

Modeling Gel Effect in Branched Polymer Systems: Free-Radical Solution Homopolymerization of Vinyl Acetate

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ABSTRACT: In this work a comprehensive mathematical framework is developed for modeling gel effect in branched polymer systems with application in the solution polymerization of vinyl acetate. This model is based on sound principles such as the free-volume theory for polymer chains diffusion. The model predictions for monomer conversion and number- and weight-average molecular weights were found to be in good agreement with published data in the literature. Moreover, the joint molecular-weight distribution–long chain branching distribution is calculated by direct numerical integration of a large system of nonlinear

ordinary integral-differential equations describing the mass conservation of macromolecular species in a batch reactor. This allows studying the effect of process conditions such as initiator and solvent concentration on the product quality. It is believed that this work might contribute to a more rational design of polymerization reactors. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2171–2185, 2009

Key words: theory; radical polymerization; diffusion; molecular-weight distribution; modeling; simulation; vinyl acetate

INTRODUCTION

The free-radical polymerization of vinyl acetate (VAC) is an industrial process with significant financial interest because branched polymers with diverse end-use properties are produced. The importance of the VAC free-radical polymerization has led to numerous experimental^{1–6} and theoretical^{7–20} studies. The main characteristic of this process is the existence of autoacceleration phenomena (gel effect) at high conversion. These autoacceleration phenomena are caused by a decrease in the termination rate constants at high conversion because of the small mobility of polymer chains.

Autoacceleration phenomena, such as the gel effect in polymerization reactors, have been the subject of numerous studies.^{21–60} These studies could be

classified as deterministic models or stochastic models based on comprehensive modeling techniques and recently reviewed in Ref. 61. The deterministic models are based either on the free-volume theory^{62–64} or on the reptation theory^{65–68} for polymer diffusion, both combined with the Smoluchowski⁶⁹ model to describe the variation of the diffusion controlled kinetic rate constants with process conditions. The main difficulty in building a deterministic model for the specific process is the coexistence of both branched and linear polydispersed polymers in the reaction mixture. A model for the gel effect in free-radical polymerization necessitates a comprehensive theory for diffusion describing the variation of diffusion coefficients with process conditions. The challenge in our case is to describe the variation of diffusion coefficients as a function of the process conditions in the reaction mixture containing both polydispersed linear and branched chains.

The aim of this work is to overcome these difficulties and propose a unique model based on the free-volume theory to describe the solution free-radical homopolymerization of VAC. This work is organized as follows: In the following section the kinetic mechanism along with the polymerization rate functions are briefly reviewed, the mathematical model

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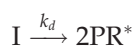
for the gel effect is presented, and the model parameters are given. In the fourth section, results are discussed and the effect of process conditions on product quality is thoroughly investigated. Finally, conclusions are drawn.

MODEL DEVELOPMENT

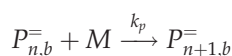
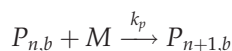
Kinetic mechanism and polymerization rate functions

A general kinetic mechanism of chemically initiated free-radical polymerization leading in long-chain-branched polymers, such as VAC, includes the following steps:^{1-21,70-73}

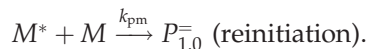
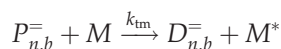
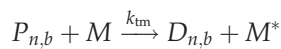
Initiation



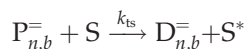
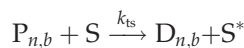
Propagation



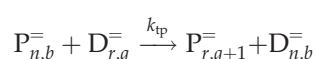
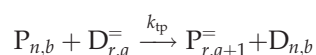
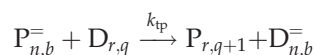
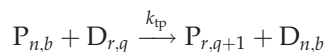
Chain transfer to monomer



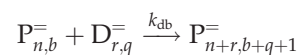
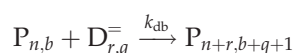
Chain transfer to solvent



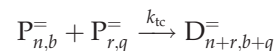
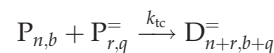
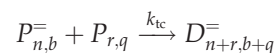
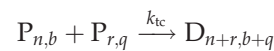
Chain transfer to polymer



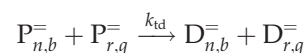
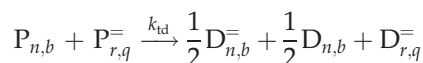
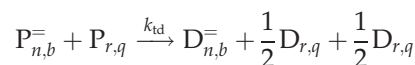
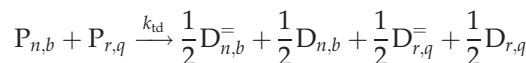
Reaction of terminal double bond



Termination by combination



Termination by disproportionation



All symbols used are explained in the "Nomenclature" section.

Following most researchers in the field, we assume that isothermal conditions and absence of mixing in the batch reactor are due to the intensive stirring and cooling by a jacketed reactor or a cooling coil inside the reactor. One-phase conditions were assumed, as the reaction mixture is a homogeneous solution or even a homogenous gel because of the presence of a good solvent. Based on the above mechanism one could derive the following equations describing the conservation of species in a batch reactor:

Initiator

$$\frac{1}{V} \frac{d(VI)}{dt} = -k_d I \quad (1)$$

Monomer-fractional monomer conversion (X)

$$\frac{1}{V} \frac{d(VM)}{dt} = r_M = -(k_p + 2k_{tm})P_{00}^T - k_{ts}SP_{00}^T - k_I PR^* M; \quad X = \frac{(M_0 V_0 - MV)}{M_0 V_0} \quad (2)$$

Solvent

$$\frac{1}{V} \frac{d(VS)}{dt} = -k_{ts} P_{00}^T S \quad (3)$$

Macromolecular species balance

$$\frac{1}{V} \frac{d(VG)}{dt} = r_G, \quad G = P_{n,b}; P_{n,b}^-; D_{n,b}; D_{n,b}^- \quad (4)$$

$$r_{P_{n,b}} = (k_I PR^* M + k_{ts} P_{00}^T) \delta(n-1, b) + k_p M (P_{n-1,b} - P_{n,b}) - AP_{n,b} + k_{tp} n D_{n,b-1} P_{00}^T + k_{db} \sum_{r=1}^{n-1} \sum_{q=0}^{b-1} P_{r,q} D_{n-r,b-q-1}^- - k_{db} P_{n,b} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} D_{r,q}^- \quad (5)$$

$$r_{P_{n,b}^-} = k_{tm} M P_{00}^T \delta(n-1, b) + k_p M (P_{n-1,b}^- - P_{n,b}^-) - AP_{n,b}^- + k_{tp} n D_{n,b-1}^- P_{00}^T + k_{db} \sum_{r=1}^{n-1} \sum_{q=0}^{b-1} P_{r,q} D_{n-r,b-q-1}^- - k_{db} P_{n,b}^- \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} D_{r,q}^- \quad (6)$$

$$r_{D_{n,b}} = (A - k_t P_{00}^T) P_{n,b} - k_{tp} n D_{n,b} P_{00}^T + \frac{1}{2} k_{tc} \sum_{r=1}^{n-1} \sum_{q=1}^{b-1} P_{r,q} P_{n-r,b-q-1} + \frac{1}{2} k_{td} P_{00}^T P_{n,b} \quad (7)$$

$$r_{D_{n,b}^-} = (A - k_t P_{00}^T) P_{n,b}^- - k_{tp} n D_{n,b}^- P_{00}^T + k_{db} D_{n,b}^- P_{00}^T + \frac{1}{2} k_{tc} \sum_{r=1}^{n-1} \sum_{q=1}^{b-1} P_{r,q}^- (P_{n-r,b-q-1}^- + 2P_{n-r,b-q-1}) + \frac{1}{2} k_{td} P_{00}^T (P_{n,b}^- + 2P_{n,b}^-) \quad (8)$$

where

$$A = k_{tm} M + k_{ts} S + k_t P_{00}^T + k_{tp} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} r D_{r,q} \quad (9)$$

P_{00}^T is the concentration of total "live" polymer:

$$P_{00}^T = \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} P_{r,q} \quad (10)$$

and $\delta(n, b)$ is the Kronecker delta: $\delta(n, b) = \delta(n) \delta(b)$.

