

Active Centers of $TiCl_3$ Catalysts for Propene Polymerization

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Summary

Publications reporting numbers of active centers in $TiCl_3$ propylene polymerization catalysts are very contradictory. Experimental data from the beginning of the sixties are reevaluated by the author. It is concluded that $TiCl_3$ -catalysts from the Hoechst type (and probably from the Stauffer AA-type) have, after an initial period of polymerization, numbers of active centers in the range of percentage of total $TiCl_3$. This value increases with temperature. By cooling during polymerization some metal polymer bonds, probably active centers, disappear.

Conversion versus time and molecular weight versus conversion for propene polymerization

20-25 years ago we studied the polymerization of propylene with the so called Hoechst catalyst¹⁾. This catalyst system is described in patents and shortly in scientific publications of Hoechst^{1,2)}. The preparation of this catalyst has the following steps:

Reaction of $TiCl_4$ with Al-organic compounds (preferably $AlEt_2Cl$ or $Al_2Et_3Cl_3$) at low temperature for several hours. Aging of the precipitate at temperature above $80^\circ C$. This violet $TiCl_3$ catalyst is combined with $AlEt_2Cl$. For details see the patents²⁾, also ³⁾.

The Hoechst catalyst is a modified Ziegler catalyst, especially developed for propylene polymerization. This catalytic system has been used by some big polypropylene producers. In the past this catalyst system had the greatest economic importance under all propylene polymerization catalysts. With the Hoechst catalyst diethyl-aluminium-monochloride was introduced in a commercial process for the first time. In a recent publication by PINO and MÜHLHAUPT⁴⁾ entitled "The stereospecific polymerization of propylene. A survey 25 years after discovery" the chapters 2 and 3 were devoted to the catalyst development. In these chapters many catalysts, papers, patents were mentioned except the important Hoechst catalyst.

Many scientists working at university and industry laboratories, at first NATTA⁵⁾, describe time-conversion curves for propylene polymerization⁶⁻¹³⁾. Most assume that the rate of polymerization is linearly proportional to the number of active centers. Increase of rate means increase of number of active centers, decrease of rate means decrease of that number. We doubted this idea and felt that some physical effects also contribute to the rate. For instance we argued that the decline of rate in Fig. 1 could be the consequence of reduced monomer concentration at the catalyst surface with increasing conversion and/or reduced mass transfer to the catalyst.

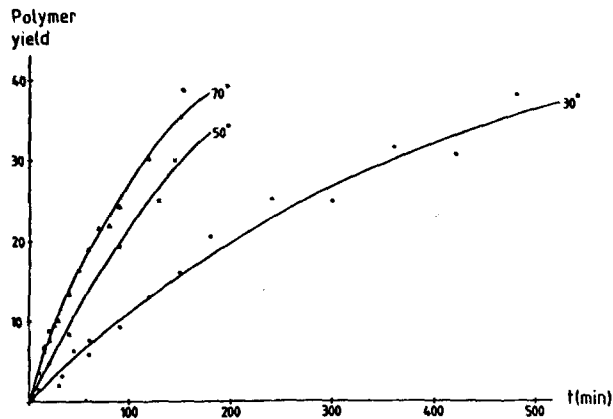


Fig.1: Polymer yield (rel. units) versus time for 30, 50 and 70°C polymerization temp.

If physical effects are not the cause for the decline we have to assume a decrease of the numbers of active centers during polymerization or decrease of activity. We have pointed out that in contrary to the early publications from the NATTA school the molecular weights of polypropylene depend strongly on conversion and polymerization temperature (Fig.2), experiments with the Hoechst catalyst.

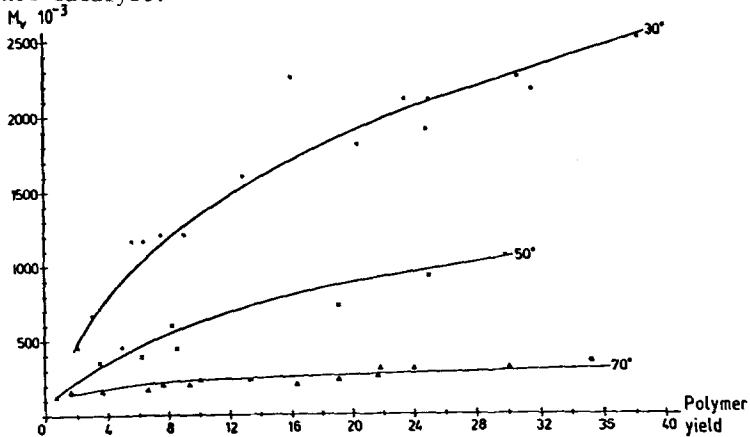


Fig.2: Viscosimetric molecular weight versus polymer yield

The dependence is low at 70°C and strong at 30°C. The author interpreted this strong dependence of molecular weight on conversion by assuming that the formation of a polymer molecule takes a long time. Further he assumed that during polymerization new active centers are formed and chain transfer reactions are not important. This last statement obviously was correct only to some extent.

