DAICEL

The Best Solution for You

DAICEL

Confidential

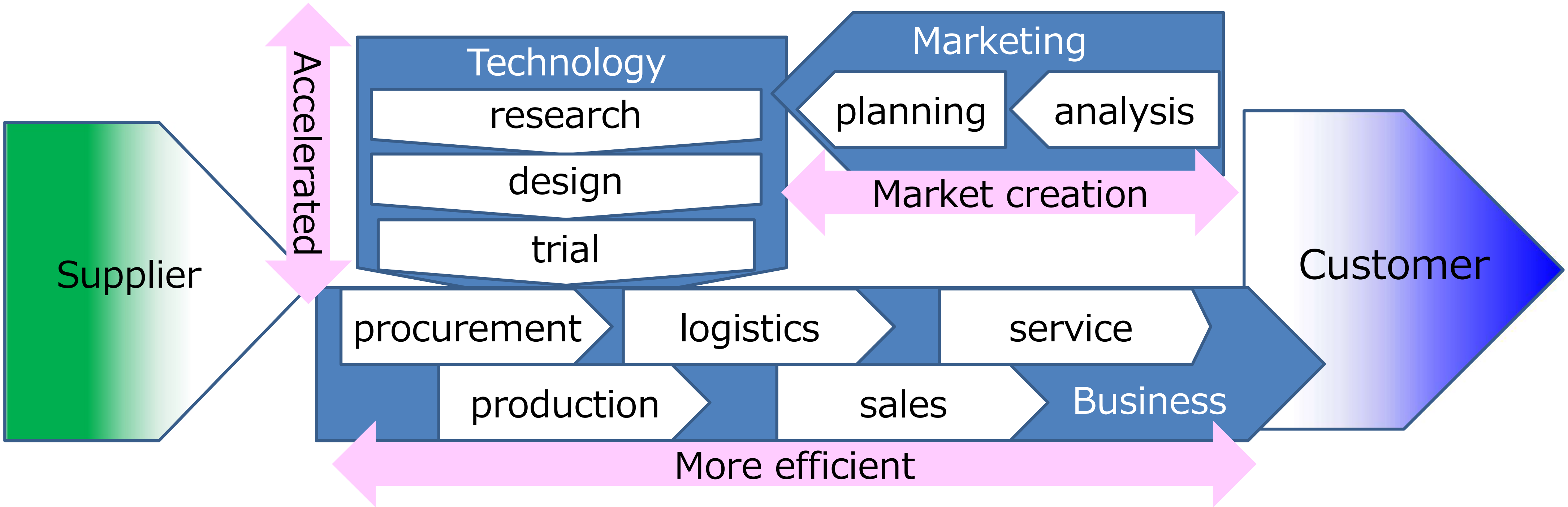
# Optimization of operating conditions for continuous flow processes

**Keywords:Optimization,Flow-shop scheduling,chemical-process**

DAICEL CORPORATION
Production Management Headquarters
Process Technology Division
Simulation Department
Tomohide Ina

# Role of simulation department

**Providing optimal solution for technical issues in our every business division (from marketing to commercialization) by the collaboration of each elemental digital technology.**



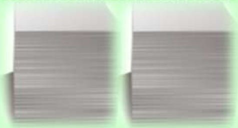

From Daicel medium-term strategy report, *Accelerate2025-*Ⅱ

# Development using Simulation

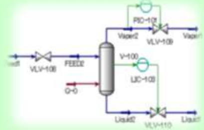
**The Objective is reducing design time and development cost by using Simulation from initial design stage.**

Plan → Material design → Process design → Plant design → commercial operation

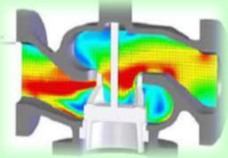
◇AI(Using Process technical document)



