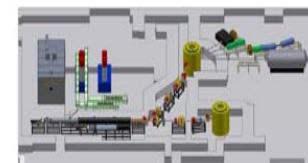


Solvent Penetration in Tripodal Organo-Silicon Dendrimers



Low Energy Neutron Source

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Abstract

Dendrimers, or dendritic polymers are macromolecules that are constructed by linking together molecular units (dendrons) that have one "input" connection and two or more "output" connections [1]. Starting from a central core, a series of macromolecules may be created with sizes that grow geometrically with each "generation." These structures are attractive for a number of potential applications (including catalysis, drug delivery, molecular-scale batteries, etc.). The most common dendrimers are based on 2:1 dendrons such as PAMAM (Poly amido amine). There has recently been some controversy regarding the effect of solvent strength and pH on the structure of PAMAM dendrimers [2,3,4]. In this work we consider the structure of dendrimers based on 3:1 (tripodal) dendrons and investigate the impact of solvent strength on the size of, and solvent penetration into, the dendrimers using Small Angle Neutron Scattering (SANS). A novel method for the analysis of the SANS data is also presented.

Intensity Scaling Analysis

To investigate unambiguously the effect of solvent quality on the structure of these dendrimers, we introduce a novel model-independent method for comparing the data from different solvents. We introduce this "Intensity Scaling Analysis" by considering the standard interpretation of dilute solutions in terms of a form factor $f(q)$ (describing intrinsic structure of isolated molecules) and a structure factor $S(q,v)$ (which describes the concentration-dependent correlations among molecules). In the following, v refers to the volume fraction of the molecule in solution and $\Delta\rho$ refers to the scattering-length density contrast between the solvent and dendrimer.

$$I(q) = S(q,v)F(q, \Delta\rho, v) + B_{s,v}$$

$$= v\Delta\rho^2 S(q,v)f(q) + B_{s,v}$$

At large q , where $S(q,v)$ is equal to 1 the intensity of two experiments performed on the same material in different solvents may be related linearly as follows (if the form factor does not change).

$$I_2 = mI_1 + b$$

$$m = \frac{v_2\Delta\rho_2^2}{v_1\Delta\rho_1^2} \quad b = B_2 - B_1 \left(\frac{v_2\Delta\rho_2^2}{v_1\Delta\rho_1^2} \right)$$

Below we demonstrate that this analysis clearly shows that the structure of the G3 dendrimer does not change when the solvent is changed from d-DCM to d-toluene.

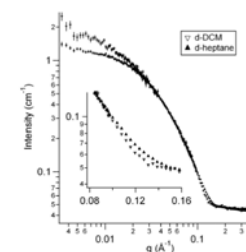


Figure 4: When the same scaling analysis used in figure 3 is applied to data collected in d-heptane and d-DCM the two SANS curves do not fall on top of each other. This unambiguously demonstrates that the structure is different in d-heptane than in d-DCM. In this case we find that the dendrimer's mean diameter shrinks by roughly 10% +/- 3% in d-heptane (since the larger solvent molecules do not penetrate into the dendrimer as effectively as the smaller d-DCM and d-toluene).

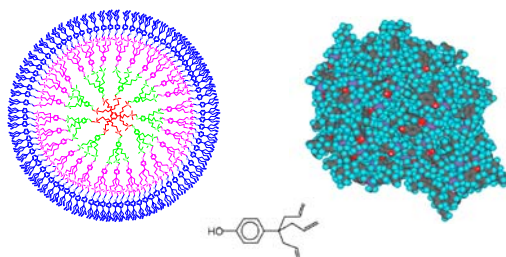


Figure 1: Schematic diagram G3 dendrimer structure in this series. The dendron used to develop the dendrimer is shown in the middle above, where the tripodal nature of the family is clearly seen. On the right we show a space-filling Molecular dynamics model of the G3 structure.

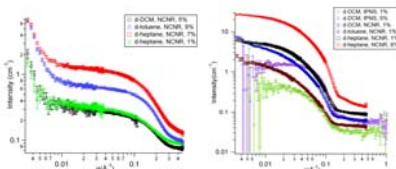


Figure 2: SANS data for the first (left figure) and third (right figure) generation dendrimers in various solvents. Data were collected at either the Intense Pulsed Neutron Source (IPNS) at Argonne or the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD. The upturn in the G1 data at low Q reflects a slight tendency of these materials to aggregate. The dominant influence of the different solvents is to change the overall intensity of the scattering, due to changes in scattering-length density contrast, but we show in the following that changes in the dendrimer structure also arise in some cases. We also note that, particularly in the case of the third generation samples (G3), these scattering curves would be easily measured on the LENS SANS instrument.

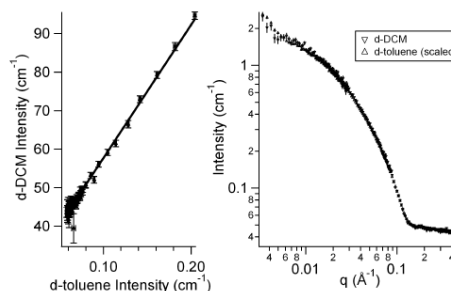


Figure 3: SANS data for third generation dendrimers in d-toluene and d-DCM (dichloromethane) where the former has been scaled by a factor reflecting the different scattering contrasts expected for the two solvents. The left-hand figure shows how accurately the linear intensity relationship described above works for this case. The extent of overlap between the two curves seen over the full range of q in the right-hand figure unambiguously demonstrates that the structure of the dendrimer does not change significantly upon changing the solvent from d-DCM to d-toluene.

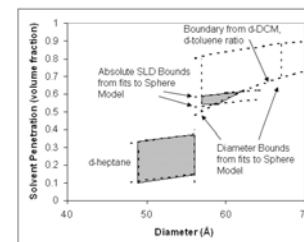


Figure 5: Although models of the scattering which assume uniform spheres do not accurately describe the scattering data for these materials, they can be used to set rough boundaries on the size of the dendrimers and the SLD contrast between the dendrimers and the solvent. Such modeling indicates that the SLD contrast is less than expected if one assumes the solvent to be fully excluded from the interior of the dendrimer. By assuming this reduction is due to solvent penetration, we are able to estimate the fraction of the dendrimer volume "filled" by the solvent. Note that the fit parameters from figure 3 provide further constraints on this quantity. It is clear from this analysis that both the d-DCM and d-toluene fill a larger fraction of the dendrimer volume than the d-heptane, a likely cause of the size difference noted above.

Conclusions

A novel method for the analysis of the SANS data is also presented. Using this method we demonstrate that the structure of the G3 tripodal dendrimer is identical in d-DCM and d-toluene solvents, but that the macromolecular structure changes when the molecule is suspended in d-heptane.

Comparison of the SLD contrasts indicate that d-heptane penetrates into the dendrimer to a smaller degree than does either d-DCM or d-toluene which is likely the cause of the contraction of the dendrimer in d-heptane.

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The Low Energy Neutron Source at the Indiana University Cyclotron Facility is funded by:

