

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 π -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 π -Conjugated Molecules

Recent Selected Publications

Jiang, Y.; Kibune, M.; Tosaka, M.; Yamago, S., Practical Synthesis of Dendritic Hyperbranched Polyacrylates and Their Topological Block Polymers by Organotellurium-Mediated Emulsion Polymerization in Water, *Angew. Chem. Int. Ed.*, **62**, e202306916 (2023).

Tosaka, M.; Takeuchi, H.; Kibune, M.; Tong, T.; Zhu, N.; Yamago, S., Stochastic Simulation of Controlled Radical Polymerization of Dendritic Hyperbranched Polymers, *Angew. Chem. Int. Ed.*, **62**, e202305127 (2023).

Terabayashi, T.; Kayahara, E.; Mizuhata, Y.; Tokitoh, N.; Nishinaga, T.; Kato, T.; Yamago, S., Synthesis of Twisted $[n]$ Cycloparaphenylenes by Alkene Insertion, *Angew. Chem. Int. Ed.*, **62**, e202214960 (2023).

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**, 1331-1335 (2022).

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).

Stochastic Simulation of Controlled Radical Polymerization Forming Dendritic Hyperbranched Polymers

The formation process of hyperbranched polymers (HBPs) based on the reversible deactivation radical polymerization (RDRP) using a branch-inducing monomer, evolmer, was investigated by stochastic simulation. Our original simulation program successfully reproduced the change of dispersities (D_s) during the polymerization process. Based on the simulation, we found that the observed D_s ($\approx 1.5-2$) are due to the distribution of the number of branches instead of undesired side reactions. We further found that the branch structures are well controlled, so the majority of HBPs have structures close to the ideal one (Fig. 1). The simulation also suggested that, if we pay attention to individual molecules, the branch density slightly changes depending on molecular weight. This trend was experimentally confirmed by synthesizing HBPs with an evolmer having a phenyl group and analyzing the signal intensity from multiple detectors in size exclusion chromatography.

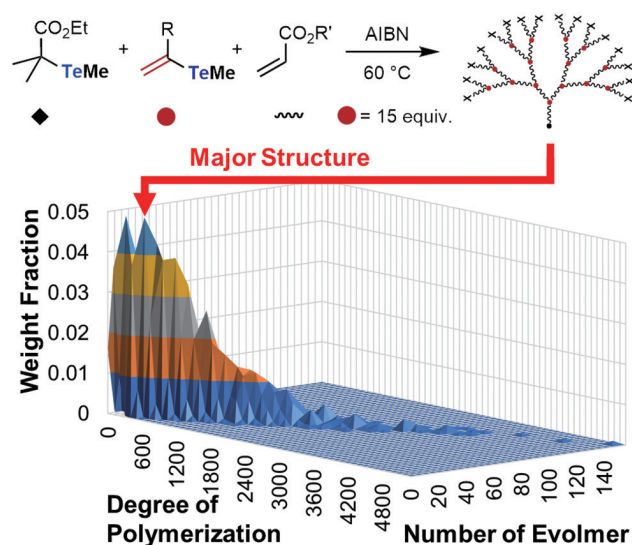


Figure 1. Weight distribution of simulated structure of HBP.

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) $_2$ - $[n]$ CPP] with $n = 4, 6,$ and 8 were synthesized. Single-crystal X-ray diffraction analyses revealed that the strips formed by the π -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 π -conjugated molecules.

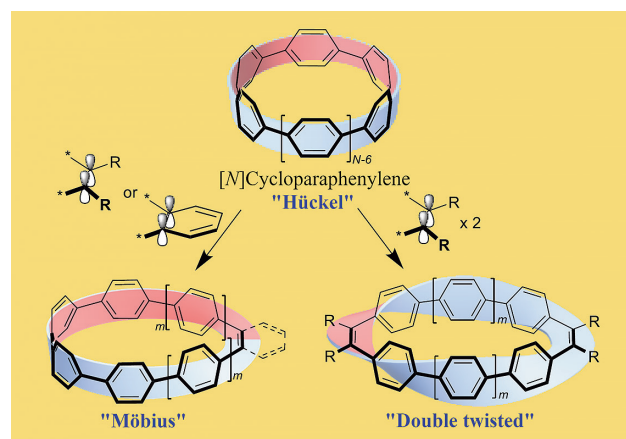


Figure 2. Insertion of alkene or *ortho*-phenylene units into a CPP skeleton.