MOLECULARLY DISPERSED DENDRIMERS
IN A POLYMERIC MATRIX

Barry J. Bauer , Ty J. Prosa[†], Da-Wei Liu, Catheryn L. Jackson, Donald A. Tomalia[*], and Eric J. Amis

National Institute of Standards and Technology
Polymers Division, Gaithersburg, MD 20899

[†]Presently: Kutztown University
Department of Physical Science
Kutztown, PA 19530

[*]Michigan Molecular Institute
Midland, MI 48640

Introduction

Dendrimers represent a new class of macromolecules developed in recent years [1]. They are synthesized in a stepwise manner, with each set of two reactions producing a new "generation" which typically doubles the number of branch points, end groups, and molecular mass.   Poly(amido amine) dendrimers (PAMAM) were among the first dendritic structures synthesized and can be produced with high molecular mass. Small angle x-ray scattering (SAXS) and small angle neutron (SANS) scattering show that large PAMAM dendrimers are spherical in shape with a very uniform interior and a rather sharp interface [2]. The interior of a dendrimer, although densely packed with dendrimer units, has considerable room for solvent molecules as well as "guest" molecules, e.g. solvated molecules [3]. It has been shown that dendrimers can disperse molecules in a solvent in a way similar to micellar structures.

Depending on the solvent and ionic conditions, dendrimers can form a regular array, giving a lattice-like structure in solution [4]. This nanoscopic structure, however, is in dynamic equilibrium, and is not fixed in space or time. It is of great interest to find if dendrimers could similarly be dispersed in a polymeric matrix, forming stable nanoscopic structures.

There have been reports of small dendrimers (M_w < 2000 g/mol) that have miscibility with linear polymers [5], and hyperbranched molecules that are miscible with linear polymers [6]. But there are no reports of large dendrimers that are uniformly dispersed in a polymer. Preliminary reports from our laboratory have shown that miscible blends and interpenetrating polymer networks (IPN) are possible [7].

Experimental

All amounts described in this report are mass fractions. The mass fraction designation is omitted for simplicity. The uncertainties of the values reported here were calculated from the experimental standard deviation, and are plotted in the figures as error bars only when the uncertainty limits are larger than the size of the symbol. The R_g values and uncertainties in methanol are from reference [2]. The values for the IPNs were calculated from the positions of the higher order features and are reported as a relative range of ± 10 % which is typical of such measurements.

PAMAM dendrimers were synthesized by reported methods [1] and were obtained from Dendritech (Michigan Molecular Institute, Michigan) as a solution in methanol [8]. The solutions were diluted with methanol to produce the desired concentration. The IPNs were prepared by dissolving the dendrimers in 2-hydroxyethylmethacrylate (HEMA) containing approximately 1 % ethylene glycol dimethacrylate with AIBN as an initiator. They were polymerized at 35 °C for 72 h and at 70 °C for an additional hour.

The SAXS experiments of solutions were performed at the Polymers Division 10 m SAXS facility at NIST [9]. The SAXS of the IPNS was carried out at the Advanced Polymers Participating Research Team (AP-PRT) beamline X27C (NIST/SUNY Stony Brook/GE/Allied Signal/Montell/Air Force Laboratory) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) [10]. The spectrometers give 2-D data sets, which are corrected for dark current and empty beam contributions. The IPN samples were soaked in aqueous HBr to increase the x-ray contrast. The isotropic scattering in the form I(q) results from circular averaging the data sets around the beam center.

Samples of thickness approximately (60-80) nm were ultramicrotomed at –80 °C, transferred to carbon-coated Cu grids of 200 mesh, and stained with OsO_4 vapors by exposing the grid to a 4 % aqueous solution at room temperature for 1 h. The images were obtained at magnification of 17,000X or less on a Philips 400T model TEM operated at 120 kV using low-dose conditions.

