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POLYMERIZATION OF PROPENE WITH ^{t}BuNSiMe$_2$C$_5$Me$_4$TiMe$_2$: EFFECTS OF TRIALKYLALUMINIUMS AS ADDITIVES

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ABSTRACT. Propene was polymerized at 0 °C with ^{t}BuNSiMe$_2$C$_5$Me$_4$TiMe$_2$/MAO. Kinetic features and other parameters indicated quasi-living polymerization. Effects of various trialkylaluminiums as additives have been investigated; it was found that compounds with more bulky groups like ^{i}Bu$_3$Al, Oct$_3$Al increased the activities significantly whereas Me$_3$Al and Et$_3$Al reduced the activities of the catalyst system. The triad sequence in the ^{13}C NMR spectrum confirmed a syndiotactic-enriched atactic polypropene.

KEY WORDS: Polymerization of propene, ^{t}BuNSiMe$_2$C$_5$Me$_4$TiMe$_2$, Trialkylaluminiums, Syndiotactic-enriched atactic polypropene

INTRODUCTION

Soon after Ziegler and Natta discovered heterogeneous olefin polymerization catalysts in the mid-1950s, efforts were directed towards devising homogeneous catalysts that would prove amenable for polymerization studies. In 1959, Natta *et al.* [1] and Breslow *et al.* [2] reported that the metallocene Cp$_2$TiCl$_2$ (Cp = cyclopentadienyl) could be activated for olefin polymerization by Et$_3$Al or Et$_2$AlCl. These soluble catalysts polymerized ethylene but were inactive for propylene and exhibited much lower activities than the heterogeneous systems. This situation changed dramatically in the early 1980s when Sinn and Kaminsky [3, 4] discovered that partially hydrolyzed Me$_3$Al called methylaluminoxane (MAO), activated group IV metallocenes for polymerization of ethylene and α-olefins. This discovery has stimulated a renaissance in single-site catalysis, with olefin polymerization clearly receiving most attention.

Metallocene analogues that have received much commercial attention are the *ansa*-monocyclopentadienyl-amido (CpA) group IV catalysts developed concurrently by Dow [5] and Exxon [6]. The generalized structure for the CpA catalyst is shown in Figure 1.

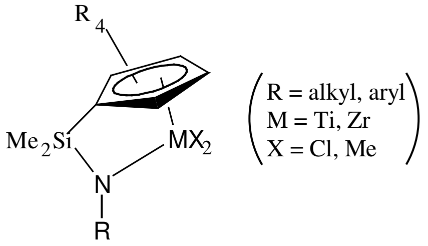

Figure 1. The CpA catalyst.

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One of the key features of the catalysts is the open nature of the catalyst active sites, which allows them to incorporate other olefins into polyethylene. It has been established that the open nature of the coordination site and electronic effects provided by the amido ligation are the likely origin of the high molecular weights found with Scollard and McConville's "living" catalysts containing bis-amido ligands [7]. In 1990, Okuda reported a novel type of metallocene catalyst, in which N-base ligands were attached to cyclopentadiene rings [8].

There are conflicting reports in the literature on the stereospecificity of CpA catalysts for propene polymerization and the influence of the counterion on the stereospecificity. Canich reported [9] that certain MAO-activated chiral and achiral CpA metal dichlorides gave crystalline polypropylene (PP) with high isotacticities ([mmmm] > 75%) whereas McKnight *et al.* reported that they were unable to obtain isotactic polymers under similar conditions [10]. Turner reported [11] that conversion of the zirconium dichloride complex to the dimethyl derivative and activation with $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ gave a syndiotactic microstructure with a racemic dyad content > 90%. In another report [12], MAO-activated catalysts yielded atactic polypropylene, whereas activation with $[Ph_3C^+][B(C_6F_5)_4^-]$ and Al^iBu_3 yielded a polymer that could be fractionated to give 30% of a syndiotactically enriched ([rrrr] = 80%) fraction.

In view of the fact that several challenges still exist for further elaboration of CpA olefin polymerization, we report, under "living" conditions, the polymerization of propylene with $^tBuNSiMe_2C_5Me_4TiMe_2$ **1** activated with MAO and other trialkylaluminiums as additives.

EXPERIMENTAL

Materials. All operations were carried out under nitrogen atmosphere using standard Schlenk techniques. Dried MAO was prepared from a toluene solution of MAO by vacuum drying followed by hexane or heptane washing as reported in detail previously [13]. Propene from Mitsubishi petrochemical was purified by bubbling it through a $NaAlH_2{}^iBu_2$/1,2,3,4-tetrahydronaphthalene solution.

Synthesis of [$\eta^1:\eta^5$-tert-butyl(dimethylsilyltetramethyl-cyclopentadienyl)amido]dimethyl titanium [5, 6, 14] ***(1)***

Preparation of $C_5HMe_4SiMe_2Cl$

A soluton of butyllithium (58 mL of 1.5 M solution in hexane; 87 mmol) was added to a solution of tetramethylcyclopentadiene (10 g, 82 mmol) in hexane (200 mL at 0 °C within 1 h. After stirring for 3 h at room temperature, the solvent was removed under vacuum and washed with hexane several times to obtain $Li(C_9H_{13})$. A solution of dichlorodimethylsilane (38 mL) in THF (100 mL) was added to the suspension of $Li(C_9H_{13})$ in THF (200 mL) at –78 °C. The resultant suspension was stirred for 8 h at room temperature. The solvent and excess dichlorodimethylsilane were removed under vacuum. After precipitation of lithium chloride with pentane and filtering it off, solvent was removed to give; 14.26 g (66 mmol, 80%) of $C_5HMe_4SiMe_2Cl$ as a light yellow oil.

^1H NMR (C_6D_6; ref. C_6H_6, 7.15 ppm): 2.95 (s, 1H, C_5HMe_4), 1.91 (s, 6H, C_5HMe_4), 1.71 (s, 6H, C_5HMe_4), 0.13 (s, 6H, $Si(CH_3)_2$).

Preparation of $^tBuNHSiMe_2C_5HMe_4$

2 eq. of tert-butylamine was added to a solution of $C_5HMe_4SiMe_2Cl$ (14.26 g, 66 mmol) in THF (150 mL) at 0 °C over a period of 1 h. After stirring overnight a yellow suspension was produced. After removal of the solvent, the product was extracted with pentane. The extract was

filtered and removal of the solvent gave 11.95 g (45 mmol, 68%) of $^tBuNHSiMe_2C_5HMe_4$ as yellow oil.

^1H NMR (C_6D_6; ref. C_6H_6, 7.15 ppm) 2.75 (s, 1H, C_5HMe_4), 2.01 (s, 6H, C_5HMe_4), 1.84 (s, 6H, C_5HMe_4), 1.09 (s, 9H, $C(CH_3)_3$), 0.40 (s, 1H, -NH-), 0.10 (s, 6H, $Si(CH_3)_2$).

Synthesis of $^tBuNSiMe_2C_5Me_4TiCl_2$

A solution of butyllithium (65 mL of 1.5 M solution in hexane) was added to a solution of $^tBuNHSiMe_2C_5HMe_4$ (11.95 g, 45 mmol) in ether (150 mL at –78 °C. After the mixture was warmed to room temperature, the reaction mixture was stirred for 6 h. The solvent was removed and washed with ether several times to obtain the salt $Li_2[^tBuNSiMe_2C_5Me_4]$ (20 g, 44 mmol) as a white solid. A solution of dilithium salt (4.0 g, 16 mmol) in THF (60 mL was added to a suspension of $TiCl_3.3THF$ (5.9 g, 16 mmol) in THF (60 mL) at –78 °C. The mixture was stirred overnight and warmed to room temperature. Solid $PbCl_2$ (5.5 g) was added to the mixture, which was stirred for 2 h. The solvent was removed and the residue was extracted with pentane. The extract was filtered and pentane was removed from the filtrate to give $^tBuNSiMe_2C_5Me_4TiCl_2$ (5.90 g, 16 mmol, 36%) as a yellow solid.

^1H NMR (C_6D_6: ref. C_6H_6, 7.15 ppm): 2.00 (s, 6H, C_5HMe_4), 1.99 (s, 6H, C_5HMe_4), 1.42 (s, 9H, $C(CH_3)_3$), 0.43 (s, 6H, $Si(CH_3)_2$).

