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# Novel Sparse-Matrix Representation for Free-Radical Polymerization Simulations

Yadunandan L Dar,<sup>1\*</sup> Vijay R. Tirumala,<sup>2,3</sup> Gerard T. Caneba,<sup>4\*</sup> and Derrick C.  
Mancini<sup>5</sup>

Department of Chemical Engineering

Michigan Technological University

1400 Townsend Drive, Houghton, MI 49931

Fax: 908-487-3213

and

Experimental Facilities Division

Argonne National Laboratories

9700 S. Cass Avenue, Argonne, IL 60439

Fax: 630-252-9303

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<sup>1</sup> Current address: Corporate Research, National Starch and Chemical Company, 10 Finderne Avenue, Bridgewater, NJ 08807; fax: 908-685-7400; email: yadunandan.dar@nstarch.com

<sup>2</sup> Experimental Facilities Division, Argonne National Laboratories, 9700 S. Cass Av., Argonne, IL 60439; email: vijay@aps.anl.gov

<sup>3</sup> Department of Chemical Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931; email: vrtiruma@mtu.edu

<sup>4</sup> Department of Chemical Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931; email: Caneba@mtu.edu

<sup>5</sup> Experimental Facilities Division, Argonne National Laboratories, 9700 S. Cass Av., Argonne, IL 60439; email: mancini@aps.anl.gov

## Summary

The mathematical modeling and simulation of free radical polymerization can provide significant insight into the process and resulting products. Modeling free radical polymerization kinetics requires the solution of mass (mole) balance equations for all species in the system with appropriate models for the reaction rates. The number of equations involved can be very large for high molecular weight polymers. This is the reason why methods based on averaging techniques like the methods of moments have been utilized for these systems. These methods greatly reduce the number of equations and hence the computational complexity of the models. However, these methods also result in a loss of detail, especially related to complexities in the molecular weight distributions of living and terminated polymer chains. This communication describes a novel method that reduces the large number of equations in such a model to a very small number of vector equations without any loss in information. This method is amenable to solution by relatively simple computational approaches, but would be best solved on a processor optimized for vector processing. Further, this representation can lend itself to leveraging the sparseness of the vectors used in the models to further reduce computational complexity. The model has been simulated for the bulk polymerization of methyl methacrylate and the results agree well with experimental data and simulation results from the literature for low molecular weights. This system would be uniquely useful in deriving detailed kinetic information for complex polymerization systems e.g. controlled free radical polymerization approaches.

## 1. Introduction

Free radical polymerization (FRP) reactions exhibit a range of complex kinetic events. The conversion of monomer to polymer significantly changes the density and viscosity of the reaction mixture, which affect transport properties and reaction kinetics. These changes are strongly dependent on the polymer concentration as well as polymer chain length and chain length distribution.

Several researchers<sup>[1]</sup> have tried to model FRP and its associated thermodynamic and kinetic phenomena by trying to account for such changes explicitly. They did so by considering polymer species of different chain lengths to be individual reactive species and modeled the kinetics of polymerization by solving the mass balance equations for all the species.<sup>[2]</sup> This can lead to thousands, even millions, of equations in complex polymerizations, making averaging approaches necessary for simulation procedures to be computationally viable.

This problem has been partly addressed by the *method of moments* (MOM) approach, which was computationally less intensive. The approach transforms the mass balance equations for all polymeric species to equations modeling moments of the molecular weight distribution (typically the zeroth, first and second moments).<sup>[3]</sup> The solution of these equations can accurately simulate well-behaved and non-complex polymerization reactions with certain limitations. These limitations have prevented the application of this approach in modeling complex polymerization processes. For example, MOM works

best for polymerizations with unimodal molecular weight distributions and cannot accurately describe shoulders or multiple peaks in molecular weight distributions usually associated with many FRP systems. In addition, it has been observed that the reaction rate coefficients can change by several orders of magnitude as the average chain length changes during the reaction, and could be very different for different chain lengths even at the same average polymer concentration<sup>[1]</sup>. The actual dependence of rate coefficients on system parameters cannot be modeled explicitly using the MOM approach. This can result in the failure of this approach to precisely model even relatively simple real-world systems.<sup>[4]</sup>

