Homo- and copolymerization of ethylene and propylene using a heterogeneous chromium catalyst system

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Homo- and copolymerization of ethylene and propylene was carried out using a heterogeneous $Cr(CH_3COO)_3/AlEt_2Cl$ catalytic system in toluene at 40°C. Homopolymerization was studied at atmospheric pressure and followed by measuring the volume of monomer consumed. Copolymerization was carried out at low pressure in a closed system and the progress of the reaction was studied by monitoring the change in monomer pressure. Random copolymers were obtained despite the catalytic system being heterogeneous.

(Keywords: homopolymerization; copolymerization; ethylene; propylene; heterogeneous chromium catalyst; random copolymer)

INTRODUCTION

Homopolymers and copolymers of ethylene and propylene are important commercially and efforts directed towards finding novel and more efficient catalysts for the synthesis of the desired materials have been reported in numerous patents and publications[1,2]. Two different types of catalyst systems have been widely applied commercially: the Ziegler–Natta and the metal alkyl-free catalysts.

Generally Ziegler–Natta catalysts are formed by reacting a metal alkyl (or hydride) and a transition-metal salt. While many transition-metal salts, in combination with a certain metal alkyl (or hydride), show some activity in the polymerization of ethylene or propylene, only those of Ti and V are of industrial importance and have been widely studied. Cr salts such as $CrCl_2$, $CrCl_3$ and $Cr(acac)_3$ have also been used but their activities are generally low (acac = acetylacetonate).

A metal alkyl-free catalyst is one that consists of a transition-metal salt, alone or in combination with a second component, and does not contain added base-metal alkyl. The Phillips catalyst prepared by impregnating a silica–alumina or a silica support with CrO_3 is one of the most widely investigated. The various modifications of the Phillips catalyst and a number of other chromium-based catalysts such as the bis(triphenylsilyl)chromate and chromocene have been reviewed recently[3]. However, these chromium compounds are only widely used in the polymerization of ethylene.

In recent patent literature, Battelle[4] have reported the preparation of a new chromium catalyst from reacting $Cr(CH_3COO)_3H_2O$ with acetic acid and acetic anhydride. The product in combination with $AlEt_2Cl$ shows extremely high activity in polymerizing ethylene. We have since successfully used the catalyst for both the homopolymerization of propylene and random copolymerization of ethylene and propylene[5]. Recent investigations showed that the same chromium catalyst could be prepared from a variety of starting materials[6]. Based on the results of elemental analysis, i.r., d.s.c. and bulk magnetic susceptibility measurements, the compound appears to have a polymeric structure with two types of bridging acetate groups and with the empirical formula of $Cr(CH_3COO)_3$.

This paper reports more detailed results of the homo- and copolymerization of ethylene and propylene using such a catalytic system.

EXPERIMENTAL

Materials

Research-grade ethylene, propylene and toluene (from Takachiho Chemical Co.) were further purified according to the usual procedures. Nitrogen of high purity (from Nippon Sanso) was further 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.

Preparation of $Cr(CH_3COO)_3$

Commercial $Cr(CH_3COO)_3H_2O$ was refluxed in a mixture of acetic acid and acetic anhydride for 4 h. The excess acetic acid and acetic anhydride were removed under reduced pressure to give a bright-green fine powdery product.

Polymerization and analytical procedures

Homopolymerization was carried out at 40°C in a 300 ml glass reactor equipped with a magnetic stirrer. A known weight (around 30 mg) of $Cr(CH_3COO)_3$ was dispersed in 80 ml toluene in the reactor under nitrogen. Two different procedures have been utilized. In the first method, the reactor was degassed *in vacuo* before the monomer gas, at atmospheric pressure, was introduced

