

# 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

Li, X.; Kato, T.; Nakamura, Y.; Yamago, S., The Effect of Viscosity on the Coupling and Hydrogen-Abstraction Reaction between Transient and Persistent Radicals, *Bull. Chem. Soc. Jpn.*, **94**, 966-972 (2021).

Park, B.; TosaKa, M.; Yamago, S., Crystallization of Isotactic Poly(*N,N*-diethyl acrylamide) Synthesized by Ytterbium Triflate/H<sub>2</sub>O Catalyzed Stereoselective Radical Polymerization, *Polym. J.*, **53**, 533-538 (2021).

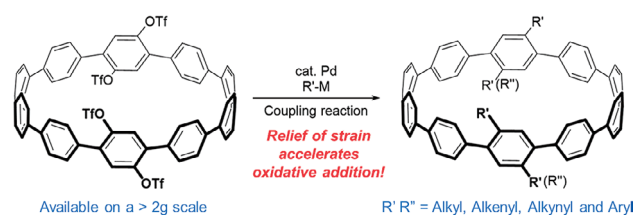
Imamura, Y.; Fujita, T.; Kobayashi, Y.; Yamago, S., Tacticity, Molecular Weight, and Temporal Control by Lanthanide Triflate-Catalyzed Stereoselective Radical Polymerization of Acrylamides with an Organotellurium Chain Transfer Agent, *Polym. Chem.*, **11**, 7042-7049 (2020).

Kayahara, E.; Nakano, M.; Sun, L.; Ishida, K.; Yamago, S., Syntheses of Tetrasubstituted [10]Cycloparaphenylenes by a Pd-catalyzed Coupling Reaction. Remarkable Effect of Strain on the Oxidative Addition and Reductive Elimination, *Chem. Asian J.*, **15**, 2451-2455 (2020).

Lu, Y.; Yamago, S., Synthesis of Structurally Controlled, Highly Branched Polymethacrylates by Radical Polymerization Through the Design of a Monomer Having Hierarchical Reactivity, *Macromolecules*, **53**, 3209-3216 (2020).

## Syntheses of Tetrasubstituted [10]Cycloparaphenylenes by a Palladium-catalyzed Coupling Reaction. Remarkable Effect of Strain on the Oxidative Addition and Reductive Elimination

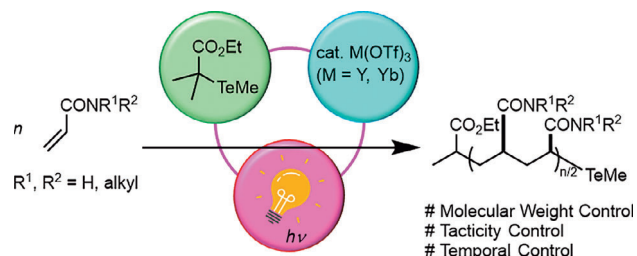
A small library of tetrasubstituted [10]cycloparaphenylene ([10]CPP) derivatives bearing alkyl, alkenyl, alkynyl and aryl substituents was constructed by a palladium-catalyzed cross-coupling reaction starting from tetratriflate [10]CPP, which was readily available in high yields on a >2 g scale. The CPP skeleton increases the reactivity of aryl triflate for oxidative addition to the palladium species, and the tetratriflate [10]CPP was found to be 10 times more reactive than its linear paraphenylene analogue, as determined by competition experiments. Theoretical calculations suggested that the accumulation of the small strain relief from each paraphenylene unit not involved in the reaction is responsible for the observed enhancement of reactivity.



**Figure 1.** Synthesis of tetrasubstituted [10]cycloparaphenylene derivatives bearing alkyl, alkenyl, alkynyl and aryl substituents.

## Tacticity, Molecular Weight, and Temporal Control by Lanthanide Triflate-catalyzed Stereoselective Radical Polymerization of Acrylamides with an Organotellurium Chain Transfer Agent

Polymerization of *N,N*-dimethylacrylamide, *N*-isopropylacrylamide, *N,N*-diethylacrylamide, and acrylamide while controlling both molecular weight and stereoregularity was achieved by organotellurium-mediated radical polymerization (TERP) in the presence of  $Y(OTf)_3$  or  $Yb(OTf)_3$  as a Lewis acid catalyst. In previous works, dual-control reactions have been limited to the synthesis of low-molecular-weight polyacrylamides. On the other hand, the current conditions could overcome this limitation. We could demonstrate the high compatibility of the TERP chain transfer agent and dormant species to the Lewis acid by nearly complete end-group fidelity. Stereoblock copolymers consisting of atactic and isotactic PDEAA blocks were also successfully synthesized. Temporal control while maintaining dual control was also accomplished by using photoactivation of organotellurium species. The effect of tacticity on the polymer structure in the gas phase was studied for the first time by ion mobility spectrometry, revealing that the collision cross section increased as the meso diad selectivity of the polyacrylamide increased.



**Figure 2.** Polymerization of acryl amide with controlled tacticity, molecular weight, and temporal progress.