



Synthesis and characterization of hydrophobic and mesoporous silicate–silsesquioxane hybrid copolymers



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ABSTRACT

Mesoporous and hydrophobic silicate–silsesquioxane hybrid copolymers were synthesized from tetraethoxysilane and methyltrimethoxysilane by hydrolysis and condensation polymerization using a basic catalyst. The porosity and hydrophobicity of the calcined copolymers were studied by measuring the adsorption isotherms of water and using several other techniques, such as solution and solid-state ²⁹Si-NMR spectroscopy, small-angle X-ray scattering (SAXS), and ¹H-MAS NMR spectroscopy. The porous structure of the calcined polymers was influenced by the branched polymer structure and the high condensation ratio of the rigid polymer framework. The hydrophobicity of the polymers depended on the number of residual silanol groups and the degree of polymer branching. The highly branched polymer had an indented surface that caused the polymer to exhibit relatively hydrophobic characteristics owing to segregation of the silanol groups.

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1. Introduction

Hydrophobic porous silica and silsesquioxane are potential candidates for catalysts [1], membranes [2], chemical sensors [3], and low-dielectric-constant insulators [4–13]; further, they have applications in optics [14] and biotechnology [15,16]. These materials perform particularly well as esterification catalysts and low-dielectric-constant insulators.

Kim and Jeong [17] synthesized a silicate–silsesquioxane hybrid resin from tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS) by hydrolysis and condensation polymerization to give a low-dielectric-constant thin film. The Si–OH groups in this film induced the weak physisorption of H₂O molecules, which resulted in a relatively high dielectric constant. de Theije et al. [18] proposed that the prevention of water adsorption is crucial to obtain a low dielectric constant.

In studies on catalysts for the transesterification reaction, which has potential utility in the synthesis of biodiesels [19], and for oxidation reactions, which facilitate the use of hydrogen peroxide as an oxidant, the presence of trace amounts of water and the polarity of the porous silicate surface have been observed to inhibit reaction and affect product selectivity [20–26]. Sasidharan and

Bhaumik [19] reported the synthesis of hybrid silica-based porous aerogels by co-condensation of methyltriethoxysilane (MTES) and TEOS precursors using aqueous ammonia and showed that the aerogels are excellent catalyst supports for transesterification reactions of fatty acid esters with methanol. Palazzi et al. [24] described the co-condensation of MTES and TEOS precursors to produce a less hydrophilic catalyst support for the oxidation of olefins with hydrogen peroxide. The less hydrophilic catalyst support and partial methylation of the silica surface tended to increase the reaction productivity and reduce the consumption of hydrogen peroxide.

For hydrophobic silica, the sol–gel process is a versatile method for the economical preparation of silicate–silsesquioxane films on a variety of substrates. Several authors used this methodology to synthesize hydrophobic silica nanoparticles [27–29] and surfaces [30–32]. Another common route involves the use of alkyl–alkoxy compounds as co-precursors. MTMS is a widely used co-precursor in conjunction with tetramethoxysilane (TMOS) [33–35]; moreover, MTES has been used with TEOS [36]. Rao et al. [37] investigated the synthesis of superhydrophobic silica aerogels using MTMS as the precursor. Duan et al. [38] developed hydrophobic and porous silica aerogels by reacting the Si–OH groups in an aerogel with a silsesquioxane oligomer.

A surfactant-templated approach was adopted as a synthetic strategy for porous and hydrophobic silicate–silsesquioxane compounds in previous studies [13,18] because, unlike other methods,

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this approach allows the synthesis of compounds with both small, uniform pores and high porosities. However, residues from the template after volatilizing the sacrificial template material at a high temperature are a major concern. Hydrophobicity has been discussed as an important property, especially for the application of low-dielectric-constant insulators. High dielectric constants have been assumed to be due to Si–OH groups inside a low-dielectric-constant material [17]. Although the characterization of Si–OH groups by solid-state ^{29}Si -NMR spectra has been reported, more extensive studies on surface Si–OH species and the relationship between H_2O and Si–OH species are required [38].

The primary aim of this study was to obtain an MTMS–TEOS copolymer with a highly porous structure and hydrophobic characteristics by using common and simple alkoxy silane monomers in a non-templated synthesis procedure, and to ascertain the origin of the aforementioned characteristics. For this purpose, we investigated a polymerization process based on the modified Stöber method [39] and kinetic growth models [40] using a basic catalyst. This approach afforded a high condensation ratio and a branched polymer of MTMS and TEOS. The hydrophobicity and ordered structure of the porous copolymer is discussed using water and nitrogen gas adsorption–desorption isotherms, dielectric constants, small-angle X-ray scattering (SAXS), and ^{29}Si -NMR and ^1H NMR measurements.

2. Experimental section

2.1. Sample preparation

The polymer samples were prepared using different basic catalysts to investigate the effect of catalyst $\text{p}K_{\text{a}}$ (CH_3NH_2 , $\text{p}K_{\text{a}} = 10.7$; $(\text{CH}_3)_4\text{NOH}$, $\text{p}K_{\text{a}} \geq 13$) on the hydrophobicity and porosity of the dried polymer.

