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Research Note

Simulation of Styrene Radical Polymerization in Batch Reactor: A Modified Kinetic Model for High Conversion

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In this paper, bulk and suspension free radical polymerization of styrene in batch reactor has been modelled. This research contains two parts. In the first part, the derivation of a mathematical model from kinetics of reactions was performed. The solution of this mathematical model required roughly 10000-50000 stiff-differential equations to be solved simultaneously. However, the number of equations were reduced to only five non-stiff differential equations and six algebraic equations using moment model and quasi-steady-state assumption. Due to an enormous increase in viscosity during polymerization, the system translates into diffusion-controlled state, which causes gel and glassy effects. These effects along with initiator cage effect influence termination rate constant, propagation rate constant and initiator efficiency, respectively. In the second part, effective rate constants were defined as a function of free volume and temperature in order to describe gel and glassy effects in the model. The efficiency of initiators was also defined as a function of free volume and temperature in the same manner to account for cage effect. The model presented here has been solved by Matlab software. Also Matlab optimization software was used to obtain the adjustable parameters of effective rate constants. The model predicted the monomer conversion, number and weight average molecular weights as a function of time with a high rate of accuracy particularly at high conversions. Results were in good agreement with experimental data obtained from different sources. The predictions were found to be better than the so far published models including Marten-Hamielec [1] and Vivaldo-Lima [2] models.

INTRODUCTION

At high monomer conversions in radical polymerization, the termination, propagation and initiation reactions can become diffusion-controlled due to highly viscous reaction medium. Diffusion-controlled phenomena have been related to the well-known gel and glassy effects [3]. Several semi-emperical models have been reported dealing with the mathematical description of diffusion-controlled kinetic rate constants in free radical polymerization [1,2,4,5]. Among these models Marten-Hamielec [1] and Vivialdo-Lima [2] models have proven to be the most successful in predicting conversion and molecular weight particularly at low and medium conversion. In this work, a model has been presented which modifies the various assumptions made in Marten-Hamielec and Vivaldo-Lima models in order to achieve better agreement between theoretical predictions and experimental values, particularly at high conversions.

KINETICS OF FREE-RADICAL POLYMERIZATION

The general description of the reactions involved in initiated bulk or suspension polymerization can be written as follows [6]:

Initiator decomposition	$I \xrightarrow{kd} 2R^0$
Initiation	$R^0 + M \xrightarrow{ki} R_1$
Propagation	$R_x + M \xrightarrow{k_p} R_{x+1}$
Termination by disproportionation	$R_x + R_y \xrightarrow{k_{td}} P_x + R_y$
Termination by combination	$R_x + R_y \xrightarrow{k_{tc}} P_{x+y}$
Chain transfer to monomer	$R_x + M \xrightarrow{k_m} R_1 + P_x$

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Table 1. Differential equations of the model.

$\frac{dI}{dt} = -K_d I - (\frac{I}{V})\frac{dV}{dt}$
$\frac{dM}{dt} = -K_i M R^0 - (K_p + K_m)M \sum_{x=1}^{\infty} R_x - (\frac{M}{V})\frac{dV}{dt}$
$\frac{dR_1}{dt} = -K_i M R_0 + K_p M R_1 - K_t R_1 \sum_{x=1}^{\infty} R_x + (K_s S + K_m M) \sum_{x=2}^{\infty} R_x - (\frac{R_1}{V})\frac{dV}{dt}$
$\frac{dR_x}{dt} = -K_p M R_x + K_p M R_{x-1} - (K_m M + K_s S)R_x - K_t R_x \sum_{y=1}^{\infty} R_y - (\frac{R_x}{V})\frac{dV}{dt}$
$\frac{dP_x}{dt} = (K_s S + K_m M)R_x + K_{td} R_x \sum_{y=1}^{\infty} R_y + (\frac{K_{tc}}{2}) \sum_{y=1}^{x=1} R_y R_{x-y} - (\frac{P_x}{V})\frac{dV}{dt}$

Table 1 shows the differential equations of the model, which have been suggested, based on the free radical polymerization kinetics. In derivation of these equations, the following assumptions were made to simplify the mathematical descriptions:

1. Reactions of polymerization are elementary and irreversible;
2. The reaction rate constant is independent of chain length;
3. There is no temperature gradient and the reactor is well mixed.