Averaging procedures have been suggested<sup>[5]</sup> to overcome this limitation but the problem cannot be solved unless the chain length dependence is factored explicitly for individual species. The use of averaging approaches results in a loss of detail in the simulation of systems with multimodal or broad molecular weight distributions, often seen in many industrial products. Several researchers have used averaging techniques together with the MOM approach. Teymour et al<sup>[6, 7]</sup> developed the so-called numerical fractionation (NF) techniques to overcome the limitations of the MOM approach and applied it to gel-forming systems. Butte et al modified the method developed by Kumar and Ramakrishna (KR method)<sup>[8]</sup> to predict chain length distribution in bulk<sup>[9]</sup> and emulsion<sup>[10]</sup> polymerization systems. Both the methods use the MOM on small partitions of the chain length distributions to overcome the problems associated with the approach. Though these methods have been successful at providing detailed chain length distribution information, they cannot accurately describe the chain length distribution unless the

population balance equations for each individual species in the system are solved explicitly.<sup>[7]</sup>

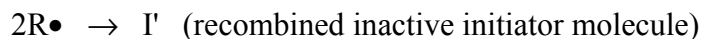
The approach described in this communication is directed towards such explicit consideration of the chain length effects on kinetic parameters, while facilitating the application of suitable computation techniques that reduce the time and efforts needed for the simulation. This approach is based on a sparse matrix<sup>[11]</sup> representation of the polymerization kinetics. A sparse matrix is one that has a large number of zero elements (>> 50 %). Use of sparse-matrix-specific solution techniques can greatly simplify the storage and CPU requirements for solving large number of equations in such a model. The first step in the utilization of these techniques is the development of an efficient sparse matrix representation of the mass balance equations. This representation can then be subjected to sparse matrix manipulation techniques like partitioning and tearing to reduce solution effort and time.<sup>[12, 13]</sup> These techniques use concepts from graph theory<sup>[14]</sup> to model information flows in large systems of equations.<sup>[15, 16, 17]</sup> The approach described in this communication does not employ, but is amenable, to such solution methods and could serve as a powerful tool in the modeling, simulation, and understanding of chain polymerization processes.

## **2. Free Radical Polymerization Kinetics**

Free radical polymerization is a type of chain polymerization, wherein monomer repeat units add on to a propagating radical chain. Steps in this process include chain initiation,

typically initiated by a radical initiator activated either by temperature or radiation; chain propagation (addition of monomer units); chain transfer to monomer, solvent, initiator, polymer, or chain transfer agent; and chain termination by combination or disproportionation. The details for each step are well known and have been widely discussed in the literature.<sup>[18]</sup> Recapping briefly, a typical free radical polymerization reaction comprises of the following steps:

## 2.1 Initiation



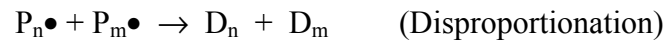
where I is the initiator molecule, R• is the primary initiator free radical, M is a monomer molecule, and P<sub>1</sub>• is the polymer radical of chain length one. It is typical to not include the initiator fragment when describing the polymer chain length. The gas is typically nitrogen or oxygen, evolved during an elimination reaction leading to radical generation from azo compounds or peroxides.

## 2.2 Propagation



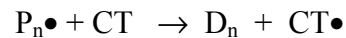
where  $P_n\bullet$  is a polymer radical of chain length  $n$  and  $P_{n+1}\bullet$  is a radical of chain length  $n+1$ .

### 2.3 Termination



where  $D_m$ ,  $D_n$ , and  $D_{n+m}$  are polymer chains (not radicals) of chain length  $m$ ,  $n$ , and  $m+n$  respectively.

