

Mathematical Modeling of Diffusion-Controlled Free-Radical Terpolymerization Reactions

Anastasios Keramopoulos, Costas Kiparissides

Department of Chemical Engineering, Chemical Process Engineering Research Institute, Aristotle University of Thessaloniki, P.O. Box 472, 540 06 Thessaloniki, Greece

Received 4 April 2002; accepted 4 June 2002

ABSTRACT: A comprehensive mathematical model is developed to describe the kinetics and molecular and compositional developments in a free-radical terpolymerization batch reactor. This model is based on a fairly general kinetic mechanism, including chain-transfer and terminal double-bond reactions. We take into account the effects of diffusion-controlled phenomena (i.e., gel, glass, and cage effects) on polymerization kinetics by extending our previous model on diffusion-controlled reactions to terpolymerization systems. Triple moments for the live and dead trivariate chain-length terpolymer composition distributions are introduced to describe the molecular and compositional developments in the

terpolymerization system. The predictive capabilities of this model are demonstrated by simulation of the free-radical, bulk terpolymerization of butyl acrylate/methyl methacrylate/vinyl acetate under different experimental conditions. It is shown that the model predictions are in good agreement with experimental data on monomer conversion, average molecular weights, and terpolymer composition, as reported by Dube and Penlidis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 161–176, 2003

Key words: modeling; radical polymerization; diffusion

INTRODUCTION

Free-radical multicomponent polymerizations have been met with growing interest by both the polymer industry and academia. The synthesis of multicomponent polymers is of significant economic importance because of the great diversity of polymer grades that can be produced by variation of the number and relative concentrations of the monomers in the reaction mixture. This enhanced flexibility can lead to the production of polymers with desired physical, chemical, and mechanical properties. Free-radical random multicomponent polymers are typically obtained as a mixture of macromolecules with different compositions, chain lengths, degrees of branching, and chain sequence characteristics. Controlling the polymer chain microstructure and, thus, the end-use properties of the polymer requires a thorough understanding of the polymerization kinetics and physical transport processes occurring during polymerization.

In the open literature, a very limited number of experimental kinetic studies have been published^{1,2} on free-radical terpolymerizations. In a recent publication by Dube and Penlidis,³ the experimental investigation of the butyl acrylate (BuA)/methyl methacrylate (MMA)/vinyl acetate (VAc) system was reported.

Moreover, there are a lack of publications dealing with the modeling of free-radical multicomponent polymerizations. Gao and Penlidis⁴ recently reported the development of a software package for simulating bulk and solution free-radical terpolymerizations. They claimed that their work was the first attempt to model free-radical terpolymerization kinetics. Model predictions were shown to be in good agreement with experimental measurements on monomer conversion, terpolymer composition, and average molecular weights (MWs) for the BuA/MMA/VAc system. However, no details were presented with regard to the kinetic mechanism and the values of the various kinetic rate constants used in the simulations.

In this article, a comprehensive mathematical model is developed to describe kinetic and molecular weight (MW) developments in free-radical terpolymerizations. The model takes into account the effects of diffusion-controlled phenomena (e.g., gel, glass, and cage effects) on polymerization kinetics. The termination and propagation rate constants and the initiator efficiency are expressed in terms of the corresponding intrinsic rate constant and a diffusion-controlled term. The generalized free-volume theory of Vrentas and Duda^{5–7} is employed to estimate the self-diffusion coefficients of the various reactive species (e.g., monomers, initiator, and polymer chains) and the observed decrease in the respective kinetic rate constant (e.g., termination, propagation) caused by diffusional limitations. The ability of this mathematical model to describe diffusion-controlled reactions in free-radical ter-

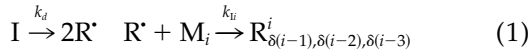
Correspondence to: C. Kiparissides (cypress@alexandros.cperi.certh.gr).

polymerizations is demonstrated by its application to the batch, bulk terpolymerization of BuA/MMA/VAc. To our knowledge, this is the first attempt to model kinetic and MW developments up to high conversions in free-radical terpolymerizations by consideration of the effect of all diffusion-controlled reactions on the polymerization kinetics.

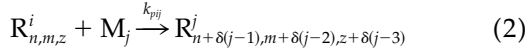
KINETIC MODEL DEVELOPMENTS

In this study, a comprehensive kinetic mechanism was employed to describe all the elementary reactions occurring in a chemically initiated free-radical terpolymerization. Thus, besides the conventional reactions (e.g., initiation, propagation, and termination), the terpolymerization mechanism included chain transfer to monomer, polymer, and chain-transfer agent and terminal double-bond reactions. Specifically, the following elementary reactions were considered:

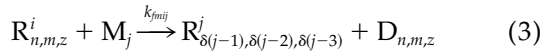
Chain-initiation reactions:



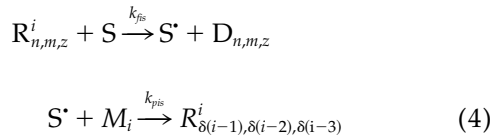
Propagation reactions:



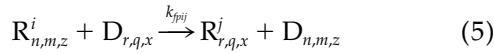
Chain transfer to monomer reactions:



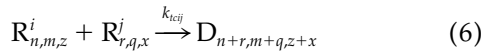
Chain transfer to modifier reactions:



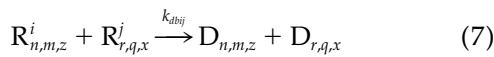
Chain transfer to polymer reactions:



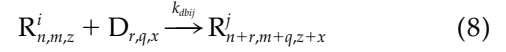
Termination by combination reactions:



Termination by disproportionation reactions:



Terminal double-bond polymerization reactions:



where the symbols I, R^\cdot , M_j ($j = 1, 2, 3$), and S denote the initiator, primary radicals, monomer, and modifier (i.e., chain-transfer agent) molecules, respectively. The terpolymerization mechanism comprises four chain-initiation, nine propagation, nine chain transfer to monomer, three chain transfer to modifier, nine chain transfer to polymer, six termination by combination, six termination by disproportionation, and nine terminal double-bond reactions; that is a total of 55 elementary reactions. Depropagation reactions and penultimate monomer effects are assumed to be negligible.

The symbols $R_{n,m,z}^i$ and $D_{n,m,z}$ denote the live and dead terpolymer chains, respectively. The subscripts n , m , and z represent the degrees of polymerization for the monomers M_1 , M_2 , and M_3 . Finally, the superscript i refers to the ultimate monomer unit of the live polymer chains, which can be of type M_1 , M_2 , or M_3 .

Terpolymerization rate functions

The net rates of production of the live and dead terpolymer chains can be obtained by consideration of all of the relevant elementary reactions according to which live and dead polymer chains are generated or/and consumed. On the basis of the previous comprehensive kinetic mechanism, the following general rate functions for the molecular species $R_{n,m,z}^1$, $R_{n,m,z}^2$, $R_{n,m,z}^3$ and $D_{n,m,z}$ can be derived. For live terpolymer chains of type i of total length $n + m + z$,

$$r_{R_{n,m,z}^1} = \left(k_{i1} PR^\cdot M_1 + \sum_{j=1}^3 k_{fmi1} M_1 R_{000}^j + k_{f1s} S R_{000}^1 \right) \\ \times \delta(n-1, m, z) + \sum_{j=1}^3 k_{pji1} M_1 R_{n-1, m, z}^j \\ - \sum_{j=1}^3 k_{p1j} M_j R_{n,m,z}^1 - A_1 R_{n,m,z}^1 + \sum_{j=1}^3 k_{fpi1} R_{000}^j n D_{n,m,z} \\ - \sum_{j=1}^3 k_{db1j} R_{n,m,z}^1 \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} \sum_{x=0}^{\infty} D_{r,q,x} \\ + \sum_{j=1}^3 k_{dbj1} \sum_{r=0}^n \sum_{q=0}^m \sum_{x=0}^z D_{r,q,x} R_{n-r, m-q, z-x}^j \quad (9)$$

$$\begin{aligned}
 r_{R_{n,m,z}^2} &= \left(k_{I2} PR^* M_2 + \sum_{j=1}^3 k_{f_{mj2}} M_2 R_{000}^j + k_{f_{2s}} SR_{000}^2 \right) \\
 &\times \delta(n, m-1, z) + \sum_{j=1}^3 k_{p_{j2}} M_2 R_{n,m-1,z}^j - \sum_{j=1}^3 k_{p_{2j}} M_j R_{n,m,z}^2 \\
 &- A_2 R_{n,m,z}^2 + \sum_{j=1}^3 k_{f_{pj2}} R_{000}^j m D_{n,m,z} - \sum_{j=1}^3 k_{db_{2j}} R_{n,m,z}^2 \\
 &\times \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} \sum_{x=0}^{\infty} D_{r,q,x} + \sum_{j=1}^3 k_{db_{j2}} \sum_{r=0}^n \sum_{q=0}^m \sum_{x=0}^z D_{r,q,x} R_{n-r,m-q,z-x}^j
 \end{aligned} \quad (10)$$

$$\begin{aligned}
 r_{R_{n,m,z}^3} &= \left(k_{I3} PR^* M_3 + \sum_{j=1}^3 k_{f_{mj3}} M_3 R_{000}^j + k_{f_{3s}} SR_{000}^3 \right) \\
 &\times \delta(n, m, z-1) + \sum_{j=1}^3 k_{p_{j3}} M_3 R_{n,m,z-1}^j \\
 &- \sum_{j=1}^3 k_{p_{3j}} M_j R_{n,m,z}^3 - A_3 R_{n,m,z}^3 + \sum_{j=1}^3 k_{f_{pj3}} R_{000}^j z D_{n,m,z} \\
 &- \sum_{j=1}^3 k_{db_{3j}} R_{n,m,z}^3 \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} \sum_{x=0}^{\infty} D_{r,q,x} \\
 &+ \sum_{j=1}^3 k_{db_{j3}} \sum_{r=0}^n \sum_{q=0}^m \sum_{x=0}^z D_{r,q,x} R_{n-r,m-q,z-x}^j
 \end{aligned} \quad (11)$$

For dead copolymer chains of total length $n + m + z$,

$$\begin{aligned}
 r_{D_{n,m,z}} &= \sum_{i=1}^3 \left(A_i - \sum_{j=1}^3 k_{t_{cij}} R_{000}^j \right) R_{n,m,z}^i \\
 &- \sum_{i=1}^3 k_{f_{pi1}} R_{000}^i n D_{n,m,z} - \sum_{i=1}^3 k_{f_{pi2}} R_{000}^i m D_{n,m,z} \\
 &- \sum_{i=1}^3 k_{f_{pi3}} R_{000}^i z D_{n,m,z} \\
 &+ \frac{1}{2} \sum_{i=1}^3 \sum_{j=1}^3 k_{t_{cij}} \sum_{r=1}^{n-1} \sum_{q=1}^{m-1} \sum_{x=1}^{z-1} R_{r,q,x}^i R_{n-r,m-q,z-x}^j \\
 &- \sum_{i=1}^3 \sum_{j=1}^3 k_{db_{ij}} R_{000}^i D_{n,m,z}
 \end{aligned} \quad (12)$$

where

$$\begin{aligned}
 A_i &= \sum_{j=1}^3 (k_{f_{mij}} M_j + k_{t_{ij}} R_{000}^j) + k_{f_{is}} S \\
 &+ k_{f_{pi1}} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} \sum_{x=0}^{\infty} r D_{r,q,x} + k_{f_{pi2}} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} \sum_{x=0}^{\infty} q D_{r,q,x} \\
 &+ k_{f_{pi3}} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} \sum_{x=0}^{\infty} x D_{r,q,x}
 \end{aligned} \quad (13)$$

R_{000}^i denotes the total concentration of live polymer chains of type i :

$$R_{000}^i = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{z=0}^{\infty} R_{n,m,z}^i \quad (14)$$

$\delta(n, m, z)$ is Kronecker's delta, given by

$$\delta(n, m, z) = \delta(n) \cdot \delta(m) \cdot \delta(z)$$

$$\delta(i) = 1 \text{ for } i = 0, \delta(i) = 0 \text{ for } i \neq 0 \quad (15)$$

Application of the fundamental molar conservation equation to all live and dead polymer chains present in the polymerization mixture typically results in an infinite system of differential equations. To reduce the high dimensionality of the numerical problem, several mathematical techniques have been proposed in the literature.⁸ The method of moments is a commonly employed technique that allows for the reduction of the infinite system of dynamic molar balance equations into a low-order system of differential moment equations. The method of moments is based on the statistical representation of the average molecular properties [e.g., number-average molecular weight (M_n), weight-average molecular weight (M_w), terpolymer composition] in terms of the leading moments of the number chain-length distributions of live and dead polymer chains.

