Polymerization of Styrene in the Presence of Polybutadiene: Determination of the Molecular Structure

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ABSTRACT: This work experimentally and theoretically determines the molecular macrostructure of the polymer mixture that is developed (at relatively low conversions) in a solution polymerization of styrene (St) in presence of polybutadiene (PB). The reaction was carried out at 70°C in a batch-stirred tank reactor. From samples taken along the reaction, the three polymeric components of high-impact polystyrene (HIPS) (i.e., polystyrene —PS—, residual PB, and graft copolymer) were first separated from each other by solvent extraction. Then, the graft copolymer was ozonized to isolate the St branches. The molecular weight distributions (MWDs) of the total HIPS, the three HIPS components, and the grafted St branches were determined by the size exclusion chromatography (SEC). For the graft copolymer and the total HIPS, the variation of the St mass fraction with molecular weights was also determined by SEC. All measurements were compared with theoretical estimates, and a reasonable agreement is observed. For the theoretical estimates, the mathematical model of Estenoz, D. A.; Valdez, E.; Oliva, H. M.; Meira, G. R. (J Polym Sci 1996, 59, 861) was extended to compare the MWD of the St branches with the MWD of the free PS. For the sought experimental conditions, these two distributions had very similar results but in a bulk industrial process, larger discrepancies are to be expected. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1950–1961, 1999

Key words: high-impact polystyrene; molecular weight distribution; graft copolymer; grafted branches

INTRODUCTION

High-impact polystyrene (HIPS) is a heterogeneous material obtained by polymerizing styrene (St) in the presence of polybutadiene (PB). It consists of rubber particles dispersed in a vitreous polystyrene (PS) matrix. When produced via the bulk process, the rubber particles are approximately 2 μm in diameter and themselves heterogeneous, presenting typical salami structures due to the inclusion of vitreous microocclusions. Accumulated at the interfaces, the graft copolymer improves the material toughness by preventing the phase separation. The interrelationships between morphology and mechanical properties were considered in several publications.[1–7]

In the bulk process, the salami morphology is formed during the well-stirred prepolymerization stage, and more specifically, during the phase inversion period.[8] The graft copolymer must be generated at early stages of the prepolymerization to favor the phase inversion and control the morphology. To this effect, a chemical initiator capable of inducing grafting and with a short mean life compared to the total polymerization is required. The prepolymerization is followed by

the main polymerization stage, where conversion is increased from around 30–75%. During this second stage, the temperature is raised, the reaction is thermally initiated, and a gentle stirring is required to avoid destroying the salami structure that must remain essentially unchanged until the final product.

In a recent publication,[9] an interpretation on the vital role of the graft copolymer in the development of the salami structure was presented. It was concluded that the microoocclusions observed in the rubber particles are a mixture of low molecular weight PS and St branches of single-branched copolymer molecules, with their butadiene (Bd) chains embedded in the rubber phase. Also, graft copolymer molecules containing two or more St branches accumulate at the external particle interface, with their St branches embedded in the continuous phase.

In the mentioned publication,[9] it was assumed that the graft copolymer contained only T grafts (i.e., with each St branch attached to a single Bd chain). However, H grafts, consisting of St branches attached onto two Bd chains, are also produced.[10] T grafts are generated by a transfer of a nonprimary copolymer radical and by a combination termination between a PS homoradical with a (primary or nonprimary) rubber radical. H grafts are only produced by combination termination between two nonprimary rubber radicals or between a primary with a nonprimary rubber radical.

The molecular structure of HIPS is described by the molecular weight distribution (MWD) of the homopolymers (free PS and unreacted PB), together with the joint distribution of molecular weights/chemical composition/branching frequency of the graft copolymer. For measuring such characteristics, the three polymer components of HIPS must be first quantitatively separated from each other by solvent extraction, and then their distributions can be determined by size exclusion chromatography (SEC). The difficulties of such a procedure are as follows. (a) At high conversions, the rubber phase may contain micro- and/or macrogels that are difficult to characterize; (b) when obtained via the bulk process, it is in practice impossible to extract all the occluded PS, thus contaminating the unreacted PB and the graft copolymer; and (c) no methods are at present available in SEC for determining the multivariate distribution of the graft copolymer.

Huang and Sundberg[11] have calculated the evolution of the St grafting efficiency along a HIPS process by using standard dual-detection SEC (i.e., containing a differential refractometer and an UV absorbance detector). To this effect, reaction samples were dissolved and directly injected into the chromatograph, thus avoiding the slow and relatively inaccurate solvent extraction procedure. In the described experiment,[11] the PB chains were substantially larger than the free PS or the grafted branches. For this reason, the chromatograms of the three HIPS components could be reasonably well deconvoluted from the total chromatogram through commercial peak-fitting software. From the original PB mass and the areas under the individual chromatograms, the St grafting efficiency could be determined.[11]

In the experimental article by Fischer and Hellmann,[9] the three HIPS components were isolated by solvent extraction, and the global MWD obtained by adding together their individual distributions compared with the MWD of the total polymer mixture. No details on the solvent separation techniques nor on the SEC methods were provided. Also, it was verified that the MWDs obtained in the bulk process were very similar to the MWDs observed in an equivalent solution polymerization.[9] This is rather fortunate because it enables the analysis of an experimentally simpler solution polymerization and derives conclusions regarding the bulk process. Finally, it was shown[9] that for a solution polymerization at 70°C, the MWD of the grafted St branches is very similar to the MWD of the free PS. This result was used to estimate the number of grafted St branches per PB chain. Previously, other authors had directly assumed without evidence that the MWD of the St branches should coincide with the MWD of the free PS.[11,12]

Apart from the analytical methods, several mathematical models were proposed to estimate the molecular structure that is developed during the synthesis of HIPS. In particular, the MWDs of PS and PB, together with the joint molecular weight–chemical composition distribution of the graft copolymer, were theoretically predicted in our previous publications.[10,13–15] However, in such works only the MWD of the free PS and the St grafting efficiency (i.e., the mass of grafted St divided by the total mass of polymerized St) were experimentally validated. So far, no comparisons between the measured and estimated MWDs in HIPS were reported.

The present work investigates polymerization in solution of St in the presence of PB. It aims at determining the molecular macrostructure that is

developed at low conversions, with particular emphasis on the graft copolymer characteristics. A solution process was preferred to a bulk process to avoid the contamination by the low molecular weight PS that is occluded in the rubber particles. All measurements are compared with theoretical estimates. The developed mathematical model assumes a homogeneous polymerization, and it is therefore strictly applicable to a solution process.

EXPERIMENTAL

A batch polymerization of St in the presence of medium-*cis*-1,4 PB was carried out in a dilute toluene solution by using *tert*-butyl peroctoate (TBPO) as initiator. The MWD of the initial PB was measured by SEC and is presented in Figure 1(a). A three-neck 1-L glass reactor was employed. The reaction was well stirred, and the temperature was controlled at 70°C. The PB (Intene Enichem, Italy), the solvent (E. M. Science, Darmstadt, Germany), and the initiator (Akzo Chemicals, Itupeba, Brazil) were used as received. The St (monomer grade) was vacuum-distilled.

The reaction was carried out as follows. First, 3.42 g of PB were dissolved in toluene at room temperature for 24 h, and the solution was loaded into the reactor. Then, the monomer and the initiator were added, and the remaining solvent was incorporated until 500 mL were completed. Thus, the initial reaction volume was $V = 0.5$ L. The initial concentrations of monomer, of Bd repetitive units, and of initiator resulted in: $[St]^0 = 2.93$ mol/L, $[B^*]^0 = 0.127$ mol/L, and $[I_2]^0 = 0.00187$ mol/L, respectively. The rubber concentration was chosen deliberately low (about 2.3% in weight of rubber with respect to the pure monomer) to ensure homogeneous conditions throughout the reaction.

Samples (by triplicate) were taken at 8, 12, and 16 h of reaction. The global results are presented in Table I. In Figures 1–2, the distributions for the samples taken at 12 and 16 h are shown.

Conversion was determined from 20-mL samples as follows. The polymer was first precipitated in 200 mL of methanol containing hydroquinone as inhibitor and dry ice to lower the temperature. Then, the polymer was dried under vacuum at 60°C until constant weight. The polymerized monomer mass and the conversion were calculated after subtraction of the original PB mass.

The PS mass and the St grafting efficiency were gravimetrically determined by extracting the PS from the total HIPS through a 50/50 mixture of methyl ethyl ketone/dimethylformamide (MEK/DMF).[11] The mass of grafted St was obtained directly from the St grafting efficiency. The PB mass, the copolymer mass, and the Bd grafting efficiency (i.e., the mass of grafted PB divided by the initial PB mass) were determined through a second solvent extraction procedure applied to the undissolved rubber components. This second procedure was carried out as follows. (a) A measure of 50 mL of petroleum ether (Fisher Scientific) containing 0.035 g of hydroquinone as inhibitor were added to the rubber precipitate and agitated for 12 h; (b) the soluble portion containing the unreacted PB was precipitated in 10 mL of methanol, dried, and weighed; and (c) the mass of grafted PB was determined by subtraction of the residual PB from the initial PB mass. The PB mass (a few milligrams per sample) could not be totally recuperated. For this reason, errors by defect in the PB mass (and by excess in the Bd grafting efficiency) were expected. In the first rows of Table I, the conversion (x), the global masses of free PS (G_{PS}), residual PB (G_{PB}), graft copolymer (G_C), and grafted St (G_{GS}), together with the St and Bd grafting efficiencies (E_{St}, E_{Bd}), are presented.

