Influence of the nature of monomers on the activity of supported titanium catalysts in the α-olefin polymerization

N. M. Gul'tseva*, T. M. Ushakova, A. M. Aladyshev, L. N. Raspopov, and I. N. Meshkova

Institute of Chemical Physics of Academy of Science, Kosigina 4, 117977 Moscow, Russian Federation

SUMMARY

Ethylene and propylene co-polymerization and sequential polymerization with high activity supported titanium catalysts were studied. Specific rate of homopolymerization and co-polymerization constants for ethylene and propylene were determined by using the derived values of the solubility constants for monomers in nascent polymers. The reason of the increased rate of co-polymerization upon enriching the monomers mixture with propylene, the effect of activation of ethylene polymerization upon preliminary polymerization of propylene may be in the increasing number of active sites due to enlarged content of amorphous phase in the nascent polymer product.

INTRODUCTION

The co-polymerizations of ethylene with α-olefins in the presence of heterogeneous (1,2,4) and homogeneous (4,5) complex catalysts are known to be accompanied by the effect of increased polymerization rate for ethylene in the presence of co-monomers: propylene (1,2,3), butene (2), hexene-1 (1,4,5), and methylpentene-1(3) The activation of co-polymerization of ethylene with α-olefins was explained by: the change in the k_p value due to modification of an active site, C_p (4); the increase in the amount of active sites, $[C_p]$(3); and the change in the monomer concentration in the vicinity of the centers of polymer chain propagation (3).

Aiming at elucidating the influence of nature of monomer on activity of complex catalysts for α-olefin polymerization, in the present work we investigated the kinetics of co-polymerization and sequential polymerization of ethylene and propylene by the supported titanium-magnesium catalyst (TMC); the effect of increased polymerization rate of ethylene in the presence of co-monomers was tentatively explained by the data on

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*Corresponding author

relative reactivity of monomers and by specific activity of TMC in sequential polymerizations. To determine the role of diffusion limitations in the investigated processes, we compared the specific activities of catalysts in the gas phase polymerization of ethylene and propylene, as well as those in an inert solvent and in liquid monomer (for propylene).

EXPERIMENTAL

The homo- and co-polymerizations of ethylene and propylene were carried out with the catalyst $MgCL_2$/DIBP/$TiCL_4$-$ALEt_3$ and the stereoregulating agent, phenyltrietoxysilane (PTES). The titanium content in the catalyst was 2.3 wt.%. Ethylene and propylene were of polymerization grade purity.

The liquid phase polymerizations were carried out in dried n-heptane of spectral purity grade (6). The polymerization and co-polymerization conditions for ethylene and propylene were as follows: temperature $70^{\circ}C$; mole ratios: $ALEt_3$:Ti=320, $ALEt_3$:PTES=20. The experimental procedure of polymerization was described elsewhere (7,8).

The kinetic method (9) was used in the studies on co-polymerizations.In the case of the multistage sequential polymerization and co-polymerization the first stage of polymerization were performed in n-heptane (or in liquid propylene), the further stages were carried out in a gas phase.The composition of ethylene-propylene co-polymers, besides the kinetic method (9), was also established by using the NMR ^{13}C spectra as described elsewhere (10). The spectra were registered with the Bruker HM-400 device at the frequency 100.6 MHz and $100^{\circ}C$.The spectra were taken by using the 3-5 wt.% solutions of ethylene-propylene co-polymers in o-dichloroben zene.To stabilize magnetic field, hexadeuterodimethylsulfoxide was added to the co-polymer solution. The crystallization degree (α) of polymer products was determined by X-ray method.

RESULTS AND DISCUSSION

According to the obtained kinetic data, the homo- and co-polymerization of ethylene in the presence of TMC has the pronounced non-stationary character (Fig.1).During co-polymerization process, upon admission of the monomers mixture of the given composition, some constant concentrations of α-olefins are achieved within the reaction zone (Fig.2.),i.e. at some certain moment the consumption rate for the mixture of monomers, dm/dt, and the rate of monomers inlet in co-polymer ($W = \omega_{C_2H_4} + \omega_{C_3H_6}$) are equalized. By choosing the monomers ratio, at which dm/dt=W (fig.2,curve4') in the presence of TMC one may prepare the co-polymers of constant composition equal to the composition of a replenishing mixture $N_{C_3H_6}/N_{C_2H_4}$;

