Bulk thermal copolymerization of styrene/*p*-methylstyrene: Modelling diffusion-controlled termination and propagation using free-volume theory

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Herein is reported the development of a kinetic model for the bulk thermal copolymerization of styrene/*p*-methylstyrene (PMS). Free-volume theory has been used to model diffusion controlled termination and propagation. This kinetic model is in reasonable agreement with published rate and molecular weight data on thermal homopolymerization of styrene[1] and PMS[2] as well as with data for the copolymerization of these monomers[3].

(Keywords: copolymerization; diffusion; free-volume theory)

INTRODUCTION

Batch kinetic data on the thermally-initiated bulk copolymerization of styrene/PMS and the homopolymerization of each of these monomers have been reported earlier[1–3]. The objective of the present study was to develop a kinetic model and to use the free-volume theory to model diffusion-controlled termination and propagation reactions for this system. Such an approach has already been used to model the copolymerization of styrene/acrylonitrile[4] and methyl methacrylate (MMA)/PMS[5] with reasonable success. The present model includes segmental-diffusion controlled termination at low polymer concentrations.

MODEL DEVELOPMENT

Mechanism of copolymerization

Penultimate effects have been ignored in all chemically controlled reactions, i.e. the reactivity of the polymer radical is assumed to depend solely on its terminal monomer unit. The reactions considered in the model include:

Initiation:

$$\left.\begin{aligned} M_1 + M_1 &\underset{k_{-\mathrm{I}1}}{\overset{k_{\mathrm{I}1}}{\rightleftharpoons}} Z_1 \\ M_2 + M_2 &\underset{k_{-\mathrm{I}2}}{\overset{k_{\mathrm{I}2}}{\rightleftharpoons}} Z_2 \\ M_1 + M_2 &\underset{k_{-\mathrm{I}3}}{\overset{k_{\mathrm{I}3}}{\rightleftharpoons}} Z_3 \end{aligned}\right\} \text{Diels–Alder adducts}$$

$$\left.\begin{aligned} Z_1 + M_1 &\xrightarrow{k_{\mathrm{T}11}} T \\ Z_1 + M_2 &\xrightarrow{k_{\mathrm{T}12}} T \end{aligned}\right\} \text{Cyclic trimers}$$

$$\left.\begin{aligned} Z_2 + M_1 &\xrightarrow{k_{\mathrm{T}21}} T \\ Z_2 + M_2 &\xrightarrow{k_{\mathrm{T}22}} T \\ Z_3 + M_1 &\xrightarrow{k_{\mathrm{T}31}} T \\ Z_3 + M_2 &\xrightarrow{k_{\mathrm{T}32}} T \end{aligned}\right\} \text{Cyclic trimers}$$

$$\left.\begin{aligned} Z_1 + M_1 &\xrightarrow{k_{\mathrm{S}11}} 2R_1^{\bullet} \\ Z_1 + M_2 &\xrightarrow{k_{\mathrm{S}12}} 2R_1^{\bullet} \\ Z_2 + M_1 &\xrightarrow{k_{\mathrm{S}21}} 2R_1^{\bullet} \\ Z_2 + M_2 &\xrightarrow{k_{\mathrm{S}22}} 2R_1^{\bullet} \\ Z_3 + M_1 &\xrightarrow{k_{\mathrm{S}31}} 2R_1^{\bullet} \\ Z_3 + M_2 &\xrightarrow{k_{\mathrm{S}32}} 2R_1^{\bullet} \end{aligned}\right\} \text{Monoradicals}$$

A similar initiation mechanism has been employed for the thermal copolymerization of styrene/acrylonitrile by Kirchner *et al.*[6]. The initiation mechanism has not been verified in this investigation, but rather has been used to derive a limiting rate expression which is third-order in monomer. The details are given later.

Propagation:

$$R_{r,1}^{\bullet} + M_1 \xrightarrow{k_{11}} R_{r+1,1}^{\bullet}$$

$$R_{r,2}^{\bullet} + M_1 \xrightarrow{k_{21}} R_{r+1,1}^{\bullet}$$

$$R_{r,1}^{\bullet} + M_2 \xrightarrow{k_{12}} R_{r+1,2}^{\bullet}$$

$$R_{r,2}^{\bullet} + M_2 \xrightarrow{k_{22}} R_{r+1,2}^{\bullet}$$

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The total rate of polymerization (R_p) can be defined as

$$R_p = k_{p0}[M][R^\bullet] \tag{1a}$$

where

$[M] = [M_1] + [M_2]$ = total monomer concentration

and

$[R^\bullet] = \sum_{i=1}^{2} \sum_{s=1}^{\infty} [R^\bullet_{s,i}]$ = total radical concentration

R_p can also be expressed as

$$R_p = \sum_{i=1}^{2} \sum_{j=1}^{2} k_{ij}[M_i][R_j] \tag{1b}$$

where

$$[R_i] = \sum_{s=1}^{\infty} [R_{s,i}] \qquad i = 1,2$$

For long copolymer chains, the rate of addition of monomer **1** to a polymer radical having monomer **2** as its chain end can be set equal to the rate of addition of monomer **2** to a radical having monomer **1** as its chain end and therefore

$$k_{21}[M_1][R_2^\bullet] = k_{12}[M_2][R_1^\bullet] \tag{1c}$$

Using equations (1a), (1b) and (1c) and some algebra, one has for k_{p0}

$$k_{p0} = k_{11}k_{22}(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)/(k_{22} r_1 f_1 + k_{11} r_2 f_2) \tag{1}$$

where

$$r_i = k_{ii}/k_{ij} \qquad i \neq j$$

and f_1 and f_2 are monomer mole fractions.

