

**Project Title:**

**Computational Studies on Olefin Polymerization Catalyzed by Cationic Rare-earth Metal Complex**

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1. **Background and purpose of the project, relationship of the project with other projects**

The discovery of new catalysts can result in breakthroughs in various areas. Novel catalysts can facilitate novel reactions that have been previously considered impossible, and can thus help us to make innovative functional materials that cannot be made by previous means.

To develop new generations of catalysts which complement or are superior to the existing ones, exploring the potential of untapped elements or complexes with unprecedented structures and desired properties has been a long-standing research strategy of both academic and industrial scientists. So far, extensive studies have been carried out on the utilization of d-block transition metals, whereas rare earth metals have received much less attention. Compared to most d-block transition metals, rare earth metals possess unique physical and chemical properties. The synthesis of organo rare earth metal complexes having new structures is thus of great interest and importance. Recently, with development of further research on the organo rare earth metal complexes, its application range is gradually expanded including information, energy and new materials etc. The design and application of organo rare earth metal complexes as catalysts for polymerization and organic synthesis have occupied an especially important place in the development of a

sustainable global development strategy. The catalysis research of novel organo rare earth metal complexes has both theoretical and practical significance. Especially in novel polymer materials, rare-earth metal catalysts show outstanding advantage and draw more and more interests. Some research groups such as Hessen group in Holland, Okuda group in Germany, Carpentier group in France, Hou group in Japan, and so on, have done many representative work. In addition, some researchers in China also made prominent contribution in the field of olefin polymerization. Numerous olefin polymerization complex catalysts have been synthesized. Among these new complexes, cationic rare earth alkyl complexes have been reported to act as a new family of polymerization catalysts, and which showed excellent activity and selectivity for the polymerization and copolymerization of a wide range of olefins, such as syndiospecific polymerization and copolymerization of styrene with ethylene, dienes and other olefins. In view of the difficulties in detecting and separating active species, it is very hard to clarify some elementary and key properties in polymerization process. Therefore, numerous computational studies have been widely and successfully conducted to investigate the polymerization mechanism of various olefins catalyzed by group 4 and late transition metal complexes. These theoretical studies effectively

promote the design and development of homogeneous transition metal catalyst. In contrast, computational studies on reactions related by rare-earth metal catalysts have been much less extensively explored despite recent progress.

## 2. Specific usage status of the system and calculation method

During the fiscal year 2012, part of specified computational resources was used.

Some properties on active species and reaction mechanism will be investigated and clarified through using some model softwares, such as Gaussian09, ADF and so on.

The QM/MM ONIOM Methods will be used to exploring larger systems, such as third molecules monomer insertion, the interaction between the counteranion and cationic active species)

## 3. Result

We have computationally studied the regio- and stereoselectivity of the polymerization of 1-hexene catalyzed by the dicationic rare-earth metal complexes  $[(\text{Pr-trisox})\text{L}(\text{CH}_2\text{SiMe}_3)]^{2+}$  (Ln = Sc and Y). At both chain initiation and propagation stages, 1,2-insertion has been found to be kinetically favorable over 2,1-insertion. The kinetic priority of 1,2-insertion pattern is mainly due to the absence of repulsive interaction between the ancillary ligand and the  $\text{CH}_3(\text{CH}_2)_3$  group of 1-hexene moiety in the insertion transition state and the resulting stronger binding between the metal center and the 1-hexene motif. The stereoselectivity has been found to follow chain-end mechanism, and the iso-specific insertion of 1-hexene observed experimentally is mainly controlled by kinetics. The insertion reaction catalyzed by dicationic active species is easier than that by monocationic species both kinetically and energetically, which is in agreement with the higher activity of the dicationic species observed

experimentally. The features of frontier molecular orbitals of the two kinds of species could also account for their different activities. The origin of difference in activity between the scandium active species and its yttrium analogue has been also computationally investigated. It has been found that the scandium-catalyzed insertion reaction has kinetic preference over the yttrium-catalyzed reaction and that the generation of scandium active species is easier compared with that of yttrium analogue. These results could help understand better the higher activity of the scandium complex than its yttrium analogue and develop rare earth polymerization catalysts.

## 4. Conclusion

The RICC provided enough calculation resources for the investigations on olefin co(polymerization) mediated by cationic rare-earth metal alkyl complex catalysts. Our computational studies have offered important information for the development of novel rare-earth catalysts and new organic reaction.

## 5. Schedule and prospect for the future

A series of novel rare-earth-metal complex catalysts have been synthesized and been successfully applied to olefin (co)polymerization and C-H functionalization of pyridines and anisoles. In the process of exploring the reaction mechanism, numerous DFT calculations need to be executed and computational resources is necessary. Due to larger reaction systems containing rare-earth metal, it is necessary to use large scales computational resources.

I have been a RICC general user, and we wish to continue using the system.

**Fiscal Year 2012 List of Publications Resulting from the Use of RICC**

**[Publication]**

**Xiaohui Kang**, Yuming Song, Yi Luo,\* Gang Li, Zhaomin Hou,\* Jingping Qu\* “Computational Studies on Isospecific Polymerization of 1-Hexene Catalyzed by Cationic Rare Earth Metal Alkyl Complex Bearing a  $C_3$  *i*Pr-trisox Ligand” *Macromolecules* **2012**, *45*, 640–651