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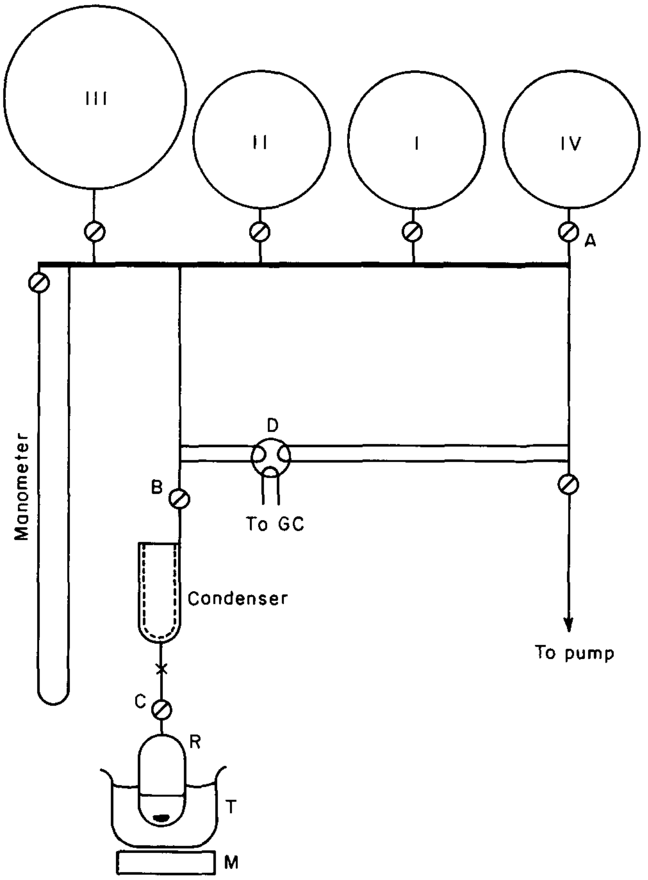


Figure 1 Apparatus for copolymerization at low pressure. The schematic diagram is not drawn to scale and only the essential components are shown. Reservoir flask I is for storing ethylene, II for propylene, III for mixing the monomers, and IV (with calibrated volume) for the monomer mixture used in copolymerization. D is a multi-way tap which is connected to a gas chromatograph. R, Reactor; M, magnetic stirrer; T, thermostated bath. The condenser was maintained at −10°C with acetone–dry ice mixture to prevent the vaporization of toluene into the gas line. Only taps A, B and C were opened during copolymerization

followed by the measured amount of $AlEt_2Cl$ solution. In the second method the measured amount of $AlEt_2Cl$ was first added into the reactor and the mixture was agitated for about 30 min until the colour of the mixture turned from green to pale yellow. The reactor was then degassed before the introduction of monomer gas.

Copolymerization was carried out at 40°C in a 100 ml glass reactor connected to a gas line with a reservoir flask containing ethylene and propylene mixture of known composition. The set-up of the apparatus is as shown in *Figure 1*. Measured amounts of $Cr(CH_3COO)_3$ and $AlEt_2Cl$ were first mixed in 20 ml toluene in the reactor under nitrogen. The reactor was then degassed *in vacuo* followed by the introduction of monomer mixture whose composition has been determined by gas chromatography. The progress of the polymerization was followed by recording the drop in pressure at different reaction times.

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.

RESULTS AND DISCUSSION

The mixture of $Cr(CH_3COO)_3/AlEt_2Cl$ in toluene is heterogeneous but very highly dispersed. Homopolymerization was carried out at 40°C using different Al/Cr ratios. In each case, the rate of ethylene polymerization is very much higher than that of propylene. *Figure 2* shows the typical kinetic curves of homopolymerization. In the case of ethylene polymerization, the rate increases rapidly to a maximum within 10 min. In contrast, the rate of propylene polymerization decreases with time.

As mentioned earlier, two polymerization procedures have been used. The first procedure involves saturating the solvent containing the dispersed chromium catalyst with the monomer gas before the addition of $AlEt_2Cl$. In the second procedure, the chromium complex is allowed to react with $AlEt_2Cl$ for a specific time before introducing the monomer gas. In the first procedure, polymerization of ethylene begins after the co-catalyst has reacted with the chromium catalyst, producing a colour change within a short period. In the second procedure, polymerization of ethylene begins almost instantly as the co-catalyst and catalyst have been allowed to react for some time. While both procedures have no effect on the maximum rate of ethylene polymerization, only the second procedure can polymerize propylene and copolymerize ethylene and propylene.

