ALLA N. KLYAMKINA, ALEXANDER M. ALADYSHEV,
POLINA M. NEDOREZOVA, VALENTINA I. TSVETKOVA,
IRINA L. DUBNIKOVA
Semenov Institute of Chemical Physics
Russian Academy of Science
4, Kosygin Street, 117977 Moscow, Russia

Some aspects of propylene and ethylene copolymerization over titanium—magnesium and metallocene catalysts*)

Summary — Propylene/ethylene copolymers were prepared over two complex catalyst systems: (i) an $AlEt_3$-activated $MgCl_2$-supported titanium catalyst $TiCl_4/MgCl_2$ with dibutyl phthalate and propyltrimethoxysilane used as respectively internal and external donors and (ii) two methylaluminoxane (MAO)-activated, unsupported zirconocene catalyst systems differing in indenyl ligand structure, *viz.*, $Me_2SiInd_2ZrCl_2$ and $[Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2]ZrCl_2$ (rac:meso = 1:2). The olefins were copolymerized (Table 1) in liquid propylene at 50—60°C at constant ethylene overpressures (above C_3 pressure) varying over 0.3 to 3 atm corresponding to ethylene concentrations of 0.07 to 0.69 mol/L in the liquid phase. The copolymers contained 1.6-18% of C_2 mers. Catalyst activity (Fig. 1) and kinetics of copolymerization (Fig. 1) were studied and the microstructure, molecular weight characteristics (Table 2) and mechanical properties (Tables 3, 5) of the resulting copolymers were determined. IR spectra (recorded, not included) are discussed. The comonomer reactivity coefficients were evaluated for the copolymerizations run over the three catalytic systems.

Key words: propylene/ethylene copolymerization, titanium—magnesium catalysts, metallocenes, copolymers.

Isotactic polypropylene (*i*-PP) has been widely used because of its low cost and good physical properties. However, poor impact strength of *i*-PP, particularly at low temperatures, is a limitation. One common method of modifying *i*-PP properties is to introduce small amounts of ethylene into the polymer chain. Random propylene-ethylene copolymers, with a low ethylene content, are an interesting class of semicrystalline materials. Low-ethylene polypropylene is characterized by a lower crystallinity, lower melting temperatures but a higher impact strength than those of *i*-PP [1—3]. The degree of modification of copolymer properties is related to the total ethylene content and to the type of comonomer distribution along the polypropylene based chain [2]. Slow cooling of the melt is known to result in the copolymer crystallized as a mixture of α- and γ-crystals [4]. The development of the γ-form is determined by interruption of isotactic PP-sequences as the comonomer is being inserted into the polymer chain, and the γ-form content increases as the ethylene content is increased.

The heterogeneous supported titanium catalysts tend to produce stereoregular α-olefin sequences, *i.e.*, block sequences of ethylene and propylene with compositional heterogeneity, which contribute to undesired crystallinity. Uniform propylene-ethylene copolymers are prepared over homogeneous vanadium catalysts. Metallocene catalysts, in combination with polymethylaluminoxane (MAO), developed for olefin polymerization, have opened new opportunities for synthesis of copolymers having controllable structure and properties [5—7]. By changing catalyst composition and structure, it is possible to produce uniform homo- or copolymers "programmed" so as to be endowed with desired properties.

In this work, a *quasi*-static method was used for the production of copolymers. Ethylene-propylene copolymers were obtained in a liquid propylene medium by using both modern titanium—magnesium and metallocene catalysts.

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EXPERIMENTAL

Copolymerization procedure

To prepare ethylene-propylene copolymers, we used a $TiCl_4/MgCl_2$ catalyst (TMC) containing 2.3% Ti in combination with $AlEt_3$. Dibutyl phthalate and propyltrimethoxysilane (D) were used as internal and external donors. The MAO-activated ansa-metallocenes of C_2 symmetry, $Me_2SiInd_2ZrCl_2$ (MC-1) and $Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2ZrCl_2$ (rac: meso = 1:2) (MC-2), were used as metallocene catalysts.

