

# KINETIC STUDY OF GAS-PHASE POLYMERIZATION OF PROPENE BY THE INHIBITION METHOD USING CARBON MONOXIDE\*

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## ABSTRACT

The inhibition method using CO to determine the active center concentration  $C^*$  in olefin polymerization and the kinetics of gas-phase polymerization of propene were studied. The reliability of the method when used in gas-phase polymerization of propene is proved and the influencing factor of the method is found to be the "repeating inhibition" of CO to the active centers.

The  $C^*$ , the rate constant  $k_p$  and the activation energy were determined from the experimental results. We concluded that the  $C^*$  decreases with polymerization time and coincides with the decay rate of the polymerization.

## INTRODUCTION

Up to now the method of determining active center concentration in the Ziegler-Natta polymerization kinetics has not been thoroughly studied. Recently, Tait et al.<sup>[1]</sup> have devised a new method which involves simultaneous rate and adsorption measurements. Keii et al.<sup>[2]</sup> have also used a similar method. But the reliability of the method and the factors influencing the determination of  $C^*$  etc. are not concerned.

On the other hand, the gas-phase polymerization of propene is of great industrial importance since it has the advantages of high catalyst efficiency, simple process and safe operation. There are, however, relatively few reports on gas-phase polymerization of propene and no report on the work with complex-type (i. e. Solvay type)  $TiCl_3$  catalyst system have been published.

Following our previous work<sup>[3]</sup>, we have carried out studies on the inhibition method using CO and the gas-phase polymerization of propene, and found out the main factor influencing the method and the reliability of the method when used in gas-phase polymerization of propene with complex-type catalyst. We have also determined the  $C^*$ , the  $k_p$  and the activation energy and compared the above values with those in the slurry polymerization.

## EXPERIMENTAL PART

### Materials

Catalyst and propene: the same as reported previously<sup>[3]</sup>. Carbon Monoxide: purity

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99.2%, a product of Beijing Analysis Instrument Factory.

### *Polymerization apparatus and procedure*

The polymerization were carried out in a 500 ml glass reactor under a constant pressure of 850—870 mmHg with catalyst Al / Ti = 4(mol). The revolution of the stirrer was maintained at  $300 \pm 10$  rpm. In order to prevent catalyst from caking, about 15 ml of glass beads (2.0—2.2 mm diameter) as the dispersion aid were added into the reactor. Under a nitrogen stream, Al ( $C_2H_5$ )<sub>2</sub> Cl, catalyst and a little hexane (2—4 ml) were admitted into the reactor and mixed for 10 min. Then, the mixture was dried in vac. for 1 h, propene was introduced and the polymerization was started. The polymerization rate was measured by the rate drop of the single tube mercury column of propene tank. The relative error of the rate measurement did not exceed  $\pm 2\%$ .

## RESULT AND DISCUSSION

### *Kinetic behaviour of the complex-type catalyst in gas-phase polymerization of propene*

The rate-time curves of gas-phase polymerization of propene with complex-type catalyst belong to the decay type (Fig. 1). In the case with AlEt<sub>2</sub>Cl as cocatalyst, the polymerization rate at the same temperature is the same as that in slurry polymerization<sup>[3]</sup> along the whole curve, but in this procedure the induction period exhibiting the preliminary formation of active centers is not observed.

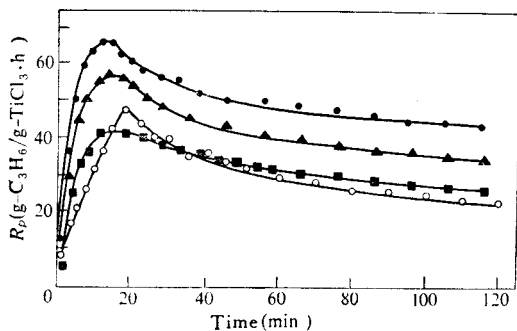


Fig. 1 Rate-time curves of gas-phase polymerization of propene with different co-catalyst at different temperature

Cocatalyst: ●, ▲, ■ AlEt<sub>2</sub> Cl; ○ AlEt<sub>3</sub>  
 Temperature: ● 60°C; ▲, ○ 50°C; ■ 40°C

The external diffusion could be neglected in the experiment according to the result of Doi et al.<sup>[4]</sup>. We have examined the influence of the produced polymer on monomer diffusion by means of the intermission of polymerization<sup>[2]</sup>. After drawout of the monomer, the rate still drops during the intermission of polymerization. This indicates that the rate decay in the polymerization is attributed mainly to chemical course. Meanwhile, the Thiele Modules  $\alpha$  calculated = 0.08, which is  $\ll 1$ , therefore, the kinetic data in our experiments could be considered as the performance characteristic of the catalyst system.

