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EFFECT OF POLYBUTADIENE COMPOSITION ON THE GLASS TRANSITION TEMPERATURE OF SBS BLOCK COPOLYMERS

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ABSTRACT

Gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis techniques were used to study the molecular characteristics of six commercially available styrene-butadiene-styrene (SBS) block copolymers which are mostly used for modifying bitumen. The *cis*-1,4, *trans*-1,4, and 1,2-*vinyl* units in the polybutadiene (PB) parts and the styrene contents of the SBS block copolymers were investigated by means of ^{1}H-NMR spectra. In addition, carbon and hydrogen contents were estimated using ^{1}H-NMR measurements. These estimated values were confirmed using the results of elemental analysis (EA). The glass transition temperatures (T_g) of SBS block copolymers were obtained using differential scanning calorimetry (DSC). The SBS block copolymers used in this study have different structural properties such as molecular weight and linearity. However, it is observed that the T_g-onset values are directly proportional to the percentage of the 1,2-*vinyl* units and inversely proportional to the percentage of the *trans*-1,4 units in the SBS block copolymers.

Keywords: SBS, Block copolymers; GPC, NMR,· Glass trantision temperature

1. INTRODUCTION

Block copolymer term is used to explain copolymers with long series or different monomers in the same continuous chain. The properties of block copolymers are related to the length of the sequence of repeating, or their domains. The domains in commercial block copolymers of styrene and butadiene are suitably long such that the products are flexible. SBS block copolymers are a type of thermoplastic elastomers which exhibit both the properties of plastic and rubber [1-4]. These properties provide SBS block copolymers a variety of application fields such as plastic modification, adhesives and especially bitumen modification [5-11]. Commercial SBS block copolymers are classified into two groups as linear and radial polymers. Radial SBS block copolymers are also called branched or star polymers [4, 12]. Scheme 1 shows that SBS block polymers comprise polybutadiene mid-block and polystyrene (PS) end blocks. The polybutadiene part is responsible for the elasticity of the whole polymer. On the other hand, the polystyrene part increases the strength and rigidity of the polymer [2, 13].

Due to the structural benefits, SBS block polymers are widely used for modifying bitumen [5, 12, 13]. Bitumen is a residue of crude oil refining process. The properties of bitumen such as adhesivity, impermeability, and low cost make it most suitable binder in road paving. In addition, fatigue and aging properties of bitumen restrict its applications in industrial processes. SBS block copolymers enable swelling up to nine times its initial volume in maltene phase of bitumen and its continuous polymer phase helps to make polymer modified bitumen [7, 15-17]. SBS block copolymers improve the physical properties of bitumen to prevent rutting and cracking of asphalt in low or high temperature. Among polymers used for modified bitumens, SBS block copolymers provide higher performance such as penetration value, softening point and ductility value [18-20].

