Emulsion Copolymerization Modelling
for the Production of
Nitrile Rubber in a Continuous Reactor Train

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Introduction

The objective is to develop a dynamic model in order to simulate emulsion copolymerization of AN-Bd (Nitrile Rubber) in a series of CSTR's.

The model will act as a practical tool that can be used by industry to predict production rate and product quality, as well as in various on-line control and optimization applications.

Typical model predictions will include conversion, polymerization rate, copolymer composition, molecular weight, branching frequencies, and particle number and size.

The effect of impurities within the reactor is of considerable concern, as they can drastically affect reactor performance and product quality. Thus, our model will consider both monomer and water soluble impurities.

Reaction Mechanism

Multiphase system: polymer particles, aqueous phase (continuous phase), and monomer droplets.

Redox Initiation

$$I + Fe^{2+} \xrightarrow{k_1} R^g_{in} + Fe^{3+} + Y^-$$
$$Fe^{3+} + RA \xrightarrow{k_2} Fe^{2+} + RA^+$$
$$R^g_{in} + M_j \xrightarrow{k'_{p_{j_w}}} R^g_{1,j}$$

Propagation

$$R^g_{n,j} + M_j \xrightarrow{k_{p_{jj_p}}} R^g_{n+1,j}$$

Termination

$$R^g_{n,j} + R^g_{m,i} \xrightarrow{k_{tc}} P_{(n+m)}$$
$$R^g_{n,j} + R^g_{m,i} \xrightarrow{k_{td}} P_n + P_m$$

Water-Soluble Impurities

$$R^g_{n,j} + Z_k \xrightarrow{k_{z_jk}} P_k$$

Monomer-Soluble Impurities

$$R^g_{n,j} + MSI_k \xrightarrow{k_{fmsi_{kj}}} P_k$$

Chain Transfer Agent

$$R^g_{n,j} + CTA_k \xrightarrow{k_{fcta_{kj}}} P_{n,j} + CTA^g_k$$

Transfer to Monomer

$$R^g_{n,j} + M_j \xrightarrow{k_{fm_{jj}}} P_{n,j} + M^g_j$$

Transfer to Polymer

$$R^g_{n,j} + M_j \xrightarrow{k_{fp_{jj}}} P_{n,j} + M^g_j$$

Terminal/ Internal Double Bonds

$$R^g_{n,j} + P^{ter}_{m,j} \xrightarrow{k^*_{p_{jj}}} R^g_{n+m,j}$$
$$R^g_{n,j} + P^{int}_{m,j} \xrightarrow{k^{**}_{p_{jj}}} R^g_{n+m,j}$$

Model Formulation*

Initiator Balance:

$$\frac{dN_I}{dt} = F_{I,in} - \frac{N_I}{V_w} q_w - R_I V_w \quad , \quad \frac{dN_{Fe^{2+}}}{dt} = F_{Fe^{2+},in} - \frac{N_{Fe^{2+}}}{V_w} q_w - R_{Fe^{2+}} V_w$$
$$\frac{dN_{RA}}{dt} = F_{RA,in} - \frac{N_{RA}}{V_w} q_w - R_{RA} V_w \; , \quad \frac{dN_{Fe^{3+}}}{dt} = F_{Fe^{3+},in} - \frac{N_{Fe^{3+}}}{V_w} q_w - R_{Fe^{3+}} V_w$$
$$\frac{dN_{Fe}}{dt} = F_{Fe,in} - \frac{N_{Fe}}{V_w} q_w$$

Monomer Balance:

$$\frac{dN_{m_j}}{dt} = F_{m_j,in} - \frac{N_{m_j}}{V_R} q_T - \left(R_{p_{j_w}} V_w + R_{p_{j_p}} V_p \right)$$

Bound Polymer Balance:

$$\frac{dN_{pol_j}}{dt} = F_{pol_j,in} - \frac{N_{pol_j}}{V_p} q_p + \left(R_{p_{j_w}} V_w + R_{p_{j_p}} V_p \right)$$

Water-soluble Impurities (WSI) Balance:

$$\frac{dN_z}{dt} = F_{z,in} - \frac{N_z}{V_w} q_w - k_z [Z] [R^g]_w V_w$$

Monomer -soluble Impurities (MSI) Balance:

$$\frac{dN_{msi}}{dt} = F_{msi,in} - \frac{N_{msi}}{V_R} q_T - k_{fmsi} [MSI]_p Y_o V_p$$

Chain Transfer Agent (CTA) Balance:

$$\frac{dN_{cta}}{dt} = F_{cta,in} - \frac{N_{cta}}{V_R} q_T - k_{fcta_p} [CTA]_p Y_o V_p$$

Rates of Polymerization:

$$R_{p_{j_p}} = \frac{k_{p_{AA_p}} k_{p_{BA_p}} \left(r_1 [M_A]_p^2 + [M_A]_p [M_B]_p \right)}{k_{p_{BA_p}} r_1 [M_A]_p + k_{p_{AA_p}} r_2 [M_B]_p} Y_o$$
$$R_{p_{j_w}} = \frac{k_{p_{AA_w}} k_{p_{BA_w}} \left(r_1 [M_A]_w^2 + [M_A]_w [M_B]_w \right)}{k_{p_{BA_w}} r_1 [M_A]_w + k_{p_{AA_w}} r_2 [M_B]_w} [R^g]_w$$

