



Dendronized polystyrene supports for new catalytic systems

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ABSTRACT

New catalytic systems based on tris(dimethylvinyl)methyl substituted polystyrene were prepared. Dendronized polystyrenes were obtained by modification of poly(styrene-co-chloromethylstyrene) precursors with $\text{LiC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$. Platinum was attached to the polymers via coordination to vinyl groups located on carbosilane moieties. Such the catalytic system makes an interesting alternative for heterogenous platinum catalysts (Pt/charcoal, Pt/C_{act} and Pt/Al₂O₃) and also to Karstedt's catalyst, when used in hydrosilylation of vinylsilanes.

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1. Introduction

An effective recovery of catalysts from reagents/products mixture is very important aspect of large scale chemical synthesis. Therefore, the preparation of new supports for commonly used catalytic systems is under unceasing study. Soluble [1] and cross-linked [2] polymers can be used as scaffolds for the catalysts (including the membrane processes [3]). Polystyrene (frequently as a cross-linked resin) is one of the most popular polymer supports, due to its availability, facile functionalization and chemical inertness [4]. Platinum complexes, bound to polystyrene functionalized with thiomethyl [5], propargyl [6] and amine [7] groups, were used to catalyze hydrosilylation reactions. Preparation of Pt metal colloids anchored on the surface of polystyrene was also reported [8]. However, organic polymers usually show a solvent swelling dependent performance, which impacts the catalytic activity of the supported species. On the other hand catalysts based on dendrimeric supports (especially the periphery-functionalized ones [9]) offer perfectly regularly distributed and available catalytic sites. Still, the preparation of dendrimers having regular structure and high molecular weight is not easy. Branched groups immobilized on polymeric supports are thus a compromise since they can provide the polymeric system with so called dendritic effect [10]. Dendronization of a polymer gives a swelling-like effect, due to the separation of polymer chains and weakening of inter-chain interactions. The swelling properties depend on the type of terminal groups on dendrimeric moiety. Linear-hyperbranched copolymers consisting of polystyrene and dendritic polycarbosi-

lane side grafts [11] and linear blocks [12] were described in the literature. In this paper is reported the synthesis of Pt-catalytic system supported on polystyrene modified with tris(dimethylvinyl)methyl (V_{Si}) groups of branched structure, corresponding to carbosilane dendrons of 1st generation.

Sterically overloaded tris(trimethylsilyl)methane ("trisyl") and its derivatives, due to the exceptional steric hindrance and structural versatility, have been studied extensively in organometallic chemistry [13]. More recently, these moieties have found their place in the field of polymer chemistry, and have been applied for preparation of novel polymeric materials [14] and catalytic systems [15]. Trisyl-type moieties were also recently applied for the synthesis of carbosilane scaffolds for new platinum catalysts [16]. Tris(trimethylsilyl)methyl ligand became known of providing steric protection to macromolecular systems. Its presence results in dramatic changes of properties (an increase of the glass transition temperature and thermal resistance enhancement), reflecting a substantial decrease of polymer chain mobility. Due to its steric bulk, trisyl-type substituents are also expected to increase free volume within the polymeric material and exert an effect similar to the one described for dendritic side-groups.

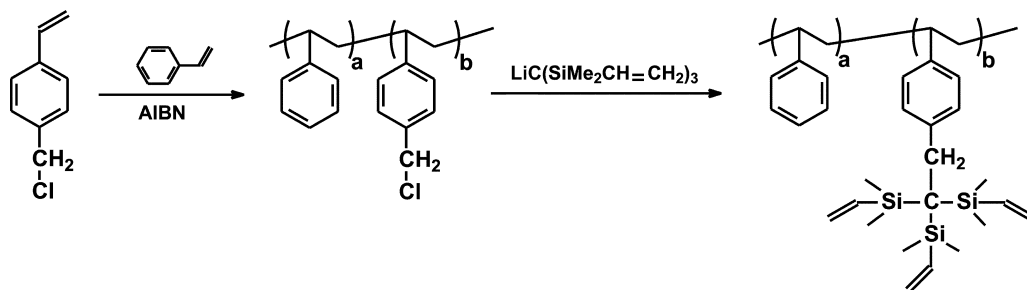
2. Results and discussion

2.1. Preparation of polystyrenes grafted with carbosilane dendritic groups

The method [14a] reported earlier for modification of poly(styrene)-co-(chloromethylstyrene) precursors have been applied for the preparation of poly(styrene)-co-[1,1,1-tris(dimethylvinyl)ethylstyrene] (Scheme 1). Linear poly(styrene)-co-(chloromethylsty-

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Scheme 1. Preparation of polystyrenes grafted with tris(dimethylvinyl)ethyl groups.

rene) polymers of random distribution of chloromethyl groups along the polymer chain were obtained with 44% average yield by radical polymerization of styrene and chloromethylstyrene, catalyzed by azoisobutyronitrile (AIBN). Two distinct types of poly(styrene)-*co*-(chloromethylstyrene) were used. The first one (I-A) contained 30% of chloromethylated units. The other one (II-A) had 7% of functionalized aromatic rings and molecular weight higher than I-A (Table 1). High molecular weight was expected to facilitate polymer precipitation from the reaction mixture and improve the regeneration and reuse.

Poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrenes] were prepared by reaction of their chloromethyl-precursors with organolithium reagent $\text{LiC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$. The method affords for preparation of polystyrenes of various degree of monomeric units substituted with bulky carbosilane groups. The grafting occurs easily at 70 °C, under the atmosphere of dry inert gas. The yield of chloromethyl group conversion can be confirmed by ^1H NMR (Fig. 1). After modification of polystyrene with tris(dimethylvinyl)methylolithium, all chloromethyl groups (4.5 ppm) disappeared and formation of new type CH_2 groups was detected (peak at 3.15 ppm). Molecular weight, as could be expected, increased after modification with V_{Si} (Table 1). Absolute values of M_n , obtained from light scattering measurements, correspond to the growing size of a random coil after the modification of polystyrene with V_{Si} . Masses obtained from SEC measurements show discrepancies caused by the changes in the hydrodynamic volume of molecules in two different solvents. Polymer dispersity was generally enlarged, which is typical since the hydrodynamic volume can change a lot after modification of a polymer, especially with a highly sterically hindered group like V_{Si} .

The studied poly(styrene)-*co*-(chloromethylstyrene) precursors (Fig. 2, Table 2) exhibit the thermal behaviour typical of polystyrenes [17]. The first step of thermal decomposition of a polymer sample (dried to constant weight prior to the thermogravimetric analysis)

starting at about 100 °C, corresponds to evaporation of traces of residual monomer and solvents on polymer softening during devitrification. The second one, close to 400 °C, indicates total decomposition of polystyrene due depolymerization of the main chain. The weight of poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)-ethylstyrene] having 30% of aromatic rings substituted with carbosilane moieties (I-B), was stable at low temperatures. The main decomposition process occurred above 400 °C. In spite of the fact that the glass transition of poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] was observed at 129 °C (Fig. 3), and the relaxation of polymer chains could take place before the main degradation process, no distinct weight decrease, that might correspond to the release of entrapped volatiles, was observed. It may point to the existence of the postulated quasi-dendritic effect, exerted by V_{Si} groups in poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene]. Polystyrene chains are shifted apart due to steric hindrance effect brought about by large tris(dimethylvinyl)ethyl groups. The residue left after thermal decomposition of I-B is very small (4.1 wt%, Table 2). It is expected that tris(dimethylvinyl)methyl group, like its tris(trimethylsilyl)methyl analogue [14b], decomposes at the temperature range close to 450 °C. Formation of dimethylvinylsilane or divinyltetramethyldisilane, instead of tris(dimethylvinylsilyl)methane or tris(dimethylvinylsilyl)ethane, is postulated due to the difference in the bond length between inner Si-C and outer Si-CH₃ [13a,18]. It may not be excluded that the removal of traces of entrapped solvent, as well as carbosilane group decomposition, adds to the main chain decomposition process. Still, no solvent residue was detected by ^1H NMR in dried I-B (Fig. 1).

DSC measurements confirmed, the reported earlier [14a,14c], increase of glass transition temperature after modification of polymer with sterically hindered V_{Si} groups (Table 1). The increase is significant for polymer I-B, having 30% of 1,1,1-tris(dimethylvinyl)ethylstyrene units (35 °C), and also detectable for II-B with only 7% of substituted aromatic rings (6 °C).

Table 1
Characteristics of polystyrene supports

Polymer	^a (mol%)	^b (mol%)	^c (%)	^d (mol%)	M_n^e	M_w/M_n^e	M_n^f	M_w/M_n^f	M_n^g	M_w/M_n^g	Tg (°C)	Y (%)
I-A	70.0	30.0	1.0	30	16000	1.6	22200	1.5	15000	1.6	94	49
I-B	70.0	–	–	0	31500	1.9	39800	2.0	33000	2.1	129	85
II-A	93.0	7.0	0.2	7	66800	1.9	41400	1.7	64000	1.3	105	39
II-B	93.0	–	–	0	45600	2.4	47800	2.3	94000	1.8	111	90

Tg – Glass transition temperature.

Y – Reaction yield.

^a Styrene.

^b 4-Vinylbenzylchloride.

^c $[\text{AIBN}]/[\sum(\text{CH}_2=\text{CH}-)] \times 100\%$.

^d The amount of chloromethyl groups in the product found by ^1H NMR.

^e found by SEC in toluene.

^f found by SEC in CH_2Cl_2 .

^g found by light scattering.

