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Softening of Octyl-modified Phenylsilsesquioxanes

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Abstract

Octyl-modified phenylsilsesquioxanes were prepared from phenyltriethoxysilane and octyltriethoxysilane by two-step acid-base catalysed sol-gel process. Resulting silsesquioxanes were characterized by scanning electron microscopy, X-ray diffraction analysis, gel permeation chromatography and Fourier-transform infrared spectroscopy, while the thermal properties were investigated by differential scanning calorimetry and thermogravimetric analysis. Morphology of polysilsesquioxanes was found to greatly depend on ratio of alkoxides, presumably because of poor miscibility of long alkyl chains which results in a less homogeneous initial mixture. Long alkyl chains also present steric hindrance to condensation of phenyltriethoxysilane eventually preventing the formation of particles. Incomplete condensation caused the decrease of softening temperature from 160°C to ~50°C and overall poorer thermal stability of polysilsesquioxanes. Decrease in initial temperature of degradation by at least 150°C is probably caused by alkyl chains exposed on the surface of the particles. Increased solvent content improves incorporation of octyl chains due to better solubility and yields polysilsesquioxanes with a more regular structure and a more homogeneous particle size distribution. On the other hand it adversely influences the level of condensation and the softening temperature.

KEY WORDS:
organic-inorganic hybrid material
polysilsesquioxanes
sol-gel process
thermal properties

KLJUČNE RIJEČI:
organsko-anorganski hibridni materijal
polisilseskvioksani
sol-gel postupak
toplinska svojstva

Omekšavanje fenilsilseskvioksana modificiranih oktilnim lancima

Sažetak

Fenilsilseskvioksani modificirani oktilnim lancima pripravljeni su od feniltrietoksisilana i oktiltrietoksisilana dvostupanjskim kiselobaznim sol-gel postupkom. Nastali silseskvioksani karakterizirani su pretražnom elektronskom mikroskopijom, rendgenskom difrakcijskom analizom, kromatografijom na propusnom gelu i spektroskopijom u infracrvenom području s Fourierovim transformacijama, dok su njihova toplinska svojstva ispitivana razlikovnom pretražnom kalorimetrijom i termogravimetrijskom analizom. Ustanovljeno je da morfologija polisilseskvioksana uvelike ovisi o omjeru polaznih alkoksida, vjerojatno zbog slabe topljivosti dugih alkilnih lanaca i time nehomogenije početne smjese. Dugački alkilni lanci također sterički ometaju kondenzaciju feniltrietoksisilana, što konačno onemogućava nastajanje čestica. Nepotpuna kondenzacija uzrokuje sniženje omekšavališta sa 160 °C na ~50 °C i općenito slabiju toplinsku postojanost nastalih polisilseskvioksana. Sniženje početne temperature razgradnje za 150 °C vjerojatno je posljedica izloženosti alkilnih lanaca na površini čestica. Povećan udio otapala poboljšava ugradnju oktilnih lanaca zbog njihove bolje topljivosti i daje polisilseskvioksane pravilnije strukture i homogenije raspodjele čestica. No dodatak otapala negativno utječe na stupanj kondenzacije i omekšavalište polisilseskvioksana.

Introduction

Organic-inorganic hybrid materials unite properties of organic and inorganic materials, resulting in materials with hardness and stability of inorganic glasses and also flexibility and low-temperature processing of polymeric materials.[1,2] Wide application potential has caused ever growing interest in these materials in the recent years. Polysilsesquioxanes, $RSiO_{3/2}$ (where R stands for an organic group), are a class of hybrid materials with unique thermal, optical and mechanical properties,[3-5] mostly prepared by sol-gel process[6-11] from trifunctional organically modified alkoxysilanes, $RSi(OR')_3$ (OR' – an alkoxy group). The composition and consequently the properties of the polysilsesquioxanes can be easily modified by addition of different precursors in the starting mixture.[8] Among polysilsesquioxanes, phenylsilsesquioxanes (PhSSQs) have drawn much attention, and synthesis of $PhSiO_{3/2}$ particles was reported (Ph stands for a phenyl group, C_6H_5).[9-11] In previous research it was demonstrated that $PhSiO_{3/2}$ particles prepared by the two-step acid-base catalysed sol-gel process exhibit glass transition and softening when heated.[11] In this manner transparent thick films were formed by electrophoretic deposition and subsequent heat treatment of the particles,[12] and convex-shaped $PhSiO_{3/2}$ microlens arrays could be obtained on a hydrophobic-hydrophilic-patterned surface.[13] Thin coatings based on PhSSQ with improved adhesion to polycarbonate substrate were also prepared by dip-coating.[14] PhSSQ nanoparticles can be used as a component of flame-retardant systems,[15] while surface-sulfonated PhSSQs are prospective solid proton-conducting electrolytes.[16,17] Softening temperature of PhSSQs depends on the level of condensation, which can be controlled by conditions of synthesis,[18] co-condensation with alkyl-alkoxysilanes[19] or use of diphenylalkoxysilanes.[20]

In this paper, influence of alkyl modification of PhSSQ with octyl chain is presented. The influence of precursor ratio and solvent content on morphology, thermal properties and level of condensation of resulting hybrid polysilsesquioxanes was investigated.

