

New catalytic systems based on fluorine-containing titanium(IV) alkoxides for the synthesis of ultrahigh-molecular-weight polyethylene and olefin elastomers*

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The catalytic activity of the systems based on titanium(IV) alkoxides ($\text{Ti}(\text{OPr}^i)_4$, $\text{Ti}(\text{OPr}^i)_2(\text{OCH}(\text{CF}_3)_2)_2$, and $\text{Ti}(\text{OCH}(\text{CF}_3)_2)_4$) and mixtures of alkylaluminum chlorides (Et_2AlCl or $\text{Et}_3\text{Al}_2\text{Cl}_3$) with dibutylmagnesium in ethylene polymerization and ethylene copolymerization with propylene and 5-ethylidene-2-norbornene was studied. Ultrahigh-molecular-weight polyethylene with the molecular weight reaching $4.9 \cdot 10^6$ Da was found to be formed in the homopolymerization reaction, whereas copolymerization gives ter-copolymers containing propylene (up to 35 mol.%) and 5-ethylidene-2-norbornene (4.3 mol.%) units.

Key words: titanium, alkoxides, fluorinated alcohols, polymerization, ultrahigh-molecular-weight polyethylene, polyolefin elastomers.

Ultrahigh-molecular-weight polyethylene (UHMWPE) is characterized by a combination of such unique properties as high strength, rigidity, and wear resistance and a low friction coefficient at a high chemical stability.¹ Owing to these factors, this polymer is one of the most promising construction materials that finds wide use in various industrial areas. As all polyolefins, UHMWPE is inferior to polyamide polymers and carbon fibers in thermal stability but retains all unique consumer properties at low temperatures, which predetermines prospects of its application in cryogenic technology, under Arctic conditions, and in outer space. The extremely high viscosity of the polymer melts caused by high molecular weights and a high degree of entanglement of the macromolecules^{1,2} impede, to a high extent, its processing by the methods usual for thermoplastics. One of the methods for the solution of this problem is the synthesis of a UHMWPE powder with a low degree of entanglement of macromolecules. The morphology of this powder is close to that of single-crystal mats³ and, hence, it can be processed by the solvent-free solid-phase method to form highly strength oriented materials.^{4,5} The modern state of the studies aimed at developing catalysts for the UHMWPE synthesis was considered in

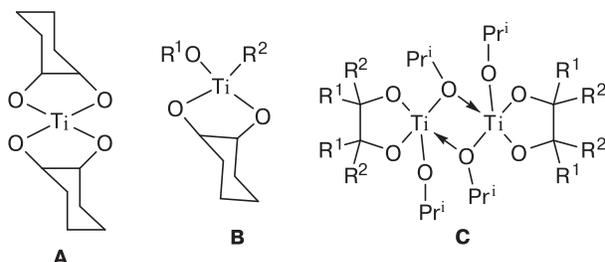
the review.⁶ In particular, the titanium complexes with phenoxyimine,⁷ TADDOL,⁸ and saligenine^{9,10} ligands are used for these purposes. We have previously shown that the reactor UHMWPE powder with the required morphology can be prepared on the titanium complexes with the ligands of the OO type activated by a mixture of Et_2AlCl and Bu_2Mg .^{11–15}

One of the purposes of the present study is the modification of the ligand environment of the transition metal with retention of a sufficiently high activity in the co- and homopolymerization of olefins and dienes and, undoubtedly, consumer properties of the synthesized polymers.

In the most cases, the reactions of ethylene with simple alkoxides of Group IV metals (and di(alkoxo)titanium complexes of a more complicated structure but without haloid ligands) activated by the organoaluminum compounds result in the formation of butenes, most probably, *via* the metallocyclic mechanism.^{16–19} The ability of titanium alkoxides to dimerize ethylene can be used for the development of tandem catalytic systems for the synthesis of linear low-density polyethylene (LLDPE). For example, the catalytic system $\text{Ti}(\text{OBu})_4/\text{AlEt}_3$ —MAO/ $\text{SiO}_2/\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (MAO is polymethylalumoxane, and Ind is indenyl) produces LLDPE with the activity up to $(1.9–5.6) \cdot 10^3$ kg, and the degree of inclusion of comonomers (predominantly but-1-ene) reaches 6.3%.²⁰

* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 90th birthday.

