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# Active Centers of $TiCl_3$ Catalysts for Propene Polymerization Comments to G. Bier, Pol. Bull. *7*, 177–184 (1982)

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It is stated by BIER in his paper (1982) that using $^{14}CO$ we obtained understated values of the number of active centers ($C_p$) and, consequently, overstated values of the propagation rate constants ($K_p$). Earlier we published (BUKATOV et al. 1977) a number of arguments in favour of the quantitative determination of $C_p$ with the help of $^{14}CO$. We may add the following.

1. High values of $K_p$ obtained with the use of $^{14}CO$ (BUKATOV et al. 1982) for titanium-magnesium catalysts for propene polymerization are in good agreement with those obtained on the base of the data on polymer molecular mass in a short time of polymerization (5s)(SUZUKI et al. 1979; SHEPELEV et al. 1981; KASHIWA and YOSHITAKE, 1982).

2. Modification of the method for determination of $C_p$ using $^{14}CO$ and $^{14}CO_2$ (WARZELHAN et al. 1982) only 2-3 times increases $C_p$, while our data on $C_p$ values are two orders higher than those of BIER (1982).

3. BIER's data on $C_p$ (8-9 % of titanium content) considerably exceed those obtained by COOVER et al. (1966), JUNG and SCHNECKO (1972)(less than 1% of titanium content) with the same method of polymerization quenching by radioactive alcohol. BIER explains these differences by the use of different catalysts. The catalyst $TiCl_3$(AA) used by JUNG and SCHNECKO (1972) is claimed to develop in the beginning phase longer than the Hoechst catalyst ($TiCl_3$(H)) used by BIER. So, according to BIER, the correct determination of $C_p$ is to be made after the catalyst development phase from the linear dependence of the number of metal polymer bonds (MPB) on polymer yield (G) in the range of sufficiently high G, rather than in the region of low G, as it was made by COOVER et al. (1966), JUNG and SCHNECKO (1972). Such a supposition of BIER is not in accordance with his own data (BIER et al., 1962) obtained for catalyst $TiCl_3$(H) and NATTA's catalyst $TiCl_3$(N). The latter is obtained by reduction of $TiCl_4$ with hydrogen and has a longer development phase compared to $TiCl_3$(AA), and especially to $TiCl_3$(H). However, it does not correspond to the data of BIER et al. (1962)(Fig.).

It should be noted that such a dependence of the MPB number

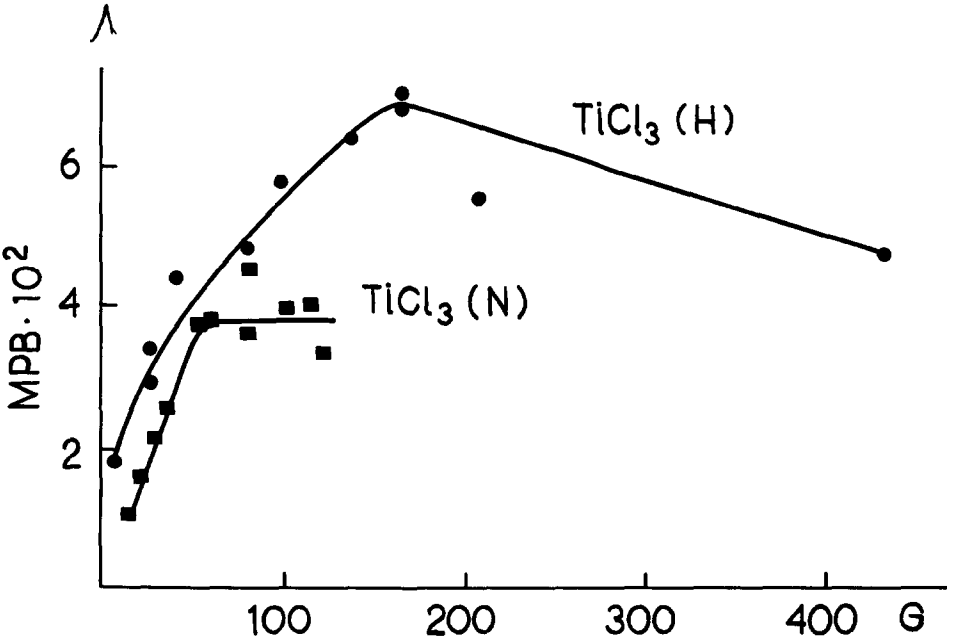


Fig. MPB (mol/molTi) versus G (gPP/gTi) plotted by us according to data of BIER et al. (1962)

on G (with a sharp curvature up to MPB number decrease) is hard to be accounted for. It was observed by nobody, but BIER, and is likely to be caused by some methodic drawbacks. On this account, the found by BIER (1982) MPB disappearance during polymerization is not worth serious discussion.

4. BIER was not quite exact when discussing Fig. 2a in BUKATOV et al.(1977). We attribute the fact that the curve at 30°C is above the curve at 50°C to the different values of Kp at 30 and 50°C.

BIER, G., HOFFMANN, W., LEHMANN, G. and SEYDEL, G.: Macromol. Chem. 58, 1 (1962)
BIER, G.: Polymer Bulletin 7, 177 (1982)
BUKATOV, G.D., CHUMAEVSKII, N.B., ZAKHAROV, V.A., KUZNETSOVA, G.I. and YERMAKOV, Yu.I.: Makromol. Chem. 178, 953 (1977)
BUKATOV, G.D., ZAKHAROV, V.A. and YERMAKOV, Yu.I.: Makromol. Chem. 179, 2097 (1978)
BUKATOV, G.D., SHEPELEV, S.N., ZAKHAROV, V.A., SERGEEV, S.A. and YERMAKOV, Yu.I.: Makromol. Chem. 183, 2657 (1982)
COOVER, H.W., GUILLET, J.E., COMBS, R.L. and JOYNER, F.B.: J. Polym. Sci., A1, 4, 2583 (1966)
JUNG, K.A. and SCHNECKO, H.: Makromol. Chem. 154, 227 (1972)
KASHIWA, N. and YOSHITAKE, J.: Makromol. Chem. Rapid Commun. 3, 211 (1982)
SHEPELEV, S.N., BUKATOV, G.D., ZAKHAROV, V.A. and YERMAKOV, Yu.I.: Kinetika i Kataliz 22, 258 (1981)
SUZUKI, E., TAMURA, M., DOI, Y. and KEII, T.: Makromol. Chem. 180, 2235 (1979)
WARZELHAN, V., BURGER, T.F., STEIN, D.J.: Makromol. Chem. 183, 489 (1982)

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