

Calculation of Molecular Weight Distribution from Molecular Weight Moments in Free Radical Polymerization

Timothy J. Crowley and Kyu Yong Choi*

Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742

A novel method is presented for the calculation of weight chain length distribution in free radical polymerization of vinyl monomers. In the proposed method, polymerization kinetic equations and molecular weight moment equations are used in conjunction with a function that defines the weight fraction of polymer in a finite chain length interval. The entire range of molecular weight is divided into a finite number of intervals, and the weight fractions of polymers in these intervals are calculated. It is also possible to predict a chromatogram obtainable by gel permeation chromatography. A numerical example is presented and compared with experimental data to illustrate the usage of the proposed method.

1. Introduction

Control of polymer molecular weight distribution (MWD) is important in industrial polymerization processes because a polymer's end-use properties are strongly dependent on its MWD. Often in practice, a single molecular weight average (e.g., weight average molecular weight or number molecular weight) is controlled to yield the target polymer properties such as tensile strength, impact strength, etc. In other cases, the control of a single molecular weight average is insufficient, and it is necessary to control the polymer molecular weight distribution. In certain situations, it is often desired to control the amount of polymers in certain molecular weight ranges (Bersted and Anderson, 1990). The breadth of polymer MWD is measured by the ratio of weight average molecular weight to number average molecular weight (i.e., polydispersity). Although polydispersity is a useful and convenient measure of polymer molecular weight distribution, a polydispersity value itself does not contain enough information about a complete differential molecular weight distribution. It is possible that polymers of different chain length distribution can have the same polydispersity value but exhibit significantly different end-use properties.

If a polymerization kinetic model is available, molecular weight averages and molecular weight distribution can be calculated by numerical integration of the polymer material balances or by using the moment generating function, z -transform, continuous variable transformation, and the method of molecular weight moments (Ray, 1972 and references therein; Schork et al., 1993). Certain polymerization systems have also been modeled using statistical descriptions such as Markov chain approaches and numerical Monte Carlo methods (Storti et al., 1992; Chistov and Georgiev, 1995). The molecular weight distribution can also be calculated by integrating an instantaneous chain length distribution, which is obtained from the dead polymer mass balance equation, to a desired conversion (Xie et al., 1991). The differential molecular weight distribution can also be approximated by fitting a prespecified chain length distribution function with molecular weight averages (Herdan, 1953; Gloor, 1978). For the control of polymerization processes, it is often desirable to monitor the weight distribution on-line with reaction time.

Stochastic estimation methods such as the extended Kalman filtering technique can be used for such purposes.

The kinetic approach to MWD modeling has been applied to many free radical polymerization systems of varying complexity including vinyl chloride polymerization (Xie et al., 1991), styrene polymerization (Schuler and Suzhen, 1984), and copolymerization systems (Xie and Hamielec, 1993). Ellis et al. (1988) developed a method for calculating the MWD of a linear homopolymer using the continuous variable approximation and a finite element method. Notable in their work is the inclusion of chain length dependent termination and propagation. In their work, the theoretically infinite domain of polymer chain lengths is replaced with a finite range having an upper bound of 10^6 . The partial differential equations for dead polymer concentration were solved at discrete chain-length points, and they found that 15 finite elements with two discretization points per element provided adequate resolution of both unimodal and bimodal molecular weight distributions.

From a practical standpoint, the chosen mathematical description of a polymer's molecular weight distribution should be that which can be best correlated with the polymer's end-use properties. In the absence of such information, it may be desirable to model and control the entire MWD, and such modeling requires the choice of discrete chain lengths at which the polymer differential equations are to be solved. In previous literature, the number of discrete chain lengths is chosen to be large enough to provide good resolution of the MWD without introducing an excessively large computational burden, and the maximum chain length is chosen somewhat arbitrarily.

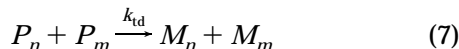
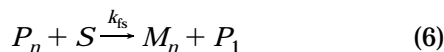
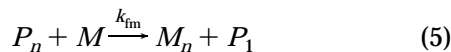
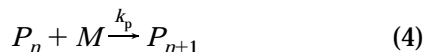
In this paper, we present a new simple computational method for calculating polymer molecular weight distribution that is an extension of the method of molecular weight moments. This method calculates the weight fraction of polymer in a specified molecular weight range rather than at a single chain length and enables the use of a consistent, quantitative criterion for selecting the maximum chain length for MWD modeling. The proposed method is tested on an experimentally measured MWD from the solution polymerization of methyl methacrylate (MMA).

