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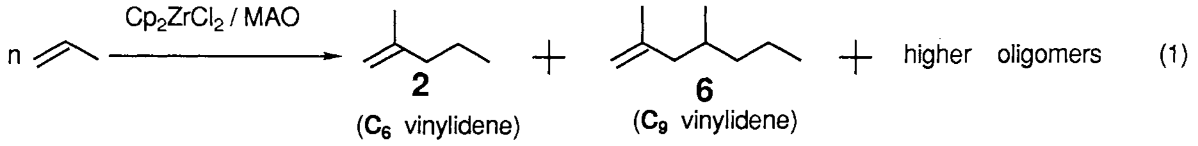
On the Mechanism of Oligomerization of Propylene by $(C_5Me_5)_2MCl_2$/Methylalumoxane Catalysts (M=Zr, Hf)

Takaya MISE,* Akiko KAGEYAMA, Shinya MIYA,† and Hiroshi YAMAZAKI*
The Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama 351-01
†Chisso Petrochemical Corp., 5-1 Goikaigan, Ichihara, Chiba 290

In the oligomerization of propylene by $(C_5Me_5)_2MCl_2$ (M=Zr,Hf) /methylalumoxane, formation of abnormal oligomers such as 1-pentene(C_5), 2,4-dimethyl-1-pentene(C_7), 4-methyl-1-heptene(C_8), and 2,4,6-trimethyl-1-heptene(C_{10}) besides normal oligomers such as 4-methyl-1-pentene(C_6) and 4,6-dimethyl-1-heptene(C_9) is indicative of the mixing of unusual β-CH_3 and usual β-H transfer terminations from each growing carbon chain which was initiated by insertion of propylene into either M-H or M-Me bond.

Homogeneous Ziegler-Natta olefin polymerization catalysts consisting of combinations of titanium, zirconium, or hafnium metallocenes with methylalumoxane(MAO) (Kaminsky type catalyst) have high performance for producing atactic, isotactic, and syndiotactic polypropylene,1) and they provide good models for studying the relationship between the ligand structure and the catalytic activity and specificity. Previously we prepared all members of methyl substituted zirconocene dichlorides of $(C_5H_{5-n}Me_n)_2ZrCl_2$ (n=0-5) and employed them for propylene polymerization in combination with MAO (Al/Zr=4,000).2) Although only atactic polypropylene was obtained with these catalysts, it was noted that both catalytic activity and molecular weight of the polymers obtained were markedly influenced by the numbers and the positions of the methyl groups on the cyclopentadienyl (Cp) rings. In addition, analysis of unsaturated end groups of the polymers revealed that the presence of double bond of vinylidene type for n=0-3, vinyl type for n=5, and both types for n=4. If we assumed β-H elimination in the termination steps, sterically unfavorable secondary (2,1-) insertion of propylene for bulky substituent systems (n=4 and 5) must be considered in the propagation steps, in contrast with the regular primary (1,2-) insertion for less bulkier systems (n=0-3).

It has been known that in Kaminsky type catalyst system decrease of the amount of MAO to metallocenes (Al/M<100) results in the formation of oligomers instead of polymers.3a) Again, dimer having a double bond of terminal vinyl type, 4-methyl-1-pentene has been formed mainly by bulkier $Cp^*{}_2ZrCl_2$ system,3b) whereas that of vinylidene type, 2-methyl-1-pentene formed exclusively by Cp_2ZrCl_2.3a) With expectation of resolving the above mechanistic conflict in both oligomerization and polymerization, we examined the oligomerization of propylene in some detail (Eqs. 1 and 2). Distribution of low boiling fractions (up to C_{10}) of oligomers produced by Cp_2ZrCl_2



