Characterization of several HTPB binder samples by NMR, GPC and OH-number

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Abstract

Hydroxyl terminated polybutadiene (HTPB) continues to be the first choice as pre-polymer for an elastomer binder for high performance solid rocket propellants and plastic bonded high explosive charges. Cured with isocyanates to polyurethane elastomers, so-called HTPB binders have unique properties: high strain capacity with suitable values of young modulus, excellent low temperature properties with a glass-rubber transition temperature in the range of -75°C to -85°C (HTPB binders without plasticizer) determined using DMA at 0.1Hz, low hygroscopicity, and good ageing behaviour, when protected by adapted antioxidant functionality. Further on, curing behaviour is well controllable and pot life is adjustable to the needs. In detail the achievable property spectrum depends on the structure of the chains, the cis-trans-vinyl ratio of C=C double bonds, the mean molar mass or mean chain length and the mean number of OH groups per molecule and their positions along the chains.

Several HTPB samples were characterised with three analytical methods: (1) NMR (nuclear magnetic resonance) spectroscopy in ^{1}H and ^{13}C mode to retrieve several information such as mean molecular mass of the HTPB, ratio of cis, trans and vinyl isomers and their molecular environment, and with assumptions, also the mean number of OH groups per molecule; (2) GPC (gel permeation chromatography) to determine the molar mass distribution and the mean molar masses Mn, Mw, Mz as well as polydispersity D (relative to polystyrene standards); (3) the so-called OH number (OH-n) or hydroxyl value and the equivalent mass Eqm are obtained by acetylation of OH groups and back-titration of surplus acetic acid with potassium hydroxide solution (KOH). Discussion of the results in terms of suitability of and differences between the individual HTPB lots is included.

1. Introduction

The properties and characteristics of the polyol pre-polymer for polyurethane bonded composite rocket propellants and also for PBX (plastic bonded high explosives) are determining the quality of these products. The glass-rubber transition temperature region and the strain capacity are such properties strongly influenced by the pre-polymer type [1]. To achieve low glass-transition temperatures, the polymer must be as less polar as possible. One must be aware that plasticizers cannot compensate unsuitable properties of the basic elastomeric system with respect to both strain capacity and strength [2]. This low polarity demand is guiding directly to polybutadiene or isoprene rubbers [3]. Therefore, the first choice to fulfil low glass-transition temperatures is the hydroxyl-terminated polybutadiene (HTPB) as polyol. Further, the network formed with polyisocyanates in polyaddition reaction must have long enough sliding chains between the cross-link points. Therefore, only the ends of the pre-polymer should bear OH-groups to create the network. This is not the case with HTPB materials. Different HTPB types exist with different mean numbers of OH-groups per molecule. They range between 2.1 and 2.8. It is clear from elastomer mechanics that the higher the mean OH functionality per mole-

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cule, the lower the performance of the propellant with respect to strain capacity and glass-rubber transition temperature. This cannot be compensated by addition of plasticizers.

In this work, we have investigated several HTPB samples of very different origin and of different quality with respect to hydroxyl value (so-named OH number), equivalent mass, molar mass distribution, number averaged mean molar mass, the average OH numbers per polymer chain and further configuration properties of the samples as trans to cis to vinyl ratios.

2. Materials

Several HTPB types were investigated, which are not named in full in this paper. The types are listed in Table 1. HTLO type means type HTPB R45 HTLO or similar to this type. Measurements made are indicated. ^{1}H-NMR and ^{13}C-NMR spectra were recorded. With GPC the mean molar masses Mn, Mw and Mz were determined from the molar mass distribution functions relative to polystyrene calibration standards.

Table 1: The types of HTPB pre-polymers investigated.

Number	Sample (typically named)	Remarks	Measured in		
			NMR	OH-n	GPC
1a	HTPB-M1, type R45 M	first determ.	x	x	x
1b	HTPB-M2, type R45 M	second determ.			x
1c	HTPB-M3, type R45 M	third determ.			x
2a	HTPB-H, type HTLO	first determ.	x	x	x
2b	HTPB-H, type HTLO	second determ.		x	x
2c	HTPB-H, type HTLO	third determ.		x	x
3	HTPB-C, R45 M type		x	x	x
4	HTPB-1_VO, HTLO type	old material	x	x	x
5	HTPB-2_AB, HTLO type	older material	x	x	x
6	HTPB-3_AQ, HTLO type	older material	x	x	x
7	HTPB-4_OB, HTLO type	old material	x	x	x
8a	HTPB-E, HTLO type	fresh material	x	x	x
8b	HTPB-E, HTLO type	fresh material		x	

Some of the samples have been measured several times and the results are compared individually. Some of the lots contain an antioxidant, very probably of the phenolic type like Vulkanox^{TM} BHT (2,6-di-tert.-butyl-4-methylphenol), M = 220.4 g/mol) or Vulkanox^{TM} BKF (2,2´-methylene-bis-(4-methyl-6-tert.-butyl-phenol), M = 340.6 g/mol). Both are on the market under several brand names.

The name HTPB indicates that the pre-polymer was obtained from butadiene. It consists of about 40 to 60 butene units and is “end capped” by –OH groups. The backbone has so called 1,4 units with trans and cis double bonds and also 1,2 units as vinyl side groups. The ratio is around 60:20:20 for trans to cis to vinyl. Because of the atactic configuration of vinyl side groups in standard HTPB types, they can be seen as comb-type polymer. Fig. 1 shows some ‘idealized’ configurations of polybutadiene (cis-1,4, trans-1,4 and 1,2 polybutadiene) and a randomly polymerized polybutadiene.

HTPB is commonly produced by polymerization of 1,3-butadiene [4]. The ratio of isomers and the mean molar mass (number averaged) of HTPB depend on the synthesis route and the catalyst used [4, 5].

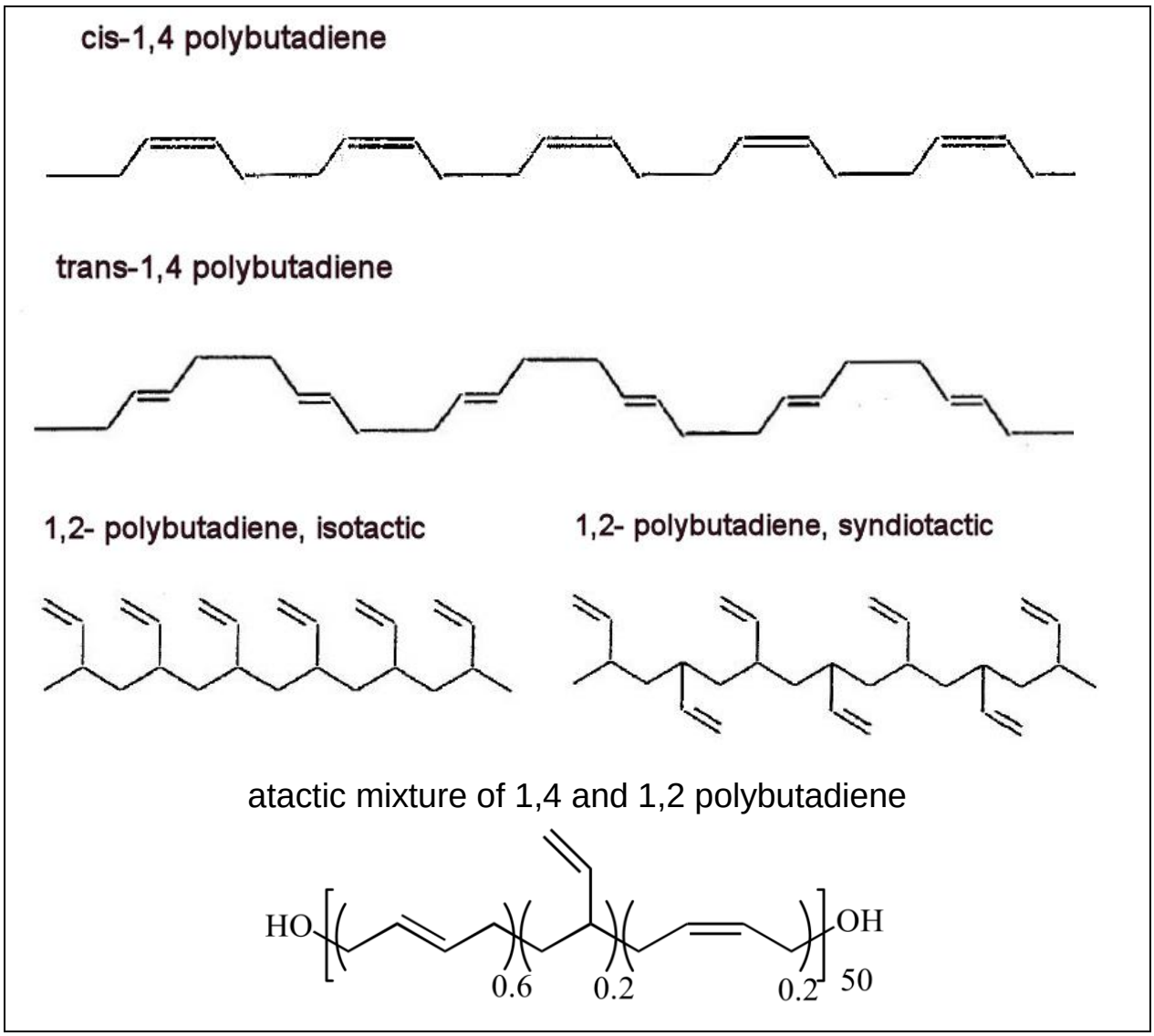

Fig. 1: 'Idealized' configurations of polybutadiene and a randomly polymerized polybutadiene used in HTPB. The atactic example is typical for the HTPB qualities used for CRP and PBX.

3. Methods

3.1 Nuclear magnetic resonance (NMR)

The used spectrometer components are from company Bruker: Avance II 400 MHz console; Spectrospin 400/89 magnet system (wide bore magnet, unshielded, nitrogen and helium cooled); the operating and evaluation software is Bruker TOPSPIN 2.1; the probe is a Bruker 400 MHz multinuclear inverse z-gradient, type VSP 400. The resonance frequencies of ^{1}H and ^{13}C are 400.13 MHz and 100.62 MHz, respectively. The temperature at the probe during measurements was the room temperature of about 23°C.

The HTPB samples were dissolved in deuterium enriched trichloromethane (99.8 % D), transferred into NMR test tubes (diameter 5 mm) and measured with several NMR techniques. The

chemical shifts of ^{13}C were predicted using the software package ChemDraw Ultra 5.0 [6]. The measurement conditions and parameters are listed in Table 2.

Table 2: Parameters of ^{1}H NMR and ^{13}C NMR measurements.

Parameter	Conditions / values
Pulse program for ^{1}H analyses (name/s)	zg [7] and cosyqf [8, 9]
Pulse program for ^{13}C analyses (name/s)	zgig [10, 11] and jmod [12]
Pulse program for $^{1}H^{13}C$ analyses (name/s)	hmqcetgp [13] and hmbcetgpnd [14]
Chemical shift of solvent in ^{1}H spectra	δ = 7.24
Chemical shift of solvent in ^{13}C spectra	δ = 77.0
Recorded chemical shift region for ^{1}H spectra	δ = - 1 to δ = 12
Recorded chemical shift region for ^{13}C spectra	δ = - 10 to δ = 230

Figures 2 to 5 show all chemical structures of butene units terminated by -OH groups. Figure 6 is an example of a polymer chain, each butene unit indicated with numbers for the C atoms. Thus NMR signals (e. g. in ^{13}C inverse gated spectra) can be assigned to functional groups much easier and misunderstandings can be prevented. R, R_1 and R_2 represent further chain elements or terminating -OH groups.

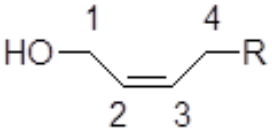

Fig. 2: Terminal *cis*-2-butene unit, with primary terminal HO-CH_2-

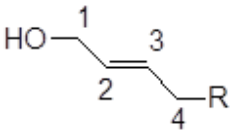

Fig. 3: Terminal *trans*-2-butene unit, with primary terminal HO-CH_2-

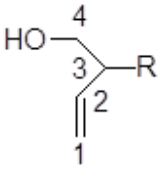

Fig. 4: Terminal 1-butene unit (vinyl), with primary terminal HO-CH_2-

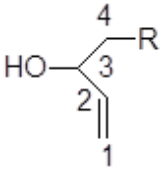

Fig. 5: Terminal 1-butene unit (vinyl), with secondary terminal HO-CH-

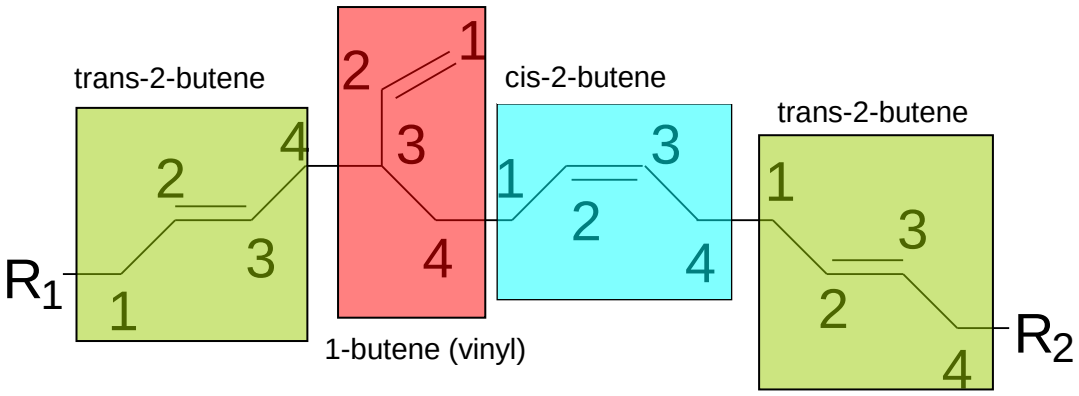

Fig. 6: Chain section of alternating *trans*-2-butene (green), 1-butene (red) and *cis*-2-butene units (blue).

The ^{13}C NMR spectra of the HTPB samples are used to determine the properties described in the following and the methods are based on the integrated signals. For this the coupling be-

tween ^{13}C and ^{1}H must be supressed by special pulse programs. However, then the nuclear Overhauser effect (NOE) may change the intensities of the different ^{13}C atoms in different extent and the integrated peaks could not be used for quantitative evaluation. In this case, a special pulse technique allows to suppress the NOE, the so-called inversed gated decoupling technique.

By approved procedures, two characteristic properties of HTPB can be determined from the NMR spectra: (1) the mean molar masses of the HTPB samples and (2) the mean ratio of the three isomers; (3) a third property based on assumptions is the mean number of OH groups per HTPB molecule. In the following, the corresponding three procedures are described.

Procedure 1
Determination of mean molar mass of the HTPB samples. This mean molar mass corresponds to the mean molar mass Mn obtained by osmometry for example or by GPC when using absolute calibration.

