



TITANIUM(4+) COMPLEXES WITH TETRAARYLDIOXOLANE LIGANDS AS THE CATALYSTS FOR THE SYNTHESIS OF ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE

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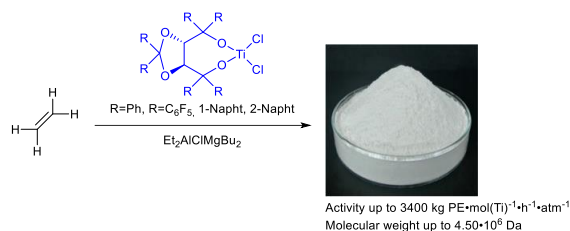
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Abstract

Titanium(4+) complexes with tetraaryldioxolane-dimethanol (TADDOL) ligands were obtained. Their catalytic activity in the ethylene polymerization was evaluated. It was shown that, in the presence of Al activators, the resulting compounds catalyze the ethylene polymerization highly efficiently (up to 3400 kg PE·mol(Ti)⁻¹·h⁻¹·atm⁻¹), resulting in the formation of ultra-high-molecular-weight polyethylene (UHMWPE) with a molecular weight of up to 4.50 10⁶ Da.

Key words: post-metallocene catalysts, titanium, organoaluminum activators, ultra-high-molecular-weight polyethylene.



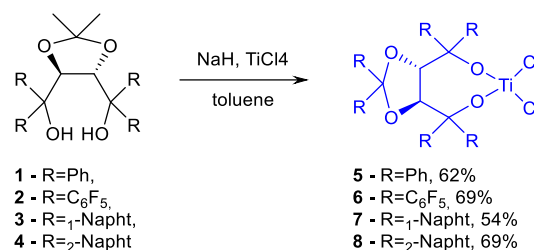
Introduction

Catalytic polymerization of olefins is one of the most intensively studied synthetic reactions in the last fifty years [1–8]. Such attention is caused by the rapidly developing market for consumption of polyolefins, which are the most popular synthetic macromolecules. Nowadays, most polyethylenes and polypropylenes are synthesized using the heterogeneous multicenter Ziegler–Natta catalysts, which represent complex systems containing titanium or vanadium compounds (for example, TiCl₄, VOCl₃, VCl₄), organoaluminum activators or cocatalysts (Lewis acids, namely, trimethylaluminum (AlMe₃), triisobutylaluminum (AlⁱBu₃)), modifying additives (organic compounds of various compositions used in catalysis for the addition to the supported catalyst), as well as a mineral carrier, usually magnesium chloride. Nevertheless, the last decade has witnessed an increased industrial demand for single-site olefin polymerization catalysts, which allow the control over different properties of resulting polymers, such as microstructure, molecular weight, molecular weight distribution, glass transition and melting temperature. Earlier we have shown [9–11] that titanium TADDOL complexes in the presence of methylaluminoxane (MAO) are capable of polymerizing ethylene and propylene. This work presents the data on the use of a binary cocatalyst (Et₂AlCl/ⁱBu₂Mg), which differs in its nature from the standard cocatalysts used in the olefin polymerization, since it allows replacing expensive activators (alkylaluminoxanes and perfluorophenylborates) for conventional organometallic compounds. The post-metallocene titanium(4+) complexes with TADDOL ligands were obtained, which, in the presence of organoaluminum and organomagnesium cocatalysts, led to the formation of UHMWPE. The physicochemical properties of the resulting polymeric samples, the effect of the composition of the cocatalysts on the activity of the catalytic systems, and the

properties of the resulting polymers were studied. The possibility of synthesizing UHMWPE with the titanium(+4) complexes obtained was evaluated, and the possibility of its processing into high-strength high-modulus oriented yarns was demonstrated.

Results and discussion

Individual titanium dichloride complexes LTiCl₂ were obtained by the sequential treatment of TADDOL ligands with sodium hydride and titanium tetrachloride (Scheme 1).



Scheme 1. Synthesis of the titanium(4+) complexes with TADDOL ligands.

