A versatile one-pot strategy for the synthesis of organosilicon-functionalized polyolefins

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Abstract

We report a facile *one-pot* catalytic strategy for the synthesis of organosilicon-functionalized polyolefins — a long-standing challenge in polymer science. This streamlined approach integrates the hydrosilylation of polybutadiene with subsequent hydrogenation of the resulting silyl-functionalized intermediates, all under unified reaction conditions. The developed protocol exhibits exceptional functional group tolerance, enabling the incorporation of a broad spectrum of organic moieties that are typically incompatible with conventional copolymerization or post-polymerization methods. Remarkably, the degree of functionalization can be precisely tuned simply by adjusting the stoichiometric ratio of the organosilicon reagent to vinyl groups. This level of control, versatility, and simplicity has not been demonstrated previously in the functionalization of polyolefins. The methodology paves the way for the tailor-made design of advanced silicon-containing polyolefins

with attractive functional groups, opening new avenues for applications in materials science, surface engineering, and beyond.

Introduction

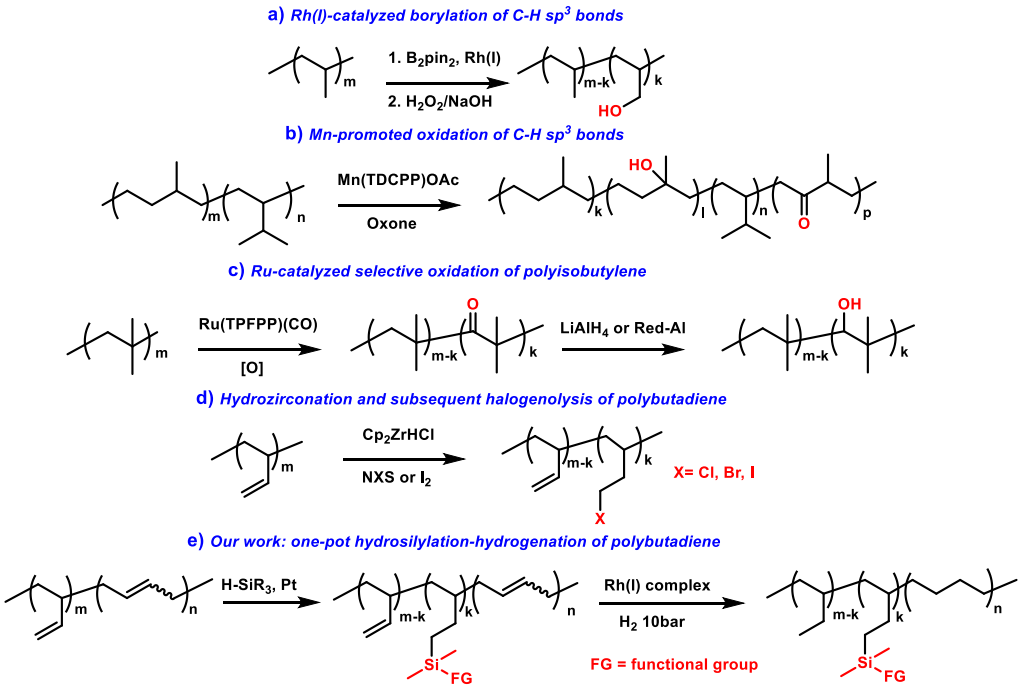
Polymeric materials, due to the ability to precisely adjust their properties to specific applications, have undoubtedly become indispensable elements of our everyday life [1-2]. Among synthetic polymers, polyolefins are one of the most important groups. The massive global production of over 400 million tons per year of more than 300 different grades of polyolefins reveals their significance in the world economy. This is largely due to their outstanding properties including high physicochemical resistance, ease of processability, and production from inexpensive feedstocks. Therefore, polyolefins have found a wide range of applications in almost every field of daily life [3-5]. However, polyolefins exhibit poor compatibility with nitrogen- or oxygen-containing compounds and inorganic materials, as a consequence of their hydrophobicity caused by the lack of functional groups. This limits their suitability for applications requiring good surface adhesion, toughness, solvent resistance, or miscibility with polar group-containing polymers, and many others [6-7]. These drawbacks can be overcome by the incorporation of even low amounts of functional groups into the hydrocarbon backbones, which may significantly expand the number of potential applications, making these new materials more versatile and valuable products. Nevertheless, developing a universal and straightforward methodology for the synthesis of functional polyolefins remains a major challenge [4, 7-8]. There are two synthetic pathways leading to functional polyolefins: direct copolymerization of an olefin with a functional comonomer [5, 9-11] and the post-polymerization modification [4, 6-8]. The copolymerization approach seems to be more straightforward and economically favorable. However, not all functionalities can be easily incorporated through a copolymerization reaction, as organic functional groups may poison the metal center, which is called “the polar monomer problem”. Even though some particular types of catalysts are tolerant to the presence of organic groups, the number of monomers that undergo copolymerization is strictly limited for each catalytic system. Furthermore, each reaction system requires an individual approach and careful selection of the catalyst, as well as precise optimization of the reaction conditions.

Consequently, the direct transfer of an optimized copolymerization methodology for one monomer to another remains a significant challenge or is not even possible [4-7, 9-11]. In recent years, the post-polymerization modification has gained increasing attention. This process relies on the chemical functionalization of well-defined polymers [4, 6-8]. Since the most common polyolefins such as polyethylene or polypropylene contain only single carbon-carbon and carbon-hydrogen bonds, any functionalization requires the cleavage of these units which remains challenging due to high bond dissociation energies [4, 6-8]. Nevertheless, a few strategies providing direct activation of $C(sp^3)$-H units have been developed. For example, Hillmyer, Hartwig and co-workers developed a protocol based on Rh(I)-catalyzed borylation of polyolefins (PP, PEE, LLDPE) using B_2pin_2, followed by oxidation of the resulting alkyl boronate esters, which resulted in the formation of hydroxyl-containing [13-15] or polar group-bearing polyolefins [15] (**Scheme 1a**). Hillmyer's group also reported direct oxyfunctionalization of polyethylene-alt-propylene (PEP) in the presence of [Mn(TDCPP)OAc] as a catalyst and oxone as an oxidizing agent in a biphasic reaction system (**Scheme 1b**). This methodology also enabled the incorporation of hydroxyl groups to tertiary carbon atoms and ketone functionalities but this required long reaction time [16]. Recently, Hartwig and co-workers reported two independent methodologies leading to functionalized polyolefins. The first one involves the use of nickel complex $[Ni(Me_4Phen)_3](BPh_4)_2]$ and *m*-CPBA as an oxidant enabling the hydroxylation of a wide range of polyethylenes of various microstructures and molar masses. However, the selectivity of the process was poor, which was manifested by the incorporation of chlorine from the solvent into the polymer chain and the formation of ester units *via* Baeyer-Villiger oxidation [17]. The inconveniences were overcome by the application of ruthenium-porphyrin catalyst [Ru(TPFPP)(CO)] and 2,6-dichloropyridine *N*-oxide as an oxidizing agent, which ensured the selective formation of hydroxyl- and carbonyl-containing polyethylenes (**Scheme 1c**) [18]. This methodology has also been successfully applied in the oxyfunctionalziation of polyisobutene (PIB) [19]. Unfortunately, the aforementioned reactions are highly sophisticated, require the use of high metal loading and enable the introduction of only one type of functional group. Therefore, they cannot be considered as universal synthetic tools. Taking the above into account, the development of a

