Supramolecular Polymers from a Cyclodextrin Dimer and Ditopic Guest Molecules

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(Received November 24, 2004; CL-041416)

Novel supramolecular polymers have been prepared from a β-cyclodextrin dimer and ditopic guest dimers having adamantyl groups. A guest dimer (**C0**) with a 4,4′-bipyridinium group as a stiff spacer between adamantyl groups gave linear supramolecular polymers with high molecular weight, although guest dimer (**C2**) with flexible methylene spacers gave cyclic supramolecular polymers in aqueous solutions.

The field of supramolecular chemistry is now extending to supramolecular polymer chemistry.[1] There have been some papers on the construction of supramolecular polymers using hydrogen bonding,[2–5] coordination by metals,[6] crown ether–ammonium systems,[7,8] and calix[*n*]arenes.[5,9] However, in biological systems, more complicated and sophisticated systems of supramolecular polymers, such as viruses, phages, microtubules, and microfilaments, play important roles in realizing unique structures and functions.[10] We have been trying to design and construct larger and more complicated and/or higher order supramolecular polymers using host–guest systems. Previously, we reported preparation and structures of cyclodextrins (CDs) having a hydrocinnamoyl group (6-HyCiO–CD) or a cinnamoyl group (6-CiO–CD) as a guest.[11] Although HyCiO–β-CD was found to form intramolecular complexes, CiO–α-CD formed intermolecular complexes to give supramolecular oligomers with a degree of polymerization up to three. When the supramolecular complexes were stabilized by attaching bulky stoppers, cyclic tri[2]rotaxanes, daisy chain necklaces, were obtained.[12] To obtain larger complexes, formation of small cyclic complexes should be avoided. Therefore, we have decided to use a CD dimer and guest dimers with various flexibilities. Although there are many papers on the cooperative binding of guests by CD dimers,[13] there are few on the formation of intermolecular complexes of CD dimers with guests.[14] More recently, while we were preparing for this manuscript, Liu et al. reported intermolecular complexes of CD dimers with fullerene.[15] Now we found that a CD dimer formed supramolecular polymers with ditopic guest molecules. The products have been characterized by ROESY and vapor pressure osmometry.

β-CD was bound by a phthaloyl group as a spacer because a benzene ring is rigid enough to give intermolecular complexation with guest dimers, prepared by the reaction of 6-amino-β-CD with phathalic acid using DCC in DMF. The guest dimers have two adamantyl groups as the guests because the adamantyl groups have higher association constant with β-CD. A model compound, adamantane carbomethylpyridinium bromide (**1**) or *N*-methyl-*N*′-(1-adamantylcarbonylmethyl)-4,4′-bipyridinium dibromide (**2**), has been found to bind to a β-CD cavity with an association constant of $10^4\,M^{-1}$. Guest dimers, **C0** and **C2**, were prepared by the reaction of bipyridine derivatives with 1-adamantylbromomethylketone, which three kinds of dimers have different spacer groups between adamantanes end group (Figure 1). **C0** is rather stiff, because a 4,4′-bipyridinium group is used as a spacer. In contrast, **C2** are more flexible than **C0** because of the existence of methylene groups in the spacer groups.

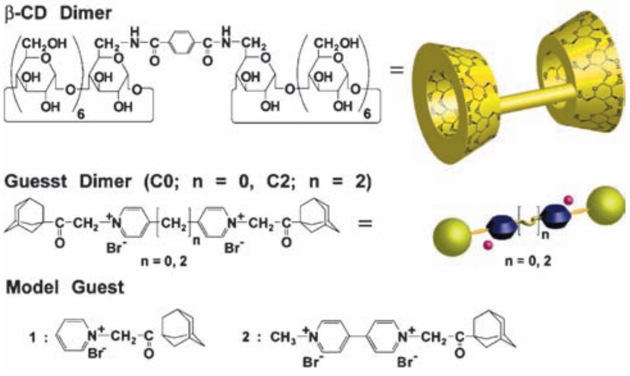

Figure 1. Structures of β-CD dimer and guest dimers.

