Templating Nanoporosity in Polyorganosilicates Using Reactive Dendrimers

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ABSTRACT: It is shown that macroscopic phase separation of an otherwise immiscible dendrimer in a typical organosilicate can be kinetically hindered by incorporation of the dendrimers in a chemical network. Subsequent removal of sacrificial dendritic templates by thermolysis results in formation of nanoporous organosilicates. The phase separation of a dendritic diol in an organosilicate was studied by light microscopy. It was shown that macroscopic phase separation of such dendrimers could be drastically hindered by addition of a small amount of a triisocyanate, resulting in the formation of a polyurethane network bearing dendritic wedges at moderate temperatures. Curing of the organosilicate at elevated temperatures creates an interpenetrating network, in which the phase separation of dendrimers is prohibited because of topological constraints. Small-angle X-ray scattering revealed that pore sizes of approximately 12 nm can be generated upon thermolysis even in a matrix containing 70 wt % of dendrimer. The results were in qualitative agreement with field emission SEM images of the cross section of the coatings.

Continuing drive toward miniaturization in chip manufacturing represents significant challenges to the chemical industry, particularly regarding developments of new types of photoresists[1] and interlayer dielectrics.[2] In the latter case traditional layers, based on silicon dioxide with dielectric constants k of 3.9−4.2, must be replaced with new types of materials with significantly lower k values, especially for features of 90 nm and below. Because of very low dielectric constant of air ($k = 1$), inclusion of nanocavities in the matrix system has been the method of choice for decreasing k values. As the matrix, various types of organic polymers[3] and inorganic resins, mostly polyorganosilicates,[4] have been tested which are applied by spin-on technologies as opposed to chemical vapor deposition methods commonly used for application of conventional dielectric layers.

To template nanoporosity in the matrix system, various types of organic porogens have been used which are thermally decomposed at elevated temperatures leaving nanocavities.[5] To produce ultralow dielectric materials ($k < 2$), a significant amount of porogens must be added to the spin-on formulations. However, at relatively high porogen loading (typically above 35 wt %) macroscopic phase separation is observed, which hampers the application of this method to template large level of nanopores. Attempts have been made to increase the solubility of the porogens with the solvent (mostly alcohols in the case of polyorganosilicates) and matrix, and thus prevent macroscopic phase separation at high loadings, by using different types of organic materials with different chemical structure such as star-shaped poly(ϵ-caprolactone),[6] triblock copolymers,[7] poly(methyl methacrylate)s,[8] and hyperbranched polyesters.[9]

Here we present a new concept for suppressing macroscopic phase separation, which is not based on favoring thermodynamic by increasing solubility, but aims to hamper nucleation and growth by introducing topological constrains. In general, the size of cavities is determined by nucleation/phase separation process which takes place during spin-coating and/or subsequent matrix hardening. The idea is to use functionalized porogens, i.e., dendrimers, able to undergo rapid cross-linking reaction before macroscopic phase separation sets in. After the curing step of the matrix an interpenetrating network is formed which topologically hinders the macroscopic phase separation of porogens. To demonstrate the power of our approach, we use Fréchet-type dendrimers[10] that macroscopically phase separate from a typical organosilicates already during the spin-coating process. We have shown previously that reaction of dendritic diols, i.e., generation four (G4-diol), shown in Figure 1, with a triisocyanate, i.e., Desmosdur RFE, results in the formation of polyurethane networks bearing dendritic wedges.[11]

