BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (6), 1802—1806 (1979)

Molecular Weight Distribution and Kinetics of Low-temperature Propene Polymerization with Soluble Vanadium-based Ziegler Catalysts

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(Received November 8, 1978)

A kinetic study has been carried out on the low-temperature polymerization of propene with the soluble catalyst system, VCl_4 and alkylaluminium ($AlEt_2Cl$, $AlEt_2Br$, or $AlEt_3$). The rate coefficients of the elementary reactions were evaluated at −78 °C. The molecular weight distribution function was derived on the basis of the polymerization mechanism. The theoretical distribution curves and experimental distribution curves obtained by use of a gel permeation chromatography agree, supporting the mechanism proposed for the coordination polymerization.

The molecular weight distribution (MWD) of polymers depends on the kinetic scheme of polymerization. Flory[1] and Bamford *et al.*[2] derived some distribution functions related to kinetic parameters for vinyl polymerization. Since the advent of gel permeation chromatography,[3] detailed kinetic investigations on the basis of the MWD data of polymers produced have been carried out for various models of polymerization, such as the radical polymerization of styrene with benzoyl peroxide as initiator[4] and the radiation-induced polymerization of styrene[5] and α-methylstyrene.[6] Agreement between the theoretical and experimental MWD curves can be regarded as evidence for the proposed kinetic scheme. However, this type of investigation does not seem to have been applied to the coordination polymerizaton of α-olefin with Ziegler-type catalysts.

In the present study, carrying out the polymerization of propene with the soluble catalyst mixture of VCl_4 with alkylaluminium [$AlEt_2Cl$, $AlEt_2Br$, or $AlEt_3$ ($Et{=}C_2H_5$)] at −78 °C, we compare the experimental MWD curves with a theoretical one derived from a proposed kinetic scheme. The catalyst system, $VCl_4/AlEt_2Cl$[8] or $VCl_4/AlEt_2Br$,[7] at −78 °C gives the syndiotactic form of polypropylene, whereas $VCl_4/AlEt_3$[10] gives the stereoirregular (atactic) form of polypropylene.

The kinetic scheme for polymerization is discussed, values being then determined for the rate coefficients of elementary reactions along the scheme.

Kinetic Scheme

The mechanism of syndiotactic polymerization of propene with the soluble catalyst system $VCl_4/AlEt_2Cl$ has been extensively investigated by Natta and coworkers.[8–11] Their kinetic data[9,10] on the polymerization and spectroscopic data[11] of the catalyst system suggest the following mechanistic features concerning the polymerization of propene. The catalytically active vanadium formed by the reaction of VCl_4 with $AlEt_2Cl$ is only a small fraction (less than 1%) of the total amount of vanadium[9] and a trivalent state.[11] The polymerization of propene takes place *via* two successive reactions, propene monomer coordination to the active vanadium and the subsequent insertion of the coordinated monomer into the growing chain attached to the metal.[10] The molecular weight of the growing chain is restricted either by the propene monomer coordinated or by the attack of alkylaluminium.[9,10] The chain transfer with monomer may be caused by a hydrogen transfer from the growing chain to the coordinated monomer with the subsequent formation of a new growing chain and a dead polymer. In the chain transfer with alkylaluminium, the growing chain attached to the vanadium may be replaced by the alkyl group on aluminium. In both cases the number of polymerization centers remains unchanged. For the purpose of calculation, the above reactions are written as follows.

Coordination to monomer

$$R_n + M \overset{K_m}{\rightleftarrows} C_n \tag{1}$$

Propagation

$$C_n \xrightarrow{k_p} R_{n+1} \tag{2}$$

Chain transfer with monomer

$$C_n \xrightarrow{k_{tm}} R_1 + Y_n \tag{3}$$

Chain transfer with alkylaluminium

$$R_n + A \xrightarrow{k_{tal}} R_1 + Z_n \tag{4}$$

Here C_n and R_n represent the growing chain with n units attached to the active vanadium metal with and without the monomer coordinated, respectively. M, A, Y_n, and Z_n represent the propene monomer, alkylaluminium, polymer with n units and polymer molecule with n units attached to inactive aluminium metal, respectively.

