

The Chemical Reactivity of Sol–Gel Materials: Hydrobromination of Ormosils

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Received June 23, 2000. Revised Manuscript Received October 10, 2000

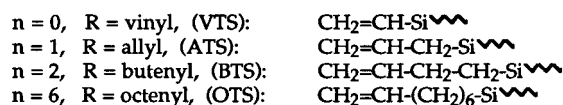
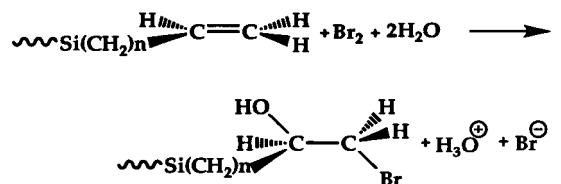
The chemical reactivity of sol–gel materials prepared via base catalysis from mixtures of $\text{Si}(\text{OEt})_4$ and $\text{RSi}(\text{OEt})_3$, where R is an n -alkenyl group bearing the double bond at the terminal position, was studied through the double-bond hydrobromination addition reaction. The reactivity and kinetics were studied as a function of the length of R and as a function of variations in the material preparation procedure. The initial reaction rates and the total capacity of the materials to act as “bromine sponges” depend inversely on the size of R. This behavior is interpreted, among other parameters, in terms of the formation of early micellar structures of the hydrolyzed $\text{RSi}(\text{OEt})_3$ species. Of the various R residues studied, the most efficient bromine sponge is the allyl residue.

1. Introduction

Chemical reactivity of sol–gel materials can be induced and tailored by one of three methods: direct physical entrapment of a reactive dopant;^{1,2} covalent anchoring of a reactive residue to the surface;^{2–4} and copolymerization of monomers providing the supportive matrix, with monomers providing the desired reactivity.^{2,3} Practically all major families of chemical reactions have found their way into sol–gel materials via at least one of these methods, with examples including catalysis,^{5a} photochemistry,^{5b} biochemistry,^{5c,d} and electrochemistry.^{5e,f} Many applications have been developed with these families of reactions, and perhaps the most advanced one, using all of these families of reactions, is chemical sensing.⁶

Here, we report the results of a study aimed at understanding some of the elementary features that dictate the reactivity of sol–gel materials. Specifically, we studied the hydrobromination of a series of organically modified sol–gel silicas (ormosils) bearing double

Scheme 1. Reaction of the Olefin Residue with Bromine under Aqueous Conditions



bonds. The materials have been prepared by the copolymerization of $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ (TEOS) with $\text{RSi}(\text{OCH}_2\text{CH}_3)_3$ (RTS) under base catalysis conditions, where R is one of the homologous groups of the vinyl (VTS), allyl (ATS), n -3-butenyl (BTS), and n -7-octenyl (OTS) residues. Under aqueous conditions, olefins react with bromine in conformity with Markovnikov's rule⁷ as shown in Scheme 1, resulting in a bromohydrin. This series of materials was taken especially for the purpose of analyzing the relation between the length of R and the accessibility of the interface of the material to an incoming reactive species (bromine, in this case, Scheme 2). As we shall see below, unlike solution chemistry in which changes in reactivity of a homologous series either follow a gradually changing structural parameter or are indifferent to it (if the residue does not play an important role in the reaction), the picture is much more complex when it comes to sol–gel materials.

On the practical side, we have demonstrated with this study the ability of reactive sol–gel materials to act as detoxification sponges of hazardous chemicals, converting in this case bromine to the more benign hydrobromic acid. There is a wide demand for chemical sponges for a variety of purification needs in the environment, in

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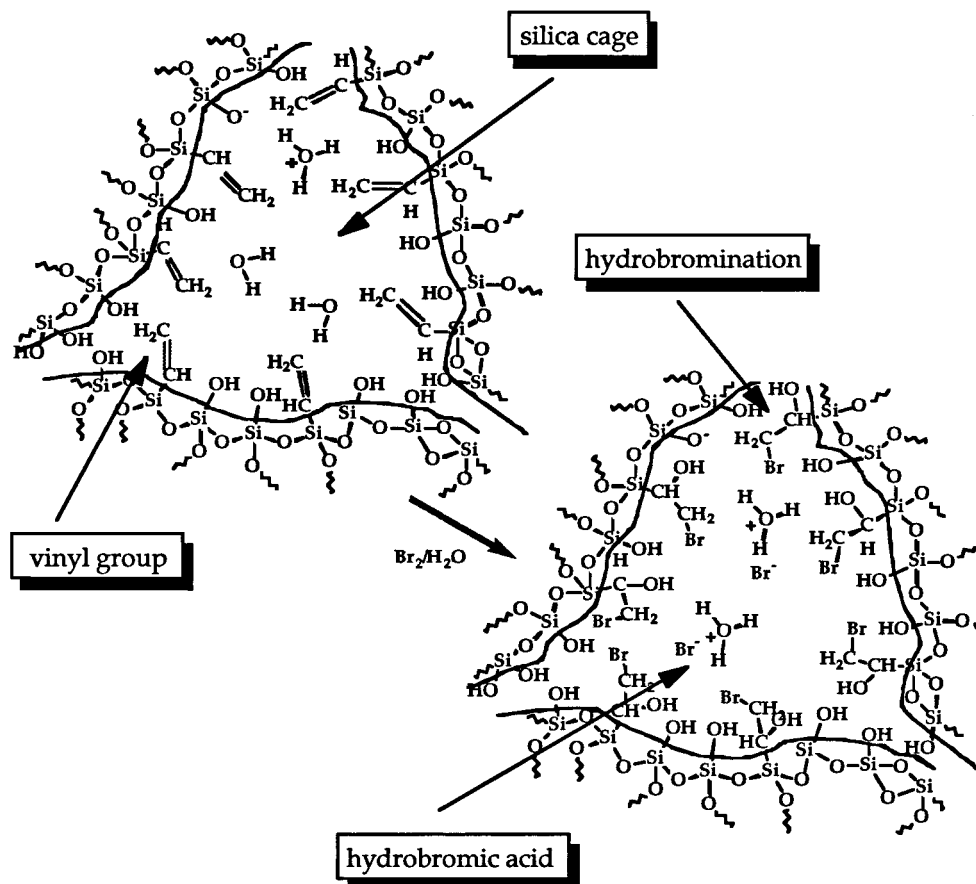
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Scheme 2. Schematic View of the Reaction Inside a Pore, between the Interface of the Material and the Incoming Bromine (VTS)

medicine, and in the chemical industry. The advantages of sol-gel materials (listed intensively, e.g., in refs 2–4 and 8) render them particularly suitable for designing such sponges,⁹ more of which are currently being developed in our laboratory. Finally, some previous relevant studies in the context of this report include the bromination of octa(vinylsilsesquioxane) in carbon tetrachloride,¹⁰ the hydrobromination of pervinyloctasil-sesquioxane with HBr,¹¹ and the gas-phase bromination of a network prepared with 1,2-bis(triethoxysilyl)ethylene.¹² Also related is the study of spacer effects on sol-gel-bound ruthenium(II) catalysts.¹³

2. Experimental Details

Chemicals. Tetraethoxysilane (TEOS), vinyltriethoxysilane (VTS), allyltriethoxysilane (ATS), and ethyltriethoxysilane

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(ETS) were obtained from Aldrich. 4-Butenyltriethoxysilane (BTS) was obtained from Gelest. Bromine (99.5%) was obtained from Merck. These chemicals were used without further purification. 7-Octenyltriethoxysilane (OTS) was synthesized by stirring octenyltrichlorosilane (from Gelest) with an excess of ethanol (EtOH) under dry N₂ at 35 °C for 48 h. The product was distilled at 135 °C, and its structure was confirmed by ¹³C and ¹H nuclear magnetic resonance (NMR) spectroscopy, Gas chromatography–mass spectroscopy (GC–MAS), and elemental analysis. *Hazards:* Bromine and all alkoxy silanes should be handled in a well-ventilated fume hood and with gloves.

