Polysiloxanes as supports for transition metal catalysts*)

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Abstract: This article reviews the potential applicability of polysiloxanes as supports for transition metal catalysts. Unique physicochemical properties of polysiloxanes suggest their usefulness as catalyst supports. Polysiloxanes of various macromolecular topologies – linear and star-shaped and hyperbranched – with the functional side groups capable of binding transition metals were prepared. These polymers were used as carriers for palladium and rhodium complexes. The activities of so-immobilized complexes of transition metals in model reactions were comparable to that of the corresponding homogeneous complexes of these metals.

Keywords: polysiloxanes, polymer-supported catalysts, palladium, rhodium, immobilized catalysts.

Polisiloksany jako nośniki katalizatorów na bazie metali przejściowych

Streszczenie: Przedstawiono przegląd potencjalnych zastosowań polisiloksanów jako nośników katalizatorów opartych na metalach przejściowych. Unikatowe właściwości fizykochemiczne polisiloksanów wskazują na ich przydatność w charakterze nośników katalizatorów. Otrzymano polisiloksany o różnych topologiach makrocząsteczek – liniowych, gwiaździstych i hiperrozgałęzionych – zawierających boczne grupy funkcyjne zdolne do wiązania metali przejściowych. Polimery te wykorzystano jako nośniki kompleksów palladu i rodu. Immobilizowane kompleksy metali przejściowych w modelowych reakcjach wykazały aktywność porównywalną z aktywnością katalizatorów homogenicznych.

Słowa kluczowe: polisiloksany, polimerowe nośniki katalizatorów, pallad, rod, katalizatory immobilizowane.

Immobilization (heterogenization) of catalysts aims to obtain catalysts which combine the advantages of homogeneous catalysts (high activity, selectivity) and heterogeneous ones (stability, easy separation from the reaction medium and reusability in multiple reaction cycles). One of the most promising areas of research in this domain is the use of soluble polymers as catalyst carriers [1]. The main factor that makes the polymer matrix an interesting alternative to the inorganic carriers is the ability to control the structure of the support (the size and conformation of the molecules, the density of the groups capable of anchoring the catalyst), its solubility in the reaction medium, as well as the thermal and chemical resistance. The structure of the support affects the capacity, catalytic activity and selectivity of the obtained catalysts. The catalysts immobilized on soluble polymers may act as homogeneous catalysts and thus may have similar catalytic activity and stereoselectivity to the parent small molecular complexes. When the reaction is completed, the catalyst can be separated by the techniques known in polymer chemistry, such as addition of a non-solvent, freezing, membrane filtration, centrifugation, or preparative size-exclusion chromatography. The use of soluble polymers for classical and combinatorial synthesis, and catalysis has recently been reviewed [2–6].

Recyclable catalysts allow for significant savings in expensive metal complex. The concentration of the immobilized catalyst is easier to control. High density of ligands on the surface of the support makes possible the synthesis of multifunctional catalysts in which more than one active species is bound to the carrier. Supported analogs of toxic, explosive, or odorous reagents are safer and more convenient to handle than the corresponding soluble chemicals.

Furthermore, supported catalysts can also be more resistant towards side reactions, such as reduction, autooxidation, or hydrolysis. It is possible to stabilize highly reactive compounds, which cannot exist as separate species in solution.

Despite these advantages, polymeric supports are not yet used on a large scale in industrial processes. The major drawbacks that prevent their potential use are insufficient stability of immobilized catalysts and gradual loss of activity due to leaching of metal and/or ligand. Moreover, the immobilized systems often exhibit lower catalytic activity than homogeneous catalysts due to poor accessibility of the active sites, steric effects of the matrix, and a carrier-solvent incompatibility or due to inhomogeneities resulting from the formation of the different bonds between the carrier and the complex. Immobilization of chiral catalysts often results in lower activities

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and enantioselectivities as compared to those observed for their homogeneous counterparts [5].

Synthesis of the polymeric carrier involves the copolymerization of monomers functionalized with a suitable ligand or the grafting of ligands on a pre-formed polymer support. Organic polymers, such as polystyrene, polyethylene, poly(ethylene oxide), poly(vinylpyridine), and others, have been commonly used as supports for catalysts [7]. Immobilization of catalysts on polymeric carriers usually involves covalent binding of the metal with a functional group on the polymer, as a result of ligand exchange between a soluble metal complex and the polymer. This mini review presents the current state of knowledge on the applicability of polysiloxanes as supports for transition metal catalysts and is focused mainly on the research done in our laboratory.

POLYSILOXANES AS SUPPORTS FOR CATALYSTS

Polysiloxanes are known for their unusual conformational flexibility, which is advantageous, as the chain may easily adopt optimal conformation for catalytic centers to be accessible for the reagents. Polysiloxanes are also chemically and thermally stable (except in the presence of strong acids and bases) and well soluble in many organic solvents. They may also be relatively easily separated from the reaction mixture. Low surface tension suggests their use in phase-transfer catalysis. Easy modification in side groups provides flexibility in the choice of ligands [8]. The controlled synthesis of copolymers of various topologies (linear, grafted, branched, dendritic) allows the adjustment of the polysiloxane structure to the requirements of the process. These features make them interesting potential supports for transition metal catalysts.

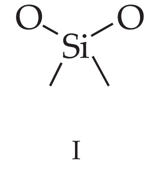
The reports on the use of polysiloxanes as catalyst supports are very scarce and their applicability has not been systematically studied. Siloxane-supported rhodium catalysts of hydroformylation were prepared by Farrell *et al.* [9]. However, while more than 90 % of the polymer could be recovered after the reaction, analysis showed that significant rhodium metal loss occurred. Poly(phenylsiloxane) complexed $Cr(CO)_3$ was used as a stereoselective hydrogenation catalyst but again the extensive metal leaching was observed [10]. Polysiloxane supported zirconium complexes were tested as catalysts in olefin polymerization [11]. A chiral vanadium(IV) Lewis acid catalyst covalently bound to the dimethylpolysiloxane chain was proven to be active in Diels-Alder reactions [12]. Polysiloxanes were used as a scaffold for support of Cinchona alkaloids useful as ligands for Sharpless' asymmetric dihydroxylation reaction [13]. Polysiloxane with pendant aryldiamine ligands was examined as a support for an organonickel catalyst which proved to be active in Kharasch addition [14]. In all cases, linear polysiloxanes were used. The dependence of the catalytic activity and stability on the topology of the macromolecules and the type and density of the anchoring groups is unknown.

Recently, we studied the application of soluble polysiloxanes of various topologies, *i.e.*, linear, star-shaped and hyperbranched, having various functional groups, for immobilization of transition metals [15–17] and enzymes [18] in order to throw some light on the carrier structure-catalyst activity relationship.

SYNTHESIS OF WELL-DEFINED FUNCTIONALIZED POLYSILOXANES

Where the control of the macromolecular structure is not essential, polysiloxanes are usually prepared by equilibration of a mixture of linear and cyclic oligomers obtained from the hydrolysis of chlorosilanes (this is the least expensive method for the synthesis of these polymers) [19]. If the topology and size of macromolecule is important, the use of controlled polymerization method is required. The best method for the control of the structure of polysiloxanes is anionic ring opening polymerization of cyclotrisiloxanes [20, 21]. Due to the ring strain, the Si-O bond breaking in the monomer and its addition to the growing chain is much faster than the competing processes of chain transfer. When the proper initiator system is used, for example, BuLi/THF (THF – tetrahydrofuran), in the kinetically controlled step of the process the siloxane polymer may be obtained with a yield of over 90 %. The resulting polymer has a molecular weight controlled by monomer to initiator ratio and has a low molecular weight distribution, typical for living systems [19].

The use of various functional monomers in copolymerization with hexamethylcyclotrisiloxane allows to control the density and distribution of side groups in the chain [Formulas (I)–(V)]. Depending on the reaction conditions the polymer of random, block, alternating or gradient distribution of ligands can be obtained [22].