heterogeneous and homogeneous catalysts (1-5), the extremum in the dependence of catalytic activity upon the ratio of α-olefin and ethylene monomer concentrations within the reaction zone, F, is observed (Fig.1). Together with co-polymerization of C_2H_4 and C_3H_6, the sequential multistage homopolymerization of these monomers has been investigated. By assuming that admission of monomer to the active sites is possible only through the polymer layer formed on the catalyst surface in the course of polymerization (11,12), the values of the specific rate of homopolymerization of ethylene and propylene ($K_{ef}=W/C_m Q_{Me}$, where W - polymerization rate, in mole/min; Q_{Me} - gram of transition metal; Cm - monomer concentration, in mole/l) were determined by usingthe derived values of the solubility constants (K_H) for monomers in the amorphous portions of the samples of the nascent isotactic polypropylene and the ultra-high-molecular-weight polyethylene (UHMWPE) (dry and in the presence of n-heptane).The equations giving the $K_{H(C_3H_6)}$ and $K_{H(C_2H_4)}$ values as a function of temperature, are presented in Table 1.

It was shown that the specific polymerization rate calculated by using the C_3H_6 and C_2H_4 solubility constants in polymer, and in polymer with solvent (n-heptane and liquid propylene) for gas phase and suspension process, are essentially the same. (Fig.3)

In the course of the studies on the sequential homo- and co-polymerization of ethylene and propylene in the presence of TMC both for the suspension and gas phase processes, the following results were obtained:

-the ethylene polymerization is activated not only in the presence of the propylene co-monomer, but as well uponpreliminary polymerization of propylene, complete removal of the residual C_3H_6 from the reaction zone, and its substitution by ethylene (Fig.4a);

-for the two-stage process $C_2H_4 \longrightarrow C_3H_6$, the specific propylene polymerization rate was found to be smaller than that for the one-stage polymerization of C_3H_6 (Fig.4b);

-the preliminary homopolymerization of propylene (ethylene) has no influence on the specific rate of co-monomers inlet into a polymer chain in the course of co-polymerization (Fig.5). From the data on the composition of co-polymers it follows that, inspite of the fact whether the homopolymerization of mono mers precedes co-polymerization, or not in the presence of TMC the polymers of the same composition are formed(Fig 6) The values of r_1 and r_2 for the suspension process of co-polymerization and

$$f = \omega_{C_3H_6} / \omega_{C_2H_4} = (dm/dt \ N_{C_3H_6} / \ dm/dt \ N_{C_2H_4} = N_{C_3H_6} / N_{C_2H_4}$$
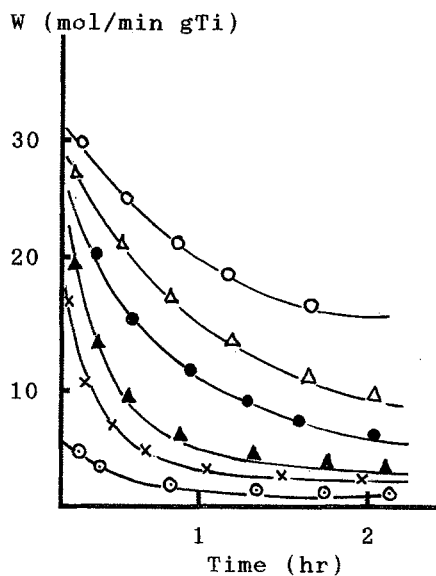
W (mol/min gTi)

Fig.1. Typical rate time plots for homo- and co-polymerization of ethylene and propylene using TMC at 70 $^\circ$C, n-heptane homopolymerization:$\triangle$-C_2H_4

$\odot$-C_3H_6

O,●,▲,✕ -co-polymerization of C_2H_4 and C_3H_6

$N_{C_3H_6} / N_{C_2H_4}$:O-0.18;, ●-1;▲-2.7;

✕ -5.45
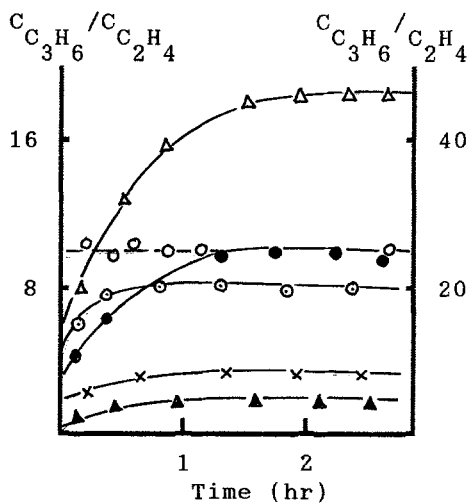
Fig.2.Variation of monomer mixture composition in n-heptan with time

70 $^\circ$C; $N_{C_3H_6} / N_{C_2H_4}$: ▲-0.18;

✕ -0.26; $\odot$ -1; ●,o -2.7; $\triangle$ -5.45; -before co-polymerization

$P_{C_3H_6} / P_{C_2H_4}$ =5.75

According to the kinetic data (9), this means that the relative reactivity of co-monomers in the presence of TMC is time-independent, and co-polymerization is brought about by the same active sites.