The overall rates of propagation, R_p, and chain transfer, R_t, are given by

$$\begin{aligned} R_p &= k_p\sum_1^{\infty}[C_n] = k_pK_m\sum_1^{\infty}[R_n][M] \\ &= k_p\left(\frac{K_m[M]}{1+K_m[M]}\right)\sum_1^{\infty}([C_n]+[R_n]) \end{aligned} \tag{5}$$

$$R_t = (k_{tm}K_m[M]+k_{tal}[A])\sum_1^{\infty}[R_n] \tag{6}$$

The number average degree of polymerization of the isolated polymers, $\bar{P}_n$, at a given time, t, is given by

$$\bar{P}_n = \frac{\int_0^t R_p \mathrm{d}t}{\sum_1^{\infty}([C_n]+[R_n])+\int_0^t R_t \mathrm{d}t} \tag{7}$$

If we assume the steady-state conditions under which $R_{\rm p}$ and $R_{\rm t}$ remain constant during the course of polymerization, the reciprocal of $\bar{P}_n$ can be expressed as

$$\frac{1}{\bar{P}_n} = \left(\frac{1+K_{\rm m}[{\rm M}]}{k_{\rm p}K_{\rm m}[{\rm M}]}\right)\cdot\frac{1}{t} + \frac{R_{\rm t}}{R_{\rm p}} \tag{8}$$

Under the conditions that $t \gg 0$, Eq. 8 can be approximated as

$$\frac{1}{\bar{P}_n} \simeq \frac{R_{\rm t}}{R_{\rm p}} = \frac{k_{\rm tm}}{k_{\rm p}} + \frac{k_{\rm ta1}}{k_{\rm p}K_{\rm m}}\cdot\frac{[{\rm A}]}{[{\rm M}]} \tag{9}$$

We now derive the MWD function in this polymerization. The formation of the growing chain with n units is given by

$$\frac{{\rm d}[{\rm R}_n+{\rm C}_n]}{{\rm d}t} = k_{\rm p}K_{\rm m}[{\rm M}]([{\rm R}_{n-1}]-[{\rm R}_n]) - (k_{\rm tm}K_{\rm m}[{\rm M}]+K_{\rm ta1}[{\rm A}])[{\rm R}_n] \tag{10}$$

When the polymerization is stationary, *i.e.*, $[{\rm C}_n]$ and $[{\rm R}_n]$ remain constant during the course of polymerization, the right-hand side of Eq. 10 is zero. Thus we have

$$[{\rm R}_n] = \beta[{\rm R}_{n-1}] = \beta^{n-1}[{\rm R}_1] \tag{11}$$

with

$$\beta = \frac{k_{\rm p}K_{\rm m}[{\rm M}]}{k_{\rm p}K_{\rm m}[{\rm M}]+k_{\rm tm}K_{\rm m}[{\rm M}]+k_{\rm ta1}[{\rm A}]} \tag{12}$$

The rate of formation of the polymer with n units is given by

$$\frac{{\rm d}[{\rm Y}_n+{\rm Z}_n]}{{\rm d}t} = (k_{\rm tm}K_{\rm m}[{\rm M}]+k_{\rm ta1}[{\rm A}])[{\rm R}_n] \tag{13}$$

For a low conversion of monomer the concentration of polymer, $[{\rm Y}_n+{\rm Z}_n]$, may be expressed as a function of t.

$$[{\rm Y}_n+{\rm Z}_n] = (k_{\rm tm}K_{\rm m}[{\rm M}]+k_{\rm ta1}[{\rm A}])\beta^{n-1}[{\rm R}_1]t \tag{14}$$

Thus, we have the mole fraction of polymer with n units, $X(n)$

$$X(n) = (1-\beta)\beta^{n-1} \tag{15}$$

which is the same as the MWD function derived by Flory.[1)]

Experimental

Reagents. Propene (Mistubishi Petrochemical Co. 99.7 % purity, the impurity being propane) was dried by passing through columns of NaOH and P_2O_5. Heptane (reagent grade) was dried by refluxing over sodium metal under nitrogen atmosphere after distillation. Alkylaluminiums (Japan Aluminium Alkyl Co.) and VCl_4 (Wako Pure Chemicals) were used without further purification.