### 2.4 Chain Transfer



where  $CT$  is the chain transfer agent, which could be a monomer molecule, a polymer chain, an impurity, or a chain transfer agent added to increase transfer rates.

Modeling and simulation approaches for the reaction thermodynamics and kinetics of FRP have also been extensively reviewed.<sup>[1]</sup> The approach used to model the polymerization kinetics is described briefly in the next section.

### 3. Modeling Free Radical Kinetics

Kinetics of free radical polymerization are conventionally modeled as a set of mass (or mole) balance equations. These ordinary differential equations (ODEs) can be solved individually for each polymer species or converted into equations based on the moments of the polymer chain length distribution. Models for kinetic rate constants, sometimes called “gel-effect” models, are used to determine the rate coefficients as a function of polymer concentration, chain length, and other reaction parameters. During polymerization, the system density changes with an increase in conversion as the monomer and polymer densities are typically different.

Chain transfer has been neglected in the following analysis, but can be added as an additional term in the mass balance for each polymer species if it is important in the reaction schema, as discussed by Penlidis et al.<sup>[19]</sup> The following equations represent the kinetics of this system.<sup>[20]</sup>

$$\frac{1}{V} \frac{d([I]V)}{dt} = -k_d [I] \quad (1)$$

$$\frac{1}{V} \frac{d([M]V)}{dt} = -k_p [M]P \quad (2)$$

$$\frac{1}{V} \frac{d([R]V)}{dt} = 2fk_d [I] - k_t [R][M] \quad (3)$$

$$\frac{1}{V} \frac{d([P_1])}{dt} = k_i [R][M] - k_p [M]P_1 - k_t [P_1]P \quad (4)$$



$$\frac{1}{V} \frac{d([P_n]V)}{dt} = k_p [M] ([P_{n-1}] - [P_n]) - k_t ([P_n]) P \quad (5)$$

$$\frac{1}{V} \frac{d([D_n]V)}{dt} = k_{td} [P_n] P + \frac{1}{2} k_{tc} \sum_{m=1}^{n-1} [P_m] [P_n] \quad (6)$$

$$x = \frac{[M]_0 V_0 - [M]V}{[M]_0 V_0} \quad (7)$$

$$V = \frac{V_0}{(1 + \beta)} (1 - \varepsilon x + \beta) \quad (8)$$

$$\varepsilon = \frac{(\rho_p - \rho_m)}{\rho_p} \quad (9)$$

$$\beta = \frac{f_s}{(1 - f_s)} \quad (10)$$

$$f_s = \frac{V_{solvent}}{V_0} \quad (11)$$

where,

- $[I]$  - Initiator concentration (mol.L<sup>-1</sup>)
- $[M]$  - Monomer concentration (mol.L<sup>-1</sup>)
- $[R]$  - Primary initiation radical concentration (mol.L<sup>-1</sup>)
- $[P_1]$  - Primary polymer radical concentration (mol.L<sup>-1</sup>)
- $[P_n]$  - Concentration of polymer radical of length n (mol.L<sup>-1</sup>)
- $[D_n]$  - Concentration of dead polymer molecule of length n (mol.L<sup>-1</sup>)
- $[M_0]$  - Initial monomer concentration (mol.L<sup>-1</sup>)

$x$	-	Conversion
$V_0$	-	Initial volume (L)
$V$	-	Volume (L)
$V_{solvent}$	-	Volume of solvent (L)
$\varepsilon$	-	Relative change in density as defined above
$\beta$	-	Relative fraction of solvent defined as $f_s/(1-f_s)$
$f_s$	-	Fraction of solvent volume
$\rho_p$	-	Density of polymer ( $\text{g.cm}^{-3}$ )
$\rho_m$	-	Density of monomer ( $\text{g.cm}^{-3}$ )
$k_p$	-	Propagation rate constant ( $\text{L.mol}^{-1}.\text{sec}^{-1}$ )
$k_{tc}$	-	Rate constant for termination by combination ( $\text{L.mol}^{-1}.\text{sec}^{-1}$ )
$k_{td}$	-	Rate constant for termination by disproportionation ( $\text{L.mol}^{-1}.\text{sec}^{-1}$ )
$k_t$	-	Rate constant for termination (combination and disproportionation) ( $\text{L.mol}^{-1}.\text{sec}^{-1}$ )
$k_d$	-	Rate constant for initiation ( $\text{sec}^{-1}$ )