All the data shown here are won with a relatively high catalyst concentration: 2,5 mMol TiCl_3 /100 cm and 5 mMol AlEt_2Cl /100 cm.

Metal polymer bonds (MPB) and active centers

It is possible to get more exact informations on the kinetics of polymerization by determination of the number of active centers and also by determination of metal polymer bonds (MPB). During the fifties and sixties only

the number of MPB could be determined. Since 1972 it is known by ERMAKOV and ZAKHAROV¹⁴⁾ (Institute of Catalysis, Novosibirsk Siberian branch USSR, Academy of Sciences), that certain compounds as CO, CO₂ only or preferably react with titanium organic compound but not or only very slowly with aluminium organic compounds. This method, with ¹⁴CO and ¹⁴CO₂, was applied for the determination of active centers by these authors together with several co-authors from the Novosibirsk group in successive publications with experimental and theoretical content¹⁴⁾.

By a combination of the method of the Novosibirsk authors and the well known MPB determination it should be possible to gain real insight into the polymerization reaction. Unfortunately not many combined data are available. We found only a single curve in ¹⁴c), Fig. 1, page 104, where it is shown by 3 points, that the number of active centers is constant during polymerization in the range of 1 pro mille.

Because some of the data of the Novosibirsk authors obviously did not agree with our work from the beginning of the sixties, the author has reevaluated the data on MPB-determination. In Fig. 3 the development of MPB during polymerization in dependence of polymer amount is shown.

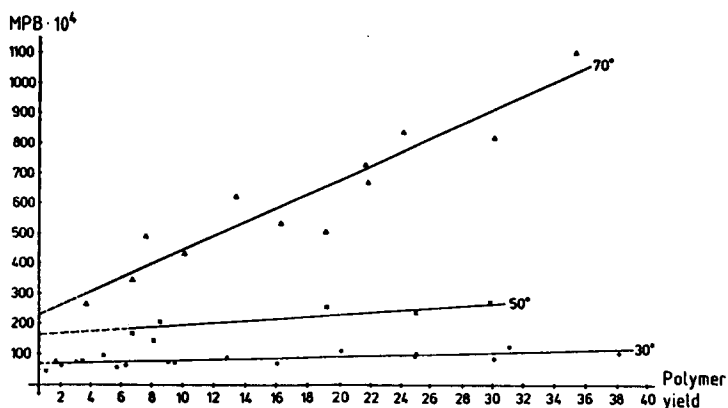


Fig.3: MPB development during polymerization

In the beginning of the curve the experimental data are scattering strongly. This can be attributed to the fact that in the first minutes the catalyst with active centers is built up and that it was not looked carefully enough on the reproduction conditions in this starting phase. After this phase the development of MPB obviously proceeds linearly with polymer amount. The increase is strong at 70°C and low at 30°C. By extrapolating conversion towards zero one gets numbers of MPB which very probably correlate to the numbers of active centers in the catalyst - with exception of the starting phase. These numbers correspond to a percentage of active centers of the TiCl₃ at 30°C of about 2-2,5%, at 50° of about 6%, at 70° of about 8-9%. These numbers are not too exact. There is no doubt, however, that there is a temperature dependence. These numbers include all active centers, tactic and atactic centers. We learn from Fig. 3 that with increasing polymerization temperature the number of active centers increase as well as the chain transfer reactions. Both influence the molecular weights.

In a publication of the Novosibirsk team^{14a)} Fig. 2a, the MPB conversion values meet at low conversion and point on the pars pro mille range. The 30° curve is located between the 50 and 70° curve which seems not to be very probable. However the authors used the TiCl₃-AlR₃-catalyst. In case of

$AlEt_2Cl$ containing catalysts the Novosibirsk authors confirm the temperature dependence of this catalyst type. The exact values for the active centers are shown in Table 3 of ¹⁴g). These values are two orders of magnitudes lower than our values. The Novosibirsk authors regard the temperature dependence as a consequence of adsorption equilibria of al-R compounds on solid catalyst¹⁴ⁱ). This interpretation seems to be questionable. On the improvement of the CO method V. WARZELHAN (BASF) and others are working¹⁵). These authors found that the experimental procedure of the Novosibirsk authors result in too low active center numbers and too high rate constants.

