

# Bulk Polymerization of Styrene in Presence of Polybutadiene: Calculation of Molecular Macrostructure

D. A. ESTENOZ,<sup>1</sup> E. VALDEZ,<sup>1</sup> H. OLIVA,<sup>2</sup> and G. R. MEIRA<sup>1,\*</sup>

<sup>1</sup>INTEC (CONICET and Universidad Nacional del Litoral), Santa Fe (3000), Argentina and

<sup>2</sup>Facultad de Ingeniería, Universidad del Zulia, Maracaibo, Venezuela

## SYNOPSIS

In our previous publication the detailed molecular macrostructure generated in a solution polymerization of styrene (St) in the presence of polybutadiene (PB) at 60°C, was theoretically calculated. In this work, an extended kinetic mechanism that incorporates monomer thermal initiation, chain transfer to the rubber, chain transfer to the monomer, and the gel effect is proposed, with the aim of simulating a bulk high-impact polystyrene (HIPS) process. The mathematical model enables the calculation of the bivariate weight chain-length distributions (WCLDs) for the total copolymer and for each of the generated copolymer topologies and the univariate WCLDs for the free polystyrene (PS), the residual PB, and the crosslinked PB topologies. These last topologies are characterized by the number of initial PB chains per molecule; copolymer topologies are characterized by the number of PS and PB chains per molecule. The model was validated with published literature data and with new pilot plant experiments that emulate an industrial HIPS process. The literature data correspond to a dilute solution polymerization at a constant low temperature with chemical initiation and a bulk polymerization at a constant high temperature with thermal initiation. The new experiments consider different combinations of prepolymerization temperature, initiator concentration, and solvent concentration. One of the main conclusions is that most of the initial PB is transformed into copolymer. For example, for a prepolymerization temperature of 120°C with addition of initiator, the experimental measurements indicate that the final total rubber mass is approximately three times higher than the initial PB. Also, according to the model predictions, the final weight fractions are: free PS, 0.778; graft copolymer, 0.220; initial PB, 0.0015; and purely crosslinked PB, 0.0005. The final graft copolymer exhibits the following characteristics: average molecular weights,  $\bar{M}_{n,C} = 492,000$  and  $\bar{M}_{w,C} = 976,000$ ; average weight fraction of St, 0.722; and average number of PS and PB branches per molecule, 5.19 and 1.13, respectively. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

High-impact polystyrene (HIPS) is a composite material with a rubbery disperse phase. In its industrial synthesis, bulk styrene monomer (St) is polymerized in the presence of about 6% in weight of dissolved polybutadiene (PB),<sup>1</sup> with or without the addition of small quantities of solvent and/or initiator. The process is homogeneous only up to about 6% of monomer conversion, and thereafter is het-

erogeneous. From the beginning of the heterogeneous period until the point of phase inversion, the continuous phase is rich in the rubber; the disperse phase is practically pure PS. The phase inversion occurs at about 15–20% conversion (when the phase volume ratio is close to unity), and thereafter the vitreous matrix remains as the continuous phase. The graft copolymer tends to accumulate at the interfaces, stabilizing the heterogeneous mixture and favoring the phase inversion.

Two main stages constitute the bulk HIPS process. The first (prepolymerization) stage is carried out at a lower temperature (e.g., 90°C) and under conditions of good agitation to facilitate the phase

\* To whom correspondence should be addressed.

inversion. In the second (finishing) stage, agitation becomes unimportant, temperature is raised, and initiation is by thermal monomer decomposition. When solvent is added to lower viscosity, a final devolatilization stage at a higher temperature is required to eliminate the solvent and the residual monomer. In general, the aim seems to be to favor the normal (trifunctional) grafting, while minimizing crosslinking.<sup>2-6</sup> Many experimental works have been published on the synthesis and characterization of HIPS.<sup>2-21</sup> The simpler bulk homopolymerization of St (without rubber) has also been extensively studied.<sup>22-27</sup>

In spite of its industrial importance, only relatively crude mathematical models on the HIPS synthesis have been published.<sup>28-34</sup> In Ludwico and Rosen<sup>35,36</sup> grafting reactions were neglected, but the partition of monomer and initiator between phases is taken into consideration to calculate the global polymerization rate. Except for these publications, all others (including the present) treat the bulk process as if it were homogeneous. Strictly speaking, polymerization rate, particle morphology, and molecular parameters all depend on the partition between phases of reagents and products. However, according to Ludwico and Rosen,<sup>35,36</sup> the partition coefficients for monomer and initiator are close to unity; and this in part justifies the homogeneous hypothesis.

Consider previous mathematical models that include the rubber grafting.<sup>28-34</sup> Brydon et al.<sup>28</sup> studied the polymerization of St with PB in dilute solution and at low temperatures. The kinetics only considered chemical initiation, propagation, rubber attack by the primary radical, and combination termination of the styryl radicals. Other researchers have also studied the solution process, but include transfer reactions to the monomer and to the rubber.<sup>29-31</sup> Chern and Poehlein's model distinguishes some global copolymer classes.<sup>31</sup> With gross assumptions and through a statistical approach, Tung and Wiley<sup>32</sup> calculated the molecular weight distribution (MWD) of the comblike copolymer topologies that are produced in a HIPS process. Such topologies were classified according to the number of PS branches per PB chain. The aim of the study was to compare the theoretical MWD with the measured MWD by size exclusion chromatography (SEC). Peng,<sup>33</sup> in a both theoretical and experimental work, studied the isothermal bulk polymerization of St with PB through a mathematical model that assumed thermal monomer initiation, propagation, transfer to the monomer and to the rubber, combination termination, and crosslinking of butadiene

radicals. The model adequately predicted the total mass of grafted S. The global number of grafting points and crosslinks were also calculated. The concentration of unreacted repetitive units of B was assumed constant, and the volume contraction was neglected.

In the first part of this series,<sup>34</sup> a model based on the simple kinetics of Brydon et al.<sup>28</sup> for a solution polymerization of St in the presence of PB at 60°C, was developed. The model distinguished between each of the consumed and produced polymer species, with the aim of calculating the detailed molecular macrostructure of the reaction mixture. More specifically, it was possible to calculate the MWD of the final homopolymers (residual PB and free PS), together with the bivariate weight chain-length distributions (WCLD) of the global copolymer and of the individual copolymer topologies. Such topologies were specified by the number of PS and PB chains per molecule. In the present work, the detailed macrostructure is again estimated, but through an extended mechanism valid for a nonisothermal bulk polymerization. The model considers the gel effect, the volume contraction, and a kinetic mechanism that incorporates thermal initiation, termination by disproportionation, transfer to the rubber and to the monomer, and crosslinking between primary B radicals.

## MATHEMATICAL MODEL

### Kinetic Mechanism

Consider the global mechanism presented in the first column of Table I. The following nomenclature is adopted:  $S_n$  characterizes an accumulated PS molecule of chain length  $n$ ;  $P$  represents any polymer molecule with at least one unreacted unit of B;  $P_0^\bullet$  represents a primary rubber radical generated on graft copolymer or on (initial or crosslinked) PB; and  $P_n^\bullet$  is a nonprimary copolymer radical, with a new growing branch containing  $n$  repetitive units of St.

Note the following: (a) even though termination by disproportionation is negligible in St polymerization ( $k_{td}, k'_{td}, k''_{td} \simeq 0$ ), it is here included for generality reasons; (b) the reactivity of styryl radicals is unaffected by molecular weight or copolymer composition; (c) intramolecular termination is neglected due to the extremely low probability that two free radicals may simultaneously occur in the same molecule; (d) the rates of propagation, chain transfer, and termination by combination are assumed independent of chain length; (e) a reduction

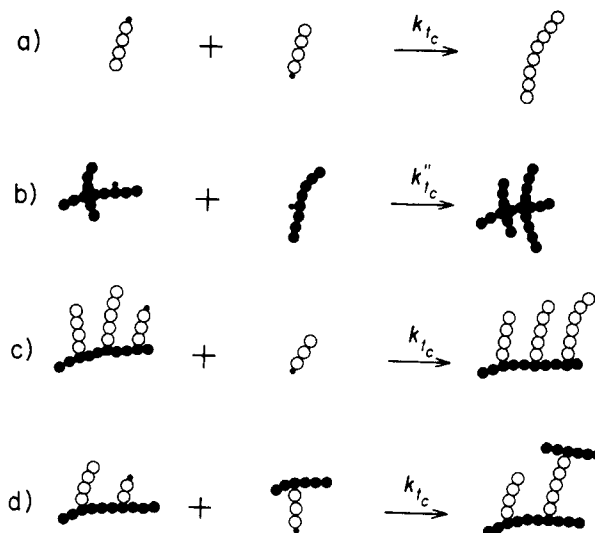
**Table 1 Adopted Kinetic Mechanism**

Global Kinetics ( $n, m = 1, 2, 3, \dots$ )	Detailed Kinetics ( $p, p_1, s, s_1 = 0, 1, 2, \dots$ ) ( $q, q_1, b, b_1, n, m = 1, 2, 3, \dots$ )
<b>Initiation:</b>	
$I_2 \xrightarrow{k_d} 2I^*$	$I_2 \xrightarrow{k_d} 2I^*$
$3St \xrightarrow{k_{10}} 3S_1^*$	$3St \xrightarrow{k_{10}} 3S_1^*$
$I^* + St \xrightarrow{k_{11}} S_1^*$	$I^* + St \xrightarrow{k_{11}} S_1^*$
$I^* + P \xrightarrow{k_{12}} P_0^*$	$I^* + P_{(p,q)}(s, b) \xrightarrow{k_{12}} P_{0(p,q)}^*(s, b)$
$P_0^* + St \xrightarrow{k_{13}} P_1^*$	$P_{0(p,q)}^*(s, b) + St \xrightarrow{k_{13}} P_{1(p,q)}^*(s, b)$
<b>Propagation:</b>	
$S_n^* + St \xrightarrow{k_p} S_{n+1}^*$	$S_n^* + St \xrightarrow{k_p} S_{n+1}^*$
$P_n^* + St \xrightarrow{k_p} P_{n+1}^*$	$P_{n(p,q)}^*(s, b) + St \xrightarrow{k_p} P_{n+1(p,q)}^*(s, b)$
<b>Transfer:</b>	
$S_n^* + St \xrightarrow{k_{1M}} S_n + S_1^*$	$S_n^* + St \xrightarrow{k_{1M}} S_n + S_1^*$
$P_n^* + St \xrightarrow{k_{1M}} P + S_1^*$	$P_{n(p-1,q)}^*(s-n, b) + St \xrightarrow{k_{1M}} P_{(p,q)}(s, b) + S_1^*$
$P_0^* + St \xrightarrow{k_{1M}} P + S_1^*$	$P_{0(p,q)}^*(s, b) + St \xrightarrow{k_{1M}} P_{(p,q)}(s, b) + S_1^*$
$S_n^* + P \xrightarrow{k_{10}} S_n + P_0^*$	$S_n^* + P_{(p,q)}(s, b) \xrightarrow{k_{10}} S_n + P_{0(p,q)}^*(s, b)$
$P_n^* + P \xrightarrow{k_{10}} P + P_0^*$	$P_{n(p-1,q)}^*(s-n, b) + P_{(p_1,q_1)}(s_1, b_1) \xrightarrow{k_{10}} P_{(p,q)}(s, b) + P_{0(p_1,q_1)}^*(s_1, b_1)$
<b>Termination:</b>	
$S_n^* + S_m^* \xrightarrow{k_{tc}} S_{n+m}$	$S_n^* + S_m^* \xrightarrow{k_{tc}} S_{n+m}$
$P_m^* + S_n^* \xrightarrow{k_{tc}} P$	$P_{m-n(p-1,q)}^*(s-m, b) + S_n^* \xrightarrow{k_{tc}} P_{(p,q)}(s, b)$
$P_m^* + P_n^* \xrightarrow{k_{tc}} P$	$P_{m-n(p-p_1-1,q-q_1)}^*(s-s_1-m, b-b_1) + P_{n(p_1,q_1)}^*(s_1, b_1) \xrightarrow{k_{tc}} P_{(p,q)}(s, b)$
$P_0^* + P_n^* \xrightarrow{k_{tc}'} P$	$P_{0(p-p_1-1,q-q_1)}^*(s-s_1-n, b-b_1) + P_{n(p_1,q_1)}^*(s_1, b_1) \xrightarrow{k_{tc}'} P_{(p,q)}(s, b)$
$P_0^* + S_n^* \xrightarrow{k_{tc}'} P$	$P_{0(p-1,q)}^*(s-n, b) + S_n^* \xrightarrow{k_{tc}'} P_{(p,q)}(s, b)$
$P_0^* + P_0^* \xrightarrow{k_{tc}'} P$	$P_{0(p-p_1,q-q_1)}^*(s-s_1, b-b_1) + P_{0(p_1,q_1)}^*(s_1, b_1) \xrightarrow{k_{tc}'} P_{(p,q)}(s, b)$
$S_n^* + S_m^* \xrightarrow{k_{td}} S_n + S_m$	$S_n^* + S_m^* \xrightarrow{k_{td}} S_n + S_m$
$P_m^* + S_n^* \xrightarrow{k_{td}} P + S_n$	$P_{m(p-1,q)}^*(s-m, b) + S_n^* \xrightarrow{k_{td}} P_{(p,q)}(s, b) + S_n$
$P_m^* + P_n^* \xrightarrow{k_{td}} P + P$	$P_{m(p-1,q)}^*(s-m, b) + P_{n(p_1-1,q_1)}^*(s_1-n, b_1) \xrightarrow{k_{td}} P_{(p,q)}(s, b) + P_{(p_1,q_1)}(s_1, b_1)$
$P_0^* + S_n^* \xrightarrow{k_{td}'} P + S_n$	$P_{0(p,q)}^*(s, b) + S_n^* \xrightarrow{k_{td}'} P_{(p,q)}(s, b) + S_n$
$P_0^* + P_n^* \xrightarrow{k_{td}'} P + P$	$P_{0(p,q)}^*(s, b) + P_{n(p_1-1,q_1)}^*(s_1-n, b_1) \xrightarrow{k_{td}'} P_{(p,q)}(s, b) + P_{(p_1,q_1)}(s_1, b_1)$
$P_0^* + P_0^* \xrightarrow{k_{td}'} P + P$	$P_{0(p,q)}^*(s, b) + P_{0(p_1,q_1)}^*(s_1, b_1) \xrightarrow{k_{td}'} P_{(p,q)}(s, b) + P_{(p_1,q_1)}(s_1, b_1)$

of the termination rate constant with conversion is included, to consider the autoacceleration or gel effect by controlled macromolecular diffusion<sup>37</sup>; and (f) different types of  $S_1^*$  radicals are generated, but they all propagate with the rate of a generic  $S_n^*$  radical. With reference to item (d), and considering the bulk polymerization of St, some recent publications<sup>38,39</sup> stress the dependence of the termination rate on the produced MWD. This effect should be relatively unimportant in the HIPS process, however, because most dead polymer is generated at high temperatures during the termination stage; and under such conditions, chain transfer instead of combination termination is the dominant mechanism.

