"Topo-polymers. Polymers with catenane or rotaxane structure in the main chain"

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Conventional polymers are made up of units called monomers connected by some kind of chemical bond. That is, if you trace the top of a molecule from one end to another with your finger, there is one or more uninterrupted chains of chemical bonds. In contrast, we focused on mechanical connections between dogs and collars and cows and nose rings, which we often see in the macro world (Fig. 1), and aimed to synthesize a polymer with this connection entered in the structure of the main chain ("topopolymer"). Figures 2a and 2b show the schematic structure of the polymer we targeted. In Figure 2a, the spectacle-type unit apparently serves as the basic skeleton, and the two rings of the spectacles interlock with her separate spectacle-type units to form the main chain of the polymer. Also, in Fig. 2b, the L-shaped unit with a dumbbell-shaped part and a ring part becomes the basic skeleton, and the adjacent unit is connected to the adjacent unit in the relationship of a dog and a collar to form a polymer main chain. It goes without saying that the main chain structure of a polymer has a great influence on the thermal and solution physical properties, as well as the optical and electronic physical properties. Since the polymer shown in Fig. 2 has a completely new main chain structure, it is of interest not only from the viewpoint of synthetic chemistry but also from various physical properties.

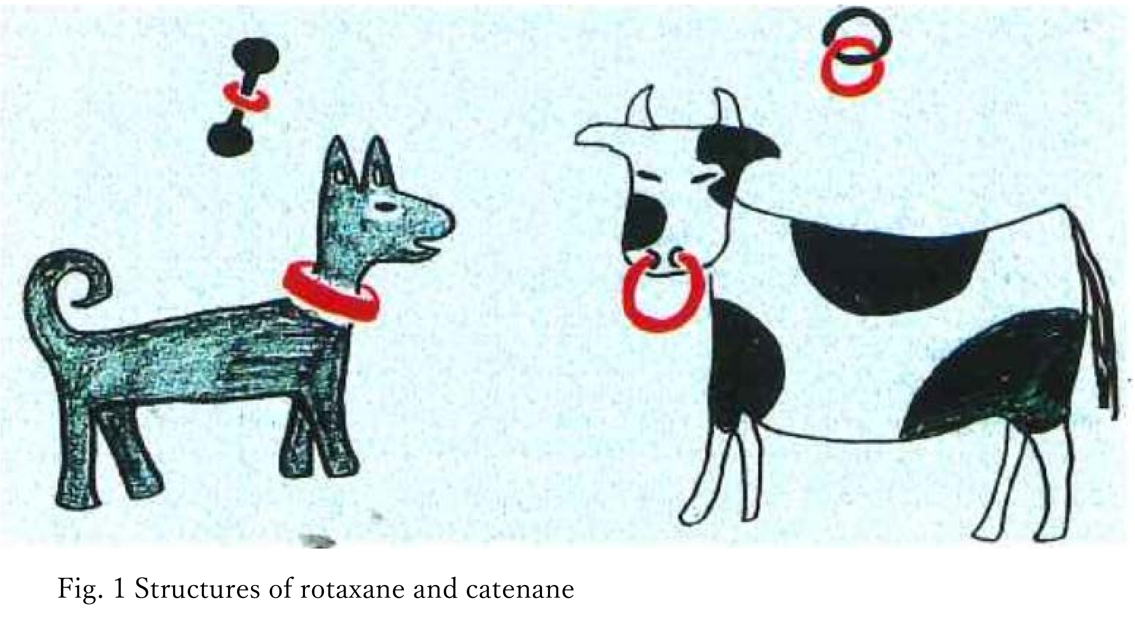

