Homo- and copolymerization of ethylene and propylene with a soluble chromium catalyst

Kazuo Soga*, Shian-Ing Chen, Takeshi Shiono and Yoshiharu Doi
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Yokohama 227, Japan
(Received 5 November 1984; revised 17 December 1984)

Polymerization of ethylene and propylene was carried out with a soluble $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalytic system in toluene. The system was found to be active only for ethylene polymerization. From e.s.r. measurements of the catalytic system combined with some qualitative experiments, the active species was determined to be Cr^{2+}. The reason why it should be incapable of polymerization of propylene was also discussed. The catalytic system showed some activity for ethylene–propylene copolymerization to give a random copolymer with a narrow molecular weight distribution.

(Keywords: polymerization; ethylene; propylene; catalytic system; active species; random copolymer)

INTRODUCTION

Ziegler–Natta catalyst for the stereospecific polymerization of α-olefins generally consist of a transition metal compound in combination with a metal alkyl component. Many transition metal salts show some activity in the polymerization of one or more olefins, but relatively few systems are of industrial importance. The most widely studied metal salts are those of Ti and V.

Battelle[1] has recently reported a series of new catalytic systems for ethylene polymerization, in which $Cr(CH_3COO)_3 \cdot H_2O$ combined with $AlEt_2Cl$ apparently shows the highest activity. More recently, we have reported the preliminary results on the polymerization of ethylene and/or propylene by using the above mentioned catalyst. The catalyst actually showed very high activity for ethylene polymerization, but there do seem to be some difficulties in discussing the mechanism of polymerization because of the heterogeneity of the catalytic system[2].

From such a viewpoint, we have developed a soluble chromium catalytic system composed of $Cr(C_{17}H_{35}COO)_3$ and $AlEt_2Cl$. This paper reports the detailed results of the homo- and copolymerization of ethylene and propylene together with some analytical results for the catalyst itself.

EXPERIMENTAL

Materials

Research grade ethylene, propylene and toluene (from Takachiho Chemical Co.) were further purified according to the usual procedures. $Cr(C_{17}H_{35}COO)_3$ was extra pure reagent purchased from Kanto Chemical Co. Nitrogen of ultra high purity (from Nippon Sanso Co., 99.9989%) was purified by passing through a molecular sieve 3A column cooled at −196°C. The other chemicals (research grade) were commercially obtained and used without further purification.

Polymerization and analytical procedures

The homopolymerization was carried out in a 300 ml glass reactor equipped with a magnetic stirrer. In the reactor were placed the measured amounts of $Cr(C_{17}H_{35}COO)_3$ and toluene under nitrogen. The reactor was then degassed *in vacuo* followed by introduction of either ethylene or propylene. After the mixture was agitated for about 10 min at the polymerization temperature, a given amount of an alkylaluminium was added. In the case of copolymerization, in a 200 ml stainless steel reactor equipped with a magnetic stirrer were placed the measured amounts of $Cr(C_{17}H_{35}COO)_3$, toluene and an alkylaluminum under nitrogen at room temperature. The reactor was cooled with liquid nitrogen, degassed *in vacuo*, and then given amounts of purified monomers were introduced. The polymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The precipitated polymer was washed with methanol, followed by drying *in vacuo* at room temperature.

The e.s.r. spectra were recorded with a VARIAN E-12 ESR spectrometer at a microwave frequency of 9.528 GHz. C^{13} n.m.r. spectra were recorded on a JOEL 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 pulse of 13.5 s, 7.0 s repetition rate and 5000 Hz sweep width. The molecular weight distribution of the copolymer was measured at 140°C with a SHOWA DENKO GPC fitted with a Shodex 80M column (AD-80M/S), using 1,2-dichlorobenzene as solvent. D.s.c. measurements were made with a SHIMAZU SC-30 instrument at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Homopolymerization of ethylene and propylene was first carried out at 30°C in the $Cr(C_{17}H_{35}COO)_3$ solution in

0032-3861/85/121888-03$03.00

toluene in the absence of alkylaluminum compounds, and it was found that neither ethylene nor propylene were polymerized in this system. Then a homopolymerization was conducted under similar conditions in the presence of of $AlEt_3$ or $AlEt_2Cl$. The results obtained (*Table 1* and *Figure 1*) indicate that these homogeneous catalytic systems are active only for ethylene polymerization, and that the activity using $AlEt_2Cl$ is much higher than that obtained using $AlEt_3$ as cocatalyst.

