Thermal behavior of ethylene copolymers with di- and tri-alkenylsilsesquioxane comonomers synthesized by post-metallocene catalysts

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Abstract

This paper reported thermal properties of ethylene copolymers with di- and tri-alkenylsilsesquioxanes (POSS) synthesized by bis(phenoxy-imine) Ti, Zr, V, and V salen-type complexes. Ethylene copolymers with multi-alkenyl POSS obtained by such complexes contain multi-alkenyl POSS incorporated into the polymer chain as a side group. They were characterized by different thermal behavior depending on the kind of multi-alkenyl POSS comonomer, and type of the catalyst used, as well as polymerization conditions and thus the structure of the copolymer chain. Ethylene/POSS copolymers differed in incorporation of POSS into the polymer chain, content of specific unsaturation groups, and molecular weight, as well as heterogeneity of polymer chain compositions. The incorporation of multi-alkenyl POSS into the polymer chain affected melting and crystallization processes of copolymers in different ways. The POSS units could act as a nucleating agent of macromolecules. The increasing POSS content in E/POSS copolymers resulted in increasing thermal stability of obtained products, regardless of the kind of multi-alkenylsilsesquioxanes used. Thermal stability of such copolymers increased with decreasing content of trisubstituted vinylene groups (internal saturations) as well. The highest improvement of thermal stability over 85 °C in comparison with PE was observed in case of E/POSS copolymers synthesized by bis(phenoxy-imine) zirconium catalyst. The composition heterogeneity of E/POSS copolymers was found to affect markedly thermal stability of E/POSS copolymers.

Introduction

One of the most promising methods for improving thermal stability of polyolefins is development of new materials containing polyhedral oligomeric silsesquioxanes (POSS) [1, 2]. POSS are a class of interesting nano-scale units for the synthesis of organic–inorganic hybrid materials [3–9]. Indeed, incorporation of POSS into polymer chain results in improvement of physicochemical properties, such as mechanical properties [10], thermal stability [1], thermo-oxidative resistance [1], and flammability [11, 12] in comparison with unmodified polymers.

A typical POSS molecule is composed of a Si–O cage and several reactive or unreactive organic groups attached to Si atoms. POSS compounds containing at least one reactive substituent can be introduced into the polymer chain via polymerization or reactive grafting methods. Mono-functional POSS macromonomers can be incorporated into the polymer chain as pendant side groups, internal and/or end groups in the main chain [6–8].

As regards copolymers of olefins with POSS, many investigations were focused on the effect of the completely condensed silicon–oxygen T_8 POSS core with one reactive substituent with cyclopentyl or *iso*-butyl as non-reactive substituents [1, 13, 14]. Mono-functional POSS units incorporated into the polymer chain improved thermal stability of obtained materials [8, 13, 14] and could act as nucleating agents, which accelerate crystallization process of copolymers [7].

In case of ethylene copolymers with multi-alkenylsilsesquioxanes up to this moment, there are no literature data

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describing their thermal stability. It should be noted that thermal properties of such materials could depend not only on the kind and incorporation level of POSS comonomer but also on the microstructure of copolymer macromolecules. Ethylene copolymers with multi-alkenyl POSS could differ not only in the kind and number of substituents but also in the type of silicon–oxygen cage. Moreover, the way of POSS incorporation could significantly influence on thermal behavior of obtained polymeric products.

The purpose of the present work was to study comprehensively the influence of the structure of di- and tri-functional silsesquioxane comonomers with different structure of POSS core (completely or incompletely condensed silicon–oxygen cage of POSS) and different substituents attached to POSS core on thermal behavior of ethylene/POSS copolymers synthesized by bis(phenoxy-imine) Ti, Zr, V, and V salen-type complexes. In case of the previous research, it was found that through careful selection of functional POSS comonomer, its amount, type of catalyst, and polymerization conditions (ethylene pressure) make it possible to obtain a polymeric product with different structural characteristics (i.e, molecular weight, type and content of unsaturation groups, heterogeneity of copolymer macromolecules). The relationship between structure and content of multi-alkenylsilsesquioxanes incorporated into the copolymer, as well as the microstructure of copolymer macromolecules and their thermal properties of the products, was determined.

Experimental

Materials

Ethylene copolymers with di- and tri-alkenylsilsesquioxane comonomers were prepared according to the procedures as published previously [4, 5]. The phenyl-substituted di(hex-5-enyl) double-decker silsesquioxane (POSS-6-2) and *iso*-butyl-substituted tri-decenyl-silsesquioxane (POSS-10-3) which contained the incompletely condensed silicon–oxygen T_4D_3 were used as comonomers (Fig. 1). These POSS compounds were copolymerized with ethylene over
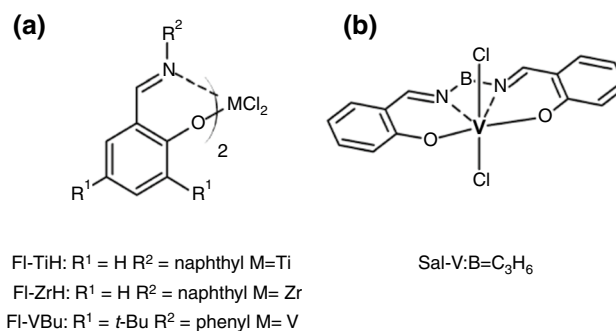
bis(phenoxy-imine) Ti, Zr, and V as well as V salen-type complexes are shown in Fig. 2.

E/POSS copolymers had various content of silsesquioxanes incorporated into the polymer chain (C_{POSS}) which fell within the range of 1.03–7.57 mass%, as determined by the ^1H NMR method [4, 5]. The structure of obtained E/POSS copolymers including different unsaturation groups is shown in Scheme 1.

