

Kinetics of Bulk Styrene Polymerization Catalyzed by Symmetrical Bifunctional Initiators

K. Y. CHOI,* W. R. LIANG,† and G. D. LEI, *Department of
Chemical and Nuclear Engineering, University of Maryland, College
Park, Maryland 20742*

Synopsis

The kinetics of bulk styrene polymerization catalyzed by symmetrical bifunctional initiators [2,5-dimethyl-2,5-bis(benzoyl peroxy) hexane] is studied. Being characterized by the presence of two peroxide groups of equal thermal stabilities, this bifunctional initiator system shows complex initiation, propagation, and termination reaction pathways. The kinetic model for bulk styrene polymerization with the bifunctional initiator is presented and compared with experimental data. The experimental data indicate that the model is quite satisfactory in describing the polymerization rate and polymer molecular weights for bulk styrene polymerization catalyzed by the symmetrical bifunctional initiator.

INTRODUCTION

The use of bifunctional initiators containing two labile groups (e.g., peroxy or azo) is a new way of optimizing polymer properties and polymerization processes. The decomposition characteristics of such initiators depend upon the stability of the labile groups and the nature of hydrocarbon bridge between them. Generally, there are two types of bifunctional initiators: (I) symmetrical bifunctional initiators containing two labile groups of equal stability and (II) unsymmetrical bifunctional initiators containing two labile groups of significantly different thermal stabilities. Under proper polymerization conditions, such bifunctional initiators can be used to enhance polymerization rates and to control polymer molecular weights more effectively than conventional monofunctional initiators.¹⁻³ For instance, the polymerization temperature can be varied during the reactor operation to better control the radical concentrations through sequential decomposition of labile groups of different thermal stabilities. Such nonisothermal reaction leads to the formation of polymers having considerably high molecular weight at high reaction rate. Since the bifunctional initiator molecule contains more than one labile group, the initiation, propagation, termination and chain transfer reaction pathways become quite complicated. In order to describe the kinetics of free radical polymerization catalyzed by such bifunctional initiators, it is important to have a quantitative kinetic model which can predict the progress of polymerization and the resulting polymer properties. Unfortunately, however,

*To whom correspondence should be addressed.

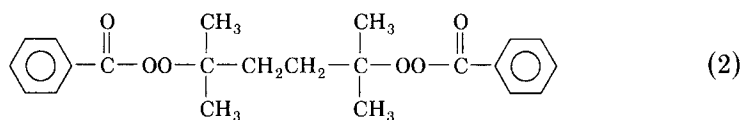
†On leave from Taiyuan University of Technology, Taiyuan, China.

there is a dearth of open literature on the kinetic modeling of the free radical polymerizations catalyzed by bifunctional initiators.^{3,4} In this paper, we shall derive a detailed mathematical model of polymerization kinetics for symmetrical bifunctional initiator. The model prediction of polymerization rates and polymer molecular weight properties are compared with experimental data.

The bifunctional initiator considered in the present study is the diperoxyester of the following structurally symmetrical form:

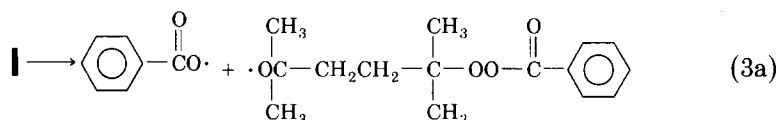


where R_1 and X represent hydrocarbon ligands. The specific initiator system chosen in our experimental study is commercially available 2,5-dimethyl-2,5-bis(benzoyl peroxy) hexane:



(I)

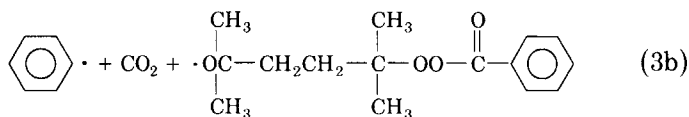
Upon heating, the initiator decomposes into two radical species as follows:



(II)

(III)

or



(IV)

(III)

The route that the peroxyester proceeds will depend on the stability of the phenyl radical (IV). Radical species (II) and (III) may further react via decarboxylation and β -scission reaction, respectively; however, there will be no net change in radical concentrations by such reactions. For the initiator shown in (2), the decomposition activation energies of the two peroxides are almost identical.^{5,6} When the hydrocarbon bridge between the peroxides is long, the stability of the second peroxide may change upon decomposition of the first peroxide.² The kinetic model we shall develop in this paper can be used to describe the polymerizations catalyzed by any of those initiators.

Kinetic Scheme

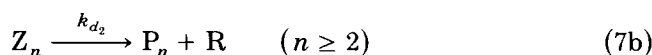
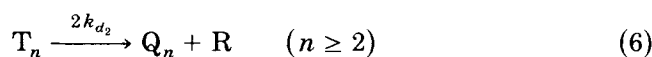
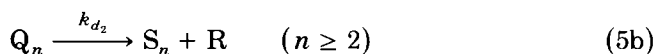
A mechanism of polymer formation in free radical polymerization initiated by bifunctional initiators is called poly-recombinational polymerization be-

TABLE I
Polymeric Species in Free Radical Polymerization Catalyzed by Symmetrical
Bifunctional Initiator^a

