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Analysis by size exclusion chromatography of the graft terpolymer present in MBS

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Abstract The molar mass distribution (MMD) and branching distribution (BD) of the graft terpolymer present in MBS (methyl methacrylate-butadiene-styrene, MMA-B-St) were estimated by size exclusion chromatography (SEC) with a series of three detectors: a UV photometer, a specific viscometer (SV), and a differential refractometer (DR). A solvent extraction procedure was employed to isolate the main MBS constituents: unreacted polybutadiene (PB), a PMMA-PS free copolymer (FC), and the PB-*g*-(PMMA-PS) graft terpolymer (GT). The FC was analyzed by UV + DR, yielding an almost uniform St mass fraction. The analysis of the GT involved the following assumptions: (i) the composition of the grafted branches coincides with that of the FC; (ii) the volumetric contractions of the molecules are represented by the Zimm–Stockmayer equations for randomly branched homopolymers; (iii) the low molar mass fraction exhibits a single branch per molecule; and (iv) the Mark–Houwink–Sakurada (MHS) parameters of the hypothetical homologous linear terpolymer are estimated by weighting the MHS constants of the PB and FC according to their mass fractions in the GT. The data treatment employed also enabled the branching exponent (ε) that relates the geometric and hydrodynamic contraction factors to be estimated, yielding $\varepsilon \approx 1.45$.

Keywords Size exclusion chromatography (SEC) · Graft terpolymer · Methyl methacrylate-butadiene-styrene (MBS) · Branching distribution (BD) · Branching exponent

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Introduction

Graft copolymers are a class of copolymers with a backbone of a certain chemical nature and side chains (or branches) of a different chemical nature [1]. Graft copolymers exhibit some of the properties of block copolymers but are generally easier to synthesize, and are applied as impact-resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers [2]. In general, well-defined molecular characterizations of graft polymers are required to develop successful polymerization strategies and improve understanding of their structure–property relationships [3].

MBS is a heterogeneous material that is typically employed as an impact modifier. It can be synthesized by radical copolymerization of styrene (St) and methyl methacrylate (MMA) in the presence of polybutadiene (PB) [4–11]. MBS is a blend of a linear St-MMA random copolymer (or free copolymer, FC), a fraction of unreacted PB, and the graft terpolymer (GT). The GT consists of a PB backbone with one or more grafted branches of St-MMA. In our previous publications [8, 9], simple and detailed mathematical models were developed for the solution (or bulk) batch copolymerization of St and MMA in the presence of PB. The models are able to predict the monomer conversion and the grafting efficiencies, together with the macromolecular structure of the evolving blend, i.e., (i) the molar mass distribution (MMD) of each polymeric component of the blend, (ii) the chemical composition distribution (CCD) of the FC and GT, and (iii) the branching distribution (BD) of the GT. Furthermore, the bivariate chain length distributions of the GT topologies were estimated, with each of the different topologies characterized by the number of branches per molecule [9].

The molecular characterization of branched polymers has been performed on many occasions, due to the effect of branches on the thermomechanical properties of polymers [12–16]. Branches can be long or short. Even though such a classification is still a matter of controversy, a branch is considered long when its length is similar to that of the main chain [17]. Long chain branches (LCB) and short chain branches (SCB) can be generated during radical polymerizations. While LCB are produced by chain intermolecular transfer to polymers or by reactions with double bonds, SCB are mainly produced when the growing radicals undergo intramolecular hydrogen transfer (or "backbiting"). The presence of SCB can affect the degree of crystallinity in semicrystalline polymers, which in turn influences the melting point, glass-transition temperature, and elastic modulus. In contrast, LCB normally affect rheological properties such as the sedimentation behavior, the intrinsic viscosity, and the viscosity and elasticity of the polymer melt. Three techniques are commonly used to determine the degree of LCB: ^{13}C nuclear magnetic resonance (NMR) spectroscopy, multidetection size exclusion chromatography (SEC), and infrared (IR) spectroscopy. Branching in up to a few percent of the monomer units of a poly(*n*-butyl acrylate) obtained by emulsion polymerization has been observed by ^{13}C NMR spectroscopy [18–20]. Solid-state ^{13}C NMR is less sensitive than solution NMR, but the latter technique requires fully soluble samples (i.e., with no gel present). More recently, melt-state ^{13}C NMR has been used to characterize randomly branched polyacrylates with degrees of branching of around 2 % of the repeating units [21]. Even though ^{13}C NMR cannot normally discriminate between long and short branches, it has been possible to distinguish short branches with up to six carbons in polyolefins [22, 23].

A size-exclusion chromatography–Fourier transform infrared spectroscopy (SEC-FTIR) technique was developed for the analysis of high-density polyethylene copolymers. For the calibration of SCB, this technique employs complete spectral regions from FTIR in a multilinear regression method. It can resolve reasonably low degrees of SCB but, due to signal-to-noise limitations, it is inapplicable to very low degrees of branching (<5 CH_3/1000C) [24, 25].