### The reaction mechanism between CO and the polymerization system

The change of the polymerization rate resulted from the addition of a preconcerted small amount of CO during the polymerization is shown in Fig. 2. After the rapid depression to a

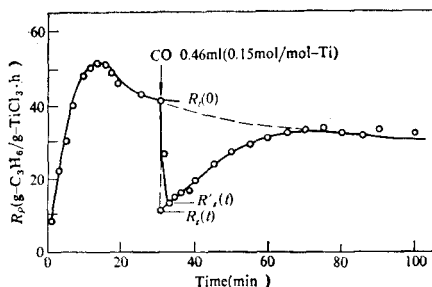
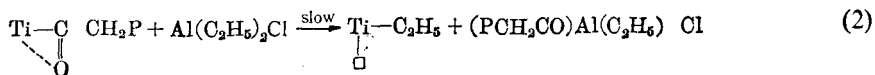
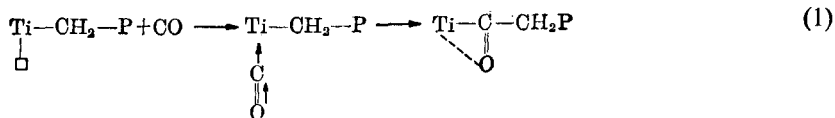


Fig. 2 Change in the rate depressed by the addition of CO during the gas-phase polymerization of propene  
Temperature: 50°C      Cocatalyst: AlEt<sub>2</sub>Cl

minimum value ( $R'_p(t)$ ) in 2–5 min, the rate increases gradually to reach its original value. The chemical function of CO interpreted by Keii<sup>[2]</sup> as follows:



where  $\square$  is a free coordination site and  $-\text{CH}_2\text{P}$  is a polymer chain.

The first reaction has been reported<sup>[2]</sup>. In order to confirm the latter reaction, we have designed the following experiment: intermitting the polymerization course, then adding 50 ml hexane to the reactor and drawing out the solvent after stirring 2 min. Repeating this operation five times to remove the free alkylaluminum in the system, then the polymerization is started again and CO is added (Fig. 3). We have noticed that the change of the rate is different from the case without the above treatment. The rate is not recovered rapidly after dropping to the minimum value and maintained there for a period of time; when the amount of CO reaches a certain extent, the polymerization is completely stopped and the rate could not be recovered to its original value.

The above experimental results illustrate that the chain transfer of the free alkylaluminum in the system plays a leading role for rapidly recovering the polymerization rate after depression and that the active centers could be inhibited completely. The elimination of free AlEt<sub>2</sub>Cl causes the chain transfer to weaken greatly and the inhibited active centers are not regenerated quickly, therefore, the rate is not recovered rapidly. When the inhibited

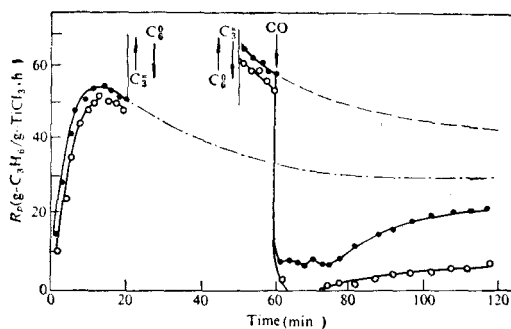


Fig. 3 Influence of the addition of CO after washing free alkylaluminium on polymerization rate (50°C)  
 — ● —  $[CO]/[Ti] = 0.02$  mol/mol, in the mixture washed out,  $[Al]$  is 59.4% of the added amount, the ether is 80.5% of the added amount  
 — ○ —  $[CO]/[Ti] = 0.03$  mol/mol, in the mixture washed out  $[Al]$  is 47.8% of the added amount, the ether is 79.3% of the added amount

active centers are partly regenerated, the rate is gradually increased. The phenomenon that the rate is not recovered to its original value may be attributed to that the amount of residual alkylaluminium is not enough to regenerate all the inhibited active centers.