Sample-1 was prepared from MTMS and TEOS (MTMS:TEOS = 1.0:1.0 mol ratio) with methylamine as the catalyst. A mixture of aqueous methylamine solution (11.21 g of 25 wt%), distilled water (476.0 g), and methanol (496.1 g) was stirred at 60 °C. A mixture of MTMS (85.7 g, 0.629 mol), TEOS (131.0 g, 0.629 mol), and methanol (400.0 g) was added dropwise over 2 h at 60 °C with vigorous stirring. After completion of the addition, the solution was stirred at 60 °C under N_2 for 4 h and then cooled in ice/water. To neutralize the basic catalyst, 60% HNO_3 (9.48 g) was added with vigorous stirring, and then butyl acetate (500 g) and distilled water (500 g) were added. The organic phase, which included the copolymer, was washed with distilled water three times, and methylamine in the aqueous phase was washed out as a nitric acid salt. The solvent was removed from the organic phase and was replaced with propylene glycol monopropyl ether (PGPE) to afford a 10 wt% PGPE solution of sample-1 as a clear solution suitable for spin coating.

Sample-2 was prepared from MTMS and TEOS (MTMS:TEOS = 1.0:1.0 mol ratio) with tetramethyl ammonium hydroxide (TMAH) as the catalyst. A mixture of aqueous TMAH solution (32.9 g of 25 wt%), distilled water (476.0 g), and methanol (474.4 g) was stirred at 60 °C. The remainder of the synthesis was the same as the method described for sample-1, and a 10 wt% PGPE solution of sample-2 was obtained as a clear solution suitable for spin coating. The PGPE solution of 1 or 2 was spin coated on silicon wafers, then prebaked at 200 °C for 1 h in a N_2 oven (sample-1a or sample-2a), and subsequently heated at a rate of 5 °C/min to 400 °C, where the temperature was maintained for 2 h under N_2 (sample-1b or 2b). The powder samples for the measurement of gas adsorption/desorption and solid-state NMR were prepared by scraping the polymer film off the Si wafer with a knife.

2.2. Gas adsorption and desorption

The specific surface area of the solid polymer samples was measured using the BET method with nitrogen gas as the adsorbate on a Quantachrome Autosorb-1 instrument at -196 °C [41]. Prior to measurement, all samples were outgassed at 200 °C and 0.0133 Pa.

The water vapor adsorption and desorption isotherms of the solid polymer samples were measured with a Quantachrome Hydrosorb-1000 instrument at 25 °C after pre-evaluation at 60 °C for 3 h. The measured P/P_0 range was 0.05–0.99. The pore size distribution over the radius range of 1–100 nm was calculated from the adsorption isotherms using the BJH method [42].

2.3. Measurement of dielectric constants

Thin films of sample-1 or 2 were prepared by spin coating the solutions onto boron-doped silicon wafers. After spin coating, the wafers were heated on a hot plate at 80 °C for 1 min and then at 200 °C for 1 h in a N_2 oven. The wafers were then heated in the N_2 oven at a rate of 5 °C/min to 400 °C, where the temperature was maintained for 2 h. Five aluminum electrodes were deposited on the sample film by vacuum evaporation, and the area of the electrodes was accurately measured. The thickness of the thin film sample used for calculating the dielectric constant was measured using spectroscopic ellipsometry.

The dielectric constants were measured using a metal/insulator, i.e., a thin film of sample-1 or 2/metal structure, with the top electrode patterned using a mask. Capacitance vs. frequency (C–F) measurements were performed using a Yokogawa Hewlett–Packard HP16451B electrode and an HP4284A Precision LCR meter. The values reported here were obtained at a frequency of 100 Hz. The dielectric constant (k value) of the film was measured in the following sequence.

First measurement: The first k value ($k_{1\text{st}}$) was measured under the initial ambient conditions.

Second measurement: After the measurement of $k_{1\text{st}}$, the sample wafer was placed on a hot plate in a dry N_2 flow box and heated at 200 °C for 30 min to remove moisture from the film. The second k value ($k_{2\text{nd}}$) of the dried sample was then measured at 25 °C in a dry N_2 flow box.

2.4. Solution-state ^{29}Si -NMR spectroscopy

The procedure for solution-state ^{29}Si -NMR measurements is described in previous studies [43]. ^{29}Si -NMR spectroscopy was performed on a Bruker 500 Avance spectrometer (99.36 MHz for ^{29}Si) equipped with a 10 mm BBO probe. The sols were studied as prepared in 10 mm Teflon tubes with benzene- d_6 as the lock solvent. The ^{29}Si -NMR signal was enhanced by DEPT [44] using a 40 ms delay and a third ^1H pulse of 25°. A recycling delay of 10 s (acquisition time = 1.1 s) was confirmed to be sufficient. Under these conditions, spectra with good signal-to-noise ratios were obtained.

2.5. Solution and solid-state small-angle X-ray scattering (SAXS)

Solution and solid-state SAXS measurements were performed using a Kratky-type camera and a Cu $K\alpha$ radiation source (Rigaku RU-200) operating at 50 kV and 200 mA. The beam was monochromated through a Ni filter and then collimated by a U-slit of 70 mm \times 25 mm and a receiving slit of 0.14 mm. The diffracted intensities (arbitrary units) were registered simultaneously on a scintillation counter (Rigaku, RAD-C) for the 2θ angles of 0.08°–6.00°. The powder samples for the scattering experiments were packed in quartz capillary tubes. The relative scattering

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