Our aim is to test whether such types of reactions, simultaneously occurring during the spin-coating process, could hamper macroscopic phase separation of the dendrimers in a common polyorganosilicate, i.e., poly(methylphenylsiloxane) resin (GR150F). A typical formulation is prepared by dissolving a stoichiometric amount of G4-diol and Desmodur RFE ([−NCO]/[−OH]) = 1) in dichlorobenzene (DCB) and adding an appropriate amount of GR150F. After mixing some amount of catalyst, i.e., dibutyltin acetate, the solution is immediately spin-coated onto glass substrate. Because of extremely fast reactions between alcohols and isocyanates, we expect that reaction products of G4-diol and Desmodure RFE are already formed in the solution.[12] During the spin-coating process and solvent evaporation a polyurethane network is formed, essentially swelled with GR150F. The coated glass substrate is then thermally heated in two steps. First the sample is heated for 2 h at 200 °C, resulting in hardening of GR150F resin and formation of an interpenetrating network of siloxane and polyurethane chains bearing dendritic wedges.[13] In the second step, the coated substrate is heated at 530 °C for 2 h, leading to thermal decomposition of the organic fraction and formation of nanocavities.[14]

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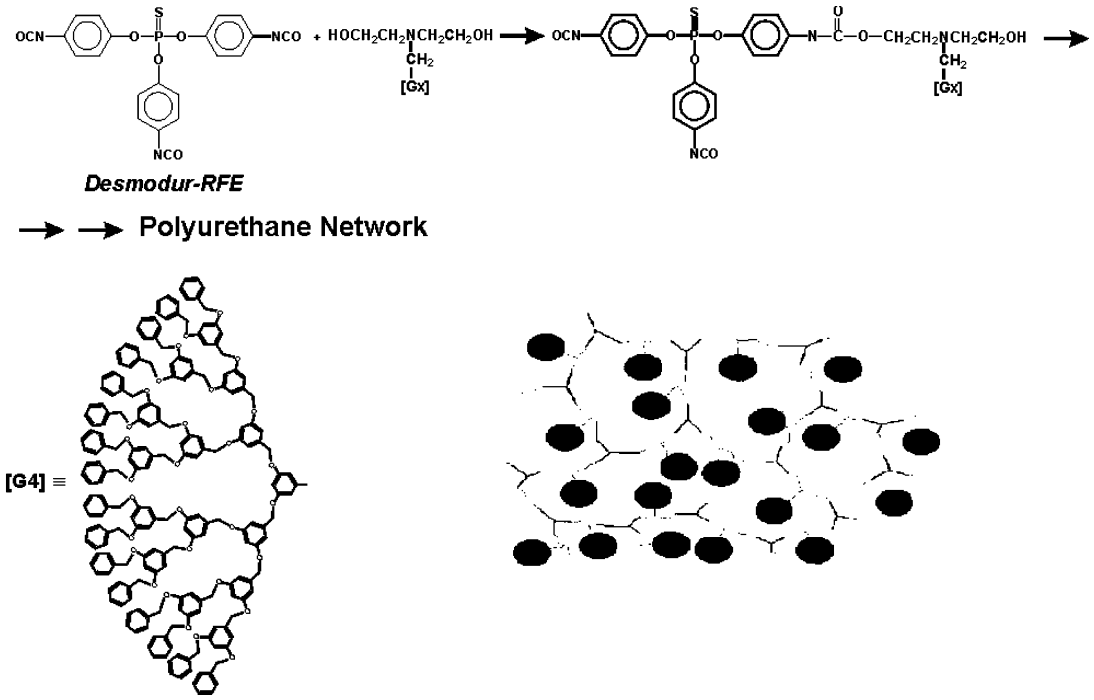

Figure 1. Synthetic scheme showing the chemical structure of dendritic diol and triisocyanate used in this study and the reaction involved in the formation of polyurethane network. Inset shows a schematic representation of such networks bearing dendritic wedges.