Figure 1 illustrates some of the mechanisms that generate the different classes of inactive polymer molecules. For example, PS homopolymer may be produced by combination termination [Fig. 1(a)]. By reaction of two primary rubber radicals, a pure crosslink is obtained. When such rubber radicals are PB homoradicals, then crosslinked PB is generated [Fig. 1(b)]. PS branches may be linked onto a PB chain by one end ("T" grafting) or onto two different PB chains by both ends ("H" grafting). T grafts may be produced by chain transfer (not shown), or by combination termination [Fig. 1(c)]. H grafts can be created only by combination termination [Fig. 1(d)]. While T grafting does not alter the total number of copolymer plus (residual or crosslinked) PB molecules, H grafting and pure crosslinking both reduce such number. Clearly, H grafting is a special kind of crosslinking that involves a PS chain.

In the second column of Table I, the detailed kinetics is presented. It can be shown that by appropriate summations on the independent variables  $p$ ,  $p_1$ ,  $q$ ,  $q_1$ ,  $s$ ,  $s_1$ ,  $b$ , and  $b_1$ , the global kinetics in the first column of Table I may be recuperated. As in Estenoz and Meira,<sup>34</sup> a copolymer topology is characterized by the pair of integers  $(p, q)$ , where  $p \geq 1$  and  $q \geq 1$ , respectively, indicate the number of PS and PB chains per molecule. The residual (unreacted) PB and the crosslinked PB are considered special topologies with  $(p = 0, q = 1)$  and  $(p = 0, q = 2, 3, \dots)$ , respectively. The following nomenclature is utilized:  $P_{(p,q)}$  indistinctly represents an inactive accumulated copolymer of topology  $(p, q)$ , a residual PB of topology  $(0, 1)$ , or a pure crosslinked PB of topology  $(0, q)$ ;  $P_{(p,q)}(s, b)$  represents a molecular species of  $P_{(p,q)}$  containing  $s$  repetitive units of St and  $b$  repetitive units of B [in particular,  $P_{(0,1)}(0, b)$  represents the unreacted PB, and  $P_{(0,q)}(0, b)$  the crosslinked PB with  $q > 1$ ];  $P_{0(p,q)}^*(s, b)$  represents a primary rubber radical



**Figure 1** Possible mechanisms for obtaining: (a) free PS; (b) crosslinked PB; (c) T grafted copolymer; and (d) H grafted copolymer.

generated from an accumulated  $P_{(p,q)}(s, b)$  species [in particular,  $P_{0(0,1)}^*(0, b)$  and  $P_{0(0,q)}^*(0, b)$  are primary PB radicals]; and  $P_{n(p,q)}^*(s, b)$  represents a nonprimary copolymer radical generated from  $P_{0(p,q)}^*(s, b)$ , with a new growing branch containing  $n$  repetitive units of St.

Due to the possibility of pure crosslinking as in Figure 1(b), any combination of  $p$  and  $q$  is theoretically possible. In contrast, and as a consequence of a simpler kinetics, in Estenoz and Meira<sup>34</sup>  $p \geq q - 1$  was verified.

There is a single trifunctional branching point per T graft, and two trifunctional branching points per H graft or pure crosslink. It can be proven that the total number of trifunctional branching points per  $P_{(p,q)}(s, b)$  molecule is  $2(q - 1)$ .

Table II presents the nomenclature of the univariate and bivariate chain-length distributions that are calculated by our new mathematical model. In the case of the univariate distributions, the chain lengths can be simply transformed into molecular weights. Also, for any copolymer topology or for the total copolymer, the independent variables  $(s, b)$  may be transformed into  $(M, w_S)$ , where  $M (= sM_S + bM_B)$  is the molecular weight and  $w_S (= sM_S/M)$  is the copolymer composition or weight fraction of St. For example, the WCLD for the total copolymer  $G_C(s, b)$  yields the bivariate distribution of molecular weight and chemical composition  $G_C(M, w_S)$ . After such transformation, uniformly distributed points along the original independent variables  $s$  and  $b$  result in unevenly distributed points along  $M$  and

**Table II Nomenclature for Univariate and Bivariate Chain-Length Distributions**

Polymer Type	NCLD	WCLD
Free PS	$[S_n]V \equiv N_{PS}(n)$	$G_{PS}(n)$
Original PB	$[P_{(0,1)}(0, b)]V \equiv N_{PB}(n) \quad (n = b)$	$G_{PB}(n)$
Crosslinked PB of topology (0, q)	$[P_{(0,q)}(0, b)]V \equiv N_{(0,q)}(0, b) \quad (q > 1)$	$G_{(0,q)}(0, b)$
Total crosslinked PB	$N_{XB}(n)$	$G_{XB}(n)$
Copolymer of topology (p, q)	$[P_{(p,q)}(s, b)]V \equiv N_{(p,q)}(s, b)$	$G_{(p,q)}(s, b)$
Total copolymer	$N_C(s, b)$	$G_C(s, b)$

$w_S$ . For this reason, an appropriate discretization with a simultaneous heights transformation is required to represent the bivariate distribution by means of a continuous surface.

From the bivariate distribution of a given copolymer topology  $G_{(p,q)}(M, w_S)$  and after appropriate summations, the MWD represented by  $G_{(p,q)}(M)$  and the chemical composition distribution (CCD) represented by  $G_{(p,q)}(w_S)$  can be obtained.<sup>34</sup> Similarly, for the total copolymer,  $G_C(M)$  and  $G_C(w_S)$  can be derived from  $G_C(M, w_S)$ . From  $G_C(M)$  and  $G_C(w_S)$ , the average molecular weights and the global mass fraction of St in the copolymer can be calculated. However, due to the loss of information introduced by the change in independent variables, it is numerically preferable to obtain such averages directly from the bivariate WCLD.<sup>34</sup>

### Homogeneous Model

From the global kinetics of Table I and assuming a homogeneous polymerization, the mathematical model of Appendix A can be derived. We have called this part of the model the basic module. It allows the calculation of not only most of the global variables (such as conversion, initiator concentration, and number-average molecular weight of the total copolymer), but also the univariate NCLDs (number CLDs) for free PS, the residual PB, and the total crosslinked PB. The basic module is self-sufficient in the sense that it may be independently solved by standard numerical methods appropriate for "stiff" differential equations.

The part of the model based on the detailed kinetics of Table I is termed the copolymer distribution module (CDM). This module is derived in Appendix B. It calculates the bivariate distributions of the total copolymer and of the individual topologies, together with the univariate distributions of each crosslinked PB topology. The final expressions are eqs. (B.24) and (B.26), and (B.27)–(B.29). For their resolution, the basic module results are required. Note that eq. (B.27) directly calculates the

bivariate distribution for the total copolymer, without the need for obtaining each of the individual topology distributions.

In the basic module and in the CDM, discrete distributions must be calculated. To avoid integrating a differential equation for every possible chain length, many molecular species can be lumped together at fixed chain-length intervals. In the present work,  $\Delta s = 200$  and  $\Delta b = 600$  were sought, with the aim of producing approximately 100 independent points in each chain-length axis. This discretization was proven insufficient for the low molecular weight components, however; and for this reason the first interval had to be further divided into 100 subintervals.

In the CDM, a very large number of differential equations must be solved. For example, in the integration of eq. (B.24), 250,000 differential equations must be solved at the end of the simulation. This corresponds to the independent calculation of 25 copolymer topologies with 10,000 points in their corresponding bivariate distribution. To integrate the CDM, an "ad hoc" numerical method with fixed (and larger) integration steps was applied. For each fixed time interval, it essentially consists in "distributing" the newly generated PS branches and pure crosslinks among the produced rubber radicals. Through this crude procedure, relatively accurate results can be obtained, however. The reason for this is that the reacted masses are all accurately estimated in the basic module, and therefore possible integration errors are not accumulated along the solution.

The proposed model does not include an energy balance. However, nonisothermal reactions can be simulated through the use of standard or modified Arrhenius expressions for the kinetic constants.<sup>23,27,33</sup> When imposing a temperature profile, we shall assume that the reactor cooling/heating system is ideal, in the sense that it is capable of exactly following such a profile.

The computer program was written in Watcom™ Fortran for a 486 IBM compatible PC. A typical

simulation consumed about 3 s to solve the basic module, 14 min to calculate the bivariate distribution of the total copolymer through eq. (B.27), and 7 h to solve the bivariate distributions of the generated copolymer topologies [eq. (B.24)].

## SIMULATED ISOTHERMAL EXAMPLES

### Low-Temperature Solution Case

The simulation presented in Estenoz and Meira<sup>34</sup> was reattempted here. It was based on run 8 of Brydon et al.,<sup>10,28</sup> that considers a reaction carried out up to 18% conversion at 60°C in dilute benzene solution with benzoyl peroxide (BPO) as initiator. The kinetic constants are presented in the second column of Table III. For the reactions contemplated in the simpler mechanism of Estenoz and Meira, the same values for the kinetic constants were adopted.<sup>34</sup> Simulation results are not presented here because they practically coincide with those of Estenoz and Meira.<sup>34</sup> (A maximum deviation of 1.8% in one of the predicted global values was observed.) This confirms that at low temperatures and conversions

chemical initiation dominates thermal initiation, while most of the dead polymer (free PS and graft copolymer) is produced by combination termination (rather than by chain transfer).

### High-Temperature Bulk Case

Following Peng,<sup>33</sup> the bulk polymerization of St with 5% PB at 150°C and without chemical initiation was simulated. From the reported molecular weight averages for the initial PB ( $\bar{M}_{n,PB}^o$  104,000 and  $\bar{M}_{w,PB}^o$  237,000),<sup>33</sup> a "most probable" or Schulz-Flory MWD with the same  $\bar{M}_{n,PB}^o$  but  $\bar{M}_{w,PB}^o/\bar{M}_{n,PB}^o = 2$  was assumed.

The kinetic constants presented in the third column of Table III were adopted. They coincide with those in Peng,<sup>33</sup> except for the ratio  $k_{fM}/k_{fG}$  that was set to 7.5 instead of 13, for a better adjustment of the measurements. The reaction rates not contemplated in Peng,<sup>33</sup> were set to zero.

The level of grafting, defined in Peng<sup>33</sup> as the total mass of grafted St with respect to the initial PB mass, was simulated and experimentally mea-

**Table III** Empyred Kinetic Constants

	Low Temperature Solution Case ( $T = 60^\circ\text{C}$ )	High Temperature Bulk Case ( $T = 150^\circ\text{C}$ )	Experimental Nonisothermal Examples ( $70^\circ\text{C} \leq T \leq 150^\circ\text{C}$ )
$k_d$	$2.0 \times 10^{-6}$ (BPO), <sup>34</sup>	0	$9.13 \times 10^{13} e^{-29,608/RT}$ (TBPO) <sup>a</sup>
$k_{i0}$	$6.2 \times 10^{-14}$ , <sup>33</sup>	$9.03 \times 10^{-10}$ , <sup>33</sup>	$2.10 \times 10^6 e^{-15,000/T}$ , <sup>b,24,26,27,33,40</sup>
$k_{i1}$	140, <sup>34</sup>	0	$8.37 \times 10^5 e^{-2,650/T}$ , <sup>34</sup>
$k_{i2}$	88 <sup>34</sup>	0	$5.27 \times 10^5 e^{-2650/T}$ , <sup>34</sup>
$k_{i3}$	160, <sup>34</sup>	1415, <sup>33</sup>	$9.56 \times 10^5 e^{-2,600/T}$ , <sup>34</sup>
$k_p$	160, <sup>34</sup>	1415, <sup>33</sup>	$9.56 \times 10^5 e^{-2600/T}$ , <sup>b,24,26,27,33,40</sup>
$k'_{fM}, k''_{fM}, k'''_{fM}$	0.0048, <sup>40</sup>	$257000 e^{-(13.5+1.26x)}$ , <sup>33</sup>	$7.81 \times 10^6 e^{-6435/T}$ , <sup>b,24,26,27,33,40</sup>
$k_{fG}$	0.032, <sup>40</sup>	$\frac{k'_{fM}}{7.5}$ , <sup>b</sup>	$1.11 \times 10^{10} e^{-8898/T}$ , <sup>b,24,26,27,33,40</sup>
$k_{t_c}, k'_{t_c}, k''_{t_c}$	$6.4 \times 10^6$ , <sup>34</sup>	$2.25 \times 10^8 e^{-0.86x-14.8x^2+0.58x^2}$ , <sup>33</sup>	$1.66 \times 10^9 e^{-(843/T)-2(C_1x+C_2x^2+C_3x^3)}$ , <sup>c,37</sup>
$k_{t_d}, k'_{t_d}, k''_{t_d}$	0	0	0

<sup>a</sup> Obtained from manufacturer data.

<sup>b</sup> Adjusted in this work.

<sup>c</sup>  $C_1 = 2.57 - 0.00505T$ ;  $C_2 = 9.56 - 0.0176T$ ;  $C_3 = -3.03 + 0.00785T$ .

sured in that publication. In our nomenclature, this variable is represented by:  $(G_{ST} + G_{SH}/G_{PB}^0)$  [see eqs. (A.30) and (A.31)]. In Figure 2(a), the levels of grafting presented in Peng<sup>33</sup> are compared with our predictions, and practically coincident results are observed. Further simulation results by our new model are presented in Figures 2(b–d). In Figure 2(b), the total mass of topology (1, 1) starts to fall at around 80% conversion due to the grafting-over-grafting process. In Figures 2(c) and (d), the MWDs of the final polymer constituents at 98% conversion are presented.

## EXPERIMENTAL

### Nonisothermal Examples

Five nonisothermal batch polymerizations were carried out by one of us (H.O.) to validate the proposed model. Essentially, the experiments involved a (well-stirred) prepolymerization stage interrupted at 30% conversion, followed by an unstirred finishing stage in small glass ampoules at 150°C for 8 h. For the prepolymerization, different combinations of temperatures, initiator concentrations, and solvent concentrations were used (indicated in the first rows of Table IV). In the two experiments where solvent was incorporated, this component was eliminated in a final devolatilization stage. Consider first the employed reagents.

Styrene from Chevron was utilized, after elimination of the stabilizer (terbutylcatechol) as follows: a 10% water solution of NaOH was added, the mixture was washed several times with demineralized water, and the monomer was finally dried with silica gel.

Approximately 6% in weight of medium-*cis* anionic PB from Enichem was used. The polymer was assumed linear, and its MWD determined by SEC (ALC/GPC 244 from Waters Assoc.), after a calibration with narrow PB standards from Polyscience, Inc. The distribution was used as shown, without adjustment to any specific analytical expression. The average molecular weights resulted in  $\bar{M}_{n,PB}^0$  of 115,385 and  $\bar{M}_{w,PB}^0$  of 221,154. The concentration of unreacted B units in the initial PB was  $[B^*]^0 = 1.02$  mol/L.

*tert*-Butyl peroxoate (TBPO) from Akzo Chemicals was the employed (liquid) initiator. Its purity (89.29%) was determined as in ASTM D 2340-82. It implies the addition of NaI followed by a titration (with sodium thiosulfate) of the liberated iodine. In benzene solutions, the manufacturer reported initiator half-lives of 1 and 10 h at 92° and 74°C, re-

spectively. The experiments with higher prepolymerization temperatures did not include chemical initiation.

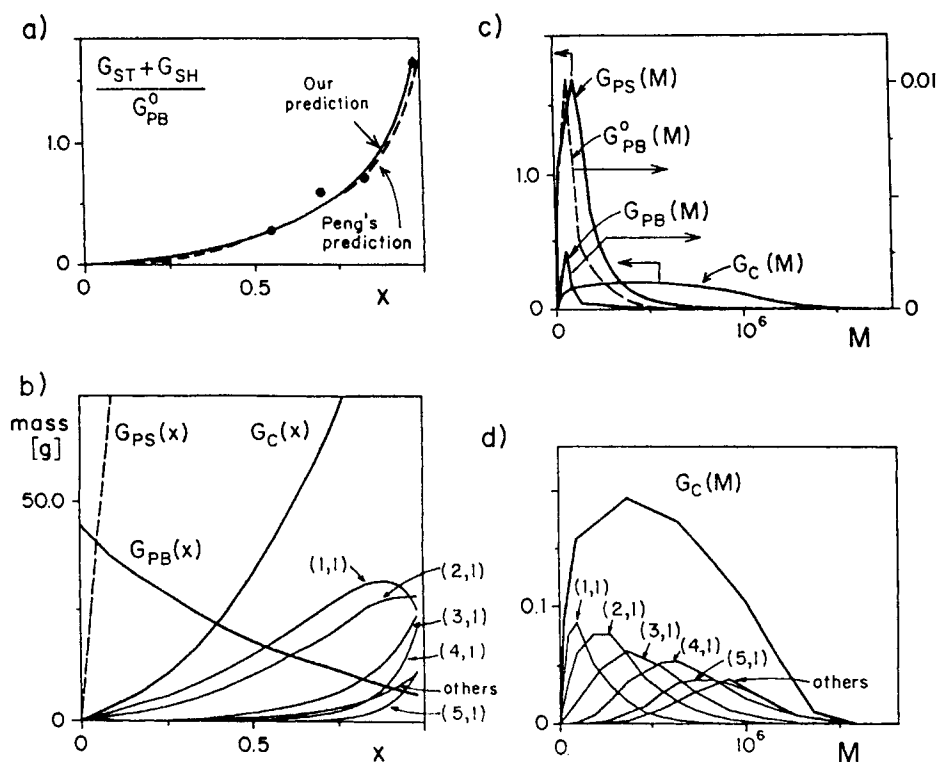
A Polygard<sup>TM</sup> mixture of di/trinonyl-phenylphosphite and tri-isopropanol amine from Uniroyal was used as the antioxidizing agent to protect the rubber during the dissolution period.

In the experiments with prepolymerization temperature at 120°C, 10% in volume of ethyl benzene solvent was added to prevent “hot points” and/or reaction runaways.

The dissolution and prepolymerization stages were carried out in a 2.5-L stainless steel Büchi Autoclave BEP 280 reactor fit with a turbine stirrer. The dissolution stage was implemented as follows: all reagents were loaded, except for the initiator; nitrogen was bubbled to eliminate oxygen, maintaining a residual pressure of 75 kPa; the dissolution operation involved 3 h at 70°C, with stirring at 250 rpm; and a sample was finally taken to verify solution homogeneity. The prepolymerization stage involved the following steps: the reactor was depressurized to allow initiator addition (when required); a nitrogen purge was implemented and the stirring speed was set at 125 rpm; temperature was increased from 70°C at 1°C/min until the required prepolymerization temperature (90° or 120°C) was reached; the  $30 \pm 2.00\%$  conversion point was detected by linear extrapolation of the conversion plot (in turn estimated by gravimetry of the solid contents). Defining the initial time at the start of the dissolution period, the time at the end of the prepolymerization stage was determined.

For the finishing stage, the prepolymer was first loaded into 5-mm o.d. glass tubes by means of a vacuum pump. The ampoules were sealed and maintained for 8 h in an isothermal bath at 150°C. The final conversions were not measured, but assumed to be 95% or higher. The glass ampoules were then introduced into cold water and broken. The product was recuperated in the form of “spaghettis.” In the experiments where solvent was added, the devolatilization stage consisted of heating the “spaghettis” up to 140°C, compressing the melt into thin films, and maintaining the films under vacuum at 80°C for 15 min.

The final product was analyzed to determine: the total mass of copolymer plus initial or purely cross-linked PB, by gravimetry; the St grafting efficiency (i.e., percent of grafted St with respect to the total polymerized St), by gravimetry; and the average molecular weights of the free PS, via SEC. For one of the samples, the total mass of copolymer plus PB



**Figure 2** A simulated high-temperature bulk polymerization. (a) The level of grafting from Peng<sup>33</sup> is compared with our prediction. (b) Masses of free PS ( $G_{PS}$ ), of residual monomer ( $G_{PB}$ ), of total copolymer ( $G_C$ ), and of individual topologies. (c) MWDs for the final polymer constituents. (d) MWDs of the generated copolymer topologies. All unidentified and nonreacting topologies are lumped together in the curves indicated others.

was also estimated through the analysis of the final particle morphology.

In the gravimetric method, a solvent extraction technique similar to that described in Peng<sup>33</sup> was employed. The basic assumption was that all free PS could be dissolved in methyl ethyl ketone (MEK), while the copolymer and the PB homopolymer both remained insoluble. Unfortunately, the procedure is expected to provide estimations in excess,<sup>33</sup> due to the impossibility of completely dissolving the free PS occluded in the rubber particles. This error is in part compensated for by the low molecular weight copolymer that is inevitably washed out by the solvent. The technique involved the following steps:  $0.200 \pm 0.001$  g of HIPS were loaded into a centrifuge tube containing 10 mL of MEK. The tube was shaken for 2 h, and centrifuged for 3 h. The soluble portion was poured on an aluminum plate and 10 mL of MEK were added into the insolubles. The dispersion was shaken for 12 h, centrifuged for 3 h, and the solubles separated as before. A final cycle of solvent addition, 2 h agitation, 3 h centrifugation, and solubles extraction was implemented. The

metal plates and the centrifuge tube were dried under vacuum until constant weight. The total mass of insolubles (i.e., final copolymer plus initial or purely crosslinked PB) was obtained from the weight of the centrifuge tube. The free PS was obtained by adding the solid contents of all extracted solutions. The grafted PS was determined by subtracting the insolubles' weight from the initial PB mass; and the St grafting efficiency was finally calculated.

Bearing in mind the errors in excess of the gravimetric method with regard to total rubber mass, this quantity was independently estimated from electron microscopy of the final particle morphology. The measurement involved a discretization of the micrographs. The relative amount of rubber with respect to the total mass was determined from the fraction of the rubber area with respect to the total area. To this effect, all darker areas were assumed to be either copolymer or PB, and a compensation for the variation in the densities between the two homopolymers was also introduced. Finally, the ratio between the final and initial rubber contents could be calculated.



Table IV Experimental Conditions and Global Results

Experimental conditions	Experiment				
	1	2	3	4	5
Prepolymerization temperature (°C)	90	90	90	120	120
St (wt %)	94.000	93.991	93.972	84.600	84.591
PB (wt %)	6.000	5.999	5.998	5.400	5.399
Solvent (wt %)	0	0	0	10	10
Initiator (wt %)	0	0.01	0.03	0	0.01
<b>Measurements and predictions</b>					
Time for $x = 0.3$ (min)	890.0	620.0	510.0	470.0	400.0
Rubber ratio at $x = 0.95$	(893.0)	(630.0)	(530.0)	(471.0)	(401.8)
	1.67 <sup>a</sup>	2.41 <sup>a</sup>	3.04 <sup>a</sup>	3.43 <sup>a</sup>	4.23 <sup>a</sup>
	(1.61) <sup>b</sup>	(1.74) <sup>b</sup>	(1.91) <sup>b</sup>	(3.33) <sup>b</sup>	(3.44) <sup>b</sup>
$\bar{M}_{n,PS} \times 10^{-3}$ at $x = 0.95$	94.00 <sup>d</sup>	83.50 <sup>d</sup>	88.30 <sup>d</sup>	70.60 <sup>d</sup>	68.30 <sup>d</sup>
$\bar{M}_{w,PS} \times 10^{-3}$ at $x = 0.95$	278.3 <sup>d</sup>	233.4 <sup>d</sup>	227.2 <sup>d</sup>	193.4 <sup>d</sup>	178.1 <sup>d</sup>
St grafting efficiency <sup>e</sup> at $x = 0.95$	0.043 <sup>a</sup>	0.090 <sup>a</sup>	0.13 <sup>a</sup>	0.155 <sup>a</sup>	0.212 <sup>a</sup>
	(0.041)	(0.050)	(0.061)	(0.155)	(0.164)

The predicted values are indicated in parentheses after the experimental measurements.

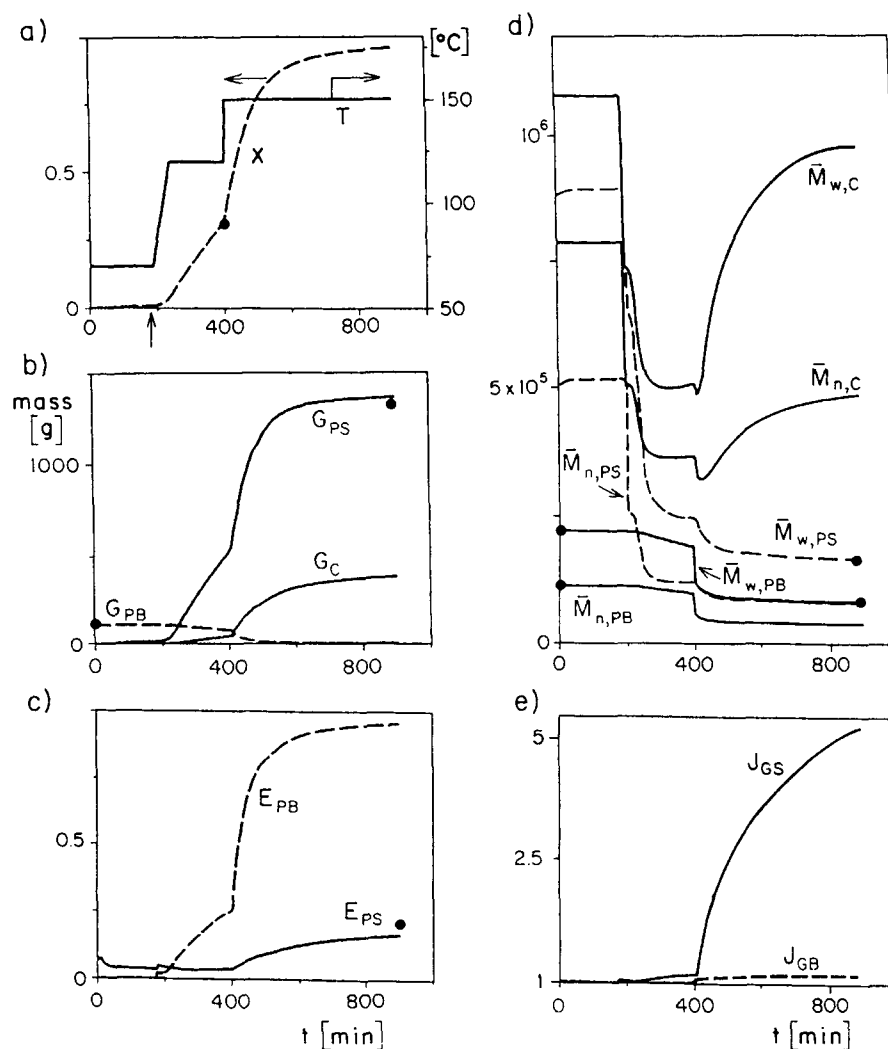
<sup>a</sup> Estimated by gravimetry.

<sup>b</sup> Obtained from  $(G_C + G_{PB} + G_{XB})/G_{PB}^0$ .

<sup>c</sup> Estimated from particle morphology.

<sup>d</sup> Estimated from SEC measurements.

<sup>e</sup> Ratio of graft bound St mass and total bound St mass.



**Figure 3** Evolution of the main variables in experiment 5: (a) applied temperature profile and resulting conversion; (b) accumulated masses of unreacted PB, free PS, and copolymer; (c) grafting efficiencies; (d) average molecular weights; (e) average numbers of PB and PS chains per copolymer molecule.

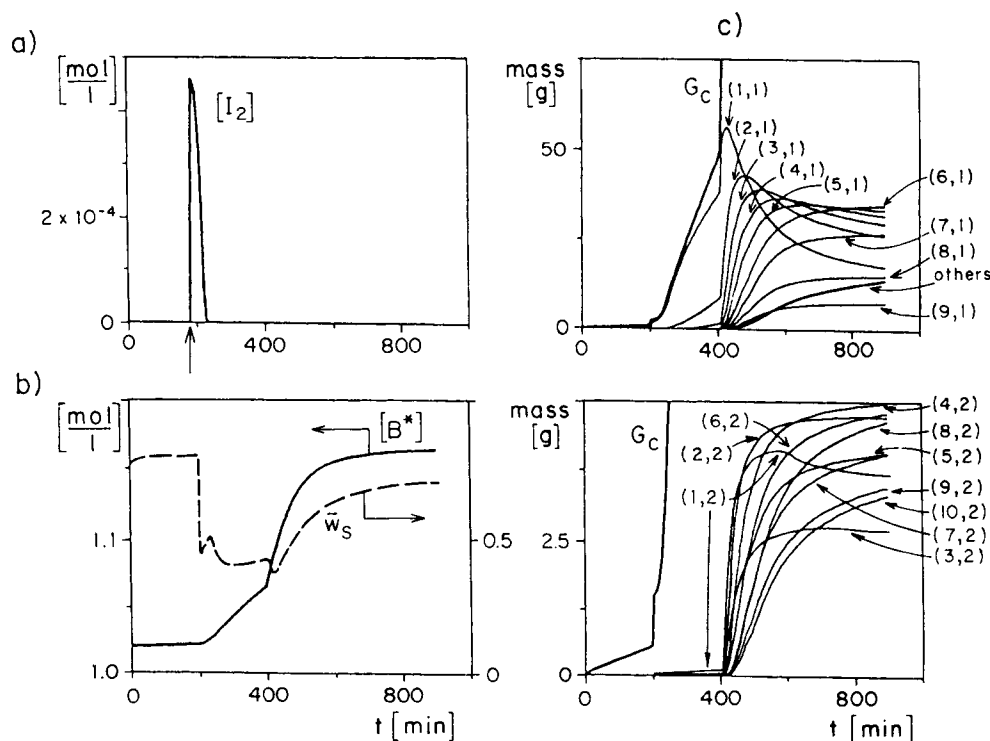
For the PS average molecular weights, a Du Pont LC 870 size exclusion chromatograph fitted with Zorbax™ PSM 60S and PSM 1000S columns, was employed. The PS samples were taken from the first extraction of the St grafting efficiency determination.

