Laboratory of Polymer Synthesis Chemistry

Professor: Sadahito Aoshima

Associate Professor: Shokyoku Kanaoka

URL: http://www.chem.sci.osaka-u.ac.jp/lab/aoshima/index.html/
E-mail: aoshima@chem.sci.osaka-u.ac.jp

Synthesis of Functional Polymers by Precision Polymerization

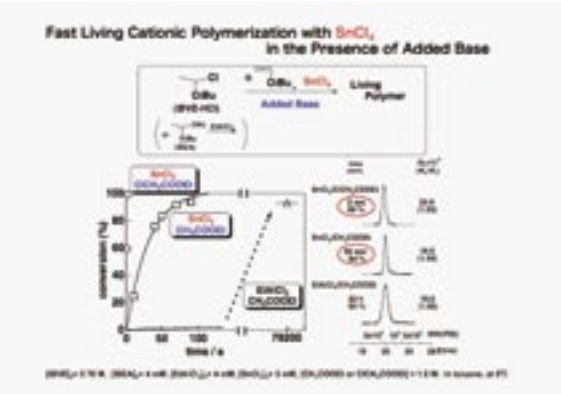
In recent years, the great interest in creating advanced polymer materials with specific functions and/or excellent performance, similar to biopolymers, has stimulated studies on nano-organized self-assemblies using various stimuli-responsive (or amphiphilic) block copolymers. Our group pioneered the design and synthesis of a new series of stimuli-responsive polymers by living cationic polymerization of several functional monomers using environmentally benign catalysts in the presence of an added base. Recent representative studies, summarized here, include ultrafast living polymerization carried out in seconds using conventional Lewis acids; living polymerization using Fe-based environmentally benign catalysts including a solid catalyst; and the selective synthesis and self-association of well-defined stimuli-responsive star-shaped polymers, which are effective in the preparation of catalytic Au nanoclusters.

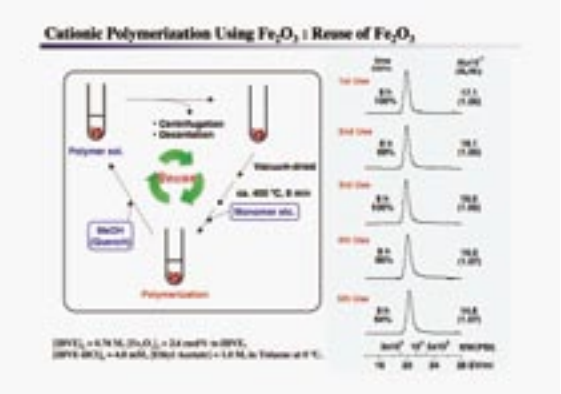
(i) Precision Polymerization with Environmentally Benign Catalysts

An Array of Effective Lewis Acids for Living Systems and Fast Living Polymerization: We have explored a wide variety of Lewis acids combined with Lewis bases, demonstrating successful living polymerization with acids consisting of Al, Sn, Ti, Zr, Hf, Zn, Ga, In, Si, Ge, Bi, Sb, Nb, or Ta. A notable example was the ultrafast living cationic polymerization of vinyl ethers (VEs) using $SnCl_4$ in the presence of a weak Lewis base. The $SnCl_4/ClCH_2COOC_2H_5$ system was complete in a couple of seconds: the reactions are 5 orders of magnitude faster than the previous system.

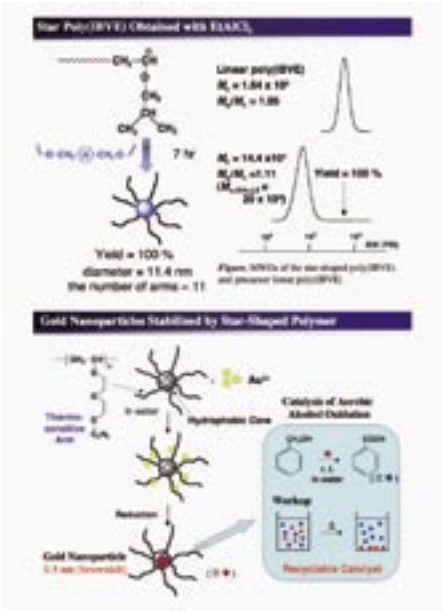
Living Cationic Polymerization using Fe-Based Environmentally Benign Catalysts: Encouraged by the expansion of initiating systems, we examined the cationic polymerization of VEs with $FeCl_3$, one of the less toxic metal halides. For example, the combination of $FeCl_3$ and 1,3-dioxolane permitted living cationic polymerization of isobutyl VE (IBVE) in toluene at 0 ºC, with the reaction being completed in 2-3 s. The product polymers had very narrow MWDs, and the M_n increased in direct proportion to monomer conversion.

