SANS Analysis of a Novel Star-Shaped Dendrimer[1)]

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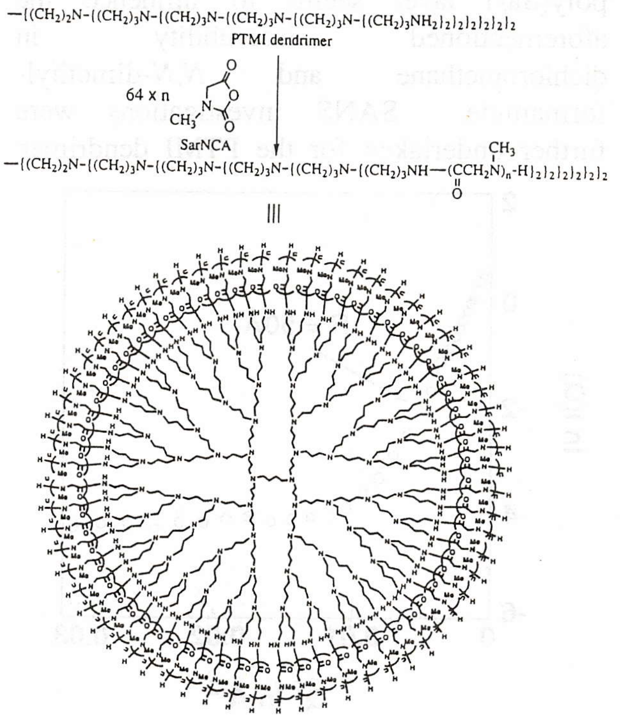
Since spherical molecules have some remarkable features such as a molecular capsule and a ball bearing, fullerene, dendrimers, and microspheres have been paid much attention in a wide range of fields from molecular science to materials science. Diameters of common dendrimers (ca. < 10 nm) are intermediate between those of fullerene (7 Å) and microspheres (0.1 - 10 μm). Homodendrimers are generally known to have a limitation of molecular size due to increasing defects of branching or incomplete coupling of high-generational dendrons. Especially, dendrimers with a short interbranch-point distance have a small molecular size, whereas small dendrimers possess attractive characters, e.g., a molecular capsule and regulated molecular shape. Poly(trimethyleneimine) (PTMI) dendrimer[2)], namely poly(propyleneimine) dendrimer[3)], is an important dendrimer for the purpose of derivatization to enlarge the globular shape by introducing a block structure.

A novel AB_n-type dendrimer/linear polymer block copolymer, i.e., poly(trimethyleneimine) dendrimer (poly(propyleneimine) dendrimer)-*block*-(polysarcosine)$_{64}$ (**1**), was synthesized by ring-opening polymerization of sarcosine *N*-carboxyanhydride initiated by 64-NH_2-terminal poly(trimethyleneimine) dendrimer as a macroinitiator. **1** has narrow molecular weight distributions ($M_w/M_n = 1.0_1$-1.0_3, by size exclusion chromatography) and controlled polysarcosine chain lengths by monomer/dendrimer feed molar ratios.

1 was soluble in methanol, dimethyl sulfoxide, and water in a concentration of 1.0 g/L. Poly(Sar) homopolymer was also dissolved in these solvents. Contrary to our prediction, **1** was insoluble in dichloromethane and *N,N*-dimethylformamide, which are solvents for poly(Sar). It is probably due to formation of a relatively dense shell of poly(Sar) (*vide infra*).

Molecular size and shape of the linear polymer-hyperlinked dendrimer **1** was examined by a SANS study[4)]. SANS is a powerful methodology to determine size and shape of a nanoscale physical structure.

The SANS measurements were made using the cold neutron small-angle scattering instrument WINK at the High Energy Accelerator Research Organization, Tsukuba, Japan. The instrument was operated at a neutron radiation of 1-16 Å wavelength at 25 °C, using a rectangular quartz cell of dimensions 22 x 40 x 2 mm. The SANS



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intensities were obtained as a function of scattering vector Q (= $(4\pi/\lambda)\sin(\theta/2)$, where λ and θ are the neutron radiation wavelength and the scattering angle, respectively). The radii were calculated from a slope of a representation of intensity I(Q) versus Q^2 in the Guinier regime ($I(Q) = I_0\exp(-R_G{}^2Q^2/3)$) and an equation ($R_G{}^2 = 3R^2/5$) for a spherical particle model, where I_0, R_G, and R are a constant, a radius of gyration, and a radius of a spherical particle, respectively.

