Thur. Jan. 17th

FY2018's 4st, CREST Workshop

Computational molecular technology towards chain shuttling polymerization by using Red Moon method

Yuichi Suzuki

Chain shuttling polymerization (CSP) (Reshown)

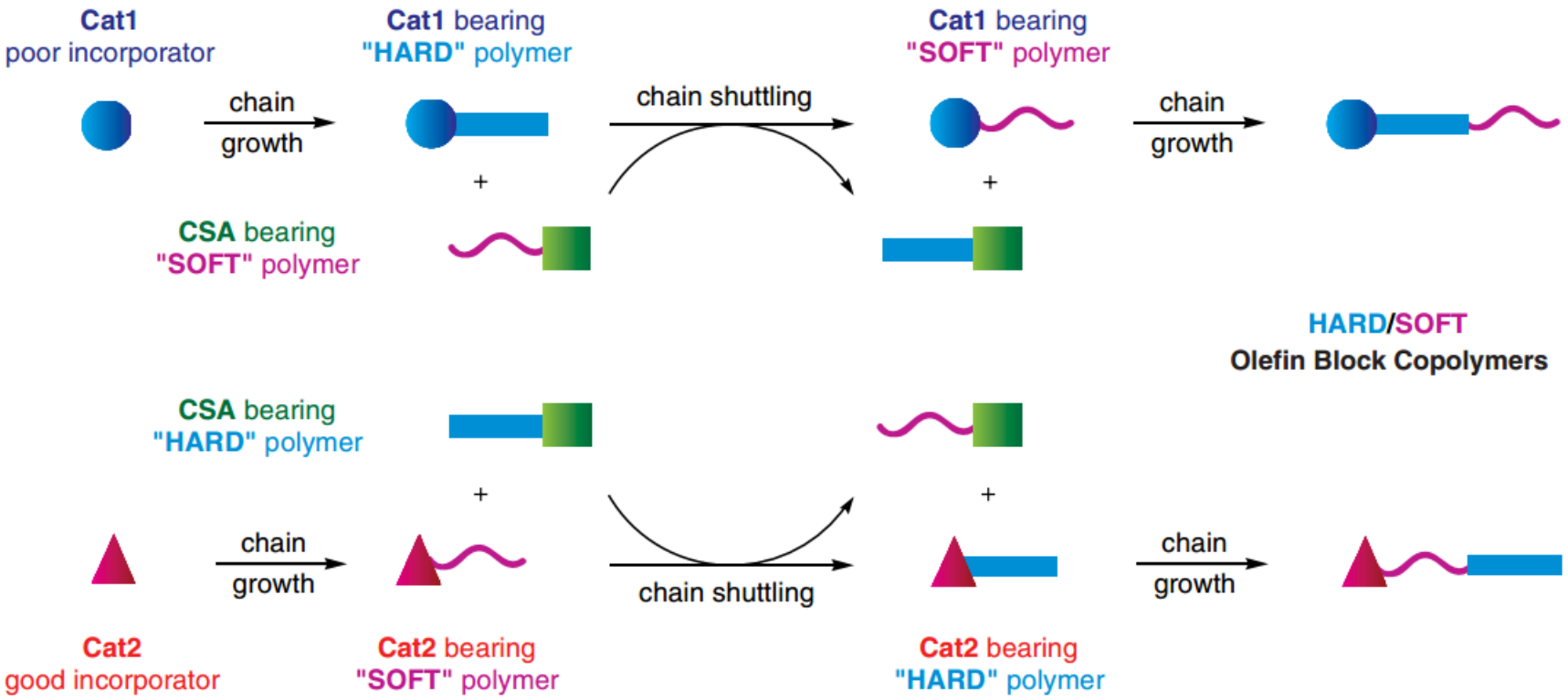


Fig. 1. Depiction of the likely chain shuttling mechanism in a single reactor, dual-catalyst approach. **Cat1** (solid circles) and **Cat2** (solid triangles) represent catalysts with high and low monomer selectivity, respectively, whereas the **CSA** (solid squares) facilitates the chain shuttling reaction. …

Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714–719.

Procedure towards the realization of CSP simulation

Hf catalyst system

I. Ethylene IP simulation.
II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

} Complete!! (by Dr. Matsumoto)

III. Ethylene and 1-octene IP simulation.
IV. CCTP simulation with ethylene and 1-octene as monomers, and with $ZnEt_2$ as CTA.

Zr catalyst system

I. Ethylene IP simulation. ← Complete!! (presented at my last CREST-WS)
II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

CSP system with Hf and Zr catalysts

I. CSP simulation in which the ethylene and 1-octene IP occurs on the Hf catalyst, and the ethylene IP occurs on the Zr catalyst, accompanying with chain transfer by $ZnEt_2$ as CSA.

IP: insertion polymerization
CCTP: coordinative chain transfer polymerization
CTA: chain transfer agent
CSP: chain shuttling polymerization
CSA: chain shuttling agent

Test RM simulation of CSP for CREST meeting

Hf catalyst system

I. Ethylene IP simulation.

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

Complete!!
(by Dr. Matsumoto)

III. Ethylene and 1-octene IP simulation.

IV. CCTP simulation with ethylene and 1-octene as monomers, and with $ZnEt_2$ as CTA.

Zr catalyst system

I. Ethylene IP simulation.

Complete!!
(presented at my last CREST-WS)

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

RM simulation requested for the final report of CREST (15/9/2018).

CSP system with Hf and Zr catalysts

I. CSP simulation in which the ethylene and 1-octene IP occurs on the Hf catalyst, and the ethylene IP occurs on the Zr catalyst, accompanying with chain transfer by $ZnEt_2$ as CSA.