The relative content of unsaturation groups in the range of 0.321–1.032 and 0.196–1.764 for vinyl ($A_{908/2020}$) and trisubstituted vinylene groups ($A_{800/2020}$), respectively, was determined by FT-IR method [4, 5]. Molecular weight (M_w) for E/POSS copolymers evaluated on an Alliance 135 GPCV 2000 apparatus was in the range of $165–1135 \times 10^3$ g mol^{-1}, and it depended on the type of organometallic complex used in (co)polymerization, as well as polyreaction condition [4, 5]. It should be noted that neat polyethylenes obtained under the same conditions were used as reference material.

Thermal properties of E/POSS copolymers

Thermal stability studies under dynamic (non-isothermal) conditions employed the thermogravimetric analysis (TGA) in air atmosphere (gas flow 50 mL min^{-1}) with the use of a TG/DSC1 Mettler Toledo device. Before the analysis, the oven of the device was purged with air. (Co)polymer powders (5 mg) were placed in a ceramic pan and heated from

(a)   **(b)**

Fl-TiH: R^1 = H R^2 = naphthyl M=Ti
Fl-ZrH: R^1 = H R^2 = naphthyl M= Zr
Fl-VBu: R^1 = *t*-Bu R^2 = phenyl M= V

Sal-V:B=C$_3$H$_6$

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

Fig. 1 Structures of di- (**a**) and tri- (**b**) comonomers

POSS-6-2: R = −Si(CH$_3$)$_2$C$_4$H$_8$CH=CH$_2$ POSS-10-3: R = −Si(CH$_3$)$_2$C$_4$H$_{16}$CH=CH$_2$
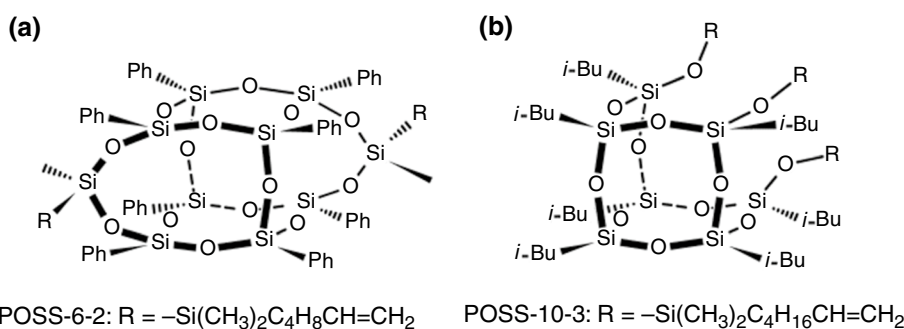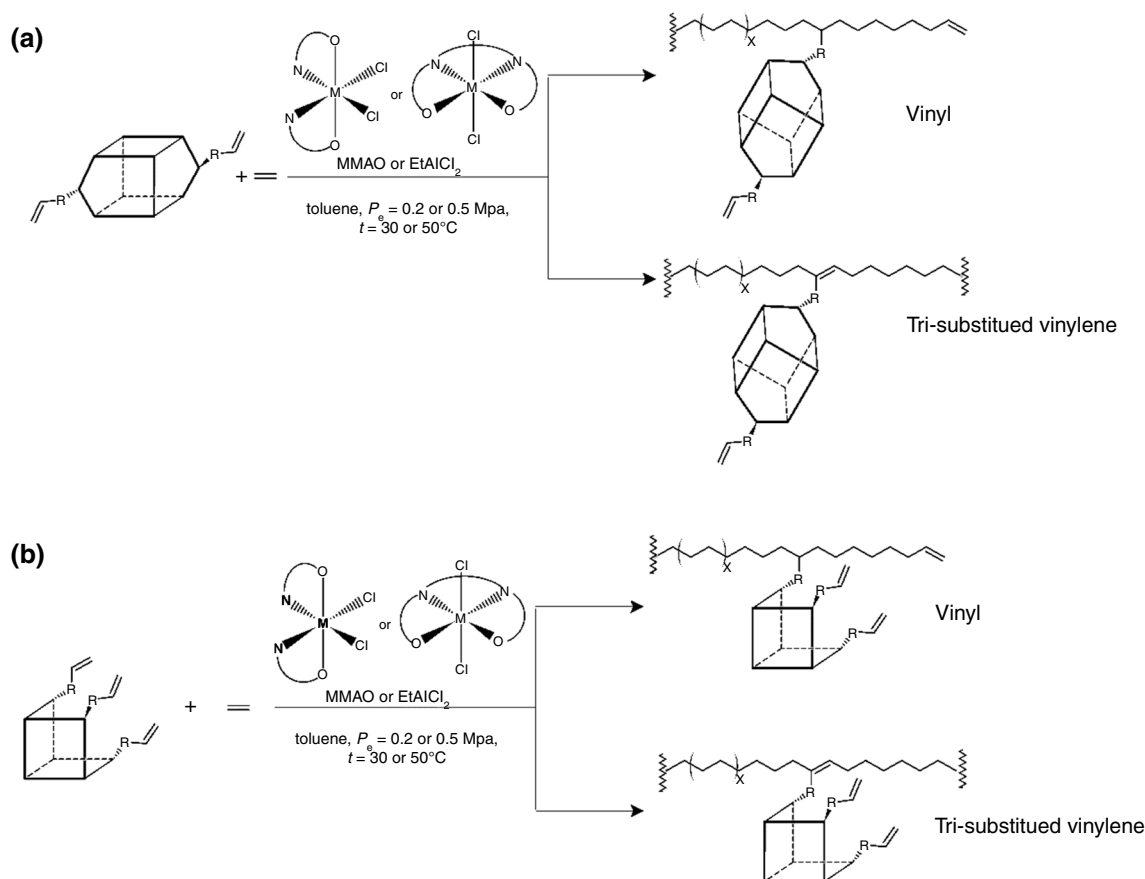
Scheme 1 Schematic structure of ethylene with **a** di- or **b** tri-alkenylsilsesquioxanes obtained over bis(phenoxy-imine) and salen-type complexes including different unsaturation groups

the room temperature up to 500 °C at the heating rate of 10 °C min⁻¹. The T_5 and T_{30} parameters define the temperatures at which 5 and 30% of the sample mass are lost, respectively, as well as there were determined the temperatures at the maximum rate of weight loss (T_{max}) for all studied (co) polymers.