Results and Discussion

The SAXS of G10 dendrimers in solution at 1 % and 26 % and in the IPNs at 1 % and 10 % are shown in figure 1. The uncertainty limits are one standard deviation based on the goodness of the fits of a circular average. None of the curves shows an abrupt increase in intensity at low q. This is an indication that there is no clustering of the dendrimers either in solution or in the IPN.
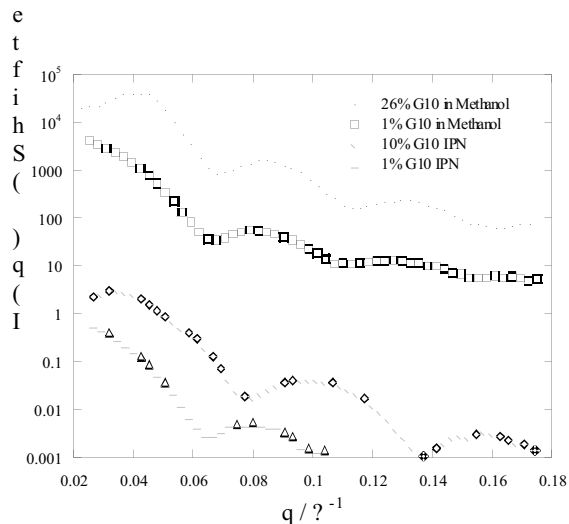

Figure 1. SAXS of PAMAM G10 dendrimer in solution and in an IPN, both low and high concentration.

All curves show higher order features in the scattering, characteristic of their sphere-like shapes [2]. The positions of these features can be used to estimate the size of the dendrimers, even at high concentration [11]. In going from 1 % to 26 % in methanol, a peak at low q (q   0.04 Å^{-1}) appears. This is due to the correlation formed between the positions of the dendrimers. It has been shown that this is due to the tendency of the dendrimers to avoid overlapping. The positions of the higher order features do not shift, however. This suggests that the dendrimer size remains constant in this concentration range. This has been seen before in poly(propylene imine) dendrimers [11].

For the IPNs, the 1 % dendrimer sample is quite similar to that of the solution. The second higher order feature of the IPN is difficult to distinguish due to the weak scattering of this sample. As one goes to a 10 % dendrimer IPN, the higher order features are shifted to higher q. This indicates that the dendrimer size has decreased. This shifting is also present for 10 % and 25 % IPNs of G6 and G11. These concentrations are below the overlap concentration of the dendrimers themselves, suggesting that the presence of polymer instead of solvent promotes the shrinkage of the dendrimers.

Figure 2 is a plot of the R_g of dendrimers in solution and in IPNs for G6 through G11 dendrimers. At 1 % dendrimer concentration, the R_g values for solutions and IPNs are nearly identical, but there is a significant decrease in R_g of the dendrimers at 10 % loading of the IPNs. The dendrimers in IPNs at high concentrations have segment concentrations near that of a bulk PAMAM dendrimer without solvent.

IPNs made by polymerizing a network around linear chains are strongly pushed towards phase separation [12,13]. It has been shown that when the network size becomes smaller than the linear chain size, the linear chains contract in size and eventually form large clusters. The difference may be related to the very compact, spherical size of the dendrimers. They seem to shrink in size, but remain molecularly dispersed in the polymeric matrix.
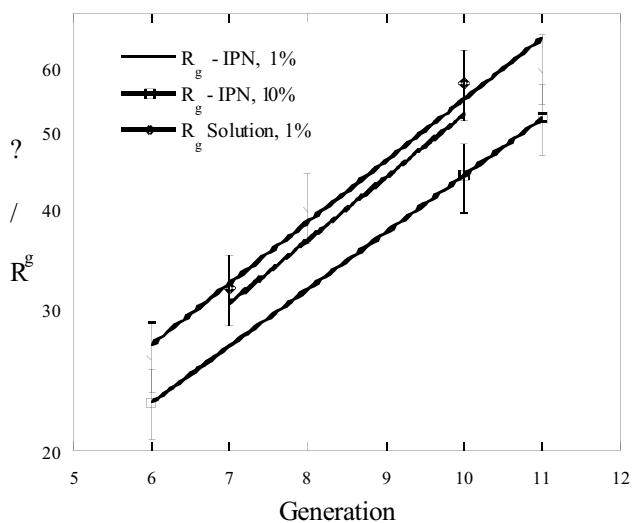
Figure 2. Radius-of-gyration of G10 PAMAM dendrimers in solution and in blends at different concentrations.

