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Synthesis of Mononuclear (TACN)Fe Complexes Having Weakly Coordinated Solvent and Application to Atom Transfer Radical Polymerization.

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1. Introduction

Transition metal catalyzed Atom Transfer Radical Polymerization (ATRP) is a representative example of controlled radical polymerization (CRP), which is an important methodology to construct well-defined polymers.[1)] In ideal cases, good catalysts for ATRP should; 1) access to polymers with the desired molecular weight and narrow molecular weight distribution, 2) give high reaction rate and durability to achieve complete monomer conversion in the construction of block co-polymers, 3) have versatile applicability to several monomers, and 4) give minimum residual heavy and toxic metal catalysts in the product.[2)] To develop the new ATRP catalyst which has all these features, we focused on the iron which is low toxicity and abundant in the earth.

2. Previous work

2.1. TACN coordinated Fe catalyst

We have reported the synthesis of a trinuclear iron complex having 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN) ligand, $[(Me_3TACN)Fe(\mu\text{-}Cl)_3Fe(Me_3TACN)]$ $[Me_3TACNFeCl_3]$, as an environmentally friendly and reusable catalyst for well-controlled ATRP of styrene. This complex has a great advantage as the catalyst facilely removable from the polystyrene formed. Furthermore, the catalyst recovered is reusable for five times. In contrast, there are problems in relatively low reaction rate and less controllable ATRP of methacrylates and acrylates.[3)] Recently, we have developed a neutral mononuclear coordinatively unsaturated Fe(II)-complexes, $(iPr_3TACN)FeCl_2$ and $(iPr_3TACN)FeBr_2$ as highly efficient and environmentally friendly catalysts for the ATRP.[4)] These iron catalysts showed high performance in well-controlled ATRP of styrene, methacrylates such as methyl methacrylate (MMA), and acrylates such as butylacrylate (BA). The high reactivity of these catalysts led to well-controlled polymerization and block copolymerization even with lower catalyst concentration. However, efficient removal of these catalysts from the polymer produced was prevented due to their neutral structure. In this presentation we wish to report the synthesis of new iron complexes bearing various TACN ligands to develop a useful "perfect" catalyst which can fulfill all requirements for ideal ATRP catalysts described above.

3. This work

3.1. Experimental method

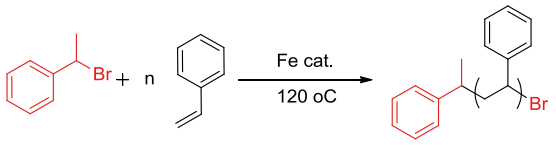
In this presentation, we want to show that treatment of dinuclear complex $[(Me_3TACN)Fe(\mu\text{-}Br)_3Fe(Me_3TACN)]Br$ (**1**) with a two-electron donor liagnd such as MeCN, PhCN and pyridine led to the formation of some complex which has higher reactivity toward polymerization. Catalyst reactivity was evaluated by the reaction time, molecular distribution of polymer, and monomer versatility. GPC-MS was used for analysis of obtained polymer. The molecular structures of **2-4** were determined by X-ray diffraction analysis, ^1H NMR spectroscopy, and elemental analysis.

3.2. Polymerization of Styrene

To verify the character of these catalyst, we tried polymerization of Styrene first, because, Styrene is known as an easier monomer to control over radical polymerization, results are summarized in Table 1. In this trial, Entry **2-4**

showed relatively high reactivity toward

polymerization of styrene, conversion reached > 90% within 6 hours at 120 °C (Table 1, entries 2~4), in contrast, polymerization mediated by **1** required for 48 hrs to complete the reaction.



Entry	Ligand	time(h)	Conv(%)	M_w/M_n	M_n(exp.)
1	---	48	76	1.3	21000
2	MeCN	6	96	1.3	24000
3	PhCN	6	92	1.3	24000
4	Pyridine	6	90	1.3	24000

Conversion plot over Styrene polymerization mediated by Entry **1** and **2** revealed that there should be some active species in reaction medium. (Time vs Conv. shown in Figure B)

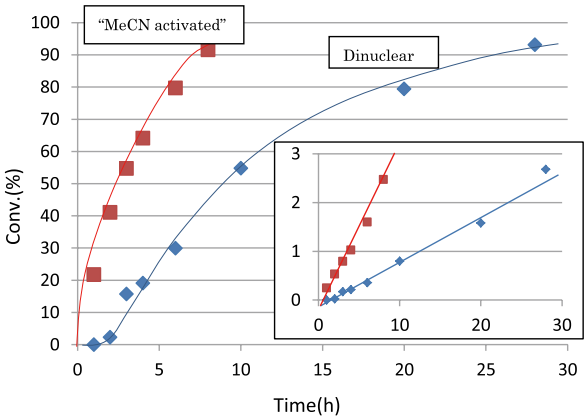


Figure B. Time vs Conv. of Styrene polymerization

3.3. Catalyst removal

On the next, we tried to separate the catalyst from prepared poly-Styrene, because if after precipitation in MeOH catalyst forms dinuclear species, it is possible to separate catalyst from polymer easily. It should be noted that only 22 ppm of iron residue was detected in the formed polymer after precipitation with MeOH; this means that 99.5 % of the charged iron catalyst was removed by precipitation. The reason why the iron species was easily separated by precipitation is ascribe to regeneration of ionic dinuclear complex **1** while precipitation. The catalyst was proved to be reusable for polymerization of styrene by treatment of the recovered **1** with MeCN prior to use as shown in Table 2.

3.4. Monomer versatility

As I mentioned, monomer versatility is very important or synthesizing of block co-polymer, then next we tried polymerization of Methylmethacrylate (MMA). Previously we tried to control MMA polymerization but the resulted polymer has broad molecular weight distribution (M_w/M_n = ~2.0). In contrast, using MeCN activated catalyst, molecular weight distribution of obtained polymer was very narrow (M_w/M_n = ~1.34).

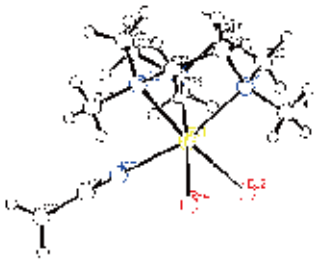


Figure A. ORTEP drawing of $(Me_3TACN)FeBr_2(MeCN)$

3.5. catalytic active species

To reveal the active species of this system, we tried to isolate catalytic active species. Finally, we could isolated mononuclear iron complex (ORTEP drawing of $(Me_3TACN)FeBr_2(MeCN)$ complex is shown in Figure A). This complex was charactalized by X-ray crystallography and 1H-NMR analysis. Surely, this complex has very high reactivity and could complete Styrene polymerization within 6 hours. This complex may catalytic active species.

4. Reference

1) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921-2990; M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689-3746.2) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2007**, *107*, 2270-2299; M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009,** *109*, 4963-5050.3) H. Nagashima e, M. Kawamura, Y. Sunada, H. Kai, N. Koike, A. Hamada, H. Hayakawa, J. Ren-Hua,. *Adv. Synth. Catal.*, **2009**, *351*, 2086.4) H. Nagashima, S. Niibayashi, H. Hayakawa, J. Ren-Hua,. *Chem. Commun.*, **2007**, 1855.