No single chromatographic mechanism is currently capable of efficiently separating complex polymers according to molar mass, chemical composition, or number of branches per molecule. Combining multiple separation mechanisms (such as adsorption, desorption, and exclusion) can improve the molecular characterization of complex polymers [26]. For example, a two-dimensional liquid chromatography method has been developed for determining the MMD and LCB distribution of long branched polymers [27], where each dimension is chosen to maximize the separation efficiency according to the molar mass or number of branches. In liquid chromatography under critical conditions of enthalpic interactions, the fractionation system can be adjusted to separate the polymer molecules according to their topology or chemical composition, but without discriminating by molar mass [28, 29]. This selective fractionation enables further quantification and molecular characterization of each constituent through the application of a second analytical technique (e.g., SEC). Unfortunately, these techniques are highly specific to the analyzed polymeric material and difficult to implement in comparison to the standard SEC technique.

The molecular characterization of complex polymers is improved by multidetection SEC, which involves the combined use of a differential refractometer (DR), an ultraviolet (UV) detector, a specific viscosity (SV) detector, and/or a light scattering (LS) photometer [12–16, 30–34]. For example, an SEC fitted with a DR and a dual-wavelength UV detector has been used to characterize a PS-PB-PMMA block terpolymer [31]. The method enabled the determination of the instantaneous and global compositions, the mass fractions of the three polymer constituents, and the MMD.

The characterization of branched polymers by SEC requires the use of a SV detector in order to relate the intrinsic viscosity to the molar mass of each eluting fraction. In solution, a branched molecule exhibits a smaller hydrodynamic volume than a linear molecule of the same molar mass (M). At a given M, the geometric and viscometric contraction factors g and g' are respectively defined by [35, 36]:

$$g \equiv \frac{R^2_{\mathrm{g,b}}(M)}{R^2_{\mathrm{g,l}}(M)} \leq 1; \qquad (M = M_{\mathrm{b}} = M_{\mathrm{l}}) \tag{1.a}$$

$$g' \equiv \frac{[\eta]_{\mathrm{b}}(M)}{[\eta]_{\mathrm{l}}(M)} = \frac{[\eta]_{\mathrm{b}}(M)}{\mathrm{K}M^{\alpha}} \leq 1; \qquad (M = M_{\mathrm{b}} = M_{\mathrm{l}}), \tag{1.b}$$

where R^2_{g} is the average squared radius of gyration, $[\eta]$ is the intrinsic viscosity, and (K, α) are the Mark–Houwink–Sakurada (MHS) constants of the homologous linear terpolymer. The subscripts "b" and "l" indicate branched and linear molecules, respectively. Zimm and Stockmayer [35] developed the following approximate expression for a randomly branched polymer with trifunctional branch units that is dissolved in a θ solvent:

$$g = \left[\left(1 + \frac{b_{\mathrm{n}}}{7}\right)^{1/2} + \frac{4\, b_{\mathrm{n}}}{9\,\pi}\right]^{-1/2}, \tag{2}$$

where b_{n} is the number-average number of branch units per molecule, corresponding to a variety of molecules of fixed M. Both contraction factors are related through the semi-empirical expression [37]

$$g' = g^{\varepsilon}, \tag{3}$$

where the exponent ε is a measure of molecular drainability. Unfortunately, this exponent is only known for a few polymer–solvent systems, and it was seen to depend on M [38]. Typically, values of ε are in the range 0.5–1.5, with $\varepsilon \approx$

0.5 for star-like polymers and $\varepsilon \approx 1$ for comb polymers [16, 39]. However, values of $\varepsilon > 1.5$ have also been reported [13, 40, 41]. For branched polymers, knowledge of this exponent is useful for calculating the number of branches by SEC/(SV + DR). A theoretical study of the errors introduced in the SEC analysis of branched polymers has been recently published [42].

Polystyrenes with complex architectures, such as regular combs and centipedes, were characterized by SEC with static and dynamic LS, and viscometric detection, in order to measure their radii of gyration, hydrodynamic radii, and intrinsic viscosity, respectively. A value of $\varepsilon \approx 0.9$ was found [32]. SEC with triple detection (SV+LS + DR) was used to check the validity of the universal calibration concept in the separation of branched polyacrylates [33]. A reasonable separation according to M was only observed for highly branched molecules [33], contradicting other theoretical results [34]. A two-dimensional liquid chromatography system that combines temperature gradient interaction chromatography with SEC with (LS + DR + SV) detection was used to determine the molar masses and average number of branches of a mixture of regular star-shaped and linear PS [34]. In our previous publications [12, 13], we employed SEC with (DR + SV) to analyze the graft copolymer present in high-impact polystyrene. In those articles, the MMD, BD, and CCD of the graft copolymer were estimated with the aid of a polymerization model.

In the work reported in the present paper, the GT present in an MBS polymer synthesized in our laboratory was analyzed by SEC with SV + UV + DR detection, with the aim of estimating its MMD and BD. In this paper, we first present the measurement model and data processing methodology employed. The experimental section contains a brief description of the synthesis procedure and fractionation by solvent extraction. Finally, the SEC system and characterization results are presented and discussed.

Measurement model and data processing procedure

Assume that the (linear) FC can be perfectly separated from the (branched) GT through an appropriate fractionation procedure. Then, both MBS constituents are independently analyzed by SEC, as described in what follows.

