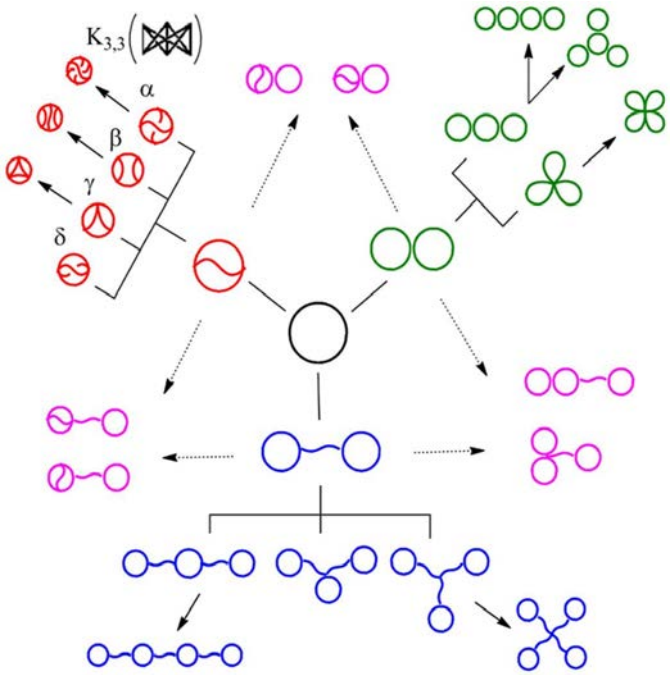
Topological Polymer Chemistry:Endless attractions with macromolecular designing

The fascinating developments have now been ongoing in topological polymer chemistry, since a variety of topologically defined and formidably complex polymer constructions have become accessible along with diverse synthetic protocols introduced during the first two decades of this century [1,2]. Thereupon, the precision designing of static and dynamic properties and functions of non-linear polymer substrates, assisted with the explicit computational simulations by the expanding capacity, has proceeded to uncover unprecedented topology effects based upon topological geometry conjectures, intriguingly counterintuitive to Euclidian geometry commonsenses.



Professor Tezuka group have so far demonstrated an *electrostatic self-assembly and covalent fixation* (ESA-CF) procedure as a powerful synthetic technique for diverse topological polymers, shown in **Scheme** above, where ion-paired self-assemblies by linear or non-linear polymers are employed as key intermediates [3]. A series of complex multicyclic topologies of either *spiro*-, *bridged*- and *fused*-forms have successfully been constructed by the ESA-CF protocol in conjunction with recently developed effective linking chemistries,

including alkyne-azide addition (*click*) and olefin metathesis (*clip*) reactions. Notably, in particular, a topologically significant fused-tetracyclic $K_{3,3}$ graph polymer topology, which is known as a prototypical non-planar graph in topological geometry, and remarkably identified in cyclic polypeptides (cyclotides) of diverse biofunctions, has been constructed through the programmed ESA-CF polymer folding by using a uniform-size dendritic polymer precursor. Furthermore, the programmed polymer folding, invoked with the concurrent breakthrough of the precision AI prediction of protein folding, has now evolved into an emerging frontier in topological polymer chemistry [4, 5, 6].

References

1) *Topological Polymer Chemistry: concepts and practices*, Y. Tezuka, T. Deguchi, eds., Springer Japan,Tokyo, 2021.

2) *Topological Polymer Chemistry: Progress of cyclic polymers in synthesis, properties and functions*, Y. Tezuka ed., World Scientific, Singapore, 2013.

3) Y. Tezuka, *Acc. Chem. Res.*, **50**,2661 (2017).

4) Y, Tezuka, *Isr. J. Chem. (Rosarium Philosophorum – Macromlecules)*, **60**, 67 (2020).

5) Y. Tezuka, *React. Funct. Polym.*, **148**, 104489 (2020).

6) K. Kyoda, T. Yamamoto, Y. Tezuka, *J. Am.Chem. Soc.*, **141**, 7526 (2019).

Yasuyuki Tezuka is a Professor Emeritus of Tokyo Institute of Technology. He obtained a BS (1976) and a MS (1978) degree in synthetic chemistry at The University of Tokyo. He moved to Ghent University (Belgium) in 1979 as a fellowship student of Belgian (Flemish) government, and completed his doctorate study in Belgium in 1982. He then returned to Japan to start an academic carrier as an assistant professor at Nagaoka University of Technology, and promoted to an associate professor in 1991. In 1994, he moved to Tokyo Institute of Technology (Department of Organic and Polymeric Materials), where he served as a full professor from 2003 to his official retirement in 2019. He received Tokyo Tech Award of Best Teacher, 2004, The Award of the Society of Polymer Science, Japan (2010), and SPSJ Award for Outstanding Achievement in Polymer Science and Technology (2018). He served as an Asian Editor (2006-2011) and continued as an Editor-in-Chief (2012-2018) for Reactive and Functional Polymers. He has currently held the position of Honorary Editor of the journal. His research activities have been focusing on ***topological polymer chemistry***, designing topologically unique macromolecular architectures, and uncovering their topology effects.