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High Resolution Transmission Electron Microscopy of Melamine-formaldehyde Aerogels and Silica Aerogels

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The goal of the high resolution transmission electron microscopy (HRTEM) was to image the structure of two tetramethyl orthosilicate (TMOS) and two melamine-formaldehyde (MF) aerogels at the single polymer chain level^{1,2}. With this level of structural resolution we hoped to interrelate each aerogel's structure with its physical properties and its method of synthesis. Conventional single-step base catalysed TMOS aerogels show strings of spheroidal particles linked together with minimal necking. The spheroidal particles range from 86-132 Å and average 113 ± 10 Å in diameter². In contrast the TMOS aerogels reported on here were made by a two step method. After extended silica chains are grown in solution under acidic conditions with a substoichiometric amount of water, the reaction is stopped and the methanol hydrolysed from TMOS is removed. Then base catalysis and additional water are added to cause gel formation in a nonalcoholic solvent. The aerogels that were imaged in this study were characterized at Lawrence Livermore National Laboratory as follows:

<u>Name</u>	<u>Composition</u>	<u>Density (gm/cc)</u>	<u>Method of Synthesis</u>	<u>BET (meter²/ gm)</u>
TT47-4	TMOS	0.009	2 step	574
JP95-6	TMOS	0.030	2 step	~630
CA1218E	MF	0.16	pH ~2.0	970
CA0104N	MF	0.13	pH ~0.5	850

The MF aerogels were prepared for HRTEM by fracturing them on a stereo microscope stage with a razor knife so that fractured pieces with smooth flat surfaces could be selected for platinum-carbon replication. The two silica (TMOS) aerogels were both transparent and difficult to see. These aerogels were fractured on a stereo microscope stage with tweezers. After fracturing, aerogel pieces were loaded onto the stage of the Balzers 300. The Balzers was evacuated to 5×10^{-8} torr and the cold finger located over the sample was cooled to -185°C fifteen minutes before the sample stage was cooled to about -185°C. The specimens were platinum-carbon (Pt-C) replicated at an almost vertical angle (80°) and backed with a rotary deposited carbon film at a 100° angle. The silica (TMOS) and MF aerogel samples were replicated as follows:

<u>Name</u>	<u>Pt-C film thickness</u>	<u>Carbon film thickness</u>
TT47-4	9.5Å	120Å
JP95-6	9.5Å	111Å
CA1218E	9.5Å	128Å
CA0104N	9.5Å	130Å

The silica replicas were removed with dilute hydrofluoric acid and the MF replicas were removed from the MF aerogel in one to two weeks with a saturated KOH solution heated at 55°-70°C. The replicas were washed on water and then picked up on 300 or 400 mesh copper grids without a support film. The replicas were imaged in a JEM 100CX TEM with a 2625Å depth of field and with a 6.6Å resolution (3). Kodak 4489 film was used and image reversals and prints were made as previously described (3).

From previous work a 9.5Å thick Pt-C film increases the average polysiloxane chain of ~4.1Å (4,5) by roughly 5.5Å to a Pt-C coated average chain thickness of 9.6Å (1, 3). It is assumed that the average unbranched MF chain thickness is between 2-6 Å and its width is increased by a 9.5 Å thick Pt-C film by 5.5Å. A Pt-C coated single MF chain should average between 7.5-11.5Å.

TT47-4, Silica Aerogel

This is the lowest density aerogel (0.4 % solids) that has been imaged and because of this low density two to four layers beneath its surface have been preserved in the replica (see Fig. 1). The connector diameters range from about 20Å to 132Å with the largest diameter fraction 60-132Å. The connector lengths are greater in TT47-4 than the connector lengths in JP95-6. The connectors produced by the two step method in both TT47-4 and JP95-6 aerogels are more uniform than in the one step colloidal silica aerogel previously reported^{2,6}. The connectors in TT47-4 are not composed of bundled linear chains. Instead, the connectors are composed of a high frequency of silica chain ends growing out of its surface. This suggests that side chain growth, branching, and connections between the side chains has thickened the connectors during the second step of this two step method of synthesis. This would also explain why a fraction of this aerogel's mass is excluded from nitrogen adsorption (574 M²/gm).

JP95-6, Silica Aerogel

This aerogel was ~1.3 % solids and had a density 3.33 times that of TT47-4. In this aerogel there appear to be more connectors per volume and the connectors appear to be shorter than in TT47-4 (see Fig. 2). Connector diameters range from 20Å to 160Å and these connectors are composed of a high frequency of silica chain ends growing out of their surface. This also suggests, like TT47-6, that side chain growth, branching, and connections between the side chains has thickened the connectors during the second step of this two step method of synthesis. This would also explain why this aerogel also has a fraction of its mass excluded from nitrogen adsorption (~630 M²/gm). This two step aerogel has the lowest heat conduction of any two step silica aerogel with a higher or lower density. At roughly 60-70 mg/cc or 2.6-3.0% solids the conduction of heat by the silica network becomes a major factor. At lower densities heat conduction by convection through the pores is more important. The pores in JP95-6 (~1.3 % solids) are smaller than they are in TT47-4 (0.4 % solids) suggesting why JP95-6 is a better insulator.

CA1218E, Melamine-Formaldehyde Aerogel

This aerogel is formed from the addition of formaldehyde to the amino groups of melamine under basic conditions. Formaldehyde can react forming as many as six hydroxymethyl (-CH₂OH) groups linked to melamine. This melamine-formaldehyde adduct is then polymerized at a pH of ~2.0 forming a transparent aerogel of 0.16 gm/cc. This polymeric aerogel has very thin connectors (12-20Å) with frequent branching and pores that are smaller than the opaque MF aerogel CA0104N. This aerogel has a 970 M²/gm surface area. This surface area is similar to the RF #559 aerogel (905 M²/gm) previously thought to be polymeric. the RF#559 aerogel was constructed of small branched clusters (20-40Å) where as CA1218E MF aerogel is composed of 12-20Å chains with frequent branching. The size of the melamine-formaldehyde chain estimated in the introduction did not take into account that as many as six hydroxymethyl (-CH₂OH) groups can be attached to a single melamine. This would thicken the chains and so would short side chains frequently formed along a connector.

CA0104N, Melamine-Formaldehyde Aerogel

This melamine-formaldehyde aerogel was polymerized at a pH of ~ 0.5 forming an opaque aerogel of 0.13 gm/cc with a surface area of 850 M²/gm. The connectors in this aerogel are longer and the pores are much larger than those in CA1218E. The connectors are composed of groups of chains that are more highly branched and/or clustered than CA1218E (see Fig. 4). This branching and/or clustering effect could explain why this aerogel has a slightly lower surface area than CA1218E (850 M²/gm). This aerogel looks more like CA1218E and is also distinctly different from aerogel RF#559.

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FIGURE CAPTIONS

Figure 1 TT47-4 silica aerogel replicated with 9.5Å Pt-C and backed with 120Å of carbon. Magnification 242,000x

Figure 2 JP95-6 silica aerogel replicated with 9.5Å Pt-C and backed with 111Å of carbon. Magnification 242,000x

Figure 3 CA1218E melamine-formaldehyde aerogel replicated with 9.5Å Pt-C and backed with 128Å of carbon. Magnification 242,000x

Figure 4 CA0104N melamine-formaldehyde aerogel replicated with 9.5Å Pt-C and backed with 130Å of carbon. Magnification 242,000x

Fig. 1 TT47-4 silica aerogel

Fig. 2 JP95-6 silica aerogel

Fig. 3 CA1218E MF aerogel

Fig.4 CA0104N MF aerogel

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