versatile, functional group-tolerant methodology for the synthesis of functionalized polyolefins is still highly desired and is also one of the most important challenges facing synthetic polymer chemists today. Since the C(sp^3)-H functionalization and copolymerization processes have significant limitations, novel approaches and development of innovative synthetic strategies are essential to overcome these obstacles. We postulate that polybutadiene (**PB**) is an excellent precursor for the synthesis of functionalized polyolefins due to its low cost resulting from large-scale industrial production and high content of easily modifiable C=C bonds, which are reactive in a wide range of various catalytic and stoichiometric reactions [21-27]. Moreover, the microstructure and molar mass of **PB** can be precisely controlled through anionic polymerization [28-29]. Therefore, also in this area, several alternative strategies leading to organofunctionalized polyolefins based on the transformations of C=C units present in **PB** have been described in the literature. For example, **PB** can be easily functionalized *via* thiol addition, but it is very difficult to control the reaction due to its radical mechanism. This usually also leads to the formation of many side products, including the cyclization of neighboring vinyl groups [22-23]. Barner-Kowollik and co-workers reported the synthesis of polyolefins equipped with bromine atoms and alkoxyether groups *via* an electrophilic functionalization cascade of **PB** containing predominantly 1,4-addition units [24]. In contrast, Tang's group developed a novel protocol leading to halogenated polyhydrocarbons through the addition of Schwartz's reagent (Cp_2ZrHCl), followed by the halogenolysis of the hydrozirconated macromolecular intermediate (**Scheme 1d**). Nonetheless, the efficiency of halogen incorporation into polymer chains decreases significantly from iodine to chlorine [25]. Recently, we reported the synthesis of functionalized polymeric precursors bearing high content of side H-Si [26] and HC≡C-Si [27] through *one-pot* hydrosilylation of **PB** with chlorodimethylsilane, followed by Red-Al®-promoted Si-Cl reduction, or a Grignard reaction, respectively. The synthesized precursors were successfully modified with a wide gamut of functional modifiers *via* transition metal-catalyzed reactions. Unfortunately, Pt-mediated hydrosilylation of **PB** enabled the functionalization of only 1,2-vinyl groups. Therefore, both the polymeric precursors and the final products still contained unsaturated C=C units in the backbone [26-27]. Despite this, the synthesis of functionalized

polyolefins through catalytic modification of polybutadienes seems to be a much more functional group-tolerant process compared to polymerization reaction. Unfortunately, its biggest drawback is that 1,4-addition moieties show lower reactivity than 1,2-vinyl ones. Hence, the modification of all unsaturated units present in the polybutadiene chain with simultaneous precise selectivity control still remains a challenge.

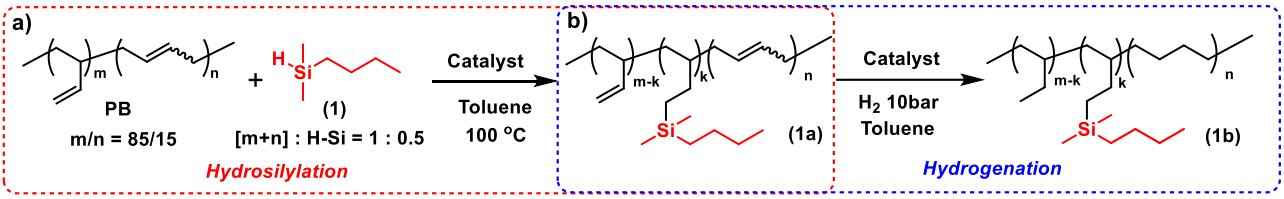
In this work, we present a simple and very efficient synthetic protocol leading to functionalized, unique polyolefins obtained on the basis of a sequence of two consecutive reactions: hydrosilylation of polybutadiene and subsequent hydrogenation of the functionalized polymer product (**Scheme 1e**). The developed approach, due to its high versatility, enables the incorporation of a wide range of functional groups into polymer chains with precise control of the functionalization degree. Moreover, it is particularly worth emphasizing that the presented methodology is tolerant towards the various organic moieties introduced into the **PB** structure during catalytic functionalization and its subsequent hydrogenation. It also provides direct access to novel, previously undescribed materials equipped with desired functional groups and reactivity, which can be further exploited in tailored applications. To the best of our knowledge on this subject, such polyolefins are not accessible *via* the aforementioned polymerization, copolymerization, and post-polymerization processes.



Scheme 1. Recent advances in the post-polymerization synthesis of functionalized polyolefins.

Results and discussion

Considering the specific chemical properties of polyolefins (polyethylene, polypropylene) resulting from the presence of saturated hydrocarbon chains and the application potential of organofunctional polymers of this type, we undertook work aimed at developing a versatile methodology leading to novel functionalized polymeric materials in the simplest and the most efficient way. Since the hydrosilylation reaction itself and the known and commonly used catalytic systems have an extraordinary tolerance to a wide range of functional groups, it is commonly used in the functionalization of molecular compounds and macromolecular systems both in laboratory practice and in large-scale industrial processes (production of silane coupling agents, functionalization of polysiloxanes, cross-linking of silicone rubbers) [30-34]. Therefore, in this work, hydrosilylation was also selected as the main synthetic tool, enabling the introduction of organic and organometallic functional groups into hydrocarbon chains. As a starting polymer, we chose commercially available polybutadiene containing ~85 % of 1,2-vinyl and 15 % of 1,4-cis/trans moieties. The initial studies relied on the hydrosilylation of **PB** with $HSiBuMe_2$ (**1**) in the presence of Pt and Rh-based complexes (**Scheme 2a**), whose catalytic activity is well known [30,33,35-37]. Hydrosilylation of **PB** offers to control the number of functional groups attached to the main chain by adjusting the stoichiometry between the vinyl groups and silane, which means a maximum 85 % of the moieties in the case of the selected starting material. For comparison, modification of polyolefins through C(sp^3)-H activation leads to the functionalization of up to several mol% [6-8, 13-19].



Scheme 2. *One-pot* synthesis of polyolefin through hydrosilylation and subsequent hydrogenation.

