INTERNATIONAL STANDARD

ISO 21561-1

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

Part 1: ^{1}H-NMR and IR with cast-film method

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

Partie 1: Méthode ^{1}H-NMR et IR avec film moulé

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

This first edition of ISO 21561-1, together with ISO 21561-2, cancels and replaces ISO 21561:2005, which has been technically and nominally revised with the following changes:

— the descriptions of D's were modified in 4.6.2;

— some terms and expressions were revised to be aligned with those in the ISO 21561-2 to be (ATR method);

— it also incorporates the Amendment, ISO 21561:2005/Amd 1:2010.

ISO 21561 consists of the following parts, under the general title *Styrene-butadiene rubber (SBR)*:

— *Part 1: ^{1}H-NMR and IR with cast-film method*

— *Part 2: FTIR with ATR method*

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

Part 1: ^{1}H-NMR and IR with cast-film method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International 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.

CAUTION — Certain procedures specified in this International Standard may involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This part of ISO 21561 specifies procedures for the quantitative determination of the microstructure of the butadiene and the content of styrene in solution-polymerized SBR (S-SBR) by ^{1}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 trans, cis and vinyl contents are expressed in mol % relative to the butadiene. These methods are applicable only for raw rubber.

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

NOTE 2 Only “vinyl”, “trans” and “cis” are used in this part of ISO 21561. However, the expression of vinyl, trans and cis mean as follows in general:

— vinyl: vinyl unit, vinyl bond, 1,2-unit, 1,2-bond, 1,2-vinyl-unit or 1,2-vinyl-bond;

— trans: 1,4-trans unit, 1,4-trans bond, trans-1,4 unit or trans1,4 bond;

— cis: 1,4-cis unit, 1,4-cis bond, cis-1,4 unit or cis-1,4 bond.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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}H-NMR spectrum of the sample solution is measured at a 15 ppm sweep width.

With the peak areas obtained from ^{1}H-NMR, calculate the microstructure of the butadiene portion and the styrene content by the 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 Ethanol-toluene azeotrope (ETA).

3.2.3 Acetone.

3.3 Apparatus

3.3.1 ^{1}H-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 antioxidants in accordance with ISO 1407, using 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 (3.2.1). The concentration of this sample solution shall be selected according to the resolution of the spectrometer used.

3.5.3 Measure the ^{1}H-NMR spectrum of the S-SBR solution and a solvent blank [deuterated chloroform (3.2.1)] 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

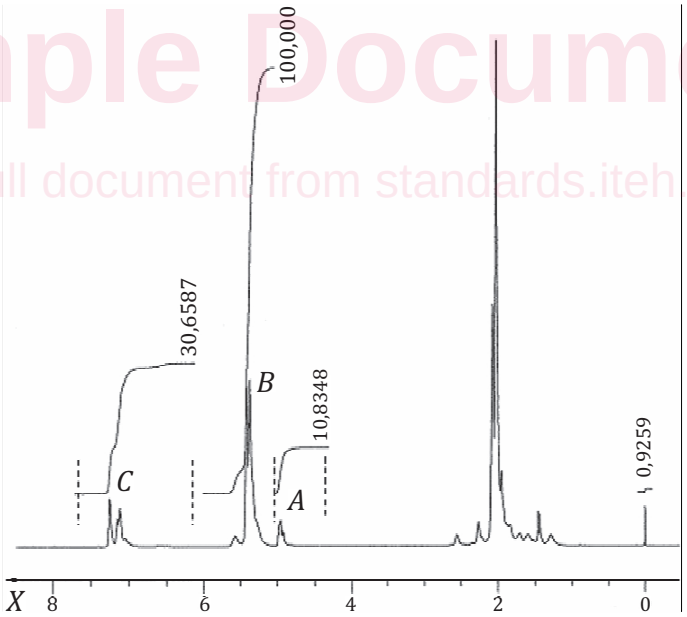
Pulse repetition	4 s to 30 s
Accumulation	32 times to 256 times

3.6 Determination of the microstructure

3.6.1 Integrate the signal intensities of the ^{1}H-NMR spectrum over each of the areas *A*, *B* and *C* defined in Table 1. Figure 1 gives an example of a ^{1}H-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 Text ^{1}H-NMR spectrum for an S-SBR

3.6.2 Normalize the solvent blank measured in 3.5.3 using Formula (1) and subtract it from the signal intensity of the solvent determined from the integrated signal intensity of area *C*: