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ACID-CATALYZED TIME-EFFICIENT SYNTHESIS OF RESORCINOL-FORMALDEHYDE AEROGELS AND CROSSLINKING WITH ISOCYANATES

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Introduction

Aerogels are open-cell foams derived from supercritical fluid (SCF) drying of wet gels. Their large internal void space is responsible for low thermal conductivity, high surface area and high acoustic impedance. Most aerogels are based on inorganic metal or semimetal oxide frameworks. Pekala and co-workers¹⁻⁴ synthesized resorcinol-formaldehyde (RF) organic aerogels by poly-condensation of resorcinol with formaldehyde in the presence of Na₂CO₃ as base catalyst, followed by drying with SCF CO₂. Low-density RF aerogels prepared by this method exhibit high porosities (>80%), high surface areas (400-900 m²g⁻¹), ultrafine cell-size (<500 Å) and densities as low as 0.03 g cm⁻³. The major drawback though, has been the length of the preparation procedure that typically spans several days.

Looking at the mechanism of the process, the RF gel formation has been associated with two major reactions: (1) formation of hydroxymethyl derivatives of resorcinol; and, (2) condensation of those derivatives to methylene (-CH₂-) and methylene ether (-CH₂-O-CH₂-) bridges. The effect of the resorcinol to catalyst (R/C) ratio on the final aerogel structure has been studied extensively. That ratio was typically varied in the range between 50-300. Formation of particles connected with large necks was reported for low and for very high (~1500) R/C ratios.⁵⁻⁷ The final pore structure and the gelation time depend strongly on the sol pH;⁸ at low pHs, precipitation rather than gelation was reported.

The extensive literature on base-catalyzed RF aerogels has obscured attempts towards acid-catalyzed processing.⁹⁻¹³ Recently, Brandt and Fricke reported an aqueous acetic acid catalyzed route for RF gel synthesis, where they still allowed a two-day period for gelation and aging.¹⁰

Reasoning that not only hydroxy methylation of resorcinol, but also subsequent condensation to methylene and methylene ether bridges should be all acid-catalyzed processes, we undertook a systematic look at the reaction of resorcinol with formaldehyde in CH₃CN, developing a time-efficient method that yields within a few hours (as opposed to weeks) gels indistinguishable from those reported in the literature. The -OH groups of resorcinol in the resulting gels are reactive with di- and tri-isocyanate crosslinkers in analogy to silica, leading to isocyanate-derived polymer crosslinked RF aerogels, which are more robust, and more resistive to shrinkage than their native (non-crosslinked) counterparts.

Experimental

The RF sol was prepared by mixing resorcinol with formaldehyde in CH₃CN in four different mol ratios (1:2, 1:3, 1:5 and 1:10). For example the sol with 1:2 ratio was prepared by mixing at room temperature two solutions; solution "A" containing 0.337 g (0.003 mol) of resorcinol, 0.477 mL (0.006 mol) of a formaldehyde solution (37%, methanol stabilized from Aldrich), and 11.5 mL CH₃CN, and solution "B" containing 0.636 mL CH₃CN and 0.03 mL conc. HCl. The mixture (sol) was poured into polypropylene molds (Wheaton polypropylene Omni-Vials, Part No. 225402, 1 cm in diameter) and is capable of gelling within 90 min at room temperature (followed by a 24 h aging period), but the entire gelation/aging process can be accelerated by placing in an 80 °C oven for just one hour. The resulting wet gels were washed with CH₃CN, acetone and were either dried with SCF CO₂ or were crosslinked with Desmodur N3200 (a diisocyanate) or Desmodur N3300 (a triisocyanate) in the presence or absence of triethylamine (TEA) as a catalyst, according to published procedures.¹⁴⁻¹⁶

Results and Discussion

¹³C-NMR of the RF reaction mixture in CD₃CN (Figure 1) shows that the products formed are essentially the same as the products reported in the literature from the base-catalyzed route. The characteristic difference, however, is that under acid-catalysis condensation of resorcinol with formaldehyde occurs immediately after mixing even at room temperature.

Hard gels are produced within one hour at 80 °C, and further aging is not even necessary. ¹³C-NMR peak assignment supports protonation of formaldehyde to [H₂C⁺OH] that gives electrophilic aromatic substitution with resorcinol (Scheme 1). The hydroxy group of the hydroxy methylated product can be protonated further, becoming prone to lose water yielding either additional electrophilic aromatic substitution, or, condensation with another hydroxymethylated resorcinol to form methylene ether bridges. Solid ¹³C-NMR of the final RF-aerogels shows that almost all the condensation leads to -CH₂- rather than to -CH₂-O-CH₂- bridging.

