

SMALL-ANGLE NEUTRON SCATTERING FROM METAL ION-CONTAINING PAMAMOS DENDRIMER NETWORKS

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Introduction

There has been considerable interest recently in the development and understanding of nanocomposites based on the use of dendrimers as the host matrix. An important design intent in this direction is to take advantage of functionalized dendrimer interiors that can advantageously complex with an added constituent, resulting in a nanocomposite using the dendrimer as a template. Materials for applications ranging from microelectronics, catalysts, functional membranes, molecular sensors, and so forth, have been proposed or are under development.¹⁻⁴ Whereas previous work has been largely based upon nanocomposites composed of random dendrimer aggregates, crosslinked dendrimer-based networks were chosen for this work. In order to better define the fundamentals of such systems, crosslinked dendrimers modified with either Au³⁺ or Cu²⁺ were prepared and their morphologies were characterized. A representative of a radially-layered copolymeric poly(amidoamine-organosilicon) (PAMAMOS) dendrimers consisting of five interior layers of polyamidoamine (PAMAM) and one exterior layer of organosilicon (OS) branch cells, i.e., (PAMAMOS [4,1]DMOMS) was selected as the host dendrimer. The OS layer in this instance was a dimethoxy-methylsilane (DMOMS).

A principal supposition in the selection of this system was that the nitrogen moieties contained in the dendrimer interior would be highly interactive with the added metallic ions.⁵ The selected dendrimer was also a reasonable compromise between having potential economics and yet a large enough core structure to enable the possibility of the formation of a suitable nanocomposite. Because imaging of these materials by transmission electron microscopy usually proves to be very difficult, scattering techniques were relied upon to provide the key information on the resulting microstructures.

Experimental

Sample Preparation

Crosslinked poly(amidoamine-organosilicon), PAMAMOS dendrimer thick films, (0.5 to 2) mm thick, were prepared from dimethoxymethylsilyl-terminated PAMAMOS dendrimers⁶⁻⁸ via moisture hydrolysis of their CH₃O-Si groups followed by condensation of the resulting silanols into interdendrimer siloxy bridges.⁹⁻¹¹ In the first phase of the procedure, the films were cast under ambient conditions from about a mass fraction 20 % PAMAMOS/methanol solutions, following which the crosslinking was completed by heating in a vacuum oven at 65 °C for about 20 hours. The resulting clear and transparent films were then exposed to solutions of metal salts in D₂O, and the salts were allowed to diffuse in at room temperature.^{4, 6,7} For Au³⁺ and Cu²⁺, AuHCl₄ and CuSO₄ solutions, respectively, were utilized. In all examined cases this obeyed Case II diffusion kinetics and the depth of salt penetration could be easily monitored by simple optical microscopy. The concentrations are kept within 1 % of the reported values and the temperatures were kept in a 1 °C range of the stated value.

Alternatively, via an *in-situ* method, a methanol solution of desired salt was added directly into the solution of precursor PAMAMOS dendrimer in the same solvent, and crosslinking was performed in the same manner as described above. Notably, the crosslinking via this procedure was always

faster than when the salt was not present, indicating initial formation of cation-silanolates, which more rapidly underwent silanol condensation reaction. In another significant difference from the samples prepared by the salt diffusion into the preformed dendrimer-based networks technique, the samples obtained by this approach had continuous distribution of metal cations at a macroscopic level throughout entire bulk of the films. Thus, while cross-cuts of the films containing Cu²⁺, for example, may typically showed two blue surface layers surrounding colorless Cu²⁺-free middle section, the corresponding samples prepared by the *in-situ* method were always continuously blue throughout their entire cross sections.

The PAMAMOS thick films were then prepared for small-angle neutron scattering (SANS) by exposing them to D₂O for sufficient time (typically several days) to permit the samples to approach the equilibrium level of uptake by diffusion. The location of D₂O between interior dendrimer branches with or without added metallic ions results in SANS characteristics indicative of the microstructures of the prepared nanocomposites.^{5, 12}

Small-Angle Neutron Scattering

The SANS experiments were performed at the 8 m facility at the National Institute of Standards and Technology Center for Cold Neutron Research (Gaithersburg, Maryland).^{13,14} A sample to detector distance of 203 cm was maintained throughout the study, operating at a wavelength, $\lambda = 5 \text{ \AA}$, with a wavelength spread of $\Delta\lambda/\lambda = 0.14$. The number of counts was corrected for detector efficiency, background scattering, and empty cell for each pixel of the two-dimensional detector plane. Absolute scattering intensities were calculated by use of a H₂O standard and the experimental transmission values. Circular averaging the two-dimensional data sets of the absolute intensities results in the values of the absolute scattering intensity as a function of the scattering vector Q (with $Q = (4\pi/\lambda) \sin(\theta/2)$, θ being the scattering angle). The data processing was carried out with the software provided by the Center for Neutron Research at NIST.¹⁵ The uncertainties of the scattering as one standard deviation of the counts is smaller than the symbols in the plots and is not shown. The characteristic spacing is calculated from the peak position as $D = 2\pi/Q_{\text{max}}$ and is typically in the range $\pm 10 \%$.