Polymerization Procedure. A three-neeked glass flask with a magnetic stirrer was used as a reactor. Propene was condensed into heptane in the reactor kept at −78 °C with methanol–Dry Ice. The amount of heptane used was adjusted to be 100 ml as the total volume of solution. Prescribed amounts of alkylaluminium and VCl_4 were charged one after the other. Polymerization was timed from the addition of the VCl_4 component, and quenched at a given time by introducing 100 ml of an ethanol solution of hydrochloric acid cooled at −78 °C. The polymers obtained were washed several times with 200—300 ml ethanol and dried *in vacuo* at room temperature.

Gel-permeation Chromatography Analysis. Molecular weight distributions of polymers were measured by gel permeation chromatography (GPC) (Waters Associates, Model 200) with the use of five polystyrene gel columns (10^7, 10^6, 10^5, 10^4, and 10^3 Å pore sizes) and *o*-dichlorobenzene as a solvent at 135 °C. The solvent flow rate was maintained at 1.0 ml/min. A molecular weight calibration curve was obtained on the basis of the universal calibration,[12,13)] with 10 standard samples of monodisperse polystyrene of molecular weights 2100—2610000. From the GPC data, the number-average and weight-average molecular weights ($\bar{M}_{\rm n}$, $\bar{M}_{\rm w}$) were obtained by standard procedures by using the data at 1/2 count (2.5 ml elution volume).

Results and Discussion

The polymerization results obtained at −78 °C under various conditions are summarized in Tables 1, 2, and 3 for the $VCl_4/AlEt_2Cl$, $VCl_4/AlEt_2Br$, and $VCl_4/AlEt_3$ catalysts, respectively. Polymerization was carried out in the range of a low conversion of propene monomer up to several percents. The concentration of monomer may be regarded as constant during the course of polymerization. Kinetic analysis for the polymerization was made from the data given in the Tables.

Polymerization Rate. The time dependence of the yields of polymers produced in the course of polymerizations with different catalyst systems is shown in Fig. 1. The yield-time curves are almost linear with no induction periods. This shows that the formation of the polymerization centers is complete just after the start of polymerization and the number of the centers remains constant during the course of polymerization.

The polymer yields at a given polymerization time were of first-order, as anticipated, with respect to the amount of vanadium tetrachloride at a constant concentration of alkylaluminium. On the other hand, it was found that the relationship between polymerization rate and propene monomer concentration is not of simple first-order kinetics. The polymerization rate, $R_{\rm p}$, increased to a constant value with increase in monomer

TABLE 1. POLYMERIZATION RESULTS OBTAINED AT −78 °C UNDER DIFFERENT EXPERIMENTAL CONDITIONS WITH $VCl_4/AlEt_2Cl$ CATALYST SYSTEM

Sample	$AlEt_2Cl$ (mol/l)	C_3H_6 (mol/l)	Polymerization period (h)	Polymer yield (g)	$\bar{M}_{\rm n}$ ($\times 10^4$)	Q ($\bar{M}_{\rm w}/\bar{M}_{\rm n}$)
A-1	0.05	8.4	0.5	0.05	2.39	1.4
A-2	0.05	8.4	0.75	0.14	2.32	1.5
A-3	0.05	8.4	1.0	0.19	2.99	1.5
A-4	0.05	8.4	2.0	0.49	3.06	1.5
A-5	0.05	8.4	3.0	0.72	3.19	1.5
A-6	0.05	8.4	4.0	1.01	3.73	1.6
A-7	0.05	8.4	5.0	1.39	3.58	1.7
A-8	0.05	8.4	7.0	2.00	4.07	1.7
A-9	0.03	8.4	3.0	0.52	3.28	1.5
A-10	0.10	8.4	3.0	0.99	2.93	1.6
A-11	0.15	8.4	3.0	0.96	3.06	1.7
A-12	0.20	8.4	3.0	0.97	2.68	1.8
A-13	0.25	8.4	3.0	0.94	2.87	1.6
A-14	0.05	1.2	3.0	0.23	1.92	1.9
A-15	0.05	2.4	3.0	0.46	2.27	1.7
A-16	0.05	4.8	3.0	0.66	2.97	1.7
A-17	0.05	11.7	3.0	0.66	—	—

VCl_4 concentration of 0.01 mol/l, polymerization solution of 0.1 l.