The corresponding reaction rates for the moments can be obtained from eqs. (5)–(8) by multiplying each term by $n^k b^l$ and adding over the total variation of n and b . This results in a low-order system of ordinary differential equations. Based on the above polymerization rate function one could give the following equations for a batch reactor by applying the method of moments for the bivariate chain length-degree of branching distribution:^{74–78}

Chain length–degree of branching distribution moments' definition

$$\lambda_{k,l} = \sum_{n=0}^{\infty} \sum_{b=0}^{\infty} n^k b^l P_{n,b}; \quad \lambda_{k,l}^- = \sum_{n=0}^{\infty} \sum_{b=0}^{\infty} n^k b^l P_{n,b}^-; \quad \mu_{k,l} = \sum_{n=0}^{\infty} \sum_{b=0}^{\infty} n^k b^l D_{n,b}; \quad \mu_{k,l}^- = \sum_{n=0}^{\infty} \sum_{b=0}^{\infty} n^k b^l D_{n,b}^- \quad (11)$$

Moments balances

$$\frac{1}{V} \frac{d(V \lambda_{k,l})}{dt} = r_{\lambda_{k,l}}; \quad \frac{1}{V} \frac{d(V \lambda_{k,l}^-)}{dt} = r_{\lambda_{k,l}^-}; \quad k, l = 0, 1, 2 \quad (12)$$

$$\frac{1}{V} \frac{d(V \mu_{k,l})}{dt} = r_{\mu_{k,l}}; \quad \frac{1}{V} \frac{d(V \mu_{k,l}^-)}{dt} = r_{\mu_{k,l}^-}; \quad k, l = 0, 1, 2 \quad (13)$$

where

$$r_{\lambda_{k,l}} = (k_I PR^* M + k_{ts} S \lambda_{0,0}^T) \delta(l) + k_p M \left[\sum_{i=0}^k \binom{k}{i} \lambda_{i,l} - \lambda_{k,l} \right] - A' \lambda_{k,l} + k_{tp} \lambda_{0,0}^T \sum_{j=0}^l \binom{l}{j} \mu_{k+1,j} - k_{db} \lambda_{k,l} \mu_{0,0}^- + k_{db} \sum_{i=0}^k \binom{k}{i} \sum_{p=0}^l \binom{l}{p} \sum_{j=0}^p \binom{p}{j} \lambda_{i,j} \mu_{k-i,p-j}^- \quad (14)$$

$$r_{\lambda_{k,l}^-} = k_{tm} M \lambda_{0,0}^T \delta(l) + k_p M \left[\sum_{i=0}^k \binom{k}{i} \lambda_{i,l}^- - \lambda_{k,l}^- \right] - A' \lambda_{k,l}^- + k_{tp} \lambda_{0,0}^T \sum_{j=0}^l \binom{l}{j} \mu_{k+1,j}^- - k_{db} \lambda_{k,l}^- \mu_{0,0}^- + k_{db} \sum_{i=0}^k \binom{k}{i} \sum_{p=0}^l \binom{l}{p} \sum_{j=0}^p \binom{p}{j} \lambda_{i,j}^- \mu_{k-i,p-j}^- \quad (15)$$

$$r_{\mu_{k,l}} = (A' - k_t \lambda_{0,0}^T) \lambda_{k,l} + \frac{1}{2} k_{tc} \sum_{i=0}^k \binom{k}{i} \sum_{j=0}^l \binom{l}{j} \lambda_{i,j} \lambda_{k-i,l-j} + \frac{1}{2} k_{td} \lambda_{k,l} \lambda_{0,0}^T - k_{tp} \mu_{k+1,l} \lambda_{0,0}^T \quad (16)$$

$$r_{\mu_{k,l}^-} = (A' - k_t \lambda_{0,0}^T) \lambda_{k,l}^- + \frac{1}{2} k_{tc} \sum_{i=0}^k \binom{k}{i} \sum_{j=0}^l \binom{l}{j} \lambda_{i,j}^- \times (\lambda_{k-i,l-j}^- + 2\lambda_{k-i,l-j}) + \frac{1}{2} k_{td} (2\lambda_{k,l}^- + \lambda_{k,l}) \lambda_{0,0}^T - k_p^* \mu_{k,l}^- \lambda_{0,0}^T - k_{tp} \mu_{k=1,l}^- \lambda_{0,0}^T \quad (17)$$

where

$$A' = k_{tm} M + k_{ts} S + k_t \lambda_{0,0}^T + k_{tp} \mu_{1,0}^T \quad (18)$$

$$\lambda_{k,l}^T = \lambda_{k,l} + \lambda_{k,l}^-; \quad \mu_{k,l}^T = \mu_{k,l} + \mu_{k,l}^-; \quad k, l = 0, 1, 2 \quad (19)$$

A detailed presentation of the moments' method as applied in the VAC polymerization is given elsewhere.⁷⁹ The number and the weight-average degree

of polymerization (\bar{X}_n , \bar{X}_w) as well as the number-average degree of branching (\bar{B}_n) are given as follows:

$$\begin{aligned}\bar{X}_n &= \frac{\mu_{10} + \mu_{10}^- + \lambda_{10} + \lambda_{10}^-}{\mu_{00} + \mu_{00}^- + \lambda_{00} + \lambda_{00}^-}; \\ \bar{X}_w &= \frac{\mu_{20} + \mu_{20}^- + \lambda_{20} + \lambda_{20}^-}{\mu_{10} + \mu_{10}^- + \lambda_{10} + \lambda_{10}^-}; \\ \bar{B}_n &= \frac{\mu_{01} + \mu_{01}^- + \lambda_{01} + \lambda_{01}^-}{\mu_{00} + \mu_{00}^- + \lambda_{00} + \lambda_{00}^-}\end{aligned}\quad (20)$$

Based on the polymerization rate functions and the method of moments one could calculate the bivariate chain length–degree of branching distribution by directly solving the macromolecular mass balances [eqs. (4)–(10)]. These mass balances consist of a large nonlinear system of integral-differential equations. More specifically, the continuous variable approximation (CVA) was implemented to decrease the number of equations of the algebraic “live” radical mass balance system.⁵⁸ By applying the CVA, the discrete system is transformed into a continuous variable system by expanding the concentration of “live” radicals having chain length n , in Taylor expansion, truncated after the second term:

$$\begin{aligned}[P_{n-1,b}] &= [P_{n,b}] - \left. \frac{\partial [P_{n,b}]}{\partial x} \right|_{x=n}; \\ \left. \frac{\partial [P_{n,b}]}{\partial x} \right|_{x=n} &= \frac{([P_{n,b}] - [P_{n-\eta\text{step},b}])}{\eta\text{step}}\end{aligned}\quad (21)$$

where “ η step” is the chain length step used in the discretization.

Implementation of the CVA reduces the number of mass balances of “live” radicals to be solved and transforms them into an ordinary differential equations system with respect to chain length which can be directly solved using the above finite difference scheme. The summations to infinite were calculated by using the method of moments. The summations to a finite number were transformed into integrals using the CVA and calculated using standard methods of numerical analysis.⁵⁸ This results in a continuous integral-differential system. A detailed presentation of the computational methodology for solving these balances in the case of diffusion controlled polymerization reactions by using standard methods of numerical analysis such as the fourth-order variable step Runge-Kutta method was given in our previous work.⁵⁸

Modeling gel effect

An isothermal homogenous solution or homogenous gel was assumed because of intensive stirring and the presence of the solvent. Under these uniform

conditions (absence of temperature or concentration gradients) diffusion is described by self diffusion coefficients. The starting point in this analysis is the Smoluchowski equation⁶⁹ utilized by most workers in the field to express the overall termination kinetic rate constant in terms of the “live” radicals self-diffusion coefficient:

$$\frac{1}{k_{te,j}} = \frac{1}{k_{t0}} + \frac{1}{4\pi N_A r_t \bar{D}_{p,j}} = \frac{1}{k_{t0}} + \frac{r_t^2 P_{0j}}{3\bar{D}_{p,j}}; \quad j = l \text{ or br} \quad (22)$$

where N_A is the Avogadro number, k_{t0} stands for the total intrinsic termination rate constant ($k_{t0} = k_{tc0} + k_{td0}$) defined at zero conversion and involving two short chains, P_{0b} and P_{0l} represent the total concentration of “live” branched and linear radicals, respectively, and r_t represents the effective reaction radius for the termination reaction calculated by the excess chain end mobility theory.^{33–36,39,40}

In eq. (22), two effective termination rate constants, $k_{te,j}$ are considered, one for linear terminating chains, $k_{te,l}$, and the second for branched terminating chains, $k_{te,br}$.