Propylene-ethylene copolymerizations were carried out in the bulk of propylene at 50—60°C in a 400-mL stainless steel reactor equipped with a mechanical stirrer [3, 8]. The reactor was charged with liquid propylene to 2/3 of the reactor capacity. First, a cocatalyst and an external donor (in the case of TMC) and then a catalyst were introduced into the reactor and a suitable amount of ethylene was added to provide the required ethylene concentration in the reaction zone. The ethylene pressure in different runs was varied from 0.3 to 3 atm above the propylene pressure in the reactor. This range corresponds to the variation of ethylene concentration in the liquid phase from 0.07 to 0.69 mol/L. The pressure of ethylene, the temperature and the rate of stirring were kept constant during a copolymerization run. Copolymerization rate was controlled by ethylene consumption from a known-volume vessel.

Methods of polymer characterization

The average composition of copolymers was controlled on the basis of consumption of ethylene during the experiment and analysis of IR spectra recorded according to [9]. Partial contents of ethylene and propylene were evaluated from the relative intensities of IR absorption bands at 720 cm^{-1} (methylene sequences $[(CH_2)_n$ where $n \geq 5]$ and ethylene block forming) or 730 cm^{-1} (which characterized isolated ethylene units present in the polymer chain) and 1377 cm^{-1} or 1167 cm^{-1}.

The methods used to study the molecular-weight, thermophysical and mechanical characteristics of copolymers were as described elsewhere [3].

RESULTS AND DISCUSSION

With TMC as catalyst, the resulting copolymers contained 1.6 to 12 mol % of ethylene. Loading a small quantity of ethylene in the reaction medium was found to result in a considerably increased polymer product forming rate (Table 1). A representative kinetic curve for propylene-ethylene copolymerization in the liquid propylene medium over the TMC-Et_3Al/D catalytic system is shown in Fig. 1a. Incorporation of ethylene into the copolymer is seen to follow a non-stationary course. Increasing the ethylene content in the reaction medium was found not to affect the speed of catalytic system deactivation.

Table 1. **Conditions of propylene-ethylene copolymerization on TMC—Et_3Al/D catalytic system in liquid propylene medium**

$P(C_2H_4)$ atm	$[C_2H_4]$ mol/L	Copol. time min	Activity kg EP/ (g cat · h)	Activity kg EP/ (mmol Ti · h)	C_2H_4 in copolymer wt. %
0	0	60	3.0	6.3	0
0.3	0.07	40	4.0	8.4	1.6
0.4	0.09	90	4.4	9.2	3
1.2	0.27	50	6.0	12.5	6
1.4	0.32	75	8.0	16.7	8
2.6	0.59	60	9.0	18.8	12

Copolymerization temperature, 50°C. Ti-Mg catalyst, 0.015 g/L. Et_3Al — 1.0 g/L. Al/D (mol/mol), 15—20.