TABLE 2. POLYMERIZATION RESULTS OBTAINED AT −78 °C WITH $VCl_4/AlEt_2Br$ CATALYST SYSTEM

Sample	$AlEt_2Br$ (mol/l)	C_3H_6 (mol/l)	Polymerization period (h)	Polymer yield (g)	$\overline{M}_n$ ($\times 10^3$)	Q ($\overline{M}_w/\overline{M}_n$)
B-1	0.050	8.4	2.0	0.06	3.34	2.3
B-2	0.050	8.4	3.0	0.08	5.17	3.0
B-3	0.050	8.4	5.0	0.10	6.58	2.7
B-4	0.050	8.4	6.5	0.16	5.50	2.6
B-5	0.015	8.4	3.0	0.05	—	—
B-6	0.025	8.4	3.0	0.09	4.24	2.5
B-7	0.075	8.4	3.0	0.04	4.61	1.7
B-8	0.100	8.4	3.0	0.04	4.40	1.6
B-9	0.200	8.4	3.0	0.03	3.34	1.6
B-10	0.025	4.8	3.0	0.06	3.02	2.0
B-11	0.025	12.3	3.0	0.14	4.93	2.3

VCl_4 concentration of 0.01 mol/l, polymerization solution of 0.1 l.

TABLE 3. POLYMERIZATION RESULTS OBTAINED AT −78 °C WITH $VCl_4/AlEt_3$ CATALYST SYSTEM

Sample	$AlEt_3$ (mol/l)	C_3H_6 (mol/l)	Polymerization period (h)	Polymer yield (g)	$\overline{M}_n$ ($\times 10^5$)	Q ($\overline{M}_w/\overline{M}_n$)
C-1	0.025	8.4	0.5	0.30	2.57	1.6
C-2	0.025	8.4	1.0	0.49	3.43	1.8
C-3	0.025	8.4	1.5	0.92	5.45	2.0
C-4	0.025	8.4	2.5	1.25	7.55	2.0
C-5	0.025	8.4	3.0	1.43	7.75	2.0
C-6	0.005	8.4	3.0	1.08	6.81	2.1
C-7	0.015	8.4	3.0	0.83	5.97	2.4
C-8	0.100	8.4	3.0	0.57	4.86	2.6
C-9	0.150	8.4	3.0	0.40	3.46	2.6
C-10	0.200	8.4	3.0	0.47	3.82	2.2
C-11	0.025	1.2	2.5	0.22	2.74	2.1
C-12	0.025	4.8	2.5	0.82	5.74	2.0
C-13	0.025	11.9	2.5	1.42	10.7	1.8

VCl_4 concentration of 0.001 mol/l, polymerization solution of 0.1 l.

concentration, [M].[14] $1/R_p$ is plotted against $1/[M]$ for the respective catalyst system in Fig. 2. The linearity of the plots indicate that Eq .5 is applicable to the polymerization of propene with soluble vanadium-based catalysts. The values of the coordination equilibrium constant of monomer, K_m, were determined from the slopes and the intercepts of the straight lines. The results are given in Table 4.

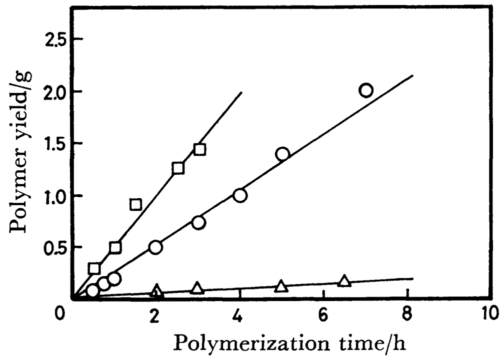

Fig. 1. Polymer yield-time curves of the polymerizations with different catalyst systems.

(○); $VCl_4/AlEt_2Cl$ system (samples A-1—A-8), (△); $VCl_4/AlEt_2Br$ system (samples B-1—B-4), (□); $VCl_4/AlEt_3$ system (samples C-1—C-5).

For experimental conditions see Tables 1—3.

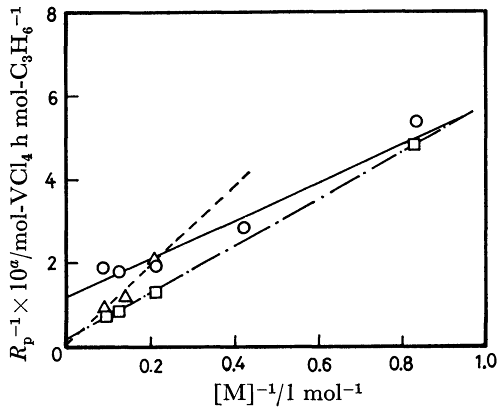

Fig. 2. Plots of the reciprocal of polymerization rate, R_p^{-1}, against the reciprocal of propene monomer concentration, $[M]^{-1}$.

(○); $VCl_4/AlEt_2Cl$ system ($a=1$ for $R_p^{-1}\times 10^a$), (△); $VCl_4/AlEt_2Br$ system ($a=0$ for $R_p^{-1}\times 10^a$), (□); $VCl_4/AlEt_3$ system ($a=2$ for $R_p^{-1}\times 10^a$).

−78 °C, $[AlEt_2Cl]=[AlEt_2Br]=0.05$ mol/l or $[AlEt_3]=0.025$ mol/l.

The effect of alkylaluminium concentration on the polymerization rate is complicated (Fig. 3). The polymerization rate rises to a maximum value followed by a gradual fall with increase in the concentration of alkylaluminium, *i.e.*, in the Al/V ratio. The polymerization rate is correlated with the following function of the concentration of alkylaluminium [A].

$$R_p \propto \frac{K_A[A]}{(1+K_A[A])^2} \tag{16}$$

TABLE 4. RATE COEFFICIENTS OF ELEMENTARY REACTIONS IN THE POLYMERIZATION OF PROPENE WITH $VCl_4/AlEt_2X$ (X=Cl, Br, Et) CATALYST SYSTEMS AT −78 °C

	$AlEt_2Cl$	$AlEt_2Br$	$AlEt_3$
K_m(l·mol^{-1})	0.26±0.03	0.02±0.01	0.04±0.01
K_A(l·mol^{-1})	6.8±0.3	31±3	46±2
k_p(h^{-1})	(4.3±1.0)×10^3	(2.5±1.2)×10^2	(5.3±0.6)×10^4
k_{tm}(h^{-1})	5.4±0.1	1.7±0.1	2.3±0.3
k_{tal}(l·mol^{-1}·h^{-1})	18±6.5	3.5±2.0	9.0±1.5

The value of the constant, K_A, decreases in the order: $AlEt_3 > AlEt_2Br > AlEt_2Cl$ (Table 4). The order appears to correspond to the reducing powers of the alkylaluminium for VCl_4. Though we can not present a conclusive explanation for Eq. 16, alkylaluminium seems to take part in the deactivation of polymerization centers as well as in the formation of the centers through the alkylation and complexation of VCl_4. This is supported by the obervation of Lehr[15] that higher Al/V ratios result in some reduction of vanadium to its divalent state at −78 °C in the $VCl_4/Al(i\text{-}Bu)_3$ catalyst system. The influence of the alkylaluminium concentration on the polymerization rate is thus understandable as a result of the change in the number of polymerization centers, $\sum_1^\infty([C_n]+[R_n])$.

