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Supramolecular Polymers Polymeric Betains Oligomers

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Supramolecular Polymers
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Oligomers

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Cyclodextrin-Based Supramolecular Polymers

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Abstract Supramolecular polymers were prepared by inclusion of a guest in cyclodextrin via a covalent bond. The structures of the supramolecular oligomers and polymers were determined by X-ray studies, NMR measurements, absorption and circular dichroism spectra. The sizes of the supramolecular polymers were determined by vapor pressure osmometry and pulsed-field gradient NMR. Although hydrocinnamoyl β-cyclodextrin formed an intramolecular complex, hydrocinnamoyl α-cyclodextrin formed intermolecular complexes. Cinnamoyl β-cyclodextrin gave a cyclic dimer and cinnamoyl α-cyclodextrin formed a cyclic trimer. α-Cyclodextrin with cinnamic amide at the secondary hydroxyl side gave supramolecular polymers. Formation of the complexes of cyclodextrins with various polymers has also been described.

Keywords Cyclodextrin · Host-guest interactions · Inclusion complex · Molecular tube · Polyrotaxane · Supramolecular polymer

1 Introduction

In recent years, supramolecular chemistry has been expanding to include supramolecular polymer science [1, 2]. Conventional polymers, such as vinyl polymers and condensation polymers, are made up of covalent bonds. However, supramolecular polymers are made up of non-covalent bonds. The first supramolecular polymers were reported by Lehn et al. [1, 3–5], in which each building block is linked by three hydrogen bonds (Fig. 1). In this case, on average, several building blocks are linked together to form supramolecular oligomers. Later, Meijer et al. [6–8] reported supramolecular polymers formed by four hydrogen bonds in each unit (Fig. 2). In this case, high molecular weight (higher than 10×10^4) supramolecular polymers were obtained. The concentrated solutions are viscous-like solutions of conventional polymers. In addition, the viscosity can be controlled by their concentrations, temperature, and even the addition of a monofunctional unit.

These supramolecular polymers remind us of the discussion concerning the existence of macromolecules over 70 years ago by Staudinger et al. Although macromolecules made up of covalent bonds are of course ubiqui-

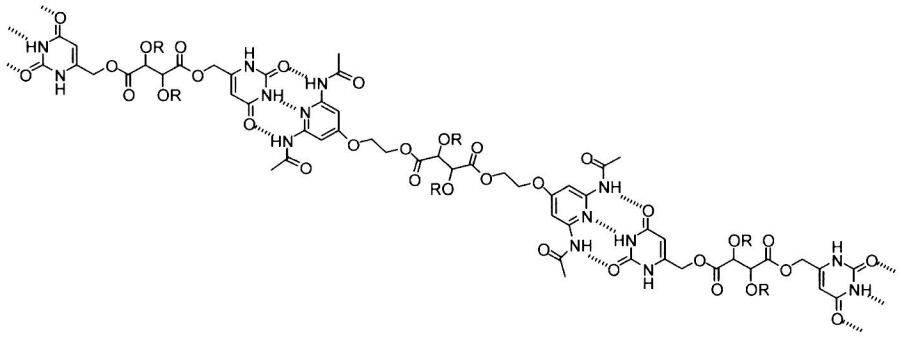

Fig. 1 Supramolecular polymer of bifunctional ureido pyrimidinone derivative reported by Lehn

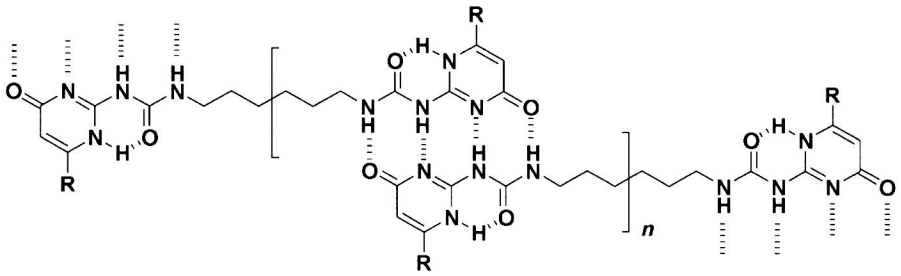

Fig. 2 Supramolecular polymer reported by Meijer

tous in nature and the synthetic world, "macromolecules" made up of non-covalent bonds are also ubiquitous in nature, especially in living creatures and are important in the synthetic world as well.

