

ROLE OF ORGANOMETAL AND MONOMER IN THE FORMATION OF ACTIVE CENTERS AT STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

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Kinetic scheme of polymerization of propylene catalysed by titanium trichloride-triethylaluminium system was worked out on the basis of literature data. It was proved experimentally that the rate of formation of active centers is high even at low temperatures and monomer concentrations. Active centers are probably formed by an interaction of catalytic components not requiring the presence of monomer; the product contains aluminium as an unremovable component of the system and exhibits a considerable catalytic activity even after repeated washing with the solvent. An increase in a number of active centers with triethyl aluminium concentration at low $[Al]/[Ti]$ ratios can be due to the shortage of the cocatalyst which is consumed by alkylation reactions of titanium trichloride. The efficiency of alkylations leading to the formation of active centers is, however, very low.

Since the discovery of Ziegler-Natta systems the structure of active centers and mechanism of their formation from the catalytic components has been continuously discussed in the literature¹. Some authors consider the alkylation of transition metal compound as a necessary condition for the formation of active centers²⁻⁵; the others ascribe their formation to chemisorption of the cocatalyst on the catalyst surface^{6,7}. Besides this, it has been shown that even if a seemingly simple catalytic system is used for the homopolymerization of an olefin it is necessary to consider simultaneous function of several types of active centers^{1,2}.

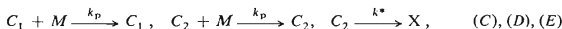
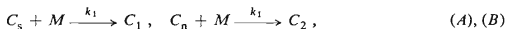
The aim of this study was to make a contribution for the elucidation of chemism of active centers formation. This should make the estimation of their number more reliable.

THEORETICAL

Let us assume, according to Keii and coworkers⁷, that the real active centers of polymerization are formed by an irreversible reaction between monomer and the equilibrium surface complex of titanium trichloride with an organoaluminium component (cocatalyst). In order to simplify the derivation of kinetic equations let us assume that we are working at such a high aluminium triethyl concentration that all potential centers on the surface of titanium trichloride form a complex with the cocatalyst. However, these potential centers formed on highly activated catalysts are not of the same quality. Certain part of them C_s (mol/mol $TiCl_3$), after complexation with the

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cocatalyst, form by reaction with monomer M so-called stationary active centers of polymerization; the number of which C_1 (mol/mol $TiCl_3$) does not change with time. The other active centers C_n (mol/mol $TiCl_3$) are transformed by the same reaction to so called nonstationary active centers of polymerization (C_2) which cease by a monomolecular (or a pseudomonomolecular) reaction forming product X . Furthermore, let us assume that all active centers of polymerization react with monomer in the propagation step and that this bimolecular reaction have the same rate constant (k_p in $mol^{-1} l min^{-1}$) for both type of centers; the reactivity of the polymerization active center therefore depends neither on its type nor on the polymer chain length connected to it. A simplified mechanism can be schematically described as follows: (the abbreviations are identical with the symbols used for the relative numbers of centers)



where k_1 represents rate constant of the transformation of potential centers to polymerization centers by reaction with monomer ($l mol^{-1} min^{-1}$) and k^* is the rate constant of deactivation of nonstationary polymerization centers (min^{-1}). By deriving and solving the corresponding differential equations for a constant monomer concentration, we obtain:

$$C_1 = C_{s,0}(1 - e^{-k_1 M \tau}), \quad (1)$$

$$C_2 = C_{n,0} \frac{k_1 M}{k^* - k_1 M} (e^{-k_1 M \tau} - e^{-k^* \tau}), \quad (2)$$

$$C = C_1 + C_2, \quad (3)$$

$$C/C_{s,0} = 1 - e^{-k_1 M \tau} + \frac{(C_{n,0}/C_{s,0})k_1 M}{k^* - k_1 M} (e^{-k_1 M \tau} - e^{-k^* \tau}), \quad (4)$$