The last two expressions in Table 1 represent an infinite number of differential equations since x can vary from 2 to infinity. Therefore, a rigorous solution requires roughly 10000-50000 stiff differential equations to be solved simultaneously [7]. This large number of equations can be reduced to a set of fewer non-linear differential equations by the method of moments. In this method, the kth moment of the live radical and the dead polymer concentration are defined as:

$$\mu_k = \sum_{x=1}^{\infty} x^k p_x, \tag{1}$$

$$\lambda_k = \sum_{x=1}^{\infty} x^k R_x, \tag{2}$$

where λ_0 represents the total concentration of free radicals and μ_0 denotes the total polymer concentration. Consequently, the number of equations will reduce to nine stiff differential equations and three algebraic equations. To eliminate the stiff condition of the equations, quasi-steady-state assumption was made to reduce the number of equations to six non-stiff differential and five algebraic equations. The quasi-steady-state assumes that the rate of change of radical concentration is almost zero [7-10]. Table 2 shows the final simplified mathematical model.

EFFECT OF MASS TRANSFER ON KINETICS OF FREE RADICAL POLYMERIZATION

In bulk polymerization systems, the viscosity of the medium increases enormously as the reaction proceeds. Therefore, the termination and propagation reactions are affected by the diffusion phenomena. Both diffusion-controlled termination and propagation reactions have been reported to be related to gel and glassy effects, respectively. Also because of the "cage effect" an initiator efficiency has to be defined to account for the fraction of primary free radicals that are successfully involved in the initiation of the polymerization.

Table 2. The final simplified mathematical model.

$\lambda_0 = \left[\frac{2fK_d I}{(K_t + K_p \varepsilon \frac{M}{M_0})}\right]^{\frac{1}{2}}$
$\lambda_1 = \frac{2fK_d I + (K_p M + K_m M)\lambda_0}{K_m M + (K_t + K_p \varepsilon \frac{M}{M_0})\lambda_0}$
$\lambda_2 = \lambda_1 + \frac{2K_p M \lambda_1}{K_m M + (K_1 + K_p \varepsilon \frac{M}{M_0})\lambda_0}$
$\frac{d\mu_1}{dt} = K_m M \lambda_1 + K_t \lambda_0 \lambda_1 - K_p \mu_1 \lambda_0 \varepsilon \frac{M}{M_0}$
$\frac{d\mu_0}{dt} = K_m M \lambda_0 + K_{td} \lambda_0^2 + K_{tc} \frac{\lambda_0^2}{2} - \mu_0 \lambda_0 \varepsilon K_p \frac{M}{M_0}$
$\frac{dM}{dt} = -K_p M \lambda_0 (M_0 + \varepsilon M)/M_0$
$\frac{d\mu_2}{dt} = K_m M \lambda_2 + K_t \lambda_0 \lambda_2 + K_{tc} \lambda_1^2 - K_p \mu_2 \lambda_0 \varepsilon \frac{M}{M_0}$
$\frac{dI}{dt} = -K_d I - K_p I \lambda_0 \varepsilon M/M_0$
$X = \frac{M_0 V_0 - MV}{M_0 V_0} = \frac{M_0 - M}{M_0 + \varepsilon M}$
$\bar{M}_n = M_m \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0}$
$\bar{M}_W = M_m \frac{\mu_2 + \lambda_2}{\mu_1 + \lambda_1}$
$V = V_0(1 + \varepsilon X)$

Cage Effect

Initiation step involves generation of active primary radicals. However, not all of these radicals can approach the monomer molecules to initiate the reaction, due to a "cage effect". It is believed that owing to the very close proximity of the generated radicals, only part of them can escape from their "cages". Thus, an initiator efficiency factor is defined to account for cage effect. In this work, 2, 2′-Azobisisobutyronitrile (AIBN) has been selected as a radical initiator. The efficiency of AIBN has been defined as a function of temperature and total free volume as follows:

$$f = 0 - 89.91\ \exp(-14.24\ \text{kJ mol}^{-1}/RT), \tag{3}$$

$$f = \left[1 + (\frac{1}{f_0} - 1)\exp\left[0.158\left(\frac{1}{V_f} - \frac{1}{V_{f0}}\right)\right]\right]^{-1}, \tag{4}$$

in which f_0 is the initial initiator efficiency defined as the function of temperature only and f is the efficiency of the initiator during the polymerization reaction.

