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Polysiloxane microcapsules, microspheres and their derivatives[*)]

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Abstract: The paper summarizes progress in synthesis of polysiloxane microspheres, as well as in preparation of their functional and ceramic derivatives. Synthesis of microcapsules with polysiloxane shells is also discussed. Structure and most important properties of the microparticles are analyzed. Presented routes used for formulation of microspheres include preparation the particles by a sol-gel process from the functional (*e.g.*, containing vinyl groups alkoxysilanes) and by cross-linking of polyhydrosiloxanes with low molar mass or oligomeric divinyl compounds (in many instances also polysiloxanes). The mini-review describes also synthesis of polysiloxanes from polyhydrosiloxanes and divinyl compounds in a process involving hydrolysis of ≡SiH groups to ≡SiOH silanols and their dehydrocondensation, carried out in dispersed systems. Synthesis of modified polysiloxane microspheres yielding the particles with controlled hydrophobic/hydrophilic balance [presence of the hydrophobic $(CH_3)_3Si–$ or $≡SiOCH(CH_3)_2$ and hydrophilic siloxane groups] is discussed. Preparation of the functionalized particles with epoxy, amine, and vinyl groups is presented. The paper describes modification of the routes of synthesis of the polysiloxane particles was yielding hybrid particles with the core-shell structure, in which polysiloxanes constitute the particles' cores or shells. In the latter case, the particles had the structure of polysiloxane microcapsules containing encapsulated inorganic or organic material. Preparation of composed microspheres, which in addition to polysiloxane contain a significant fraction of organic material is described. The paper depicts polysiloxane microspheres as an attractive preceramic material. Selected applications of polysiloxane based particles as carriers of catalysts, optical diffusers and phase-change microspheres are discussed.

Keywords: polysiloxane microspheres, polysiloxane microcapsules, functionalized microparticles, synthesis of polysiloxane microparticles, carriers of catalysts, phase-change materials, preceramic materials.

Polisiloksanowe mikrokapsułki, mikrosfery i ich pochodne

Streszczenie: Przedstawiono rozwój syntezy polisiloksanowych mikrosfer i ich funkcjonalnych oraz ceramicznych pochodnych. Omówiono syntezę mikrokapsułek z polisiloksanową otoczką, analizowano strukturę i najważniejsze ich właściwości. Opisano metody wykorzystane do formowania mikrosfer, obejmujące wytwarzanie mikrosfer w procesach zol-żel z komponentów funkcjonalnych (np. alkoksy-

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silanów zawierających grupy winylowe), sieciowania polihydrosilanów oraz o małej masie molowej lub oligomerycznych substratów diwinylowych (w większości wypadków także polisiloksanów). Poniższy mini przegląd literatury dotyczy także syntezy polisiloksanów z polihydrosiloksanów i komponentów diwinylowych w procesie hydrolizy grup ≡SiH do ≡SiOH i następnej ich dehydrokondensacji w dyspersji wodnej. Syntetyzowanie modyfikowanych mikrosfer polisiloksanowych umożliwia otrzymanie cząsteczek o kontrolowanym bilansie hydrofilowo-hydrofobowym [obecność grup hydrofobowych $(CH_3)_3Si$– lub $\equiv SiOCH(CH_3)_2$ i hydrofilowych grup siloksanowych]. Omówiono wytwarzanie cząsteczek zawierających epoksydowe, aminowe i winylowe grupy funkcyjne. Opisano modyfikacje metod syntezy polisiloksanowych cząsteczek, prowadzące do cząsteczek hybrydowych o strukturze rdzeń-otoczka, w których polisiloksany tworzą otoczkę lub rdzeń, a także syntezę polisiloksanowych mikrokapsułek zawierających enkapsulowany organiczny bądź nieorganiczny materiał. W artykule przedstawiono polisiloksanowe mikrosfery jako atrakcyjny preceramiczny materiał o potencjalnym zastosowaniu w charakterze nośników katalizatorów, dyfuzorów optycznych i zmiennofazowych mikrosfer.

Słowa kluczowe: polisiloksanowe mikrosfery, polisiloksanowe mikrokapsuły, sfunkcjonalizowane mikrocząsteczki, synteza polisiloksanowych mikrocząsteczek, nośniki katalizatorów, materiały zmiennofazowe, materiały preceramiczne.

Polysiloxanes attract attention of many researchers. This interest is due to several important properties of polymers, which belong to the above-mentioned class. In particular, polysiloxanes are physiologically neutral, resistant to water and water vapors, to oxygen, are permeable by gasses, their mechanical properties could be controlled, their properties make them suitable for various applications [1–11]. Polysiloxanes are used as sealants, coatings (including antifouling coatings), medical implants, components in electronics, ceramic precursors, and many others [12–18]. Polysiloxanes are used very often as bulk materials, which, like many other polymers, only after the properly chosen processing are converted into final products.

In recent years, however, there is noticed a growing interest in polysiloxane and polysiloxane related materials shaped into nanoparticles, microparticles and microcapsules. The reason of the above-mentioned interest is due to a quite large specific surface (S_{sp}) of materials, which consists of microparticles. For example, in the case of spherical non-porous microspheres the specific surface can be expressed by a simple formula:

$$S_{sp} = \frac{6}{d \cdot D} \tag{1}$$

where: d and D – density and diameter of microspheres, respectively. Taking into account that density of polysiloxane is 0.965 g/cm^3, the specific surface of non-porous microspheres with $D = 1$ μm should be 6.2 m^2/g. Obviously, the specific surface of porous microparticles could be even by 2–3 orders of magnitude larger. Thus, the polysiloxane microspheres and their modified derivatives are good candidates for carriers of active substances (various catalysts, enzymes, compounds and nanoparticles with antimicrobial activity). Moreover, the polysiloxane microspheres with tailored surface properties could be used as well dispersible fillers modifying mechanical, thermal, optical and other properties of various polymers. Ceramized polysiloxane microspheres are excellent candidates for preparation of the stress-free ceramics.