Transfer to monomer and other small molecule(s):

$$R^\bullet_{r,1} + M_1 \xrightarrow{k_{f11}} R_{1,1} + P_r$$

$$R^\bullet_{r,1} + M_2 \xrightarrow{k_{f12}} R_{1,2} + P_r$$

$$R^\bullet_{r,2} + M_1 \xrightarrow{k_{f21}} R_{1,1} + P_r$$

$$R^\bullet_{r,2} + M_2 \xrightarrow{k_{f22}} R_{1,2} + P_r$$

$$R^\bullet_{r,1} + S \xrightarrow{k_{f1S}} P_r + S^\bullet$$

$$R^\bullet_{r,2} + S \xrightarrow{k_{f2S}} P_r + S^\bullet$$

Equating the total rate of transfer to monomer to $k_{fm}[M][R^\bullet]$ and using equation (1c) and the definition of f_i and r_i ($i = 1,2$), one has for k_{fm}, the pseudo transfer to monomer rate constant

$$k_{fm} = \frac{k_{21}k_{f11}f_1^2 + f_1 f_2(k_{21}k_{f12} + k_{12}k_{f21}) + k_{12}k_{f22}f_2^2}{(k_{21}f_1 + k_{12}f_2)} \tag{2}$$

Termination by combination:

$$\left.\begin{aligned} &R^\bullet_{r,1} + R^\bullet_{s,1} \xrightarrow{k_{t11}} P_{r+s} \\ &R^\bullet_{r,1} + R^\bullet_{s,2} \xrightarrow{k_{t12}} P_{r+s} \\ &R^\bullet_{r,2} + R^\bullet_{s,2} \xrightarrow{k_{t22}} P_{r+s} \end{aligned}\right\} \text{chemically-controlled termination}$$

$$R^\bullet_{r,i} + R^\bullet_{s,j} \xrightarrow{k_{tc}} P_{r+s} \qquad i = 1,2 \text{ and } j = 1,2 \text{ diffusion-controlled termination}$$

Termination by disproportionation is considered negligible[1,7]. Equating the total rate of termination to $k_{tc0}[R^\bullet]^2$, one has for k_{tc0} (chemically-controlled termination rate constant)

$$k_{tc0} = \frac{(k_{t11}k_{21}^2 f_1^2 + 2k_{t12}k_{21}k_{12}f_1 f_2 + k_{t22}k_{12}^2 f_2^2}{(k_{21}f_1 + k_{12}f_2)^2} \tag{3}$$

In the above reactions M_1 and M_2 are the two monomers styrene and PMS respectively. S represents any unidentified small molecule. It could be (i) a Diels–Alder adduct, (ii) cyclic trimer or any other by-product of the thermal initiation reactions. There is evidence that chain transfer to small molecules other than monomer is significant; however, the identity of these molecules is not certain, but is likely an intermediate in the thermal initiation mechanism[1].

Diffusion-controlled termination and propagation

The data of North and Reed[8], Ludwico and Rosen[9], Chiantore and Hamielec[2] and copolymerization data on styrene/PMS[3] all indicate that an initial increase in the termination constant k_t occurs with conversion at low polymer concentrations. This behaviour has been explained theoretically by North and Reed[8] and also by Mahabadi and O'Driscoll[10]. Both have derived the following relation for very low monomer conversions

$$\frac{k_t}{k_{t0}} = \frac{k_{tseg}}{k_{t0}} = (1 + \delta c) \tag{4}$$

where k_{t0} is the value of k_t in pure monomer, c is the polymer concentration, k_{tseg} is the segmental diffusion-controlled termination rate constant and δ is a proportionality constant. A theoretical derivation of δ and its measurement are presented in ref. 10. δ increases with the size of the macroradical or in other words, the larger the macroradical, the more dependent is its size and termination constant on polymer concentration. In a thermodynamically 'good' solvent an increase in the polymer concentration decreases the size of the macroradical coil and results in an increased chain end concentration gradient, across which segmental diffusion takes place[10].

As the polymer concentration increases further, translational diffusional resistance becomes the controlling resistance and k_t decreases rapidly with increasing conversion. The point of transition from segmental to translational diffusion control has been identified by a critical concentration, c_1, at which $k_{tseg} = k_{ttrans}$, where k_{ttrans} is the translational diffusion-controlled k_t, by Tulig and Tirrell[11]. Marten and

Hamielec (MH model)[12] defined the point of transition on the basis of chain entanglements by identifying a parameter K_3 given by

$$K_3 = \bar{M}^m_{\mathrm{wcr1}} \exp(A/V_{\mathrm{Fcr1}}) \qquad (5)$$

where

$\bar{M}_{\mathrm{wcr1}}$ is the accumulated weight-average molecular weight of the polymer at the point of entanglement;

V_{Fcr1} is the free volume fraction at $\bar{M}_{\mathrm{w}} = \bar{M}_{\mathrm{wcr1}}$;

A and m are adjustable parameters.

The MH model used free-volume theory to predict the self-diffusion coefficient of the entangled macroradical.

According to Bueche[13], the diffusion coefficient D_{p} of a polymer molecule of molecular weight M diffusing in a matrix of monodisperse polymer of the same molecular weight is given by

$$D_{\mathrm{p}} = \frac{\phi_0 \Psi^2}{K_2 M^n} \exp(-A/V_{\mathrm{F}}) \qquad (6)$$

where ϕ_0 is the jump frequency, Ψ is the jump distance, K_2 is a constant and V_{F} is the free volume fraction and is given by:

$$V_{\mathrm{F}} = (0.025 + a_{\mathrm{p}}(T - T_{\mathrm{gp}}))\frac{V_{\mathrm{p}}}{V_{\mathrm{T}}} + (0.025 + a_{\mathrm{M}}(T - T_{\mathrm{gm}}))\frac{V_{\mathrm{M}}}{V_{\mathrm{T}}} + (0.025 + a_{\mathrm{s}}(T - T_{\mathrm{gs}}))\frac{V_{\mathrm{S}}}{V_{\mathrm{T}}}$$

where subscripts m, p and s denote monomer, polymer and solvent (or a second monomer), respectively, T is polymerization temperature, T_{g} is glass transition temperature, V is volume, V_{T} is total volume, $a = a_{\mathrm{l}} - a_{\mathrm{g}}$; a_{g} is expansion coefficient for the glassy state and a_{l} is the same for the liquid state.

Assuming that the termination constant k_{t} is proportional to the diffusion coefficient under translational diffusion-controlled conditions and following Marten and Hamielec[12] one has

$$\frac{k_{\mathrm{t}}}{k_{\mathrm{t}}^*} = \left(\frac{\bar{M}_{\mathrm{wcr1}}}{\bar{M}_{\mathrm{w}}}\right)^n \exp\left(-A\left(\frac{1}{V_{\mathrm{F}}} - \frac{1}{V_{\mathrm{Fcr1}}}\right)\right) \qquad (7)$$

where k_{t}^* is the value of k_{t} at $\bar{M}_{\mathrm{w}} = \bar{M}_{\mathrm{wcr1}}$ and n is an adjustable parameter.

