

**BAM** Bundesanstalt für  
Materialforschung und -prüfung

## Forschungsbericht 213

High Resolution NMR Spectroscopy  
for the Determination of Elastomers,  
Blends and Thermoplastic Elastomers

– Carbon and Proton NMR Spectra Catalogue –

Dr. Jürgen Kelm



Berlin 1995

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# Preface

This paper was written in the „Federal Institute for Materials Research and Testing“ ( BAM ), Berlin, in the former sub-department 3.4 „ Organic-Chemical Investigations“.

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## Summary

NMR is a powerful method for structure elucidation and determination of polymers in solution. Soluble polymers can be studied by high resolution techniques - just as small molecules - provided there is sufficient segmental motion to average out some of the linebroadening effects. The resonance lines remain broader, however, which can result in peak overlapping, especially for proton spectra. Carbon NMR is favoured in this field because of the larger spectral range and the feasibility of getting single lines by proton broad-band decoupling. One particularly important use of NMR is the determination of the microstructure of the polymer chain.

The application of high resolution NMR to solid polymers was not possible until the development of techniques like magic angle spinning, high power proton decoupling and cross polarization. The linebroadening effects in thermoplastic and duroplastic polymers, however, are only reduced to some extent. The spectra show relatively broad lines, with typical linewidths of 100 - 500 Hz, which are roughly 10 to 100 times larger than in the liquid state. Different from thermoplastic and duroplastic polymers the spectra of elastomers have a much better resolution if the measurements are performed well above the glass transition temperature. This condition is fulfilled at room temperature for many elastomers. Above  $T_g$  linebroadening effects are averaged out by segmental motions, comparable to the liquid phase. By raising the temperature the resolution can be increased further which especially improves the spectra of elastomers with relatively high glass transition temperatures.

Fillers can influence the linewidth of the spectra. The effect is twofold. First, the filler particles, e.g. carbon black, introduce microscopic inhomogeneities by susceptibility variations. Second, the molecular mobility of the polymer chains is reduced. Both effects can be averaged out to a great extent by magic angle spinning and high power decoupling, however. Therefore the filler has no detrimental influence on the resolution of the solid-state elastomer spectra. As a consequence, no decomposition procedures are necessary prior to the NMR investigation. The sample can be measured in its original molecular state.

This was the starting point for a thorough and comprehensive investigation of filled elastomers using the solid state technique in order to find out the possibilities and limits. The experiment turned out to be very successful. This led us to the idea to put all the spectra together in form of a spectra catalogue. The collection contains the most important standard and special commercial rubber types. In order to complement the solid state NMR part two chapters on blends and thermoplastic elastomers are added. Proton and carbon solution spectra of the raw rubbers are also included. Especially important is the interpretation of the spectra, in order not to display only "fingerprints".

A short version has been published already in the journal *Kautsch. Gummi, Kunstst.*, volume 46, first issue, 1993.

## Zusammenfassung

Die NMR-Spektroskopie ist bei der Strukturaufklärung und -bestimmung von löslichen Polymeren zu einer führenden Methode geworden. In Lösung werden linienverbreiternde Effekte wie die Anisotropie der chemischen Verschiebung oder die Dipol-Wechselwirkung ausgemittelt, und es werden hochaufgelöste NMR-Spektren beobachtet. Bei festen Proben sind besondere Experimente erforderlich, um Spektren guter Auflösung zu erhalten: „Magische Rotation“, „Hochleistungsentkopplung“ und „Querpolarisierung“. Trotzdem bleiben die Linien breiter als in Lösung. Im festen Stoff gibt es noch andere Effekte, die für eine Linienverbreiterung sorgen. Konformationsvariationen, Packungsunterschiede oder lokal auftretende Suszeptibilitätsschwankungen sorgen für eine Dispersion der chemischen Verschiebung, die nicht zu beseitigen ist. Diese Effekte machen sich besonders bei thermoplastischen und duroplastischen Polymeren bemerkbar und führen dort zu typischen Linienbreiten zwischen 100 und 500 Hz.

Im Gegensatz dazu erhält man bei Elastomeren Spektren mit erheblich besserer Auflösung, wenn weit oberhalb der Glasatemperatur gemessen wird. Da die Glasatemperaturen niedrig liegen, ist diese Bedingung für viele Elastomere schon bei Raumtemperatur erfüllt. Oberhalb von  $T_g$  setzen Bewegungen von Kettensegmenten ein, die ähnlich wie in Lösung zu einer Ausmittlung der linienverbreiternden Effekte führen. Durch Erhöhung der Meßtemperatur kann die Auflösung weiter gesteigert werden, was sich besonders bei Elastomeren mit hoher Glasatemperatur günstig auswirkt.

Da Elastomere weitmaschig vernetzt sind, entsprechen die Festkörperspektren von Vulkanisaten weitgehend den Lösungsspektren der Rohkautschuke. Trotz der größeren Linienbreite (typischer Wert: 30 Hz) bleiben viele Merkmale des Lösungsspektrums erhalten und ermöglichen nach wie vor eine detaillierte Beschreibung des unlöslichen Makromoleküls.

Typisch für Gummiprodukte ist ihr hoher Anteil an anorganischen Füllstoffen. Die Wechselwirkung zwischen Füllstoff und Polymer führt zu einer erheblichen Linienverbreiterung im NMR-Spektrum, insbesondere bei aktiven Füllstoffen, weil die molekulare Beweglichkeit dadurch eingeschränkt wird und die Füllstoffpartikel durch Suszeptibilitätseffekte das Magnetfeld am Kernort beeinflussen. Durch magische Rotation und Hochleistungsentkopplung jedoch wird der Einfluß auf die Linienbreite weitgehend ausgemittelt.

Aus diesen Gründen hat sich die Festkörper-NMR-Methode bei der Bestimmung von Kautschuken in Vulkanisaten sehr bewährt. In diesem Spektrenatlas sind die Ergebnisse zusammengestellt. Er umfaßt die meisten kommerziellen Elastomere, Elastomer Blends und thermoplastische Elastomere. Enthalten sind auch die Protonen- und Kohlenstoff-Lösungsspektren der löslichen Kautschuke. Besonderer Wert wird darauf gelegt, nicht bloße „fingerprints“ darzustellen, sondern jedes Spektrum möglichst weitgehend zu interpretieren. Dazu kann in vielen Fällen auf NMR-Literatur zurückgegriffen werden.

Eine Kurzfassung der Arbeit mit repräsentativen Beispielen ist in der Zeitschrift Kautsch. Gummi, Kunstst., Band 46 (1993), Heft 1, erschienen.

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# 1. Introduction

Elastomers are macromolecular materials which return rapidly to approximately their initial dimensions and shape after substantial deformation by a weak stress when the stress is released. They are made by vulcanization of rubber molecules. Rubbers are amorphous polymers with low glass transition temperatures. By vulcanization the polymer chains are crosslinked – through a change in their chemical structure – forming a wide-meshed network. Quite a lot of vulcanization processes can be distinguished, but the most general and most important is the sulfur vulcanization, even today. The peroxide cure is also of wider applicability; other processes are only limited to special rubber types.

Rubbers are well-known for a long time now, but nevertheless there are a lot of current efforts in research and development to cope with new demands of application. Improvements refer to, e.g., processing, heat resistance, ozone and weather resistance, oil and chemical resistance, gas permeability, low-temperature flexibility or electrical properties. In this sense it is and remains a modern and high-tech material.

High quality standards have generally become more and more important because of different reasons, e.g., a changed attitude towards environment and resources, severe demands for the safety of technical systems and plants, the increasing division of labour or new regulations of liability. To contribute to a high level of quality is one of the main tasks of the Federal Institute for Materials Research and Testing. To this end chemical analysis is indispensable. In the field of rubbers it is not only the polymer that determines the suitability of an elastomer, but quite a lot of accompanying substances, like fillers, pigments, plasticisers, curing agents, antioxidants, stabilizers and processing aids. Therefore a complete analysis is very laborious and time – consuming<sup>1,2</sup>. To what extent chromatographic and spectrometric methods are used, however, depends on the special problem to be solved, of course.

The main interest of this paper, however, is the rubber molecule. Since many years it is common practise to use spectrometry for determining chemical structures. Infrared (IR) spectrometry is widely known and used for the identification of polymers<sup>3</sup>. Specific absorption bands, their intensities, and their patterns (fingerprints) are used for this purpose. The interpretation is made, as a rule, by comparison with a collection of reference spectra. One problem is that copolymers and mixtures of homopolymers generally cannot be distinguished. Another problem can arise from the filler. The situation has been improved considerably with the introduction of newer IR instrumentation (FTIR), but preparation procedures for filled vulcanizates are still in use by which the polymer is

transformed into the soluble form and freed from the other, disturbing components<sup>4</sup>. To accomplish this vulcanizates can be treated by standardized thermal decomposition methods, which frequently cause, in addition to chain rupture, a change in the original structure. Therefore – in order not to fail – the interpretation has to take these deviations into account.

An alternative approach to the determination of rubbers is nuclear magnetic resonance (NMR) spectrometry. NMR is a powerful method for structure elucidation and determination of polymers in solution. Soluble polymers can be studied by high resolution techniques – just as small molecules – provided there is sufficient segmental motion to average out some of the linebroadening effects. The resonance lines, remain broader, however, which can result in peak overlapping, especially for proton spectra. Carbon NMR is favoured in this field because of the larger spectral range and the feasibility of getting single lines by proton broad-band decoupling. One particularly important use of NMR is the determination of the microstructure of the polymer chain<sup>5</sup>. The polymerization of conjugated dienes, e.g., can produce structures with various combinations of geometrical and configurational isomerism: 1,3-butadiene can give 1,4 or 1,2 enchainment; the 1,4 structures may be *cis* or *trans*, the 1,2 structures may occur in isotactic or syndiotactic sequences.

The application of high resolution NMR to solid polymers was not possible until the development of techniques like magic angle spinning, high power proton decoupling and cross polarization<sup>6-12</sup>. The linebroadening effects in thermoplastic or duroplastic polymers, however, are only reduced to some extent. The spectra show relatively broad lines, with typical linewidths of 100 – 500 Hz, which are roughly 10 to 100 times greater than in the liquid state. Besides the mechanisms like dipolar coupling and chemical shift anisotropy there are other effects in organic solids that cause linebroadening, for instance variations in intramolecular conformations, bond angles, intermolecular packing and geometries of local sources of magnetic susceptibility anisotropy. These effects cause a dispersion in chemical shift values that cannot be removed by decoupling and magic angle spinning<sup>13</sup>. Nevertheless NMR has been used extensively for the following subjects: determination of insoluble polymers, investigation of solid-state reactions like crosslinking or curing, surface analysis, observation of crystalline and amorphous domains, elucidation of the structure of polymer blends, investigation of polymer dynamics (spin relaxation).

Different from thermoplastic and duroplastic polymers the spectra of elastomers have a much better resolution if

the measurements are performed well above the glass transition temperature<sup>14,15</sup>. This condition is fulfilled at room temperature for many elastomers. Above  $T_g$  line-broadening effects are averaged out by segmental motions, comparable to the liquid phase. By raising the sample temperature the resolution can be increased further which improves the spectra especially for elastomers like fluoro rubbers or nitrile rubbers with relatively high glass transition temperatures or butyl rubber with relatively slow segmental motions<sup>16</sup>.

Fillers can influence the linewidths of the spectra. The effect is twofold. First, the filler particles, e.g. carbon black, introduce microscopic inhomogeneities by susceptibility variations. Second, the molecular mobility of the polymer chains is reduced. Both effects can be averaged out to a great extent by magic angle spinning and high power decoupling, however<sup>17</sup>. Therefore the filler has no detrimental influence on the resolution of solid-

state elastomer spectra. As a consequence, no decomposition procedures are necessary prior to the NMR investigation. The sample can be measured in its original molecular state.

This was the starting point for a thorough and comprehensive investigation of filled elastomers using the solid state technique in order to find out the possibilities and limits. The experiments turned out to be very successful. This led us to the idea to put all the spectra together in form of a spectra catalogue. A short version has been published already<sup>18</sup>. The collection contains the most important standard and special commercial rubber types. In order to complement the solid state NMR part two chapters on blends and thermoplastic elastomers are added. Proton and carbon solution spectra of the raw rubbers are also included. Mainly the carbon spectra are used for the interpretation of the solid state spectra and for comparison, too.

## 2. Fundamentals

### NMR (Nuclear Magnetic Resonance)

Nuclei that act as though they are spinning possess angular momentum and a magnetic moment  $\mu$ . In a magnetic field the nuclear dipoles, like gyroscopes in a gravitational field, undergo precession about the field direction. The frequency of this so-called Larmor precession  $\omega_0$  depends on the magnetic field  $H_0$ .

By a well-known relationship, the Larmor frequency is given by

$$\omega_0 = \gamma H_0$$

$\gamma$  is the gyromagnetic ratio.

By applying a second oscillating magnetic field, at right angles to  $H_0$ , the nuclear spins can be made to flip over if the oscillation frequency  $\nu$  fulfils the resonance condition

$$2 \pi \nu = \omega_0 = \gamma H_0$$

### Chemical shift

The resonance frequency for a nucleus is not a fixed value, but depends on the chemical surrounding. This "chemical shift" has its origin in the magnetic screening or shielding produced by electrons. Thus a nucleus experiences not the applied magnetic field  $H_0$  but rather a field  $H_i$  :

$$H_i = H_0 (1 - \sigma_i)$$

The shielding constants  $\sigma_i$  are found to be rather small (roughly  $10^{-5}$  for protons and  $< 10^{-3}$  for most other nuclei).

The measurement of absolute chemical shifts is not possible because it would require measurements of a nucleus stripped of all electrons. For applications of chemical interest, however, it is only necessary to determine the displacements relative to a reference compound (TMS, tetramethylsilane, for proton and carbon NMR spectrometry). As the chemical shifts are proportional to the magnetic field strength it is customary to report the values in a dimensionless scale (ppm, parts per million) which gives the same results for different spectrometers:

$$\delta = \frac{\nu_{\text{substance}} - \nu_{\text{standard}}}{\nu_{\text{standard}}} \times 10^6$$

### Scalar spin-spin coupling

Besides the chemical shift there is another effect that splits resonance lines into multiplets. It is commonly

called indirect spin-spin coupling or scalar spin-spin coupling. This type of coupling is explained by an interaction of neighbouring nuclei. The interaction occurs via slight polarizations of the spins or orbital motions of the valence electrons. Spin-spin coupling is not affected by the tumbling of the molecules and, unlike the chemical shift, is independent of the applied field  $H_0$ .

In the liquid phase, most often in solutions, chemical shifts and scalar couplings can be measured readily. Linebroadening effects like the dipolar coupling or the anisotropy of chemical shift are averaged out by strong molecular motions. In solids, however, these effects broaden the resonance lines extensively which results in wide-line spectra. Typical linewidths are 1 Hz in solution and 10 kHz in solids.

### Dipolar spin-spin coupling

As already mentioned, the resonance frequency of a nucleus is dependent on the local magnetic field. Besides the applied field  $H_0$ , screened by the electrons, one has to consider local fields coming from magnetic dipoles. This is the so-called dipolar spin-spin coupling, shown for a carbon-proton pair in fig. 1. The magnetic moment  $\mu$  of the hydrogen nucleus  $^1\text{H}$  produces a local magnetic field  $h_{\text{loc}}$  at the site of the carbon nucleus  $^{13}\text{C}$ .

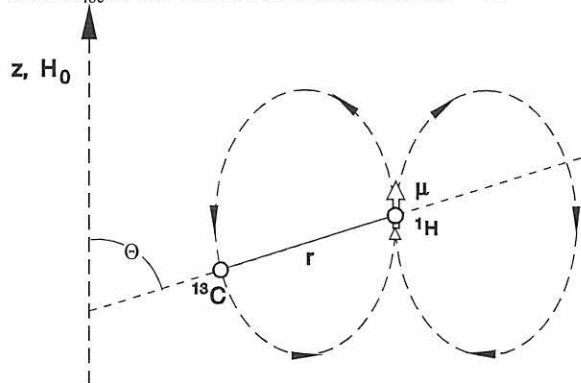


Fig. 1: Dipolar spin-spin coupling

The z-component of this local field is given by the following relation:

$$h_{\text{loc}} \sim \mu (3 \cos^2 \Theta - 1) / r^3$$

According to distance and orientation different local fields have to be expected, which, because of poor molecular mobility, cannot be averaged out and will lead to considerable linebroadening. Similar to the broadening by different internal magnetic fields, also different internal electrical field gradients may broaden the resonance line of nuclei having a nuclear quadrupole moment.

## Chemical shift anisotropy (CSA)

Another effect that determines the line width in solids is the chemical shift anisotropy (CSA). The resulting magnetic field at a carbon nucleus depends upon the shielding caused by surrounding electrons. In general, the electron density is not symmetric. Thus the chemical shift of a carbonyl carbon, e.g., depends, upon whether the C = O bond is lined along the magnetic field or perpendicular to it, or is in some other orientation. In a liquid with rapid molecular motion only an average, or isotropic chemical shift,  $\sigma_i$ , is observed. In an amorphous solid or crystal powder, however, a complicated broad lineshape is observed that arises from the sum of all possible shifts. Although information concerning bonding and molecular symmetry are contained in the CSA line shape, the overlap in a complex system makes interpretation difficult<sup>19</sup>. The line width induced by CSA interactions are directly proportional to  $H_0$ , so that higher fields do not improve resolution. As for the dipolar coupling the angle dependence is described by the term

$$\Delta\sigma \sim (3 \cos^2 \Theta - 1)$$

## Magic angle spinning (MAS)

The angle dependence is the same for all anisotropic interactions, as described. The angle  $\Theta$  has a different meaning depending upon the type of interaction being considered. For dipolar coupling, the angle is between a vector joining the dipoles and the direction of  $H_0$ . In the case of CSA interactions, it is the angle between the bond axis and  $H_0$  and finally, the angle in quadrupolar interactions is between the quadrupolar moment and the direction of the electric field gradient. In each case, if the angle  $\Theta$  is chosen that

$$3 \cos^2 \Theta - 1 = 0$$

all anisotropic contributions to the NMR spectrum will reduce to zero. This angle,  $54^\circ 44'$ , is the so-called magic angle. In a static solid sample the molecules are oriented in all possible directions from  $0^\circ$  to  $180^\circ$ , of course. The only way to meet the condition of magic angle for all interactions is to rotate the macroscopic sample about an axis, which is tilted against the field direction at  $54^\circ 44'$ . Then, in the time average, all anisotropic interactions are no more effective<sup>6</sup>. The spinning frequency must be at least comparable to the chemical shift anisotropy, however. For  $^{13}\text{C}$ , e.g., spinning rates of some kHz are necessary. Carbonyl or aromatic groups have anisotropies of up to 200 ppm, aliphatic groups of roughly 50 ppm (10 kHz / 2,5 kHz for  $\nu_0 = 50$  MHz). Therefore spinning sidebands are characteristic of solid-state NMR.

## High power decoupling

The intensities become relatively high when the spinning frequency is smaller than the chemical shift anisotropy.

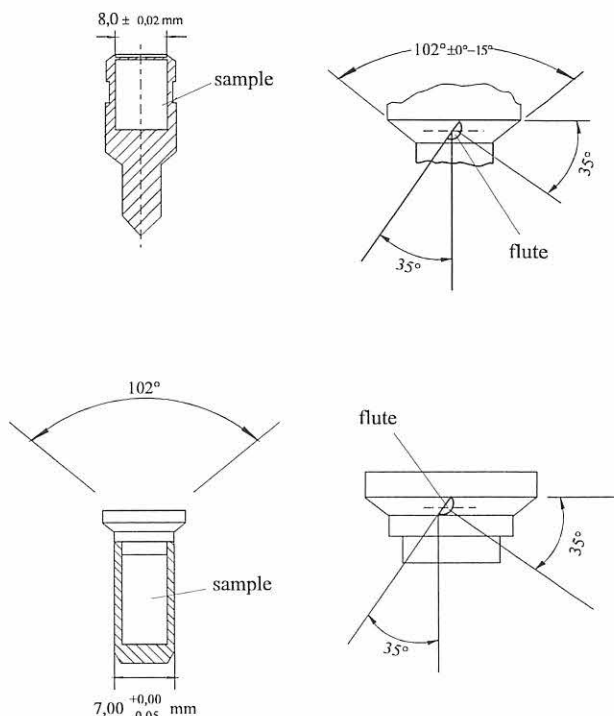


Fig. 2: MAS rotor types (according to Varian)  
upper: conical design, lower: cylindrical design

One of the most crucial components of solid state NMR is the high speed rotor. Experimentally, magic angle spinning can be achieved in a variety of ways. Basically two rotor types have been used: the conical design ("mushroom") after Andrew and Beams and the cylindrical construction employing separate bearing and drive systems after Lowe (fig. 2)<sup>20</sup>. The Andrew / Beams rotors have the principal advantage of simplicity of construction. However, it is impossible to optimize both the drive efficiency and stability. The principal disadvantage of such spinners is the difficulty of routinely obtaining dynamic balance at high speeds, especially with inhomogeneous samples, like powders. Therefore the cylindrical design using dual gas bearing and separate gas drive is favoured today. It requires, however, a high dimensional stability of the rotor material and an extreme precision of machining. Therefore plastics which are important for the other rotor type have to be excluded - except for the rotor end caps. Only materials like ceramics, e. g. silicates, aluminium oxide or silicon nitride, meet the heavy requirements. In addition to the better spinning performance of the cylindrical rotor type ceramic spinner assemblies open up new fields of application. As the differential thermal expansion is very low variable temperature operation becomes possible. De



pending on the rotor diameter rotation frequencies up to about 25 kHz can be obtained<sup>21</sup>.

Theoretically, it is possible to remove all the above anisotropic interactions by sample spinning at the magic angle. Realistically, normal spinning rates of up to 5 kHz are sufficient to attenuate or remove linebroadening due to CSA, but are far too slow for the dipolar coupling where approximately 20 kHz are necessary. For atomic nuclei with a low natural abundance the dipolar fields come from hetero spins, for <sup>13</sup>C in organic solids, e.g., from protons. In such cases a simple means of removing such coupling is to decouple the two spin systems. This technique is well known from high resolution liquid NMR. The main difference is the extremely high rf power applied as the interactions are much bigger in solids. By applying a strong decoupling rf pulse to the <sup>1</sup>H nuclei resulting in rapid spin flips the coupling is averaged out.

### Cross Polarization (CP)

Another problem with solid samples are the spin-lattice relaxation times  $T_1$ . Unfortunately, long  $T_1$  times are typical of solids due to the reduced molecular mobilities. This means very long pulse delays in Fourier-transformation experiments of less abundant nuclei and therefore only small numbers of accumulation in a given time which was a severe limitation in the past. The CP experiment is a solution to this problem. The basic idea is to use the strong spin polarization of abundant spins like protons in organic samples to enhance the weak polarization of rare spins like <sup>13</sup>C by polarization transfer [7]. As the resonance frequencies are different in a static field  $H_0$  the polarization cannot be transferred directly between the two spin systems. This is only possible in the so-called rotating frame if the Hartmann-Hahn condition is fulfilled:

$$\gamma_C H_{1,C} = \gamma_H H_{1,H}$$

$H_{1,C}$  and  $H_{1,H}$  are the amplitudes of the alternating magnetic fields applied simultaneously,  $\gamma_C$  and  $\gamma_H$  the gyromagnetic ratios [8]. The rotating frame is a coordinate system which rotates at the NMR resonance frequency about  $H_0$ . In this system the effect of  $H_0$  appears eliminated; the alternating fields  $H_{1,C}$  and  $H_{1,H}$  become static and play the same role as  $H_0$  in the laboratory frame. The Hartmann-Hahn condition permits exactly matched energy-conserving mutual spin flips between carbons and protons. In terms of the spin temperature concept a thermal contact is established by the cross polarization process. The result is a net transfer of polarization from the cold proton reservoir to the hot carbon spins during

the contact time. The point is that the spin-lattice relaxation time  $T_1$  is no more decisive for the relaxation behaviour, but other relaxation times become effective. After the CP contact the <sup>13</sup>C polarization decreases much more quickly than in the normal experiment allowing considerably more accumulations in a given time.

The following equations describe the dynamics of the CP experiment<sup>11</sup>:

$$\begin{aligned} M(t) &= M_0 \lambda^{-1} \left\{ 1 - \exp\left(-\frac{\lambda t}{T_{CH}}\right) \right\} \exp\left(-\frac{t}{T_{1\rho}({}^1H)}\right) \\ M(t) &= M_0 \lambda^{-1} f(t) \\ &\text{with} \\ \lambda &= 1 + \frac{T_{CH}}{T_{1\rho}({}^{13}C)} - \frac{T_{CH}}{T_{1\rho}({}^1H)} \\ f(t) &= \exp\left(-\frac{t}{T_{1\rho}({}^1H)}\right) - \exp\left[-t\left(\frac{1}{T_{CH}} + \frac{1}{T_{1\rho}({}^{13}C)}\right)\right] \end{aligned}$$

With increasing contact time  $t$  the signal intensities as a measure of the magnetization  $M(t)$  go through a maximum and then drop off again. Usually the cross polarization time  $T_{CH}$  is much shorter than the relaxation times of the rotating frame  $T_{1\rho}({}^1H)$  and  $T_{1\rho}({}^{13}C)$  - otherwise the experiment would be a failure - so <sup>1</sup>H and <sup>13</sup>C spins reach a common spin temperature which then relaxes to the lattice via  $T_{1\rho}^{-1}({}^1H)$ . The rate  $T_{1\rho}^{-1}({}^{13}C)$  can be ignored in this discussion. The rate of cross polarization depends on the dipolar interaction between <sup>13</sup>C and <sup>1</sup>H. Thus, for an ideal system quarternary carbons are polarized more slowly than protonated carbons, but then lose polarization at a common rate, provided there is sufficient spin diffusion. Spin diffusion among the proton spins averages out the individual values so that  $T_{1\rho}({}^1H)$  is typical of a specific domain which dimensions are estimated at approximately 2 nm.

As the efficiency of cross polarization for a given contact time depends on  $T_{CH}$  and  $T_{1\rho}({}^1H)$  the measurement will not properly represent the whole sample. This implies that the CP experiment discriminates between different parts of the sample. It is clear that relative intensities will only accurately quantify the carbons at long contact times when, unfortunately, some carbons will have considerably less intensity than their maximum<sup>22</sup>.

As an example a signal intensity plot from a CP experiment as a function of contact time for a blend of polypropylene and EPDM, a thermoplastic elastomer, is shown (fig. 3).

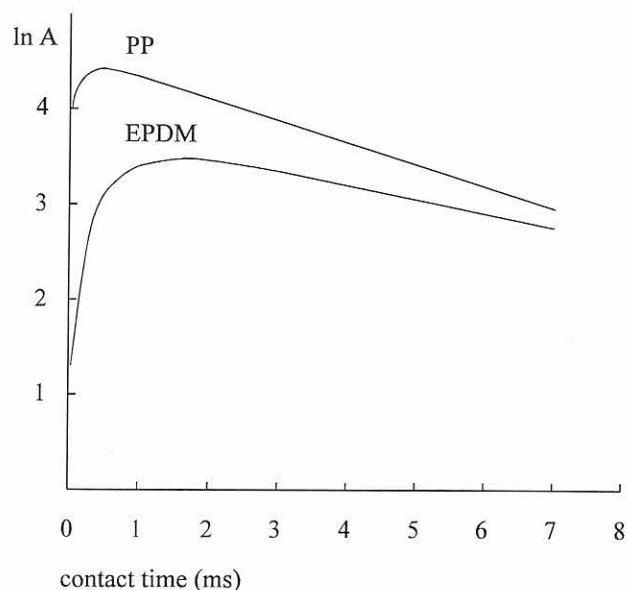
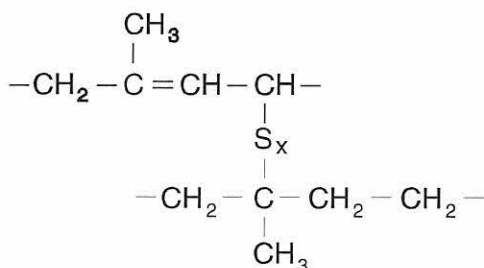


Fig. 3: Cross Polarization of a blend of PP and EPDM for representative signals; A: peak height, not normalized.

The cross polarization for polypropylene is very effective; the maximum is reached after about 0.5 ms. In the logarithmic presentation, the decrease is described by a straight line, as expected. The EPDM signals, on the other hand, grow much more slowly and reach their maximum after about 2 ms. The reason for the different behaviour is the different molecular mobility of the thermoplastic and elastomeric domains. Thermoplastic elastomers are discussed below in more detail.

### NMR of elastomers, blends and thermoplastic elastomers

By the introduction of crosslinks the chemical surrounding of some carbons is changed resulting in additional resonances shifted more or less away from the original position. As an example for network structures two natural rubber chains, linked together by a sulfur bridge  $S_x$ , are shown:



As the network is wide-meshed, i.e., only one crosslink per about 100 monomer units, and as there are different reaction paths the intensity of the "crosslink peaks" is rather low. Nevertheless solid state NMR was used intensively in this field<sup>23-27</sup>.

