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Please cite as: CHEMIK 2013, **67**, 12, 1173–1180

## Introduction

Immobilization (heterogenization) of catalysts aims to obtain catalysts which combine the advantages of homogeneous catalysts (high activity, selectivity) and heterogeneous ones (stability, ease of separation from the reaction medium and the possibility of re-use in subsequent reaction cycles). One of the most promising directions of research in this field is the use of polymers as catalyst carriers [1]. The main factor that causes the polymer matrix is an interesting alternative to the inorganic carriers is the ability to control the structure of the support (the size and stiffness of the molecules, the density of the groups anchoring catalyst). This makes possible to control its solubility in the reaction medium, the chemical and thermal resistance as well as the capacity, and consequently, catalytic activity and selectivity of the obtained catalysts. Particularly interesting group of supports are soluble polymers. By using such catalysts, organic reactions can be carried out in a homogeneous manner and thus may have similar catalytic activity and stereoselectivity as the homogeneous parent system. When the reaction is completed, the catalyst can be separated by either solvent or heat precipitation, membrane filtration, centrifugation, or 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 or enzyme. Immobilized catalyst is easier to distribute and control its concentration, for example, in combinatorial reactions. High density of ligands on the surface of the support makes possible the synthesis of multifunctional catalysts in which more than one active agent 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 allow the use of a wider range of solvents, they can also be more resistant towards side reactions deactivating the catalyst, such as reduction, autooxidation, or hydrolysis. It is possible to stabilize highly reactive coordinatively unsaturated 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 main reason for this is insufficient stability of immobilized catalysts and loss of activity due to leaching of metal and/or ligand. In addition, 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 complex. Immobilization of chiral catalysts often results in lower activities 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 usually been 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.

Methods for the immobilization of biocatalysts (enzymes) on polymers are more complex and comprise a number of techniques ranging from physical adsorption through a covalent bond formation to the trapping and encapsulation in the polymer network [8, 9].

Potential benefits of the biocatalyst immobilization include mainly the higher resistance to temperature, pH variation and poisoning/contamination of the catalyst. The ease of separation from the reaction mixture and the possibility of reuse are also of great importance. Moreover, the enhanced activity of the enzyme is often observed, due to a better availability of catalytic sites resulting from a conformational change imposed by the formation of a covalent bond to polymer.

However, the process of immobilization of enzymes also has its disadvantages, such as the additional cost of the carrier and additional reagents and increased mass transfer resistance (due to diffusion limitations). It should be emphasized that there is no universal method for the immobilization of any enzyme or for all uses of the particular enzyme. Selection of the optimal procedure, carrier, or even a suitable enzyme is strongly dependent on the chosen process. The immobilization method must be adjusted individually for each system. Immobilization of the enzyme can thus be too expensive and time-consuming, especially, when the enzyme itself is inexpensive.

## Polysiloxanes as supports for catalysts

Polysiloxanes are known for their extreme conformational flexibility, which may be 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. Excellent surface properties suggest their potential in phase-transfer catalysis. Easy modification in side groups provides flexibility in the choice of ligands [10]. The synthesis of various topologies (linear, branched, brushes, dendrimers) is possible and allows the adjustment of the support structure to the requirements of the process. These features make them interesting potential supports for transition metal catalysts. In addition, hydrophobic character of polysiloxanes in combination with hydrophilicity of enzymes, would make the resulting hybrids amphiphilic and increase the solubility of enzymes in organic solvents.

The reports on the use of polysiloxanes as catalyst supports are very scarce. To our best knowledge, there are no reports on the covalent binding of enzymes with soluble polysiloxanes. All reports concern the use of polysiloxanes as transition metal supports. Siloxane-supported rhodium catalysts of hydroformylation were prepared by Farrell et al. [11]. 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  $\text{Cr}(\text{CO})_3$  was used as a stereoselective hydrogenation catalyst [12]. Polysiloxane-supported zirconium complexes were tested as catalysts in olefin polymerization [13]. A chiral vanadium(IV) Lewis acid catalyst covalently bound to the dimethylpolysiloxane chain has proven to be active in Diels-Alder reactions [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 synthesis and 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].

### 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 siloxane oligomers obtained in 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 (Fig. 1.) [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 (Fig. 1). Extremely important is the proper choice of the initiator system. One of the simplest and most commonly used is the BuLi/THF. Under optimal conditions, in the kinetically controlled step of the process, the polymer may be obtained with a yield of over 90%. The resulting polymer has a molecular weight corresponding to the monomer to initiator ratio used and has a narrow molecular weight distribution [19].

