NISTIR 6151

Preparation and Characterization of Polymer/Dendrimer Blends
Progress Report 3/31/98

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U.S. DEPARTMENT OF COMMERCE
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U.S. DEPARTMENT OF COMMERCE
William M. Daley, Secretary

TECHNOLOGY ADMINISTRATION
Gary R. Bachula, Acting Under Secretary
for Technology

NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Raymond G. Kammer, Director

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General Information

Throughout this report some conventions will be used when describing uncertainties in measurements. Plots of small angle scattering data have been calculated from circular averaging of two dimensional files. The uncertainties are calculated as the estimated standard deviation of the mean. In cases where the limits are smaller then the plotted symbols, the limits are left out for clarity. Fits of the scattering data are made by a least squares fit of the data giving an average and a standard deviation to the fit, this is true for fit values such as radius of gyration and exponents. Temperatures are given as expected ranges of values based on previous work.

All concentrations are calculated from weighed samples and are reported as mass fractions. Volume fractions are calculated from reported densities reported by the manufacturers. The conventional notation, "molecular weight", has been replaced by "relative molecular mass" in most cases. Rarely, the conventional notation is used to conform to previous publications.

Abbreviations for technical terms appear the first time they occur, except in the references. The abbreviations are ACS, American Chemical Society; PMSE, Polymer Material Science and Engineering; ANTEC, Society of Plastic Engineers Annual Technical Conference; LANSCE, Los Alamos Neutron Science Center; NIST-ERATO, National Institute of Standards and Technology - Exploratory Research for Advanced Technology.

Dendrimer Interpenetrating Polymer Networks

NIST: Barry J. Bauer, Andreas Topp, Ty J. Prosa, Dawei Liu, Catheryn L. Jackson, and Eric J. Amis

Outside Collaborators: Donald Tomalia, MMI

Objectives:

To synthesize and characterize interpenetrating polymer networks (IPNs) containing dendrimers that are molecularly dispersed

Technical Description:

Use IPN techniques to prepare molecularly dispersed moderate to large size poly(amido amine) (PAMAM) dendrimers in a polymeric matrix. Use small angle xray scattering (SAXS) to measure the radius of gyration of dendrimers and the correlations between dendrimers. Use transmission electron microscopy (TEM) to measure dendrimer size and dispersion.

Summary Report:

The IPNs were prepared by dissolving the dendrimers in 2-hydroxyethylmethacrylate (HEMA) containing a mass fraction of approximately 1 % ethylene glycol dimethacrylate with azo-bis isobutyronitrile as an initiator. They were polymerized at 35 °C for 72 hours and at 70 °C for an additional hour. The nominal temperature stability was ± 1 °C for both the synthesis and later scattering studies. The SAXS experiments were performed on IPNs that were soaked in HBr. The HBr should preferentially go to the amine groups in the dendrimer, changing the electron density enough to give sufficient x-ray contrast.

Figure 1 shows the SAXS results of an IPN with 10 % by mass G11 PAMAM dendrimer as a Guinier plot. The low q scattering gives the radius of gyration of (60 ± 6) Å calculated as described earlier. The shoulder at higher q is due to higher order features in the scattering of sphere-like objects. This demonstrates that the dendrimers are molecularly dispersed in the poly(2-hydroxyethylmethacrylate) matrix. Calculation of the standard deviation of the scattering data is described previously.

Figure 2 is a TEM of samples of thickness approximately (60 to 80) nm that 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 0.04 g/g 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. The individual dendrimers can be seen and have a size and shape consistent with the SAXS results.

There is no sign of large aggregates, indicating that the dendrimers are molecularly dispersed.

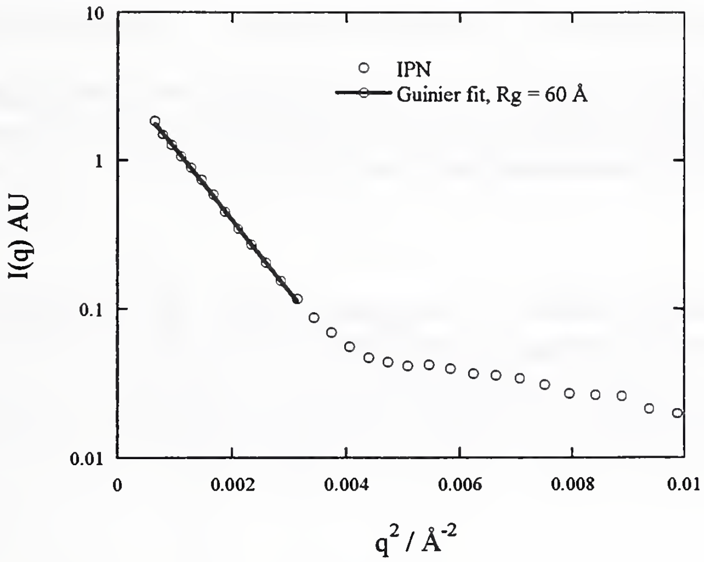

Figure 1. SAXS of an IPN with 10 % of a G11 dendrimer incorporated in a Guinier plot. The low q scattering gives the radius of gyration of (60 ± 6) Å. The shoulder at higher q is due to higher order features in the scattering of sphere-like objects.

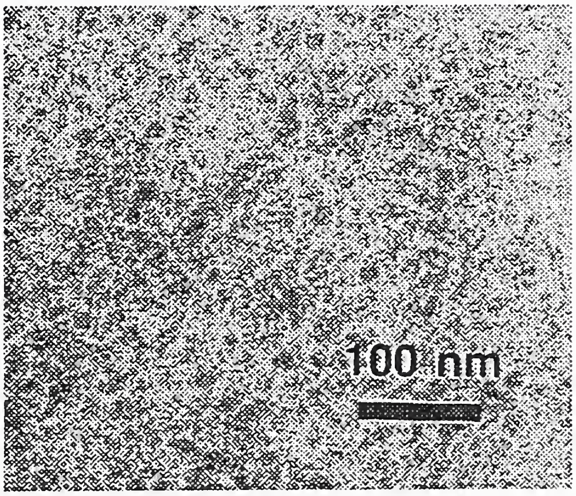

Figure 2 is a TEM of the same sample. The individual dendrimers can be easily seen in the matrix. The thickness of the film causes several layers of dendrimers to be seen. There is no sign of large aggregates, the dendrimers appear to be molecularly dispersed.

Future Plans:

To synthesize materials with a variety of available dendrimers and to continue SAXS and TEM to characterize them.

Publications:

"Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks", Barry J. Bauer, Andreas Topp, Ty J. Prosa, Da-Wei Liu, Catheryn L. Jackson, and Eric J. Amis, ANTEC '98 Proceedings, April 1998.

Presentations:

"Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks", Barry J. Bauer, ANTEC '98, April 1998.

Ternary Dendrimer Blends

NIST: Barry J. Bauer, Andreas Topp, Dawei Liu, Brett Ermi, Kathleen Barnes, Alan I. Nakatani, and Eric J. Amis

Outside Collaborators: Aissa Ramzi, DSM, Rolf Scherrenberg, DSM

Objectives:

To measure the effect of hydrophobically modified dendrimers on the miscibility of a polymer blend.

Technical Description:

Ternary blends of polystyrene-d (PSD) and poly(vinylmethyl ether) PVME are modified by incorporation of between 1 and 10 % dendrimer. SANS is used to locate the phase boundaries and a Rheometer is used to measure the dynamic response. Atomic Force Microscopy (AFM) is used to follow the kinetics of phase separation of a thin film.

Summary:

A hydrophobically modified dendrimer was synthesized from a G5 poly(propylene imine) (PPI) dendrimer with $-NH_2$ terminal groups by addition of 80 mass % excess 1,2-epoxy octane in vacuum at 140°C for 8 h. The excess 1,2-epoxy octane was distilled off in vacuum at 95°C. Blends were made with PSD and PVME by solution in toluene, evaporation of the solvent, drying in vacuum, and pressing into disks.

Figure 3 shows the SANS from blends with and without added dendrimer. At 120 °C all samples have scattering typical of miscible blends. At 130 °C, however, the scattering of the sample without dendrimer has changed significantly, now having a shape typical of a blend that has undergone phase separation. Under these conditions, the presence of the dendrimer has given the sample stability.

Using a controlled stress rheometer we monitor the viscoelastic parameters of the blends as a function of temperature, dendrimer content and dendrimer type (by chemical modification) Preliminary results show that the addition of 1 mass % chemically modified dendrimer (generation 5) show an unexpectedly large increase in dynamic viscosity over that of the pure blend as shown in Figure 4. This is in contrast to the relatively low increase in viscosity seen with the addition of silica type fillers to the blend. We also note that the temperature of phase separation in the blend seems unaffected by the dendrimer addition in this blend.

Figure 5 displays two AFM topographical images of phase separating thin film blends (L ~ 800 Å, $\phi_{PS} = 0.30$) of PS and PVME after annealing for 10 min. and at 160 °C, which is in the two phase region of the phase diagram. The addition of a mass fraction of 1 %

G5 modified dendrimer (figure 6) to the blend has a dramatic effect on the observed phase separated morphology. The phase separation is much more rapid with the incorporation of the dendrimer.

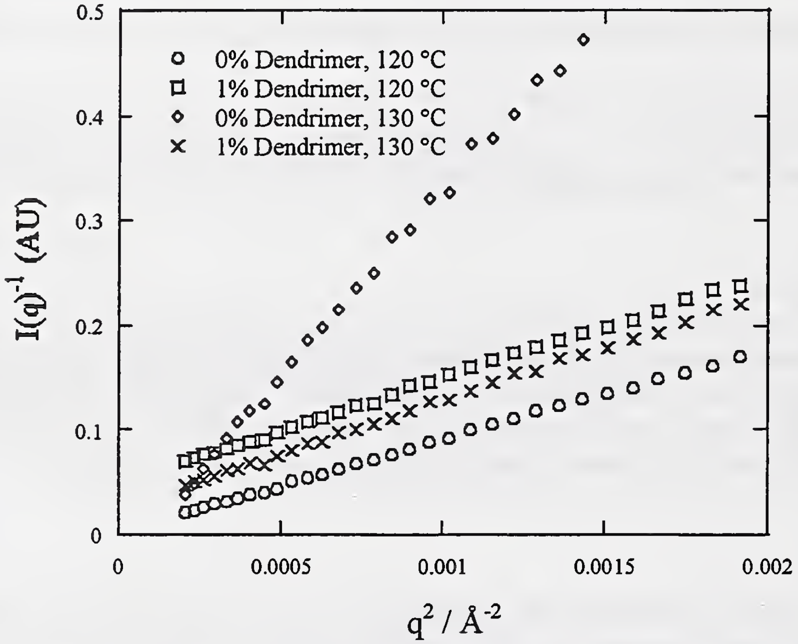

Figure 3. SANS from 3:7 PSD/PVME blends that contain an amount of (0 and 1) mass % PPI-C_8 dendrimer

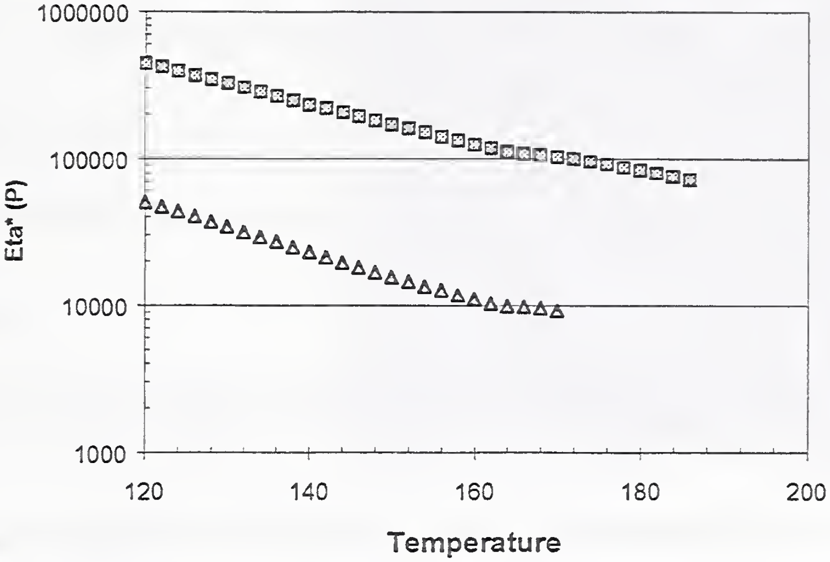

Figure 4. Viscosity of a binary PSD/PVME blend (triangles) and a PSD/PVME blend with a mass fraction of 1 % dendrimer addition (squares) at a frequency of 0.1 rad/s while increasing the temperature from 120 °C at a rate of 1 °C/min.

