

Bulk and Suspension Polymerization of Styrene in the Presence of *n*-Pentane. An Evaluation of Monofunctional and Bifunctional Initiation

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SYNOPSIS

The plasticizing effect of *n*-pentane on the rate of bulk free radical polymerization of styrene and molecular weight distribution development has been modeled on the basis of the free volume theory for both monofunctional and bifunctional initiation. A strong decrease in the reaction rate in the late stages of the polymerization, due to the displacement of the onset of the gel effect, has been observed for both types of initiation. This decrease in the polymerization rate limited the terminal conversion to values well below 100% for monofunctional initiation. However, in bifunctionally initiated polymerization, terminal conversions close to 100% were obtained in spite of the decrease in reaction rate. Contrary to what was expected, the molecular weight distribution obtained at terminal conversion was almost completely insensitive to these changes in polymerization rate. This phenomenon is explained in terms of limited transfer to monomer reactions when *n*-pentane is present in the system. In suspension polymerization, the limiting conversion and plasticizing effects of *n*-pentane in monofunctionally initiated systems, caused enhanced coalescence leading to suspension set-up. In bifunctionally initiated systems this enhanced coalescence was completely overcome by the short duration of the particle growth stage, owing to high polymerization rates, and stable suspensions were achieved. For these systems the particle size distributions obtained were similar to that of suspension polystyrene without *n*-pentane.

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INTRODUCTION

Traditional manufacture of expandable polystyrene (EPS) in bead form involves two different processes. First, free radical aqueous suspension polymerization of styrene is carried out at temperatures between 80 and 90°C with the aid of monofunctional initiators, such as azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO).¹ The batch polymerization is carried out in a stirred reactor bearing a dispersed phase hold-up (ϕ = volume of disperse phase/total volume) in the range of 0.4 to 0.6, until the conversion where the beads become glassy because of the fact that the glass-transition temperature, T_g , of the monomer/polymer mix increases reaching the polymerization temperature, T .²

During this process, the dispersed droplets reach a critical viscosity ($\mu_{cr1} \sim 100$ cp) at about 30% conversion, depending on the molecular weight and T , from which droplet coalescence overcomes the droplet breakage caused by the agitation system. As a result the mean particle size (MPS) starts to increase rapidly.³ The particle growth is controlled to the desired final size with the aid of suspending agents that may be insoluble inorganic powders such as zinc oxide and tricalcium phosphate (TCP), or water-soluble polymers, such as polyvinyl alcohol (PVA), hydroxyethyl cellulose (HEC), or polyvinyl pyrrolidone (PVP). Particle growth stops at a second critical viscosity ($\mu_{cr2} \sim 10^6$ cp) reached at about 70% conversion, due to the elastic nature of the particle collisions at this viscosity level that averts coalescence. This point is commonly referred to as the identity point and the growth stage as the "sticky stage." From the identity point on, the suspension

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is stable and the polymerization proceeds until the beads become glassy.⁴

The second process, called the impregnation stage, consists of a high temperature-high pressure cycle ($T_i > T_g$) in which the blowing agent, commonly *n*-pentane, is loaded in the reactor and diffuses into the softened beads. In addition, exhaustion of the residual monomer is achieved simultaneously, with the aid of a finishing monofunctional initiator of higher half life than the one used during the polymerization process.

Depending on the impregnation temperature (T_i) and pressure (P_i), a minimum time must be allowed for the diffusion of the blowing agent to reach the core of the beads and for complete monomer exhaustion.¹ At the end of the impregnation stage the suspension is cooled down to room temperature and the polymer is separated from the water in a centrifuge and then dried at low temperatures.

The main productivity limitation of these two processes consists of the long batch times necessary to carry them to completion. Polymerization with monofunctional initiators at higher temperatures, as a means to increase productivity, has not succeeded due to both lower molecular weights of the product (out of the processing range), and the enhanced particle coalescence observed at higher temperatures.⁵ Moreover, addition of blowing agent before the glassy point, as another means to increase productivity in the commercial manufacture of EPS, has not been reported as yet.

Recently, suspension polymerization of styrene with bifunctional initiators at temperatures above and below the T_g of polystyrene, has been studied at length.⁶ In this study, it has been demonstrated that, due to the sequential decomposition characteristics of bifunctional initiators, the polymer molecules experience multiple reinitiation/propagation/termination cycles. As a result, it is possible to achieve simultaneously high polymerization rates and high molecular weights.

In the same study, it was demonstrated that suspension polystyrene with the molecular weight characteristics of expandable polystyrene is obtained with bifunctional initiator 1,4-bis(terbutyl peroxy-carbo) cyclohexane (TBPCC), at 105°C, in a batch cycle 75% shorter than that obtained through the traditional monofunctional initiation system.⁶ Moreover, the enhanced particle coalescence observed at such a polymerization temperature was completely overcome by the great real-time reduction of the particle growth stage.

In this article, the early presence of *n*-pentane in the polymerization mix, in both monofunctionally

and bifunctionally initiated systems, is studied from two points of view:

1. its effect on polymerization rate and molecular weight distribution development in bulk/solution polymerization of styrene; and
2. its effect on suspension stability, mean particle size, and particle size distribution in suspension polymerization of styrene.

The kinetic phenomena observed in this study are modeled and simulated to compare with the experimental data obtained.

Reaction Schemes

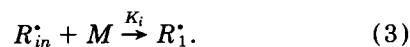
It has been shown elsewhere that both bulk and suspension free radical polymerization proceed through the same kinetic mechanism throughout the entire conversion range.⁷ The well known set of elementary reactions involved in monofunctionally initiated bulk or suspension polymerization of styrene, considered in this study, can be written as follows.⁸

Monofunctional System

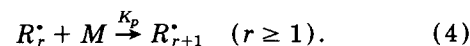
Thermal initiation:



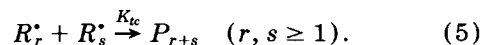
Chemical initiation:



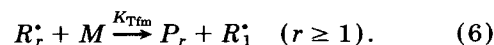
Propagation:



Termination by combination:

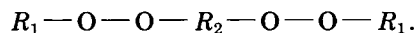


Transfer to monomer:

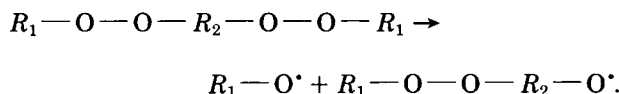


In the above scheme: *I* is a monofunctional initiator; R_{in}^* are the primary radicals; R_i^* are growing radicals of chain length *i*; *M* is styrene monomer; and P_i represents dead polymer molecules of chain length *i*.

A symmetrical bifunctional initiator molecule can be represented as:



The peroxide groups in such a diperoxide compound can undergo homolytic rupture of the O—O bonds by increasing the energy of the system. The primary homolysis of a diperoxide can be written as:



From this reaction two different radicals are formed, one similar to the radicals of monofunctional initiation, and one bearing an undecomposed peroxide. Upon polymerization, these two primary radicals will lead to the formation of two different populations of propagating radicals, with and without terminal undecomposed peroxide, respectively.

When termination by combination is the dominant bimolecular termination mechanism, such as for polystyrene, these two radical populations will yield three different polymer populations: (1) dead polymer; (2) temporarily dead polymer with one terminal peroxide group; and (3) temporarily dead polymer with two undecomposed peroxide groups (one at each end). Because the terminal peroxide groups in these temporarily dead polymer populations can further undergo homolysis of the O—O bond, they will act as macroinitiators in subsequent stages of the polymerization, experiencing, as a result, a new initiation/propagation/termination cycle that may lead to the formation of either dead or temporarily dead polymer molecules again.

This multiple reinitiation/propagation/termination phenomenon is responsible for the possibility of achieving high reaction rates and high molecular weights simultaneously in free radical polymerization with bifunctional initiators.^{9,10}

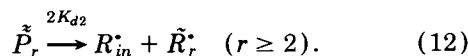
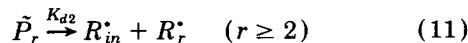
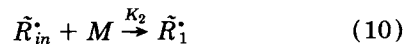
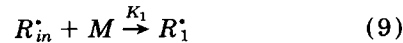
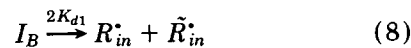
The set of elementary reactions involved in bifunctionally initiated free radical bulk or suspension polymerization of styrene considered in this study can be written as follows.⁸

Bifunctional System

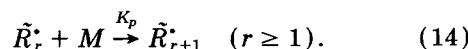
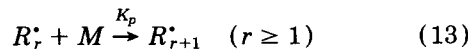
Thermal initiation:



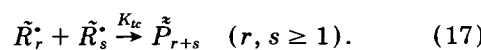
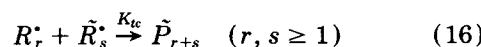
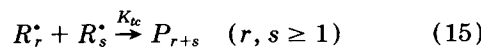
Chemical initiation:



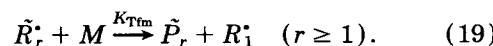
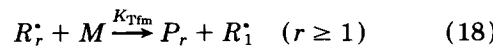
Propagation:



Termination by combination:



Transfer to monomer:



Here I_B is the bifunctional initiator; R_{in}^{\cdot} are primary radicals with one undecomposed peroxide; \tilde{R}_i^{\cdot} are growing radicals of chain length i with one terminal peroxide group; and \tilde{P}_r and $\tilde{\tilde{P}}_r$ are temporarily dead polymer molecules with one and two terminal peroxide groups, respectively. The rest of the species are the same as in the monofunctional scheme.