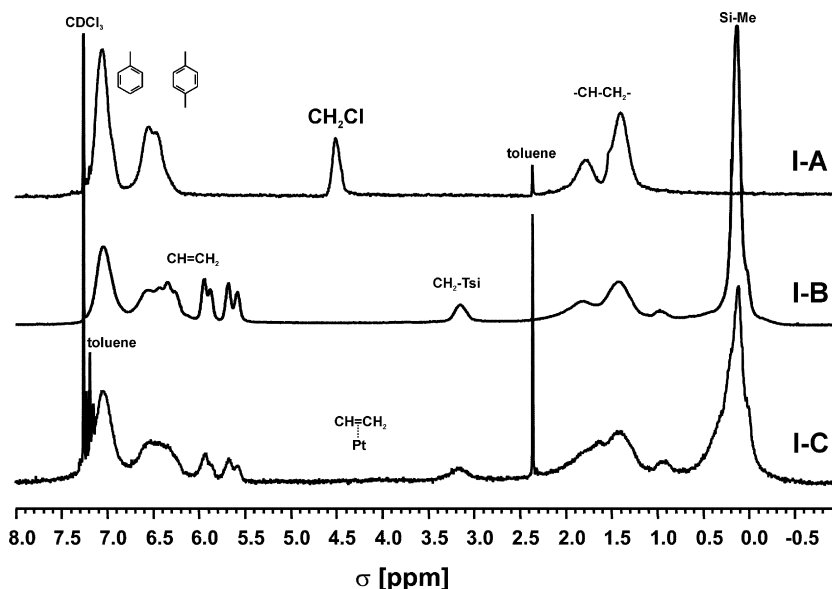


Fig. 1. ^1H NMR spectra of poly(styrene)-*co*-(chloromethylstyrene) (I-A), poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] (I-B), and platinum bound to poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] (I-C).

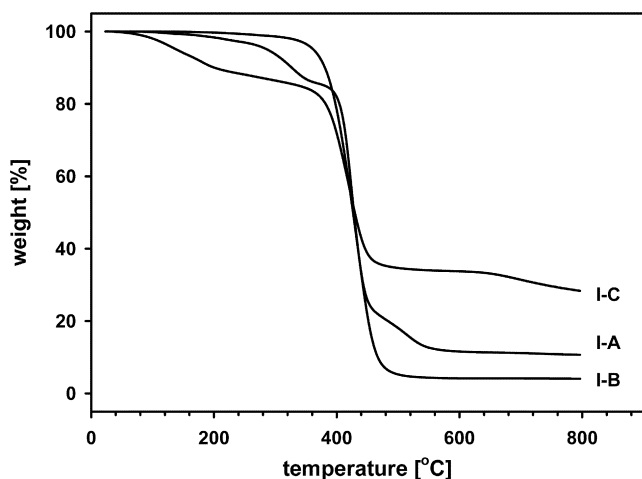


Fig. 2. TGA analysis of poly(styrene)-*co*-(chloromethylstyrene) (I-A), poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] (I-B), and platinum bound to poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] (I-C).

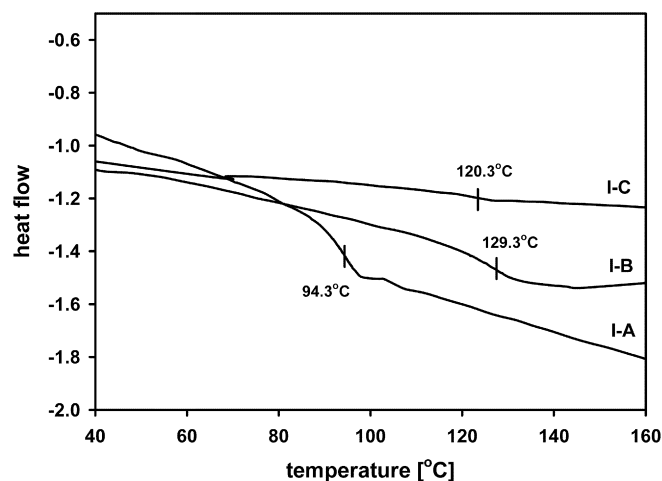


Fig. 3. DSC analysis of poly(styrene)-*co*-(chloromethylstyrene) (I-A), poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] (I-B), and platinum bound to poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] (I-C).

Table 2
Weight decrease during thermogravimetric analysis (Fig. 2)

Polymer	Δ_1 (%)	Δ_2 (%)	Δ_3 (%)	Δ_4 (%)
I-A	14.4	65.2	9.7	10.7
I-B	6.5	86.6	2.8	4.1
I-C	17.5	47.3	6.7	28.5
II-A	9.1	87.8	1.3	1.7
II-B	7.9	89.9	1.0	1.2

Δ_1 – at 60–370 °C.

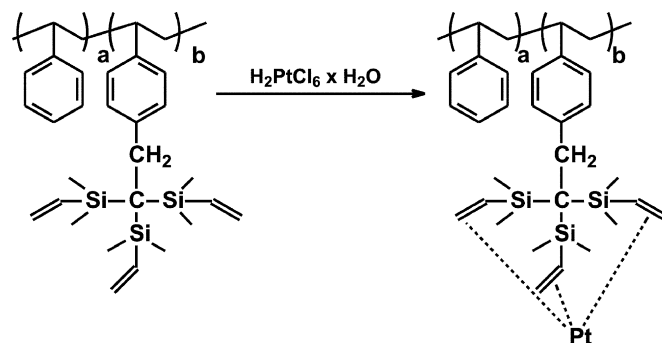
Δ_2 – at 370–480 °C.