For the molecular weight determinations, a Waters Associates ALC244 size exclusion chromatograph fitted with a differential refractometer, an UV detector at 254 nm, and a full set of μ-Styragel columns was employed. The carrier solvent was tetrahydrofurane at 1.0 mL/min, and the temperature controlled at 30°C. In Figure 1(a–d), the MWDs of the individual HIPS components and the total HIPS are represented. The areas under the MWDs were made proportional to their gravimetrically determined masses. The unreacted PB is represented separately in Figure 1(a) and (b), because of its small mass with respect to the other components. The MWD of the total HIPS was obtained by simply injecting a diluted sample of the reaction mixture into the chromatograph. For the homopolymers, individual molecular weight calibrations employing PS and PB standards were used. For determining the instantaneous molecular weights and chemical compositions of the graft copolymer and the total HIPS, a procedure for dual-detection SEC was applied.[16] To this effect, the detectors were first calibrated by injecting known masses of PS and PB standards. The effective molecular weights of
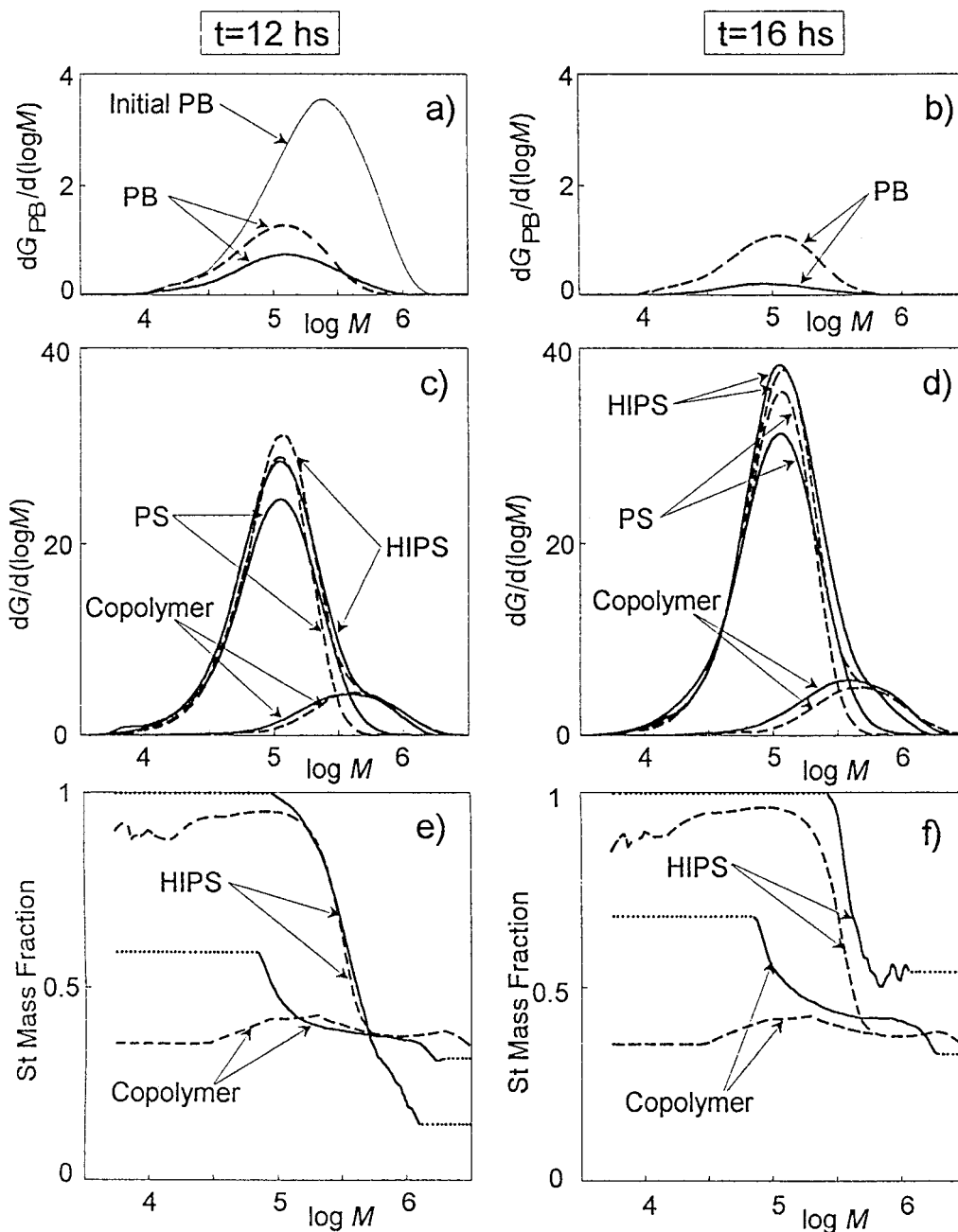
Figure 1 Measurements (in continuous trace) and theoretical predictions (in discontinuous trace) of the samples taken at 12 and 16 h. (a, b) MWD for the residual PB; (c, d) MWD for the total HIPS, the free PS, and the graft copolymer; (e, f) chemical composition versus molecular weights for the copolymer and HIPS. In (a), the initial MWD of PB is also represented.

the copolymer and the total HIPS were obtained by interpolation between the homopolymer molecular weight calibrations, according to the instantaneous St mass fraction.[16] In Figure 1(e–f), the variation of the St mass fraction with molecular weights for the graft copolymer and for the total HIPS are presented. For the total HIPS, the instantaneous (and average) compositions have no physical meaning, but they were included here to provide for an extra check of the theoretical predictions. As expected,[16] the instantaneous St composition is very noisy at the chromatogram tails.

Table I   Experimental Results and Theoretical Predictions[a]

Output Variables		$t = 8$ h		$t = 12$ h		$t = 16$ h	
		Meas.	Model	Meas.	Model	Meas.	Model
x	—	8.82	9.72	13.39	13.56	17.60	16.88
G_{PS}	[g]	12.61	13.78	19.22	19.20	24.73	23.74
G_{PB}	[g]	1.017	1.413	0.71	1.107	0.18	0.922
G_C	[g]	3.244	3.034	3.904	3.776	5.334	4.482
G_{GS}	[g]	0.841	1.027	1.194	1.483	2.092	1.897
E_{St}	[%]	6.25	6.93	5.85	7.17	7.80	7.40
E_{Bd}	[%]	70.26	58.70	79.24	67.63	94.77	73.04
HIPS:							
$\bar{M}_n$	[g/mol]	84,600	80,000	77,400	81,000	66,500	82,800
$\bar{M}_w$	[g/mol]	169,000	176,400	164,000	179,000	152,000	184,000
$\bar{M}_w/\bar{M}_n$	—	2.00	2.20	2.11	2.21	2.29	2.21
St Mass %	[%]	79.72	81.24	85.65	85.80	88.70	88.30
PS:							
$\bar{M}_n$	[g/mol]	68,300	70,500	72,500	72,800	74,200	75,000
$\bar{M}_w$	[g/mol]	132,000	110,000	129,000	114,000	132,000	118,000
$\bar{M}_w/\bar{M}_n$	—	1.93	1.56	1.78	1.57	1.78	1.57
PB:							
$\bar{M}_n$	[g/mol]	91,900	84,500	81,400	75,700	70,700	70,000
$\bar{M}_w$	[g/mol]	210,000	157,000	167,000	135,000	131,000	122,000
$\bar{M}_w/\bar{M}_n$	—	2.29	1.85	2.05	1.78	1.85	1.74
Copolymer:							
$\bar{M}_n$	[g/mol]	346,000	336,000	287,000	345,000	290,000	357,000
$\bar{M}_w$	[g/mol]	654,000	525,000	572,000	558,000	577,000	594,000
$\bar{M}_w/\bar{M}_n$	—	1.89	1.56	1.99	1.62	1.99	1.66
St Mass %	[%]	40.00	33.85	40.00	38.74	46.00	44.26
J_{Bd}	#/molec.	1.71	1.03	1.36	1.03	1.34	1.04
St Branches:							
$\bar{M}_n$	[g/mol]	—	72,600	79,600	75,300	73,300	78,000
$\bar{M}_w$	[g/mol]	—	111,000	157,000	116,000	157,000	121,000
$\bar{M}_w/\bar{M}_n$	—	—	1.67	1.97	1.54	2.14	1.55
J_{St}	#/molec.	—	1.58	1.11	1.81	1.55	1.99
$J\ (=J_{St} + J_{Bd})$	#/molec.	—	2.61	2.47	2.84	2.89	3.03