P_n :	· —————]
Q_n :	· ————— CO—OOCR ₁
S_n :	· —————
T_n :	R ₁ COO—OC ————— CO—OOCR ₁
Z_n :	[————— CO—OOCR ₁
M_n :	[—————]

^a. = free radical; —————] polymer chain with inactive chain end.

cause polymers formed in the early stages of polymerization contain undecomposed peroxide groups and these polymers participate in the reaction through reinitiation, propagation, chain transfer, and termination. As shown in Table I, six different polymeric species (P_n , Q_n , S_n , T_n , Z_n , and M_n) can be defined in accordance with the nature of the end units of the polymer chains. Note that P_n , Q_n , and S_n are the growing (or live) polymer radicals with n -monomer units and T_n , Z_n , and M_n are the inactive polymers with n -monomer units. However, Q_n , T_n , and Z_n species carry undecomposed peroxide groups (—CO—OOCR₁) on the chain ends. Thus such polymers can be reconverted to active radical species via additional thermal decomposition of the peroxides. The decomposition reactions of the primary diperoxyester initiator (I) and the polymeric initiators can be described as following:

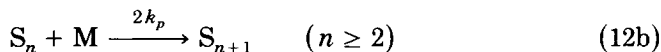
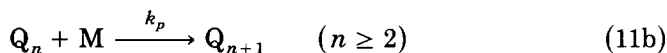
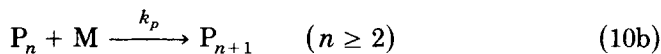
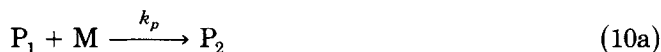


where k_{d_1} and k_{d_2} denote the decomposition rate constants of the peroxide groups in the primary initiators and in the polymers, respectively. Note that both the primary initiator (I) and the polymeric species T_n have dual functionality because they contain two undecomposed peroxides. Here, it is assumed that the decomposition of primary radical species R' to diradical species is negligible. In styrene polymerization under 110°C the effect of thermal initiation is negligible⁷ and thus is not included in the above initiation scheme. For the bifunctional initiator shown in (2), the decomposition activation energies of the two peroxides have been found almost identical.⁶ It is also assumed that the thermal stability of the peroxides in polymer chains is independent of polymer chain length.¹

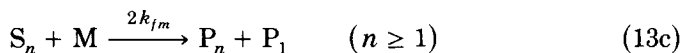
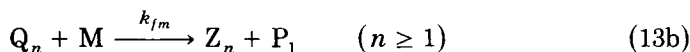
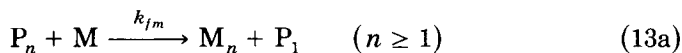
The initiation reactions by the primary radicals take place as follows:



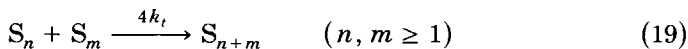
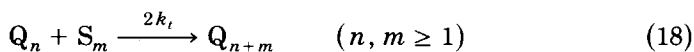
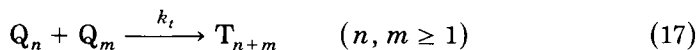
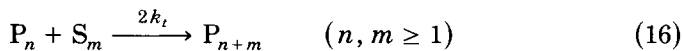
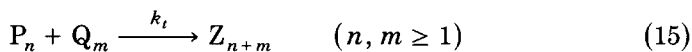
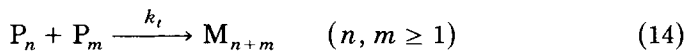
The propagation reactions are:



where the propagation rate constants are also assumed to be independent of polymer chain length. Since species S_n contains two radicals per molecule, the propagation and termination reactions involving these polymers occur twice as fast as those involving the other polymeric species. The following chain transfer reactions to monomer also occur:



When the termination of growing polymer chains occurs exclusively by combination mechanism (e.g., styrene polymerization), the following termination reactions will take place:



Note that various reactive polymeric species (e.g., Q_n , T_n , and Z_n) containing undecomposed peroxide groups are formed by the combination termination reactions and these species, upon subsequent decomposition and polymerization, will lead to the formation of polymers having extended polymer chain lengths. The termination by primary radicals is assumed negligible in the above scheme. In eqs. (14)–(19), the combination termination rate constants for the macroradical species are assumed to be identical.

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 is referred to as gel effect. Although the gel effect in styrene polymerization is not as strong as that in methyl methacrylate polymerization, the gel effect becomes important at high conversion or low solvent volume fraction. In this study, the gel effect correlation suggested by Friis and Hamielec⁸ for bulk styrene polymerization is used:

$$g_t \equiv \frac{k_t}{k_{t0}} = \exp[-2(Bx + Cx^2 + Dx^3)] \quad (20a)$$

where x and k_{t0} denote the monomer conversion and the termination rate constant at zero monomer conversion, respectively, and

$$B = 2.5882 - 3.4852 \times 10^{-3}T \quad (K)$$

$$C = 4.3108 - 1.2635 \times 10^{-2}T \quad (K)$$

$$D = -4.6488 + 1.9026 \times 10^{-2}T \quad (K) \quad (20b)$$

The coefficients have been determined by using the optimal parameter estimation method for the experimental monomer conversion data.

