
**Styrene-butadiene rubber (SBR) —
Determination of the microstructure of
solution-polymerized SBR**

*Caoutchouc styrène-butadiène (SBR) — Détermination de la
microstructure du SBR polymérisé en solution*

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 21561 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

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Styrene-butadiene rubber (SBR) — Determination of the microstructure of solution-polymerized SBR

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies procedures for the quantitative determination of the microstructure of the butadiene units and the content of styrene units in solution-polymerized SBR (S-SBR) by $^1\text{H-NMR}$ spectrometry as an absolute method and by IR spectrometry as a relative method. The styrene content is expressed in mass % relative to the whole polymer. The 1,4-trans, 1,4-cis and 1,2-vinyl contents are expressed in mol % relative to the butadiene units.

NOTE IR spectrometry can also give absolute values of microstructure by calibration with S-SBRs of known absolute microstructure obtained by $^1\text{H-NMR}$ spectrometry.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1407, *Rubber — Determination of solvent extract*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

3 NMR method (absolute method)

3.1 Principle

3.1.1 A small quantity of an extracted S-SBR is dissolved in deuterated-chloroform.

3.1.2 A $^1\text{H-NMR}$ spectrum of the sample solution is measured at a 15 ppm sweep width. The peak areas of the 1,4-bond (the sum of the 1,4-trans bond and 1,4-cis bond) and the 1,2-vinyl bond of the butadiene portion are determined along with the peak area of styrene. The microstructure of the butadiene portion and the styrene content are then calculated using theoretical formulae.

3.2 Reagents

3.2.1 Deuterated chloroform, CDCl_3 , containing 0,03 % of tetramethyl silane (TMS) as internal standard. The purity of the CDCl_3 itself shall be > 99,8 %.

3.2.2 Anhydrous ethanol-toluene azeotrope (ETA).

3.2.3 Acetone.

3.3 Apparatus

3.3.1 **¹H-NMR spectrometer:** Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer with a resonance frequency of 150 MHz or higher.

3.3.2 **Extraction apparatus,** as described in ISO 1407.

3.3.3 **Vacuum oven,** operated at 50 °C to 60 °C.

3.3.4 **Analytical balance,** accurate to 0,1 mg.

3.4 Sampling

The raw rubber shall be sampled in accordance with ISO 1795.

3.5 Procedure

3.5.1 Extract rubber additives such as extender oil and antioxidant in accordance with ISO 1407, using anhydrous ETA or acetone as the extraction solvent. Dry the extracted S-SBR under vacuum in the oven at 50 °C to 60 °C.

3.5.2 Take 15 mg to 50 mg of the extracted S-SBR and dissolve it completely in 0,5 ml of deuterated chloroform containing 0,03 % of TMS. The concentration of this sample solution shall be selected according to the resolution of the spectrometer used.