Gel Effect

Gel effect has been attributed to the decrease of termination rate constant which is caused by the reduction of the polymer chain mobility. This phenomenon leads to a broader molecular weight distribution. In the present work, the combination termination rate constant has been assumed to be a function of temperature, free volume and average molecular weight and propagation-diffusion as described below [1,2]:

$$k_{tc} = k_{tc}^{0}\left(\frac{M_{wcr}}{M_w}\right)^{m} \exp\left[-A\left(\frac{1}{V_f} - \frac{1}{V_{fcr}}\right)\right] + C_{rd}k_p[M], \tag{5}$$

where $[M]$ denotes the monomer concentration, A, m and C_{rd} are adjustable parameters and M_{wcr} and V_{fcr} are critical values of M_w and V_f, respectively. The term $C_{rd}k_p[M]$ accounts for the propagation-diffusion termination [2]. The critical values are given by [1]:

$$K_{cr} = 9.6\exp(1929/T), \tag{6}$$

$$K(X) = M_w(X)^{0.5}\exp(A/V_f(X)). \tag{7}$$

A critical value K_{cr} for the system, denoting the onset of the translational diffusion-controlled termination reactions, was defined as a function of temperature only. According to Marten-Hamielec when $K(X)$ equals K_{cr}, then V_f and M_W take their critical values, i.e., V_{fcr} and M_{wcr}, respectively. It should be noted that termination rate constant by disproportionation was neglected.

Glassy Effect

Glassy effect has been related to the decrease of the propagation rate constant caused by a decrease of the mobility of monomer molecules. The glassy effect appears in polymerization taking place at temperatures below the glass transition temperature of the polymer. The propagation rate constant is a function of temperature and free volume as follows [1]:

$$k_p = k_p^0 \exp\left[-\left[\frac{1}{V_f} - \frac{1}{V_{fcr2}}\right]\right]. \tag{8}$$

Here V_{fcr2} is the free volume of the system at a critical conversion where the reaction mix becomes glassy, which is given by:

$$V_{fcr2} = \frac{1}{7.4847 - 9.38215 \times 10^{-8}T^3}. \tag{9}$$

Calculation of Free Volume

To calculate the overall available free volume, the sum of the individual contribution must be taken Therefore, considering [2], this quantity is obtained from the following equation:

$$V_f = \sum_{i=1}^{N}[0.025 + \alpha_i(T - T_{gi})\frac{V_i}{V_t}], \tag{10}$$

where i = monomer, polymer, ..., N.

RESULT AND DISCUSSION

The mathematical model presented in Table 2 was simulated by Matlab package and the adjustable parameters that were used by Marten-Hamielec and optimized by the toolbox facility in the package using experimental data from the literature. The obtained adjustable parameters are as follows:

$$A = 0.385, \quad m = 1.7072, \quad C_{rd} = 135.$$

Chemical kinetics and physical parameters depicted in Tables 3 and 4 were used in the mathematical model.

Figures 1 to 6 show the model predictions for the variation of extent of polymerization versus time at three different temperatures and initiator concentrations. The range of temperature and initiator concentration covered was 333.15 – 353.15 (°K) and 0.0212 – 0.05 (gmole/l), respectively. Comparison between the model predictions and experimental data indicates an excellent agreement, especially at high conversions, which was very good compared to earlier models

