Bulk Polymerization of Styrene in the Presence of Polybutadiene. The Use of Bifunctional Initiators

D. A. ESTENOZ,[1] G. P. LEAL,[2] Y. R. LOPEZ,[2] H. M. OLIVA,[2] and G. R. MEIRA[1,*]

[1]INTEC (CONICET and Universidad Nacional del Litoral), Santa Fe (3000), Argentina, and
[2]Facultad de Ingeniería, Universidad del Zulia, Maracaibo, Venezuela

SYNOPSIS

This work experimentally and theoretically investigates the use of bifunctional initiators in the synthesis of high-impact polystyrene (HIPS). The experimental design involved a series of nonisothermal bulk polymerizations of styrene (St) in the presence of polybutadiene (PB). The performance of three commercial initiators [2,5-dimethyl-2,5 bis(2-ethylhexanoyl peroxy) hexane or L-256; 2,5 dimethyl-2,5 bis(benzoyl peroxy) hexane or L-118; and ethyl 3,3 di(t-butyl peroxide) butirate or L-233] were compared to the performance of a standard monofunctional initiator (terbutylperoctoate or TPBO), and to the blank case (i.e., without initiator). From samples taken along the prepolymerization period, the phase inversion point and the 30% conversion point were estimated. For the final product, the free polystyrene (PS) molecular weights and the St grafting efficiency were measured. A mathematical model was developed that predicts the evolution of the MWDs for the free PS, the residual PB, and the graft copolymer, together with the chemical composition distribution for the total graft copolymer. Compared to the monofunctional case, the L-256 initiator induces phase inversion and rubber grafting at low conversions. Also, it shortens the prepolymerization times by around 38%, without affecting the molecular characteristics of the final product. L-118 also shortens prepolymerization time with respect to TBPO; but is not as effective as L-256 or TBPO in promoting rubber grafting. At the polymerization end, the final molecular characteristics are practically independent of the initiator type because most of the polymerization is induced by monomer initiation. Due to its slow decomposition rate, the L-233 initiator is less effective that TBPO for reducing prepolymerization times and for promoting phase inversion. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

High impact polystyrene (HIPS) is produced by polymerizing styrene (St) in the presence of a dissolved polybutadiene (PB) rubber. Even though St is capable of thermally initiating, monofunctional initiators of short mean lifes are normally added at the start of the polymerization to induce rubber grafting. The generation of graft copolymer at low conversion is important to favor phase inversion. This transition occurs at around 20% conversion, and it consists of a change from a disperse PS phase into a disperse rubber-rich phase.

The use of bifunctional initiators has been widely investigated in relation to St homopolymerization. Choi and Lei[1] and Kim and Choi[2] developed detailed kinetic models for the bulk St homopolymerization with symmetrical and asymmetrical diperoxyester bifunctional initiators. They showed that operating at high temperatures, it is possible to obtain high reaction rates and molecular weights, with relatively narrow molecular weight distributions (MWDs). Villalobos et al.[3] theoretically and experimentally investigated the polymerization of St with the following bifunctional initiators: 2,5 dimethyl-2,5 bis (2 ethylhexanol peroxy) hexane, Lupersol-256, or L-256; 1,1-di(t-butyl-peroxy) cyclohexane, or Lupersol-331-80B; and 1,4-bis (t-butyl peroxycarbo) cyclohexane, or D-162. Compared to the standard monofunctional case, bifunctional initiators reduced polymerization times as much as 75%, without sub-

Table I The Adopted Kinetic Mechanism

Global Kinetics	Detailed Kinetics
$(i, j = 0, 1, 2, \ldots), (n, m = 1, 2, 3, \ldots)$	$(i, j, s, s_1 = 0, 1, 2, \ldots), (b, b_1, n, m = 1, 2, 3, \ldots)$

Initiation

$3S \xrightarrow{k_{i0}} 2S_1^\bullet$	$3S \xrightarrow{k_{i0}} 2S_1^\bullet$
$I^{(2)} \xrightarrow{f_1 k_{d1}} I^{\bullet(0)} + \tilde{I}^{\bullet(1)}$	$I^{(2)} \xrightarrow{f_1 k_{d1}} I^{\bullet(0)} + \tilde{I}^{\bullet(1)}$
$I^{\bullet(0)} + S \xrightarrow{k_{i1}} S_1^{\bullet(0)}$	$I^{\bullet(0)} + S \xrightarrow{k_{i1}} S_1^{\bullet(0)}$
$\tilde{I}^{\bullet(0)} + S \xrightarrow{\tilde{k}_{i1}} S_1^{\bullet(0)}$	$\tilde{I}^{\bullet(0)} + S \xrightarrow{\tilde{k}_{i1}} S_1^{\bullet(0)}$
$\tilde{I}^{\bullet(1)} + S \xrightarrow{\tilde{k}_{i1}} S_1^{\bullet(1)}$	$\tilde{I}^{\bullet(1)} + S \xrightarrow{\tilde{k}_{i1}} S_1^{\bullet(1)}$
$\tilde{S}_n^{\bullet(0)} + S \xrightarrow{\tilde{k}_{i1}} S_{n+1}^{\bullet(0)}$	$\tilde{S}_n^{\bullet(0)} + S \xrightarrow{\tilde{k}_{i1}} S_{n+1}^{\bullet(0)}$
$\tilde{S}_n^{\bullet(1)} + S \xrightarrow{\tilde{k}_{i1}} S_{n+1}^{\bullet(1)}$	$\tilde{S}_n^{\bullet(1)} + S \xrightarrow{\tilde{k}_{i1}} S_{n+1}^{\bullet(1)}$
$I^{\bullet(0)} + P^{(i)} \xrightarrow{k_{i2}} P_0^{\bullet(i)} + IH^{(0)}$	$I^{\bullet(0)} + P^{(i)}(s, b) \xrightarrow{k_{i2}} P_0^{\bullet(i)}(s, b) + IH^{(0)}$
$\tilde{I}^{\bullet(0)} + P^{(i)} \xrightarrow{\tilde{k}_{i2}} P_0^{\bullet(i)} + H\tilde{I}^{(0)}$	$\tilde{I}^{\bullet(0)} + P^{(i)}(s, b) \xrightarrow{\tilde{k}_{i2}} P_0^{\bullet(i)}(s, b) + H\tilde{I}^{(0)}$
$\tilde{I}^{\bullet(1)} + P^{(i)} \xrightarrow{\tilde{k}_{i2}} P_0^{\bullet(i)} + H\tilde{I}^{(1)}$	$\tilde{I}^{\bullet(1)} + P^{(i)}(s, b) \xrightarrow{\tilde{k}_{i2}} P_0^{\bullet(i)}(s, b) + H\tilde{I}^{(1)}$
$S_n^{(1)} \xrightarrow{f_2 k_{d2}} \tilde{S}_n^{\bullet(0)} + I^{\bullet(0)}$	$S_n^{(1)} \xrightarrow{f_2 k_{d2}} \tilde{S}_n^{\bullet(0)} + I^{\bullet(0)}$
$S_n^{(2)} \xrightarrow{f_2 k_{d2}} \tilde{S}_n^{\bullet(1)} + I^{\bullet(0)}$	$S_n^{(2)} \xrightarrow{f_2 k_{d2}} \tilde{S}_n^{\bullet(1)} + I^{\bullet(0)}$
$H\tilde{I}^{(1)} \xrightarrow{f_2 k_{d2}} I^{\bullet(0)} + \tilde{I}^{\bullet(0)}$	$H\tilde{I}^{(1)} \xrightarrow{f_2 k_{d2}} I^{\bullet(0)} + \tilde{I}^{\bullet(0)}$
$P^{(i)} \xrightarrow{f_2 k_{d2}} \tilde{P}_n^{\bullet(i-1)} + I^{\bullet(0)}$	$P^{(i)}(s, b) \xrightarrow{f_2 k_{d2}} \tilde{P}_n^{\bullet(i-1)}(s - n, b) + I^{\bullet(0)}$
$P_0^{\bullet(i)} + S \xrightarrow{k_{i3}} P_1^{\bullet(i)}$	$P_0^{\bullet(i)}(s, b) + S \xrightarrow{k_{i3}} P_1^{\bullet(i)}(s, b)$
$\tilde{P}_n^{\bullet(i)} + S \xrightarrow{k_{i1}} P_{n+1}^{\bullet(i)}$	$\tilde{P}_n^{\bullet(i)}(s, b) + S \xrightarrow{k_{i1}} P_{n+1}^{\bullet(i)}(s, b)$

Propagation

$S_n^{\bullet(0)} + S \xrightarrow{k_p} S_{n+1}^{\bullet(0)}$	$S_n^{\bullet(0)} + S \xrightarrow{k_p} S_{n+1}^{\bullet(0)}$
$S_n^{\bullet(1)} + S \xrightarrow{k_p} S_{n+1}^{\bullet(1)}$	$S_n^{\bullet(1)} + S \xrightarrow{k_p} S_{n+1}^{\bullet(1)}$
$P_n^{\bullet(i)} + S \xrightarrow{k_p} P_{n+1}^{\bullet(i)}$	$P_n^{\bullet(1)}(s, b) + S \xrightarrow{k_p} P_{n+1}^{\bullet(i)}(s, b)$

Transfer

$S_n^{\bullet(0)} + S \xrightarrow{k_{fM}} S_n^{(0)} + S_1^{\bullet(0)}$	$S_n^{\bullet(0)} + S \xrightarrow{k_{fM}} S_n^{(0)} + S_1^{\bullet(0)}$
$S_n^{\bullet(1)} + S \xrightarrow{k_{fM}} S_n^{(1)} + S_1^{\bullet(0)}$	$S_n^{\bullet(1)} + S \xrightarrow{k_{fM}} S_n^{(1)} + S_1^{\bullet(0)}$
$P_0^{\bullet(i)} + S \xrightarrow{k_{fM}'} P^{(i)} + S_1^{\bullet(0)}$	$P_0^{\bullet(i)}(s, b) + S \xrightarrow{k_{fM}'} P^{(i)}(s, b) + S_1^{\bullet(0)}$
$P_n^{\bullet(i)} + S \xrightarrow{k_{fM}} P^{(i)} + S_1^{\bullet(0)}$	$P_n^{\bullet(i)}(s - n, b) + S \xrightarrow{k_{fM}} P^{(i)}(s, b) + S_1^{\bullet(0)}$
$S_n^{\bullet(0)} + P^{(i)} \xrightarrow{k_{fG}} S_n^{(0)} + P_0^{\bullet(i)}$	$S_n^{\bullet(0)} + P^{(i)}(s, b) \xrightarrow{k_{fG}} S_n^{(0)} + P_0^{\bullet(i)}(s, b)$
$S_n^{\bullet(1)} + P^{(i)} \xrightarrow{k_{fG}} S_n^{(1)} + P_0^{\bullet(i)}$	$S_n^{\bullet(1)} + P^{(i)}(s, b) \xrightarrow{k_{fG}} S_n^{(1)} + P_0^{\bullet(i)}(s, b)$
$P_n^{\bullet(i)} + P^{(j)} \xrightarrow{k_{fG}} P^{(i)} + P_0^{\bullet(j)}$	$P_n^{\bullet(i)}(s - n, b) + P^{(j)}(s_1, b_1) \xrightarrow{k_{fG}} P^{(i)}(s, b) + P_0^{\bullet(j)}(s_1, b_1)$

(continued)

Table I *Continued*

Global Kinetics	Detailed Kinetics
$(i, j = 0, 1, 2, \ldots)$, $(n, m = 1, 2, 3, \ldots)$	$(i, j, s, s_1 = 0, 1, 2, \ldots)$, $(b, b_1, n, m = 1, 2, 3, \ldots)$

Termination

Global Kinetics	Detailed Kinetics
$S_n^{\bullet(0)} + S_m^{\bullet(0)} \xrightarrow{k_{t_c}} S_{n+m}^{(0)}$	$S_n^{\bullet(0)} + S_m^{\bullet(0)} \xrightarrow{k_{t_c}} S_{n+m}^{(0)}$
$S_n^{\bullet(0)} + S_m^{\bullet(1)} \xrightarrow{k_{t_c}} S_{n+m}^{(1)}$	$S_n^{\bullet(0)} + S_m^{\bullet(1)} \xrightarrow{k_{t_c}} S_{n+m}^{(1)}$
$S_n^{\bullet(1)} + S_m^{\bullet(1)} \xrightarrow{k_{t_c}} S_{n+m}^{(2)}$	$S_n^{\bullet(1)} + S_m^{\bullet(1)} \xrightarrow{k_{t_c}} S_{n+m}^{(2)}$
$P_m^{\bullet(i)} + S_n^{\bullet(0)} \xrightarrow{k_{t_c}} P^{(i)}$	$P_{m-n}^{\bullet(i)}(s - m, b) + S_n^{\bullet(0)} \xrightarrow{k_{t_c}} P^{(i)}(s, b)$
$P_m^{\bullet(i)} + S_n^{\bullet(1)} \xrightarrow{k_{t_c}} P^{(i+1)}$	$P_{m-n}^{\bullet(i)}(s - m, b) + S_n^{\bullet(1)} \xrightarrow{k_{t_c}} P^{(i+1)}(s, b)$
$P_m^{\bullet(i)} + P_n^{\bullet(j)} \xrightarrow{k_{t_c}} P^{(i+j)}$	$P_{m-n}^{\bullet(i)}(s - s_1 - m, b - b_1) + P_n^{\bullet(j)}(s_1, b_1) \xrightarrow{k_{t_c}} P^{(i+j)}(s, b)$
$P_0^{\bullet(i)} + P_n^{\bullet(j)} \xrightarrow{k''_{t_c}} P^{(i+j)}$	$P_0^{\bullet(i)}(s - s_1 - n, b - b_1) + P_n^{\bullet(j)}(s_1, b_1) \xrightarrow{k''_{t_c}} P^{(i+j)}(s, b)$
$P_0^{\bullet(i)} + S_n^{\bullet(0)} \xrightarrow{k''_{t_c}} P^{(i)}$	$P_0^{\bullet(i)}(s - n, b) + S_n^{\bullet(0)} \xrightarrow{k''_{t_c}} P^{(i)}(s, b)$
$P_0^{\bullet(i)} + S_n^{\bullet(1)} \xrightarrow{k''_{t_c}} P^{(i+1)}$	$P_0^{\bullet(i)}(s - n, b) + S_n^{\bullet(1)} \xrightarrow{k''_{t_c}} P^{(i+1)}(s, b)$
$P_0^{\bullet(i)} + P_0^{\bullet(j)} \xrightarrow{k'_{t_c}} P^{(i+j)}$	$P_0^{\bullet(i)}(s - s_1, b - b_1) + P_0^{\bullet(j)}(s_1, b_1) \xrightarrow{k'_{t_c}} P^{(i+j)}(s, b)$

stantial changes in the final product quality. Yoon and Choi[4] and Choi et al.[5] investigated the St homopolymerization with L-256. A mathematical model involving initiation, propagation, transfer, and termination was developed that appropriately reproduced the experimental results. Kim et al.[6] experimentally investigated the high temperature St polymerization with the asymmetrical initiator 4-[(*tert*-butylperoxy)carbonyl]-3-hexyl-6-[7-((*tert*-butylperoxy)carbonyl)heptyl] cyclohexene, showing that it was possible to simultaneously obtaining high reaction rates and high molecular weights. Similar conclusions were observed when a bulk St polymerization was carried out in a continuous stirred tank reactor.[7,8] Yoon and Choi[9] and González et al.[10] studied the bulk polymerization of St with mixtures of mono- and bifunctional initiators. Compared to the use of standard monofunctional initiators, initiator mixtures allowed to reduce polymerization time without affecting the final product quality.

