Macromolecules

Volume 19, Number 12 December 1986

Polymerization of Ethylene and Propylene with $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$/Metal Chloride Catalysts

Kazuo Soga,* Shiang-Ing Chen, Yoshiharu Doi, and Takeshi Shiono

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan. *Received January 21, 1986*

ABSTRACT: A $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl/MgCl_2$ catalyst was prepared by modifying the Battelle-type catalyst with $MgCl_2$ dissolved in 2-ethyl-1-hexanol (2-EHA), and the polymerization of ethylene was carried out in toluene at 20–40 °C. The rate of polymerization markedly increased with increasing Mg/Cr molar ratio. The polyethylene obtained without $MgCl_2$ had a very broad polydispersity, whereas the polyethylenes in the presence of $MgCl_2$ had extremely high molecular weights with narrow polydispersities. The polymerization of ethylene was also performed with various types of metal chlorides under similar conditions. The activity of the catalyst was strongly dependent upon the metal chloride used as modifier. A clear correlation was observed between the activity and the electronegativity of the metal ion in the metal chloride.

Introduction

We have previously investigated the effect of carriers (metal chlorides, MCl_x, such as $MgCl_2$, etc.) on the rate of olefin polymerization by using the soluble $Ti(OBu)_4/AlEt_2Cl$ catalyst combined with a variety of MCl_x and found an important correlation between the activity and the electronegativity of the metal ion in MCl_x.[1,2] The application of the rule to the Battelle-type catalyst[3] markedly improved the activity for ethylene polymerization; the modified catalysts ($Cr(OAc)_3/AlEt_2Cl/MgCl_2$[4] and $Cr(OBu)_4/AlEt_2Cl/MgCl_2$)[5] were 10 times more active than the original catalysts ($Cr(OAc)_3/AlEt_2Cl$ and $Cr(OBu)_4/AlEt_2Cl$). These catalytic systems are, however, not easy to handle, owing to either insolubility in usual organic solvents (in the case of $Cr(OAc)_3$) or instability (in the case of $Cr(OBu)_4$).

On the other hand, chromium stearate [$Cr(C_{17}H_{35}COO)_3$] is stable in air and soluble in usual organic solvents. The soluble $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalyst in toluene has shown some activity for ethylene polymerization.[6]

We are thus encouraged to develop a catalyst for ethylene polymerization with enhanced activity by modifying the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ system with suitable metal chlorides. Development of such an easy-to-handle catalytic system could be important for industrial applications. This paper reports the results of ethylene and propylene polymerization using the catalyst.

Experimental Section

Research grade ethylene (Toa Nenryo Kogyo Co. Ltd.), propylene (Mitsubishi Petrochemical Co.), $Cr(C_{17}H_{35}COO)_3$ (Kanto Chemical Co. Ltd.), 2-ethyl-1-hexanol (2-EHA), and toluene (Takachiho Chemical Co.) were purified according to the usual procedures.[2] Ultrahigh-purity nitrogen (Nippon Sanso Co.) was further purified by passing it through a 3A molecular sieve column. Other chemicals (research grade) were commercially obtained and used without further purification.

Polymerization and Analytical Procedures

Into a 300-cm^3 glass reactor equipped with a magnetic stirrer were introduced measured amounts of $Cr(C_{17}H_{35}COO)_3$, MCl_x (dissolved in 2-EHA, 1.5×10^{-1} M), and toluene (solvent) under nitrogen. The reactor was degassed, followed by introduction of either ethylene or propylene (1 atm). After the mixture was agitated for 10 min at the polymerization temperature, a prescribed amount of alkylaluminum was added. The polymerization was terminated by adding acidic methanol. The precipitated polymer was washed with methanol, followed by drying in vacuo at room temperature. ^{13}C NMR spectra were recorded on a JEOL JNM PS-100 spectrometer operating at 25.14 MHz with full proton noise decoupling. The instrument was equipped with a PET-100 FT system. Spectra were recorded at 120 °C with 13.5-s pulses, a 7.0-s repetition rate, and a 5000-Hz sweep width. The molecular weight distribution of the polymer was measured at 145 °C by GPC, using 1,2,4-trichlorobenzene as solvent.