Differential scanning calorimetry (DSC) measurements were performed by using a DSC1 Mettler Toledo instrument at the heating and cooling rate of 10 °C min⁻¹ at nitrogen atmosphere with the gas flow 30 mL min⁻¹. Products in an amount of 5 mg were placed in an open aluminum pan (40 μl) and heated up to 170 °C, cooled to room temperature, and then heated again to 170 °C in order to remove their thermal history. The melting temperature (T_m), crystallization temperature (T_c), and heat of fusion (ΔH_f) values were obtained for the samples formerly melted and recrystallized, which then were heated up to 170 °C. The percentage crystallinity degree was calculated using the equation: $X_c = \Delta H_f \times (100/290)$ [15].

The successive self-nucleation and annealing (SSA) experiments were conducted by using a DSC1 Mettler Toledo instrument at nitrogen atmosphere with the gas flow

of 30 mL min⁻¹. The samples were heated up to 170 °C and maintained at this level for 20 min, and then they were cooled down to 0 °C at the rate of 5 °C min⁻¹. The heating–annealing–cooling cycles were repeated for temperatures from 140 to 67 °C at 3 °C intervals [16, 17].

The thickness values for various lamellae can be calculated from the Gibbs–Thomson equation [18]:

$$T_m = T_m^0 \left(\frac{1 - 2\sigma_e}{\Delta H_f \cdot L_{GT}} \right)$$

The lamellar thickness L_{GT} was determined from the peak of each lamellar thickness distribution. The following parametric values were used in calculations [19–21]: T_m^0—equilibrium melting temperature of a perfect crystal is 145.5 °C, ΔH_f—heat of fusion per unit volume for a perfect crystal is 290 J cm⁻³, and σ_e—crystallite specific surface free energy is 90 mJ m⁻².

In turn, the DI values can be obtained through calculation of the ratio of the melting enthalpy (ΔH_m) of each peak to the melting enthalpy (ΔH_m^{max}) of the maximum peak in the SSA curves of the copolymer.

Results and discussion

Melting and crystallization behavior of E/POSS copolymers synthesized by complexes bearing phenoxy-imine or salen ligands

In our previous work [3–5], it was found that ethylene/multi-alkenylsilsesquioxane copolymers synthesized over post-metallocene catalytic systems were characterized by higher POSS incorporation level, as well as higher molecular weight and broad molecular dispersion in comparison with corresponding E/POSS copolymers obtained by *ansa*-metallocene. In addition, the content of specific unsaturation groups present in the E/POSS copolymers depended on the kind of post-metallocene complexes used in polymerization process, what was confirmed by FT-IR analysis. Differences in the structure of E/POSS copolymers obtained using bis(phenoxy-imine) Ti, Zr, V, or V salen-type complexes significantly affected their thermal properties.

In this study, we investigated the influence of composition of E/POSS copolymers on their melting and crystallization behavior. Selected ethylene copolymers with POSS-6-2 or POSS-10-3 copolymers synthesized over bis(phenoxy-imine) Ti, Zr, V, and V salen-type catalysts were evaluated by differential scanning calorimetry (DSC). The values of the crystallinity degree (X_c), onset, peak, and endset melting temperatures (T_{mo}, T_{mp}, and T_{me}, respectively), and onset, peak, and endset crystallization temperatures (T_{co}, T_{cp}, and T_c, respectively) for neat polyethylenes and for E/POSS copolymers are presented in Table 1.

The melting temperatures (T_{mp}) for ethylene/POSS copolymers in most cases were lower than that for neat PE (Table 1). The values of T_{mp} were found generally decreased with the increase of POSS content in copolymer. Noteworthy is that E/POSS copolymers synthesized by bis(phenoxy-imine) Ti and Zr complexes with low POSS content were characterized by higher T_{mp} values in comparison with this value for PE (Table 1, items 1, 2, 4, 6, 7, and 9).

It was found that the incorporation of POSS comonomer into the polymer chain resulted in narrowing of endothermal peaks, what could suggest the homogeneity of E/POSS copolymers (Table 1).

It should be noted that crystallinity degrees (X_c) of E/POSS copolymers generally decreased with increasing POSS content in the polymer chain regardless of the kind of POSS comonomer used (Table 1), what is associated with the irregular order of macromolecules after incorporation of POSS units.