Material Preparation Procedures. Samples were prepared by the “two-step” procedure¹⁴ without added cosolvent.¹⁵ We recall that the main role of a cosolvent in the sol-gel process is to homogenize the starting solution, which otherwise is composed of two phases. Without a cosolvent, as the reaction proceeds, more and more ethanol is generated until a homogeneity finally is reached.¹⁵ The procedure was carried out as follows: A mixture of 0.008 mol of RTS (1.70 mL of VTS, 1.80 mL of ATS, 1.95 mL of BTS, and 1.97 g of OTS) and 2.65 mL of TEOS (0.012 mol) was stirred for 1 min in a vial, and then 1.45 mL of distilled water and 0.015 mL of 1 N HCl (0.04 mol of water and 0.015 mmol of HCl) were added. The vial was sealed, and the solution was mixed for 5 h at 35 °C (50 °C for OTS). Subsequently, 0.99 mL of distilled water and 0.47 mL of 0.095 N NH₄OH (0.045 mol of water and 0.04 mmol of NH₄-OH) were added, and the mixture was stirred for an additional 15 min in the sealed vial; the mixture was then left to gel (10 min to 2 h). After gelation, the gel was left to age at 35 °C for 24 h and dried at 120 °C for 24 h [resulting in a final TEOS/

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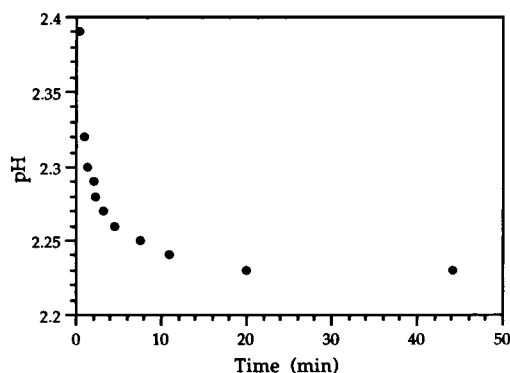


Figure 1. Hydrobromination kinetics of VTS (prepared without EtOH) following the pH as HBr is released.

RTS/water/HCl/NH₄OH molar ratio of 1.5:1:10:(1.9 × 10⁻³): (5 × 10⁻³). The different xerogels thus obtained are termed according to the RTS monomer that led to them, namely, VTS, ATS, BTS, and OTS. For comparison, samples were also prepared with the same compositions but with ethanol (ethanol/water = 1:1), which was added at the first stage as a cosolvent. For blank tests, samples were prepared with ethyltriethoxysilane (ETS, 1.70 mL, 0.008 mol) in the same manner as described above.

Material Characterization. Surface area measurements were carried out on samples that were degassed overnight at 100 °C. These surface areas were determined by nitrogen sorption on a Micromeritics ASAP 2000 instrument, and the results were interpreted according to the Brunauer–Emmett–Teller (BET) equation.¹⁶ True density measurements were determined with a Quantachrome Multipycnometer-4AC232 instrument, using helium as the displacing fluid. All samples were pretreated with a flow of helium for 15 min.

Hydrobromination Procedure. A specific amount of the material (crushed to a fine powder with a particle size of around 10 μm) containing 1 mmol of double bonds (e.g., 0.17 g of VTS) was placed in a 100-mL round-bottom flask to which 10 mL of distilled water was added, and the slurry was stirred for an hour in order to ensure penetration of the solvent into all pores. Fresh bromine solutions were prepared by dissolving 0.21 g of Br₂ in 50 mL of distilled water (0.026 M), 50 mL of the bromine solution in water was added to the ormosil powder (double bond/Br₂ = 1:1.3), and the mixture was stirred at room temperature. In the course of the reaction, HBr evolved (Schemes 1 and 2), and so the stirring was continued until the pH reached a constant value (e.g., pH 2.17 for ATS), within 0.5 h. A typical HBr release profile is shown in Figure 1 (and it does not follow a simple zero- or first-order rate law).

