



Titanium and vanadium catalysts with oxazoline ligands for ethylene-norbornene (co)polymerization



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ABSTRACT

A series of catalysts, (Py-ox)TiCl₄, (Py-box)TiCl₄, (Py-ox)VCl₃, (Py-box)VCl₃, SIL/(Py-ox)VCl₃, SIL/(Py-box)VCl₃, with 2-(1,3-oxazolin-2-yl)pyridine (Py-ox) and 2,6-bis(1,3-oxazolin-2-yl)pyridine (Py-box) ligands, silica support modified by 1-[3-(triethoxysilyl)propyl]pyridinium ethylchloroaluminate ionic liquid (SIL), activated by AlEt₂Cl, AlEtCl₂, and methylaluminoxane (MMAO) were studied in ethylene polymerization and ethylene-norbornene copolymerization. Single-crystal X-ray diffraction is given for both Py-ox and Py-box. The complexation was confirmed by NMR and ESI-MS methods. All complexes were found to be active in ethylene polymerization with better performance of the vanadium catalysts. Properties of polyethylene (PE) obtained using these catalysts are characterized by the molecular weight (M_w) within the range of $1.5\text{--}2.4 \times 10^6$ g/mol, narrow molecular weight distribution ($1.9 < M_w/M_n < 2.9$), melting temperature ($131 < T_m < 144$ °C), and crystallinity degree ($42 < X < 81\%$). The supported SIL/(Py-box)VCl₃ catalyst activated by AlEt₂Cl shows the best activity in ethylene polymerization (8120 kg PE/mol_V h) and copolymerization with norbornene (7135 kg Cop/mol_V h). The vanadium systems show high norbornene (NB) incorporation within the range of 17–40 mol% at low NB concentration (0.5–1.5 mol/L). Copolymer is characterized by M_w from 107 to 960×10^3 g/mol and narrow M_w/M_n (1.6–2.6). Glass transition temperature (T_g up to 61 °C) depends linearly on the amount of comonomer incorporated.

1. Introduction

There is a need to design of new polymer materials of specific properties, which is one of the most interesting challenges of modern science. In case of polyolefins, this can be achieved by control of (co) polymerization reaction and proper choice of amount of reagents. For this purpose, new designed transition metal compounds give a chance to be applied as pre-catalysts for synthesis of highly-specialized synthetic polymers [1–4].

Nowadays, there is some interest in vanadium complexes because they enable to obtain: polymers of high molecular weight and narrow molecular weight distribution, copolymers of ethylene with higher 1-olefins or cyclic olefins with higher comonomer incorporation in the polymer chain [2,4–12]. On the other hand, the vanadium compounds are not so extensively studied, because so far they reveal low activity in (co)polymerization reactions in comparison to titanium and zirconium analogues [12–14]. The main reason of low activity is an intrinsic instability of V-C bond so that the active forms of vanadium species are reduced to those less active or inactive, which mostly leads to catalyst deactivation during polymerization reaction [7,8,15,16]. This problem

can be solved when a reactivating agent is added to reaction medium, which prevents reduction of vanadium to lower states. Ethyl trichloroacetate (ETA) is the most commonly used for this purpose, like also chlorinated hydrocarbons [9,15–17].

Another method to improve the stability of active site, and thus to increase the catalyst activity, is introduction to the catalyst structure nitrogen, oxygen or phosphine atoms, which act as the electron donors. Such catalyst complexes should ensure not only high yield in (co) polymerization reaction, but also polymer product with desired characteristic [9,15–18]. Therefore, search for proper ligands for the catalyst complexes is indispensable for development of technology.

The promising alternative for metallocene complexes commonly applied in polymerization reactions can be compounds consisted of transition metal and oxazoline or bis(oxazoline) ligands [19,20]. These type of ligands are applied in asymmetric catalytic processes for over two decades [21]. The most important benefits of their applications are: easy synthesis, accessible chiral precursors, and ability to coordinate various metals, such as Cu, Pd, Fe, Zn, Mg, Ni, or Sc [21–26]. Commonly applied Py-box is usually tridentate ligand, although literature report bidentate (involving pyridine and one oxazoline nitrogen atoms)

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or monodentate [21,22]. Oxazoline complexes are applied in various reactions including cyclopropanation, allylic substitution, hydrosilylation, epoxidation, Diels-Alder, aldol-like and Michael reactions [23,27–29]. However, their application in olefin polymerization is merely recognized [19,20,30].