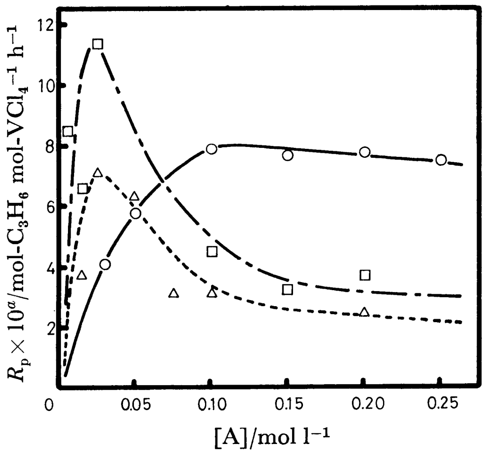

Fig. 3. Influence of alkylaluminium concentration, [A], on polymerization rate, R_p.
(○); $VCl_4/AlEt_2Cl$ system ($a=0$ for $R_p \times 10^a$), (△); $VCl_4/AlEt_2Br$ system ($a=-1$ for $R_p \times 10^a$), (□); $VCl_4/AlEt_3$ system ($a=1$ for $R_p \times 10^a$).
−78 °C, [M] = 8.4 mol/l.

Average Molecular Weight. The number-average molecular weghts, $\overline{M}_n$, of polymers produced increase with the polymerization time, attaining constant values in a few hours for all the catalyst systems (Tables 1—3). The plots of $1/\overline{M}_n$ *vs.* $1/t$ are shown for different catalyst systems in Fig. 4. The linearity of plots indicates that the experimental results are satisfactorily correlated by Eq. 8, which is a linear form of Eq. 7. Using the values of K_m given in the preceding section, we can estimate the values of the propagation rate coefficient of monomer, k_p, from the slopes of the straight lines. The values of k_p for different catalyst systems are summarized in Table 4.

The values of $\overline{M}_n$ of the polymers produced at 3 h increase with increase in the concentration of propene monomer, [M]. The dependence of the value of $\overline{M}_n$ on [M] is given by Eq. 9. The relation between the value of $\overline{M}_n$ of the polymers produced and the concentration of alkylaluminiums, [A], also follows Eq. 9 (Figs. 5—7). The values of intercepts of both straight lines in the respective figure agree closely with each other. This suggests that the chain terminating steps other than the transfer with monomer and alkylaluminium is not significant in the polymerization. The values of the rate coefficients of the chain transfers, k_{tm} and

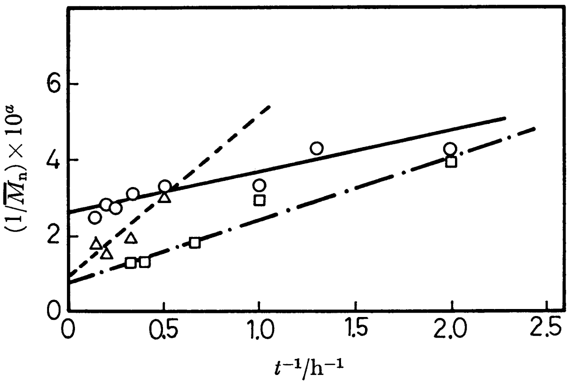

Fig. 4. Plots of $1/\overline{M}_n$ *vs.* $1/t$.
(○); $VCl_4/AlEt_2Cl$ system ($a=5$ for $1/M_n \times 10^a$, samples A-1—A-8), (△); $VCl_4/AlEt_3Br$ system ($a=4$ for $1/M_n \times 10^a$, samples B-1—B-4), (□); $VCl_4/AlEt_3$ system ($a=6$ for $1/M_n \times 10^a$, samples C-1—C-5).
For experimental conditions see Table 1—3.