Composite materials containing the microcapsules with polysiloxane shells and phase change cores are suitable for fabrication of products ensuring thermal control in packaging, clothes, and construction applications.

The minireview provides information on recent progress in synthesis/preparation and determination of properties of polysiloxane and polysiloxane derived microparticles and on their selected applications.

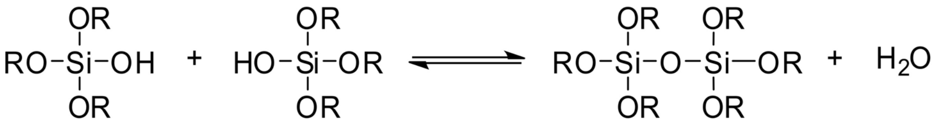
SYNTHESIS OF POLYSILOXANE MICROSPHERES

Sol-gel method – from silica to polysiloxane microspheres

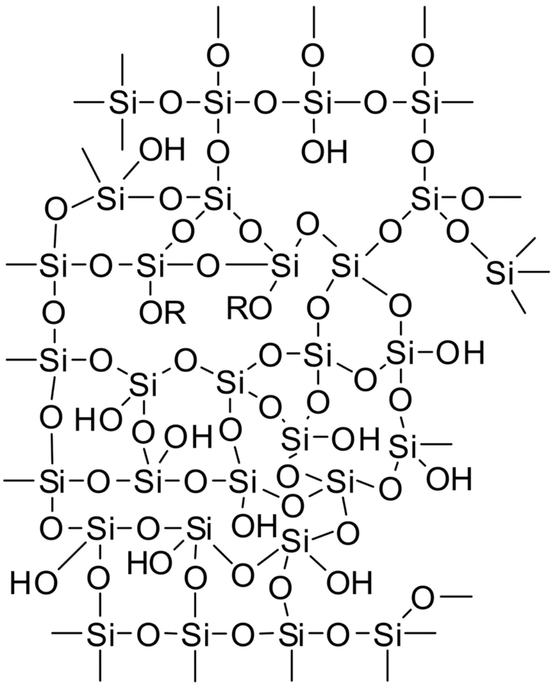
The first and still often used syntheses of polysiloxane microspheres are based on reactions similar to those responsible for synthesis of nanosilica by the Stöber method [19]. Starting materials for Stöber syntheses are tetraalkoxysilanes. The process is carried out in the presence of ammonia used as a catalyst and consists of the hydrolysis of alkoxysilane (Scheme A) and condensation polymerization depicted in Scheme B.

Scheme A. Hydrolysis of alkoxysilane

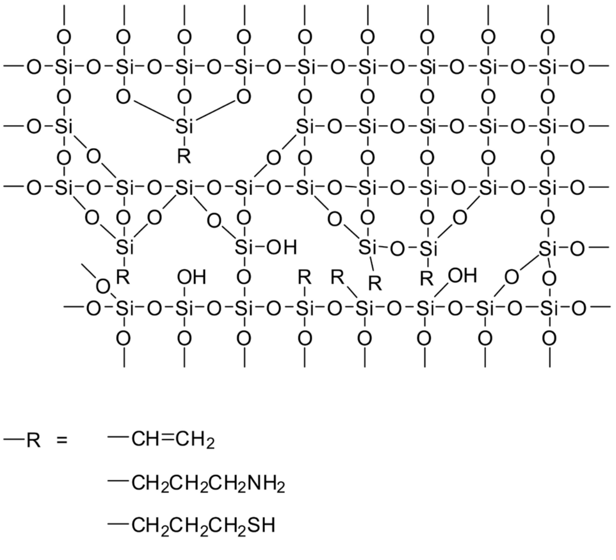
The products of condensation shown in Scheme B are further hydrolyzed and prone to subsequent condensation reactions forming a network containing ≡SiOSi≡ and ≡SiOC≡ as well as some ≡SiOH groups, which remain unreacted being hidden in defects of the structure of the relatively rigid network (see Scheme C).



Scheme B. Condensation of alkoxysilanes containing –OH groups



Scheme C. Cross-linked polysiloxane containing hydroxyl groups



Scheme D. Chemical structures in cross-linked alkyltrialkoxysilanes

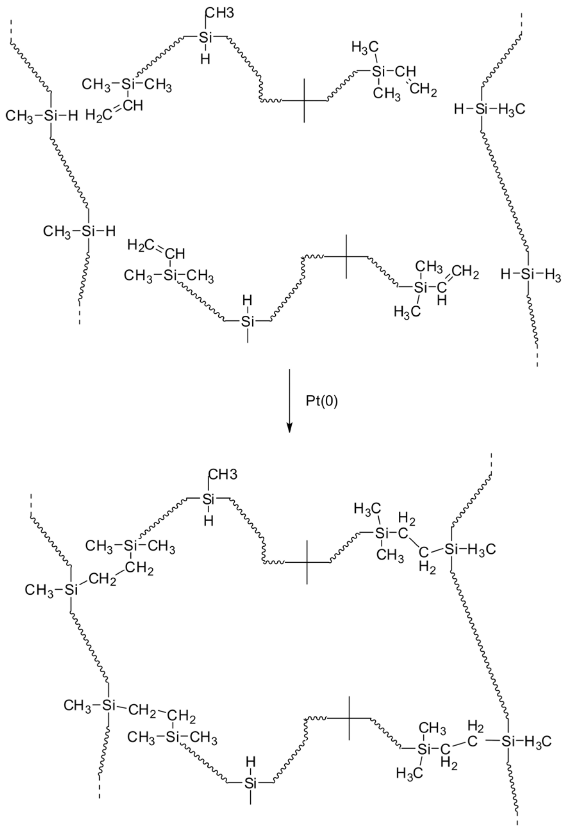
The above described process yields uniform spherical particles with diameters ranging from 30 nm to 2 μm [19, 20]. Diameters of synthesized particles and possible presence of particle aggregates depend on concentration and chemical structure of tetraalkoxysilanes, catalysts (*e.g.*, ammonia or NaOH), pH, and temperature [21–28]. Nowadays the original Stöber method is optimized for the high yield mass production of silica particles with controlled size and porosity.

