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171

Polymer Synthesis

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Polymer Synthesis

With contributions by

Y. Furusho · Y. Ito · N. Kihara · K. Osakada · M. Suginome

T. Takata · D. Takeuchi



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Polyrotaxanes and Polycatenanes: Recent Advances in Syntheses and Applications of Polymers Comprising of Interlocked Structures

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Abstract Syntheses and applications of interlocked polymers, polyrotaxanes, and polycatenanes, including corresponding oligomers are reviewed with emphasis on (i) synthesis of interlocked polymers consisting of interlocked structures as the monomer-linking units (genuine “topological” polymers), and (ii) application of the interlocked polymers in both bulk and molecular levels. Further, the review also refers to a few important polyrotaxanes and polycatenane which are still unknown despite many synthetic challenges attempted so far. The review mainly summarizes the recent progress in the chemistry of polyrotaxanes and polycatenanes during this decade, in terms of kind of ring systems.

Keywords Poly(oligo)rotaxane poly(oligo)catenane · Synthesis · Application · Interlocked polymer

1

Introduction—Chemistry of Polyrotaxanes and Polycatenanes: An Overview

Mechanical bonding characteristic of interlocked molecules such as rotaxanes and catenanes assures high freedom and mobility of the whole molecule or its components, as predicted from their unique structures. Meanwhile, complete separation of their components to each other requires energy as high as that for covalent bond breaking. Therefore, the so-called “topological bond” between the components can be regarded as a “soft but strong bond” in comparison with the typical covalent bond. The interlocked molecules having such characteristic features are expected to have special or extraordinary physical and chemical properties.

The chemistry of rotaxanes and catenanes has progressed well in accordance with the interest in their unique structures and the expectation to development as the parts of molecular machines or molecular device, whereas

that of polymers comprising these structures as the key repeating units, i.e., interlocked polymers, has progressed less well. The chemistry of [2]rotaxanes and [2]catenanes has recently stressed their applications by utilizing the vast amount of studies as their background, while both synthesis and application of the interlocked polymers have been studied simultaneously.

Although characteristic properties in mechanical and/or rheological aspects have been assigned to the interlocked polymers in the bulk state, the ring size of the wheel component included seems to exert a serious influence, as well as that by the freedom of the component. As a way of looking at the polymer properties, the effect of the entangled polymer chain plays an important role. That is, it can be considered that an elastic property exists based on the interlocked polymer chains as highly interpenetrated ones which may be associated with the properties of rubber and interpenetrating polymers, when a big wheel is used. Meanwhile, when a wheel component is connected with the chain polymers, bonding between the wheel component and the polymer chain results in producing the crosslinked points that can move on the chain. Such a type of “topological crosslinking” can provide special mobility to the polymer, because it is distinguished from both physical and chemical crosslinkings with little mobility.

As mentioned above, studies from the viewpoint of material science and technology of these new type of polymers are progressing, particularly since the start of the twenty-first century, and various unique properties are expected for the polymers characterized by the interlocked structures.

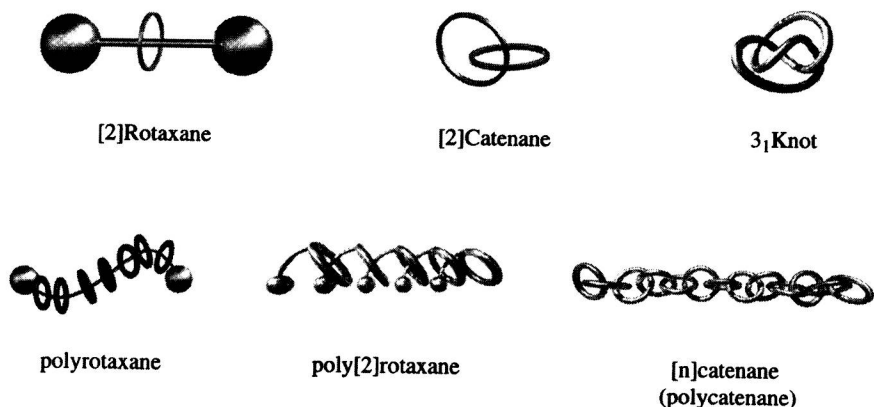
There are reviews including two comprehensive articles of Gibson [1] and Stoddart [2] on the polyrotaxanes and polycatenanes [3–12], in addition to a lot of review articles and books on the rotaxanes and catenanes [13–28]. Short reviews on the applications of polyrotaxanes are also reported [29–38].