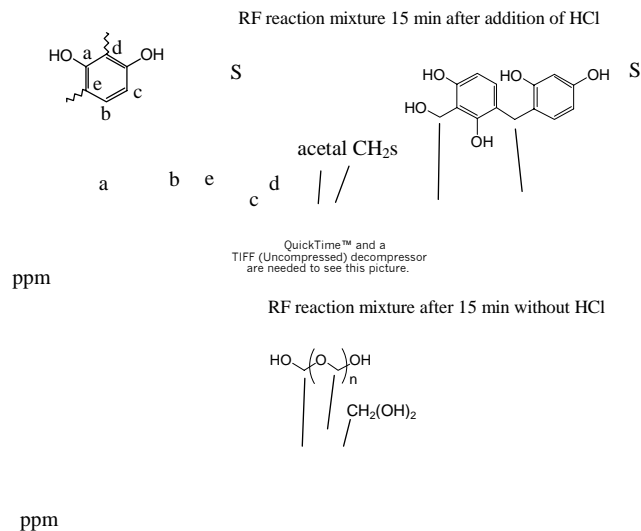
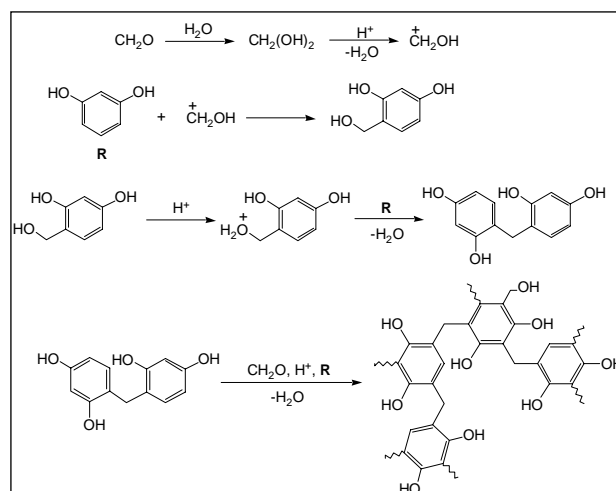


Figure 1. Comparative ¹³C-NMR spectra of a 1:2 mol ratio mixture of R:F in CD₃CN (S). Evidently, much faster reaction takes place in the presence of HCl. The peak assignment was according to ref. 17.



Scheme 1. Proposed mechanism for the acid-catalyzed RF gelation.

RF wet gels can be dried directly with SCF CO₂ to aerogels, or they can be first crosslinked with isocyanate using the -OH functionality of resorcinol as the focal point for the surface attachment of the isocyanate, according to chemistry discussed recently in conjunction with silica aerogels.¹⁴⁻¹⁶ Figure 2 shows a photograph of two typical RF aerogels, one prepared with a 1:3 and another one with a 1:5 R/F mole ratio, and of their corresponding isocyanate-treated counterparts. The densities of the two native aerogels are 0.180 and 0.154 g cm⁻³, while the densities of the corresponding crosslinked samples are 0.120 and 0.148 g cm⁻³, respectively. The fact that the isocyanate-treated RF aerogels have lower densities than the densities of the corresponding native aerogels, is attributed to the significant shrinkage experienced by the latter.

Isocyanate-treated RF aerogels remain close to the volume of the mold. Based on density and dimension considerations (see Figure 2), isocyanate-treated RF aerogels consist of 51-54% w/w of diisocyanate-derived polymer.

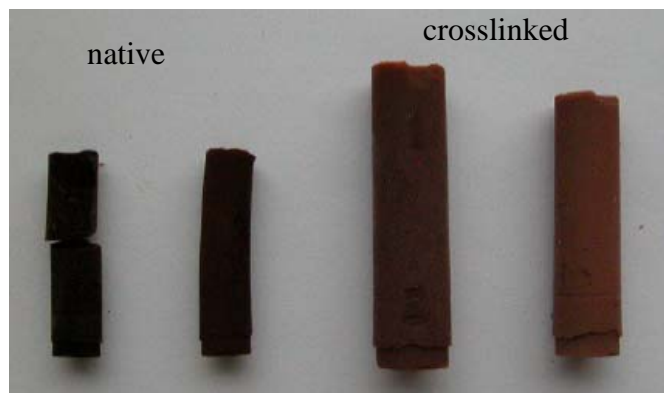


Figure 2. Photographs of two native acid-catalyzed RF aerogels (left), and of corresponding isocyanate crosslinked samples (right). *From left:* First sample (broken): R/F mole ratio=1:3; sample diameter: 0.64 cm; bulk density=0.180 g cm⁻³. Second sample: R/F mole ratio=1:5; sample diameter: 0.64 cm; bulk density=0.154 g cm⁻³. Third sample: R/F mole ratio=1:3; sample crosslinked with Desmodur N3300 in the presence of 0.1% w/w TEA catalyst; sample diameter=0.93 cm; bulk density=0.120 g cm⁻³. Fourth sample: R/F mole ratio=1:5; sample crosslinked with Desmodur N3200 in the presence of 0.1% w/w TEA catalyst; sample diameter=0.84 cm; bulk density=0.148 g cm⁻³. (Treatment with isocyanate minimizes shrinking.)

