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Feature article

Mechanically linked supramolecular polymer architectures derived from macromolecular [2]rotaxanes: Synthesis and topology transformation

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ABSTRACT

This review article deals with the construction and function of dynamic macromolecular systems having mechanically linked polymer chains which can undertake a topology transformation to induce structure and property changes. Synthesis of a macromolecular [2]rotaxane (M2R) possessing a macromolecular switch function is first described, which is a structure-definite ideal polyrotaxane consisting of one polymer axle and one macrocycle wheel. Its application to the synthesis of rotaxane cross-linked polymers (RCP) and topology-transformable polymers is discussed along with their properties, where the rotaxane-linking of polymer chains plays a crucial role. The M2R-based cross-linker is prepared and applied to the synthesis of RCPs by adding it into radical polymerization systems of vinyl monomers. RCPs have high stretchability and toughness. Rotaxane-linked block copolymers and cyclic polymers synthesized by introducing polymer chains onto the wheel and axle components of M2R are subjected to the topology transformation using the switch function of M2R to cause remarkable structure and property changes.

Contents

1. Introduction

As the Nobel Prize in Chemistry 2016 was awarded to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa for the design and synthesis of molecular machines, mechanically linked molecules whose components are interlocked without the atoms connecting directly with each other, have attracted lots of interest and have been developed for the last three decades [1–11]. The combination of organic chemistry and supramolecular chemistry made it possible to build various mechanically interlocked molecules (Fig. 1).

Among them, the rotaxane comprising dumbbell shaped units

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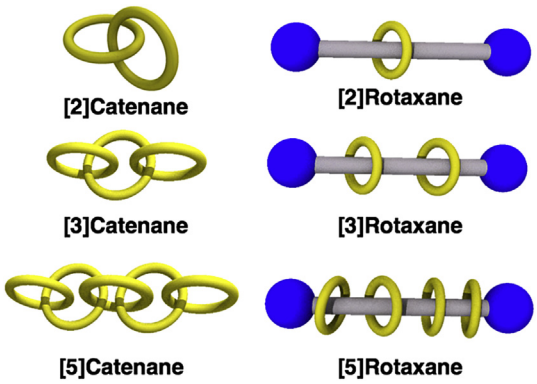

Fig. 1. Structures of catenanes and rotaxanes as the typical mechanically interlocked molecules.

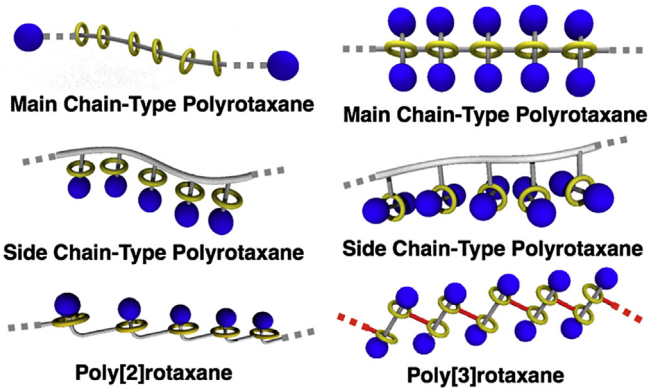

Fig. 2. Structures of typical polyrotaxanes.

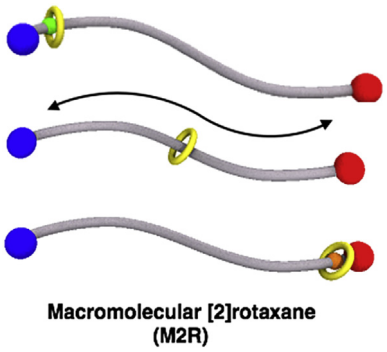

Fig. 3. Macromolecular [2]rotaxane (M2R) and macromolecular switch based on M2R.

and threaded wheels is characterized by high freedom and mobility of its components. The successful construction of molecular switches, molecular machines, and so on originates from the unique characteristics of the rotaxane's components. Therefore, the integration of rotaxane units seems more interesting. The polymer comprising the rotaxane structure as the repeating units, called a polyrotaxane, is actually attracting considerable attention owing to its wide range of usefulness based on the dynamic nature via cooperative interactions (Fig. 2).

