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SPECTRAL AND THERMAL CHARACTERIZATION OF STYRENE-BUTADIENE COPOLYMERS WITH DIFFERENT ARCHITECTURES

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Three types of styrene-butadiene copolymers ? two block copolymers (poly(styrene-*b*-butadiene-*b*-styrene) linear triblock copolymer, poly(butadiene-*b*-styrene)$_4$ star block copolymer) and a poly(butadiene-*co*-styrene) random copolymer have been investigated by Fourier transform infrared (FT-IR) spectrometry, nuclear magnetic resonance (^{13}C NMR) spectrometry, dynamical mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) in order to find correlations between their macromolecular structures and physical properties. The main spectral (FT-IR and ^{13}C NMR features which discriminate between block and random copolymers have been established. A band at 1702 cm^{-1} was found to be typical for the random copolymer, while the extinction coefficients of some bands (699 cm^{-1}(PS), 966 cm^{-1} (*trans* PB), 2848 cm^{-1} (PB) and 2920 cm^{-1} (PB) cm^{-1}) are different for star copolymer in comparison with the corresponding linear block copolymer. The relations for composition determination from ^{13}C NMR data for each type of copolymer were established. DSC and DMTA analyses were used to compare the degrees of mixing at the interface in the block copolymers and to examine the supermolecular structure of the block copolymers. The domain disruption temperature (T_{DD}) has been detected.

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1. Introduction

The block copolymers, which become phase separate due to thermodynamic immiscibility of the constituent blocks, are the subject of a large interest during the last decades due to their unique morphologies and useful properties. The numerous possibilities of variation of architecture and properties within this polymer class allow manufacturing of plastic materials with tailor-made properties for specific applications.

Of special interest are the so-called thermoplastic elastomers which are composed of glassy outer blocks and rubbery inner blocks. Some typical examples of such copolymers are the copolymers containing styrenic and elastomeric blocks. The elastomeric inner blocks can be unsaturate (poly(styrene-*b*-isoprene-*b*-styrene) (SIS); poly(styrene-*b*-butadiene-*b*-styrene) (SBS)) or saturate (poly(styrene-*b*-(ethylene-co-propylene)-*b*-styrene) (SEPS), poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS).

If the styrene content in the block-copolymer is small enough the block-copolymer will have a microphase separated morphology. This morphology can be proved by the existence of two glass transition temperatures [1] corresponding to the glassy and elastomeric phases. The separation of the outer glassy polystyrene (PS) blocks into discrete domains results in materials that behave as crosslinked rubbers at low temperatures but can be processed as thermoplastics at higher temperatures. The glassy PS domains act as reinforcing filler and provide physical crosslinks for the elastomeric network [2,3]. By heating to temperatures above their glass transition temperature (T_g) the rigid domains can be weakened. Therefore such materials can be processed at elevated temperatures like conventional thermoplastics, e.g. by extrusion or injection moulding.

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Such block-copolymers which are composed of glassy outer blocks and rubbery inner blocks, have a variety of practical applications: as impact modifiers [4,5] as matrices for conductive materials [6], as additives for the improvement rheological and mechanical properties of bitumen [7], as compatibilisers in polymer blends [8], etc. A typical example of succesfuly comercialised thermoplastic elastomers are the Kraton block-copolymers which are used in compounds, hot melt and tape adhesives, sealants and coatings. Kraton polymers give unique properties to bitumen enabling performance and longevity advantages when using this modified bitumen as a binder for paving roads and runways or when producing waterproofing materials for roofs and bridges.

Depending on temperature and PS content, the (minor) outer PS blocks can have different morphologies: cylindrical (in SBS Kraton 1102 [9,10], in SEBS Kraton G1652 with 29 wt. % styrene [11], PS-PIB-PS poly(styrene-*b*-isobutylene-*b*-styrene with 30 mol% styrene [12] or with 25-30 wt.% styrene [13]), body-centered cubic lattice (poly(styrene)–poly(ethylene-co-butylene)–poly(styrene) Kraton 1657 with 13 vol.% styrene [14]). It is accepted that these structures are equilibrium morphologies [15]. When the material is heated up to the order-disorder transition temperature (T_{ODT}) the PS domains disappear and the morphology of the copolymer changes to a disorganised/homogeneous one.

Due to the low content of PS component, it has been reported that the determination of T_g by DSC methods may be difficult for SBS copolymers (Kraton 1101 and Kraton 1102 [7,9,16,17]. However, for a Kraton copolymer 1102 SBS, other authors have determined by DSC the glass transition of the PS phase around 90 °C [3] while the NMR studies, for the same copolymer, have shown that the glass transition process spreads over the 50 ÷150 °C range: the T_g, as detected from the fraction of protons participating in the solid like component of the magnetic relaxation curve, spread over a broad temperature interval. The fraction of protons, was found to decrease to zero, over the 50 ÷ 50 °C range. It was assumed that segmental fluctuations of polystyrene take place around 50 °C and they start affecting the outer part of the cylinders first [3].

Hacaloglu et al. [18] have studied the differences between the properties of linear (block) and random styrene-butadiene copolymers. However, few studies have been performed with the aim of establishing the differences between the linear (block) and star styrene-butadiene copolymers [19,20]. It was found that star copolymers with PS-PIB arms have better mechanical properties than the corresponding linear block copolymers [19]. Shim and Kennedy [20] have studied the differences between star-blocks consisting of 5-21 polystyrene-polyisobutylene PS-PIB arms emanating from cyclosiloxane cores and the linear triblocks PS-PIB-PS of comparable arm molecular weight and compositions. They found that, compared with linear bloc copolymers, the star-block copolymers have higher tensile strength for lower molecular weight of the PS segment, can maintain their strength to higher temperature, have lower melt viscosity and, consequently, better processability and higher tolerance toward diblock-contamination. Additionally to these features, the flexural modulus of a nine armed polystyrene-polydiene star block-copolymer was found to be less than that exhibited by linear PS-polydiene-PS copolymer for temperatures approaching T_g of polyisoprene (PI), feature which may be due to the high segment density of PI near the center of the nine armed star block copolymer [21].

