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A NEW SYNTHETIC ROUTE TO ORGANIC AEROGELS*

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ABSTRACT

The aqueous, sol-gel polymerization of melamine with formaldehyde, followed by supercritical extraction, leads to the formation of a new type of organic aerogel. Synthetic conditions (e.g. reaction time, pH) affect the density, transparency, and microstructure of the resultant aerogels. Unlike previous organic aerogels based upon resorcinol-formaldehyde, the melamine-formaldehyde aerogels are both colorless and transparent. Low densities (0.1-0.8 g/cc), high surface areas (~1000 m^2/g), and optical clarity are only a few of the promising characteristics of this new material.

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INTRODUCTION

Aerogels are a special class of low density, open-cell foams. These materials have continuous porosity, ultrafine cell/pore sizes (< 500 Å), and a solid matrix composed of interconnected colloidal-like particles or polymeric chains with characteristic diameters of 100 Å. This microstructure is responsible for the unusual acoustic, mechanical, optical, and thermal properties of these materials [1,2].

The hydrolysis and condensation of metal alkoxides (e.g. tetramethoxy silane) is the most common synthetic route for the formation of *inorganic aerogels* [3-5]. Our research has focused on sol-gel polymerizations that lead to *organic aerogels*. The reaction pathway, microstructure, and properties of these new materials are analagous to their inorganic counterparts. Furthermore, our organic aerogels are distinctly different from the 'aerogels' that Kistler prepared from nitrocellulose, cellulose, agar, and egg albumin [6].

Previous work has shown that organic aerogels can be formed from the base catalyzed, aqueous polymerization of resorcinol (1,3 dihydroxy benzene) with formaldehyde [7-10]. Although resorcinol-formaldehyde (RF) aerogels exhibit minimal light scattering, these materials are dark red in color and have a large absorption coefficient within the visible spectrum. The color centers in RF aerogels result from oxidation products (e.g. quinones) formed during the sol-gel polymerization. Their presence has limited the use of these materials in certain optical applications where an aerogel is required to be both colorless and transparent.

In order to circumvent this problem, we are forming colorless gels from the aqueous polycondensation of melamine (2,4,6 triamino s-triazine) with formaldehyde. Synthetic conditions (e.g. pH, reaction time) affect both the transparency and microstructure of the resultant melamine-formaldehyde (MF) aerogels. This paper describes in detail the synthesis and characterization of these new organic aerogels.

EXPERIMENTAL

The polycondensation of 3-6 moles of formaldehyde (37.6 %; methanol stabilized; J.T. Baker) with 1 mole of melamine (99+ %; Aldrich Chemical) was carried out in deionized and distilled water using 10-100 millimoles of sodium hydroxide as a base catalyst. The above slurry was heated for 10-15 mins. at 70 °C to form a clear solution. This solution was allowed to cool to 45 °C, at which time, concentrated hydrochloric acid (36.5%) was added. If the solution was heated too long at 70 °C or the pH was not properly adjusted, a white precipitate was formed and a gel could not be obtained. To form transparent gels, the pH of the MF solution was required to be 1.5-1.8 when measured at 23 °C. Outside of this range, translucent or opaque gels were formed.

The pH adjusted, melamine-formaldehyde solution was poured into 23 x 85 mm glass vials, sealed, and cured under various conditions. Solutions containing ≥ 20 % reactants gelled in less than 24 hours at room temperature, while solutions containing 7 % reactants gelled in approximately 4 weeks at a cure temperature of 85-95 °C. As the reaction progressed, all formulations acquired a light blue haze.

In preparation for supercritical drying, the crosslinked gels were removed from their glass vials and placed in an ammonium hydroxide solution to neutralize the HCl within the pores. The gels were then exposed to a 50:50 mixture of acetone:water, followed by a 75:25 mixture, and finally 100% acetone. Multiple exchanges with fresh acetone were used to remove residual water from the gels.

The acetone-filled, MF gels were dried in a jacketed pressure vessel (Polaron Equipment Ltd., Watford, England) using carbon dioxide as the supercritical fluid (T_c= 31 °C; P_c= 1100 psi). Details of this procedure have been described elsewhere [7,8]. MF aerogels removed from the pressure vessel were transparent, indicative of the ultrafine cell size (< 500 Å) of these porous solids. All samples were stored in dessicators to inhibit moisture adsorption and prevent cracking.

RESULTS AND DISCUSSION

Melamine is a hexafunctional monomer capable of reaction at each of the amine hydrogens. Under alkaline conditions, formaldehyde adds to the above positions to form hydroxymethyl (-CH_2OH) groups. In the second part of the polymerization, the solution is acidified to promote condensation of these intermediates, leading to gel formation. The principal crosslinking reactions include the formation of (1) diamino methylene (-$NHCH_2NH$-) and (2) diamino methylene ether (-$NHCH_2OCH_2NH$-) bridges [11,12]. Figure 1 outlines the MF reaction and depicts the formation of a crosslinked polymer network.

At present, the role of solution pH (acidification) and its effects upon gel clarity are not totally understood. All melamine-formaldehyde solutions develop a blue haze as they cure. This phenomenon is associated with Rayleigh scattering from MF "clusters" generated in solution. These "clusters" contain surface functional groups (e.g. -CH_2OH) that eventually crosslink to form a gel. We believe that the aggregation and crosslinking processes are strongly pH dependent. Thus, only a small pH window exists for the preparation of transparent gels.