Radical Concentrations:

$$Y_o = \frac{\bar{n} N_p}{N_A V_p} \quad , \quad [R^g]_w = \sum_{j=1}^{j_{cr}} [R^g_{j,A}]_w + \sum_{j=1}^{j_{cr}+2} [R^g_{j,B}]_w + [R^g_m]$$

Particle Nucleation:

$$\frac{d\left(N_p V_w\right)}{dt} = F_{N_p,in} - \frac{N_p V_w}{V_R} q_T + \left[\frac{d\left(N_{mic} V_w\right)}{dt} + \frac{d\left(N_{hom} V_w\right)}{dt} \right] - k_F N_p^2 V_w$$
$$\frac{dN_{hom}}{dt} = \left([M_B]_w \left(k_{p_{AA_w}} [R^g_{j_{cr}/2,A}]_w + k_{p_{BA_w}} [R^g_{j_{cr}/2,B}]_w + \sum_{j=j_{cr}/2+1}^{j_{cr}-1} k_{p_{AA_w}} [R^g_{j,A}]_w \right) + k_{p_{AA_w}} [M_A]_w [R^g_{j_{cr}-1,A}]_w \right) N_A$$
$$\frac{dN_{mic}}{dt} = N_A \left(\rho_{des} + \frac{k_{crm} [R^g]_w^{cap}}{r_{mic}} \right) \frac{A_m}{A_m + \varepsilon A_p}$$

Partitioning Approach (Preliminary):

$$K_{j_{mw}} = \frac{[M_j]_m}{[M_j]_w}, \quad K_{j_{wp}} = \frac{[M_j]_w}{[M_j]_p}, \quad [M_j]_w = \frac{N_{m_j}}{K_{j_{mw}} V_m + V_w + \frac{V_p}{K_{j_{wp}}}}$$

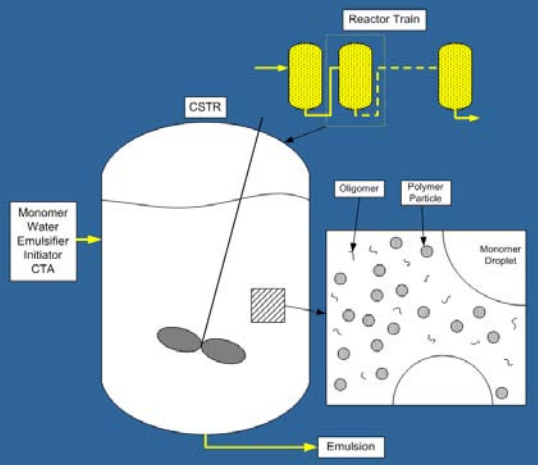
Moment Balances:

$$\frac{d\left(V_p Q_o\right)}{dt} = Q_{o,in} q_{p,in} - Q_o q_p + \left(\tau + \frac{\beta}{2} - \frac{k_p^{**} Q_1}{k_p [M]_p} - \frac{k_p^* Q_o}{k_p [M]_p} \right) k_p [M]_p Y_o V_p$$
$$\frac{d\left(V_p Q_1\right)}{dt} = Q_{1,in} q_{p,in} - Q_1 q_p + \left(\tau - \frac{k_{td} Y_o}{k_p [M]_p} \right) k_p [M]_p Y_o V_p$$
$$\frac{d\left(V_p Q_2\right)}{dt} = Q_{2,in} q_{p,in} - Q_2 q_p + \left(\gamma + 2 \left(1 + \frac{k_p^* Q_1 + k_p^{**} Q_2}{k_p [M]_p} \right) \frac{\xi}{\lambda} + \beta \left(\frac{\xi}{\lambda} \right)^2 \right) k_p [M]_p Y_o V_p$$

Molecular Weight:

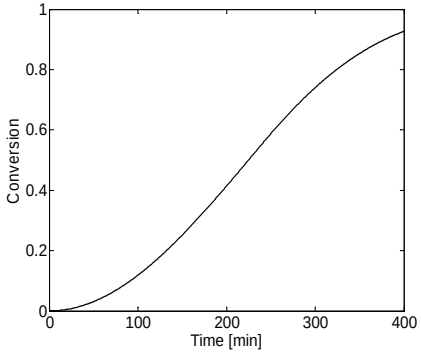
$$\bar{M}_n = MW_{eff} \frac{Q_1}{Q_o}, \quad \bar{M}_w = MW_{eff} \frac{Q_2}{Q_1}$$
$$MW_{eff} = \sum MW_j \bar{F}_j$$

*The equations shown here are a representative sample of the complete model. Other important equations include volume change in each phase, solvent and emulsifier balances, and branching moments and frequencies.



Results

Results are preliminary, as the model is in the troubleshooting/development phase. A plot of monomer conversion as a function of time is as follows:



The figure above is representative of the model's predictive capability under batch operation. Predictions not shown are those of number- and weight-average molecular weight, tri- and tetra-functional branching, polymerization rate, and particle size and number.

Future Work

MASc project commenced in September 2006

Immediate Future Steps

- Extensions to CSTR's
- Testing with batch/CSTR data
- Critical comparison of different approaches for calculating the average number of radicals per particle, monomer/CTA/MSI concentrations in each phase, and particle nucleation
- Parameter sensitivity analysis and parameter estimation

Long-term Future Steps

- Evaluation of the model for on-line model predictive optimization and control scenarios
- Possible model reduction studies
- Relation of model outputs to rubber application indicators (i.e. Mooney viscosity). Such relations would act to facilitate the prediction of grade change effects.

References

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