

Molecular Weight Distribution in Continuous Stirred Tank Vinyl Acetate Emulsion Polymerization

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Synopsis

Emulsion polymerization typically produces polymers of high molecular weight with broad distributions of molecular size. Many models have been proposed that use either a Flory type distribution, resulting in a polydispersity of two, or a distribution function to represent the breadth of the distribution. In this work, a model for the distribution of molecular weights is derived as an approximation from a detailed molecular weight model that was previously developed. The model is found to approximate the distribution of molecular weights well for several emulsifier concentrations in continuous stirred tank emulsion polymerization of vinyl acetate. An analysis is also conducted of the transformation of gel permeation chromatography data to weight and number fractional distributions of the molecular sizes.

INTRODUCTION

The molecular weight distribution is one of the key structural characteristics of polymer physical properties and a criterion for quality control. Furthermore, it reflects a history of the kinetics involved in a specific polymerization process. In 1969, Katz et al.¹ derived a set of partial differential equations which describes events of polymer chain growth based on probability distributions. However, their solution requires extensive numerical computation, and for the steady state zero-one radical system, the molecular weight distribution obtained has the form of a most probable distribution. Since that development, the molecular weight distribution in emulsion polymerization has been an attractive subject of experimental and theoretical investigations. This heterogeneous polymerization method gives higher average molecular weights and larger polydispersity ratios than other polymerization techniques. The higher molecular weights and broadness of the distribution are due to the compartmentalization of the propagating radicals in the particles and radical desorption and absorption phenomena. The compartmentalization means that every particle in emulsion polymerization acts as a minibatch reactor, i.e., a segregated reactor. As early as 1969, Graessley et al.²⁻⁴ investigated average molecular weights and the molecular weight distribution for vinyl acetate solution polymerization, including the effects of mixing. Based on their theoretical development, Friis and Hamielec⁵ derived a moment equation for the average molecular weight. These investigators approximated the broad molecular weight distribution by using a logarithmic normal distribution for vinyl acetate polymerization. In 1980, Lichti et al.⁶ developed a significant theoretic-

cal concept for the molecular weight distribution in emulsion polymerization. They demonstrated the broadness of the polydispersity as a function of the average number of radicals per particle by considering the compartmentalization of the free radicals. Their theory gives important information accounting for the large polydispersities which are commonly observed in emulsion polymerization.

For styrene emulsion polymerization, Lin et al.⁷ used a most probable distribution to approximate the molecular weight distribution. However, by definition this distribution results in a polydispersity of 2.

Nomura and Harada⁸ observed that radical capturing mechanisms are responsible for the large polydispersity values. In 1982, Baade et al.⁹ formulated a theoretical expression by following the calculations of Bamford and Tompa¹⁰ in homogeneous vinyl acetate continuous polymerization, but this equation was not properly formulated for segregated continuous polymerization reactors. Continuous emulsion polymerization is one type of segregated, i.e., macromixed, polymerization system which undergoes radical desorption and absorption by diffusion. In 1985, Taylor and Reichert¹¹ explained the polydispersity broadness again by using a segregated reactor model which makes use of the residence time distribution. Their goal was to investigate the micro- and macromixing effects on the molecular weight distribution. The simulation results were in good agreement with the experimental data.

Despite the above efforts, no explicit form for the molecular weight distribution in continuous vinyl acetate emulsion polymerization or continuous styrene emulsion polymerization has been developed. The main difficulty for this arises from the complex nature of the kinetic mechanisms which include radical transfer effects and multiple propagation steps, i.e., the terminal double bond reaction, and the method of solution of the two mass balances for dead polymer and living polymer chains. These two mass balance equations cannot be solved without a consideration of the heterogeneous initiation mechanism which accounts for radical absorption into particles and desorption from particles.

In a previous work,¹² a model to predict non-steady-state average molecular weights which includes a heterogeneous initiation mechanism has been developed. In this paper, an explicit equation for the molecular weight distribution is developed from the two mass balances of the previously developed molecular weight model,¹² and this theoretical result is compared with experimental data taken from gel permeation chromatographic separation of solubilized polymer in tetrahydrofuran solvent.

EXPERIMENTAL

Reagent grade vinyl acetate (VAc) was supplied by Fisher Scientific Co. and further purified by distillation in a rotary evaporator at a reduced pressure of 30 mm Hg to remove inhibitor. Sodium dodecyl sulfate (SDS) of 99% purity was obtained from Sigma Chemical Co. and used without further purification. Initiator, potassium persulfate (PPS), was obtained from J. T. Baker Chemical Co. and used directly as obtained. Water was purified by reverse osmosis, then deionized, and passed over a carbon filter before use. Nitrogen, bubbled

through a strongly alkaline pyrogallol solution to remove trace oxygen, was used to purge the reactor, as oxygen acts as a radical scavenger.

