



## BROMINATION OF SOME STYRENE-DIENE BLOCK COPOLYMERS

E. BUZDUGAN,\* P. GHIOCA, E. G. BADEA and S. SERBAN

Chemical Research Institute ICECHIM, Spl. Independentei 202, 77208 Bucharest, Romania

N. STRIBECK

Institut für Technische und Makromolekulare Chemie, Universität Hamburg, 20146 Hamburg, Germany

(Received 18 June 1996; accepted in final form 22 October 1996)

**Abstract**—The bromine addition at the polydiene block double bonds of a radial styrene-butadiene (SBS) and a linear styrene-isoprene (SIS) block copolymer (thermoplastic elastomers), in tetrahydrofurane solution at 0°C, has been investigated by IR spectroscopy. In both cases the bromine reacts exclusively with the polydiene middle block double bonds; the polystyrene blocks are unaffected. The bromine reacts preferentially with the 1,4-type (*cis* and *trans*) double bonds of the polybutadiene block of SBS. At low bromination level (below 5%) the bromine reacts mainly with the 1,4-*cis* type double bonds of polyisoprene block of SIS, while at higher bromination level the bromine presents the same reactivity towards the 1,4-type (*cis* and *trans*) and vinylic (3,4-type) double bonds. © 1997 Elsevier Science Ltd

### INTRODUCTION

Thermoplastic elastomers based on styrene-diene block copolymers exhibit the melt processing characteristics of thermoplastic materials and many of the physical properties of vulcanized rubber. This behavior is a consequence of the thermodynamic incompatibility of polystyrene and polydiene (polybutadiene or polyisoprene), resulting in a two-phase structure of glassy polystyrene domains dispersed in a rubbery polydiene matrix.

Since in the styrene-diene block copolymer the polydiene blocks are unsaturated, they can participate in many additional reactions like hydrogenation, halogenation, etc.

Bromine addition at the double bonds of polydiene blocks may be interesting for at least two reasons: On one hand, styrene-diene block copolymers having brominated polydiene blocks (called brominated block copolymers) are useful intermediate materials for subsequent chemical reactions such as grafting or substitution reactions [1], the result of which are polymers with expected new properties as compared with the base copolymer.

On the other hand, brominated block copolymers may be important for a better understanding of the morphology of thermoplastic rubbers in general. If investigated by small-angle X-ray scattering (SAXS) the polystyrene block has a higher electron density than the polydiene (polybutadiene or polyisoprene) block. By bromination of the polydiene block the electron density of the polydiene phase increases until zero contrast for equal electron densities and at higher bromination level it is even possible to realize a contrast inversion.

### EXPERIMENTAL

#### Materials

Two commercial products, both supplied by CAROM S.A., Onesti, Romania were studied. CAROM TS 30 is a radial styrene-butadiene block copolymer; CAROM TLI 30 is a linear styrene-isoprene triblock copolymer.

The radial SBS block copolymer CAROM TS30 has four arms each consisting of an outer polystyrene and an inner polybutadiene block. The styrene content is 30%, the total molecular mass  $M_w = 135,000$  g/mol, the molecular mass of the polybutadiene block is  $M_w = 24,000$  g/mol. According to IR spectroscopy [2] its polybutadiene block contains 34.7% 1,4-*cis* units, 52.1% 1,4-*trans* units and 13.2% 1,2 (*vinyl*) units.

The SIS triblock copolymer CAROM TLI 30 has a polyisoprene middle block and two polystyrene end blocks. The styrene content is 30%, the total molecular mass  $M_w = 105,000$  g/mol, the molecular mass of the polyisoprene block is  $M_w = 73,500$  g/mol. According to IR spectroscopy [3-5] its polyisoprene block contains 88.9% 1,4-*cis* units, 2.1% 1,4-*trans* units and 9.0% 3,4 (*vinyl*) units.

#### Bromination

Details concerning the bromination technique were published elsewhere [1]. The bromination reactions were carried out in tetrahydrofurane (THF) solution at 0°C. The amount of bromine needed for a certain bromination degree of the polydiene block was added dropwise as THF solution into the reaction vessel containing the block copolymer solution. The bromination reactions were monitored recording the optical density of the reaction mixture. After the total consumption of bromine (constant value of optical density), the brominated block copolymers were recovered from THF solution by spin-casting. The brominated block copolymers were characterized by elemental analysis and IR spectroscopy.