*Synthesis of $^tBuNSiMe_2C_5Me_4TiMe_2$ (**1**)*

MeLi (20 mL of 1.4 M solution in ether) was added to a solution of $^tBuNSiMe_2C_5Me_4TiCl_2$ (5.90 g, 16 mmol) in ether (150 mL) at –60 °C. The mixture was stirred overnight and warmed to ambient temperature (below 20 °C) spontaneously. The solvent was removed and the residue was extracted with pentane. The extract was filtered and concentrated and kept at –30 °C for 2 days. Light yellow crystals of $^tBuNSiMe_2C_5Me_4TiMe_2$ (1.6 g, 5.0 mmol, 34 %) was obtained.

^1H NMR (C_6D_6; ref. C_6H_6, 7.15 ppm): 1.96 (s, 6H, C_5HMe_4), 1.87 (s, 6H, C_5HMe_4), 1.56 (s, 9H, $C(CH_3)_3$), 0.50 (s, 6H, $Si(CH_3)_2$), 0.43 (s, 6H, $Ti(CH_3)_2$).

Polymerization procedure

Polymerization of propene was conducted in a 200 mL glass reactor by semi-batch and batch method. In a semi-batch method, gaseous olefin was introduced into the reactor under atmospheric pressure. After toluene was saturated with the olefin, polymerization was started by successive addition of prescribed amounts of cocatalyst and catalyst (MAO = 8.0 mmol, Ti = 20 μmol, Al/Ti = 400 mol/mol). Olefin pressure (1 atm.) and temperature (0 °C) were kept constant during the polymerization, and the consumption rate of olefin was monitored by a gas flow meter. In a batch system, a measured amount of olefin was made to flow into the pre-prepared solvent before the addition of catalysts. For both systems, the polymerizations were conducted for 1 h and terminated by addition of acidic methanol. The polymer obtained was washed many times with methanol, and dried in *vacuo* at 60 °C for 6 h.

Analytical procedure. ^1H NMR spectra of the ligands and catalysts were recorded at room temperature on a Lambda-300 spectrometer operated at 300 MHz in pulse Fourier-Transform mode.

Molecular weight and molecular weight distribution of poly(olefin)s were determined against PS standard with universal calibration, by a Waters 150CV at 140 °C using *o*-dichlorobenzene as solvent. ^{13}C NMR spectra were recorded at 130 °C on a Lambda-500 spectrometer operated at 125.65 MHz, in pulse Fourier-Transform mode. The spectra were obtained at 130 °C in a 5.0 mm o.d. tube. Sample solutions were prepared in 1,1,2,2-tetrachloroethene-d_2 to contain up to 10% by weight. The central peak of 1,1,2,2-tetrachloroethene-d_2 (74.47 ppm) was used as an internal reference.

RESULTS AND DISCUSSION

*Propene polymerization with **1**/ MAO*

Kinetic features

Living polymerizations of propene with ^{t}BuNSiMe$_2$C$_5$Me$_4$TiMe$_2$/MAO at 0 °C were investigated, and the dependence of molecular weight on polymerization time was determined by sampling during the polymerization under an atmospheric pressure of propene. The M_n and M_w/M_n values were plotted against polymerization time as illustrated in Figure 2. The M_n value increased with increasing polymerization time while at the same time a constant narrow molecular weight distribution (MWD) was kept. However, the straight line did not pass through the origin. This result suggests the presence of chain transfer in quasi-living polymerization with this system. The GPC curves of the polypropene sampled at time intervals are indicated in Figure 3.