More environmentally benign catalysts were employed to examine the cationic polymerization. Iron oxides with a base induced living polymerization of IBVE, producing polymers with very narrow MWDs. The catalyst maintained its activity after the polymerization and it was possible to reuse it repeatedly. Such a heterogeneous solid catalyst has never been reported before in living cationic polymerization.





(ii) Synthesis of Well-Controlled Stimuli-Responsive Polymers



Being able to carry out the living cationic polymerization of several functional monomers with considerable efficiency led to a new series of water-soluble or stimuli-responsive polymers. Living cationic polymerization with an added base permitted the selective preparation of polymers with various shapes and different sequence distributions of monomer units, including (i) stimuli-responsive (or amphiphilic) diblock and triblock copolymers, (ii) gradient and graft copolymers, (iii) end-functionalized polymers, and (iv) star-shaped polymers (see below).

Star-Shaped Polymers: Base-stabilized living cationic polymerization permitted the selective preparation of star-shaped polymers. This is the first example of the selective preparation of star-shaped polymers with a narrow MWD in quantitative yields *via* a polymer-linking reaction by any polymerization mechanism. Well-defined star-shaped polymers with thermosensitive arms were prepared, and proved to be effective in the preparation of gold nanoclusters with narrow size distribution. The polymer-supported Au nanocluster of less than 4 nm catalyzed aerobic alcohol oxidation reactions. The thermosensitive phase transition of the arm chains, when heated, caused only the star polymer/Au cluster to be precipitated in the reaction mixture. This cluster could be redissolved in water, and no negative aggregation was observed. Such stability and straightforward separation procedures allowed repeated reuse of the Au cluster several times, at least. The reused cluster induced alcohol oxidation with similar reactivity in each run.

References (main papers in 2005-2007)

1. Double Thermosensitive Diblock Copolymers of Vinyl Ethers with Pendant Oxyethylene Groups: Unique Physical Gelation, Sugihara, S. et al., *Macromolecules* **2005**, *38*, 1919-1927.
2. Fast Living Cationic Polymerization Accelerated by $SnCl_4$. I. New Base-Stabilized Living System for Various Vinyl Ethers with $SnCl_4$/$EtAlCl_2$, Yoshida, T. et al., *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 468-472.
3. Instant Living Cationic Polymerization using $SnCl_4$/$EtAlCl_2$ with a Weak Lewis Base: Ultrafast Polymerization in Seconds, Yoshida, T. et al., *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4288-4291.
4. Living Cationic Polymerization of Azobenzene-Containing Vinyl Ether and Its Photoresponsive Behavior, Yoshida, T. et al., *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5138-5146.
5. Quantitative Synthesis of Star-Shaped Poly(vinyl ether)s with a Narrow Molecular Weight Distribution by Living Cationic Polymerization, Shibata, T. et al., *J. Am. Chem. Soc.* **2006**, *128*, 7497-7504.
6. Fast Living Cationic Polymerization of Vinyl Ethers with Iron(III) Chloride in the Presence of a Cyclic Ether: Most Active and Environmentally Benign Catalyst for the Living Cationic Polymerization of Vinyl Ethers, Kanazawa, A. et al., *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5795-5800.
7. New Stage in Living Cationic Polymerization: An Array of Effective Lewis Acid Catalysts and Fast Living Polymerization in Seconds, Aoshima, S. et al., *J. Polym. Sci., Part A: Polym. Chem. (Highlight)* **2007**, *45*, 1801-1813.
8. Heterogeneously Catalyzed Living Cationic Polymerization of Isobutyl Vinyl Ether Using Iron (III) Oxide, Kanazawa, A. et al., *J. Am. Chem. Soc.* **2007**, *129*, 2420-2421.
9. Thermosensitive Gold Nanoclusters Stabilized by Well-Defined Vinyl Ether Star Polymers: Reusable and Durable Catalysts for Aerobic Alcohol Oxidation, Kanaoka, S. et al., *J. Am. Chem. Soc.* **2007**, *129*, 12060-12061.
10. Synthesis of Stimuli-Responsive Polymers by Living Polymerization: Poly(*N*-Isopropylacrylamide) and Poly(Vinyl Ether)s, Aoshima, S. et al., *Adv. Polym. Sci.* **2007**, in press.