3.5.3 Transfer 0,5 ml of the S-SBR sample solution into an NMR tube for measurement.

3.5.4 Measure the ¹H-NMR spectrum of the S-SBR solution under the following conditions:

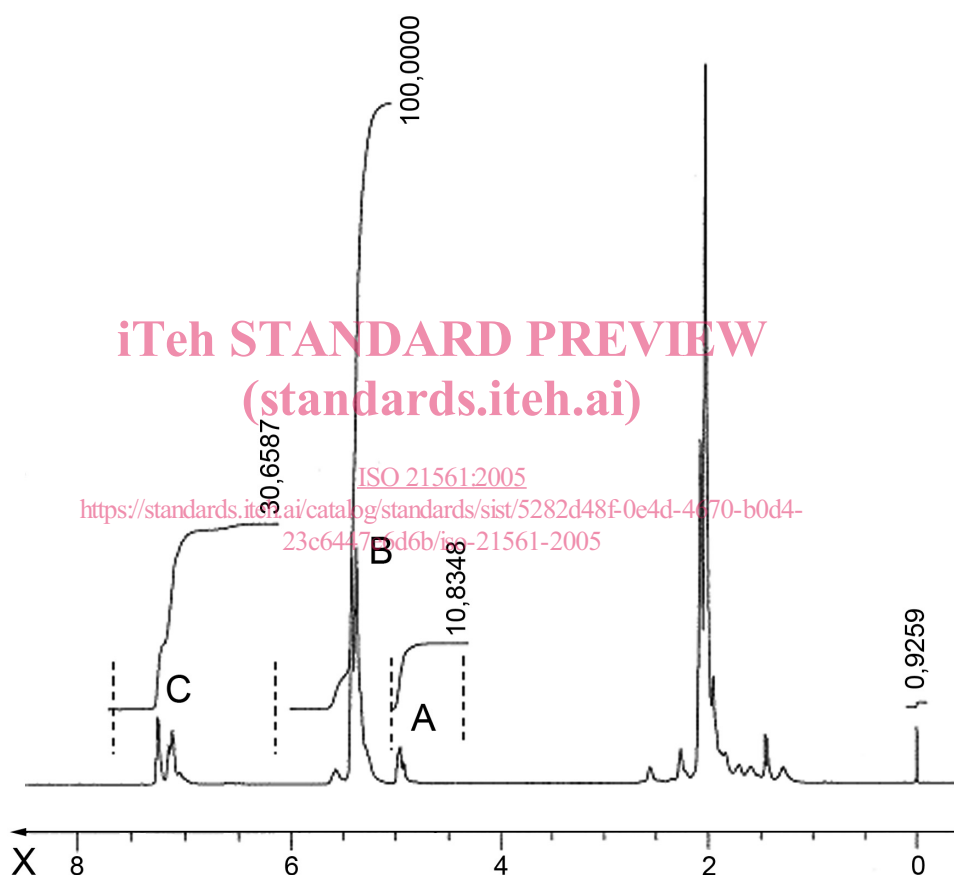
Mode	single-pulse mode
Measurement temperature	room temperature to 50 °C
No. of data points	32 k
Offset	5 ppm
Sweep width	15 ppm or wider
Flip angle	30° pulse
Pulse repetition	4 s to 30 s
Accumulation	32 times to 256 times

3.6 Determination of the microstructure

3.6.1 Integrate the signal intensities of the ¹H-NMR spectrum over each of the areas A, B and C defined in Table 1. Figure 1 gives an example of a ¹H-NMR spectrum showing the areas A, B and C.

Table 1 — Definition of signal integration areas

Area	Signal integration range
A	From 4,3 ppm to minimum intensity point around 5,0 ppm
B	From minimum intensity point around 5,0 ppm to minimum intensity point around 6,1 ppm
C	From minimum intensity point around 6,1 ppm to 7,7 ppm
TMS _{blank}	Integrated signal intensity of TMS in CDCl ₃ containing TMS
CD _{blank}	From 6,1 ppm to 7,7 ppm in CDCl ₃ containing TMS
TMS	Integrated signal intensity of TMS in S-SBR sample solution

**Key**

X shift (ppm)

A, B, C signal integration areas

Figure 1 — Example of a ¹H-NMR spectrum for an S-SBR

3.6.2 Measure as a solvent blank the ¹H-NMR spectrum of the deuterated chloroform containing 0,03 % of TMS. The TMS blank is normalized using Equation (1) and subtracted from the signal intensity of the solvent determined from the integrated signal intensity of area C:

$$C_{\text{calib}} = C - CD_{\text{blank}} \times (TMS/TMS_{\text{blank}}) \quad (1)$$

3.6.3 Calculate the content of each microstructure component (1,4-bond and 1,2-vinyl bond) of the butadiene portion and the styrene content, using Equations (2) to (4):

$$\% \text{ St} = \frac{(C_{\text{calib}}/5) \times 104}{(C_{\text{calib}}/5) \times 104 + (B/2 + A/4) \times 54} \times 100 \quad (2)$$

$$\% \text{ Bd}_{1,2} = \frac{A/2}{B/2 + A/4} \times 100 \quad (3)$$

$$\% \text{ Bd}_{1,4} = \frac{B/2 - A/4}{B/2 + A/4} \times 100 \quad (4)$$

where

C_{calib} is the integrated signal intensity of area C compensated for the effect of CHCl_3 in CDCl_3 ;

% St is the styrene content of the SBR, in mass %;

% $\text{Bd}_{1,2}$ is the 1,2-vinyl bond content of the butadiene portion of the SBR, in mol %;

% $\text{Bd}_{1,4}$ is the 1,4-bond content of the butadiene portion of the SBR, in mol %.

4 IR method (relative method)

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4.1 Principle

4.1.1 A small quantity of extracted S-SBR is dissolved in cyclohexane and coated on a KBr plate.

4.1.2 The IR spectrum of the S-SBR sample on the KBr plate is measured over the range $1\,200\text{ cm}^{-1}$ to 600 cm^{-1} . From the absorbances at four specified wavelengths, the contents of the 1,4-trans bond, the 1,4-cis bond, the 1,2-vinyl bond and the styrene unit are calculated using Hampton's method (see Reference [1] in the Bibliography).