This work is the first attempt to investigate the convenience of employing bifunctional initiators in the bulk HIPS process. In our previous publication,[11] the same process was investigated for the blank case (i.e., without chemical initiation), and when using a standard monofunctional initiator (*tertbutyl* peroctoate or TBPO). The previous experimental results[11] are here reproduced for comparison reasons. The mathematical model of Estenoz et al.[11] is extended to the special case of bifunctional initiation.

The total copolymer characteristics are here estimated. (In Estenoz et al.,[11] the bivariate chain length distributions of the different generated topologies— characterized by the number of PS and PB chains per molecule—were also calculated.)

MATHEMATICAL MODEL

Kinetic Mechanism

The proposed kinetics involves initiation via symmetrical bifunctional initiators, thermal initiation, propagation, transfer to the monomer, transfer to the rubber, and combination termination. Consider the global kinetic mechanism presented in the left column of Table I. The following nomenclature is adopted:

$I^{(2)}$: $R_1 - O - O - R_2 - O - O - R_1$. Bifunctional initiator.

$I^{\bullet(0)}$: Primary radical of the type $R_1 - O^{\bullet}$, without unreacted peroxide groups.

$\tilde{I}^{\bullet(0)}$: Primary radical of the type $HO - R_2 - O^{\bullet}$, without unreacted peroxide groups.

$\tilde{I}^{\bullet(1)}$: Primary radical of the type $^{\bullet}O - R_2 - O - O - R_1$, with one unreacted peroxide group.

$IH^{(0)}$: $R_1 - OH$. Inert molecule, generated by attack to the polymer.

$H\tilde{I}^{(1)}$: $HO - R_2 - O - O - R_1$. Secondary mono-

functional initiator, generated by attack to the polymer.

$H\tilde{I}^{(0)}$: $HO - R_2 - OH$. Inert molecule, generated by attack to the polymer.

$S_s^{(i)}$: Linear homopolymer of chain length s, with $i = 0$, 1, or 2 unreacted peroxide groups at the chain ends.

$\tilde{S}_s^{\bullet(i)}$: Primary homoradical generated by decomposition of $S_s^{(i+1)}$, with $i = 0$ or 1 unreacted peroxide groups.

$S_s^{\bullet(i)}$: Non-primary PS homoradical of chain length s, with $i = 0$ or 1 unreacted peroxide groups.

$P^{(i)}$: Copolymer with $i = 0, 1, 2, 3, \cdots$ unreacted peroxide groups at the grafted branch ends.

$P_0^{\bullet(i)}$: Primary radical produced by attack to a butadiene repetitive unit (B) present either in the residual PB or in the accumulated $P^{(i)}$.

$\tilde{P}_n^{\bullet(i)}$: Primary copolymer radical, generated by decomposition of $P^{(i+1)}$.

$P_m^{\bullet(i)}$: Copolymer radical with m repetitive units of St in the active branch, generated by propagation of $P_0^{\bullet(i)}$ or $\tilde{P}_n^{\bullet(i)}(n < m)$.

The following has been assumed: (a) intramolecular termination is neglected due to the extremely low probability that two free radicals may simultaneously occur in the same chemical species; (b) all peroxide groups present in the bifunctional initiator exhibit the same thermal stability; (c) the thermal stability of unreacted peroxide groups incorporated into the accumulated homo- and copolymer is unaffected by the polymer characteristics; (d) all different types of $S_1^{\bullet(i)}$ radicals react like a generic $S_s^{\bullet(i)}$; and (e) propagation and transfer to the rubber are unaffected by chain length or conversion.

Note the following: (a) when two homoradicals terminate, the PS molecule may contain 0, 1, or 2 unreacted peroxide groups; (b) unreacted peroxide groups are introduced into the copolymer by termination between a polymer radical and a homoradical containing one unreacted peroxide group at its chain end; (c) a PS branch may be linked onto a single PB chain by one end (T grafting), or onto two different PB chains by both ends (H grafting); (d) T-grafts are produced by transfer of nonprimary copolymer radicals, or by combination termination between a PS homoradical and a (primary or nonprimary) rubber radical; (e) H-grafts are only created by combination termination between copolymer radicals; and (f) while T grafting does not alter the total number of copolymer plus residual PB mole-

cules, H grafting (a special kind of crosslinking), reduces such number.

Consider now the detailed kinetic mechanism presented in the right column of Table I. Copolymer species are distinguished by the number of repetitive St units, the number of repetitive B units, and the number of unreacted peroxide groups. The following nomenclature is employed:

$P^{(i)}(s, b)$: $P^{(i)}$ copolymer or unreacted PB molecule with s repetitive units of St and b repetitive units of B. In the case of PB, it is $i = s = 0$.

$P_0^{\bullet(i)}(s, b)$: Primary radical generated by attack to a B unit of $P^{(i)}(s, b)$.

$\tilde{P}_n^{\bullet(i)}(s, b)$: Primary radical generated by decomposition of a peroxide group located at the end of a grafted branch (of chain length n) present in $P^{(i+1)}(s + n, b)$.

$P_m^{\bullet(i)}(s, b)$: Nonprimary copolymer radical with m repetitive units of St in the active branch, generated from $P_0^{\bullet(i)}(s, b)$ or $\tilde{P}_n^{\bullet(i)}(s, b)(m > n)$.

From the detailed kinetics, and after summation over all possible ss and bs, the global mechanism can be recuperated.

Homogeneous Model

From the kinetics of Table I and assuming an homogeneous bulk polymerization, the mathematical model of Appendixes A and B was developed. The derivation is similar to that of Estenoz et al.,[11] with the difference that here it is necessary to compute the number of unreacted peroxide groups present in each of the accumulated molecular species.

From the global kinetics, the Basic Module of Appendix A was derived. The part of the model based on the detailed kinetics of Table I, we have called Total Copolymer Bivariate Distribution Module (or simply Copolymer Module), and is presented in Appendix B. Except for the copolymer macrostructure that must be estimated through the Copolymer Module, all other distributions and variables (including the number average molecular weight for the total copolymer) are simulated through the Basic Module.

The nomenclature that is used to characterize the polymer mixture is given in what follows.

$G_{PS}^{(i)}(s)$: Weight chain length distribution (WCLD) for the free PS containing $i = 0$, 1 or 2 terminal peroxide groups.

$G_{PS}(s)$: $\left(= \sum_{i=0}^{2} G_{PS}^{(i)}(s)\right)$ WCLD for the total free PS.

$G_{PB}(b)$: WCLD for the unreacted PB. (The initial distribution $G_{PB}^{0}(b)$ is assumed known.)

$G_C^{(i)}(s, b)$: Set of bivariate WCLDs for the copolymer containing $i = 0, 1, 2, 3, \cdots$ unreacted peroxide groups.

$G_C(s, b)$: $\left(= \sum_{i} G_C^{(i)}(s, b)\right)$ Copolymer WCLD.

For the PS and PB homopolymers, the corresponding weight molecular weight distributions (WMWDs) can be obtained from $G_{PS}(s)$ and $G_{PB}(b)$, by replacing the chain lengths (s or b) for their molecular weights (sM_S or bM_B). For the total copolymer, the bivariate molecular weight-chemical composition distribution $G_C(M, w_S)$ may be obtained from $G_C(s, b)$, by replacing the independent variables (s, b) for (M, w_S), where M ($=sM_S + bM_B$) is the copolymer molecular weight, and w_S ($=sM_S/M$) is the weight fraction of polymerized St in the graft copolymer, or copolymer composition. In this transformation, uniformly distributed points along the original (s, b) axes result in being unevenly distributed along (M, w_S). For this reason, a simultaneous heights transformation must be implemented if $G_C(M, w_S)$ is to be represented by a continuous surface. From $G_C(M, w_S)$ and after appropriate summations, the univariate distributions of molecular weight $G_C(M)$, and of chemical composition $G_C(w_S)$ can be obtained.[12] From $G_C(M)$ and $G_C(w_S)$, the average molecular weights and the global copolymer composition can be further calculated. However, due to loss of information introduced by the change in independent variables, it is numerically preferable to obtain such averages directly from $G_C(s, b)$.[12]

The proposed model does not include an energy balance. However, nonisothermal reactions and the gel effect can be simulated through the use of standard or modified Arrhenius expressions for the kinetic constants.[1-11] When imposing a temperature profile, it will be assumed that the reactor cooling/heating system is ideal in the sense that it is capable of exactly following such profile.

The Basic Module is self-sufficient from the calculation point of view. In this case, eqs. (A.1)–(A.3), (A.6), (A.8)–(A.10), (A.21)–(A.24), (A.28), (A.29), (A.31), (A.32), (A.35)–(A.40), (A.74)–(A.77), (A.80)–(A.82), (A.85), and (A.86)–(A.90) must be simultaneously solved. For the Copolymer Module, eq. (B.26) must be integrated utilizing the Basic Module

results. To avoid the calculation at every possible chain length, many molecular species may be lumped together at fixed chain length intervals (e.g.: $\Delta s = 200$ and $\Delta b = 600$).

The Basic Module can be solved by standard numerical methods, appropriate for "stiff" differential equations. In the Copolymer Module, a large number of differential equations (approximately 10,000) must be integrated; and for this reason, a cruder numerical method was employed. In this case, fixed integration time intervals were adopted. For each time interval of the Copolymer Module, the total mass of grafted St and the total number of grafting points were accurately estimated through the Basic Module. With this precaution, possible integration errors in the Copolymer Module are not accumulated along the solution. The computer program was written in Watcom™ FORTRAN for a 486 IBM compatible PC.

EXPERIMENTAL WORK

A series of 12 nonisothermal batch experiments were carried out with different combinations of initiator type, initiator concentration, and prepolymerization temperature (see first four columns of Table II). The following bifunctional initiators were evaluated: L-256; 2,5-dimethyl-2,5 bis(benzoyl peroxy) hexane (or L-118); and ethyl 3,3-di(*t-butyl* peroxide) butyrate (or L-233). For comparison, the experiments reported in Estenoz et al.[11] for the blank and the TBPO cases are reconsidered.

In general, the experiments were carried out as explained in Estenoz et al.[11] Prepolymerization temperatures of 90 and 120°C were investigated. The dissolution and prepolymerization stages were carried out in a 2.5-L stainless steel Büchi Autoclave BEP 280 stirred-tank reactor. The finishing stage was carried out under nonagitated conditions, in 5-mm o.d. glass ampoules. For the experiments with prepolymerization at 120°C, the applied temperature profiles are represented in Fig. 1(a). In the rubber dissolution stage, all reagents (except for the initiator) were agitated during 3 h at 70°C. At the start of the prepolymerization, the initiator was added, and the temperature was increased at 1°C/min until 90°C or 120°C was reached. The prepolymerization stage was interrupted when $30 \pm 2.0\%$ conversion was detected. To this effect, a linear extrapolation of the conversion plots was implemented on line. The prepolymer was then forced into glass ampoules by means of a vacuum pump, the ampoules were

Table II   Experimental Conditions and Global Results

Experiment No.	Final Prepolymerization Temperature (°C)	Initiator Type	Initiator Concentr. (mol/L)	Prepolymerization Time (min)	$\bar{M}_{n,\mathrm{PS}}$ (×10⁻³)	$\bar{M}_{w,\mathrm{PS}}$ (×10⁻³)	St Grafting Efficiency	Average Particle Diameter (μm)
1	90	none (blank)	—	890 (893)	94.0 (85.5)	278.3 (250.2)	0.043 (0.091)	0.6
2	90	TBPO	0.0046	620 (630)	83.5 (80.1)	233.4 (239.1)	0.090 (0.097)	1.1
3	90	TBPO	0.0135	510 (530)	88.3 (79.4)	227.2 (232.4)	0.130 (0.121)	
4	120	none (blank)	—	497 (495)	70.6 (68.1)	193.4 (199.3)	0.155 (0.155)	
5	120	TBPO	0.0046	444 (443)	68.3 (70.7)	178.1 (204.7)	0.212 (0.158)	1.5
6	120	L-256	0.0046	363 (369)	80.6 (67.5)	212.3 (190.3)	0.203 (0.168)	1.4
7	120	L-118	0.0046	401 (408)	65.4 (68.4)	171.4 (195.6)	0.183 (0.162)	2.0
8	120	L-233	0.0046	480 (476)	— (69.1)	— (197.4)	— (0.159)	
9	90	L-256	0.0023	451 (470)	90.9 (89.4)	258.3 (236.2)	0.054 (0.099)	0.7
10	90	L-256	0.0046	378 (381)	89.3 (87.3)	252.9 (232.1)	0.086 (0.125)	1.8
11	90	L-256	0.0068	341 (334)	88.3 (84.4)	227.1 (230.4)	0.105 (0.135)	1.6
12	90	L-256	0.0135	305 (300)	66.8 (81.2)	176.7 (220.1)	0.281 (0.141)	3.3

The theoretical predictions are indicated in parentheses.

sealed, and for the finishing stage the ampoules were maintained at 150°C during 8 h. The final conversion was in all cases 95% or higher. For the experiments with prepolymerization at 120°C, 10% in volume of ethyl benzene solvent was added to prevent "hot points" and/or reaction runaways. In such cases, the solvent was extracted from the reaction product in a final devolatilization operation.

The reagents were basically obtained as in our previous work.[11] St monomer from Chevron was utilized, after an appropriate elimination of the stabilizer. Approximately 6% in weight of medium-*cis* PB from Enichem was dissolved into the monomer. The rubber was analyzed by size exclusion chromatography (SEC), and the resulting MWD is represented in Figure 7 with a linear horizontal axis. The distribution was used as shown, without adjustment to any analytical expression. The average molecular weights resulted $\bar{M}^0_{n,\mathrm{PB}}$ = 115,385 and $\bar{M}^0_{w,\mathrm{PB}}$ = 221,154. A Polygard™ mixture of di/trinonyl-phenyl-phosphite and tri-isopropanol amine from Uniroyal was added as antioxidizing agent, to protect the rubber during the dissolution period.

The commercial initiators were used as provided by the manufacturer. The purity of L-256, L-118, and TBPO were determined as in ASTM D2340-82. For L-233, the nominal manufacturer's concentration was directly adopted, because the mineral oil supplied with the reagent interfered with the purity measurement.

The final product was analyzed to determine the total mass of copolymer plus initial or purely crosslinked PB, by gravimetry; the St grafting efficiency (or percent of grafted St with respect to the total polymerized monomer), by gravimetry; the average molecular weights of the free PS, by SEC; and the number average rubber particle diameter, by scanning electron microscopy. As explained in Estenoz et al.,[11] the grafting efficiency is expected to be in excess, due to the difficulty of completely extracting the PS occluded in the rubber particles. The final results are presented in Table II.

