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A new catalyst for ethylene polymerization based on the oxidation product of dibenzenetitanium(0) with fullerene

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A catalyst for ethylene polymerization under mild conditions (room temperature, pressure below atmospheric) was obtained for the first time on the basis of the oxidation product of dibenzenetitanium(0) with fullerene. Polyethylene formed in the reaction was characterized by IR and Raman spectra. Molecular mass of the product (1 634 000), melting point (133 °C) and the degree of crystallinity (79.4%) were determined. These values are typical of medium-pressure polyethylene. The catalyst reacts with molecular nitrogen with formation of an air-stable compound (N/Ti = 0.2). It is assumed that the oxidation state of titanium in the catalytically active site is above zero, but not higher than three.

Key words: dibenzenetitanium(0), fullerene, ethylene, polymerization, molecular nitrogen.

Previously[1,2] we have shown, that ditoluenetitanium(0) does not react with pure ethylene, but ethylene polymerization occurs in the presence of oxygen. The catalyst of the process is an oxygen-containing titanium (II) complex formed as a result of ditoluenetitanium(0) oxidation with oxygen.[2] In the present work, an attempt to use fullerene as the dibenzenetitanium(0) oxidant was undertaken.

Experimental

Dibenzenetitanium(0) was synthesized by co-condensation of titanium atoms evaporated in high vacuum (10^{-5} Torr) with a solid benzene matrix cooled with liquid nitrogen.[1—3] After thawing, a red solution of dibenzenetitanium(0) in benzene (λ_{max} = 512 nm) was transferred to a reaction flask in an inert atmosphere, the excess of unconsumed titanium being filtered through the glass filter.

Reaction of dibenzenetitanium(0) with fullerene was carried out in vacuum (1.3 Pa) at 20 °C by mixing red solution of dibenzenetitanium(0) in benzene ($6 \cdot 10^{-5}$ mol Ti mL^{-1}, 1 mL, 0.06 mmol) with a solution of fullerene in benzene. Benzene (2 mL) was distilled *in vacuo* onto fullerene (0.055 g, 0.076 mL) with freezing, resulting in a saturated bright violet solution containing incompletely dissolved fullerene. The reactants were mixed using a vacuum setup and magnetically stirred. After 5—10 min, the soulution became pale violet and a black precipitate formed (**1**).

Ethylene polymerization was carried out in a 0.08-L reactor on a glass vacuum setup. Before the experiments, the reaction flask was freezed to the temperature of liquid nitrogen and evacuated. After thawing and warming of the solution to room temperature, it was saturated for several minutes with ethylene with vigoruous magnetic stirring at a pressure of 72 kPa. The quantity of ethylene absorbed was determined by the pressure method. The reaction product was washed with benzene in the vacuum setup until benzene washings became colorless to remove excess of fullerene.

The molecular mass of polyethylene was determined by viscosimetry using a capillary Ostwald viscometer in decalin at 135±0.5 °C. Initially, the time of effluence (t_0) of the pure solvent (20 mL) was measured, then a sample of polyethylene (0.01—0.02 g) was dissolved in the same volume of decalin and the time of effluence of the solution was determined (t_1). From these measurements, the reduced viscosity was calculated $\eta_{red} = [(t_1/t_0) - 1]C$, where C is the concentration of the polymer solution (g (100 mL)$^{-1}$). The reduced viscosities were determined at four concentrations, diluting successively the solution with 5 mL of decalin. Based on the data obtained, the dependence of the reduced viscosity of the polymer solution on concentration was plotted. From the intercept on the ordinate axis, the characteristic viscosity η was found, which is the limiting value of the reduced viscosity at the zero concentration. The molecular mass of polyethylene was calculated by the Staudinger equation[4] $[\eta] = 4.6 \cdot 10^{-4} M_w^{0.73}$.

Thermophysical characteristics of the product (the melting point T_m, the crystallization temperature T_{cr}, the degree of crycstallinity W) were determined by DSC using a Perkin—Elmer DSC-7 instrument with a heating rate of 10 deg min^{-1}. Here the results of second scanning are presented.

The degree of crystallinity was calculated using the formula $W = (\Delta H_m/\Delta H_m{}^0) \cdot 100\%$, where ΔH_m is the heat of melting of the polymer sample studied, $\Delta H_m{}^0$ = 293 J g^{-1} is the heat of melting of crystalline polyethylene.[5]

IR spectra were recorded on a FTIR-spectrometer Perkin—Elmer Spectrum 100 by diffuse reflection technique at 3000—700 cm^{-1}. Raman spectra were recorded on a Nicolet NXR 9610 spectrofotometer.

