

Fatty Acid Modified Dendrimers in Bulk and Solution: Single-Chain Neutron Scattering from Dendrimer Core and Fatty Acid Shell

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ABSTRACT: Small-angle neutron scattering (SANS) has been applied to extract the single-chain form factors of the fatty acid (FA) and the dendrimer components in bulk and dilute solution of fatty acid modified poly(propyleneimine) dendrimers (Astramol). The fatty acid chains were covalently or noncovalently linked to the end groups of two generations, G3 and G5. Bulk samples were prepared under contrast match conditions of mixtures of dendrimer-*h*/FAH and dendrimer-*h*/FAD to obtain the form factor of the fatty acid components. The solutions were prepared with deuterated fatty acid modified dendrimers in decalin solvent using the contrast match technique. Mixtures of decalin-*h* and decalin-*d* were used to match either the dendrimer or FA components. The dendrimer core of both G3 and G5 appears collapsed, without the incorporation of a significant amount of solvent. The G3 FA portion has a size closer to that of the bulk than that of a collapsed FA shell. The G5 dendrimer has the opposite trend.

Introduction

Dendrimers are a new class of macromolecules constructed with highly regular branching, having a tree-like structure that emanates from a central core.^{1–6} The unique structure of these three-dimensional polymers is a result of the control of their size, shape, molecular weight, topology, and surface chemistry to an extent unprecedented in polymer science.^{7,8} The multistep synthesis of dendritic macromolecules differs from that of the related family of hyperbranched polymers.^{9,10} The synthetic methods cause dendrimers to be highly uniform, while hyperbranched polymers are randomly branched.

While a large variety of novel dendritic structures have been synthesized,^{11–14} the thorough investigation of the physical properties of these materials has lagged behind. This is unfortunate, since a number of reports have appeared suggesting exciting and unusual behavior.^{15–17} For example, a maximum in intrinsic viscosity with molecular weight has been found.¹⁸ This is consistent with the dendrimer obtaining a globular structure as the molecular weight of the dendrimer increases. The main problem with many physical studies of dendrimers is that only small quantities are usually available. Recently, DSM in The Netherlands developed a method of synthesis that can produce large amounts of dendritic molecules. These dendrimers are commercially available and are based on poly(propyleneimine) molecules (Astramol).^{4,19}

In recent years, the synthesis of these macromolecules has progressed, and it is becoming a major area of interest from both an industrial and academic standpoint. Particularly, the chemistry of the end groups has been one of the main areas of research interest. Indeed, many different ways of end group modification have

been reported on different dendritic polymers.²⁰ For poly(propyleneimine) dendrimers, a wide range of modification reactions have been performed,^{21–24} leading to new materials such as a “dendritic box”,²² liquid crystalline structures,^{6,25,26} dye extraction agents,²⁷ chiral dendrimers,^{28–31} and dendrimers with catalytic sites.^{32–35} The modification of the dendrimer’s end groups not only changes their chemical properties but also dramatically changes their physical behavior and material properties.^{36–38} An example is the modification with fatty acids, which also leads to interesting new applications.^{24,27,39,40}

In this paper, the end groups of poly(propyleneimine) dendrimers were modified with octadecanoic or octadecanoic-*d*₃₅ acid groups. Small-angle neutron scattering (SANS) has been used to obtain quantitative information about the FA and the dendrimer components in bulk and in dilute solution. By using the contrast matching method,^{41–43} the average size and shape of each of the components can be isolated and measured.

Theoretical Background

Many authors^{44–49} have reported the measurement of single-chain form factors in concentrated solutions and in bulk. The measurements give the configuration of an individual chain using SANS. The samples are composed of mixtures of normal hydrogenated and deuterium-labeled polymers. For the labeled dendrimers in this study, an analogy can be made to labeled polymer solutions.⁵⁰ Such a treatment has been used by Koberstein⁵¹ and by Williams et al.⁵² on polyelectrolyte systems.