Various molecular weight dependencies have been proposed to describe the diffusion-controlled k_{t}. According to Bueche[13], $n = 3.5$ for a large entangled diffusing macromolecule. However, his analysis does not account for a polydisperse polymer environment. In the context of reptation theory, k_{t} scales as M^{-1} for a growing macroradical of molecular weight M[14]. Reptation theory does not apply at very high conversions where polymer/polymer friction is significant[15]. Soh and Sundberg[16] used an exponent of 2.4 in their chain length dependent model. Marten and Hamielec have used a value of $n = 1.75$ to model the bulk and solution polymerization of MMA[12] and styrene[17]. The MH model, though perhaps less rigorous than the Soh and Sundberg model, appears reasonably to model homo- and copolymerizations to limiting conversion[4,5,12,17].

The present copolymerization model uses the MH model equations to account for diffusion-controlled termination and propagation.

Equation (4) has been used at low conversions until equation (5) is satisfied whereafter equation (7) is used to model k_{t}. It should be noted that this represents an attempt to account for segmental diffusion control before the macroradical chains are entangled. However, the situation where translational diffusion control occurs before chain entanglement may not be accounted for.

At very high conversions, as the polymer chains become essentially immobilized, the chain ends of the growing macroradicals move by 'reaction diffusion'[15]. Following Stickler[15] the following expression for the 'reaction diffusion coefficient' D_{R}, can be written:

$$D_{\mathrm{R}} = \frac{n_{\mathrm{s}} l_0^2}{6} k_{\mathrm{p}}[\mathrm{M}] \qquad (8)$$

where n_{s} is the average number of monomeric units in a polymer segment; l_0 is the length of monomeric unit.

Substituting the expression for mutual diffusion coefficient in the Smoluchowski equation, one has[15]:

$$k_{\mathrm{t}} = \frac{8\pi N_{\mathrm{A}}}{1000} \cdot \frac{\phi n_{\mathrm{s}} l_0^2}{6} \cdot k_{\mathrm{p}}[\mathrm{M}] = Z k_{\mathrm{p}}[\mathrm{M}] \qquad (9)$$

where N_{A} is Avogadro's number

$\phi = \left(\frac{6V_{\mathrm{M}}}{\pi N_{\mathrm{A}}}\right)^{1/3}$ is the reaction radius

V_{M} is the molar volume of monomer

The contribution of 'reaction diffusion' is negligible until very high conversions near limiting conversions are reached[15]. For polymerizations at a temperature above the glass-transition temperature of the polymer, termination by reaction diffusion is likely not limiting.

Propagation is also a diffusion-controlled reaction at high conversions. Following Marten and Hamielec[12], the diffusion-controlled propagation rate constant is given by:

$$k_{\mathrm{p}} = k_{\mathrm{p0}} \exp\left[-B\left(\frac{1}{V_{\mathrm{F}}} - \frac{1}{V_{\mathrm{Fcr2}}}\right)\right] \text{ at } x \geqslant x_{\mathrm{crit2}} \qquad (10)$$

where

$$V_{\mathrm{F}} = V_{\mathrm{Fcr2}} \text{ at } x = x_{\mathrm{crit2}}$$

and B is an adjustable parameter.

The propagation rate constants k_{11} and k_{22} are assumed to be equal in this model, as was assumed in ref. 3. As shown earlier[3], this system exhibits negligible composition drift with $r_1 = 0.971 \pm 0.001$ and $r_2 = 0.907 \pm 0.013$. Hence, all the propagation constants become diffusion-controlled at the same V_{F} and k_{p0} does not depend on conversion.

KINETIC MODEL

Rate of thermal initiation, $\mathrm{R_I}$

Application of the stationary-state hypothesis to the intermediates $\mathrm{Z_1}$, $\mathrm{Z_2}$ and $\mathrm{Z_3}$ and considering the limiting case where the radical initiation rate is third order in monomer concentration[3] gives:

$$R_{\mathrm{I}} = (k_{\mathrm{I}} f_1^3 + k_{\mathrm{II}} f_2^3 + k_{\mathrm{III}} f_1^2 f_2 + k_{\mathrm{IV}} f_1 f_2^2)[\mathrm{M}]^3 \qquad (11)$$

where [M] is the total monomer concentration

$$k_{\mathrm{I}}=\frac{2k_{\mathrm{I}1}k_{\mathrm{S}11}}{k_{-\mathrm{I}1}},\quad k_{\mathrm{II}}=\frac{2k_{\mathrm{I}2}k_{\mathrm{S}22}}{k_{-\mathrm{I}2}}$$

$$k_{\mathrm{III}}=2\left(\frac{k_{\mathrm{I}1}k_{\mathrm{S}12}}{k_{-\mathrm{I}1}}+\frac{k_{\mathrm{I}3}k_{\mathrm{S}31}}{k_{-\mathrm{I}3}}\right), k_{\mathrm{IV}}=2\left(\frac{k_{\mathrm{I}2}k_{\mathrm{S}21}}{k_{-\mathrm{I}2}}+\frac{k_{\mathrm{I}3}k_{\mathrm{S}32}}{k_{-\mathrm{I}3}}\right)$$

Rate of monomer consumption

$$\frac{dx}{dt}=k_{\mathrm{p}}(1-x)\left[\frac{R_{\mathrm{I}}}{k_{\mathrm{tc}}}\right]^{1/2} \tag{12}$$

$$V=V_0(1-\varepsilon x) \tag{13}$$

where x is the total molar conversion of monomer.

V is the volume of the reacting mixture.

$\varepsilon=\rho_{\mathrm{M}}(1/\rho_{\mathrm{M}}-1/\rho_{\mathrm{cop}})$

ρ_{cop} = density of copolymer.

$\rho_{\mathrm{M}}=\rho_1\rho_2(f_1M_{\mathrm{m}1}+f_2M_{\mathrm{m}2})/(f_1M_{\mathrm{m}1}\rho_2+f_2M_{\mathrm{m}2}\rho_1)$

$M_{\mathrm{m}1}$ and $M_{\mathrm{m}2}$ are the molecular weights of the monomers.

ρ_1 and ρ_2 are the densities of the monomers.

