

Division of Materials Chemistry

– Polymer Controlled Synthesis –

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CHEN, Dongyang University of St. Andrews, Scotland, 15 October–17 November

SOE, Myo Min University of Yangon, Myanmar, 16 November–13 December

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

Selected Publications

Lu, Y.; Yamago, S., One-step Synthesis of Dendritic Highly Branched Polystyrenes by Organotellurium-mediated Copolymerization of Styrene and a Dienyl Telluride Monomer, *Angew. Chem. Int. Ed.*, **58**, 3952-3956 (2019).

Fan, W.; Yamago, S., Synthesis of Structurally Controlled Poly(N-vinyl amide)s and Poly(vinyl amine)s and Their Block Copolymers Using Organotellurium-mediated Radical Polymerization, *Angew. Chem. Int. Ed.*, **58**, 7113-7116 (2019).

Li, X.; Ogiwara, 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).

Strain-Induced Double Carbon–Carbon Bond Activations of Cycloparaphenylenes by a Platinum Complex: Application to the Synthesis of Cyclic Diketones

The carbon–carbon (C–C) bond activation of [n]cycloparaphenylenes ([n]CPPs) by a transition-metal complex was achieved. The Pt⁰ complex Pt(PPh₃)₄ regioselectively cleaves two C–C σ bonds of [5]CPP and [6]CPP to give cyclic dinuclear platinum complexes in high yields. Theoretical calculations revealed that the relief of ring strain drives the reaction. The cyclic complex was further transformed into a cyclic diketone by using a CO insertion reaction. The mechanism of the formation of the dinuclear platinum(0) complexes was elucidated with DFT calculations, which suggested a stepwise pathway. Both steps of forming the mononuclear platinum complex and the cyclic dinuclear complex were found to be highly exothermic and have low activation energies. The DFT studies also explained regioselectivity of the reaction. The activation of the more strained [5]CPP was significantly faster compared with that of less strained [6]CPP. Consistent with the proposed strain-induced process, larger CPPs, such as [7]CPP and [8]CPP, did not show reactivity.

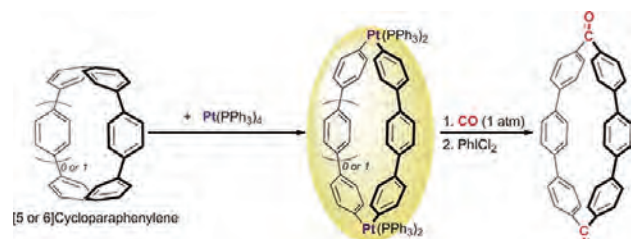


Figure 1. Carbon–Carbon Bond Activations of Cycloparaphenylenes by a Platinum Complex.

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 dienylyl 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.

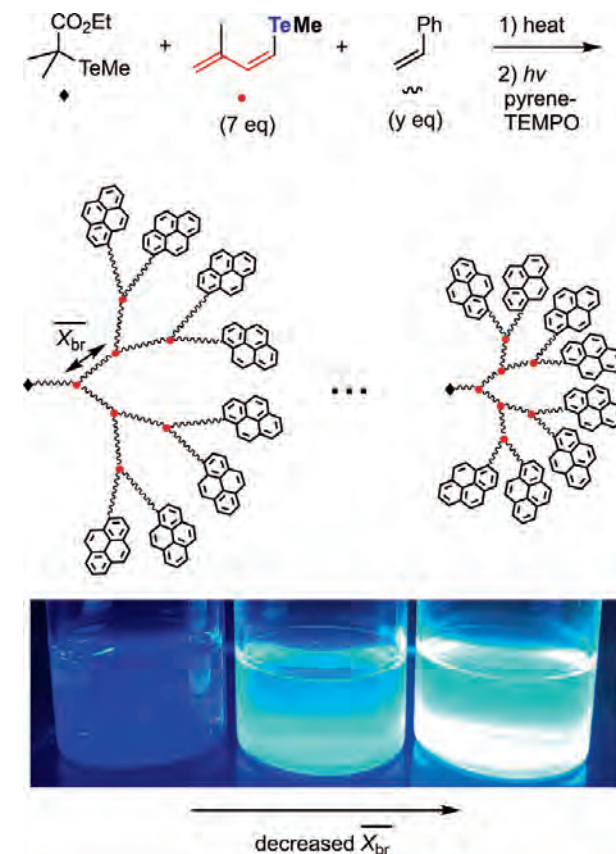


Figure 2. End group transformation of the highly branched polystyrene.