Suppose we have an incompressible blend of two polymer species, designated P and S, in which a volume fraction “*x*” of the P species are labeled by substituting the hydrogen atoms by deuterium. The coherent scattering cross section per unit sample volume is given by^{49,50}

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$$\frac{d\Sigma}{d\Omega}(q,x) = x(1-x)(a_H - a_D)^2 N_P S_S(q) + \left[a_H(1-x) + a_D x - a_S \frac{V_P}{V_S} \right]^2 \frac{S_T(q)}{V} \quad (1)$$

where a_H and a_D are the coherent neutron scattering lengths for the normal (hydrogenated) and labeled (deuterated) monomer units of the P species, a_S is the neutron scattering length of the monomer unit of the species S, V is the total volume of the sample, and V_P and V_S are the monomer specific volumes of the P and S species. The factor $S_S(q)$ is the single-chain form factor

$$S_S(q) = \langle |\sum_j \exp(i\mathbf{q} \cdot \mathbf{r}_j)|^2 \rangle \quad (2)$$

and $S_T(q)$ is the interference scattering which is the total scattering from samples without mixed H and D-labeled polymers ($x = 0$ or $x = 1$).

$$S_T(q) = \langle |\sum_{M,j} \exp(i\mathbf{q}(\mathbf{R}_M + \mathbf{r}_j))|^2 \rangle \quad (3)$$

Here the brackets $\langle \dots \rangle$ indicate an ensemble average, \mathbf{R}_M is the position of the center of mass of the M th polymer of the P species chains, \mathbf{r}_j is the position of the j th monomer of the M th polymer chain relative to \mathbf{R}_M , N_P is the total number of polymer chains, and \mathbf{q} is the wavevector for the momentum transfer, $q = 4\pi\lambda^{-1} \sin(\theta/2)$ (λ is the wavelength and θ is the angle of scatter). It is clear from eq 1 that the interference scattering term, $S_T(q)$, is proportional to the total scattering $d\Sigma/d\Omega(q)$ from a blend where the P species are fully labeled ($x = 1$). It gives information on the phase structure and the dimensions of the individual phases. The single-chain form factor $S_S(q)$ gives information on the configuration of the individual labeled chain from which we get the radius of gyration, R_g . In the case of fatty acid modified dendrimers, the form factor is the total factor of all fatty acid molecules (16 for G3 and 64 for G5) that are bonded to a single dendrimer core.

Experimental Methods

Synthesis of Samples. In this study, the third (G3) and fifth (G5) generation of poly(propyleneimine) dendrimers (Astramol),^{4,19} with $y = 16$ and 64 primary amine groups (DAB-dendr-(NH₂)_y), were modified with octadecanoic acid.

In one set of samples, ammonium salts were synthesized by protonation of the dendrimer's amine end groups by the fatty acid, forming to the "noncovalently bonded" samples. For these samples, about 2.5 mmol of octadecanoic acid was added to an amine-equivalent amount of poly(propyleneimine) dendrimer in 20 mL of toluene. The mixture was heated to 60 °C until a homogeneous solution was formed. The solvent was removed carefully with a rotary evaporator at 60 °C and 2 kPa.

In the other set of samples, the dendrimer's amine groups were reacted with the acid group to form amides giving the "covalently bonded" samples. About 2.5 mmol of fatty acid (H or D) was added to an amine-equivalent amount of poly(propyleneimine) dendrimer and 20 mL of xylene. The mixture was heated to 160 °C while stirring, under a slow stream of nitrogen in a two-necked flask with a gas inlet and a Dean-Stark trap. After 1 h at 160 °C, all of the xylene was distilled off, after which the product was allowed to cool to room temperature.

The thermal properties of the FAD samples have been analyzed by differential scanning calorimetry (DSC). For this purpose a Perkin-Elmer DSC-7 equipped with a CCA-7 nitrogen cooling accessory was used.¹⁹ Temperature calibration

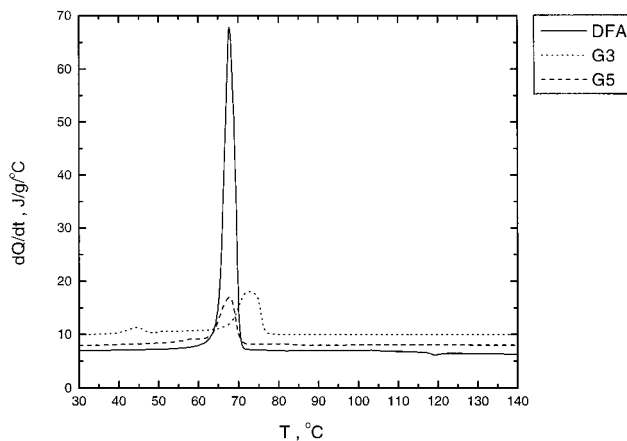


Figure 1. DSC heating flow curves for covalently modified generations G3 and G5 dendrimers with deuterated fatty acid. The curve corresponding to pure deuterated fatty acid is also included.

was performed using indium and lead. Indium was also used for energy calibration. A scanning rate of 10 °C/min and a sample mass of approximately 5 mg were used throughout.

