Solution and Quasi-Bulk Copolymerizations of Styrene and Methyl Methacrylate in the Presence of Polybutadiene: Mathematical Model

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ABSTRACT: A mathematical model was developed for simulating the batch copolymerization of styrene (St) and methyl methacrylate (MMA) in the presence of polybutadiene (PB). It was adjusted to the measurements of three reactions carried out at 65°C, with initial comonomers ratio at the azeotropic condition, THF as solvent, and benzoyl peroxide as initiator. The measurements included: (a) conversions and grafting efficiencies by gravimetry; (b) molecular weight distributions (MWDs) by size exclusion chromatography; and (c) global mass fractions of St in the co- and terpolymer, by UV-Vis spectroscopy. The model predicts the MWDs of the three polymeric components of MBS: free St-MMA copolymer, St-MMA-g-PB graft terpolymer (GT), and residual PB. In addition, it predicts the bivariate chain length distributions of the different GT topologies, with each topology characterized by the number of branches per molecule. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 899–919, 2010

Key words: graft copolymer; molecular weight distribution; modelling

INTRODUCTION

Brittle thermo-plastics such as polymethylmethacrylate (PMMA), polystyrene (PS), or styrene-acrylonitrile copolymer (SAN) improve their impact resistance by incorporation of rubber particles into their continuous vitreous matrixes. Other properties such as optical transparency and elastic modulus may be deteriorated, however. Methyl methacrylate (MMA)/Butadiene (Bd)/Styrene (St) polymer (MBS) is used for improving the impact resistance of PVC for bottles, without affecting transparency or heat stability. MBS contains dispersed rubber particles in a matrix consisting of a free copolymer (FC) of St-MMA. The rubber particles are themselves heterogeneous, with vitreous FC occlusions and a continuous phase of unreacted polybutadiene (PB) and a graft terpolymer (GT) containing St-MMA branches grafted onto PB chains.

MBS is produced through a free-radical copolymerization of St and MMA in the presence of a PB-based rubber. The process can be either a bulk copolymerization, a two-stage emulsion process, or a bulk-suspension process.[1–3] By accumulating at the interfaces, the GT determines the particle morphology and mechanical properties of the final material.

Many publications[4–47] have investigated on the homopolymerizations of MMA or St in the presence of PB rubbers. In the case of high-impact polystyrene (HIPS), both experimental[15–30] and theoretical[31–47] articles have been reported. Except for the mathematical model by Casis et al.,[35] all the other models[36–47] have considered the bulk process as if were homogeneous. This hypothesis has been justified by the fact that the partition coefficients of the low molar mass species (the St monomer and the initiator) are both close to unity.[46,47] For the solution polymerization of St in the presence of PB at 60°C, Brydon et al.[32] developed a simple kinetic scheme that included: chemical and thermal initiation, propagation, termination by combination, and transfer reactions to the monomer, to the rubber and to the solvent. Estenoz and Meira[39] adopted such scheme, and developed a mathematical model for calculating the detailed molecular structure of the evolving polymer mixture. The model was tested under nonisothermal conditions;[40] and it was proven that the molecular weight distributions (MWDs) of the grafted PS branches are close to the MWDs of the free PS.[41] (Without experimental evidence, other authors[14,30,44] had previously assumed identical MWDs for the FC and grafted branches.).

The bulk and solution copolymerizations of St and MMA have been investigated in several

TABLE I
The Investigated Copolymerizations: Recipes, Final Measurements and Model
Predictions (in Parentheses)

	Experiment 1	Experiment 2	Experiment 3
Recipe			
MMA (g)	94.5	94.5	391.0
St (g)	136.7	136.6	546.1
PB (g)[a]	–	8.6	34.0
BPO (g)	4.5	4.5	2.0
THF (g)	246.75	233.85	98.6
Final Product Characteristics and Model Predictions (in Parentheses)			
x (%)	42.9 (40.4)	41.4 (40.5)	20.9 (21.3)
E(%)	–	21.6^{b} (20.4)	20.4^{b} (19.5)
E_{PB}(%)	–	– (94.0)	78.6 (74.3)
Unreacted PB			
$\overline{M}_{n,PB}$(g/mol)	–	– (31,000)	92,600 (56,000)
$\overline{M}_{w,PB}$(g/mol)	–	– (43,500)	192,000 (90,900)
FC			
$\overline{p}_{St,FC}$	0.48	0.49^{c} and 0.45^{d}	0.52^{c} and 0.40^{d}
	(0.54)	(0.54)	(0.54)
$\overline{M}_{n,FC}$	31,200 (30,600)	32,000 (26,500)	127,800 (134,000)
$\overline{M}_{w,FC}$	51,800 (54,300)	50,900 (47,200)	188,900 (229,000)
GT			
$\overline{p}_{St,GT}$	–	– (0.39)	0.30 (0.33)
$\overline{p}_{MMA,GT}$	–	– (0.32)	– (0.31)
$\overline{M}_{n,GT}$	–	– (241,000)	296,000 (381,000)
$\overline{M}_{w,GT}$	–	– (483,000)	622,000 (666,000)
$\overline{r}_n$	–	– (5.11)	1.90^{e} (1.70)
$\overline{r}_w$	–	– (9.45)	– (2.53)
$\overline{r}_{n,SM}$	–	– (5.62)	– (1.83)
$\overline{r}_{n,PB}$	–	– (1.09)	– (1.12)

[a] Of $\overline{M}_{n,PB}$ = 101900 g/mol; $\overline{M}_{w,PB}$ = 218200 g/mol; and MWD represented in Fig. 3b.
[b] Average of three determinations.
[c] SEC measurements.
[d] Off-line UV-Vis measurements.
[e] Experimental value.

opportunities.[48–57] Kuo and Chen[56] determined the azeotropic condition and associated kinetics constants. In a review on free-radical copolymerizations, Gao and Penlidis[57] presented a mathematical model that is applicable to the copolymerization of St and MMA.

In our preliminary publication,[58] a simple mathematical model was developed for the batch and solution copolymerization of St and MMA in the presence of PB. It predicts the monomer conversion, grafting efficiencies, average molecular weights (of the FC, GT, and unreacted PB); but it does not calculate the molecular characteristics of the different GT topologies.

In this work, a homogeneous mathematical model is presented for a free-radical copolymerization of St and MMA in the presence of PB. Some of the model parameters were adjusted to measurements from three experiments. As far as the authors are aware, this is the first model capable of predicting the detailed macromolecular structures of the three polymeric components of MBS.

EXPERIMENTAL WORK

Three batch copolymerizations of St-MMA with benzoyl peroxide (BPO) as initiator were carried out at 65°C, up to conversions of around 30% (to investigate the prepolymerization stage), and with 58% in weight of St with respect to the total comonomers (the azeotropic composition) (Table I). Experiment 1 was a solution copolymerization without rubber. Experiment 2 was a solution copolymerization with 1.8% in weight of PB. Experiment 3 was a quasi-bulk copolymerization, with about 3% in weight of PB and 10% in volume of tetrahydrofuran (THF). In Experiment 3, the initial concentration of initiator was lower than in the other two experiments, to counterbalance for a higher expected "gel effect." Because of its low initial rubber concentration, the quasi-bulk Experiment 3 was expected to have remained homogeneous until relatively high conversions.

The St (technical grade from Petrobras Energía S.A., Pto. San Martín, Argentina), and the MMA (Aldrich, purity 98%) were vacuum-distilled before

the reactions. The BPO initiator (Riedel-Haën, analytical grade, purity >98%), and the THF (Sintorgan, purity 99%), were used as received.

Experiments 1 and 2 were carried out in a 500 mL stirred glass reactor, and their temperatures were maintained constant by introducing the reactor in an isothermal oil bath. Experiment 3 was carried out in a 2 L stainless-steel reactor, fit with a turbine-type stirrer, an external heating jacket, and an internal cooling coil. The temperature was manually-controlled by manipulating the flow rate of the internal cooling water and the temperature of the external heating oil. In Experiment 3, the samples were taken by means of a special device fit in the reactor bottom.

In Experiment 1 without rubber, the comonomers were directly charged into the reactor. In Experiments 2 and 3, a glass flask was used to predissolve the rubber in the comonomers-solvent mixture (at room temperature). Before the copolymerizations, the dissolved oxygen was eliminated by bubbling nitrogen for 10 min. into the comonomers mixtures (or into the comonomers/rubber mixtures). Then, the temperature was raised to 65°C and the polymerizations were started when loading the initiator. The reaction times were in all cases 8 h. Along the reactions, several (20 mL) samples were taken. Aliquots of these samples were used to determine the global comonomers conversion (by vacuum-drying the reaction mixtures at room temperature until constant weight, and then subtracting the original PB mass). In the remaining sample fractions, the total polymer was first precipitated in 200 mL of methanol containing liquid air and hydroquinone as inhibitor. Then, the precipitates were vacuum-dried and cold-stored in dark until their analyses. For the dry samples of Experiments 2 and 3, a sequence of two solvent extraction-gravimetry procedures was applied to isolate the three polymeric components of MBS.

The first solvent extraction procedure enabled the separation of the FC from the GT + unreacted PB. The technique was as follows: (a) 0.3 g of total dry polymer were loaded in a centrifuge tube, mixed for 12 h with 10 mL of methyl ethyl ketone (MEK), and the tube was centrifuged for 2 h at 10,000 rpm; (b) the soluble fraction containing the FC was separated by decantation, another 10 mL of MEK were added into the insoluble fraction, and the procedure was repeated; (c) the two supernatant solutions were mixed together, and the FC was precipitated in methanol, and dried until constant weight; (d) the contents of the centrifuge tube were dried under vacuum, and the mass of insoluble (GT + unreacted PB) was determined; and (e) the mass of grafted St-MMA was obtained from the difference between the insoluble mass and the initial PB mass. Finally, the comonomers grafting efficiency was calculated from the ratio between the mass of grafted St-MMA and the total mass of polymerized St-MMA.

The second solvent extraction procedure was applied to the aforementioned precipitate, to isolate the unreacted PB from the GT. First, 10 mL of petroleum ether were added to dissolve the PB but not the GT. The system was agitated and centrifuged. The soluble portion was separated from the GT precipitate, and the procedure was repeated twice. The PB solutions were mixed together, and the total unreacted PB was isolated by solvent evaporation. The mass of grafted PB was determined from the difference between the initial and unreacted PB masses. The PB grafting efficiency was obtained from the ratio between the mass of grafted PB and initial PB mass.

The isolated polymer components were analyzed by size exclusion chromatography (SEC), to determine their MWDs, the mass fractions of St in the FC and GT, and the average number of branches per molecule in the GT. The chromatograph was a Waters Breeze fitted with a Waters model 1515 pump, and a full set of 6 μ-Styragel columns (of nominal fractionation range 10^2–10^7 g/mol). The detectors were a Waters 440 UV spectrophotometer at 254 nm and a Viscotek 200 detector [consisting of an on-line specific viscometer (SV) in parallel with a differential refractometer (DR)]. The carrier solvent was THF at room temperature and at 1 mL/min. The UV and DR sensors were calibrated by injecting known masses of narrow PS, PMMA, and PB standards. The same standards were used to obtain their corresponding molar mass calibrations, that resulted: $\log(M_{PS}) = 11.78$–$0.1600\ V$; $\log(M_{PMMA}) = 11.8$–$0.1604\ V$; and $\log(M_{PB}) = 11.32$–$0.1530\ V$, where V is the elution volume.