In this study, trivariate distributions were introduced to describe the molecular and compositional developments in the terpolymerization system. Accordingly, the corresponding moments of live and dead chain-length terpolymer composition (CLTC) distributions are defined:

$$\lambda_{k,l,w}^i = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{z=1}^{\infty} n^k m^l z^w R_{n,m,z}^i$$

$$i = 1, 2, 3 \text{ and } k, l, w = 0, 1, 2$$

$$\mu_{k,l,w} = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{z=1}^{\infty} n^k m^l z^w D_{n,m,z} \quad (16)$$

To calculate the rate functions for the moments $\lambda_{k,l,z}^i$ and $\mu_{k,l,z}$, all terms in eqs. (9)–(12) were multiplied by the term $n^k m^l z^w$, and the resulting expressions were summed up with respect to the total variations of n , m , and z (i.e., degrees of polymerization). Thus, the following expressions for the moment rate functions, $r_{\lambda_{k,l,w}^1}$, $r_{\lambda_{k,l,w}^2}$, $r_{\lambda_{k,l,w}^3}$, and $r_{\mu_{k,l,w}}$ were obtained:

$$\begin{aligned} r_{\lambda_{k,l,w}^1} &= k_{11}PR'M_1 + \sum_{j=1}^3 k_{fmj1}M_1\lambda_{000}^j + k_{f1s}S\lambda_{000}^1 \\ &+ \sum_{j=1}^3 k_{pj1}M_1 \sum_r \binom{k}{r} \lambda_{r,l,w}^j - \sum_{j=1}^3 k_{p1j}M_j\lambda_{k,l,w}^1 - A_1'\lambda_{k,l,w}^1 \\ &+ \sum_{j=1}^3 k_{fpj1}\lambda_{000}^j\mu_{k+1,l,w} - \sum_{j=1}^3 k_{db1j}\lambda_{k,l,w}^1\mu_{000} \\ &+ \sum_{j=1}^3 k_{dbj1} \sum_r \sum_q \sum_x \binom{k}{r} \binom{l}{q} \binom{w}{x} \mu_{r,q,x} \lambda_{k-r,l-q,w-x}^j \quad (17) \end{aligned}$$

$$\begin{aligned} r_{\lambda_{k,l,w}^2} &= k_{12}PR'M_2 + \sum_{j=1}^3 k_{fmj2}M_2\lambda_{000}^j + k_{f2s}S\lambda_{000}^2 \\ &+ \sum_{j=1}^3 k_{pj2}M_2 \sum_r \binom{1}{r} \lambda_{k,r,w}^j - \sum_{j=1}^3 k_{p2j}M_j\lambda_{k,l,w}^2 - A_2'\lambda_{k,l,w}^2 \\ &+ \sum_{j=1}^3 k_{fpj2}\lambda_{000}^j\mu_{k,l+1,w} - \sum_{j=1}^3 k_{db2j}\lambda_{k,l,w}^2\mu_{000} \\ &+ \sum_{j=1}^3 k_{dbj2} \sum_r \sum_q \sum_x \binom{k}{r} \binom{l}{q} \binom{w}{x} \mu_{r,q,x} \lambda_{k-r,l-q,w-x}^j \quad (18) \end{aligned}$$

$$\begin{aligned} r_{\lambda_{k,l,w}^3} &= k_{13}PR'M_3 + \sum_{j=1}^3 k_{fmj3}M_3\lambda_{000}^j + k_{f3s}S\lambda_{000}^3 \\ &+ \sum_{j=1}^3 k_{pj3}M_3 \sum_r \binom{w}{r} \lambda_{k,l,r}^j \\ &- \sum_{j=1}^3 k_{p3j}M_j\lambda_{k,l,w}^3 - A_3'\lambda_{k,l,w}^3 \\ &+ \sum_{j=1}^3 k_{fpj3}\lambda_{000}^j\mu_{k,l,w+1} - \sum_{j=1}^3 k_{db3j}\lambda_{k,l,w}^3\mu_{000} \\ &+ \sum_{j=1}^3 k_{dbj3} \sum_r \sum_q \sum_x \binom{k}{r} \binom{l}{q} \binom{w}{x} \mu_{r,q,x} \lambda_{k-r,l-q,w-x}^j \quad (19) \end{aligned}$$

$$\begin{aligned} r_{\mu_{k,l,w}} &= \sum_{i=1}^3 \left(A_i' - \sum_{j=1}^3 k_{tcij}\lambda_{000}^j \right) \lambda_{k,l,w}^i - \sum_{i=1}^3 k_{fpi1}\lambda_{000}^i\mu_{k+1,l,w} \\ &- \sum_{i=1}^3 k_{fpi2}\lambda_{000}^i\mu_{k,l+1,w} - \sum_{j=1}^3 k_{fpi3}\lambda_{000}^j\mu_{k,l,w+1} + \frac{1}{2} \sum_{i=1}^3 \sum_{j=1}^3 \\ &\times k_{tcij} \sum_r \sum_q \sum_x \binom{k}{r} \binom{l}{q} \binom{w}{x} \lambda_{r,q,x}^i \lambda_{k-r,l-q,w-x}^j \\ &- \sum_{i=1}^3 \sum_{j=1}^3 k_{dbij}\lambda_{000}^i\mu_{k,l,w} \quad (20) \end{aligned}$$

where

$$\begin{aligned} A_i' &= \sum_{j=1}^3 (k_{fmij}M_j + k_{tij}\lambda_{000}^j) + k_{fis}S \\ &+ k_{fpi1}\mu_{100} + k_{fpi2}\mu_{010} + k_{fpi3}\mu_{001} \quad (21) \end{aligned}$$

From the general moment rate eqs. (17)–(21), one can easily derive the rate functions for the leading moments of live and dead CLTC distributions. In Tables I and II, the analytical expressions for live (e.g., $r_{\lambda_{000}^1}$, $r_{\lambda_{000}^2}$, $r_{\lambda_{000}^3}$, $r_{\lambda_{100}^1}$, $r_{\lambda_{100}^2}$, $r_{\lambda_{100}^3}$) and dead (e.g., $r_{\mu_{000}}$, $r_{\mu_{100}}$, $r_{\mu_{010}}$, $r_{\mu_{001}}$, $r_{\mu_{110}}$, $r_{\mu_{101}}$) polymer chains are reported.

Reactor design equations

On the basis of the previous moment rate functions, one can easily derive the following design equations for a batch free-radical terpolymerization reactor. For the initiator

$$\frac{d(VI)}{dt} = -Vk_dI \quad (22)$$

For the monomers

$$\begin{aligned} \frac{d(VM_1)}{dt} &= Vr_{M1} = -\{[(k_{p11} + k_{f11})\lambda_{0,0,0}^1 + (k_{p21} + k_{f21})\lambda_{0,0,0}^2 \\ &+ (k_{p31} + k_{f31})\lambda_{0,0,0}^3]M_1 + k_{11}R'M_1\}V \quad (23) \end{aligned}$$

$$\begin{aligned} \frac{d(VM_2)}{dt} &= Vr_{M2} = -\{[(k_{p12} + k_{f12})\lambda_{0,0,0}^1 \\ &+ (k_{p22} + k_{f22})\lambda_{0,0,0}^2 + (k_{p32} + k_{f32})\lambda_{0,0,0}^3]M_2 + k_{12}R'M_2\}V \quad (24) \end{aligned}$$

$$\begin{aligned} \frac{d(VM_3)}{dt} &= Vr_{M3} = -\{[(k_{p13} + k_{f13})\lambda_{0,0,0}^1 + (k_{p23} + k_{f23})\lambda_{0,0,0}^2 \\ &+ (k_{p33} + k_{f33})\lambda_{0,0,0}^3 + k_{13}R'M_3\}V \quad (25) \end{aligned}$$

For the modifier (chain-transfer agent)

TABLE I
Rate Functions for the Moments of Live Terpolymer Chains of the CLTC Distribution

