European Polymer Journal Vol. 16, pp. 937 to 940
Pergamon Press Ltd 1980. Printed in Great Britain

THE NUMBER OF PROPAGATING SPECIES AND SOME RATE CONSTANTS OF ELEMENTARY ACTS FOR THE POLYMERIZATION OF ETHYLENE AND α-OLEFINS USING SUPPORTED ZIEGLER CATALYSTS

A. A. BAULIN, A. G. RODIONOV, S. S. IVANCHEV and N. M. DOMAREVA
"Plastpolymer", Okhta Research and Production Association, Leningrad, U.S.S.R.

(*Received* 12 *February*; *revised* 14 *April* 1980)

Abstract—Concentrations of propagating species (PS) and chain propagation constants (k_p) were determined for the polymerizations of ethylene, propylene, butene-1 and hexene-1 using $TiCl_4/MgO–Al(C_2H_5)_3$ (**I**) and $TiCl_4/Al_2O_3$, $SiO_2–Al(C_2H_5)_3$ (**II**) catalytic systems. The concentrations of propagating species for all monomers and a particular catalytic system are close. They give an idea of high degree of application of transition metal ($\simeq$35–39% of total Ti for system **I** and $\simeq$20–23% for system **II**). Values of k_p for ethylene, propylene, butene-1, hexene-1 at 70° for system I are 2440 ± 240, 4.8 ± 0.5, 4.6 ± 0.5 and 2.5 ± 0.3 l/mol·sec respectively. For system **II**, k_p values for the first three monomers are 110 ± 11, 1.0 ± 0.1 and 0.13 ± 0.01 l/mol·sec. These results indicate the relation of reactivity of propagating species and chemical nature of the support to the surface of which they are fixed. Rate constants for chain transfer to monomer or triethyl aluminium and spontaneous disproportionation (at 70°) were compared for the polymerizations of ethylene and propylene using catalytic system I.

INTRODUCTION

Previously [1, 2] we established that polymerization of ethylene using Ziegler catalysts on mineral supports is characterized by a high degree of application of transition metal included into the propagating species and, for magnesium-containing supports, by high reactivity of propagating species in the elementary reactions, primarily chain propagation, Information about the kinetics of α-olefin polymerization using catalysts of this type is not available.

This paper deals with determination and comparison of propagating species and some rate constants for elementary reactions in the polymerizations of ethylene, propylene, butene-1 and hexene-1 using $TiCl_4–Al(C_2H_5)_3$ catalytic system supported by magnesium oxide and aluminosilicate.

EXPERIMENTAL

Supported catalysts were prepared by treatment of magnesium oxide and aluminosilicate by titanium tetrachloride at 140° [3]. Catalyst activation by triethyl aluminium was carried out during polymerization. Procedures for the determination of specific surface of supported catalysts (S_{sp}), titanium content, reagent purity and polymerization kinetics have been described [4, 5].

Concentrations of propagating species on the surface of supported catalysts were determined by chain termination with methanol labelled by tritium in the OH group taking into account "non-active" metal-polymer bonds produced on the polymer by chain transfer by triethyl aluminium. Correction for the kinetic isotope effect was made by means of the isotopic exchange reaction of ordinary hydrogen and tritium [1, 2]. An automatic liquid SL-30 scintillating spectrometer was used for assays of C_2H_5OT and polyolefin samples produced with this stopper. The number of metal-polymer bonds was determined using a quoted formula [1].

The intrinsic viscosities [η] of polyethylene and polypropylene were measured in decalin at 135°, of polybutene in decalin at 115° and of polyhexene in cyclohexene at 25°. The viscosity-average molecular weights ($\bar{M}_\eta$) of polyolefin samples were calculated from [η] values using formulae given for polyethylene [1], polypropylene [6], polybutene [7] and polyhexene [8]. The stereoregularity (I_{st}) of polypropylene was determined as the proportion insoluble in boiling *n*-heptane and that of polybutene as the proportion insoluble in boiling diethyl ether [9]. The distribution factor for polypropylene was determined, based on its $\bar{M}_w$ and $\bar{M}_n$ values found by high temperature GPC. Waters glass packed chromatograph was used with *o*-dichlorobenzene as solvent at 130°.

RESULTS AND DISCUSSION

Figure 1 shows kinetic curves for the polymerization of ethylene and α-olefins using supported catalysts. They express the relation of effective rate constant of polymerization (k_{ef}) and process time. k_{ef} Values were calculated according to [4, 10]. k_{ef} Is the polymerization rate of a monomer corrected for concentration in the reaction zone. It is equal to the product of the concentration of propagating species (C_p^x) and k_p.

Figure 1 shows that, when ethylene is replaced by α-olefins, there is rapid decrease of polymerization rate for both supported catalysts. For α-olefins this difference of catalytic activity is not very great; thus for system **I**, the difference between maximum k_{ef} values for ethylene and propylene is about 600, whereas for propylene and hexene-1 this factor is <2. For propylene and butene-1, catalytic activities of the

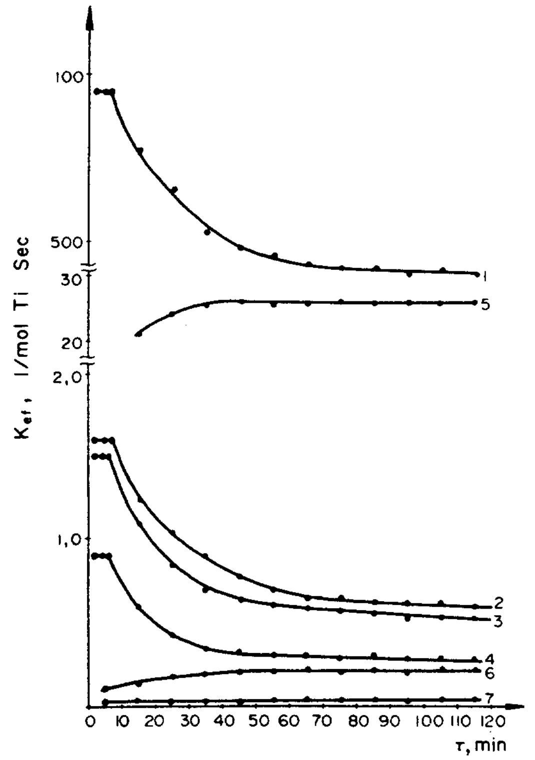

Fig. 1. Kinetic curves for polymerization of olefins using $TiCl_4/MgO-Al(C_2H_5)_3$ (1–4) and $TiCl_4/Al_2O_3$, $SiO_2-Al(C_2H_5)_3$ (5–7) systems. Curves 1,5—ethylene; curves 2,6—propylene; curves 3,7—butene-1; curve 4—hexene-1. Polymerization conditions are similar to those of Table 1.

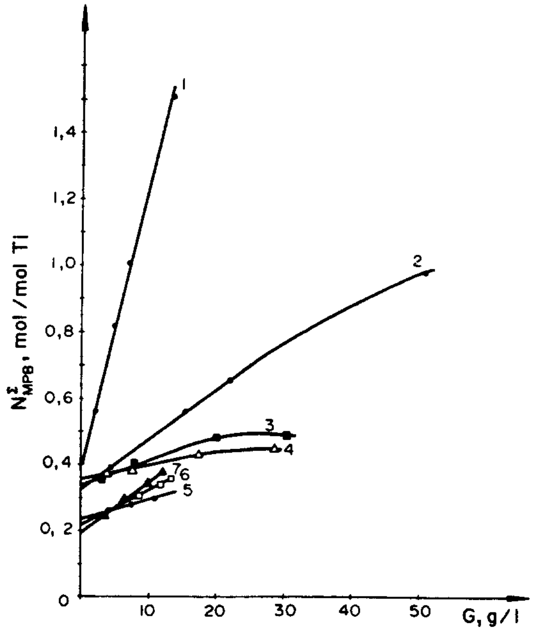

Fig. 2. Relation of the number of metal-polymer bonds and polyolefin yield for the polymerizations of olefins using $TiCl_4/MgO-Al(C_2H_5)_3$ (1–4) and $TiCl_4/Al_2O_3$, $SiO_2-Al(C_2H_5)_3$ (5–7) catalytic systems. Concentration of $Al(C_2H_5)_3 = 0.2$ g/l, all other polymerization conditions and symbols for curves are similar to those in Fig. 1.