Consider some of the experimental results of Table IV. The average molecular weights of the final free PS are similar to the average molecular weights of the original PB. Also, the ratio of the final total rubber (i.e., copolymer plus PB) with respect to the initial PB mass is relatively high. If the average molecular weights of the grafted St chains are similar to those of the free PS, then the previous arguments suggest that at the end of the polymerization, most

of the PB must have been transformed into graft copolymer, with more than one graft per original PB chain.

### Model Adjustment

The adopted kinetic parameters are presented in the last column of Table III. Their adjustment was obtained as follows. The expressions for  $k_d$ ,  $k_{i1}$ ,  $k_{i2}$ ,  $k_{i3}$ , and the termination constants were taken from published data. The parameters  $k_{io}$ ,  $k_{fm}$ ,  $k_p$ , and  $k_{fg}$  were adjusted within the values referenced in Table III, to fit the experimental measurements presented in Table IV.



**Figure 4** Evolution of more global variables in experiment 5: (a) initiator concentration; (b) global mass fraction of St in the copolymer and total concentration of unreacted B units; (c) masses of generated topologies.

All measured variables were estimated through the basic module; and due to the very short simulation times required, the adjustment could be interactively performed. Only experiments 2 and 5 were used for the adjustment. These experiments employ the same initiator concentration but different pre-polymerization temperatures, thus allowing an adequate fit of the exponential terms. In a first stage,  $k_{io}$ ,  $k_{fM}$ , and  $k_p$  were adjusted through the following procedure: the pre-polymerization times were fit with  $k_{io}$  and  $k_p$ , and the  $\bar{M}_n$ 's of the free PS were fit with  $k_{fM}$ ; if the predictions for  $\bar{M}_{w,PS}$  differed from the measurements, then a new set of parameters was found in the first step; otherwise, convergence was reached. The second stage involved the adjustment of  $k_{fg}$  using the measured St grafting efficiencies ( $E_{PS}$ ). The latter stage is relatively independent from the former, because variations of  $k_{fg}$  have little effect on the St homopolymerization, and therefore on the first-adjusted measurements.

### Simulation Results

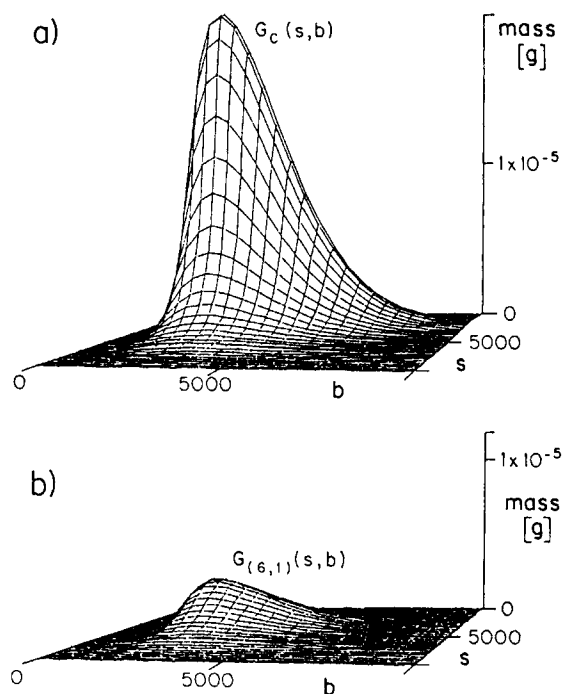
As can be observed in Table IV, a reasonable agreement between predicted and measured values for all five experiments was obtained. The greater differ-

ences appear in the final rubber ratio and in the final St grafting efficiency ( $E_{PS}$ ), because (as explained before) the gravimetric measurements are expected to be in excess.

Consider in the following the detailed results of experiment 5 presented in Figures 3–6 and in Table IV. In Figs. 3 and 4, the time evolution of most global variables are presented.

In the dissolution stage, the rate of polymerization is low due to the relatively slow thermal monomer decomposition at 70°C [Figs. 3(a,b)]. The negligible amount of copolymer generated in this stage is mainly topology (1, 1), with a smaller contribution of topology (1, 2). This copolymer mixture presents a relatively high molecular weight [Fig. 3(d)] because: at 70°C the PS branches are principally produced by combination termination; and at the beginning of the polymerization, the high molecular weight fractions of the initial PB are the first to react, due to their highest grafting probability. (For the same reason, the average molecular weight of the residual PB diminishes monotonically along the polymerization.)

The pre-polymerization stage started at  $t = 180$  min, with the addition of the chemical initiator and the simultaneous temperature increase at 1°C/min



**Figure 5** Experiment 5: Final bivariate NCLDs for the (a) total copolymer and the (b) most abundant copolymer topology.

until 120°C was reached. At the beginning of this stage, a dramatic decrease in the molecular weights of the accumulated free PS is observed [Figs. 3(a,d)]. This is due to the initiator decomposition and to the fact that at increased temperatures, transfer to the monomer predominates with respect to termination. Due to its relatively short half-life, the initiator is totally consumed within an hour, while the monomer conversion is still below 10% [Figs. 3(a) and 4(a)]. Possibly, the main role of the initiator is to increase the amount of graft copolymer produced at the beginning of the polymerization, thus favoring the processes of phase separation and phase inversion. Experimentally, the prepolymerization finished at  $t = 400$  min. This time differs slightly from the simulated value (401.8 min), because the computer program waited until 30% conversion was reached before commencing the finishing stage.

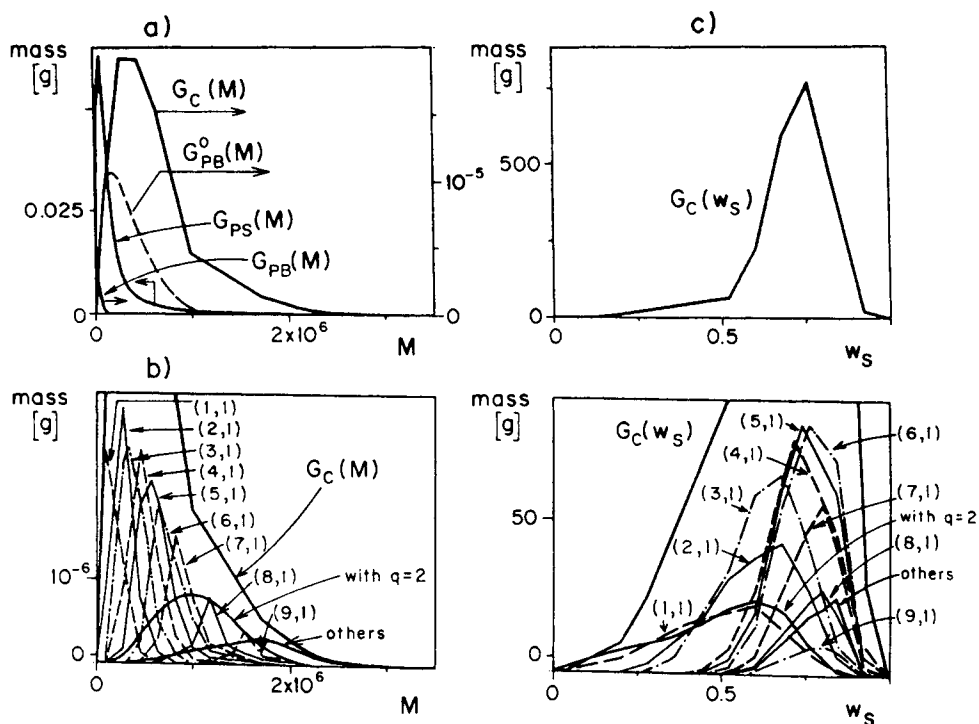
The sudden temperature rise at the start of the finishing stage determined a great increase in the rates of polymerization and grafting, and a further decrease in the molecular weights when transfer to the monomer becomes dominant. Grafting-over-grafting also becomes important at this stage, as is indicated by the increments in: the masses of free PS and copolymer [ $G_{PS}$  and  $G_C$  in Fig. 3(b); eqs. (A.29) and (A.54)]; the PB and PS grafting efficien-

cies [ $E_{PB}$  and  $E_{PS}$  in Fig. 3(c); eqs. (A.55) and (A.56)]; the number of PS and PB branches per molecule [ $J_{GS}$  and  $J_{GB}$  in Fig. 3(e); eqs. (B.29) and (A.57)]; and the masses of generated topologies [Fig. 4(c)]. The copolymer molecular weights first drop due to the new (shorter) PS branches, but then rapidly grow as a consequence of the grafting-over-grafting process [Fig. 3(d)]. At the start of the finishing stage, the most abundant topology was (1, 1). But at the end of the polymerization, the most abundant topologies resulted in (6, 1), (5, 1), and (4, 1). At 150°C, an increased level of crosslinking between primary rubber radicals is evidenced by the production of copolymer with two PB chains per molecule [lower half of Fig. 4(c)]. A negligible amount of crosslinked PB was produced, and for this reason it is not presented in the results. Due to computer memory limitations, the higher topologies presenting a very low mass (and mainly produced during the second half of the polymerization) were lumped into the curve named "others" [Fig. 4(c)]. If the mass of this curve had been significant, then it would have been necessary to increase the number of individual topologies.

In Fig. 4(b), the global mass fraction of St in the accumulated copolymer ( $\bar{w}_S$ ) and the total concentration of unreacted B units ( $[B^*]$ ) present in the copolymer or in the (original or crosslinked) PB are represented. As expected,  $\bar{w}_S$  grows in the finishing stage, when grafting-over-grafting becomes important. The rise in  $[B^*]$  is a consequence of the volume contraction, and in fact a small drop of 0.89% was observed in the total moles of unreacted B units.

Consider now in more detail the product quality at 95% conversion, i.e. at the polymerization end. The weight percent of the main polymer constituents resulted in: free PS, 77.8%; graft copolymer, 22.0%; initial PB, 0.15%; and purely crosslinked PB, 0.05%. The average molecular weights of the final PS and the copolymer resulted in:  $\bar{M}_{n,PS} = 69,400$ ;  $\bar{M}_{w,PS} = 171,500$ ;  $\bar{M}_{n,C} = 492,400$ ; and  $\bar{M}_{w,C} = 976,000$ . The final average copolymer contains a 72.2% in weight of St, 5.19 PS chains per molecule, and 1.13 PB chains per molecule.

Finally, consider in Figs. 5 and 6 the predicted distributions at the end of the polymerization. Figure 5 represents the final bivariate WCLDs for the total copolymer and for the most abundant topology (1, 6). Smooth surfaces are observed in both cases. In Figure 6(a) the MWDs of the final polymer constituents and of the original PB are represented. Figure 6b illustrates how the final copolymer MWD is built up of the individual topology distributions. In that figure, all species with two PB chains per molecule



**Figure 6** Final univariate distributions in experiment 5: (a) MWDs for the final polymer constituents and for the original PB; (b) MWDs for the final copolymer and main topologies; (c) CCDs for the final copolymer (upper curve) and for the main topologies (lower curves).

were added together in the curve named with  $q = 2$ . The curve termed others indicates the lumped (unidentified) topologies. As expected, high topologies also exhibit relatively large molecular weights. In Figure 6(c), the CCD for the total copolymer and main topologies are represented. The larger the number of PS branches per molecule, the higher the corresponding average composition.

## CONCLUSIONS

This work constitutes the first attempt at estimating the detailed molecular macrostructure generated in a bulk polymerization of St in the presence of PB. The model was validated with literature results and through a batch polymerization designed to emulate a nonisothermal bulk HIPS process. An important result is that at the end of the polymerization, practically all the rubber is transformed into copolymer. Most of the final copolymer contains between two and seven PS branches grafted onto a single PB chain; and less than 10% of the molecules contain two or more PB branches that are produced via crosslinking (by reaction of two primary rubber radicals or by *H* grafting). *H* grafting occurs prin-

cipally at the beginning of the polymerization, when termination is mainly by combination. The graft copolymer produced at the beginning of the polymerization may play an important role by accumulating at the interfaces and favoring the phase separation and phase inversion. Crosslinking of primary rubber radicals is important at the final stages of the polymerization when the rubber radical concentration becomes significant vis-à-vis the residual monomer concentration. Crosslinking of rubber radicals may "explode" above 98% conversion, and further experiments are required to determine the real significance of this process.

With the present analytical technology, it is impossible to verify the predicted distributions for each of the generated copolymer topologies. Even the analysis of the total copolymer is complicated because of the impossibility of quantitatively extracting the occluded PS and the PB homopolymer from the copolymer. After an appropriate copolymer isolation and neglecting the effect of branching on hydrodynamic volume, then it should be possible to estimate the univariate distributions of molecular weights and composition via dual-detection SEC.<sup>41</sup> Furthermore, by combining SEC with thin-layer chromatography and/or with gra-

dient high-performance liquid chromatography, it may be feasible to measure the bivariate distributions of molecular weight and chemical composition.

Possible extensions of the mathematical model are:

1. simulation of an industrial (and continuous) HIPS process, with the aim of optimizing polymer properties and/or process conditions;
2. extensions to other graft polymerizations such as the production of ABS (acrylonitrile BSt) via the emulsion process; and
3. relaxation of the homogeneous hypothesis, with calculation of the polymerization in two phases and estimation of the developed particle morphology.

The authors wish to acknowledge: CONICET, Universidad Nacional del Litoral, CONDES-LUZ, and Universidad del Zulia for their financial support; and INDESCA (Venezuela) for the molecular weight determinations.

## APPENDIX A: BASIC MODULE

The material balances that follow may be written on the basis of the global mechanism of Table I.

### Main Balances

#### Initiator

$$\frac{d}{dt}([I_2]V) = -fk_d[I_2]V. \quad (\text{A.1})$$

#### Monomer

Call  $[S^*]$  and  $[P^*]$  the total concentrations of  $S_n^*$  and  $P_n^*$  radicals, respectively, that is:

$$[S^*] = \sum_{n=1}^{\infty} [S_n^*] \quad (\text{A.2})$$

$$[P^*] = \sum_{n=1}^{\infty} [P_n^*] \quad (\text{A.3})$$

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

$$\begin{aligned} \frac{d}{dt}([St]V) &= -R_p V \\ &= -k_p[St]([S^*] + [P^*])V \quad (\text{A.4}) \end{aligned}$$

where  $R_p$  is the global rate of St consumption.

### Unreacted B Units

Let us represent with  $B^*$  any unreacted B unit present in the copolymer or in the (initial or crosslinked) PB. Every time a  $P$  molecule is attacked, one  $B^*$  unit is consumed; and when a  $P_0^*$  radical terminates, one  $B^*$  unit is regenerated. Thus,

$$\begin{aligned} \frac{d}{dt}([B^*]V) &= -\{k_{i2}[I^*] + k_{fg}([S^*] + [P^*])\}[B^*]V \\ &\quad + \{k'_{fM}[St] + k''_{td}([S^*] + [P^*]) \\ &\quad + k'_{td}[P_0^*]\}[P_0^*]V. \quad (\text{A.5}) \end{aligned}$$

### Radical Species

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

$$\begin{aligned} \frac{d}{dt}\{[I^*]V\} &= \{2fk_d[I_2] \\ &\quad - (k_{i1}[St] + k_{i2}[B^*])[I^*]\}V \simeq 0 \quad (\text{A.6}) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt}\{[S_1^*]V\} &= \{k_{i1}[S][I^*] + 3k_{io}[St]^3 \\ &\quad - k_p[St][S_1^*] + k'_{fM}[St][P_0^*] + k_{fM}[St] \\ &\quad \times ([S^*] + [P^*])\}V - \{k_{fg}[B^*] \\ &\quad + (k_{tc} + k_{td})([S^*] + [P^*]) + (k''_{tc} + k''_{td})[P_0^*] \\ &\quad + k_{fM}[St]\}[S_1^*]V \simeq 0 \quad (\text{A.7}) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt}\{[S_n^*]V\} &= k_p[St][S_{n-1}^*]V \\ &\quad - \{(k_p[St] + k_{fM}[St] + k_{fg}[B^*] \\ &\quad + (k_{tc} + k_{td})([S^*] + [P^*]) \\ &\quad + (k''_{tc} + k''_{td})[P_0^*]\}[S_n^*]V \simeq 0 \\ &\quad n = 2, 3, 4, \dots \quad (\text{A.8}) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt}\{[P_0^*]V\} &= \{k_{i2}[I^*] + k_{fg}([S^*] + [P^*])\}[B^*]V \\ &\quad - \{k_{i3}[St] + k'_{fM}[St] + (k'_{tc} + k'_{td})[P_0^*] \\ &\quad + (k''_{tc} + k''_{td})([S^*] + [P^*])\}[P_0^*]V \simeq 0 \quad (\text{A.9}) \end{aligned}$$

$$\frac{d}{dt}\{[P_1^*]V\} = k_{i3}[St][P_0^*]V$$

$$\begin{aligned}
 & - \{ (k_p[St] + k_{fM}[St] + k_{fG}[B^*]) \\
 & + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
 & + (k''_{t_c} + k''_{t_d})[P_0^*] \} [P_1^*] V \simeq 0 \quad (\text{A.10})
 \end{aligned}$$

$$\begin{aligned}
 \frac{d}{dt} \{ [P_n^*] V \} & = k_p[St][P_{n-1}^*] V \\
 & - \{ (k_p[St] + k_{fM}[St] + k_{fG}[B^*]) \\
 & + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
 & + (k''_{t_c} + k''_{t_d})[P_0^*] \} [P_n^*] V \simeq 0 \\
 & \quad n = 2, 3, 4, \dots \quad (\text{A.11})
 \end{aligned}$$

From eq. (A.6), one obtains:

$$[I^*] = \frac{2fk_d[I_2]}{k_{i1}[St] + k_{i2}[B^*]} \quad (\text{A.12})$$

Adding up eq. (A.7) with eq. (A.8) over all  $n$ 's; and eq. (A.10) with eq. (A.11) over all  $n$ 's, it can be written:

$$\begin{aligned}
 \frac{d}{dt} \{ [S^*] V \} & = \{ k_{i1}[St][I^*] + 3k_{i0}[St]^3 \\
 & + k'_{fM}[St][P_0^*] + k_{fM}[St][P^*] \} V \\
 & - \{ (k_{t_c} + k_{t_d})([S^*] + [P^*]) + (k''_{t_c} + k''_{t_d})[P_0^*] \\
 & + k_{fG}[B^*] \} [S^*] V \simeq 0 \quad (\text{A.13})
 \end{aligned}$$

$$\begin{aligned}
 \frac{d}{dt} \{ [P^*] V \} & = k_{i3}[St][P_0^*] V - \{ k_{fM}[St] + k_{fG}[B^*] \\
 & + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
 & + (k''_{t_c} + k''_{t_d})[P_0^*] \} [P^*] V \simeq 0. \quad (\text{A.14})
 \end{aligned}$$

From eq. (A.4), the global rate of monomer consumption is:

$$R_p = k_p[St]([S^*] + [P^*]). \quad (\text{A.15})$$

This rate is the result of three contributions:

$$R_p = R_{PPS} + R_{PST} + R_{PSH} \quad (\text{A.16})$$

where  $R_{PPS}$ ,  $R_{PST}$ , and  $R_{PSH}$ , respectively represent the consumption of monomer incorporated into: the accumulated free PS; the accumulated copolymer through  $T$  grafting; and the accumulated copolymer through  $H$  grafting. To find expressions for such individual rates, define first the molar ratio of free St homoradicals with respect to the total St radicals:

$$\varphi = \frac{[S^*]}{[S^*] + [P^*]}. \quad (\text{A.17})$$

The propagation rate of St with  $S^*$  is  $\varphi R_p$ ; the propagation rate of St with  $P^*$  is  $(1 - \varphi)R_p$ . Thus, the generation rate of PS homopolymer is obtained by multiplying  $\varphi R_p$  with the probability of  $S^*$  to transfer or terminate, resulting in:

$$\begin{aligned}
 R_{PPS} & = \varphi R_p \\
 & \times \frac{(k_{fM}[St] + k_{fG}[B^*] + k_{t_d}([S^*] + [P^*]) \\
 & + k_{t_c}[S^*] + k''_{t_d}[P_0^*])[S^*]}{(k_{fM}[St] + k_{fG}[B^*] \\
 & + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
 & + (k''_{t_c} + k''_{t_d})[P_0^*])[S^*]} \quad (\text{A.18})
 \end{aligned}$$

Similarly,  $R_{PSH}$  may be obtained by multiplying the rate of propagation of  $P^*$  with the probability of that copolymer radical to terminate either with another  $P^*$  or with a primary rubber radical  $P_0^*$ ; yielding:

$$\begin{aligned}
 R_{PSH} & = (1 - \varphi)R_p \frac{(k_{t_c}[P^*] + k''_{t_c}[P_0^*])[P^*]}{(k_{fM}[St] + k_{fG}[B^*] \\
 & + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
 & + (k''_{t_c} + k''_{t_d})[P_0^*])[P^*]} \quad (\text{A.19})
 \end{aligned}$$

Styrene is incorporated into T grafts through two possible mechanisms: combination of  $S^*$  with  $P^*$  or  $P_0^*$ ; or deactivation of  $P^*$  by transfer or disproportionation. Such contributions are respectively represented by the first and second terms in the right-hand side of the following expression:

$$\begin{aligned}
 R_{PST} & = R_p \varphi \frac{(k_{t_c}[P^*] + k''_{t_c}[P_0^*])[S^*]}{(k_{fM}[St] + k_{fG}[B^*] \\
 & + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
 & + (k''_{t_c} + k''_{t_d})[P_0^*])[S^*]} \\
 & + R_p \frac{(1 - \varphi)(k_{fM}[St] + k_{fG}[B^*] \\
 & + k_{t_d}([S^*] + [P^*]) \\
 & + k''_{t_d}[P_0^*] + k_{t_c}[S^*])[P^*]}{(k_{fM}[St] + k_{fG}[B^*] \\
 & + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
 & + (k''_{t_c} + k''_{t_d})[P_0^*])[P^*]} \quad (\text{A.20})
 \end{aligned}$$

Define now the following dimensionless kinetic parameters:

$$\beta = \frac{k_{t_c} R_p}{(k_p [St])^2} \quad (\text{A.21})$$

$$\tau = \frac{k_{fM}}{k_p} + \frac{k_{fG}[B^*]}{k_p [St]} + \frac{k_{t_d} R_p}{(k_p [St])^2} + \frac{k_{t_d}'' R_p}{(k_p [St])^2} + \gamma \tau_1 \quad (\text{A.22})$$

$$\tau_1 = \frac{k_{t_c}'' R_p}{(k_p [St])^2} \quad (\text{A.23})$$

$$\gamma = \frac{[P_0^*]}{[S^*] + [P^*]} \quad (\text{A.24})$$

$$\alpha = \tau + \beta. \quad (\text{A.25})$$

Introducing eqs. (A.15), (A.17), and (A.21)–(A.25) into eqs. (A.18)–(A.20), one finds:

$$R_{pPS} = \varphi R_p \frac{\tau - \gamma \tau_1 + \beta \varphi}{\alpha} \quad (\text{A.26})$$

$$R_{pST} = (1 - \varphi) R_p \frac{2\beta \varphi + \gamma \tau_1 \frac{\varphi}{1 - \varphi} + \tau - \gamma \tau_1}{\alpha} \quad (\text{A.27})$$

$$R_{pSH} = (1 - \varphi) R_p \frac{\beta(1 - \varphi) + \gamma \tau_1}{\alpha}. \quad (\text{A.28})$$

Call  $G_{PS}$ ,  $G_{ST}$ , and  $G_{SH}$  the accumulated masses of polymerized monomer associated to  $R_{pPS}$ ,  $R_{pST}$ , and  $R_{pSH}$ , respectively. Such masses may be obtained by integration of:

$$\begin{aligned} \frac{d(G_{PS})}{dt} &= R_{pPS} M_S V \\ &= \varphi R_p \frac{\tau - \gamma \tau_1 + \beta \varphi}{\alpha} M_S V \end{aligned} \quad (\text{A.29})$$

$$\begin{aligned} \frac{d(G_{ST})}{dt} &= R_{pST} M_S V = (1 - \varphi) R_p \\ &\times \frac{2\beta \varphi + \gamma \tau_1 \frac{\varphi}{1 - \varphi} + \tau - \gamma \tau_1}{\alpha} M_S V \end{aligned} \quad (\text{A.30})$$

$$\begin{aligned} \frac{d(G_{SH})}{dt} &= R_{pSH} M_S V \\ &= (1 - \varphi) R_p \frac{\beta(1 - \varphi) + \gamma \tau_1}{\alpha} M_S V. \end{aligned} \quad (\text{A.31})$$

The monomer conversion can be calculated from:

$$x = \frac{[St]^o V^o - [St] V}{[St]^o V^o} \quad (\text{A.32})$$

where superscript  $o$  indicates initial condition.

### Volume

For the evolution of reaction volume ( $V$ ), assume the following: a homogeneous bulk polymerization, simple volume addition, and a constant rubber volume (i.e., negligible grafting). Then, one can write:

$$V = V_S^o(1 - \epsilon x) + V_{PB}^o \quad (\text{A.33})$$

with:

$$\epsilon = \frac{V_S^o - V_{PS}^f}{V_S^o} \quad (\text{A.34})$$

where  $\epsilon$  is the PS homopolymer volume contraction factor;  $V_{PS}^f$  is the final volume of the free and grafted PS at full conversion; and  $V_S^o$  and  $V_{PB}^o$  are the initial pure St and pure PB volumes, respectively.

Equations (A.1), (A.4), (A.5), (A.9), (A.12)–(A.14), (A.21)–(A.25), and (A.29)–(A.34) can be simultaneously solved to find  $[I_2]$ ,  $[B^*]$ ,  $V$ ,  $\tau$ ,  $\tau_1$ ,  $\beta$ ,  $\gamma$ ,  $\varphi$ ,  $\alpha$ ,  $R_p$ ,  $G_{PS}$ ,  $G_{ST}$ ,  $G_{SH}$ , and  $x$ .

### NCLD of Free PS

The accumulated NCLD for the free PS can also be found from the global mechanism of Table I. A mass balance for each of the accumulated PS species yields:

$$\begin{aligned} \frac{d}{dt} ([S_n] V) &= \{k_{fM}[St] + k_{fG}[B^*] \\ &+ k_{t_d}([S^*] + [P^*]) + k_{t_d}''[P_0^*]\} [S_n^*] V \\ &+ \frac{k_{t_c}}{2} \sum_{m=1}^{n-1} [S_m^*][S_{n-m}^*] V \quad n = 1, 2, 3, \dots \end{aligned} \quad (\text{A.35})$$

Inserting eqs. (A.13), (A.15), (A.17), and (A.21)–(A.25) into eq. (A.7), one obtains:

$$[S_1^*] = \frac{\varphi R_p \alpha}{k_p [St](1 + \alpha)}. \quad (\text{A.36})$$

Similarly, inserting eqs. (A.13), (A.15), (A.17), and (A.21)–(A.25) into eq. (A.8) and solving the resulting recurrency formula, one finds:



$$[S_n^*] = \frac{\varphi R_p}{k_p [St]} \frac{\alpha}{(1 + \alpha)^n} \quad n = 2, 3, 4, \dots \quad (\text{A.37})$$

Inserting eqs. (A.36) and (A.37) into eq. (A.35), and remembering the definitions of  $\varphi$ ,  $\tau$ ,  $\tau_1$ ,  $\beta$ ,  $\gamma$ , and  $\alpha$ , one can obtain:

$$\frac{d}{dt} ([S_n]V) = \varphi R_p \alpha \left[ \tau - \gamma \tau_1 + \frac{1}{2} \beta \varphi \alpha n \right] (1 + \alpha)^{-n} V \quad n = 1, 2, 3, \dots \quad (\text{A.38})$$

For sufficiently high values of  $n$ ,  $(1 + \alpha)^{-n} \simeq e^{-\alpha n}$ . Thus, the NCLD of the accumulated free PS may be obtained by integration of:

$$\begin{aligned} \frac{d}{dt} ([S_n]V) &= \frac{dN_{PS}(n)}{dt} \\ &= \left[ R_p V \varphi (\tau - \gamma \tau_1) + \frac{R_p V \varphi^2 \beta}{2} \alpha n \right] \alpha e^{-\alpha n} \\ & \quad n = 1, 2, 3, \dots \quad (\text{A.39}) \end{aligned}$$

The right-hand side of eq. (A.39) represents the NCLD of the instantaneously produced PS. Such NCLD is the sum of two distributions: the "most probable" distribution [ $\alpha e^{-\alpha n}$ ], with  $\bar{M}_n = M_S/\alpha$  and polydispersity  $\simeq 2$  weighted by the molar rate [ $R_p V \varphi (\tau - \gamma \tau_1)$ ]; and the normalized binomial distribution [ $\alpha^2 n e^{-\alpha n}$ ], with  $\bar{M}_n = 2M_S/\alpha$  and polydispersity  $\simeq 1.5$  weighted by the molar rate [ $R_p V \varphi^2 \beta / 2$ ]. Note that at all times, the instantaneous  $\bar{M}_w$  of [ $\alpha e^{-\alpha n}$ ] coincides with the instantaneous  $\bar{M}_n$  of [ $\alpha^2 n e^{-\alpha n}$ ]. When  $\tau = 0$  (i.e., for  $k_{fm}$ ,  $k_{fg}$ ,  $k_{td}$ ,  $k'_{td} = 0$ ), then the most probable part of the distribution becomes zero, yielding the instantaneous distribution of our previous publication.<sup>34</sup> Similarly, when  $\beta = 0$  (i.e.,  $k_{tc} = 0$ ), then the part of the distribution with polydispersity 1.5 becomes zero.