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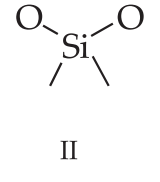

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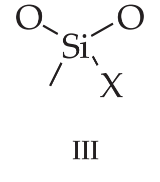

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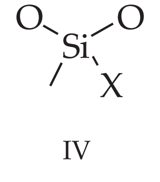

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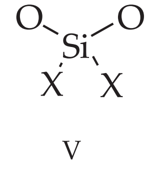

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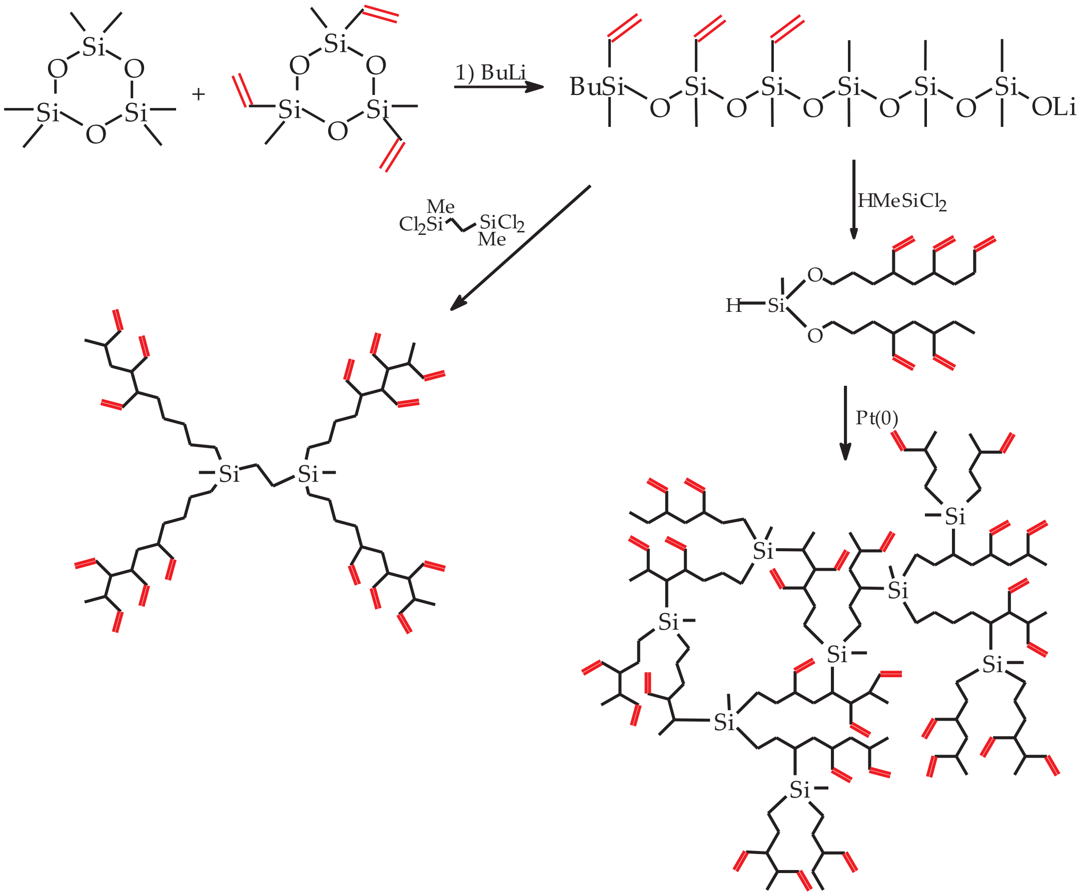
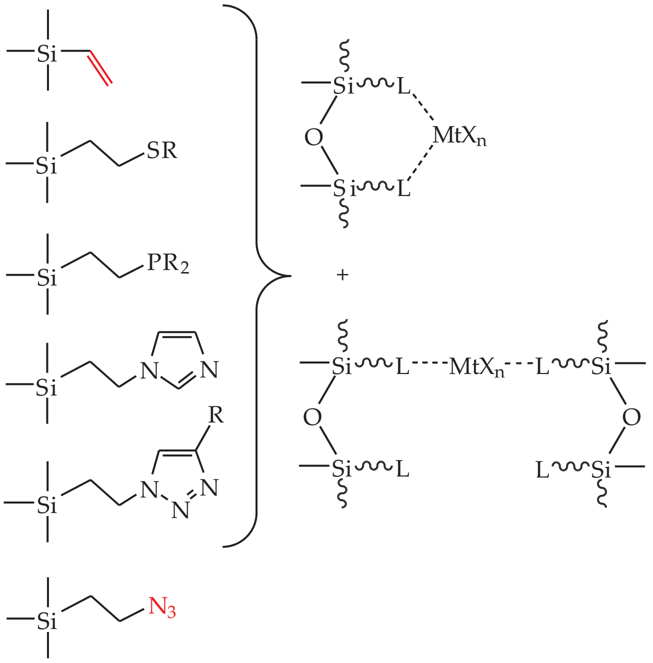