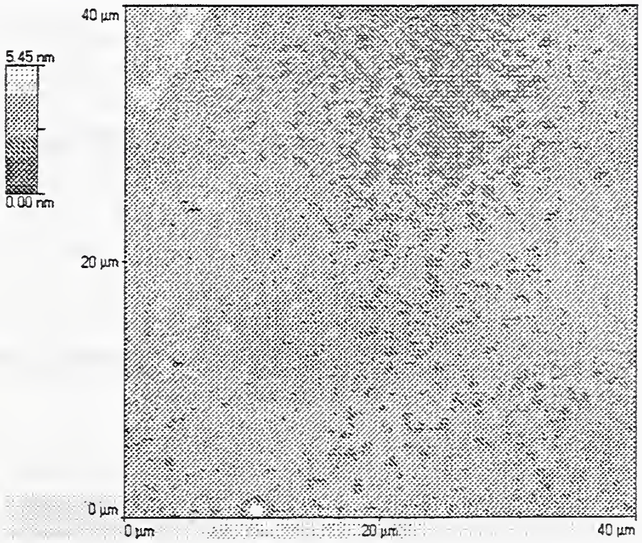

Figure 5. PS/PVME blend annealed at 160 °C for 10 min.

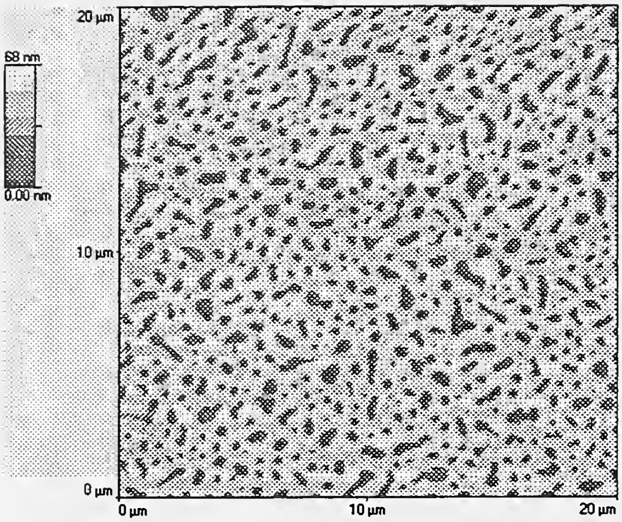

Figure 6. PS/PVME/Dendrimer blend annealed at 160 °C for 10 min.

Future Plans:

To measure the domain size by TEM and to compare the effects filler particles of similar size on the phase diagrams. To measure the kinetics of phase separation by time resolved temperature jump light scattering.

Publications:

"Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks", Barry J. Bauer, Andreas Topp, Ty J. Prosa, Da-Wei Liu, Catheryn L. Jackson, and Eric J. Amis, ANTEC '98 Proceedings, April 1998.

Presentations:

"Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks", Barry J. Bauer, ANTEC '98, April 1998.

SANS Study of Fatty Acid Modified Dendrimers

NIST: Barry J. Bauer, Eric J. Amis

Outside Collaborators: Aissa Ramzi, DSM Rolf Scherrenberg, DSM, Jacques Joosten, DSM

Objectives:

To evaluate the morphology of chemically modified dendrimers in the bulk and in solution. To determine if these dendrimers form a miscible blend with a variety of polyolefins.

Technical Description:

Use SANS to measure the type and size of the morphology in the bulk. Contrast matching techniques are used to measure the single dendrimer scattering in the bulk and in solution. Power law scattering from dendrimer/polyolefin blends determines if there if miscibility.

Summary Report:

Divergent dendrimers are formed by a stepwise addition of generations to a core, most commonly doubling the molecular weight, branch points and terminal groups in each step. The terminal groups are sites for further chemical reactions, and recently, hydrophylic dendrimers have been reacted with fatty acids to form hydrophylic-hydrophobic structures.

Figure 7 is a plot of the SANS results for the samples at 30 °C They show multiple peaks in the scattering, indicating microphase separation. The features were strongest for the G5 and G3 samples and more sharply defined for the covalent than for the ionic. In well annealed samples, the peak positions have a ratio of 1:2:3 which is characteristic of lamellar microstructure.

As the temperature is increased, there is a phase transition at about 60 °C for the ionic samples. The transition temperatures are approximately 110 °C for the G1 covalent and 90 °C for the G3 and G5. Figure 8 is a plot of the scattering from a G5 covalent dendrimer at 100 °C. In one case pure deuterated fatty acid dendrimer is used and in the other a mixture of H and D at the match point for the dendrimer core is used. In both cases the dendrimer core is hydrogenated. In the matched case the scattering no longer has the prominent peak that is present in the unmatched case. The pure deuterated dendrimer no longer shows multiple peaks, with only one “correlation hole” peak showing incipient ordering. In the match case, single dendrimer scattering can give the sizes of the fatty acid portion of the dendrimers. A Guinier plot of the scattering gives $R_g = (17.8 \pm 0.9)$ Å for G3 and $R_g = (23.4 \pm 1.1)$ Å for G5. The shoulder at higher q shows that the fatty acids form a hollow shell around the dendrimer.

Figure 9 is a plot of the SANS from blends of the dendrimers with various polyolefins. The limiting power law of -4 indicates that the samples are phase separated and not miscible. Generations G1, G3, and G5 were all immiscible and annealing did not change the miscibility. The low q scattering suggests that the phase size is large, greater than 500 Å in all cases.

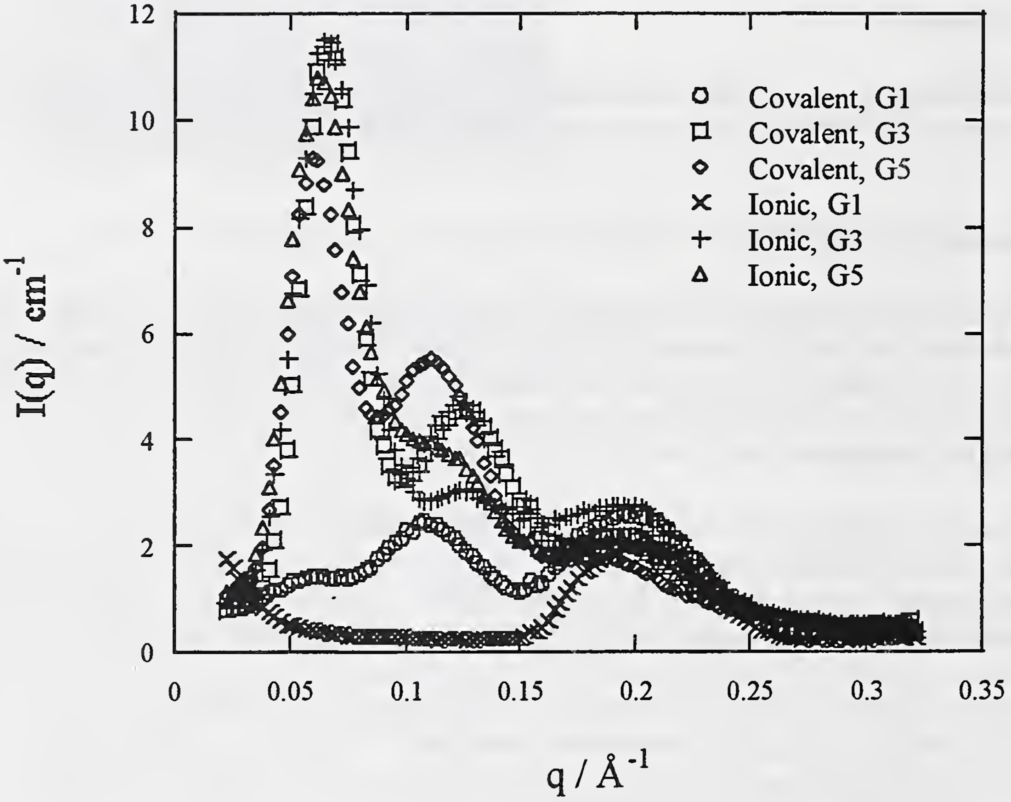

Figure 7. SANS of ionic and covalent hydrophobically modified dendrimers at 30 °C

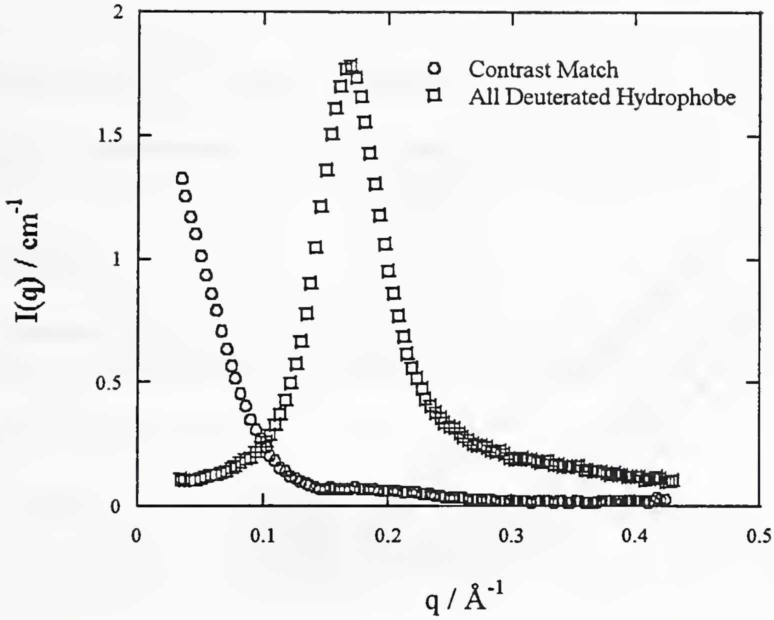

Figure 8. SANS of G5 covalent hydrophobically modified dendrimers at 100 °C under matched and unmatched conditions.