$$\begin{aligned}
 r_{\lambda_{000}^1} &= k_{I1}PR^*M_1 + (k_{fm21}\lambda_{000}^2 + k_{fm31}\lambda_{000}^3)M_1 + (k_{p21}\lambda_{000}^2 + k_{p31}\lambda_{000}^3)M_1 - (k_{p12}M_2 + k_{p13}M_3)\lambda_{000}^1 + (k_{fp21}\lambda_{000}^2 + k_{fp31}\lambda_{000}^3)\mu_{100} \\
 &\quad - [k_{fm12}M_2 + k_{fm13}M_3 + (k_{ic11} + k_{id11})\lambda_{000}^1 + (k_{ic12} + k_{id12})\lambda_{000}^2 + (k_{ic13} + k_{id13})\lambda_{000}^3 + k_{fp12}\mu_{010} + k_{fp13}\mu_{001}]\lambda_{000}^1 - [k_{db12}\lambda_{000}^1 \\
 &\quad + k_{db13}\lambda_{000}^1 - k_{db21}\lambda_{000}^2 - k_{db31}\lambda_{000}^3]\mu_{000} \\
 r_{\lambda_{000}^2} &= k_{I2}PR^*M_2 + (k_{fm12}\lambda_{000}^1 + k_{fm32}\lambda_{000}^3)M_2 + (k_{p12}\lambda_{000}^1 + k_{p32}\lambda_{000}^3)M_2 - (k_{p21}M_1 + k_{p23}M_3)\lambda_{000}^2 + (k_{fp12}\lambda_{000}^1 + k_{fp32}\lambda_{000}^3)\mu_{010} \\
 &\quad - [k_{fm21}M_1 + k_{fm23}M_3 + (k_{ic21} + k_{id21})\lambda_{000}^1 + (k_{ic22} + k_{id22})\lambda_{000}^2 + (k_{ic23} + k_{id23})\lambda_{000}^3 + k_{fp21}\mu_{100} + k_{fp23}\mu_{001}]\lambda_{000}^2 - [k_{db21}\lambda_{000}^2 \\
 &\quad + k_{db23}\lambda_{000}^2 - k_{db12}\lambda_{000}^1 - k_{db32}\lambda_{000}^3]\mu_{000} \\
 r_{\lambda_{000}^3} &= k_{I3}PR^*M_3 + (k_{fm13}\lambda_{000}^1 + k_{fm23}\lambda_{000}^2)M_3 + (k_{p13}\lambda_{000}^1 + k_{p23}\lambda_{000}^2)M_3 - (k_{p31}M_1 + k_{p32}M_2)\lambda_{000}^3 + (k_{fp13}\lambda_{000}^1 + k_{fp23}\lambda_{000}^2)\mu_{001} \\
 &\quad - [k_{fm31}M_1 + k_{fm32}M_2 + (k_{ic31} + k_{id31})\lambda_{000}^1 + (k_{ic32} + k_{id32})\lambda_{000}^2 + (k_{ic33} + k_{id33})\lambda_{000}^3 + k_{fp31}\mu_{100} + k_{fp32}\mu_{010}]\lambda_{000}^3 - [k_{db31}\lambda_{000}^3 \\
 &\quad + k_{db32}\lambda_{000}^3 - k_{db13}\lambda_{000}^1 - k_{db23}\lambda_{000}^2]\mu_{000} \\
 r_{\lambda_{100}^1} &= k_{I1}PR^*M_1 + (k_{fm11}\lambda_{000}^1 + k_{fm21}\lambda_{000}^2 + k_{fm31}\lambda_{000}^3)M_1 + k_{f1s}S\lambda_{000}^1 + k_{p11}M_1\lambda_{000}^1 + k_{p21}M_1(\lambda_{000}^2 + \lambda_{100}^2) + k_{p31}M_1(\lambda_{000}^3 + \lambda_{100}^3) \\
 &\quad - (k_{p12}M_2 + k_{p13}M_3)\lambda_{100}^1 - [k_{fm11}M_1 + k_{fm12}M_2 + k_{fm13}M_3 + (k_{ic11} + k_{id11})\lambda_{000}^1 + (k_{ic12} + k_{id12})\lambda_{000}^2 + (k_{ic13} + k_{id13})\lambda_{000}^3 + k_{f1s}S \\
 &\quad + k_{fp11}\mu_{100} + k_{fp12}\mu_{010} + k_{fp13}\mu_{001}]\lambda_{100}^1 + (k_{fp11}\lambda_{000}^1 + k_{fp21}\lambda_{000}^2 + k_{fp31}\lambda_{000}^3)\mu_{200} - (k_{db12} + k_{db13})\lambda_{100}^1\mu_{000} + k_{db11}\lambda_{000}^1\mu_{100} \\
 &\quad + k_{db21}(\mu_{000}\lambda_{100}^2 + \mu_{100}\lambda_{000}^2) + k_{db31}(\mu_{000}\lambda_{100}^3 + \mu_{100}\lambda_{000}^3) \\
 r_{\lambda_{100}^2} &= k_{I2}PR^*M_2 + (k_{fm12}\lambda_{000}^1 + k_{fm22}\lambda_{000}^2 + k_{fm32}\lambda_{000}^3)M_2 + k_{f2s}S\lambda_{000}^2 + (k_{p12}\lambda_{000}^1 + k_{p32}\lambda_{000}^3)M_2 - (k_{p21}M_1 + k_{p23}M_3)\lambda_{100}^2 - [k_{fm21}M_1 \\
 &\quad + k_{fm22}M_2 + k_{fm23}M_3 + (k_{ic21} + k_{id21})\lambda_{000}^1 + (k_{ic22} + k_{id22})\lambda_{000}^2 + (k_{ic23} + k_{id23})\lambda_{000}^3 + k_{f2s}S + k_{fp21}\mu_{100} + k_{fp22}\mu_{010} + k_{fp23}\mu_{001}]\lambda_{100}^2 \\
 &\quad + (k_{fp12}\lambda_{000}^1 + k_{fp22}\lambda_{000}^2 + k_{fp32}\lambda_{000}^3)\mu_{110} - (k_{db21} + k_{db23})\lambda_{100}^2\mu_{000} + k_{db12}(\mu_{000}\lambda_{100}^1 + \mu_{100}\lambda_{000}^1) + k_{db22}\lambda_{000}^2\mu_{100} + k_{db32}(\mu_{000}\lambda_{100}^3 \\
 &\quad + \mu_{100}\lambda_{000}^3) \\
 r_{\lambda_{100}^3} &= k_{I3}PR^*M_3 + (k_{fm13}\lambda_{000}^1 + k_{fm23}\lambda_{000}^2 + k_{fm33}\lambda_{000}^3)M_3 + k_{f3s}S\lambda_{000}^3 + (k_{p13}\lambda_{000}^1 + k_{p23}\lambda_{000}^2)M_3 - (k_{p31}M_1 + k_{p32}M_2)\lambda_{100}^3 - [k_{fm31}M_1 \\
 &\quad + k_{fm32}M_2 + k_{fm33}M_3 + (k_{ic31} + k_{id31})\lambda_{000}^1 + (k_{ic32} + k_{id32})\lambda_{000}^2 + (k_{ic33} + k_{id33})\lambda_{000}^3 + k_{f3s}S + k_{fp31}\mu_{100} + k_{fp32}\mu_{010} + k_{fp33}\mu_{001}]\lambda_{100}^3 \\
 &\quad + (k_{fp13}\lambda_{000}^1 + k_{fp23}\lambda_{000}^2 + k_{fp33}\lambda_{000}^3)\mu_{101} - (k_{db31} + k_{db32})\lambda_{100}^3\mu_{000} + k_{db13}(\mu_{000}\lambda_{100}^1 + \mu_{100}\lambda_{000}^1) + k_{db23}(\mu_{000}\lambda_{100}^2 + \mu_{100}\lambda_{000}^2) + \\
 &\quad k_{db33}\lambda_{000}^3\mu_{100} \\
 r_{\lambda_{010}^1} &= k_{I1}PR^*M_1 + (k_{fm11}\lambda_{000}^1 + k_{fm21}\lambda_{000}^2 + k_{fm31}\lambda_{000}^3)M_1 + k_{f1s}S\lambda_{000}^1 + (k_{p21}\lambda_{010}^2 + k_{p31}\lambda_{010}^3)M_1 - (k_{p12}M_2 + k_{p13}M_3)\lambda_{010}^1 - [k_{fm11}M_1 \\
 &\quad + k_{fm12}M_2 + k_{fm13}M_3 + (k_{ic11} + k_{id11})\lambda_{000}^1 + (k_{ic12} + k_{id12})\lambda_{000}^2 + (k_{ic13} + k_{id13})\lambda_{000}^3 + k_{f1s}S + k_{fp11}\mu_{100} + k_{fp12}\mu_{010} + k_{fp13}\mu_{001}]\lambda_{010}^1 \\
 &\quad + (k_{fp11}\lambda_{000}^1 + k_{fp21}\lambda_{000}^2 + k_{fp31}\lambda_{000}^3)\mu_{110} - (k_{db12} + k_{db13})\lambda_{010}^1\mu_{000} + k_{db11}\lambda_{000}^1\mu_{010} + k_{db21}(\mu_{000}\lambda_{010}^2 + \mu_{010}\lambda_{000}^2) + k_{db31}(\mu_{000}\lambda_{010}^3 \\
 &\quad + \mu_{010}\lambda_{000}^3) \\
 r_{\lambda_{010}^2} &= k_{I2}PR^*M_2 + (k_{fm12}\lambda_{000}^1 + k_{fm22}\lambda_{000}^2 + k_{fm32}\lambda_{000}^3)M_2 + k_{f2s}S\lambda_{000}^2 + k_{p12}M_2(\lambda_{000}^1 + \lambda_{010}^1) + k_{p22}M_2\lambda_{000}^2 + k_{p32}M_2(\lambda_{000}^3 + \lambda_{010}^3) \\
 &\quad - (k_{p21}M_1 + k_{p23}M_3)\lambda_{010}^2 - [k_{fm21}M_1 + k_{fm22}M_2 + k_{fm23}M_3 + (k_{ic21} + k_{id21})\lambda_{000}^1 + (k_{ic22} + k_{id22})\lambda_{000}^2 + (k_{ic23} + k_{id23})\lambda_{000}^3 + k_{f2s}S \\
 &\quad + k_{fp21}\mu_{100} + k_{fp22}\mu_{010} + k_{fp23}\mu_{001}]\lambda_{010}^2 + (k_{fp12}\lambda_{000}^1 + k_{fp22}\lambda_{000}^2 + k_{fp32}\lambda_{000}^3)\mu_{020} - (k_{db21} + k_{db23})\lambda_{010}^2\mu_{000} + k_{db12}(\mu_{000}\lambda_{010}^1 \\
 &\quad + \mu_{010}\lambda_{000}^1) + k_{db22}\lambda_{000}^2\mu_{010} + k_{db32}(\mu_{000}\lambda_{010}^3 + \mu_{010}\lambda_{000}^3) \\
 r_{\lambda_{010}^3} &= k_{I3}PR^*M_3 + (k_{fm13}\lambda_{000}^1 + k_{fm23}\lambda_{000}^2 + k_{fm33}\lambda_{000}^3)M_3 + k_{f3s}S\lambda_{000}^3 + (k_{p13}\lambda_{010}^1 + k_{p23}\lambda_{010}^2)M_3 - (k_{p31}M_1 + k_{p32}M_2)\lambda_{010}^3 - [k_{fm31}M_1 \\
 &\quad + k_{fm32}M_2 + k_{fm33}M_3 + (k_{ic31} + k_{id31})\lambda_{000}^1 + (k_{ic32} + k_{id32})\lambda_{000}^2 + (k_{ic33} + k_{id33})\lambda_{000}^3 + k_{f3s}S + k_{fp31}\mu_{100} + k_{fp32}\mu_{010} + k_{fp33}\mu_{001}]\lambda_{010}^3 \\
 &\quad + (k_{fp13}\lambda_{000}^1 + k_{fp23}\lambda_{000}^2 + k_{fp33}\lambda_{000}^3)\mu_{011} - (k_{db31} + k_{db32})\lambda_{010}^3\mu_{000} + k_{db13}(\mu_{000}\lambda_{010}^1 + \mu_{010}\lambda_{000}^1) + k_{db23}(\mu_{000}\lambda_{010}^2 + \mu_{010}\lambda_{000}^2) + \\
 &\quad k_{db33}\lambda_{000}^3\mu_{010} \\
 r_{\lambda_{001}^1} &= k_{I1}PR^*M_1 + (k_{fm11}\lambda_{000}^1 + k_{fm21}\lambda_{000}^2 + k_{fm31}\lambda_{000}^3)M_1 + k_{f1s}S\lambda_{000}^1 + (k_{p21}\lambda_{001}^2 + k_{p31}\lambda_{001}^3)M_1 - (k_{p12}M_2 + k_{p13}M_3)\lambda_{001}^1 - [k_{fm11}M_1 \\
 &\quad + k_{fm12}M_2 + k_{fm13}M_3 + (k_{ic11} + k_{id11})\lambda_{000}^1 + (k_{ic12} + k_{id12})\lambda_{000}^2 + (k_{ic13} + k_{id13})\lambda_{000}^3 + k_{f1s}S + k_{fp11}\mu_{100} + k_{fp12}\mu_{010} + k_{fp13}\mu_{001}]\lambda_{001}^1 \\
 &\quad + (k_{fp11}\lambda_{000}^1 + k_{fp21}\lambda_{000}^2 + k_{fp31}\lambda_{000}^3)\mu_{101} - (k_{db12} + k_{db13})\lambda_{001}^1\mu_{000} + k_{db11}\lambda_{000}^1\mu_{001} + k_{db21}(\mu_{000}\lambda_{001}^2 + \mu_{001}\lambda_{000}^2) + k_{db31}(\mu_{000}\lambda_{001}^3 \\
 &\quad + \mu_{001}\lambda_{000}^3) \\
 r_{\lambda_{001}^2} &= k_{I2}PR^*M_2 + (k_{fm12}\lambda_{000}^1 + k_{fm22}\lambda_{000}^2 + k_{fm32}\lambda_{000}^3)M_2 + k_{f2s}S\lambda_{000}^2 + (k_{p12}\lambda_{001}^1 + k_{p32}\lambda_{001}^3)M_2 - (k_{p21}M_1 + k_{p23}M_3)\lambda_{001}^2 - [k_{fm21}M_1 \\
 &\quad + k_{fm22}M_2 + k_{fm23}M_3 + (k_{ic21} + k_{id21})\lambda_{000}^1 + (k_{ic22} + k_{id22})\lambda_{000}^2 + (k_{ic23} + k_{id23})\lambda_{000}^3 + k_{f2s}S + k_{fp21}\mu_{100} + k_{fp22}\mu_{010} + k_{fp23}\mu_{001}]\lambda_{001}^2 \\
 &\quad + (k_{fp12}\lambda_{000}^1 + k_{fp22}\lambda_{000}^2 + k_{fp32}\lambda_{000}^3)\mu_{011} - (k_{db21} + k_{db23})\lambda_{001}^2\mu_{000} + k_{db12}(\mu_{000}\lambda_{001}^1 + \mu_{001}\lambda_{000}^1) + k_{db22}\lambda_{000}^2\mu_{001} + k_{db32}(\mu_{000}\lambda_{001}^3 \\
 &\quad + \mu_{001}\lambda_{000}^3) \\
 r_{\lambda_{001}^3} &= k_{I3}PR^*M_3 + (k_{fm13}\lambda_{000}^1 + k_{fm23}\lambda_{000}^2 + k_{fm33}\lambda_{000}^3)M_3 + k_{f3s}S\lambda_{000}^3 + k_{p13}M_3(\lambda_{000}^1 + \lambda_{001}^1) + k_{p23}M_3(\lambda_{000}^2 + \lambda_{001}^2) + k_{p33}M_3\lambda_{000}^3 \\
 &\quad - (k_{p31}M_1 + k_{p32}M_2)\lambda_{001}^3 - [k_{fm31}M_1 + k_{fm32}M_2 + k_{fm33}M_3 + (k_{ic31} + k_{id31})\lambda_{000}^1 + (k_{ic32} + k_{id32})\lambda_{000}^2 + (k_{ic33} + k_{id33})\lambda_{000}^3 \\
 &\quad + k_{f3s}S + k_{fp31}\mu_{100} + k_{fp32}\mu_{010} + k_{fp33}\mu_{001}]\lambda_{001}^3 + (k_{fp13}\lambda_{000}^1 + k_{fp23}\lambda_{000}^2 + k_{fp33}\lambda_{000}^3)\mu_{002} - (k_{db31} + k_{db32})\lambda_{001}^3\mu_{000} \\
 &\quad + k_{db13}(\mu_{000}\lambda_{001}^1 + \mu_{001}\lambda_{000}^1) + k_{db23}(\mu_{000}\lambda_{001}^2 + \mu_{001}\lambda_{000}^2) + k_{db33}\lambda_{000}^3\mu_{001}
 \end{aligned}$$