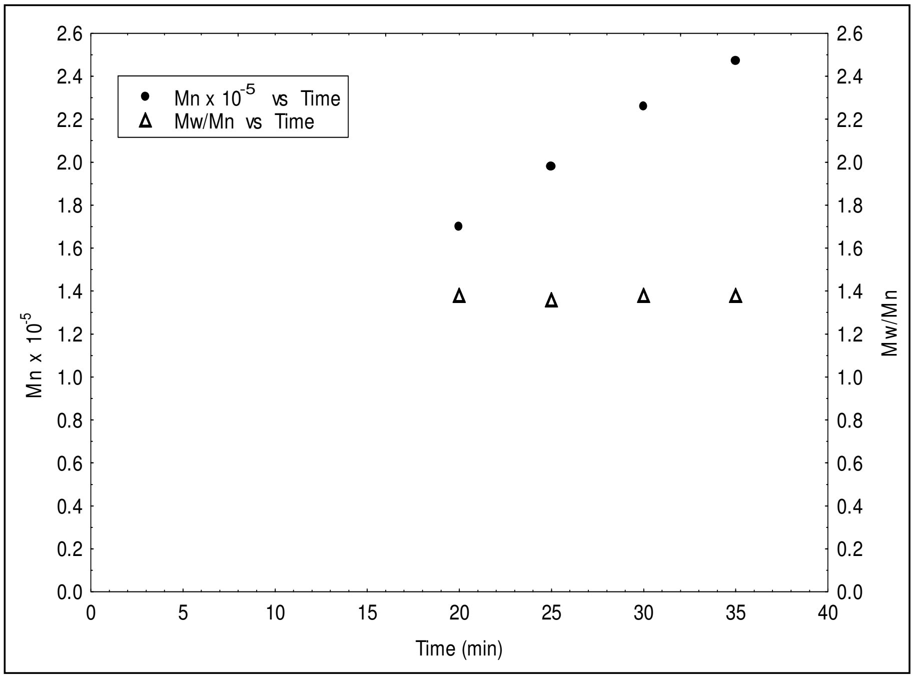


Figure 2. M_n and M_w/M_n against time for the polymerizatio propene with **1**/ MAO at 0 °C.

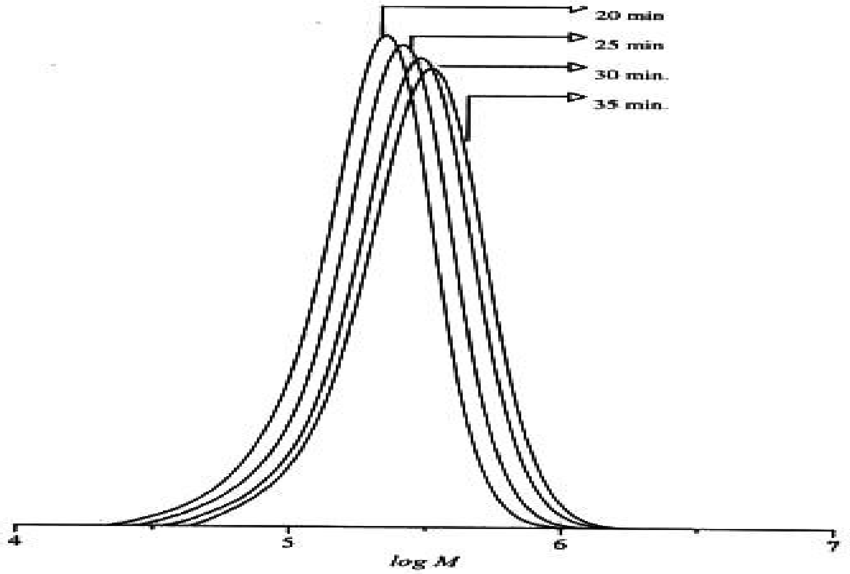


Figure 3. GPC curves of polypropene obtained with **1**/MAO.

An attempt was made to further confirm the living nature of **1**/MAO using a batch process, in which measured amounts of monomer were used for polymerization. The results shown in Table 1 indicated a conversion range between 92-98%. The number of polymer chains slightly increased with increasing the concentration of propene.

Table 1. Results of polymerization of propene with **1**/ MAO at 0 °C[a].

Run	Propene (mol/L)	Yield (g)	Conversion (%)	[b]M_n x 10^{-5}	M_w/M_n[b]	[c]N (μmol)
1	0.25	0.30	92	0.39	1.39	8
2	0.50	0.59	94	0.60	1.36	10
3	1.00	1.25	98	1.08	1.37	12
4	2.00	1.85	97	1.36	1.38	13

[a]Polymerization conditions: Ti = 20 μmol, toluene = 30 mL, Al/Ti = 400 mol/mol, time = 1 h. [b]Determined by GPC using PS standards with universal calibration. [c]Number of polymer chains calculated from yield and M_n.

The values of MWD, conversion, and polymer chains show that the catalyst system gave long life-time polymer chain. However, there is an indication of slight chain transfer since the graph of M_n against time did not pass through the origin (Figure 2). GPC curves of the polymers were determined as shown in Figure 4.