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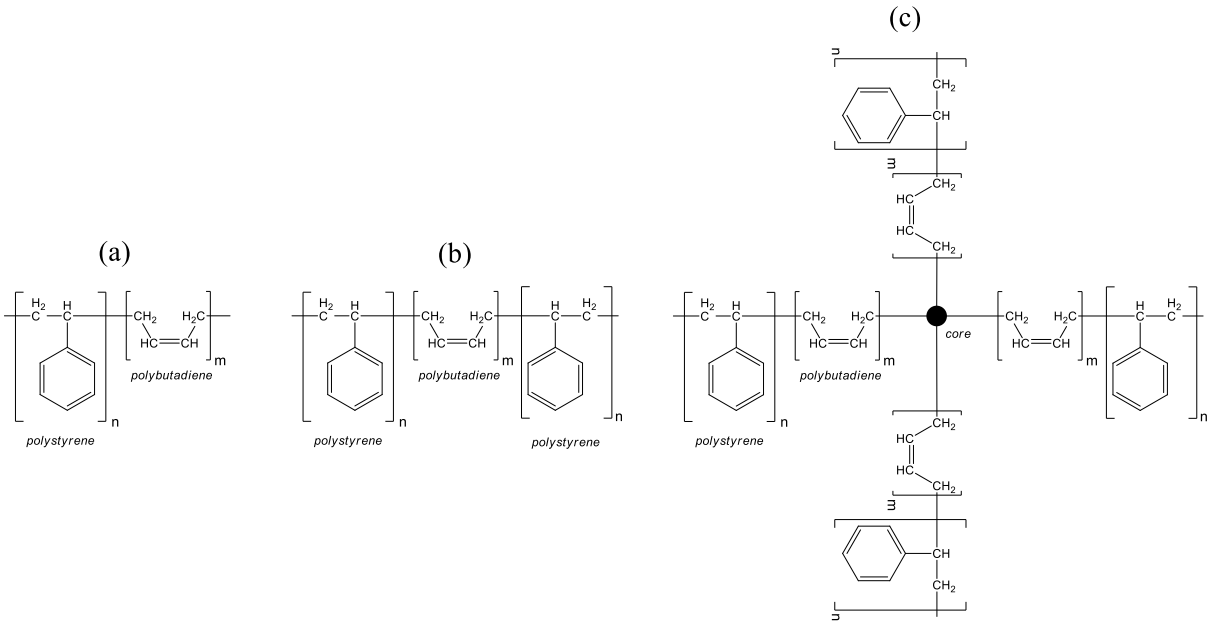
Commercially available SBS block copolymers for modification of bitumen contain approximately 30% styrene and 70% butadiene. However, the SBS block copolymers exhibit different physical properties such as glass transition temperature [16]. Since the thermal sensitivity of bitumen causes cracking at low temperature, glass transition temperature is one of the most important parameter for bitumen used in asphalt pavement [17, 21]. In this study, we report the structural characterization of six different commercial SBS block copolymers by means of GPC, ^{1}H-NMR, ^{13}C-NMR, and elemental analysis techniques and the effects of molecular structure on T_g values.



Scheme 1. The structures of SBS block copolymers: (a) Diblock; (b) Triblock; (c) Radial

2. MATERIALS AND METHODS

Six different commercially available SBS block copolymers were obtained from various sources and used without any further purification. Among the SBS block copolymers SBS-1 is a linear diblock copolymer. SBS-2, SBS-3, SBS-4, and SBS-5 correspond to linear triblock copolymers, and SBS-6 shows a radial copolymer.

2.1. GPC measurements

Molecular weight distributions of all SBS block copolymers were determined using an Agilent 1000 Series GPC system with a Refractive Index detector and PLgel 5 µm MIXED-D column at a flow rate 0.5 mL/min., at 25 °C. The samples were dissolved in THF and passed the solution through a 0.45 micrometer pore diameter teflon filter. THF butylated hydroxy toluene (BHT) was added as a flow marker. A calibration curve based on linear polystyrene standards was used to determine the molecular weights of SBS block copolymers.

2.2. NMR Analysis

^{1}H-NMR and ^{13}C-NMR spectroscopy measurements were performed on a Varian 600 MHz spectrometer at room temperature (23,5 ±5 °C) in $CDCl_3$. The solvent peaks appearing at 7.26 ppm in ^{1}H-NMR spectra and at 77.2 ppm in ^{13}C-NMR spectra were used as internal references.

2.3. Elemental Analysis

Elemental analysis measurements were performed on a Thermo Finnigan Flash 1112 Series EA Model instrument.

2.4. DSC Measurements

DSC analyses were performed using a Perkin Elmer DSC8000. The experiments were carried out for all SBS block copolymers under nitrogen at a heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. GPC measurements

The weight average molecular weights (Mw), the number average molecular weights (Mn) and the polydispersity index (PDI), Mw/Mn ratio, for all SBS block copolymers are shown in Table 1. When PDI is equal to 1, polymer chains have identical molecular weight and length. Narrow distribution is more desirable for polymers. On the other word, if PDI is close to 1, the molecular properties of polymer chains are more identical in polymer domains [22]. Table 1 shows that SBS-1 has the lowest molecular weight and SBS-6 has the highest molecular weight among all SBS block copolymers. The molecular weight of radial SBS-6 is at least two times higher than the linear SBS block copolymers.