Analysis of the FC by UV + DR detection

The FC is a linear random copolymer with St and MMA units, so a SEC configuration with DR + UV detection allows efficient estimation of its MMD and CCD. The measurement model is described by [43]

$$A^{\mathrm{FC}}(V) = \left\{ \mathrm{k}_{\mathrm{UV,PS}}\ p_{\mathrm{St}}^{\mathrm{FC}}(V) \right\}\ G^{\mathrm{FC}}(V) \tag{4.a}$$

$$n^{\mathrm{FC}}(V) = \left\{ \mathrm{k}_{\mathrm{DR,PS}}\ p_{\mathrm{St}}^{\mathrm{FC}}(V) + \mathrm{k}_{\mathrm{DR,PMMA}} \left[1 - p_{\mathrm{St}}^{\mathrm{FC}}(V) \right] \right\}\ G^{\mathrm{FC}}(V), \tag{4.b}$$

where V represents the elution volume, $A^{\mathrm{FC}}(V)$ and $n^{\mathrm{FC}}(V)$ are the baseline-corrected UV and DR chromatograms, respectively, $p_{\mathrm{St}}^{\mathrm{FC}}(V)$ is the instantaneous mass fraction of St in the FC, $G^{\mathrm{FC}}(V)$ is the instantaneous mass concentration, $k_{\mathrm{UV,PS}}$ is the calibration constant of the UV detector for PS (which includes the specific UV absorptivity of PS and the UV detector gain), and $k_{\mathrm{DR,PS}}$ and $k_{\mathrm{DR,PMMA}}$ are the calibration constants of the DR detector (which includes the corresponding specific refractive indices and the DR gain) for PS and PMMA, respectively. In particular, Eq. 4.a assumes that the UV absorption by the MMA units is negligible in comparison to the UV absorption by the St units.

From Eqs. 4.a and 4.b, one obtains

$$G^{\mathrm{FC}}(V) = \frac{1}{k_{\mathrm{DR,PMMA}}}\ \ n^{\mathrm{FC}}(V) - \frac{k_{\mathrm{DR,PS}} - k_{\mathrm{DR,PMMA}}}{k_{\mathrm{DR,PMMA}}\, k_{\mathrm{UV,PS}}}\ A^{\mathrm{FC}}(V) \tag{5.a}$$

$$p_{\mathrm{St}}^{\mathrm{FC}}(V) = \frac{k_{\mathrm{DR,PMMA}}\ \left[A^{\mathrm{FC}}(V) \big/ n^{\mathrm{FC}}(V) \right]}{k_{\mathrm{UV,PS}} - \left(k_{\mathrm{DR,PS}} - k_{\mathrm{DR,PMMA}} \right)\ \left[A^{\mathrm{FC}}(V) \big/ n^{\mathrm{FC}}(V) \right]}. \tag{5.b}$$

Note that $G^{\mathrm{FC}}(V)$ is calculated from a linear combination of the chromatogram heights. In contrast, $p_{\mathrm{St}}^{\mathrm{FC}}(V)$ involves a nonlinear transformation due to the signal ratio $A^{\mathrm{FC}}(V)$ / $n^{\mathrm{FC}}(V)$; for this reason, large errors are to be expected at the chromatogram tails. The distribution of St mass fraction in the FC, $G^{\mathrm{FC}}(p_{\mathrm{St}}^{\mathrm{FC}})$, can be obtained from $G^{\mathrm{FC}}(V)$ and $p_{\mathrm{St}}^{\mathrm{FC}}(V)$. When a molar mass calibration of the FC, $M^{\mathrm{FC}}(V)$, is available, then the MMD of the FC, $G^{\mathrm{FC}}(M^{\mathrm{FC}})$, can be calculated from $G^{\mathrm{FC}}(V)$ and $M^{\mathrm{FC}}(V)$ [43].

Analysis of the GT by SV + UV + DR detection

The branched GT macromolecules contain a PB backbone and poly(St-MMA) branches similar to the FC. With a UV + DR + SV configuration, the measurement model is described as follows (the superscript "GT" is omitted to simplify the notation) [43, 44]:

$$A(V) = \left\{ k_{\mathrm{UV,PS}}\ p_{\mathrm{St}}(V) \right\}\ G(V) \tag{6.a}$$

$$n(V) = \left\{ \begin{array}{r} k_{\mathrm{DR,PS}}\ p_{\mathrm{St}}(V) + k_{\mathrm{DR,PMMA}}\, p_{\mathrm{MMA}}(V) + \\ + k_{\mathrm{DR,PB}}\ \left[1 - p_{\mathrm{St}}(V) - p_{\mathrm{MMA}}(V) \right] \end{array} \right\}\ G(V) \tag{6.b}$$

$$\eta_{\mathrm{sp}}(V) = \left\{ [\eta]_{\mathrm{b}}(V) \right\}\ G(V), \tag{6.c}$$

where $k_{DR,PB}$ is the DR calibration constant for PB (which includes the corresponding specific refractive index and the DR gain), $p_{St}(V)$ and $p_{MMA}(V)$ are the instantaneous mass fractions of St and MMA in the GT, $G(V)$ is the instantaneous mass concentration of the GT, and $[\eta]_b(V)$ is the instantaneous weight-average intrinsic viscosity of the GT.

