The NMR Spectroscopic Evaluation of Immobility of a Crowd of Porphyrin Rings Combined with Dendritic Poly(L-lysine)s

Tamaki Kato, Naoki Maruo, Hideo Akisada,† Toru Arai, and Norikazu Nishino*
Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550
†*Department of Environmental Chemistry, Faculty of Engineering, Kyushu Kyoritsu University, Kitakyushu, 807-8585*

(Received February 16, 2000; CL-000160)

Since the dendritic poly(L-lysine)s combining eight to thirty-two free base-porphyrins showed split circular dichroism at the Soret band in toluene/*N*,*N*-dimethylformamide (9/1, v/v), the immobility of porphyrin rings was evaluated by ^{1}H NMR measurements in terms of the peak width at half-height and spin-lattice relaxation time.

We previously reported the synthesis of interesting macromolecules, namely dendritic poly(L-lysine)s combining a crowd of porphyrin rings in a certain stratum (Figure 1).[1–3] The porphyrin rings in such a complex macromolecule showed split circular dichroism (CD) in some nonpolar solvents, while *N*,*N*-dimethylformamide (DMF), a good solvent to the polyamide linkage, induced no CD at porphyrin absorption band. In contrast, the increasing content of toluene, a poor solvent to polyamide, afforded extremely strong split CD at the Soret band. For example, compound **2** showed no CD in DMF but strong split CD ($[\theta]_{410} - [\theta]_{428}$= 1.6 × 10^6 deg cm^2 dmol^{-1}) in toluene/DMF (9/1, v/v) (Figure 2).[1] The CD experiments suggested that toluene decreased the mobility of porphyrin rings in dendritic poly(L-lysine)s and affected to immobilize at least a pair of porphyrin rings in right handed sense according to Nakanishi's "exciton chirality method".[4] The elucidation of such solvent-depending arrangement of porphyrin rings by various physicochemical measurements is necessary for the design of functional materials based on dendritic polymers.

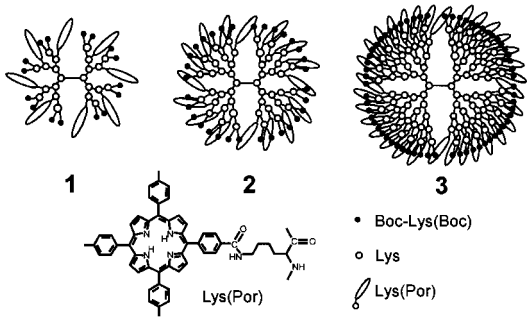

Figure 1. Illustration of dendritic poly(L-lysine)s combining porphyrins.

In order to understand the relationship between solvent conditions and split CD, we attempted to evaluate the immobility of the porphyrin rings on dendritic poly(L-lysine)s by ^{1}H NMR measurements in the present study. Especially, the peak width at half-height and the spin–lattice relaxation time (T_1) in the NMR spectra are often determined to evaluate the mobility of a specific functional group in a macromolecule.[5–10] We determined them in various mixed solvents of toluene-d_8 and DMF-d_7 by considering the effect of toluene on the strong split CD of the porphyrin rings on dendritic poly(L-lysine)s.

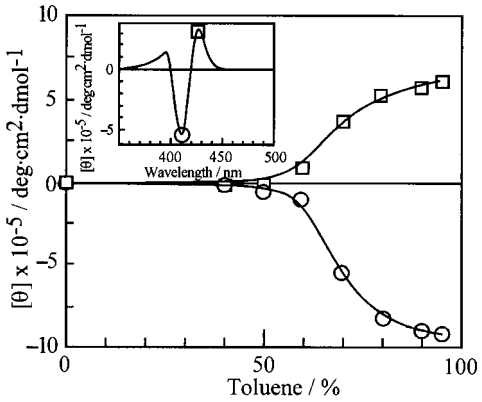

Figure 2. Intensity of CD peaks of **2** at 410 nm (○) and 428 nm (□) on toluene content. Inset: CD spectra of **2** in toluene/DMF(7/3, v/v).