From the above polymerization schemes note that n -pentane should not act as a chain transfer agent at the polymerization temperatures being used, because hydrogen abstraction from saturated hydrocarbons at this temperature level is very unlikely. Its role in the polymerization kinetics, therefore, may be limited to its plasticizing effect as an inert solvent in the system. However, its influence over the extent of the transfer to monomer reactions will be addressed herein.

Kinetic Modelling

Detailed derivation of the corresponding kinetic models, based on the above polymerization schemes, have been reported elsewhere.⁸ The development of the kinetic models mentioned, are based on the ap-

plication of the method of moments to the mass balances for each of the existing species in the polymerization mix.

Following this procedure, applying the steady-state hypothesis for radical concentration, the long

chain approximation for monomer consumption, and simplifying by considering that $Y_2 \gg Y_1 \gg Y_0$, the following set of algebraic and ordinary differential equations are obtained for each mode of initiation.

Monofunctional Initiation

Monomer consumption:

$$\frac{1}{V} \frac{d([M]V)}{dt} = -K_p[M]Y_0$$

Initiator consumption:

$$\frac{1}{V} \frac{d([I]V)}{dt} = -K_d[I]$$

Initiation rate:

$$R_I = 2fK_d[I] + 2K_{th}[M]^3$$

Moments of the live polymer concentration distributions:

Zeroth

$$Y_0 = \frac{(R_I)^{1/2}}{(K_{tc})^{1/2}}$$

First

$$Y_1 = \frac{R_I + K_p[M]Y_0}{K_{Tfm}[M] + K_{tc}Y_0}$$

Second

$$Y_2 = \frac{R_I + 2K_p[M]Y_1}{K_{Tfm}[M] + K_{tc}Y_0}$$

Bifunctional Initiation

$$\frac{1}{V} \frac{d([M]V)}{dt} = -K_p[M]Y_{T0}$$

$$\frac{1}{V} \frac{d([I_B]V)}{dt} = -2K_{d1}[I]$$

$$R_I = f\{2K_{d1}[I_B] + K_{d2}(\tilde{Q}_0 + 2\tilde{Q}_0^*)\} + 2K_{th}[M]^3$$

$$\tilde{R}_I = 2fK_{d1}[I_B]$$

$$Y_0 = \frac{R_I + fK_{d2}\tilde{Q}_0 + K_{Tfm}[M]\tilde{Y}_0}{K_{tc}Y_{T0}}$$

$$\tilde{Y}_0 = \frac{\tilde{R}_I + 2fK_{d2}\tilde{Q}_0}{K_{Tfm}[M] + K_{tc}Y_{T0}}$$

$$Y_1 = \frac{R_I + fK_{d2}\tilde{Q}_1 + K_p[M]Y_0}{K_{Tfm}[M] + K_{tc}Y_{T0}}$$

$$\tilde{Y}_1 = \frac{\tilde{R}_I + 2fK_{d2}\tilde{Q}_1 + K_p[M]\tilde{Y}_0}{K_{Tfm}[M] + K_{tc}Y_{T0}}$$

$$Y_2 = \frac{R_I + fK_{d2}\tilde{Q}_2 + 2K_p[M]Y_1}{K_{Tfm}[M] + K_{tc}Y_{T0}}$$

$$\tilde{Y}_2 = \frac{\tilde{R}_I + 2fK_{d2}\tilde{Q}_2 + 2K_p[M]\tilde{Y}_1}{K_{Tfm}[M] + K_{tc}Y_{T0}}$$

Moments of the dead and temporarily dead polymer concentration distributions:

Zeroth

$$\frac{1}{V} \frac{d(Q_0 V)}{dt} = \frac{1}{2} K_{tc} Y_0^2 + K_{Tfm} [M] Y_0$$

$$\frac{1}{V} \frac{d(\tilde{Q}_0 V)}{dt} = \frac{1}{2} K_{tc} \tilde{Y}_0^2 + K_{Tfm} [M] \tilde{Y}_0$$

$$\frac{1}{V} \frac{d(\tilde{\tilde{Q}}_0 V)}{dt} = K_{tc} Y_0 \tilde{Y}_0 + K_{Tfm} [M] \tilde{Y}_0 - K_{d2} \tilde{\tilde{Q}}_0$$

$$\frac{1}{V} \frac{d(\tilde{\tilde{Q}}_0 V)}{dt} = \frac{1}{2} K_{tc} \tilde{Y}_0^2 - 2K_{d2} \tilde{\tilde{Q}}_0.$$

First

$$\frac{1}{V} \frac{d(Q_1 V)}{dt} = K_{tc} Y_1 Y_0 + K_{Tfm} [M] Y_1$$

$$\frac{1}{V} \frac{d(\tilde{Q}_1 V)}{dt} = K_{tc} \tilde{Y}_1 Y_0 + K_{Tfm} [M] \tilde{Y}_1$$

$$\frac{1}{V} \frac{d(\tilde{\tilde{Q}}_1 V)}{dt} = K_{tc} (\tilde{Y}_1 Y_0 + Y_1 \tilde{Y}_0) + K_{Tfm} [M] \tilde{Y}_1 - K_{d2} \tilde{\tilde{Q}}_1$$

$$\frac{1}{V} \frac{d(\tilde{\tilde{Q}}_1 V)}{dt} = K_{tc} \tilde{Y}_1 \tilde{Y}_0 - 2K_{d2} \tilde{\tilde{Q}}_1.$$

Second

$$\frac{1}{V} \frac{d(Q_2 V)}{dt} = K_{tc} (Y_1^2 + Y_2 Y_0) + K_{Tfm} [M] Y_2$$

$$\frac{1}{V} \frac{d(\tilde{Q}_2 V)}{dt} = K_{tc} (\tilde{Y}_1^2 + \tilde{Y}_2 \tilde{Y}_0) + K_{Tfm} [M] \tilde{Y}_2$$

$$\frac{1}{V} \frac{d(\tilde{\tilde{Q}}_2 V)}{dt} = K_{tc} (\tilde{Y}_2 Y_0 + 2Y_1 \tilde{Y}_1 + Y_2 \tilde{Y}_0) + K_{Tfm} [M] \tilde{Y}_2 - K_{d2} \tilde{\tilde{Q}}_2$$

$$\frac{1}{V} \frac{d(\tilde{\tilde{Q}}_2 V)}{dt} = K_{tc} (\tilde{Y}_1^2 + \tilde{Y}_2 \tilde{Y}_0) - 2K_{d2} \tilde{\tilde{Q}}_2.$$

In the preceding sets of equations: V is the total volume of the reaction mix; f is the initiator and macroinitiator efficiencies, d/dt represents rate of change with time; and $[\]$ indicates concentration. The i -th moment ($i = 0, 1, 2$) of the live (both with and without terminal peroxide), dead, and temporarily dead polymer concentration distributions, appearing in the above equations, are defined as:

$$Y_i = \sum_{r=1}^{\infty} r^i [R_r] \quad \text{for live polymer}$$

$$\tilde{Y}_i = \sum_{r=1}^{\infty} r^i [\tilde{R}_r] \quad \text{for live polymer with one terminal undecomposed peroxide group}$$

$$Q_i = \sum_{r=1}^{\infty} r^i [P_r] \quad \text{for dead polymer}$$

$$\tilde{Q}_i = \sum_{r=1}^{\infty} r^i [\tilde{P}_r] \quad \text{for temporarily dead polymer with one terminal undecomposed peroxide group}$$

$$\tilde{\tilde{Q}}_i = \sum_{r=1}^{\infty} r^i [\tilde{\tilde{P}}_r] \quad \text{for temporarily dead polymer with two terminal undecomposed peroxide groups}$$

$$Y_{T0} = Y_0 + \tilde{Y}_0 \quad \text{total radical concentration (} Y_0 \text{ for monofunctional initiation).}$$

The simultaneous numerical solution of the above equations through the use of a standard library subroutine (LSODE) has been the base for the development of the simulation programs MONOFUN and BIFUN, for bulk and suspension polymerization of styrene through monofunctional and bifunctional

initiators, respectively. From the integrated values of the variables involved in the kinetic models described, monomer conversion and molecular weight averages as a function of the polymerization time are calculated in both programs as:

$$X_t = \frac{[M]_0 - [M]_t}{[M]_0} \quad (20)$$

$$M_{n(t)} = \frac{MW_M \{ \sum Q_{1(t)} + \sum Y_{1(t)} \}}{\sum Q_{0(t)} + \sum Y_{0(t)}} \quad (21)$$

$$M_{w(t)} = \frac{MW_M \{ \sum Q_{2(t)} + \sum Y_{2(t)} \}}{\sum Q_{1(t)} + \sum Y_{1(t)}} \quad (22)$$

Here X is the monomer conversion; MW_M is the molecular weight of monomer; M_n and M_w are the number-average and weight-average accumulated molecular weights of polymer; subindex 0 means initial value; subindex t means integrated value at time t ; and the summations are over the different species present for the bifunctional system and over the only specie present for the monofunctional one. The details of the simulation program BIFUN may be found elsewhere.⁸

Because both simulation programs based their treatment of the diffusion controlled termination and propagation reactions at high monomer conversions on the free volume theory, similar modifications have been introduced to both programs in order to account for the presence of n -pentane, fed into the reaction mix in batch fashion at some point in the reaction coordinate. The treatment may be described as follows.