Equations 6.a–6.c cannot be solved for the four unknowns G, p_{St}, $[\eta]_b$, and p_{MMA}. To circumvent this problem, let us assume that the composition of the grafted branches coincides with the average mass fraction of St in the FC, $\overline{p}_{St}^{FC}$. In this case, one can write

$$\frac{p_{MMA}(V)}{p_{St}(V)} = \frac{1-\overline{p}_{St}^{FC}}{\overline{p}_{St}^{FC}} = f = \text{constant} \tag{7}$$

with $\overline{p}_{St}^{FC}$ obtained by averaging $p_{St}^{FC}(V)$ across the whole range of V. From Eqs 6.a, 6.b, and 7, one obtains

$$G(V) = \frac{1}{k_{DR,PB}}\, n(V) - \frac{k_{DR,PS} + f\ k_{DR,PMMA} - (1+f)(1)\ k_{DR,PB}}{k_{UV,PS}\, k_{DR,PB}} A(V) \tag{8.a}$$

$$p_{St}(V) = \frac{k_{DR,PB}\ \left[A(V)/n(V)\right]}{k_{UV,PS} - \left\{k_{DR,PS} + f\ k_{DR,PMMA} - (1+f)\ k_{DR,PB}\right\}\ \left[A(V)/n(V)\right]}. \tag{8.b}$$

$[\eta]_b(V)$ and $p_{MMA}(V)$ can then be calculated from Eqs. 6.c and 7, respectively.

The distribution of the St mass fraction in the GT, $G(p_{St})$, is obtained from $G(V)$ and $p_{St}(V)$. As in the case of the FC, note that (i) Eq. 6.a assumes that the UV absorption is only determined by the St units and (ii) $p_{St}(V)$ can exhibit high oscillations at the chromatogram tails.

Assume that a universal calibration, $J(V)$, was developed from a set of narrow PS standards. Then, from Eq. 6.c and $J(V)$, the following expression can be derived that enables the instantaneous number average molar mass, $M_n(V)$ to be calculated [45]:

$$J(V) = [\eta]_b(V) M_n(V) = \frac{\eta_{sp}(V)}{G(V)} M_n(V). \tag{9}$$

The MMD of the GT, $G(M_n)$, can then be estimated from $G(V)$ and $M_n(V)$.

In order to estimate the BD of the GT, $G(b_n)$, the following steps are proposed: (i) calculate $[\eta]_b(M_n)$ from $[\eta]_b(V)$ and $M_n(V)$; (ii) obtain $g(M_n)$ from Eqs. 1.b and 9 and the known parameters K, α, and ε; (iii) calculate $b_n(M_n)$ from Eq. 2; and (iv) estimate $G(b_n)$ from $G(V)$ and $b_n(V)$. Unfortunately, SEC with SV detection only provides semiquantitative estimates of the BD because (a) while the Zimm–Stockmayer expression (Eq. 2) was developed for molecules of equal M, it is applied to molecules eluting at equal V, (b) $M_n(V)$ is highly oscillatory at both chromatogram tails due to errors in the signal ratio of Eq. 9, (c) errors in the parameters ε, α, and K directly affect the estimates, and (d) further data processing is required to transform the (continuous) estimates $b_n(M_n)$ and $G(M_n)$ into a (discrete) distribution, $W(b)$, where W indicates the mass fraction and b only adopts integer values. As far as the authors are aware, no value of ε has been published so far for the GT contained in MBS and dissolved in THF. In the "Appendix," a novel procedure for obtaining an independent estimate of ε is proposed.

Figure 1 depicts a flow sheet of the calculation procedure employed. In that figure, a black bar indicates that the output variable was obtained by combining two input variables of common abscissas. For example, $G(M_n)$ is obtained by combining $G(V)$ and $M_n(V)$. The upper section of Fig. 1 presents the calculation procedure for estimating the MMD of the FC and the parameter f. The lower section of Fig. 1 presents the calculation procedure for characterizing the GT, including its MMD, BD, and the intermediate ε parameter.

Experimental work

A bulk copolymerization of distilled St (technical grade, Petrobras Energía S.A., Buenos Aires, Argentina) and MMA (99 %, Aldrich, St. Louis, MO, USA) was carried out at 60 °C in a 1-L stirred-tank reactor in the presence of high-*cis*-1,4 PB (Intene Enichem, Roma, Italy) of average molar masses $\overline{M}_n =$ 101,900 g/mol and $\overline{M}_w =$ 218,200 g/mol. The mixture of comonomers was close to the azeotropic composition (of 58 wt.% St), in order to produce an almost uniform FC composition. Four samples were withdrawn during the polymerization, at the following mass conversions (x): 16.4, 17.7, 18.5, and 20.9 %. The GT was isolated from the bulk polymer through a solvent fractionation procedure that involved a few steps [8, 9]. In the first step, methyl ethyl ketone was used to remove the FC from the whole sample. In the second step, petroleum ether was

