Supramolecular Polymers Formed by Bifunctional Cyclodextrin Derivatives

Atsuhisa Miyawaki, Yoshinori Takashima, Hiroyasu Yamaguchi, and Akira Harada*
Department of Macromolecular Science, Graduate School of Science,
Osaka University, Toyonaka, Osaka 560-0043

(Received April 10, 2007; CL-070387; E-mail: harada@chem.sci.osaka-u.ac.jp)

The mixture of monofunctional and bifunctional cyclodextrin derivatives formed branched supramolecular polymers, which showed an increase in the viscosity of aqueous solution. However, a monofunctional cyclodextrin derivative did not form viscous solutions. It is caused by the crosslinking of linear supramolecular polymers through hetero-type inclusion and some intermolecular interactions.

Preparation of supramolecular structures in aqueous environments is one of the most versatile approaches for developing new dynamic systems.[1] Many kinds of supramolecular polymers linked by appropriate interactions including metal coordinations, hydrogen bonds, and/or hydrophobic interactions have been reported by the efforts of synthetic chemists in recent years.[2] Previously, we reported preparations and structures of water-soluble cyclic tri[2]rotaxanes (daisy chain necklaces) and linear supramolecular polymers formed by cyclodextrins (CDs) having a cinnamoyl group and a cinnamamide group as a guest part.[3] However, the viscosity of supramolecular polymers is lower than that excepted from the molecular weight of supramolecular polymers. Herein, we have prepared 3-cinnamoylaminohexanamide-α-CD (**1**) bearing a pentyl group and 3-N^{α}-cinnamoly-aminohexancarbonyl-N^{ε}-cinnamoyl-lysinamide-α-CD (**2**) bearing two guest parts and have investigated the formation of linear and hyperbranched supramolecular polymers, respectively. This is the first example of the formation of fibrous supramolecular polymers by cyclodextrin-based host–guest systems.

The physical properties of supramolecular polymers formed by each mono-substituted CD (**1** and **2**) were investigated by viscosity measurements under dilute conditions (Figure 1). The η_{sp}/C value of compound **1** moderately increased with an increase in the concentration and reached 3.9 cm^3 g^{-1} at 80 mM. However, the η_{sp}/C value of compound **2** was too low to be measured[4] because of the low solubility in aqueous solutions, whereas compound **2** was easily solubilized in 20 mM aqueous solutions of compound **1**, which reached the saturated concentration at 14.1 mM. Mixtures of **1** and **2** showed a dramatic increase in the viscosity with an increase in the molar ratio of compound **2**. The η_{sp}/C value of the mixture of **1** and **2** (**2**/**1** = 0.7) is 1.4 times larger than that of compound **1** at 34.1 mM. Compound **2** affects the elevation of viscosity of aqueous solutions, which was caused by the formation of branched supramolecular polymer. These results are in agreement with the self-diffusion coefficients of supramolecular complexes determined from pulsed field gradient spin-echo (PFG) NMR measurements.[5]

^{1}H NMR spectra of mixtures of **1** and **2** were measured to verify the formation of branched supramolecular polymer (Figure 2). Mixtures of **1** and **2** showed that protons of the cinnamoyl group of compound **2** shifted to upfield significantly with an increase in the molar ratio of compound **2**. The electro-

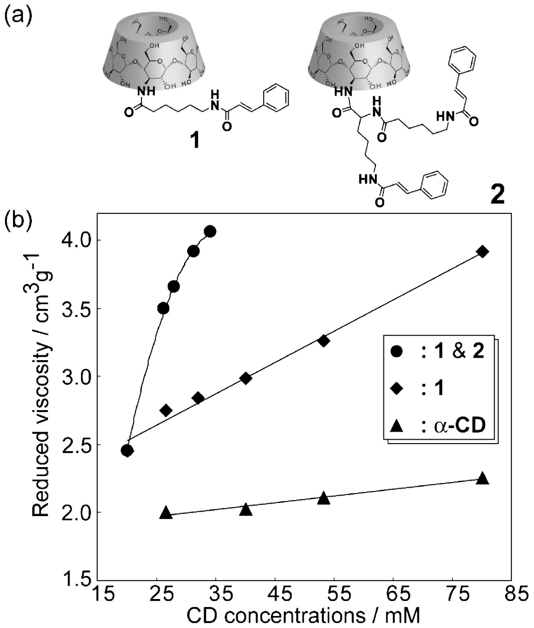

Figure 1. (a) Chemical structures of compounds **1** and **2**. (b) Reduced viscosity of α-CD (triangle), compound **1** (rhombic), and mixtures of **1** and **2** (circle) in H_2O at 25 °C.