At the beginning of the polymerization the value of the termination rate constant, K_{tc} , is given by:

$$K_{tc0} = A_{tc} \exp(-E_{tc}/RT). \quad (23)$$

The monomer conversion at which the n -pentane is introduced to the reaction mix is denoted as $X_{ad}(C_5)$. Upon polymerization, the total volume of the system, temperature and conversion dependent, is calculated as:

$$V(X) = V_m(X) + V_p(X) \quad (\text{for } X < X_{ad}) \quad (24)$$

or

$$V(X) = V_m(X) + V_p(X) + V_{C5} \quad (\text{for } X \geq X_{ad}) \quad (25)$$

where the subindexes m , p and $C5$, denote monomer, polymer, and n -pentane, respectively, and (X) de-

notes the value at conversion X . Note that because the mass of n -pentane does not change with conversion its volume is only temperature dependent.

The free volume of the species i in the reaction mix (monomer, polymer, and n -pentane) is calculated as a function of conversion as¹¹:

$$VF_i(X) = \{ 0.025 + \alpha_i(T - T_{gi}) \} \times (V_i(X)/V(X)) \quad (26)$$

where α_i is the thermal expansion coefficient of the specie i ; T is the polymerization temperature; and T_{gi} is the glass-transition temperature of the specie i . The free volume of the system at any monomer conversion is, then, given by:

$$VF(X) = VF_m(X) + VF_p(X) \quad (\text{for } X < X_{ad}) \quad (27)$$

or

$$VF(X) = VF_m(X) + VF_p(X) + VF_{C5}(X) \quad (\text{for } X \geq X_{ad}). \quad (28)$$

A critical value K_{cr} for the system, denoting the onset of the translational diffusion controlled termination reactions, is defined as a function of temperature only. For every increment in conversion the parameter K is calculated as¹²:

$$K(X) = M_w(X)^M \exp(A/VF(X)) \quad (29)$$

where M and A are adjustable parameters.

When $K \leq K_{cr}$ the termination rate constant is considered to increase linearly with conversion due to an increase in the segmental diffusion rate of the growing polymer chains as the concentration of polymer in the system increases and the coil sizes decrease.

Accordingly¹³:

$$K_{tcs}(X) = K_{tc0}(1 + \delta[P](X)). \quad (30)$$

Here K_{tcs} is the segmental diffusion controlled termination rate constant and δ is a parameter related to the rate of diffusion of the growing polymer chains and the quality of the solvent (monomer plus solvent if present). For homopolymerization of styrene this effect can be completely neglected in which case $K_{tcs} = K_{tc0}$ (i.e., $\delta = 0$).¹⁴

At the conversion at which K becomes greater than K_{cr} , VF and M_w take their critical values (VF_{cr}

and M_{wcr}) and from then on the termination rate constant is considered to decay exponentially according to¹²:

$$K_{tc}(X) = K_{tcs}(M_{Mcr}/M_w(X))^N \times \exp(-A(1/VF(X) - 1/VF_{cr})) \quad (31)$$

where N is an adjustable parameter.

Whenever a free radical polymerization is carried out at temperatures below the T_g of the polymer being formed ($T < T_{gp}$), the T_g of the reaction mix (T_{gmix}), which depends on monomer conversion and polymer molecular weight, will equal the polymerization temperature at a critical conversion X_{cr} from which the reaction mix becomes glassy. In the vicinity of X_{cr} the propagation reaction becomes diffusion controlled because the diffusion of monomer to the reactive centre through the glassy polymer matrix is extremely slow. This phenomenon, referred to as the glassy effect, is modeled by decreasing the propagation rate constant for $X > X_{cr}$, as¹²:

$$K_p(X) = K_{p0} \exp(-B(1/VF(X) - 1/VF_{cr2})) \quad (32)$$

Here VF_{cr2} is the free volume of the system at X_{cr} , and B is an adjustable parameter.

On the bases of this treatment the expected effect of n -pentane on the reaction rate can be now explained. Upon addition of n -pentane, the free volume of the system increases and so does the molecular mobility of the polymer chains. Because the small molecules of n -pentane diffuse across the polymer coils, the plasticizing effect thus induced facilitates the translational diffusion of the growing radicals necessary to approach each other and terminate. As a result, the onset of the translational diffusion controlled termination reactions is delayed and a decrease in the polymerization rate must be expected according to the decrease of both $[M]$ and R_f . The decrease in the polymerization rate will proceed up to the conversion at which the free volume of the system is such that the termination reactions become translational diffusion controlled in spite of the plasticizing effect of n -pentane. However, if the concentration of n -pentane is high enough this point may never be reached, in which case a progressive decay of the polymerization rate must be observed.

With regard to the propagation reaction, the increase in free volume caused by the presence of n -pentane may be such that the critical free volume

for the diffusion of monomer to the propagating centre may not be reached. That is, the T_{gmix} may never reach the polymerization temperature (i.e., the polymerization mix does not become glassy) due to the strong plasticizing effect caused by the high molecular mobility (low T_g) of n -pentane. In such cases K_p will not fall.

Because the onset of the diffusion controlled termination reaction occurs at a larger free volume than the onset of the diffusion control propagation reaction, the following scenarios are possible depending on the amount of n -pentane in the reaction mix:

1. Delay of the onset of both diffusion controlled termination and propagation reactions. In this case, the gel effect and the glassy effect occur at higher conversion than in the absence of n -pentane with the consequent decrease in the polymerization rate during the delay until the system autoaccelerates.
2. Delay of the onset of diffusion controlled termination and absence of glassy effect. In this case, the gel effect will occur at higher conversions than in the absence of n -pentane with the consequent decrease in polymerization rate during the delay. However, once the gel effect occurs the autoacceleration must lead to terminal conversions approaching 100%.
3. Absence of both gel and glassy effects. In such case the polymerization rate will decrease progressively according to the decrease in $[M]$ and $[I]^{1/2}$.

In all three cases lower molecular weights at terminal conversions should be expected inasmuch as the larger build-up of molecular weight occurs during the gel effect because of the longer radical mean life before termination caused by the lower translational diffusion of the growing radicals. In the limiting case, when the radicals remain alive due to immobility in the glassy medium, this phenomenon is referred to as radical trapping.¹⁵

In a recent publication, Yoon and Choi¹⁶ developed a very comprehensive kinetic model for the bulk polymerization of styrene using the symmetrical bifunctional initiator 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxy) hexane. Important features of their model include the accounting for a decrease in the initiator efficiency with increasing level of initiator and monomer conversion. Unfortunately, this model does not account for diffusion-controlled propagation and for the effect of inert solvent on diffusion-controlled termination.

EXPERIMENTAL

Styrene (Aldrich Chemical) was washed and distilled following standard procedures.⁸ Monofunctional initiator benzoyl peroxide (Lucidol-BPO, Pennwalt-Lucidol Co.), and bifunctional initiator 1,4-bis(terbutyl peroxycarbo)cyclohexane (Initiator D-162, Akzo-Chemie) were used without any further purification. Chloroform and methanol, both reactive grade, were used as polystyrene solvent and nonsolvent, respectively. *n*-Pentane analytical grade (Aldrich Chemical) was employed in all studies.

All isothermal bulk polymerizations of styrene with and without *n*-pentane were carried out in 5-mm (o.d.) glass ampoules. The ampoule contents were degassed through the standard freeze-thaw cycles and sealed under a maximum pressure of 10^{-4} Torr.

The ampoules containing the reaction mix and *n*-pentane for the experiments at $X_{ad} = 0$, and the experiments without *n*-pentane ($X_{ad} = 1$) were sealed in the standard way described, whereas the ampoules containing the reaction mix for the experiments at $X_{ad} = 0.5$ were sealed with a microsyringe at the top, containing the required amount of *n*-pentane. Polymerizations were carried out by immersing the ampoules in an oil bath at the required temperature. The ampoules were removed from the bath at the required times and immediately quenched in liquid nitrogen. Based on the conversion

data for the experiments without *n*-pentane, the *n*-pentane was added to the ampoule mix through the microsyringe, at the time at which $X = 0.5$. After addition, the new reaction mix was homogenized through agitation, to avoid possible phase separation.

