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Molecular Characterization of Styrene-Butadiene-Styrene Block Copolymers (SBS) by GPC, NMR, and FTIR

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Summary

This paper deals with the characterization of styrene-butadiene-styrene (SBS) block copolymers at molecular level through different techniques. SBS molecular weight distributions (MWD) were measured by Gel Permeation chromatography (GPC) in tetrahydrofuran (THF) solvent and using a calibration curve based on mono-dispersed polystyrene standards; afterwards, the relative molecular weights obtained by GPC were adjusted using a correction factor based on Mark-Houwink-Sakurada parameters for SBS in THF. Quantitative characterization of polybutadiene (PB) structures in SBS was made by solid-state ^{13}C Nuclear Magnetic Resonance (NMR). A novel method using Fourier transform infrared spectroscopy (FTIR) has been developed for characterizing the SBS composition. This method covers the determination of composition in SBS ranging from 20 to 75wt% of polybutadiene (PB) and was performed based on a FTIR calibration curve, which was prepared using mixtures of polystyrene (PS) and polybutadiene (PB) of known compositions.

Keywords

SBS, block copolymer, NMR, FTIR, GPC

Introduction

Styrene-Butadiene (SB) block copolymers are an important class of thermoplastic elastomers [1-3]. A variety of SB, with different molecular architectures and block lengths as well, is manufactured commercially in large volumes with a high degree of control over the molecular characteristics to produce block copolymers with particular domain microstructures suitable for specific applications. These SB copolymers are synthesized through anionic polymerization via either sequential or coupling methods. For instance, to produce SBS tri-block copolymers, in both methods, the synthesis comprises initiation of styrene polymerization using a mono-anionic organolithium compound to form living polystyryl anion, followed by addition of a butadiene monomer to form living SB di-block. In the sequential method, a second quantity of styrene is added to the living SB di-block in order to complete the formation of SBS tri-block copolymer. The coupling process differs from the sequential one in that the tri-block copolymer is terminated by coupling two living SB di-blocks using difunctional compounds such as dicarboxilic acid esters, phosgene, etc. The efficiency of each method depends on the temperature, polarity of the solvent, and presence of impurities (water, alcohol, etc). Generally speaking, coupling process produces more symmetrical end blocks and highly monodisperse block copolymers compared to the sequential one. The polarity of the solvent used in the polymerization can be also adjusted in order to control the microstructure of the polybutadiene segment, for example, adding polar species (ethers, amines, ketals, or orthoesters) to the typically used solvents (cyclohexane, benzene, etc) [4].

As can be seen from the brief description of the synthesis procedure for the SB copolymers, a great variety and complexity of structures can be obtained for these materials, which would stimulate studies on the molecular characterization of these SB copolymers. However, few papers in the literature [5-7] deal with the characterization of SB block copolymers at molecular level by different techniques. Therefore, the aim of this work is to perform molecular characterizations of commercial SBS block copolymers concerning their molecular weights, PB microstructure, and PB and PS contents using GPC, Solid-state ^{13}C NMR, and FTIR, respectively.

Experimental

Materials

Commercial grades of SBS block copolymers used in this work were obtained from various sources and are listed in Table 1.

Table 1. SBS used in this work

Designation used here	Supplier designation	Molecular architecture*	Supplier
KD 1152	Kraton D-1152	Tri-block	Kraton Polymers
KD 1151	Kraton D-1151	Tri-block	Kraton Polymers
KD 1186	Kraton D-1186	Star-block	Kraton Polymers
VECTOR	Vector 6241	Tri-block	Dexco Polymers
TR1091	Cariflex TR-1091C	Tri-block	Petroflex S.A.

* according to the supplier.

Methods

Gel Permeation Chromatography (GPC) analysis

Determination of average molecular weights and of the molecular weight distribution for the SBS copolymers by Gel Permeation Chromatography (GPC) were performed using a High Performance Liquid Chromatography HPLC Waters 410C equipped with a Refraction Index (RI) detector and three Waters Ultrastyragel Columns (10^3, 10^4,