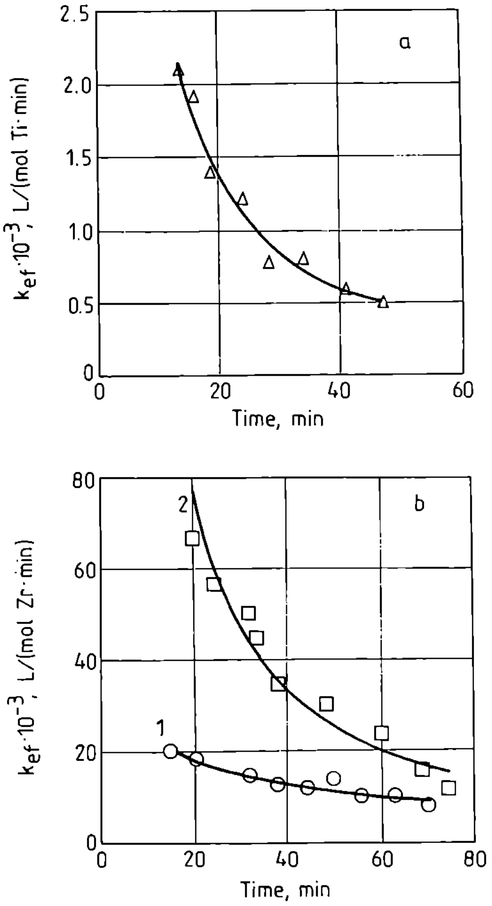

Fig. 1. The effective rate of ethylene incorporation in copolymer vs. time: a — copolymerization over $TiCl_4/MgCl_2$-based catalytic system; ethylene content in copolymer, 12 mol %; b — copolymerization over $Me_2SiInd_2ZrCl_2$/MAO catalytic system; ethylene content in copolymer: 1 — 8 mol %, 2 — 18 mol %

The Finemann-Ross [10] interrelation between the copolymer composition and the molar ratio of monomers in the reaction zone allowed to evaluate the constants of the ethylene and propylene reactivity ratios: r_e = 4.8 and

$r_p = 0.39$; $r_e \cdot r_p = 1.87$. These data correlate well with the literature values [11, 12].

Table 2. **The composition and properties of copolymers**

C_2H_4 in copolymer mol %	K, %	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	M_w/M_n	T_m, °C	Macrotacticity, %	Content of fraction soluble in *n*-heptane wt. %
0	62	776	109	7.1	165	96	1.0
1.6	60	—	—	—	161	88	1.3
3	57	950	150	6.3	160	89	2.4
6	49	786	144	5.5	145	88	6.0
8	50	913	149	6.1	144	88	—
12	46	882	133	6.6	143	85	8.1

K is the degree of crystallinity evaluated from X-ray method analysis.

The copolymer property data are listed in relation to the ethylene content in the copolymer (Table 2). Some increase in M_w and M_n and a narrowing of molecular-weight distribution (*MWD*) can be observed in the copolymers at the investigated compositions. The low-*M* fraction content in the copolymers was calculated by *n*-heptane fractionation. The cold *n*-heptane soluble fraction content was maximum 8 wt. %. When the ethylene content was increased from 1.6 to 12 mol %, the total crystallinity degree decreased from 60 to 46%. When the content of ethylene was raised to 6 mol %, T_m fell noticeably and the temperature range of melting broadened. This fact may be attributed to the decrease in the length of regular PP-blocks in the copolymers. Macrotacticity (D_{998}/D_{973}), which characterizes the long isotactic blocks content in the polymer chain, decreased with the rise in ethylene content. At higher ethylene contents (6—12 mol %), T_m was only marginally dependent on the copolymer composition. In the copolymers enriched in ethylene, an increase in the fraction of short PP blocks in copolymers manifested itself in the accumulation of the crystalline phase with a low T_m.

IR spectrum analysis showed the copolymers with ethylene contents of 1.6—3 mol % to have isolated ethylene units in the polymer chain. The copolymers containing more ethylene units are characterized by the formation of ethylene blocks. Taking into account the copolymerization constants obtained and the absence of IR spectral band at 1894 cm^{-1} (polyethylene crystalline phase characterized), we can conclude that, in the copolymers with ethylene contents higher than 3 mol %, there are ethylene blocks involving 2 or more monomer units in the polymer chain. The fraction of single isolated ethylene units is rather slight. As the content of ethylene in the copolymer was increased from 1.6 to 12 mol %, the calculated mean length of polypropylene sequences decreased from 44 to 8.5 monomer units.

Table 3. **Mechanical characteristics of PP and of propylene-ethylene copolymers**

Ethylene in copolymer mol %	E, MPa	σ_y, MPa	σ_{br}, MPa	ε_{br}, %	a, kJ/m^2
0	1200	31	32	550	8
1.6	1150	30	34	620	14
3	1100	28	31	650	17
6	950	24	30	600	—
8	850	22	31	820	—
12	670	17	24	850	30

E — Young's modulus. σ_y — stress at yield. σ_{br} and ε_{br} — stress and elongation at break, respectively. *a* — Izod impact strength.