Tetraethoxysilane (TEOS) is the most often used substrate for synthesis of silica particles by the Stöber method. Syntheses in which at least some part of TEOS were replaced with alkyltrialkoxysilanes yield hybrid microspheres containing structural elements: of silica and of the cross-linked siloxane [29–33]. Chemical structure of such microspheres is shown in Scheme D.

The presence of large alkyl substituents leads to defects in silica structure. Presence of unreacted ≡SiOH groups is also possible in the network.

Microspheres by cross-linking, carried out in emulsion, of polydimethylsiloxane related copolymer containing hydromethylsiloxane constitutional units and terminated with vinyl end-groups at both ends

Microspheres composed of cross-linked polydimethylsiloxane could be prepared also by cross-linking of linear polysiloxanes equipped with needed reactive groups (*e.g.*, vinyl and hydromethylsiloxane) [34]. The synthesis of the



Scheme E. Cross-linking of polysiloxanes containing hydromethylsilane and vinyl groups

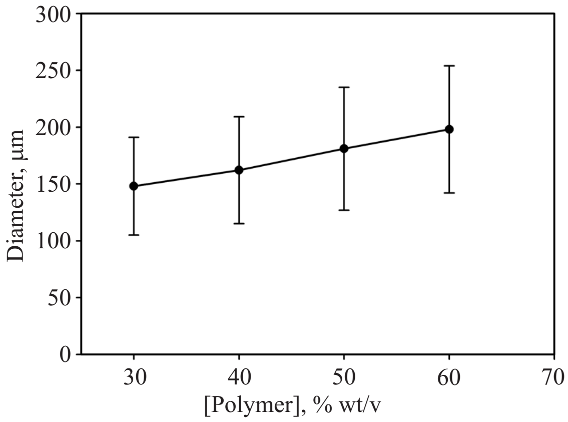


Fig. 1. Diameters of cross-linked polysiloxane microspheres as a function of the concentration of polysiloxane with vinyl and hydromethylsiloxane end-groups in chloroform solution (based on Ref. [34])

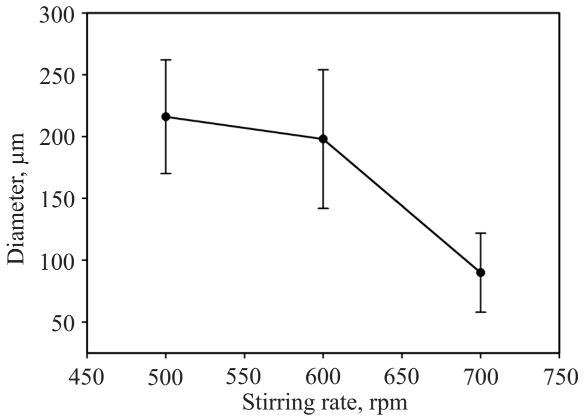
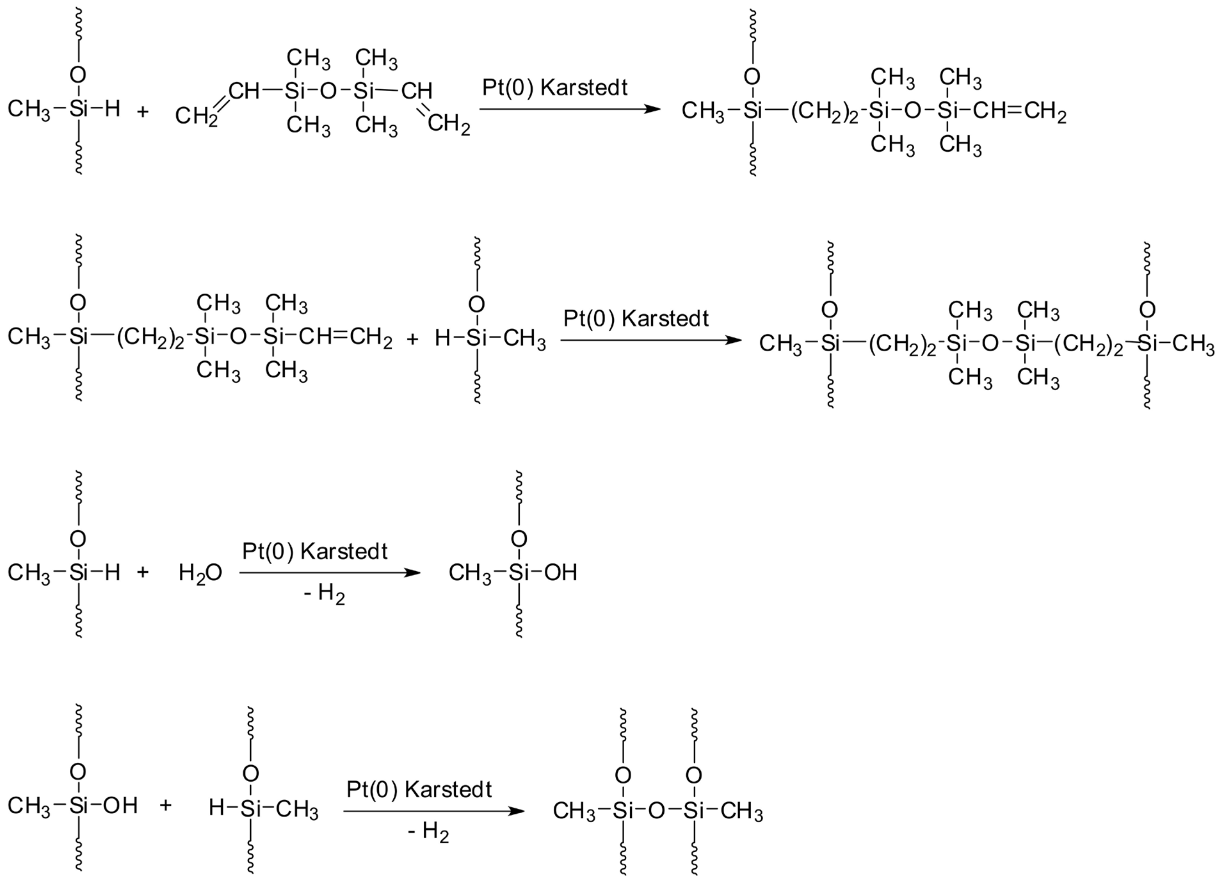


