



Preceramic polysiloxane networks obtained by hydrosilylation of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane

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ABSTRACT

Preceramic polysiloxane networks were prepared by hydrosilylation of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4^{Vi}) with a series of linear hydrogensiloxanes as well as with a cyclic hydrogensiloxane, namely 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) at various hydrogensiloxane/ D_4^{Vi} molar ratios in the starting reaction mixture. FTIR spectroscopic measurements conducted during the processes as well as for the reaction products allowed to reveal that the rate of D_4^{Vi} hydrosilylation as well as its efficiency are influenced by the type of hydrogensiloxane used and by the reactants molar ratio. Ceramic yields determined at 1000 °C by thermogravimetric analyses were higher for D_4^{Vi} – D_4^H than for D_4^{Vi} –linear hydrogensiloxane networks (86–89% vs 65–76%, respectively). Preceramic polysiloxanes prepared as well as the products of their pyrolysis obtained after thermal investigations were monolithic, pore-less materials.

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1. Introduction

Fabrication of silicon carbon fibers from polycarbosilane [1] followed by their successful commercialization [2] have brought about a great scientific interest in polymeric ceramic precursors. Silicon-containing macromolecular compounds are particularly intensively studied since their pyrolysis provides a range of ceramic materials, some of which have already found technical applications as e.g. heating elements in glow plugs for diesel engines, brake disks for motorbikes and resistant to high temperatures coatings for glass and oxide fibers [3].

Polysiloxanes, i.e. compounds whose molecules contain alternating silicon and oxygen atoms, meet several requirements that preceramic polymers should fulfill. Thus, they can be easily synthesized by ring-opening polymerization of cyclic siloxane monomers or by polycondensation of the appropriate compounds [4,5]. Due to film-forming properties, polysiloxanes are applied to produce a variety of functional coatings [5]. Additionally, cross-linked polysiloxanes can be prepared *via* polycondensation of the properly designed monomers or *via* cross-linking of the polymers containing relevant reactive groups. This feature is particularly important since it is known that in order to get high yields of ceramic materials it is necessary to use cross-linked polymers as precursors [6].

Pyrolysis of polysiloxanes conducted at the temperatures between 800 °C and 1300 °C results in the formation of silicon

oxycarbides [3,7,8]. These are amorphous materials whose composition corresponds to that of silica in which some of oxygen atoms are replaced by carbon ones and hence they can be represented by the general formula SiC_xO_{4-x} ($0 \leq x \leq 4$). In practice, however, it is very difficult to obtain stoichiometric oxycarbides. Two-phase Si–C–O systems composed of silicon oxycarbides and free carbon, often called “black glasses”, are formed instead [3,7,8]. With respect to conventional quartz glass, such glasses exhibit advantageous properties: higher glass transition temperature, better mechanical properties and higher resistance to crystallization [3]. At temperatures higher than 1300 °C, silicon oxycarbides transform first to SiC and SiO_2 , then to SiC and C [7]. Therefore “black glasses” cannot be produced during conventional glass fabrication which requires high temperatures. Thus, the preceramic polymer route is the only one for the preparation of these materials.

In most of the literature reports concerning the synthesis and characterization of Si–C–O systems, polysiloxanes obtained by the sol–gel method which involves hydrolysis of alkoxyalkylsilanes followed by polycondensation of alkylhydroxysilanes formed have been used as precursors [9–13]. Such reactions are usually carried out in alcoholic solutions of the reactants under conditions of acid or base catalysis.

Hydrosilylation, i.e. catalytic addition of Si–H bond to multiple carbon–carbon or carbon–heteroatom bonds [14], can be an attractive alternative to the sol–gel method. However, even though this process has been applied to obtain various organosilicon compounds [14], examples of its use for the preparation of preceramic polysiloxanes are rather scarce. Michalczyk et al. have shown that the products of

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hydrosilylation of 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^{Vi}) with 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) are excellent potential ceramic precursors since their pyrolysis results in high ceramic yields [15]. Yoshida and co-workers have studied pyrolytic behaviour of polymer networks obtained by hydrosilylation of D_4^{Vi} with poly(methylsiloxane) [16] and compared it to that of the pre-ceramic materials prepared by hydrosilylation of D_4^{Vi} with D_4^H as well as that of the materials synthesized by the sol–gel method [17].

In the present work, D_4^{Vi} has been hydrosilylated with a series of linear hydrogensiloxanes and – for comparison – with D_4^H . Hydrosilylation products have been studied by IR spectroscopy which has made it possible to determine efficiency of the hydrosilylation process in the investigated systems under adopted experimental conditions. FTIR technique has been also applied to monitor hydrosilylation reactions. The aim of the studies has been to verify, whether the products of D_4^H hydrosilylation with linear hydrogensiloxanes are good candidates for ceramic precursors. Their suitability for this application has been evaluated based on thermogravimetric analyses. Surface morphology of the materials has been examined by scanning electron microscopy.

2. Experimental

2.1. Chemicals

1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4^{Vi}) as well as all hydrogensiloxanes applied in the experiments: 1,1,3,3-tetramethyldisiloxane ($^HMM^H$), 1,1,3,3,5,5-hexamethyltrisiloxane ($^HMDM^H$), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane ($^HMD_2M^H$) and 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) were purchased from ABCR, Germany.