At each elution volume, the instantaneous mass fractions of St in the FC and in the GT were determined from the signals ratio between the UV and DR chromatograms; and then the global average compositions were calculated.[59] For such measurements, the sensors were calibrated with known masses of PS, PMMA, and PB homopolymers. Calling $G(V)$ the total homopolymer concentration, the DR calibrations resulted: $s_{DR,PS}(V) = 5745\ G(V)$; $s_{DR,PMMA}(V) = 2640\ G(V)$; $s_{DR,PB}(V) = 5637\ G(V)$. At 254 nm, the UV sensor "sees" the St repeating units, but not the B or MMA repeating units. Thus, the UV spectrophotometer calibration for PS resulted: $s_{UV,PS}(V) = 99191\ G(V)$. The global mass fractions of St in the FC and GT were also independently determined off-line with a UV-Vis spectrophotometer at 260 nm (Perkin–Elmer, spectrum Lambda 40). In this case, the PS mass calibration resulted: $A_{PS} = 4.3846\ C_{PS}$, where A_{PS} and C_{PS} are respectively, the light absorbance of PS at 260 nm and the PS concentration.
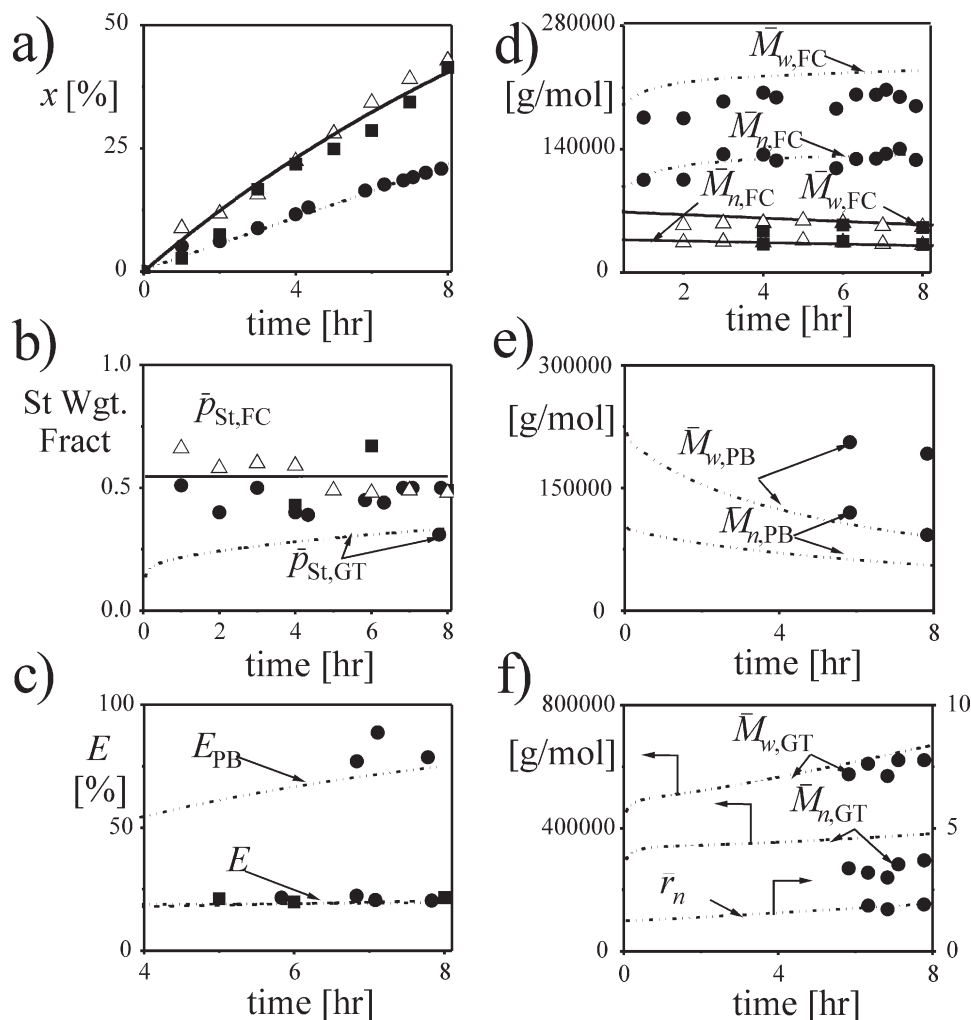
Figure 1 Experiments 1–3: The measurements (in symbols) are compared with the model predictions; as follows: Experiment 1 (—△—), Experiment 2 (---■---), Experiment 3 (---●---). (a) Gravimetric conversion. The simulation results of Exps 1 and 2 both coincide. (b) Mass fractions of St in the FC ($\bar{p}_{St,FC}$) and in the GT ($\bar{p}_{St,GT}$). (c) Comonomer grafting efficiencies (E) and PB grafting efficiency (E_{PB}) of Experiment 2 and 3. (d) Average molecular weights of the FC. (e) For Experiments 2 and 3: average molecular weights of the residual PB. (f) For Experiment 3: average molecular weights and average number of branches per molecule of the GT.

The molecular weights of the linear FC were obtained by interpolation (with the St mass fractions) between the direct calibrations of PS and PMMA. However, the corresponding homopolymer calibrations were almost coincident; and therefore the calculated FC molar masses were little affected by the (almost constant) instantaneous composition.

The GT molecular weights were estimated from the instantaneous intrinsic viscosity $[\eta](V)$ (in turn, obtained from the ratio between the SV and DR signals), and a "universal" calibration given by $\log\{[\eta]M\} = 18.82804–0.33507V$ (obtained from the set of PS standards). At each GT molar mass, the average number of trifunctional branches per molecule, $r(M)$, was determined with the following assumptions: (a) the GT behaves as a pseudo-homopolymer of constant composition; and (b) its low molar mass

fraction exhibits a single branch per molecule.[59] The calculation of $r(M)$ involved: (a) the measurements $[\eta](M)$; (b) the use of the Zimm-Stockmayer expressions[60] for randomly-branched homopolymers with long trifunctional branches; and (c) the expression: $g(r) = \{[\eta](M)/(K\,M^{\alpha})\}^{1/\varepsilon}$. In this last expression, g is the ratio between the squared radii of gyration of a branched GT molecule with respect to its linear homologue of the same molar mass; $K = 1.706 \times 10^{-4}$ dL/g and $\alpha = 0.728$ are the Mark-Houwink constants of the linear homologue; and $\varepsilon = 1.45$ is a structure exponent.[59]

The measurements are represented in Figure 1, and the final product characteristics are reproduced in Table I. Figure 1(a) presents the evolution of the global comonomers conversion. Despite the long reaction times, the final conversions are all quite low

as a consequence of the selected temperature and initiator concentrations. The low polymerization rate of Experiment 3 was caused by its lower initiator concentration. The polymerization rate of Experiment 1 without rubber is generally higher than that of Experiment 2; as a consequence of the relatively low reinitiation rate of primary rubber radicals. Figure 1(b) presents the average mass fraction of St in the FC ($\overline{p}_{St,FC}$) for all three experiments, and a single measurement of the average mass fraction of St in the GT ($\overline{p}_{St,GT}$) for Experiment 3. The values of $\overline{p}_{St,FC}$ are close to the expected azeotropic ratio (shown in horizontal dashed trace). In Experiment 3, the compositions are somewhat lower than expected, possibly due to an imperfect isolation of the three polymeric components with the applied solvent extraction technique. Figure 1(c) presents the comonomers grafting efficiency (E) of Experiments 2 and 3, and the PB grafting efficiency (E_{PB}) of Experiment 3. While E is around 20% in both reactions with the rubber, E_{PB} is around 75% in Experiment 3. Figure 1(d) presents the average molecular weights of the FC in the three reactions. In Experiment 3, the FC molecular weights are high and grow with time due to a moderate gel effect. In Experiments 1 and 2, the FC molar masses are relatively lower and slightly decreasing with time. This is expected in solution polymerizations without gel effect, when the initiator consumption is slower than the comonomers consumption.[61] Figure 1(e,f) show the measurements of Experiment 3 only. The molecular weights of the residual PB [Fig. 1(e)] decrease with time, due to the higher probability of grafting of the higher molar mass fractions. For the GT, [Fig. 1(f)] presents the average molar masses and average number of trifunctional branching points per molecule. While $\overline{M}_{w,GT}$ shows a slow final increase; the final GT exhibits around two trifunctional branching points per molecule.

MATHEMATICAL MODEL

The kinetic mechanism is presented in Table II. It consists of chemical and thermal initiation, propagation, chain transfer to the comonomers and to the rubber, and terminations by recombination and disproportionation. Rubber grafting is produced by abstraction of an allylic hydrogen of a butadiene (B) repetitive unit, caused by attack of a primary initiator radical ($I^\bullet$) or by a growing St-MMA chain. The following reactions are neglected: propagation with internal double bonds, intramolecular reactions, degradation, and reactions with impurities. In all cases, both the FC and the grafted St-MMA branches are considered as pseudo-homopolymers of "effective" chain lengths n and c, respectively. This assumption

is justified by the fact that the reactions were carried out at the azeotropic conditions. Other kinetic assumptions are: (a) the reactivity of a macroradical only depends on the nature of its terminal unit, and it coincides with the reactivity of the corresponding primary monomer radical; (b) the rates of propagation, chain transfer, and termination are independent of chain length; (c) all ungrafted B repeating units exhibit a common reactivity; and (d) termination reactions are difussion-controlled.

The following nomenclature is employed in the Global Kinetics of Table II: I_2 is the initiator molecule; S, M are the St and MMA comonomers, respectively; $S_1^\bullet$, $M_1^\bullet$ are primary St and MMA radicals; $TS_1^\bullet$, $TM_1^\bullet$ are primary St- or MMA-terminated terpolymer radicals; $S_n^\bullet$, $M_n^\bullet$ are St- or MMA-terminated copolymer radicals with n repetitive units; C_n is a FC molecule with n repetitive units; T represents either a GT or an unreacted PB molecule; $T_0^\bullet$ is a primary rubber radical generated on a PB or GT molecule; $TS_n^\bullet$, $TM_n^\bullet$ are nonprimary terpolymer radicals with a growing chain of n repetitive units terminating in a St or MMA radical, respectively. Consider the nomenclature of the Detailed Kinetics of Table II. GT molecules are classified into several r topologies, each of which are characterized by the number of trifunctional branching points per molecule ($r = 1, 2...$). A generic GT molecule is represented by $T_{(r)}(c,b)$ where r is the topology, c is the number of repetitive units of St-MMA, and b is the number of repetitive units of B. The unreacted PB is considered as a special case of $T_{(r)}(c,b)$, with $r = c = 0$.

For a hypothetical species $T_{(3)}(14,16)$, Figure 2 shows two possible configurations a (more frequent) T-grafted structure with a single PB chain [Fig. 2(a)], and a (less frequent) H-grafted structure with a St-MMA crosslink between two PB chains [Fig. 2(b)]. T-grafts are formed when a growing GT radical terminates by either disproportionation, by recombination with a growing FC radical, and by chain transfers (to the monomer and the FC). H-grafts are formed when two GT radicals terminate by recombination. Finally, $T_{0(r)}^\bullet(c,b)$ represents a primary rubber radical generated from $T_{(r)}(c,b)$, with $T_{(0)}^\bullet(0,b)$ as a special case of primary PB radical; and $TS_{n(r)}^\bullet(c,b)$, $TM_{n(r)}^\bullet(c,b)$ are nonprimary terpolymer radicals with a growing chain ending either in a St or a MMA radical. Considering a branched GT molecule as an equivalent branched homopolymer, then its topology (r) coincides with the total number of branches b_n; independently of whether they are T- or H-grafts. In addition, the following is verified in the GT: $r = r_{SM} + r_{PB} - 1$, where r_{SM} is the number of poly(St-MMA) chains, and r_{PB} is the number of PB chains.

The mathematical model consists of two modules in series: the Basic Module presented in Appendix A

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TABLE II
Adopted Kinetic Mechanism

Global kinetics	Detailed kinetics
Initiation	
$I_2 \xrightarrow{k_d} 2I^\bullet$	$I_2 \xrightarrow{k_d} 2I^\bullet$
$I^\bullet + S \xrightarrow{k_{i1S}} S_1^\bullet$	$I^\bullet + S \xrightarrow{k_{i1S}} S_1^\bullet$
$I^\bullet + M \xrightarrow{k_{i1M}} M_1^\bullet$	$I^\bullet + M \xrightarrow{k_{i1M}} M_1^\bullet$
$I^\bullet + T \xrightarrow{k_{i2}} T_0^\bullet$	$I^\bullet + T_{(r)}(c,b) \xrightarrow{k_{i2}} T_{0(r)}^\bullet(c,b)$
$3S \xrightarrow{k_{i0S}} 2S_1^\bullet$	$3S \xrightarrow{k_{i0S}} 2S_1^\bullet$
$3M \xrightarrow{k_{i0M}} 2M_1^\bullet$	$3M \xrightarrow{k_{i0M}} 2M_1^\bullet$
$T_0^\bullet + S \xrightarrow{k_{i3S}} TS_1^\bullet$	$T_{0(r)}^\bullet(c,b) + S \xrightarrow{k_{i3S}} TS_{1(r)}^\bullet(c,b)$
$T_0^\bullet + M \xrightarrow{k_{i3M}} TM_1^\bullet$	$T_{0(r)}^\bullet(c,b) + M \xrightarrow{k_{i3M}} TM_{1(r)}^\bullet(c,b)$
Propagation	
$S_n^\bullet + S \xrightarrow{k_{pSS}} S_{n+1}^\bullet$	$S_n^\bullet + S \xrightarrow{k_{pSS}} S_{n+1}^\bullet$
$S_n^\bullet + M \xrightarrow{k_{pSM}} M_{n+1}^\bullet$	$S_n^\bullet + M \xrightarrow{k_{pSM}} M_{n+1}^\bullet$
$M_n^\bullet + M \xrightarrow{k_{pMM}} M_{n+1}^\bullet$	$M_n^\bullet + M \xrightarrow{k_{pMM}} M_{n+1}^\bullet$
$M_n^\bullet + S \xrightarrow{k_{pMS}} S_{n+1}^\bullet$	$M_n^\bullet + S \xrightarrow{k_{pMS}} S_{n+1}^\bullet$
$TS_n^\bullet + S \xrightarrow{k_{pSS}} TS_{n+1}^\bullet$	$TS_{n(r)}^\bullet(c,b) + S \xrightarrow{k_{pSS}} TS_{n+1(r)}^\bullet(c,b)$
$TS_n^\bullet + M \xrightarrow{k_{pSM}} TM_{n+1}^\bullet$	$TS_{n(r)}^\bullet(c,b) + M \xrightarrow{k_{pSM}} TM_{n+1(r)}^\bullet(c,b)$
$TM_n^\bullet + M \xrightarrow{k_{pMM}} TM_{n+1}^\bullet$	$TM_{n(r)}^\bullet(c,b) + S \xrightarrow{k_{pMS}} TS_{n+1(r)}^\bullet(c,b)$
$TM_n^\bullet + S \xrightarrow{k_{pMS}} TS_{n+1}^\bullet$	$TM_{n(r)}^\bullet(c,b) + M \xrightarrow{k_{pMM}} TM_{n+1(r)}^\bullet(c,b)$
Transfer to the comonomers	
$S_n^\bullet + S \xrightarrow{k_{fmSS}} C_n + S_1^\bullet$	$S_n^\bullet + S \xrightarrow{k_{fmSS}} C_n + S_1^\bullet$
$S_n^\bullet + M \xrightarrow{k_{fmSM}} C_n + M_1^\bullet$	$S_n^\bullet + M \xrightarrow{k_{fmSM}} C_n + M_1^\bullet$
$M_n^\bullet + M \xrightarrow{k_{fmMM}} C_n + M_1^\bullet$	$M_n^\bullet + M \xrightarrow{k_{fmMM}} C_n + M_1^\bullet$
$M_n^\bullet + S \xrightarrow{k_{fmMS}} C_n + S_1^\bullet$	$M_n^\bullet + S \xrightarrow{k_{fmMS}} C_n + S_1^\bullet$
$TS_n^\bullet + S \xrightarrow{k_{fmSS}} T + S_1^\bullet$	$TS_{n(r-1)}^\bullet(c-n,b) + S \xrightarrow{k_{fmSS}} T_{(r)}(c,b) + S_1^\bullet$
$TS_n^\bullet + M \xrightarrow{k_{fmSM}} T + M_1^\bullet$	$TS_{n(r-1)}^\bullet(c-n,b) + M \xrightarrow{k_{fmSM}} T_{(r)}(c,b) + M_1^\bullet$
$TM_n^\bullet + M \xrightarrow{k_{fmMM}} T + M_1^\bullet$	$TM_{n(r-1)}^\bullet(c,b) + M \xrightarrow{k_{fmMM}} T_{(r)}(c,b) + M_1^\bullet$
$TM_n^\bullet + S \xrightarrow{k_{fmMS}} T + S_1^\bullet$	$TM_{n(r-1)}^\bullet(c,b) + S \xrightarrow{k_{fmMS}} T_{(r)}(c,b) + S_1^\bullet$
$T_0^\bullet + M \xrightarrow{k'_{fmM}} T + M_1^\bullet$	$T_{0(r)}^\bullet(c,b) + M \xrightarrow{k'_{fmM}} T_{(r)}(c,b) + M_1^\bullet$
$T_0^\bullet + S \xrightarrow{k'_{fmS}} T + S_1^\bullet$	$T_{0(r)}^\bullet(c,b) + S \xrightarrow{k'_{fm}} T_{(r)}(c,b) + S_1^\bullet$
Transfer to the rubber	
$M_n^\bullet + T \xrightarrow{k_{fgM}} C_n + T_0^\bullet$	$M_n^\bullet + T_{(r)}(c,b) \xrightarrow{k_{fgM}} C_n + T_{0(r)}^\bullet(c,b)$
$S_n^\bullet + T \xrightarrow{k_{fgS}} C_n + T_0^\bullet$	$S_n^\bullet + T_{(r)}(c,b) \xrightarrow{k_{fgS}} C_n + T_{0(r)}^\bullet(c,b)$
$TM_n^\bullet + T \xrightarrow{k_{fgM}} T + T_0^\bullet$	$TM_{n(r-1)}^\bullet(c-n,b) + T_{(r)}(c,b) \xrightarrow{k_{fgM}} T_{(r)}(c,b) + T_{0(r)}^\bullet(c,b)$
$TS_n^\bullet + T \xrightarrow{k_{fgS}} T + T_0^\bullet$	$TS_{n(r-1)}^\bullet(c-n,b) + T_{(r)}(c,b) \xrightarrow{k_{fgS}} T_{(r)}(c,b) + T_{0(r)}^\bullet(c,b)$