Fig. 1 Structures of rotaxane and catenane

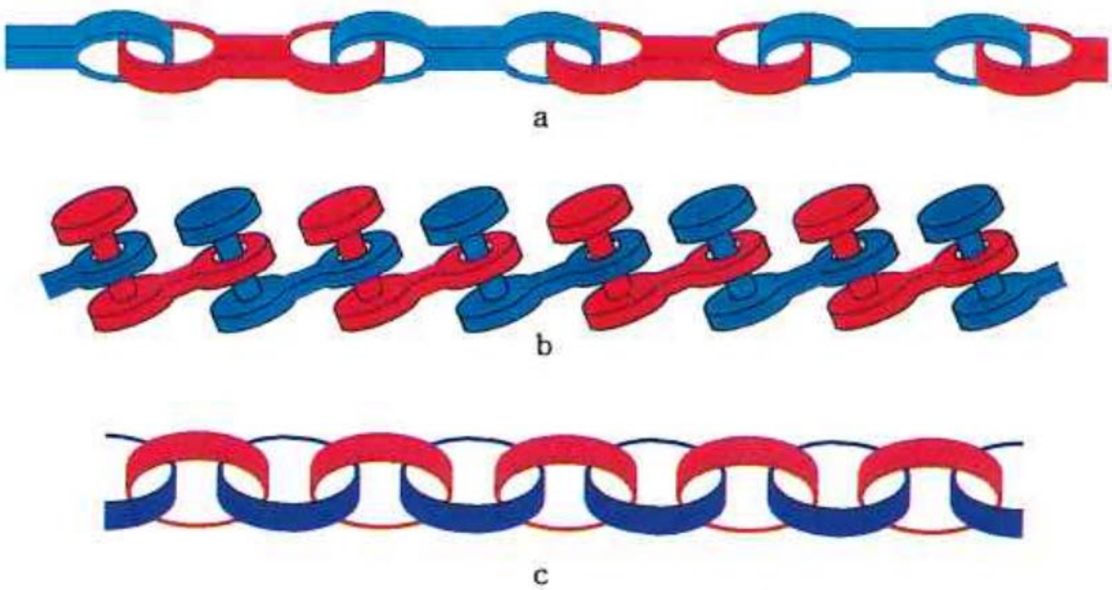

Fig. 2 Topo-polymers

Substances with the structures of cattle and nose rings and dogs and collars are called catenane and rotaxan, respectively, and are compounds that have long been targeted in the field of synthetic chemistry. In recent years, many integration strategies utilizing supramolecular interactions have been developed, with high yields of [2] or [3] catenane and [2] or [3] rotaxane consisting of two or three constituent units. In the last few years, Stoddart et al. of the United Kingdom have greatly developed the method of connecting rings one by one, and up to five rings have interlocked [5] catenane. [n] Catenane (Fig. 2c), which interlocks innumerable rings, is also an ancient target of synthesis. However, the structure in which these innumerable rings are connected is chain-reacted or continuous. At present, synthesis of [n] catenane is not possible because we don't have any polyaddition reactions or polycondensation reactions forming a catenane structure at each step.

We designed the molecular structure in Figure 2ab from the perspective of being easier to synthesize than [n] catenane. Furthermore, as a monomer necessary for its synthesis, we considered [2] catenane and [2] rotaxane with one condensation functional group on each unit in the molecule. Polycondensation of these compounds, either directly or with other bifunctional monomers, should result in the formation of macromolecules with the structures shown in Figures 2a and 2b.

