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CALCULATION OF MOLECULAR WEIGHT DISTRIBUTION IN STYRENE POLYMERIZATION INITIATED BY A BINARY INITIATOR SYSTEM

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Abstract – A computational scheme is presented for the calculation of molecular weight distribution in styrene polymerization initiated by a binary initiator system. In this paper, the method of finite molecular weight moment is presented by calculation of the polymer chain length distribution. This method is compared with the method of integrating an infinite number of polymer population balance equations. The results of the two methods show a reasonably good agreement. It is possible to produce polymer having the same molecular weight distribution.

Key words: Polystyrene, Molecular Weight Distribution, MWD, Binary Initiator

INTRODUCTION

To date, only single monofunctional initiators such as benzoyl peroxide (BPO) or azobisisobutyronitrile (AIBN) have been researched. However, in order to produce polymers of various grades in a more effective way, a variety of more complex initiator systems [Yoon, 1996] are used in many industrial free radical polymerization processes. By using the mixture of monofunctional initiators with considerably different thermal decomposition characteristics, it is quite possible to reduce reaction time, while increasing the monomer conversion and the polymer molecular weight by the use of the unique characteristics of the mixed initiator system. To be more specific, it is possible to achieve semi-sequential decomposition of the initiator when the polymerization temperature is optimally changed. In this way, by using such complex initiator systems, polymer reactor engineers can improve the performance of the polymerization reactor without any major hardware modification.

Polymer molecular weight distribution (MWD) is one of the most valuable polymer properties involving the physical, mechanical and rheological properties of industrial polymers. Many industrial polymerization processes usually use molecular weight averages and polydispersity to characterize polymer molecular weight properties. It is quite common for two polymers of different chain length distribution to have identical molecular weight averages. A slight variation in high or low molecular weight fractions of polymer can sometimes make a significant difference in the polymer's end-use properties. Accordingly, it is often necessary in practice to predict or control not the molecular weight averages but the entire chain length distribution.

In modern industrial polymerization processes, polymerization process conditions are so designed and operated that they can produce polymers of desired molecular weight properties having minimum variance from their target values. For this purpose the relation between a polymer's molecular properties and reaction conditions must be established quantitatively. Here it is possible to utilize a detailed polymerization process model. For our main goal of predicting and controling the polymer molecular weight distribution in a given polymerization process, it is necessary to get an appropriate computational method to predict the chain length distribution in the progress of reaction. Once a polymerization kinetic model is available, it is possible to calculate molecular weight average and MWD by numerical integration of the polymer population balance equations or by putting into use a moment generating function, z-transform, continuous variable transformation, and the method of molecular weight moment [Ray, 1972; Schork et al., 1993]. In addition, certain polymerization systems have been modeled by statistical descriptions, such as Markov chain approaches and numerical Monte Carlo methods [Storti et al., 1992; Christov and Georgiev, 1995]. It is also possible to calculate the MWD by integrating an instantaneous chain length distribution to a desired conversion [Xie et al., 1991]. When a prespecified chain length distribution function with molecular weight averages [Herdan, 1953; Gloor, 1978] can be fitted, it is also possible to approximate the differential MWD.

Previous reports have dealt with a new method called the method of *finite molecular weight moments* to calculate the chain length distribution in free radical polymerization of styrene [Crowley and Choi, 1997]. In this method, the weight fraction of polymers in a finite chain interval, instead of the concentration or weight fraction of polymer with a certain length, is calculated in thermal polymerization of styrene where combination termination is the primary mode of chain termination. Here, it is the major advantage of the method of finite molecular weight moments that the differential equation for the weight fraction of any finite chain length interval can be expressed clearly in terms of process variables.

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This paper shows that the method of finite molecular moments can be applied to styrene polymerization initiated by a binary initiator system. It also proposes a detailed analysis of polymer chain length distribution by changing binary initiator fraction. In addition, it is also suggested that a mixed initiator fraction is an important control variable for new polymers which have different MWD.

COMPUTATIONAL PROCEDURE

A binary initiator system consists of two popular monofunctional initiators of different thermal decomposition characteristics, i.e., t-butyl peroxide (TBPO) and t-butyl perbenzoate (TBPB). The former is a slow initiator which decomposes at a moderate rate at higher temperature; the latter is a fast initiator which readily decomposes at lower temperature. For the styrene polymerization catalyzed by the mixed initiators, it is assumed that the primary radicals generated by the decomposition of the two initiators are indistinguishable in their activities. At high reaction temperatures, thermal initiation becomes important. According to the mechanism proposed by Hui and Hamielec [1972], the thermal initiation reaction is third order with respect to styrene monomer.

