Polymer tubules prepared

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THREAD several cyclodextrins (CDs) onto a single polymer chain, and they efficiently self-assemble. Harada and co-workers have taken advantage of this to build tubular polymeric structures. On page 516 of this issue[1], they show how last year's molecular necklace[2] becomes this year's molecular tubing, preparing supramolecular complexes in which a series of α-CD molecules are almost perfectly aligned. Their latest finding is that one can use the reactivity of the CD's terminal hydroxyl groups to establish covalent bonds among them, so that the individual receptor cavities combine to form a long polysaccharide-based tube about a nanometre across.

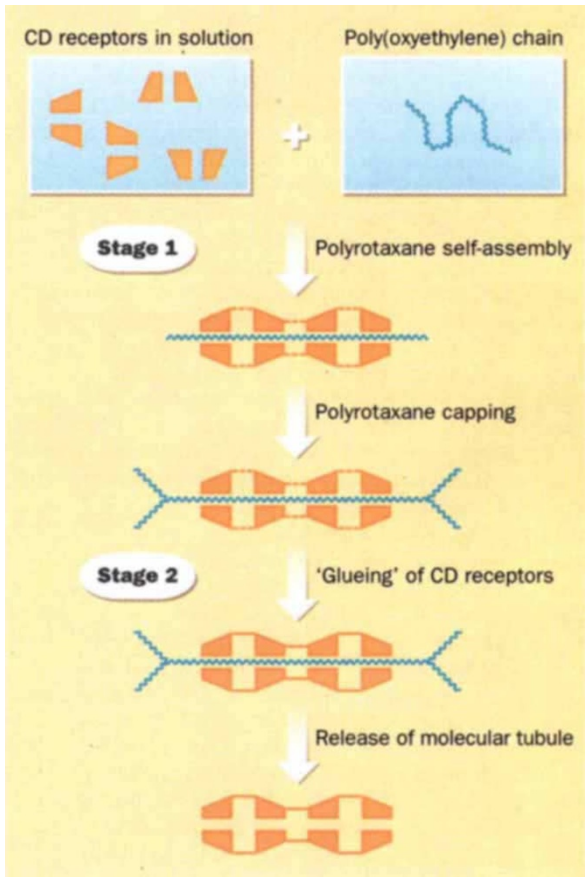
The cyclodextrins, which are composed of sugar units, are a class of natural receptor molecules without a known natural function. But their ability to bind organic substrates in aqueous media, coupled with a shape very suggestive of a lampshade, has fascinated chemists for decades. Among other applications, chemically modified CDs have been proposed as artificial enzymes.

From the smallest cyclodextrin (α-CD) come the rotaxanes, an intriguing class of supramolecular complexes in which one or more cyclic components (the beads) are threaded by a linear subunit. Bulky terminal groups prevent the escape of the beads. The cavity diameter of α-CD (~5 Å) is ideal for threading on extended aliphatic $[-(CH_2)_n-]$ or ethyleneoxy $[-(CH_2CH_2O)_n-]$ chains, and several rotaxanes containing only one trapped bead have been made[3–8]. The groups of Harada[2] in Japan, and Wenz[9] in Germany, last year expanded the idea to the preparation of polyrotaxanes in which numerous α-CD units are trapped after appropriate capping of the chain ends.

In Harada's polyrotaxanes[2], the threaded CDs are well packed, essentially covering the entire length of the polyethyleneoxy chain. The stopper groups at the ends of the chain keep the CDs in close contact with each other, as well as preventing their dissociation. The assembly of such structures is probably assisted by extensive hydrogen bonding among the –OH groups that line the CD cavity openings. At this point, the tubular structure is already in place; one only needs to 'glue' each CD to its two neighbours in the polyrotaxane, remove the stopper groups and extract the threading chain, to make the molecular polytubes (see figure).

This is precisely what Harada and co-workers have accomplished, using epichlorohydrin in basic medium as the chemical glue. In the presence of epichlorohydrin and base, the CD hydroxyl groups react to form covalent bonds between neighbouring units. A larger excess of base leads to the removal of the capping groups and to the subsequent release of the tubular CD-based polymers[1].

Molecular self-assembly is crucial to the success of this approach. The polyrotaxane structure, which can be considered as the precursor of the tubular polymer, essentially assembles itself, and the threading chain provides a support along which the α-CD units can develop favourable hydrogen bonding interactions. Capping of the polyrotaxane keeps the aligned CD units in place, ready to undergo the cross-linking reaction that yields the tubular polymer. Obviously, polymerization of freely dissolved α-CD would not produce these remarkable tubular structures. Harada and co-workers are pioneering the use of molecular self-assembly followed by chemical reactions for the construction of nanometre-sized structures of controlled shape and size.



Building designer polymer tubes out of cyclodextrin units. In stage 1, dotted lines represent hydrogen bonds; in stage 2, these are replaced by covalent bonds between adjacent CDs.

These hollow, cylindrical polymers are reminiscent of fibrillar or tubular structures found in living systems. But they are singularly small; their internal diameter is about 5 Å and their external diameter about 15 Å. Even the outer diameter is smaller than the average external diameter of the DNA helix (20 Å). Other relevant biological structures, such as microfilaments and microtubules, are much larger, with external diameters of 70 and 250 Å, respectively. The development of similar procedures for the organized polymerization of the higher CDs, β-CD and γ-CD, would give us tubular polymers with internal diameters of 6.5 and 8 Å. The length of the molecular tubes could probably be controlled by adjusting the length of the polymeric chains that template the formation of the precursor polyrotaxanes.

'Designer' polymeric tubes should be welcomed in separation technology, as they could be used in the manufacture of chromatographic or filtration media containing pores of well-defined molecular sizes. These structures may also serve as microreactors, a sort of organic zeolites (see the News and Views article by Davis[10]) with, perhaps, catalytic properties for a number of reactions. The reactivity of molecules included in these tubular polymers is expected to differ considerably from that observed in homogeneous media.

Without a doubt, these novel structures pose many research challenges; they constitute an excellent example of what supramolecular chemistry can accomplish. □

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