



Formation of polysilsesquioxane network by vapor-phase method in the spatially limited system of cross-linked polymer pores



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ABSTRACT

This paper presents novel types of polysilsesquioxane (PSQ)–polymer composites formed through polycondensation of ethyltriethoxysilane in the spatially limited system of polymer pores in the presence of acid or base catalysts vapors. In addition, it gives an insight into the architecture of the PSQ network. It is shown that PSQ formed under acidic conditions is mainly composed of long ladder-like structures, whereas small three and four-membered rings are dominating structural units in the base set PSQ. Theoretical calculations extend the common interpretation of the ²⁹Si NMR spectra according to which signals at ca. –47, –55, and –65 ppm can be simply attributed to T¹, T², and T³ Si atoms, respectively. Moreover, they indicate that T¹ and T⁰ ²⁹Si NMR signals should be easily distinguishable from T², and T³ (and among each other), since T⁰ is placed upfield (–31.5 ppm) as compared to the other mentioned ²⁹Si signals.

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1. Introduction

The sol-gel technique is commonly used to synthesize a wide range of solid-state materials with random branching from solution-state precursors. It involves all processes starting from the formation of sol (a colloidal suspension) and its gelation, until formation of a gel (i.e., a continuous solid skeleton enclosing a continuous liquid phase) [1]. These processes as well as the produced materials are still one of the most widely studied fields in materials chemistry [2]. There are numerous different precursors, which can be used for the sol-gel processes, but one of the most widely used are silica alkoxides. They are moderately reactive, therefore catalysts must be applied to increase their relative rate of hydrolysis and condensation reactions, which influence the structure of the resulting gel. Gelation of silica precursors conventionally takes place in aqueous solutions of desired pH. Nevertheless, Nishiyama et al. presented an alternative, highly efficient route of the synthesis of porous siliceous materials which involves supplying the silica precursors from the vapor phase under acidic or basic conditions [3–7]. On the other hand, it has been demonstrated that siliceous phase can be successfully produced

within a polymer beads when only catalysts are provided in the vapor phase of the desired composition [8]. This vapor-phase strategy has a great advantage, especially in the case of the polymer-drug-silica composites synthesis, since it prevents the release of the incorporated drug during the precursor gelation [9–11].

Although in the latter method the gelation of the silica precursor takes place in the presence of the vapor mixture of water and ammonia or water and hydrochloric acid, the silica precursor exists in the liquid state within the pore system of the polymeric support. Hence, the mechanism of sol-gel reactions in the presence of catalyst vapors should not significantly differ from the conventional route in the aqueous solutions. In addition, different processing conditions (i.e., acidic or basic) should affect the mechanism of silica precursor transformation. Indeed, it was previously demonstrated that the acid and base set silica gels anchored within the polymer matrix and produced by the use of the vapor-phase method differ significantly from each other in the molecular constitutions [8]. Consequently, the polymer-silica composites as well as the final silica gels obtained after removal of the polymer matrix exhibit different porosity and morphology. Moreover, those silica gels are also different from these produced earlier from TEOS or Na-silicate introduced into the polymeric support in the presence of aqueous NH₄OH or HCl solutions [12–14].

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In addition to acid and base catalysts, many other factors affect the mechanism of the silica precursor transformation (i.e., the rates of its hydrolysis and condensation) and thus the structure of silica gels. The silica precursor used in a synthesis is of a great importance. The most common silica alkoxides used in the sol-gel technique are tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS). However, even in this case, the process of the precursor transformation and SiO₂ formation are highly complex, and other factors (such as temperature, solvent type, precursor-to-solvent ratio, mixing rate, drying and ageing conditions, presence of the additives etc.) influence their final structure, porosity and texture. These effects are described in detail in many reviews [1,2]. A simple SiO₂ precursor can be replaced by the so-called organoalkoxysilane precursors, in which an organic group (or groups, R) bonded directly to the silicon atom is present. Also in this case, the type of organic unit R (non-polymerizable, e.g., aliphatic groups, or polymerizable, e.g., vinyl group) [15–21] strongly influences the sol-gel process and thus it has structural implications on the resulting gel. Such organically modified silica precursors are widely used in the synthesis of organic–inorganic hybrid materials. These materials are still of a great interest in the scientific and industrial communities due to the endless possibilities of designing and tailoring their characteristics such as hydrophobicity, flexibility, porosity, stability, structure, morphology, texture etc. Therefore, the studies concerning the sol-gel chemistry of organoalkoxysilanes in various conditions are constantly needed.

