



Copolymers of ethylene with monoalkenyl- and monoalkenyl (siloxy)silsesquioxane (POSS) comonomers – Synthesis and characterization

Paweł Groch^a, Katarzyna Dziubek^{a,*}, Krystyna Czaja^a, Beata Dudziec^b, Bogdan Marciniec^{b,c}

^a Opole University, Faculty of Chemistry, Oleska 48, 45-040 Opole, Poland

^b Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89B, 61-614 Poznań, Poland

^c Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, Umultowska 89C, 61-614 Poznań, Poland

ARTICLE INFO

Keywords:

Copolymerization

Ethylene

Polyhedral oligomeric silsesquioxane (POSS)

Metallocene

ABSTRACT

The hybrid ethylene/POSS copolymers were obtained using the *rac*-Et(Ind)₂ZrCl₂ catalyst activated by MAO. A series of monoalkenyl- and monoalkenyl(siloxy)silsesquioxanes derivatives with different structures of reactive alkenyl substituent and types of non-reactive groups attached to the T₈ POSS cage was used as comonomers. The kind and concentration of the POSS comonomer in the reaction feed as well as extended reaction time were found to strongly influence the catalyst efficiency and incorporation of POSS units into polymer chains. The comonomer reactivity was significantly dependent on the length of the alkenyl reactive substituent in the POSS molecule and it was highest for the POSS structures with medium-length of the alkenyl substituent due to their steric and inductive effects of the silicon-oxygen cage. The molecular weight as well as the kind and the content of unsaturated end groups in copolymers were dependent on the kind and amount of POSS comonomer in the reaction feed. The change in melting temperature, crystallinity degree, crystallization temperature and morphology of copolymers was observed as compared to neat polyethylene (PE).

1. Introduction

The hybrid organic-inorganic materials have attracted much attention for more than ten years, both from the academic and industrial points of view, because of their interesting physicochemical and mechanical properties. Such materials combine the features of organic and inorganic materials and thus could turn out to be useful in various application areas [1–3].

Polyhedral oligomeric silsesquioxanes (POSS) make one of the most interesting examples of the organic-inorganic compounds, and their advantageous features have contributed to the rapid progress in the research on their synthesis and applications. A POSS contains an inorganic core consisting of the silicon and oxygen atoms which usually has the form of a cage. Various substituents may be attached to each corner silicon atom, thus the properties of POSS can be modified in the wide range by the structural control [4].

Developing new POSS-containing polymeric materials with improved thermal stability and resistance to oxidation [5–10] has been one of the most promising application fields for POSS compounds. Significant opportunities have been provided by copolymerization of alkenylsilsesquioxanes with olefins. However, the number of literature data concerning coordination (co) polymerization of such monomers with the use of organometallic catalysts is still limited [5–10]. It is thus very difficult to determine

* Corresponding author.

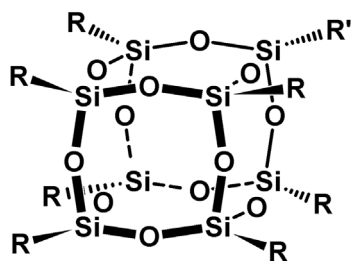
E-mail address: katarzyna.dziubek@uni.opole.pl (K. Dziubek).

<http://dx.doi.org/10.1016/j.eurpolymj.2017.03.038>

Received 28 September 2016; Received in revised form 13 February 2017; Accepted 15 March 2017

Available online 18 March 2017

0014-3057/ © 2017 Elsevier Ltd. All rights reserved.



- | | |
|--------------------|---|
| a) R= <i>i</i> -Bu | R'= -OSi(CH ₃) ₂ CH ₂ CH=CH ₂ |
| b) R= <i>i</i> -Bu | R'= -OSi(CH ₃) ₂ C ₄ H ₈ CH=CH ₂ |
| c) R= <i>i</i> -Bu | R'= -OSi(CH ₃) ₂ C ₈ H ₁₆ CH=CH ₂ |
| d) R= Cy | R'= -OSi(CH ₃) ₂ C ₈ H ₁₆ CH=CH ₂ |
| e) R= <i>i</i> -Bu | R'= -CH=CH ₂ |
| f) R= <i>i</i> -Bu | R'= -CH ₂ CH=CH ₂ |
| g) R= <i>i</i> -Bu | R'= -C ₄ H ₈ CH=CH ₂ |
| h) R= <i>i</i> -Bu | R'= -C ₈ H ₁₆ CH=CH ₂ |
| i) R= Cy | R'= -CH ₂ CH=CH ₂ |
| j) R= Cy | R'= -C ₄ H ₈ CH=CH ₂ |