Typical of elastomers are high molecular mobilities. As a result the above mentioned linebroadening effects are averaged out to some extent. The situation is comparable to the liquid state. Obviously the molecular chain segments are undergoing a considerable amount of random reorientational motions to produce motional narrowing. Thus, experiments were performed on solid polyisoprene and polybutadiene raw rubbers using the common liquid NMR instrumentation<sup>28</sup>. For filled, crosslinked samples this method will fail, however. Sometimes the resolution can be improved by rubber sample swelling in suitable solvents<sup>29</sup>; but generally the solid state technique has to be used for successful measurements.

Depending on glass transition temperature and structure the resolution of solid state elastomer spectra can vary considerably. Fortunately, we found striking improvements in cases of bad resolution after raising the temperature of the measurement up to about 80°C. In fig. 4 the spectra of natural rubber and butyl rubber are shown. As the scalar coupling is used as a measure of resolution the experiments were performed without decoupling. In spite of nearly the same glass transition temperatures, about -70°C, the resolution at room temperature is quite different. Only for natural rubber the scalar couplings are resolved. This is achieved for butyl rubber not before the temperature is raised. Butyl rubbers appear to be an exception among elastomers. Spin-lattice relaxation times  $T_1$  and nuclear Overhauser enhancement (NOE) measurements showed that the average backbone segmental motion is about two orders of magnitude slower<sup>31</sup>.

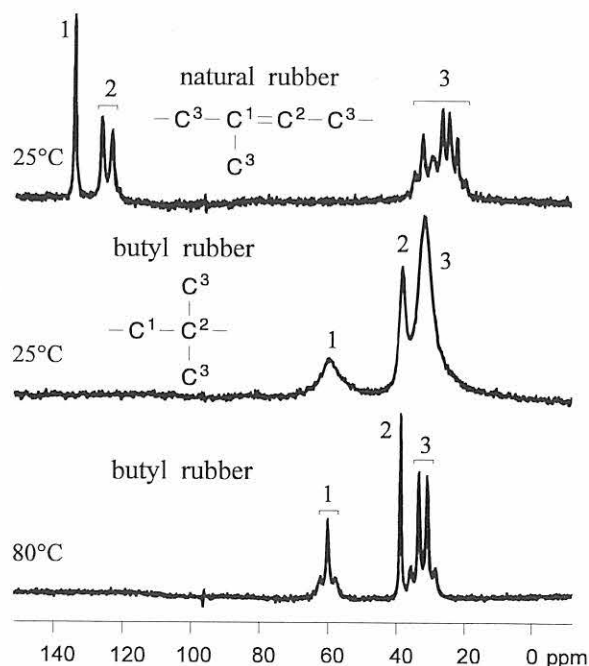


Fig. 4: Influence of temperature on resolution; experiments with MAS, without decoupling



High resolution  $^{13}\text{C}$  spectra of solid polymers can principally be obtained by two ways: from normal Bloch decays (SPE: single pulse excitation) of the carbon magnetization, just as in liquid NMR, or from cross polarization. In both cases, MAS and high power proton decoupling are used. In the field of polymers both techniques complement each other. For semicrystalline and glassy materials the use of SPE is relatively inefficient due to the long  $T_1$ 's, which prevents short repetition times. Cross polarization gives a signal theoretically four times larger than the normal experiment, and circumvents the  $T_1$  problem. Elastomeric systems behave differently. Because of their much greater segmental mobility, elastomers have shorter spin-lattice relaxation times - in the order of seconds - making SPE, the normal experiment feasible. Moreover, cross polarization is not effective for elastomers and their blends, because the static dipolar coupling necessary for the contact between the  $^1\text{H}$  and  $^{13}\text{C}$  spin system has been eliminated or greatly reduced by molecular motion.

A special case are thermoplastic elastomers. They are usually block copolymers having a two-phase morphol-

ogy. These blocks can be arranged in random or in ordered fashion in a copolymer. Physical mixtures or chemically interacted mixtures of hard and soft polymers are also possible. At the service temperature one of the blocks is viscous or rubbery; this is the soft segment. The other is of a glassy, crystalline or polar nature; this is the hard segment. It is the intermolecular association of the hard segments which provides the thermo-reversible physical crosslinks in the polymer. As solids NMR is highly sensitive to molecular mobilities - with respect to relaxation and linebroadening - heterogeneous systems like thermoplastic elastomers are particularly interesting to the NMR specialist. Commercial types can be mainly attributed to five basic classes: styrenic block copolymers, polyolefin blends, polyurethanes, polyetheresters and polyetheramides<sup>32</sup>. It turns out that it is advantageous to use both solid state experiments, SPE and CP. The spectra yield complementary results. The hard phases require CP operation with relatively short contact times at or near room temperature, whereas the mobile segments are accentuated by longer contact times or an SPE experiment, mostly at higher temperatures.

## 3. Experimental

### Materials and preparation

The spectra catalogue contains the following elastomers, blends and thermoplastic elastomers (class designations and abbreviations according to ISO 1629<sup>33</sup>):

#### Elastomers

Class M - rubbers having a saturated chain of the polymethylene type: acrylate rubbers (ACM), chlorinated polyethylene (CM), chlorosulfonated polyethylene (CSM), ethylene-propylene copolymer (EPM), ethylene-propylene-diene terpolymers (EPDM), ethylene-vinylacetate copolymer (EVM), fluorocarbon rubbers (FPM)

Class O - rubbers having oxygen in the polymer chain: epichlorohydrin rubber (CO), ethylene oxide-epichlorohydrin copolymer (ECO)

Class Q - rubbers having silicone in the polymer chain: silicone rubber (MQ), phenylsilicone rubber (PVMQ), fluorosilicone rubber (FVMQ)

Class R - rubbers having an unsaturated chain: butadiene rubbers (BR), chloroprene rubber (CR), butyl rubber (IIR), bromobutyl rubber (BIIR), chlorobutyl rubber (CIIR), isoprene rubbers (IR), nitrile rubbers (NBR), hydrogenated nitrile rubbers (HNBR), natural rubbers (NR), epoxidized natural rubbers, polynorbornene, polyoctenamers, styrene-butadiene-rubbers (SBR)

Class T - rubbers having sulfur in the polymer chain: polysulfide rubber (OT)

Class U - rubbers having carbon, oxygen, and nitrogen in the polymer chain (urethane rubbers): polyester rubbers (AU), polyether rubber (EU)

#### Blends

BIIR/NR, BIIR/SBR, BR/SBR, BR/CR, BR/IR, CR/NR, CR/BIIR, CR/SBR, EPDM/NR, EPDM/SBR, NBR/NR, NBR/SBR, polyoctenamer/SBR, FPM/HNBR

#### Thermoplastic elastomers

- styrene block copolymers
- polyolefin blends
- polyurethanes
- polyetheresters
- polyetheramides

Samples of raw rubbers were normally cut into small pieces as far as possible. Samples of vulcanizates were ground by an ultracentrifugal mill (Retsch ZM 1) after immersion in liquid nitrogen. In case of sticky samples sometimes the addition of zinc oxide proved to be successful. Then the crushed material was extracted accord-

ing to standard procedures in order to remove antioxidants, accelerators, plasticisers, and other low molecular additives. Next the extracted material was dried, preferably under vacuum at 50 °C. After preparation raw rubber samples were solved in deuterated solvents, tetrahydrofurane, dimethylsulfoxide, dimethylformamide, but mainly chloroform. With one exception, FVMQ, all polymers were soluble. Increasing the temperature facilitated the solving process in some cases. The solutions were filled into 5 mm-diameter sample tubes.

Powdered or granular samples of the vulcanizates, approximately of 0,5 mm size or finer, were loaded into 7 mm-diameter rotors. The rotor used was the dual gas bearing type described in the chapter on magic angle spinning. There were two rotor options, one for ambient temperature, the other for high temperatures. The ambient temperature rotor consisted of a ceramic body and a top cap made of a fluorocarbon polymer. The high temperature type was a three-part assembly: the ceramic body, a bottom cap with a threaded rod and a top screw cap, both made of polyimide. The ceramic rotor body consisted of a silicate or aluminum oxide in every case.

#### NMR Spectrometry

Solution and solid state spectra were carried out on a Varian XL-200 spectrometer operating at 200 MHz for protons and 50 MHz for carbons. Solution <sup>1</sup>H and <sup>13</sup>C spectra were normally obtained at ambient temperature; for the urethane rubbers, however, temperatures up to 100°C were employed. For convenience the chemical shift scale was adjusted via solvent peaks, for instance the chloroform residue in deuteriochloroform at 7,24 ppm for <sup>1</sup>H-NMR and the deuteriochloroform triplet at 77 ppm for <sup>13</sup>C-NMR.

Solid state <sup>13</sup>C-NMR spectra were obtained using a PLE probe (pneumatic load/eject). Adjustments of the magic angle or the Hartmann-Hahn match, e.g., were performed using reference compounds like hexamethylbenzene and adamantane. The solid state experiment employed an 11 μs carbon 90° pulse, CP contact times of 200 and 3000 μs, proton high power decoupling of 45 kHz, recycle delay time of 1 s, and MAS rotor frequencies between 2500 and 3000 Hz. The CP spectra were normally measured at 30°C, the SPE spectra at 80°C. For the detection of minor structural features, for instance of isoprene units in butyl rubber, measurement times up to 72 hours were necessary depending on the filler content. The chemical shifts were adjusted by using hexamethylbenzene as an external secondary reference, with the aromatic signal at 132,1 ppm. The rotor resonances, due to the polymeric parts, were eliminated by using an interactive subtraction routine.

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## 4. <sup>13</sup>C-NMR Spectra of Vulcanizates and Raw Rubbers

### ACRYLATE RUBBER (ACM)

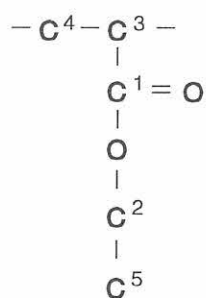
#### 1. Ethyl acrylate rubber

Acrylate rubbers are copolymers having two components: acrylic acid esters (95 - 99%) and the reactive cure site (1 - 5%). The acid esters are mainly ethyl or butyl acrylate and methoxy or ethoxy ethyl acrylate. The saturated chemical structure of acrylate elastomers does not allow the use of common curing systems. In order to enable the vulcanization reactive co-monomers are added, e.g., monomers with an active chlorine group or epoxy and

carboxy groups. A different type is a copolymer of ethylene and methyl acrylate.

The interpretation of the spectrum of ethyl acrylate rubber is straightforward. The backbone peaks 3 and 4 show tacticity splittings. Their assignment was verified by DEPT experiments.

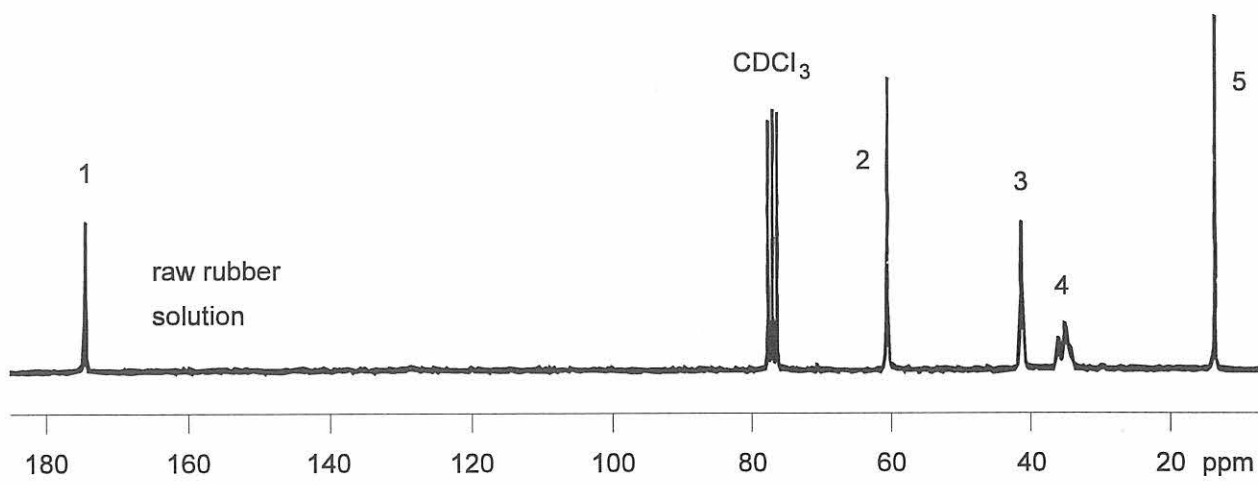
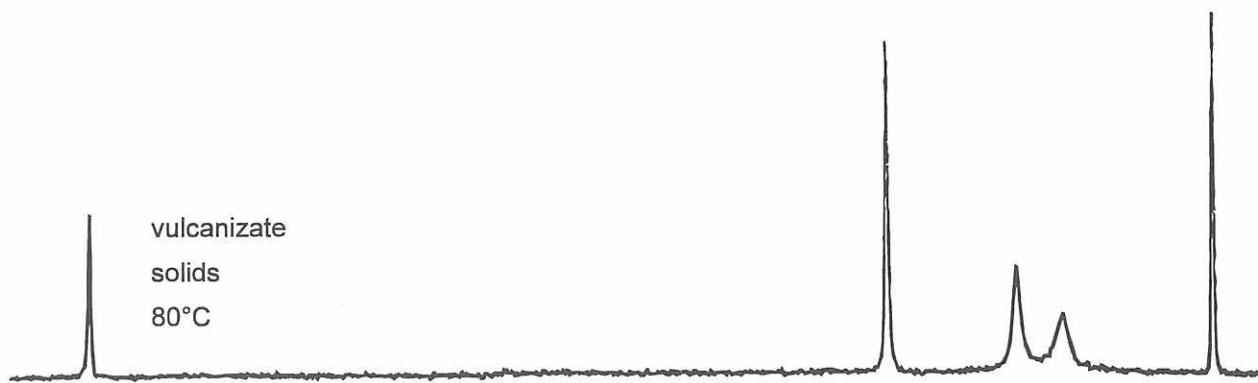
#### Assignments<sup>1,2</sup>:



#### References:

<sup>1</sup> K. J. Ivin, S. Pitchumani, C. R. Reddy and S. Rajadurai, Eur. Polym J. 17,341 (1981)

<sup>2</sup> A. Simmons, A. Natansohn, A. Eisenberg, J. Polym. Sci., Polym. Chem. Ed. 25, 2221 (1987)



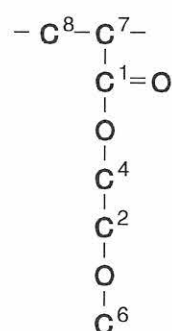
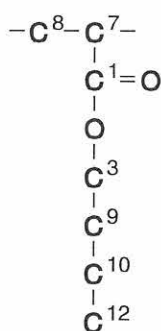
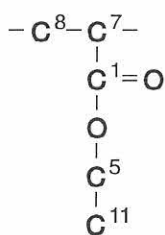
# ACRYLATE RUBBER (ACM)

## 2. Ethyl acrylate – butyl acrylate – methoxyethyl acrylate terpolymer

Acrylate elastomers are speciality elastomers. Their use in hot oil and high temperature applications determine the choice of the monomers. By combining ethyl acrylate, butyl acrylate and methoxy ethyl acrylate it is possible to achieve high performance properties in connection with

low temperature flexibility. The interpretation of the spectrum is straightforward. The peaks were assigned by comparison with the homopolymers, by using the DEPT experiment and by performing increment calculations.

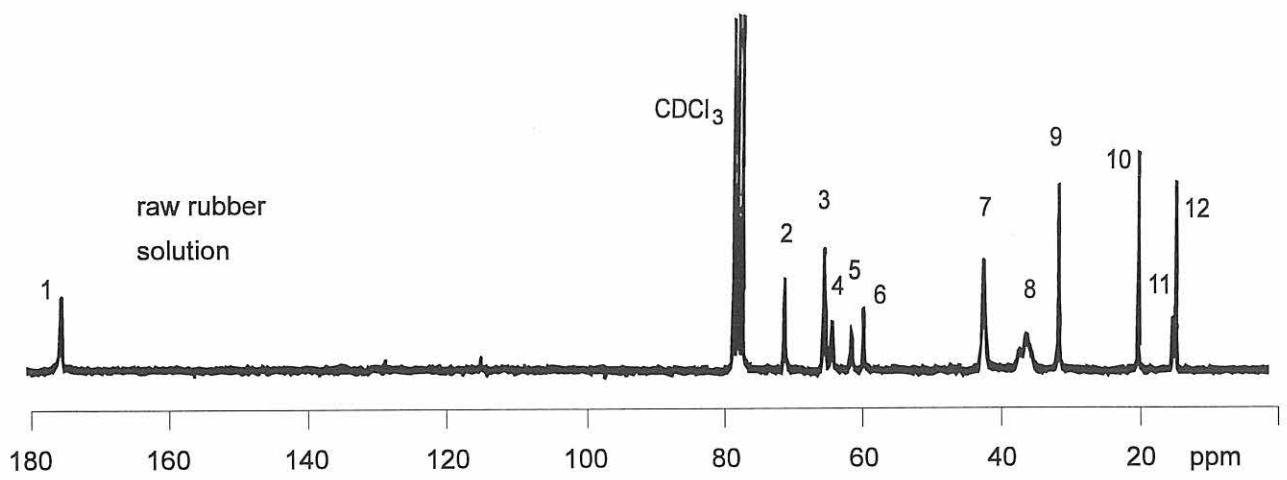
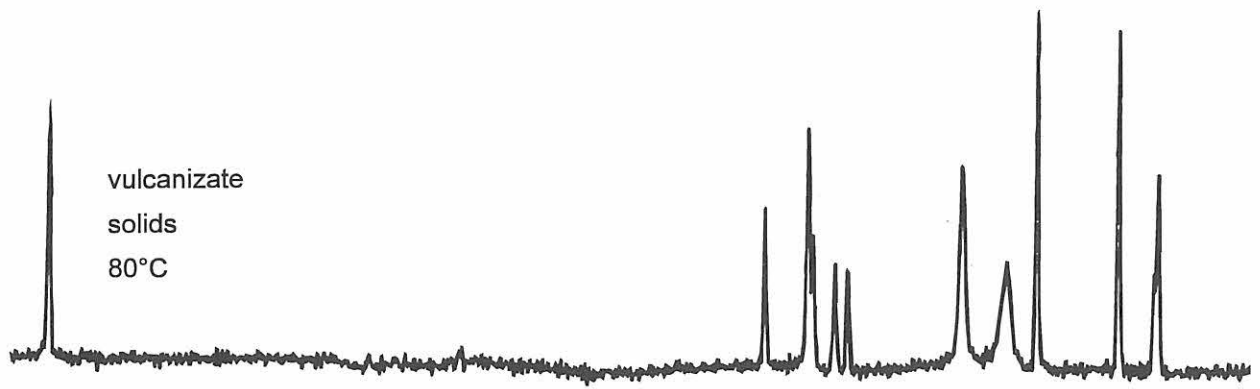
### Assignments<sup>1</sup>:



### References:

<sup>1</sup> see references of ACM, example 1: ethyl acrylate rubber

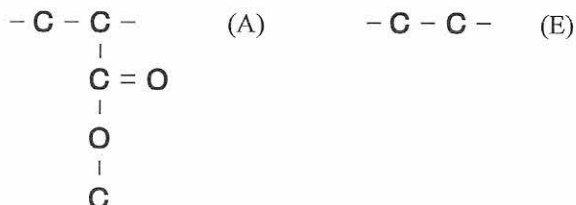




# ACRYLATE RUBBER (ACM)

## 3. Ethylene-methyl acrylate copolymer

The combination of an acrylate monomer with ethylene is another way to high performance properties:



Normally a third carboxylic monomer of small amount is incorporated to provide cure sites along the chain. The monomer units A and E are arranged in different sequences. The spectrum is interpreted on the basis of triads; it is assumed that the acrylate units are polymerized only in normal head-to-tail addition. The observed carbon atom is marked by an asterisk. The small peak at 41,5 ppm is due to AAA sequences. Correspondingly the main contribution to peak 5 comes from AAE sequences.

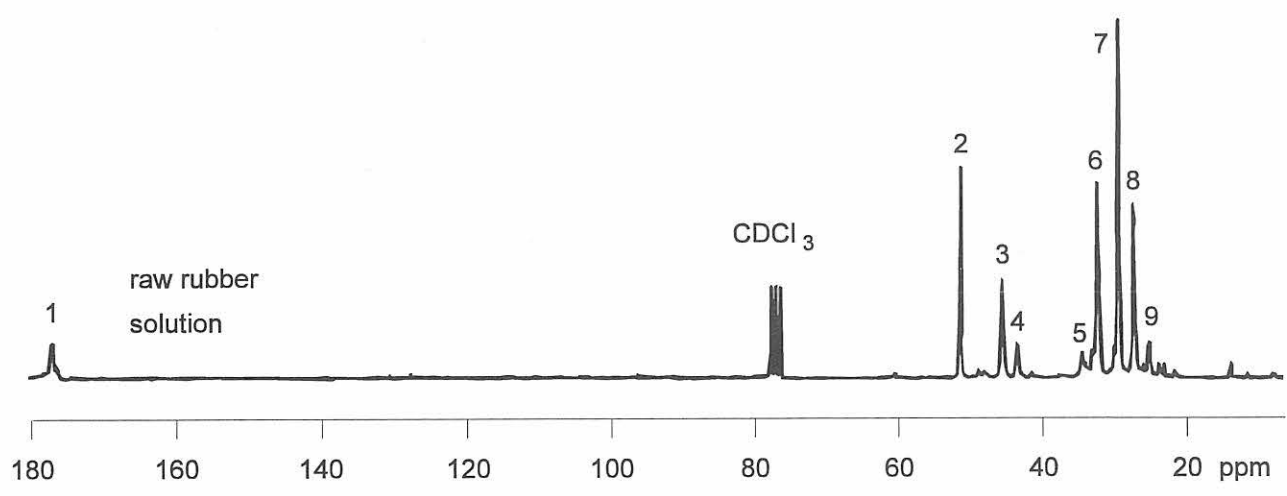
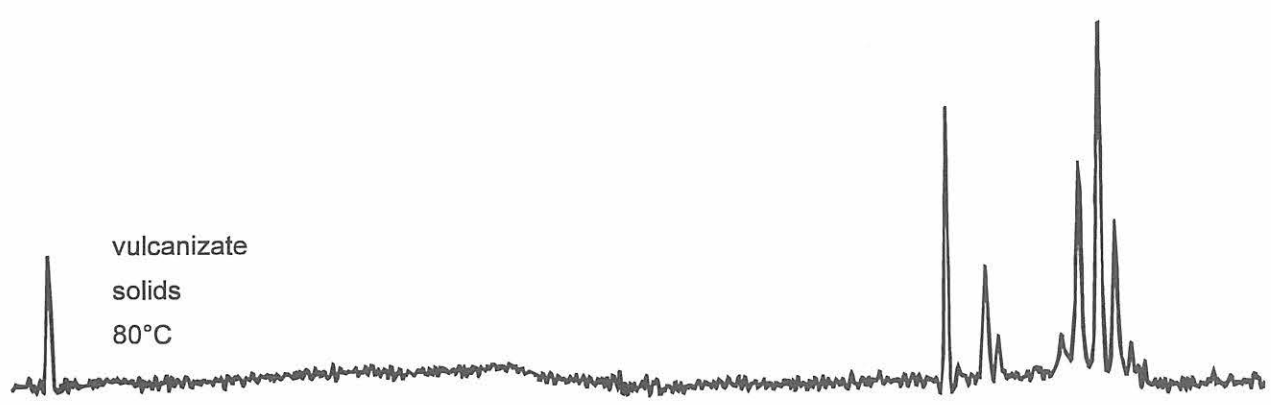
### Assignments<sup>1,2</sup>:

- |   |  |
|---|--|
| signal 1: C = O                                   | 6: CH <sub>2</sub> (AEE, AEA, EAE, EAA: <u>CCC</u> *CC, CCC* <u>CC</u> ) |
| 2: OCH <sub>3</sub>                               | 7: CH <sub>2</sub> (EEA, EEE : CCC*CC)                                   |
| 3: CH (EAE: CCC*CC)                               | 8: CH <sub>2</sub> (AEE, EEA : <u>CCC</u> *CC, CCC* <u>CC</u> )          |
| 4: CH (AAE, EEA: <u>CCC</u> *CC, CCC* <u>CC</u> ) | 9: CH <sub>2</sub> (AEA: <u>CCC</u> *CC)                                 |
| 5: CH <sub>2</sub> (AAA, AAE: CCC* <u>CC</u> )    |  |

### References:

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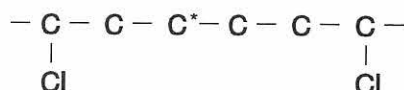


# CHLORINATED POLYETHYLENE (CM)

Chlorinated polyethylene is made by chlorination of polyethylene. The strong tendency of pure polyethylene to crystallize is reduced by the introduction of the chlorine atom ending up with an amorphous polymer. The chlorine concentration differs from 20% to 40%. The chlorination results in polymers which consist of unmodified methylene units and chlorinated methylene co-units. Low crystallinity and elastomeric properties are typical of a random distribution of the structure units.

The spectrum is rather complex. A lot of lines is not fully resolved, especially the peaks between 57 and 67 ppm.

Therefore the interpretation can only give rough assignments. A special nomenclature is used for the interpretation of the spectrum. The carbons are designated by T (tertiary carbon: CH) and S (secondary carbon: CH<sub>2</sub>). The distance of the observed carbon C\* to the next tertiary carbon bearing a chlorine atom is given by small letters (c<sup>+</sup> stands for a distance of at least c), e.g., bSc stands for



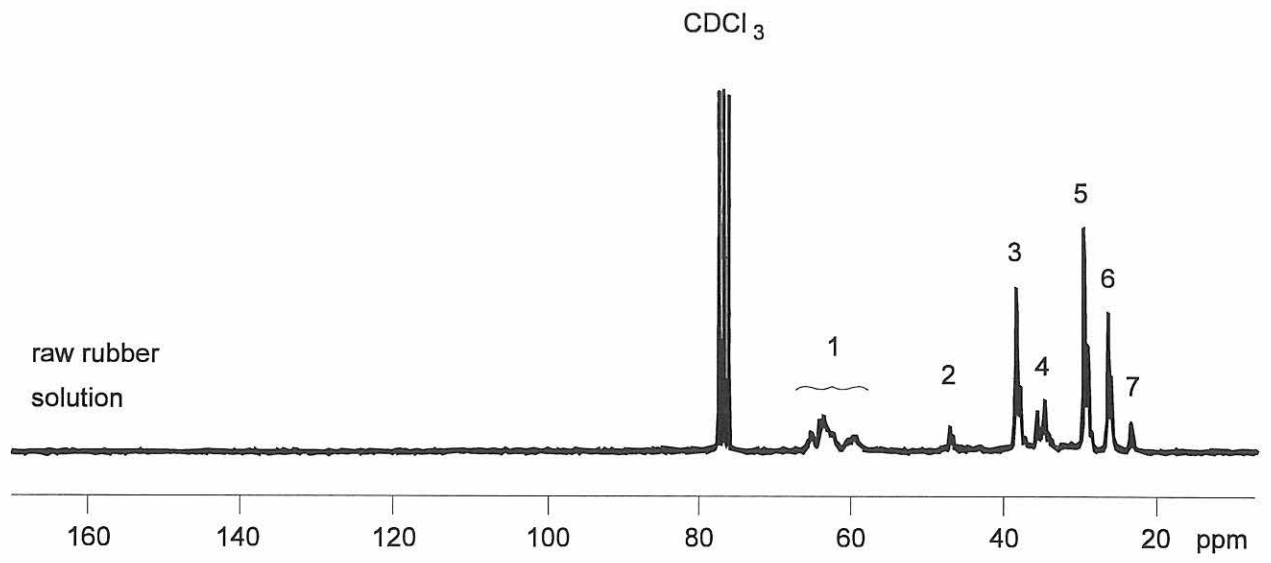
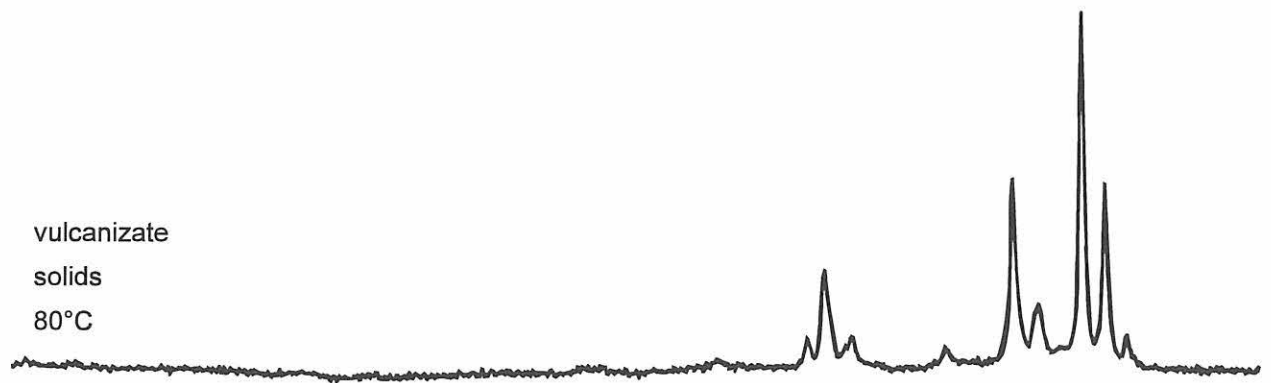
## Assignments<sup>1,2</sup>:

signal	1:	T (different surroundings)	5:	c <sup>+</sup> Sc <sup>+</sup>
	2:	aSa	6:	bSc <sup>+</sup>
	3:	aSc <sup>+</sup>	7:	bSb
	4:	aSb		

## References:

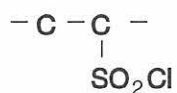
<sup>1</sup> F. Keller and C. Mügge, *Plaste Kautsch.* 24, 88 (1977); *ibid.* 24, 239 (1977)

<sup>2</sup> B. H. Chang, R. Zeigler and A. Hiltner, *Polym. Eng. Sci.* 28, 1167 (1988)



# CHLOROSULFONATED POLYETHYLENE (CSM)

Corresponding to CM the chlorine content of commercial CSM rubbers ranges from 20% to 40%. Different from chlorinated polyethylene CSM has additional chlorosulfonyl groups with a concentration of about 1% in order to facilitate vulcanization:



Vulcanizates of CSM are highly resistant to the influences of ozone, oxygen, weather, heat, oil and chemicals in connection with good mechanical properties.