Consider the prepolymerization times presented in the fifth column of Table II. Such times are shortened by chemical initiation. For a given initiator and temperature, prepolymerization time is reduced when the initiator concentration is increased. In Figure 1(b), the conversion measurements corresponding to prepolymerizations at 120°C, are represented. The L-256 and L-118 initiators produce faster polymerizations than TBPO. Note, however, that compared to the bifunctional initiators and for identical molar concentrations, TBPO has only one-half of active peroxides. Due to its relatively slow
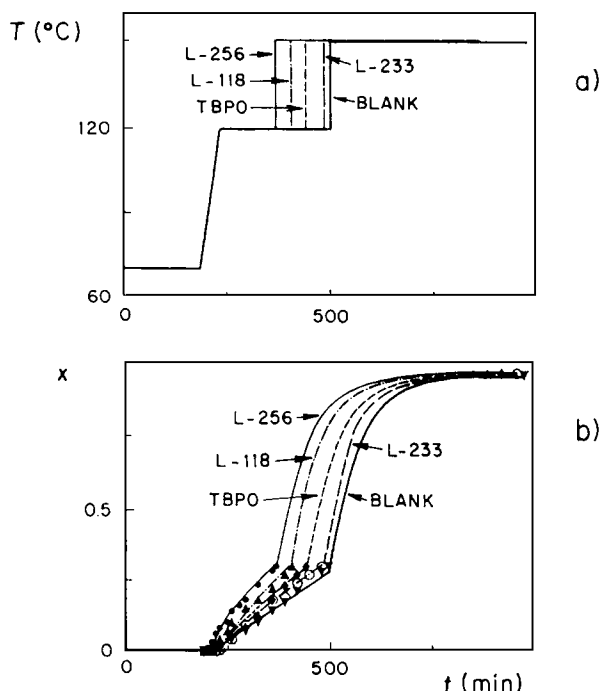
Figure 1 Experiments 4-8. (a) Applied temperature profiles. (b) Evolution of conversion.

decomposition rate, L-233 exhibits longer prepolymerization times than TBPO.

For an adequate polymer quality, the phase inversion must occur during the agitated prepolymerization period; and the aim is to produce a clear transition at the lowest possible conversion. Because one of the objectives of the work was to investigate the ability of chemical initiators to induce phase inversion, the prepolymerization period was especifically monitored.

To estimate the phase inversion point, the viscosity of reactor samples taken along the prepolymerization were determined via a Brookfield viscometer at 25°C. A minimum in the viscosity curve is indicative of such transition. In Figure 2, viscosity measurements are represented vs. conversion. Note that the curves in Figure 2 are not simulation results and were simply obtained by joining together the experimental points. (The present homogeneous model is incapable of predicting viscosities and particle sizes.) For the prepolymerization at 120°C [Fig. 2(a)], it is seen that the faster L-256 and L-118 initiators provide two superimposed viscosity minima at around 10% conversion. TBPO also produces a clear minimum (at an increased conversion), but monotonically increasing measurements are observed for the L-233 and blank cases. For its slow

decomposition rate, it was decided to discard the L-233 initiator in all that follows.

Consider now the final product characteristics presented in Table II. It is seen that PS molecular weights decrease as the prepolymerization temperature is raised. This is because at higher temperatures, the largest fraction of the polymer is produced by transfer to the monomer rather than by combination termination. For a given prepolymerization temperature, the final PS molecular weights are practically independent on the initiator type. The reason for this is that the relatively small amount of PS produced by chemical initiation compared to the PS mass produced by monomer initiation. This "dilution" effect is less dramatic in the St grafting efficiency, however, because primary initiator radicals are more effective than polystyryl radicals to induce rubber attack.

In the last column of Table II, the average diameters of the final rubber particles are presented. Near total conversion, average diameters are strongly related to the number density (large densities imply small average diameters, and viceversa). Average diameters and number density are mainly determined during the prepolymerization, and more specifically during the phase inversion period. Many interrelated variables determine the phase transi-
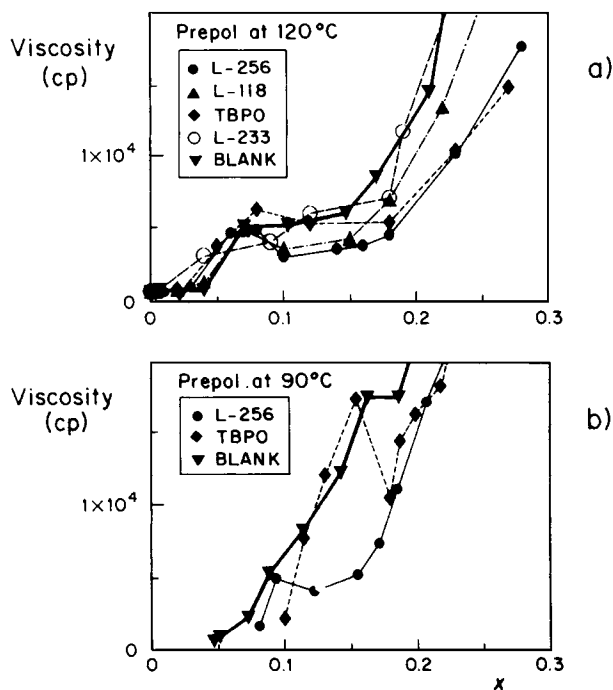

Figure 2 Viscosity measurements for Experiments 4-8 (a); and for Experiments 1, 2, and 10 (b).

tion; for example: agitation, viscosity, grafting efficiency, copolymer characteristics, temperature, polymerization rate, etc. The present homogeneous model is incapable of predicting particle size; and for this reason no further attempts will be here made to interpret such measurements.

SIMULATION RESULTS

The adopted kinetic parameters are presented in Table III. For the blank and monofunctional initiator cases (Experiments 1–5), the parameters in Table III were also employed, but with the mathematical model in Estenoz et al.[11]

The expressions for k_d, k_{d1}, k_{d2}, k_{t_c}, k'_{t_c} and k''_{t_c} were directly adopted from the references in Table III. For k_{i1}; $\tilde{k}_{i1}$; k_{i2}, $\tilde{k}_{i2}$, and k_{i3}, the relationships

of Table III between k_p and such initiation constants were adopted. The expressions for k_{io}, k_{f_M}, k'_{f_M}, k''_{f_M}, k_p, and k_{f_G} were adjusted in this work. Also, the efficiencies f, f_1, and f_2 were specifically adjusted to each initiator type. The Basic Module alone allowed the parameter adjustment, because it estimates all the measured values. Due to the short simulation times required (of the order of 5 s), a fast interactive adjustment was possible. After the adjustment, the Copolymer Module was run to estimate the copolymer characteristics. For the Copolymer Module, calculation times of about 5 min per experiment were observed.

The parameter adjustment was based on Experiments 6 and 10. They involve a fixed L-256 concentration at the two prepolymerization temperatures. Except for the initiator efficiencies, the resulting parameter set was then directly applied to

Table III Employed Kinetic Constants

k_d (TBPO)	$[\text{s}^{-1}]$	$9.2 \times 10^{13} e^{-14850/T}$	Ref. (8)
k_{d1}, k_{d2} (L-256)	$[\text{s}^{-1}]$	$1.1 \times 10^{15} e^{-15953/T}$	Ref. (8)
k_{d1}, k_{d2} (L-118)	$[\text{s}^{-1}]$	$5.6 \times 10^{16} e^{-18694/T}$	Ref. (8)
k_{d1}, k_{d2} (L-233)	$[\text{s}^{-1}]$	$3.8 \times 10^{15} e^{-18397/T}$	Ref. (8)
k_{t_c}, k'_{t_c}, k''_{t_c}	$\left[\dfrac{\text{L}}{\text{mol s}}\right]$	$1.7 \times 10^9 e^{-843/T - 2(C_1 x + C_2 x^2 + C_3 x^3)}$;[a]	Ref. (13)
$k_{i1} = \tilde{k}_{i1} = k_p$	$\left[\dfrac{\text{L}}{\text{mol s}}\right]$		Ref. (1, 11)
$k_{i2} = \tilde{k}_{i2} = 0.63 k_p$	$\left[\dfrac{\text{L}}{\text{mol s}}\right]$		Ref. (11)
$k_{i3} = k_p$	$\left[\dfrac{\text{L}}{\text{mol s}}\right]$		Ref. (11)
k_{i_o}	$\left[\dfrac{\text{L}^2}{\text{mol s}}\right]$	$2.2 \times 10^5 e^{-13809/T}$;[b]	Ref. (3, 14)
f_1, f_2 (L-256)		0.5;[b]	
k_p	$\left[\dfrac{\text{L}}{\text{mol s}}\right]$	$9.0 \times 10^5 e^{-2650/T}$;[b]	Ref. (3, 15)
k_{f_M}, k'_{f_M}, k''_{f_M}	$\left[\dfrac{\text{L}}{\text{mol s}}\right]$	$4.2 \times 10^6 e^{-6477/T}$;[b]	Ref. (15)
k_{f_G}	$\left[\dfrac{\text{L}}{\text{mol s}}\right]$	$3.0 \times 10^6 e^{-8950/T}$;[b]	
f (TBPO)		0.5;[b]	
f_1, f_2 (L-118)		0.5;[b]	
f_1, f_2 (L-233)		0.6;[b]	

[a] $C_1 = 2.57 - 0.00505\ T$; $C_2 = 9.56 - 0.0176\ T$; $C_3 = -3.03 + 0.00785\ T$.
[b] Adjusted in this work.

all other experiments. The adjustment with Experiments 6 and 10 was as follows. First, k_{i_o}, f_1 (L-256), f_2 (L-256), and k_p were selected to fit the conversion curves. Then, k_{f_M} was modified to fit the $\bar{M}_{n,PS}$ measurements; and the afterwards the predictions for $\bar{M}_{w,PS}$ were checked against the measurements. Different combinations of the kinetic parameters were iteratively selected, until appropriate estimation of conversion and the molecular weight averages. The final step was to adjust k_{f_G} to the observed grafting efficiency. (Grafting reactions have a negligible effect on conversion and on the free PS characteristics.)

Apart from the model predictions in Table II, the evolution of the main global variables is presented in Figures 1(b) and 3 to 6. They are all represented against conversion (x), except for Figure 3, which is represented against time (t). Also, they all correspond to the experiments with prepolymerization at 120°C, except for Figure 6(b), which illustrates some of the 90°C prepolymerizations. A reasonable agreement between predictions and measured values is in general observed. The greater differences appear in the grafting efficiencies, where relatively large measurement errors were *a priori* expected.

Figure 3 shows the evolution of the accumulated polymer masses. The curves for the PS masses in Figure 3(a) are similar in shape to those of the global St conversions in Figure 1(b). In Figure 3(b), it is observed that all final PB masses practically coincide at about 10% of its initial value. This indicates that at the polymerization end most graft copolymer must have been produced by attack from a monomer-initiated free radical. During the prepolymerization, different rates of PB consumption (and, therefore, of grafting) are observed, with the fastest PB consumption corresponding to the L-256 case. Accordingly, the largest copolymer production during the prepolymerization also corresponds to L-256 [Fig. 3(c)].

Figure 4(a) shows the evolution of the PS molecular weights. At the beginning of the process (dissolution stage), the initiator is not yet added and the temperature is low (70°C). Under such circumstances, combination termination dominates, transfer to the monomer is low, and the initial molecular weights are high. At the prepolymerization temperature of 120°C, most polymer is produced by transfer to the monomer, and the accumulated molecular weights are considerably reduced. Molecular weights are further reduced when chemical initiation is employed. TBPO and L-256 are totally consumed during the first part of the prepolymerization, and this explains the observed minima in the PS molec-
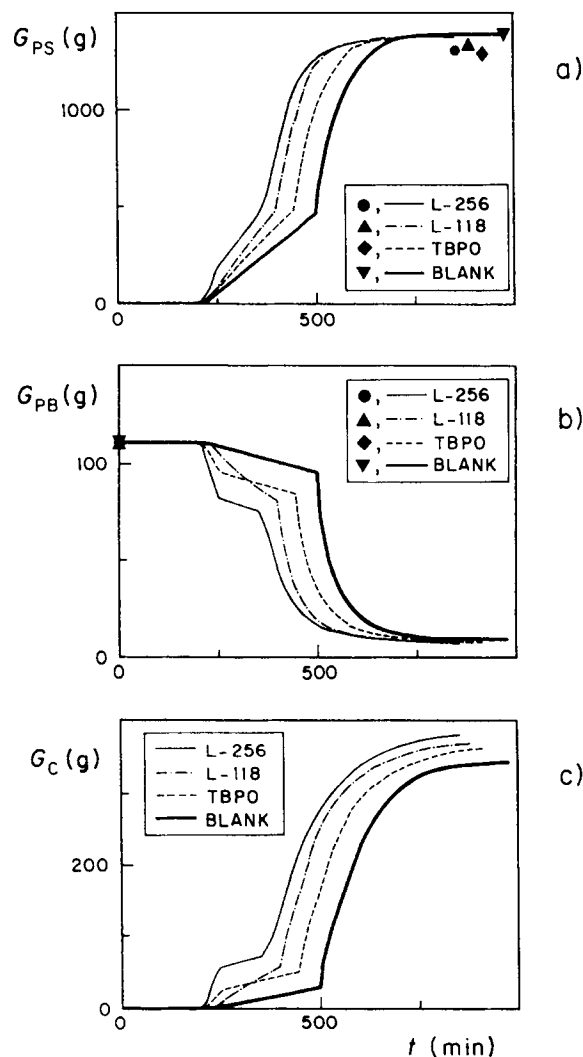

Figure 3 Experiments 4–7. Total masses of free PS (a); residual PB (b); and graft copolymer (c).

ular weights. During the finishing stage at 150°C, transfer to the monomer dominates. Also, the total free radical concentration increases due to an increased monomer decomposition combined with a decreased termination (in turn, a consequence of the gel effect). Thus, PS molecular weights decrease during the finishing stage. The discontinuities in the curves at 30% conversion are indicative of the temperature step changes applied at the beginning of the finishing stage.