The lack of any literature reports concerning the gelation of organoalkoxysilane precursors introduced into the polymeric support in the presence of catalyst vapors, encouraged us to thoroughly investigate this problem. The silica precursor chosen for this study is alkoxysilane modified with ethyl functional group, i.e., ethyltriethoxysilane (ETEOS) since it serves as a model for the study of sol-gel chemistry in the presence of catalyst vapors of other organoalkoxysilane precursors with more complex R substituents. As a result of ETEOS gelation, polysilsesquioxane (PSQ) composed of a repeated C₂H₅–SiO_{1.5} unit is formed, i.e., a single silicon atom is attached to C₂H₅– unit in a network of up to three siloxane bond (commonly known as polyethylsilsesquioxane) [19,22]. This product is gaining more and more popularity and it is increasingly used as an ingredient of skin care composition, e.g., face powders, skin specialistic serum, lipsticks etc. [23]. It is also one of the fillers for the preparation of adhesive formulations having excellent dielectric properties [24]. Therefore, it is desirable and even necessary to thoroughly investigate polyethylsilsesquioxane especially on the molecular level. As a result of gelation, polysilsesquioxane (PSQ) composed of a repeated C₂H₅–SiO_{1.5} unit is formed, i.e., a single silicon atom is attached to C₂H₅– unit in a network of up to three siloxane bond [19,22]. The polymeric support selected in this study is non-ionic Amberlite XAD7HP, which has a well-developed permanent porous structure even in the dry state and is of moderately polar character. Thus, it ensures the specific microenvironment for gelation of organoalkoxysilane precursor. To initiate the gelation of ETEOS, a vapor mixture of H₂O and HCl or H₂O and NH₃ of the desired compositions were used at ambient temperature.

The aim of this study is to present a sol-gel chemistry of organoalkoxysilanes in the presence of catalyst vapors and to investigate the PSQ network formed in the spatially limited system of polymer pores. Thus, one of our major objectives is to identify the molecular constitutions of PSQ network obtained at acidic or basic conditions. Additionally, the project provides results pertaining to the structural differences between acid and base set polymer-PSQ composites. To achieve these objectives the obtained materials were characterized by ²⁹Si nuclear magnetic resonance (²⁹Si NMR), X-ray diffraction (XRD), positron annihilation lifetime spectroscopy (PALS), scanning electron microscopy (SEM), as well as nitrogen

sorption porosimetry (LN₂). Interpretation of the NMR measurements was supported by performing theoretical calculations of the chemical shifts of silicon nuclei.

2. Experimental

2.1. Materials

Amberlite XAD7HP resin (labeled here as XAD7) is a polymeric adsorbent of moderately polar character supplied as white insoluble beads. To retard bacterial growth, beads are saturated with salts (NaCl and Na₂CO₃). Therefore, prior to the experiment XAD7 beads were thoroughly rinsed with distilled water as the manufacturer suggests, and dried at 80 °C under vacuum until no weight loss was observed (i.e., for 12 h). The average particle size of the washed and dried Amberlite XAD7 was 0.30 ± 0.12 mm. For further investigation, the polymer beads were used as received, without fractionation. Ethyltriethoxysilane (ETEOS, > 97% (GC)) was used without further purification as the PSQ precursor. Both Amberlite XAD7HP and ETEOS were supplied by Sigma-Aldrich, while ammonium solution (NH₄OH, 25%) and hydrochloric acid (HCl, 36–38%) by POCH, Poland.

2.2. Preparation of polymer-PSQ composites

Composites were prepared by swelling method using preformed polymer beads as a support [12]. At first, dry XAD7 beads were wetted, drop by drop with ETEOS (1.9 g of ETEOS per 1 g of XAD7) which was completely absorbed during swelling of polymer, i.e. no excess ETEOS left outside the polymer beds. These XAD7 beads saturated with ETEOS (XAD7-ETEOS) were left for 24 h at room temperature in a sealed container. In the next step, XAD7-ETEOS beads were exposed to the vapor mixture of water and ammonia to initiate the hydrolysis and condensation of the introduced precursor [8]. For this purpose the freshly prepared ammonia solution was poured into a sealed container (10 cm³ 3.25 M NH₃aq per 1 g of XAD7-ETEOS) and XAD7-ETEOS beads were immediately placed directly over the solution and the container was tightly closed. XAD7-ETEOS beads were kept in the catalyst vapors at room temperature for 24 h or 72 h. The XAD7 beads which contained PSQ species, were dried at 80 °C under vacuum for 12 h. The composite prepared for 24 h was labeled as CB-1, and for 72 h – as CB-3 and they are referred to as base set composites (BSCs). The CA-1 and CA-3 composites were prepared in similar way, except that gelling of ETEOS was performed in the vapor mixture of water and hydrochloric acid (10 cm³ 2 M HCl per 1 g of XAD7-ETEOS). Their common name used throughout the text is acid set composites (ASCs). CB-3 and CA-3 materials were stored in the closed vessels at ambient pressure and temperature over a period of one year. The stored materials were denoted by adding “Y” to their initial labels. The measurements were carried out both before and after storage. To investigate the catalyst effect on parent XAD7 beads (i.e., without precursor), they were also exposed to ammonia or HCl vapors at the same conditions for 72 h. The base and acid set polymer beads were denoted as PB-3 and PA-3, respectively.

2.3. Methods of characterization

All investigated materials were characterized by the measurements of nitrogen adsorption–desorption at –196 °C using the ASAP 2420 V2.09 adsorption analyzer (Micromeritics, Norcross, GA) (low temperature nitrogen adsorption–desorption method; LN₂). Prior to the measurements, samples were outgassed for 6 h in the degas pot of the adsorption instrument at 80 °C. The specific surface areas, S_{BET}, were determined from the N₂ adsorption data by the

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