With the kinetic scheme proposed above, the rate expressions for various reaction steps take the following forms:

For initiator:

$$\frac{dI}{dt} = -2k_{d_1}I \quad (21)$$

$$\frac{dR}{dt} = 2f_1k_{d_1}I - k_{i_1}RM + f_1k_{d_2}(Q + 2T + Z) \quad (22)$$

$$\frac{dR'}{dt} = 2f_2k_{d_1}I - k_{i_2}R'M \quad (23)$$

where f_1 and f_2 are the initiator efficiencies which indicate the fraction of primary radicals (R and R') being involved in chain initiation. It is assumed that the initiator efficiencies are constant during the course of polymerization.

For growing polymers:

$$\begin{aligned} \frac{dP_1}{dt} = & k_{i_1}RM + k_{d_2}Z_1 + k_{f_m}M(P - P_1 + Q + 2S + 2S_1) - k_pMP_1 \\ & - k_tP_1(P + Q + 2S) \end{aligned} \quad (24a)$$

$$\begin{aligned} \frac{dP_n}{dt} = & k_{d_2}Z_n + k_{f_m}M(2S_n - P_n) + k_pM(P_{n-1} - P_n) \\ & - k_tP_n(P + Q + 2S) + 2k_t \sum_{m=1}^{n-1} P_{n-m}S_m \quad (n \geq 2) \end{aligned} \quad (24b)$$

$$\frac{dQ_1}{dt} = k_{i_2}R'M - k_{d_2}Q_1 - k_{f_m}MQ_1 - k_pMQ_1 - k_tQ_1(P + Q + 2S) \quad (25a)$$

$$\begin{aligned} \frac{dQ_n}{dt} = & k_{d_2}(2T_n - Q_n) - k_{f_m}MQ_n + k_pM(Q_{n-1} - Q_n) \\ & - k_tQ_n(P + Q + 2S) + 2k_t \sum_{m=1}^{n-1} Q_{n-m}S_m \quad (n \geq 2) \end{aligned} \quad (25b)$$

$$\frac{dS_1}{dt} = k_{d_2}Q_1 - 2k_{f_m}MS_1 - 2k_pMS_1 - 2k_tS_1(P + Q + 2S) \quad (26a)$$

$$\begin{aligned} \frac{dS_n}{dt} = & k_{d_2}Q_n - 2k_{f_m}MS_n + 2k_pM(S_{n-1} - S_n) - 2k_tS_n(P + Q + 2S) \\ & + 2k_t \sum_{m=1}^{n-1} S_{n-m}S_m \quad (n \geq 2) \end{aligned} \quad (26b)$$

For temporarily inactive polymers:

$$\frac{dT_n}{dt} = -2k_{d_2}T_n + \frac{k_t}{2} \sum_{m=1}^{n-1} Q_{n-m}Q_m \quad (n \geq 2) \quad (27)$$

$$\frac{dZ_1}{dt} = -k_{d_2}Z_1 + k_{f_m}MQ_1 \quad (28a)$$

$$\frac{dZ_n}{dt} = -k_{d_2}Z_n + k_{f_m}MQ_n + k_t \sum_{m=1}^{n-1} P_{n-m}Q_m \quad (n \geq 2) \quad (28b)$$

For monomers and dead polymers:

$$\frac{dM}{dt} = -k_{i_1}RM - k_{i_2}R'M - k_{fm}M(P + Q + 2S) - k_pM(P + Q + 2S) \quad (29)$$

$$\frac{dM_n}{dt} = k_{fm}MP_n + \frac{k_t}{2} \sum_{m=1}^{n-1} P_{n-m}P_m \quad (n \geq 2) \quad (30)$$

where P , Q , S , T , and Z are the total concentrations of the corresponding polymeric species, i.e.,

$$\begin{aligned} P &= \sum_{n=1}^{\infty} P_n, & Q &= \sum_{n=1}^{\infty} Q_n, & S &= \sum_{n=1}^{\infty} S_n \\ T &= \sum_{n=2}^{\infty} T_n, & Z &= \sum_{n=1}^{\infty} Z_n \end{aligned} \quad (31)$$

The number average polymer chain length (X_N) and the weight average polymer chain length (X_W) are determined by using the molecular weight moments defined by

$$\lambda_{\xi, k} \equiv \sum_{n=j}^{\infty} n^k \xi_n \quad [\xi = P, Q, S, Z(j=1); T(j=2)] \quad (32a)$$

$$\lambda_k^d \equiv \sum_{n=2}^{\infty} n^k M_n \quad (32b)$$

where $\lambda_{\xi, k}$ and λ_k^d denote the k th moment and polymeric species ξ and dead polymers, respectively. The average chain length are defined by

$$X_N = \frac{\sum_{\xi} \lambda_{\xi, 1} + \lambda_1^d}{\sum_{\xi} \lambda_{\xi, 0} + \lambda_0^d} \quad (\xi = P, Q, S, T, Z) \quad (33a)$$

$$X_W = \frac{\sum_{\xi} \lambda_{\xi, 2} + \lambda_2^d}{\sum_{\xi} \lambda_{\xi, 1} + \lambda_1^d} \quad (\xi = P, Q, S, T, Z) \quad (33b)$$

Using the rate expressions for various species, one can derive the following molecular weight moment equations:

Polymeric species P_n :

$$\frac{d\lambda_{P,0}}{dt} \left(= \frac{dP}{dt} \right) = k_{i_1}RM + k_{d_2}Z + k_{f_m}M(Q + 4S) - k_tP(P + Q) \quad (34a)$$

$$\begin{aligned} \frac{d\lambda_{P,1}}{dt} &= k_{i_1}RM + k_{d_2}\lambda_{Z,1} + k_{f_m}M(P - \lambda_{P,1} + Q + 2S + 2\lambda_{S,1}) \\ &\quad + k_pMP + k_t[2P\lambda_{S,1} - (P + Q)\lambda_{P,1}] \end{aligned} \quad (34b)$$

$$\begin{aligned} \frac{d\lambda_{P,2}}{dt} &= k_{i_1}RM + k_{d_2}\lambda_{Z,2} + k_{f_m}M(P - \lambda_{P,2} + Q + 2S + 2\lambda_{S,2}) \\ &\quad + k_pM(2\lambda_{P,1} + P) \\ &\quad + k_t[4\lambda_{S,1}\lambda_{P,1} + 2\lambda_{S,2}P - (P + Q)\lambda_{P,2}] \end{aligned} \quad (34c)$$

Polymeric species Q_n :

$$\frac{d\lambda_{Q,0}}{dt} \left(= \frac{dQ}{dt} \right) = k_{i_2}R'M + k_{d_2}(2T - Q) - k_{f_m}MQ - k_tQ(P + Q) \quad (35a)$$

$$\begin{aligned} \frac{d\lambda_{Q,1}}{dt} &= k_{i_2}R'M + k_{d_2}(2\lambda_{T,1} - \lambda_{Q,1}) - k_{f_m}M\lambda_{Q,1} + k_pMQ \\ &\quad + k_t[2\lambda_{S,1}Q - (P + Q)\lambda_{Q,1}] \end{aligned} \quad (35b)$$

$$\begin{aligned} \frac{d\lambda_{Q,2}}{dt} &= k_{i_2}R'M + k_{d_2}(2\lambda_{T,2} - \lambda_{Q,2}) \\ &\quad - k_{f_m}M\lambda_{Q,2} + k_pM(2\lambda_{Q,1} + Q) \\ &\quad + k_t[4\lambda_{S,1}\lambda_{Q,1} + 2\lambda_{S,2}Q - (P + Q)\lambda_{Q,2}] \end{aligned} \quad (35c)$$

Polymeric species S_n :

$$\frac{d\lambda_{S,0}}{dt} \left(= \frac{dS}{dt} \right) = k_{d_2}Q - 2k_{f_m}MS - 2k_t[S(P + Q) + S^2] \quad (36a)$$

$$\frac{d\lambda_{S,1}}{dt} = k_{d_2}\lambda_{Q,1} - 2k_{f_m}M\lambda_{S,1} + 2k_pMS - 2k_t(P + Q)\lambda_{S,1} \quad (36b)$$

$$\begin{aligned} \frac{d\lambda_{S,2}}{dt} &= k_{d_2}\lambda_{Q,2} - 2k_{f_m}M\lambda_{S,2} + 2k_pM(2\lambda_{S,1} + S) \\ &\quad + k_t[4\lambda_{S,1}^2 - 2(P + Q)\lambda_{S,2}] \end{aligned} \quad (36c)$$

Polymeric species T_n :

$$\frac{d\lambda_{T,0}}{dt} \left(= \frac{dT}{dt} \right) = -2k_{d_2}T + \frac{k_t}{2}Q^2 \quad (37a)$$

$$\frac{d\lambda_{T,1}}{dt} = -2k_{d_2}\lambda_{T,1} + k_t\lambda_{Q,1}Q \quad (37b)$$

$$\frac{d\lambda_{T,2}}{dt} = -2k_{d_2}\lambda_{T,2} + k_t(\lambda_{Q,2}Q + \lambda_{Q,1}^2) \quad (37c)$$

Polymeric species Z_n :

$$\frac{d\lambda_{Z,0}}{dt} \left(= \frac{dZ}{dt} \right) = -k_{d_2}Z + k_{fm}MQ + k_tPQ \quad (38a)$$

$$\frac{d\lambda_{Z,1}}{dt} = -k_{d_2}\lambda_{Z,1} + k_{fm}M\lambda_{Q,1} + k_t(\lambda_{P,1}Q + \lambda_{Q,1}P) \quad (38b)$$

$$\frac{d\lambda_{Z,2}}{dt} = -k_{d_2}\lambda_{Z,2} + k_{fm}M\lambda_{Q,2} + k_t(\lambda_{P,2}Q + 2\lambda_{P,1}\lambda_{Q,1} + \lambda_{Q,2}P) \quad (38c)$$

Dead polymers:

$$\frac{d\lambda_0^d}{dt} = k_{fm}M(P - P_1) + \frac{k_t}{2}P^2 \quad (39a)$$

$$\frac{d\lambda_1^d}{dt} = k_{fm}M(\lambda_{P,1} - P_1) + k_tP\lambda_{P,1} \quad (39b)$$

$$\frac{d\lambda_2^d}{dt} = k_{fm}M(\lambda_{P,2} - P_1) + k_t(P\lambda_{P,2} + \lambda_{P,1}^2) \quad (39c)$$

An application of quasi-steady state approximation to live radical species leads to the following algebraic equations:

$$k_tP^2 + k_tQP - 2f_1k_{d_1}I - f_1k_{d_2}(Q + T + 2Z) - k_{fm}M(Q + 4S) = 0 \quad (40a)$$

$$k_tQ^2 + (k_tP + k_{d_2} + k_{fm}M)Q - 2(f_2k_{d_1}I + k_{d_2}T) = 0 \quad (40b)$$

$$2k_tS^2 + 2(k_tP + k_tQ + k_{fm}M)S - k_{d_2}Q = 0 \quad (40c)$$

Those equations are solved simultaneously by the Newton-Raphson method. In order to compute the molecular weight averages, various moment equations are solved with material balance equations by the fourth-order Runge-Kutta method.