We therefore decided to use a precise amount of **1**, sufficient to functionalize 50 % of all unsaturated groups present in **PB**, which is significantly more than can be achieved through C(sp^3)-H activation approaches. The reactions were monitored using *real-time* FT-IR spectroscopy by observing the band

corresponding to the H-Si bond to find the most active catalysts for complete hydrosilane conversion. Exemplary FT-IR spectra are presented in **Figure 1**, and the results are summarized in **Table 1**. The model reaction showed that all the examined rhodium and platinum complexes turned out to be effective hydrosilylation promoters. However, Pt-based catalysts revealed significantly higher catalytic activity than Rh(I) complex (reaction profiles are provided in Supporting Information).

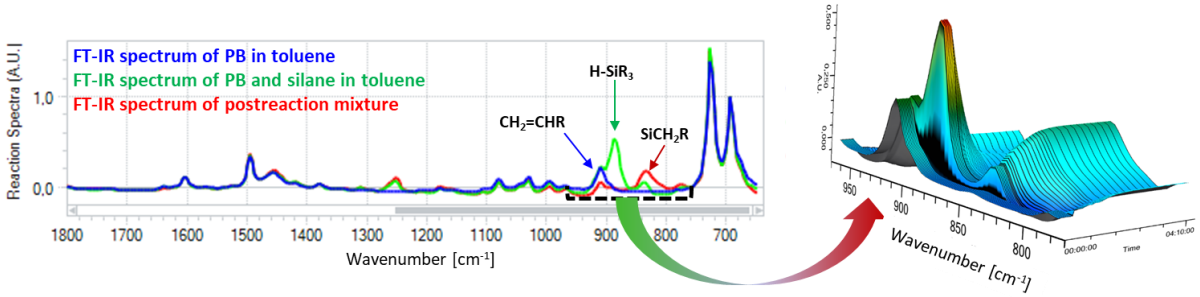


Figure 1. Exemplary FT-IR spectra of starting mixture (PB + **1** in toluene) and postreaction mixture.

The ^{1}H NMR spectrum recorded for **1a** confirmed the complete disappearance of the H-Si signal, partial conversion of the unsaturated groups, and formation of a characteristic signal originating from the formed $SiCH_2$ units, regardless of the catalyst used. It should be emphasized that only vinyl groups were functionalized *via* hydrosilylation, which is consistent with the literature data [26, 27, 33]. Moreover, the ^{29}Si NMR spectrum revealed a significant downfield shift of the peak corresponding to **1** (from -13.06 ppm to 2.95 ppm). Therefore, NMR analysis clearly confirmed the successful functionalization of **PB** with **1**. Furthermore, the GPC analysis showed that the Pt-catalyzed reactions had no influence on the polymer dispersity index (*Đ*) in contrast to the rhodium-promoted reaction, which was demonstrated by an increase in the *Đ* value from 1.44 to 2.29. This indicates that the Rh(I)-catalyzed hydrosilylation could be accompanied by side processes such as crosslinking or chain scission. On the other hand, H_2PtCl_6 enabled complete silane conversion in the shortest time. Therefore, Speier's catalyst was selected for further hydrosilylation reactions.

Table 1. The results of the PB hydrosilylation with **1**

Entry	Catalyst	Silane conv. [%]	Reaction time h:min	M_n [g × mol^{-1}]	*Đ*
1	H_2PtCl_6 in 2-propanol[a]	99	2:30	5430	1.46

2	$Pt_2(dvds)_3$[b]	99	4:20	5480	1.48
3	H_2PtCl_6 in 1-octanol/ 1-octanal[c]	99	3:40	5450	1.46
4	[{Rh(μ-Cl)(COD)}$_2$]	87	24:00	6320	2.29

[a]Speier's catalyst, [b]Karstedt's catalyst, [c]Lamoreaux catalyst

After successful hydrosilylation tests, the next stage of the planned synthetic pathway was hydrogenation. It should be mentioned that we recently reported systematic studies on the transition metal-catalyzed hydrogenation of nonfunctionalized synthetic rubbers [38]. We found that H_2PtCl_6 can promote very high hydrogenation yields, regardless of the type of **PB** microstructure and its molecular weight. Based on our previous findings, H_2PtCl_6 seemed to be the best choice for the hydrogenation reaction of partially-functionalized **PBs**. Thus, the post-hydrosilylation mixture containing **1a** was subsequently subjected to hydrogenation tests without any isolation procedure. The hydrogenation trials were carried out under mild conditions*, i.e.* 80 ºC and 10 bars of hydrogen (**Scheme 2b**). The previously established hydrogenation conditions were sufficient for the complete **PB** hydrogenation [38]. The results of the transition metal-catalyzed hydrogenation of **1a** are summarized in **Table 2**. Unfortunately, Pt catalysts did not show activity in the second step of the synthetic route. Therefore, we then decided to increase the Pt content in the reaction system to $5x10^{-4}$ Pt and 10^{-3} mol Pt per remaining C=C units. Nevertheless, in this case, H_2PtCl_6 was also found to be inactive in the hydrogenation of partially silylated rubber. The addition of the Lamoreaux catalyst also did not bring any positive effect. Considering the above, it seems that the presence of the incorporated organosilicon groups has a highly unfavorable effect on the hydrogenation process, which can be explained mainly by steric hindrance around the unsaturated units caused by the introduced side organosilicon groups. The second reason may be the lowered C=C moieties content responsible for the stabilization of the metal nanoparticles in the solution, while the scarcity of the former results in metal aggregation and reduced active area of such catalyst. Therefore, the partially functionalized **PB** exhibited a completely different reactivity in the hydrogenation reaction compared to the raw polybutadiene. In view of the literature data, Rh(I) complexes are commonly known as efficient hydrogenation catalysts. Consequently, we decided to employ [$RhCl(PPh_3)_3$] and [{Rh(μ-Cl)(COD)}$_2$], which have proven to be highly active hydrogenation promoters of polybutadiene

rubbers [38]. Our previous studies revealed that the introduction of additional PPh_3 equivalents into the reaction system is necessary to stabilize the complex in the homogeneous phase and promote the full conversion of unsaturated units. If there is no phosphine in the hydrogenation system, the heterogeneous metal particles precipitate. Surprisingly, the catalytic hydrogenation of the partially silylated rubber exhibited the opposite behavior. The presence of a phosphine ligand in the reaction system led to lower hydrogenation yields compared to the ligand-free processes (**Table 2, entries 4-10**). This indicates the higher efficiency of heterogeneously-driven hydrogenation over the homogeneous one. We postulate that the bulky organosilicon groups were responsible for the hindered coordination of the C=C units present in the modified polymer to the rhodium center. Moreover, $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ showed higher catalytic activity than commonly applied Wilkinson's complex, and ultimately enabled complete conversion of all unsaturated units present in **1a** structure (**Table 2**). This was confirmed by NMR (Fig. S7 in ESI) and FT-IR (Fig. S10 in ESI) analyses, as well as demonstrated by a high ***N*** factor value (**Table 2**). Considering the above, $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ was selected as most efficient a hydrogenation catalyst precursor for further experiments. Additionally, **Table 2** provides values of the α factor which describes the ratio of protons from the saturated CH_n units to all the protons in the main polymer chain. This parameter precisely demonstrates the actual degree of polymer saturation, even if hydrogenation has not been completed. The general formula is presented in **Figure 2**.

