

Generation of Efficient Solutions in Multiobjective Optimization for Copolymerization Processes

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Abstract

In this work, the free radicals solution copolymerization in a continuous stirred tank reactor (CSTR) is modeled, with the aim of simulating an industrial process and improving the final polymer quality, which is measured in terms of molecular weight averages and final conversion. A multiobjective optimization problem was formulated using conflicting performance objectives in polymerization systems, such as maximize monomer conversion and minimize molecular weight distribution. The dynamic mass balances were developed for initiator, monomer radicals, and polymer for CSTR, respectively. A simultaneous optimization approach was selected to solve the dynamic optimization problem. A nonlinear programming model was obtained when orthogonal collocation on finite elements was used for time domain. Two methods have been implemented: Weighted Sum and Normal Boundary Intersection. A Pareto curve is presented and some strategies are proposed to select suitable operating policies in an open-loop environment.

Key words: Pareto Set, PAN, NBI, Weighted Sum

1. Introduction

Productivity maximization avoiding the product quality compromising is the top priority for the process industries. Hence, a trade-off between these two requirements usually emerges. This is not an exception for polymers, so that, the product quality needs to be maintained. The quality product is specified within a very short range, and its productivity is enhanced keeping the product specification within that given narrow range. Polymerization processes are quite complex in nature; the operating variables of a polymerization reactor system commonly influence molecular parameters of the product in conflicting ways. For instance, the average molecular weights determine several physical properties, e.g. strength and impact resistance, and they can be treated as an indirect measurement of product quality, whereas the polymerization time is a direct measurement of productivity. The simultaneous minimization of polymerization time and maximization of molecular weight distribution (M_w) can lead to the goal of productivity maximization without affecting the product quality. Thus, the study of the phenomena that occurs into the polymerization reactors is an important requirement, where the mathematical modeling and multicriteria optimization techniques represent useful tools to achieve this purpose. In this work it is formulated a multiobjective optimization problem using conflicting performance

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objectives in copolymerization systems, such as maximizing monomer conversion, minimizing molecular weight distribution, and computing the optimal rates of monomer feed, which ensure the satisfaction of the product quality. These copolymerization systems depicted two conflicting objectives, and framed an ideal platform applied to multiobjective optimization problem (MOOP) for copolymerization of acrylonitrile (AN) and vinyl acetate (VA) systems in a continuous stirred tank reactor (CSTR). Several studies [1-3] have been reported in the open literature on the kinetics, steady-state and dynamic modeling, simulation, optimization, and control of copolymerization systems. Czajlik et al. [1] and Wiles et al. [2] presented an elaborate kinetic investigation of the polymerization of AN, methyl acrylate (MA) and dimethylformamide (DMF) systems. They reported overall rate constants values at different temperature gradients and the monomer reactivity ratios as well. Vallecillo-Gomez et al. [3] presented a study for the free radicals solution copolymerization, system AN-VA, with the objective of finding the characteristic correlations parameters which are used to determine the auto-acceleration reaction phenomenon [4] called "gel effect". It occurs at small solvent concentrations. This phenomenon arises as a consequence of the viscosity increase into the reaction medium, due to the formation of polymer molecules and it commonly occurs when small solvent concentrations are presented. The result is a rate constant termination decrease and a conversion increase. These authors observed that temperature improves monomers conversion and monomers fraction, however, an increment in operation temperature increases poly-dispersity and reduces average molecular weight. Benyahia et al. [5], presented a multicriteria optimization formulation for styrene (St) and butyl acrylate to determine the dynamic optimal feed rate profile necessary to produce core-shell latex particles with specific end-use properties depending on the considered application, e.g. paints or adhesives. The model proposed by the authors predicts the global monomer conversion, the M_w , the particle size distribution and the residual monomers mass fraction. An evolutionary algorithm to determine the Pareto set was applied, and a unique solution was selected and experimentally implemented. Gomes et al. [5] reported optimal control policies for emulsion terpolymerization of St, methyl methacrylate (MMA) and MA, which were determined in a semi-batch reactor using the multi-objective dynamic optimization method. They used a dynamic model for the design of optimal control for the reaction system, and an approach on the control vector parameterization was implemented for constrained optimization. Six variables were used as manipulated variables: three monomers feed rates (St, MMA and MA), surfactant and initiator feed rates and the reactor temperature as well. Their results showed that the optimization procedure could simultaneously minimize the reaction time and monomer flows to obtain the desired composition of the polymers, particle size distribution and M_w . The research showed high temperature influence on M_w , due to the effect of the diffusion of the radical ends. The effect is observed not only through diffusion or reptation for the concentrated case, but also propagation, which lengthens the radical chain and effectively moves the radical end in spatial position.