Consider now the molecular weights of the residual PB and graft copolymer presented in Figure 4(b) and (c). PB molecular weights monotonically decrease from their initial value, since (at each chain length) the probability of branching is proportional to the mass of bound B, rather than to the moles of
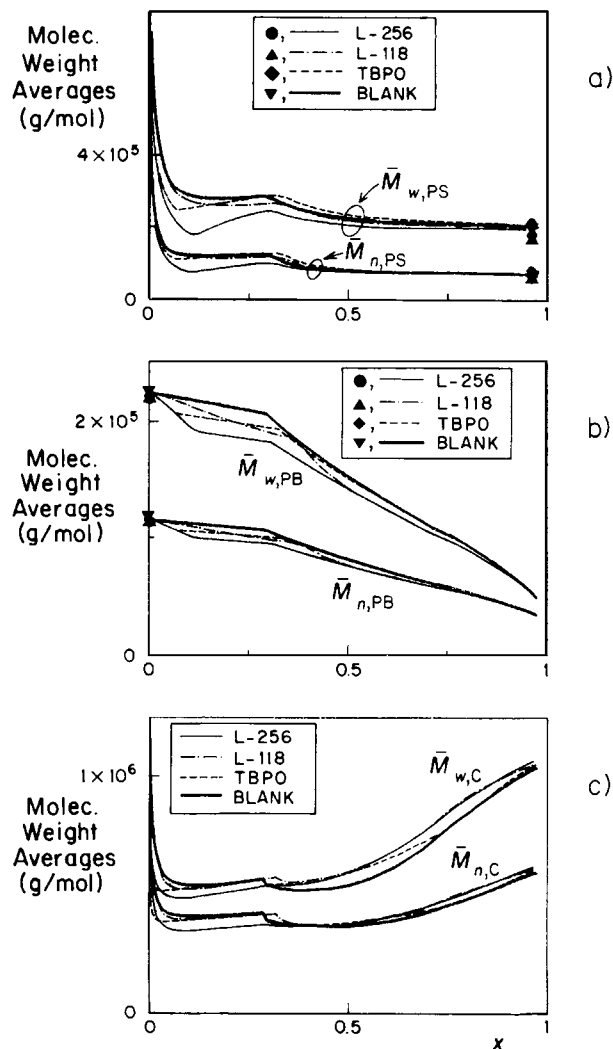
Figure 4 Experiments 4–7. Average molecular weights for the free PS (a); the residual PB (b); and the graft copolymer (c).

PB species [Fig. 4(b)]. Thus, at the beginning of the polymerization, graft copolymer based on the longest PB chains is produced. As it was shown in our previous publication,[11] the MWD of the instantaneously produced PS is at all times similar to the MWD of the instantaneously grafted branches. Also, the amount of H-grafts with respect to T-grafts increases as the temperature is decreased.[11] For all above reasons, high molecular weight copolymer is produced during the initial dissolution stage. During the prepolymerization, copolymer molecular weights drop as a consequence of an increased production of T-type molecules with shorter PB chains and shorter grafted branches. In the finishing stage, the shortest grafted chains are produced. However, the copolymer molecular weights increase due to the

"graft-over-graft" process, in turn, produced by an increased rate of chain transfer to the polymer. For this reason, at final conversion several branches are (in the average) grafted onto each PB chain.

In Figure 5(a), the concentration evolution for the original initiators and corresponding by-products are presented. While TBPO and L-256 are totally consumed during the first part of the prepolymerization, unreacted L-118 still remains during the finishing stage. Also, only TBPO and L-256 produce important amounts of graft copolymer at low conversions, thus explaining their good phase inversion performance. The molar concentrations of the secondary products generated from L-256 and
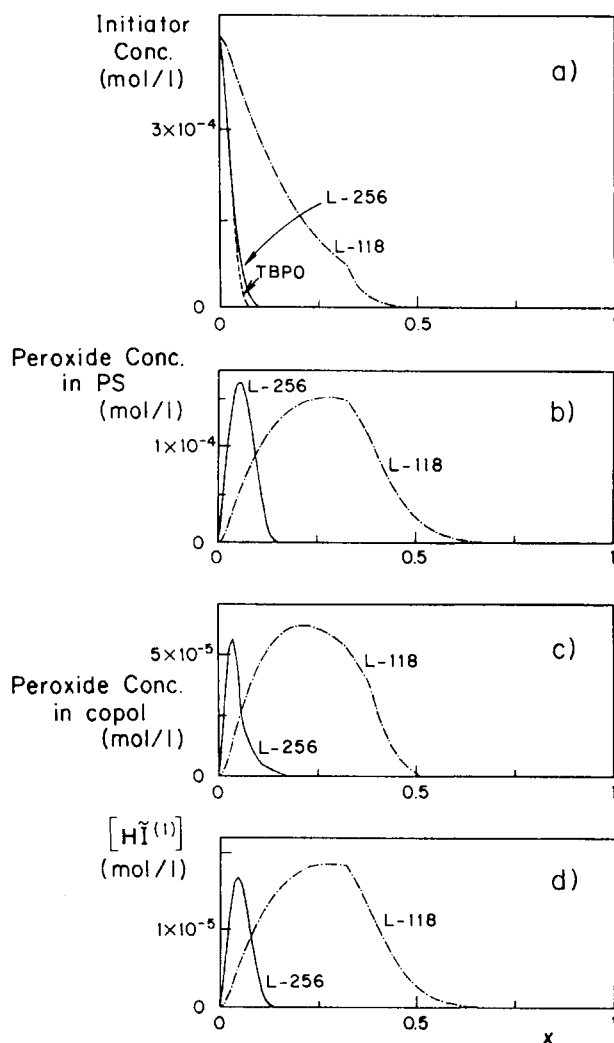
Figure 5 Experiments 5–7. Concentration of initiators and by-products. (a) Evolution of TBPO, L-256, and L-118. (b) Total peroxides in the accumulated PS. (c) Total peroxides in the accumulated copolymer. (d) Secondary initiator.
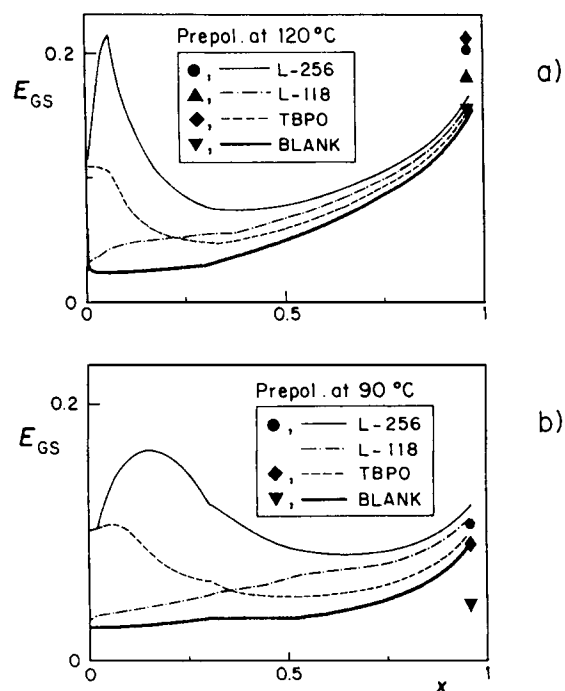
Figure 6 Styrene grafting efficiencies for Experiments 4–7 (a); and for Experiments 1, 2, and 10 (b).

L-118 are presented in Figure 5(b)–(d). Figure 5(b) represents the total active peroxide groups present in the free PS (in the form of one or two peroxide groups per molecule). Figure 5(c) shows the active peroxide groups accumulated in the copolymer (in the form of one or more peroxide groups per molecule). Figure 5(d) illustrates the concentration of the secondary (monofunctional) initiators. As expected, bifunctional initiators are consumed before their corresponding by-products.

Figure 6(a) and (b) respectively show the grafting efficiencies for all the prepolymerizations at 120°C and for some of the 90°C prepolymerizations. For TBPO and L-256, the initial grafting efficiencies practically coincide. But soon after, the L-256 efficiency rapidly increases, presenting a large maximum at around 15% conversion as a consequence of decomposition of the active peroxides accumulated in the free PS.

In Figure 7, the final product quality corresponding to experiment 6 is presented. Even though not shown, similar results were observed for the other simulated examples. Figure 7(a) shows the estimated MWDs. The final PS molecular weights result somewhat larger than the original PB molecular weights. Also, while the residual PB tends to an oligomer, copolymer molecular weights tend to very large values. (Above 95% conversion, other aspects

not included in the present model should be taken into consideration for a more accurate estimation of the product quality.) Figure 7(b) shows the bivariate chain length distribution for the final copolymer. From such distribution, the univariate distributions of molecular weights (M) and of chemical composition (w_S) were obtained [Fig. 7(a) and (c)]. From Figure 7(c), the global weight fraction of polymerized St in the total copolymer may be calculated; resulting $\bar{w}_S = 0.74$. Also, the MWD of the accumulated PS should be similar to the MWD of accumulated grafted branches.[11] Therefore, approximately five St branches per PB chain must be present in the final copolymer. It should be noted that by integration of the third to fifth terms of eq. (B.24), the exact number of grafted branches could be calculated. From this value and with the moles of copolymer obtained from eq. (A.86), then the av-
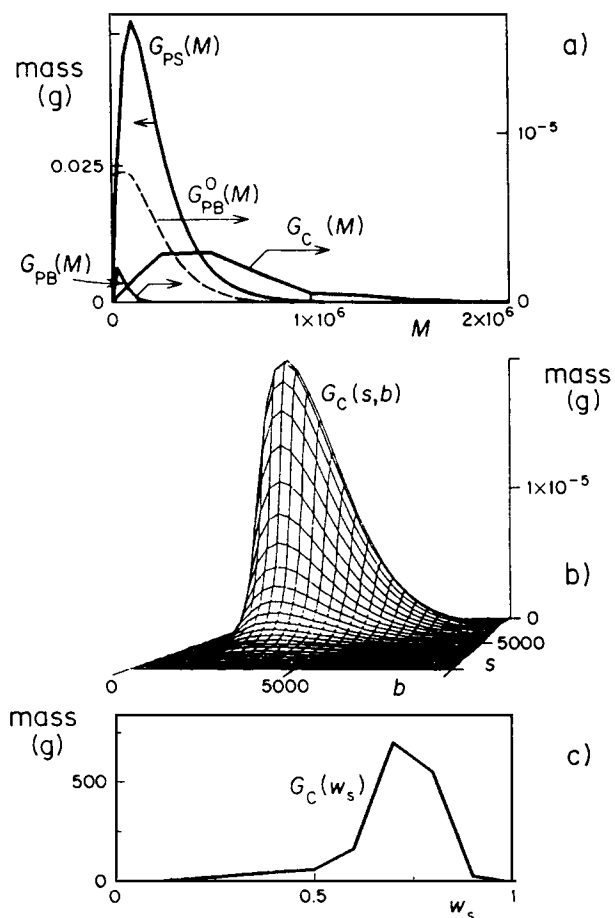

Figure 7 Molecular macrostructure for the final polymer mixture in Experiment 6. (a) MWDs. (b) Bivariate chain length distribution for the final copolymer. (c) Chemical composition distribution for the final copolymer.

erage number of branches per copolymer molecule could be more accurately estimated.

CONCLUSIONS

This work experimentally and theoretically investigated the use of bifunctional initiators in the bulk HIPS process. For the experimental design, several combinations of initiator types, initiator concentrations, and prepolymerization temperatures were tested. For the theoretical analysis, a new mathematical model was developed, that requires to follow the evolution of all initiator by-products.

An early production of graft copolymer via chemical initiation is important for favoring phase inversion at low conversions. To this effect, initiator lifetimes must be short compared to prepolymerization times. L-233 lifetimes proved excessively long at the sought prepolymerization temperatures; and for this reason L-233 was early discarded in the present investigation. In the case of L-118, the prepolymerization rates were appropriately increased with respect to TBPO, but it exhibited a relatively poor capacity for generating graft copolymer.

The main result is that L-256 can be advantageously employed in the bulk HIPS polymerization. Compared to the use of a standard monofunctional initiator (TBPO), prepolymerization times may be shortened by around 38%, and the phase inversion periods are produced at lower conversions.

The final molecular macrostructure proved quite independent of the initiator type. This does not necessarily imply similar mechanical properties however, because noticeable differences in the average particle sizes were observed.

APPENDIX A: BASIC MODULE

Balances for the Nonpolymeric Reagents and Products

Initiator and Secondary Initiator

$$\frac{d}{dt}([I^{(2)}]V) = -f_1 k_{d1}[I^{(2)}]V \qquad (A.1)$$

$$\frac{d}{dt}([H\tilde{I}^{(1)}]V)$$
$$= -f_2 k_{d2}[H\tilde{I}^{(1)}]V + \tilde{k}_{i2}[I^{\cdot(1)}][B^*]V \quad (A.2)$$

Monomer

Assuming the "long chain approximation" (by which propagation is the only monomer-consuming reaction), one can write:

$$\frac{d}{dt}([St]V) = -R_p V$$

$$= -k_p[St]([S^{\cdot}] + [P^{\cdot}])V \quad (A.3)$$

where R_p is the global St polymerization rate, and

$$[S^{\cdot}] = \sum_{n=1}^{\infty} [S_n^{\cdot}] = \sum_{n=1}^{\infty} \{[S_n^{\cdot(0)}] + [S_n^{\cdot(1)}]\} \quad (A.4)$$

$$[P^{\cdot}] = \sum_{n=1}^{\infty} [P_n^{\cdot}] = \sum_{n=1}^{\infty} \sum_{i=1}^{\infty} [P_n^{\cdot(i)}]. \quad (A.5)$$

represent the total concentrations of $S_n^{\cdot}$ and $P_n^{\cdot}$, respectively.

Unreacted B Units

$$\frac{d}{dt}([B^*]V)$$

$$= -\{k_{i2}[I^{\cdot(0)}] + \tilde{k}_{i2}([\tilde{I}^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}]) + k_{f_G}([S^{\cdot}]$$

$$+ [P^{\cdot}])\}[B^*]V + k'_{f_M}[St][P_0^{\cdot}]V \quad (A.6)$$

with

$$[P_0^{\cdot}] = \sum_{i=1}^{\infty} [P_0^{\cdot(i)}]. \quad (A.7)$$

Radical Species

Consider the mass balances of all free radicals appearing in the global kinetics. Such balances, together with the pseudosteady-state assumption (by which all derivatives may be set to zero), provide:

$$\frac{d}{dt}\{[I^{\cdot0}]V\}$$

$$= \left\{ f_1 k_{d1}[I^{(2)}] + f_2 k_{d2}\left[\sum_{n=1}^{\infty}([S_n^{(1)}] + 2[S_n^{(2)}])\right.\right.$$

$$\left.\left. + \sum_{i=1}^{\infty} i[P^{(i)}]\right] - (k_{i1}[St] + k_{i2}[B^*])[I^{\cdot(0)}]\right\}V \simeq 0$$

$$(A.8)$$

$$\frac{d}{dt}\{[\tilde{I}^{\cdot(0)}]V\} = \{f_2 k_{d2}[\tilde{I}H^{(1)}]$$

$$- (\tilde{k}_{i1}[St] + \tilde{k}_{i2}[B^*])[\tilde{I}^{\cdot(0)}]\}V \simeq 0 \quad (A.9)$$

$$\frac{d}{dt}\{[\tilde{I}^{\cdot(1)}]V\} = \{f_1 k_{d1}[I^{(2)}]$$

$$- (\tilde{k}_{i1}[St] + \tilde{k}_{i2}[B^*])[\tilde{I}^{\cdot(1)}]\}V \simeq 0 \quad (A.10)$$

$$\frac{d}{dt}\{[S_1^{\cdot(0)}]V\}$$

$$= \{k_{i1}[I^{\cdot(0)}][St] + \tilde{k}_{i1}[\tilde{I}^{\cdot(0)}][St] + 2k_{i0}[St]^3$$

