^{-6}–1.76 × 10^{-5} M; [Al] = 1.3–1.4 × 10^{-2} M. [b] Based on the dyad distribution.[27]

Table 2. Calculated triad distribution and reactivity ratios.

Cat. (*T*[°C])	EEE	PEE + EEP	PEP	EPE	EPP + PPE	PPP	Fit [× 10^{-3}][a]	Calcd parameters			
First-order Markovian model								r_1	r_2		
1/MAO (0)	8.6	25.0	18.2	19.6	22.3	6.3	16.1	3.99	0.097		
1/MAO (20)	5.6	20.9	19.6	16.8	26.6	10.5	36.5	4.98	0.085		
2/MAO (0)	0.8	10.8	37.4	35.9	13.8	1.3	8.6	1.34	0.021		
2/MAO (20)	1.3	13.6	35.4	35.8	12.8	1.1	9.4	2.46	0.014		
3/MAO (0)	1.0	12.3	37.7	39.3	9.1	0.6	7.0	2.13	0.009		
3/MAO (20)	2.3	17.3	33.2	37.1	9.5	0.6	9.4	4.89	0.007		
Second-order Markovian model								r_{11}	r_{22}	r_{12}	r_{21}
1/MAO (0)	8.6	24.8	17.6	20.0	19.9	9.1	3.0	4.04	0.157	0.085	4.10
1/MAO (20)	5.5	19.3	19.1	16.9	23.6	15.6	0.9	5.32	0.141	0.075	4.72
2/MAO (0)	3.0	8.8	37.4	35.9	11.8	3.2	6.6	6.29	0.058	0.018	1.09
2/MAO (20)	3.4	11.3	35.4	35.8	10.5	3.6	8.7	7.61	0.053	0.011	2.05
3/MAO (0)	2.7	10.4	37.7	39.3	7.2	2.7	6.1	6.79	0.057	0.007	1.80
3/MAO (20)	2.8	15.8	33.2	37.1	8.1	3.0	2.6	6.66	0.039	0.006	4.48
Alternating-site model								r_1	r_2	r'_1	r'_2
2/MAO (0)	0.9	10.6	37.4	35.9	13.6	1.6	7.0	1.14	0.048	1.88	0.012
2/MAO (20)	2.3	12.7	35.4	35.8	11.9	21.9	8.9	2.01	0.12	6.54	0.005

[a] χ^2 values.

PP sequences in copolymers made with catalyst **1**/MAO are isotactic,[19] provide strong experimental support for the "chain-skipping" hypothesis[9] according to which, following an olefin insertion, the polymer chain skips back to its initial coordination site—even in the presence of ethene.

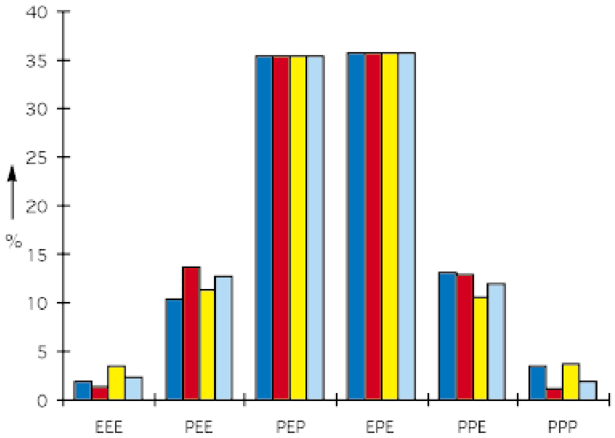

Figure 2. Triad distribution for E/P copolymer from **2** at 20°C. Dark blue: experimental data, red: according to first-order Markovian model, yellow: according to second-order Markovian model, pale blue: according to the alternate site model.