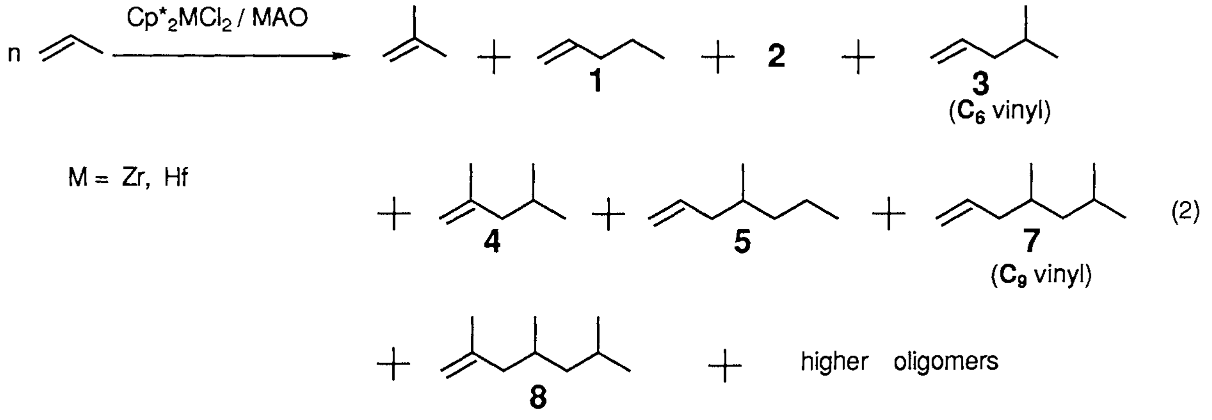


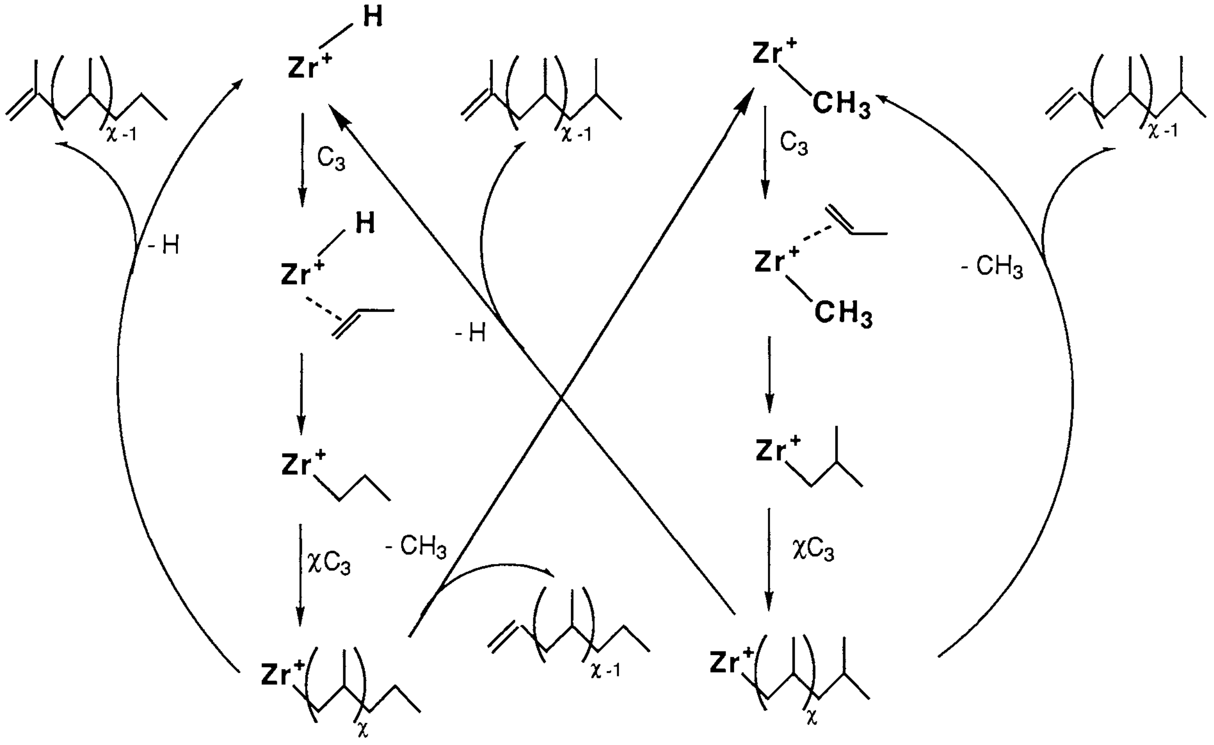
Table 1. Oligomerization of Propylene[a)]

