CHEMISTRY LETTERS, pp.327-329, 1972. Published by the Chemical Society of Japan

ZIEGLER-NATTA PROPYLENE POLYMERIZATION IN GAS PHASE: PRODUCTION OF HIGHLY ISOTACTIC POLYMERS

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The isotacticities of the polypropylenes produced with $TiCl_3$-$AlEt_3$ catalyst without solvent were 6∿7% higher than those obtained in the case with n-heptane solvent. In the case of $TiCl_3$-$AlEt_2Cl$ catalyst there was no such a difference due to the presence of the solvent.

While some Zigler-Natta polymerizations in dry system are interesting in practical view1), there were reported few fundamental studies made on them. One of the present authors (T.K.), in collaboration with Kanetaka, studied the initial stage of α-olefin polymerization with the $TiCl_3$-alkylaluminum catalyst in dry system.2-3) Lipman and Norrish used mixed vapors of $TiCl_4$ and $AlEt_3$, as catalyst for ethylene polymerization.4)

In this letter, the presence authors would like to point out that the propylene polymerization with the $TiCl_3$-$AlEt_3$ catalyst, in the absence of solvent, gives highly isotactic polymers.

The apparatus and procedure used were essentially the same as reported in the previous paper.5) The reactor used was a three necked 500ml glass flask, which was equipped with a magnetic stirrer with two Teflon blades. In order to assure good dispersion of the catalyst, about 10 ml of glass beads (1.5mm dia.) was admitted to the flask. About 0.2-0.5g of $TiCl_3$ was admitted onto the bed of beads, about 1-5ml of n-heptane solution of alkylaluminum (20 wt%) was scattered over the $TiCl_3$,and n-heptane was thoroughly evacuated. The polymerization was started by introducing propylene. The stirring speed was 400 r.p.m.. After the polymerization was quenched usually, the produced polymers were dried overnight at room temperature in a evacuated oven, and the isotacticity of the polymers was determined by the method of Luongo,6) which is based on the comparison of 995 cm^{-1} band with 947 cm^{-1} one of IR spectra.

Figure 1 shows the kinetic curves (polymerization rate, R, versus time,t) obtained with the two catalyst systems, $TiCl_3$-$AlEt_3$ and $TiCl_3$-$AlEt_2Cl$, in the presence or absence of n-heptane solvent. Besides the stationary rate, the rate of polymerization without solvent is lower than that in the case with n-heptane solvent. In the case of the $TiCl_3$-$AlEt_2Cl$ catalyst there is no such a difference due to solvent, excepting the initial stage of polymerization.