#### 4. A Novel Sparse Matrix Representation

Equation (1)-(11) can be converted to a set of four mass-balance vector ODEs (Equation (12)-(15)) after some manipulation. The assembly of matrices used in these equations can then be implemented on a computer using relatively straightforward matrix manipulations.<sup>[21]</sup> Derived originally from the material balance equations for all the species in a polymerization process, these equations completely address the kinetics of

free radical polymerization. As explained earlier, chain transfer and other side reactions can also be added as separate terms to Equation (12)-(15) when applicable. All one-dimensional matrices are denoted by a single bar (-) over their name whereas, all two-dimensional matrices are denoted by double bars (=) over the variable name, as typically used in vector notation. All symbols used have been described earlier, except  $\lambda_0$ , which is the sum of the concentrations of all polymer radicals of all chain lengths.

$$\frac{d[I]}{dt} = \left\{ -k_d + \frac{\varepsilon k_p(1-x)\lambda_0}{(1-\varepsilon x + \beta)} \right\} [I] \quad (12)$$

$$\frac{dx}{dt} = k_p(1-x)\lambda_0 \quad (13)$$

$$\frac{d[\bar{P}]}{dt} = \bar{\bar{A}} \cdot [\bar{P}^*] - (k_{td} + k_{tc}) \bar{P} \cdot \bar{I}_{n,1}^T \cdot [\bar{P}] + \frac{\varepsilon k_p(1-x)\lambda_0}{(1-\varepsilon x + \beta)} [\bar{P}] \quad (14)$$

$$\frac{d[\bar{D}]}{dt} = k_{td} \bar{Q} \cdot \bar{I}_{1,n} \cdot [\bar{P}] + k_{tc} \cdot \bar{\bar{C}} \cdot [\bar{P}] + \frac{\varepsilon k_p(1-x)\lambda_0}{(1-\varepsilon x + \beta)} [\bar{D}] \quad (15)$$

Where,

$$\bar{\bar{A}} = \begin{bmatrix} 2fk_d[I] & -k_p[M] & 0 & & & & \\ 0 & k_p[M] & -k_p[M] & 0 & & & \\ & 0 & \cdot & \cdot & \cdot & & \\ & & \cdot & \cdot & \cdot & & \\ & & 0 & k_p[M] & -k_p[M] & 0 & \\ & & & 0 & k_p[M] & -k_p[M] & \end{bmatrix}$$

$$\bar{Q} = \begin{bmatrix} P_0 \\ P_1 \\ \cdot \\ \cdot \\ P_n \\ 0 \\ \cdot \\ \cdot \\ 0 \end{bmatrix}$$

$$\bar{P} = \begin{bmatrix} P_0 \\ P_1 \\ \cdot \\ \cdot \\ P_n \end{bmatrix}$$

$$\bar{P}^* = \begin{bmatrix} 1 \\ P_0 \\ P_1 \\ \cdot \\ \cdot \\ P_{n-1} \end{bmatrix}$$

$$\bar{D} = \begin{bmatrix} D_0 \\ D_1 \\ \cdot \\ \cdot \\ D_{2n} \end{bmatrix}$$