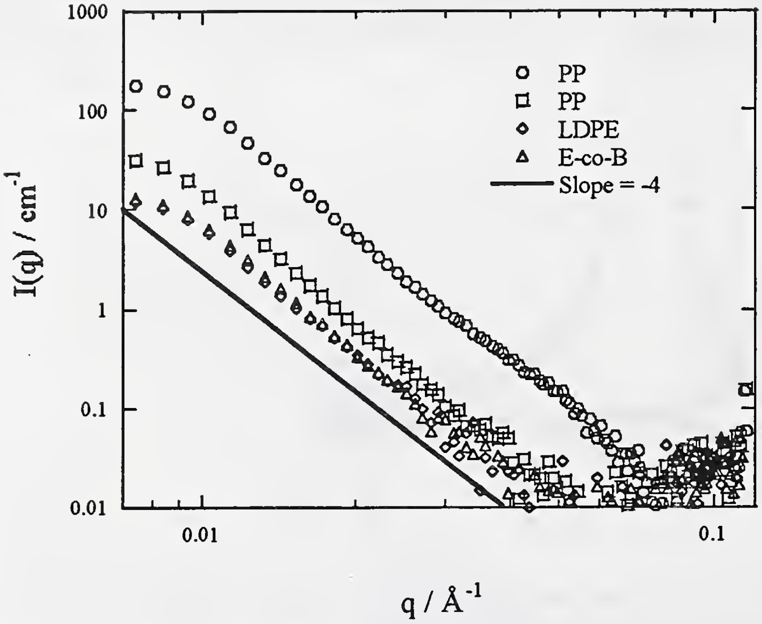

Figure 9. SANS of blends of polyolefins with fatty acid modified dendrimers. PP, Polypropylene, (PP); low density polyethylene, (LDPE); ethylene- butylene random copolymer (E-co-B)..

Future Plans:

To try to form monolayers on surfaces and characterize them by neutron and x-ray reflectivity. Dendrimers with other surface chemistries will be used to find miscible blends.

Publications:

“SANS Study of Fatty Acid Modified Dendrimers”, Aissa Ramzi, Barry J. Bauer, Rolf Scherrenberg, Jacques Joosten, and Eric J. Amis, ACS PMSE Preprints, 79, August 1998.

Presentations:

“SANS Study of Fatty Acid Modified Dendrimers”, Aissa Ramzi, Fall 1998 ACS National Meeting, August 1998.

SANS of Polystyrene Hypergrafts

NIST: Andreas Topp, Barry J. Bauer, Eric J. Amis,

Outside Collaborators: Mario Gauthier, U Waterloo, S. Chio, U Md, Robert M. Briber, U. Md.

Objectives:

To measure the size and segment density distribution of polystyrene (PS) hypergrafts in solution and in blends, and to compare them to dendrimers

Technical Description:

Use SANS to measure the radius of gyration of PS hypergrafts generations G0 to G3 in cyclohexane-d12 and in blends with linear PSD and to look for higher order features in the scattering indicative of uniformity.

Summary Report:

Hypergraft polymers are made by taking linear polystyrene and placing chloromethyl groups on the aromatic rings. "Living" anionic PS is then recated with the chloromethylated PS, grafting one PS chain for every two or three PS repeat units. This forms the "zeroth" generation, G0. Further reactions produce hypergraft polymers up to G3. The largest have R_g values up to 225 Å and relative molecular mass up to 2.8 X 10^7 g/mol. These highly grafted polymers have an internal structure with branching densities comparable to dendrimers, but have much higher relative molecular masses generated in many fewer synthetic steps.

Figure 10 is the SANS results for a G3 hypergraft in cyclohexane-d12 above and below the phase separation temperature, and in blends with linear PSD. The solution scattering has low q scattering that con be fit with a Guinier plot giving the R_g. The blend has a similar scattering profile, which also can be used to measure R_g. The R_g in solution is the largest. Upon phase separation, the Rg becomes smaller, and a low q peak forms indicating a correlated dendrimer-dendrimer distance in the concentrated phase. In the blend, the Rg is still smaller, indicating a collapse.

Figure 11 is a plot of the R_g of hypergraft generations G0 through G3 versus molecular weight in cyclohexane. The power law in this region is 0.22 ± 0.02 which can be compared to the lines labeled "Linear Chain" which is data from linear chains in cyclohexame and "Uniform Sphere" which is calculated for pure PS spheres with a density of 1.04 g cm^{-3}. The R_g is smaller than linear polymers of the same molecular weight, and the G3 hypergraft approached the bulk density. It is clear that hypergraft molecules can have high densities like dendrimers, but with larger molecular weights and R_g.

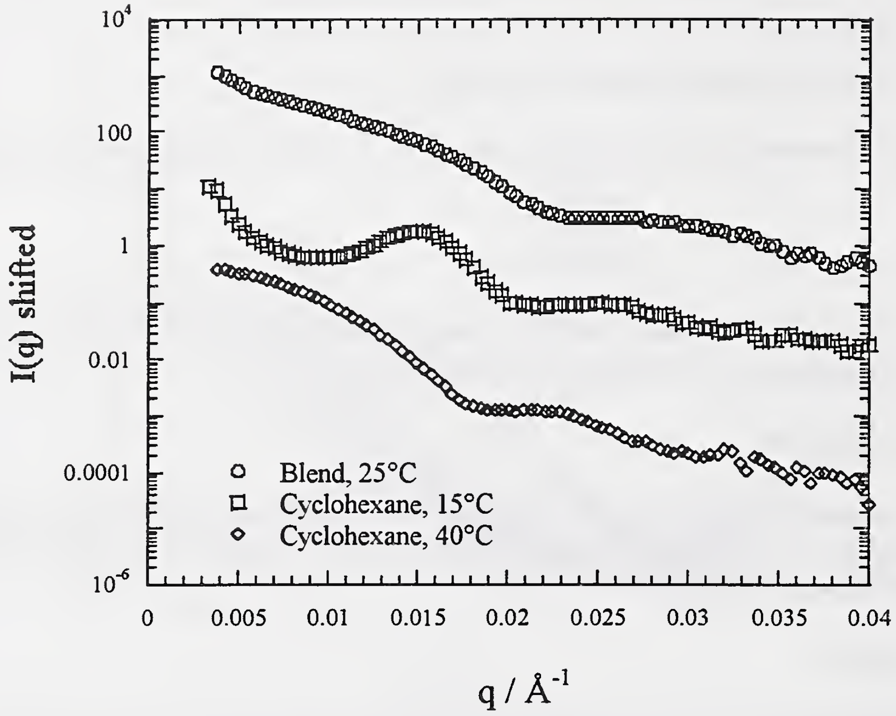

Figure 10. SANS of hypergraft G3 in cyclohexane-d12 solution and in blends with linear PSD. All results are for mass fractions < 1 %.

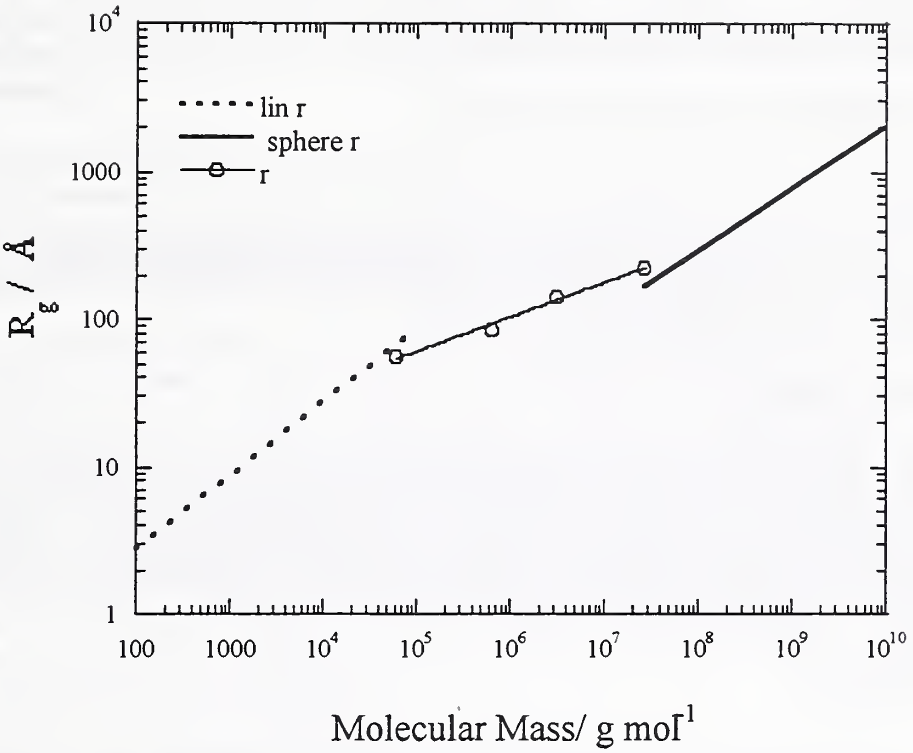

Figure 11. R_g of hypergraft G0 through G3 in cyclohexane-d12 along with linear polystyrene in cyclohexane and bulk PS.

Future Plans:

To make blends with poly(vinyl methylether)-d3 and to use SANS to generate phase diagrams that will define the effects of branching on miscibility.

Publications:

None

Presentations:

"Small Angle Neutron Scattering of Solutions of Arborescent Graft Polymers", Sangwook Choi, LANSCE User Meeting, August 1997.

"Small Angle Neutron Scattering of Solutions of Arborescent Graft Polymers", Sangwook Choi, APS Meeting, March, 1998.

High Resolution SAXS Studies of PAMAM Dendrimers

NIST: Ty J. Prosa, Barry J. Bauer, Eric J. Amis

Outside Collaborators: Donald Tomalia (MMI)

Objectives:

To extract information about intramolecular dendrimer composition from SAXS in order to better assess potential applications. This includes dendrimer size, shape, size dispersity and distribution of internal segment density profiles.

Technical Description:

SAXS from dilute solutions of various dendrimers in methanol were investigated at the newly commissioned National Synchrotron Light Source's Advanced Polymers-Participating Research Team (AP-PRT) beamline at the Brookhaven National Laboratory. The combination of high x-ray flux and improved resolution has allowed for experimental data suitable for detailed quantitative analysis.

Summary Report:

SAXS from dilute solutions of dendrimers exhibit scattering features that depend primarily on the intramolecular structure within the individual dendrimers. Previous SAXS studies from this laboratory reported on scattering data of sufficient quality to measure R_g and to suggest that at large generations, dendrimers exhibit additional features consistent with a sphere-like molecular organization. However, these measurements were not of sufficient quality to allow one to distinguish between competing models with varying segment density distributions.

PAMAM dendrimers of generation 3 - 10 (G3 - G10) were prepared as solutions in methanol, mass fraction = 1 % dendrimer, and data was collected at the AP-PRT beamline. We were able to obtain measurements of sufficient quality to identify three basic scattering characteristics of the dendrimer molecules:

The absence or presence of secondary scattering features is suggestive of an evolving intramolecular structure. The star-like organization of the G3 dendrimer is shown in figure 12. This profile is compared to a model that mimics the molecular architecture within these dendrimers. It includes chains with ideal flexibility that exhibit Gaussian chain statistics. While this model is in qualitative agreement with the overall shape of scattering curve, there are significant differences which disqualify it as a good model for describing the internal structure of this molecule. The lack of identifiable secondary scattering features is a consistent feature present in molecules with a star-like architecture. A progression away from star-like behavior is observed by a growth in both the number and quality of secondary features as seen in the G4 - G9 dendrimers. For G10 dendrimers, the quantity and quality of secondary features resembles scattering from a sphere-like entity (see the Iq^4 plot of figure 13). This progression of features as a function of generation suggest a star-like molecular organization for low generation dendrimers that slowly evolves to a more compact uniform sphere-like organization for the larger dendrimer generations.

The evolution of scattering power-law behavior from q^{-2} for G3 to q^{-4} for G10 is reflective of the sharpness of the boundary between particle and the solvent components of the solution. Again, this scattering progression is consistent with an evolution from a star-like to a sphere-like molecular organization as a function of generation.