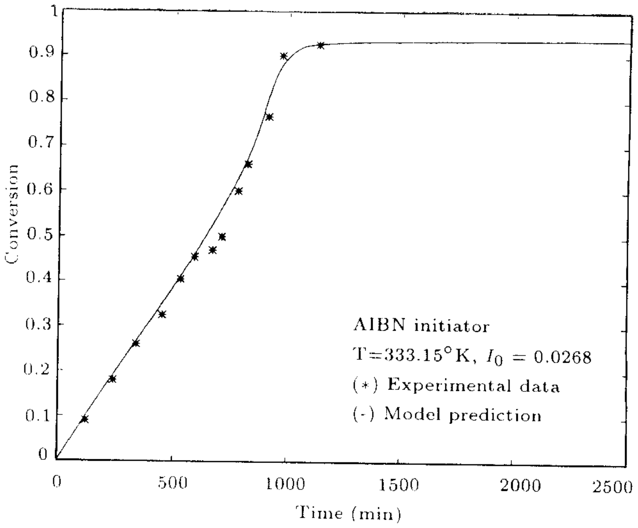

Figure 1. Variation of conversion versus time in polymerization of styrene at 60°C, $[I_0] = 0.0268$ (gmol AIBN/l), data of [1].

Table 3. Physical parameters used in the model.

	Styrene	**Polystyrene**
$\alpha(^\circ C^{-1})$	0.001	0.00048
$T_g(^\circ K)$	185	366.65
d (kg/l)	$0.924 - 0.000918(T - 273.15)$	$1.084 - 0.000605(T - 273.15)$

eported elsewhere. In Marten-Hamielec model, the greement between predicted and experimental data is bserved but only at conversions below 85% [1]. The xperimental data used in Figures 1 to 6 are the same ata that have been used by Marten-Hamielec and Vivaldo-Lima in their own models. The comparison with the experimental molecular weight data and the theoretical prediction have been illustrated in Figures 7 to 10. The agreement between M_w and M_n values is excellent. It should be noted that Marten-Hamielec

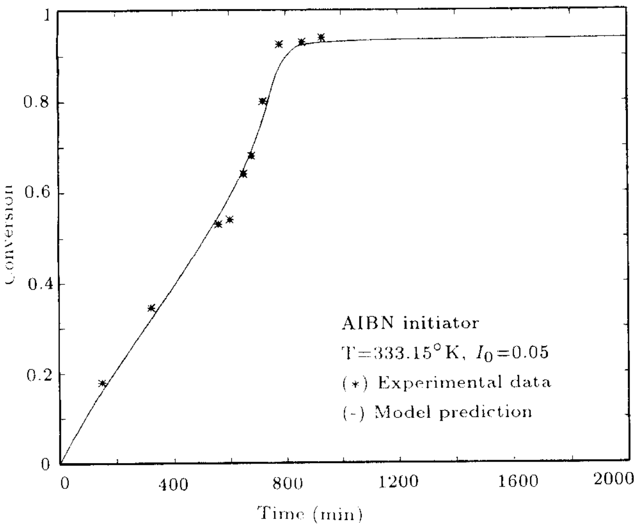

Figure 2. Variation of conversion versus time in polymerization of styrene at 60°C, $[I_0] = 0.05$ (gmol AIBN/l), data of [1].

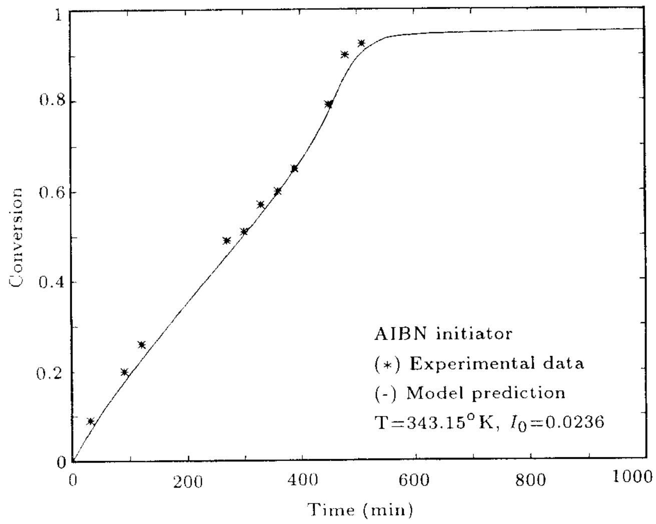

Figure 4. Variation of conversion versus time in polymerization of styrene at 70°C, $[I_0] = 0.0236$ (gmol AIBN/l), data of [4].