Table 1. GPC measurements of SBS block copolymers

Sample	*Mw*	*Mn*	*Mw/Mn*
SBS-1	133.720	128.040	1.04
SBS-2	228.420	208.220	1.10
SBS-3	235.450	223.010	1.06
SBS-4	235.590	226.100	1.04
SBS-5	185.800	176.950	1.05
SBS-6	490.380	455.690	1.08

3.2. ^{13}C-NMR Analysis

The ^{13}C-NMR measurements were used to qualify the carbon atoms in the SBS block copolymers. As shown in Figure 1, the carbon atoms of aromatic rings for all SBS block copolymers were observed in the region 145 and 128-125 ppm. The alkenyl carbons of 1,2-*vinyl*-butadiene were observed at 144, 143, 115 and 114 ppm. The peaks appearing at 132-129 ppm shows the double bonds of *cis*-1,4-butadiene and *trans*-1,4-butadiene. The aliphatic carbon atoms appeared in the region 44-14 ppm [23, 24].

3.3. ^{1}H-NMR Analysis

The ^{1}H-NMR spectroscopy measurements were used to determine the percentage of polystyrene and polybutadiene in the SBS block copolymers. In addition, the compositions of 1,2-*vinyl*-butadiene, *trans*-1,4-butadiene, and *cis*-1,4-butadiene in polybutadiene parts were quantified using the integrations of ^{1}H-NMR spectra.

Figure 2 shows that the aromatic ring hydrogens for all SBS block copolymer samples were observed in the region 7.25-6.25 ppm. The alkenyl hydrogens of *cis*-1,4-butadiene and *trans*-1,4-butadiene appeared at around 5.43 and 5.38 ppm, respectively. The peaks appearing at around 5.55 and 4.98 ppm confirmed that the presence of alkenyl hydrogens in 1,2-*vinyl*-butadiene structure. The aliphatic hydrogens in SBS block copolymer chains appeared in the region 2.20-0.80 ppm [23-25].