Table 2. The results of the **1a** hydrogenation

Entry	Catalyst	[M] : [C=C] mol : mol	Hydrogenation of 1,2-units [%]*	Hydrogenation of 1,4 units [%]*	Total hydrogenation [%]*	N^* [%]	α^* [%]
1	H_2PtCl_6	0.0002	-	-	-	48	77
2	H_2PtCl_6	0.0005	-	-	-	48	77
3	H_2PtCl_6	0.001	-	-	-	48	77
4	$RhCl(PPh_3)_3$ + 5eq PPh_3	0.0005	31	13	25	60	85
5	$RhCl(PPh_3)_3$ + 5eq PPh_3	0.001	42	15	34	65	86
6	$RhCl(PPh_3)_3$	0.001	53	50	52	75	90
7	$[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ + 5eq PPh_3	0.0005	31	16	29	61	85
8	$[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ + 5eq PPh_3	0.001	99	99	99	99	>99
9	$[\{Rh(\mu\text{-}Cl)(COD)\}_2]$	0.0005	50	30	44	70	89
10	$[\{Rh(\mu\text{-}Cl)(COD)\}_2]$	0.001	99	99	99	99	>99

* calculated on the basis of NMR integrals, N - Total conversion of the unsaturated units after second step, α – Total saturation of the main polymer chain.

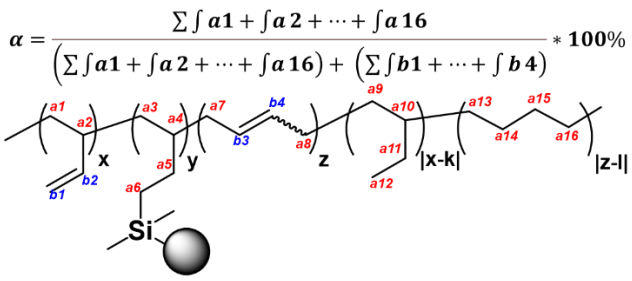
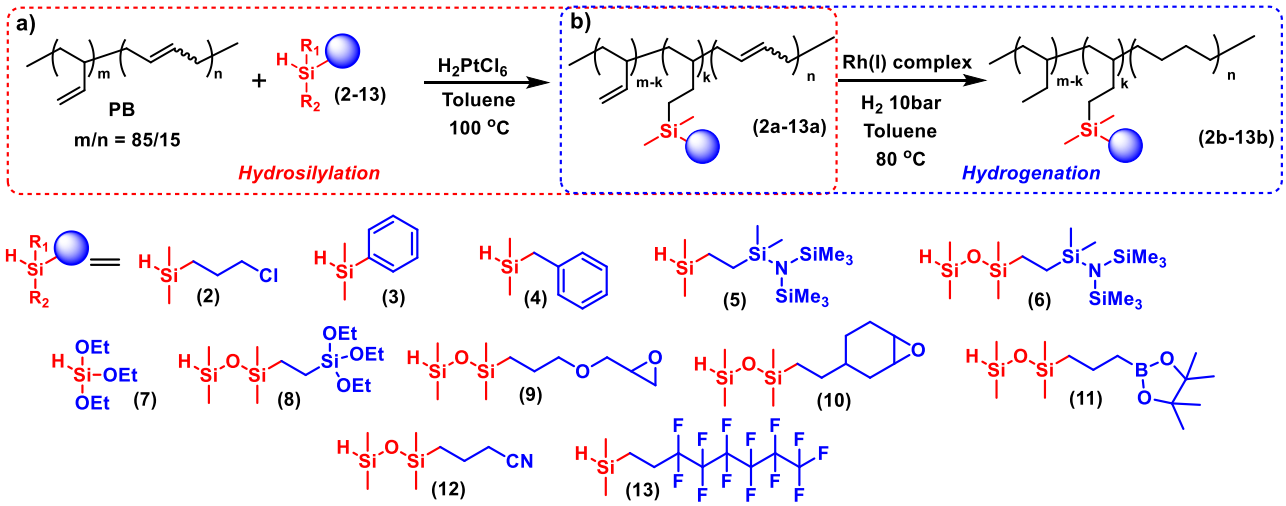


Figure 2. The structure of the product obtained through one-pot methodology and general formula for the α factor calculation.

Having the hydrogenation conditions established, the functionalization of **PB** was carried out using a wide range of organofunctional hydrosilanes and hydrosiloxanes (**Scheme 3**). The selected organosilicon modifiers contained key functional groups whose introduction into the polymer chain should significantly change the physicochemical properties of obtained macromolecular materials or enable their further transformations [39-42].



Scheme 3. *One-pot* synthesis of polyolefins through hydrosilylation of PB with functional silanes and subsequent hydrogenation.

Moreover, the high silicon atom content can also provide additional benefits such as flame-retardant properties and/or increased thermal resistance [43-44]. Hydrosilylations of **PB** with compounds **2-13** was carried out under the same conditions as in the case of the previously described model reaction. The results are summarized in **Table 3**. The data presented therein indicate that the type of functional group present in the modifier's structure has a significant effect on the hydrosilylation process.

However, the kinetic curves of the reaction course using *real-time* FT-IR spectroscopy revealed that despite the occurring structural effects, under the established conditions full conversion of the most tested organosilicon modifiers is possible towards their incorporation into the polymer chain within a relatively short time i.e. less than 10 hours for most compounds. However, a significantly lower reactivity in this process was observed for compounds **7** and **12**. The decreased reactivity of **12** can be attributed to the coordination properties of the nitrile group and its interaction with the catalyst. Moreover, a higher platinum content was required to achieve full silane conversion (**Table 3, entry 13**). On the other hand, a lower reactivity of **7** can be simply explained by steric hinderance caused by triethoxysilyl groups. In general, from a practical point of view, the established conditions for **PB** modification can be considered very favorable due to the relatively low temperature and short reaction times, except for the aforementioned examples. Based on our previous studies and available literature data, the bulkiness and electronic properties of substituents directly bonded to the silicon atom have a significantly greater impact on the hydrosilylation efficiency compared to the substituents separated from the $HSiMe_2$ unit [30, 35-36, 45]. Nevertheless, no universal trend was observed that could directly describe the influence of the functional group type on reactivity. All reaction profiles recorded by FT-IR, as well as the NMR, FT-IR, and GPC analyses of the obtained silicon-containing polymeric intermediates (**2a-13a**) are available in ESI. After the successful incorporation of silanes into **PB** chains, the partially functionalized polymers were subjected to hydrogenation without any purification procedure. The second step was carried out using the previously selected [{Rh(μ-Cl)(COD)}$_2$] at a temperature of 80°C and under 10 bar hydrogen pressure. The results are summarized in **Table 3**.

Table 3. *One-pot* synthesis of functionalized polyolefins

Entry	Silane	Hydrosilylation time[a]	Hydrogenation of 1,2-units [%]*	Hydrogenation of 1,4 units [%]*	Total hydrogenation [%]*	Isolated yield [%]	N^* [%]	α^* [%]
1	2	5:20	99	99	99	92	99	>99
2	3	9:15	99	75	93	95	96	>99
3	4	6:50	99	66	90	93	95	99
4	5	13:50	99	75	94	87	97	>99
5	6	7:20	95	75	90	86	95	98
6	7	19:40	17	0	13	-	52	81
7	8	4:15	85	36	70	-	85	95
8	8	4:15	99	68	91[d]	87	96	99

9	9	5:50	53	14	42	-	71	89
10	9	5:50	99	76	94[d]	85	97	>99
11	10	4:50	99	65	90	89	95	98
12	11	13:30	99	62	91	88	95	99
13	12[b]	20:10	0	0	0	-	48	79
14	12[b]	20:10	99	19	82[e]	85	91	97
15	13[c]	10:50	80	32	66	-	83	94
16	13[c,f]	6:00	99	50	86	93	93	98

[a] Reaction time required to achieve 99% conversion of silane – determined by *real-time* FT-IR, [*]calculated on the basis of NMR integrals, *N* - Total conversion of the unsaturated units after *one-pot* synthesis, *α* – Total saturation of the main polymer chain, Reaction conditions: Hydrosilylation 95 °C in toluene, 10^{-4} mol H_2PtCl_6 / mol silane, [H-Si] : [C=C] = [0.5] : [1], Hydrogenation - 80 °C, 10 bar H_2, 18h, 0.001 mol [{Rh(μ-Cl)(COD)}$_2$]/ mol C=C, [b] $5x10^{-4}$ mol H_2PtCl_6 / mol silane, [c] $2x10^{-4}$ mol H_2PtCl_6 / mol silane, [d] 0.002 mol [{Rh(μ-Cl)(COD)}$_2$]/ mol C=C, [e] 0.002 mol [$RuCl_2(PPh_3)_3$]/ mol C=C, [f] reaction performed in α,α,α,-trifluorotoluene.

Spectroscopic analyses of the materials obtained by this protocol revealed successful syntheses of organosilylfunctionalized polyolefins with a very low content of remaining unsaturated units. It should be emphasized that in all reactions a total or a nearly complete consumption of 1,2-units was observed, which was not the case in the hydrogenation efficiency of the 1,4-units. This observation is consistent with our previous studies [38]. We noticed that only triethoxysilyl-containing intermediate (**Table 3, entry 6**) and nitrile-group bearing modifier (**Table 3, entry 13**) showed poor hydrogenation progress compared to the others. In contrast, the case of **7a** can be explained by the steric hindrance of the triethoxysilyl groups, which are in close proximity to C=C groups, hindering their interactions with the catalyst. However, in the case of **8a** hydrogenation, also containing a triethoxysilyl moiety, but bonded to the main polymer chain *via* a disiloxane spacer, much higher conversion of C=C units was observed. This confirms the influence of the -$Si(OEt)_3$ steric effect on the hydrogenation efficiency of C=C bonds. On the other hand, the presence of nitrile side groups in the polymer intermediate **12a** led to the deactivation of the rhodium catalyst (**Table 3, entry 13**). It could be explained by the formation of stable chelates in which polymer chains bearing numerous side nitrile act as multidonating ligands, ultimately sterically deactivating the metal center toward the hydrogenation of C=C units. According to the literature, Ru-based catalysts exhibit catalytic activity in the hydrogenation of nitrile rubbers [46-47]. Therefore, we applied [$RuCl_2(PPh_3)_3$] as a hydrogenation catalyst, which enabled full hydrogenation of 1,2-vinyl units and partial saturation of the 1,4-moieties, ultimately achieving an 82 % total hydrogenation yield, corresponding to 97 % main chain saturation (**Table 3, entry 14**). It should also be noted that the application of polar groups-bearing modifiers resulted in lower hydrogenation efficiency, which was particularly observed for the modifiers equipped with -$Si(OEt)_3$ (**8**) and glycidyl (**9**) groups. Such oxygen-rich polymers

required higher rhodium loading to be hydrogenated. The application of $2x10^{-3}$ mol Rh/C=C led to the complete conversion of 1,2-vinyl units and higher consumption of 1,4-units, ultimately resulting in hydrogenation yields of 91 % and 94 % for **8b** and **9b**, respectively. An issue was encountered in the case of perfluorinated modifier **13**, the incorporation of which resulted in the **13a** separation from toluene during the hydrosilylation. Consequently, the hydrogenation occurred in a biphasic system, leading to only 66 % total hydrogenation of the C=C bonds. To counteract this, the catalytic test was repeated with a fluorinated reaction medium, *i.e.* α,α,α-trifluorotoluene. This simple change allowed the reaction to be carried out under homogeneous conditions and boosted the overall hydrogenation yield from 66 to 86 %. Apart from **12a**, [{Rh(μ-Cl)(COD)}$_2$] proved to be highly effective and tolerant to functional groups. This must be underlined that the combination of hydrosilylation and subsequent hydrogenation of **PB** under *one-pot* conditions enabled complete or near-total saturation of the polymer C=C bonds, as evidenced by the very high α factor values (**Table 3**). As a consequence, a library of novel organofunctionalized polyolefins was obtained with high isolation yields (85-95%). All materials were characterized using ^{1}H NMR, 2D HSQC, ^{29}Si NMR, FT-IR spectroscopy, and GPC measurements. **Figure 3** presents exemplary ^{1}H NMR spectra of the starting **PB**, Polymer **2a**, and Polymer **2b**. The spectrum of **2a** showed partial conversion of unsaturated units, along with the appearance of new characteristic peaks confirming the partial functionalization of **PB** with silane. Finally, analysis of **2b** (**Figure 3c**) revealed a complete disappearance of the olefinic peaks and an increase of proton signals in the aliphatic range, accompanied by the creation of a new signal at ~0.8 ppm corresponding to the formed -CH_3 units. Additionally, ^{29}Si NMR spectra (**Figure 4**) revealed a disappearance of the peak located at -4.23 ppm, originating from **2**, and the appearance of a new signal at the lower field, originating from **2a** and **2b**, respectively. Moreover, the silicon NMR spectra did not exhibit any additional peaks, clearly indicating a high selectivity of the hydrosilylation process and the absence of side reactions such as dehydrogenative silylation, formation of siloxanes, or α-isomer. The NMR spectra of all products (**1b-13b**) and intermediates (**1a-13a**) are available in Supporting Information. The successful transformation of **PB** into organofunctionalized polyolefins was also confirmed by GPC measurements. The results of GPC analysis clearly indicate an increase

