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Active Centers of $TiCl_3$ Catalysts for Propene Polymerization[1] Answer to Bukatov et al.[2] Pol. Bull. *11*, 91–92, 1983

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Extrapolating the linear part of the MPB-conversion towards zero conversion we [1] have found between 30 and 70°C polymerization temperature active centers 2 - 8.5 % of total Ti. For 60° C about 7 % are concluded. These numbers mean total activity (tactic + atactic centers). The same extrapolation method has been applied to experimental values of JUNG and SCHNECKO [3]. Active centers in the same region result. The latter authors have used slightly different catalysts systems. The developed $TiCl_3$ catalyst exhibits active centers within the percentage range. This author did not apply the mentioned extrapolation method in his earlier papers. The percentage figure is in contrast to the 1 ‰ active centers figure of the Novosibirsk authors [2]. These authors have determined the number of active centers by the ^{14}C method [4]. WARZELHAN et al. [5] have modified this method. They found 1.2 % active centers. WARZELHAN applied the same system like JUNG and SCHNECKO. The same catalyst system also has been applied in the work of the Novosibirsk authors. In their remarks BUKATOV et al. don' t mention this 1.2 % result. This 1.2 % figure can be raised considerably by activation of the catalyst (private communication). WARZELHAN has determined only the active centers for the tactic polymer. Therefore his figure has to be smaller than the numbers of BIER. Considering this there is a good agreement between the the numbers of BIER and WARZELHAN.

The Novosibirsk authors as well as COOVER et al. [6] find intensive chain transfer reactions even at low conversions of the polymerization runs. We establish, hovever, only minor chain transfer at low conversions. The steep increase of molecular weight especially in the starting phase of polymerization is not in concordance with an intensive chain transfer reaction. MPB is the sum of active centers and of inactive metal-polymer bounds. COOVER probably has attributed too many of the total MPB to the inactive molecules, which means to chain transfer reaction.

NATTA et al. [7], in their first publications, mainly worked with the system $TiCl_3(H) + AlR_3$. They concluded that $TiCl_3$ is a typical inorganic catalyst with a fixed number of active centers, which do not change during polymerization.

Growth starts from Al-R compound. This assumption has to be revised. $TiCl_3$ is altered chemically in two ways at least. It is alkylated and reduced partially by the AlR_3 compound. The reduction is accompanied probably by a loss of MPB - and active center -, in analogy to the well known reaction $RTiCl_3 \rightarrow TiCl_3$ + hydrocarbon. We have described [1] that under special conditions a certain loss of MPB results, which has been explained by a loss of active centers. BUKATOV et al. [2] have commented this observation as not worth serious discussion. They claim no change of active centers when increasing or lowering the polymerization temperature. Apparently, NATTA's statement that $TiCl_3$ catalysts do not change still is accepted by them.

We don' t know exactly the increase of active centers at the start of the polymerization. Some of them may be occluded in the bigger catalyst particles, and they may get free in the dispersion phase. Dispersion of catalyst into smaller particles has been described several times. Eventually, new Ti-R groups are built up during polymerization. It has to be considered also that propylene oligomers resulting from $Ti(C_3)_nR$ are lost after treatment with the radioactive stopping agent, with a consequent loss of MPB or active centers. Such loss may be higher relatively at low conversion.

Newer publications on high-activity $TiCl_3$ carrier catalysts clearly show that different catalysts exhibit different rate constants and that the number of active centers may decrease drastically during reaction.

We are convinced that all known important $TiCl_3$ based catalysts for propylene polymerization are dynamic rather than static systems, with inclusion of the Al-organic compounds. The individual catalysts are changing during polymerization.

Some experimental mistakes may be included in our data. However, the bulk of our results on $TiCl_3$-AlR based propylene polymerization did not agree with the experimental results as well with the conclusions of the Novosibirsk authors in the same field. Their idea of direct determination of active centers was excellent. Because of the clear discrepancy of the mutual results our paper [1] has been published, and it has been presented at the Makromolekulares Kolloquium 1982 in Freiburg. WARZELHAN et al. have demonstrated that the original method of the Novosibirsk authors is not satisfactory. The improved method yields conclusive results.

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