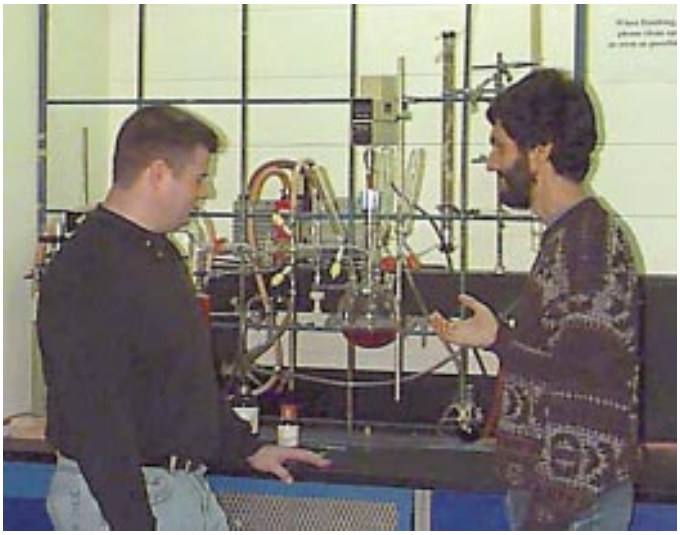
# ARBORESCENT GRAFT POLYMERS

Arborescent graft polymers (AGP) are a new class of polymer molecules with potential for use as drug delivery systems, monomolecular micelles for catalyst dispersions, waste water treatment and flow modifiers. AGP's are highly branched (i.e. treelike or arborescent) macromolecules synthesized by successive generations of functionalization and grafting reactions [1]. These molecules fall into a class of controlled architecture polymers that have generated considerable research interest in recent years and include dendrimers, arborescent, and hyper-branched polymers [2]. The applications envisaged for these types of polymers are based on exploiting the highly branched architecture of the polymers and require an understanding of the size and shape of the molecules in solutions and mixtures with other polymers. Small-angle neutron scattering (SANS) has been used to provide the foundation for understanding the shape-property relationships in these systems.

The chain architecture of AGP's is shown schematically in Fig. 1. The synthesis goal is to provide methods for producing polymers with controllable size, shape and functionality for use in such applications as coatings, membranes, drug release systems and flow modifiers. By synthesizing molecules with an outside shell of a hydrophilic polymer and an inner core of a hydrophobic polymer these molecules can act as water dispersible monomolecular micelles which can absorb organic molecules from waste water or help to disperse water insoluble



**Andy Kee (left) and Mario Gauthier (right) discussing the synthesis of arborescent polymers.**

catalyst systems. In order to design APG's for specific applications it is necessary to have detailed information on the intermolecular density profile, molecular size and shape in solutions and in mixtures with other polymers. We have been using small angle neutron scattering (SANS) to measure the size and shape of APG's under a range of different conditions.

SANS curves for a series of polystyrene AGP's as a function of generation in deuterated cyclohexane at 30°C is shown in

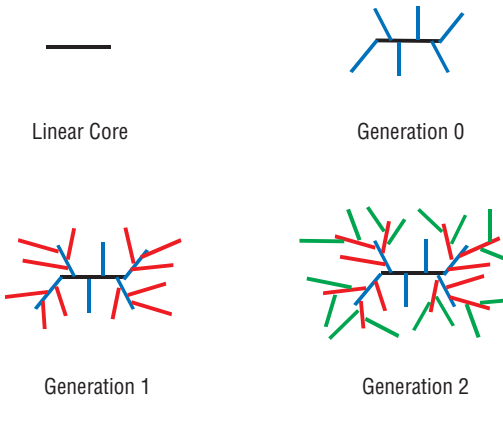



**FIGURE 1. Schematic of arborescent graft polymer chain architecture.**

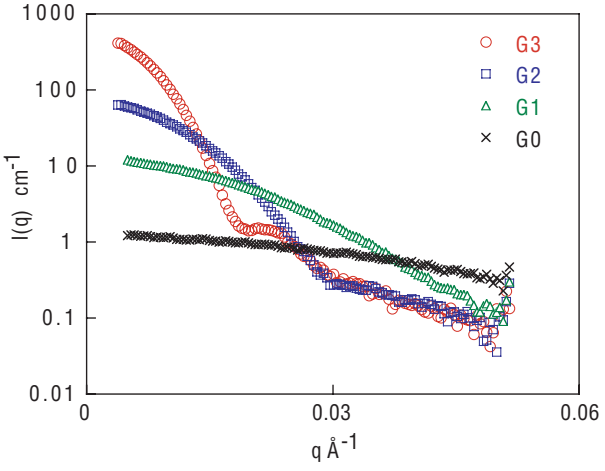



**FIGURE 2. SANS data for all generations of arborescent graph polystyrenes in deuterated cyclohexane.**

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Fig. 2. The radii of gyration ($R_g$) of the polymers were measured and are plotted as a function of generation in Fig. 3.