TABLE II *Continued*

Global kinetics	Detailed kinetics

Termination by combination

$S_n^\bullet + S_m^\bullet \xrightarrow{k_{tcSS}} C_{n+m}$ $S_n^\bullet + S_m^\bullet \xrightarrow{k_{tcSS}} C_{n+m}$

$S_n^\bullet + M_m^\bullet \xrightarrow{k_{tcSM}} C_{n+m}$ $S_n^\bullet + M_m^\bullet \xrightarrow{k_{tcSM}} C_{n+m}$

$M_n^\bullet + M_m^\bullet \xrightarrow{k_{tcMM}} C_{n+m}$ $M_n^\bullet + M_m^\bullet \xrightarrow{k_{tcMM}} C_{n+m}$

$TS_n^\bullet + S_m^\bullet \xrightarrow{k_{tcSS}} T$ $TS_{n-m(r-1)}^\bullet(c-n,b) + S_m^\bullet \xrightarrow{k_{tcSS}} T_{(r)}(c,b)$

$TS_n^\bullet + M_m^\bullet \xrightarrow{k_{tcSM}} T$ $TS_{n-m(r-1)}^\bullet(c-n,b) + M_m^\bullet \xrightarrow{k_{tcSM}} T_{(r)}(c,b)$

$TM_m^\bullet + S_m^\bullet + \xrightarrow{k_{tcMS}} T$ $TM_{m-n(r-1)}^\bullet(c-n,b) + S_n^\bullet \xrightarrow{k_{tcSM}} T_{(r)}(c,b)$

$TM_n^\bullet + M_m^\bullet \xrightarrow{k_{tcMM}} T$ $TM_{n-m(r-1)}^\bullet(c-n,b) + M_m^\bullet \xrightarrow{k_{tcMM}} T_{(r)}(c,b)$

$TS_n^\bullet + TS_m^\bullet \xrightarrow{k_{tcSS}} T$ $TS_{n-m(r-r_1-1)}^\bullet(c-c_1-n,b-b_1) + TS_{m(r_1-1)}^\bullet(c_1,b_1) \xrightarrow{k_{tcSS}} T_{(r)}(c,b)$

$TS_n^\bullet + TM_m^\bullet \xrightarrow{k_{tcSM}} T$ $TS_{n-m(r-r_1-1)}^\bullet(c-c_1-n,b-b_1) + TM_{m(r_1-1)}^\bullet(c_1,b_1) \xrightarrow{k_{tcSM}} T_{(r)}(c,b)$

$TM_n^\bullet + TM_m^\bullet \xrightarrow{k_{tcMM}} T$ $TM_{n-m(r-r_1-1)}^\bullet(c-c_1-n,b-b_1) + TM_{m(r_1-1)}^\bullet(c_1,b_1) \xrightarrow{k_{tcMM}} T_{(r)}(c,b)$

$T_0^\bullet + S_n^\bullet \xrightarrow{k''_{tcS}} T$ $T_{0(r-1)}^\bullet(c-n,b) + S_n^\bullet \xrightarrow{k''_{tcS}} T_{(r)}(c,b)$

$T_0^\bullet + M_n^\bullet \xrightarrow{k''_{tcM}} T$ $T_{0(r-1)}^\bullet(c-n,b) + M_n^\bullet \xrightarrow{k''_{tcM}} T_{(r)}(c,b)$

$T_0^\bullet + TS_n^\bullet \xrightarrow{k''_{tcS}} T$ $T_{0(r-r_1-1)}^\bullet(c-c_1-n,b-b_1) + TS_{n(r_1-1)}^\bullet(c_1,b_1) \xrightarrow{k''_{tcS}} T_{(r)}(c,b)$

$T_0^\bullet + TM_n^\bullet \xrightarrow{k''_{tcM}} T$ $T_{0(r-r_1-1)}^\bullet(c-c_1-n,b-b_1) + TM_{n(r_1-1)}^\bullet(c_1,b_1) \xrightarrow{k''_{tcM}} T_{(r)}(c,b)$

Termination by disproportionation

$S_n^\bullet + S_m^\bullet \xrightarrow{k_{tdSS}} C_n + C_m$ $S_n^\bullet + S_m^\bullet \xrightarrow{k_{tdSS}} C_n + C_m$

$S_n^\bullet + M_m^\bullet \xrightarrow{k_{tdSM}} C_n + C_m$ $S_n^\bullet + M_m^\bullet \xrightarrow{k_{tdSM}} C_n + C_m$

$M_n^\bullet + M_m^\bullet \xrightarrow{k_{tdMM}} C_n + C_m$ $M_n^\bullet + M_m^\bullet \xrightarrow{k_{tdMM}} C_n + C_m$

$TS_n^\bullet + S_m^\bullet \xrightarrow{k_{tdSS}} T + C_m$ $TS_{n(r-1)}^\bullet(c-n,b) + S_m^\bullet \xrightarrow{k_{tdSS}} T_{(r)}(c,b) + C_m$

$TS_n^\bullet + M_m^\bullet \xrightarrow{k_{tdSM}} T + C_m$ $TS_{n(r-1)}^\bullet(c-n,b) + M_m^\bullet \xrightarrow{k_{tdSM}} T_{(r)}(c,b) + C_m$

$TM_n^\bullet + S_m^\bullet \xrightarrow{k_{tdMS}} T + C_m$ $TM_{n(r-1)}^\bullet(c-n,b) + S_m^\bullet \xrightarrow{k_{tdMS}} T_{(r)}(c,b) + C_m$

$TM_n^\bullet + M_m^\bullet \xrightarrow{k_{tdMM}} T + C_m$ $TM_{n(r-1)}^\bullet(c-n,b) + M_m^\bullet \xrightarrow{k_{tdMM}} T_{(r)}(c,b) + C_m$

$TS_n^\bullet + TS_m^\bullet \xrightarrow{k_{tdSS}} T + T$ $TS_{n(r-1)}^\bullet(c-n,b) + TS_{m(r-1)}^\bullet(c_1-m,b_1) \xrightarrow{k_{tdSS}} T_{(r)}(c,b) + T_{(r_1)}(c_1,b_1)$

$TS_n^\bullet + TM_m^\bullet \xrightarrow{k_{tdSM}} T + T$ $TS_{n(r-1)}^\bullet(c-n,b) + TM_{m(r-1)}^\bullet(c_1-m,b_1) \xrightarrow{k_{tdSM}} T_{(r)}(c,b) + T_{(r_1)}(c_1,b_1)$

$TM_n^\bullet + TM_m^\bullet \xrightarrow{k_{tdMM}} T + T$ $TM_{n(r-1)}^\bullet(c-n,b) + TM_{m(r-1)}^\bullet(c_1-m,b_1) \xrightarrow{k_{tdMM}} T_{(r)}(c,b) + T_{(r_1)}(c_1,b_1)$

$T_0^\bullet + S_n^\bullet \xrightarrow{k''_{tdS}} T + C_n$ $T_{0(r-1)}^\bullet(c,b) + S_n^\bullet \xrightarrow{k''_{tdS}} T_{(r)}(c,b) + C_n$

$T_0^\bullet + M_n^\bullet \xrightarrow{k''_{tdM}} T + C_n$ $T_{0(r-1)}^\bullet(c,b) + M_n^\bullet \xrightarrow{k''_{tdM}} T_{(r)}(c,b) + C_n$

$T_0^\bullet + TS_n^\bullet \xrightarrow{k''_{tdS}} T + T$ $T_{0(r-1)}^\bullet(c,b) + TS_{n(r_1-1)}^\bullet(c_1-n,b_1) \xrightarrow{k''_{tdS}} T_{(r)}(c,b) + T_{(r_1)}(c_1,b_1)$

$T_0^\bullet + TM_n^\bullet \xrightarrow{k''_{tdM}} T + T$ $T_{0(r-1)}^\bullet(c,b) + TM_{n(r_1-1)}^\bullet(c_1-n,b_1) \xrightarrow{k''_{tdM}} T_{(r)}(c,b) + T_{(r_1)}(c_1,b_1)$

(based on the Global Kinetics of Table II), and the GT Topology Module of Appendix B (based on the Detailed Kinetics of Table II). The main model assumptions are: (a) homogeneous reaction conditions; (b) pseudo-stationary states for all radical species; and (c) use of pseudo-rate constants for calculating the weight-chain length distributions (WCLD) of the FC and grafted GT branches. The hypothesis of system homogeneity in the bulk reaction is supported by the low employed rubber concentration,
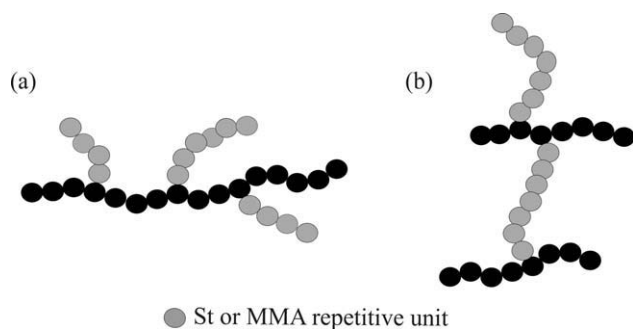
(a)   (b)

● St or MMA repetitive unit

Figure 2 Two possible configurations of the hypothetical GT species $T_3(14,16)$, where 3 is the number of trifunctional branching points, 14 are the number of St-MMA units (gray circles), and 16 are the number of B units (black circles). Molecule (a) exhibits 3 "T" branches; and molecule (b) exhibits a single "T" branch and a single "H" branch.

and by the assumption that initiator and the comonomers are evenly partitioned between the phases.

The Basic Module calculates the following global variables: concentrations of reagents and products; monomer conversion (x); mass fractions of St in the FC ($\bar{p}_{St,C}$) and in the GT ($p_{St,GT}$); comonomers grafting efficiency (E); and PB grafting efficiency (E_{PB}). Additionally, it estimates the number-chain length distributions (NCLDs) and WCLDs of the FC and residual PB; the number-average number of St-MMA chains per GT molecule ($\bar{r}_{n,SM}$), and the number-average number of PB chains per GT molecule ($\bar{r}_{n,PB}$). The GT Topology Module calculates the bivariate WCLDs of each topology [eq. (B23)], and the WCLDs of the total GT [eq. (B24)].

For the numerical resolution, the set of (algebraic and differential) eqs. (A1, A6–A8, A19–A23, A41–A45, A48, and A49) was first solved by standard methods appropriate for "stiff" systems. The average polymer properties were calculated from the obtained uni- and bivariate distributions. The differential equations involving all distributions (i.e., the univariate WCLDs of the FC and unreacted PB, and the bivariate WCLDs of the different GT topologies) were integrated through an "ad hoc" finite difference method with a fixed integration step of 1 s. Also, many molecular species were lumped together at fixed chain length intervals, to avoid integrating a differential equation for every possible chain length. Thus, while the univariate WCLDs contained 10,000 points (with chain length intervals of 50 repeating units), the bivariate WCLD of each GT topology was represented by a 500 × 500 matrix (with 100 repeating units per point for the St-MMA branches and with 500 repeating units per point for the PB branches). At each integration step, all the newly-generated GT branches were "distributed" among the produced rubber radicals. Despite the relatively crude procedure employed, relatively accurate

results were obtained, however, because the global masses of each polymer component were accurately estimated in the Basic Module, and therefore integration errors in the distribution calculations were not accumulated along the solution. The computer program was written in Fortran for a Pentium IV PC. A typical run involved about 3 s for the global variables and 1 h for the WCLDs.