Conversion of the ampoule contents were determined gravimetrically by dissolving the samples in chloroform, and precipitating the polymer with a tenfold excess of methanol. The slurry was vacuum filtered and washed thoroughly with methanol. The polymer was recovered and dried under vacuum at 100°C for 24 h to eliminate all traces of solvent, nonsolvent, and *n*-pentane.

The molecular weight distribution of selected samples were determined by size exclusion chromatography (SEC) using tetrahydrofuran as the carrier solvent in a Waters Scientific Model-150 GPC/ALC.

Model predictions for the all the experiments carried out were performed with the modified versions of the MONOFUN and BIFUN simulation programs, described above using the kinetic rate constants and model parameters values given in Table I. The modified versions of these programs were named MONOPEN and BIPEN simulation programs.

Suspension polymerizations were carried out in a 1-gal stainless steel pilot plant reactor vessel, scaled-down from plant data of two different com-

Table I Values of the Parameters Used in Simulations

Parameter and Value Used	Units	Ref.
Monofunctional system (BPO)		
$K_d = 2.2896 \times 10^{14} \exp(-27233/RT)$	min ⁻¹	6
$f = 0.6$		6
Bifunctional system (TBPCC)		
$K_{d1} = 2.117 \times 10^{14} \exp(-28064/RT)$	min ⁻¹	10
$K_{d2} = 3.850 \times 10^{20} \exp(-40022/RT)$	min ⁻¹	10
$f = 0.7$		10
Both systems		
$K_p = 6.128 \times 10^8 \exp(-7068/RT)$	L/mol-min	13
$K_{tco} = 7.550 \times 10^{10} \exp(-1677/RT)$	L/mol-min	13
$K_{Tfm} = 6.128 \times 10^8 \exp(-13450/RT)$	L/mol-min	13
$K_{th} = 1.314 \times 10^7 \exp(-27440/RT)$	min ⁻¹	10
<i>n</i> -Pentane		
$T_g = 123^\circ\text{K}$; $\alpha = 0.00079$ (1/°K); $d = 0.649 - 0.00115$ ($T^\circ\text{C}$) kg/L		22
Styrene		
$T_g = 185^\circ\text{K}$; $\alpha = 0.001$ (1/°K); $d = 0.924 - 0.000918$ ($T^\circ\text{C}$) kg/L		13
Polystyrene		
$T_g = 370^\circ\text{K}$; $\alpha = 0.00048$ (1/°K); $d = 1.084 - 0.000605$ ($T^\circ\text{C}$) kg/L		13
Gel and glassy effect parameters		
$K = 9.44 \exp(1929/T)$; $A = 0.348$; $M = 0.5$; $N = 1.75$; $B = 1.0$		13
$\delta = 0(X < X_{ad})$; $\delta = 1(X \geq X_{ad})$; $VF_{cr2} = 0.0465$; $D = 1.75$		This work

Table II Reactor Internal Arrangement and Operating Conditions

Recipe	
Initial volume @ 25°C (deionized water + styrene)	$v_0 = 3200$ cc
Dispersed phase volume fraction (@ 25°C)	$\Phi = 0.4$
Initiator concentration (BPO or TBPCC)	$[I]_0 = 0.01$ mol/L-styrene
Suspending agent (TCP) concentration	$[TCP]_0 = 7.5$ g/L-styrene
<i>n</i> -Pentane concentration	$[C_5]_{xad} = 0, 7.5, 15$ wt % (wrt styrene)
Operating Conditions	
Polymerization temperature	$T_p = 90, 105^\circ\text{C}$
Polymerization pressure ($X < X_{ad}$)	$P_0 = 275$ KPa
Polymerization pressure ($X \geq X_{ad}$)	$P = 825$ KPa
Polymerization time (monofunctional, bifunctional)	$t_m = 8$ h, $t_b = 6$ h
Agitation speed	$N = 275$ rpm
Geometrical Parameters	
Liquid height (<i>Z</i>) to tank diameter (<i>T</i>) ratio	$Z/T = 1.2$
Impeller diameter (<i>D</i>) to tank diameter (<i>T</i>) ratio	$D/T = 0.6$
Impeller type (turbine)	4-blade, 45° pitch
Number of impellers	$N_o = 2$
Position of bottom impeller (from reactor bottom)	$H_1 = T/4$
Position of top impeller (from reactor bottom)	$H_2 = (2/3)Z$
Blade width	$W_I = 0.2 D$
Number and position of baffles (offset $T/44$)	$Bf = 4$, every 90°
Baffle width	$W_B = T/12$

mercial manufacturers of expandable polystyrene (Industrias Resistol, S.A., and PlastiFab Ltd.). The MPS and PSD of the resulting beads were determined by sieving the samples through an adequate set of different mesh sizes. The terminal conversion of the PS beads was determined gravimetrically following the same procedure described above.

Impregnation efficiency was determined gravimetrically, quantifying the volatile contents of the beads (corrected for residual monomer), after expanding and melting the beads in vacuum at 180°C for 12 h.

The internal arrangement and reactor operating conditions can be seen in Table II. Details of the scale-down procedure for EPS pilot plant reactors have been published elsewhere.⁶

RESULTS AND DISCUSSION

Monofunctionally Initiated Systems

The effect of the concentration of *n*-pentane, added from the beginning of the polymerization ($X_{ad} = 0$), on the styrene bulk polymerization rate and molecular weight distribution development, was studied first. Figure 1 shows the experimental and model

results of conversion history for bulk PS initiated with BPO (0.01 mol/L) at 90°C. In the absence of *n*-pentane ($[C_5] = 0$) the curve shows the onset of

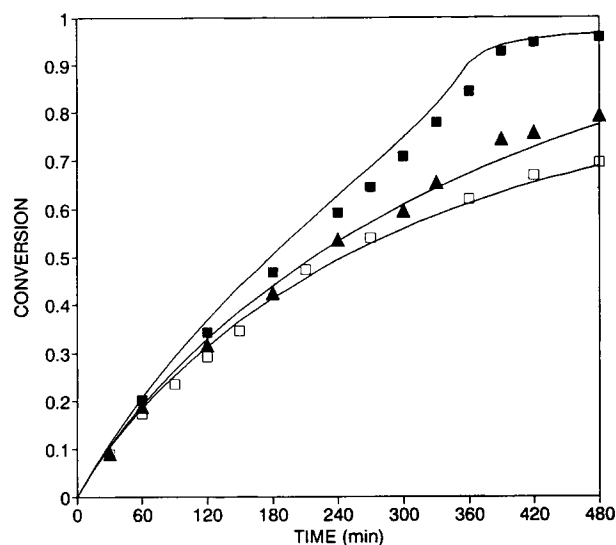


Figure 1 Effect of *n*-pentane concentration, $X_{ad} = 0\%$, on polymerization rate of styrene initiated with [BPO] = 0.01 mol/L at 90°C. Experimental monomer conversion for 0 (■), 7.5 (▲), and 15.0 (□) wt % *n*-pentane. Model predictions (—).

the gel effect at about 50% conversion. When 7.5 wt % *n*-pentane is present, two main differences in the conversion history are observed: first an initial slight decrease in the polymerization rate and second no occurrence of gel effect.

The initial decrease in polymerization rate, in addition to the lower monomer and initiator concentrations due to the presence of *n*-pentane in the system, is due to an increase in the segmental diffusion controlled termination rate, caused by the decrease in growing polymer coil sizes in the pentane-plasticized system. This decrease in the coil sizes is brought about by the fact that the monomer/pentane mix is a poorer solvent for polystyrene than the pure monomer is [solubility parameters $\delta_S = 9.3$, $\delta_{C_5} = 7.08$, $\delta_{PS} = 8.72-9.11$ (cal/cc)^{1/2}].¹⁷ In a poorer solvent, the coil sizes decrease and the segmental diffusion increases.

This behaviour was modelled by giving δ [in eq. (30)] a value of $\delta = 1$ to account for the increase in the segmental diffusion of the smaller coils.

The lack of the gel effect is clear in the curve and was well simulated by the increase in the free volume of the system caused by the *n*-pentane. The onset for the translational diffusion controlled termination is not reached due to the plasticizing effect of the small pentane molecules that increases the translational diffusion of the growing polymer chains. The limiting conversion observed is due to the decrease in the overall rate of reaction due to the low monomer concentration in the system and very low initiator concentration in the late stages of the reaction ($t_{1/2} = 1.5$ h @ 90° for BPO).

The glassy effect does not occur in this system since the T_g of polystyrene with 7.5 wt % of *n*-pentane is well below 90°C ($T_{gPS} = 97^\circ\text{C}$, $T_{gC_5} = -150^\circ\text{C}$).