As expected there is no indication of chlorosulfonyl groups in the spectrum. Therefore the spectrum of CSM can be interpreted like that of CM using the same nomenclature.

## Assignments<sup>1</sup>:

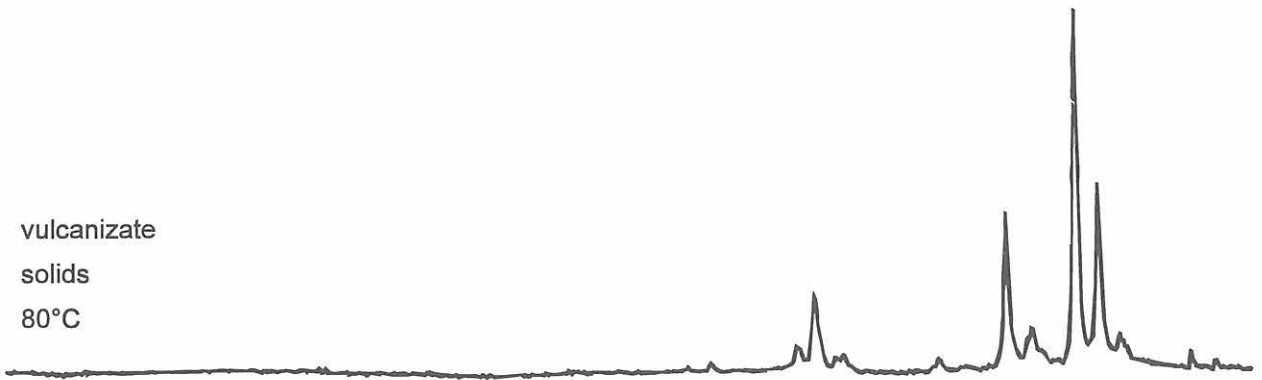
- signal 1: T (different surroundings)  
2: aSa  
3: aSc<sup>+</sup>  
4: aSb  
5: c<sup>+</sup>Sc<sup>+</sup>  
6: bSc<sup>+</sup>  
7: bSb

## References:

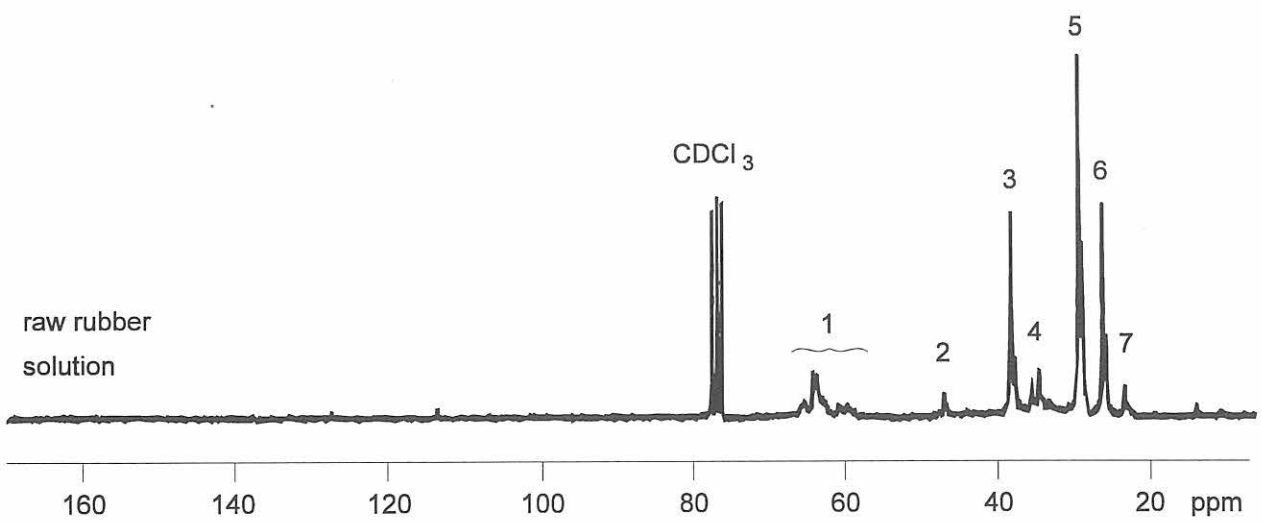
<sup>1</sup> see references of CM



vulcanizate  
solids  
80°C



raw rubber  
solution



# ETHYLENE-PROPYLENE COPOLYMER (EPM)

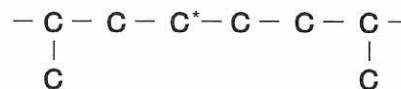
EPM is a copolymer of ethylene and propylene:



By incorporating propylene units in statistical distribution the crystallization of polyethylene segments is prevented. Both the ratio of ethylene and propylene monomers and the length of methylene sequences determine the physical and chemical properties. As the polymer is totally saturated it can only be vulcanized by peroxide curing sys-

tems. As a result, vulcanizates are extremely resistant to attack by ozone, oxygen and weather.

The spectrum is interpreted by use of a special nomenclature<sup>1</sup>. The carbons are designated by T (tertiary carbon: CH), S (secondary carbon: CH<sub>2</sub>) and P (primary carbon: CH<sub>3</sub>). The distance of the observed carbon C\* to the next tertiary carbon atom is given by small letters (d<sup>+</sup> stands for a distance of at least d; for CH<sub>3</sub>: distance of the adjacent CH to the next CH), e.g., bSc stands for



## Assignments<sup>2,3</sup>

signal	1:	aSa	9:	cSd <sup>+</sup>
	2:	caSc, caSd <sup>+</sup>	10:	d <sup>+</sup> Sd <sup>+</sup>
	3:	d <sup>+</sup> aSc	11:	bSc
	4:	d <sup>+</sup> aSd <sup>+</sup>	12:	bSd <sup>+</sup>
	5:	aSb	13:	bSb
	6:	cTc, cTd <sup>+</sup>	14:	bPb, bPc <sup>+</sup>
	7:	d <sup>+</sup> Td <sup>+</sup>	15:	c <sup>+</sup> Pc <sup>+</sup>
	8:	bTc, bTd <sup>+</sup> , cSc		

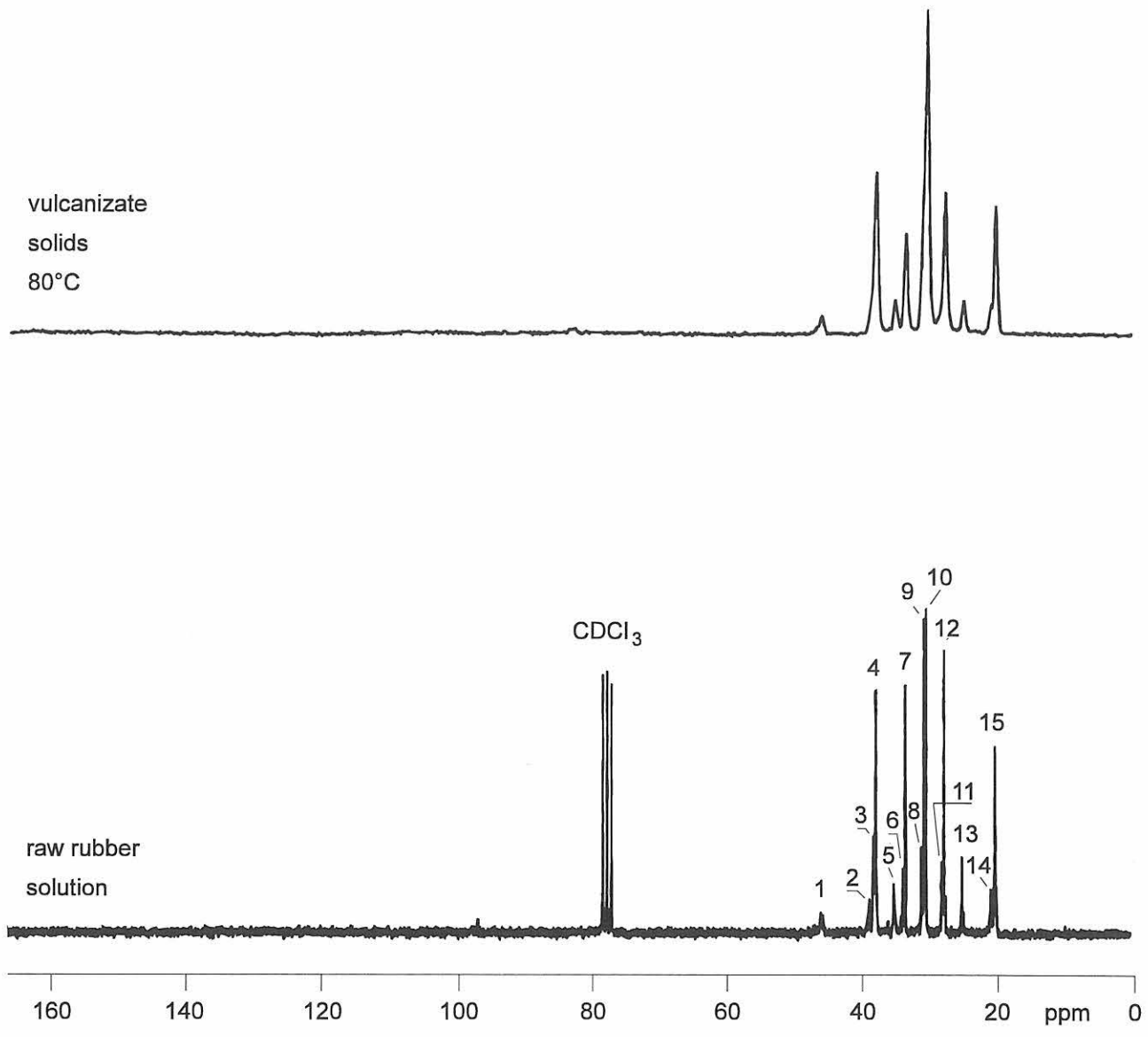
## References:

<sup>1</sup> C. J. Carman and K. C. Baranwal, Rubber Chem. Technol. 48, 705 (1975)

<sup>2</sup> L.G. Yechevskaya, G.D. Bukatov, V.A. Zakharov and A. V. Nosov, Makromol. Chem. 188, 2573 (1987)

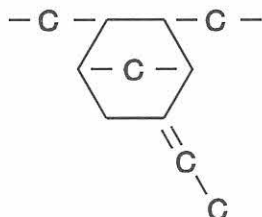
<sup>3</sup> V. B. F. Mathot, Ch. C. M. Fabrie, G. P. J. M. Tie-

mersmathoone and G. v. d. Velden, J. Polym. Sci., Polym. Phys. Ed. 28, 2509 (1990)



# ETHYLENE-PROPYLENE-DIENE-TERPOLYMER (EPDM)

1. D = ethylidene norbornene:



EPDM consists of ethylene and propylene, like EPM, and a small amount (2 - 9% of weight) of a third diene monomer which makes the polymer capable of sulfur vulcanization. Three dienes are used commercially: ethylidene norbornene, dicyclo-pentadiene and hexadiene.

These components are combined in such a manner as to produce a rubber with a completely saturated backbone and pendant unsaturation. From this point of view, vulcanizates of EPDM show the same behaviour as EPM elastomers.

The nomenclature for interpreting this spectrum is the same as for EPM. In addition to the major resonances small peaks can be identified that are uniquely assignable to ethylidene norbornene. This holds not only true for the solution spectrum, but also for the solid state spectrum of a carbon black filled vulcanizate (about 50 phr). The peak positions are the same. As the peaks 1, 2, 3 and 19 are free from overlapping they are best suited for the identification of ethylidene norbornene.

## Assignments<sup>1,2</sup>:

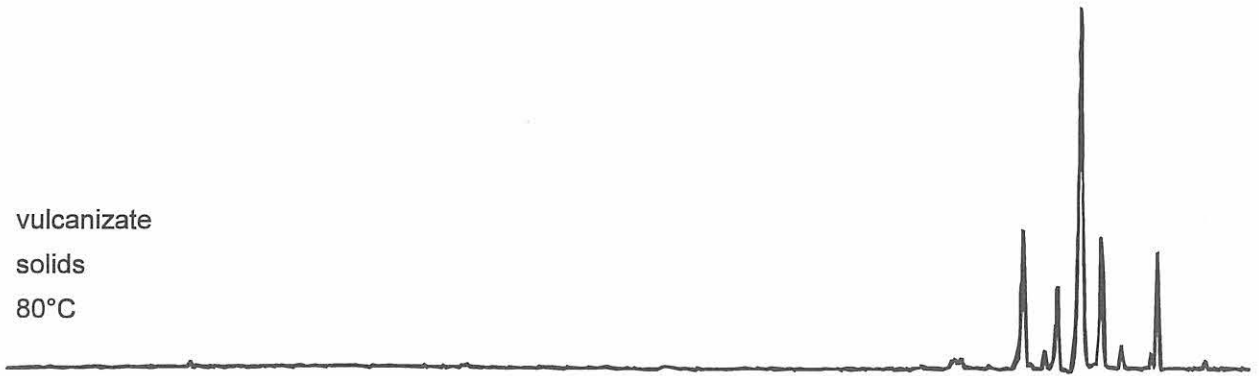
signal	1:	D	11:	bTc, bTd <sup>+</sup> , cSc
	2:	D	12:	cSd <sup>+</sup>
	3:	D	13:	d <sup>+</sup> Sd <sup>+</sup>
	4:	aSa	14:	bSc
	5:	caSc, caSd <sup>+</sup>	15:	bSd <sup>+</sup>
	6:	d <sup>+</sup> aSc	16:	bSb
	7:	d <sup>+</sup> aSd <sup>+</sup>	17:	bPb, bPc <sup>+</sup>
	8:	aSb	18:	c <sup>+</sup> Pc <sup>+</sup>
	9:	cTc, cTd <sup>+</sup>	19:	D
	10:	d <sup>+</sup> Td <sup>+</sup>		

## References:

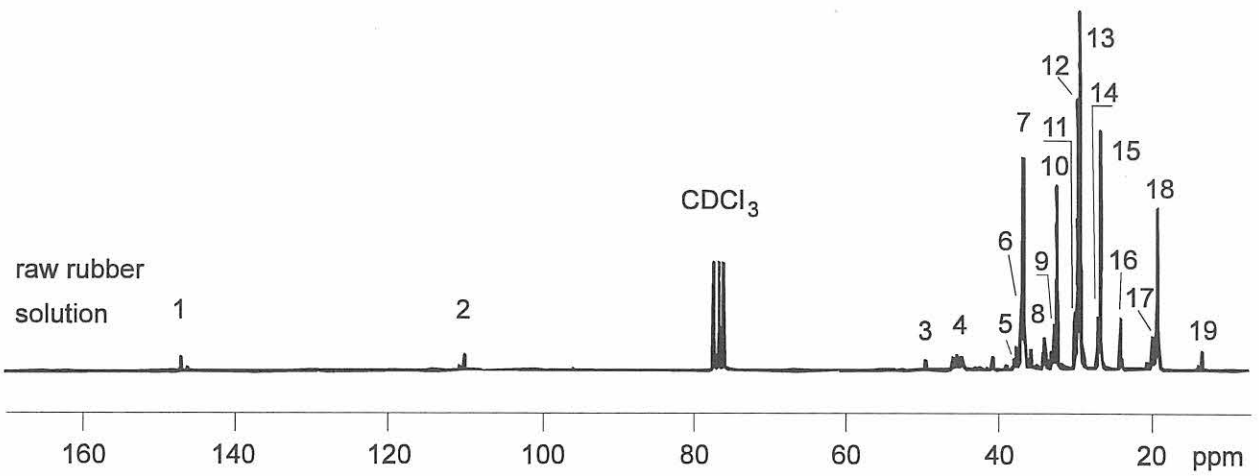
<sup>1</sup> see references of EPM

<sup>2</sup> G. v. d. Velden, *Macromolecules* 16, 85 (1983)

vulcanizate  
solids  
80°C

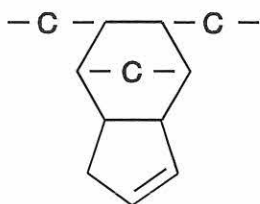


raw rubber  
solution



# ETHYLENE-PROPYLENE-DIENE TERPOLYMER (EPDM)

2. D = dicyclopentadiene:



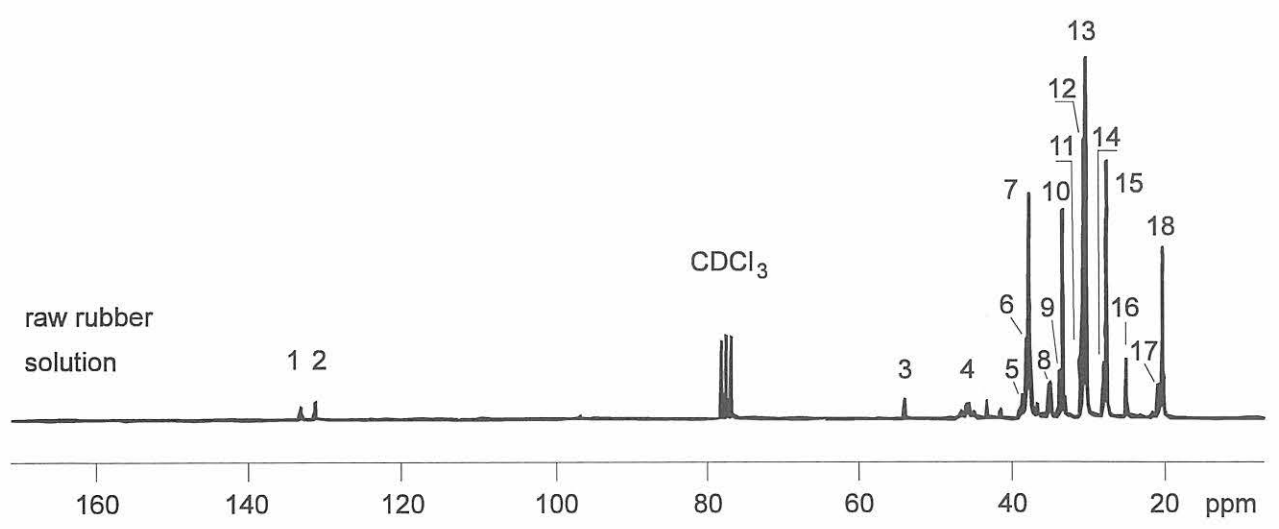
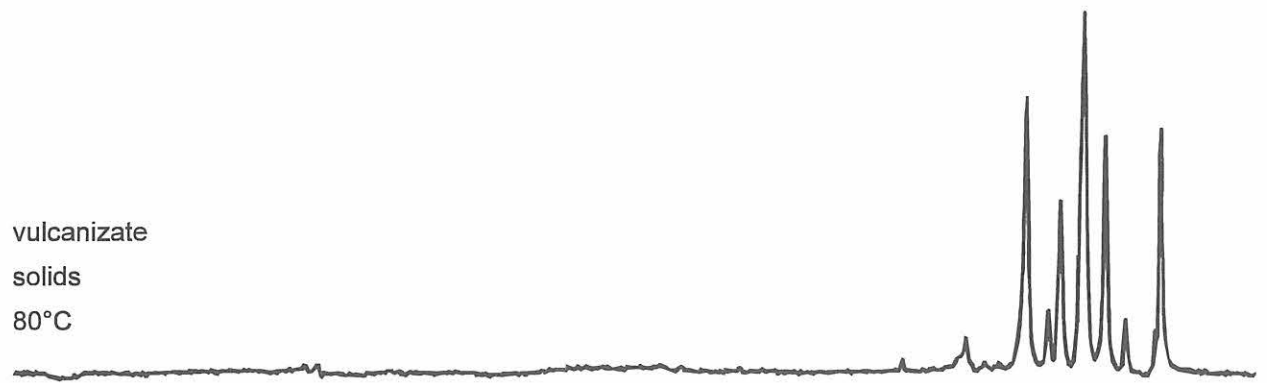
The nomenclature for interpreting the spectrum is the same as for EPM. The signals 1, 2 and 3 are due to dicyclopentadiene. They can be detected in solution and in solid state. As with ethylidene norbornene the peak positions are the same indicating that quite a lot of diene structures is not affected during vulcanization.

## Assignments<sup>1</sup>:

signal	1:	<b>D</b>	10:	<b>d<sup>+</sup>Td<sup>+</sup></b>
	2:	<b>D</b>	11:	<b>bTc, bTd<sup>+</sup>, cSc</b>
	3:	<b>D</b>	12:	<b>cSd<sup>+</sup></b>
	4:	<b>aSa</b>	13:	<b>d<sup>+</sup>Sd<sup>+</sup></b>
	5:	<b>caSc, caSd<sup>+</sup></b>	14:	<b>bSc</b>
	6:	<b>d<sup>+</sup>aSc</b>	15:	<b>bSd<sup>+</sup></b>
	7:	<b>d<sup>+</sup>aSd<sup>+</sup></b>	16:	<b>bSb</b>
	8:	<b>aSb</b>	17:	<b>bPb, bPc<sup>+</sup></b>
	9:	<b>cTc, cTd<sup>+</sup></b>	18:	<b>c<sup>+</sup>Pc<sup>+</sup></b>

References:

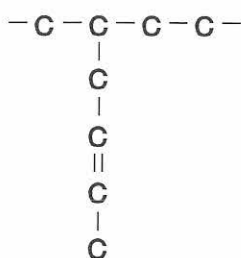
<sup>1</sup> see references of EPDM, D = ethylidene norbornene





# ETHYLENE-PROPYLENE-DIENE TERPOLYMER (EPDM)

3. D = hexadiene:



The nomenclature for interpreting the spectrum is the same as for EPM. The peaks 1, 2 and 18 are due to hexadiene. They are present in the solution and in the solid state spectrum as with the other dienes. Summarizing the results for EPM and EPDM it can be stated that solid state NMR can be used for distinguishing EPM and EPDM elastomers and for determining the diene present.

## Assignments<sup>1</sup>:

signal	1:	<b>D</b>	10:	<b>bTc, bTd<sup>+</sup>, cSc</b>
	2:	<b>D</b>	11:	<b>cSd<sup>+</sup></b>
	3:	<b>aSa</b>	12:	<b>d<sup>+</sup>Sd<sup>+</sup></b>
	4:	<b>caSc, caSd<sup>+</sup></b>	13:	<b>bSc</b>
	5:	<b>d<sup>+</sup>aSc</b>	14:	<b>bSd<sup>+</sup></b>
	6:	<b>d<sup>+</sup>aSd<sup>+</sup></b>	15:	<b>bSb</b>
	7:	<b>aSb</b>	16:	<b>bPb, bPc<sup>+</sup></b>
	8:	<b>cTc, cTd<sup>+</sup></b>	17:	<b>c<sup>+</sup>Pc<sup>+</sup></b>
	9:	<b>d<sup>+</sup>Td<sup>+</sup></b>	18:	<b>D</b>

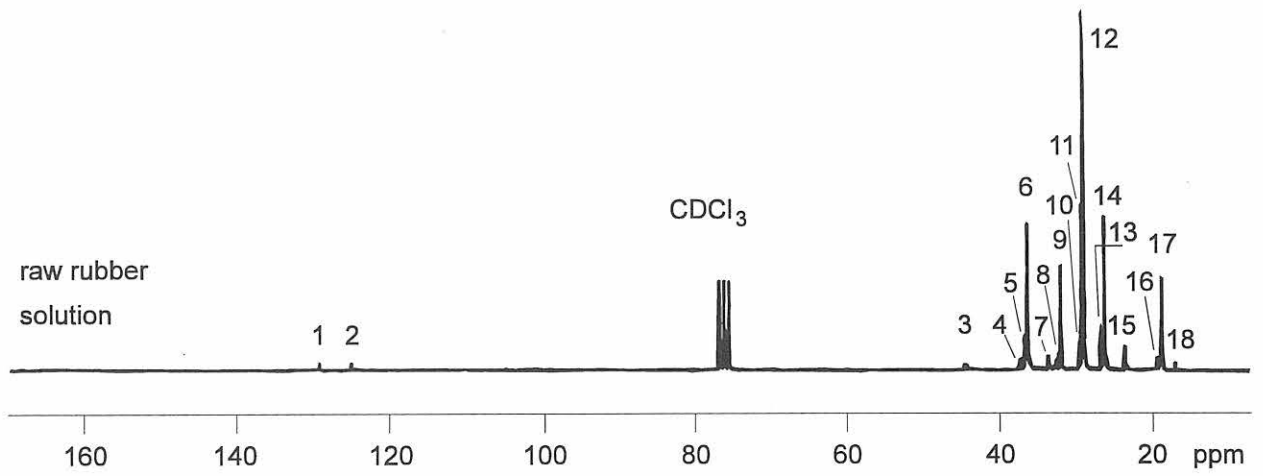
## References:

<sup>1</sup> see references of EPDM, D = ethylidene norbornene

vulcanizate  
solids  
80°C



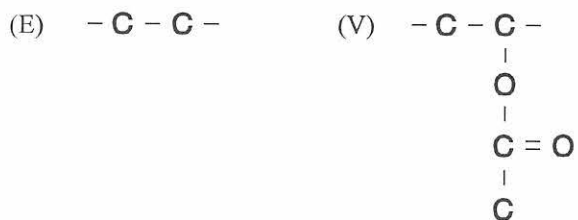
raw rubber  
solution



# ETHYLENE-VINYLAACETATE RUBBER (EVM)

Rubberlike copolymers of ethylene and vinylacetate are made with vinylacetate contents from about 40% to 70%. Beyond this range the copolymer behaves like a thermo-

plastic polymer. Different from ISO 1629: 1987 the abbreviation EVM ist used instead of EAM following a proposal of DIN ISO 1629 (draft from May 1990).



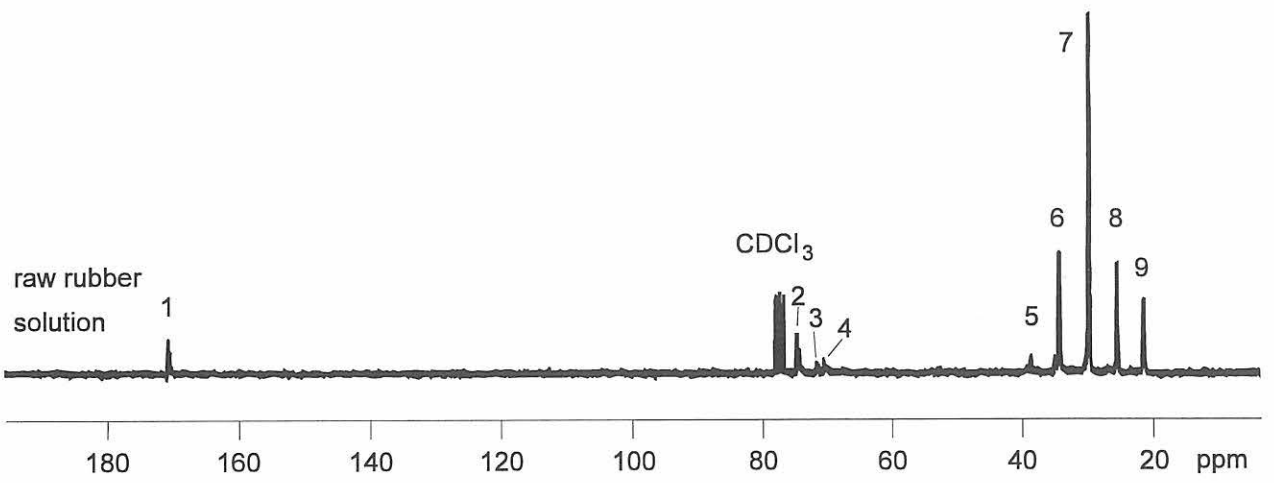
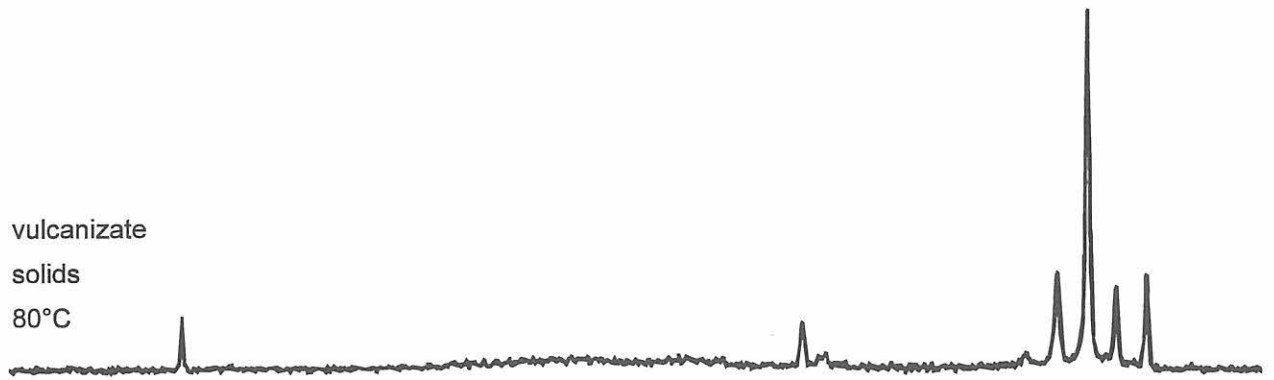
The monomer units are arranged in different sequences. The spectrum is explained on the basis of triads. The interpretation is analogous to that of ethylene-methylacrylate copolymer (ACM). The carbon atom under consideration is marked by an asterisk and the tertiary carbon is underlined. There is no indication of VVV sequences. The corresponding peak would appear at 68 ppm.