1. Record of a ^{13}C-spectrum by inverse gated decoupling to obtain the chemical shifts of HTPB signals without splitting by ^{1}H coupling and without intensity distortion by NOE;

2. Determination of the cumulative signal area between $\delta \approx 113$ and $\delta \approx 145$, which is the ^{13}C shift region of -CH=CH- of cis and of -CH=CH- of trans groups and of $-CH=CH_2$ of vinyl groups; this integral value is called $I_{C=Call}$, it represents the whole sample;
   The number of butene units in the whole sample is defined as $N_{butene} = Kb * I_{C=Call}/2$, with Kb as proportionality constant, whereby the definition is based on using one sp^2-C for one butene unit in the molecule;

3. Calculate the signal area between $\delta \approx 57$ and $\delta \approx 66$ of ^{13}C-atoms, which bear each one terminating OH group. This integral value is called I_2 and represents the whole sample;

4. With the assumption that per HTPB chain (non-branched) only at its two ends a terminating $-CH_2-OH$ group exists, the integral value I_2 corresponds exactly to two $-CH_2-OH$ groups per HTPB molecule. Then the number of HTPB molecules $N_{molecule}$ in the whole sample is defined as
   $N_{molecule} = Kn * I_2/2$, with Kn as proportionality constant;

5. Divide the number of butene units in the whole sample obtained in step 2 by the number of molecules $N_{molecules}$ in the sample from step 4; this gives the number of butene units per molecule:
   $N_{butene/molecule} = N_{butene} / N_{molecule} = Kb/Kn * I_{C=Call}/2 / I_2/2$
   The proportionality factors are equal by using this NMR technique and the mean number of butene units per molecule is obtained;

6. Multiply the result of step 5 with the molar mass of a single butene unit (M = 54.1 g/mol);

7. Add the molar mass of two OH groups (M = 34.01 g/mol) to the result from step 6; this gives the mean molar mass of one HTPB molecule.

Procedure 2
Determination of the ratio of the isomers trans, cis and vinyl in the HTPB sample.

1. Record of a ^{13}C spectrum with inverse gated decoupling to obtain all HTPB signals without splitting by ^{1}H coupling and without intensity distortion by NOE;

2. Determination of the cumulative signal area between $\delta \approx 113$ and $\delta \approx 145$, which is the ^{13}C shift region of -CH=CH- of cis and of -CH=CH- of trans groups and of -

$CH=CH_2$ of vinyl groups; this integral value is called $I_{C=Call}$, it represents all sp^2-C atoms in the whole sample;

3. Determination of the partial integrals of the signals in the shift regions:
   (1) $\delta \approx 113 – 118$, for $=CH_2$ of 1-butene units, integral value is named $I_{CH2\text{-}vinyl}$
   (2) $\delta \approx 126 – 135$, for –CH=CH- of *cis*-2-butene and for –CH of *trans*-2-butene units together, integral value is named $I_{CH\ cis+trans}$
   (3) $\delta \approx 138 – 145$, for –CH= of 1-butene units, integral value is named $I_{CH\text{-}vinyl}$

4. Add together cut out areas of both sp^2-C vinyl units to obtain the corresponding ^{13}C signal integral of vinyl $-CH=CH_2$ in the whole sample; this integral value is named $I_{vinyl;}$ $I_{vinyl} = I_{CH2vinyl} + I_{CHvinyl}$

5. Divide the area of ^{13}C of 1-butene units (result of step 4) by total area of ^{13}C in the shift region of the -C=C- groups (from step 2), to get the relative content G_{vinyl} of 1-butene in the sample;
   $G_{vinyl} = I_{vinyl} / I_{C=Call}$;

6. Determine the signal integral of both $-CH_2-$ groups of *cis*-2-butene units in the shift region $\delta \approx 24$ - 28.5; this integral value is named I_{cis};

7. Determine the signal integral of both $-CH_2-$ groups of *trans*-2-butene units in the shift region $\delta \approx 29.4$ - 33.5; this integral value is named I_{trans};

8. Add area value of $-CH_2-$ ^{13}C assigned to *cis*-2-butene (result of step 6) to area value of $-CH_2$ ^{13}C assigned to *trans*-2-butene (result of step 7); this gives an area value proportional to total number of $-CH_2-$ of cis 2-butene and trans 2-butene; this integral value is named $I_{cis+trans}$;

9. Determine the parts of signal integrals of shift region $\delta \approx 24$ - 28.5 (*cis*-2-butene) and of shift region $\delta \approx 29.4$ - 33.5 (*trans*-2-butene) by dividing the signal integrals obtained in step 6 and step 7 by the summed up signal integral of step 8:
   $P_{trans} = I_{trans} / I_{cis+trans}$ $P_{cis} = I_{cis} / I_{cis+trans}$;

10. Multiply signal integral from $\delta \approx 126$ - 135 ($-CH=CH-$) of *cis*-2-butene and *trans*-2-butene units with either part P_{cis} or P_{trans} and divide by the result from step 2 to get corresponding relative contents G_{cis} and G_{trans} of *cis*-2-butene and of *trans*-2-butene, respectively, in the sample;
    $G_{trans} = I_{CHcis+trans} * P_{trans} / I_{C=Call}$; $G_{cis} = I_{CHcis+trans} * P_{cis} / I_{C=Call}$.

Procedure 3

Determination of the mean number of -OH groups per molecule is based on the assumption that signals in the chemical shift regions $\delta \approx 55 – 57$ and $\delta \approx 66 – 70$ were caused by ^{13}C attached to additional -OH groups

1. Record of a ^{13}C spectrum with inverse gated decoupling to obtain all HTPB signals without splitting by ^1H coupling and without intensity distortion by NOE ;

2. Calculate the ^{13}C signal area of $–CH_2-OH$ between $\delta \approx 57$ and $\delta \approx 66$;

3. The area value of step 2 represents two OH groups per molecule under the assumption that termination of chains occurs on both ends, that means with $–CH_2-OH$; this area value is called I_{OHend}, it is formally identical to I_2 from procedure 1; the number of $-CH_2-OH$ end groups in the whole sample is called $N_{OHend} = K_{OH} * I_{OHend}$ with K_{OH} as proportionality factor; the number of 'OHend' groups per molecule is formally calculated by $N_{OHend/molecule} = K_{OH} * I_{OHend} / Kn * I_2/2 = 2$;

4. Determination of ^{13}C peak areas in the shift regions $\delta \approx 55 - 57$ and $\delta \approx 66 - 70$; These peaks are assumed to originate from additional -CH-OH; the summed-up area value is called I_{OHadd}; the number of additional OH end groups per molecule is obtained by: $N_{OHadd/molecule} = I_{OHadd} / I_{OHend}/2$;

5. Addition of the results of steps 3 and 4 to the total mean number of OH-groups per molecule: $N_{OHall/molecule} = N_{OHend/molecule} + N_{OHadd/molecule} = 2 + N_{OHadd/molecule}$.

3.2 Gel permeation chromatography (GPC)

GPC is used to analyse a polymeric sample according to its composition of molecules of different length or of molar mass. For this, the sample must be soluble in a suitable solvent. A small amount of solution is injected in a column set with porous material, which serves as separation device according to the size (hydrodynamic volume) of the polymeric molecules. Because the size of the polymeric molecule is determined by its molar mass, one gets finally a molar mass distribution of this polymeric sample [15, 16]. Applications of GPC for nitrocellulose can be found in [17, 18].

3.2.1 Instrumentation

The instrumentation of the GPC apparatus:
Agilent Series 1100 consisting of isocratic pump, injection block, auto-sampler, refractive index detector 1100RID, column oven
Solvent degasser from company PSS, Mainz, Germany

Column set: SDV columns from company PSS, Mainz, Germany
SDV: modified styrene-divinylbenzene copolymer network
Pre-column for protecting the main column set:
PSS precolumn SDV 5µ, 8 mm in diameter and 50 mm long
Separation columns (particle size 5µm, pore size in Å) in series
PSS SDV 5 µ 50Å
PSS SDV 5 µ 100Å
PSS SDV 5 µ 1000Å
PSS SDV 5 µ 100 000Å
The dimensions of the separation columns: 8 mm in diameter and 300 mm long.

Sample solvent and eluent:	tetrahydrofurane (THF) not stabilised, with 0.2 mass-% TFA (trifluoro acetic acid)
Flow:	1.0 ml/min
Temperature of column oven:	35°C
Temperature of RID detection cell:	35°C

Typical polymer sample concentration in THF	0.5 to 3 mg/ml
Typical sample injection volume	100µl

The used calibration standards for the column set are narrowly distributed polystyrene standards in the molar mass range from 162 to1210000 g/mol (as peak molar mass Mp), obtained from company PSS, Mainz, Germany. All results are relative to these standards.

Software: PSS WinGPCUniChrom, from company PSS, Mainz, Germany.

3.2.2 Calibration of the column set

In Fig. 7 the schematic GPC calibration curve is shown as the decadic logarithm of molar mass as function of elution volume Ve. The solid curve is the ideal calibration curve, if the separation of the molecules follows perfectly the size exclusion process.

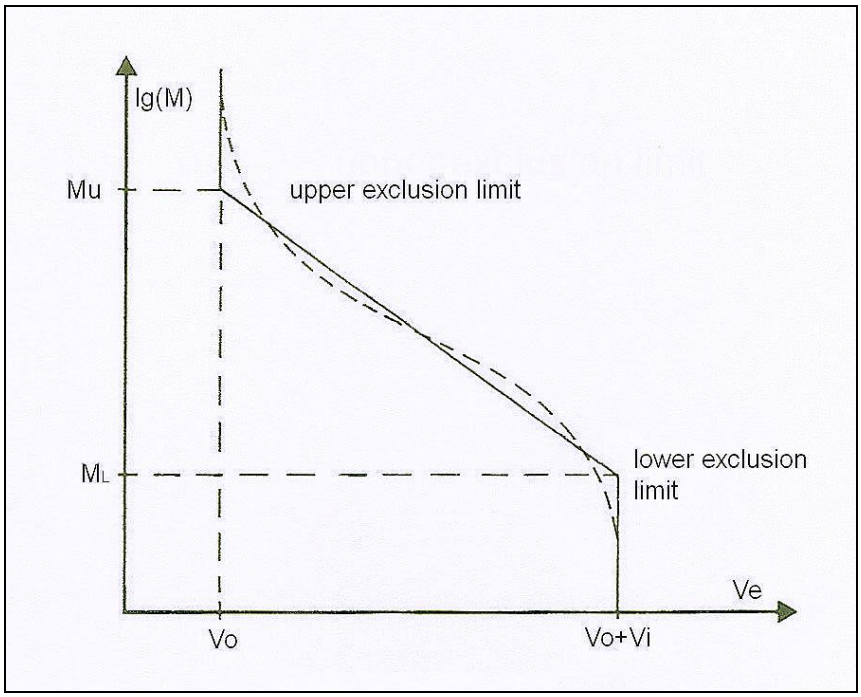

Fig. 7: Idealized exclusion behaviour of a GPC column set, solid line, and the typical appearance of the real size exclusion behaviour, broken line.

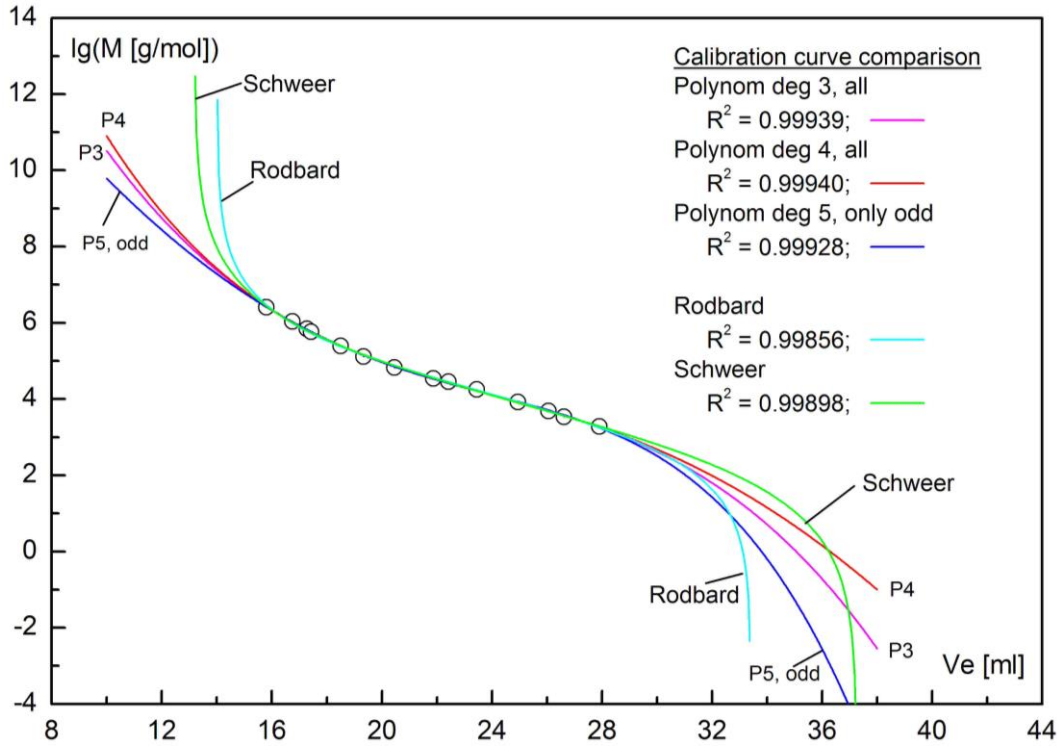

Fig. 8: Comparison of some polynomial calibration curves with Rodbard and Schweer equations. The lack of correctly regarding the exclusion limits with polynomials can be seen clearly especially at the upper exclusion limit.

Molecules greater than the largest pores elute at first and appear all together at the beginning of the chromatogram; they are in size above the upper size exclusion limit M_U. Molecules smaller than the smallest pores elute last and appear all together at the end of the chromatogram; they are in size below the lower size exclusion limit M_L. The broken curve is the general appearance of a real calibration curve. Vo is the outer column volume between the gel particles (=mobile phase), Vi is inner volume of the column, means the volume of the pores inside the gel particles. More details about calibration can be found in [15, 19].

The often found S shape of the calibration curve, lg(Mp [g/mol]) versus elution volume Ve, can mostly be described by a polynomial of degree 3 or 5. One should use only odd degrees [5]. The general calibration equation is given in Eq.(1). The polynomial is shown in Eq.(2). In Fig. 8 the polynomial of degree 3 and 5 are compared and also some special calibration equations developed by Rodbard [20, 21] and Schweer [22].

It can be seen that polynomials have not a good definition of the exclusion limits, whereas the other two equations show pronounced exclusion limits. The Rodbard equation is given in Eq.(3) and it seems quite good solution if one must operate near the exclusion limits.

$$\lg(M(Ve)) = f(Ve) \tag{1}$$

$$\lg(M(Ve)) = a_0 + a_1 \cdot Ve + a_2 \cdot Ve^2 + a_3 \cdot Ve^3 + a_4 \cdot Ve^4 + a_5 \cdot Ve^5 \tag{2}$$

Rodbard [20] has proposed a calibration equation, which has intrinsically the pronounced S shape. For large M values Ve approaches Vo, the upper exclusion limit. With M going to zero Ve becomes Vt = Vo+Vi, the lower exclusion limit. The built-in limit regions simulate the real situation much better than polynomials. But up to now the companies offering GPC evaluation software have installed only the polynomial calibration possibility. With polynomials a linear fit algorithm can be used, with Rodbard equation a non-linear fit procedure must be employed.

$$\lg(M(Ve)) = \lg\left(c \cdot \left(\frac{Vi}{Ve - Vo} - 1\right)\right) \quad \text{with } Ve \geq Vo \tag{3}$$

Ve elution volume (retention volume)
Vo volume between gel particles of column set (mobile phase)
Vi inner pore volume of column set
Vt total elution volume Vt of column set, Vt = Vo +Vi
M molar mass at Ve(M)
c scaling constant with the dimension of molar mass

In Table 3 one set of calibration data used is compiled. Fig. 9 shows elugrams of some of the used standards, and in Fig. 10 the calibration curve is shown, established with a polynomial of degree 3 and of degree 5. Together with the elugram distribution of HTPB sample, see Fig. 11, the MMD of the HTPB samples can be established. The procedure is described in section 3.2.3.