$$+ k_{f_M}[St]([S^{\cdot}] + [P^{\cdot}])\}V - \{k_p[St] + k_{f_G}[B^*]$$

$$+ k_{t_c}([S^{\cdot}] + [P^{\cdot}]) + k_{t_c}''[P_0^{\cdot}]$$

$$+ k_{f_M}[St]\}[S_1^{\cdot(0)}]V \simeq 0 \quad (A.11)$$

$$\frac{d}{dt}\{[\tilde{S}_n^{\cdot(0)}]V\} = f_2 k_{d2}[S_n^{(1)}]V$$

$$- \tilde{k}_{i1}[St][S_n^{\cdot(0)}]V \simeq 0 \quad n = 1, 2, \cdots \quad (A.12)$$

$$\frac{d}{dt}\{[S_n^{\cdot(0)}]V\}$$

$$= \{\tilde{k}_{i1}[St][\tilde{S}_{n-1}^{\cdot(0)}] + k_p[St][S_{n-1}^{\cdot}]\}V$$

$$- \{(k_p[St] + k_{f_M}[St] + k_{f_G}[B^*]$$

$$+ k_{t_c}([S^{\cdot}] + [P^{\cdot}]) + k_{t_c}''[P_0^{\cdot}]\}[S_n^{\cdot(0)}]V \simeq 0$$

$$n = 2, 3, 4, \cdots \quad (A.13)$$

$$\frac{d}{dt}\{[S_1^{\cdot(1)}]V\}$$

$$= \tilde{k}_{i1}[\tilde{I}^{\cdot(1)}][St]V - (k_p[St] + k_{t_c}([S^{\cdot}] + [P^{\cdot}])$$

$$+ k_{t_c}''[P_0^{\cdot}] + k_{f_G}[B^*] + k_{f_M}[St])[S_1^{\cdot(1)}]V \simeq 0$$

$$(A.14)$$

$$\frac{d}{dt}\{[\tilde{S}_n^{\cdot(1)}]V\} = 2f_2 k_{d2}[S_n^{(2)}]V$$

$$- \tilde{k}_{i1}[St][\tilde{S}_n^{\cdot(1)}]V \simeq 0 \quad n = 1, 2, \cdots \quad (A.15)$$

$$\frac{d}{dt}\{[S_n^{\cdot(1)}]V\}$$

$$= \{\tilde{k}_{i1}[St][\tilde{S}_{n-1}^{\cdot(1)}] + k_p[St][S_{n-1}^{\cdot(1)}]\}V$$

$$- \{k_p[St] + k_{t_c}([S^{\cdot}] + [P^{\cdot}]) + k_{t_c}''[P_0^{\cdot}]$$

$$+ k_{f_M}[St] + k_{f_G}[B^*]\}[S_n^{\cdot(1)}]V \simeq 0$$

$$n = 2, 3, \cdots \quad (A.16)$$

$$\frac{d}{dt}\{[P_0^{\cdot(i)}]V\}$$

$$= \{k_{i2}[I^{\cdot(0)}] + \tilde{k}_{i2}([I^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}])$$

$$- k_{f_G}([S^{\cdot}] + [P^{\cdot}])\}[B^{*(i)}]V - \{k_{i3}[St] + k_{f_M}'[St]$$

$$+ k_{t_c}'[P_0^{\cdot}] + k_{t_c}''([S^{\cdot}] + [P^{\cdot}])\}[P_0^{\cdot(i)}]V \simeq 0 \quad (A.17)$$

$$\frac{d}{dt}\{[P_1^{\cdot(i)}]V\}$$

$$= k_{i3}[St][P_0^{\cdot(i)}]V - \{k_p[St] + k_{f_M}[St] + k_{f_G}[B^*]$$

$$+ k_{t_c}([S^{\cdot}] + [P^{\cdot}]) + k_{t_c}''[P_0^{\cdot}]\}[P_1^{\cdot(i)}]V \simeq 0 \quad (A.18)$$

$$\frac{d}{dt}\{[\tilde{P}_n^{\cdot(i)}]V\} = k_{d2}(i + 1)[P_n^{i+1}]V$$

$$- \tilde{k}_{i1}[St][\tilde{P}_n^{\cdot(i)}]V \simeq 0 \quad n = 1, 2, \cdots \quad (A.19)$$

$$\frac{d}{dt}\{[P_n^{\cdot(i)}]V\}$$

$$= \{\tilde{k}_{i1}[St][\tilde{P}_{n-1}^{\cdot(i)}] + k_p[St][P_{n-1}^{\cdot(i)}]\}V$$

$$- \{k_p[St] + k_{f_M}[St] + k_{f_G}[B^*] + k_{t_c}([S^{\cdot}] + [P^{\cdot}])$$

$$+ k_{t_c}''[P_0^{\cdot}]\}[P_n^{\cdot(i)}]V \simeq 0 \quad n = 2, 3, \cdots \quad (A.20)$$

where $[B^{*(i)}]$ is the molar concentration of total B units present in the PB or copolymer molecules containing $i = 0, 1, \cdots$ peroxide groups and $[B^*] = \sum_i [B^{*(i)}]$. (For PB, it is clearly $i = 0$).

To obtain the global concentration of PS homoradicals, add first eq. (A.11) with eq. (A.13) over all ns. Then, considering eq. (A.12), it results:

$$\frac{d}{dt}\{[S^{\cdot(0)}]V\}$$

$$= \frac{d}{dt}\sum_{n=1}^{\infty}\{[S_n^{\cdot(0)}]V\}$$

$$= \{(k_{i1}[I^{\cdot(0)}] + \tilde{k}_{i1}[\tilde{I}^{\cdot(0)}])[St] + 2k_{i0}[St]^3$$

$$+ f_2 k_{d2}\sum_{n=1}^{\infty}[S_n^{(1)}] + k_{f_M}[St][P^{\cdot}] + k_{f_M}'[S^{\cdot}][P_0^{\cdot}]\}V$$

$$- \{k_{t_c}([S^{\cdot}] + [P^{\cdot}]) + k_{t_c}''[P_0^{\cdot}]$$

$$+ k_{f_G}[B^*]\}[S^{\cdot(0)}]V \simeq 0. \quad (A.21)$$

Similarly, adding up eq. (A.14) with (A.16) over all ns, and bearing in mind eq. (A.15), one finds:

$$\frac{d}{dt}\{[S^{\cdot(1)}]V\} = \frac{d}{dt}\sum_{n=1}^{\infty}\{[S_n^{\cdot(1)}]V\} = \tilde{k}_{i1}[\tilde{I}^{\cdot(1)}][St]$$

$$+ 2k_{d2}\sum_{n=1}^{\infty}[S_n^{(2)}]V - \{k_{t_c}([S^{\cdot}] + [P^{\cdot}]) + k_{t_c}''[P_0^{\cdot}]$$

$$+ k_{f_G}[B^*]\}[S^{\cdot(1)}]V. \quad (A.22)$$

From eqs. (A.21) and (A.22), the total concentration of homoradicals may be obtained:

$$\frac{d}{dt}\{[S^\cdot]V\}$$

$$= \{k_{i1}[I^{\cdot(0)}][St] + \tilde{k}_{i1}([\tilde{I}^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}])[St]$$

$$+ 2k_{i0}[St]^3 + f_2k_{d2}\left(\sum_n [S_n^{(1)}] + 2\sum_n [S_n^{(2)}]\right)$$

$$+ k'_{f_M}[St][P_0^\cdot] + k_{f_M}[St][P^\cdot]\}V$$

$$- \{k_{t_c}([S^\cdot] + [P^\cdot]) + k''_{t_c}[P_0^\cdot] + k_{f_G}[B^*]\}[S^\cdot]V \simeq 0. \quad (A.23)$$

To obtain the total PB radicals and copolymer radicals, first add eqs. (A.17)–(A.20) over all *i*s, resulting:

$$\frac{d}{dt}\{[P_0^\cdot]V\} = \{k_{i2}[I^{\cdot(0)}] + \tilde{k}_{i2}([\tilde{I}^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}])$$

$$+ k_{f_G}([S^\cdot] + [P^\cdot])\}[B^*]V - \{k_{i3}[St] + k'_{f_M}[St]$$

$$+ k'_{t_c}[P_0^\cdot] + k''_{t_c}([S^\cdot] + [P^\cdot])\}[P_0^\cdot]V \simeq 0 \quad (A.24)$$

$$\frac{d}{dt}\{[P_1^\cdot]V\} = k_{i3}[St][P_0^\cdot]V - \{(k_p[St] + k_{f_M}[St]$$

$$+ k_{f_G}[B^*] + k_{t_c}([S^\cdot] + [P^\cdot]) + k''_{t_c}[P_0^\cdot]\}[P_1^\cdot]V \simeq 0 \quad (A.25)$$

$$\frac{d}{dt}\{[\tilde{P}_n^\cdot]V\} = k_{d2}\sum_i i[P_n^{(i)}]V - \tilde{k}_{i1}[St][\tilde{P}_n^\cdot]V \simeq 0$$

$$n = 1, 2, \cdots \quad (A.26)$$

$$\frac{d}{dt}[P_n^\cdot]V = \{k_{i1}[St][\tilde{P}_{n-1}^\cdot] + k_p[St][P_{n-1}^\cdot]\}V$$

$$- \{k_p[St] + k_{f_M}[St] + k_{f_G}[B^*] + k_{t_c}([St] + [P^\cdot])$$

$$+ k''_{t_c}[P_0^\cdot]\}[P_n^\cdot]V \simeq 0. \quad n = 2, 3, \cdots \quad (A.27)$$

Then, adding eq. (A.25) with eq. (A.27) over all *n*s, and considering eq. (A.26), the total concentration of PB plus copolymer radicals is obtained:

$$\frac{d}{dt}\{[P^\cdot]V\} = \left\{k_{i3}[St][P_0^\cdot] + f_2k_{d2}\sum_i i[P^{(i)}]\right\}V$$

$$- \{k_{f_M}[St] + k_{f_G}[B^*] + k_{t_c}([S^\cdot] + [P^\cdot])$$

$$+ k''_{t_c}[P_0^\cdot]\}[P^\cdot]V \simeq 0. \quad (A.28)$$

From eqs. (A.23) and (A.28), the total concentration of macroradicals results:

$$\frac{d}{dt}\{([S^\cdot] + [P^\cdot])V\}$$

$$= \left\{[k_{i1}[I^{\cdot(0)}] + \tilde{k}_{i1}([\tilde{I}^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}])][St] + 2k_{i0}[St]^3\right.$$

$$+ k_{i3}[St][P_0^\cdot] + f_2k_{d2}\left[\sum_n ([S_n^{(1)}] + 2[S_n^{(2)}])\right]$$

$$\left. + \sum_i i[P^{(i)}]\right\}V + k'_{f_M}[St][P_0^\cdot]V$$

$$- \{k_{t_c}([S^\cdot] + [P^\cdot]) + k''_{t_c}[P_0^\cdot] + k_{f_G}[B^*]\}$$

$$\times ([S^\cdot] + [P^\cdot])V \simeq 0. \quad (A.29)$$

Peroxide Groups

The total concentration of peroxide groups is:

$$[Pe] = 2[I^{(2)}] + [H\tilde{I}^{(1)}] + [Pe]_{PS} + [Pe]_C \quad (A.30)$$

with

$$[Pe]_{PS} = \sum_{n=1}^\alpha \{[S_n^{(1)}] + 2[S_n^{(2)}]\} \quad (A.31)$$

$$[Pe]_C = \sum_{i=1}^\alpha i[P^{(i)}] \quad (A.32)$$

where $[Pe]_{PS}$ and $[Pe]_C$ respectively represent the molar concentration of peroxide groups accumulated in the free PS and in the copolymer.

Peroxide groups are consumed only by decomposition reactions. Therefore, it can be written:

$$\frac{d\{[Pe]V\}}{dt} = -\{f_1k_{d1}[I^{(2)}] + f_2k_{d2}([H\tilde{I}^{(1)}]$$

$$+ [Pe]_{PS}) + [Pe]_C)\}V. \quad (A.33)$$

From eqs. (A.33) and (A.1), the total peroxide groups contained in $H\tilde{I}^{(1)}$, PS, and the copolymer may be calculated from the following difference:

$$\frac{d}{dt}\{([H\tilde{I}^{(1)}] + [Pe]_{PS} + [Pe]_C)V\} = f_1k_{d1}[I^{(2)}]V$$

$$- f_2k_{d2}\{[H\tilde{I}^{(1)}] + [Pe]_{PS} + [Pe]_C\}V. \quad (A.34)$$

Inserting eqs. (A.2) into (A.34), one finds:

$$\frac{d}{dt}\{([Pe]_{PS} + [Pe]_C)V\} = f_1k_{d1}[I^{(2)}]V - f_2k_{d2}([Pe]_C$$

$$+ [Pe]_{PS})V - \tilde{k}_{i2}[I^{\cdot(1)}][B^*]V. \quad (A.35)$$

On the basis of the global mechanism of Table I, the following balances for the accumulated peroxide groups contained in PS with 1 and 2 peroxide group per molecule, may be written:

$$\frac{d}{dt}\{[Pe^{(1)}]_{PS}V\}$$

$$= \frac{d}{dt}\left\{\sum_{n=1}^{\infty}[S_n^{(1)}]V\right\}$$

$$= (k_{f_M}[St] + k_{f_G}[B^*])[Pe^{(1)}]_{PS}V$$

$$+ k_{t_c}[S^{\cdot(0)}][S^{\cdot(1)}]V - f_2 k_{d2}[Pe^{(1)}_{PS}]V \quad (A.36)$$

$$\frac{d}{dt}\{[Pe^{(2)}]_{PS}V\} = \frac{d}{dt}\left\{\sum_{n=1}^{\infty}2[S_n^{(2)}]V\right\}$$

$$= k_{t_c}[S^{\cdot(1)}][S^{\cdot(1)}]V - f_2 k_{d2}[Pe^{(2)}]_{PS}V. \quad (A.37)$$

Conversion and Volume

The monomer conversion can be calculated form

$$x = \frac{[St]^0 V^0 - [St]V}{[St]^0 V^0} \quad (A.38)$$

where the superscript "0" indicates initial conditions.

The evolution of reaction volume (V) is obtained as in Estenoz et al.[11] from:

$$V = V_{St}^0(1 - \epsilon x) + V_{PB}^0 \quad (A.39)$$

with

$$\epsilon = \frac{V_{St}^0 - V_S^f}{V_{St}^0} \quad (A.40)$$

where V_{St}^0 and V_{PB}^0 are the initial St and PB volumes, respectively; ϵ is the (St) volume contraction factor; and V_S^f is the final volume of free and grafted St at full conversion.

Equations (A.1)–(A.3), (A.6), (A.8)–(A.10), (A.21), (A.22), (A.24), (A.29), (A.31), (A.32), and (A.35)–(A.40) can be simultaneously solved to find the evolutions of $[I^{(2)}]$, $[H\tilde{I}^{(1)}]$, $[St]$, $[B^*]$, $[S^{\cdot(0)}]$, $[S^{\cdot(1)}]$, $[P_0^{\cdot}]$, $[P^{\cdot}]$, $[S^{\cdot}]$, $[Pe^{(1)}]_{PS}$, $[Pe^{(2)}]_{PS}$, $[Pe]_{PS}$, $[Pe]_C$, x, and V.