catalytic systems towards ethylene and α-olefins can be explained by kinetic features of the propagation, C^{*}_{p} and k_p. Data required for their calculation are also shown in Fig. 2. It illustrates the relation of the total number of metal-polymer bonds (N^{Σ}_{MPB}) ("active" Ti-C and "non-active" Al-C bonds formed as result of chain transfer by triethyl aluminium) and polyolefin yield (G). Relevant results are shown in Table 1 (calculations were done according to a published method [1, 2]).

Table 1 shows that the actual maximum concentrations of propagating species (1) for all monomers for the selected catalytic system are close. These concentrations characterize high degree of application of the transition metal ($\simeq$35–39% of total Ti for system I and $\simeq$20–23% of total Ti for system II). High C^{*}_{p} value for magnesium oxide supported catalyst corresponds to those for titanium and magnesium catalytic systems of different types known from the literature. Thus, based on the example of catalysts produced by the reduction of titanium tetrachloride with solvated magnesium organic compounds, Haward [11] has shown that the concentration of the propagating species can reach 60% for the ethylene polymerization [12] and approximately 40% for the propylene polymerization [13]. Bohm [14] has supposed the possibility of application of 70% of all Ti atoms for the ethylene polymerization using titanium–magnesium catalyst in the propagating species. The composition of this catalyst is similar to that of Haward [11]. However k_p values coincide with those for the ethylene polymerization using common Ziegler catalysts [14].

Our k_p values for different monomers are significantly different, excluding propylene–butene-1 for system I. k_p Values which are different for a monomer polymerized on I and II catalytic systems indicate the relation of the reactivity of the propagating species and the chemical nature of the support. In this case the promoting action of MgO support was confirmed for ethylene polymerization using system I. This action was previously established when using supported catalysts with higher titanium content than in this paper [1].

The promoting influence of the support upon the reactivity of the propagating species follows from the comparison of k_p values for ethylene with catalytic system I (2440 ± 240 l/mol·sec) and for initial $TiCl_4-Al(C_2H_5)_3$ unsupported catalytic system. At 70°, k_p is 232 ± 12 l/mol·sec (molar ratio of Al/Ti = 1:1) [2].

The conclusion to be drawn from these results is that the number of propagating species on the surface of a supported catalyst depends only upon catalyst structure. The nature of the monomer does not significantly influence this number. These results are different from those of Yung and Schnecko for $TiCl_3 \cdot 0.3\ AlCl_3-Al(C_2H_5)_2Cl$ catalytic system for which the stationary concentrations of propagating species for ethylene–propylene–butene-1 series decreased, being 0.0102, 0.0047 and 0.0028 mol/mol Ti [15]. The proximity of C^{*}_{p} values obtained by us becomes clear if one takes into account the structural features of both studied catalysts. It was shown [4] that the effective radius of pores of MgO supported catalysts in the range of 60–1500 Å, S_{sp} is 20–30 m^2/g; those for Al_2O_3, SiO_2 supported catalysts are in the range of

Table 1. Kinetic features of propagating reaction for olefin polymerization using supported ziegler catalysts and some molecular parameters of polyolefins

