

# Division of Materials Chemistry

## – Polymer Controlled Synthesis –

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## Scope of Research

Our research focuses on creation of new organic molecules with potential as key reagents and materials for future science and technologies. Furthermore, we have been developing new organic and polymeric materials based on our tailor-made molecules. For example, we are developing a new living radical polymerization method using heavier heteroatom compounds as controlling agents. Another topic is the synthesis of cycloparaphenylenes, hoop-shaped  $\pi$ -conjugated molecules, based on new synthetic strategies. We also study various condensed states of polymers by both static and dynamic methods to understand the relationship between structure and physical properties.



### KEYWORDS

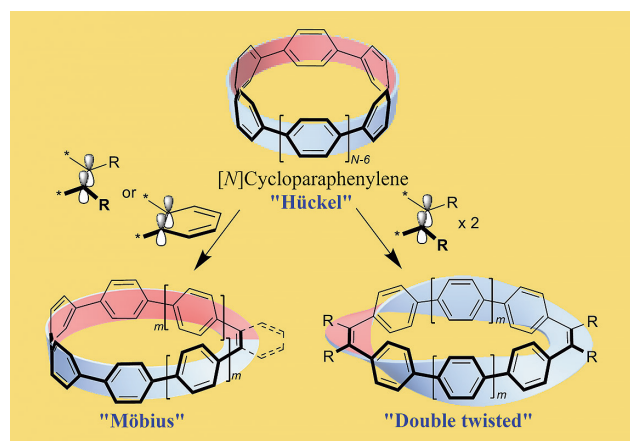
Organic Synthesis      Polymer Synthesis      Living Radical Polymerization  
Polymer Properties      Curved  $\pi$ -Conjugated Molecules

### Recent Selected Publications

- Jiang, Y.; Fan, W.; Tosaka, M.; Yamago, S., Controlled Synthesis of High-Molecular-Weight Polystyrene and Its Block Copolymers by Emulsion Organotellurium-Mediated Radical Polymerization, *ACS Macro Lett.*, **11**(12), 1331-1335 (2022).
- Park, B.; Tosaka, M.; Yamago, S., Crystallization of Isotactic Poly(*N,N*-diethyl acrylamide) Synthesized by Ytterbium Triflate/ $H_2O$  Catalyzed Stereoselective Radical Polymerization, *Polym. J.*, **53**, 533-538 (2021).
- Jiang, Y.; Fan, W.; Tosaka, M.; Cunningham, M. F.; Yamago, S., Fabrication of Structurally Controlled Poly(*n*-Butyl Acrylate) Particles by ab initio Emulsion Organotellurium-mediated Radical Polymerization. Synthesis of High Molecular Weight Homo and Block Copolymers, *Macromolecules*, **54**, 10691-10699 (2021).
- Imamura, Y.; Yamago, S., Role of Lewis Acids in Preventing the Degradation of Dithioester-Dormant Species in the RAFT Polymerization of Acrylamides in Methanol to Enable the Successful Dual Control of Molecular Weight and Tacticity, *Polym. Chem.*, **12**, 5336-5341 (2021).
- Li, X.; Ogihara, T.; Nakamura, Y.; Yamago, S., Evidence for Polarity- and Viscosity-Controlled Pathways in the Termination Reaction in the Radical Polymerization of Acrylonitrile, *Macromolecules*, **54**, 4497-4506 (2021).

## Synthesis of Twisted [N]Cycloparaphenylene by Alkene Insertion

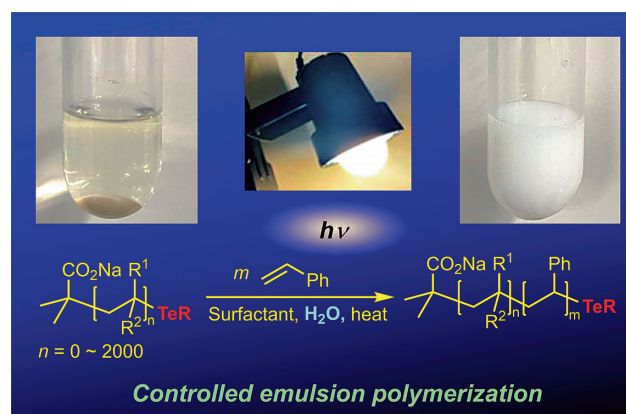
By fusing CPP precursors and alkene or *ortho*-phenylene groups via coupling reactions, mono-alkene-inserted [N] cycloparaphenylenes **1** [(ene)-[N]CPP] with  $N = 6, 8,$  and  $10,$  mono-*ortho*-phenylene-inserted [6]CPP **2**, and di-alkene-inserted [N]CPP **3** [(ene)<sub>2</sub>-[N]CPP] with  $N = 4, 6,$  and  $8$  were synthesized. Single-crystal X-ray diffraction analyses revealed that the strips formed by the  $\pi$ -surfaces of **1** and **2** exhibited a Möbius topology in the solid state. The Möbius topology in the parent **1** and **2** in a solution was lost due to the free rotation of the paraphenylene unit even at low temperatures. On the other hand, ene- [6]CPP **4** with eight 1-pyrrolyl groups preserved the Möbius topology even in a solution. Despite a twist, **1** has in-plane conjugation and possesses a unique size dependence of the electronic properties; i.e., the opposite size dependency of the HOMO-LUMO energy relative to conventional  $\pi$ -conjugated molecules.



**Figure 1.** Insertion of alkene or *ortho*-phenylene units into a CPP skeleton.

## Controlled Synthesis of High-Molecular-Weight Polystyrene and Its Block Copolymers by Emulsion Organotellurium-Mediated Radical Polymerization

Despite recent developments in reversible-deactivation radical polymerization, the synthesis of high-molecular-weight (HMW) polymers, particularly polystyrenes (PSts) and block copolymers, has been a formidable challenge. We have successfully synthesized structurally controlled HMW PSts and block copolymers consisting of HMW PSt segments by emulsion organotellurium-mediated radical polymerization (TERP). The hydrophilicity of the organotellurium group of TERP chain transfer agents (CTAs) was found to be important for successful control of molecular weight; CTAs **1b** and **1c** with di- and tetraethylene glycol units were suitable. By using **1b** and **1c** along with hexadecyltrimethylammonium bromide (CTAB) as the surfactant, PSts with MWs over 1 million and with low dispersity ( $D < 1.6$ ) were synthesized with monomer conversion exceeding 96%. Because of the high monomer conversion, high end-group fidelity, and rapid monomer diffusion to polymer particles, we could successfully synthesize also HMW block copolymers with low dispersity by the addition of a second monomer after converting the first monomer without isolating the macroinitiators. This method provides a valuable route for fabricating polymer materials based on HMW PSts.



**Figure 2.** Emulsion TERP giving high molecular weight homo ( $M_n > 1 \times 10^6$ ) and block copolymer ( $M_n > 4 \times 10^5$ ) with narrow dispersity ( $D < 1.6$ ).