NCLD of the Free PS

Define the following molar ratios:

$$\varphi = \frac{[S^{\cdot}]}{[S^{\cdot}] + [P^{\cdot}]} \quad (A.41)$$

$$\varphi_0 = \frac{[S^{\cdot(0)}]}{[S^{\cdot}]} \quad (A.42)$$

$$\varphi_1 = \frac{[S^{\cdot(1)}]}{[S^{\cdot}]} \quad (A.43)$$

$$\gamma = [P_0^{\cdot}]/[S^{\cdot}] + [P^{\cdot}] \quad (A.44)$$

and the following dimensionless kinetic parameters:

$$\beta = \frac{k_{t_c}R_p}{(k_p[St])^2} \quad (A.45)$$

$$\tau = \frac{k_{f_M}}{k_p} + \frac{k_{f_G}[B^*]}{k_p[St]} + \gamma\tau_1 \quad (A.46)$$

$$\tau_1 = \frac{k_{t_c}''R_p}{(k_p[St])^2} \quad (A.47)$$

$$\alpha = \tau + \beta. \quad (A.48)$$

The NCLD of the accumulated free PS can be found from the global mechanism of Table I. For $n = 1, 2, 3, \ldots$, the mass balance for all possible PS species with 0, 1, and two peroxide groups per molecule result:

$$\frac{d}{dt}([S_n^{(0)}]V) = \{k_{f_M}[St] + k_{f_G}[B^*]\}[S_n^{\cdot(0)}]V$$

$$+ \frac{k_{t_c}}{2}\sum_{m=1}^{n-1}[S_m^{\cdot}][S_{n-m}^{\cdot}]V \quad (A.49)$$

$$\frac{d}{dt}\{[S_n^{(1)}]V\} = (k_{f_M}[St] + k_{f_G}[B^*])[S_n^{\cdot(1)}]V$$

$$+ k_{t_c}\sum_{m=1}^{n-1}[S_m^{\cdot(0)}][S_{n-m}^{\cdot(1)}]V - f_2 k_{d2}[S_n^{(1)}]V \quad (A.50)$$

$$\frac{d}{dt}\{[S_n^{(2)}]V\} = \frac{k_{t_c}}{2}\sum_{m=1}^{n-1}[S_m^{\cdot(1)}][S_{n-m}^{\cdot(1)}]V$$

$$- 2f_2 k_{d2}[S_n^{(2)}]V. \quad (A.51)$$

Adding up eqs. (A.49)–(A.51), the following balance for the total free PS species can be obtained:

$$\frac{d}{dt}\{[S_n]V\} = (k_{f_M}[St] + k_{f_G}[B^*])[S_n^{\cdot}]V$$

$$+ \frac{k_{t_c}}{2}\sum_{m=1}^{n-1}[S_m^{\cdot}][S_{n-m}^{\cdot}]V - f_2 k_{d2}\{[S_n^{(1)}] + 2[S_n^{(2)}]\}V$$

$$n = 2, 3, \cdots \quad (A.52)$$

For solving eqs. (A.49)–(A.51), expressions for the free radical concentrations must be developed. Consider first the homoradicals without peroxide groups.

Insert eqs. (A.21) and (A.45)–(A.48) into (A.11), to obtain:

$$[S_1^{\bullet(0)}] = \frac{[S^{\bullet(0)}]k_p[St]\alpha - f_2k_{d2}\sum_n [S_n^{(1)}]}{k_p[St](1 + \alpha)} . \quad (A.53)$$

From eqs. (A.12), (A.13), and (A.45)–(A.48), one finds:

$$[S_n^{\bullet(0)}] = \frac{f_2k_{d2}[S_{n-1}^{(1)}] + k_p[St][S_{n-1}^{\bullet(0)}]}{k_p[St](1 + \alpha)}$$

$$n = 2, 3, \cdots \quad (A.54)$$

Solving this last recurrency formula, it results:

$$[S_n^{\bullet(0)}] = \frac{f_2k_{d2}}{k_p[St]} \sum_{i=1}^{n-1} \left[\frac{[S_{n-i}^{(1)}]}{(1 + \alpha)^i}\right]$$

$$+ \frac{1}{(1 + \alpha)^{n-1}} [S_1^{\bullet(0)}] \quad n = 2, 3, \cdots \quad (A.55)$$

Replacing eq. (A.53) into (A.55), one finds:

$$[S_n^{\bullet(0)}] = \frac{f_2k_{d2}}{k_p[St]} \sum_{i=1}^{n-1} \frac{[S_{n-i}^{(1)}]}{(1 + \alpha)^i} + \frac{\alpha}{(1 + \alpha)^n} [S^{\bullet(0)}]$$

$$- \frac{f_2k_{d2}}{k_p[St]} \frac{\sum\limits_{n=1}^{\alpha} [S_n^{(1)}]}{(1 + \alpha)^n} \quad n = 2, 3, \cdots \quad (A.56)$$

Adding up eq. (A.56) over all ns, the following can be proven:

$$\sum_{i=1}^{n-1} \frac{[S_{n-1}^{(1)}]}{(1 + \alpha)^i} = \frac{\sum\limits_{n=1}^{\alpha} [S_n^{(1)}]}{(1 + \alpha)^n} . \quad (A.57)$$

Substituting into eq. (A.56), one finally obtains:

$$[S_n^{\bullet(0)}] = \frac{\alpha}{(1 + \alpha)^n} [S^{\bullet(0)}] \quad n = 2, 3, \cdots \quad (A.58)$$

Let us develop similar expressions for $[S_1^{\bullet(1)}]$ and $[S_n^{\bullet(1)}]$. Inserting eqs. (A.22) and (A.45)–(A.48) into (A.14), it yields:

$$[S_1^{\bullet(1)}] = \frac{[S^{\bullet(1)}]k_p[St]\alpha - 2f_2k_{d2}\sum_n [S_n^{(2)}]}{k_p[St](1 + \alpha)} . \quad (A.59)$$

From eqs. (A.15), (A.16), and (A.45)–(A.48), one can write:

$$[S_n^{\bullet(1)}] = \frac{2f_2k_{d2}[S_{n-1}^{(2)}] + k_p[St][S_{n-1}^{\bullet(1)}]}{k_p[St](1 + \alpha)}$$

$$n = 2, 3, \cdots \quad (A.60)$$

Operating as before, the following is obtained:

$$[S_n^{\bullet(1)}] = \frac{\alpha}{(1 + \alpha)^n} [S^{\bullet(1)}] \quad n = 2, 3, \cdots \quad (A.61)$$

Adding up eqs. (A.58) and (A.61), it gives:

$$[S_n^{\bullet}] = \frac{\alpha}{(1 + \alpha)^n} [S^{\bullet}] \quad n = 2, 3, \cdots \quad (A.62)$$

Replacing now the definitions of eqs. (A.3) and (A.41)–(A.43) into eqs. (A.58), (A.61), and (A.62), it can be written:

$$[S_n^{\bullet}] = \frac{\varphi R_p}{k_p[St]} \frac{\alpha}{(1 + \alpha)^n} \quad n = 2, 3, \cdots \quad (A.63)$$

$$[S_n^{\bullet(0)}] = \varphi_0[S_n^{\bullet}] \quad n = 2, 3, \cdots \quad (A.64)$$

$$[S_n^{\bullet(1)}] = \varphi_1[S_n^{\bullet}] \quad n = 2, 3, \cdots \quad (A.65)$$

Inserting eqs. (A.63)–(A.65) into eqs. (A.49)–(A.52), and remembering the definitions of τ, τ_1, β, γ, and α, the following balances for the PS species may be finally written:

$$\frac{d}{dt}([S_n^{(0)}]V) = \varphi\varphi_0 R_p\alpha\{(\tau - \gamma\tau_1) + \tfrac{1}{2}\beta\varphi_0\varphi\alpha n\}$$

$$\times (1 + \alpha)^{-n}V \quad n = 1, 2, \cdots \quad (A.66)$$

$$\frac{d}{dt}([S_n^{(1)}]V) = \varphi\varphi_1 R_p\alpha\{(\tau - \gamma\tau_1) + \beta\varphi_0\varphi\alpha n\}$$

$$\times (1 + \alpha)^{-n}V - f_2k_{d2}[S_n^{(1)}]V \quad n = 1, 2, \cdots$$

$$(A.67)$$

$$\frac{d}{dt}([S_n^{(2)}]V) = R_p\frac{\beta}{2}(\varphi\varphi_1\alpha)^2 n(1 + \alpha)^{-n}V$$

$$- 2f_2k_{d2}[S_n^{(2)}]V \quad n = 1, 2, \cdots \quad (A.68)$$

$$\frac{d}{dt}([S_n]V) = \varphi R_p\alpha[\tau - \gamma\tau_1 + \tfrac{1}{2}\beta\varphi\alpha n](1 + \alpha)^{-n}V$$

$$- f_2k_{d2}\{[S_n^{(1)}] + 2[S_n^{(2)}]\}V \quad n = 1, 2, \cdots \quad (A.69)$$

For sufficiently high values of n, then: $(1 + \alpha)^{-n} \simeq e^{-\alpha n}$. Thus, the NCLD of the accumulated free PS with 0, 1, and 2 peroxide groups, together with the NCLD for the total free PS may be obtained by integration of:

$$\frac{d}{dt}([S_n^{(0)}]V)$$

$$= \left\{\varphi\varphi_0 R_p V(\tau - \gamma\tau_1) + R_p \frac{V(\varphi\varphi_0)^2}{2}\beta\alpha n\right\}\alpha e^{-\alpha n}$$

$$n = 1, 2, \cdots \quad \text{(A.70)}$$

$$\frac{d}{dt}([S_n^{(1)}]V)$$

$$= \left\{\varphi\varphi_1 R_p V(\tau - \gamma\tau_1) + R_p V \frac{\varphi^2\varphi_0\varphi_1}{2}\beta\alpha n\right\}\alpha e^{-\alpha n}$$

$$- f_2 k_{d2}[S_n^{(1)}]V \quad n = 1, 2, \cdots \quad \text{(A.71)}$$

$$\frac{d}{dt}([S_n^{(2)}])V = \left\{R_p \frac{V(\varphi\varphi_1)^2}{2}\beta\alpha n\right\}\alpha e^{-\alpha n}$$

$$- 2f_2 k_{d2}[S_n^{(2)}]V \quad n = 1, 2, \cdots \quad \text{(A.72)}$$

$$\frac{d}{dt}([S_n]V) = \left[\varphi R_p V(\tau - \gamma\tau_1) + \frac{R_p V\varphi^2\beta}{2}\alpha n\right]\alpha e^{-\alpha n}$$

$$- f_2 k_{d2}\{[S_n^{(1)}] + 2[S_n^{(2)}]\}V \quad n = 1, 2, \cdots \quad \text{(A.73)}$$

To calculate the corresponding WCLDs, multiply eqs. (A.70)–(A.73) by the molecular weights (nM_S), and replace n by s, to obtain:

$$\frac{d}{dt}G_{\text{PS}}^{(0)}(s) = \left[\varphi\varphi_0 R_p V(\tau - \gamma\tau_1) + R_p \frac{V(\varphi\varphi_0)^2}{2}\beta\alpha s\right]$$

$$\times \alpha e^{-\alpha s}sM_S \quad s = 1, 2, \cdots \quad \text{(A.74)}$$

$$\frac{d}{dt}G_{\text{PS}}^{(1)}(s) = \left\{\left[\varphi\varphi_1 R_p V(\tau - \gamma\tau_1) + R_p V \frac{\varphi^2\varphi_0\varphi_1}{2}\beta\alpha s\right]\right.$$

$$\left.\times \alpha e^{-\alpha s} - f_2 k_{d2}[S_s^{(1)}]V\right\}sM_S \quad s = 1, 2, \cdots \quad \text{(A.75)}$$

$$\frac{d}{dt}G_{\text{PS}}^{(2)}(s)] = \left\{\left[R_p \frac{V(\varphi\varphi_1)^2}{2}\beta\alpha s\right]\alpha e^{-\alpha s}\right.$$

$$\left.- 2f_2 k_{d2}[S_s^{(2)}]V\right\}sM_S \quad s = 1, 2, \cdots \quad \text{(A.76)}$$

$$\frac{d}{dt}G_{\text{PS}}(s)V = \left\{\left[\varphi R_p V(\tau - \gamma\tau_1) + \frac{R_p V\varphi^2\beta}{2}\alpha s\right]\alpha e^{-\alpha s}\right.$$

$$\left.- f_2 k_{d2}\{[S_s^{(1)}] + 2[S_s^{(2)}]\}V\right\}sM_S \quad s = 1, 2, \cdots$$

$$\text{(A.77)}$$

Injecting the evolution of R_p, V, φ, φ_0, φ_1, γ, τ, τ_1, β, and α; eqs. (A.74)–(A.77) may be integrated to respectively calculate the WCLDs for the PS without peroxide groups, the PS with one peroxide groups, the PS with two peroxide groups, and the total PS.