For continuous operation, two separate feed streams were prepared. One is the solution of vinyl acetate (1.333 L), SDS (9.6 g for a 0.01 mol/L water concentration) and distilled water (2.0 L). Two other surfactant concentrations were used as the major experimental parameter varied; 0.03 and 0.05 mol/L water were the others. The other feed is the initiator solution (1.35 L water and 9.12 g of PPS for the initiator concentration of 0.01 mol/L water used here). To start up the reactor, the feed streams were introduced to a 1-L glass kettle reactor which was initially filled with 294 mL of distilled water. The two feed streams were continuously supplied to the stirred tank reactor at constant flow rates with a duplex-head Masterflex pump (Cole-Parmer Co.) through silicone tubing. Flow rates were 7 mL/min for monomer solution and 2.8 mL/min for initiator solution to give a residence time of 30 min. The reactor temperature was maintained at $60 \pm 2^\circ\text{C}$. The basic design follows that of Kiparissides et al.¹³ The conversion of the effluent emulsion was measured continuously by a Mettler Paar DMA 35 densitometer. Samples of the effluent emulsion were quenched by concentrated hydroquinone solution, and were stored in 10-mL sampling bottles. Samples were taken every 10 min for analysis of molecular weights. Molecular weights were determined after coagulation and drying of the samples.

Molecular weights were determined by gel permeation chromatography (GPC) using a Waters Associates Model GPC I with a differential refractometer and three 7.8 mm \times 30 cm columns packed with ultra-styragel having nominal pore sizes 1×10^3 , 1×10^5 , 1×10^6 Å. Tetrahydrofuran was used for the solvent. Further experimental details are available elsewhere.^{12,14}

GPC has found widespread applications in determining molecular weight distributions of thermoplastic polymers. The experimental chromatogram obtained from a GPC unit is a continuous curve of relative mass concentration vs. elution time. The experimental GPC chromatogram does not represent the true molecular weight distribution. In many cases, a calibration curve is developed from standard samples having relatively narrow molecular weight distributions and which have been well characterized by one or more of the absolute methods such as light scattering and osmotic methods. By means of calibration, a differential molecular weight distribution curve vs. elution time is generated by a regression method [Fig. 1(C)]. In this experiment, the detector utilized is a differential refractometer, for which the mass concentration is assumed to be proportional to the instrument response ΔRI :

$$\text{MASS} = \delta \cdot \Delta RI$$

The proportionality factor δ is dependent on the sample solubility in THF solvent. This solubility factor is a function of the sample molecular weights. Since this factor is unknown, the sample chromatogram characterized by the known standard curve was normalized [Fig. 1(F)]. This chromatogram gives a weight fractional distribution of the subject polymer sample. To calculate a mole fractional distribution, the obtained weight fractional distribution was divided into very narrow regions to give negligible molecular weight differences for each region. The width of the regions is dependent on the differential