Market of plastics for high-tech engineering constantly searches new material of specific properties. The interest is focused, in particular for cyclic olefins copolymers (COCs). The most versatile and common COCs are copolymers of ethylene with norbornene. These plastics are a promising group of thermoplastics, from high crystalline solids to thermoplastic elastomers, depending on the degree of norbornene incorporation and the microstructure of copolymer [3,11,31]. They are used as materials in medical and diagnostic equipment, electronic devices, as packaging films, etc. [3,32–34]. In general, all literature reports on the catalysts used in the copolymerization of ethylene with norbornene concern homogeneous complexes [31,32], and only there are few data on heterogeneous compounds [35,36].

In contrast, in industry, heterogeneous catalyst systems are preferred for practical reasons, because they increase catalyst stability, enables to control polymer microstructure and morphology as well as to eliminate reactor fouling [37,38]. So far, many methods have been developed to immobilize transition metal compounds on a solid support, but one of them, the so-called supported ionic liquid (SIL), seems to be interesting. In this method, a thin layer of ionic liquid (IL) containing dissolved catalyst is anchored on a solid, porous, organic or inorganic carrier [10,39–42]. The SIL systems combine the advantages of homogeneous and heterogeneous catalysis, while reducing their disadvantages [39,40]. The SIL systems were successfully applied in both polymerization reactions of ethylene and copolymerization of ethylene with 1-olefins and cyclic olefins [10,41,43].

The aim of this work is to search for catalysts for olefin (co)polymerization that, activated by using inexpensive organometallic compounds, would give a stable and efficient catalytic system that produces a polymer with desired properties.

2. Experimental section

2.1. Materials

Substrates for syntheses as well as methods of purification of solvents are given in [Supplementary Material](#). Ionic liquid, 1-[3-(triethoxysilyl)propyl]pyridinium chloride, was obtained according to the published procedure [43].

2.2. Instruments

^{13}C NMR and ^1H NMR spectra of the ligands and complexes, and ^{13}C NMR spectra of the polymers were recorded on a Bruker Ultrashield spectrometer (400 MHz) in dimethyl sulfoxide- d_6 and *o*-dichlorobenzene- d_4 solvent, respectively. Total norbornene incorporation in polymer was calculated using equation: $\text{Mol NB\%} = [1/3(2\text{IC}_7 + \text{IC}_1/\text{C}_4 + \text{IC}_2/\text{C}_3)/\text{ICH}_2] \times 100\%$ where: ICH_2 , IC_7 , IC_1/C_4 , IC_2/C_3 are total area of the ^{13}C NMR signal at 26–31, 31–34, 36–42 and 43–50 ppm.

Atomic absorption spectrometry (AAS) using an ICE 3500 model (Thermo Electron Corporation) was used to determine amount of V element.

The melting temperatures, crystallinity, and glass transition temperatures of the polymers were measured by differential scanning calorimetry DSC 2010 TA instrument calorimeter equipped with an automated sampler. The data were collected with the heat/cool/heat cycle at a heating rate of 10 °C/min under a nitrogen atmosphere. The polyethylene crystallinity degree was calculated using the equation: $X = (\text{DH}_f/\text{DH}_{f,c}) \times 100\%$, where DH_f is enthalpy of fusion of the polyethylene sample, $\text{DH}_{f,c}$ is enthalpy of fusion of standard (290 J/g), and X is crystallinity degree, %.

Gel permeation chromatography was used to determine molecular weight and molecular-weight distribution of polymer samples on Waters Alliance GPCV 2000 apparatus using 1,2,4-trichlorobenzene as the solvent at 142 °C. The data were analyzed using polystyrene calibration curves.

Elemental analysis (EA) was performed using apparatus EA 1108 (Fisons Instruments).