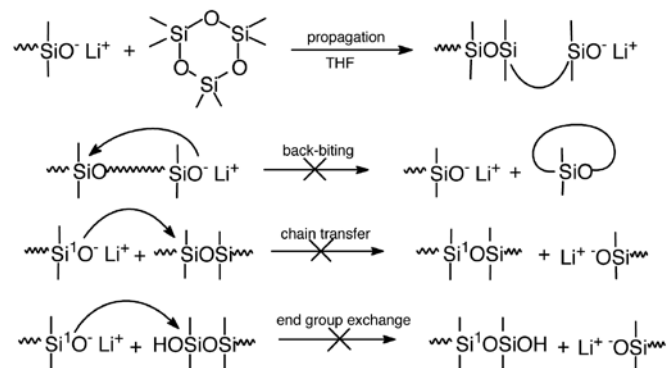


Fig. 1. Controlled anionic ring opening polymerization of cyclotrisiloxanes

The use of various functional monomers allows to control the density and distribution of side groups in the chain (Fig. 2). In the controlled copolymerization of functional cyclotrisiloxanes with hexamethylcyclotrisiloxane one can extend the control of the distribution of functional groups along the chain. Depending on the reaction conditions the polymer of random, block, alternating or gradient distribution of ligands can be obtained (Fig. 3) [22].

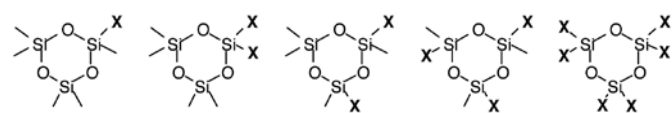


Fig. 2. Functional cyclotrisiloxanes

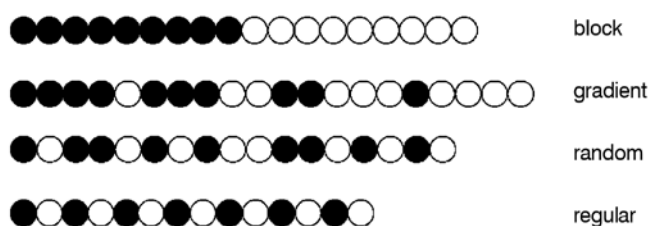


Fig. 3. Possible distributions of ligands along the polymer chain

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 Figure 4 [15, 23].

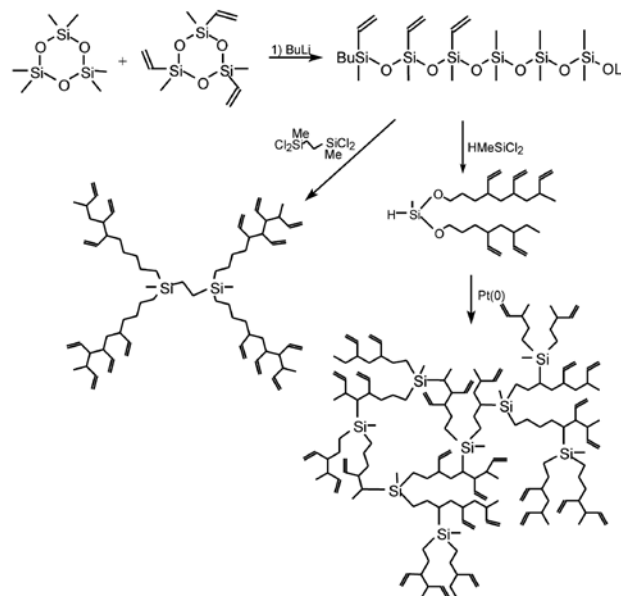


Fig. 4. Synthesis of complex polysiloxane topologies

### 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 [24]. One of the most important precursor groups is the vinyl group [10, 22, 24]. This group, which in addition to the susceptibility to modification is also an effective ligand transition metals. In our work we used this group as both a ligand anchoring metals as well as a precursor for the synthesis of other ligands such as phosphine and sulfide groups and the epoxy function used for binding the enzyme (Fig. 6). Increasingly important is becoming the azide group, mainly due to its use in so-called “click chemistry” [25]. Chemical transformations of this group led to triazole and primary amino ligands (Fig. 7).

