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

Part 2:
FTIR with ATR method

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

Partie 2: Méthode FTIR avec ATR

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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 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 analysis*.

This first edition of ISO 21561-2 cancels and replaces ISO 21561:2005, which has been technically revised. It also incorporates Amendment ISO 21561:2005/Amd.1:2010.

ISO 21561 consists of the following parts, under the general title *Styrene-butadiene rubber (SBR) — Determination of the microstructure of solution-polymerized 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 2:
FTIR with ATR method

WARNING — Persons using this part of ISO 21561 should be familiar with normal laboratory practice. This part of ISO 21561 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 part of ISO 21561 might 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 Fourier Transform Infrared Spectrometry (FTIR) with Attenuated Total Reflection (ATR) method. The styrene content is expressed in mass % relative to the whole polymer. The vinyl, trans and cis contents are expressed in mol % relative to the butadiene content. This method is only applicable to raw rubbers.

NOTE 1 Precision as shown in Annex A may not be obtained for S-SBRs containing polystyrene block or styrene content more than 45 mass %.

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

3 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 wavelengths are used to determine the content of each component by using the specific formulae presented in this part of ISO 21561.

4 Apparatus

4.1 FTIR, of the following specifications:

— Detector: Deuterium Tri-Glycine Sulfate (DTGS) or Tri-Glycine Sulfate (TGS);

— Number of scans: 32;

— Resolution: 2 cm^{-1};

— Range of wavelength: 600 cm^{-1} to 1 800 cm^{-1}.

4.2 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 preferable.

5 Calibration

5.1 FTIR

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

5.2 ATR

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

6 Sampling

6.1 Prepare the test sample in accordance with ISO 1795.

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

6.2 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.

7 Procedure for measuring ATR spectrum

7.1 Set up FTIR according to the manufacturer's instruction manual.

7.2 Set ATR in a sample chamber of FTIR.

7.3 Measure the background spectrum with the conditions shown in 4.1.

7.4 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 4.2. The contact between the test piece and the crystal affects the absorbance of ATR spectra.

7.5 Measure the sample spectrum with the conditions shown in 4.1.

7.6 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.

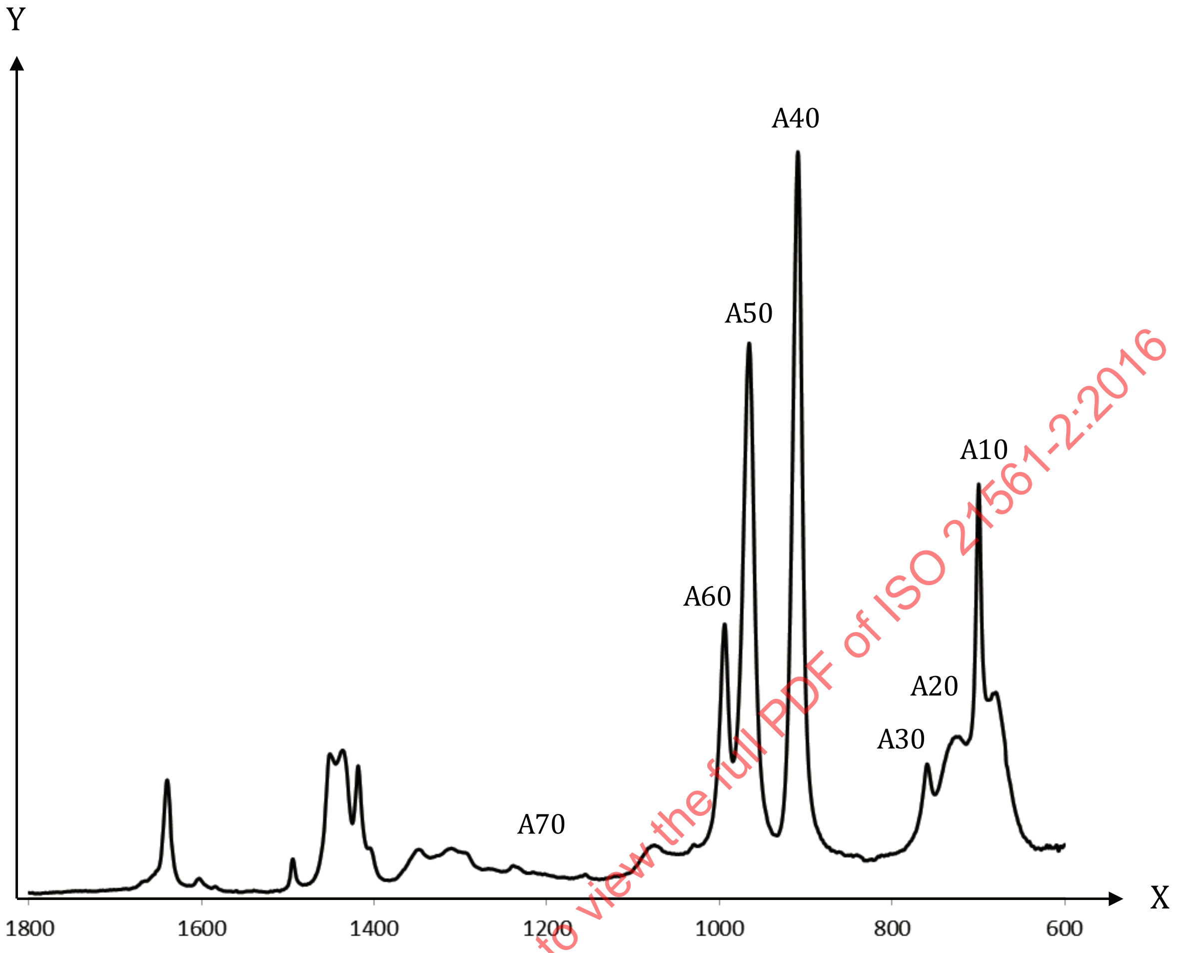
8 Determination of the microstructure of butadiene and the styrene content