2. Computational Procedure

Let us consider the following kinetic scheme for free radical polymerization of methyl methacrylate where

* To whom correspondence should be addressed.

termination is via disproportionation only



where I is the initiator, R is the primary radical, P_n is the live polymer radical with n repeating units, M_n is the dead polymer with n repeating units, and S is the solvent. For the calculation of molecular weight, the following molecular weight moments are defined for live polymers and dead polymers respectively as

$$\lambda_k^1 \equiv \sum_{n=1}^{\infty} n^k P_n \quad \text{and} \quad \lambda_k \equiv \sum_{n=2}^{\infty} n^k M_n \quad (8)$$

where λ_k^1 and λ_k denote the k th moment of live and dead polymers, respectively. The number average and weight average polymer molecular weights are defined as

$$\bar{M}_n = M_0 \frac{\lambda_1^1 + \lambda_1}{\lambda_0^1 + \lambda_0} \quad \text{and} \quad \bar{M}_w = M_0 \frac{\lambda_2^1 + \lambda_2}{\lambda_1^1 + \lambda_1} \quad (9)$$

M_0 is the molecular weight of monomer. Since the concentration of live polymers is far smaller than the concentration of dead polymers, the contribution of live polymer moments to overall polymer molecular weight is negligibly small. Thus, eq 9 is often reduced to

$$\bar{M}_n \approx M_0 \frac{\lambda_1}{\lambda_0} \quad \text{and} \quad \bar{M}_w \approx M_0 \frac{\lambda_2}{\lambda_1} \quad (10)$$

These molecular weight averages can be easily calculated by solving the dynamic molecular weight moment equations together with the kinetic equations. Experimentally, polymer molecular weight is measured most conveniently by gel permeation chromatography (GPC). The resulting chromatogram (detector signal vs retention time) represents the weight distribution of polymer because the detector (e.g., UV or RI detectors) signal is mass dependent. The columns used in GPC are calibrated on polymer standards of narrow molecular weight distribution or by the universal calibration method using Mark-Houwink constants.

The limitation of using the molecular weight moment equations is that only molecular weight averages are calculated and a complete molecular weight distribution is not obtainable. In the following, we present a new method to calculate chain length distribution directly from the kinetic equations. Let us define the following

$$f_{(m,n)} \equiv \frac{\sum_{i=m}^n iM_i}{\sum_{i=2}^{\infty} iM_i} = \frac{\text{weight of polymer with chain lengths from } m \text{ to } n}{\text{total weight of polymer}} \quad (11)$$

which represents the weight fraction of polymer with chain lengths from m to n . The contribution of live polymers to the total weight of polymer has been neglected in eq 11. During polymerization, the concentration of dead polymers changes, and hence $f_{(m,n)}$ changes with time. Using eq 11, we can derive a differential equation for $f_{(m,n)}$:

$$\begin{aligned} \frac{df_{(m,n)}}{dt} &= \frac{1}{\lambda_1} \sum_{i=m}^n i \frac{dM_i}{dt} - \frac{\sum_{i=m}^n iM_i}{\lambda_1^2} \frac{d\lambda_1}{dt} \\ &= \frac{1}{\lambda_1} \sum_{i=m}^n i \frac{dM_i}{dt} - \frac{f_{(m,n)}}{\lambda_1} \frac{d\lambda_1}{dt} \end{aligned} \quad (12)$$