## Assignments<sup>1-3</sup>:

- |        |  |  |
|--------|--|--|
| signal | 1: C = O   | 6: CH <sub>2</sub> (VEE, VEV, EVE, EVV: <u>CCC</u> *CC, CCC* <u>CC</u> ) |
|        | 2: CH (EVE: <u>CCC</u> *CC)                          | 7: CH <sub>2</sub> (EEV, EEE : CCC*CC)                                   |
|        | 3, 4: CH (VVE, EVV: <u>CCC</u> *CC, CCC* <u>CC</u> ) | 8: CH <sub>2</sub> (VEE, EEV : <u>CCC</u> *CC, CCC* <u>CC</u> )          |
|        | 5: CH <sub>2</sub> (VVE : <u>CCC</u> * <u>CC</u> )   | 9: CH <sub>2</sub> (VEV: <u>CCC</u> * <u>CC</u> ), CH <sub>3</sub>       |

## References:

- <sup>1</sup> B. Ibrahim, A. R. Katritzky, A. Smith and D. E. Weiss, J. Chem. Soc., Perkin II 1974, 1537 (1974)
- <sup>2</sup> M.-F. Grenier-Loustalot, Eur. Polym. J. 21, 361 (1985)
- <sup>3</sup> H. N. Cheng and G. H. Lee, Polym. Bull. 19, 89 (1988)



# FLUORORUBBER (FPM)

## 1. Copolymer of vinylidene fluoride and hexafluoropropylene

Fluoroelastomers are used because of their outstanding heat and fluid resistance. Simultaneously they retain their good mechanical properties better than most other elastomers. Introduced to meet the needs in the aerospace industry for a high-performance sealing elastomer the use has spread quickly to other industries.

The standard fluororubber is a copolymer of vinylidene fluoride (VF<sub>2</sub>) and hexafluoropropylene (HFP):



The monomer ratio is about 75 : 25. The monomers are arranged rather regularly along the chain (head-to-tail), the HFP units are isolated.<sup>1</sup>

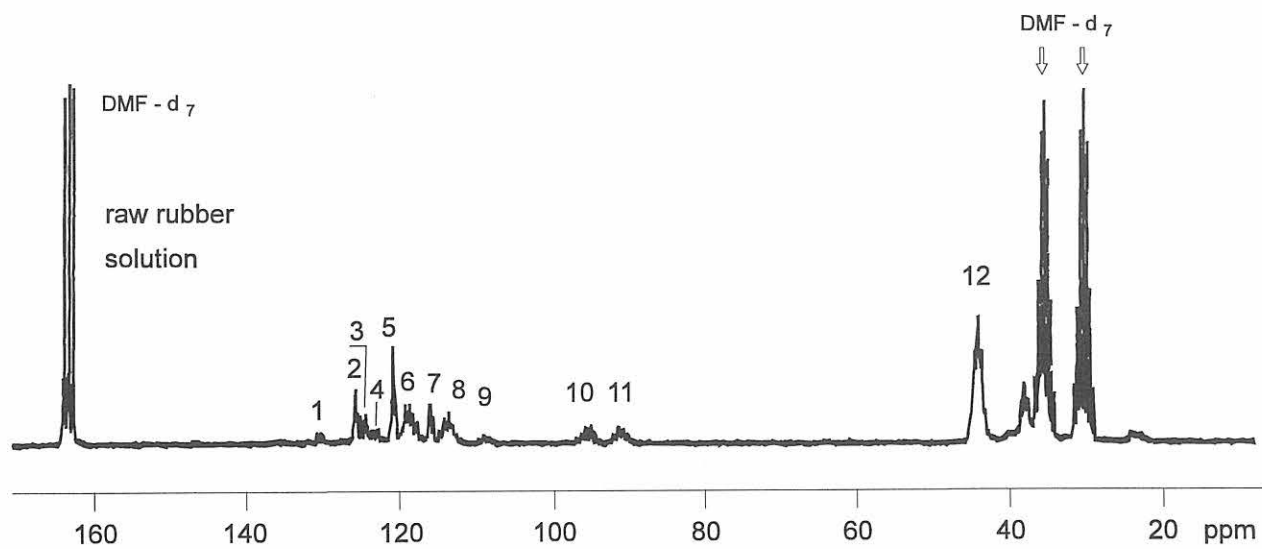
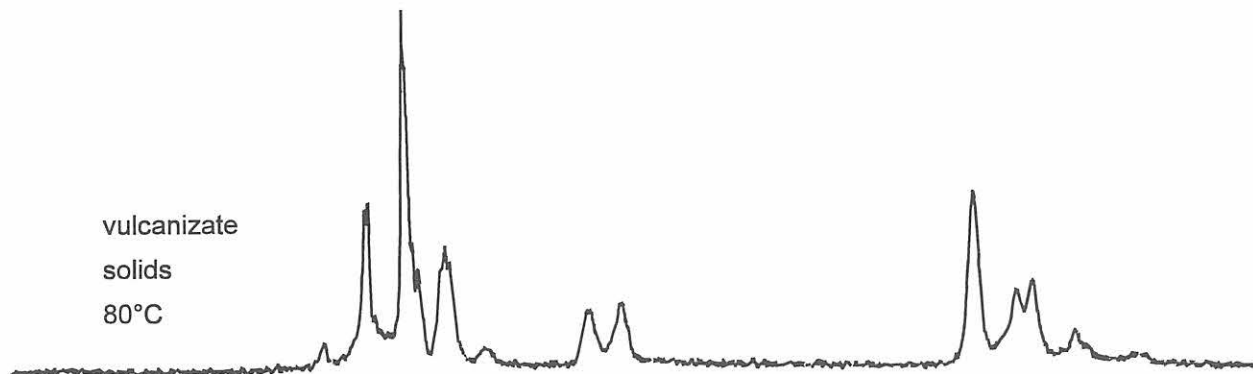
C-F couplings in the spectrum are dominating, C-H couplings play only a minor part. One has to distinguish between two sets of coupling constants, i.e., <sup>1</sup>J (C,F) and <sup>3</sup>J (C, F). The CF resonance, e.g., is split into two peaks by <sup>1</sup>J (C, F) coupling and each of them into a multiplet by the coupling with the adjacent CF<sub>2</sub> and CF<sub>3</sub> groups. This is the reason for overlapping and makes it difficult to analyse the spectrum in detail. For a better insight a fluorine decoupled spectrum was taken into consideration. Besides, the spectrum was compared with that of polyvinylidene fluoride. The assignments are tentative. For the CH<sub>2</sub> part no detailed interpretation is given. But the main peak at 44 ppm can be explained easily, as it is also found in the spectrum of polyvinylidene fluoride. It is due to longer sequences of VF<sub>2</sub>.

### Assignments:

signal 1, 3, 6, 8:	CF <sub>3</sub>
2, 5, 7:	CF <sub>2</sub> of longer VF <sub>2</sub> sequences
4, 6, 8:	CF <sub>2</sub> of VF <sub>2</sub> in different surroundings
6, 8, 9:	CF <sub>2</sub> of HFP
10, 11:	CF
12:	CH <sub>2</sub>

### References:

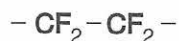
<sup>1</sup> W. W. Schmiegell, Kautschuk Gummi Kunststoff 31, 137 (1978)



# FLUORORUBBER (FPM)

## 2. Terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene

Additionally to vinylidene fluoride and hexafluoropropylene this FPM rubber has tetrafluoroethylene units in the polymer chain:



The result is a higher level of fluorine in the polymer backbone which improves the fluid resistance generally

but deteriorates the low-temperature flexibility<sup>1</sup>. Therefore a compromise has to be made according to the application. The addition of tetrafluoroethylene makes the spectrum even more complex. New chemical shifts and new sources of spin-spin coupling come into play. Some similarities to example 1 can be noticed, but a detailed interpretation is not given.

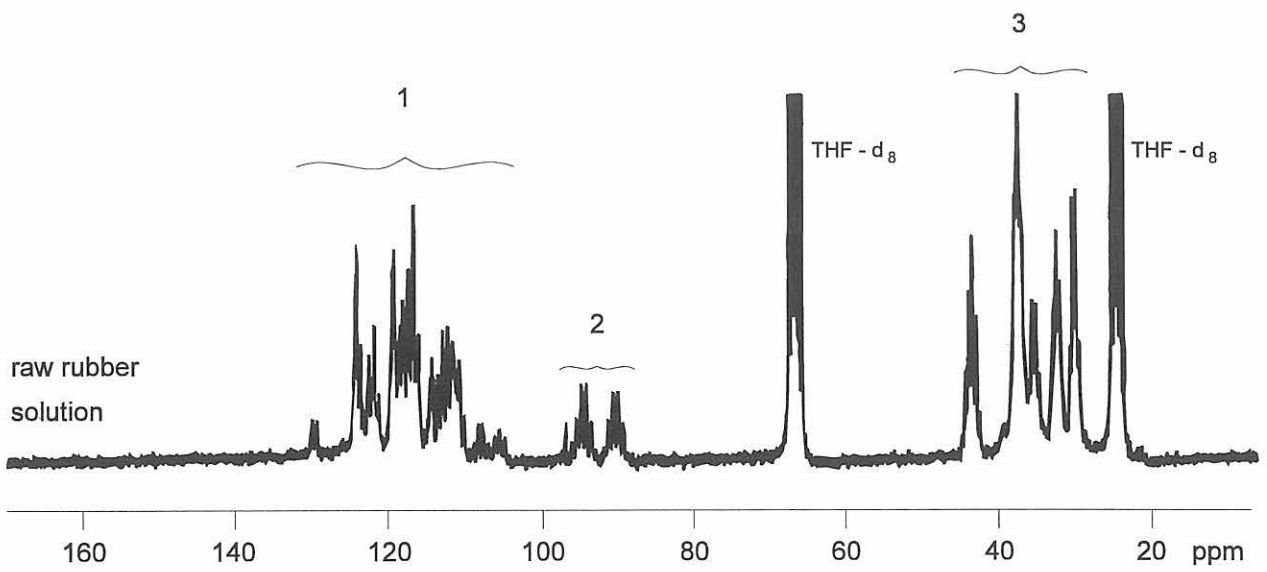
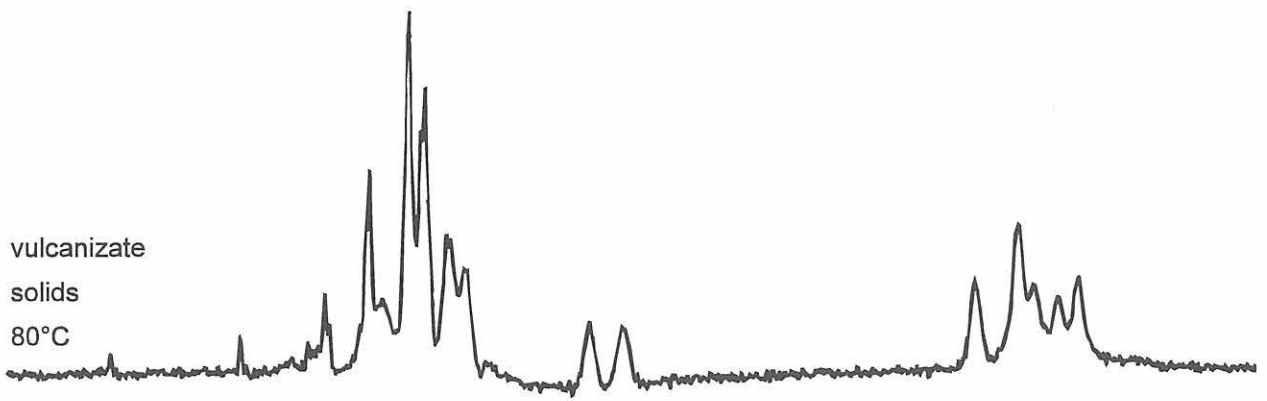
### Assignments:

signal 1:	<b>CF<sub>2</sub>, CF<sub>3</sub></b>
2:	<b>CF</b>
3:	<b>CH<sub>2</sub></b>

### References:

<sup>1</sup> G. Streit and S. Dunse, Kautsch., Gummi, Kunstst. 38, 471 (1985)





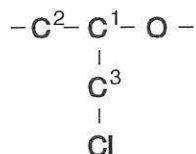
## EPICHLOROHYDRIN RUBBER (CO)

CO consists of polyepichlorohydrin. Polyether elastomers are speciality elastomers. They are mainly used for automotive applications because of their outstanding properties, e.g., resistance against swelling and heat as well as low permeability to gas and fuel. The glass transition temperature is relatively high resulting in low-temperature flexibility.

In the spectrum of CO three resonances are found, due to the backbone CH (1) and CH<sub>2</sub> (2) and side chain. The spectrum should give information about the microstruc-

ture of the chain. Actually, the resonance 2 shows up as a doublet corresponding to isotactic and syndiotactic diads with the isotactic peak at lower field. The small tacticity effect is explained by the influence of the ether bridge. More splittings, even for the methine carbon, can be resolved when going to a higher resonance frequency (90 MHz). Then the spectrum reveals information about triad and tetrad sequences<sup>1</sup>. The solid state spectrum shows rather broad lines. The peaks marked by asterisks are aniso-tropy bands.

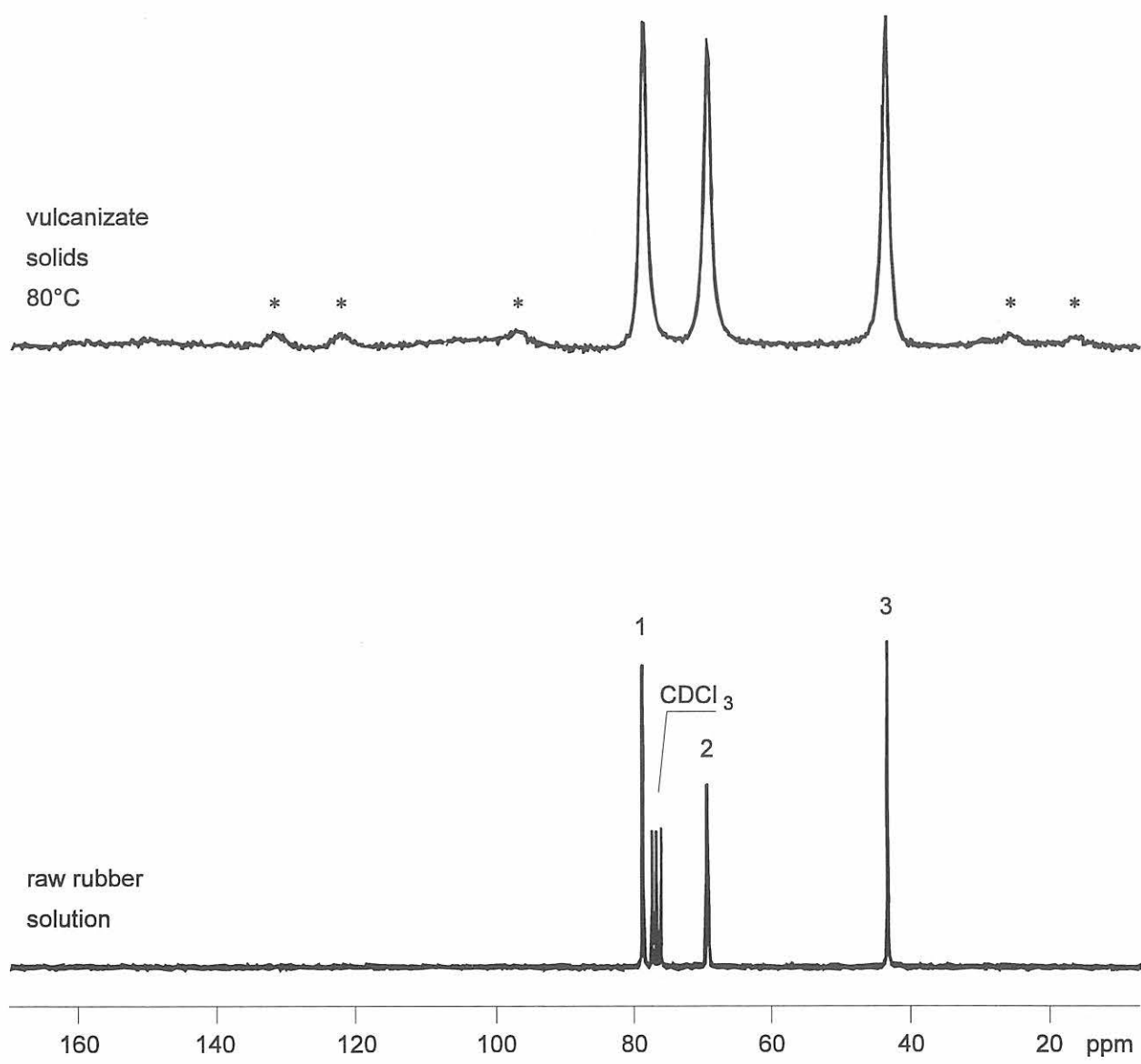
### Assignments<sup>1, 2</sup>:



### References:

<sup>1</sup> H. N. Cheng and D. A. Smith, J. Appl. Polym. Sci. 34, 909 (1987)

<sup>2</sup> H. N. Cheng in "Catalysis in Polymer Synthesis", ACS Symposium Series 496, 157 (1992)



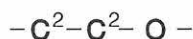
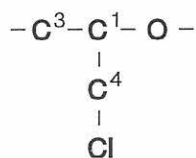
# ETHYLENE OXIDE - EPICHLOROHYDRIN COPOLYMER (ECO)

ECO is a copolymer of epichlorohydrin (P) and ethylene oxide (E). By introducing ethylene oxide the glass transition temperature is lowered. By using ECO a compromise can be achieved between high polarity and low-temperature flexibility.

In the spectrum of ECO four resonance regions can be observed, due to epichlorohydrin (1, 3, 4) and ethylene

oxide (2). The splittings are explained by the presence of different sequences of the units P and E: PPP, PPE, PEP, EPP, PEE, EPE, EEP and EEE. Additionally, tacticity effects have to be considered. Regions 1 and 3 (backbone of P) have sequence effects and tacticity mixed together; region 4 is only sensitive to sequence effects. The spectrum corresponds to a copolymer with E units dominating.

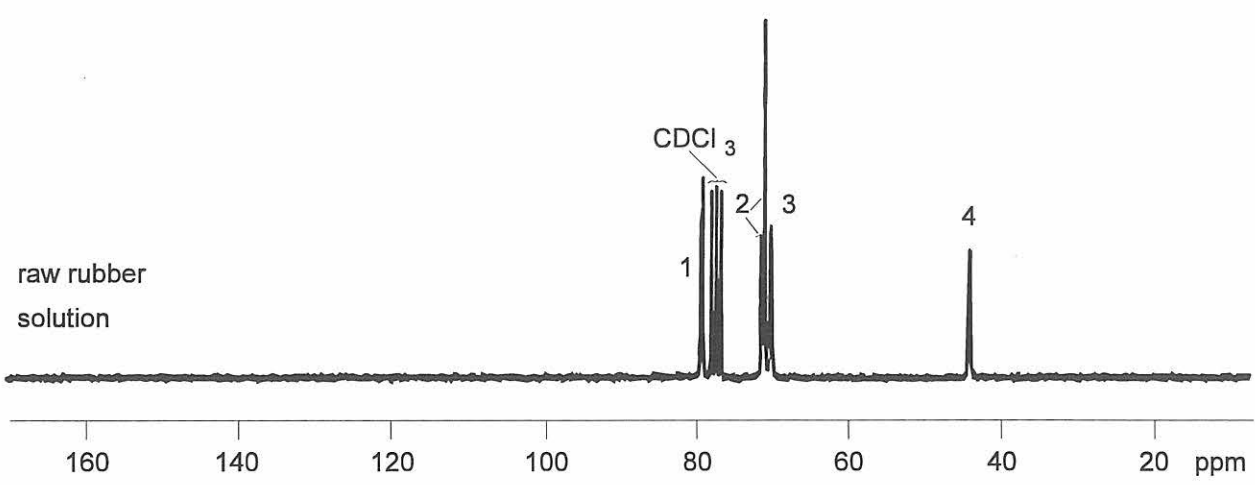
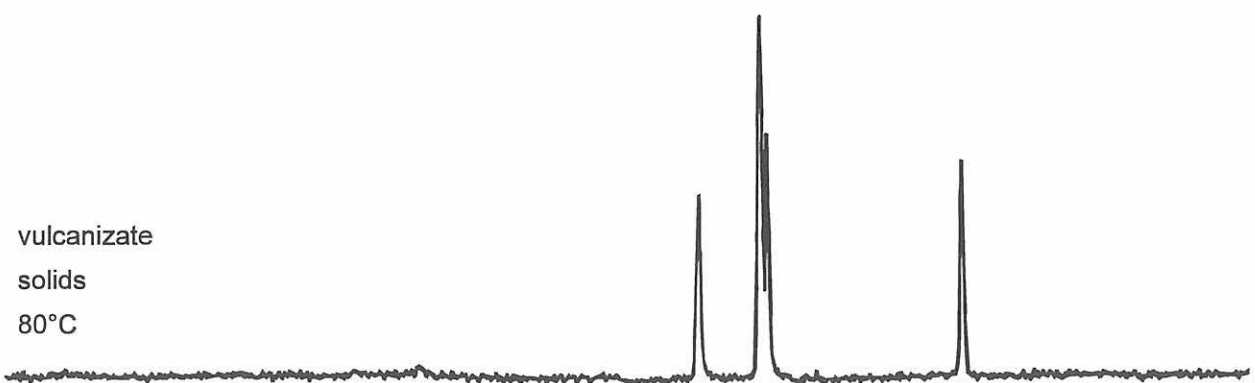
## Assignments<sup>1,2</sup>:



## References:

<sup>1</sup> H. N. Cheng and D. A. Smith, Makromol. Chem. 192, 267 (1991)

<sup>2</sup> see reference No. 2 of CO



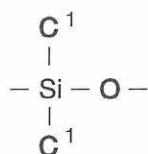
# SILICON RUBBER (Q)

## 1. MQ

Silicon rubbers are used in extreme temperature applications. They withstand sustained service from temperatures as low as  $-85^{\circ}\text{C}$  up to  $+260^{\circ}\text{C}$ . Principally there are three different types: silicon rubber with methyl groups on the polymer chain (MQ), with phenyl and methyl groups (PMQ) and with fluoro and methyl groups (FMQ). Additionally a vinyl group (V) may be present in low concentration. MQ consists of dimethyl polysiloxane.

It is the standard silicon rubber. A substitution of an end methyl group by a vinyl group makes it amenable to blending with other rubbers (VMQ)<sup>1</sup>. As the concentration is too low MQ and VMQ cannot be distinguished from each other by NMR means. Corresponding to the regular linkage of the structure unit the spectrum shows only one resonance. The small satellite peaks are due to scalar coupling between carbon and silicon.

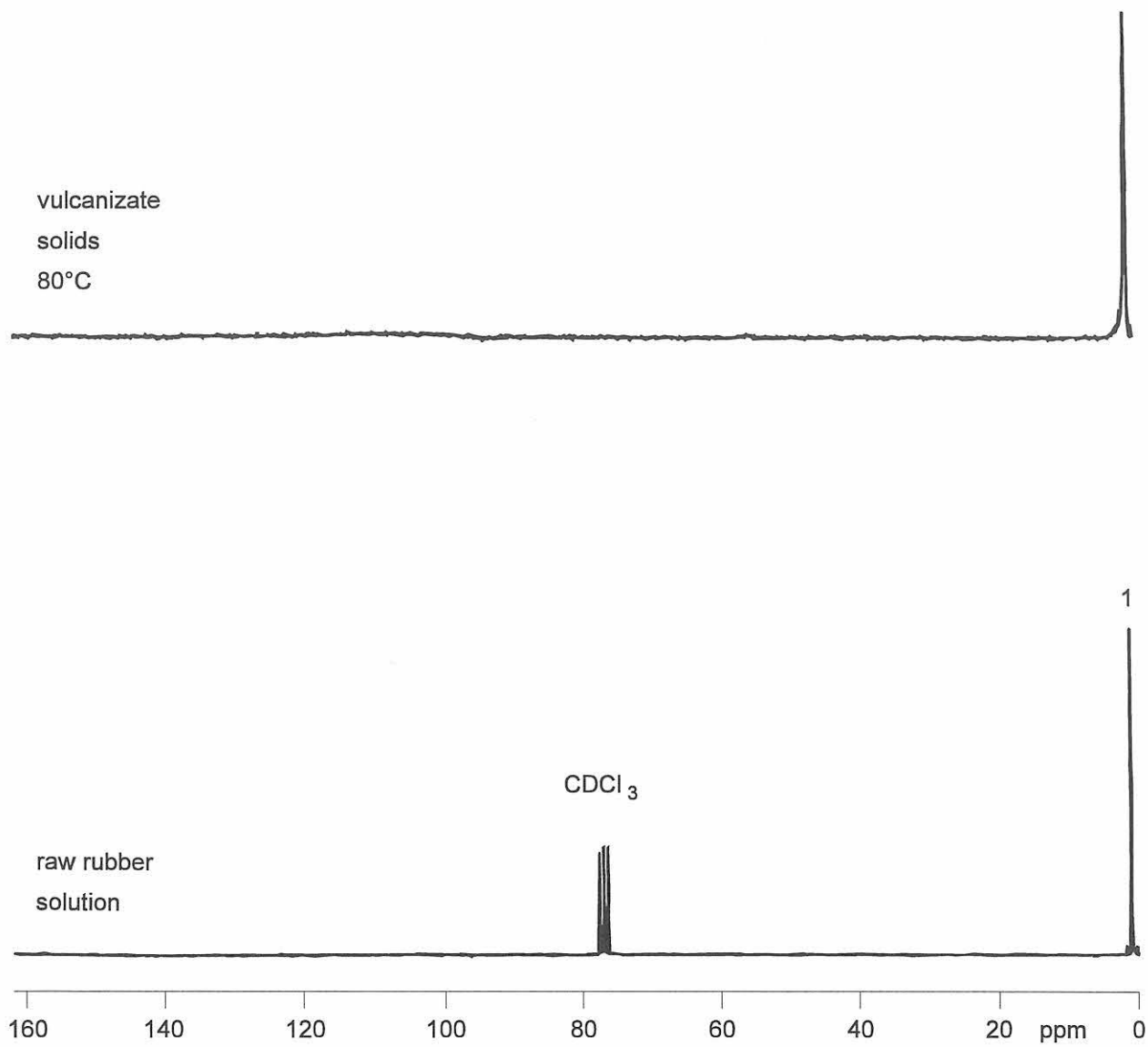
### Assignments<sup>2</sup>:



### References:

<sup>1</sup> D. R. Salverson, Gummi, Asbest, Kunstst. 42, 640 (1989)

<sup>2</sup> R. B. Taylor, B. Parbhoo and D. M. Fillmore in "The Analytical Chemistry of Silicones", edited by A. L. Smith, John Wiley & Sons, New York, 1991



# SILICON RUBBER (Q)

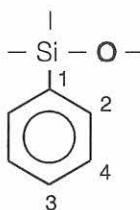
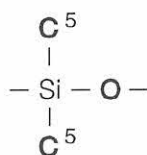
## 2. PVMQ

PVMQ consists of dimethyl siloxane, units with phenyl groups and a third component of vinyl structure. Introducing the phenyl groups improves especially the low-temperature applications<sup>1</sup>.

As with VMQ the vinyl carbons are not observable. The spectrum displays the methyl resonance at 1 ppm, accompanied by spin-spin satellites, according to MQ.

Because of equivalence there are four aromatic peaks: C<sub>1</sub>, C<sub>ortho</sub>, C<sub>meta</sub> and C<sub>para</sub>. They can be assigned by use of increments and intensity considerations. The question arises whether there are methyl phenyl or diphenyl siloxane groups. The answer is given by Si-NMR unambiguously: diphenyl siloxane<sup>2</sup>.