IP: insertion polymerization
CCTP: coordinative chain transfer polymerization
CTA: chain transfer agent
CSP: chain shuttling polymerization
CSA: chain shuttling agent

rf_input.dat (input file to RF program)

rf_input.dat

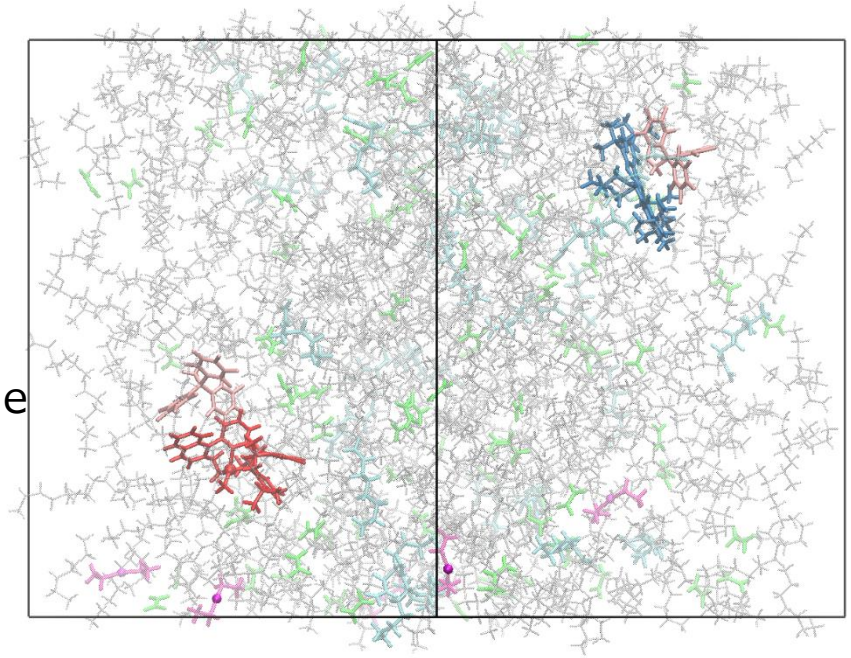
```
#-----------monomer insertion------------
#Reaction 1 (HFB-MIC + EXX ---> HFB-ERC-MTX)
ReactID=1 Ea=0.0 dE=-17.3
"COND = distance(:HFB@Hf; :EXX@C1)<3.8
       && distance(:HFB@Hf; :EXX@C2)<3.8
       && dihedral(:MIC@C1; :HFB@Hf; :EXX@C1; :EXX@C2)
       =[-60.0,60.0]
       && angle(:HFB@N; :HFB@Hf; :EXX@C1)>100.0
       && distance(:HFB@Hf; :MIC@C1)<2.4"
"ACTION =
   createBond :HFB@Hf :EXX@C1;
   createBond :EXX@C2 :MIC@C1;
   deleteBond :HFB@Hf :MIC@C1;
   ModifyResByPrepin :EXX ./parms/erc.prepin;
   ModifyResByPrepin :MIC ./parms/mtx.prepin"
#Reaction 2 (HFB-EIC + EXX ---> HFB-ERC-ETX)
ReactID=2 Ea=0.0 dE=-17.3
"COND = distance(:HFB@Hf; :EXX@C1)<3.8
       && distance(:HFB@Hf; :EXX@C2)<3.8
       &&
dihedral(:EIC@C1; :HFB@Hf; :EXX@C1; :EXX@C2)=[-
60.0,60.0]
   deleteBond :HFB@Hf :EIC@C1;
   ModifyResByPrepin :EXX ./parms/erc.prepin;
   ModifyResByPrepin :EIC ./parms/etx.prepin"
…
```

```
#-----------polymer exchange------------
#Reaction 4 (HFB-MIC + ZN-EIZ ---> HFB-EIC + ZN-MIZ)
ReactID=4 Ea=0.01 dE=0.0
"COND = distance(:HFB@Hf; :EIZ@C1)<2.8
       && distance(:MIC@C1; :ZN@Zn)<2.8
       && distance(:HFB@Hf; :MIC@C1)<2.4
       && distance(:HFB@Hf; :HFB@N)<5.0
       && distance(:ZN@Zn; :EIZ@C1)<2.4"
"ACTION =
   createBond :HFB@Hf :EIZ@C1;
   createBond :ZN@Zn :MIC@C1;
   deleteBond :HFB@Hf :MIC@C1;
   deleteBond :ZN@Zn :EIZ@C1;
   ModifyResByPrepin :MIC ./parms/miz.prepin;
   ModifyResByPrepin :EIZ ./parms/eic.prepin"
…
#Reaction 9 (HFB-ERC-P1 + ZN-ERZ-P2 --->
                                HFB-ERC-P2 + ZN-ERZ-P1)
ReactID=9 Ea=0.01 dE=0.0
"COND = distance(:HFB@Hf; :ERZ@C1)<2.8
       && distance(:ERC@C1; :ZN@Zn)<2.8
       && distance(:HFB@Hf; :ERC@C1)<2.4
   deleteBond :HFB@Hf :ERC@C1;
   deleteBond :ZN@Zn :ERZ@C1;
   ModifyResByPrepin :ERC ./parms/erz.prepin;
   ModifyResByPrepin :ERZ ./parms/erc.prepin"
```

The reaction patterns over 70 in total are needed to treat all of the elementary reactions for CSP simulation in the current format of RF input, but the 19 patterns were only considered to realize the CSP simulation in the minimum reaction scheme.