#### IR spectroscopy

In order to record IR absorption spectra, measurements were carried out on a SPECORD M 80 (Carl Zeiss Jena)

\*To whom all correspondence should be addressed.

spectrometer using films of 50  $\mu\text{m}$  thickness obtained from chloroform solutions on KBr window.

For the brominated SBS samples the peaks were assigned considering the following characteristic absorption bands [1, 2, 6, 7]:

- 540  $\text{cm}^{-1}$  for the C—Br bond;
- 714  $\text{cm}^{-1}$  for the 1,4-*cis* structural units (shifted for SBS block copolymer; for pure polybutadiene being 730  $\text{cm}^{-1}$ );
- 910  $\text{cm}^{-1}$  for the 1,2 (*vinyl*) structural units;
- 965  $\text{cm}^{-1}$  for the 1,4-*trans* structural units;
- 1600  $\text{cm}^{-1}$  for the phenylic ring as internal standard [6, 7].

For the brominated SIS samples the peaks were assigned considering the following characteristic absorption bands (3–7):

- 540  $\text{cm}^{-1}$  for the C—Br bond;
- 836  $\text{cm}^{-1}$  for the total 1,4-type (*cis* + *trans*) structural units;
- 890  $\text{cm}^{-1}$  for the 3,4 (*vinyl*) structural units;
- 1090  $\text{cm}^{-1}$  for the 1,4-*cis* structural units;
- 1150  $\text{cm}^{-1}$  for 1,4-*trans* structural units;
- 1600  $\text{cm}^{-1}$  for phenylic ring as internal standard [6, 7].

The absorption band at 935  $\text{cm}^{-1}$ , corresponding to 1,2-type vinyl isoprene structural units [5, 7], is missing for both the unbrominated and the brominated SIS samples.

## RESULTS AND DISCUSSION

The elemental analysis indicates that the experimental bromine content was practically the same as the theoretical, predicted bromination level. For both the brominated SBS and SIS, the entire amount of bromine from the reaction mixture was consumed in the reaction with the block copolymers.

All samples were soluble in the usual solvents (toluene, benzene, THF, chloroform, etc.) irrespective of the bromination level, therefore, the bromination reaction of SBS and SIS is not accomplished by crosslinking side-reactions.

### Brominated SBS

Since the absorption peak at 1600  $\text{cm}^{-1}$ ,  $D_{1600}$ , of the phenylic ring of styrene structural units is a very stable and reproducible peak, this was chosen as internal standard.

Figure 1 shows the ratio between absorbance of the C—Br bond at 540  $\text{cm}^{-1}$ ,  $D_{540}$ —which is the total absorbance at 540  $\text{cm}^{-1}$  diminished with the ab-

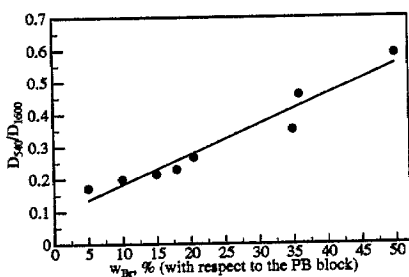


Fig. 1. Ratio of C—Br absorbance at 540  $\text{cm}^{-1}$  to phenylic ring absorbance at 1600  $\text{cm}^{-1}$  ( $D_{540}/D_{1600}$ ) vs bromination degree of SBS.

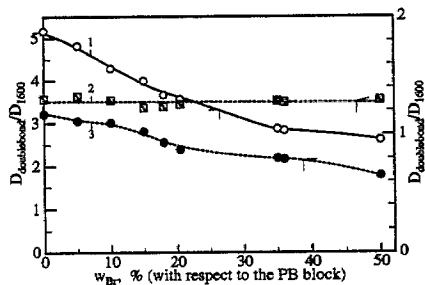


Fig. 2. Double-bond absorbance/phenylic ring absorbance vs bromination degree of brominated SBS. (1) —○— 1,4-*trans* (965  $\text{cm}^{-1}$ ), the left hand side axis of ordinates. (2) —□— vinyl (910  $\text{cm}^{-1}$ ), the right hand side axis of ordinates. (3) —●— 1,4-*cis* (714  $\text{cm}^{-1}$ ), the right-hand side axis of ordinates.

sorbance registered at the same wave-number in the IR spectrum of the base block copolymer assigned to the phenylic ring of styrene structural units—to  $D_{1600}$  vs bromination degree of polybutadiene block determined by elemental analysis.

