

## Effect of the cocatalyst on the copolymerization of ethylene and propylene with high activity Ziegler-Natta catalyst

J. Koivumäki<sup>1,\*</sup>, J. V. Seppälä<sup>1</sup>, and L. Kuutti<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Helsinki University of Technology, SF-02150 Espo, Finland

<sup>2</sup>Technical Research Centre of Finland, Laboratory of Biotechnology, SF-02150 Espoo, Finland

### SUMMARY

Ethylene and propylene were copolymerized in n-heptane in the presence of high activity heterogeneous Ziegler-Natta catalyst to study the effect of the cocatalyst on the microstructure and molecular weight of the copolymer. Seven aluminium alkyls of structure  $\text{Al}((\text{CH}_2)_n\text{CH}_3)_3$ , where  $n = 0, 3, 5, 7$  or  $11$ , and one of structure  $\text{Al}(\text{C}(\text{CH}_3)_3)_3$ , were used as cocatalysts. The effect of the Al/Ti mole ratio was also studied. Modern molecular modelling techniques were used to calculate the volume of the cocatalyst and the electron density around aluminium. The size of the cocatalyst molecule was found to have a marked effect on the activity of the catalyst: the smaller the cocatalyst the higher the activity. Higher electron density around aluminium increased the randomness of the copolymer.

### INTRODUCTION

Titanium catalysts contain two kinds of active polymerization species, of which  $\text{Ti}^{2+}$  species are active only for ethylene and  $\text{Ti}^{3+}$  species are normally active for both ethylene and propylene(1,2). If the growing polymer chain end is an ethylene unit, the  $\text{Ti}^{2+}$  species can also effect the addition of propylene(3).  $\text{Ti}^{3+}$  species can further be divided into two groups with different monomer reactivities(4). One group has two vacancies and the other only one. The first group, which is more reactive for propylene, can be selectively deactivated with a donor and the amount of propylene in the product thereby decreased(5).

The composition and microstructure of ethylene-propylene copolymer prepared under identical conditions depend not only on the cocatalyst but on the chemical composition of the total catalyst system, including the presence and type of the carrier(6,7). Moreover, if the catalyst is prepared with grinding, the composition of the copolymer will further be affected by the grinding time(8). If, for example, over-reduction of titanium is prevented, moderately random copolymers will be obtained(9). But if the catalyst contains considerable amounts of  $\text{Ti}^{2+}$  species, the copolymer will tend to have long ethylene sequences.(10,11)

The chemical nature of the support influences both the activity and selectivity of the catalyst system. The polymerization species of  $\text{TiCl}_4\text{-AlEt}_3$  catalyst are more selective towards ethylene on aluminium silicate than on magnesium oxide.(12) Supports that contain magnesium are not only used to increase the surface area but also to stabilize the  $\text{Ti}^{3+}$  polymerization species with the production of moderately random copolymer.(13,14)

The aluminium alkyl strongly affects the polymerization kinetics. The activity reaches maximum at low Al/Ti mole ratios and decreases at high mole ratios.(15) Higher aluminium alkyl concentration also tends to decrease the overall rate of polymerization and to increase the decay rate if the alkyl concentration increases beyond a certain limit(16). Böhm(17) explains this tendency in terms of a competition

\*Corresponding author

of the monomer and the aluminium alkyl for the same active sites of the titanium and its consequent overreduction.(3) Study of different cocatalysts has suggested that the decay rate decreases if the size of the alkyl group attached to aluminium increases.(18)

We carried out ethylene-propylene copolymerization using  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalyst without any donor (i.e. mainly atactic polypropylene is formed), and with various aluminium alkyls as cocatalysts. Our main purpose was to study how the structure of the aluminium alkyl influences the microstructure of the copolymer, the catalyst activity, the molecular weight and molecular weight distribution of the polymer. Molecular modelling was employed as a tool for a better understanding of the role of the cocatalyst.