EXPERIMENTAL

Polymerization experiments were performed using pyrex test tubes under nitrogen atmosphere. Styrene (Aldrich Chemical) was purified by standard method. The bifunctional initiator (2,5-dimethyl-2,5-bis(benzoyl peroxy)

TABLE II
 Numerical Values of Kinetic Constants^{6,10}

$k_{d_1} = 7.111 \times 10^{16} \exp(-36,800/RT) \text{ (s}^{-1}\text{)}$
$k_{d_2} = 7.111 \times 10^{16} \exp(-36,800/RT) \text{ (s}^{-1}\text{)}$
$f_1 = f_2 = 0.7$
$k_p = 1.051 \times 10^7 \exp(-7,060/RT) \text{ (L/mol s)}$
$k_{t0} = 1.260 \times 10^9 \exp(-1,680/RT) \text{ (L/mol s)}$
$k_{i_1} = k_{i_2} \approx k_p$
$k_{fm} = 4.033 \times 10^4 \exp(-10,280/RT) \text{ (L/mol s)}$
$M_0 = 8.728 \text{ mol/L}$

hexane [Luperox 118]) was supplied by the Pennwalt-Lucidol Company. The polymer samples were dissolved in benzene and precipitated by adding excess methanol. This procedure was repeated several times to ensure that unreacted monomer was completely extracted from the polymer. The samples were dried *in vacuo* and the monomer conversion was measured by gravimetric method. The molecular weight and molecular weight distribution of polystyrene samples were determined by gel permeation chromatography using tetrahydrofuran as a solvent. In order to confirm the isothermal reaction conditions, several test experiments were performed by inserting a thermocouple into the test tube and monitoring the temperature of reaction mixture during the course of polymerization. For the temperature range 90–120°C, the maximum temperature difference between the oil bath and the reaction mixture was less than 1.5°C.

DISCUSSION OF RESULTS

The effect of polymerization temperature on monomer conversion and polymer molecular weight was first studied. The numerical values of kinetic

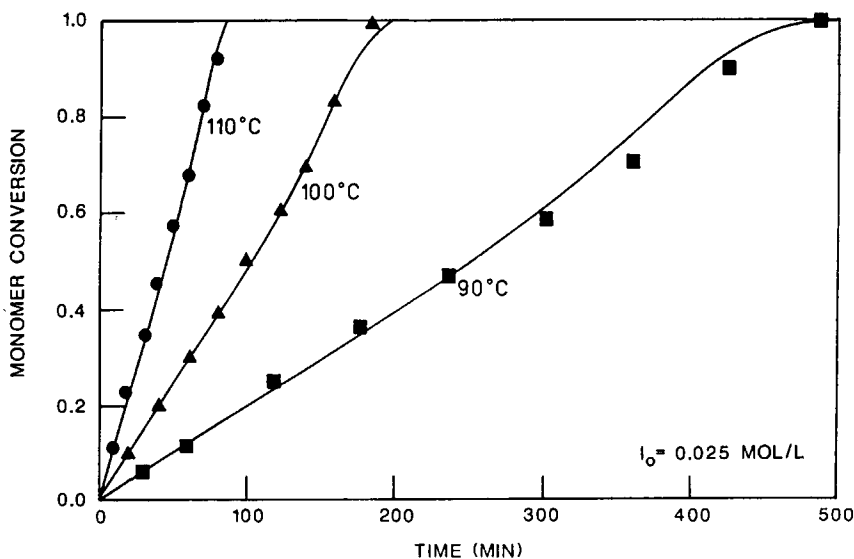


Fig. 1. The effect of temperature on monomer conversion: (—) model prediction; (●, ▲, ■) experimental data; $I_0 = 0.025 \text{ mol/L}$.

parameters used in our numerical simulation are listed in Table II. Figure 1 shows the monomer conversion profiles at three different temperatures (i.e., 90, 100, 110°C). The agreement between predicted and experimental data is excellent for the entire range of monomer conversion. Figure 2 also shows that the predicted number average molecular weight (M_N) agrees very well with the experimental data. However, the weight average molecular weight (M_W) predicted by the model is satisfactory at low to intermediate monomer