Analyses of the Hydrobromination. The reaction yields in terms of both the percentage of double bonds that have reacted and the total Br/Si molar ratios were calculated from the amount of HBr that was produced by the reaction. This, in turn, was determined from the difference between the initial pH and the final value. A blank test to determine the release of HBr from alkylated silica, which does not contain double bonds (ETS, under the same reaction conditions), was also carried out. The amount of HBr released in this case was found to be very small (0.027 mmol), but it was taken into account. Another blank test was performed in order to determine the amount of adsorbed HBr, which was found negligible. The surface Br/Si molar ratio was determined from elemental analysis of the surface, carried out with a JEOL JXA-8600 electron probe microanalyzer equipped with a NORAN Vantage automation system. This method gave the ratio between the external surface-bonded bromine and surface Si atoms to a depth of 1 μm.

Structural evidence for the hydrobrominated residues was obtained with solid-state ¹³C NMR spectroscopy using the cross-polarization/magic-angle spinning (CP MAS) technique.¹⁷

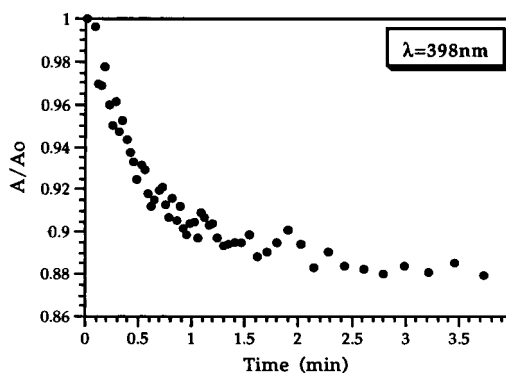


Figure 2. Hydrobromination kinetics characterized by following the decrease of Br₂ relative absorption (A/A_0) while it reacts with VTS.

Table 1. Physical Properties of the Ormosils before Reaction

| ormosil | preparation method | surface area (m ² /g) | pore size (Å) (±5 Å) | true density (g/cm ³) (±0.02 g/cm ³) |
|---------|--------------------|----------------------------------|----------------------|--|
| VTS | with cosolvent | 722 (±4) | 26 | 1.58 |
| | without cosolvent | 864 (±18) | 26 | 1.86 |
| ATS | with cosolvent | 655 (±8) | 22 | 1.52 |
| | without cosolvent | 564 (±7) | 22 | 1.75 |
| BTS | with cosolvent | 437 (±6) | 22 | 1.56 |
| | without cosolvent | <1 | <10 | 1.70 |
| OTS | with cosolvent | <1 | <10 | 1.30 |
| | without cosolvent | <1 | <10 | 1.39 |

The spectra were measured at 125.76 MHz with a Bruker DMX-500 digital F NMR spectrometer equipped with a BL-4 probe head and a high-resolution/high-performance (HPHP) ¹H preamplifier for solids. All CP MAS spectra were calibrated with an external spectra reference (carbonyl at 176.03 ppm). A vacptppm (variable-amplitude cross-polarization/two-pulse phase-modulation ¹H decoupling) pulse program was used. Samples were placed in 4-mm zirconia rotors and spun at a rate of 11.0 kHz.

Reaction Kinetics. The initial rates of reaction were determined by following the decrease in the bromine absorption at 398 nm in a 1 cm glass cuvette using an HP-8453 spectrophotometer. This was carried out by placing an amount of the desired sample containing 0.1 mmol of double bonds in the cuvette, adding 1 mL of H₂O, and leaving the solution to mix for an hour to reach equilibrium. Then, 3 mL of 0.01 M bromine solution in water was added, and the measurement was started. This procedure was repeated three times for each sample, and the average value was calculated. A typical result is shown in Figure 2. It is seen (compare with Figure 1) that the release profile of HBr from the pores is, as expected, much slower than the intrapore reaction rate of the hydrobromination.

3. Results

Starting Materials. The physical properties of the different materials are collected in Table 1. The main points to note are that the surface areas decrease with the increasing length of the R group, that the surface area of BTS is greatly affected by the addition of a cosolvent, that the average pore size tends to decrease with increasing R length, that the densities decrease with increasing length of R when no cosolvent is used, and that the use of a cosolvent decreases the densities.

