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# A SYNTHETIC ROUTE TO ORGANIC AEROGELS - MECHANISM, STRUCTURE, AND PROPERTIES

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Résumé - En catalyse basique, la réaction en voie aqueuse du résorcinol avec le formaldehyde est assimilable à une voie sol-gel, dans laquelle des "clusters" de polymère à surface fonctionnelle sont formés. La nature covalente de la reticulation ntre ces "clusters" produit des gels qui sont séchés sous des conditions hypercritiques pour obtenir des aerogels organiques de faible densité (≤ 200 mg/cc). Les aerogels sont transparents et sont constitués de cellules dont la taille est inférieure à 1000 Å. Leur microstructure est constituée par des particules quasi colloïdales interconnectées, dont le diamètre varie entre 30 et 100Å. La taille de la particule, la taille de la cellule, la surface spécifique et la densité des aerogels de resorcinol-formaldehyde (R.F.) sont grandement déterminées par la concentration en catalyseur du mélange. Les aerogels R.F. sont sous plusieurs angles similaires à ceux de silice, encore qu'une comparaison de leurs propriétés mécaniques respectives suggère l'existence de subtiles différences

Abstract - The base catalyzed, aqueous reaction of resorcinol with formaldehyde follows a sol-gel pathway in which surface functionalized polymer "clusters" are formed. The covalent crosslinking of these "clusters" produces gels which are dried under supercritical conditions to obtain low density, organic aerogels (≤ 200 mg/cc). The aerogels are transparent and have cell sizes less than 100Å. Their microstructure consists of interconnected colloidal-like particles with diameters of 30-100 Å. The particle size, cell size, surface area, and density of resorcinol-formaldehyde (RF) aerogels are largely determined by the catalyst concentration in the mixture. RF aerogels are similar to silica aerogels in many ways, yet a comparison of their mechanical properties suggests subtle morphological differences.

## 1 - INTRODUCTION

Sol-gel processing of metal alkoxides in the common route for the production of two different materials : (1) inorganic xerogels which are heat treated to form coatings, fibers, or composites /1,4/ and /2/ inorganic aerogels which have low density, high porosity, and ultrafine cell sizes /5,6/. In the first process, the xerogel is formed from the slow evaporation of solvent from an alcogel. Large capillary forces are exerted as the liquid-vapor interface moves through the gel, and these forces cause macroscopic shrinkage. The resulting xerogel has high surface area and continuous porosity. These parameters allow the material to be sintered into full density coatings at relatively low temperatures.

In the formation of inorganic aerogels, shrinkage of the alcogel is minimized by supercritical drying. Above the critical point of the solvent which occupies the pores of the gel, capillary forces are reduced to zero /7/. Inorganic aerogels retain the morphology of the original alcogels. Their high surface area, continuous porosity, and low density lead to potential applications as phonic and thermal insulators, filters, and catalyst supports /8,10/.
After reviewing the sol-gel chemistry of alkoxysilanes (i.e. TMOS and TEOS), our research group concluded that organic chemistry could be used to produce new low density materials in a similar fashion /11,13/. In our view, four important requirements must be satisfied to produce gels via a sol-gel route. These requirements are outlined in Table I.
The synthesis of organic aerogels via a sol-gel route involves the polycondensation reaction of resorcinol (1,3 dihydroxybenzene) with formaldehyde under alkaline conditions. In this reaction, resorcinol serves as a trifunctional monomer capable of electrophilic aromatic substitution in the 2,4 and 6 ring positions. Formaldehyde is difunctional and forms covalent bridges between the resorcinol rings leading to high crosslinking densities. The resultant sol is composed of polymer "clusters" with diameters of 30-100 Å. Favorable solvent-polymer and ionic interactions are responsible for the stabilization of these "clusters". The "clusters" crosslink to form gels through the condensation of surface functional groups such as the hydroxymethyl ($-CH_2OH$) species.