In contrast to the results obtained with the *tert*-butyl-substituted catalyst **1**/MAO, the methyl-substituted catalyst **2**/MAO produced copolymers that show triad distributions with up to 70% EPE and PEP triads in approximately the same ratio (Figure 2). The copolymerization parameters and in particular the product of the reactivity ratios $r_1r_2 = 0.028-0.034$ are unusually small for copolymers obtained from metallocenes.[11] As is typically observed for homogeneous catalysts the mass distribution is narrow ($M_n/M_w = 1.7-2.5$) for both catalyst systems. The triad distribution obtained by using catalyst **2**/MAO indicates a highly alternating monomer distribution. The percentage of alternating structures can be estimated to be 81% from the triad distribution.[20]

A mechanistic model was derived to interpret the comonomer distribution of the copolymers produced from catalysts (such as **1**/MAO and **2**/MAO) that have two different coordination sites. For this model, the standard copolymerization equations were written for each catalyst site, and it was assumed that the sites alternate with each insertion to give two states, M and M′ [Figure 1; Eqs. (1)–(4)].[21] This two-state model yields two sets of reactivity ratios r_1, r_2 and r_1', r_2', which can be derived from the experimental triad distribution in terms of the probabilities of each insertion step.

$$\text{M-E} + \text{E} \xrightarrow{k_{11}} \text{M'-E-E} = \text{M'-E} \qquad \text{M'-E} + \text{E} \xrightarrow{k'_{11}} \text{M-E-E} \tag{1}$$

$$\text{M-E} + \text{P} \xrightarrow{k_{12}} \text{M'-P-E} = \text{M'-P} \qquad \text{M'-E} + \text{P} \xrightarrow{k'_{12}} \text{M-P-E} \tag{2}$$

$$\text{M-P} + \text{E} \xrightarrow{k_{21}} \text{M'-E-P} \qquad \text{M'-P} + \text{E} \xrightarrow{k'_{21}} \text{M-E-P} \tag{3}$$

$$\text{M-P} + \text{P} \xrightarrow{k_{22}} \text{M'-P-P} \qquad \text{M'-P} + \text{P} \xrightarrow{k'_{22}} \text{M-P-P} \tag{4}$$

The experimental triad distribution of copolymers from catalyst **2**/MAO gave satisfactory fits to all three statistical models (Table 2, Figure 2). Copolymerization parameters obtained from the first-order Markovian model $r_1r_2 = 0.026-0.034$ and the second-order Markovian model are indicative of an alternating structure, as observed. Copolymerization parameters obtained from the alternating-site model show a large difference in the copolymerization parameters for the two sites (r_1,r_2 vs r_1',r_2'), which suggests that the reactivity ratios towards ethene and propene are different at the two reaction sites. While it is not necessary to invoke the switching model to fit the triad distribution (the first-order model is adequate), the derived reactivity ratios from the switching model are illuminating. In particular, for the polymer obtained at 20°C, $r_1 = 2.01$ and $r_2 = 0.12$—values that are close to those observed for the unsubstituted catalyst **4**/MAO ($r_1 = 1.3$ and $r_2 = 0.20$).[17] In contrast, for the other site $r_1' = 6.54$ and $r_2' = 0.005$, which suggests a much larger preference for ethene insertion at this coordination site.

The E/P copolymerization with the symmetrical substituted complex **3**/MAO was investigated in order to determine if the reactivity ratios for this catalyst would match those derived from the switching-site model with **2**/MAO (r_1', r_2'). The copolymers obtained from **3**/MAO show also a triad distribution with predominant EPE and PEP triads. A degree of alternation of 83% (polymerization at 0°C) can be estimated. The experimental triad distribution of copolymers from catalyst **3**/MAO gave satisfactory fits to both first- and second-order Markovian statistical models (Table 2), and the copolymerization parameters (r_1r_2 values of 0.027–0.047) indicate an alternating structure. The reactivity ratios ($r_1 = 2.13-4.95$; $r_2 = 0.007-0.009$) are similar to those derived for r_1' and r_2' from the switching-site model for **2**/MAO, but the mechanism for alternating monomer incorporation by **3**/MAO *cannot be that as proposed for* **2**/MAO because **3**/MAO has two enantiotopic coordination sites which will have identical reactivity ratios. Preliminary analysis of the microstructure reveals that polymers derived from **2**/MAO are *isotactic*, while those from **3**/MAO are *atactic*,[12] strongly implicating different mechanisms for catalysts **2**/MAO and **3**/MAO.