The ability of simple titanium(IV) alkoxides in the presence of organoaluminum compounds to catalyze the polymerization of conjugated dienes has been known very long ago.^{21–23} However, these compounds were rarely used in the catalysis of olefin polymerization. Titanium(IV) tetrabutylate activated by MAO and Me₃Al polymerizes propylene with a high yield and isotacticity up to 45%.²⁴ The homo- and heteroleptic complexes (**A** and **B**) in the presence of Et₃Al₂Cl₃ catalyze the formation of low-molecular-weight polyethylene.²⁵



B: R¹ = Prⁱ, Et, Bu; R² = OPrⁱ, OEt, OBU, Cl

C: R¹ = R² = Ph, C₆H₅, Me, CF₃; R¹ = Ph, R² = C₆F₅

The situation cardinally changes when using mixtures of alkylaluminum chlorides and dibutylmagnesium as activators. It is shown that Ti(OPrⁱ)₄ in the presence of a mixture of Et₂AlCl and Bu₂Mg is an efficient catalytic system that polymerizes propylene²⁶ and copolymerizes ethylene with higher olefins.²⁷

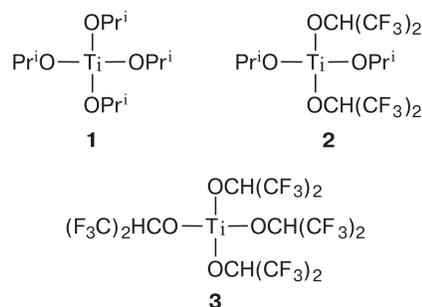
The introduction of fluorine atoms is an evident method for the modification of the Ti(OPrⁱ)₄ precatalyst without substantial complication of its structure. The fluorine-containing organic compounds often possess unique physical, biological, and chemical properties.^{28,29} A significant chemical stability of the C—F bond and a strong electron-acceptor effect of the CF₃ group predetermine the reasonable use of fluorine-containing ligands for the formation of post-metallocene catalysts of olefin polymerization. Taking into account the tendency of alkoxo complexes to dimerization and even to the formation of complicated molecular associates, it can be concluded that the enhancement of acidity of alkoxo ligands would favor the formation of non-associated molecular complexes. In fact, the p*K*_a values for isopropyl alcohol and its hexafluorinated analog are 15.3 and 9.3, respectively (calculated using the Advanced Chemistry Development (ACD/Labs) Software V11.02).

Another positive aspect of application of fluorine-containing ligands appears in ethylene copolymerization with higher olefins, propylene, and unconjugated dienes. The previous study of the copolymerization of ethylene and hex-1-ene using the titanium complexes with 1,2-diolate ligands (compounds **C**) showed that the complexes with the fluorinated ligands exceeded the non-fluorinated analogs in both the activity and comonomer content and

also in regularity of the distribution of the comonomeric units in the macromolecule.¹⁴

Results and Discussion

Fluorine-containing titanium(IV) alkoxides were synthesized by the exchange reaction of titanium(IV) tetraisopropylate **1** with hexafluoroisopropyl alcohol using known procedures.^{30–31} The compositions and structures of synthesized compounds **2** and **3** were determined from elemental analysis and ¹H and ¹⁹F NMR spectroscopy data.



The catalytic activity of titanium alkoxides was studied on the model reaction of ethylene polymerization. Mixtures of Et₂AlCl or Et₃Al₂Cl₃ with di-*n*-butylmagnesium in the molar ratio Al : Mg = 3 : 1 were used as activators.