Results and Discussion

Plotted as scattered intensity versus scattering vector Q, two series of SANS curves are shown in Figures 1 and 2 for, respectively, increasing Au³⁺ and Cu²⁺ content in samples prepared by the *in-situ* method. The scattering is similar in kind to that generally observed for small-angle scattering from multiple spheres (See, for example, ref. 16.). In both figures, the resulting core-to-core spacing for the neighboring PAMAMOS dendrimers is 37 Å ($Q_{\text{max}} = 0.17 \text{ \AA}^{-1}$). This result was confirmed by small-angle X-ray scattering (SAXS). The addition of either ionic Au or Cu results in both an increase in the dendrimer core-to-core spacing and a broadening of its distribution. The well defined SANS peaks are indicative of a fairly high degree of order in the crosslinked PAMAMOS network.

For Au-containing samples, the average spacing increases from 37 Å to about 45 Å with an increase of Au content to a mass fraction of 1.2 %. In the case of the Cu-containing samples, the increase in core-to-core spacing is to about 53 Å over a range of mass fraction (0 to 16.7) % Cu²⁺. The rise in scattered intensity at low Q suggests that a portion of the metallic ions resides outside the PAMAM dendrimer interior in the OS matrix as the ionic content is increased, although the increasing intensity of the peak suggests that a major portion of the Cu²⁺ is partitioned into the dendrimer interiors.

While the scattered intensity in low Q portion of the SANS curve for the Cu-containing samples steadily increases, the curves for the Au-containing samples indicate first an increase followed by a partial decrease with increasing content. This is most likely related to the partial reduction of Au and resulting precipitation of Au⁰ that result in Au³⁺ being subtracted from the population that is presumably associated with D₂O during SANS. Indeed, both preliminary SAXS and HRTEM indicate the formation of Au⁰ particles

on the order of 14 nm in size as Au content is increased. No precipitation of Cu^0 , however, was observed in the samples.

In contrast to the results for the *in-situ* samples, the samples prepared by post-polymerization *diffusion* into the pre-crosslinked networks yield very different SANS results. These are characterized by pronounced diffuse scattering at low Q with a gradual decrease to a base line background at about the Q equivalent to the core-to-core distance. No distinct peak associated with the crosslinked PAMAMOS is observed. These results are consistent with the existence of a fairly random distribution of the metallic constituents with no preferential concentration in the dendrimer interiors.

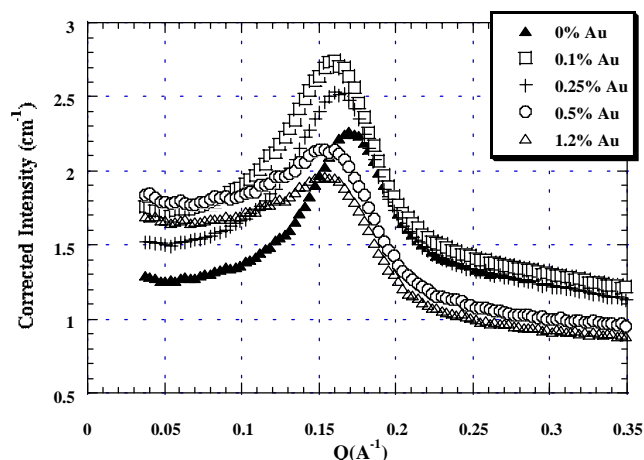


Figure 1. Small-angle neutron scattering from PAMAMOS[4,1]DMOMS networks made by the *in-situ* technique with increasing mass fraction Au. Data is plotted as corrected intensity (cm^{-1}) versus scattering vector, Q (\AA^{-1}).

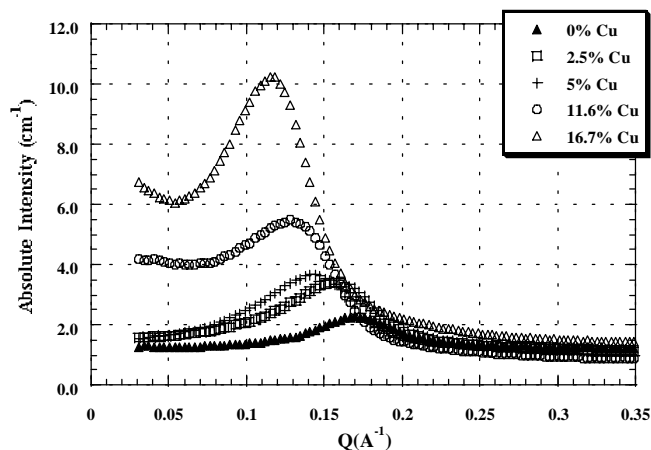


Figure 2. Small-angle neutron scattering from PAMAMOS[4,1]DMOMS networks made by the *in-situ* technique with increasing mass fraction Cu^{2+} content. Data is plotted as absolute intensity (cm^{-1}) versus scattering vector, Q (\AA^{-1}).

Conclusions

1. The studied crosslinked PAMAMOS dendrimer networks gave strong evidence of a fairly high degree of order, as indicated by the SANS, which showed a core-to-core distance of about 37 \AA .

2. The addition of Au^{3+} or Cu^{2+} in solution before crosslinking of the PAMAMOS dendrimers via the *in-situ* method resulted in a nanocomposite microstructure with a preference in distribution for the dendrimer interiors, however, increasing metallic content led to some distribution to the surrounding crosslink matrix. For example, a content of about mass fraction 5% Cu^{2+} appears to be an upper practical limit, above which a significant portion of the ionic content is no longer centralized in the dendrimer interiors.
3. The *in-situ* method of preparing the PAMAMOS-based dendrimer nanocomposites more readily resulted in a distribution favoring ionic content in the dendrimer interiors when compared to the post-crosslinking *diffusion* method.

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