Computational model and details

- Model system:
  - Ion Pair (Hf-cat.+anion) ×1
  - Ion Pair (Zr-cat.+anion) ×1
  - heptane (solvent) ×480
  - ethylene ×90
  - 1-octene ×30
  - $ZnEt_2$ ×5
- MM parameters:
  General AMBER Force Field (GAFF)
  + FF prepared by Dr. Matsumoto
  + modified LJ for ethylene and 1-octene
- MD Calculation:
  NVT-MD (400K) (based on experiment[2])
- Unit Cell Size:
  56.6 Å ×56.6 Å ×55.6 Å



[1] Ahmadi, M; Nasresfahani, A; *Macromol. Theory Simul.* **2015**, *24*, 311
[2] Arriola, D, J; Carnahan, E. M; Hustad, P. D; Kuhlman, R. L; Wenzel, T. T; *Science*, **2006**, *312*, 714

RM simulation result (shown by movie)

<Total 500 RM cycle (50 sec.)>

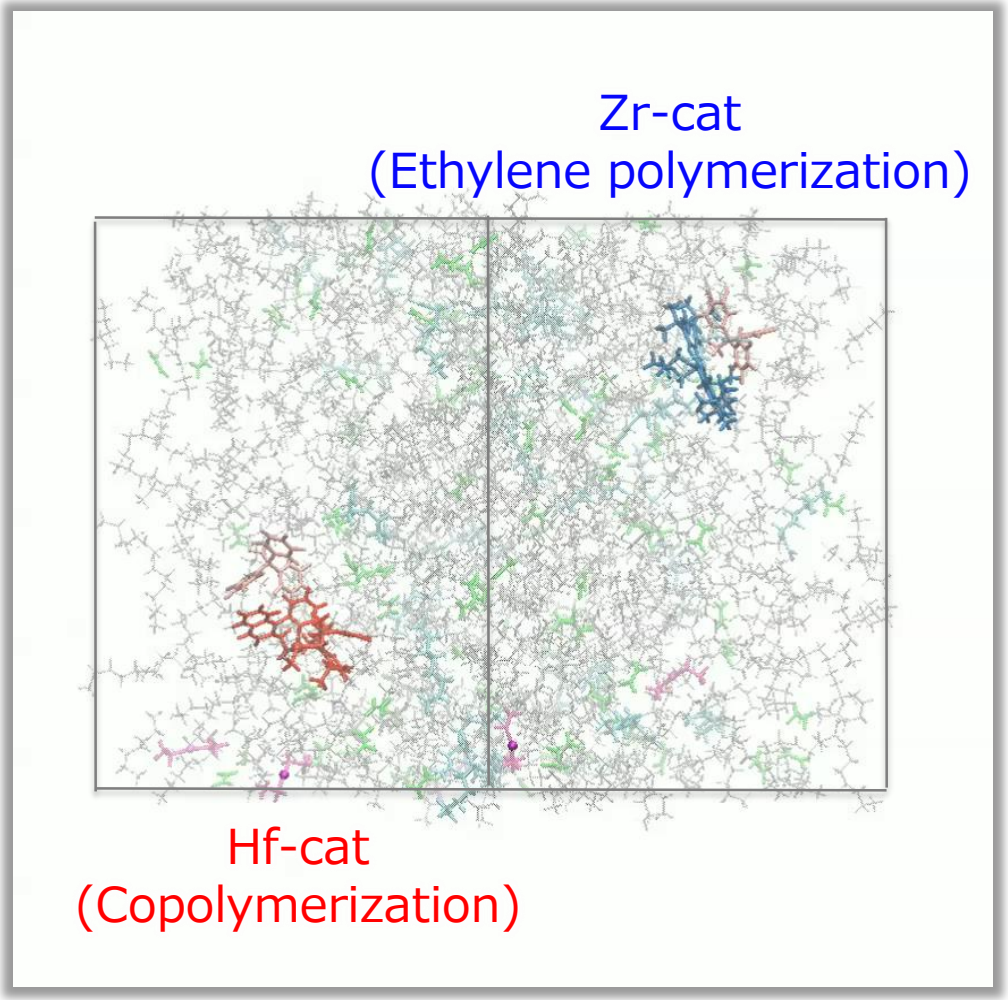
1. **0～199 cycle** (0～19 sec.)
   octene×2 and ethylene×3 inserted on Hf, copolymerization

2. **200 cycle** (20 sec.)
   transfer of copolymer to Zn

3. **370 cycle** (37 sec.)
   transfer of copolymer from Zn to Zr

4. **371～449 cycle** (37~45 sec.)
   ethylene×3 inserted on Zr

5. **450 cycle** (45 sec.)
   transfer of block copolymer(?) produced on Zr to Zn



Procedure towards the realization of CSP simulation

Hf catalyst system

I. Ethylene IP simulation.

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

Complete!!
(by Dr. Matsumoto)

III. Ethylene and 1-octene IP simulation.

IV. CCTP simulation with ethylene and 1-octene as monomers, and with $ZnEt_2$ as CTA.

The present target simulation which was requested for the CREST meeting (09/12/2018).