The experimental points are fitted well by a straight line, consequently—after a suitable calibration—the absorption IR spectroscopy may be used for bromination degree determination of brominated SBS, which is an easier way than the elemental analysis.

The double bonds of the polybutadiene block of SBS are either in the main chain because of the 1,4-type structural units (*cis* and *trans*) or as —CH=CH<sub>2</sub> in side groups because of the 1,2-type, vinyl, butadiene structural units. These three types of butadiene structural units are distributed randomly in a polybutadiene block of SBS. The bromine reacts with the polybutadiene block double bonds by addition and for every bromine molecule addition a double bond disappears. When we are talking about polybutadiene block microstructure of brominated SBS, this is in fact the microstructure of the butadiene structural units which did not react with bromine.

The ratio for 1,4-*cis* structural units,  $D_{714}/D_{1600}$ , and for 1,4-*trans* structural units,  $D_{965}/D_{1600}$ , both decrease with increasing the bromination level of the polybutadiene block of SBS, while the ratio  $D_{910}/D_{1600}$  corresponding to the vinylic 1,2-type structural units remains practically unchanged (Fig. 2). Results in the bromination reaction of SBS, up to a 50% bromination level of polybutadiene block, react almost exclusively with the main-chain double bonds of 1,4-*cis* and 1,4-*trans* butadiene structural units.

The curves 1 ( $D_{965}/D_{1600}$ ) and 3 ( $D_{714}/D_{1600}$ ) are more or less parallels, indicating the same reactivity of 1,4-type structural unit double bonds, irrespective of their *trans* or *cis* structure.

The curve 2 ( $D_{910}/D_{1600}$ ) is a straight line parallel with the abscissa, indicating that the side-double bonds of *vinyl* (1,2-type) butadiene structural units are insensitive towards bromine addition.

The microstructure of the double-bond containing (unbrominated) butadiene structural units of base and brominated SBS were computed according to [2], using the following equations:

$$1,4\text{-}cis = cis \cdot 100 / (cis + trans + vinyl), \text{ in } \% \quad (1)$$

$$1,4\text{-trans} = \text{trans} \cdot 100 / (\text{cis} + \text{trans} + \text{vinyl}), \text{ in } \% \quad (2)$$

$$1,2(\text{vinyl}) = \text{vinyl} \cdot 100 / (\text{cis} + \text{trans} + \text{vinyl}), \text{ in } \% \quad (3)$$

where:

$$\text{cis} = 17.459D_{714} - 0.151D_{910} \quad (4)$$

$$\text{trans} = 4.292D_{965} - 0.454D_{714} - 0.129D_{910} \quad (5)$$

$$\text{vinyl} = 3.745D_{910} - 0.07D_{714} \quad (6)$$

$D_{714}$ ,  $D_{910}$ ,  $D_{965}$  are the peak intensity of IR absorption spectra of 1,4-*cis*, *vinyl* (1,2-type) and 1,4-*trans* type structural units, respectively.

In Fig. 3 is shown the microstructure of unbrominated butadiene structural units of brominated SBS vs bromination level of polybutadiene block.

Considering the total double bonds remaining after bromination, the proportion of 1,4 type *cis* + *trans* decreases and the 1,2-type increases with bromination degree. The curves 1 and 2 for 1,2-type and for 1,4-type (*cis* + *trans*) butadiene structural units, respectively, were calculated considering that the bromine reacts exclusively with polybutadiene blocks, and with bromine react exclusively the double bonds of 1,4-type butadiene structural units. The agreement between theoretical curves and experimental points is very good. Results, on the one hand, with bromine show reaction only of the double bonds of the 1,4-type butadiene structural units, which is in agreement with the above-mentioned conclusion. On the other hand, the bromine reacts exclusively with the polybutadiene block; the polystyrene blocks being unaffected by bromination of SBS.