Ratio of the number of MPB to the number of active centers

In several publications the cited authors argue¹⁴) that the number of MPB is one or two orders of magnitudes higher than the number of active centers. It seems to be quite clear, however, from Fig. 3 that each conversion point and each temperature has a different ratio MPB active center. This ratio is not constant. In one publication the Novosibirsk authors¹⁴ⁱ) mention that the percentage of polypropylene molecules based on chain transfer is 4-10% and 5,5-13% of all molecules. This is a very low figure. The author assumes this is concluded from a very early stage of polymerization. In the same paper it is stated: "The numbers of MPB at polymer yield 100 g/g Ti are one to two orders higher than the number of propagation center Cp^* determined by using ¹⁴CO". If we look on Fig. 3 we find that at 100 g polymer per g titanium the MPB at 30 and 50°C -this is in the middle of the curve- are near to the number of active centers and that at 70°C the MPB number is triple of the active center number. If we use lower amounts of catalyst for the same polypropylene amount, the ratio MPB to active centers is higher because we shift to right in Fig. 3. Ratio MPB/number of active centers depends essentially on the catalyst, on number of Cp^* , on conversion and on polymerization temperature.

Change of temperature during polymerization

The Novosibirsk authors say that by changing polymerization temperature during a run one reaches the rate reproducibly and fast according to the corresponding temperature. The Russian authors used catalyst systems based on $TiCl_3.AlR_3$. These results are not in accordance with our earlier results, where we used a catalyst system on the $TiCl_3.AlR_2Cl$ base (Hoechst catalyst). We found that by starting polymerization at high temperature (70°C) -making more active centers- and cooling to lower temperature one gets a higher polymerization rate than with a original low temperature run. However this high rate does not stand for the whole run but decreases gradually to the value of the original temperature run. See Fig. 4:

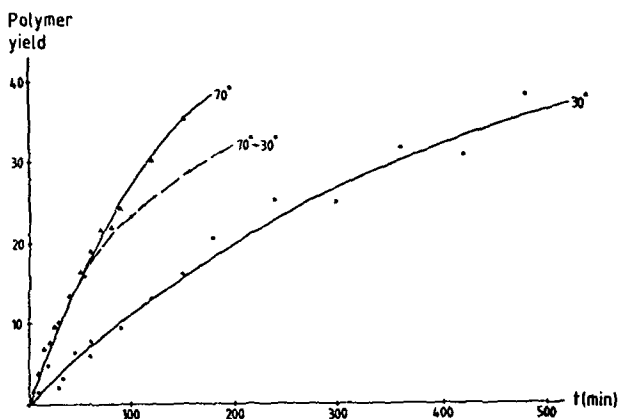


Fig. 4: Polymer yield versus time and temperature

If we discuss the MPB development in the series with different polymerization temperature we find a slow decrease of the number of MPB. This means that metal polymer bonds disappear, Fig. 5:

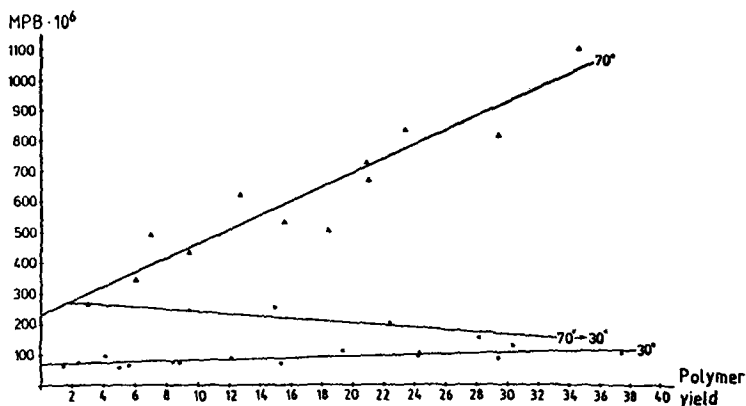


Fig. 5: MPB versus time and temperature

Discussion of the active centers, MPB and rate

The rate of propylene polymerization is highest in the beginning in spite the fact, that the active centers are not fully developed. Eventually we have highly active centers in this phase as shown by BÖHM¹⁶⁾ for an ethylene catalyst. Centers of different activities for polypropylene are described by WARZELHAN et al¹⁵⁾.

If one assumes that the extrapolation as shown in Fig. 3 gives the number of active centers and that after the beginning period no additional active centers are built up during the polymerization, the difference between active center and MPB are the molecules with Al-organic end groups, formed by chain transfer reaction of the Ti-polymer with the co-catalyst. This chain transfer is low at 30° and higher at 70°C, but not extremely high. At the end of the polymerization at 70° we have 4 Al-organic MPB per 1 titanium MPB according to this interpretation. It seems that chain transfer is connected with the propagation.