Zr catalyst system

I. Ethylene IP simulation.

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

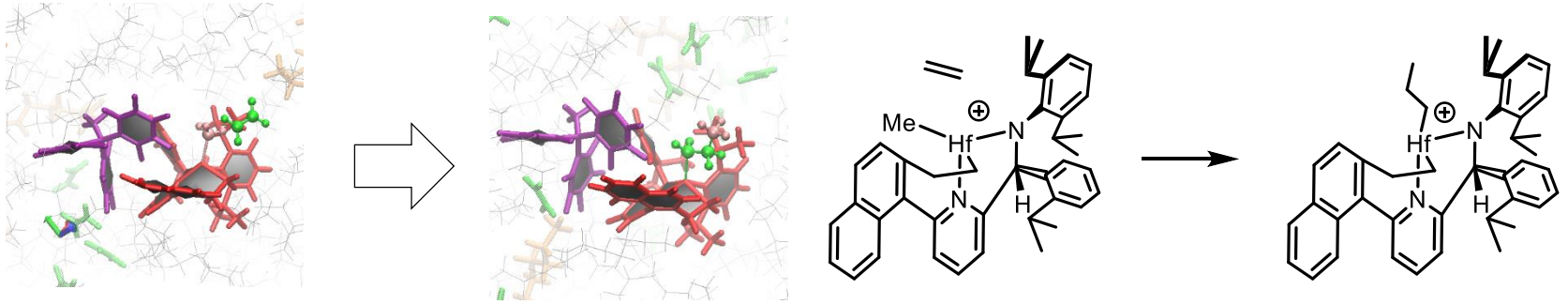
CSP system with Hf and Zr catalysts

I. CSP simulation in which the ethylene and 1-octene IP occurs on the Hf catalyst, and the ethylene IP occurs on the Zr catalyst, accompanying with chain transfer by $ZnEt_2$ as CSA.

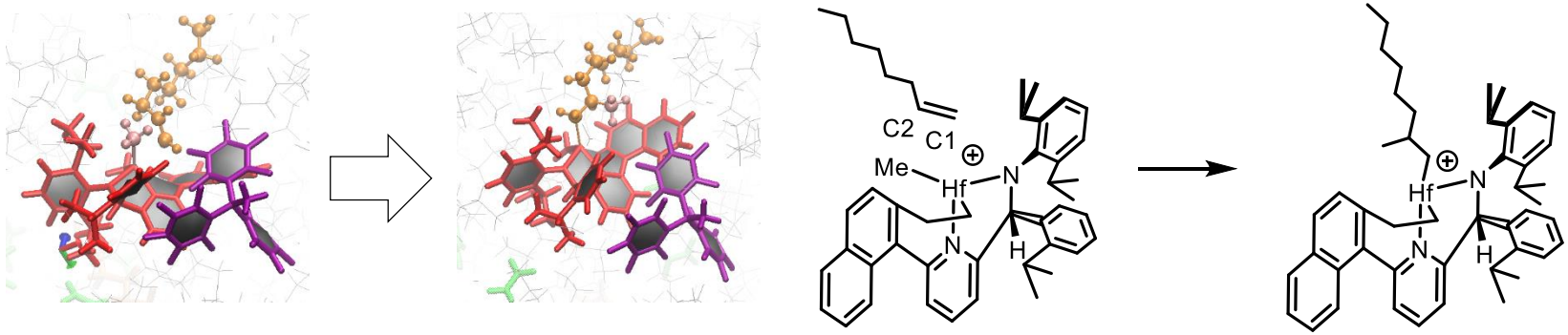
IP: insertion polymerization
CCTP: coordinative chain transfer polymerization
CTA: chain transfer agent
CSP: chain shuttling polymerization
CSA: chain shuttling agent

Reaction scheme (by Ms. Misawa)