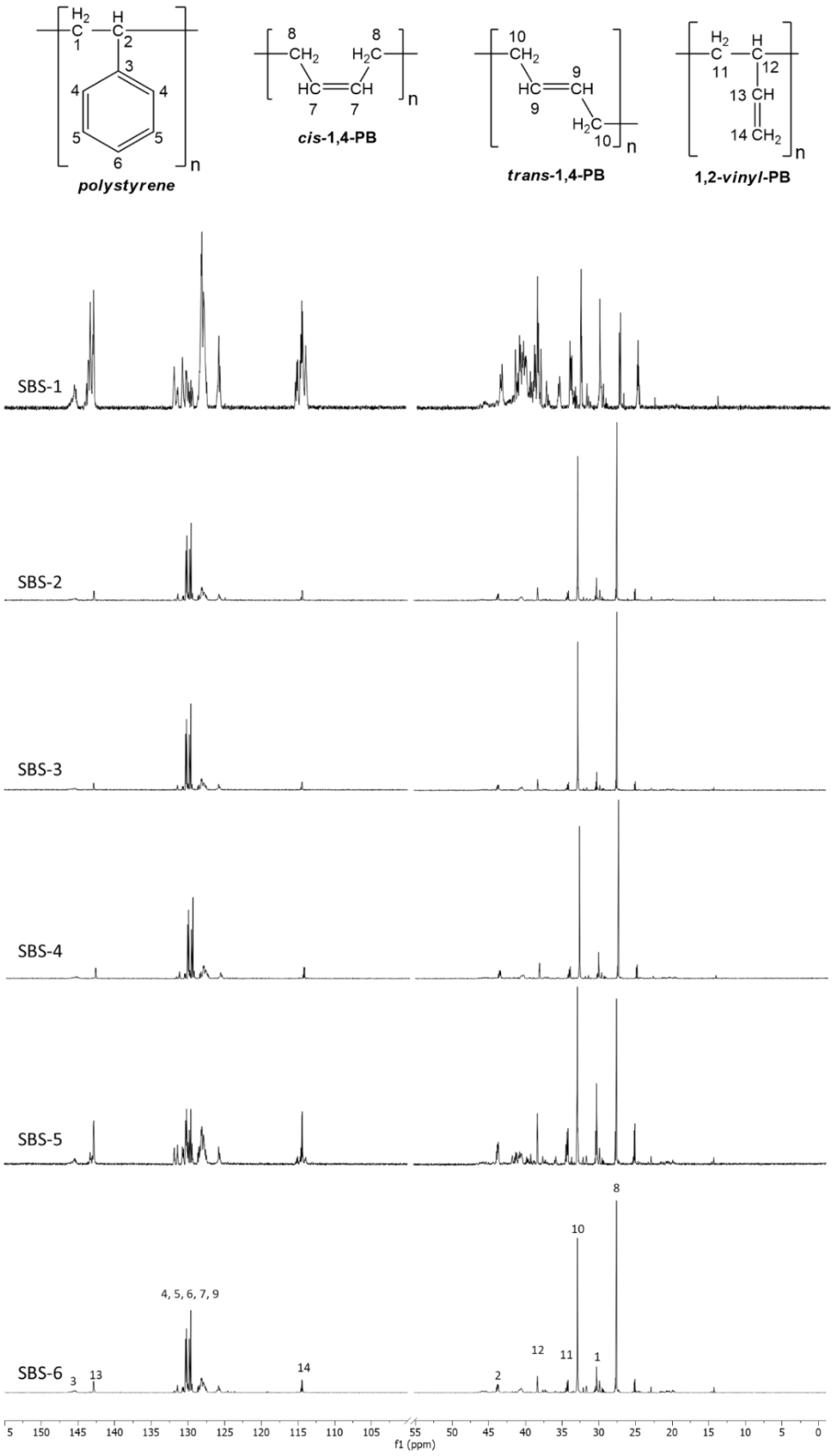


Figure 1. ^{13}C-NMR spectra of the SBS block copolymers

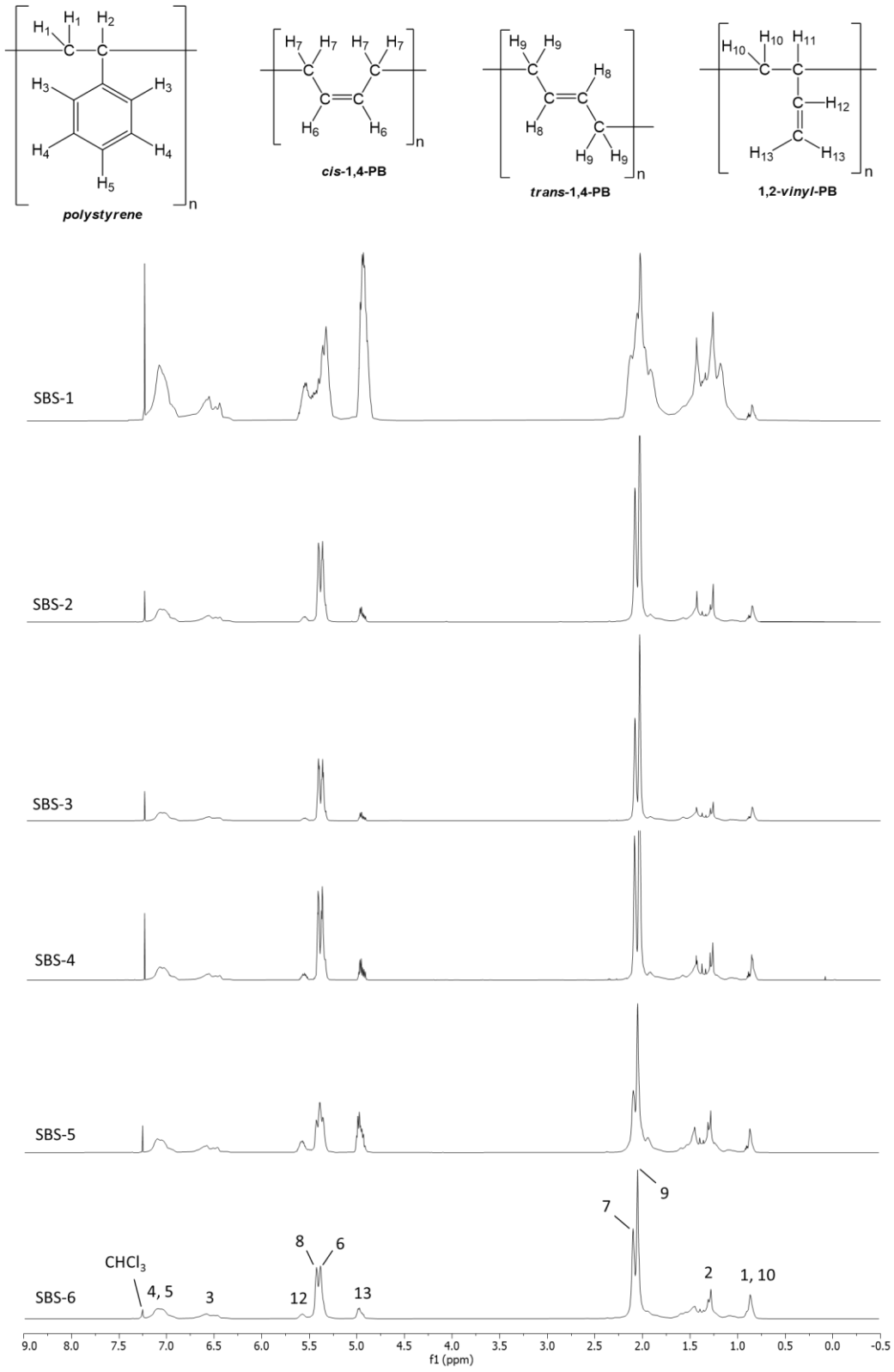


Figure 2. ^{1}H-NMR spectra of the SBS block copolymers

Figure 3 is an example to show the integration of the ^{1}H-NMR spectrum of SBS-2 for the rest of SBS block copolymers. The contents of styrene and butadiene were analysed according to the integration values. In addition, the compositions of 1,2-*vinyl*, *trans*-1,4 and *cis*-1,4 butadiene conformations in SBS block copolymers were estimated using the ^{1}H-NMR spectra and the results are shown in Table 2. In order to analyse the styrene contents in SBS block copolymers and the compositions of polybutadiene parts, the following equations (1-8) were used [24, 25]. The estimated styrene and butadiene contents are given in Table 3.