For the larger generation dendrimers ($G > 8$), the dendrimer molecules exhibit scattering profiles that possess a large number of resolvable secondary features. By comparing to models consisting of either a distribution of uniform molecular spheres or a single ellipsoidally shaped molecule, one can estimate the amount of polydispersity in molecular size and shape. Figure 13 shows a fit to the PAMAM G10 data for a distribution of spheres with an average radius = 69.5 Å and a standard deviation of the distribution = 4.2 Å. The effects of polydispersity in particle size can be discerned by comparing the fit of the data with a model that consists of a single ellipsoidally shaped particle with a major axis = 72.3 Å and a minor axis = 61.5 Å. These fits are comparable and suggest that the estimated spherical polydispersity in particle size is likely overestimated when any polydispersity in shape is present.

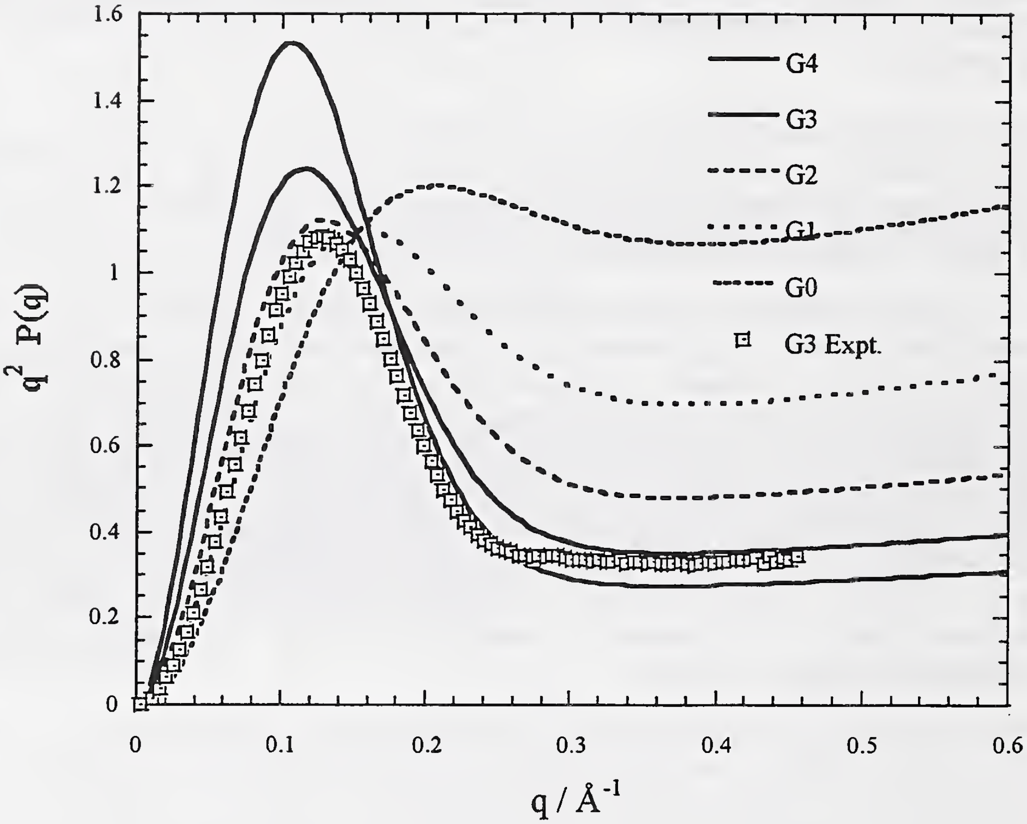

Figure 12. Kratkey plot of PAMAM G3 compared to a branched chain model with Gaussian behavior of the subchains called the ``soft sphere'' model.

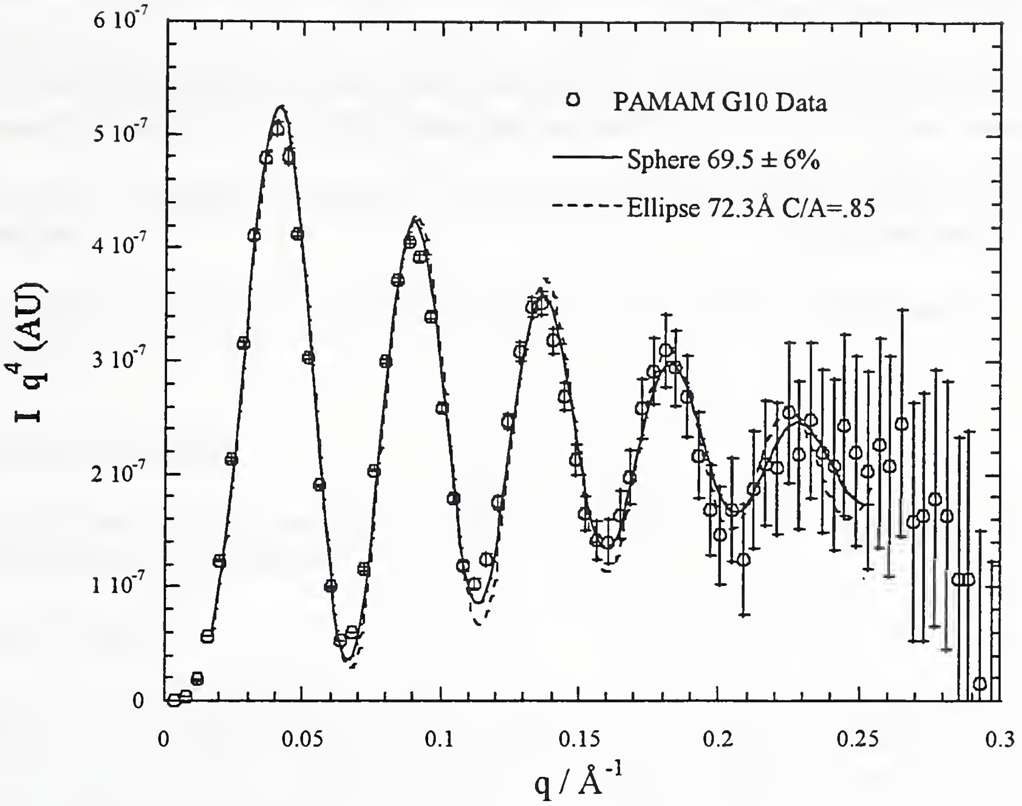

Figure 13. PAMAM G10 SAXS fit by a model consisting of a distribution of uniform spheres and a model consisting of a single ellipsoidally shaped particle.

Future Plans:

To continue to characterize dendrimers from various sources as to their size and homogeneity.

Publications:

"A SAXS Study of the Internal Structure of Dendritic Polymer Systems", Ty J. Prosa, Barry J. Bauer, Eric J. Amis, Donald A. Tomalia, Rolf Scherrenberg, *JPS Physics*, **35**, 2913, (1997).

Presentations:

"A SAXS Study of Correlations within Dendritic Polymer Systems" APS Meeting, March 1997.

“A SAXS Study of the Internal Structure of Dendritic Polymer Systems”, Ty J. Prosa, NIST-ERATO Meeting, June 1997.

“SANS and SAXS Investigations of the Internal Structure of Dendritic Molecules”, B. J. Bauer, Fall 1997 ACS National Meeting, September 1997.

"SAXS Analysis of Dilute Dendrimer Solutions: From Stars to Spheres", Ty Prosa, APS Meeting, March 1998.

Interactions of Dendrimers at High Concentration

NIST: Andreas Topp, Barry J. Bauer, Ty J. Prosa, Eric J. Amis,

Outside Collaborators: Rolf Scherrenberg, DSM

Objectives:

To measure the effect of crowding on the size and amount of interpenetration of dendrimers

Technical Description:

Use SANS and SAXS to measure the changes in dendrimer size and interpenetration by monitoring peak size and shape.

Summary Report:

Solutions of the poly(propylene imine) dendrimers $DAB(PA)_{32}$ and $DAB(PA)_{64}$ in methanol are investigated with SANS experiments over the range of dendrimer mass fraction $0.01 \leq x \leq 0.80$. Scattering functions from dilute solution are extrapolated to $x \to 0$ to yield the single particle scattering function $P(q)$, which is used to calculate the structure factor $S(q)$ of the dendrimer solutions. The values for the radius of gyration of the dendrimers in dilute solution are $R_g^+ (DAB(PA)_{32}) = (12.4 \pm 0.2)$ Å and $R_g^+ (DAB(PA)_{64}) = (15.6 \pm 0.2)$ Å. The segment density of the two generations in dilute solution, ρ^+, has the value $\rho^+ = (0.35 \pm 0.03)$ g cm^{-3}, leaving a large fraction of the dendrimers average volume accessible for solvent molecules. We define the 'dilute solution regime' for dendrimers to reach to a concentration at which the dendrimer volume fraction, ϕ^+, first equals the value $\phi^+ = 0.64$ (ϕ^+ calculated from R_g^+). At this concentration, the spatial arrangement of the dendrimers can be described as a random close packing.

For higher concentrations, the experimental scattering functions appear to be self-similar up to a mass fraction of $x \approx 0.60$, indicating that the spatial arrangement is unchanged in this concentration range. Figure 14 shows that in this concentration range, the normalized shape of the scattering is constant. The observations are consistent with a proposed model for highly concentrated dendrimer solutions, which assumes that the individual dendrimers collapse to maintain a volume fraction of $\phi \approx 0.64$, which is the volume fraction of random close packing for hard sphere systems. The collapse is followed experimentally by observing the average dendrimer-dendrimer distance up to $x = 0.60$.

Preliminary SAXS data give further evidence of the dendrimer collapse. Figure 15 shows that a higher order feature (second peak) can be resolved. The position of this feature defines the radius of the dendrimer described as a sphere. The fact that the feature moves to higher q shows that the dendrimers are decreasing in size as the concentration increases.

The absolute peak intensities decreases with increased concentration, however. This is best described as a certain amount of interpenetration of the dendrimers.

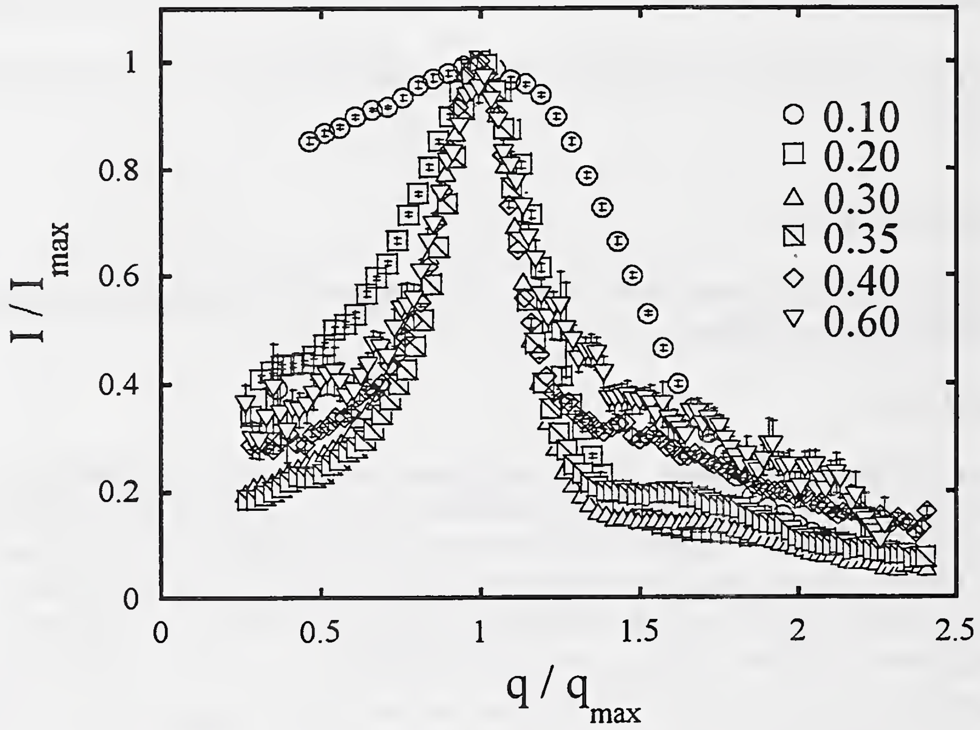

Figure 14. Normalized plot of SANS scattering from a G5 dendrimer in the intermediate concentration range.