[a] The first block of measurements is based on global gravimetric determinations; the second block is based on SEC analyses, and the third block is based on ozonolysis–SEC.

Since a value of this variable along the complete chromatogram range is required to estimate the molecular weights at the chromatogram tails, the compositions were approximated by horizontal lines obtained by extrapolation of the last calculated values [dotted horizontal lines in Figure 1(e) and (f)]. In the midchromatogram sections, the weight fraction of St is approximately constant. This is because the number of grafted St chains per copolymer molecule is proportional to the PB chain length.

Even though not shown here to simplify Figure 1(c–d), the added MWD of the individual HIPS components was seen to be close to the experimental MWD of total HIPS. The total HIPS is basically free PS at the low molecular weights,

and graft copolymer at the high molecular weights. For the sample taken at 16 h, the copolymer MWD appears above the MWD of HIPS. This inconsistency can be due to errors in the solvent extraction procedure. Also, for the same reason, the St mass fraction of the copolymer and the total HIPS do not coincide at the high molecular weight end.

In the midsection of Table I, the averages for the individual components and the total HIPS are presented. Although PS molecular weights are practically constant along the prepolymerization, PB molecular weights fall with time because of the larger grafting probability of longer, with respect to the shorter, PB chains.
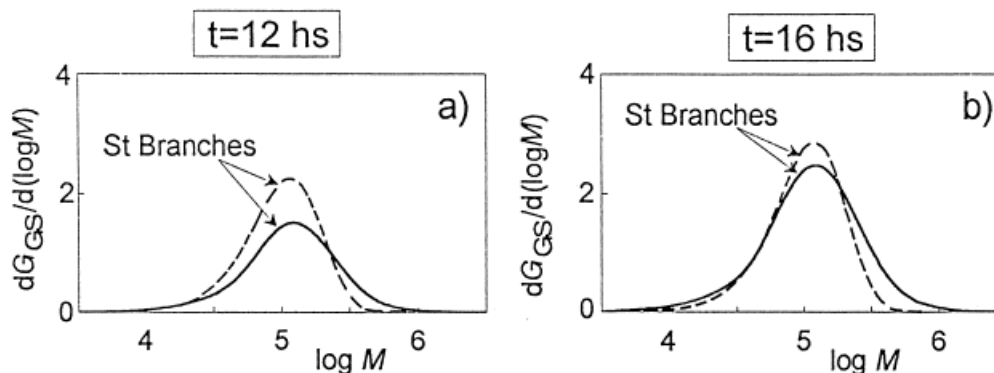
Figure 2   MWDs of the St branches for the samples taken at 12 and 16 h. Measurements are in continuous trace, whereas theoretical predictions are in discontinuous trace.

To isolate the St branches from the graft copolymer, all Bd double bonds were selectively destroyed by ozonolysis, following a technique similar to that described in Tanaka.[17] An ozone generator from Griffin Technics Corp. was used. The produced ozone-rich gas was bubbled through the rubber solution. The emerging gas was washed in a 5% solution of IK (Fisher Scientific) in a 1 : 1 acetic acid–water mixture. Bubbling times were optimized through FTIR, by verifying the integrity of the aromatic ring, with simultaneous disappearance of the Bd double bonds. A slight color change in the IK solution was indicative of the operation end. The applied procedure was as follows. (a) A measure of 0.2 g of rubber (copolymer plus unreacted PB) was dissolved into 100 mL of methylene chloride; (b) ozonated oxygen was blown into this solution at $-78°C$ for about 5 min, until the uptake of ozone ceased; (c) the produced ozonide groups were reduced into alcohols and water by means of a solution of lithium aluminum hydride (Aldrich) in ether, and since this reaction can be violent, the solution was first added slowly at 0°C, and then the reaction was completed in a reflux condenser at 45°C for 30 min; (d) the hydride in excess was eliminated by reaction with water, and the resulting alluminate was dissolved in HCl; (e) the organic phase was separated from the water phase by decantation; (f) the St branches were precipitated from the organic solution with methanol; and (g) the precipitate was dried under vacuum until constant weight.

In Figure 2, the MWDs of the grafted branches are represented. Their average molecular weights are shown in Table I. The areas under the distributions were made proportional to the mass of grafted St. The St branches corresponding to the 8 h sample could not be totally dissolved, and therefore, they were not analyzed. This was possibly due to crosslinking induced by partial destruction of the phenyl rings.

Consider now the calculation of the average number of branches per copolymer molecule. The moles of St branches and of copolymer were estimated from the ratios of their masses to their number-average molecular weights. The moles of grafted Bd were obtained from the difference between the initial and residual PB moles. The number of St branches per copolymer molecule J_{St} was estimated from the ratio of the moles of St branches to the moles of copolymer. The number of Bd branches per copolymer molecule J_{Bd} was calculated from the ratio-grafted Bd moles to copolymer moles. Finally, the total number of branches per copolymer molecule J was obtained by the addition of J_{St} with J_{Bd}.