All titanium(IV) alkoxides in the presence of the binary cocatalysts {Et₂AlCl + Bu₂Mg} or {Et₃Al₂Cl₃ + Bu₂Mg} exhibited fairly high activity in ethylene polymerization (Table 1). The obtained results showed that the introduction of fluorine atoms into Ti^{IV} alkoxides led to a noticeable but insignificant increase in the catalytic activity. The use of the activator containing ethylaluminum sesquichloride makes it possible to form the most active catalytic systems: the maximum activity is 3.47 · 10⁶ (g of PE) (mole of Ti h atm)⁻¹ was detected for titanium tetrakis(hexafluoroisopropylate) **3**.

The nature of the organoaluminum component of the activator exerts a much more pronounced effect on the molecular weight of the formed polyethylene (see Table 1). Ethylaluminum sesquichloride (Et₃Al₂Cl₃) with a higher Lewis acidity compared to diethylaluminum chloride (Et₂AlCl), favors the formation of ultrahigh-molecular-weight polymers. A similar regularity was observed earlier for the titanium complexes with the 2-hydroxymethylphenol^{9,10} and diol^{11–15} ligands.

The melting points (135–141 °C) and degrees of crystallinity (61.4–83.3%) are typical of UHMWPE.^{1,2} The low values of bulk densities of the reactor UHMWPE powders indirectly indicate nonuniformity of the particles in sizes and porosity of the structure. This morphology (including molecular weight and, mainly, degree of entanglement of macromolecules of the polymer among other factors) provides the possibility of solvent-free processing

Table 1. Activity of Ti^{IV} alkoxides in ethylene polymerization and some properties of the prepared polyethylene samples^a

Entry	Catalytic system	<i>A</i> ^b	Yield/g	Bulk density of PE/g cm ⁻³	M.p. ^c /°C	χ ^d (%)	<i>M_v</i> · 10 ⁶ /Da
1	1/Et ₂ AlCl/Bu ₂ Mg	2.57 · 10 ⁶	4.49	0.059	135 (130)	61.4/41.1	1.59
2	1/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	2.97 · 10 ⁶	5.19	0.053	140 (135)	75.1/47.2	3.34
3	2/Et ₂ AlCl/Bu ₂ Mg	2.65 · 10 ⁶	4.63	0.077	136 (131)	75.1/61.7	1.02
4	2/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	3.17 · 10 ⁶	5.55	0.082	141 (134)	77.6/57.8	4.00
5	3/Et ₂ AlCl/Bu ₂ Mg	2.61 · 10 ⁶	4.56	0.080	136 (132)	83.3/72.3	0.82
6	3/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	3.47 · 10 ⁶	6.08	0.086	141 (134)	79.0/57.8	4.90

^a Polymerization conditions: in 100 mL of toluene at 30 °C for 30 min, ethylene pressure 1.7 atm, amount of the used titanium precatalyst 5 · 10⁻⁶ mol. In all experiments, the molar ratio is Ti : Al : Mg = 1 : 300 : 100.

^b Catalyst activity, (g of polyethylene) (mole of Ti h atm)⁻¹.

^c The temperature of the second melting is given in parentheses.

^d The degree of crystallinity was determined by the DSC data for the first and second meltings.

Table 2. Tensile strength (σ) and elasticity modulus (*E*) of oriented UHMWPE films

Entry ^a	Catalytic system	σ	<i>E</i>
		GPa	
2 ^b	1/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	2.0	105.0
4	2/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	1.9	119.3
6	3/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	2.1	125.9

^a The numeration corresponds to Table 1.

^b According to the data of Ref. 10.

to high-strength and high-modulus films. The mechanical characteristics (tensile strength and elasticity modulus) of the prepared films are given in Table 2.