The curve for 15 wt % *n*-pentane in the initial polymerization mix shows the similar initial decrease in polymerization rate and absence of gel effect, with lower terminal conversion, as the former curve. The initial decrease in polymerization rate was explained and satisfactorily modelled as for the system with 7.5% pentane inasmuch as the coil sizes must decrease more in the poorer solvent at higher concentrations of *n*-pentane. The absence of gel effect was also satisfactorily explained and simulated by the larger increase in the free volume of the system that averts the onset of the diffusion controlled termination. The lower terminal conversion is, then, due to the decrease in the polymerization rate as $[M]$ and $[I]$ decrease.

The evolution of the molecular weight averages with conversion for the three cases is shown in Fig-

ure 2. In this figure it is remarkable how the molecular weight averages are similar throughout the entire conversion range, but especially at high conversions, in spite of the absence of gel effect for the systems with *n*-pentane. Even though this behaviour can be partially explained by the low polymerization rates experienced by the systems with *n*-pentane at high conversions ($X > 50\%$), along with the low radical concentration in the system caused by the initiator depletion (which reduces the termination rate in chemically controlled termination) lower molecular weights than for the system without *n*-pentane should be expected. Therefore, another phenomenon must also be responsible for the molecular weight buildup in the systems with *n*-pentane.

The effect of solvents in the extent of the chain transfer reactions have been reported elsewhere. For donor-acceptor systems it has been shown that the presence of nonpolymerizing strong electron donor solvents inhibits chain transfer reactions by either solvation of free monomer or by secondary complex formation with the acceptor monomer.^{18,19}

For the case at hand, since *n*-pentane is a stronger electron donor than styrene and even though styrene cannot be considered as an electron acceptor, pentane solvation of free monomer can obstruct the hydrogen abstraction necessary for chain transfer to monomer to occur. In such a case, the extent of chain

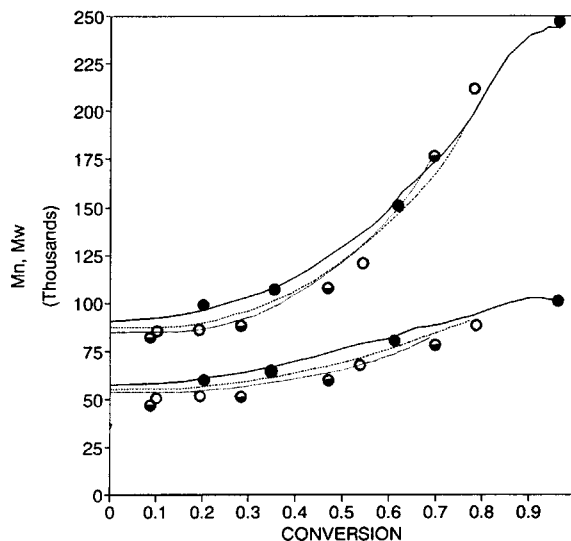


Figure 2 Effect of *n*-pentane concentration, $X_{ad} = 0\%$, on molecular weight distribution development of polystyrene initiated with $[BPO] = 0.01$ mol/L at 90°C. Experimental M_n and M_w for 0 (●), 7.5 (○), and 15.0 (◐) wt % *n*-pentane. Model predictions for 0 (—), 7.5 (— —), and 15.0 (···) wt % *n*-pentane.

transfer to monomer reactions will depend on the *n*-pentane concentration, and the extraordinary molecular weight buildup in the systems with *n*-pentane can be explained.

In order to account for this effect, the transfer to monomer rate constant was considered to decrease with *n*-pentane concentration in the system according to:

$$K_{Tfm} = K_{Tfm0} \exp(-D \cdot V F_{C_5}) \quad (33)$$

where K_{Tfm0} is the transfer to monomer rate constant for the system without *n*-pentane and D is an adjustable parameter. This model was included in the simulation programs MONOPEN and BIPEN where the value of D was fit to 1.75 (see Table I), with which the simulated molecular weight averages described the actual trend. All simulations reported herein were performed with the above treatment.

The effect of the conversion of addition of *n*-pentane on styrene bulk polymerization rate and molecular weight distribution development was studied. Figure 3 shows the experimental and model results for conversion history for the systems with 7.5 wt % *n*-pentane added at 0, 50, and 100% conversion. The curves for $X_{ad} = 0$ and 100% conversion were discussed above (curves for 7.5% and 0% pentane in Fig. 1).

When pentane is added at 50% conversion an immediate decrease in the polymerization rate is observed

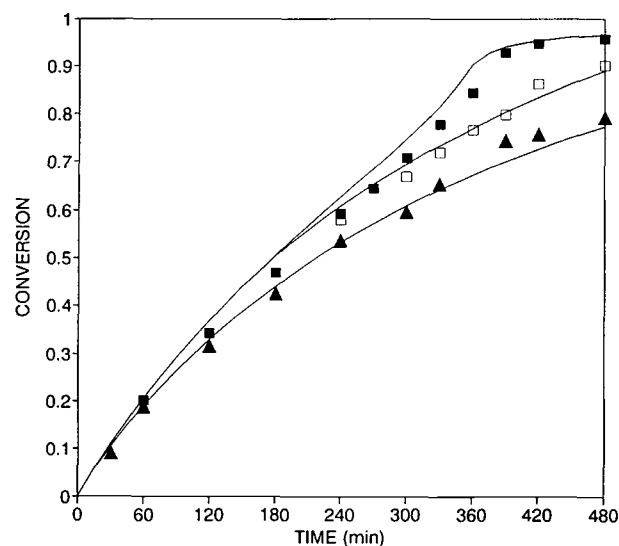


Figure 3 Effect of conversion of addition of *n*-pentane, $[C_5] = 7.5$ wt %, on polymerization rate of styrene initiated with $[BPO] = 0.01$ mol/L at 90°C . Experimental monomer conversion for $X_{ad} = 0\%$ (\blacktriangle), 50% (\square), and 100% (\blacksquare). Model predictions (—).

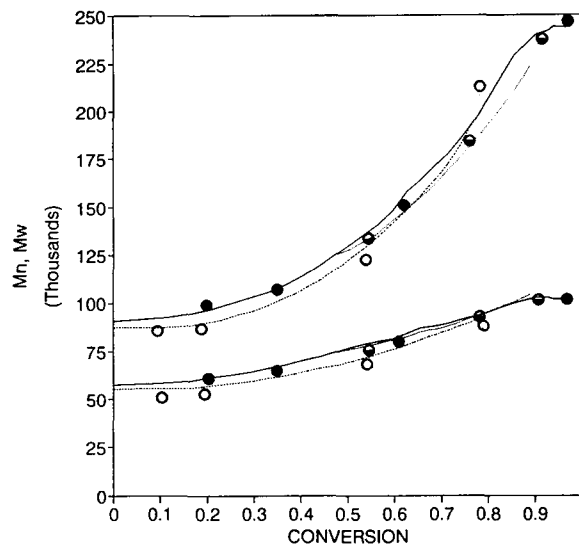


Figure 4 Effect of conversion of addition of *n*-pentane, $[C_5] = 7.5$ wt %, on molecular weight distribution development of polystyrene initiated with $[BPO] = 0.01$ mol/L at 90°C . Experimental M_n and M_w for $X_{ad} = 0\%$ (\circ), 50% (\ominus), and 100% (\bullet). Model predictions for $X_{ad} = 0\%$ (---), 50% ($\bullet\bullet\bullet$), and 100% (—).

and the onset of the gel effect is delayed to conversions above 70% where a marginal increase in polymerization rate occurs. For this system the limiting terminal conversion (ca. 90%) is higher than for the system where $X_{ad} = 0$ but lower than for the system without *n*-pentane. This higher terminal conversion is obtained because of the higher initial polymerization rate and the weak gel effect experienced.

Figure 4 shows the evolution of the molecular weight averages for the three cases considered. The M_n and M_w curves for $X_{ad} = 0$ and 100% have been discussed above (curves for 7.5% and 0% pentane in Fig. 2). As seen in this figure the initial fall in molecular weights following the addition of *n*-pentane at 50% conversion and subsequent molecular weight build-up were properly described by the model. This behaviour is well explained by the delayed weak gel effect observed, along with limited transfer to monomer reactions from the point of addition on *n*-pentane.

Once the effect of *n*-pentane on polymerization rate (R_p) and molecular weight distribution development was established, suspension polymerizations with 7.5 wt % of *n*-pentane added at 0, 50, and 100% were carried out under the same polymerization conditions ($T = 90^\circ\text{C}$, $[BPO] = 0.01$ mol/L-styrene) in order to evaluate the effect of pentane, R_p , and MWD development on suspension stability,

mean particle size (MPS), and particle size distribution (PSD).

