JOURNAL OF MATERIALS SCIENCE 24 (1989) 3221–3227

# Organic aerogels from the polycondensation of resorcinol with formaldehyde

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The polycondensation of resorcinol with formaldehyde under alkaline conditions results in the formation of surface functionalized polymer "clusters". The covalent crosslinking of these "clusters" produces gels which are processed under supercritical conditions to obtain low density, organic aerogels ($\leqslant 0.1\ \mathrm{g\,cm^{-3}}$). The aerogels are transparent, dark red in colour, and consist of interconnected colloidal-like particles with diameters of approximately 10 nm. The polymerization mechanism, structure and properties of the resorcinol–formaldehyde aerogels are similar to the sol–gel processing of silica.

## 1. Introduction

Gels are a unique class of materials which exhibit solid-like behaviour resulting from a continuous, three-dimensional framework extending throughout a liquid. This framework consists of molecules interconnected through multifunctional junctions. These junctions can be formed through covalent crosslinking, crystallization, ionic interactions, hydrogen bonding, or chain entanglements. In some cases, junction formation is reversible and the gels revert to liquid-like behaviour upon a change in temperature [1–5].

Gels have been synthesized for a variety of applications, and scientists from many disciplines have studied their properties. Electrophoresis of protein mixtures is performed with crosslinked polyacrylamide gels [6]. Chromatographic packings are composed of styrene–divinyl benzene gel particles [7]. Hydrogels containing 2-hydroxyethyl methacrylate are used in many soft contact lens applications [8]. In each of these examples, the gel framework is tailored to the specific end use. For example, the molecular weight between crosslinks partially determines the water content of a soft contact lens.

In other cases, gels serve only as an intermediate phase in materials processing. High modulus fibres are made by solution spinning a polyethylene/decalin solution, quenching the filaments to form a gel, and stretching to a high draw ratio [9]. Gels produced from the phase separation of dilute polymer solutions serve as precursors to membranes and low density foams [10–13].

Sol–gel processing of ceramics has gained considerable attention because various metal oxides can be formed from gels at relatively low temperatures when compared to conventional melt processing [14]. In the case of silica gels, the solvent is slowly evaporated to form a dry, porous xerogel which can be sintered into a glass. If the solvent is removed from the silica gel via supercritical drying, a transparent low density foam results. Foams of this type are referred to as "inorganic aerogels".

The small cell size ($< 50$ nm) of the silica gel necessitates supercritical drying. Large capillary forces at the liquid–vapour interface cause the silica gel to shrink or crack if the solvent is removed by evaporation. In the case of supercritical drying, no surface tension is exerted across the pores, and the dry aerogel retains the original morphology of the silica gel.

The silica gels are produced from the polycondensation of tetramethoxy silane (TMOS) or tetraethoxy silane (TEOS) in the presence of an acid or base [15, 16]. Under acidic conditions, linear or slightly branched polymers are formed which entangle and then crosslink to form a gel. Under alkaline conditions, the reaction produces branched polymeric "clusters" which crosslink together. The size of the "clusters" and their interpenetration can be manipulated under appropriate reaction conditions. The latter mechanism is similar to gel formation from the destabilization of colloids [17].

The silica gels are unaffected by the solvent which fills their pores. The gel can be exchanged into an organic solvent from its original alcohol–water environment without swelling or deswelling. This behaviour contrasts sharply with gels such as crosslinked polystyrene where the solvent interaction parameter, $\chi$, determines the equilibrium swelling behaviour [18].

Interestingly, Iler [19] states that "there is no relation or analogy between silicic acid polymerized in an aqueous system and condensation-type organic polymers". In this paper, a synthetic route for the production of organic gels with properties similar to silica gels is described. The reaction involves the polycondensation of resorcinol (1,3-dihydroxy benzene) with formaldehyde under alkaline conditions. The resorcinol–formaldehyde (RF) gels are unaffected by solvent exchanges in contrast to conventional polymeric gels (e.g. crosslinked polystyrene). In addition, the gels can be supercritically dried to form transparent, ultrafine cell size ($< 100$ nm), low density foams. We