$$\bar{I}_{1,n} = [1 \quad 1 \quad \cdot \quad \cdot \quad 1]$$

$$\bar{C} = \begin{bmatrix} P_0 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ P_1 & 0 & & & & & \cdot \\ P_2 & P_1 & 0 & & & & \cdot \\ \cdot & P_2 & 0 & & & & \cdot \\ \cdot & \cdot & P_2 & 0 & & & \cdot \\ P_n & \cdot & P_3 & 0 & & & \cdot \\ 0 & P_n & \cdot & \cdot & 0 & & \cdot \\ \cdot & 0 & P_n & \cdot & \cdot & & \cdot \\ \cdot & & 0 & \cdot & \cdot & 0 & \cdot \\ \cdot & & & 0 & \cdot & P_{n-1} & \cdot \\ \cdot & & & & 0 & P_n & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot & 0 & P_n \end{bmatrix}$$

Most of the matrices used here are one-dimensional and require minimum computing resources for both storage and processing. Bottlenecks in computation will mainly arise from handling the larger two-dimensional matrices. It can be seen that the large 2-D matrices used ( $A$  and  $C$ ) are sparse with occupancies much lower than 50 %. These equations can now be solved on a platform that facilitates vector or parallel solution techniques, along with a suitable numerical algorithm and methods for the utilization of sparse matrix techniques.

The dimensions of each matrix used are shown in Table 1 as a function of  $n$ , the chain length of the longest active radical chain in this process. Note that the maximum chain length of any molecule is twice of  $n$ , which would be created due to termination by combination.

**Table 1.** Dimensions of Matrices used in Equation (12)-(15)

<b>Matrix</b>	<b>Dimension (row x column)</b>
<i>A</i>	$(n+1) \times (n+1)$
<i>C</i>	$(2n+1) \times (n+1)$
<i>D</i>	$(2n+1) \times 1$
<i>I</i>	$1 \times n$
<i>P</i>	$(n+1) \times 1$
<i>P*</i>	$(n+1) \times 1$
<i>Q</i>	$(2n+1) \times 1$

The occupancies of matrices *A* and *C* can be calculated using Equation (16) and (17) respectively.

$$\text{Occupancy for } A = \frac{2n}{(n+1)^2} \quad (16)$$

$$\text{Occupancy for } C = \frac{n+2}{4n+2} \quad (17)$$

It can be seen that matrix *A*, being a predominantly block diagonal matrix, has very low occupancy at higher values of *n* (from 0.039 for *n*=50, to 0.0002 for *n*=10,000), whereas matrix *C* has an average occupancy of 0.25, for all *n*.

## 5. Results

The approach was validated by simulating the bulk polymerization of methyl methacrylate<sup>[16]</sup> based on the kinetic parameters used by Chiu et al.<sup>[22]</sup> Simulations were run in a MATLAB (Mathworks, Inc) environment on a Sun Blade 1000 processor, with a 6 GB system memory. The physical parameters used for the simulation are shown in Table 2.

**Table 2.** Parameters used for the simulation of methyl methacrylate bulk polymerization (Chiu et al<sup>[22]</sup>)

Parameter	Description	Value
$\rho_{MMA}$	Density of methyl methacrylate (MMA)	$0.973-1.164 \times 10^{-3}(T-273.16) \text{ g.cm}^{-3}$
$\rho_{PMMA}$	Density of poly(MMA)	$1.2 \text{ g.cm}^{-3}$
$MW_{MMA}$	Molecular weight of MMA	$88 \text{ gm.mol}^{-1}$
$k_{p0}$	Intrinsic rate constant for chain propagation	$2.95 \times 10^7 e^{(-4353/RT)} \text{ L.mol}^{-1}.\text{sec}^{-1}$
$k_{t0}$	Intrinsic rate constant for chain termination	$5.88 \times 10^9 e^{(-701/RT)} \text{ L.mol}^{-1}.\text{sec}^{-1}$
$k_d$	Rate constant for initiator decomposition	$6.32 \times 10^{16} e^{(-15430/T)} \text{ sec}^{-1}$
$F$	Fractional initiator efficiency	0.58