$$\frac{d(VS)}{dt} = -V(k_{f1s}\lambda_{0,0,0}^1 + k_{f2s}\lambda_{0,0,0}^2 + k_{f3s}\lambda_{0,0,0}^3)S \quad (26)$$

For moments of live and dead chain-length distributions

For volume contraction

$$\frac{d(V\lambda_{k,l,z}^i)}{dt} = Vr_{\lambda_{k,l,z}^i} \quad i = 1, 2, 3 \quad (28)$$

$$\frac{d(V)}{dt} = -V\left[r_{M1}(MW_1)\left(\frac{1}{d_1} - \frac{1}{d_p}\right) + r_{M2}(MW_2)\right.$$

$$\left.\frac{d(V\mu_{k,l,z})}{dt} = Vr_{\mu_{k,l,z}} \quad (29)\right.$$

$$\left. + \left(\frac{1}{d_2} - \frac{1}{d_p}\right) + r_{M3}(MW_3)\left(\frac{1}{d_3} - \frac{1}{d_p}\right)\right] \quad (27)$$

For the fractional monomer conversion

$$X = \frac{V_0(M_{10} + M_{20} + M_{30}) - V(M_1 + M_2 + M_3)}{V_0(M_{10} + M_{20} + M_{30})} \quad (30)$$

From the leading moments of the dead CLTC distribution, the cumulative number-average composition of monomer i in the terpolymer chains can be calculated:⁸

$$F_{ni} = \frac{\mu_{I_i}}{\sum_{i=1}^3 \mu_{I_i}} \quad (31)$$

where the index I_i is a (1×3) row vector that has its i element equal to one and the other two elements equal to zero.

Similarly, one can calculate the cumulative M_n and M_w of the terpolymer:

$$M_n = \left(\frac{\sum_{i=1}^3 \mu_{I_i}}{\mu_{0,0,0}} \right) \times \sum_{i=1}^3 F_{ni} MW_i \quad (32)$$

$$M_w = \left[\frac{\left(\sum_{i=1}^3 \sum_{j=1}^3 MW_j \mu_{I_i+I_j} \right)}{\left(\sum_{j=1}^3 MW_j \mu_{I_j} \right)} \right] \times \sum_{i=1}^3 F_{ni} MW_i \quad (33)$$

where MW_i is the molecular weight of monomer i .

Diffusion-controlled reactions

In free-radical polymerizations, self-termination reactions involving two live polymer chains can become diffusion-controlled because of the dramatic increase in the viscosity of the reaction medium. As a result, the termination rate constant can decrease by several orders of magnitude. This phenomenon is known as the *gel effect*. Moreover, the monomer conversion can reach a limiting value (i.e., <100%) because of the decrease in the propagation rate constant caused by the decrease in the mobility of monomer molecules. This phenomenon is known as the *glass effect*. Finally, at high monomer conversions, the chain-initiation reactions can also become diffusion-controlled, resulting in a decrease in the initiator efficiency. Thus, in any comprehensive kinetic modeling study, the diffusion of the various reactive species (e.g., monomers, initiator, and polymer chains) has to be adequately described by consideration of the continuous change of the transport properties of the reaction medium during polymerization.

The generalized free-volume theory of Vrentas and Duda⁵⁻⁷ is generally accepted as one of the most successful approaches for the calculation of the molecular diffusion coefficients of the various reactive species in a polymerization medium. Thus, following the recent developments on modeling diffusion-controlled reac-

tions in a multicomponent mixture,^{5,9} the monomer self-diffusion coefficients in a pentad mixture (i.e., monomers M_1 , M_2 , and M_3 ; solvent; and polymer chains) can be expressed as

$$D_{m1} = D_{01} \exp \left[-\gamma_m \frac{\omega_1 V_1^* + \omega_2 V_2^* \xi_{1p} / \xi_{2p} + \omega_3 V_3^* \xi_{1p}}{\xi_{3p} + \omega_s V_s^* \xi_{1p} / \xi_{sp} + \omega_p V_p^* \xi_{1p}} \right] \frac{1}{V_{FH}} \quad (34)$$

$$D_{m2} = D_{02} \exp \left[-\gamma_m \frac{\omega_1 V_1^* \xi_{2p} / \xi_{1p} + \omega_2 V_2^* + \omega_3 V_3^* \xi_{2p}}{\xi_{3p} + \omega_s V_s^* \xi_{2p} / \xi_{sp} + \omega_p V_p^* \xi_{2p}} \right] \frac{1}{V_{FH}} \quad (35)$$

$$D_{m3} = D_{03} \exp \left[-\gamma_m \frac{\omega_1 V_1^* \xi_{3p} / \xi_{1p} + \omega_2 V_2^* \xi_{3p} / \xi_{2p} + \omega_3 V_3^*}{\omega_s V_s^* \xi_{3p} / \xi_{sp} + \omega_p V_p^* \xi_{3p}} \right] \frac{1}{V_{FH}} \quad (36)$$

where the subscripts 1, 2, 3, s , and p refer to the three monomers, the solvent, and the terpolymer, respectively. γ_m is a parameter that is introduced to account for the overlap between free-volume elements (i.e., free volume shared by neighboring molecules). D_{0i} , ω_i , and V_i^* denote the respective preexponential constant of the diffusion coefficient, the weight fraction, and the specific critical hole free volume of species i in the mixture. Notice that the value of V_i^* can be estimated by the group contribution method of Haward¹⁰ on the basis of the chemical composition of the species of interest.

The parameter ξ_{ip} is defined as the ratio of the critical molar volume of the jumping unit of species i to that of the jumping unit of the polymer:

$$\xi_{ip} = V_i^* MW_i / V_{pj} \quad (37)$$

where V_i is the critical volume of the jumping unit of species i and V_{pj} is the critical molar volume of the jumping unit of the polymer. Because of the inherent difficulty in determining the MW of the polymer jumping unit, an empirical expression was developed¹¹ for its calculation in terms of the glass-transition temperature of the terpolymer (T_{gp}):

$$V_{pj} = [0.6224 T_{gp} - 86.95] \quad T_{gp} \geq 295 \text{ K} \quad (38)$$

$$V_{pj} = [0.0925 T_{gp} + 69.47] \quad T_{gp} \leq 295 \text{ K} \quad (39)$$

Finally, V_{FH} is the average free volume of the mixture, given as the weighted sum of the free volumes of the five components in the reaction mixture:^{5,9}

$$V_{FH} = [\alpha_{p0} + \alpha_p (T - T_{gp})] V_p^* \omega_p + \sum_{i=1}^3 [\alpha_{mi0} + \alpha_{mi} \times (T - T_{gmi})] V_i^* \omega_i + [\alpha_{s0} + \alpha_s (T - T_{gs})] V_s^* \omega_s \quad (40)$$

where α_i and α_{i0} denote the difference in the thermal expansion coefficient above and below T_{gp} and the fractional free volume of species i at T_{gp} , respectively.

To calculate T_{gp} , it is necessary to take into consideration the sequence distribution of monomers M_1 , M_2 , and M_3 in the terpolymer chains. Thus, according to Johnston¹² T_{gp} for a random terpolymer is given by the following equation:

$$\frac{1}{T_{gp}} = \sum_{i=1}^3 \frac{F_{wi}P_{ii}}{T_{gpi}} + \frac{F_{w1}P_{12} + F_{w2}P_{21}}{T_{gp12}} + \frac{F_{w1}P_{13} + F_{w3}P_{31}}{T_{gp13}} + \frac{F_{w2}P_{23} + F_{w3}P_{32}}{T_{gp23}} \quad (41)$$

where F_{wi} and T_{gpi} denote the weight-average terpolymer composition and the glass-transition temperature of the i th homopolymer, respectively. P_{ij} is the probability that a live polymer chain ending in an i monomer unit will react with monomer j . Finally, T_{gpij} is the glass-transition temperature of a strictly alternating copolymer of monomers i and j .

