Modeling of Free-Radical Polymerization of Styrene by Bifunctional Initiators

A detailed kinetic model for the bulk styrene polymerization initiated by symmetrical diperoxyester bifunctional initiators is presented. When chain termination occurs via a combination termination mechanism, six distinct polymeric species are identified in accordance with the nature of the polymer end units. It is shown that the unequal thermal decomposition characteristics of the peroxides of the bifunctional initiator system lead to the formation of polymers having considerably higher molecular weight than those obtained by the monofunctional intiator systems. It has also been found that high monomer conversion, high molecular weight, and narrow molecular weight distribution can be obtained simultaneously by using the bifunctional initiators at high reaction temperatures. This is due to the reinitiation and propagation of inactive polymers carrying undecomposed peroxides. The molecular-weight-increasing effect of the bifunctional initiator is more pronounced at high reaction temperatures. The new possibilities of increasing the monomer conversion and controlling the polymer molecular weight properties more effectively through the use of bifunctional initiators are discussed.

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Introduction

The application of multifunctional initiators to industrial free-radical polymerizations of vinyl or styrenic monomers is a relatively new area of research. In contrast to the conventional free-radical polymerization initiators such as benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) having only one labile peroxide or azo group, multifunctional initiators contain more than one labile group (peroxide and/or azo) having distinctively different thermal decomposition characteristics. Although the use of "finishing" catalysts having high activation energies together with main monofunctional initiators is not uncommon in many industrial free-radical polymerization processes in order to enhance the monomer conversion, such mixed initiator systems or single conventional monofunctional initiator systems do not produce polymers of substantially high molecular weight, narrow molecular weight distribution (MWD), and high monomer conversion simultaneously (Kamath and Harpell, 1978).

By using properly chosen multifunctional initiators and polymerization conditions, the conversion of monomers and the polymer molecular weight can be significantly increased in a well-controlled manner. This has not been possible with conventional monofunctional free-radical initiators. Some multifunctional initiators have also been used successfully for block copolymerizations via sequential monomer incorporation techniques (Piirma and Chou, 1979; Gunesin and Piirma, 1981; Waltz and Heitz, 1978). Therefore, it is believed that the innovative application of multifunctional free-radical initiators opens a new avenue for tailor-making polymers or modifying polymer properties without requiring significant reactor equipment modifications. Recently O'Driscoll and Bevington (1985) analyzed the effect of multifunctional initiators on polymer molecular weight distribution in free-radical polymerization using both Schultz-Flory distribution function and Monte Carlo simulation methods. They demonstrated that altering the molecular weight distribution was possible by inducing the sequential decomposition of two labile groups in a bifunctional initiator.

In this paper, we present a detailed kinetic model for the free-

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radical polymerization of styrene catalyzed by bifunctional initiators that contain two labile peroxide groups. The effect of unequal thermal stabilities of peroxide groups on the monomer conversion, polymer molecular weight, and MWD are examined for various polymerization conditions.

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

$$R_1COO\text{—}OOCXCOO\text{—}OOCR_1 \qquad (1)$$

where R_1 and X represent hydrocarbon ligands. The specific initiator system chosen in our numerical simulation study is the diperoxyester studied by Prisyazhnyuk and Ivanchev (1970):

$$\underset{(I)}{CH_3(CH_2)_6COO\text{—}OOC[CH_2CHCl]COO\text{—}OOC(CH_2)_6CH_3} \qquad (2)$$

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

$$I \xrightarrow{\Delta} \underset{(R)}{CH_3(CH_2)_6COO\cdot} + \underset{(R')}{\cdot OOC\,[CH_2CHCl]COO\text{—}OOC(CH_2)_6CH_3} \qquad (3)$$

where the primary radical species R' carries an undecomposed peroxide group that may decompose further during the course of polymerization. It is assumed that the peroxide groups of the same structure in the symmetrical primary initiator as shown in Eq. 1 have the same decomposition rate constant when the ligand between the peroxides is small. If the bridge (i.e., hydrocarbon ligand X) between the peroxide groups is short enough for an inductive effect to be transmitted, the thermal stability of a group will change considerably when the neighboring group decomposes (Ivanchev, 1979). For the bifunctional initiator shown above, it has been found that the decomposition activation energy of the peroxide group in R' is quite different from that of the peroxides in the original initiator I. When the radical species R' is involved in subsequent polymerization, polymers carrying labile peroxide end groups will be formed and such polymers are called reactive polymers or polymeric initiators. As will be shown in the following discussion, the existence of two radical species (R and R') creates quite complex reinitiation, propagation, and termination reaction kinetics. As a result, the polymers produced by the bifunctional initiator will have some unique properties. It is the objective of this paper to present a detailed kinectic model of the free-radical polymerization of styrene catalyzed by the bifunctional initiator system of the type of Eq. 1 and to characterize the polymerization behavior in a quantitative manner.

Kinetic Modeling

A mechanism of polymer formation in free-radical polymerization initiated by bifunctional initiators is called poly-recombinational polymerization because reactive macromolecules formed in the early stages of polymerization participate in the reaction through reinitiation, propagation, and termination. As shown in Table 1, 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 (—COO—OOCR$_1$) on the chain ends. Thus such polymers can be reconverted to active radical species by additional thermal decomposition of the peroxides. The decomposition reactions of the primary diperoxyester initiator I and the polymeric initiators can be described as follows:

Table 1. Polymeric Species

P_n: ●———OOCR$_1$
Q_n: ●———COO—OOCR$_1$
S_n: ●———●
T_n: R$_1$COO—OOC———COO—OOCR$_1$
Z_n: R$_1$COO———COO—OOCR$_1$
M_n: R$_1$COO———OOCR$_1$

● free radical; ——— polymer chain

$$I \xrightarrow{2k_{d_1}} R + R' \qquad (4)$$

$$Q_1 \xrightarrow{k_{d_2}} S_1 + R \qquad (5.a)$$

$$Q_n \xrightarrow{k_{d_2}} S_n + R \quad (n \geq 2) \qquad (5.b)$$

$$T_n \xrightarrow{2k_{d_2}} Q_n + R \quad (n \geq 2) \qquad (6)$$

$$Z_n \xrightarrow{k_{d_2}} P_n + R \quad (n \geq 2) \qquad (7)$$

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 β-scission reaction, induced decomposition (chain transfer to initiator), decarboxylation reaction, and cyclization reaction do not occur. The decomposition of primary radical species R' to diradical species is also assumed to be negligible. In styrene polymerization under 100°C, the effect of thermal initiation is negligible (George, 1967) and thus is not included in the above initiation scheme. According to Ivanchev (1979), the decomposition rate constants of more stable peroxides (i.e., peroxides in Q_n, T_n, and Z_n) are independent of polymer chain length.

The initiation of polymer chain propagation by the primary radicals takes place as follows:

$$R + M \xrightarrow{k_{i_1}} P_1 \qquad (8)$$

$$R' + M \xrightarrow{k_{i_2}} Q_1 \qquad (9)$$

The propagation reactions are:

$$P_1 + M \xrightarrow{k_p} P_2 \tag{10a}$$

$$P_n + M \xrightarrow{k_p} P_{n+1} \quad (n \geq 2) \tag{10b}$$

$$Q_1 + M \xrightarrow{k_p} Q_2 \tag{11a}$$

$$Q_n + M \xrightarrow{k_p} Q_{n+1} \quad (n \geq 2) \tag{11b}$$

$$S_1 + M \xrightarrow{2k_p} S_2 \tag{12a}$$

$$S_n + M \xrightarrow{2k_p} S_{n+1} \quad (n \geq 2) \tag{12b}$$

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.

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

$$P_n + P_m \xrightarrow{k_t} M_{n+m} \quad (n, m \geq 1) \tag{13}$$

$$P_n + Q_m \xrightarrow{k_t} Z_{n+m} \quad (n, m \geq 1) \tag{14}$$

$$P_n + S_m \xrightarrow{2k_t} P_{n+m} \quad (n, m \geq 1) \tag{15}$$

$$Q_n + Q_m \xrightarrow{k_t} T_{n+m} \quad (n, m \geq 1) \tag{16}$$

$$Q_n + S_m \xrightarrow{2k_t} Q_{n+m} \quad (n, m \geq 1) \tag{17}$$

$$S_n + S_m \xrightarrow{4k_t} S_{n+m} \quad (n, m \geq 1) \tag{18}$$

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 to be negligible in the above scheme. In Eqs. 13–18, the combination termination rate constants for the macroradical species are assumed to be identical. In this kinetic scheme, chain transfer reactions have also been ignored.

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 the gel effect. Although the gel effect in styrene polymerization is not as strong as that in methyl methacrylate polymerization, the gel effect is not quite negligible at high conversion or low solvent volume fraction. In this study, the gel effect correlation suggested by Friis and Hamielec (1976) for bulk styrene polymerization is used:

$$g_t = \frac{k_t}{k_{to}} = \exp\left[-2(Bx + Cx^2 + Dx^3)\right] \tag{19}$$

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

$$B = 2.57 - 5.05 \times 10^{-3} T\,(\mathrm{K})$$
$$C = 9.56 - 1.76 \times 10^{-2} T\,(\mathrm{K})$$
$$D = -3.03 + 7.85 \times 10^{-3} T\,(\mathrm{K})$$

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

For initiator:

$$\frac{dI}{dt} = -2k_{d_1} I \tag{20}$$

$$\frac{dR}{dt} = 2f_1 k_{d_1} I - k_{i_1} R M + k_{d_2}(Q + 2T + Z) \tag{21}$$

$$\frac{dR'}{dt} = 2f_2 k_{d_1} I - k_{i_2} R' M \tag{22}$$

where f_1 and f_2 are the initiator efficiencies that 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:

$$\frac{dP_1}{dt} = k_{i_1} R M - k_p M P_1 - k_t P_1 (P + Q + 2S) \tag{23}$$

$$\frac{dP_n}{dt} = k_p M(P_{n-1} - P_n) + k_{d_2} Z_n - k_t P_n (P + Q + 2S) + 2k_t \sum_{m=1}^{n-1} P_{n-m} S_m \quad (n \geq 2) \tag{24}$$

$$\frac{dQ_1}{dt} = k_{i_2} R' M - k_p M Q_1 - k_{d_2} Q_1 - k_t Q_1 (P + Q + 2S) \tag{25}$$

$$\frac{dQ_n}{dt} = -k_{d_2} Q_n + 2k_{d_2} T_n + k_p M(Q_{n-1} - Q_n) - k_t Q_n (P + Q + 2S) + 2k_t \sum_{m=1}^{n-1} Q_{n-m} S_m \quad (n \geq 2) \tag{26}$$

$$\frac{dS_1}{dt} = k_{d_2}Q_1 - 2k_pMS_1 - 2k_tS_1(P + Q + 2S) \quad (27)$$

$$\frac{dS_n}{dt} = k_{d_2}Q_n + 2k_pM(S_{n-1} - S_n) - 2k_tS_n(P + Q + 2S) + 2k_t\sum_{m=1}^{n-1} S_{n-m}S_m \quad (n \geq 2) \quad (28)$$