The simulation results for conversion vs. time and  $k_p/k_t$  calculations used for the model are shown in Figure 1. The simulation results have been compared to experimental data generated by Marten and Hamielec.<sup>[23]</sup> The reaction rate coefficients were modeled using the CCS model developed by Chiu et al.<sup>[22]</sup> The parameters used in modeling the rate

coefficients have been summarized in Table 2 for reference. The dependence of kinetic rate coefficients on these parameters is described in Equation (18) and (19). The derivation of the equations as well as details about the parameters used and their significance has been discussed by Chiu et al in detail. Each rate coefficient is modeled as a function of the intrinsic reaction rate coefficients and parameters that model the impact of changes in concentration and diffusivities.

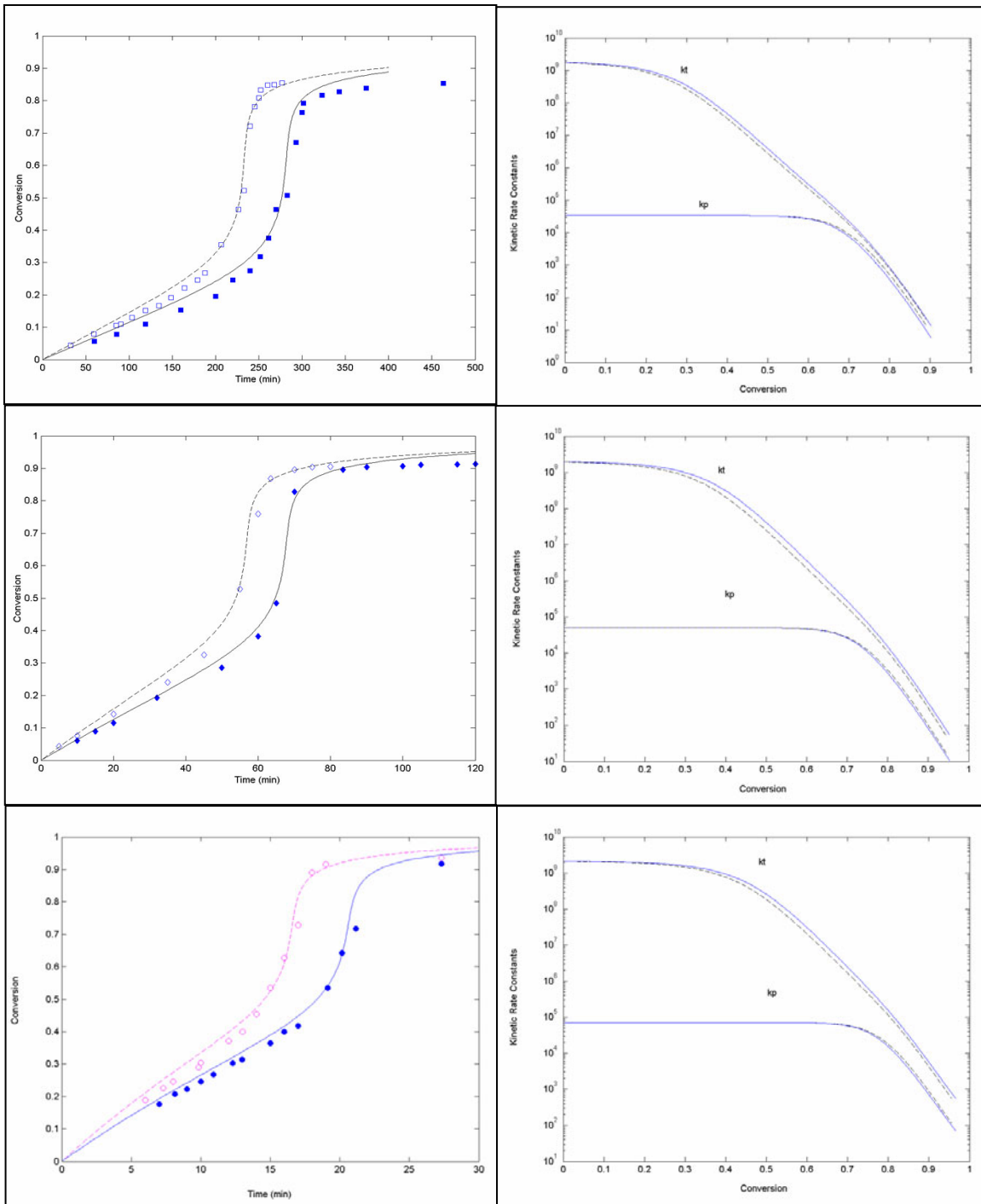
$$k_t = \frac{k_{t0}}{[1 + k_{t0} \theta_t \lambda_0 \exp(-\frac{2.3\phi_m}{A+B})]} \quad (18)$$