It is worth-while to point out the fact discovered in the test that, the polymerization rate even increases instead of depression after elimination of the free alkylaluminium. In some experiments, a little hexane (10–30 ml/g-Ti) is added during the polymerization, showing that it does not influence the rate and hence excludes the possibility that the residual solvent may cause the rate to increase. We propose that the increase of the rate may be attributed to the removal of the catalyst poison  $AlEt_2Cl$  produced during the polymerization and the removal of a part of the ether which blocks up the active centers.

#### *The reliability of the inhibition method using CO*

The inhibition method involves the use of an inhibitor to "titrate" the active centers, simultaneously to determine the drop of the polymerization rate and evaluate the concentration of active center by the amount of CO, when the rate is decreased to zero. Therefore, the key of the reliability of the method lies in whether there is a stoichiometrical reaction between CO and the active centers. We discuss this problem in three aspects:

- (1) The stoichiometrical reaction between CO and the active center in the case of "single time inhibition"

Yermakov et al.<sup>[5]</sup> reported that a pre-coordination stage occurred before CO inserts the titanium-polymer bond, thus, we could consider that the amount of CO molecule reacting with an active center in the case of "single time inhibition" depends on the stoichiometrical reaction of adsorption that CO coordinates with the active center. According to the analysis and calculation on the adsorption structure of CO on the surface of  $\delta$ - $TiCl_3$ <sup>[6]</sup>, we could infer that CO coordinates mainly in linear type:  $M \leftarrow C \equiv O$ , in other words, one CO molecule inserts one active center.

(2) The influence of "repeating inhibition" on the stoichiometrical reaction between CO and the active centers

We noticed the fact that even though CO added reaches 20% of Ti in the catalyst, the residual CO content is always smaller than that in raw material propene at the later period of the reaction, in other words, all of the CO added is consumed. In addition, if the added amount of CO is close to or exceeds  $[C^*]$ , the rate is not recovered rapidly after depression and can not be decreased to zero, "terrace" stages appear in the curve (Fig. 4). It shows that the residual CO content in the gas-phase decreases gradually when analysed at different time along "terrace" stage, finally being smaller than the CO content in the raw material.

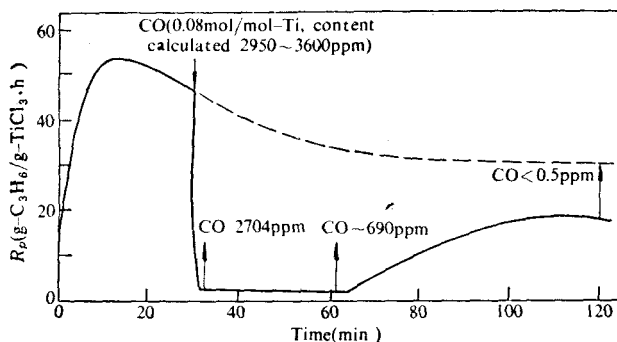
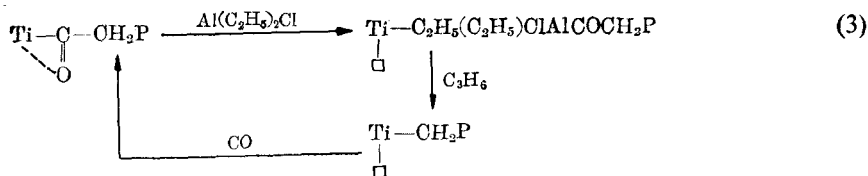


Fig. 4 Change of residual CO content in the gas-phase when excessive amount of CO is added

We consider that the above phenomena may be attributed to the "repeating inhibition" of CO into the active centers, which is interpreted as follows:



The analysis on the residual amount of CO in the gas-phase during the rate recovery when different amount of CO were added shows clearly that the residual amount of CO does not exceed 1% of its added amount if the CO added is less than  $[C^*]$ , and the rate recovers rapidly after depression (Fig. 5 (a)). Therefore the reaction is mainly the insertion of CO into Ti-CH<sub>2</sub>P bond during the rate decrease and the transition of Ti-C-P into AlEt<sub>2</sub>Cl during

the rate recovery. If the amount of CO added is close to or exceeds  $[C^*]$ , the residual amount of CO at the "terrace" stage increases, and the rate does not recover fast (Fig. 5 (b)), in this condition, the influence of "repeating inhibition" may take place and these data are not used,

the zero point of rate drop was obtained by extrapolation (see Fig. 6).