The polymerization recipe and reactor operating conditions employed (see Table II), correspond to the scaled-down system selected to obtain an MPS of 0.60 mm when monofunctional initiation with BPO (0.01 mol/L) at 90°C is used and no pentane is added during polymerization.⁶

Figure 5 shows the PSD obtained for the system with $X_{ad} = 100\%$ (reference system with no pentane added). The MPS obtained was 0.598 mm with a PSD variation coefficient, $CV = 0.511$. The variation coefficient (CV) characterizes the spread of the distribution and is defined as σ/MPS , where σ is the standard deviation of the distribution. The reference system then reproduced the MPS expected from the scaled-down procedure (target size 0.6 mm).⁶

The large spread of the distribution and its bimodal character are characteristics of suspension polymerizations carried out in small pilot reactors.²⁰ In large commercial reactors unimodal distributions with variation coefficients ranging from 0.25 to 0.35 are obtained when this MPS is produced.⁶

The systems with $X_{ad} = 0$, and 50%, both yielded suspension set-up after 6 and 6.5 h of polymerization, respectively. This behaviour can be explained in terms of the conversion curves shown in Figure 3. For the system without *n*-pentane ($X_{ad} = 100\%$), the particle growth stage, occurring between 30 and 70% conversion, lasts for a total of 3 h. When pentane is added from the beginning of the polymeriza-

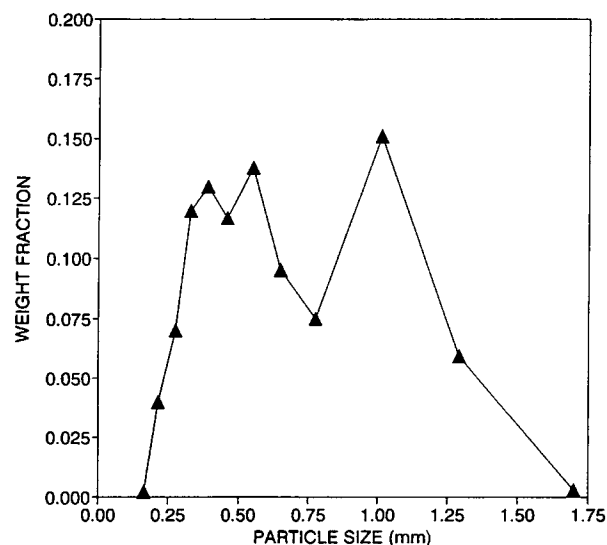


Figure 5 Particle size distribution for suspension polystyrene beads initiated with $[\text{BPO}] = 0.01 \text{ mol/L}$ at 90°C without *n*-pentane. Reference system (see Table II for reactor operating conditions).

tion ($X_{ad} = 0$) the critical viscosity for particle growth is reached after about 2 h of polymerization. From then on particle coalescence is enhanced, even in the presence of a suspending agent. Since the viscosity of the beads is lower in this system than for the system without *n*-pentane because of the plasticization of the matrix, the decrease in the polymerization rate prevents the system from reaching the identity point. As a result, coalescence continues indefinitely until suspension set-up (total coalescence of the beads) occurs.

When *n*-pentane is added at 50% conversion ($X_{ad} = 50\%$), the beads are half way through the growth stage. In this case the plasticization of the beads and the decrease in polymerization rate delay the attainment of the identity point. As a result the particle growth stage is extended for at least two more hours, which is enough for total coalescence of the beads to occur.

In addition, the diffusion of *n*-pentane through the suspending agent-protected surface of the beads seems to increase the coalescence rate. This may be due to the diffusion mechanism of *n*-pentane in the monomer/polymer particles. It has been shown that when *n*-pentane is added to the suspension at high conversions, it diffuses very rapidly into the periphery of the beads (diffusion coefficient D about $1.0 \times 10^{-6} \text{ cm}^2/\text{s}$) where it concentrates. After almost complete *n*-pentane uptake in a few minutes, the pentane starts to diffuse more slowly toward the core of the beads (D from 2.0×10^{-7} to $1.0 \times 10^{-10} \text{ cm}^2/\text{s}$, depending on the degree of conversion).²¹

As a consequence of this diffusion mechanism, after addition of *n*-pentane at 50% conversion, most of the *n*-pentane added will concentrate on the periphery of the beads plasticizing them to such an extent that the surface viscosity of the particles decreases to levels at which particle coalescence is very effective. The net results are suspension instability and total coalescence.

In an attempt to stabilize these systems, the experiments were repeated after increasing the suspending agent concentration twofold. Although the initial suspensions seemed more stable, total coalescence occurred after 7 h of polymerization. Moreover, an experiment with $X_{ad} = 90\%$ was also attempted under the same conditions in which the resulting beads were extremely large (MPS > 2.5 mm) and completely deformed. This corroborated the effect of the diffusion mechanism of *n*-pentane in the coalescence rate.

It is obvious that the marginal increase in productivity achieved at $X_{ad} = 90\%$ with respect to the current manufacturing processes in which *n*-pen-

tane is added at the glassy point (about 96% conversion) does not compensate for the instability problems observed.

In light of these results and because the systems with early addition of *n*-pentane cannot be taken to higher terminal conversions by increasing the initiator concentration without lowering the molecular weights of the product and in turn its processing characteristics and mechanical properties, it is not surprising that early addition of *n*-pentane to the monofunctionally initiated suspension polymerization of PS has not found general use in industry.

Bifunctionally Initiated Systems

As in the case of monofunctionally initiated systems, the effect of the concentration of *n*-pentane [added from the beginning ($X_{ad} = 0$)] on styrene polymerization rate (R_p) and molecular weight distribution development (MWD) was studied first. Ampoule bulk polymerizations were carried out at $T = 105^\circ\text{C}$, using TBPCC (0.01 mol/L) as bifunctional initiator.

Figure 6 shows the experimental and model results for conversion history for systems with 0, 7.5, and 15 wt % *n*-pentane. The first remarkable feature observed in these curves is that, in spite of the *n*-pentane concentration, all the systems reach terminal conversions close to 100%. For the system without *n*-pentane the onset of the gel effect occurs

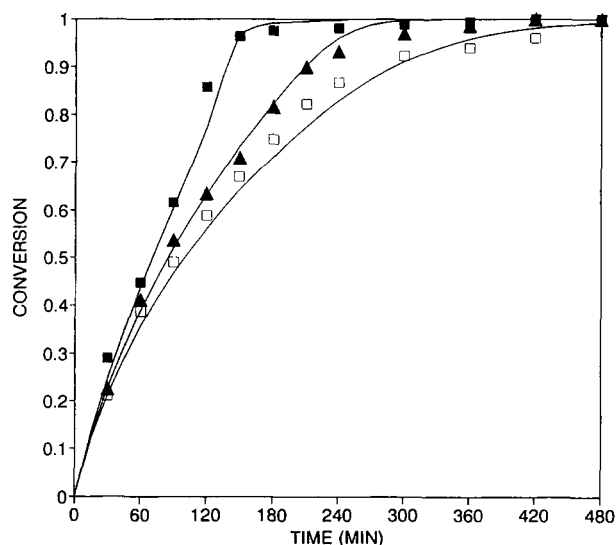


Figure 6 Effect of *n*-pentane concentration, $X_{ad} = 0\%$, on polymerization rate of styrene initiated with [TBPCC] = 0.01 mol/L at 105°C . Experimental monomer conversion for 0 (■), 7.5 (▲), and 15.0 (□) wt % *n*-pentane. Model predictions (—).

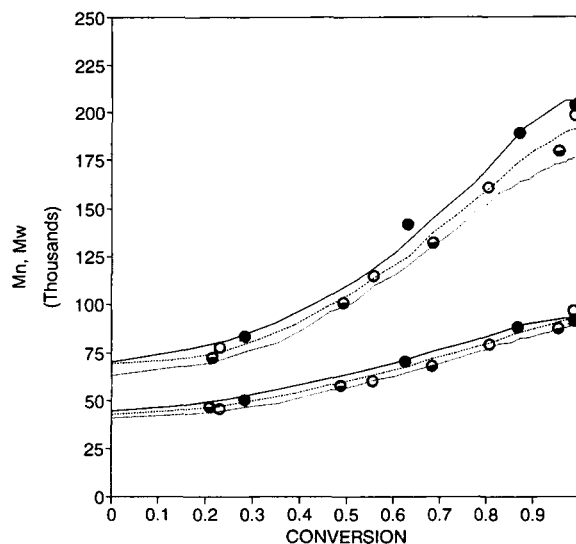


Figure 7 Effect of *n*-pentane concentration, $X_{ad} = 0\%$, on molecular weight distribution development of polystyrene initiated with [TBPCC] = 0.01 mol/L at 105°C . Experimental M_n and M_w for 0 (●), 7.5 (○), and 15.0 (●) wt % *n*-pentane. Model predictions for 0 (—), 7.5 (---), and 15.0 (⋯) wt % *n*-pentane.

at about 50% conversion and because the polymerization temperature T is above the T_g of polystyrene, no glassy effect occurs. Note that for this system 97% conversion is reached after only 2.5 h of polymerization.