The normalized MWDs and averages of the grafted St chains are similar to those of the free PS. For the copolymer, J_{Bd} values larger than unity are indicative of H grafting. Measurements indicate a moderate decrease in J_{Bd} along the reaction. This could only be possible if the ratio of T to H grafting increased in time, when the grafting-over-grafting process remained still unimportant. However, at a constant reaction temperature, a relatively constant T to H grafting ratio is to be expected, and therefore the decreasing values of J_{Bd} are probably due to errors in the PB mass.

In the described experiment, the accuracy of most measurements is directly affected by the solvent extraction procedure. Many adjustments were necessary to optimize the (vital) first separation of that procedure. The presented St graft-

ing efficiency exhibits a reproducibility of ±3%. In the second solvent extraction, the two rubber components were isolated, and a reproducibility of ±5% in the PB grafting efficiency was observed. However, the accuracy of this last determination is suspected to be rather low, as the consequence of (a) the propagation of errors from the first step; (b) the low masses of recuperated PB; and (c) the possible contamination with low molecular weight PS. In spite of all the difficulties, the solvent extraction procedure was in general adequate. This was evidenced by the fact that the total HIPS chromatogram (obtained independently from the solvent extraction) was quite similar to that obtained by adding together the chromatograms of the individual HIPS components. (Note that if a bulk, rather than a solution, polymerization had been analyzed, then the accuracy of the solvent extraction would have dropped with respect to the given values. This is because it is in practice impossible to completely extract the occluded PS from the rubber particles, with a resulting contamination of the rubber fraction with low molecular weight PS.)

In the ozonolysis–SEC determination, the low masses of recuperated graft copolymer determined that duplicates could not be taken. Also, the gravimetric determinations in ozonolysis–SEC were unfortunately unreliable, and for this reason were not presented in this work. Finally, to check on the accuracy of the average molecular weights, an independent SEC calibration was performed that involved the use of an on-line viscometer (a Viscotek 200) in combination with a universal calibration. Deviations on the order of ±8% with respect to the presented values were observed. This can be considered satisfactory, bearing in mind the numerous sources of errors involved.

MATHEMATICAL MODEL AND SIMULATION RESULTS

The adopted kinetic scheme is presented in eqs. (A1)–(A21) of the Appendix. It is identical to the mechanism adopted in our previous publication,[13] but it also includes the chain transfer reactions to the solvent. Also, our previous mathematical model[13] was extended to calculate the MWD of the grafted branches (see Appendix) and obtain the variation of the chemical composition with the molecular weights for the graft copolymer and for the total HIPS (not presented here for space reasons).

The MWDs of the free PS and the St branches were determined by numerical integration of eqs. (A39) and (A41), respectively. The two distributions are in principle different, but in many situations they almost coincide, as explained in the Appendix.

The kinetic constants were obtained from the Arrhenius expressions presented in Estenoz et al.[13] The transfer to the solvent reactions were not considered in the said publication, and the following was here adopted[18] as $k_{ft} = k'_{ft} = 9.87 \times 10^{14} e^{-27073/RT} = 0.0044$ L/mol s at 70°C.

In Table I and Figures 1 and 2, all theoretical predictions are compared with the measurements, and in general, a quite reasonable agreement is observed. The differences in the Bd grafting efficiency, in the areas under the MWDs of PB and in J_{Bd}, are all the consequence of the large experimental errors (by defect) in G_{PB}. The predictions for the average number of grafted St chains per copolymer molecule (J_{St}) are above the measured values. The differences in J_{Bd} and J_{St} are compensated in the total J, however.

Measurements and predictions indicate that PS molecular weights are similar to the molecular weights of the St branches and that they vary little along the polymerization. The relatively (minor) variations in the experimental copolymer molecular weights were not confirmed by the theoretical predictions. According to the model, the copolymer molecular weights slightly increase as a consequence of an incipient grafting-over-grafting process, which more than compensates for the reduction in the grafted PB chain lengths. The differences are small and within experimental errors, however. As expected, at the high-molecular weight end of Figure 1(e–f), the theoretical functions for the St mass fractions both converge to a common curve. This is not observed in the SEC measurements, however, because of the large errors in composition at the chromatogram tails.

According to the model, the MWD of the St branches are similar to the MWD of the free PS. This is because the two sufficient conditions developed in the last section of the Appendix for the two distributions to coincide are almost verified. With regard to condition (1) of eq. (A42), a maximum relative variation of 3% was observed between the T_1/T_2 and T_3/T_4. With regards to condition (2) of eq. (A43b), a maximum variation of 7% in the St grafting efficiency was observed.

To analyze a situation where the MWDs of the free PS and the St branches could appreciably differ, the same polymerization was simulated, but with a varying temperature and extending the reaction to almost complete conversion. The applied temperature profile was sought to emulate an industrial process.[13] First, the temperature was increased at 1°C/min from 70 to 90°C; then the prepolymerization was carried out at 90°C until 30% conversion was reached, and finally, a step change to 120°C was applied until 95% conversion was obtained. The varying values of the kinetic constants were calculated through the employed Arrhenius expressions. The simulation results indicated that at the end of the polymerization, the $\bar{M}_n$ and $\bar{M}_w$ values for the free PS were, respectively, 21 and 22% larger than the same averages for the St branches. In this case, the conditions of eqs. (A42) and (A43) were not verified, because, for example, a fivefold increase in the St grafting efficiency was observed.