For temporarily inactive polymers:

$$\frac{dT_n}{dt} = -2k_{d_2}T_n + \frac{k_t}{2}\sum_{m=1}^{n-1} Q_{n-m}Q_m \quad (n \geq 2) \quad (29)$$

$$\frac{dZ_n}{dt} = -k_{d_2}Z_n + k_t\sum_{m=1}^{n-1} P_{n-m}Q_m \quad (n \geq 2) \quad (30)$$

For monomers and dead polymers:

$$\frac{dM}{dt} = -k_{i_1}RM - k_{i_2}R'M - k_pM(P + Q + 2S) \quad (31)$$

$$\frac{dM_n}{dt} = \frac{k_t}{2}\sum_{m=1}^{n-1} P_{n-m}P_m \quad (n \geq 2) \quad (32)$$

where P, Q, S, T, and Z are the total concentrations of the corresponding polymeric species, that is,

$$P = \sum_{n=1}^{\infty} P_n, \quad Q = \sum_{n=1}^{\infty} Q_n, \quad S = \sum_{n=1}^{\infty} S_n \quad T = \sum_{n=2}^{\infty} T_n \quad Z = \sum_{n=2}^{\infty} Z_n \quad (33)$$

For primary radicals and live polymeric species (P_n, Q_n, and S_n) quasi-steady state approximation will be employed. In order to compute the molecular weight averages of polymers, the following molecular weight moments are used:

$$\lambda_{\xi,k} \equiv \sum_{n=j}^{\infty} n^k \xi_n \quad [\xi = P, Q, S(j = 1); T, Z(j = 2)] \quad (34a)$$

$$\lambda_k^d \equiv \sum_{n=2}^{\infty} n^k M_n \quad (34b)$$

where $\lambda_{\xi,k}$ and λ_k^d denote the kth moment of polymeric species ξ and dead polymers, respectively. The overall number-average chain length X_N and weight-average chain length X_W are defined by

$$X_N = \frac{\sum_\xi \lambda_{\xi,1} + \lambda_1^d}{\sum_\xi \lambda_{\xi,0} + \lambda_0^d} \quad (\xi = P, Q, S, T, Z) \quad (35)$$

$$X_W = \frac{\sum_\xi \lambda_{\xi,2} + \lambda_2^d}{\sum_\xi \lambda_{\xi,1} + \lambda_1^d} \quad (\xi = P, Q, S, T, Z) \quad (36)$$

The number-average and weight-average chain lengths of each polymeric species are also given by

$$X_{N,\xi} = \frac{\lambda_{\xi,1}}{\lambda_{\xi,0}}, \quad X_{W,\xi} = \frac{\lambda_{\xi,2}}{\lambda_{\xi,1}} \quad (\xi = P, Q, S, T, Z) \quad (37)$$

$$X_{N,d} = \frac{\lambda_1^d}{\lambda_0^d}, \quad X_{W,d} = \frac{\lambda_2^d}{\lambda_1^d} \quad (38)$$

The polydispersity is a measure of molecular weight distribution broadening and is defined by

$$PD = \frac{X_W}{X_N} \quad (39)$$

Using the rate expression derived above, one can derive the molecular weight moment equations. They take the following forms.

Polymeric species P_n:

$$\frac{d\lambda_{P,0}}{dt}\left(= \frac{dP}{dt}\right) = k_{i_1}RM + k_{d_2}Z - k_tP(P + Q) \quad (40)$$

$$\frac{d\lambda_{P,1}}{dt} = k_{i_1}RM + k_pMP + k_{d_2}\lambda_{Z,1} + k_t[2P\lambda_{S,1} - (P + Q)\lambda_{P,1}] \quad (41)$$

$$\frac{d\lambda_{P,2}}{dt} = k_{i_1}RM + k_pM(2\lambda_{P,1} + P) + k_{d_2}\lambda_{Z,2} + k_t[4\lambda_{S,1}\lambda_{P,1} + 2\lambda_{S,2}P - (P + Q)\lambda_{P,2}] \quad (42)$$

Polymeric species Q_n:

$$\frac{d\lambda_{Q,0}}{dt}\left(= \frac{dQ}{dt}\right) = k_{i_2}R'M + k_{d_2}(2T - Q) - k_tQ(P + Q) \quad (43)$$

$$\frac{d\lambda_{Q,1}}{dt} = k_{i_2}R'M + k_pMQ + k_{d_2}(2\lambda_{T,1} - \lambda_{Q,1}) + k_t[2\lambda_{S,1}Q - (P + Q)\lambda_{Q,1}] \quad (44)$$

$$\frac{d\lambda_{Q,2}}{dt} = k_{i_2}R'M + k_pM(2\lambda_{Q,1} + Q) + k_{d_2}(2\lambda_{T,2} - \lambda_{Q,2}) + k_t[4\lambda_{S,1}\lambda_{Q,1} + 2\lambda_{S,2}Q - (P + Q)\lambda_{Q,2}] \quad (45)$$

Polymeric species S_n:

$$\frac{d\lambda_{S,0}}{dt}\left(= \frac{dS}{dt}\right) = k_{d_2}Q - 2k_tS(P + Q) - 2k_tS^2 \quad (46)$$

$$\frac{d\lambda_{S,1}}{dt} = k_{d_2}\lambda_{Q,1} + 2k_pMS - 2k_t(P + Q)\lambda_{S,1} \quad (47)$$

$$\frac{d\lambda_{S,2}}{dt} = k_{d_2}\lambda_{Q,2} + 2k_pM(2\lambda_{S,1} + S) + k_t[4\lambda_{S,1}^2 - 2(P + Q)\lambda_{S,2}] \quad (48)$$