### Assignments<sup>1</sup>:

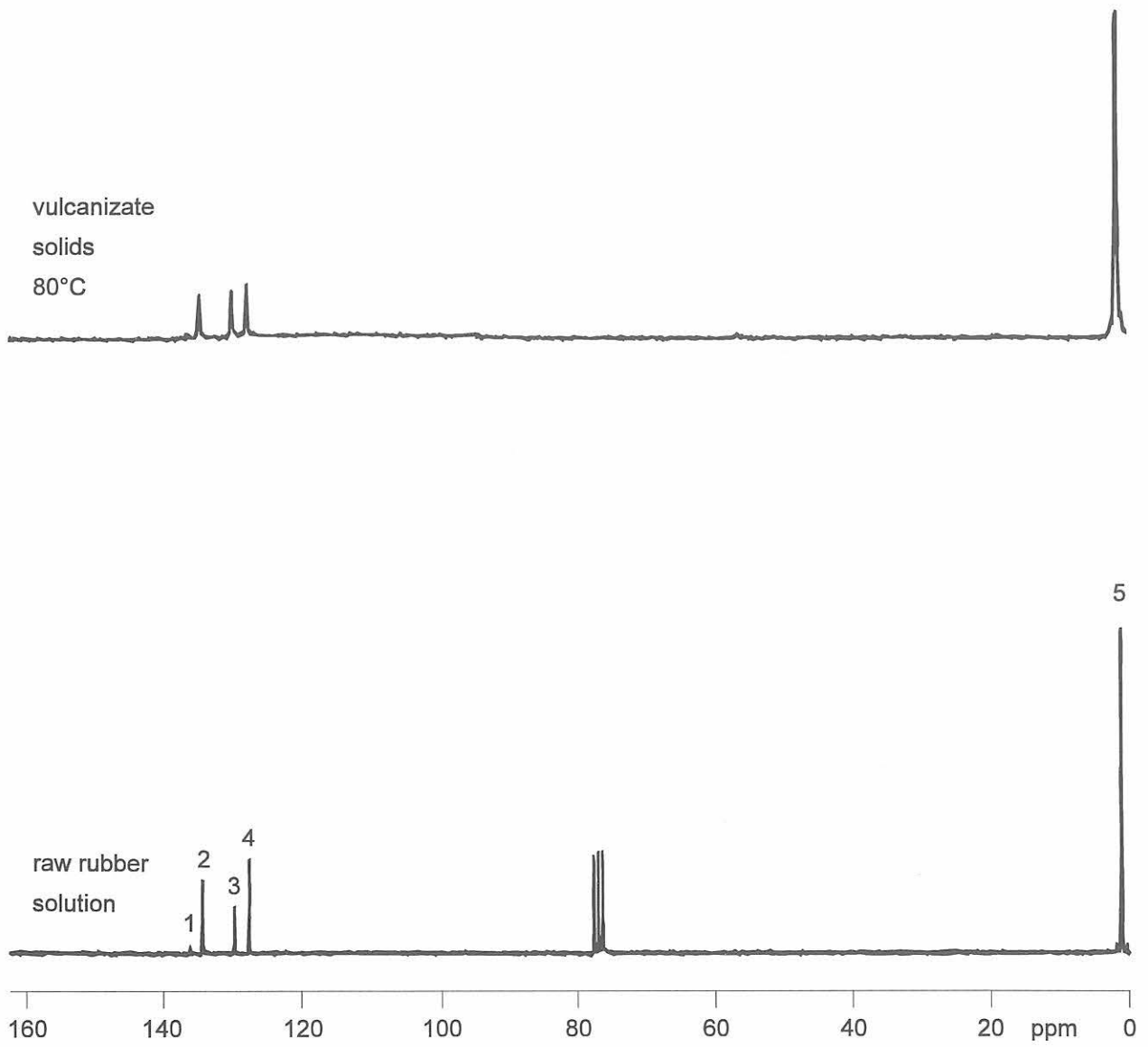


### References:

<sup>1</sup> see references of MQ

<sup>2</sup> courtesy of Dr. H. Jancke, BAM, Berlin





# SILICON RUBBER (Q)

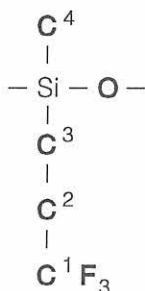
## 3. FVMQ

The main structure unit is methyl trifluoropropyl siloxane. Again the vinyl has not to be considered for spectral assignments. This polymer is used for applications with solvents and fuel. By increasing the polarity swelling is reduced<sup>1,2</sup>.

FVMQ is unsolvable in common solvents. Only the solid state spectrum is shown. The spin-spin coupling of fluo-

rine is easily detected at 127 ppm and 28 ppm. Only a small peak is observed at 1 ppm, the position of methyl resonances of MQ, supposedly due to end groups. The other assignments are straightforward.

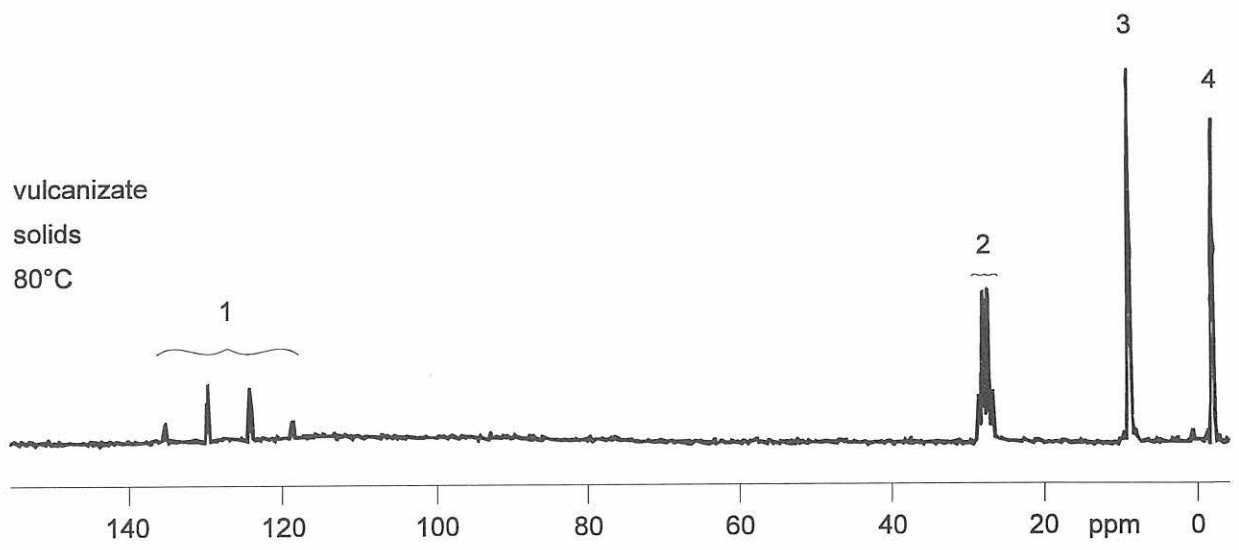
### Assignments<sup>1</sup>:



### References:

<sup>1</sup> see references of MQ

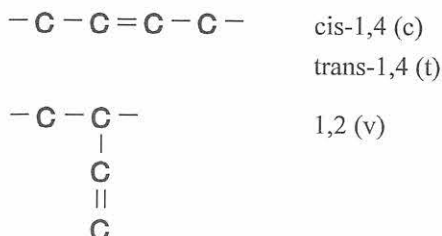
<sup>2</sup> G. Streit, S. Dunse, Kautschuk Gummi Kunststoff 38, 471 (1985)



# BUTADIENE RUBBER (BR)

## 1. BR with high cis content (>90%), standard type

Butadiene rubber consists of polybutadiene. Three isomers have to be considered:



For convenience c, t and v stand also for the corresponding concentrations. The microstructure depends on the catalyst used for polymerisation.

The standard type is a BR with high cis content (>90%). The higher this content the lower is the glass transition temperature. By increasing v and t the glass transition temperature goes up. The structure units are arranged in different sequences. According to the range of chemical shift influence diads or triads are considered. The unit under consideration is underlined; the observed carbon is marked by an asterisk if necessary. In the case of diads the assignment refers to the first or last atom of the structure unit, i.e., the linkage atom.

The solid state spectrum resembles very much the solution counterpart. An interesting feature is the obvious difference of trans content. This is explained by cis/trans isomerization during vulcanization.

### Assignments<sup>1-3</sup>

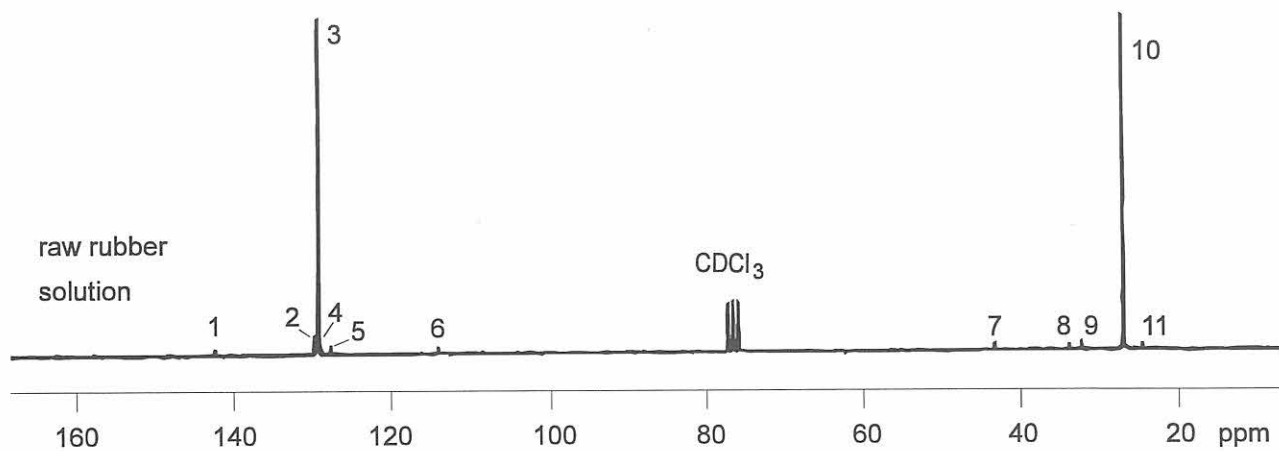
signal	1: =CH (v)	7: CH (v)
	2: CH=C*H (ccv, ctc, vcc)	8: CH <sub>2</sub> (v)
	3: C*H=CH (ccc, tcc)	9: CH <sub>2</sub> (tc, tt, ct, tt, vc)
	4: C*H=CH (cct, cv)	10: CH <sub>2</sub> (cc, ct, cc, tc)
	5: C*H=CH (vcc)	11: CH <sub>2</sub> (cv)
	6: =CH <sub>2</sub> (v)	

### References:

<sup>1</sup> P. T. Suman and D. D. Werstler, J. Polym. Sci., Polym. Chem. Ed. 13, 1963 (1975)

<sup>2</sup> K.-F. Elgert, G. Quack and B. Stützel, Polymer 16, 154 (1975)

<sup>3</sup> G. v. d. Velden, C. Didden, T. Veermans and J. Beulen, Macromolecules 20, 1252 (1987)



# BUTADIENE RUBBER (BR)

## 2. Polybutadiene with approximately $c=35\%$ , $t=55\%$ , $v=10\%$

As mentioned in example 1 the microstructure depends on the catalyst. Cobalt, titanium and neodymium catalysts, e.g., lead to polybutadienes with  $c > 90\%$ . By choosing lithium catalysts polybutadienes with different

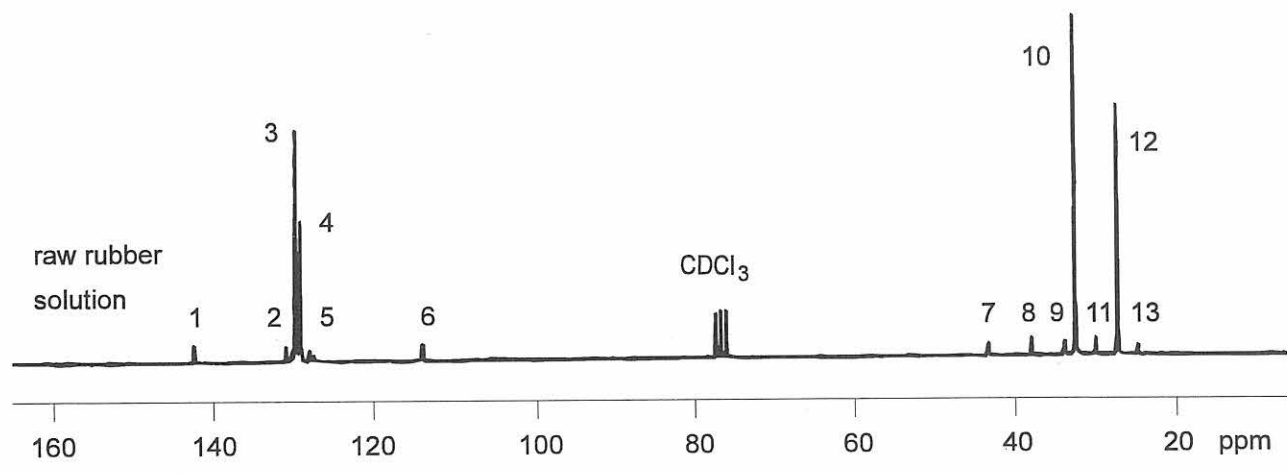
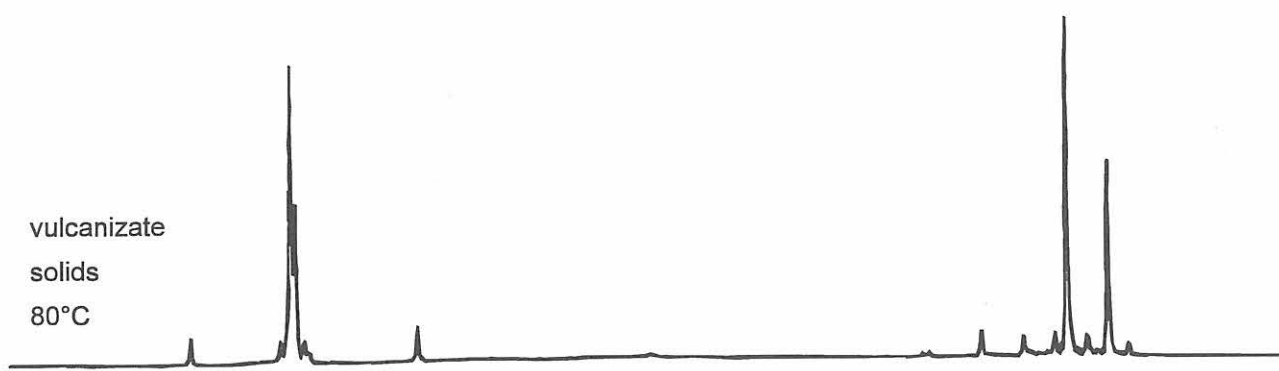
cis content can be produced like the example shown here. Such polybutadienes are used, e. g., as impact modifiers in thermoplastic polymers.

### Assignments<sup>1</sup> (see example 1 for general remarks):

signal	1: =CH (v)	7: CH (v)
	2: CH=C*H (ctv, ttv)	8: CH <sub>2</sub> (vt)
	3: CH=C*H (vtt, vtc, ccv, tev, ctc, ctt, vcc, vct, ttc, ttt)	9: CH <sub>2</sub> (v)
	4: C*H=CH (ctv, ttv, ccc, tcc, cct, tct, ccv, tev)	10: CH <sub>2</sub> (tc, tt, ct, tt, vc)
	5: C*H=CH (vtc, vtt, vcc, vct)	11: CH <sub>2</sub> (tv)
	6: =CH <sub>2</sub> (v)	12: CH <sub>2</sub> (cc, ct, cc, tc)
		13: CH <sub>2</sub> (cv)

### References:

<sup>1</sup> see references of BR, example 1: standard type



# BUTADIENE RUBBER (BR)

## 3. Polybutadiene with high vinyl content

In parts the spectrum is rather complex. Therefore no detailed interpretation is given<sup>1</sup>. The nomenclature for the assignments is the same as for example 1. Additionally r and m are introduced for syndiotactic and isotactic diads.

From the peak at 25 ppm and missing peak at 30 ppm (cv respectively iv) the conclusion can be drawn that the polymer has cis, but no trans structures.

### Assignments<sup>2-4</sup> (for general remarks see example 1):

signal	1: =CH (v)	8: CH <sub>2</sub> (c <u>vc</u> )
	2: CH <sub>2</sub> (c <u>v</u> , v <u>c</u> )	9: CH <sub>2</sub> (v <u>vc</u> -r)
	3: =CH <sub>2</sub> (v)	10: CH <sub>2</sub> (c <u>vc</u> )
	4: CH (c <u>vc</u> )	11: CH <sub>2</sub> (v <u>vc</u> -m)
	5: CH (c <u>vv</u> ), CH <sub>2</sub> (v <u>vc</u> , v <u>v</u> )	12: CH <sub>2</sub> (c <u>c</u> , c <u>c</u> )
	6: CH (v <u>vv</u> )	13: CH <sub>2</sub> (c <u>v</u> )
	7: CH <sub>2</sub> (c <u>vv</u> -r)	

### References:

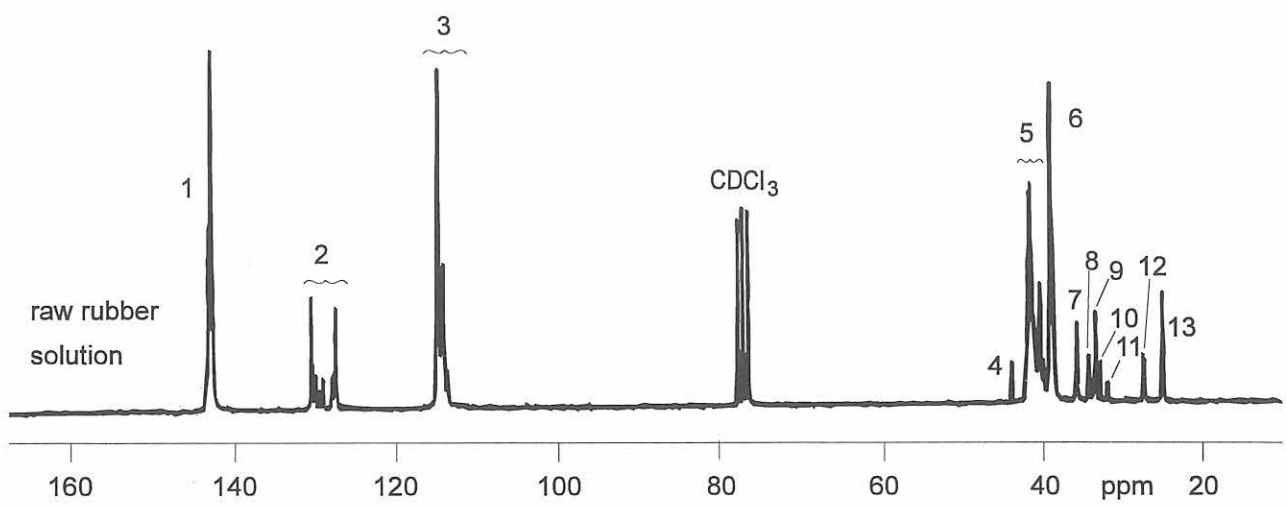
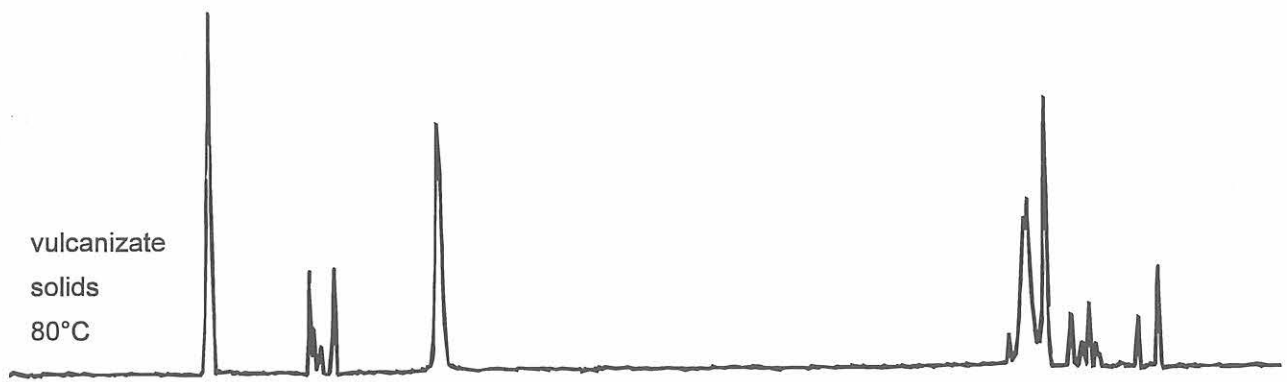
<sup>1</sup> For a detailed assignment of the backbone peaks 5 and 6 see Y. Gao, Z. Zhou and Z. Feng, Science in China, Series B 33, 777 (1990)

<sup>2</sup> Y. Alaki, T. Yoshimoto, M. Imanari and M. Takeuchi, Rubber Chem. Technol. 46, 350 (1973)

<sup>3</sup> Bywater, Polym. Comm. 24, 203 (1983)

<sup>4</sup> H. Sato, K. Takebayashi and Y. Tanaka, Macromolecules 20, 2418 (1987)



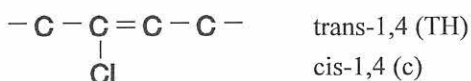


# CHLOROPRENE RUBBER (CR)

Some outstanding properties of CR are good resistance to weathering, ozone and chemicals and very good resistance to aging.

CR consists of polychloroprene. The polymer is predominantly trans-1,4-polychloroprene in regular head-to-tail placement. But there are major irregularities: inverted trans-1,4 units and cis-1,4 units. Other minor irregularities include 1,2, isomerized 1,2 and 3,4 units.

For the interpretation of the spectrum following structure units are distinguished (C-CCl is tail (T), C-C is head (H)<sup>1</sup>):



Different triads can be defined:

- A: TH - TH - TH, HT - HT - HT
- B: HT - TH - TH, HT - HT - TH
- C: TH - TH - HT, TH - HT - HT
- D: HT - TH - HT, TH - HT - TH
- E: HT - c - TH
- F: TH - TH - c

The assignments refer to the middle unit, the observed carbon is marked by an asterisk if necessary.

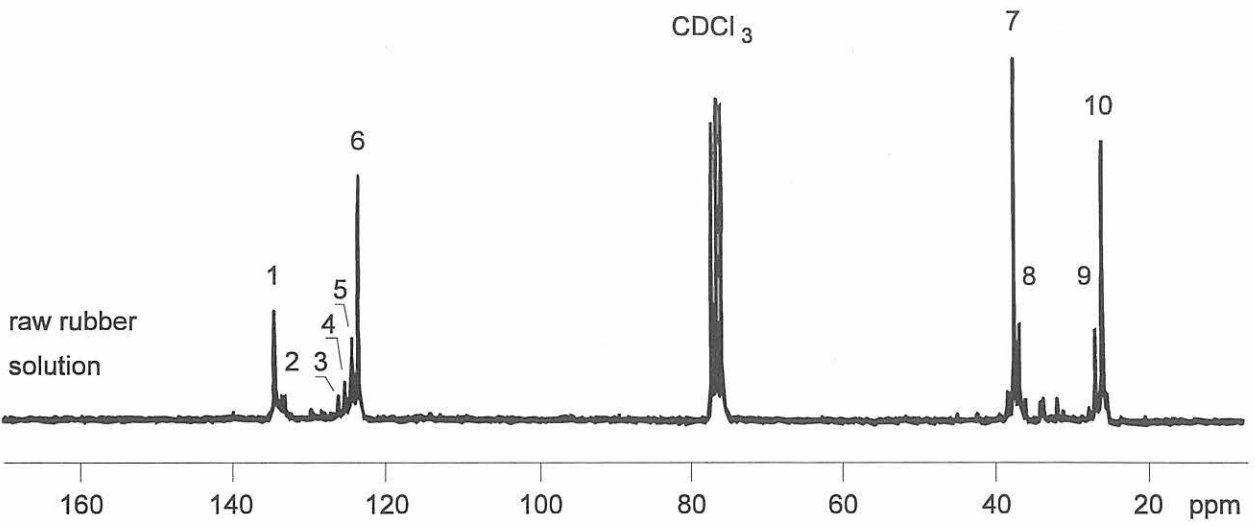
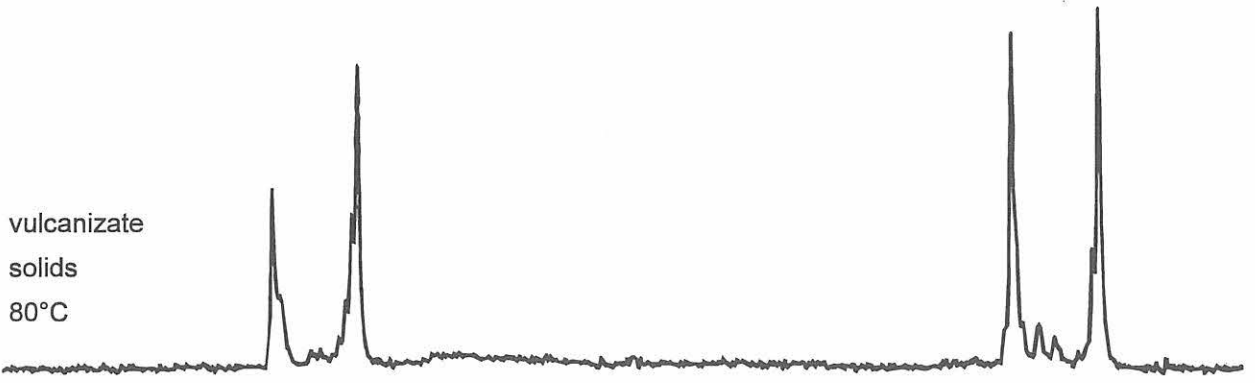
## Assignments<sup>1,2</sup>:

- |        |                              |  |
|--------|------------------------------|--|
| signal | 1: CCl (A)                   | 6: CH (A)                                    |
|        | 2: CCl (different sequences) | 7: C <sup>*</sup> H <sub>2</sub> - CCl (A,C) |
|        | 3: CH (E)                    | 8: C <sup>*</sup> H <sub>2</sub> - CCl (B,D) |
|        | 4: CH (D)                    | 9: C <sup>*</sup> H <sub>2</sub> - CH (C,D)  |
|        | 5: CH (B,C,F)                | 10: C <sup>*</sup> H <sub>2</sub> - CH (A,B) |

## References:

<sup>1</sup> M. M. Coleman, D. L. Tabb and E. G. Brame, Rubber Chem. Technol. 50, 49 (1977)

<sup>2</sup> R. Petiaud and Q. T. Pham, J. Polym. Sci., Polym. Chem. Ed. 23, 1343 (1985).



## BUTYL RUBBER (IIR)

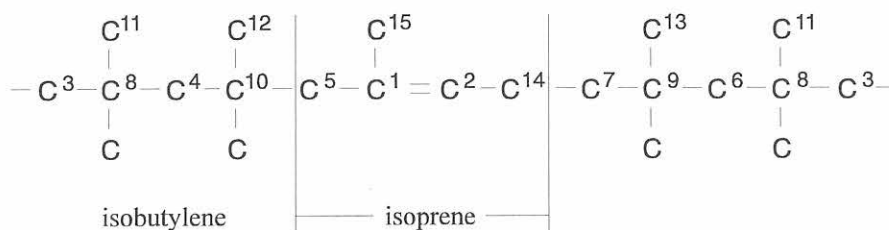
Butyl rubber is a copolymer of isobutylene and isoprene containing less than 3 mol-% incorporated isoprene groups. It provides excellent air retention, energy absorption and resistance to attack by chemicals, steam, ozone and weathering. Because of the double bonds IIR is capable of sulfur vulcanization. The incorporation of isoprene into the isobutylene chain alters the chemical shifts in the neighbourhood. So the minor peaks are due to isoprene itself and to its direct neighbours. The main peaks (3, 8, 11) are assigned to "undisturbed" isobutylenes. Taking the variation of the chemical shifts

into account following conclusions about the microstructure were drawn<sup>1</sup>:

- The isobutylene units are arranged head-to-tail.
- The isoprene units are incorporated head-to-tail in 1,4-mode.
- The isoprene units have predominantly E geometry.

The solid state experiment is able to reveal the minor structures, too; corresponding peaks, however, are very small and are partly obscured by adjacent major structure peaks. The peaks marked by asterisks are anisotropy bands.