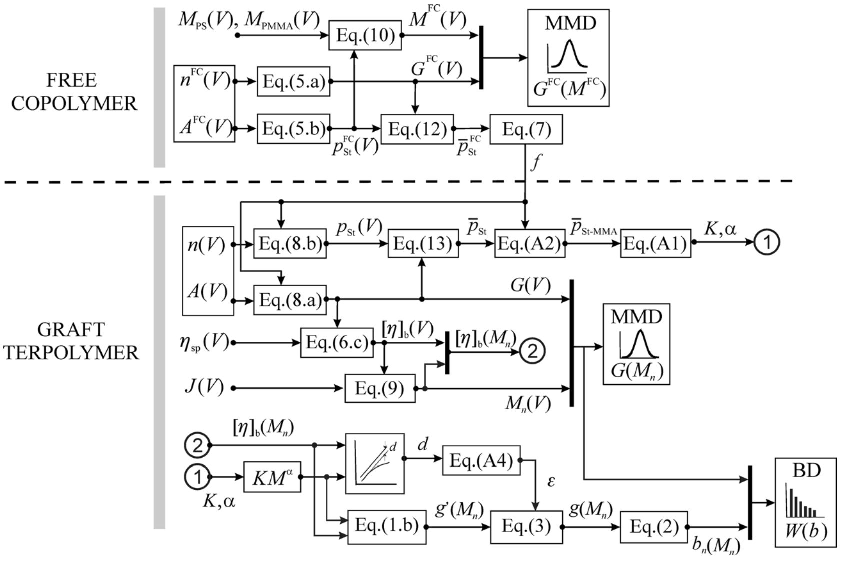

Fig. 1 Proposed data treatment procedure. The main outputs are the MMD of the FC and the MMD and BD of the GT

used to extract the unreacted PB from the remaining PB-GT mixture. For more experimental details, see [8, 9].

For each sample, the residual PB was analyzed by SEC/DR, the FC by SEC/(UV + DR), and the GT by SEC/(SV + UV + DR). All measurements were carried out at room temperature in a chromatograph fitted with a set of six μ-Styragel columns (HR1-6, 7.8 mm×300 mm, 5 μm, Waters, Milford, MA, USA), a differential refractometer (Waters 2414), a differential viscosity detector (Viscotek, model 200, Malvern Instruments, Malvern, UK), and a UV sensor (Waters 440, at 254 nm). The detector temperatures were stabilized at 30 °C. The carrier solvent was THF (HPLC grade) at 1 mL/min. Samples were dissolved in THF at a nominal concentration of 1.0 mg/mL. The injected volumes were 0.25 mL.

The following molar mass calibrations were determined from commercial sets of narrow standards: $\log M_{PS}(V)=11.78–0.1600\,V$; $\log M_{PMMA}(V)=11.80–0.1604\,V$; and $\log M_{PB}(V)=11.32–0.1530\,V$. The instantaneous molar mass of the FC, $M^{FC}(V)$, was calculated by interpolation between $\log M_{PS}(V)$ and $\log M_{PMMA}(V)$ as follows [43]:

$$\log M^{FC}(V) = p^{FC}_{St}(V)\ \log M_{PS}(V) + \left[1{-}p^{FC}_{St}(V)\right]\ \log M_{PMMA}(V). \qquad (10)$$

However, within experimental error, the calibrations of PMMA and PS were almost coincident, so $\log M_{PS}(V)\approx \log M_{PMMA}(V)\approx \log M^{FC}(V)$.

A set of eight PS standards in the range 1800–1,500,000 g/mol were measured by (SV + DR), leading to the following linear universal calibration:

$$\log J(V) = 18.83{-}0.3351\ V. \qquad (11)$$

The UV and DR detector gains were calibrated with narrow standards of PS, PMMA, and PB. Five concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 mg/mL) of each standard were injected, and the areas under the baseline-corrected DR and UV chromatograms were linearly correlated with the concentrations. The following parameters were estimated from the slopes of the linear correlations: $k_{UV,PS}$=99191; $k_{DR,PS}$=5745, $k_{DR,PB}$=4037; and $k_{DR,PMMA}$=2640.

Results and discussion

Analysis of the FC samples by (UV + DR)

Figure 2 shows the baseline-corrected DR and UV chromatograms of the FC. It is apparent that $A(V)$ is almost proportional to $n(V)$ across the range of the chromatogram, indicating an almost constant St mass fraction except at the chromatogram tails, where large errors are expected. For each sample, the average St mass fraction in the FC, $\overline{p}^{FC}_{St}$, was calculated via

$$\overline{p}^{FC}_{St} = \frac{\sum G^{FC}(V)\, p^{FC}_{St}(V)}{\sum G^{FC}(V)}, \qquad (12)$$

where $G^{FC}(V)$ and $p^{FC}_{St}(V)$ were calculated using Eqs 5.a and 5.b, respectively. For all of the samples analyzed, $\overline{p}^{FC}_{St}$ ranged from 0.47 to 0.51 (Table 1), i.e., slightly below the azeotrope (0.58). The values of f in Table 1 were calculated by placing the $\overline{p}^{FC}_{St}$ values into Eq. 7. Even though f ranged from 0.96 to 1.12, $f \cong 1$ was adopted throughout this work for the sake of simplicity.

The MMD of the FC, $G^{FC}(M^{FC})$, was obtained from $G^{FC}(V)$ and $M^{FC}(V)$. The global number- and weight-average molar masses of the FC ($\overline{M}^{FC}_{n}$ and $\overline{M}^{FC}_{w}$, respectively) slightly increased with x (see Table 1). In all cases, the dispersity index $\overline{M}^{FC}_{w}/\overline{M}^{FC}_{n}$ remained below 2.

