

# **A Small-angle Scattering Study of the Solution Properties of Dendrimer-like Star Polymers\***

**John A Pople**

Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center,  
Stanford University, Stanford, CA 94309

**Alice P Gast**

Dept. of Chemical Engineering, Stanford University, Stanford, CA 94305

**Mikael Trollsås, Hans Claesson and James L Hedrick**

IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120

## *Abstract*

The solution properties of poly( $\epsilon$ -caprolactone) dendritic polymers are investigated by small angle neutron scattering (SANS) techniques. Comparisons of the scattering function in the intermediate region of the SANS patterns with molecular dynamic simulations indicate that the dendritic polymers are relatively extended in their conformation. We report a decay exponent, which scales as  $1/\nu$ , of  $-1.2$ , which suggests a conformation more extended than star polymers, approaching the case of sea urchins. Guinier plots of SANS patterns yield radius of gyration measurements  $R_g \sim 30\text{\AA}$ , which increase with generation number. Modeling the scattering profiles according to a 'blob' model yields values of the random walk persistence length  $\langle \xi_E \rangle \sim 10\text{\AA}$ , which decreases with increasing polymerization generation.

*Keywords:* Dendrimer, star polymer, polymer solution, small-angle neutron scattering.

*Presented at 217<sup>th</sup> American Chemical Society National Meeting  
March 21 - 25, 1999 Anaheim, California*

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\* Work supported by Department of Energy contract DE-AC03-76SF00515

## Introduction

Dendritic polymers are relatively novel materials synthesized by a discrete, step wise series of bifurcations emanating from a central core.<sup>[1-4]</sup> The functional end groups can usually be bonded reliably, and this leads to a high degree of control over the regularity and structure of the final dendritic polymer. There are a wealth of available applications for these systems, including: small scale catalysts,<sup>[5]</sup> magnetic resonance imaging agents<sup>[6]</sup> and drug delivery systems.<sup>[7]</sup>

Most of the considerations of the structure of dendrimers to date have been theoretical.<sup>[8-11]</sup> One of the first analyses of dendrimers was by de Gennes and Hervet, who predicted a hollow core for a dendrimer using a self consistent mean field theory.<sup>[8]</sup> Other workers have deduced structural properties from Monte-Carlo simulations which suggest that the dendrimer core is not hollow, and that the density of segments decreases monotonically from the core at low generation numbers, whilst a local maximum occurs for higher generations at a distance comparable to  $R_g$ .<sup>[9-10]</sup>

This contrasts with the case of star polymers. The absence of the fixed bifurcation points of the dendrimer structure which occur with each successive generation leads to a characteristically steeper decay of the radial density profile for star polymers than for dendrimers.<sup>[11]</sup> Grest and co-workers presented a molecular dynamics simulation of star polymers and concluded that the chains were more elongated than expected, leading to a decay of  $I(q)$  in the intermediate scattering region with an index of  $-5/3$ .<sup>[11-12]</sup> Since the polymers we are studying are hybrid structures that are similar to star branched polymers, it is interesting to compare their structures with those of stars.

Limited experimental characterization of dendritic polymer systems has also been performed.<sup>[13-15]</sup> A small angle X-ray scattering (SAXS) study of poly(propyleneimine) dendrimers in solutions of methanol by Prosa *et al* revealed that the generation of the dendrimer had little or no effect on the density distribution.<sup>[13]</sup> Calculation of the radius of gyration of 3rd generation poly(amidoamine) dendrimers with molecular weights of 14 200, 58 000 and 116 000 gave respective measurements of  $R_g \sim 15\text{\AA}$ ,  $30\text{\AA}$  and  $35\text{\AA}$ .<sup>[13]</sup>

A SANS study of poly(propyleneimine) dendrimers in aqueous solution by Scherrenberg and co-workers revealed that the dendrimers behaved as soft molecules with possible interpenetration at higher concentration.<sup>[14-15]</sup> Electrostatic repulsion dominated as the solvent pH was lowered resulting in a stretching of the molecules and a behaviour more characteristic of harder particles.<sup>[14]</sup> It was further shown that the dimension of the dendrimers increased linearly with the generation number (roughly as  $M^{1/3}$ ) independent of the character of the end group and of the solvent used. The dendritic polymer was thus concluded to be in a folded, rather than an extended, conformation, exhibiting a relatively homogeneous density distribution.<sup>[15]</sup>

The purpose of this study is to experimentally determine, using SANS techniques, first order structural parameters concerning the conformation of dendrimer-like star poly( $\epsilon$ -caprolactone) polymers up to the third generation, in solutions of deuterated toluene.

