Division of Materials Chemistry
– Polymer Controlled Synthesis –

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Scope of Research

Our research focuses on creation of new organic molecules which would become 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. One such topic is the development of new living radical polymerization method utilizing heavier heteroatom compounds as controlling agents. The other topic is the synthesis of cycloparaphenylenes, hoop-shaped π-conjugated molecules, based on new synthetic strategy. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.

KEYWORDS

Organic Synthesis
Polymer Synthesis
Living Radical Polymerization
Polymer Properties
Conjugated π-molecules

Selected Publications

Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S., Selective and Random Syntheses of [*n*]Cycloparaphenylenes (*n* = 8–13) and Size-Dependence of Their Electronic Properties, *J. Am. Chem. Soc*., **133,** 8354-8361 (2011).

Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S., Size-Selective Encapsulation of C_{60} by [10]Cycloparaphenylene. Formation of the Shortest Fullerene-Peapod, *Angew. Chem. Int. Ed*., **50,** 8342-8344 (2011).

Kayahara, E.; Yamada, H.; Yamago, S., Generation of Carbanions via Stibin-Metal and Bismuthine-Metal Exchange Reaction and Its Applications to Precision Synthesis of ω-End Functionaized Polymers, *Chem. Eur. J*., **17,** 5272-5280 (2011).

Nakamura, Y.; Kitada, Y.; Kobayashi, Y.; Ray, B.; Yamago, S., Quantitative Analysis of the Effect of Azo Initiators on the Structure of α-Polymer Chain Ends in Degenerative Chain Transfer-Mediated Living Radical Polymerization Reactions, *Macromolecules*, **44,** 8388-8397 (2011).

Yamago, S., Precision Polymer Synthesis by Degenerative Transfer Controlled/Living Radical Polymerization Using Organotellurium, Organostibine, and Organobismuthine Chain Transfer Agents, *Chem. Rev.*, **109,** 5051-5068 (2009).

Tosaka, M., A Route for the Thermodynamic Description of Strain-Induced Crystallization in Sulfur-Cured Natural Rubber, *Macromolecules*, **42,** 6166-6174 (2009).

Formation of the Shortest Fullerene-Peapod

Cycloparaphenylenes (CPPs) are hoop-shaped π-conjugated molecules in which paraphenylene units are linked in a cyclic manner. They represent the simplest structural unit of armchair carbon nanotubes (Figure 1). Based on the analogy to layered carbon networks with curved surfaces, the concave cavity of the CPPs should act as a host for π-conjugated molecules with a convex surface, such as fullerenes. Such a host–guest complex would be a suitable model for elucidating convex–concave π–π interactions. We found that [10]CPP selectively encapsulated C_{60} forming the shortest fullerene-peapod, [10]CPP⊃C_{60}, among several CPPs prepared by the method we have developed (Figure 2). This finding opens the possibility of utilizing CPPs as size- and shape-selective host molecules for various guest molecules, such as higher fullerenes, metallofullerenes, and carbon nanotubes. Such complementary host–guest chemistry will be useful for the size- and shape-selective separation of higher fullerenes and carbon nanotubes.

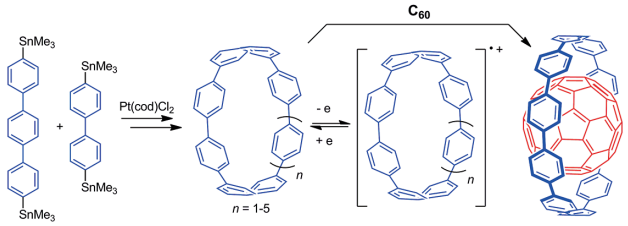

Figure 1. Synthesis and properties of CPPs.

Controlled Copolymerization of (Meth)acrylates and Vinyl Ethers by TERP, SBRP, and BIRP

Synthesis of structurally well-defined macromolecules with controlled molecular weights, molecular weight distributions, functional groups, and monomer sequences by controlled polymerization has been a significant challenge. Such macromolecules would lead to the development of new polymeric materials with improved or novel properties. Random copolymers comprised of (meth)acrylates and vinyl ethers with controlled molecular weights and polydispersities were successfully synthesized by using organotellurium-, organostibine-, and organobismuthine-mediated living radical polymerizations, which are abbreviated as TERP, SBRP, and BIRP, respectively. Highly alternating copolymers were formed for the first time by employing excess amount of vinyl ethers over (meth)acrylates (Figure 2). Several new block copolymers were synthesized by combining the alternating copolymerization and living radical or living cationic polymerization. These methods open new possibilities for providing novel functional polymers in materials science.

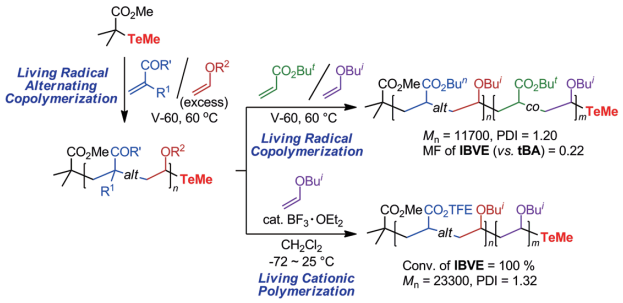

Figure 2. Controlled copolymerization of (meth)acrylates and vinyl ethers by using TERP, SBRP, and BIRP.