

# Organic-Inorganic Hybrid Structures with Dendrimers: A Small Angle X-ray Scattering Study on a Mesoscopic Model System

Franziska Gröhn, Yvonne A. Akpalu, Barry J. Bauer, and Eric J. Amis

*Polymers Division, National Institute of Standards and Technology*

The combination of organic and inorganic matter on size scales of nanometers produces unique natural materials, like seashell or bone. In nanocomposites, the combination of the optical and electrical properties of the inorganic colloid with the mechanical properties, propensity for self-assembly, and functional groups of the organic compound can result in a variety of potential applications. These range from optical and electrical to medical and information storage materials. Thus, the synthetic design of such hybrid nanostructures has generated great interest. Inspired by nature, the method of polymer nanotemplating, i.e. templating a growing inorganic crystal within a polymeric matrix, has been evaluated as an effective synthetic route. However, the success of such materials requires an understanding of their formation mechanisms and properties. Therefore it is necessary to study model systems that provide a well-defined polymeric template and the possibility for a full characterization of the nanostructures. We have been investigating dendrimers, organic molecules with a size between (1 and 15) nm, as “model nanoreactors.” Small angle x-ray scattering (SAXS) has been used for the characterization of the resulting hybrid structures.

In aqueous solution, charged dendrimers attract oppositely charged metal ions, as is depicted in Figure 1. Chemical reactions can be performed on the inorganic precursors attached to the dendrimer, producing colloid structures that are controlled by the dendrimer. SAXS data for an unmodified generation 9 (G9) dendrimer and for the corresponding dendrimer-gold hybrid-particles are also shown in Figure 1. The different particle characteristics can

be measured by Fourier transformation of the scattering curve  $I(q)$  into real space, i.e. the pair distance distribution functions  $P(r)$  (program ITP, *Indirect Transformation for the Calculation of P(r)*, O.Glatter). The shape of  $P(r)$  for the unmodified dendrimer corresponds to a homogenous sphere of 13 nm diameter. In contrast,  $P(r)$  for the hybrid particle is typical of a layered sphere with a maximum dimension of 13 nm. This result proves that the gold is indeed formed inside of the dendrimer as indicated in the schematic. Furthermore, modeling of the  $P(r)$  reveals that the gold particle inside the dendrimer is located with an offset from the center. The 4 nm diameter of the gold particle is in agreement with SAXS and transmission electron microscopy (TEM) results.

The G9 dendrimer was loaded with gold salt corresponding to a gold-ion to end-group ratio of 1:1, i.e. 2048 gold atoms per one dendrimer. Assuming the formation of one gold colloid per dendrimer molecule upon reduction, one would expect a size of 4 nm for this gold particle consisting of 2048 gold atoms. This is