By applying the quasi-steady-state assumption to live polymer radicals, one can obtain the following

$$P_i = (1 - \alpha) P \alpha^{i-1} \quad (13)$$

where P is the total concentration of polymer radicals and α is the probability of propagation defined as

$$\alpha \equiv \frac{k_p M}{k_p M + k_t P + k_{tm} M + k_{ts} S} \quad (14)$$

Equation 13 is known as the most probable distribution. If chain termination occurs by disproportionation only (e.g., methyl methacrylate polymerization), the following differential equation for λ_1 is obtained from the kinetic model equations for the polymerization system described by eqs 1-7:

$$\frac{d\lambda_1}{dt} = (2 - \alpha) k_p M P \quad (15)$$

The mass balance for dead polymer of chain length i can be derived as

$$\frac{dM_i}{dt} = \frac{1 - \alpha}{\alpha} k_p M P_i \quad (16)$$

Then, the summation term in eq 12 becomes

$$\sum_{i=m}^n i \frac{dM_i}{dt} = \frac{(1 - \alpha)}{\alpha} k_p M \sum_{i=m}^n i P_i \quad (17)$$

It is easy to show that

$$\sum_{i=m}^{\infty} iP_i = \left[\frac{m(1-\alpha) + \alpha}{(1-\alpha)^2} \right] P_m \quad (18)$$

Then

$$\sum_{i=m}^n iP_i = \left[\frac{m(1-\alpha) + \alpha}{(1-\alpha)} \right] \alpha^{m-1} P - \left[\frac{(n+1)(1-\alpha) + \alpha}{(1-\alpha)} \right] \alpha^n P \quad (19)$$

Substitution of eq 19 into eq 17 yields

$$\sum_{i=m}^n i \frac{dM_i}{dt} = \left[\frac{m(1-\alpha) + \alpha}{\alpha} \right] \alpha^{m-1} - \left[\frac{(n+1)(1-\alpha) + \alpha}{\alpha} \right] \alpha^n \Big] k_p MP \quad (20)$$

Finally, eq 12 becomes

$$\frac{df_{(m,n)}}{dt} = \left[\frac{m(1-\alpha) + \alpha}{\alpha} \right] \alpha^{m-1} - \left[\frac{(n+1)(1-\alpha) + \alpha}{\alpha} \right] \alpha^n - (2-\alpha)f_{(m,n)} \Big] \frac{k_p MP}{\lambda_1} \quad (21)$$

Equation 21 represents how the weight fraction of polymer in a certain chain length interval changes with reaction time. To calculate the polymer chain length distribution, eq 21 is then solved simultaneously with eq 15 and the kinetic modeling equations (i.e., mass balance equations for monomer, initiator, solvent). The higher order moment equations can also be solved together to compute the molecular weight averages. If number chain length distribution is also desired, a function similar to $f_{(m,n)}$ can be defined and solved.

At this point, it is necessary to assign appropriate values to m and n and to replace the infinite chain length domain with a finite range bounded by a maximum chain length which we will denote n_{\max} . For a batch polymerization reactor, this is accomplished by integrating eq 21 along with other mass balance equations up to the final desired conversion and repeating this off-line integration until the search value of n_{\max} satisfies the following criterion:

$$f_{(2, n_{\max})}|_{x=x_f} = 0.999 \quad (22)$$

The physical meaning of this criterion is that polymer produced in the chain length range from 2 to n_{\max} represents 99.9% of all polymer which will be produced during the batch polymerization. The minimum chain length of interest may be assumed to be 2 though a larger value could be used if desired. After selecting maximum and minimum chain lengths, it is necessary to divide this finite chain length interval into subintervals as an approximate description of the entire molecular weight distribution. Since the computing time required for using the proposed method is very small, one can use as many chain length intervals as desired. We have found it convenient to divide the finite chain length range using the GPC calibration curve relating chain length to elution time. This is accomplished by calculating the elution times corresponding to the maximum and minimum chain lengths. This elution time range is then divided into equal time subintervals.

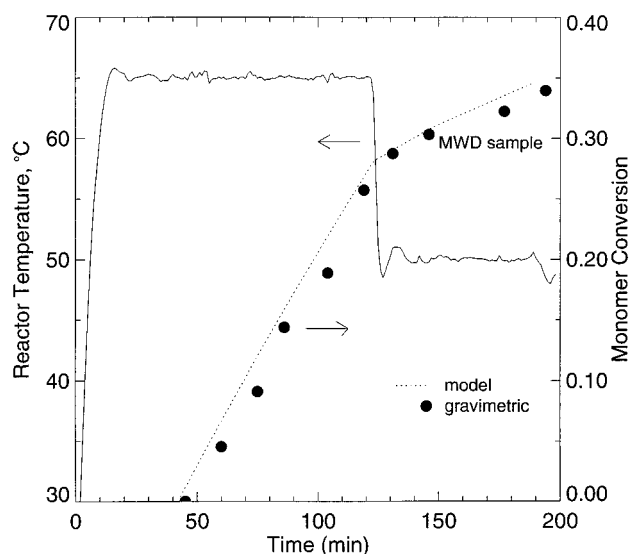


Figure 1. Reactor temperature and monomer conversion profiles; $I_0 = 0.046$ mol/L, monomer volume fraction = 0.5.

Twenty intervals were chosen for the following example in this paper. The weight fraction of polymer in a given elution subinterval is determined from the GPC chromatogram simply by calculating the area of the chromatogram in that subinterval and dividing this area by the total chromatogram area. The corresponding model prediction of polymer weight fraction in a given elution time subinterval is found by calculating the chain lengths corresponding to the elution times which bound the subinterval, substituting these chain length values for m and n in eq 21 and integrating the model.

3. Example

To illustrate the proposed computational method, a batch free radical solution polymerization of methyl methacrylate (MMA) has been carried out in a 4 L jacketed stirred tank reactor. The reactor was initially charged with 500 mL of MMA (Rohm and Haas), 500 mL of ethyl acetate (Aldrich) as solvent, and 9 g of Vazo 67 (DuPont) initiator. The monomer was used as supplied without purification. The reactor was heated to 65 °C, regulated at that temperature to 27% monomer conversion, and then decreased to 50 °C to intentionally broaden the molecular weight distribution. Figure 1 represents the experimental reactor temperature and monomer conversions measured off-line using the gravimetric method. Also shown in Figure 1 is the monomer conversion curve predicted by the kinetic model. The observed induction period is due to inhibitors in the monomer. In our model simulation, the end of the induction period was set as the initial reaction time. Molecular weight measurements were made with a Waters GPC system equipped with an RI detector and three Ultrastyrigel columns (one 10^4 Å, one 10^3 Å, and a linear column). Narrow MWD poly(methyl methacrylate) standards were used for column calibration and the resulting calibration equation is

$$\log nM_0 = 22.007 - 1.936t_e + 0.078t_e^2 - 0.0012t_e^3 \quad (23)$$

where n represents polymer chain length corresponding to an elution time, t_e , in minutes. The following kinetic parameters have been used for model calculations (units in mol, L, K, min): $k_d = 1.14 \times 10^{19} \exp(-34\,277/RT)$,

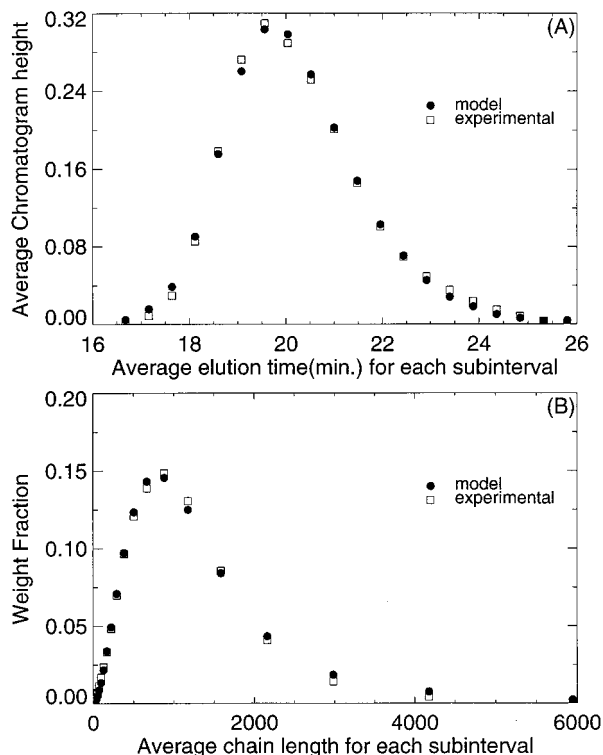


Figure 2. Calculated and experimentally measured molecular weight distributions.