The system with 7.5 wt % *n*-pentane shows a delay in the onset of the gel effect to conversions above 70%. The weak gel effect experienced by this system caused by the enhanced free volume and the plasticization of the polymer matrix, well represented by the kinetic model, was capable of carrying the polymerization to completion in about 6 h.

For the system with 15 wt % *n*-pentane, a more delayed and weaker gel effect occurs. The occurrence of this weak gel effect is only noticeable in that the reaction rate does not fall according to the decrease in $[M]$ and $[I]^{1/2}$. For this system the moderated autoacceleration experienced was capable of carrying the polymerization to completion in about 8 h. In addition, for the two systems with *n*-pentane, the contribution of the thermal initiation of styrene to the total initiation rate, at this temperature level, prevented lower terminal conversions caused by dead end polymerization after virtual initiator depletion at 4 h ($t_{1/2} = 0.5$ h @ 105°C).⁶

The experimental and model results for the effect of *n*-pentane concentration on MWD development for the above systems is shown in Figure 7. Note that in spite of the high reaction rates reached (al-

most four times higher than for monofunctional initiation), the weight average molecular weight of the final products are only 15–20% lower than for the monofunctional case. The M_w obtained for all three cases are still within the range for adequate processing of EPS (M_w from 180,000 to 250,000).⁶ Moreover, the final M_n obtained is similar for both monofunctionally and bifunctionally initiated systems.

These results demonstrate the ability of bifunctional initiators to produce high molecular weight polymer at very high reaction rates. Note also in Figure 7 that the model results closely follow the actual trend, which indicates that the model for enhanced free volume and limited chain transfer to monomer for polymerization in the presence of n -pentane applies as well for bifunctional initiation.

The effect of the conversion of addition of n -pentane (7.5 wt %) on R_p and MWD development, in bulk polymerization of styrene initiated with bifunctional initiator TBPCC (0.01 mol/L) at 105°C, was studied. Figure 8 shows the conversion history for $X_{ad} = 0, 50,$ and 100%. The curves for 0 and 100% have been discussed above (curves for 7.5 and 0% n -pentane in Fig. 6).

For the system in which n -pentane is introduced at 50% conversion, the curve, as expected, shows an intermediate behaviour between the systems with $X_{ad} = 0\%$ and $X_{ad} = 100\%$ and the conversion approaches 100% at about 5 h. In this curve, an im-

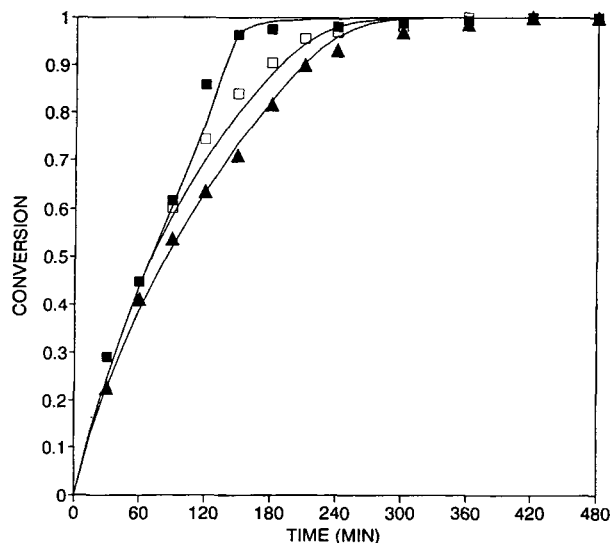


Figure 8 Effect of conversion of addition of n -pentane, $[C_s] = 7.5$ wt %, on polymerization rate of styrene initiated with $[TBPCC] = 0.01$ mol/L at 105°C. Experimental monomer conversion for $X_{ad} = 0\%$ (\blacktriangle), 50% (\square), and 100% (\blacksquare). Model predictions (—).

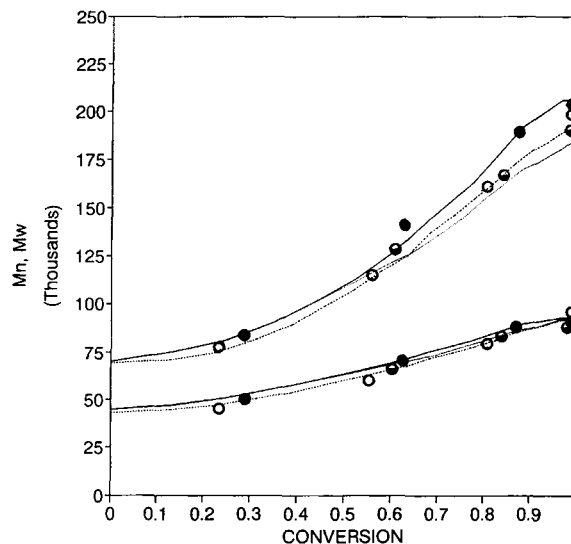


Figure 9 Effect of conversion of addition of n -pentane, $[C_s] = 7.5$ wt %, on molecular weight distribution development of polystyrene initiated with $[TBPCC] = 0.01$ mol/L at 105°C. Experimental M_n and M_w for $X_{ad} = 0\%$ (\circ), 50% (\bullet), and 100% (\bullet). Model predictions for $X_{ad} = 0\%$ (---), 50% ($\bullet\bullet\bullet$), and 100% (—).

mediate decrease in the polymerization rate is observed upon addition of n -pentane, followed by a delayed and weak gel effect that yields a reaction rate similar to that for the curve of $X_{ad} = 0\%$, but only at slightly higher conversions equal to the difference in conversions at the addition point. In Figure 9, the experimental and model results for the evolution of the molecular weight averages for this system and the other two discussed previously (see Fig. 7 for 0 and 7.5 wt % pentane) are shown. Note the similarity of the M_n curves for all three systems. The model M_w curve for the system with $X_{ad} = 50\%$ crosses the curve for $X_{ad} = 0\%$ at about 70% conversion due to the higher polymerization rate of the former at similar gel effect strength. In actuality, the experimental results show that this behaviour occurs at higher conversions.

The model predictions shown in Figures 8 and 9 for the bifunctionally initiated system, closely follow the actual behaviour of the system, which indicates that the model for enhanced free volume and limited transfer to monomer applies also for additions of n -pentane at intermediate conversions.

After establishing the effect of the concentration and conversion of addition of n -pentane on R_p and MWD development, suspension polymerizations [at 105°C using bifunctional initiator TBPCC (0.01 mol/L-styrene) under the same scaled-down conditions as for the monofunctional system] were car-

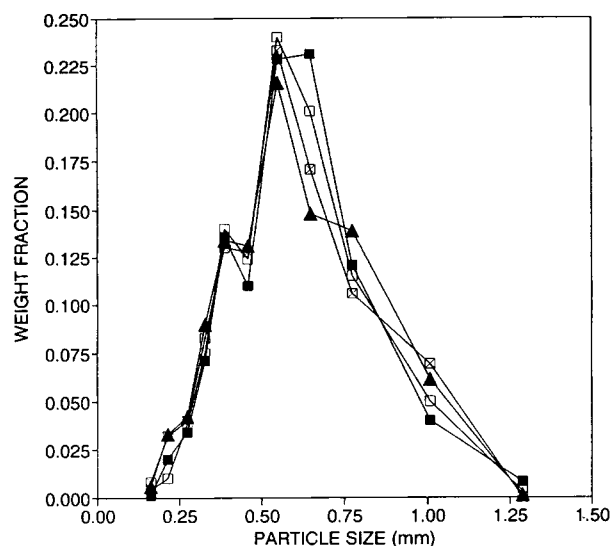


Figure 10 Effect of conversion of addition of *n*-pentane, $[C_5] = 7.5$ wt %, on particle size distribution for suspension polystyrene beads initiated with $[TBPCC] = 0.01$ mol/L at 105°C . Experimental results for $X_{ad} = 0\%$ (■), 50% (□), 90% (⊗), and 100% (▲) (see Table II for reactor operating conditions).

ried out to evaluate the effect of these variables on suspension stability, MPS, and PSD.

Figure 10 shows the particle size distributions of the beads obtained for $X_{ad} = 0, 50, 90,$ and 100% conversion under the described conditions.

The similarity of the four distributions obtained is remarkable. The mean particle sizes calculated from the above distributions all were less than the 0.6 -mm mean size of the monofunctional reference system (see Fig. 5). In addition, the spread of the PSDs obtained (CV) varied from 0.319 to 0.359 , which means that both smaller MPS and narrower PSD are obtained at high polymerization rates, even at temperatures above the T_g of polystyrene. More-

over, the final conversions reached were above 99% for all four products. And the impregnation efficiency (defined as the mass of *n*-pentane in the dry beads divided by the initial mass of *n*-pentane loaded to the reactor) was above 95% for all three products bearing *n*-pentane. Table III summarizes all the experimental results for these systems.