To calculate the self-diffusion coefficients of “live” radicals one has to resort to either the free-volume theory or to the reptation theory. In our previous work⁵⁸ it was shown that both theories are able to describe free-radical homopolymerization in spite of their inherent differences (for example, consideration of individual chain lengths in reptation theory versus average molecular weights in free volume) According to our previous work,⁵⁸ based on Vrentas and Duda free-volume theory^{62–64} one can derive the following equation to describe the concentration and temperature dependence of the macromolecular mean self-diffusion coefficient in a semidilute polymer solution:

$$\begin{aligned}\bar{D}_{p,l} &= \left(D_{p0} / \bar{X}_{lr}^2 \right) \\ &\times \exp \left[-\gamma \left(\omega_m V_m^* + \omega_s V_s^* \xi_{23} + \omega_p V_p^* \xi_{13} \right) / (V_F \xi_{13}) \right]\end{aligned}\quad (23)$$

$$V_F / \gamma = \sum_{i=1}^3 \frac{K_{1i}}{\gamma} (K_{2i} - T_{gi} + T) \omega_i \quad (24)$$

where D_{p0}' is a preexponential factor, \bar{X}_{lr} represents the average degree of polymerization of the linear “live” radicals, and subscripts p , m , and s represent the “dead” polymer, monomer, and solvent, respectively. D_{p0} is an adjustable parameter including the effect of segmental diffusion, V_F is the average hole free volume per kg of the solution, and γ is an overlap factor, which is introduced, because the same free volume is available to more than one molecule. V_i^* is the specific critical hole free volume of the i th component required for a diffusion jump and ξ_{i3}

TABLE I
Kinetic Rate Constants for the Solution
Polymerization of VAC^{2,14}

$k_d = 4.5 \times 10^{14} \exp(-30,000/RT) [s^{-1}]$ (AIBN)
$k_d = 2.85 \times 10^{-6} [s^{-1}]$ (BPO, 60°C)
$k_p = 7 \times 10^7 \exp(-6300/RT) [L \text{ mol}^{-1} \text{ s}^{-1}]$
$k_{tm} = k_p \times 1.42 \times 10^{-2} \exp(-2700/RT) [L \text{ mol}^{-1} \text{ s}^{-1}]$
$k_{ts} = k_p \times 3.4 \times 10^{-5} [L \text{ mol}^{-1} \text{ s}^{-1}]$ (<i>t</i> -butanol)
$k_{td0} = 0 [L \text{ mol}^{-1} \text{ s}^{-1}]$
$k_{tco} = 2.7 \times 10^{10} \exp(-2800/RT) [L \text{ mol}^{-1} \text{ s}^{-1}]$
$k_{tpo} = k_p \times 7 \times 10^{-3} \exp(-2700/RT) [L \text{ mol}^{-1} \text{ s}^{-1}]$
$k_{tp} = k_{tpo} \exp(-0.282 M/S) [L \text{ mol}^{-1} \text{ s}^{-1}]$
$k_{db} = k_p \times 0.66$

represents the ratio of the critical molar volume of the jumping unit of *i*th low-molecular-weight substance to that of the polymer. K_{1i} and K_{2i} are free-volume parameters for *i*th component and T_{gi} is the glass transition temperature. In the above equations ω_i represents the weight fraction of *i*th substance. The above equation describes the diffusion of linear chains in a ternary polymer solution containing not only polymer and monomer but also solvent. The Vrentas–Duda free-volume theory describes the self-diffusion coefficients adequately both in solution and gel state.

Graessley and coworkers^{80,81} have shown that the self-diffusion coefficient ($\bar{D}_{p,br}$) of monodisperse three-arm star polybutadiene in a melt depends on the number average degree of polymerization (\bar{X}_b) as

$$\bar{D}_{p,br} \propto (e^{-a\bar{X}_b}) \quad (25)$$

Equation (23) has to be modified by taking into account Graessley and coworkers' results to describe the diffusion of branched "live" radicals:

$$\bar{D}_{p,br} = D'_{p0} (e^{-a\bar{X}_b}) \times \exp \left[-\gamma \left(\omega_m V_m^* + \omega_s V_s^* \zeta_{23} + \omega_p V_p^* \zeta_{13} \right) / (V_F \zeta_{13}) \right] \quad (26)$$

where α is an adjustable parameter including the effect of segmental diffusion and \bar{X}_b represents the number-average degree of polymerization of the branched "live" radicals.

Following most workers in the field it is assumed in this work that the residual termination rate con-

stant is proportional to the frequency of monomer addition to the radical chain end:

$$k_{t, \text{reac}} = Ak_p M \quad (27)$$

If the self-diffusion coefficients are calculated, then we can calculate the termination kinetic rate constants for branched and linear "live" radicals ($k_{t,br}$, $k_{t,l}$) by using the Smoluchowski equation [eq. (22)] along with the residual termination correction [eq. (27)]. The termination kinetic rate constants for branched and linear "live" radicals are given by

$$k_{t,br} = k_{t,br} + k_{t, \text{reac}}; \quad k_{t,l} = k_{t,l} + k_{t, \text{reac}} \quad (28)$$

The overall kinetic rate constant ($k_t = k_{tc} + k_{td}$) is calculated as

$$k_t = (k_{t,br} P_{0b} + k_{t,l} P_{0l}) / P_{00}^T \quad (29)$$

where P_{0b} and P_{0l} represent the total concentration of "live" branched and linear radicals, respectively. These quantities as well as the number-average degree of polymerization ($\bar{X}_{l,r}$, \bar{X}_b) appearing in eq. (23) and (26) can be directly calculated from the corresponding polymerization functions by using the method of moments. Finally, it is assumed in this work that the cage effect and the glass effect are minimal because of the presence of a solvent.

Model parameters

Estimation of kinetic rate parameters has been the subject of extensive experimental investigation as reviewed by Taylor and Reichert.¹³ In this work the kinetic rate constants of Hamer and Ray¹⁴ were adopted. The values of the kinetic rate constants are summarized in Table I. The thermophysical properties of the solution constituents are given in standard references.^{82–85} Initial reactor volume was assumed to have a value equal to 1 L.

The free-volume parameters used in this work are summarized in Table II.⁸⁶ Free-volume parameters for VAC were set equal to the free-volume parameters of methyl acetate according to our previous work. The *t*-butyl alcohol free-volume parameter ($K_{22} - T_{g2}$) was directly estimated by using the

TABLE II
Monomer, Solvents, and Polymer Free-Volume-Theory Parameters⁸⁶

A. Monomer	$V_m^* (\times 10^3 \text{ m}^3/\text{kg})$	$K_{11}/\gamma [\times 10^6 \text{ m}^3/(\text{kg K})]$	$K_{21} - T_{g1} (\text{K})$
Vinyl acetate	0.855	1.25	-38.5
B. Solvents	$V_s^* (\times 10^3 \text{ m}^3/\text{kg})$	$K_{12}/\gamma [\times 10^6 \text{ m}^3/(\text{kg K})]$	$K_{22} - T_{g2} (\text{K})$
<i>t</i> -Butyl alcohol	0.967	0.72	-56.6
Toluene	0.917	2.20	-102.72
C. Polymer	$V_p^* (\times 10^3 \text{ m}^3/\text{kg})$	$K_{13}/\gamma [\times 10^7 \text{ m}^3/(\text{kg K})]$	$K_{23} - T_{g3} (\text{K})$
PVAC	0.728	4.33	-258.2

Doolittle equation⁸⁷ and the Goletz–Tassios correlation⁸⁸ for the prediction of pure solvent viscosity versus temperature data combined with the Vrentas–Duda equation.^{62–64} The parameter (K_{12}/γ) was calculated by fitting *t*-butyl alcohol viscosity–temperature data.⁸⁴ The parameter ξ is defined as the ratio of the critical molar volume of the solvent jumping unit to that of the polymer jumping unit. The parameter ξ_{13} (vinyl acetate–PVAC) was set equal to 0.6 according to our previous work.⁸⁹ The solvent–polymer parameter ξ_{23} was set equal to 0.86 for toluene and equal to 0.97 for *t*-butyl alcohol by using the predictive options of Vrentas–Duda theory.^{62–65,86} D_{p0}' [eq. (26)] was set equal to 10^{-4} m²/s for simplicity.