#### Brominated SIS

The polyisoprene block double bonds of SIS are either in the main chain because of the 1,4-type structural units (mainly *ca* 90% of *cis* and a small proportion of *trans*) or as  $-\text{C}(\text{CH}_3)=\text{CH}_2$  in side groups because of the 3,4-type, *vinyl*ic, isoprene structural units. These three types of isoprene structural units are distributed randomly in the polyisoprene block of SIS. In a similar manner with SBS, the bromine reacts with the polyisoprene block double bonds by addition and for every bromine molecule addition a double bond disappears. Also, discussing the polyisoprene block microstructure of

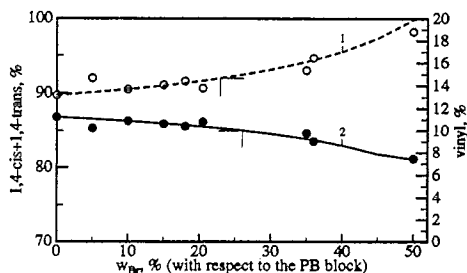


Fig. 3. Microstructure of unbrominated butadiene structural units vs bromination degree of SBS. (1) *vinyl*-type double bonds; ○ experimental data, — theoretical curve computed considering that react only the 1,4-type double bonds. (2) Total 1,4-type (*cis* + *trans*) double bonds; ● experimental data, — theoretical curve computed considering that react only the 1,4-type double bonds.

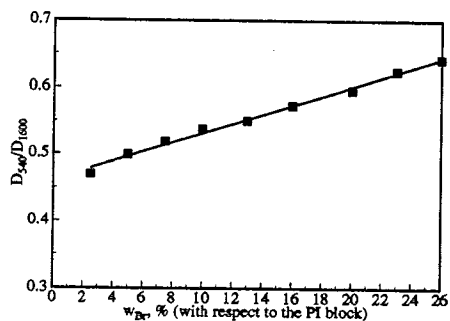


Fig. 4. Ratio of C—Br absorbance at  $540\text{ cm}^{-1}$  to phenylic ring absorbance at  $1600\text{ cm}^{-1}$  ( $D_{540}/D_{1600}$ ) vs bromination degree of SIS.

brominated SIS, this is in fact the microstructure of the isoprene structural units which did not react with bromine.

As for brominated SBS, the ratio between absorbance of the C—Br bond at  $540\text{ cm}^{-1}$ ,  $D_{540}$  to  $D_{1600}$ , the absorbance of the phenylic ring of styrene structural units—the internal standard for IR spectra evaluation—were calculated after subtraction of the absorbance at  $540\text{ cm}^{-1}$  of the IR spectrum of unbrominated SIS (Fig. 4).

Since the  $D_{540}/D_{1600}$  ratio is a straight line as a function of SIS bromination level (determined by elemental analysis), the IR spectroscopy can be used for the quantitative determination of the bromination degree of the polyisoprene block, after calibration.

Figure 5 shows the unsaturation of the polyisoprene block of brominated SIS vs bromination degree. The experimental points were computed using the following equation:

$$\text{unsaturation} = 100[(D_{890} + D_{1090} + D_{1150})/D_{1600}]_i / [(D_{890} + D_{1090} + D_{1150})/D_{1600}]_0, \text{ in } \%, \quad (8)$$

where  $[(D_{890} + D_{1090} + D_{1150})/D_{1600}]_i$  is the ratio between absorbances of vinyl (3,4-type), 1,4-*cis* and 1,4-*trans*-type isopren structural units, respectively, and internal standard absorbance of brominated SIS having a certain bromination level; and  $[(D_{890} + D_{1090} + D_{1150})/D_{1600}]_0$  is the ratio between absorbances of vinyl (3,4-type), 1,4-*cis* and 1,4-*trans*-type isopren structural units, respectively, and internal standard absorbance of unbrominated SIS.

The unsaturation of brominated SIS computed

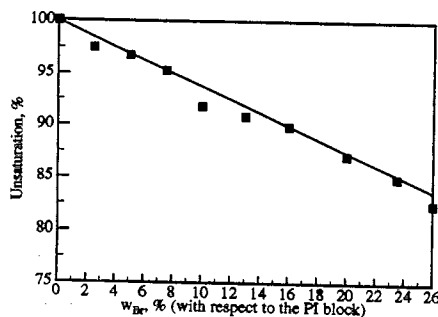


Fig. 5. Unsaturation of polyisoprene block of SIS vs bromination level. ■ Experimental data. — Theoretical curve.