The failure to polymerize when a transition-metal compound and solvent mixture was first saturated with propylene before the addition of co-catalyst has also been

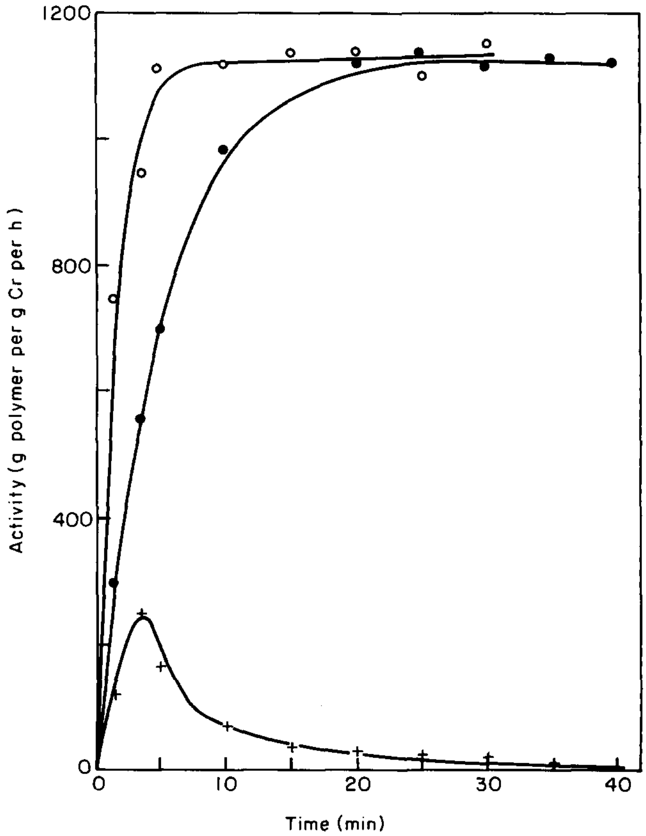


Figure 2 Kinetic curves of homopolymerization. Polymerization conditions: monomer pressure, 101 kPa (760 torr); and Al/Cr = 10. Ethylene was polymerized using the first procedure (●) and the second procedure (○), while propylene was polymerized by the second procedure (+)

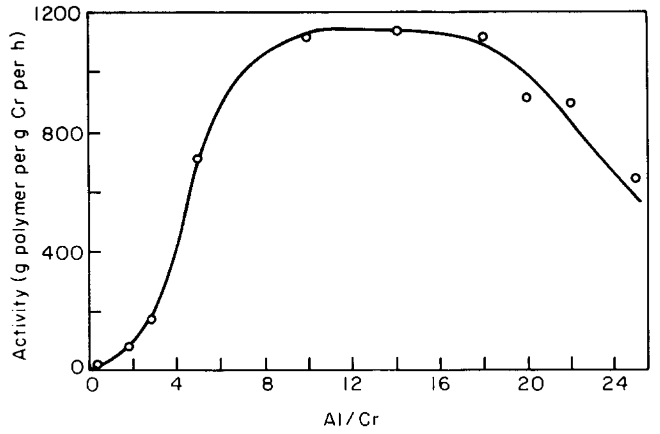


Figure 3 Effect of varying Al/Cr ratio on the maximum rate of ethylene polymerization. Monomer pressure, 101 kPa; other conditions as described in 'Experimental' section

Table 1 Effect of pre-reaction time of catalyst and co-catalyst[a]

Reaction time (min)	Amount of propylene in copolymer (mol%)	Average activity (g copolymer per g Cr per h)
5	40	5
30	40	34
60	41	32
300	40	33
1200	41	16

[a] Monomer mixture for the copolymerization contains 43.6% ethylene and 56.4% propylene. Al/Cr = 10. Mol% propylene in copolymer was determined from ^{13}C n.m.r.[13] The catalyst and co-catalyst were mixed at room temperature while the copolymerization was carried out at 40°C

observed in a number of other cases[7-9]. As it has been shown that the oxidation state of Cr in the active catalyst is II[5,9], the formation of a stable complex between the Cr^{2+} species and propylene has been suggested as a possible cause. However, such a proposal alone cannot satisfactorily explain the occurrence of propylene polymerization by the second procedure. In the first procedure there was no colour change, indicating that the co-catalyst and the catalyst had not reacted. Thus it appears that propylene may inhibit the reaction of Cr(III) acetate and $AlEt_2Cl$. Once reduction to Cr(II) had occurred, by the second procedure, polymerization of propylene becomes possible.

Figure 3 summarizes the effect of varying the Al/Cr ratio on the activities of the catalyst system towards homopolymerization. The activity increases with Al/Cr ratio and attains a maximum when the Al/Cr molar ratio is around 8. Further increase in Al/Cr ratio up to 18 does not produce significant change in activity. However, activity appears to drop at much higher Al/Cr ratio.

