

MODELING AND ANALYSIS FOR COPOLYMERIZATION SYSTEMS OF ACRYLONITRILE – VINYL ACETATE.

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INTRODUCTION

Due to the importance of the commercial polymer production, it is necessary to understand the phenomenon that happens in polymerization reactors. Actually all acrylic fibers are made from acrylonitrile copolymers containing one or more additional monomers that improve the fiber properties. The uniformity of the polymer is a significant difficulty and defines the quality of final product, which is fundamental to develop products destined to special applications. One of the copolymer preparation methods is the free radicals addition polymerization, where continuous tank and tubular reactors are the most used industrial equipments for this type of reactions. Under this context it is important to develop a mathematical model that predicts the characteristics of the polymer and reactor behavior with the aim of determining the operation conditions for the process design, operation and process modifications. In this work, the mathematical analysis of the system Acrylonitrile (AN)-Vinyl Acetate (VA) is presented, and we carry out a comparison between our modeling results and experimental data from Fujimoto (1967) and other industrial process (confidential). To decrease the polydispersivity of the polymer obtained at the outlet of the tank and tubular reactors, we proposed easy operative modifications.

METHODOLOGY

In this paper, we have considered the chemical kinetics for the free radical copolymerization system AN-VA proposed by Masson (1995), where the reactions that take place in this copolymerization are: initiation, propagation and termination by radical combination and chain transfer to solvent. To make more manageable the kinetic equations we apply the "long chain hypothesis" (LCH) and the quasi-steady-state-approximation (QSSA) to the rate expressions. The solution technique for the model of tank reactor, at steady state conditions proposed by Hamer and Ray (1981) was made as reference. The mathematical solution for the tubular reactor was developed using Runge-Kutta method. For both reactors the rate constants are:

$$k_d = \hat{k}_d \exp\{-E_d / RT\} \quad \text{(Dissociation of initiator)}$$

$$k_{p_{ij}} = \hat{k}_{p_{ij}} \exp\{-E_{p_{ij}} / RT\} g_{p_{ij}} \quad i, j = 1, 2 \quad \text{(Propagation)}$$

$$k_{t_{ii}} = \hat{k}_{t_{ii}} \exp\{-E_{t_{ii}} / RT\} g_{t_{ii}} \quad i = 1, 2 \quad \text{(Radical termination)}$$

$$k_{t_{12}} = \phi(k_{t_{11}} k_{t_{22}})^{1/2}$$

Where the gel effect parameters g_{iii} are computed using the empirical correlations of Friis and Hamielec and Ross and Laurence. The Table 1 shows the mathematical model of the copolymerization mechanism for CSTR and Tubular reactors.

The total concentration of polymer was obtained by

$$P = \frac{k_{p21}M_1}{k_{p12}M_2}Q \quad Q = k_p \left[\frac{2f_i k_d I}{k_{t11} \left(\frac{k_{p21}M_1}{k_{p12}M_{21}} \right)^2 + 2k_{t12} \left(\frac{k_{p21}M_1}{k_{p12}M_{21}} \right) + k_{t22}} \right]^{1/2}$$

Table 1.

CSTR	Tubular
$V \frac{dI}{dt} = (I_f - I)q - k_d IV$	$\frac{dI_{(t)}}{dt} = -k_d I \quad I_{(0)} = If$
$V \frac{dM_1}{dt} = (M_{1f} - M_1)q - M_1(k_{p11}P + k_{p21}Q)V$	$\frac{dM_{1(t)}}{dt} = -M_1(k_{p11}P + k_{p21}Q) \quad M_{1(0)} = M_{1f}$
$V \frac{dM_2}{dt} = (M_{2f} - M_2)q - M_2(k_{p12}P + k_{p22}Q)V$	$\frac{dM_{2(t)}}{dt} = -M_2(k_{p12}P + k_{p22}Q) \quad M_{2(0)} = M_{2f}$
Energy balance for both CSTR and Tubular reactors	
$V \frac{dT}{dt} = (T_f - T)q + \frac{V}{\rho C_p} [(-\Delta H_{p11} k_{p11} P M_1) + (-\Delta H_{p21} k_{p21} Q M_1) +$ $+ (-\Delta H_{p12} k_{p12} P M_2) + (-\Delta H_{p22} k_{p22} Q M_2)] - \frac{hA_c}{\rho C_p} (T - T_c)$	