The effective radius for the termination reaction was calculated by using the excess chain end mobility theory as developed by Soh and Sundberg.^{33–36} They derived an equation for the termination rate constant by assuming that the chain end of a “live” macroradical is free to move in a relatively limited spherical region of radius r_t with the node of a chain entanglement at the center. For the calculation of r_t they developed the following equation:

$$r_t = \left\{ \ln \left[1000\tau^3 / \left(N_A \lambda_{00}^T \pi^{3/2} \right) \right] \right\}^{0.5} / \tau \quad (30)$$

where

$$\tau = (3/2j_c\delta^2)^{0.5} \quad (31)$$

δ is the average root-mean-square end-to-end distance per square root of the number of monomer units in a chain and can be measured experimentally. j_c is the entanglement spacing and is equal to the average number of monomer units in a dangling chain. j_c could be written in terms of the critical degree of polymerization for entanglement of pure polymer, x_{c0} , and the volume fraction of polymer ϕ_p as^{39,40}

$$j_c^{-1} = j_{c0}^{-1} + 2\phi_p/x_{c0} \quad (32)$$

where j_{c0} is a critical value corresponding to zero conversion. The values of the δ and x_{c0} parameters can be found elsewhere.⁹⁰ These parameters were set in this work equal to 6.9 Å and 100, respectively. The value of j_{c0} could be calculated from eqs. (30) and (31) assuming that at time zero (i.e., $x = 0$ and $t = 0$) the effective reaction radius, r_t , is equal to the mean-square radius of gyration as determined by Graessley and Mittelhauser.⁹¹

Finally, this model includes as adjustable parameters the initiator efficiency f and the quantities D_{p0} and α [see eqs. (23)–(26)]. Additionally, the chain transfer to solvent kinetic rate constant and the

residual termination parameter A could be treated as adjustable parameters.

RESULTS AND DISCUSSION

Two different sets of experimental data reported in the literature were used to estimate the model adjustable parameters with the aid of nonlinear regression analysis. The first set includes the experimental data of McKenna and Villanueva.¹⁷ These workers studied the solution polymerization of VAC in toluene at 60°C by using as initiators the azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO). They reported extensive data on monomer conversion, number-average molecular weight, and polydispersity for different toluene initial concentrations. The aim of this work is to test the ability of this model to describe experimental data even in the case of minimal gel effect as the small conversion data of McKenna and Villanueva.¹⁷

The model adjustable parameters for this case include the kinetic rate constant of chain transfer to toluene along with initiators efficiencies and the gel parameters [D_{p0} and a , see eqs. (23)–(26)]. The effect of residual termination was not considered because of the observed small degree of monomer conversion. Standard methods of numerical analysis were used.⁹² Molecular-weight data were scaled by multiplying the experimental data and the predictions of the model with appropriate constants (weights) to be in the same order of magnitude with conversion data. The resulting fitting is illustrated in Figures 1–4. The estimated parameters are summarized in Table III. The estimated chain transfer to solvent kinetic rate constant has a value equal to $2.7 \times 10^{-4} k_p$. This value is inside the limits of $1.75 \times 10^{-4} k_p$ to $2.8 \times 10^{-4} k_p$ reported for the solution polymerization of VAC in toluene reported in the Polymer Handbook.⁷³ The initiator efficiencies for AIBN and BPO were found equal to 1.8×10^{-4} and 3.7×10^{-4} . These surprising small values for initiators efficiencies could be attributed to the selected values of $k_p/k_t^{0.5}$. More specifically, the reported values¹³ in the literature for $k_p/k_t^{0.5}$ at 60°C varied from 0.286 to 1.39 (L mol⁻¹ s⁻¹)^{0.5}. The used value of $k_p/k_t^{0.5}$ in this work is equal to 0.286 (see Table I). However, it was suggested that propagating radicals in VAC solution homopolymerizations might form complexes with aromatic solvents such as the toluene.¹⁷ The possibility of this variation being due to an influence of chain transfer to solvent on k_p was dismissed because there were no remarkable differences in the rate constants found for benzene and deuterated benzene for either VAC or methyl methacrylate polymerization.¹⁷ The formation of these complexes and their possible influence on $k_p/k_t^{0.5}$, not taken into account to our knowledge in the open literature,

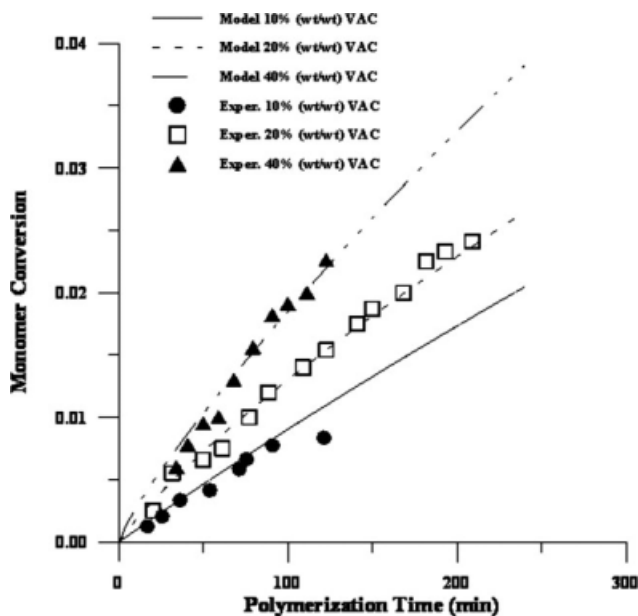


Figure 1 Monomer conversion versus polymerization time for different monomer initial concentrations. Solvent: Toluene. Initiator: 0.004 mol/L AIBN. Polymerization temperature: 60°C. Experimental data from McKenna and Villanueva.¹⁷

could explain the small values for initiator efficiency observed in this work.

The estimated values of D_{p0} and a were found equal to 1.14×10^{-10} m²/s and 0.0158, respectively. The results obtained for the solution polymerization

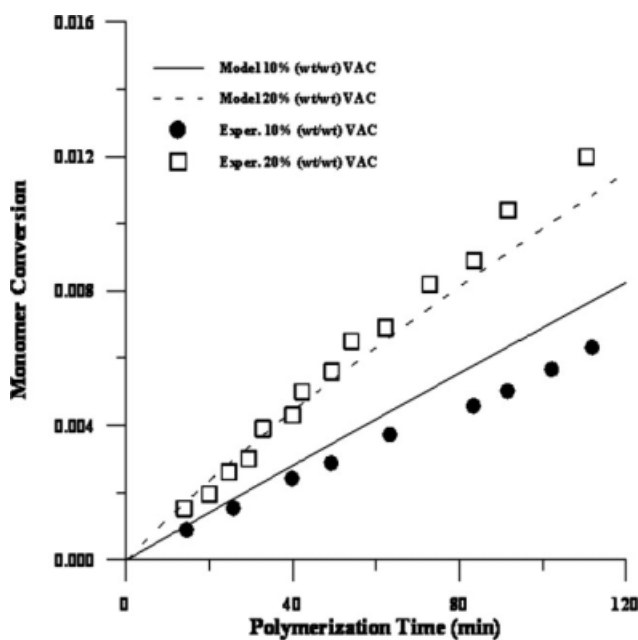


Figure 2 Monomer conversion versus polymerization time for different monomer initial concentrations. Solvent: Toluene. Initiator: 0.004 mol/L BPO. Polymerization temperature: 60°C. Experimental data from McKenna and Villanueva.¹⁷

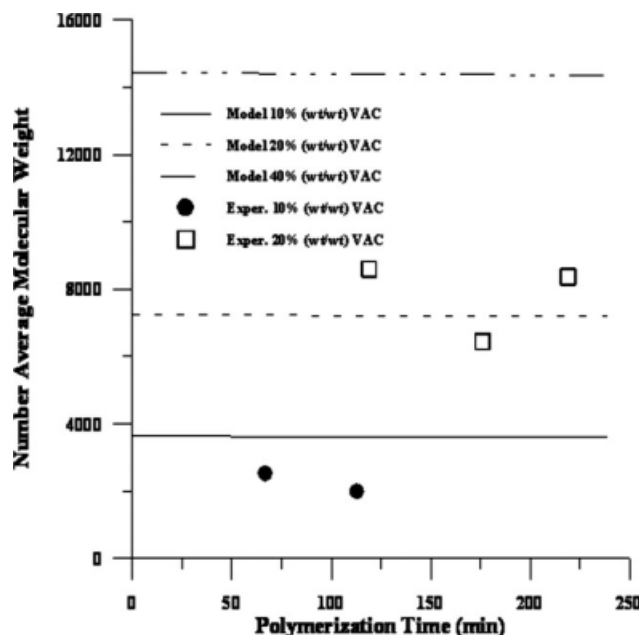


Figure 3 Number-average molecular weight versus polymerization time for different monomer initial concentrations. Solvent: Toluene. Initiator: 0.004 mol/L AIBN. Polymerization temperature: 60°C. Experimental data from McKenna and Villanueva.¹⁷

of VAC in toluene were further validated by examining the solution polymerization of VAC in *t*-butyl alcohol as studied by Graessley and coworkers.² These workers studied the solution polymerization of VAC 60°C by using AIBN as initiator and *t*-butyl

