Segment Density Profiles in Dendrimers by SANS Analysis

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Dendrimer is in the limelight as new polymer materials since "Starburst-Dendritic Macromolecules" were synthesized by Tomalia et al. in 1984.[1]

We synthesized two dendrimers of fifth generation (G 5) with OH end groups. Poly (amido amine) dendrimer (PAMAM) comprises only hydrophilic units of amido-amine, while poly (trimethyleneimine) / mono (amido amine) layer-block dendrimer (PTMIN) is composed of hydrophobic core and hydrophilic shell as shown in Fig. 1. In this report, we discuss about the segment density and the solvent-filled void of the interia of the dendrimer in aqueous solutions by means of SANS method using external contrast variation technique.[2,3] The SANS measurements were carried out at room temperature using the small/medium-angle neutron diffractometer WINK in KEK. We choose dilute concentration of 1wt%, where the interdendrimer structure factor S(Q) can be ignored.

We observed that SANS intensities I(Q) vary with the mixing ratio of D_2O/H_2O in the 0-50%H_2O,. The apparent radii of gyration, which are obtained from the Guinier regions, decrease as the increase of the H_2O concentration. Similar result was observed for the both dendrimers. That means existence of segment distribution in dendrimer and solvent penetration into dendrimer. This is consistent with the results from Stuhrmann plot.[4]

We assume that spherical G 5 dendrimers consist of five concentric layers with each radius R_i as shown in Fig. 2. We assumed that each layer in the model has a homogeneous scattering length density (sld) ρ_i. Then, I(Q) is given by the following expression:

$$I(Q) \cong n_P P(Q) = n_P \left[\sum_{i=1}^{4} \left(\frac{4\pi R_i^3}{3} \right) (\rho_i - \rho_{i+1}) \left\{ \frac{3J_1(QR_i)}{QR_i} \right\} + \left(\frac{4\pi R_5^3}{3} \right) (\rho_5 - \rho_S) \left\{ \frac{3J_1(QR_5)}{QR_5} \right\} \right]^2, \quad (1)$$

where n_p is the number density of dendrimers, P(Q) intradendrimer structure factor, $J_1(x)$ the first order Bessel function, and ρ_s the mean coherent neutron sld of the solvent.[5] The contributions from the water penetrated into each layer are described by,

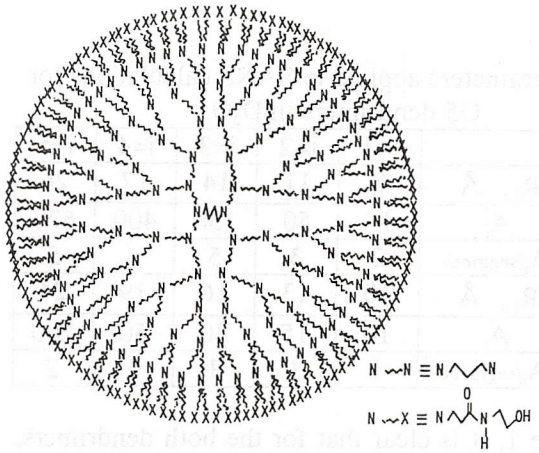

Fig. 1 Chemical structure of G5 PTMIN dendrimer with OH end groups.

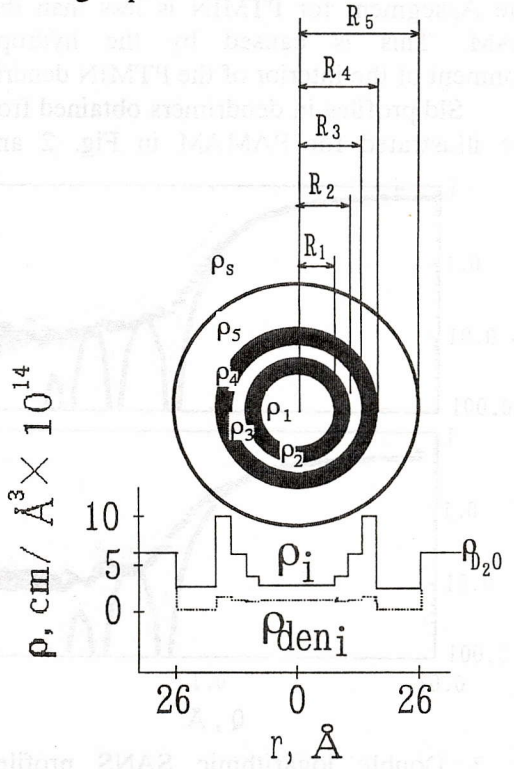

Fig. 2 Definition of concentric five layer model (upper) and sld profile (lower) of PAMAM in D_2O as a function of radial distance from the center.

$$\rho_i = \rho_{deni} + A_i \rho_S , \qquad (2)$$

where ρ_{deni} is the mean coherent neutron sld of dendrimer segment in the i-th layer and A_i the number density of solvent in the i-th layer.

