

# Grafting of Styrene onto Polybutadiene: Calculation of the Molecular Macrostructure

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## SYNOPSIS

The radical-induced grafting of styrene onto polybutadiene at 60°C and in dilute solution is theoretically investigated, with the aim of estimating the detailed molecular macrostructure of the evolving polymer mixture. To this effect, the kinetic mechanism proposed by Brydon et al. [*J. Polym. Sci. Polym. Chem. Ed.*, **11**, 3255 (1973) and **12**, 1011 (1974)] was extended to evaluate the bivariate weight chain-length distribution (WCLD) for each of different copolymer topologies generated along the polymerization. Each molecular topology is characterized by two integers: the number of grafted styrene chains and the number of incorporated butadiene chains. Apart from the bivariate WCLDs for every topology and for the total copolymer, the molecular weight distributions of the accumulated polystyrene and of the unreacted polybutadiene are calculated. The model predictions of global variables (monomer conversion, polymer production, average molecular weights, grafting efficiencies, and average number of graft sites per reacted polybutadiene molecule) closely match the experimental measurements in the cited publications. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polymerization under the presence of polybutadiene (PB) onto which grafting can be induced is industrially important, because valuable materials like HIPS, ABS, and MBS are produced in this fashion. Surprisingly, however, few publications on the kinetics and mathematical modeling of such polymerization have appeared.<sup>1-5</sup> Other (mainly experimental) works on the grafting of styrene (S) onto PB or closely related reactions, are listed in Refs. 6-10.

In Brydon et al.,<sup>1,2</sup> the grafting of S onto PB in benzene solution at 60°C and with benzoyl peroxide as initiator was investigated. According to the proposed mechanism, the standard S kinetics is followed<sup>2</sup>:

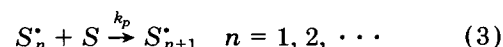
Initiator decomposition:



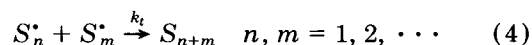
Primary radical attack on monomer:



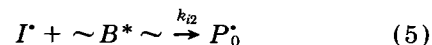
Homopolymer propagation:



Homopolymer-forming termination (by combination):



Primary radical attack on an unreacted internal butadiene unit ( $B^*$ ), contained either in the free PB or the copolymer:

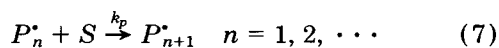


Butadiene radical attack on monomer:

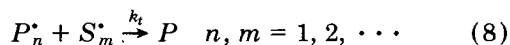


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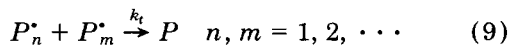
Copolymer radical propagation:



Copolymer-forming termination 1 (by combination):



Copolymer-forming termination 2 (by combination):



In the above mechanism, the grafted polymer chain is initiated only by direct attack of the initiator (primary) free radical on the preformed rubber backbone and the growing long-chain free radical is incapable of adding to the rubber. This last fact was experimentally verified in Ref. 1, where it was proved that with a different initiator (AIBN) the *S* was polymerized but no graft copolymer was detected. Manaresi et al.,<sup>3</sup> in an experimental and theoretical paper, proposed an extended mechanism that included chain-transfer reactions to the rubber and to the monomer. An even more detailed mechanism, capable of distinguishing among different copolymer types, was proposed by Chern and Poehlein<sup>4</sup> based on the same experimental evidence of Refs. 1 and 2. Through these extended mechanisms, the evolution of accumulated grafting efficiencies for the polymerized *S* could be derived.<sup>3,4</sup> In Sundberg et al.,<sup>5</sup> the grafting process of *S* onto a *PB* latex was presented. The kinetic scheme neglects eq. (8) and the chain transfer to the rubber and monomer, but includes the chain transfer to a transfer agent. This last reaction is important in emulsion processes, where otherwise excessively high molecular weight material is produced.<sup>5</sup>

This work aims at theoretically estimating the detailed molecular macrostructure of the polymer mixture generated in a solution polymerization of *S* under the presence of *PB*. The mathematical model herein developed assumes the relatively simple kinetics of Brydon et al.,<sup>1,2</sup> but extends it in the sense of computing each of the possible molecular structures of the dead copolymer *P*. Some of the experimental results presented in the Refs. 1 and 2 and here utilized to validate the new extended model.

## BASIC CONSIDERATIONS

A copolymer radical is either deactivated by a *PS* radical (termination 1) or by another copolymer

radical (termination 2). In the first case, a new *S* branch grafted at one end onto a single *B* chain is produced. In the second, the new *S* branch links two *B* chains belonging to different preexistent molecules.

We shall classify each of the copolymer molecules into different topologies that will be characterized by the pair of integers (*p*, *q*), where *p* and *q*, respectively, indicate the number of *S* and *B* chains. The following nomenclature will characterize an accumulated global topology, an accumulated molecular species within a topology, and a new copolymer radical:

- $P_{(p,q)}$  represents an inactive copolymer molecule of topology (*p*, *q*);
- $P_{(p,q)}(s, b)$  represents a molecular species of  $P_{(p,q)}$ , with *s* repetitive units of *S* and *b* repetitive units of *B*; and
- $P_{r(p,q)}^*(s, b)$  represents an activated  $P_{(p,q)}(s, b)$  species, with a new growing branch containing *r* repetitive units of *S*. Note that the repeating units in the new chain are not included in *s*.

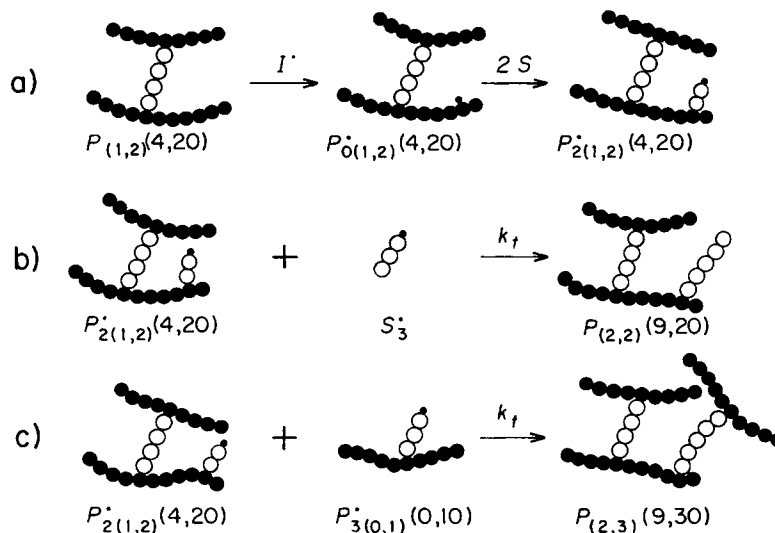
To illustrate the nomenclature above, Figure 1(a) represents the production of a copolymer radical, and in Figure 1(b) and (c), the two termination types are presented.

Any *S* branch in the dead copolymer has either one or both ends grafted onto different *B* chains, and intramolecular reactions are not considered. Thus, the following relationship between the number of *S* and *B* chains in any dead copolymer molecule is verified:

$$p \geq q - 1 \quad (q = 1, 2, \dots) \quad (10)$$

Also, it may be proven that in a given (*p*, *q*) topology the number of grafting points per molecule is  $p + q - 1$ .

For the total accumulated copolymer, we shall indicate with *n* and *g* the number of moles and its mass, respectively. These same properties, but for a given topology, will be represented by  $n_{(p,q)}$  and  $g_{(p,q)}$ . Finally, at molecular species level within a topology (i.e., for any combination of *p*, *q*, *s*, and *b*), then  $n_{(p,q)}(s, b)$  and  $g_{(p,q)}(s, b)$ , respectively, represent the moles and mass of  $P_{(p,q)}(s, b)$ . Alternatively, for fixed values of (*p*, *q*), but arbitrary values of (*s*, *b*),  $n_{(p,q)}(s, b)$  and  $g_{(p,q)}(s, b)$  can be, respectively, interpreted as the bivariate number- and weight-chain-length distribution (NCLD and WCLD) of topology (*p*, *q*).



**Figure 1** Illustration of nomenclature: (a) generation of a copolymer radical; (b, c) formation of a deactivated copolymer by terminations 1 and 2. (●) B unit; (○) S unit; (•) free radical.

A univariate WCLD completely specifies an homopolymer macrostructure. At the beginning of the reaction, the WCLD of the base *PB* is assumed known. We shall represent this distribution by  $g_{PB}^o(b)$ , where the supraindex “o” indicates initial conditions. The WCLD of the free accumulated *PS* will be represented by  $g_{PS}(s)$ . The total *PB* and *PS* masses can be, respectively, obtained through  $g_{PB} = \sum_{b=1}^{\infty} g_{PB}(b)$  and  $g_{PS} = \sum_{s=1}^{\infty} g_{PS}(s)$ .

For the total copolymer, the bivariate chain length distributions will be

$$n(s, b) = \sum_{q=1}^{\infty} \sum_{p=1}^{\infty} n_{(p,q)}(s, b);$$

$$g(s, b) = \sum_{q=1}^{\infty} \sum_{p=1}^{\infty} g_{(p,q)}(s, b) \quad (11)$$

and, therefore,

$$n = \sum_{s=1}^{\infty} \sum_{b=1}^{\infty} n(s, b); \quad g = \sum_{s=1}^{\infty} \sum_{b=1}^{\infty} g(s, b) \quad (12)$$

For any dead copolymer molecule, the independent variables  $s$  and  $b$  are related to the molecular weight ( $M$ ) and to the weight fraction of *S* ( $w_S$ ) through

$$M = sM_S + bM_B \quad (13)$$

and

$$w_S = \frac{sM_S}{M} \quad (0 \leq w_S \leq 1) \quad (14)$$

where  $M_S$  and  $M_B$  are the molecular weights of *S* and *B*, respectively. For the total copolymer, a topology, and a species within a topology, and their moles and masses are interrelated by

$$n = \frac{g}{\bar{M}_n}; \quad n(s, b) = \frac{g(s, b)}{sM_S + bM_B};$$

$$n_{(p,q)}(s, b) = \frac{g_{(p,q)}(s, b)}{sM_S + bM_B} \quad (15)$$

where  $\bar{M}_n$  is the copolymer number-average molecular weight (NAMW).