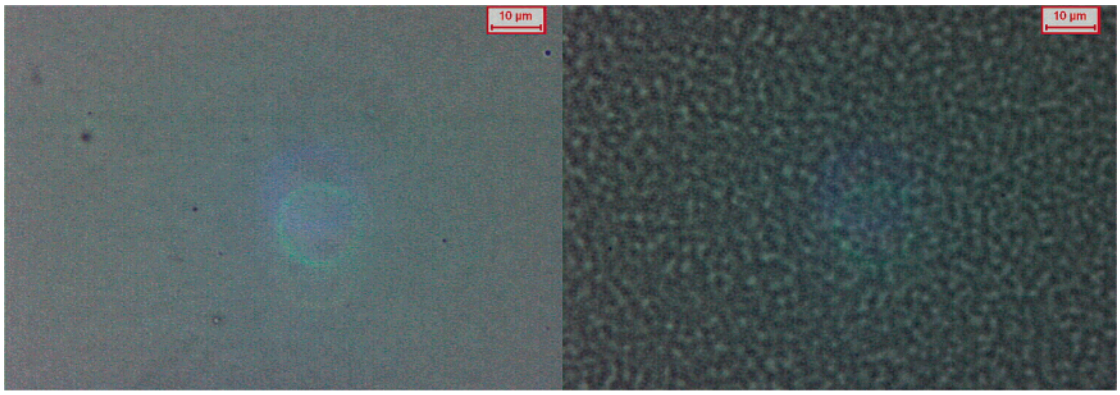

Figure 2. Light microscopy image of a spin-coated film prepared from a formulation containing 70 wt % of dendrimers with respect to GR150 and a stoichiometric amount of Desmodur RFE, designated as GR150F/PUN70. As the reference system, the image is shown of a sample prepared from the same formulation but without Desmodur RFE (designated as GR150F/Ref70). Both images are taken after spin-coating and before thermal heating at elevated temperatures.

Figure 2 shows the light microscopy image of a spin-coated film prepared from a formulation containing 70 wt % of dendrimer and a stoichiometric amount of Desmodur RFE, designated as GR150F/PUN70. As the reference sample the image is shown of the same formulation but without Desmodur RFE, designated as GR150F/Ref70. Both images are taken after spin-coating and before heating at elevated temperatures.

First of all, it should be stated that the coatings without Desmodur RFE appeared milky white, indicative of macroscopic phase separation. This is also reflected in the light microscopy image of GR150/Ref70 showing a clear two-phase structure. In fact, investigations at lower loadings have indicated that the macroscopic phase separation already occurs above 10 wt % dendrimer in GR150F. In contrast, samples containing Desmodur RFE all appeared transparent even at a dendrimer loading of 70 wt %. This is also evident from the microscopy image of GR150F/PUN70, which shows no structure at least on a microscopic scale.

The fact that addition of Desmodur RFE yielded transparent films encouraged us to study these coatings at smaller length scales using more advanced techniques, such as small-angle X-ray scattering (SAXS) and field emission scanning electron microscopy (FESEM). Figure 3 reveals the SAXS profiles recorded from the coating GR150F/PUN70 after heating at 200 °C, i.e., temperature at which GR150F starts to cross-link and eventually vitrify, and subsequent annealing at 530 °C, i.e., temperature at which more than 85 wt % of organic phase is lost. The steep decay of the scattering intensity detected here suggests indeed the presence of a two-phase morphology. However, it should be noted that the intensity decay in this range has a slope of −2.5, whereas for an ideal two-phase morphology with well-defined interfaces this value should be −3. After annealing at 530 °C, the profile indicates a change in scattering behavior, not only with respect to the overall scattering intensity (invariant Q) but also in the variation of the scattering intensity.