The improved properties were attributed to a combination of three factors [20,21]: 1) the star-block copolymers combines two types of crosslinking sites, a physical crosslink which disappear when heating above T_g of the hard segment, and a chemical crosslinking site which survives heating and helps to distribute the applied stress more evenly to the hard PS domains. 2) the larger number of glassy PS domains per volume unit leads to more finely dispersed “filler” particles. (3) the more uniformly dispersed hard domains allow for better phase separation.

This paper deals with a comparative spectral study of three types of styrene-butadiene copolymers (two blocks and one random) in order to establish correlations between their molecular structure, morphology, and some of the thermal properties.

2. Experimental

2.1 Materials

Three types of styrene-butadiene copolymers supplied by CAROM-Oneşti chemical mark-Romania have been studied: poly(styrene-*b*-butadiene-*b*-styrene) linear triblock copolymer, poly(butadiene-*b*-styrene)$_4$ star block copolymer and poly(butadiene-*co*-styrene) random copolymer (having the butadiene and styrene units randomly distributed along the macromolecular chain). Their characteristics and macromolecular structure are shown in Table 1 and Fig. 1.

Table 1. The characteristics of the studied styrene-butadiene copolymers.

Copolymer	Characteristics	Symbol
Poly(Styrene-*b*-Butadiene-*b*-Styrene) linear triblock copolymer	Linear; 30 wt. % styrene; Shear modulus G=6,3 MPa; T_g^{PS}=75 ºC (DSC); T_g^{PS}=98 ºC (DMTA); T_g^{PB}=-87 ºC (DMTA). Mw=65470 g/mol (GPC)	BS-lin
Poly(Butadiene-*b*-Styrene]$_4$ star copolymer	Star; 30 wt.% styrene; Shear modulus G=15,4 MPa; T_g^{PS}=80 ºC (DSC); T_g^{PB}=-93 ºC (DMTA), Mw=172300 g/ mol (GPC)	BS-star
Copolymer Styrene-Butadiene Random	Random; 25÷30 wt. % styrene; Shear modulus G=6,4 MPa; T_g=-28 ºC (DMTA), Mw=104300 g/mol (GPC)	BS-random

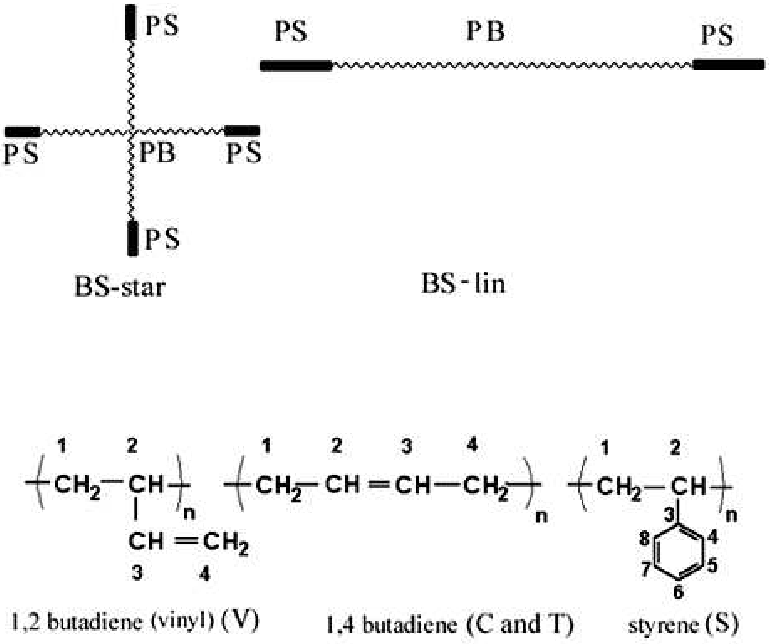

Fig. 1. Macromolecular structures and monomeric units of the styrene-butadiene block-copolymers. The length of each block is direct proportional with molecular weight of the block. 1,2 butadiene (*vinyl*) (V), *cis* (C) 1,4 butadiene, *trans* (T) 1,4 butadiene and *styrene* (S) units are shown.

The two block copolymers have been synthesized using the sequential anionic polymerisation method in a hydrocarbonated solvent. The basis of this method stands in the fact that, during the reaction, the "active centers" can maintain their activity if any impurities are removed from the solvent. The polymerisation reaction was performed in toluene. As initiator n-butyl litium was used. During the first step of the polymerisation reaction PS^-Li^+ was obtained by adding n-butyl litium. After this step butadiene was added in order to obtain a diblock PS-*b*-PB having the PB chain end active. By adding styrene in solution PS-*b*-PB-*b*-PS is obtained. A small amount of water was added in order to dezactivate the initiator.

The second step was different for the star copolymer: after the diblock PS-*b*-PB with active PB chain end was obtained, a coupling agent ($SiCl_4$) was added in the solution. Depending on the $SiCl_4$ amount various amounts of star copolymers with 3 or 4 arms were obtained. The probability of obtaining star copolymers with four arms is maximal. One important parameter of the polymerisation process is the temperature, which should not be above 60°C when PS^-Li^+ is formed. All chemicals used are high purity reagents.