Following the developments of Keramopoulos and Kiparissides,⁹ the translational diffusion coefficient of the polymer chains can be expressed as

$$D_p = \frac{D_{p0}}{M_w^2} \exp \left[-\gamma \frac{\omega_1 V_1^* / \xi_{1p} + \omega_2 V_2^* / \xi_{2p} + \omega_3 V_3^*}{\xi_{3p} + \omega_s V_s^* / \xi_{sp} + \omega_p V_p^*} \right] \quad (42)$$

where D_{p0} is a preexponential factor calculated at zero polymer concentration from the Stokes–Einstein diffusion equation:

$$D_p = k_B T / (6\pi\eta_{\text{mix}}R_H) \quad (43)$$

where k_B is the Boltzmann constant and η_{mix} is the solution viscosity of the three monomers and the solvent (if present). According to the one-constant method of Grunberg and Nissan,¹³ η_{mix} is given by

$$\ln \eta_{\text{mix}} = \sum_i x_i \ln \eta_i + \sum_{i \neq j} x_i x_j G_{ij} \quad (44)$$

where x_i and η_i are the molar fraction and viscosity of i component, respectively. G_{ij} is a binary interaction parameter for the monomer pair (i, j) . Its value can be calculated with the group contribution method.¹³ The polymer hydrodynamic radius, R_H , depends on the intrinsic viscosity of the terpolymer solution and on the M_w of the terpolymer.^{9,14}

To account for the segmental diffusion of the growing polymer chains, the translational diffusion coefficient,

D_p , is usually multiplied by a correction factor, F_{seg} .⁹

$$D_{pe} = F_{\text{seg}} D_p \quad (45)$$

where D_{pe} is the effective diffusion coefficient of the polymer chains. F_{seg} accounts for the probability that two live polymer chains will react when their active centers come into close proximity.^{9,15} In deriving the previous equations, we assumed that the mass fraction of the initiator was very small compared to the mass fractions of the monomers and terpolymer chains.

Diffusion-controlled initiation reaction

Following the developments described in our previous publication,⁹ one can show that the diffusion-controlled initiator efficiency can be expressed as

$$f^{-1} = f_0^{-1} + (k_{i10}[M_1] + k_{i20}[M_2] + k_{i30}[M_3])r_{12}^3 \div (3r_{I1}f_0D_I) = f_0^{-1}(1 + f_D^{-1}) \quad (46)$$

where r_{I1} and r_{I2} are the radii of the initiator reaction and the diffusion spheres, respectively. f_0 denotes the initiator efficiency at zero monomer conversion, and D_I is the diffusion coefficient of the primary radicals, as given by the following equation:⁹

$$D_I = D_{I0} \exp \left[-\gamma_I \frac{\omega_1 V_1^* \xi_{1p} / \xi_{1p} + \omega_2 V_2^* \xi_{2p} / \xi_{2p} + \omega_3 V_3^* \xi_{3p}}{\xi_{3p} + \omega_s V_s^* \xi_{sp} / \xi_{sp} + \omega_p V_p^* \xi_{1p}} \right] \quad (47)$$

From eqs. (46) and (47), one can easily conclude that the overall initiator efficiency, f , depends on the monomer concentrations $[M_1]$, $[M_2]$, and $[M_3]$ and on D_I , which in turn, depends on the free volume of the reaction mixture. Thus, at very low monomer conversions, the contribution of the diffusion-controlled term, f_D^{-1} , to the overall initiator efficiency will not be important and, thus, $f \approx f_0$. However, at high monomer conversions, the f_D^{-1} term in eq. (46) will be significant (e.g., $f_D^{-1} \gg 1$) and, thus, $f \approx f_D f_0$. In the latter case, the overall initiator efficiency will decrease with the extent of the terpolymerization.

Diffusion-controlled termination reaction

Following the original work of Achilias and Kiparissides¹⁶ the termination rate constants (k_{t11} , k_{t22} and k_{t33}) can be expressed as follows:

$$k_{tii} = k_{tii}^d + k_{tii}^{\text{res}} \quad (48)$$

TABLE III
Kinetic Rate Constants for the BuA/MMA/VAc
Terpolymerization

$k_{p11} = 1.08 \times 10^9 \exp(-4156/RT)$ (L/mol/min) ²¹
$k_{p22} = 2.95 \times 10^7 \exp(-4353/RT)$ (L/mol/min) ²²
$k_{p33} = 4.2 \times 10^9 \exp(-6300/RT)$ (L/mol/min) ²⁰
$r_{12} = 0.298, r_{21} = 1.789, r_{13} = 5.939$
$r_{31} = 0.0262, r_{23} = 24.025, r_{32} = 0.0261^3$
$k_{tc11} = 7.854 \times 10^8$ for $T = 70^\circ\text{C}$ (L/mol/min) ¹⁹
$k_{tc11} = 4.429 \times 10^8$ for $T = 50^\circ\text{C}$ (L/mol/min)
$k_{td22} = 5.88 \times 10^9 \exp(-701/RT)$ (L/mol/min) ²²
$k_{tc33} = 1.62 \times 10^{12} \exp(-6300/RT)$ (L/mol/min) ²⁰
$k_{td11} = 0, k_{tc22} = 0, k_{td33} = 0$
$\phi_{12} = \phi_{13} = \phi_{23} = 1.0$
$k_{fm11} = k_{fm12} = k_{fm13} = 1.74 \times 10^7 \exp(-7786/RT)$ (L/mol/min) ²³
$k_{fm22} = k_{fm21} = k_{fm23} = 2.796 \times 10^{11} \exp(-18233/RT)$ (L/mol/min) ¹⁶
$k_{fm33} = k_{fm31} = k_{fm32} = 1.0206 \times 10^6 \exp(-6300/RT)$ (L/mol/min) ²⁴
$k_{fp11} = 3.596 \times 10^3 \exp(-4156/RT)$ (L/mol/min) ³³
$k_{fp22} = 4.425 \times 10^3 \exp(-4353/RT)$ (L/mol/min) ³²
$k_{fp23} = 2.947 \times 10^3 \exp(-4353/RT)$ (L/mol/min) ³²
$k_{fp32} = 3.860 \times 10^7 \exp(-6300/RT)$ (L/mol/min) ³²
$k_{fp33} = 9.912 \times 10^5 \exp(-6300/RT)$ (L/mol/min) ²⁴
$k_d = 6.32 \times 10^{16} \exp(-30660/RT)$ (1/min) ¹⁶

where the subscript i refers to the terminal unit of live polymer chains. k_{tii}^d and k_{tii}^{res} denote the diffusion-controlled termination rate constant between two live polymer chains of the same type (e.g., having the same terminal unit) and the so-called residual termination rate constant, respectively.

Accordingly, k_{tii}^d can be expressed in terms of the intrinsic termination rate constant, k_{t0ii} , and a diffusion-controlled term:⁹

$$\frac{1}{k_{tii}^d} = \frac{1}{k_{t0ii}} + \frac{1}{4\pi r_{ti} D_{pe} N_A} \quad (49)$$

where r_{ti} is an effective termination radius for the live polymer chains.^{9,16}

To account for the mobility of the growing polymer chains caused by the monomer propagation reactions, a phenomenon known as residual termination, a residual termination rate constant, k_{tii}^{res} , is defined:^{9,16}

$$k_{tii}^{res} = A_i k_{p_{ii}} [M_i] \quad (50)$$

where A_i is a proportionality rate constant that can be estimated from the volume-swept-out model.^{9,17}

Finally, the various cross termination rate constants appearing in the terpolymerization kinetic model (e.g., $k_{t12} = k_{t21}, k_{t13} = k_{t31}, k_{t23} = k_{t32}$) are calculated with the following equation:

$$\phi_{ij} = k_{tij} / [2(k_{tii} k_{tjj})^{1/2}] \quad (51)$$

Diffusion-controlled propagation reaction

At very high conversions, the propagation reactions become diffusion-controlled as well. In this work, the propagation rate constants (k_{p11} , k_{p22} and k_{p33}) were

TABLE IV
Physical and Transport Properties for the BuA/MMA/VAc Terpolymerization

$d_{m1} = 0.9255 - 1.075 \times 10^{-3}(T - 273.15)$ (g/cm ³) ²⁵
$d_{m2} = 0.968 - 1.225 \times 10^{-3}(T - 293.15)$ (g/cm ³) ¹⁶
$d_{m3} = 0.9584 - 1.3276 \times 10^{-3}(T - 293.15)$ (g/cm ³) ²⁶
$d_{p1} = 1.085 - 6.05 \times 10^{-4}(T - 273.15)$ (g/cm ³)
$d_{p2} = 1.212 - 8.45 \times 10^{-4}(T - 273.15)$ (g/cm ³) ²⁷
$d_{p3} = 1.211 - 8.496 \times 10^{-4}(T - 273.15)$ (g/cm ³) ²⁶
$MW_1 = 128.17, MW_2 = 100.13, MW_3 = 86.09, M_{II} = 68.1, f_0 = 0.58$
$\delta_1 = \delta_2 = \delta_3 = 6.9 \text{ \AA};^{28} X_{c01} = 200, X_{c02} = 100, X_{c03} = 256^{29}$
$\epsilon_{110}/D_{10} = 10.08, \epsilon_{120}/D_{10} = 372.38, \epsilon_{130}/D_{10} = 54.24$ (s/cm ²) (Calcd.)
$\alpha_p = F_{n1}\alpha_{p1} + F_{n2}\alpha_{p2} + (1 - F_{n1} - F_{n2})\alpha_{p3}$
$\alpha_{p1} = 4.8 \times 10^{-4}, \alpha_{p2} = 3.0 \times 10^{-4}, \alpha_{p3} = 5.0 \times 10^{-4}$ (K ⁻¹) ²⁹
$\alpha_{m1} = 1.19 \times 10^{-3},^{19} \alpha_{m2} = 2.9 \times 10^{-4}, \alpha_{m3} = 5.1 \times 10^{-4}$ (K ⁻¹) ²⁹
$\alpha_{p0} = 0.025, \alpha_{m10} = 0.025, \alpha_{m20} = 0.011, \alpha_{m30} = 0.070^{29}$
$T_{gm1} = 185.15 \text{ K},^{19} T_{gm2} = 159.15 \text{ K},^{30} T_{gm3} = 109.0 \text{ K}^{29}$
$T_{gp1} = 218.0 \text{ K},^{19} T_{gp2} = 388.15 \text{ K},^{29} T_{gp3} = 305.15 \text{ K}^{29}$
$V_{m1}^* = 0.904, V_{m2}^* = 0.868, V_{m3}^* = 0.840$ (cm ³ /g) (Calcd.)
$V_{p1}^* = 0.842, V_{p2}^* = 0.788, V_{p3}^* = 0.748, V_I^* = 0.912$ (Calcd.)
$r_{e1} = 15.4, r_{e2} = 17.0, r_{e3} = 16.0 \text{ \AA}, r_e = F_{n1}r_{e1} + F_{n2}r_{e2} + (1 - F_{n1} - F_{n2})r_{e3}^{31}$
$\gamma_{m1} = \gamma_{m2} = 0.30, \gamma_{m3} = 0.60, \gamma_I = 0.95, \gamma_p = 0.65, a_{seg} = 0.20$
$\gamma_p = 0.40$ ([I] = 0.01, $T = 50^\circ\text{C}$), $\gamma_p = 0.60$ ([I] = 0.071, $T = 50^\circ\text{C}$), $\gamma_p = 0.95$ ($T = 70^\circ\text{C}$)
$D_{m10} = 6.4 \times 10^{-10}, D_{m20} = 4.96 \times 10^{-10},^{16} D_{m30} = 2.0 \times 10^{-8}$ (dm ² /min)
$\log \eta_1 = 610.73 \times \left(\frac{1}{T} - \frac{1}{287.20}\right)$ cP, ³² $\log \eta_2 = 453.25 \times \left(\frac{1}{T} - \frac{1}{254.92}\right)$ cP ¹⁶
$\log \eta_3 = 457.89 \times \left(\frac{1}{T} - \frac{1}{235.35}\right)$ cP, $G_{12} = 0.159, G_{13} = 0.288, G_{23} = 0.129$ (Calcd.)