Table 1 Thermal properties of PE and E/POSS copolymers synthesized over post-metallocene complexes

Entry	Cat	(Co)polymers	X_c/%	Melting temperature[c]/°C			Crystallization temperature[c]/°C			ΔT/°C	$t_{1/2}$/min	G/min^{-1}
				T_{mo}	T_{mp}	T_{me}	T_{co}	T_{cp}	T_{ce}			
1	FI-TiH[e,f]	PE	50.8	125.6	137.4	143.0	123.1	116.6	105.1	18.0	1.67	0.60
2[a]		E/POSS-6-2*	52.8	125.8	136.5	142.3	123.4	117.6	106.8	16.6	1.25	0.80
3[b]			52.5	124.8	137.3	143.3	123.1	116.6	104.4	18.7	1.42	0.70
4[a]		E/POSS-10-3	50.5	123.7	137.1	144.1	122.8	116.9	104.6	18.2	1.63	0.61
5[b]			45.1	124.0	138.1	141.2	122.3	116.2	105.1	17.2	1.53	0.65
6	FI-ZrH[e]	PE	62.7	123.1	137.9	143.7	122.7	115.7	103.7	19.0	1.70	0.59
7[a]		E/POSS-6-2*	69.6	123.6	137.7	143.2	122.8	116.9	105.5	17.3	1.32	0.76
8[b]			59.6	123.9	136.8	142.5	122.8	117.7	107.2	15.6	1.25	0.80
9[a]		E/POSS-10-3	68.5	125.5	136.8	142.6	123.2	116.8	105.3	17.9	1.32	0.76
10[b]			60.6	123.4	135.6	140.4	123.1	117.2	107.4	15.7	1.33	0.75
11	FI-VBu[d]	PE	58.3	125.6	137.4	143.1	121.9	116.3	107.6	14.3	1.53	0.65
12[a]		E/POSS-6-2	53.0	124.3	135.6	138.4	125.5	118.4	111.4	14.1	2.50	0.40
13[b]			52.8	120.4	131.0	137.9	125.8	116.7	106.1	19.7	2.72	0.37
14[a]		E/POSS-10-3	54.5	124.8	136.0	141.3	126.5	118.5	107.6	18.9	1.93	0.52
15[b]			57.8	124.8	133.6	137.9	125.1	118.8	109.9	15.2	1.62	0.62
16	Sal-V[d]	PE	57.6	126.4	136.6	141.9	122.1	116.8	109.2	12.9	1.42	0.70
17[a]		E/POSS-6-2	54.7	125.1	133.2	139.2	124.8	119.0	110.5	14.3	2.32	0.43
18[b]			51.2	123.0	133.0	136.1	125.2	117.6	104.2	21.0	2.57	0.39
19[a]		E/POSS-10-3	52.9	123.9	129.5	136.9	125.3	115.3	111.1	14.2	2.38	0.42
20[b]			50.5	123.8	133.1	138.9	123.6	118.2	105.8	17.8	2.60	0.39

[POSS]: [a]1.67×10^{-3} and [b]6.67×10^{-3} mol dm^{-3}, data were obtained by [c]DSC, p_e = [d]0.2 and [e]0.5 MPa, T_r = [f]30 °C, 50 °C, t_r = 30 min. * [3]

In case of E/POSS copolymers obtained by FI-TiH and FI-ZrH catalysts, the peak crystallization temperature values (T_{cp}) were generally shifted toward higher temperatures in comparison with neat PE and increased with increasing content of POSS in copolymer, what indicated that the POSS units effectively accelerated the crystallization process (Table 1, items 1–10).

The changes of T_{cp} values for E/POSS copolymers synthesized by FI-VBu and Sal-V catalyst were unsystematic (Table 1, items 11–20). The T_{co} and T_{ce} values of copolymers obtained by post-metallocene vanadium complexes generally were higher in comparison with neat polyethylene, regardless of kind of POSS used. These results suggested that the crystallization process of those copolymers started early and ran faster than for neat PE (Fig. 3, Table 1, items 11–20).

In order to better understand the influence of POSS units on the crystallization process of E/POSS copolymers, the relative crystallinity of polymer X as a function of time was determined. In addition, we calculate $t_{1/2}$ and the growth rate (G) which is the reciprocal of the crystallization half time $G = (t_{1/2})^{-1}$. The crystallization half time ($t_{1/2}$) is one of the most interesting and important parameters in the investigation of crystallization kinetics. It is defined as the time required to reach a relative crystallinity of 50%. The $t_{1/2}$ can

be calculated from equation. X_t and $X_{t\infty}$ are the relative crystallinity at specific time and infinite time, respectively.

$$X = \frac{X_t}{X_{t_\infty}}$$

In turn, the reciprocal of $t_{1/2}$ determines the crystallization rate. In Table 1, are shown the values of $t_{1/2}$ and G for all of the obtained polymeric products. It should be noted that the ethylene copolymers with multi-alkenylsilsesquioxanes synthesized by FI-TiH and especially FI-ZrH complexes were characterized by higher the crystallization rate in comparison with neat polyethylene (Table 1, items 1–10). These results confirmed the influence of POSS derivatives on the crystallization rate of copolymers as a nucleating agent.

