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# Analysis of a Styrene–Butadiene Graft Copolymer by Size Exclusion Chromatography

## II. Determination of the Branching Exponent with the Help of a Polymerization Model\*

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A styrene–butadiene graft copolymer is analyzed by size exclusion chromatography (SEC) with on-line viscometry with the aim of estimating the  $\epsilon$  exponent that relates the two branching parameters through  $g^\epsilon = g'$ . Three copolymer samples synthesized in a solution polymerization of styrene in the presence of polybutadiene were analyzed. Theoretical predictions on the branching characteristics were obtained with the help of a detailed polymerization model that is presented in the first part of this series. The  $\epsilon$  exponent was adjusted by comparing the experimental variation of  $g'$  along molecular weights with the expected theoretical function. For tetrahydrofuran solutions at 25°C, a value of  $\epsilon = 2$  was obtained. The resulting average number of trifunctional branching points per molecule are in accord with independent determinations by gravimetry, ozonolysis, and SEC.

**Keywords:** Size exclusion chromatography; Branching parameter; Styrene–Butadiene; Graft copolymer; Branching distribution; High-impact polystyrene

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## INTRODUCTION

In this work, the branching characteristics of a graft copolymer containing only trifunctional branching points are analyzed by size exclusion chromatography (SEC) with a specific viscosity sensor and a mass detector. From the signal ratio, the instantaneous intrinsic viscosity  $[\eta]_b(V)$  is obtained, where the subscript b indicates branched polymer and  $V$  is the elution volume. From  $[\eta]_b(V)$  and the universal calibration  $\log([\eta]M)$  vs.  $V$ , the  $V$ -molecular weight ( $M$ ) transformation is found. Compared to light-scattering detectors, viscosity estimates of  $M$  are less affected by the chemical composition. From  $[\eta]_b(V)$  and the  $V$ - $M$  transformation,  $[\eta]_b(M)$  is obtained. The instantaneous  $g'$  branching parameter is then determined from

$$g'(M) \equiv [\eta]_b(M_b)/[\eta]_l(M_l) = [\eta]_b(M_b)/KM_1^\alpha \leq 1; \quad (M = M_l = M_b) \quad (1)$$

where the subscript l indicates a linear (block copolymer) homologue of the same molar mass and chemical composition as the analyzed branched copolymer, and  $K, \alpha$  are the Mark-Houwink coefficients of the linear homologue. The  $g$  branching parameter (based on the radius of gyration) is related to  $g'$  through:

$$[g(M)]^\varepsilon = g'(M); \quad (M = M_l = M_b) \quad (2)$$

where  $\varepsilon$  is an empirical exponent that (except for a few homopolymers), it is in general unknown. Finally, the instantaneous number-average number of trifunctional branching points per molecule along molecular weights  $r_n(M)$  can be obtained from  $g$ ; but to this effect a theoretical interrelationship is required. Such relationship is available for homopolymers<sup>[1]</sup>

$$g(M) = \left[ \left( 1 + \frac{r_n(M)}{7} \right)^{1/2} + \frac{4r_n(M)}{9\pi} \right]^{-1/2} \leq 1; \quad (M = M_l = M_b) \quad (3)$$

but unfortunately no equivalent expression has been derived for graft copolymers.

For many branched polymers, the degree of branching increases monotonically with molecular weights. This is rather fortunate, since

it ensures a fractionation by degree of branching. Under ideal conditions, SEC fractionates by hydrodynamic volume. In the first part of this series,<sup>[2]</sup> the ideal SEC analysis of a styrene (St)–butadiene (Bd) graft copolymer was theoretically investigated. To simulate the fractionation of the different molecular topologies, the Zimm-Stockmayer model and the universal calibration concept were adopted.<sup>[2]</sup> It was concluded that errors in the molecular weight distribution (MWD) and in the degree of branching distribution (DBD) are low because the instantaneous MWDs and DBDs are narrow, and their averages vary monotonically with elution volume. In contrast, very large errors are encountered when estimating the chemical composition distribution (CCD).<sup>[2]</sup>