Many kinds of molecular interactions, such as hydrogen bonding, ionic interactions, van der Waals interactions, and hydrophobic interactions can be used for the design and construction of supramolecular polymers [1–12]. The most important interaction in biological systems are Host-Guest interactions, such as enzyme-substrate, antigen-antibody, microtubules, microfilaments, and flagella. Recently, many kinds of supramolecular polymers have been designed and constructed by synthetic methods. In this Chapter, the authors would like to introduce some supramolecular polymers constructed through Host-Guest systems, especially using cyclodextrins as hosts and some benzene derivatives as guests.

2
Supramolecular Polymers in the Solid State

X-ray crystallography has been a major source of information for the three-dimensional structure of the host-guest complexes. First attempts in the use

of single-crystal X-ray diffraction were applied to α-cyclodextrin (α-CD) and β-cyclodextrin (β-CD) by French and Rundl [13]. James et al. [14] reported the crystallographic data for several α-CD complexes, but their resolution for structural analysis of the iodine complex was very low. After several years, Hybl et al. [15] reported the structure of the complex of α-CD with potassium acetate for a full X-ray structure. Since then, there have been numerous reports on crystal structures of cyclodextrins and their inclusion complexes, as summarized in several reviews [16–20]. Crystal structures of CDs and their inclusion complexes were classified into cage-, channel-, and layer-type structures. These classes are dependent on the relationship between CDs and the included guest molecules. Recently, some monosubstituted CDs were synthesized to give the catalytic activity and the formation of the supramolecular complex. For example: in the crystal structure, 6-*O*-(*tert*-butylthio)-β-CD molecules was arranged along a screw axis and the *tert*-butylmercaptan group was inserted into the next β-CD cavity to form a helically extended polymeric structure [21]. This modified CD behaves not only as a donor of the guest group but also as an acceptor. These types of structure may be termed "supramolecular polymer" in the solid state. This section focuses on the crystal structures of monosubstituted CDs.

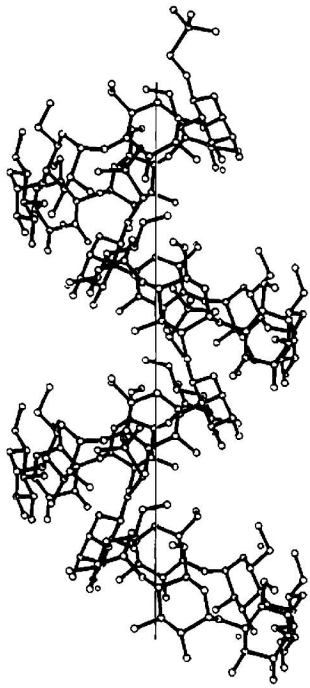

Fig. 3 The crystal structure of 6-*O*-(*tert*-butylthio)-β-CD drawing a helical polymer related by the 2_1 screw axis

2.1
Crystal Structure of 6-*O*-(*tert*-Butylthio)-β-Cyclodextrin

The structure of 6-(*tert*-butylthio)-β-CD was characterized by Tabushi et al. [21]. The compound of 6-*O*-(*tert*-butylthio)-β-CD was prepared from the reaction of 6-*O*-(*p*-toluenesulfonyl)-β-CD with *tert*-butylmercaptan and recrystallized in water. This is the first example of the determination of crystal structure of monosubstituted CD derivatives and the first evidence concerning the supramolecular polymer of an inclusion complex of a monosubstituted CD. The crystal structure of 6-*O*-(*tert*-butylthio)-β-CD was arranged around the two-fold axis to yield a polymeric structure, in which the *tert*-butyl group is intermolecularly included in the cavity of CD (Fig. 3).