To calculate the WCLD for the free PS, multiply eq. (A.39) by the molecular weights ( $nM_S$ ), obtaining:

$$\begin{aligned} \frac{d}{dt} G_{PS}(n) &= \left[ \frac{R_p V \varphi M_S}{\alpha} (\tau - \gamma \tau_1) + \frac{R_p V \varphi^2 \beta M_S}{2} n \right] \alpha^2 n e^{-\alpha n} \\ & \quad n = 1, 2, 3, \dots \quad (\text{A.40}) \end{aligned}$$

Injecting the evolution of  $R_p$ ,  $V$ ,  $\varphi$ ,  $\gamma$ ,  $\tau$ ,  $\tau_1$ ,  $\beta$ , and  $\alpha$ , eq. (A.40) may be integrated to find  $G_{PS}(n)$ . The

above derivation for eqs. (A.39) and (A.40) is an extension of the "classical" approach for the MWD development in linear homopolymerizations.<sup>38</sup>

### NCLD of Residual Unreacted PB

In the global mechanism of Table I,  $P$  either represents the accumulated copolymer, or the total accumulated PB (unreacted or crosslinked). Consider now the reactions involving the initial PB only, and furthermore the reactions of each possible chain length  $n$ . If  $N_{PB}(n)$  is the NCLD of the residual PB, then  $nN_{PB}(n)$  for  $n = 1, 2, \dots$  represents the total moles of  $B^*$  in each chain-length class. A primary rubber radical  $P_0^*$  is formed whenever a  $B^*$  unit is attacked. Because that attack is proportional to the  $B^*$  contents of each  $P$  species, then the fraction of  $P_0^*$  radicals corresponding to primary residual PB radicals of chain length  $n$  is  $\{nN_{PB}(n)/[B^*]V\}$ . Therefore,  $\{[P_0^*]nN_{PB}(n)/[B^*]V\}$  represents the concentration of primary residual PB radicals of chain length  $n$ ; and the following individual species balance can be written:

$$\begin{aligned} \frac{d}{dt} N_{PB}(n) &= -\{k_{i2}[I^*] + k_{fg}([S^*] + [P^*])\}nN_{PB}(n) \\ & \quad + \{k'_{fm}[St] + k'_{td}([S^*] + [P^*]) \\ & \quad + k'_{td}[P_0^*]\}[P_0^*] \frac{nN_{PB}(n)}{[B^*]} \\ & \quad n = 1, 2, 3, \dots \quad (\text{A.41}) \end{aligned}$$

Introducing eqs. (A.9), (A.14), (A.15), (A.17), and (A.21)–(A.25) into eq. (A.41), results in:

$$\begin{aligned} \frac{dN_{PB}(n)}{dt} &= -\left\{ R_p V (1 - \varphi) \left( \tau - \gamma \tau_1 + \beta \varphi + \frac{\gamma \tau_1 \varphi}{1 - \varphi} \right) \right\} \\ & \quad \times \frac{nN_{PB}(n)}{[B^*]V} - \{R_p V (1 - \varphi) [\beta (1 - \varphi) + 2\gamma \tau_1]\} \\ & \quad \times \frac{nN_{PB}(n)}{[B^*]V} - \left\{ \frac{R_p^2 \gamma^2 V k'_{td}}{(k_p [St])^2} \right\} \frac{nN_{PB}(n)}{[B^*]V} \\ & \quad n = 1, 2, 3, \dots \quad (\text{A.42}) \end{aligned}$$

It can be shown that the first, second, and third terms in the right-hand side of eq. (A.42), respectively represent the consumption of original PB molecules due to T grafting, H grafting, and crosslinking. Multiplying eq. (A.42) by the molecular weights ( $nM_B$ ), an expression enabling the calculation of the WCLD for the residual PB is obtained:

$$\begin{aligned} \frac{dG_{PB}(n)}{dt} = & - \left\{ R_p V(1 - \varphi) \left( \tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi} \right) \right. \\ & + R_p V(1 - \varphi) [\beta(1 - \varphi) + 2\gamma\tau_1] + \frac{R_p^2 \gamma^2 V k'_c}{(k_p [St])^2} \left. \right\} \\ & \times \frac{n^2 N_{PB}(n) M_B}{[B^*] V} \quad n = 1, 2, 3, \dots \quad (\text{A.43}) \end{aligned}$$

The total moles and mass of residual PB may be obtained as follows:

$$N_{PB} = \sum_n N_{PB}(n) \quad (\text{A.44})$$

$$G_{PB} = \sum_n G_{PB}(n). \quad (\text{A.45})$$

### NCLD of Total Crosslinked PB Homopolymer

Consider the calculation of the NCLD for the total accumulated crosslinked PB homopolymer, that is, containing two or more PB chains per molecule. Let us represent such NCLD by  $N_{XB}(n)$ . New crosslinked PB is produced whenever two primary (crosslinked or unreacted) PB radicals react together, and is consumed when a primary PB radical is grafted or crosslinked onto a copolymer. With a similar treatment to eq. (A.41), the following balance may be written:

$$\begin{aligned} \frac{d}{dt} N_{XB}(n) = & - \{ k_{i2} [I^*] + k_{fc} ([S^*] + [P^*]) \} n N_{XL}(n) \\ & + \{ k'_{fm} [St] + k'_{fd} ([S^*] + [P^*]) + k'_{fd} [P_0^*] \} \\ & \times [P_0^*] \frac{n N_{XL}(n)}{[B^*]} + \frac{k'_{fc}}{2} [P_0^*]^2 \\ & \times \sum_{m=1}^{n-1} \frac{m(N_{XB}(m) + N_{PB}(m))}{[B^*]} \\ & \times \frac{(n - m)(N_{XB}(n - m) + N_{PB}(n - m))}{[B^*]} \\ & \quad n = 1, 2, 3, \dots \quad (\text{A.46}) \end{aligned}$$

where  $\{ [P_0^*] n N_{XL}(n) / [B^*] \}$  represents the moles of primary crosslinked PB radicals of chain length  $n$ . Introducing eqs. (A.9), (A.14), (A.15), (A.17), and (A.21)–(A.25) into eq. (A.46), produces:

$$\begin{aligned} \frac{dN_{XB}(n)}{dt} = & - \left\{ R_p V(1 - \varphi) \left( \tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi} \right) \right\} \\ & \times \frac{n N_{XB}(n)}{[B^*] V} - \{ R_p V(1 - \varphi) [\beta(1 - \varphi) + 2\gamma\tau_1] \} \\ & \times \frac{n N_{XB}(n)}{[B^*] V} - \left\{ \frac{R_p^2 \gamma^2 V k'_c}{(k_p [St])^2} \right\} \left[ \frac{n N_{XB}(n)}{[B^*] V} \right. \\ & - \sum_{m=1}^{n-1} \frac{m(N_{XB}(m) + N_{PB}(m))}{[B^*] V} \\ & \left. \times \frac{(n - m)(N_{XB}(n - m) + N_{PB}(n - m))}{[B^*] V} \right] \\ & \quad n = 1, 2, 3, \dots \quad (\text{A.47}) \end{aligned}$$

Multiplying eq. (A.47) by the molecular weights ( $nM_B$ ), an expression for the WCLD of the total crosslinked PB can be obtained:

$$\begin{aligned} \frac{dG_{XB}(n)}{dt} = & - \left\{ R_p V(1 - \varphi) \left( \tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi} \right) \right. \\ & + R_p V(1 - \varphi) [\beta(1 - \varphi) + 2\gamma\tau_1] \\ & + \frac{R_p V k'_c \gamma}{(k_p [St])^2} \left. \right\} \frac{n^2 N_{XB}(n) M_B}{[B^*] V} \\ & + \{ R_p V(1 - \varphi) [\beta(1 - \varphi) + 2\gamma\tau_1] \} \left[ \frac{n^2 N_{XB}(n) M_B}{[B^*] V} \right. \\ & - n M_B \sum_{m=1}^{n-1} \frac{m(N_{XB}(m) + N_{PB}(m))}{[B^*] V} \\ & \left. \times \frac{(n - m)(N_{XB}(n - m) + N_{PB}(n - m))}{[B^*] V} \right] \\ & \quad n = 1, 2, 3, \dots \quad (\text{A.48}) \end{aligned}$$

The total moles and mass of crosslinked PB may be calculated as follows:

$$N_{XB} = \sum_n N_{XB}(n) \quad (\text{A.49})$$

$$G_{XB} = \sum_n G_{XB}(n). \quad (\text{A.50})$$

### Total Copolymer Molecules

A global balance for the  $P$  molecules (i.e., graft copolymer + residual PB + crosslinked PB) is:

$$\begin{aligned}
 \frac{d}{dt}([P]V) &= \frac{dN}{dt} = -[B^*]\{k_{i2}[I^*] + k_{fg}([S^*] + [P^*])\} \\
 &+ \{k_{fm}[St] + k_{fg}[B^*] + k_{td}([S^*] \\
 &\quad + [P^*]) + k'_{td}[P^*_0]\} \\
 &\times [P^*]V + k_{tc}[S^*][P^*]V + k'_{tc}[S^*][P^*_0]V \\
 &+ \frac{k_t}{2}[P^*][P^*]V + k'_{tc}[P^*][P^*_0]V \\
 &+ \{k'_{fm}[St] + k'_{td}([S^*] + [P^*]) + k'_{td}[P^*_0]\}[P^*_0]V \\
 &\quad + \frac{k'_{tc}}{2}[P^*_0][P^*_0]V \quad (A.51)
 \end{aligned}$$

where  $N$  are the total moles of  $P$ . Introducing eqs. (A.9), (A.14), (A.15), (A.17), and (A.21)–(A.25) into eq. (A.51):

$$\begin{aligned}
 \frac{dN}{dt} &= -\frac{R_p V(1-\varphi)}{2} [\beta(1-\varphi) + 2\gamma\tau_1] \\
 &\quad - \frac{R_p^2 \gamma^2 k'_{tc}}{2(k_p[St])^2} V. \quad (A.52)
 \end{aligned}$$

The total moles of graft copolymer ( $N_C$ ) may be found from the following expression:

$$N_C = N - N_{PB} - N_{XB} \quad (A.53)$$

where  $N$ ,  $N_{PB}$ , and  $N_{XB}$  can be determined through eqs. (A.52), (A.44), and (A.49). Similarly, the total copolymer mass  $G_C$  may be obtained from:

$$G_C = G_{PB}^0 - G_{PB} - G_{XB} + G_{ST} + G_{SH} \quad (A.54)$$

where the initial PB mass  $G_{PB}^0$  is known *a priori*, and the evolution of  $G_{PB}$ ,  $G_{XB}$ ,  $G_{ST}$ , and  $G_{SH}$  can be followed through eqs. (A.30), (A.31), (A.45), and (A.50).

### Global Derived Variables

From the previous results, several global parameters can be calculated.

#### St Grafting Efficiency

$$E_{PS} = \frac{G_{ST} + G_{SH}}{G_{PS} + G_{ST} + G_{SH}}. \quad (A.55)$$

#### PB Grafting Efficiency

$$E_{PB} = \frac{G_{PB}^0 - G_{PB}}{G_{PB}^0}. \quad (A.56)$$

### Average Number of PB Chains per Copolymer Molecule

$$J_{GB} = \frac{N_{PB}^0 - N_{PB} - N_{XB}}{N_C} \quad (A.57)$$

where the initial number of PB moles ( $N_{PB}^0$ ) is known *a priori*.

### Number Average MW for Total Copolymer

$$\bar{M}_{n,C} = \frac{G_C}{N_C}. \quad (A.58)$$

## APPENDIX B: COPOLYMER DISTRIBUTIONS MODULE

Let us represent with  $B_{(p,q)}^*(s, b)$  any unreacted B unit in  $P_{p,q}(s, b)$ . Considering that a  $P_{(p,q)}(s, b)$  molecule contains  $(b - p - q + 1)$  unreacted B units, then one can write:  $[B_{(p,q)}^*(s, b)] = (b - p - q + 1)[P_{(p,q)}(s, b)]$ . From the extended mechanism of Table I, the mass balances for every possible radical species together with the pseudo-steady-state assumption yield:

$$\begin{aligned}
 \frac{d}{dt} \{ [P_{0(p,q)}^*(s, b)] V \} \\
 &= \{ k_{i2}[I^*] + k_{fg}([S^*] + [P^*]) \} [B_{(p,q)}^*(s, b)] V \\
 &\quad - \{ k_{i3}[St] + k'_{fm}[St] + (k'_{tc} + k'_{td})[P^*_0] \\
 &\quad + (k''_{tc} + k''_{td})([S^*] + [P^*]) \} \\
 &\quad \times [P_{0(p,q)}^*(s, b)] V = 0 \\
 &\quad p, s = 0, 1, 2, \dots; b, q = 1, 2, 3, \dots \quad (B.1)
 \end{aligned}$$

$$\begin{aligned}
 \frac{d}{dt} \{ [P_{1(p,q)}^*(s, b)] V \} \\
 &= k_{i3}[St][P_{0(p,q)}^*(s, b)] V - \{ (k_p[St] + k_{fm}[St] \\
 &\quad + k_{fg}[B^*] + (k_{tc} + k_{td})([S^*] + [P^*]) \\
 &\quad + (k''_{tc} + k''_{td})[P^*_0] \} [P_{1(p,q)}^*(s, b)] V = 0 \\
 &\quad p, s = 0, 1, 2, \dots; b, q = 1, 2, 3, \dots \quad (B.2)
 \end{aligned}$$

$$\frac{d}{dt} \{ [P_{n(p,q)}^*(s, b)] V \}$$

$$\begin{aligned}
&= k_p[St][P_{n-1(p,q)}^*(s, b)]V \\
&\quad - \{ (k_p[St] + k_{fM}[St] + k_{fG}[B^*] \\
&\quad + (k_{t_c} + k_{t_d})([S^*] + [P^*]) \\
&\quad + (k_{t_c}'' + k_{t_d}'')[P_0^*] \} \\
&\quad \times [P_{n(p,q)}^*(s, b)]V = 0 \quad n = 2, 3, 4, \dots; \\
&\quad p, s = 0, 1, 2, \dots; \quad b, q = 1, 2, 3, \dots \quad (\text{B.3})
\end{aligned}$$

Comparing eqs. (A.9) and (B.1), one finds:

$$\frac{[P_{0(p,q)}^*(s, b)]}{[P_0^*]} = \frac{[B_{(p,q)}^*(s, b)]}{[B^*]}$$

$$p, s = 0, 1, 2, \dots; \quad b, p = 1, 2, 3, \dots \quad (\text{B.4})$$

indicating that the fraction of primary radicals generated from  $P_{(p,q)}(s, b)$  (with respect to the total number of primary rubber radicals) coincides with the molar fraction of unreacted  $B^*$  units in that particular species (with respect to the total number of  $B^*$  units). In eqs. (A.41) and (A.46), similar relationships to eq. (B.4), but specific to the residual and the total crosslinked PB, were more intuitively introduced.