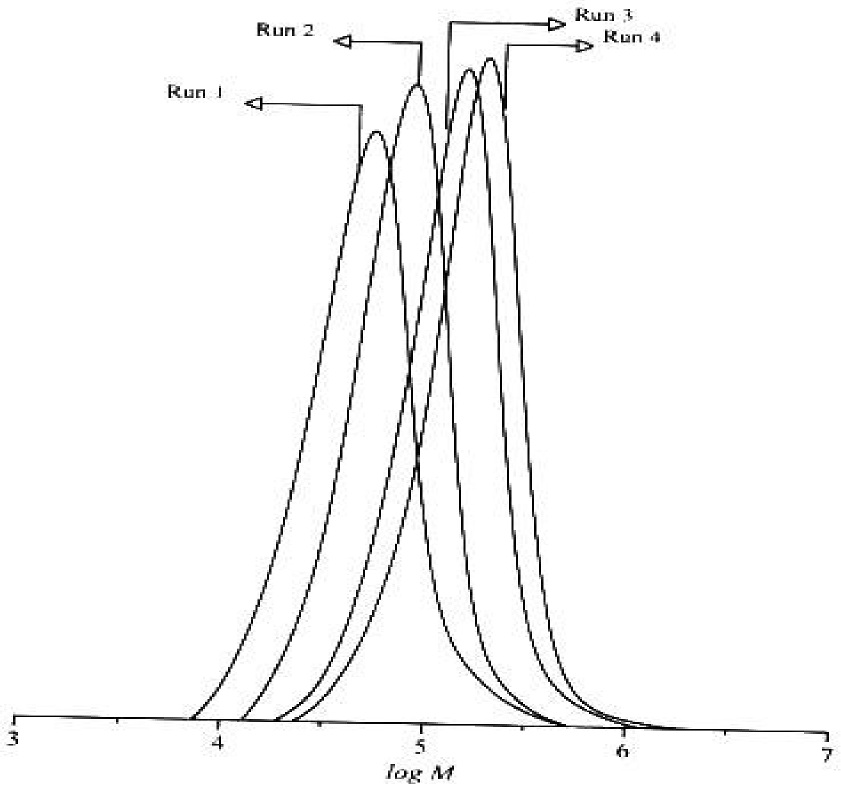


Figure 4. GPC curves of polypropene of runs 1-4 from Table 1.

Effects of trialkylaluminiums as additives on ***1****/ MAO system investigated*

Trialkylaluminiums such as ${}^{i}Bu_3Al$, Oct_3Al, Me_3Al and Et_3Al were investigated as additives during polymerization of propene with the **1**/MAO system. Activities and molecular weight were significantly lowered with additives such as Me_3Al and Et_3Al or by an excess MAO itself. MAO itself contains some Me_3Al. Therefore, adding more of Me_3Al further suppressed the activity of the system lower than when additive was not used. From Table 2, it is obvious that all the trialkylaluminiums generally increased the number of polymer chains, which was larger than the number of Ti complex (20 μmol) employed. This observed phenomenon indicates that the chain transfer occurred with these alkylaluminiums. The kinetic profiles displayed in Figure 5 and summarized in Table 2 showed that the addition of ${}^{i}Bu_3Al$ and Oct_3Al increased the activity whereas Me_3Al and Et_3Al decreased it.

A plausible mechanism of the additive effects is represented in the Scheme 1. Bulky ${}^{i}Bu_3Al$ and Oct_3Al coordinate to the counter anion rather than the cationic Ti species, which weakens the interaction between cationic Ti species and the counter anion and which eventually enhances catalytic activity. On the other hand, less bulky Me_3Al and Et_3Al preferentially coordinate to the Ti species, and which retards propagation rate.

Bulkier ^{i}Bu$_3$Al showed higher activity than linear Oct$_3$Al, while the number of polymer chains with ^{i}Bu$_3$Al was more than that with Oct$_3$Al. This shows that the chain transfer ability of ^{i}Bu$_3$Al is higher than that of Oct$_3$Al. Nevertheless, the chain transfer ability of Oct$_3$Al is not negligible as reported by Hagihara and Co-workers [15]. The yield obtained with Et$_3$Al was much lower than the amount of propene consumed and the M_n value was about 5000. This result indicated a possible formation of some methanol soluble oligomers with Et$_3$Al, and which could not be recovered by reprecipitation. Based on this, it is believed that the chain transfer ability of Et$_3$Al is much higher than other trialkylaluminiums.