The investigation of the catalytic activity of the resulting compounds (Table 1) allowed us to draw the following conclusions. The titanium complexes in the presence of MAO used as a cocatalyst in the Al_{MAO}/M ratio up to 2000 catalyze the polymer formation with an activity of up to 700 kg PE·mol(Ti)⁻¹·h⁻¹·atm⁻¹. The application of a mixture of Et₂AlCl and ⁱBu₂Mg as a cocatalyst leads to an increase in the catalytic activity up to 3450 kg PE·mol(Ti)⁻¹·h⁻¹·atm⁻¹. It was also established that an increase in the volume of the aryl substituents located in the close proximity to the metal center, achieved by replacing phenyl groups with the naphthyl ones, leads to a decrease in the catalytic activity of the complexes.

Table 1. Catalytic activity of the titanium(4+) TADDOL complexes in the ethylene polymerization^a

| Exp. | Complex | Activator, Al/Mg/Ti | Activity, kg PE·mol(Ti) ⁻¹ ·h ⁻¹ ·atm ⁻¹ | M _v , 10 ⁶ Da ^b |
|------|----------|--|---|--|
| 1 | 5 | MAO, 500 | 482 | 2.10 |
| 2 | 5 | MAO, 1000 | 550 | 1.87 |
| 3 | 5 | MAO, 2000 | 640 | 1.55 |
| 4 | 5 | Et ₂ AlCl/Bu ₂ Mg, 300/100 | 2700 | 4.23 |
| 5 | 6 | MAO, 1000 | 612 | 3.21 |
| 6 | 6 | MAO, 2000 | 700 | 2.93 |
| 7 | 6 | Et ₂ AlCl/Bu ₂ Mg, 300/100 | 3450 | 4.97 |
| 8 | 7 | MAO, 2000 | 266 | 2.33 |
| 9 | 7 | Et ₂ AlCl/Bu ₂ Mg, 300/100 | 1178 | 3.17 |
| 10 | 8 | MAO, 2000 | 365 | 1.20 |
| 11 | 8 | Et ₂ AlCl/Bu ₂ Mg, 300/100 | 980 | 2.27 |

^a polymerization conditions: ethylene pressure 1.7 atm., toluene as a solvent, polymerization time 30 min, C(Ti) = 5·10⁻⁶ mol/L, temperature 30 °C;

^b molecular weights were determined using the viscometric method.

The melting temperatures of the polymers obtained varied in the range of 135–142 °C and their molecular weights ranged from 1.20·10⁶ to 4.97·10⁶ Da.

The processing of the resulting UHMWPE reactor powders in the presence of precatalysts **5–8** into high-modulus oriented films was accomplished by preparing monolithic samples under pressure and shear deformation at a temperature below the melting point of the polymer, followed by the uniaxial stretching.

The films obtained using the synthesized catalytic systems (experiments 4 and 7, Table 1) feature an elastic modulus of 140.00 GPa and a tensile strength of 2.25 GPa. It should be noted that the films obtained in these experiments are characterized by a single-stage rupture pattern, indicating the homogeneity of the samples, while the close values of tensile elongation and elastic modulus for a series of the samples with the same orientational draw ratio confirm the high quality of the nascent UHMWPE reactor powders obtained over the catalytic system with the suggested precatalyst.

Conclusions

Thus, the resulting titanium(4+) complexes with tetraaryldioxolane-dimethanol ligands, in the presence of organoaluminum activators, serve as highly effective catalysts for the synthesis of high-molecular-weight polyethylene, with the activity up to 3400 kg PE·mol(Ti)⁻¹·h⁻¹·atm⁻¹. The polymers obtained over these titanium complexes represent UHMWPE, with a molecular weight of up to 4.50·10⁶ Da. The film yarns obtained using catalysts **5** and **7** feature an elastic modulus of 140.00 GPa and a tensile strength of 2.25 GPa. The mechanical characteristics of the oriented film yarns obtained in this work using the synthesized titanium(+4) complexes are not inferior to those obtained using the earlier reported catalytic systems [12] (the experiments were carried out under the same conditions). For comparison, the value of an elastic modulus for

commercially available gel-spun oriented UHMWPE fiber is 113 GPa [13].

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Electronic supplementary information

Electronic supplementary information (ESI) available online: [the experimental section](#). For ESI, see DOI: 10.32931/foXXXXx.

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