Table 3: One complete set of calibration data used for a specified column set and instrument configuration. Given is the peak molar mass of narrowly distributed polystyrene standards and the associated elution volumes Ve. The logarithm to base 10 is abbreviated by lg. Because the polystyrene standards have small D values near one, Mp ≈ Mn ≈ Mw.

Ve [ml]	lg(Mp [g/mol])	Mp [g/mol]
21.72	6.222716471	1670000
22.5	5.980457892	956000
23.23	5.720985744	526000
24.16	5.397940009	250000
25.03	5.152288344	142000
25.62	5.00000	100000
26.46	4.819543936	66000
27.26	4.645422269	44200
28.12	4.447158031	28000
29.13	4.195899652	15700
30.22	3.960470778	9130
30.87	3.815577748	6540
31.53	3.691965103	4920
32.36	3.540329475	3470
33.53	3.357934847	2280
34.99	3.096910013	1250
37.77	2.675778342	474
39.42	2.424881637	266
40.84	2.209515015	162

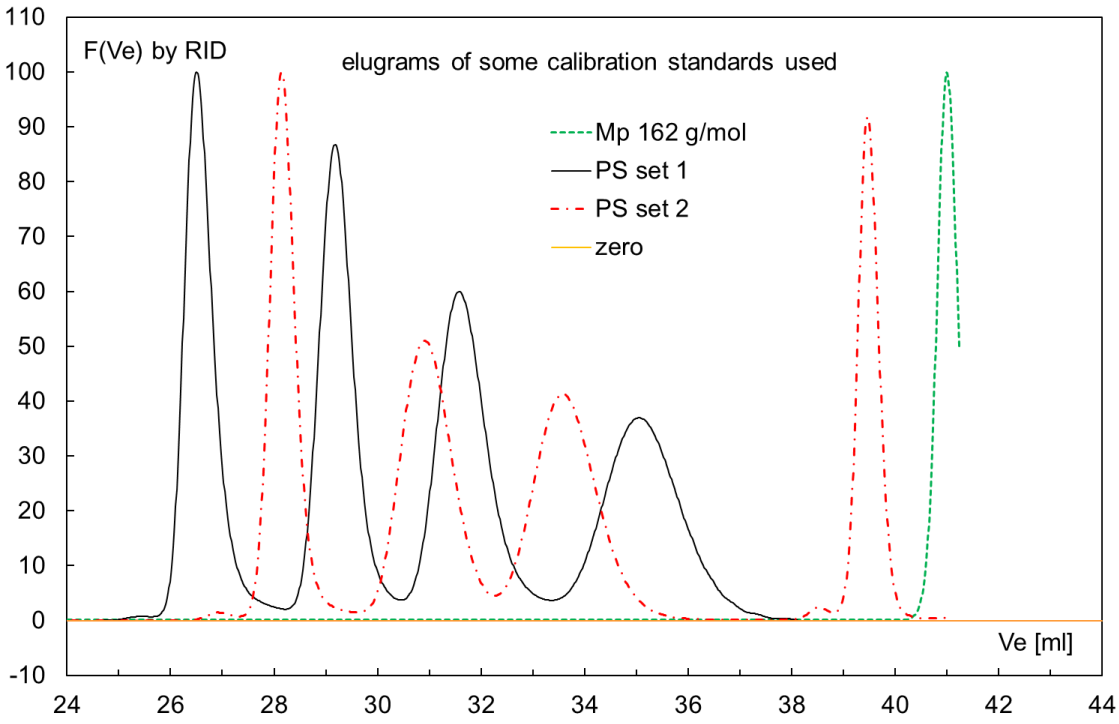

Fig. 9: Elugram of some of the polystyrene calibration standards used.

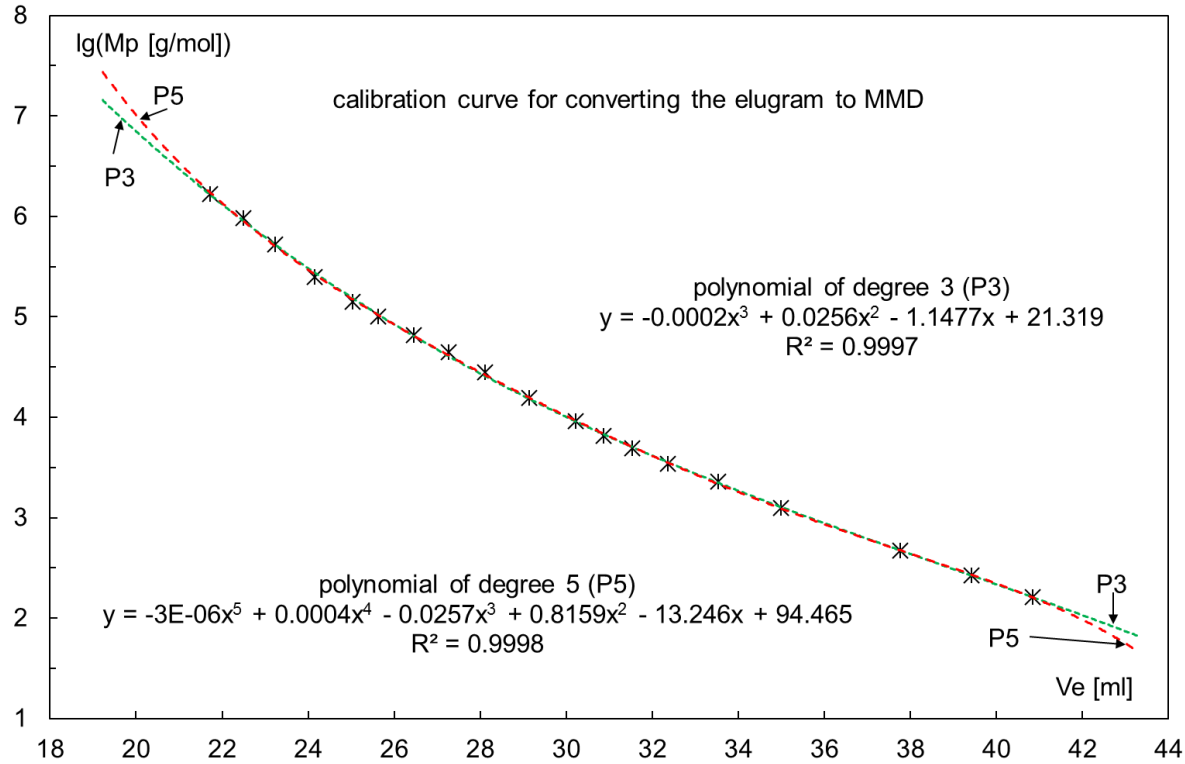

Fig. 10: Calibration curve established as lg(Mp [g/mol]) against elution volume. The curve is very well defined by using many polystyrene standards.

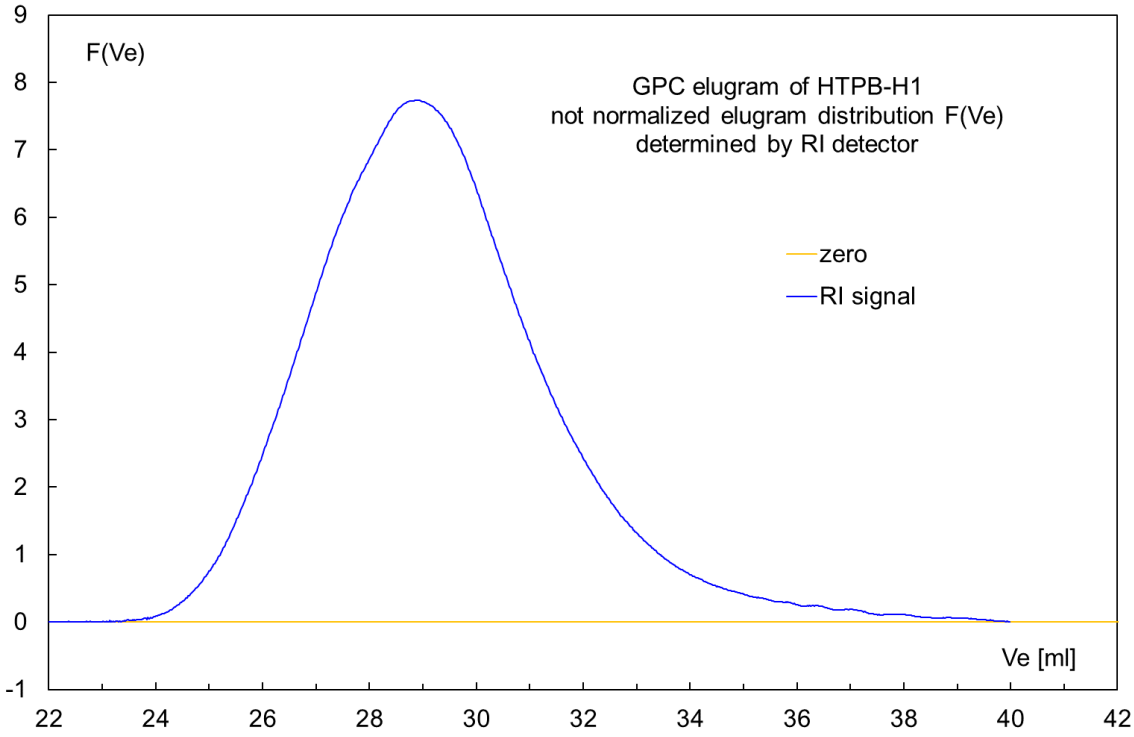

Fig. 11: Example of an elugram in GPC. Intensity F(Ve) of RI detector against eluted volume Ve. The intensity of the RI signal is proportional to the mass concentration in the eluent element in the detector measurement cell. Eluent was THF (tetrahydrofuran). The long chains or molecules with the large hydrodynamic volume leave the column set at low Ve values, because they are retained only by diffusion into and out of the bigger pores of the set.

3.2.3 Conversion of the elugram distribution to molar mass distribution

The amount of polymeric material in an element of elugram distribution (ED) must be the same in the assigned element of the molar mass distribution (MMD). This is expressed in Eq.(4)

$$F(Ve) \cdot dVe = -A \cdot y(M) \cdot dM \tag{4}$$

F(Ve) intensity in ED at Ve
dVe elution volume element at Ve, ranging from Ve to Ve+dVe
y(M) intensity in MMD at M
dM molar mass element at M, ranging from M to M+dM

The general calibration function is written as in Eq.(5) shown. Later the derivatives given in Eq.(6) are needed.

$$lg(M(Ve)) = f(Ve) \tag{5}$$

$$\left.\begin{aligned} \frac{\partial lg(M(Ve))}{\partial Ve} &= \frac{\partial f(Ve)}{\partial Ve} \\ \frac{dM(Ve)}{dVe} &= \frac{\partial f(Ve)}{\partial Ve} \cdot ln(10) \cdot M(Ve) \end{aligned}\right\} \tag{6}$$

Using Eq.(4) and Eq.(6, second) the following Eq.(7) is obtained.

$$F(Ve) \cdot dVe = -A \cdot ln(10) \cdot \frac{\partial f(Ve)}{\partial Ve} \cdot M(Ve) \cdot y(M) \cdot dVe \tag{7}$$

Using B = A ln(10), the Eq.(8) results, with the abbreviation hy(M) given in Eq,(9).

$$F(Ve) = -B \cdot \frac{\partial lg(M(Ve))}{\partial Ve} \cdot hy(M) \tag{8}$$

$$hy(M) = M(Ve) \cdot y(M) \tag{9}$$

Finally the connection between ED and MMD is obtained, Eq.(10). It becomes clear that all hy(M) are a function of lg(M(Ve)). The statistical character von hy(M) is determined by the type of detection used.

$$\left.\begin{aligned} hy(M) \cdot dlg(M(Ve)) &= -F(Ve) \cdot dVe \frac{1}{B} \\ hy(M) \cdot \frac{dM(Ve)}{M(Ve)} &= -F(Ve) \cdot dVe \frac{1}{A \cdot ln(10) \cdot lg(e)} \end{aligned}\right\} \tag{10}$$

If the intensity F(Ve) is mass-sensitive (mass concentration), which means the detector recognizes the mass of the polymer molecules in its detection volume element and produces an averaged signal, then the mass of polymer molecules of the polymer fraction is determined, which is present in the ED element F(Ve) dVe. Therefore y = m and the polymer fraction mass (of polymer molecules) averaged MMD hm(M) is obtained.

If the intensity F(Ve) is number-sensitive (number concentration), which means the detector recognizes the number of polymer molecules in its detection volume element and produces an averaged signal, then the number of polymer molecules of the polymer fraction is determined,

which is present in the ED element F(Ve). Therefore y = n and the polymer fraction number (of polymer molecules) averaged MMD hn(M) is obtained.

3.2.4 Mean molar masses and other definitions

The mean molar masses can be interpreted as so-named moments of molar mass distribution functions (density functions). If one uses the corresponding type of density function, the mean molar mass is always the arithmetic mean of the distribution. In other words, they are a 'center of gravity' quantity for the corresponding distribution. Here the definitions of the mean molar masses My and the corresponding molar mass distribution (MMD) functions $hy_i(M)$ are given. The polymer fraction i is assumed to be molecularly uniform, means it only consists of molecules with molar mass M_i and the number of mols in this fraction is n_i. The polymer sample is characterized by molar mass distribution (MMD) functions $hy_i(M)$, which can be of different kind. The index y defines the attribute of the distribution function. In the following the $hn_{u,i}$ and $hm_{u,i}$ and $hz_{u,i}$ are un-normalized distribution functions.

MMD related to the mol numbers in the polymer fractions, $hn_i(M)$

$$hn_i(M) = \frac{hn_{u,i}(M)}{\sum_i hn_{u,i}(M)} = \frac{\frac{hm_{u,i}(M)}{M_i}}{\sum_i \frac{hm_{u,i}(M)}{M_i}} \qquad \sum_i hn_i(M) = 1$$

$hn_i(M)$ polymer fraction mol number related normalized molar mass distribution;
n_i is the mol number in polymer fraction i.

The quantity $hn_i(M)$ gives the frequency (=normalized number) of molecules with a molar mass M_i in the polymer fraction i. If one considers the distribution as continuous, the differential formulation is taken.

$$hn(M) = \frac{hn_u(M)}{\int_{Ma}^{Me} hn_u(M)\cdot dM} = \frac{\frac{hm_u(M)}{M}}{\int_{Ma}^{Me} \frac{hm_u(M)}{M}\cdot dM} \qquad \int_{Ma}^{Me} hn(M)\cdot dM = 1$$

The quantity hn(M)dM gives the mol number fraction (=normalized mol number) of molecules with a molar mass in the range from M to M+dM.