Table 2. Effects of alkylaluminium additives on propene polymerization with **1**/ MAO at 0 °C^a.

Run	Alkyl aluminium	Yield (g)	Activity^b	^bM_n x 10^{-5}	M_w/M_n^{c}	^{d}N (μmol)
1	^{e}	2.23	223	1.57	1.33	18
2	^{i}Bu$_3$Al	4.99	499	0.59	1.72	87
3	Oct$_3$Al	4.24	424	0.95	1.55	46
4	Et$_3$Al	0.66	066	0.05	1.63	130
5	Me$_3$Al	2.09	209	0.62	1.43	36

^{a}Polymerization conditions: Ti = 20 μmol, toluene = 30 mL, Al/Ti = 400 mol/mol, propene = 1 atm. ^{b}Activity = kg-PP mol-Ti^{-1} h^{-1}. ^{c}Determined by GPC using PS standards with universal calibration. ^{d}Number of polymer chains calculated from yield and M_n. ^{e} No additive.

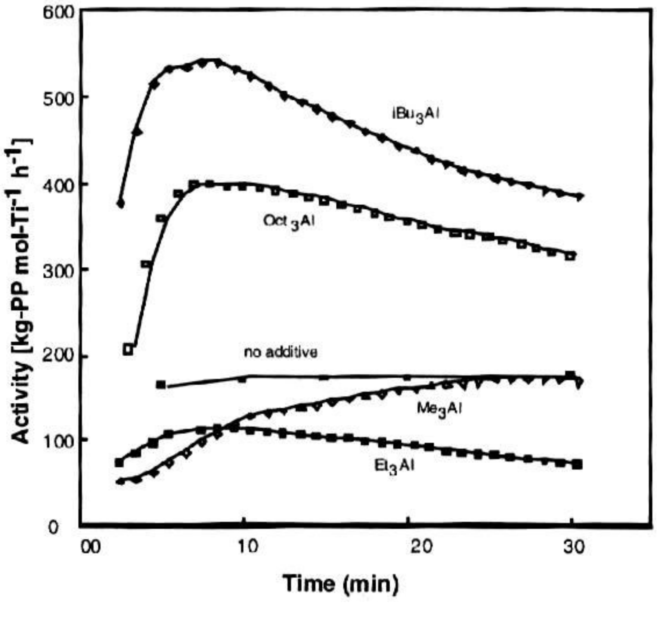
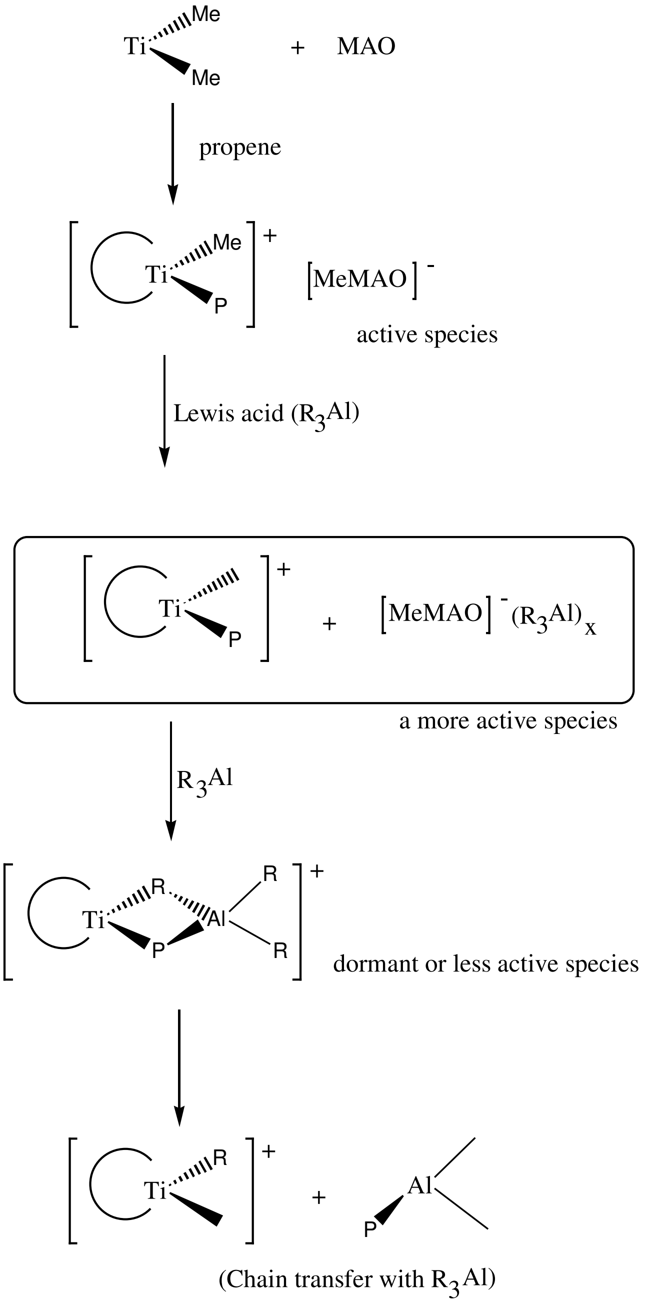