2.2 Investigation methods

The copolymers have been studied by Fourier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR), Dynamical Mechanical Thermal Analysis (DMTA) and Differential Scanning Calorimetry (DSC).

a) The IR spectra of the copolymers have been recorded with an FT-IR apparatus Nicolet Protegé 460, in solid state. The copolymers were mixed with potassium bromide. Other series of samples were recorded by means of a Perkin-Elmer 577 apparatus using thin copolymer films obtained by solvent casting on KBr tablets. To obtain approximately the same thickness of the films, the concentration of all copolymer solutions was the same of 1 wt.%.

b) The ^{13}C NMR spectras have been recorded a Bruker Avance apparatus (400MHz) in $CDCl_3$, at room temperature.

c) Dynamical Mechanical Thermal Analysis, in single cantilever bending mode, was done using a DMA DX04T tester at a frequency of 1 Hz and 2 °C /min heating rate. The specimens for DMTA testing (dimensions 11.8 mm × 2.00 mm × 11.00 mm) were produced in a laboratory micro-injection molding machine (DSM). The barrel temperature was 150 °C and that of mold 25 °C.

d) The DSC curves were recorded with a DSC 12 E Mettler apparatus, under N_2 flow (50 cm^3/min), with 10 °C /min heating rate.

2.3 Results and discussion

2.3.1. FT-IR results

The FT-IR spectra and the IR absorption frequencies are presented in the Fig. 2 and Table 2, respectively.

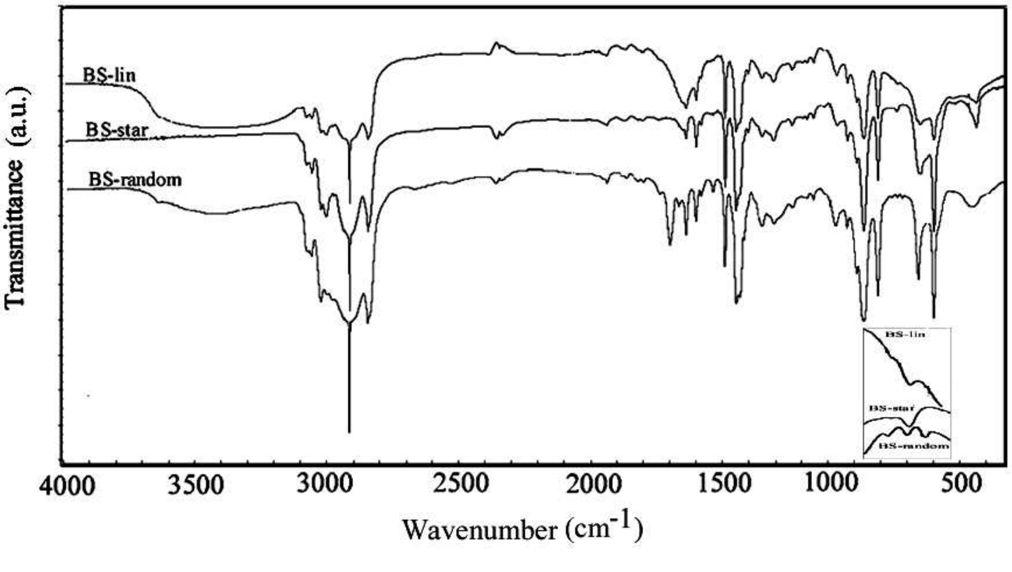

Fig. 2. FT-IR spectra of the studied copolymers.

Table 2. The frequencies (cm^{-1}) of the bands observed in the FT-IR spectra of the studied copolymers.

BS-lin	BS-star	BS-random	Assignments and observations
540 573 sh	540 573 sh	540-575	- PS units. For BS-lin, the shoulder is much more clearly evidenced in comparison with the others copolymers
699	698	699	Out-of-plane bending of the CH groups in the aromatic ring, all the 5 hydrogen carbons oscillating in phase. Typical for monosubstituited aromatic ring [22,23]. Strong and well evidenced in all copolymers.
727	728	726	Bending vibrations (wagging) of the CH groups in the *cis*-PB units [23,24].
748, 755 761 - 839 860 sh	748, 755 - - 842 -	759 - - 821 840 860	Deformation vibrations of the CH groups in the aromatic ring [22]. The band at 821cm^{-1} appears only in the random copolymer (BS-random). Possibly asigned to the CH groups in the *cis*-PB and *trans*-PB units.
911	911	911	Out-of-plane (wagging) vibrations of the CH$_2$ groups near the double bond of the *vinyl*-PB units. Strong and well evidencied in all copolymers. [22-25].
966	965	966	Out-of-plane (wagging) vibrations of the CH groups near the double bond in *trans*-PB units [22-25].
994	992	993	Out-of-plane bending of the –CH= groups in *vinyl*-PB units [22-24].
1028	1027	1029	PS units and stretching vibrations in *cis*-PB units ν(C-C) [25]
1070	1068	1074	PS
1154 1181	1155 1181	1155 1181	PS PS
1238	1238	1236	*cis*-PB [25]
1266 1311	1266 1312	sh 1310	PS or CH$_2$ twisting vibrations in *trans*-PB or *cis*-PB units [25]. Deformation vibrations of the CH units in *cis*-PB units δ(=CH) [25]
1351	1351	1351	Deformation vibrations (wagging) of the CH$_2$ groups in *trans*-PB and *cis*-PB units [25]
1403	1403	-	Deformation vibrations in *cis*-PB units δ(=CH) [25]
1419 sh	1419 sh	1419	Deformation vibrations δ(CH$_2$=) in *vinyl*-PB units [25]
1451, (1437 sh) 1492	1451, (1437 sh) 1492	1450, 1437 1493	Strong and well evidenced in all copolymers. can be attributed to the deformation vibrations of the CH$_2$ groups in *cis*-PB and *trans*-PB units [25]. The band at 1451 cm^{-1} could also be assigned to the *vinyl*-PB δ(CH) in CH$_2$=CH-. The bands 1451 cm^{-1} and 1493 cm^{-1} may be also attributed to the stretching vibrations of the carbons in the aromatic ring [22].
1583	1582	1582	Assigned to the stretching vibrations of the carbons in the aromatic ring [22]. Well evidenced in all copolymers.
1601	1601	1602	Assigned to the stretching vibrations of the carbons in the aromatic ring [22]. Well evidenced in all copolymers.
1639	1639	1638	Stretching vibrations ν(C=C) in *vinyl*-PB group [25]
1650	1651	1650 sh?	Stretching vibrations ν(C=C) in *cis*-PB group [25]
1666 sh	1666w	1666	Well evidenced especially in BS-random. Can be assigned to the stretching vibrations ν(C=C) in *cis*-PB or *trans*-PB units.
-	-	1702	Appears only for BS-random
1941	1941	1940	PS units
2848	2848	2848	Symmetrical stretching vibrations of the CH$_2$ groups in PB-units ν(CH$_2$) [25].
2920	2917	2918	Asymmetrical stretching vibrations of the CH$_2$ groups in PB-units ν(CH$_2$). [25].
2978	2976	2977	Symmetrical stretching vibrations ν(CH$_2$=) in *vinyl*-PB units [25]
3005 3024	3005 3024	3001 3025	these bands are assigned to the stretching vibrations of the CH$_2$ groups in PB units and CH groups in the aromatic ring. Due to the overlapping of these bands the assignement is more difficult.
3060	3060	3061	
3080	3079	3073	Symmetrical stretching vibrations ν(CH$_2$=) in *vinyl*-PB units [25]
3104	3104	3102	