Cat.	C_4	C_5(**1**)	dimer C_6(**2**) vinylidene	dimer C_6(**3**) vinyl	C_7(**4**)	C_8(**5**)	trimer C_9(**6**) vinylidene	trimer C_9(**7**) vinyl	C_{10}(**8**)	Higher oligomers (g)
	Oligomers (mmol)									
Cp_2ZrCl_2	0.16[b)]	-	15.63	-	-	-	4.76	-	-	0.53
$Cp^*_2ZrCl_2$	2.95	0.59	0.93	7.00	2.11	2.42	-	6.73	1.52	3.68
$Cp^*_2HfCl_2$	2.66	0.71	0.24	10.06	0.50	2.13	-	5.49	0.17	0.89

a)Reaction conditions: cat. 0.05 mmol, Al / M = 40, propylene 4 kg / cm^2, benzene 20 ml, 2 h, 50°C.
b) Isobutene of this amount is ascribed to the impurity of propylene used.

and $Cp^*_2MCl_2$ (M=Zr, Hf) /MAO system (Al/M=40) was determined by quantitative GC analysis and is shown in Table 1. They (C_4-C_{10}) are characterized by comparison of the GC retention time, GC-MS spectra, and ^1H NMR spectra with those of authentic samples which are commercially available or prepared by the literature method.[4)] In Cp_2ZrCl_2 catalyst system, oligomers having a double bond of vinylidene type, 2-methyl-1-pentene (C_6, **2**) and 2,4-dimethyl-1-heptene (C_9, **6**) were produced exclusively.[5)] However, in $Cp^*_2MCl_2$ catalyst system, the formations of isobutene (C_4) and abnormal oligomers, 1-pentene (C_5, **1**), 2,4-dimethyl-1-pentene (C_7, **4**), 4-methyl-1-

heptene (C_8, **5**) and 2,4,6-trimethyl-1-heptene (C_{10}, **8**) were observed in fairly large amounts besides oligomers having a double bond of vinyl type, 4-methyl-1-pentene (C_6, **3**) and 4,6-dimethyl-1-heptene (C_9, **7**) together with a small amount of **2**. It is worth noting that the ratios of C_{3n-1}/C_{3n+1} oligomers depend on the number of propylene oligomerized and on the kind of catalyst metal. The one carbon decrement in the oligomerization could be explained only by a β-methyl transfer termination from a growing chain which was initiated by insertion of propylene into M-H bond as illustrated in Scheme 1[6] (χ=1,2) and inversely the one carbon increment by a β-H transfer termination from a growing chain which was initiated by insertion of propylene into a M-CH_3 bond (χ=0,1,2). Proposed mechanism in Scheme 1 interprets reasonably well the production of every isomers obtained in the oligomerization of propylene . Thus, we suggest the β-methyl transfer as an important step in oligomerization and polymerization[7] of propylene by $Cp^*{}_2MCl_2$ /MAO system.[8] Such type of β-methyl transfer in oligomerization was reported by Watson et al.[9] for the lanthanide system $Cp^*{}_2LuMe{\cdot}Et_2O$ and recently by Teuben et al.[10] for the cationic group 4A systems $[Cp^*{}_2MMe(THT)]^+$ (M=Zr,Hf; THT=tetrahydrothiophene), although formation of $C_{3n\pm1}H_{6n\pm2}$ (n≥2) such as **4**, **5**, and **8** had not been mentioned in these reports.



Scheme 1.

It is uncertain whether electronic or steric effect is the main reason for the predominant β-Me elimination mechanism in oligomerization and polymerization in $Cp^*{}_2MCl_2$ /MAO catalyst system. But, it might be interpreted by assuming that interaction of β-methyl group with metal is more preferred than that of β-H atom since a mutual repulsion between the β-methyl group on growing carbon chain and methyl substituents on Cp ring becomes enormous.