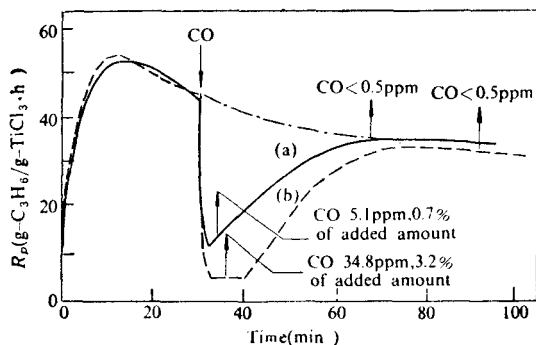


Fig. 5 Change of residual CO content in gas-phase when added amount of CO is smaller than or close to  $[C^*]_t$

(a) Added  $[CO]/[Ti] = 0.02$  mol/mol, content calculated 948—1058 ppm

(b) Added  $[CO]/[Ti] = 0.03$  mol/mol, content calculated 1358—1722 ppm

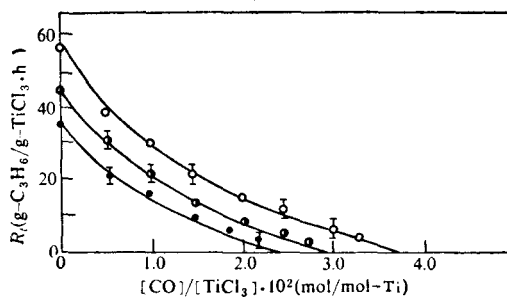


Fig. 6 Relation between polymerization rate and the amount of CO added at different time

Cocatalyst:  $AlEt_2Cl$ . Temperature:  $50^\circ C$

Determination time: —○— 5 min, —◐— 30 min, —●— 60 min

After excessive amount of CO is added the polymerization rate will decrease to a minimum value (at least by 98%) within 2 min, therefore, we assume that the active centers have been inhibited completely at 2.5 min. And we have compared the residual amount of CO determined by chromatography this moment with the theoretical residual amount of CO calculated according to  $[C^*]_t$  (Tab. 1), showing that the relative error between these two data is only 3.5—3.6%. If the  $[C^*]_t$  determined is indicated as the active  $Ti^{3+}$  concentration  $[Ti^*]_t$ , then the consumed CO moles coincide with the active  $Ti^*$  moles in the system, their ratio being  $0.93—0.94 \approx 1$ , which further proves that the influence of “repeating inhibition” could be avoided and the stoichiometrical relation that each active center is inhibited by only one CO molecule could be essentially established in our determination.

### (3) The analysis on other related factors

1. Through infra-red test, it could be approved that alkylaluminium does not react

**Table 1** Comparison between residual amount of CO determined by chromatography and that calculated according to  $[C^*]_t$ 

| No.   | The amount of CO added |      |                  | Analysis time after addition of CO (min) | Residual amount of CO determined (ml) | Residual amount of CO calculated (ml) | Related error between the two values (%) | CO 2.5 (min)         |
|-------|------------------------|------|------------------|------------------------------------------|---------------------------------------|---------------------------------------|------------------------------------------|----------------------|
|       | $[CO]/[Ti]$ (mol/mol)  | (ml) | Calculated (ppm) |                                          |                                       |                                       |                                          | $[Ti^*]_t$ (mol/mol) |
| GA-77 | 0.08                   | 2.87 | 3622             | 2.5                                      | 1.68                                  | 1.62                                  | 3.6                                      | 0.93                 |
| GA-83 | 0.08                   | 2.44 | 3412             | 2.5                                      | 1.43                                  | 1.38                                  | 3.5                                      | 0.94                 |

Note: CO is added at 30 min after polymerization starting and  $[C^*]_t = 0.0289$  mol/mol Ti this moment

with CO; 2. Within  $40^\circ\text{C}$ – $60^\circ\text{C}$ , it is shown by experiment that the determination was not influenced by temperature; 3. According to Fig. 3, the polymerization is stopped by 12 min when excessive amount of CO is added after  $AlEt_2Cl$  is washed out, therefore the copolymerization proposed by Caunt<sup>[7]</sup> does not take place in our experiment.