Thermal stability of E/POSS copolymers

The structure of ethylene copolymers with multi-alkenyl-silsesquioxane comonomers should also affect the thermal stability of such materials. We found here that the linear copolymers of ethylene with POSS-6-2 and E/POSS-10-3 obtained under 0.5 MPa were characterized by a significantly higher thermal stability than polyethylene as evidenced by higher values of T_5, T_{30}, and T_{max} (Table 2, items 1–10).
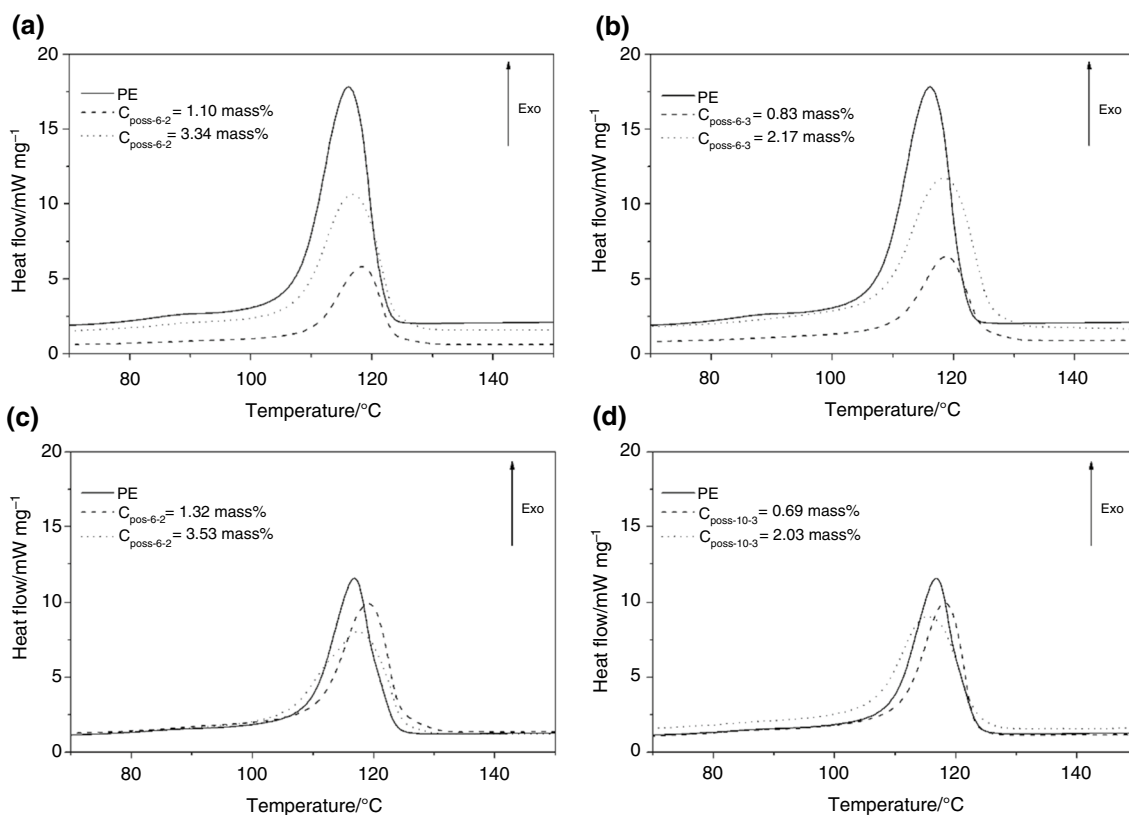
Fig. 3 The DSC curves of polyethylene, E/POSS-6-2, and E/POSS-10-3 copolymers obtained by FI-VBu (**a**, **b**) and Sal-V (**c**, **d**)

Table 2 Physicochemical properties for ethylene/POSS copolymers obtained over bis(phenoxy-imine) Ti, Zr, V and V salen-type complexes

Item	Catalyst	(Co)polymers	p_e/MPa	C_{POSS}*/mass%	T_5/°C	T_{30}/°C	T_{max}/°C	$M_w \times 10^{-3}$*/g mol^{-1}	M_w*/M_n	Unsaturation groups*	
										$A_{908/2020}$	$A_{800/2020}$
1	FI-TiH	PE	0.5	0	397.0	457.0	468.1	1050	12.7	0.231	0
2[a]		E/POSS-6-2		4.01	363.3	450.5	471.4	946	4.1	0.321	0.259
3[b]				7.57	379.6	452.6	472.6	558	3.6	0.534	0.520
4[a]		E/POSS-10-3		1.03	392.6	447.4	470.9	–	–	0.577	0.196
5[b]				1.75	376.8	448.5	462.0	–	–	0.697	0.428
6	FI-ZrH	PE		0	300.9	426.8	458.4	1135	7.1	0.298	0
7[a]		E/POSS-6-2		1.48	378.1	436.8	461.8	358	8.3	0.668	0.334
8[b]				5.09	386.3	435.9	460.3	198	5.6	1.180	1.764
9[a]		E/POSS-10-3		1.03	387.0	432.4	468.1	572	11.6	0.902	0.196
10[b]				1.22	347.0	433.3	468.6	–	–	1.037	0.428
11	FI-VBu	PE	0.2	0	347.5	435.7	468.2	348	1.5	0.251	0
12[b]		E/POSS-6-2		3.34	310.8	438.9	463.9	180	3.8	0.407	0.043
13[b]		E/POSS-10-3		2.17	313.8	429.2	458.7	228	4.1	0.557	0.918
14	Sal-V	PE		0	360.4	425.0	461.7	364	1.8	0.216	0
15[b]		E/POSS-6-2		3.53	304.7	432.5	463.2	577	1.6	0.472	0.923
16[b]		E/POSS-10-3		2.03	316.5	430.7	454.9	164	5.7	0.505	0.722

Concentration of POSS in reaction feed: [a] 1.67×10^{-3} mol dm^{-3}, [b] 6.67×10^{-3} mol dm^{-3}, reaction time: 30 min. The measurement was carried out at a heating rate of 10 °C min^{-1} from 25 to 500 °C in air. *[4, 5]

However, the FI-ZrH complexes allowed to obtain (co) polymers characterized by the highest thermal stability out of all polymeric products synthesized by post-metallocene catalysts studied (Table 2, items 1–10). Moreover, thermal stability of ethylene copolymers with di-alkenylsilsesqui-oxanes (POSS-6-2) improved markedly with the increasing content of POSS comonomer regardless of the type of catalyst (Table 2, items 2 and 3, and 7 and 8).