MMD related to the mass (not molar mass!) in the polymer fractions, $hm_i(M)$

$$hm_i(M) = \frac{hm_{u,i}(M)}{\sum_i hm_{u,i}(M)} = \frac{\frac{hz_{u,i}(M)}{M_i}}{\sum_i \frac{hz_{u,i}(M)}{M_i}} \qquad \sum_i hm_i(M) = 1$$

$hm_i(M)$ polymer fraction mass related normalized molar mass distribution
$m_i = M_i * n_i$
m_i is the mass of polymer fraction i

$$hm_i(M) = \frac{hn_i(M)\cdot M_i}{\sum_i hn_i(M)\cdot M_i}$$

$$hm(M) = \frac{hm_u(M)}{\int_{Ma}^{Me} hm_u(M)\cdot dM} = \frac{\frac{hz_u(M)}{M}}{\int_{Ma}^{Me} \frac{hz_u(M)}{M}\cdot dM} \qquad \int_{Ma}^{Me} hm(M)\cdot dM = 1$$

The quantity hm(M)dM gives the mass fraction of molecules with a molar mass in the range from M to M+dM.

MMD related to the z attributes of the polymer fractions, $hz_i(M)$

$$hz_i(M) = \frac{hz_{u,i}(M)}{\sum_i hz_{u,i}(M)} \qquad \sum_i hz_i(M) = 1$$

$hz_i(M)$ polymer fraction z-weight related normalized molar mass distribution;
$z_i = M_i * m_i = M_i * M_i * n_i$
z_i is the mass m_i of fraction i multiplied with molar mass M_i
z_i is the z mass (or generally said the z-weight) of polymer fraction i

$$hz_i(M) = \frac{hm_i(M)\cdot M_i}{\sum_i hm_i(M)\cdot M_i} = \frac{hn_i(M)\cdot M_i \cdot M_i}{\sum_i hn_i(M)\cdot M_i \cdot M_i}$$

$$hz(M) = \frac{hz_u(M)}{\int_{Ma}^{Me} hz_u(M)\cdot dM} = \frac{\frac{hm_u(M)}{M}}{\int_{Ma}^{Me} \frac{hm_u(M)}{M}\cdot dM} \qquad \int_{Ma}^{Me} hz(M)\cdot dM = 1$$

The quantity hz(M)dM gives the z-mass fraction of molecules with a molar mass in the range from M to M+dM. The mean molar mass Mx is obtained directly from the distribution function with the same attribute x according to the equation for the calculation of the center of gravity of the distribution.

Mean molar mass Mn

Mn is the mean molar mass averaged according to the mol numbers n_i in the polymer fractions i (mol number weighing). Mn is the arithmetic mean of the $hn_i(M)$ or hn(M) distribution. Often named number average or number averaged mean molar mass.

$$Mn = \frac{\sum_i hn_{u,i}(M)\cdot M_i}{\sum_i hn_{u,i}(M)} = \frac{\sum_i hm_{u,i}(M)}{\sum_i \frac{hm_{u,i}(M)}{M_i}}$$

or

$$Mn = \frac{\sum_i hn_i(M)\cdot M_i}{\sum_i hn_i(M)} = \sum_i hn_i(M)\cdot M_i \qquad \text{with normalized distribution } hn_i(M)$$

$$Mn = \frac{\int_{Ma}^{Me} M\cdot hn(M)\cdot dM}{\int_{Ma}^{Me} hn(M)\cdot dM} = \int_{Ma}^{Me} M\cdot hn(M)\cdot dM \qquad \text{with normalized distribution } hn(M)$$

Mean molar mass Mw

Mw is the mean molar mass averaged according to the mass of the polymer fraction i (mass weighing). Mw is the arithmetic mean of $hm_i(M)$ or hm(M) distribution. Often named mass average (weight average) or mass averaged (weight averaged) mean molar mass. The term weight average in the sense of mass average should be omitted because it interfers with the term statistical weight.

$$Mw = \frac{\sum_i hm_i(M) \cdot M_i}{\sum_i hm_i(M)} = \sum_i hm_i(M) \cdot M_i \qquad \text{with normalized distribution } hm_i(M)$$

$$Mw = \frac{\int_{Ma}^{Me} M \cdot hm(M) \cdot dM}{\int_{Ma}^{Me} hm(M) \cdot dM} = \int_{Ma}^{Me} M \cdot hm(M) \cdot dM \qquad \text{with normalized distribution hm(M)}$$

Mean molar mass Mz

Mz is the mean molar mass averaged according to the z-mass (z-weight) of the polymer fraction i (z weighing). Mz is the arithmetic mean of the $hz_i(M)$ or hz(M) distribution. z stands for German 'Zentrifuge' (centrifuge) because a mean molar mass of this statistical weight was determined via the sedimentation equilibrium obtained with an analytical centrifuge.

$$Mz = \frac{\sum_i hz_i(M) \cdot M_i}{\sum_i hz_i(M)} = \sum_i hz_i(M) \cdot M_i \qquad \text{with normalized distribution } hz_i(M)$$

$$Mz = \frac{\int_{Ma}^{Me} M \cdot hz(M) \cdot dM}{\int_{Ma}^{Me} hz(M) \cdot dM} = \int_{Ma}^{Me} M \cdot hz(M) \cdot dM \qquad \text{with normalized distribution hz(M)}$$

3.3 OH number and equivalent mass

The OH-number is an important characterizing quantity for hydroxyl-terminated pre-polymers, which are used to create elastomers via polyaddition reaction with polyisocyanates. To form a defined elastomer also the isocyanate number NCO-n of the polyisocyanate must be known,to mix both in the wished equivalent ratio Req = NCO/OH. The OH-number may be called also OH-n or hydroxyl number or hydroxyl value.

The OH-number is defined as the amount of (solid) KOH (potassium hydroxide) in mg, which is equivalent to the (molar) amount of acetic acid, which is bonded during the acetylation process by one gram of polyol. For the acetylation, acetic acid anhydride is used in a solvent as N-methyl pyrrolidone (NMP), somewhat in excess. The not used acetic anhydride or acetic acid is determined by normalized KOH solution in methanol. As reference, the same solution of reagents is used without the polyol and the same treatment. The detailed descriptions of this analytical procedure can be found elsewhere, for example in DIN norms [23] or ASTM E 1899-08. The OH-number is then determined according to Eq.(11), whereby KOH_R and KOH_S are the consumption of KOH solution expressed in milli-mol of KOH for the reference and the sample, respectively. The molar mass of 56.106 mg/mmol given is the one of KOH.

$$OH-n=\left(KOH_R-KOH_S\right)[mmol]\cdot\frac{56.106\,mg/mmol}{E\ [g]} \tag{11}$$

In this way, the molar amount of OH groups can be determined in a polyol. Mostly this quantity is not needed in practical application, one uses the equivalent mass Eqm (equivalent weight) of the material, which carries just one OH group per molecule, see Eq.(12). The molar mass of 56.106 given is the one of KOH. The equivalent mass has the unit of g/mol-eq.

$$Eqm=\frac{1000\,mg}{g}\cdot\frac{56.106\,g/mol}{OH-n\ [mg/g]} \tag{12}$$

Another important characteristic quantity is the average amount of OH groups per average chain length. To get this, the 'true' (means not relative to any standard) number averaged mean molar mass Mn of the polyol is needed. The OH-functionality F-OH of the polyol can be calculated by dividing the (true) molar mass Mn with the equivalent mass Eqm, see Eq.(13).

$$F-OH=\frac{Mn}{Eqm} \tag{13}$$

4. Results

4.1 Nuclear magnetic resonance spectroscopy (NMR)

The ^1H spectra show three regions of interest:

1. ^1H attached to aliphatic carbon ($\delta \approx 1.0 - 2.3$);
2. ^1H attached to carbon of $-CH_2$-OH groups ($\delta \approx 3.3 - 4.2$);
3. ^1H attached to carbon atoms with a double bond ($\delta \approx 4.8 - 5.7$).

More detailed assignments of ^1H signals are given in Table 4. Examples of spectra are given in Figures 12 and 12a.

Table 4: Assignments of the ^1H chemical shifts of the HTPB pre-polymers. The considered proton is underlayed.

Chemical shift region observed	Origin
≈1.00 to 1.60	-C<u>H</u>$_2$- groups of 1-butene units, aliphatic area, i. e. bound to C-4 (see figure 6)
≈1.80 to 2.30 ≈2.00 to 2.30	-C<u>H</u>$_2$- groups of *cis*-2 and *trans*-2-butene units, aliphatic area, i. e. bound to C-1 or C-4 (see figure 6), overlapped by –C<u>H</u>- (C-3) and –C<u>H</u>$_2$- (C-4) of 1-butene units
≈3.30 to 3.70	-C<u>H</u>$_2$-OH of 1-butene terminating groups (see figure 4)
≈3.90 to 4.10	-C<u>H</u>$_2$-OH of *trans*-2-butene terminating groups (see figure 3)
≈4.10 to 4.20	-C<u>H</u>$_2$-OH of *cis*-2-butene terminating groups (see figure 2)
≈4.80 to 5.00	C<u>H</u>$_2$ groups of 1-butene units, double bond area, i. e. bound to C-1 (see figure 6)
≈5.00 to 5.45	C<u>H</u> groups of *cis*-2 and *trans*-2-butene units, double bond area, i. e. bound to C-2 and C-3 (see figure 6)
≈5.47 to 5.70	C<u>H</u> groups of 1-butene units, double bond area, i. e. bound to C-2 (see figure 6)

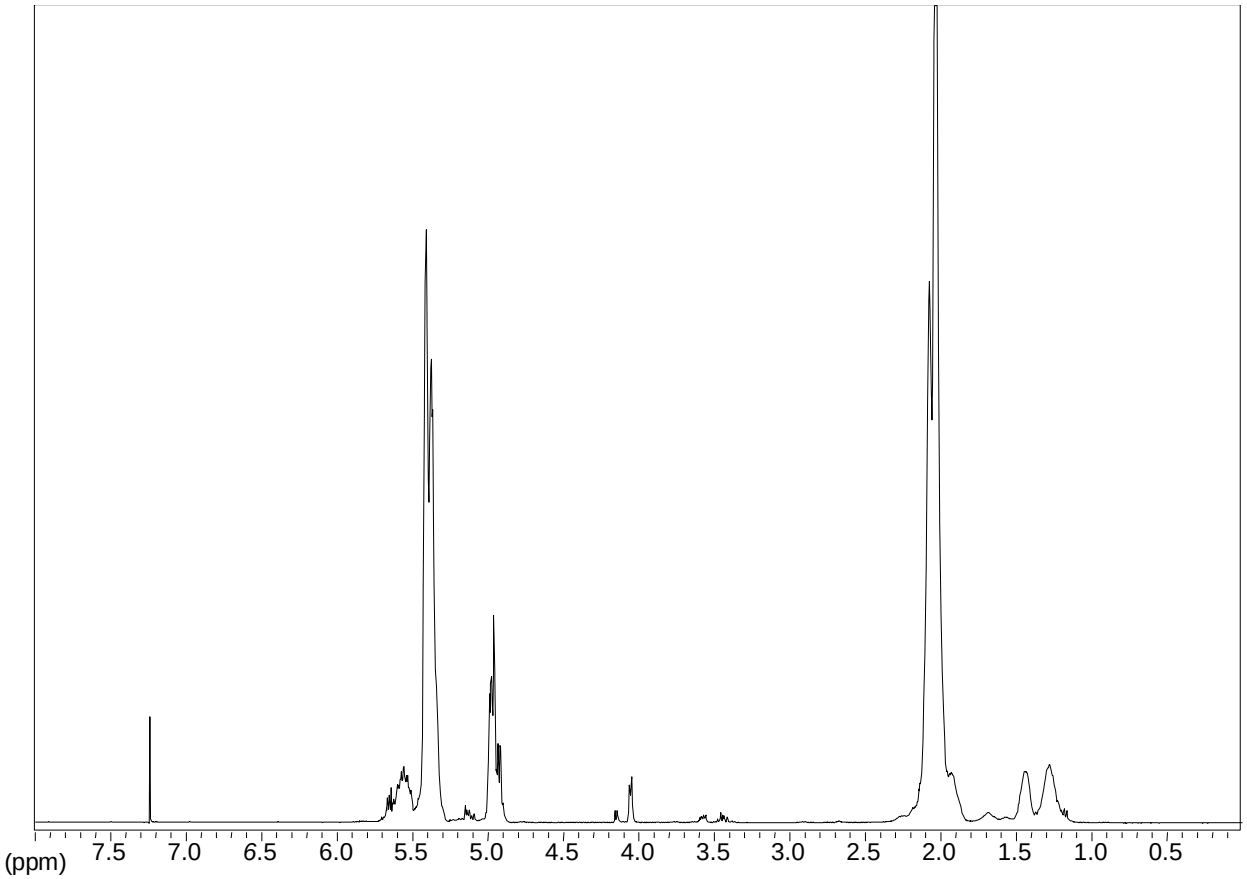

Fig. 12: ^{1}H spectrum of a typical HTPB pre-polymer sample, in total.

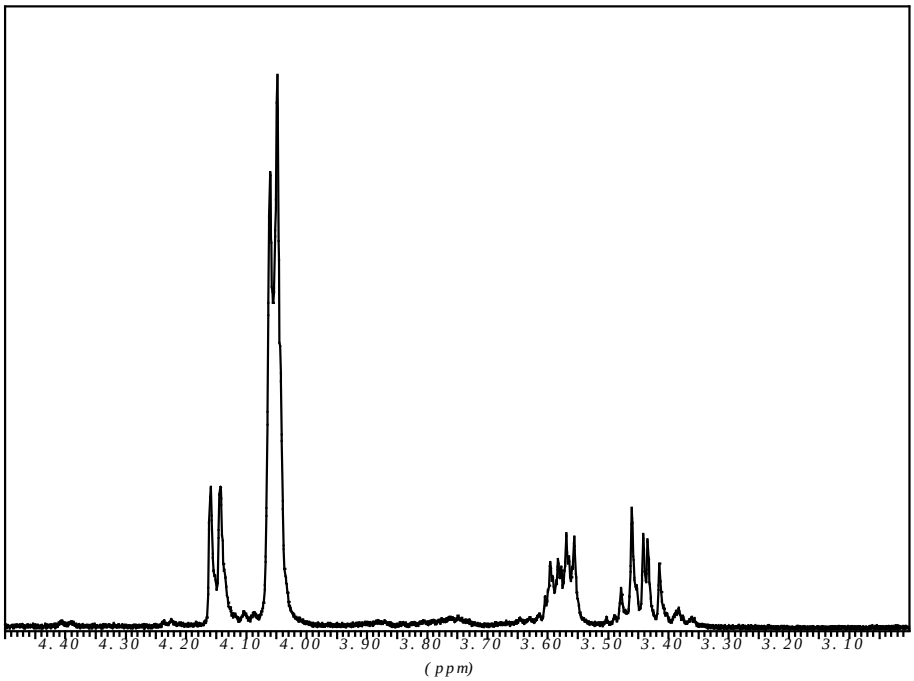

Fig. 12a: ^{1}H spectrum of a typical HTPB pre-polymer sample, clipping-out of the –OH region.