Figure 1 shows the first heating run for the covalently modified generations G3 and G5 dendrimers and deuterated fatty acid (FAD). The peak temperature of the melting region for G3 and G5 was 72 and 68 °C, respectively, and the peak temperature for FAD was 68 °C. The standard uncertainty of the measurements is typically ± 0.2 °C as is determined by repeated runs. This small variation of the peak temperature, most probably connected with different thermal history of the samples, indicates that melting temperature of the fatty acid is not strongly dependent on dendrimer generation or attachment. On the other hand, the melting enthalpy of G3 (70 J/g) and G5 (60 J/g) is considerably smaller as compared with that of FAD (200 J/g), implying that the attachment of the fatty acid chain to the dendrimer lowers the ability of the fatty acid to crystallize.

Small-Angle Neutron Scattering. SANS experiments were carried out on the 8 m (NG1) and 30 m (NG7) instruments of the National Institute of Standards Technology Center for Cold Neutron Research in Gaithersburg, MD.⁵³ The wavelength λ of the incident beam was 6 Å. Two different configurations were used: $D_{ss} = 4.10$ m, $D_{sd} = 3.60$ m and $D_{ss} = 3.92$ m, $D_{sd} = 1.30$ m for the NG1 and NG7 instruments, respectively (D_{ss} is the source-sample distance and D_{sd} is the sample-detector distance). These configurations correspond to scattering wavevectors q varying between $2 \times 10^{-2} \text{ \AA}^{-1} < q < 0.17 \text{ \AA}^{-1}$ (NG1) and $2 \times 10^{-2} \text{ \AA}^{-1} < q < 0.45 \text{ \AA}^{-1}$ (NG7) (with $q = (4\pi/\lambda) \sin(\theta/2)$, θ being the scattering angle). The observed scattering intensity at a given temperature was collected over a two-dimensional detector and was corrected for empty cell, background radiation, and detector inhomogeneity. It is then normalized against H₂O, which serves as a secondary standard, to give the absolute intensity. Finally, it is circularly averaged to give the q dependence of the coherent scattering cross section, $d\Sigma/d\Omega(q)$, in absolute units (cm^{-1}). The standard uncertainties are calculated as the estimated standard deviation of the mean, and the total combined standard uncertainty is not given as comparisons are made with data obtained under the same conditions. In cases where the limits are smaller than 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. All temperatures reported are within ± 1 °C as determined by previous experience.

The bulk samples were melted at approximately 100 °C for the ionic and 130 °C for the covalent and placed in 1 or 2 mm quartz liquid cells. For the solutions, the dendrimers were added to the match solvent mixture and dissolved at 90 °C. The solutions were kept at this temperature during the SANS experiments.

Table 1. Molecular Characteristics of Generations G3 and G5 Poly(propyleneimine) Dendrimers, Fatty Acid Chains (FAH and FAD), and Decalin

molecule	structure	a^a (10^{-12} cm)	M^b (g/mol)	V^c (10^{-23} cm ³)	density (g/cm ³)
G3	C ₈₈ H ₁₉₂ N ₃₀	14.792	1688	267.94	1.00
G5	C ₃₇₆ H ₈₁₆ N ₁₂₆	62.792	7092	1177.49	1.00
FAH	C ₁₈ H ₃₅ O	-0.540	267	52.78	0.835
FAD	C ₁₈ D ₃₅ O	35.895	320	52.78	0.944
decalin- <i>h</i>	C ₁₀ H ₁₈	-0.082	138.25	20.57	0.896
decalin- <i>d</i>	C ₁₀ D ₁₈	18.656	156.25	20.57	1.013

^a Coherent neutron scattering length. ^b Molar mass. ^c Specific volume.^{54,57}