## EXPERIMENTAL

Apparatus and method of copolymerization: Copolymerizations were performed in n-heptane in a 1-dm<sup>3</sup> reactor at 40°C for 40 min under a constant overpressure of 1,0 bar. The only variables were the type and amount of cocatalyst.

The cocatalyst was pumped into the reactor (2,5 mmol/dm<sup>3</sup> or 25 mmol/dm<sup>3</sup>) at the polymerization temperature and the monomer feed was started immediately thereafter. A mixture of ethylene and propylene with a molar ratio of 1/1,4 and total flow rate of 2 dm<sup>3</sup>/min was bubbled through the reactor 5 minutes before the catalyst was added.

After polymerization, the reactor was degassed and the reaction medium was washed with diluted hydrochloric acid and water and precipitated with acetone. The product was dried under vacuum at 60°C overnight.

The reactor temperature was controlled with a thermostat connected to a Pt-100 resistance thermometer. Reactor pressure and the feed of ethylene and propylene were controlled with electronic pressure and mass flow controllers. Accuracy of the pressure control was  $\pm 0,03$  bar and the reactor temperature  $\pm 0,1^\circ\text{C}$ .

Chemicals: The catalyst was a supported Ziegler-Natta catalyst of type  $\text{MgCl}_2/\text{TiCl}_4$ . Titanium content of the catalyst was 7 wt.-%. The aluminium alkyls were 10 wt.-% solutions in n-heptane (from Schering AG).

n-Heptane was grade GR (from J.T. Baker) and was further purified with molecular sieves,  $\text{CuO}$  and  $\text{Al}_2\text{O}_3$  before use. Ethylene was grade 2.7 (from AGA) and propylene 2.5 (from Messer Griesheim) and both were further purified before entering the reactor by being conducted them through columns containing molecular sieves,  $\text{CuO}$  and  $\text{Al}_2\text{O}_3$ .

Polymer characterization: The microstructure of the copolymers was determined with a Jeol GSX-400 nuclear magnetic spectrometer according to Cheng(19). Molecular weight distributions were investigated with a Waters high-temperature GPC device equipped with two Shodex mixed bed columns with exclusion limit for polystyrene  $5 \times 10^7$  and one Shodex column with exclusion limit for polystyrene  $2 \times 10^8$ . Solvent 1,2,4-trichlorobenzene was used at a flow rate of 1,0 cm<sup>3</sup>/min. The columns were calibrated universally with broad molecular weight distribution low density polyethylenes and monomer composition of the copolymers was taken into account according to the literature(20).

Molecular modelling: The computational studies utilized standard aspects of quantum mechanical MNDO (Modified Neglect of Diatomic Overlap) calculations(21), which was available for MOPAC(22). MOPAC was used here for SCF (Self-Consistence Field) calculations and geometry optimizations of the aluminium alkyl compounds. SCF convergence and energy minimization criteria were limited to the program default values (the keywords used were T, GEO-OK and PRECISE). All the input files to MOPAC were created using the CHEM-X molecular modelling system. CHEM-X is a fully-integrated, expandable system with a range offering specialized functions(23).

One of the modules, ChemQM, provides an interface between CHEM-X and MOPAC. The volume of the cocatalyst compound was evaluated as the volume of the sum of the van der Waals radii of all atoms in the compound. The calculations were made with the CHEM-X molecular modelling system.

## RESULTS AND DISCUSSION

Compounds used as cocatalysts and the results of the molecular modelling are listed in Table 1. The volume of the cocatalyst molecule is taken to measure the size of the cocatalyst and the charge of the aluminium atom measures the electron density with a lower charge then indicating higher electron density. The results of the polymerizations and the polymer properties are summarized in Table 2.

Table 1. Compounds used as cocatalysts.

Alkyl	Formula	Specific charge of Al atom in electrons	Volume in Å <sup>3</sup>
TMA	Al(CH <sub>3</sub> ) <sub>3</sub>	0,6212	59
TEA	Al(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	0,6864	99
TPA	Al((CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	0,6779	137
TBA	Al((CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ) <sub>3</sub>	0,6773	185
TIBA	Al(CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub>	0,6677	183
THA	Al((CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub> ) <sub>3</sub>	0,6768	263
TOA	Al((CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> ) <sub>3</sub>	0,6767	331
TDDA	Al((CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub> ) <sub>3</sub>	-(*	501

\*) Compound contains too many atoms to be calculated with CHEM-X

### Effect of cocatalyst on the catalyst activity

Figure 1 shows the activity of the catalyst as a function of the volume of the cocatalyst molecule and the Al/Ti mole ratio. A linear correlation can be seen between the

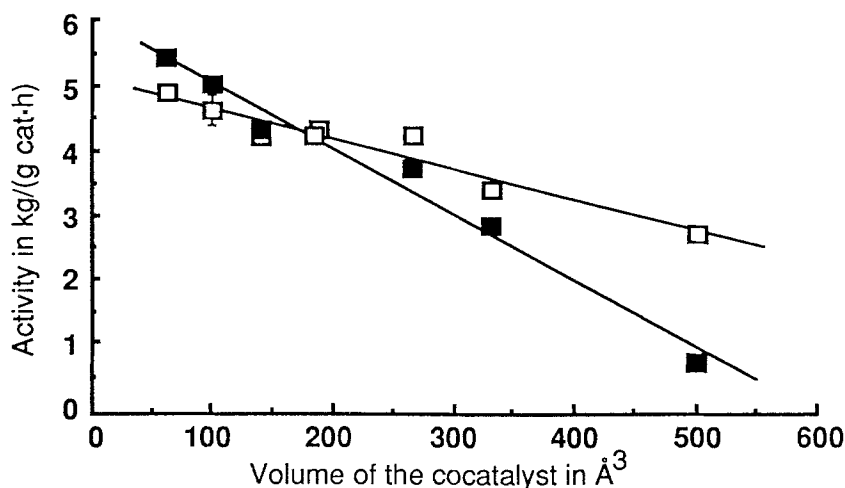


Figure 1. Relationships between the volume of the cocatalyst and the activity of the catalyst; ■ Al/Ti=100, □ Al/Ti=1000.

Table 2. Results of the polymerizations.

Alkyl	Al/Ti	Activity <sup>(*)</sup> in kg/(g cat.h)	Ethylene content in mole-%	PPP	Monomer triad in mole fractions			PEE	EEE	Random index <sup>(**)</sup> in mole-%	$\bar{M}_w$ in kg/mol		$\bar{M}_w/\bar{M}_n$		
					PPE	EPE	PEP				1	2 <sup>(***)</sup>	1	2	
TMA	100	5.4	49	0.13	0.16	0.24	0.10	0.17	0.20	67	195	20	9.8		
	1000	4.9	53	0.12	0.14	0.21	0.09	0.19	0.25	64	158	18	178	21	8.8
TEA	100	5.0	51	0.14	0.14	0.22	0.08	0.19	0.23	63	155	20	132	18	7.8
	100	5.0	52	0.13	0.14	0.21	0.09	0.19	0.24	63	190	20	176	18	9.5
	100	5.1	53	0.13	0.14	0.21	0.08	0.20	0.24	63	200	21	189	20	9.5
	1000	4.6	51	0.15	0.14	0.19	0.09	0.17	0.26	59	175	16			10.9
	1000	4.9	48	0.16	0.15	0.19	0.09	0.17	0.24	60	159	15			10.6
	1000	4.3	51	0.16	0.15	0.18	0.08	0.17	0.26	58	159	15	151	16	10.6
TPA	4000	3.0	53	0.16	0.13	0.19	0.07	0.16	0.29	55	183	17	178	18	10.8
	100	4.3	51	0.12	0.14	0.24	0.08	0.18	0.24	64	216	19			11.4
	1000	4.2	45	0.17	0.16	0.19	0.09	0.16	0.23	60	281	19	283	21	14.8
	100	4.3	54	0.10	0.14	0.23	0.09	0.19	0.25	65	265	22	240	20	12.0
TBA	1000	4.3	56	0.12	0.14	0.20	0.08	0.18	0.28	59	352	24	327	25	14.7
TIBA	100	4.2	56	0.09	0.13	0.22	0.10	0.21	0.25	66	283	23			12.3
	1000	4.2	54	0.11	0.13	0.22	0.09	0.17	0.28	61	306	25	321	25	12.2
THA	100	3.7	54	0.11	0.14	0.22	0.08	0.19	0.26	64	254	23			11.0
	1000	4.2	54	0.11	0.13	0.21	0.06	0.19	0.30	60	364	29	344	24	12.6
	100	2.8	62	0.07	0.11	0.21	0.07	0.22	0.32	61	288	26	269	23	11.1
TOA	1000	3.4	61	0.08	0.12	0.21	0.06	0.20	0.32	60	262	25	226	23	10.5
TDDA	100	0.7	73	0.02	0.07	0.19	0.05	0.22	0.45	53	327	36	314	43	9.1
	1000	2.7	63	0.06	0.09	0.19	0.07	0.22	0.37	57	287	30	236	27	9.6