Fig. 1. Molecular structures of POSS comonomers used; monoalkenyl(siloxy)silsesquioxanes: (a) POSS-(*i*-Bu)₇(OSi(CH₃)₂CH₂CH=CH₂), (b) POSS-(*i*-Bu)₇(OSi(CH₃)₂C₄H₈CH=CH₂), (c) POSS-(*i*-Bu)₇(OSi(CH₃)₂C₈H₁₆CH=CH₂), (d) POSS-(Cy)₇(OSi(CH₃)₂C₈H₁₆CH=CH₂), and monoalkenylsilsesquioxanes: (e) POSS-(*i*-Bu)₇(CH=CH₂), (f) POSS-(*i*-Bu)₇(CH₂CH=CH₂), (g) POSS-(*i*-Bu)₇(C₄H₈CH=CH₂), (h) POSS-(*i*-Bu)₇(C₈H₁₆CH=CH₂), (i) POSS-(Cy)₇(CH₂CH=CH₂), and (j) POSS-(Cy)₇(C₄H₈CH=CH₂).

even a generic correlation between the structure of the POSS comonomer and the properties of the obtained hybrid copolymers.

The purpose of the present work was to comprehensively study the influence of the structure of monofunctional silsesquioxane comonomers on the performance of the ethylene/POSS copolymerization process in which the *rac*-ethylenebis(indenyl)zirconium dichloride catalyst (*rac*-Et(Ind)₂ZrCl₂) activated by methylaluminoxane (MAO) was used. Monoalkenyl- and monoalkenyl(siloxy)silsesquioxanes (without or contained the dimethylsiloxy spacer which connected the alkenyl substituent with the POSS cage, respectively) with different substituents attached to the corner silicon atoms in the T₈ POSS cage were applied as comonomers (Fig. 1). The studied POSS derivatives contained seven *iso*-butyl (*i*-Bu) or cyclohexyl (Cy) substituents as non-reactive groups. In turn, the reactive *n*-alkenyl substituents were different from each other in the length. It should be noted that, to the best of our knowledge, that type POSS derivatives have not been used until now in copolymerization with ethylene over metallocene catalysts.

Moreover, there is no comparative report available, which would present the relation between the POSS structure and the activity of a catalytic system, (co)monomer reactivity in copolymerization in ethylene, (co)monomer incorporation degree as well as physicochemical properties of the copolymer products obtained.

2. Experimental

2.1. Materials

Chlorosilanes (Aldrich), anhydrous magnesium sulphate (Aldrich), calcium hydride (Aldrich), triethylamine (Fluka), silica gel 60 (Fluka), 1,3,5,7,9,11,14-heptaisobutyltricyclo-[7.3.3.15,11]heptasiloxane-*endo*-3,7,14-triol (trisilanolisobutyl POSS) (Hybrid Plastics), methylaluminoxane (MAO, 10 wt.%, Sigma-Aldrich), *rac*-ethylenebis-(1- η^5 -indenyl)-zirconium dichloride (*rac*-Et(Ind)₂ZrCl₂, Sigma-Aldrich), 1,2-dichlorobenzene-*d*₄ (POCH Gliwice), chloroform-*d* (99.8%, Deutero GmbH), hydrochloric acid (35–38%, POCH Gliwice) and methanol (POCH Gliwice) were used as purchased. Pure grade *n*-pentane (Chempur), *n*-hexane (Chempur) and THF (Chempur) were dried prior to use over CaH₂ and stored under argon. Ethylene (Grade 3.5, Air Liquide) and nitrogen (Messer) were used after passing through a column with the sodium metal supported on Al₂O₃. Toluene (POCH Gliwice) was refluxed over sodium. 1,2,4-Trichlorobenzene (TCB, 99 wt.%) (Aldrich) was purified by distillation.

2.2. Synthesis and NMR characterization of 1-alkenyl- and 1-alkenyl(dimethylsiloxy)-3,5,7,9,11,13,15-hepta(*iso*-butyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxanes (monoalkenyl- and monoalkenyl(siloxy)silsesquioxanes)

All syntheses were conducted under argon atmosphere using standard Schlenk-line and vacuum techniques.

Depending whether the alkenyl group was attached directly to the POSS core (monoalkenylsilsesquioxanes) or via –SiO– spacer (monoalkenyl(siloxy)silsesquioxanes), the methodology for their syntheses varied. It was based on hydrolytic condensation of incompletely condensed trisilanolisobutyl POSS or consecutive hydrolytic condensation followed by hydrolysis of its intermediate chlorosubstituted derivative and second condensation reaction with the respective alkenylchlorosilane. This synthetic methodology for the synthesis of monofunctional silsesquioxanes is well-documented [2]. It was applied in the modified version described by Marciniak et al. [11] and analytically pure compounds were isolated with the yield of 89–97%. The structure and synthetic route to 1-alkenyl(dimethylsiloxy)-3,5,7,9,11,13,15-hepta(*iso*-butyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxanes is shown in Scheme 1 [12].

All synthesized compounds were characterized by NMR analysis.

Download English Version:

<https://daneshyari.com/en/article/5159787>

Download Persian Version:

<https://daneshyari.com/article/5159787>

[Daneshyari.com](https://daneshyari.com)