Let us consider the following kinetic scheme for free radical polymerization of styrene where termination is via combination only as follows:

Initiation by initiators:

$$I_A \xrightarrow{k_{dA}} 2R \tag{1a}$$

$$I_B \xrightarrow{k_{dB}} 2R \tag{1b}$$

$$R+M \xrightarrow{k_i} P_1 \tag{1c}$$

Thermal initiation:

$$3M \xrightarrow{k_m} 2P_1 \tag{2}$$

Propagation:

$$P_n+M \xrightarrow{k_p} P_{n+1}\ (n \geq 1) \tag{3}$$

Chain transfer to monomer:

$$P_n+M \xrightarrow{k_{fm}} M_n+P_1\ (n \geq 1) \tag{4}$$

Termination

$$P_n+P_m \xrightarrow{k_t} M_{n+m}\ (n, m \geq 1) \tag{5}$$

where R is the primary radical, P_n the live polymer with n-repeating units, and M_n the dead polymer with n-repeating units.

In high conversion free radical polymerization, the termination reactions involving polymeric radicals become diffusion controlled and the termination rate constant decreases considerably with increase in monomer conversion. This phenomenon, which is referred to as the gel effect, has been studied by many workers in the past. In this study, the empirical gel effect correlation suggested by Peng [1990] for bulk styrene polymerization is used according to:

For temperature $\leq$ 130 °C and all x

$$g_t = \exp[-x\ A_2\ \exp(A_1/T)]$$

For temperature > 130 °C and x < 0.65

$$g_t = \exp[-x\ A_2\ \exp(A_1/403)] \tag{6}$$

For temperature > 130 °C and x $\geq$ 0.65

$$g_t = \exp[-x\ A_2\ \exp(A_1/T)]$$

where

$$A_1 = 1000x$$
$$A_2 = 4.42549\ \exp(-1.9837x)$$

The rate equation of polymeric species represents a system of an infinite number of differential equations. For the calculation of molecular weight, the following molecular weight moments are defined for live polymers and dead polymers, respectively, as

$$\lambda_k^l = \sum_{n=1}^{\infty} n^k P_n \quad \text{and} \quad \lambda_k = \sum_{n=2}^{\infty} n^k M_n \tag{7}$$

where λ_k^l 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

$$\overline{M_n} = M_0 \frac{\lambda_1^l + \lambda_1}{\lambda_0^l + \lambda_0} \quad \text{and} \quad \overline{M_w} = M_0 \frac{\lambda_2^l + \lambda_2}{\lambda_1^l + \lambda_1} \tag{8}$$

M_0 is the molecular weight of monomer. Since the concentration of live polymers is far smaller than that of dead polymers, the concentration of live polymers moments to overall polymer molecular weight is negligibly small. Thus, Eq. (8) is often reduced to

$$\overline{M_n} \simeq M_0 \frac{\lambda_1}{\lambda_0} \quad \text{and} \quad \overline{M_w} \simeq M_0 \frac{\lambda_2}{\lambda_1} \tag{9}$$

These molecular weight averages can be easily calculated by solving the dynamic weight moment equations together with the kinetic equations. Experimentally, polymer molecular weight is measured most conveniently by gel permeation chromatography (GPC).

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. For the calculation of a complete polymer chain length distribution, the polymer population balance equations need to be solved. To calculate the dead polymer molecular weight distribution, Eq. (19) can be solved directly; however, this method is not practical because of very large values of i. Or we can use the method of finite molecular weight moments as described in the following. Let us define the following function

$$f_{(m,n)} = \frac{\text{Weight of polymer with chain lengths from m to n}}{\text{Total weight of polymer}}$$

$$= \frac{\sum_{i=m}^{n} i\,M_i}{\sum_{i=2}^{\infty} i\,M_i} \tag{10}$$

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. (10). As the total number of chain length intervals increases, the resulting chain length distribution will approach a continuous distribution. During polymerization, the concentration of dead polymers changes, and hence $f_{(m,n)}$ changes with time. Using Eq. (10), we can derive a differential equation for $f_{(m,n)}$:

$$\frac{df_{(m,n)}}{dt} = \frac{1}{\lambda_1}\sum_{i=m}^{n} i\frac{dM_i}{dt} - \frac{f_{(m,n)}}{\lambda_1}\frac{d\lambda_1}{dt} \tag{11}$$

when this equation, for any given values of m and n, is solved together with the mass balance equations for a polymerization process, we can obtain the discrete polymer chain length distribution.