Fig. 2. Diameters of cross-linked polysiloxane microspheres as a function of stirring rate during synthesis (based on Ref. [34])

microspheres was performed in an emulsion of functionalized polydimethylsiloxane diluted with chloroform. The process consists in mixing the above-mentioned solution with solution of platinum catalyst, and emulsifying this mixture in water solution of poly(vinyl alcohol) (1.5 % wt/v). The cross-linking proceeds in droplets of polymer solution. The reaction is carried out for 8 h at 45 °C with continuous stirring with the rate in a range from 500 to 700 rpm. The process of cross-linking is outlined in Scheme E.

It is worth noting that the diameter of produced microspheres is a function of the concentration of polymer in the feed and of the rate of stirring. Diameters of microspheres increased with the increasing concentration of polymer in chloroform solution (see Fig. 1). Apparently,



Scheme F. Reactions involved in synthesis of cross-linked polysiloxane microspheres from linear polysiloxanes with some hydromethyl groups

the more concentrated and thus, more viscous polymer solution yielded the larger droplets. It should be also noted that the higher rate of stirring leads to the smaller microspheres (see Fig. 2). Evidently, the faster is the stirring the more efficiently dispersed is the polymer solution.

The process allowed synthesis of the cross-linked polydimethylsiloxane microspheres with diameters in a range from 90 to about 220 μm. The microspheres, after modification of their surfaces, were used as fillers toughening the epoxy resins.

Microspheres by cross-linking of polyhydromethylsiloxane with 1,3-divinyltetramethyldisiloxane

Cross-linked polydimethylsiloxane microspheres with functional ≡SiOH and ≡Si–CH=CH$_2$ groups were synthesized by the catalytic [Pt(0) Karstedt catalyst] hydrosilylation, hydrolysis and dehydrocondensation reactions involving polyhydromethylsiloxane (PHMS) and 1,3-divinyltetramethyldisiloxane (DVTMDS) [35]. The reactions contributing to formation of the microspheres are depicted in Scheme F.

The process included two stages, which did not differ with respect to chemical reactions but to the physical state of the polymerizing system (see Fig. 3).

In a typical synthesis, during the first step the cross-linking of a mixture of PHMS and DVTMDS (mass ratio 4.45 : 1.00) dissolved in chloroform (concentration of reagents 58 % wt/v) initiated with the Karstedt catalyst [$3.4 \cdot 10^{-5}$ wt % of Pt(0) with respect to siloxane reagents] was carried out at 45 °C, with stirring for 9 min, *i.e.*, before gelation started. In a separate experiments it was found that in the above-described system the gelation begins 13 min after the onset of reaction. Then, the mixture containing the partially cross-linked polysiloxane was homogenized (7500 rpm) in water solution of poly(vinyl alcohol) (preheated to 45 °C, proportion of the organic/polysiloxane phase to water was 4.2 % v/v) and the reaction was continued for 48 h. Thereafter, the microspheres were isolated by centrifuging, purified by several times repeated washing with water, isolation by centrifugation and, eventually, lyophilized. Diameters of obtained microspheres were in a range from 3.2 to 15.1 μm, depending on concentration/proportion of reagents and the rate of stirring [35].

^{29}Si and ^{13}C MAS NMR spectra revealed that microspheres contained the structural units shown in Table 1.

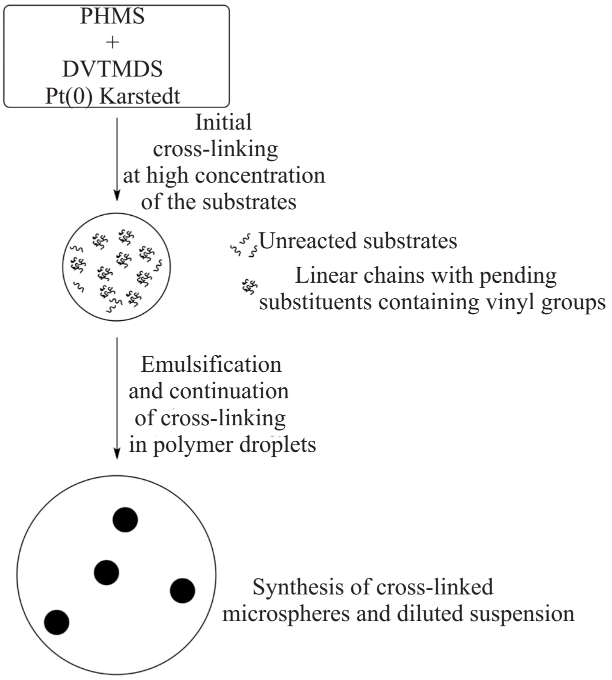


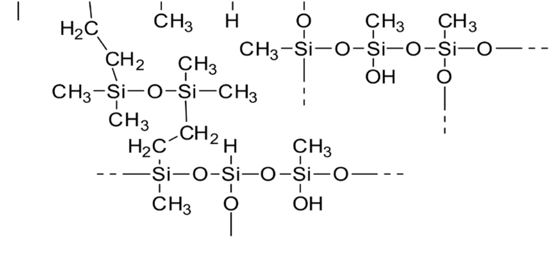
Fig. 3. Preparation of cross-linked polysiloxane microspheres by cross-linking polyhydromethylsiloxane with 1,3-divinyltetramethylsiloxane (based on data from Ref. [35])