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The resorcinol-formaldehyde (RF) gels are red in color and transparent indicative of both a small cell (pore) size and "clusters" size. The supercritical extraction of solvent from the pores of the gel results in organic aerogels. This paper describes the chemistry, structure, and properties of RF aerogels in detail.

TABLE I
Sol-gel requirements
- Multifonctional monomers
- High degree of crosslinking
- Surface functional groups
- Particle stabilization

## 2 - EXPERIMENTAL PROCEDURES

### 2.1 - GEL PREPARATION AND SUPERCRITICAL DRYING

Gel preparation has been described previously /14/. Briefly, resorcinol and formaldehyde were mixed in deionized and distilled water at a molar ratio of 1:2. Sodium carbonate was then added as the base catalyst. The RF solution was poured into 23 x 85 mm glass vials or ampules which were tightly sealed and placed into an oven to cure at 85-95°C. Depending upon the % solids and catalyst level, gel times varied from several hours to days. Typically, the RF gels were cured for 7 days and then removed from their glass containers and placed in a dilute acid solution at 45°C. The acid treatment increased the modulus of the gels through additional crosslinking provided by the condensation of hydroxymethyl groups to form ether bridges.

In preparation for supercritical drying, the gels were exchanged into an organic solvent which was compatible with liquified carbon dioxide (e.g. acetone, methanol, or isopropanol). The solvent-filled gels were placed into a jacketed pressure vessel (Polaron Equipment Ltd., Watford, England) which was then filled with carbon dioxide. After the carbon dioxide was completely exchanged for the solvent in the pores of the gels, the vessel was heated 15°C above the critical temperature ($T_C$ = 31°). The samples were maintained at 46°C for a minimum of 4 hours, and then the pressure was slowly released through an exit valve. At atmospheric pressure, the samples were removed and held in front of a light source to ensure that the aerogels were transparent.

### 2.2 - AEROGEL CHARACTERIZATION

All mass and dimensional measurements were made after the aerogels were dessicated for 24 hours at room temperature. The high surface area of the aerogels and the presence of many hydrophilic groups caused a 2-8 % mass increase if the materials were not dried properly. Selected samples were submitted for surface area analysis and microscopic examination. BET surface areas were obtained from nitrogen adsorption analysis (Digisorb 2600). Prior to analysis, samples were evacuated ($10^{-5}$ Torr) for 24 hours at 25°C to remove adventitious moisture and contaminants from the surface of the aerogels. Some samples were dried under vacuum at 200°C for 4 hours ; however, no significant differences in surface areas were noted between these two procedures. The standard deviation for surface area mesurements was generally ± 12 % of the reported values.

The morphology of the RF aerogels was examined with scanning electron microscopy (Hitachi S-800) and transmission electron microscopy (Jeol 200 CX). SEM was performed on uncoated samples because the sputter deposition of a thin, conductive gold coating was found to distort the aerogel structure. Samples were prepared for TEM by atomizing an RF aerogel/ methanol mixture on to a Formvar $^R$ grid. Thin sections of the aerogel were analyzed at an accelerating voltage of 80 kV. Re-wetting of the RF aerogels with methanol did not damage the microstructure observed with TEM.

### 2.3 - MECHANICAL PROPERTIES

The strength and modulus of RF aerogels were measured in uniaxial compression at a strain rate of 0.1%/sec using an Instron (Model # 1125). The aerogels were machined into 10 x 10 x 10 $mm^3$ rectangular prisms for testing. All measurements were conducted under ambient conditions at 22-25°C. The relative humidity was generally 50-70 % during the experiments, and no special precautions were taken to prevent moisture adsorption by the aerogels.

The compressive strength of RF aerogels was calculated at the point on the stress-strain curve where the curve deviated from linearity by 0.2 % strain. Although no fundamental reason exists for choosing the 0.2 % strain offset, we have found it to be a convenient way to characterize the strenght of many different low density materials which exhibit a variety of responses at higher compressive strains. The compressive modulus of the aerogels was calculated from the slope of the stress-strain curve in the linear elastic region.