◇Process simulation

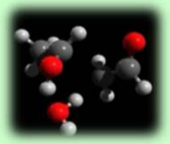


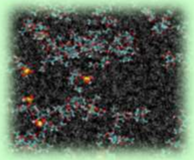
◇CAE
Fluid Simulation



◇Materials Informatics

◇Computational Science
QM・MD・Coarse-grained Simulation





**Improve design accuracy**

【Previous】
- Lab: Design, Experiment → Pilot: Design, Experiment → Plant: Specification confirmed

【Now】
- Lab: Design, simulation, Experiment → Pilot: Design, simulation, Experiment → Plant: Specification confirmed

**Reduce design time**

# Computational Science Team

**Supporting research and development**
**providing theoretical material design and process design based on principles**

Needs → Theory → Modeling → Calc. → Analysis → Elucidation → Factor identification → Prediction Design → Functional Evaluation → Propose

## Theoretical Material Design

### Basic theories

- Quantum mechanics
- Thermodynamics
- Statistical mechanics
- Fluid mechanics

### Numerical solutions

- Molecular orbital method
- Density functional theory
- Molecular dynamics method
- Monte Carlo method
- Dissipative particle dynamics method
- CFD (lattice method/particle method)

### Cluster PC

CPU Num. : 2216
Comp.Power :
95TFLPS

➡FY 2022 plan (GPU)
: 625TFLOPS

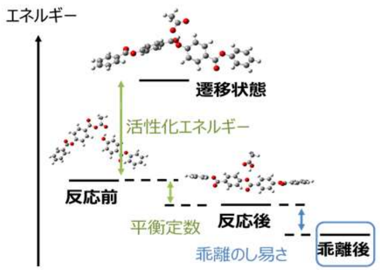
### Joint research

・MEXT Fugaku project
・Osaka university
・University of Hyogo

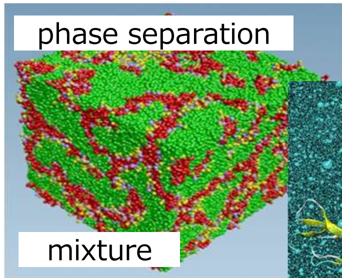
### Goal

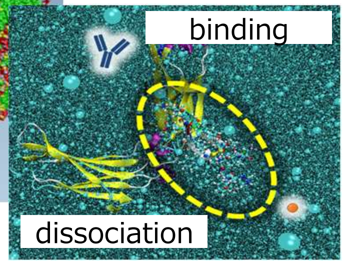
**Realizing specific functions by controlling the constituent elements and structures of matter**

**Reaction process**

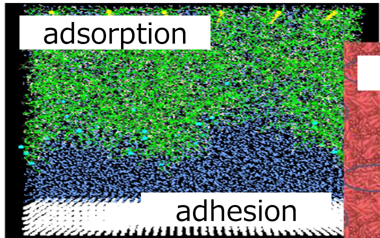


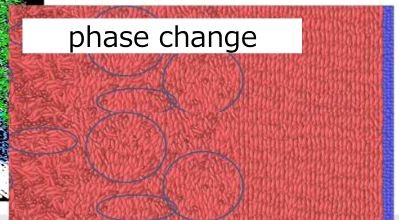

**Bulk**




**Surface**



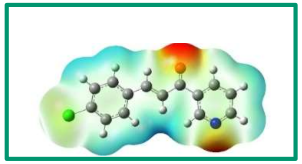




etc.

# Materials Informatics Team

◇ Mission: Explore advanced materials informatics technology for the laboratory scale and deepen the technology through joint research with university research institutes. We build and provide model technology, material libraries, and physical property maps.

Material information



A.I.

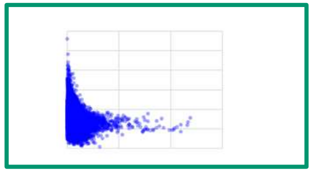
Physical properties

3.0, 8.0, 11.0….
True, False,True….

Model tech.