The ROESY spectrum of the mixture of the β-CD dimer (5 mM) and the guest dimer (**C0**) (5 mM) showed that the peaks of methylene and methine protons of adamantane were correlating well with inner proton peaks of β-CD (C3-*H* and C5-*H*), indicating that an adamantane part is included in a cavity of β-CD. The guest dimer (**C2**) also showed cross peaks between adamantane and β-CD in the ROESY spectra.

Generally, NMR methods were used to determine stoichiometries and association constants in host–guest chemistry.[1,16] In contrast, VPO (vapor pressure osmometry) is more sensitive to the number of species.[17] Recently, the technique of VPO has been used to estimate association constants of supramolecular complexes.[18] We measured the molecular weight (M_n) of a 1:1 mixture of the cyclodextrin dimer and ditopic guest molecules by VPO at 40 °C and estimated the sizes of supramolecular polymers. When we use **C0** as a guest, M_n increased with an increase in the concentrations, although molecular weights of the reference compounds (**1**), which cannot form supramolecular polymers, were independent of the concentrations. The M_n for **C0** and β-CD dimer at 3 mM is about 3000, indicating the formation of a 1:1 complex. However, the M_n for **C0** and β-CD dimer over 10 mM is more than 90000 and reached saturation, indicating the formation of supramolecular polymers with high molecular weights. When **C2** was used as a guest dimer, M_n saturated at almost 15000 even in concentrated solutions over 8 mM, although the ^{1}H NMR showed that all the adamantane moieties are included and no free (non-included) adamantane groups could be detected, suggesting that the **C2** formed cyclic oligomers with the β-CD dimers. These results indicated that **C0** formed linear supramolecular polymers of high molecular weight with the cyclodextrin dimer because of its stiffness and **C2** formed cyclic oligomers with the β-CD dimer because of their flexibility.

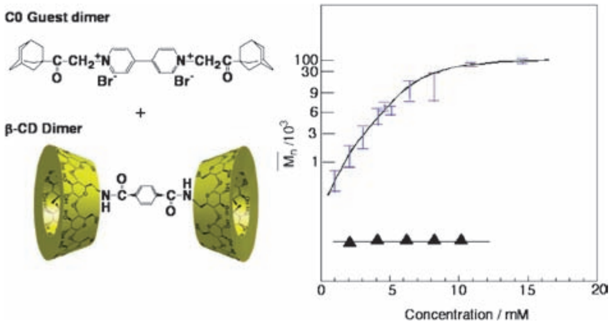

Figure 2. Concentration dependence of number-average molecular weight for 1:1 mixtures of β-CD dimer and guest dimer **C0** (bar) and model compound (**1**) (triangle) in aqueous solutions at 40 °C by VPO measurements.

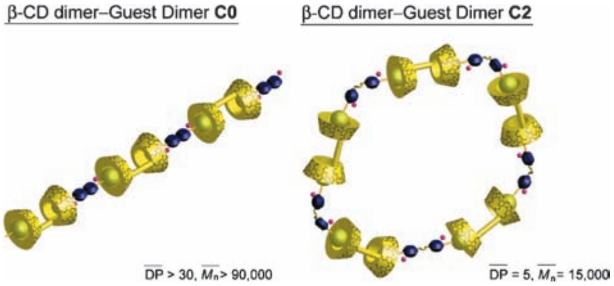

Figure 3. Proposed structures of supramolecular polymers constructed by β-CD dimer and guest dimer **C0**, and β-CD dimer and guest dimer **C2**.

In conclusion, a cyclodextrin dimer forms supramolecular polymers with a stiff ditopic guest molecule to give high molecular weight supramolecular polymers, and the dimer gives cyclic supramolecular oligomers with flexible ditopic guest molecules. Now we are studying the dynamic aspects and properties of the supramolecular polymers.

This work was partially supported by a Grant-in-Aid No. S14103015 for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Published on the web (Advance View) February 5, 2005; DOI 10.1246/cl.2005.320