Hydrobromination. Evidence for the hydrobromination of the double bonds and clues to the location of

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Table 2. ^{13}C CP MAS NMR Chemical Shifts before and after Hydrobromination

| sample ^a | structure ^b | C ¹ (ppm) | C ² (ppm) | other carbons |
|---|---|----------------------|----------------------|--|
| VTS | $\text{C}^1\text{H}_2=\text{C}^2\text{H}-\text{Si}$ | 129 | 135 ^c | |
| VTS + Br ₂ /H ₂ O | $\text{Br}-\text{C}^1\text{H}_2-\text{C}^2\text{H}(\text{OH})-\text{Si}$ | 36 ^c | 63 | 137 (C ¹), ^{c,d} 127(C ²) ^{c,d} |
| ATS | $\text{C}^1\text{H}_2=\text{C}^2\text{H}-\text{C}^3\text{H}_2-\text{Si}$ | 115 | 130 | 19 (C ³), 67 ^{c,e} |
| ATS + Br ₂ /H ₂ O | $\text{Br}-\text{C}^1\text{H}_2-\text{C}^2\text{H}(\text{OH})-\text{C}^3\text{H}_2-\text{Si}$ | 38 ^c | 67 | 19 (C ³) |
| BTS | $\text{C}^1\text{H}_2=\text{C}^2\text{H}-\text{C}^3\text{H}_2-\text{C}^4\text{H}_2-\text{Si}$ | 114 | 139 | 26 (C ³), 11(C ⁴) ^d , 67 ^{c,e} |
| BTS + Br ₂ /H ₂ O | $\text{Br}-\text{C}^1\text{H}_2-\text{C}^2\text{H}(\text{OH})-\text{C}^3\text{H}_2-\text{C}^4\text{H}_2-\text{Si}$ | 37 ^c | 73 ^c | 25 (C ³), 7(C ⁴) ^c , 65 ^{c,e} |
| OTS | $\text{C}^1\text{H}_2=\text{C}^2\text{H}-(\text{C}^3-\text{H}_2)_5-\text{C}^8\text{H}_2-\text{Si}$ | 114 | 138 | 22-33 (C ³⁻⁷), 12(C ⁸) |
| OTS + Br ₂ /H ₂ O | $\text{Br}-\text{C}^1\text{H}_2-\text{C}^2\text{H}(\text{OH})-(\text{C}^3-\text{H}_2)_5-\text{C}^8\text{H}_2-\text{Si}$ | - | - | 138 (C ¹), ^d 114 (C ²), ^d 22-33 (C ³⁻⁷), 11(C ⁸) |

^a Samples prepared without cosolvent. ^b Si = matrix surface. ^c Broad signal. ^d Signals from unreacted double bonded carbons. ^e Signals from residual unhydrolyzed OEt groups.

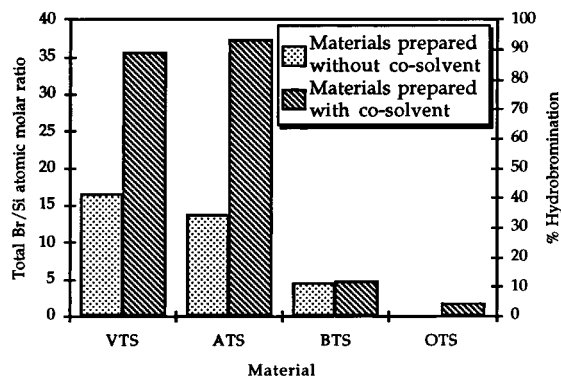


Figure 3. Reaction yield in terms of percent of hydrobromination (i.e., % double bonds reacted) and in terms of total Br/Si atomic molar ratio for the different materials.

the Br and OH in the alkyl chain were extracted from the solid-state ^{13}C NMR spectra of the samples prepared without cosolvent, and the chemical shifts are collected in Table 2. For example, in ATS, one sees the double bond before the reaction at 130 ppm, which is attributed to the C¹ terminal carbon of the allyl group, and at 115 ppm, which is attributed to the C².^{18a} The carbon bonded to the silicon atom, C³, appears at 19 ppm, in agreement with the results of White et al.^{18b} After the reaction, the signal from the brominated C¹ undergoes a large shift to a higher field, 38 ppm, that from the hydroxylated C² appears at 67 ppm, and that from C³ remains practically unaffected. The NMR results confirm that only one reaction occurred, e.g., the hydrobromination of the double bond. In the case of OTS prepared without cosolvent, no reaction occurred. In the case of ETS, used as a blank, no reaction was observed, implying that the matrix itself is inert toward Br₂ and that the only reaction was the hydrobromination.