The mechanical property data of *i*-PP and copolymers with various contents of ethylene units were calculated from stress-strain curves (σ—ε) (Table 3). Deformation of *i*-PP is characterized by a sharp occurrence of plastic flow and necking. Similarly to homopolymers, the copolymers containing 1.6 to 6 mol % of ethylene undergo deformation with necking. At higher ethylene contents, the σ—ε curves follow substantially modified courses. Copolymers enriched in ethylene show a tendency to a macrohomogeneous plastic flow. Young's modulus *E* and yield stress σ_y linearly decreased as the content of ethylene was increased in the copolymer. Elongations at break ε_{br} of the copolymers are higher than those of *i*-PP, especially in the case of the copolymers tending to undergo a homogeneous deformation.

Increasing the irregularity of molecular structure in modified PP causes a decrease in the crystalline phase content and in the degree of item perfection. The mechanical properties of the copolymer vary as a result of changes in the copolymer crystalline structure. The mechanical properties were found to depend on the α-phase content in the copolymer.

Interesting results were obtained in studying ethylene-propylene copolymerization by using homogeneous catalytic systems based on *ansa*-metallocenes.

Table 4. **Propylene-ethylene copolymerization over Me_2Si-Ind_2ZrCl_2—MAO catalytic system in liquid propylene medium**

$[C_2H_4]$ mol/L	Activity kg EP/ (g cat · h)	Activity kg EP/ (mmol Zr · h)	C_2H_4 in copolymer mol %	$M_w \cdot 10^{-3}$	M_w/M_n
0	182	80	0	58	1.9
0.14	170	75	1.8	100	2.5
0.28	220	97	8	99	2.5
0.69	364	160	18	98	2.5

Copolymerization temperature, 50°C. [MC] = $1 \cdot 10^{-6}$ mol/L. Al/Zr = 12000.

The results achieved with copolymerization run over MC-1/MAO are shown in Table 4. The ethylene content in the copolymer was varied from 1.8 to 18 mol %. Increasing the ethylene content in the reaction mixture led to an increase in the rate of copolymer production. Thus, with ethylene concentration in the liquid phase increased from 0.14 to 0.69 mol/L, the catalytic activity rose by a factor of 2. The kinetic curves for propylene-ethylene copolymerization over MC-1/MAO are shown in Fig. 1b. The process is non-stationary as in the case of copolymerization with TMC. The increase of ethylene concentration in the reaction medium led to an increase in the effective rate of ethylene incorporation into the copolymer and at the same time to a more sharp decrease during copolymerization.

Interestingly, introduction of a small amount of ethylene led to a noticeable increase in the copolymer molecular weight: M_w rose to 100000, whereas under the same conditions M_w of isotactic PP did not exceed 58000. Neither M_w nor *MWD* depend on the ethylene content in the polymer chain.

One possible reason for the production of an isotactic PP with a low molecular weight on this catalytic system may be the low catalyst regioselectivity which could lead to anomalous insertions of monomer units into the growing polymer chain of type 2-1 and 1-3. Such insertions are known to be followed by interactions of a next propylene unit with the polymer chain that occur at a much lower rate. As a result, temporarily deactivated active centers are formed in the catalytic system. One possibility is that ethylene activates the catalyst sites blocked by 2,1-insertion [13]. As a result, the rate of copolymerization and the copolymer M_w rise under ethylene filling.

IR spectral data allow to conclude that the copolymer chains synthesized over MC-1/MAO contain mostly isolated ethylene units. In the copolymers obtained, the average length of long polypropylene sequences varied from 50 to 5 monomer units, as the ethylene content was increased from 1.8 to 18 mol %.