CONCLUSIONS

This work theoretically and experimentally analyzed the molecular characteristics of the homopolymers and the graft copolymer that are generated in a batch solution polymerization of St in presence of PB, at relatively low conversions. The controlled production of graft copolymer during the first stages of the bulk HIPS process is of great industrial interest, because of the importance of that component in developing the particle morphology and improving the final material properties.

According to the developed model, the normalized MWD of the St branches is in general similar to the normalized MWD of the free PS. Thus, similar (but not identical) distributions are to be expected when nonisothermal polymerizations are carried out to high conversions. But for the isothermal and low-conversion process that was here investigated, the two MWDs are practically coincident because the sufficient conditions of eqs. (A42) and (A43) are verified.

Computer-model predictions can be combined with SEC measurements of the total polymerization mixture to provide a simple and direct estimation of the grafting efficiencies and other molecular characteristics, without resorting to the slower and relatively inaccurate solvent extraction techniques. This will be the subject of a future communication.

APPENDIX: WEIGHT CHAIN-LENGTH DISTRIBUTION OF THE GRAFTED POLYSTYRENE BRANCHES

Consider the kinetic mechanism that follows.

Chemical Initiation:
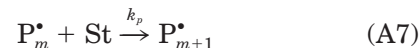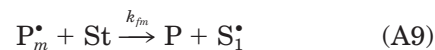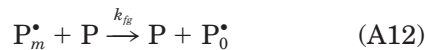
$$I_2 \xrightarrow{k_d} 2I^\bullet \tag{A1}$$

$$I^\bullet + St \xrightarrow{k_{i1}} S_1^\bullet \tag{A2}$$

$$I^\bullet + P \xrightarrow{k_{i2}} P_0^\bullet \tag{A3}$$

Thermal Initiation:

$$3\ St \xrightarrow{k_{i0}} 2\ S_1^\bullet \tag{A4}$$

Propagation:

$$S_n^\bullet + St \xrightarrow{k_p} S_{n+1}^\bullet \tag{A5}$$

$$P_0^\bullet + St \xrightarrow{k_{p0}} P_1^\bullet \tag{A6}$$

$$P_m^\bullet + St \xrightarrow{k_p} P_{m+1}^\bullet \tag{A7}$$

Transfer to the Monomer:

$$S_n^\bullet + St \xrightarrow{k_{fm}} S_n + S_1^\bullet \tag{A8}$$

$$P_m^\bullet + St \xrightarrow{k_{fm}} P + S_1^\bullet \tag{A9}$$

$$P_0^\bullet + St \xrightarrow{k'_{fm}} P + S_1^\bullet \tag{A10}$$

Transfer to the PB or the Copolymer:

$$S_n^\bullet + P \xrightarrow{k_{fg}} S_n + P_0^\bullet \tag{A11}$$

$$P_m^\bullet + P \xrightarrow{k_{fg}} P + P_0^\bullet \tag{A12}$$

Transfer to the Solvent:

$$S_n^\bullet + T \xrightarrow{k_{ft}} S_1^\bullet + S_n \tag{A13}$$

$$P_m^\bullet + T \xrightarrow{k_{ft}} S_1^\bullet + P \tag{A14}$$

$$P_0^\bullet + T \xrightarrow{k_{ft}'} S_1^\bullet + P \tag{A15}$$
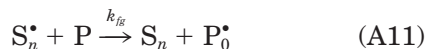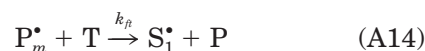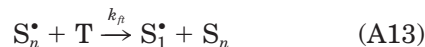
Termination by Combination:

$$S_n^\bullet + S_s^\bullet \xrightarrow{k_{tc}} S_{n+s} \tag{A16}$$

$$P_{m-n}^\bullet + S_n^\bullet \xrightarrow{k_{tc}} P \quad (m > n) \tag{A17}$$

$$P_{m-p}^\bullet + P_p^\bullet \xrightarrow{k_{tc}} P \quad (m > p) \tag{A18}$$

$$P_0^\bullet + P_m^\bullet \xrightarrow{k_{tc}''} P \tag{A19}$$

$$P_0^\bullet + S_n^\bullet \xrightarrow{k_{tc}''} P \tag{A20}$$

$$P_0^\bullet + P_0^\bullet \xrightarrow{k_{tc}'} P \tag{A21}$$
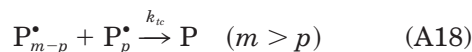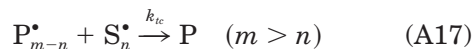
where I_2 is the chemical initiator; I_2 is a primary initiator radical; P is either the copolymer or the residual PB; $P_0^\bullet$ is a primary rubber radical; $P_n^\bullet$ is a radical produced from $P_0^\bullet$ with a growing branch containing n repetitive units of St; $S_1^\bullet$ is a PS homoradical of unity chain length obtained by initiation or transfer reactions; S_n is a PS molecule of chain length n; $S_n^\bullet$ is a PS homoradical of

chain length n; and T is the solvent. In the above mechanism, n, $s = 1, 2, \ldots$ both represent the chain length of a polystyryl radical or a free PS molecule, whereas m, $p = 1, 2, \ldots$ both represent the chain length of a newly grafted St chain.