Compounds **1**-**3** were prepared by the method described previously.[1] The ^{1}H NMR measurements were carried out using JEOL JNM-A500 (500 MHz) with a concentration of 0.2% at 30 °C. The peak widths at half-height of all peaks in the NMR spectra of compounds **1**–**3** in DMF-d_7 were wider than those of Boc-Lys(Por)-OH, a reference compound, and were further gradually broadened along with the increase in toluene-d_8 content (Figure 3). In toluene-d_8/DMF-d_7 (9/1, v/v), all peaks measured in the NMR were significantly broadened than those in DMF-d_7. For example, the peak width at half-height of the proton peak in **2** due to the β-pyrrole proton was 150 Hz in toluene-d_8/DMF-d_7 (9/1, v/v), while it was less than 60 Hz when the toluene-d_8 content did not exceed 70% (Figure 3). Such solvent dependent peak width broadening was also observed for **1** and **3** (Figure 3). It should be noted that the

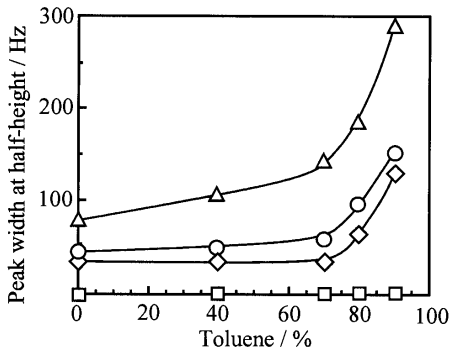

Figure 3. Peak widths of β-pyrrole protons at half-height of **1** (◇), **2** (○), **3** (△), and Boc-Lys(Por)-OH (□) on toluene content.

intermolecular aggregation is negligible because the sample dilution (1/10) caused almost no change in peak width. The peak widths for Boc-group at half-height from **1**, **2**, and **3** also showed almost same solvent dependence (data not shown). Actually, the peak width for Boc-group of **2** was 230 Hz in toluene-d_8/DMF-d_7 (9/1, v/v) and it became less than 30 Hz when the toluene-d_8 content was decreased to 70%. The peak widths at half-height of the peaks due to the pyrrole and Boc-groups in Boc-Lys(Por)-OH, a reference compound, did not exceed 20 Hz in any toluene-d_8 content. The observation of solvent dependence in CD study[1] was discussed to be attributed to the immobilization of porphyrin rings in toluene-rich solvent, and again confirmed by NMR measurements. The increasing content of toluene could enforce the backbone of poly(L-lysine)s to shrink together with porphyrin rings. In addition, the peak widths at half-height of the proton peaks in **1**, **2**, and **3** attributed to the β-pyrrole proton in toluene-d_8/DMF-d_7 (7/3, v/v) became more broadened consistently with the growth in molecular weights of dendritic poly(L-lysine)s (Figure 4). The crowdedness of porphyrin rings and the thickness of dendritic poly(L-lysine)s may reduce the mobility of the porphyrin rings and Boc-group on the surface of the dendritic macromolecule.

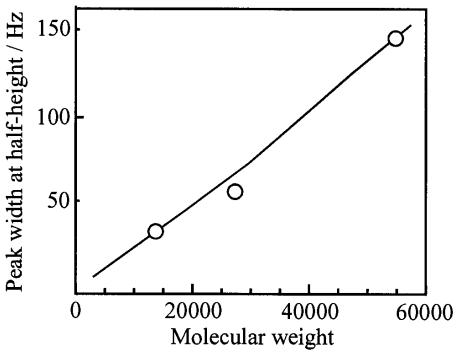

Figure 4. Dependence of peak widths of β-pyrrole protons at half-height on molecular weight in toluene / DMF (7/3, v/v).

If the overall mobility of the dendritic poly(L-lysine) molecule was significantly depressed in toluene-d_8/DMF-d_7 (9/1, v/v), the porphyrin rings might be brought in different environments. In such situation, the significant broadening may not reflect the precise mobility of the porphyrin rings in the dendrimer because each porphyrin ring in different environments does not show the same chemical shift. To ascertain the immobility of the porphyrin rings in dendritic poly(L-lysine)s depending on the toluene-d_8 content, we carried out the T_1 measurement. The T_1 of the peak attributed to the β-pyrrole proton of compound **2** was 1900 ms in DMF-d_7. When the toluene-d_8 content increased to 70%, T_1 value was decreased a little to 1830 ms. The T_1 value significantly decreased to 1470 ms in toluene-d_8/DMF-d_7 (9/1, v/v) (Figure 5). Again, we observed the dependence of T_1 on toluene-d_8 content.