$$k_p = \frac{k_{p0}}{[1 + k_{p0} \theta_p \lambda_0 \exp(-\frac{2.3\phi_m}{A+B})]} \quad (19)$$

**Table 3:** Parameters for Calculation of Rate Coefficients (From Chiu et al<sup>[22]</sup>)

Polymerization Temperature, °C	$[I_0]$ mol.L <sup>-1</sup>	$\theta_t$ , min	$\theta_p$ , min	A	B
50	0.0258	1.5e3	3.5e3	0.134	0.03
50	0.01548	2.33e3	3.5e3	0.134	0.03
70	0.0258	49	2.5e2	0.152	0.03
70	0.01548	83	2.5e2	0.152	0.03
90	0.0258	3.8	30	0.163	0.03
90	0.01548	6.3	30	0.163	0.03

The CCS model was chosen to model the rate coefficients as it has been used by the creators to adequately predict the polymerization system simulated here. The model and others based on it were also highly successful in simulating a variety of FRP systems;



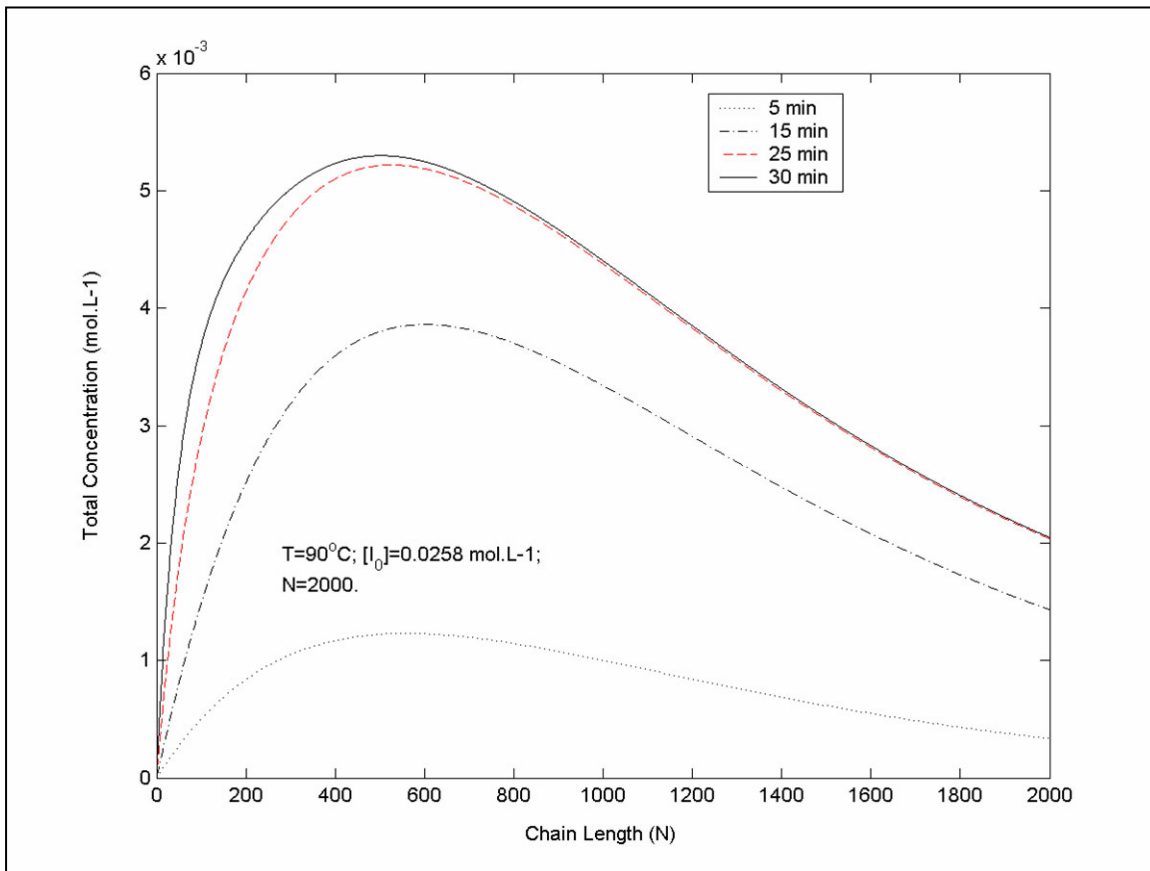
**Figure 1:** Conversion (left) and kinetic rate coefficient (right) histories of MMA bulk polymerization at 50°C (top panel), 70°C (middle panel), and 90°C (bottom panel), at two initiator loadings:  $[I_0] = 0.0258$  mol/L (hollow markers) and 0.01548 mol/L (solid markers). Markers are experimental values<sup>23</sup> and lines are simulation results.