## Experimental

### Materials

The materials studied here are dendrimer-like star polymers, based on aliphatic polyesters and synthesized by a divergent growth approach as has been previously

described.<sup>[4]</sup> A hexa-hydroxy-functional 2,2 bis(hydroxymethyl)propionic acid (bis-MPA) derivative was used as the initiator for the stannous-2-ethylhexanoate catalyzed living ring opening polymerization of poly( $\epsilon$ -caprolactone), to form a semicrystalline polymer with six arms.<sup>[4]</sup> Three generations of this polymer were employed in this study with degrees of polymerization (DP) of 20, (G1-20, G2-20 and G3-20) with the latter generations being produced by repeated iterations of the original synthesis process. Initiation and functionalization of the polymerizing process was monitored by nuclear magnetic resonance (NMR), and the molecular weights of the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> generations were 14 200, 42 300 and 96 000 respectively.

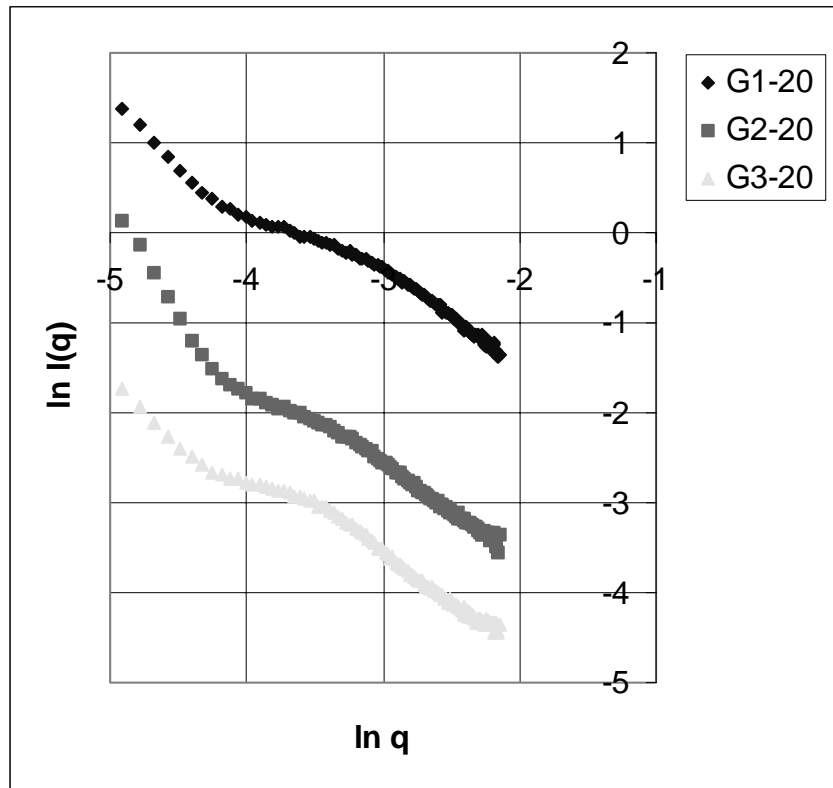
The dendrimers are prepared in solution of deuterated toluene at 5% by weight. A series of concentration dependent solutions (1%, 5% and 10% by weight) are also prepared using G2-15 (a 2<sup>nd</sup> generation dendrimer with DP 15). All SANS data collected in this report were collected at ambient temperature.

### Neutron scattering

Small angle neutron scattering (SANS) was performed at beamline NG7 the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD. The incident wavelength of the neutrons was  $\lambda = 9\text{\AA}$ , and the energy resolution of the source was  $\lambda/\Delta\lambda \sim 0.15$ . The liquid samples were contained in quartz cells which had an active path length of 1mm. Data were collected on a 2-dimensional multiwire detector which was positioned 3.6m away from the sample holder, providing a  $q$  range:  $0.001\text{\AA}^{-1} < q < 0.1\text{\AA}^{-1}$ . These data were corrected for background scattering and scattering from the empty quartz cell, and normalized against a water standard to give absolute intensity measurements.

### *Results and Discussion*

Figure 1 shows the scattering profiles for G1-20, G2-20 and G3-20. The characteristic shape of each of the scattering curves, with a slope at low  $q$ , in the Porod region, and a slope at higher  $q$ , with two inflections between, is reminiscent of the scattering curves simulated by the molecular dynamics studies of Grest *et al.*<sup>[11]</sup> In their simulation the intermediate scattering region evidenced a decay exponent (given by  $1/\nu$ ) of  $-5/3$ , giving  $\nu \sim 3/5$ : characteristic of a star polymer in a good solvent.<sup>[11]</sup> Hirata and Tsunashima show that  $\nu \sim 1$  for sea urchin molecules, where the arms are rodlike and fully extended.<sup>[16]</sup> In our experimental data we find  $\nu \sim 5/6$ , (Table 1) which is intermediate between these two cases. We interpret these exponents in the light of the simulations as evidence that the chains making up the dendrimers are highly extended in their conformation: a degree of stretching which is typical in the highly crowded scenario associated with a confined star-like geometry.<sup>[17]</sup>



**Figure 1:** Scattering profiles for a series of 5% w/w solutions of the series of poly( $\epsilon$ -caprolactone) dendritic polymers in deuterated toluene. The degree of polymerization of each polymer branch is 20. The scattering profiles have been displaced along the ordinate for clarity.