2. Problem formulation

2.1 Process description

The traditional poly(acrylonitrile) (PAN) manufacturing process is carried out in a CSTR at 333.15 K using water and DMF as medium, the process is depicted in Figure 1. The total weight of water and DMF is three times higher than those monomers. Azobisisobutyronitrile (AIBN), 2% wt on the basis of the monomers, is used as initiator. Monomers AN (M_{1f}) and MA (M_{2f}), initiator and solvent (S_f) are continuously added to the CSTR system. The residence time was set at 12 hours according to an industrial case of study, whereas the molar basis was represented by $M_{1f} + M_{2f} + S_f = 10$ [3].

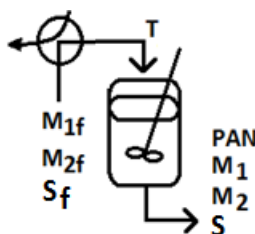


Figure 1. Copolymerization reactor system

2.2 Kinetic model and material balances

Besides chemical kinetics, physical phenomenon related to the diffusion of several chemical reactive species is important in free-radical polymerization reactions. In fact, at high monomer conversions, almost all elementary reactions might become diffusion-controlled. Reactions which are influenced by diffusion phenomenon include live macroradicals termination [6], propagation of a growing chain, and chemical initiation reactions. Diffusion-controlled termination, propagation, and initiation reactions have been related to the gel, glass, and cage effects. During the last 35 years, several models have been published, [7] they deal with the mathematical description of diffusion-controlled kinetic rate constants in free-radical polymerization. The proposed mathematical model was based on the classical kinetic mechanism for free-radical solution copolymerization reactions, where the propagation and termination steps are extended to allow reactions between different types of monomer and living macro-radicals. The reaction mechanism is presented in appendix A. For the purpose of this study, the gel effect parameters were taken from Vallecillo-Gomez et al. [3].

Assuming that the copolymerization occurs in a CSTR without volume change in the reacting mixture, the mol balances can be written for the monomer conversion, initiator, monomers concentration and the zeroth moment of growing radical distributions. Appendix B contains the material balances. This mathematical model features a wide variation in the numerical values of the system states; they span a number of magnitude orders. To improve the numerical robustness of the model, and to reduce potential difficulties related to the numerical integration and optimization, the model was properly scaled.

2.3 Multiobjective optimization problem

In the present work, we formulate a MOOP using conflicting performance objectives in copolymerization system, such as to minimize molecular weight distribution, f_{Mw} , and to maximize monomer conversion, f_X , as follows:

$$\min_u f_{Mw} = \int_0^t (Mw^d - Mw)^2 dt, \text{ and } \max_u \int_0^t X dt \quad (1)$$

where Mw^d stands for the desired value of molecular weight. The MOOP is subject to a set of nonlinear ordinary differential equations (see Appendix B) for the states of the system and it can be represented in a vector form as $dy/dt = \mathbf{F}(\mathbf{y}, \mathbf{u})$, $\mathbf{y}(0) = \mathbf{y}_0$, where the state vector includes monomer conversion, initiator, primary initiator radical, monomers concentration and the leading moments of the Mw , $\mathbf{y}(t) = [X(t), I(t), R(t), M1(t), M2(t), \lambda_0(t), \zeta_0(t)]$ and two monomer feed rates were used as manipulated variables, $\mathbf{u} = [M_{1f}(t), M_{2f}(t)]$. Tsoukas et al. [13] found that the monomer addition is a more effective manipulated variable for composition distribution narrowing than temperature. Any vector \mathbf{y} satisfying the constraint equations is termed a feasible solution, the control or path constraints insure that a non-manipulated variable is outside of a feasible region due to a very high or low flow rate.