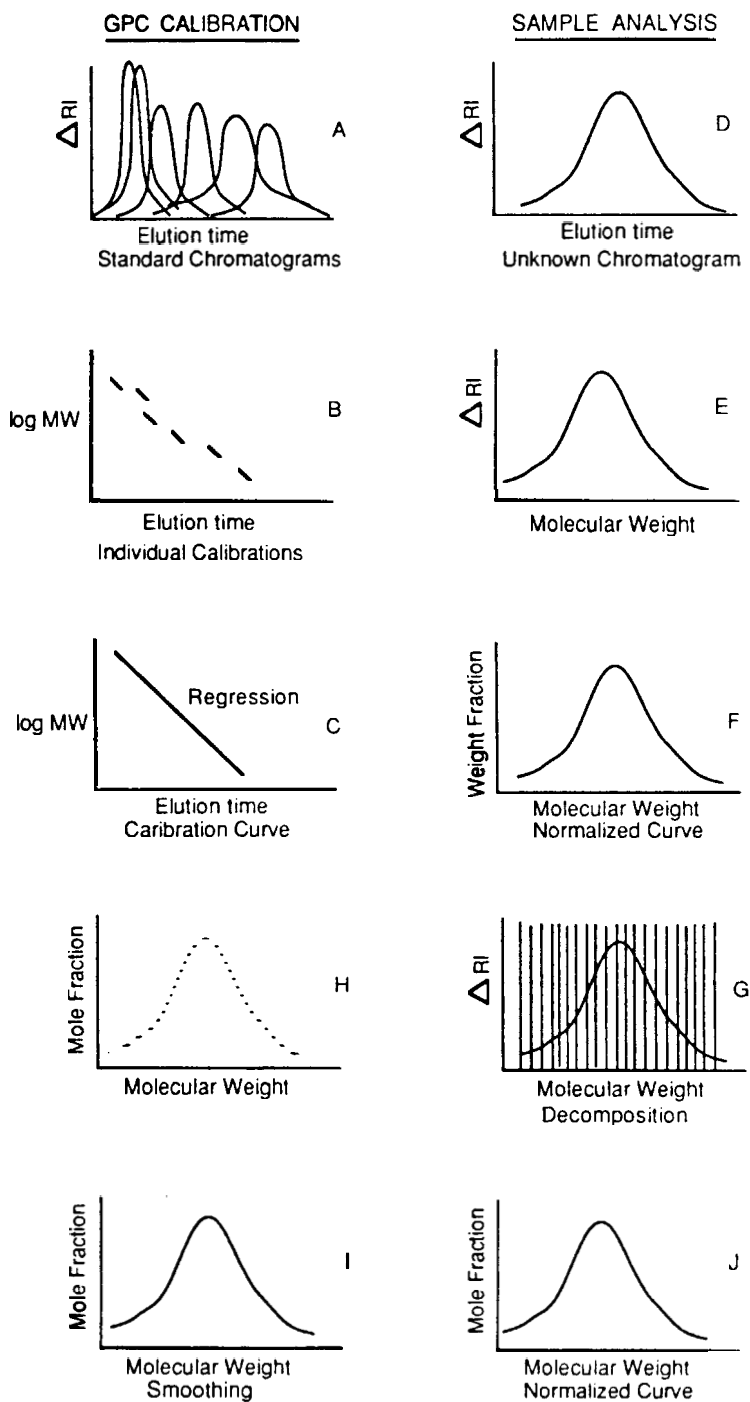


Fig. 1. Experimental procedure for sample analysis of molecular weight distribution.

slope of the cumulative weight fractional distribution. From each sliced area, a differential mole fraction was calculated by dividing the sliced area with the corresponding molecular weight. This discrete distribution was smoothed by a cubic spline method. The total area of this smoothed chromatogram was calculated by using the Gauss-Legendre quadrature formula and normalized to give an area of 1.0 [Fig. 1(I)]. Since the molecular weight range of the distribution is so wide, the smoothed curve by the cubic spline method was equally divided into approximately 200 pieces. For each piece, the Gauss-Legendre quadrature formula using 20 collocation points was applied.

THEORETICAL FORMULATION

The dead and living polymer mass balances from the previous development¹² are:

$$\frac{d[P_j]}{dt} = (A_2) \cdot [P_j^*] - (A_3 + A_4 + 1/\theta) \cdot [P_j] \quad (1)$$

$$\begin{aligned} \frac{d[P_j^*]}{dt} = & (A_1) \cdot [P_{j-1}^* - P_j^*] - (A_2 + A_5 + 1/\theta) \cdot [P_j^*] \\ & + (A_3) \cdot [P_j] + K_{pp} \left[\sum_{m=1}^{j-1} P_{j-m}^* P_m \right] \end{aligned} \quad (2)$$

where the A_i are simplified notations and defined in the Appendix. (The notation from the previous work¹² has been retained throughout this paper.) The first step in converting the above two equations to a tractable continuous function is to apply the continuous variable approximation as used by Zeman and Amundson.¹⁵ In that approximation, the polymer chain length n is considered as a continuous rather than a discrete variable. The difference term between living polymer concentrations in eq. (2) is expanded in a Taylor series:

$$[P_{j-1}^* - P_j^*] = -\frac{\partial [P_j^*]}{\partial j} + \frac{1}{2} \frac{\partial^2 [P_j^*]}{\partial j^2} + \dots \quad (3)$$

This series is truncated with the first-order term, and, using the steady state approximation, the dead polymer concentration in eq. (2) is substituted by using eq. (1). The simplified equation (2) forms a single differential equation:

$$\begin{aligned} (A_1) \frac{\partial [P_j^*]}{\partial j} + \left[(A_2 + A_5 + 1/\theta) - \frac{A_2 \cdot A_3}{A_3 + A_4 + 1/\theta} \right] \cdot [P_j^*] \\ = \left[\frac{K_{pp} \cdot A_2}{A_3 + A_4 + 1/\theta} \right] \cdot \left[\sum_{m=1}^{j-1} P_{j-m}^* P_m^* \right] \end{aligned} \quad (4)$$

The following expression for the above summation term now can be substituted:

$$\left[\sum_{m=1}^{j-1} P_{j-m}^* P_m^* \right] = \left[\sum_{m=0}^j P_{j-m}^* P_m^* \right] - 2[P_0^*][P_j^*] \quad (5)$$

This discrete function is related to a continuous function by the Euler-MacLaurin series summation formula resulting in

$$\begin{aligned} \left[\sum_{m=0}^j P_{j-m}^* P_m^* \right] &\approx \left[\int_0^j P_{j-m}^* \cdot P_m^* dm \right] + \frac{1}{2} \cdot ([P_j^*][P_0^*] + [P_0^*][P_j^*]) \\ &+ \sum_{m=1}^n \frac{B_{2m}}{(2m)!} \left[[P_{j-m}^* P_m^*]^{(2m-1)} \right. \\ &\quad \left. - [P_{j-m}^* P_m^*]^{(2m-1)} \right]_{m=0} + \dots \quad (6) \\ &\quad (j, n = 1, 2, 3, \dots) \end{aligned}$$

where the B_m are the Bernoulli numbers. If the degree of polymerization is large ($j \rightarrow \infty$), the last summation terms may be neglected for the following reason:

The derivative terms in the above summation terms, $\partial P^*(\infty)/\partial j$ and $\partial P^*(0)/\partial j$, are negligible compared to the integral term because the polymer concentrations which have zero and infinite repeating units are each very small.

As a result, we may approximate the above discrete function as a continuous integrodifferential equation by combining eq. (4) and (5) to give

$$\frac{\partial [P_j^*]}{\partial j} + C_1 \cdot [P_j^*] = C_2 \cdot \left[\int_0^j P_{j-m}^* \cdot P_m^* dm \right] \quad (7)$$

where

$$C_1 = \frac{(A_2 + A_5 + 1/\theta) \cdot (A_3 + A_4 + 1/\theta) - A_2 \cdot A_3 + K_{pp} \cdot A_2 [P_0^*]}{A_1 \cdot (A_3 + A_4 + 1/\theta)}$$

$$C_2 = \frac{K_{pp} \cdot A_2}{A_1 \cdot (A_3 + A_4 + 1/\theta)}$$

This integrodifferential equation can be solved by use of the Laplace transformation. The result is

$$[P_j^*] = \frac{2 \cdot [P_0^*] \cdot e^{-C_1 \cdot j} \cdot I_1 \left[\sqrt{4C_2 \cdot [P_0^*]} \cdot j \right]}{\sqrt{4C_2 \cdot [P_0^*]} \cdot j} \quad (8)$$

where the $[P_0^*]$ represents the monomeric radical concentration in the particles which was derived in the previous work.¹² I_1 is the modified Bessel function of the first kind. The above solution has the same form as that of Zeman and Amundson,¹⁵ which was developed for modeling bulk polymerization by consideration of multiple propagation steps.

Therefore, the weight and number fractional distributions are calculated by using the above molecular weight distribution equation for the living polymer concentration. The dead polymer concentration is related to the living polymer concentration by eq. (1). Weight fractional distribution is

$$\begin{aligned}\bar{W}_j &= \frac{\text{weight of polymer of length } j \text{ units}}{\text{total polymer weight}} \\ &= \frac{j \cdot [P_j] + j \cdot [P_j^*]}{\sum_{j=1}^{\infty} j \cdot [P_j] + \sum_{j=1}^{\infty} j \cdot [P_j^*]} \\ &= \frac{j \cdot [P_j^*] \cdot [(A_2 + A_3 + A_4 + 1/\theta)/(A_3 + A_4 + 1/\theta)]}{[M_1] + [M_1^*]}\end{aligned}\quad (9)$$

The number fractional distribution is then

$$\begin{aligned}\bar{N}_j &= \frac{[P_j] + [P_j^*]}{\sum_{j=1}^{\infty} [P_j] + \sum_{j=1}^{\infty} [P_j^*]} \\ &= \frac{[P_j^*] \cdot [(A_2 + A_3 + A_4 + 1/\theta)/(A_3 + A_4 + 1/\theta)]}{[M_0] + [M_0^*]}\end{aligned}\quad (10)$$

In addition, from the molecular weight distribution of eq. (8), a theoretical polydispersity ratio is developed. When a molecular weight distribution (population density) is known, the weight average molecular weight and number average molecular weight can be expressed in terms of the population density. Specifically

$$\bar{M}_n = \frac{(\text{MW}) \int_0^{\infty} jP(j) dj}{\int_0^{\infty} P(j) dj}\quad (11)$$

$$\bar{M}_w = \frac{(\text{MW})^2 \int_0^{\infty} j^2P(j) dj}{(\text{MW}) \int_0^{\infty} jP(j) dj}\quad (12)$$