Material library

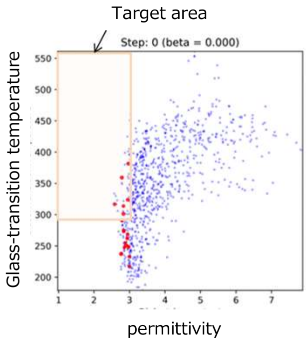
Property map

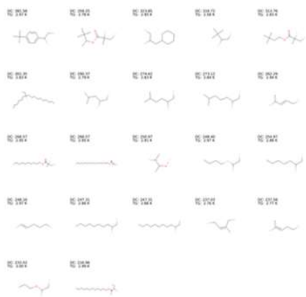


# Application examples of materials informatics

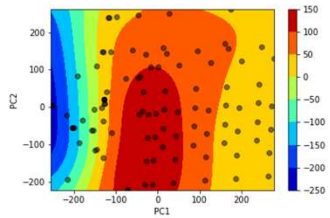
**The predictive models have been developed for "materials-physical properties" targeting the laboratory scale. To do so, there are various studies with various departments as shown below.**

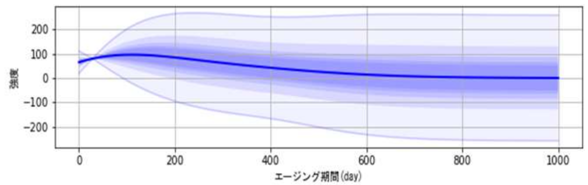
## Examples of MI for data on polymer material



## Examples of providing MI technology for material preparation recipes



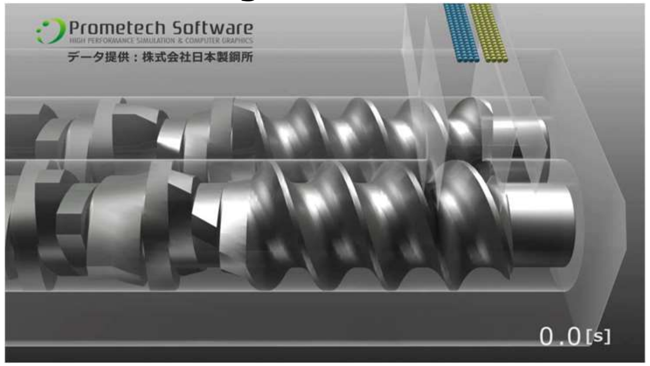
Example of a concrete manufacturing method.