E/POSS copolymers obtained by the bis(phenoxy-imine) zirconium and titanium catalytic systems were characterized by higher thermal stability than monoalkenyl- and monoalkenyl(siloxy)silsesquioxanes obtained over *rac*-Et(Ind)$_2$ZrCl$_2$ [1]. Noteworthy is that the values of T_5 and T_{30} of the copolymers E/POSS obtained in the presence of post-metallocene catalyst were usually lower than for neat polyethylene, regardless of the kind and share of POSS comonomer used. However, the FI-TiH and FI-ZrH complexes allowed to obtain (co)polymers characterized by the highest thermal stability out of all polymeric products synthesized by post-metallocene catalysts studied (Table 2, items 1–10).

In case of copolymers produced by the FI-ZrH/MAO catalytic system, a significant increase was found in T_5 parameter, even by 46.1–86.1 °C, depending on the kind and content of multi-alkenyl POSS in copolymer, in comparison with neat polyethylene (Table 2, items 6–10, Fig. 4a, b). It could thus be concluded that incorporation of POSS units increased the initial temperature of thermal decomposition

of copolymer materials. However, changes in T_{30} parameter were less significant (Table 2, items 6–10).

The high thermal stability of E/POSS copolymers could be explained by possible formation of a ceramic layer on the surface of the materials during thermal degradation of POSS units. These phenomena could be explained by limitation of the heat flux to the sample, oxygen diffusion toward the copolymers, and the volatile degradation gases from the sample [15].

Meanwhile, the increase in POSS-10-3 content resulted in a significant reduction in the thermal stability of its copolymer with ethylene. It should be noted that POSS-10-3 comonomer contained incompletely condensed silicon–oxygen cage T$_4$D$_3$ clearly more susceptible to degradation in contrast to POSS-6-2 with fully condensed cage T$_8$.

In turn, post-metallocene vanadium complexes (bearing phenoxy-imine and salen-type ligands) used for ethylene copolymerization with POSS performed under $p_e = 0.2$ MPa resulted in obtaining copolymers characterized by the lowest values of the characteristic parameters (Table 2, items 11–16). These copolymers proved to be less thermally stable than neat polyethylene and other samples of E/POSS copolymers studied irrespective of POSS comonomer type.

It should be noted that significant differences in thermal stability of obtained E/POSS copolymers could be explained by different contents of POSS units in the copolymer macromolecules, the M_w values of E/POSS copolymers, and also by specific POSS–POSS interactions and
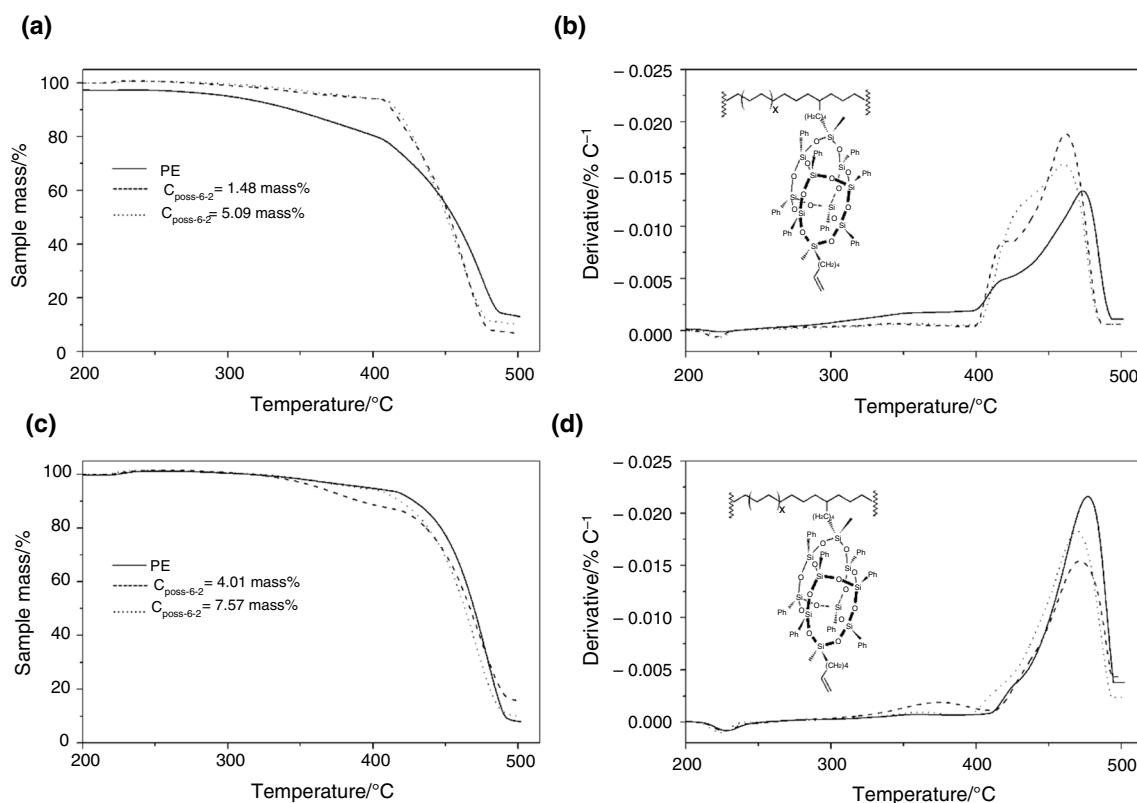
Fig. 4 TGA and DTA curves of polyethylene and E/POSS-6-2 copolymers synthesized by FI-ZrH (**a**, **b**) and FI-TiH (**c**, **d**) complexes

POSS–polyethylene sequences, which was associated with different distributions of POSS units in the copolymer materials (Table 2). However, noteworthy is that E/POSS copolymers synthesized by V salen-type complex, despite the fact that they contained a similar POSS incorporation level ($C_{POSS-10-3}$ = 2.03 mass% and $C_{POSS-6-2}$ = 3.53 mass%, respectively) and content of unsaturation groups (vinyl end group 0.505 and 0.472, trisubstituted vinylene 0.722 and 0.923, respectively), were characterized by different thermal stability (Table 2, items 15 and 16). The T_5 value of E/POSS-10-3 was higher by 15 °C than this TGA parameter for E/POSS-6-2 copolymer, although the former contained a not fully condensed cage. Despite a similar way of incorporation of POSS comonomers (as a side group of the main chain), the thermal stability of E/POSS copolymers differed considerably and was dependent on the type of catalyst used.