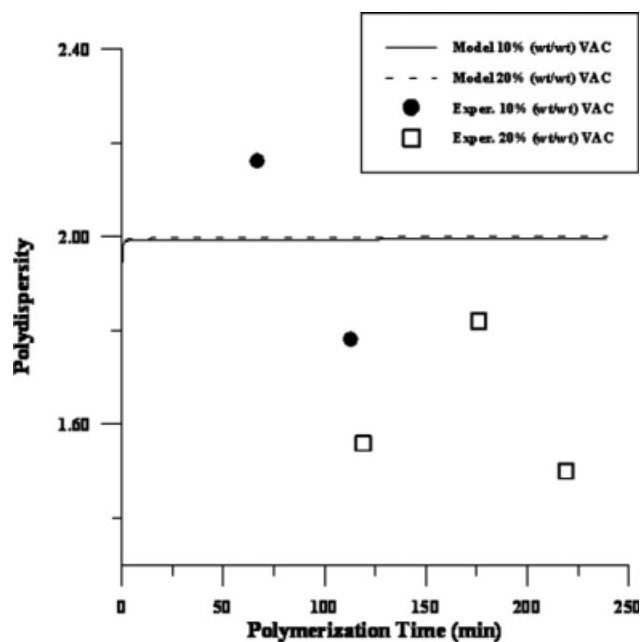


Figure 4 Polydispersity versus polymerization time for different monomer initial concentrations. Solvent: Toluene. Initiator: 0.004 mol/L AIBN. Polymerization temperature: 60°C. Experimental data from McKenna and Villanueva.¹⁷

TABLE III
Estimated Model Parameters at 60°C

System	Initiator	Initiator efficiency, f	D_{p0} (m ² /s)	α	Kinetic rate constant of chain transfer to solvent, k_{ts} (L mol ⁻¹ s ⁻¹)	Residual termination parameter, A
A. VAC/toluene	AIBN	1.8×10^{-4}	1.14×10^{-10}	0.018	$2.7 \times 10^{-4} k_p$	–
	BPO	3.7×10^{-4}	1.14×10^{-10}	0.018	$2.7 \times 10^{-4} k_p$	–
B. VAC/ <i>t</i> -butyl alcohol	AIBN (Case 1)	0.1	3.98×10^{-9}	0.007	–	562.3
	AIBN (Case 2)	0.101	3.98×10^{-9}	0.0067	–	602.5

alcohol as a solvent. Moreover, they carried out an experimental parametric analysis for solvent and initiator concentrations by measuring the monomer conversion as well as the number- and weight-average molecular weights at different times. Their data include three different initial initiator concentrations (4.2×10^{-4} , 1×10^{-3} , and 1.6×10^{-3} gmol/L AIBN) and three initial solvent concentrations (initial solvent/monomer mole ratio equal to 2–6). The model adjustable parameters include initiator efficiency AIBN, residual termination parameters as well as the gel parameters (D_{p0} and a). To demonstrate the predictive abilities of the model, two separate numerical experiments were carried out. The first numerical experiment (Case 1) includes parameter estimation by using all the experimental data of Graessley and coworkers.² The resulting fitting is illustrated in Figures 5–10. The second numerical experiment (Case 2) includes parameter estimation by using only a part of the experimental data (two

different initial initiator concentrations: 1×10^{-3} and 1.6×10^{-3} gmol/L AIBN, and two initial solvent concentrations: initial solvent/monomer mole ratio equal to 2–3). The estimated parameters are illustrated in Table III. The estimated parameters of the two numerical experiments are shown to be in excellent agreement, thus justifying the predictive ability of the model as a good fitting could also be obtained between the experimental data not used in the parameter estimation and model predictions. The initiator efficiency (f) and the residual termination parameter (A) were found equal to 0.1 and 562.3, respectively. The initiator efficiency for AIBN in *t*-butyl alcohol has higher value than the observed value for the VAC polymerization in toluene. The reported value for this initiator efficiency by most workers in the field is equal to 0.5. The discrepancy between this value and the reported value could be attributed to a discrepancy in the used value of

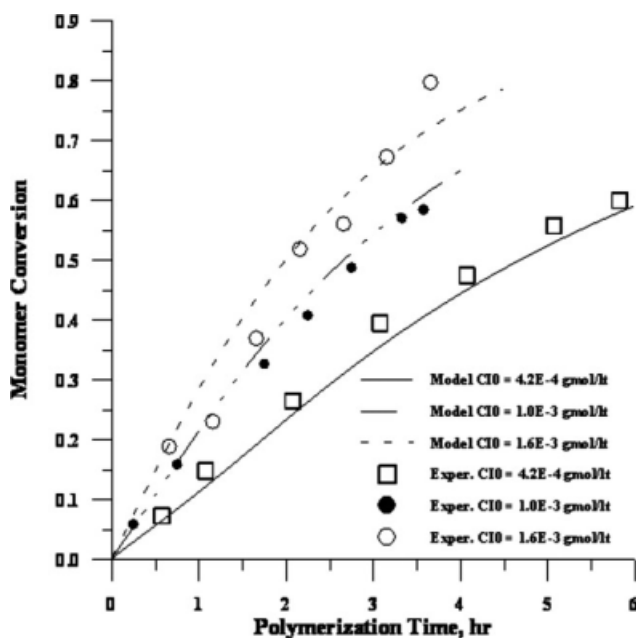


Figure 5 Monomer conversion versus polymerization time for different initial initiator concentrations. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Initiator: AIBN. Polymerization temperature: 60°C. Experimental data from Chatterjee et al.²

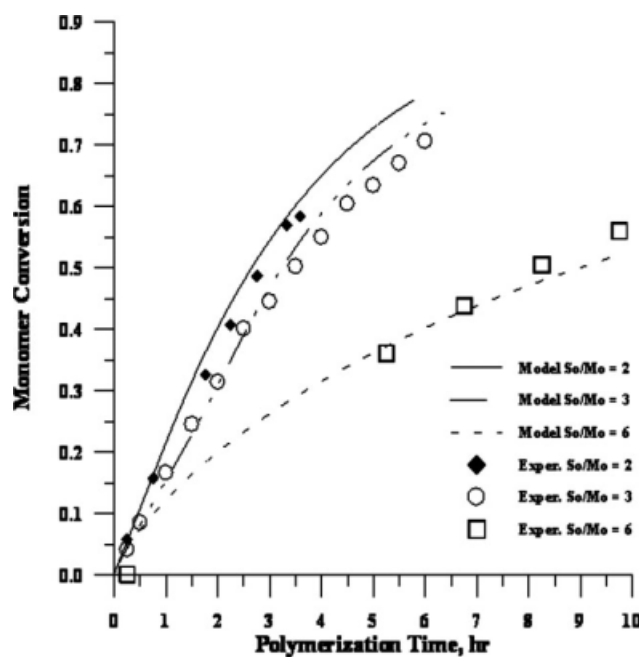


Figure 6 Monomer conversion versus polymerization time for different initial solvent concentrations. Solvent: *t*-butyl alcohol. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Experimental data from Chatterjee et al.²

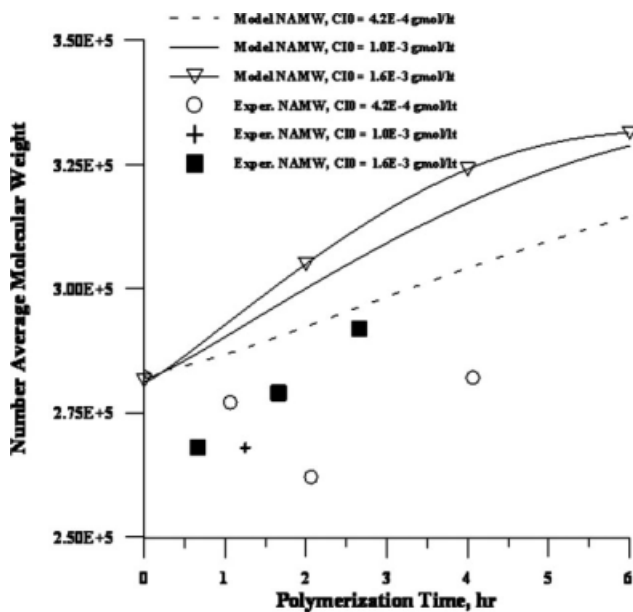


Figure 7 Number-average molecular weights versus polymerization time for different initial initiator concentrations. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Initiator: AIBN. Polymerization temperature: 60°C. Experimental data from Chatterjee et al.²

$k_p/k_t^{0.5}$ because of the possible effect of solvent. More specifically, several workers¹⁻²⁰ reported different values for $k_p/k_t^{0.5}$ for the solution homo-polymerization of VAC in different solvents. This effect could