As discussed above, we consider that this method is reliable when used in gas-phase polymerization of propene and mainly affected by the "repeating inhibition" of CO to the active centers. The main advantage of the method lies in the possible determination of active center concentration at the different time in the polymerization course. Besides, the apparatus used are simple and the operation is convenient.

#### *Determination of $C^*$ , $k_p$ in gas-phase polymerization of propene with the complex-type catalyst*

Fig. 2 shows the change of the polymerization rate after adding CO, by means of plotting the rate ( $R$ ) of the earlier stage of the recovery course against time ( $t$ ) and using least-square fit method, the residual rate  $R_{t(t)}$  just inhibited by CO is obtained.

Figs. 6 and 7 show the relation between the residual rate  $R_t$  and the amount of CO added, we have a curve fitting the above relation according to a nonlinear equation  $Y = a + be^{-x}$  and have evaluated  $[C^*]_t$  by the minimum amount of CO necessary to stop the polymerization.

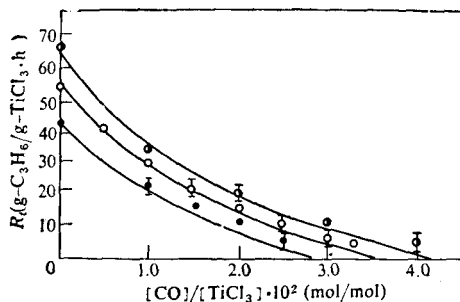


Fig. 7 Relation between polymerization rate and the amount of CO added at different temperature

Cocatalyst:  $AlEt_2Cl$ , CO is added at 15 min after Polymerization starting

Temperature: —●—  $60^\circ\text{C}$ , —○—  $50^\circ\text{C}$ , —●—  $40^\circ\text{C}$

Following results are obtained by determination on  $C^*$ ,  $k_p$ :

(a) All curves in Fig. 6 and 7 are of the same type at different temperatures and time, but change with the catalyst system. For instance, it is deviated from above type when co-catalyst  $AlEt_3$  is used as shown in Fig. 8, which has been testified on "finger-print" character of Tait's<sup>(11)</sup>. In fact, the extent of the curves winding shows the activity distribution of active centers in the system and may be related to the surface heterogeneity of catalyst, perhaps there are two kinds of active centers.

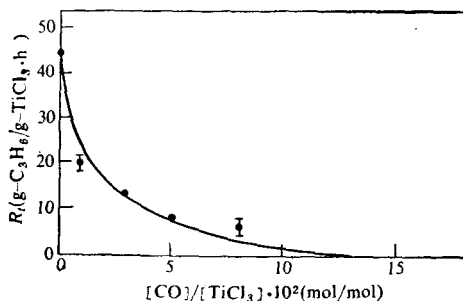


Fig. 8 Relation between polymerization rate and the amount of CO added in the case with  $AlEt_3$  as cocatalyst

Temperature: 50°C, CO is added at 20 min after polymerization starting

(b) At the same temperature, the  $C^*$  decreases with the polymerization time in the period of rate decay and the  $k_p$  remains constant (Tab. 2). Fig. 9 shows that the decrease of  $C^*$  coincides with the decay rate  $R_p$  of the polymerization within the same time interval (15—60 min). Because both  $R_p$  and  $C^*$  are mainly second order decay, it proves that the decay rate is resulted from the decrease of  $C^*$ .

Table 2 Determination of  $C^*$  and  $k_p$  for gas-phase polymerization of propene with complex-type catalyst

| Catalyst system                                                              | Temperature<br>(°C) | [M]<br>(mol/l) | $\bar{R}_t(O)$<br>(g-C <sub>3</sub> H <sub>6</sub> /<br>g-TiCl <sub>3</sub> ·h) | Inhibited<br>time<br>(min) | $[C^*]_t \cdot 10^2$<br>(mol/mol-Ti) | $k_p$<br>(l/mol·s) |
|------------------------------------------------------------------------------|---------------------|----------------|---------------------------------------------------------------------------------|----------------------------|--------------------------------------|--------------------|
| TiCl <sub>3</sub> /                                                          | 40                  | 0.04453        | 42.70                                                                           | 15                         | 2.95                                 | 32.10              |
| TiCl <sub>4</sub> /                                                          |                     | 0.04308        | 53.88                                                                           | 15                         | 3.56                                 | 35.78              |
| Bu <sub>2</sub> O-                                                           | 50                  | 0.04285        | 43.58                                                                           | 30                         | 2.89                                 | 35.84              |
| AlEt <sub>2</sub> Cl                                                         |                     | 0.04281        | 36.35                                                                           | 60                         | 2.41                                 | 35.88              |
|                                                                              | 60                  | 0.04167        | 65.47                                                                           | 15                         | 4.08                                 | 39.21              |
| TiCl <sub>3</sub> /TiCl <sub>4</sub><br>/Bu <sub>2</sub> O-AlEt <sub>3</sub> | 50                  | 0.04272        | 44.25                                                                           | 20                         | 13.0                                 | 8.11               |

(c) With  $AlEt_2Cl$  as cocatalyst, the polymerization rate usually attains a maximum value at 12—18 min, so the  $[C^*]_t$  determined at 15 min is equal to the max concentration  $C^*_{max}$  of active centers in the system.  $C^*_{max}$  increases with the raise of temperature and

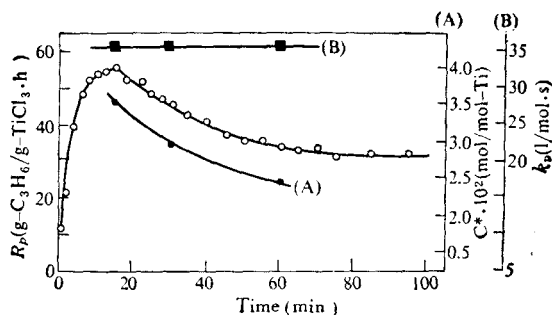


Fig. 9 Change of polymerization rate  $R_p$ ,  $C^*$  and  $k_p$  with time

could be interpreted in terms of more active centers being transferred from the potential active sites with the raise of temperature.

(d) The determined values are the same order of the other authors' <sup>(1,3,7)</sup> using different methods with the same catalyst system. When  $\text{AlEt}_3$  is used as cocatalyst,  $C^*$  is above  $10 \cdot 10^{-2}$  mol/mol-Ti,  $\text{AlEt}_2\text{Cl}$  as cocatalyst,  $C^*$  is  $2 \cdot 10^{-2}$  —  $5 \cdot 10^{-2}$  mol/mol-Ti.

(e) There is no appreciable difference between the values of  $C^*$  in the gas-phase and in slurry polymerization, but the value of  $k_p$  is 5—7 times larger correspondingly (Tab. 2). It may be deduced that the activity of the catalyst will increase if the gas-phase polymerization is carried out with a monomer concentration equal to that of the slurry polymerization.

#### *The activation energy for gas-phase polymerization with complex-type catalyst*

The apparent activation energy evaluated  $E_a$  (5.5 kcal/mol) is about half of that in slurry polymerization, which is in accordance with Григорьев's<sup>[8]</sup> and Keii's<sup>[9]</sup> change law and relative ratio. In addition, the activation energy for chain propagation  $E_p$  (2.1 kcal/mol) and the frequency factor  $A_p$  ( $9.0 \cdot 10^2$  l/mol·s) are smaller than those in slurry polymerization.

The decrease of  $E_a$  in gas-phase polymerization is resulted from the drop of both  $E_p$  and  $\Delta E$ . The depression of  $E_p$  may be attributed to the elimination of the resistance of solvent molecules. On the other hand, there is no transfer of medium around alkylaluminum in gas-phase polymerization, which limits the transformation extent of the potential sites to active centers with the rise of temperature and thus causing the  $\Delta E$  value to drop.

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