2.2
Crystal Structure of 6-*O*-(Phenylthio)-β-Cyclodextrin and 6-*O*-(Phenylsulphinyl)-β-Cyclodextrin

Tabushi and Kamitori et al. [22] also reported that a substituted group was intermolecularly included in the cavity of another CD (Fig. 4). They carried out the X-ray crystallographic study of two compounds, 6-*O*-phenylthio-β-

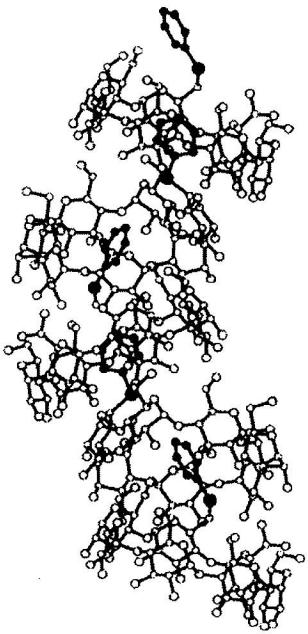

Fig. 4 The crystal structure of 6-deoxy-6-(phenylthio)-β-CD. The phenyl group is shown with *filled circles*. The molecules are arranged along a 4-fold screw axis, and the phenyl group is inserted into the cavity of an adjacent β-CD from its secondary hydroxyl side

CD and 6-*O*-phenylsulphinyl-β-CD. From the molecular structure of 6-*O*-phenylthio-β-CD, it was found that the phenyl group enters the center of the CD cavity from the side of secondary hydroxyl groups. In the case of 6-*O*-phenylsulphinyl-β-CD, the guest phenylsulphinyl group was more deeply included in the host CD cavity than that of 6-*O*-phenylthio-β-CD. In the packing structures, the molecules are arranged around the screw axis to give a unique polymeric inclusion column structure formed from a single species acting both as a guest and as a host. The macrocycles in helical columns are related by a four-fold screw axis for 6-*O*-phenylthio-β-CD and by a two-fold screw axis for 6-*O*-phenylsulphinyl-β-CD.

2.3 Crystal Structure of 2-*O*-[(*S*)-2-Hydroxypropyl]-β-Cyclodextrin, 6-*O*-[(*R*)-2-Hydroxypropyl]-β-Cyclodextrin, and 6-*O*-[(*S*)-2-Hydroxypropyl]-β-Cyclodextrin

Harata et al. [23] reported that the crystal structure of 2-*O*-[(*S*)-2-hydroxypropyl]-β-CD was solved by X-ray diffraction (Fig. 5). The molecules are arranged in a herring-bone fashion to form a cage-type packing structure. The hydroxypropyl group is inserted into the cavity of an adjacent molecule related by a two-fold screw axis.

In the crystal structures of 6-*O*-[(*R*)-2-hydroxypropyl]- and 6-*O*-[(*S*)-2-hydroxypropyl]-β-CD, the 2-hydroxypropyl group is inserted into the β-CD cavity of the next β-CD related by the two-fold screw axis, and a helically extended polymeric structure is formed by repetition of the intermolecular inclusion (Fig. 6). The hydroxyl group of the substituent group penetrates through the β-CD ring from the secondary hydroxyl side and is linked to an

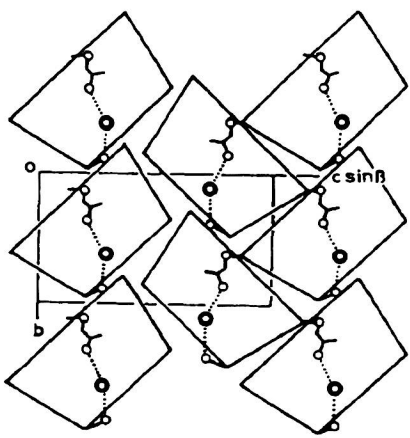

Fig. 5 Packing structure of 2-*O*-[(*S*)-2-hydroxypropyl]-β-CD. Hydrogen bonds involving the hydropropyl group are shown by *dotted lines*

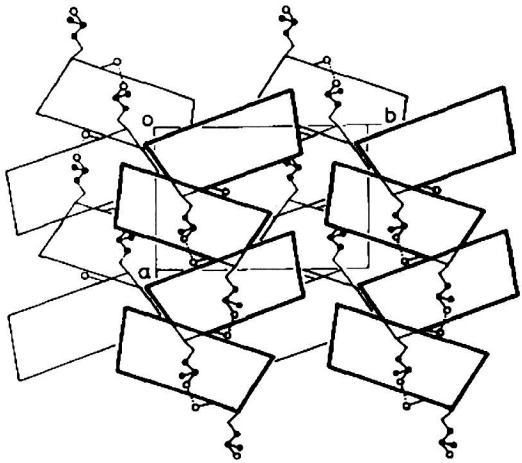

Fig. 6 A schematic drawing of the packing in the crystal viewed along the *c*-axis in 6-*O*-[(*R*)-2-hydroxypropyl]- and 6-*O*-[(*S*)-2-hydroxypropyl]-*β*-CD

HO-6 group by a hydrogen bond. Comparison of intermolecular contacts of the substituent group indicates that the (*S*)-2-hydroxypropyl group is better fitted to the cavity than the (*R*)-2-hydroxy-propyl group.