Values for parameter r_1 for **3**/MAO (2.13–4.95) are close to reported values for other *ansa*-metallocene catalysts,[16, 17] but the r_2 values (0.007–0.009) are unusually small. This suggests that either k_{22} is small or k_{21} is large. Preliminary propene homopolymerization results for **3**/MAO indicate its activity towards propene polymerization is comparable to that of **1**/MAO and **2**/MAO, implying that k_{22} is not negligible. Therefore, the small ratio of k_{22} to k_{21} is likely due to a relatively large value for k_{21}. The parameters obtained by fitting to a second-order Markovian model point to similar interpretations: unusually small r_{22} and r_{12} values indicate a small ratio of propene versus ethene insertion into a propene-terminated chain. Presumably the encumbered ligand framework enforces a placement of a propene-terminated polymer chain such that the ratio of propene versus ethene insertion becomes uncommonly small. Further studies are underway to clarify the factors leading to alternating structures formed by these types of catalysts. While we had originally assumed that a dual site catalyst (such as **2**/MAO) would be necessary for preparing alternating EP copolymers, the remarkable implication of the results with the catalyst **3**/MAO is that it appears possible to design catalysts with symmetric coordination sites that are capable of producing alternating structures of ethene and propene.[11]

In summary, we report the alternating copolymerization of ethene and propene with symmetric and nonsymmetric catalysts of type $[\{(RCp)(Me_2C)(Flu)\}ZrMe_2]$/MAO.[11] These studies show the potential of metallocenes for preparing copolymers of defined sequence distributions by controlling the reactivity ratios of olefins through appropriate ligand design.

Experimental Section

General: Copolymerizations were carried out in a mixture of propene (100 mL) and toluene (20 mL) with a constant supply of ethene at a pressure sufficient to give the desired E/P feed ratio.[22, 23] The reactions were started by injecting a solution of metallocenedimethyl and MAO in toluene (20 mL) under Ar pressure into an autoclave charged with propene (100 mL) and saturated with ethene at a total pressure of 5650 – 11 030 hPa. Low conversion and constant total pressure ensured a constant monomer feed. After 30 – 60 min the reaction was quenched by injection of methanol (20 mL). The copolymers were precipitated in methanol (200 mL) and dried at 40 °C under reduced pressure. Quantitative ^{13}C NMR spectra of polymer (300 mg) dissolved in a mixture of dichlorobenzene with 10% $[D_6]$benzene (4 mL) were used for compositional analyses. The monomer feed was calculated by using the fugacity equation and the experimentally estimated fugacity coefficient for ethene and propene.[23, 24]

$(3,4\text{-}Me_2Cp)(Me_2C)(Flu)$: 3,4,6,6′ tetramethylfulvene was prepared from 1,2-dimethylcyclopentadienyl-Li[25] and acetone/pyrrolidine in methanol.[26] $(3,4\text{-}Me_2Cp)(Me_2C)(Flu)$ was synthesized from 3,4,6,6′ tetramethylfulvene and fluorenyllithium according to reported procedures.[4] ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.71$ (d, 2H; arom.), 7.34 – 7.16 (m, 6H; arom.), 5.87 (s, 1H; CH), 4.09 (s, 1H; CH); 3.09 (s, 2H; CH_2), 2.01 (s, 3H; CH_3), 1.89 (s, 3H; CH_3), 1.01 (s, 6H; CH_3).

3: $[\{(3,4\text{-}Me_2Cp)(Me_2C)(Flu)\}ZrCl_2]$ was synthesized from Li salt of the ligand and $ZrCl_4$ in CH_2Cl_2.[4] The resulting red crystals were treated with 2.2 equiv of MeLi in ether. Extraction with pentane gave **3,** which was recrystallized once from toluene/pentane. $\delta = 8.07$ (d, 2H; arom.), 7.50 (d, 2H; arom.), 7.32 (m, 2H; arom.), 7.07 (m, 2H; arom.), 5.15 (s, 2H; CH), 1.89 (s, 6H; CH_3), 1.87 (s, 6H; CH_3), −1.17 (s, 6H; CH_3). C,H analysis: calcd for $C_{25}H_{28}Zr$ (419.75): C 71.53, H 6.74; found: C 71.27, H 7.01.

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[21] Full details of this model will be reported elsewhere.

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