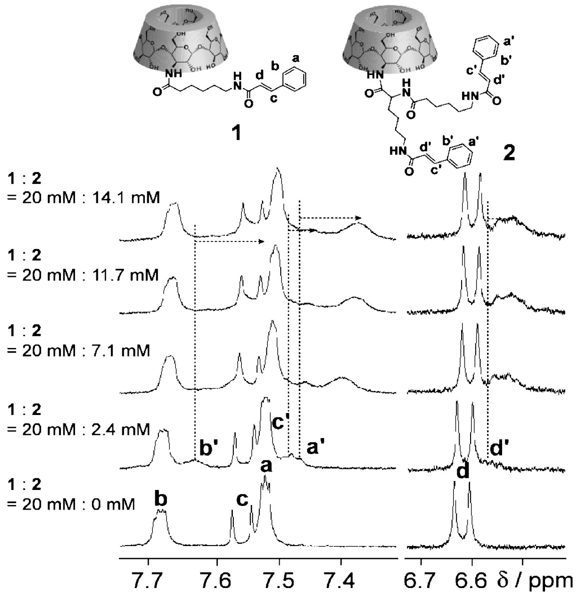

Figure 2. ^{1}H NMR spectra of mixtures of **1** and **2** at various ratios in D_2O at 30 °C.

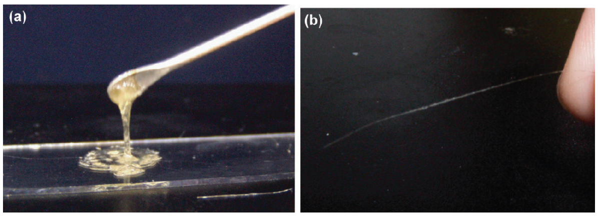

Figure 3. Photographs for the mixture of **1** and **2** (a) thread-forming property (40 wt %) (b) freestanding fiber.

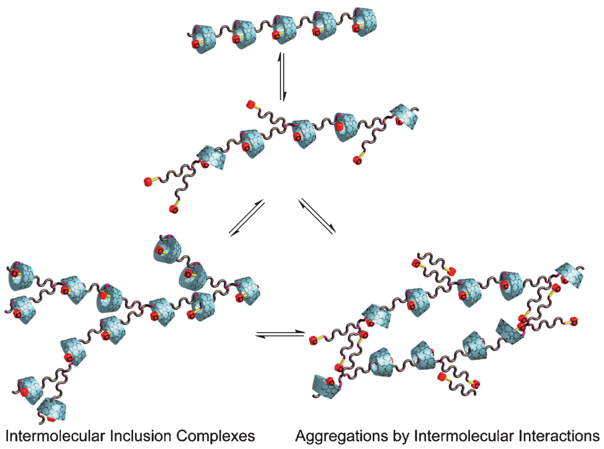

Figure 4. Schematic illustration of fibrous supramolecular polymers formed by **1**–**2** complexes in aqueous solution.

spray ionization (ESI) mass spectra of the mixture of **1** and **2** showed the species of potassium cation adducts of **1** with **2** ($[M_1 + M_2 + K]^+$ and $[2M_1 + M_2 + K]^+$). These results indicate that mixtures of **1** and **2** formed hetero-type supramolecular complexes. Compounds **1** and **2** were also found to form supramolecular polymers, respectively, by ESI mass spectrometry, ^{1}H NMR spectroscopy, and ROESY NMR spectroscopy. The ESI spectra of compounds **1** and **2** showed the species of supramolecular complexes with at least 5 mer. Considering their chemical structures, we suppose that compound **1** formed linear type and compound **2** formed hyperbranched type supramolecular polymers.