## 3 - RESULTS AND DISCUSSION

### 3.1 - REACTION CHEMISTRY AND KINETICS

Resorcinol reacts with formaldehyde under alkaline conditions to form mixtures of addition and condensation products. These intermediate products can react further to form a tightly crosslinked polymer network. The principal reactions include /1/ the formation of hydroxymethyl derivatives at the 2,4, and/or 6 ring positions of resorcinol, and /2/ the condensation of the hydroxymethyl derivatives to form methylene and methylene ether bridged compounds /15,16/. Figure 1 shows a schematic diagram of the reaction of resorcinol with formaldehyde under conditions used in this study.

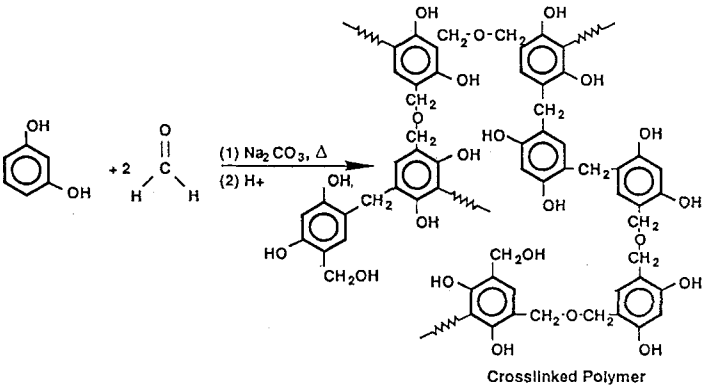



Figure 1. A crosslinked polymer network from the reaction of resorcinol with formaldehyde.

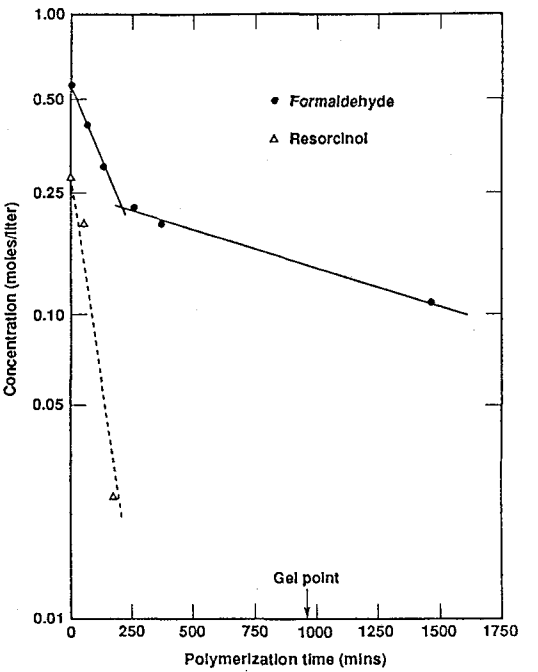



Figure 2. Free monomer in the RF reaction as a function of the polymerization time at 85°C. Sample was prepared at a target density of 50 mm/cc with [[Resorcinol] /[Catalyst] = 200.

The catalyst concentration affects both the reaction kinetics and resultant aerogel properties. Figure 2 shows the amount of unreacted formaldehyde and resorcinol in a 5 % solids solution as a function of the polymerization time at 85°C /14,17/. Approximately 60 percent of the original formaldehyde is consumed after 200 minutes, and an abrupt change in the rate of formaldehyde consumption follows. At this point in the polymerization,

approximately 90 percent of the initial resorcinol is reacted. These data indicate that the nucleation and growth of polymer "clusters" is nearly complete. Henceforth, the rate-limiting step becomes the interconnection of the "clusters". Eventually, a gel is formed at approximately 950 minutes, but formaldehyde is still able to participate in addition and crosslinking reactions.