Experimental

Preparation of modified particles

Octyl-modified PhSSQ particles were prepared by two-step acid-base catalysed sol-gel procedure, using ethanol (EtOH) as solvent, according to Figure 1. Phenyltriethoxysilane, $C_6H_5Si(OC_2H_5)_3$, and octyltriethoxysilane, $C_8H_{17}Si(OC_2H_5)_3$, provided by Shinetsu, were used as starting materials. Molar ratio of silanes : EtOH : H_2O (0.01% HCl): H_2O (4% NH_4OH) = 1 : 20 : 20 : 180 were used. The influence of solvent quantity was also studied, varying molar ratio of ethanol to silanes in 0-100 range. Ratio of phenyl and octyl alkoxysilanes and designation of modified PhSSQs are given in Table 1. Unmodified octylsilsesquioxane, $C_8H_{17}SiO_{3/2}$ (OcSSQ) was also prepared.

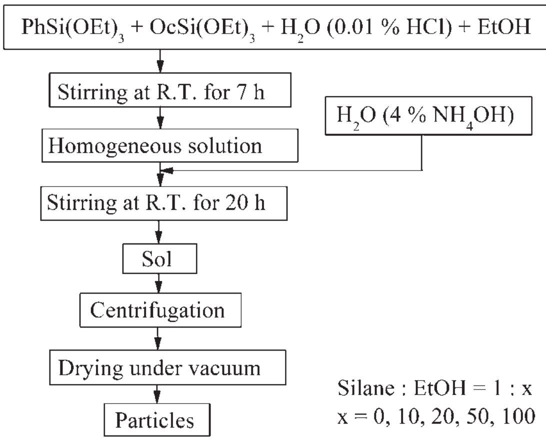

FIGURE 1 - Synthesis of modified PhSSQs

TABLE 1 - Influence of ratios of phenyl (Ph) and octyl (Oc) alkoxysilanes and ethanol: silane ratio on appearance of modified PhSSQs

Designation	Ph:Oc	EtOH : silane	Appearance
PhSSQ	1 : 0	20	Powder
PhOc02Et00	0.8 : 0.2	0	Powder
PhOc02(Et20)		20	
PhOc02Et50		50	
PhOc03	0.7 : 0.3	20	Powder + amorphous
PhOc04Et10	0.6 : 0.4	10	Rubbery + powder
PhOc04(Et20)		20	Rubbery
PhOc04Et50		50	Tacky rubber
PhOc04Et100		100	Viscous fluid
OcSSQ	0 : 1	20	Viscous fluid

Ethanol and 0.01% HCl were mixed in a reaction vessel, and when the mixture was homogeneous phenyl- and octylalkoxysilane were added and left to stir for 7 hours. Obtained clear sol was added to 4% NH_4OH and left to stir for additional 20 hours. The resulting suspension was centrifuged at 10 000 rpm for 30 minutes, supernatant fluid was decanted and in cases when it was not transparent kept for analysis. The silsesquioxanes were dried under vacuum.

Instrumental methods

Morphology of polysilsesquioxanes was investigated on gold-sputtered samples by scanning electron microscopy (SEM) with 20 kV accelerating voltage on *JEOL JSM-5300* microscope.

Glass transition temperature was measured by differential scanning calorimetry (DSC) on *Perkin Elmer Pyris* 1 instrument equipped with Intercooler unit, on samples weighing ~5 mg, under protective nitrogen atmosphere. Specimens were cooled to starting temperature of -20°C and heated to 200°C with the heating/cooling rate of 20 K/min, except for samples OcSSQ, PhOc04Et50 and PhOc04Et100, which were cooled to -50°C with cooling rate of 2 K/min and heated to 100°C with 20 K/min. All samples were heated from start to end temperature twice, to check the reversibility of the glass transition.

Thermal stability of polysilsesquioxanes was investigated by combined differential thermal and thermogravimetric analysis (DTA-TGA) on *Rigaku Thermo plus 8120* instrument on specimens weighing ~5 mg, with heating rate of 10 K/min in temperature interval 25-900°C and air flow of 200 ml/min.

The level of condensation of polysilsesquioxanes was investigated by gel permeation chromatography (GPC) on *Shimadzu* system (*LC-10AD* pump, *RID-6A* detector, *CTO-10A* column oven) with a combination of two *Shodex* silica-gel columns (*CF-310HQ* and *GF-7MHQ*) and tetrahydrofuran (THF) as an eluent, at 40°C. Particles were prepared as 0.2 weight% solution in THF, while supernatant fluid was diluted with THF in 3 : 1 weight ratio. Prior to analysis the samples were filtered through a membrane filter with 0.45 µm pore size.

The level of ordering was determined by X-ray diffraction (XRD) on *Shimadzu XRD-6000* instrument.