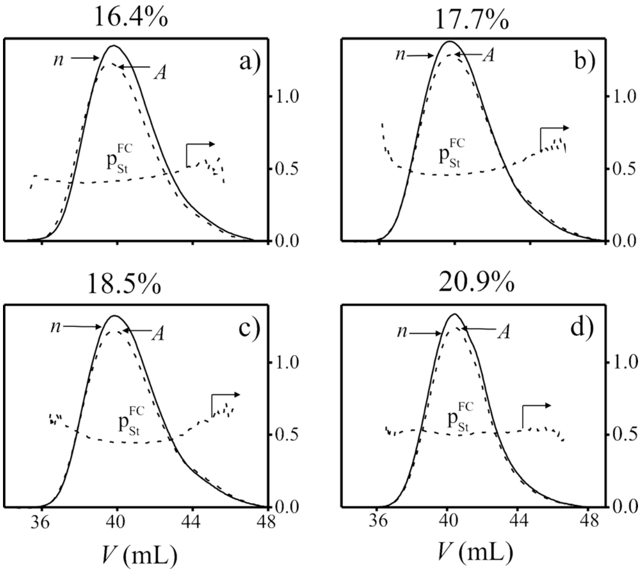

Fig. 2 **a–d** Analysis of the FC. The UV and DR chromatograms correspond to four samples taken at the following mass conversions (x): **a** 16.4 %, **b** 17.7 %, **c** 18.5 %, and **d** 20.9 %. The instantaneous St mass fractions in the FC, $p_{St}^{FC}(V)$, are almost constant in the mid-chromatogram range

Analysis of the GT samples by (SV + UV + DR)

The baseline-corrected chromatograms of all the analyzed GT samples are presented in Fig. 3, together with the evolution of the instantaneous St mass fractions calculated via Eq. 8.b, with $f=1$. In all cases, $p_{St}(V)$ is almost constant in the mid-chromatogram range. The average St mass fraction in the GT, $\overline{p}_{St}$, was calculated using

$$\overline{p}_{St} = \frac{\sum G(V) p_{St}(V)}{\sum G(V)}. \tag{13}$$

Table 1 presents the global averages of the GT. As expected, the average molar masses, $\overline{M}_n$ and $\overline{M}_w$, are significantly higher than those of the FC. The dispersity indices are also higher than in the case of the FC, with $\overline{M}_w/\overline{M}_n$ >3.

In Figure 4, the MHS plots of the four GT samples (continuous curves) are compared with the MHS plot of the hypothetic linear terpolymer (continuous straight lines). Following the approach presented in the "Appendix," the dashed straight lines correspond to the tangents (taken at low M values) to the curves of $\log([\eta]_b)$ vs. $\log M$. For each sample, the vertical distance between both straight lines (i.e., the difference between their intercepts) is indicated by d. In all cases, the d values were close to 0.06 (see Table 1). Thus, according to Eq. A4, $\hat{\varepsilon} = 24.1\ d \cong 1.45$.

The evolutions of the number of branches per molecule, $b_n(\log M)$, were obtained from Eqs 1.b, 2, and 3 (see Fig. 4). For all samples, $b_n(\log M)$ increases. The poor viscosity detector signal at low M prevents adequate estimation of b_n, so these values were assumed to be equal to 1. The global average number of trifunctional branches per molecule, $\overline{b}_n$, was calculated via

$$\overline{b}_n = \frac{\sum b_n(\log M)\, G(\log M)\, M^{-1}}{\sum G(\log M)\, M^{-1}}. \tag{14}$$

Only a moderate increase in $\overline{b}_n$ with the conversion was observed (see Table 1).

Figure 5 shows the MMDs and the BDs of the GT samples taken at low and high conversions (16.4 and 20.9 %, respectively). The MMDs were determined from $G(V)$ and $M_n(V)$, and the BDs were calculated by combining $b_n(M)$ with $G(M)$. In all samples, the largest mass fraction corresponds to macromolecules with a single branch ($b=1$). The average molar masses and average degree of branching are presented in Table 1. As expected, the average number of branches per molecule increases with conversion.

Figure 6 presents the chromatograms of each of the MBS components (FC, GT, and PB) and of the total sample (TS) at 16.4 and 20.9 % conversion. In all cases, the areas under the chromatograms were made proportional to the measured masses. The chromatograms of the different MBS components are all contained within those of the TS. As expected, the major component is the FC (72 % at 16.4 % and 68 % at 20.9 % conversion), followed by the GT (27 % at 16.4 % and 25.5 % at 20.9 % of conversion), and by minor amounts of residual PB (1.7 % at 16.4 % and 7 % at 20.9 % of

Table 1 Free copolymer (FC) and graft terpolymer (GT): main global characteristics

Free copolymer					Graft terpolymer					
x (%)	$\overline{M}_n^{FC}$ (g/mol)	$\overline{M}_w^{FC}$ (g/mol)	$\overline{p}_{St}^{FC}$ (−)	f (−)	$\overline{M}_n$ (g/mol)	$\overline{M}_w$ (g/mol)	$\overline{p}_{St}$ (−)	$\overline{b}_n$ (−)	d (−)	ε (−)
16.4	129460	203120	0.47	1.12	142200	615860	0.43	1.51	0.062	1.49
17.7	132800	209720	0.48	1.08	119470	583000	0.40	1.55	0.060	1.45
18.5	139180	221150	0.50	1.00	208500	795410	0.30	1.74	0.062	1.49
20.9	142620	225590	0.51	0.96	208190	792000	0.31	1.89	0.060	1.45