$$\frac{dP}{d\tau} = k_p C c M, \quad (5)$$

where M is monomer concentration ($mol l^{-1}$); τ the time elapsed since the addition of monomer (min); C_2 the number of nonstationary active centers of polymerization (mol/mol $TiCl_3$); P the amount of monomer consumed by polymerization (mol) and c is the amount of titanium trichloride (mol); subscript 0 denotes the values at $\tau = 0$. The analysis of equation (4) shows that the number of active centers and subsequently also the polymerization rate in dependence on time proceed through a maximum which is defined by

$$\tau_{max} = \frac{\ln [k_1 M + (C_{s,0}/C_{n,0})(k_1 M - k^*)/k^*]}{k_1 M - k^*}. \quad (6)$$

For sufficiently long periods of time the number of polymerization centers attains the value $C = C_{s,0}$ and then the polymerization proceeds at a constant rate. Let us compare the scheme given before with the experimental results presented by Keii and coworkers⁷. These authors quote that the deactivation constant (k^*) is, especially at low temperatures ($< 57^\circ C$), practically independent of monomer concentration and reaches the value of about $0.026 min^{-1}$ at $44^\circ C$. Activation energy of deactivation is $2-3 kcal mol^{-1}$. From the time dependence of the rate

of polymerization at different monomer concentrations⁷ (M in mol l⁻¹) it is possible to calculate the rate constant of formation of polymerization centers ($k_1 = 0.51 \text{ mol}^{-1} \text{ l min}^{-1}$ at 44°C) and the ratio of the numbers of the stationary to nonstationary centers ($C_{s,0}/C_{n,0}$) being ≈ 0.35 . Activation energy of polymerization center formation given by the authors mentioned above is 9 kcal mol⁻¹. The experimental values of τ_{max} (min) quoted by Keii and coworkers⁷ for the polymerization in heptane at 44°C and the values calculated according to the equations and quantities quoted above are in good agreement (p_M denotes monomer pressure in Torr)

| | | | | | |
|----------------------------|-------|-------|-------|-------|-------|
| p_M | 300 | 380 | 450 | 560 | 660 |
| M | 0.189 | 0.240 | 0.285 | 0.350 | 0.415 |
| τ_{max} (exp) | 22 | 17 | 16 | 15 | 13.5 |
| τ_{max} (calc) | 21.8 | 18.5 | 16.4 | 14.3 | 12.7 |

If we use the above given values of activation energies then the equation (4) shows that with decreasing temperature and monomer concentration the time period needed for attaining maximum number of polymerization centers (τ_{max}) increases and simultaneously the maximum attainable number of polymerization centers ($C/C_{s,0}$)_{max} decreases. From the shape of curves it is evident (Fig. 1) that at higher temperatures and monomer concentrations the periods of increasing polymerization rate are so short that they may not be noticed if we employ the methods generally used for following these reactions. The problem of study of initial stages of polymerization can be solved in two ways: either by slowing down the polymerization rate by working at low temperatures and low concentration of reactants or by employing the methods suitable for following fast reactions. As it is indicated above, we have adopted the first possibility. The apparatus provided for the work at constant monomer concentration has not been used and all propylene was dosed at the beginning of reaction; this, in fact, made the evaluation of kinetic curves slightly more complicated. On the assumption that the polymerization is of first order with respect to monomer, it is necessary to use as a parameter characterizing the number of active centers—the ratio of polymerization rate and instantaneous monomer concentration or the slope of the time dependence of $\ln(M_0/M)$.