The composition of polysilsesquioxanes and supernatant fluid was determined by Fourier-transform infrared spectroscopy (FTIR) on *Perkin Elmer Spectrum GX* instrument. The powdery samples were prepared as KBr tablets, with sample 1 weight % (2 mg of sample for 200 mg of KBr) of the tablet. Viscous or liquid samples were spread on silicon wafer

Results and discussion

Well-defined spherical particles were formed only for the octyl-phenyl ratio 0.2, while higher ratios produced a solid phase which was either completely amorphous (ratio 0.4) or a mixture of particles and the amorphous phase (ratio 0.3), as shown in Figure 2. (Term *amorphous* here denotes simply the appearance, not the crystallinity: particles are also non-crystalline.) It is presumed that the silsesquioxane structure is disturbed by presence of large octyl chains. The morphology of PhOc02 particles, $(C_6H_5)_{0.8}(C_8H_{17})_{0.2}SiO_{3/2}$, depends on the solvent content: particle size distribution becomes more homogeneous with increased quantity of solvent, as shown in Figure 3. This can be ascribed to improved solubility of octyl chains which yields a more homogeneous starting solution. But increased quantity of solvent softens the particles so they become soluble in mixture of water and ethanol, as shown in Figure 3 d).

Glass transition temperatures, T_g, of modified PhSSQs can be determined by DSC, but the effect is fairly small and easily overlapped by other thermal effects, which limits the precision of this method. DSC investigation of hybrid polysilsesquioxanes showed a glass transition superimposed with endothermic effect at 50-60°C, which is probably due to evaporation of ethanol and water produced by further condensation of silanol and residual ethoxy groups at temperatures above the

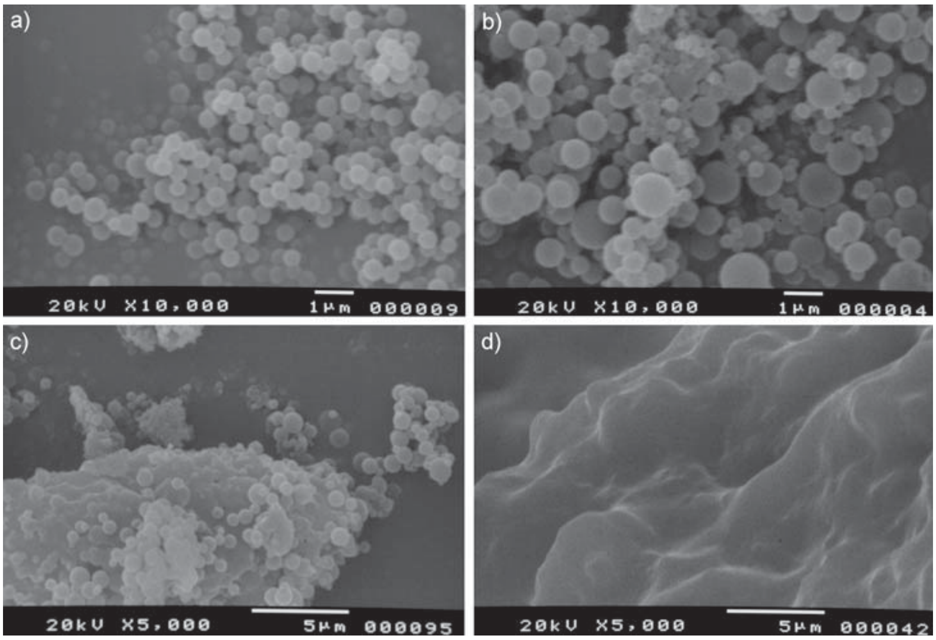

FIGURE 2 - Morphology of alkyl-modified polysilsesquioxanes: a) Ph-SSQ; b) PhOc02; c) PhOc03; d) PhOc04

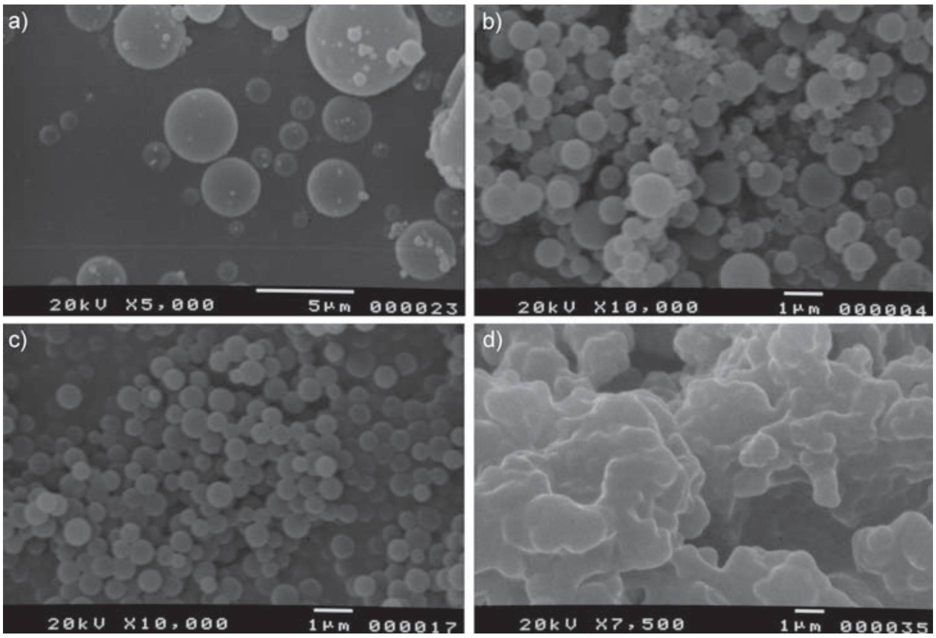

FIGURE 3 - Morphology of PhOc02 particles prepared with different quantities of ethanol: a) PhOc02Et00; b) PhOc02Et20; c) PhOc02Et50; d) PhOc02Et50 dispersed in water and ethanol

