A Mechanism of the Syndiotactic Polymerization of α-Olefin

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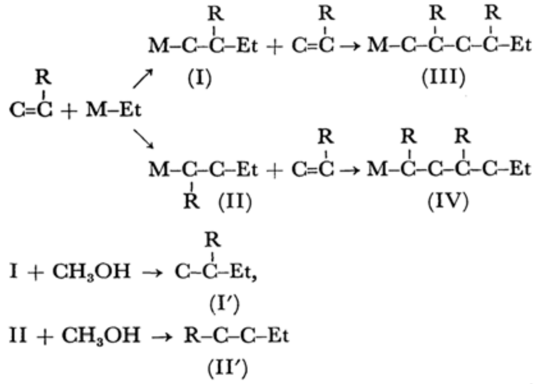
In connection with the initiation step of the polymerization of α-olefin, the insertion reactions of olefins into metal-ethyl bond in Ziegler-type catalysts were studied.[1] An olefin was reacted with a catalyst in a high concentration, and then, after a certain reaction time, the catalyst mixture was decomposed by methanol. The insertion processes of an olefin into a metal-ethyl bond may be formulated as follows:



$$\mathrm{C{=}\overset{R}{C}} + \mathrm{M{-}Et} \nearrow \underset{\text{(I)}}{\mathrm{M{-}C{-}\overset{R}{C}{-}Et}} + \mathrm{C{=}\overset{R}{C}} \rightarrow \underset{\text{(III)}}{\mathrm{M{-}C{-}\overset{R}{C}{-}C{-}\overset{R}{C}{-}Et}}$$

$$\searrow \underset{\text{(II)}}{\mathrm{M{-}\underset{R}{C}{-}C{-}Et}} + \mathrm{C{=}\overset{R}{C}} \rightarrow \underset{\text{(IV)}}{\mathrm{M{-}\overset{R}{C}{-}C{-}\overset{R}{C}{-}C{-}Et}}$$

$$\mathrm{I} + \mathrm{CH_3OH} \rightarrow \underset{\text{(I')}}{\mathrm{C{-}\overset{R}{C}{-}Et},}$$

$$\mathrm{II} + \mathrm{CH_3OH} \rightarrow \underset{\text{(II')}}{\mathrm{R{-}C{-}C{-}Et}}$$

The hydrocarbons thus liberated were identified by gas-liquid chromatography.

The catalyst system containing titanium gave exclusively a metal alkyl (I), which was related to the isotactic polymerization of α-olefins. Unlike as in the titanium system, propylene was polymerized to a syndiotactic polymer with a vanadium catalyst at a low temperature.[2]

The method described in a former paper[1] was used in this vanadium catalyst system. However, in the case of propylene, neither metal alkyl (I) nor (II) were detected at a low temperature. Butene-1 and higher olefins could not be polymerized with this catalyst.[3] Pentene-1 could be reacted with vanadium tetrachloride and diethylaluminum chloride catalysts. After methanolysis, *n*-heptane (from metal alkyl (II)) and a small amount of 3-methylhexane (from metal alkyl (I)) were obtained. The results are summarized in Table 1. At −70°C, where the syndiotactic polymerization of propylene proceeded, almost ten times as much (II) as metal alkyl (I) was obtained. The fact that the yield of the metal alkyls decreased with the reaction time indicates that the second step of the insertion of pentene-1 into metal alkyls (I) and (II) occurred slowly.

Recently Zambelli *et al.*[4] succeeded in copolymerizing ethylene and butene-1 with a syndiospecific catalyst, and they obtained an almost alternating copolymer. This may be explained, in our opinion, by the consideration that the insertion of butene-1 into a sterically-hindered secondary metal alkyl bond is difficult, while ethylene is easily inserted into the secondary metal alkyl bond and forms the primary metal alkyl bond again.

According to this mechanism, almost every experimental result with the syndiospecific catalyst can be clearly explained.

1) A bulky olefin, such as butene-1 or pentene-1, can not be polymerized, for the steric hindrance of the alkyl substituent attached closely to vanadium interrupts the coordination of the approaching monomer.

2) The syndiotacticity in the case of the polymerization of propylene is caused by the monomer attack on the secondary metal alkyl bond from the less hindered site.

3) The addition of anisole to the reaction system increases the tendency of the insertion reaction to the secondary metal alkyl bond, as is shown in Table 1.

Table 1. Insertion reaction of pentene-1 into metal-ethyl bond in VCl_4-$AlEt_2Cl$ catalyst

Reaction		Products		Additive (mmol)
Temp. (°C)	Time (min)	3-Methyhexane(mmol)	*n*-Heptane	
−70	5	0.0105	0.0422	
−70	10	0.0126	0.0392	
−70	360	0.0040	0.0141	
−70	10	0.0137	0.135	Anisole 1.0
−70	40	0.0150	0.115	Anisole 1.0
−70	360	0.0022	0.103	Anisole 1.0

VCl_4, 1.00 mmol, $AlEt_2Cl$, 3.00 mmol
pentene-1, 4.5 mmol
Solvent, toluene; Total volume, 10 m*l*

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[1] Y. Takegami, T. Suzuki and T. Okazaki, This Bulletin, to be published, No. 4 (1969).

[2] A. Zambelli, G. Natta and I. Pasquon, *J. Am. Chem. Soc.*, **84**, 1488 (1962).

[3] A. Zambelli, G. Natta and I. Pasquon, *J. Polymer Sci.*, **C4**, 411 (1963).

[4] A. Zambelli, A. Lety, C. Tosi and I. Pasquon, *Makromol. Chem.*, **115**, 73 (1968).