The Promotive Effect of the Metal Chelate Compounds in the Triethylaluminum-Vanadium Tetrachloride Catalyst

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Nickel-, cobalt-, titanium-, and chromium acetylacetonate have been used as transition metal components of Ziegler-type catalysts in the polymerizations of alpha-olefines and of 1, 3-conjugated dienes.[1] The Ziegler catalyst containing ferric acetylacetonate is active in the oligomerization of 1, 3-butadiene to produce a linear trimer[2] and in the co-oligomerization of 1, 3-butadiene with ethylene to produce 1, 4-hexadiene.[3] In the isomerization polymerization of 2-butene, the addition of ferric acetylacetonate to the catalytic system promotes the isomerization of 2-butene to 1-butene, and the yield of poly-1-butene is increased.[4,5]

1) N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers," Interscience Publ., New York (1959).
2) M. Hidai, Y. Uchida and A. Misono, This Bulletin, **38**, 1243 (1965).
3) G. Hata, *J. Am. Chem. Soc.,* **86**, 3903 (1964).
4) Toyo Rayon Co., French Pat. 1415239 (1965).
5) A. Shimizu, T. Otsu and M. Imoto, Abstract Papers presented at the 14th Symposium on Polymer Science, Kyoto, October, 1965, p. 256.

In this communication, we wish to report that the addition of a small amount of ferric acetylacetonate to the catalytic system consisting of triethylaluminum and vanadium tetrachloride causes a remarkable increase in the yields of polypropylene and polybutene. The polymerization of propylene was carried out at an atmospheric pressure in the presence of catalysts consisting of 7.3 mmol of triethylaluminum, 4 mmol of vanadium tetrachloride, and various quantities of

TABLE 1. POLYMERIZATION OF PROPYLENE (50°C, 2 hr)

Ferric acetylacetonate mmol	Yield of polymer g
0	9.8
0.0043	19.7
0.07	23.8
0.25	18.5
1.0	11.7
4.0	0.8

ferric acetylacetonate, with benzene as a solvent. The results are shown in Table 1.

It was found that the maximum yield of the polymer was obtained by adding a proper quantity of the acetylacetonate. The most favorable order of adding the three components of the catalyst to the reaction system is when vanadium tetrachloride is added to an admixture of triethylaluminum and ferric acetylacetonate. If the metal chelate compounds are added in the order of reacting first with vanadium tetrachloride, the polymerization activity of the resulting catalytic system is rather decreased. The activity of the catalytic system containing ferric acetylacetonate in the polymerization of propylene is kept at a high level for a relatively long time, and the yields of the polymer increase linearly with the reaction time. The absorption of propylene takes place faster than in the case of the catalytic system without ferric acetylacetonate.

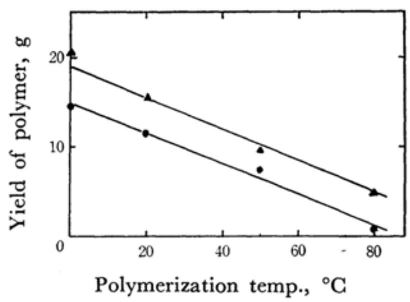

Fig. 1. Relation between the reaction temperature and the yield of polymer in polymerizing propylene for 1 hr in the presence of Et_3Al-VCl_4 (●) and Et_3Al-$Fe(C_5H_7O_2)_3$-VCl_4 (▲), respectively.

The relation between the yield of the polymer and the reaction temperature is shown in Fig. 1. In both cases, the yield of the polymer decreased linearly as the temperature increased. It was observed that the increment of the yield by the addition of the acetylacetonate were almost same the temperature range studied. When, in place of ferric acetylacetonate, ferric ethylacetoacetate was added to the system as a metal chelate compound, the yield of polypropylene was twice that obtained by using the system without an iron chelate component. The promotive effect of the iron chelate compounds was also observed in the polymerization of 1-butene (Table 2). The addition of other metal chelate compounds, *e. g.*, sodium,

Table 2. Polymerization of butene-1 (50°C, 1 hr)

Ferric acetylacetonate mmol	Yield of polymer g
0	5.7*
0.05	21.8
0.1	21.4
0.5	14.8
1.0	9.0
2.0	2.9

* Polymerization was carried out for 2 hr.

Table 3. Polymerization of propylene with the catalysts containing various metal acetylacetonates (50°C, 2 hr, Et_3Al 7.3 mmol, VOl_4 4 mmol)

Metal acetylacetonate	mmol	Yield of polymer g
$Na(C_5H_7O_2)$	0.5	22.0
$Be(C_5H_7O_2)_2$	0.5	13.5
$Al(C_5H_7O_2)_3$	1.0	14.1
$Sr(C_5H_7O_2)_2$	1.0	19.7
$Cu(C_5H_7O_2)_2$	0.1	18.5
$Ca(C_5H_7O_2)_2$	0.5	15.2
none	—	8.6

beryllium, aluminum, copper, strontium, or calcium acetylacetonate, also caused an increase in the yield of the polymer, provided an adequate quantity of the chelate compound was added to the system (Table 3).

It is interesting that a small quantity of the metal chelate compound caused a remarkable increase in the activity of the catalyst. Generally, the metal chelate compounds are readily reduced to a lower valent state by the action of triethylaluminum, and in the absence of a ligand capable of stabilizing the lower valent state, a black precipitate, probably a metallic species, was separated. It is considered that the existence of the small quantity of the metallic species effectively increases the activity, or that a certain interaction of triethylaluminum with the metal chelate compound gives a new complex, which then acts to form a more active catalyst. However, there is no conclusive explanation for the mechanism of the promotive effect of the metal chelate compounds on the catalyst composed of triethylaluminum and vanadium tetrachloride.