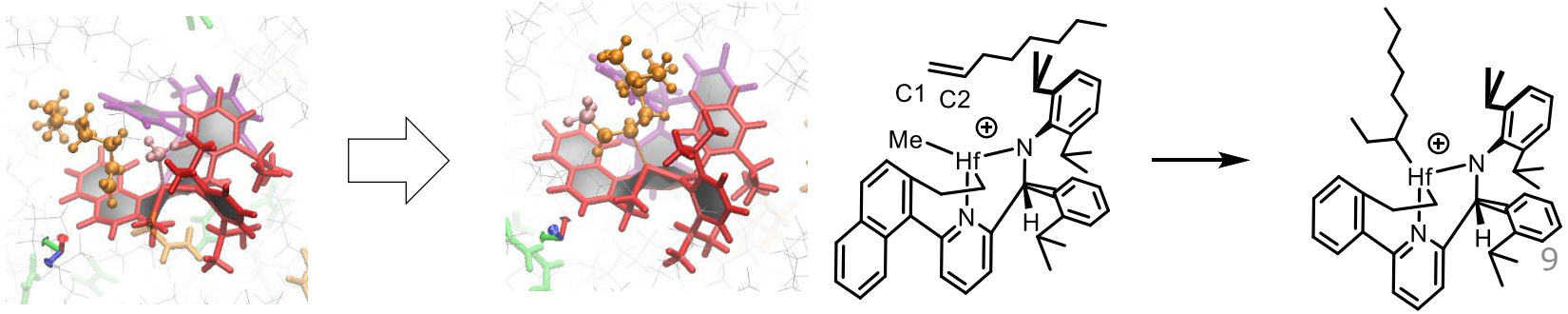
(i) trans ethylene insertion



(ii) trans-1,2-octene insertion



(iii) trans-2,1-octene insertion

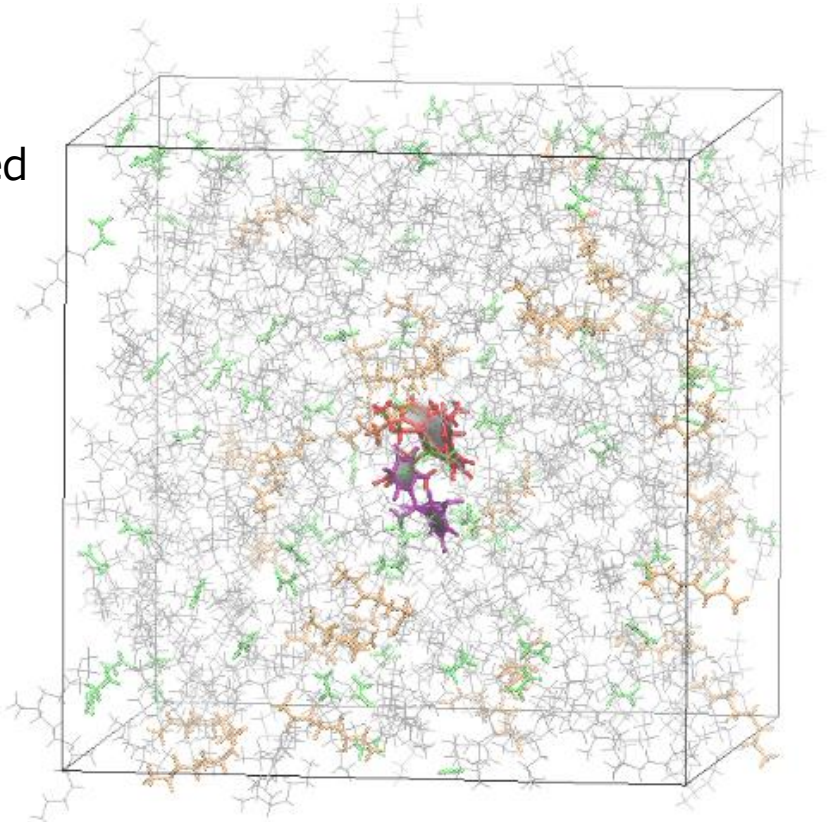


Computational model and details (by Ms. Misawa)

- Model system:
  - Ion Pair (Hf-cat.+anion) ×1
  - heptane (solvent) ×480
  - ethylene ×90

  (0.855 mol/L: a bit higher than the estimated ethylene density of 0.572 mol/L in ref[1])
  - 1-octene ×30

  (0.285 mol/L: a bit higher than the estimated 1-octene density of 0.200 mol/L in ref[1])
- MM parameters:
  General AMBER Force Field (GAFF)
  + FF prepared by Dr. Matsumoto
  + modified LJ for ethylene and 1-octene
- MD Calculation:
  NVT-MD (400K) (based on experiment[2])
- Unit Cell Size:
  55.9 Å 55.9 Å ×55.9 Å



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

RM simulation results (shown by Movie)

<Total 750 RM cycle (75 sec.)>

1. **0～260 cycle** (0～26 sec.)
   ethylene × 4 inserted

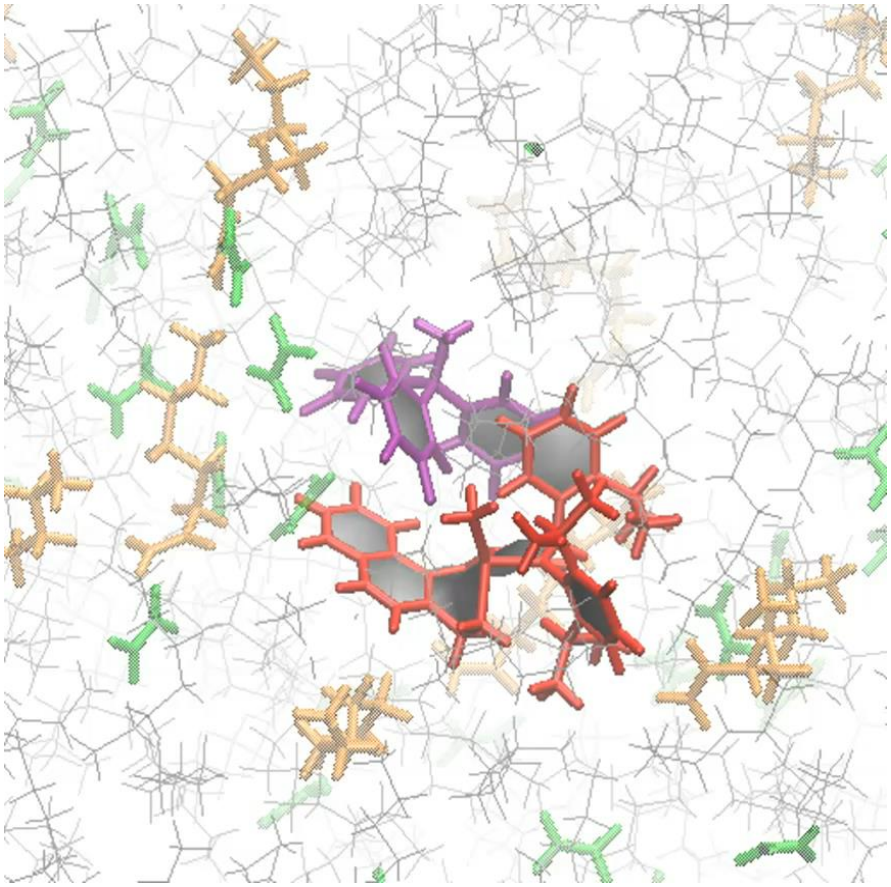
2. **370 cycle** (37 sec.)
   octene × 1 (trans-1,2)

3. **500 cycle** (50 sec.)
   ethylene × 1 inserted

4. **500～580 cycle** (50~58 sec.)
   octene × 2 inserted (trans- and cis-1,2)

5. **600 cycle** (60 sec.)
   ethylene × 1 inserted

5. **660～720 cycle** (66~72 sec.)
   octene × 2 inserted (both trans-1,2)



Red : Hf-cat
Purple : anion
Green : ethylene
Orange : 1-octene
Gray : heptane

Temp. : 400K
Box size : 55.9 Å × 55.9 Å × 55.9 Å

Ethylene IP simulation with termination reaction

Hf catalyst system

I. Ethylene IP simulation.

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

Complete!!
(by Dr. Matsumoto)

III. Ethylene and 1-octene IP simulation.

IV. CCTP simulation with ethylene and 1-octene as monomers, and with $ZnEt_2$ as CTA.

Zr catalyst system

I. Ethylene IP simulation.

RM simulation with termination reaction by H_2 molecule, which was requested for the CREST meeting (09/12/2018).

