PROBING THE LOCATION OF THE TERMINAL GROUPS OF A DENDRIMER

Dendrimers represent a new class of macromolecules developed in recent years. Typically, a dendrimer structure has a tri- or tetrafunctional core, which is surrounded by several "generations" of stepwise added trifunctional monomers, leaving the last generation with a large number of terminal units as shown in Fig. 1. The molecular weight doubles with each generation, leading to high molecular weights, and causing the dendrimer to become very compact and crowded.

Many of the potential technological applications of dendrimers depend on their segment density distribution. Previous scattering studies have shown that dendrimers have uniform interiors and are quite spherelike in their shape [1]. The location of the terminal groups is also of importance, since they are usually different chemically from the rest of the dendrimer. This invites a number of applications such as the support of catalysts or drugs or their use as hyperfunctional crosslink sites. The accessibility of these terminal groups depends on their location compared to the other dendrimer units.

The location of the terminal units can be determined by labeling the last generation of the dendrimer with deuterium and using contrast matching techniques. Figure 1 shows the labeled groups in red and the rest of the dendrimer in blue. By choosing the proper mix of h- and d- solvents, the interior of the dendrimer will be matched, making only the labeled end groups visible in small angle neutron scattering (SANS).

A sixth generation polyamidoamine (PAMAM) dendrimer was reacted with acrylonitrile (vinyl-d3) to give the deuterium labeling for the SANS. Ethylene diamine was reacted with the dendrimer to give a labeled seventh generation dendrimer. A similar reaction was used to make a seventh and eighth generation dendrimer without labeling. Solutions of unlabeled eighth generation dendrimer were made in mixtures of CH_3OH and CD_3OH for determination of the match point. Three samples were analyzed, an unlabeled dendrimer in CD_3OH (high contrast), an unlabeled dendrimer in the match mixture (dendrimer matched), and the labeled dendrimer in the match mixture (interior matched).

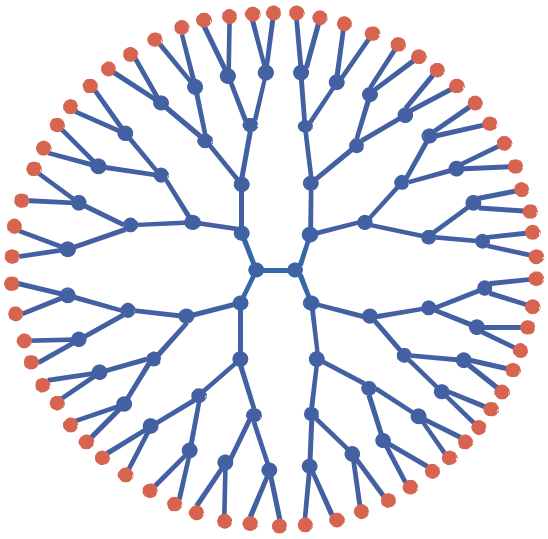

FIGURE 1. Dendrimer structure with labeled terminal units.

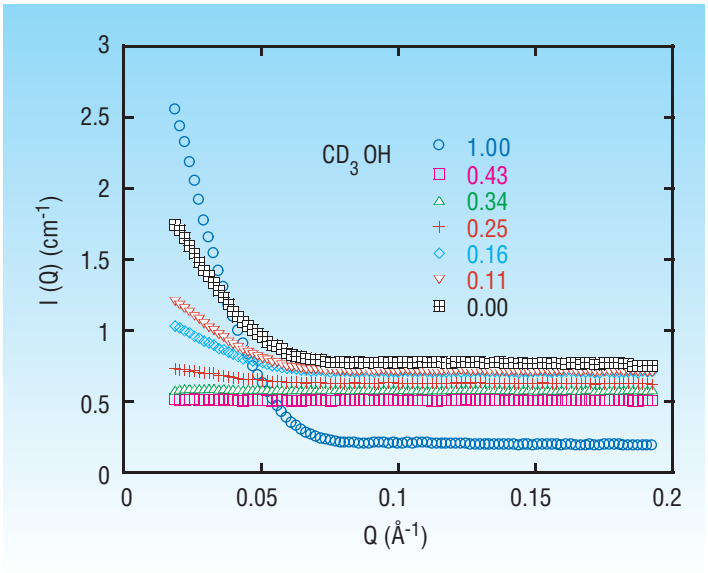

FIGURE 2. SANS from G8 dendrimer in CD_3OH/CH_3OH mixtures.

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SANS was performed at the 30 m facilities at NIST. The spectrometers were operated at a wavelength of $\lambda = 6$ Å, and a wavelength spread of $\Delta\lambda/\lambda = 0.15$.

