NANOCOMPOSITES OF MOLECULARLY DISPERSED POLYAMIDOAMINE (PAMAM) DENDRIMERS

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Introduction

Dendrimers are highly branched polymers promoted as new materials with unique physical properties compared to linear polymers (1-2). To exploit their unique structure, applications for dendritic polymers have been proposed in areas ranging from biomedical to materials science. Dendrimers are grown in a stepwise manner from a central core to different "generations" using many types of chemical reactions, resulting in a variety of end groups and chemical structures. The generations are designated as GX, where X is the generation number. Poly(amidoamine) (PAMAM) dendrimers have interior branches containing tertiary amine and amide groups, while the terminal units on the dendrimers can be functionalized with primary amines, hydroxyls, or other groups. These different terminal groups can make the dendrimer soluble in many different solvents. Miscibility of these dendrimers in a polymeric matrix would also be expected to depend on the terminal groups present on the dendrimer.

The size and distribution of PAMAM dendrimers in solution have been studied using small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) (3). These measurements have shown that the dendrimers are spherical in shape and well dispersed in solution. A TEM study of PAMAM dendrimers (G5 through G10) in our laboratory (4) successfully utilized biological type staining methods (5) to image individual dendrimer molecules for the first time. We have also recently prepared "dendrimer nanocomposites" in a polymer matrix using an interpenetrating polymer network (IPN) method (6-7). SAXS and TEM results show that PAMAM dendrimers can be uniformly dispersed in an IPN of hydroxyethyl methacrylate (HEMA) at mass fractions of 1 % and 10 %. For the TEM, the G11 dendrimers were prepared at a mass fraction of 10 % and were stained using osmium tetraoxide (6-7).

In this study, we determined the size, shape and morphological distribution of PAMAM dendrimers (G8 to G10) in an IPN matrix by TEM after staining the dendrimers with sodium phosphotungstic acid (NaPTA). All concentration ratios mentioned in this paper are mass fractions. At low dendrimer concentrations (1 % to 2 %) and for lower generation dendrimers (G8), we found that NaPTA stain produced much greater contrast than OsO_4 for dendrimers within the IPN. The uniformity of the distribution of dendrimers in the IPN was easier to determine by TEM at low concentrations, since the overlapping of the molecules due to the nominal section thickness of 70 nm was less prominent. The measurements of average size from TEM are consistent with those from SAXS for the dendrimers within the IPN, and an average size of PAMAM dendrimers in the polymer IPN are compared to those in methanol solution.

Experimental

PAMAM dendrimers of G8 through G10 were obtained from Dendritech (Michigan Molecular Institute) (8) as a solution in methanol. These dendrimers have amine groups (-NH2) as terminal units. The solutions were diluted in methanol to obtain the desired concentration. The dendrimer-IPN soluitios were prepared by dissolving 1 % or 2 % dendrimers in 2-HEMA containing 0.5 % of ethylene glycol dimethacrylate with AIBN as an initiator. They were polymerized at 35 ^{o}C for 14 h and at 50 ^{o}C for 3 h, and an additional hour at 70 ^{o}C.

Dendrimer blends were stained with a 2 % aqueous phosphotungstic acid (PTA) solution that has been neutralized with sodium hydroxide (pH = 7), for 1 d and dried for 3 d in air. The blends looked optically transparent, even after NaPTA staining. Electron transparent films of 60 nm to 80 nm thickness were cryo-microtomed at –30 ^{o}C, transferred to carbon coated Cu TEM grids, and the morphology of these materials was studied using TEM (Philips EM 400T) operated at 120 kV under low-dose conditions. A description of the experimental conditions for the SAXS data presented has been given previously (6).

Results and Discussion

The size, shape and distribution of PAMAM (G8, G9 and G10) dendrimers in IPN matrix are easily visualized by TEM after staining with NaPTA, as shown in Figure 1. The differentially stained PAMAM dendrimers appear as dispersed particles with darker contrast than the IPN matrix without any significant agglomeration or clustering, as shown in Figure 1a-c for G8 to G10, respectively. The image contrast of dendrimers in TEM is due to the fact that NaPTA preferentially reacts with the amine groups in the PAMAM dendrimers rather than the IPN matrix. NaPTA is most widely used in negative staining biological systems, where an electron-dense heavy-metal salt in solution provides contrast by surrounding a small particle (5). PTA has also been used to stain a number of different polymers, mainly polyamides and polyesters, in bulk to reveal crystalline lamella and fiber morphology, as summarized by Sawyer and Grubb (9).