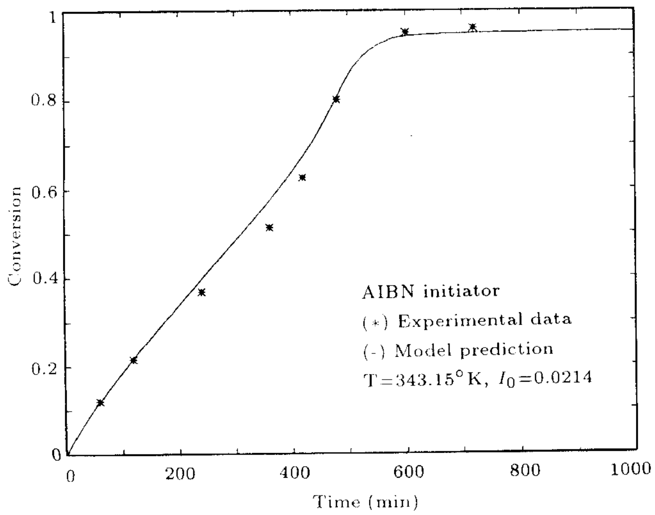

Figure 3. Variation of conversion versus time in polymerization of styrene at 70°C, $[I_0] = 0.0214$ (gmol AIBN/l), data of [4].

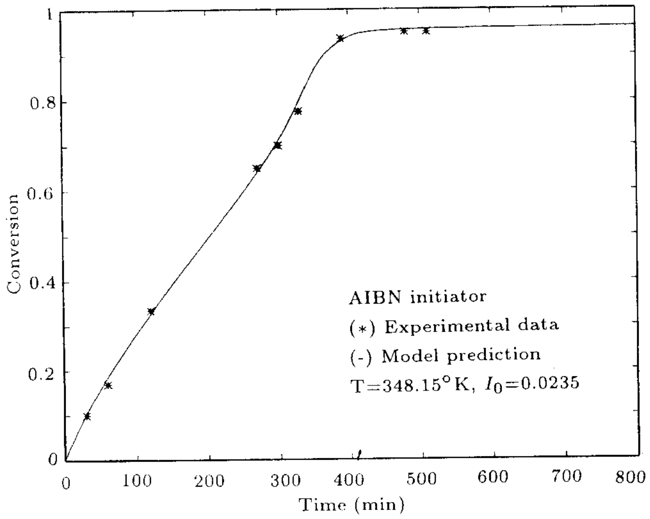

Figure 5. Variation of conversion versus time in polymerization of styrene at 75°C, $[I_0] = 0.0235$ (gmol AIBN/l), data of [4].

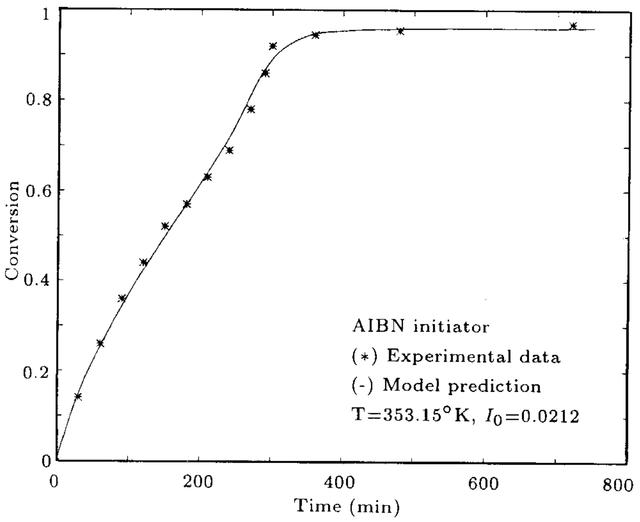

Figure 6. Variation of conversion versus time in polymerization of styrene at 80°C, $[I_0] = 0.0212$ (gmol AIBN/l), data of [4].