Δ_3 – at 480–800 °C.

Δ_4 – residue left at 800 °C.

2.2. Platinum catalyst preparation

Platinum was bound to $-\text{CH}=\text{CH}_2$ groups of trisilated supports in reaction with $\text{H}_2\text{PtCl}_6 \times 6\text{H}_2\text{O}$ (Scheme 2), using the literature procedure [19]. The molar ratio $[-\text{CH}=\text{CH}_2]/[\text{H}_2\text{PtCl}_6] = 3$ was used,



Scheme 2. Preparation of platinum catalysts on V_{Si} -modified polystyrene supports.

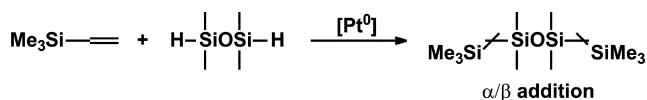
according to the known stoichiometry of $[\text{Pt}]/[-\text{CH}=\text{CH}_2]$ in Pt-2,4-divinyl-tetramethyldisiloxane complex (Karstedt's catalyst) [20]. The samples with Pt coordinated to vinyl groups, after neutraliza-

tion with NaHCO_3 , and drying to constant weight under high vacuum at room temperature, are brown solids that dissolve well in toluene and CH_2Cl_2 to give transparent pale brown solutions. It was found that there is a certain limiting amount of Pt, that can be introduced into poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene]. Above this amount insoluble materials were formed. The coordination of Pt occurs most probably involving vinyl groups that can belong to tris(dimethylvinyl)methyl dendritic groups, situated at different polystyrene chains or adjacent V_{Si} -lated styrene units of the same macromolecule (Scheme 2 represents only a simplified and general idea). Coordination of Pt to only a part of the theoretical number of vinyl groups in copolymers was confirmed by ^1H NMR [disappearance of a part of “free” vinyl groups and formation of a broad multiplet in the range 3.9–4.2 ppm (the chemical shift close to the one typical for vinylsiloxanes with Pt coordinated to $-\text{CH}=\text{CH}_2$ [16,21]). The amount of platinum in the catalyst, assuming that Pt coordinates to 3 $-\text{CH}=\text{CH}_2$ moieties, was calculated on the basis of the relative decrease of “free” vinyl groups in ^1H NMR spectrum [their number (related to Me groups) was compared to those in the precursor]. For the polymer I-C containing 30% of 1,1,1-tris(dimethylvinyl)ethylstyrene units, only ~50% of the total amount of vinyl groups can take part in the coordination to Pt. Under the same conditions all vinyl groups of carbosilane dendrimer of IInd generation coordinated to Pt [16a]. Increasing the reaction temperature to 90 °C, the yield of Vi-Pt coordination increases but the polymer suffers much on inter/intra-chain coordination. Cross-linked gels (which cannot be neutralized with NaHCO_3 and thus tested, but can be still effectively swelled to be analyzed with ^1H NMR) are formed. The efficient use of $\text{CH}_2=\text{CH}-$ groups for Pt coordination depends on the amount of 1,1,1-tris(dimethylvinyl)ethylstyrene units in polystyrene chain. Only 20% of $\text{CH}_2=\text{CH}-$ were involved with Pt in sample II-C, obtained with 7% V_{Si} -containing polystyrene (II-B). The result supports the postulated interchain coordination. X-ray fluorescence (XRF) studies confirmed the amount of platinum estimated on the basis of ^1H NMR (10.7 wt% of Pt for I-C and 4.3% of Pt wt for II-C by XRF and, respectively, 13.4 wt% and 2.2 wt% by ^1H NMR).

As a consequence of interchain coordination a sort of physical cross-linking occurs, and hinders the mobility of polymeric chains. In spite of careful drying to constant weight (under vacuum at room temperature) a certain amount of solvent remains confined within the polymer-bound catalyst (Fig. 1). Flexible poly(methylvinyl-*co*-dimethyl)siloxanes [16b], once transformed into Pt complexes, showed an increase of glass transition temperature. No glass temperature increase can be discerned for Pt-coordinated poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] system. In fact no definite Tg can be detected. The weak slope of I-C DSC trace at 120 °C (Fig. 3) cannot be ascribed to devitrification. Polystyrenes are not crystalline and therefore another phenomenon reported for polysiloxane systems [16b] – the disappearance of the crystalline phase on Pt coordination to vinyl groups – could not be observed. The weight decrease due to entrapped volatiles evaporation at low temperatures [lost weight% is slightly higher than the one observed for poly(styrene-*co*-chloromethylstyrene) (Fig. 2, Table 2)] proves loosening of the coordination network to some extent. The weight of residue, left after TGA analysis, corresponds to the expected one (calculated taking into account the residue left after TGA analysis of I-B, the amount of Pt calculated from ^1H NMR and the amount of volatiles in I-C, released at low temperatures).

2.3. The studies of catalytic activity

The activity of Pt-coordinated poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] catalysts was tested in a model reaction of hydrosilylation of trimethylvinylsilane with 1,1,3,3-tetra-



Scheme 3. Model hydrosilylation reaction.

thylidisiloxane (Scheme 3). A solution of both reagents in toluene ($[\text{Si}-\text{H}] = 0.55 \text{ mol/dm}^3$, $[\text{Si}-\text{H}]/[-\text{CH}=\text{CH}_2] = 1$) was prepared and the solution of the immobilized platinum catalyst I-C in toluene (0.33 mol/dm^3 [Pt], $[\text{Pt}]/[-\text{CH}=\text{CH}_2] = 1.7 \times 10^{-3}$) was added at selected conditions. The composition of the reaction mixture was studied by FT-IR and the progress of Si-H bonds conversion was followed (disappearance of the characteristic Si-H band at 2100 cm^{-1}). The catalyst was found to be active at room temperature, giving reproducible results (Fig. 4). The increase of the reaction temperature to 40 °C was found to be of great advantage – complete conversion of Si-H groups was observed after 1 h (Fig. 5). The inter-chain coordination phenomenon did not cause a significant decrease of activity (usually, a decrease of catalytic activity is observed after ligand immobilization in polymeric system [22]). A comparable studies, performed at room temperature with Pt coordinated to monomeric tris(dimethylvinyl)methane, indicated hardly any deactivation of catalyst after grafting of carbosilane “ligands” onto polystyrene (Fig. 6). The amount of 1,1,1-tris(dimethylvinyl)ethylstyrene units seems to be the activity controlling factor. High molecular weight polystyrene II-B with 7% 1,1,1-tris(dimethylvinyl)ethylstyrene units was prepared with a purpose of cost-effectiveness due to the expected efficient and uncomplicated separation of the supported Pt catalyst II-C by precipitation. However, small amount of V_{Si} “ligands” makes the catalytic sites of II-C locked up among polystyrene chains, resulting in restricted diffusion of reagents/products and inferior catalytic performance. The activity of catalyst II-C was much poorer to I-C at the same $[\text{Pt}]/[-\text{CH}=\text{CH}_2]$ ratio [only 3% Si-H conversion after 90 min at room temperature (and respectively, 19% after 25 h) was observed].

The activity of new catalytic systems was compared to those of Karstedt’s catalyst, as well as a number of commercially available heterogeneous platinum catalysts (supported on non-polymeric substrates). A solution in toluene of the immobilized platinum catalyst I-C ($[\text{Pt}]/[-\text{CH}=\text{CH}_2] = 1.7 \times 10^{-3}$), or appropriate amounts of heterogeneous catalysts or Pt-divinyltetramethyldisiloxane complex, were added to the reaction mixture. The composition of the reaction mixture was studied by FT-IR. Once the reaction was completed the mixture was analyzed with ^1H NMR to examine the selectivity of the α/β addition of Si-H to the double bond.

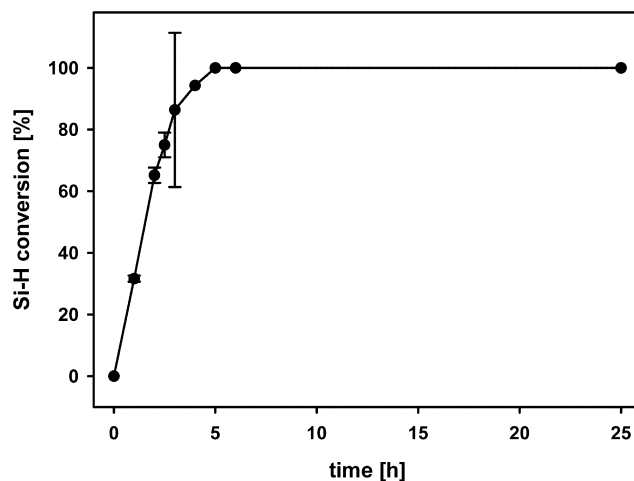


Fig. 4. Conversion of Si-H groups in I-C catalyzed hydrosilylation of trimethylvinylsilane with 1,1,3,3-tetraethylidisiloxane at room temperature.

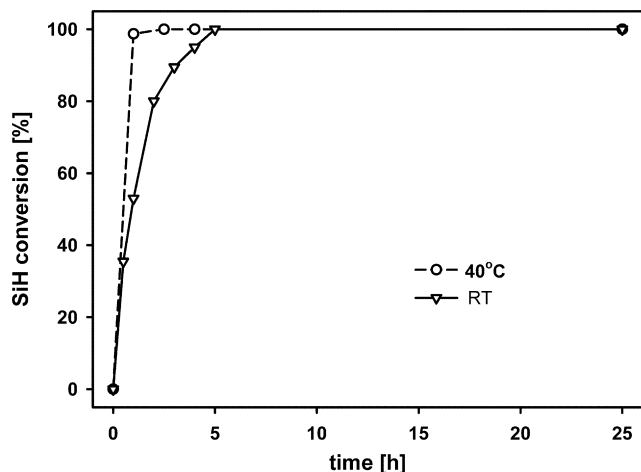


Fig. 5. Temperature dependent conversion of Si-H groups in I-C catalyzed hydrosilylation of trimethylvinylsilane with 1,1,3,3-tetramethyldisiloxane.