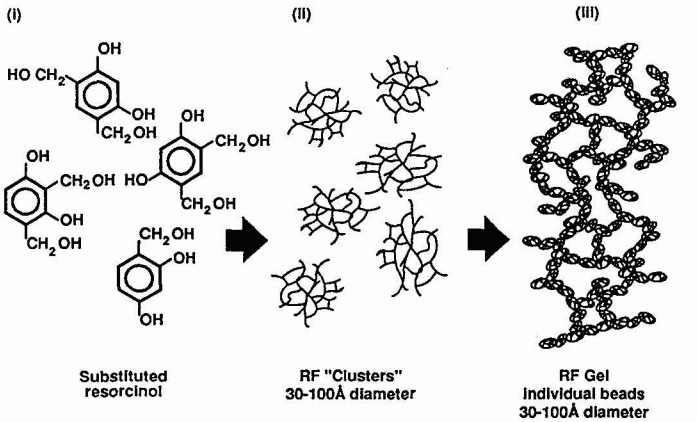



Figure 3. A shematic diagram of the RF gelation mechanism.

The use of a different catalyst concentration in the RF formulation changes the absolute amount of formaldehyde remaining in solution at various polymerization times ; however, the same trends for nucleation, growth, and gelation are observed. Figure 3 depicts the sol-gel chemistry of an RF mixture.

3.2 - STRUCTURE AND PROPERTIES

Figure 4 displays an RF aerogel after supercritical drying. The aerogel is dark red in color and transparent. The latter property indicates that both the cell size and characteristic particle size (referred to as "cluster" size in the gel phase) of the aerogel are less than 1/20th the wavelength of visible light.

RF aerogels were examined by SEM to reveal their morphology. Figure 5 shows that the aerogels have an open cell structure with continuous porosity. The observed cell size is less than 1000 Å --- far below the typical value for foams made from phase-inversion or blowing processes /18,19/.

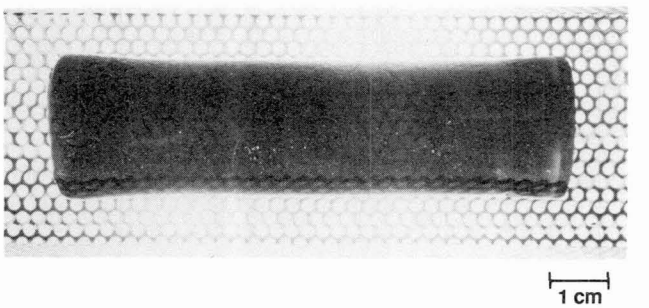



Figure 4. A transparent RF aerogel on a perforated metal screen.

TEM reveals that the aerogel microstructure is composed of interconnected colloidal-like particles. The size of these particles is controlled to a large extent by the catalyst concentration used in the RF formulation. Figure 6 shows the microstructure of aerogels synthesized from a 5% solids mixture at two different catalyst concentrations. As the catalyst concentration is increased by a factor of 4, the particles are observed to decrease in diameter from approximately 100 Å to 30 Å.

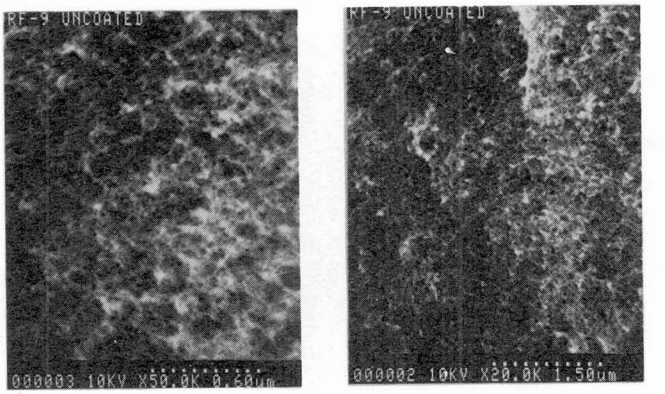



Figure 5. Scanning electron micrographs of an RF aerogel.