With TMC under investigation, as well as with another

Table.1 Solubility of C_2H_4 and C_3H_6 in the isotactic poly propylene and UHMWPE as a function of temperature.

Polymer	$/1-\alpha/,\%$	Monomer	K_H
Polypropylene	62	C_2H_4	$K_H = 1.42 \ 10^{-3} e^{1750/RT}$
		C_3H_6	$K_H = 3.31 \ 10^{-3} e^{2500/RT}$
UHMWPE	31	C_2H_4	$K_H = 6.2 \ 10^{-3} e^{730/RT}$
		C_3H_6	$K_H = 7.96 \ 10^{-3} e^{1335/RT}$

* The solubility constants for ethylene and propylene in both swollen in the solvent polymers were found to be larger than those in dry nascent polymers and close to $K_{H(C_2H_4)}$ and $K_{H(C_3H_6)}$ in n-heptane (7,13).
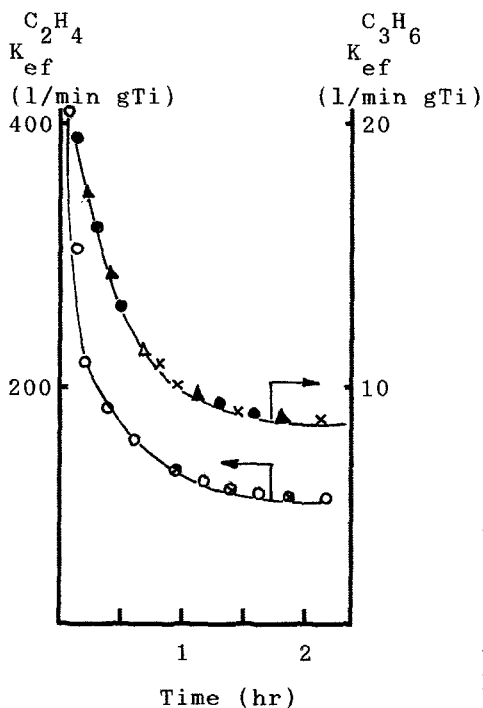

C_2H_4
K_{ef}
(l/min gTi)

C_3H_6
K_{ef}
(l/min gTi)

Fig 3. Kinetic curves of ethylene and propylene polymerization using TMC.
Ethylene polymerization: in n-heptane,

$K_{H(C_2H_4)} = 0.0796$ mol/l atm (O);

without solvent (◐)

$K_{H(C_2H_4 \text{ in UHMWPE})} = 0.059$ mol/l atm

Propylene polymerization:
in n-heptane,

$K_{H(C_3H_6)} = 0.325$ mol/l atm (●);

in liquid propylene (▲)
without solvent
$K_{H(C_3H_6 \text{inPP})} = 0.13$ mol/l atm (✗)

Time (hr)

$\overset{C_2H_4}{K_{ef}}$
(1/min g Ti)

$\overset{C_3H_6}{K_{ef}}$
(1/min g Ti)

$\overset{C_2H_4}{K_{ef}}$
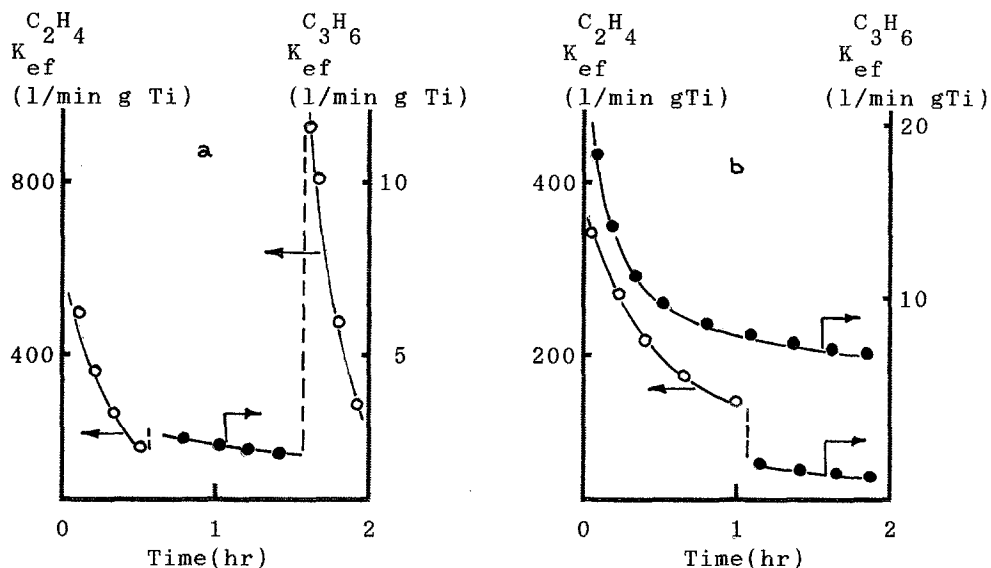(1/min gTi)