Figure 3 is a TEM of an IPN consisting of 10 % PAMAM G11 dendrimer in PHEMA. Individual dendrimers can be seen in the matrix. This microtomed sample is thick enough to have more than one layer of dendrimers visible, causing an overlapping image. Lower magnification images of this sample showed that the large scale dendrimer concentration was uniform, without signs of clustering. This is in agreement with the SAXS results which showed no strong upturn in the scattering at low angle.
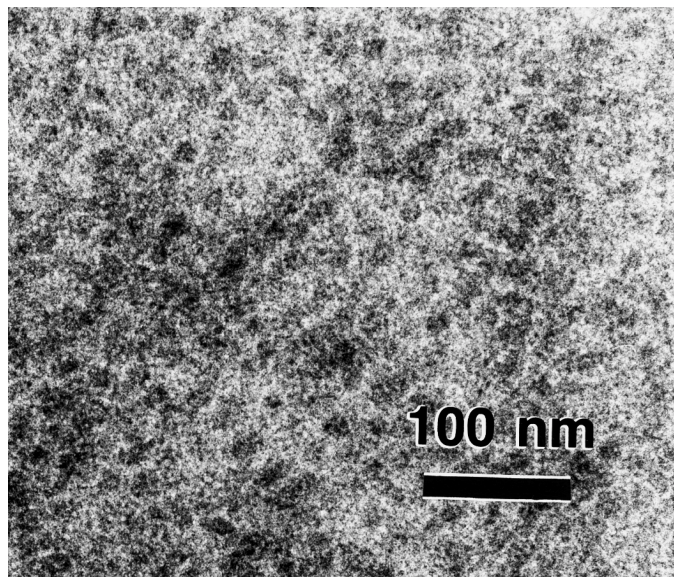

Figure 3. TEM of an IPN of 10 % G11 PAMAM dendrimer in a matrix of PHEA.

Conclusions

PAMAM dendrimers from generation 6 through 11 can be dispersed on a molecular level with IPN techniques. They remain unclustered up to 25 % dendrimer. This is in stark contrast to linear polymers which readily phase separate when made into IPNs. The compact globular structure of the dendrimers may possibly be responsible for this behavior. When placed in sufficient quantity, they shrink in size in the polymeric matrix approaching bulk density. Still, there a truly uniform distribution, with no signs of clustering.

References and Comments
1. Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.
2. Prosa, T. J.; Bauer, B. J.; Amis, E. J.; Tomalia, D. A.; Scherrenberg, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 2913.
3. Bauer, B. J.; Topp, A.; Tomalia, D. A.; Amis, E. J., *American Chemical Society PMSE Proceedings* **1998**, *79*, 312.
4. Ramzi, A.; Scherrenberg, R.; Brackman, J.; Joosten, J.; Mortensen, K. *Macromolecules*, **1998**, 31, 1621.
5. Carr, P. L.; Davies, G. R.; Feast, W. J.; Stainton, N. M.; Ward, I. M., *Polymer*, **1996**, *37*, 2395.
6. Massa, D. J.; Shriner, K. A.; Turner, S. A.; Voit, B. I., *Macromolecules*, **1995**, *28*, 3214.
7. Bauer, B. J.; Topp, A.; Prosa, T. J.; Liu, D.; Jackson, C. J.; Amis, E. J., *SPE ANTEC*, **1998**, *98*, 2065.
8. Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.
9. Barnes, J. D.; Mopsic, F., *Ann. Tech. Conf. SPE Proc.*, **1988**, *12*, 1179.
10. Hsaio, B.;Chu, B.;Yeh, F., *NSLS Newsletter*, **1997**, *July*, 1.
11. Prosa, T. J.;Bauer, B. J.; Topp, A.; Amis, E. J.; Scherrenberg, R., *American Chemical Society PMSE Proceedings* **1998**, *79*, 307.
12. Bauer, B. J.; Briber, R. M., in "Advances in Interpenetrating Polymer Networks Volume IV", pages 45-76, **1994**.
13. Briber, R. M.; Liu, X. D.; Bauer, B. J., *Science*, **1995**, *268*, 395.