NN	Monomer	C_M* (mol/l)	Yield (kg/g Ti)	k_{ef}^{max}, (l/mol Ti·sec)	C_p^x, (mol/mol Ti)	k_p, (l/mol·sec)	I_{st}	$\overline{M}_\eta \cdot 10^{-3}$	$\bar{v}_\eta \cdot 10^{-3}$†
Catalytic system $TiCl_4/MgO$ (contains 0.2% Ti)–$Al(C_2H_5)_3$ (**I**)									
1	C_2H_4	0.216	484.2	952	0.39 ± 0.02	2440 ± 240	—	2660	95
2	C_3H_6	1.20	6.7	1.60	0.33 ± 0.02	4.8 ± 0.5	7.3	68.5	1.6
3	C_4H_8	1.30	8.0	1.55	0.34 ± 0.02	4.6 ± 0.5	48.0	420	7.5
4	C_6H_{12}	1.50	6.0	0.91	0.36 ± 0.02	2.5 ± 0.3	not. det.	609.	7.3
Catalytic system $TiCl_4/Al_2O_3$, SiO_2 (contains 3.6% Ti)–$Al(C_2H_5)_3$ (**II**)									
1	C_2H_4	0.216	19.5	25.2	0.23 ± 0.01	110 ± 11	—	3035	108
2	C_3H_6	1.20	0.9	0.22	0.22 ± 0.01	1.0 ± 0.1	9.9	146.4	3.5
3	C_4H_8	1.30	0.2	0.026	0.20 ± 0.01	0.13 ± 0.01	58.3	460	8.2

* Monomer concentration of the reaction zone. † Average rate of polymerization.

Polymerization conditions: temperature 70°, solvent = n-heptane (0.1 l); concentration of solid catalysts = 0.2–0.8 g/l; concentration of $Al(C_2H_5)_3$ = 0.2–0.4 g/l; polymerization time = 2 hr.

80–90 Å and S_{sp} is 200 m^2/g. S_{sp} of $TiCl_4/MgO$ catalyst used here is 22.5 m^2/g therefore it is easy to calculate that the number of propagating species for 1 m^2 of its surface is $7.2 \cdot 10^{-7}$ mol for ethylene and $6.6 \cdot 10^{-7}$ mol for hexene. If the cross section of the polyhexene molecule is 100 Å^2 (we know that the cross section of the isotactic polypropylene molecule is ≃35 Å^2 [16]), it is easy to show that the total area of simultaneously propagating polyhexene macrochains does not exceed 40% of the surface of MgO supported catalyst. Allowing for this information and the dimensions of catalyst pores, it is possible to understand that in our case the difference of geometric dimensions of olefin molecules does not practically influence the concentration of propagating species during polymerization [15].

This difference is apparently caused by the propagation of polyolefin macrochains. It means that k_p decreases when ethylene is replaced by α-olefins as a result of the action of steric factors at the stage of formation of the π-complex of the olefin molecule and Ti atom included into propagating species. The absence of a large difference between k_p values for the polymerizations of propylene and butene-1 using system **I** is related to its low stereospecifity. Propylene has lower stereospecifity than butene-1. k_p Of isotactic polypropylene macrochains are known to be much higher than those of atactic polypropylene [13]. Our values mean higher selectivity of the supported catalytic systems for ethylene relative to α-olefins, compared with common Ziegler catalysts. k_p Values for the polymerizations of ethylene, propylene and butene-1 (e.g. $TiCl_3 \cdot 0.3\, AlCl_3$–$Al(C_2H_5)_2Cl$ system are 78.1, 18.0 and 7.3 l/mol·sec at 60° respectively [15]. For k_p we note that α-olefins are considered to be effective for polymerization because, compared to polyethylene, the resulting polyolefins swell at 70° and even partially dissolve in n-heptane which is used as solvent. As a consequence, the concentration of monomers at the propagating species can change. However this factor is not limiting because the shape of the polymerization kinetic curves using the selected catalyst (see Fig. 1) is identical for all olefins and it does not depend on the accumulated polymer in the reaction medium and on the increase of the viscosity of the system.