The zeroth moment of the distribution, $\int_0^{\infty} P(j) dj$, is the total integral molar concentration of polymer; the first moment $(\text{MW}) \int_0^{\infty} jP(j) dj$ is the total integral mass concentration; (MW) is the molecular weight of the repeating unit (vinyl acetate molecular weight). The polydispersity ratio (PD) can then

be calculated from $\overline{M}_w/\overline{M}_n$:

$$PD = \frac{\left[\int_0^\infty j e^{-c_1 j} I_1 \left[\sqrt{4C_2 [P_0^*]} j \right] dj \right] \left[\int_0^\infty \frac{1}{j} e^{-c_1 j} I_1 \left[\sqrt{4C_2 [P_0^*]} j \right] dj \right]}{\left[\int_0^\infty e^{-c_1 j} I_1 \left[\sqrt{4C_2 [P_0^*]} j \right] dj \right]^2} \quad (13)$$

RESULTS AND DISCUSSION

To investigate the effect of the surfactant concentration on the molecular weight distribution, distributions at a polymerization time of 300 min around the steady state for each surfactant concentration are chosen for examination from the available data.¹² This corresponds to 10 reactor residence times from startup, well past the point at which steady operation is achieved. The results are presented in Figures 2 and 3. Figure 2 represents the weight fractional distributions. Their maximum peak positions are exactly related to their weight average molecular weights, which are observed in Table I. Although the maximum peak position at a surfactant concentration of 0.01 mol/L water is very close to that at 0.03 mol/L water, it has higher weight fractions in the low molecular weight region. As a result, it has a much lower weight average molecular weight. The number fractional distribution of Figure 3 is correlated with the number average molecular weight in a similar way.

In order to compare the molecular weight distributions obtained from gel permeation chromatographic separation with the theoretical distribution equation (9), experimental values of the average molecular weights around the steady state values of 240 and 300 min reaction times (eight and 10 reactor residence times) are chosen because the experimental data show relatively good agreement with the results for the average molecular weights in previous work.¹²

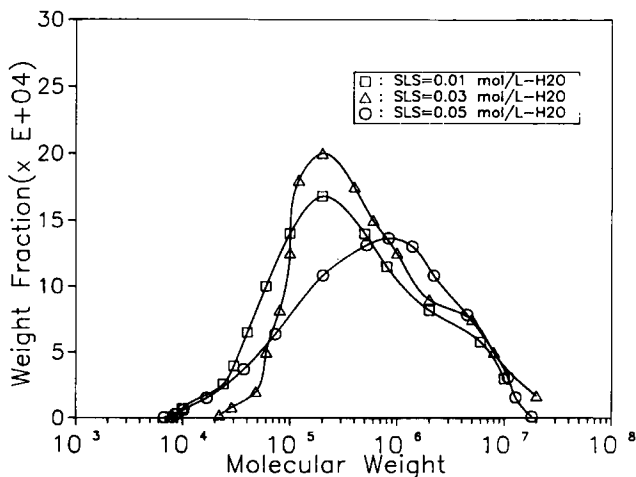


Fig. 2. Comparison of weight fractional distributions from experiments at different surfactant concentrations at a reaction time of 300 min.

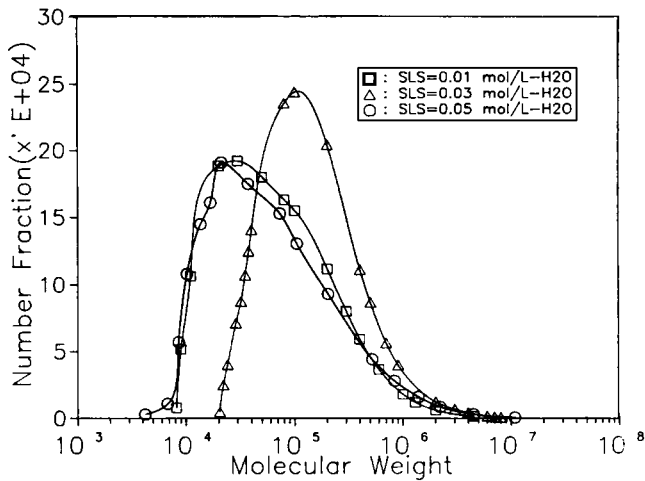


Fig. 3. Comparison of number fractional distributions from experiments at different surfactant concentrations at a reaction time of 300 min.