T = temperature.

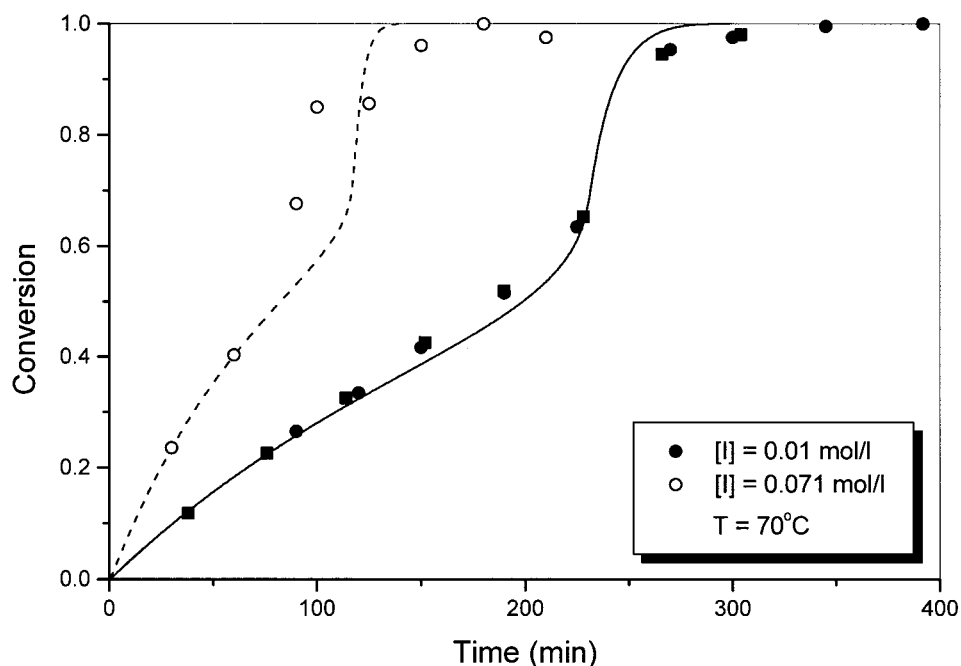


Figure 1 Predicted and experimental conversion–time histories for the BuA/MMA/VAc terpolymerization (polymerization temperature = 70°C, experimental data from ref. 3).

expressed as in the original article of Achilias and Kiparissides,¹⁶ considering the correction of Litvinenko and Kaminsky:¹⁸

$$\frac{1}{k_{pii}} = \frac{1}{k_{p0ii}} + \frac{1}{4\pi D_{mi} r_{mi} N_A} \quad (52)$$

The effective reaction radius, r_{mir} , is assumed to be equal to the termination reaction radius, r_{tir} , whereas the monomer diffusion coefficients are calculated from eqs. (34)–(36).

Finally, the various cross-propagation rate constants were estimated in terms of the respective reactivity

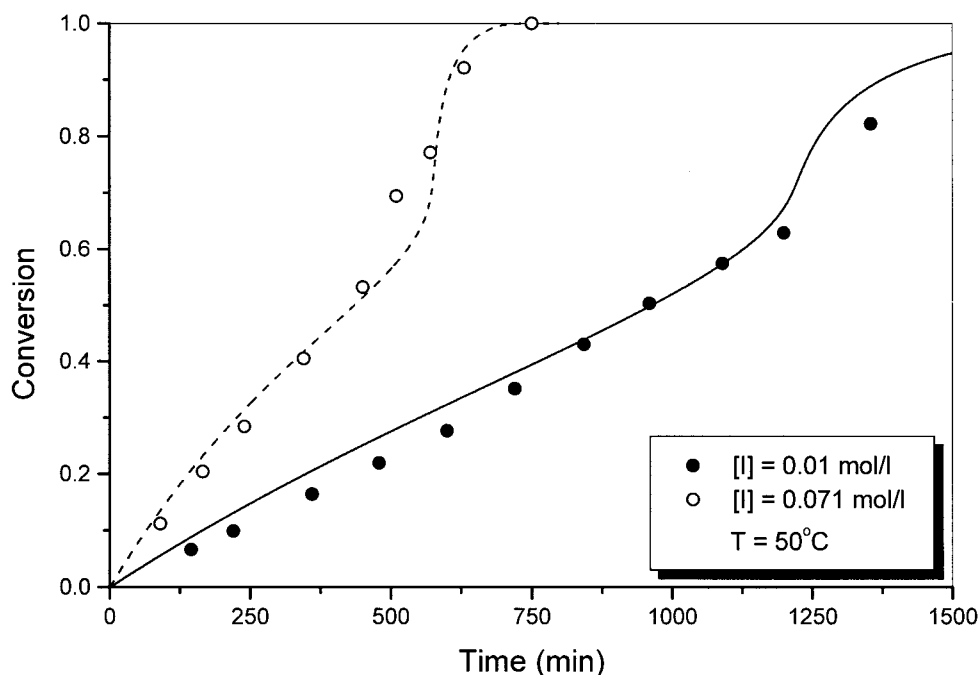


Figure 2 Predicted and experimental conversion–time histories for the BuA/MMA/VAc terpolymerization (polymerization temperature = 50°C, experimental data from ref. 3).

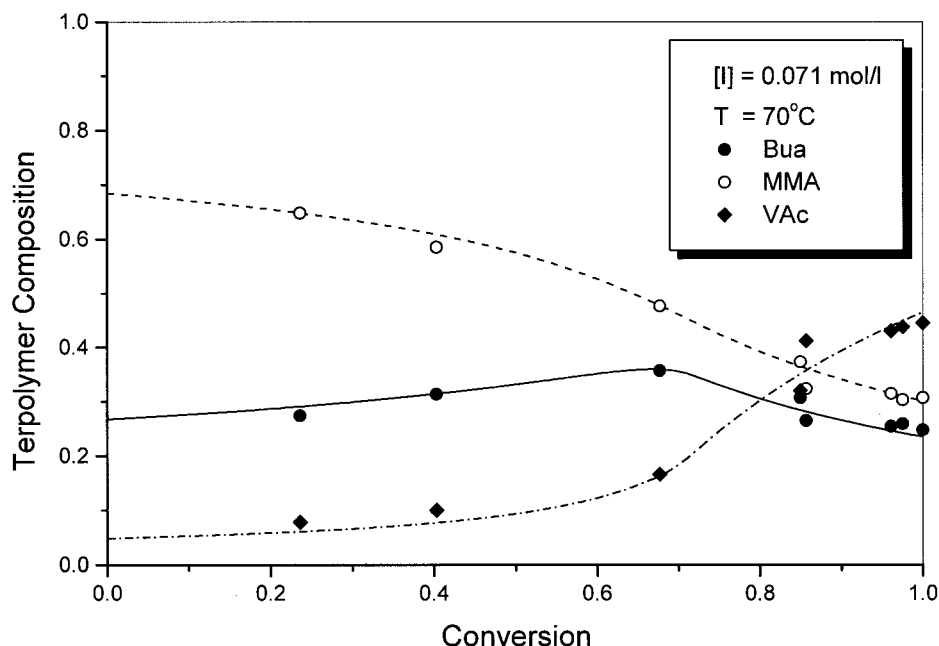


Figure 3 Cumulative copolymer composition of the three monomers with respect to the overall monomer conversion (polymerization temperature = 70°C, $[I_0] = 0.071M$ AIBN).

ratios (i.e., r_{12} , r_{21} , r_{13} , r_{31} , r_{23} , r_{32}) and the values of k_{p11} , k_{p22} , and k_{p33} :

$$r_{ij} = k_{pji}/k_{pjj} \quad (53)$$

RESULTS AND DISCUSSION

The bulk free-radical terpolymerization of BuA/MMA/VAc was assumed to proceed in a single phase at 70 and 50°C in the presence of 2,2'-azobisisobutyronitrile (AIBN) initiator. Model predictions were compared with the experimental data of Dube and Penlidis³ on monomer conversion, terpolymer composition, and average MWs for two initial initiator concentrations.

The self-termination of live polymer chains, ending in either a BuA or VAc monomer unit, was assumed to occur exclusively by combination,^{19,20} whereas the termination of live polymer chains, ending in a MMA monomer unit, was assumed to occur exclusively by disproportionation.⁹ Chain-transfer reactions to monomer and polymer molecules were also included in the kinetic mechanism. In Table III, the numerical values of all kinetic rate constants employed in the simulation of the terpolymerization system are reported. The values of all physical and transport properties employed for the calculation of the diffusion-controlled terms are presented in Table IV.

In Figures 1 and 2, conversion-time histories are shown for the two initial initiator concentrations and the two different temperatures. Continuous and

broken lines represent model predictions, whereas discrete points denote experimental conversion measurements. A good agreement exists between model predictions and experimental measurements. In Figures 3 and 4, the cumulative terpolymer composition is plotted with respect to the overall monomer conversion for the two different temperatures and an initial initiator concentration of 0.071 mol/L. An excellent agreement exists between experimental results and model predictions. In Figures 5–8, model predictions (continuous and broken lines) and experimental measurements (discrete points) on M_n and M_w are plotted for the two initial initiator concentrations of 0.01 and 0.071 mol/L and the two temperatures of 50 and 70°C. A fairly good agreement exists.

Because of the lack of an accurate value for the refractive index increment for this specific terpolymer system, the experimental measurements on MW averages should be considered as general trends rather than exact values. Moreover, Dube and Penlidis reported that during the experiments, there were clear indications of nonisothermal conditions, which resulted in higher conversions at the center of the ampule because of the higher temperature level.⁴ This is an additional reason to consider the experimental MW measurements only as general indications.

