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Mechanistic Studies of Co-polymerization *via* ZnR_2-mediated Chain shuttling between Zr and Hf Catalysts

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Introduction

Chain shuttling co-polymerization is a method of producing olefin block co-polymers with desired properties using dual catalysts *via* a chain shuttling agent. Arriola[1] *et al.* reported the first olefin block co-polymers with alternative semicryatalline and amorphous segments having precisely adjusted architecture prepared by the changing concentration ratio of 1-alkene and ethylene. The role of chain shuttling agent (CSA) , $ZnEt_2$ in this reaction, is to transfer the polymer chains between two catalysts which generate hard or soft polymers. These high performance polymers show excellent elastomeric properties due to low glass transition temperature and high melting temperature and they can be used as commercial thermoplastic polymers. The overall mechanism of the reaction is shown below.

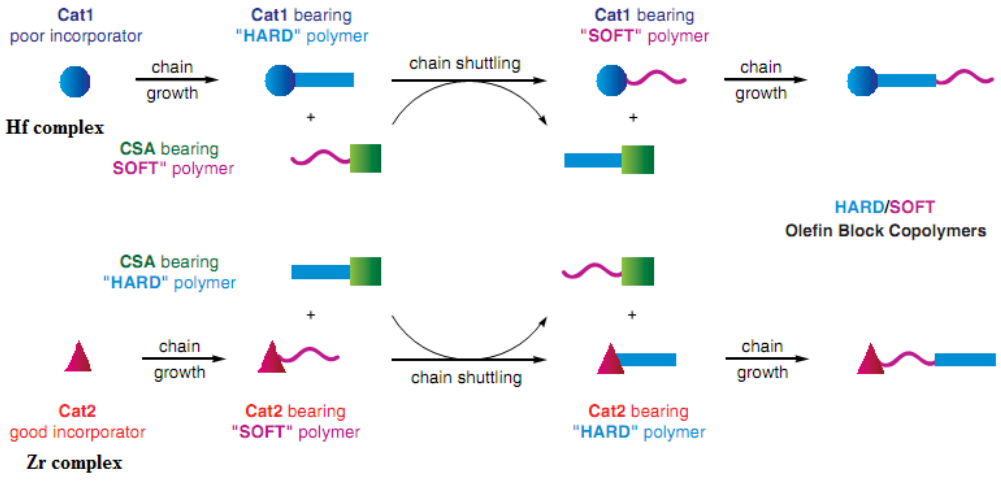
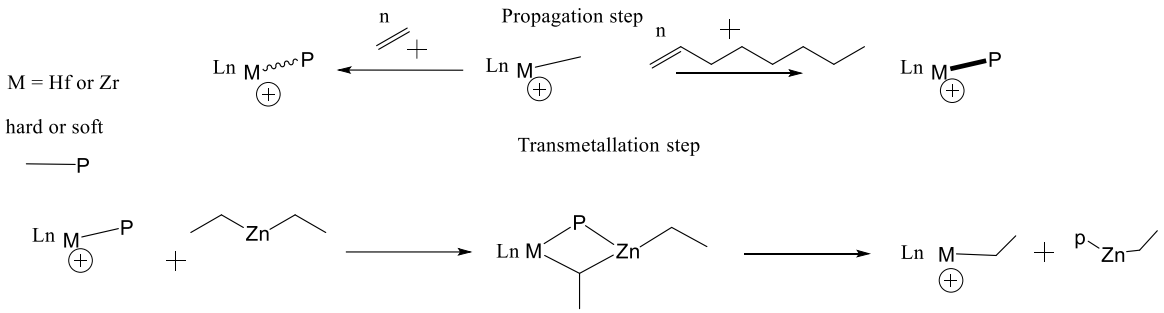


Figure 1. The proposed mechanism of chain shuttling reaction reported by Arriola *et al.* Blue circle and red triangle represent two catalysts. Green square represents $ZnEt_2$. Hard and soft polymers are indicated by the blue and pink tails of the catalysts and CSA, respectively.

Up to our knowledge, no complete reaction profile has been proposed except the reaction mechanism of the propagation step of Hf complex by the same group.[2] In this regard, we have studied the complete reaction mechanism of propagation by Zr catalyst and Hf catalyst including the ligand exchange or transmetallations. We proposed a general pathway for the reaction which is given below using DFT (M06/LANL2DZ and 6-31G(d)) methods.



Scheme 1. Proposed mechanism in this study.

Results and Discussion

We observed that the insertion of ethylene with the Zr catalyst as a model propagation step is thermodynamically more favorable compared to that of 1-octene with the Hf catalyst. There are four reaction pathways for the ethylene insertion with the Zr catalyst dependent on the structure of the Zr complex. We also investigated four reaction pathways for the 1-octene insertion with the Hf catalyst in which 1-octene attacks to the Hf complex from different directions. Though the corresponding activation barriers are between 7 and 12 kcal/mol for the ethylene insertion with the Zr catalyst, those of 1-ocetene insertion with the Hf catalyst, are between 19 to 28 kcal/mol. The current studies also indicate that Hf catalyst can rearrange to another catalyst by insertion of ethylene into the Hf-C(naphthyl moiety in the pincer ligand) bond with an activation barrier of 1 kcal/mol which can much more effectively catalyze the propagations. During the transmetallation process between the catalyst and $ZnEt_2$ it is also suggested that a four-membered intermediate exists with high stability. All the other possibilities of the reaction can be seen in the poster.

Conclusions

In the chain shuttling reaction mechanism, we have proposed all possibilities for the propagations of catalysts as well as the selectivity of monomers using DFT method. We observed that *in situ* formed Hf complex can also catalyze the propagation process. Moreover, the four-membered ring intermediates between catalyst and $ZnEt_2$ *via* transmetallation process are also studied. We believe that our work could understand the possibilities of reaction mechanism in depth insight.

References

1. D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, Science, **2006**, 312, 714

2. R. D. J. Froese, P. D. Hustad, R.L. Kuhlman, T. T. Wenzel, J. Amer. Chem. Soc. 2007, 129, 7831.