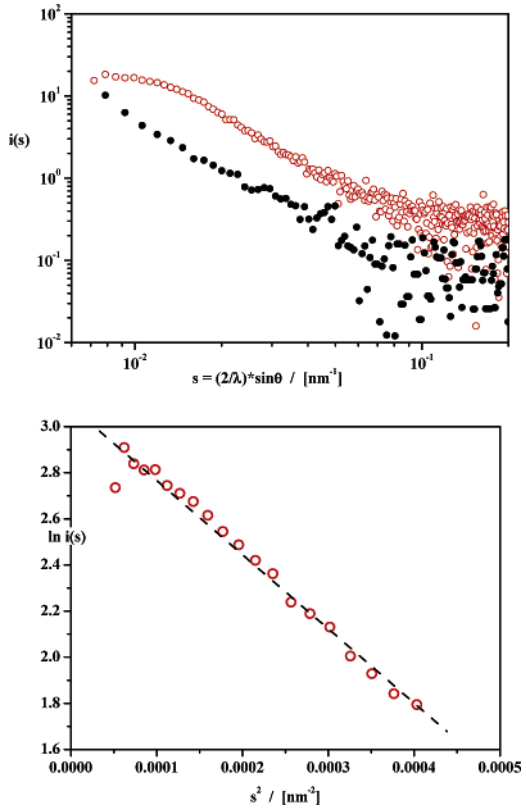

Figure 3. SAXS profiles (top) recorded of spin-coated films of GR150F/PUN70 after curing at 200 °C (dots) and annealing at 530 °C (circles); the Guinier plot (bottom) representation of the data recorded from the coating GR150F/PUN70 after annealing at 530 °C.

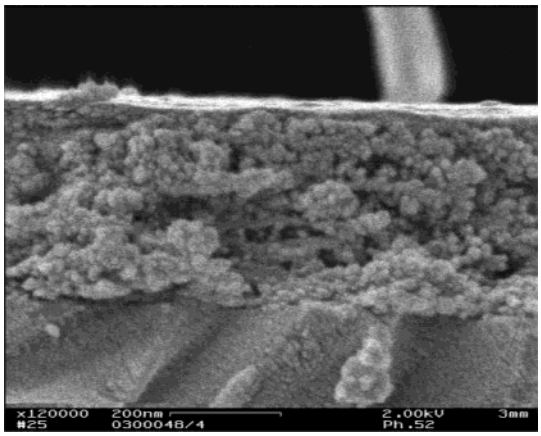

Figure 4. FESEM image of cross section of coating GR159F/PUN70 after annealing at 530 °C. Pores with a size larger than 50 nm are believed to be the result of sample preparation, i.e., breakage of the sample to obtain a cross section.

The SAXS profiles reveal a rather well-defined scattering profile, which does not indicate the presence of a two-phase structure with large dimensions but rather suggests the presence of relatively well-defined pores. An estimate for the dimension of these structures can be obtained from the Guinier plot representation in Figure 3 which reveals a radius of gyration (R_G) of ~9 nm. The latter is related to the pore radius (R) via $R = \sqrt{5/3}R_G$ and thus yields a dimension of $R \sim 12$ nm.

Figure 4 shows the FESEM image of the cross section of the coating GR150F/PUN70 after annealing at 530 °C.

It is clear from the FESEM image in Figure 4 that a porous structure is obtained upon annealing at 530 °C. Furthermore, there seems to be a reasonable agreement with SAXS results regarding the pore sizes. There are, however, some larger pores (size >50 nm) present, which are believed to be the result of sample preparation, i.e., breakage of the sample to obtain a cross section.

Indeed, the results so far seem to indicate that introducing a cross-linking reaction can kinetically hinder phase separation of otherwise immiscible dendrimers in a typical organosilicate. The chemical reaction occurs simultaneously during the spin-coating process and accompanying rapid solvent evaporation, which results in the fixation of dendrimers in a polyurethane network. The network formation in such type of addition polymerization involves two distinct steps: chain extension process up to the gel point and cross-linking reaction thereafter.[15] The first step involves the formation of polyurethane oligomers bearing dendritic wedges that might have a higher solubility in the organosilicate matrix than dendritic diiols. To investigate whether this factor is (also) involved in suppressing phase separation of dendrimers, we repeated the experiments, but instead of using a triisocyanate (Desmodur RFE), we added a diisocyanate, i.e., Bisphenol-F diisocyanate. We have shown previously that reaction of dendritic diiols with this particular diisocyanate results in oligomerization.[16] A spin-coated sample of 70 wt % dendrimer in GR150F with a stoichiometric amount of Bisphenol-F diisocyanate appeared milky white, indicating that chain extension alone cannot hinder nucleation and growth of dendrimers.