glass transition. Since glass transitions proved to be irreversible once the sample was heated above T_g, the endothermic effect could not be removed, and thus T_g could only be determined very roughly. In order to determine the temperature interval of the glass transition, softening of the particles was inspected by SEM after isothermal treatment for 10 minutes at selected temperatures (usually 50, 100, 150 and 200°C). Specimens whose T_g could not be determined by DSC were isothermally treated in the DSC cell to achieve more precise temperature control prior to SEM observation. An example is given in Figure 4, which shows irreversible softening and merging of particles into an amorphous mass after heating at given temperature. The specimens heated at lower temperatures showed no change in appearance.

Glass transition temperatures/intervals are given in Table 2. Increased content of large octyl groups prevents condensation of phenyltriethoxysilane and leads to lower T_g. The amorphous hybrid polysilsesquioxanes did not exhibit a glass transition, and it was marked as below room temperature (<RT). Irreversibility of glass transitions indicates further condensation within polysilsesquioxanes during heating above T_g. Increased solvent content also results in decreased T_g, possibly due to lesser degree of condensation from more dilute solutions.

The thermal stability of octyl-modified PhSSQs decreases significantly in comparison with unmodified PhSSQs, and the initial temperature of degradation, T_d, is somewhat lowered with increasing alkyl content, as can be seen from thermogravimetric and DTA curves in Figure 5, and Table 2. For comparison, DTA curve of OcSSQ ($C_8H_{17}SiO_{3/2}$) is also given (Figure 5b). It can be seen that OcSSQ starts to degrade at much lower temperature in comparison with PhSSQ ($C_6H_5SiO_{3/2}$), but octyl-modified PhSSQs shows exothermal degradation effect at temperature comparable to that of OcSSQ. Presumably octyl chains remain exposed on the surface of the modified PhSSQ particles. The

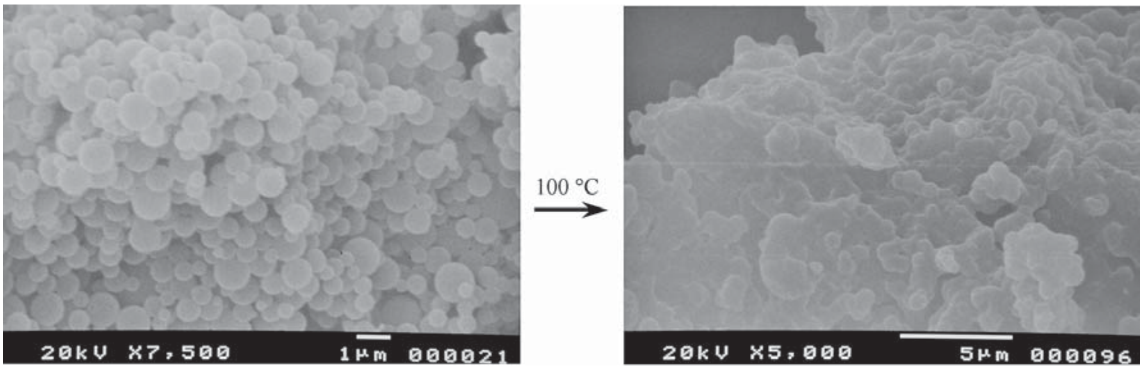

FIGURE 4 - Softening behaviour of PhOc02 as determined by SEM

TABLE 2 - Glass transition temperature, T_g, as determined by DSC or SEM, and initial temperature of degradation, T_d, temperature at which 50% of sample has degraded, T_{50}, and weight content of residue at 800°C, w, determined from TGA curves

Material	T_g / °C	T_d / °C	T_{50} / °C	w / %	$w(SiO_2)$ / %
PhSSQ	~160	~400	633	43.33	46.51
PhOc02Et00	150	~250	598	45.45	44.05
PhOc02Et20	50-100		594	42.90	
PhOc02Et50	50-100		598	41.74	
PhOc03	~50	~230	567	38.84	42.91
PhOc04Et10	Non-detectable	~220	496	41.59	41.83
PhOc04Et20	<RT	~220	514	42.64	
PhOc04Et50	<RT	~220	497	40.25	
PhOc04Et100	<RT	~215	484	36.36	
OcSSQ	<RT	~60	396	33.38	36.35

temperature at which 50% of sample has degraded, T_{50}, and weight content of residue at 800°C, w, are also given in Table 2. T_{50} shows similar decrease with increased octyl content of modified silsesquioxanes as T_d, while for w there is no clear trend. For comparison, theoretical content of SiO_2 in fully condensed polysilsesquioxanes, $w(SiO_2)$, is also given in Table 2. For $w < w(SiO_2)$, it is probable that condensation is not complete, and the residual –OH groups add to mass loss. For $w > w(SiO_2)$, incomplete combustion of carbon char could be the cause. Both effects are probably present in all samples, and they balance out differently in different cases.