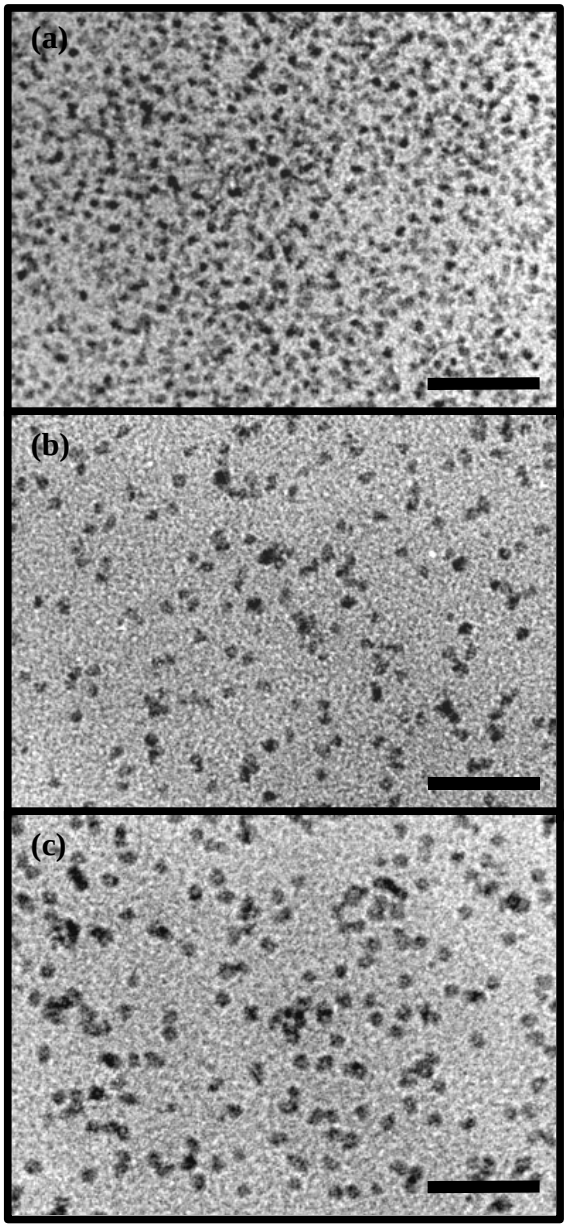

Figure 1. TEM images of PTA stained dendrimers in IPN; (a) 2 % G8 in IPN; (b) 1 % G9 in IPN; (c) 1 % G10 in IPN. The scale bars indicate 100nm.

The area fraction of dispersed dendrimers to IPN matrix in the electron micrographs looks much higher than the real mass fraction of dendrimers in blends. This is because the microtomed thin sections (nominal thickness of 70 nm) are still much thicker than the dendrimer diameter, so that more than one layer of dendrimers can be projected into the resultant two-dimensional image. This may also result in overlapped dendrimers in some regions of the image. Even though some of dendrimers show a slight polyhedral shape, the typical shape of stained dendrimers in the IPN is roughly spherical.

A comparison to results using OsO_4 stain for the 1 % G10 dendrimer in the IPN is shown in Figure 2. The dendrimers are visible in this image, but the differentiation between dendrimer and matrix is much less apparent than seen in Figure 1c for the same sample stained with NaPTA.

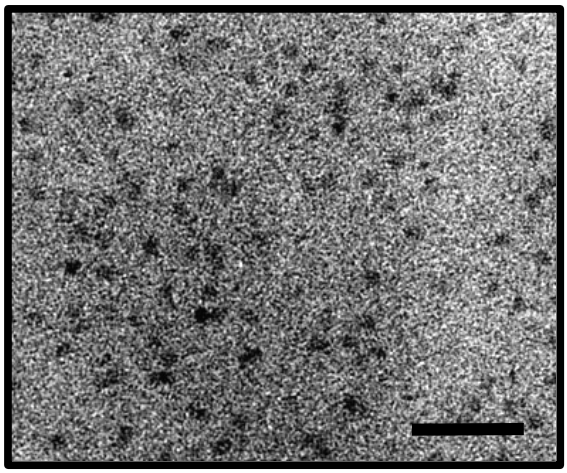

Figure 2. TEM image of osmium stained 1 % G10 in IPN. The scale bar indicates 100 nm.

The average sizes of dendrimers in the IPN measured by TEM and the size data from SAXS are summarized in Table 1. The average sizes from TEM were obtained by measuring the diameters on a highly magnified electron micrograph and calculating the mean value with ± being one standard deviation. The average size measured by SAXS was obtained from a plot of R_g of dendrimers in IPN and in solution with one standard deviation calculated as described elsewhere (3, 6). The radius of gyration, R_g, was converted to a sphere radius assuming a uniform density sphere model, as $R= R_g/\sqrt{0.6}$. The average sizes of dendrimers in IPN measured using TEM are well matched with the values obtained from SAXS. This result is also consistent with the measured values for individual dendrimers in the absence of any solvent using TEM (4). As compared with the SAXS data, when the concentration of dendrimers is relatively low (1 % to 2 %), the average sizes of dendrimers in IPN and in methanol solution are nearly identical.

Table 1. Size Measurements on PAMAM Dendrimers in IPN from TEM and SAXS (nm)

Dendrimers	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 from SAXS	**9.6±1.0**		**13.7±1.4**
The average size on a surface from TEM	**10.2±0.8**	**12.4±0.5**	**14.7±1.1**
The average size in methanol from SAXS	**10.4±1.0**	**12.7±1.3**	**14.8±1.5**

Conclusions

PAMAM dendrimers are well distributed in the IPN matrix at 1 % to 2 % and visible as individual molecules as observed by TEM of thin sections stained with NaPTA. The TEM results concur with previous SAXS data on these materials, but also demonstrate that large clumps or aggregates of dendrimers are not present, information that is difficult to extract from SAXS alone. From the stained images, the overall shape of dendrimers in the IPN matrix remains spherical without a measurable change in size or shape. As compared with the average size of dendrimers in solution, using the polymeric matrix as a host for the dendrimers does not appear to affect the size and shape of dendrimers at relatively low-mass fraction of dendrimers.

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