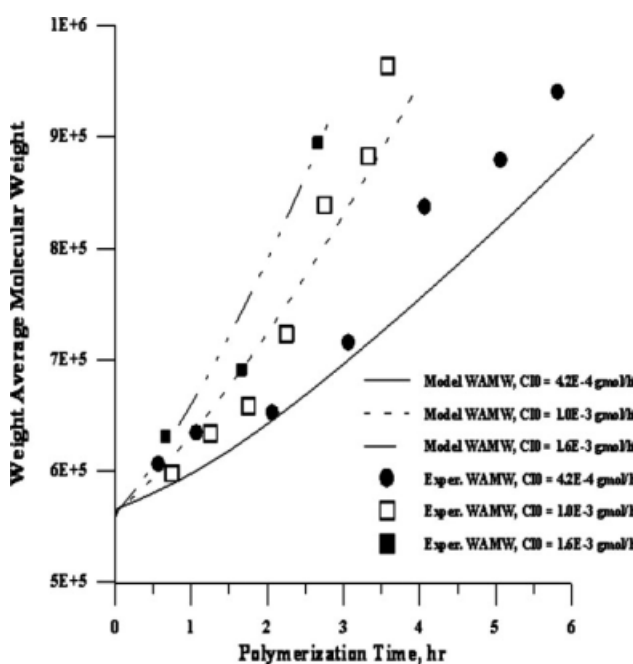


Figure 8 Weight-average molecular weights versus polymerization time for different initial initiator concentrations. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Initiator: AIBN. Polymerization temperature: 60°C. Experimental data from Chatterjee et al.²

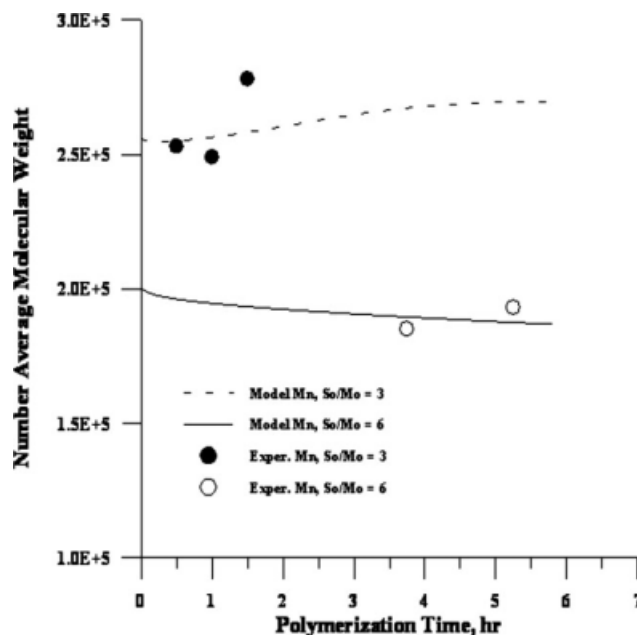


Figure 9 Number-average molecular weights for different initial solvent concentrations. Solvent: *t*-butyl alcohol. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Experimental data from Chatterjee et al.²

explain the observed discrepancy from the nominal value of 0.5.

The estimated values for the D_{p0} and a (gel parameters) were found equal to $3.98 \times 10^{-9} \text{ m}^2/\text{s}$ and 0.007. These values are almost in the same order with the previously observed ones for the solution polymerization of VAC in toluene (Table III).

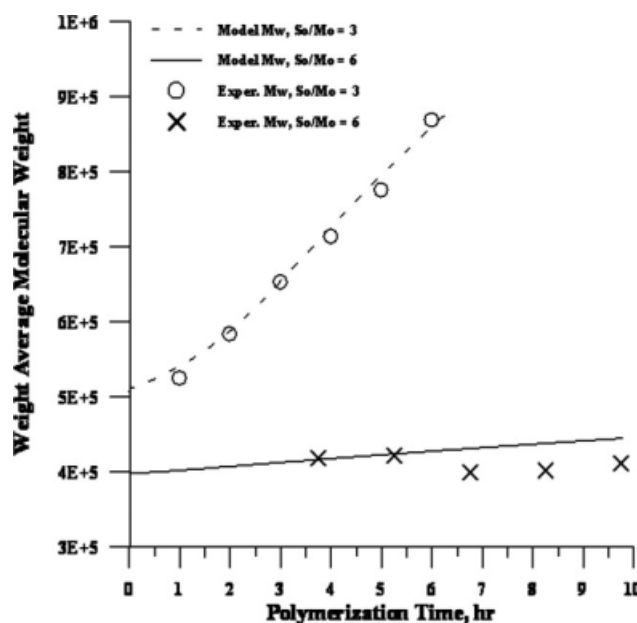


Figure 10 Weight-average molecular weights for different initial solvent concentrations. Solvent: *t*-butyl alcohol. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Experimental data from Chatterjee et al.²

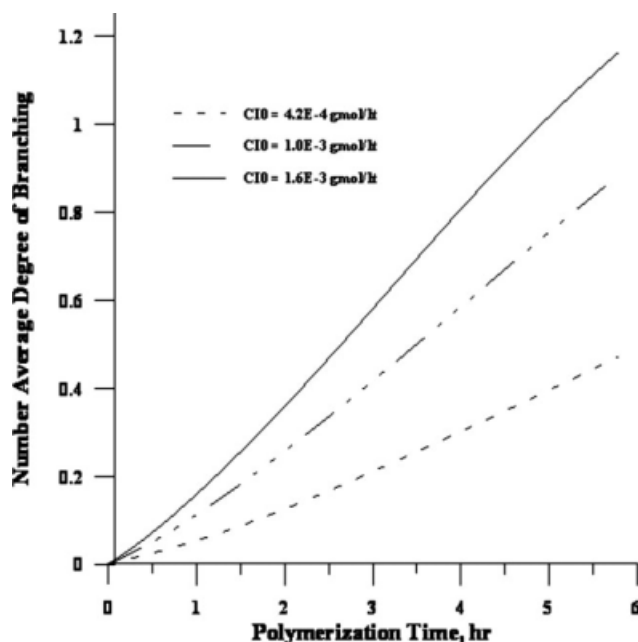


Figure 11 Number average degree of branching for different initial initiator concentrations. Initiator: AIBN. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Polymerization temperature: 60°C.

In Figure 11, the effect of initiator concentration on the number-average degree of branching is studied. A maximum mean value of 1.2 branches per molecule is observed for the experimental conditions of Graessley and coworkers. This figure indicates that although a considerable part of “dead” polymer

consists of linear molecules with zero degree of branching there are also polymer molecules with long chain branches. The degree of long chain branching is better illustrated by calculating the joint degree of branching–molecular-weight distribution (DB-MWD).

The development of a comprehensive model for the solution homopolymerization of VAC allows us to study thoroughly the effects of the process conditions on the product quality by calculating DB-MW distribution. In Figures 12–14 the effects of the initial initiator and solvent concentration on DB-MW distribution for a specific degree of monomer conversion are shown. $D_{t(n,b)}$ denotes summed concentration (sum of species with and without a terminal double bond) of “dead” polymer having n monomer units and b number of branches. For monomer conversion equal to 0.5, the MWD was calculated for different degrees of branching by directly solving the corresponding mass balances by using standard methods of numerical analysis.⁵⁸

As shown in Figures 12–14, the amount of “dead” polymer significantly decreases as the degree of branching increases. Although the initial initiator concentration has a small effect on product quality (see Figs. 12 and 13) for a given monomer conversion, the initial solvent concentration has a profound effect (see Figs. 13 and 14).

More specifically, as shown in Figures 13 and 14, the maximum of MWD-DB shifts to smaller values while the amount of “dead” polymer having branches decreases, as initial solvent concentration

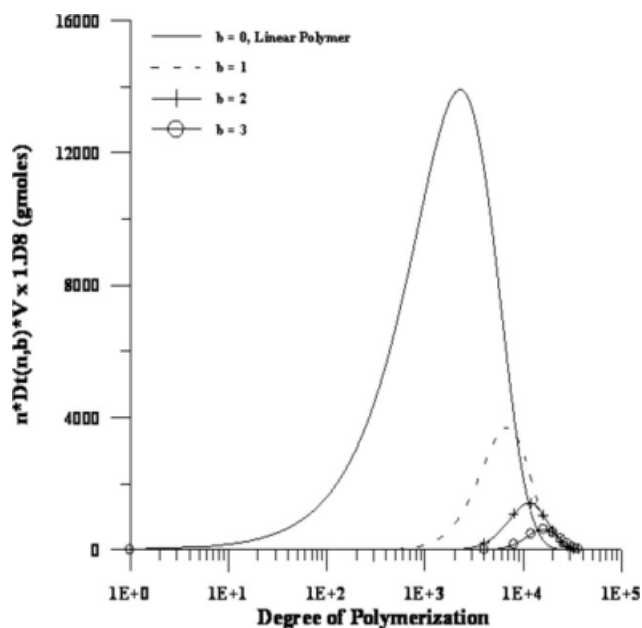


Figure 12 Joint degree of branching–molecular-weight distribution. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Initiator: 0.00042 mol/L AIBN. Polymerization temperature: 60°C. Monomer conversion: 0.5.