Copolymerizations were carried out using the set-up outlined earlier. The catalyst and co-catalyst were allowed to react in the reactor for various reaction times before introducing the monomer mixture at a total initial pressure of 450±5 torr. As shown in *Table 1*, optimum activity is attained after 30 min to 5 h. Prolonged reaction time, however, leads to a drop in activity. All the copolymerizations were terminated after 30 min when the pressure change is less than 10% of the initial total pressure; thus the monomer mixture composition is approximately constant. The average activity expressed as grams of copolymer per gram of Cr per hour was calculated from the total yield of copolymer divided by the weight of Cr in the catalyst multiplied by 2.

Table 2 summarizes the effect of Al/Cr ratios on the rate of copolymerization. The optimum ratio is within the range from 5 to 10. At much higher Al/Cr ratio, the activity decreases.

Under conditions of constant volume and temperature, the total monomer pressure P is directly proportional to the total number of moles of ethylene and propylene in the mixture, n, as

$$P = n\frac{RT}{V}$$

The rate of monomer consumed per unit time is given by

$$-\frac{\Delta n}{\Delta t} = -\frac{\Delta P}{\Delta t}\frac{V}{RT} \qquad (1)$$

The activity of the catalyst system can be expressed as the number of moles copolymerized per gram of chromium in the catalyst per hour.

Figure 4 shows typical kinetic curves of copolymerization using different mol% propylene in the monomer mixture at 40°C and Al/Cr = 10. The activity of the catalyst system increases sharply to a maximum

Table 2 Effect of varying Al/Cr ratio on copolymerization[a]

Al/Cr	Amount of propylene in copolymer (mol%)	Average activity (g copolymer per g Cr per h)
2	50	6.0
5	51	27.4
8	48	28.3
10	53	27.0
15	43	12.1
20	40	11.2

[a] Monomer mixture in the gaseous phase contained 38.4% ethylene and 61.6% propylene. Catalyst and co-catalyst were allowed to react for 60 min before the introduction of monomer mixture

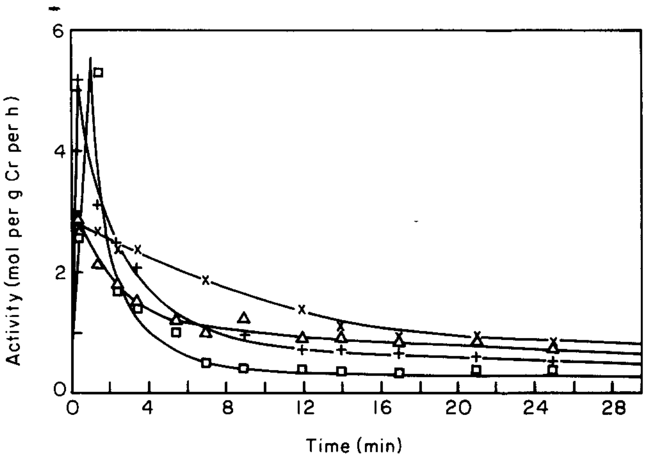
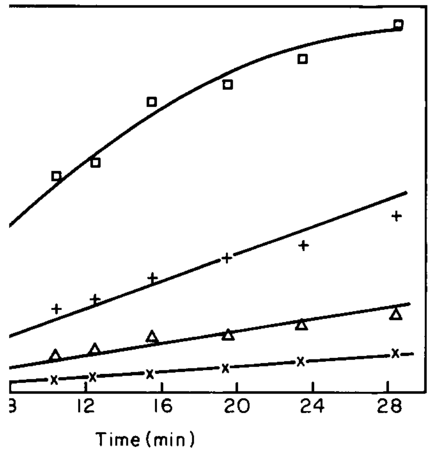


Figure 4 Kinetic curves of copolymerization with $Cr(CH_3COO)_3/AlEt_2Cl$ catalyst system using monomer mixture with different mol% propylene. Al/Cr = 10. Catalyst and co-catalyst are allowed to react for 60 min before introducing monomer. Other conditions as described under 'Experimental' section. Propylene content in the monomer mixture: (□) 83%, (+) 73%, (△) 37% and (×) 31%



l,)−1 *versus t*. Copolymerization conditions as ontent in the monomer mixture: (□) 83%, (+)) 31%

then decreases to a steady state. The seems to decrease with the mol% e final steady-state activity shows the addition, at lower mol% propylene, ie maximum activity occurs more

le that the active centres initially :action of the $AlEt_2Cl$ and the Cr(III) ıble as shown by the results of *Table 1*. *re 4* can be interpreted as follows. As into the solvent and reach the active erogeneous catalyst, polymerization itial rise in activity could be due to the : catalyst particle which exposes new 's new centres to be formed. At this ntres appear to be unstable, possibly ıral changes, and the activity decreases