Figure 9 illustrates the variation of the termination rate constants k_{t11} , k_{t22} , and k_{t33} with respect to the overall monomer conversion for the two different temperatures. All three termination rate constants exhibited a significant decrease with conversion, character-

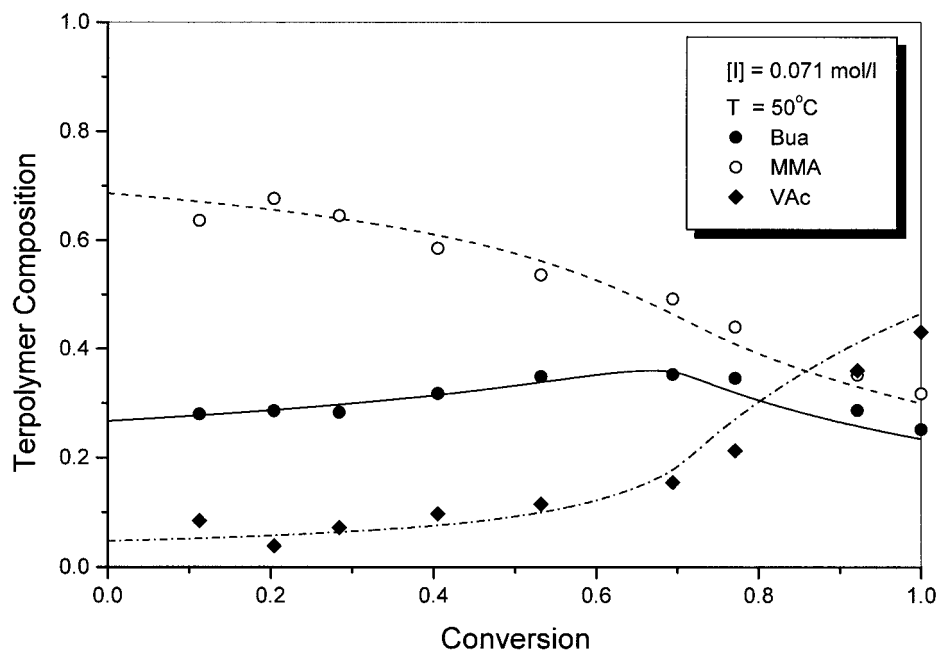


Figure 4 Cumulative copolymer composition of the three monomers with respect to the overall monomer conversion (polymerization temperature = 50°C , $[I_0] = 0.071\text{M}$ AIBN).

istic of a polymerization system in which termination reactions are diffusion-controlled. Finally, in Figure 10, the variation of the propagation rate constants k_{p11} , k_{p22} , and k_{p33} with respect to the overall monomer conversion is depicted. The propagation rate constants did not significantly vary with overall monomer conversion. These results are explained by the fact

only the VAc was present at significant concentrations at high conversions (e.g., $> 70\%$).

CONCLUSIONS

In this article, a comprehensive mathematical framework is presented for modeling diffusion-controlled free-rad-

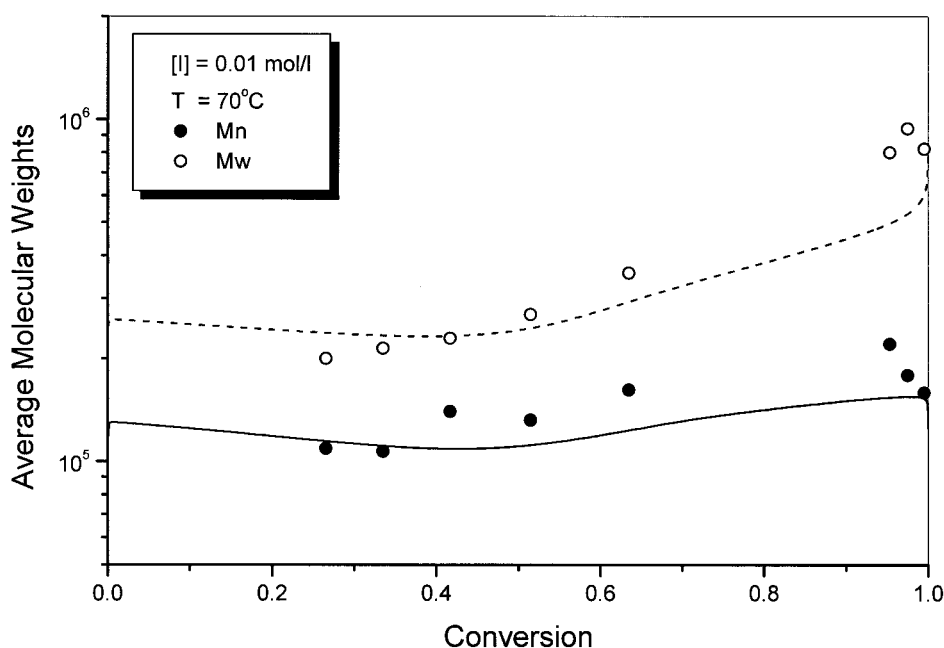


Figure 5 Predicted and experimental M_w and M_n with respect to the overall monomer conversion (polymerization temperature = 70°C , $[I_0] = 0.01\text{M}$ AIBN).

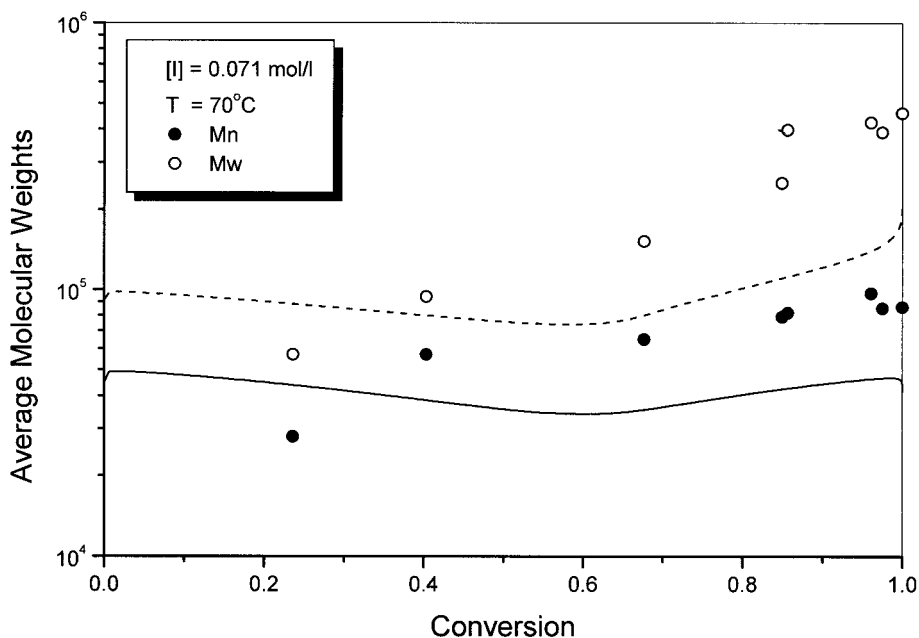


Figure 6 Predicted and experimental M_w and M_n with respect to the overall monomer conversion (polymerization temperature = 70°C, $[I_0] = 0.071M$ AIBN).

ical terpolymerization reactions. The variation of initiator efficiency and termination and propagation rate constants with conversion is theoretically described with the so-called parallel model. According to the latter model, the kinetic parameters of interest are expressed in terms of a reaction-limited and a diffusion-limited term. Trivariate distributions for live and dead polymer chains are employed to describe the molecular and compositional

developments in the terpolymerization reactor. The predictive capabilities of the proposed model are demonstrated via the simulation of the experimental results of Dube and Penlidis³ on the bulk terpolymerization of BuA/MMA/VAc. Model predictions were found to be in very good agreement with experimental measurements on monomer conversion, cumulative terpolymer composition, and M_n and M_w .

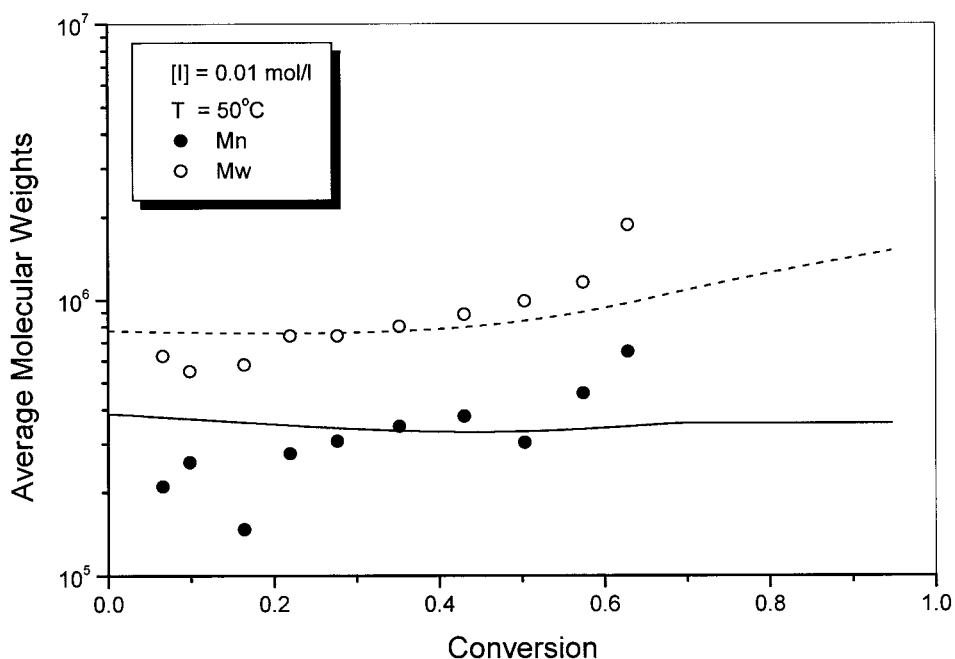


Figure 7 Predicted and experimental M_w and M_n with respect to the overall monomer conversion (polymerization temperature = 50°C, $[I_0] = 0.01M$ AIBN).

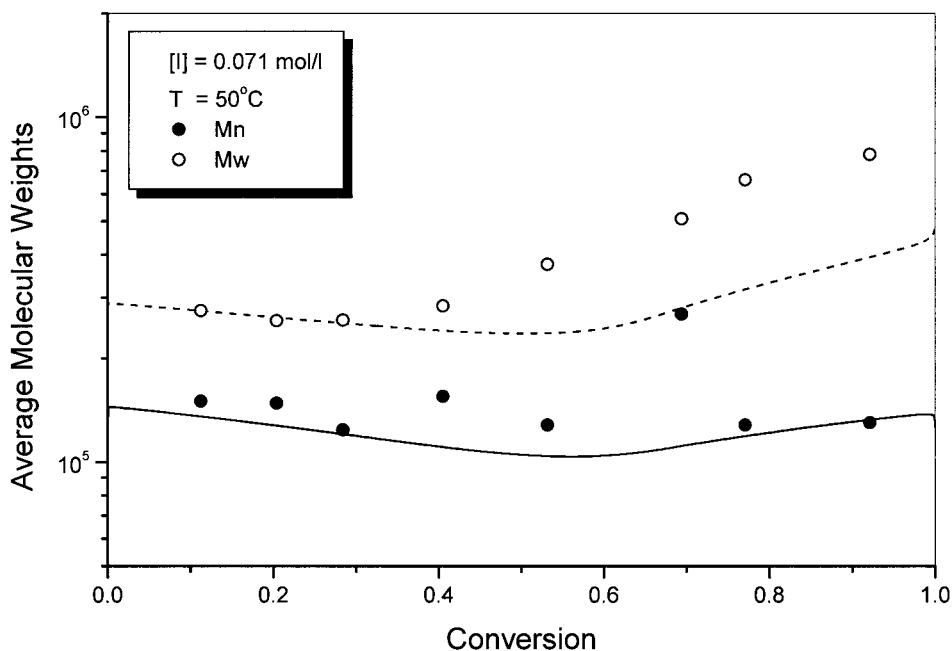


Figure 8 Predicted and experimental M_w and M_n with respect to the overall monomer conversion (polymerization temperature = 50°C, $[I_0] = 0.071M$ AIBN).