2.4 Crystal Structure of 6-*O*-(6-Cyclo(L-histidyl-L-leucyl))-*β*-Cyclodextrin

In the molecular structure of 6-*O*-(6-cyclo(L-histidyl-L-leucyl)-*β*-CD, the cyclo(L-histidyl-L-leucyl) group is included in the center of the CD cavity

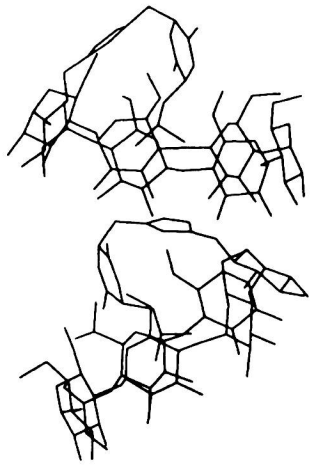

Fig. 7 The crystal structure of 6-*O*-(6-cyclo(L-histidyl-L-leucyl)-*β*-CD along the *b*-axis

from the side of the primary hydroxyl groups (Fig. 7) [24]. In the packing structure, the molecules are arranged around the two-fold screw axis to give the unique polymeric inclusion column structure formed from a single species acting both as a guest and as a host. The structure of 6-*O*-(6-cyclo(L-histidyl-L-leucyl)-β-CD was arranged along the two-fold screw axis and the cyclo(L-histidyl-L-leucyl) group is inserted into the β-CD cavity.

2.5 Crystal Structure of 6-*O*-Azido-α-Cyclodextrin, 6-*O*-Allyl-α-Cyclodextrin and 6-*O*-[(6-Aminohexyl)Amino]-β-Cyclodextrin

The X-ray crystal structures of 6-*O*-azido-α-CD and 6-*O*-allyl-α-CD were determined by Hanesian et al. [25]. Azido and allyl groups of each CD unit are included in the cavity of adjacent units from the secondary hydroxyl group side to form along the two-fold screw axis (Fig. 8). 6-*O*-[(6-Aminohexyl)amino]-β-CD is arranged along the two-fold screw axis parallel to the *c* crystal axis forming a polymeric column structure (Fig. 9) [26]. 6-Aminohexyl chain groups are inserted into the cavity of the adjacent β-CD moiety from the secondary side. All the atoms of the chain exhibit large thermal motion. The nitrogen atom is found near the secondary hydroxyl group rim of host β-CD and forms a hydrogen-bond with a water molecule. The end of the nitrogen atom in the substituted group was also hydrogen-bonded to

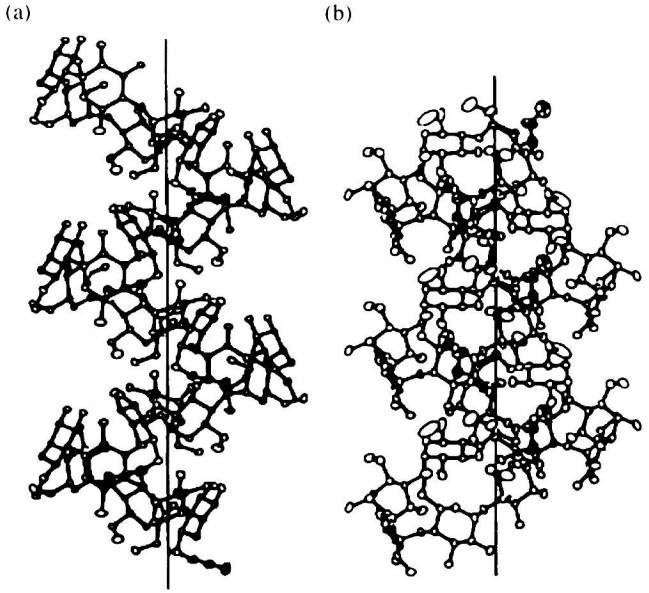

Fig. 8 The crystal structures of 6-*O*-azido-α-CD and 6-*O*-allyl-α-CD drawing a helical polymer penetrated by the 2_1 screw axis