Call B^* any unreacted repeating unit of Bd (present in the copolymer or in the initial PB) that contains an unreacted double bond and call $[S^\bullet] = \sum_n [S_n^\bullet]$ and $[P^\bullet] = \sum_n [P_n^\bullet]$ the global concentrations of $S_n^\bullet$ and $P_m^\bullet$, respectively. From eqs. (A1)–(A21), the following global material balances may be written

$$\frac{d}{dt}\{[I_2]V\} = -k_d[I_2]V \tag{A22}$$

$$\frac{d}{dt}\{[St]V\} = -k_p([S^\bullet] + [P^\bullet])[St]V \tag{A23}$$

$$\frac{d}{dt}\{[T]V\} = -\{k_{ft}([S^\bullet] + [P^\bullet]) + k_{ft}'[P_0^\bullet]\}[T]V \tag{A24}$$

$$\frac{d}{dt}\{[B^*]V\} = -\{k_{i2}[I^\bullet] + k_{fg}([S^\bullet] + [P^\bullet])\}[B^*]V$$
$$+ \{k_{fm}'[St] + k_{ft}'[T]\}[P_0^\bullet]V \tag{A25}$$

$$\frac{d}{dt}\{[I^\bullet]V\} = \{2fk_d[I_2]$$
$$- (k_{i1}[St] + k_{i2}[B^*])[I^\bullet]\}V \cong 0 \tag{A26}$$

$$\frac{d}{dt}\{[S^\bullet]V\} = k_{i1}[St][I^\bullet]V$$
$$+ 2k_{i0}[St]^3V + (k_{fm}'[St] + k_{ft}'[T])[P_0^\bullet]V$$
$$+ (k_{fm}[St] + k_{ft}[T])[P^\bullet]V - \{k_{fg}[B^*] + k_{tc}''[P_0^\bullet]$$
$$+ k_{tc}''([S^\bullet] + [P^\bullet])\}[S^\bullet]V \cong 0 \tag{A27}$$

$$\frac{d}{dt}\{[P^\bullet]V\} = k_{p0}[St][P_0^\bullet]V - k_{fm}[St][P^\bullet]V$$
$$- \{k_{ft}[T] + k_{fg}[B^*] + k_{tc}''[P_0^\bullet] + k_{tc}([S^\bullet]$$
$$+ [P^\bullet])\}[P^\bullet]V \cong 0 \tag{A28}$$

$$\frac{d}{dt}\{[P_0^\bullet]V\} = \{k_{i2}[I^\bullet] + k_{fg}([S^\bullet] + [P^\bullet])\}[B^*]V$$
$$- \{k_{p0}[St] + k_{fm}'[St] + k_{ft}'[T] + k_{tc}'[P_0^\bullet]$$
$$+ k_{tc}''([S^\bullet] + [P^\bullet])\}[P_0^\bullet]V \cong 0. \tag{A29}$$

Equations (A22)–(A29) may be simultaneously solved to calculate the concentration of the main reagents and global radicals.

Consider now a derivation of the expressions required to calculate the weight chain-length distributions (WCLDs) of the free PS [indicated by $G_{PS}(n)$] and the grafted St branches [indicated by $G_{GS}(n)$]. From the mass balances for $S_n^\bullet$ and $P_m^\bullet$, the following can be obtained[13]:

$$[S_n^\bullet] = \frac{R_p\phi}{k_p[St]}\frac{\alpha}{(1+\alpha)^n} \quad n = 1, 2, 3, \ldots \quad \text{(A30)}$$

$$[P_m^\bullet] = \frac{R_p(1-\phi)}{k_p[St]}\frac{\alpha}{(1+\alpha)^m} \quad m = 1, 2, 3, \ldots \quad \text{(A31)}$$

with

$$R_p = k_p([S^\bullet] + [P^\bullet])[St] \quad \text{(A32)}$$

$$\phi = \frac{[S^\bullet]}{[S^\bullet] + [P^\bullet]} \quad \text{(A33)}$$

$$\alpha = \tau + \beta \quad \text{(A34)}$$

$$\tau = \frac{k_{fm}}{k_p} + \frac{k_{ft}[T]}{(k_p[St])} + \frac{k_{fg}[B^*]}{(k_p[St])} + \gamma\tau_1 \quad \text{(A35)}$$

$$\beta = \frac{k_{tc}R_p}{(k_p[St])^2} \quad \text{(A36)}$$

$$\gamma = \frac{[P_0^\bullet]}{[S^\bullet] + [P^\bullet]} \quad \text{(A37)}$$

$$\tau_1 = \frac{k_{tc}''R_p}{(k_p[St])^2} \quad \text{(A38)}$$

To calculate $G_{PS}(n)$, a mass balance for every possible S_n ($n = 1, 2, \ldots$) must be first written, and then eqs. (A30)–(A38) must be replaced, yielding[13]

$$\frac{d}{dt}\{G_{PS}(n)\} = T_1(t) \times D_1(n, t) + T_2(t) \times D_2(n, t)$$
$$n = 1, 2, 3 \ldots \quad \text{(A39a)}$$

with

$$T_1(t) = R_p V M_{St}\frac{\phi(\tau - \gamma\tau_1)}{\alpha} \quad \text{(A39b)}$$

$$D_1(n, t) = \alpha^2 n e^{-\alpha n} \quad \text{(A39c)}$$

$$T_2(t) = R_p V M_{St}\frac{\phi^2\beta}{\alpha} \quad \text{(A39d)}$$

$$D_2(n, t) = \frac{\alpha^3}{2}n^2 e^{-\alpha n} \quad \text{(A39e)}$$

where $T_1(t)$, $T_2(t)$ (in g/s) represent the instantaneous mass rate of production of PS chains by transfer reactions and by combination termination, respectively; $D_1(n, t)$ represents a (normalized) most probable or Schulz–Flory WCLD of $\bar{M}_n = M_{St}/\alpha$; $D_2(n, t)$ represents a normalized binomial WCLD of $\bar{M}_n = 2M_{St}/\alpha$; and M_{St} (in g/mol) is the monomer molecular weight.