4.1.3 IR spectrometry can also give absolute values of microstructures by calibration with S-SBRs of known absolute microstructure obtained by $^1\text{H-NMR}$ spectrometry.

4.2 Reagents

4.2.1 Anhydrous ethanol-toluene azeotrope (ETA).

4.2.2 Acetone.

4.2.3 Cyclohexane.

4.3 Apparatus

4.3.1 **IR spectrophotometer:** Fourier transform infrared (FT-IR) spectrophotometer or double-beam IR spectrophotometer.

4.3.2 **Extraction apparatus,** as described in ISO 1407.

4.3.3 **Vacuum oven,** operated at $50\text{ }^\circ\text{C}$ to $60\text{ }^\circ\text{C}$.

4.3.4 **Analytical balance,** accurate to 0,1 mg.

- 4.3.5 20 ml sample vial, with cap.
- 4.3.6 Pasteur pipette and 10 ml pipette.
- 4.3.7 KBr plate, for IR spectrophotometry.
- 4.3.8 Holder, for KBr plate.
- 4.3.9 Metal spacer, of 0,1 mm thickness.

4.4 Sampling

The raw rubber shall be sampled in accordance with ISO 1795.

4.5 Procedure

4.5.1 Preparation of sample solution

4.5.1.1 Extract extender oil and antioxidant from the S-SBR in accordance with ISO 1407, using anhydrous ETA or acetone. Dry the extracted S-SBR in a vacuum oven at 50 °C to 60 °C.

4.5.1.2 Put 0,2 g of extracted S-SBR sample in a 20 ml sample vial.

4.5.1.3 Add 10 ml of cyclohexane to the sample vial using the 10 ml pipette. Place the cap on the vial and shake to dissolve the S-SBR completely.

4.5.2 Preparation of film coating

4.5.2.1 Place the 0,1 mm thick metal spacer on the KBr plate and spread the sample solution uniformly in the spacer hole using the Pasteur pipette.

4.5.2.2 Remove any excess sample solution from the spacer, leaving a film of uniform thickness. As film thickness affects absorbance, adjust the volume of sample solution accordingly.

4.5.2.3 Dry the sample solution on the KBr plate.

4.5.2.4 Remove the spacer from the KBr plate and place the KBr plate in the holder ready for insertion in the IR spectrophotometer.

NOTE Details of the equipment and procedure for preparing the film coating are given in Annex A.

4.5.3 Measurement of IR spectrum

4.5.3.1 Measurement by Fourier transform IR spectrophotometer

4.5.3.1.1 Measure the background spectrum of a blank KBr plate from 1 200 cm⁻¹ to 600 cm⁻¹.

4.5.3.1.2 Measure the spectrum of the sample KBr plate from 1 200 cm⁻¹ to 600 cm⁻¹.

4.5.3.1.3 In order to ensure good reproducibility, the maximum absorbance for the sample spectrum shall be in the range 0,10 to 0,15.

4.5.3.1.4 An example of an FT-IR spectrum is shown in Figure 2.

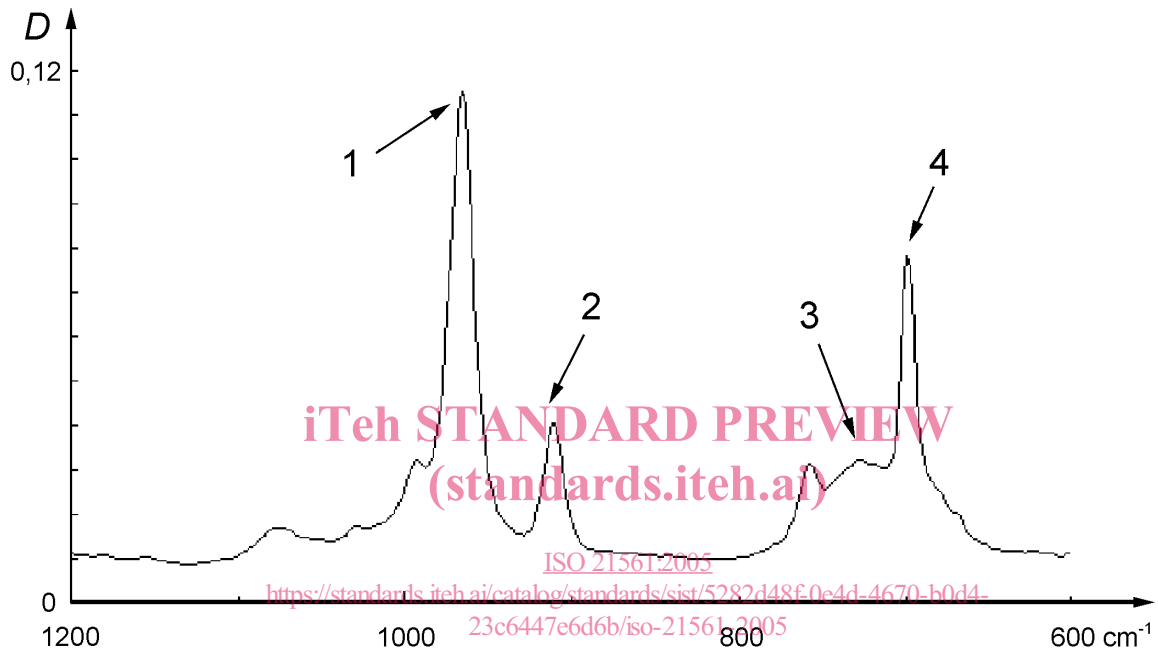
4.5.3.2 Measurement by double-beam IR spectrophotometer