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TABLE I Formulations examined in this study

| Formulation | % Solids | Concentrations of molar | | | Theoretical density ($g cm^{-3}$) | Actual density ($g cm^{-3}$) |
|---|---|---|---|---|---|---|
| | | Resorcinol | Formaldehyde | $Na_2CO_3$ | | |
| A | 5.0 | 0.29 | 0.58 | 0.0029 | 0.050 | 0.079 |
| B | 5.0 | 0.29 | 0.58 | 0.0019 | 0.050 | 0.073 |
| C | 5.0 | 0.29 | 0.58 | 0.0015 | 0.050 | 0.070 |
| D | 4.0 | 0.24 | 0.47 | 0.0012 | 0.040 | 0.054 |
| E | 3.5 | 0.21 | 0.41 | 0.0010 | 0.035 | 0.044 |
| F | 2.0 | 0.12 | 0.24 | 0.0006 | 0.020 | 0.030 |

propose that these foams, which heretofore have never been reported, are "organic aerogels".

## 2. Materials and methods

### 2.1. Gel preparation

Resorcinol (98% purity) was purchased from Aldrich Chemical Co. and used as-received. Formaldehyde was obtained from J. T. Baker Chemical Co. as an aqueous solution (37.6%; methanol stabilized). Sodium carbonate monohydrate was supplied by Mallinckrodt, Inc. All solutions were prepared from water which had been deionized and distilled. A typical gel formulation contained 0.29 M resorcinol, 0.57 M formaldehyde and 1.5–4.0 mM sodium carbonate for a total of 5.0% solids. In some cases, gels were synthesized at concentrations as low as 2.0% solids, but the molar ratio of formaldehyde : resorcinol was held at a constant value of 2. Other dihydroxy and trihydroxy benzene compounds (e.g., catechol, phloroglucinol) were also found to form gels. Table I displays the various formulations examined in this study.

After weighing out the desired formulation, the solution was stirred and the initial pH was recorded. A pH range of 6.5–7.4 was studied. At an initial pH $< 6.0$, an opaque gel or a precipitate was formed upon heating. Mixtures with an initial pH $> 7.5$ were not evaluated. The pH of all formulations was lowered as the condensation reaction progressed.

The RF mixture was decanted into 19 mm × 107 mm glass ampules (10 $cm^3$ capacity). The ampules were sealed with an acetylene torch, and placed in an oven at $85 \pm 3°C$ for 7 days. The solution progressively changed colour from clear to yellow to orange to deep red as a function of the reaction time. Gel time was a function of the percent solids in the mixture and the catalyst level. Solutions containing 5.0 and 3.5% solids (Formulations C and E) gelled in approximately 16 and 30 h, respectively. The extended 7-day cure was found to be necessary so that the gels could support their own weight and be handled in subsequent processing.

Upon completion of the cure cycle, the glass ampules were removed from the oven and cooled to room temperature. A small amount of liquid from syneresis was usually located at the top of the gel. In addition, the gels were always darker at the gel–air interface as a result of slight oxidation. After scribing the bottom of the glass ampules with a SiC tipped pencil, a red-hot glass rod was used to shatter the glass. The gels did not adhere to the glass walls of the ampules and were easily removed.

### 2.2. Solvent exchange

After removal from the ampules, the RF gels were placed in an agitated bath of 0.125% trifluoroacetic acid at 45° C for 3 days (pH = 1.9 at room temperature). The acid wash assisted in further condensation of hydroxymethyl groups ($-CH_2OH$) remaining in the gels to form ether bridges between resorcinol molecules [20]. The acid wash treatment resulted in an obvious increase in the compressive modulus of the gels.

In preparation for critical point drying, the acid-filled gels were then placed into an agitated acetone bath at 45° C. Multiple exchanges with fresh acetone were used to remove the residual water. Usually, nine RF gels were placed in 4 litres of fresh acetone on a daily basis for 4 days. The acetone was heated to accelerate the diffusion of water from the gel. Other solvents which were successfully used in the exchange process included methanol, isopropanol and amyl acetate. Presumably, any solvent which is miscible with carbon dioxide can be used in the exchange step.

It should be noted that the RF gels remained transparent independent of the refractive index of the solvent used in the exchange. This finding indicated that the cell size of the gels was less than the wavelength of visible light.

### 2.3. Critical point drying

Nine acetone-filled gels were placed on perforated stainless steel racks in an 85 mm diameter × 300 mm long jacketed pressure vessel (Polaron Equipment Ltd, Watford, England). Trapped air was slowly bled from the vessel while it was filled with liquified carbon dioxide at 900 psi and a jacket temperature of 14° C. The jacket temperature was controlled to $\pm 0.5°C$ with a circulating bath containing 50/50 ethylene glycol/water.