The influence of solvent ratio on thermal stability is illustrated in Figure 6 and in Table 2. Thermal stability of PhOc02 particles is not greatly influenced by increased ethanol content in the starting mixture, only w decreases indicating lesser degree of condensation within the particles. PhOc04 polysilsesquioxanes, $(C_6H_5)_{0.6}(C_8H_{17})_{0.4}SiO_{3/2}$, show somewhat greater influence of ethanol content on thermal stability, as T_d and T_{50} as well as w decrease with increased ethanol content. The only exception is PhOc04Et10, possibly because of its two-phase morphology (rubbery and powdered phase). From the differential thermogravimetric (DTG) curves (Figure 7) it is obvious that both PhOc02 and PhOc04 samples degrade in two steps, of which the first (400-500°C) probably corresponds to a species richer in octyl chains. For PhOc02 samples content of these species increases with increased ethanol content, but this effect is much less pronounced for PhOc04 samples.

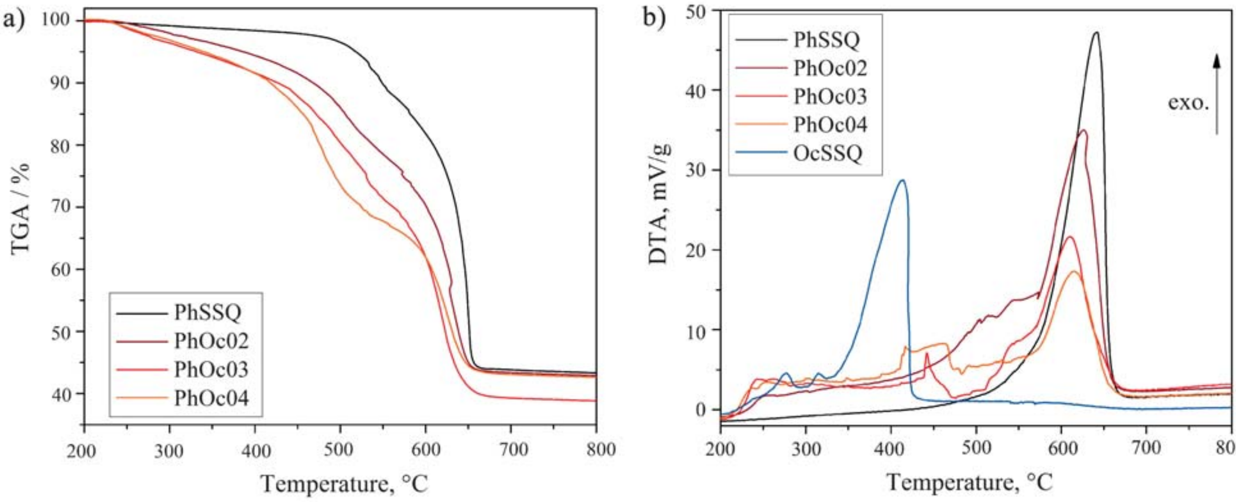

FIGURE 5 - Thermogravimetric (a) and DTA (b) curves for octyl-modified PhSSQs

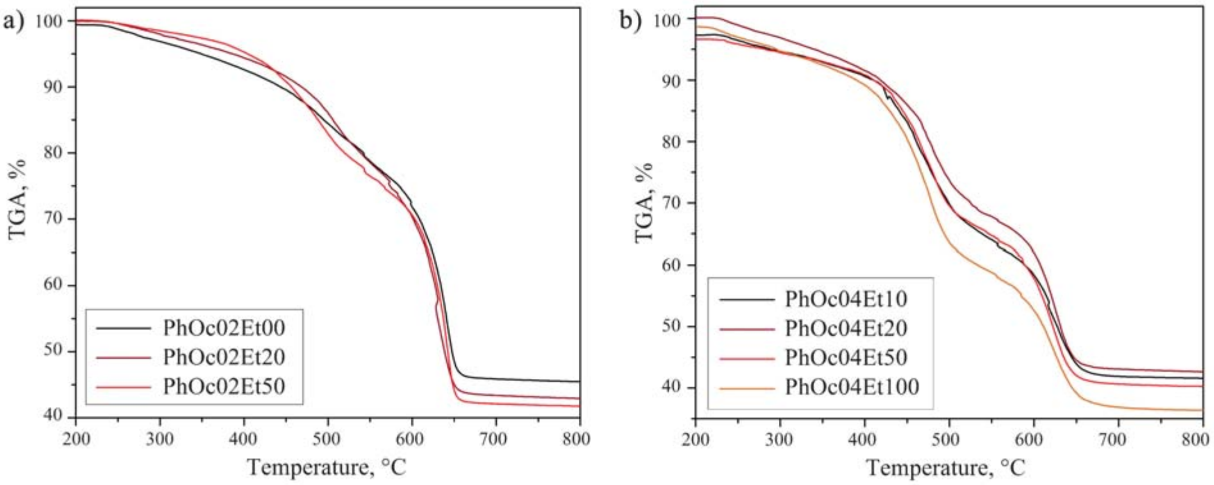

FIGURE 6 - Thermogravmetric curves for a) PhOc02 and b) PhOc04 polysilsesquioxanes