Molecular weight development

Modelling for linear copolymer chains, the following equations are obtained for r_{N} and r_{W} (instantaneous number and weight average chain lengths)[3] and r_{WR} (weight-average chain length of the macroradicals):

$$r_{\mathrm{N}}=1/(\tau+\beta/2) \tag{14}$$

$$r_{\mathrm{W}}=2(\tau+1.5\beta)/(\tau+\beta)^2 \tag{15}$$

$$r_{\mathrm{WR}}=2/(\tau+\beta) \tag{16}$$

where

$$\tau=\frac{k_{\mathrm{fm}}}{k_{\mathrm{p}}}+(\Phi_1^{\bullet}B_1x+\Phi_2^{\bullet}B_2x) \tag{17}$$

$$\Phi_1=k_{21}f_1(k_{21}f_1+k_{12}f_2)$$

$$\Phi_2=k_{12}f_2/(k_{21}f_1+k_{12}f_2)$$

where $\Phi_1^{\bullet}$ and $\Phi_2^{\bullet}$ are fractions of polymer radicals of types 1 and 2

$$B_1=k_{\mathrm{f1S}}/k_{\mathrm{p}}$$

$$B_2=k_{\mathrm{f2S}}/k_{\mathrm{p}}$$

and

$$\beta=k_{\mathrm{tc}}R_{\mathrm{p}}/(k_{\mathrm{p}}[\mathrm{M}])^2 \tag{18}$$

Also

$$\bar{r}_{\mathrm{N}}=x\Bigg/\int_0^x\frac{\mathrm{d}x}{r_{\mathrm{N}}} \tag{19}$$

and

$$\bar{r}_{\mathrm{W}}=\frac{1}{x}\int_0^x r_{\mathrm{W}}\mathrm{d}x \tag{20}$$

where $\bar{r}_{\mathrm{N}}$ and $\bar{r}_{\mathrm{W}}$ are the accumulated number- and weight-average chain lengths.

Three regions of conversion have been identified in the present model. These are:

Interval 1: $x=0$ to the point where equation (5) is satisfied

$$\left.\begin{aligned}&k_{\mathrm{tc}}=k_{\mathrm{tc}0}(1+\delta c)\\&k_{\mathrm{p}}=k_{\mathrm{p}0}\\&k_{\mathrm{tc}}=k_{\mathrm{tc}}^{*}\text{ where equation (5) is satisfied.}\end{aligned}\right\} \tag{21}$$

Interval 2: After equation (5) is satisfied

$$\left.\begin{aligned}&k_{\mathrm{tc}}=k_{\mathrm{tc}}^{*}\exp\left(-A\left(\frac{1}{V_{\mathrm{F}}}-\frac{1}{V_{\mathrm{Fcr}1}}\right)\right)+Zk_{\mathrm{p}}[\mathrm{M}]\\&k_{\mathrm{p}}=k_{\mathrm{p}0}\end{aligned}\right\} \tag{22}$$

Interval 3: $x\geqslant x_{\mathrm{crit}2}$

$$\left.\begin{aligned}&k_{\mathrm{tc}}=k_{\mathrm{tc}}\text{ as in interval 2}\\&k_{\mathrm{p}}=k_{\mathrm{p}0}\exp\left(-B\left(\frac{1}{V_{\mathrm{F}}}-\frac{1}{V_{\mathrm{Fcr}2}}\right)\right)\end{aligned}\right\} \tag{23}$$

It should be noted that for this high temperature copolymerization of styrene/PMS, $Zk_{\mathrm{p}}[\mathrm{M}]$ in equation (22) is negligible.

RESULTS AND DISCUSSION

Parameter estimation

The calculation of free-volume fraction requires values for the T_{g} of the monomers and the copolymer. The equation used to calculate the V_{F} for copolymerization follows:

$$\begin{aligned}V_{\mathrm{F}}=&[0.025+a_{\mathrm{M}1}(T-T_{\mathrm{gM}1})]\frac{V_{\mathrm{M}1}}{V_{\mathrm{T}}}\\&+[0.025+a_{\mathrm{M}2}(T-T_{\mathrm{gM}2})]\frac{V_{\mathrm{M}2}}{V_{\mathrm{T}}}\\&+[0.025+a_{\mathrm{p}}(T-T_{\mathrm{gP}})]\frac{V_{\mathrm{P}}}{V_{\mathrm{T}}}\end{aligned}$$

where M1 refers to styrene, M2 to PMS and P to the copolymer.

Fedor's relation was used to estimate the $T_{\mathrm{gM}1}$ and $T_{\mathrm{gM}2}$ values[18]. The melting and boiling points of the two monomers were obtained from Kaeding *et al.*[19]. $a_{\mathrm{M}1}$ and $a_{\mathrm{M}2}$ were both set at 0.001 and a_{P} at 0.00048 as these values have been used earlier to model the homopolymerization of styrene at low temperatures[17].

A rigorous theoretical calculation of δ requires parameters that are unavailable in the literature[10]. The plots of k_{tc} as a function of conversion obtained in ref. 3 were used to estimate δ. Assuming a linear relationship between k_{tc} and c at low conversions ($x\leqslant 0.1$), δ was found to be approximately equal to 0.001 ($\mathrm{l\,g^{-1}}$). This value of δ compares well with those found by Dionisio *et al.*[20] for styrene polymerization at 77°C and was found to be largely independent of temperature and comonomer compositions, permitting a single value to be used in the model. Equation (7) was used in intervals 2 and 3 without the molecular weight dependence as the data showed no evidence of M_{W} changing significantly with conversion. Thus

$$k_{\mathrm{tc}}=k_{\mathrm{tc}}^{*}\exp\left[-A\left(\frac{1}{V_{\mathrm{F}}}-\frac{1}{V_{\mathrm{Fcr}1}}\right)\right] \tag{24}$$

Equation (24) has been used by Soh and Sundberg[16] for low temperature styrene polymerizations up to moderate to high conversions. Schulz[21] gives $n_s = 10$ and $l_0 = 0.25$ nm and these values were used for modelling MMA polymerization by Stickler[15]. These values, when employed here for the high temperature thermal copolymerization of styrene/PMS, gave an insignificant contribution.