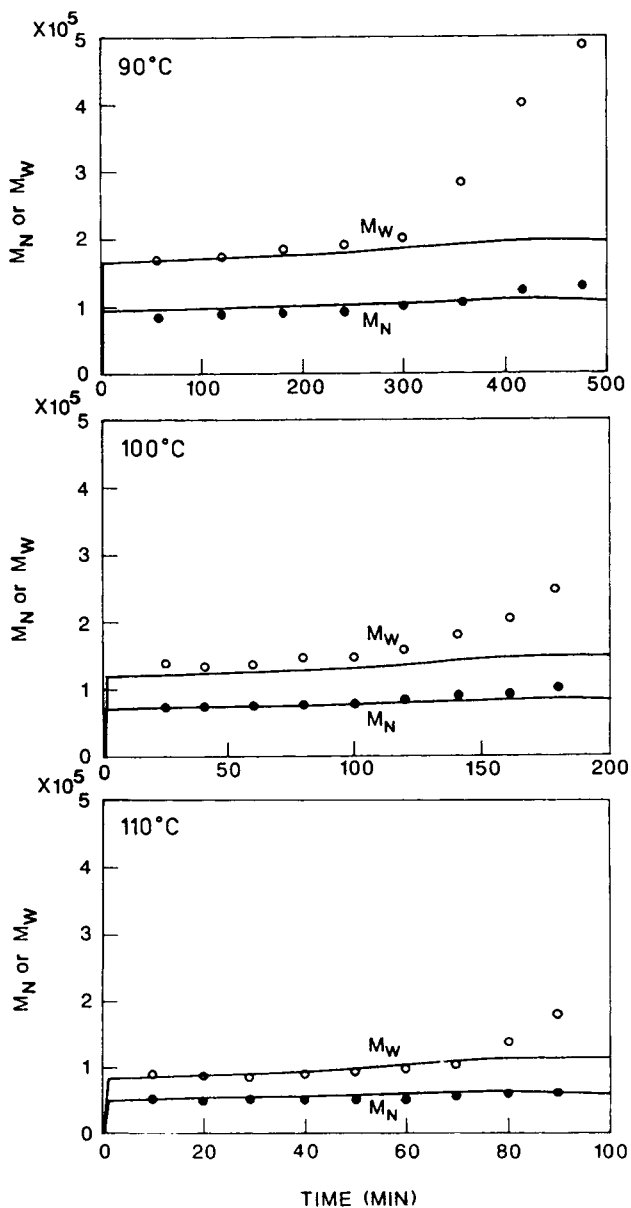


Fig. 2. The effect of temperature on molecular weights: (—) model prediction; (O, ●) experimental data; $I_0 = 0.025$ mol/L.

conversion ($\sim 60\%$) for 90 and 100°C . At 110°C , the predicted M_w value is quite good up to about 90% conversion. The similar phenomenon of rapidly increasing M_w at high monomer conversion was also reported in the literature for bulk styrene polymerization with AIBN.⁹ This indicates that the gel effect is rather strong in bulk styrene polymerization at about 60–90% of monomer conversion. It is also interesting to observe that the polydispersity (M_w/M_n) at near complete conversion tends to increase with a decrease in polymerization temperature.

The effect of initiator concentration was also studied at 100°C . Figure 3 shows predicted and experimentally observed monomer conversion profiles for three different initiator concentrations. Again, excellent agreement between the model prediction and experimental data has been obtained. The number average molecular weight (M_n) predicted by the model at different initiator concentration is quite satisfactory up to very high monomer conversion as shown in Figure 4. However, the predictions of M_w values tend to become poor with a decrease in initiator concentration.

It is also interesting to note that the polydispersity (M_w/M_n) is almost always less than about 2.5 when the bifunctional initiator is used. In bulk styrene polymerization with monofunctional initiators such as AIBN under similar reaction conditions, polydispersity value increases rapidly to above 3.0 as monomer conversion increases to high values.⁹ Thus, our experimental data suggests that relatively narrower molecular weight distribution can be obtained by the use of symmetrical bifunctional initiator.

The composition distribution of polymerizing mixture at three different reaction temperatures is illustrated in Figure 5. The concentrations of live polymeric species (e.g., P_n , Q_n , S_n) are very small (10^{-6} – 10^{-10} mol/L). Figure 5 indicates that a significant amount of polymeric species containing unde-

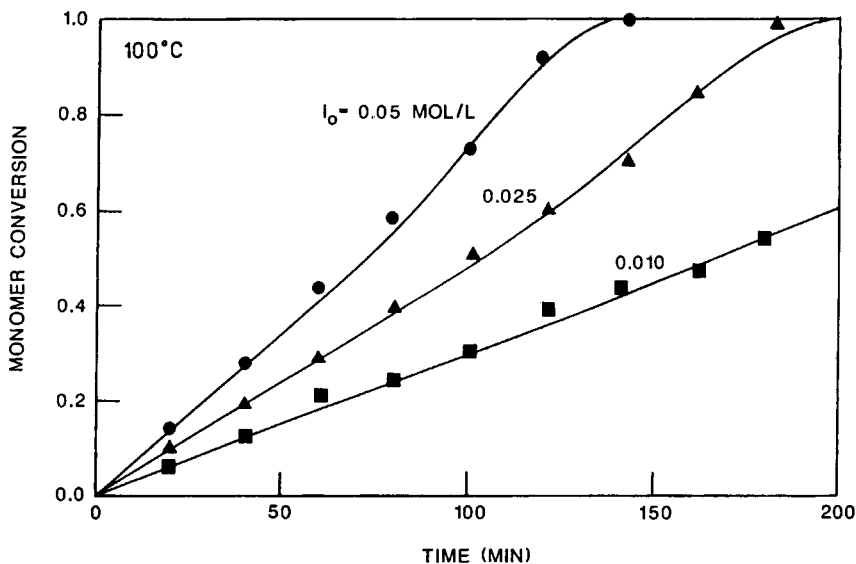


Fig. 3. The effect of initiator concentration on monomer conversion, 100°C : (—) model prediction; (●, ▲, ■) experimental data.