By replacing eqs. (A.21)–(A.25) into eq. (B.2), and considering eqs. (A.14), (A.15), (A.17), and (B.4), one can write:

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

$$p, s = 0, 1, 2, \dots; \quad b, q = 1, 2, 3, \dots \quad (\text{B.5})$$

Similarly, introducing eqs. (A.15), (A.17), (A.21)–(A.25), and (B.5) into eq. (B.3), one finds:

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

$$n = 2, 3, 4, \dots; \quad p, s = 0, 1, 2, \dots; \\
b, q = 0, 1, 2, \dots \quad (\text{B.6})$$

In the following, a material balance for every possible  $P_{(p,q)}(s, b)$  species will be derived. This is equivalent to obtaining the bivariate NCLD for every copolymer topology plus the univariate NCLD for the residual PB and for every crosslinked PB topology. A mass balance for  $P_{(p,q)}(s, b)$  yields:

$$\frac{d}{dt} ([P_{(p,q)}(s, b)]V) = T_1 + T_2 + T_3 + T_4 + T_5$$

$$p, s = 0, 1, 2, \dots; \quad b, q = 1, 2, 3, \dots \quad (\text{B.7a})$$

with:

$$T_1 = -[B_{(p,q)}^*(s, b)]\{k_{i2}[I^*] + k_{fG}([S^*] + [P^*])\} \quad (\text{B.7b})$$

$$\begin{aligned}
T_2 = &\{k_{fM}[St] + k_{fG}[B^*] + k_{t_d}([S^*] + [P^*]) \\
&+ k_{t_d}''[P_0^*]\} \sum_{m=1}^s [P_{m(p-1,q)}^*(s - m, b)]V \\
&+ k_{t_c} \sum_{m=2}^s \sum_{n=1}^{m-1} [P_{n(p-1,q)}^*(s - m, b)][S_{m-n}^*]V \\
&+ k_{t_c}'' \sum_{m=1}^s [P_{0(p-1,q)}^*(s - m, b)][S_m^*]V \quad (\text{B.7c})
\end{aligned}$$

$$\begin{aligned}
T_3 = &\frac{k_{t_c}}{2} \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=2}^s \sum_{n=1}^{m-1} \\
&\times [P_{m-n(p-p_1-1, q-q_1)}^*(s - s_1 - m, b - b_1)] \\
&\times [P_{n(p_1, q_1)}^*(s_1, b_1)]V + k_{t_c}'' \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=2}^s \\
&\times [P_{m(p-p_1-1, q-q_1)}^*(s - s_1 - m, b - b_1)] \\
&\times [P_{0(p_1, q_1)}^*(s_1, b_1)]V \quad (\text{B.7d})
\end{aligned}$$

$$\begin{aligned}
T_4 = &\{k_{fM}'[S] + k_{t_d}''([S^*] + [P^*]) + k_{t_d}'[P_0^*]\} \\
&\times [P_{0(p,q)}^*(s, b)]V \quad (\text{B.7e})
\end{aligned}$$

$$\begin{aligned}
T_5 = &\frac{k_{t_c}'}{2} \sum_{q_1=1}^{q-1} \sum_{p_1=0}^p \sum_{b_1=1}^{b-1} \sum_{s_1=1}^s [P_{0(p-p_1, q-q_1)}^*(s - s_1, b - b_1)] \\
&\times [P_{0(p_1, q_1)}^*(s_1, b_1)]V \quad (\text{B.7f})
\end{aligned}$$

where  $T_1$  represents the rate of disappearance of the accumulated  $P_{(p,q)}(s, b)$  species by generation of  $P_{0(p,q)}^*(s, b)$  radicals;  $T_2$  represents the rate of generation of  $P_{(p,q)}(s, b)$  copolymer by grafting of a new  $T$  branch of length  $m$  onto an accumulated  $P_{(p-1,q)}(s - m, b)$  species;  $T_3$  represents the rate of generation of  $P_{(p,q)}(s, b)$  copolymer by linking  $P_{(p-p_1-1, q-q_1)}(s - s_1 - m, b - b_1)$  and  $P_{(p_1, q_1)}(s_1, b_1)$ , with a new  $H$  branch of length  $m$ ;  $T_4$  represents the rate of generation of  $P_{(p,q)}(s, b)$  by deactivation of primary  $P_{0(p,q)}^*(s, b)$  radicals; and  $T_5$  represents the rate of generation of  $P_{(p,q)}(s, b)$  copolymer or pure crosslinked PB by direct crosslinking between  $P_{0(p-p_1, q-q_1)}^*(s - s_1, b - b_1)$  and  $P_{0(p_1, q_1)}^*(s_1, b_1)$ . In eq. (B.7), unreacted PB molecules  $P_{(0,1)}(0, b)$  can only be consumed or generated (by deactivation of primary PB radicals), and therefore  $T_1, T_4 \neq 0$ , but  $T_2 = T_3 = T_5 = 0$ . Similarly, for purely crosslinked PB molecules  $P_{(0,q)}(0, b)$ :  $T_1, T_4$ ,

$T_5 \neq 0$ , but  $T_2 = T_3 = 0$ . Let us now find alternative expressions for each of the  $T_i$  terms in eq. (B.7).

### First Term or Disappearance of $P_{(p,q)}(s, b)$

Equation (B.7b) may be rewritten as follows:

$$T_1 = -\left\{\frac{[B_{(p,q)}^*(s, b)]}{[B^*]}\right\}\{[k_{i2}[I^*] + k_{fg}([S^*] + [P^*])[B^*]V] \quad (\forall p, q, s, b). \quad (B.8)$$

The second factor of eq. (B.8) represents the rate of generation of new grafting points (or of primary radicals  $P_{0(p,q)}^*(s, b)$ , while the first factor "distributes" such grafting points among the accumulated  $P_{(p,q)}(s, b)$  species, proportionately to their  $B^*$  contents. Introducing eqs. (A.9), (A.14), (A.15), (A.17), and (A.21)–(A.25) into eq. (B.8), one can write:

$$T_1 = -\left\{\frac{[B_{(p,q)}^*(s, b)]}{[B^*]}\right\}\left\{\left[R_p V(1 - \varphi) \times \left(\tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi}\right)\right] + [R_p V(1 - \varphi)(\beta(1 - \varphi) + 2\gamma\tau_1)] + \left[\frac{R_p^2 V k'_{tc} \gamma^2}{(k_p [St])^2}\right] + \left[R_p V \gamma \left(\frac{k'_{fm}}{k_p} + \frac{k'_{td}}{(k_p [St])^2} + \frac{k'_{td} \gamma}{(k_p [St])^2}\right)\right]\right\} \quad (\forall p, q, s, b). \quad (B.9)$$

Consider the second factor in the right-hand side of eq. (B.9). It can be proven that the first term represents the rate of generation of new  $T$  grafting sites; the second term represents the same rate, but of new  $H$  grafting sites; the third term represents the rate of consumption of active sites by direct crosslinking of two PB radicals without St intervention; the fourth term represents the rate of regeneration of free PB by deactivation of primary B radicals due to transfer or termination.

### Second Term or Production of $P_{(p,q)}(s, b)$ with a New T-Grafted PS Chain

Equations (A.37) and (B.6) may be rewritten as follows:

$$[S_{m-n}^*] = \frac{\alpha\varphi R_p}{k_p [St]} \frac{1}{(1 + \alpha)^{m-n}} \quad (B.10)$$

$$[P_{m(p,q)}^*(s - m, b)] = \frac{(1 - \varphi)R_p}{k_p [St]} \frac{\alpha}{(1 + \alpha)^m} \frac{[B_{(p,q)}^*(s - m, b)]}{[B^*]} \quad (B.11)$$

$$[P_{n(p,q)}^*(s - m, b)] = \frac{(1 - \varphi)R_p}{k_p [St]} \frac{\alpha}{(1 + \alpha)^n} \frac{[B_{(p,q)}^*(s - m, b)]}{[B^*]} \quad (B.12)$$

where  $m$  represents the chain length of the new St branch.

Replacing eqs. (B.10)–(B.12) into (B.7c), and considering eqs. (A.15), (A.17), and (A.21)–(A.25), one obtains:

$$T_2 = R_p(1 - \varphi)\alpha \sum_{m=1}^s \frac{[B_{(p-1,q)}^*(s - m, b)]}{[B^*]} \times \left[ \left( \tau - \gamma\tau_1 + \gamma\tau_1 \frac{\varphi}{1 - \varphi} \right) \frac{1}{(1 + \alpha)^m} + \beta\varphi\alpha m \frac{1}{(1 + \alpha)^m} \right] V \quad (\forall p, q, s, b) \quad (B.13)$$

and therefore:

$$T_2 = R_p(1 - \varphi)\alpha \sum_{m=1}^s \frac{[B_{(p-1,q)}^*(s - m, b)]}{[B^*]} \times \left[ \left( \tau - \gamma\tau_1 + \gamma\tau_1 \frac{\varphi}{1 - \varphi} \right) e^{-\alpha m} + \beta\varphi\alpha m e^{-\alpha m} \right] V \quad (\forall p, q, s, b). \quad (B.14)$$

### Third Term or Production of $P_{(p,q)}(s, b)$ with a New H-Grafted PS Chain

Equation (B.6) may be written:

$$[P_{m-n(p-1,q-q_1)}^*(s - s_1 - m, b - b_1)] = \frac{(1 - \varphi)R_p\alpha}{k_p [St]} \frac{1}{(1 + \alpha)^{m-n}} \frac{[B_{(p-1,q-q_1)}^*(s - s_1 - m, b - b_1)]}{[B^*]} \quad (B.15)$$

$$[P_{n(p_1,q_1)}^*(s_1, b_1)] = \frac{(1 - \varphi)R_p\alpha}{k_p [St]} \frac{1}{(1 + \alpha)^n} \frac{[B_{(p_1,q_1)}^*(s_1, b_1)]}{[B^*]} \quad (B.16)$$

$$[P_{m(p-p_1-1,q-q_1)}^*(s - s_1 - m, b - b_1)]$$

$$= \frac{(1 - \varphi)R_p\alpha}{k_p[St]} \frac{1}{(1 + \alpha)^m} \frac{[B_{(p-p_1-1, q-q_1)}^*(s - s_1 - m, b - b_1)]}{[B^*]} \quad (\text{B.17})$$

Replacing eqs. (B.15)–(B.17) into eq. (B.7d), and considering eqs. (A.15), (A.17), (A.21)–(A.25), and (B.4), results in:

$$T_3 = R_p(1 - \varphi)^2 \frac{\beta}{2} \alpha \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=2}^s \times \frac{[B_{(p-p_1-1, q-q_1)}^*(s - s_1 - m, b - b_1)]}{[B^*]} \times \frac{[B_{(p_1, q_1)}^*(s_1, b_1)]}{[B^*]} m\alpha e^{-\alpha m} V + R_p(1 - \varphi)\gamma\tau_1\alpha \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=2}^s \times \frac{[B_{(p-p_1-1, q-q_1)}^*(s - s_1 - m, b - b_1)]}{[B^*]} \times \frac{[B_{(p_1, q_1)}^*(s_1, b_1)]}{[B^*]} e^{-\alpha m} V \quad (\forall p, q, s, b). \quad (\text{B.18})$$

**Fourth Term or Regeneration of  $P_{(p,q)}(s, b)$  by Deactivation of  $P_{0(p,q)}(s, b)$**

Introducing eqs. (A.15), (A.17), (B.4), and (B.5) into (B.7e), one finds:

$$T_4 = R_p V \gamma \left[ \frac{k'_{fd}}{k_p} + \frac{k''_{fd}}{(k_p[St])^2} + \frac{k'_{fd}\gamma}{(k_p[St])^2} \right] \frac{[B_{(p,q)}^*(s, b)]}{[B^*]} \quad (\forall p, q, s, b). \quad (\text{B.19})$$

**Fifth Term or Production of  $P_{(p,q)}(s, b)$  by Direct Crosslinking of Two Rubber Radicals**

From eqs. (A.15), (A.17), (B.4), and (B.5), one can write:

$$P_{0(p-p_1, q-q_1)}^*(s - s_1, b - b_1) = \frac{\gamma R_p}{k_p[St]} \frac{[B_{(p-p_1, q-q_1)}^*(s - s_1, b - b_1)]}{[B^*]} \quad (\text{B.20})$$

$$P_{0(p_1, q_1)}^*(s_1, b_1) = \frac{\gamma R_p}{k_p[St]} \frac{[B_{(p_1, q_1)}^*(s_1, b_1)]}{[B^*]} \quad (\text{B.21})$$

Then, replacing eqs. (B.20) and (B.21) into eq. (B.7f), the following is obtained:

$$T_5 = \frac{R_p^2 \gamma^2 k'_{tc}}{2(k_p[St])^2} \times \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \frac{[B_{(p-p_1, q-q_1)}^*(s - s_1, b - b_1)]}{[B^*]} \times \frac{[B_{(p_1, q_1)}^*(s_1, b_1)]}{[B^*]} \quad (\forall p, q, s, b). \quad (\text{B.22})$$

Introducing eqs. (B.9), (B.14), (B.18), (B.19), and (B.22) into eq. (B.7a), an expression for the evolution of the moles of  $P_{(p,q)}(s, b)$  species may be finally encountered:

$$\frac{d}{dt} N_{(p,q)}(s, b) = - \left\{ R_p(1 - \varphi) \left( \tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi} \right) + R_p(1 - \varphi) [\beta(1 - \varphi) + 2\gamma\tau_1] + \frac{R_p^2 \gamma^2 k'_{tc}}{(k_p[St])^2} \right\} \frac{[B_{(p,q)}^*(s, b)]}{[B^*]} V + \left\{ R_p V(1 - \varphi) \left( \tau - \gamma\tau_1 + \gamma\tau_1 \frac{\varphi}{1 - \varphi} \right) \times \sum_{m=1}^s \frac{[B_{(p-1, q)}^*(s - m, b)]}{[B^*]} \alpha e^{-\alpha m} + R_p V \varphi(1 - \varphi)\beta + \sum_{m=1}^s \frac{[B_{(p-1, q)}^*(s - m, b)]}{[B^*]} \alpha^2 m e^{-\alpha m} V \right\} + \left\{ R_p V(1 - \varphi)\gamma\tau_1 \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^s \times \frac{[B_{(p-p_1-1, q-q_1)}^*(s - s_1 - m, b - b_1)]}{[B^*]} \times \frac{[B_{(p_1, q_1)}^*(s_1, b_1)]}{[B^*]} \alpha e^{-\alpha m} + R_p V(1 - \varphi)^2 \frac{\beta}{2} \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^s \times \frac{[B_{(p-p_1-1, q-q_1)}^*(s - s_1 - m, b - b_1)]}{[B^*]} \times \frac{[B_{(p_1, q_1)}^*(s_1, b_1)]}{[B^*]} \alpha^2 e^{-\alpha m} \right\} + \left\{ \frac{R_p^2 V \gamma^2 k'_{tc}}{2(k_p[St])^2} \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \right.$$

$$\begin{aligned} & \times \frac{[B_{(p-1,q-q_1)}^*(s-s_1, b-b_1)]}{[B^*]} \\ & \times \frac{[B_{(p_1,q_1)}^*(s_1, b_1)]}{[B^*]} \left. \right\} q, b = 1, 2, 3, \dots; \\ & p, s = 0, 1, 2, \dots \quad (\text{B.23}) \end{aligned}$$