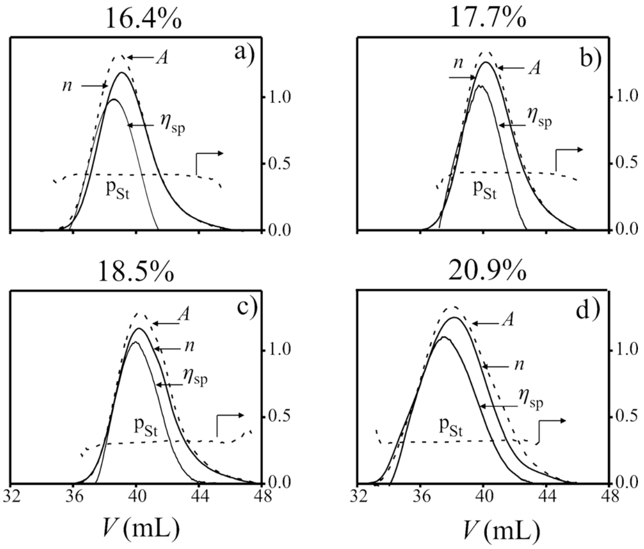

Fig. 3 Analysis of the GT. The SV, UV, and DR chromatograms, and the instantaneous St mass fractions, for the four analyzed samples

conversion). The greatest variation corresponds to the PB, possibly due to incomplete extraction. Accordingly, and due to its low mass, it is difficult to quantify residual PB by gravimetry. A more precise determination of the amount of residual PB could be achieved by liquid chromatography under critical conditions of enthalpic interaction [29].

Conclusions

SEC with on-line DR + UV + SV detection was used to characterize the main MBS components. The FC was analyzed by DR and UV at 254 nm, and exhibited an almost uniform St

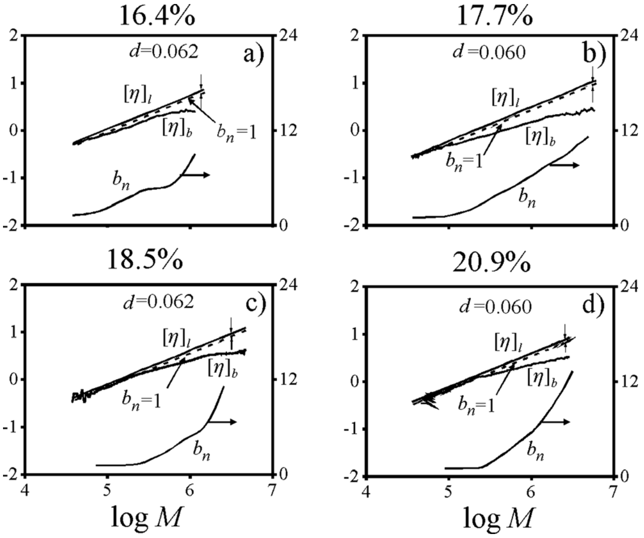

Fig. 4 Branching characteristics of the GT. MHS plots for the GT (log $[\eta]_b$) and for the homologous linear terpolymer ($\log[\eta]_l$). The slope of log $[\eta]_b$ (at low *M*) is indicated by *dashed lines*. Also represented is the evolution of the number of branches per molecule (b_n) with *M*

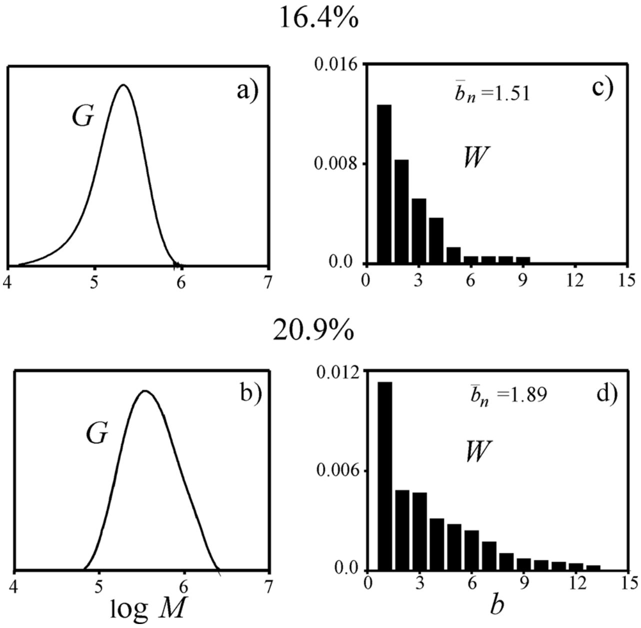

Fig. 5 a–d Characterization of the GT at conversions of 16.4 and 20.9 %: molar mass distributions (**a**, **b**) and discrete branching distributions (**c**, **d**)

mass fraction (as a consequence of the azeotropic copolymerization), with an average value close to 50 %. The evaluation of the MMD of the FC is reliable because the direct molar mass calibrations of PS and PMMA in THF are almost coincident.

