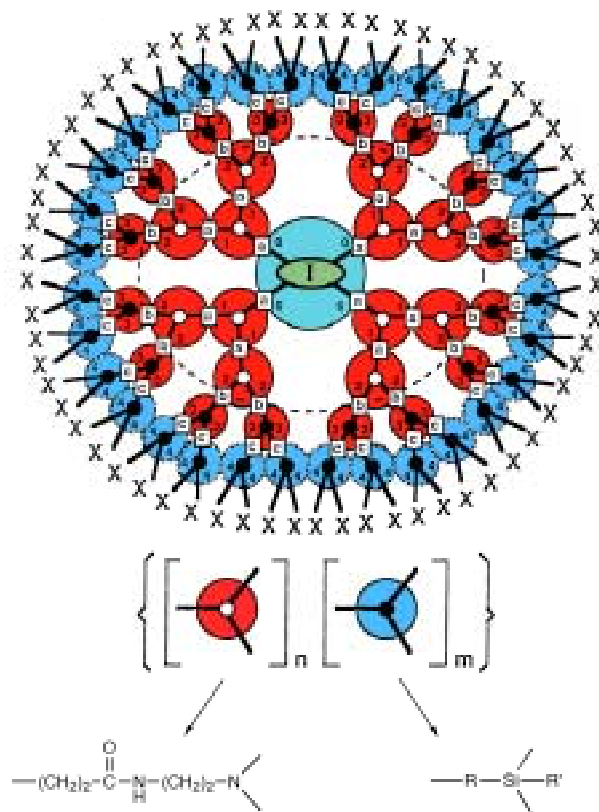


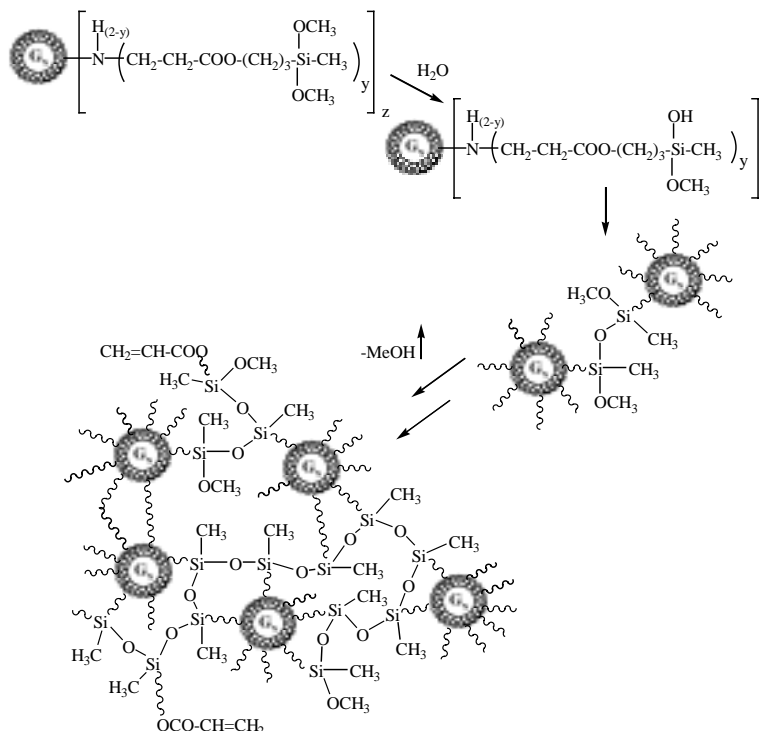
# PAMAMOS DENDRIMERS

Radially layered poly(amidoamine-organosilicon) (PAMAMOS) dendrimers are inverted unimolecular micelles that consist of hydrophilic, nucleophilic polyamidoamine (PAMAM) interiors and hydrophobic organosilicon (OS) exteriors.<sup>1,2</sup> A generalized two-dimensional projection of the structure of these nano-scaled, globular macromolecules is shown below:



**Figure 1:** Generalized structure of a perfect PAMAMOS dendrimer containing radially layered red (PAMAM) branch cells in the interior and blue (OS) branch cells in the molecular exterior.

This unique new family of dendrimers was discovered by Dr. Petar Dvornic and his colleagues at Michigan Molecular Institute in the 1990s.<sup>1</sup> It includes many compositional and functional variants,<sup>1</sup> among which are those with alkoxyethyl end-groups ( $X = Si-OR$  in Figure 1). These dendrimers are exceptionally useful precursors for the preparation of honeycomb-like networks<sup>3-5</sup> with nanoscopic PAMAM and OS domains. The formation of such networks is illustrated in Figure 2.