10^5 Angstroms) at a flow rate of 1 mL/min, sample concentration of 0.1 wt% in tetrahydrofuran (THF), and temperature of 40°C. According to this procedure, the SBS molecular weights were determined using a calibration curve based on mono-dispersed polystyrene standards (Shodex Standard). Afterwards, the SBS molecular weights relative to the polystyrene standards were adjusted using a correction factor based on Mark-Houwink-Sakurada parameters for SBS in THF, according to ASTM D 3593 method. In this method, a polybutadiene corresponding molecular weight is obtained based on the polystyrene corresponding molecular weight, determined according to the GPC calibration curve, using the following equation:

$$\log_{10} M_B = \left(\frac{1}{1+a_B}\right)\log_{10}\left(\frac{K_S}{K_B}\right) + \left(\frac{1+a_S}{1+a_B}\right)\log_{10} M_S \qquad \text{(equation 1)}$$

where: S and B indexes refer to polystyrene and polybutadiene phases, respectively; *K* and *a* are constants for a given polymer/solvent system at a specified temperature and *M* is the corrected molecular weight. For the tetrahydrofuran at 40°C, the PS constants are $K_S = 1.050 \times 10^{-4}$ dL.g^{-1} and $a_S = 0.731$ and the PB constants are $K_B = 5.781 \times 10^{-4}$ dL.g^{-1} and $a_B = 0.670$.

Finally, the molecular weight for the SBS copolymer can be accurately obtained by taking into account the molecular weights corresponding to PS (GPC analysis) and PB (equation 1) and the weight fraction of each component in the SBS copolymer, through the following equation:

$$M_{SBS} = w_S.M + w_B.M_B \qquad \text{(equation 2)}$$

where: w_i is the weight fraction of the *i* component in the copolymer.

Nuclear Magnetic Resonance (NMR) measurements

The NMR measurements were performed on a VARIAN/INOVA spectrometer operating at frequencies of 100 MHz for ^{13}C and 400 MHz for ^1H, using a 7-mm MAS double-resonance probe head. The MAS spinning frequency was set at 4 kHz. In all measurements only 4.0-μs π/2 pulse for ^{13}C nuclei excitation and ^1H decoupling (~ 50 kHz) were used. Due to the large difference between the PB and PS mobilities, the spin-lattice relaxation times of these two moieties are very different. This feature allowed the selective excitation of the PB ^{13}C nuclei using a short recycle delay (2 s), permitting observing only the ^{13}C PB spectra of the SBS block copolymers.

Fourier transforms infrared spectroscopy (FTIR) measurements

Fourier transform infrared spectroscopy (FTIR) analyses were performed in a Perkin-Elmer spectrophotometer, model Spectrum 1000. A calibration curve was obtained based on PB/PS standard compositions previously prepared and was used to obtain the amount of polystyrene and polybutadiene in the SBS copolymer. The PB/PS standard mixtures in the range from 20 to 75wt% of PB were prepared by casting from toluene solution (5wt%/vol.) on Sodium Chloride (NaCl) mono-crystal disks. The peaks at the wave-number of 966 cm^{-1} relative to the C—H *oop* bending of trans alkenes and 699 cm^{-1} relative to C—H *oop* bending in monoalkylated aromatics were selected as the most suitable ones for analysis of polybutadiene (PB) and polystyrene (PS), respectively.

Results and Discussion

NMR Analysis

In this work NMR measurements were used to quantify the relative amount of the different PB isomers in the SBS block copolymers. Because quantification is needed, the more appropriate excitation technique is the direct polarization of the ^{13}C nuclei with the use of high power ^{1}H decoupling during the acquisition. Actually, ^{1}H spectra obtained at high MAS spinning frequency (> 15 kHz) would also be very appropriated, but this requires a high-spinning MAS probe, which is not available in our laboratory. Besides, to quantify the relative amount of the different PB isomers is desirable to obtain a spectrum that contains exclusively the PB contribution. In other words, it is necessary to suppress the signal from the PS phase. Because the ^{13}C T_1 relaxation time of the PS phase is much longer than in the PB phase, this selection can be achieved by setting the recycle delay to a short value (2 s), in such a way that after the excitation the PB magnetization has completely recovery after this time, while the PS magnetization is still in the transverse plane. Thus, after some dummy scans, the signal observed is almost exclusively due to the PB phase. Figure 1 shows the solid-state ^{13}C NMR spectrum for a neat PB. The line assignments were based on typical chemical shift values of the chemical structures shown as inset. Figure 2 shows the solid-state ^{13}C NMR spectra for the series of SBS employed in this study. The quantification of the PB structures in the neat PB and in SBS copolymers was made via integration of the following peaks: 1,2-*vinil* carbon # 1 (40-37 ppm); 1,2-*vinil* carbon # 4 (120-110 ppm); 1,4-*cis* carbons # 1 and # 4 (29-27 ppm); 1,4-*trans* carbons # 1 and # 4 (34-32 ppm).