Table 1. Structural units in cross-linked polysiloxane microspheres and relevant signals in ^{29}Si and ^{13}C MAS NMR spectra (based on data from Ref. [35])

Structural unit	δ, ppm
^{13}C MAS NMR	
$\underline{\mathrm{C}}\mathrm{H}_3$	-3.2, -0.2, +0.9
$\underline{\mathrm{C}}\mathrm{H}_2$	+9.1, +11.5
^{29}Si MAS NMR	
$\mathrm{CH_3\underline{\mathbf{Si}}(OSi)_3}$	-66.6
$\mathrm{CH_3\underline{\mathbf{Si}}(OH)(OSi)_2}$	-56.5
$\mathrm{CH_3\underline{\mathbf{Si}}(H)(OSi)_2}$	-36.8
$\mathrm{CH_3\underline{\mathbf{Si}}(CH_2)(OSi)_2}$	-20.3
$\mathrm{(CH_3)_2\underline{\mathbf{Si}}(CH_2)(OSi)}$ and $\mathrm{(CH_3)_3\underline{\mathbf{Si}}O}$	+8.0

The above-mentioned NMR data combined with IR absorption signals (cm^{-1} at max) of the following linkages: 776 Si–C (str), 841 Si–C (rock), 906 Si–OH (str), 1029, 1106, 1139 Si–O (str), 1276 CH$_3$ (sym def), 1416 CH$_3$ (asym def), 2175 Si–H (str), 2916, 2972 C–H (str), 3430 O–H (str), fully support the following structure of polymer in the microspheres (see Scheme G).

Integration of signal intensities in the NMR spectra allowed determination of the fractions of the initial ≡SiH groups converted during synthesis into the ≡SiO– and



Scheme G. Chemical structure of polysiloxane microspheres produced from polysiloxanes with some hydromethyl groups

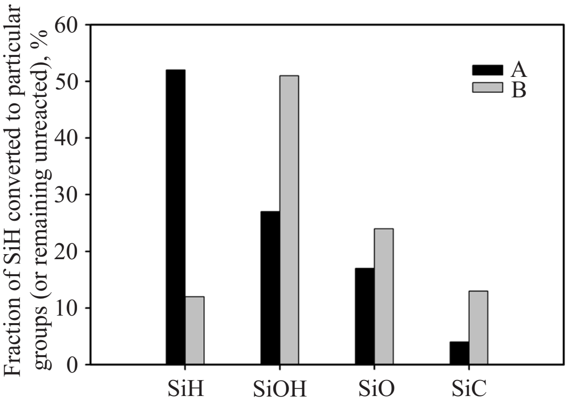


Fig. 4. Fractions of structural elements in the cross-linked polysiloxane microspheres (based on data from Ref. [35]); sample A was obtained without initial cross-linking in concentrated solution, sample B with the initial cross-linking carried out for 9 min

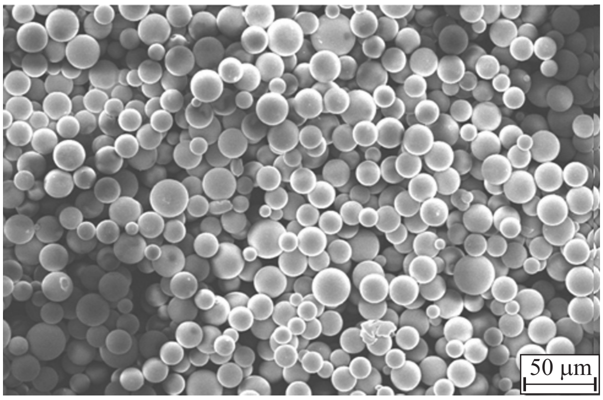


Fig. 5. SEM microphotograph of the cross-linked polysiloxane microspheres

≡SiC≡ and those remaining unreacted (as ≡SiH). Example fractions of these groups are shown in Fig. 4.

Plots in Fig. 4 reveal importance of the primary cross-linking in concentrated solution. Samples A and B were obtained without and with initial cross-linking in concentrated solution (carried out for 9 min). The first cross-linking step in high concentration of reagents assures high conversion of ≡SiH groups and their involvement in formation of the network.

SEM microphotograph shown in Fig. 5 shows that indeed, the product is in the form of spherical particles.