In eq. (B.23),  $m$  represents the chain length of the instantaneously grafted PS chains. Multiplying eq. (B.23) by the corresponding molecular weights ( $sM_S + bM_B$ ), the mass of each  $P_{(p,q)}(s, b)$  species can be finally obtained from:

$$\begin{aligned} & \frac{d}{dt} G_{(p,q)}(s, b) \\ & = - \left\{ R_p(1-\varphi) \left( \tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1-\varphi} \right) \right. \\ & \quad \left. + R_p(1-\varphi) [\beta(1-\varphi) + 2\gamma\tau_1] + \frac{R_p^2\gamma^2k'_{tc}}{(k_p[St])^2} \right\} \\ & \quad \times (sM_S + bM_B) \frac{[B_{(p,q)}^*(s, b)]}{[B^*]} V \\ & \quad + \left\{ R_p V(1-\varphi) \left( \tau - \gamma\tau_1 + \gamma\tau_1 \frac{\varphi}{1-\varphi} \right) \right. \\ & \quad \times \sum_{m=1}^s \frac{[B_{(p-1,q)}^*(s-m, b)]}{[B^*]} \alpha e^{-\alpha m} \\ & \quad \left. + R_p V\varphi(1-\varphi)\beta \right. \\ & \quad \times \sum_{m=1}^s \frac{[B_{(p-1,q)}^*(s-m, b)]}{[B^*]} \alpha^2 m e^{-\alpha m} V \\ & \quad \left. + R_p V(1-\varphi)\gamma\tau_1 \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^s \right. \\ & \quad \times \frac{[B_{(p-p_1-1,q-q_1)}^*(s-s_1-m, b-b_1)]}{[B^*]} \\ & \quad \times \frac{[B_{(p_1,q_1)}^*(s_1, b_1)]}{[B^*]} \alpha e^{-\alpha m} \\ & \quad \left. + R_p V(1-\varphi)^2 \frac{\beta}{2} \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^s \right. \\ & \quad \times \frac{[B_{(p-p_1-1,q-q_1)}^*(s-s_1-m, b-b_1)]}{[B^*]} \\ & \quad \times \frac{[B_{(p_1,q_1)}^*(s_1, b_1)]}{[B^*]} \alpha^2 e^{-\alpha m} + \frac{R_p^2 V \gamma^2 k'_{tc}}{2(k_p[St])^2} \\ & \quad \times \sum_{q_1=1}^{q-1} \sum_{p_1=0}^{p-1} \sum_{b_1=1}^{b-1} \frac{[B_{(p-p_1,q-q_1)}^*(s-s_1, b-b_1)]}{[B^*]} \end{aligned}$$

$$\begin{aligned} & \times \frac{[B_{(p_1,q_1)}^*(s_1, b_1)]}{[B^*]} \left. \right\} (sM_S + bM_B) \\ & q, b = 1, 2, 3, \dots; p, s = 0, 1, 2, \dots \quad (\text{B.24}) \end{aligned}$$

Equation (B.24) not only calculates the bivariate WCLD of every generated copolymer topology, but also the univariate WCLD of the residual PB, and the univariate WCLD of every crosslinked PB topology ( $p = 0, q > 1$ ). To prove that eq. (B.24) includes the mass balance of the residual PB, consider the balance of  $P_{(0,1)}(0, b)$ . In this case,  $G_{(0,1)}(0, b)$  can be replaced by  $G_{PB}(n)$ ; and  $B_{(0,1)}^*(0, b)$  by  $nN_{PB}(n)$ ; the first and the fourth terms of eq. (B.24) are non-zero, while all remaining terms are zero (evidenced by the negative values of  $p$  in these terms). Thus, eq. (A.42) is recuperated.

To prove that eq. (B.24) also includes the purely crosslinked PB as a special case, consider the following independent mass balance to calculate the univariate WCLD for every crosslinked PB topology ( $q = 2, 3, \dots$ ):

$$\begin{aligned} & \frac{d}{dt} G_{(0,q)}(0, b) \\ & = -bM_B [B_{(0,q)}^*(0, b)] \{ k_{i2}[I^*] + k_{fg}([S^*] + [P^*]) \} \\ & \quad + \{ k'_{fM}[St] + k'_{td}([S^*] + [P^*]) + k'_{td}[P_0^*] \} \\ & \quad \times bM_B [P_{0(0,q)}^*(0, b)] V + \frac{k'_{tc}}{2} bM_B \\ & \quad \times \sum_{q_1=1}^{q-1} \sum_{b_1=1}^{b-1} [P_{0(0,q-q_1)}^*(0, b-b_1)] \\ & \quad \times [P_{0(0,q_1)}^*(0, b_1)] V \quad q = 2, 3, \dots \quad (\text{B.25}) \end{aligned}$$

Introducing eqs. (A.9), (A.14), (A.15), (A.17), (A.21)–(A.25), and (B.4) into eq. (B.25):

$$\begin{aligned} & \frac{d}{dt} G_{(0,q)}(0, b) \\ & = - \left\{ R_p(1-\varphi) \left( \tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1-\varphi} \right) \right. \\ & \quad \left. + R_p(1-\varphi) [\beta(1-\varphi) + 2\gamma\tau_1] + \frac{R_p^2\gamma^2k'_{tc}}{(k_p[St])^2} \right\} bM_B \\ & \quad \times \frac{[B_{(0,q-q_1)}^*(0, b)]}{[B^*]} V + \frac{R_p^2 V \gamma^2 k'_{tc}}{2(k_p[St])^2} \\ & \quad \times \sum_{q_1=1}^{q-1} \sum_{b_1=1}^{b-1} \frac{[B_{(0,q-q_1)}^*(0, b-b_1)]}{[B^*]} \end{aligned}$$

$$\times \frac{[B_{(0,q)}^*(0, b_1)]}{[B^*]} \} bM_B \quad q, b = 1, 2, 3, \dots \quad (\text{B.26})$$

It is easy to see that eq. (B.26) is included in eq. (B.24), where the terms involving St grafting are zero ( $T_2, T_3 = 0$ ). Now if eq. (B.26) is added over all  $q$ 's, an expression allowing the calculation of the WCLD for the total crosslinked PB may be obtained. It is simple to prove that such expression coincides with eq. (A.48).

### WCLD of Total Copolymer

Consider the calculation of the total copolymer WCLD, without the need of obtaining each of the generated topologies. Adding up eq. (B.24) over all  $p$ 's and  $q$ 's, one finds:

$$\begin{aligned} \frac{d}{dt} G_C(s, b) = & - \left\{ R_p(1 - \varphi) \left( \tau - \gamma\tau_1 + \beta\varphi + \frac{\gamma\tau_1\varphi}{1 - \varphi} \right) \right. \\ & \left. + R_p(1 - \varphi) [\beta(1 - \varphi) + 2\gamma\tau_1] + \frac{R_p^2\gamma^2k'_t}{(k_p[St])^2} \right\} \\ & \times \frac{bN_C(s, b)}{V[B^*]} V(sM_S + bM_B) \\ & + \left\{ R_p V(1 - \varphi) \left( \tau - \gamma\tau_1 + \gamma\tau_1 \frac{\varphi}{1 - \varphi} \right) \right. \\ & \times \sum_{m=1}^s \frac{bN_C(s - m, b)}{[B^*]V} \alpha e^{-\alpha m} + R_p V\varphi(1 - \varphi)\beta \\ & \times \sum_{m=1}^s \frac{bN_C(s - m, b)}{[B^*]V} \alpha^2 m e^{-\alpha m} + R_p V(1 - \varphi)\gamma\tau_1 \\ & \times \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^s \frac{bN_C(s - s_1 - m, b - b_1)}{[B^*]V} \\ & \times \frac{bN_C(s_1, b_1)}{V[B^*]} \alpha e^{-\alpha m} + R_p V(1 - \varphi)^2 \frac{\beta}{2} \\ & \times \sum_{b_1=1}^{b-1} \sum_{s_1+m=1}^s \frac{bN_C(s - s_1 - m, b - b_1)}{V[B^*]} \\ & \times \frac{bN_C(s_1, b_1)}{V[B^*]} \alpha^2 e^{-\alpha m} + \frac{R_p^2 V \gamma^2 k'_t}{2(k_p[St])^2} \\ & \left. \times \sum_{b_1=1}^{b-1} \frac{bN_C(s - s_1, b - b_1)}{V[B^*]} \frac{bN_C(s_1, b_1)}{V[B^*]} \right\} \\ & \times (sM_S + bM_B) \quad s, b = 1, 2, 3, \dots \quad (\text{B.27}) \end{aligned}$$

### Global Derived Variables

The number of PS branches per copolymer molecule is  $pP_{(p,q)}(s, b)$ . Therefore, the following averages can be obtained.

### Average Number of Grafted S Chains per Reacted PB Molecule

$$J = \frac{\sum_{q=1}^{\infty} \sum_{p=1}^{\infty} \sum_{b=1}^{\infty} \sum_{s=1}^{\infty} pP_{(p,q)}(s, b)}{N_{PB}^0 - N_{PB}} \quad (\text{B.28})$$

### Average Number of Grafted S Chains per Copolymer Molecule

$$J_{GS} = \frac{\sum_{q=1}^{\infty} \sum_{p=1}^{\infty} \sum_{b=1}^{\infty} \sum_{s=1}^{\infty} pP_{(p,q)}(s, b)}{N_C} \quad (\text{B.29})$$

### REFERENCES

1. J. L. Amos, *Polym. Eng. Sci.*, **14**, 1 (1974).
2. S. L. Aggarwal and R. A. Livigni, *Polym. Eng. Sci.*, **17**, 498 (1977).
3. S. G. Turley and H. Keskkula, *Polymer*, **21**, 466 (1980).
4. E. T. C. Mui, V. B. Boateng, J. F. Fullers, and J. L. White, *J. Appl. Polym. Sci.*, **27**, 1395 (1982).
5. K. Sardelis, H. J. Michelis, and G. Allen, *J. Appl. Polym. Sci.*, **28**, 3255 (1983).
6. G. Cigna, S. Matarrese, and G. F. Biglione, *J. Appl. Polym. Sci.*, **20**, 2285 (1976).
7. J. P. Fisher, *Angew. Chem. Int. Ed.*, **12**, 428 (1973).
8. J. L. Refregier, J. L. Locatelli, and G. Riess, *Eur. Polym. J.*, **10**, 139 (1974).
9. D. J. Stein, G. Fahrback, and H. Adler, Crosslinking Reaction in High Impact Polystyrene Rubber Particles, *Adv. in Chem. Ser. (ACS)*, **142**, 148 (1975).
10. A. Brydon, G. M. Burnett, and G. G. Cameron, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 3255 (1973).
11. A. Gasperowicz and W. Laskowski, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2875 (1976).
12. T. O. Craig, R. M. Quick, and T. E. Jenkins, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 441 (1977).
13. V. D. Enal'ev, V. I. Mel'nichenko, O. P. Bovkunenko, E. I. Egovora, N. G. Podosenova, and V. P. Budtov, *J. Polym. Sci. Technol.*, **11**, 59 (1980).
14. J. P. Kennedy and J. M. Delvaux, *Adv. Polym. Sci.*, **38**, 141 (1981).
15. V. K. Gupta, G. S. Bhargava, and K. K. Bhattacharyya, *J. Macromol. Sci.-Chem.*, **A.16**, **6**, 1107 (1981).
16. R. A. Hall, R. D. Hites, and P. Plantz, *J. Appl. Polym. Sci.*, **27**, 2885 (1982).
17. R. A. Hall, *J. Appl. Polym. Sci.*, **36**, 1151 (1988).
18. Y. Okamoto, H. Miyagi, and M. Kakugo, *Macromolecules*, **24**, 5639 (1991).



19. H. Tobita, *Macromolecules*, **25**, 2671 (1992).
20. H. Oliva, *Rev. Téc. Univ. Zulia (Venezuela)*, **16**, 67 (1993).
21. H. Oliva, G. Pariacano, and J. Polo, *Rev. Téc. Univ. Zulia (Venezuela)*, **6**, 43 (1993).
22. S. Molnar, *J. Polym. Sci.*, **10**, 2245 (1972).
23. F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.*, **27**, 489 (1982).
24. K. Y. Choi and G. D. Lei, *AIChE J.*, **33**, 2067 (1987).
25. K. Y. Choi, W. R. Liang, and G. D. Lei, *J. Appl. Polym. Sci.*, **35**, 1547 (1988).
26. K. J. Kim, W. Ling, and K. Y. Choi, *Ind. Eng. Chem. Res.*, **28**, 131 (1989).
27. M. A. Villalobos, A. E. Hamielec, and P. E. Wood, *J. Appl. Polym. Sci.*, **42**, 629 (1991).
28. A. Brydon, G. M. Burnett, and G. G. Cameron, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1011 (1974).
29. V. Manaresi, V. Passalacqua, and F. Pilati, *Polymer*, **16**, 520 (1975).
30. D. C. Sundberg, J. Arndt, and M. Y. Tang, *J. Dispersion Sci. Technol.*, **5**, 433 (1984).
31. Ch. Sh. Chern and G. W. Poehlein, *Chem. Eng. Commun.*, **60**, 101 (1987).
32. L. H. Tung and R. M. Wiley, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1413 (1973).
33. F. M. Peng, *J. Appl. Polym. Sci.*, **40**, 1289 (1990).
34. D. A. Estenoz and G. R. Meira, *J. Appl. Polym. Sci.*, **50**, 1081 (1993).
35. W. A. Ludwico and S. L. Rosen, *J. Appl. Polym. Sci.*, **19**, 757 (1975).
36. W. A. Ludwico and S. L. Rosen, *J. Appl. Polym. Sci., Polym. Chem. Ed.*, **14**, 2121 (1976).
37. N. Friis and A. E. Hamielec, *ACS Symp. Ser.*, **24**, 82 (1976).
38. B. O'Shaughnessy and J. Yu, *Macromolecules*, **27**, 5079 (1994).
39. P. A. Clay and R. G. Gilbert, *Macromolecules*, **28**, 552 (1995).
40. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley, New York, 1989, p. II.85.
41. R. O. Bielsa and G. R. Meira, *J. Appl. Polym. Sci.*, **46**, 835 (1992).

Received November 1, 1994

Accepted June 25, 1995