T. M. USHAKOVA, N. M. GUL'TSEVA,
I. N. MESHKOVA, Y. A. GAVRILOV
Institute of Chemical Physics
Russian Academy of Sciences
Moscow, Russia

Random and block copolymerization of ethylene and α-olefins with Ziegler-Natta catalysts

Summary — The kinetics of ethylene polymerization and of its successive copolymerization with propylene under varying conditions of comonomer addition into the reaction medium and with changing the comonomer addition sequence has been investigated in the presence of high-active magnesium-supported titanium catalyst. To determine correctly the rate of incorporation of ethylene into copolymer chain and of the ethylene/propylene copolymerization rates it was necessary to determine also the concentration of this monomer in the vicinity of active centre, this concentration being different from that in the polymerization medium because of monomer access to catalyst being limited by the previously formed polymer. Therefore, the solubilities of ethylene and propylene in isotactic polypropylene and in UHMWPE were determined both in the presence and in the absence of a hydrocarbon solvent. The corresponding dissolution rates were determined as a function of temperature.

It was found that the activating effect of olefin comonomer on the ethylene polymerization rate is not due to a modification of active centres caused by the addition of a second monomer (both the copolymer composition and the copolymerization rate constants r_1 and r_2 in the gaseous phase and in the suspension process are independent of the sequence of comonomer addition to the reaction zone), but it is due to an increase in the active centres concentration (confirmed experimentally by the method of polymerization inhibition by the addition of carbon monoxide to the reaction medium). It is assumed that this is due to an increase in the degree of utilization of the catalyst surface area caused by an increase in the proportion of the amorphous polymer phase formed in the vicinity of active centres (almost completely amorphous ethylene-propylene copolymer is synthetized there) what favours monomer solubility in the polymer layer formed on the catalyst.

Copolymerization of ethylene with α-olefins is a major field of Ziegler-Natta catalysis. Incorporation of α-olefin fragments into the polyethylene (PE) chain modifies the structure and properties of polyethylene. Linear polyethylene is formed by copolymerization of ethylene with small amounts of *n*-hexene. Modification of polypropylene (PP) by ethylene fragments improves frost resistance. The α-olefin comonomer influences not only the structure of polymer products but also the kinetic parameters of the polymerization process.

Copolymerization of ethylene with α-olefins (propylene, butene, 1-hexene, 4-methyl-1-pentene) over heterogeneous [1—3] and homogeneous [4] complex catalysts is well known to be accompanied by the effect of increased polymerization rate for ethylene.

Activation of copolymerization of ethylene with α-olefins has been explained by a change of the propagation constant owing to modification [4] and rise in the number of active sites [3].

To elucidate the nature of activation of ethylene polymerization by α-olefins over TMC ($MgCl_2/DIBP/TiCl_4$-$AlEt_3$ and a stereoregulation agent, phenyltriethoxysilane) a complex investigation was undertaken on

(*i*) the kinetics of ethylene and propylene sequential homo- and copolymerization in the suspension and the gas phase processes by a kinetic method [5];

(*ii*) the solubility processes for comonomers in nascent isotactic PP and ultra-high molecular-weight polyethylene (UHMWPE), dry and in the presence of *n*-heptane;

(*iii*) the determination of the number of active sites in the polymerization process of ethylene after a preliminary "inhibited polymerization" of propylene with CO.

With TMC, as also with other catalysts, an extremum was observed in the catalytic activity plotted against *F*, the propylene concentration within the reaction zone (Fig. 1).

To estimate the specific rates of ethylene and propy-

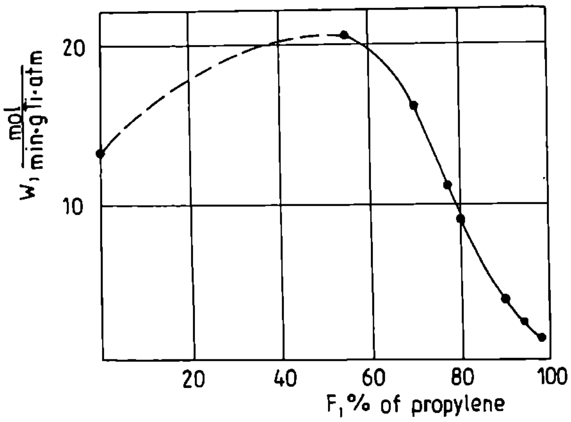

Fig. 1. TMC catalyst activity plotted against propylene concentration (F) within the reaction zone in copolymerization process (70°C, n-heptane)

lene incorporation into the copolymer chain in the copolymerization process, it was necessary to determine monomer concentrations in the vicinity to the centre of polymer chain propagation.