MODIFICATION OF POLYSILOXANE MICROSPHERES

Functionalization of cross-linked polysiloxane microspheres

Cross-linked polysiloxane microspheres obtained in the process involving polyhydromethylsiloxane and 1,3-divinyltetramethyldisiloxane (earlier described) contain the high fraction of ≡SiOH groups produced by hydrolysis of ≡SiH groups in polyhydromethylsiloxane (from 20 to 67 % of the primary SiH groups) [35]. These

T a b l e 2. Structural units in functionalized cross-linked polysiloxane microspheres and relevant signals in ^{29}Si and ^{13}C MAS NMR spectra (based on data from Ref. [35])

Structural unit	δ, ppm
Microspheres functionalized with (3-aminopropyl)-triethoxysilane	
^{13}C MAS NMR	
$\underline{\mathbf{C}}\mathrm{H_3Si}$	-2.4
$\underline{\mathbf{C}}\mathrm{H_2Si}$, $\underline{\mathbf{C}}\mathrm{H_3CH_2O}$	+9.7
$\mathrm{CH_2}\underline{\mathbf{C}}\mathrm{H_2CH_2}$	+27.5
$\underline{\mathbf{C}}\mathrm{H_2N}$	+45.15
$\mathrm{CH_3}\underline{\mathbf{C}}\mathrm{H_2O}$	+50.1
^{29}Si MAS NMR	
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(OSi)_3}$	-66.8
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(OH)(OSi)_2}$	-58.4
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(CH_2)(OSi)_2}$	-20.6
$\mathrm{(CH_3)_2}\underline{\mathbf{Si}}\mathrm{(CH_2)(OSi)}$ and $\mathrm{(CH_3)_3}\underline{\mathbf{Si}}\mathrm{O}$	+8.5
Microspheres functionalized with (3-glycidyloxypropyl)-trimethoxysilane	
^{13}C MAS NMR	
$\underline{\mathbf{C}}\mathrm{H_3Si}$	-3.4
$\underline{\mathbf{C}}\mathrm{H_2Si}$	+8.7
^{29}Si MAS NMR	
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(OSi)_3}$	-67.3
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(OH)(OSi)_2}$	-58.1
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(CH_2)(OSi)_2}$	-21.75
$\mathrm{(CH_3)_2}\underline{\mathbf{Si}}\mathrm{(CH_2)(OSi)}$ and $\mathrm{(CH_3)_3}\underline{\mathbf{Si}}\mathrm{O}$	+7.9
Microspheres functionalized with dimethylvinylchlorosilane	
^{13}C MAS NMR	
$\underline{\mathbf{C}}\mathrm{H_3Si}$	-0.1, +0.1
$\underline{\mathbf{C}}\mathrm{H_2Si}$	+9.3
$\underline{\mathbf{C}}\mathrm{H_2{=}CH}$	+132.1
$\mathrm{CH_2{=}}\underline{\mathbf{C}}\mathrm{H}$	+139.0
^{29}Si MAS NMR	
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(OSi)_3}$	-66.7
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(OH)(OSi)_2}$	-57.2
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(H)(OSi)_2}$	-36.7
$\mathrm{CH_3}\underline{\mathbf{Si}}\mathrm{(CH_2)(OSi)_2}$	-21.5
$\mathrm{(CH_3)}\underline{\mathbf{Si}}\mathrm{(CH{=}CH_2)(OSi)_2}$	-3.1
$\mathrm{(CH_3)_2}\underline{\mathbf{Si}}\mathrm{(CH_2)(OSi)}$ and $\mathrm{(CH_3)_3}\underline{\mathbf{Si}}\mathrm{O}$	+8.3

groups could be used for further functionalization of the microspheres. Functionalization was carried out in reaction of the microspheres with alkylalkoxy or alkylchlorosilanes, in which alkyl substituents were bearing amine, epoxy, and vinyl groups: (3-aminopropyl)-triethoxysilane, (3-glycidyloxypropyl)trimethoxysilane and dimethylvinylchlorosilane [35]. The reactions were carried out in toluene [for (3-aminopropyl)triethoxysilane and (3-glycidyloxypropyl)trimethoxysilane] or, in dichloromethane containing $N(CH_2CH_3)_3$ added as proton scavenger for dimethylvinylchlorosilane. The functionalization was monitored by ^{13}C and ^{29}Si MAS (magic angle spinning) NMR spectroscopy. Structures of observed groups and positions of their relevant signals in the NMR spectra are shown in Table 2.

Efficiency of functionalization is shown in Table 3.

Table 3. Efficiency of functionalization of the cross-linked polysiloxane microspheres (based on data from Ref. [35])

Modifying silane (M)	M/SiOH	M attached mol %	Fraction of SiOH involved in binding alkoxysilane mol %
(3-Aminopropyl)-triethoxysilane	1.79	–	62
(3-Glycidyloxypropyl)-trimethoxysilane	0.67	99	–
Dimethylvinyl-chlorosilane	3.45	8.7	–

The microspheres with ammonium cations were obtained by reacting their ≡SiOH groups with functional chlorosilanes, for example, with *N*-[3-(dimethylchlorosilyl)-propyl]-imidazole hydrochloride or with 3-chloropropylmethyldichlorosilane. In the latter case the chloropropyl groups attached to the microspheres are subjected to further reaction with *n*-octyldimethylamine [36].

Cross-linked polysiloxane microspheres with tailored hydrophilicity

Microspheres synthesized by cross-linking polyhydromethylsiloxane in emulsion (see earlier text) contain a significant amount of ≡SiOH groups making them hydrophilic. Tailoring of hydrophilic/hydrophobic balance of the microspheres could be controlled either during synthesis in emulsion, which is carried out in presence of *iso*-propanol, or by post-modification of microspheres containing ≡SiOH groups [35, 37]. In the first case, dehydrocondensation involving ≡SiH groups of polyhydromethylsiloxane and *iso*-propanol leads to formation of the $\equiv Si{-}OCH(CH_3)_2$ groups whereas, in the latter, in reaction of ≡SiOH and $ClSi(CH_3)_3$ the hydrophobic $\equiv Si{-}O{-}Si(CH_3)_3$ groups are formed.

Hydrophobic/hydrophilic balance of the microspheres was determined using Rose Bengal as a probe. Rose Bengal, a fluorescent dye, being more efficiently adsorbed on hydrophobic surfaces is often used for this purpose [38, 39].