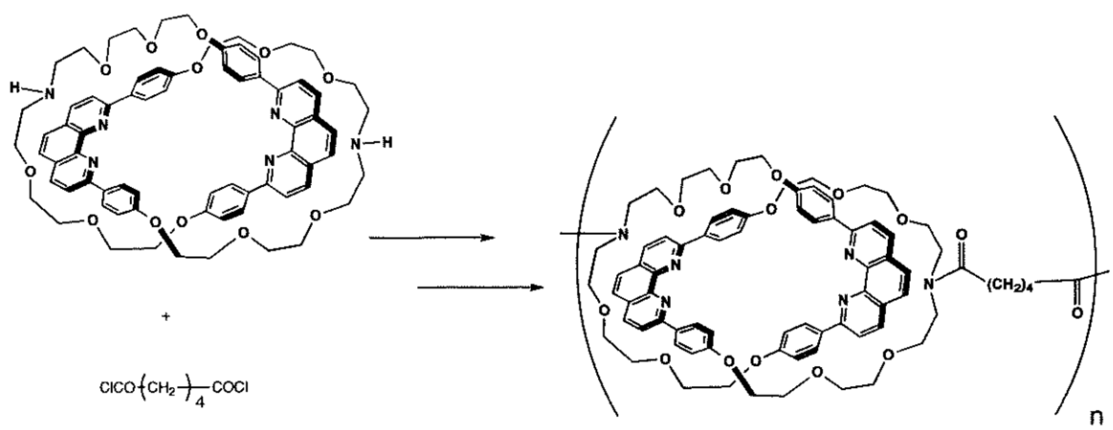


Fig. 3 Structure of a bi-functional [2] catenane and the polymerization scheme to a topo-polymer

Figure 3 shows the structure of the bifunctional [2] catenane we synthesized and the scheme of the polymerization reaction using it. First, a catenane structure is constructed using a hexaethylene glycol chain containing an amino group protected with a benzyloxycarbonyl group in a part of the ring, and finally deprotection is performed to make two rings in each of the two rings in one molecule. A bifunctional [2] catenane with one secondary amino group in each unit was synthesized. A polycondensation reaction between this and adipoyl dichloride was carried out in the presence of copper ions to obtain a polymer with a molecular weight of several hundred thousand (GPC / polystyrene equivalent) [3,4,5]. When the same reaction was carried out without adding copper ions, the molecule was cyclized within the molecule, and a pretzel (a type of German bread) type molecule was formed. Copper ions are thought to form a complex with two phenanthroline rings and keep the amino groups in the catenane away from each other. [4]

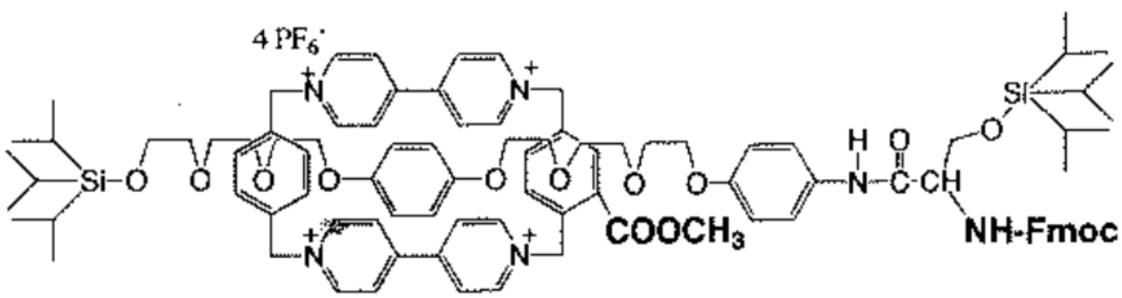


Fig. 4 Structure of a bi-functional [2] rotaxane

On the other hand, the structure of the bifunctional [2] rotaxane synthesized as a monomer for the synthesis of polymer shown in Fig. 2b is shown in Fig. 4. It has a protected amino group in a dumbbell part and a carboxylate group in the ring part, so it is a kind of amino acid. Both protecting groups are deprotected and used as a monomer for polycondensation reaction, or only the carboxylate group is converted to a carboxylic acid group and then applied to peptide solid-phase polymerization to introduce a rotaxane structure at an arbitrary position in the polypeptide chain. This is currently under investigation. [6)]

It goes without saying that the physical properties of organic compounds largely depend on the molecular structure. However, in order to create completely new physical properties, it is necessary to change the molecular structure from a conceptual point rather than just modifying it. In this study, we introduced an attempt to introduce a catenane structure and a rotaxane structure into the main chain of a polymer. From now on, we plan to proceed with synthetic research and perform various physical property measurements.

References

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5) Recently, another group independently published a result of a synthesis of a polymer with a similar structure. J.-L. Weidmann, J. -M. Kern, J.-P. Sauvage, Y. Geerts, D. Muscat and Müllen, J. Chem. Soc., Chem. Commun., 1996, 1243.

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