$k_p = 4.2 \times 10^8 \exp(-6300/RT)$, $k_{fm} = 1.74 \times 10^{13} \times \exp(-17957/RT)$, $k_{fs} = 6.12 \times 10^{10} \exp(-15702/RT)$, $k_{td} = g_t \times 1.06 \times 10^{11} \exp(-2800/RT)$, $f_i = 0.21$ (initiator efficiency factor). The gel effect parameter (g_t) accounts for diffusion-controlled termination and is correlated with free volume (Ross and Laurence, 1976):

$$g_t = 0.10575 \exp[17.15(v_f - 0.01715(T - 273.2))] \quad \text{for } v_f \geq v_{fcr} \quad (24)$$

$$g_t = 2.3 \times 10^{-6} \exp[75v_f] \quad \text{for } v_f \leq v_{fcr} \quad (25)$$

Here, the free volume (v_f) and the critical free volume (v_{fcr}) are given by

$$v_f = 0.025 + 0.001(T - 167)\phi_m + 0.001(T - 181)\phi_s + 0.001(T - 387)\phi_m \quad (26)$$

$$v_{fcr} = 0.186 - 2.96 \times 10^{-4}(T - 273.16) \quad (T \text{ in K}) \quad (27)$$

Using eq 22, a value for n_{max} was found to be 8612. After this step, the minimum chain length was changed to 20 because column separation of molecular weights less than 2000 was poor. The GPC elution time range corresponding to this chain length range is from 16.42 to 26.0 min, and therefore, the elution time subinterval for 20 weight fractions is 0.48 min. A sample for molecular weight analysis was taken from the reactor at 146 min, corresponding to 30% monomer conversion. We break up the polymer chain length distribution into 20 intervals. This requires 21 differential equations, 20 for the weight fraction function ($f_{(m,n)}$) and one for the first moment for dead polymers (λ_1). Parts A and B of Figure 2 show respectively a graphical comparison of the experimental and model predicted GPC chromatograms and the polymer's weight chain length distribution curves. The experimental normalized chro-

matogram heights in Figure 2A are calculated by dividing the actual GPC chromatogram heights by the total chromatogram area such that the normalized chromatogram area then equals unity. The model predicted chromatogram heights can then be calculated by simply dividing the model predicted weight fractions by the elution time subinterval which in this example corresponds to 0.48 min. Notice that excellent agreement between the predicted and the experimentally measured MWDs has been obtained ($\bar{M}_w(\text{predicted}) = 96975$; $\bar{M}_w(\text{measured}) = 97582$; polydispersity(predicted) = 2.15; polydispersity(measured) = 2.15), supporting the validity of the proposed computational method.

4. Concluding Remarks

In this paper, a simple new method is presented for the calculation of weight chain length distribution using the kinetic rate equations, molecular weight moment equations, and the function that defines the weight fraction of polymer in a finite chain length interval. We name the proposed method the method of finite molecular weight moments. The proposed computational method can be viewed as an extension of the method of moments because low-order molecular weight moments are needed. It enables one to compute the weight fraction of polymer in any molecular weight range. The molecular weight averages can be computed using the chain length distribution obtained or directly solving the molecular weight moment equations that are calculated with the function $f_{(m,n)}$. It should also be pointed out that the proposed method is based on several important assumptions including quasi-steady-state approximation for live polymers and chain length independent termination, which may not be always applicable to certain free radical polymerization processes. In this paper, we have considered disproportionation termination only for illustrative purpose; however, the proposed method, with minor modification of the polymer population balance equations, is applicable to polymerization systems with combination termination. This method may be a useful control tool for polymerization processes in which customary molecular weight averages are inadequate for correlations to desired end-use properties. This issue will be addressed in our forthcoming paper.

Acknowledgment

Partial financial support by the sponsors of the Chemical Process Systems Laboratory of the Institute of Systems Research at the University of Maryland is gratefully acknowledged.