In order to understand the effect of POSS incorporation into the polymer chain as a side group by different complexes bearing phenoxy-imine and salen ligands on thermal stability, unsaturation group analysis was performed [5]. The content of specific unsaturation groups in E/POSS copolymers was found to influence significantly on the thermal stability of obtained polymeric products. It should be noted that the C=C bonds in the main chain due to their high reactivity toward oxygen resulted in the degradation process of polymeric products. The content of C=C bonds (vinyl and trisubstituted vinylene groups) occurring in E/POSS copolymers increased, depending on the type of catalyst used as follows: FI-TiH > FI-ZrH > FI-VBu ~ Sal-V (Table 2). These results were in line with the thermal stability evaluated by the study of thermogravimetric analysis (Table 2). Interesting is that the content of trisubstituted vinylene groups (internal unsaturations) present in E/POSS copolymers obtained by both vanadium complexes was generally much higher in comparison with the content of specific unsaturation groups in copolymers obtained using bis(phenoxy-imine) titanium and zirconium complexes (Table 2).
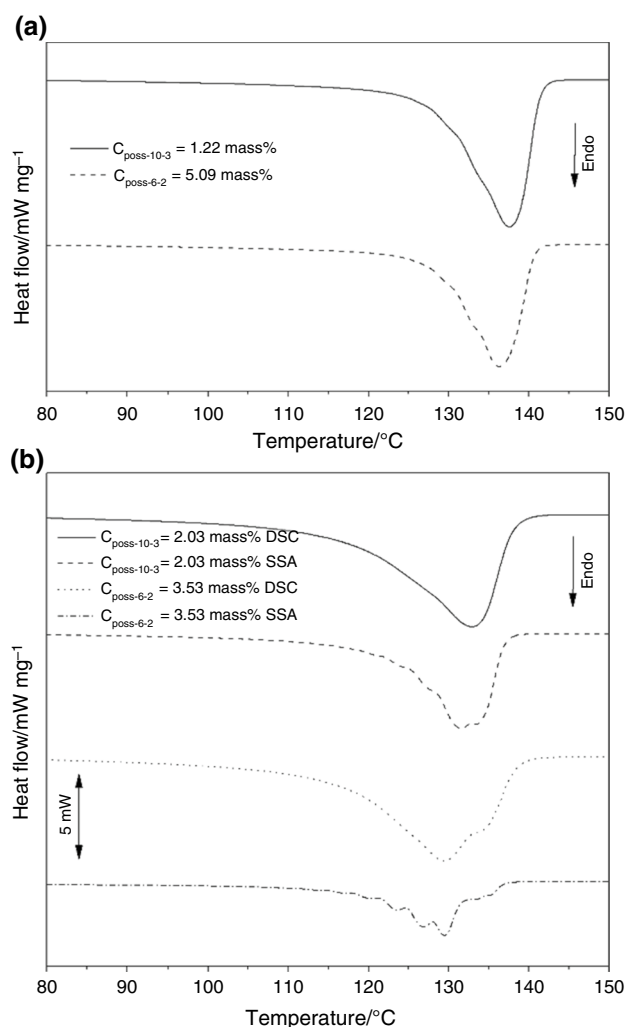
Thermal stability and heterogeneity of E/POSS copolymers

In order to explain the differences in thermal properties for E/POSS copolymers synthesized by bis(phenoxy-imine) zirconium and V salen-type complexes with a similar incorporation level and content of unsaturation groups, SSA analysis was performed. Already in the above described studies of copolymer crystallization were found that the increasing content of POSS in copolymer chain resulted in broadening of the exothermic peak corresponding to the polymer crystallization process (Fig. 3, Table 1, items 11–20) in

contrast to products obtained by FI-TiH and FI-ZrH catalysts (Table 1, items 1–10). It could be thus concluded that copolymers obtained by post-metallocene vanadium catalysts (FI-VBu and Sal-V) were characterized by more heterogeneous compositions (Table 1, items 11–20).

SSA analysis confirmed that the ethylene copolymers with di- or tri-alkenylsilsesquioxane obtained by FI-ZrH contained relatively homogeneous compositions independently of the comonomer incorporation level (Fig. 5 a).

In turn, the copolymers obtained by V salen-type complex were characterized by multiple melting peaks which were observed in the SSA curves of copolymer samples, although they were characterized by a comparable and even smaller incorporation degree of POSS units than copolymers obtained by FI-ZrH (Fig. 5 b). Moreover, there was also observed a difference in the number of peaks, their location, and intensity (Fig. 5).

The V salen-type/Et_2AlCl catalytic system produced E/POSS copolymers with seven and eleven thermal fractionation melting peaks in the range 104–135 °C and 102–136 °C for E/POSS-10-3 and E/POSS-6-2, respectively (Fig. 5). Those results indicated that the composition of E/POSS-6-2 copolymer (C_{POSS} = 3.53 mass%) was much more heterogeneous in comparison with hybrid materials with a slightly lower POSS-10-3 content (C_{POSS} = 2.03 mass%). For evaluation of the heterogeneity of hybrid materials, the concept of dispersity index (DI) was very often used [22–24] (Fig. 6).