The FTIR technique is a convenient method for identifying the isomeric composition of polybutadiene, but in the standard analysis the determination of the relative amount

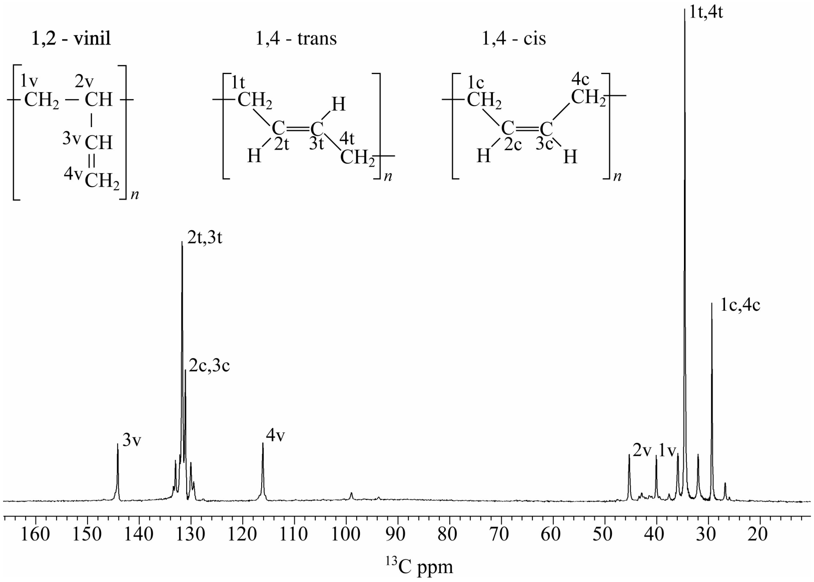


Figure 1. ^{13}C Solid-state NMR spectrum of neat PB.

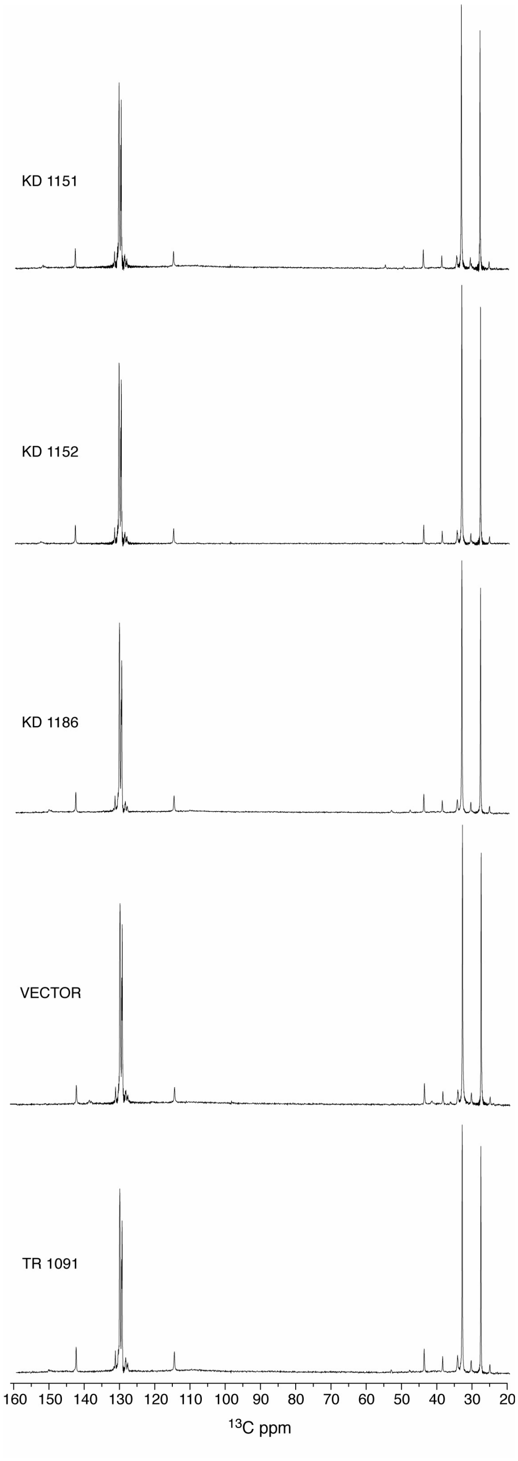
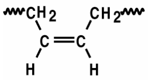
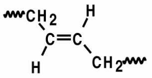
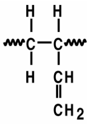