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Results and Discussion

Bisarenetitanium(0) complexes are extremely sensitive to oxygen.[1—3] Mixing, using a vacuum setup, of a red solution of dibenzenetitanium(0) in benzene with a bright violet saturated solution of fullerene containing undissolved fullerene in benzene affords a fine dark precipitate **1**, the solution becomes pale violet. Then ethylene was added to the system with stirring. The kinetics of ethylene polymerization in the presence of complex **1** in the initial period of the reaction is presented in Fig. 1. Polymerization begins with short induction period (5 min). The profile of the kinetic curve suggests its steady-state character. The rate of polymerization retains during the first four hours, after which it begins to decrease. The duration of polymerization process is 113 h under these conditions. The yield of polyethylene after the first hour is 13 g (g Ti)$^{-1}$, the final yield of polyethylene is 396 g (g Ti)$^{-1}$. After completion of the reaction, the excess of fullerene was removed from the product by washing with benzene in a vacuum setup until the colorless benzene washings were obtained.

The reaction product formed in the form of film covering the walls of the reaction vessel. The film color varied from pale brown to beige depending on its thickness. This can probably be explained by the presence of catalyst **1** remained. The melting point of polyethylene determined by DSC is 133 °C. The molecular mass of polymer determined by viscosimetry is 1 634 kDa.

It should be noted that in contrast to previous work[2] the use of fullerene instead of oxygen changes the properties of polyethylene formed: the polymer represents a film coating rather than separate spherical particles as in case of oxygen-containing catalyst.

The elemental analysis of the polyethylene film obtained gives (%): C, 88.00; H, 11.32; the residue 0.1. The existence of the residue indicates the presence of titanium in the product. According to the elemental analysis data (H/C = 1.544), the product obtained is characterized by increased content of carbon compared with common polyethylene, which could be explained by the presence of both polyethylene and fullerene.

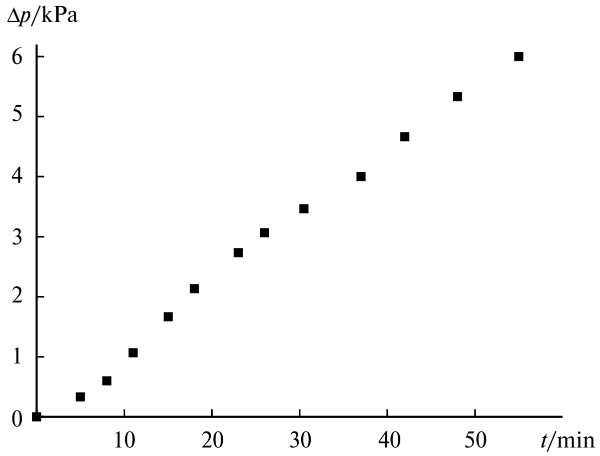

Fig. 1. The time dependence of ethylene consumption during its polymerization in the presence of catalyst **1** in the initial period of the reaction. Reaction conditions: 22 °C, pressure 72 kPa, benzene (3 mL), $6 \cdot 10^{-5}$ mmol of Ti, $7.6 \cdot 10^{-5}$ mmol of fullerene.

Indeed, the following absorption bands are present in the IR spectra of the film formed, ν/cm^{-1}: 718 (δ(CH_2)) (medium), 728 (δ(CH_2)) (medium), 1183 (C_{60}) (weak), 1430 (C_{60}) (weak), 1462 (δ(CH_2)) (medium), 1472 (δ(CH_2)) (medium), 2850 (ν(CH_2)) (strong), 2918 (ν(CH_2)) (strong). The spectrum observed comprises two spectra: a spectrum characteristic of polyethylene,[6] and a spectrum of fullerene.[7] Weak absorption bands at 1183 and 1432 cm^{-1} are referred to vibrations of the fullerene molecule.[7]

The polyethylene component is in the crystalline state. The crystallinity of polyethylene is confirmed by splitting of absoption bands of scissor and rocking vibrations of CH_2 by 10 cm^{-1} (doublets at 1462, 1472 cm^{-1} and 728, 718 cm^{-1}, respectively).[8] According to DSC data, the degree of crystallinity of polyethylene film is 79.4% (ΔH_m = = 232.7 J g^{-1}), and T_{cr} = 111.16 °C. No adsorption bands at 1378 and 2960 cm^{-1} typical of the Me groups are present in the IR spectra, which suggests the linear nonbranched structure of polyethylene obtained.[8]

Half-widths of the absorption bands of the stretching vibrations of C—H at 2918 and 2850 cm^{-1} in the IR spectra of polyethylene obtained on catalyst **1** are 13.5 and 9 cm^{-1}, respectively, which is ~30% smaller than in the case of the Zeigler catalysts.[9]

The Raman spectrum of the product (ν/cm^{-1}): 278 (C_{60}) (strong), 436 (C_{60}) (weak), 497 (C_{60}) (strong), 711 (C_{60}) (weak), 773 (C_{60}) (weak), 1063 (polyethylene) (weak), 1108 (C_{60}) (weak), 1131 (polyethylene) (weak), 1249 (C_{60}) (weak), 1286 (polyethylene) (medium), 1438 (polyethylene, δ(CH_2)) (medium), 1468 (C_{60}) (strong), 1574 (C_{60}) (medium), 2844 (polyethylene, ν(CH_2)) (strong), 2881 (polyethylene, ν(CH_2)) (strong). It consisted of the spectra of polyethylene and fullerene. The frequences and intensities of the observed fullerene bands are in agreement with the literature data.[10] The characteristics of polyethylene bands in the Raman spectrum measured are also in agreement with the published ones.[6]