Results and Discussion

Polymerization of Ethylene. We have previously investigated the polymerization of ethylene and propylene with the homogeneous $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalyst system in toluene solvent.[6] The results obtained are summarized as follows: (1) The catalyst system shows some activity for ethylene polymerization (the best rate is 150 g of PE/(g of Cr·h)) but not for propylene polymerization. (2) The active species for ethylene polymerization is Cr^{2+}.

The present study was mainly aimed at the activation of the catalyst by modifying it with suitable metal chlo-

0024-9297/86/2219-2893$01.50/0

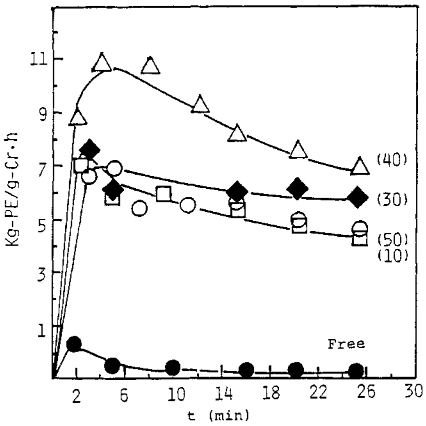

Figure 1. Kinetic curves of ethylene polymerization with the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$/2-EHA catalyst system. Polymerization conditions: 30 °C; ethylene pressure = 1 atm; toluene = 100 mL; $Cr(C_{17}H_{35}COO)_3$ = 21 mg; $[AlEt_2Cl]$ = 0.12 M Al/Cr = 520). Numbers in the figure indicate the Mg/Cr molar ratio.

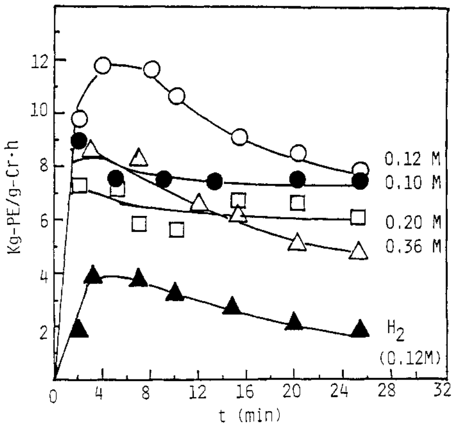

Figure 2. Kinetic curves of ethylene polymerization in the presence of different concentrations of $AlEt_2Cl$. Polymerization conditions as in Figure 1.

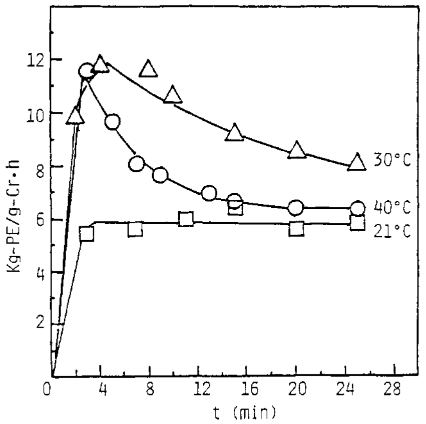

Figure 3. Temperature dependence of the rate of ethylene polymerization. Polymerization condition as in Figure 1.

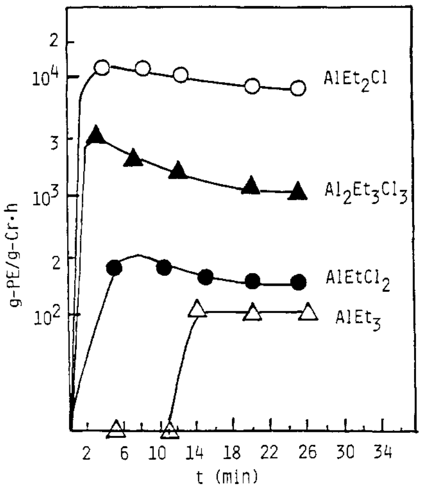

Figure 4. Kinetic curves of ethylene polymerization with the $Cr(C_{17}H_{35}COO)_3/MgCl_2$/2-EHA catalyst system in the presence of various kinds of alkylaluminums. Polymerization conditions as in Figure 1.