Table 1 shows the isotacticities and the molecular weights of the poly-

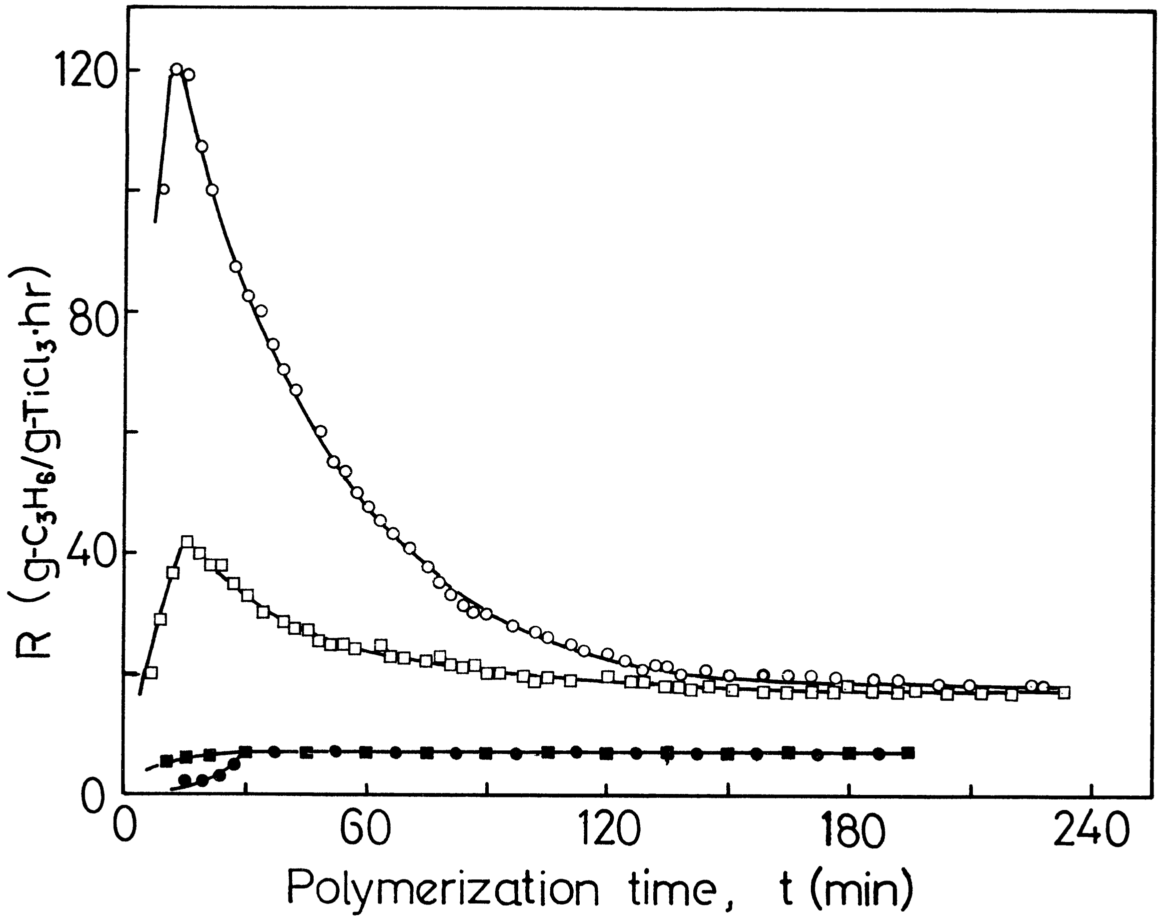

Figure 1. Time dependence of Polymerization rate
P = 76 cmHg, 41°C,

(□) $TiCl_3$-$AlEt_3$ system, without solvent, $TiCl_3$=1.5mmol, $AlEt_3$=3.9mmol.
(○) $TiCl_3$-$AlEt_3$ system, n-heptane 200ml, $TiCl_3$=3.2mmol, $AlEt_3$=3.2mmol.
(■) $TiCl_3$-$AlEt_2Cl$ system, without solvent, $TiCl_3$=2.5mmol, $AlEt_2Cl$=9.5mmol.
(●) $TiCl_3$-$AlEt_2Cl$ system, n-heptane 200ml, $TiCl_3$=3.2mmol, $AlEt_2Cl$=3.2mmol.

propylenes produced with various systems. The table clearly shows that the isotacticities of the polymers produced with $TiCl_3$-$AlEt_3$ catalyst without solvent are 6~7% higher than those obtained in the case with the solvent. In the case of the $TiCl_3$-$AlEt_2Cl$ catalyst there is no such a difference.

The enhancement of isotacticity, thus observered with the $TiCl_3$-$AlEt_3$ catalyst, can be explained on the basis of our theory of two kinds of polymerization centers in the catalyst; highly isotactic polymers was formed only at the stable sites, the other sites being unstable and capable of producing polymers of low steric order.[7)]

The detailed discussion of these polymerizations will be reported soon.

Table 1. Isotacticities of polypropylene produced with various catalyst systems at 41°C, 76 cmHg.

$TiCl_3$ (mmol)	alkylaluminum (mmol)	n-heptane (ml)	stationary rate (g-C_3H_6/g-$TiCl_3$ hr)	isotacticity[a)] (%)	Mv[a,b)] ($\times10^{-4}$)
1.5	TEA 0.3	0	2.5	88.0	30.5
1.5	TEA 0.7	0	7.5	87.5	25.0
1.5	TEA 1.5	0	13.0	88.0	-
1.5	TEA 3.9	0	17.0	87.5	24.0
1.5	TEA 6.0	0	16.5	89.0	22.0
3.2	TEA 3.2	200	17.0	81.5	30.0
3.2	TEA 6.4	200	17.0	81.0	-
2.5	DEAC 2.5	0	3.7	93.0	38.0
2.5	DEAC 3.2	0	4.8	94.0	36.2
2.5	DEAC 6.0	0	5.8	92.0	35.6
2.5	DEAC 9.5	0	6.8	92.5	34.5
2.5	DEAC 15.0	0	6.7	92.5	36.0
3.2	DEAC 3.2	200	6.5	92.5	43.0
3.2	DEAC 6.4	200	6.8	93.0	-

TEA: triethylaluminum, DEAC: diethylaluminum chloride

a) The values obtained from total polymers produced at 90 min.

b) The values of Mv were calculated from measured intrinsic viscocity by means of Kinsinger's equation.[8)]

Materials

AA-$TiCl_3$ (aluminum reduced and ground, supplied by Toho Titanium Co., the surface area: 17 m^2/g)

$AlEt_3$, $AlEt_2Cl$ (Ethyl Corp.) was used as a 20% solution of n-heptane.

Propylene (Mitsubishi Petrochem. Co., 99.6% purity)

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(Received January 26, 1972)