The degree of hydrobromination was determined, as indicated above, from the amount of the released HBr. Figure 3 shows the results obtained for the various ormosils, and it is seen that, in general, the longer chains correspond to lower yields. ATS prepared with a cosolvent is the most efficient bromine sponge (with a 93% yield, and VTS is almost as good). It is also seen that, in general, homogenization of the reaction mixture with a cosolvent results in higher reactivity yields compared to those of the materials prepared without initial homogenization. The total Br/Si atomic molar ratio calculated from the released HBr (Figure 3) was compared to the particle external surface Br/Si atomic molar ratio, as determined from the elemental analysis

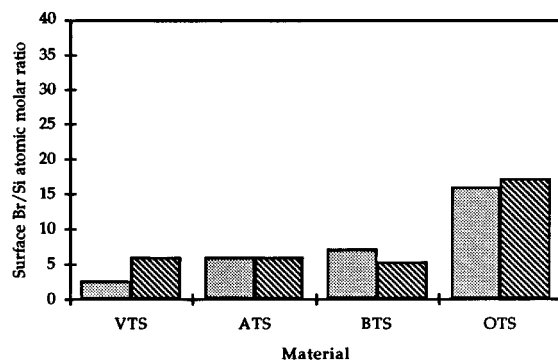


Figure 4. The external surface Br/Si molar ratio of the different material determined from elemental analysis (in scale with Figure 3).

measurements (Figure 4). The surface Br/Si atomic molar ratio for samples prepared with no cosolvent increases with increasing length of the alkenyl group, whereas the total Br/Si atomic molar ratio decreases. For samples prepared with EtOH as a cosolvent, the surface Br/Si atomic ratio is similar for VTS, ATS, and BTS and is greater for OTS.

Initial Reaction Rates. Figure 5 shows the initial rates of Br₂ disappearance (as determined from the decrease in the Br₂ optical absorption). It is seen that, in general, this rate decreases with increasing length of R. It is also seen that the samples prepared with cosolvent (Figure 5A) react more slowly than those prepared without cosolvent (Figure 5B). (The analytical method used here is more sensitive than the determination of pH, and therefore, the very slow kinetics of OTS in Figure 4B, which is due mainly to interfacial octenyl residues (see next section), is not seen in Figure 3.)

4. Discussion

The main observation is that, perhaps counterintuitively, as the chain length carrying the double bond gets longer, the reaction yields and rates decrease. This is counterintuitive because one would expect that longer chains would mean better accessibility of the reactive moiety because of their better exposure. This, in fact, is not the case, and the double bond becomes less accessible for bromine as the alkenyl chain becomes longer. We propose that this observation is best interpreted in terms of two opposing trends. The first is the tendency to concentrate the nonpolymerizable residues of trialkoxysilane monomers at the interface of the forming pores. More of these residues are expected to be found on the pore walls than in the bulk, because the trialkoxy tails will polymerize with each other (and