Results and Discussion

Bulk Samples. In eq 1, for the case of bulk samples, the fatty acid is species P, both H and D forms, and the dendrimer core is species S. The dendrimers are fully hydrogenated (Dend) while a volume fraction “*x*” of hydrogenated fatty acid (FAH) is replaced by a deuterated fatty acid (FAD). By analogy to a polymer solution, the dendrimer molecules are treated as “solvent” molecules in the calculation of the contrast factor. In the bulk experiments, we used generations G3 and G5 of the covalently bonded samples. The scattering length and the specific volume for molecule N are defined as

$$a_N = \sum_i b_i \quad (4)$$

and

$$V_N = \frac{M_N}{\rho N_A} \quad (5)$$

where \sum_i denotes summation of the scattering lengths, b_i , of the different atoms in the molecule, and M_N , ρ , and N_A are the molar mass of the molecule, the density, and Avogadro's number, respectively. Table 1 summarizes the parameters characterizing the macromolecules studied in this work: Dend, FAH, FAD, decalin-*h*₁₈, and decalin-*d*₁₈. Scattering lengths are taken from ref 54.

The fatty acid form factor $S_S(q)$ was measured in bulk for the covalent samples. The volume fraction, *x*, of deuterated fatty acid mixed with hydrogenated fatty acid and dendrimer molecules has been determined where the second term in eq 1 is zero (i.e., to avoid the interchain scattering):

$$x = \frac{a_{\text{FAH}} - a_{\text{Dend}} \frac{V_P}{V_S}}{a_{\text{FAH}} - a_{\text{FAD}}} \quad (6)$$

The match point, *x*, is found to be approximately equal to 0.092 for G3 and G5. In all of the contrast matched bulk samples, covalently linked samples were used to avoid exchange of fatty acids. Thus, the scattering cross section of eq 1 becomes

$$\frac{d\Sigma}{d\Omega}(Q) = K_N N_P S_S(Q) \quad (7)$$

K_N is the contrast factor which is related to the scattering lengths by

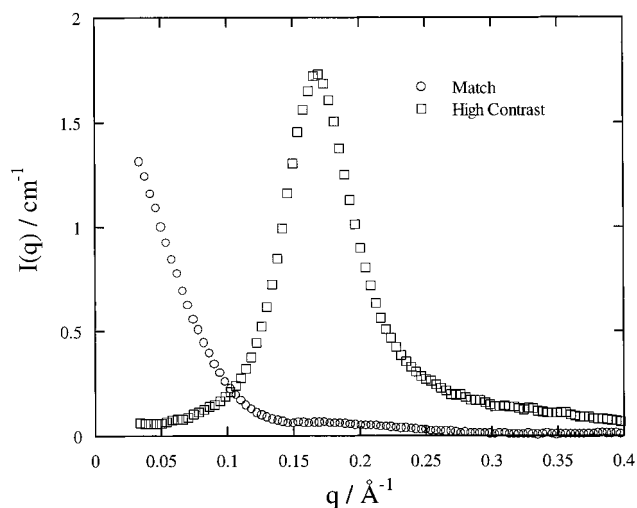


Figure 2. SANS of G5 dendrimers covalently modified with fatty acid at $T = 100$ °C in bulk. The figures show the total scattering (\square) and the matched sample (\circ).

$$K_N = \left(a_{\text{FAH}} - a_{\text{Dend}} \frac{V_P}{V_S} \right) \left(a_{\text{Dend}} \frac{V_P}{V_S} - a_{\text{FAH}} \right) \quad (8)$$

The contribution to the total scattering by incoherent scattering has to be removed before any data analysis is done. We have done this in two ways. For the solid samples, the q range extends to values greater than 0.4 \AA^{-1} . At this point the single-chain scattering approaches zero. An average value of the scattering beyond 0.4 \AA^{-1} is subtracted, and only the low- q data are used in the fits ($0.034 \text{ \AA}^{-1} < q < 0.087 \text{ \AA}^{-1}$). Since the solutions are dilute, slight variations in this subtraction do not affect the calculated R_g . The standard uncertainty in the baseline was taken to be $\pm 0.02 \text{ cm}^{-1}$ in all cases, and the standard uncertainty of the baseline was propagated through all of the fits. This value was estimated from the standard deviation in the fits of pure solvents. For the solutions, high- q data were not available, so the incoherent contribution was calculated by taking weighted values of the dendrimer along with experimental values of the contributions from decalin-*h*₁₈ and decalin-*d*₁₈. The standard uncertainty in the baseline was taken to be $\pm 0.05 \text{ cm}^{-1}$ for the solutions.

Figure 2 is a plot of the scattering from a G5 sample at 100 °C, both in the match conditions and for high contrast (pure dendrimer-*h*/FAD). The high contrast sample has a prominent peak in the SANS which is typical of the “correlation hole” effect seen in block copolymers.⁴¹ The matched sample has scattering characteristic of a single dendrimer, with all of the interchain effects being removed.

