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Characterizations of Sugar Ball in Solution by SANS and NSE

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Overall static and dynamic characterizations of the dendrimer are expected to be modified through changing the internal and terminal chemical structures of the dendrimer. In the present study, the aqueous solutions of the fifth generation glycopeptide-type sugar ball at 1 and 10 wt% dendrimer concentrations, which show different small-angle neutron scattering profiles, were measured by neutron spin echo. The diffusion behaviors were found to depend on dendrimer concentration, as well as for the solutions of fifth generation poly(amido amine) dendrimer with hydroxyl terminals. A slow relaxation mode was obtained at high concentration but the fast and slow modes were at low concentration. It was concluded that the slow mode is translational diffusion of dendrimer and the fast one due to segment motion in dendrimer. Since the fast mode was found for both dendrimer solutions, that will be specific dynamics originated by amido-amine unit in dendrimer, which is common in both dendrimers.

KEYWORDS: sugar ball, dendrimer, small-angle neutron scattering, neutron spin echo, dynamics

§1. Introduction

Dendrimer, which is one of three-dimensional highly-branched polymers, has been given attention as a novel class of macromolecules.[1,2] In recent years, numerous effort has been given for the developments on synthesis, characterization and theoretical analysis for dendrimers.

Static structural investigations on dendrimer were performed by means of small-angle neutron scattering (SANS). Bauer *et al.*[3] discussed the size of poly(amido amine) (PAMAM) dendrimer by SANS. SANS studies of solutions with added acid were done for PAMAM dendrimer by Briber *et al.*[4] and for poly(propylene imine) dendrimer by Ramzi *et al.*[5] They discussed intermolecular interactions as a function of dendrimer and ion concentrations. SANS experiments by Scherrenberg *et al.*[6] were performed for poly(propylene imine) dendrimer with two types of terminals and the dimension of the dendrimer was determined. The density profiles of PAMAM dendrimer by Imae and coworkers[7,8] and of layer-block dendrimer by Pötschke *et al.*[9] were investigated by means of the external contrast variation of SANS. Topp *et al.*[10] synthesized partially deuterated PAMAM dendrimer and discussed the spatial distribution of terminals of the dendrimer by SANS.

Only few studies have been made on dynamic behavior of dendrimer. Dynamics by quasielastic neutron scattering was studied by Stark *et al.*[11] for carbosilane dendrimer with perfluorohexyl terminals. Funayama *et al.*[12] discussed dependence of dynamics on concentration of PAMAM dendrimer with hydroxyl terminals by neutron spin echo (NSE). Overall characterizations of dendrimer are expected to be modified through changing the internal or terminal chemical structure of dendrimer.[13]

In this study, SANS and NSE measurements were performed for the aqueous solutions of the fifth generation PAMAM dendrimer with glycopeptide terminals. Obtained results were then compared with those of the fifth generation PAMAM dendrimer with hydroxyl terminals, which was discussed in the separate paper.[12] The terminals of both dendrimers are hydrophilic but have difference as regarding spatial conformation of themselves.

§2. Experimental Section

2.1 *Materials*

The fifth generation sugar ball (galactose-having glycopeptide-type PAMAM dendrimer), as shown in Fig. 1, was synthesized according to the previous method.[14,15] 1 and 10 wt% solutions of sugar ball were prepared in 99.75 % deuterium oxide, which was purchased from Wako Pure Chemical Industries, Ltd. From dynamic light scattering (DLS) measurements for a 1 wt% solution of sugar ball, the translational diffusion coefficient D_0 and the hydrodynamic radius R_h were decided to be 4.4×10^{-11} m^2 s^{-1} and 54 Å, respectively.

2.2 *Measurements*

The SANS experiments were made using the SANS-U diffractometer at JRR-3M (Tokai, Japan). The instrument was operated at room temperature (~ 25 °C). The incident neutron beam wavelength was $\lambda = 7.0$ Åwith a wavelength resolution $\Delta\lambda/\lambda = 10$ %. The sample-detector was placed in 1, 4 and 8 m. The solutions were contained in the rectangular quartz cells. For aqueous dendrimer solutions, the SANS intensity $I(Q)$ as a func-

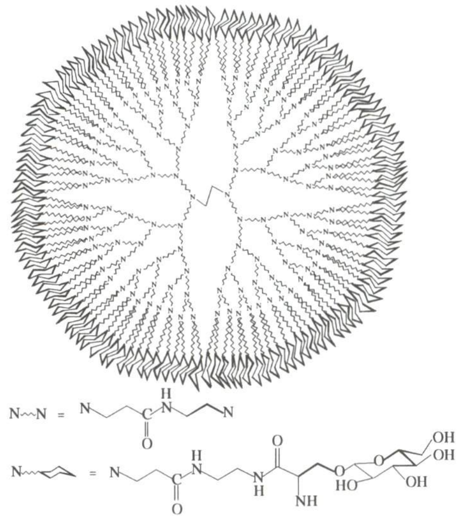

Fig. 1. Chemical structure of the fifth generation galactose-having glycopeptide-type sugar ball.

tion of scattering vector Q is expressed as[16)]

$$I(Q) = N_\mathrm{p} P(Q) S(Q), \tag{2.1}$$

where N_p is the number density of dendrimer, $P(Q)$ is the form factor and $S(Q)$ is the interdendrimer structure factor.