Table 1 shows that polyolefins with high $\overline{M}_\eta$ are prepared using supported catalytic systems. It is interesting to note that the change of $\overline{M}_\eta$ for the series polyethylene, polypropylene, polybutene and polyhexene prepared under similar conditions has a specific nature: $\overline{M}_\eta$ of polypropylene is sharply decreased compared to that of polyethylene and then $\overline{M}_\eta$ of polybutene and polyhexene are significantly increased. Further work is required for adequate interpretation of this result, particularly study of the molecular weight distributions of polyolefins. This information has been obtained by us only for polyethylene [1, 17] and polypropylene prepared using catalytic system **I**. Good agreement between $\overline{M}_\eta$ and $\overline{M}_w$ was established. For $\overline{M}_\eta = (50\text{–}70) \cdot 10^3$ the distribution factor is hardly changed and is 5.9. As far as the kinetic system for propylene polymerization is similar to that for ethylene, our experimental data allow us to determine the kinetic conditions for limiting reactions for polypropylene using $TiCl_4/MgO$–$Al(C_2H_5)_3$ and

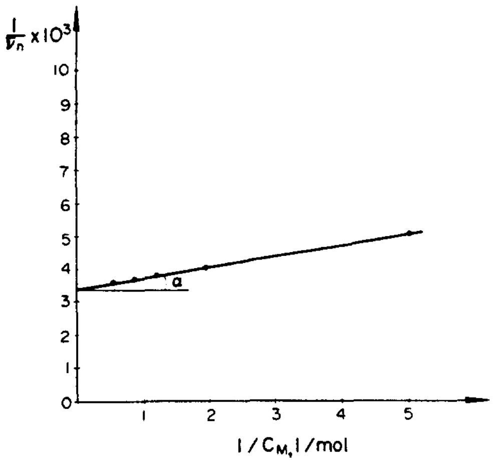

Fig. 3. The effect of monomer concentration on the number-average degree of polymerization of polypropylene using $TiCl_4/MgO–Al(C_2H_5)_3$ catalytic system. Concentration of $Al(C_2H_5)_3 = 0.2$ g/l, all other polymerization conditions are similar to those in Fig. 1.

to compare them with similar results for polyethylene [1]. The kinetic system for polymerization and the procedures for these calculations have been given in detail [1, 18]. In this paper we limit ourselves to the indication that the rate of chain transfer to triethyl aluminium (W_0^{Al}) was determined from the slope $N_{MPB}^{\Sigma} = f(G)$ curve 2, Fig. 2).

Rate constant (k_0^{Al}) was calculated using the equation:

$$W_0^{Al} = k_0^{Al} \cdot C_p^x \cdot C_{Al}^{1/2},$$

where C_{Al} is the concentration of triethyl aluminium in the reaction zone. The increase of metal-polymer bonds was related to the time corresponding to the initial stationary portion of kinetic curve 2 (Fig. 1, $\tau = 7$ min) for which the constant maximum concentration of the propagating species used for the calculation ($C_p^x = 0.33$ mol/mol Ti) is relevant. Chain transfer constant for propylene (k_0^M) was found from the intercept on the ordinate by the straight line expressing

$$1/\bar{\nu}_n = f\left(\frac{1}{C_M}\right),$$

where $\bar{\nu}_n$ is number-average polymerization rate (see Fig. 3), from

$$1/\bar{\nu}_n = \frac{k_0^M}{k_p} \left(\text{when } \frac{I}{C_M} = 0\right).$$

Rate constant for spontaneous disproportionation (k_0^{sp}) was calculated from the slope of the straight line of Fig. 3 using

$$\mathrm{tg}\alpha = \frac{k_0^{Al} \cdot C^{1/2} + k_0^{sp}}{k_p}$$

Rate constants for chain limiting reactions for the polymerization of propylene are shown in Table 2.