MODEL ADJUSTMENT AND SIMULATION RESULTS

Most of the model parameters were directly taken from literature (Table III). The adjusted parameters were determined following a procedure similar to that of Estenoz et al. (1996) for the HIPS process. It was as follows. First, the homopropagation rate constants (k_{pSS} and k_{pMM}) were adjusted to fit the conversion measurements within reported literature values. [Fig. 1(a)]. Then, the rate constants of initiation and of chain transfer to the rubber (k_{i2} and k_{fgS}, respectively) were adjusted to fit the measurements of the comonomers grafting efficiency E [Fig. 1(c)]. As shown in the bottom of Table III, all the resulting parameters were within expected literature ranges.

In the simulation results of Figure 1 and Table I, a reasonable agreement is observed between the measurements and model predictions. According to the model, $\overline{M}_{w,PB}$ falls more rapidly than $\overline{M}_{n,PB}$ [Fig. 1(e)], due to the higher probability of grafting of the longer PB chains. The mass fraction of St in the GT increases monotonically [Fig. 1(b)], due to a reduction in the molar masses of the newly-grafted PB chains combined with an increased grafting-over-grafting process. For the same reasons, $\overline{M}_{w,GT}$ increases more rapidly than $\overline{M}_{n,GT}$ [Fig. 1(f)]. In Table I, the simulation results indicate that the final GT of Experiment 2 exhibits in average 5.11 total chains per molecule, and 1.09 PB chains per molecule. For Experiment 3, the same averages are 1.70 and 1.12, respectively.

Figure 3 presents some additional model predictions for the quasi-bulk Experiment 3. Figure 3(a) shows the time evolutions of the total masses of FC (G_{FC}), GT (G_{GT}), and PB (G_{PB}). Note that despite the low final conversion, most of the original PB was transformed into GT. Figure 3(b) presents the MWD of the original PB as measured by SEC ($G_{PB}^0 (M)$), together with the simulated final MWDs of the residual PB ($G_{PB} (M)$), FC ($G_{FC} (M)$), and GT ($G_{GT} (M)$). The areas under these MWDs are shown proportional to their experimental mass fractions. For the total final GT, Figure 3(c) shows the MWDs of each of the generated GT topologies (where the topologies with $r > 6$ were lumped together under "others"). The most abundant topology contains a single St-MMA branch per molecule, and the higher topologies exhibit increasingly higher molecular weights.

TABLE III
Kinetic Parameters at $T = 65°C$

Parameter	Value	Units	Reference
F	1		62
k_d	2.5×10^{-6}	(s^{-1})	63
$k_{i1S} = k_{i3S} = k_{PSS}$	287	$(L\ mol^{-1}\ s^{-1})$	a
$k_{i1M} = k_{i3M} = k_{pMM}$	629	$(L\ mol^{-1}\ s^{-1})$	b
k_{i1M}/k_{i2}	1.2	–	–
k_{i2}	524	$(L\ mol^{-1}\ s^{-1})$	This work
k_{i0S}	62.0×10^{-15}	$(L^2\ mol^{-2}\ s^{-1})$	35
k_{i0M}	16.7×10^{-10}	$(L^2\ mol^{-2}\ s^{-1})$	64
r_S	0.523	–	64
r_M	0.47	–	64
k_{pSM}	(k_{pSS}/r_S)	$(L\ mol^{-1}\ s^{-1})$	–
k_{pMS}	(k_{pMM}/r_M)	$(L\ mol^{-1}\ s^{-1})$	–
$k_{fmSS} = k'_{fmS}$	2×10^{-2}	$(L\ mol^{-1}\ s^{-1})$	65
$k_{fmSM} = k_{fmMS}$	1.6×10^{-2}	$(L\ mol^{-1}\ s^{-1})$	65
k_{fgS}	0.096	$(L\ mol^{-1}\ s^{-1})$	c
k_{fgM}	0.40	$(L\ mol^{-1}\ s^{-1})$	d
$k_{fmMM} = k'_{fmM}$	3.52×10^{-2}	$(L\ mol^{-1}\ s^{-1})$	64
$k_{tcSS} = k''_{tcS}$	$1.94 \times 10^6 e^{-(C_1\psi_i + C_2\psi_i^2 + C_3\psi_i^3)\,e}$	$(L\ mol^{-1}\ s^{-1})$	64
$k_{tcMM} = k''_{tcd}$	$2.0 \times 10^6 \frac{1}{1-\psi_i} e^{-(A_1\psi_i + A_2\psi_i^2)\,f}$	$(L\ mol^{-1}\ s^{-1})$	64
$k_{tcSM} = k_{tcMS}$	$6.0 \times 10^8 e^{-(C_1\psi_i + C_2\psi_i^2 + C_3\psi_i^3)\,e}$	$(L\ mol^{-1}\ s^{-1})$	56
$k_{tdSS} = k''_{tdS}$	0	$(L\ mol^{-1}\ s^{-1})$	–
$k_{tdSM} = k_{tdMS}$	$2.0 \times 10^6 \frac{1}{1-\psi_i} e^{-(A_1\psi_i + A_2\psi_i^2)\,f}$	$(L\ mol^{-1}\ s^{-1})$	64
$k_{tdMM} = k''_{tdM}$	$11.9 \times 10^6 \frac{1}{1-\psi_i} e^{-(A_1\psi_i + A_2\psi_i^2)\,f}$	$(L\ mol^{-1}\ s^{-1})$	64

a,b,c,d Adjusted in this work between the following literature limits: $80 < k_{pSS} < 480$ L mol s^{-1}; $290 < k_{pMM} < 900$ L mol s^{-1}; $0.0016 < k_{fgS} < 0.096$ L mol s^{-1}; $0.14 < k_{fgSM} < 0.44$ L mol s^{-1} for cis-2-butene, as proposed by Cameron and Qureshi.[14]

e $C_1 = 2.57 - 0.00505T$; $C_2 = 9.56 - 0.0176\ T$; $C_3 = -3.03 + 0.00758T$.

f $A_{1(60°C)} = -5.48$; $A_{2(60°C)} = -2.72$; ψ'_i: polymer volume fraction.[66]
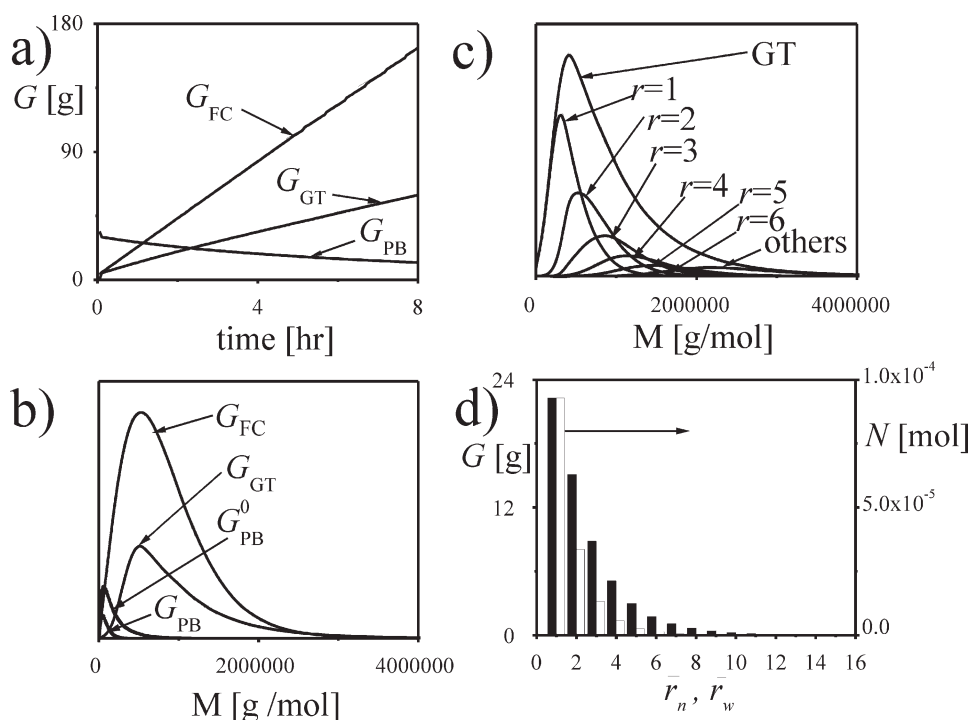

Figure 3 Model predictions of Experiment 3. (a) Time evolution of the total masses of FC, GT, and PB. (b) MWDs of the polymeric components of the final MBS, and MWD of the initial PB (G_{PB}^0). (c) MWDs of the final total GT and corresponding topologies. (d) Distribution of chain branching in the final GT.

For the total final GT, Figure 3(d) shows the (weight and number-based) distributions of chain branching. Their corresponding (weight and number-based) averages are 2.53 and 1.70, respectively.

CONCLUSIONS

A global mathematical model was developed for the bulk free-radical copolymerization of St and MMA in the presence of PB, carried out at the azeotropic comonomers ratio. The model involved the adjustment of four kinetic constants, and it predicts the detailed molecular structure of the evolving polymer mixture.

At present, it is impossible to verify the model predictions on the molecular characteristics of the generated GT topologies; and even the analyses of the isolated polymeric components is subject to contamination errors, due to the imperfect fractionation by solvent-extraction. The analysis of the total polymer could perhaps be improved by two-dimensional liquid chromatography (i.e., by combining size exclusion with adsorption/desorption). This technique could in principle isolate the homopolymer distributions from the bivariate distribution of molar mass and composition of the GT.

NOMENCLATURE

B	butadiene repetitive unit
b	number of B repetitive units
B^*	unreacted B
C_n	FC with n pseudo-repetitive units
DR	differential refractometer
E	comonomers grafting efficiency
E_{PB}	PB grafting efficiency
FC	free St-MMA copolymer
f	initiator efficiency
f_M, f_S	molar fractions of MMA and St in the comonomers mixture [eqs. (A28, A29)]
$G_B, G_{GT},$ G_{FC}, G_{gB}	total masses of PB, GT, FC, and grafted St-MMA branches
I_2	initiator
$I^\bullet$	primary initiator radical
k_d	initiator decomposition rate constant
k_{fg}	pseudo-rate constant of transfer to the rubber [defined by eq. (A35)]
$k_{fgM}; k_{fgS}$	rate constant of transfer to the rubber by MMA- and St-ended radicals
k_{fm}	pseudo-rate constant of chain transfer to the monomers [defined by eq. (A34)]
$k_{fmMM}; k_{fmMS};$ $k_{fmSS}; k_{fmSM};$ $k_{fmM}; k_{fmS}$	rate constants of chain transfer to the monomers
$k_{i2}; k_{i1M}; k_{i1S};$ $k_{i3M}; k_{i3S};$	initiation rate constants
$k_{i0M}; k_{i0S}$	thermal initiation rate constants
k_p	pseudo-rate constant of propagation [eq. (A33)]
$k_{pMM}; k_{pSS};$ $k_{pMS}; k_{pSM}$	propagation rate constants
$k_{tc}; k_{tc}''$	pseudo-rate constants of re-combination termination [eqs. (A37) and (A39)]
$k_{tcMM}; k_{tcMS};$ $k_{tcSS}; k_{tcM}'';$ $k_{tcS}''; k_{tc}''$	rate constants of termination by recombination
$k_{td}; k_{td}''$	pseudo-rate constants of termination by disproportionation [eqs. (A36) and (A38)]
$k_{tdMM}; k_{tdMS};$ $k_{tdSS}; k_{tdM}'';$ $k_{tdS}''; k_{td}''$	rate constants of termination by disproportionation
MMA,M	methyl methacrylate
M	molecular weight
$M^\bullet$	generic MMA-ended FC radical
$M_1^\bullet$	primary MMA radical
$M_n^\bullet$	MMA-ended radical containing n pseudo-repetitive units into growing chain
$\overline{M}_n$	number-average molecular weight
$\overline{M}_w$	weight-average molecular weight
MWD	molecular weight distribution
N	number of moles
NCLD	number-length chain distribution
PB	polybutadiene
$\overline{p}_{St,FC}; \overline{p}_{St,GT}$	mass fractions of St in the FC and in the GT
r_M, r_S	reactivity ratios of MMA and St radicals
r	Number of trifunctional points
$\overline{r}_{n,PB}, \overline{r}_{w,PB}$	Average-number and weight of PB chains per molecule in the GT
$\overline{r}_{n,SM}, \overline{r}_{w,SM}$	Average-number and weight of Poly(St-MMA) chains per molecule in the GT
$R^\bullet$	generic free radical
R_p	global rate of comonomers consumption
R_{pgB}	rate of incorporation of St and MMA onto the GT
R_{pFC}	rate of generation of FC
St,S	styrene
$S^\bullet$	generic St-ended radical
$S_1^\bullet$	St primary radical
$S_n^\bullet$	St-ended radical with n pseudo-repetitive units in the growing chain
SEC	size exclusion chromatography
SV	specific viscosity
T	GT or unreacted PB molecule
$T_{0(r)}^\bullet$	primary T radical of topology r
$T^\bullet$	nonprimary GT

$T_{(r)}$ terpolymer of topology r (the unreacted PB has $r = c = 0$)