8.1 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.

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

Notation for absorbance	Microstructure component	Remarks
A10	Styrene	Measure the absorbance at the peak maximum from 695 cm^{-1} to 700 cm^{-1}.
A20	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}.
A30	Styrene	Measure the absorbance at the peak maximum from 755 cm^{-1} to 761 cm^{-1}.
A40	Vinyl	Measure the absorbance at the peak maximum from 905 cm^{-1} to 912 cm^{-1}.
A50	Trans	Measure the absorbance at the peak maximum from 962 cm^{-1} to 967 cm^{-1}.
A60	Vinyl	Measure the absorbance at the peak maximum from 991 cm^{-1} to 996 cm^{-1}.
A70	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

8.2 Calculation of microstructures

8.2.1 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.

8.2.2 Base line correction of each absorbance peak

Obtain the absorbance of each of the peaks A11 to A61 with corrected base lines by using Formulae (1) to (6):

$$A11 = A10 - A70 \quad (1)$$

$$A21 = A20 - A70 \quad (2)$$

$$A31 = A30 - A70 \quad (3)$$

$$A41 = A40 - A70 \quad (4)$$

$$A51 = A50 - A70 \quad (5)$$

$$A61 = A60 - A70 \quad (6)$$

8.2.3 Ratio of absorbance

Obtain the ratios of the absorbances A12 to A62 by using Formulae (7) to (12):

$$A12 = (A11)/(A11 + A21 + A31 + A41 + A51 + A61) \quad (7)$$

$$A22 = (A21)/(A11 + A21 + A31 + A41 + A51 + A61) \quad (8)$$

$$A32 = (A31)/(A11 + A21 + A31 + A41 + A51 + A61) \quad (9)$$

$$A42 = (A41)/(A11 + A21 + A31 + A41 + A51 + A61) \quad (10)$$

$$A52 = (A51)/(A11 + A21 + A31 + A41 + A51 + A61) \quad (11)$$

$$A62 = (A61)/(A11 + A21 + A31 + A41 + A51 + A61) \quad (12)$$

8.2.4 Second order terms

Calculate the second order terms which are the squares of A12 to A62.

8.2.5 Styrene content and microstructures in mass % by regression formulae

The content (mass %) of each microstructure component is expressed by the following regression Formulae (13) to (16):

$$S_m = 9{,}0 + 12{,}9 \times (A12) + 25{,}9 \times (A12)^2 - 111{,}2 \times (A22) + 412{,}5 \times (A22)^2 + 105{,}0 \times (A32) + 891{,}9 \times (A32)^2 - 0{,}5 \times (A42) - 21{,}5 \times (A42)^2 - 30{,}7 \times (A52) + 28{,}9 \times (A52)^2 + 24{,}5 \times (A62) - 47{,}2 \times (A62)^2 \quad (13)$$

$$V_m = 32{,}9 + 5{,}3 \times (A12) - 12{,}9 \times (A12)^2 - 183{,}6 \times (A22) + 1\,168{,}4 \times (A22)^2 + 13{,}2 \times (A32) - 572{,}5 \times (A32)^2 + 33{,}7 \times (A42) + 3{,}5 \times (A42)^2 - 90{,}5 \times (A52) + 33{,}5 \times (A52)^2 + 129{,}6 \times (A62) + 168{,}9 \times (A62)^2 \qquad (14)$$

$$T_m = 42{,}5 - 16{,}3 \times (A12) - 18{,}8 \times (A12)^2 + 61{,}4 \times (A22) - 1\,368{,}2 \times (A22)^2 - 65{,}1 \times (A32) - 127{,}7 \times (A32)^2 - 19{,}6 \times (A42) + 14{,}9 \times (A42)^2 + 93{,}3 \times (A52) - 13{,}9 \times (A52)^2 - 129{,}8 \times (A62) - 116{,}6 \times (A62)^2 \qquad (15)$$

$$C_m = 15{,}6 - 1{,}9 \times (A12) + 5{,}8 \times (A12)^2 + 233{,}5 \times (A22) - 212{,}6 \times (A22)^2 - 53{,}1 \times (A32) - 191{,}7 \times (A32)^2 - 13{,}6 \times (A42) + 3{,}1 \times (A42)^2 + 27{,}9 \times (A52) - 48{,}5 \times (A52)^2 - 24{,}3 \times (A62) - 5{,}1 \times (A62)^2 \qquad (16)$$

where

S_m is the styrene content of the S-SBR, in mass %;

V_m is the vinyl content of the S-SBR, in mass %;

T_m is the trans content of the S-SBR, in mass %;

C_m is the cis content of the S- SBR, in mass %.