Polymeric species T_n:

$$\frac{d\lambda_{T,0}}{dt}\left(=\frac{dT}{dt}\right)=-2k_{d_2}T+\frac{k_t}{2}Q^2 \tag{49}$$

$$\frac{d\lambda_{T,1}}{dt}=-2k_{d_2}\lambda_{T,1}+k_t\lambda_{Q,1}Q \tag{50}$$

$$\frac{d\lambda_{T,2}}{dt}=-2k_{d_2}\lambda_{T,2}+k_t(\lambda_{Q,2}Q+\lambda_{Q,1}^2) \tag{51}$$

Polymeric species Z_n:

$$\frac{d\lambda_{Z,0}}{dt}\left(=\frac{dZ}{dt}\right)=-k_{d_2}Z+k_tPQ \tag{52}$$

$$\frac{d\lambda_{Z,1}}{dt}=-k_{d_2}\lambda_{Z,1}+k_t(\lambda_{P,1}Q+\lambda_{Q,1}P) \tag{53}$$

$$\frac{d\lambda_{Z,2}}{dt}=-k_{d_2}\lambda_{Z,2}+k_t(\lambda_{P,2}Q+2\lambda_{P,1}\lambda_{Q,1}+\lambda_{Q,2}P) \tag{54}$$

Dead polymers:

$$\frac{d\lambda_0^d}{dt}=\frac{k_t}{2}P^2 \tag{55}$$

$$\frac{d\lambda_1^d}{dt}=k_tP\lambda_{P,1} \tag{56}$$

$$\frac{d\lambda_2^d}{dt}=k_t(P\lambda_{P,2}+\lambda_{P,1}^2) \tag{57}$$

Applying the quasi-steady state approximation to live radical species leads to the following algebraic expressions for P, Q, and S (live polymeric radical species):

$$P=\frac{1}{2k_t}(-k_tQ+\{(k_tQ)^2 + 4k_t[2f_1k_{d_1}I+k_{d_2}(Q+2T+2Z)]\}^{1/2}) \tag{58}$$

$$Q=\frac{1}{2k_t}\{-(k_tP + k_{d_2})+[(k_tP+k_{d_2})^2+8k_t(f_2k_{d_1}I+k_{d_2}T)]^{1/2}\} \tag{59}$$

$$S=\frac{1}{2k_t}\{-k_t(P+Q)+[k_t^2(P+Q)^2+2k_tk_{d_2}Q]^{1/2}\} \tag{60}$$

Model Simulations and Discussion

The proposed kinetic model for the free-radical polymerization catalyzed by the bifunctional initiator system has been used to simulate isothermal batch bulk polymerization of styrene using the diperoxide initiator of the type shown in Eq. 1. The numerical values of kinetic constants and standard polymerization conditions are given in Table 2. Note that the decomposition activation energies of the two peroxide groups differ considerably. The monofunctional initiators M1 and M2 are hypothetical ones used for the purpose of comparison with the bifunctional initiator system. The behavior of the monofunctional initiator M2 is similar to that of popular AIBN. The modeling equations and moment equations derived in the previous section were solved by the fourth-order Runge-Kutta method.

Table 2. Numerical Values of Kinetic Constants and Base Operating Conditions

$k_{d_1}=8.90\times10^{10}\exp(-23{,}473/RT)$, s^{-1} $k_{d_2}=5.59\times10^{14}\exp(-30{,}387/RT)$, s^{-1} $f_i=0.23,\ i=1,2$	Prisyazhnyuk & Ivanchev (1970)
$k_p=1.051\times10^{7}\exp(-7{,}060/RT)$, 1/mol · s $k_t=1.260\times10^{9}\exp(-1{,}680/RT)$, 1/mol · s	Brandrup & Immergut (1975)
$k_{i_1}=k_{i_2}\approx k_p$	
$I_0=0.025$ mol/L (bifunctional initiator) $I_0=0.050$ mol/L (monofunctional initiators) $M_0=8.728$ mol/L	
For monofunctional initiators	
M1: $k_d=8.90\times10^{10}\exp(-23{,}473/RT)$, s^{-1} M2: $k_d=5.59\times10^{14}\exp(-30{,}387/RT)$, s^{-1}	

Figure 1 shows the fractional conversions of the primary initiators (species I in Eq. 2) for the bifunctional initiator and for the two monofunctional initiators at three different temperatures. The initiator M1 is a fast (or low-temperature) initiator and M2 is a slow (or high-temperature) initiator. Note that the decomposition rate of the peroxides in the bifunctional initiator

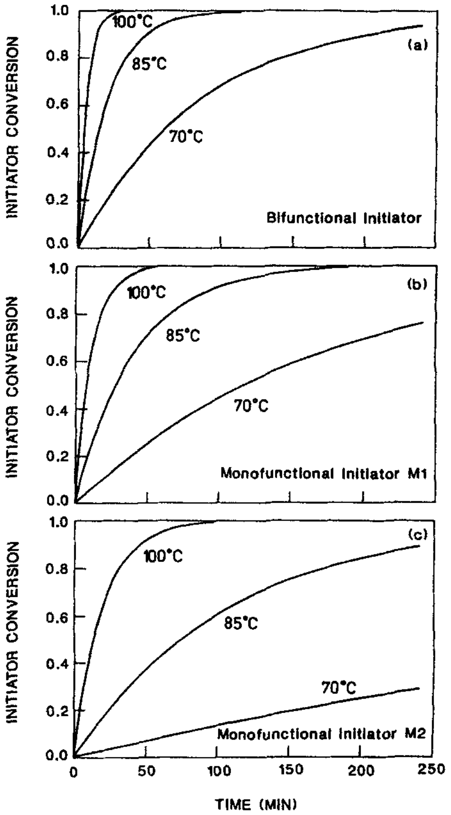

Figure 1. Conversion profiles of primary initiators for different reaction temperatures