in both M_n and M_w values when compared to starting **PB**, which is manifested by a shift of the molecular weight distribution curves towards higher molar masses. The molecular weight distribution plots of **PB** and selected polymers are presented in **Figure 5**. Furthermore, no significant change in value of $Đ$ index was observed, usually recorded $Đ$ values were generally close to those of the reference sample or slightly increased, depending on the type of incorporated functional groups. Therefore, GPC analysis revealed neither peak multiplication nor the formation of low molecular weight fractions which clearly confirmed high selectivity of the developed procedure with simultaneous exclusion side reactions such as chain scission and polymer crosslinking.

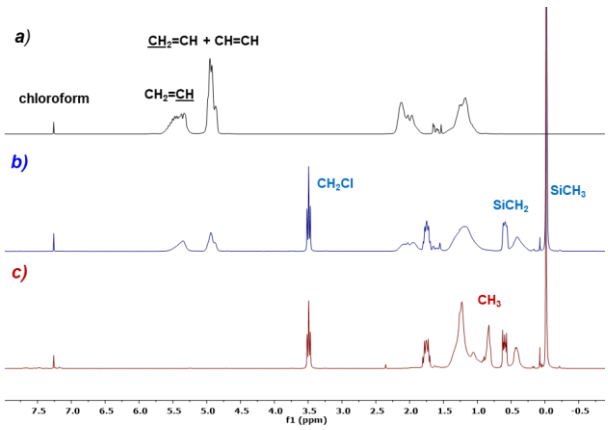


Figure 3. Exemplary ^{1}H NMR spectra of a) **PB**, b) polymer **2a** and c) polymer **2b**

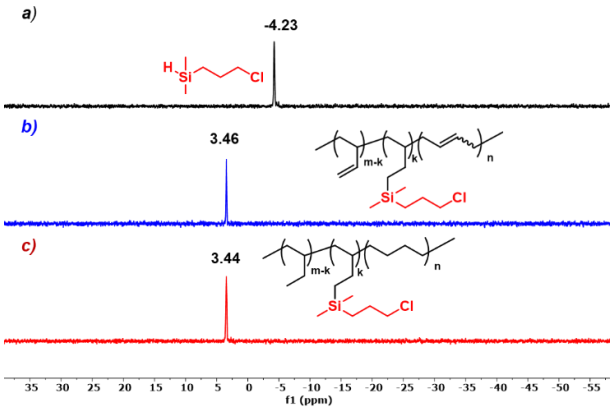


Figure 4. Exemplary ^{29}Si NMR spectra of a) **2**, b) polymer **2a** and c) polymer **2b**

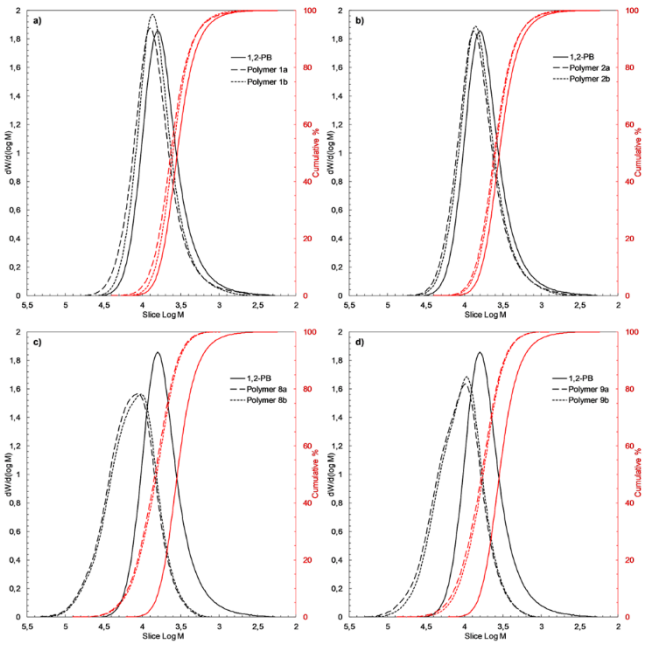


Figure 5. Exemplary GPC Molecular weight distribution curves of **PB** and selected samples.

The main goal of this work was to develop a universal and functional group-tolerant methodology allowing control of the degree of polyolefin functionalization. Our approach demonstrates the feasibility of the incorporation of a high content of functional groups, contrary to the direct C(sp^3)-H functionalization. However, most papers on the synthesis of organofunctionalized polyolefins report the functionalization degree up to several mol%. Therefore, selected organosilicon modifiers were also tested in the presence of a lower hydrosilane amount than described above, namely 30 % in relation to all unsaturated units present in the starting **PB**. The results are listed in **Table 4.**

Table 4. One-pot synthesis of functionalized polyolefins with 30%-functionalization degree

Entry	Silane	Hydrosilylation time[a]	Hydrogenation of 1,2-units [%]*	Hydrogenation of 1,4 units [%]*	Total hydrogenation [%]*	Isolated yield [%]	N^* [%]	α^* [%]
1	1	2:30	99	34	87	95	91	97
2	2	9:00	99	58	92	92	94	98
3	4	6:30	99	12	84	93	88	96
4	10	5:10	99	60	91	89	93	98

Reaction conditions: Hydrosilylation 95 °C, 10^{-4} mol H_2PtCl_6 per mol silane; [H-Si] : [C=C] = [0.3] : [1] Hydrogenation - 80 °C, 10 bar H_2, 18h, 0.001 mol [{Rh(μ-Cl)(COD)}$_2$]/ mol C=C, [a] Reaction time required to achieve 99% conversion of silane – determined by *real-time* FT-IR, *calculated on the basis of NMR integrals, *N* - Total conversion of the unsaturated units after *one-pot* synthesis, *α* – Total saturation of the main polymer chain.

The performed experiments revealed that the number of functional groups can be easily controlled by adjusting the ratio between organosilicon compound and vinyl groups in the **PB** structure. In all cases, complete incorporation of the organosilicon modifiers into the polymer chain was observed, as

confirmed by FT-IR and NMR analyses. Additionally, these 30%-functionalized polymers demonstrated excellent hydrogenation activity for 1,2-vinyl units, further confirming the simplicity and universality of the developed synthetic protocol. Nevertheless, even the small amount of remaining 1,4-units had no significant impact on the α values, and the obtained products can still be classified as organofunctionalized polyolefins. Furthermore, NMR and GPC measurements confirmed that the developed *one-pot* procedure is highly selective, as no traces of chain scission, cross-linking, isomerization, dehydrogenative silylation, were detected.