In summary, we have presented a concept for templating a high level of nanoporosity in a typical organosilicate, using in-situ cross-linking of dendrimers, preventing them from macroscopic phase separation. It should be noted that both formulation and morphology of nanoporous silicate need to be modified before they can be used for low-*k* dielectric applications. For example, a different dendritic structure is required to facilitate more efficient degradation and depletion process. Also, the chemical structure of polyorganosilicate examined here must be optimized in order to ensure the lowest possible *k* value for the matrix. It was not our intention to develop an ideal material ready to use, but rather to present the main results demonstrating the basic feasibility of our concept.

Experimental Section

The triisocyanate Desmodur RFE was obtained from Bayer and recrystallized from dichloromethane to give white crystals with isocyanate functionality of three. Poly(methylphenylsiloxane) resin under the trade name GR150F was obtained from Techneglas. Dendritic wedges were synthesized according to the procedure described previously.[15] The spin-on formulations were prepared by dissolving an appropriate amount of GR150F in carefully dried dichlorobenzene (DCB) followed by adding a stoichiometric amount of dendritic diol and Desmodur RFE ([−NCO]/[−OH] = 1). After mixing some amount of catalyst, i.e., dibutyltin acetate, the solutions were immediately spin-coated at 3000 rpm onto a glass substrate. Samples were cured in an oven under nitrogen for 2 h at 200 °C and 2 h at 530 °C.

Light microscopy experiments were conducted on a Zeiss Axiophot microscope operating in phase contrast mode.

The small-angle X-ray scattering (SAXS) experiments were performed at ambient conditions with a modified Kratky setup, attached to a conventional sealed tube X-ray source (40 kV and 50 mA), which provides line-focused, Ni-filtered Cu Kα

radiation (0.154 nm). The Kratky setup is equipped with an entrance slit of 40 μm and features a sample-to-detector distance of 288 mm. The scattering patterns from the samples and the background scattering were recorded with a position-sensitive detector (MBRAUN 50M). Since the thickness of the spin-coated films on the glass substrate is below 20 μm, the resulting scattering intensity is very low, and it is essential to obtain reliable data featuring a very good statistics. Consequently, exposure times in the range of 2−3 days had to be employed. Moreover, subtraction of the background signal—originating from the camera and the glass substrate—appears to be crucial and demands careful determination of the transmission values. For this purpose, the signal recorded from a PE reference sample was used for intensity calibration, whereas sample transmissions were derived from its attenuation. For calibration of the scattering vector, $q = 2\pi s = (4\pi/\lambda) \sin \vartheta$, the position of the (attenuated) primary beam was recorded without beamstop. SAXS data processing including subtraction of the transmission-weighted background signal was performed with subroutines of the FFSAXS software, developed by Vonk. In this step, the overall background signal (including parasitic scattering from the SAXS camera and contributions from the glass substrate) was subtracted from the scattering pattern in order to minimize statistical errors at high s.

Scanning electron microscopy images were measured using a FESEM Leo Gemini 982 operating at a beam voltage of 2 kV.

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(12) The dilution level of dendrimers and Desmodur RFE in DCB is well below the critical concentration for gelation so percolation in solution is prohibited.

(13) In this temperature range the polyurethane network is still thermally stable while GR-150F resin chemically cross-links. There is also a possibility that the siloxane resins interfere with the formation of polyurethane networks. This is, however, not probable because it is well-known that the rate of chemical reaction between R−OH and −NCO groups is much faster than reaction between Si−OH and −NCO groups.

(14) Thermogravimetric analysis has indicated that at this temperature the weight loss of the organic phase is more than 85 wt %.

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