To get a better insight into these results, the e.s.r. spectra were taken at 30°C with various systems. The spectrum of the $Cr(C_{17}H_{35}COO)_3$ solution in toluene displayed a broad signal with a *g* factor of 1.972 attributable to Cr^{3+}. By adding $AlEt_2Cl$ to the system the colour of the solution gradually changed from deep blue to light orange, and the e.s.r. signal diminished gradually and was completely gone after several minutes. When $AlEt_3$ was added to the original system, the colour of the solution changed to light orange and then dark blue, and the spectrum displayed a new signal with a *g* factor of 1.989. It has a hyperfine structure of 8 lines plus weak satellites which is typical of Cr^{1+} complexes[3].

On the other hand, when ethylene or propylene was added to the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ system, the colour of the solution slowly changed from light orange to water white, and the final system displayed a weak e.s.r. signal attributed to Cr^{1+}.

These observations combined with the results shown in *Figure 1* suggest that the oxidation state of the Cr in the active catalyst is II. To throw light upon this point the effect of oxygen on the activity was examined by adding some amounts of air to the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalytic system during the ethylene polymerization (*Figure 2*).

In the case of the polymerization at 30°C, where the activity decreased gradually with an increase in the reaction time, the activity was quickly recovered by adding some amounts of oxygen. Whereas in the case of the polymerization at 0°C where the activity was stable, no change was observed in the activity. Therefore the above assumption seems to be reasonable.

The apparent activation energy of the polymerization was then measured with the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalytic system in the temperature range between *ca.* −20°C and 10°C where no deactivation takes place during the polymerization (*Figures 3* and *4*).

The apparent activation energy was thus obtained to be approximately 8.5 kcal mol^{-1}, which is not dissimilar to those energy values obtained with the usual Ziegler–Natta catalysts based on titanium.

The polyethylene produced was confirmed as being a high-density linear polyethylene having a very high molecular weight.

Why is polymerization of propylene not possible with the present catalyst? The phenomenon is similar to that observed when using a Ti^{2+} catalyst[4,5]. As mentioned above, no discussion could be found in the oxidation behaviour of the $Cr(C_{17}H_{35}COO)_3$ catalyst between the catalytic systems containing ethylene and propylene. Therefore, the lack of propylene polymerization with the present catalyst might not be attributed to the over-reduction of the Cr species. One plausible interpretation may be the formulation of a stable complex, e.g. π-allyl complex, between the Cr^{2+} species and propylene. The

Table 1 Results of homopolymerization of ethylene and propylene[a]

Cocatalyst	Al/Cr	Monomer	Polymer yield (g polymer/ g catalyst.hour
$AlEt_3$	100	Ethylene	14
$AlEt_2Cl$	100	Ethylene	150
$AlEt_2Cl$	100	Propylene	0

[a] Polymerization was carried out at 30°C for 80 min using 80 mg of $Cr(C_{17}H_{35}COO)_3$ and 100 ml of toluene

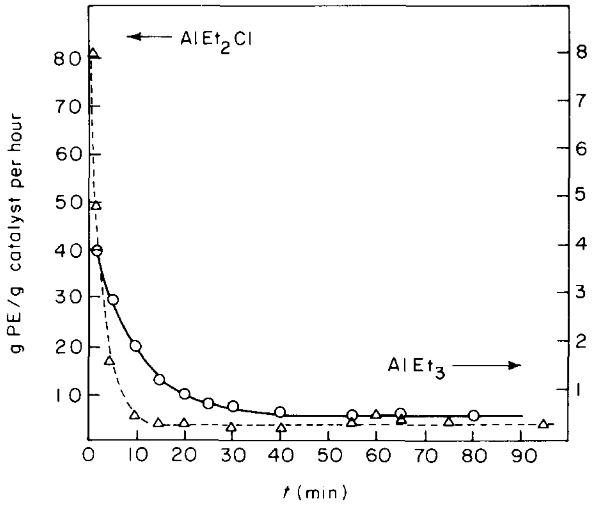

Figure 1 Time courses of ethylene polymerization at 30°C. Polymerizations were carried out with the $Cr(C_{17}H_{35}COO)_3$ (80 mg)/ $AlEt_2Cl$(Al/Cr = 100) catalytic system in 100 ml of toluene under 1 atm of ethylene. (○) $AlEt_2Cl$; (△) $AlEt_3$