The molecular characterization of the GT involved the calculation of the St mass fraction, the MMD, and the BD. The GT branches were assumed to be similar to the FC, with

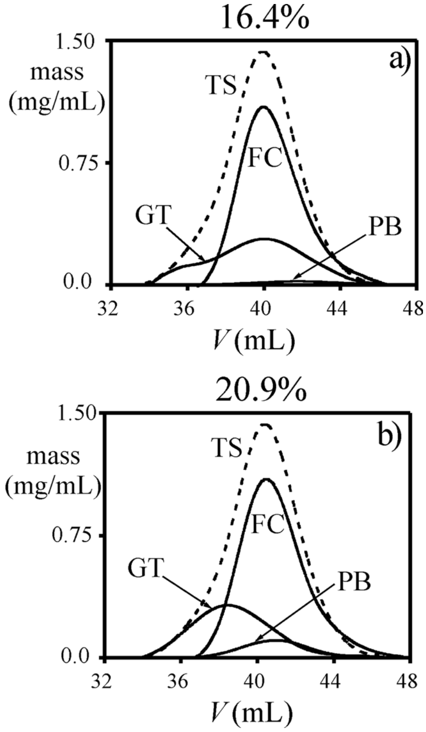

Fig. 6 Instantaneous masses of the MBS components at conversions of 16.4 and 20.9 %

an St mass fraction of around 50 % (i.e., $f \cong 1$). Based on the DR and UV measurements only, the St mass fractions of the GT samples ranged from 30 to 43 %. For the determination of the MMD, the SV signal and the universal calibration were also required.

A more complex level of data treatment was necessary to estimate the BD of the GT (Fig. 1). A novel graphical procedure was proposed to estimate the exponent ε, on the basis of (i) the DR, UV, and SV signals, (ii) the universal calibration, and (iii) the MHS parameters of the homologous linear terpolymer. The method assumed that the GT exhibits a single branch at low molar masses. A value of $\varepsilon = 1.45$ was estimated. It was then possible to calculate the contraction factor g from $(g')^{1/\varepsilon}$, which was converted into branches per molecule through the Zimm–Stockmayer theory. The GT contains between 1 and 13 branches per molecule, with number averages of between 1.51 and 1.89 branches per molecule, and with the average increasing with monomer conversion.

Appendix. Proposed procedure for estimating ε

The proposed method is based on comparing the MHS plot of the GT with that of a hypothetical linear terpolymer (LT) containing an St-MMA copolymer chain linked to a PB chain. The MHS constants of the LT (K and α) are obtained by adding the contributions from both blocks [46]:

$$\log K_{\mathrm{LT}} = \bar{p}_{\mathrm{St-MMA}} \log K_{\mathrm{St\text{-}MMA}} + \left(1 - \bar{p}_{\mathrm{St-MMA}}\right) \log K_{\mathrm{PB}} \tag{A1.a}$$

$$\alpha_{\mathrm{LT}} = \bar{p}_{\mathrm{St-MMA}}\, \alpha_{\mathrm{St\text{-}MMA}} + \left(1 - \bar{p}_{\mathrm{St-MMA}}\right) \alpha_{\mathrm{PB}}, \tag{A1.b}$$

where $\bar{p}_{\mathrm{St-MMA}}$ is the average mass fraction of St-MMA in the GT; $K_{\mathrm{St\text{-}MMA}}$, $\alpha_{\mathrm{St\text{-}MMA}}$, K_{PB}, and α_{PB} are the MHS constants of the St-MMA copolymer and PB, respectively. The following values were adopted: $\{K_{\mathrm{St\text{-}MMA}} = 8.213 \times 10^{-5}$ dL/g, $\alpha_{\mathrm{St\text{-}MMA}} = 0.750\}$ [47], and $\{K_{\mathrm{PB}} = 4.57 \times 10^{-4}$ dL/g, $\alpha_{\mathrm{PB}} = 0.693\}$ [48]. In Eqs. A1.a and A1.b, $\bar{p}_{\mathrm{St-MMA}}$ was calculated from the average St fractions in the FC and in the GT as follows:

$$\bar{p}_{\mathrm{St-MMA}} = \cfrac{\cfrac{\bar{p}_{\mathrm{St}}}{\mathrm{FC}}}{\bar{p}_{\mathrm{St}}} = (1 + f)\ \bar{p}_{\mathrm{St}}. \tag{A2}$$

At low M values, the GT is assumed to exhibit a single St-MMA branch ($b_{\mathrm{n}} = 1$) and, according to Eq. 2, $g = 0.9089$. From Eqs. 1.b and 3, one can write

$$\log[\eta]_{\mathrm{b}}(M) = \varepsilon\ \log(0.9089) + \log(K) + \alpha\ \log M \qquad (at\ low M). \tag{A3}$$

The left-hand side of Eq. A3 represents the (nonlinear) MHS plot of the GT, while the last two terms of Eq. A3 correspond to the (linear) MHS plot of the LT. Thus, at low M values, the term $\varepsilon \log(0.9089)$ represents the difference between both MHS plots. The estimated value of ε ($\widehat{\varepsilon}$) is then calculated via

$$\hat{\varepsilon} = \frac{d}{\log(0.9089)} = 24.1\ d \qquad (at\ low M), \tag{A4}$$

where d is the vertical distance from the straight line (corresponding to the MHS plot of the LT) to the tangent (at low M) to the curve of $\log[\eta]_{\mathrm{b}}$ vs. $\log M$. Also, d is the difference between the intercepts of both straight lines.

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