An initial parameter search for styrene thermal homopolymerization, at temperature levels of 140°C and 170°C using experimental low to moderate conversion *versus* time data, yielded a value of $A = 0.85$. A sixth-order Runge–Kutta differential equation solver within a Gauss–Marquadt optimization scheme was used to fit the conversion–time profiles. This value of A was also found to fit experimental low to moderate conversion–time profiles for PMS thermal homopolymerizations at temperatures of 120°C, 140°C and 160°C and all the thermal copolymerization data reported earlier[3]. A was then fixed at 0.85 and B and $X_{\mathrm{crit}2}$ were next estimated by visually fitting all the conversion–time data available on this system, since the parameter estimation routine proved to be inefficient because of the high correlation between B and $X_{\mathrm{crit}2}$. A value of 0.5 for B was found to fit adequately all of the conversion–time data. The temperature dependence of K_3 was determined using all of the reported data[1,2] as well as the data measured by the authors[3]. *Figures 1* and *2* show K_3 and $V_{\mathrm{Fcr}2}$ plotted as functions of temperature. $V_{\mathrm{Fcr}2}$ is observed to be almost independent of temperature. *Figure 3* shows a typical variation of k_{tc} and the reaction diffusion termination

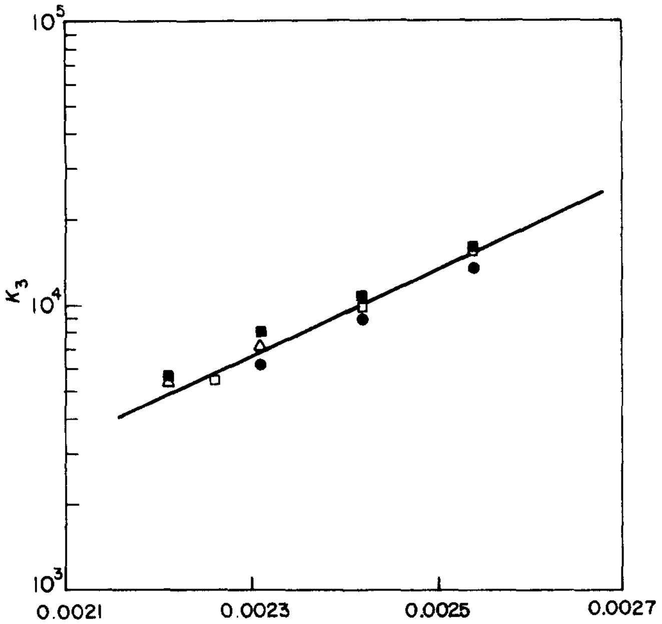

Figure 1 Measured (f_1: ●, 0; △, 0.2; ■, 0.75; □, 1.0) and predicted K_3 vs. (1/T) (K^{-1}) with $A = 0.85$

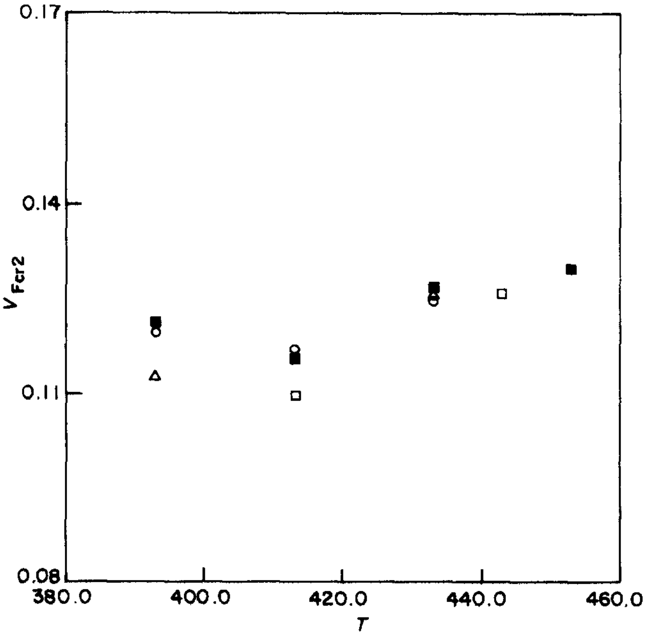

Figure 2 Measured (f_1: ○, 0; △, 0.2; ■, 0.75; □, 1.0) $V_{\mathrm{Fcr}2}$ vs. T (K) with $B = 0.5$

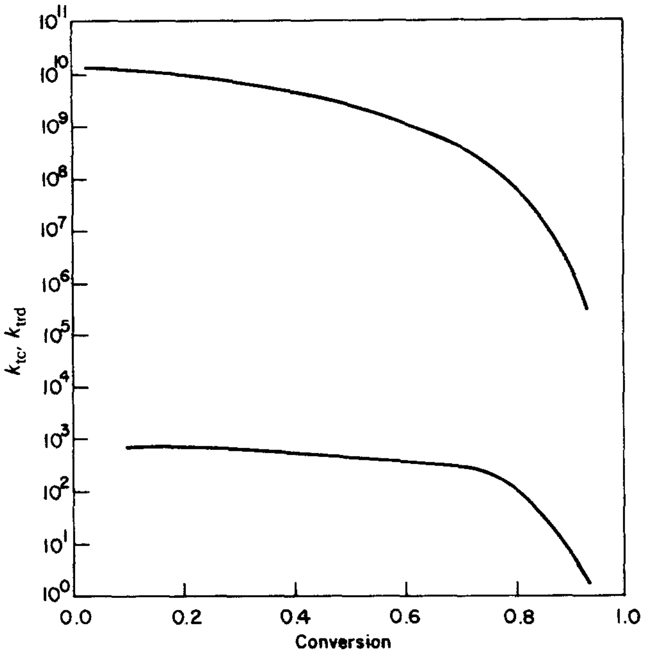

Figure 3 Predicted ($f_{10} = 0.2$, $T = 140$°C) change in k_{tc} (a) (upper curve) and k_{trd} (b) (lower curve) (l mol^{-1} min^{-1}) with conversion

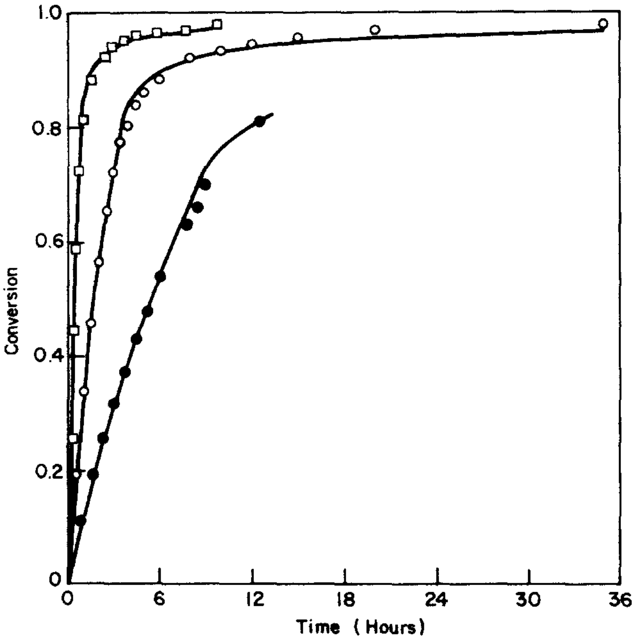

Figure 4 Measured (●, 120°C; ○, 140°C; □, 170°C; $f_{10} = 1$) and predicted conversion vs. time

constant, k_{trd}, with conversion, k_{tc} is observed to fall by about five decades over the entire conversion range and k_{trd} remains negligibly small in comparison throughout.

