



# On the synthesis and structure of resorcinol-formaldehyde polymeric networks – Precursors to 3D-carbon macroassemblies



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## ABSTRACT

With the new impetus towards the development of hierarchical graphene and CNT macro-assemblies for application in fields such as advanced energy storage, catalysis and electronics; there is much renewed interest in organic carbon-based sol–gel processes as a synthetically convenient and versatile means of forming three dimensional, covalently bonded organic/inorganic networks. Such matrices can act as highly effective precursors, scaffolds or molecular ‘glues’ for the assembly of a wide variety of functional carbon macro-assemblies. However, despite the utility and broad use of organic sol–gel processes – such as the ubiquitous resorcinol-formaldehyde (RF) reaction, there are details of the reaction chemistries of these important sol–gel processes that remain poorly understood at present. It is therefore both timely and necessary to examine these reactions in more detail using modern analytical techniques in order to gain a more rigorous understanding of the mechanisms by which these organic networks form. The goal of such studies is to obtain improved and rational control over the organic network structure, in order to better direct and tailor the architecture of the final inorganic carbon matrix. In this study we have investigated in detail, the mechanism of the organic sol–gel network forming reaction of resorcinol and formaldehyde from a structural and kinetic standpoint, by using a combination of real-time high field solution state nuclear magnetic resonance (NMR), low field NMR relaxometry and differential scanning calorimetry (DSC). These investigations have allowed us to track the network formation processes in real-time, gain both detailed structural information on the mechanisms of the RF sol–gel process and a quantitative assessment of the kinetics of the global network formation process. It has been shown that the mechanism, by which the RF organic network forms, proceeds via an initial exothermic step correlated to the formation of a free aromatic aldehyde. The network growth reaction then proceeds in a statistical manner following a first order Arrhenius type kinetic relationship – characteristic of a typical thermoset network poly-condensation process. And despite the relative complexity and ill-defined nature of the formaldehyde starting material, the final network structure is to a large extent, governed by the substitution pattern of the resorcinol molecule.

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## 1. Introduction

Sol–gel chemistries are widely employed as a convenient and versatile means of forming three-dimensional (3-D), covalently bonded organic networks [1]. Such organic sol–gels are the precursor to a family of low density, carbon aerogels [2] and xerogels [3,4] with exceptional mechanical, thermal and electrical properties. These inorganic carbon ‘foams’ have, over the last 30 years, received much attention for their potential to serve as inorganic electrolytes [5], thermally resistant barrier layers [6], electrodes for

energy storage [7], catalysts [8], separation media [9] and even fusion fuel carriers [10]. The renewed interest in the last 5 years in applications of the sol–gel process for the formation of inorganic carbon architectures is largely the result of the push toward the formation of hierarchical 3-D macro-assemblies of novel allotropes of carbon [11–13]. Recently it has been demonstrated that both carbon-nanotubes and graphene can be successfully formed into high surface area 3-D macro-assemblies through the application of relatively simple organic sol gel reactions to form, amongst other things, ultra-low density aerogels with unique mechanical, thermal, and electrical properties [12,13].

Organic sol–gel processes are typically based on the poly-condensation of multifunctional small molecule precursors in the

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presence of a suitable solvent, to form a 3-D organic polymeric network. The solvent can be subsequently removed or exchanged resulting in the formation of a xerogel or aerogel structure, respectively – which may be further processed or modified thermally or chemically. The addition of functional, secondary additives such as graphene oxide or single-walled carbon nanotubes during the network forming reaction allow the covalent incorporation of additional carbon architecture into the organic network and is the basis of the synthetic route for the formation of a family of functional 3-D carbon macro-assemblies [13]. By far the most widely employed organic sol–gel process in the field of inorganic, low-density carbon architectures remains the solvent-mediated resorcinol-formaldehyde (RF) polycondensation reaction [14]. It is significant that, despite its utility and broad use [14], there are details of the reaction chemistry of the RF sol–gel process that remain poorly understood. While over the last 40 years there has been a concerted effort to define mechanisms and kinetic dependences of inorganic sol–gel processes [15–18], there has been much less progress in understanding organic, sol–gel reactions. There are a number of publications on the early stage reaction mechanisms of the RF reaction [19–22], however the mechanisms proposed are general (see Fig. 1), make large assumptions about the purity and state of the starting material and provide virtually no information on the kinetics of the network formation process.

With new impetus towards the development of hierarchical graphene and CNT macro-assemblies for application in fields such as advanced energy storage and catalysis, there is much renewed interest in the organic sol–gel process. It is therefore both timely and necessary to examine these reactions in more detail and gain a more rigorous understanding of the mechanisms by which the initial organic network form, with the goal of obtaining improved control over the organic gel structure. Indeed there is evidence that imperfections in the final inorganic carbon aerogel structures (e.g. the presence of residual organic regions, microscopic nodes and micro-scale occlusions) are directly related to non-idealities in the organic precursor network [23].