Equations (13) and (14) allow the changing of the independent variables from  $(s, b)$  into  $(M, w_S)$ . We shall call  $g(M, w_S)$  and  $g_{(p,q)}(M, w_S)$  the bivariate molecular weight/chemical composition distributions (MW/CCDs) for the total copolymer and for topology  $(p, q)$ , respectively. These functions can be obtained from the bivariate NCLD or WCLDs and are, strictly speaking, discrete distributions with unevenly spaced points along the horizontal axes. For this reason, appropriate procedures must be applied when “continuous” surfaces are employed to represent them.<sup>11</sup> After the transformations, the original WCLDs are, in general, irrecoverable from their derived MW/CCDs.

For a given topology or for the total copolymer, the univariate molecular weight distributions  $g_{(p,q)}(M)$  and  $g(M)$  are obtained by integration of the corresponding bivariate MW/CCDs:

$$g_{(p,q)}(M) = \sum_{w_S} q_{(p,q)}(M, w_S);$$

$$g(M) = \sum_{w_S} g(M, w_S) \quad (16)$$

Similarly, the univariate chemical composition distributions are obtained from

$$g_{(p,q)}(w_S) = \sum_M g_{(p,q)}(M, w_S);$$

$$g(w_S) = \sum_M g(M, w_S) \quad (17)$$

The average molecular weights of the total copolymer can be obtained from  $g(M)$ . However, it is numerically preferable to directly calculate such averages from the bivariate WCLD, as follows:

$$\bar{M}_n = \frac{\sum_{b=1}^{\infty} \sum_{s=1}^{\infty} g(s, b)}{\sum_{b=1}^{\infty} \sum_{s=1}^{\infty} \frac{g(s, b)}{(M_S s + M_B b)}};$$

$$\bar{M}_w = \frac{\sum_{b=1}^{\infty} \sum_{s=1}^{\infty} g(s, b) (M_S s + M_B b)}{\sum_{b=1}^{\infty} \sum_{s=1}^{\infty} g(s, b)} \quad (18)$$

Similarly, the global  $S$  mass fraction in the total copolymer is found from

$$\bar{w}_S = \frac{\sum_{b=1}^{\infty} \sum_{s=1}^{\infty} \frac{g(s, b) s M_S}{(M_S s + M_B b)}}{\sum_{b=1}^{\infty} \sum_{s=1}^{\infty} g(s, b)} \quad (19)$$

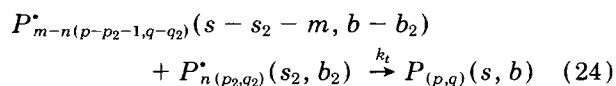
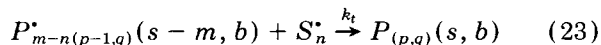
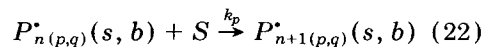
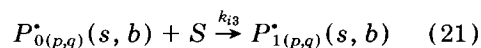
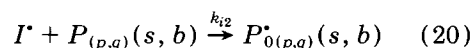
All the previous distributions and averages characterized the accumulated polymer mixture along the reaction. Time ( $t$ ) is not explicitly incorporated to simplify the notation.

Integers  $p$  and  $q$  unambiguously characterize the basic configuration of topologies with  $p = 1$  and arbitrary  $q$ . For example,  $P_{(5,1)}$  represents a comblike molecule with five  $PS$  branches bound onto a single  $PB$  chain. This is not the case, however, of topologies with  $p \geq 2$ , and, for example,  $P_{(3,2)}$  englobes any of the six possible configurations illustrated in Figure

2. Configurations (a)–(c) are discarded in our treatment because intramolecular termination is highly improbable and therefore not contemplated in the kinetics. Configurations (d)–(f) are all possible, but will be hereafter “lumped” into the single (3, 2) category. Note that the relationship  $p \geq q - 1$  does not hold for configurations (a)–(c).

### MATHEMATICAL MODEL

To compute the evolution of the generic species  $P_{(p,q)}(s, b)$ , we shall replace the set of global eqs. (5)–(9) by the following:



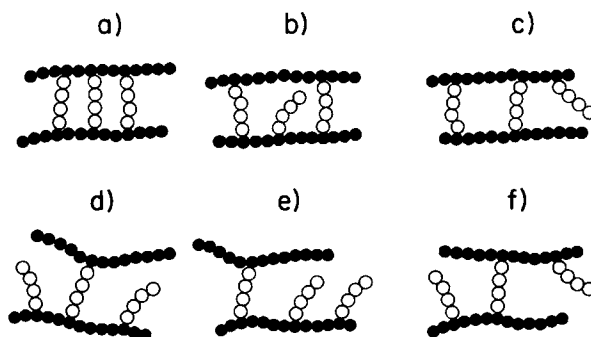
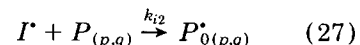
with the indexes varying as follows:

$$p, p_2, s, s_2 = 0, 1, 2, \dots \quad (25)$$

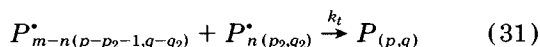
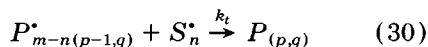
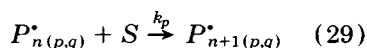
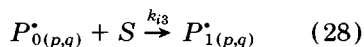
$$q, q_2, b, b_2, n, m = 1, 2, 3, \dots \quad (26)$$

Note that in eqs. (20)–(26) we have considered the  $PB$  as a special case of copolymer. Thus,  $P_{0(0,1)}^*(0, b)$  represents an attacked  $PB$  molecule.

By summation of eqs. (20)–(24) over all possible  $s$  and  $b$  values, the topology-level kinetics is obtained:



**Figure 2** Possible configurations of topology (3, 2). Only configurations (d)–(f) are feasible with the proposed kinetic mechanism: (●)  $B$  unit; (○)  $S$  unit.



where  $p$ ,  $p_2$ ,  $n$ ,  $q$ ,  $q_2$ , and  $m$  are varied as in eqs. (25) and (26). Finally, by summation over all indexes  $p$ ,  $p_2$ ,  $q$ ,  $q_2$ , eqs. (5)–(9) may be recuperated from eqs. (27)–(31).

From the extended mechanism of eqs. (1)–(4) and (20)–(26), a dynamic mass balance for each of the intervening species can be developed (see Appendix) and an analytical expression for the instantaneous univariate NCLD that characterizes both the free  $PS$  and the new  $S$  branches incorporated into the copolymer can be derived. Two modules constitute our computer model. The first (Basic Module) allows the prediction of global variables such as conversion. The second (Distributions Module) allows the evaluation of the evolving polymer macrostructure.

### Basic Module

The equations presented in this section could be directly obtained from the global mechanism of eqs. (1)–(9), but we shall here make use of the extended treatment considered in the Appendix. For the constant reaction volume ( $V$ ), eq. (A.1) provides

$$\frac{d[I_2]}{dt} = -fk_d[I_2] \quad (32)$$

where  $[\cdot]$  indicates molar concentration.

Define the monomer conversion as  $x = ([S]^\circ - [S])/[S]^\circ$ . Its evolution may be obtained considering eqs. (A.2) and (A.16), resulting in

$$\begin{aligned} \frac{dx}{dt} &= -\frac{1}{[S]^\circ} \frac{d[S]}{dt} \\ &= k_p(1-x)([S^*] + [P^*]) = \frac{R_p}{[S]^\circ} \quad (33) \end{aligned}$$

with

$$[S^*] = \sum_{n=1}^{\infty} [S_n^*] \quad (34)$$

$$[P^*] = \sum_{q=1}^{\infty} \sum_{p=0}^{\infty} \sum_{b=1}^{\infty} \sum_{s=0}^{\infty} \sum_{n=1}^{\infty} \{P_{n(p,q)}^*(s, b)\} \quad (35)$$

$$R_p = k_p \left( \frac{2fk_d}{k_t} \right)^{1/2} [S][I_2]^{1/2} \quad (36)$$

where  $R_p$  is the global  $S$  polymerization rate, while  $[S^*]$  and  $[P^*]$  are the total concentrations of  $S$  homoradicals and copolymer radicals, respectively.

From eqs. (5) and (A.15), the concentration of (unreacted)  $B$  units still containing a double bond ( $B^*$ ), and present either in the free  $PB$  or in the copolymer may be found from

$$\begin{aligned} \frac{d[B^*]}{dt} &= -k_{i2}[I^*][B^*] \\ &= -\frac{2fk_d[I_2]}{\left(\frac{k_{i1}}{k_{i2}}[S] + [B^*]\right)} [B^*] \quad (37) \end{aligned}$$

The accumulated mass of bound  $S$  can be classified as free  $PS$  ( $g_{PS}$ ) or as grafted  $S$ . In this last case, one can further distinguish the mass incorporated into the dead copolymer by termination 1 ( $g_{GS1}$ ) from that incorporated by termination 2 ( $g_{GS2}$ ). As in Brydon et al.,<sup>1,2</sup> the  $PS$  grafting efficiency is defined by

$$E_{PS} = \frac{g_{GS1} + g_{GS2}}{g_{PS} + g_{GS1} + g_{GS2}} \quad (38)$$

The same grafting efficiency, but for the instantaneously polymerized  $S$ , is also defined by

$$F = (R_{pGS1} + R_{pGS2})/R_p \quad (39)$$

where  $R_{pGS1}$  and  $R_{pGS2}$  are the polymerization rates yielding  $g_{GS1}$  and  $g_{GS2}$ . An expression for  $F$  may be obtained by replacing (A.18) into (A.27), yielding, as in Refs. 1 and 2,

$$F = 1 - \left[ \frac{k_{i1}[S]}{k_{i1}[S] + k_{i2}[B^*]} \right]^2 \quad (40)$$

The evolution of the different polymerized masses of  $S$  are obtained from eqs. (36) and (A.23)–(A.27), producing

$$\begin{aligned} \frac{d(g_{PS})}{dt} &= \left\{ k_p[S] \left[ \frac{2fk_d[I_2]}{k_t} \right]^{1/2} (1-F) \right\} M_S V \\ &= R_{pPS} M_S V \quad (41) \end{aligned}$$

$$\begin{aligned} \frac{d(g_{GS1})}{dt} &= \left\{ 2k_p[S] \left[ \frac{2fk_d[I_2]}{k_t} \right]^{1/2} \right. \\ &\quad \left. \times (1-F)^{1/2} [1 - (1-F)^{1/2}] \right\} M_S V \\ &= R_{pGS1} M_S V \end{aligned} \quad (42)$$

$$\begin{aligned} \frac{d(g_{GS2})}{dt} &= \left\{ k_p[S] \left[ \frac{2fk_d[I_2]}{k_t} \right]^{1/2} \right. \\ &\quad \left. \times [1 - (1-F)^{1/2}]^2 \right\} M_S V \\ &= R_{pGS2} M_S V \end{aligned} \quad (43)$$

where  $R_{pPS}$  is the rate of free *PS* production.