Hydrophobicity of microspheres with certain fractions of ≡SiOH groups replaced by $\equiv Si{-}O{-}CH(CH_3)_2$ or $\equiv Si{-}O{-}Si(CH_3)_3$ groups increased in the following order: not modified microspheres(0) < 13 % of ≡SiOH replaced with $\equiv Si{-}O{-}CH(CH_3)_2$ < 42 % of ≡SiOH replaced with $\equiv Si{-}O{-}CH(CH_3)_2$ < 15 % ≡SiOH replaced by $\equiv Si{-}O{-}Si(CH_3)_3$ [38].

SELECTED APPLICATIONS OF CROSS-LINKED POLYSILOXANE MICROSPHERES

Cross-linked polysiloxane microspheres as preceramic materials

It is well known that pyrolysis of organosilicon polymers (*e.g.*, polysiloxanes, polysilsesquioxanes, polycarbosiloxanes, and polycarbosilanes) carried out in air yields ceramic materials rich in SiO_2 and in oxycarbide phases [40]. These materials have very good thermal, chemical and mechanical properties. They withstand temperatures up to 1500 °C. However, the ceramization process is inevitably accompanied with evolution of volatile products and loss of volume (linear shrinkage from 20 to 30 %). Significant shrinkage leads to distortion of shape and mechanical stress resulting in the unwanted cracks. The above-mentioned problem could be alleviated by filling the preceramic matrix with passive fillers, which do not change their volume on heating. The best candidates for this purpose are the ceramic silicon oxycarbide particles, because their thermal expansion coefficient matches that of the ceramics formed by heating of the preceramic matrix. Preferably, the fillers should have a regular shape, *e.g.* spherical, making their packing easier. Recently, fabrication of ceramic silicon oxycarbide (SiOC) microspheres was reported [41]. The SiOC microspheres were obtained by ceramization of the cross-linked polysilane microspheres, synthesis of which was described earlier of this paper. Detailed description of the process was given in Ref. [41]. Samples of the preceramic microspheres were heated in argon atmosphere from room to the predetermined high temperatures. The heating rate was 10 °C/min from room to the selected 400, 700 and 1000 °C maximum temperatures. In the latter case, the ceramic material was obtained. The samples were kept at the maximum temperatures for 1 hour. Then, the heating was switched off and the samples were cooled down to the room temperature in flowing argon.

It is worth noting that after heating the microspheres retained their spherical shape and were free of cracks (Fig. 6).

Chemical structure of preceramic microspheres and microspheres fabricated by the ceramization process were determined by ^{29}Si MAS NMR [41]. Mol fractions of various silicon-containing units present in these microspheres are shown in Figs. 7 and 8.

The microspheres heated at 400 °C remained white and they contained the same chemical groups as the pristine

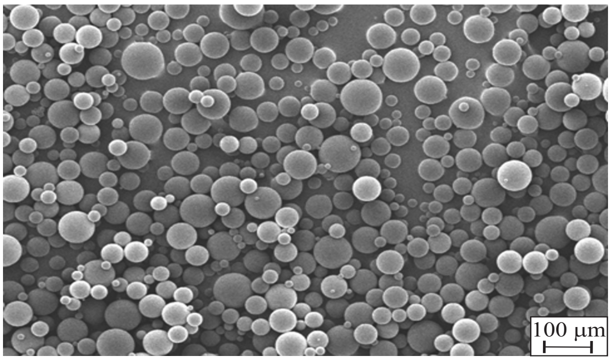


Fig. 6. SEM microphotograph of the microspheres obtained from the cross-linked particles heated at 700 °C

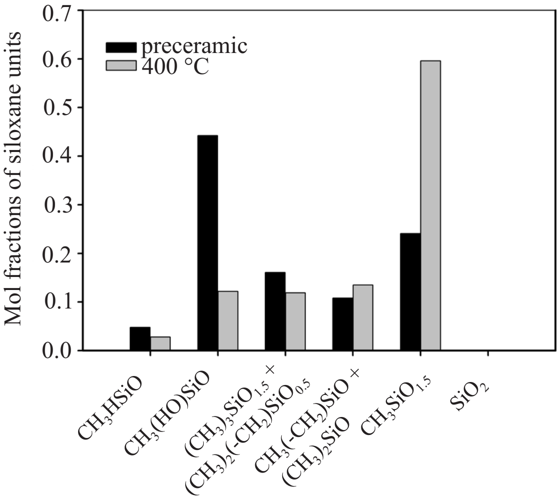


Fig. 7. Chemical structure of the polysiloxane microspheres obtained by cross-linking polyhydromethylsiloxane with 1,3-divinyltetramethylsiloxane (based on data from Ref. [41])

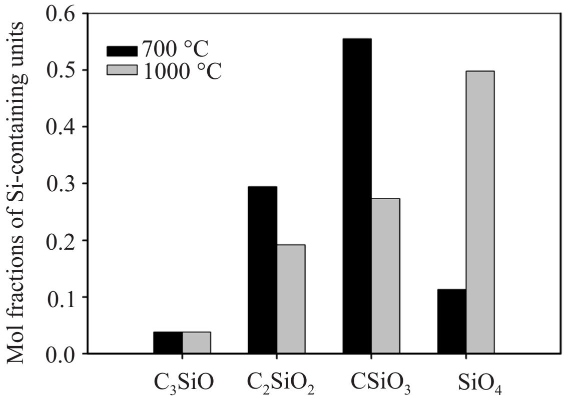


Fig. 8. Chemical structure of the microspheres obtained from the cross-linked particles heated at 700 °C

polysiloxane microspheres (see Fig. 7). However, it should be noted that heating at 400 °C led to significant reduction of the fraction of $CH_3(HO)SiO$ and increase of the $CH_3SiO_{1.5}$ of units, which is due to dehydrocondensation reaction (last reaction in Scheme F).