# CAE team

**We simulate complicated phenomenon in production process**
**→ contribute to development or design of process**

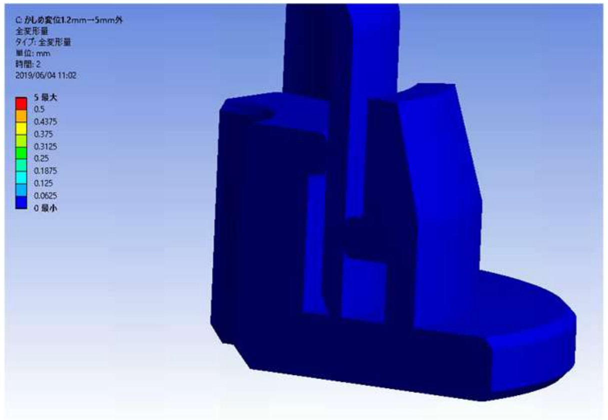
## ○Fluid simulation

**Twin-screw kneading machine**



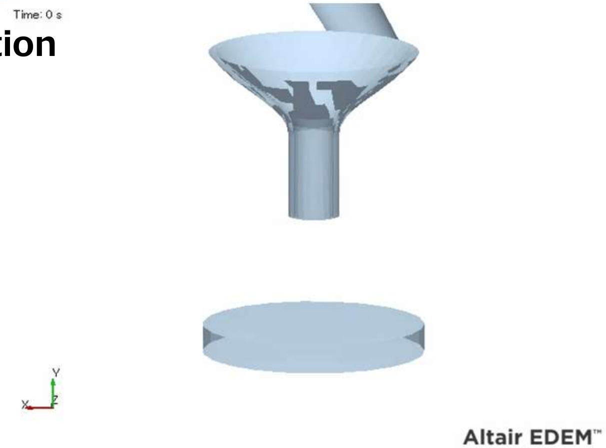

## ○Structural analysis

**Metal working**



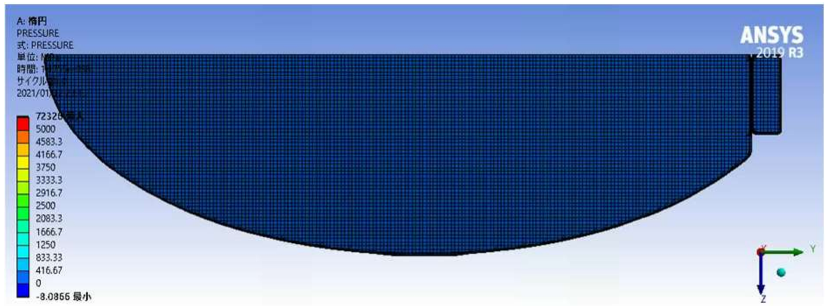
## ○Powder simulation

**Powder Transportation**




## ○Detonation analysis

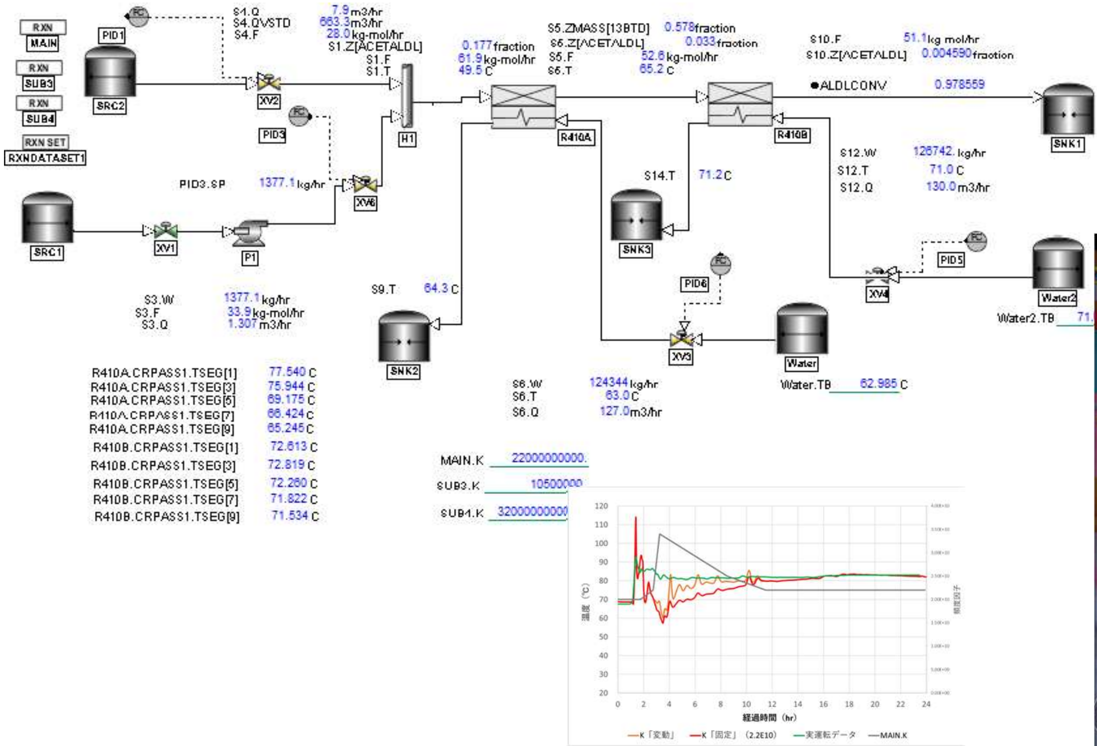
**Pressure distribution in vessel**



# CAE team

**We simulate complicated phenomenon in production process**
**→ contribute to development or design of process**

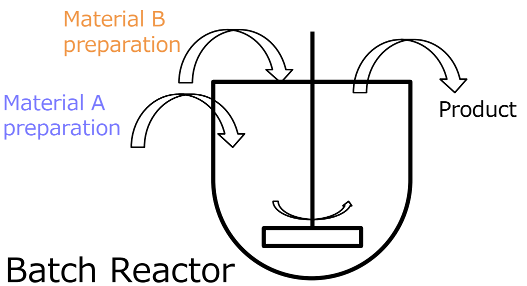
## ○Process simulation



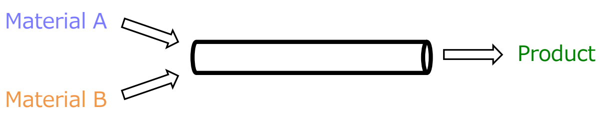

## ○ Operation training simulation

# Outline and background of the assignment

- ◇ We are designing a polymerization reactor in a polymer manufacturing process using two kinds of monomers.
