두 기능성 개시제의 이성분 혼합에 의한 스틸렌 중합

윤 원 중, 최 규 용*
경원대학교 화학공학과, 메린랜드대학교 화학공학과 *

Free Radical Polymerization of Styrene with a Binary Mixture of Symmetrical Bifunctinal Initiators

Won Jung Yoon and Kyu Yong Choi*
Dept. of Chem. Eng., Kyungwon University, Dept. of Chem. Eng., University of Maryland*

Introduction

Bifunctinal initiators containing two labile groups of equal or unequal thermal stabilities are frequently used in the polymer industry for the synthesis of vinyl polymers. In our previous reports, we have presented the kinetic models for the styrene polymerization with a single symmetrical bifunctional initiator and with a single unsymmetrical bifunctional initiator[1-5]. Although these models were developed for styrene polymerization, they can be used for other vinyl monomer polymerizations with mimor modifications. One of the potential advantages of using bifunctional initiators, in particular unsymmtrical ones, in free radical polymerization is that high polymerization rate and high polymer molecular weight can be readily obtained simulataneously by employing appropriate reactor temperature programming.

Since there are a few symmetrical bifunctional initiators available in commercial quantity, it is of practical interest to form *in sutu* unsymmetry of initiator functions by mixing more than one symmetrical bifunctional initiators of different thermal stabilities. Quite obviously, one can expect that the resulting reaction kinetics will be quite complicated because there are reported reinitiation, propagation, chain transfer, and chain termination reactions due to the presence of undecomposed labile groups residing in the polymer chain ends. Here, we need a model that can provide an accurate prediction of polymerization rate and resulting polymer molecular weight properties. we shall present a kinetic model for free radical styrene polymerization with a binary mixture of symmetrical bifunctional initiators. Polymerization experiments have also been carried out under various reaction conditions in order to validate the proposed kinetic model.

Reaction Kinetics

The specific bifunctional initiators used in our experimental study are 2,5-dimethyl-2,5-bis (benzoyl peroxy) hexane [Luperox 118: Initiator I_A] and 2,5-dimethyl- 2,5-bis

(2-ethyl hexanoyl peroxy) hexane [Lupersol 256: Initiator I_B]. The peroxide group in Luperox 118 has a half-life of 9.9 hr at 100°C whereas the peroxide group in Lupersol 256 has a half-life of 21 min at 100°C. Thus, Luperox 118 is a relatively *slow* bifunctional initiator and Lupersol 256 is a *fast* initiator. Primary radicals are generated by homolytic scission reactions.

When styrene is polymerized by these radicals, undecomposed peroxides will be redistributed in the polymers via propagation, chain transfer and termination reactions. For the modeling of the polymerization kinetics, we shall use a molecular species modeling approach wherein polymer molecules are identified by the type of their end units. Table I shows ten polymeric species present in the reaction mixture. The formation of these species is due to the presence of two different peroxide groups which are redistributed in polymer chains through chain transfer and termination reactions. Note that there are two polymeric radical species (Q_n and S_n) containing an undecomposed peroxide and five inactive polymer species containing either one or two undecomposed peroxides (U_n, V_n, W_n, U_n' and V_n'). Table II shows various reactions occurring in the reactor.

Table I Polymeric Species

Symbols	Note
P_n: ⊢——•	live polymer without peroxides
Q_n: A——•	live polymer with undecomposed peroxide A
S_n: B——•	live polymer with undecomposed peroxide B
T_n: •——•	polymeric diradical
M_n: ⊢——⊣	dead polymer
U_n: ⊢——A	inactive polymer with undecomposed peroxide A
V_n: ⊢——B	inactive polymer with undecomposed peroxide B
W_n: A——B	inactive polymer with undecomposed peroxides A and B
U_n': A——A	inactive polymer with two undecomposed peroxides A
V_n': B——B	inactive polymer with two undecomposed peroxides B

Table II A Kinetic Model with a Binary Mixture of Symmetrical Bifunctional Initiators