EXPERIMENTAL

Chemicals and Methods. Titanium trichloride; a commercial product of Toho Titanium Comp. (Japan), type TAC-141 (*Ia*) and of Stauffer Chem. Comp. (USA), type AA (*Ib*); the sample (*Ic*) was prepared in our Institute by reduction of titanium tetrachloride with hydrogen on tungsten spiral and ground in hydrocarbon medium under inert atmosphere in an Attritor type ball mill⁸; heptane suspension was used for polymerizations. Triethylaluminium (Sherring, BRD) containing about 95% of active component was used for polymerizations as a heptane solution. Gaseous propylene (Slovnaft, Czechoslovakia) was stored in a glass container sealed to a vacuum line. Eventual traces of water and oxygen were removed by passing it through a tube with a sodium mirror. Heptane was fractionally distilled, washed with sulphuric acid and with water to neutral reaction and then distilled with sodium; it was stored over calcium hydride in a glass container sealed to a vacuum line. Nitrogen was freed from water and oxygen by the standard procedure which secured that the concentration of each impurity did not exceed 10 p.p.m. The determination of titanium trichloride (*I*) and triethylaluminium concentrations in heptane was described earlier⁹. The determination of titanium and aluminium in their mixture was done photometrically¹⁰. Chlorine was determined argentometrically.

Apparatus and Procedure. Polymerizations were performed in a thermostated glass vessel, holding effectively 30 ml, joined to a high-vacuum line through a ground joint. Reaction mixture was stirred electromagnetically. An inlet to the vessel (through which the reaction vessel was evacuated or the solvent dosed) was provided with a glass valve for monomer dosing and with a three-way valve for dosing catalyst components and finally with a mercury pressure gauge which was designed to provide for keeping the volume of reaction vessel (including the vapour phase) during measurement constant. For experiments, in which I after interaction with triethylaluminium was washed with heptane, the reaction vessel was also provided with a vertical stainless steel tube; the lower end of which was generally above the level of reaction mixture. The upper part of the reaction vessel was equipped with a tombac bellow (the lift was about 5 cm) to which the stainless steel tube was joined. The bellow provided for a vertical lift of the tube under high vacuum. The assembled apparatus was evacuated for at least 1 h at 10^{-5} Torr. The required amount of heptane from the container was condensed at first to a graduated bulb and then to the reaction vessel. The solvent was cooled down to -78°C and the evacuated reaction vessel filled with purified nitrogen. Triethylaluminium solution and then the suspension of I were syringed into the reaction vessel. After that the inert gas from the cooled reaction mixture was removed by evacuation. The reaction vessel was brought to the required temperature and the catalyst components were let to react for a certain period of time; the reaction led to a slight increase of pressure as a result of gaseous products formation (predominantly ethane)^{9,11}. In the meantime the required amount of monomer was condensed at -78°C in a small calibrated tube and at a required moment, after opening an appropriate valve, was quickly distilled into the reaction volume. It was found that the gas-liquid equilibrium was established within 2 min from the time of monomer dosage. The monomer to polymer conversion was followed easily by measuring the pressure as in the concentration range of propylene used the partial pressure of monomer was a linear function of its amount. The experiments, at which I after interaction with triethylaluminium was washed with heptane, were performed in the following way: After a certain time of interaction the suspension was let to sedimentate; then most of the liquid phase was removed and approximately the same volume of solvent was distilled in and finally the contents were stirred. This procedure was usually repeated four-times. After these operations the catalyst was either analyzed for titanium and aluminium or used for the polymerization described above. Polymerization experiments at which monomer concentration was about 2.3 mol l^{-1} were carried out in dilatometers; the procedure was described earlier¹².

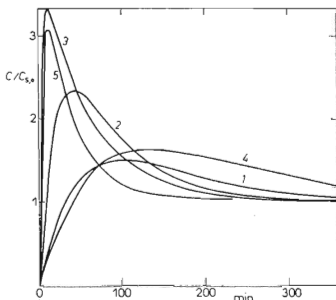


FIG. 1

Course of the Relative Number of Active Centers

M_0 (mol l^{-1}): 1 0.1; 2, 4, 5 0.35; 3 2.3; temperature ($^{\circ}\text{C}$): 1, 2, 3 15; 4 -10; 5 50. The curves were constructed by using the data published by Keii and coworkers⁷.