Table 2 shows that, for polymerization of propylene, the absolute values of k_0^M and k_0^{Al} are lower than those for ethylene (respectively 4.1 and 1.6 times). However although k_p for propylene is less than that for ethylene (≈ 500 times), sharp decrease of $\bar{M}_n$ is observed on going from polyethylene to polypropylene (see Table 1). The rate of spontaneous disproportionation for propylene polymerization remains significantly lower than those of other limiting reactions of macrochains. In this case k_0^{sp} for polypropylene is twice that for polyethylene. It indicates high lability of the Ti-C bond when the propylene part is connected with the Ti atom. It can be explained by the positive inductive effect of the methyl group of the propylene molecule.

Table 2. Kinetic features for chain limiting reactions in homopolymerization of ethylene [1] and propylene using $TiCl_4/MgO–Al(C_2H_5)_3$ system. Polymerization conditions are similar to those of Table 1.

No.	Monomer	$k_0^M \cdot 10^2$ (l/mol·sec)	$k_0^{Al} \cdot 10^2$ ($l^{1/2}/mol^{1/2}$·sec)	$k_0^{sp} \cdot 10^4$ (sec^{-1})
1	C_2H_4	6.64	2.30	4.4
2	C_3H_6	1.63	1.45	9.9

Acknowledgement—The authors express their gratitude to V. N. Sokolov who carried out radiometric measurements

REFERENCES

1. A. A. Baulin, V. N. Sokolov, A. S. Semyonova, N. M. Chirkov and L. F. Shalaeva, *Vysokomolek. Soedin.* **A17**, 46 (1975).
2. A. A. Baulin, M. A. Budanova, S. S. Ivanchev, V. N. Sokolov and B. V. Eropheev, *Dokl. Ak. Nauk SSSR* **247**, 1170 (1979).
3. N. M. Korobova, M. I. Leitman, E. Ya. Paramonkov, L. G. Stefanovitch, A. A. Baulin, N. M. Chirkov and A. S. Semyonova, *Plast. Massy* **N3**, 3 (1973).
4. A. A. Baulin, A. S. Semyonova, L. G. Stephanovitch, N. M. Chirkov and A V. Stapheev, *Vysokomolek. Soedin.* **A16**, 2688 (1974).
5. A. G. Rodionov, A. A. Baulin, A. L. Goldenberg, Yu. M. Zavialov, I. N. Andreeva and S. S. Ivanchev, *Plast. Massy* **N4**, 11 (1979).
6. I. Moraglio, *Chem. Ind.* **41**, 10 (1959).
7. S. S. Stivala, R. J. Valles and D. W. Tevi *J. appl. Polym. Sci.* **7**, 97 (1963).
8. F. C. Lin, S. S. Stivala and I. A. Biesenberger, *J. appl. Polym. Sci.* **17**, 1073 (1973).
9. G. Natta, P. Pino and G. Mazzanti, *Gazz. chim. ital.* **87**, 528 (1957).
10. A. A. Baulin, E. I. Novikova, G. Ya. Malkova, V. L. Maximov, L. I. Vyshinskaya and S. S. Ivanchev, *Vysokomolek. Soedin.* **A22**, 181 (1980).
11. R. N. Haward, A. N. Roper and K. L. Fletcher, *Polymer* **14**, 365 (1973).
12. D. G. Boucher, I. W. Parsons and R. N. Haward, *Macromolek. Chem.* **175**, 3461 (1974).
13. K. A. Gardner, I. W. Parsons and R. N. Haward, *J. Polym. Sci. Polym. Chem. Ed.* **16**, 1683 (1978).
14. L. L. Bohm, *Polymer* **19**, 553 (1978).
15. K. A. Yung and H. Schnecko, *Makromolek. Chem.* **154**, 227 (1972).
16. Yu. V. Kissin and N. M. Chirkov, *Eur. Polym. J.* **6**, 267 (1970).
17. A. A. Baulin, L. F. Shalaeva and S. S. Ivanchev, *Dokl. Ak. Nauk SSSR* **231**, 413 (1976).
18. L. A. Novokshonova, V. I. Tsvetkova and N. M. Chirkov, *Vysokomolek. Soedin.* **7**, 898 (1965).