Figure 2. Normalized ^{13}C solid-state NMR spectra of SBS copolymers.

of each isomeric structure in the SBS copolymer may be significantly inaccurate. This is mostly due to the overlapping of a polystyrene peak with cis-1,4-polybutadiene. In contrast, the NMR analysis using the parameters for selectively obtaining the PB spectra is more quantitative because the lines from the different isomers are very well resolved. Table 2 shows relative amount of each isomeric component of PB in the SBS block copolymers as well as for neat PB as extracted from the NMR results. The results for pure PB was used to obtain the FTIR calibration curve for quantification of [PB]/[PS] in SBS.

Table 2. Structure compositions of PB in SBS determined by solid-state ^{13}C MAS NMR.

	Composition (molar %)		
			
	1,4-*cis*	1,4-*trans*	1,2-*vinil*
PB	39.4	51.2	9.4
SBS KD 1152	39.4	52.8	7.8
SBS KD 1151	39.7	53.2	7.1
SBS KD 1186	39.4	52.7	7.8
SBS VECTOR	36.4	51.3	12.3
SBS TR 1091	39.4	51.6	9.0

FTIR Analysis

Figure 3 shows the FTIR calibration curve used for the determination of the SBS styrene/butadiene monomer composition. This curve covers the determination of composition in the range of 20-75wt% of polybutadiene. The absorbance ratio at 966 cm^{-1} vs. 699 cm^{-1} is linearly related to the ratio [PB]/[PS] and can be expressed by the equation obtained from linear fit of the FTIR experimental data: $(A_{966\,cm^{-1}} / A_{699\,cm^{-1}}) = 0.42695\,[PB]/[PS] - 0.01514$. The PB or PS content (wt.%) in the SBS copolymer can be obtained by combining the relation above with the following relation: $[PB] + [PS] = 1$, where the contents within the square brackets represent the weight fraction of the copolymer components. It is important to mention that the absorption at 966 cm^{-1} that is relative to 1,4-*trans* structure in PB could be used in this analysis because the content of the *trans* structure of the different types of SBS are very close (Table 2). However, if one wants to determine the composition of a SBS copolymer containing different contents of 1,4-*trans* structures, this fact must be taken into account. The FTIR spectra for some of the PB/PS standard mixtures are shown in Figure 4 pointing out the PB and PS absorptions that were used for the FTIR calibration curve.

Figure 5 shows the FTIR spectra for the different SBS copolymers used in this study and Table 3 shows the quantitative results of the SBS copolymer compositions obtained by FTIR analysis using the calibration curve (Figure 3).

Table 3. SBS compositions determined by FTIR.

	Abs. $_{966\ cm^{-1}}$	Abs. $_{699\ cm^{-1}}$	Abs. $_{966\ cm^{-1}}$ / Abs. $_{699\ cm^{-1}}$	[PB] / [PS] (wt% / wt%)
SBS KD 1152	0.8866	0.8390	1.0591	71.6 / 28.4
SBS KD 1151	0.5955	0.6171	0.9648	69.7 / 30.3
SBS KD 1186	0.5528	0.5648	0.9788	70.0 / 30.0
SBS VECTOR	0.9767	1.4668	0.6659	61.5 / 38.5
SBS TR 1091	0.8281	1.2019	0.6890	62.2 / 37.8

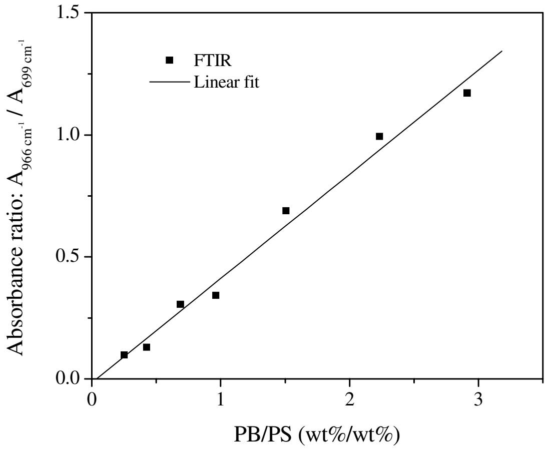


Figure 3. FTIR calibration curve based on polybutadiene/polystyrene standards for determination of SBS butadiene/styrene monomer composition.