4.5.3.2.1 Place blank KBr plates in both the sample and reference paths, and measure the background spectrum from 1 200 cm^{-1} to 600 cm^{-1} in the absorbance mode.

4.5.3.2.2 Place the sample KBr plate in the sample path and a blank KBr plate in the reference path. Measure the sample spectrum from 1 200 cm^{-1} to 600 cm^{-1} in the absorbance mode.

4.5.3.2.3 In order to ensure good reproducibility, the maximum absorbance for the sample spectrum shall be in the range 0,10 to 0,15.

4.5.3.2.4 Produce a difference spectrum for the calculation of the microstructure by subtracting the background spectrum from the sample spectrum.



Key

- 1 1,4-trans
- 2 1,2-vinyl
- 3 1,4-cis
- 4 styrene

Figure 2 — An example of an FT-IR spectrum for an S-SBR

4.6 Determination of microstructure

4.6.1 Measurement of absorbance corresponding to each microstructure component

Measure the absorbance values at the wave numbers corresponding to the microstructure components as specified in Table 2. For “1,4-cis”, the absorption peak is weak and the wave number of the peak is affected by the styrene content of the polymer.

Table 2 — Measurement of absorbances for each microstructure component of S-SBR

Notation for absorbance	Microstructure component	Wave number cm ⁻¹	Remarks
D_{trans}	1,4-trans bond	967	Measure the absorbance at the peak maximum.
D_{vinyl}	1,2-vinyl bond	911	Measure the absorbance at the peak maximum.
D_{cis}	1,4-cis bond	724	The wave number at this peak maximum is affected by the nature of the polymer, such as the styrene content. When the peak maximum is visible, read off the absorbance at the peak maximum from 720 cm ⁻¹ to 740 cm ⁻¹ . The absorbance at 724 cm ⁻¹ is not necessary in this case. If the styrene content is over 30 %, the peak of the 1,4-cis bond is hidden between the two large styrene absorptions at 755 cm ⁻¹ and 699 cm ⁻¹ . In this case, measure the absorbance value at 724 cm ⁻¹ .
D_{styrene}	Styrene	699	Measure the absorbance at the peak maximum.

4.6.2 Calculation

4.6.2.1 General

The content of each microstructure component in the S-SBR is calculated from the absorbances (D_{trans} , D_{vinyl} , D_{cis} and D_{styrene}) of the sample at the corresponding wave numbers by the equation given by Hampton [1].

4.6.2.2 Normalization

Normalize the measured absorbances using the following equations:

$$\% D_{\text{trans}} = \frac{D_{\text{trans}}}{D_{\text{trans}} + D_{\text{vinyl}} + D_{\text{cis}} + D_{\text{styrene}}} \times 100 \quad (5)$$

$$\% D_{\text{vinyl}} = \frac{D_{\text{vinyl}}}{D_{\text{trans}} + D_{\text{vinyl}} + D_{\text{cis}} + D_{\text{styrene}}} \times 100 \quad (6)$$

$$\% D_{\text{cis}} = \frac{D_{\text{cis}}}{D_{\text{trans}} + D_{\text{vinyl}} + D_{\text{cis}} + D_{\text{styrene}}} \times 100 \quad (7)$$

$$\% D_{\text{styrene}} = \frac{D_{\text{styrene}}}{D_{\text{trans}} + D_{\text{vinyl}} + D_{\text{cis}} + D_{\text{styrene}}} \times 100 \quad (8)$$