NCLD of the Residual PB

Call $N_{PB}(b)$ the moles of PB with b units of B. From the kinetic mechanism of Table I, it can be written:

$$\frac{d}{dt}N_{\text{PB}}(b) = -\{k_{i2}[I^{\cdot(0)}] + \tilde{k}_{i2}([\tilde{I}^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}])$$

$$+ k_{f_G}([S^{\cdot}] + [P^{\cdot}])\}bN_{\text{PB}}(b) + k'_{f_M}[St][P_0^{\cdot}]\frac{bN_{\text{PB}}(b)}{[B^*]}$$

$$b = 1, 2, 3, \cdots \quad \text{(A.78)}$$

Introducing eqs. (A.3), (A.24), (A.28), (A.41), and (A.44)–(A.48) into eq. (A.78), it results:

$$\frac{dN_{\text{PB}}(b)}{dt} = -\left\{R_p V(1 - \varphi)\left(\tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi}\right)\right\}$$

$$\times \frac{bN_{\text{PB}}(b)}{[B^*]V} - \left\{R_p V(1 - \varphi)[\beta(1 - \varphi) + 2\gamma\tau_1]\right\}$$

$$\times \frac{bN_{\text{PB}}(b)}{[B^*]V} - \left\{\frac{R_p^2\gamma^2 Vk'_{t_c}}{(k_p[St])^2}\right\}\frac{bN_{\text{PB}}(b)}{[B^*]V} + f_2 k_{d2}$$

$$\times \left(\sum_{i=1}^{\infty} i[P^{(i)}]\right)\frac{bN_{\text{PB}}(b)}{[B^*]V} \quad b = 1, 2, 3, \cdots \quad \text{(A.79)}$$

Multiplying each of eqs. (A.79) by the molecular weights (bM_B), an expression enabling the calculation of the WCLD for the residual PB, is obtained:

$$\frac{dG_{\text{PB}}(b)}{dt} = -\left\{R_p V(1 - \varphi)\left(\tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi}\right)\right.$$

$$+ R_p V(1 - \varphi)[\beta(1 - \varphi) + 2\gamma\tau_1] + \frac{R_p^2\gamma^2 Vk'_{t_c}}{(k_p[St]^2)}$$

$$\left.- f_2 k_{d2}\left(\sum_{i=1}^{\infty} i[P^{(i)}]\right)\right\}\frac{b^2 N_{\text{PB}}(b)M_B}{[B^*]}$$

$$b = 1, 2, 3, \cdots \quad \text{(A.80)}$$

The total moles and mass of the residual PB are therefore:

$$N_{\text{PB}} = \sum_b N_{\text{PB}}(b) \quad \text{(A.81)}$$

$$G_{\text{PB}} = \sum_b G_{\text{PB}}(b). \quad \text{(A.82)}$$

Total Copolymer Molecules

A global balance for the $P^{(i)}$ molecules (either PB or copolymer) gives

$$\frac{d}{dt}([P^{(i)}]V) = -\{k_{i2}[I^{\cdot(0)}] + \tilde{k}_{i2}([\tilde{I}^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}])$$

$$+ k_{fG}([S^{\cdot}] + [P^{\cdot}])\}[B^{*(i)}]V + f_2 k_{d2} i[P^{(i)}]V$$

$$+ (k_{fM}[St] + k_{fG}[B^*])[P^{\cdot(i)}]V + k'_{fM}[St][P_0^{\cdot(i)}]V$$

$$+ k_{t_c}\{[S^{\cdot(0)}][P^{\cdot(i)}] + [S^{\cdot(1)}][P^{\cdot(i-1)}]\}$$

$$+ \frac{k_{t_c}}{2}\sum_{j=1}^{i}[P^{\cdot(j)}][P^{\cdot(i-j)}]V + k''_{t_c}\{[S^{\cdot(0)}][P_0^{\cdot(i)}]$$

$$+ [S^{\cdot(1)}][P_0^{\cdot(i-1)}]\}V + \frac{k'_{t_c}}{2}\sum_{j=1}^{i}[P_0^{\cdot(j)}][P_0^{\cdot(i-j)}]V$$

$$i = 0, 1, 2, \cdots \quad (A.83)$$

Adding over all all is, one finds:

$$\frac{d}{dt}([P]V) = \frac{dN}{dt} = -[B^*]\{k_{i2}[I^{\cdot(0)}]$$

$$+ \tilde{k}_{i2}([I^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}]) + k_{fG}([S^{\cdot}] + [P^{\cdot}])\}V$$

$$- f_2 k_{d2}\sum i[P^{(i)}]V + \{k_{fM}[St] + k_{fG}[B^*]\}[P^{\cdot}]V$$

$$+ k_{t_c}[S^{\cdot}][P^{\cdot}]V + k''_{t_c}[S^{\cdot}][P_0^{\cdot}]V + \frac{k_{t_c}}{2}[P^{\cdot}][P^{\cdot}]V$$

$$+ k''_{t_c}[P^{\cdot}][P_0^{\cdot}]V + k'_{fM}[St][P_0^{\cdot}]V$$

$$+ \frac{k'_{t_c}}{2}[P_0^{\cdot}][P_0^{\cdot}]V \quad (A.84)$$

where N are the total moles of P. Introducing eqs. (A.3), (A.24), (A.28), (A.41), and (A.44)–(A.48) into eq. (A.84), it results:

$$\frac{dN}{dt} = -\frac{R_p V(1-\varphi)}{2}[\beta(1-\varphi) + 2\gamma_1]$$

$$- \frac{R_p^2 \gamma^2 k'_{t_c}}{2(k_p[St])^2}V. \quad (A.85)$$

The total moles of graft copolymer (N_C) may be found from:

$$N_C = N - N_{PB} \quad (A.86)$$

where N and N_{PB} can be determined through eqs. (A.84) and (A.81), respectively.

The grafted St mass (G_{GS}) can be calculated from:

$$G_{GS} = M_S[St]_0 V^0 x - G_{PS}. \quad (A.87)$$

Finally, the total copolymer mass (G_C) may be obtained from:

$$G_C = G_{GS} + G_{PB}^0 - G_{PB} \quad (A.88)$$

where the initial PB mass G_{PB}^0 is *a priori* known, and the evolution of G_{PB} can be followed through eqs. (A.82).

Other Global Variables

From the above results, the St grafting efficiency and the number average molecular weight for the total copolymer may be found from:

$$E_{GS} = \frac{G_{GS}}{G_{PS} + G_{GS}} \quad (A.89)$$

$$\bar{M}_{n,C} = \frac{N_C}{G_C}. \quad (A.90)$$

APPENDIX B: TOTAL COPOLYMER BIVARIATE DISTRIBUTION MODULE

From the extended mechanism of Table I, the mass balances for each of the PB or copolymer radicals, together with the pseudosteady-state assumption, yields:

$$\frac{d}{dt}\{[P_0^{\cdot(i)}(s, b)]V\}$$

$$= \{k_{i2}[I^{\cdot(0)}] + \tilde{k}_{i2}([\tilde{I}^{\cdot(0)}] + [\tilde{I}^{\cdot(1)}])$$

$$+ k_{fG}([S^{\cdot}] + [P^{\cdot}])\}[B^{*(i)}(s, b)]V$$

$$- \{k_{i3}[St] + k'_{fM}[St] + k'_{t_c}[P_0^{\cdot}]$$

$$+ k''_{t_c}([S^{\cdot}] + [P^{\cdot}])\}[P_0^{\cdot(i)}(s, b)]V \simeq 0$$

$$i, s = 0, 1, 2, \ldots; \quad b = 1, 2, 3, \cdots \quad (B.1)$$

$$\frac{d}{dt}\{[P_1^{\cdot(i)}(s, b)]V\}$$

$$= k_{i3}[St][P_0^{\cdot(i)}(s, b)]V - \{k_p[St] + k_{fM}[St]$$

$$+ k_{fG}[B^*] + k_{t_c}([S^{\cdot}] + [P^{\cdot}]) + k''_{t_c}[P_0^{\cdot}]\}$$

$$\times [P_1^{\cdot(i)}(s, b)]V \simeq 0$$

$$i, s = 0, 1, 2, \ldots; \quad b = 1, 2, 3, \cdots \quad (B.2)$$

$$\frac{d}{dt}\{[\tilde{P}_n^{\cdot(i)}(s, b)]V\}$$

$$= f_2 k_{d2} N_{BR}^{(1)}(n) - \tilde{k}_{i1}[St][\tilde{P}_n^{\cdot(i)}(s, b)]V \simeq 0$$

$$n = 2, 3, 4, \ldots; \quad i, s = 0, 1, 2, \ldots;$$

$$b = 1, 2, 3, \cdots \quad (B.3)$$

$$\frac{d}{dt}\{[P_n^{\bullet(i)}(s,b)]V\}$$

$$= \tilde{k}_{i1}[St][\tilde{P}_{n-1}^{\bullet(i)}(s,b)]V + k_p[St][P_{n-1}^{\bullet(i)}(s,b)]V$$

$$- \{k_p[St] + k_{f_M}[St] + k_{f_G}[B^*]$$

$$+ k_{t_c}([S^\bullet] + [P^\bullet]) + k_{t_c}''[P_0^\bullet]\}$$

$$\times [P_n^{\bullet(i)}(s,b)]V \simeq 0$$

$$n = 2, 3, 4, \ldots; \quad i, s = 0, 1, 2, \ldots;$$

$$b = 1, 2, 3, \cdots \quad (B.4)$$

where $B^{*(i)}(s,b)$ is any unreacted B unit of $P^{(i)}(s, b)$; and $N_{BR}^{(1)}(n)$ are the moles of grafted chains of length n, containing one unreacted peroxide group. Equations (B.1) and (A.24) provide:

$$\frac{[P_0^{\bullet(i)}(s,b)]}{[P_0^\bullet]} = \frac{[B^{*(i)}(s,b)]}{[B^*]}$$

$$b = 1, 2, 3, \ldots; \quad i, s = 0, 1, 2, \cdots \quad (B.5)$$

Introducing eqs. (A.18) and (A.44)–(A.48) into eq. (B.2); and then considering eq. (B.5) and the fact that $\sum_i i[P^{(i)}] = \sum_n N_{BR}^{(1)}(n)$, one finds:

$$[P_1^{\bullet(i)}(s,b)] = \frac{k_p[St]\alpha[P^\bullet][B^{*(i)}(s,b)]/[B^*]}{k_p[St](1 + \alpha)}$$
$$+ k_{d2}\sum_n N_{BR}^{(1)}(n)$$

$$b = 1, 2, 3, \ldots; \quad i, s = 0, 1, 2, 3, \cdots \quad (B.6)$$

Similarly, eqs. (B.4) and (B.3) provide:

$$[P_n^{\bullet(i)}(s,b)]$$

$$= \frac{k_p[St][P_{n-1}^{\bullet(i)}(s,b)] + k_{d2}N_{BR}^{(1)}(n-1)}{k_p[St](1 + \alpha)}$$

$$n = 2, 3, 4, \ldots; \quad b = 1, 2, 3, \ldots;$$

$$i, s = 0, 1, 2, \cdots \quad (B.7)$$

Remembering the case of eq. (A.56), and after substitution of eqs. (B.6), (A.41)–(A.44), and (A.3), eq. (B.7) may be transformed into:

$$[P_n^{\bullet(i)}(s,b)]$$

$$= \frac{(1-\varphi)R_p}{k_p[St]}\frac{\alpha}{(1+\alpha)^n}\frac{[B^{*(i)}(s,b)]}{[B^*]}$$

$$i, s = 0, 1, 2, \ldots; \quad b = 0, 1, 2, \ldots;$$

$$n = 2, 3, 4, \cdots \quad (B.8)$$

To calculate the bivariate distribution of the accumulated copolymer, the following mass balance must be written:

$$\frac{d}{dt}[P^{(i)}(s,b)]V = T_1 + T_2 + T_3 + T_4 + T_5$$

$$i, s = 0, 1, 2, \ldots; \quad b = 1, 2, 3, \cdots \quad (B.9a)$$

with:

$$\Gamma_1 = -[B^{*(i)}(s,b)]\{k_{i2}[I^{\bullet 0}] + \tilde{k}_{i2}([\tilde{I}^{\bullet(0)}]$$

$$+ [\tilde{I}^{\bullet(1)}]) + k_{f_G}([S^\bullet] + [P^\bullet])\}V$$

$$- k_{d2}i[P^{(i)}(s,b)]V \quad (B.9b)$$

$$T_2 = \{k_{f_M}[St] + k_{f_G}[B^*]\}\sum_{m=1}^{s}[P_m^{\bullet(i)}(s-m,b)]V$$

$$+ k_{t_c}\sum_{m=2}^{s}\sum_{n=1}^{m-1}[P_n^{\bullet(i)}(s-m,b)][S_{m-n}^{\bullet(0)}]V$$

$$+ k_{t_c}\sum_{m=2}^{s}\sum_{n=1}^{m-1}[P_n^{\bullet(i-1)}(s-m,b)][S_{m-n}^{\bullet(0)}]V$$

$$+ k_{t_c}''\sum_{m=1}^{s}[P_0^{\bullet(i)}(s-m,b)][S_m^{\bullet(0)}]V$$

$$+ k_{t_c}''\sum_{m=1}^{s}[P_0^{\bullet(i-1)}(s-m,b)][S_m^{\bullet(1)}]V \quad (B.9c)$$

$$T_3 = \frac{k_{t_c}}{2}\sum_{j=1}^{i}\sum_{b_1=1}^{b-1}\sum_{s_1+m=2}^{s}\sum_{n=1}^{m-1}[P_{m-n}^{\bullet(j)}(s-s_1$$

$$- m, b - b_1)][P_n^{\bullet(i-j)}(s_1,b_1))]V$$

$$+ k_{t_c}''\sum_{j=1}^{i}\sum_{b_1=1}^{b-1}\sum_{s_1+m=2}^{s}[P_m^{\bullet(j)}(s-s_1-m,b-b_1)]$$

$$\times [P_0^{\bullet(i-j)}(s_1,b_1))]V \quad (B.9d)$$

$$T_4 = k_{f_M}'[St]P_0^{\bullet(i)}(s,b)V \quad (B.9e)$$

$$T_5 = \frac{k_{t_c}'}{2}\sum_{j=1}^{i}\sum_{b_1=1}^{b-1}\sum_{s_1=1}^{s}[P_0^{\bullet(j)}(s-s_1,b-b_1)]$$

$$\times [P_{0(p_1,q_1)}^{\bullet(i-j)}(s_1,b_1))]V. \quad (B.9f)$$

Consider now each of the terms in eq. (B.9a).

First Term

Equation (B.9b) may be rewritten to yield:

$$T_1 = -\left\{\frac{[B^{*(i)}(s,b)]}{[B^*]}\right\}\{[k_{i2}[I^{\bullet(0)}] + \tilde{k}_{i2}([\tilde{I}^{\bullet(0)}]$$

$$+ [\tilde{I}^{\bullet(1)}]) + k_{f_G}([S^\bullet] + [P^\bullet])][B^*]V\}$$

$$- k_{d2}i[P^{(i)}(s,b)]V \quad (\forall i, s, b). \quad (B.10)$$

Introducing eqs. (A.24), (A.28), (A.41), and (A.44)–(A.48) into eq. (B.10), one obtains:

$$T_1 = -\left\{\frac{[B^{*(i)}(s,b)]}{[B^*]}\right\}\left\{R_p V(1-\varphi)\left(\tau - \gamma\tau_1\right.\right.$$

$$+ \beta\varphi + \frac{\gamma\tau_1\varphi}{1-\varphi}\right) + R_p V(1-\varphi)(\beta(1-\varphi)$$

$$+ 2\gamma\tau_1) + \frac{R_p^2 V k'_{t_c}\gamma^2}{(k_p[St])^2} + R_p V\gamma\frac{k'_{fM}}{k_p}$$

$$\left. + f_2 k_{d2}\sum_i i[P^{(i)}]\right\} \quad (\forall i, s, b). \quad (B.11)$$

Second Term

Equations (A.63), (A.64), and (B.8) may be rewritten as follows:

$$[S^{\bullet(0)}_{m-n}] = \frac{\varphi\varphi_0 R_p}{k_p[St]}\frac{\alpha}{(1+\alpha)^{m-n}} \quad (B.12)$$

$$[S^{\bullet(1)}_{m-n}] = \frac{\varphi\varphi_1 R_p}{k_p[St]}\frac{\alpha}{(1+\alpha)^{m-n}} \quad (B.13)$$

$$[P^{\bullet(i)}_m(s-m,b)]$$

$$= \frac{(1-\varphi)R_p}{k_p[St]}\frac{\alpha}{(1+\alpha)^m}\frac{[B^{*(i)}(s-m,b)]}{[B^*]} \quad (B.14)$$

$$[P^{\bullet(i)}_n(s-m,b)]$$

$$= \frac{(1-\varphi)R_p}{k_p[St]}\frac{\alpha}{(1+\alpha)^n}\frac{[B^{*(i)}(s-m,b)]}{[B^*]}. \quad (B.15)$$

Replacing eqs. (B.12)–(B.15) into (B.9c), and considering eqs. (A.41)–(A.44), one finds:

$$T_2 = R_p(1-\varphi)\alpha\sum_{m=1}^s\frac{[B^{*(i)}(s-m,b)]}{[B^*]}\left[\left(\tau - \gamma\tau_1\right.\right.$$

$$+ \gamma\tau_1\frac{\varphi\varphi_0}{1-\varphi}\right)\frac{1}{(1+\alpha)^m} + \beta\varphi\varphi_0\alpha m\frac{1}{(1+\alpha)^m}\right]V$$

$$+ R_p(1-\varphi)\alpha\sum_{m=1}^s\frac{[B^{*(i-1)}(s-m,b)]}{[B^*]}$$

$$\times\left[\gamma\tau_1\frac{\varphi\varphi_1}{1-\varphi}\frac{1}{(1+\alpha)^m} + \beta\varphi\varphi_1\alpha m\frac{1}{(1+\alpha)^m}\right]V$$

$$(\forall i, s, b) \quad (B.16)$$

and therefore:

$$T_2 = R_p(1-\varphi)\alpha\sum_{m=1}^s\frac{[B^{*(i)}(s-m,b)]}{[B^*]}\left[\left(\tau - \gamma\tau_1\right.\right.$$

$$+ \gamma\tau_1\frac{\varphi\varphi_0}{1-\varphi}\right)e^{-\alpha m} + \beta\varphi\varphi_0\alpha me^{-\alpha m}\right]V$$

$$+ R_p(1-\varphi)\alpha\sum_{m=1}^s\frac{[B^{*(i-1)}(s-m,b)]}{[B^*]}$$

$$\times\left[\gamma\tau_1\frac{\varphi\varphi_1}{1-\varphi}e^{-\alpha m} + \beta\varphi\varphi_1\alpha me^{-\alpha m}\right]V$$

$$(\forall i, s, b) \quad (B.17)$$

where m represents the chain length of the newly generated branches.