Figure 5. Rate-time profiles of additive effects of alkylaluminium on propene polymerization with **1**/ MAO at 0 °C.



Scheme 1. A plausible scheme of interaction between active species and alkylaluminium.

*Molecular structure of polypropene obtained with **1**/MAO*

The ^{13}C NMR spectrum of polypropene obtained in Run 3 (Table 1) is shown in Figure 6. The resonances attributable to regioirregular units are very weak in the spectrum, which indicates that the polymer produced was regioregular [15].

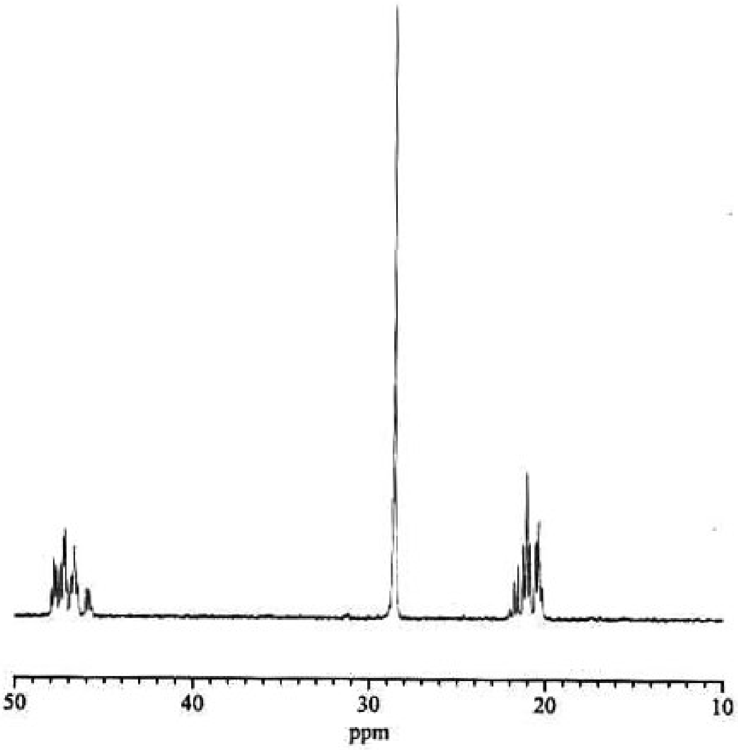


Figure 6. ^{13}C NMR spectrum of PP (Run 3) using **1**/MAO.

The spectrum of methyl region is shown in Figure 7. The triad sequence distribution was determined from relative intensities of the methyl group in the main chain using ^{13}C NMR and found as follows: mm = 32.11 %, mr = 11.78 %, rr = 56.11 %. The observed values almost fit to the calculated ones using Bernoullian model [16]. Although the rr content is slightly high statistically, the polymer obtained was confirmed to be a syndiotactic-enriched atactic polypropylene.