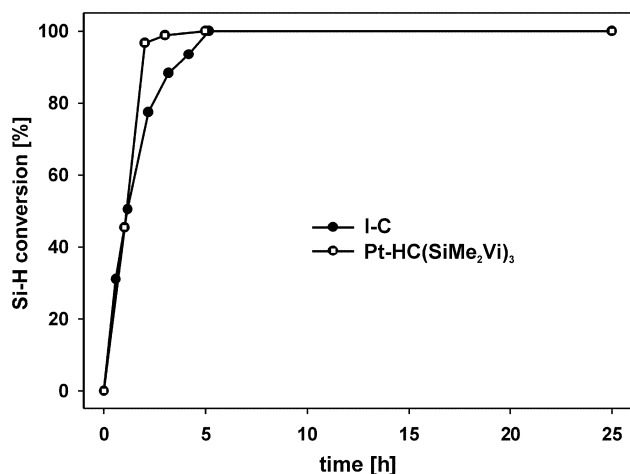


Fig. 6. Conversion of Si-H groups in I-C and Pt-HC(SiMe₂Vi)₃ [platinum complex with tris(dimethylvinyl)methane] catalyzed hydrosilylation of trimethylvinylsilane with 1,1,3,3-tetramethyldisiloxane at room temperature.

The comparable studies of catalytic activity (Fig. 7) were carried out at room temperature (the first hour). Then the reaction temperature was increased to 40 °C. Karstedt's catalyst was found to be the most active one, and hydrosilylation of 1,1,3,3-tetramethyldisiloxane proceeded very fast in its presence. After short initial period (about 2 min) an exothermic reaction took place. The reaction mixture turned pale brown due to the formation of colloidal platinum. FT-IR spectrum recorded after 5 min proved complete disappearance of Si-H band. Heterogenous catalysts were less active at room temperature. The best result was obtained with platinum supported on active carbon (10% of Si-H conversion after 1 h at room temperature). The polymer bound Pt catalyst I-C was more effective (35% of Si-H conversion on average after 1 h at room temperature). The activity of all catalysts increased at elevated temperatures. For most of them 100% Si-H conversion was reached within 5 h. I-C was more active at 40 °C than all other heterogenous catalysts. The effect can be supposedly assigned to more efficient reagent/product diffusion from the active site.

In spite of the distinct difference in catalyst activity, the ratio of α/β addition to C=C bond (Table 3) is comparable for all the studied species, including Pt-divinyltetramethyldisiloxane complex (0.03 on average, values found for products obtained at room temperature for Karstedt's catalyst and 40 °C for other catalysts).

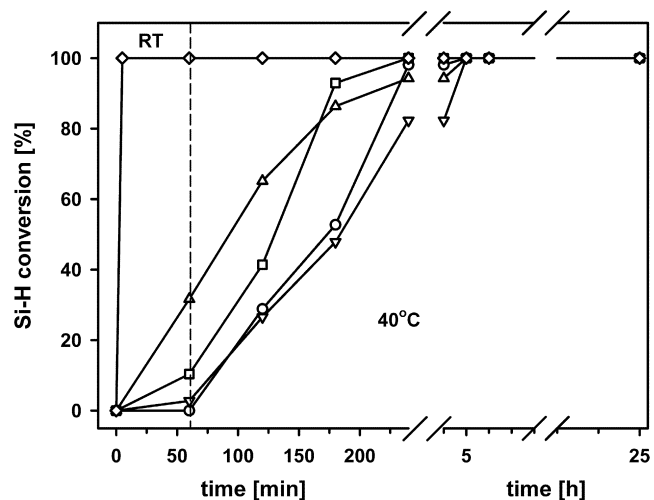


Fig. 7. Comparative study of catalyst activity in hydrosilylation of trimethylvinylsilane with 1,1,3,3-tetramethyldisiloxane at room temperature and after temperature increase to 40 °C. Δ – I-C, ∇ – Pt/charcoal, \square – Pt/C_{akt}, \diamond – Karstedt's catalyst, \circ – Pt/Al₂O₃.

Table 3

Selectivity of Si-H addition across C=C bond at 40 °C

Catalyst	α (%)	β (%)
Pt/Al ₂ O ₃	2.8	97.2
Pt/charcoal	2.4	97.6
Pt/C _{akt}	3.9	96.1
I-C	3.1	96.9
Karstedt's catalyst	3.2 ^a	96.8 ^a

^a Reaction carried out at room temperature.