## Distributions Module

### Free *PS*

Multiplying eqs. (A.31) by the molecular weight ( $sM_S$ ), an expression for the instantaneous WCLD is obtained. Its finite difference approximation is

$$\begin{aligned} \Delta g_{PS}(s) &= R_{pPS} \frac{\beta^3}{2} s^2 e^{-\beta s} M_S V \Delta t; \\ s &= 1, 2, 3, \dots \end{aligned} \quad (44)$$

where  $\Delta g_{PS}(s)$  represents the WCLD produced during the (short) time interval  $\Delta t$ . Equation (44) indicates that the instantaneous WCLD may be represented by the (single-parameter and normalized) distribution of chain lengths ( $\beta^3/2 \times s^2 e^{-\beta s}$ ) with  $s = 1, 2, \dots$  multiplied by its mass ( $R_{pPS} M_S V \Delta t$ ). The kinetic parameter  $\beta$ , defined in eq. (A.28), is also related to the instantaneous NAMW through Reference 12:

$$\bar{M}_{n,PS_{inst}} = 2M_S/\beta \quad (45)$$

The polydispersity of the instantaneous *PS* is  $\bar{M}_{w,PS_{inst}}/\bar{M}_{n,PS_{inst}} = 1.5$ , and the molecular weight distribution of the total free *PS* is found by simple accumulation:

$$g_{PS}(s) \simeq \sum_{t_k} \Delta g_{PS}(s) \quad s = 1, 2, 3, \dots \quad (46)$$

where (even though not explicitly indicated),  $\Delta g_{PS}(s)$  and  $g_{PS}$  are a function of the discrete time  $t_k = 0, 1, 2, \dots, k$ .

## Copolymer Topologies

The evolving macrostructure for each of the different copolymer topologies can be calculated through a balance involving the disappearance (due to grafting) of inactive species present in the *PB* or in the accumulated bivariate distributions and the generation of new copolymer species via grafting reactions.

After solving the Basic Module, the bivariate NCLDs of the accumulated copolymer topologies can be calculated through eq. (A.48) in conjunction with eqs. (A.24), (A.25), (A.32), and (A.33). To simplify the computer implementation of eqs. (A.48), and also to provide a clearer interpretation of its terms, the mentioned equation will be now rederived. This more "intuitive" approach considers the appearance and disappearance of accumulated copolymer species, with incorporation of complete new *S* branches and without consideration of intermediate growing radicals. It is based on the following results: (a) the instantaneous new masses of *S* incorporated onto the copolymer by terminations 1 and 2 may be calculated through eqs. (42) and (43); (b) the normalized NCLDs of the newly generated *PS* homopolymer and of the grafted *S* branches (by terminations 1 or 2) are all identical (see Appendix), and (c) for any generic species of the free *PB* or the copolymer, the number of new grafting sites are proportional to their  $B^*$  contents.

At the beginning of each  $\Delta t$ , the set of bivariate NCLDs for each of the accumulated topologies is assumed known. Also included in this set is the NCLD of the unreacted *PB* [represented by  $n_{(0,1)}(0, b)$ ]. From the complete set of NCLDs, the corresponding WCLDs of unreacted *B* units only can be calculated as follows:

$$\begin{aligned} g_{B^*(p,q)}(s, b) &= (b - p - q + 1) n_{(p,q)}(s, b) M_B \\ &\quad \text{(for all } p, q, s, b) \end{aligned} \quad (47)$$

because any copolymer molecule has  $(b - p - q + 1)$  unreacted *B* units.

The total mass of unreacted *B* units can be obtained by integration of eqs. (47) like in eqs. (A.33) or directly from

$$g_{B^*} = [B^*] M_B V \quad (48)$$

with  $[B^*]$  determined through eq. (37).

At each sampling interval, the variation in the number of moles of the accumulated generic species  $P_{(p,q)}(s, b)$  may be calculated through

$$\begin{aligned} \Delta n_{(p,q)}(s, b) = & -\Delta n_{(p,q)}(s, b)|_{c_1} + \Delta n_{(p,q)}(s, b)|_{g_1} \\ & - \Delta n_{(p,q)}(s, b)|_{c_2} + \Delta n_{(p,q)}(s, b)|_{g_2} \\ & \text{(for all } p, q, s, b) \end{aligned} \quad (49)$$

where subindex  $c_1$  indicates instantaneous consumption (by termination 1) of the accumulated  $P_{(p,q)}(s, b)$  molecules (which includes the  $PB$  as a special case); subindex  $g_1$  indicates instantaneous generation of  $P_{(p,q)}(s, b)$  due to the same reaction; and subindexes  $c_2, g_2$ , respectively, indicate consumption and generation of  $P_{(p,q)}(s, b)$  by termination 2. In what follows, expressions for each of the terms in eq. (49) will be derived.

Consider the first two terms in the right-hand side of eq. (49). The new grafted mass of  $S$  due to termination 1 is obtained from eq. (42) by differentiation of the "continuous"  $g_{GS1}(t)$  function, yielding

$$\Delta g_{GS1} = R_{pGS1} M_S V \Delta t \quad (50)$$

For every mole of new  $S$  branches, 1 mol of old accumulated polymer is consumed and 1 mol of new copolymer is generated. Thus, the following can be written

$$\Delta n|_{c_1} = \Delta n|_{g_1} = \frac{\Delta g_{GS1}}{\bar{M}_{n,branch}} \quad (51)$$

where  $\bar{M}_{n,branch}$  is the NAMW of the new  $S$  branch; that as in eq. (45) is given by

$$\bar{M}_{n,branch} = \frac{2M_S}{\beta} \quad (52)$$

Introducing eqs. (50) and (52) into eq. (51), one finds

$$\Delta n|_{c_1} = \Delta n|_{g_1} = R_{pGS1} V \Delta t \frac{\beta}{2} \quad (53)$$

Since a single grafting point per  $S$  branch is produced through termination 1, then  $\Delta n|_{c_1}$  also represents the instantaneous total number of new grafting sites. These points are "distributed" among all possible  $PB$  or copolymer species proportionately to the molar fraction of their unreacted  $B$  units. Thus, one can write

$$\begin{aligned} \Delta n_{(p,q)}(s, b)|_{c_1} = \Delta n|_{c_1} \frac{g_{B^*(p,q)}(s, b)}{g_{B^*}} \\ \text{(for all } p, q, s, b) \end{aligned} \quad (54)$$

Termination 1 maintains the number of  $B$  chains in the original parental molecule ( $q$ ) and its  $B$  contents ( $b$ ). A new generic  $P_{(p,q)}(s, b)$  species is generated by incorporation of an  $S$  branch of arbitrary length  $m$  onto an accumulated  $P_{(p-1,q)}(s-m, b)$  species. At each  $m$ , the molar fraction of new  $S$  chains is represented by  $(\beta^2 m e^{-\beta m})$ . Therefore,

$$\begin{aligned} \Delta n_{(p,q)}(s, b)|_{g_1} \\ = \Delta n|_{g_1} \sum_{m=1}^s \frac{g_{B^*(p-1,q)}(s-m, b)}{g_{B^*}} \beta^2 m e^{-\beta m} \\ \text{(for all } p, q, s, b) \end{aligned} \quad (55)$$

Consider now the consumption and generation of  $P_{(p,q)}(s, b)$  by the mechanism of termination 2. At each sampling interval  $\Delta t$ , the total new  $S$  mass may be found by differentiation of the continuous  $g_{GS2}(t)$  function obtained from eq. (45), resulting in

$$\Delta g_{GS2} = R_{pGS2} M_S V \Delta t \quad (56)$$

For every mole of new  $S$  linking chains, 2 mol of accumulated polymer are consumed and 1 mol of new copolymer is generated. Therefore,

$$\frac{1}{2} \Delta n|_{c_2} = \Delta n|_{g_2} = \frac{\Delta g_{GS2}}{\bar{M}_{n,branch}} \quad (57)$$

where  $\bar{M}_{n,branch}$  is the NAMW of the new linking chains. Introducing eqs. (56) and (52) into eq. (57), one finds

$$\frac{1}{2} \Delta n|_{c_2} = \Delta n|_{g_2} = R_{pGS2} V \Delta t \frac{\beta}{2} \quad (58)$$

The moles of new linking chains is one-half the moles of new grafting sites, and these new grafting sites are distributed among all possible  $PB$  or copolymer species proportionately to their  $B^*$  contents. Therefore,

$$\begin{aligned} \Delta n_{(p,q)}(s, b)|_{c_2} = \Delta n|_{c_2} \frac{g_{B^*(p,q)}(s, b)}{g_{B^*}} \\ \text{(for all } p, q, s, b) \end{aligned} \quad (59)$$

To evaluate the generation of a  $P_{(p,q)}(s, b)$  species by termination 2, we shall imagine a two-step process. In step 1, the final inactive branch of chain length  $m$  is linked at one end onto the accumulated species  $P_{(p_1,q_1)}(s_1, b_1)$ . In step 2, the free end of this intermediate species is linked onto the accumulated species  $P_{(p_2,q_2)}(s_2, b_2)$ . The following relationships

must be verified for all possible combinations of  $p_1$ ,  $p_2$ ,  $q_1$ ,  $q_2$ ,  $s_1$ ,  $s_2$ ,  $m$ ,  $b_1$ , and  $b_2$ :

$$p_1 + p_2 + 1 = p; \quad q_1 + q_2 = q; \\ s_1 + s_2 + m = s; \quad b_1 + b_2 = b \quad (60)$$

and, therefore,  $p_1 = p - p_2 - 1$ ;  $q_1 = q - q_2$ ;  $s_1 = s - s_2 - m$ ; and  $b_1 = b - b_2$ .