It is seen that the introduction of fluorine atoms into the structures of titanium(IV) alkoxides is accompanied by an increase in the elasticity modulus of the oriented films. For comparison, the modulus for the commercially available UHMWPE fiber produced by the gel spinning is 113 GPa.*

The results of studying the activity of titanium alkoxides 1–3 in the presence of the binary activators in the copo-

lymerization of ethylene, propylene, and 5-ethylidene-2-norbornene (ENB) are presented in Table 3.

The compositions and structures of the prepared copolymers were studied by ¹H NMR spectroscopy using a described procedure.³² The spectrum of the ter-copolymer synthesized using the 3/Et₃Al₂Cl₃+Bu₂Mg catalytic system (see Table 3, entry 6) is shown in Fig. 1. The spectra of the copolymers in a range of 0.4–0.9 ppm exhibit signals of the methyl groups from the propylene fragments. The signals in a range of 0.9–2.8 ppm correspond to protons of the methylene and methine groups (three protons of propylene units (CH₂–CH), four protons of ethylene fragments (CH₂–CH₂), and 11 protons of ENB). The range from 4.8 to 5.4 ppm contains signals from the olefin protons of ENB as two peaks caused by the presence of the *E* and *Z* conformational isomers.

According to the data in Table 3, the introduction of fluorine atoms into the alkoxy groups of the precatalyst exerts a negative effect on the activity of the catalytic systems and on the degree of inclusion of the comonomers. However, the molecular weights of the copolymers obtained on precatalysts 2 and 3 substantially exceeds the values obtained for the non-fluorinated analog (see Table 3).

Table 3. Activity of Ti^{IV} alkoxides in the copolymerization of ethylene (Et), propylene (P), and 5-ethylidene-2-norbornene (ENB)^a

Entry	Catalytic system	<i>A</i> /g (mole of Ti h atm) ⁻¹	Polymer composition	M.p./°C	χ (%)	<i>M_w</i>	<i>M_w</i> / <i>M_n</i>
1	1/Et ₂ AlCl/Bu ₂ Mg	3.720 · 10 ⁶	60.7 (Et)—35.0 (P)—4.3 (ENB)	98.6	11.2	0.2 · 10 ⁵	6.85
2	1/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	3.210 · 10 ⁶	63.6 (Et)—34.0 (P)—2.4 (ENB)	102.1	15.1	1.4 · 10 ⁵	6.24
3	2/Et ₂ AlCl/Bu ₂ Mg	1.010 · 10 ⁶	68.3 (Et)—30.7 (P)—1.0 (ENB)	93.9	6.8	0.8 · 10 ⁵	6.15
4	2/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	7.80 · 10 ⁵	67.3 (Et)—31.5 (P)—1.2 (ENB)	107.7	9.5	4.8 · 10 ⁵	4.82
5	3/Et ₂ AlCl/Bu ₂ Mg	1.280 · 10 ⁶	66.0 (Et)—32.3 (P)—1.7 (ENB)	94.8	5.7	1.6 · 10 ⁵	4.91
6	3/Et ₃ Al ₂ Cl ₃ /Bu ₂ Mg	2.250 · 10 ⁶	65.5 (Et)—33.4 (P)—1.1 (ENB)	112.5	9.4	4.1 · 10 ⁵	4.55

^a Copolymerization conditions: the process is carried out in a medium of liquefied propylene at 0 °C for 30 min, the amount of the used titanium precatalyst is 5 · 10⁻⁶ mol, *V*(ENB) = 5 mL, and the total pressure of the monomers is 8.7 atm. In all experiments, the molar ratio is Ti : Al : Mg = 1 : 300 : 100, and the percent ratio of ethylene to propylene in the initial reaction mixture is 10 : 90.

* https://www.teijinaramid.com/wp-content/uploads/2018/12/18033TEI-Prodbroch-Endumax_LR.pdf.