- ◇ Until now, we have been using a semi-batch method, but we are planning to change to a continuous process from the perspective of productivity and quality stability.
- ◇ The desired values for the polymer produced are conversion, molecular weight (number average degree of polymerization), and reactivity ratio.
- ◇ Although the polymerization reaction rate formula is known from previous investigations, it is complicated as described later.
- ◇ In order to control the quality of the final product, we want to optimize the reactor volume and monomer flow rate.



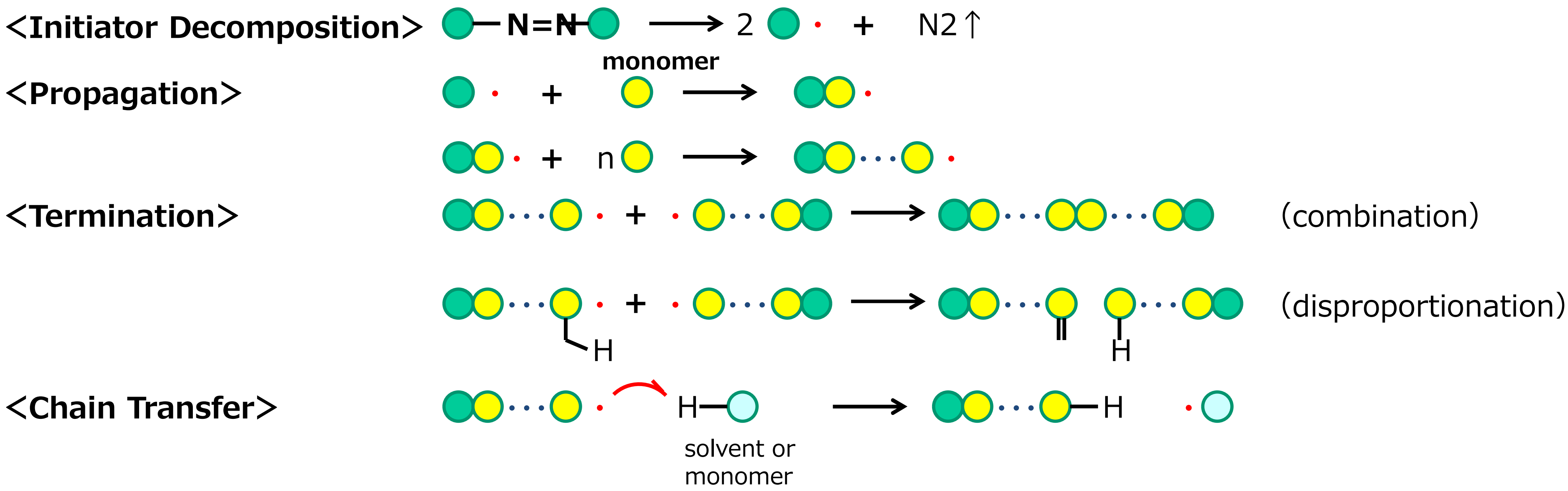

Batch Reactor




Continuous Reactor

# Radical polymerization reaction mechanism

- ◇ In the reaction mechanism of radical polymerization, four reactions proceed.
- ◇ The initiator decomposes to generate initiating radicals, which react with monomers to grow the polymer.
- ◇ The radicals disappear by recombination or disproportionation of the propagating radicals. In addition, the chain transfer reaction also stops the reaction.