In the first step of termination 2,  $\Delta n|_{g_2}$  mol of new  $S$  chains react with an equal number of moles of accumulated  $P_{(p_1, q_1)}(s_1, b_1)$  species proportionately to their  $B^*$  contents. Remembering the NCLD of the  $S$  chains, the moles of new intermediate species  $P_{(p-p_2, q-q_2)}(s-s_2, b-b_2)$  may be obtained in a similar fashion to eq. (55), yielding

$$\Delta n_{(p-p_2, q-q_2)}(s-s_2, b-b_2)|_{g_2} \\ = \Delta n|_{g_2} \sum_{s_2 m=1}^s \frac{g_{B^*}^{(p-p_2-1, q-q_2)}(s-s_2-m, b-b_2)}{g_{B^*}} \\ \times \beta^2 m e^{-\beta m}$$

$$p_2 = 0, 1, \dots, p-1; \quad q_2 = 1, 2, \dots, q-1; \\ s_2 = 0, 1, \dots, s; \quad b_2 = 1, 2, \dots, b \quad (61)$$

In the second step, the intermediate species react with an equal number of accumulated  $P_{(p_2, q_2)}(s_2, b_2)$  species, providing the same total moles of new  $P_{(p, q)}(s, b)$  molecules. Also, each intermediate species can react with any other copolymer or free  $PB$  molecule, with the sole restriction that eqs. (60) must be verified. Therefore,

$$\Delta n_{(p, q)}(s, b)|_{g_2} = \Delta n|_{g_2} \sum_{q_2=1}^{q-1} \sum_{p_2=0}^{p-1} \sum_{b_2=1}^b \sum_{s_2+m=1}^s \\ \times \frac{g_{B^*}^{(p-p_2-1, q-q_2)}(s-s_2-m, b-b_2)}{g_{B^*}} \\ \times \frac{g_{B^*}^{(p_2, q_2)}(s_2, b_2)}{g_{B^*}} \times \beta^2 m e^{-\beta m} \\ \text{(for all } p, q, s, b) \quad (62)$$

Replacing eqs. (53)–(55), (58), (59), and (62) into eq. (49), the finite difference equivalent of eq. (A.48) is recuperated. Also, for each of the produced topologies, the instantaneous bivariate WCLD may be obtained from  $\Delta n_{(p, q)}(s, b)$  as follows:

$$\Delta g_{(p, q)}(s, b) = \Delta n_{(p, q)}(s, b)(M_{Ss} + M_B b) \\ \text{(for all } p, q, s, b) \quad (63)$$

Finally, the set of accumulated WCLDs are obtained by addition of the instantaneous WCLDs, yielding

$$g_{(p, q)}(s, b) = \sum_{i_k} \Delta g_{(p, q)}(s, b) \\ \text{(for all } s, b, p, q) \quad (64)$$

where it should be noted that  $\Delta g_{(p, q)}(s, b)$  can be either positive or negative.

### Residual PB

The WCLD of the instantaneously consumed  $PB$  may be obtained by first multiplying eqs. (A.50) by the molecular weights ( $bM_B$ ) and then taking finite differences:

$$\Delta g_{(0,1)}(0, b) = \Delta g_{PB}(b) = -(R_{PGS_1} + 2R_{PGS_2}) \\ \times \frac{\beta}{2} \frac{g_{PB}(b)}{g_{B^*}} b M_B V \Delta t \quad (b = 1, 2, 3, \dots) \quad (65)$$

The WCLD of the unreacted  $PB$  is therefore given by

$$g_{PB}(b) = g_{PB}^0(b) + \sum_{i_k} \Delta g_{PB}(b) \\ (b = 1, 2, 3, \dots) \quad (66)$$

with  $\Delta g_{PB}(b)$  being always negative. The total remaining mass of  $PB$  ( $g_{PB}$ ) is obtained by simple integration of  $g_{PB}(b)$  in all  $b$ 's.

### More Derived Variables

Apart from the average molecular weights and average chemical compositions, other global variables can be estimated from the Distributions Module:

(a)  $PB$  grafting efficiency ( $E_{PB}$ ):

$$E_{PB} = \frac{g_{PB}^0 - g_{PB}}{g_{PB}^0} \quad (67)$$

(b) average number of grafted  $S$  chains per reacted  $PB$  molecule ( $J_1$ ):

$$J_1 = \frac{\sum_{q=1}^{\infty} \sum_{p=1}^{\infty} \sum_{s=0}^{\infty} \sum_{b=1}^{\infty} p n_{(p, q)}(s, b)}{\sum_{b=1}^{\infty} \frac{[g_{PB}^0(b) - g_{PB}(b)]}{M_B b}} \quad (68)$$



(c) average number of grafted  $S$  chains per copolymer molecule ( $J_2$ ):

$$J_2 = \frac{\sum_{q=1}^{\infty} \sum_{p=1}^{\infty} \sum_{s=0}^{\infty} \sum_{b=1}^{\infty} pn_{(p,q)}(s, b)}{\sum_{q=1}^{\infty} \sum_{p=1}^{\infty} \sum_{s=0}^{\infty} \sum_{b=1}^{\infty} n_{(p,q)}(s, b)} \quad (69)$$

Note that to calculate these global variables the complete polymer macrostructure must be first estimated.

### Computer Implementation

After solving the Basic Module, the Distributions Module can be attempted. Instead of investigating all possible integers  $s$  and  $b$ , it is sufficient to concentrate their masses into a reduced set of fictitious points, taken at regular intervals of  $\Delta s$  and  $\Delta b$ .

Any nonzero topology generated along the polymerization should be allowed to undergo a grafting reaction. In practice, the apparition of a new topology is justified when enough accumulation of possible parental topologies is observed. The check for termination 1 simply implies the addition of a new branch onto all accumulated topologies. The check for termination 2 is more complex since it involves the cross-linking between all possible molecular pairs.

### SIMULATION EXAMPLE

The computer program was written in FORTRAN for a VAX11/780 machine with VMS operating system. A computation time of around 23 h was required to simulate a typical run.

The simulation of Reference Run No. 8 of Brydon et al.<sup>1,2</sup> will be presented here, which considers the polymerization of  $S$  at 60°C in dilute benzene solution with benzoyl peroxide as initiator and under the presence of a high *cis*-1,4-PB. The batch polymerization was carried out in a small reaction tube of  $V = 0.025L$ . The initial reagent concentrations were (1)

$$[S]^0 = 1.53 \text{ mol/L}; \quad [I_2]^0 = 0.025 \text{ mol/L}; \\ [B^*] = 0.53 \text{ mol/L} \quad (70)$$

and the WCLD of the base  $PB$  was assumed to be Schulz-Flory, with  $\bar{M}_{n,PB} = 145,000$  and total mass  $g_{PB}^0 = 0.7155 \text{ g}$ .<sup>1</sup> Therefore, one can write<sup>12</sup>

$$g_{PB}^0(b) = g_{BP}^0 \tau^2 b e^{-\tau b} \quad (71)$$

with

$$\tau = \frac{M_B}{\bar{M}_{n,PB}} = \frac{54.09}{145,000} = 3.73 \times 10^{-4} \quad (72)$$

The Basic Module parameters were adjusted as indicated below. The kinetic factor in eq. (36) was estimated from the measurements  $x$  vs.  $t$  presented in Ref. 1 and reproduced in Figure 3(a), yielding

$$R_1 = k_p \left( \frac{2fk_d}{k_t} \right)^{0.5} = [(2fk_d)^{0.5}] \left[ \frac{k_p}{k_t^{0.5}} \right] \\ = 3.81 \times 10^{-5} \frac{L^{0.5}}{\text{mol}^{0.5} \text{ s}} \quad (73)$$

For the Distributions Module, the values of  $(2fk_d)^{0.5}$ ,  $(k_p/k_t^{0.5})$ , and  $k_{i2}/k_{i1}$  must be known. For their adjustment, the measurements of  $E_{PB}$ ,  $J_1$ , and  $\bar{M}_{n,PB}$  presented in Refs. 1 and 2 were utilized [see Fig. 3(c)-(e)], resulting in

$$(2fk_d)^{0.5} = 1.9 \times 10^{-3} \text{ s}^{-0.5}; \\ \frac{k_p}{k_t^{0.5}} = 0.02 \left( \frac{L}{\text{mol s}} \right)^{0.5} \quad (74)$$

$$\frac{k_{i2}}{k_{i1}} = 0.63 \quad (75)$$

The values in eqs. (73) and (74) respond, for example, to the following combination of individual parameters:

$$f = 0.9; \quad k_p = 160 \frac{L}{\text{mol s}}; \quad k_t = 64 \times 10^6 \frac{L}{\text{mol s}}; \\ k_d = 2 \times 10^{-6} \text{ s}^{-1} \quad (76)$$