Scheme A

Previously we discussed the methods for the controlled synthesis of linear polysiloxanes. Using functional reagents which react with the active ends of the polymer chain more complex macromolecular structures can be obtained, like star-shaped or hyperbranched as illustrated in Scheme A [15, 23].

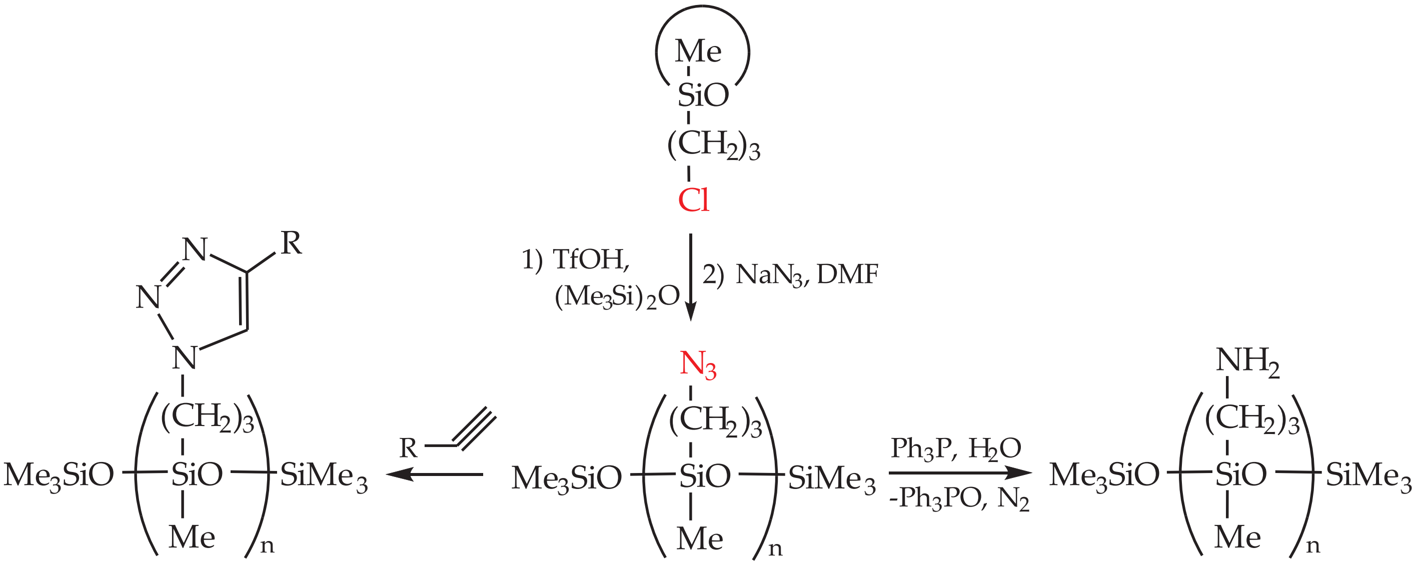


Scheme B

INTRODUCTION OF CATALYST ANCHORING GROUPS

As mentioned above, polysiloxane having groups binding a catalyst, is prepared by polymerization of the monomer containing the corresponding groups or, in the first stage, the polymer with precursor groups is obtained which are then converted into the appropriate ligands by the reaction on polymer (Scheme B). One of the most versatile precursor functions is the vinyl group [8, 22, 24]. It is not only susceptible to diverse modifications but also is itself an effective ligand binding transition metals. Increasingly important is becoming the azide group, mainly due to its use in so-called "click chemistry" [25].