Figure 3 is a plot of the same G5 samples at 30 °C. The high contrast sample now has three prominent peaks. The crystallization that has taken place upon cooling has produced a very regular structure with long-range order. The nature of the morphology from TEM and SANS will be discussed elsewhere.⁵⁵ The match point sample has developed features that appear to be the result of mismatched contrast. Instead of a smooth curve such as is shown in Figure 1, shoulders appear in the matched sample. These shoulders are in positions similar to those of the high contrast sample.

Figure 4 shows the effect of temperature on the scattering of the matched G5 sample. There is a clear transition near the melting point found by DSC. Upon

Table 2. Radii of Gyration of the Core (Dendrimer) and the Shell (Fatty Acid Chains) for Generations G3 and G5 Extracted from Guinier Fits ($0.034 \text{ \AA} < q < 0.087 \text{ \AA}^{-1}$)

component	generation	type	R_g (\AA)			
			dendrimer ^a	collapsed ^b	bulk	solution
dendrimer	5	covalent	13.9	10.9		9.3 ± 2.0
	5	ionic	13.9	10.9		8.3 ± 1.7
	3	covalent	9.3	6.7		5.7 ± 1.9
	3	ionic	9.3	6.7		7.3 ± 1.3
fatty acid	5	covalent		18.9	24.2 ± 0.4	17.9 ± 0.9
	5	ionic		18.9		19.2 ± 0.8
	3	covalent		11.8	18.5 ± 0.4	16.3 ± 0.9
	3	ionic		11.8		19.3 ± 0.9

^a From ref 57. ^b Calculated from data in Table 1.

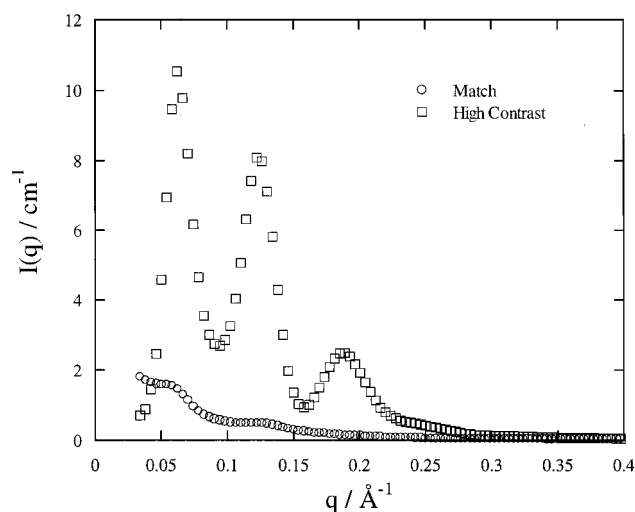


Figure 3. SANS of G5 dendrimers covalently modified with fatty acid at $T = 30 \text{ }^\circ\text{C}$ in bulk. The figures show the total scattering (\square) and the matched sample (\circ).

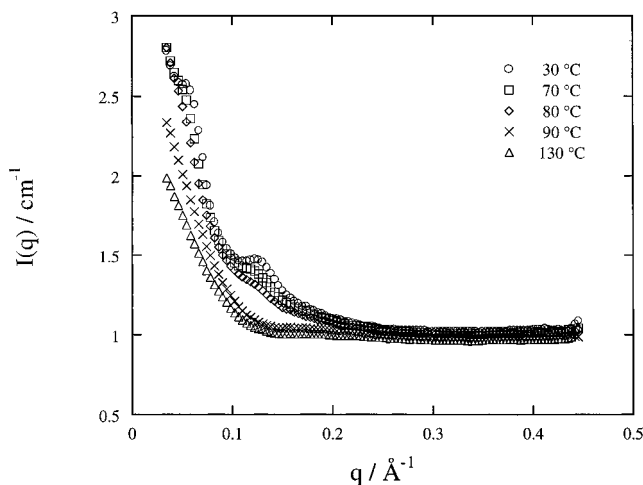


Figure 4. SANS of G5 dendrimers covalently modified with fatty acid between $T = 30$ and $130 \text{ }^\circ\text{C}$ in bulk. The shape of the scattering curve changes between 80 and $90 \text{ }^\circ\text{C}$.