:ion of many transition-metal alkyl ›bserved to involve a bimolecular assume this was the case in the present the point of maximum activity, then se of active centre concentration, C, y equation (2), assuming no further ;enerated:

$$-dC/dt = kC^2 \qquad (2)$$

rate constant for the bimolecular cess such as the following:

l∿∿P ⟶ Polymer + Inactive products

or CH_3

uation (2) between $t=0$ where $C=C_0$, ıum activity, and $t=t$, where $C=C_t$,

$$1/C_t = kt + (1/C_0) \qquad (3)$$

ymerization experiment, the monomer tained at approximately constant rerall activity of copolymerization, A_t, he active centre concentration, C_t. The

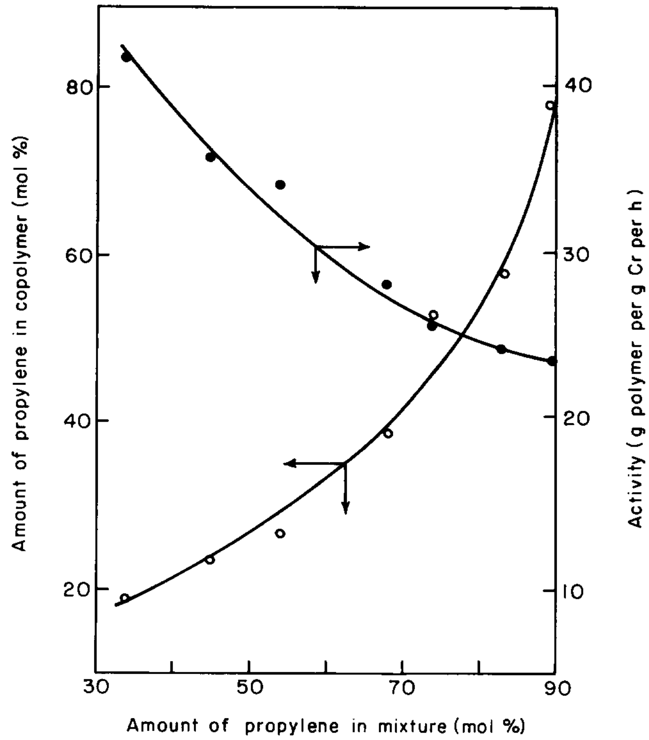


Figure 6 Effect of mol% propylene in the monomer mixture upon the composition of the copolymer and the average activity over 30 min. Polymerization conditions as in *Figure 4*

maximum activity A_0 is likewise proportional to C_0, thus

$$A_0/A_t = C_0/C_t = C_0kt + 1 \qquad (4)$$

$$(A_0/A_t) - 1 = C_0kt \qquad (5)$$

Figure 5 shows that, when the monomer mixture contains a low percentage of propylene, the decay of the active centres occurs at a very slow rate and appears to fit the second-order equation. However, as the propylene content increases beyond 73%, the decline of active centre concentration occurs much more rapidly and is not adequately fitted by equation (5) at high deactivation levels. Without further information on the nature of the active centres and the mechanism of reaction, it is difficult to interpret these kinetic curves at this stage.

The average activity was markedly dependent upon the composition of the monomer mixture, higher average activity being attained at lower mol% propylene as shown in *Figure 6*, while, as expected, the mol% propylene in the copolymer increases with the mol% propylene in the monomer mixture used. The series of copolymers have been characterized by ^{13}C n.m.r. and examined by d.s.c. and the results show that the monomers were distributed fairly randomly in the copolymers[13].

CONCLUSIONS

Homopolymerization of propylene and copolymerization of propylene and ethylene using the Battelle chromium acetate catalyst can be carried out if the catalyst is allowed to react with $AlEt_2Cl$ first before the introduction of monomer. Varying the ratio of Al/Cr within the range 8–18 does not affect the rate of homopolymerization, while the activity of copolymerization was not affected by varying Al/Cr in the range 5–10. The mol % propylene in the monomer mixture affects the kinetics of copolymerization. The average rate decreases with increasing mol % propylene.

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