RESULTS AND DISCUSSION

Fig. 2 shows the dependences of $\ln(M_0/M)$ vs time for three types of activated titanium chloride (Ia, Ib Ic; see Experimental) at temperatures -10°C , 15°C and 50°C . If the polymerization is not controlled by diffusion of monomer to the catalyst surface, the slope decrease of these curves is a result of the decrease of the number of active centers. The dependence of the curve slope vs time reasonably obeys the equation

$$\ln(k - k_r)/(k_0 - k_r) = -k^*\tau,$$

(where k_0 , k and k_r are experimentally determined rate constants of polymerization at time 0, τ , and ∞ , respectively) described by Keii and coworkers^{7,13}. In contrast to the observation of the authors cited⁷ we have not observed the stage of increasing rate constant at the beginning of the polymerization which could be ascribed to a relatively slow formation of active centers; this was so even at low monomer concentra-

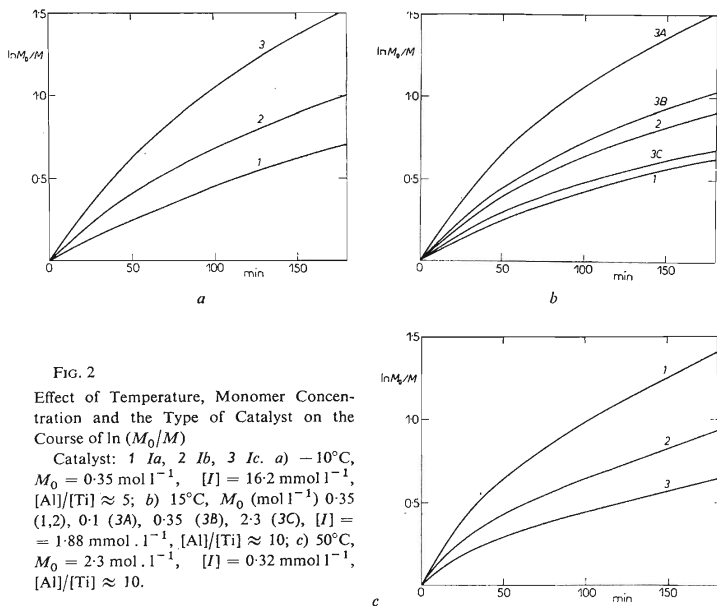


FIG. 2

Effect of Temperature, Monomer Concentration and the Type of Catalyst on the Course of $\ln(M_0/M)$

Catalyst: 1 Ia, 2 Ib, 3 Ic. a) -10°C , $M_0 = 0.35 \text{ mol l}^{-1}$, $[I] = 16.2 \text{ mmol l}^{-1}$, $[\text{Al}]/[\text{Ti}] \approx 5$; b) 15°C , $M_0 (\text{mol l}^{-1})$ 0.35 (1,2), 0.1 (3A), 0.35 (3B), 2.3 (3C), $[I] = 1.88 \text{ mmol l}^{-1}$, $[\text{Al}]/[\text{Ti}] \approx 10$; c) 50°C , $M_0 = 2.3 \text{ mol l}^{-1}$, $[I] = 0.32 \text{ mmol l}^{-1}$, $[\text{Al}]/[\text{Ti}] \approx 10$.

tions as can be seen in Fig. 2b, curves 3A–C. Different courses of the last mentioned curves are discussed below. Our results demonstrate that the active centers are most likely formed by an interaction of catalytic components – titanium trichloride (*I*) and triethylaluminium – without the participation of monomer. This interaction is, in the temperature range studied, sufficiently fast. The explanation given by Mezhi-kovskij and coworkers^{14,15} can be accepted as one of the possible explanations of the accelerated stages of the polymerization observed by the authors mentioned. These authors found that even in the presence of traces of water (or alcohol) an inhibition period of polymerization was observed. The length of inhibition period increased with the amount of these polar compounds.