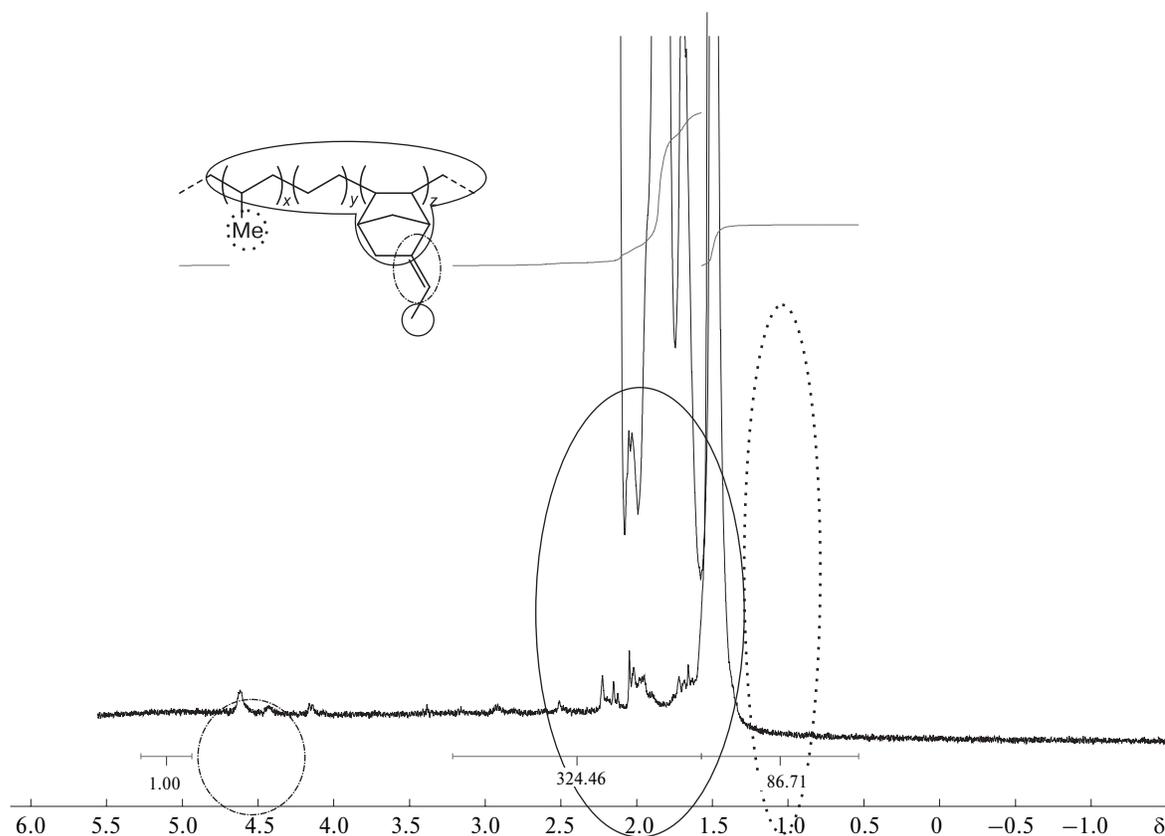


Fig. 1. ^1H NMR spectrum (400 MHz, CDCl_3) of the ethylene—propylene—5-ethylidenenorbornene copolymer prepared on the $3/\text{Et}_3\text{Al}_2\text{Cl}_3/\text{Bu}_2\text{Mg}$ catalytic system (see Table 3, entry 6).

With increasing the number of fluorine-containing fragments in the precatalyst, the molecular weight distribution of the copolymers decreases appreciably remaining, nevertheless, polymodal.

It can be assumed that the fluorine atoms can enter into the noncovalent interaction with the hydrogen atoms of the propagating polymer chain as it takes place in the case of the phenoxyimine complexes of Group IV metals with the fluorine-containing phenoxyimine ligands.^{33–36} This interaction results in the stabilization of a catalytically active particle, an increase in the molecular weight of the polymer, and narrowing of the polydispersity index.