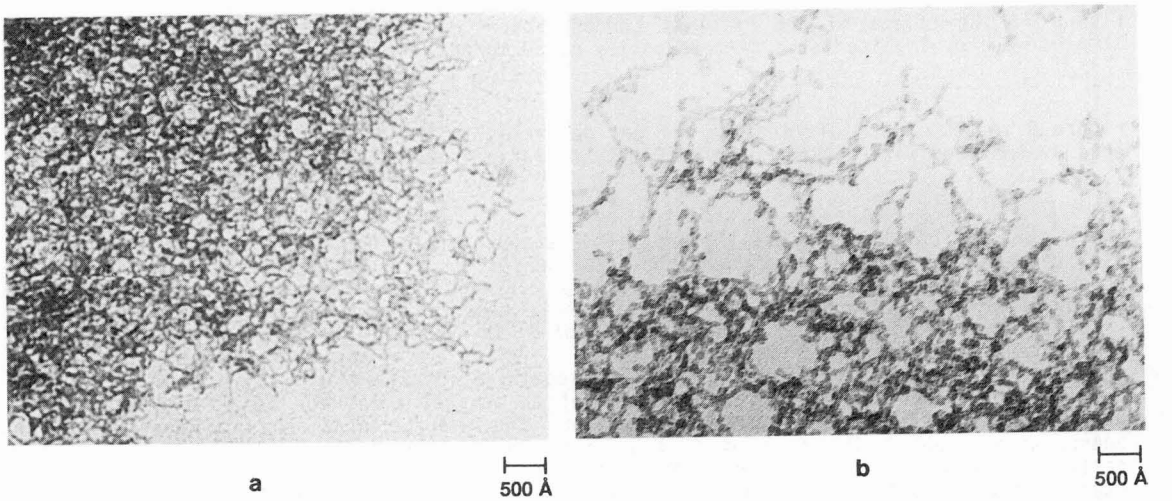
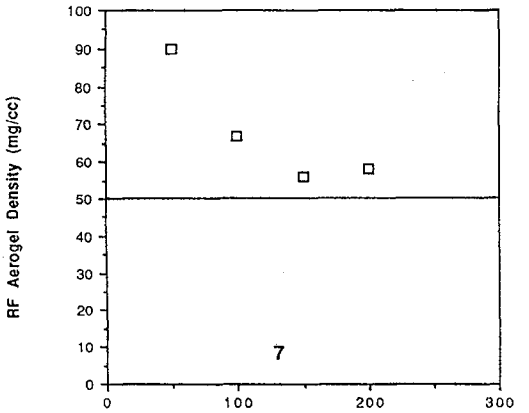



Figure 6. Transmission electron micrographs of RF aerogels synthesized at a target densities of 50 mg/cc with 2 different catalyst concentrations. [Resorcinol]/[Catalyst] ratio equals (a) 50 and (b) 200.

The effect of the catalyst concentration upon the interconnected particle size and presumably the size of "clusters" formed prior to gelation suggests an autocatalytic growth mechanism. After the base catalyst activates the resorcinol ring through hydrogen abstraction, formaldehyde can add to the ring in either the 2,4, or 6 positions. The reaction rate of this substituted resorcinol molecule toward bridge formation or further substitution is faster than the original addition of formaldehyde to resorcinol. After a bridge is formed between two resorcinol rings, this dimer is tetra-functional and has a higher probability of further reaction than an individual resorcinol molecule in solution. The above mechanism leads to the preferential growth of polymer "clusters", the total number of which are determined by the initial catalyst concentration.

