Morphological study of dendritic polymer templates for the formation of inorganic nanoclusters in amorphous and crystalline polymer composites

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The unique ability of highly branched polyamidoamine (PAMAM) dendrimers as stabilizers and templates for the formation of inorganic nanoclusters has been demonstrated. [1, 2] To get uniformity in the physical properties of polymer nano-composites, homogeneous distribution of dendrimers in a polymer matrix is an important issue. In this study, we investigate the morphological behavior of PAMAM dendrimers in amorphous and crystalline polymers using conventional transmission electron microscopy (TEM) with staining and small angle X-ray scattering (SAXS).

To disperse dendrimers uniformly in an amorphous interpenetrating polymer networks (IPN), the dendrimers were dissolved in 2-hydroxyethylmethacrylate (HEMA) and the monomer was polymerized. For the synthesis of metal nanoclusters, the dendrimer-polymer networks swollen in water were placed into aqueous solutions of inorganic metal salts for one week and the metal salts were washed out by water or hydrochloric acid. The network pieces were transferred into a solution of reducing agent, and then washed again with water, and dried in vacuum. To observe the dendrimers in crystallized polymer, hydrolytically stable gels were formed by dissolving portions of the vinyl surfone terminated poly(ethylene glycol) and 5 % dendrimers into polar solutions of water, methanol or DMSO, and cured.

SAXS data were collected at the Advanced Polymer Beam Line at Brookhaven National Laboratory, X27C as described elsewhere.[2] For TEM, cryo-microtomed electron transparent thin sections were stained by aqueous phosphotungstic acid (PTA) solution on Cu TEM grids and observed using a TEM. The measured diameters of various generations of dendrimers using SAXS and TEM are summarized in table 1.

When a 1 % PAMAM G9 in PHEMA IPN was stained with PTA, individual dendrimers are revealed, having dark contrast in the electron micrograph. They appear to be well dispersed in the matrix, as shown in Figure 1a. The formation of Pt nanoclusters in the PAMAM dendrimers in the PHEMA is confirmed by unstained TEM images. They reveal the dark contrast of Pt nanoparticles in the matrix (Fig. 1b). When these samples are stained with PTA, it is clearly demonstrated that Pt colloids with the darkest contrast are formed inside of the G9 PAMAM dendrimers that have a lighter gray color, as shown in Figure 1c. In other samples comprised of crystallized PEG with spherulitic crystal structures, PAMAM dendrimers are incorporated in the inter PEG lamellar crystals with amorphous portion of PEG chains (Figure 2). Figure 2a is the RuO_4 stained image showing the center of a spherulite radiating crystal lamellae. RuO_4 has stained the amorphous regions containing more free volume than chain folded crystal lamellae. In a crystallized PEG and G8 dendrimer network, spherical dendrimers are distributed in amorphous regions between PEG lamellar crystals, as shown in a PTA stained image of Fig. 2b.

Reference:

1. Gröhn, F.; Bauer, B. J.; Akpalu, Y. A.;Jackson, C. L.; Amis, E. J. *Macromolecules* **2000**, *33*, 6042-6050.
2. Gröhn , F.; Kim, G.; Bauer B. J.; Amis E. J Macromolecules, **2001,** 34, 2179

Table 1. Size measurements on PAMAM dendrimers in IPN from TEM and SAXS (Unit: nm)

Dendrimenrs	G7	G8	G9	G10
The average size in IPN from TEM		9.6±0.4	11.7 ±0.8	14.7±1.6
The average size in IPN form SAXS	8.0 ±0.8	9.6 ±1.0		13.7±1.3

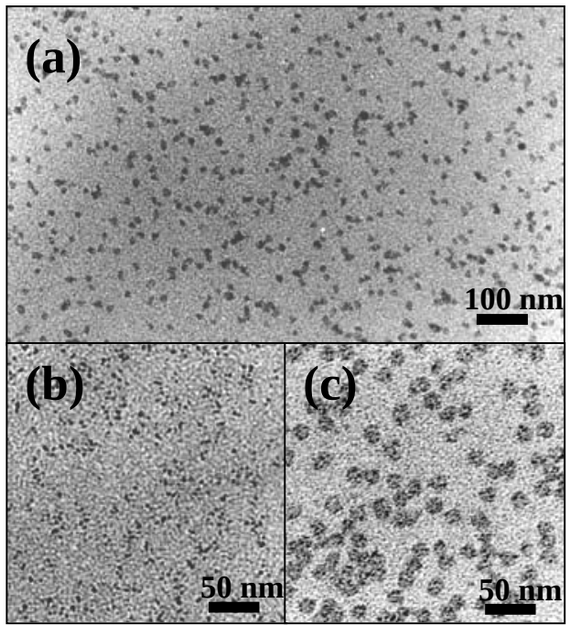

Figure 1. TEM images of (a) PTA stained G9 dendrimers in PHEMA; (b) Pt nanocolloids formed in a G9 dendrimers/PHEMA composite; (c) after PTA staining the sample imaged in (b)

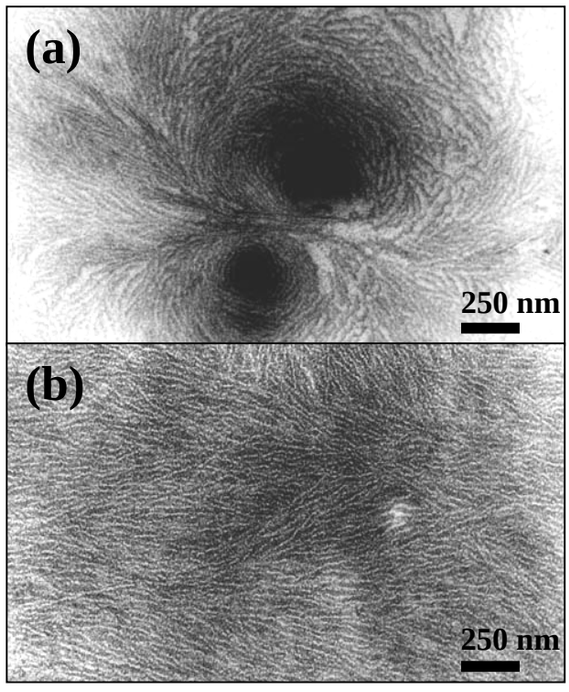

Figure 2. TEM images of G8 dendrimers in PEG spherulites; (a) RuO4 stained; (b) PTA stained