crystallization, the density of the FA phase increases, changing the contrast factor, causing a mismatch. But the effect is small, even a 10% increase in the density will not add a significant contribution from the second term. Another possibility is that upon crystallization there is a segregation of the FAH and FAD dendrimers into H- and D-rich regimes. Such segregation upon crystallization has been seen for other isotopically labeled polymers such as polyethylene.⁵⁶

If segregation is occurring, then there is no longer a match condition, and a contribution of the total scat-

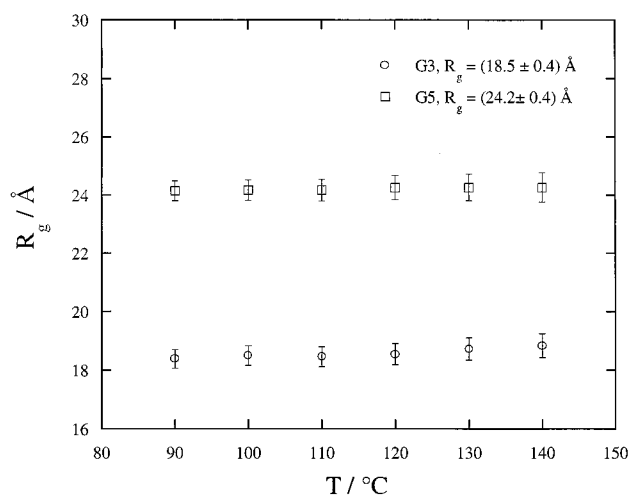


Figure 5. R_g of G3 and G5 dendrimers under matched conditions between 90 and $140 \text{ }^\circ\text{C}$.

tering will affect the match curve. If this is the case, then one of the assumptions used in generating the contrast match equations has been violated.^{49,50} The original assumption was that H and D substitution affects only the scattering contrast and not the spatial placement of the molecules. We will therefore only apply the equation to samples above the transition. Figure 5 shows the R_g values of the FA portions of the G3 and G5 samples in the bulk between 90 and $140 \text{ }^\circ\text{C}$. The values are independent of temperature in this range and are 18.5 ± 0.4 and $24.2 \pm 0.4 \text{ \AA}$, respectively.

In Figure 2 for the contrast match sample, there is a weak peak appearing at $q \approx 0.17 \text{ \AA}^{-1}$. This has been seen previously for large dendrimers⁵⁷ and is a higher order feature in the scattering of spherulike objects. It is not a result of mismatched samples since it is in a different position from the high contrast peak. Figure 6 is a Kratky plot of the scattering from the FA portion of the G5 dendrimer along with a uniform sphere and a thin shell having the same R_g . The SANS curve is smeared due to instrumental effects, and there can also be smearing due to polydispersity in the dendrimer shape as has been seen with dendrimers before.⁵⁸ This shape polydispersity can be present even if the molecular weight is monodisperse. However, it does seem that the scattering is between that of a sphere and a thin shell, which is consistent with a hollow structure (matched dendrimer) with a shell (FA).

Solution Samples. Solutions were made up of mixed decalin- h_{18} and decalin- d_{18} to match either the dendrimer or the FA of the covalent and ionic samples of both G3 and G5 dendrimers. Figure 7 is a log-log plot of scattered intensity of the dendrimer matched samples

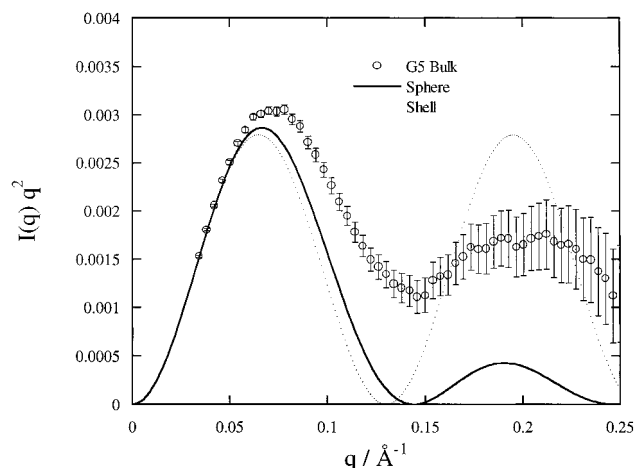


Figure 6. Kratky plots of the scattering from a G5 dendrimer under match conditions along with the theoretical scattering from a uniform sphere and a thin shell with the same R_g .