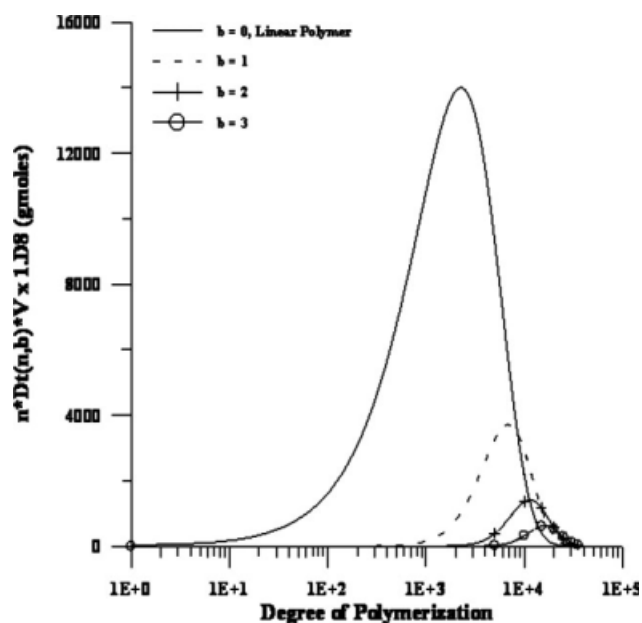


Figure 13 Joint degree of branching–molecular-weight distribution. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Monomer conversion: 0.5.

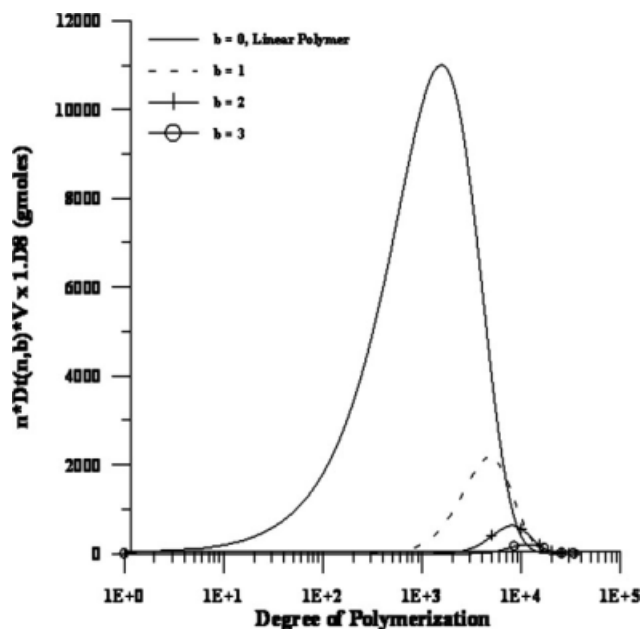


Figure 14 Joint degree of branching–molecular-weight distribution. Solvent: *t*-butyl alcohol, $S_0/M_0 = 6$. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Monomer conversion: 0.5.

increases. This is attributed to the fact that increasing initial solvent concentration not only promotes chain transfer to solvent reactions but also reduces the propagation rate causing a further decrease in the mean molecular weight of produced “dead” polymer. In other words, the concentration of “dead” polymer increases while mean molecular

weights decrease. This decrease in mean molecular weights causes a further reduction in the “dead” polymer having a higher degree of branching because of a reduction of transfer to polymer reaction rate. As a result of the variation of both initial solvent and monomer concentrations, the maximum value of MWD, corresponding to the number-average molecular weight, shifts to smaller values of polymerization degree while there is less accumulation to higher degrees of both polymerization and branching causing a further decrease in polydispersity and weight-average molecular weights. These observations are in accordance with the experimental observations of Graessley and coworkers² as shown in Figures 7–10.

In Figures 15–17 the effect of initial solvent concentration on terminal double bonds is investigated by plotting the MWD for “dead” polymer. Symbol $D(s)$ denotes “dead” polymer total concentration having s monomer units (sum of species having a different degree of branching). As initial solvent increases, or initial monomer concentration decreases, the position of the MWD maximum (see Fig. 15) for polymer having no terminal double bonds shifts to higher polymerization degrees because of the reduction of transfer to monomer reactions rate causing the formation of terminal double bonds. However, the effect of monomer increase causes the opposite result on polymer with terminal double bonds (Fig. 16). The overall effect as shown in Figure 17 for the total MWD is a shift of its

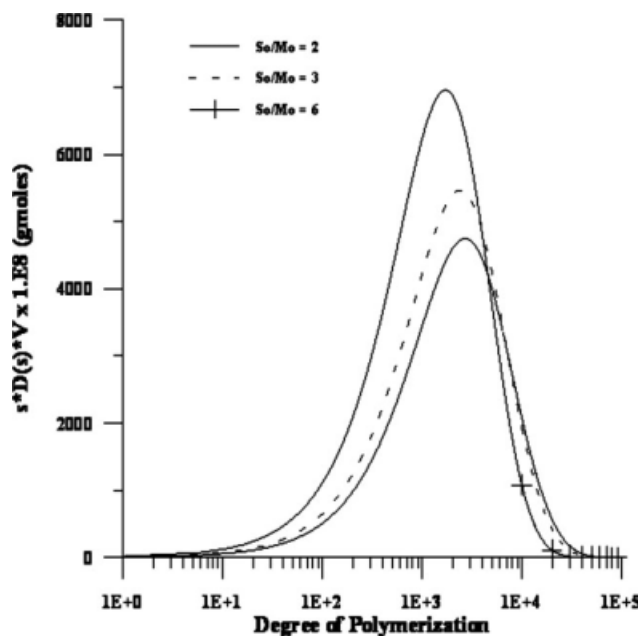


Figure 15 Molecular-weight distribution—no terminal double bonds as a function of initial solvent concentration. Solvent: *t*-butyl alcohol. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Monomer conversion: 0.5.

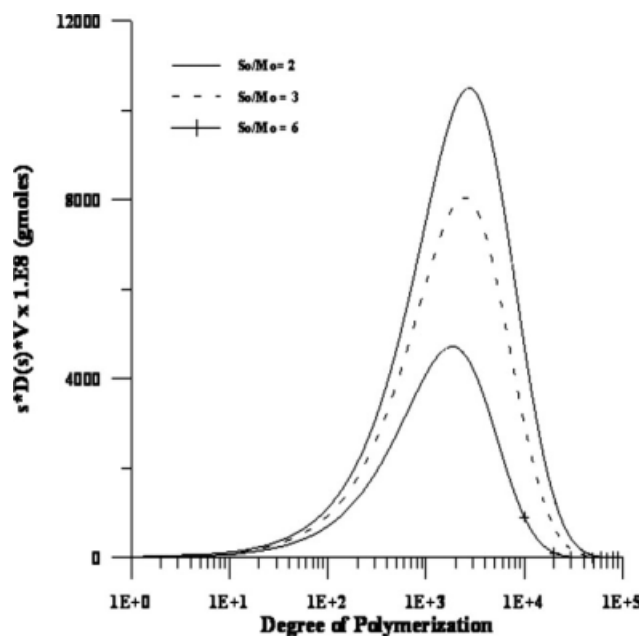


Figure 16 Molecular-weight distribution—with terminal double bonds as a function of initial solvent concentration. Solvent: *t*-butyl alcohol. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Monomer conversion: 0.5.