w, sh, s stands for weak, shoulder, strong.

ν and δ stands for: stretching and bending vibrations.

In the IR spectra of the copolymers there are many bands which can be attributed to more than one absorbing group. However, several bands can be attributed with a high degree of confidence to one single absorbing unit and can be used for qualitative and quantitative analysis. Such are the bands attributed to the C=C groups (ν C=C) (1639 cm^{-1} *vinyl* ; 1650 cm^{-1} *cis*) [24], to the =CH- groups (727 cm^{-1} *cis*-PB CH_{wag}, 966 cm^{-1} *trans*-PB CH_{wag}, 1311 cm^{-1} *cis* δ(=CH) [24], to the $–CH_2$- groups (1419 cm^{-1} *vinyl*-PB δ CH_2) [24], to the carbon atoms in the aromatic ring (1493 cm^{-1} $\nu_{C=C}$)) to the aromatic ring (1582 cm^{-1}, 1601 cm^{-1}, 1492 cm^{-1}).

The bands corresponding to the CH out-of-plane vibrations, typical for substituents at double bond, are located at 727 cm^{-1} *cis*-PB, 966 cm^{-1} *trans*-PB, 993 cm^{-1} *vinyl*-PB [24]. The stretching vibrations of the CH and CH_2 groups are located in the 2800-3100 cm^{-1} [24].

The IR spectra of the BS-lin and BS-star copolymers are quite similar. Due to the statistical structure of the random copolymer (BS-random), there are dissimilarities between the spectra of the BS-lin (BS-star) and BS-random.

In the block copolymers there is a clear band at 540 cm^{-1} (corresponding to the styrene units) while for the random copolymer there is a large band, centered at 550 cm^{-1}. Due to the interactions between PB and PS units in the random copolymer, which are not so important in block copolymers due to the domain structure, this band is larger in BS-random copolymer.

For the same reason the band at 840 cm^{-1} (attributed to the PS units) has a complex structure being splitted in three bands (821, 840 and 860 cm^{-1}) for the BS-random copolymer while for the two block copolymers this band has a more simple structure (see Table 2 and the detail in Figure 2). The presence of the bands at 1666 and 1702 cm^{-1} in the BS-random spectra, which are not present in the IR spectra of the PB and PS, can be also attributed to the stronger interactions between the PB and PS units in the BS-random copolymer.

The band at 759 cm^{-1} (attributed to the PS units) has a more complicated structure in the block copolymers while in the random copolymer its structure is simpler. Thus, for the BS-lin copolymer three bands can be observed (at 748, 755 and 761 cm^{-1}) while for the BS-star copolymer only two bands appear at 748 and 755 cm^{-1}. The presence of the band at 761 cm^{-1} only for the BS-lin copolymer can be attributed to the differences in the molecular structure of the two block copolymers (see Figure 1).

In order to find out whether the spectral extinction coefficients (ε(ν)) have similar values for the two block copolymers (BS-lin and BS-star), the spectral extinctions E of the IR bands of the BS-star copolymer have been plotted against the spectral extinction of the same bands in the BS-lin copolymer.

$$E = \ln (1/T) = \varepsilon(\nu)\, c\, d \qquad (1)$$

where E is tha spectral extinction, T the transmittance, c the concentration of the absorbing unit at the frequency ν, and d is the film thickness.

From the following considerations the obtained plot should be a straight line passing through the origin of the axes: the concentration of the absorbing units in the copolymer film is direct proportional with the relative number (molar concentration) of these units in the copolymer. Owing to the fact that the BS-star and BS-lin copolymers have the same relative number of the absorbing units (see NMR results) the ratio between the concentration of the absorbing units in BS-star copolymer film and the corresponding concentration in BS-lin copolymer film should be the same for all the absorbing units (IR bands) considered. In consequence, as the film thicknesses d^{star} and d^{lin} are constant, the $E^{star} / E^{lin} = \varepsilon^{star}(\nu)/\varepsilon^{lin} (\nu) \cdot c^{star}/c^{lin} \cdot d^{star}/d^{lin}$ should be constant and the above mentioned plot should be a straight line passing through the origin of the axes.

In order to have this comparison more accurate, an additional star block copolymer (Kraton type from Shell), with similar composition and macromolecular structure as the BS-star copolymer (see NMR results) was used.

From the Figure 3 it can be seen that, although stright lines are obtained, for some bands (699 cm^{-1} (PS), 966 cm^{-1} (*trans* PB), 2848 cm^{-1} (PB) and 2920 cm^{-1} (PB) the extinction coefficients are higher for both star copolymers (BS-star and Kraton).

These differences between the extinction coefficients are connected with the different macromolecular structures of the BS-lin and BS-star copolymers. The fact that the extinction coefficients of PS at 699 cm^{-1} and PB at 966 cm^{-1} are influenced by the macromolecular structure of these copolymers has already been reported elsewhere [23].