The mechanical data obtained for the copolymers produced over MC-1 show that even a small amount of ethylene units in PP resulted in essential modification (Table 5). The ethylene units included into the polypropylene chain allow to prepare materials that are quite different as regards Young's modulus, stress at yield, and elongation at break. The homopolymer synthesized over MC-1 was brittle (elongation at break ε_{br}, 4.2%). The deformation on stretching a copolymer containing a small quantity of ethylene is characterized by necking and, at an ethylene content of about 8 mol %, the copolymer becomes a more elastic material with ε_{br} equal to 200%.

Table 5. Mechanical characteristics of PP and propylene-ethylene copolymers produced over $Me_2SiInd_2ZrCl_2$/MAO catalytic system

Ethylene in copolymer, mol %	*E*, MPa	σ_y, MPa	ε_y, %	σ_{br}, MPa	ε_{br}, %
0	1900	—	—	36	4.2
1.8	1300	26.8	7.3	22.4	9
8	600	17	10.7	13	200
18	30	2.5	19.5	3.1	350

E — Young's modulus. σ_y and ε_y — stress and elongation at yield, respectively. σ_{br} and ε_{br} — stress and elongation at break, respectively.

To obtain copolymers with higher molecular weights, we used the catalytic system based on MC-2. Alkyl substituents in position 2 and aryl substituents in position 4 in indenyl ligands are known to suppress the chain termination reaction from β-H transfer to a coordinated olefin and to reduce the extent of anomalous insertion of a monomer into the polymer chain and thus to increase M_w of the polypropylene produced [14].

Copolymerizations over the MC-2/MAO catalytic system were carried out at 60°C in the bulk of propylene to prepare copolymers with ethylene contents varying from 3 to 14 mol % and a higher molecular weight (M_w = 10^6). The copolymerization rate increased moderately under ethylene filling. The yield of the copolymer was equal to 500—530 kg EP/(g cat · h).

The ethylene and propylene reactivity ratios were determined in the copolymerization run over the MC-based catalytic systems. For MC-1/MAO, r_e = 4.3; r_p = 0.22; $r_e \cdot r_p$ = 0.95. For MC-2/MAO, r_e = 3.1; r_p = 0.32; $r_e \cdot r_p$ = 0.99. The data obtained suggest that, in contrast to most heterogeneous titanium catalysts which have a tendency to form long crystallizable ethylene sequences, these metallocene catalysts produced copolymers with the comonomer randomly incorporated into the polymer chain.

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REFERENCES

1. Simonazzi T., Cecchin G., Mazzulo S.: *Progress in Polymer Science* 1991, **16**, 303.
2. Galli P.: IUPAC International Symposium on Macromolecules, 7—12 September 1980, Firenze (Italy) 1980, Preprints, **1**, 10.
3. Dubnikova I. L. *et al.*: *Polymer Science, Ser. A* 1995, **37**, No. 12, 1238.
4. Avella M. *et al.*: *Macromol. Chem.* 1986, **187**, 1927.
5. Brintzinger H. H. *et al.*: *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 1143.
6. Kaminsky W.: *Macromol. Chem. Phys.* 1996, **197**, 3907.
7. Galiberti M. *et al.*: Proceedings of MetCon '98, Houston (TX, USA), June 10—11, 1998.
8. Aladyshev A. M. *et al.*: *Polymer Science* 1991, **33**, No. 8m 1595.
9. Kissin Y. V.: Isospecific Polymerization of Olefins, New York, Springer 1985, 307.
10. Faineman M., Ross S. D.: *J. Polymer Science* 1950, **51**, No. 5, 429.
11. Yechevskaya L. G., Zakharov V. A.: STEPOL '94 International Symposium, Milano (Italy), 6—10 June 1994, Abstracts, 165.
12. Kravchenko R., Waymouth R. M.: *Macromolecules* 1998, **31**, 1.
13. Schupfner G., Kaminsky W.: *J. Mol. Cat. A* 1995, **102**, 59.
14. Spaleck W. *et al.*: *Organometallics* 1994, **13**, 954.