Thus we could find out clear relationship between the split CD and the mobility measured by NMR in terms of the peak width at half-height and T_1 on the circumstances of the crowd of porphyrin rings on a dendritic poly(L-lysine). Tomoyose et al. demonstrated that the mobility of the porphyrin ring in the center of the dendrimer remains almost intact upon increment of the number of generations, whereas protons in the exterior

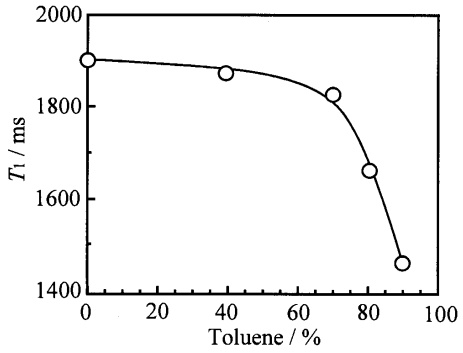

Figure 5. Spin-lattice relaxation time (T_1) of β-pyrrole protons on Toluene content.

surface become less mobile by the ^{1}H NMR T_1 measurement.[6] Meltzer et al. demonstrated that the T_1 values of the terminal carbons were decreased with increasing molecular weight but the T_1 values of the carbons in the molecular interior were found to decrease initially with molecular weight but were independent of molecular weight above the second generation of their dendrimers in their ^{13}C NMR T_1 measurement.[7] In our study, the mobility of porphyrin ring and Boc-group was decreased according to the number of generation, probably because that they exist near the surface of the macromolecule and tend to be effected by the solvent conditions.

In the present study, we succeeded to evaluate the immobility of the porphyrin rings in dendritic poly(L-lysine)s depending not only on the molecular size but also on the solvent component by NMR measurements. Both of the results of the evaluation were consistent with the assumption made by CD experiment and suggested that the crowdedness around the porphyrin rings caused the immobility.

References and Notes

1 N. Maruo and N. Nishino, *Kobunshi Ronbunshu*, **54**, 731 (1997).
2 N. Maruo, M. Uchiyama, T. Kato, T. Arai, H. Akisada, and N. Nishino, *Chem. Commun.*, **1999**, 2057.
3 T. Kato, M. Uchiyama, N. Maruo, T. Arai, and N. Nishino, *Chem. Lett.*, **2000**, 144.
4 K. Nakanishi and N. Berova, in "Circular Dichroism-Principles and Applications," ed. by K. Nakanishi, N. Berova, and R. W. Woody, VCH Publishers, Inc., New York (1994), Chap. 13, p. 361; X. Huang, B. H. Rickman, B. Borhan, N. Berova, and K. Nakanishi, *J. Am. Chem. Soc.*, **120**, 6185 (1998); S. Matile, N. Berova, K. Nakanishi, J. Fleischhauer, and R. W. Woody, *J. Am. Chem. Soc.*, **118**, 5198 (1996).
5 A. M. Naylor, W. A. Goddard III, G. E. Kiefer, and D. A. Tomalia, *J. Am. Chem. Soc.*, **111**, 2339 (1989).
6 Y. Tomoyose, D.-L. Jiang, R.-H. Jin, T. Aida, T. Yamashita, K. Horie, E. Yashima, and Y. Okamoto, *Macromolecules*, **29**, 5236 (1996).
7 A. D. Meltzer, D. A. Tirrell, A. A. Jones, P. T. Inglefield, D. M. Hedstrand, and D. A. Tomalia, *Macromolecules*, **25**, 4541 (1992).
8 A. D. Meltzer, D. A. Tirrell, A. A. Jones, and P. T. Inglefield, *Macromolecules*, **25**, 4549 (1992).
9 J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, and E. W. Meijer, *Science*, **266**, 1226 (1994).
10 D.-L. Jiang and T. Aida, *J. Am. Chem. Soc.*, **120**, 10895 (1998).