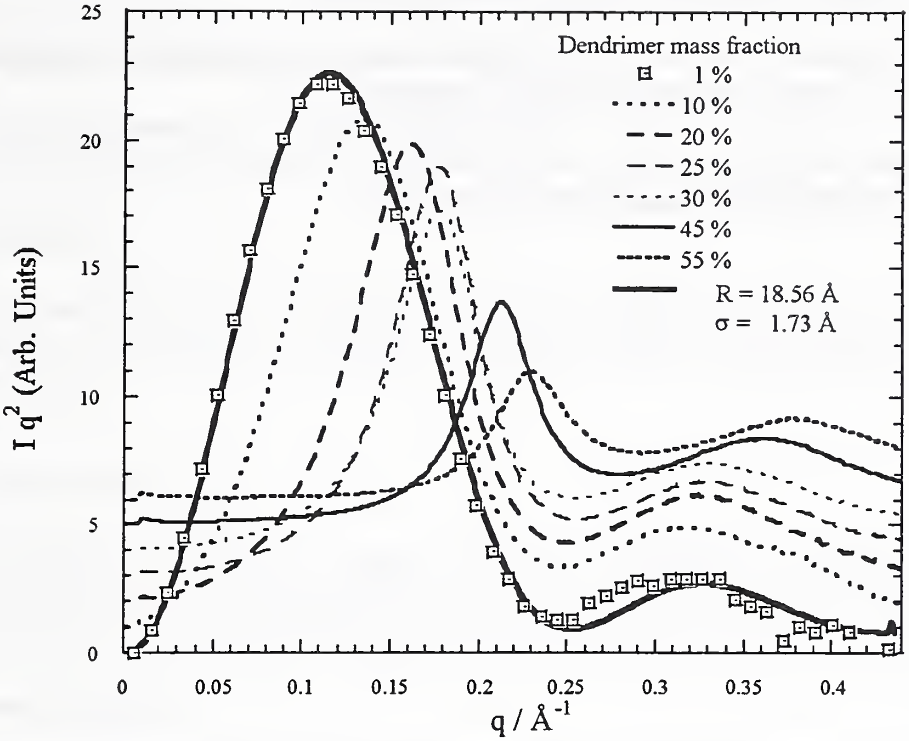

Figure 15. SAXS scattering from a G5 dendrimer in the intermediate concentration range.

Future Plans:

A paper has been written and will be submitted for publication soon. Fully deuterated dendrimers will be obtained to directly measure the size and segment density distribution in concentrated solution and in the bulk.

Publications:

"Small Angle Neutron Scattering from Dilute and Concentrated DAB(PA)$_x$ Dendrimer Solutions", A Topp, B.J. Bauer, E.J. Amis, ACS PMSE Preprints, **1997**, *77*, 82.

"Size Changes and Interpenetration within Concentrated Dendrimer Solutions", Ty J. Prosa, Barry J Bauer, Andreas Topp, Eric J. Amis and Rolf Scherrenberg. ACS PMSE Preprints, Fall 1998.

Presentations:

“Small Angle Neutron Scattering from Dilute and Concentrated DAB(PA)$_x$ Dendrimer Solutions”, Andreas Topp, NIST-ERATO Meeting, June 1997.

“Small Angle Neutron Scattering from Dilute and Concentrated DAB(PA)x Dendrimer Solutions“, A. Topp, ACS National Meeting, September 1997.

“Size Changes and Interpenetration within Concentrated Dendrimer Solutions”, Ty J. Prosa, Fall 1997 Fall ACS National Meeting, August 1998.

The Effect of Solvent Quality on Dendrimer Size

NIST: Andreas Topp, Barry J. Bauer, Eric J. Amis,

Outside Collaborators: Donald Tomalia, MMI

Objectives:

To measure the effect of solvent strength of the radius of gyration of dendrimers in solution. To evaluate the variation in dendrimer size for possible applications as size standards.

Technical Description:

Use SANS to measure the radius of gyration of moderate to large size PAMAM dendrimers in solvents ranging from very good (H_2O) to very poor (n-butanol) and in mixed solvent pairs (methanol/acetone) and in varying acid and salt concentrations in H_2O.

Summary Report:

The average dimensions of PAMAM dendrimers of generation numbers G5 and G8 are measured by small angle neutron scattering (SANS) as a function of solvents of different quality, of the composition of mixtures of a good solvent and a non-solvent, and of temperature. The radius of gyration of the G8 dendrimer, R_g, decreases for the series of solvents $D(CD_2)_mOD$ (with $m = 0, 1, 2, 4$) by approximately 10 % with decreasing solvent quality as is shown in figure 16.

The amount of swelling of PAMAM dendrimers, as reflected by R_g, is not influenced by the composition of mixtures of methyl alcohol/acetone in the full range of solubility of the dendrimers. In the temperature range $-10\ °C \leq T \leq 50\ °C$, the dimensions of the G8 and G5 dendrimer are constant within $\approx$ 5 % of the R_g value as is shown in figure 17. The average segment densities have been calculated for G5 and G8 under various solvent conditions, with the dendrimers containing volume fractions of solvent between 0.43 and 0.60.

To determine whether the volume of dendrimers in aqueous solutions is strongly affected by changes in solution conditions, we measured the SANS from G8 PAMAM dendrimers in D_2O. Since PAMAM dendrimers contain both primary and tertiary amines, their charged density can be manipulated by varying the solution pH. The stoichiometric ratios of added HCl and NaOH to the total number of terminal groups of the dendrimer are noted α and β, respectively. Values of α greater than 1 correspond to a partial ionization of the tertiary amines of the dendrimer interior. Once charged, dendrimer interactions are screened upon addition of salt. For all conditions studied, we find that the scattered intensity can be fitted with the form factor of a sphere with a radius of gyration, $R_g = 42$ Å ± 5 % R_g. Thus we conclude that the size of the dendrimers is only slightly sensitive to the charge density of the molecules or ionic strength of the solvent, see figure 18.

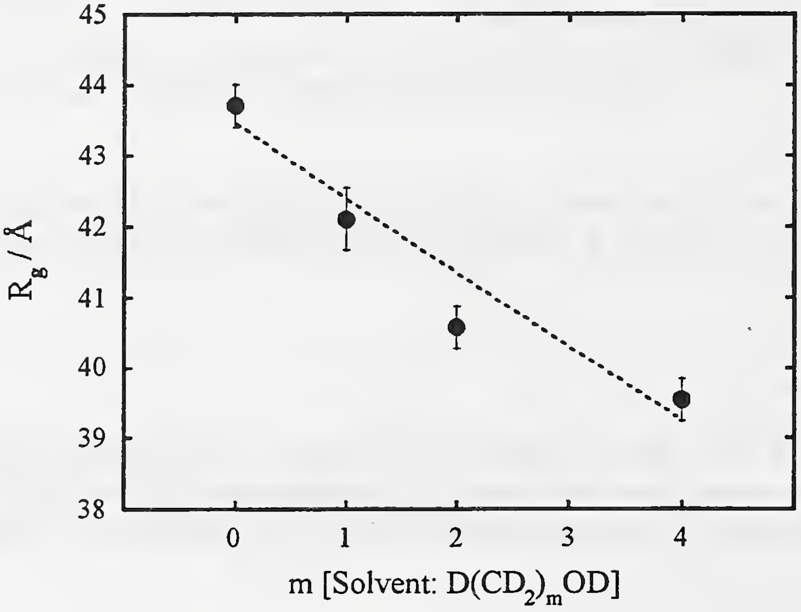

Figure 16. Plot of the radius of gyration of G5 PAMAM dendrimers, versus the composition of the solvent, x_s . (○) $T = 20$ °C; (□) $T = 50$ °C.

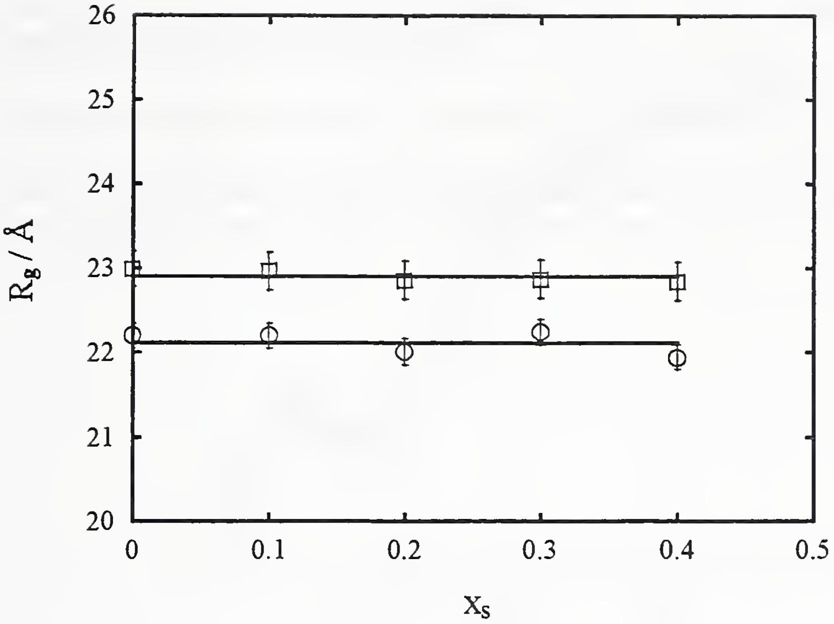

Figure 17. Radius of gyration of a G5 dendrimer in methanol-acetone mixtures; ☐ T = 50°C; ○ T = 20 °C.

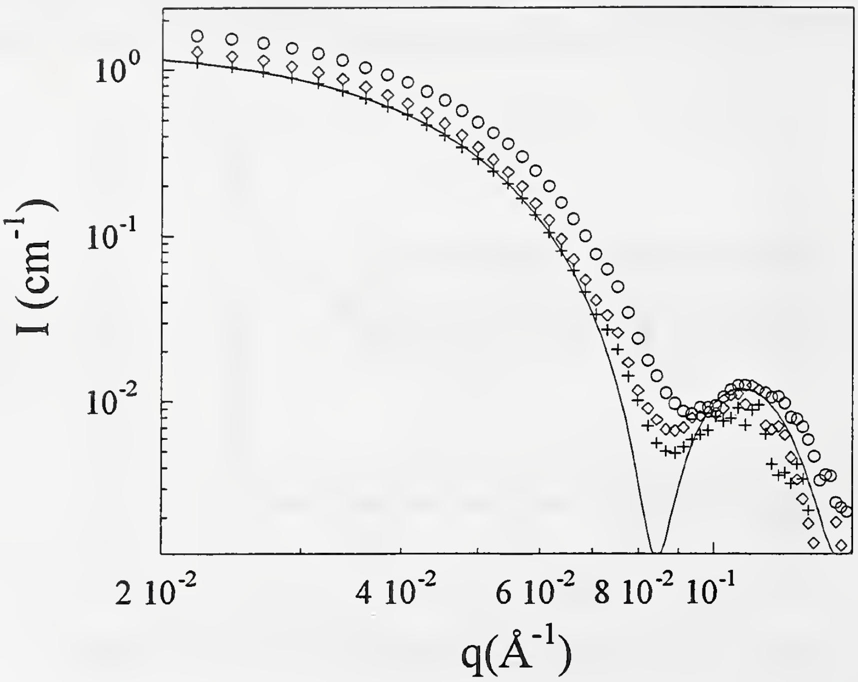

Figure 18. Effect of ionic strength and pH on G8 PAMAM dendrimers. Approximate dendrimer mass fraction is 3 %. Concentration of added NaCl is noted Cs. Symbols represent β = 0.1 Cs = 0 mol/L(Circles); α = 1 Cs = 0.5 mol/L (Crosses); α = 2 Cs = 0.5 mol/L (Diamonds). Solid line represents a non-linear least-squares fit to the data (α = 1 Cs = 0.5 mol/L) of a dense sphere with Rg = 42 Å.