\*) Extrapolated linearly from 40 min to 60 min

\*\*) Random index=(EEP+EPE+PEP+PPE)/(EEP+EPE+PEP+PPE+EEE+PPP)

\*\*\*) Two parallel samples

volume of the cocatalyst and the activity of the catalyst: the greater the volume i.e., the larger the alkyl group, the lower the activity. The long alkyl groups in the cocatalyst molecule appear to sterically preventing aluminium from getting close enough to titanium to form an active centre. By contrast, there was no correlation between the catalyst activity and the electron density around aluminium. As is also shown in Figure 1, the activity decreases more sharply with the smaller Al/Ti mole ratio. Perhaps this is because the activity maximum as a function of the cocatalyst concentration does not lie in the same area for different cocatalysts.

#### Effect of cocatalyst on the microstructure

In comparing the microstructure of different copolymers, it is important that the overall ethylene content is at the same level. Here the comparison is made in this way for TMA, TEA, TIBA, TBA and THA. From the Table 2 it can be seen that with TEA as cocatalyst the amounts of the EEE homopolymer blocks are smaller with smaller Al/Ti mole ratio and the fractions of the EPE triads are smaller at the higher Al/Ti mole ratio. The same trend is not seen for the PEP triads, which remain nearly constant in amount. All the triad data are combined in Figure 2, where they are displayed as random indexes. The random index is seen to decrease when the specific charge of the aluminium increases, that is, when the electron density around aluminium is decreasing. The random index is also lower when the amount of cocatalyst is increased. This is in good correlation with the other studies where when overreduction of titanium is prevented moderately random copolymers are obtained.(9)

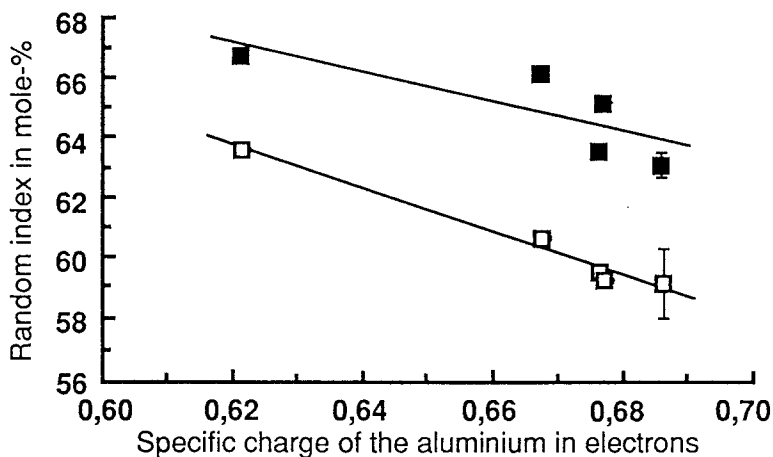


Figure 2. The effect of specific charge of the aluminium on the random index of the copolymer; ■ Al/Ti=100, □ Al/Ti=1000.