The RF gels were allowed to stand in the liquified carbon dioxide for a minimum of 4 h before flushing the system. After partial exchange of the acetone with carbon dioxide, the gels were buoyant as observed through the window of the Polaron. After this initial induction period, carbon dioxide was drained from the vessel to a level just above the RF gels. The vessel was then refilled with carbon dioxide. This drain/refill procedure was conducted four times daily. The RF gels were also flushed with carbon dioxide in a flow-through manner for a minimum of 4 h $day^{-1}$ to assist in removing acetone from the pores of the RF gel and replacing it with carbon dioxide. In this process, diffusion was solely responsible for removal of the acetone. Three days were generally required to remove all acetone from the RF gels.

At this point, the $CO_2$ valve and exit valve of the pressure vessel were closed and the jacket temperature was increased to 45° C. The critical point for $CO_2$ is 1100 psi at 31° C. Carbon dioxide was vented manually from the system at pressures greater than 1300 psi. Dry RF aerogels were subsequently recovered by slowly bleeding the Polaron to atmospheric pressure while maintaining the temperature at 45° C.

The RF aerogels were held in front of a high intensity white light to ensure that the drying process was successful. If the acetone was not completely exchanged with $CO_2$, the aerogels were opaque in the region where the acetone had been present.

### 2.4. Characterization techniques

The consumption of formaldehyde was determined as a function of polymerization time using a titration procedure [21]. Approximately 10 g of an RF solution or pulverized gel was added to 100 ml of 90% ethanol. This solution was titrated with 0.2 N hydrochloric acid to a greenish-yellow endpoint using bromophenol blue as an indicator. To this mixture, 25 ml of 5% hydroxylamine hydrochloride solution was added. The resulting acidic solution was allowed to stand for 1/2 h while hydrochloric acid was liberated during the reaction with free formaldehyde. The solution was titrated with 0.1 N sodium hydroxide to a final endpoint at a pH of 3.4. One ml of 0.1 N sodium hydroxide was equivalent to 0.0030 g of formaldehyde.

Molecular weight distributions for aliquots from the RF polymerization were obtained by gel permeation chromatography (GPC). Polystyrene standards (Pressure Chemical) were used to calibrate the Bimodal PSM 60S and PSM 1000S columns (Dupont). In addition, a resorcinol novolac polymer was used to evaluate the columns. This polymer was synthesized under acidic conditions at a formaldehyde : resorcinol mole ratio of 0.8. It contained no hydroxymethyl groups and was not capable of crosslinking by itself.

All GPC experiments were performed in inhibitor-free tetrahydrofuran at a flow rate of $1.0 \text{ ml min}^{-1}$. Samples were not filtered before injection. A UV detector set at 273 nm monitored the molecular weight profiles.

Thermal analysis of RF gelation was performed with a differential scanning calorimeter (Perkin–Elmer DSC 7) attached to a PE 3700 data station. All samples were placed in DSC pans with a silicone o-ring seal so that they could be scanned above the boiling point of the solution. Sample size was approximately 65 mg. Heating rates varied from $3\text{–}12° \text{K min}^{-1}$.

All infrared spectra were recorded on a Digilab FTS-40 spectrophotometer attached to a 3240-SPC computer station. A vibratome was used to cut 0.25 mm thick pieces from the RF aerogels. These thin samples were dessicated for 24 h and then placed between two sodium chloride windows. IR spectra were acquired between 4000 and $500 \text{ cm}^{-1}$ using 64 scans.

Surface areas of the RF aerogels were obtained from nitrogen adsorption analysis (Digisorb 2600). In order to remove gaseous or liquid contaminants, all samples were placed under vacuum ($10^{-5}$ torr) for 24 h at 25° C prior to analysis. The standard deviation for surface area measurements was typically ± 2% of the reported values.

Scanning electron microscopy (Hitachi S-800) and transmission electron microscopy (Jeol 200 CX) were used to examine the morphologies of RF aerogels. SEM was performed on uncoated samples at an accelerating voltage of 10 kV. TEM samples were atomized onto Formvar grids and analysed at 80 kV.