Future Plans:

A paper has been written and will be submitted for publication soon. A related project on the effect of ionic strength on dendrimer size and virial coefficient has been completed and a paper is being written.

Publications:

“Effect of Solvent Quality on Single Particle Dimensions of PAMAM Dendrimers”, Andreas Topp, Barry J. Bauer, Donald A. Tomalia, and Eric J. Amis, in preparation.

“Effect of Solvent Quality on the Molecular Dimensions of PAMAM Dendrimers”, Barry J. Bauer, Andreas Topp, Donald A. Tomalia, and Eric J. Amis, ACS PMSE Preprints, 79.

Presentations:

"Dendrimers and Dendrimer/Polymer Blends", Barry J. Bauer Spring 1997 Center for Interfacial Engineering Meeting, May 1997.

"Dendrimer Solutions and Blends", Barry J. Bauer, 1997 NIST-ERATO Meeting, June 1997.

"Effect of Solvent Quality on the Molecular Dimensions of PAMAM Dendrimers", Barry J. Bauer, Andreas Topp, Donald A. Tomalia, and Eric J. Amis, Fall 1997 ACS Meeting, September 1997.

Evaluation of Dendrimers as Model Polyelectrolyte Systems

NIST: Giovanni Nisato, Robert Ivkov, Barry J. Bauer, Eric J. Amis

Objectives:

To determine the potential of dendrimers as a suitable model substance for studies of macroions in solution.

Technical Description:

Use SANS to measure the changes in solution structure that accompany variations of solution ionic strength, dendrimer charge density, and dendrimer volume fraction, ϕ, in good solvent (D_2O).

Summary Report:

Model polyelectrolyte systems should consist of molecules with 1) uniform size and shape, 2) ionizable surfaces that can support large variations of charge density, and 3) remain soluble over a wide range of conditions to allow sampling over a sufficiently large parameter space. Dendrimers are macromolecules that are believed to possess such characteristics and are potentially ideal model systems for exploring the physics of macroions.

We obtained SANS data on generation 5 (G5) polyamidoamine (PAMAM) dendrimers obtained from Dendritech, Inc., Midland, MI. The theoretical 128 terminal amine ($-NH_2$) groups on a G5 PAMAM dendrimer were ionized to the ($-NH_3^+$) form through the addition of acid. We approximate the extent of ionization by the stoichiometric ratio, α, of added HCl to the total number of terminal groups in solution.

Generally, the total scattering, $I(q)$, from a solution of interacting particles can be written as, $I(q) = \kappa^2 P(q)S(q)$ where κ is the contrast, $P(q)$ is the single particle form factor (intraparticle interference), and $S(q)$ is the solution structure factor (interparticle interference). In systems of non-interacting particles, $S(q) = 1$, and the total scattering reflects the nature of the individual particles. However, if the scattering particles are charged, $S(q) > 1$, and the scattered intensity will exhibit features that reflect interparticle effects.

We show that the dendrimers studied behave as weakly interacting particles in dilute solutions in D_2O, but that the addition of acid charges the dendrimers (Figure 19). Scattering from charged dendrimer solutions exhibits a peak that scales with the exponent (0.32 ± 0.01) of the volume fraction, ϕ, indicating liquid-like ordering. The interactions can further be manipulated by the addition of salt which screens the electrostatic repulsions (Figure 20). Extrapolations of these data to $q = 0$ yield the osmotic compressibility. For the system studied, we find positive values of these quantities. Taken together, these results suggest that PAMAM dendrimers are good candidates for model colloids since there is a large parameter space over which these solutions can be manipulated and measured. Comparisons of these data with theoretical models are ongoing.

Figure 19 shows the effect of the addition of HCl to solutions of G5 PAMAM dendrimers with volume fraction ϕ = 4.2 %. Symbols represent $\alpha = 0$ (open circles), $\alpha = 0.06$ (squares), $\alpha = 0.1$ (diamonds), $\alpha = 0.3$ (triangles), $\alpha = 0.5$ (inverted triangles), $\alpha = 1$ (filled circles). The inset shows the peak position, q^* as a function of dendrimer concentration. For comparison, the expected results for simple cubic (SC), body-centred cubic (BCC), and face-centred cubic (FCC) packing for spheres with radius, R = 31Å are shown. Figure 20 shows the effect of the addition of NaCl to charged dendrimer solutions, $\alpha = 0$ and ϕ = 4 volume %. Added salt concentrations are 1.0 mol/L (circles), 0.1 mol/L (squares), 0.050 mol/L (diamonds), 0.025 mol/L (triangles), 0.005 mol/L (inverted triangles), 0.0 mol/L (crosses). Note that at 1 mol/L NaCl, we recover single particle scattering. The inset shows a plot the inverse of I(0) extrapolated from data shown in the Figure. Lines are drawn as visual aids. Circles in the inset refer to data from dendrimer in pure D_2O (α = 0, no added salt). The slope is indicative of the interparticle interactions in the solution. A positive slope indicates repulsive interactions.

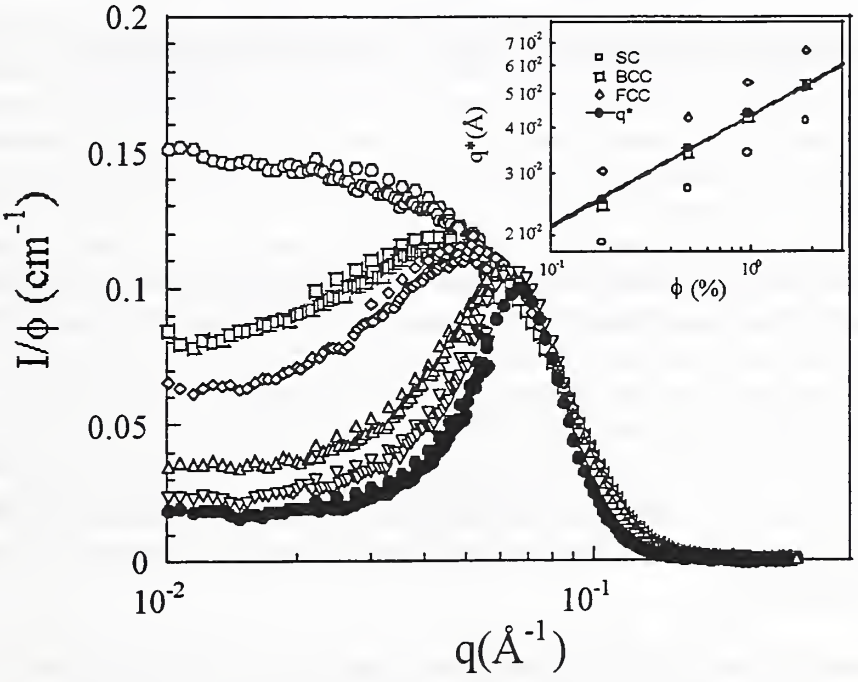

Figure 19. Effect of HCl addition on G5 PAMAM Dendrimers.

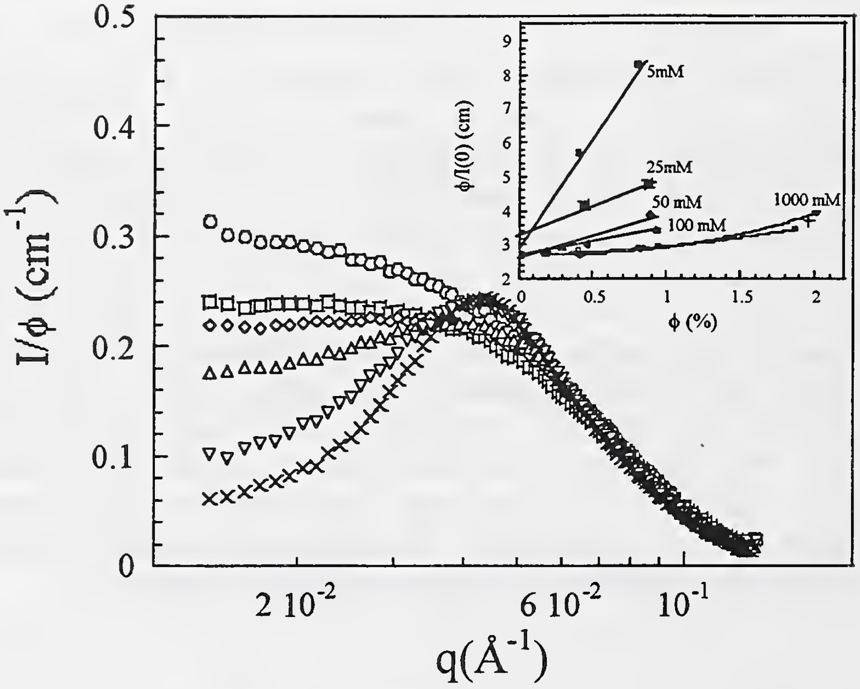

Figure 20. The effect of NaCl and HCl addition on G5 PAMAM dendrimers.

Publications:

"Interactions of Charged PAMAM Dendrimers in Solution: A Small Angle Neutron Scattering Study," Giovanni Nisato, Robert Ivkov, Barry J. Bauer, Eric J. Amis, PMSE Preprints, August 1998.

Presentations:

"SANS Investigation of the Structure of Charged Dendrimer Solutions," G. Nisato, Colloid, Macromolecular, and Polyelectrolyte Gordon Research Conference, Ventura California, February 1998.

"Characterization of Charged PAMAM Dendrimer Interactions in Solution by Small Angle Neutron Scattering," R. Ivkov, Fall 1998 ACS National Meeting, August 1998.

TEM of Dendrimers

NIST: Catheryn L. Jackson, Barry J. Bauer, Eric J. Amis

Outside Collaborators: Henri D. Chanzy, CNRS, Frank P. Booy, NIH, Donald A. Tomalia, MMI

Objectives:

To obtain real space images of dendrimers with resolution to make size measurements using the methods familiar to biological TEM. To determine the smallest size dendrimers that can be reasonably imaged by TEM.

Technical Description:

We have characterized the size, shape and size distribution of PAMAM dendrimer molecules using the technique of positive and negative staining in the TEM. To study the dendrimers in solution using the cryo-TEM method and determine the scope of possible future studies.

Summary:

Individual dendrimer molecules of PAMAM from generation ten (G10) to G5 were obtained by conventional TEM after staining with aqueous sodium phosphotungstate, examples for G10 and G5 are shown in Figure 21 and 22. The dendrimers were resolved as separate, beam-stable entities and their sizes and distribution of sizes were statistically analysed and compared with data from small angle x-ray scattering (SAXS) in solution, shown in Figure 23. To a first approximation, the dendrimers appeared circular in projection and the diameters conformed to a Gaussian distribution which broadened somewhat with increasing generation number. Aqueous G10 dendrimers were also characterized by examination in the frozen, hydrated state after quench-freezing in liquid ethane (cryo-TEM) and the data compared with the results of the staining experiments. Cryo-TEM, in general, confirmed the staining experiments but suggested that in the native state, there is more variability in the shapes of the dendrimers, with polyhedral shapes occurring quite frequently. In addition, cryo-TEM suggests that limited regions of close-packed arrays of dendrimer molecules may exist in solution.