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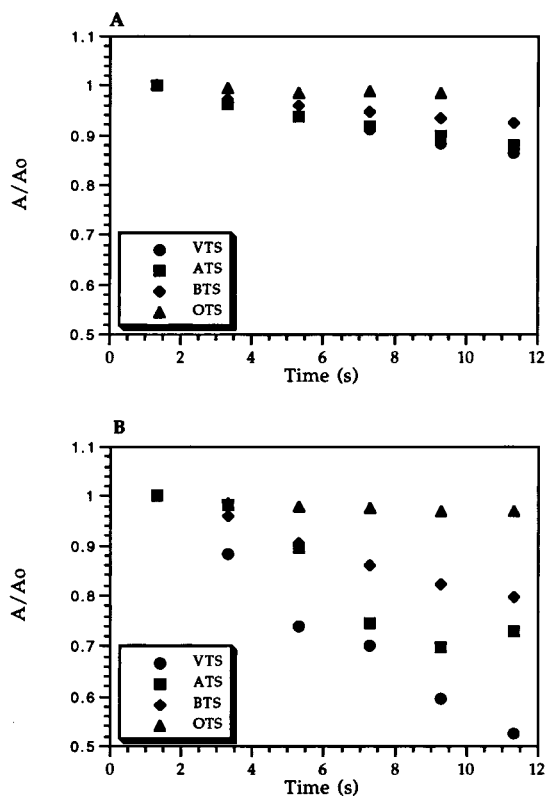
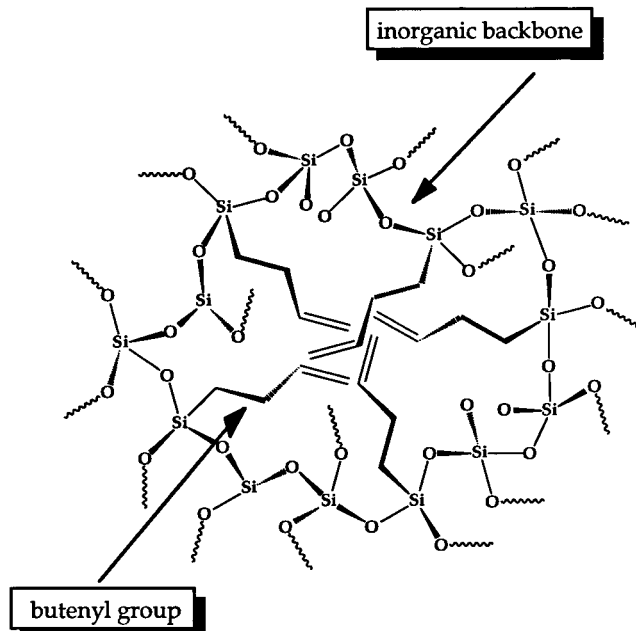


Figure 5. Initial rate of Br₂ disappearance: (A) samples prepared with cosolvent and (B) samples prepared without cosolvent.

with the tetraalkoxy monomer), tending to direct the alkenyl heads away from the polymerizing microenvironment. This explains the accessibility and exposure of the alkenyl residues to reaction within the porous materials, as is illustrated in Scheme 2 for the vinyl groups. The second, opposing trend, which buries the chains and reduces their accessibility, is proposed to be the formation of micellar-like structures at the very early stages of the sol-gel process. At this stage, the hydrolyzed monomers tend to arrange themselves such that the polar $-\text{Si}(\text{OH})_3$ groups form the head of the micelle and the hydrophobic alkenyl chain is buried within the core of that micelle. Further polymerization with (hydrolyzed) TEOS, it is suggested, then freezes this structure; this is illustrated in Scheme 3. Thus, the pore network should be more accessible to incoming molecules for the shorter-chain materials and less accessible to the longer ones (Figures 3 and 5); this is also generally seen for the penetrability of nitrogen shown in Table 1. Also seen in this table is that, although OTS has the lowest true density, it reveals no N₂-adsorption-detectable porosity. The low density, it is proposed, is all due to internal pores that might be closed, or at least bottlenecked, which could also explain the lack of reactivity.

Corroborative evidence for the assumption of micelle formation comes from a comparison of the materials prepared with ethanol as cosolvent to those prepared without it. As this solvent disrupts the formation of micelles, its use should enhance reactivity and increase the accessibility to nitrogen. This is, indeed, generally the case: for OTS, which showed no detectable HBr release, some residual reactivity is detected upon the addition of a cosolvent (Figure 3); and even for the vinyl

Scheme 3. Schematic View of the Possible Micellar Structures, Shown for BTS (without cosolvent)



and allyl groups there is an improvement in performance, suggesting that micellar structures might be generated to some extent even with these residues. As seen in Table 1, homogenization with ethanol has a particularly marked effect on the nitrogen adsorption of the BTS materials but not on the reactivity (Figure 3). This example demonstrates, once again, that N₂-BET values might sometimes be of no relevance to other adsorbed molecules under different conditions (N₂ at cryogenic temperatures vs Br₂ at room temperature; cf., the major difference between CO₂ and N₂ adsorption values¹⁹).