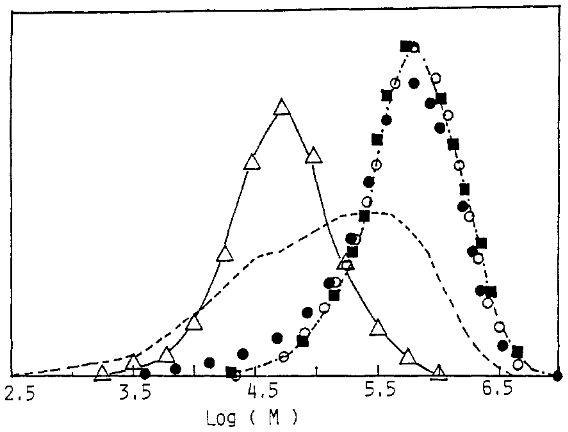

Figure 5. Molecular weight distribution curves of polyethylenes obtained at 30 °C with the $Cr(C_{17}H_{35}COO)_3/MgCl_2/AlEt_2Cl$ catalyst system: (---) A; (■); (---) C; (○) D; (●) E; (△) F. Polymerization conditions were as follows (variables given only in A): (A) Mg/Cr = 0, $[AlEt_2Cl]$ = 0.12 M (Al/Cr = 520), 25 min ($\bar{M}_n = 3.8 \times 10^3$, $Q \doteqdot 18.5$); (B) 40, 0.12 M (520), 25 (3.6×10^5, 2); (C) 40, 0.20 M (870), 25 (3.6×10^5, 2); (D) 40, 0.36 M (1560), 25 (3.6×10^5, 2); (E) 40, 0.12 M (520), 4 (3.6×10^5, 2); (F) 40, 0.12 M (520), 25 (3.2×10^4, 2) in the presence of 100 Torr of hydrogen.

rides. Polymerization of ethylene was first carried out with the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ system in toluene by adding $MgCl_2$. Typical kinetic curves of ethylene polymerization performed under various conditions are shown in Figures 1–3. The rate of polymerization was markedly dependent upon the Mg/Cr mole ratio, the concentration of $AlEt_2Cl$, and the polymerization temperature. The optimum conditions were thus obtained at around 30 °C with Mg/Cr = 40 and $[AlEt_2Cl]$ = 0.12 M (Al/Cr = 520). Polymerization of ethylene was also carried out under the same conditions at 8 atm of ethylene for 1 h to give an activity of approximately 150 kg of PE/(g of Cr·h). This maximum activity can compare with those previously obtained with the $Cr(CH_3COO)_3/MgCl_2/AlEt_2Cl$ (120 kg of PE/(g of Cr·h) at $P_{C_2H_4}$ = 8 atm, Mg/Cr = 40)[4] and $Cr(OBu)_4/MgCl_2/AlEt_2Cl$ (182 kg of PE/(g of Cr·h) at $P_{C_2H_4}$ = 8 atm, Mg/Cr = 40) catalyst systems.[5] The use of $AlEt_3$, $Al_2Et_3Cl_3$, or $AlEtCl_2$ in place of $AlEt_2Cl$ caused a remarkable decrease in the polymerization activity, as shown in Figure 4. Figure 5 illustrates the molecular weight distribution curves of polyethylenes obtained at 30 °C with the $Cr(C_{17}H_{35}COO)_3/MgCl_2/AlEt_2Cl$ catalyst system. All the polymers obtained were identified by IR and ^{13}C NMR spectra to be linear high-density polyethylenes. The polyethylene (A) obtained without $MgCl_2$ shows a very broad polydispersity ($Q \doteqdot 18.5$) with a considerably low molecular weight, whereas the polyethylenes (B, C, D, and E) obtained with $MgCl_2$ show narrow polydispersities ($Q \doteqdot 2$) with high molecular weights. It should be noted that the polymers obtained at 4 and 25 min (E and B) show approximately the same molecular weight distribution curves. Therefore, the lifetime of the living polymer is quite short and is limited by transfer reactions. Changing the concentration of $AlEt_2Cl$ (B, C, and D) has no effect