Heating at 700 °C and 1000 °C yielded brownish and black microspheres, respectively, which suggests formation of the free carbon. Indeed, combination of elemental analysis and ^{29}Si MAS NMR data obtained during the above-mentioned and more recent studies revealed that in addition to siloxane and silicon oxycarbide units the particles contain free carbon in amount up to 20 wt % [41, 42].

Cross-linked polysiloxane microspheres as solid supports for adsorption of proteins and carriers of covalently immobilized platinum and palladium catalysts

The cross-linked polysiloxane microspheres with tailored surface properties could be used for fabrication of functional microparticles. Microspheres with adsorbed and covalently immobilized immunoglobulins and other proteins are useful components of diagnostic kits and devices [43–47]. Recent studies revealed that γ-globulins could be efficiently adsorbed onto the hydrophobized microspheres (see earlier text) yielding particles with surface concentration of adsorbed protein up to 16 mg/m^2 [36, 37].

Polysiloxane microspheres were tested also as carriers of platinum [Pt(0), Pt(II)] and palladium [Pd(II)/Pd(0)] catalysts [48–51]. The systems (polysiloxane microspheres)-Pt(0) and -Pt(II) were used as catalysts of the hydrosilylation of phenylacetylene and hydrogenation of cinnamaldehyde [49]. The palladium catalyst immobilized on the polysiloxane microspheres was used for carbonylative Suzuki-Miyaura cross-coupling of aryl iodides with phenylboronic acids [50, 51].

In the case of immobilization of the platinum catalysts the microspheres were first functionalized by the reaction of –OH groups of the microspheres with *N*-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane. Thereafter, they were converted to the microsphere-catalyst system in reaction with K_2PtCl_4. Platinum II attached to the polysiloxane microspheres was reduced to Pt(0) in reaction with $NaBH_4$. Palladium catalyst was obtained by functionalization of the polysiloxane microspheres with (3-aminopropyl)triethoxysilane and subsequent immobilization of Pd(II) in reaction with $PdCl_2(MeCN)_2$ [51]. It has been shown that at the conditions of the Suzuki-Miyaura cross-coupling reactions part of the immobilized Pt(II) is converted into Pt(0) containing clusters.

Phase-change microcapsules with cross-linked polysiloxane shells

Chemical reactions involved in synthesis of polysiloxane microspheres by cross-linking of polyhydromethylsiloxane with 1,3-divinyltetramethyldisiloxane could be used also for fabrication of microcapsules with cross-linked polysiloxane shells. The phase-change microcapsules with paraffin (*n*-eicosane) cores were synthesized using this approach [52]. The process did consist of three stages. During the first one the cross-linking of polyhydromethylsiloxane (PHMS) with 1,3-divinyltetramethyldisiloxane (DVTMDS) was carried out in THF, using the Karstedt Pt(0) complex as a catalyst. The reaction was carried out at 45 °C until the solution became viscous, but did not form yet the macroscopic gel. At this stage the reacting solution of polyhydromethylsiloxane and 1,3-divinyltetramethyldisiloxane was mixed with solution of *n*-eicosane in *iso*-propanol and the reaction was continued at 45 °C for 5 more minutes. Thereafter, the mixture was added to water containing poly(vinyl alcohol) (reaction mixture : water = 0.8 : 1 v/v), homogenized and diluted with six-fold excess of water containing poly(vinyl alcohol). Then, the reaction was continued for 70 hours, with stirring, at 45 °C. Eventually, the formed microcapsules were isolated by sedimentation and several times were washed with fresh portions of water. SEM microphotograph of the microcapsules is shown in Fig. 9.

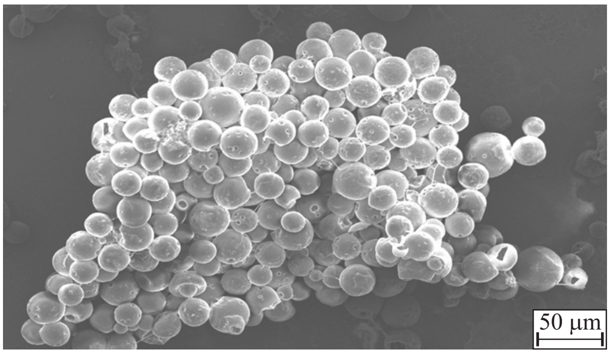


Fig. 9. Microcapsules with cross-linked polysiloxane shells and *n*-eicosane cores

Depending on proportions of used reagents the microspheres with diameters from 5.9 to 22.9 μm were obtained. Phase change temperatures (melting and crystallization of *n*-eicosane in the microspheres) were in the range 35–42 °C and 34–22 °C, respectively; the heat of melting was up to 160 J/g.

CONCLUSIONS

Cross-linking of polyhydromethylsiloxane with 1,3-divinyltetramethyldisiloxane, carried out in emulsion, did open a simple and convenient way for synthesis of the library of microspheres and microcapsules. The library contains soft polysiloxane microspheres with controlled hydrophobic/hydrophilic balance, varied porosity, particles with amine, epoxide and vinyl functions as well as hard ceramic microspheres.

Post-synthesis modification of the pristine cross-linked polysiloxane microspheres containing ≡SiH and ≡SiOH functions during their reactions with alkoxy- or chlorosilanes bearing various functional groups, allows for synthesis of functionalized microparticles. These particles were used as carriers of proteins as well as platinum and palladium catalysts. The cross-linked polysiloxane microspheres could be converted to the silicon oxycarbide ceramic microspheres – potential fillers for fabrication of ceramic materials.

The method, similar to those used for synthesis of cross-linked polysiloxane microspheres allowed obtaining microcapsules loaded with *n*-eicosane. The microcapsules were suitable for application as phase-change materials appropriate for maintaining temperature within the range from 22 °C to 42 °C.

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