NOMENCLATURE

A proportionality rate constant (cm^3/mol)
 AIBN 2,2'-azobisisobutyronitrile
 d density (g/cm^3)
 D diffusion coefficient (cm^2/s)
 $D_{n,m,z}$ concentration of dead polymer with $n + m + z$ monomer units

f initiator efficiency

F_n cumulative number average terpolymer composition
 F_{seg} factor representing the probability of two radicals reacting when their active centers come into close proximity

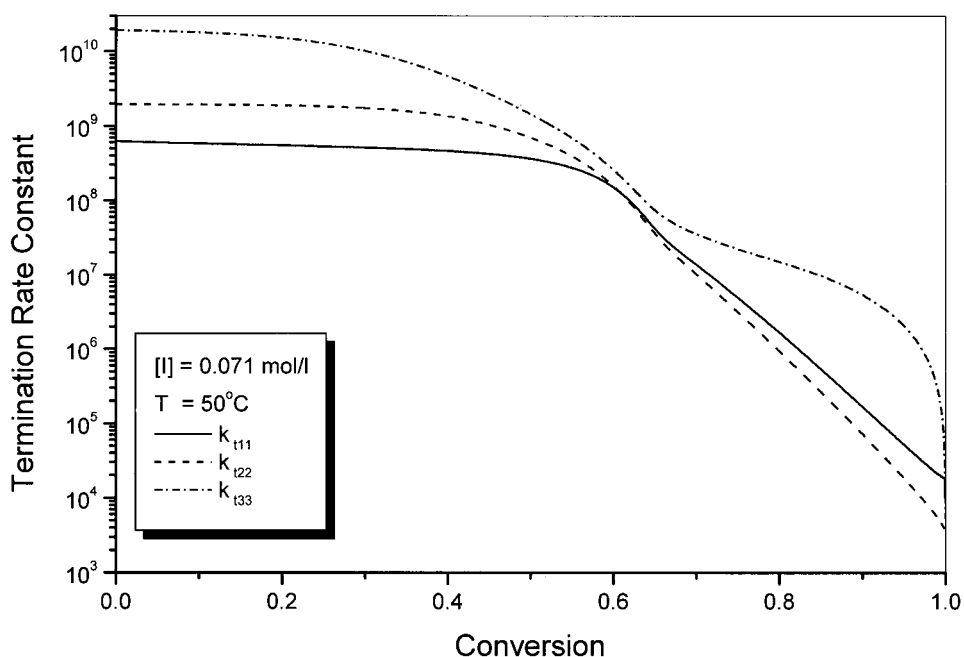


Figure 9 Variation of the termination rate constants with respect to the overall monomer conversion (polymerization temperature = 50°C, $[I_0] = 0.071M$ AIBN).

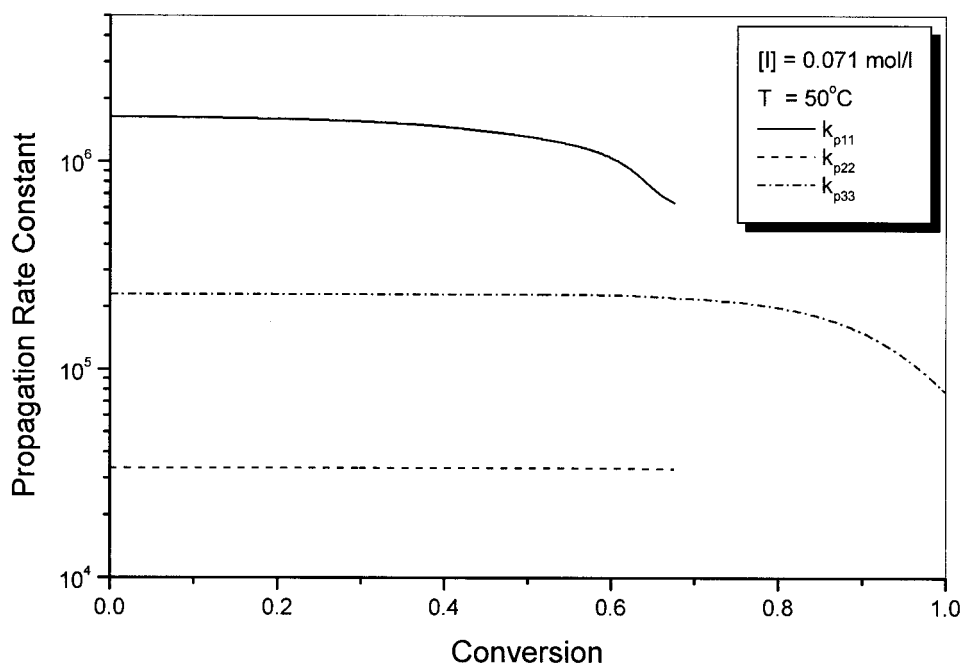


Figure 10 Variation of the propagation rate constants with respect to the overall monomer conversion (polymerization temperature = 50°C, $[I_0] = 0.071M$ AIBN).

F_w	cumulative weight-average terpolymer composition	R	universal gas constant (1.9872 cal/mol/K)
G_{ij}	binary interaction parameter for the calculation of the viscosity of a mixture	$R\cdot$	primary radical
I	initiator concentration (mol/L)	r_B	distance of the chain end from the sphere center (Å)
j_c	entanglement spacing	r_e	segment length (Å)
k_B	Boltzmann constant (1.3806×10^{-23} J/K)	R_H	hydrodynamic radius (cm)
k_d	initiator decomposition rate constant (L/mol/min)	r_{I1}	radius of the initiator reaction sphere (cm)
k_{dp}	terminal double-bond reaction rate constant (L/mol/min)	r_{I2}	radius of the initiator diffusion sphere (cm)
k_{fm}	chain transfer to monomer/chain-transfer agent rate constant (L/mol/min)	r_{ij}	reactivity ratio
k_{fp}	chain transfer to polymer rate constant (L/mol/min)	r_M	production rate of monomer (mol/cm ³ /min)
k_i	initiation reaction rate constant (L/mol/min)	$R_{n,m,z}$	concentration of a live radical with $n + m + z$ monomer units
k_p	propagation rate constant (L/mol/min)	r_t, r_m	effective reaction radii (cm)
k_t	termination reaction overall rate constant (L/mol/min)	S	solvent concentration (mol/cm ³)
k_{tc}	termination by combination rate constant (L/mol/min)	T	temperature (K)
k_{td}	termination by disproportionation rate constant (L/mol/min)	T_g	glass-transition temperature (K)
k_t^d	diffusion-controlled termination rate constant (L/mol/min)	V	reactor volume
k_t^{res}	residual termination rate constant (L/mol/min)	V^*	critical hole free volume (cm ³ /g)
M	monomer concentration (mol/cm ³)	V_{FH}	average free volume of the mixture (cm ³ /g)
M_n	number-average molecular weight	V_{pj}	molar volume of the copolymer jumping unit (cm ³ /g)
M_w	weight-average molecular weight	X	conversion
MW	molecular weight	X_{c0}	critical degree of polymerization for entanglements
N_A	Avogadro's number (6.023×10^{23} molecules/mol)	x_i	molar fraction of monomer i

Greek letters

α	difference in thermal expansion coefficients above and below T_g (1/K)
α_{i0}	fractional free volume at the glass-transition temperature of component i

- α_{seg} parameter for the calculation of segmental diffusion
- γ overlap factor
- δ average root-mean-square end-to-end distance per square root of the number of the monomer units in a chain (\AA)
- ϵ_t proportionality constant ($= k_{t0}/k_{p0}$)
- η viscosity (cP)
- $[\eta]$ intrinsic viscosity of the polymer (cm^3/g)
- λ moments of the live radical distribution
- μ moments of the dead polymer distribution
- ξ ratio of the critical molar volume of the jumping unit to the critical molar volume of the polymer jumping unit
- τ parameter for the calculation of the termination radius
- ϕ volume fraction
- ϕ_t crosstermination rate parameter
- ω weight fraction

Subscripts

- I* initiator
- m* monomer
- p* polymer
- s* solvent
- t* termination
- 0 initial conditions
- 1 BuA
- 2 MMA
- 3 VAc

Superscripts

- * critical
- 1 terminal monomer unit BuA in a live polymer chain
- 2 terminal monomer unit MMA in a live polymer chain
- 3 terminal monomer unit VAc in a live polymer chain

References

- Schoonbrood, H. A. S.; Van den Reijen, B.; de Kock, J. B. L.; Manders, B. G.; Van Herk, A. M.; German, A. L. *Macromol Rapid Commun* 1995, 16, 119.
- Buback, M.; Kowollik, C. *Macromol Chem Phys* 1999, 200, 1764.
- Dube, M. A.; Penlidis, A. *Macromol Chem Phys* 1995, 196, 1101.
- Gao, J.; Penlidis, A. *Macromol Chem Phys* 2000, 201, 1176.
- Neogi, P. *Diffusion in Polymers*; Marcel Dekker: New York, 1996; p 143.
- Vrentas, J. S.; Duda, J. L. *J Polym Sci Polym Phys Ed* 1977, 15, 403.
- Vrentas, J. S.; Duda, J. L. *J Polym Sci Polym Phys Ed* 1977, 15, 417.
- Achilias, D. S.; Kiparissides, C. *J Macromol Sci Rev Macromol Chem Phys* 1992, 32, 183.
- Keramopoulos, A.; Kiparissides, C. *Macromolecules* 2002, 35, 4155.
- Haward, R. N. *J Macromol Sci Rev Macromol Chem* 1970, 4, 191.
- Hong, S. U. *J Appl Polym Sci* 1996, 61, 833.
- Johnston, N. W. *J Macromol Sci Rev Macromol Chem* 1976, 14, 215.
- Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases & Liquids*, 4th ed.; McGraw-Hill: New York, 1988; p 474.
- Crowley, T. J.; Choi, K. Y. *J Comp Chem Eng* 1999, 23, 1153.
- North, A. M. *Macromol Chem* 1965, 83, 15.
- Achilias, D. S.; Kiparissides, C. *Macromolecules* 1992, 25, 3739.
- Buback, M.; Huckestein, B.; Russel, G. T. *Makromol Chem Phys* 1994, 195, 539.
- Litvinenko, G. I.; Kaminsky, V. A. *Prog React Kinet* 1994, 19, 139.
- Dube, M. A.; Rilling, K.; Penlidis, A. *J Appl Polym Sci* 1991, 43, 2137.
- Konstadinidis, K.; Achilias, D. S.; Kiparissides, C. *Polymer* 1992, 33, 5019.
- Van Herk, A. M. *Macromol Theory Simul* 2000, 9, 433.
- Achilias, D. S.; Kiparissides, C. *J Appl Polym Sci* 1988, 35, 1303.
- Maeder, S.; Gilbert, R. G. *Macromolecules* 1998, 31, 4410.
- Nagasubramanian, K.; Graessley, W. W. *Chem Eng Sci* 1970, 25, 1549.
- Lyons, R. A.; Hutovic, J.; Piton, M. C.; Christie, D. I.; Clay, P. A.; Manders, B. G.; Kable, S. H.; Gilbert, R. G. *Macromolecules* 1996, 29, 1918.
- Schmidt, A. D. Ph.D. Thesis, University of Wisconsin-Madison, 1981.
- Tefera, N.; Weickert, G.; Westertep, K. R. *J Appl Polym Sci* 1997, 63, 1663.
- Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980; p 331.
- Soh, S. K.; Sundberg, D. C. *J Polym Sci Polym Chem Ed* 1982, 20, 1345.
- Jones, K. M.; Bhattacharya, D.; Brash, J. L.; Hamielec, A. E. *Polymer* 1986, 27, 602.
- Aharoni, S. M. *Macromolecules* 1986, 19, 426.
- Polymer Handbook*, 3rd ed.; Brandrup, J.; Immergut, E., Eds.; Wiley: New York, 1989.
- Plessis, C.; Arzamendi, G.; Leiza, J. R.; Alberdi, J. M.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. *J Polym Sci Part A: Polym Chem* 2001, 39, 1106.