In fact, syntheses and applications of a variety of polyrotaxanes, mainly of the main-chain-type, have been studied so far directed toward the development of innovative polymeric materials using the dynamic nature of the components besides the construction of

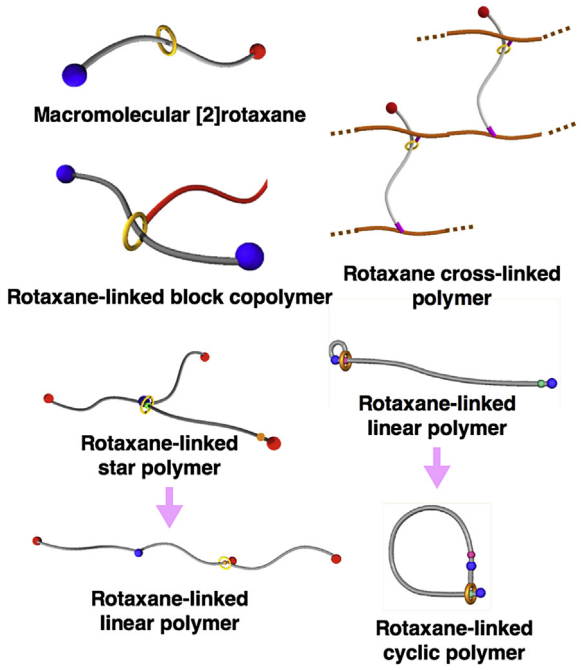

Fig. 4. Dynamic macromolecular systems derived from M2R.

novel polymers. Several comprehensive reviews and books published cover them [5,8–11]. Although many polyrotaxanes have been reported in these two decades, few structure-definite polyrotaxanes have appeared, presumably because of the synthetic difficulty. In particular, synthesis of a structure-definite polyrotaxane comprising one polymeric axle and one threaded wheel, the simplest polyrotaxane named as a macromolecular [2]rotaxane (M2R), has still been a big challenge, because M2R would possess a great potential in the development of dynamic polymeric materials driven by *e.g.* a macromolecular switch (Fig. 3) based on the controllable location and mobility of the components.

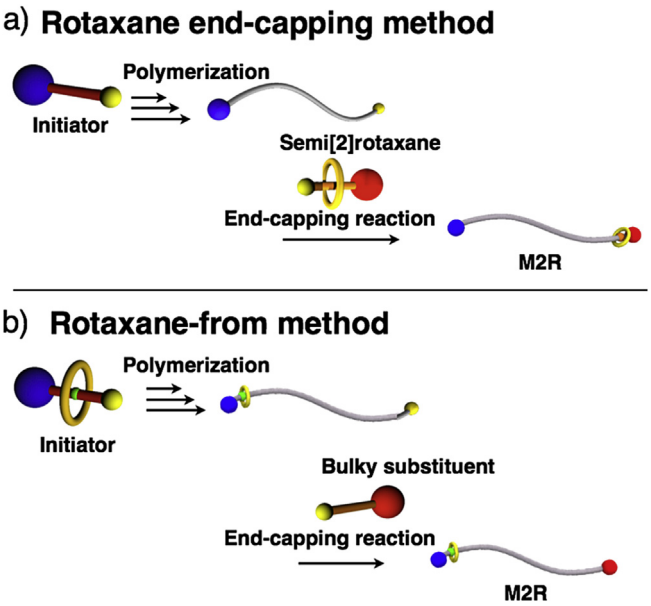

Fig. 5. Synthetic strategies for **M2R** via rotaxane end-capping method and rotaxane-from method.