In the particular case of the St–Bd graft copolymer, no values have been published for the  $\varepsilon$  exponent of Eq. (2). The reasons for this are: (a) for a graft copolymer,  $\varepsilon$  depends on several variables such as the composition distribution, the sequence-length distribution, the number of branches per molecule, the temperature, and the solvent nature; and (b) no practical theory relating  $\varepsilon$  with other more basic physicochemical parameters has been developed. It is generally accepted that  $\varepsilon$  ranges between 0.5 and 1.5 or 2. The lower limit of 0.5 is observed for star-branched polymers or for polymers with low degrees of long-chain branching under theta conditions.<sup>[3]</sup> The upper limit has been observed in low-density polyethylenes with higher degrees of branching in good solvents.<sup>[4,5]</sup> More recently, it has been suggested that  $\varepsilon$  is a function of molecular weights.<sup>[5]</sup>

In this work, three graft copolymer samples previously investigated in Ref. [6] are reanalyzed with the aim of estimating the  $\varepsilon$  exponent in Eq. (2). To this effect, SEC with on-line viscometry is combined with theoretical predictions on the degrees of branching by the mentioned polymerization model.<sup>[2]</sup> One of the samples (the 16 h sample) was theoretically investigated in the first part of this series.<sup>[2]</sup> From the value of  $\varepsilon$ , the DBDs for the three samples are calculated.

## EXPERIMENTAL

The copolymer samples were synthesized and analyzed in Estenoz *et al.*<sup>[6]</sup> Consider now some of our previous results,<sup>[6]</sup> which are

reproduced in the first rows of Table I. A solution polymerization of St in the presence of polybutadiene PB was carried out at 70°C, and using *tert*-butyl peroctoate as chemical initiator.<sup>[6]</sup> Samples were taken at 8, 12, and 16 h, and the monomer conversions are presented in Table I. The graft copolymer was isolated from the polystyrene (PS) and PB homopolymers by solvent extraction. The copolymer global St mass fraction was determined by SEC fitted with a differential refractometer and an UV photometer.<sup>[6]</sup> The global number of branches from St and Bd was obtained from independent determinations of the total copolymer moles, the moles of grafted St branches (isolated by ozonolysis), and the moles of grafted PB.<sup>[6]</sup> In Table I, the global number-average number of trifunctional branching points per copolymer molecule  $\bar{r}_n$  (rather than the total number of branches) is shown.

A Waters ALC244 chromatograph fitted with a complete set of six  $\mu$ -Styragel columns, a Viscotek 200 viscometer, and Unical v. 4.01 software, was employed. The raw measurements were the instantaneous specific viscosity and the instantaneous mass. The carrier solvent was tetrahydrofuran (THF) at 1 mL/min. The temperature was 25°C. For all samples, the injection volume was 0.25 mL, and the nominal concentration was 1.0 mg/mL. An independent calibration of the refractive index detector allowed *a posteriori* corrections of the instantaneous concentration. From a set of narrow PS standards, the following (linear) universal calibration was determined:  $\log([\eta]M_1) = 18.09 - 0.3041 V$ . From the mass chromatogram and the  $V$ - $M$  transformation, the MWDs of Figure 1 and the molecular weight averages of Table I were produced. The areas under the

TABLE I Global characteristics of the analyzed St-Bd graft copolymer samples

	Sample taken at		
	8 hs	12 hs	16 hs
Monomer conv. (%) <sup>a</sup>	8.8	13.4	17.6
Global St mass fract. <sup>a</sup>	0.40	0.40	0.46
$\bar{r}_n^a$	—	1.47	1.89
$\bar{M}_n$ (g/mol)	230000	235000	276000
$\bar{M}_w$ (g/mol)	534000	559000	598000
$\bar{r}_n$ (SEC)	1.37	1.44	2.15
$\bar{r}_n$ (theoretical)	1.60	1.82	1.99
$\bar{r}_w$ (SEC)	2.53	2.73	3.74
$\bar{r}_w$ (theoretical)	2.12	2.61	3.02

<sup>a</sup> Obtained from Estenez *et al.*<sup>[6]</sup>

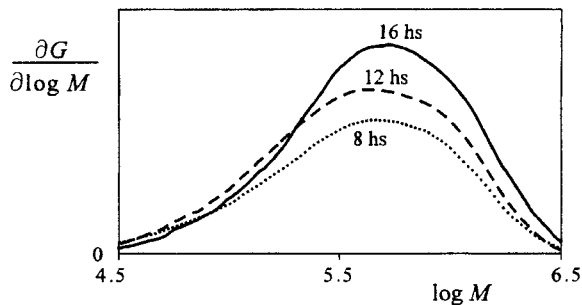


FIGURE 1 MWDs of the three investigated St-Bd graft copolymer samples. The parameter indicates the sampling time in a solution polymerization of St in the presence of PB. In the ordinates,  $G$  indicates mass. The areas under the curves are made proportional to the graft copolymer mass at the indicated sampling time.

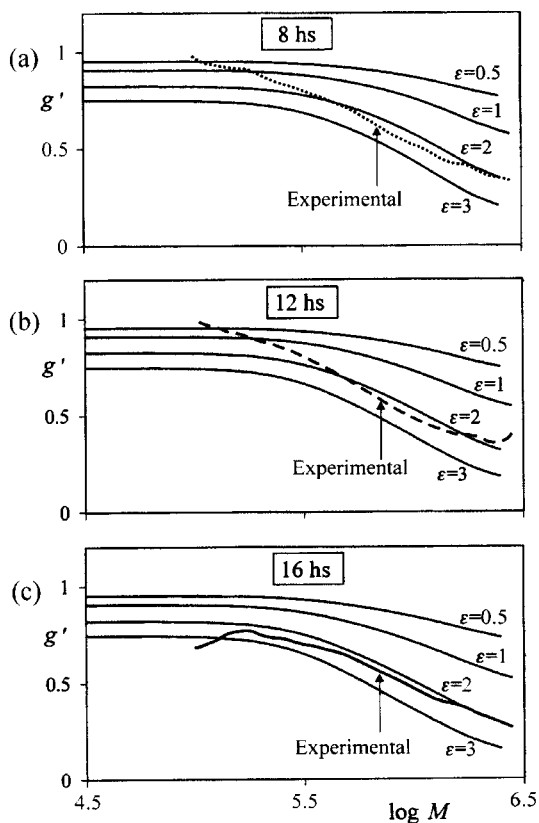


FIGURE 2 Experimental and theoretical  $g'(M)$  functions for the three investigated graft copolymer samples. The theoretical functions were found by raising  $g(M)$  to the indicated  $\epsilon$  exponents. The best overall fit is observed for  $\epsilon = 2$ .

distributions of Figure 1 were made proportional to the copolymer masses at the given sampling times.

The  $g'(M)$  functions were obtained through Eq. (1). The following Mark-Houwink constants (corresponding to a linear St-Bd block copolymer with a global St mass fraction of 40%) were adopted:<sup>[7]</sup>  $K = 3.2 \times 10^{-4}$  dL/g and  $\alpha = 0.693$ . In Figure 2, the experimental  $g'(M)$  functions are presented. Several factors explain the relatively large errors observed at the low molecular weight ends of  $g'(M)$ : the lower sensitivity of viscosity sensors to low molar masses; the contamination of the copolymer samples with low molecular weight polystyrene;<sup>[6, 8]</sup> and uncertainties in the adopted Mark-Houwink constants.

## ESTIMATION OF $\varepsilon$ AND DEGREE OF BRANCHING DISTRIBUTION

To estimate  $\varepsilon$ , the experimental  $g'(M)$  functions of Figure 2 are compared with equivalent theoretical functions. First, the theoretical  $g(M)$ 's were obtained, and then the theoretical  $g'(M)$ 's were calculated from  $[g(M)_{\text{theor.}}]^\varepsilon$ . Consider the determination of  $g(M)_{\text{theor.}}$ .

In the first part of this series,<sup>[2]</sup> a detailed polymerization model is presented. Copolymer molecules are classified into  $r = 1, 2, \dots, 16$  topologies, where  $r$  indicates the number of trifunctional branching points per molecule. For each topology, the MWD was predicted.<sup>[2]</sup> From the mentioned set of MWDs,<sup>[2]</sup> the bivariate distribution  $x(r, M)$  for the total copolymer was obtained, where  $x$  indicates molar fraction. As in Ref. [2] Eq. (3) was applied to each copolymer topology, yielding:  $g_{r=1} = 0.909$ ;  $g_{r=2} = 0.840$ ; *etc.*, where  $g_r$  stresses the fact that the calculation involves only topology  $r$ . Finally,  $g(M)_{\text{theor.}}$  for the total copolymer was found from<sup>[1]</sup>

$$g(M)_{\text{theor.}} = \sum_r x(r, M)g_r; \quad (r = 1, 2, \dots) \quad (4)$$

In Figure 2,  $g(M)_{\text{theor.}}$  is presented as  $g'(M)$  with  $\varepsilon = 1$ . Such functions were then raised to the powers of 0.5, 2, and 3, and the

resulting  $g'(M)_{\text{theor.}}$  are also represented in Figure 2. Clearly, none of these curves exactly reproduce the measurements. However, by neglecting the  $g'(M)$  measurements at low  $M$  values,  $\varepsilon = 2$  is seen to provide a reasonable overall fit.

The possible variation of  $\varepsilon$  with molecular weights was obtained from the experimental  $g'(M)$  and the theoretical  $g(M)$  functions, as follows:

$$\varepsilon(M) = \frac{\log [g'(M)_{\text{exper.}}]}{\log [g(M)_{\text{theor.}}]} \quad (5)$$

and the resulting curves are presented in Figure 3. At high  $M$  values, all curves converge to  $\varepsilon = 2$ ; while at low  $M$  values, no clear tendency is shown. Thus, a global  $\varepsilon = 2$  seems again to be a good compromise.

To estimate a "chromatographic" DBD, the function relating the number-average number of trifunctional branching points per molecule with the molecular weights  $r_n(M)$  is required. To obtain the experimental  $r_n(M)$  functions, Eq. (3) with  $g(M)$  estimated from  $[g'(M)_{\text{exper.}}]^{1/2}$  was applied to our St-Bd graft copolymer. This may be justified as follows: THF is a good solvent for both the St and the Bd chains, thus reducing the inter- and intramolecular interactions; and the solubility parameters for PS and PB are close  $17.5 \text{ MPa}^{0.5}$ ,<sup>[9]</sup> thus indicating a low interaction between the different copolymer chains. To obtain the theoretical  $r_n(M)$ , the following was applied:

$$r_n(M) = \sum_r x(r, M)r; \quad (r = 1, 2, \dots) \quad (6)$$

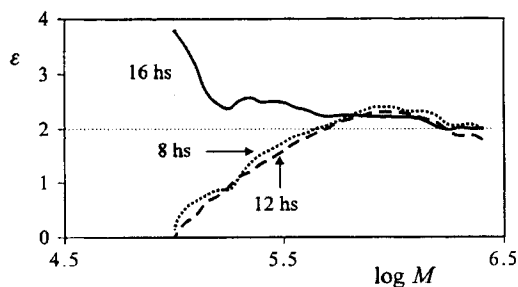


FIGURE 3 Calculated variation of the branching exponent with molecular weights for the three investigated samples.



where  $x(r, M)$  is the previously-defined bivariate distribution. In Figure 4, the experimental  $r_n(M)$  functions are compared with their theoretical equivalents.

The experimental and theoretical DBDs are presented in Figure 5, while their corresponding global number- and weight averages ( $\bar{r}_n$  and  $\bar{r}_w$ , respectively) are given in Table I. Again, a reasonable agreement between theory and measurements is observed. To produce the experimental DBDs, the MWDs of Figure 1 and the experimental  $r_n(M)$  functions of Figure 4 were used. Since the sought distributions are discrete, the masses at  $r=1, 2, \text{etc.}$ , were found by integrating the areas under the mass chromatograms with  $r_n$ 's between 1 and 2, between 2 and 3, *etc.* The theoretical DBDs were directly obtained from the polymerization model.<sup>[2]</sup>

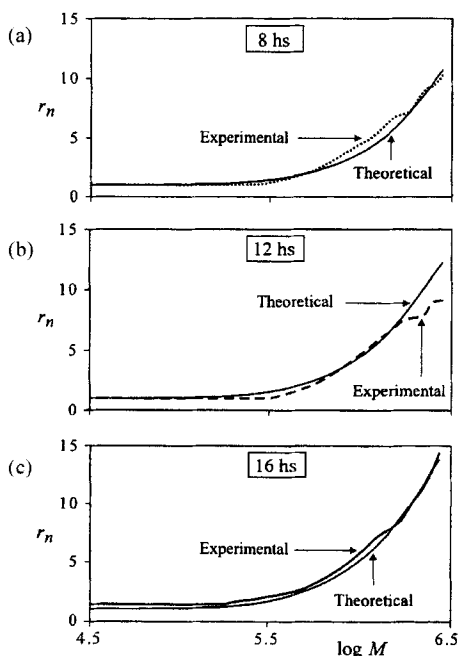


FIGURE 4 Experimental and theoretical variation of the number-average number of trifunctional branching points per molecule with molecular weights, for the three investigated samples.

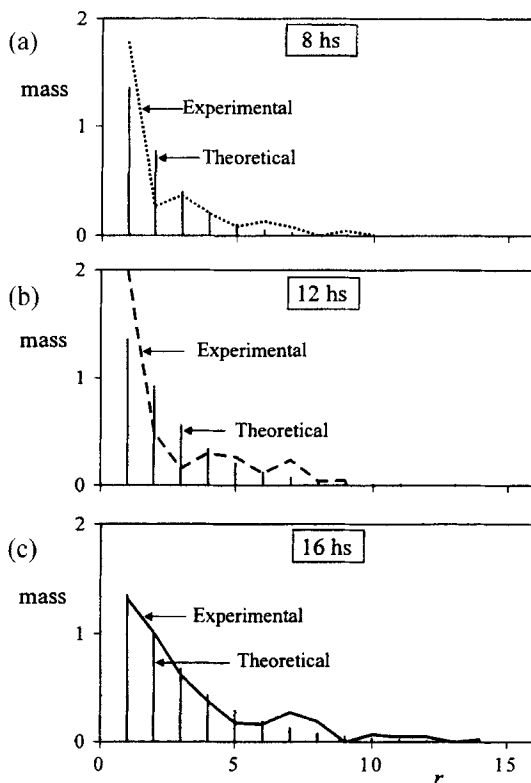


FIGURE 5 Experimental and theoretical degrees of branching distributions, for the three investigated samples.

## CONCLUSIONS

SEC measurements can be considerably enriched when combined with polymerization model predictions on the detailed molecular macrostructure. An St-Bd graft copolymer produced in an HIPS process at low conversions was analyzed. A branching exponent  $\varepsilon = 2$  was found for copolymer solutions in THF at 25°C. The estimated value is at the upper limit of the  $\varepsilon$  range. This may be explained by an increased viscosity of the graft copolymer with respect to an equivalent branched homopolymer, as a consequence of the intramolecular incompatibility between St and Bd branches.

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