1.1

Structures of Interlocked Polymers

Scheme 1 illustrates the simplest structures of rotaxane, catenane, and knot besides polyrotaxane and polycatenane. From the fact that the main chain-type polyrotaxane at the left side is the only interlocked polymer synthesized so far among the three polymers shown at the bottom of the scheme, progress in synthesis of interlocked polymers appears to be sluggish judging from the level of activity in synthetic polymer chemistry in the world.

More detailed general structures of the representative polyrotaxanes and polycatenanes are shown in Scheme 2. Polyrotaxanes can be categorized into two types: one is the polyrotaxanes consisting of the main chains of covalent type as shown in the top four examples (A–D), while the other involves the polyrotaxanes of which monomer linking units are constructed by the rotaxane structure as shown in the following two structures (E, F). The essen-



Scheme 1

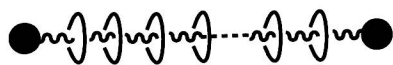
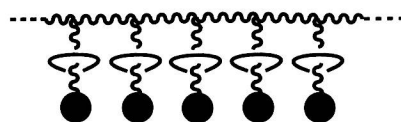
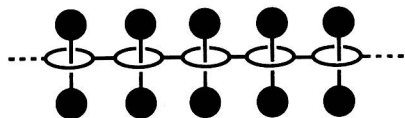
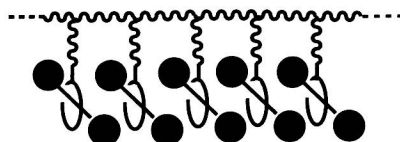
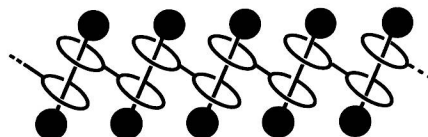
tial difference in main chain structure between the two types of polyrotaxanes should cause large differences in their physical or mechanical properties. The former polyrotaxanes (A–D) are further divided into main chain-type (A, B) and side chain-type (C, D). As mentioned above, poly[2]rotaxane (E) as one of the latter is an unknown polymer which has still been encouraging the many synthetic challenges made so far aside. Meanwhile, synthesis of the neighboring poly[3]rotaxane (F) has very recently been achieved. Genuine polyrotaxane seems to be one of the polyrotaxanes like the former “topological polyrotaxanes”, which may reflect their truly unique structures to their properties.

In addition to three typical structures of poly[2]catenanes (G–I), polycatenane (i.e., [n]catenane) of which the structure is comprised only of wheel components is simply interlinked like a “chain” (J). The polycatenane is one of the most difficult goals in the synthesis of unknown interlocked polymers, like poly[2]rotaxane as already pointed out, although it will be accomplished in the near future because so much effort has been made by synthetic chemists, and this will be continued.

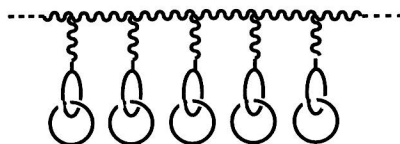
1.2

Wheel Component

It is vital that simple and cheap synthesis of interlocked polymers is achieved in order to make progress in the chemistry of polyrotaxanes and polycatenanes. Since bulk property is essential in polymer science, difficulty in synthesis of interlocked polymers should be avoided, this being different from the case of molecular materials such as molecular devices functioning at a molecular level. Both polyrotaxanes and polycatenanes as well as both rotaxanes and catenanes are becoming easy to synthesize with the progress