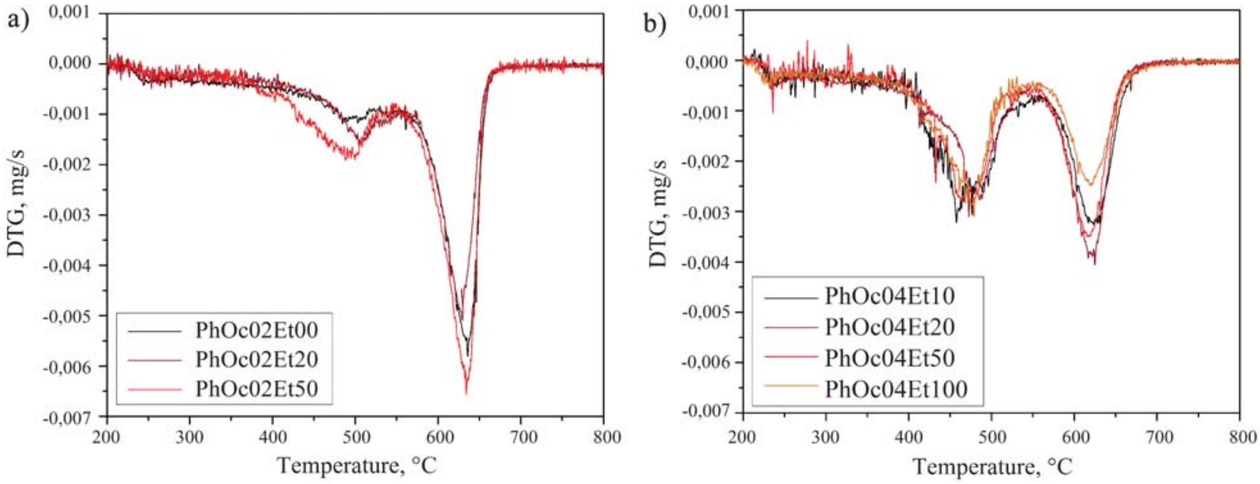

Figure 7 - Differential thermogravimetric curves for a) PhOc02 and b) PhOc04 polysilsesquioxanes

The adverse influence of the increased content of octyl chains and of solvent quantity on level of condensation of the hybrid particles was also determined by GPC (Figure 8). Supernatant fluid of all modified PhSSQs was milky, indicating remaining monomers and oligomers in the supernatant fluid, which was confirmed by GPC. Subsequently, FTIR analysis of PhOc02 supernatant fluid was performed and the presence of both octyl- and phenyl-silane monomers, $C_6H_5Si(OC_2H_5)_3$ and $C_8H_{17}Si(OC_2H_5)_3$, was confirmed. Monomer is also present in

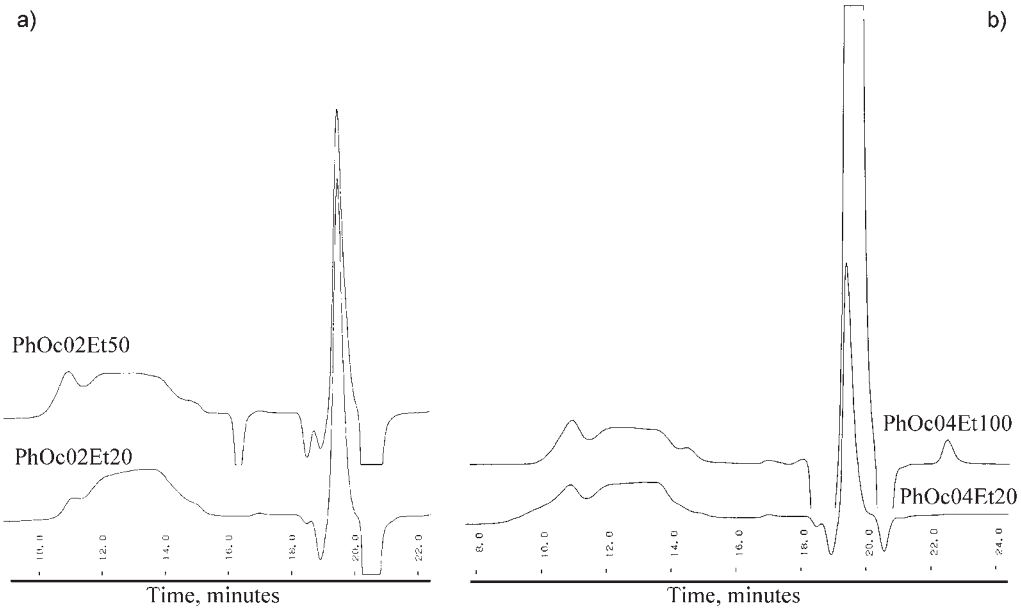

FIGURE 8 - GPC curves of a) PhOc02 and b) PhOc04 polysilsesquioxanes

the modified PhSSQs (peak at ~19 min) and cannot be removed by washing with a mixture of water and ethanol, which indicates that it is trapped within the polysilsesquioxane structure.

The level of ordering in modified PhSSQs can be determined by XRD.[21,22] Diffraction maxima correspond to interplanar distances between repeating structures, *d*, which are calculated from Bragg equation:

$$d \quad \frac{\lambda}{2\sin\theta} \tag{1}$$

where λ is the wavelength of X-rays, λ(CuKα) = 0.15418 nm, and θ is the angle of diffraction. In PhSSQs, position of the first maximum corresponds to interval of long-range ordering within the material (Figure 9), and this distance increases with the increasing content of long octyl chains since silsesquioxane structure has to accommodate them. The parameters determined from the patterns are given in Table 3. It can be seen that interplanar distance, *d*, decreases with increasing solvent content, presumably because better solubility and homogeneity allow more regular arrangement of bulky octyl chains.

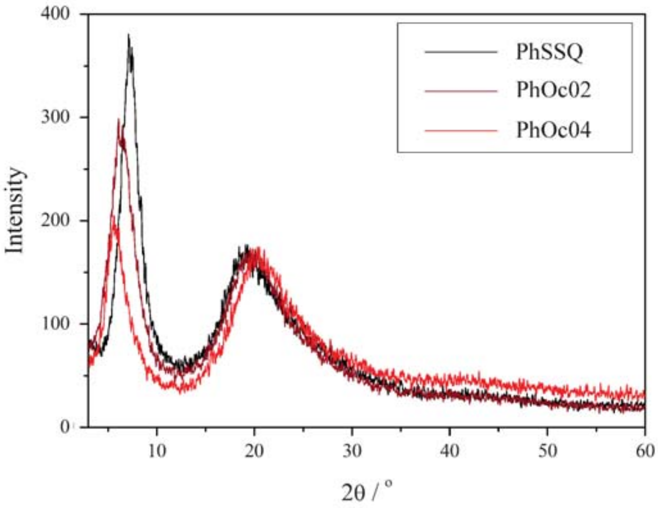

FIGURE 9 - XRD spectra of octyl-modified PhSSQ

TABLE 3 - Interplanar distance, *d*, calculated from the position of the first diffraction maximum by Bragg equation, and ratio of areas of Ph-Si band (~730 cm^{-1}) and Si-C band (698 cm^{-1}) as determined from FTIR spectra

Material	*d* / nm	Ratio
PhSSQ	1.24	1.53
PhOc02Et00	1.49	1.30
PhOc02Et20	1.45	1.32
PhOc02Et50	--	1.18
PhOc03	1.56	1.21
PhOc04Et10	1.63	1.21
PhOc04Et20	1.56	1.01

Composition of alkyl-modified PhSSQ was determined by FTIR, which confirmed the presence of alkyl chains (C-H bands in 3000-2800 cm^{-1} range). Bands characteristic of phenyl group at 1595 and 1430 cm^{-1} are visible in spectra of all samples, as is the wide band characteristic for Si-O bonds between 1200 and 1000 cm^{-1}. The spectra of some samples are given in Figure 10. The decreased intensity of 1595 and 1431 cm^{-1} bands and the Ph-Si band (~730 cm^{-1}) can be used as a measure of modification, as illustrated in Figure 11. Since band intensity (area) depends on the sample preparation (KBr tablet thickness and homogeneity), the most quantitative measure is the ratio of areas of adjoining Ph-Si and Si-C bands (698 cm^{-1}), which is given in Table 3. The smaller the ratio, the greater quantity of alkyl chains in the sample, but more precise determination is impractical since the Ph-Si band overlaps with another band at ~740 cm^{-1}. It seems that there is some influence of ethanol ratio on modification of the samples, but of course the shortcomings of this method should be kept in mind. The samples prepared with larger quantity of ethanol apparently contain more octyl chains, presumably because of improved solubility of octyltriethoxysilane.