(a) $I_{0,B}$ = 0.025 mol/L
(b) $I_{0,M1}$ = 0.050 mol/L
(c) $I_{0,M2}$ = 0.050 mol/L

is higher than that in the monofunctional initiators because of the dual functionality of the bifunctional initiator molecule. The effect of polymerization temperature on the fractional conversion of monomer for the bifunctional system and for the monofunctional systems M1 and M2 is illustrated in Figures 2a, 2b, and 2c. Here, the identical initial concentrations of peroxides in the primary initiators were used for both bifunctional and monofunctional initiators (i.e., $I_{0,B} = \frac{1}{2}I_{0,M1} = \frac{1}{2}I_{0,M2}$). At low temperature (70°C), the monomer conversion obtained by using the bifunctional initiator is higher than that yielded by the monofunctional initiator M2 and slightly lower than that yielded by the monofunctional initiator M1. At high temperature (100°C), the bifunctional initiator yields higher monomer conversion than does the monofunctional initiator M1 and slightly lower than does the monofunctional initiator M2. This illustrates that the bifunctional initiators having two peroxide groups can be used for a broader range of polymerization temperatures than the two monofunctional initiators when the same initial concentration of peroxides is used to obtain high monomer conversion. Figure 2b shows that the monomer conversion levels off at only about 60% at 100°C. This is due to the premature decomposition of the initiator, as shown in Figure 1b. Such a phenomenon is called dead-end polymerization and is undesirable because of poor initiator usage. When the bifunctional initiator is used at high temperatures, the monomer conversion increases continuously even if the conversion of the primary initiator is also very high, Figure 1a. This effect is due to the reinitiation, propagation, and termination of polymeric initiators formed during the course of polymerization; the polymerization is first initiated by the primary radicals formed during the initial cleavage of the peroxide group in the initiator. Subsequently, the polymerization is reinitiated by the radicals formed during the decomposition of more stable peroxide groups on the polymer chain ends, Eqs. 5, 6, and 7. As shown in Figure 3, at 70°C the reaction mixture consists mainly of inactive polymeric species (T_n, Z_n, and M_n) and unreacted monomers. At higher temperatures, however, the decomposition of thermally more stable peroxide groups in the polymers is facilitated, and the rapid generation of more radicals results. Consequently, the overall monomer conversion increases considerably even after the original initiator species I has been completely consumed. In Figure 3, the concentrations of live polymeric species (P_n, Q_n, and S_n) are not shown because their weight fractions are extremely low: $10^{-3}\%$ at low temperature to $10^{-8}\%$ at high temperature.

The effect of bifunctional initiator concentration on the monomer (styrene) conversion is illustrated in Figure 4. As expected, the use of high initiator concentration leads to high monomer conversion. The experimental data of monomer conversion shown in Figures 2a and 4 are from Prisyazhnyuk and Ivanchev (1970). Note that the prediction of the proposed kinetic model agrees quite well with the experimentally observed monomer conversion data.

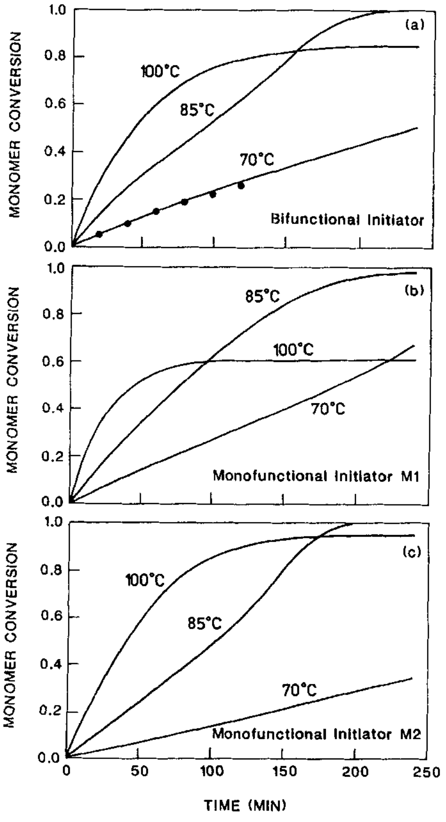

Figure 2. Effect of polymerization temperature on monomer conversion with various initiators.

(a) $I_{0,B} = 0.025$ mol/L
(b) $I_{0,M1} = 0.050$ mol/L
(c) $I_{0,M2} = 0.050$ mol/L
● Data of Prisyazhnyuk and Ivanchev (1970); 70°C, $I_{0,B} = 0.025$ mol/L

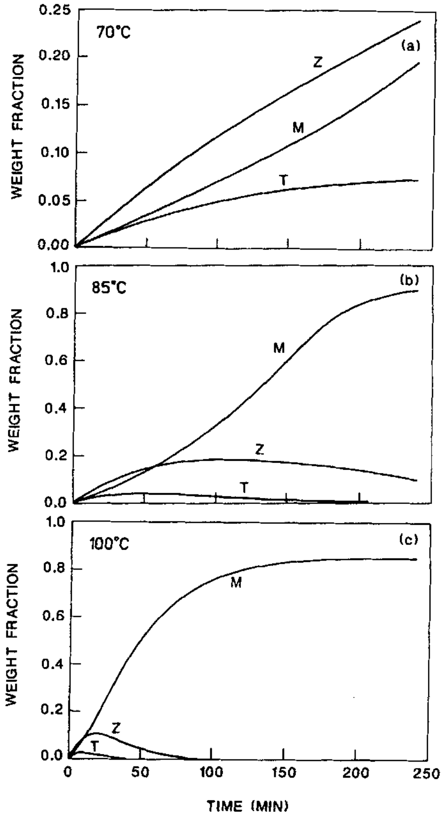

Figure 3. Effect of temperature on the composition distribution of polymeric species for bifunctional initiator system.