Figure 2 is a plot of SANS of dendrimer solutions with different CD_3OH contents. The intensity is the strongest in pure CD_3OH, weakens as CH_3OH is added and increases again when pure CH_3OH is used. The coherent scattering intensity varies as $I \approx (b_S - b_D)^2$ where b_D is the contrast of the dendrimer and b_S is the average contrast of the solvent mixture.

Figure 3 is a plot of the square root of the scattered intensity versus solvent composition with the values to the right made negative so that a straight line can be put through all of the data points. The zero intersection is at a mass fraction of 60.5 CH_3OH which was the composition used in the matching experiments.

Figure 4 is a plot of the SANS of the three G7 samples. The circles give the scattering from the high contrast sample, showing strong scattering typical of large spherical dendrimers. The diamonds show the SANS of the same dendrimer, but under match conditions. This sample has no measurable coherent scattering signal, demonstrating that the match conditions have been achieved. The labeled dendrimer SANS is given by the squares. The scattering is weak because only the labeled terminal groups scatter.

A Guinier analysis of the scattering of the high contrast sample gives the radius of gyration (R_g) of the whole dendrimer, and the labeled - contrast match sample gives the R_g of only the terminal groups. The R_g of the whole dendrimer is (34.2 ± 0.2) Å, while the R_g of the terminal groups is (39.3 ± 1.0) Å.

The terminal groups of a seventh generation PAMAM dendrimer are 15 % larger than the average of all of the units. Therefore, the terminal units of a dendrimer are concentrated in the outer shell of a dendrimer.

REFERENCES

[1] T. J. Prosa, B. J. Bauer, E. J. Amis, D. A. Tomalia, R. Scherrenberg, J. Polym. Sci.: Polym. Phys. **35**, 2213, (1997).

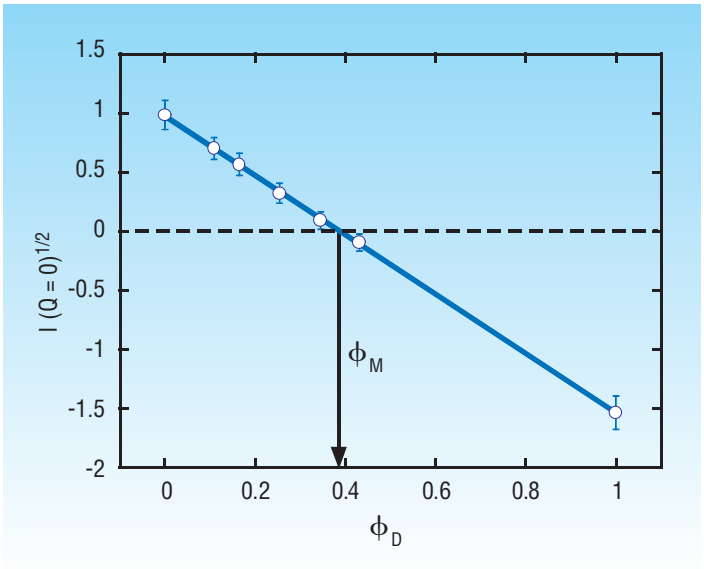

FIGURE 3. Location of the match point.

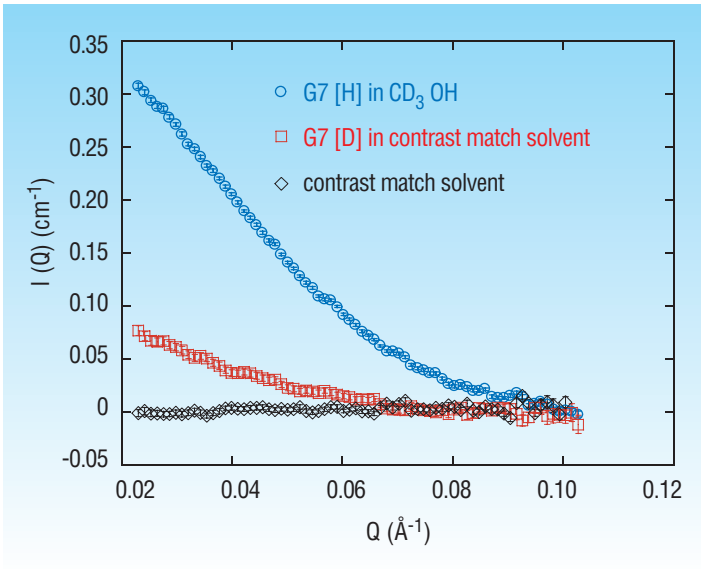

FIGURE 4. SANS of labeled and unlabeled G7 dendrimer in match and high contrast solvents.