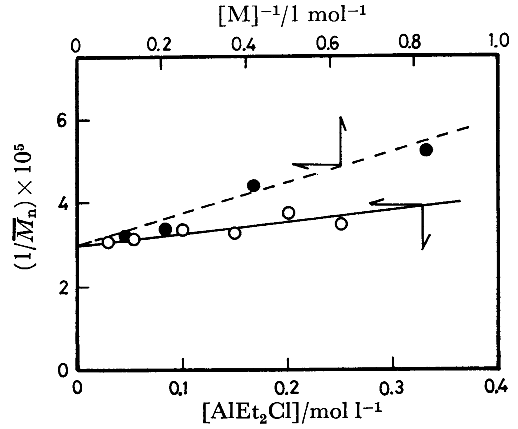

Fig. 5. Plots of $1/\overline{M}_n$ *vs.* 1/[M] and *vs.* [A] for $VCl_4/AlEt_2Cl$ system.
(●); Samples A-14—A-16 and A-5, (○); Samples A-9—A-13 and A-5.
For experimental conditions see Table 1.

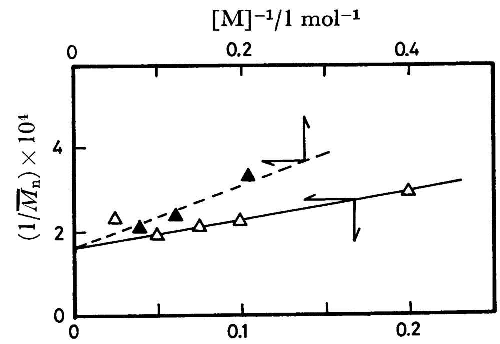

Fig. 6. Plots of $1/\overline{M}_n$ *vs.* 1/[M] and *vs.* [A] for $VCl_4/AlEt_2Br$ system.
(▲); Samples B-10, B-11 and B-2, (△); Samples B-6—B-9 and B-2.
For experimental conditions see Table 2.

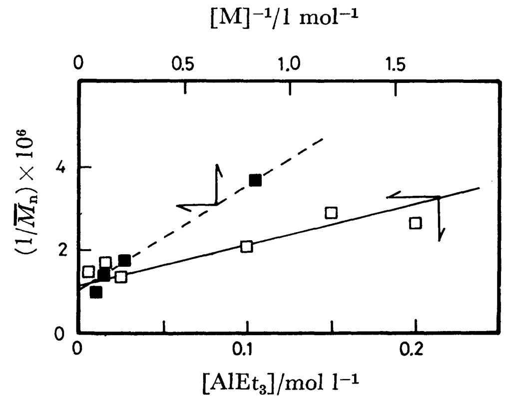

Fig. 7. Plots of $1/\overline{M}_n$ vs. $1/[M]$ and vs. [A] for $VCl_4/AlEt_3$ system.
(■); Samples C-11—C-13 and C-4.
(□); Samples C-5—C-10.
For experimental conditions see Table 3.

k_{tal}, may be obtained from the intercepts and slopes of the straight lines. The values of k_{tm} and k_{tal} are given in Table 4 with the experimental deviation for each catalyst system.

The rate coefficients of the elementary reactions are remarkably affected by the type of alkylaluminium used. The mole fraction of syndiotactic dyads of the polypropylene produced decreases as follows.[7]

$$AlEt_2Cl\ (86) > AlEt_2Br\ (65) > AlEt_3\ (50) \qquad (17)$$

The remarkable influence of the type of alkylaluminium on the elementary reaction rates and stereospecificity may be interpreted in terms of the bimetallic structure of the polymerization center, first proposed by Zambelli *et al.*,[11] in which the alkylaluminium complexed with alkylvanadium chloride regulates the catalytic capability.

Molecular Weight Distributions. Comparison has been made between the theoretical and experimental MWD curves of the polypropylene samples. Three nomalized GPC curves of samples A-8, B-4 and C-5 are shown in Fig. 8 by solid lines. The polypropylene samples were prepared by the polymerization with different catalyst systems. The weight fraction of polymer is plotted against common logarithms of molecular weight. For the sake of comparison the theoretical MWD curves of the three samples were calculated from a plot of $42 \cdot n^2 \cdot [X(n)]$ vs. $\log(42 \cdot n)$, with $[X(n)]$ by means of Eq. 15 and the values of β (0.99865 for sample A-8, 0.98915 for sample B-4 and 0.99995 for sample C-5) were determined using the kinetic parameters (Table 4), taking the conditions for the preparation into consideration. The results are shown in Fig. 8 by dotted lines. The modes of curves and the values of maxima are in close agreement between theory and experiment, except sample B-4 prepared with $VCl_4/AlEt_2Br$ system. The shoulder at the higher molecular weights observed in the GPC curve of sample B-4 may be due to the coexistence of $AlEt_2Cl$ formed by the halogen interchange between VCl_4 and $AlEt_2Br$.

