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Tri-alkenyl polyhedral oligomeric silsesquioxanes as comonomers and active center modifiers in ethylene copolymerization catalyzed by bis(phenoxy-imine) Ti, Zr, V and V salen-type complexes

Paweł Groch[a,*], Katarzyna Dziubek[a], Krystyna Czaja[a], Marzena Białek[a], Dariusz Man[b]

[a] *Opole University, Faculty of Chemistry, Oleska 48, 45-052, Opole, Poland*
[b] *Opole University, Institute of Physics, Oleska 48, 45-052, Opole, Poland*

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ABSTRACT

In copolymerization of ethylene (E) with tri-alkenyl-silsesquioxanes (POSS-6-3 and POSS-10-3) were used bis (phenoxy-imine) titanium, zirconium and vanadium catalysts, as well as salen-type vanadium catalysts. There were obtained copolymers with POSS-R-3 units as side branches of polymer chains. The type of employed bis (phenoxy-imine) titanium, zirconium and vanadium catalysts and salen-type catalyst of vanadium determined the copolymer chain termination reactions, as well as the mechanism of modification of the active species by the POSS-R-3 comonomer. POSS-R-3 comonomers caused selective poisoning of bis(phenoxy-imine) zirconium catalyst and they provided protection against tight contact with $[\text{Me-MMAO}]^-$ counter anion. Concentration of the precursor of the active site and Ti(III) complex was found decreased in the system with bis(phenoxy-imine) titanium catalyst and POSS-R-3. There were formed different catalytic species characterized by diamagnetic properties for bis(phenoxy-imine) vanadium due to the presence of POSS-R-3. Our findings were based on results from the following methods: FT-IR, ^{1}H NMR, ^{1}H-^{1}H NOESY, EPR and GPC.

1. Introduction

Organic-inorganic hybrid materials have attracted great interest in recent years due to their combined properties derived from organic and inorganic components [1]. An excellent example of organic-inorganic compounds are polyhedral oligomeric silsesquioxanes (POSS) which, moreover, can be introduced into polymers to produce many novel hybrid polymeric materials with advantageous properties [2].

Generally, POSS can be introduced into polymers by physical or chemical methods [3]. Particular attention should be paid to chemical approach which offers the possibility of avoiding inter alia macroscopic phase separation which is a common problem in composites [3]. Incorporation of POSS cages into polymer chains via chemical bonds makes it possible to obtain unique polymeric materials with different structural characteristics and interesting physiochemical properties.

In the past few years there were published quite many reports on preparation of hybrid POSS-containing copolymers by use of mono-, di- and multi-functional POSS comonomers [4–7]. The incorporation way of silsesquioxane units into polymer chains is dependent on the functionality of the former one. Mono-functional POSS comonomers could act mostly as pendant or end groups of the main chain [7]. In case of POSS which contains two or more reactive groups, it is also possible to obtain bead-like copolymers or cross-linked materials [6,8–10]. Multifunctional POSS derivatives perform as nanosized cross-linkers [11–13] or they make precursors of amphiphilic materials [14].

In general, POSS derivatives were successfully incorporated into a wide range of polymers via polycondensation [10,15], polyaddition [4], radical polymerization [7], Friedel-Crafts reaction [16], “click chemistry” [17,18] or ring-opening polymerization [5]. However, information on copolymers with di- and multi-alkenylsilsesquioxanes is rather limited [4,8,19–23]. Available literature data on coordinative copolymerization of olefins with POSS are also scarce [6,8,19,24–27]. Available reports cover mainly metallocene-produced copolymers of ethylene or propylene with mono- [24–27], di- [8] and multi-alkenylsilsesquioxanes [6]. Within that area, we found out in our previous work that a tri-alkenylsilsesquioxane with incompletely condensed POSS cage could act not only as a comonomer but also as a modifier of metallocene species. Strong interaction between open POSS cage and metallocene catalyst increased concentrations of precursors and active species at a very low activator/catalyst molar ratio (Al/Zr = 10 mol/mol) which is unusual for metallocene catalysts [6].

We were the first ones to report that ethylene copolymers with

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[*] Corresponding author.
E-mail address: pgroch@uni.opole.pl (P. Groch).

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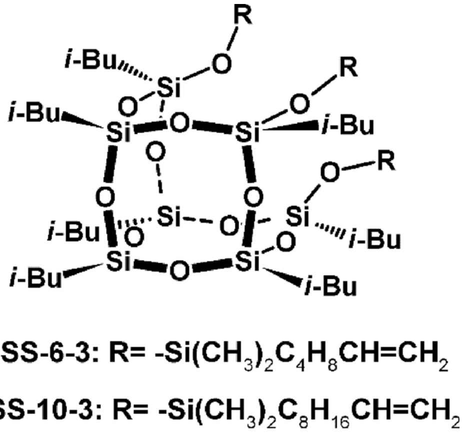

Fig. 1. Structures of tri-alkenyl-silsesquioxane comonomers.

mono- or di-alkenylsilsesquioxanes could be successfully prepared over the bis(phenoxy-imine) titanium, zirconium complexes and salen-type complex of zirconium [8,19]. These unique catalysts produced materials with interesting properties which would open up new applications [28,29]. For ethylene/POSS copolymerization, bis(phenoxy-imine) titanium or zirconium and zirconium salen-type catalysts offered the possibility to synthesize polymeric materials which contained higher incorporation degrees of POSS comonomers and advantageous structural and thermal properties as compared to metallocene-produced copolymers [27].