Comparison between model prediction and experimental data

Figure 4 shows the bulk rate data for styrene after Hui[1] at 120°C, 140°C and 170°C. The agreement between predicted and experimental data is reasonable. *Figure 5* shows the comparison between model prediction and experimental conversion data for PMS after Chiantore and Hamielec[2] obtained at 120°C, 140°C and 160°C. The agreement is again reasonable. *Figures 6, 7, 8* and *9* compare model prediction with experimental conversion data on copolymerization of styrene/PMS[3]. Reasonable agreement is observed for copolymerization covering the entire composition range. *Figures 10, 11* and *12* compare model predictions with experimental $\bar{M}_w$ data for two different compositions of the copolymer. Reasonable agreement is observed. Similar agreement is found in *Figure 13* where the experimental $\bar{M}_N$ data are compared with model prediction for a copolymer composition of 20% styrene. However agreement between model prediction and $\bar{M}_N$ data for copolymer with a styrene content of 75%, in *Figure 14*, is rather poor. One reason for this discrepancy could be the inadequacy of equation (17) to model chain transfer reactions to oligomers and other byproducts of thermal initiation.

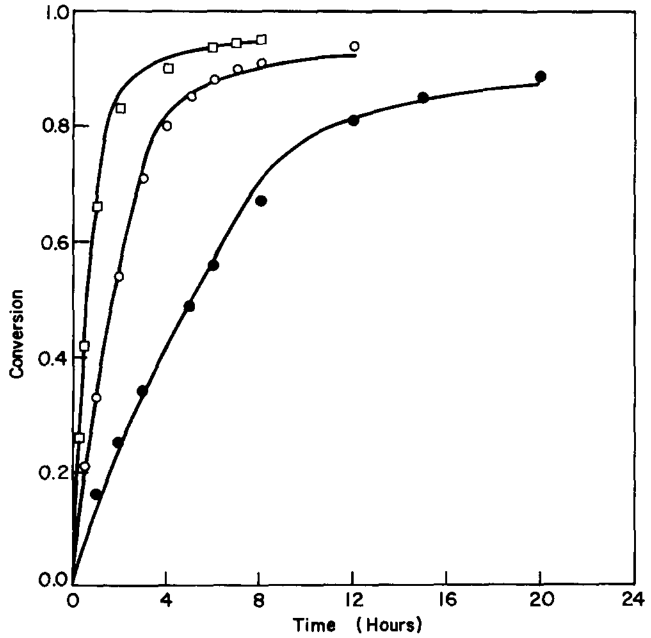

Figure 5 Measured (●, 120°C; ○, 140°C; □, 170°C; $f_{10}=0$) and predicted conversion vs. time

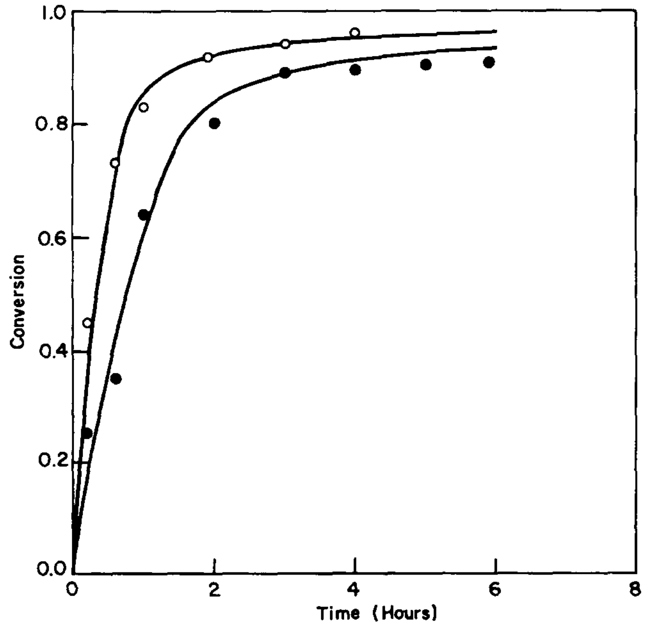

Figure 6 Measured (●, 120°C; ○, 140°C; $f_{10}=0.2$) and predicted conversion vs. time

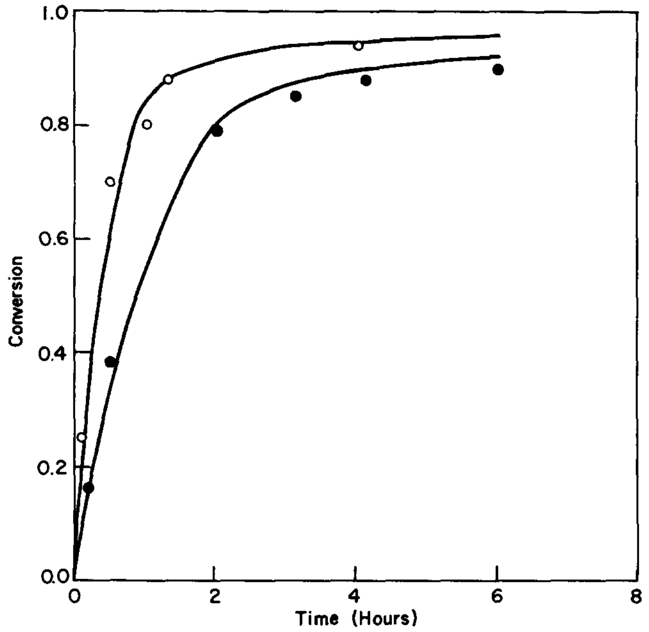

Figure 7 Measured (●, 160°C; ○, 180°C; $f_{10}=0.2$) and predicted conversion vs. time