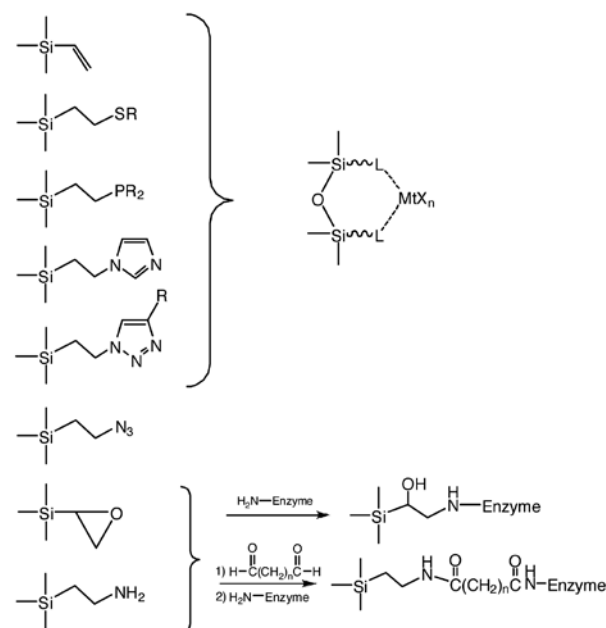


Fig. 5. Ligands binding a catalyst and the precursor groups to be transformed to the proper ligand

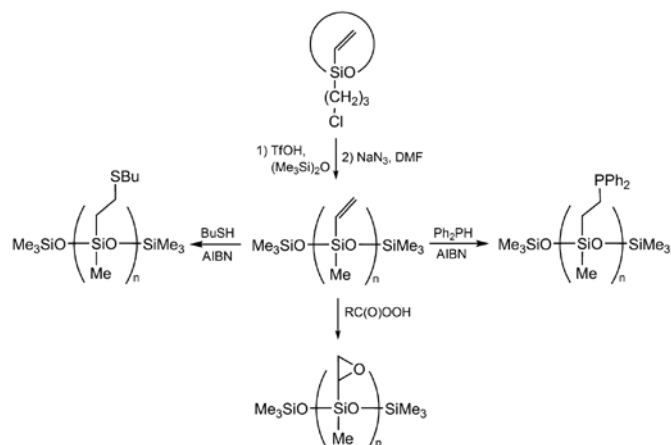


Fig. 6. Modifications of the vinyl group

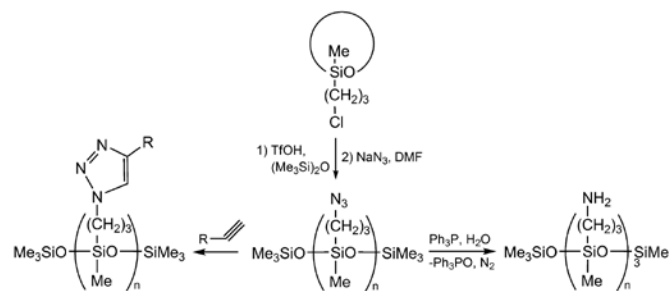


Fig. 7. Modifications of the azide group

### Immobilization of catalysts

Immobilization of metals on polysiloxanes with vinyl, butylthio and diphenylphosphinyl groups involved a ligand exchange between soluble palladium,  $\text{PdCl}_2(\text{PhCN})_2$ , and rhodium,  $[\text{RhCl}(\text{CO})_2]_2$ , complexes with functional polysiloxane in toluene solution. The reaction progress was controlled by solution decolorization and precipitation of the polymeric complex. The metal may be bound intramolecularly by two adjacent ligands in the chain or intermolecularly by ligands belonging to two polymer chains. Possible structures of complexes of the polymers are shown in Figure 8. Intermolecular bonds cause cross-linking of the polymer, and its insolubility, but the process is reversible, as in the reaction medium the coordination bonds can be broken. Immobilized catalysts were analyzed by far-infrared spectroscopy,  $^{29}\text{Si}$  NMR, X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS). XRF spectroscopy confirmed the metal content in the polymers in accord with the theoretical prediction. For palladium, all the methods proved the presence of metal in the polymers. The content of rhodium was too small for IR and NMR to clearly show its presence. The XPS spectra proved that the oxidation state of the metal does not change upon immobilization. Thermogravimetric Analysis (TGA) showed that the polysiloxanes containing metals are stable up to 200°C.