$TM^\bullet$ MMA-ended GT radical

$TM_1^\bullet$ primary MMA-ended GT radical

$TM_n^\bullet$ nonprimary MMA-ended GT radical, with n repetitive units of St and MMA in the new growing chain

$T_{(r)}(c,b)$ GT molecule of topology r, with c pseudo-repeating units of St or MMA, and b units of B

$T_{(0)}(c,b)$ unreacted PB

$TS^\bullet$ St-ended GT radical

$TS_1^\bullet$ primary St-ended GT radical

$TS_n^\bullet$ nonprimary St-ended GT radical with n pseudo-repetitive units of St or MMA

$TM_{n(r)}^\bullet(c,b)$, $TS_{n(r)}^\bullet(c,b)$ MMA-ended and St-ended non primary GT radical

UV   ultraviolet

x total comonomers conversion

$[\ ]$ molar concentration

Greek symbols

$\alpha, \beta, \gamma, \tau_1, \tau$ dimensionless kinetic parameters

ϕ_{St}, ϕ_M molar fraction of S- and M-ended radicals

φ ratio of total M- and St-ended FC radicals concentration and the total free radicals concentration [eq (A26)]

ψ_i polymer volume fraction

APPENDIX A: BASIC MODULE

From the Global Kinetics of Table II, the following mass balances are derived:

Initiator

$$\frac{d([I_2]V)}{dt} = -k_d[I_2]V \tag{A1}$$

Comonomers

Call $[M^\bullet]$, $[S^\bullet]$, $[TM^\bullet]$, and $[TS^\bullet]$ the total concentrations of $[M_n^\bullet]$, $[S_n^\bullet]$, $[TM_n^\bullet]$, and $[TS_n^\bullet]$, radicals respectively; i.e:

$$[M^\bullet] = \sum_{n=1}^{\infty} [M_n^\bullet] \tag{A2}$$

$$[TM^\bullet] = \sum_{n=1}^{\infty} [TM_n^\bullet] \tag{A3}$$

$$[S^\bullet] = \sum_{n=1}^{\infty} [S_n^\bullet] \tag{A4}$$

$$[TS^\bullet] = \sum_{n=1}^{\infty} [TS^\bullet] \tag{A5}$$

With the "long chain approximation," the comonomers molar balances are:

$$\frac{d([S]V)}{dt} = -R_{pS}V = -\left\{ k_{pSS}[S]([S^\bullet] + [TS^\bullet]) + k_{pMS}[S]([M^\bullet] + [TM^\bullet]) \right\}V \tag{A6}$$

$$\frac{d([M]V)}{dt} = -R_{pM}V = -\left\{ k_{pMM}[M]([M^\bullet] + [TM^\bullet]) + k_{pSM}[M]([S^\bullet] + [TS^\bullet]) \right\}V \tag{A7}$$

where R_{pS}, R_{pM} are the global rates of consumption of St and MMA, respectively.

Unreacted B units

Let us represent with B^* any unreacted B unit contained either in the GT or in the PB. Thus,

$$\begin{aligned}
\frac{d([B^*]V)}{dt} = & -\left\{ k_{i2}[I^\bullet] + k_{fg\,S}([S^\bullet] + [TS^\bullet]) \right. \\
& + k_{fg\,M}([M^\bullet] + [TM^\bullet]) \Big\} [B^*]V \\
& + \{ k'_{fm\,S}[S] + k'_{fm\,M}[M] + k''_{td\,S}([S^\bullet] + [TS^\bullet]) . \\
& + k''_{td\,M}([M^\bullet] + [TM^\bullet]) \} [T_0^\bullet]V
\end{aligned} \tag{A8}$$

Radical Species

With the pseudo-steady state assumption, the following mass balances can be written:

$$\frac{d([I^\bullet]V)}{dt} = \{ 2fk_d[I_2] - (k_{i1S}[S] + k_{i1\,M}[M] + k_{i2}[B^*])[I^\bullet] \}V = 0 \tag{A9}$$

$$\begin{aligned}
\frac{d([S_1^\bullet]V)}{dt} = & \left(k_{i1S}[S][I^\bullet] + 2k_{i0S}[S]^3 \right)V - \left(k_{pSM}[M] + k_{pSS}[S] \right)[S_1^\bullet]V \\
& + \left\{ k_{fmMS}([M^\bullet]+[TM^\bullet]) + k_{fmSS}([S^\bullet] + [TS^\bullet]) + k'_{fMS}[T_0^\bullet] \right\}[S]V \\
& - \left\{ (k_{tdSS} + k_{tcSS})([S_n^\bullet] + [TS_n^\bullet]) + (k_{tdSM} + k_{tcSM})([M_n^\bullet] + [TM_n^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet] \right\}[S_1^\bullet]V = 0 \tag{A10}
\end{aligned}$$

$$\frac{d([S_n^\bullet]V)}{dt} = (k_{pSS}[S_{n-1}^\bullet] + k_{pMS}[M_{n-1}^\bullet])[S]V - (k_{pSS}[S] + k_{pSM}[M] + k_{fmSS}[S]$$
$$+ k_{fmSM}[M] + k_{fg}[B^*])[S_n^\bullet]V - \{(k_{tdSS} + k_{tcSS})([S^\bullet] + [TS^\bullet])$$
$$+ (k_{tdSM} + k_{tcSM})([M^\bullet] + [TM^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet]\}[S_n^\bullet]V = 0$$
$$n = 2, 3 \cdots \quad (A11)$$

$$\frac{d([TS_1^\bullet]V)}{dt} = k_{i3S}[S][T_0^\bullet]V - \{k_{pSS}[S] + k_{pSM}[M] + k_{fmSS}[S] + k_{fmSM}[M]$$
$$+ k_{fgS}[B^*] + (k_{tdSS} + k_{tcSS})([S^\bullet] + [TS^\bullet])$$
$$+ (k_{tdSM} + k_{tcSM})([M^\bullet] + [TM^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet]\}[TS_1^\bullet]V = 0 \quad (A12)$$

$$\frac{d([TS_n^\bullet]V)}{dt} = (k_{pSS}[TS_{n-1}^\bullet] + k_{pMS}[TM_{n-1}^\bullet])[S]V - \{k_{pSS}[S] + k_{pSM}[M]$$
$$+ k_{fmSS}[S] + k_{fmSM}[M] + k_{fgS}[B^*] + (k_{tdSS} + k_{tcSS})([S^\bullet] + [TS^\bullet])$$
$$+ (k_{tdSM} + k_{tcSM})([M^\bullet] + [TM^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet]\}[TS_n^\bullet]V = 0$$
$$n = 2, 3 \ldots \quad (A13)$$

$$\frac{d([M_1^\bullet]V)}{dt} = (k_{i1M}[M][I^\bullet] + 2k_{i0M}[M]^3)V - (k_{pMM}[M] + k_{pMS}[S])[M_1^\bullet]V$$
$$+ \{k_{fmSM}([S^\bullet] + [TS^\bullet]) + k_{fmMM}([M^\bullet] + [TM^\bullet])$$
$$k'_{fmS}[T_0^\bullet]\}[M]V - \{(k_{tdMM} + k_{tcMM})([M^\bullet] + [TM^\bullet])$$
$$+ (k_{tdSM} + k_{tcSM})([S^\bullet] + [TS^\bullet]) + (k''_{tdM} + k''_{tdM})[T_0^\bullet]\}[M_1^\bullet]V = 0 \quad (A14)$$

$$\frac{d([M_n^\bullet]V)}{dt} = (k_{pMM}[M_{n-1}^\bullet] + k_{pSM}[S_{n-1}^\bullet])[M]V - (k_{pMS}[S] + k_{pMM}[M] + k_{fmMM}[M]$$
$$+ k_{fmMS}[S] + k_{fgM}[B^*])[M_n^\bullet]V - \{(k_{tdMM} + k_{tcMM})([M^\bullet] + [TM^\bullet])$$
$$+ (k_{tdSM} + k_{tcSM})([S^\bullet] + [TS^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet]\}[M_n^\bullet]V = 0$$
$$n = 2, 3 \quad (A15)$$

$$\frac{d([TM_1^\bullet]V)}{dt} = k_{i3M}[M][T_0^\bullet]V - \{k_{pMM}[M] + k_{pMS}[S] + k_{fmMM}[M] + k_{fmMS}[S]$$
$$+ k_{fgM}[B^*] + (k_{tdMM} + k_{tcMM})([M^\bullet] + [TM^\bullet])$$
$$+ (k_{tdMS} + k_{tcMS})([S^\bullet] + [TS^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet]\}[TM_1^\bullet]V = 0 \quad (A16)$$

$$\frac{d([TM_n^\bullet]V)}{dt} = (k_{pMM}[TM_{n-1}^\bullet] + k_{pSM}[TS_{n-1}^\bullet])[M]V - \{k_{pMM}[M] + k_{pMS}[S] +$$
$$k_{fmMM}[M] + k_{fmMS}[S] + k_{fgM}[B^*] + (k_{tdMM} + k_{tcMM})([M^\bullet] + [TM^\bullet])$$
$$+ (k_{tdMS} + k_{tcMS})([S^\bullet] + [TS]^\bullet) + (k''_{tdM} + k''_{tcM})[T_0^\bullet]\}[TM_n^\bullet]V = 0$$
$$n = 2, 3 \ldots \quad (A17)$$

$$\frac{d([T_0^\bullet]V)}{dt} = \{k_{i2}[B^*][I^\bullet] - k_{i3S}[T_0^\bullet][S] - k_{i3M}[T_0^\bullet][M] - k'_{fmM}[M][T_0^\bullet]$$
$$- k'_{fmS}[S][T_0^\bullet] + k_{fgS}[B^*]([S^\bullet] + [TS^\bullet]) + k_{fgM}[B^*]([M^\bullet] + [TM^\bullet])\}V$$
$$- \{(k'_{tcM} + k'_{tdM})([M^\bullet] + [TM^\bullet]) + (k'_{tcS} + k'_{tdS})([S^\bullet] + [TS^\bullet])\}[T_0^\bullet]V = 0 \quad (A18)$$

From eq. (A9), one obtains:

$$[I^\bullet] = \frac{2fk_d[I_2]}{(k_{i1S}[S] + k_{i1M}[M] + k_{i2}[B^*])} \quad (A19)$$

Adding up eqs. (A10) and (A11); eqs. (A12) and (A13); eqs. (A14) and (A15); and eqs. (A16) and (A17) over all possible n's, the following expressions for the total free-radicals are obtained:

$$\frac{d([S^\bullet]V)}{dt} = \left\{ k_{i1S}[S][I^\bullet] + 2k_{i0S}[S]^3 - k_{pSM}[M][S^\bullet] + k_{pMS}[S][M^\bullet] \right.$$
$$+ k_{fmMS}[S][M^\bullet] - k_{fmSM}[S^\bullet][M] + \left(k_{fmSS}[TS^\bullet] + k_{fmMS}[TM^\bullet] \right.$$
$$\left. + k'_{fMS}[T_0^\bullet] \right)[S] \Big\} V - \left\{ k_{fgS}[B^*] + (k_{tdSS} + k_{tcSS})([S^\bullet] + [TS^\bullet]) \right.$$
$$+ (k_{tdSM} + k_{tcSM})([M^\bullet] + [TM^\bullet]) + (k'_{tdS} + k'_{tcS})[T_0^\bullet] \Big\}[S^\bullet]V = 0 \tag{A20}$$

$$\frac{d([TS^\bullet]V)}{dt} = \left\{ \left(k_{i3S}[T_0^\bullet] + k_{pMS}[TM^\bullet] \right)[S] - k_{pMS}[TS^\bullet][M] \right\}V - \left\{ k_{fmMS}[M] \right.$$
$$+ k_{fmSS}[S] + k_{fgS}[B^*] + (k_{tdSS} + k_{tcSS})([S^\bullet] + [TS^\bullet])$$
$$+ (k_{tdSM} + k_{tcSM})([M^\bullet] + [TM^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet] \Big\}[TS^\bullet]V = 0 \tag{A21}$$

$$\frac{d([M^\bullet]V)}{dt} = \left\{ k_{i1M}[M][I^\bullet] + 2k_{i0M}[M]^3 + (k_{pSM} + k_{fmSM})[M][S^\bullet] - \right.$$
$$(k_{pMS} + k_{fmMS})[S][M^\bullet] + (k_{fmSM}[TS^\bullet] + k_{fmMM}[TM^\bullet]$$
$$\left. + k'_{fmM}[T_0^\bullet] \right)[M] \Big\}V - \left\{ k_{fg}[B^*] + (k_{tdMM} + k_{tcMM})([M^\bullet] + [TM^\bullet]) \right.$$
$$+ (k_{tdSM} + k_{tcSM})([S^\bullet] + [TS^\bullet]) + (k''_{tdM} + k''_{tdM})[T_0^\bullet] \Big\}[M^\bullet]V = 0 \tag{A22}$$

$$\frac{d([TM^\bullet]V)}{dt} = \left\{ \left(k_{i3M}[T_0^\bullet] + k_{pSM}[TS^\bullet] \right)[M] - k_{pMS}[TM^\bullet][S] \right\}V -$$
$$\left\{ k_{fmMM}[M] + k_{fmMS}[S] + k_{fgM}[B^*] + (k_{tdMM} + k_{tcMM})([M^\bullet] + [TM^\bullet]) \right.$$
$$+ (k_{tdMS} + k_{tcMS})([S^\bullet] + [TS^\bullet]) + (k''_{tdS} + k''_{tcS})[T_0^\bullet] \Big\}[TM^\bullet]V = 0 \tag{A23}$$

Equations (A1), (A6–A8), (A18–A23) must be solved together for calculating the evolutions of [I₂], [S], [M], amd [B*].