The NSE measurements were performed at room temperature (~ 25 °C) using NSE spectrometer at JRR-3M. Neutrons with wavelength $\lambda = 7.1$ Å$(\Delta\lambda/\lambda = 18\%)$ were used in the present measurements. The solutions were filled in the rectangular quartz cells. The intermediate correlation functions $I(Q,t)$ were normalized by elastic scattering intensity $I(Q,0)$ at each Q, where t is time. In simple system, where there is a relaxation time due to the translational diffusion D of particle, $I(Q,t)/I(Q,0)$ is given by a single-exponential equation[17)] such as

$$I(Q,t)/I(Q,0) = \exp(-\Gamma(Q)t), \tag{2.2}$$

where $\Gamma(Q)$ is a decay rate, which is expressed as

$$\Gamma(Q) = DQ^2. \tag{2.3}$$

§3. Results and Discussion

Observed SANS intensities $I(Q)$ for 1 and 10 wt% solutions of sugar ball are given in Fig. 2 as a function of scattering vector Q. The SANS profiles depend on dendrimer concentration. This dependence is due to interdendrimer structure factor $S(Q)$. The interdendrimer interaction can be almost neglected for a dilute solution as 1 wt%.[5,7,8)] $I(Q)$ for a 1 wt% solution can, consequently, be approximated to $N_\mathrm{p}P(Q)$ in Eq. (2.1). Then NSE measurements were carried out for the Q range $(0.02 \le Q \le 0.1)$ of interest, where remarkable effect of $S(Q)$ were exhibited. Fuller discussion of $S(Q)$ will be presented in the succeeding paper.

The normalized intermediate correlation functions $I(Q,t)/I(Q,0)$ for sugar ball solutions were obtained at $Q = 0.02$ to 0.1 Å^{-1} and $t = 0.15$ to 15 ns. The results for a 10 wt% solution can be obeyed to a single-exponential equation in Eq. (2.2), as seen in Fig. 3 (a). Nevertheless, $I(Q,t)/I(Q,0)$ for a 1 wt% solution don't become unity with extrapolation to $t \to 0$ under Eq. (2.2), as shown

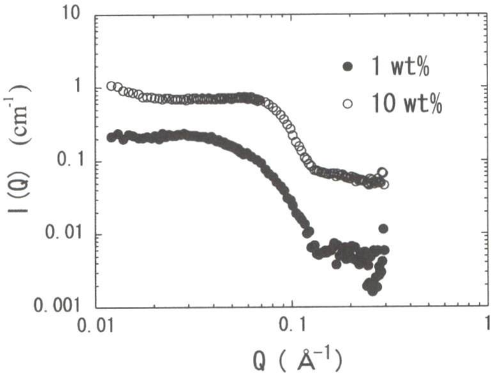

Fig. 2. Double logarithmic plots of SANS intensities $I(Q)$ versus scattering vector Q for 1 and 10 wt% solutions of the fifth generation sugar ball.

in Fig. 3 (b). The contribution of the fast mode has to be, therefore, considered using a double-exponential equation written as

$$\begin{aligned} I(Q,t)/I(Q,0) &= f_\mathrm{S}\exp(-\Gamma_\mathrm{S}(Q)t) \\ &\quad + f_\mathrm{F}\exp(-\Gamma_\mathrm{F}(Q)t), \\ f_\mathrm{S} + f_\mathrm{F} &= 1 \end{aligned} \tag{3.1}$$

and,

$$\Gamma_\mathrm{S}(Q) = D_\mathrm{S}Q^2, \Gamma_\mathrm{F}(Q) = D_\mathrm{F}Q^2, \tag{3.2}$$

where f is a fraction of the contribution of the each decay mode, and subscripts S and F denote fast and slow modes, respectively.[12,19,20)] The results for a 1 wt% solution could be fitted better with Eq. (3.1) than Eq. (2.2). Figure 3 (b) shows the fit curves obtained from Eq. (3.1). This indicates that dynamic behavior for a dilute dendrimer solution has two modes with different values of decay time and is different from that of a semidilute solution. Furthermore, the dependence of dynamics on dendrimer concentration for sugar ball solutions is similar to that of PAMAM dendrimer with hydroxyl terminals.[12)]