3. Conclusions

A new polymeric support based on multifunctional, exceptionally sterically hindered carbosilane moieties, grafted onto linear poly(styrene-co-chloromethylstyrene), was prepared. It offers well accessible, coordination-active sites ($-\text{CH}=\text{CH}_2$ moieties) that can be used for preparation of novel catalysts. Tris(dimethylvinylsilyl)methyl groups exert quasi-dendritic effect to polystyrene. The swelling effect and increased chain separation were confirmed by thermal characteristics (TGA, DSC). Platinum was attached to the synthesized poly(styrene-co-[1,1,1-tris(dimethylvinyl)ethylstyrenes]) via coordination to vinyl groups. The polymer-bound metal complex was tested in hydrosilylation of vinylsilanes. The support structure and Pt load was correlated with the catalyst performance. Deficiency of V_{Si} substituents and thus coordination sites, affects both the catalyst preparation and its efficiency. The structure/activity reciprocity was optimized. The catalyst based on polystyrene substituted in 30% with V_{Si} groups does not show any substantial activity impedence due to ligand immobilization onto a polymer chain. It has a temperature dependent performance, but is reasonably active at room temperature and can be considered as an alternative for traditional platinum catalysts. Additionally, it shows high selectivity, comparable to the one found for Karstedt's catalyst.

4. Experimental

4.1. Analysis and general methodology

All reactions were performed using standard Schlenk or syringe techniques under an atmosphere of argon. NMR spectra of

polymeric precursors were recorded, in CDCl_3 as a solvent, on Bruker AC-200 MHz (^1H NMR) or DRX-500 MHz (^{13}C , ^{29}Si and ^{195}Pt NMR) spectrometers with TMS and K_2PtCl_6 as appropriate references. Size exclusion chromatography (SEC) traces were recorded using a Agilent 1100 Series isocratic pump, degasser, autosampler thermostatic box for columns, and set of 2 X PLGel 5 μm MIXED columns at 27 °C. Wyatt Optilab rEX interferometric refractometer and MALLS (Multiangle Laser Light Scattering) DAWN EOS Laser Photometer (Wyatt Technology Corp., USA) were applied as detectors. Methylene chloride was used as the eluent, at a flow rate of 0.8 ml/min. M_n and M_w/M_n were calculated from the experimental traces using WYATT ASTRA V 4.90.07 program. Parallel measurements were effected with LDC Analytical refractometer IV instrument [RI detector, two columns SDV 8 \times 300 (5 μm and 104 Å porosity) and SDV 8 \times 300 (5 μm and 100 Å porosity), eluent – toluene (0.7 ml/min)]. Molecular masses were derived from a calibration curve based on polystyrene standards. Thermogravimetric analyses were performed by use of a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) in nitrogen atmosphere (heating rate 10 °C/min, resolution 3, sensitivity 3). Differential Scanning Calorimetry traces were recorded with a 2920 Modulated DSC apparatus (TA Instruments) calibrated against indium and copper in nitrogen atmospheres in the temperature ranges: –50 °C to 150 °C (first and second heating). Samples of about 10 mg were placed in hermetic aluminum pans and heated/cooled at 10 °C/min. IR spectra were recorded using a FT-IR ATI Mattson spectrometer or Nicolet 380. X-ray fluorescence measurements for the analysis of Pt amount in I-C and II-C were carried out with Canberra XRF Spectrometer, Model 1510.

4.1.1. Reagents

Poly(styrene)-*co*-(chloromethylstyrene) precursors were prepared with styrene (99%, Aldrich) and 4-vinylbenzylchloride (90%, Aldrich). The monomers were freshly distilled, azoisobutyronitrile (AIBN) catalyst (Aldrich) was crystallized from methanol and dried under vacuum before use. Tris(dimethylvinylsilyl)methane was prepared as previously described [16a]. Trimethylvinylsilane (97%), MeLi (1.6 M in diethyl ether), hexachloroplatinic(IV) acid hydrate were purchased from Aldrich. Platinum catalysts used for comparative studies were bought from the respective suppliers [Pt/charcoal (10 wt%, Fluka), Pt/activated carbon (10 wt%, Aldrich) and Pt/alumina (5 wt%, Alfa)]. Platinum divinyltetramethyldisiloxane complex (Karstedt's catalyst, 3% solution in xylenes) and 1,1,3,3-tetramethyldisiloxane (97%) were bought from ABCR. All solvents were dried prior to their use according to the literature procedures [23].

4.2. Preparation of polystyrene supports

4.2.1. Synthesis of poly(styrene-*co*-chloromethylstyrenes)

Monomers were placed under argon in a Schlenk's flask and diluted with toluene. The mixture was degassed by freeze-thaw method (repeated three times) in order to remove traces of oxygen. AIBN was added and the closed flask was placed with magnetic stirring at 60 °C in an oil bath. The mixture was heated for 72 h and then concentrated under reduced pressure to leave viscous, syrupy oils. The products were precipitated into methanol. A white, solid precipitate was collected, dissolved in small amount of CH_2Cl_2 and precipitated again into methanol. The purified product was dried under vacuum for 16 h at room temperature.

NMR: ^1H (σ ppm): 1.35 CH_2 (polymer chain), 1.85 CH (polymer chain), 4.5 CH_2Cl , 6.5 Ar, 7.0 Ar.

^{13}C (σ ppm): 40.26 CH_2 (polymer chain), 43.68 CH (polymer chain), 46.32 CH_2Cl , 125.74 Ar, 127.98 Ar, 134.72 Ar, 145.16 Ar.