In our opinion, penetration of the monomer to active sites is possible only by migration through the polymer film covering the catalytic particles and concentration of the monomer near the active sites depends on monomer solubility in the nascent polymer. Propylene solubility in PE is the only one reported in the literature [6].

Absorption equipment was used to determine the absorbed gas quantity (ethylene or propylene by PP or UHMWPE) by the manometric method.

Gases are well known to dissolve only in the amorphous portions of polymers and their solubilities are proportional to the content of the amorphous phase in nascent polymer products [7]. Crystallization degrees (α) were determined by X-ray method for UHMWPE and isotactic PP (Table 1).

Solubility constants for monomers in the amorphous portions of nascent dry isotactic PP and UHMWPE samples were calculated as

$$Q_m = Q_{mo} - PV_{gas}/RT \qquad (1)$$

$$Q_m = K^{mon/pol} V_{pol}(1 - \alpha)P \qquad (2)$$

$$K^{mon/pol} = Q_m / V_{pol}(1 - \alpha)P, \text{ mol/L·atm} \qquad (3)$$

where Q_{mo} — *monomer introduced into reactor, mols;* Q_m — *monomer absorbed by polymer, mols;* V_{pol} — *polymer volume, L;* V_{gas} — *volume of gas phase in the reactor, L;* p — *monomer pressure, atm;* α — *crystallization degree of polymer.*

T a b l e 1. SOLUBILITY CONSTANTS OF ETHYLENE AND PROPYLENE AS FUNCTIONS OF TEMPERATURE

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

Variations in ethylene and propylene solubility constants in dry UHMWPE and isotactic PP with temperature were found to obey the Arrhenius law (Table 1). The solubility constants of ethylene and propylene in the presence of a solvent (*n*-heptane) were also determined. The monomer introduced into the reactor becomes distributed between the polymer, solvent, polymer with solvent, and gas phase:

$$Q_m = Q_{mo} - K^{mon/solv}(V_{liqo} - V_{liq/pol}) - PV_{gas}/RT \qquad (4)$$

where: V_{liqo} — *volume of solvent introduced into reactor, L;* $V_{liq/pol}$ — *volume of solvent contained in swollen polymer, L; and* $K^{mon/solv}$ — *ethylene or propylene solubility constants in solvent.*

The value of $V_{liq/pol}$ was most difficult to determine. Slow evacuation of the solvent from a polymer sample after interaction of the polymer with the solvent allowed to measure the volume of swollen and to calculate the volume of solvent in swelling polymer ($V_{liq/pol}$). Relaxation processes promoted in the system after the solvent had been removed, reduced the volume of swollen polymer and the measured value $V_{liq/pol}$ was incorrect.

EPR spectroscopy has been used to compare the correlation time of stable radical (2,2,6,6-tetramethylpiperidine) [7] in dry PP, *n*-heptane and in swollen PP after removal of solvent (Table 2). Viscosity of the polymer system, swollen PP after removal of *n*-heptane, was found to be lower than that of dry PP and different from that of *n*-heptane.

T a b l e 2. CORRELATION TIMES OF STABLE RADICAL IN *n*-HEPTANE-SWOLLEN PP AFTER REMOVAL OF SOLVENT AND DRY PP

System	τ, s^{-1}
Dry PP	$28.8 \cdot 10^{-10}$
Swollen PP after removal of *n*-heptane	$9.0 \cdot 10^{-10}$
n-Heptane	$1.0 \cdot 10^{-11}$

The present experimental data have allowed to estimate the solubility constants for monomers in nascent polymer products (PP and UHMWPE) in the presence of a solvent and to find that the solubility constants of C_2H_4 and C_3H_6 in the polymer—solvent—monomer system are close to those for monomers in the solvent—monomer system.

The solubility constants of ethylene and propylene in nascent dry isotactic PP and UHMWPE were necessary in order to estimate the specific rates of ethylene incorporation into the copolymer chain and copolymerization constants of ethylene and propylene in the gas phase process.

Sequential homo- and copolymerization of ethylene and propylene over TMC was investigated. The resulting kinetic data showed the specific rate of ethylene incorporation into the copolymer chain to be greater than that of ethylene homopolymerization; preliminary homopolymerization of propylene had no influence on the specific rate of ethylene incorporation into the copolymer chain (Fig. 2).