Now, one compares the diffusion coefficient D for a 10 wt% solution estimated from Eqs. (2.2) and (2.3) with D_S for a 1 wt% solution from Eqs. (3.1) and (3.2), since both diffusion behaviors are of slow relaxation modes. Figure 4 shows diffusion coefficients of slow modes for 10 and 1 wt% solutions as a function of Q. Around high Q region, the values of diffusion coefficients are approximately constant for both dendrimer concentrations. The averaged value are somewhere corresponding to the translational diffusion coefficient D_0 determined from DLS, as mentioned in Experimental section. For lower Q ranges, however, the diffusion coefficient increases with decreasing Q. That is more prominent for a 10 wt% solution. The averaged distance between molecules, if the dendrimers are assumed to disperse homogeneously in the solution at 10 wt%, is evaluated about 120 Å, equivalent to $Q \approx 0.05$ Å^{-1}. Q-dependence of the diffusion coefficient was found below $Q \sim 0.05$ for a 10 wt% solution. Therefore it was explained by the effect of interdendrimer interaction, as well as that for PAMAM dendrimer reporting separately.[12)] The optimum values of the other parameters except Γ_S and D_S on Eqs. (3.1) and (3.2) considered fast and slow modes for a 1 wt%

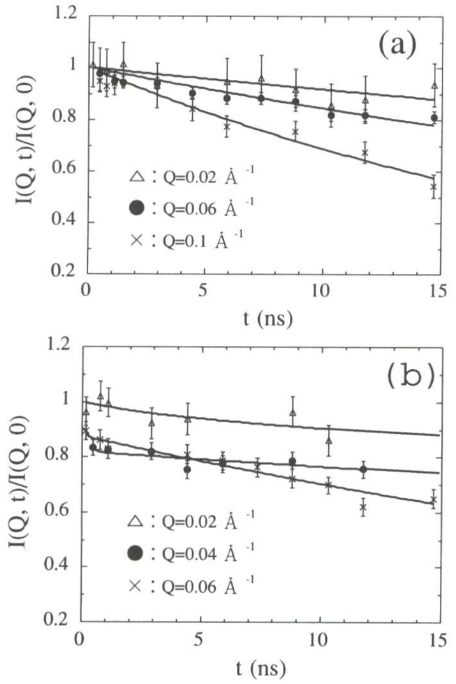

Fig. 3. Normalized intermediate correlation functions $I(Q,t)/I(Q,0)$ as a function of time t for 10 wt% (a) and 1 wt% (b) solutions of fifth generation sugar ball: Solid lines are Eqs. (2.2) (a) and (3.1) (b), respectively.

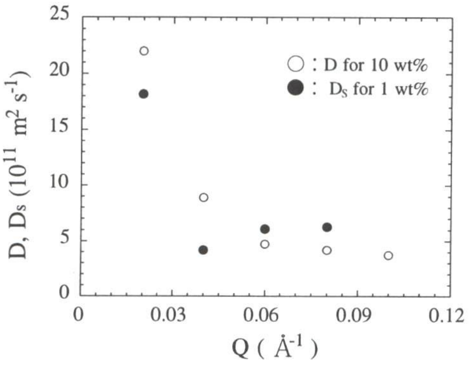

Fig. 4. Diffusion coefficient D or D_S as a function of Q for 1 and 10 wt% solutions of the fifth generation sugar ball.

Table I. Parameters obtained from the theoretical equations (Eqs. (3.1) and (3.2)) for a 1 wt% solution of the fifth generation sugar ball.

Q (Å^{-1})	f_S	f_F	Γ_F (ns^{-1})	D_F ($10^{-11} \times$ m^2 s^{-1})
0.02	0.96	0.04	0.43	1100
0.04	0.82	0.18	4.9	3100
0.06	0.87	0.13	12	3200
0.08	0.77	0.23	1800	280000

solution are listed in Table I. The contribution f_F (0.23) of the fast mode at high Q is large as compared with one (0.04) at low Q, suggesting that the fast mode is owing to the microscopic motion. In the present system, the segment motion in sugar ball is taken as the microscopic one. Moreover, the contributions f_F of the fast mode are much smaller than f_S of the slow mode. For a 10 wt% solution, the fast mode can not be observed, because the contribution of the fast mode is much lower as compared with that of slow mode including the effect of interdendrimer interaction. The fast mode at a dilute solution was also observed for PAMAM dendrimer with hydroxyl terminals.$^{12)}$ Since the fast mode was actually found for the solutions of both dendrimers with different terminals, it seems reasonable to conclude that segment motion is specific dynamics originated by amido-amine unit in dendrimer, which are included in both dendrimers.

§4. Conclusions

The dynamics were found to depend on concentration of sugar ball in solutions, as well as that of PAMAM dendrimer with hydroxyl terminals.$^{12)}$ Namely, the effects of terminals on dynamic behavior was not observed by the view of NSE experiments, although static behavior by SANS depends on nature of terminals.$^{18)}$ The dynamics of dendrimers consisting of amido-amine unit might be caused by properties of internal chemical structure.

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