Third Term

Equation (B.8) provides:

$$[P^{\bullet(j)}_{m-n}(s-s_1-m, b-b_1)]$$

$$= \frac{(1-\varphi)R_p}{k_p[St]}\frac{\alpha}{(1+\alpha)^{m-n}}$$

$$\times\frac{[B^{*(j)}(s-s_1-m, b-b_1)]}{[B^*]} \quad (B.18)$$

$$[P^{\bullet(i-j)}_n(s_1, b_1)]$$

$$= \frac{(1-\varphi)R_p}{k_p[St]}\frac{\alpha}{(1+\alpha)^n}\frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]} \quad (B.19)$$

$$[P^{\bullet(j)}_m(s-s_1-m, b-b_1)]$$

$$= \frac{(1-\varphi)R_p\alpha}{k_p[St]}\frac{1}{(1+\alpha)^m}$$

$$\times\frac{[B^{*(j)}(s-s_1-m, b-b_1)]}{[B^*]}. \quad (B.20)$$

Replacing eqs. (B.18–B.20) into eq. (B.9d), and considering eqs. (B.5) and (A.41)–(A.48), it results:

$$T_3 = R_p(1-\varphi)^2\frac{\beta}{2}\alpha$$

$$\times\sum_{j=1}^i\sum_{b_1=1}^{b-1}\sum_{s_1+m=2}^s\frac{[B^{*(j)}(s-s_1-m, b-b_1)]}{[B^*]}$$

$$\times\frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]}me^{-\alpha m}V + R_p(1-\varphi)\gamma\tau_1\alpha$$

$$\times\sum_{j=1}^i\sum_{b_1=1}^{b-1}\sum_{s_1+m=2}^s\frac{[B^{*(j)}(s-s_1-m, b-b_1)]}{[B^*]}$$

$$\times\frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]}e^{-\alpha m}V \quad (\forall i, s, b). \quad (B.21)$$

Fourth Term

Introducing eqs. (A.3), (A.44), and (B.5) into (B.9e), one finds:

$$T_4 = R_p V \gamma \left[\frac{k'_{fM}}{k_p}\right] \frac{[B^{*(i)}(s, b)]}{[B^*]} \quad (\forall i, s, b). \quad (B.22)$$

Fifth Term:

With eqs. (A.3), (A.44), and (B.5), eq. (B.9f) provides:

$$T_5 = \frac{R_p^2 \gamma^2 k'_{t_c}}{2(k_p[St])^2} \sum_{j=1}^{i} \sum_{b_1=1}^{b-1} \frac{[B^{*(j)}(s - s_1, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]} \quad (\forall i, s, b). \quad (B.23)$$

Introducing eqs. (B.11), (B.17), (B.21), (B.22), and (B.24) into eq. (B.9a), an expression for the evolution of the moles of the generic species $P^i(s, b)$ may be finally encountered:

$$\frac{d}{dt} N^{(i)}(s, b)$$

$$= -\left\{\left[R_p V(1 - \varphi)\left(\tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi}\right)\right.\right.$$

$$+ R_p V(1 - \varphi)[\beta(1 - \varphi) + 2\gamma\tau_1]$$

$$\left.+ \frac{R_p^2 V \gamma^2 k'_{t_c}}{(k_p[St])^2} - f_2 k_{d2} \sum_i i[P^{(i)}]V\right] \frac{[B^{*(i)}(s, b)]}{[B^*]}\right\}$$

$$- \{f_2 k_{d2} i[P^{(i)}(s, b)]V\}$$

$$+ \left\{R_p V(1 - \varphi)\left(\tau - \gamma\tau_1 + \gamma\tau_1 \frac{\varphi\varphi_0}{1 - \varphi}\right)\right.$$

$$\times \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]} \alpha e^{-\alpha m}$$

$$+ R_p V \varphi\varphi_0(1 - \varphi)\beta \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]}$$

$$\left.\times \alpha^2 m e^{-\alpha m}\right\}$$

$$+ \left\{R_p V \gamma\tau_1 \varphi\varphi_1 \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]} \alpha e^{-\alpha m}\right.$$

$$+ R_p V \varphi\varphi_1(1 - \varphi)\beta$$

$$\left.\times \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]} \alpha^2 m e^{-\alpha m}\right\}$$

$$+ \left\{R_p V(1 - \varphi)\gamma\tau_1\right.$$

$$\times \sum_{j=1}^{i} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^{s} \frac{[B^{*(j)}(s - s_1 - m, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]} \alpha e^{-\alpha m} + R_p V(1 - \varphi)^2 \frac{\beta}{2}$$

$$\times \sum_{j=1}^{i} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^{s} \frac{[B^{*(j)}(s - s_1 - m, b - b_1)]}{[B^*]}$$

$$\left.\times \frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]} \alpha^2 e^{-\alpha m}\right\}$$

$$+ \left\{\frac{R_p^2 V \gamma^2 k'_{t_c}}{2(k_p[St])^2} \sum_{j=1}^{i} \sum_{b_1=1}^{b-1} \frac{[B^{*(j)}(s - s_1, b - b_1)]}{[B^*]}\right.$$

$$\left.\times \frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]}\right\}$$

$$b = 1, 2, 3, \ldots; \quad i, s = 0, 1, 2, \cdots \quad (B.24)$$

In eq. (B.24), m represents the chain-length of the instantaneously grafted St chains. The first term in the right-hand side of eq. (B.24) represents the rate of disappearance of accumulated $P^{(i)}(s, b)$ species by generation of $P_0^{*(i)}(s, b)$ radicals; the second term represents the rate of disappearance of $P^{(i)}(s, b)$ species by decomposition of a peroxide group [generation of $\hat{P}_n^{*(i-1)}(s - n, b)$]; the third term represents the rate of generation of $P^{(i)}(s, b)$ copolymer, by grafting of a new T branch of length m with a peroxide group onto an accumulated $P^{(i-1)}(s - m, b)$ species; the fourth term represents the rate of generation of $P^{(i)}(s, b)$ by grafting of a new T branch of length m without peroxide groups onto an accumulated $P^{(i)}(s - m, b)$ species; the fifth term represents the rate of generation of $P^{(i)}(s, b)$, by linking $P^{(j)}(s - s_1 - m, b - b_1)$ and $P^{(i-j)}(s_1, b_1)$ with a new H branch of length m; and the sixth term represents the generation rate of $P^{(i)}(s, b)$ by direct crosslinking between $P^{(j)}(s - s_1, b - b_1)$ and $P^{(i-j)}(s_1, b_1)$.

Multiplying each of eqs. (B.24) by the corresponding molecular weights, the evolution of the bivariate WCLDs for every possible number of peroxide groups i, are obtained:

$$\frac{d}{dt} G^{(i)}(s, b)$$

$$= -\left\{\left[R_p V(1 - \varphi)\left(\tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi}\right)\right.\right.$$

$$+ R_p V(1 - \varphi)[\beta(1 - \varphi) + 2\gamma\tau_1]$$

$$+ \frac{R_p^2 V \gamma^2 k'_{t_c}}{(k_p[St])^2} - f_2 k_{d2} \sum_i i[P^{(i)}]V \bigg] \frac{[B^{*(i)}(s, b)]}{[B^*]} \bigg\}$$

$$\times (sM_S + bM_B) - \{f_2 k_{d2} i[P^{(i)}(s, b)]V\}$$

$$\times (sM_S + bM_B) + \bigg\{ R_p V(1 - \varphi)\bigg(\tau - \gamma\tau_1$$

$$+ \gamma\tau_1 \frac{\varphi\varphi_0}{1 - \varphi}\bigg) \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]} \alpha e^{-\alpha m}$$

$$+ R_p V \varphi\varphi_0 (1 - \varphi)\beta \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]}$$

$$\times \alpha^2 m e^{-\alpha m}\bigg\}(sM_S + bM_B)$$

$$+ \bigg\{ R_p V \gamma\tau_1 \varphi\varphi_1 \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]} \alpha e^{-\alpha m}$$

$$+ R_p V \varphi\varphi_1 (1 - \varphi)\beta \times \sum_{m=1}^{s} \frac{[B^{*(i)}(s - m, b)]}{[B^*]}$$

$$\times \alpha^2 m e^{-\alpha m}\bigg\}(sM_S + bM_B) + \bigg\{ R_p V(1 - \varphi)\gamma\tau_1$$

$$\times \sum_{j=1}^{i} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^{s} \frac{[B^{*(j)}(s - s_1 - m, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]} \alpha e^{-\alpha m} + R_p V(1 - \varphi)^2 \frac{\beta}{2}$$

$$\times \sum_{j=1}^{i} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^{s} \frac{[B^{*(j)}(s - s_1 - m, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]} \alpha^2 e^{-\alpha m}\bigg\}(sM_S + bM_B)$$

$$+ \bigg\{ \frac{R_p^2 V \gamma^2 k'_{t_c}}{2(k_p[St])^2} \times \sum_{j=1}^{i} \sum_{b_1=1}^{b-1} \frac{[B^{*(j)}(s - s_1, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^{*(i-j)}(s_1, b_1)]}{[B^*]}\bigg\}(sM_S + bM_B)$$

$$b = 1, 2, 3, \ldots; \quad i, s = 0, 1, 2, \cdots \quad \text{(B.25)}$$

Finally, the global bivariate WCLD for the total copolymer is obtained by adding up eqs. (B.25) for all is, resulting:

$$\frac{d}{dt} G(s, b)]$$

$$= -\bigg\{ \bigg[R_p V(1 - \varphi)\bigg(\tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi}\bigg)$$

$$+ R_p V(1 - \varphi)[\beta(1 - \varphi) + 2\gamma\tau_1]$$

$$+ \frac{R_p^2 V \gamma^2 k'_{t_c}}{(k_p[St])^2} - f_2 k_{d2} \sum_i [P^{(i)}]V \bigg] \frac{[B^*(s, b)]}{[B^*]} \bigg\}$$

$$\times (sM_S + bM_B) - \bigg\{ f_2 k_{d2} \sum_i i[P^{(i)}(s, b)]V \bigg\}$$

$$\times (sM_S + bM_B) + \bigg\{ R_p V(1 - \varphi)\bigg(\tau - \gamma\tau_1$$

$$+ \gamma\tau_1 \frac{\varphi}{1 - \varphi}\bigg) \sum_{m=1}^{s} \frac{[B^*(s - m, b)]}{[B^*]} \alpha e^{-\alpha m}$$

$$+ R_p V \varphi(1 - \varphi)\beta \sum_{m=1}^{s} \frac{[B^*(s - m, b)]}{[B^*]}$$

$$\times \alpha^2 m e^{-\alpha m}\bigg\}(sM_S + bM_B) + \bigg\{ R_p(1 - \varphi)V\gamma\tau_1$$

$$\times \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^{s} \frac{[B^*(s - s_1 - m, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^*(s_1, b_1)]}{[B^*]} \alpha e^{-\alpha m} + R_p V(1 - \varphi)^2 \frac{\beta}{2}$$

$$\times \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^{s} \frac{[B^*(s - s_1 - m, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^*(s_1, b_1)]}{[B^*]} \alpha^2 e^{-\alpha m}\bigg\}(sM_S + bM_B)$$

$$+ \bigg\{ \frac{R_p^2 V \gamma^2 k'_{t_c}}{2(k_p[St])^2} \times \sum_{b_1=1}^{b-1} \frac{[B^*(s - s_1, b - b_1)]}{[B^*]}$$

$$\times \frac{[B^*(s_1, b_1)]}{[B^*]}\bigg\}(sM_S + bM_B)$$

$$b = 1, 2, 3, \ldots; \quad s = 0, 1, 2, \cdots \quad \text{(B.26)}$$

REFERENCES

1. K. Y. Choi and G. D. Lei, *AIChE J.*, **33**(12), 2067 (1987).
2. K. J. Kim and K. Y. Choi, *Chem. Eng. Sci.*, **44**(2), 297 (1989).
3. M. A. Villalobos, A. E. Hamielec, and P. E. Wood, *J. Appl. Polym. Sci.*, **42**, 629 (1991).
4. W. J. Yoon and K. Y. Choi, *Polymer*, **33**(21), 4582 (1992).
5. K. Y. Choi, W. R. Liang, and G. D. Lei, *J. Appl. Polym. Sci.*, **35**, 1547 (1988).
6. K. J. Kim, W. Liang, and K. Y. Choi, *Ind. Eng. Chem. Res.*, **28**, 131–138 (1989).
7. K. J. Kim and K. Y. Choi, *Chem. Eng. Sci.*, **43**(4), 965 (1988).
8. K. Y. Choi, *Polym. Eng. Sci.*, **26**(14), 975 (1986).

9. W. J. Yoon and K. Y. Choi, *J. Appl. Polym. Sci.,* **46**(8), 1353 (1992).

10. I. M. González, G. R. Meira, and H. Oliva, *J. Appl. Polym. Sci.,* to appear.

11. D. A. Estenoz, E. Valdez, H. Oliva, and G. R. Meira, *J. Appl. Polym. Sci.,* to appear.

12. D. A. Estenoz and G. R. Meira, *J. Appl. Polym. Sci.,* **50,** 1081 (1993).

13. F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.,* **27,** 489 (1982).

14. F. M. Peng, *J. Appl. Polym. Sci.,* **40,** 1289 (1990).

15. J. Brandrup and E. H. Immergut, *Polymer Handbook,* 3rd ed., J. Wiley & Sons, New York, 1989, p. II.85.