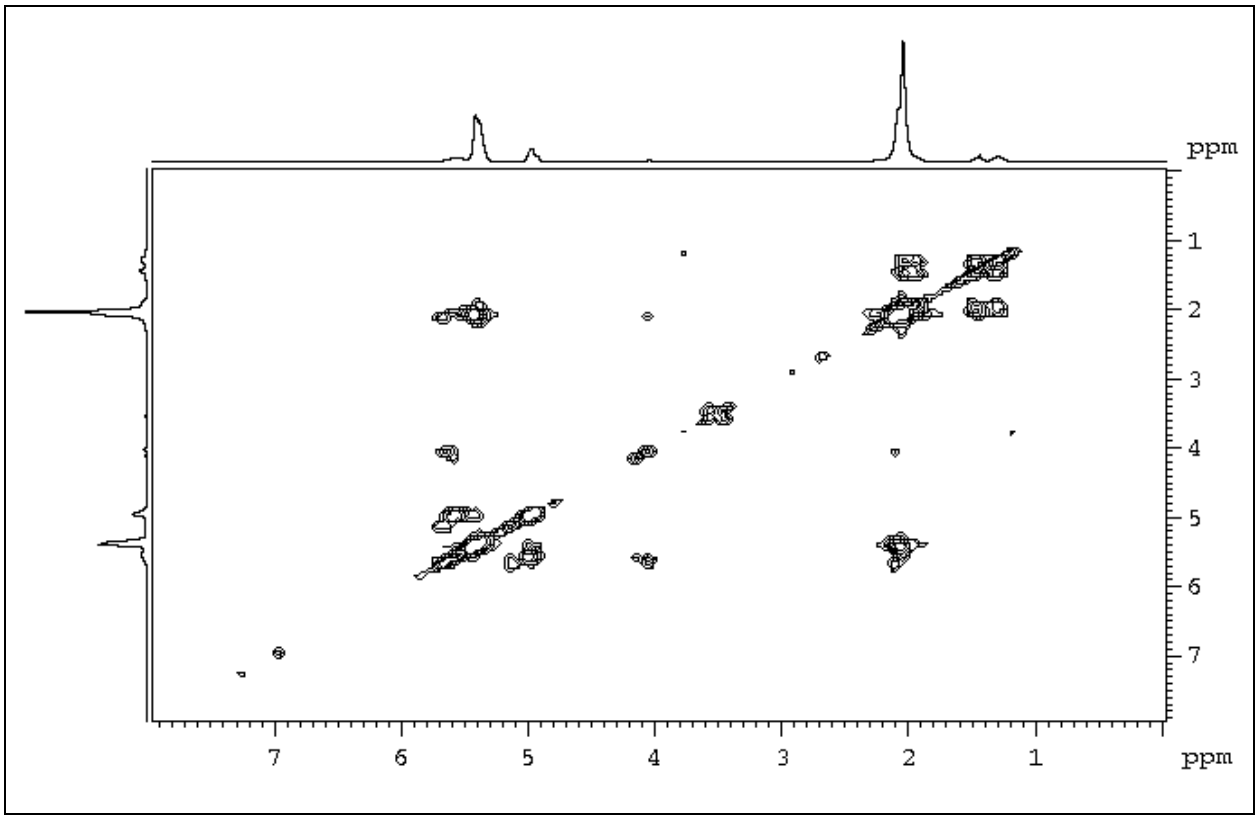

Fig. 13: ^{1}H-^{1}H **CO**rrelated **S**pectroscop**Y** (COSY) spectrum of a typical HTPB pre-polymer sample.

Because of many overlapping effects in the ^{1}H spectra, the focus is laid now on proton decoupled ^{13}C spectra and correlation spectra, as shown in Figure 13 and in the following. The predicted shifts of ^{13}C signals correspond all with recorded ^{13}C spectra obtained with inverse gated decoupling from protons, see Table 5. An example of a ^{13}C spectra with inverse gated decoupling between ^{1}H-^{13}C is presented in Figure 14.

A ^{1}H-^{13}C **H**eteronuclear **M**ultiple **Q**uantum **C**oherence (HMQC) spectrum as presented in Figure 16 shows cross peaks for protons that are bonded to carbons directly. The spectrum should be read as follows:

1. Choose one projection (e. g. ^{1}H spectrum);
2. draw an orthogonal line from one peak maximum of projected spectrum (i. e. shift of ^{1}H signal) from upper abscissa into the HMQC spectrum to find out how many cross peaks can be detected on this line. If there is more than one cross peak, overlapping in the ^{1}H spectrum occurs;
3. draw a second line that is orthogonal to the first one with origin in the cross peak to find the correlating ^{13}C signal on the left ordinate.

Since there are no signals visible, which correspond with terminal–CH-OH (there are neither corresponding signals at $\delta \approx 73$ in ^{13}C inverse gated spectra, nor J modulated spin echo (JMSE) spectra (Figure 15) nor cross signals in correlation spectra (Figure 16) the structure shown in Figure 5 is not detectable.

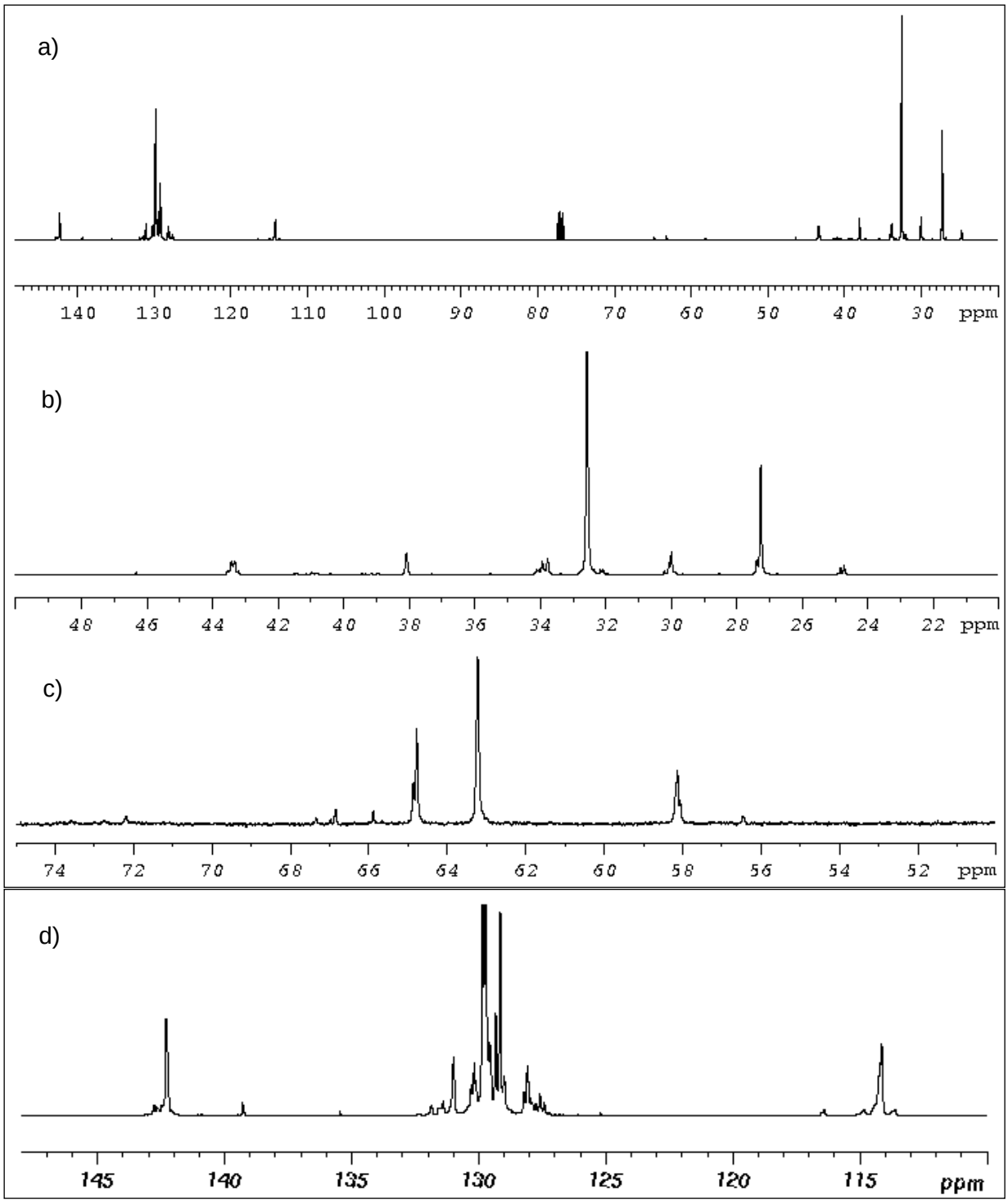

Fig. 14: ^{13}C-spectrum with inverse gated decoupling from protons of a typical HTPB pre-polymer sample, with clipping-out of three regions of interest.

a) Total spectrum including sp^2 C atoms, of sp^3 C atoms without bonded oxygen and without the $-CH_2-OH$ region;
b) Aliphatic carbon (sp^3) without bonded oxygen;
c) $–CH_2-OH$ region;
d) Region of sp^2 carbon.

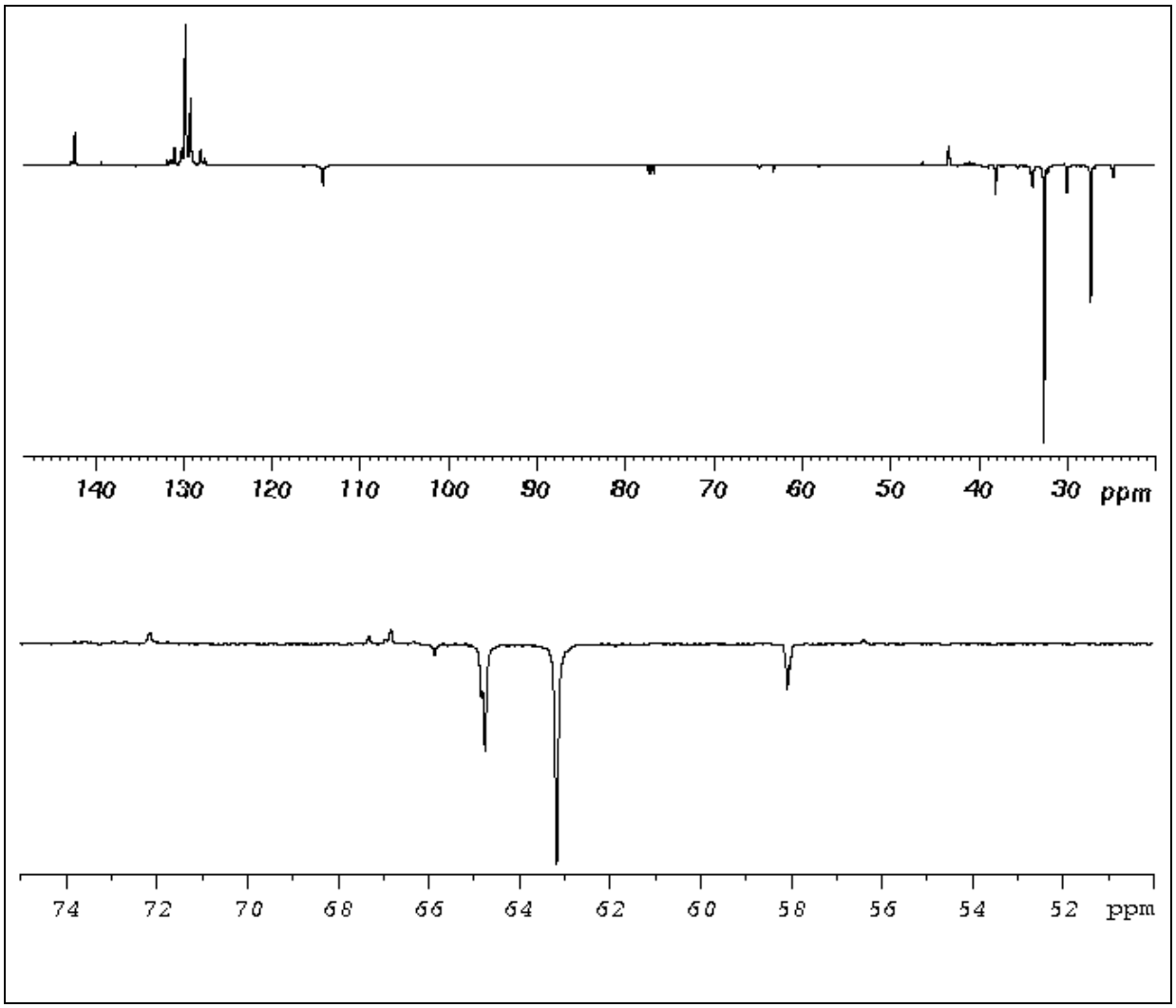

Fig. 15: Top part shows the total spectrum:
^{13}C JMSE spectrum of a typical HTPB pre-polymer sample; positive signals are: -CH, negative signals are: $-CH_2$.
The bottom part shows parts of the top part:
(1) the clipping-out of the region of terminating CH_2-OH groups in the shift range 58 to 65 /66, with negatively oriented intensities;
(2) the peaks of the assumed additional C-OH with positive oriented intensities.

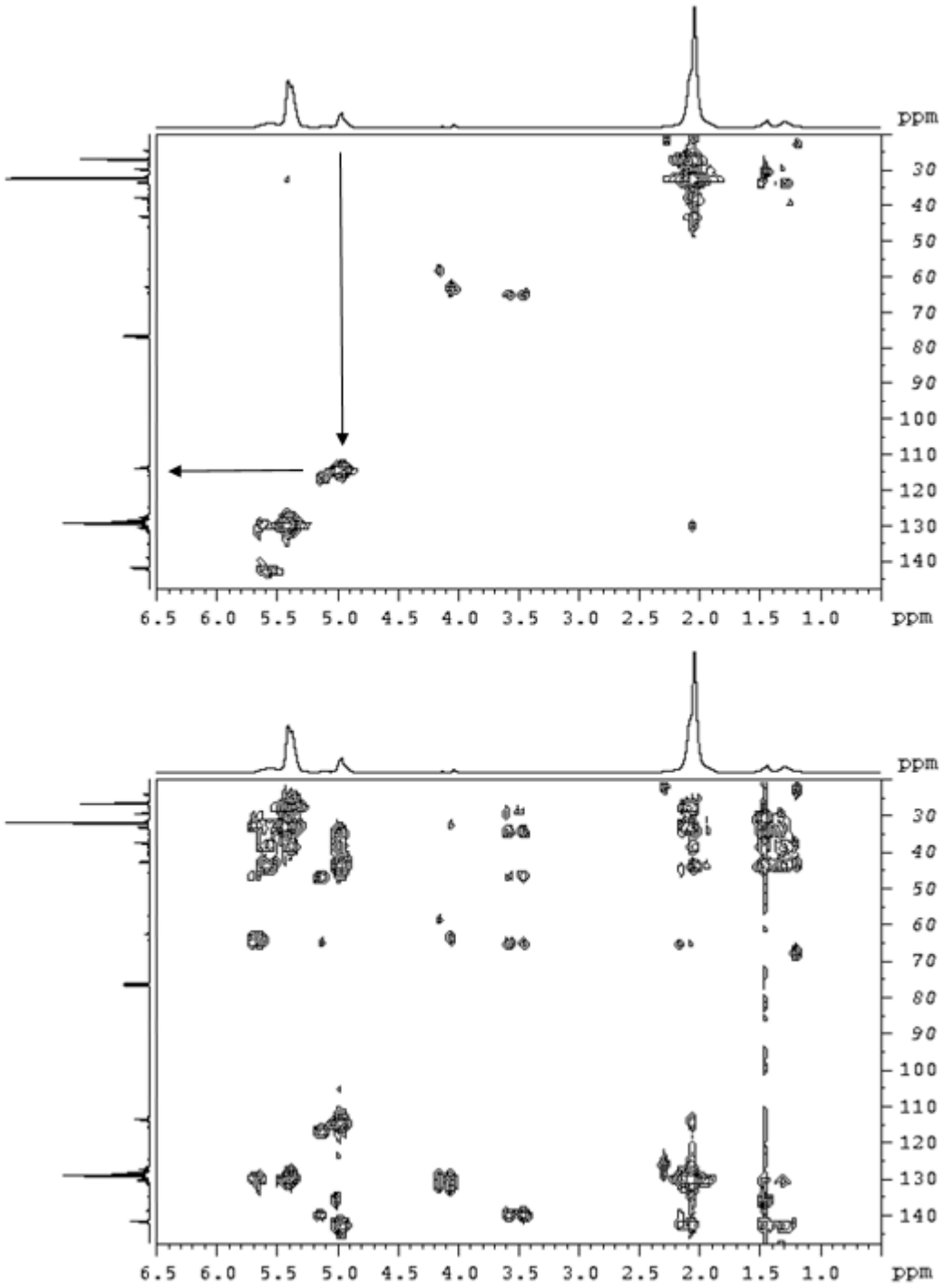

Fig. 16: Top: ^{1}H-^{13}C **H**eteronuclear **M**ultiple **Q**uantum **C**oherence (HMQC) spectrum, shows directly bonded nuclei as ^{13}C - ^{1}H;
Bottom: ^{1}H-^{13}C **H**eteronuclear **M**ultiple **B**ond **C**orrelation (HMBC) spectrum of a typical HTPB pre-polymer sample. This technique shows interactions between two selected nuclei across several chemical bonds including directly bonded nuclei.