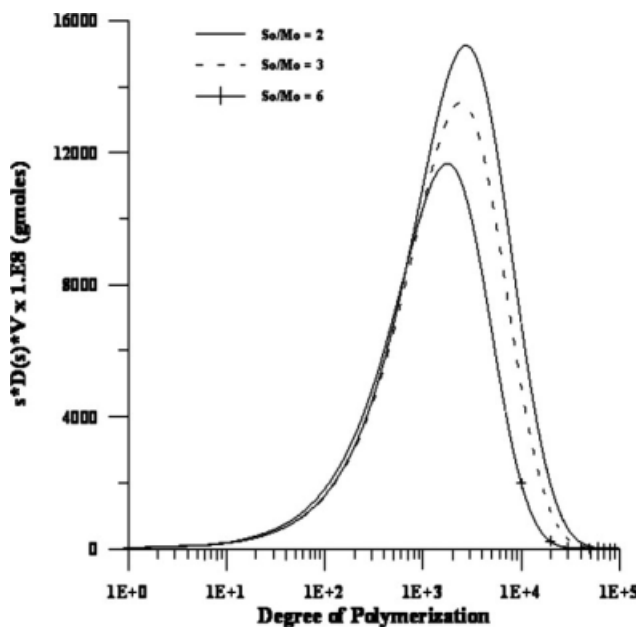


Figure 17 Total molecular-weight distribution as a function of initial solvent concentration. Solvent: *t*-butyl alcohol. Initiator: 0.001 mol/L AIBN. Polymerization temperature: 60°C. Monomer conversion: 0.5.

maximum to smaller degrees of polymerization as solvent concentration increases. This combined effect is attributed to the total effect of initial reactant concentration on the polymerization mechanism.

Finally, in Figures 18 and 19 the effect of polymerization time on product quality is studied by plotting the MWD as a function of monomer conver-

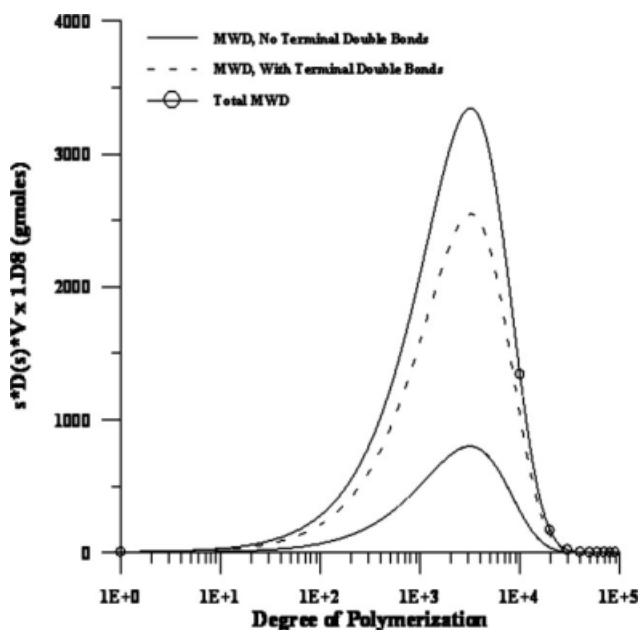


Figure 18 Molecular-weight distribution. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Initial AIBN concentration: 0.0016 gmol/L. Polymerization temperature: 60°C. Monomer Conversion: 0.1.

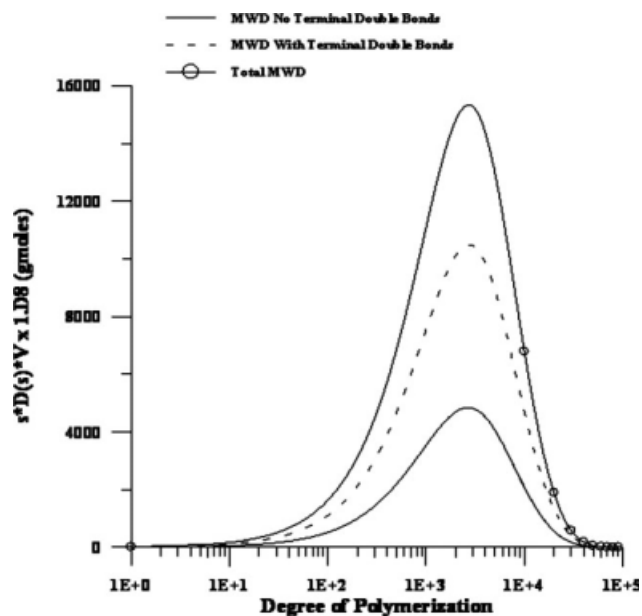


Figure 19 Molecular-weight distribution. Solvent: *t*-butyl alcohol, $S_0/M_0 = 2$. Initial AIBN concentration: 0.0016 gmol/L. Polymerization temperature: 60°C. Monomer conversion: 0.5.

sion corresponding to different polymerization times. As polymerization time proceeds or conversion increases both the maximum values of the distributions increase because of addition of more polymer chains while their positions, corresponding to the number-average molecular weights remain almost unaffected. Moreover, there is a significant accumulation near the tail of the distribution curve corresponding to weight-average molecular weight. This results in an increase in polydispersity in all type of chains, including "dead" polymer with terminal double bonds as polymerization time proceeds.

CONCLUSIONS

In this work a comprehensive mathematical framework for modeling the gel effect in branched polymer systems with application to the solution polymerization of VAC was developed. This model was based on sound principles such as the free-volume theory for polymer diffusion and was successfully applied to simulate experimental data for VAC polymerization in toluene and *t*-butyl alcohol at 60°C, published in the literature. All the model adjustable parameters have a clear physical meaning. Moreover, the effects of process conditions on the product quality were thoroughly studied by calculating the joint LCB-MW distribution as a function of initial reactant concentrations. It is believed that this work might contribute to the more rational design of polymerization reactors.

George Verros thanks Ms. Kate Somerscales for her help in preparing the manuscript.

NOMENCLATURE

A	residual termination adjustable parameter
\bar{B}_n	number-average degree of branching
$D_{n,b}; D_{n,b}$	"dead" polymer having n monomer units and b number of branches; its concentration
$D_s; D_s$	"dead" polymer having s monomer units (sum of species with different degrees of branching); its concentration
$D_{t(n,b)}$	total concentration (sum of species with and without a terminal double bond) of "dead" polymer having n monomer units and b number of branches
$D_{p0}; D'_{p0}$	free-volume theory preexponential parameter
$\bar{D}_{p,0}$	self-diffusion coefficient of linear "live" radicals
$\bar{D}_{p,br}$	self-diffusion coefficient of "live" radicals having different degree of branching
f	initiator efficiency
$I; I$	initiator; its concentration
j_c	entanglement spacing
k_d	initiator decomposition kinetic rate constant
k_{db}	terminal double-bond reaction kinetic rate constant
k_p	propagation rate kinetic rate constant
k_{t0}	intrinsic termination rate constant defined at zero conversion and involving two short chains
k_{tm}	chain transfer to monomer kinetic rate constant
k_{tp}	chain transfer to polymer kinetic rate constant
k_{ts}	chain transfer to solvent kinetic rate constant
k_{tc}	termination by combination kinetic rate constant
k_{td}	termination by disproportionation kinetic rate constant
K_{1i}	free-volume parameter
K_{2i}	free-volume parameter
$M; M$	monomer; its concentration
\bar{M}_n	number-average molecular weight
\bar{M}_W	weight-average molecular weight
N_A	Avogadro number
P_{00}^T	total concentration of "live" radicals
P_{0b}	total concentration of "live" radicals with branches
P_{0l}	total concentration of linear "live" radicals
$P_{n,b}; P_{n,b}$	"live" polymer having n monomer units and b number of branches; its concentration

$PR^*; PR^*$	primary radical from the fragmentation of the initiator; its concentration
r_t	effective termination reaction radius
R	universal gas constant
$S; S$	solvent agent; its concentration
t	time
T	temperature
T_G	glass transition temperature
V	reactor volume
V_F	specific free volume
V_i^*	specific critical hole free volume of the i th substance
x_{c0}	critical degree of polymerization for entanglement of pure polymer
X	fractional monomer conversion
\bar{X}_n	number-average degree of polymerization
\bar{X}_W	weight-average degree of polymerization
\bar{X}_b	number-average degree of polymerization of the branched "live" radicals
\bar{X}_{lr}	number-average degree of polymerization of the linear "live" radicals

Greek symbols

α	free-volume theory adjustable parameter
γ	overlap factor
δ	average root-mean-square end-to-end distance per square root of the number of monomer units in a chain
$\delta(n)$	Kronecker delta
λ_{kl}	"live" polymer distribution moments
μ_{kl}	"dead" polymer distribution moments
τ	auxiliary parameter
ϕ_p	volume fraction of polymer
ω	weight fraction

Subscripts

b	number of long-chain branches in a polymer chain
m	monomer
n	number of monomer units in the polymer chain
o	initial conditions
p	polymer
s	solvent

Superscripts

T	total (sum of all species with and without a terminal double bond)
$=$	terminal double bond incorporated into a macromolecule

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