Initiation:

$$I_A \xrightarrow{2k_{d_A}} R_1 + R_A$$
$$I_B \xrightarrow{2k_{d_B}} R_2 + R_B$$
$$R_A \xrightarrow{k_{d_A}} R_1 + R'$$
$$R_B \xrightarrow{k_{d_B}} R_2 + R'$$
$$R_1 + M \xrightarrow{k_i} P_1$$
$$R_2 + M \xrightarrow{k_i} P_1$$
$$R_A + M \xrightarrow{k_i} Q_1$$
$$R_B + M \xrightarrow{k_i} S_1$$
$$R' + M \xrightarrow{2k_i} T_1$$
$$Q_n \xrightarrow{k_{d_A}} R_1 + T_n \quad (n \geq 1)$$
$$S_n \xrightarrow{k_{d_B}} R_2 + T_n \quad (n \geq 1)$$
$$U_n \xrightarrow{k_{d_A}} R_1 + P_n \quad (n \geq 2)$$
$$V_n \xrightarrow{k_{d_B}} R_2 + P_n \quad (n \geq 2)$$
$$W_n \xrightarrow{k_{d_B}} R_2 + Q_n \quad (n \geq 2)$$
$$W_n \xrightarrow{k_{d_A}} R_1 + S_n \quad (n \geq 2)$$
$$U_n' \xrightarrow{2k_{d_A}} R_1 + Q_n \quad (n \geq 2)$$
$$V_n' \xrightarrow{2k_{d_B}} R_2 + S_n \quad (n \geq 2))$$
$$3M \xrightarrow{k_{thM}} 2P_1$$

Propagation ($n \geq 1$):

$$P_n + M \xrightarrow{k_p} P_{n+1}$$
$$Q_n + M \xrightarrow{k_p} Q_{n+1}$$
$$S_n + M \xrightarrow{k_p} S_{n+1}$$
$$T_n + M \xrightarrow{2k_p} T_{n+1}$$

Chain transfer ($n \geq 1$):

$$P_n + M \xrightarrow{k_{fm}} M_n + P_1$$
$$Q_n + M \xrightarrow{k_{fm}} U_n + P_1$$
$$S_n + M \xrightarrow{k_{fm}} V_n + P_1$$
$$T_n + M \xrightarrow{2k_{fm}} P_n + P_1$$

Termination ($n, m \geq 1$):

$$P_n + P_m \xrightarrow{k_t} M_{n+m}$$
$$P_n + Q_m \xrightarrow{k_t} U_{n+m}$$
$$P_n + S_m \xrightarrow{k_t} V_{n+m}$$
$$P_n + T_m \xrightarrow{2k_t} P_{n+m}$$
$$Q_n + Q_m \xrightarrow{k_t} U_{n+m}'$$
$$Q_n + S_m \xrightarrow{k_t} W_{n+m}$$
$$Q_n + T_m \xrightarrow{2k_t} Q_{n+m}$$
$$S_n + S_m \xrightarrow{k_t} V_{n+m}'$$
$$S_n + T_m \xrightarrow{2k_t} S_{n+m}$$
$$T_n + T_m \xrightarrow{4k_t} T_{n+m}$$

Results and Discussion

When the two symmetrical bifunctional initiators are mixed, the initiator mixture composition is a new free parameter one can use to regulate the polymerization rate. With the total initiator concentration fixed at 0.01 mol/L, the polymerization experiments were carried out at 100°C for five different initiator compositions. Figure 1 shows the monomer conversion profiles where y_A is the more fraction of Luperox 118 (*slow initiator*). Here, solid lines represent the model simulations. As shown, excellent agreements between the model predictions and the experimental data have been obtained for all the cases studied. It is seen that when pure Lupersol 256 is used (i.e., y_A =0.0) at 100°C, dead end polymerization occurs, limiting the final monomer conversion to 90%. When the slow initiator is used alone (i.e., y_A =1.0), high monomer conversion is obtained but quite longer reaction time is required. As Luperox 118 is added to Lupersol 256, the polymerization rate decreases to some extent but no dead end polymerization occurs and higher monomer conversion is obtained in less reaction time than with Luperox 118 alone. The reason for the disappearance of dead end polymerization is that after the depletion of less stable peroxide B in Lupersol 256 there is a continuing supply of radicals by the slowly decomposing Luperox 118.

The effect of initiator composition is more clealy seen in Figure 2 where 50/50 (mole ratio) mixture of the symmetrical bifunctional initiators is used at fixed total initiator concentration (0.02 mol/L). Also shown are the monomer conversion profiles with a single symmetrical bifunctional initiator. At 90°C, the monomer conversion with the mixture is almost the same as that with pure Lupersol 256 becauses at this temperature Luperox 118 (slow initiator) decomposes only a little. As the reaction temperture is increased (e.g., 110°C), the initiator mixture clearly shows its effect. Thus, one can obtain the monomer conversion of 0.6-1.0 in much reduced reaction time by using a mixture of these symmetrical bifunctional initiators. Notice that with Lupersol 256 alone at 110°C, the final monomer conversion is limited to only 65% because of the occurrence of dead end polymerization.

