Division of Materials Chemistry
- Polymer Controlled Synthesis -

http://www.scl.kyoto-u.ac.jp/~yamago/index.html

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Visitors

Dr SCHAPER, Andreas	Philipps University in Marburg, Germany, 11 September–1 October 2006
Dr WU, Ming-Chien	National Cheng Kung University, Taiwan, 1 July 2006
Dr CHOW, Tahsin	Academia Sinica, Taiwan, 27 April 2006
Dr AMEDURI, Bruno	Ecole Nationale Supérieure de Chemie de Montpellier, France, 1 September 2006
Prof STUDER, Armido	Westfläische Wilhelms University, Germany, 23 October 2006
Prof CRICH, David	University of Illinois at Chicago, USA, 19 December 2006

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, 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 2006)

Presentations

"Recent Advances in Radical Reactions of Organotellurium Compounds", Yamago S, 16th IUPAC International Conference on Organic Synthesis, Merida, Mexico, 11–15 June (Invited).

"Effects of Heteroatoms in Highly Controlled Living Radical Polymerizations", Yamago S, 2nd Pacific Conference on Radical Chemistry, Daejoen, Korea, 5–8 November (Invited).

"Recent Developments in Organotellurium-Mediated Living Radical Polymerization", Yamago S, 2006 Japan-Taiwan Joint Symposium on Organic Chemistry, Kyoto, Japan, 22–23 April (Invited).

"Electron Microscopy and Diffraction of Radiation-Sensitive Nanostructured Materials", Schaper AK, Yoshioka T, Ogawa T, Tsuji M, IMC16, The 16th International Microscopy Congress, Sapporo, Japan, 3–8 September, and other 2 presentations.

"Self-Assembly of Nano-Sized Arrays on Highly Oriented Thin Films of Poly(tetrafluoroethylene)", Tosaka M, Tsuji M, Kohjiya S, Nagayama K, THERMEC'2006, International Conference on Processing & Manufacturing of Advanced Materials, Vancouver, Canada, 4–8 July (Invited).

Grants

Yamago S, Synthesis of Organic Nano-Molecules by New Living Radical Polymerizations, PRESTO Program, Japan Science and Technology Agency, 1 November 2002–31 March 2006.

Yamago S, Bond Transformation Reactions through Dynamic Interaction of Group 14 Metal-Tellurium Bonds, Grant-in-Aid on Priority Areas, 1 April 2004–31 March 2006.

Highly Efficient Organobismuthine-Promoters for Living Radical Polymerization

The synthesis of functionalized macromolecules with defined structures by living radical polymerization (LRP) is becoming increasingly important since radicals are compatible with a wide variety of polar functional groups, which do not lend themselves to ionic and metal-catalyzed polymerization conditions. While several systems have been developed to conduct LRP, the invention of a new system presents an excellent opportunity to control, with greater precision, molecular structure and to functionalize polymer end-groups. During the course to search more efficient promoters for LRP using organoheteroatom compounds, we found that organobismuthines are most efficient promoters through dual activation mechanisms, namely, thermal generation and degenerative transfer. Both conjugated and unconjugated vinyl monomers are polymerized to give well-defined polymers with predetermined molecular weights and low polydispersity indexes.

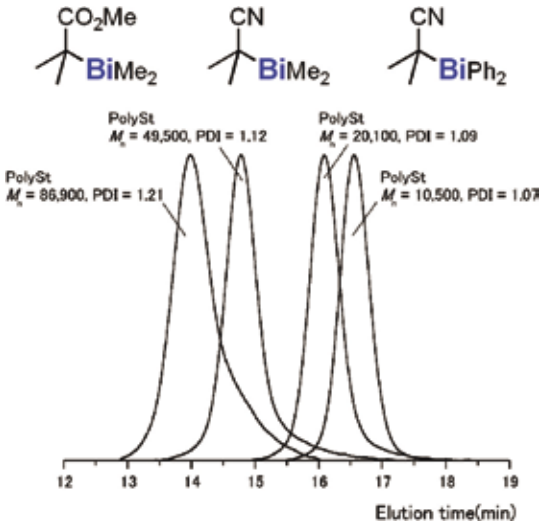

Figure 1. Structures of novel organobismuthine mediators (top) and GPC traces of polystyrene prepared by the mediator and styrene (bottom).

Dialkylphosphates as New Stereo-Directing Protecting Groups in Oligosaccharide Synthesis

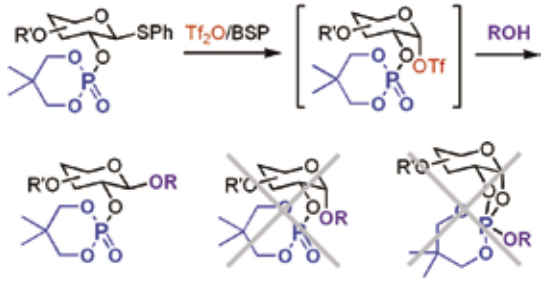

Figure 2. Stereoselective synthesis of 1,2-*trans*-glycoside using C-2 dialkylphosphate protected thioglycosides.

Stereoselective formation of a glycosidic linkage is one of the most important tasks in synthetic carbohydrate chemistry, because the structure of glycosides plays crucial role in many of important biological processes involving oligosaccharides. To date, 1,2-*trans*-glycosides have been prepared so far by intramolecular neighboring group participation of the C2-acyl protective groups, but this method has serious drawbacks due to the formation of an orthoester side product. We found that dialkylphosphates served as excellent stereo-directing groups for 1,2-*trans*-glycoside synthesis. As the phosphates can be removed after glycosylation, they can be used as stereo-directing protective groups. In addition to this, we found that these protective groups can be used in the iterative glycosylation reactions. Therefore, a variety of oligosaccharides that possess the 1,2-*trans*-glycosidic linkage can be synthesized under a set of glycosylation conditions.

Yamago S, Invention of New Radical Chemistry of "Heavy" Group 15 Heteroatom Compounds, Grant-in-Aid for Scientific Research, (A) (2), 1 April 2005–31 March 2008.

Yamago S, Novel Iterative Synthetic Transformations by Repetitious Uses of Heteroatom Compounds, Grant-in-Aid on Priority Areas, 1 April 2006–31 March 2007.

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.

Yamago S, Precision Control of Organotellurium-Mediated Living Radical Polymerization (TERP), Mitsubishi Foundation Grant, 1 October 2006–30 September 2007.

Yamago S, Creation of Functional Organic Materials by Organobismuthine-Mediated Living Radical Polymerization, Industry-University Joint Research for Innovative Seeds Program, Japan Science and Technology Agency, 1 September 2006–31 August 2007.

Tsuji M, High-Resolution TEM of the Shish-Kebab Structure in Uniaxially Oriented Polyesters, Grant-in-Aid for Scientific Research, (C) (2), 1 April 2004–31 March 2007.

Tosaka M, Dissipative Structures Induced by Oriented Polymer Thin Films, Tokuyama Science Foundation Grant, 10 May 2006–31 May 2007.