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) solution in xylene (2% Pt) was supplied by Aldrich, Poland.

All the chemicals were used in the experiments without any further purification.

2.2. Preparation procedures

All the hydrosilylation experiments were conducted under dry Ar atmosphere. Before the process, reaction flask was de-aerated and filled with Ar. All the chemicals were then introduced into it under Ar atmosphere.

In a typical hydrosilylation procedure, 1 ml (2.9×10^{-3} mol) of D_4^{Vi} and the appropriate amount of a selected hydrogensiloxane were introduced into the reaction flask. After that, the necessary volume of Karstedt's catalyst solution was added using a Hamilton micro-syringe so that the Pt (from the catalyst) to SiH (from hydrogensiloxane) molar ratio in the reaction mixture was equal to 1×10^{-5} . The reactions were carried out at the temperature of 28 °C by magnetic stirring of the reactants for 48 h. The products obtained were dried under vacuum (10^{-3} Torr) until constant mass in order to remove un-reacted starting substances.

For all the hydrogensiloxanes, two series of hydrosilylation experiments differing in molar ratios of the reactants were conducted. In experimental series 1, excessive amounts of hydrogensiloxanes with respect to D_4^{Vi} were used. In these experiments, hydrogensiloxane/ D_4^{Vi} molar ratio was equal to 3 for linear compounds ($^HMM^H$, $^HMDM^H$ and $^HMD_2M^H$) and 2 for the cyclic compound (D_4^H). The experimental series 2 was performed at lower hydrogensiloxane/ D_4^{Vi} molar ratios: 1.5 for $^HMM^H$, $^HMDM^H$ and $^HMD_2M^H$ and 1 for D_4^H . Additional hydrosilylation processes (experimental series 3) were carried out for only two hydrogensiloxanes, namely: $^HMDM^H$ and $^HMD_2M^H$. In these reac-

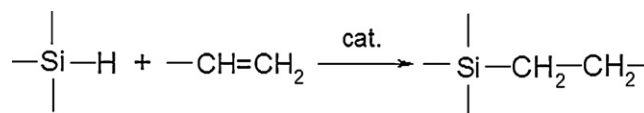


Fig. 1. Schematic representation of hydrosilylation of vinyl compounds.

tions, molar ratio of these compounds to D_4^{Vi} was equal to 0.75.

Hydrosilylation processes conducted at lower hydrogensiloxane/ D_4^{Vi} molar ratios (experimental series 2 and 3) were monitored by FTIR spectroscopy (Section 2.3). Reaction mixtures were sampled at selected time intervals (after 1 h, 4 h, 24 h, 26 h, 48 h of the process), IR spectra of the samples were measured and compared to those recorded for the starting reaction mixtures. Spectra analysis (see Section 2.3) enabled us to follow the consumption of SiH bonds during reactions performed in various systems.

It should be noted that hydrosilylation products were glassy solids, except for those obtained with $^HMDM^H$ and $^HMD_2M^H$ at their molar ratio to D_4^{Vi} equal to 0.75 (experimental series 3) which were viscous liquids.

2.3. Characterization methods

FTIR spectra in the middle infrared range were recorded on a BioRad FTS60v spectrometer. Spectra of the solid samples (most hydrosilylation products, see Section 2.2) were measured in the range of 400–4000 cm^{-1} , in the transmission mode using a standard KBr pellet technique. For liquids (all the starting compounds and hydrosilylation products obtained in experimental series 3) as well as to follow hydrosilylation course (see Section 2.2) ATR technique on ZnSe crystal at the incident beam angle of 45° was employed. The range of ATR measurements was 550–4000 cm^{-1} and the obtained spectra were ATR-corrected using WinIR™ software. Transmission spectra were collected after 256 and ATR ones after 64 scans. Resolution of all the IR measurements was equal to 4 cm^{-1} .

Quantitative analysis used to monitor the consumption of SiH bonds during hydrosilylation (see Section 2.2) was performed on baseline-corrected spectra. The area of the band corresponding to SiH stretching vibrations at $\sim 2100 \text{ cm}^{-1}$ to that originating from CH in Si–CH₃ group symmetric bending vibrations at 1259 cm^{-1} ratios were calculated. Si–CH₃ groups do not take part in the reaction. Hence, their concentration in the reaction mixture stayed constant during the whole hydrosilylation process.

Thermogravimetric analysis of hydrosilylation products was conducted on a Derivatograph C (MOM Budapest, Hungary) instrument. The studies were carried out in the temperature range of 30–1000 °C, in the flow of gaseous argon. The heating rate was equal to 10 °/min. Approximately 30 mg of the sample was applied in the measurements.

SEM analysis was carried out on a Nova Nanosem 200, FEI Co. microscope system. The powders were attached to the SEM stubs using conductive silver paste and vacuum-sputtered with a thin carbon layer.

3. Results and discussion

As has been already mentioned, hydrosilylation is a process of catalytic addition of SiH group to a multiple carbon–carbon or carbon–heteroatom bond [14]. When vinyl compounds take part in this reaction, its products contain ethylene (–CH₂–CH₂–) spacers in their structure. This is shown schematically in Fig. 1.

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