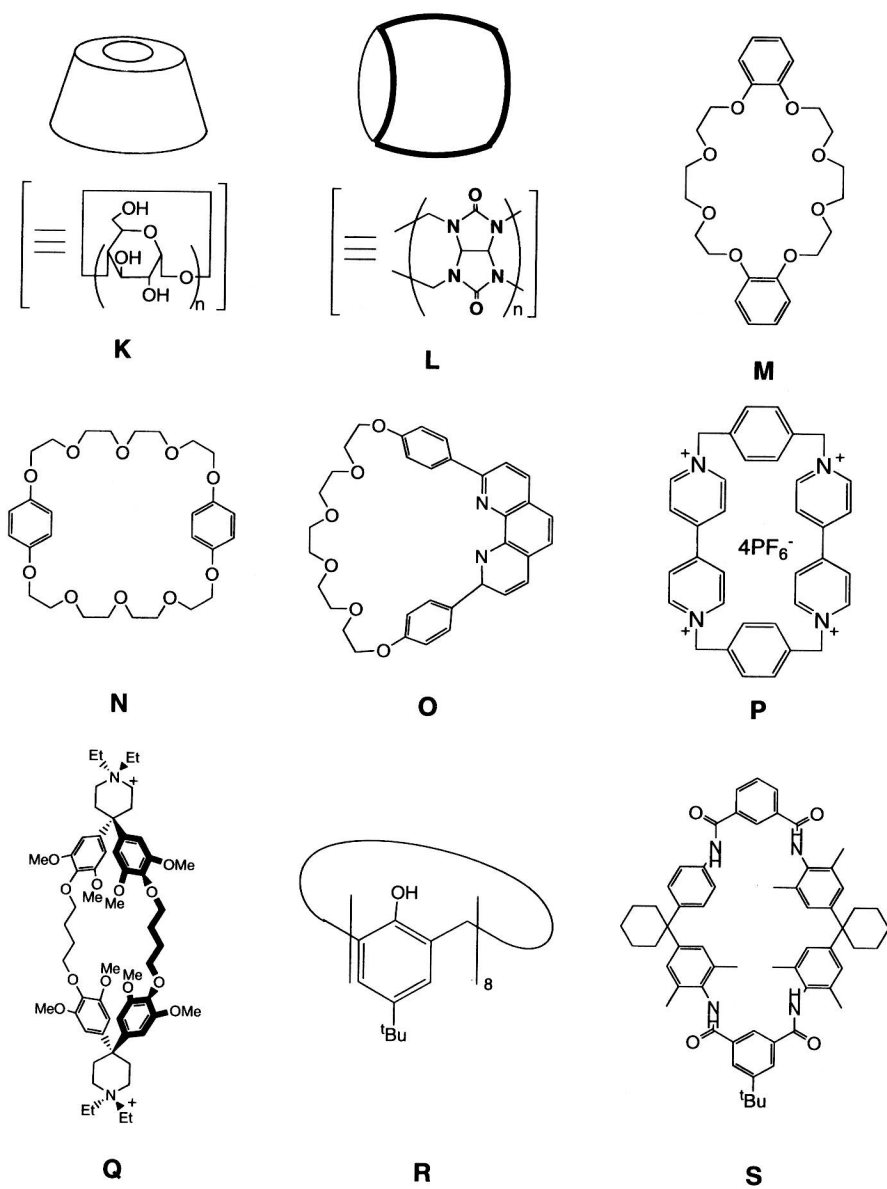
Main Chain-Type Polyrotaxane, **A**Side Chain-Type Polyrotaxane, **C**Main Chain-Type Polyrotaxane, **B**Side Chain-Type Polyrotaxane, **D**Poly[2]rotaxane, **E**Poly[3]rotaxane, **F**

Typical Structures of Polyrotaxanes

Poly[2]catenane, **G**Poly[2]catenane, **I**Poly[2]catenane, **H**Polycatenane, [n]Catenane, **J**