though some have criticized the boundary conditions used.<sup>[24]</sup> Other models have been



discussed as more capable and applicable to more generic systems.<sup>[24, 25]</sup> However, the CCS model was selected to validate this approach as it has been shown to work well for the system being simulated and it was relatively simple to integrate into the model. The utilization of more complex models can be incorporated at a later stage to provide more information on system specific kinetics as needed.

It can be seen that the conversion-time data correlates well with the experimental data, even during the onset of the gel effect. The rate coefficients change as the volume fraction of polymer increases in the reaction. The results also agree well with the simulation results presented by Chiu et al.



**Figure 2:** Population distributions at various times of MMA polymerization at 90°C, and at  $[I_0] = 0.0258 \text{ mol/L}$ .

The chain length distributions for all polymeric species in the system (newly generated radicals as well as terminated polymer) for reaction time of 5, 15, 25, and 30 minutes are shown in Figure 2. Note that the average chain lengths are much lower than the experimental system since the distributions are all clipped at  $N_{max}$ .

The unique feature of this approach is the inherent utilization of sparse matrices in this representation. The incorporation of mathematical techniques that further exploit the sparseness of the larger two-dimensional matrices used in this approach would greatly reduce the computational resources needed for the simulation. The ongoing and future work will be targeted towards taking advantage of some of these features. This work includes developing a more efficient implementation, using the appropriate level of computer resources, as well the incorporation of sparse matrix manipulation techniques for simulation using large values ( $> 10,000$ ) of  $N_{max}$ .

## **6. Conclusions**

A novel, sparse-matrix based representation of FRP kinetics was developed and implemented in a MATLAB environment on available computational resources. The MATLAB environment was chosen not for efficient computation but for its ease of implementation and analysis. The methodology was validated by comparing the simulation results from this approach to experimental data as well as other simulation results. The results correlate very well with conversion vs. time data from both the experimental and simulation results (using another modeling approach) for the chosen

test system. The comparison of the molecular weight data was only possible at lower chain lengths due to computational limitations. Ongoing and future efforts will include the optimization of the computational implementation to address this shortcoming. This approach provides detailed kinetic information on the population distribution of the system at any given time, including computed distributions of living and termination polymer chains. This level of detail could be very useful in the simulation of complex free radical polymerization approaches.

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