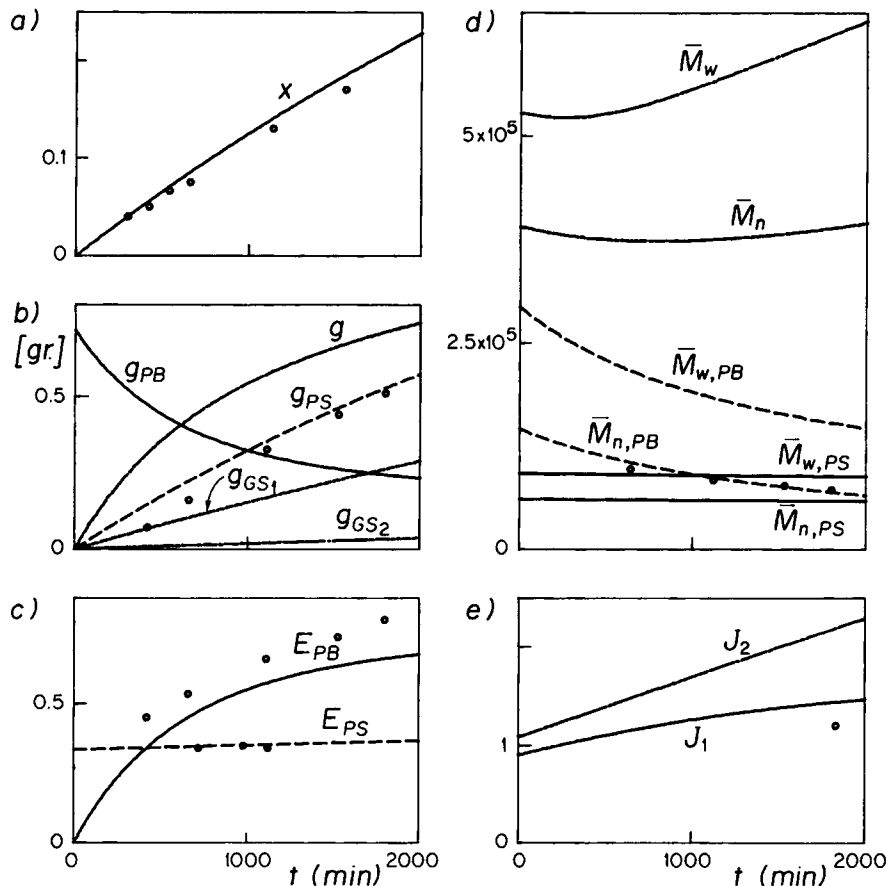
These rate constants are close to those determined in Ref. 4 also and fall within the following literature ranges<sup>13</sup>:

$$1.6 \times 10^{-6} \text{ s}^{-1} \leq k_d \leq 2.76 \times 10^{-6} \text{ s}^{-1};$$

$$80 \frac{L}{\text{mol s}} \leq k_p \leq 376 \frac{L}{\text{mol s}};$$

$$29.4 \times 10^6 \frac{L}{\text{mol s}} \leq k_t \leq 72 \times 10^6 \frac{L}{\text{mol s}}$$

For the Distributions Module, the total polymerization time was discretized into 400 intervals of  $\Delta t = 5 \text{ min}$  each, while the chain lengths  $s$  and  $b$  were



**Figure 3** Simulated example: parameters adjustment. The experimental points for  $x$ ,  $g_{PS}$ ,  $E_{PB}$ ,  $E_{PS}$ ,  $\bar{M}_{n,PB}$ , and  $J_1$  (taken from Refs. 1 and 2), are compared to the model predictions. Also represented are the simulated evolutions of  $g_{GS1}$ ,  $g_{GS2}$ ,  $g$ ,  $g_{PB}$ ,  $\bar{M}_{n,PS}$ ,  $\bar{M}_{w,PB}$ ,  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $J_2$ .

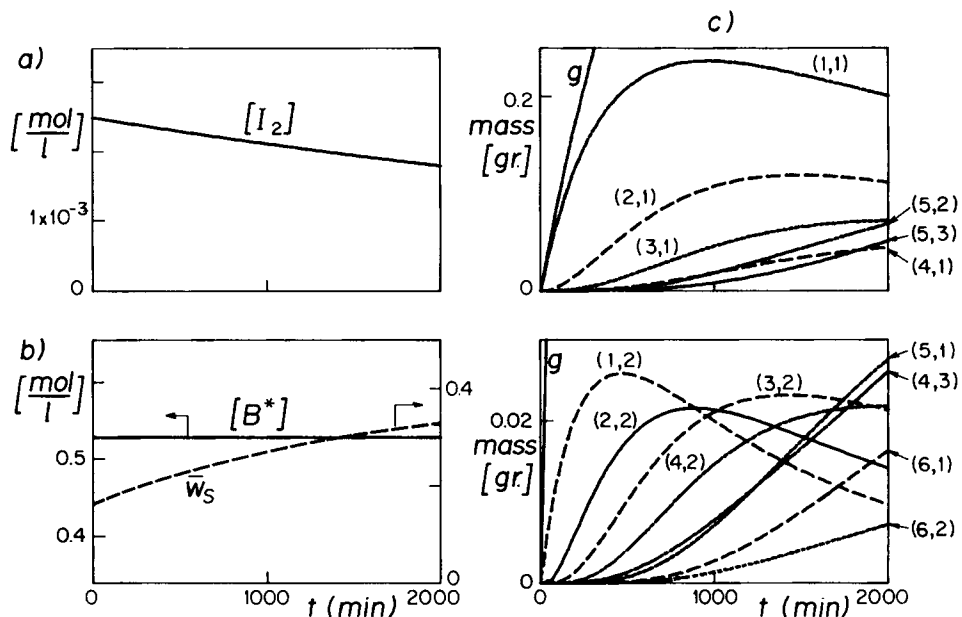
discretized into 100 intervals of  $\Delta s = 200$  and  $\Delta b = 600$ .

The simulation results are presented in Figures 3–6. At the final experimental time ( $t = 1800$  s), the measurements were<sup>2</sup>  $x = 0.19$ ,  $g_{PS} = 0.50$  g,  $E_{PB} = 80\%$ ,  $E_{PS} = 33\%$ ,  $\bar{M}_{n,PB} = 71,600$ , and  $J_1 = 1.1$ . With regard to Figures 3 and 4, the following can be mentioned:

1. The simulated results match the experimental points rather well, in spite that only three kinetic parameters were adjusted within expected ranges.
2.  $g_{PS}$ ,  $g_{GS1}$ , and  $g_{GS2}$  grow more or less linearly with time. For this reason,  $x(t)$  is also approximately linear and  $E_{PS}$  remains practically constant. The shape of  $E_{PB}$  is a consequence of  $g_{PB}(t)$ .
3. The WCLD of the free PS (and therefore of the grafted S chains) remains practically con-

stant along the polymerization, as suggested by the evolutions of  $\bar{M}_{n,PS}$  and  $\bar{M}_{w,PS}$ .  $\bar{M}_{n,PB}$  decreases as a consequence of the higher probability of larger PB molecules to induce grafting. The copolymer molecular weights first decrease (mainly due to the drop in  $\bar{M}_{n,PB}$ ), then increase as a consequence of the grafting-over grafting process.

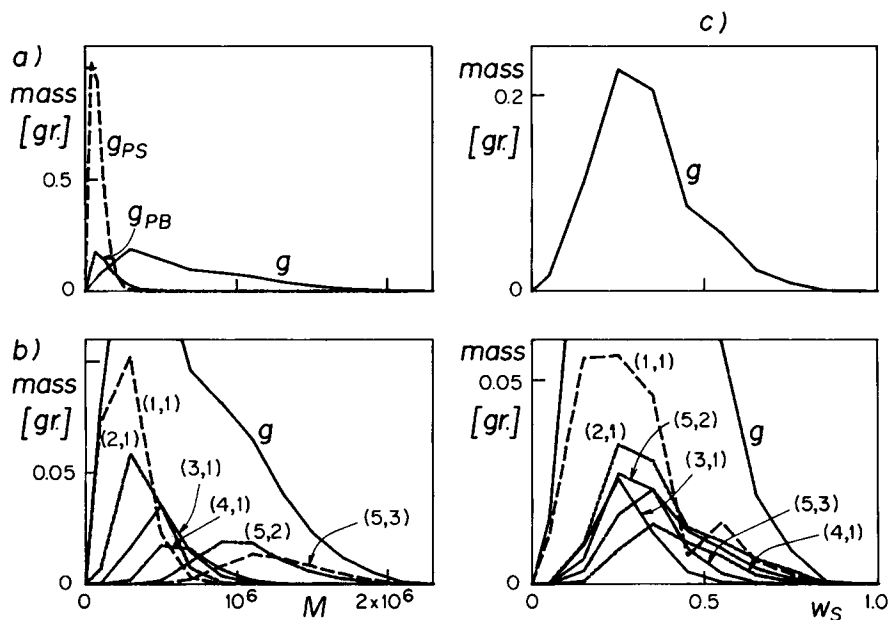
4. The average number of grafted S chains per copolymer molecule ( $J_2$ ) increases almost linearly with time, while the average copolymer composition ( $\bar{w}_S$ ) also increases, due to the drop in  $g_{PB}$  in combination with the grafting-over grafting process. As expected,  $[B^*]$  remains practically constant.
5. In Figure 4(c), the evolution of the more abundant copolymer topologies is illustrated. At the final time, these topologies count for more than 97% of the total copolymer mass. The remaining 3% corresponds to the sum of



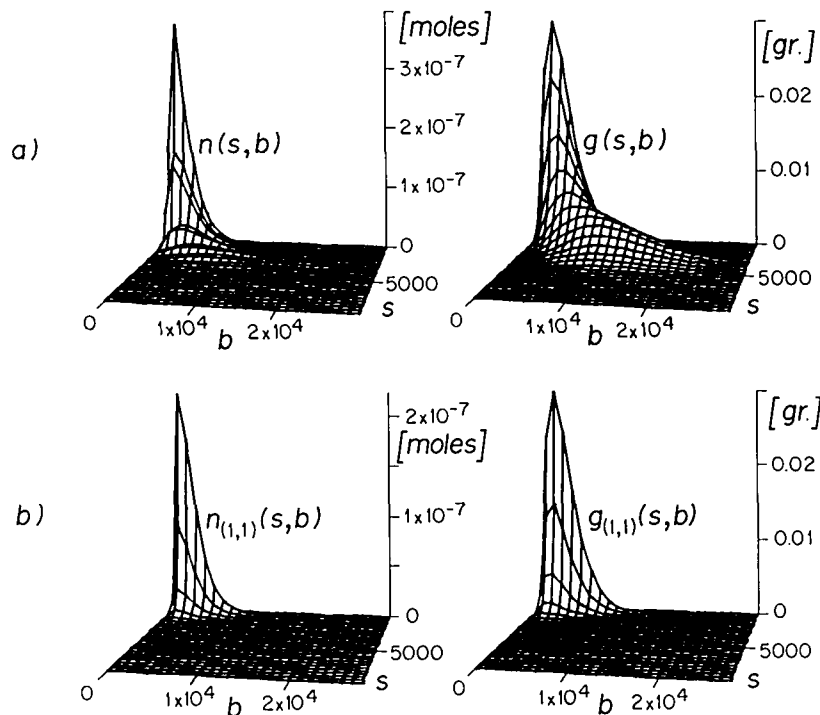
**Figure 4** Simulated example: more theoretical predictions. In (c), the mass evolution of the more abundant topologies are represented in two different scales together with the evolution of the total copolymer mass ( $g$ ).

all higher topologies. The higher topologies observed [but not represented in Fig. 4(c)] were  $P_{(7,1)}$  and  $P_{(7,4)}$ . The higher the conversion, the higher the topologies that tend to accumulate.

