

NANOPARTICLE FORMATION WITHIN DENDRIMER-CONTAINING POLYMER NETWORKS: ROUTE TO NEW ORGANIC-INORGANIC HYBRID MATERIALS

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Introduction

Due to quantum-size effects, inorganic nanoparticles have unique and size-dependent optical, electrical and magnetic properties that can lead to a wide variety of practical applications. In solution, discrete nanoparticles of differing chemical compositions with narrow size distribution can be synthesized in a classical way using surfactants to stabilize the growing colloidal structure or in a more controlled way via the synthesis in confined reaction media such as microemulsions or block copolymer micelles. However, certain applications may require a solid polymeric matrix in order to combine the special colloidal effects with the mechanical properties of the surrounding polymer.

Recently, polyamidoamine (PAMAM) dendrimers, polymer molecules in the size range of (1 to 15) nm, have been successfully used as stabilizers and templates for inorganic nanoclusters in aqueous or methanol solution.¹ The aim of this study is to investigate “dendrimer nanotemplating” transferred to solid materials. Recently, it has been shown that PAMAM dendrimers can be uniformly dispersed in a hydrophilic polymer network by the use of an interpenetrating polymer network synthesis.²

Experimental

PAMAM dendrimers^{3,4} were obtained from Dendritech (Michigan Molecular Institute) as a solution in methanol.⁵ The dendrimer-polymer networks were prepared by dissolving the dendrimers in 2-hydroxyethyl methacrylate (HEMA) containing a mass fraction of (0.5 or 1) % ethylene glycol dimethacrylate with AIBN as an initiator for the methacrylate. They were polymerized at 35 °C for 72 h and at 70 °C for an additional hour.

The dendrimer-polymer networks were swollen in water and cut into small pieces and were placed into aqueous solutions of H₂PtCl₆ or Cu(NO₃)₂ (2·10⁻⁶ M to 1·10⁻⁴ M) for one week.⁶ Afterwards, the network was transferred in water or 0.1 M hydrochloric acid, with this solution replaced every day for about two weeks, until no further gold salt was washed out, as was judged by eye from the color of the solution. For the synthesis of metal nanoclusters, the network pieces were transferred into a solution of reducing agent, e.g. sodium borohydrate in 0.2 M NaOH solution, and then washed again with water and finally dried in vacuum.

SAXS data were collected at the Advanced Polymer Beamline at Brookhaven National Laboratory, X27C as described elsewhere. The scattering curves I(q) were Fourier transformed into the pair distance distribution function P(r) using the program ITP (*Indirect Transformation for the Calculation of P(r)*) by O. Glatter.^{7,8,9}

Samples were ultramicrotomed at -30° C with a range of thickness from (60 to 80) nm and transferred to carbon-coated copper grids, 200 mesh. Staining of these thin sections was performed by inverting the grid on a drop of aqueous phosphotungstic acid solution that had been neutralized with NaOH (mass fraction of 2 % phosphotungstic acid). The grid was then blotted on filter paper and air-dried. TEM images were obtained with a Phillips 400 T at 120 kV using low-dose conditions at a magnification of 17000 X and 36000 X.

Results and Discussion

Networks containing dispersed dendrimers are clear and transparent materials, in a dried as well as in a water-swollen state. When exposed to metal-salt solutions, the swollen polymer networks turn into the color of the solution, e.g. yellow and brown using H₂AuCl₄ and H₂PtCl₆, respectively, indicating the diffusion of the metal salt solution into the network. In case of copper salt, the network turns dark blue, which in addition indicates the coordination of the copper ions to the dendrimer amine groups.

Figure 1 shows results for dendrimer-polymer networks containing a mass fraction of 1% dendrimers generation 7 to 10 (G7 to G10) after loading with H₂PtCl₆. The scattering curves exhibit the features typical of the form factors of these higher generation dendrimers in solution, i.e., sphere form factors.¹⁰ This result demonstrates that the PtCl₆²⁻ ions are indeed accumulated inside the dendrimer. In addition, it can be seen from the scattering curves that the dendrimers are well-dispersed inside the polymer matrix and no aggregates are detected. This is in agreement with recent SAXS and TEM characterization of these unmodified dendrimer-polymer networks under staining with phosphotungstic acid.² The same result is found for loading the networks with copper ions.