In this formulation our aim is to compute the two monomers feed rates as time function in order to drive the molecular weight to its desired value, and simultaneously maximize total monomer conversion in a short period of time. Then we use Weighted Sum method (WS) [8] and the Normal Boundary Intersection technique (NBI) [9] for generating the Pareto frontier, in which one of the solutions should be an "ideal" solution, also known as compromise solution. In the weighting method, the weighted sum of the objective function is optimized. The problem is stated as follows: $\min (w_1 \times f_{Mw} + w_2 \times (-f_X))$, through the weight variations w_i different efficient solutions were obtained. The NBI method provides means for obtaining an even distribution of Pareto optimal points for a consistent variation in the user-supplied parameter vector \mathbf{w} , even with a nonconvex Pareto optimal set. The approach is formulated as follows:

$$\min_{z \in Z, \mu} \mu \quad \text{subject to} \quad \boldsymbol{\psi} \mathbf{w} + \mu \mathbf{n} = \mathbf{F}(z) - \mathbf{F}^0 \quad (2)$$

where $\boldsymbol{\psi}$ is a $m \times m$ pay-off matrix in which the i th column contains the vector $\mathbf{F}(z_i^*) - \mathbf{F}^0$, and $\mathbf{F}(z_i^*)$ is the vector of the objective functions evaluated at the minimum of the i th objective function. The diagonal elements of $\boldsymbol{\psi}$ are zeros, \mathbf{w} is a vector of scalars so that $\sum w_i = 1$ and $\mathbf{w} \geq \mathbf{0}$, $\mathbf{n} = -\boldsymbol{\psi} \mathbf{e}$, where $\mathbf{e} \in R^k$ is a column vector of ones in the criterion space, \mathbf{n} is called a quasi-normal vector. Since each component of $\boldsymbol{\psi}$ is positive, the negative sign ensures that \mathbf{n} points out towards the origin of the criterion space, \mathbf{n} gives the property to the NBI method that for each \mathbf{w} , a solution point is independent of the way the objective functions are scaled. As \mathbf{w} is systematically modified, the solution of (1) yields an even distribution of Pareto optimal points representing the complete Pareto set. Then, using the simultaneous approach [10] for solving the dynamic optimization problem and its constraints, these were converted into a nonlinear

programming (NLP) problem by approximating the states \mathbf{y} and control \mathbf{u} variables by the application of the method of orthogonal collocation on finite elements for handling the time coordinate.

3. Results

The rate constants and parameters required for describing the gel effect are given in [3], and are not being repeated here for the sake of brevity. Similarly, the values of the different parameters to integrate the model equations are also extensively reported in [1-4]. Using the proposed MOOP algorithm described in the above sections, 40 Pareto points are plotted in Figure 2(a) within the normalized bi-objective space. A compromise solution was obtained by determining the Pareto solution which is closest to the utopia point according to the approach suggested in [8]. As can be seen from the results displayed in Figure 2(a) acceptable polymer conversion and molecular weight distribution values were obtained by setting a trade-off between the addressed conflicting objectives. This compromise solution has dynamic optimal responses for the dimensionless feed rates optimal profiles, dimensionless monomers concentration and molecular weight, as illustrated in Figures 2(b) to 2(d), whereas Figures 2(e) to 2(g) displayed the dynamic optimal responses when WS technique is applied. These operating conditions are termed as WS operating policies. Table 1 lists the dimensionless values of the objective functions, f_{Mw} and f_x , and the necessary time to reach Mw^d . The numerical results for the addressed cases were obtained by using a 2 GB RAM, Intel Corei5 and 2.67 GHz PC. Table 1 summarizes the parameters used for the two addressed cases. The NLP problem was solved using the CONOPT NLP solver embedded in the GAMS algebraic modeling system [11]. The discretization scheme required 15 finite elements with three internal collocation points for the time coordinate.

4. Discussion

The most informative format to present the results of copolymerization for bi-objective optimization problem is the Pareto set, as depicted in Figure 2(a). It easily permits to determine the trade-offs among performance objectives produced by different control schemes. Due to the characteristics of the Pareto frontier, it is possible to find an alternative trajectory of the feed rates close to utopia point, i.e. it is possible to move from a specific point of the Pareto set improving f_x objective with a little reduction of f_{Mw} . For certain start-up policies, it might not be possible to reach the desired steady state, leading to obtain a multiple steady state system.