The catalyst concentration also affects the final density of aerogels synthesized from gels with the same solids content. Figure 7 shows that aerogels dried from gels synthesized at high catalyst concentrations have higher densities than their low catalyst counterparts. The high catalyst gels experience more shrinkage during supercritical drying even though their modulus is higher than the low catalyst gels. Presumably, the higher modulus results from better interconnection between "clusters" in the high catalyst gels. Nevertheless, the increased shrinkage during supercritical drying suggests that the interparticle crosslinking density is low. This discrepancy is under further investigation.

The above data indicate that RF aerogels will most closely approximate their theoretical densities at low catalyst concentrations. Figure 8 compares actual RF aerogel densities to



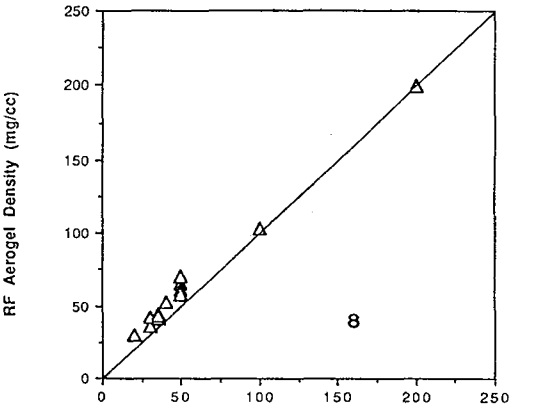




Figure 7. The effect of the catalyst concentration upon final RF aerogel densities. All samples were synthesized at a target density of 50 mg/cc.

Figure 8. A comparison of final RF aerogel densities to their target densities. All samples were synthesized with a [Resorcinol]/[Catalyst] ratio = 200.

their theoretical values at a [Resorcinol]/[Catalyst] ratio of 200. The solid line of the plot represents the ideal case where the final densities match the theoretical densities. Above 100 mg/cc, target densities are readily achieved. Below 50 mg/cc, the aerogels are approximately 33 % higher in density than their expected values. Lower concentrations of catalyst can be used, but eventually a point is reached where only opaque gels or precipitates are formed.

In order to further characterize the above aerogels, BET surface areas were measured. Figure 9 shows a 60% increase in the surface area of an aerogel after the catalyst concentration was raised four-fold. The TEM data show that the average particle size decreases from approximately 100 Å to 30 Å over this same range. This decrease in particle diameter partially explains the increased surface area per gram of aerogel ; however, other factors such as the porosity of individual particles and the size of necks between them must be quantified before a detailed model of the microstructure can be proposed.

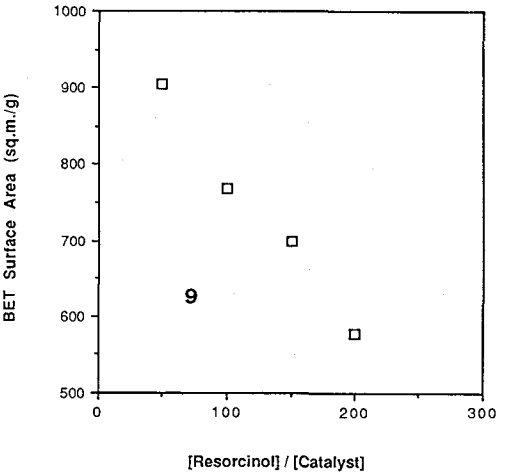
If the [Resorcinol]/[Catalyst] ratio is held constant for gel formulations varying in solids content, the surface areas of the resultant aerogels remain relatively constant. Figure 10 displays the surface areas of aerogels ranging in density from 30-200 mg/cc. These data indicate that the average particle size is approximately the same for each aerogel; however, the average cell size must be increasing as the density is lowered.