In this study we have investigated the mechanism of the organic sol–gel network forming reaction of resorcinol and formaldehyde from a structural and kinetic standpoint by using a combination of real-time high field solution state nuclear magnetic resonance (NMR), low field NMR relaxometry and differential scanning calorimetry (DSC). These investigations have allowed us to track the network formation processes in real-time, gain both detailed structural information on the mechanisms of the RF sol–gel process and a quantitative assessment of the kinetics of the global network formation process.

## 2. Experimental

### 2.1. Materials

All reagents were used without further purification. Resorcinol (99%), formaldehyde (37% in water), DMSO- $d_6$  and TMS were purchased from Aldrich Chemical Co. Sodium carbonate (anhydrous) was purchased from J.T. Baker Chemical Co.

### 2.2. Preparation and sampling of resorcinol-formaldehyde gels

11 wt. % resorcinol-formaldehyde (RF) aqueous gels were prepared in the following manner: 0.625 g of resorcinol was dissolved in 7.181 g of demineralized, purified water in a 20 mL glass vial. To this, 0.900 g of 37% aqueous formaldehyde solution was added under constant stirring. Finally 0.03 g of sodium carbonate catalyst was massed into the solution under constant agitation and immediately on dissolution, sealed and stored at temperatures ranging

from 25 to 50 °C. 'T<sub>0</sub>' for each system was defined as 2 min after storage at the appropriate temperature to allow for thermal equilibration. 200  $\mu$ L (or 200 mg if gelled) aliquots were collected along a series of time intervals from T<sub>0</sub> to T <sub>$\infty$</sub>  (24–96h, dependent on the analysis temperature) during the gelation process and immediately quenched in 5 mL vials containing 1 mL DMSO- $d_6$ /(0.03%)TMS and dried in 0.5 g sodium sulfate. Gelled aliquots were swelled in DMSO- $d_6$ /TMS by sonication prior to storage. These aliquots in deuterated DMSO were stored in liquid nitrogen in order to quench any reactivity until such time as they were analysed by NMR and DSC. 11 wt. % aqueous RF samples for T<sub>2</sub> relaxometry analysis were prepared in the same manner as the 20 mL stock solutions, with 1 mL aliquots being transferred to 5 mm NMR tubes for in-situ analysis and the addition of the catalyst to the solution defined as T<sub>0</sub>.

### 2.3. High field NMR measurements

Proton detected spectra were acquired immediately after being brought to 25 °C from liquid nitrogen temperatures with a Bruker Avance III NMR spectrometer operating at 600 MHz and TopSpin 3.0 software, with samples sealed in high resolution 5.0 mm Norell™ tubes rated for 600 MHz. All NMR spectra were collected with a Bruker Triple Resonance Broadband liquid capable gradient probe. NMR chemical shift reference: <sup>1</sup>H NMR, HD<sub>2</sub>SOCD<sub>3</sub>: 2.50 ppm; C<sub>4</sub>H<sub>12</sub>Si: 0.00 ppm. All spectra were acquired at 298 K to impede further reaction progress during NMR acquisition. 1-D <sup>1</sup>H NMR spectra were collected with solvent suppression using the WATERGATE-W5 suppression sequence [24] with a total acquisition time (aq) of 183 s, a 2 s relaxation delay (d1) at 32 scans and 2 Hz exponential line broadening.

### 2.4. Low field T<sub>2</sub> relaxometry

All T<sub>2</sub> relaxometry studies were performed on a low field Bruker Minispec™ spectrometer under static conditions using the Carr-Purcell-Meiboom-Gill (CPMG) spin echo method [25] with ninety degree pulse lengths of  $\tau_P = 2.25 \mu$ s and recycle delays of 15 s. T<sub>2</sub> values were obtained from the mono-exponential fits of a train of collected FID's generated from the CPMG sequence. 2 g Samples of 11 wt. % resorcinol-formaldehyde solution were prepared in 5 mm borosilicate NMR tubes and allowed to equilibrate at the analysis temperature, in the probe for 2 min. T<sub>2</sub> measurements were then taken at variable time intervals (from 5 min to 12) hours over a total time period of 48 h, at temperatures of 30, 35, 40, 45 and 50  $\pm$  0.1 °C respectively. For each temperature, the values of T<sub>2</sub> were plotted as a function of time and fitted to an exponential decay curve to yield an effective rate of gelation of the system.

### 2.5. DSC analysis

All DSC characterization was carried out using a Perkin–Elmer Diamond DSC operating in non-modulated mode using power-compensation. Six milligram samples of 11 wt. % resorcinol-formaldehyde solution were prepared in sealed hermetic pans. The samples prepared at 293 K prior to analysis and were analysed using an isothermal temperature program with an initial 2 min hold a 293 K followed by a jump to 348 K and a hold time of 20 min, under a N<sub>2</sub> purge flow.

## 3. Results and discussion

### 3.1. Solution state <sup>1</sup>H NMR characterization of organic precursors

In order to accurately study and assess the mechanism of the resorcinol-formaldehyde poly-condensation reaction, the purity

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