Modelling and Simulation of ARGET ATRP of BMA solution in Continuous Stirred Tank Reactor

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ABSTRACT

ARGET ATRP (**Activators Regenerated by Electron Transfer** Atom Transfer Radical Polymerization) has received widespread attention for its ability to improve upon the faults associated with the conventional ATRP method. In this project mathematical models are developed for the CSTR version of this process. The simulation of the model provides some important insights into the system which can be used to control the process.

OBJECTIVES

- Develop a Kinetic model of commercially available BMA undergoing ARGET ATRP in a continuous stirred tank reactor.
- Determine the steady state point of the system to study the dynamics.
- Develop a controller to control the ARGET ATRP process of BMA in CSTR.

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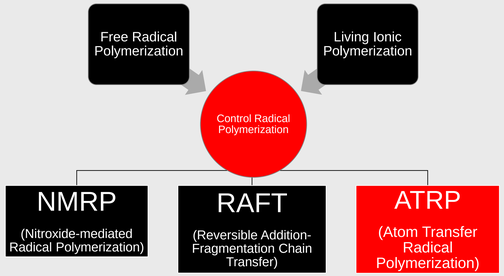
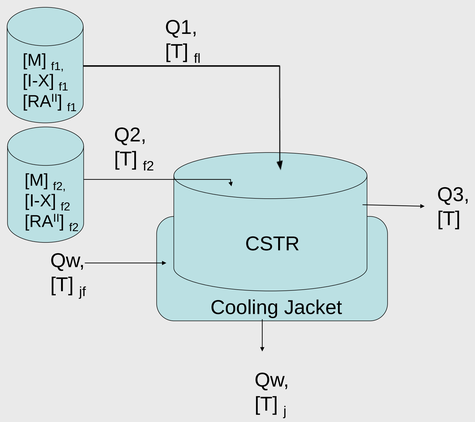
INTRODUCTION



ATRP - Catalyst used is sensitive to air and humidity, which does not facilitate the handling of catalyst.
AGET ATRP -Higher oxidation state catalyst is used instead of the lower oxidation state catalyst and the activators are produced by reduction of catalyst with reducing agent.
ARGET ATRP - Reduces the amount of catalyst required and Improved Oxygen Tolerance.

PROCESS DESCRIPTION



Butyl Methacrylate – **monomer [M]**
Ethyl 2-bromoisobutryate (EBiB) – **initiator [I-X]**
Tin(II) 2-ethylhexanoate ($Sn(EH)_2$)- **reducing agent [RA^{II}]**
Copper(II) bromide tris[(2-pyridryl)methyl]amine complex ($CuBr_2$/TPMA)- **deactivator [A-X]**

PROCESS DESCRIPTION

1. (Reduction of deactivator species)
   $RA^{II} + A - X \xrightarrow{kr1} A + RA^{III}$
2. (Activation of initiator)
   $I - X + A \xrightarrow{ka,0} I\cdot + A - X$
3. (Initiation)
   $I\cdot + M \xrightarrow{kp} R_1\cdot$
4. (Propagation. Where i≥1)
   $R_i\cdot + M \xrightarrow{kp} R_{i+1}\cdot$
5. (Termination)
   $R_i\cdot + R_j\cdot \xrightarrow{ktc} P_{i+j}$
   $R_i\cdot + R_j\cdot \xrightarrow{ktd} P_i + P_j$

*(Transfer)
$M + R_i\cdot \xrightarrow{ktrm} P_i + M\cdot$
*(Deactivation of Monomer Radical)
$M\cdot + A - X \xrightarrow{kda,0} M - X + A$
*(Activation of Dormant Monomer)
$M - X + A \xrightarrow{ka,0} M\cdot + \boxed{A - X}$

Persistent Radical Effect

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NSERC and Department of Chemical Engineering, Ryerson University for financial support.

KINETIC MODELLING

The CSTR system exchanges mass and energy with its surrounding, and has non-constant thermodynamic properties (**Non-Isothermal**).

Mass Balance

$$\frac{d[N]}{dt} = f(k,[N]) + \dot{N}_i - \dot{N}$$

Where N= c * V
N ,molar flow rate (mol/s)
c ,molar concentration (mol/L)
V ,volume (L)
Q ,volumetric flow rate (L/s)

$$V\frac{d[c]}{dt} = f(k,[N]) + c_iQ_i - cQ - c\frac{d[V]}{dt}$$

$$\frac{d[c]}{dt} = f(k,[N]) + \frac{c_i}{(\frac{V}{Q_i})} - \frac{c}{(\frac{V}{Q})} - \frac{c}{V}\frac{d[V]}{dt}$$

PROCESS CONTROL

Develop the model in State space form

$$\dot{x} = f(x,u,v)$$
$$\frac{dx}{dt} = f(x,u,v)$$
$$Y = Cx + e$$

Where,

x = state variables (arises in dynamic material or energy balance) eg. [I] , [M] , T

u = Manipulated variable eg (Catalyst,[M],flow rates of stream entering/leaving the process)

v = disturbance

Y = output variable eg. temperature, Mw, PDI (Đ)

U = PID/Model Predictive Controller

KINETIC MODELLING

Energy Balance

Reactor

$$\frac{dT}{dt} = \frac{-\Delta H_r R_p}{\rho_m Cp_{mix}} + \frac{UA(T-T_j)}{\rho_m Cp_{mix} V} + \frac{[T]_{f1}}{(\frac{V}{Q_1})} + \frac{[T]_{f2}}{(\frac{V}{Q_2})} - \frac{[T]}{(\frac{V}{Q_3})} - \frac{[T]}{V}\frac{dV}{dt}$$

Where
ρ_m, density of monomer
Cp_{mix}, specific heat capacity of the mixture
ΔH_r, enthalpy of the reaction
U, internal energy

Cooling Jacket

$$\frac{dT_j}{dt} = \frac{UA(T-T_j)}{\rho_w Cp_w V_{jack}} + \frac{Q_w}{V_{jack}}(T_{jf} - T_j)$$

Where
ρ_w, density of water
Cp_w, specific heat capacity of the water
V_{jack}, volume of jacket

REMARKS

1. ARGET ATRP reduces the amount of catalyst required
2. To fully realize the potential of ARGET, it must be studied not only in lab scale batch reactions but also in CSTR processes which are more commonly employed in industry.
3. Control of polymerization is needed to obtain low PDI and low number average molecular weight.

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