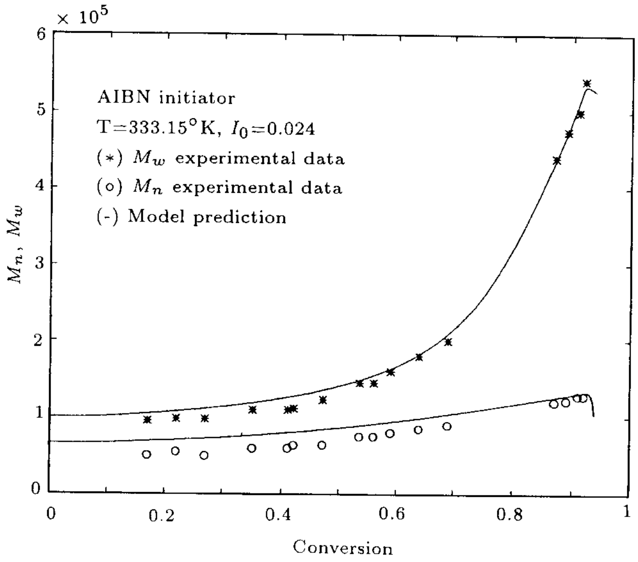

Figure 7. Variation of M_w and M_n versus conversion in polymerization of styrene at 60°C, $[I_0] = 0.024$ (gmol AIBN/l), data of [1].

model predictions for M_n is relatively good but for M_w is unsatisfactory.

The poor prediction by Marten-Hamielec could be attributed mainly to two factors:

Table 4. Kinetic constants used in the model.

k_p^0 (l/min)	$6.128 \times 10^8 \exp(-7068/RT)$
k_{tc}^0 (l/mol.min)	$7.55 \times 10^{10} \exp(-1677/RT)$
k_m (l/mol.min)	$6.128 \times 10^8 \exp(-13450/RT)$
k_d (min^{-1})	$12 \times 10^{16} \exp(-30714.02/RT)$
R(cal/mol.k)	1.987

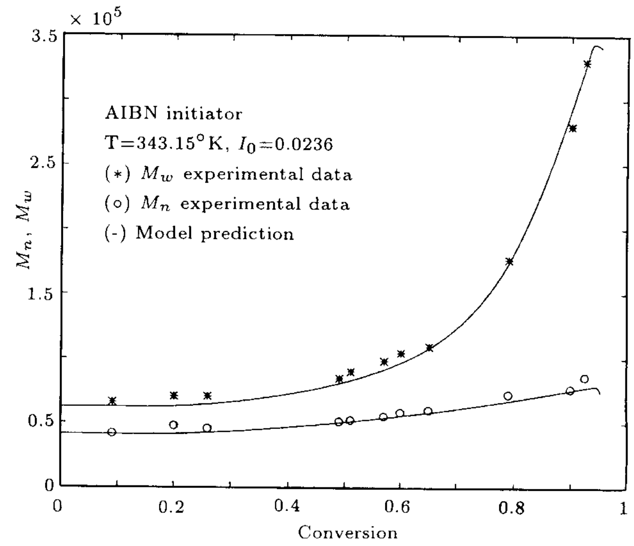

Figure 8. Variation of M_w and M_n versus conversion in polymerization of styrene at 70°C, $[I_0] = 0.0236$ (gmol AIBN/l), data of [4].

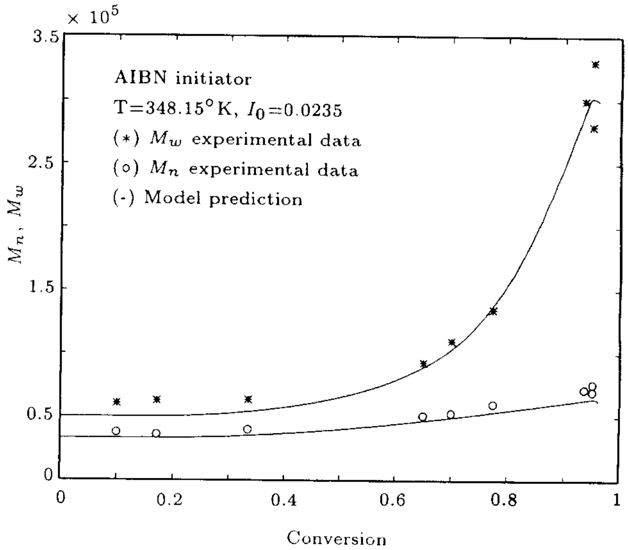

Figure 9. Variation of M_w and M_n versus conversion in polymerization of styrene at 75°C, $[I_0] = 0.0235$ (gmol AIBN/l), data of [1].