To analyze the quality parameters (polydispersivity and average molecular weight), we have applied the moments technique (Ray 1972). The moments of the molecular weight distributions for a compolymerization system are defined as

$$\psi_{ij} = \sum_i^n \sum_j^m (nw_1)i(mw_2)jP_{n,m}$$

Where the number average molecular weight and weight average molecular weight through the moments of the molecular weight distributions is performed by using

$$Mn = \frac{\Psi^1}{\Psi^0} \quad \text{Number average molecular weight.}$$

$$Mw = \frac{\hat{\Psi}^1}{\hat{\Psi}^0} \quad \text{Weight average molecular weight.}$$

For determining these average quantities, the concentration of growing polymer chains is calculated by

$$P_{n,m} = \alpha_a P_{n-1,m} + \frac{\gamma \alpha_a}{r_1} Q_{n-1,m} \quad Q_{n,m} = \frac{\alpha_b}{\gamma r_2} P_{n,m-1} + \alpha_b Q_{n,m-1}$$

The reaction rate of the concentration of dead polymer chains is defined by

$$r_{Mn,m} = Kt_{11} \sum_r^n \sum_q^m P_{r,q} P_{n-r,m-q} + 2Kt_{12} \sum_r^n \sum_q^m P_{r,q} Q_{r,q} + Kt_{22} \sum_r^n \sum_q^m Q_{r,q} Q_{n-r,m-q} + K_{fs1} \sum_r^n \sum_q^m P_{r,q} + K_{fs2} \sum_r^n \sum_q^m Q_{r,q}$$

Using the generation functions and convolution theorem we obtain

$$\Theta = \theta(Kt_{11}G^2 + 2Kt_{12}G\Phi + Kt_{22}\Phi + K_{fs1}G + K_{fs2}\Phi) \quad (\text{Tank reactors})$$

$$\frac{d\Theta_{(t)}}{dt} = Kt_{11}G^2 + 2Kt_{12}G\Phi + Kt_{22}\Phi + K_{fs1}G + K_{fs2}\Phi \quad (\text{Tubular reactors})$$

Applying the definition of the moments, we can get the equations for CSTR and Tubular reactors (Table 2).

Table 2.

Moments for CSTR	Moments for Tubular
$\Psi^0 = [\Theta]_{s=u=1}$	$\Psi^0(t) = [\Theta]_{s=u=1}$
$\Psi^1 = \left[\frac{\partial \Theta}{\partial u} \right]_{s=u=1}$	$\Psi^1(t) = \left[\frac{\partial \Theta}{\partial u} \right]_{s=u=1}$
$\dot{\Psi}^0 = \left[\frac{\partial \Theta}{\partial u} \right]_{s=u=1}$	$\dot{\Psi}^0(t) = \left[\frac{\partial \Theta}{\partial u} \right]_{s=u=1}$
$\dot{\Psi}^1 = \left[\frac{\partial \Theta}{\partial u} \right]_{s=u=1} + \left[\frac{\partial^2 \Theta}{\partial u^2} \right]_{s=u=1}$	$\dot{\Psi}^1(t) = \left[\frac{\partial \Theta}{\partial u} \right]_{s=u=1} + \left[\frac{\partial^2 \Theta}{\partial u^2} \right]_{s=u=1}$

And the polydispersity can be computed by

$$\text{Polydispersity} = \frac{Mw}{Mn}$$

Case of study: Copolymerization AN-VA for acrylic fiber applications.

A solution polymerization reactor system is formed by 3 CSTR reactors in series. The non reacting monomers at the exit of the 3rd reactor are evaporated and recycled to the first reactor, each reactor have initiator feeding. One problem of this reaction system is the variability in the uniformity of the polymer; this situation is a significant difficulty in the new tendency of the global acrylic fiber market. To reduce this variability we propose keep constant the mass ratio between the monomers in the feed of each reactor, feeding the reactors 2 and 3 with additional quantity of the more reactive monomer.