ESI-Q-TOF-MS analysis was performed on a micrOTOF-Q II system (Bruker Daltonics, Bremen, Germany), equipped with an automatic syringe pump (KD Scientific Inc., Holliston, MA, USA) for direct infusion. The mass spectrometer was running at 4.0 kV at a desolvation temperature of 150 °C and system was operating in the positive ion mode. The instrument was calibrated using an internal calibration standard ESI-L low concentration tuning mix solution (Agilent Technologies). Data were processed via Bruker Data analysis software version 4.0 SP 5. Full scan and MS/MS analysis were measured in the range m/z 50–1100. MS/MS experiments were conducted using nitrogen as collision gas, at low energy to confirm the main fragmentation pathways of studied complexes. All calculated m/z values of the vanadium complexes were based on the naturally most abundant ^{51}V isotope, whereas the values of the titanium complexes were based on the most abundant ^{48}Ti isotope. Dried acetonitrile was used as a sample solvent and samples were directly infused in MS system at a flow rate 3 $\mu\text{L}/\text{min}$. The nebulizing gas (nitrogen) pressure was 0.04 MPa, and dry gas flow rate set at 4 L/min.

2.3. Synthesis of ligands

The syntheses of 2-(1,3-oxazolin-2-yl)pyridine (Py-ox) and 2,6-bis(1,3-oxazolin-2-yl)pyridine (Py-box) were performed mainly according to Stokes et al. [44] and Zhu et al. [45], respectively. Structure confirmation is given in Data in Brief [46].

2.4. Synthesis of titanium complexes

All steps were carried out in inert argon atmosphere. A stoichiometric amount of titanium(IV) chloride in toluene was added dropwise to a stirred solution of the Py-ox or Py-box ligand (1.0 mmol) in dichloromethane or toluene. The reaction mixture was stirred overnight at room temperature. The complex precipitated and the solvents were removed by filtration in glove-box and the residue was washed several times with hexane, and then dried in vacuum. The final titanium complexes were in the form of beige solid (Py-ox)TiCl₄ or yellow solid (Py-box)TiCl₄.

(Py-ox)TiCl₄, yield 77%. ^{13}C NMR (400 MHz, DMSO- d_6) δ 164.07, 149.58, 148.50, 137.96, 126.77, 122.01, 43.07, 40.84 (Fig. 1S). ^1H NMR (400 MHz, DMSO- d_6) δ 8.62 (1H, d), 8.00–7.97 (2H, m), 7.60 (1H, t), 3.73 (2H, t), 3.60 (2H, q) (Fig. 2S). Elemental analysis of C₈H₁₀N₂OCl₄Ti results: calculated C 28.44%, H 2.39%, N 8.29%, experimental: C 28.24%, H 2.45%, N 8.19%. MS (m/z) 361 ($\text{M}^+ + \text{Na}$), 303 ($\text{M}^+ - \text{Na} - \text{Cl}$), 207 (Py-ox + Na + Cl), 171 (Py-ox + Na), 148 (Py-ox).

(Py-box)TiCl₄, yield 68%. ^{13}C NMR (400 MHz, DMSO- d_6) δ 163.81, 148.97, 139.94, 124.80, 43.15, 41.28 (Fig. 3S). ^1H NMR (400 MHz, DMSO- d_6) δ 8.20 (3H, m), 3.86 (4H, t), 3.69 (4H, q) (Fig. 4S). Elemental analysis of C₁₁H₁₄N₃O₂Cl₄Ti results: calculated C 32.47%, H 2.72%, N 10.33%, experimental: C 32.29%, H 2.77%, N 10.26%. MS (m/z) 431 ($\text{M}^+ + \text{Na}$), 397 ($\text{M}^+ + \text{Na} - \text{Cl}$), 361 ($\text{M}^+ + \text{Na} - 2\text{Cl}$), 240 (Py-box + Na), 218 (Py-box).

2.5. Synthesis of vanadium complexes

To a stirred solution of the corresponding ligand (1.0 mmol) in dichloromethane was added a stoichiometric amount of solution vanadium(III) chloride in THF. The reaction mixture was stirred overnight at room temperature and dried under reduced pressure. The residue

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