In Figures 2(b) and 2(c) the stair lines stand for the feed monomer rates optimal profile and these describe the dynamic optimal operating policies leading to obtain the Mw^d and polymer conversion desired, when NBI and WS techniques are respectively applied. In this case, from Figures 2(d), 2(g) and the second column of Table 1, the result shows 11% reduction of the required time to reach the compromise solution. These Figures depicts further reduction in the polymerization time, which can be achieved by using larger monomer fractions, M_{f2}/M_{f1} , throughout the time. In fact, the first case (NBI method) has achieved its target value about 0.6315 dimensionless time, whereas 0.7105 are required using the WS technique. Because of the

higher reactivity ratios, larger monomer conversion emerges as Soane and Sharma have described in [12]. Moreover, the slope of the classical s-shaped gel effect curve changes rather quickly helping to explain the reduction in polymerization. This saving in polymerization time translates into a reduction of heating/cooling utilities resulting in increased process profit.

In Table 1, the obtained compromise optimal solution for the two-objective-function problem from the NBI technique is not equal to the one obtained from WS method in the single objective function problem. Generally, the relative value of the weights reflects the relative importance of the objectives; however the misunderstanding of the theoretical and practical meaning of the weights could lead to the process of intuitively selecting non-arbitrary weights by inefficient task. Although these results indicate an acceptable performance of the proposed open loop control strategy, several issues need to be addressed before any industrial-scaling could take place. The experimental validation of the nonlinear reactor model is essential even in a pilot plant. The kinetic parameters used in this reactor model were obtained from the literature [1-4]. These parameters should be fine-tuned using results of experiments on a pilot reactor. In this case, the accurate measurements of the output variables should be continuously available for feedback control. This can be done easily for the reactor temperature but not for the remaining outputs. Periodic laboratory analysis of solution polymer concentration, polymer composition, and molecular weight are usually available, but a significant sampling dead time is introduced. For control purposes, the required measurements can be obtained either by improved online instrumentation such as an online viscometer or by using a state estimator to infer the polymer properties between the measurements. The estimator can be implemented in the form of a modified Kalman filter as shown for example in [14].

Table 1. Dimensionless values for optimal solution

<i>Method</i>	<i>Time to reach M_w^d</i>	f_{M_w}	f_x
NBI	0.6315	0.2348	0.3494
Weighted Sum	0.7105	0.5532	0.4365

Conclusions

The proposed multiobjective optimization formulation permits to obtain a flexible implementation of the process operation limits, like monomer rates constraints as well as different objective functions, which increase the desired polymerization conditions. The dynamic optimal operation of the monomers feed rates demanded less polymerization processing time when using NBI technique. The optimization results imply an economical process profit due to the quantity of auxiliary services that could be required.