4.2.2. Grafting tris(dimethylvinylsilyl)methyl dendritic groups on polystyrene backbone

$\text{LiC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$ (LiV_{Si}) have been prepared as 0.15 M solution in THF, from MeLi and $\text{HC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$ ($[\text{MeLi}]/[\text{V}_{\text{Si}}] = 1.1$) as described earlier [16a]. It was added via a canula to a solution of poly(styrene)-*co*-(chloromethylstyrene) in THF ($[-\text{CH}_2\text{Cl}] = 0.1 \text{ mol/dm}^3$, $[-\text{CH}_2\text{Cl}]/[\text{LiV}_{\text{Si}}] = 0.67$). The mixture was stirred for 24 h at 70 °C. Volatiles were removed under reduced pressure, and the product was dissolved in a small amount of CH_2Cl_2 and precipitated into a large amount of methanol, separated and dried for 8 h under vacuum at room temperature to leave solid poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene].

NMR ^1H (σ ppm): 0.1 SiMe, 0.95 CH (polymer chain – V_{Si} modified units), 1.35 CH_2 (polymer chain), 1.85 CH (polymer chain – styrene units), 3.15 $\text{CH}_2\text{V}_{\text{Si}}$, 5.8 $\text{CH}_2=$, 6.25 $-\text{CH}=\text{}$, 6.5 Ar, 7.0 Ar.

^{13}C (σ ppm): 1.37 SiMe, 40.31 CH_2 (polymer chain), 44.05 CH (polymer chain), 125.62 Ar, 127.92 Ar, 130.73 $-\text{CH}=\text{}$, 139.23 Ar, 141.91 $\text{CH}_2=$, 145.15 Ar.

^{29}Si (σ ppm): –3.70 SiMe_2Vi .

4.3. Formation of Pt(0)-[$\text{CH}_2=\text{CH}$] complexes at poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene]

A solution of poly(styrene)-*co*-[1,1,1-tris(dimethylvinyl)ethylstyrene] ($[\text{CH}_2=\text{CH}-] = 0.2 \text{ mol/dm}^3$) in toluene was prepared in a flask, equipped with a magnetic stirrer. H_2O ($[\text{CH}_2=\text{CH}-]/[\text{H}_2\text{O}] = 0.73$), and then H_2PtCl_6 was added ($[\text{CH}_2=\text{CH}-]/[\text{Pt}] = 3.0$). The mixture was stirred at 50 °C for 2 h. Once cooled down to room temperature, the solution was admixed with NaHCO_3 ($[\text{Na}]/[\text{Pt}] = 7.3$). After filtration, solvents were removed and the product was dried under vacuum to leave brown solid.

NMR ^1H (σ ppm): 0.1 SiMe, 0.95 CH (polymer chain – V_{Si} modified units), 1.35 CH_2 (polymer chain), 1.65 CH (polymer chain – styrene units), 3.15 $\text{CH}_2\text{V}_{\text{Si}}$, 3.9–4.2 $-\text{CH}=\text{CH}_2 \cdot \text{Pt}$, 5.8 $\text{CH}_2=$, 6.25 $\text{CH}=\text{}$, 6.5 Ar, 7.0 Ar.

^{13}C (σ ppm): 1.23 SiMe, 40.0 CH_2 (polymer chain), 45.11 CH (polymer chain), 54.43 $-\text{CH}=(\text{Vi} \cdot \text{Pt})$, 58.78 $\text{CH}_2=(\text{Vi} \cdot \text{Pt})$, 125.78 Ar, 127.85 Ar, 130.62 $-\text{CH}=\text{}$, 137.53 Ar, 141.26 $\text{CH}_2=$, 145.50 Ar.

^{29}Si (σ ppm): –3.77 SiMe_2Vi .

^{195}Pt (σ ppm): broad peak around –6000.

4.4. Kinetic studies – hydrosilylation of trimethylvinylsilane with 1,1,3,3-tetramethyldisiloxane

A solution of trimethylvinylsilane and 1,1,2,2-tetramethyldisiloxane ($[\text{CH}_2=\text{CH}-]/[\text{H}_2\text{O}] = 1.0$) in toluene ($[\text{CH}_2=\text{CH}-] = 0.65 \text{ mol/dm}^3$) was prepared and its reference FT-IR spectrum was recorded (the concentration of samples utilized in the kinetic studies with solutions of I-C or Karstedt's catalyst was adjusted by addition of toluene into "0" sample in order to match the amount of solvent in the subsequent kinetic samples). Platinum catalyst ($[\text{Pt}]/[\text{CH}_2=\text{CH}-] = 5 \times 10^{-4}$, as a solid for Pt/ Al_2O_3 , Pt/Charcoal and Pt/ C_{act} or 0.18 M solution in toluene for I-C, or as 3% solution in xylenes for Karstedt's catalyst) was added to the reaction mixture. The reaction was carried out at given temperature. The composition of the reaction mixture was studied by FT-IR. Once the reaction was completed the mixture was analyzed with ^1H NMR to examine the selectivity of the α/β addition to the double bond during the reaction.

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