MWD of the FC

From eqs. (A6) and (A7), the global rate of comonomers consumption is:

$$R_p = R_{pSFC} + R_{pM} \tag{A24}$$

This rate is also the result of the following contributions:

$$R_p = R_{pFC} + R_{pgB} \tag{A25}$$

where R_{pFC}, R_{pgB} respectively represent the rates of incorporation of the generic pseudo-comonomer into the FC and into the GT branches. Let us define the following fraction of FC free radicals:

$$\varphi = \frac{[M^\bullet] + [S^\bullet]}{[M^\bullet] + [TM^\bullet] + [S^\bullet] + [TS^\bullet]} \tag{A26}$$

The rate of propagation of either MMA or St with $TM^\bullet$ or $TS^\bullet$ is $(1 - \varphi)R_p$. The rate of generation of FC is given by:

$$R_{pFC} = \varphi R_p \left\{ k_{fmMM}[M][M^\bullet] + k_{fmSS}[S][S^\bullet] + \left(k_{fgM}[M^\bullet] + k_{fgS}[S^\bullet] \right)[B^*]. \right.$$
$$+ k_{fSM}[M][S^\bullet] + k_{fMS}[S][M^\bullet] + k_{tdSM}([S^\bullet] + [TS^\bullet])[M^\bullet]$$
$$+ k_{tdMS}([M^\bullet] + [TM^\bullet])[S^\bullet] + k_{tdMM}([M^\bullet] + [TM^\bullet])[M^\bullet]$$
$$+ k_{tdSS}([S^\bullet] + [TS^\bullet])[M^\bullet] + k''_{tdM}[T_0^\bullet][M^\bullet] + k''_{tdS}[T_0^\bullet][S^\bullet] + k_{tcSS}[S^\bullet]^2$$
$$+ k_{tcMS}[S^\bullet][M^\bullet] + k_{tcMM}[M^\bullet]^2 \Big\} \times \left\{ k_{fmMM}[M][M^\bullet] + k_{fmSS}[S][S^\bullet] \right.$$
$$+ \left(k_{fgM}[M^\bullet] + k_{fgS}[S^\bullet] \right)[B^*] + k_{fSM}[M][S^\bullet] + k_{fMS}[S][M^\bullet]$$
$$+ k_{fSM}[M][S^\bullet] + k_{fMS}[S][M^\bullet] + k_{tdSM}([S^\bullet] + [TS^\bullet])[M^\bullet]$$
$$+ k_{tdMS}([M^\bullet] + [TM^\bullet])[S^\bullet] + k_{tdMM}([M^\bullet] + [TM^\bullet])[M^\bullet]$$
$$+ k_{tdSS}([S^\bullet] + [TS^\bullet])[M^\bullet] + k''_{tdM}[T_0^\bullet][M^\bullet] + k''_{tdS}[T_0^\bullet][S^\bullet] + k_{tcSS}[S^\bullet]^2$$
$$+ k_{tcMS}[S^\bullet][M^\bullet] + k_{tcMM}[M^\bullet]^2 + k_{tcMM}[TM^\bullet][M^\bullet] + k_{tcSS}[TS^\bullet][S^\bullet]$$
$$+ k''_{tcS}[T_0^\bullet][S^\bullet] + k''_{tcM}[T_0^\bullet][M^\bullet] \Big\}^{-1} \tag{A27}$$

Then, the rate of incorporation of St and MMA onto can be calculated from eq. (A24)

Define the following comonomer molar fractions:

$$f_{St} \equiv \frac{[S]}{[M] + [S]} = \frac{[S]}{[C]} \quad (A28)$$

$$f_{MMA} \equiv \frac{[M]}{[M] + [S]} = \frac{[M]}{[C]} \quad (A29)$$

where [C] is the total comonomers concentration.

The molar fractions of St- and MMA-ended free-radicals are defined by:

$$\phi_{St} = \frac{[S^\bullet] + [TS^\bullet]}{[R^\bullet]} \quad (A30)$$

$$\phi_{M} = \frac{[M^\bullet] + [TM^\bullet]}{[R^\bullet]} \quad (A31)$$

$$[R^\bullet] = [S^\bullet] + [M^\bullet] + [TS^\bullet] + [TM^\bullet] \quad (A32)$$

For calculating the MWD of the FC, the copolymerization is treated as a pseudo-homopolymerization. Considering eqs. (A28–A32) and the material balances of eqs. (A6–A23), the pseudo-rate constants are estimated from[62]:

$$k_p = k_{pSS}f_{St}\phi_{St} + k_{pSM}f_M\phi_{St} + k_{pMM}f_M\phi_M + k_{pMS}f_{St}\phi_M \quad (A33)$$

$$k_{fm} = k_{fmSS}f_{St}\phi_{St} + k_{fmSM}f_M\phi_{St} + k_{fmMM}f_M\phi_M$$
$$+ k_{fmMS}f_{St}\phi_M \quad (A34)$$

$$k_{fg} = k_{fgS}\phi_{St} + k_{fgM}\phi_M \quad (A35)$$

$$k_{td} = k_{tdSS}(\phi_{St})^2 + k_{tdSM}\frac{[M^\bullet][S^\bullet]}{([M^\bullet] + [S^\bullet])^2}$$
$$+ k_{tdMM}(\phi_M)^2 \quad (A36)$$

$$k_{tc} = k_{tcSS}(\phi_{St})^2 + k_{tcSM}\frac{[M^\bullet][S^\bullet]}{([M^\bullet] + [S^\bullet])^2} + k_{tcMM}(\phi_M)^2 \quad (A37)$$

$$k''_{td} = k''_{tdS}\phi_{St} + k''_{tdM}\phi_M \quad (A38)$$

$$k''_{tc} = k''_{tcS}\phi_{St} + k''_{tcM}\phi_M \quad (A39)$$

The total polymerization rate can be written in terms of the total concentrations of comonomers and radicals, yielding:

$$R_p = k_p[R^\bullet][C] \quad (A40)$$

After Estenoz et al. (1996), the following dimensionless kinetic parameters are defined:

$$\gamma = \frac{[T_0^\bullet]}{[M^\bullet] + [S^\bullet] + [TM^\bullet] + [TS^\bullet]} \quad (A41)$$

$$\tau_1 = \frac{k'_{tc}R_p}{(k_p[C])^2} \quad (A42)$$

$$\tau = \frac{k_{fm}}{k_p} + \frac{k_{fg}[B^*]}{k_p[C]} + \frac{k_{td}R_p}{(k_p[C])^2} + \frac{k''_{td}R_p[T_0^\bullet]}{(k_p[C])^2[R^\bullet]} + \gamma\tau_1 \quad (A43)$$

$$\beta = \frac{k_{tc}R_p}{(k_p[C])^2} \quad (A44)$$

$$\alpha = \tau + \beta \quad (A45)$$

Inserting eqs. (A41–A45) into (A24) and (A26), it results:

$$R_{pFC} = \phi R_p \frac{\tau - \gamma\tau_1 + \beta\phi}{\alpha} \quad (A46)$$

$$R_{pgB} = (1 - \phi)R_p \frac{2\beta\phi + 2\tau_1\frac{\phi}{1-\phi} + \tau - \gamma\tau_1}{\alpha} \quad (A47)$$

The masses of polymerized St and MMA contained in the FC and in the GT branches (G_{FC} and G_{gB} respectively), are obtained through:

$$\frac{d(G_{FC})}{dt} = R_{pC}M_{eff}V = \phi R_p \frac{\tau - \gamma\tau_1 + \beta\phi}{\alpha}M_{eff}V \quad (A48)$$

$$\frac{d(G_{gB})}{dt} = R_{pgB}M_{eff}V$$
$$= (1 - \phi)R_p \frac{2\beta\phi + 2\tau_1\frac{\phi}{1-\phi} + \tau - \gamma\tau_1}{\alpha}M_{eff}V \quad (A49)$$

with the molar mass of the "effective" pseudo-repetitive unit (M_{eff}) given by:

$$M_{eff} = \overline{p}_{St,C}M_{St} + \left(1 - \overline{p}_{St,C}\right)M_{MMA} \quad (A50)$$

where $\overline{p}_{St,C}$ is the average weight fraction of St in the FC; and M_{St} and M_{MMA} are the molecular weights of St and MMA, respectively.

Equations (A1), (A6–A8), (A19–A23), (A41–A45), and (A48, A49) were simultaneously solved for calculating $[I_2]$, $[S]$, $[M]$, $[B^*]$, τ, τ_1, β, γ, ϕ, α, R_p, G_{FC}, and G_{gB}.

The NCLD of the FC is obtained from the Global Kinetics of Table II. The molar balance of each pseudo-copolymer species provides:

$$
\frac{d[C_n]V}{dt} = \left\{ [S]\left(k_{fmSS}[S_n^\bullet] + k_{fmMS}[M_n^\bullet]\right) + [M]\left(k_{fmSM}[S_n^\bullet] + k_{fmMM}[M_n^\bullet]\right) + [B^*]\left(k_{fgM}[M_n^\bullet] + k_{fgS}[S_n^\bullet]\right) \right.
$$
$$
+ k_{tcSS}\sum_{m=1}^{n-1}[S_m^\bullet][S_{n-m}^\bullet] + k_{tdSS}[S_n^\bullet]([S^\bullet]+[TS^\bullet]) + k_{tcSM}\sum_{m=1}^{n-1}[M_m^\bullet][S_{n-m}^\bullet] + k_{tdSM}[S_n^\bullet]([M^\bullet]+[TM^\bullet])
$$
$$
\left. + k_{tdMM}[M_n^\bullet]([M^\bullet]+[TM^\bullet]) + k_{tdMS}[M_n^\bullet]([S^\bullet]+[TS^\bullet]) + \left(k''_{tdS}[S_n^\bullet] + k''_{tdM}[M_n^\bullet]\right)[T_0^\bullet] \right\}V
$$
$$
n = 1,2,3\cdots \qquad (A51)
$$

Inserting eqs. (A20), (A22), (A27), and (A41–A45) into eqs. (A10) and (A14), it results:

$$
[C_1^\bullet] = \frac{\varphi R_p \alpha}{k_p[C](1+\alpha)^n} \qquad (A52)
$$

Similarly, inserting eqs. (A20), (A22), and (A41–A45) into eqs. (A11) and (A15), one finds:

$$
[C_n^\bullet] = \frac{\varphi R_p}{k_p[C](1+\alpha)^n}\frac{\alpha}{(1+\alpha)^n} \qquad n = 2,3,4\cdots \quad (A53)
$$

Inserting eqs. (A52) and (A53) into eq. (A51), and bearing in mind the definitions of φ τ, τ_1, β, γ, and α, one obtains:

$$
\frac{d[C_n]V}{dt} = \varphi R_p \alpha\left[\tau - \tau_1 + \frac{1}{2}\varphi\beta\alpha n\right](1+\alpha)^{-n}V
$$
$$
n = 1,2,3,4\cdots \qquad (A54)
$$

For high values of n, it is $(1+\alpha)^{-n} \cong e^{-\alpha n}$. Thus, the NLCD of the free pseudo-copolymer is obtained by integration of:

$$
\frac{d[C_n]V}{dt} = \frac{dN_C(n)}{dt} = \left[R_p V\varphi(\tau - \gamma\tau_1) + \frac{R_p V\varphi^2\beta}{2}\alpha n\right]\alpha e^{-\alpha n}
$$
$$
n = 1,2,3,4\cdots\cdots \qquad (A55)
$$

An expression for the WCLD of the FC $[G_{FC}(n)]$ is obtained by multiplying each of eq. (A54) by the corresponding molecular weights (nM_{eff}), yielding:

$$
\frac{dG_{FC}(n)}{dt}
$$
$$
= \left[\frac{R_{pC}V\varphi\,M_{eff}}{\alpha}(\tau - \gamma\tau_1) + \frac{R_p V\varphi^2\beta M_{eff}}{2}n\right]\alpha^2 n e^{-\alpha n}
$$
$$
n = 1,2,3,4\cdots \qquad (A56)
$$

Equation (A56) was solved by integration, after injecting the evolutions of R_p, φ, γ, τ, τ_1, β and α.