To obtain $G_{GS}(m)$, note from eqs. (A1)–(A21) that a St branch of length m is generated through any of the following reactions: (a) transfer of a copolymer radical of length m to the monomer, solvent, PB, or copolymer; (b) termination of two growing branches of lengths n and $m - n$; (c) termination of a growing branch of length n with a growing PS radical of length $m - n$; and (d) termination of a primary rubber radical with a growing branch of chain length m or with a growing PS radical of chain length m. Thus, the following may be written

$$\frac{d}{dt}\{G_{GS}(m)\} = \Bigg\{(k_{fm}[St] + k_{ft}[T] + k_{fg}[B^*])[P_m^\bullet]V$$
$$+ \frac{k_{tc}}{2}\sum_{n=1}^{m-1}[P_n^\bullet][P_{m-n}^\bullet]V + k_{tc}\sum_{n=1}^{m-1}[P_n^\bullet][S_{m-n}^\bullet]V$$
$$+ k_{tc}''[P_0^\bullet][S_m^\bullet]V + k_{tc}''[P_0^\bullet][P_m^\bullet]V\Bigg\}m M_{St}$$
$$m = 1, 2, 3, \ldots \quad \text{(A40)}$$

Inserting eqs. (A30)–(A38) into eq. (A40) and considering that for sufficiently large values of m, $(1 + \alpha)^{-m} \cong e^{-\alpha m}$, then eq. (A40) yields

$$\frac{d}{dt}\{G_{GS}(m)\} = T_3(t) \times D_1(m, t) + T_4(t) \times D_2(m, t)$$
$$m = 1, 2, 3, \ldots \quad \text{(A41a)}$$

with

$$T_3(t) = R_p V M_{St} \frac{(1 - \phi)\tau + \gamma\tau_1\phi}{\alpha} \quad \text{(A41b)}$$

$$T_4(t) = R_p V M_{St} \frac{2\beta\phi(1 - \phi) + (1 - \phi)^2\beta}{\alpha} \quad \text{(A41c)}$$

where the normalized distributions $D_1(m, t)$ and $D_2(m, t)$ are as in eqs. (A39c, e), but with n replaced by m; T_3 (in g/s) represents the mass rate of generation of grafted St chains by transfer reactions or by combination termination between a primary rubber radical with either a St homoradical or with a nonprimary rubber radical; and T_4 (in g/s) represents the mass rate of generation of grafted St chains by combination termination between a nonprimary rubber radical with either a St homoradical or with another nonprimary rubber radical.

The right-hand sides of eqs. (A39a) and (A41a) represent the instantaneous WCLD of the free PS and of the St branches, respectively. Such distributions are themselves made up of two primary distributions. Each primary distribution is in turn the product of a generation rate T_i ($i = 1, \ldots, 4$) with a normalized WCLD. All four normalized distributions have a single and common parameter α. Two limiting cases can be distinguished. When the polymerization is carried out at low temperatures (e.g., between 60 and 70°C), then most of the dead polymer is produced by combination termination. In this case, it results in $\tau \cong \gamma \cong T_1 \cong T_3 \cong 0$, and the most probable contribution to the instantaneous distribution becomes negligible. At higher temperatures (e.g., between 90 and 200°C), most of the dead polymer is produced by transfer reactions; it results in $\beta \cong T_2 \cong T_4 \cong 0$, and therefore, the binomial contribution to the instantaneous distribution becomes negligible.

The instantaneous distributions of eqs. (A39a) and (A41a) are in principle different because in general $T_1 \neq T_3$ and $T_2 \neq T_4$. The normalized and cumulative WCLD of the St branches $[G_{GS}(m, t)/G_{GS}(t)]$ will, however, coincide with the normalized and cumulative WCLD of the free PS $[G_{PS}(m, t)/G_{PS}(t)]$ when the following conditions are verified. (1) The instantaneous and normalized WCLDs are identical, and (2) the ratio between the mass production rates of free PS and of the St branches is a constant. To satisfy condition (1), it is sufficient that

$$T_1(t)/T_2(t) = T_3(t)/T_4(t). \quad \text{(A42)}$$

Similarly, to satisfy condition (2), it is sufficient that either

$$[T_1(t) + T_2(t)]/[T_3(t) + T_4(t)] = \text{constant} \quad \text{(A43a)}$$

or equivalently, that the St grafting efficiency must be constant, for instance,

$$E_{St}(t) = \text{constant.} \quad \text{(A43b)}$$

To prove the equivalence between eqs. (A43a) and (A43b), note that E_{St} can be obtained from $G_{PS}(n, t)$ and $G_{GS}(m, t)$ as follows:

$$E_{St}(t) = \frac{\sum_n G_{GS}(n, t)}{\sum_n [G_{PS}(n, t) + G_{GS}(n, t)]}$$

$$= \frac{\int_0^t \sum_n [T_3(\tau) \times D_1(n, \tau) + T_4(\tau) \times D_2(n, \tau)] \, d\tau}{\int_0^t \sum_n \{[T_1(\tau) + T_3(\tau) \times D_1(n, \tau) + [T_2(\tau) + T_4(\tau)] \times D_2(n, \tau) \, d\tau}$$

$$\text{(A44)}$$

Since $\sum_n D_1(n, \tau) \, d\tau = \sum_n D_2(n, \tau) \, d\tau = 1$; then eq. (A44) becomes

$$E_{St}(t) = \frac{\int_0^t [T_3(\tau) + T_4(\tau)] \, d\tau}{\int_0^t [T_1(\tau) + T_2(\tau) + T_3(\tau) + T_4(\tau)] \, d\tau}$$

$$\text{(A45)}$$

Now, if eq. (A43b) is true, then from eq. (A45) it is sufficient that $(T_1 + T_2)/(T_3 + T_4)$ must be a constant. Alternatively, if eq. (A43a) is true, then eq. (A45) implies that E_{St} must be a constant. Finally, it should be noted that eqs. (A43) are both verified when eq. (A42) is transformed into $(T_1/T_2) = (T_3/T_4) = \text{constant}$.

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