## 3. Results and discussion

### 3.1. Reaction chemistry and kinetics

Resorcinol undergoes all of the typical reactions of phenol, but at a much faster rate because of the enhanced electron density in the 2,4,6 ring positions. Electron densities at the various ring positions explain the relative reactivities and the regioselectivity in electrophilic substitution. Although the 2 position of resorcinol has the highest electron density, it is sterically hindered by the adjacent hydroxyl groups so that substitution occurs primarily in the 4 and 6 positions [22].

Resorcinol reacts with formaldehyde under alkaline conditions to form mixtures of addition and condensation compounds which can react further to form a crosslinked network. The principal reactions involved include (1) the formation of hydroxymethyl derivatives of resorcinol, (2) the condensation of the hydroxymethyl derivatives to form methylene and methylene ether bridged compounds and (3) the disproportionation of the methylene ether bridges to form methylene bridges plus formaldehyde as a by-product. These reactions have been studied extensively by NMR [23, 24]. Figure 1 shows a schematic diagram of the reaction of resorcinol with formaldehyde under conditions used in this study.

The RF reaction was monitored by titrating free formaldehyde as a function of polymerization time using the hydroxylamine hydrochloride procedure. The rate of the reaction was found to depend upon the catalyst level; however, the reaction was found to be first order only during the initial 3 h. Figure 2 shows the kinetic data for formulations A through C. The inflection point at 3 h shows that approximately 60% of the original formaldehyde has been consumed, and it probably represents the point at which the majority of the RF "clusters" have been formed. The reaction then depends primarily upon the crosslinking of these "clusters" to form a gel. The latter reaction would be expected to be the slow, rate-determining step for gelation.

In order to pursue this concept further, aliquots were removed during the polymerization of formulation C and subjected to GPC analysis. The samples were diluted to 0.5% in tetrahydrofuran and stored at 3° C until being analysed the next day. A UV detector set at 273 nm was used to monitor the eluting species. In all cases, the only detectable peak was assigned to unreacted resorcinol. Quantitative analysis of the data showed that greater than 90% of the original resorcinol

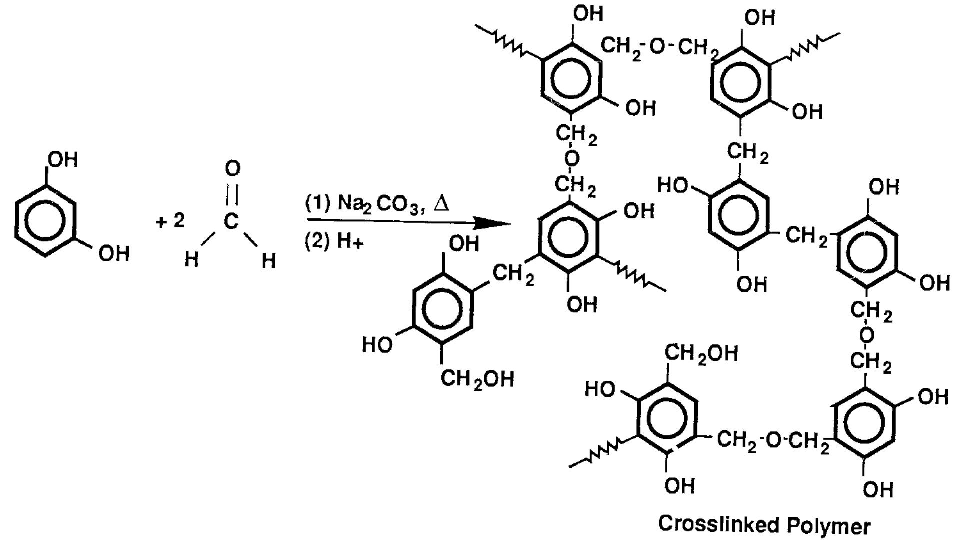

*Figure 1* A schematic diagram of the reaction of resorcinol with formaldehyde.

had reacted after 3 h of polymerization. This result corroborates the titration data and suggests that the RF "clusters" are completely formed after 3 h.

The RF "clusters" also absorb at the above wavelength; however, they were not detectable by GPC. Apparently, the RF "clusters" were adsorbed onto the packing material during the analysis. In order to test this hypothesis, a resorcinol novolac polymer which does not contain any hydroxymethyl groups was injected into the GPC columns and species of varying molecular weights were resolved. This experiment showed that the GPC columns could separate low molecular weight, branched polymers provided that they do not adsorb onto the column packing material.