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

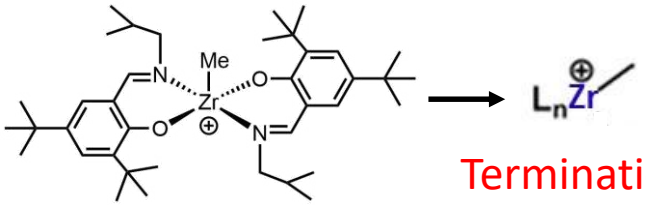
CSP system with Hf and Zr catalysts

I. CSP simulation in which the ethylene and 1-octene IP occurs on the Hf catalyst, and the ethylene IP occurs on the Zr catalyst, accompanying with chain transfer by $ZnEt_2$ as CSA.

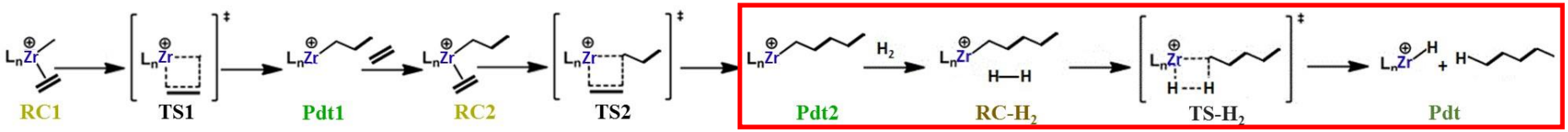
IP: insertion polymerization
CCTP: coordinative chain transfer polymerization
CTA: chain transfer agent
CSP: chain shuttling polymerization
CSA: chain shuttling agent

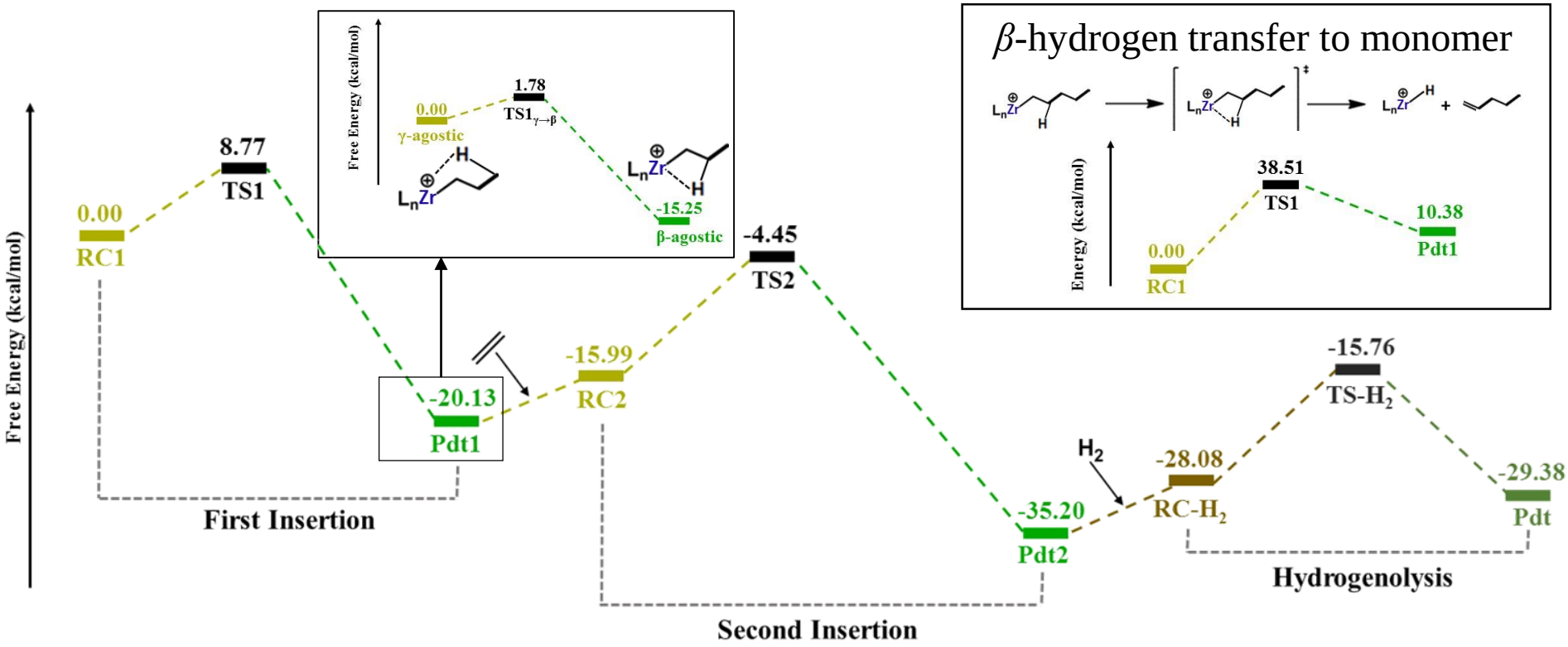
Termination reaction by H_2 molecule (by Dr. Saha)