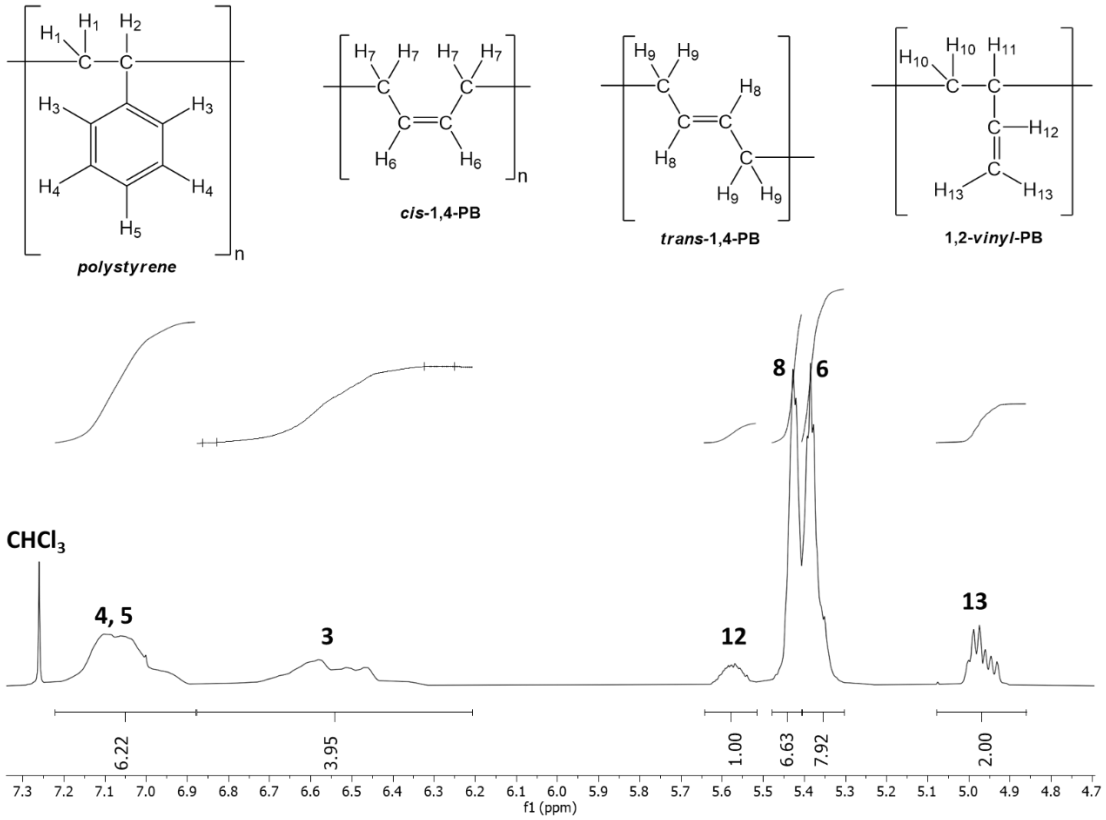


Figure 3. ^{1}H-NMR integration for SBS-2

$$N_1 = \frac{H_6/2}{H_6/2 + H_8/2 + (H_{12}+H_{13})/3} \times 100 \quad (1), \qquad N_2 = \frac{H_8/2}{H_6/2 + H_8/2 + (H_{12}+H_{13})/3} \times 100 \quad (2), \qquad N_3 = \frac{(H_{12}+H_{13})/3}{H_6/2 + H_8/2 + (H_{12}+H_{13})/3} \times 100 \quad (3)$$

$$N_4 = \frac{(H_3+H_4+H_5)/5}{H_6/2 + H_8/2 + (H_{12}+H_{13})/3 + (H_3+H_4+H_5)/5} \times 100 \quad (4), \qquad N_5 = \frac{H_6/2 + H_8/2 + (H_{12}+H_{13})/3}{H_6/2 + H_8/2 + (H_{12}+H_{13})/3 + (H_3+H_4+H_5)/5} \times 100 \quad (5)$$

$$S\% = \frac{N_4 \times Mw_S}{N_4 \times Mw_S + N_5 \times Mw_B} \times 100 \quad (6), \qquad B\% = \frac{N_5 \times Mw_B}{N_4 \times Mw_S + N_5 \times Mw_B} \times 100 \quad (7)$$

N_1= mole ratio of *cis*-1,4-butadiene for polybutadiene part, N_2= mole ratio of *trans*-1,4-butadiene for polybutadiene part, N_3= mole ratio of 1,2-*vinyl*-butadiene for polybutadiene part, N_4= mole ratio of styrene for SBS block copolymer, N_5= mole ratio of butadiene for SBS block copolymer, H_6= ratio of ^{1}H-NMR integral for *cis*-1,4-butadiene unit, H_8= ratio of ^{1}H-NMR integral for *trans*-1,4-butadiene unit, H_{12} and H_{13}= ratios of ^{1}H-NMR integral for 1,2-*vinyl* butadiene unit, H_3, H_4, and H_5= ratios of ^{1}H-NMR

integral for aromatic unit, Mw_S= Molecular weight of styrene, Mw_B= Molecular weight of butadiene, Mw_{SBS}= Molecular weight of SBS block copolymer, S%= Styrene content of SBS block copolymer by weight. B%= Butadiene content of SBS block copolymer by weight.