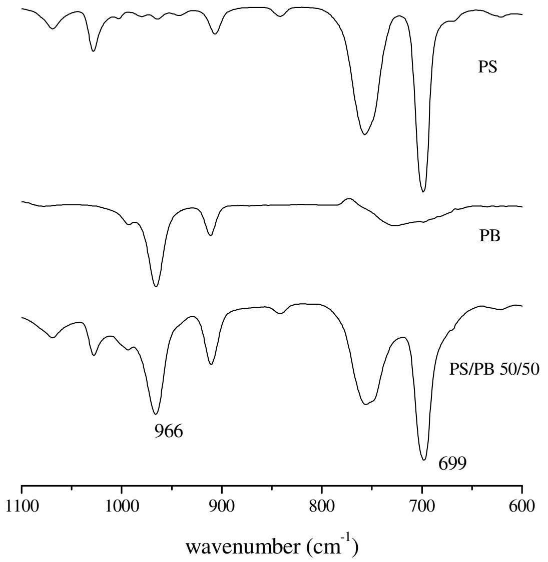


Figure 4. FTIR spectra for neat PB and PS, and for a PB/PS 50/50 (wt%/wt%) mixture, emphasizing the PB and PS absorptions, which were used to make the FTIR calibration curves.

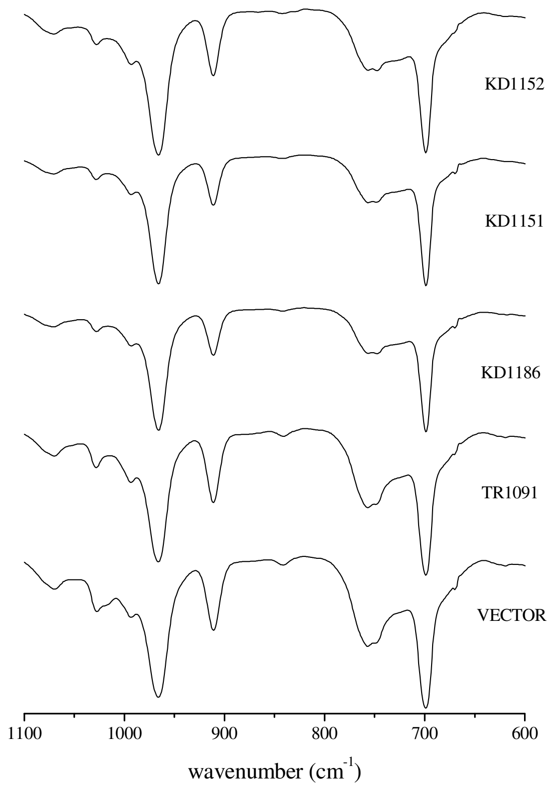


Figure 5. FTIR spectra for the SBS block copolymers.

GPC Analysis

Figure 6 shows the GPC molecular weight distribution curves obtained for the SBS block copolymers relative to polystyrene standards (Figure 7). It can be seen from molecular weight distribution curves in Figure 6 that there are more than one peak for each SBS copolymer, which is associated to different polymer species with different molecular weights.

The SBS KD1152 molecular weight distribution curve presents two peaks: one with higher intensity (peak a) and a second one (peak b) with lower intensity and with half of molecular weight of the most intense peak. The peak with highest intensity refers to the major tri-block molecular species contained in this SBS copolymer whereas the less intense peak is believed to correspond to di-block molecular species. The molecular weight relation between these two peaks (2:1) supports this argument. The di-block fraction that was found for this SBS is probable the result of segments that did not undergo the coupling process during polymerization.