RESULTS AND CONCLUSIONS

The prediction of the model for the copolymerization system AN-VA was consistent. the model simulation are similar to the experimental data obtained in a laboratory CSTR reactor (Figures 1-3). Taking as reference these results the simulation of the tubular reactor was made. In Table 4 we show the comparison between 3 CSTR and Tubular reactor, where with less time we can obtain the same total monomers conversion with higher weight average molecular weight but a greater value of polydispersity. For the Case of study modeling results are presented in Figures 4 – 6. The principal conclusion

PRE

of the analysis of the proposed operative modification made to CSTR reactors, is than allowed to reduce the variability in the molecular weight distributions at the outlet of each reactor in 89.6% less than the original system (Table 3), and also we can have a major control in the mole fraction of monomer 2 in the polymer formed. These results are important because the final levels were similar to the target values for a high quality product. The better system is the tubular reactor, with lower time reaction, higher conversion, higher average molecular weights and low equipment investment. We have no presence of gel effect at all conversions reported in this paper, experimentally we founded it at 105 and 7 minutes of time reaction with mass ratios of solvent – monomers of 2 and 1 respectively.

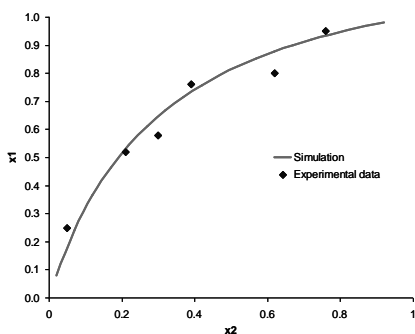


Figure 1. Conversion reaction between both monomers.

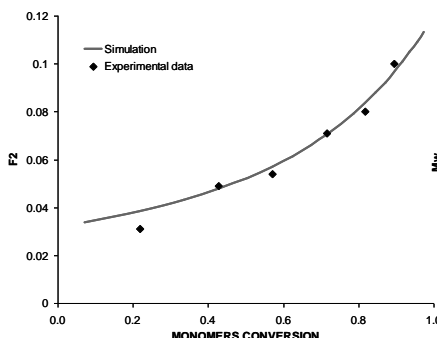


Figure 2. Monomer 2 in polymer formed vs. Total monomers conversion

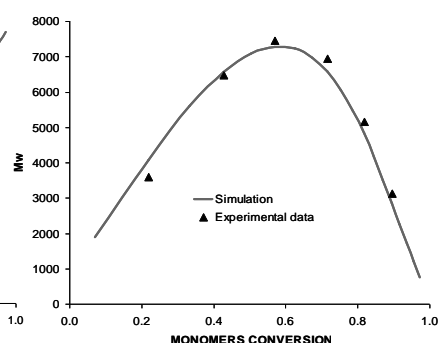


Figure 3. Weight Average Molecular Weight (WAMW) vs total monomers conversion.

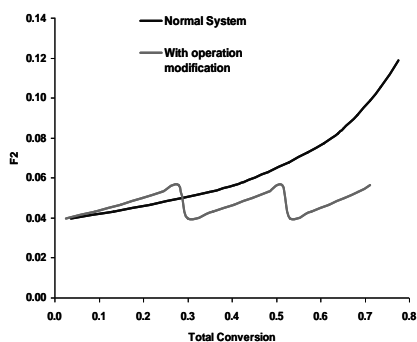


Figure 4. Monomer 2 in polymer formed vs. Total monomers conversion

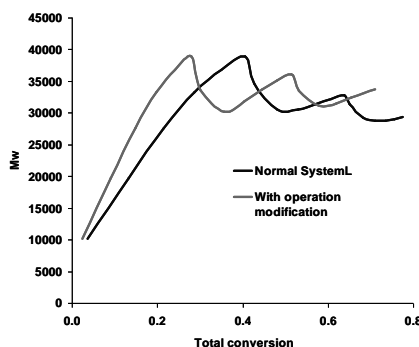


Figure 5. Weight Average Molecular Weight (WAMW) vs total monomers conversion.

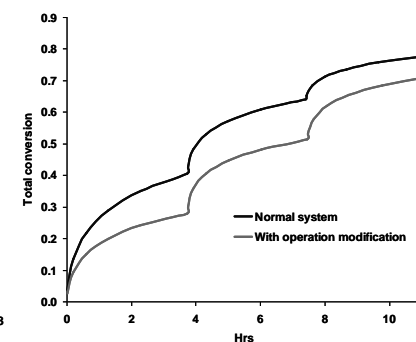


Figure 6. Total conversion vs. Time

Table 3. Case of study. Simulation 3 CSTR reactor in series

	Polydispersivity	Mw
Normal system		
Outlet of first reactor	1.84	38858.6
Outlet of second reactor	1.97	32804.9
Outlet of third reactor	2.177	29294.8
Operative modification		
Outlet of first reactor	1.84	38858.6
Outlet of second reactor	1.853	36021.1
Outlet of third reactor	1.875	33637.9

Table 4. Case of study. Simulation of a Tubular reactor

Parameter	3 CSTR series (real system)	Tubular Reactor (simulation)
Time reaction (hrs)	11.6	3.75
Conversion	0.55	0.53
Weight average molecular weight	26500 gr/mol	41,000 gr/mol
Comonomer concentration	0.075	0.076
Outlet Polymer content in solution	0.14	0.16

The solution methodology is quite flexible, since it also allows to calculate the effecto in polymerization kinetics of chain transfer to monomer, initiator o other agents, diverse termination types, gel effect, and inhibition.