Thus, compound **1** is the catalyst for ethylene polymerization. It should be noted that the rate of polymerization and the yield of the polymer is higher in the case of the fullerene-containing catalyst **1** than in the case of oxygen-containing titanium comlex[2] under similar conditions, *i.e.*, catalyst **1** is more efficient in polyethylene polymerization.

The mechanism of the interaction of fullerene with dibenzenetitanium(0) is unclear. It can be assumed that the interaction results in the formation of fullerene-containing titanium compound like charge-transfer complex.

The titanium—fullerene compounds have been described previously.[11] Since fullerene is the proton acceptor, one may assume that the oxidation state of titanium(0) increases in the formation of compound **1** and a low-valent titanium compound (with the oxidation state <4) forms. Then the polymerization process proceeds similarly to the described one.[2]

The assumption on the low oxidation state of titanium is proved by the fact that compound **1** reacts with molecular nitrogen. We found that 20 min after introduction of nitrogen into the vessel containing the dibenzenetitanium(0)—fullerene reaction product, air-stable brown solid nitrogen-containing product is formed. According to elemental analysis data, it contains 0.2 nitrogen atom per 1 titanium atom. It is known[12] that titanium if present in the oxidation states not higher than three reacts with molecular nitrogen. We have found that dibenzenetitanium(0) itself does not react with molecular nitrogen. Therefore, the ability of compound **1** to react with molecular nitrogen suggests the oxidation of titanium(0) with fullerene resulting in formation of a low valent titanium compound in the oxidation state above zero, but not higher than three.

Thus, for the first time we obtained the catalyst **1** for ethylene polymerization based on the oxidation product of dibenzenetitanium(0) with fullerene. This is the first example of occurence of fullerene in the catalytic system for ethylene polymerization. The use of the catalyst **1** provides a principal possibility for the preparation of fullerene composites with polymers not by concentration of a polymer solution on a fullerene support,[13] but by polymerization of a monomer in the presence of fullerene-containing complex **1**. At the same time, the ability of complex **1** to react with molecular nitrogen with formation of a stable nitrogen-containing compound was shown.

References

1. G. G. Tairova, O. N. Krasochka, V. I. Ponomaryov, E. F. Kvashina, Yu. A. Shvetsov, E. M. Lisetsky, D. M. Kirykhin, L. O. Atovmyan, Yu. G. Borod´ko, *Trans. Metals Chem.*, 1982, **7**, 189.
2. E. F. Kvashina, O. N. Efimov, N. V. Chapysheva, O. S. Roshchupkina, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 2043 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 2115].
3. F. W. Benfield, M. L. Green. J. S. Ogden, D. Yong, *J. Chem. Soc., Chem. Commun.*, 1973, 866.
4. N. Gaylord, H. Mark, *Linear and Stereoregular Addition Polymers*, Interscience Publishers, New York—London, 1959, 566 pp.
5. B. Wunderlich, *Macromolecular Physics*, Academic Press, New York—San Francisco—London, 1976, 363 pp.
6. A. Kh. Kuptsov, G. N. Zhizhin, *Furie-KR and Furie-IK spectry polimerov* [*Handbook of Fourier Transform Raman and Infrared Spectroscopy of Polymers*], Fizmatlit, Moscow, 2001, p. 2 (in Russian).
7. H. Kuzmany, R. Winkler, T. Pichler, *J. Phys.: Condens. Matter.*, 1995, **7**, 6601.
8. J. Dechant, R. Danz, R. Kimmer, R. Schmolke, *Ultrarotspektroskopishe Untersuchungen an Polymeren*, Ed. J. Dechant, Akademie Verlag, Berlin, 1972, 369 pp.
9. A. N. Panin, Z. M. Dzhabieva, P. M. Nedorezova, N. M. Bravaya, *J. Polym. Sci., A, Polym. Chem.*, 2001, **39**, 1915.
10. A. Rosenberg, *Solid State Commun.*, 1995, **95**, 729.
11. V. V. Burlakov, A. V. Usatov, K. A. Lyssenko, M. Yu. Antipin, Yu. N. Novikov, V. B. Shur, *Eur. J. Inorg. Chem.*, 1999, 1855.
12. T. A. Bazhenova, A. E. Shilov, *Ros. Khim. Zh.*, 1995, **39**, 50 [*Mendeleev Chem. J.* (*Engl. Transl.*), 1995, **39**].
13. D. V. Konarev, R. N. Lyubovskaya, *Russ. Chem. Rev.*, 1999, **68**, 19.

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