

Division of Materials Chemistry

– Polymer Controlled Synthesis –

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*New Research Field
Development Project

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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 Properties

Polymer Synthesis

Curved π -Conjugated Molecules

Living Radical Polymerization

Selected Publications

Li, X.; OgiHara, T.; Abe, M.; Nakamura, Y.; Yamago, S., The Effect of Viscosity on the Diffusion and Termination Reaction of Organic Radical Pairs, *Chem. Eur. J.*, **25**, 9846-9850 (2019).

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).

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).

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).

One-Step Synthesis of Dendritic Highly Branched Polystyrenes by Organotellurium-Mediated Copolymerization of Styrene and a Dienyl Telluride Monomer

By a one-step copolymerization of dienyly telluride (DT) and styrene (St) in the presence of organotellurium chain transfer agent (CTA) at thermal condition, dendritic highly branched polystyrenes (HB-PSts) were successfully synthesized. The molecular weight, branching density, and dendritic generation were easily controlled by the ratio of CTA, DT, and St with maintaining low dispersity ($D < 2.2$). The branching efficiency estimated by a deuterium-labeling experiment showed that DT quantitatively (>95%) served as the branching point. The end group fidelity was determined by the end group transformation to pyrene derivative and was proved to be high (ca. 90%). Intrinsic viscosity of the HB-PSt was significantly lower than that of linear polystyrenes and were easily tuned by the branching number and branching density. The method is compatible of various functional groups, and furthermore, chloro and acetoxy-substituted styrenes were also used as comonomer. A tadpole block copolymer was also synthesized by starting from linear PSt as a macroinitiator.

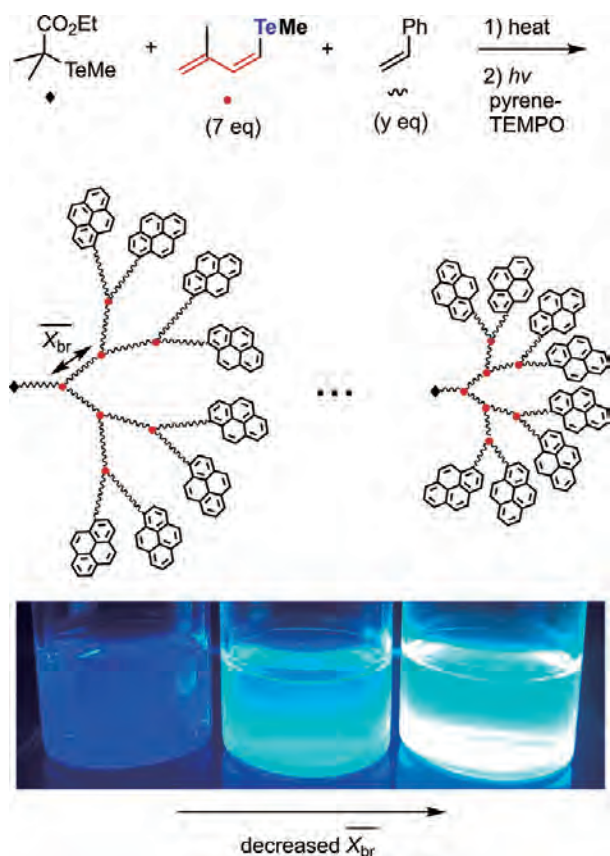


Figure 1. End group transformation of the highly branched polystyrene.

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.

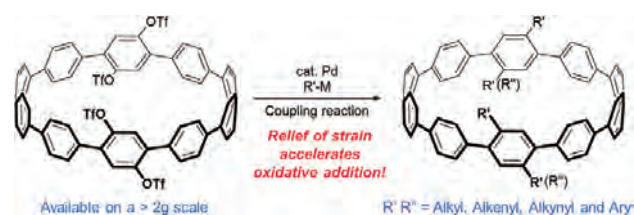


Figure 2. Synthesis of tetrasubstituted [10]cycloparaphenylene derivatives bearing alkyl, alkenyl, alkynyl and aryl substituents.