Table 5: ^{13}C chemical shift (δ) assignment of HTPB samples observed in the investigated samples. Underlayed is the carbon in consideration. The predictions were made with Chem Draw Ultra 5.0.

δ predicted	δ region recorded	Origin Carbon atom and functional group (butene unit)	Predicted and recorded neighbour unit/ units (carbon atom)
25.3	23.8 to 25.7	C-1/C-4, i. e. -CH_2- (*cis*-2-butene)*	1-butene (C-4), i. e. -CH_2-
27.3 to 27.7	25.6 to 28.2	C-1/C-4, i. e. -CH_2- (*cis*-2-butene)*	*cis*-/*trans*-2-butene (C-1/C-4), i. e. -CH_2-
31.3 to 31.6	29.1 to 31.0	C-1/C-4, i. e. -CH_2- (*trans*-2-butene)*	1-butene (C-4), i. e. -CH_2-
33.3 to 33.7	30.8 to 33.5	C-1/C-4, i. e. -CH_2- (*trans*-2-butene)	*cis*-/*trans*-2-butene (C-1/C-4), i. e. -CH_2-
34.8 to 35.1	33.2 to 36.0	C-4, i. e. -CH_2- (1-butene)	*cis*-/*trans*-2-butene (C-1/C-4), i. e. -CH_2-
37.1 to 37.6	37.5 to 38.7	C-4, i. e. -CH_2- (1-butene)	1-butene (C-3/C-4), i. e. –CH-/-CH_2-
38.8 to 39.1	38.7 to 42.5	C-3, i. e. –CH- (1-butene)	
39.3 to 39.6	37.5 to 38.7	C-4, i. e. -CH_2- (1-butene)	
41.0 to 43.8	42.1 to 45.3	C-3, i. e. –CH- (1-butene)	
60.0	57.5 to 59.0	C-1/C-4, i. e. -CH_2- (*cis*-2-butene)*	-OH
66.0	62.5 to 63.9	C-1/C-4, i. e. -CH_2- (*trans*-2-butene)	-OH
67.5 to 67.8	64.3 to 65.3	C-4, i. e. -CH_2- (1-butene)	-OH
111.3 to 114.5	112.5 to 116.2	C-1, i. e. =CH_2 (1-butene)*	
	116.2 to 117.5	C-1, i. e. =CH_2 (1-butene)* unit terminated by -OH	
128.4 to 132.4	126.0 to 135.0	C-2/C-3, i. e. -CH= (*cis*-/*trans*-2-butene)	*cis*-/*trans*-2-butene (C-1/C-4), i. e.-CH_2- 1-butene (C-3/C-4), i. e. –CH-/ -CH_2-
140.6 to 142.0	138.7 to 140.5	C-2, i.e. -CH= (1-butene)* unit terminated by -OH	
	140.5 to 144.5	C-2, i.e. –CH= (1-butene)*	*cis*-/*trans*-2-butene (C-1/C-4), i. e. -CH_2- 1-butene (C-3/C-4), i. e. –CH-/ -CH_2-

* The assignment is certain, no overlapping of signal/s caused by carbon atom/s of other butene unit/s

There are a few signals in the chemical shift region between $\delta = 55$ and $\delta = 70$, which are not mentioned in Table 5. These signals could be assigned to further –C-OH, but there is no clear proof for this assumption. These signals could be arise also from –C-O-R. But because

it is known from practice that HTPB has more than two OH groups per molecule, here the assumption is followed that these signals originate from some additional OH groups along the HTPB backbone. The areas of these signals are added to the number of "OH end capped" ^{13}C and finally one gets an average number of total OH-groups per molecule greater than two. This is valid for all HTPB types, because they can be cured to a three-dimensional cross-linked elastomer with only two-functional isocyanates.

Table 6: Calculated mean number of OH groups per molecule in HTPB pre-polymer samples assuming 2 OH-groups at the ends and some between the ends.
*) The signal at $\delta \approx 70$ may be an overlapping of several substituents.

Number	Sample	Number of terminal $-CH_2-OH$ and additional C-OH	Remarks
1	HTPB M, type R45M	2 + 0.22 = 2.22	
2	HTPB H, type HTLO	2 + 0.28 = 2.28	
3	HTPB C, R45 type	2 + 0.25 = 2.25	
4	HTPB-1_VO	2 + 0.29 = 2.29	
5	HTPB-2_AB	2 + 0.26 = 2.26	
6	HTPB-3_AQ	2 + 0.32 = 2.32	
7	HTPB-4_OB	2 + 0.24 = 2.24	
8	HTPB E	2 + 1.34 = 3.34	*) Signal at $\delta \approx 70$ (integral value 1.12

Table 7: Mean molar masses M_{NMR} of HTPB pre-polymer samples.

Number	Sample	Area corresponding to two $-CH_2-OH$ groups	Mean number of butene units per HTPB chain	M_{NMR} [g/mol] with two OH groups per molecule	All OH groups per molecule	M_{NMR} [g/mol] with all OH groups per molecule
1	HTPB M, type R45M	107.315	53.66	2937	2.22	2941
2	HTPB H, type HTLO	107.4426	53.72	2940	2.28	2945
3	HTPB C	129.0775	64.54	3526	2.25	3530
4	HTPB-1_VO	103.3462	51.67	2829	2.29	2834
5	HTPB-2_AB	112.4789	56.24	3077	2.26	3081
6	HTPB-3_AQ	117.0018	58.5	3199	2.32	3204
7	HTPB-4_OB	118.8388	59.42	3249	2.24	3253
8	HTPB E	113.25	56.63	3098	3.34	3121

According to MIL-H-85497 (AS) [24] the mean molar mass of HTPB should be between 2500 to 3600 g/mol (or Dalton). This was determined by GPC using HTPB standards. These standards were obtained by fractionating a normal HTPB polymer sample and the fractions were characterized by vapour osmometry and the mean molar masses Mn of these fractions were obtained. The fractions were used to calibrate the column set of the GPC. The standard

types HTPB R45 M and HTPB R45 HTLO have M_{NMR} values in this demanded range. This is valid also for the other samples investigated.

Table 8: Mean molecular ratio of butene isomers contained in the HTPB pre-polymer samples

Num.	Sample	Corresponding areas	Type of isomer	Relative content cis : trans : vinyl [%]
1	HTPB-M, type R45M	24.846	*cis*-2-Butene	23.1
		59.75	*trans*-2-Butene	55.7
		22.719	1-Butene	21.2
	area sum	*107.315*		*100*
2	HTPB-H, type HTLO	25.5156	*cis*-2-Butene	23.7
		59.0535	*trans*-2-Butene	55.0
		22.8735	1-Butene	21.3
	area sum	*107.4426*		*100*
3	HTPB-C, similar to R45M type	30.4954	*cis*-2-Butene	23.6
		71.6285	*trans*-2-Butene	55.5
		26.9536	1-Butene	20.9
	area sum	*129.0775*		*100*
4	HTPB-1_VO	23.631	*cis*-2-Butene	22.9
		58.162	*trans*-2-Butene	56.3
		21.5532	1-Butene	20.8
	area sum	*103.3462*		*100*
5	HTPB-2_AB	26.1287	*cis* 2-Butene	23.2
		62.8689	*trans* 2-Butene	55.9
		23.4812	1-Butene	20.9
	area sum	*112.4788*		*100*
6	HTPB-3_AQ	27.2208	*cis*-2-Butene	23.3
		65.1387	*trans*-2-Butene	55.6
		24.6423	1-Butene	21.1
	area sum	*117.0018*		*100*
7	HTPB-4_OB	27.0631	*cis* 2-Butene	22.8
		67.0861	*trans* 2-Butene	56.4
		24.6897	1-Butene	20.8
	area sum	*118.8389*		*100*
8	HTPB E	26.4684	*cis* 2-Butene	23.3
		62.9212	*trans* 2-Butene	55.6
		23.8604	1-Butene	21.1
	area sum	*113.25*		*100*

4.2 Gel permeation chromatography (GPC)

In Table 9 the mean molar masses, the maximum value of the MMD and the polydispersity are listed. The values are not very different between the types. The types R45M seem to have somewhat higher Mn values than the HTLO types and their D values are smaller. The MMD are shown in the Figures 17 to 22. Small differences are recognizable. Some of the lots have an added antioxidant, which is appearing in the MMDs as small peaks at low M values.

Table 9: Mean molar masses Mn, Mw and Mz as well as peak maximum value Mp of the MMD and the polydispersity D, determined from the molar mass distribution function (MMD) obtained by GPC measurements. Calibration of the separation column set by narrowly distributed polystyrene standards.

number	type (typically named)	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]	Mp [g/mol}	D = Mw/Mn
1a	HTPB-M1, type R45 M	5629 ± 61	12339 ± 95	23890 ± 930	10184 ± 11	2.19. ± 0.04
1b	HTPB-M2, type R45 M	5795 ± 169	12104 ± 42	22270 ± 441	9929 ± 28	2.09 ± 0.05
1c	HTPB-M3, type R45 M	5306 ± 47	11351 ± 67	20950 ± 222	9599 ± 93	2.14 ± 0.01
2a	HTPB-H1, type R45 HTLO	4721 ± 5	13001 ± 106	28170 ± 263	9243 ± 73	2.75 ± 0.02
2b	HTPB-H2, type R45 HTLO	4714 ± 32	12498 ± 29	27110 ± 586	8717 ± 35	2.66 ± 0.03
2c	HTPB-H3, type R45 HTLO	5013 ± 131	12268 ± 80	25460 ± 33	8830 ± 30	2.45 ± 0,05
3	HTPB-C, R45 M type	5018 ± 103	12275 ± 38	24660 ± 246	9684 ± 75	2.45 ± 0.05
4	HTPB-1_VO, HTLO type	4687 ± 14	11076 ± 145	20780 ± 890	9599 ± 26	2.36 ± 03
5	HTPB-2_AB, HTLO type	4524 ± 5	11314 ± 54	21840 ± 430	9269 ± 55	2.50 ± 0.01
6	HTPB-3_AQ, HTLO type	4822 ± 6	12399 ± 41	26890 ± 22	9024 ± 48	2.57 ± 0.01
7	HTPB-4_OB, HTLO type	4491 ± 71	10584 ± 4	19490 ± 78	9509 ± 22	2.36 ± 0.04
8a	HTPB-E, HTLO type	4752 ± 42	11191 ± 77	21700 ± 515	9163 ± 112	2.36 ± 0.0

The relative ratio of cis, trans and vinyl conformations in the HTPB samples are compiled in Table 8, calculated from the peak areas of corresponding isomers found with ^{13}C NMR. There are not much differences between the samples in the ratios. Only in the total area of the peaks of all isomers one recognizes some differences. HTPB-C has a value significantly higher than the values of HTPB-M and HTPB-H.

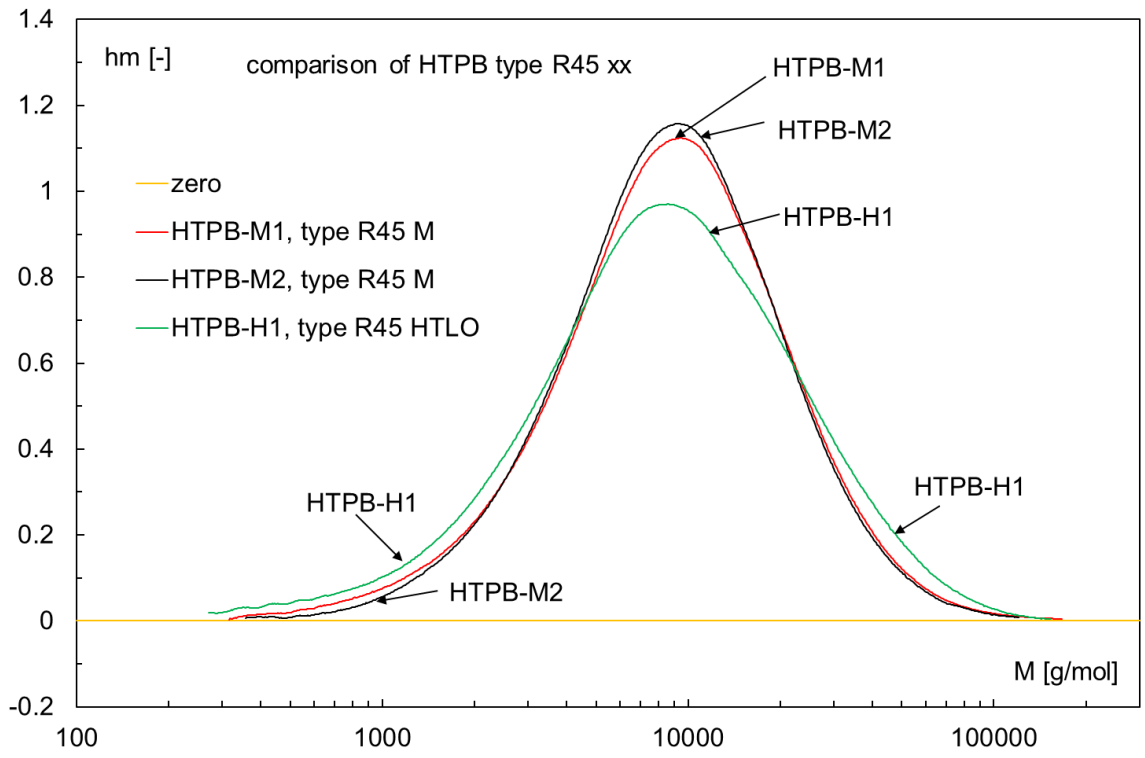

Fig. 17: MMD of HTPB samples of type R45M and HTLO. The polydispersity D = Mw/Mn of type R45M is smaller than the one of type HTLO, the values are in average 2.15 to 2.65. The MMD of type R45 M is somewhat shifted to high M values, recognizable by molar mass Mp of the maximum of MMD.

