

# 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

## Selected Publications

- Nakamura, Y.; Yamago, S., Termination Mechanism in the Radical Polymerization of Methyl Methacrylate and Styrene Determined by the Reaction of Structurally Well-defined Polymer End Radicals, *Macromolecules*, **48**, 6450-6456 (2015).
- Patel, V. K.; Kayahara, E.; Yamago, S., Practical Synthesis for  $[n]$ Cycloparaphenylenes ( $n = 5, 7-12$ ) by  $H_2SnCl_4$ -Mediated Aromatization of 1,4-Dihydroxycyclo-2,5-diene Precursors, *Chem. Eur. J.*, **21**, 5742-5749 (2015).
- Toriumi, N.; Muranaka, A.; Kayahara, E.; Yamago, S.; Uchiyama, M., In-Plane Aromaticity in Cycloparaphenylene Dications: A Magnetic Circular Dichroism and Theoretical Study, *J. Am. Chem. Soc.*, **137**, 82-85 (2015).
- Sugihara, Y.; Yamago, S.; Zetterlund, P., An Innovative Approach to Implementation of Organotellurium-Mediated Radical Polymerization (TERP) in Emulsion Polymerization, *Macromolecules*, **48**, 4312-4318 (2015).
- Gros, A.; Tosaka, M.; Huneau, B.; Verron, E.; Poompradub, S.; Senoo, K., Dominating Factor of Strain-induced Crystallization in Natural Rubber, *Polymer*, **76**, 230-236 (2015).

## Modular Synthesis of Mid-Chain-Functionalized Polymers by Photoinduced Diene- and Styrene-Assisted Radical Coupling Reaction of Polymer-End Radicals

An array of precisely located functional groups in natural macromolecules, such as nucleotides and proteins, plays a pivotal role in their well-defined three-dimensional structure and numerous functions. Therefore, controlling the position and number of reactive functional groups in a structurally well-defined synthetic polymer has been an important challenge in order to create novel functional polymer materials with enhanced or new properties. Photo-irradiation of structurally well-defined “living” polymers prepared by organotellurium-mediated living radical polymerization in the presence of dienes or styrenes induced selective polymerend coupling reaction with the concomitant insertion of the dienes or styrenes with >90% coupling efficiency. The number of inserted dienes or styrenes could be highly controlled to two molecules when acrylic polymers were used. Therefore, various mid-chain-functionalized polymers with well-controlled molecular and macromolecular structure in terms of their molecular weight, molecular weight distribution, functionality, and position were successfully synthesized by employing functionalized dienes or styrenes. The method was applied to the facile synthesis of mid-chain-functionalized telechelic polymers and a 4-miktoarm star polymer with a well-controlled structure.

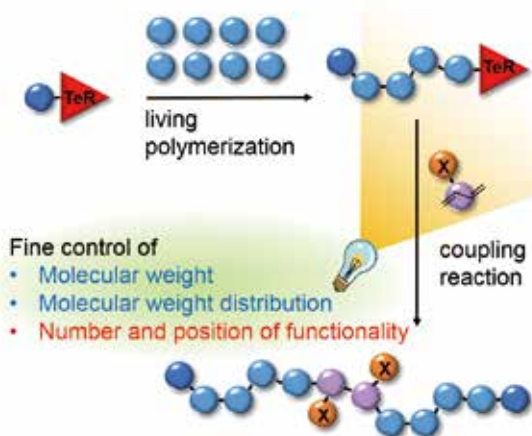


Figure 1. Novel synthetic strategy for mid-chain-functionalized polymers.

## Practical Synthesis of [n]Cycloparaphenylenes (n = 5, 7–12) by H<sub>2</sub>SnCl<sub>4</sub>-mediated Aromatization of 1,4-Dihydroxycyclo-2,5-diene Precursors

Cyclic precursors of cycloparaphenylenes (CPPs) containing 1,4-dihydroxy-2,5-cyclohexadien-1,4-diyl units were prepared by modifying the synthesis method of corresponding 1,4-dimethoxy derivatives, which was developed by Jasti and co-workers. Reductive aromatization of the diyl moieties by SnCl<sub>2</sub>/2HCl took place under mild conditions and afforded CPPs incorporating 5 or 7–12 phenylene units with good yield. Highly strained [5]CPP was synthesized at more than 0.3 g. <sup>119</sup>Sn NMR spectroscopy clarified the *in situ* formation of an ate complex, H<sub>2</sub>SnCl<sub>4</sub>, upon mixing a 2:1 ratio of HCl and SnCl<sub>2</sub>, which serves as a highly active reducing agent under nearly neutral conditions. When more than two equivalents of HCl, in relation to SnCl<sub>2</sub>, were used, acid-catalyzed decomposition of the CPP precursors took place. The stoichiometry of HCl and SnCl<sub>2</sub> was found to be critical in achieving the desired aromatization reaction of highly strained CPP precursors.

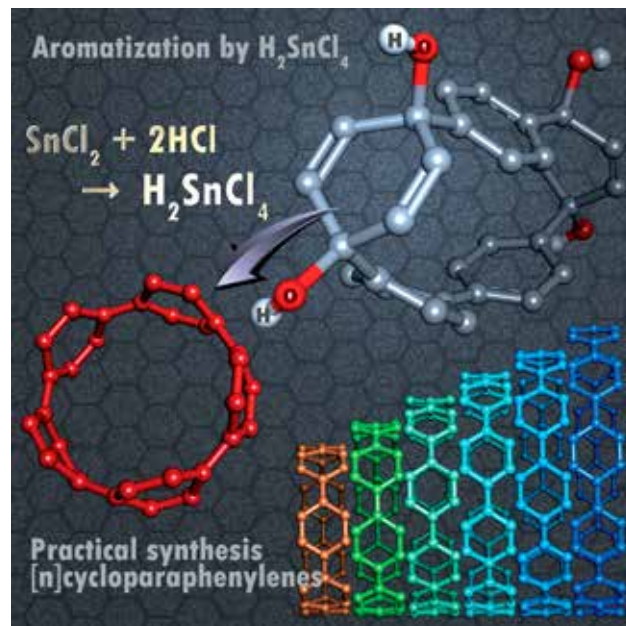


Figure 2. Synthesis of [n]Cycloparaphenylenes (n = 5, 7–12)