Nomenclature

$f_{(m,n)}$ = weight fraction of polymer in the chain length interval from m to n
 f_i = initiator efficiency factor
 g_t = gel effect parameter
 I = initiator concentration, mol L^{-1}
 k_d = initiator decomposition rate constant, min^{-1}
 k_{fm} = chain transfer to monomer rate constant, $L \text{ mol}^{-1} \text{ min}^{-1}$
 k_{fs} = chain transfer to solvent rate constant, $L \text{ mol}^{-1} \text{ min}^{-1}$
 k_i = initiation rate constant, $L \text{ mol}^{-1} \text{ min}^{-1}$
 k_p = propagation rate constant, $L \text{ mol}^{-1} \text{ min}^{-1}$
 k_{td} = disproportionation termination rate constant, $L \text{ mol}^{-1} \text{ min}^{-1}$
 M = monomer concentration, mol L^{-1}
 M_n = dead polymer concentration with n repeating units, mol L^{-1}

\bar{M}_n = number average molecular weight, g mol⁻¹
 \bar{M}_w = weight average molecular weight, g mol⁻¹
 M_0 = molecular weight of monomer, g mol⁻¹
 n_{\max} = maximum chain length for molecular weight distribution modeling
 P = total concentration of live polymer radicals, mol L⁻¹
 P_n = live polymer concentration with n repeating units, mol L⁻¹
 R = gas constant, cal mol⁻¹K⁻¹
 S = solvent concentration, mol L⁻¹
 T = temperature, K
 t_e = GPC elution time, min
 v_f = free volume
 v_{fcr} = critical free volume
 x = monomer conversion
 x_f = final monomer conversion

Greek Letters

α = probability of propagation
 λ_k^l = k th moment of live polymer molecular weight
 λ_k = k th moment of dead polymer molecular weight distribution
 ϕ_m = volume fraction of monomer
 ϕ_p = volume fraction of polymer
 ϕ_s = volume fraction of solvent

Literature Cited

- Bersted, B. H.; Anderson, T. G. Influence of Molecular Weight and Molecular Weight Distribution on the Tensile Properties of Amorphous Polymers. *J. Appl. Polym. Sci.* **1990**, *39*, 499.
 Christov, L.; Georgiev, G. An Algorithm for Determination of the Copolymer Molecular Weight Distribution by Markov Chain Simulation. *Macromol. Theory Simul.* **1995**, *4*, 177.

- Ellis, E. G.; Taylor, T. W.; Gonzalez, V.; Jensen, K. F. Estimation of the Molecular Weight Distribution in Batch Polymerization. *AIChE J.* **1988**, *34* (8), 1341.
 Gloor, W. E. The Numerical Evaluation of Parameters in Distribution Functions of Polymers from Their Molecular Weight Distributions. *J. Appl. Polym. Sci.* **1978**, *22*, 1177.
 Herdan, G. Fitting of Polymer Distributions of Molecular Weight by the Method of Moments. *J. Polym. Sci.* **1953**, *10* (1), 1.
 Ray, W. H. On the Mathematical Modeling of Polymerization Reactors. *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C8* (1), 1. Ross, R. T.; Laurence, R. L. Gel Effect and Free Volume in the Bulk Polymerization of Methyl Methacrylate. *AIChE Symp. Ser.* **1976**, *72*, 74.
 Schork, F. J.; Desphande, P. B.; Leffew, K. W. *Control of Polymerization Reactors*; Marcel-Dekker: New York, 1993.
 Schuler, H.; Suzhen, Z. Real Time Estimation of the Chain Length Distribution in a Polymerization Reactor. *Chem. Eng. Sci.* **1985**, *40* (10), 1891.
 Storti, G.; Polotti, G.; Cocaini, M.; Morbidelli, M. Molecular Weight Distribution in Emulsion Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 731.
 Xie, T.; Hamielec, A. E. Modeling Free Radical Polymerization Kinetics-Evaluation of the Pseudo-Kinetic Rate Constant Method. *Makromol. Chem., Theory Simul.* **1993**, *2*, 421.
 Xie, T. Y.; Hamielec, A. E.; Wood, P. E.; Woods, D. R. Experimental Investigation of Vinyl Chloride Polymerization at High Conversion: Molecular-Weight Development. *Polymer* **1991**, *32* (6), 1098.

Received for review October 4, 1996

Revised manuscript received December 30, 1996

Accepted January 5, 1997*

IE960623E

* Abstract published in *Advance ACS Abstracts*, February 15, 1997.