For the SBS KD1151 molecular weight distribution curve, besides the peaks that are related to the tri-block (peak c) and the di-block (peak d) molecular species, a third peak (peak e) was observed with a molecular weight that is two times the molecular weight of the tri-block peak. This peak is probably related to pent-block species that is supposed to be associated with di-vinyl benzene contamination during polymerization,

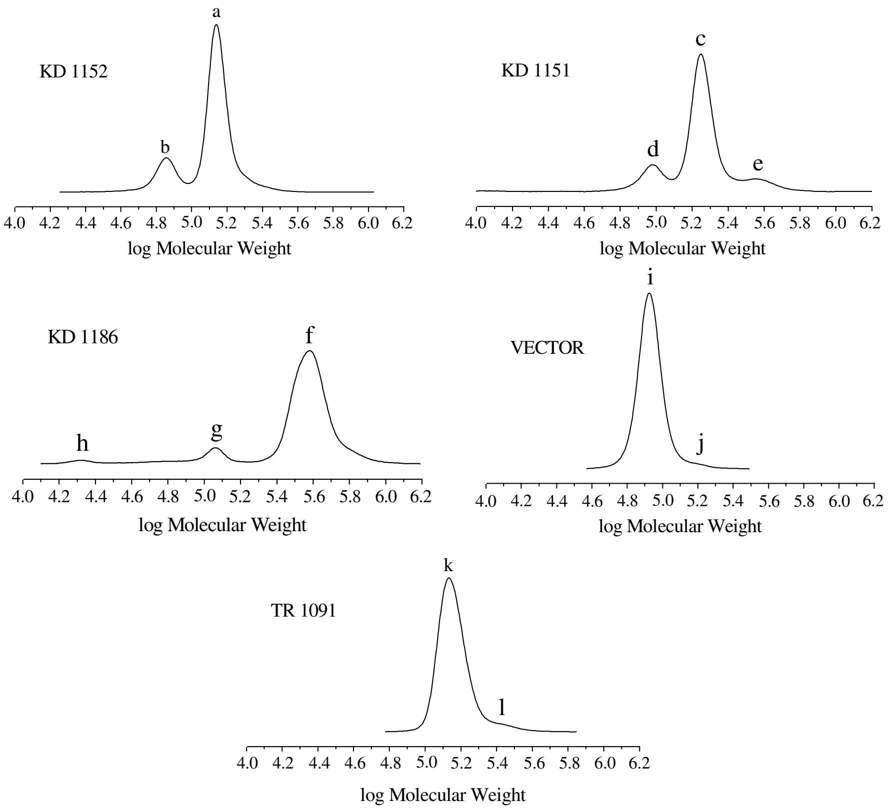


Figure 6. Molecular weight distribution curves relative to polystyrene standards obtained by GPC for the SBS block copolymers.

which would cause bi-lateral grown of PS blocks on the first stage of the polymerization causing the appearance of pent-block species.

The SBS KD1186 molecular weight distribution curve presents three peaks, the most intense one (peak f) correspond to radial species and the second more intense peak refers to the di-block species (peak g). According to the molecular weight relation between these two peaks (3:1), the SBS KD1186 is expected to be a tri-arm star block copolymer. The third peak with the lowest intensity (peak h) is probably associated to the PS block, which coupling failed during this SBS polymerization. It is important to mention that the "linear-polystyrene-equivalent" molecular weight of a star-block copolymer is significantly different from the one measured for a linear tri-block copolymer with the same molecular weight [6-7].

The SBS VECTOR and the TR1091 molecular weight distribution curves present two peaks each one, which are associated to the tri-block molecular species (most intense peaks) (peaks i and k, respectively) and to the pent-block molecular species (less intense peaks) (peaks j and l, respectively).

The molecular weights for each polymer specimen in the SBS copolymers with their respective weight fractions, determined via integration of the GPC curves presented in Figure 6, are shown in Table 4.

Table 4. SBS molecular weights determined by GPC.

	Molecular weight (g.mol^{-1})	Polymer specimen (relative amount)
SBS KD1152	M_n = 142,000 M_w = 146,000	tri-block (81 wt%)
	M_n = 70,000 M_w = 71,000	di-block (16 wt%)
	M_n = 280,000 M_w = 283,000	pent-block (3 wt%)
SBS KD1151	M_n = 179,000 M_w = 182,000	tri-block (78 wt%)
	M_n = 93,000 M_w = 94,000	di-block (15 wt%)
	M_n = 387,000 M_w = 392,000	pent-block (7 wt%)
SBS KD1186	M_n = 381,000 M_w = 405,000	star-block (88 wt%)
	M_n = 114,000 M_w = 115,000	di-block (10 wt%)
	M_n = 21,000 M_w = 21,000	polystyrene (2wt%)
SBS VECTOR	M_n = 84,000 M_w = 88,000	tri-block (96 wt%)
	M_n = 164,000 M_w = 165,000	pent-block (4 wt%)
SBS TR1091	M_n = 139,000 M_w = 143,000	tri-block (95 wt%)
	M_n = 292,000 M_w = 295,000	pent-block (5 wt%)