Investigations on the sequential polymerization $C_2H_4 \rightarrow C_3H_6$ and $C_2H_4 \rightarrow C_3H_6 \rightarrow C_2H_4$ gave the following results:

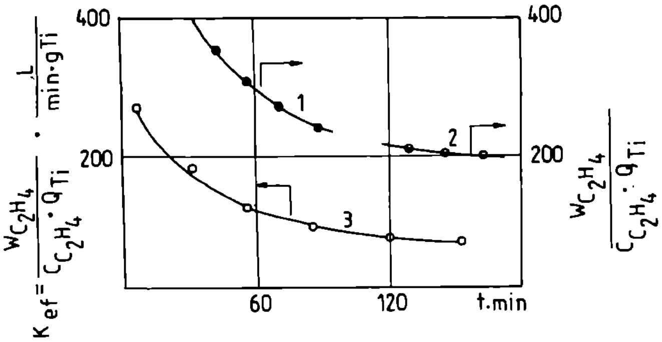

Fig. 2. Specific rates of ethylene incorporation into the copolymer chain and of ethylene homopolymerization. 1 — ethylene and propylene copolymerization; 2 — ethylene and propylene copolymerization after propylene polymerization; 3 — ethylene homopolymerization

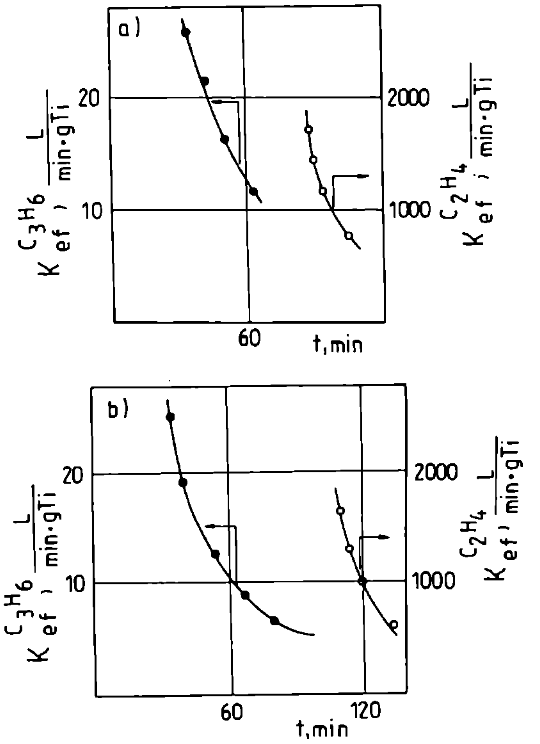

Fig. 3. Kinetic plots of sequential polymerization $C_3H_6 \rightarrow C_2H_4$

	Time of C_3H_6 polymerization, min	*PP coating, g PP/g Ti*
a	*60*	*420*
b	*100*	*480*

(*i*) ethylene polymerization was activated not only in the presence of propylene comonomer, but also upon preliminary polymerization of propylene, complete removal of residual C_3H_6 from the reaction zone, and its substitution by ethylene (Figs. 3, 4);

(*ii*) the ethylene specific rate increased irrespective of the quantity and composition of the polymer covering the catalytic particles and irrespective of the time of propylene polymerization (Figs. 3, 4).

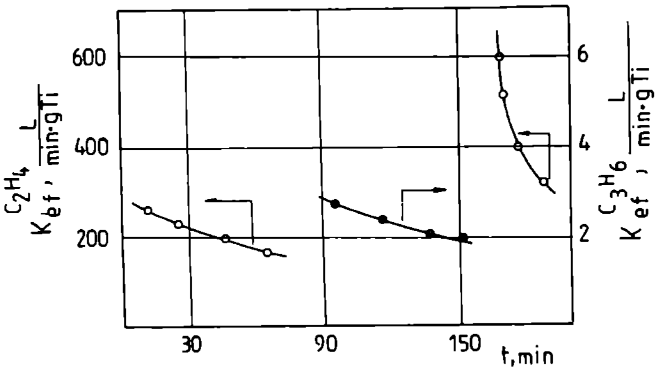

Fig. 4. Kinetic plots of sequential polymerization $C_2H_4 \rightarrow C_3H_6 \rightarrow C_2H_4$; time of C_3H_6 polymerization 150 min, polymer coating 370 + 110 g/g Ti

From the copolymer composition data follows that, whether or not homopolymerization of monomers precedes copolymerization, copolymers of the same composition are formed in the presence of TMC (Fig. 5). The values of r_1 and r_2, respectively, for the suspension and the gas-phase copolymerizations after propylene and ethylene homopolymerization are close in magnitude (Table 3).

The nature of the ethylene Cp is thus seen to remain unaffected by the action of propylene nor is the nature of propylene Cp changed in the presence of ethylene.