6. Consider the mass evolution of topologies with one  $B$  chain ( $p = 1$ ). At the investigated conversions, the primary "T-shaped" topology  $P_{(1,1)}$  is always the most abundant, followed by  $P_{(2,1)}$ ; this, in turn, is followed by  $P_{(3,1)}$  and



**Figure 5** Simulated example: univariate distributions at  $t = 2000$  min. (a) WCLDs of free  $PS$ , unreacted  $PB$ , and copolymer. (b) WCLDs of more abundant topologies, with  $g(M)$  shown for comparison. (c) CCDs for total copolymer and individual topologies (in two different scales).



**Figure 6** Simulated example: bivariate NCLDs and WCLDs at  $t = 2000$  min (a) for total copolymer and (b) for most abundant (1, 1) topology.

so on. For an arbitrary number of  $S$  branches enough accumulation of topology  $(p_1, 1)$  is required before topology  $(p_1 + 1, 1)$  can start being produced. The maxima in  $P_{(1,1)}$  and  $P_{(2,1)}$  indicate that at higher conversions all “lower” topologies tend to disappear, with the copolymer molecular weights tending to infinity.

7. Consider the evolution of molecules with two  $B$  chains ( $p = 2$ ). At the final time, topology  $P_{(5,2)}$  is more abundant than is the primary (“H-shaped”) topology  $P_{(1,2)}$ . Clearly, the “primary” (1, 1) and (1, 2) topologies are the first in their series to be consumed.

Consider the univariate and bivariate distributions at the final simulated time, represented in Figures 5 and 6. The observed discontinuities are a consequence of the continuation procedure associated with the transformation of independent variables  $(s, b)$  into  $(w_S, M)$ .

1. In Figure 5(a), The WCLDs of the free  $PS$ , the unreacted  $PB$ , and the total copolymer are illustrated. The areas under these curves represent their masses at  $t = 2000$  min.
2. Figure 5(b) represents the WCLDs of the more abundant topologies. As expected, higher

topologies also exhibit the higher molecular weights.

3. In Figure 5(c), the CCDs for the total copolymer ( $g$ ) and more abundant topologies are represented. Topology (1, 1) shows a bimodality, as a consequence of the WCLD in each of its two constituent chains. For all higher topologies, the expected multimodalities are smeared off, thus each exhibiting a single maximum.
4. In Figure 6(a), the bivariate number and WCLDs for the final copolymer are represented. High molecular weight species are only “visible” in the WCLD. In Figure 6(b), the same bivariate distributions but for the most abundant (1, 1) topology are represented. As expected, its contribution toward the total copolymer is mainly at the low molecular weight end.

## DISCUSSION

As far as the authors are aware, this is the first attempt to theoretically predict the evolution of a detailed graft copolymer macrostructure. In particular, the polymerization of  $S$  in presence of  $PB$  and in

dilute solution (i.e., with no “gel” effect) was investigated, and this is because a relatively simple kinetics is capable of adequately interpreting the available experimental data.<sup>1,2</sup> The model is consistent in the sense that the global predictions of the Basic Module may be also recuperated by appropriate integration of the Distributions Module results.

Model predictions proved in excellent agreement with global experimental measurements.<sup>1,2</sup> The Distributions Module is capable of estimating the polymer macrostructure and other important averages such as the number of grafted *S* chains per copolymer molecule ( $J_2$ ). The simulation results related to the copolymer macrostructure are presently impossible to verify, but it is expected that theoretical developments like this work may spur parallel developments in copolymer analysis techniques and vice versa.

Remembering Figure 2, it is clear that with the pair of ( $p, q$ ) integers only it is impossible to completely specify a complex copolymer configuration. But when (as in our case) the final number of grafted chains is relatively low, then enough information may still be available from the sought specification.

In a future communication, and in order to apply the technique to other polymerization systems, the kinetic model will be extended to include (a) termination by disproportionation; (b) radical transfer to a modifier or some other small molecule; and (c) attack of the *S* radical onto the base *PB* to generate a new branch. It can be proven that in such a model the NCLD of the instantaneous free *PS* still coincides with that of the new grafted branches and that its shape can be represented by a two-parameter binomial distribution.<sup>14</sup> Even with the treated kinetics, other extensions of the present approach are also possible. For example, to simulate the bulk polymerization of *S* in the manufacture of HIPS, then the problems of polymerization in two phases and diffusional control by “gel effect” should have to be taken into consideration.

The authors acknowledge CONICET and Universidad Nacional del Litoral (Argentina) for their financial support.

## APPENDIX: THE DISTRIBUTIONS MODULE

### Mass Balance

From the extended mechanism of eqs. (1)–(4) and (20)–(26), the material balance for each of the intervening

species may be developed. The balances for the initiator and monomer are

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

$$\frac{d}{dt} ([S]V) = -R_pV = -k_p[S]([S^*] + [P^*])V \quad (\text{A.2})$$

where  $[S^*] = \sum_{n=1}^{\infty} [S_n^*]$  is the total concentration of growing homoradicals and  $[P^*] = \sum_{q=1}^{\infty} \sum_{p=0}^{\infty} \sum_{b=1}^{\infty} \sum_{s=0}^{\infty} \sum_{n=1}^{\infty} [P_{n(p,q)}^*(s, b)]$  is the total concentration of copolymer radicals. In eq. (A.2), the “long-chain approximation” has been assumed; i.e., propagation is the only monomer-consuming reaction. Consider now the final products’ balances at the molecular species level:

Residual *PB*:

$$\begin{aligned} \frac{d}{dt} ([P_{(0,1)}(0, b)]V) \\ = -k_{i2}[I^*]b[P_{(0,1)}(0, b)]V \quad b = 1, 2, 3, \dots \end{aligned} \quad (\text{A.3})$$

Free *PS*:

$$\begin{aligned} \frac{d}{dt} ([S_s]V) = \frac{1}{2}k_t \sum_{m=1}^s [S_m^*][S_{s-m}^*]V \\ s = 1, 2, 3, \dots \end{aligned} \quad (\text{A.4})$$

Accumulated copolymer:

$$\frac{d}{dt} ([P_{(p,q)}(s, b)]V) = T_1 + T_2 + T_3 \quad (\text{A.5a})$$

with

$$T_1 = -k_{i2}[I^*](b - p - q + 1)[P_{(p,q)}(s, b)]V \quad (\text{A.5b})$$

$$T_2 = k_t \sum_{m=1}^s \sum_{n=1}^m [P_{n(p-1,q)}^*(s - m, b)][S_{m-n}^*]V \quad (\text{A.5c})$$

$$\begin{aligned} T_3 = \frac{k_t}{2} \sum_{q_2=1}^q \sum_{p_2=0}^{p-1} \sum_{b_2=1}^b \sum_{s_2+m=1}^s \sum_{n=1}^m [P_{m-n(p-p_2-1,q-q_2)}^* \\ (s - s_2 - m, b - b_2)][P_{n(p_2,p_2)}^*(s_2, b_2)]V \\ p, s = 0, 1, 2, \dots; \quad b, q = 1, 2, 3, \dots; \end{aligned} \quad (\text{A.5d})$$

In eq. (A.5b),  $(b - p - q + 1)[P_{(p,q)}(s, b)]$  is the molar concentration of unreacted *B* units in  $P_{(p,q)}(s, b)$ .

The mass balances for the individual radical species together with the pseudo-steady-state assumption (by which all equations may be set to zero) provide

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

$$\frac{d}{dt} \{[S_1^*]V\} = \{k_{i1}[S][I^*] - k_p[S][S_1^*] - k_t[S_1^*]([S^*] + [P^*])\}V = 0 \quad (\text{A.7})$$

$$\frac{d}{dt} \{[S_s^*]V\} = \{k_p[S][S_{s-1}^*] - (k_p[S] + k_t([S^*] + [P^*]))[S_s^*]\}V = 0$$

$$s = 2, 3, 4, \dots \quad (\text{A.8})$$

$$\frac{d}{dt} \{[P_{0(p,q)}^*(s, b)]V\} = \{-k_{i3}[S][P_{0(p,q)}^*(s, b)] + k_{i2}[I^*](b - p - q + 1)[P_{(p,q)}(s, b)]\}V = 0$$

$$p, s = 0, 1, 2, \dots; \quad b, q = 1, 2, 3, 4, \dots \quad (\text{A.9})$$

$$\frac{d}{dt} \{[P_{1(p,q)}^*(s, b)]V\} = \{k_{i3}[S][P_{0(p,q)}^*(s, b)] - k_p[S][P_{1(p,q)}^*(s, b)] - k_t[P_{1(p,q)}^*(s, b)]([S^*] + [P^*])\}V = 0$$

$$p, s = 0, 1, 2, \dots; \quad b, q = 1, 2, 3, \dots; \quad (\text{A.10})$$

$$\frac{d}{dt} \{[P_{n(p,q)}^*(s, b)]V\} = \{k_p[S][P_{n-1(p,q)}^*(s, b)] - k_t[P_{n(p,q)}^*(s, b)]([S^*] + [P^*])\}V = 0$$

$$n = 2, 3, 4, \dots; \quad p, s = 0, 1, 2, \dots; \quad b, q = 1, 2, 3, \dots \quad (\text{A.11})$$

where  $[B^*] = \sum_{q=1}^{\infty} \sum_{p=0}^{\infty} \sum_{b=1}^{\infty} \sum_{s=0}^{\infty} (b - p - q + 1)[P_{(p,q)}(s, b)]$  is the total concentration of unreacted repetitive units of  $B$  (present in the  $PB$  and in the copolymer).