Conclusions

The morphology of polysilsesquioxanes prepared by copolymerization of phenyltrialkokysilane with octyltrialkoxysilane was found to greatly depend on the ratio of alkoxides, presumably because of poor miscibility of long alkyl chains resulting in a less homogeneous initial mixture. The size of alkyl chains also presents sterical hindrance to condensation of phenylsilsesquioxanes, so the softening temperature

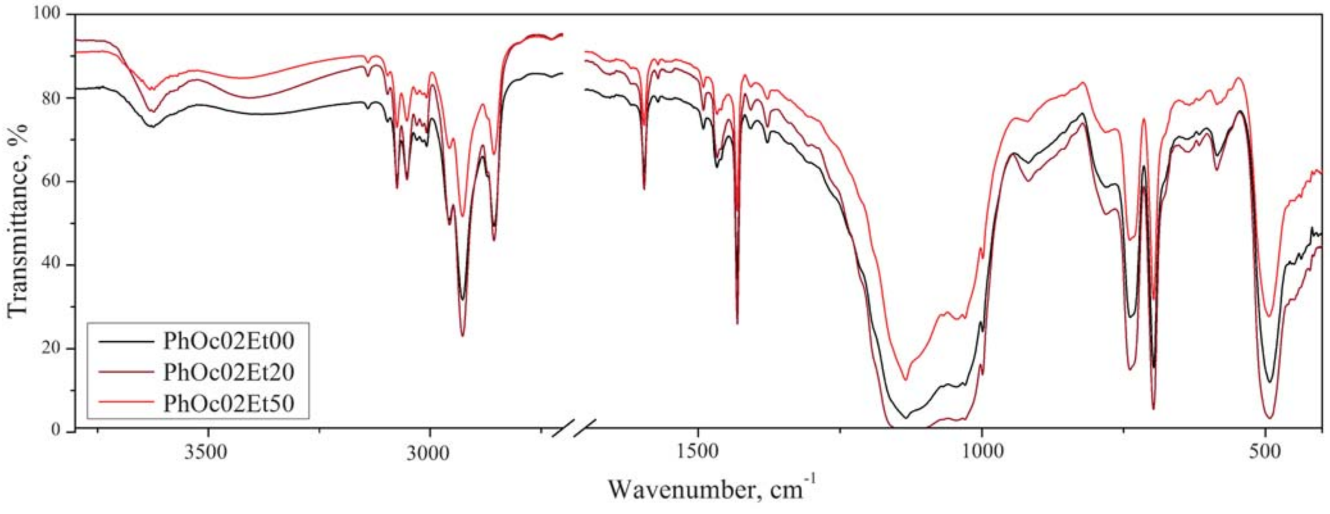

FIGURE 10 - FTIR spectra of PhOc02 polysilsesquioxanes

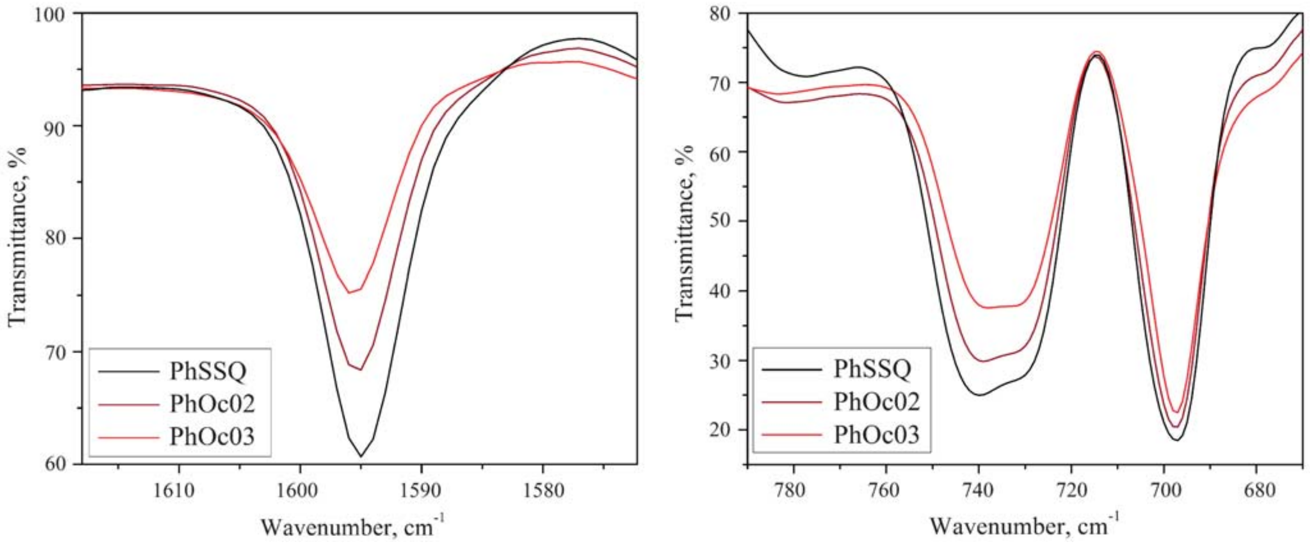

FIGURE 11 - Characteristic bands for semiquantitive analysis of octyl-modification of PhSSQs.

decreases from 160°C for unmodified particles to ~50°C for the modified ones. Decreased condensation level of modified phenylsilsesquioxanes was confirmed by GPC. Increased solvent content and consequently improved solubility of octyltrialkoxysilane yields polysilsesquioxanes with a more regular structure (as determined by XRD) and a more homogeneous particle size distribution. On the other hand it also decreases both softening temperature and level of condensation. The thermal stability of modified particles decreased as expected, with degradation starting at temperature corresponding to degradation of octylsilsesquioxanes, so it can be supposed that long alkyl chains remain exposed on the surface of the particles.

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