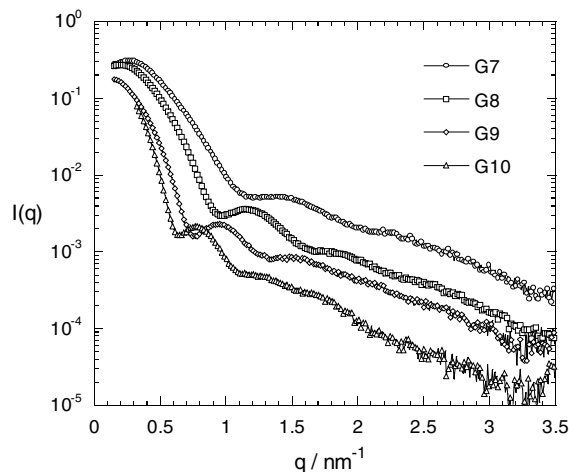


Figure 1. SAXS of dendrimer-polymer networks containing a mass fraction of 1% dendrimers generation 7 to 10 after loading with H₂PtCl₆

Figure 2 shows SAXS data for a metal-salt loaded network containing a mass fraction of 10 % G8 dendrimer. In this case, the interparticle correlation becomes evident within the q-range covered by the measurement. The peak at low q is caused by a peak in the interparticle structure factor S(q) and the position allows for the determination of an experimental interparticle distance d_{exp}. In a simple approximation this is given by d_{exp} = (3/2)^{1/2}2π/q_{max}. The data in Figure 2 yield an experimental inter-dendrimer distance of (19 ± 1) nm. This value for d_{exp} can further be compared to the distance expected for uniform particle distribution d_{uni}. For a mass fraction (which can be regarded as roughly equal to the volume fraction) of 10 % G8 dendrimers, the expected distance for uniform distribution d_{uni} = (1/φ·v_{den})^{1/3} (φ volume fraction, v_{den} dendrimer volume) is d_{uni} = 19.1 nm. This result confirms the assumption of a homogeneous distribution of dendrimers within the polymer network. Further, the scattering curves for the samples with 1 % mass fraction of G7 and G8 dendrimer in Figure 1 also show slight peaks at low q, giving approximate inter-dendrimer spacings of d_{exp} = (32 ± 1) nm and d_{exp} = (39 ± 2) nm, for G7 and G8, respectively. These again correspond to the expected distances for uniform particle distribution of d_{uni} = 32.2 nm for G7 and d_{uni} = 41 nm for G8. Thus the spacing between the dendrimers is apparently controlled as expected by the dendrimer concentration within a range from (1 to 10) %. For G9 and G10 (mass fraction of 1 % dendrimer), d_{uni} does not lie within the q-range of the SAXS measurement and could not be checked.

Reduction of metal salt inside the polymer-dendrimer network results in metal clusters of nanometer size, as can be seen by the dark red or brown color of the polymer network for the gold and the platinum samples, respectively. TEM images of gold colloids obtained upon reduction of a polymer-dendrimer network show that the metal colloids that are formed are well-dispersed in the polymer matrix.

The size range of the gold colloids is (4.0 to 4.3) nm. It is interesting to compare the size of the gold colloids to previous dendrimer nanoclusters in aqueous solution. In solution, we found that the maximum possible loading with gold ions without causing aggregation of dendrimers corresponded to a molar ratio of dendrimer end groups to gold ions of 1:1. The gold ions added per dendrimer molecule could then be reduced to form one colloidal particle (“fixed-loading law”). The resulting colloid sizes were approximately 3.2 nm

corresponding to 1000 atoms for G8 and 4.0 nm corresponding to 2000 atoms for G9. Thus, the colloids formed in the dendrimers within a polymer matrix are remarkably larger for the same G8 dendrimer. It is also the case here that the gold salt concentration in the surrounding solution was an order of magnitude larger than necessary for stoichiometric loading. Colloids of 4 nm size consist of about 2000 gold atoms. We note that this corresponds to the total number of chargeable amine groups of one dendrimer molecule (primary and tertiary ones) and could be consistent with the electrostatic-attraction mechanism. This would be in contrast to nanotemplating in solution, and yield a maximum loading with gold ions which is twice as high. Since these dendrimers are fixed in the polymer matrix and cannot aggregate upon loading with metal salt they are evidently stabilized to this higher loading level which yields larger metal nanoparticles than could be obtained in solution.

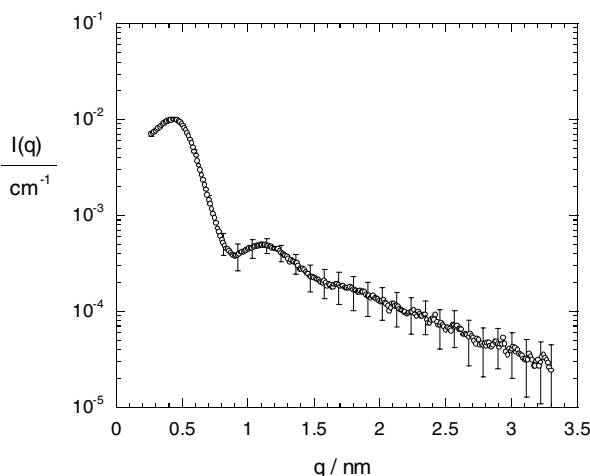


Figure 2. SAXS data for a metal-salt loaded network containing a mass fraction of 10 % G8 dendrimer.