$I_{0,B} = 0.025$ mol/L

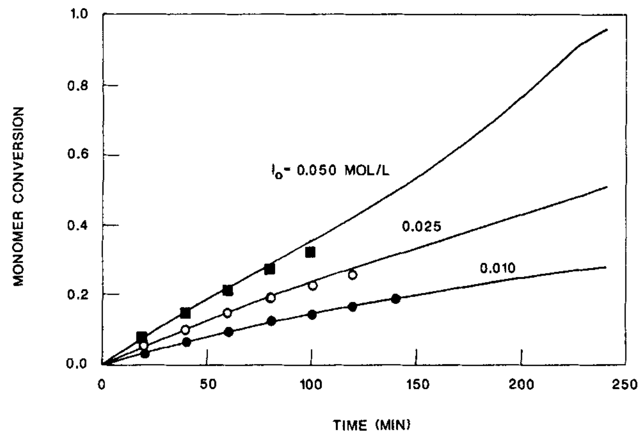

Figure 4. Effect of bifunctional initiator concentration on monomer conversion at 70°C.
Data of Prisyazhnuk and Ivanchev (1970), 70°C

Figures 5a and 5b show the ratios of total primary radical concentrations in the bifunctional initiator system to that in the monofunctional initiator systems M1 and M2, respectively, during the course of polymerization. The initial total number of moles of peroxide groups in the bifunctional initiator and the monofunctional initiator systems is identical. During the early reaction period, the fast monofunctional initiator M1 generates more primary radicals than the bifunctional initiator; however, as polymerization proceeds, the bifunctional initiator system generates free radicals continuously through the cleavage of more stable peroxides in the polymeric species (Q_n, T_n, Z_n). Therefore, the radical concentration ratio increases with monomer conversion. When the slow monofunctional initiator M2 is used, the rate of free radical generation during the early reaction period is much slower than that of the bifunctional initiator system, which contains two peroxides of high and low decomposition activation energies, Figure 5b. As reaction continues, more radicals are generated in the monofunctional initiator system M2, whereas the radicals are continuously consumed in the bifunctional initiator system. As a result, the ratio decreases monotonically with polymerization, as shown in Figure 5b. One can observe similar phenomena in Figures 6a and 6b for total live polymeric radical concentrations. Notice that at high temperature (100°C) the polymeric radical concentration increases more rapidly relative to the fast monofunctional initiator M1, Figure 6a. As the polymerization proceeds, the growth of the live polymeric species is terminated by radical termination reactions.

The dramatic effect of the bifunctional initiator on the polymer molecular weight properties is illustrated in Figure 7a. When compared with the number-average chain length (NACL) of polystyrenes produced by the monofunctional initiators, Figures 7b and 7c, the NACL obtained by the bifunctional initiator is considerably higher, particularly at high polymerization temperatures. Neither monofunctional initiator M1 nor M2 produces polymers having molecular weights as high as those obtained by the bifunctional initiator at high polymerization rate. Although high molecular weight may be obtained by using a very low concentration of monofunctional initiators, this will reduce the polymerization rate significantly, resulting in much longer reaction time. Figure 7a also illustrates that although the NACL is lower at higher reaction temperature during the early reaction stage, the polymer molecular weight increases continuously with reaction time, notably at higher polymerization temperatures. This is due to the continuous reinitiation of polymeric species Q_n, T_n, and Z_n, which contain undecomposed peroxide groups, and the termination reactions of these long polymer chains. During the early reaction period, polymer formation is primarily due to the cleavage of less stable peroxides; however as monomer conversion increases, more stable peroxides residing in active and inactive polymer chains decompose, resulting in a significant increase in the overall degree of polymerization. Clearly, this molecular weight increase with the bifunctional initiator system is due to the combination termination mode, which allows the formation of reactive polymer chain ends that can

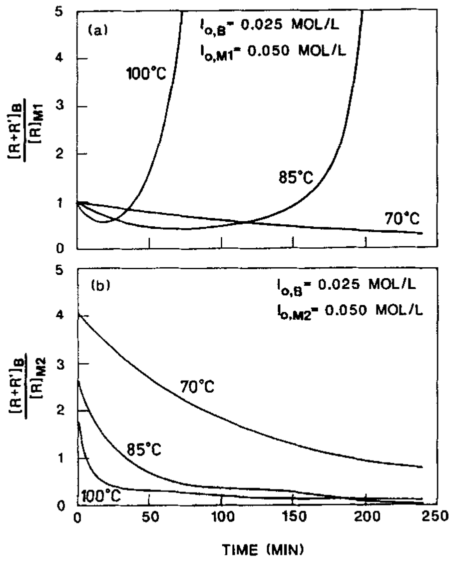

Figure 5. Primary radical concentration ratios at different styrene polymerization temperatures.

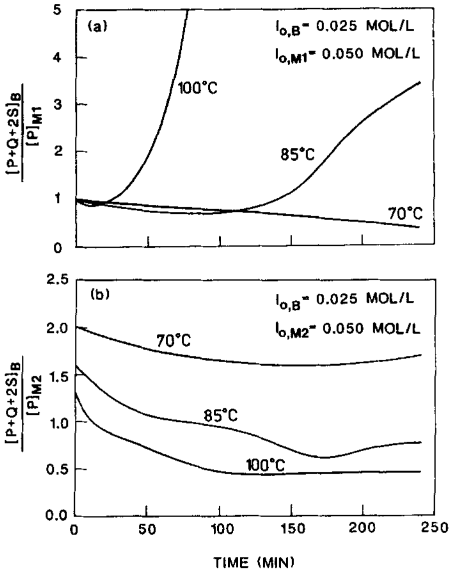

Figure 6. Growing polymer radical concentration ratios at different styrene polymerization temperatures.