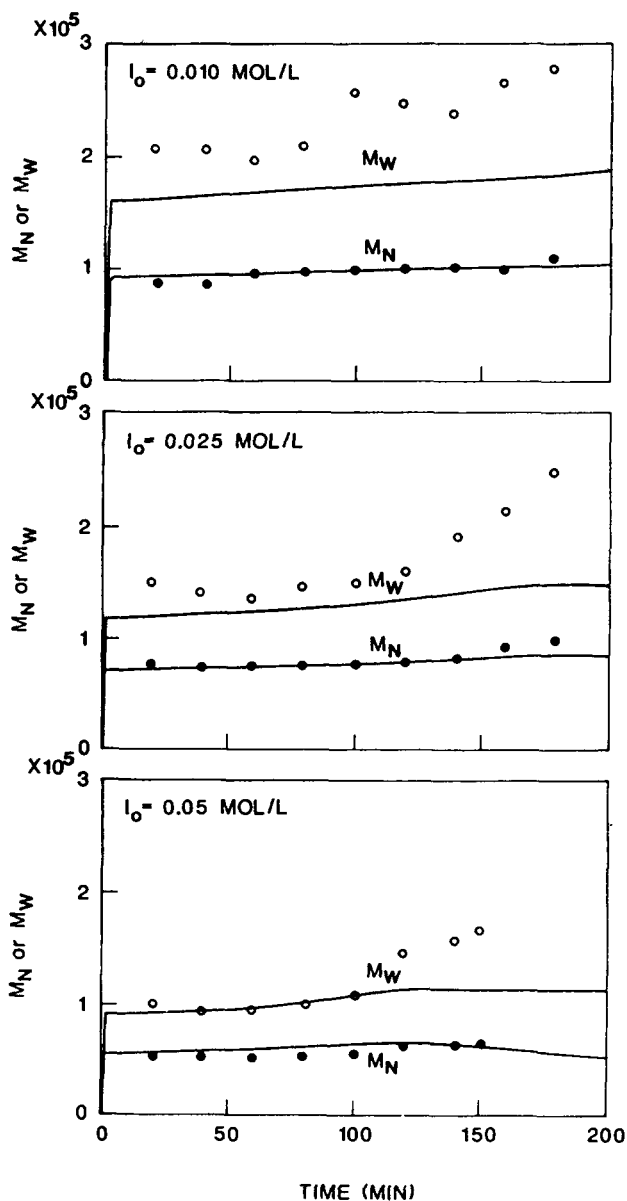


Fig. 4. The effect of initiator concentration on molecular weights, 100°C: (—) model prediction; (○, ●) experimental data.

composed peroxides is present at high monomer conversion. Such polymers can be used as polymeric initiators in performing block copolymerization with other monomers. The molecular weight of various polymeric species at three different temperatures are also shown in Figure 6. Note that diradical species (S_n) have high molecular weights until very high monomer conversion is reached. The contributions of those live polymers (i.e., P_n, Q_n, S_n species) to overall molecular weight are negligible due to their low concentrations in the

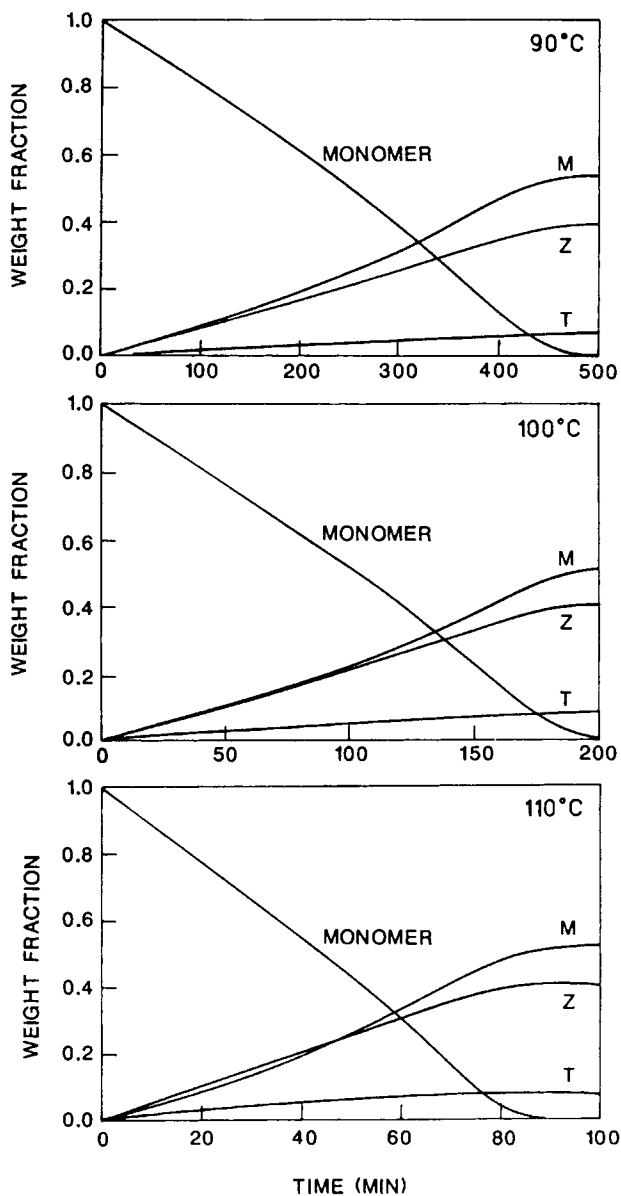


Fig. 5. Composition profiles of various species at different reaction temperatures, $I_0 = 0.025$ mol/L.

reaction mixture. For dead or inactive polymers, the molecular weight decreases as the number of peroxides in the polymer chains decreases (i.e., $M_{N,T} > M_{N,Z} > M_{N,M}$).