### Assignments<sup>1,2</sup>:

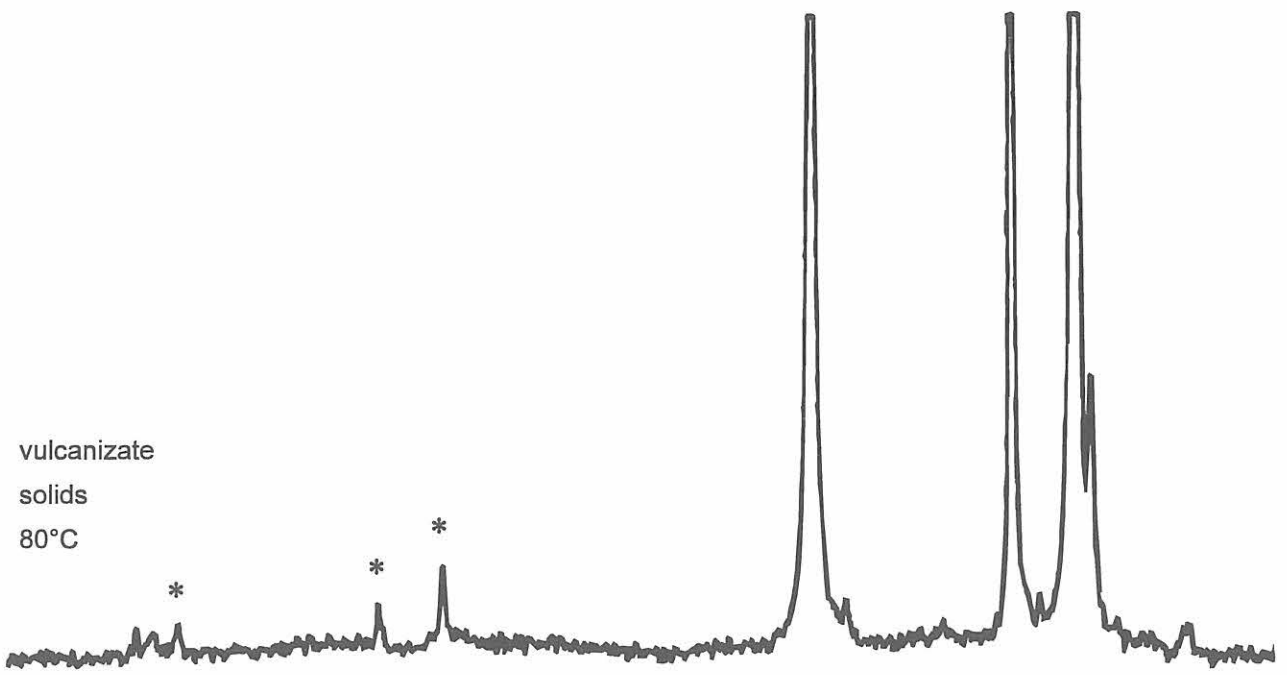


### References:

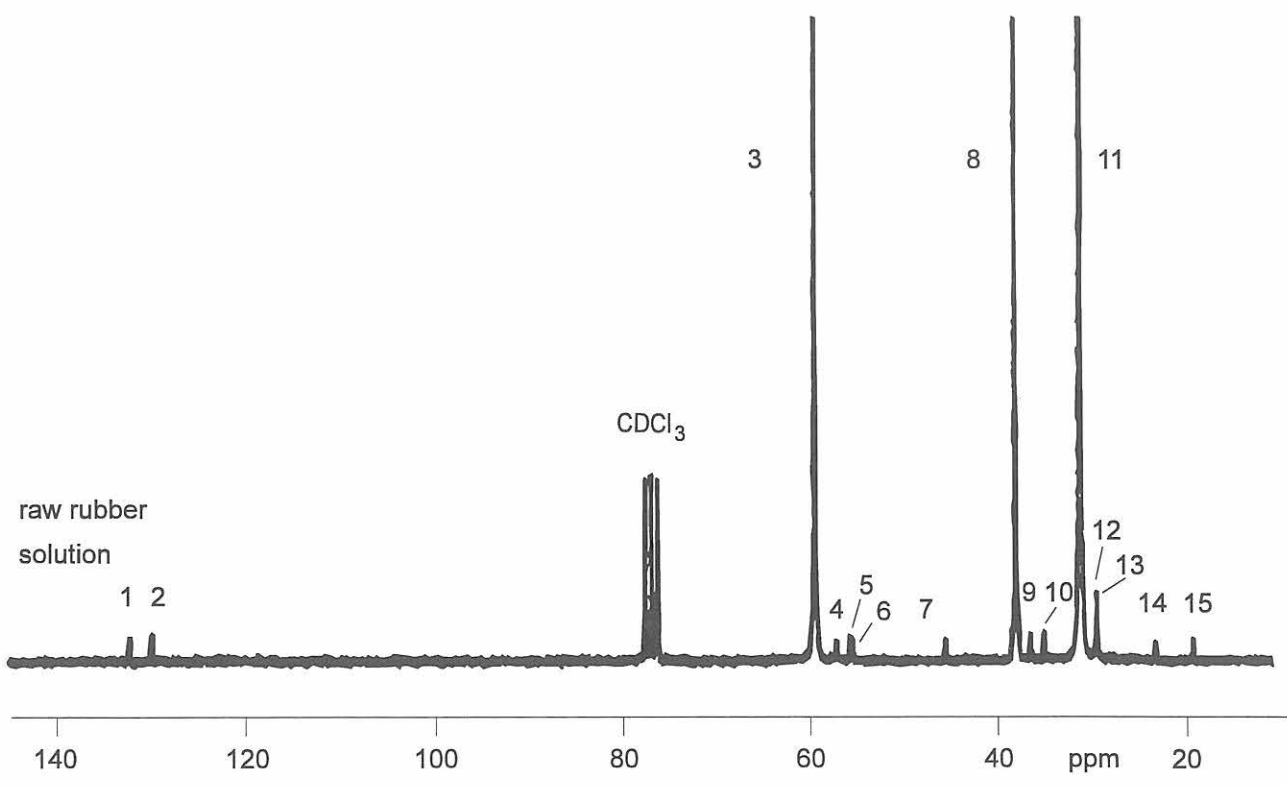
<sup>1</sup> C. Y. Chu and R. Vukov, *Macromolecules* 18, 1423 (1985)

<sup>2</sup> I. Kuntz and K. D. Rose, *J. Polym. Sci., Polym. Chem. Ed.* 27, 107 (1989)

vulcanizate  
solids  
80°C



raw rubber  
solution



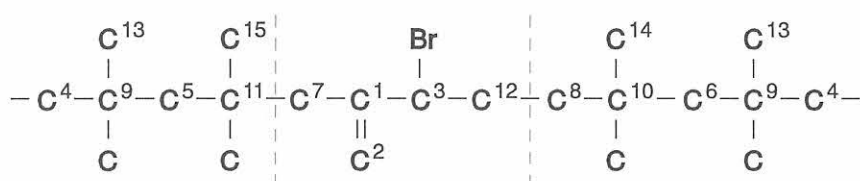
## BROMOBUTYL RUBBER (BIIR)

The halobutyls retain all of the basic properties of regular butyl rubber with the additional benefits of faster cure rates, co-vulcanization with other polymers, improved heat resistance and the ability to crosslink with zinc oxide alone.

Halogenated butyl rubber is made by bromination or chlorination of butyl rubber. The halogen atom is exclusively incorporated in the isoprene unit. Molecular structure investigations have shown that current commercial halogenation procedures produce a special isomer as major compound: it is the exomethylene allylic halide isomer<sup>1</sup>.

Almost all halobutyl curing systems contain zinc oxide as curing agent. Therefore, defining the role played by zinc oxide in the crosslinking process, has been the subject of considerable research activities. Different from other elastomers all the original structures of the halogenated isoprenes are affected. They are - except crosslinking - mainly transferred to conjugated diene units<sup>2</sup>. In the solid state spectrum the original olefinic resonances have disappeared, instead diene peaks can be detected (a, b, c; the fourth peak about 116 ppm is hidden in the noise). The peaks marked by asterisks are anisotropy bands.

### Assignments<sup>1,3</sup>:

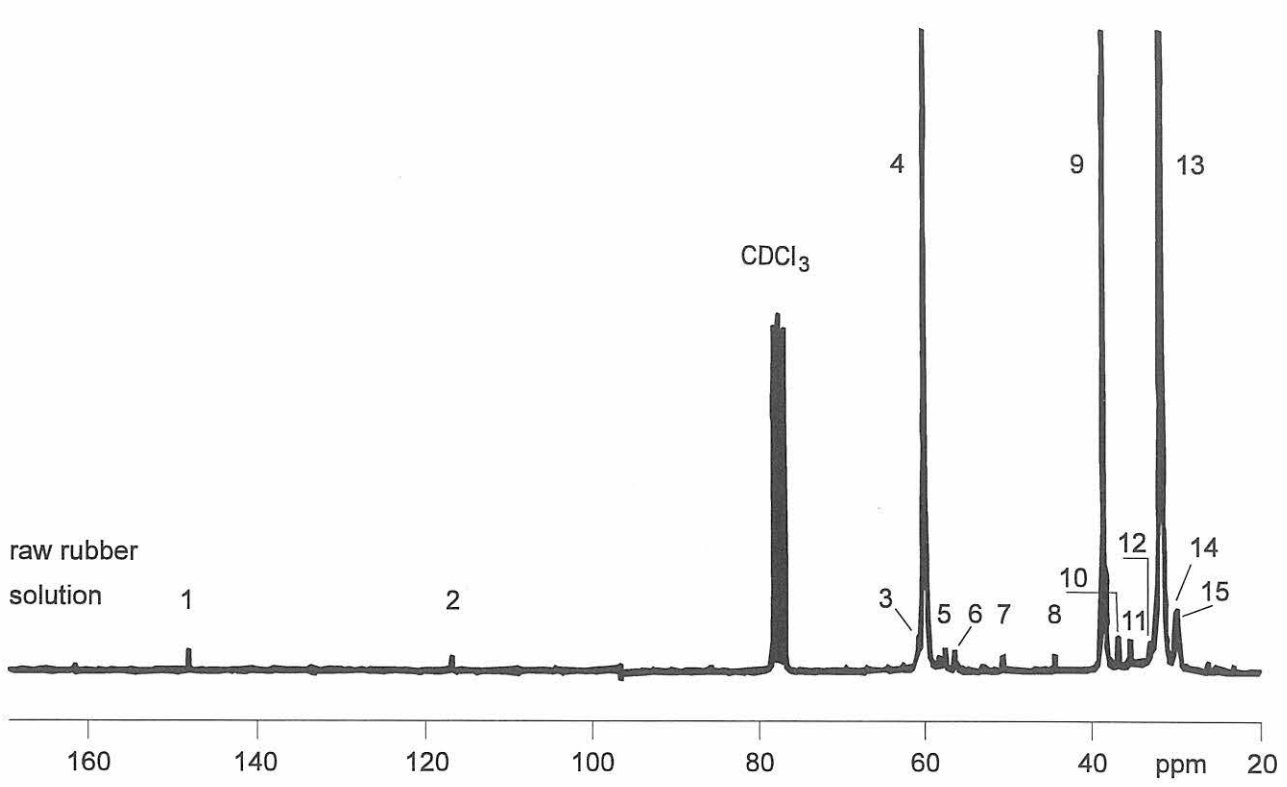
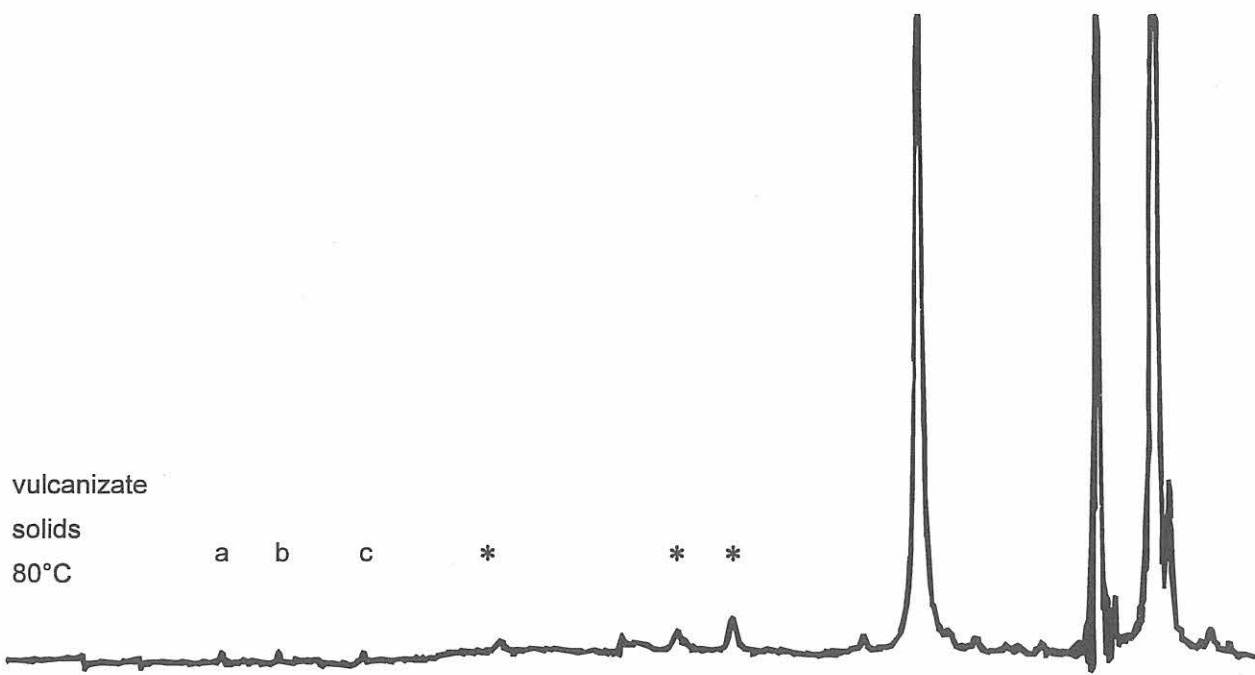


### References:

<sup>1</sup> C. Y. Chu, K. N. Watson and R. Vukov, Rubber Chem. Technol. 60, 636 (1987)

<sup>2</sup> I. J. Gardner and J. V. Fusco, presented at a meeting of the Rubber Division, American Chemical Society, Montreal, Quebec, Canada, May 26-29, 1987

<sup>3</sup> D. M. Cheng, I. J. Gardner, H. C. Wang, C. B. Frederick, A. H. Dekmezian and P. Hous, Rubber Chem. Technol. 63, 265 (1990)

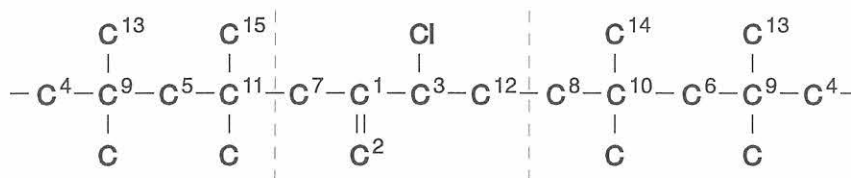


## CHLOROBUTYL RUBBER (CIIR)

Many of the properties of bromobutyl and chlorobutyl elastomers are essentially the same. However, the more active cure sites in bromobutyl rubber generally provide faster cures and better blending behaviour.

The description given for BIIR vulcanization reactions holds true for CIIR, too<sup>1</sup>. The solid state spectrum is the same. As with BIIR three diene resonances (a, b, c) can be detected. The peaks marked by asterisks are anisotropy bands.

### Assignments<sup>2</sup>:

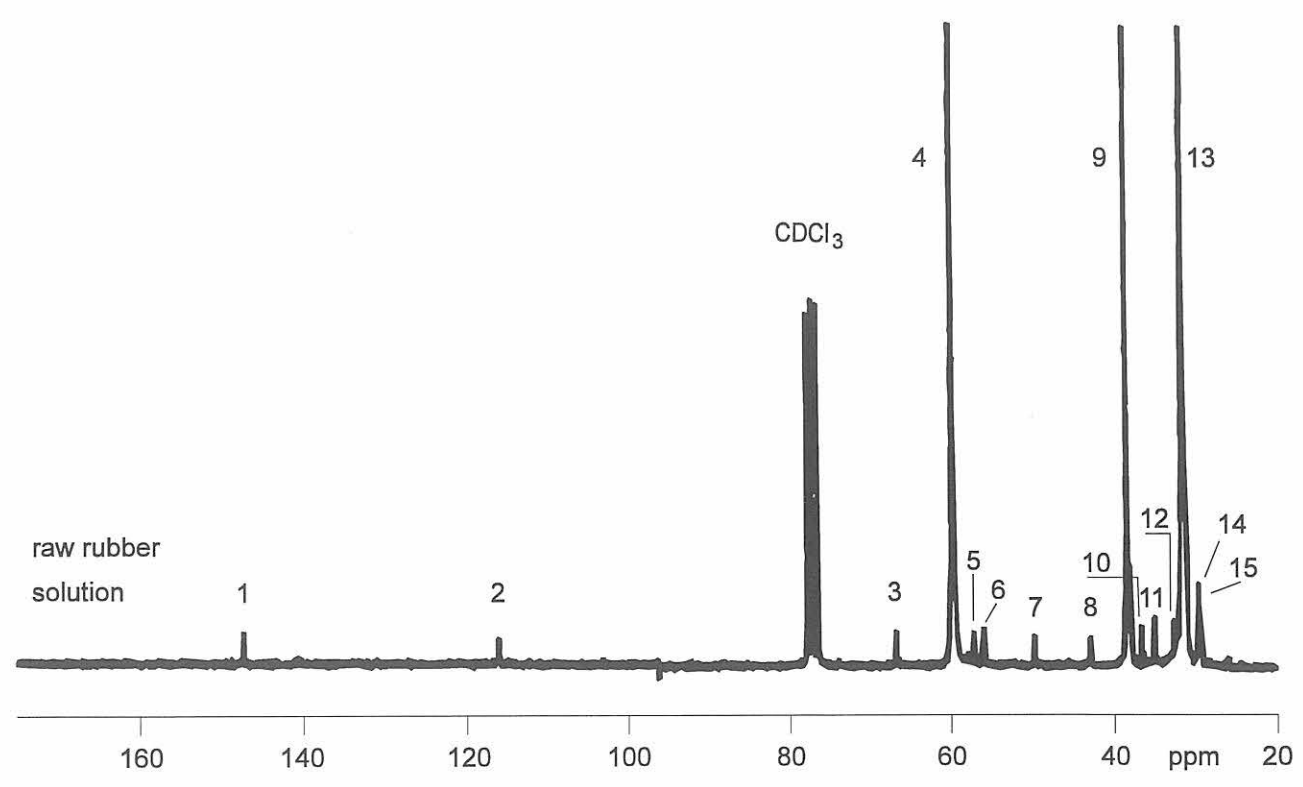
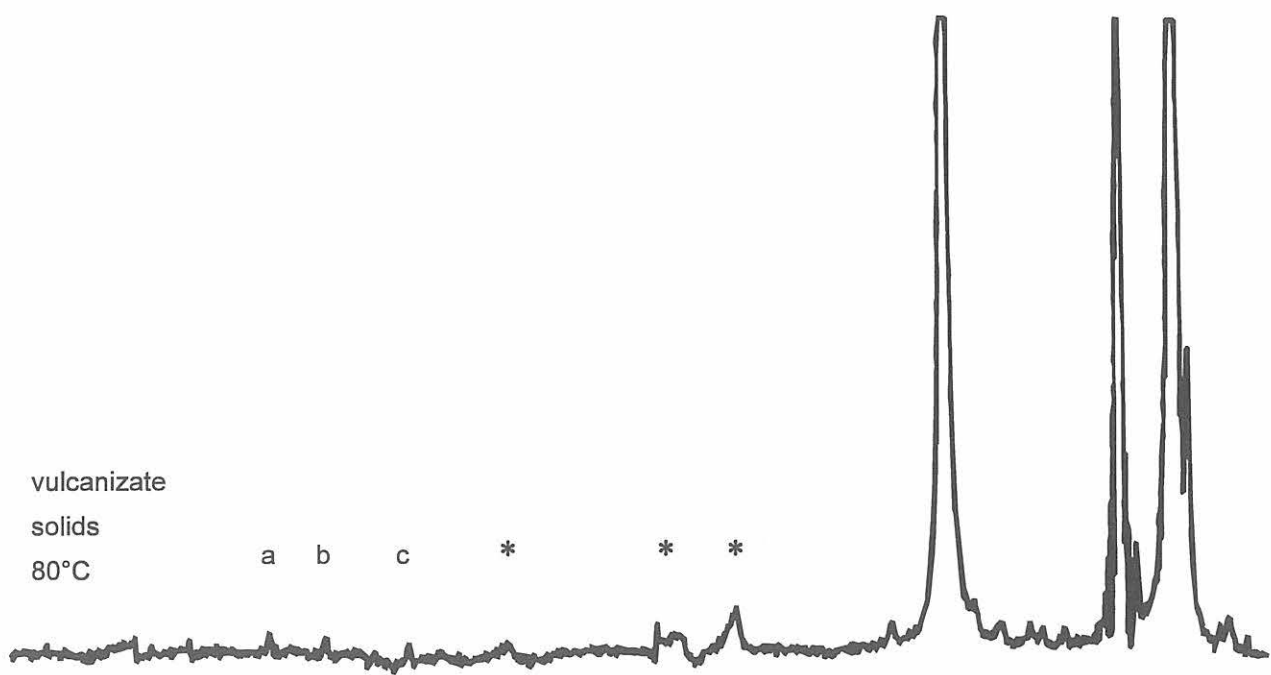


### References:

<sup>1</sup> I. J. Gardner and J. V. Fusco, presented at a meeting of the Rubber Division, American Chemical Society, Montreal, Quebec, Canada, May 26-29, 1987

<sup>2</sup> C. Y. Chu, K. N. Watson and R. Vukow, Rubber Chem. Technol. 60, 636 (1987)





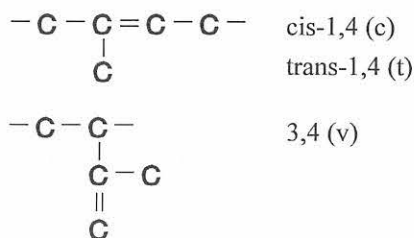
# ISOPRENE RUBBER (IR)

## 1. Li - IR

Isoprene rubber has many characteristics similar to natural rubber, but it is superior in some areas such as ease of mixing, cure rate uniformity, rate of contamination or reproducibility of physical properties.

The starting material is isoprene. Two processes have been developed using different catalysts leading to rubbers with high cis-1,4 content.

Minor structures are trans-1,4 and 3,4 units; 1,2 units are not observed:



Lithium containing catalysts lead to rubbers with about 90% cis content. The main signals clearly correspond to natural rubber. The minor structures are easily recognizable, in solution and in solid state.

For an unambiguous assignment the observed carbon atom is marked by an asterisk if necessary. In the case of diads the observed atom is the first or last carbon of the underlined unit, i.e., the atom linked to the other unit.

### Assignments<sup>1-3</sup>:

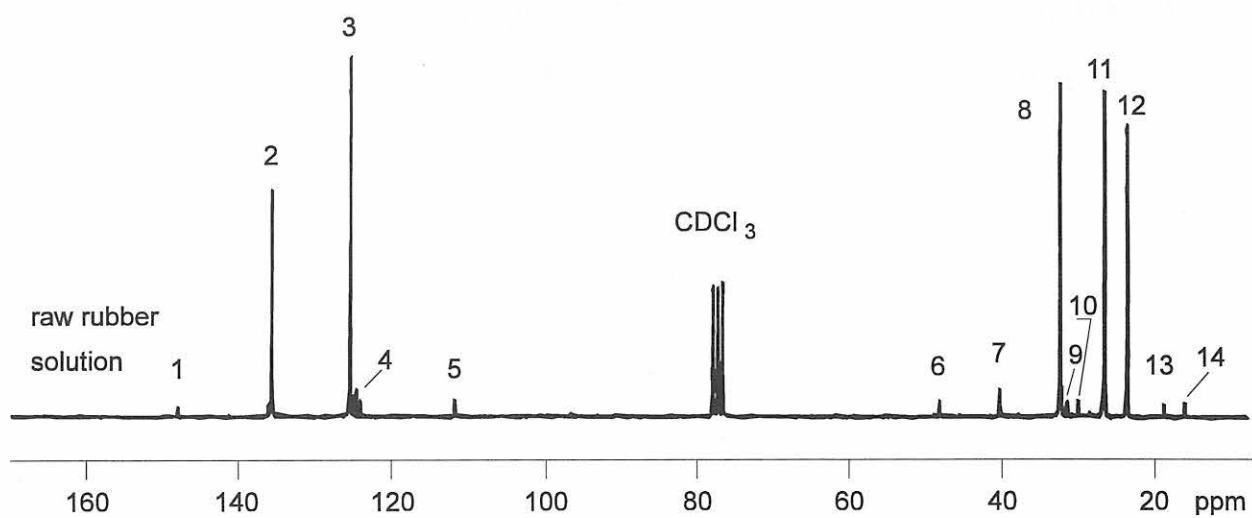
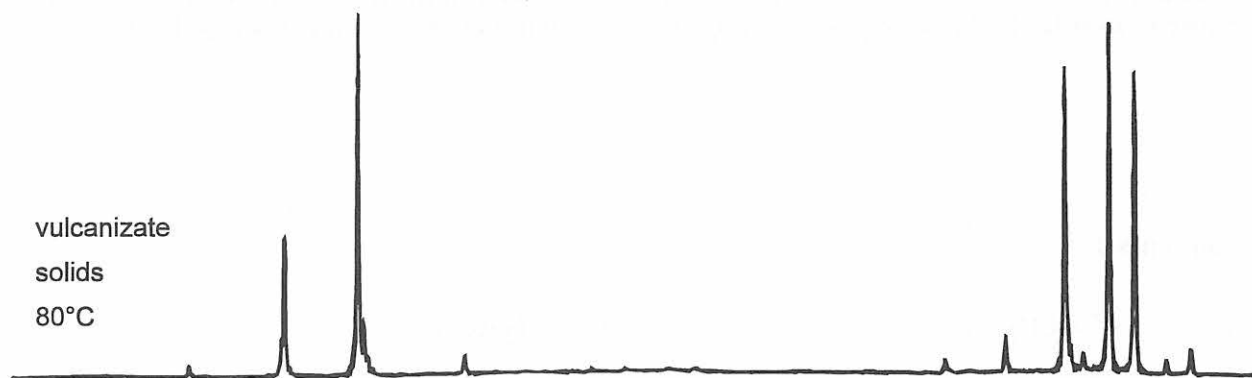
signal	1: C* = CH <sub>2</sub> (v)	8: CH <sub>2</sub> ( <u>cc</u> , <u>tc</u> )
	2: C* = CH (c, t)	9: CH <sub>2</sub> ( <u>vc</u> , <u>cv</u> )
	3: C = C*H (c)	10: CH <sub>2</sub> ( <u>cv</u> )
	4: C = C*H (t)	11: CH <sub>2</sub> ( <u>cc</u> , <u>tc</u> , <u>ct</u> )
	5: C = C*H <sub>2</sub> (v)	12: CH <sub>3</sub> (c)
	6: CH (v)	13: CH <sub>3</sub> (v)
	7: CH <sub>2</sub> ( <u>ct</u> )	14: CH <sub>3</sub> (t)

### References:

<sup>1</sup> H. Sato, A. Ono and Y. Tanaka, Polymer 18, 581 (1977)

<sup>2</sup> A. S. Khatchaturov, E. R. Dolinskaya, L. K. Prozenko, E. L. Abramenko and V. A. Kormer, Polymer 18, 871 (1977)

<sup>3</sup> D. H. Beebe. Polymer 19, 231 (1978)



# ISOPRENE RUBBER (IR)

## 2. Ti - IR

In contrast to Li-IR the use of titanium containing catalysts leads to isoprene rubbers with cis contents of about 98%. Therefore this rubber is very similar to natural rubber.

The spectra show the similarity to Li-IR, naturally at a lower concentration level. The minor peaks are assigned

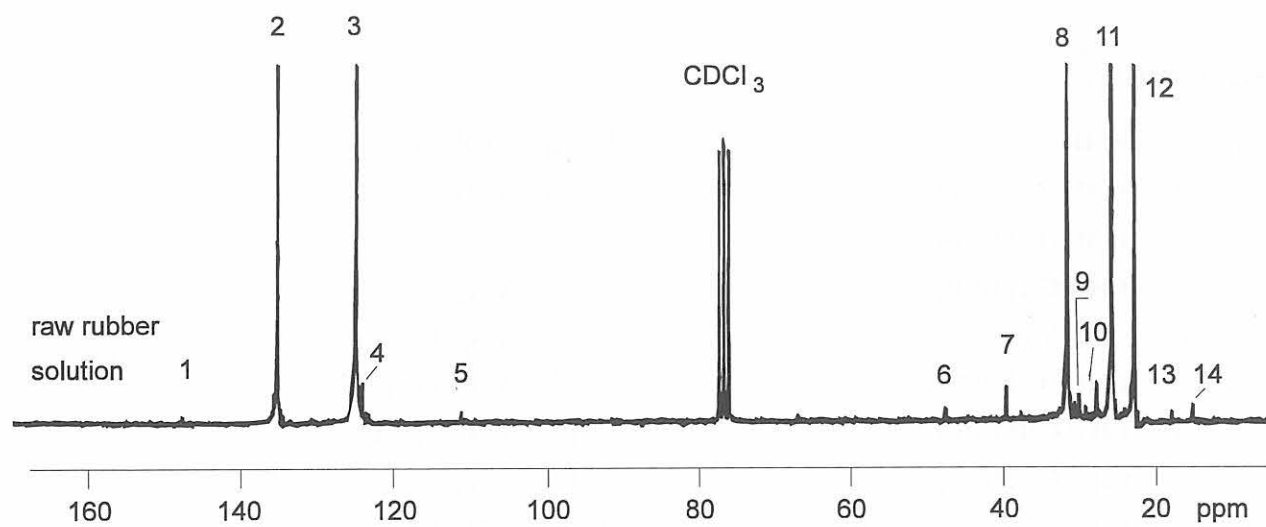
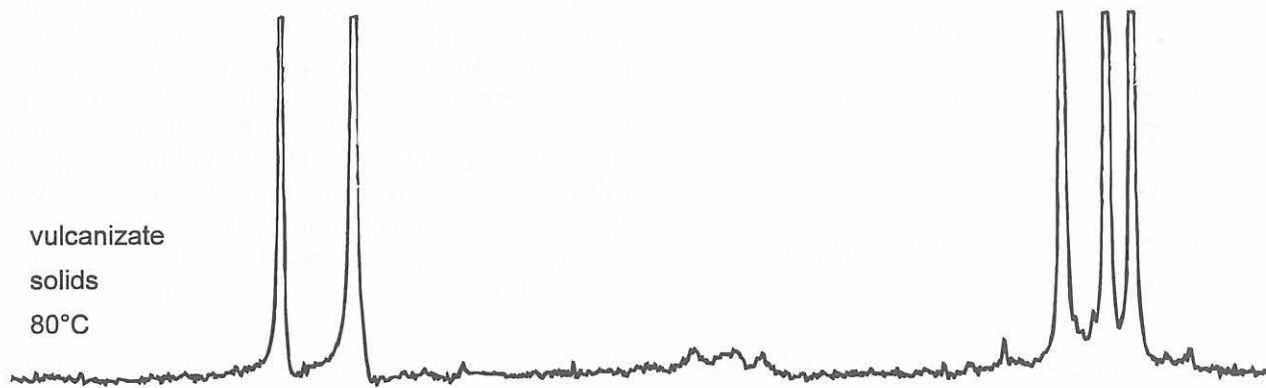
to trans-1,4 and 3,4 units, as well. In the solid state spectrum some of the peaks are no more recognizable, especially of 3,4 units. The concentration of trans units may have increased during vulcanization by cis/trans isomerization. The spectral difference from natural rubber becomes very small. The three resonances in the middle of the solid state spectrum are anisotropy bands.