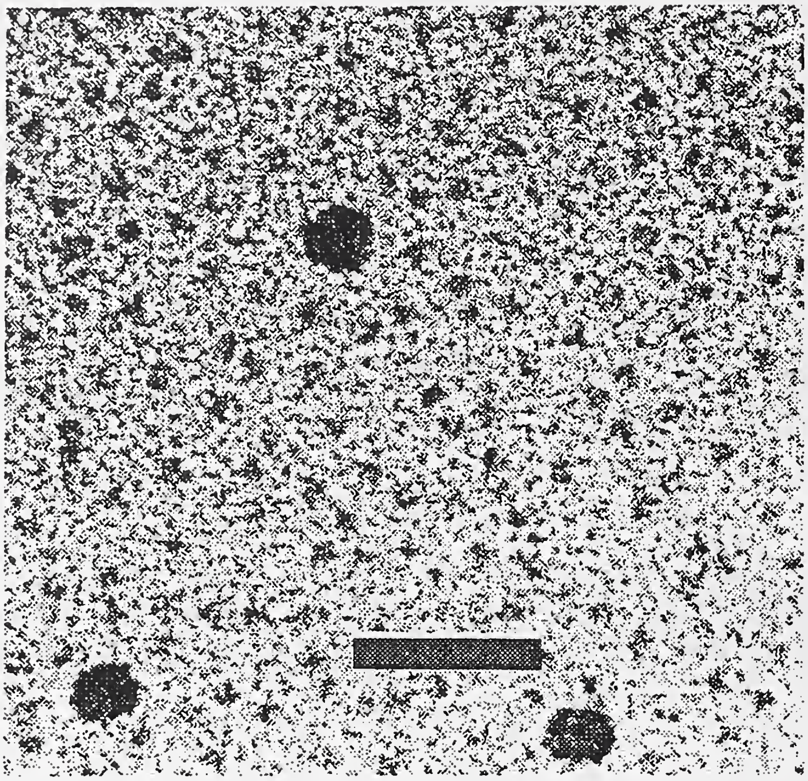

Figure 21. TEM of G5 PAMAM dendrimer. Large shaped are G10 dendrimer. Insert is 50 nm.

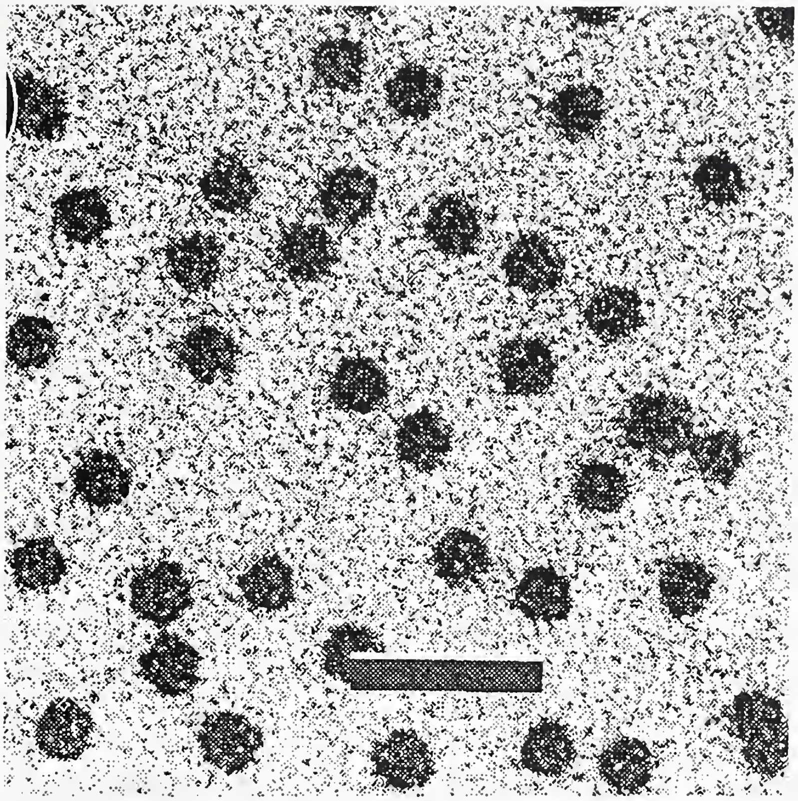

Figure 22. TEM of G10 PAMAM dendrimer. Insert is 50 nm.

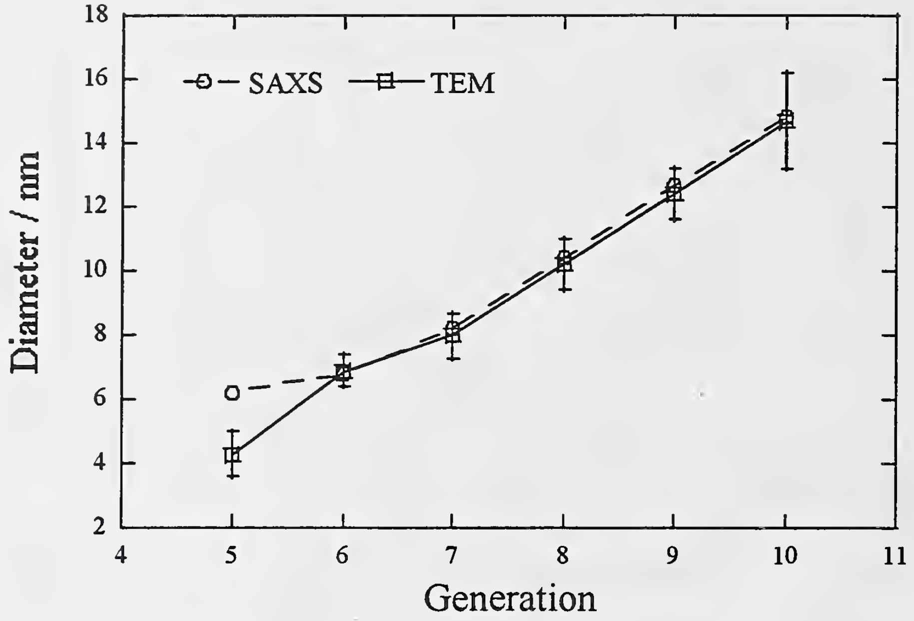

Figure 23. Comparison of TEM and SAXS measurements of dendrimer diameter.

Future Plans:

Continue to characterize dendrimers of other types by conventional TEM, when the size range is suitable (>5 nm in diameter).

Publications:

C. L. Jackson, H. D. Chanzy, F. P. Booy, B. Drake, D. A. Tomalia, B. J. Bauer and E. J. Amis, "Visualization of Dendrimer Molecules by Transmission Electron Microscopy (TEM): Staining Methods and Cryo-TEM of Vitrified Solutions", Macromolecules, submitted.

C. L. Jackson, H. D. Chanzy, F. P. Booy, D. A. Tomalia, and E. J. Amis, "Characterization of Dendrimer Molecules by Staining and Cryoelectron Microscopy Techniques", ACS PMSE Preprints, **1997**, *77*, 222.

Presentations:

"Characterization of the Structure of Dendrimer Molecules by Transmission Electron Microscopy and Scattering Techniques", Catheryn L. Jackson, North Carolina State University, Materials Science and Engineering Department, Raleigh, NC, October 1997.

"Characterization of Dendrimer Molecules by Staining and Cryoelectron Microscopy Techniques", Catheryn L. Jackson, Fall 1998 ACS Meeting, September 1997.

"Characterization of Polymer Micellar Suspensions and Dendrimer Solutions by Cryo-electron Microscopy" (co-authors H. D. Chanzy and F. P. Booy), Catheryn L. Jackson, NIST-ERATO Meeting, June 1997.

Thin Film Studies of Dendrimers and Dendrigrafts

NIST: Alamgir Karim, Barry J. Bauer, Dawei Liu, Jack Douglas, Eric J.Amis

Outside Collaborators: Donald Tomalia, MMI, Rui Yin, MMI

Objectives:

To measure the effect of branching on the interfacial thickness with linear polymers and the kinetics of dewetting. To see if monolayers of dendrimers can be formed on a surface ad how the thickness varies with generation.

Technical Description:

Use neutron reflectivity to measure interfacial thickness, optical microscopy to follow dewetting of thin films, and xray reflectivity to measure the thickness of monolayers.

Summary Report:

A measure of the adhesion between a dendrigraft molecule and a polymer molecule without performing mechanical tests is the interfacial width between layers of two such materials. To this end, neutron reflection, a technique with nanometer resolution was used to measure the interface width between a deuterated polymer, polystyrene and PEOX. Samples were prepared by spin coating from selective solvents. Measurements were performed on PEOX's ranging from linear to the highest branching content, G3. It was observed that the interface thickness increased slightly from (40 ± 5) Å for linear PEOX to (50 ± 5) Å for the third generation dendrigrafts. While these widths are typical of immiscible polymers, the variation of interfacial width with branching content may be related to entropic reasons, which deems further investigation, see figure 24.

Monolayer films of dendrimers have been the subject of much recent scrutiny. Here we use X-Ray reflectivity (XR) to characterize spin coated dendrimer films prepared from very dilute solutions (mass fraction, 0.1 %). Dry films of generation G3 through G11 were measured by XR for this study. In general, the reflectivities are characterized by well defined minimas for G3 through G10 films, indicative of smooth films with nominal rms surface roughness (< 10 Å). On the other hand, the minima for the G11 is strongly damped, which indicates that the surface is rough. The reflectivity from G6 has a bimodal distribution suggestive of possible thinner regions within the film. This trend is confirmed for G7 and higher, and the break in thickness with generation number is shown in the plot. The plot also shows that the film thicknesses up to G5 correlate well with individual dendrimer size up to G6, as measured by other techniques, such as SAXS and TEM. Thus, the film thicknesses suggest that the dendrimer films are monolayers up to generation 5. See figure 25

As discussed, our preliminary studies indicate that the branching of dendrigraft molecules influences interfacial widths with polystyrene in the bilayer film experiments. At higher temperatures (T>120 deg. C), the pure PEOX films tended to dewet and both the final dewetting morphology and the kinetics seemed to be strongly influenced by branching. As shown, the linear PEOX dewets like regular polymer molecules to form classic Vorronoi-tessellation patterns, however the higher generation shows multiple shell-like break up structure which might be related to its higher viscosity.