CONCLUDING REMARKS

In this paper, a detailed kinetic model for bulk styrene polymerization initiated by symmetric bifunctional initiator is presented and compared with

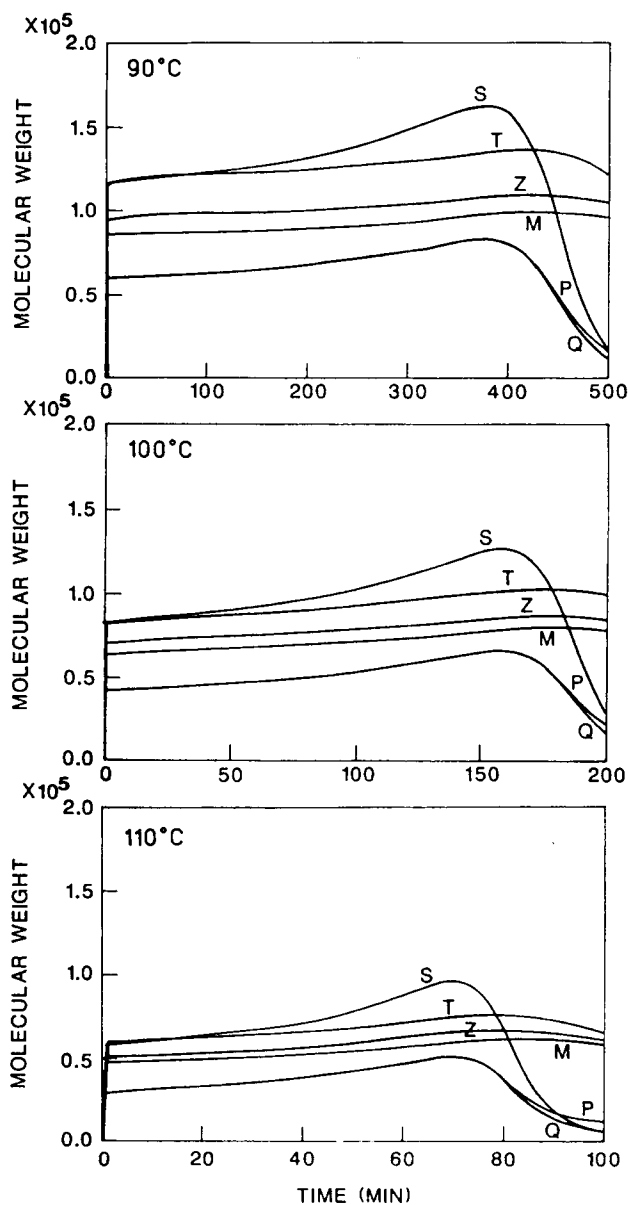


Fig. 6. Molecular weight profiles of various polymeric species at different temperatures, $I_0 = 0.025$ mol/L.

experimental data. In the proposed kinetic model, complex initiator, propagation, termination, and chain transfer reactions by various polymeric species are considered. The experimental results indicate that the proposed kinetic model can satisfactorily describe the progress of reaction and the resulting polymer molecular weight for the experimental conditions employed. The gel effect was quite clearly observed at high monomer conversion; however, the polydispersity was less than 2.5 even at complete monomer conversion. Al-

though the model was tested on the symmetrical bifunctional initiator in which two peroxide groups have identical decomposition activation energies, the proposed model can also be used for the polymerizations catalyzed by semi-symmetrical initiators in which the decomposition activation energy of one of the two peroxide groups is affected by the decomposition of neighboring peroxide group.

This work was supported in part by the National Science Foundation (CBT-85-52428) and by the Systems Research Center at the University of Maryland. We also thank the Pennwalt-Lucidol Company for the generous donation of initiators for this study. Computing time provided by the Computer Science Center at the University of Maryland is also acknowledged. Financial support for W. R. Liang by the Chinese government is also appreciated.

References

1. S. S. Ivanchev, *Polym. Sci. USSR*, **20**, 2157 (1979).
2. A. I. Prisyazhnyuk and S. S. Ivanchev, *Polym. Sci. USSR*, **12**(2), 514 (1970).
3. K. Y. Choi and G. D. Lei, *AIChE J.*, **33**(12), 2067 (1987).
4. K. F. O'Driscoll and J. C. Bevington, *Eur. Polym. J.*, **21**(12), 1039 (1985).
5. V. R. Kamath, private communication (1986).
6. Technical Bulletin, Pennwalt-Lucidol Company (1986).
7. M. H. George, in *Vinyl Polymerization*, G. E. Ham, Ed., Marcel Dekker, New York, 1967, vol. 1.
8. N. Friis and A. E. Hamielec, *Am. Chem. Soc. Symp. Ser.*, **24**, 82 (1976).
9. F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.*, **27**, 489 (1982).
10. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.

Received July 2, 1987

Accepted August 17, 1987