Conclusions

In summary, an effective *one-pot* methodology leading to organosilicon-functionalized polyolefins was developed. The reported synthetic protocol enabled the efficient incorporation of reactive or specific functional groups, the introduction of which into polyolefin chains is very difficult or even impossible using conventional and previously described copolymerization or polyolefin post-modification techniques. This approach is highly versatile and exhibits excellent functional group tolerance (eg. glycidyl, chloroalkyl, alkoxysilyl, silylamine, nitrile, boronate ester, alkyl, aryl and perfluorinated chain), which in effect enables designing the properties of this type of macromolecular materials for specific applications by introducing the desired moieties, e.g. a combination of reactive or inert ones. Moreover, it can be easily expanded to a variety of other organic and organometallic units, due to the wide commercial availability of a variety of organosilicon compounds. Importantly, the ability to precisely control the degree of polymer functionalization through reaction stoichiometry was confirmed. We believe that the developed approach will find applications in the synthesis of materials with precisely tailored properties. The presented methodology is based on well-known catalysts that are commercially available, which is undoubtedly a significant advantage of the developed synthetic protocol. Further development of the reported methodology will be focused on finding more active catalysts simultaneously suitable for their immobilization on solid supports. This will reduce costs, enabling the technology transfer from the laboratory to industry scale, and ultimately, reaching the consumer market.

Data availability

The data that support the findings of this study are available in the ESI of this article.

Author contributions

Rafał Januszewski - Conceptualization, Methodology, Investigation, Data curation, Writing - original draft, Writing - Review & Editing, Funding acquisition.

Bartosz Orwat – Investigation, Writing - Review & Editing

Michał Dutkiewicz - Investigation

Ireneusz Kownacki - Writing - Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] M. Stürzel, S. Mihan, R. Mülhaupt, From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.,* 2016, **116** 1398–1433.

[2] P.D. Goring, C. Morton, P. Scott, End-functional polyolefins for block copolymer synthesis. *Dalton Trans.,* 2019, **48**, 3521-3530.

[3] M. Quasim, M. S. Bashir, S. Iqbal, Q. Mahmood, Recent advancements in α-diimine-nickel and -palladium catalysts for ethylene polymerization. *Eur. Polym. J.,* 2021, **160**, 110783.

[4] C. M. Plummer, L. Li, Y. Chen, The post-modification of polyolefins with emerging synthetic methods. *Polym. Chem.,* 2020, **11**, 6862-6872.

[5] C. Chen, Designing catalysts for olefin polymerization and copolymerization: beyond electronic and steric tuning. *Nat. Rev. Chem.,* 2018, **2**, 6–14.

[6] N.K. Boaen, M.A. Hillmyer, Post-polymerization functionalization of polyolefins. *Chem. Soc. Rev.,* 2005, **34**, 267–275.

[7] G. M. Rodriguez, M. M. Díaz-Requejo, P. J. Pérez, Metal-Catalyzed Postpolymerization Strategies for Polar Group Incorporation into Polyolefins Containing C–C, C═C, and Aromatic Rings. *Macromolecules* 2021, **54**, 4971–4985.

[8] A.D. Mohanty, C. Bae, Chapter One - Transition Metal-Catalyzed Functionalization of Polyolefins Containing CC, CC, and CH Bonds. *Adv. Organomet. Chem.,* 2015, **64**, 1-39.

[9] C. Tan, C. Chen, Emerging Palladium and Nickel Catalysts for Copolymerization of Olefins with Polar Monomers. *Angew. Chem. Int. Ed.*, 2019, **131**, 7268-7276.

[10] J. Chen, Y. Gao, T.J. Marks, Early Transition Metal Catalysis for Olefin–Polar Monomer Copolymerization. *Angew. Chem. Int. Ed*., 2020, 59, 14726–14735.

[11] L. Guo, S. Dai, X. Sui, C. Chen, Palladium and Nickel Catalyzed Chain Walking Olefin Polymerization and Copolymerization. *ACS Catal.*, 2016, **6**, 428−441.

[12] S. J. Blanksby and G. B. Ellison, Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.*, 2003, **36**, 255–263.

[13] Y. Kondo, D. Garcıa-Cuadrado, J.F. Hartwig, N.K. Boaen, N.L. Wagner, M.A. Hillmyer, Rhodium-Catalyzed, Regiospecific Functionalization of Polyolefins in the Melt. *J. Am. Chem. Soc*., 2002, **124**, 1164–1165.

[14] C. Bae, J.F. Hartwig, N.K. Boaen, R.O. Long, K.S. Anderson, M.A. Hillmyer, Catalytic Hydroxylation of Polypropylenes. *J. Am. Chem. Soc.*, 2005, **127**, 767–776.

[15] C. Bae, J.F. Hartwig, H. Chung, N.K. Harris, K.A. Switek, M.A. Hillmyer, Regiospecific Side-Chain Functionalization of Linear Low-Density Polyethylene with Polar Groups. *Angew. Chem. Int. Ed.*, 2005, **44**, 6410–6413.

[16] N.K. Boaen, M.A. Hillmyer, Selective and Mild Oxyfunctionalization of Model Polyolefins. *Macromolecules* 2003, **36**, 7027–7034.

[17] A. Bunescu, S. Lee, Q. Li, J.F. Hartwig, Catalytic Hydroxylation of Polyethylenes. *ACS Cent. Sci.* 3 (**2017**) 895−903.

[18] L. Chen, K.G. Malollari, A. Uliana, D. Sanchez, P.B. Messersmith, J.F. Hartwig, Selective, Catalytic Oxidations of C–H Bonds in Polyethylenes Produce Functional Materials with Enhanced Adhesion.
Chem, 2021, **7**, 137-145.

[19] L. Chen, K.G. Malollari, A. Uliana, J.F. Hartwig, Ruthenium-Catalyzed, Chemoselective and Regioselective Oxidation of Polyisobutene. *J. Am. Chem. Soc.*, 2021, **143**, 4531-4535.

[20] J.P. Dilcher, H. Jürgens, G.A. Luinstra, Sequential postmodifications of polybutadiene for industrial applications, in multi-component and sequential reactions in polymer synthesis, in: P. Theato (Ed.), Advances in Polymer Science, vol. 269, Springer, Cham, 2015.

[21] C Tan, G. Si, C. Zou, C. Chen, Functional Polyolefins and Composites. *Angew. Chem. Int. Ed.*, 2025, **64**, e202503026.

[22] N. Brummelhuis, C. Diehl, H. Schlaad, Thiol−Ene Modification of 1,2-Polybutadiene Using UV Light or Sunlight. *Macromolecules* 2008, **41**, 9946–9947.

