Division of Materials Chemistry
– Polymer Controlled Synthesis –

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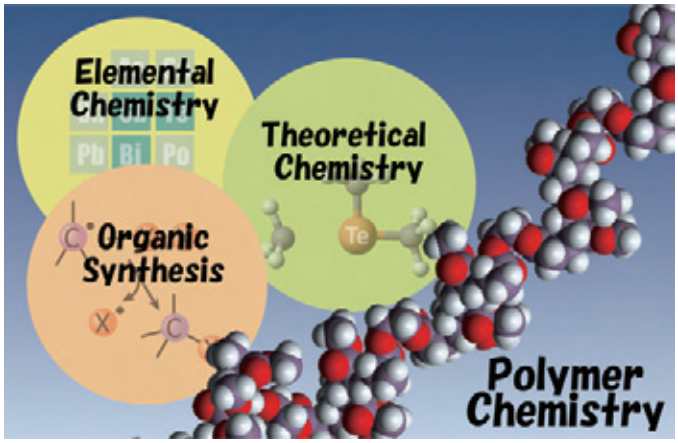
Scope of Research

Synthesis of structurally well-defined macromolecules has attracted great deal of attention, because such molecules would clarify structure-property relationship of polymers and lead to the development of new functional materials. Our research program focuses on development of new synthetic methods, which enable precise control of polymers and oligomers in terms of their size and structure. 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

Yamago S, Watanabe Y, Iwamoto T: Synthesis of [8]Cycloparaphenylene from a Square-Shaped Tetranuclear Platinum Complex [(cod)Pt(4,4'-biphenyl)]4, *Angew. Chem. Int. Ed.*, **49,** 757-759 (2010).

Mishima E, Yamada T, Watanabe H, Yamago S: Precision Synthesis of Hybrid Block Copolymers by Organotellurium-Mediated Successive Living Radical and Cationic Polymerizations, *Chem. Asian J.*, DOI:10.1002/asia.201000402 (in press).

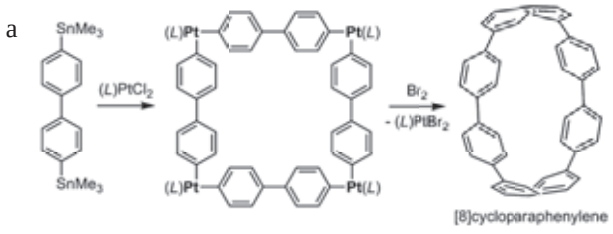
Yamago S: Precision Polymer Synthesis by Degenerative Transfer Controlled/Living Radical Polymerization Using Organotellurium, Organostibine, and Organobismuthine Chain Transfer Agents, *Chem. Rev.*, **109,** 5051-5068 (2009).

Yamago S, Ukai Y, Matsumoto A, Nakamura Y: Organotellurium-Mediated Controlled/Living Radical Polymerization Initiated by Direct C-Te Bond Photolysis, *J. Am. Chem. Soc.*, **131,** 2100-2101 (2009).

Kayahara E, Yamago S: Development of an Arylthiobismuthine Cocatalyst in Organobismuthine-Mediated Living Radical Polymerization. Applications for Synthesis of Ultrahigh Molecular Weight Polystyrenes and Polyacrylates, *J. Am. Chem. Soc.*, **131,** 2508-2513 (2009).

Novel Synthetic Strategy of Cycloparaphenylenes

Cycloparaphenylenes are hoop-shaped π-conjugated molecules consisting from *p*-disubstituted benzene rings, and are the simplest structural unit of armchair carbon nanotubes. Due to their unique structure associated with expected unique properties, they have attracted the attention of various disciplines ranging from basic chemistry to material science. However, although they have a simple structure, their synthesis has been a significant challenge. We have succeeded in the selective synthesis of [8]cycloparaphenylene based on a new synthetic strategy (Figure 1).



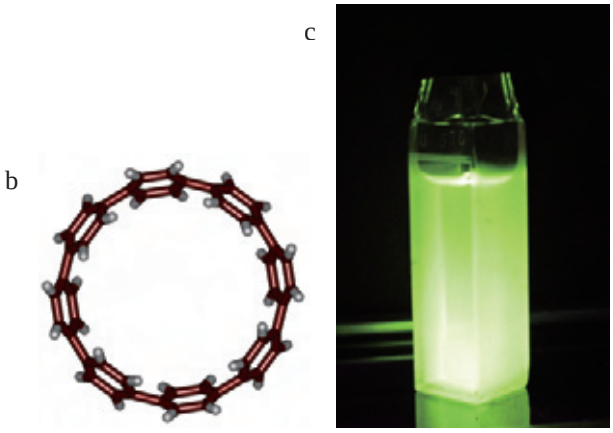


Figure 1. (a) Synthetic route, (b) computer-generated structure, and (c) luminescence of [8]cycloparaphenylene.

Hybrid Polymerization Method Mediated by Organotellurium Compounds

Living radical polymerization has become an indispensable method for the controlled synthesis of functionalized polymers, but applicability of this method is still limited to the certain class of vinyl monomers. We have already reported that organotellurium compounds are excellent controlling agents for living radical polymerization. Now we found that they also serve as efficient controlling agents for living cationic polymerization. Furthermore, living polymers, such as poly(meth)acrylates, prepared by organotellurium-mediated living radical polymerization were used for living cationic polymerization of vinyl ethers (Figure 2). This method enables access to new hybrid copolymers, which are difficult to synthesize by other methods.

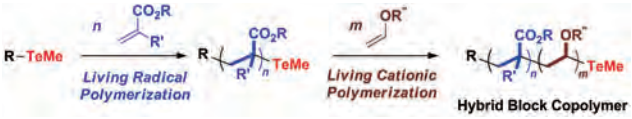


Figure 2. Synthesis of hybrid block copolymers by successive living radical and cationic polymerizations.