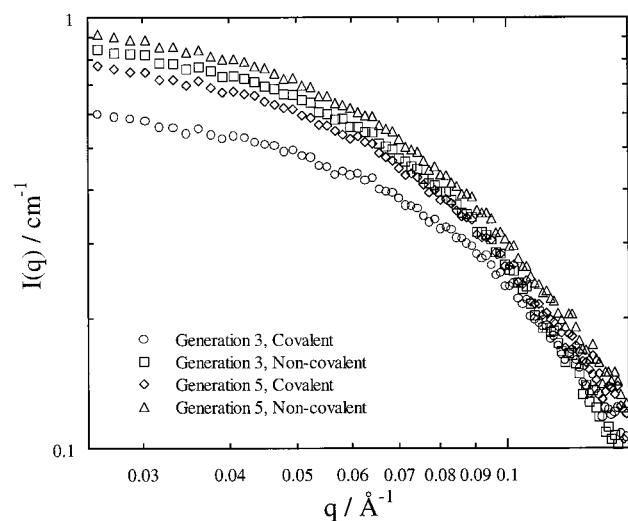


Figure 7. log-log plots of scattering from covalent and noncovalent G3 and G5 dendrimers.

G3 and G5, both covalent and noncovalent. The curves come together at high q but diverge at low q due to differences in R_g . Table 1 gives the parameters used in calculating the contrast match conditions. Fits were made as previously described, and the results are listed in Table 2. Also listed in Table 2 are the R_g values of the dendrimer that makes up the core as measured by SANS in D_2O .^{57,59} Calculations can be made from the data in Table 1 to give the size of dendrimer or fatty acid if the molecule was collapsed to bulk density, with all solvent being excluded from the molecule. These calculations assume the dendrimer is a sphere and the fatty acid is a hollow shell with the interior the size of a collapsed dendrimer.

The size of the dendrimer core in decalin solvent is close to the value of the collapsed structure and is always considerably lower than the value measured for the dendrimer alone in a good solvent. Due to the small size and the weak scattering of the samples at a match condition, the standard uncertainties are relatively large, but it does seem that the hydrophilic dendrimer cores collapse in the hydrophobic solvent. While the hydrophobic FA shell allows the dendrimers to be dispersed, the solvent does not enter the core. There is no consistent difference between the ionic and covalent results for the dendrimer core due to the large standard

uncertainties, but for the fatty acid shell, the covalent R_g is smaller than that of a noncovalent R_g of a dendrimer of the same type. For the covalent samples, the R_g is larger in the bulk than in solution.

The size of the FA shell shows differences between the G3 and G5 samples. The G3 FA shell for the covalent sample has a $R_g = 18.5 \pm 0.4 \text{ \AA}$ in the bulk, $16.3 \pm 0.9 \text{ \AA}$ in decalin, and 11.8 \AA if the whole structure was collapsed. The ionic version in decalin has $R_g = 19.3 \pm 0.3 \text{ \AA}$. Therefore, the solution size is expanded, as in the bulk. The G5 FA shell for the covalent sample has a $R_g = 24.2 \pm 0.4 \text{ \AA}$ in the bulk, $17.9 \pm 0.9 \text{ \AA}$ in decalin, and 18.9 \AA if the whole structure was collapsed. The ionic version in decalin has $R_g = 19.2 \pm 0.8 \text{ \AA}$. Therefore, the solution size is closer to that of a collapsed molecule. There is a general trend for the FA portions of the ionic samples to be larger than for the covalent samples, but the differences are small.

Conclusions

Contrast matching techniques have been used to measure the dendrimer and FA portions of fatty acid modified dendrimers. In the bulk, there is a dramatic change in the scattering shape, having a strong peak typical of a "correlation hole" of a block copolymer for the high contrast sample to that of single molecule scattering in the matched sample. Above the melting point of the FA chains, single-chain scattering allows calculation of R_g values, but below the melting point, the scattering still contains features of the high contrast scattering. This may be due to segregation of the H and D upon crystallization, and it prevents the calculation of R_g values. For the G5 sample, high q scattering shows a higher order feature typical of spherelike objects. The shape seems to be a result of a hollow sphere structure.

Solution scattering with matched dendrimer or FA gives the calculation of R_g of the two parts of the FA modified dendrimers. In decalin, the dendrimer core appears collapsed, without the incorporation of a significant amount of the solvent. The G3 FA portion has a size closer to that of the bulk than that of a collapsed FA shell. The G5 dendrimer has the opposite trend.

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