Structural analysis of spherical water-soluble dendrimer by SANS

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Abstract

Small-angle neutron scattering (SANS) data for aqueous solutions of the fifth-generation poly(amido amine) dendrimer with hydroxyl end groups have been analyzed on the basis of the dendrimer geometry and the SANS theory. The calculation using a five-layer model with water penetration was the best fit with the observed one. At the exterior region in the dendrimer, the segment chains were extended, and the segment density was smaller. Therefore, the solvent-filled void was larger there. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The determination of dendrimer geometry, especially, the segment density and the solvent-filled void in dendrimer is meaningful in connection with the ability of the dendrimer doping small molecules. Some investigators have discussed the density distribution in dendrimers [1–4]. While it has been predicted that a segment distribution function has the highest density on the periphery [1], on the contrary, the highest density at the center and a decaying profile to the edge of dendrimer have been inferred [2,4]. On a report of Meltzer et al. [3], whole dendrimer density is lowest at the fifth- and sixth-generations, whereas the surface layer density increases with increasing generation.

Imae et al. [5] have visualized a spherical texture of the fifth-generation poly(amido amine) dendrimer (PAMAM) with hydroxyl end groups by an atomic force microscopy and elucidated the steric repulsion force acting between the dendrimers from surface force measurement. It has been found from the external contrast variation of small-angle neutron scattering (SANS) for aqueous dendrimer solutions that the apparent radius of gyration of the dendrimer is decreased as H_2O content in H_2O/D_2O mixed solvent is increased [6]. This means the water penetration into the dendrimer, indicating the existence of the solvent-filled void in the dendrimer. In the present work, the numerical

analysis of SANS is reported and the structural density distribution in the dendrimer is discussed.

2. Theoretical aspect

The SANS intensity $I(Q)$ for an aqueous dendrimer solution is written by

$$I(Q) = n_p P(Q) S(Q) \tag{1}$$

as a function of scattering vector amplitude Q [7]. n_p is the number density of dendrimers, and $P(Q)$ is the intradendrimer structure factor which depends on the dendrimer geometry. $S(Q)$, the interdendrimer structure factor, is supposed to be unity, when an aqueous dendrimer solution is so dilute as 1.0 wt.%.

The intraparticle structure factor for a hard sphere of radius R is described by

$$P(Q) = \left[\frac{4\pi R^3}{3} \left(\rho - \rho_s \right) \frac{3J_1(QR)}{QR} \right]^2, \tag{2}$$

where, ρ and ρ_s are the mean coherent neutron scattering length densities of a spherical particle and the solvent, respectively, and $J_1(x) = (\sin x - x \cos x)/x^2$ is the first-order Bessel function.

Supposing that a spherical dendrimer consists of concentric layers, as depicted in Fig. 1. The fifth-generation dendrimer consists of five layers, since the layers can be equalized to generations of a dendrimer. Then the intradendrimer structure factor is contributed by the terms from an

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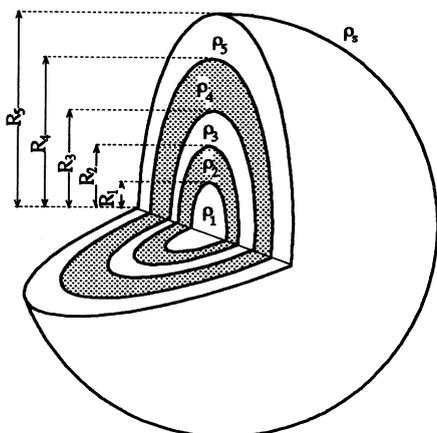
Fig. 1. Geometric definition of the spherical particle with concentric structure.

internal core of the radius R_1 and the surrounding shells with thickness of $R_i - R_{i-1}$ as follows:

$$P(Q) = \left| \sum_{i=1}^{4} \frac{4}{3} \pi R_i^3 (\rho_i - \rho_{i+1}) \frac{3 J_1(QR_i)}{QR_i} \right.$$

$$\left. + \frac{4}{3} \pi R_5^3 (\rho_5 - \rho_s) \frac{3 J_1(QR_5)}{QR_5} \right|^2, \tag{3}$$

where ρ_i is the mean coherent neutron scattering length density in the ith layer of a dendrimer.

If the solvent penetrates into the dendrimers, the mean coherent neutron scattering length density of a particle in Eq. (2) and an ith layer in Eq. (3) includes the contribution from the dendrimer and the penetrating solvent as

$$\rho = \rho_{den} + A\rho_s \tag{4}$$

and

$$\rho_i = \rho_{den_i} + A_i \rho_s, \tag{5}$$

respectively, where ρ_{den} is the mean coherent neutron scattering length density of the dendrimer, and A is the number density of the solvent in the dendrimer. The subscript i means the ith layer of a dendrimer.

If the mean coherent neutron scattering length density of the solvent water is changed by mixing D_2O with H_2O in the external contrast variation method,

$$\rho_s = (1 - \alpha)\rho_{H_2O} + \alpha\rho_{D_2O}, \tag{6}$$

where $1 - \alpha$ is the fractional number of H_2O molecules in the solvent, that is, percentage H_2O. ρ_{H_2O} and ρ_{D_2O} are the mean coherent neutron scattering length densities of H_2O and D_2O, respectively.