It would be of interest to evaluate the need for the detailed kinetic model as proposed from different angle. To do so, let us assume that we view the mixture of the symmetrical bifunctional initiators as simply a mixture of two types of peroxide A and B in *hypothetical* monofunctional initiators[6]. Since the decomposition of these peroxide is solely due to thermal activation, we may expect that the monomer conversion or the polymerization rate could be predicted with a simple kinetic model. Thus, we carried out the simulations of the kinetic model for a binary mixture of *hypothetical* monofunctional initiators. The overall accuracy of the simplified model is reasonably good for the monomer conversion. However, Figure 3 shows that the predicted molecular weight values, in praticular M_w values, are significantly lower than the experimental values. Quite obviously, this is because in real polymerization system there is an additional chain length extension mechanism due to the combination termination of growing polymer radicals containing undecomposed peroxide. When such peroxides in the polymer chains are decomposed and engaged in propagation and termination reactions, much larger polymer molecules are produced.

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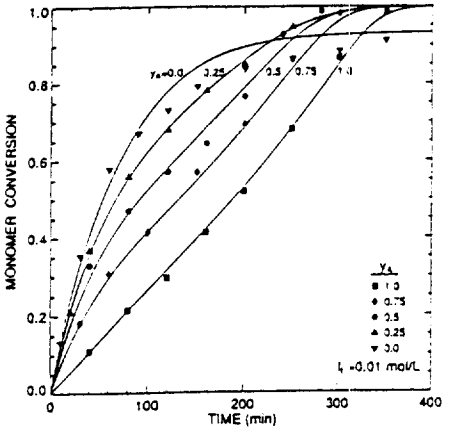

Figure 1 Effect of initiator mixture composition on monomer conversion (I_t = 0.01 mol/L, 100°C).

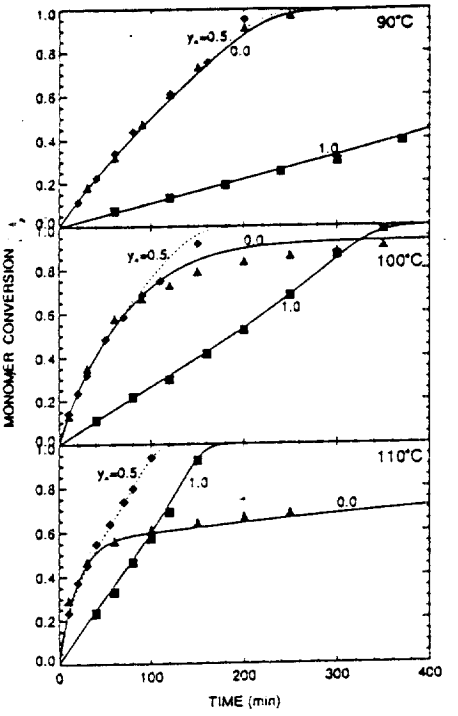

Figure 2 Monomer conversion profiles for initiator mixture and single initiators: (♦) I_t = 0.02 mol/L, y_A = 0.5; (■) [Luperox 118] = 0.01 mol/L; (▲) [Lupersol 256] = 0.01 mol/L.

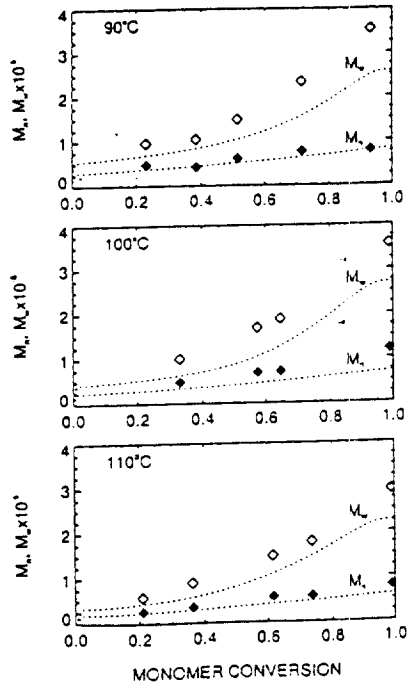

Figure 3 Molecular weight profiles predicted by a simple model (I_t = 0.02 mol/L).