# Radical polymerization reaction rate formula①

◇ When the raw material monomers are A and B, the above schematic diagram is converted into the form of the formula.

◇ The initiator decomposition and propagation reactions are as follows. Combination of A and B has 6 growth reactions.

<Initiator Decomposition>

$I \rightarrow 2R\cdot \qquad r = d[R\cdot]/dt = 2 \cdot f \cdot d[I]/dt = 2 \cdot f \cdot kd\ [I] \qquad (1)$

<Propagation>

$R\cdot + A \xrightarrow[kia]{} PA\cdot \qquad r = d[A]/dt = -ki[R\cdot]\cdot[A] \qquad (2)$

$R\cdot + B \xrightarrow[kib]{} PB\cdot \qquad r = d[B]/dt = -ki[R\cdot]\cdot[B] \qquad (3)$

$PnA\cdot + A \xrightarrow[kpaa]{} PnAA\cdot \qquad r = d[A]/dt = -kpaa[PnA\cdot]\cdot[A] \qquad (4)$

$PnA\cdot + B \xrightarrow[kpab]{} PnAB\cdot \qquad r = d[B]/dt = -kpab[PnA\cdot]\cdot[B] \qquad (5)$

$PmB\cdot + A \xrightarrow[kpba]{} PmBA\cdot \qquad r = d[A]/dt = -kpba[PnB\cdot]\cdot[A] \qquad (6)$

$PmB\cdot + B \xrightarrow[kpbb]{} PmBB\cdot \qquad r = d[A]/dt = -kpbb[PnB\cdot]\cdot[B] \qquad (7)$

# Radical polymerization reaction rate formula②



◇ When the raw material monomers are A and B, the above schematic diagram is converted into the form of the formula.

◇ There are six chain transfer reactions.

<Chain Transfer>

$$PnA\cdot + A \xrightarrow{kraa} PnA + A\cdot \qquad r = d[P\cdot]/dt = -kraa\,[PnA\cdot]\cdot[A] \tag{8}$$

$$PnA\cdot + B \xrightarrow{krab} PnA + B\cdot \qquad r = d[P\cdot]/dt = -krab\,[PnA\cdot]\cdot[B] \tag{9}$$

$$PmB\cdot + A \xrightarrow{krba} PmB + A\cdot \qquad r = d[P\cdot]/dt = -krba\,[PmB\cdot]\cdot[A] \tag{10}$$

$$PmB\cdot + B \xrightarrow{krbb} PmB + B\cdot \qquad r = d[P\cdot]/dt = -krbb\,[PmB\cdot]\cdot[B] \tag{11}$$

$$PnA\cdot + S \xrightarrow{ksa} PnA + S\cdot \qquad r = d[P\cdot]/dt = -ksa\,[PnA\cdot]\cdot[S] \tag{12}$$

$$PmB\cdot + S \xrightarrow{ksb} PmB + S\cdot \qquad r = d[P\cdot]/dt = -ksb\,[PmB\cdot]\cdot[S] \tag{13}$$

# Radical polymerization reaction rate formula③

◇ When the raw material monomers are A and B, the above schematic diagram is converted into the form of the formula.

◇ There are eight termination reactions as follows.