Approximate values of activation energies of polymerization were calculated from initial rates of polymerization (Fig. 2). The values depend on the type of *I*: for *Ia* – 15.2; *Ib* – 11.9 and for *Ic* – 10.0 kcal mol⁻¹ were calculated. It can be seen that activation energies for *Ia* and *Ib* are distinctly higher. If we assume that the active centers are formed by interaction of catalytic components, then the numbers of active centers should increase with temperature as a result of increasing conversion of exchange reaction^{9,11}. This increase has been confirmed by the majority of studies^{16–18} based on radiochemical determination of the number of metal–polymer bonds; on the other hand also the opposite information can be found in the literature^{19,20}. If in the course of interaction of *I* with triethylaluminium the catalyst crystal lattice is partially destroyed^{9,11} it can be expected that the presence of aluminium trichloride will ease this destruction. Aluminium trichloride can be transformed by a reaction with the cocatalyst to a soluble form (ethylaluminium dichloride or diethylaluminium chloride) and the place of its location can become a source of further destruction of titanium trichloride crystal lattice leading to the formation of active centers. Therefore the presence of aluminium trichloride may manifest itself in a steeper dependence of the number of active centers on temperature. Of course, it can not be ruled out that the activation energy of propagation will be different for different types of *I*.

If the polymerization is of the first order with monomer, as it is generally accepted, then the rate constant of polymerization referred to unit amount of titanium trichloride should be independent of monomer concentration. However the slopes of curves 3A–C in Fig. 2b, recalculated for unit amount of titanium trichloride, tend to decrease slightly with increasing monomer concentration. But on the other hand the rate constant of deactivation of nonstationary active centers (k^*) is independent of the monomer concentration; this is in good agreement with the results given by Keii and coworkers⁷. This also indicates that the polymerization is chemically controlled. One of the possible explanation is that the propagation reaction is two-step reaction as it is assumed by the number of authors¹. The first step is the reversible formation of π -complex on a titanium vacancy of an active center and the second is the insertion of monomer into the transition metal–carbon bond. If we assume that the rate determining step is the intramolecular insertion, then the polymerization can be of first order reaction with monomer only if equilibrium constant of π -complex formation is extremely low and therefore the occupation of vacancies on titanium by monomer negligible. This may not be so at low temperatures and higher monomer concentrations and therefore noticeable deviations from the first order

reaction with respect to monomer may be observed. Experimental confirmation of this hypothesis will, however, need further measurements. If the cocatalyst chemisorption on the catalyst surface takes place, then this phenomenon, at low organometal concentrations, manifests itself in an increase of polymerization rate with cocatalyst concentration. If organometal concentration is high enough a constant rate is attained. Even if this mechanism can not be ruled out, especially at systems comprising cocatalyst of low alkylation power²¹ (e.g. ethylaluminium dichloride, diethylaluminium chloride), it seems to be proved that alkylation of a transition metal compound is a necessary step in the process of active center formation at systems comprising cocatalyst of high alkylation power (triethylaluminium). If we do not consider a possible presence of impurities which could effect the shape of the polymerization rate *vs* organometal concentration dependence, it is possible to put forward an alternative explanation of the increase of polymerization rate with organometal concentration: At highly activated catalyst, the conversion of the exchange reaction (substitution of chlorine in *I* for an alkyl from organometal), when using triethylaluminium, is unusually high. Thus at *Ic* if an excess of triethylaluminium is used¹¹ then up to 20% of total chlorine is replaced. If we assume, in accordance with Rodriguez and coworkers²², that two equivalents of triethylaluminium are consumed for each exchange reaction, then in order to attain maximum conversion of the substitution reaction the $[Al]/[Ti]$ ratio of at least 1.2 would be needed. At lower ratio values only a partial utilisation of active center should be obtained and, in addition to it, most of the organometal should be transformed to diethylaluminium chloride which is formed as a second product of the exchange reaction and makes the catalytic system substantially less active than the system comprising triethylaluminium. With increasing cocatalyst concentration the polymerization rate should increase as long as the system does not contain free triethylaluminium; this is in accord with experimental data presented by Keii and coworkers⁷. These authors also observed that at high polymerization temperatures a higher organometal concentration is needed in order to attain maximum polymerization rate. They explain this by a reversible sorption of triethyl aluminium on the titanium trichloride surface (Langmuir's type of chemisorption). The observed dependence can also be explained by an increase of conversion of the exchange reaction with temperature^{9,11} and therefore the required amount of organometal is higher.

