# Division of Materials Chemistry
## - Polymer Controlled Synthesis -

http://www.scl.kyoto-u.ac.jp/~yasuyuki/

Prof
YAMAGO, Shigeru
(D Sc)

Assoc Prof
TSUJI, Masaki
(D Eng)

Assist Prof
TOSAKA, Masatoshi
(D Eng)

Assist Prof
NAKAMURA, Yasuyuki
(D Sc)

### Students

KAYAHARA, Eiichi (D2)
MISHIMA, Eri (D1)
UEKI, Kazuya (M2)
YAMADA, Hiroto (M2)
WATANABE, Yoshiki (M2)
YANG, Junyue (M2)
IWAMOTO, Takahiro (M1)
KITADA, Yukie (M1)
KONISHI, Shota (M1)
KONDO, Noriaki (UG)
HORIE, Keita (UG)
YASUDA, Ryosuke (UG)

## Scope of Research

Our research program focuses on development of new synthetic methods, which enable precise control of polymers in terms of their size and structure. Our attention is especially directed to control of reactive carbon species, such as carbon centered radicals and carbocations, and organometallic species with the aid of synthetic organic chemistry, element chemistry, computational chemistry, and so on. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.

## Research Activities (Year 2009)

### Publications

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).

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).

### Presentations

Organotellurium-Mediated Controlled/Living Radical Polymerization Initiated by Carbon-Tellurium Bond Photolysis, Yamago S, 2009 International Symposium on Nano Structures: Synthesis, Characterization and Application (3rd Korea-Japan Joint Seminar: Precisely Synthesis and Applications), Gwanjyu, Korea, 7–10 October 2009 (invited lecture).

Recent Advances in Organoheteroatom-Mediated Controlled/Living Radical Polymerization, Yamago S, The 1st Federation of Asian Polymer Societies (FAPS) Polymer Congress, Nagoya, Japan, 20–23 October 2009 (invited lecture).

Taming Controlled/Living Radical Polymerization Reactions Using Organoheteroatom Compounds, Yamago S, 4th Pacific Symposium on Radical Chemistry, Shanghai, China, 19–22 November 2009 (invited lecture).

Organotellurium-Mediated Controlled/Living Radical Polymerization Initiated by Carbon-Tellurium Bond Photolysis, Yamago S, Ukai Y, Matsumoto A, Nakamura Y, 11th Pacific Polymer Conference, Cairns, Australia, 6–10 December 2009 (invited lecture).

### Grants

Yamago S, Precise Control of Radical Reactions Using Synergetic Effects of “Heavy” Heteroatom Compounds, Grant-in-Aid on Priority Areas, 1 October 2006–31 March 2010.

## New Methods for Precison Polymer Synthesis by Controlled/Living Radical Polymerization (LRP)

LRP is now recognized as one of the most effective methods for the synthesis of advanced polymeric materials with well-defined structure. However, their application for the synthesis of high molecular weight polymers has been extremely difficult, because polymer end radicals are always subjected to irreversible termination reaction. We have developed a new cocatalyst, diphenyl (2,6-dimesitylphenylthio) bismuthine, in organobismuthine-mediated LRP. Both low and high molecular weight polystyrenes and poly(butyl acrylate)s with controlled molecular weights ($M_n$s) and low polydispersity indices (PDIs) were synthesized by the addition of a catalytic amount of the cocatalyst to an organobismuthine chain transfer agent (CTA). Structurally well-defined polymers with $M_n$s in the range of $1.0 \times 10^4$~$2.8 \times 10^6$ and PDIs of 1.06~1.43 were successfully prepared under mild thermal conditions.

We have also developed a photo-induced LRP in the presence of organotellurium CTAs by direct carbon-tellurium photolysis. The photo-activation of the organotellurium dormant species proceeded under weak intensity UV-vis light, and the polymerization proceeded at mild conditions, such as 0 °C. The polymerization shows high versatility in terms of monomer families and functional groups and, thus, provides a powerful method for the controlled synthesis of new polymer materials.

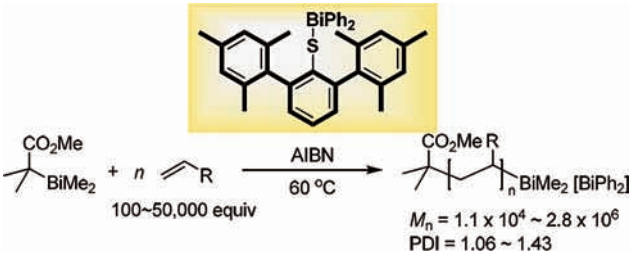



**Figure 1.** Controlled/living radical polymerization in the presence of a thiobismuthine cocatalyst

## The First Synthesis of [8]Cycloparaphenylene

Cycloparaphenylenes have attracted the attention due to their unique structures having a distorted π system and potential applications in material science, since they are the simplest structural unit of armchair carbon nanotubes. Although they have a simple structure, their synthesis has been a significant challenge. We have succeeded in the synthesis of [8]cycloparaphenylene, which is the smallest cycloparaphenylene so far synthesized, based on a new synthetic route. Our synthetic strategy is to use a square-shaped tetra(*para*-substituted oligoaryl)platinum complex as a precursor for [4n]cycloparaphenylene. Once the complex is formed, multiple reductive elimination of platinum gives [4n]cycloparaphenylene. As a proof of principle for this strategy, we examined and succeeded in the synthesis of [8]cycloparaphenylene (n = 2). [8] Cycloparaphenylene possesses strong fluorescent emission at around 540 nm.

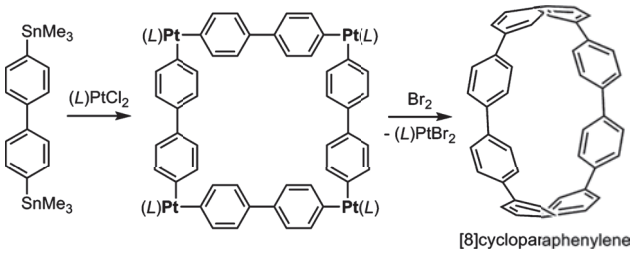
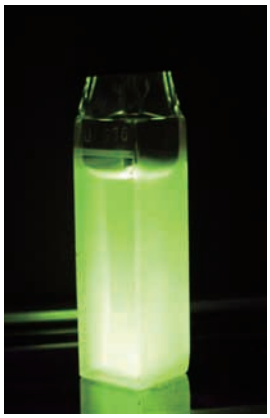



**Figure 2.** Synthesis of [8]cycloparaphenylene and its fluorescent emission in chloroform



Yamago S, Development of Photo-Induced Living Radical Polymerization Reaction and Its Applications, Torey Science Foundation, Torey Science and Technology Grant, 1 April 2008–31 March 2010.

Yamago S, Design and Synthesis of Novel Polymers for Drug Delivery, Uehara Memorial Foundation Research Grant, 1 April 2009–31 March 2010.

Yamago S, Creation of Novel Nano-System through Hierarchization of High Density Polymer Brushes, CREST, 1 October 2009–31 March 2014.

Tosaka M, Formation of Nanoparticle Arrays Using Alignment of Polymer Molecules, Grant-in-Aid for Scientific Research (C), 1 April 2008–31 March, 2011.