1. V_{fcr2} is considered as a fixed value independent of temperature variation;
2. The efficiency of initiator is also assumed to be constant.

The first factor could be the main cause of deviation at high conversions between Marten-Hamielec model predicted conversion values and the experimental data. The second factor is believed to cause deviation between predicted M_w values and the experimental data at high conversions. In the present model, V_{fcr2} has been defined as a function of temperature as shown in Equation 9. Furthermore, a novel correlation

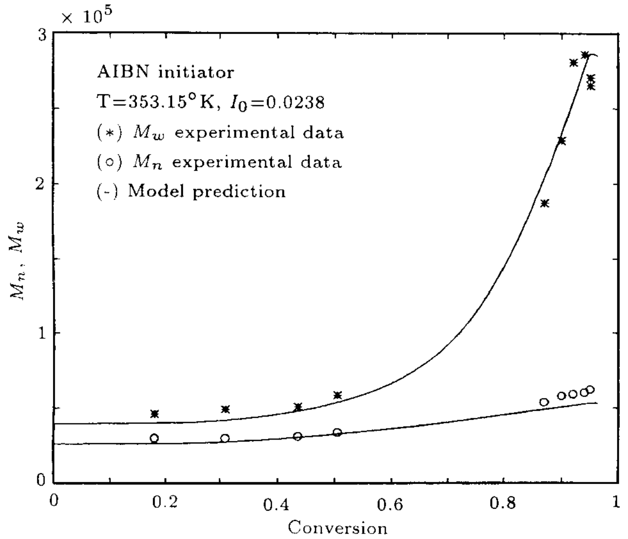

Figure 10. Variation of M_w and M_n versus conversion in polymerization of styrene at 80°C, $[I_0] = 0.0238$ (gmol AIBN/l), data of [1].

for initiator efficiency has been employed (Equations 3 and 4).

In Vivaldo-Lima model, two different termination constants are considered for M_n and M_w predictions, which is not justified in terms of polymerization mechanism. The agreement between the Vivaldo-Lima model predictions and the experimental data is just good. Moreover, in Vivaldo-Lima model, V_{fcr2} is a temperature-independent value and f_0 (initial initiator efficiency) is considered as a fixed value independent of temperature while in the model presented here f_0 is defined as a function of temperature (Equation 3). In addition, the correlation between f and free volume employed in Vivaldo-Lima model could be considered as another cause of deviation. It must be emphasized, that in the model presented here only one termination constant is considered.

CONCLUSION

A new kinetics model for free radical polymerization of styrene has been developed. The model is a modification of the earlier models presented namely, Marten-Hamielec and Vivaldo-Lima models. In this model, V_{fcr2} and f_0 are considered as a function of temperature, while in earlier models these values have been assumed to be constant. Also the initiator efficiency, f, is defined by a correlation which leads to better prediction than the correlation used by Vivaldo-Lima model. The model illustrates an excellent agreement with the experimental data at high conversions compared to the earlier models reported.

NOMENCLATURE

A	constant
C_{rd}	constant
d	density
f	initiator efficiency
I	initiator concentration
k_d	initiator decomposition kinetic constant
k_p	propagation kinetic constant
k_m	chaintransfer to monomer kinetic constant
k_{td}	termination by disproportionation kinetic constant
k_{tc}	termination by combination kinetic constant
m	constant
M_w	weight-average molecular weight
M_n	number-average molecular weight
M_{wcr}	critical value of M_w for gel effect
P	concentration of polymer
R	concentration of free radicals
T	temperature
T_g	glass transition temperature
V_f	total free volume
V_{fcr}	critical total free volume for gel effect
V_{fcr2}	critical total free volume for glassy effect
V	volume of reacting mixture

Greek Letter

ε	fractional volume change
λ	moments of live radical distribution
μ	moments of dead polymer distribution

Subscripts

0	initial conditions at $t = 0$
x, y	chain length

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