The DI values calculated for each separated peak were different, although greater dissimilarity was observed for E/POSS-6-2 copolymer, what is associated with the heterogeneity of comonomer distribution along the main chain [22]. The DI values clearly indicated that the E/POSS-6-2 copolymer was more heterogeneous in comparison with E/POSS-10-3, while both were obtained by vanadium catalyst. It should be explained that ethylene/POSS-6-2 copolymers contained shorter ethylene sequence lengths which recrystallized in shorter lamellar; therefore, many additional peaks appeared in the SSA curves due to the segregation of the crystallizable sequence lengths.

The relative share of lamellas with different thicknesses was determined by the ΔH_m values for each peak in the SSA curves (Fig. 6). It should be noted that neat E/POSS-10-3 samples had narrow distribution of lamellar thickness in the range from 7.5 to 30.7 nm and the highest fraction

Fig. 5 Comparison of SSA curves of ethylene copolymers with POSS-6-2 or POSS-10-3 comonomer obtained by complex: bis(phenoxy-imine) zirconium (**a**) or V salen-type (**b**)
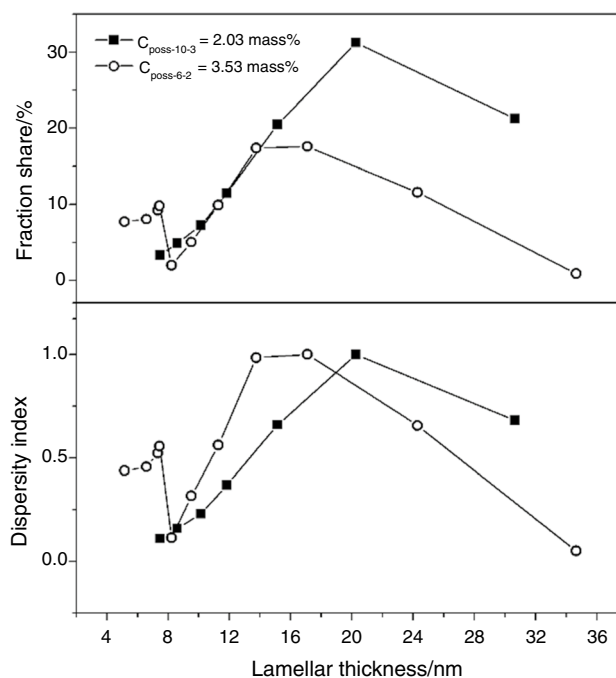
Fig. 6 Comparison of lamellar thickness with different DI values and fraction share for E/POSS copolymers synthesized over V salen-type complex

occurred at lamellar thicknesses (l_n) around 20.3 nm in contrast to E/POSS-6-2 copolymers which contained the lamellar size from 5.2 to 34.6 nm with the highest fraction at $l_n = 17.1$ nm. In addition, the V salen-type complex allowed to obtain the E/POSS-6-2 copolymers with larger lamellar size in contrast to *rac*-Et(Ind)$_2$ZrCl$_2$/MAO catalytic system ($l_n = 4.6–16.9$ nm) [3].

It should be noted that fraction was characterized by the lowest lamellar thicknesses, what could be assigned to self-aggregation of POSS. This phenomenon was confirmed by our previous findings [7].

The more heterogeneous composition of E/POSS-6-2 copolymers obtained by V-catalysts resulted in their lower thermal stability compared to E/POSS-10-3 counterparts, although the latter contained less stable incompletely condensed silicon–oxygen cage. These results were in line with the thermal stability evaluated by TGA method (Table 2, items 12 and 13 as well as 15 and 16).

Conclusions

Thermal properties of ethylene copolymers with di- and tri-alkenylsilsesquioxanes synthesized by bis(phenoxy-imine) Ti, Zr, V, and V salen-type complexes were investigated in detail by DSC and TGA techniques. All these copolymers contained silsesquioxane comonomers only as side groups of the main chain, regardless of comonomer functionality. The kind and content of multi-alkenylsilsesquioxane units incorporated into the polymer chain, as well as the structure of macromolecules, significantly influenced on thermal stability of obtained copolymers.

The peak melting temperature (T_{mp}) of copolymers obtained by bis(phenoxy-imine) Ti, Zr, V, and V salen-type complexes generally decreased with increasing POSS content. However, lower POSS incorporation level in copolymers synthesized by bis(phenoxy-imine) titanium and zirconium complexes caused a significant shift of T_{mp} values toward higher temperature than polyethylene. These results were associated with a strong interaction between POSS units and polyethylene sequences.

The crystallinity degree (X_c) of copolymers obtained over bis(phenoxy-imine) Ti and Zr catalysts was generally higher than for neat polyethylene in contrast to the copolymers synthesized over both vanadium catalysts that showed less crystallinity compared to polyethylene.

The E/POSS copolymers synthesized by FI-TiH and FI-ZrH complexes were characterized by higher crystallization rate in comparison with neat polyethylene, what confirmed the influence of POSS derivatives on the crystallization rate of copolymers as a nucleating agent.

Thermal stability of E/POSS copolymers generally increased with increasing content of silsesquioxane comonomers. However, this feature was dependent not only on the kind and content of silsesquioxane but also on POSS distribution in main copolymeric chains and the content of specific unsaturation groups. Thermal stability of E/POSS copolymers decreased with increasing content of trisubstituted vinylene groups, regardless of the kind of organometallic complexes used.

The heterogeneity of macromolecules was found to significantly influence on thermal stability of E/POSS copolymers. E/POSS-6-2 and E/POSS-10-3 copolymers obtained by V salen-type complex despite a similar POSS incorporation level and content of unsaturation groups markedly varied in heterogeneity. E/POSS-6-2 copolymer was found to be more heterogeneous than E/POSS-10-3 copolymer, what is related to lower thermal stability of this material.

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