Topology Transformation toward Cyclic, Figure-Eight-Shaped, and Cross-Linked Polymers via Dynamic Covalent Chemistry

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*JST-PRESTO*)
○Hirogi Yokochi,[1] Daisuke Aoki,[1,2] Hideyuki Otsuka[1]
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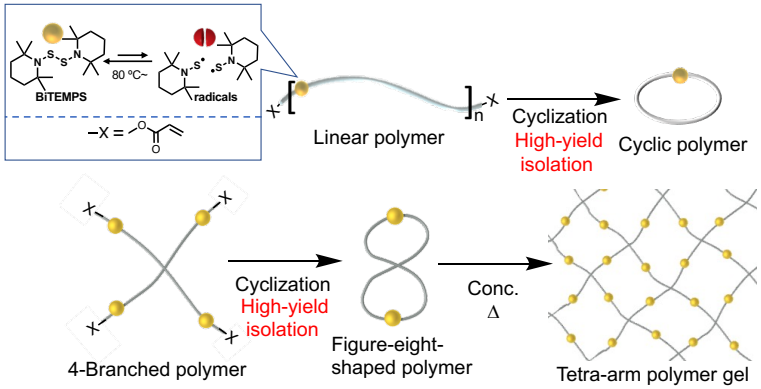
Topological transformations of polymer architectures via dynamic covalent chemistry have attracted considerable attention in recent decades, as they change the primary structure of the polymer architecture and thus the polymer properties. However, topological transformations to produce cyclic topologies remain challenging. In this study, cyclic and figure-eight-shaped polymers were synthesized based on the dynamic behavior of the bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) linkage.[1] Linear and 4-branched polymers were transformed into cyclic polymers and figure-eight-shaped polymers, using the following sequence: 1) A thiol–ene reaction was used to introduce BiTEMPS units into the terminal structures of the polymers to be cyclized; 2) an entropy-driven transformation to give the desired cyclic topology through the exchange reaction of the BiTEMPS units was induced by dilution and heating; 3) acyclic impurities with reactive groups were selectively removed via a thiol–ene click reaction with polystyrene particles that contain dangling thiol groups on their surface and subsequent simple filtration. The radicals generated by BiTEMPS upon heating are highly tolerant toward a variety of chemical species, including oxygen and olefins, and exhibit high reactivity in exchange reactions, making them applicable for various skeletons. The simplicity and substrate versatility of this procedure are demonstrated via the highly efficient gram-scale synthesis of cyclic and figure-eight-shaped polymers. Moreover, we describe the topological transformation of the obtained cyclic and/or figure-eight-shaped polymers into cross-linked polymers with precisely controlled physical properties by using their cyclic or figure-eight topology and the dynamic nature of the BiTEMPS units in their structures.



1) H. Yokochi, D. Aoki, H. Otsuka *et al*., *Macromolecules*. **2021**, *54*, 9992.