Microscopically (Figure 3), both native and crosslinked aerogels look indistinguishable and consist of agglomerations of primary and secondary particles, akin to silica aerogels. The SEM data suggest that the polymer has coated the surfaces of the particles conformally, leaving the internal empty mesoporous space intact. Indeed, the BET surface area varies in the 360-460 m² g⁻¹ range, while there is no clear distinction between isocyanate treated and non-treated samples. The skeletal density decreases from ~1.5 g cm⁻³ to ~1.27 g cm⁻³ upon treatment with isocyanate while the porosity calculated from the bulk and skeletal density data is consistently around 90±2 %.

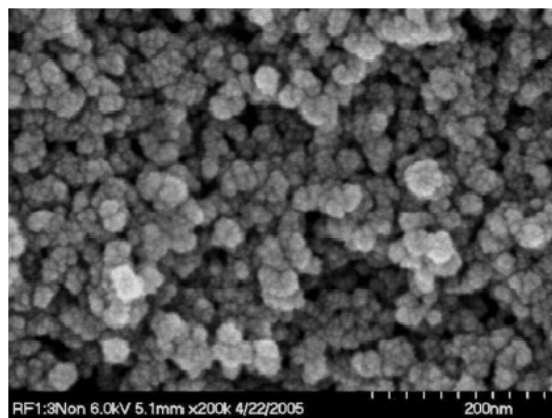


Figure 3. SEM photograph of a native acid catalyzed 1:3 RF aerogel. Isocyanate-treated samples look identical. Note that the nanostructure appears identical to that of silica aerogels of similar density.¹⁴⁻¹⁶

The uptake of isocyanate by RF gels was confirmed by infrared (IR) spectroscopy. Figure 4 compares the IR spectra of a native RF aerogel with those of gels treated with Desmodur N3200 (a diisocyanate) and Desmodur N3300 (a triisocyanate built around a isocyanurate ring), with and without a catalyst. The RF aerogel prepared by acid catalysis shows the same IR absorption pattern as that of the base (Na₂CO₃) catalyzed RF aerogels published earlier by Pekala. IR absorptions at 2942, 2842 and 1479 cm⁻¹

were associated with -CH₂- bonds, whereas the broad band at 3382 cm⁻¹ is associated with the -OH group of resorcinol. The band at 1614 cm⁻¹ represents the aromatic stretches, while the bands at 1222 cm⁻¹ and at 1092 cm⁻¹ were assigned to vibrations of the methylene ether link between phenyl rings. The IR spectrum of all RF aerogels treated with isocyanates show pronounced sharp absorptions in the 2900-3000 cm⁻¹ region assigned to aliphatic -CH₂- stretches. Samples treated with N3200 show a shoulder in the carbonyl stretch region at 1767 cm⁻¹ assigned to the diazetidinedione group, while samples treated with N3300 show the typical isocyanurate ring carbonyl stretch at 1690 cm⁻¹.

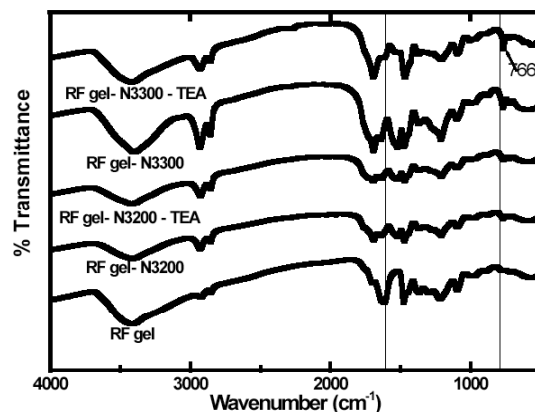


Figure 4. FTIR spectra of acid catalyzed RF aerogels prepared with a mole ratio of resorcinol to formaldehyde equal to 1:5. The isocyanate crosslinker and the use of TEA catalyst is shown by the individual spectra.

Conclusions

Mechanistically, formation of RF aerogels should proceed faster under acid catalysis, and this has been confirmed by cutting the gelation/aging time from weeks to hours. The resulting aerogels are spectroscopically indistinguishable from their base-catalyzed counterparts reported in the literature. The shrinkage noted after SCF drying is prevented by applying an isocyanate-derived conformal coating on the skeletal nanoparticles.

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