By applying the quasi-steady-state assumption (QSSA) to live polymer radicals and primary radicals, one can obtain the following:

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

$$P = \left(\frac{2k_m M^3 + 2f_{iA}\,k_{dA}\,I_A + 2f_{iB}\,k_{dB}\,I_B}{k_t}\right)^{1/2} \tag{12}$$

Where P is the total concentration of polymer radicals and f_{iA} is an A type initiator efficiency factor, f_{iB} is B type initiator efficiency factor. α is the probability of propagation defined as

$$\alpha = \frac{k_p M}{k_p M + k_t P + k_{fm} M} \tag{13}$$

Eq. (12) is known as the most probable distribution. If chain termination occurs by combination only (e.g., styrene polymerization), the following differential equation for λ_1 is obtained from the kinetic model equations for the polymerization system described by Eqs. (1)-(5). For computational convenience, the following molecular weight moment equations are changed into the probability of propagation by Eqs. (14)-(18)

$$\lambda_1' = \frac{P}{1-\alpha} \tag{14}$$

$$\lambda_2' = \frac{(1+\alpha)P}{(1-\alpha)^2} \tag{15}$$

$$\frac{d\lambda_0}{dt} = \frac{1}{2}k_t P^2 + k_{fm} MP \tag{16}$$

$$\frac{d\lambda_1}{dt} = \frac{1}{(1-\alpha)}\left[k_t P^2 + k_{fm} M P\,\alpha(2-\alpha)\right]$$
$$= (2-\alpha)\,k_p MP + (1-\alpha)\,k_t P^2 \tag{17}$$

$$\frac{d\lambda_2}{dt} = \frac{1}{(1-\alpha)^2}\left[k_t P^2(\alpha+2) + k_{fm} MP\,\alpha(\alpha^2 - 3\alpha + 4)\right] \tag{18}$$

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

$$\frac{dM_i}{dt} = k_{fm} M(1-\alpha)\,\alpha^{i-1} P + \frac{k_t}{2}(i-1)(1-\alpha)^2\alpha^{i-2}P^2 \tag{19}$$

Then the summation term in Eq. (11) becomes

$$\sum_{i=m}^{n} i\frac{dM_i}{dt} = k_{fm} M(1-\alpha)\,P\sum_{i=m}^{n} i\,\alpha^{i-1} + \frac{k_t}{2}(1-\alpha)^2 P^2 \sum_{i=m}^{n} i(i-1)\alpha^{i-2} \tag{20}$$

Finally, Eq. (11) becomes

$$\frac{df_{(m,n)}}{dt} = \frac{1}{\lambda_1}\left[k_{fm} M(1-\alpha)P\,\mathrm{sum1} + \frac{k_t}{2}(1-\alpha)^2 P^2\,\mathrm{sum2}\right] - \frac{f_{(m,n)}}{\lambda_1}\left[(2-\alpha)\,k_p MP + (1-\alpha)k_t P^2\right] \tag{21}$$

where

$$\mathrm{sum1} = \frac{\alpha^{m-1} - \alpha^n}{(1-\alpha)^2} + \frac{(m-1)\alpha^{m-1} - n\alpha^n}{(1-\alpha)} \tag{22}$$

$$\mathrm{sum2} = \frac{1}{(1-\alpha)^3}\left[\begin{array}{l}\{(m-1)(m-2)\alpha^m - 2m(m-2)\alpha^{m-1} + m(m-1)\alpha^{m-2}\} \\ -\{n(n-1)\alpha^{n+1} - 2(n+1)(n-1)\alpha^n + n(n+1)\alpha^{n-1}\}\end{array}\right]$$

Eq. (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. (12) is then solved simultaneously with the kinetic model equation. If number chain length distribution is also desired, a functional similar to $f_{(m,n)}$ can be defined and solved.

RESULTS AND DISCUSSIONS

It was necessary to prove whether the method of finite molecular weight moments we newly developed is really effective. Accordingly, we made an attempt to compare the result by solving population balance, Eq. (19) directly from n=2 to infinity by our finite method. But since solving a population balance to infinity is impossible in a practical sense, we used 12,000 as a number close to infinity.

The solid line in Fig. 1 means the result when the population balance (Eq. (19)) has been solved directly. The filled circle (●) is the result of calculation by dividing into 20 segments and the open diamond (◇) is the result by dividing into 40. Here, the value of the filled circle and open diamond represents the mean of m and n. Fig. 1 shows that the result by population balance and the result by our finite method turn out to be the same. As a result, solving 12,000 differential equations by compressing them into 20 to 40 or so, simplified the amount of calculation by about 1/500. This can also serve as a very effective method not just for easy calculation but for optimization with the target of desired molecular weight distribution.

As the result of Fig. 1 shows, it is assumed that in calculating by segment using the same interval, as many as 25 to 40 segments are needed to get an accurate curve. However,

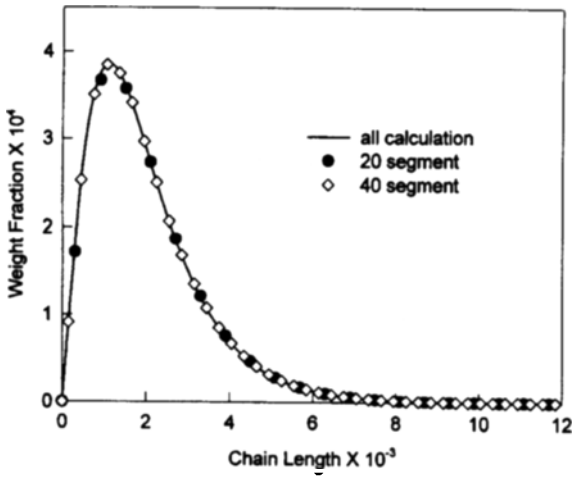

Fig. 1. Molecular weight distribution.
y_{Af}=0.0, T=150 °C, t = 60 min.

observing the curve of molecular weight distribution shows that it is important at low molecular weight. Therefore, in order to reduce the number of segments, it will be a more effective method to set the length of segment narrower in the area of low molecular weight and to set the length of segment wider in the area of high molecular weight. In this sense, the intervals suggested in the paper by Crowley and Choi [1997] might be a much more effective method.

This paper tries to explain how the method of finite molecular weight moment that we propose is different from the molecular weight distribution model using the Schulz Distribution Function. In the model using the Schulz Distribution Function, when polymer type and $\overline{M}_n$ or $\overline{M}_w$ are known, it is possible to calculate the complete molecular weight distribution. According to this model, if any polymer is the same in $\overline{M}_n$ or $\overline{M}_w$, the complete molecular weight distribution is always the same. On a practical level, however, it is not true that when the average molecular weight is the same, the molecular weight distribution is also same. This point is shown in Fig. 2 and 3.

First, model simulation was made for the selection of comparison-object. Here, y_{Af} is the mole fraction of initiator A (fast initiator). As is shown in Fig. 2, the weight average molecular weights are, respectively, 194,000 under fairly similar conditions. Fig. 3 shows that model simulation under respective reaction conditions proves the respective molecular weight distribution is actually fairly different. Fig. 3 also shows that reaction condition at y_{Af}=1.0 can produce more polymers which are low molecular weight less than $\overline{X}_n$ =1,000 and high molecular weight than $\overline{X}_n$=4,000, compared with the reaction condition at y_{Af}=0.0. Table 1 shows the molecular weight fraction and the accumulated fraction according to the respective intervals. This result proves that the molecular weight distribution model using the Schulz Distribution Function has limitations as an empirical model.

Most polymer end-users demand polymers having the same molecular weight but different molecular weight distribution for diverse uses. Of course, for the purpose of changing the molecular weight distribution, it is also possible to alter the

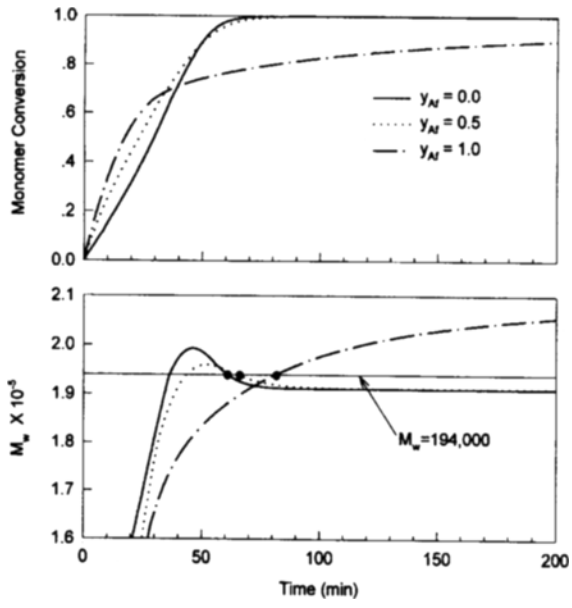

Fig. 2. Monomer conversion and molecular weight profiles at different initiator composition.
T = 152 °C, I_t = 0.01 mol/L, f_{iA} = 0.6, f_{iB} = 0.6.

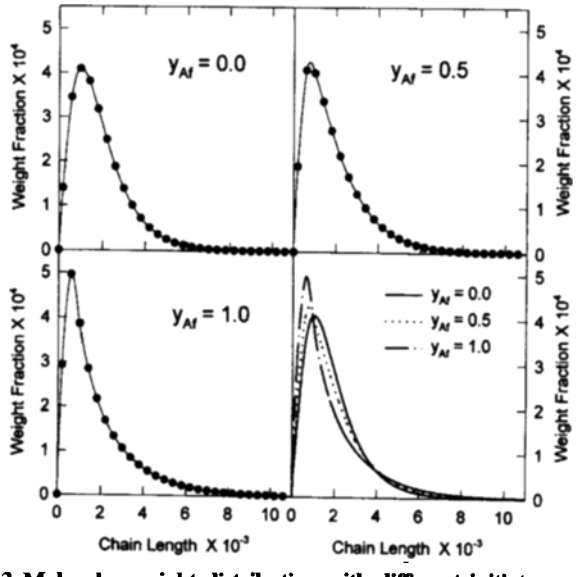

Fig. 3. Molecular weight distribution with different initiator compositions.
T = 152 °C, I_t = 0.01 mol/L, f_{Ai} = 0.6, f_{Bi} = 0.6.

average molecular weight and molecular weight distribution in consideration of reaction conditions, such as reaction temperature, initiator concentration, and reaction time.

This paper suggests that to change initiator composition using a binary mixed initiator can make it possible to produce a new grade having different molecular weight distribution. Fig. 3 is the result of molecular weight distribution through model simulation when the composition of binary mixed initiator is changed. This result shows that the weight average molecular weight is the same as 194,000; nevertheless, the molecular weight distribution is quite different. Accordingly, it is significant to produce new grades having a different molecular weight distribution by new control variable changing

Table 1. Molecular weight fraction(%) for different chain lengths

Chain length	y_{Af}=0.0		y_{Af}=0.5		y_{Af}=1.0	
	Ratio (%)	Cumulative (%)	Ratio (%)	Cumulative (%)	Ratio (%)	Cumulative (%)
2-400	5.5339	5.5339	7.5935	7.5935	11.6336	11.6336
401-800	13.7747	19.3086	16.3063	23.8998	19.7740	31.1407
801-1200	16.3210	35.6297	16.0714	39.9712	15.4060	46.8136
1201-1600	15.2221	50.8519	13.5061	53.4774	11.3468	58.1605
1601-2000	12.6820	63.5340	10.8686	64.3460	8.6311	66.7916
2001-2400	9.9304	73.4644	8.5807	72.9268	6.7369	73.5286
2401-2800	7.4906	80.9550	6.6821	79.6090	5.3328	78.8614
2801-3200	5.5156	86.4706	5.1430	84.7520	4.2509	83.1123
3201-3600	3.9945	90.4652	3.9181	88.6702	3.3996	86.5119
3601-4000	2.8583	93.3235	2.9585	91.6287	2.7221	89.2341
4001-4400	2.0265	95.3501	2.2166	93.8454	2.1800	91.4141
4401-4800	1.4262	96.7763	1.6496	95.4951	1.7450	93.1591
4801-5200	0.9976	97.7740	1.2204	96.7155	1.3956	94.5548
5201-5600	0.6942	98.4683	0.8982	97.6138	1.1151	95.6699
5601-6000	0.4809	98.9493	0.6580	98.2718	0.8900	96.5599
6001-6400	0.3319	99.2812	0.4800	98.7518	0.7095	97.2694
6401-6800	0.2282	99.5094	0.3489	99.1007	0.5650	97.8345
6801-7200	0.1564	99.6658	0.2527	99.3535	0.4494	98.2839
7201-8000	0.1797	99.8456	0.3140	99.6675	0.6406	98.9246
8001-9600	0.1213	99.9670	0.2451	99.9126	0.6555	99.5801
9601-12000	0.0288	99.9958	0.0741	99.9868	0.3169	99.8971
12001-∞	0.0042	100.0000	0.0132	100.0000	0.1029	100.0000

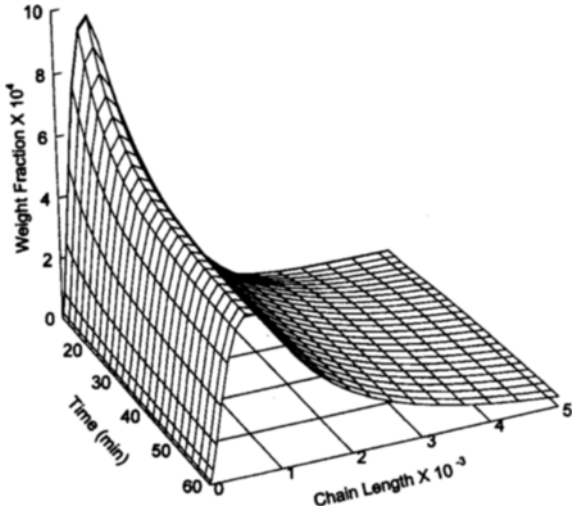

Fig. 4. Molecular weight distribution as a function of time.
y_{Af} = 1.0, T = 150 °C, t=60 min, 30 segment.

binary mixed initiator composition.

To plot the calculation of this molecular weight distribution according to time provides a large amount of definite information. As the polymer reaction goes on, the change of various reaction conditions, like those of monomer conversion and initiator concentration, keeps changing molecular weight distribution. Fig. 4 shows that low molecular weight can be produced during an initial reaction period and high molecular weight can be produced by thermal polymerization during finishing reaction period. This kind of time-based observation of molecular weight distribution shows well the process of the reaction and also proves that the control of appropriate reaction time is important in order to get a desired molecular weight distribution.

CONCLUSIONS

In this paper, a new method is presented for the calculation of weight chain length distribution in styrene polymerization initiated by a binary initiator system. This method uses the kinetic rate equations, molecular weight moment equations, and the function that defines the weight fraction of polymer in a finite chain length interval. Also, this method has the same results as that by direct integrating of the population balance. So it is possible to optimize the molecular weight distribution in a fairly simple and practical way.

Therefore, one is able to compute the weight fraction of polymer in any molecular weight range. The molecular weight averages can be computed by using the chain length distribution obtained or directly solving the molecular weight moment equations that are calculated with the function $f_{(m, n)}$. 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. It is to be noted that with some minor modifications of the model equations, one can also calculate the chain length distribution in continuous styrene polymerization processes.

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NOMENCLATURE

$f_{(m,n)}$: weight fraction of polymer in the chain length interval from m to n [-]
f_{iA} : A type initiator efficiency factor [-]
f_{iB} : B type initiator efficiency factor [-]
g_e : gel effect parameter [-]
I_A : A type initiator (TBPB) concentration [mol/L]
I_B : B type initiator (TBPO) concentration [mol/L]
I_t : total initiator concentration [mol/L]
k_{dA} : A type initiator decomposition rate constant [min^{-1}]
k_{dB} : B type initiator decomposition rate constant [min^{-1}]
k_{fm} : rate constant for chain transfer to monomer [L/mol·min]
k_i : initiation rate constant [L/mol·min]
k_m : thermal initiation rate constant [L^2/mol·min]
k_p : propagation rate constant [L/mol·min]
k_t : combination termination rate constant [L/mol·min]
M : monomer concentration [mol/L]
M_0 : molecular weight of monomer [g/mol]
M_n : dead polymer concentration with n repeating units [mol/L]
$\overline{M_n}$: number average molecular weight [g/mol]
$\overline{M_w}$: weight average molecular weight [g/mol]
P_n : live polymer concentration with n repeating units [mol/L]
P : total concentration of live polymer radicals [mol/L]
R : primary radical concentration [mol/L]
t : reaction time [min]
T : temperature [K]
x : monomer conversion [-]
y_{Af} : mole fraction of A type initiator in the initiator feed mixture, $I_A/(I_A+I_B)$ [-]

Greek Letters

α : probability of propagation [-]
λ_k : kth moment of dead polymers [mol/L]
λ_k^l : kth moment of live polymers [mol/L]

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