Adding eq. (A.7) with (A.8) over all  $s$ , eqs. (A.9) over all  $(s, b, p, q)$ , and eq. (A.10) with (A.11) over all  $(n, s, b, p, q)$ , the following balances for the total radicals may be written:

$$\frac{d}{dt} [S^*] = k_{i1}[S][I^*] - k_t[S^*]([S^*] + [P^*]) = 0 \quad (\text{A.12})$$

$$\frac{d}{dt} [P_0^*] = k_{i2}[I^*][B^*] - k_{i3}[S][P_0^*] = 0 \quad (\text{A.13})$$

$$\frac{d}{dt} [P^*] = k_{i3}[S][P_0^*] - k_t[P^*]([S^*] + [P^*]) = 0 \quad (\text{A.14})$$

where  $[P_0^*] = \sum_{q=1}^{\infty} \sum_{p=0}^{\infty} \sum_{b=1}^{\infty} \sum_{s=0}^{\infty} [P_{0(p,q)}^*(s, b)]$  is the total concentration of primary  $B$  radicals (both in the  $PB$  and in the copolymer).

### Rates of Polymerization

From eq. (A.6), one obtains

$$[I^*] = \frac{2fk_d[I_2]}{k_{i1}[S] + k_{i2}[B^*]} \quad (\text{A.15})$$

Adding up eqs. (A.12)–(A.14), and replacing into eq. (A.15), provides

$$[S^*] + [P^*] = \left( \frac{2fk_d[I_2]}{k_t} \right)^{1/2} \quad (\text{A.16})$$

Note that if eq. (A.16) is substituted into (A.2), the “classical” expression for  $R_p$  in eq. (36) is recuperated. Let us indicate with  $\varphi$  the molar fraction of the free  $PS$  radicals with respect to the total macroradicals, i.e.:

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

Replacing eqs. (A.15) and (A.16) into eq. (A.12), and remembering eq. (A.17), one obtains

$$\varphi = \frac{k_{i1}[S]}{k_{i1}[S] + k_{i2}[B^*]} \quad (\text{A.18})$$

The total rate of  $S$  consumption ( $R_p$ ) is the result of three contributions:

$$R_p = R_{pPS} + R_{pGS1} + R_{pGS2} \quad (\text{A.19})$$

where  $R_{pPS}$ ,  $R_{pGS1}$ , and  $R_{pGS2}$ , respectively, represent the moles of consumed monomer per unit time and volume incorporated into the free  $PS$ , into the copolymer through termination 1, and into the copolymer through termination 2. As in Refs. 1 and 2, we shall define the instantaneous grafted fraction of  $S$  with respect to the total polymerized  $S$  as follows:

$$F = \frac{R_{pGS1} + R_{pGS2}}{R_p} \quad (\text{A.20})$$

Consider some interrelationships between the different polymerization rates. The  $S$  monomer can propagate with either an  $S^*$  or  $P^*$  macroradical. The rate of propagation of  $S$  with  $S^*$  is  $\varphi R_p$ , while the rate of propagation of  $S$  with  $P^*$  is  $(1 - \varphi)R_p$ . Thus, the free  $PS$  generation rate can be obtained by multiplying  $\varphi R_p$  by the probability of termination between two  $S^*$  macroradicals, resulting in

$$R_{pPS} = \varphi R_p \frac{k_t[S^*][S^*]}{k_t[S^*]([P^*] + [S^*])} \quad (\text{A.21})$$

Similarly,  $R_{pGS2}$  may be found by multiplying  $(1 - \varphi)R_p$  by the probability of termination between two  $P^*$  macroradicals, yielding

$$R_{pGS2} = (1 - \varphi)R_p \frac{k_t[P^*][P^*]}{k_t[P^*]([S^*] + [P^*])} \quad (\text{A.22})$$

Then, from eq. (A.17), one can write

$$R_{pPS} = \varphi^2 R_p \quad (\text{A.23})$$

and

$$R_{pGS2} = (1 - \varphi)^2 R_p \quad (\text{A.24})$$

The rate of monomer incorporated into the copolymer by termination 1( $R_{pGS1}$ ) is obtained by adding the contributions from the  $S^*$  and  $P^*$  macroradicals. The first contribution is obtained by multiplying the probability of termination between  $S^*$  and  $P^*$  (or  $k_t[S^*][P^*]/\{k_t[S^*]([S^*] + [P^*])\}$ ) by  $\varphi R_p$ , yielding  $\varphi(1 - \varphi)R_p$ . An identical result may be obtained for  $P^*$ , and, therefore,

$$R_{pGS1} = 2\varphi(1 - \varphi)R_p \quad (\text{A.25})$$

Note that by addition of eqs. (A.23)–(A.25), eq. (A.19) may be recuperated. Similarly, the following is verified:

$$R_{pGS1} + R_{pGS2} = (1 - \varphi^2)R_p \quad (\text{A.26})$$

and eqs. (A.20) and (A.26) provide

$$F = (1 - \varphi^2) \quad (\text{A.27})$$

### NCLD of the Free PS

Define the kinetic parameter:

$$\beta = \frac{k_t R_p}{(k_p [S])^2} \quad (\text{A.28})$$

Replacing eqs. (A.15) and (A.16) and (36) into eqs. (A.7) and (A.8), and employing the definitions for  $\varphi$  and  $\beta$  of eqs. (A.18) and (A.27), one obtains

$$[S_1^*] = \frac{\varphi R_p}{k_p [S]} \frac{\beta}{1 + \beta} \quad (\text{A.29a})$$

$$[S_n^*] = \frac{\beta}{(1 + \beta)^n} \frac{\varphi R_p}{k_p [S]} \quad n = 1, 2, 3, \dots \quad (\text{A.29b})$$

Incorporating these expressions into eq. (A.4), and bearing in mind the definition of  $\beta$ , one finds

$$\frac{d}{dt} ([S_s]V) = R_p \varphi^2 \frac{\beta^3}{2} s \left( \frac{1}{1 + \beta} \right)^s V \quad s = 1, 2, 3, \dots \quad (\text{A.30})$$

Substituting eq. (A.23) into eq. (A.30), and remembering that for high values of  $s$ ,  $(1 + \beta)^{-s} \simeq e^{-\beta s}$ , then the NCLD of the accumulated PS may be obtained from

$$\frac{d}{dt} ([S_s]V) = \frac{d}{dt} [n_{PS}(s)] = R_{pPS} \frac{\beta^3}{2} s e^{-\beta s} V \quad s = 1, 2, 3, \dots \quad (\text{A.31})$$

where  $([S_s]V)$  and  $n_{PS}(s)$  indistinctly represent the NCLD of the accumulated PS. This distribution is typical of systems where molecular weights are determined by combination termination only, in the absence of transfer reactions.<sup>12</sup>

### NCLDs of the Produced Copolymer Topologies

For every topology, we aim at determining the evolution of its bivariate NCLD, represented by  $n_{(p,q)}(s, b)$ . Let us indicate with  $g_{B^*(p,q)}(s, b)$  the mass of unreacted  $B$  units contained in the generic species  $P_{(p,q)}(s, b)$ . Alternatively, for fixed values of  $(p, q)$  but arbitrary values of  $(s, b)$ ,  $g_{B^*(p,q)}(s, b)$  may be interpreted as the bivariate WCLD that considers only the mass contents of  $B^*$ . The set of these distributions may be found from the bivariate NCLDs  $n_{(p,q)}(s, b)$ , as follows:

$$\begin{aligned} g_{B^*(p,q)}(s, b) &= (b - p - q + 1) [P_{(p,q)}(s, b)] M_B V \\ &= (b - p - q + 1) n_{(p,q)}(s, b) M_B \\ &\quad (\text{for all } p, q, s, b) \quad (\text{A.32}) \end{aligned}$$

Also, the total mass of unreacted  $B$  units (indicated by  $g_{B^*}$ ) is obtained through the following integration:

$$g_{B^*} = \sum_{q=1}^{\infty} \sum_{p=0}^{\infty} \sum_{b=1}^{\infty} \sum_{s=0}^{\infty} g_{B^*(p,q)}(s, b) \quad (\text{A.33})$$

From eqs. (A.10) and (A.11), and introducing eqs. (36), (A.9), (A.15), (A.16), (A.18), (A.28), (A.32), and (A.33), one finds

$$\begin{aligned} [P_{1(p,q)}^*(s, b)] &= \frac{\beta}{(1 + \beta)} \frac{(1 - \varphi) R_p}{k_p [S]} \frac{g_{B^*(p,q)}(s, b)}{g_{B^*}} \\ b, q &= 1, 2, 3, \dots; \quad p, s = 0, 1, 2, 3, \dots \quad (\text{A.34}) \end{aligned}$$

$$\begin{aligned} [P_{n(p,q)}^*(s, b)] &= \frac{\beta}{(1 + \beta)^n} \frac{(1 - \varphi) R_p}{k_p [S]} \frac{g_{B^*(p,q)}(s, b)}{g_{B^*}} \\ n, b, q &= 1, 2, 3, \dots; \quad p, s = 0, 1, 2, 3, \dots \quad (\text{A.35}) \end{aligned}$$

Consider now each of the three terms in eqs. (A.5):

(a) *First Term, or Disappearance of Generic Species  $P_{(p,q)}(s, b)$  by Radical Attack:*

Equation (A.5b) may be rewritten:

$$\begin{aligned} T_1 &= - \left\{ \frac{(b - p - q + 1) [P_{(p,q)}(s, b)] M_B V}{[B^*] M_B V} \right\} \\ &\quad \times \{ k_{i2} [B^*] [I] V \} \quad (\text{for all } p, q, s, b) \quad (\text{A.36}) \end{aligned}$$

where the first factor in the right-hand side of eq. (A.36) represents the mass fraction of  $B^*$  units contained in the

generic species  $P_{(p,q)}(s, b)$  with respect to the total amount of  $B^*$ , whereas the second represents the number of grafting points generated per unit time [see eq. (5)]. Consider an alternative expression for this last factor. Substituting eq. (A.15), it results in

$$-k_{i2}[B^*][I']V = \frac{-k_{i2}[B^*]}{k_{i1}[S] + k_{i2}[B^*]} 2fk_d[I_2]V \quad (\text{A.37})$$