Table 2. Compositions of butadiene units in polybutadiene parts

Sample	*cis-1,4 (%)*	*trans-1,4 (%)*	*1,2-vinyl (%)*
SBS-1	23	10	67
SBS-2	48	40	12
SBS-3	47	44	9
SBS-4	48	39	13
SBS-5	35	29	36
SBS-6	49	37	14

Table 3. Styrene-butadiene contents of the SBS block copolymers

Sample	Styrene content (%)	Butadiene content (%)
SBS-1	34	66
SBS-2	32	68
SBS-3	31	69
SBS-4	31	69
SBS-5	31	69
SBS-6	31	69

3.4. Elemental Analysis

The elemental analysis results show that all SBS block copolymers have approximately 10% hydrogen content and 90% carbon by weight. The hydrogen content was also estimated using ^{1}H-NMR spectra. The mole percentage of carbon atoms and the molar ratio H/C were also calculated using ^{1}H-NMR spectra according to the following equations (12-16). The comparison between elemental analysis and ^{1}H-NMR measurements are listed in Table 4. As it is seen in the table, the values obtained from elemental analysis and ^{1}H-NMR spectroscopy are very close to each other.

$$C\% = \frac{Mw_C \times (N_4 \times \#C_S + N_5 \times \#C_B)}{Mw_C \times (N_4 \times \#C_S + N_5 \times \#C_B) + Mw_H \times (N_4 \times \#H_S + N_5 \times \#H_B)} \times 100 \quad (12), \qquad H\% = 100 - C\% \quad (13),$$

$$\text{mol } C\% = \frac{C\%}{Mw_C} \quad (14), \qquad \text{mol } H\% = \frac{H\%}{Mw_H} \quad (15), \qquad H/C = \frac{\text{mol } H\%}{\text{mol } C\%} \quad (16)$$

$\#C_S$= number of carbon atoms per styrene unit for one molecule of SBS block copolymer, $\#C_B$=number of carbon atoms per butadiene unit for one molecule of SBS block copolymer, $\#H_S$= number of hydrogen atoms per styrene unit for one molecule of SBS block copolymer, $\#H_B$=number of hydrogen atoms per butadiene unit for one molecule of SBS block copolymer, Mw_C = atomic weight of carbon, Mw_H = atomic weight of hydrogen, C% = percentage of carbon by weight, H% = percentage of hydrogen by weight, mol C% = mole percentage of carbon, mol H% = mole percentage of hydrogen, H/C = molar ratio of hydrogen.

Table 4. Elemental contents of the SBS block copolymers

Sample	*C% (EA)*	*C% (^{1}H-NMR)*	*H% (EA)*	*H% (^{1}H-NMR)*	*Mol C% (EA)*	*Mol C % (^{1}H-NMR)*	*H/C ratio (EA)*	*H/C ratio (^{1}H-NMR)*
SBS-1	90.0	89.7	10.0	10.3	7.50	7.48	1.34	1.38
SBS-2	90.0	89.9	10.0	10.1	7.50	7.49	1.34	1.35
SBS-3	90.0	89.9	10.0	10.1	7.42	7.49	1.35	1.35
SBS-4	90.0	89.9	10.0	10.1	7.50	7.49	1.34	1.35
SBS-5	90.0	89.7	10.0	10.3	7.42	7.48	1.35	1.35
SBS-6	90.0	89.7	10.0	10.3	7.25	7.48	1.38	1.34

3.5. DSC Analysis

SBS-1 and SBS-5 have higher vinyl content than the other linear and radial SBS block copolymers and therefore they have higher T_g-onset values among six SBS block copolymers. The lowest T_g-onset value of PB was observed for SBS-3. Table 5 shows SBS-1 has the highest T_g-onset value for PB.