#### Effect of cocatalyst on the molecular weight and molecular weight distribution

The molecular weight of the copolymer increases with the length of the alkyl groups in the aluminium alkyls as seen in Figure 3. This suggests that aluminium alkyls with shorter alkyl groups more eagerly act as a chain transfer agents than aluminium alkyls with longer groups. Evidently the longer group prevents the free cocatalyst molecule from getting close to the active polymer chain end. The experiments also demonstrated in the Figure 3 that the molecular weight distribution of the copolymers first increases and then decreases as a function of the cocatalyst volume. This phenomenon is probably the sum of many parameters and cannot be explained by

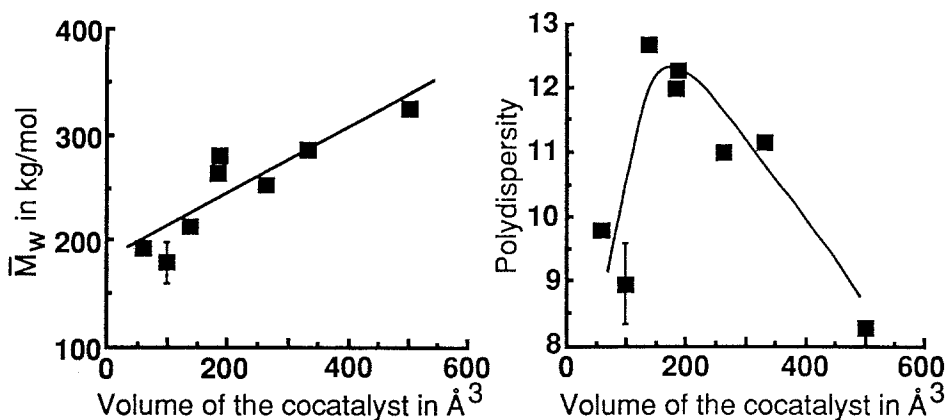


Figure 3. Relationships between the cocatalyst volume of the cocatalyst and the molecular weight and molecular weight distribution; Al/Ti=100, no hydrogen used.

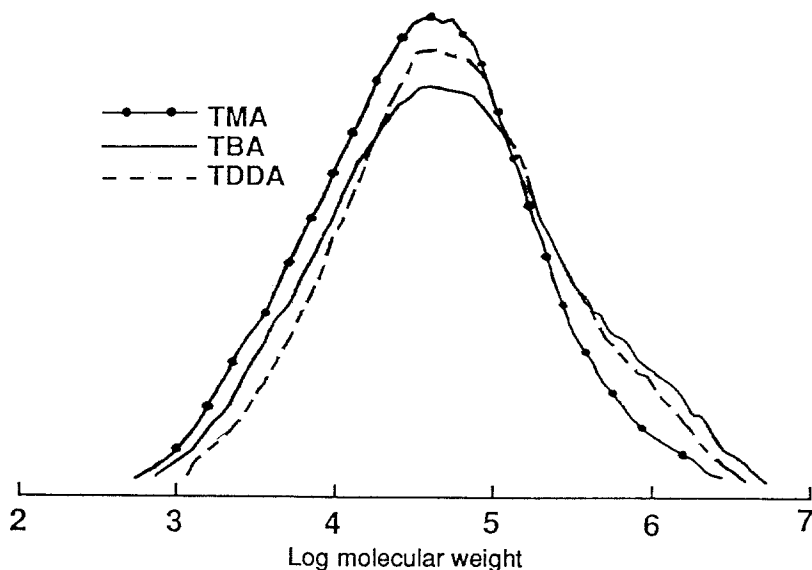


Figure 4. GPC curves of the selected samples. Al/Ti=1000, no hydrogen used.

the volume alone. At higher Al/Ti mole ratio the molecular weight distribution is broader especially with cocatalysts TPA and TBA. The molecular weight broadening is very clearly seen in Figure 4 where GPC curves of selected samples are seen.