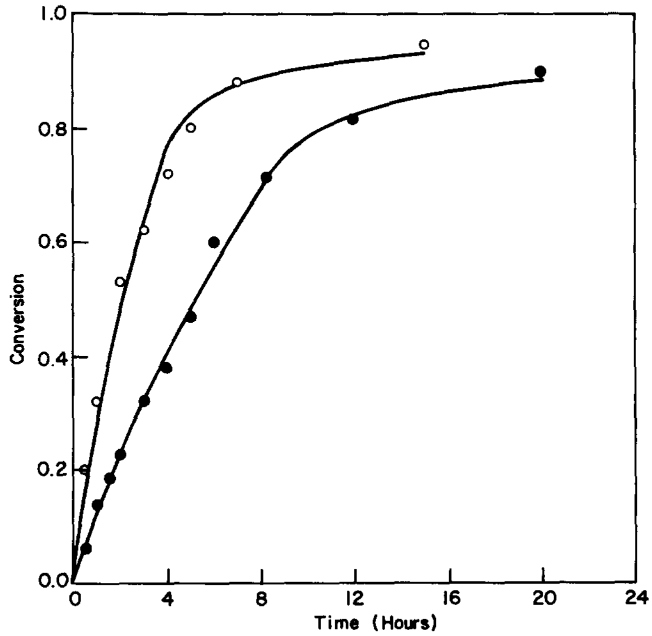

Figure 8 Measured (●, 120°C; ○, 140°C; $f_{10}=0.75$) and predicted conversion vs. time

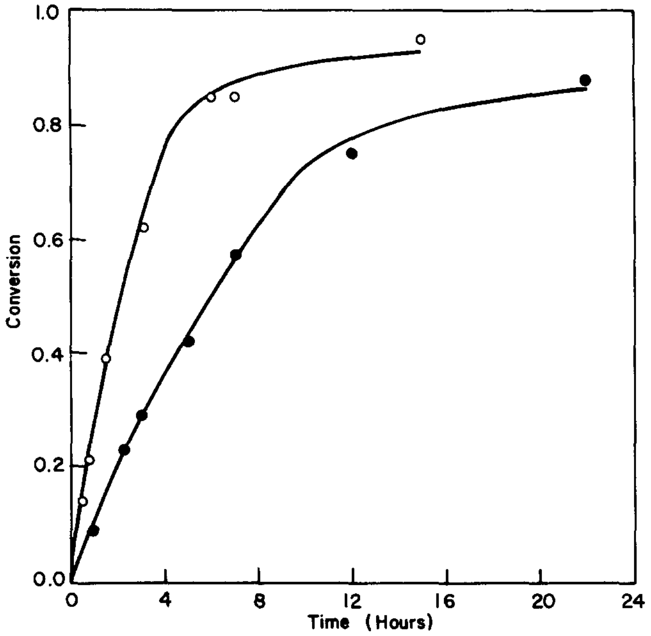

Figure 9 Measured (●, 160°C; ○, 180°C; $f_{10}=0.75$) and predicted conversion vs. time

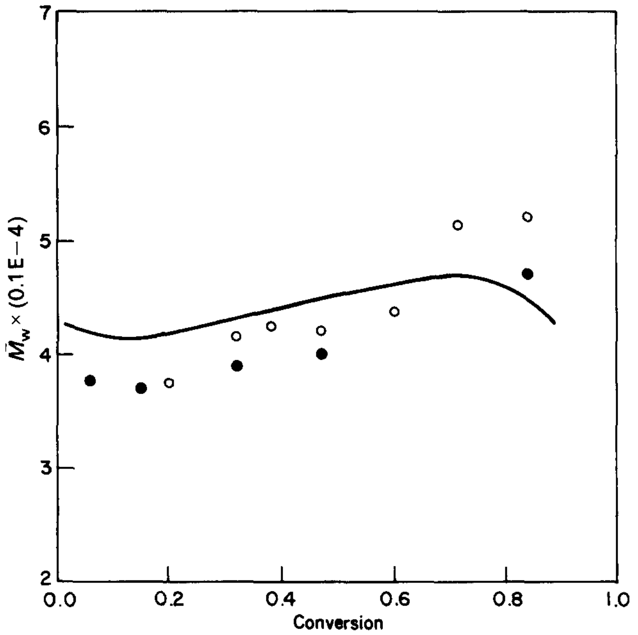

Figure 10 Measured (●, SEC; ○, LALLSP at 120°C; $f_{10}=0.2$) and predicted $\bar{M}_w$ vs. conversion at 120°C

KINETIC MODEL PARAMETERS

All chemically-controlled kinetic parameters used in this model have been listed in ref. 3. Monomer densities with their temperature dependence as used in this work are:

Density of styrene $=0.924-0.00092(T-273.1)$ g cm^{-3} (ref. 7)

Density of PMS $=0.9261-0.00092(T-273.1)$ g cm^{-3}

Density of polymer of all compositions $=1.084-0.00061(T-273.1)$ g cm^{-3} (ref. 7)

Other parameters used in this work are as follows:

$\delta=0.0011\,\mathrm{g}^{-1}$
$K_3=3.0\exp(3423/T)$
$A=0.85$
$B=0.5$
$T_{gM1}=-117.1$°C (ref. 18)
$T_{gM2}=-123.0$°C (ref. 18)
$T_{gP}(F_1=0)=113$°C (ref. 19)
$T_{gP}(F_1=0.2)=108$°C (measured)
$T_{gP}F_1=0.75)=104$°C (measured)
$T_{gP}(F_1=1.0)=100$°C (ref. 19)

where F_1 is the mole fraction of styrene in the copolymer.

Details of experimental procedure can be found in refs. 1, 2 and 3. The glass transition temperatures of the copolymers were measured by differential scanning calorimetry (d.s.c.).

