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

Part 2: Fourier transform infrared spectrometry (FTIR) with attenuated total reflection (ATR) method

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

Partie 2: Méthode par spectrométrie infrarouge à transformée de Fourier (FTIR) à réflexion totale atténuée (RTA)

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Foreword

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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 document 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 of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry.*

This second edition cancels and replaces the first edition (ISO 21561-2:2016), which has been technically revised.

The main changes are as follows:

— Clause 3 has been added;

— the units of styrene content and microstructure content of butadiene have been changed to SI units;

— the conditions of FTIR spectrum have been moved to 8.1;

— a description of regression formulae has been added in 9.2.5 and 9.2.6;

— in Table A.1, one cell has been replaced by the correct value;

— in C.3.1, the measurement conditions for ^{13}C-NMR have been corrected.

A list of all parts in the ISO 21561 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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

Part 2:
Fourier transform infrared spectrometry (FTIR) with attenuated total reflection (ATR) method

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of 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 determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document can involve the use or generation of substances, or the generation of waste, that can constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document specifies procedures for the quantitative determination of the microstructure of the butadiene portion and the content of styrene in solution-polymerized SBR (S-SBR) by Fourier transform infrared spectrometry (FTIR) with attenuated total reflection (ATR) method. The styrene content is expressed in mass fraction relative to the S-SBR. The contents of three microstructure types, i.e. vinyl, trans and cis, are expressed in mol fraction relative to the butadiene portion in the S-SBR. This method is only applicable to raw rubbers.

NOTE 1 Precision as shown in Annex A is not always possible to obtain for S-SBRs containing polystyrene block or styrene content more than 45 %.

NOTE 2 Only “vinyl”, “trans” and “cis” are used in this document. 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 are referred to in the text in such a way that some or all of their content constitutes requirements 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 1382, *Rubber — Vocabulary*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1382 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

The IR spectrum of the S-SBR sample is measured by FTIR with ATR. The absorbances that are characteristic of each microstructure component and styrene at the specified wave number are used to determine the content of each component by using the specific formulae presented in this document.

5 Apparatus

5.1 FTIR, of the following specifications:

— detector: deuterium tri-glycine sulfate (DTGS) or tri-glycine sulfate (TGS);

— resolution: 2 cm^{-1}.

5.2 ATR, of the following specifications:

— type: single bounce ATR;

— crystal: diamond;

— angle of incidence: 45°;

— sample pressure clamp: a concave or a flat-shaped clamp which is capable of maintaining a constant pressure on the sample. The use of a torque wrench is recommended.

6 Calibration

6.1 FTIR

Adjust the optical bench alignment of FTIR spectrometer according to the manufacturer's instruction manual.

6.2 ATR

Set ATR in the sample chamber of FTIR and adjust the optical alignment of ATR according to the manufacturer's instruction manual.

7 Sampling

7.1 Prepare the test sample in accordance with ISO 1795.

NOTE The extraction of ordinary extender oils by solvent is not necessary.

7.2 Cut out a test piece from the test sample. The test piece shall have a flat surface to give good contact with the ATR crystal and be approximately the same size as the crystal, usually a few square millimetres.

8 Procedure for measuring ATR spectrum

8.1 Set up FTIR according to the manufacturer's instruction manual and set up the measurement conditions as follows:

— resolution: 2 cm^{-1};

— number of scans: 32;

— range of wave number: 600 cm^{-1} to 1 800 cm^{-1}.

8.2 Set ATR with the specification in a sample chamber of FTIR.

8.3 Measure the background spectrum without sample on the ATR crystal with the conditions shown in 8.1.

8.4 Put the test piece on the ATR crystal and contact it as completely as possible to the crystal surface, preferably using the clamp specified in 5.2. The contact between the test piece and the crystal affects the absorbance of ATR spectra.

8.5 Measure the sample spectrum with the conditions shown in 8.1.

8.6 The atmosphere of the sample chamber for FTIR shall be kept consistent during the background and test piece measurements in order to avoid the influences of absorbance at 668 cm^{-1} and 723 cm^{-1} by CO_2.

9 Determination of the microstructure of butadiene and the styrene content

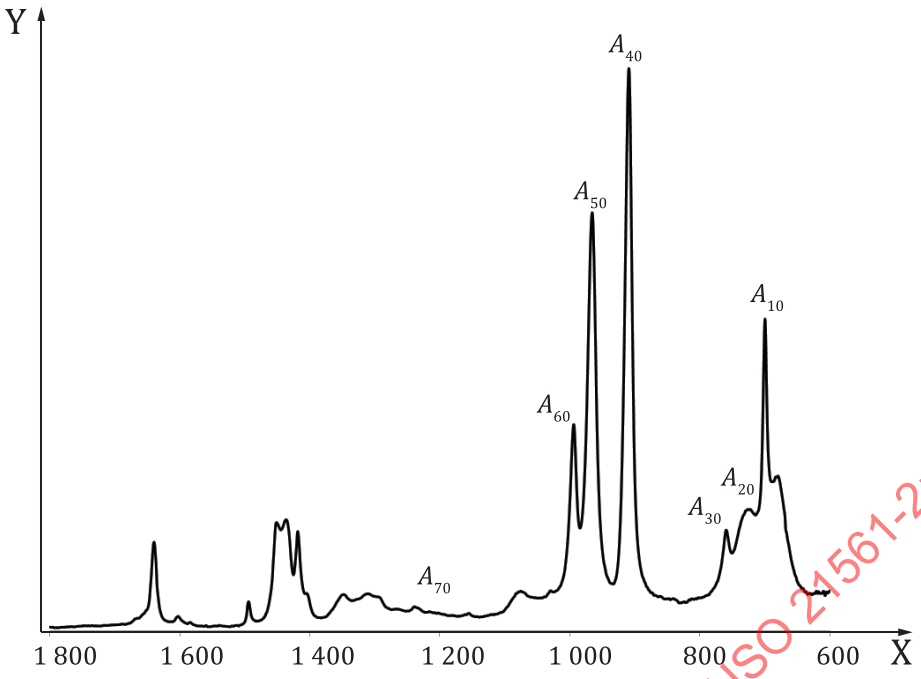
9.1 Measurement of the absorbance for each microstructure component

Measure the absorbance values at the wave numbers corresponding to the microstructure components as specified in Table 1. For cis, the absorption peaks are weak and the wave number of the peaks is affected by the styrene content of the polymer.

Figure 1 provides an example of an ATR spectrum of a typical S-SBR.

Table 1 — Measurement of absorbances for each microstructure component of S-SBR

Notation for absorbance	Microstructure Component	Remarks
A_{10}	Styrene	Measure the absorbance at the peak maximum from 695 cm^{-1} to 700 cm^{-1}.
A_{20}	Cis	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 730 cm^{-1}. If the styrene content is over 30 %, the peak of the cis bond is hidden between the two large styrene absorptions at around 758 cm^{-1} and around 698 cm^{-1}. In this case, measure the absorbance value at 726 cm^{-1}.
A_{30}	Styrene	Measure the absorbance at the peak maximum from 755 cm^{-1} to 761 cm^{-1}.
A_{40}	Vinyl	Measure the absorbance at the peak maximum from 905 cm^{-1} to 912 cm^{-1}.
A_{50}	Trans	Measure the absorbance at the peak maximum from 962 cm^{-1} to 967 cm^{-1}.
A_{60}	Vinyl	Measure the absorbance at the peak maximum from 991 cm^{-1} to 996 cm^{-1}.
A_{70}	Base line	Measure the absorbance at 1 200 cm^{-1} as zero point of each absorbance.



Key

X wave number (cm^{-1})

Y absorbance

Figure 1 — ATR spectrum of a typical S-SBR

9.2 Calculation of microstructures

9.2.1 General

The microstructure of S-SBR is calculated by using regression formulae and the measured absorbance values of the ATR spectra of each sample. The regression formulae were derived from a statistical study on the ATR spectra of various S-SBR samples with known microstructures. After adjusting the baseline of the ATR spectra, the absorbance ratio values of respective absorptions are obtained as the parameter value for microstructure calculation. The microstructure results are calculated by substituting these parameter values in the regression formulae.

9.2.2 Base line correction of each absorbance peak

Obtain the absorbance of each of the peaks A_{11} to A_{61} with corrected base lines by using Formulae (1) to (6):

$$A_{11} = A_{10} - A_{70} \quad (1)$$

$$A_{21} = A_{20} - A_{70} \quad (2)$$

$$A_{31} = A_{30} - A_{70} \quad (3)$$

$$A_{41} = A_{40} - A_{70} \quad (4)$$

$$A_{51} = A_{50} - A_{70} \quad (5)$$

$$A_{61} = A_{60} - A_{70} \quad (6)$$

9.2.3 Ratio of absorbance

Obtain the ratios of the absorbances A_{12} to A_{62} by using Formulae (7) to (12):

$$A_{12} = A_{11}/(A_{11} + A_{21} + A_{31} + A_{41} + A_{51} + A_{61}) \quad (7)$$

$$A_{22} = A_{21}/(A_{11} + A_{21} + A_{31} + A_{41} + A_{51} + A_{61}) \quad (8)$$

$$A_{32} = A_{31}/(A_{11} + A_{21} + A_{31} + A_{41} + A_{51} + A_{61}) \quad (9)$$

$$A_{42} = A_{41}/(A_{11} + A_{21} + A_{31} + A_{41} + A_{51} + A_{61}) \quad (10)$$

$$A_{52} = A_{51}/(A_{11} + A_{21} + A_{31} + A_{41} + A_{51} + A_{61}) \quad (11)$$

$$A_{62} = A_{61}/(A_{11} + A_{21} + A_{31} + A_{41} + A_{51} + A_{61}) \quad (12)$$

9.2.4 Second order terms

Calculate the second order terms which are the squares of A_{12} to A_{62}. The second order terms are expressed as ${A_{12}}^2$ to ${A_{62}}^2$ for the square of A_{12} to A_{62}.

9.2.5 Styrene content and contents of three microstructure types of butadiene portion by regression formulae

Styrene content relative to the S-SBR and the contents of three microstructure types of butadiene portion relative to the S-SBR are expressed by the regression Formulae (13) to (16).

These four regression formulae are obtained by the method shown in Annex B.

$$S_m = 9{,}0 + 12{,}9 \times A_{12} + 25{,}9 \times {A_{12}}^2 - 111{,}2 \times A_{22} + 412{,}5 \times {A_{22}}^2 + 105{,}0 \times A_{32} + 891{,}9 \times {A_{32}}^2 - 0{,}5 \times A_{42} - 21{,}5 \times {A_{42}}^2 - 30{,}7 \times A_{52} + 28{,}9 \times {A_{52}}^2 + 24{,}5 \times A_{62} - 47{,}2 \times {A_{62}}^2 \quad (13)$$

$$V_m = 32{,}9 + 5{,}3 \times A_{12} - 12{,}9 \times {A_{12}}^2 - 183{,}6 \times A_{22} + 1\,168{,}4 \times {A_{22}}^2 + 13{,}2 \times A_{32} - 572{,}5 \times {A_{32}}^2 + 33{,}7 \times A_{42} + 3{,}5 \times {A_{42}}^2 - 90{,}5 \times A_{52} + 33{,}5 \times {A_{52}}^2 + 129{,}6 \times A_{62} + 168{,}9 \times {A_{62}}^2 \quad (14)$$

$$T_m = 42{,}5 - 16{,}3 \times A_{12} - 18{,}8 \times {A_{12}}^2 + 61{,}4 \times A_{22} - 1\,368{,}2 \times {A_{22}}^2 - 65{,}1 \times A_{32} - 127{,}7 \times {A_{32}}^2 - 19{,}6 \times A_{42} + 14{,}9 \times {A_{42}}^2 + 93{,}3 \times A_{52} - 13{,}9 \times {A_{52}}^2 - 129{,}8 \times A_{62} - 116{,}6 \times {A_{62}}^2 \quad (15)$$

$$C_m = 15{,}6 - 1{,}9 \times A_{12} + 5{,}8 \times {A_{12}}^2 + 233{,}5 \times A_{22} - 212{,}6 \times {A_{22}}^2 - 53{,}1 \times A_{32} - 191{,}7 \times {A_{32}}^2 - 13{,}6 \times A_{42} + 3{,}1 \times {A_{42}}^2 + 27{,}9 \times A_{52} - 48{,}5 \times {A_{52}}^2 - 24{,}3 \times A_{62} - 5{,}1 \times {A_{62}}^2 \quad (16)$$

where

S_m is the mass fraction of styrene relative to the S-SBR, expressed in per cent;

V_m is the mass fraction of vinyl relative to the S-SBR, expressed in per cent;

T_m is the mass fraction of trans relative to S-SBR, expressed in per cent;

C_m is the mass fraction of cis relative to the S-SBR, expressed in per cent.

The styrene content is the mass fraction of styrene relative to the S-SBR.

9.2.6 Contents of three microstructure types relative to butadiene portion in the S-SBR

Contents of three microstructure types of the butadiene portion in the S-SBR are expressed by Formulae (17) to (19):

$$V = V_m/(V_m + T_m + C_m) \times 100 \quad (17)$$

$$T = T_m/(V_m + T_m + C_m) \times 100 \quad (18)$$

$$C = C_m/(V_m + T_m + C_m) \times 100 \quad (19)$$

where

V is the mol fraction of vinyl relative to the butadiene portion in the S-SBR, expressed in per cent;

T is the mol fraction of trans relative to the butadiene portion in the S-SBR, expressed in per cent;

C is the mol fraction of cis relative to the butadiene portion in the S-SBR, expressed in per cent.

10 Precision

See Annex A.

11 Test report

The test report shall include at least the following information:

a) sample details:
   1) a full description of the sample and its origin;
   2) method of preparation of test piece from the sample;
b) a reference to this document, i.e. ISO 21561-2:2024;
c) test details including any details of any procedures not specified in this document;
d) test results:
   1) the number of test pieces used;
   2) the results of the determination, expressed in % and rounded to one place of decimals;
e) date(s) of test.

Annex A
(informative)

Precision results from an interlaboratory test programme

A.1 General

The following interlaboratory test programme (ITP) was initially carried out in 2014.

All calculations to provide repeatability and reproducibility values were performed in accordance with ISO/TR 9272[1)]. Precision concepts and nomenclature are also given in ISO/TR 9272.

A.2 Precision results from the ITP

A.2.1 Programme details

The ITP was organized and conducted by Japan in 2014. Test samples were prepared in one laboratory and sent to all 16 participating laboratories.

Two S-SBRs were used in the test designated as S-33 and S-34.

The number of laboratories on which precision data for each property is based is given in the tables of precision results (Tables A.1 to A.4). The number of participating laboratories as noted in these tables is the final number after identifying certain laboratory values as outliers.

The ITP testing was conducted over a period of two sequential weeks. On a specified week, the background and determination tests for each type of rubber (n = 1 × 2) were performed in a day. One week after Day 1, the blank test and the determination tests were repeated (n = 1 × 2). All the analyses were conducted on the basis of these test results.

A.2.2 Precision results

The precision results are listed in Tables A.1 to A.4.

Repeatability: The repeatability, r, of the test method has been established as the appropriate value tabulated in Tables A.1 to A.4. Two single test results that differ by more than the value shall be considered suspect and suggest that some appropriate investigative action be taken.

Reproducibility: The reproducibility, R, of the test method has been established as the appropriate value tabulated in Tables A.1 to A.4. Two single test results that differ by more than the value shall be considered suspect and suggest that some appropriate investigative action be taken.

The precision results as determined by this ITP should not be applied to acceptance or rejection testing for any group of materials or products without documentation that the results of this precision evaluation actually apply to the products or materials tested.

1) Withdrawn and replaced by ISO 19983:2017.

Table A.1 — Precision data for styrene content of S-SBR

Sample	Mean level	S_r	r	(r)	S_R	R	(R)	No. of laboratories[a]
S-33	24,8	0,23	0,65	2,61	0,64	1,80	7,27	14
S-34	34,5	0,12	0,35	1,00	0,60	1,69	4,91	15

Key

s_r within-laboratory standard deviation (in measurement units)

r repeatability (in measurement units)

(r) repeatability (in percent of mean level)

s_R between-laboratory standard deviation (in measurement units)

R reproducibility (in measurement units)

(R) reproducibility (in percent of mean level)

[a] Number of laboratories after outliers deleted (total number of laboratories in ITP: 16).

Table A.2 — Precision data for vinyl content of S-SBR

Sample	Mean level	S_r	r	(r)	S_R	R	(R)	No. of laboratories[a]
S-33	61,1	0,35	1,00	1,64	0,80	2,25	3,69	14
S-34	42,3	0,20	0,55	1,31	0,81	2,30	5,44	15

Key

s_r within-laboratory standard deviation (in measurement units)

r repeatability (in measurement units)

(r) repeatability (in percent of mean level)

s_R between-laboratory standard deviation (in measurement units)

R reproducibility (in measurement units)

(R) reproducibility (in percent of mean level)

[a] Number of laboratories after outliers deleted (total number of laboratories in ITP: 16).

Table A.3 — Precision data for trans content of S-SBR

Sample	Mean level	S_r	r	(r)	S_R	R	(R)	No. of laboratories[a]
S-33	21,9	0,16	0,45	2,07	0,26	0,73	3,35	12
S-34	33,8	0,14	0,38	1,13	0,47	1,34	3,97	12

Key

s_r within-laboratory standard deviation (in measurement units)

r repeatability (in measurement units)

(r) repeatability (in percent of mean level)

s_R between-laboratory standard deviation (in measurement units)

R reproducibility (in measurement units)

(R) reproducibility (in percent of mean level)

[a] Number of laboratories after outliers deleted (total number of laboratories in ITP: 16).

Table A.4 — Precision data for cis content of S-SBR

Sample	Mean level	S_r	r	(r)	S_R	R	(R)	No. of laboratories[a]
S-33	17,0	0,21	0,58	3,43	0,74	2,10	12,38	13
S-34	23,5	0,24	0,69	2,95	0,95	2,69	11,45	13

Key

s_r within-laboratory standard deviation (in measurement units)

r repeatability (in measurement units)

(r) repeatability (in percent of mean level)

s_R between-laboratory standard deviation (in measurement units)

R reproducibility (in measurement units)

(R) reproducibility (in percent of mean level)

[a] Number of laboratories after outliers deleted (total number of laboratories in ITP: 16).

Annex B
(informative)

Acquisition of regression formulae for microstructure

B.1 The regression formulae for determining the microstructure were obtained by partial least squares (PLS) analysis methods.

B.2 Nineteen S-SBR samples with known microstructure shown in Table B.1 were analysed by both ^{1}H-NMR and ^{13}C-NMR spectrometry. The contents of styrene, vinyl, trans and cis were determined in accordance with Annex C. The measurements were conducted in three laboratories, and the results were averaged. These values by NMR spectrometry were used as response variables in PLS regression analysis.

B.3 ATR spectra of these samples were measured in accordance with Clause 8. The measurements were carried out once in seven laboratories.

B.4 The measured absorbances of ATR spectra were converted to ratio in accordance with 9.1 to 9.2.3.

B.5 Calculate the second order terms which are the square of A_{12} to A_{62}. A_{12} to A_{62}, and the square values of these six, are used as the explanatory variables in PLS regression analysis (see 9.2.4).

B.6 The regression Formulae (13) to (16) for determining the microstructure in Clause 9 were obtained as follows.

a) Off-the-shelf software of PLS regression (JMP® by SAS Institute Inc.[2)]) was applied.

b) The values of styrene, vinyl, trans and cis of 19 samples obtained by NMR methods in B.2 were used as response variables in PLS.

c) The values in B.5 derived from absorbance of ATR spectra by respective laboratories were used as explanatory variables in PLS.

d) The coefficients derived by the PLS regression analysis correspond to those in the Formulae (13) to (16) for styrene, vinyl, trans and cis (see 9.2.4).

Table B.1 — Microstructures of samples used for PLS regression analysis

	Styrene	Vinyl	Trans	Cis
R-01	18,1	10,2	52,2	37,6
R-02	25,7	10,3	53,8	35,9
R-03	20,7	62,8	21,4	15,7
R-04	4,8	20,1	46,4	33,5
R-05	23,2	32,6	42,2	25,2
R-06	13,4	48,1	30,9	21,0
R-07	0,0	10,6	51,9	37,5
R-08	24,8	34,5	39,7	25,8
R-09	41,4	46,1	31,2	22,7
NOTE Microstructure values were determined by ^{1}H and ^{13}C NMR spectrometry.				

2) JMP® by SAS Institute Inc. is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Table B.1 *(continued)*

	Styrene	Vinyl	Trans	Cis
R-10	34,7	56,4	24,0	19,5
R-11	36,3	41,3	33,9	24,8
R-12	41,9	34,5	39,8	25,7
R-13	26,2	9,9	53,7	36,4
R-14	0,0	55,9	24,6	19,5
R-15	0,0	70,5	16,7	12,8
R-16	8,6	37,3	37,8	24,9
R-17	4,9	77,2	12,5	10,4
R-18	25,5	49,2	29,2	21,7
R-19	29,7	30,0	44,6	25,4
NOTE Microstructure values were determined by ^{1}H and ^{13}C NMR spectrometry.				

Annex C
(informative)

Determination of microstructure by NMR spectrometry

C.1 General

Values of styrene content and contents of three microstructure types of butadiene on 19 samples to be used for obtaining the regression formulae were determined by ^{1}H-NMR spectrometry and ^{13}C-NMR spectrometry.

C.2 Determination of styrene, vinyl and sum of trans and cis by ^{1}H-NMR spectrometry

Contents of styrene, vinyl and sum of trans and cis were determined by ^{1}H-NMR spectrometry in accordance with ISO 21561-1:2015, 3.6. Formulae (C.1) and (C.2) were used additionally in this procedure.

$$V_{\mathrm{m}} = \frac{(100 - S_{\mathrm{m}}) \times V}{(V + G)} \tag{C.1}$$

$$G_{\mathrm{m}} = 100 - S_{\mathrm{m}} - V_{\mathrm{m}} \tag{C.2}$$

where

V_{m} is the mass fraction of vinyl relative to the S-SBR, expressed in per cent;

G_{m} is the sum of mass fractions of trans and cis relative to the S-SBR, expressed in per cent;

S_{m} is the mass fraction of styrene relative to the S-SBR, expressed in per cent;

V is the mol fraction of vinyl relative to the butadiene portion in the S-SBR, expressed in per cent;

G is the sum of mol fractions of trans and cis relative to the butadiene portion in the S-SBR, expressed in per cent.

C.3 Determination of trans and cis by ^{13}C-NMR spectrometry

C.3.1 Conditions for measuring ^{13}C-NMR spectra

^{13}C-NMR spectra were measured by NMR spectrometers with 100 MHz or 125 MHz under the following conditions.

— Solvent: $CDCl_3$, containing 0,3 ml/l of tetramethyl silane (TMS) as internal standard; the purity of the $CDCl_3$ > 99,8 % (atom%D).

— Sample concentration: 50 mg/ml.

— Mode: ^{1}H complete decoupling.