3. Results and discussion

Observed SANS intensities for a 1.0 wt.% solution of
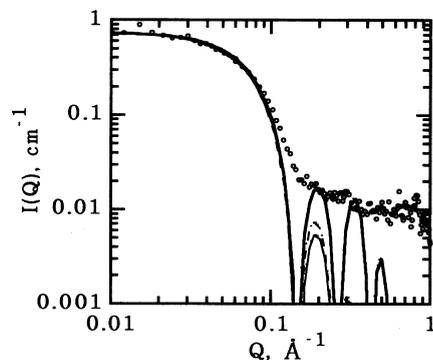
Fig. 2. Double logarithmic SANS intensity profile for a 1.0 wt.% solution of the fifth-generation PAMAM dendrimer with hydroxyl end group in D_2O. ○, observed Ref. [6]; thin solid line, calculated on hard sphere model with and without penetrated water; broken line, calculated on five-layer model without penetrated water; thick solid line, calculated on five-layer model with penetrated water.

fifth-generation PAMAM dendrimer with hydroxyl end groups in D_2O (0 v/v% H_2O) [6] are given in Fig. 2 as a function of scattering vector amplitude. The logarithmic SANS intensities are decreased first with upward curvature and then slowly, as the scattering vector amplitude is increased. The first trial of the calculation is based on the hard sphere model. The fitting curve calculated from Eqs. (1) and (2) was obtained at parameters $R = 30$ Å and $\rho = 0.5$, $\rho_s = \rho_{D_2O} = 6.4$ in 10^{-14} cm/Å^3 unit and is included in Fig. 2. However, the agreement with the observed one is not necessarily good at higher Q region.

The dendrimers are synthesized by a stepwise addition of unit to a starting core and the generations are formed. Therefore, it is assumed that the segment density in the dendrimer changes from core to exterior. Suppose that each generation is regarded as each layer, which has a mean-field density. Then Eq. (3) is applied for the fifth-generation dendrimer. The broken line in Fig. 2 represents the fitting curve with the parameters of $R_1 = 8$, $R_2 = 11$, $R_3 = 14$, $R_4 = 17$, $R_5 = 30$ in Å unit, $\rho_{den_1} = 1.4$, $\rho_{den_2} = 1.1$, $\rho_{den_3} = 1.3$, $\rho_{den_4} = 1.7$, $\rho_{den_5} = 0.2$ in 10^{-14} cm/Å^3 unit and $A_i = 0$. It is apparent that the agreement with the observed one is not found even from this model. Moreover, a value of $R_5 - R_4 = 13$ Å is too long for one generation.

The water penetration in the dendrimer has been supported from the external contrast variation of SANS for aqueous solutions of the fifth-generation PAMAM dendrimer with hydroxyl end groups [6]. Then the water penetration must be considered. Even if the contribution of the penetrated water is considered in Eq. (2) by using Eq. (4), the fitting curve is not improved, as seen in Fig. 2. However, on the five-layer model, when the parameters of $A_1 = 15$, $A_2 = 50$, $A_3 = 150$, $A_4 = 400$, $A_5 = 620$, $R_5 = 26$ in Å unit, and $\rho_{den_5} = 0.4 \times 10^{-14}$ cm/Å^3 unit are exchanged in Eq. (5), the best fitting curve is obtained, as shown in Fig. 2. The fitting is complete up to $Q = \sim 0.4$ A^{-1}.
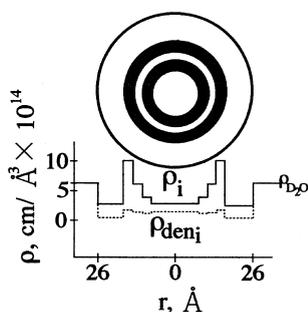
Fig. 3. Five-layer geometry (upper) and coherent neutron scattering density profile (lower) of the fifth-generation PAMAM with hydroxyl end group as a function of the radial distance from the concentric center.

A five-layer model with water penetration can be also applied to the analysis of SANS data for 1.0 wt.% solutions of the fifth-generation PAMAM dendrimer with hydroxyl end groups in 25 and 50 v/v% H_2O [6]. In Eq. (6), same parameters as those for a solution in 0 v/v% H_2O, except a $1 - \alpha(= 0.25$ or $0.5)$ value, are used for solutions of higher H_2O content. The fitting is better at lower scattering vector region, but less at higher scattering vector region.

Fig. 3 illustrates the profile of the neutron scattering length densities evaluated for the five-layer model under the consideration of water penetration. It can be elucidated that ρ_i is the largest at the fourth layer, while penetrated water is most dominant at the fifth layer. This is interpreted from the geometric structure of the dendrimer. The most exterior in concentric layers is the thickest, as seen in

Fig. 3, indicating the extension of segment chains in exterior portion of the dendritic structure as estimated. ρ_{den_i} is almost proportional to the segment density, and smaller at exterior region in the dendrimer in relation to the segment chain extension. Then, the water penetration and solvent-filled void are expected to decrease from exterior to interior. ρ_i, which is contributed by the segment density and penetrated water, becomes thus the highest at the fourth generation. It should be noted that the segment density profile in the present work is slightly different from previous reports [1–4].

Acknowledgements

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