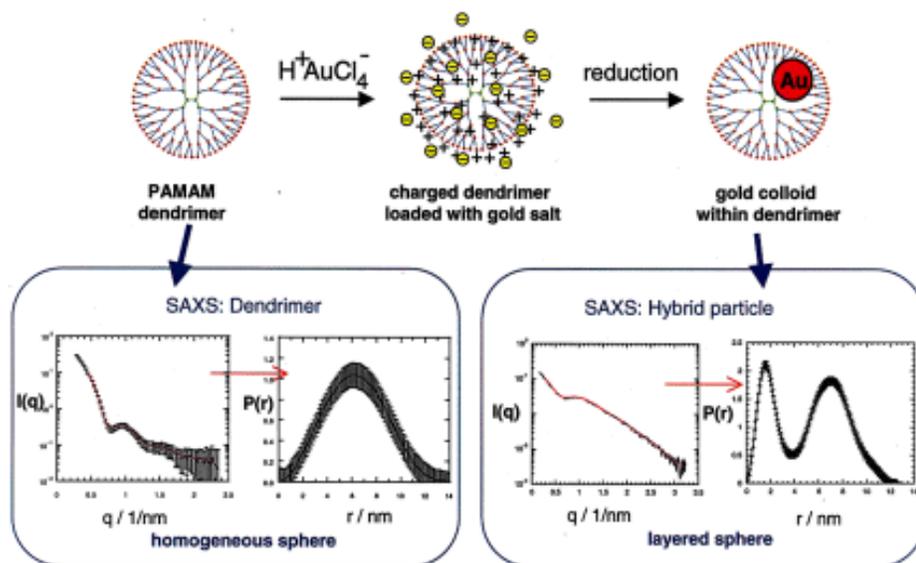


Figure 1. Schematic of Dendrimer nanotemplating in aqueous solution and small-angle x-ray scattering results for the unmodified G9 PAMAM-dendrimer and the gold containing G9 PAMAM-dendrimer. Shown are scattering curves  $I(q)$  along with fit to the data<sup>[1]</sup> and the pair distance distribution functions  $P(r)$  obtained by indirect Fourier transformation of the scattering data  $I(q)$ <sup>[2]</sup>.

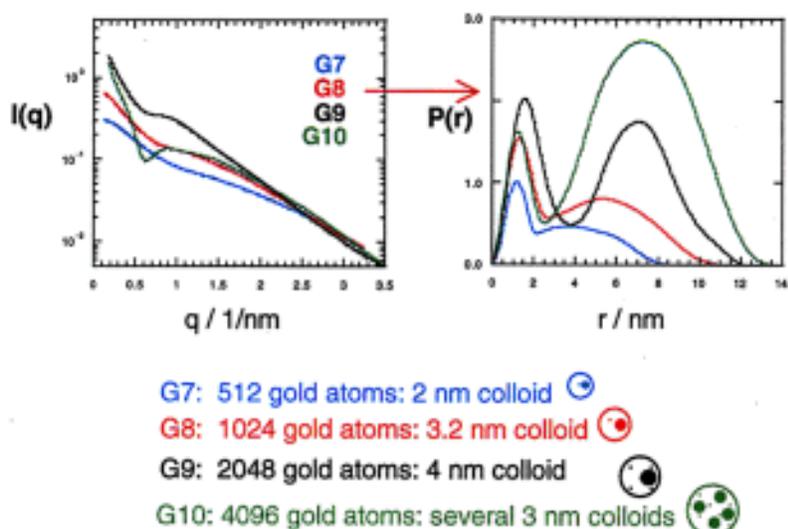


Figure 2. Generation dependence of dendrimer nanotemplating in aqueous solution: Small angle x-ray scattering curves  $I(q)^{[23]}$  and pair distance distribution functions  $P(r)^{[24]}$  for gold-dendrimer hybrid structures obtained with PAMAM dendrimers of different generation, G7 to G10.

in good agreement with the SAXS results. Thus, the postulate that the gold ions from one dendrimer form one particle is reasonable. The gold-colloid formation is indeed templated by the dendrimer. The size of the gold colloid formed is well controlled by the number of gold atoms added per dendrimer, what we refer to as “fixed loading law.” By varying the dendrimer generation (G6 to G9) or the loading ratio of gold ions per dendrimer, the size of the gold colloid can be controlled, as shown in Figure 2.

In contrast, for G10, multiple smaller gold particles inside one dendrimer are observed by SAXS and TEM. When the colloid grows inside a polymeric matrix, the elastic forces of the surrounding polymer become important in addition to the free energy of crystal formation and surface tension. The growth of a nucleated colloid is limited by the finite extension of surrounding polymer chains. For the dendrimers, the internal dendrimer segment density increases slightly as the generation number

increases. While the volume of a single gold nanocluster would double with each generation, the space available for its formation decreases. Thus for the G10 dendrimer the chain flexibility is not sufficiently high to allow for the growth of one colloidal particle. The G10 dendrimer still realizes a host-guest nanotemplating, and the different dendrimer structure results in a different colloid morphology.