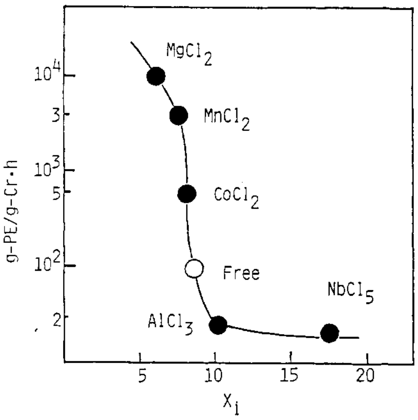

Figure 6. Relationship between stationary rate and electronegativity of the metal ion in the metal chloride. Polymerization conditions as in Figure 1.

on the polydispersity, which implies that the transfer reaction by $AlEt_2Cl$ is not dominant. Thus, the following two transfer reactions may be considered to be the main processes:

Monomolecular process

$$\mathrm{Cr{-}CH_2CH_2{-}(CH_2CH_2)_n{-}R} \rightarrow \underset{\mathbf{1}}{\mathrm{Cr{-}H}} + \mathrm{CH_2{=}CH{-}(CH_2CH_2)_n{-}R} \quad (1)$$

First-order process with respect to the monomer

$$\mathrm{Cr{-}CH_2CH_2{-}(CH_2CH_2)_n{-}R} + \mathrm{CH_2{=}CH_2} \rightarrow \underset{\mathbf{2}}{\mathrm{Cr{-}CH_2{-}CH_3}} + \mathrm{CH_2{=}CH{-}(CH_2CH_2)_n{-}R} \quad (2)$$

The effect of hydrogen on molecular weight has been examined. The polymerizatioin was performed at 30 °C for 30 min under the following conditions: P_{H_2} = 100 Torr, $P_{C_2H_4}$ = 660 Torr, Mg/Cr = 40, and [$AlEt_2Cl$] = 0.12 M (Al/Cr = 520). Addition of hydrogen caused a significant decrease in the molecular weight without chaning the polydispersity (F in Figure 5), indicating that the molecular weight of polyethylene can be controlled by adding hydrogen.

The transfer process with hydrogen can be expressed as

$$\mathrm{Cr{-}CH_2CH_2{-}(CH_2CH_2)_n{-}R} + \mathrm{H_2} \rightarrow \underset{\mathbf{1}}{\mathrm{Cr{-}H}} + \mathrm{CH_3{-}CH_2{-}(CH_2CH_2)_n{-}R} \quad (3)$$

The resulting hydride complex (**1**), reacting with the monomer, should give an alkyl group (**2**) and initiate a new chain.

$$\underset{\mathbf{1}}{\mathrm{Cr{-}H}} + \mathrm{CH_2{=}CH_2} \rightarrow \underset{\mathbf{2}}{\mathrm{Cr{-}CH_2{-}CH_3}} \quad (4)$$

A significant decrease in the activity in the presence of hydrogen (see Figure 2) suggests that the first-order process with respect to the monomer (eq 2) is the main process in the absence of hydrogen and that reaction 4 is slow.

The polymerization of ethylene was then carried out at 30 °C by using various other metal chlorides (MCl_x/Cr = 40). In Figure 6 are plotted the polymerization activities against the electronegativities of the metal ion in MCl_x. We have again obtained a similar correlation between the activity and the electronegativity of the metal ion. The polymerization activity is given by the product of k_p (propagation rate constant) and C^* (number of active species). Therefore, we must evaluate C^* to discuss the effect of MCl_x on the polymerization activity. In homogeneous catalytic systems, the C^* values are not expected to change significantly when MCl_x is varied. Actually we have found in the propylene polymerization using the $Ti(OBu)_4/AlEt_2Cl/MCl_x$ (dissolved in 2-EHA) system that the difference in the activity is mainly attributed to the magnitude of k_p.[2] Thus, we are inclined to interpret the present data similarly.