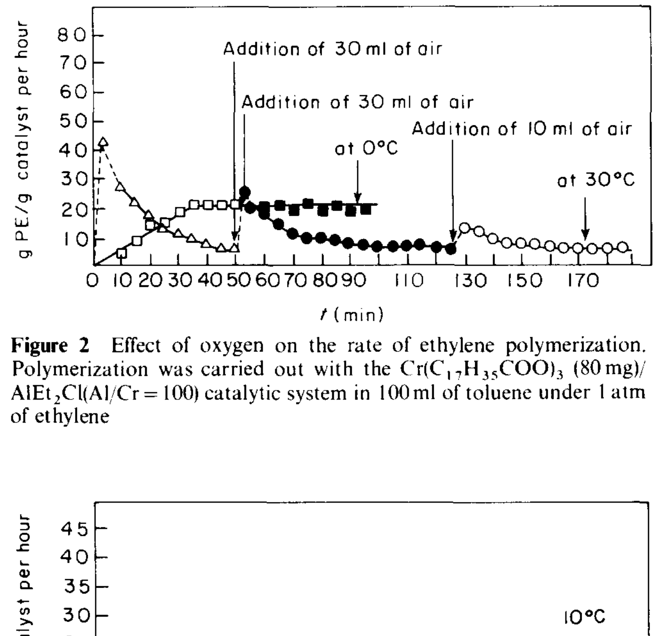

Figure 2 Effect of oxygen on the rate of ethylene polymerization. Polymerization was carried out with the $Cr(C_{17}H_{35}COO)_3$ (80 mg)/ $AlEt_2Cl$(Al/Cr = 100) catalytic system in 100 ml of toluene under 1 atm of ethylene

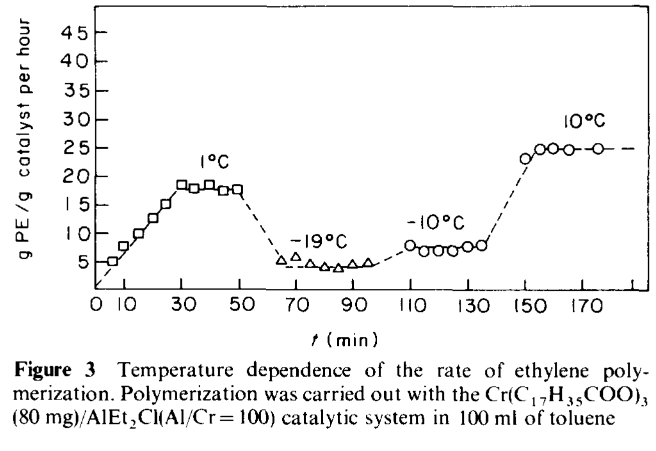

Figure 3 Temperature dependence of the rate of ethylene polymerization. Polymerization was carried out with the $Cr(C_{17}H_{35}COO)_3$ (80 mg)/$AlEt_2Cl$(Al/Cr = 100) catalytic system in 100 ml of toluene

Table 2 Results of copolymerization of ethylene and propylene[a]

Ethylene (l)	Propylene (l)	Copolymer yield (g polymer/g Cr.hour)	Propylene content in copolymer (mol%)	$\bar{M}_w$	$\bar{M}_n$	Q
2	0	504	–	–	–	–
2	4	177	10.5	30000	14600	2.0
2	6	137	11.0	22500	12000	1.9
2	8	65.4	18.3	16500	9200	1.8

[a] Copolymerization was conducted at 30°C in a 200 ml stainless steel reactor for 15 min with $Cr(C_{17}H_{35}COO)_3$ (100 mg) and $AlEt_2Cl(Al/Cr = 100)$ (11.1 mmol) in toluene (20 ml)

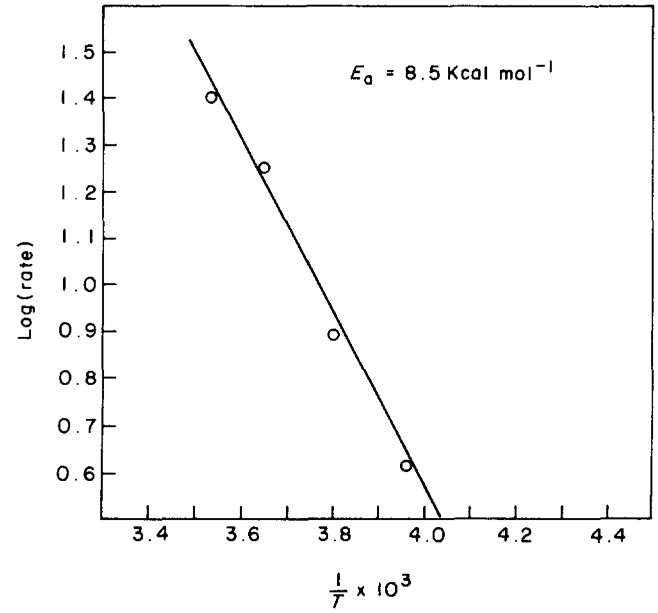

Figure 4 Plots of the rate of ethylene polymerization against the polymerization temperature. For more details see *Figure 3*