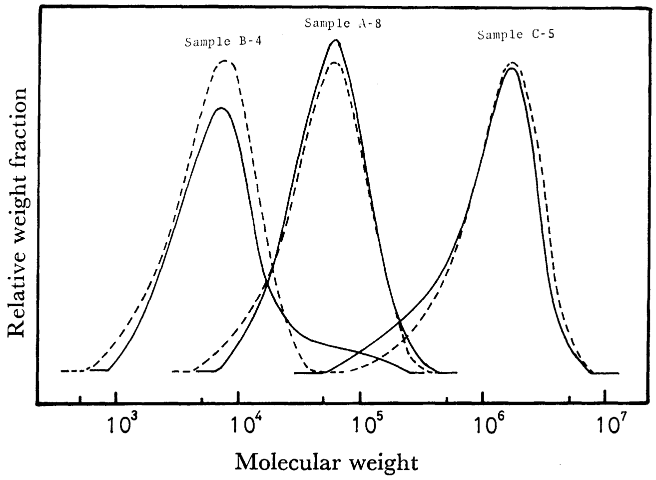

Fig. 8. Experimental and theoretical molecular weight distribution curves of polypropylenes prepared at −78 °C with different soluble vanadium-based catalysts.
(——): Experimental curves, (----) theoretical curves.

It may be concluded that the molecular weight distributions of polymers produced with soluble vanadium-based catalysts are expressed by the distribution function of Eq. 15 derived from the kinetic scheme proposed.

References

1) P. J. Flory, "Principles of Polymer Chemistry," Cornel Univ. Press, Ithaca, N. Y. (1953).

2) C. H. Bamford, W. G. Bard, A. D. Jenkins, and P. F. Onyon, "The Kinetics of Vinyl Polymerization by Radical Mechanisms," Butterworths, London, (1958).

3) J. C. Moore, *J. Polym. Sci. A-2*, **2**, 835 (1964).

4) J. A. May, Jr., and W. B. Smith, *J. Phys. Chem.*, **72**, 216 (1968).

5) S. Machi, J. Silverman, and D. Metz, *J. Phys. Chem.*, **76**, 930 (1972).

6) A. S. Chawla, and R. Y. Hung, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1271 (1975).

7) Y. Doi, M. Takada, and T. Keii, *Makromol. Chem.*, **180**, 57 (1979).

8) G. Natta, I. Pasquon, and A. Zambelli, *J. Am. Chem. Soc.*, **84**, 1488 (1962).

9) G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mognaschi, A. L. Segre, and P. Centola, *Makromol. Chem.*, **81**, 161 (1965).

10) A. Zambelli, G. Natta, I. Pasquon, and R. Signorini, *J. Polym. Sci., Part C*, **16**, 2485 (1967).

11) A. Zambelli, I. Pasquon, R. Signorini, and G. Natta, *Makromol. Chem.*, **112**, 160 (1968).

12) Z. Grubisic, P. Rempp, and H. Bonoit, *J. Polym. Sci., Part B*, **5**, 753 (1967).

13) T. Ogawa, S. Tanaka, and S. Hoshino, *Kobunshi Kagaku*, **29**, 6 (1972).

14) Further purification of monomer by bubbling in the heptane solution of $AlEt_3$ was made to remove the trace of O_2 prior to use in the VCl_4–$AlEt_2Cl$ catalyst system. However, no effect of purification was observed on the polymerization rates. It is concluded that the unusual dependence of monomer concentration on the polymerization rate can not be interpreted in terms of the inhibiting effect of O_2 trace in the monomer.

15) M. H. Leher, *Macromolecules*, **1**, 178 (1968).