Synthesis and transformations of azidopropyl groups in polysiloxane are shown in Scheme C. In the first stage, poly(3-chloropropyl)methylsiloxane was prepared by equilibration of the mixture of 3-chloropropylcyclosiloxanes in the presence of hexamethyldisiloxane as molecular weight controlling agent and CF_3SO_3H as catalyst, as described before [26]. In the second stage, polychloropropylsiloxane was modified with sodium azide in dimethylformamide (DMF) at different temperatures of 60–100 °C [27]. Finally, azido-functional polysiloxane was modified in the Huisgen cycloaddition with alkynes and in the Staudinger reduction to give 1,2,3-triazole and amino groups, respectively (Scheme C).



Scheme C

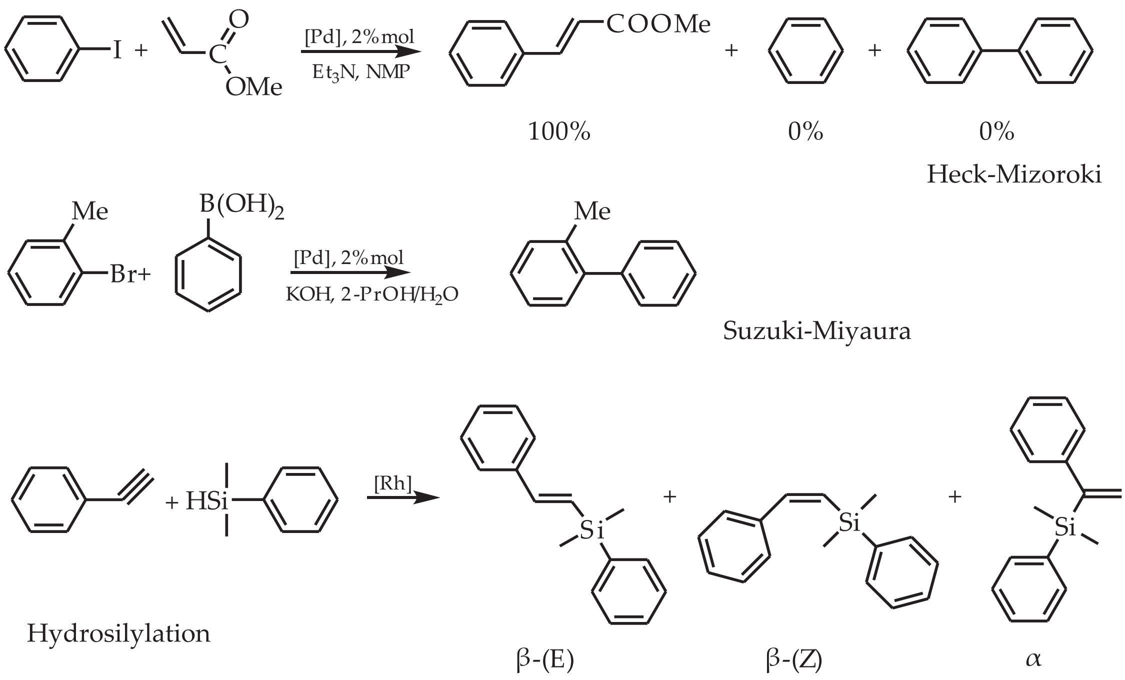
IMMOBILIZATION OF CATALYSTS

Immobilization of transition metals involved mixing of a polysiloxane solution with the solution of low molecular complex of the transition metal. In the case of palladium, the complexes used were $PdCl_2(PhCN)_2$, $Pd(OAc)_2$ or $PdCl_2(cod)$ (cod – 1,5-cyclooctadiene). In most cases the immobilization was quantitative [15]. In the case of rhodium, the $[RhCl(CO)_2]_2$ complex was used for immobilization [17]. The metal can be bound either intramolecularly by two adjacent ligands in the same chain or intermolecularly by the ligands attached to two polymer chains (see Scheme B). Intermolecular bonds cause reversible crosslinking of the polymer, and its insolubility at low temperature whereas in the reaction medium at elevated temperatures the coordination bonds can be broken and the system becomes soluble again.