Figure 3 shows photographs of a mixture of **1** and **2** in a concentrated solution. The mixture exhibits the thread-forming property (Figure 3a) and freestanding fiber was formed by wet spinning (Figure 3b). In contrast, compound **1** did not exhibit such properties. The powder X-ray diffraction (XRD) pattern of compounds **1** and **2** exhibited two broad reflections around $2\theta = 13$ and 20°, respectively. However, the mixture of **1** and **2** had fewer reflections, indicating the amorphous state.

We suppose that supramolecular polymers from mixtures of **1** and **2** mainly consist of compound **1**. Compound **2** was solubilized in the solution of compound **1**, then compound **1** forms branched supramolecular polymer including guest groups of compound **2**. The association constants were determined by UV–vis absorption spectroscopy.[6] The model system of compound **1** and compound **2** has K_1, K_1', and K_2', which were determined to be $5.7 \times 10^2\,M^{-1}$, $5.8 \times 10\,M^{-2}$, and $5.6\,M^{-1}$, respectively ($K_1 > K_1'$, K_2').[7] It should be noted that viscosity of supramolecular polymers from mixtures of **1** and **2** transcend the estimated results from association constants of model system.[8] These results suggested that the other interactions as well as inclusion effects of CD cavities have an influence on the formation of supramolecular polymers.

The proposed structures of supramolecular polymers are represented in Figure 4. We supposed that supramolecular polymers were formed through not only the formation of intermolecular inclusion complexes but also aggregations by intermolecular interactions such as hydrophobic interactions and/or hydrogen bonds. Supramolecular polymers are able to interact with other polymer chains through nonincluded guest parts in aqueous solutions especially at high concentrations since compound **2** consists of one host moiety and two guest moieties.

In conclusion, novel supramolecular polymer has been prepared from the complex of **1** and **2**. Their properties were caused by crosslinking of linear supramolecular polymer through hetero-type inclusion and some intermolecular interactions. Now, the mechanical properties of these supramolecular polymers are under investigation.

This work has been partially supported by the Center of Excellence (21COE) Program "Creation of Integrated Eco-Chemistry" of Osaka University.

References and Notes

1 a) J.-M. Lehn, in *Supramolecular Chemistry*, VCH, Weinheim, Germany, **1995**. b) J. L. Atwood, J. E. D. Davis, D. M. MacNicol, F. Vogtle, J.-M. Lehn, in *Comprehensive Supramolecular Chemistry Cyclodextrin*, Pergamon, Oxford, **1996**, Vol. 3. c) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. d) C. Fouquey, J.-M. Lehn, A.-M. Levelut, *Adv. Mater.* **1990**, *2*, 254.

2 See Supporting Information. It is available electronically on the CJS-Journal web site; http://www.csj.jp/journals/chem-lett/.

3 a) T. Hoshino, M. Miyauchi, Y. Kawaguchi, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.* **2000**, *122*, 9876. b) A. Harada, Y. Kawaguchi, T. Hoshino, *J. Inclusion Phenom. Macrocycl. Chem.* **2001**, *41*, 115. c) M. Miyauchi, Y. Kawaguchi, A. Harada, *J. Inclusion Phenom. Macrocycl. Chem.* **2004**, *50*, 57.

4 The saturated concentration of compound **2** was 2.3 mM.

5 O. E. Stejskal, J. E. Tanner, *J. Chem. Phys.* **1965**, *42*, 288.

6 K. A. Connors, A. Paulson, D. Toledo-Velasquez, *J. Org. Chem.* **1988**, *53*, 2023.

7 See Supporting Information. It is available electronically on the CJS-Journal web site; http://www.csj.jp/journals/chem-lett/.

8 a) N. Yamaguchi, L. M. Hamilton, H. W. Gibson, *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3275. b) N. Yamaguchi, H. W. Gibson, *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 143. c) H. W. Gibson, N. Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.* **2003**, *125*, 3522. d) K. Araki, R. Takasawa, I. Yoshikawa, *Chem. Commum.* **2001**, 1826. e) R. Takasawa, K. Murota, I. Yoshikawa, K. Araki, *Macromol. Rapid Commun.* **2003**, *24*, 335. f) R. K. Castellano, R. Clark, S. L. Craig, C. Nuckolls, J. Rebek, Jr., *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 12418.

Published on the web (Advance View) May 31, 2007; doi:10.1246/cl.2007.828