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, namely poly(propyleneimine) dendrimer, is an important dendrimer for the purpose of derivatization to enlarge the globular shape by introducing a block structure.

A novel ABn-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-NH2-terminal poly(trimethyleneimine) dendrimer as a macroinitiator. 1 has narrow molecular weight distributions ($M_w/M_n = 1.01-1.03$, 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. 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
intensities were obtained as a function of scattering vector \( Q \) (4π/\( λ \) sin(\( θ /2 \)), 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 \( I \) (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 \( Q = 0.024 - 0.1 \, \text{Å}^{-1} \). From equations for spherical particles described in the experimental section, the radius of \( I \) (DP = 24) was obtained to be 50 Å (Fig. 2). The calculated values of the radius of \( I \) were 39 and 89 Å, employing three-dimensionally contracted and extended Corey-Pauling-Koltun (CPK) models, respectively. Therefore, it was found that \( I \) (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 \( N,N-\text{dimethylformamide} \). SANS investigations were further undertaken for the PTMI dendrimer and PTMI dendrimer-block-oligosarcosine \( I \) (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) \( (R = 18 \, \text{Å}) \), and the latter value is acceptable for the PTMI dendrimer with two repeating units of sarcosine.

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 initiators6), instead of conventional living polymerizations producing high-molecular-weight polymers from extra-purified monomers.

Acknowledgement: The authors express their sincere gratitude to Professor M. Furusaka and Dr. T. Otomo of the High Energy Accelerator Research Organization for the SANS measurement.

References