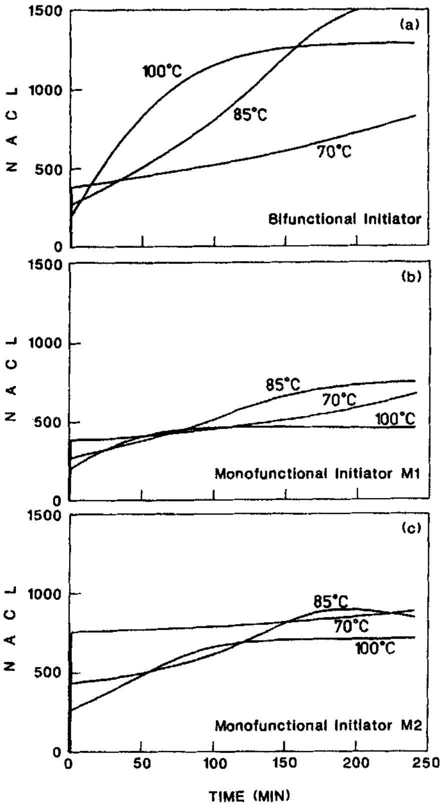

Figure 7. Effect of polymerization temperature on number-average polymer chain length for various initiator systems.

(a) $I_{0,B}$ = 0.025 mol/L
(b) $I_{0,M1}$ = 0.050 mol/L
(c) $I_{0,M2}$ = 0.050 mol/L

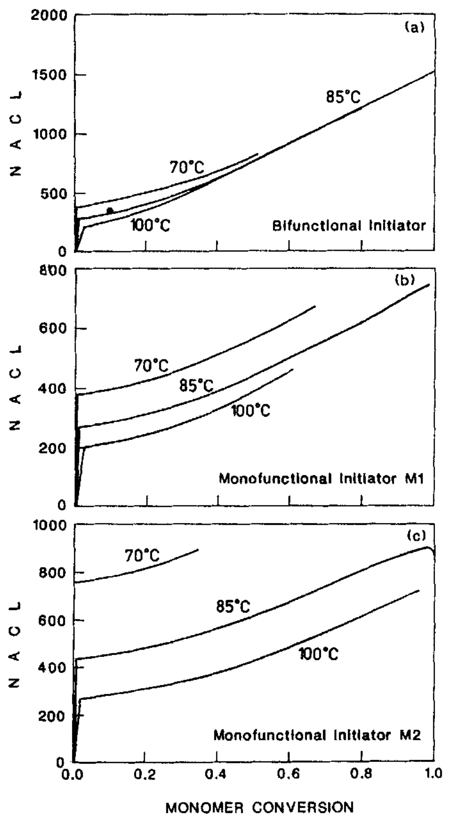

Figure 8. NACL vs. monomer conversion profiles for various initiator systems.

(a) $I_{0,B}$ = 0.025 mol/L
(b) $I_{0,M1}$ = 0.050 mol/L
(c) $I_{0,M2}$ = 0.050 mol/L
● (E), from Prizyazhnyuk and Ivanchev (1970); 10% conversion, 70°C, $I_{0,B}$ = 0.025 mol/L

grow further. From a practical point of view, the use of high polymerization temperatures in order to produce polymers of high molecular weight is advantageous in that batch polymerization time can be reduced significantly without sacrificing the molecular weight of polymers. Figures 8a, 8b, and 8c show the polymer chain length vs. monomer conversion profiles for various initiator systems. Those figures clearly show that the bifunctional initiator can be used to achieve simultaneously both high monomer conversion and high molecular weight. The only data point (E) of NACL shown in Figure 8a is from Prisyazhnyuk and Ivanchev (1970) at 10% styrene conversion with the bifunctional initiator at 70°C. More complete comparison of our model predictions with experimental data was not possible due to the lack of additional experimental data.

Figure 9 shows the polydispersity (PD = X_W/X_N) profiles for three different initiators at various reaction temperatures. The bifunctional initiator produces polymers of much narrower molecular weight distribution than the fast (or low-temperature) monofunctional initiator M2, even at high monomer conversion and high reaction temperature. This indicates that the polymerization mixture in the bifunctional initiator system consists of high molecular weight polymers having relatively equal size chain lengths (T_n, Z_n, M_n). Figure 10 shows this point. The slow monofunctional initiator M2 produces polymers having similar a molecular weight distribution, Figure 9c, to that of the bifunctional initiator system; however, the number-average molecular weight of polystyrenes yielded by the monofunctional initiator system M2 is much lower than that of the bifunctional initiator system.

The number-average chain lengths of various polymeric species have also been computed; they are shown in Figure 10 for three different polymerization temperatures. Note that the NACL of inactive polymers (T_n and Z_n) carrying undecomposed peroxides increases significantly with increase in reaction temperature. Thus, when the peroxides in such inactive polymers decompose during the course of polymerization (i.e., reinitiation), the polymerization proceeds further and much higher polymer molecular weight results as the chain growth is terminated by the combination of two growing macroradicals. At high temperature (100°C), NACL's of live polymeric species increase rapidly. Very low concentrations of those species (i.e., zero moments) are accounted for such increases in NACL. It is interesting to observe that the live polymeric species S_n containing two active radicals on both chain ends has the largest NACL, due to its dual reactivity. However, the influence of those live polymeric species on the overall polymer chain length is negligible due to their extremely low concentrations. The live polymeric species (P_n, Q_n, and S_n) are quickly converted to inactive or dead polymers of high molecular weight by combination termination.