8.2.6 Microstructures in mol %

The content (mol %) in butadiene is expressed by Formulae (17) to (19):

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

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

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

where

V is the vinyl content of the butadiene portion of the S-SBR, in mol %;

T is the trans content of the butadiene portion of the S-SBR, in mol %;

C is the cis content of the butadiene portion of the S-SBR, in mol %.

9 Precision

See Annex A.

10 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) if appropriate, method of preparation of test piece from the sample;

b) a reference to this part of ISO 21561, i.e. ISO 21561-2;

c) test details including any details of any procedures not specified in this part of ISO 21561;

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. 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 ($n = 1 \times 2$) were performed in a day. One week after Day 1, the blank test and the determination tests were repeated ($n = 1 \times 2$). 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.

Explanation of symbols for Tables A.1 to A.4:

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).

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	0,80	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

[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

[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

[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

[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 7. The measurements were carried out once in seven laboratories.

B.4 The measured absorbances of ATR spectra were converted to ratio in accordance with 8.1 to 8.2.3.

B.5 Calculate the second order terms which are the square of A12 to A62. A12 to A62, and the square values of these six, are used as the explanatory variables in PLS regression analysis (see 8.2.4.).

B.6 The regression Formulae (13) to (16) for determining the microstructure in Clause 8 were obtained as follows.

a) Off-the-shelf software of PLS regression (JMP®[1]) by SAS Institute Inc.) 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 8.2.4).

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
NOTE Microstructure values were determined by ^{1}H and ^{13}C NMR spectrometry.				

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[1] 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-09	41,4	46,1	31,2	22,7
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 butadiene microstructure 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

Content 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.

$$V_m = \frac{(100 - S_m) \times V}{(V + G)} \tag{C.1}$$

$$G_m = 100 - S_m - V_m \tag{C.2}$$

where

V_m is the vinyl content of the S-SBR, in mass %;

G_m is sum of the trans and the cis content of the S-SBR, in mass %;

S_m is the styrene content of the S-SBR, in mass %;

V is the vinyl content of the butadiene of the S-SBR in mol %;

G is the trans and cis content of the butadiene of the S-SBR in mol %.

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 with an NMR spectrometer with 400 MHz and two NMR spectrometers with 500 MHz under the following conditions:

- Solvent: $CDCl_3$, containing 0,03 % of tetramethyl silane (TMS) as internal standard; the purity of the $CDCl_3$ > 99,8 %;
- Sample concentration: 50 mg/ml;
- Mode: ^{1}H complete decoupling;

NOTE For quantitative analysis of ^{13}C-NMR, “inverse gated decoupling” is applied basically. In this analysis, however, “^{1}H complete decoupling” which is a common method for qualitative analysis was applied. The reason of using “^{1}H complete decoupling” was that, regarding ^{13}C-NMR peaks by both trans-methylene and cis-methylene carbons which were used for the quantitative analysis, the difference by Nuclear Overhauser Effect (NOE) was considered small because these methylene carbons were considered magnetically equivalent. Actually, values obtained using ^{1}H complete decoupling method were comparable to those obtained using inverse gated decoupling method, as shown in Table C.1.

- Measurement temperature: room temperature;
- Number of data points: 32 k;
- Offset:100 ppm;
- Sweep width: 250 ppm;
- Pulse width: 30°;
- Repetition time: 3 s;
- Number of scans: 5 000 times;
- Number of dummy scan: four times;
- Spinning rate: 15 Hz;
- Adjustment of the resonance of the reference peak to 0,00 ppm for TMS.

Table C.1 — Comparison on the trans and cis contents by different determination modes

Mode	Inverse gated decoupling (normally for quantitative)	^{1}H complete decoupling (normally for qualitative)
Trans (mol%)	63,2	62,4
Cis (mol%)	36,8	37,6

C.3.2 Analysis of the ^{13}C-NMR spectrum

The signals of the ^{13}C-NMR spectrum over each of the areas are defined in Table C.2.

Figure C.1 gives an example of a ^{13}C-NMR spectrum showing the areas N_a to N_f.

Each integrated value on area N_a to N_f was obtained for the determination of trans and cis contents.

Table C.2 — Definition of signal integration areas

Area	Signal integration range
N_a	From minimum intensity point around 24,7 ppm to minimum intensity point around 25,6 ppm
N_b	From minimum intensity point around 27,1 ppm to minimum intensity point around 27,7 ppm
N_c	From minimum intensity point around 29,8 ppm to minimum intensity point around 30,7 ppm
N_d	From minimum intensity point around 32,4 ppm to minimum intensity point around 33,0 ppm
N_e	From minimum intensity point around 33,8 ppm to minimum intensity point around 34,2 ppm
N_f	From minimum intensity point around 38,05 ppm to minimum intensity point around 38,35 ppm