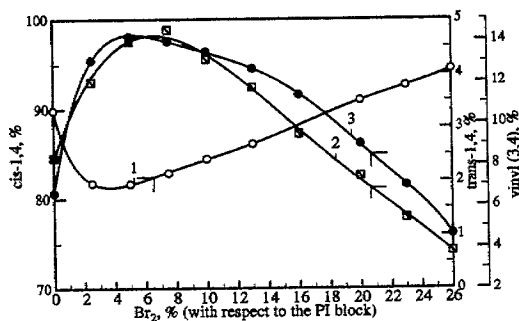


Fig. 6. Microstructure of unbrominated isoprene-structural units vs bromination degree of SIS. (1) —○— 1,4-*cis*. (2) —□— *vinyl* (3,4-type). (3) —●— 1,4-*trans*.

using the absorbance  $D_{836}$  at  $836\text{ cm}^{-1}$ , for the total 1,4-type (*cis* + *trans*) isoprene structural units instead of  $D_{1090} + D_{1150}$  (considering individually the absorbances of the two kind of 1,4-type isoprene structural units) was practically the same.

The theoretical curve on Fig. 5 was computed considering that bromine reacts exclusively with the polyisoprene block of SIS and every mol of bromine reacts with 1 mol of isoprene structural units. In other words, the theoretical unsaturation of brominated SIS is the ratio between the unbrominated isoprene structural unit content of brominated SIS to the initial isoprene structural unit content of base, unbrominated SIS. At around 70.1 wt% bromination level, with respect to the polyisoprene block, the SIS is fully brominated with 0% unsaturation.

As is observed, the agreement between experimental points and theoretical data is good, therefore, the assumption according to which in SIS bromination the bromine reacts exclusively with polyisoprene block is true.

The microstructure of unbrominated (double-bond-containing) isoprene structural units of base and brominated SIS (Fig. 6) were computed using the following equations:

$$1,4\text{cis} = \text{cis} \cdot 100 / (\text{cis} + \text{trans} + 3,4\text{vinyl}), \text{ in } \% \quad (9)$$

$$1,4\text{trans} = \text{trans} \cdot 100 / (\text{cis} + \text{trans} + 3,4\text{vinyl}), \text{ in } \% \quad (10)$$

$$3,4(\text{vinyl}) = 3,4\text{vinyl} \cdot 100 / (\text{cis} + \text{trans} + 3,4\text{vinyl}), \text{ in } \% \quad (11)$$

where:

$$\text{cis} = 16.356D_{1090} - 0.133D_{890} \quad (12)$$

$$\text{trans} = 1.292D_{1150} - 0.464D_{1090} - 0.139D_{890} \quad (13)$$

$$3,4\text{vinyl} = 1.280D_{890} - 0.173D_{1090} \quad (14)$$

$D_{890}$ ,  $D_{1090}$ ,  $D_{1150}$  are the peak intensity of IR-absorption spectra of vinyl (3,4-type), 1,4-*cis*- and 1,4-*trans*-type structural units, respectively.

At low bromination level, below 5%, the 1,4-*cis* content of unbrominated isoprene structural units decreases (curve 1), while the 1,4-*trans* (curve 3) and

3,4-type, *vinyl* (curve 2), content increases. Therefore, if the bromination reaction of SIS is carried out with small amounts of bromine, the 1,4-*cis*-type double bonds react preferentially.

At higher bromination degree the proportion of 1,4-*cis* isoprene structural units increases and the 1,4-*trans* and 3,4-type *vinyl* proportion decreases, indicating that if the bromination reaction is carried out with higher amounts of bromine, all types of double bonds will react, but the 1,4-*trans*-type double bonds seem to be the least reactive towards bromine addition.

This behavior of SIS in the bromination reaction is completely different from that of SBS when the *vinyl* double bonds are practically unaffected.

## CONCLUSIONS

1. In solution bromination of both the radial SBS and the linear SIS polystyrene blocks are unaffected. The bromine reacts exclusively with the polydiene blocks.

2. IR spectroscopy appears to be an adequate method for bromination level determination in brominated SBS and SIS.

3. SBS and SIS react in a different manner with bromine. In SIS the bromine addition almost exclusively takes place at the 1,4-type (*cis* and *trans*) double bonds of the polybutadiene block, the *vinyl* side double bonds being practically unaffected. In SIS below 5% bromination level the bromine reacts mainly with double bonds from 1,4-*cis*-type structural units of the isoprene, while at higher bromination level the bromine has practically the same reactivity towards both the double bonds of 1,4-type (*cis* and *trans*) and the ones of 3,4-type (*vinyl*).

*Acknowledgements*—The authors gratefully acknowledge the support of this study by the Romanian Ministry for Research and Technology and the German Ministry for Education and Research in the frame of the German-Romanian Cooperation in Science and Technology (Project X055.4).

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