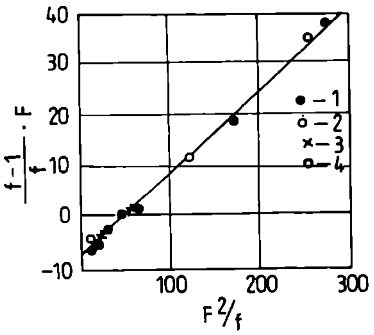

Fig. 5. Copolymer composition (f) vs. mole ratio of comonomers (F) in the reaction zone (Fineman-Ross coordinates). Copolymerization: (1) in n-heptane; (2) in gas phase after preliminary propylene homopolymerization in n-heptane; (3) in liquid propylene; (4) in gas phase after preliminary ethylene homopolymerization in n-heptane

Table 3. REACTIVITY RATIOS IN COPOLYMERIZATION OF ETHYLENE AND PROPYLENE (cf. TEXT)

r_1	r_2	$r_1 = F/f$*)
7.3 ± 0.2	0.141 ± 0.01	7.8 ± 0.2

*)Polymer composition (*f*) determined by ^{13}C-NMR method [7].,

Therefore, the polymerization activation effect of ethylene by propylene can not be related to the modification of active sites. It may be the result of a change in the number of *Cp*.

The number of active centers in the two-stage process in which ethylene polymerization precedes propylene polymerization was compared with that in ethylene polymerization (Fig. 6) by the method of "inhibited polymerization" with CO. The number of active centers after preliminary propylene polymerization was found to be greater than that in ethylene homopolymerization.

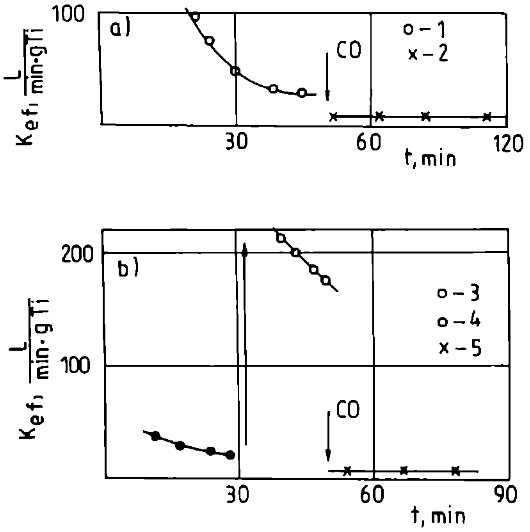

Fig. 6. The influence of CO on the specific rate of ethylene polymerization: a) ethylene homopolymerization. 1 — ethylene polymerization, 2 — ethylene polymerization in the presence of carbon monoxide; b) sequential polymerization $C_3H_6 \rightarrow C_2H_4$. 3 — propylene polymerization, 4 — ethylene polymerization, 5 — ethylene polymerization in the presence of carbon monoxide.

Polymerization process	*Moment of CO introduction minutes*	*$\Delta[CO]\cdot 10^5$ mol*	*[Cp],% mol/mol Ti*
$C_2H_4 \rightarrow CO$	*50*	*2.9*	*46.2*
$C_3H_6 \rightarrow C_2H_4 \rightarrow CO$	*50*	*6.5*	*98*

CONCLUSIONS

Rather than with modification of active sites, the effect of activation of ethylene polymerization by α-olefin is connected with a change in the number of active centres associated with the application of increased catalyst surface area.

In our opinion the increase in catalyst surface area is connected with the rising proportion of the amorphous phase in the nascent polymer product. On passing from UHMWPE to PP and practically amorphous ethylene-propylene copolymers, due to the rising proportion of the amorphous phase in the nascent polymer product, the catalytic surface accessible to monomers is increased.

REFERENCES

1. Finogenova I. T., Zakharov V. A., Bukatov G. D., Plaskunov T. K., Buniyat-Zade A. A.: *Vysokomol. Soed.* 1980, **A22**, 404.
2. Ivanchev S. S., Kryzhanovskii A. V., Gapon I. I., Ponomareva E. L.: *Vysokomol. Soed.* 1990, **A32**, 66.
3. Tait P. J. P., in: Transition Metals and Organometallics as Catalysts for Olefin Polymerization. Edited by W. Kaminsky and H. Sinn. Berlin-Heidelberg, Springer, 1988, p. 309.
4. Tsutsui T., Kashiwa N.: *Polym. Commun.* 1986, **4**, 103.
5. Firsov A. P., Meshkova I. N., Kostrova N. D., Chirkov N. M.: *Vysokomol. Soed.* 1966, **A8**, 1860.
6. Michaeles A. S., Buxler H. J.: *J. Polym. Sci.* 1959, **154**, 353.
7. Soga K., Shiono T., Doi Y.: *Polym. Bull.* 1983, **10**, 168.