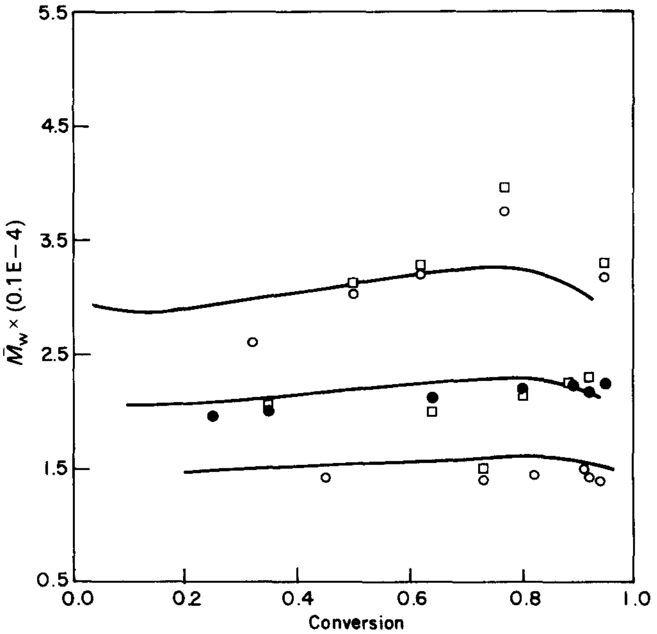

Figure 11 Measured (○, SEC; □, LALLSP at 140°C, 180°C; and ●, SEC; □, LALLSP at 160°C; $f_{10}=0.2$) and predicted $\bar{M}_w$ vs. conversion

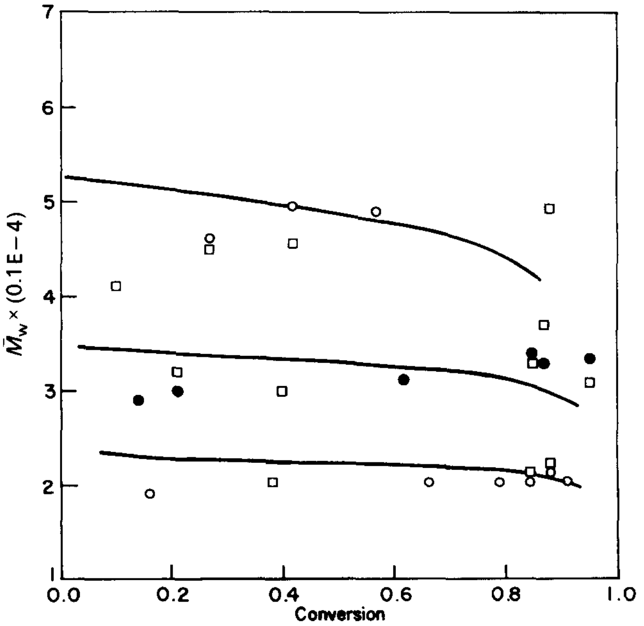

Figure 12 Measured (○, SEC; □, LALLSP at 120°C, 160°C; and ●, SEC; □, LALLSP at 140°C; $f_{10}=0.75$) and predicted $\bar{M}_w$ vs. conversion

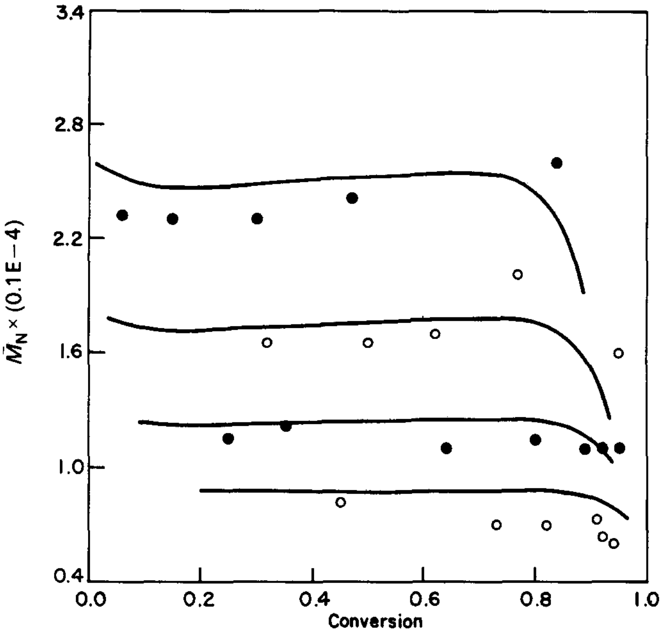

Figure 13 Measured (●, SEC at 120°C and 160°C; ○, SEC at 140 and 180°C; $f_{10}=0.2$) and predicted $\bar{M}_N$ vs. conversion

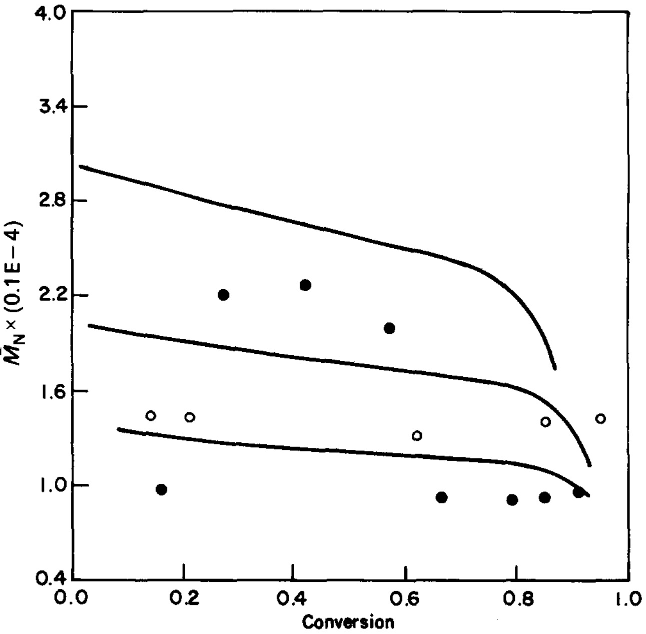

Figure 14 Measured (●, SEC at 120°C and 160°C; ○, SEC at 140°C; $f_{10}=0.75$) and predicted $\bar{M}_N$ vs. conversion

SUMMARY

A kinetic model using free-volume theory to predict diffusion-controlled propagation and termination reaction rates has been used to model the thermal bulk copolymerization of styrene/PMS and the homopolymerization of these monomers. The model seems to predict reasonably batch kinetic data (x, $\bar{M}_N$, $\bar{M}_W$ *versus* time) up to complete conversions and should find use in the design, optimization and control of reactors for the production of styrene/PMS copolymers.

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