QM Results



Termination reaction mechanism





B1 = 6-31G** (LANL2DZ +f polarization functions: Zr). [Single point SMD calculation: Solvent= Heptane, $\Delta E_{solvent}$+ G_{gas}^{Corr}]

rf_input.dat (input file to RF program)

rf_input.dat

```
#-----------monomer insertion-----------
#Reaction 1 (FIZ-MIC + ETH ---> FIZ-ERC-MTX)
ReactID=1 Ea=8.34 dE=-26.28
"COND = distance(:FIZ@Zr; :ETH@C1)<4.5
      && distance(:MIC@Ck4; :ETH@C4)<4.5"
"ACTION =
   createBond :FIZ@Zr :ETH@C1;
   createBond :MIC@Ck4 :ETH@C4;
   deleteBond :FIZ@Zr :MIC@Ck4;
   ModifyResByMol2 :MIC ./parms/MTX.mol2;
   ModifyResByMol2 :ETH ./parms/ERC.mol2"
#Reaction 2 (FIZ-ERC-MTX + ETH ---> FIZ-ERC-EMX-MTX)
ReactID=2 Ea=8.34 dE=-26.28
"COND = distance(:FIZ@Zr; :ETH@C1)<4.5
      && distance(:ERC@C1; :ETH@C4)<4.5"
"ACTION =
   createBond :FIZ@Zr :ETH@C1;
   createBond :ERC@C1 :ETH@C4;
   deleteBond :FIZ@Zr :ERC@C1;
   ModifyResByMol2 :ETH ./parms/ERC.mol2;
   ModifyResByMol2 :ERC ./parms/EMX.mol2"
```

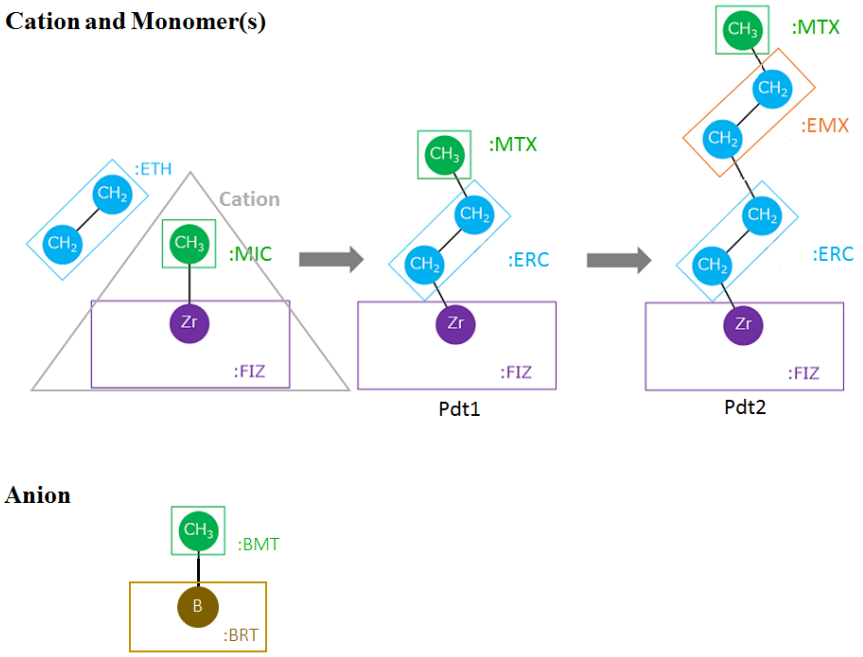


Figure. the technical approach to realize the IP reaction in the RM framework (made by Dr. Saha).

```
#-----------polymer termination-----------
#Reaction 3 (FIZ-ERC-...-MTX + H21-H22 ---> FIZ-HT1 +
HT2-EMX-...-MTX)
ReactID=3 Ea=12.32 dE=-13.62
"COND = distance(:FIZ@Zr; :H21@H1)<5.0
      && distance(:ERC@C1; :H22@H2)<5.0"
```

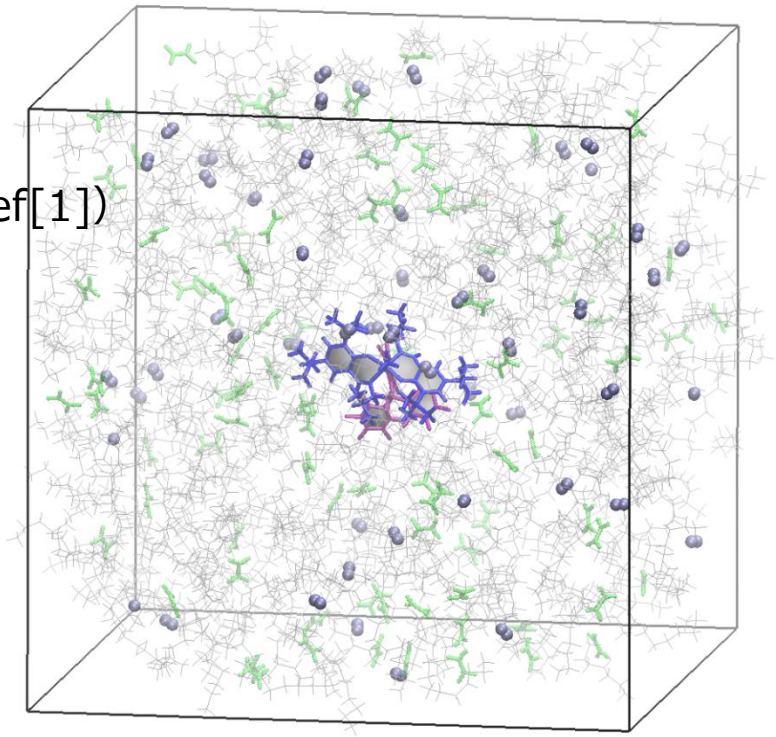
```
"ACTION =
   createBond :FIZ@Zr :H21@H1;
   createBond :ERC@C1 :H22@H2;
   deleteBond :FIZ@Zr :ERC@C1;
   deleteBond :H21@H1 :H22@H2;
   ModifyResByPrepin :ERC ./parms/EMX.prepin;
   ModifyResByPrepin :H21 ./parms/HT1.prepin;
   ModifyResByPrepin :H22 ./parms/HT2.prepin"
```