Platinum nanoparticles formed inside a G8 dendrimer in the polymer network have a size of 3 nm. This corresponds to about 1000 platinum atoms per nanocluster. With only half as many ions reduced to form one particle for the platinum as compared to the gold it is sensible to invoke the electrostatic attraction mechanism postulated above. Since the PtCl_6^{2-} is doubly charged, as compared to the single charged AuCl_4^- , this again corresponds to a one to one ratio of amine groups to ion charges.

We have also produced copper colloids inside the dendrimer network by the same procedure. TEM shows nanoparticles of 3.3 nm diameter, dispersed in the polymer matrix. More importantly, we have noted that the copper colloids produced inside the swollen polymer gel are stable for at least several days when exposed to water that may contain dissolved oxygen. This is a remarkable result, since colloidal copper particles usually are not stable in an aqueous environment in the presence of oxygen.^{11,12} This suggests an effective colloid surface stabilization is provided by the dendrimer. Previous studies on the preparation of dendrimer-stabilized metal nanoclusters have also demonstrated a stability of copper colloids in oxygen-free aqueous solution,¹ however, in air-saturated solution the clusters were converted into dendrimer coordinated copper ions overnight. The copper-dendrimer-polymer composites may thus have potential in special applications that otherwise cannot be easily realized, for example the use of a colloidal copper catalyst in aqueous solution.

For the case of platinum clusters we have used dendrimers of different generations to investigate the attachment of the ions and the reduction of the ions into metal nanoclusters. For this purpose, we produced platinum nanoclusters in polymer-dendrimer networks containing G7, G8, G9 and G10 PAMAM dendrimers, respectively, each with a dendrimer mass fraction of 1 %. Results for the salt loaded precursor samples were shown in Fig.1. For the G7 sample, after reduction, we find platinum clusters of approximately 2.4 nm diameter corresponding to about 500 platinum ions. This is consistent with the results for the G8 sample with two positively charged amine groups attracting one PtCl_6^{2-} ion and the control of particle size determined by the precursor ions on the dendrimers.

In contrast, for G9 and G10, multiple smaller platinum clusters are formed inside one dendrimer are formed. TEM shows that platinum colloids inside G9 dendrimers, where the dendrimers have been stained with phosphotungstic acid in order to visualize both, the platinum and the dendrimer both appear within the PHEMA matrix. This change in the morphology of the nanoclusters with dendrimer generation is also observed by SAXS. The pair distance distribution functions were calculated for platinum nanoclusters in dendrimer-polymer networks for both, G7 and G10. The $P(r)$ reveals a layered-sphere-structure in both cases. However, for the G7 dendrimer a deviation from a strict spherical symmetry becomes evident from the relative peak heights in the $P(r)$ functions. We have previously demonstrated that such a deviation can be caused by the location of a single metal colloid inside a dendrimer with an offset from the center. The difference in relative height of the first and second peak in $P(r)$ in G7 and G10 is due to the formation of single (off-center-placed) and multiple-particles, respectively.

For the highest generation dendrimers, it may be that the space available and the chain flexibility is not sufficiently high to allow growth of one single colloidal particle. On the other hand, the increased surface to be stabilized for multiple smaller particles is likely to be provided by the segments of the dendrimers. We can thus rationalize that the different volume conditions inside the dendrimer cause the formation of different colloid morphologies.

Conclusions

Crosslinked poly(2-hydroxyethyl methacrylate) containing dispersed PAMAM dendrimers were used as a template-matrix for the formation of inorganic nanoclusters. When swollen in aqueous solution, metal ions were attached to the dendrimers. Chemically reducing these metal ions results in gold, platinum or copper nanoclusters that are located inside the dendrimers, which are dispersed inside the polymer matrix. For G7 and G8, the size of the metal nanoclusters is controlled by the maximum number of metal ions that can be electrostatically attached. For G9 and G10, multiple colloidal particles per dendrimer are formed, as can be understood by the volume conditions inside the dendrimer and the additional influence of the polymer matrix. It has been shown that different metal nanoclusters can be produced, which opens the possibility for a wide variety of studies on model nanocomposites as well as applications in areas such as catalysis and dielectrics.

Acknowledgments

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