Squaring eq. (36) and incorporating eq. (A.27), one finds that  $2fk_d[I_2] = \beta R_p$ . Replacing this expression into eq. (A.37) and considering eq. (A.18), one can write

$$-k_{i2}[B^*][I']V = -(1 - \varphi)R_p\beta V \quad (\text{A.38})$$

Adding eq. (A.25) with twice eq. (A.24), one finds that  $(1 - \varphi)R_p = (R_{pGS1} + 2R_{pGS2})\beta/2$ . The substitution of this expression into eq. (A.38) yields

$$-k_{i2}[B^*][I']V = -\left(R_{pGS1}\frac{\beta}{2} + R_{pGS2}\beta\right)V \quad (\text{A.39})$$

where it can be easily shown that  $(R_{pGS1}\beta/2)$  are the moles of new grafting sites produced per unit time by termination 1, while  $(R_{pGS2}\beta)$  represents the same rate, but due to termination 2. Finally, replacing eq. (A.39) into (A.36) and remembering eqs. (A.32) and (A.33), one can write

$$T_1 = -(R_{pGS1} + 2R_{pGS2})\frac{\beta}{2} \frac{g_{B^*(p,q)}(s, b)}{g_{B^*}} V \quad (\text{for all } p, q, s, b) \quad (\text{A.40})$$

(b) *Second Term, or Production of Generic Species  $P_{(p,q)}(s, b)$  by Termination 1:*

Equations (A.29b) and (A.35) may be rewritten as follows:

$$[S_{m-n}^*] = \frac{\beta}{(1 + \beta)^{m-n}} \frac{\varphi R_p}{k_p[S]} \quad (\text{A.41})$$

$$[P_{n(p-1,q)}^*(s - m, b)] = \frac{\beta}{(1 + \beta)^n} \frac{(1 - \varphi)R_p}{k_p[S]} \frac{g_{B^*(p-1,q)}(s - m, b)}{g_{B^*}} \quad (\text{A.42})$$

Replacing eqs. (A.41) and (A.42) into (A.5c) and considering eqs. (A.25) and (A.28), one finds

$$T_2 = R_{pGS1} \sum_{m=1}^s \frac{g_{B^*(p-1,q)}(s - m, b)}{g_{B^*}} \frac{\beta^3}{2} \sum_{n=1}^m \left(\frac{1}{1 + \beta}\right)^m V \quad (\text{for all } p, q, s, b) \quad (\text{A.43})$$

and, therefore,

$$T_2 = R_{pGS1} \sum_{m=1}^s \frac{g_{B^*(p-1,q)}(s - m, b)}{g_{B^*}} \frac{\beta^3}{2} me^{-\beta m} V \quad (\text{for all } p, q, s, b) \quad (\text{A.44})$$

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

(c) *Third Term, or Production of Generic Species  $P_{(p,q)}(s, b)$  by Termination 2:*

Equation (A.35) provides

$$[P_{m-n(p-p_2-1,q-q_2)}^*(s - s_2 - m, b - b_2)] = \frac{\beta}{(1 + \beta)^{m-n}} \times \frac{(1 - \varphi)R_p}{k_p[S]} \frac{g_{B^*(p-p_2-1,q-q_2)}(s - s_2 - m, b - b_2)}{g_{B^*}} \quad (\text{A.45})$$

and

$$[P_{n(p_2,q_2)}^*(s_2, b_2)] = \frac{\beta}{(1 + \beta)^n} \frac{(1 - \varphi)R_p}{k_p[S]} \frac{g_{B^*(p_2,q_2)}(s_2, b_2)}{g_{B^*}} \quad (\text{A.46})$$

where  $m$  represents the chain length of the new  $S$  linking-chains. Replacing eqs. (A.45) and (A.46) into eq. (A.5d) produces

$$T_3 = R_{pGS2} \sum_{q_2=1}^q \sum_{p_2=0}^{p-1} \sum_{b_2=1}^b \sum_{s_2+m=1}^s \times \frac{g_{B^*(p-p_2-1,q-q_2)}(s - s_2 - m, b - b_2)}{g_{B^*}} \frac{g_{B^*(p_2,q_2)}(s_2, b_2)}{g_{B^*}} \times \frac{\beta^3}{2} me^{-\beta m} V \quad (\text{for all } p, q, s, b) \quad (\text{A.47})$$

Introducing eqs. (A.40), (A.44), and (A.47) into (A.5a), an expression for the evolution of the moles of the accumulated generic species  $P_{(p,q)}(s, b)$  may be finally encountered:

$$\frac{d}{dt} \{n_{(p,q)}(s, b)\} = \left[ -(R_{pGS1} + 2R_{pGS2})\frac{\beta}{2} \frac{g_{B^*(p,q)}(s, b)}{g_{B^*}} + R_{pGS1} \frac{\beta}{2} \sum_{m=1}^s \frac{g_{B^*(p-1,q)}(s - m, b)}{g_{B^*}} \beta^2 me^{-\beta m} + R_{pGS2} \frac{\beta}{2} \times \sum_{q_2=1}^q \sum_{p_2=0}^{p-1} \sum_{b_2=1}^b \sum_{s_2+m=1}^s \frac{g_{B^*(p-p_2-1,q-q_2)}(s - s_2 - m, b - b_2)}{g_{B^*}} \times \frac{g_{B^*(p_2,q_2)}(s_2, b_2)}{g_{B^*}} \times \beta^2 me^{-\beta m} \right] V \quad q, b = 1, 2, 3, \dots; \quad p, s = 0, 1, 2, \dots \quad (\text{A.48})$$



In eq. (A.48),  $m$  represents the variable chain length of the instantaneously grafted  $S$  chains. Irrespectively of the termination reaction, the normalized NCLD of such instantaneous  $S$  chains is represented by  $\beta^2 s e^{-\beta s}$ , and by comparison with eq. (A.31), it also coincides with the NCLD of the newly generated free  $PS$  molecules.

### NCLD of the Residual $PB$

For the residual  $PB$ , eq. (A.33) results in

$$g_{B^*(0,1)}(0, b) = g_{PB}(b) = b[P_{(0,1)}(0, b)]M_B V$$

$$b = 1, 2, 3, \dots \quad (\text{A.49})$$

Comparing eq. (A.3) with eqs. (A.5), it is easily seen that the former is a special case of the latter with  $p = s = 0$  and  $q = 1$ . Because the  $PB$  is only consumed and not produced, then only the  $T_1$  term in eqs. (A.5) is nonzero. Thus, in the case of the free  $PB$ , eq. (A.48) finally reduces to the following:

$$\frac{d}{dt} [n_{(0,1)}(0, b)] = \frac{d}{dt} [n_{PB}(b)]$$

$$= -(R_{PGS1} + 2R_{PGS2}) \frac{\beta}{2} \frac{g_{PB}(b)}{g_{B^*}} V$$

$$b = 1, 2, 3, \dots \quad (\text{A.50})$$

where  $n_{(0,1)}(0, b)$  or  $n_{PB}(b)$  both represent the NCLD of the unreacted  $PB$  molecules.

### NOMENCLATURE

$b$	total repetitive units of $B$ in residual $PB$ or copolymer	$g_{GS1}, g_{GS2}$	accumulated masses of grafted $S$ due to terminations 1 and 2
$B^*$	unreacted repetitive units of $B$ in $PB$ or copolymer	$g_{PB}, g_{PS}$	total masses of $PB$ and $PS$
$E_{PB}, E_{PS}$	$PB$ and $PS$ grafting efficiencies, defined by eqs. (67) and (38)	$g_{PB}(b), g_{PS}(s)$	WCLDs of $PB$ and $PS$
$f$	initiator efficiency	$g(M)$	MWD of total copolymer
$F$	instantaneous grafted fraction of $S$ , defined by eq. (39)	$g(w_S)$	CCD of total copolymer
$g$	total copolymer mass	$g_{(p,q)}(w_S)$	CCD for topology $(p, q)$
$g(s, b)$	WCLD of total copolymer	$J_1, J_2$	branching frequencies, defined by eqs. (68) and (69)
$g_{(p,q)}(s, b)$	WCLD of topology $(p, q)$	$k_d, k_{i1}, k_{i2}, k_{i3}, k_p, k_t$	rate constants
$g_{B^*}$	total mass of unreacted $B$ (in $PB$ and copolymer)	$M, M_B, M_S$	molecular weights of total copolymer and comonomers
$g_{B^*(p,q)}(s, b)$	for each topology $(p, q)$ , bivariate WCLD, where in the vertical axis only the unreacted mass of $B$ is considered	$\bar{M}_n, \bar{M}_{n,PB}, \bar{M}_{n,PS}$	NAMWs of total copolymer, $PB$ and $PS$
		$\bar{M}_w, \bar{M}_{w,PB}, \bar{M}_{w,PS}$	weight-average molecular weights of total copolymer, $PB$ , and $PS$
		MW/CCD	bivariate molecular weight/chemical composition distribution
		NAMW	number-average molecular weight
		NCLD	number chain-length distribution
		$n$	moles of total copolymer
		$n(s, b)$	bivariate NCLD of total copolymer
		$n_{(p,q)}(s, b)$	bivariate NCLD for topology $(p, q)$
		$P_{(p,q)}(s, b)$	molecular species in topology $(p, q)$ , with $s$ repetitive units of $S$ and $b$ repetitive units of $B$ . It can also represent the $PB$ when $p = s = 0$ and $q = 1$
		$P_{r(p,q)}^*(s, b)$	macroradical containing a new growing branch with $r$ repetitive units of $S$ , produced by activation of $P_{(p,q)}(s, b)$
		$R_p, R_{PPS}, R_{PGS1}, R_{PGS2}$	polymerization rates for total $S$ , $S$ generating $PS$ , grafted $S$ by termination 1, and grafted $S$ by termination 2
		$s$	total repetitive units of $S$ in free $PS$ or copolymer
		$t$	time
		$V$	reaction volume
		$w_S$	weight fraction of $S$ in a given copolymer molecule
		$\bar{w}_S$	average weight fraction of $S$ in total copolymer
		WCLD	weight chain-length distribution
		$x$	monomer conversion
		$\beta$	kinetic parameter, defined by eq. (A.28) and related to the NAMW of the instantaneously produced $S$ chains

$\phi$  molar fraction of free PS homoradicals, with respect to the total amount of macroradicals  
Supraindex "o" indicates initial value

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Received January 12, 1993

Accepted March 18, 1993