Fig. 1 shows a Guinier plot of SANS data of a D_2O solution of **1** (DP of poly(Sar) = 24) at a concentration of 1.0 wt%. We can see that logarithmic I(Q) values decrease linearly with increasing Q^2 at Q = 0.024 - 0.1 Å^{-1}. From equations for spherical particles described in the experimental section, the radius of **1** (DP = 24) was obtained to be 50 Å (Fig. 2). The calculated values of the radius of **1** were 39 and 89 Å, employing three-dimensionally contracted and extended Corey-Pauling-Koltum (CPK) models, respectively. Therefore, it was found that **1** (DP = 24) had a relatively shrink structure in an aqueous solution. The tendency to form a dense poly(Sar) layer seems to influence the aforementioned insolubility in dichloromethane and *N,N*-dimethylformamide. SANS investigations were further undertaken for the PTMI dendrimer

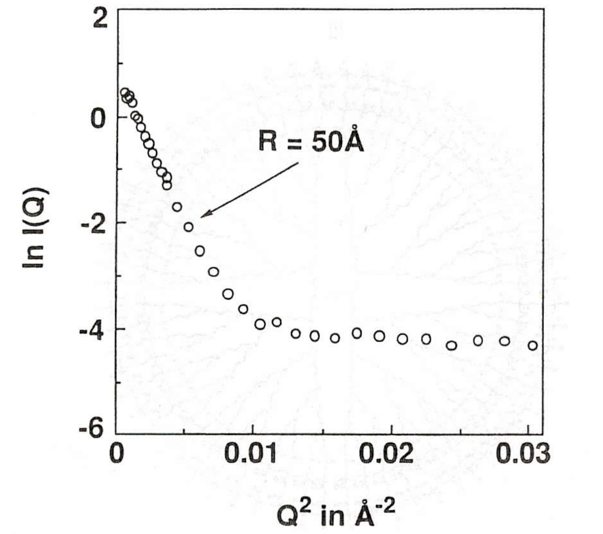

Fig. 1. Guinier plots of SANS intensity of 1.0 wt% D_2O solution of star-shaped dendrimer **1** at 25 °C.

and PTMI dendrimer-*block*-oligosarcosine **1** (DP = 2.0), to afford the radii of 17 and 22 Å, respectively. The former value is comparable to that reported by Ramzi et al.[5] (R = 18 Å), and the latter value is acceptable for the PTMI dendrimer with two repeating units of sarcosine.

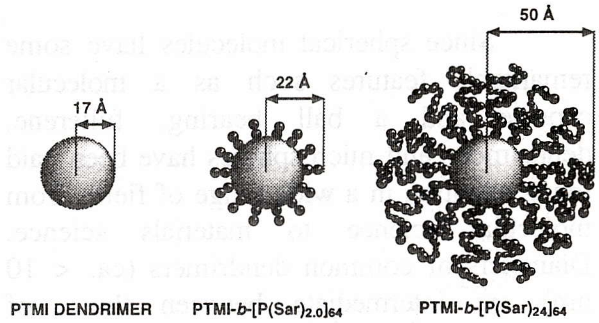

Fig. 2. Schematic illustrations of a) poly(trimethyleneimine) dendrimer and star-shaped dendrimers **1** ; b) DP of poly(Sar) = 2.0; c) DP of poly(Sar) = 24, on the basis of the SANS analysis.

The results obtained in this study have a fundamental significance that construction of nanometer-scale spherical polymers with narrow size distributions will be easily achieved by the synchronized multiple-propagation with dendritic initiators[6], instead of conventional living polymerizations producing high-molecular-weight polymers from extra-purified monomers.

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