MWD of the unreacted PB

In the Global Kinetics of Table I, T represents either the GT or the unreacted PB. Calling $N_{PB}(b)$ the NCLD of PB species of chain length b, then $b\,N_{PB}(b)$ represents the total moles of B^* at each chain length. Assuming that the number of attacked B units is proportional to the B^* contents of each chain-length class; then the fraction of $T_0^\bullet$ radicals that are primary PB radicals of chain length b is $\{bN_{PB}(b)/[B^*]V\}$. Thus, with a treatment similar to that of Estenoz et al. (1996), the following is obtained:

$$
\frac{bN_{PB}(b)}{dt} = -\left\{k_{i2}[I^\bullet] + k_{fgM}([M^\bullet]+[TM^\bullet]) + k_{fgS}([S^\bullet]+[TS^\bullet])\right\}bN_{PB}(b)
$$
$$
+ \left\{k'_{fmM}[M] + k'_{fmS}[S] + k''_{tdM}([M^\bullet]+[TM^\bullet]) + k''_{tdS}([S^\bullet]+[TS^\bullet])\right\}[T_0^\bullet]\frac{bN_{PB}(b)}{[B^*]}
$$
$$
n = 1,2,3\cdots \qquad (A57)
$$

Introducing eqs. (A18), (A21), (A23), and (A40–A45) into (A57), it results:

$$
\frac{dN_{PB}(b)}{dt} = -\left\{R_p V(1-\varphi)(\tau - \gamma\tau_1) + \beta\varphi\frac{\gamma\tau_1\varphi}{(1-\varphi)} + R_p V(1-\varphi) + 2\gamma\tau_1\right\}\frac{bN_{PB}(b)}{[B^*]}
$$
$$
- \left\{R_p V(1-\varphi)[\beta(1-\varphi) + 2\gamma\tau_1]\right\}\frac{bN_{PB}(b)}{[B^*]} \qquad n = 1,2,3\cdots \qquad (A58)
$$

The WCLD of the residual PB is calculated by multyplying each of eq. (A59) by the corresponding molecular weights (bM_B):

$$\frac{dG_{PB}(b)}{dt} = -\left\{ R_p V(1-\varphi)(\tau - \gamma\tau_1) + \beta\varphi\frac{\gamma\tau_1\varphi}{(1-\varphi)} + R_p V(1-\varphi) + 2\gamma\tau_1 \right\}\frac{bN_{PB}(b)M_B}{[B^*]}$$
$$- \left\{ R_p V(1-\varphi)[\beta(1-\varphi) + 2\gamma\tau_1] \right\}\frac{bN_{PB}(b)M_B}{[B^*]} \qquad n = 1, 2, 3\cdots \qquad \text{(A59)}$$

The total moles and mass of residual PB are given by:

$$N_{PB} = \sum_b N_{PB}(b) \qquad \text{(A60)}$$

$$G_{PB} = \sum_b G_{PB}(b) \qquad \text{(A61)}$$

Global derived variables

The total moles of T molecules (i.e.: GT + residual PB) only diminishes due to crosslinking and H grafting, providing:

$$\frac{dN_T}{dt} = -\left\{ \frac{k_{tc}}{2}([TS^\bullet] + [TM^\bullet])^2 + k''_{tc}([TS^\bullet] + [TM^\bullet])[T_0^\bullet] \right\}V \qquad \text{(A62)}$$

Introducing eqs. (A18), (A21), (A23), (A26), and (A40–A45) into (A62); it yields:

$$\frac{dN_T}{dt} = -R_p(1-\varphi)[\beta(1-\varphi) + 2\gamma\tau_1]\frac{V}{2} \qquad \text{(A63)}$$

The total GT moles (N_{GT}) are:

$$N_{GT} = N_T - N_{PB} \qquad \text{(A64)}$$

where N_{PB} and N_T are obtained through eqs. (A61) and (A62). Similarly, the total mass of GT is given by:

$$G_{GT} = G_{PB}^0 - G_{PB} + G_{gB} \qquad \text{(A65)}$$

where the initial PB mass PB (G_{PB}^0) is *a priori* known and the evolutions of G_{gB} and G_{PB} are given by eqs. (A49) and (A59), respectively.

Finally, consider the calculation of the comonomers conversion, grafting efficiencies, and averages.

Comonomers conversion

$$x = \frac{([S]_0 + [M]_0) - ([S] + [M])}{[S]_0 + [M]_0} \qquad \text{(A66)}$$

Comonomers grafting efficiency

$$E = \frac{G_{gB}}{G_{gB} + G_{FC}} \qquad \text{(A67)}$$

Average molecular weights

Free copolymer

$$\overline{M}_{n,FC} = \frac{\sum_{c=1}^{\infty} G_{FC}(c)}{\sum_{c=1}^{\infty} \frac{G_{FC}(c)}{cM_{eff}}} \qquad \text{(A68)}$$

$$\overline{M}_{w,FC} = \frac{\sum_{c=1}^{\infty} G_{FC}(c)cM_{ef}}{\sum_{c=1}^{\infty} G_{FC}(c)} \qquad \text{(A69)}$$

Unreacted PB

$$\overline{M}_{n,PB} = \frac{\sum_{b=1}^{\infty} G_{PB}(b)}{\sum_{b=1}^{\infty} \frac{G_{PB}(b)}{nM_{PB}}} \qquad \text{(A70)}$$

$$\overline{M}_{w,PB} = \frac{\sum_{b=1}^{\infty} G_{PB}(b)bM_B}{\sum_{b=1}^{\infty} G_{PB}(b)} \qquad \text{(A71)}$$

PB grafting efficiency

$$E_{PB} = \frac{G_{PB}^0 - G_{PB}}{G_{PB}^0} \qquad \text{(A72)}$$

Average number of PB chains per GT molecule

$$\overline{r}_{n,PB} = \frac{N_{PB}^0 - N_{PB}}{N_T} \qquad \text{(A73)}$$

Total number of grafted St-MMA branches

Assuming that $\overline{M}_n$ of the FC coincides with $\overline{M}_n$ of the St-MMA branches, the total moles of GT branches results:

$$N_{gB} = \frac{G_{gB}}{\overline{M}_{n,FC}} \qquad \text{(A74)}$$

Average number of grafted St-MMA branches per GT molecule

$$\bar{r}_{n,\text{SM}} = \frac{\sum_{r=1}^{\infty} \sum_{n=1}^{\infty} \sum_{b=1}^{\infty} rT_{(r)}(n,b)}{N_T} \qquad \text{(A75)}$$

Mass fractions of St in the GT ($\bar{p}_{\text{St,GT}}$) and in the FC ($\bar{p}_{\text{St,FC}}$)

$$\bar{p}_{\text{St,FC}} = \frac{\left(G_{\text{St}}^0 - G_{\text{St}}\right)}{\left(G_{\text{St}}^0 - G_{\text{St}}\right) + \left(G_{\text{MMA}}^0 - G_{\text{MMA}}\right)} \qquad \text{(A76)}$$

$$\bar{p}_{\text{St,GT}} = \bar{p}_{\text{St,FC}} \frac{G_{g_B}}{G_{g_B} + G_{\text{PB}}^0 - G_{\text{PB}}} \qquad \text{(A77)}$$

APPENDIX B. MODULE FOR THE GT AND ITS TOPOLOGIES

Consider the detailed kinetics of Table II. Adopting the pseudo-steady state assumption, the following expressions can be written for the mass balances of each of the various GT radicals:

$$\frac{d}{dt}\left\{\left[T_{0(r)}^\bullet(c,b)\right]\right\}V = \left\{k_{i2}[\text{I}^\bullet] + k_{fgS}([\text{S}^\bullet] + [\text{TS}^\bullet]) + k_{fgM}([\text{M}^\bullet] + [\text{TM}^\bullet])\right\} b\left[T_{(r)}(c,b)\right]V$$
$$- \left\{k_{i3S}[\text{S}] + k_{i3M}[\text{M}] + k_{fmS}'[\text{S}] + k_{fmM}'[\text{M}] + (k_{tdM}'' + k_{tcM}'')\right.$$
$$([\text{M}^\bullet] + [\text{TM}^\bullet]) + (k_{tdS}'' + k_{tcS}'')([\text{S}^\bullet] + [\text{TS}^\bullet])\right\}\left[T_{0(r)}^\bullet(c,b)\right]V \cong 0 \qquad \text{(B1)}$$

$$\frac{d}{dt}\left\{\left[TS_{1(r)}^\bullet(c,b)\right]\right\}V = k_{i3S}[\text{S}]\left[T_{0(r)}^\bullet(c,b)\right]V - \left\{(k_{pSS} + k_{fmS})[\text{S}] + (k_{pSM} + k_{fmSM})[\text{M}]\right\}$$
$$\left[TS_{1(r)}^\bullet(c,b)\right]V - \left\{k_{fgS}[\text{B}^*] + (k_{tcSS} + k_{tdSS})([\text{S}^\bullet] + [\text{TS}^\bullet])\right.$$
$$+ (k_{tcSM} + k_{tdSM})([\text{M}^\bullet] + [\text{TM}^\bullet])\right\}\left[TS_{1(r)}^\bullet(c,b)\right]V \cong 0 \qquad \text{(B2)}$$

$$\frac{d}{dt}\left\{\left[TM_{1(r)}^\bullet(c,b)\right]\right\}V = k_{i3M}[\text{M}]\left[T_{0(r)}^\bullet(c,b)\right]V - \left\{(k_{pMM} + k_{fmM})[\text{M}] + (k_{pMS} + k_{fmS})[\text{S}]\right\}$$
$$\left[TM_{1(r)}^\bullet(c,b)\right]V - \left\{k_{fgM}[\text{B}^*] + (k_{tcMM} + k_{tdMM})([\text{M}^\bullet] + [\text{TM}^\bullet]) +\right.$$
$$(k_{tcMS} + k_{tdMS})([\text{S}^\bullet] + [\text{TS}^\bullet])\right\}\left[TM_{1(r)}^\bullet(c,b)\right]V \cong 0 \qquad \text{(B3)}$$

$$\frac{d}{dt}\left\{\left[TS_{n(r)}^\bullet(c,b)\right]V\right\} = \left\{k_{pSS}[\text{S}]\left[TS_{n-1(r)}^\bullet(c,b)\right] + k_{pSM}[\text{M}]\left[TM_{n-1(r)}^\bullet(c,b)\right]\right\}V$$
$$- \left\{k_{pSS}[\text{S}] + k_{pSM}[\text{M}] + k_{fmS}[\text{S}] + k_{fmSM}[\text{M}] + k_{fgS}[\text{B}^*] + k_{tcSS}''[\text{T}_0^\bullet]\right.$$
$$+ (k_{tcSS} + k_{tdSS})([\text{S}^\bullet] + [\text{TS}^\bullet]) + (k_{tcSM} + k_{tdSM})([\text{M}^\bullet] + [\text{TM}^\bullet])\right\}\left[TS_{n(r)}^\bullet(c,b)\right]V \cong 0 \quad \text{(B4)}$$

$$\frac{d}{dt}\left\{\left[TM_{n(r)}^\bullet(c,b)\right]\right\} = \left\{k_{pMM}[\text{M}]\left[TM_{n-1(r)}^\bullet(c,b)\right] + k_{pMS}[\text{S}]\left[TS_{n-1(r)}^\bullet(c,b)\right]\right\}V$$
$$- \left\{k_{pMM}[\text{M}] + k_{pMS}[\text{S}] + k_{fmSM}[\text{M}] + k_{fmMS}[\text{S}] + k_{fgM}[\text{B}^*] + k_{tcMM}''[\text{T}_0^\bullet]\right.$$
$$+ (k_{tcMM} + k_{tdMM})([\text{M}^\bullet] + [\text{TM}^\bullet]) + (k_{tcMS} + k_{tdMS})([\text{S}^\bullet] + [\text{TS}^\bullet])\right\}\left[TM_{(r)}^\bullet(c,b)\right]V \cong 0 \quad \text{(B5)}$$

where $bT_{(r)}(c,b)$ is any unreacted unit of B in $T_{(r)}(c,b)$. When comparing eqs. (A18) and (B1), it yields:

$$\frac{\left[T_{0(r)}^\bullet(c,b)\right]}{[\text{T}_0^\bullet]} = \frac{\left[T_{(r)}(c,b)\right]b}{[\text{B}^*]} \qquad r,c = 0,1,2\ldots$$
$$b = 1,2\ldots \qquad \text{(B6)}$$

with:

$$[\text{T}_0^\bullet] = \sum_r \sum_c \sum_b \left[T_{0(r)}^\bullet(c,b)\right] \qquad \text{(B7)}$$

Replacing eqs. (A27) and (A41–A45) into eqs. (B4) and (B5), and considering eqs. (A21), (A23), (A28), (A40) and (B6), one can write:

$$\left[T_{1(r)}^\bullet(c,b)\right] = \frac{(1-\varphi)R_p}{k_p[\text{C}]} \frac{\alpha}{(1+\alpha)} \frac{b\lfloor T_{(r)}(c,b)\rfloor}{[\text{B}^*]}$$
$$r,c = 0,1,2\ldots \quad b = 1,2\ldots \qquad \text{(B8)}$$

Similarly, introducing eqs. (A40), (A28), and (A41–A45) into (B6) and (B7), it results:

$$\left[T_{n(r)}^\bullet(c,b)\right] = \frac{(1-\varphi)R_p}{k_p[C]}\frac{\alpha}{(1+\alpha)^n}\frac{bT_{(r)}(c,b)}{[B^*]}$$

$$n = 2,3,4 \quad r,c = 0,1,2\ldots \; b = 1,2\ldots \quad \text{(B9)}$$

Consider calculating the bivariate NCLD of each GT topology and the univariate NCLD of the residual

PB. A material balance for every possible $T_{(r)}(c,b)$ species provides:

$$\frac{d}{dt}\left[T_{(r)}(c,b)\right] = T_1 + T_2 + T_3 + T_4 \quad \text{(B10)}$$

with

$$T_1 = -\left[T_{(r)}(c,b)\right]b\left\{k_{i2}[I^\bullet] + k_{fg}[R^\bullet]\right\}V \quad \text{(B10a)}$$

$$T_2 = \left\{\left(k_{fm}[C] + k_{fg}[B^*]\right)\sum_{m=1}^{c}\left[T_{m(r-1)}^\bullet(c-m,b)\right] + (k_{tc}+k_{td})\sum_{m=2}^{c}\sum_{n=1}^{m-1}\left[T_{n(r-1)}^\bullet(c-m,b)\right]\left[C_{m-n}^\bullet\right]\right.$$

$$\left. + \left(k_{tc}'' + k_{td}''\right)\sum_{m=1}^{c}\left[T_{0(r-1)}^\bullet(c-m,b)\right]\left[C_m^\bullet\right]\right\}V \quad \text{(B10b)}$$

$$T_3 = \left\{\frac{k_{tc}}{2}\sum_{r_1=1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c}\sum_{n=1}^{m-1}\left[T_{m-n(r-r_1-1)}^\bullet(c-c_1-m,b-b_1)\right]\left[T_{n(r_1-1)}^\bullet(c_1,b_1)\right] + \right.$$

$$\left. \sum_{r_1-1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c}k_{tc}''\left[T_{m-n(r-r_1-1)}^\bullet(c-c_1-m,b-b_1)\right]\left[T_{n(r_1-1)}^\bullet(c_1,b_1)\right]\right\}V \quad \text{(B10c)}$$

$$T_4 = k_{fm}'[C]\left[T_{0(r)}^\bullet(c,b)\right]V \quad \text{(B10d)}$$

where T_1 represents the rate of disappearance of $T_{(r)}(c,b)$ by generation of $T_{(r)}^\bullet(c,b)$; T_2 represents the rate of generation of $T_{(r)}(c,b)$ via grafting of a T branch of length m onto $T_{(r-1)}$ $(c-n,b)$; T_3 represents the rate of generation of $T_{(r)}(c,b)$ by recombination of $T_{(r-r_1-1)}(c-c_1-m,b-b_1)$ and $T_{(r_1-1)}$ $(C_1, B_1$ through a new H branch of length m; and T_4 represents the rate of generation $T_{(r)}$ (c,b) by deactivation of primary $T_{(r)}^\bullet(c,b)$ radicals. In eq. (B10), note that even though the unreacted PB molecules $\lfloor T_{(r)}(0,b)\rfloor$ are normally only consumed,

they can be regenerated by deactivation of primary PB radicals. Let us now derive alternative expressions for each of the T_i terms in eq. (B10).