TABLE I
Average Molecular Weights

Average molecular weights	Expt 1,	Expt 2,	Expt 3
	[S] = 0.01 Mol/L-H ₂ O [S] = 0.03 Mol/L-H ₂ O [S] = 0.05 Mol/L-H ₂ O		
	[I] = 0.01 Mol/L-H ₂ O [I] = 0.01 Mol/L-H ₂ O [I] = 0.01 Mol/L-H ₂ O		
	(residence time = 30 min)		
$\bar{M}_w \times 10^{-6}$	1.01	1.28	1.48
$\bar{M}_n \times 10^{-5}$	2.02	2.48	1.74
PD	5.0	5.2	8.5

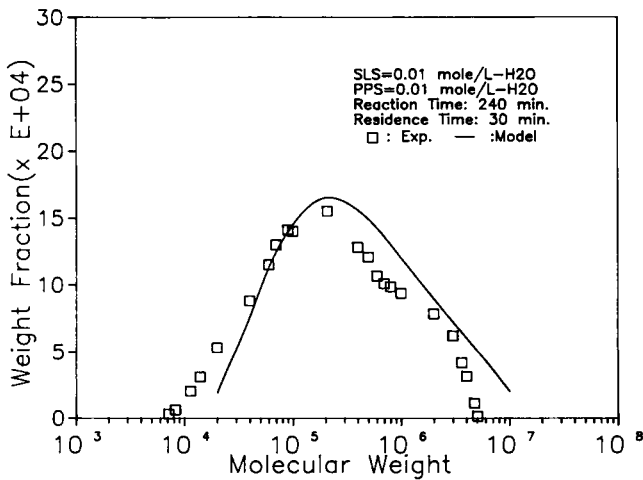


Fig. 4. Model result compared with weight fractional distribution at 0.01 surfactant concentration and 240-min reaction time.

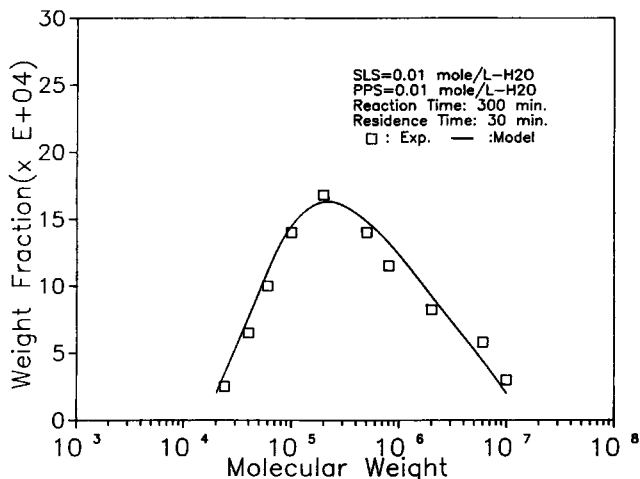


Fig. 5. Model result compared with weight fractional distribution at 0.01 surfactant concentration and 300-min reaction time.

To calculate the weight fractional distribution, we used the sum of both dead polymer and living polymer weights as the total polymer weight because all the radicals in particles are instantly deactivated by use of hydroquinone upon removal of the sample from the reactor. Comparisons of the theory and experimental results are presented in Figures 4–9. These figures show that the simplified molecular weight distribution equation gives a reasonable approximation and demonstrates that the experimental distribution provides a large polydispersity ratio. A careful observation of Figures 4–9 reveals that there are bumps in the higher molecular weight regions. The dramatic increases of molecular weight may be due to molecular branching effects from the terminal double bond reaction and radical transfer to polymer. This behavior cannot be

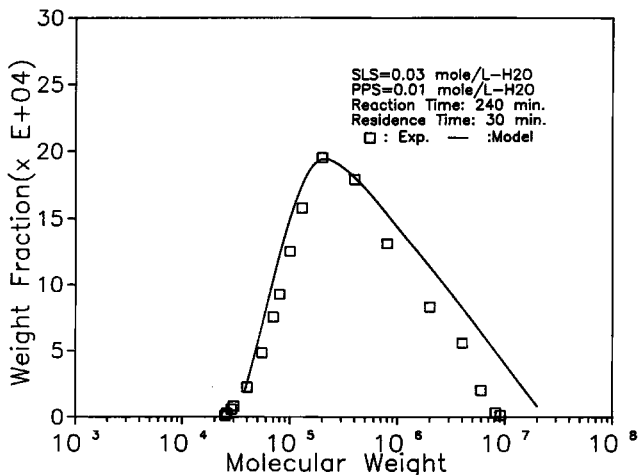


Fig. 6. Model result compared with weight fractional distribution at 0.03 surfactant concentration and 240-min reaction time.