DFT calculations were used for detailed analysis of the prepared material. The Cossee—Arlman model was chosen as the model of the reaction (Scheme 1).³⁷ The calculations were performed for cations of the complexes.

The potential energy surfaces of the 1,2-migration insertion of the ethylene molecule were calculated for the complexes. It was found that the activation energy of the transition state increased with an increase in the number of fluorine atoms in the complexes (Figs 2 and 3). It is shown that the possibility of formation of the noncovalent interaction of the fluorine atoms of the ligand environment with the hydrogen atoms of the propagating polymer chain is excluded for this geometry of the complexes.

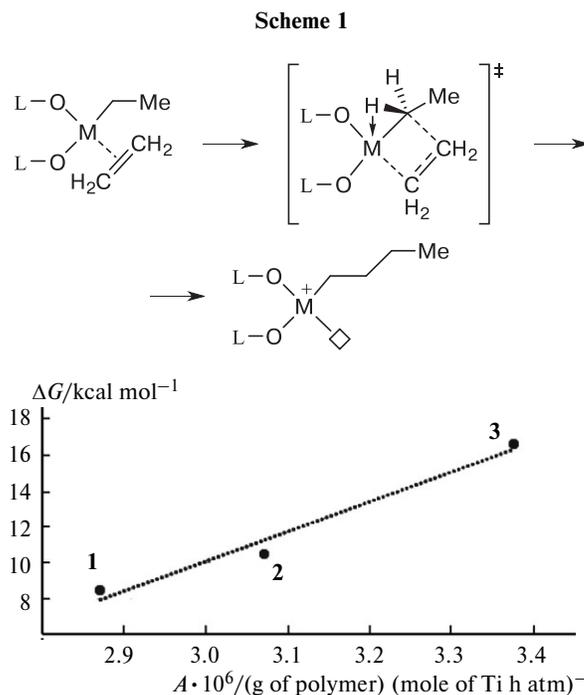


Fig. 2. Dependence of the activity of precatalysts **1–3** activated by $\text{Et}_3\text{Al}_2\text{Cl}_3$ on the activation energy of the transition state ($R^2 = 0.9721$).

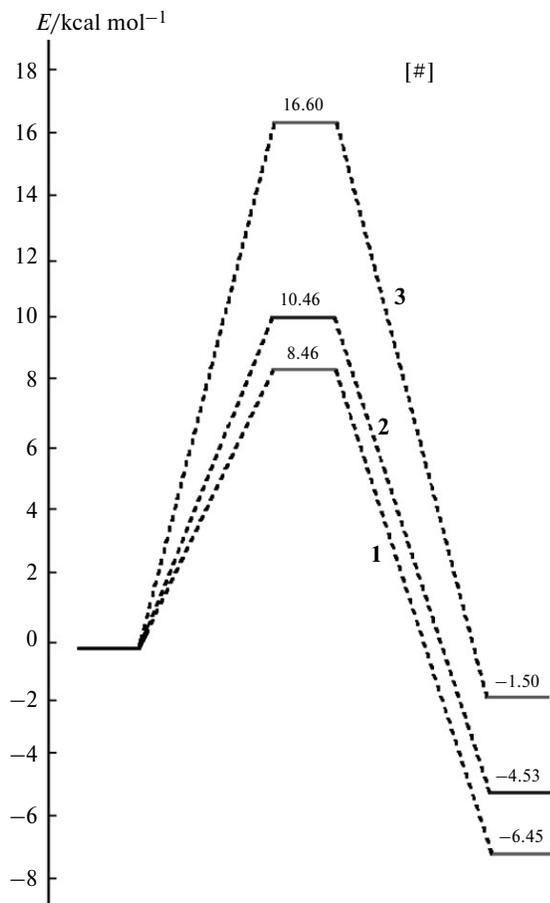


Fig. 3. Energy diagram of the 1,2-migration insertion of the ethylene molecule.