Olson *et al*. investigated a composition dependency of high vinyl polybutadiene (HVBD)/*cis*-polyisoprene (CPI) blends [26]. This study showed that T_g values are directly proportional to the percentage of the 1,2-*vinyl*-butadiene units for PB obtained from ^{1}H-NMR measurements. In our investigation, the T_g-onset values for each SBS block copolymer were plotted against the percentage of the 1,2-*vinyl*-butadiene units (Figure 5). Although all six SBS block copolymers have different structural properties such as molecular weight and linearity, the T_g-onset values are directly proportional to the percentage of the 1,2-*vinyl*-butadiene units. In addition, as it is seen in Figure 5, the results showed that the T_g-onset values are inversely proportional to the percentage of the *trans*-1,4-butadiene units.

Table 5. Glass transition temperatures

Sample	*Onset of T_g PB*
SBS-1	-42.6
SBS-2	-90.2
SBS-3	-91.8
SBS-4	-88.9
SBS-5	-69.2
SBS-6	-87.1

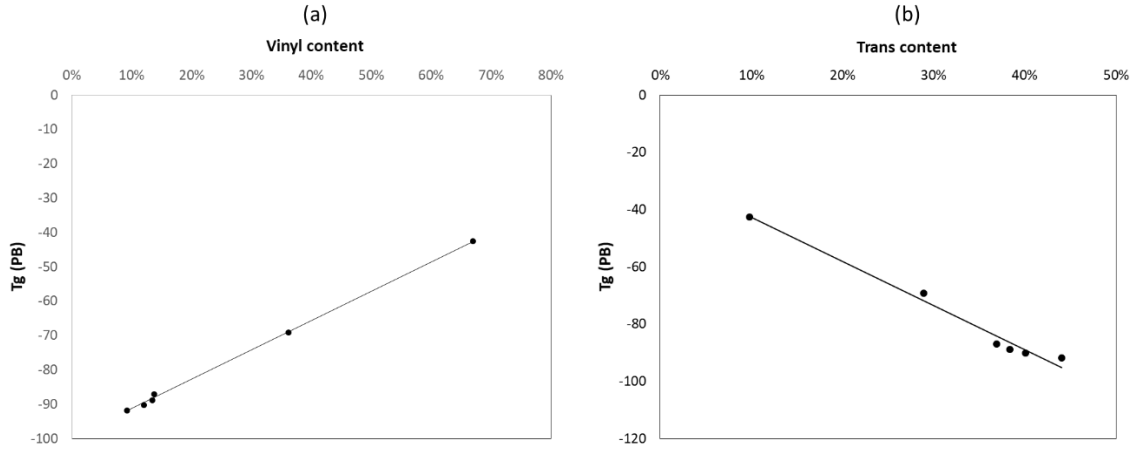


Figure 5. Linear relationship for SBS: (a) T_g-onset and 1,2-*vinyl*-butadiene content; (b) T_g-onset and *trans*-1,4-butadine content

4. CONCLUSIONS

Six commercial SBS block copolymers were characterized using NMR spectroscopy and elemental analysis. The compositions of 1,2-*vinyl*, *trans*-1,4, and *cis*-1,4 units in polybutadiene part of these copolymers were determined using ^{1}H-NMR spectroscopy. The results of the elemental analysis were compared to the ^{1}H-NMR measurements. The values obtained from elemental analysis and the ^{1}H-NMR spectroscopy are very close to each other, hence the elemental analysis results confirmed the accuracy of the calculations on ^{1}H-NMR integration.

DSC results showed that the T_g-onset values are directly proportional to the percentage of the 1,2-*vinyl* units and inversely proportional to the percentage of the *trans*-1,4 units in the SBS block copolymers which have different structural properties. Since the thermal sensitivity of bitumen causes cracking at low temperature, bitumen can be modified using SBS block copolymers which have low T_g-onset of polybutadiene. Among six SBS block copolymers, SBS-3 has the lowest 1,2-*vinyl* and the highest *trans*-1,4 butadiene units, thus SBS-3 has the lowest T_g-onset value of polybutadiene. The results of this analytical study recommend to use low 1,2-*vinyl* and high *trans*-1,4 content SBS molecules in bitumen modification as they have relatively low glass transition temperatures.

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CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

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