The formation of organic-inorganic hybrid structures has been further investigated by a different approach. Hydrophobically modified dendrimers, i.e. hydrophilic dendrimers with fatty acid chains attached to each terminal unit, can act as inverse micelles and solubilize hydrophilic molecules in hydrophobic solvent. While the plain dendrimer is a spherical molecule in solution, solubilizing the gold-salt hydrate changes the structure:

scattering results are shown in Figure 3. As seen by the data analysis displayed, the Fourier transformation of the scattering curve leads to pair distance distribution functions typical of cylinders. The cross section diameter obtained from the SAXS results is 4 nm, which is reasonable for a swollen dendrimer core filled with gold salt that produces the contrast in the x-ray experiment. The structure is further confirmed by small angle neutron scattering (SANS) in deuterated solvent

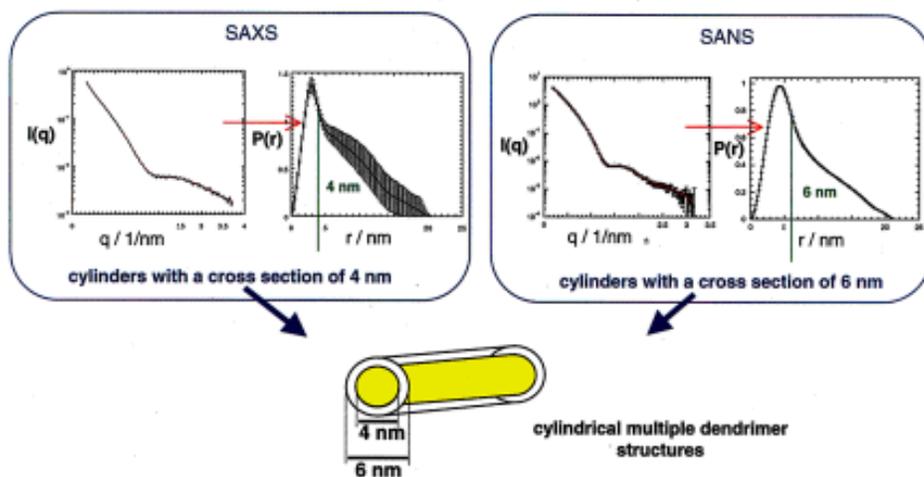


Figure 3. Hydrophobically modified dendrimer loaded with gold salt hydrate in toluene: SAXS and SANS data. Shown are scattering curves  $I(q)$  along with fit to the data<sup>[1]</sup> and the pair distance distribution functions  $P(r)$  obtained by indirect Fourier transformation of the scattering data  $I(q)$ <sup>[2]</sup>.

yielding a cylindrical structure with a total cross section diameter of 6 nm, corresponding to a two-step density profile of the swollen core (radius 2 nm) plus fatty acid chains (1 nm).

Reduction of the gold yields spherical gold particles. This may be understood by the density change of the gold with reduction. Contrary to the approach described before, in this case the gold colloids are bigger than expected when formed within one dendrimer. This also can be explained only by an intermediate connection of dendrimers.

Therefore, different types of dendrimers have been shown effective for the synthesis of organic-inorganic hybrid colloids. A complete characterization of the different hybrid particle morphologies of this model system has been performed by synchrotron small-angle x-ray scattering.

#### Acknowledgements

SAXS measurements were carried out at the Advanced Polymer Beamline X27C. We gratefully thank Feng-Ji Yeh and Lizhi Liu for their important and

continuous help with the SAXS setup that made this study possible. This work is supported in part by the U.S. Army Research office under contract number 35109-CH. We would like to thank Donald Tomalia of MMI and Rolf Scherrenberg of DSM for providing us with dendrimers and Heimo Schnablegger for discussions.

#### References

- [1] Error bars are the measured standard deviation in  $I(q)$  for the dendrimer. Errors are within the thickness of the line for the hybrid particle
- [2] Error bars are the standard deviation in the estimation of  $P(r)$ , which results from the fit to the  $I(q)$  data.
- [3] The relative standard deviation in the SAXS intensity values in the range  $0.2 \text{ nm}^{-1} < q < 1.6 \text{ nm}^{-1}$  is less than 3%. At higher wavevectors, the relative standard deviation increases with  $q$  to a maximum value of 7%. Data were collected up to a maximum value of the scattering vector magnitude  $q = 4.4 \text{ nm}^{-1}$ . In order to allow for a better comparison of the features, data are plotted here only up to a maximum value of  $q = 3.5 \text{ nm}^{-1}$ .
- [4] The relative standard deviation in the  $P(r)$  values is less than 3%.