### Assignments<sup>1</sup>:

signal	1:	$C^* = CH_2$ (v)	8:	$CH_2$ (cc, tc)
	2:	$C^* = CH$ (c, t)	9:	$CH_2$ (vc, cv)
	3:	$C = C^*H$ (c)	10:	$CH_2$ (cv)
	4:	$C = C^*H$ (t)	11:	$CH_2$ (cc, tc, ct)
	5:	$C = C^*H_2$ (v)	12:	$CH_3$ (c)
	6:	$CH$ (v)	13:	$CH_3$ (v)
	7:	$CH_2$ (ct)	14:	$CH_3$ (t)

### References:

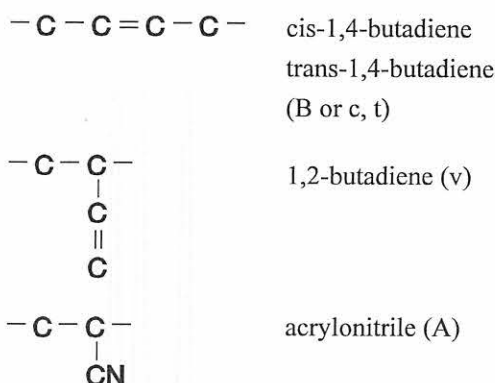
<sup>1</sup> see references of IR, example 1: Li-IR



# NITRILE RUBBER (NBR)

## 1. NBR 18

Nitrile rubbers are copolymers of butadiene and acrylonitrile:



The monomer ratio of butadiene and acrylonitrile is varied within a wide range according to special demands of application. NBR rubbers are known especially for their resistance to liquid fuels, mineral oils and greases. These properties are due to the high polarity introduced by the acrylonitrile unit. Therefore, the resistance to swell-

ing is improved going to higher levels of acrylonitrile content. But in the same way the low-temperature flexibility is diminished. Consequently, a compromise has to be established for a special application.

For the interpretation of the spectra diads and triads are considered according to the range of chemical shift influences. The unit under consideration is underlined; the observed carbon is indicated by an asterisk if necessary for clearness. In the case of diads the first or last carbon atom is considered, i.e., the carbon linked to the adjacent unit. A detailed assignment of the minor structure peaks - 1,2 and cis units - is not given. For the left-hand side of the spectrum the general abbreviation B is used, for the right-hand side the assignment differentiates between trans and cis units.

NBR 18 consists of a copolymer with 18% acrylonitrile. The configuration of butadiene is mainly trans-1,4-butadiene. The spectrum gives characteristic peak patterns, especially for the olefinic part, consisting of ABB, ABA, BBB and BBA sequences and the nitrile carbon.

### Assignments<sup>1-3</sup>:

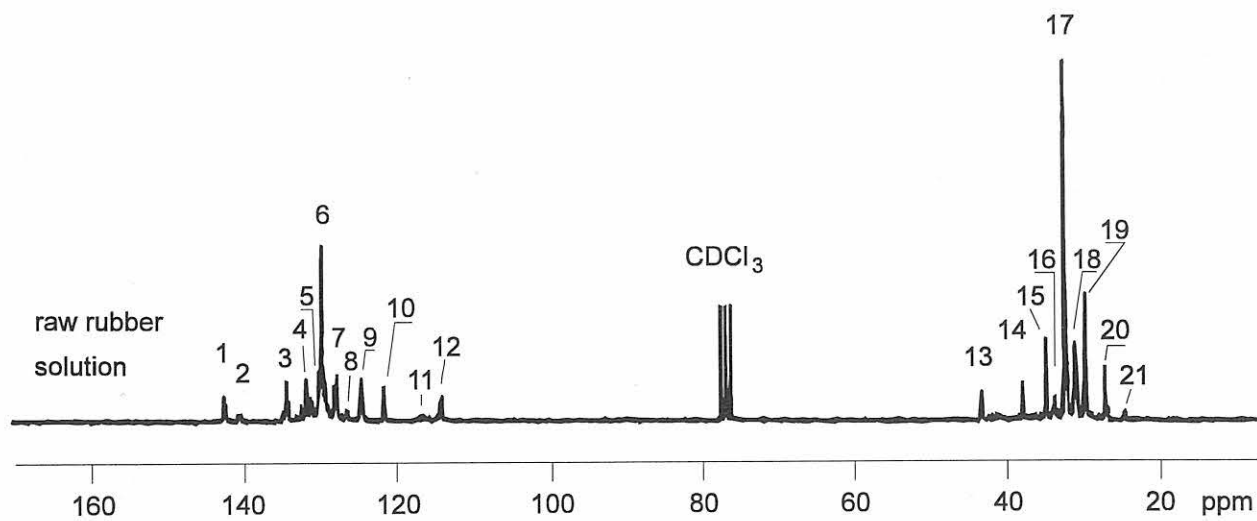
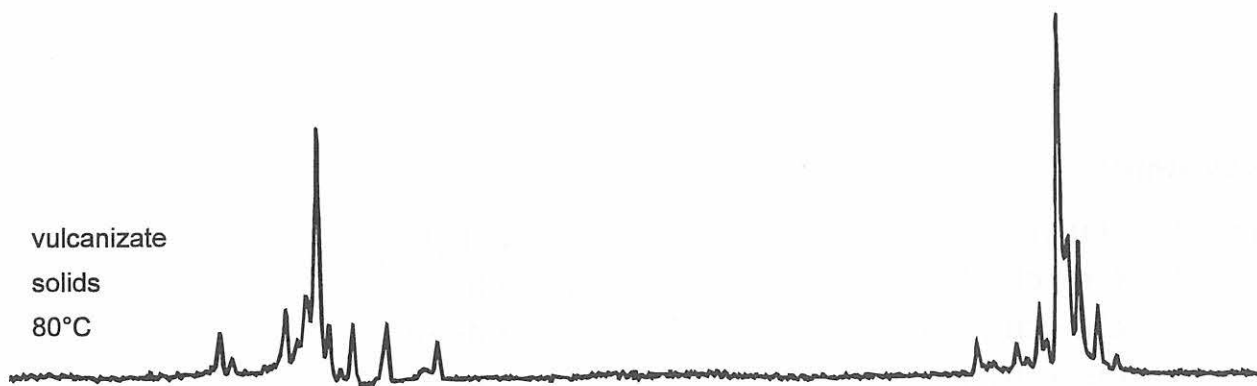
signal 1, 2:	=CH (v)	11, 12:	=CH <sub>2</sub> (v)
3:	C*H = CH (A <u>BB</u> )	13:	CH (v)
4:	C*H = CH (A <u>B</u> A)	14:	CH <sub>2</sub> (v <u>t</u> )
5:	CH = C*H (A <u>BB</u> )	15:	CH <sub>2</sub> (A <u>t</u> )
6:	=CH (B <u>BB</u> )	16:	CH <sub>2</sub> (v)
7:	C*H = CH (B <u>B</u> A)	17:	CH <sub>2</sub> (t <u>t</u> , t <u>t</u> )
8:	CH = C*H (A <u>B</u> A)	18:	CH (A <u>t</u> ), CH <sub>2</sub> (t <u>A</u> )
9:	CH = C*H (B <u>B</u> A)	19:	CH <sub>2</sub> (t <u>v</u> , t <u>A</u> )
10:	CN	20, 21:	CH <sub>2</sub> (c)

### References:

<sup>1</sup> A. R. Katritzky and D. E. Weiss, J. Chem. Soc., Perkin II 1974, 1542 (1974)

<sup>2</sup> P. Kuzay, W. Hoffmann, W. Sauer and W. Kimmer, Faserforsch. Textiltech. 26, 219 (1975)

<sup>3</sup> B. G. Willougby, Polymer Testing 8, 45 (1989)



# NITRILE RUBBER (NBR)

## 2. NBR 28

The acrylonitrile content is 28%. As with NBR 18 the olefinic peak patterns are a characteristic image of the monomer ratio. The CN resonance has nearly the same intensity as the BBB sequence resonance. The triplets on

either side of the main peak are due to ABB, ABA and BBA sequences. Peak overlapping leads to a simpler spectrum in the solid state. The fine splittings are no longer recognizable.

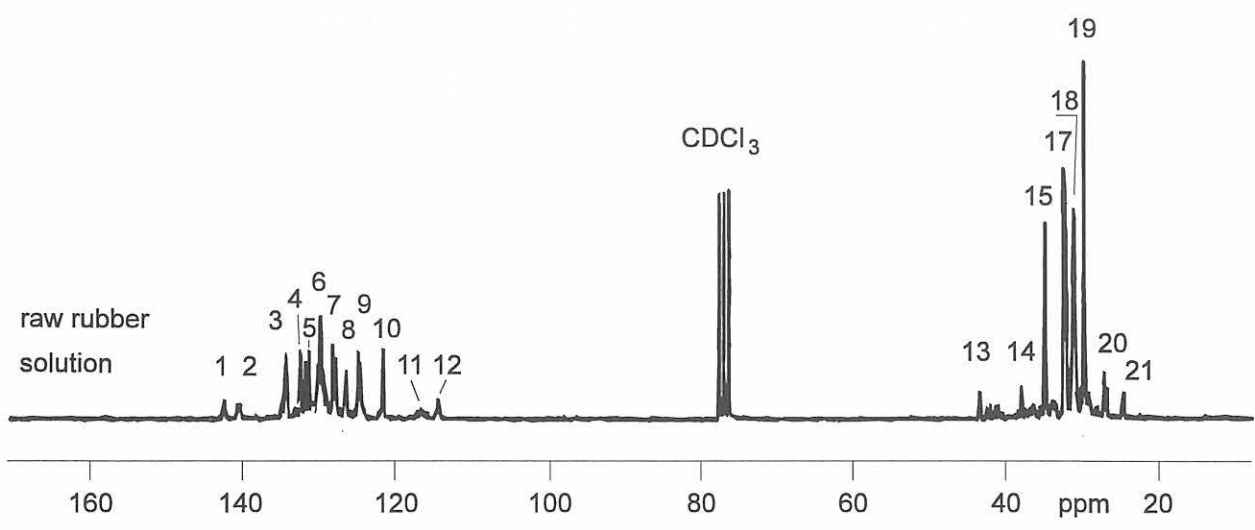
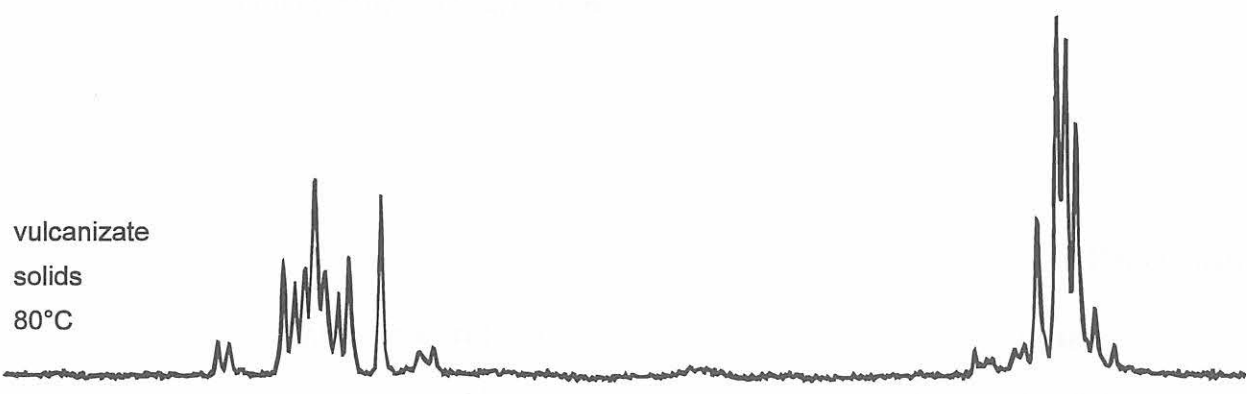
### Assignments<sup>1</sup>:

signal 1, 2:	=CH (v)	11, 12:	=CH <sub>2</sub> (v)
3:	C*H = CH (ABB)	13:	CH (v)
4:	C*H = CH (ABA)	14:	CH <sub>2</sub> (vt)
5:	CH = C*H (ABB)	15:	CH <sub>2</sub> (At)
6:	=CH (BBB)	16:	CH <sub>2</sub> (v)
7:	C*H = CH (BBA)	17:	CH <sub>2</sub> (tt, tt)
8:	CH = C*H (ABA)	18:	CH (Δt), CH <sub>2</sub> (tA)
9:	CH = C*H (BBA)	19:	CH <sub>2</sub> (tv, tΔ)
10:	CN	20, 21:	CH <sub>2</sub> (c)

### References:

<sup>1</sup> see references of NBR 18





# NITRILE RUBBER (NBR)

## 3. NBR 34

The acrylonitrile content is 34%. When going from 28% to 34% the variation in the spectrum is quite considerable, especially in the solid state spectrum. The CN peak becomes the main resonance of the left-hand side of the spectrum.

The peak of the BBB sequences has about the same intensity as the ABB and BBA resonances. The ABA resonances are now slightly more intense. The obvious intensity differences between solution and solid state spectrum are presumably due to different experimental conditions and to different resolution.

### Assignments<sup>1</sup>:

signal 1, 2: =CH (v)

3: C\*H = CH (ABB)

4: C\*H = CH (ABA)

5: CH = C\*H (ABB)

6: =CH (BBB)

7: C\*H = CH(BBA)

8: CH = C\*H (ABA)

9: CH = C\*H (BBA)

10: CN

11, 12: =CH<sub>2</sub> (v)

15: CH<sub>2</sub> (At)

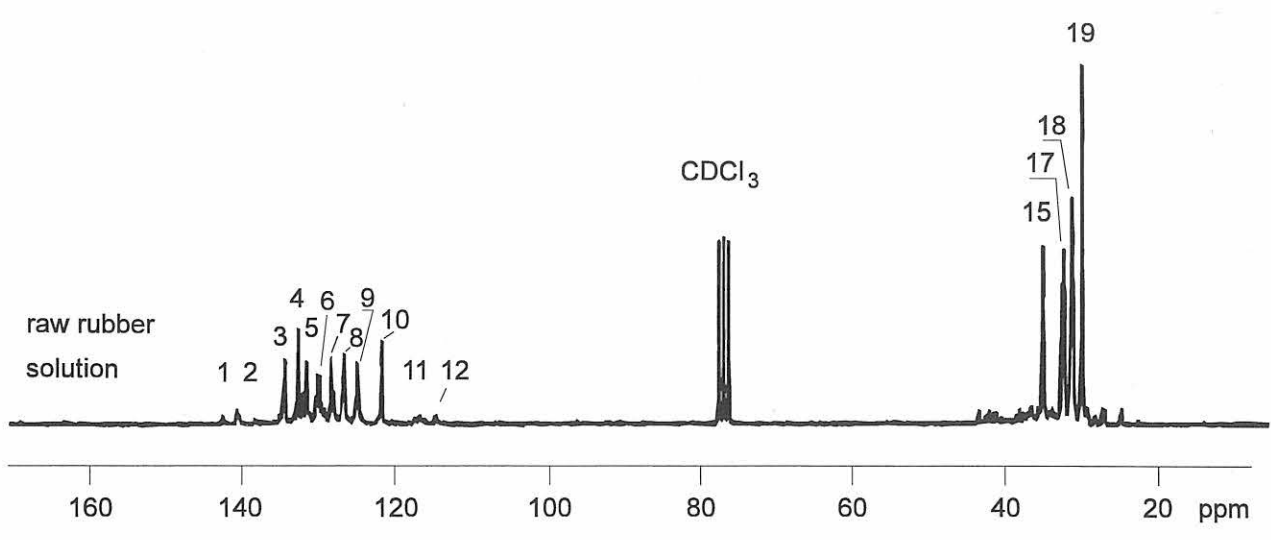
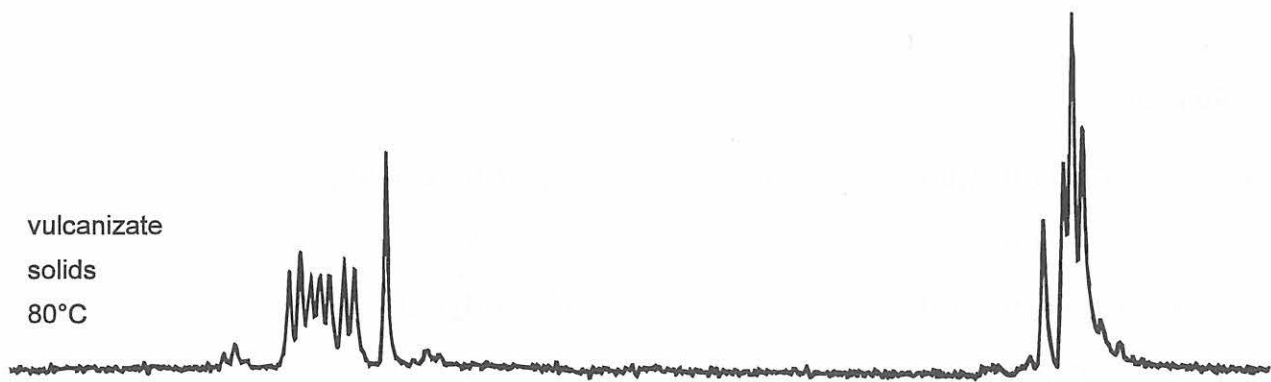
17: CH<sub>2</sub> (tt, tt)

18: CH (At), CH<sub>2</sub> (tA)

19: CH<sub>2</sub> (tv, tA)

### References:

<sup>1</sup> see references of NBR 18



# NITRILE RUBBER (NBR)

## 4. NBR 39

The acrylonitrile content is 39%. With the acrylonitrile content increasing the peaks of ABA sequences become

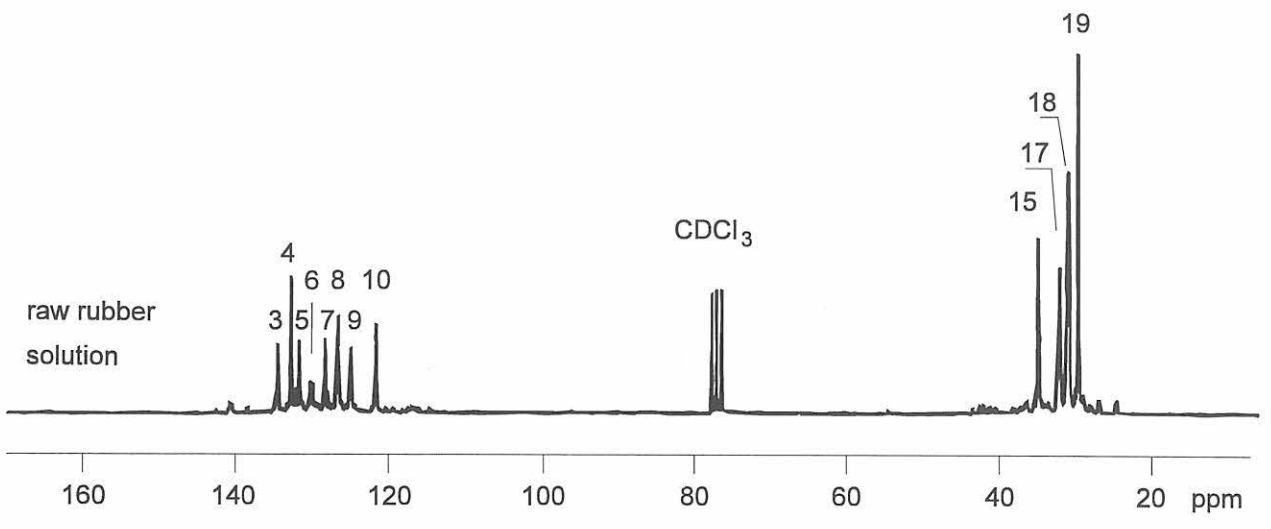
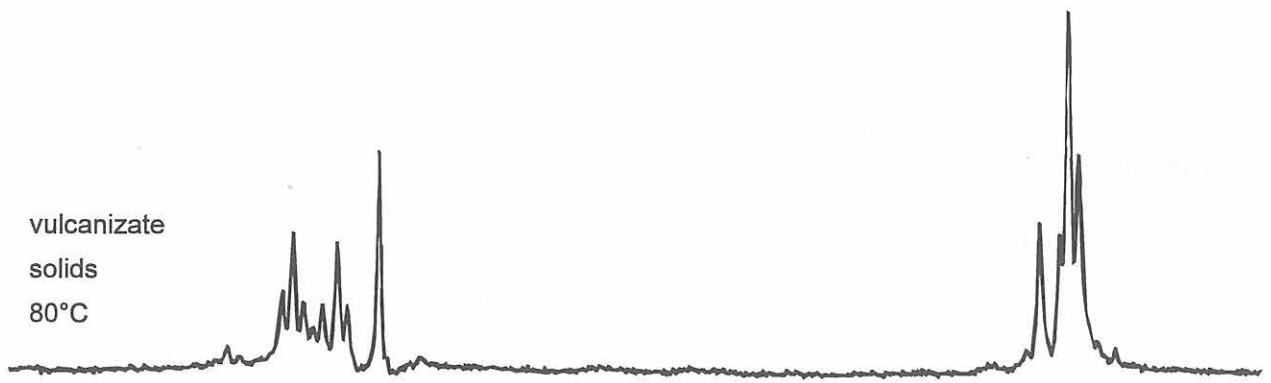
dominating besides the CN resonance. BBB sequences are negligible.

### Assignments<sup>1</sup>:

signal	3: $C^*H = CH$ ( <u>ABB</u> )	9: $CH = C^*H$ ( <u>BBA</u> )
	4: $C^*H = CH$ ( <u>ABA</u> )	10: CN
	5: $CH = C^*H$ ( <u>ABB</u> )	15: $CH_2$ ( <u>At</u> )
	6: $=CH$ ( <u>BBB</u> )	17: $CH_2$ ( <u>tt, tt</u> )
	7: $C^*H = CH$ ( <u>BBA</u> )	18: $CH$ ( <u>At</u> ), $CH_2$ ( <u>tA</u> )
	8: $CH = C^*H$ ( <u>ABA</u> )	19: $CH_2$ ( <u>tv, tA</u> )

### References:

<sup>1</sup> see references of NBR 18



# NITRILE RUBBER (NBR)

## 5. NBR 48

The acrylonitrile content is 48%. The spectrum can be explained on the basis of a copolymer with alternating butadiene and acrylonitrile units. A new peak appears at about 120 ppm. Possibly it is due to the presence of AAB or BAA sequences. There is no obvious indication of AAA

sequences. The same peak was observed for hydrogenated NBR rubbers (HNBR) with an acrylonitrile content of 45%<sup>1</sup>. This observation proves that it is a nitrile carbon resonance.

### Assignments<sup>2</sup>:

signal 4:  $C^*H = CH$  (ABA)

8:  $CH = C^*H$  (ABA)

10: CN

15:  $CH_2$  (At)

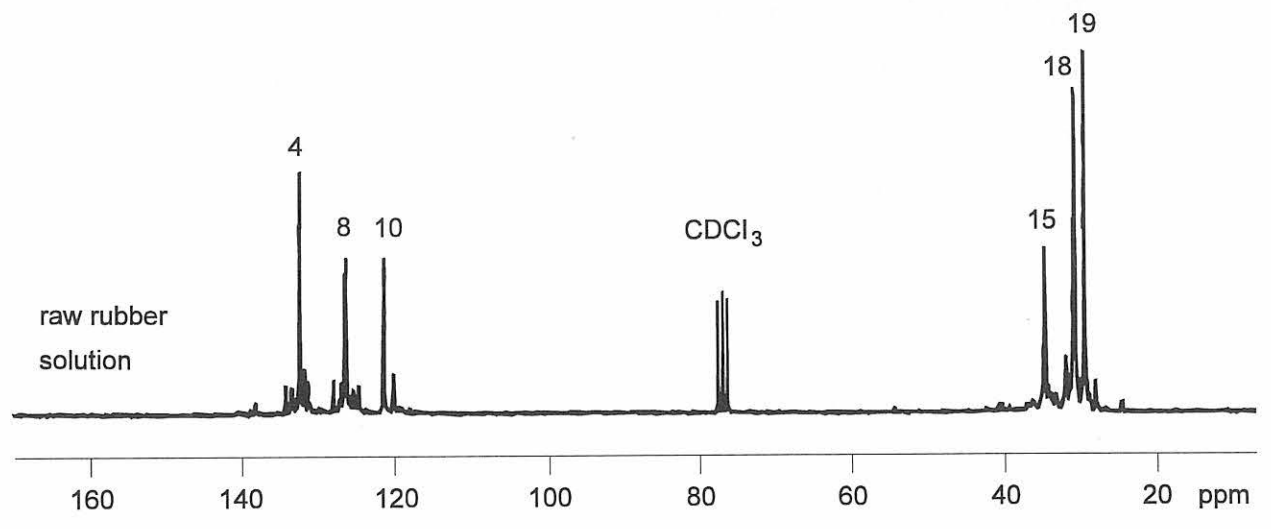
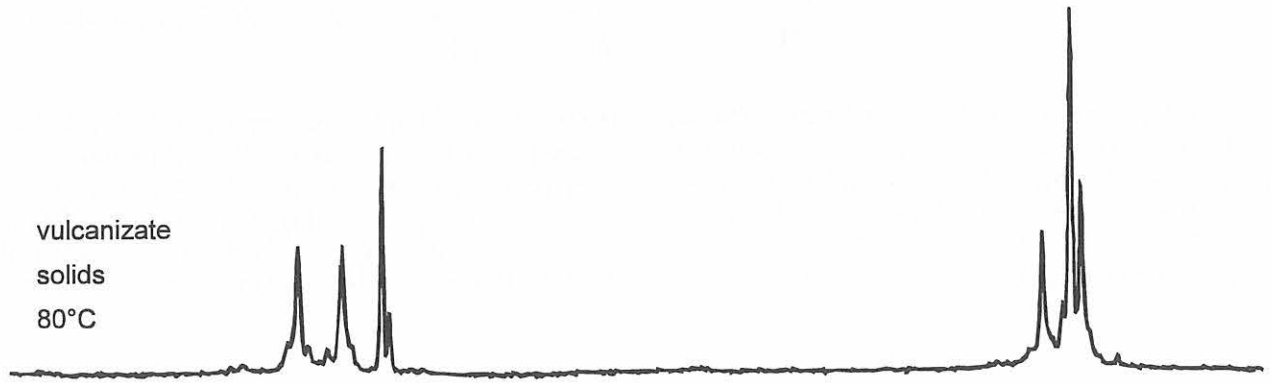
18:  $CH$  ( $\Delta t$ ),  $CH_2$  (tA)

19:  $CH_2$  (tv, t $\Delta$ )

### References:

<sup>1</sup> A. Kondo, H. Ohtani, Y. Kosugi, S. Tsuge, Y. Kubo, N. Asada, H. Inaki and A. Yoshioka, *Macromolecules* 21, 2918 (1988)

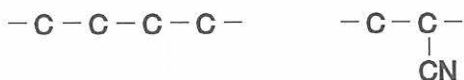
<sup>2</sup> see references of NBR 18



# NITRILE RUBBER, HYDROGENATED (HNBR)

## 1. HNBR 34

Hydrogenated NBRs have been developed to improve the thermal stability. They consist of hydrogenated butadiene units and acrylonitrile:



One can distinguish between fully and partly saturated grades. The first ones are peroxide curable and exhibit excellent aging behaviour and resistance to heat, aggressive media, ozone and weathering. The others are not that resistant, but offer the possibility of sulfur vulcanization. The partly saturated grades have double bond concentra-

tions of about 5% which is sufficient for sulfur vulcanization.