JUNG and SCHNECKO also showed a MPB versus conversion curve^{7k)} for propylene polymerization at a temperature of 60°C (Stauffer TiCl₃AA catalyst). If we recalculate this curve for our diagram, we find that the second part of the JUNG and SCHNECKO curve (higher conversion) fits exactly with our diagram. The first part of the curve, however, cuts our curves. JUNG and SCHNECKO conclude that the number of active centers at 0,5% and the additional MPB formed during the reaction are attributed only to chain transfer reactions. They explain the shape of the curve by a high chain transfer reaction in the beginning and a low one in the second part of polymerization. The author likes to offer another interpretation for the JUNG and SCHNECKO-results in the first part of the curve: The catalyst and its active centers are developed in the first phase beginning from 0,5%, and the additional MPB mean both, new active centers and chain transfer reactions. In the second part of the curve the catalyst is developed and we get the same informations as in our runs, namely the development of new Al-polymer¹⁰⁾ bounds as consequence of chain transfer reactions. COOVER and co-author¹⁰⁾ also interpreted the strong increase of MPB in the starting phase of polymerization by chain transfer reaction only.

The author's interpretation has as consequence that we have an increase of active centers in the starting phase of polymerization and that the Hoechst catalyst has active centers in the range of some percent of total TiCl₃ and that the Stauffer AA catalyst reaches the same percentage after a development phase.

It is very improbable, that Al-polymer bonds are disappearing. Therefore, we have to attribute the reduction of MPB in Fig. 5 on the reduction of titanium organic bonds. 1962 it was quite a new experimental fact that during polymerization metal polymer bounds are disappearing. It is well known that titanium organic bounds are not stable. Lowering the polymerization temperature we eventually have an increase of crystallinity of polypropylene which is connected with a mechanical stress on the catalyst-polymer bond inducing a rupture of the bond.

Growing time of polypropylene molecules

NATTA first has calculated the growth time of a polypropylene molecule. In different papers he presented slightly different values. In his extensive paper on kinetics^{5d)} he gave values from 5-12 minutes depending on conditions. The author has estimated higher growth times¹⁾ -hours for instance from the strong increase of molecular weight during polymerization, especially at temperatures of 50 and 30°C. However he did not give exact values, COOVER et al.^{10b)} estimated a growth time of seconds (70°C), CAUNT⁹⁾ of 12 minutes (60°C), JUNG and SCHNECKO of 10 minutes (60°C), CAUNT from BIER publications of 30 minutes and 1,2 hours (at 50°C), CHIEN⁸⁾ of 410 minutes (30°C), INGBERMAN and others "as long as polymerization run" (40°C). If the interpretation of Fig. 3 is correct -extrapolation of conversion zero means number of active centers and the higher values mean chain transfer reactions- it should be possible to calculate the growth time. In Fig. 3 MPB against conversion linear curves result. If MPB is plotted versus time, the system is more complicated, because the MPB-time curve is not linear, it is declining with time. This probably is just the effect of lowering the polymerization rate with conversion. Therefore the growth time of the single molecules is increasing with polymerization time. If this is true, the growth time of molecules is not constant in the kinetic scheme.

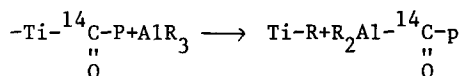
TANAKA and MORIKAWA¹⁷⁾, JACOBSEN and others¹⁸⁾ calculated the growth time of polypropylene at different temperatures. For the temperatures 30°, 50°, 70°C TANAKA found for 3 hours polymerization time the following growth times 226 min., 49 min., 25-30 min. YACOBSEN found for the same temperatures the growth times^{5h)}, 2-3^{h)}, slightly over 1 hour. The values are in agree-

ment with Fig. 3, where the sum of tactic and atactic centers is given. TANAKA and MORIKAWA found an increase of life time with polymerization time. This effect is explained above.

Termination of growth of the molecules by BH-abstraction is an additional factor. Some authors^{6,7i)} estimate, that about 10% or less of all polypropylene molecules have endgroups formed by BH-abstraction. It means this influence is smaller than the transfer by al-R compounds.

Open questions

The author tried to show that -in spite of more than 25 years research- still a number of questions in connection with the $TiCl_3$ catalysts for propylene polymerization is open. However, a lot of these uncertainties probably can be solved by systematic studies on the development of the active centers during polymerization. For instance, it is an open question whether the number of active centers after the initiation period remains constant or increases or decreases. The correct application of the ^{14}CO method should be able to answer this question. MEJZLIK and LESNA¹⁹⁾ opposed the applicability of the CO method of the Novosibirsk authors, because after stopping with CO the polymerization continues after removal of CO. The Novosibirsk authors^{14k)} explained this second polymerization by a kind of regeneration of catalyst according the equation



which means producing a new active center. Do we need such an explanation? Is it not plausible to assume that the CO attacks only the small number of active centers (in the Russian publication in the $0/00$ range of $TiCl_3$) and that the more than 99% untouched $TiCl_3$ and at least the same amount of non touched Al-organic compound are in the position to build up new active centers? This question is accessible to the experiment too. Do we have active centers of different activities? Does activity of a single center change during polymerization? Are active centers built up during polymerization and do they decay?

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