The mechanical properties of RF aerogels were measured in uniaxial compression as a function of density. As expected, both the modulus and strength increased with the aerogel bulk density as shown in Figures 11 and 12. The linear log-log plot in each case demonstrates a power-law density dependence that has been observed in many other low density materials. This relationship is expressed as

$$E \text{ or } S \propto (d)^n \qquad (1)$$

where d is the bulk density and n is a non-integer exponent that usually ranges from 2-4 [20-23]. For highly regular, geometric foam structures the exponent usually falls very close to 2.0, while for irregular, fractal type structures the value generally exceeds 3.0. In the case of the RF aerogels, the exponent is 2.5 ± 0.1 for the strength.

In comparison, the modulus of silica aerogels has been reported to show a power-law dependence with an exponent equal to 3.7 ± 0.3 [24]. Thus, our mechanical property data suggest that differences exist between the microstructure of the RF aerogels and silica aerogels. Although these differences are not generally observable with TEM or SEM, we predict that future scattering experiments will provide insight concerning this matter.



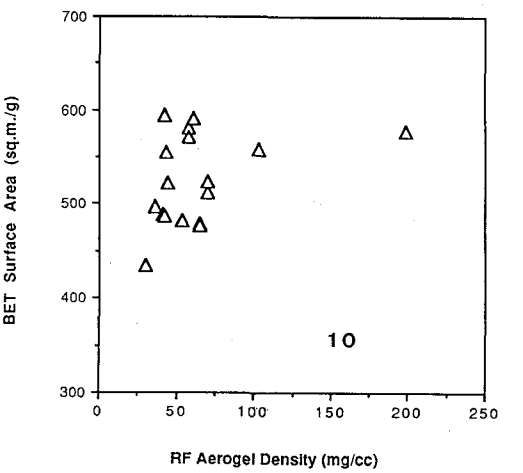
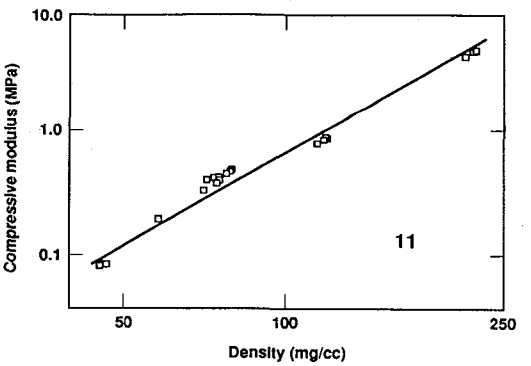




Figure 9. The effect of the catalyst concentration upon the BET surface areas of RF aerogels. Measurements were performed on the samples from Figure 7.

Figure 10. BET surface areas for RF aerogels ranging in density from 30-200 mg/cc. All samples were synthesized with a [Resorcinol]/[Catalyst] = 200.



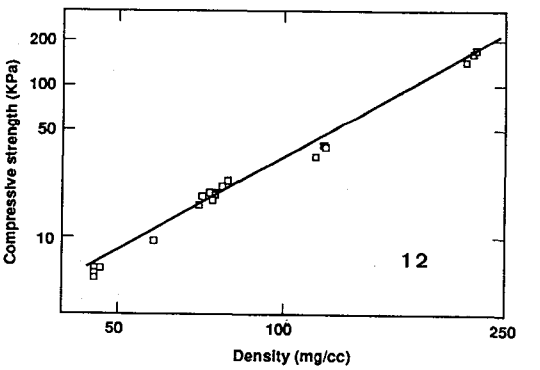




Figure 11. A log-log plot of compressive modulus vs. density.

Figure 12. A log-log plot of compressive strength vs. density.

## 4 - SUMMARY

Organic aerogels can be successfully synthesized from the base catalyzed reaction of resorcinol with formaldehyde. The catalyst concentration of this mixture dramatically affects the growth rate and size of the polymer "clusters" which crosslink to form gels. The catalyst effect manifests itself in the measurements of BET surface area, particle size, and density of the final aerogel. Although the RF aerogels appear similar to silica aerogels, a comparison of the mechanical properties of these materials suggests subtle morphological differences.

## 5 - ACKNOWLEDGMENTS

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