validity of such an interpretation was proved by the following experiment:

To the $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalytic system in toluene an atmospheric pressure of propylene was added and the mixture was agitated for 50 min at 0°C. The reactor was then evacuated *in vacuo* to remove the propylene in the reactor and the polymerization of ethylene was initiated at 0°C. In *Figure 5* the polymerization rate as a function of reaction time together with that obtained in a normal run is shown. No difference in the activity can be observed between the two systems. The result implies that the propylene coordinated with the Cr^{2+} species can be removed (or replaced) by ethylene. It may be considered therefore that the copolymerization of ethylene and propylene should proceed with the present catalyst.

From such a viewpoint, the copolymerization of ethylene and propylene was carried out in a stainless steel reactor at 30°C by using the same catalytic system. Typical results obtained are summarized in *Table 2*.

With an increase in the feed ratio of propylene/ethylene, both the activity and the molecular weight decreased to a large extent, while the content of propylene in the copolymer did alter much. It should be noted that the molecular weight distribution of the copolymer is narrow ($Q=2$), which indicates that the copolymerization proceeds over a homogeneous active species. The C^{13} n.m.r. spectrum of the copolymer (ethylene 2 l, propylene 8 l) did not display the characteristic peaks owing to long sequence of propylene units, indicating that the monomer distribution in the copolymer is extremely random. The d.s.c. curve of the copolymer (ethylene 2 l, propylene 8 l) showed a very broad melting point centred at about 60°C with T_g at −48°C.

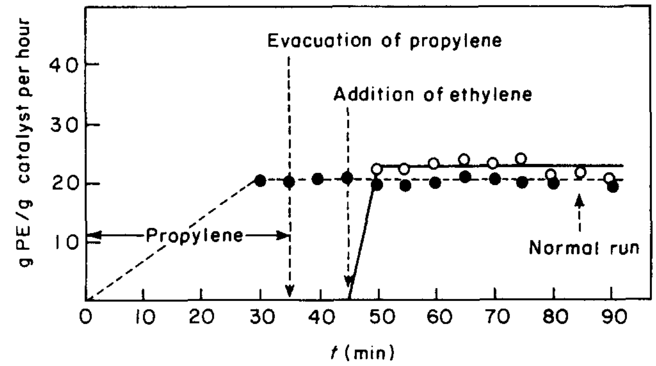

Figure 5 Time courses of ethylene polymerization at 0°C. Polymerizations were carried out with the $Cr(C_{17}H_{35}COO)_3$ (80 mg)/ $AlEt_2Cl(Al/Cr = 100)$ catalytic system in toluene. For more details see text

In conclusion, the homogeneous $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalytic system in toluene solvent showed some polymerization activity for ethylene but not for propylene. From the e.s.r. measurements of the catalytic systems combined with some qualitative experiments, the active species was determined to be Cr^{2+}. The reason why it should be incapable of polymerization of propylene was also discussed. The catalytic system showed some activity for ethylene–propylene copolymerization to give a random copolymer having a narrow molecular weight distribution.

REFERENCES

1 Alfred, C. (Batelle Memorial Institute) Ger. Offen. 2606243
2 Gan, S.-N., Chen, S.-I., Ohnishi, R. and Soga, K. *Makromol. Chem., Rapid Commun.*, 1984, **5**, 535
3 Angelescu, E., Nicolau, C. and Simon, Z. *J. Am. Chem. Soc.* 1966, **88**(17), 3910
4 Soga, K., Chen, S.-I. and Ohnishi, R. *Polym. Bull.* 1982, **8**, 473
5 Soga, K., Sano, T. and Ohnishi, R. *Polym. Bull.* 1981, **4**, 157
6 Carman, C. J. and Wilkes, C. E. *Rubber Chem. Technol.* 1971, **44**, 781