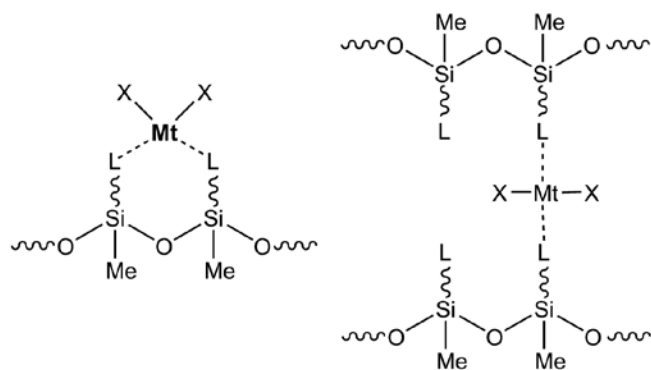


Fig. 8. Probable structures of metal complexes with polysiloxane

Among the various attempts to bind covalently the model enzyme (lipase from *Candida rugosa*) to polysiloxanes the most interesting results gave the reaction with epoxy groups (Fig. 5). Epoxy substituted polysiloxane was obtained by oxidation of the vinyl groups with percarboxylic acid (Fig. 6) [26]. However, the control of the immobilization process was very difficult and immobilized enzymes exhibited unpredictable catalytic properties. Enzyme activity was tested with a model reaction of the hydrolysis of *p*-nitrophenol palmitate.

Much better results were obtained using palladium and rhodium complexes immobilized on polysiloxanes. These catalysts were tested in a model Heck-Mizoroki [15] and Suzuki [16] reactions (Pd) and hydrosilylation (Rh) [17] (Fig. 9). In both cases, the observed catalytic activities were comparable with those of the homogeneous catalysts. The recycled palladium catalysts retain their activity despite partial loss of palladium, up to at least 10 reaction cycles. Rhodium catalysts were much less stable. As a rule, they lost activity after the first reaction cycle. The best results for both systems were obtained when linear polymers were applied as carriers. Polysiloxanes with branched structures were less effective. This can be explained by a more difficult accessibility of the metal centers bound to internal fragments of the polysiloxane side-chains. As a consequence, only the centers located in the outer part of the polymer molecule were active. 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. This is probably the result of poisoning of the catalyst. Activity of rhodium catalysts were tested in three solvents of different polarity: toluene, tetrahydrofuran and dichloroethane. The reaction progress and proportions of products were measured by gas chromatography. There were no significant differences in the activities of investigated complexes depending on the solvent. However, the selectivity of hydrosilylation significantly depends on the structure of the carrier and on the solvent. Especially the support structure affects the selectivity of the reaction carried out in toluene and dichloroethane. With the increase in branching of the polymer the fraction of  $\beta$ -(E) and  $\alpha$  forms increase (Fig. 9). Proportions of products also depend on the ligands on the silicon. For vinylsiloxanes  $\beta$ -isomer (Z) is the dominant product (70–80%). Thioalkyl and phosphinyl ligands favor formation of  $\beta$ -(Z) and  $\beta$ -(E) isomers which are produced in comparable amounts.

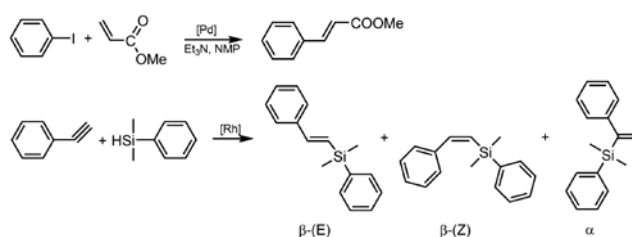


Fig. 9. Model reactions for tests of catalytic activity of Pd and Rh immobilized on polysiloxanes

### Conclusions

Functional polysiloxanes with vinyl, thioalkyl, phosphinyl, and imidazolyl side groups were good supports for palladium, giving stable and active catalysts, which activity in the Mizoroki-Heck 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 more difficult accessibility of the metal centers located at the internal fragments of

the polysiloxane chains. The reaction between the model enzyme (lipase from *Candida rugosa*) and polysiloxane with epoxy groups gave a covalent enzyme-polysiloxane compounds. However, the control of the immobilization process was very difficult and the enzyme bound to polysiloxane exhibited unpredictable, accidental catalytic activity in the model ester hydrolysis.

#### Acknowledgements

The work has been partially supported by the by the Polish Ministry of Science and Higher Education grant no. N N204 131435.

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