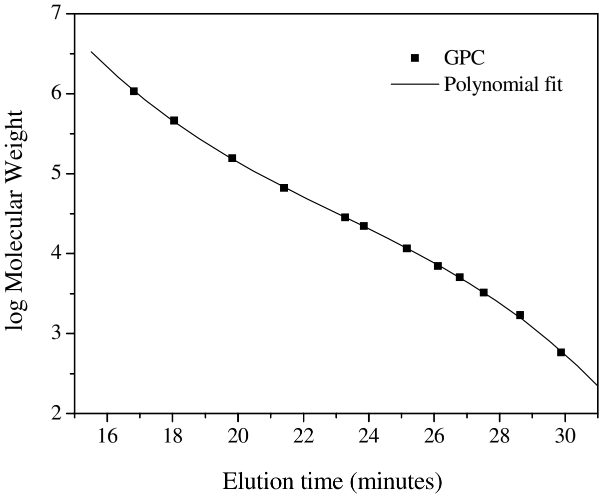


Figure 7. GPC calibration curve based on polystyrene standards for SBS molecular weight determination.

Table 5 shows the number average molecular weights for the main polymer species in each SBS copolymer, adjusted according to the procedure described in ASTM D 3593 (equations 1 and 2). The molecular weights for the PS and PB blocks in the SBS KD1152, KD1151, VECTOR and TR1091 were determined using the accurately obtained tri-block SBS copolymer molecular weights whereas the molecular weights for the PS blocks in the SBS KD1186 were determined through the accurately obtained di-block SBS copolymer molecular weight (Table 4). Note that the calculated molecular weight for the PS block in the SBS KD1186 copolymer (Table 5) is very close to the one determined by GPC (Table 4).

Table 5. SBS number average molecular weights corrected according to ASTM D 3593.

	SBS copolymer M_n ($g.mol^{-1}$)	PB block M_n ($g.mol^{-1}$) [(c)]	PS block M_n ($g.mol^{-1}$) [(c)]
SBS KD 1152	96,500 [(a)]	69,500 [(d)]	13,500 [(d)]
SBS KD 1151	125,000 [(a)]	87,400 [(d)]	18,800 [(d)]
SBS KD 1186	267,900 [(b)]	197,400 [(e)]	23,500 [(e)]
SBS VECTOR	60,900 [(a)]	37,100 [(d)]	11,900 [(d)]
SBS TR1091	103,400 [(a)]	64,000 [(d)]	19,700 [(d)]

(a) tri-block copolymer;
(b) star-block copolymer;
(c) determined according to the following relation: $M_{n(block)} = \%phase.M_{n(SBS)} / X$, where X is the number of arms of the block copolymer, i.e., X= 1 for the di-block and X= 2 for tri-block;
(d) determined from the tri-block average molecular weight;
(e) determined from the di-block average molecular weight.

Conclusions

A somewhat detailed molecular characterization of commercial grades of SBS block copolymers concerning their molecular weights, PB microstructures, and compositions was presented in this work. The isomeric compositions of PB blocks in SBS copolymers were determined using ^{13}C MAS NMR technique. For this purpose the NMR analysis, which relies on the selective observation of PB block, is more quantitative compared to the standard FTIR method. While for NMR all the PB spectra are well resolved, for FTIR there is an overlapping of a polystyrene peak with cis-1,4-polybutadiene. A simple FTIR method based on a calibration curve of PB/PS standards mixtures has been developed in order to determine the styrene/butadiene monomer composition of SBS copolymers. This method covers the determination of composition in the range of 20-75wt% of polybutadiene in SBS and is particularly dependent on the content of 1,4-*trans* structure in polybutadiene. The FTIR method developed here can be extended to other polymeric materials such as mechanical PS/PB blends and reactor-made PS/PB alloys (high impact polystyrene - HIPS). GPC analyses were useful for quantification of different SBS macromolecular species with a range of molecular weights and also allowed inferring about the polymerization method used for the SBS synthesis.

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