Another important aspect of sol-gel materials in general, and of ormosils in particular, is revealed from the comparison of the analyses of the total Br/Si atomic molar ratios of the whole material (Figure 3) and the interface (Figure 4). The comparison clearly indicates that the internal surface due to the porosity and the external surface of the material are two different entities, both chemically and physically. The two highest values of the Br/Si atomic molar ratio from Figure 3 (with cosolvent) are the short-chain VTS and ATS, which serve as an indication of the maximal possible ratio. Because the reaction yield for ATS was 93%, the maximal total Br/Si atomic molar ratio is close to 40% (reflecting the fact that 40% of the Si atoms in the material are substituted by R groups). Remaining with these two examples, it is seen that the external surface Br/Si atomic molar ratio (Figure 4) is much smaller than the total one. This can be understood if one recalls that the solvent at the reaction surface of the growing sol-gel material is strongly hydrogen-bonding (water/ethanol), so that Si-OH groups will have a preference in orienting toward this interfacial solvent, more than the hydrophobic alkenyl group. Why then is this trend reversed for the long-chain OTS? On one hand, the

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micellization, as explained above, renders the internal interface inaccessible, but on the other hand, we recall that the condensation of RTS groups is slowed for the longer R groups.²⁰ The reversal for the OTS case might therefore reflect late wrapping of the surface of the already-formed particles. Yet, this explanation is tentative in view of the recent paper of Rodriguez et al. who observed that, under different conditions, the presence of TEOS accelerated the hydrolysis of octyltriethoxy silane.²¹

An interesting observation that reflects the complexity of the studied systems is the difference in reaction rates between the ethanol-homogenized and nonhomogenized systems (Figure 5A and B, respectively). The more efficient bromine sponges in terms of capacity, namely, the homogenized materials, react *more slowly* than the nonhomogenized ones. The best interpretation we can offer relies again on the micellar structures of the hydrolyzed RSi(OEt)₃ species and is in agreement with all of the other observations given above. The nonhomogenized system is characterized by two intramaterial populations. One population is due to the formation of the initial micelles, which, as we have seen above, bury the reactive residues and decrease the capacity of the material to act as a bromine sponge. However, because of competing kinetics, the nonmicellized "RSi(OH)₃" species copolymerize with TEOS and are the ones that do offer reactivity. Then why is that reactivity faster than the reactivity found for the

homogenized systems? Note that micellization changes the RSi(OEt)₃/TEOS ratio, by removing RSi(OEt)₃ from the mixture, and this in turn, results in an environment of R that is much richer in hydrophilic Si-OH groups compared to the R-rich, more hydrophobic homogenized system. Also, because the reaction is carried out in water, which means that wetting of the pore surface is important for bringing bromine to the double bonds, it is expected and indeed found that the more hydrophilic environment of the alkenyls in the nonhomogenized materials will react faster. Figure 3 hints, at least semiquantitatively that, for instance, for ATS prepared without cosolvent, half of the double bonds are buried within a pseudo-micellar structure, while the other half is accessible for the fast reaction seen in Figure 5B.

In conclusion, as complex as this behavior and its analysis might seem, it is this complexity that opens the possibility of fine-tuning and tailoring the reactivity of sol-gel materials. Further work in this direction is in progress.

Acknowledgment. This research was supported by a grant (to H.F.-M.) from the Ministry of Science, Arts and Sports, Israel. Additional parts of this research project were supported by the Israel Science Foundation and by the Infrastructure Project (Tashtiot) of the Ministry of Science, Arts and Sports, Israel. Solid-state ¹³C NMR spectra were measured by Prof. Robert Glaser (Ben-Gurion University of the Negev) on a Bruker DMX-500 spectrometer at the University Laboratory for Magnetic Resonance.

CM000516H

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