The simulation results of free-radical styrene polymerization with different types of initiators presented in this paper indicate

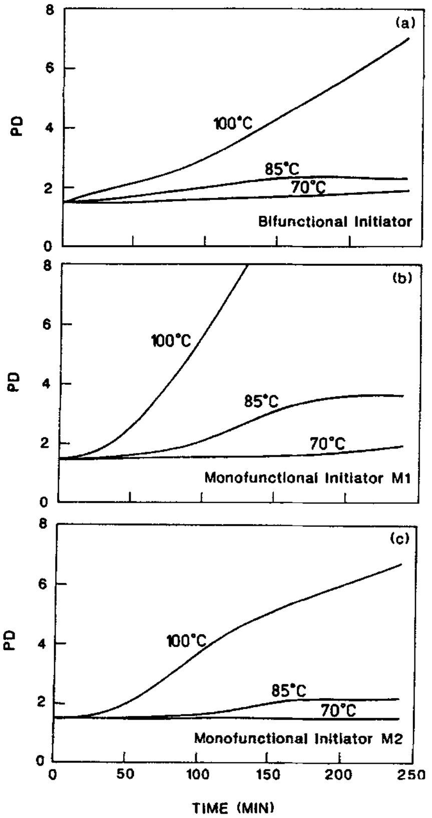

Figure 9. Effect of temperature on the polydispersity of polystyrene for various initiator systems.
(a) $I_{0,B}$ = 0.025 mol/L
(b) $I_{0,M1}$ = 0.050 mol/L
(c) $I_{0,M2}$ = 0.050 mol/L

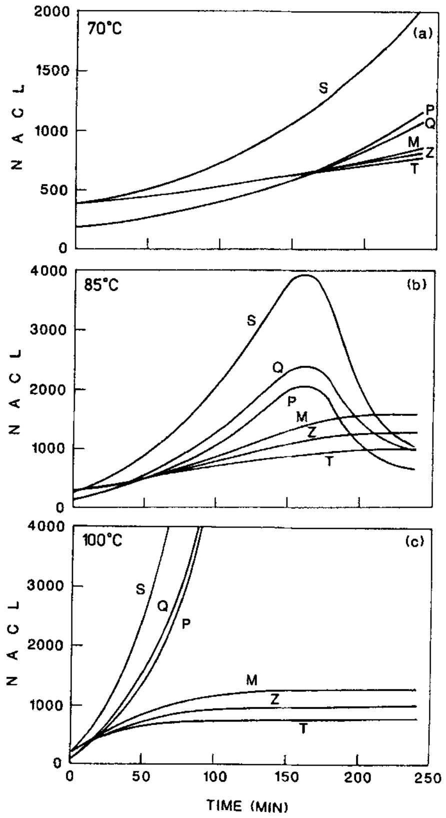

Figure 10. Effect of temperature on the number-average chain length of polymeric species.
$I_{0,B}$ = 0.025 mol/L

that the use of bifunctional initiators enables one to achieve high monomer conversion, high molecular weight, and narrow molecular weight distribution simultaneously by operating the polymerization reactors in an optimal manner. Unfortunately, a complete comparison of our model simulations with experimental data has not been made due to the lack of reported experimental data on polymer molecular weights for the bifunctional initiator system.

Concluding Remarks

This paper is the first to present a detailed kinetic model of the bulk styrene polymerization initiated by diperoxyester bifunctional initiators. When chain termination occurs via a combination termination mechanism, six distinct polymeric species are identified in accordance with the nature of the polymer end units. The overall number-average chain length and the number-average chain lengths of each polymeric species have been computed by solving the molecular weight moment equations. It has been illustrated that the unequal thermal decomposition characteristics of the peroxides of the bifunctional initiator system lead to the formation of polymers having substantially higher molecular weight than those obtained by monofunctional initiator systems. The effect of the bifunctional initiator is more pronounced at high reaction temperatures. Such a polymer chain extension phenomenon is a consequence of the extended radical lifetime via sequential decomposition of peroxides and the combination termination of long polymer chains. It has also been found that high monomer conversion, high molecular weight, and narrow MWD can be obtained simultaneously as the bifunctional initiator system is employed. The proposed model prediction was compared with the experimental data reported in the literature and the agreement was quite satisfactory. Through our model simulations, it has been demonstrated that the use of bifunctional initiators offers polymerization reaction engineers a new opportunity for improving the polymer productivity and controlling the polymer molecular weight properties more effectively than using conventional monofunctional initiators.

Acknowledgment

This research was supported in part by the Systems Research Center at the University of Maryland. The authors are also indebted to the University of Maryland Computer Science Center for computing time. Some helpful comments of V. R. Kamath (Pennwalt-Lucidol Co.) are also appreciated.

Notation

E_1 = activation energy of decomposition of less stable peroxide
E_2 = activation energy of decomposition of more stable peroxide
f_i = initiator efficiency, $i = 1, 2$
g_t = gel effect factor
I = initiator concentration
I_0 = initial initiator concentration
k_{d_i} = initiator decomposition rate constant, $i = 1, 2$
k_{i_j} = initiation rate constant, $j = 1, 2$
k_p = propagation rate constant

k_t – termination rate constant
k_{to} – termination rate constant at zero conversion
M – monomer concentration
M_0 – initial monomer concentration
PD – polydispersity
R, R' – primary radical species
x – monomer conversion
X_N – number-average chain length of polymer
X_W – weight-average chain length of polymer
$\lambda_{\xi,k}$ – kth moment of species ξ
λ_k^d – kth moment of dead polymer

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Manuscript received Dec. 22, 1986, and revision received Apr. 20, 1987.