## CONCLUSIONS

On the basis of these experiment we can conclude that the activity of the catalyst-cocatalyst system is proportional to the volume of the cocatalyst molecule calculated from the size of the alkyl groups attached to the central aluminium atom. As the size of

the alkyl group in the cocatalyst increases the activity of the catalyst system decreases.

The size of the cocatalyst molecule affects the molecular weight of the copolymer. Cocatalyst with short alkyl groups seem more eager to function as chain transfer agents than those with long alkyl groups.

The microstructure of the copolymer seem to be affected by the specific charge of the aluminium atom in the cocatalyst: the lower the specific charge (i.e., the more electrons around aluminium), the more random the copolymer. Finding that the microstructure becomes less random with increasing amount of the cocatalyst may suggest that the active centre contains more than one cocatalyst molecule. Evidently, however, the phenomenon is not explained by the specific charges alone. Future modelling of the whole active centre may give a fuller answer.

## REFERENCES

1. Soga K, Sano K, Ohnishi R (1981) *Polym Bull* 4: 157
2. Soga K, Chi S-I, Ohnishi R (1982) *Polym Bull* 8: 473
3. Kashiwa N, Yoshitake J (1984) *Makromol Chem* 185: 1133
4. Doi Y, Ohnishi R, Soga K (1983) *Makromol Chem, Rapid Commun* 4: 169
5. Soga K, Shiono T, Doi Y (1983) *Polym Bull* 10: 168
6. Baulin A, Ivanchev S, Rodionov A, Kreitsev T, Goldenberg A (1980) *Polym Sci USSR, (Engl Transl)* 22: 1630
7. Kashiwa N, Mizuno A, Minami S (1984) *Polym Bull* 12: 105
8. Terano M, Ishii K (1990) *Makromol Chem, Rapid Commun* 11: 439
9. Soga K, Ohtake M, Ohtake R, Doi Y (1984) *Polym Commun* 25: 171
10. Abis L, Bacchilega G, (1986) *Makromol Chem* 187: 1877
11. M Kakugo, Y Naito, K Mizunuma, T Miyatake (1989) *Makromol Chem* 190: 849
12. S Ivanchev, A Baulin, G Rodionov (1980) *J Polym Sci, Polym Chem Ed* 18: 2045
13. Soga K, Ohnishi R, Sano T (1982) *Polym Bull* 7: 547
14. Soga K, Ohnishi R, Doi Y (1983) *Polym Bull* 9: 299
15. Galli P, Barbé P, Noristi L (1984) *Angew Makromol Chem* 120: 73
16. Barbé P, Cecchin G, Noristi L (1987) *Adv Polym Sci* 81: 1
17. Böhm L (1978) *Polymer* 19: 553
18. Duck E, Grant D, Butcher A, Timms D (1974) *Eur Polym J* 10: 77
19. Cheng H N, (1984) *Macromolecules* 17: 1950
20. Scholte TH, Meijerink N, Schoffeleers H, Brands A (1984) *J Appl Polym Sci* 29: 3763
21. Dewar M J S, Thiel W (1977) *J Am Chem Soc* 99: 4899
22. MOPAC, QCPE-program #455 (version 5.00), A General Molecular Orbital Package, Qantum Chemistry Program Exchange, Indiana University
23. CHEM-X: Molecular modelling system , Chemical Design Ltd., Oxford, UK