BROMINATION OF SOME STYRENE–DIENE BLOCK COPOLYMERS

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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 tetrahydrofuran 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 polysoprene block of SIS, while at higher bromination level the bromine presents the same reactivity towards the 1,4-type (cis and trans) and vinyllic (3,4-type) double bonds.

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 polysoprene), 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.

Bromination 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 polysoprene) block. By bromination of the polydiene block the electron density of the polydiene phase increases until no contrast for equal electron densities and at higher bromination level it is even possible to realize a contrast inversion.

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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 \( M_n = 135,000 \) g/mol, the molecular mass of the polybutadiene block is \( M_n = 24,000 \) 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 polysoprene middle block and two polysoprene end blocks. The styrene content is 30%, the total molecular mass \( M_n = 105,000 \) g/mol, the molecular mass of the polysoprene block is \( M_n = 73,500 \) g/mol. According to IR spectroscopy [3–5] its polysoprene block contains 88.9% 1,4-cis units, 21.1% 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 tetrahydrofuran (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 SPECCORD M 80 (Carl Zeiss Jena)
spectrometer using films of 50 μm 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 cm⁻¹ for the C—Br bond;
- 714 cm⁻¹ for the 1,4-cis structural units (shifted for SBS block copolymer; for pure polybutadiene being 730 cm⁻¹);
- 910 cm⁻¹ for the 1,2 (vinylic) structural units;
- 965 cm⁻¹ for the 1,4-trans structural units;
- 1600 cm⁻¹ for the phenyl ring as internal standard [6, 7].

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

- 540 cm⁻¹ for the C—Br bond;
- 836 cm⁻¹ for the total 1,4-type (cis + trans) structural units;
- 890 cm⁻¹ for the 3,4 (vinylic) structural units;
- 1090 cm⁻¹ for the 1,4-cis structural units;
- 1150 cm⁻¹ for 1,4-trans structural units;
- 1600 cm⁻¹ for vinyl and phenyl ring as internal standard [6, 7].

The absorption band at 935 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 cm⁻¹, D₁₀₀, of the phenyl 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 cm⁻¹, D₅₄₀—which is the total absorbance at 540 cm⁻¹—diminished with the absorbance registered at the same wave-number in the IR spectrum of the base block copolymer assigned to the phenyl ring of styrene structural units—to D₅₄₀ vs bromination degree of brominated SBS. (1) —○— 1,4-trans (965 cm⁻¹), the left hand side axis of ordinates. (2) —□— vinyl (910 cm⁻¹), the right hand side axis of ordinates. (3) —●— 1,4-cis (714 cm⁻¹), the right hand side axis of ordinates.

Fig. 2. Double-bond absorbance/phenyl ring absorbance vs bromination degree of brominated SBS. (1) —○— 1,4-trans (965 cm⁻¹), the left hand side axis of ordinates. (2) —□— vinyl (910 cm⁻¹), the right hand side axis of ordinates. (3) —●— 1,4-cis (714 cm⁻¹), the right-hand side axis of ordinates.

![Fig. 1. Ratio of C—Br absorbance at 540 cm⁻¹ to phenyl ring absorbance at 1600 cm⁻¹ (D₅₄₀/D₁₀₀) vs bromination degree of SBS.](image)

![Fig. 2. Double-bond absorbance/phenyl ring absorbance vs bromination degree of brominated SBS.](image)
1,4-trans = trans·100/(cis + trans + vinyl), in % (2)
1,2(vinyl) = vinyl·100/(cis + trans + vinyl), in % (3)

where:
\[
cis = 17.459D_{114} - 0.151D_{910} \quad (4)
\]
\[
trans = 4.292D_{965} - 0.454D_{114} - 0.129D_{910} \quad (5)
\]
\[
vinyl = 3.745D_{910} - 0.07D_{114} \quad (6)
\]

\(D_{114}, D_{910}, D_{965}\) 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 unbranched butadiene structural units of brominated SBS vs bromination level of polyybutadiene 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 polyybutadiene 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 polyybutadiene block; the polystyrene blocks being unaffected by bromination of SBS.

**Brominated SIS**

The polyyisoprene 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 \(\equiv C(CH_2)_2\equiv CH_2\) in side groups because of the 3,4-type, vinyllic, isoprene structural units. These three types of isoprene structural units are distributed randomly in the polyyisoprene block of SIS. In a similar manner with SBS, the bromine reacts with the polyyisoprene block double bonds by addition and for every bromine molecule addition a double bond disappears. Also, discussing the polyyisoprene block microstructure of 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 cm\(^{-1}\), \(D_{540}\) to \(D_{1600}\), the absorbance of the phenyllic ring of styrene structural units—the internal standard for IR spectra evaluation—were calculated after subtraction of the absorbance at 540 cm\(^{-1}\) of the IR spectrum of unbranched 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 polyyisoprene block, after calibration.

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

\[
\text{unsaturation} = 100\left[\frac{D_{900} + D_{1090} + D_{1150}}{D_{1600}}\right] / \left[\frac{D_{540} + D_{1090} + D_{1150}}{D_{1600}}\right], \text{ in } %, \quad (8)
\]

where \([D_{900} + D_{1090} + D_{1150}]/D_{1600}\) is the ratio between absorbances of vinyl (3,4-type), 1,4-cis and 1,4-trans-type isoprene structural units, respectively, and internal standard absorbance of brominated SIS having a certain bromination level; and \([D_{540} + D_{1090} + D_{1150}]/D_{1600}\), is the ratio between absorbances of vinyl (3,4-type), 1,4-cis and 1,4-trans-type isoprene structural units, respectively, and internal standard absorbance of unbranched SIS.

The unsaturation of brominated SIS computed...
using the absorbance $D_{836}$ at 836 cm$^{-1}$, for the total 1,4-type ($cis$ + $trans$) isoprene structural units instead of $D_{1096}$ + $D_{1150}$ (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 polysisoprene 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 unbranminated isoprene structural unit content of brominated SIS to the initial isoprene structural unit content of base, unbranminated SIS. At around 70.1 wt% bromination level, with respect to the polisyoprene 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 polisyoprene block is true.

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

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

(9)

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

(10)

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

(11)

where:

$$cis = 0.16356D_{1096} - 0.0133D_{890}$$

(12)

$$trans = 1.292D_{1150} - 0.464D_{1096} - 0.139D_{890}$$

(13)

$$3,4-vinyl = 1.280D_{1150} - 0.173D_{890}$$

(14)

$D_{1096}$, $D_{1150}$, and $D_{890}$ 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 unbranminated isoprene structural units decreases (curve 1), while the 1,4-trans (curve 2) and 3,4-type, vinylic (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 vinylic 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 vinylic 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 bromination addition almost exclusively takes place at the 1,4-type ($cis$ and $trans$) double bonds of the polybutadiene block, the vinylic 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 (vinylic).

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