Although palladium catalysts supported on soluble siloxanes functionalized have been successfully recycled, the separation step has been rather complicated. Therefore, we decided to examine the catalytic activity of palladium supported on aminopropyl-functionalized crosslinked polysiloxane microspheres [28].

CATALYTIC ACTIVITY OF POLYSILOXANES SUPPORTED CATALYSTS

The palladium catalysts immobilized on polysiloxanes having vinyl, butylthio, and diphenylphosphinyl groups were tested in a model Heck-Mizoroki reaction,



Scheme D

while those having imidazolyl and triazolyl groups in Suzuki-Miyaura reaction (Scheme D).

Rhodium catalysts immobilized on polysiloxanes with Vi-, BuS-, and Ph_2P- groups were also tested in hydrosilylation (Scheme D). In all cases, the observed catalytic activity was comparable with that for the homogeneous catalysts except for the system with rhodium supported on sulfide ligands, as sulfur apparently poisons the catalyst [15–17, 27]. The recycled palladium catalysts retain their activity despite partial loss of palladium, up to 10 reaction cycles.

The dependence of catalytic activity on the topology of the carrier was studied most comprehensively for polysiloxanes with vinyl ligands and palladium in the Heck reaction. Comparison of catalysts supported on polysiloxanes of different structures and different ligand densities in the polymer chain showed that (i) polymers with higher density of ligands bind metal more effectively; (ii) catalysts immobilized on linear polymers are more active and more stable in recycling than those immobilized on branched structures [15]. This is probably due to easier accessibility of active centres in linear structures.

A palladium catalyst supported on polysiloxane microspheres was prepared in the reaction of $PdCl_2(MeCN)_2$ with a suspension of crosslinked polymethylsiloxane modified at the surface with aminopropylsilane. This catalyst was used in the Suzuki–Miyaura coupling of various aryl bromides with phenylboronic acids. Efficient separation of the catalyst from organic products was achieved by simple filtration due to the properties of microspheres [29]. The scanning electron microscopy (SEM) analysis shows that palladium is evenly distributed on the surface of the spheres, and its amount does not differ before and after the catalytic reaction. Negligible differences in the amounts of palladium between samples can show the lack of leaching of the metal from the support during the reaction. This demonstrates the very strong and stable bond of palladium to the NH_2 groups [29].

Rhodium catalysts were much less stable. As a rule, they lost activity after the first reaction cycle. The best results were obtained when linear polymers were applied as carriers. Polysiloxanes with more complex structures were less effective. There was no significant difference in activity depending on the ligand binding metal, with one exception: the sulfide ligands significantly reduced the activity of rhodium catalysts. The selectivity of the reaction strongly depends on its conditions (catalyst and solvent) [17].

CONCLUSIONS

Functional polysiloxanes with vinyl, thioalkyl, phosphinyl, and imidazolyl side groups appeared to be good supports for palladium, giving stable and active catalysts, which activity in the Heck-Mizoroki reaction was comparable to that of the homogeneous complex. Immobilization of rhodium also gave very active catalysts in the hydrosilylation reaction, however, they appear to be unstable due to the intensive metal leaching from the support surface. Selectivity of hydrosilylation depends on the topology of the carrier, the type of ligands and – to a lesser extent – on the solvent. For both tested metals, the best results were obtained when using linear polymers as carriers. Polysiloxanes with branched structures were less effective. This can be explained by a very limited accessibility of the metal centers located on the internal fragments of the polysiloxane chains. Palladium catalyst immobilized on crosslinked polysiloxanes showed also a high activity and its separation and recycling was proved to be much easier than that of catalysts supported on soluble polysiloxanes.

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