The kinetics of the RF reaction were studied with differential scanning calorimetry. The polymerization of formulation C was studied in sealed pressure pans by scanning from 30 to 180° C. Using Kissinger's method, a shift in the peak temperature of the reaction was studied as a function of the heating rate [25, 26]. Table II displays the DSC data. An activation energy for the overall reaction was calculated from the following equation:

$$d(\ln \beta/T^2)/d(1/T) = -E_a/R \qquad (1)$$

A plot of $\ln \beta/T^2$ against $1/T$, where $\beta$ is the heating rate in ° K min$^{-1}$, and $T$ is expressed in ° K, resulted in a straight line from which an activation energy of 11.3 kcal mol$^{-1}$ was obtained. This value is significantly lower than data reported for sodium hydroxide catalysis of the RF reaction at higher concentrations and implies that RF "cluster" formation proceeds through a different transition state [24]. Solvation effects and pH are expected to influence the energy of the transition state, and these factors may explain the above differences.

TABLE II DSC data

| Heating rate $\beta$ (° K min$^{-1}$) | Temperature at reaction peak $T$ (° K) | $\ln(\beta/T^2)$ | $(1/T) \times 10^3$ (° K$^{-1}$) |
|---|---|---|---|
| 3 | 375.8 | −10.76 | 2.66 |
| 5 | 391.8 | −10.33 | 2.55 |
| 7 | 396.3 | −10.02 | 2.52 |
| 10 | 404.3 | −9.70 | 2.47 |
| 12 | 409.8 | −9.55 | 2.44 |

### 3.2. Aerogel characterization

The density data in Table I shows that critical point drying always resulted in some shrinkage, i.e. the final aerogel densities were higher than their theoretical values. In addition, the amount of shrinkage was dependent upon the catalyst level used to prepare the

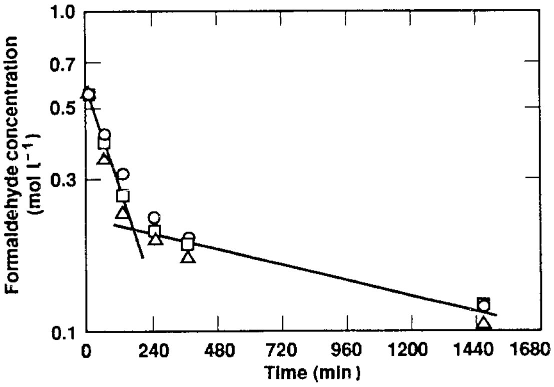

*Figure 2* Consumption of formaldehyde in the RF reaction as a function of polymerization time and catalyst level. Formulations (△) A; (□) B; (○) C.

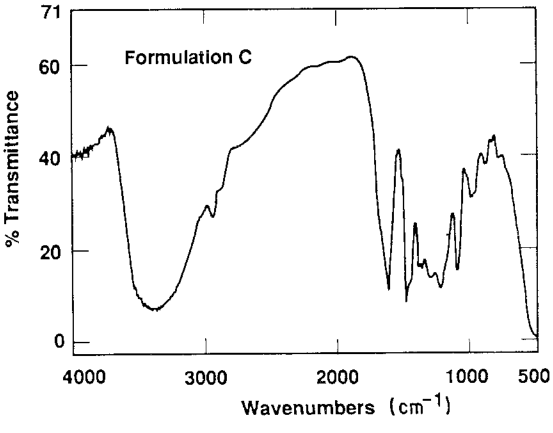

*Figure 3* IR spectrum of an RF aerogel.