Due to the differences in composition this evaluation was not made on BS-random copolymer.

We can conclude that the IR spectroscopy can be used to differentiate between copolymers with vaioust macromolecular structures. Thus, the following bands at 699 cm^{-1}(PS), 966 cm^{-1} (*trans*-PB), 2848 cm^{-1} (PB) and 2920 cm^{-1} (PB) cm-1) have higher extinction coefficients are for star copolymer than for the corresponding linear block copolymer. The band at 540 cm^{-1} is larger and the band at 840 cm^{-1} is more complex in BS-random copolymer than in the block copolymers. There are also bands typical for the BS-random copolymer (1666 cm^{-1} and 1702 cm^{-1}). The most important differences in the spectra of the three copolymers appear in the 1550-1750 cm^{-1} region.

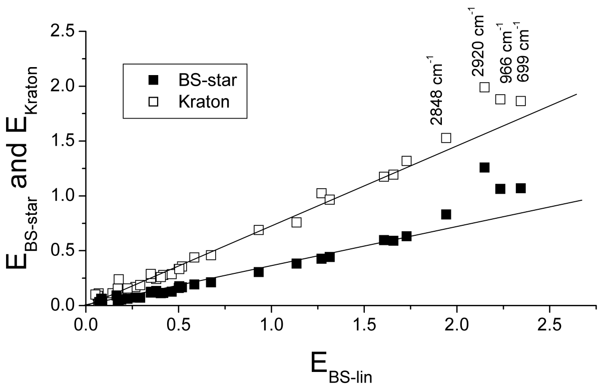

Fig. 3. The spectral extinctions (E=$\varepsilon_{(v)}$cd) of various absorption bands of the BS-star (full square) and Kraton (empty square) copolymer plotted against the spectral extinction of the same bands in the BS-lin copolymer.

2.3.2. ^{13}C NMR results

For the sake of clarity the NMR spectra have been divided in two regions in accordance with the carbon atoms responsible for the respective signals (Fig. 4):

(1) the 25÷45 ppm region corresponding to the C1 and C2 carbons in *vinyl* or styrene groups and the C1 and C4 carbons in the *cis* and *trans* units (see Fig. 1).

(2) the 125÷132 region corresponding to the C3 and C4 carbons in *vinyl* units, C2 and C3 in *cis* and *trans* units, C3÷C8 in styrene units (see Fig. 1).

In this discussion the C, T, V, and S capitals will stand for, 1,4 *cis*, 1,4 trans, *vinyl* and styrene units (see Figure 1). The S and V units will denoted by "b". The symbols "meso" (m) and "racemic" (r) will stand for consecutive S or V units having similar and opposed relative configurations, respectively.

The NMR analysis was performed considering structures containing two (diads) or three (triads) monomeric units. The monomeric unit responsible for the NMR signal will be noted with capital letters having an index showing which carbon atom in the monomeric unit is responsible for the respective signal.

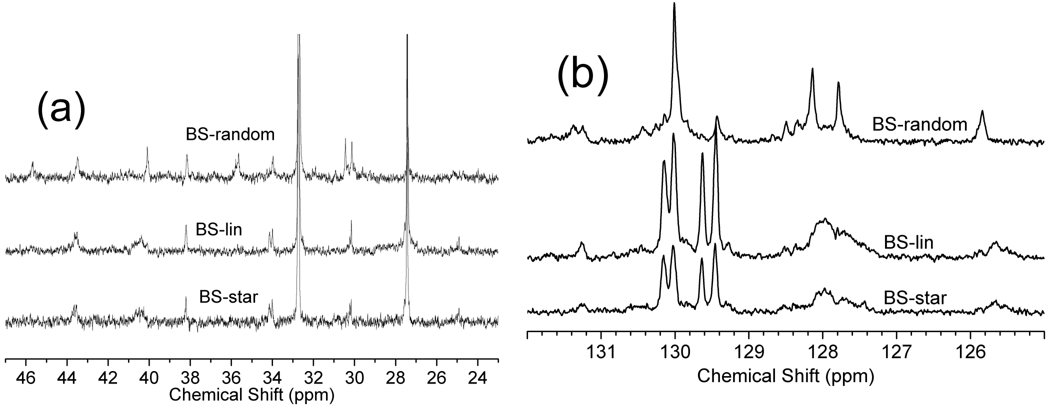

Fig. 4 : ^{13}C NMR spectra of the studied copolymers in two spectral regions: (a) 24-46 ppm and (b) 125-132 ppm.

The identification of the signals, which was based mainly on the assignment performed by Sato et all [26] but also on the assignments made by other authors [27-35] is presented in Table 3.

Table 3. Assignements of the ^{13}C NMR signals in the NMR spectra of the studied copolymers.

BS-random		BS-lin and BS-star	
Signal frequency (ppm)	Assignement	Signal frequency (ppm)	Assignement
-	-	24.90 and 25.01	C4-v
27.38	C4-1,4 and 1,4 C1	27.43	C4-1,4 and 1,4 C1
30.12	T4-v	30.15 and 30.23	T4-v
30.43	T4-s		
32.72	T4-1,4 ; 1,4-T1; 1,4-v-C1	32.72	T4-1,4 ; 1,4-T1 ; 1,4-v-C1
33.95	1.4-V1-1,4	33.99 and 34.14	1.4-V1-1,4
35.64 and 35.78	1,4-S1-1,4; 1,4-S1-b(m); 1,4-V1-b (r);b-s(r)-C1		
38.16	1,4-v-T1	38.19	1,4-v-T1
		40.37	
40.1	1,4-s-T1		
43.49	b-S2-1,4 1,4-V2-1,4	43.49 and 43.63	1.4-V2-1,4
45.66 and 45.69	1,4-S2-1,4		
114.22	V4	114.22 and 114.33	V4
125.83	S6	125.65	S6
		127.50 ÷ 128.25	S4,8 and S5,7
127.78	S4,8 and S5,7		
128.13	S4,8 and S5,7		
128.34	1,4-v-T2-t		
128.49	1.4-v-T2-c		
129.43	t-C3-c	129.44	t-C3-c
-		129.62	t-C2-c and c-C2,3-c
130.01	t-T3-c and t-T2,3-t	130.02	t-T3-c and t-T2,3-t
130.14	t-T2-c	130.14	t-T2-c
130.25			
130.43			
131.25 and 131.37	1,4-v-T3-1.4	131.26	1,4-v-T3-1.4
142.7	V3	142.58-142.76	V3
145.33	S3	145.37	S3

The copolymer composition, (percents of monomeric units) was determined by taking into account the mentioned assignments and the direct proportionality between the signal area and the number of atoms responsible for the respective signals.

If one NMR signal was produced by more than one carbon atom, the signal area was considered direct proportional with the total number of carbon atoms responsible for that signal.

A system of equations resulted that provided the percentage of various diad/triad structures and consequently the percents of the four types of the monomeric units in the copolymers (see Table 4).

The equations used in the case of BS-random copolymer is presented below (A denotes the area of the signal, the subscript stands for the frequency of the signal). Every term either denoted by “A” or by groups of two (diads)/three (triads) monomeric units stands for the number of carbons responsible for the NMR signal.

The NMR spectra were analysed using the MestRec 24 software. The numerical calculations were performed using an Microsoft Excel based software.

$$1{,}4Sb(m) = A_{42.4\div 42.95}\,[1{,}4S_2b] - A_{37.8}\,[1{,}4S_1b(r)] \tag{2}$$

$$bv1{,}4 = bv(r)C_1 + A_{31.9\div 32.3}\,[bv(m)C_1] + A_{37.2\div 37.5}\,[bv(m)T_1] + A_{38.9\div 39.1}\,[bv(r)T_1] = 0.20. \tag{3}$$

It was taken into account that $A_{33.1\div 33.9}\,[bv(r)C_1 + bs(m)C_1]=0$

$$1{,}4Vb(r) = 1{,}4vb - 1{,}4V_1b(m) = A_{114.2}\,[V] - A_{33.9\div 34.3}\,[1{,}4V_1 1.4] - A_{38.5\div 39.5}\,[bV_2b] - bv1{,}4. \tag{4}$$

It will be taken into account that: $A_{34.4\div 34.8} = 1{,}4V_1b(m) + 1{,}4sC_1 = 0$.
It will be used bv1,4 calculated with (3).

$$bs(r)C = A_{35.4\div 36.0}\,[1.4S1.4 + 1.4Sb(m) + 1.4Vb(r) + bs(r)C] - A_{45.6}\,[1.4S_2 1.4] - 1{,}4Sb(m) - 1{,}4Vb(r). \tag{5}$$

It will be used 1,4Sb(m) şi 1,4Vb(r) calculated with (2) respectively (4).

$$C = 1{,}4C_1 + A_{31.9\div 32.3}\,[bv(m)C_1] + 1{,}4vC_1 + A_{33.1\div 33.9}\,[bv(r)C_1 + bs(m)C_1] + 1{,}4sC_1 + bs(r)C_1. \tag{6}$$

It will be taken into account that: $1{,}4vC_1 = A_{33.9\div 34.3}\,[1{,}4V_1 1{,}4] - A_{38.1}\,[1{,}4vT_1]$; $A_{34.4\div 34.8} = 1{,}4V_1b(m) + 1{,}4sC_1 = 0$; It will be used $bs(r)C_1$ calculated with (4)
thus, it can be obtained:

$$C = 1{,}4C_1 + 1.05 \tag{7}$$

$$C = C_4 1{,}4 + A_{24.9}\,[C_4v] + A_{25.2}\,[C_4s] \tag{8}$$

results

$$C = C_4 1{,}4 \tag{9}$$

$$\begin{aligned} T = {} & 1{,}4T_1 + A_{37.2\div 37.5}\,[bv(m)T_1] + A_{38.9\div 39.1}\,[bv(r)T_1] + A_{38.1}\,[1{,}4vT_1] + A_{40.1}\,[1{,}4sT_1] + \\ & + A_{39.2\div 39.5}\,[bs(m)T_1] + A_{40.93\div 40.95}\,[bs(r)T_1] \end{aligned} \tag{10}$$

results

$$T = 1{,}4T_1 + 1.30 \tag{11}$$

$$T = T_4 1{,}4 + A_{30.1}\,[T_4v] + A_{30.4}\,[T_4s] \tag{12}$$

$$\text{results } T = T_4 1{,}4 + 2.1 \tag{13}$$

$$C1{,}4 + 1{,}4C = A_{27.4} = 1.20 \tag{14}$$

$$T1{,}4 + 1{,}4T = A_{32.7}[T1{,}4 + 1{,}4T + 1{,}4vC_1] - 1{,}4vC_1 \tag{15}$$

it will be taken into account that $1{,}4vC_1 = A_{33.9\div 34.3}\,[1{,}4V_1 1{,}4] - A_{38.1}\,[1{,}4vT_1]$
results

$$T1{,}4 + 1{,}4T = 9.2 \tag{16}$$

From equations 7, 9, 11, 13, 14, 16, results for BS-random: T = 64%,C = 6%, V= 9%, S=20%.

For the block copolymers (BS-lin and BS-star) the system of equations was simplified due to the macromolecular structure which is more simple for the block copolymers than for the random ones.

$$C = C_4 1{,}4 + A_{24.9}\,[C_4 v] \tag{17}$$

results

$$C = C_4 1{,}4 + 0.8 \tag{18}$$

$$1{,}4vC_1 = A_{33.99\div34.16}\,[1{,}4V_1 1{,}4] - A_{38.18}\,[1{,}4vT_1] \tag{19}$$

$$C = 1{,}4C_1 + A_{31.6\div32.13}\,[vv(m)C_1] + 1{,}4vC_1 + A_{33.3\div33.5}\,[vv(r)C_1] \tag{20}$$

It will be used $1{,}4vC_1$ calculated with (19)

results

$$C = 1{,}4C_1 + 0.9 \tag{21}$$

$$T = T_4 1{,}4 + A_{30.1}\,[T_4 v] \tag{22}$$

results

$$T = T_4 1{,}4 + 2.7 \tag{23}$$

$$T = 1{,}4T_1 + A_{37.2\div37.5}\,[vv(m)T_1] + A_{38.9\div39.1}\,[vv(r)T_1] + A_{38.1}\,[1{,}4vT_1] \tag{24}$$

results

$$T = 1{,}4T_1 + 3.4 \tag{25}$$

$$C1{,}4 + 1{,}4C = A_{27.4} = 39 \tag{26}$$

$$T1{,}4 + 1{,}4T = A_{32.7}[T1{,}4 + 1{,}4T + 1{,}4vC_1] - 1{,}4vC_1 \tag{27}$$

It will be taken into account that $1{,}4vC_1 = A_{33.9\div34.3}\,[1{,}4V_1 1{,}4] - A_{38.1}\,[1{,}4vT_1]$

results

$$T1{,}4 + 1{,}4T = 5 \tag{28}$$

From the equations 18, 21, 23, 25, 26, 28, the percentage of styrene, *cis*, *trans* and *vinyl* monomeric units can be obtained.

The compositions of the copolymers (percentage of monomeric units) it shown in the table 4.

Table 4. The compositions of the studied copolymers (percentage of monomeric units).

	T (mol %)	C (mol %)	V (mol%)	S (mol %)	S (wt. %).
BS-lin	42.5	31.6	8.6	17.3	28.7
BS-star	40.0	32.8	9.1	18.1	29.7
BS-random	64.2	6.2	9.3	20.3	32.5

From the NMR analysis it can be concluded that the compositions of the BS-lin and BS-star copolymers are quite similar. This conclusion is supported, besides the NMR calculations (see Table 4) by the direct proportionality between the signal areas corresponding to the same diad/triad structures in the BS-lin and BS-star copolymers (Fig. 5). The proportionality was also valid for a Kraton type star copolymer (with four BS arms). This conclusion agrees with the same polymerisation procedure and initial monomer concentrations used for the BS-lin and BS-star copolymers.

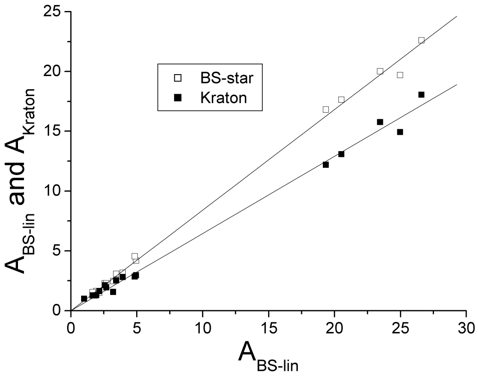

Fig. 5. The ^{13}C NMR areas of various signals for the BS-star (full square) and Kraton (empty square) copolymer plotted against the areas of the same signals in the BS-lin copolymer.

There is also an agreement between the monomer concentrations obtained by NMR analysis and the monomer concentrations used (introduced) at the beginning of the polymerisation process for the studied copolymers (BS-lin, BS-star, BS-random).

Regarding the linkage of the monomeric units, it can be concluded that in the block copolymers (BS-lin and BS-star) the *vinyl* units are mainly between 1,4 (*cis* or trans) units. Similarly, in the random copolymer (BS-random) the *vinyl* and styrene units are mainly linked between 1,4 (*cis* or trans) units.

Some differences between the NMR spectra of the block copolymers (BS-lin and BS-star) and the spectra of the random copolymer (BS-random) can be observed. Thus, due to the low content of *cis* units in BS-random the signals at 129.45, 129.63 and 130.15 ppm are less evidenced in BS-random than in the block copolymers. The signals (127.50 ÷128.25 ppm) attributed to the C4, C8, C5 and C7 carbons in styrene units (see Figure 1 and Figure 4) are much better resolved in the block copolymers due to the block structure, the interactions between styrene units being much more important in comparison with the random copolymer.

2.3.3. DSC results

In the DSC curves (see Fig. 6) the glass transition of the PS domains in the block copolymers can be detected around 75 °C for BS-lin and 80°C for BS-star copolymer. These values are lower in comparison with the usual values for bulk PS. As is expected, BS-random copolymer does not exhibit a glass transition in the studied temperature interval.

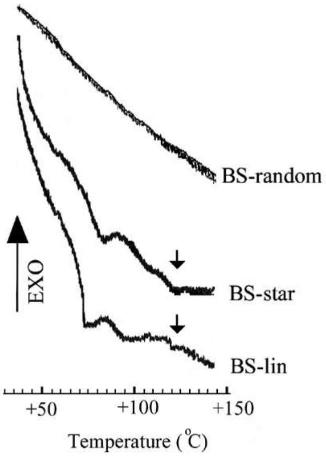

Fig. 6. DSC curves for the studied copolymers (heating rate 10°C / min).

It has been reported by many authors that the glass transition of the PS phase in such copolymers takes place at lower values comparatively with the bulk PS. For two SBS copolymers (Kraton K1102, M_w=72000 g/mol, 28.5 wt.% styrene and Kraton1101 M_w=91000 g/mol, 31 wt.% styrene) the T_g of PS phase was found to be 61 °C and 68 °C respectively [9] while for a SEBS copolymer (Kraton G1652 Mw=86800 g/mol, 29 wt.% styrene) the T_g of PS phase was found to be 83 °C [36]. This "lowering effect" was interpreted as a consequence of premature molecular motions, in polystyrene domains, induced by the PB segmental mobility [37]. Several authors have reported that ultrafine films [38] as well as systems confined to nanopores [39-41] show a lower T_g comparatively with the bulk T_g for smaller thickness or reduction of the size of nanopores. From this point of view, the copolymers with microphase separated morphology can be considered as finite confined systems. This confinement applied by the PB matrix to the PS discrete phase may decrease the T_g of PS in SBS as compared to those of the PS in the bulk. Also, the interfacial interaction and the miscible fraction at the domain boundaries lower the values of the T_g [9].