<Termination> (combination)

$$PnA\cdot + PnA\cdot \xrightarrow{kcaa} PnAAPn \qquad r = d[P\cdot]/dt = -kcaa\,[PnA\cdot]\cdot[PnA\cdot] \qquad (14)$$

$$PnA\cdot + PmB\cdot \xrightarrow{kcab} PnABPm \qquad r = d[P\cdot]/dt = -kcab\,[PnA\cdot]\cdot[PmB\cdot] \qquad (15)$$

$$PmB\cdot + PnA\cdot \xrightarrow{kcba} PmBAPn \qquad r = d[P\cdot]/dt = -kcba\,[PmB\cdot]\cdot[PnA\cdot] \qquad (16)$$

$$PmB\cdot + PmB\cdot \xrightarrow{kcbb} PmBBPm \qquad r = d[P\cdot]/dt = -kcbb\,[PmB\cdot]\cdot[PmB\cdot] \qquad (17)$$

(disproportionation)

$$PnA\cdot + PnA\cdot \xrightarrow{kdaa} PnA + PnA \qquad r = d[P\cdot]/dt = -kdaa\,[PnA\cdot]\cdot[PnA\cdot] \qquad (18)$$

$$PnA\cdot + PmB\cdot \xrightarrow{kdab} PnA + PmB \qquad r = d[P\cdot]/dt = -kdab\,[PnA\cdot]\cdot[PmB\cdot] \qquad (19)$$

$$PmB\cdot + PnA\cdot \xrightarrow{kdba} PmB + PnA \qquad r = d[P\cdot]/dt = -kdba\,[PmB\cdot]\cdot[PnA\cdot] \qquad (20)$$

$$PmB\cdot + PmB\cdot \xrightarrow{kdbb} PmB + PmB \qquad r = d[P\cdot]/dt = -kdbb\,[PmB\cdot]\cdot[PmB\cdot] \qquad (21)$$

# Radical polymerization reaction Simplified calculation method

In a radical polymerization reaction, the following four assumptions are made.

◇ The rate constant of the propagating reaction is constant regardless of the molecular weight of the propagating radical

◇ Growing radical concentration is constant. The rate of generation and disappearance of propagating radicals is equal

◇ Monomers are consumed only by the propagation reaction

◇ Even if a chain transfer reaction occurs, the polymerization rate does not decrease

The number average degree of polymerization (P) is derived as follows.

P = Monomer consumption rate ÷ Polymer production rate

The monomer consumption rate is the sum of the propagation reactions (2) to (7).

On the other hand, the polymer production rate is the sum of chain transfer reactions (8) to (13) and termination reactions (14) to (21).

Monomer consumption rate $-d[A]/dt = kpaa[PnA\cdot]\cdot[A] + kpba[PnB\cdot]\cdot[A]$ (22)

$-d[B]/dt = kpab[PnA\cdot]\cdot[B] + kpbb[PnB\cdot]\cdot[B]$ (23)

Polymer production rate

$$d[P\cdot]/dt = kraa\,[PnA\cdot]\cdot[A] + krab\,[PnA\cdot]\cdot[B] + krba\,[PmB\cdot]\cdot[A]$$

$$+ krbb\,[PmB\cdot]\cdot[B] + ksa\,[PnA\cdot]\cdot[S] + ksb\,[PmB\cdot]\cdot[S]$$

$$+ (kcaa + kdaa)\,[PnA\cdot]^2 + (kcbb + kdbb)\,[PmB\cdot]^2$$

$$+ (kcab + kcba + kdab + kdba)\,[PnA\cdot]\cdot[PmB\cdot]$$

The number average degree of polymerization

$P = (d[A]/dt + d[B]/dt) \div d[P\cdot]/dt$ (24)

Molecular Weight $Mw = P \times$ monomer average molecular weight (25)

# Theme of radical polymerization reactions

◇ In the current analysis, reaction simulations are performed for each reactor using the reaction rate formula, and the required quality (conversion, molecular weight, reactivity ratio) is satisfied by varying the monomer charging flow rate and reaction volume. The conditions are searched while performing data analysis.

Monomer A conversion:1−Qa3o／Qa,  Monomer B conversion:1−Qb3o／Qb

Molecular weight : Mw ,  Reactivity ratio : Qb3o／Qa3o

◇ **If the reaction rate formula is already determined, is it possible to determine the conditions mathematically?**