First term of eq. (B10)

The second factor of eq. (B10a) represents the rate of generation of new grafting points [or of primary radicals $T_{0(r)}^\bullet(c,b)$], while the first factor "distributes" such grafting points among the accumulated $T_{(r)}(c,b)$ species, proportionately to their $[B^*]$ contents. Introducing eqs. (A18), (A21), (A23), (A40), (A28), and (A41–A45) into (B10a), one obtains:

$$T_1 = -\left\{\frac{bT_{(r)}(c,b)}{B^*}\right\}\left\{R_pV(1-\varphi)\left(\tau-\tau_1+\beta\varphi+\frac{\gamma\tau_1\varphi}{1-\varphi}\right)\right\}$$

$$+ \left[R_pV(1-\varphi)(\beta(1-\varphi)+2\gamma\tau_1)\right]\left[\frac{(R_p)^2k_{tc}'\gamma^2}{(k_p[C])^2}\right] + \left[R_pV\gamma\left(\frac{k_{fm}'}{k_p}+\frac{k_{td}''}{(k_p[C])^2}\right)\right] \quad \text{(B11)}$$

Consider the second factor in the right-hand side of eq. (B11). While the first term represents the rate of generation of new T grafting sites, the second term represents the rate of generation of new H grafting sites; and the third term represents the rate of regen-

eration of free PB by deactivation of primary B radicals by transfer or termination.

Second term of eq. (B10)

Equations (A53) and (B9) can be rewritten as follows:

$$[C_{m-n}^{\bullet}] = \frac{\alpha R_p}{k_p[C]} \frac{1}{(1+\alpha)^{m-n}} \qquad \text{(B12)}$$

$$\left[T_{n(r)}^{\bullet}(c-m,b)\right] = \frac{(1-\varphi)R_p}{k_p[C]} \frac{\alpha}{(1+\alpha)^n} \frac{b\lfloor T_{(r)}(c-m,b)\rfloor}{[B^*]} \qquad \text{(B14)}$$

$$\left[T_{m(r)}^{\bullet}(c-m,b)\right] = \frac{(1-\varphi)R_p}{k_p[C]} \frac{\alpha}{(1+\alpha)^m} \frac{b\lfloor T_{(r)}(c-m,b)\rfloor}{[B^*]} \qquad \text{(B13)}$$

where m is the chain length of the new GT branch. Replacing eqs. (B13) and (B14) into (B10b), and considering eqs. (A40), (A28) and (A41–A45), one obtains:

$$T_2 = R_p(1-\varphi)\alpha \sum_{m=1}^{c} \frac{b\left[T_{(r)}(c-m,b)\right]}{[B^*]} \left[\left(\tau - \gamma\tau + \gamma\tau_1 \frac{\varphi}{(1-\varphi)}\right) \frac{1}{(1+\alpha)^m} + \beta\varphi\alpha m \frac{1}{(1+\alpha)^m}\right]$$

$$\forall b,c,r \qquad \text{(B15)}$$

and therefore:

$$T_2 = R_p(1-\varphi)\alpha \sum_{m=1}^{c} \frac{b\left[T_{(r)}(c-m,b)\right]}{[B^*]} \left[\left(\tau - \gamma\tau + \gamma\tau_1 \frac{\varphi}{(1-\varphi)}\right) e^{-\alpha m} \frac{1}{(1+\alpha)^m} + \beta\varphi\alpha m e^{-\alpha m}\right] V$$

$$b,c,r = 1,2,3\dots \qquad \text{(B16)}$$

Third term of eq. (B10)

Equation (B9) may be rewritten as follows:

$$\left[T_{(r-r_1-1)}^{\bullet}(c-c_1-m,b-b_1)\right] = \frac{(1-\varphi)R_p\alpha}{k_p[C]} \frac{1}{(1+\alpha)^{m-n}} \frac{\lfloor T_{(r-1)}(c-c_1-m,b-b_1)\rfloor(b-b_1)}{[B^*]} \qquad \text{(B17)}$$

$$\left[T_{n(r_1)}^{\bullet}(c_1,b_1)\right] = \frac{(1-\varphi)R_p\alpha}{k_p[C]} \frac{1}{(1+\alpha)^{m-n}} \frac{\lfloor T_{(r-1)}(c_1,b_1)\rfloor b_1}{[B^*]} \qquad \text{(B18)}$$

$$\left[T_{m(r-1)}^{\bullet}(c-c_1-m,b-b_1)\right] = \frac{(1-\varphi)R_p\alpha}{k_p[C]} \frac{1}{(1+\alpha)^m} \frac{\lfloor T_{(r-1)}(c-c_1-m,b-b_1)\rfloor(b-b_1)}{[B^*]} \qquad \text{(B19)}$$

Replacing eqs. (B17–B19) into (B10c), and considering eqs. (A25), (A42–A46) and (B6), it produces:

$$T_3 = (1-\varphi)R_p \frac{\beta}{2}\alpha \sum_{r_1=1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c} \frac{(b-b_1)\left[T_{(r-1)}(c-c_1-m,b-b_1)\right]}{[B^*]} \frac{[T_{r_1}(c_1,b_1)]b_1}{[B^*]} m\alpha e^{-\alpha m}$$

$$+ R_p(1-\varphi)\gamma\tau_1\alpha \sum_{r_1-1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c} \frac{(b-b_1)\left[T_{(r-1)}(c-c_1-m,b-b_1)\right]}{[B^*]} \frac{[T_{r_1}(c_1,b_1)]b_1}{[B^*]} e^{-\alpha m} V$$

$$c,b = 1,2,3 \qquad \text{(B20)}$$

Fourth term of eq. B10

After introducing eqs. (A41), (A26), (B8), and (B9) into (B10c), one can writte:

$$T_4 = R_p\gamma V \left[\frac{k'_{fm}}{k_p} + \frac{k''_{td}}{(k_p[C])^2} + \frac{k''_{tc}}{(k_p[C])^2}\right] \frac{b\left[T_{(r)}(c-m,b)\right]}{[B^*]}$$

$$c,b = 1,2,3 \qquad \text{(B21)}$$

Introducing eqs. (B11), (B16), (B20), (B21) into eq. (B10), the following expression is obtained for the bivariate NCLDs of the different GT topologies:

$$
\frac{d}{dt}N_{(r)}(c,b) = -\left\{\left[R_p V(1-\varphi)\left(\tau - \gamma\tau_1 + \beta\varphi\frac{\gamma\tau_1\varphi}{(1-\varphi)}\right)\right] + \left[R_p V(1-\varphi)(\beta(1-\varphi)+2\gamma\tau_1)\right]\right\}
$$

$$
\times \frac{[T_{(r)}(c,b)]}{[B^*]} + \left\{R_p(1-\varphi)\left(\tau-\gamma\tau_1+\frac{\gamma\tau_1\varphi}{(1-\varphi)}\right)\sum_{m=1}^{c}\frac{[T_{(r)}((c-m,b)]}{[B^*]}\alpha e^{-\alpha m}\right.
$$

$$
+ R_p\varphi(1-\varphi)\beta\sum_{m=1}^{c}\frac{[T_{(r)}(c-m,b)]}{[B^*]}\alpha^2 e^{-\alpha m}R_p\varphi(1-\varphi)\gamma\tau_1
$$

$$
\sum_{r_1=1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c}\frac{[T_{(r-r_1-1)}(c-c_1-m,b-b_1)]}{[B^*]}\times\frac{[T_{(r-1)}(c_1,b_1)]}{[B^*]}\alpha e^{-\alpha m} + R_p\varphi(1-\varphi)^2
$$

$$
\frac{\beta}{2}\sum_{r_1=1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c}\frac{[T_{(r-r_1-1)}(c-c_1-m,b-b_1)]}{[B^*]}\times\frac{[T_{(r-1)}(c_1,b_1)]}{[B^*]}\alpha^2 e^{-\alpha m}\right\}V
$$

$$
r,c,b = 1,2,3 \quad \text{(B22)}
$$

In eq. (B22), m represents the chain length of the instantaneously-produced branch. The bivariate WCLD is obtained through the product between each of eqs. (B22) by their corresponding molecular weights ($cM_{\text{eff}} + bM_B$), yielding:

$$
\frac{d}{dt}G_{\text{GT}(r)}(c,b) = -\left\{\begin{array}{l}\left[R_p V(1-\varphi)\left(\tau-\gamma\tau_1+\beta\varphi\frac{\gamma\tau_1\varphi}{(1-\varphi)}\right)\right]+ \\ \left[R_p V(1-\varphi)(\beta(1-\varphi)+2\gamma\tau_1)\right]\end{array}\right\}(cM_{\text{ef}}+bM_{\text{PB}})\frac{[T_{(r)}(c,b)]b}{[B^*]}
$$

$$
+\left\{R_p(1-\varphi)(\tau-\gamma\tau_1)+\frac{\gamma\tau_1\varphi}{(1-\varphi)}\sum_{m=1}^{c}\frac{[T_{(r-1)}(c-m,b)]b}{[B^*]}\alpha e^{-\alpha m}\right.
$$

$$
+ R_p\varphi(1-\varphi)\beta\sum_{m=1}^{c}\frac{[T_{(r-1)}(c-m,b)]b}{[B^*]}\alpha^2 e^{-\alpha m} + R_p\varphi(1-\varphi)\gamma\tau_1
$$

$$
\sum_{r_1=1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c}\frac{[T_{(r-r_1-1)}(c-c_1-m,b-b_1)](b-b_1)}{[B^*]}\frac{[T_{(r-1)}(c_1,b_1)]b_1}{[B^*]}\alpha e^{-\alpha m}
$$

$$
+ R_p\varphi(1-\varphi)^2\frac{\beta}{2}\sum_{r_1=1}^{r-1}\sum_{b_1=1}^{b-1}\sum_{c_1+m=2}^{c}\frac{[T_{(r-r_1-1)}(c-c_1-m,b-b_1)](b-b_1)}{[B^*]}
$$

$$
\left.\frac{[T_{(r-1)}(c_1,b_1)]b_1}{[B^*]}\alpha^2 e^{-\alpha m}\right\}(cM_{\text{ef}}+bM_{\text{PB}})V \qquad r,c,b=1,2,3 \quad \text{(B23)}
$$

Equation (B23) enables the calculation of the univariate WCLD of the GT with r trifunctional points. The WC-LD of the total GT is obtained from eq. (B23), by addition over all r's, yielding:

$$
\frac{d}{dt}G_{\text{GT}}(c,b) = -\left\{\begin{array}{l}\left[R_p V(1-\varphi)\left(\tau-\gamma\tau_1+\beta\varphi\frac{\gamma\tau_1\varphi}{(1-\varphi)}\right)\right]+ \\ \left[R_p V(1-\varphi)(\beta(1-\varphi)+2\gamma\tau_1)\right]\end{array}\right\}(cM_{\text{ef}}+bM_{\text{PB}})\frac{[T(c,b)]b}{[B^*]}
$$

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

$$
+ R_p\varphi(1-\varphi)\beta\sum_{m=1}^{c}\frac{[T(c-m,b)]b}{[B^*]}\alpha^2 e^{-\alpha m} + R_p(1-\varphi)\gamma\tau_1
$$

$$
\times\sum_{b_1=1}^{b-1}\sum_{c_1+m=1}^{c}\frac{[T(c-c_1-m,b-b_1)](b-b_1)}{[B^*]}\times\frac{[T(c_1,b_1)]b_1}{[B^*]}\alpha e^{-\alpha m}
$$

$$
+ R_p(1-\varphi)^2\frac{\beta}{2}\times\sum_{b_1=1}^{b-1}\sum_{c_1+m=1}^{c}\frac{[T(c-c_1-m,b-b_1)](b-b_1)}{[B^*]}\frac{[T(c_1,b_1)]b_1}{[B^*]}\alpha^2 e^{-\alpha m}\right\}(cM_{\text{ef}}+bM_{\text{PB}})V
$$

$$
c,b = 1,2,3 \quad \text{(B24)}
$$

Finally, the average molecular weights of the GT are:

$$\overline{M}_{n,\,GT} = \frac{\sum_{c=0}^{\infty}\sum_{b=1}^{\infty} G_T(c,b)}{\sum_{c=0}^{\infty}\sum_{b=1}^{\infty}\frac{G_T(c,b)}{(bM_B + cM_{ef})}} \tag{B25}$$

$$\overline{M}_{w,\,GT} = \frac{\sum_{c=0}^{\infty}\sum_{b=1}^{\infty} G_T(c,b)(bM_B + cM_{ef})}{\sum_{c=0}^{\infty}\sum_{b=1}^{\infty} G_T(c,b)} \tag{B26}$$

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