Polymerization of Propylene. As reported in the previous paper, the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalyst system in toluene showed no activity for propylene polymerization. However, when combined with $MgCl_2$, it was capable of catalyzing propylene polymerization to give a polypropylene having a considerable degree of isotacticity. In the following is briefly shown a typical result obtained. The polymerization was performed at 30 °C for 1 h under the following conditions: $Cr(C_{17}H_{35}COO)_3$ = 21 mg, Mg/Cr = 40, [$AlEt_2Cl$] = 0.12 M (Al/Cr = 520), toluene = 100 mL, and $P_{C_3H_6}$ = 760 Torr. After an induction period of about 30 min, polymerization took place at a rate of approximately 20 g of polymer/(g of Cr·h) to give a polypropylene with $\bar{M}_n$ = 15 000, Q ($\bar{M}_w/\bar{M}_n$) = 2.6, and 45% isotacticity (determined by the IR method).[7] The polydispersity (2.6) is very close to those of polypropylenes obtained with Kaminsky's catalyst.[8] The activity of the present catalyst for propylene polymerization is, however, much smaller than that for ethylene polymerization.

To get a better insight into this point, copolymerization of ethylene and propylene was carried out under similar conditions ($Cr(C_{17}H_{35}COO)_3$ = 20 mg, Mg/Cr = 40; $P_{C_2H_4}$ = 300 Torr, $P_{C_3H_6}$ = 460 Torr, 30 °C for 1 h). The copolymerization took place at a rate of 450 g of polymer/(g of Cr·h) to give only a random copolymer (EP rubber) containing 25 mol % propylene. Neither polypropylene nor polyethylene was produced. This result indicates that copolymerization of the two monomers occurs with the same active species. Therefore, the big difference in the activities between ethylene and propylene homopolymerizations seems to be mainly attributed to the difference in the propagation rate constants. Such a large ligand as $C_{17}H_{35}COO$ may cause an unfavorable steric effect in the chain propagation of propylene, which in turn may cause a favorable effect for isotactic polymerization.

In conclusion, the homogeneous $Cr(C_{17}H_{35}COO)_3/MgCl_2/AlEt_2Cl$ catalyst system in toluene showed a very high activity for ethylene polymerization to give a high molecular weight linear polyethylene having a very narrow polydispersity. The molecular weight of the polyethylene was found to be easily controlled by the addition of hydrogen to the catalytic system.

The catalytic system was also capable of catalyzing propylene polymerization to give a polypropylene having a considerable degree of isotacticity and a narrow polydispersity.

Registry No. 2-EHA, 104-76-7; $CH_2{=}CH_2$, 74-85-1; $Cr(C_{17}H_{35}COO)_3$, 3843-17-2; $AlEt_2Cl$, 96-10-6; $MgCl_2$, 7786-30-3; $Al_2Et_3Cl_3$, 12075-68-2; $AlEtCl_2$, 563-43-9; $AlEt_3$, 97-93-8; polypropylene, 9003-07-0; (ethylene)(propylene) (copolymer), 9010-79-1; polyethylene, 9002-88-4.

References and Notes

(1) Doi, Y.; Soga, K.; Murata, M.; Suzuki, E.; Ono, Y.; Keii, T. *Polym. Commun.* **1983**, *24*, 244.
(2) Soga, K. *History of Polyolefins*; D. Reidel: Dordrecht, The Netherlands, 1986; pp 243–256.
(3) Alfred, C. (Battelle Memorial Institute) Ger. Offen. 2 606 243, 1979.
(4) Soga, K.; Chen, S.-I.; Doi, Y.; Shiono, T. *Polymer* **1985**, *26*, 1891.
(5) Soga, K.; Chen, S.-I.; Doi, Y.; Shiono, T. *Makromol. Chem.* **1986**, *187*, 351.
(6) Soga, K.; Chen, S.-I.; Doi, Y.; Shiono, T. *Polymer* **1985**, *26*, 1885.
(7) Luongo, J. P. *J. Appl. Polym. Sci.* **1960**, *3*, 302.
(8) Kaminsky, W. Presented at the International Symposium on Future Aspects of Olefin Polymers, Tokyo, July 4–6, 1985.