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4)Authentic samples of **1**, **2**, **3**, **4**,and **6** are commercially available. Compound **7** was isolated by vacuum distillation and the structure was determined from the comparison of the NMR spectra with those mentioned in the literature.[10] Authentic samples of **5** and **8** were prepared by the literature method.[11] ^{1}H NMR (500 MHz, CDCl$_3$). **5**: δ 5.9-5.7 (m, 1H, CH$_2$=C*H*-CH$_2$-), 5.1-4.9 (m, 2H, C*H*$_2$=CH-), 2.1-2.0(m, 1H, CH$_2$=CHC*H*H-), 1.9-1.8 (m, 1H, CH$_2$=CHCH*H*-), 1.6-1.4 (m, 1H, -C*H*(CH$_3$)-), 1.4-1.3 (m, 1H, -CH(CH$_3$)C*H*HCH$_2$-), 1.4-1.2 (m, 2H, -C*H*$_2$CH3), 1.2-1.0 (m, 1H, -CH(CH$_3$)CH*H*CH$_2$-), 0.88 (t, 3H, J=7.0 Hz, -CH$_2$C*H*$_3$), 0.86 (d, 3H, J=6.7 Hz, -CH-(C*H*$_3$)-). **8**: δ 4.72 (bs,.1H, C*H*H=C(CH$_3$)-), 4.64 (bs, 1H, CH*H*=C(CH$_3$)-), 1.99 (dd, 1H, J=13.4, 6.1 Hz, =C(CH$_3$)C*H*HCH(CH$_3$)-), 1.78 (dd, 1H, J=13.4, 8.2 Hz, =C(CH$_3$)CH*H*CH(CH$_3$)-), 1.7-1.6 (m, 2H, -C*H*(CH3)-), 1.68(s, 3H, =C(C*H*$_3$)-), 1.11(ddd, 1H, J=13.4, 8.2, 5.2 Hz, -CH(CH$_3$)C*H*HCH(CH$_3$)-), 0.98 (ddd, 1H, J=13.4, 8.5, 5.8 Hz, -CH(CH$_3$)CH*H*CH(CH$_3$)-), 0.88 (d, 3H, J=6.4 Hz, CH(C*H*$_3$)), 0.85 (d, 3H, J=6.7 Hz, CH(C*H*$_3$)), 0.81 (d, 3H, J=6.7 Hz, CH(C*H*$_3$)).

5)A small amount of 2,3-dimethyl-1-butene (0.83 mmol) was formed as noted in the literature.[3a]

6)Cationic species are depicted because they have been postulated as the active intermediate in the polymerization by metallocene dichloride/ alkyl aluminium systems: J.J.Eisch, A.M.Piotrowski, S.K.Brownstein, E.J.Gabe, and F.L.Lee, *J. Am. Chem. Soc.*, **107**, 7219 (1985); R.F.Jordan, *J. Chem. Ed.*, **65**, 285 (1988); P.G.Gassman and M.R.Callstrom, *J. Am. Chem. Soc.*, **109**, 7875 (1987) and references cited therein.

7)Analysis of saturated and unsaturated end groups of the polymer produced by Cp$^*{}_2$MCl$_2$ /MAO (Al/Zr=4000) system showed the predominant presence of *i*-Pr and vinyl groups suggesting the same β-Me transfer mechanism was operating in the polymerization.

8)(C$_5$Me$_5$)(C$_5$Me$_4$H)ZrCl$_2$/MAO system (Al/Zr=20) still gave same type of oligomers such as **3** and **7** predominantly(**2**/**3**=7/93, **6**/**7**=0/100). Slightly less bulkier (C$_5$Me$_4$H)$_2$ZrCl$_2$ catalyst system (Al/Zr=20) gave polymers ($\overline{\mathrm{Mw}}$: 2060) having terminal vinyl and vinylidene type double bonds.

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