[23] B. Korthals, M.C. Morant-Minana, M. Schmid, S. Mecking, Functionalization of Polymer Nanoparticles by Thiol-Ene Addition. *Macromolecules* 2010, **43**, 8071–8078.

[24] C.M. Geiselhart, J.T. Offenloch, H. Mutlu, C. Barner-Kowollik, Polybutadiene Functionalization via an Efficient Avenue. *ACS Macro Lett.*, 2016, **5**, 1146–1151.

[25] J. Zheng, F. Liu, Y. Lin, Z. Zhang, G. Zhang, L. Wang, Y. Liu, T. Tang, Synthesis of diverse well-defined functional polymers based on hydrozirconation and subsequent anti-Markovnikov halogenation of 1, 2-polybutadiene. *Macromolecules* 2012, **45**, 1190–1197.

[26] R. Januszewski, M. Dutkiewicz, I. Kownacki, An efficient methodology for the synthesis of unique functional polyolefins. *Materials & Design* 2021, **206**, 109801.

[27] R. Januszewski, B. Orwat, M. Dutkiewicz, I. Kownacki, Structurally-unique polymeric materials obtained through catalytic post-polymerization protocols. *Mat. Today Chem.* 2022, **26**, 101073.

[28]. R. Kozak, M. Matlengiewicz, Influence of polar modifiers on microstructure of polybutadiene obtained by anionic polymerization. Part 1: Lewis base (s) aminetype polar modifiers. *Int. J. Polym. Anal. Char.*, 2015, **20**, 574-588.

[29] A. Forens, K. Roos, B. Gadenne, S. Carlotti, Anionic polymerization of butadiene by dialkylmagnesium / alkali metal alkoxide systems in apolar medium: Polybutadiene microstructure and polymerization control. *Polymer* 2020, **205**, 122864.

[30] B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluc, Hydrosilylation. A Comprehensive Review on Recent Advances, Springer, 2009.

[31] M. Zaranek, P. Pawluć, Markovnikov Hydrosilylation of Alkenes: How an Oddity Becomes the Goal. *ACS Catalysis,* 2018, **8**, 9865−9876.

[32] X. Xie, X. Zhang, H. Yang, X. Ji, J. Li, S. Ding, Iridium-Catalyzed Hydrosilylation of Unactivated Alkenes: Scope and Application to Late-Stage Functionalization. *J. Org. Chem.*, 2019, **84**, 1085–1093.

[33] R. Januszewski, M. Dutkiewicz, M. Nowicki, M. Szołyga, I. Kownacki, Synthesis and properties of epoxy resin modified with novel reactive liquid rubber-based systems. *Ind. Eng. Chem. Res.*, **2021**, 60, 2178–2186.

[34] R.J. Hofmann, M. Vlatkovic, F. Wiesbrock, Fifty Years of Hydrosilylation in Polymer Science: A Review of Current Trends of Low-Cost Transition-Metal and Metal-Free Catalysts, Non-Thermally Triggered Hydrosilylation Reactions, and Industrial Applications. *Polymers* 2017, **9**, 534.

[35] R. Januszewski, B. Orwat, J. Merna, I. Kownacki, A library of new bifunctional alkenes obtained by a highly regiodivergent silylation of 1,5-hexadiene. *RSC Adv.,* 2021, **11**, 38956–38960.

[36] J. Duszczak, K. Mituła, R. Januszewski, P. Żak, B. Dudziec, B. Marciniec, Highly Efficient Route for the Synthesis of a Novel Generation of Tetraorganofunctional Double-decker Type of Silsesquioxanes. *ChemCatChem* 2019, **11**, 1086–1091.

[37] Y. Naganawa, K. Inomata, K. Sato, Y. Nakajima, Hydrosilylation reactions of functionalized alkenes. *Tetrahedron Letters,* 2020, **61**, 151513.

[38] B. Orwat, R. Januszewski, M. Dutkiewicz, I. Kownacki, Efficient Transformation of Polybutadienes to Polyolefins: Systematic Studies on the Transition Metal-Catalyzed Hydrogenation of Synthetic Rubbers. *Ind. Eng. Chem. Res.*, 2023, **62**, 10309–10319.

[39] R. Januszewski, M. Dutkiewicz, M. Nowicki, I. Kownacki, Synthesis of novel bifunctional polyolefins and their application as hydrophobic agents for cotton fabrics. *Polym. Test.,* 2023, **126**, 108144.

[40] K. Itagaki, K. Nomura, Efficient Synthesis of Functionalized Polyolefin by Incorporation of 4-Vinylcyclohexene in Ethylene Copolymerization Using Half-Titanocene Catalysts. *Macromolecules* 2009, **42**, 5097–5103.

[41] S. M. Guillaume, Advances in the synthesis of silyl-modified polymers (SMPs). *Polym. Chem*., 2018, **9**, 1911–1926.

[42] C. Chauveau, S. Fouquay, G. Michaud, F. Simon, J.-F. Carpentier, S. M. Guillaume, Polyolefin/Polyether Alternated Copolymers: Silyl-Modified Polymers as Promising Monocomponent Precursors to Adhesives. *ACS Appl. Polym. Mater.*, 2020, **2**, 5135−5146.

[43] X. Ye, X. Jing, Y. Liu, Z. Han, F. Yang, L. Q. J. Ren, L. Meng, Z. Li, W. Wang, J. Li, Y. Li, Simultaneously Flame Retarding and Toughening of Epoxy Resin Composites Based on Two-Dimensional Polyhedral Oligomeric Silsesquioxane/Polyoxometalate Supramolecular Nanocrystals with Ultralow Loading. *ACS Appl. Mater. Interfaces*, 2024, **16**, 49763–49777.

[44] Z. Han, A. Fina, G. Camino, Chapter 12 - Organosilicon Compounds as Polymer Fire Retardants, Editor(s): Constantine D. Papaspyrides, Pantelis Kiliaris, Polymer Green Flame Retardants, Elsevier, 2014, Pages 389-418.

[45] R. Januszewski, M. Dutkiewicz, I. Kownacki, B. Marciniec, The effect of organosilicon modifier structure on the efficiency of the polybutadiene hydrosilylation process. *Catal. Sci. Technol*., 2020, **10**, 7240-7248.

[46] G. A. S. Schulz, E. Comin, R. F. de Souza, Catalytic hydrogenation of nitrile rubber using palladium and ruthenium complexes. *J. Appl. Polym. Sci*., 2007, **106**, 659−663.

[47] X. Guo, G. L. Rempel, Hydrogenation of Cis-1,4-Polybutadiene and Nitrile-Butadiene Copolymers Using Rucl(co)(ocoph)(Pph3)2 as Catalyst. *Stud. Surf. Sci. Catal.,* 1992, 73, 135−142.