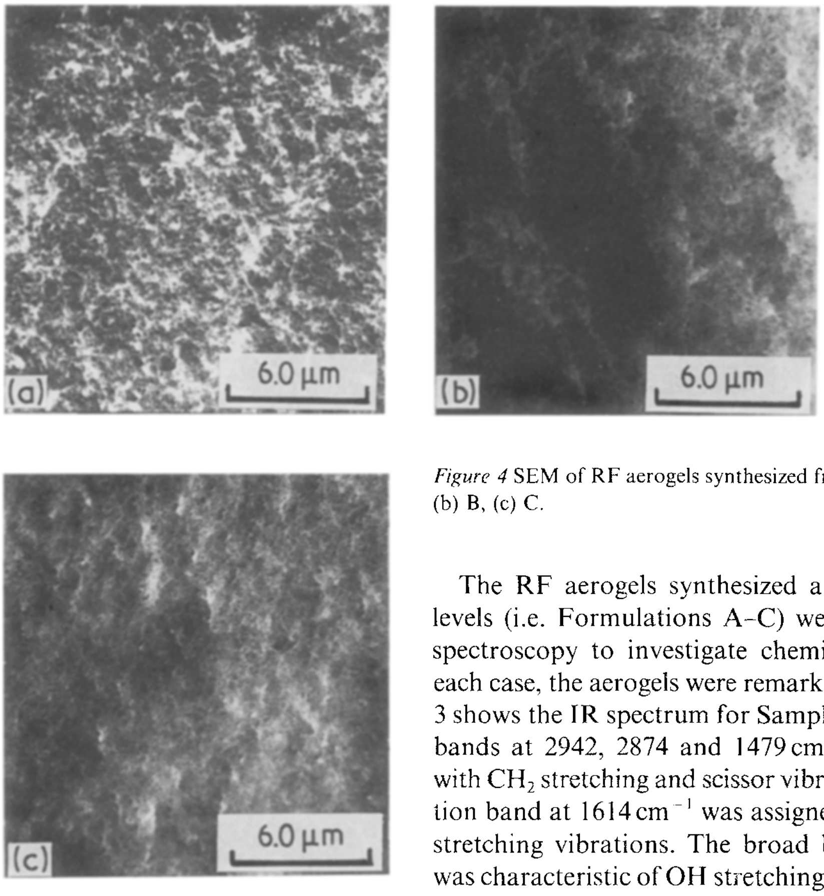

*Figure 4* SEM of RF aerogels synthesized from formulations (a) A, (b) B, (c) C.

RF aerogels. For a given formulation, greater shrinkage was experienced at the higher catalyst levels. This relationship suggests that there are differences in the size, distribution, interpenetration and chemical linking of the RF "clusters" depending upon reaction conditions.

The RF aerogels synthesized at different catalyst levels (i.e. Formulations A–C) were analysed by IR spectroscopy to investigate chemical differences. In each case, the aerogels were remarkably similar. Figure 3 shows the IR spectrum for Sample C. IR absorption bands at 2942, 2874 and 1479 cm$^{-1}$ were associated with $CH_2$ stretching and scissor vibrations. The absorption band at 1614 cm$^{-1}$ was assigned to aromatic ring stretching vibrations. The broad band at 3382 cm$^{-1}$ was characteristic of OH stretching vibrations. The IR bands at 1222 and 1092 cm$^{-1}$ were associated with $C-O-C$ stretching vibrations of methylene ether bridges between resorcinol molecules [27].

BET adsorption analysis showed substantial differences in Samples A through C. The surface area of the RF aerogels decreased as the catalyst level was lowered. The surface areas for Samples A through C