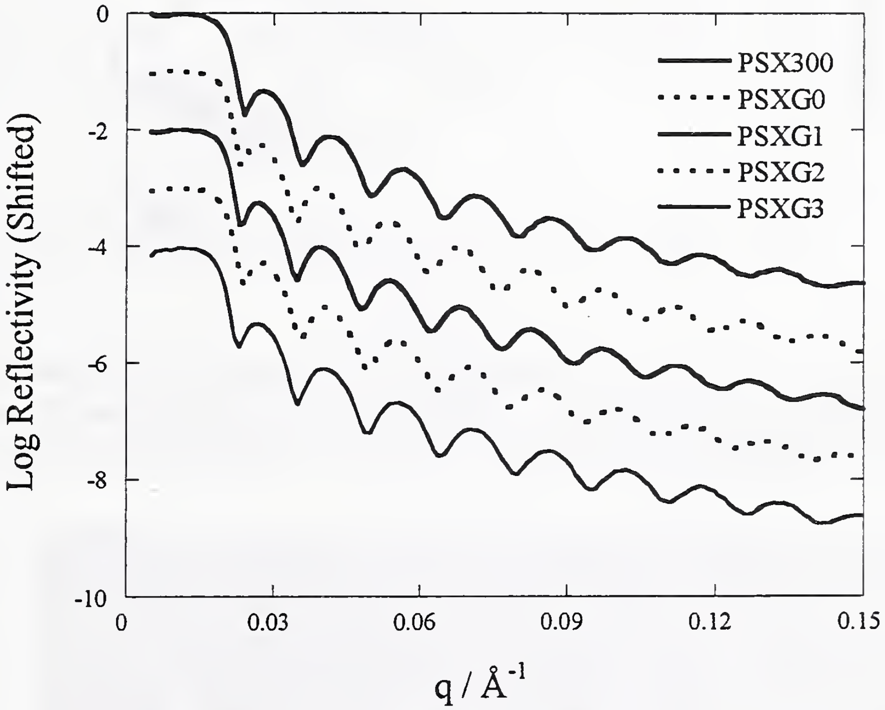

Figure 24. NR data was fit to determine interfacial thickness between deuterated polystyrene and PEOX. Interfacial thickness does not change significantly with branching, ranging from (40 ± 5) Å for linear PEOX to (50 ± 5) Å for the third generation dendrigrafts

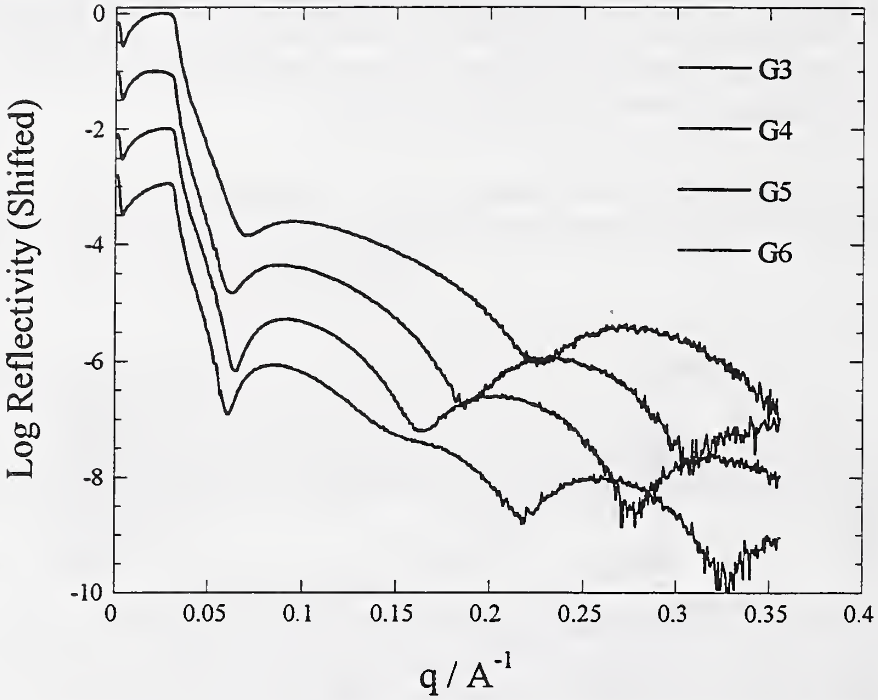

Figure 25. XR from small PAMAM dendrimers (G<6) form films that are consistent with the diameter of dendrimers measured in solution. By the sixth generation, the scattering becomes bimodal, suggesting a transition to areas of thinner films

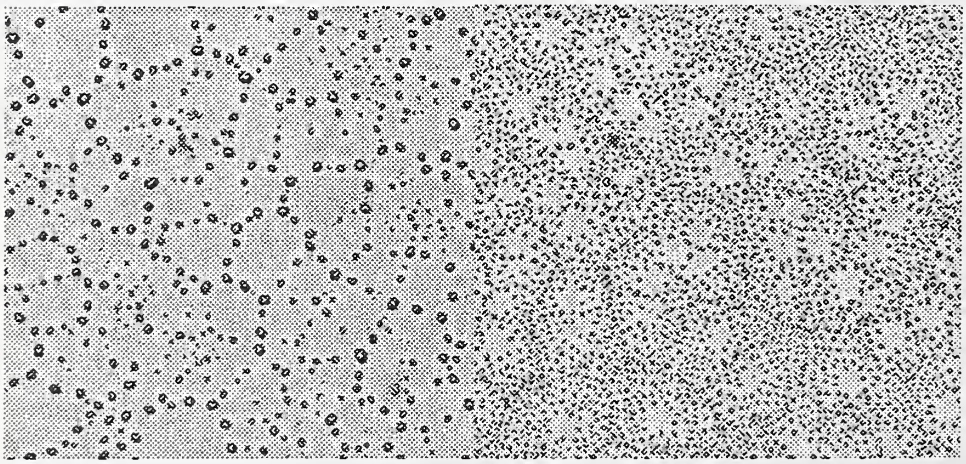

Figure 26. Optical microscopy (OM) of dewetting of linear PEOX on silicon wafers (left). These resemble classic "Vorronoi-tesselation"

patterns observed for late-stage dewetting of polymers OM of dewetting of PEOX Generation 2 (right). A novel “floral” pattern is seen

Publications:

“Influence of Generation Number on the Formation of Dendrimer Monolayers”, A. Karim, D.W. Liu, B.J. Bauer, J.F. Douglas, E.J. Amis, D.A. Tomalia, ACS PMSE Proceedings **1997**, *77*, 181.

Presentations:

“Influence of Generation Number on the Formation of Dendrimer Monolayers”, A. Karim, Fall 1997 ACS national Meeting, September 1997.

Outputs

Publications

"A SAXS Study of the Internal Structure of Dendritic Polymer Systems", Ty J. Prosa, Barry J. Bauer, Eric J. Amis, Donald A. Tomalia, Rolf Scherrenberg, J. Polymer Science, Polymer Physics, **1997**, *35*, 17.

"Small Angle Neutron Scattering from Dilute and Concentrated DAB(PA)$_x$ Dendrimer Solutions", A. Topp, B.J. Bauer, E.J. Amis, ACS PMSE Proceedings **1997**, *77*, 82.

"SANS and SAXS Investigations of the Internal Structure of Dendritic Molecules", B. J. Bauer, A. Topp, T. J. Prosa, E. J. Amis, R. Yin, Q. Qin, D. A. Tomalia, ACS PMSE Proceedings **1997**, *77*, 87.

"Influence of Generation Number on the Formation of Dendrimer Monolayers", A. Karim, D.W. Liu, B.J. Bauer, J.F. Douglas, E.J. Amis, D.A. Tomalia, ACS PMSE Proceedings **1997**, *77*, 181.

"SANS Study of Labeled PAMAM Dendrimer", E.J. Amis, A. Topp, B.J. Bauer, D.A. Tomalia, ACS PMSE Proceedings **1997**, *77*, 183.

"Characterization of Dendrimer Molecules by Staining and Cryoelectron Microscopy Techniques", C.L. Jackson, H.D. Chanzy, F.P. Booy, D.A. Tomalia, E.J. Amis, ACS PMSE Proceedings **1997**, *77*, 222.

"Dendrimer End Group Localization Determined by Counterion Mirroring", D.E. Valachovic, B.J. Bauer, E.J. Amis, D.A. Tomalia, ACS PMSE Proceedings **1997**, *77*, 230.

"Models of the Influence of Excluded Volume on the Formation of Polymer Layers", J. F. Douglas, R. Lipman, A. Karim, S. Granick, ACS PMSE Proceedings **1997**, *77*, 644.

"Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks", Barry J. Bauer, Andreas Topp, Ty J. Prosa, Da-Wei Liu, Catheryn L. Jackson, and Eric J. Amis, ANTEC Proceedings, **1998**.

Presentations

"Probing Dendrimers by Light, Neutron, and X-Ray Scattering", Eric. J. Amis, NIH Biophysics Research Colloquium, **1997**.

"Probing Dendrimers by Light, Neutron, and X-Ray Scattering", Eric. J. Amis, University of Illinois, department of Materials Science and Engineering, Urbana, **1997**.

“A SAXS Study of the Internal Structure of Dendritic Polymer Systems”, Ty J. Prosa, Spring 1997 APS National Meeting, April 1997.

“Structural Characterization of Dendrimers by Light, Neutron, and X-Ray Scattering”, Eric. J. Amis, Spring 1997 APS National Meeting, April, 1997.

“Dendrimers and Dendrimer/Polymer Blends”, Barry J. Bauer Spring 1997 Center for Interfacial Engineering Meeting, May 1997.

“Dendrimer Solutions and Blends”, Barry J. Bauer, 1997 NIST-ERATO Meeting, June 1997.

“Light, Neutron, and X-Ray Scattering of Dendrimers and Dendrimer/Polymer Blends”, Eric. J. Amis, ACS Central Region, 100 Years of Dow Chemical Co., Midland, 1997.

“Scattering Methods and Dendrimer Materials”, Eric. J. Amis, American Crystallographic Association, Session on Small Angle Scattering, St. Louis, 1997.

“SANS Study of Labeled PAMAM Dendrimer”, Barry Bauer and Andreas Topp, 1997 NIST-ERATO Meeting, June 1997.

“Small Angle Neutron Scattering from Dilute and Concentrated $DAB(PA)_x$ Dendrimer Solutions”, Andreas Topp, 1997 NIST-ERATO Meeting, June 1997.

“A SAXS Study of the Internal Structure of Dendritic Polymer Systems”, Ty J. Prosa, 1997 NIST-ERATO Meeting, June 1997.

“Small Angle Neutron Scattering from Dilute and Concentrated DAB(PA)x Dendrimer Solutions“, A. Topp, Fall 1997 ACS National Meeting, September, 1997.

“SANS ans SAXS Investigations of the Internal Structure of Dendritic Molecules”, B. J. Bauer, Fall 1997 ACS National Meeting, September, 1997.

“Influence of Generation Number on the Formation of Dendrimer Monolayers”, A. Karim, Fall 1997 ACS National Meeting, September, 1997.

“SANS Study of Labeled PAMAM Dendrimer”, A. Topp, Fall 1997 ACS National Meeting, September, 1997.

“Characterization of Dendrimer Molecules by Staining and Cryoelectron Microscopy Techniques”, C.L. Jackson, Fall 1997 ACS National Meeting, September, 1997.

“Dendrimer End Group Localization Determined by Counterion Mirroring”, D.E. Valachovic, Fall 1997 ACS National Meeting, September, 1997.

"Models of the Influence of Excluded Volume on the Formation of Polymer Layers", J. F. Douglas, Fall 1997 ACS National Meeting, September, 1997.

"Characterization of the Structure of Dendrimer Molecules by Transmission Electron Microscopy and Scattering Techniques", Catheryn Jackson, North Carolina State University, Materials Science and Engineering Department, Raleigh, NC, October, 1997.

"Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks", Barry J. Bauer, ANTEC '98, April 1998.

"Effect of Solvent Quality on the Molecular Dimensions of PAMAM Dendrimers", Barry J. Bauer, Fall 1998 ACS national Meeting, August 1998.

"Characterization of Charged PAMAM Dendrimer Interactions in Solution by Small Angle Neutron Scattering," R. Ivkov, Fall ACS National Meeting, August 1998.

"SANS Study of Fatty Acid Modified Dendrimers", Aissa Ramzi, Fall ACS National Meeting, August 1998.

"Size Changes and Interpenetration within Concentrated Dendrimer Solutions", Ty J. Prosa, Fall ACS National Meeting, August 1998.