Computational model and details

- Model system:
  - Ion Pair (Zr-cat.+anion) ×1
  - heptane (solvent) ×480
  - ethylene ×90

  (1.013 mol/L: about 2 times higher than the estimated ethylene density of 0.572 mol/L in ref[1])
  - H_2 ×50

  (0.425 mol/L: about 85 times higher than the estimated H_2 density of 0.005 mol/L in ref[1])
- MM parameters:
  General AMBER Force Field (GAFF)
  + FF prepared by Dr. Saha
  + modified LJ for ethylene
- MD Calculation:
  NVT-MD (400K) (based on experiment[2])
- Unit Cell Size:
  55.9 Å 55.9 Å ×55.9 Å



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RM simulation result (shown by movie)

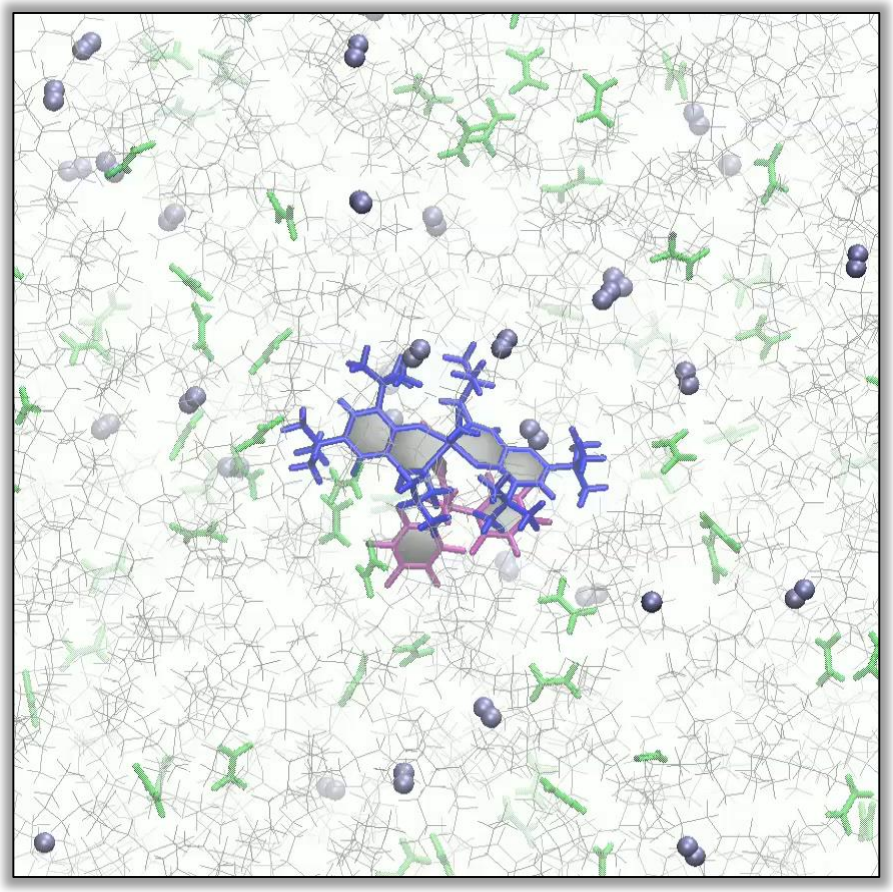
<Total 600 RM cycle (40 sec.)**>**

1. **39 cycle** (3 sec.)
   ethylene × 1 first inserted

2. **40~468 cycle** (~31 sec.)
   ethylene × 12 inserted

3. **500 cycle** (50 sec.)
   termination reaction by H_2 molecule, and elimination of polymer from Zr

4. **500~580 cycle** (50~58 sec.)
   diffusion of polymer eliminated, and stoppage state of any chemical reactions



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Zr catalyst system

I. Ethylene IP simulation.

Complete!!
(presented at my last CREST-WS)

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

The remaining targert simulations towards the realization of CSP

CSP system with Hf and Zr catalysts

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IP: insertion polymerization
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Strategy for the realization of CSP simulation (Reshown)

- The number of the reaction pattern becomes over 70 (estimated by Ms. Misawa) in the current format of input file to RF, which is almost impossible to execute RF because of the highly computational cost.
  (200 [snapshots] × 3 [distance, bond angle and dihedral angle]
  × 70 [patterns] = 42000 [number of calculations] per one RF execution)
- There are not some necessary functions in RF, e.g., "||" (or) statement for reaction conditions, and calculation of distances, bond angles and dihedral angles of atoms inbetween molecules with the same name.

➢ It is necessary to make a new format to write reaction conditions and a program similar to RF.

We are developing the Reaction Finder plus (RFplus) program to be able to include the necessary functions and solve the above problem.

➢ This development can be expected to archive to establish a generalized simulation method for complex chemical reaction systems.

Thank you for your attention.