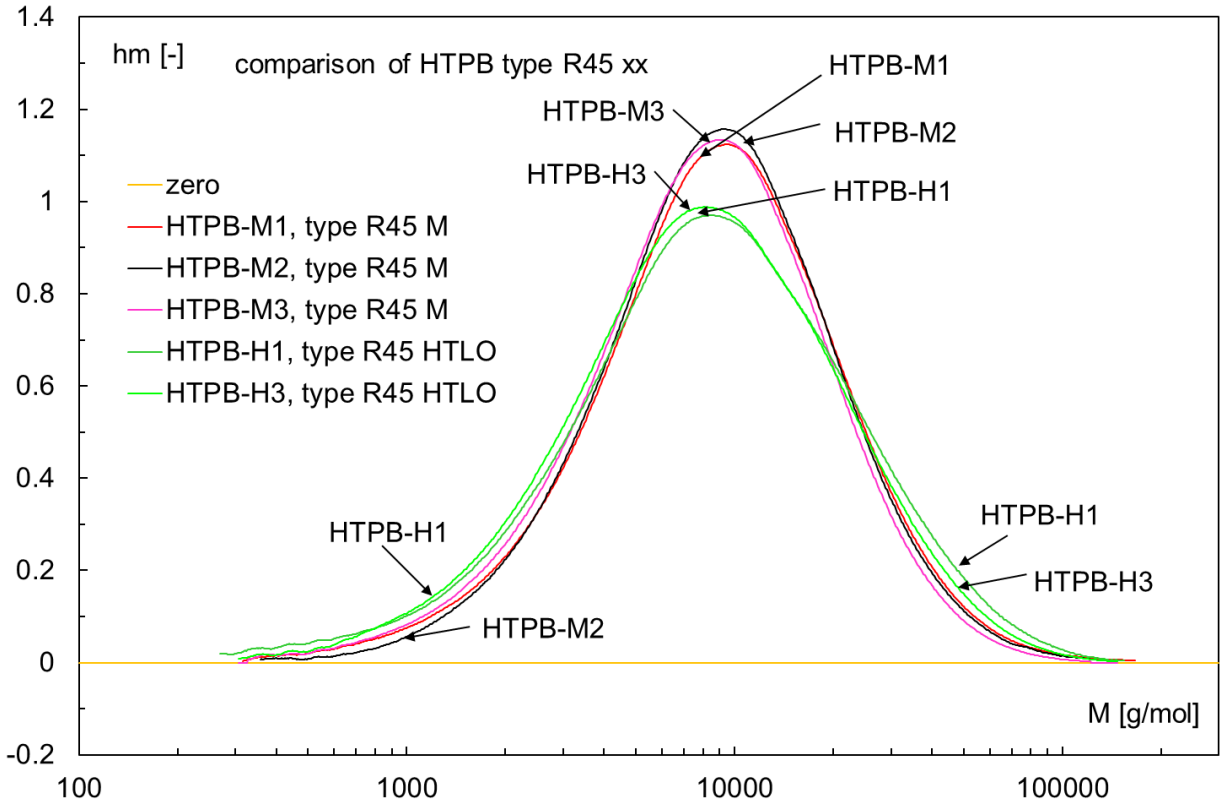

Fig. 18: MMD of HTPB samples of type R45 M and R45 HTLO in more detailed comparison of the lots and determinations. Three lots of type M (R45M) and two determinations at very different times of type H. The reproducibility of the determination is high.

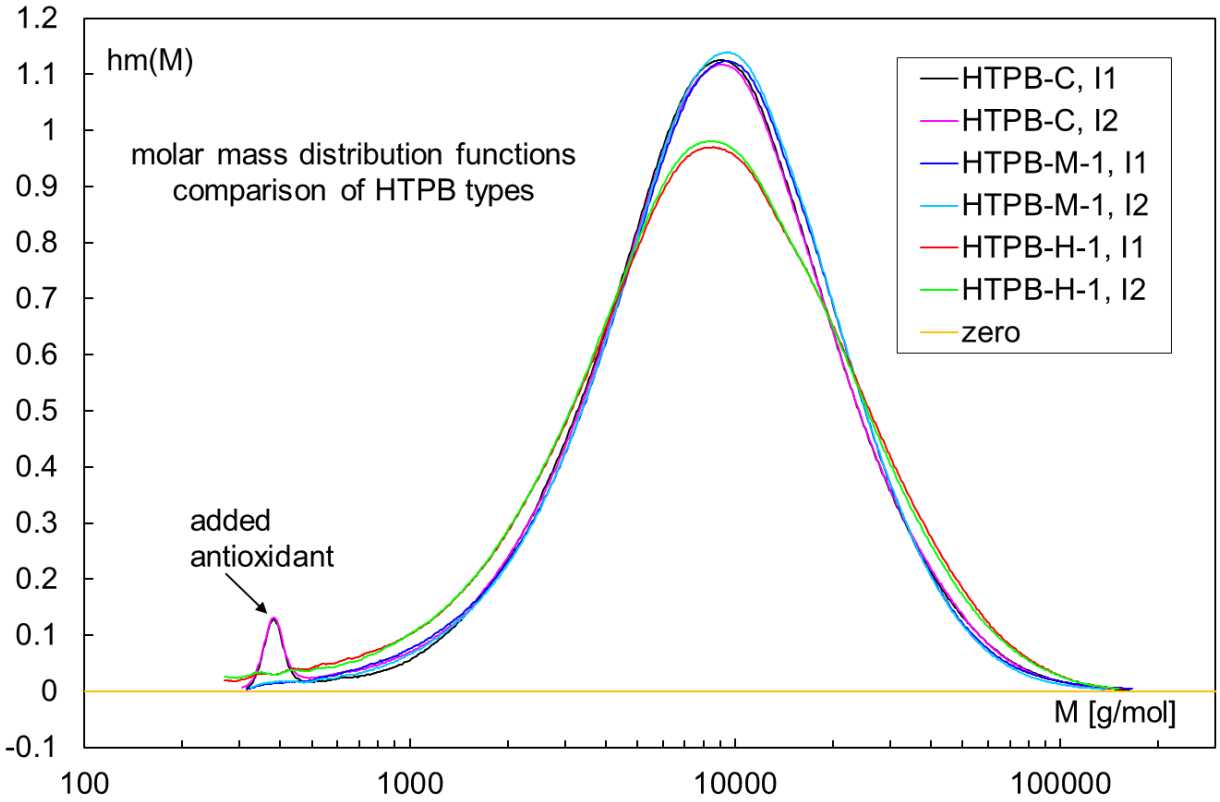

Fig. 19: MMD of HTPB samples of type R45 M and R45 HTLO. The type HTPB-C shows a small peak at small M values. It is an added antioxidant of type BKF.

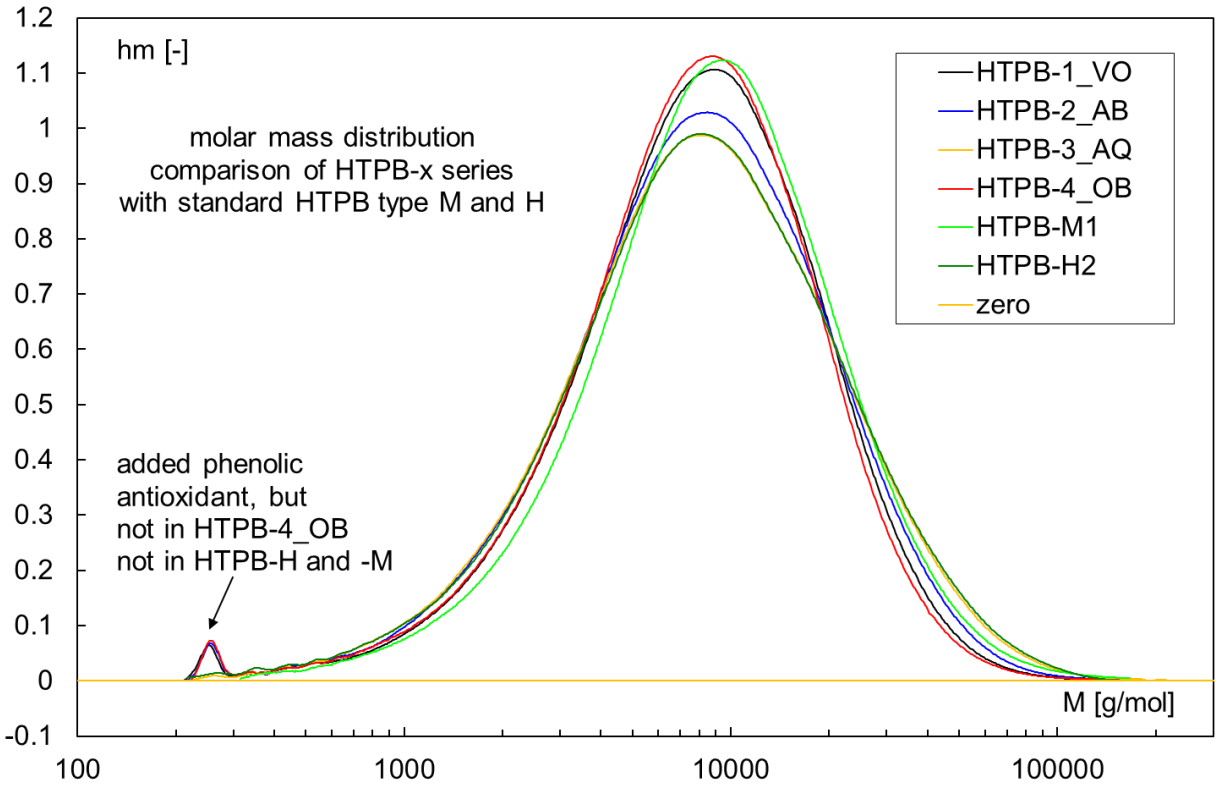

Fig. 20: MMD of HTPB samples of type R45 M and R45 HTLO. The type HTPB-VO, -AB, -AQ show a small peak at small M values. Here it is the antioxidant BHT.

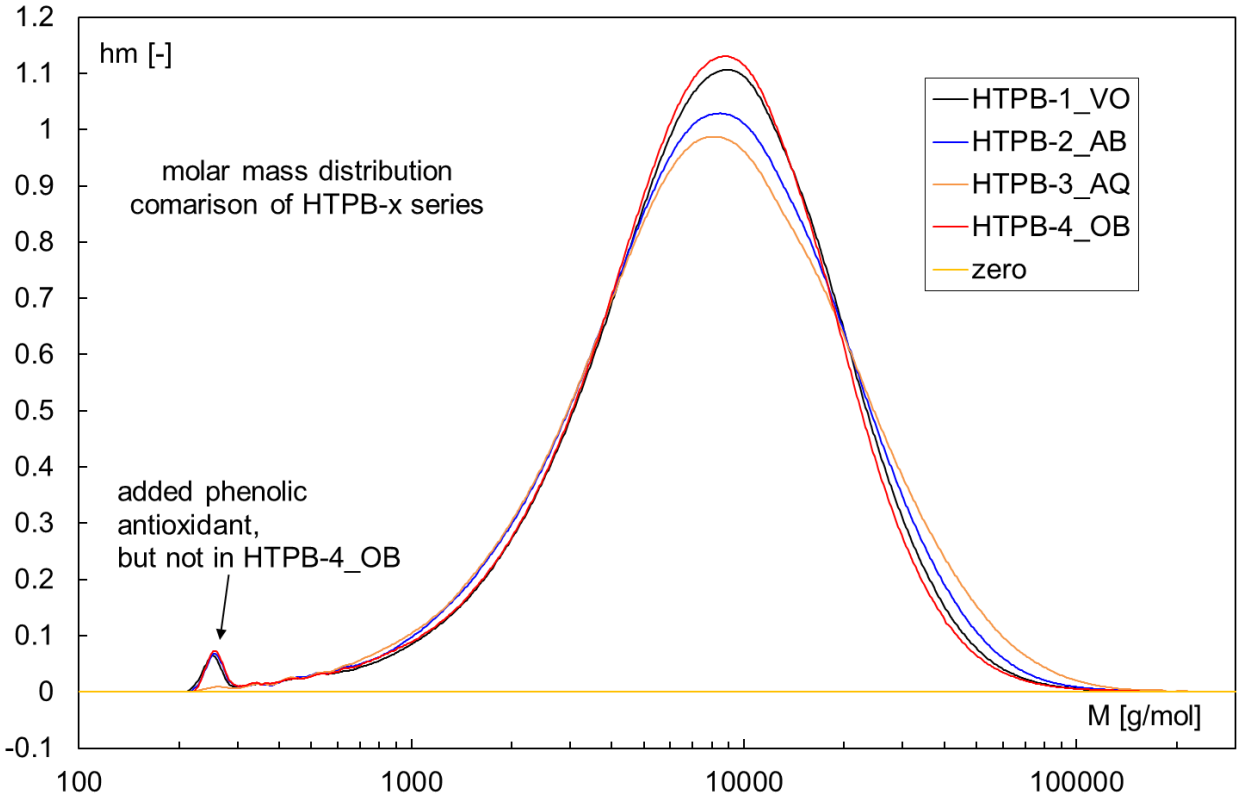

Fig. 21: MMD of HTPB samples of only type R45 HTLO. The type HTPB-VO, -AB, -AQ show a small peak at small M values. Here it is the antioxidant BHT.