Typical Structures of Polycatenanes

Scheme 2



Structures of Representative Wheel Components

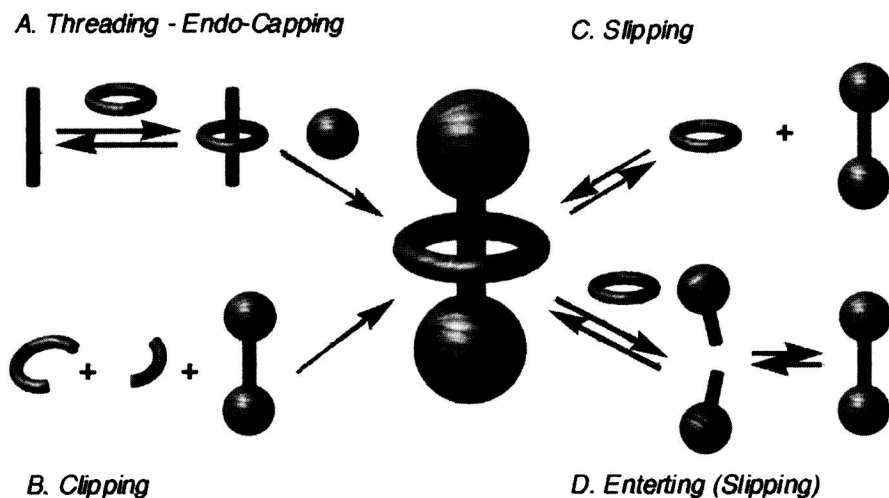
Scheme 3

of supramolecular chemistry. Even with such fortunate circumstances in recent times, the biggest problems to be overcome would be the absence of appropriate wheel components. As shown in Scheme 3, there are several examples of wheel components (K-S) which are used in the interlocked polymers among those used in rotaxanes and catenanes. Although these macrocycles are wheels good enough to be interactable with the axle components with each particular interaction, most of them suffer from synthetic difficulty and/or high cost. Creation or development of cheap or easily prepared wheel components is strongly desired.

1.3

Synthesis of Interlocked Polymers

Synthesis of polyrotaxanes and polycatenanes is performed basically by using or applying the synthetic methods for rotaxanes and catenanes.



Scheme 4

Scheme 4 summarizes the representative synthetic methods of [2]rotaxanes [17, 21]. Methods A and B are characterized by the kinetically controlled process as the final step to the rotaxane. In particular, method A is the general and most straightforward synthesis: i.e., end-capping of the axle terminal with a bulky group after threading of the axle into the wheel. Most polyrotaxanes are prepared according to this methodology. On the other hand, methods C and D at the left side undergo the thermodynamically controlled process at the equilibrium in the last step of the process. Since the procedures in the two synthetic methods completely differ from each other, the

control of the synthetic reaction is also different. The thermodynamic control process has recently attracted much attention from the viewpoint of advantages, not only in yield but in also milder reaction in accordance with progress in supramolecular chemistry.

The above-mentioned “directed” synthesis always requires a certain strong interaction between the wheel and the axle before making the interlocked bond in any method. As for the example of the wheels depicted in Scheme 3, hydrophobic interaction is the major attractive interaction in the cases of cucurbituril and cyclodextrin (A, B), thereby resulting in limitation as the wheel-axle complex formation should be done in water. In particular, it is an additional difficulty to employ the complexation in strongly acidic conditions owing to the extremely low solubility of cucurbituril.

In the case of crown ethers (M, N) which should have the number of ring members more than ca. 24, since the major attractive interaction is the hydrogen bonding with secondary ammonium ion and/or ion-dipole interaction with cationic species, the complexation should be carried out under conditions capable of encouraging such interactions. Coordination bonding to metal is the attractive interaction in the case of oligoether-macrocycles having a bidentate nitrogen ligand moiety (F). The coordination is quite stable with strong “bonding” and therefore the yield of rotaxane is usually high. Paraquat-type cationic host as the wheel component (G) requires axles having highly electron-donating property like aromatic ethers and tetrathiafulvalenes, where cation- π and/or CT interactions are the major attractive interactions. Macrocycles consisting of amide functionalities (I) make the corresponding interlocked structures with the assistance of hydrogen bonding interaction between the amide groups and the axle components. In this case, the final step reaction to rotaxane need not disturb the hydrogen bonding.

Synthesis of catenane is much more difficult than that of rotaxanes because it always depends on the final step of a ring-closing reaction with generally low efficiency. Namely, macrocycle formation at the final stage undergoes an unfavorable process with regard to entropy, and therefore the yield of catenane is usually low even by a “directed” synthesis, other than those utilizing metal-templated synthesis [16, 23, 27]. Although high yield synthesis is sometimes accessible to [2] and [3]catenanes, no polymer [n]catenane listed in Scheme 2 (J) is reported at all. The maximum number of n is 5 at present time. In contrast to polycatenane, poly[2]catenane can be easily prepared by polymerization or copolymerization of [2]catenane with polymerizable groups pre-synthesized through an efficient method.

This review mainly summarizes recent progress in the chemistry of interlocked polymers including oligomers (consisting of more than three components) in this decade. In particular, the review first describes the “genuine” interlocked polymers of which repeating units are linked through the interlocked structures—they can be called “topological polymers”—and also em-