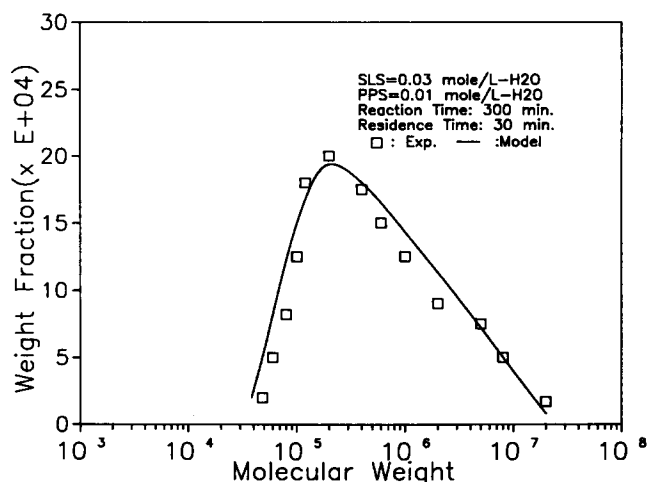


Fig. 7. Model result compared with weight fractional distribution at 0.03 surfactant concentration and 300-min reaction time.

explained without consideration of the chain length dependence of rate constants. Such a rigorous treatment was presented by Soh and Sunderberg,¹⁶ Boots,¹⁷ and Coyle and et al.¹⁸ for free radical bulk polymerization. Contrary to the simple bulk polymerization, emulsion polymerization includes extremely complicated kinetic mechanisms such that their analysis cannot be readily applied in the same manner. As previously mentioned, classical equal radical reactivity and chain length independent kinetic parameters were used here.

In the simplified size distribution equation (8), the broadness of the size distribution function is mainly dependent upon the ratio of $\sqrt{4C_2 \cdot [P_0^*]}$ and the C_1 constant. A consideration of the limiting behavior of the modified

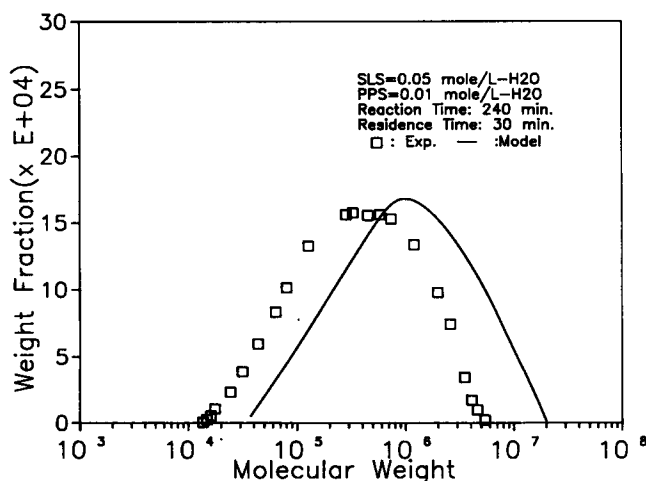


Fig. 8. Model result compared with weight fractional distribution at 0.05 surfactant concentration and 240-min reaction time.

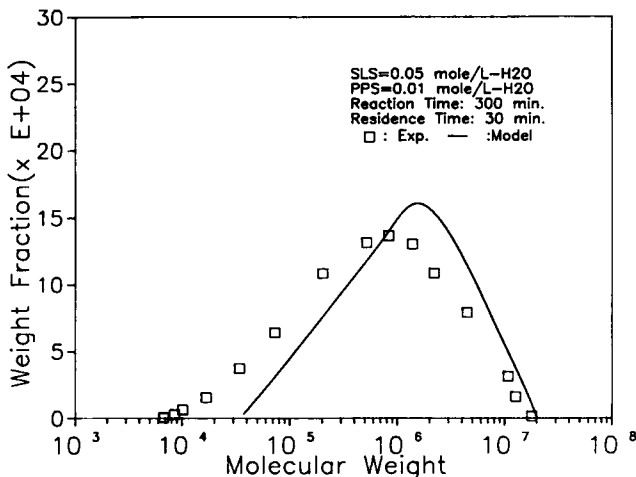


Fig. 9. Model result compared with weight fractional distribution at 0.05 surfactant concentration and 300-min reaction time.