2.3.4. DMTA results

In the DMTA spectra (tg δ versus temperature) (see Figure 7), the glass transition of the PB phase can be detected around –92 °C and –86 °C for BS-star and BS-lin respectively, being higher for the BS-lin in comparison with BS-star. The glass transition of the PS phase could be detected, at 94°C, only for BS-star copolymer. This facts can be attributed to the better intermixing of PS and PB chains at interface for BS-lin copolymer.

The glass transition of BS-random copolymer is located at around –28 °C.

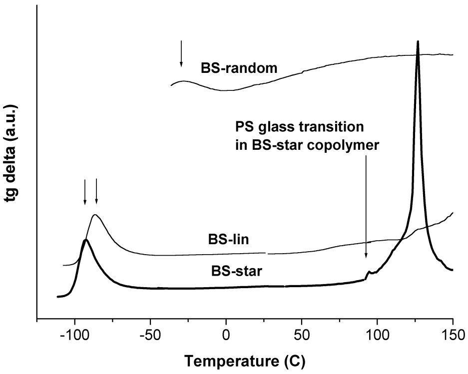

Fig. 7. DMTA spectra (tg δ versus temperature) of the styrene-butadiene copolymers. For clarity the curves have been vertically shifted. There are indicated by arrows the glass transitions of the copolymers and polystyrene phase in the BS-star copolymer.

It is interesting that the peak at 125 °C is very strong for BS-star but appears as a shoulder for BS-lin. In the DMTA curve of BS-random copolymer such peak does not appear. This peak cannot be associated with the glass transition of the PS phase which takes place at 95 °C in BS-star and probably in the same temperature interval for BS-lin

It should be noted that in DSC curves a process was observed at approximately 125 °C (see arrows in Figure 6) which is more intense for BS-star copolymer. When the samples were heated during a second run this process did not appear anymore. Some authors have connected this process with the existence of a pure PS phase mixed with the copolymer. In the opinion of the authors, this PS phase may be formed by the PS blocks which remained unreacted with PB during the polymerisation process [16].

If it is difficult to detect the T_g^{PS} for the PS domains in the copolymer it will be much more difficult to detect the T_g^{PS} of the pure (unlinked to PB) PS domains for which we can assume at least a lower volumic concentration than that of the PS domains (blocks). Thus, this assumption cannot explain the intensity of the corresponding peak for the BS-star copolymer.

From the plots of Young modulus versus temperature (Figure 8) it can be observed that the modulus of the block copolymers decreases approximately linearly with increasing temperature up to 125 °C after that it levels off.

Thus, we consider that at this temperature (125°C) the PS domains completely soften and, as a consequence of the oscillations imposed by DMTA analysis method, they start to deform but without losing their integrity in the PB matrix as long as the temperature do not exceeds T_{ODT}. This temperature (125°C) was called "Domain Disruption Temperature" [42] and was detected by DMTA experiments [42,43].

The fact that in this process are involved deformations of the PS domains, deformations imposed by the DMTA analysis method, explains why it is difficult to observe this process in DSC curves.

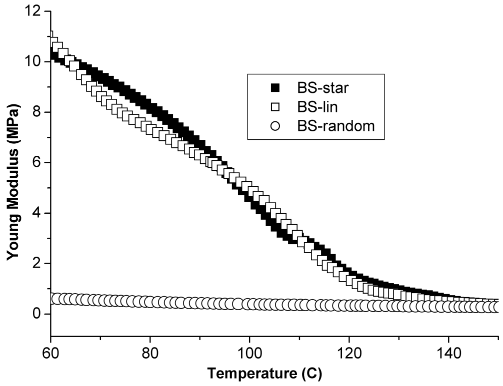

Fig. 8. Young modulus versus temperature for the three copolymers as determined from DMA measurements.

During the first DSC heating run (see Fig. 6), as a consequence of the softening of the PS domains, relaxation processes occurred which released the small mechanical energy stored in the material. These relaxation processes did not occurred during the second heating run. This is the reason why the thermal effects could be observed in DSC curves only in the first heating run.

3. Conclusions

There are differences between the FT-IR and ^{13}C NMR spectra of the random copolymer (BS-random) and block copolymers (BS-lin and BS-star). In the IR spectra of the random copolymer the band at 540 cm^{-1} is larger and the band at 840 cm^{-1} is more complex comparatively with the block copolymers. In the BS-random spectra there are bands which are not present in the spectra of the block copolymers (821 cm^{-1}, 1538 cm^{-1}, 1702 cm^{-1}). These differences can be explained by the interactions between styrene and butadiene units which are more intense for the random copolymer.

The DMTA and DSC analysis evidenced a process at 125 °C in the block copolymers which did not appeared in the random copolymer. This process consisted in the softening of the PS domains, without losing their integrity, at a temperature called "domain disruption temperature" (T_{DD})

The main differences in the mechanical and thermal properties of the block copolymers (BS-lin and BS-star) can be attributed to the differences in the supermolecular structure of the block copolymers and can be most easily evidenced by DMTA experiments. The supermolecular structure, which varies with the temperature, affects mainly the mechanical properties of the copolymers. This is why DMTA, which combines the thermal and mechanical analysis, proved to be the best method which can differentiate between the two block copolymers. Thus, it was concluded that in the BS-lin copolymer there is a better intermixing of the PB and PS chains at interface comparatively with the BS-star copolymer. Also, the PS domains in the BS-star copolymer the PS domains are smaller and more uniformly dispersed in the PB matrix.

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