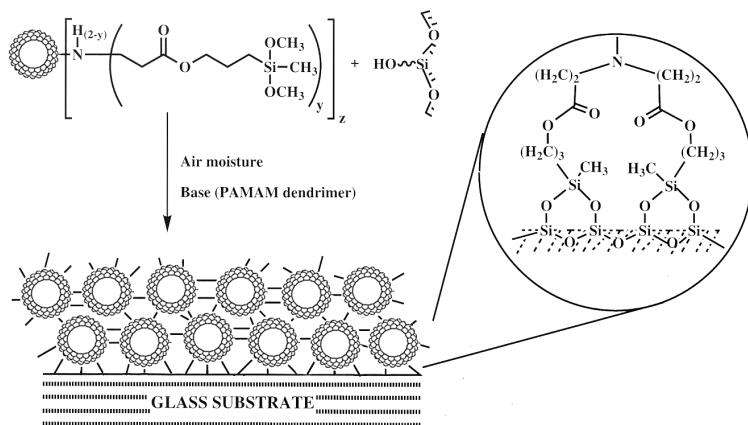


**Figure 2:** Formation of honeycomb-like nano-domained PAMAMOS dendrimer networks from alkoxy-silyl functionalized PAMAMOS dendrimers. Circular shapes represent PAMAMOS dendritic domains of generation  $G_x$ .

The precision by which the domain sizes of these dendrimer networks can be controlled is about 1 nm with actual domain sizes ranging from about 2 to about 9 nm, depending on the precursor generation used. Scanning electron microscopy (SEM), small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) studies revealed uniform three-dimensional distribution of these domains throughout the bulk of the networks.

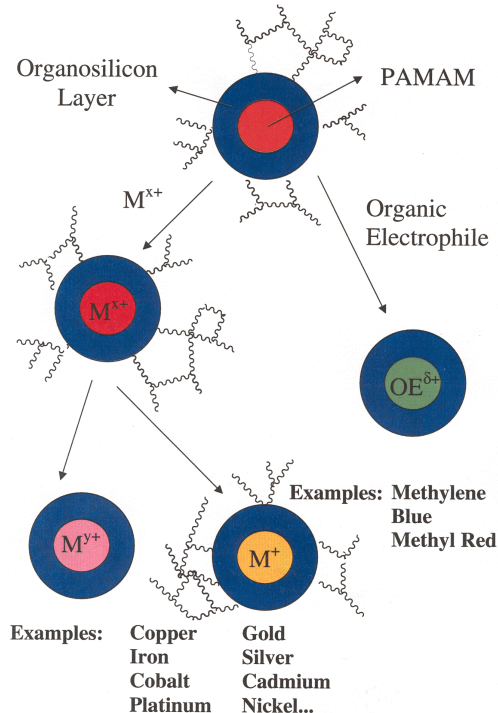
PAMAMOS dendrimer networks may be conveniently processed into self-supporting elastomeric or plastomeric films, sheets or coatings (see Figure 3) on a variety of substrates including glass, plastics, metals, paper, wood, ceramics, etc.<sup>5</sup> The properties of these objects can be controlled by: (a) the selection of PAMAMOS dendrimer precursor used for network formation; (b) the composition of the cross-linking reaction mixture; and (c) the cross-linking reaction conditions.<sup>3-5</sup> Some of important properties include:

- optical clarity, transparency and lack of visible coloration;
- insolubility (but ability to swell) in solvents, such as methanol, water, methylene chloride, THF, or acetone;
- glass temperatures ranging from below  $-50^\circ\text{C}$  to above  $100^\circ\text{C}$ ;
- mechanical properties ranging from relatively soft and flexible rubbers to very hard and scratch-resistant glasses;
- smooth surfaces whose typical roughness is less than 2 nm;
- solid surface energy of about 20-25 mN/m (i.e., similar to that of polydimethylsiloxane or paraffin waxes).



**Figure 3:** Schematic representation of a PAMAMOS dendrimer network coating on a glass substrate. If the substrate has reactive functional groups, such as Si-OH in this example, the coatings may form a permanent covalent bond with the substrate.

Nucleophilicity of PAMAM domains of these unique nanostructured dendrimer networks enables topologically controlled complexation of a wide variety of different electrophilic species.<sup>6,7</sup> Among others, these may include organic dyes, organometallic molecules and/or inorganic cations, such as: methylene blue, methyl red, various salts of  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Au}^{3+}$ ,  $\text{Rh}^{3+}$ ,  $\text{Pt}^{4+}$ , or lanthanides, such as  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , etc.<sup>6,7</sup> The complexed species can be further chemically transformed (as if in confined nano-reactors) to yield nanoscopic particles of zero-valent metals, sulfides, selenides, etc., as summarized in Figure 4.<sup>7</sup>



**Figure 4:** Schematic representation of complexation and encapsulation of guest species in nano-scaled PAMAM domains of PAMAMOS honeycomb-like networks.

This regularity of structure of PAMAMOS dendrimer networks and their ability to complex and encapsulate various guest species with nanoscopic topological precision offer unprecedented potentials for new applications in nano-lithography, electronics, photonics, chemical catalysis, etc.<sup>6</sup>

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