Guinier plots revealed radius of gyration measurements  $R_g \sim 24\text{\AA}$ ,  $33\text{\AA}$  and  $34\text{\AA}$  (Table 1). This increase is less dramatic than the increase observed in  $R_g$  with generation in the SAXS study of Prosa *et al* of poly(propyleneimine) dendrimers in solutions of methanol where the radii of gyration of 3<sup>rd</sup> generation poly(amidoamine) dendrimers with molecular weights of 14 200, 58 000 and 116 000 gave respective measurements of  $R_g \sim 15\text{\AA}$ ,  $30\text{\AA}$  and  $35\text{\AA}$ .<sup>[13]</sup>

Dendrimer solution	$M_w$	$\nu$	$R_g$ ( $\text{\AA}$ )	$\xi_E$ ( $\text{\AA}$ )
5% G1-20	14 300	0.83	24	13.3
5% G2-20	42 300	0.88	33	12.7
5% G3-20	96 000	0.79	34	11.0

**Table 1:** Characterizing parameters determined from SANS patterns for poly( $\epsilon$ -caprolactone) dendrimers with degree of polymerization 20 in each polymer branch in solution of deuterated toluene.

A study of the dependence of  $R_g$  with polymer concentration was also performed with the G2-15 solution at weight percentages of 1%, 5% and 10%. It was found that  $R_g$

decreased with increasing concentration in the sequence: 29Å, 27Å, 20Å respectively. This shows the same trend as was observed in the poly(amidoamine) dendrimers by Scherrenberg and co-workers, where concentrations of 1%, 2% and 5% in aqueous solution caused a comparable reduction in the radius of gyration of 13.9Å, 13.6Å and 12.6Å respectively, attributed to virial effects. <sup>[14]</sup>

We have also employed a relationship proposed by Edwards to calculate the screening length,  $\xi_E$ , in semi dilute solutions. <sup>[18]</sup> The relationship stipulates:

$$I(q) \propto (1 + q^2 \langle \xi_E^2 \rangle)^{1/2}$$

Using this relationship we find values for  $\xi_E$  of 13.3Å, 12.7Å and 11.0Å for the G1-20, G2-20 and G3-20 dendrimers respectively, (Table 1). The screening length can be interpreted as the persistence length over which the coils are ordered randomly, and it can be seen that  $\langle \xi_E \rangle$  decreases with increasing dendrimer generation. It is noted that this is a global parameter for the macromolecule because the architecture of the dendritic polymer is such that the inner shells of the dendrimer are likely to be more extended by reason of the fixed points of constraint imposed by each successive polymerization step. Thus it is difficult to ascribe any unambiguous interpretation to the observation that  $\langle \xi_E \rangle$  reduces as the generation number increases without knowledge of the distribution of values of  $\xi_E$  throughout the macromolecule. Nevertheless we are currently modeling the radial density profile from considerations of excluded volume effects between the neighbouring chains within a star-like polymer system in order to extract measurements of  $R_g$  and the hydrodynamic radius  $R_h$  of the dendrimer-like star polymer.

### *Conclusions*

SANS is an appropriate method for the determination of the structure of dendrimer-like polymers in solution. We observe that poly( $\epsilon$ -caprolactone) dendrimers in solutions of deuterated toluene form conformations which are relatively highly extended, ( $n \sim 5/6$ ) more so than star polymers in a good solvent, and akin to the sea urchin shapes discussed by Hirata and Tsunashima.[16] We ascribe this high degree of extension to excluded volume effects within the densely packed inner shells of the dendritic polymer. Radius of gyration measurements yield  $R_g \sim 30\text{Å}$ , which increase with generation number and decrease with concentration. Calculations of the screening length yield mean values of  $\langle \xi_E \rangle \sim 10\text{Å}$ , although the distribution of random walk persistence lengths within the macromolecule remains unknown, and is the subject of current analysis.

### *Acknowledgements*

This work was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-9808677. The SANS data in this report were collected on beamline NG7 of the NIST NCNR facility in Gaithersburg, MD and the authors thank the Eric Amis, Kathleen Barnes and Rob Ivkov, for their assistance. JAP acknowledges the support of the Stanford Synchrotron Radiation Laboratory and we acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the facilities used in these experiments.

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