In addition, the ^{13}C NMR spectrum displayed 10 peaks (Figure 7), each of which represents a different set of five stereocenters (a pentad). Therefore, from the position of each pentad in the spectrum, ^{13}C NMR experimental result in Figure 7 further supports the polymer microstructure.

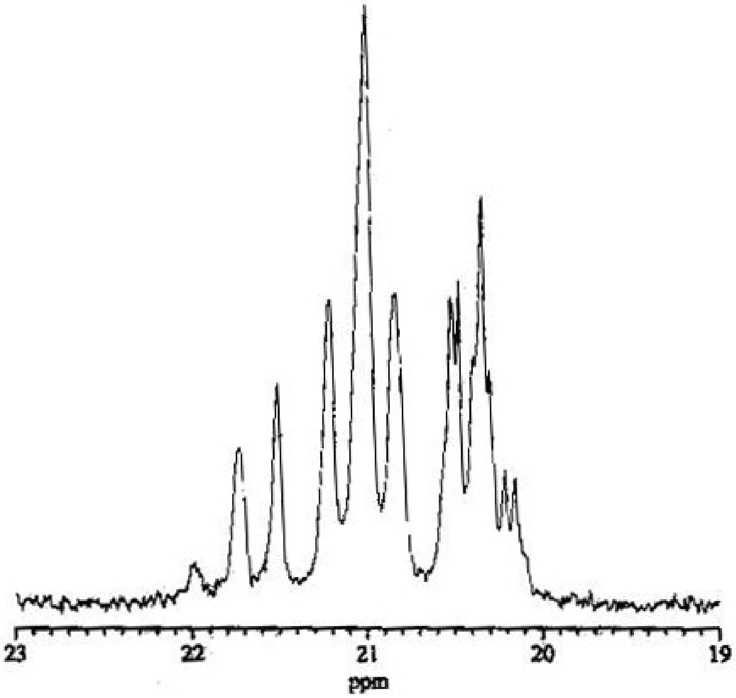


Figure 7. ^{13}C NMR spectrum of methyl region of PP (Run 3) obtained with **1**/MAO.

CONCLUSION

We have investigated the polymerization behavior of propene at 0 °C using ^{t}BuNSiMe$_2$C$_5$Me$_4$TiMe$_2$/MAO as catalyst. Various trialkylaluminiums have been adopted as additives. It has been concluded that Et$_3$Al offered the highest chain transfer ability.

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REFERENCES

1. Natta, G.; Pino, P.; Mazzanti, G.; Giannini, U. *J. Am. Chem. Soc.* **1957**, 79, 2975.
2. Breslow, D.S.; Newburg, N.R. *J. Am. Chem. Soc.* **1957**, 79, 5072.
3. Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, 18, 99.

4. Sinn, H.; Kaminsky, W.; Vollmer, H.J.; Woldt, R. *Angew. Chem. Int. Ed. Engl*. **1980**, 19, 390.
5. Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G.F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; Lai, S.Y. *The Dow Chemical Company invs*., EP 0416815 A2 **1991**, US. 401345 **1990**.
6. Canich, J.A.M. *PCT Appl. WO 91. U.S. Patent (Exxon)* 04257, April 4, **1990**.
7. Scollard, J.D.; McConville, D.H. *J. Am. Chem. Soc*. **1996**, 118, 10008.
8. Okuda, J. *Chem. Ber*. **1990**, 123, 1649.
9. Canich, J.A.M. *U.S. Patent (Exxon)* 5,026, 798, **1991**.
10. McKnight, A.L.; Masood, M.A.; Waymouth, R.M.; Straus, D.A. *Organometallics* **1997**, 16, 2879.
11. Turner, H.W.; Hlatky, G.G.; Canich, J.A.M. (Exxon), *PCT Int. Appl.* WO 93/19103, **1993**.
12. Shiomura, T.; Asanuma, T.; Sunaga, T. *Macromol. Rapid Commun*. **1997**, 18, 169.
13. Hassan, T.; Ioku, A.; Nishi, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, 34, 3142.
14. Steven, J.C. in *Catalytic Olefin Polymerization*, Keii, T.; Soga, K. (Eds.); Kadansha. Elsevier: Tokyo; **1994**, p 277.
15. Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules*, **1998**, 31, 3184.
16. Bovey, F.A.; Tiers, G.V.D. *J. Polym. Sci.* **1960**, 44, 173.