Bessel function shows that this ratio cannot be greater than 1. If this ratio is greater than 1, the molecular weight distribution diverges to infinity. When this ratio approaches 1, the distribution function produces an infinite polydispersity ratio. Therefore, the theoretical polydispersity ratio is dependent upon this ratio. Through numerical simulations, it was found that this value is a strong function of the monomeric radical concentration and the terminal double bond reaction rate constant. Thus, it is believed that the large polydispersity ratios often observed in vinyl acetate emulsion polymerization are due to these two phenomena.

CONCLUSIONS

A simplified molecular weight distribution equation was derived by using the continuous variable approximation. This distribution equation fits the experimental data, which show large polydispersity ratios, very well. The magnitude of the polydispersity ratio is correlated with the ratio of the exponential term and the modified Bessel function term. This ratio is strongly dependent upon the monomeric radical concentration in the particles and the terminal double bond reaction rate constant. Thus, the large polydispersity ratios which are typical of emulsion polymerization are due to the above two factors. The derived size distribution equation shows a mechanistic structure which represents the large polydispersity ratio.

In the experimental observations, two significant phenomena were investigated: First, higher surfactant concentration gave higher weight average molecular weights, but lower number average molecular weights were observed. In more detail, there exist higher molar concentrations of low molecular weight chains in the produced polymer at higher surfactant concentrations. Second, molecular branching from multiple propagation and radical transfer, which cause a rapid increase in higher molecular weight fractions, appears significant in most cases, although these phenomena are not represented in the theoretical size distribution equation.

APPENDIX: SIMPLIFIED NOTATION

$$A_1 = K_p[M_p]$$

$$A_2 = K_t[R_w] + K_{mf}[M_p] + K_{trp} \left[\sum_{j=1}^{\infty} P_j \right]$$

$$A_3 = K_{trp} \left[\sum_{j=1}^{\infty} P_j^* \right]$$

$$A_4 = K_{pp} \left[\sum_{j=1}^{\infty} P_j^* \right]$$

$$A_5 = K_{pp} \left[\sum_{j=1}^{\infty} P_j \right]$$

$$A_6 = 2fK_d[I_w] + K_{mf} \left[\sum_{j=1}^{\infty} P_j^* \right] [M_p] - K_2[N^*][R_w] - K_h[R_w]$$

$$A_7 = K_t[R_w] + K_{trp} \left[\sum_{j=1}^{\infty} P_j \right]$$

References

1. S. Katz, R. Shinnar, and G. M. Saidel, *Adv. Chem. Ser.*, **91**, 145 (1969).
2. W. W. Graessley, R. D. Hartung, and C. W. Uy, *J. Polym. Sci., A-2*, **7**, 1919 (1969).
3. O. Saito, K. Nagasubramanian, and W. W. Graessley, *Polym. Sci., A-2*, **7**, 1937 (1969).
4. K. Nagasubramanian and W. W. Graessley, *Chem. Eng. Sci.*, **25**, 1549 (1970).
5. N. Friis and A. E. Hamielec, *J. Appl. Polym. Sci.*, **19**, 97 (1975).
6. G. Lichti, R. G. Gilbert, and D. H. Napper, *J. Polym. Sci. Chem. Ed.*, **18**, 1297 (1980).
7. C. C. Lin, W. Y. Chiu, and L. C. Huang, *J. Appl. Polym. Sci.*, **25**, 565 (1980).
8. M. Nomura and M. Harada, *Am. Chem. Soc. Symp. Ser.*, **6**, 121 (1981).
9. W. Baade, H.-U. Moritz, and K. H. Reichert, *J. Appl. Polym. Sci.*, **27**, 2249 (1982).
10. C. H. Bamford and H. Tompa, *Trans. Faraday Soc.*, **50**, 1097 (1954).
11. T. W. Taylor and K. H. Reichert, *J. Appl. Polym. Sci.*, **30**, 227 (1985).
12. C. H. Lee and R. G. Mallinson, *AICHE J.*, **34**, 840 (1988).
13. C. Kipparissides, J. F. MacGregor, and A. E. Hamielec, *Can. J. Chem. Eng.*, **58**, 48 (1980).
14. C. H. Lee, Ph.D. thesis, University of Oklahoma (1987).
15. R. J. Zeman and N. R. Amundson, *Chem. Eng. Sci.*, **20**, 331 (1965).
16. S. K. Soh and D. C. Sunderberg, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1299 (1982).
17. H. M. Boots, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1695 (1982).
18. D. J. Coyle, T. J. Tulig, and M. Tirrell, *Ind. Eng. Chem. Fundam.*, **24**, 343 (1985).

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