In this work we present catalytic properties of different bis(phenoxy-imine) titanium, zirconium and vanadium complexes and salen-type complex of vanadium which contain complexes of group 4 and group 5 elements with [ON] and [ONNO] type ligands in the coordination copolymerization of ethylene with tri-alkenylsilsesquioxane (POSS-R-3). More specifically, *iso*-butyl-substituted tri-alkenylsilsesquioxanes which contained incompletely condensed silicon-oxygen T_4D_3 cages with different lengths of alkenyl reactive substituents were used as comonomers (POSS-6-3 and POSS-10-3, Fig. 1), and three bis(phenoxy-imine) (FI) complexes of Zr, Ti or V as the metallic center (FI-ZrH, FI-TiH, FI-V-Bu, respectively, Fig. 2a), and the salen-type complex of vanadium (Sal-V, Fig. 2b), were selected as pre-catalysts.

Based on our previous research, bis(phenoxy-imine) titanium and zirconium pre-catalysis [8,19] were activated by modified methylaluminoxane (MMAO), while ethylaluminium dichloride ($EtAlCl_2$) was used as co-catalyst for catalyst based on vanadium complexes [30,31].

There were studied effects of the type of the catalytic system, as well as of the type and concentration of the POSS-R-3 comonomer in the feed on the performance of ethylene/POSS-R-3 copolymerization and on the properties of the obtained copolymers. Copolymerizations of ethylene with POSS over bis(phenoxy-imine) Ti, Zr, V and V salen-type catalysts were carried out under optimal conditions previously determined for each catalytic system (Table S3). The properties of copolymers were characterized by nuclear magnetic resonance (^1H NMR), by Fourier transform infrared spectroscopy (FT-IR) and by gel permeation chromatography (GPC).

The nature of catalytic active sites is known to be a key factor which controls the effectiveness of catalysts in polymerization reaction and characteristics of polymeric products. Thus, the important issue of this work was to investigate the effect of silsesquioxane comonomers POSS-R-3 on any possible modification of active sites of the catalysts by spectroscopic methods: ^1H NMR and nuclear Overhauser effect spectroscopy (^1H-^1H NOESY), as well as electron paramagnetic resonance (EPR). It should be noted that oxygen atoms in the structure of MMAO and silsesquioxane comonomer are strong Lewis bases which could strongly interact with active sites of the catalysts as strong Lewis acids. Moreover, the interactions of the active site of the catalyst and MMAO are very complex as MMAO consists of a cage with up to 60–70 Al and O atoms [32,33]. Thus, there were adopted some common simplifications in studies of the influence of POSS comonomers on the performance of the catalysts and the structure of catalytic active centers.

2. Experimental section

2.1. Materials

Toluene was purchased from Chempur and it was refluxed over sodium and distilled under nitrogen prior to use. Modified methylaluminoxane (MMAO, 7 wt % solution in toluene, Sigma-Aldrich), $EtAlCl_2$ (1.0 M, Sigma-Aldrich), 1,2-dichlorobenzene-d_4 (Deutero GmbH), hydrochloric acid (35–38 %, Chempur), methanol (Chempur) and hexane (Chempur) were used as purchased. Toluene-d_8 (Deutero GmbH) was dried over molecular sieves (4 Å) and degassed by argon, and then it was stored in a glove box. Tri-alkenylsilsesquioxane derivatives were obtained as described previously by prof. B. Marciniec and his research group from the Faculty of Chemistry of UAM in Poznań [6]. Dichlorobis[*N*-(salicylidene)-1-naphthylaminato]zirconium(IV), dichlorobis[*N*-(salicylidene)-1-naphthylaminato] titanium(IV), dichlorobis[*N*-(3,5-di-*tert*-butylsalicylidene)aniline]vanadium(IV) and dichloro[*N,N'*-bis(salicylidene)propylenediamine]vanadium(IV) complexes were prepared according to previously published procedures [30,31]. Ethylene (Grade

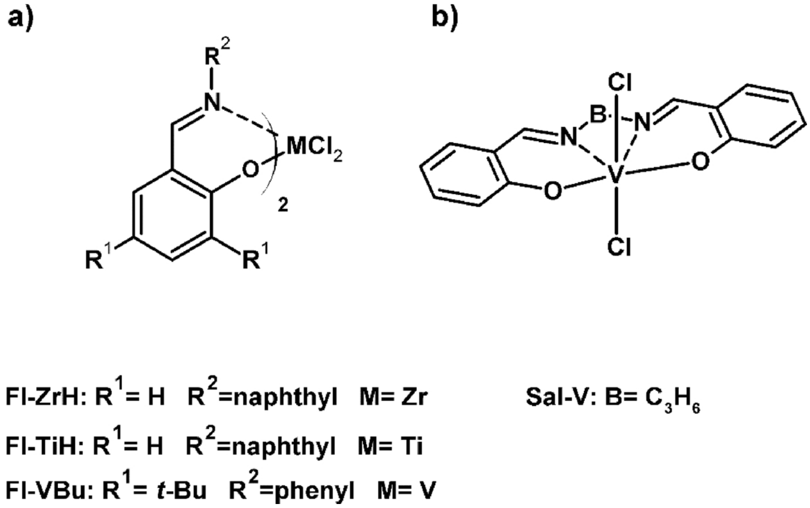

Fig. 2. Structures of bis(phenoxy-imine) (a), salen-type (b) complexes.