Experimental

Hexafluoroisopropanol (PiM-Invest, Russia) titanium(IV) tetraisopropylate, diethylaluminum chloride, ethylaluminum sesquichloride, and di-*n*-butylmagnesium (Sigma-Aldrich) were used as received. Hexane, heptane, isopropanol, and toluene were additionally purified using a known procedure.³⁸

Ethylene polymerization. The process was carried out in a 450-mL reactor (Parr Instrument Co., USA) equipped with a magnetic stirrer and inlets for loading the components of the catalytic systems and ethylene under a total pressure of ethylene and toluene vapors of 1.7 atm. The reactor was loaded with toluene (100 mL) and a necessary amount of the Al–Mg cocatalyst (1.5 mL of a 1 M solution of Et₂AlCl in hexane (1.5 · 10⁻³ mol) or 0.75 mL of a 1 M solution of Et₃Al₂Cl₃ in hexane (7.5 · 10⁻⁴ mol) and 0.5 mL of a 1 M solution of Bu₂Mg (5 · 10⁻⁴ mol) in heptane. Then the reaction mixture was saturated with ethylene until the gas flow ceased according to the indications of a Bronkhorst flowmeter (The Netherlands). Polymerization was initiated by the introduction of a solution of titanium alkoxide (5 · 10⁻⁶ mol) in toluene (1 mL). The ethylene pressure during polymerization was maintained constant (1.7 atm) using a Bronkhorst flowmeter. Polymerization was ceased by the addition of isopropanol (20 mL) to the reactor. The polymer product was filtered off, washed three times with an isoprop-

anol–10% HCl (1 : 1) mixture (total volume 150 mL), and dried *in vacuo* at 70 °C to a constant weight.

The high-strength and high-modulus film filaments from the polymer samples were produced and studied according to a described procedure.³

Copolymerization of ethylene, propylene, and 5-ethylidene-2-norbornene. The process was carried out in a 300-mL stainless steel reactor equipped with a mechanical stirrer and a steel dropping funnel with a pressure leveler. Prior to polymerization, the reactor was heated to 110 °C *in vacuo* for 1 h and filled with argon. Necessary amounts of a solution of di-*n*-butylmagnesium (0.5 mL of a 1 M solution in heptane, 5 · 10⁻⁴ mol) and 5-ethylidene-2-norbornene (5 mL, 3.71 · 10⁻² mol) were introduced into the reactor using a syringe. Propylene (36 L) was condensed using a Bronkhorst flowmeter (pressure in the reactor 5.7 atm) into the reactor precooled to 0 °C. Then ethylene was supplied to the reactor to a total pressure of 8.7 atm. Copolymerization was initiated by the combined introduction of a solution of titanium(IV) alkoxide (5 · 10⁻⁶ mol) and organoaluminum activator (1.5 mL of a 1 M solution of Et₂AlCl in hexane (1.5 · 10⁻³ mol) or 0.75 mL of a 1 M solution of Et₃Al₂Cl₃ in hexane (7.5 · 10⁻⁴ mol) in toluene (2 mL) from a dropping funnel. During copolymerization ethylene was continuously supplied to the reactor maintaining a constant pressure (ethylene pressure 3 atm). After 30 min, the ethylene supply was stopped and the gas pressure was thrown off. Isopropyl alcohol (20 mL) was introduced into the reactor, and the precipitated polymers were filtered off, washed three times with an isopropanol–10% HCl (1 : 1) mixture (total volume 150 mL), water, and pure isopropanol, and dried first in air for 6–24 h and then in a vacuum drying box at <70 °C for 6 h to a constant weight.

All manipulations with the complexes were performed using the standard Schlenk technique. ¹H NMR spectra were recorded on Bruker WP-600 and Bruker AMX-400 spectrometers. Elemental analysis was carried out on Carlo Erba-1106 and Carlo Erba-1108 instruments (Italy). DSC studies were performed on a DSM-3 differential scanning calorimeter (Mettler-Toledo, Switzerland) at a heating rate of 10 °C min⁻¹ in argon.