For generations 0 and 1 the size of the molecules is essentially equivalent under all measured conditions while for generations 2 and 3 the molecules vary in size significantly (particularly for generation 3) depending on the solvent or matrix polymer. The generation 3 molecules show the largest expansion in (deuterated) toluene which has the highest solvent power of the various systems studied. The most compact structure for the generation 3 molecule occurs in linear (deuterated) polystyrene. For comparison the $R_g$ of a sphere was calculated assuming the generation 3 molecule was collapsed to bulk density. The $R_g$ obtained was 170Å which is close to the $R_g$ of the generation 3 polymer in linear (deuterated) polystyrene. This indicates that the generation 3 molecules should be essentially non-interpenetrating and the linear polystyrene matrix chains are largely excluded from the arborescent graft molecules. These data are important for estimating the solvating power of these systems for use as monomolecular micelles and for understanding the role of entanglements in determining their flow properties.

The SANS data for generation 3 arborescent graft polymers in deuterated cyclohexane showed a clear Guinier region and a second interference peak at higher q which can be attributed to the single particle form factor (Fig. 4). A power law function was used to estimate the intermolecular density profile and calculate the scattering for comparison with experiment (see ρ(r) inset in Fig. 4).

Our neutron scattering work indicates that for the largest molecules studied (generation 3) the shape of the molecules is quite compact, and in mixtures with linear polymer chains there is relatively little interpenetration of the arborescent molecules by the linear chains. These results will help guide chemists in synthesizing new types and variations of arborescent graft polymers to exploit the unique possibilities of shape-tailored molecules for a range of applications.

## REFERENCES

[1] M. Gauthier, L. Tichagwa, J. S. Downey, and S. Gao, Macromolecules **29**, 519 (1996).

[2] D. A. Tomalia, A. M. Naylor, W. A. Goddard, Angew. Chem. Int. Ed. Engl. **29**, 138 (1990).

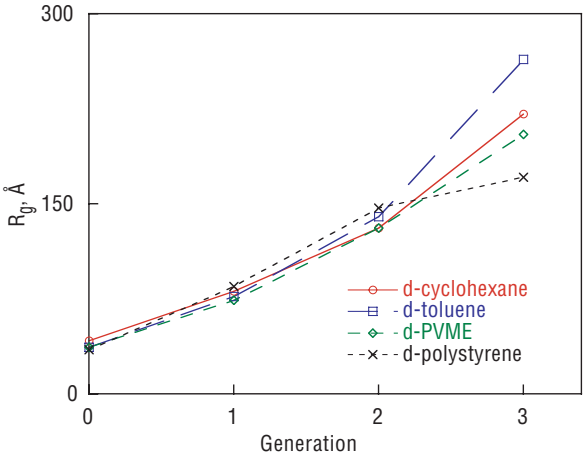


**FIGURE 3. Radius of gyration in solutions and blends for all generations.**

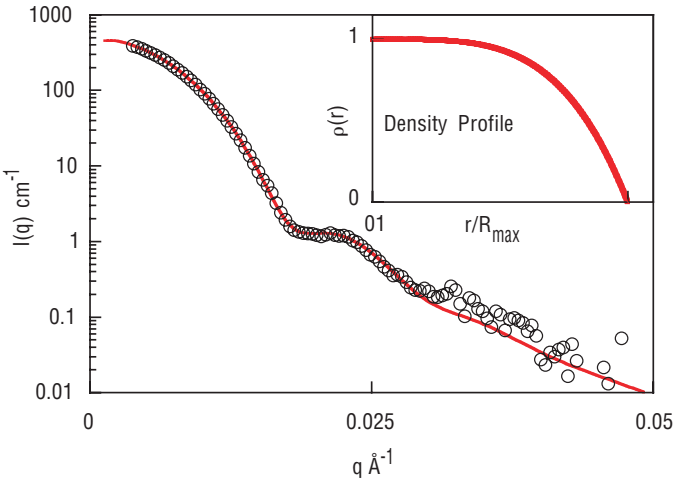


**FIGURE 4. Scattering function calculated for a power law density profile compared with SANS data for generation 3 absorscent graft polystyrene in deuterated cyclohexane.**