The explanation of the observed behaviour is as follows. In the bifunctionally initiated suspension polymerizations carried out, the MPS decreased very slightly from 0.551 mm to 0.542 mm when X_{ad} increased. This is expected inasmuch as the later the addition of *n*-pentane the shorter the duration of the particle growth stage. Based on the results given in Figure 8, it can be seen that the duration of the particle growth stage (30 – 70% conversion) is 1.2 h for $X_{ad} = 100$ and 90% , 1.4 h for $X_{ad} = 50\%$, and 1.6 h for $X_{ad} = 0\%$. Moreover, it has been shown that the spread of the distribution increases with time during the particle growth stage.²⁰ Consequently, shorter growing periods must result in narrower PSD as observed herein.

From these results, it can be concluded that the enhanced particle coalescence caused by both the early presence of *n*-pentane in the suspension system and the higher polymerization temperatures is completely overcome if substantial reductions in the particle growth time are achieved. Therefore, the main parameter controlling both MPS and PSD in suspension polymerization of styrene is the duration of the particle growth stage.

In the monofunctionally initiated system studied, the duration of the particle growth stage increases dramatically with the addition of *n*-pentane, due to a decrease in polymerization rate and limiting conversions that do not allow the system to reach the identity point. In addition, the plasticized polymer particle is more prone to coalescence than the particle without *n*-pentane. The sum of these effects

Table III Suspension Polymerization Experimental Results

Initiator Type	$[TCP]_0$ (g/Lst)	X_{ad} (%)	MPS (mm)	σ (mm)	CV (σ /MPS)	CONV (%)	Imp. ef (%)
BPO	7.5	100	0.598	0.306	0.511	96.8	—
TBPCC	7.5	0	0.551	0.176	0.319	> 99	95.4
TBPCC	7.5	50	0.550	0.178	0.324	> 99	95.9
TBPCC	7.5	90	0.543	0.195	0.359	> 99	96.1
TBPCC	7.5	100	0.542	0.196	0.361	> 99	—
TBPCC	5.0	50	0.695	0.191	0.275	> 99	95.0
TBPCC	3.5	50	0.954	0.266	0.278	> 99	97.3

(—) No *n*-pentane added.

yields suspension set-up even at high suspending agent concentrations.

In the bifunctionally initiated systems, the decrease in the polymerization rate caused by the early presence of *n*-pentane does not limit the terminal conversion and as a result the systems reach the identity point after a particle growing period that is much shorter than that of the monofunctional system without *n*-pentane. Consequently, stable suspensions are observed, and smaller MPS and narrower PSD are achieved at the end of the polymerization even with the enhanced particle coalescence caused by the particle plasticization.

From the PSD results, it may be suggested that the minimum effect on MPS and PSD observed in the bifunctionally initiated suspension polymerizations of styrene in the presence of *n*-pentane can be caused by overstabilization of the system. In spite of the results for the monofunctional system showing that the suspension is not overstabilized, two additional experiments at $X_{ad} = 50\%$ with lower suspending agent concentration, were carried out to show the response of the system to changes in stabilizer concentration.

Figure 11 shows the suspension particle size distributions obtained at different stabilizer concentrations, for the bifunctionally initiated systems (TBPCC = 0.01 mol/L, $T = 105^\circ\text{C}$), with 7.5 wt % *n*-pentane added at $X_{ad} = 50\%$. The results for

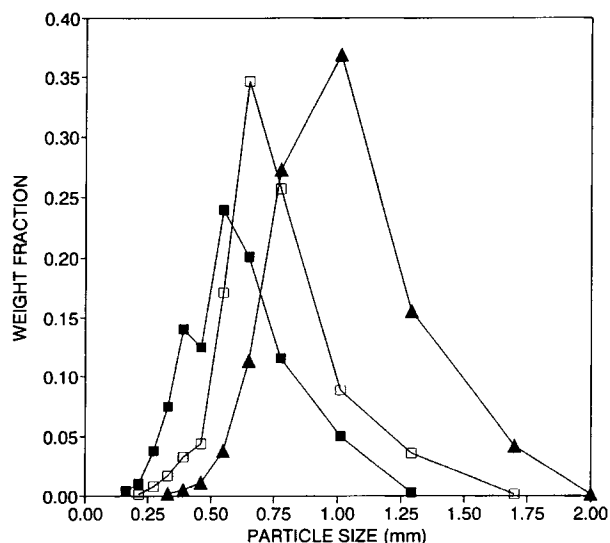


Figure 11 Effect of suspending agent concentration on particle size distribution for suspension polystyrene with early addition of *n*-pentane, $X_{ad} = 50\%$, initiated with [TBPCC] = 0.01 mol/L, at 105°C . Experimental results for [TCP] = 7.5 (■), 5.0 (□), and 3.5 (▲) g/L (styrene) (see Table II for reactor operating conditions).

MPS, PSD, terminal conversion, and impregnation efficiency of these systems are summarized in Table III.

From the results shown in Figure 11, it is obvious that the system is very sensitive to changes in stabilizer concentration and, therefore, is not overstabilized. As expected, the MPS increases as the suspending agent concentration decreases but not so the terminal conversion nor the impregnation efficiency (see Table III). Note how the distributions become unimodal at larger MPS. The shape of the PSD depending on the MPS in pilot plant reactors has been explained elsewhere.⁶

Also, from these results it has been proven that all the different commercial EPS bead sizes (0.45–2.0 mm) can be obtained in a single stage process through bifunctionally initiated suspension polymerization of styrene with early addition of *n*-pentane.

CONCLUSIONS

The modification of previously published kinetic models to account for the unique features of styrene free radical polymerization in the presence of *n*-pentane, for both monofunctional and bifunctional initiation has been reported. The modifications proposed, based on enhanced free volume and limited transfer to monomer reactions caused by the early presence of *n*-pentane in the polymerizing system, fully describe and closely follow the behaviour of the systems studied. As a result of the modifications introduced, two simulation programs that forecast monomer conversion and molecular weight distribution development for each type of initiation have been developed.

The feasibility of carrying out suspension polymerizations of styrene in the presence of *n*-pentane under different addition conditions to obtain EPS type beads in a single stage process has been demonstrated for bifunctionally initiated systems.

For monofunctionally initiated systems, enhanced particle coalescence leading to suspension set-up, caused by the early presence of *n*-pentane with the consequent inability of the system to reach the identity point, could not be overcome in any of the systems studied.

The authors wish to express their gratitude to OCMR and NSERC (Industrial Research Assistance Program), for its financial support, as well as to Industrias Resistol, S.A. (PRODESA Plant), Mexico, and PlastiFab LTD., Can-

ada, manufacturers of EPS, for their valuable plant data and permission to publish results of previous research studies performed on their behalf.

REFERENCES

1. R. B. Bishop, *Practical Polymerization for Polystyrene*, Cahners, Boston, 1971.
2. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci., A-1*, **6**, 2663 (1968).
3. J. M. Church, *Chem. Eng.*, **73**, 79 (1966).
4. K. Arai, M. Konno, Y. Matunaga, and S. Saito, *J. Chem. Eng. Jpn.*, **10**, 325 (1977).
5. M. Konno, T. Muto, and S. Saito, *J. Chem. Eng. Jpn.*, **21**, 335 (1988).
6. M. A. Villalobos, Master's thesis, McMaster University, Hamilton, Ontario, Canada, 1989.
7. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanism*, Butterworths, London, 1958.
8. M. A. Villalobos, A. E. Hamielec, and P. E. Wood, *J. Appl. Polym. Sci.*, **42**, 629 (1991).
9. K. Y. Choi and G. D. Lei, *AIChEJ*, **33**, 2067 (1987).
10. K. Y. Choi, W. R. Liang, and G. D. Lei, *J. Appl. Polym. Sci.*, **35**, 1547 (1988).
11. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
12. F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.*, **27**, 489 (1982).
13. H. K. Mahabadi and K. F. O'Driscoll, *Macromolecules*, **10**, 55 (1977).
14. D. Bhattacharya and A. E. Hamielec, *Polymer*, **27**, 611 (1986).
15. S. Zhu, Y. Tian, A. E. Hamielec, and D. R. Eaton, *Macromolecules*, **23**, 1144 (1990).
16. W. J. Yoon and K. Y. Choi, *Polymer*, **23**, 4582 (1992).
17. K. J. Sears and J. R. Darby, *The Technology of Plasticizers*, John Wiley & Sons, New York, 1982.
18. E. Tsuchida, T. Tomono, and H. Sano, *Die Makrom. Chem.*, **151**, 245 (1972).
19. S. Carter, J. N. Murrell, and E. J. Rosch, *J. Am. Chem. Soc.*, 2048 (1965).
20. M. Konno, K. Arai, and S. Saito, *J. Chem. Eng. Jpn.*, **15**, 31 (1982).
21. M. A. Villalobos, *Diffusion of Blowing Agent Into PS Beads*, Report EPR-01 to PlastiFab LTD., Calgary, Alberta, Canada (1991).
22. L. Scheffan and M. B. Jacobs, *Handbook of Solvents*, D. Van Nostrand Co. Inc., New York, 1953.

Received October 28, 1992

Accepted February 19, 1993