Bibliography

1. W. H. Ray, "The Quasi-steady-state Approximation in Continuous Stirred Tank Reactors", C. J. C. E. Vol 47, 1969.

3. W. H. Ray, T. L. Douglas and E. W. Godsalve., "Molecular Weight Distributions in Copolymer Systems. II. Free Radical Copolymerization", *Macromol.*, 4, 2, 1971.
4. W. H. Ray, "On the Mathematical Modeling of Polymerization Reactors", *Macromol.*, C8(1), 1-56, 1972.
5. A. D. Schmidt and W. H. Ray, "The Dynamic Behavior of Continuous Polymerization Reactors. I. Isothermal Solution Polymerization in CSTR" *Chem. Eng. Sci.*, 36, 1401-1410, 1981.
6. J. W. Hamer, T. A. Akramov and W. H. Ray, "The Dynamic Behavior of Continuous Polymerization Reactors. II. Nonisothermal Solution Homopolymerization and Copolymerization in a CSTR" *Chem. Eng. Sci.*, 36, 12, 1897-1914, 1981.
7. Shiro Fujimoto, "On the Velocity of Radical Copolymerization of Vinyl Acetate with Methyl Methacrylate, Styrene and Acrylonitrile", *Memories of Defense Academy Japan*, 7, 3, 1247-1254, 1967.
9. A. E. Tonelli, "Glass Transition Temperatures of Regularly Alternating Acrylonitrile-Vinyl Acetate Copolymers", *Macromol.*, 10, 3, 1977.
10. J. C. Masson, "Acrylic Fiber Technology and Applications", Marcel Dekker, Inc. USA, 1995
11. J. Brandrup, E. H. Immergut, E. A. Grulke, "Polymer Handbook", ed. Wiley Interscience, 1999.
12. A. Keramopoulos and C. Kiparissides, "Development of a Comprehensive Model for Diffusion-Controlled Free-Radical Copolymerization Reactions", *Macromol.*, 35, 4155-4166, 2002.

Nomenclature

A_c	Heat transfer area
C_p	Heat capacity
E_k	Activation energy, $k = pij, tij, d; i, j = 1, 2$
f_i	Initiator efficiency
g_k	Gel effect for rate constant, $k = pij, tii = 1, 2$
$-\Delta H_{pij}$	Enthalpy of polymerization, $i, j = 1, 2$
h	Heat transfer coefficient
I	Initiator concentration
I_f	Initiator feed concentration
$I_{(0)}$	Initiator concentration at time 0
$I_{(t)}$	Initiator concentration at time t
k_k	Reaction rate constant, $k = pij, tij, d; i, j = 1, 2$
\hat{k}_k	Pre-exponential factor, $k = pij, tij, d; i, j = 1, 2$
M_i	Monomer concentration, $i = 1, 2$
M_{if}	Monomer feed concentration, $i = 1, 2$
$M_{i(0)}$	Monomer concentration at time 0
$M_{i(t)}$	Monomer concentration at time t
Mn	Number average molecular weight
Mw	Weight average molecular weight
P	Total concentration of polymer radicals ending in M_1
Q	Total concentration of polymer radicals ending in M_2
q	Volumetric flow rate
R	Gas constant
T	Temperature
T_f	Feed temperature
T_c	Coolant temperature
t	Time
V	Reactor volume
w_i	Molecular weight of monomers, $i = 1, 2$

α_k	Probability of a chain adding another A or B monomer, $k = a, b$
γ	Ratio of reaction rate constants
ρ	Solution density
ϕ	Cross termination coefficient
G	Generating function for P
Φ	Generating function for Q
ψ_{ij}	Number molecular weight distribution
Ψ^i	Moments of number average molecular weight
$\hat{\Psi}^i$	Moments of weight average molecular weight