The experimental results for the both dendrimers are shown in Fig. 3, together with the results of the fit using eqs. (1) and (2). The parameters thus obtained by the fit is shown in table 1. In this fit, it should be noted that all parameters are reasonable values for geometry of segment in dendrimer.

Table 1 Parameters applied to SANS calculations for G5 dendrimers in D_2O.

		i=1	i=2	i=3	i=4	i=5
PAMAM	R_i, Å	8	11	14	17	26
	A_i	15	50	150	400	620
	A_i/segment	2	3	5	6	5
PTMIN	R_i, Å	10	13	16	19	24
	A_i	10	15	30	50	200
	A_i/segment	1	1	1	1	2

From table 1, it is clear that for the both dendrimers, the out-most layer is the thickest due to the extension of segment chains. The penetrated water per segment residue A_i/segment for PTMIN is less than that for PAMAM. This is caused by the hydrophobic environment of the interior of the PTMIN dendrimer.

Sld profiles in dendrimers obtained from the fit are illustrated for PAMAM in Fig. 2 and for

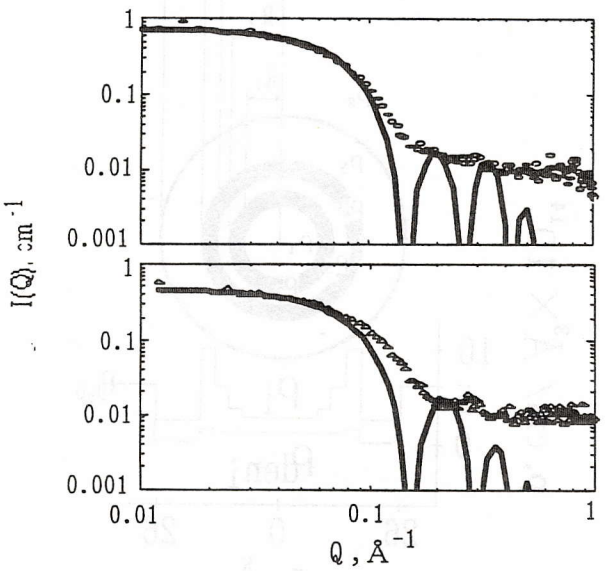

Fig. 3 Double logarithmic SANS profiles for PAMAM (upper) and PTMIN (lower) dendrimers in D_2O: plot, obserbed; solid line, calculated on five layer model with penetrated water.

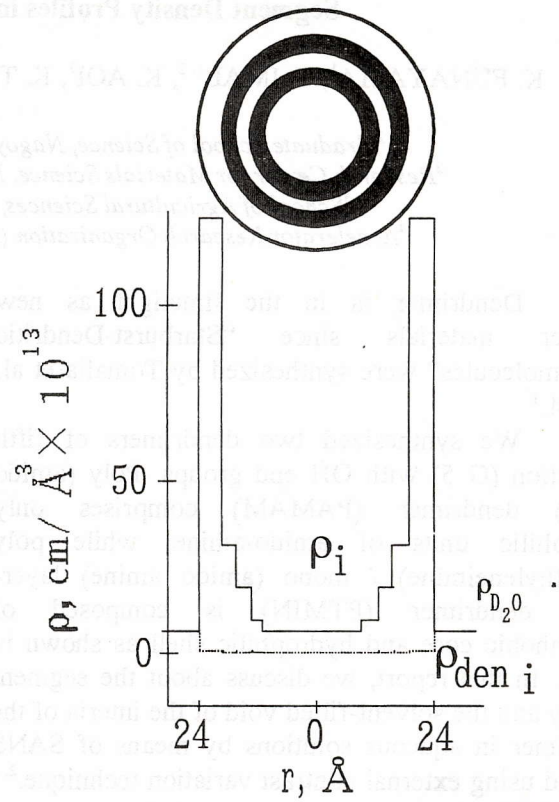

Fig. 4 Five layer geometry (upper) and sld profile (lower) of PTMIN in D_2O as a function of radial distance from the center

PTMIN in Fig. 4. For PAMAM, the sld is increased to forth layer because of increase of segment residue. However, the sld at fifth layer is significantly lower remarkably. That means that the density decrease due to segment chain extension is more dominant in comparison with the increase of segment residue at fifth layer. On another hand, the sld at fifth layer is the highest in the case of PTMIN. The reason is that density increase by segment chain extension is still prominent.

The advance of this investigation will introduce toward applications of doping small molecules into dendrimer.

References

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