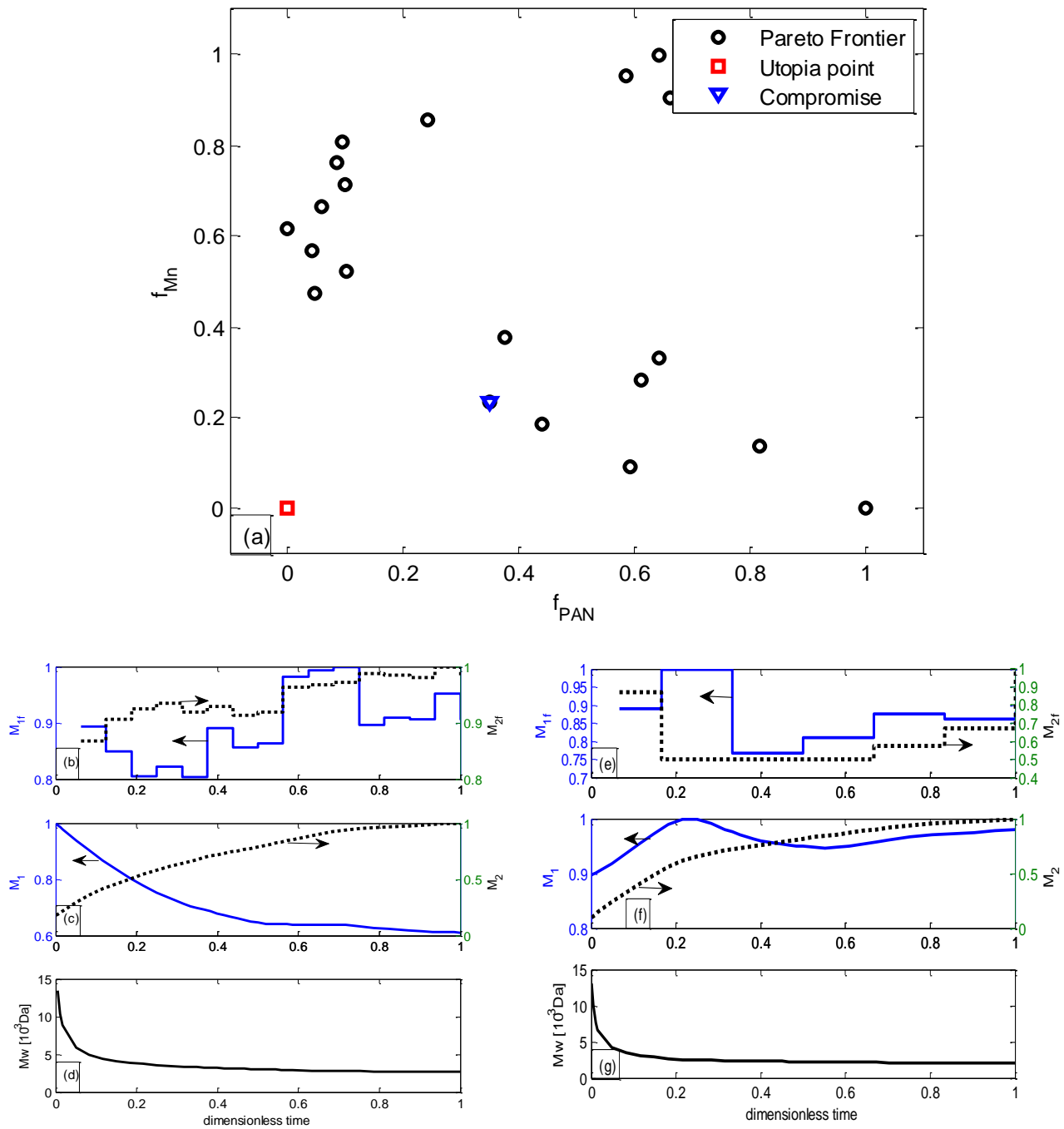
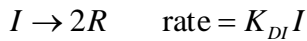


Figure 2. Plot of (a) Pareto optimal set, utopia and compromise solutions when $M_w^d = 2.5 \times 10^3$ Da, and dynamic optimal responses for compromise solution for (b) dimensionless feed rates profiles, (c) dimensionless monomers concentration and (d) molecular weight when NBI technique is used, while from (e) to (g) are dynamic optimal responses when WS method is applied.

Appendix A Copolymerization Reaction Mechanism and Kinetic Equations

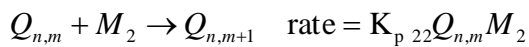
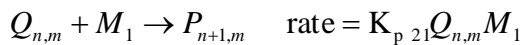
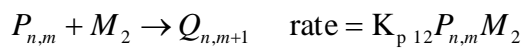
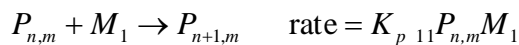
The free radical copolymerization reaction mechanism adopted here consists only of standard initiation, propagation, and termination steps. Chain-transfer reactions are neglected for convenience but can be incorporated for systems with known chain-transfer processes. The detailed mechanism is written as follows:

Initiation



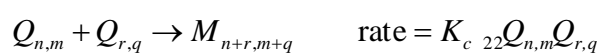
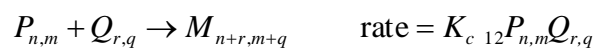
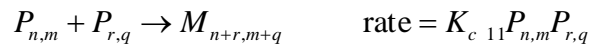
where I is the initiator, R is the primary initiator radical, M_i is the monomer.

