Ethylene Polymerization by Bisarenechrome π-Complex Compounds

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Ethylene polymerization by a binary catalyst system composed of bisarenechrome π-complex cations and an organoaluminum compound was investigated. The bisarenechrome π-complex compounds used were bisbiphenylchrome iodide, chromate, dichromate, thiocyanate, tetrathiocyano diammono chromate, etc. Instead of biphenyl, such other benzene derivatives as benzene, toluene, and mesitylene were also used as ligands.

As an organoaluminum compound, $Al(i\text{-}Bu)_3$ was the most suitable; the other organoaluminum compounds, such as $AlEt_3$ and $AlEt_2Cl$, showed less catalytic activity.

Figure 1 shows the relation of the polymerization temperature and the weights of the solid polymer formed during the initial 10 min. with the binary system of the bisbiphenylchrome compound (abbreviated as $(C_6H_5C_6H_5)_2CrX^-$) and 4 mmol. of $Al(i\text{-}Bu)_3$. As a solvent toluene was used, and the ethylene pressure was 40 kg./cm².

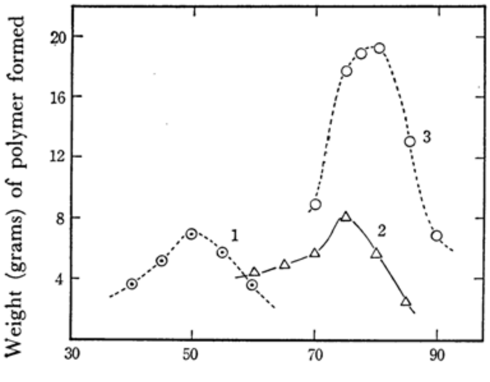

Fig. 1. 1 $(C_6H_5C_6H_5)_2Cr(NH_3)_2Cr(SCN)_4 \sim Al(i\text{-}Bu)_3$
2 $[(C_6H_5C_6H_5)_2Cr]_2CrO_4 \sim Al(i\text{-}Bu)_3$
3 $[(C_6H_5C_6H_5)_2Cr]_2Cr_2O_7 \sim Al(i\text{-}Bu)_3$

Bisbiphenylchrome dichromate showed a maximum activity at 80°C; bisbiphenylchrome chromate, at 75°C, and bisbiphenylchrome tetrathiocyano diammono chromate, at 50°C. The order of the catalytic activity of bisbiphenylchrome compounds as a component of the binary system with $Al(i\text{-}Bu)_3$ is as follows:

$$[(C_6H_5C_6H_5)_2Cr]_2Cr_2O_7 > [(C_6H_5C_6H_5)_2Cr]_2CrO_4 > [(C_6H_5C_6H_5)_2Cr][(NH_3)_2Cr(SCN)_4] > (C_6H_5C_6H_5)_2CrI$$

The same tendencies were observed for other ligands, such as benzene, toluene and mesitylene.

The orders of catalytic activities of bisarenechrome π-complex compounds with the same anion species are as follows:

X^- : I^-

$$(C_6H_6)_2CrI > (C_6H_5CH_3)_2CrI > [C_6H_3(CH_3)_3]_2CrI > (C_6H_5C_6H_5)_2CrI$$

X^- : $[(NH_3)_2Cr(SCN)_4]^-$

$$(C_6H_5C_6H_5)_2Cr[NH_3)_2Cr(SCN)_4] > [C_6H_3(CH_3)_3]_2Cr[(NH_3)_2Cr(SCN)_4] > (C_6H_5CH_3)_2Cr[(NH_3)_2Cr(SCN)_4] > (C_6H_5)_2Cr[(NH_3)_2Cr(SCN)_4]$$

It should especially be noted that bisbiphenylchrome chromate or bisbiphenylchrome dichromate alone has the catalytic activity for ethylene polymerization without the presence of an organoaluminum compound. Table I shows the results obtained at different temperatures by using bisbiphenylchrome chromate or bisbiphenylchrome dichromate. Bisbiphenylchrome chromate showed increased activity above 75°C, and bisbiphenylchrome dichromate, above 80°C. The temperature (75°C or 85°C) accorded with the temperature of the maximum catalytic activity of each binary system with Al(i-Bu)$_3$. Bisbiphenylchrome dichromate or bisbiphenylchrome chromate was inferrior to bisbenzene chrome dichromate or bisbenzenechrome chromate in catalytic activity.

Table I. Ethylene polymerization with $[(\phi_2)_2Cr]_2CrO_4$ or $[(\phi_2)_2Cr]_2Cr_2O_7$
Polymerization hour: 1 hr.

Catalyst		Temp. °C	Polymer formed, g.
$[(\phi_2)_2Cr]_2CrO_4$	0.05 g.	60	0.15
$[(\phi_2)_2Cr]_2CrO_4$	0.05 g.	75	0.45
$[(\phi_2)_2Cr]_2CrO_4$	0.05 g.	85	0.50
$[(\phi_2)_2Cr]_2CrO_4$	0.05 g.	100	0.50
$[(\phi_2)_2Cr]_2Cr_2O_7$	0.05 g.	60	0.13
$[(\phi_2)_2Cr]_2Cr_2O_7$	0.05 g.	75	0.45
$[(\phi_2)_2Cr]_2Cr_2O_7$	0.05 g.	85	0.75
$[(\phi_2)_2Cr]_2Cr_2O_7$	0.05 g.	100	0.70

Table II. Ethylene polymerization with oxidized product of bisbiphenylchrom

Polymerization temp., °C	Polymer formed, g.
75	0.55
100	0.75
150	0.60

Bisbiphenylchrome $(C_6H_5C_6H_5)_2Cr(O)$ (chrome is zero valency) showed catalytic activity for ethylene polymerization after it had been oxidized and activated by heating it above 75°C.

The results of some experiments obtained by the oxidized product of bisbiphenylchrome are shown in Table II. One procedure was as follows:

After the oxidation of $(C_6H_5C_6H_5)_2Cr$ (0.2 g.) dissolved in toluene (50 ml.) with oxygen (3 kg./cm^2) at 30°C for 1 hr. in an autoclave (100 ml.), oxygen was removed by stirring it at 75°C for 30 min. under a nitrogen atmosphere. Then ethylene was introduced up to a pressure of 40 kg./cm^2. Above 75°C, the oxidized product showed some catalytic activity, but the activity was lower than that of bisbenzene-chrome. Bisarenechromium compounds were prepared[1,2] by reducing chromium(III) chloride with benzene derivatives (benzene, toluene, mesitylene, and biphenyl) in the presence of aluminum and aluminum chloride in a sealed tube at 150°C, and by then decomposing the reduction products with methanol and water, followed by a treatment of the decomposed products with potassium salts. Bisbiphenylchromium was prepared by reducing the preceding product with $Na_2S_2O_3$.

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1) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 655 (1955).

2) E. O. Fischer and W. Hafner, *Z. anorg. allgem. Chem.*, **286**, 14b (1956).