Melamine-formaldehyde aerogels have been synthesized with densities ranging from 0.1-0.75 g/cc. Figure 2 shows an MF aerogel after supercritical drying. The aerogel is both colorless and transparent. The latter property indicates that the cell/pore size and characteristic particle size (referred to as "cluster" size in solution) are less than 1/20th the wavelength of visible light. The optical clarity of melamine-formaldehyde aerogels is equivalent to that of many silica aerogels.

The fracture surface of an MF aerogel is shown in Figure 3. SEM reveals that the aerogel is composed of interconnected particles with diameters < 500 Å. At this magnification, it is difficult to tell if the particles are composed of even smaller subunits. BET nitrogen adsorption measurements give a surface area of 970 m^2/g. Further evaluation of the aerogel microstructure is under investigation using transmission electron microscopy and small angle x-ray scattering.

SUMMARY

Organic aerogels that are both colorless and transparent have been prepared from the aqueous, sol-gel polymerization of melamine with formaldehyde. These aerogels have low densities, high surface areas, continuous porosity, and ultrafine cell/pore sizes (< 500 Å). Their organic composition provides these materials with many potential advantages over conventional inorganic aerogels (e.g. insulating properties).

ACKNOWLEDGMENTS

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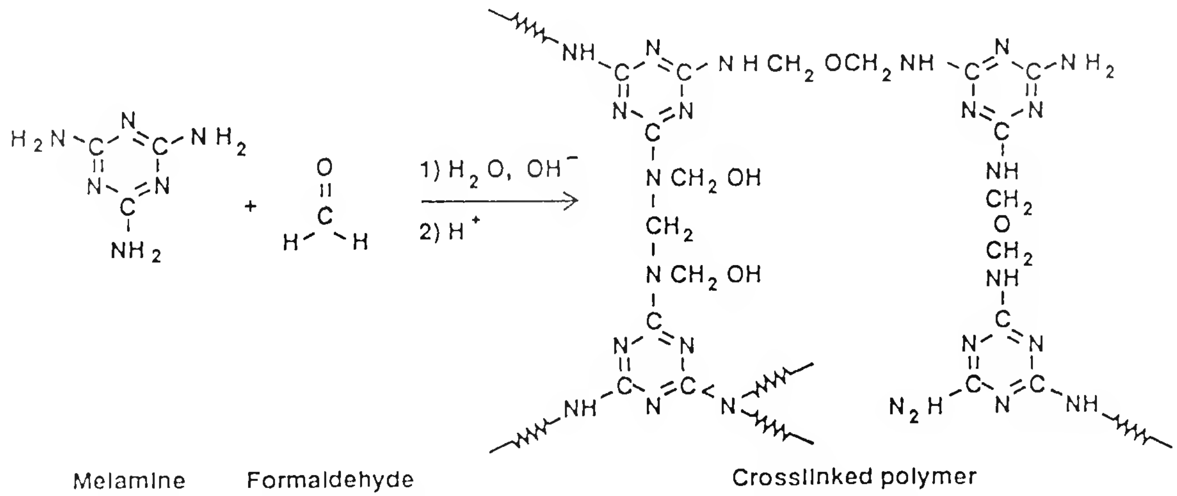

Figure 1. A schematic diagram of the reaction of melamine with formaldehyde.

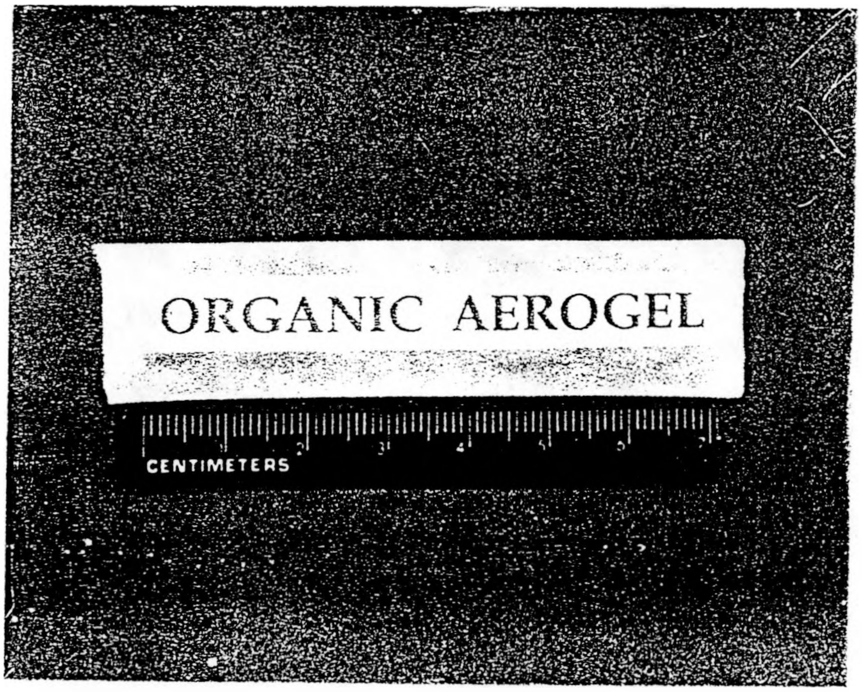

Figure 2. A 17 mm thick, transparent MF aerogel with density equals 0.3 g/cc.

Figure 3. Scanning electron micrograph of a melamine-formaldehyde aerogel.