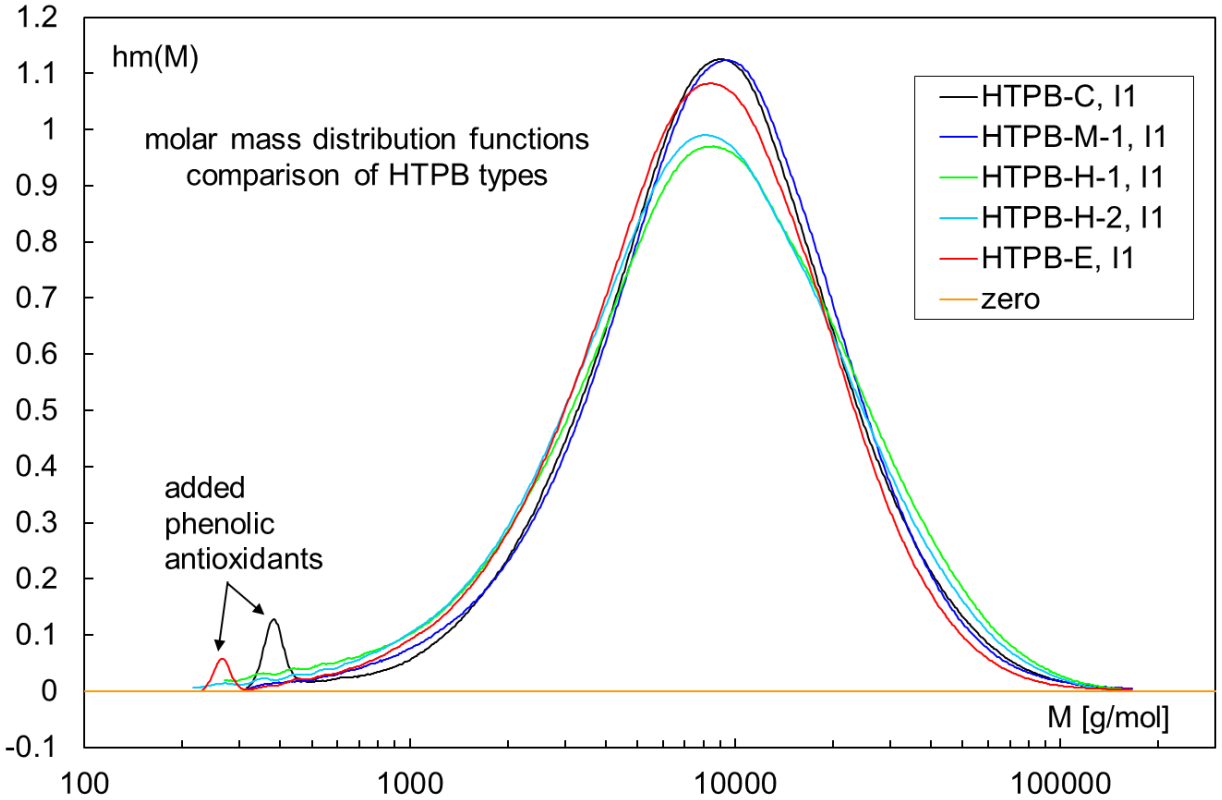

Fig. 22: MMD of HTPB samples of only type R45M and R45 HTLO. The type HTPB-C and HTPB-E show a small peak at small M values. Here it is the antioxidant BKF and BHT respectively.

4.3 OH-number and equivalent mass

The results of the determination of OH-number (hydroxyl value) and equivalent mass are compiled in Table 10. All HTPB of type R45 M have higher equivalent masses and lower OH-numbers than the types HTLO.

Table 10: OH-numbers (hydroxyl values) and equivalent masses of investigated HTPB samples.

Num-ber	Sample (typically named)	OH number [mg KOH /(g substance)]	Equivalent mass [g/mol-eq]
1a	HTPB-M1, type R45 M	41.00 ± 0.17	1368.4 ± 14.8
2a	HTPB-H1, type HTLO	47.02 ± 0.05	1193.3 ± 8.5
2b	HTPB-H2, type HTLO	48.13 ± 0.02	1166.0 ± 6.3
3	HTPB-C, R45 M type	41.60 ± 0.15	1348.5 ± 13.7
4	HTPB-1_VO, HTLO type	44.55 ± 0.27	1259.4 ± 7.7
5	HTPB-2_AB, HTLO type	48.13 ± 0.17	1165.6 ± 4.1
6	HTPB-3_AQ, HTLO type	46.39 ± 0.23	1209.4 ± 6.0
7	HTPB-4_OB, HTLO type	45.07 ± 0.08	1244.9 ± 2.3
8a	HTPB-E, HTLO type	50.46 ± 0.13	1111.6 ± 2.9
8b	HTPB-E, HTLO type	46.32 ± 0.12	1211.2 ± 3.1

5. Discussion

The results and the calculation of the characteristic parameters are compiled in Table 11.

Table 11: Comparison of results obtained from the three methods and derived quantities.

Num.	Sample type	Mn from NMR [g/mol]	Mn from GPC [g/mol]	Ratio Mn-GPC to Mn-NMR	Mean num-ber of OH groups per HTPB chain from NMR	Eqm from OH-n [g/mol-eq]	F-OH = Mn-NMR/ Eqm
1a	HTPB-M1, type R45M	2941	5629	1.91	2.22	1368.4	2.15
2a	HTPB-H1, type HTLO	2945	4721	1.6	2.28	1193.3	2.47
3	HTPB-C, R45 M type	3530	5018	1.42	2.25	1348.5	2.62
4	HTPB-1_VO	2834	4687	1.65	2.29	1259.4	2.25
5	HTPB-2_AB	3081	4524	1.47	2.26	1165.6	2.64
6	HTPB-3_AQ	3204	4822	1.5	2.32	1209.4	2.65
7	HTPB-4_OB	3253	4491	1.37	2.24	1244.9	2.64
8a	HTPB-E	3121	4752	1.52	3.34	1111.6	2.81
8b	HTPB-E	3121	4714	1.51	3.34	1211.2	2.60

Because of the calibration of the column set of the GPC apparatus with polystyrene standards, which have another behaviour in forming the hydrodynamic volume in the eluent than HTPB, the values of Mn are deviating from the ones determined with the NMR method. From the ratio of Mn-GPC to M_{NMR} one can conclude that the coil forming character is different between the HTPB samples. The HTPB-M type has a quite high Mn value compared to all others, which are mainly of type HTPB HTLO. The reason is the lower mean number of OH groups per chain. Via the OH groups along the chains the polymer coils are stabilized and also attracted or even contracted, means THF cannot expand the coil so much compared to HTPB with less OH groups per chain. This behaviour can affect also the formulation of elastomers with such samples. Besides the effect of lowering the sliding length with increasing OH number per chain the coil stabilization tends to create entanglements, which reduce further the sliding length and finally the strain capacity in cross-linked formulations.

Under the assumptions explained above, the mean number of OH groups per molecule or chain, in other words the OH-functionality F-OH can be determined also by NMR. But the determination needs more effort to get signals from OH groups, which can be evaluated well. The well recognizable ^{13}C signals of -CH=CH- groups and $–CH_2$-CH=CH-CH_2- units and those caused by -CH_2 groups connected with -OH groups (“OH-end groups”) can be used for the determination of the mean molar masses of the samples. Now one can calculate the OH functionality with these M_{NMR} values and the independently determined equivalent mass (from OH number) with good accuracy. These values show a clear trend: the R45M samples have low values between 2.15 and 2.30, whereas the HTLO types range between 2.5 and 2.85.

6. Summary and conclusion

The analytical method of determining the OH-number (hydroxyl value) as well as the equivalent mass with regard to the OH groups of the HTPB samples provides with important characterization properties. The strength of GPC, also in relative calibration, is to get the molar mass distribution (MMD) functions. Thus mean molar masses Mn, Mw and Mz can be obtained. The differences in MMD correspond in part with OH functionality of the HTPB. The more OH groups per molecule the broader is the distribution. This is caused by a different coiling behaviour of the pre-polymers.

By ^{13}C NMR spectroscopy, the HTPB substructures can be determined. Ratios of *cis*-2-butene, *trans*-2-butene and 1-butene isomers as well as mean molar masses of several HTPB samples were determined quantitatively. The mean molar masses obtained by NMR spectroscopy correspond with the requirements stated in MIL-H-85497 (AS). Contents of *cis*-2-, *trans*-2- and 1-vinyl substructures do not differ very much between the investigated samples, which may indicate similar or even same production processes. One sample seems especially treated, because the mean number of OH groups per molecule found with NMR is quite high.

In combination with OH-number and equivalent mass and the mean molar masses from NMR, the OH-functionality of the HTPB samples can be determined, which is an important quality parameter for the HTPB pre-polymers in order to get optimal strain capacity data for composite rocket propellants.

7. Abbreviations

BHT	antioxidant of phenolic type, Vulkanox™ BHT
BKF	antioxidant of phenolic type, Vulkanox™ BKF
CRP	Composite rocket propellant
ED	elugram distribution
Eqm	equivalent mass in g/mol-eq
GPC	gel permeation chromatography
HTPB	hydroxyl-terminated polybutadiene
MMD	Molar mass distribution, as function of molar mass M of the polymer
Mn	number averaged mean molar mass or polymer fraction chain number averaged mean molar mass number means the polymer mol number in the polymer fraction
Mw	mass averaged mean molar mass or polymer fraction mass averaged mean molar mass mass means the polymer mass in the polymer fraction
Mn-GPC	Mn obtained from GPC
M_{NMR}	Mean molar mass obtained from NMR, which is in character equivalent to Mn(GPC), also Mn-NMR
Mz	polymer fraction z averaged mean molar mass
D	polydispersity, D = Mw/Mn
Mp	molar mass of maximum of MMD
hm	polymer fraction mass weighted molar mass distribution
OH-n	hydroxyl number, hydroxyl value
PBX	Plastic bonded high explosive
PSS	Polymer Standards Service GMBH, Mainz, Germany
Ve	eluent volume
THF	Tetrahydrofurane, solvent and eluent in GPC
NMR [1)]	nuclear magnetic resonance (spectroscopy)
COSY	**CO**rrelation **S**pectroscop**Y**
^{1}H-^{1}H-COSY	Probing proton-proton correlation, means diploar coupling by COSY
JMSE	J-modulated spin echo spectroscopy
^{13}C JMSE	**J**-**m**odulated **s**pin **e**cho with ^{13}C carbon
HMQC	**H**eteronuclear **M**ultiple **Q**uantum **C**oherence spectroscopy
^{1}H-^{13}C-HMQC	**H**eteronuclear **M**ultiple **Q**uantum **C**oherence (between ^{1}H and ^{13}C)
HMBC	**H**eteronuclear **M**ultiple **B**ond **C**orrelation spectroscopy
^{1}H-^{13}C HMBC	**H**eteronuclear **M**ultiple **B**ond **C**orrelation (between ^{1}H and ^{13}C)
NOE	**N**uclear **O**verhauser **E**ffect

[1)] NMR specific abbreviations, for example to found in Bruker almanac 2011.

8. References

[1] T. Seyidoglu and M.A. Bohn.
Modelling of Loss Factor Curves Obtained by Torsion-DMA of HTPB and GAP Based Binders manufactured with Different Curing Agents and Plasticizers.
Paper 118, pp 118-1 to 118-26.Proc. 46th International Annual Conference of ICT on 'Energetic Materials – Performance, Safety and System Applications', June 23 to 26, 2015, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinztal, Germany, **2015**.

[2] M. Ferrapontoff Lemos, M.A. Bohn.
The effect of plasticizers on the glass-to-rubber behavior of Desmophen® 2200 based elastomers used for composite propellants.
Paper 22, pp 22-1 to 22-26.Proc. of the 46th International Annual Conference of ICT on 'Energetic Materials – Performance, Safety and System Applications', June 23 to 26, 2015, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinztal. Germany, **2015**.

[3] M.A. Bohn, G. Mußbach, S. Cerri.
Influences on the loss factor of elastomer binders and its modelling.
Paper 60, pp 60-1 to 60-43. Proc. 43rd International Annual Conference of ICT on 'Energetic Materials – Synthesis, Characterisation, Processing', June 26 to 29, 2012, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinztal. Germany, **2012**.

[4] Ullmanns Encyclopädie der technischen Chemie, 4. Auflage, Band 20, VCH Weinheim, **1981**.

[5] Enzyklopädie Naturwissenschaft und Technik, Band 4. Zweiburgen Verlag Weinheim, **1981**.

[6] CS ChemDraw Ultra 5.0, CambrigdeSoft, 100 CambridgePark Drive, Cambridge, MA 02140, USA.

[7] T.D.W Claridge, High-Resolution NMR Techniques in Organic Chemistry, Pergamon, Oxford, **1999**.

[8] W. P. Aue, E. Bartholdi, R. R. Ernst, J. Chem. Phys. 64, 2229 (**1976**).

[9] K. Nagayama et al., J. Magn. Reson. 40, 321 (**1980**).

[10] E. D. Becker, High Resolution NMR, Academic Press, New York, **1980**, Ch. 12.

[11] M. L. Martin, G. J. Martin, J. J. Delpuech, Practical NMR Spectroscopy, Heyden, London, **1984**, Ch. 9, 350-376.

[12] D. W. Bowen, T. T. Nakashima, D. L. Rabenstein, J. Magn. Reson. 45, 302-314 (**1981**).

[13] A. Bax, R. H. Griffey, B. L. Hawkins, J. Magn. Reson. 55, 301-315 (**1983**).

[14] D. O. Cicero, G. Barbato and R. Bazzo, J. Magn. Reson. 148, 209 – 213 (**2001)**.

[15] M.D. Lechner, K. Gehrke, E.H. Nordmeier.
Makromolekulare Chemie. Birkhäuser Verlag, Basel, Boston New York, 3. Auflage, **2003**.

[16] DIN 55672-1. *Gelpermeationschromatographie (GPC) – Teil 1: Tetrahydrofuran (THF) als Elutionsmittel*. August **2007**. DIN Deutsches Institut für Normung e.V., Berlin, Germany.

[17] H. Pontius, M. Dörich, M.A. Bohn.
Gel permeation chromatography of nitrocellulose (NC) and NC containing substances.
I. Parameter study in preparation of NC solutions and chromatogram evaluation.
Paper 69, pp 69-1 to 69-15. Proceed. 39th International Annual Conference of ICT on 'Energetic Materials – Processing and Product Design', June 24 to 27, 2008, Karlsruhe, Germany. ISSN 0722-4087
Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen, Germany, **2008**.

[18] H. Pontius, M. Dörich, M.A. Bohn.
Gel permeation chromatography of nitrocellulose (NC) and NC containing substances.
III. Recent results from a continued parameter study on the GPC of NC samples.
Paper 80, pp 80-1 to 80-12. Proceedings of the 40th International Annual Conference of ICT on 'Energetic Materials – Characterization, Modelling, Validation', June 23 to 26, 2009, Karlsruhe, Germany. ISSN 0722-4087.Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen. Germany, **2009**.

[19] M.A. Bohn, M. Dörich, H. Pontius.
Gel permeation chromatography of nitrocellulose (NC) and NC containing substances.
II. Remarks on calibration, molar mass distributions and mean molar masses.
Paper 70, pp 70-1 to 70-22. Proceed. of the 39th International Annual Conference of ICT on 'Energetic Materials – Processing and Product Design', June 24 to 27, 2008, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut für Chemische Technologie (ICT), 76318 Pfinztal, Germany, **2008**.

[20] D. Rodbard.
Estimation of molecular weight by gel filtration and gel electrophoresis. I. Mathematical principles.
In: N. Catsimpoolas (ed.) 'Methods of Protein Separation', Vol. 2, Plenum Press, New York, **1976,** pp 145-179.

[21] D. Rodbard.
Estimation of molecular weight by gel filtration and gel electrophoresis. II. Applications.
In: N. Catsimpoolas (ed.) 'Methods of Protein Separation', Vol. 2, Plenum Press, New York, **1976**, pp 181-218.

[22] Johannes Schweer.
Verfahren zur Molmassenbestimmung von makromolekularen Substanzen.
(Procedure to determine the molar masses of macromolecular substances).
Patent DE 40 09 559 A1, Deutsches Patentamt. Anmeldung: 24.3.**1990**; Anmelder: Bayer AG. Leverkusen, DE. Offenlegung: 26.9.1991.

[23] DIN 53240-2, Bestimmung der Hydroxylzahl Teil 2: Verfahren mit Katalysator (für die Acetylierung). November 2007. DIN Deutsches Institut für Normung eV. Beuth Verlag GmbH, 10772 Berlin, Germany.

[24] MIL-H-85497 (AS), Oct 6th **1981**.
Military specification, Naval Air Engineering Center. Engineering Specifications and Standards Department. Lakehurst, NJ, USA.