$\overset{C_3H_6}{K_{ef}}$
(1/min gTi)

a

b

Fig.4.Kinetic curves of sequential polimerization.
a)ethylene- propylene-ethylene polymerization;
b) ● - propylene polymerization; ◐,● -sequential
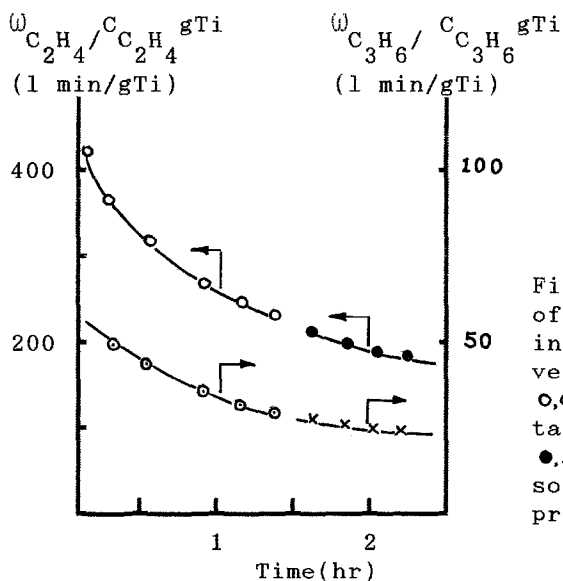ethylene-propylene polymerization

$\overset{\omega}{C_2H_4}/\overset{C}{C_2H_4}$ gTi
(1 min/gTi)

$\overset{\omega}{C_3H_6}/\overset{C}{C_3H_6}$ gTi
(1 min/gTi)

Fig.5. Plots of specific rate
of ethylene and propylene
inlet into a co-polymer chain
versus time
○,◎-co-polymerization in hep-
tane;
●,×-co-polymerization without
solvent after the preliminary
propylene homopolymerization.

for the gas phase co-polymerization after propylene (ethyle ne) homopolymerization have close magnitudes (Table.2).This implies that the nature of the ethylene Cp by the action of propylene and the nature of propylene Cp in the presence of ethylene are not changed.
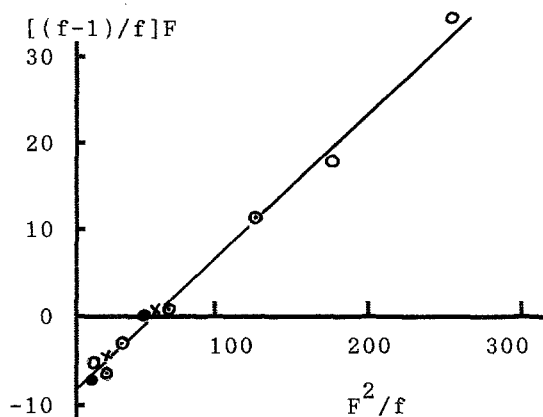

Fig.6.Variation of co-polymer composition (f) with molar ration of co-monomers (F) in the reaction zone (Fineman-Ross coordinates(14) Co-polymerization: in n-heptane (○), in gas phase after preliminary propylene homopolymerizatiom in n-heptane(⊙) and in liquid propylene (×); in gas phase after preliminary ethylene homopolymerizatiom in n-heptane (●).

Table 2 The co-polymerization constants for ethylene and propylene in the presence of TMC.

r_1	r_2	* r_1 =F/f
7.3⁻0.2	0.141⁻0.01	7.8⁻0.2

* The polymer composition (f) was determined by using the NMR ^{13}C method (10).

CONCLUSION

On the basis of our experimental data it seems reasonable to conclude that the influence of the nature of monomers on the activity of TMC in the α -olefin polymerization could not be related to modification of active sites.It may be the result of the change in the number of C_p .Transmitting from UHMWPE to polypropylene and to practically amorphous ethylene-propylene copolymers, due to enlarged content of the amorphous phase in the nascent polymer product the catalyst surface accessing for monomers is increased. In view of this, the number of C_p taking part in co-polymerization is greater than that in the homopolymerization of ethylene and propylene.

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