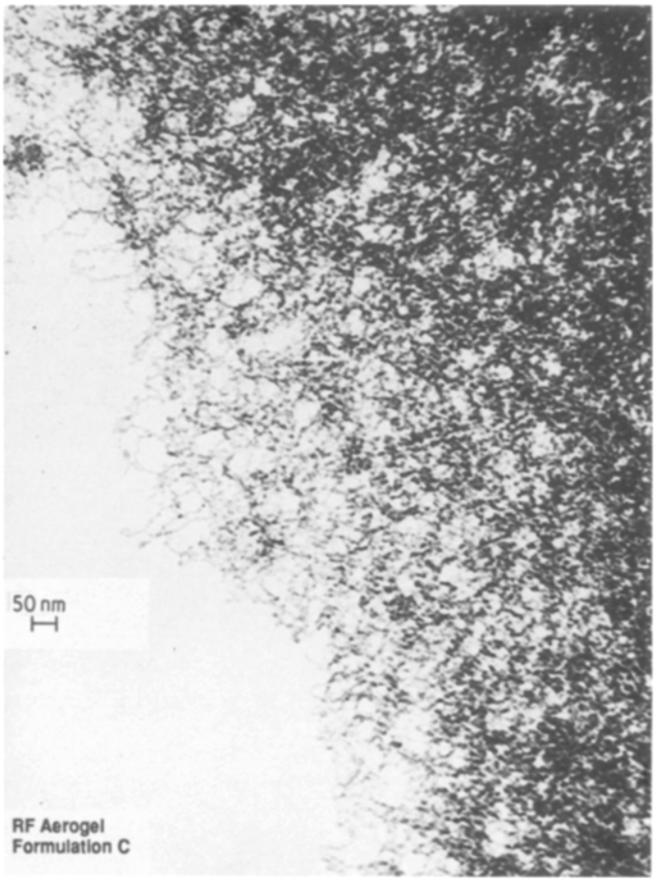

*Figure 5* TEM of an RF aerogel.

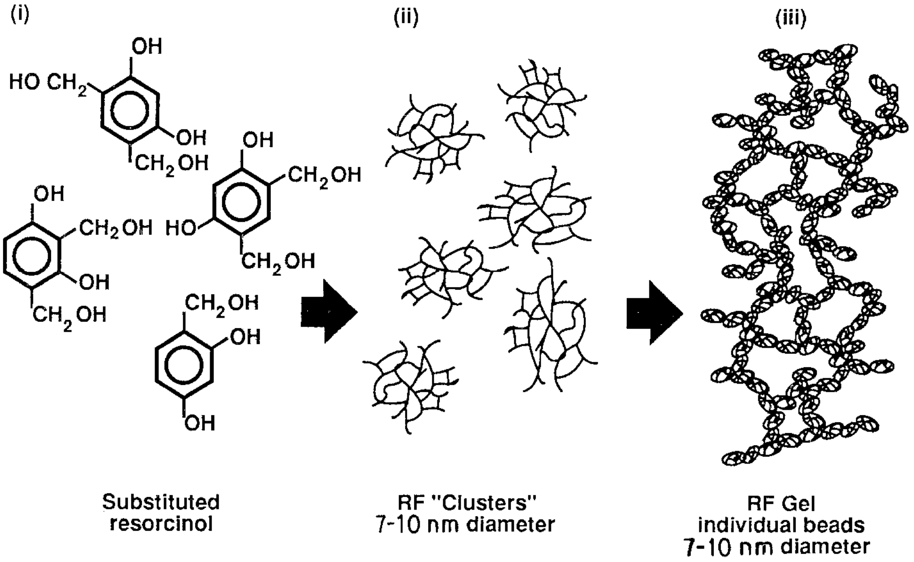

*Figure 6* A schematic diagram of the RF gelation mechanism.

were 717, 620 and $513\,\mathrm{m^2\,g^{-1}}$ respectively. These data imply that there are subtle differences in the morphologies of the RF aerogels.

An SEM examination showed no significant differences in the morphology of Samples A through C. Figure 4 shows a morphology common to all of the formulations, namely an open-celled structure with continuous porosity and cell sizes less than 100 nm. At much higher magnification, TEM examination of a thin flake from Sample C shows an interconnected bead structure. Figure 5 reveals that these beads are generally 7–10 nm in diameter with coordination numbers of 2 or 3. This structure is analogous to that reported for silica aerogels produced with a base catalyst [28]. In Samples B and C, it is hypothesized that slight differences in the diameter, surface texture and porosity of the beads account for the observed changes in surface area.

## 4. Conclusions

The above data indicate that RF aerogels are produced in a fashion similar to silica aerogels. Resorcinol reacts quickly with formaldehyde to form numerous hydroxymethyl substituted species. These species condense into surface functionalized polymer "clusters" that crosslink to form a gel. A schematic diagram of this process is shown in Fig. 6. This polymerization mechanism is analogous to that described for the polymerization of TMOS under alkaline conditions.

RF aerogels are easily produced in densities ranging from $0.035\text{–}0.100\,\mathrm{g\,cm^{-3}}$. The RF aerogels are composed of interconnected beads with diameters of 7–10 nm and cell sizes less than 100 nm. This structure is responsible for the transparency of these organic aerogels.

## Acknowledgements

The author would like to thank the following individuals for their contributions to this project: Dick Stone (sample preparation), Jim LeMay (DSC), Jack Clarkson (GPC), Suzy Hulsey (BET), Jim Yoshiyama (SEM) and Walt Bell (TEM). This work was performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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*Received 23 May*
*and accepted 13 September 1988*