Mathematical modeling of industrial multicomponent recipes for batch/semi-batch free-radical bulk/solution polymerization: Styrene/Acrylate/Methacrylate/Hydroxy (alkyl) acrylate

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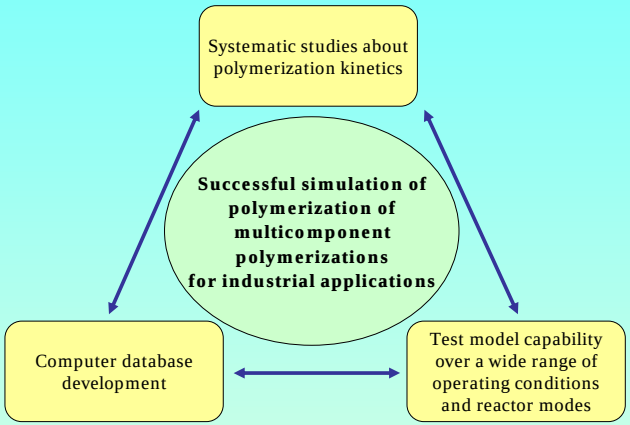
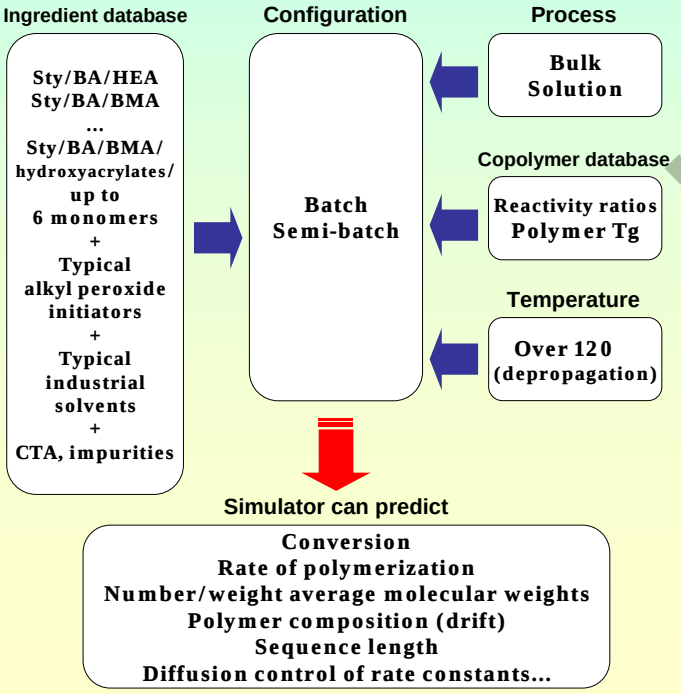
1. Introduction



2. Objectives



3. Model development (sample)

Reaction	Chemical equation	Rate equation	Pseudo rate expression
Initiation	$I \xrightarrow{k_d} 2R^{\bullet}_{in}$ $R^{\bullet}_{in} + M_i \xrightarrow{k_{p,ini}} R^{\bullet}_i$	$R_i = 2fk_d[I]$	
Propagation	$R^{\bullet}_i + M_j \xrightarrow{k_{p,ij}} R^{\bullet}_j$	$R_p = -\sum_i \frac{d(M_i)}{dt} = \sum_i \sum_j k_{p,ij}[R^{\bullet}_i][M_j]$ $= k_p[R^{\bullet}][M]$	$k_p = \sum_i \sum_j k_{p,ij}\phi^{\bullet}_i f_j$
Termination	$R^{\bullet}_i + R^{\bullet}_j \xrightarrow{k_{t,ij}}$ *Dead polymer*	$R_t = \sum_i \sum_j k_{t,ij}[R^{\bullet}_i][R^{\bullet}_j]$ $= k_t[R^{\bullet}]^2$	$k_t = \sum_i \sum_j k_{t,ij}\phi^{\bullet}_i\phi^{\bullet}_j$
Radical transfer (Monomer)	$R^{\bullet}_i + M_j \xrightarrow{k_{fm,ij}} P + R^{\bullet}_j$	$R_{fm} = \sum_i \sum_j k_{fm,ij}[R^{\bullet}_i][M_j]$ $= k_{fm}[R^{\bullet}][M]$	$k_{fm} = \sum_i \sum_j k_{fm,ij}\phi^{\bullet}_i f_j$
Radical transfer (CTA)	$R^{\bullet}_i + T \xrightarrow{k_{fCTA,i}} P + T^{\bullet}$	$R_{fCTA} = \sum_i k_{fCTA,i}[R^{\bullet}_i][T]$ $= k_{fCTA}[R^{\bullet}][T]$	$k_{fCTA} = \sum_i k_{fCTA,i}\phi^{\bullet}_i$
Radical transfer (Solvent)	$R^{\bullet}_i + S \xrightarrow{k_{fS,i}} P + S^{\bullet}$	$R_{fS} = \sum_i k_{fS,i}[R^{\bullet}_i][T]$ $= k_{fS}[R^{\bullet}][T]$	$k_{fS} = \sum_i k_{fS,i}\phi^{\bullet}_i$
Inhibition (Impurity)	$R^{\bullet}_i + Z \xrightarrow{k_{fZ,i}} P$	$R_{fZ} = \sum_i k_{fZ,i}[R^{\bullet}_i][Z]$ $= k_{fZ}[R^{\bullet}][Z]$	$k_{fZ} = \sum_i k_{fZ,i}\phi^{\bullet}_i$

*** Branching reactions to be added later**

Monomer balances

$$\frac{d(V_R[M_i])}{dt} = F_{M_i,in} - k_{p_{ij}}[R^{\bullet}_i][M_j]V_R - F_{M_i,out}$$

Initiator balance

$$\frac{d(V_R[I])}{dt} = F_{I,in} - k_d[I]V_R - F_{I,out}$$

Polymer balances

$$\frac{d(V_R[P_i])}{dt} = F_{P_i,in} + k_{p_{ij}}[R^{\bullet}_i][M_j]V_R - F_{P_i,out}$$

Radical balances

$$\frac{d(V_R[R^{\bullet}])}{dt} = 2fk_d[I]V_R - k_z[Z][R^{\bullet}]V_R - k_t[R^{\bullet}]^2V_R$$

Energy balances

$$\frac{d(V_R H)}{dt} = F_{H,in} + k_p[M][R^{\bullet}]V_R(-\Delta H_p) - UA(T_R - T_{jacket}) - F_{H,out}$$

4. Typical simulation examples

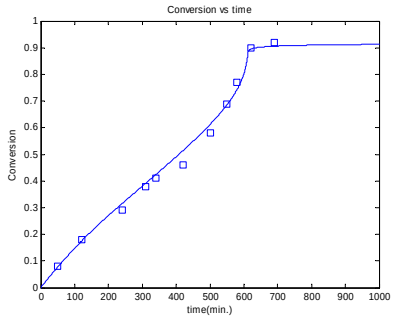


Figure 1. Simulation of conversion vs time of Styrene bulk homopolymerization (60 , [AIBN] = 0.09992 M, Data of Arai and Saito, 1976)

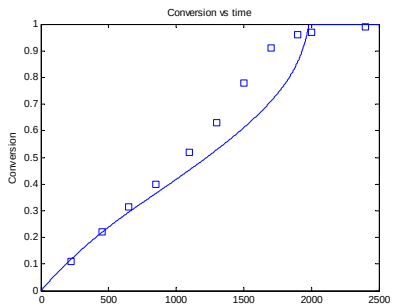


Figure 2. Simulation of conversion vs time of Styrene/BA bulk copolymerization (50 , [AIBN] = 0.05 M, f_{Sty} = 0.600, Data of Dube et al., 1990)

5. Future work plan

- MASc project started in **September, 2006**.
- Background work is based on **WATPOLY®** simulator developed by Penlidis group.
- Extensive literature search for kinetic parameters and building mathematical concepts for multicomponent modeling are currently under progress.