

Topological Polymer Chemistry

Designing Complex Macromolecular Graph Constructions

Yasuyuki Tezuka (Tokyo Institute of Technology)

Cyclic (ring) and multicyclic polymer chain architectures are topologically intriguing and have inspired expanding research interests. A class of *multicyclic* polymer topologies, including three subclasses of *spiro*-, *bridged*- and *fused*-forms, are particularly unique not only from the topological geometry viewpoint but also from their programmed folding structures of biopolymer relevance. We have so far demonstrated an *electrostatic self-assembly and covalent fixation* (ESA-CF) protocol as a powerful synthetic approach, where ion-paired linear or non-linear polymer self-assemblies are employed as key intermediates. As a showcase example, we have recently achieved the ESA-CF construction of a topologically significant *fused*-tetracyclic $K_{3,3}$ graph polymer, known as a prototypical non-planar graph in topological geometry, and remarkably identified in cyclic polypeptides (cyclotides) of diverse biofunctions, by using a uniform-size dendritic polymer precursor having six cyclic ammonium salt end groups carrying two units of a trifunctional carboxylate counteranions. Moreover, a variety of multicyclic polymer topologies of the three subclasses and their hybrid-forms, including a triply-*fused* tetracyclic and a quadruply-*fused* pentacyclic forms (unfolded tetrahedron-graph, and “shippo”-form, respectively) have been constructed through the ESA-CF process in conjunction with a tandem alkyne-azide addition, i.e., *click*, and olefin metathesis, i.e., *clip*, reactions. Upon these synthetic developments, we are now entering into an exciting new era of polymer science and polymer materials engineering based on the precision designing of polymer topologies, which appears relevant to a “Cambrian explosion period” experienced in the evolution of life systems.

References

- [1] *Topological Polymer Chemistry: Progress of cyclic polymers in synthesis, properties and functions*, Y. Tezuka ed., World Scientific, Singapore, 2013.
- [2] Heguri H, Yamamoto T, and Tezuka Y, *Angew. Chem. Int. Ed.*, **54**, 8688 (2015).
- [3] Suzuki T, Yamamoto T, and Tezuka Y, *J. Am. Chem. Soc.*, **136**, 10148 (2014).
- [4] Tomikawa Y, Yamamoto T, Tezuka Y, *Macromolecules*, **49**, 4076 (2016).