Propagation

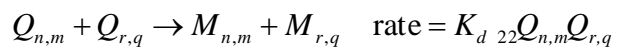
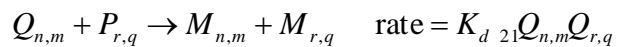
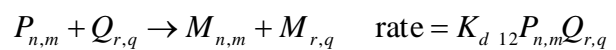


where $P_{n,m}$ is a living polymer radical, with n units of M_1 and m units of M_2 and terminal group M_1 , while $Q_{n,m}$ is a polymer living radical, with n units of M_1 and m units of M_2 and terminal group m_2 .

Termination by combination



Termination by disproportionation



where $M_{i,j}$ are the dead polymer with i units of monomer M_1 and j units of monomer M_2 and the K 's are relevant rate constants for initiation, propagation and termination steps.

Appendix B Mass Balances Equations

Assuming that the reactive mixture occupies a constant volume, the following equations can be written for the monomer conversion (X), initiator (I), primary initiator radical (R), monomers (M_1 , M_2) concentration and the both zeroth moment of growing radical distribution (λ_0, ζ_0) with terminal group M_1 and M_2 , respectively.

$$\frac{dX}{dt} = \frac{(1 + \varepsilon X)}{M_0} \left[M_1 (K_{p11}\lambda_0 + K_{p21}\zeta_0) + M_2 (K_{p12}\lambda_0 + K_{p22}\zeta_0) + \varepsilon_1 K_{p11}M_1R + \varepsilon_2 K_{p22}M_2R \right]$$

$$\frac{dI}{dt} = \frac{Q(I_0 - I)}{V} - K_{DI}I - \frac{\varepsilon I}{M_0} K$$

$$K = M_1(K_{p_{11}}\lambda_0 + K_{p_{21}}\zeta_0) + M_2(K_{p_{12}}\lambda_0 + K_{p_{22}}\zeta_0) + \varepsilon_1 K_{p_{11}} M_1 R + \varepsilon_2 K_{p_{22}} M_2 R$$

$$\frac{dR}{dt} = \frac{Q(R_0 - R)}{V} + 2fK_{D1}I - R(\varepsilon_1 K_{p_{11}} M_1 + \varepsilon_2 K_{p_{22}} M_2)$$

$$\frac{dM_1}{dt} = \frac{Q(M_{10} - M_1)}{V} - M_1(K_{p_{11}}\lambda_0 + K_{p_{21}}\zeta_0) - \frac{\varepsilon M_1}{M_0} K - \varepsilon_1 K_{p_{11}} M_1 R$$

$$\frac{dM_2}{dt} = \frac{Q(M_{20} - M_2)}{V} - M_2(K_{p_{12}}\lambda_0 + K_{p_{22}}\zeta_0) - \frac{\varepsilon M_2}{M_0} K - \varepsilon_2 K_{p_{22}} M_2 R$$

$$\begin{aligned} \frac{d\lambda_0}{dt} = \frac{Q(\lambda_{0,0} - \lambda_0)}{V} - \frac{\varepsilon \lambda_0}{M_0} K - \lambda_0 [(K_{c_{11}} + K_{d_{11}})\lambda_0 + (K_{c_{12}} + K_{d_{12}})\zeta_0] - K_{p_{12}} M_2 \lambda_0 + \\ K_{p_{21}} M_1 \zeta_0 + \varepsilon_1 K_{p_{11}} M_1 R \end{aligned}$$

$$\begin{aligned} \frac{d\zeta_0}{dt} = \frac{Q(\zeta_{0,0} - \zeta_0)}{V} - \frac{\varepsilon \zeta_0}{M_0} K - \zeta_0 [(K_{c_{12}} + K_{d_{12}})\lambda_0 + (K_{c_{22}} + K_{d_{22}})\zeta_0] + K_{p_{12}} M_2 \lambda_0 - \\ K_{p_{21}} M_1 \zeta_0 + \varepsilon_2 K_{p_{22}} M_2 R \end{aligned}$$

$$M_w = 554.7x_1^{4.109} + 546.5x_2^{3.671},$$

$$x_i = \frac{M_i}{M_1 + M_2 + S}, \quad i = 1, 2$$

Where M_w is molecular weight, x_1 , x_2 are monomers fraction of AN and VA, respectively; ε is the volume expansion factor and is equal to $(\rho_m - \rho_p) / \rho_p$, and ρ_m , and ρ_p are the average monomer mixture and copolymer density, respectively.

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