The molecular weights of the UHMWPE samples were determined by the viscosimetric method using the equation $M_w = 5.37 \cdot 10^4 \cdot [\eta]^{1.37}$ (the corresponding procedure was described in the monograph¹). DSC measurements were performed on a DSC-822e calorimeter (Mettler-Toledo, Switzerland) for the second melting of the samples, and the heating rate was 10 °C min⁻¹. The degree of crystallinity χ was calculated from the DSC data using the equation:

$$\chi = \Delta H_m / \Delta H_{100\%} \cdot 100\%,$$

where ΔH_m is the enthalpy of melting of the sample, and $\Delta H_{100\%}$ is the enthalpy of melting for the completely crystalline polyethylene equal to 288 J g⁻¹.³⁹

The molecular weight characteristics of the copolymers (weight average molecular weights (M_w), number average molecular weights (M_n), and molecular weight distribution (M_w/M_n)) were determined by gel permeation chromatography (GPC) at 135 °C on a Waters GPCV-2000 chromatograph equipped with two columns (PLgel, 5 μm and Mixed-C, 3007.5 mm) and a refractometer. 1,2,4-Trichlorobenzene served as the eluent, and the elution rate was 1 mL min⁻¹. The molecular weights of the polymers were determined from the universal calibration curve relative to the polystyrene standards with the narrow molecular

weight distribution: for polystyrene ($K = 2.88 \cdot 10^{-4}$, $\alpha = 0.64$) and for PE ($K = 6.14 \cdot 10^{-4}$, $\alpha = 0.67$).

The ^1H NMR spectra of the copolymers (as 5% solutions in CDCl_3) were recorded on a Bruker Avance-400 spectrometer. The following equations³² were used to calculate the copolymer compositions:

$$\text{ENB (mol.\%)} = \text{H}_{\text{ENB}} / [\text{H}_{\text{Et}} + \text{H}_{\text{P}} + \text{H}_{\text{ENB}}]$$

$$\text{P (mol.\%)} = \text{H}_{\text{P}} / [\text{H}_{\text{Et}} + \text{H}_{\text{P}} + \text{H}_{\text{ENB}}]$$

$$\text{Et (mol.\%)} = \text{H}_{\text{Et}} / [\text{H}_{\text{Et}} + \text{H}_{\text{P}} + \text{H}_{\text{ENB}}]$$

$$\text{H}_{\text{ENB}} = \text{IR}_3; \text{H}_{\text{P}} = 1/3 \text{IR}_1$$

$$\begin{aligned} \text{H}_{\text{Et}} &= 1/4[\text{IR}_2 - 3 \text{N}_{\text{P}} - 11 \text{H}_{\text{ENB}}] = \\ &= 1/4[\text{IR}_2 - \text{IR}_1 - 11 \text{IR}_3], \end{aligned}$$

where IR_1 is the integral intensity of signals in a range of 0.4–0.9 ppm corresponding to three protons of the methyl groups of propylene (P), IR_2 is the integral intensity of signals from the methylene and methine protons (3 protons from the propylene units ($\text{CH}_2\text{—CH}$), 4 protons from the ethylene fragments ($\text{CH}_2\text{—CH}_2$), and 11 protons from ENB) appeared in a range of 0.9–2.8 ppm, and IR_3 is the integral intensity of signals of the olefin proton of ENB in a range of 4.8–5.4 ppm.

DFT calculations. All quantum chemical DFT calculations were performed using the ORCA v.4.2.1 software.^{40,41} Geometry optimization and calculation of the thermochemical parameters were performed using the PBE0 hybrid functional⁴² and def2-TZVP basis set.⁴³ The PBE nonhybrid functional^{44,45} was applied to search for the transition state by scanning potential energy surface.

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No human or animal subjects were used in this study. The authors declare no competing interests.

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