Some of the conclusions made by Rodriguez and coworkers²² concerning the composition of solid phase after interaction of *Ic* with triethylaluminium were checked. It was found that after 2 h interaction at 50°C using $[Al]/[Ti] = 3$ with subsequent washing of a solid product of interaction the ratio Ti : Al was 1.00 : 2.52 : 0.28. The ratio of exchanged chlorine to fixed aluminium is 0.58; this value is, however, distinctly lower than that given in ref.²², but it agrees within one order with expected value 1.0. The amount of aluminium given before changes very slightly during additional washings which may indicate irreversible fixation of aluminium. After 2 h of interaction at 15°C using $[Al]/[Ti] \approx 10$ the solid phase was four-times washed with heptane and it was found that the value of initial polymerization rate was half of that when no washing was applied.

It is difficult to determine the concentration of free triethylaluminium left in the system. The calculation shows that the molar ratio of aluminium triethyl in the liquid phase to the total titanium should not be higher than 0.01. This finding can be taken as an argument that in the course of interaction an irreversible reaction between a potential active center and the organo-metal takes place, otherwise this system (practically without organometal) should exhibit an insignificant polymerization activity.

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REFERENCES

1. Boor J., jr: *Macromolecular Reviews*, Vol. 2, p. 115. Interscience, New York 1967.
2. Rodriguez L. A. M., van Looy H. M.: *J. Polymer Sci. A-1*, 4, 1951, 1971 (1966).
3. Arlman E. J., Cossee P.: *J. Catal.* 3, 99 (1964).
4. Kissin J. V., Mezhevikovsky S. M., Chirkov N. M.: *European Polymer J.* 6, 267 (1970).
5. Kissin J. V., Chirkov N. M.: *European Polymer J.* 6, 525 (1970).
6. Schnecko H., Reinmöller M., Weirauch K., Bedjagin V., Kern W.: *Makromol. Chem.* 73, 154 (1964).
7. Keii T., Soga K., Saiki N.: *J. Polymer Sci. C* 16, 1507 (1967).
8. Kummer M., Kazda A., Zlámal Z.: *Chem. průmysl* 20, 362 (1970).
9. Mejzlík J., Kvíz M., Přibyl M., Veselý K.: *Chem. průmysl* 15, 85 (1965).
10. Novák K., Mika V.: *Chem. průmysl* 7, 360 (1963).
11. Kokta B.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1967.
12. Ambrož J.: *This Journal* 24, 3703 (1959).
13. Keii T.: *Nature* 196, 160 (1962).
14. Mežikovskij S. M., Kissin J. V., Čirkov N. M.: *Vysokomolekularnyje Sojedinenija Ser. A* 9, 1243 (1967).
15. Mežikovskij S. M., Kissin J. V., Čirkov N. M.: *Vysokomolekularnyje Sojedinenija Ser. A* 9, 2006 (1967).
16. Bier G.: *Makromol. Chem.* 70, 44 (1964).
17. Lehmann G., Gumboldt A.: *Makromol. Chem.* 70, 23 (1964).
18. Kohn E., Schuurmans H. J. L., Cavender J. V., Mendelson R. A.: *J. Polymer Sci.* 58, 681 (1962).
19. Chien J. D. W.: *J. Polymer Sci. A* 1, 425 (1963).
20. Tanaka S., Morikawa H.: *J. Polymer Sci. A* 3, 3147 (1965).
21. Ingbergman A. K., Levine I. J., Turbett R. J.: *J. Polymer Sci. A-1*, 4, 2781 (1966).
22. Rodriguez L. A. M., Van Looy H. M., Gabant J. A.: *J. Polymer Sci. A-1*, 4, 1917 (1966).

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