HNBR 34 is produced by hydrogenation of NBR 34. A very detailed description is given for the right-hand side of the spectrum<sup>1</sup>. Here only a general assignment is given. 1,2 units and sequences with adjacent acrylonitrile units are neglected.

The spectra consist of four resonance groups. On the left-hand side only the CN peak is left shifted a little bit to lower field as compared to NBR. No double bonds are visible in the partly saturated types, not even in solution. The hydrogenation process produces too many different structures that the available intensity is spread too much.

### Assignments<sup>1-3</sup>:

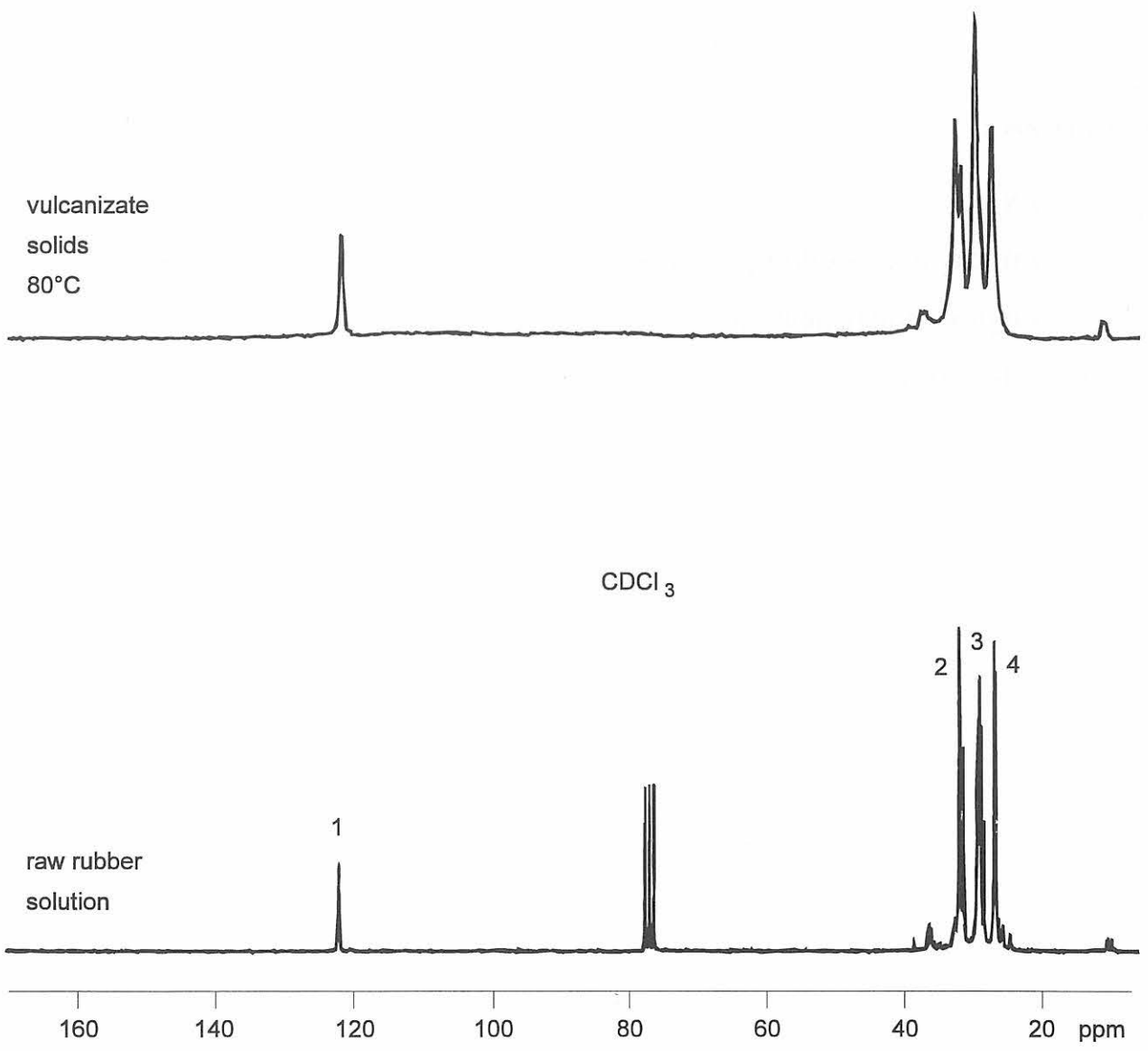
- signal 1: CN
- 2: CH, CH<sub>2</sub> (α or β to CN; CH<sub>2</sub> at lower field)
- 3: CH<sub>2</sub> (δ to CN and more distant)
- 4: CH<sub>2</sub> (γ to CN)

### References:

- <sup>1</sup> K. Kodama, R. Yoda and Y. Tanaka, Polym. Prepr. Japan 30, 2240 (1981)
- <sup>2</sup> N. A. Mohammadi and G. L. Rempel, Macromolecules 20, 2362 (1987)

- <sup>3</sup> A. Kondo, H. Ohtani, Y. Kosugi, S. Tsuge, Y. Kubo, N. Asada, H. Inaki and A. Yoshioka, Macromolecules 21, 2918 (1988)





# NITRILE RUBBER, HYDROGENATED (HNBR)

## 2. HNBR 39

HNBR 39 is produced using NBR 39 as basis material. Of course, the spectrum is interpreted like HNBR 34. It is not very much different. The little peak at about 121 ppm

may be due to AAB or BAA sequences. The small peaks at about 46 ppm and 10 ppm are due to 1,2 units (branch points and CH<sub>3</sub>).

### Assignments<sup>1</sup>:

signal 1: CN

2: CH, CH<sub>2</sub> ( $\alpha$  or  $\beta$  to CN; CH<sub>2</sub> at lower field)

3: CH<sub>2</sub> ( $\delta$  to CN and more distant)

4: CH<sub>2</sub> ( $\gamma$  to CN)

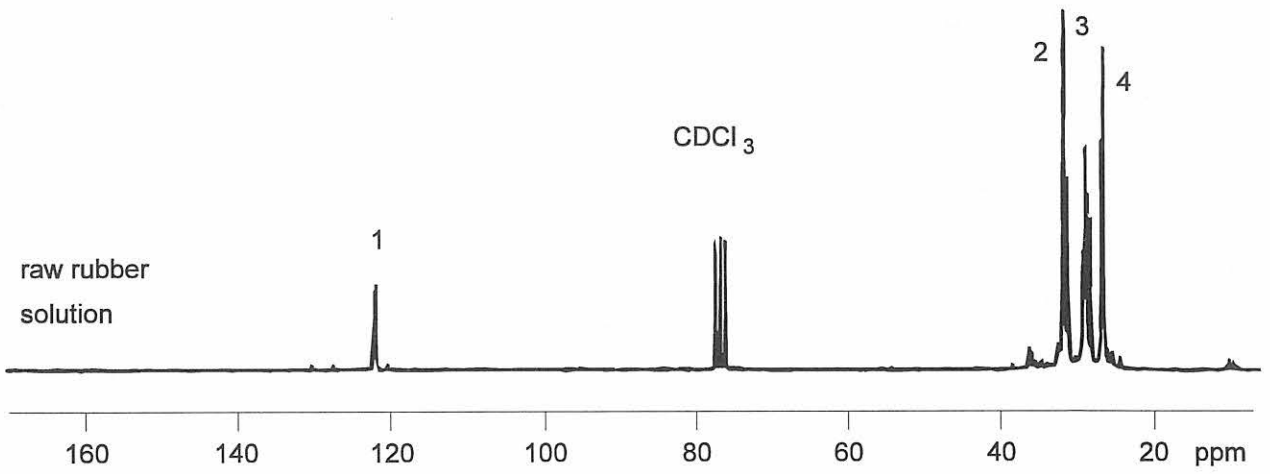
### References:

<sup>1</sup> see references of HNBR 34

vulcanizate  
solids  
80°C



raw rubber  
solution



# NATURAL RUBBER (NR)

## 1. Hevea rubber

Natural rubber is principally the name of a class of rubbers, but the most important one is Hevea rubber. Other natural rubbers are, e.g., gutta percha, guayule and chicle rubber.

Hevea rubber is known and used especially because of an excellent combination of properties like tensile strength, elasticity, low-temperature flexibility, dynamical behaviour and heat-build-up. Therefore it is indispensable in many applications, even today in spite of an extensive set of synthetic rubbers.

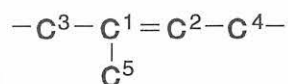
Hevea Rubber has a very regular microstructure, it consists of cis-1,4-polyisoprene. The biochemical formation starts with geranylgeranyl pyrophosphate to which isopentenyl pyrophosphate is added in cis-1,4 mode suc-

cessively. The number of trans units is estimated to be 2 - 4 per polymer chain. They can be detected in commercial samples by newer NMR instrumentation, the concentration is below 0.02%<sup>1,2</sup>.

According to the regular structure the solution spectrum consists of five resonances which are assigned readily. In the solid state spectrum three small peaks are detected additionally. Two of them (40 ppm, 16 ppm) are due to trans units, the third (30 ppm) is due to an unknown. The trans units may have been formed during vulcanization by an isomerization process (see BR).

NR was the subject of studies on vulcanization reactions and crosslinks. But this means even lower peak intensities than those of the trans units<sup>3,4</sup>.

### Assignments<sup>1,2</sup>:



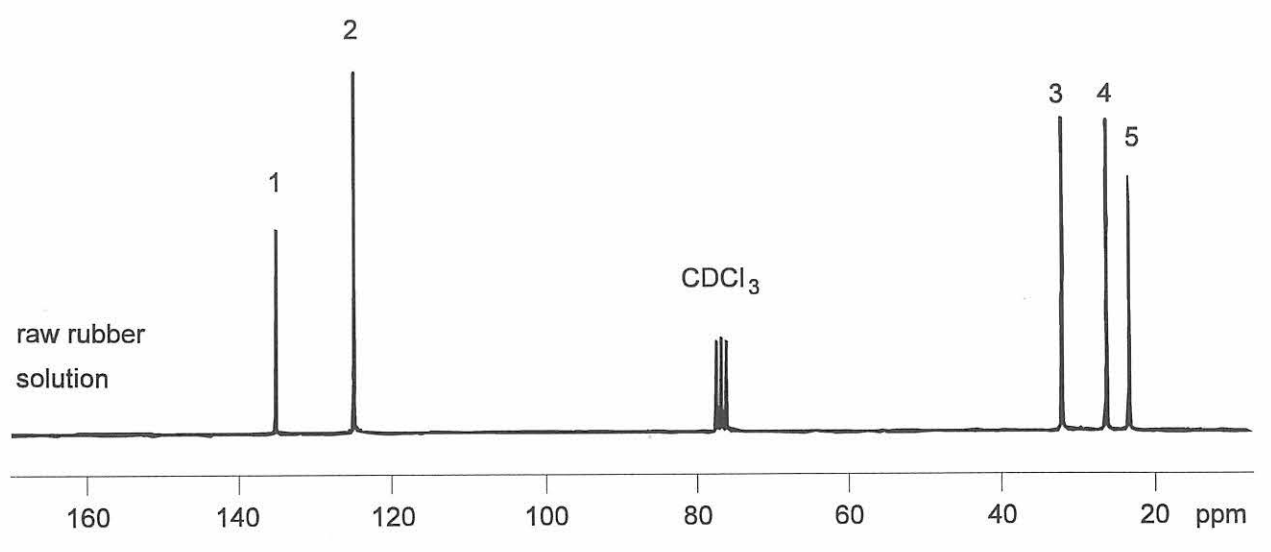
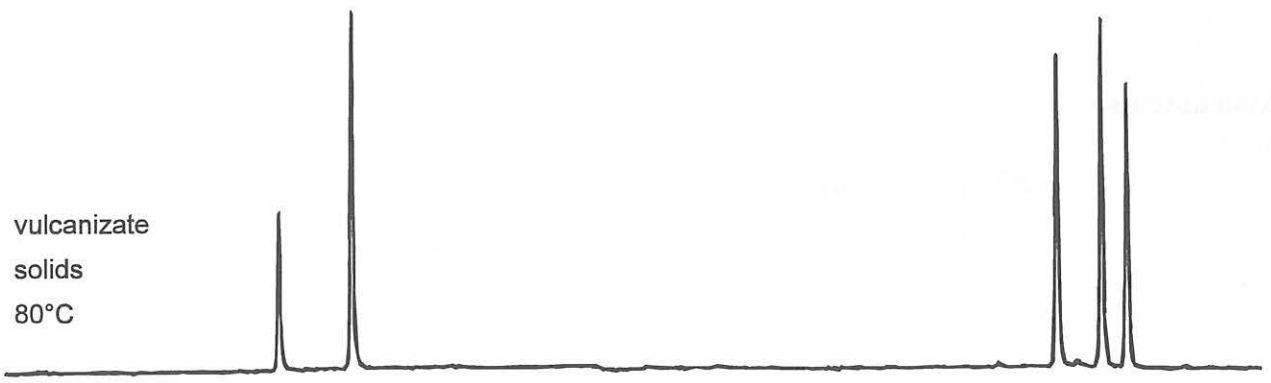
### References:

<sup>1</sup> Y. Tanaka, Nippon Gomu Kyokaishi 55, 652 (1982); translated in Intern. Polym. Sci. Technol. 10, T98 (1983)

<sup>2</sup> Y. Tanaka, Rubber Chem. Technol. 64, 325 (1991)

<sup>3</sup> M. Andreis, J. Liu and J. L. Koenig, J. Polym. Sci., Polym. Phys. Ed. 27, 1389 (1990)

<sup>4</sup> W. Gronski, H. Hasenhindl, B. Freund and S. Wolff, Kautsch. Gummi, Kunstst. 44, 119 (1991)



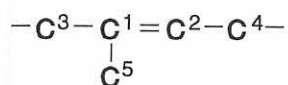
# NATURAL RUBBER (NR)

## 2. Gutta percha

Gutta percha exhibits no rubber elasticity. It was used, e.g., for the insulation of cables, but is replaced increasingly by synthetic thermoplastic polymers.

The spectrum is included for comparison. Obviously the microstructure is very regular, but in contrast to Hevea rubber gutta percha consists of trans-1,4-polyisoprene.

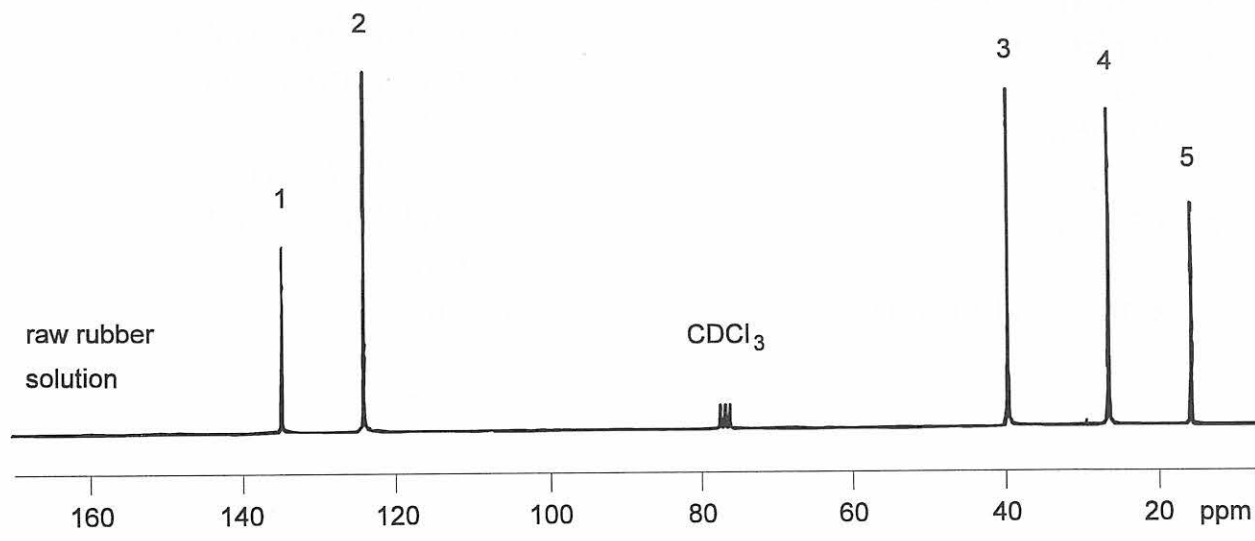
### Assignments<sup>1,2</sup>:



### References:

<sup>1</sup> M. W. Duch and D. M. Grant, *Macromolecules* 3, 165 (1970)

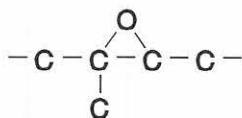
<sup>2</sup> see references No. 1 and No. 2 of Hevea rubber



# NATURAL RUBBER, EPOXIDIZED

## 1. Natural rubber with an epoxidation rate of 25% (according to specification)

More recently there has been a growing interest in the modification of natural rubber because of some outstanding properties. One possibility is epoxidation producing random copolymers containing unchanged units and epoxy co-units on the main chain:



These copolymers have a number of interesting properties. They exhibit resistance to swelling by hydrocarbon oils and retain the high strength typical of natural rubber.

The spectrum is explained on the basis of triads of epoxidized units (E) and unchanged cis-isoprene units (C). The observed carbon atom is marked by an asterisk; the assignments refer to the middle unit of the triads. The fine splittings in the olefinic range are due to pentad effects.

### Assignments<sup>1-3</sup>:

- |   |   |
|---|---|
| signal 1: $\text{C}^*=\text{CH}$ (CCE)  | 10: $\text{C}^*\text{H}_2 \text{C}=\text{CH}$ (CCC, CCE)  |
| 2: $\text{C}^*=\text{CH}$ (CCC)   | 11: $\text{C}^*\text{H}_2 \text{C} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{CH} \end{array}$ (EEC, EEE) |
| 3: $\text{C}^*=\text{CH}$ (ECC, ECE)  | 12: $\text{C}^*\text{H}_2 \text{C}=\text{CH}$ (ECC, ECE)  |
| 4: $\text{C}=\text{C}^*\text{H}$ (ECC)  | 13: $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{CH} \end{array} \text{C}^*\text{H}_2$ (CEC, EEC)          |
| 5: $\text{C}=\text{C}^*\text{H}$ (CCC, ECE)   | 14: $\text{C}=\text{CH} \text{C}^*\text{H}_2$ (CCC, ECC)  |
| 6: $\text{C}=\text{C}^*\text{H}$ (CCE)  | 15: $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{CH} \end{array} \text{C}^*\text{H}_2$ (CEE, EEE)          |
| 7: $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{C}^* \text{H} \end{array}$                       | 16: $\text{C}=\text{CH} \text{C}^*\text{H}_2$ (CCE, ECE)  |
| 8: $\text{C}^* \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ -\text{CH} \end{array}$                              | 17: $\text{CH}_3$ (C)   |
| 9: $\text{C}^*\text{H}_2 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{CH} \end{array}$ (CEC, CEE) | 18: $\text{CH}_3$ (E)   |

### References:

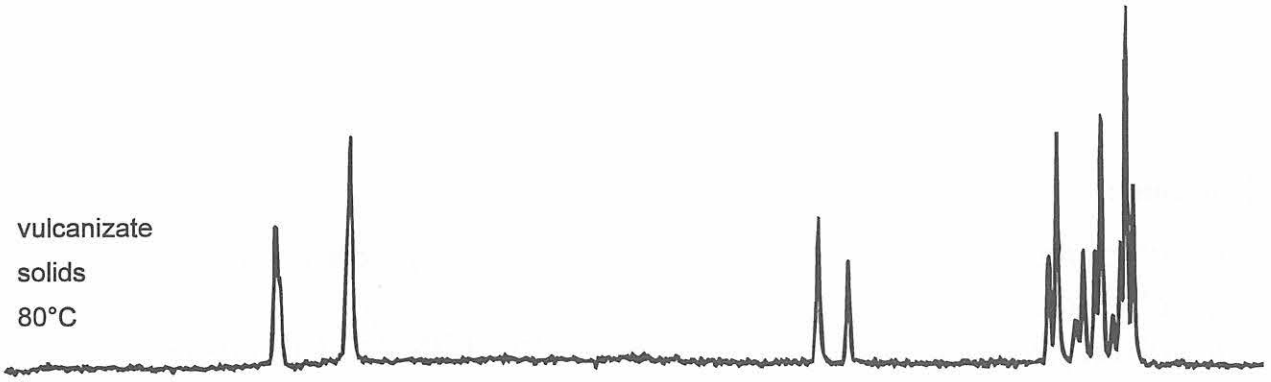
<sup>1</sup> R. V. Gemmer and M. A. Golub, J. Polym. Sci., Polym. Chem. Ed. 16, 2985 (1978)

<sup>2</sup> D. R. Burfield, K.-L. Lim, K.-S. Law and S. Ng, Polymer 25, 995 (1984)

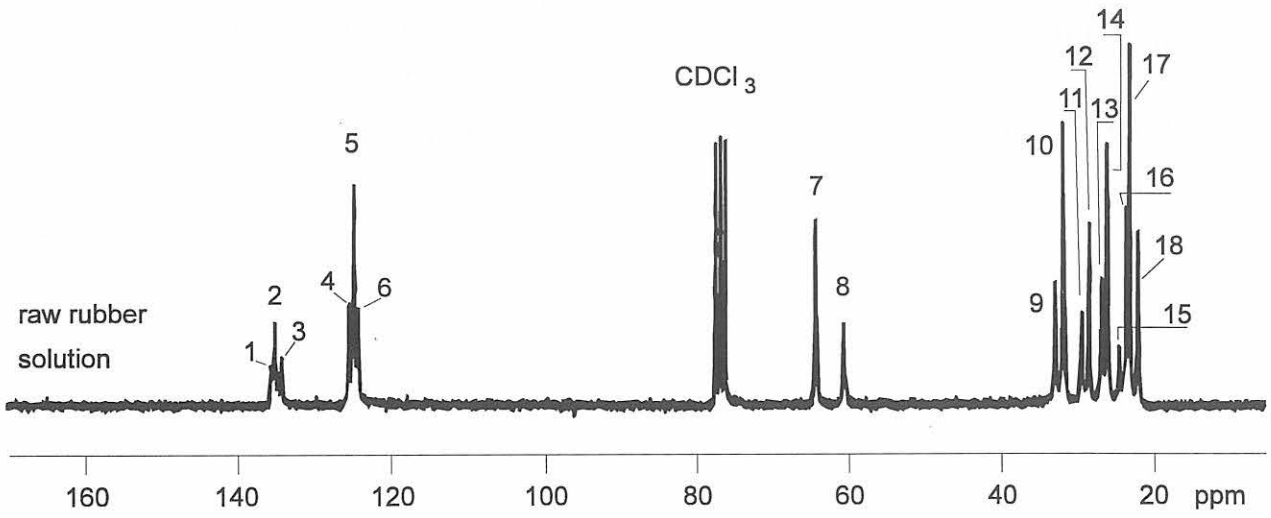
<sup>3</sup> J. H. Bradbury and M. C. S. Perera, J. Appl. Polym. Sci. 30, 3347 (1985)



vulcanizate  
solids  
80°C



raw rubber  
solution



# NATURAL RUBBER, EPOXIDIZED

## 2. Natural rubber with an epoxidation rate of 50% (according to specification)

Different from example 1 the peaks characteristic of isoprene units far away from epoxy groups are no longer the main signals in the aliphatic region (10, 14, 17). The resonances 2 and 5 are attributed to the olefinic carbons

of corresponding units, but there are deviations in chemical shift, especially for resonance 2. This is explained by pentad effects.

### Assignments<sup>1</sup>:

signal 1:  $C^*=CH$  (CCE)

2:  $C^*=CH$  (CCC)

3:  $C^*=CH$  (ECC, ECE)

4:  $C=C^*H$  (ECC)

5:  $C=C^*H$  (CCC, ECE)

6:  $C=C^*H$  (CCE)

7:  $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C - C^*H \end{array}$

8:  $\begin{array}{c} O \\ \diagdown \quad \diagup \\ C^* - CH \end{array}$

9:  $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C^*H_2 - CH \end{array}$  (CEC, CEE)

10:  $C^*H_2 - C=CH$  (CCC, CCE)

11:  $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C^*H_2 - C - CH \end{array}$  (EEC, EEE)

12:  $C^*H_2 - C=CH$  (ECC, ECE)

13:  $\begin{array}{c} O \\ \diagdown \quad \diagup \\ C - CH - C^*H_2 \end{array}$  (CEC, EEC)

14:  $C=CH - C^*H_2$  (CCC, ECC)

15:  $\begin{array}{c} O \\ \diagdown \quad \diagup \\ C - CH - C^*H_2 \end{array}$  (CEE, EEE)

16:  $C=CH - C^*H_2$  (CCE, ECE)

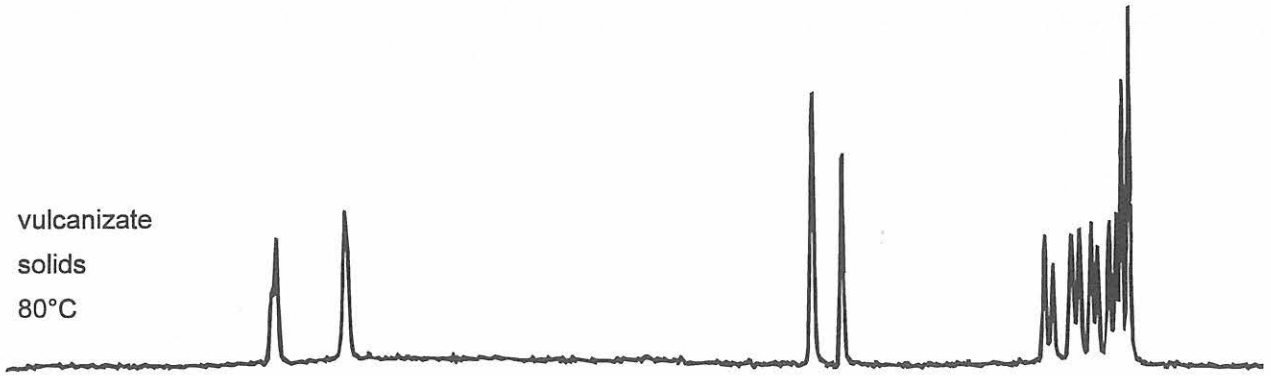
17:  $CH_3$  (C)

18:  $CH_3$  (E)

### References:

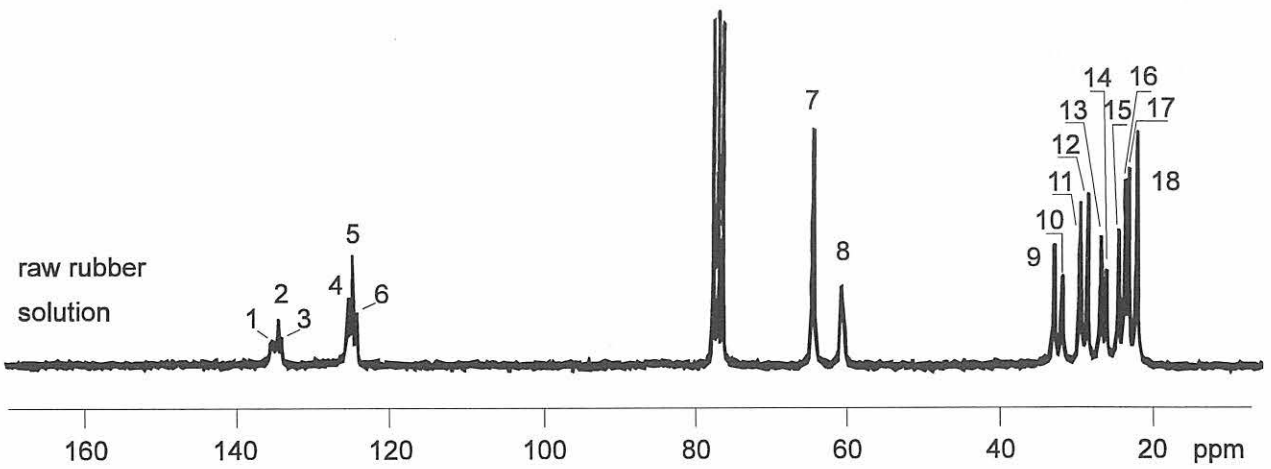
<sup>1</sup> see references of example 1

vulcanizate  
solids  
80°C



CDCl<sub>3</sub>

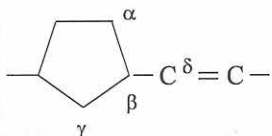
raw rubber  
solution



# POLYNORBORNENE

Polynorbornene is a speciality elastomer. The glass transition temperature is relatively high, but can be lowered by the addition of plasticisers. Typical properties are low hardness combined with high tensile strength and low compression set. Therefore it can be used, e.g., for seals, vibration elements, damping bearings or flexible couplings.

Polynorbornene is made from norbornene by a ring-opening polymerization:



The spectrum shows multiple fine splittings. The peaks can be interpreted in terms of sensitivity of the chemical shift to the cis / trans structure at the next nearest double bonds. The possibility of ring tacticity accounting for some of the fine structure cannot be entirely excluded. The cis/trans ratio can be changed by choice of the catalyst.

The first letter in brackets denotes the cis or trans structure at the nearest double bond, the second letter, at the next nearest double bond.

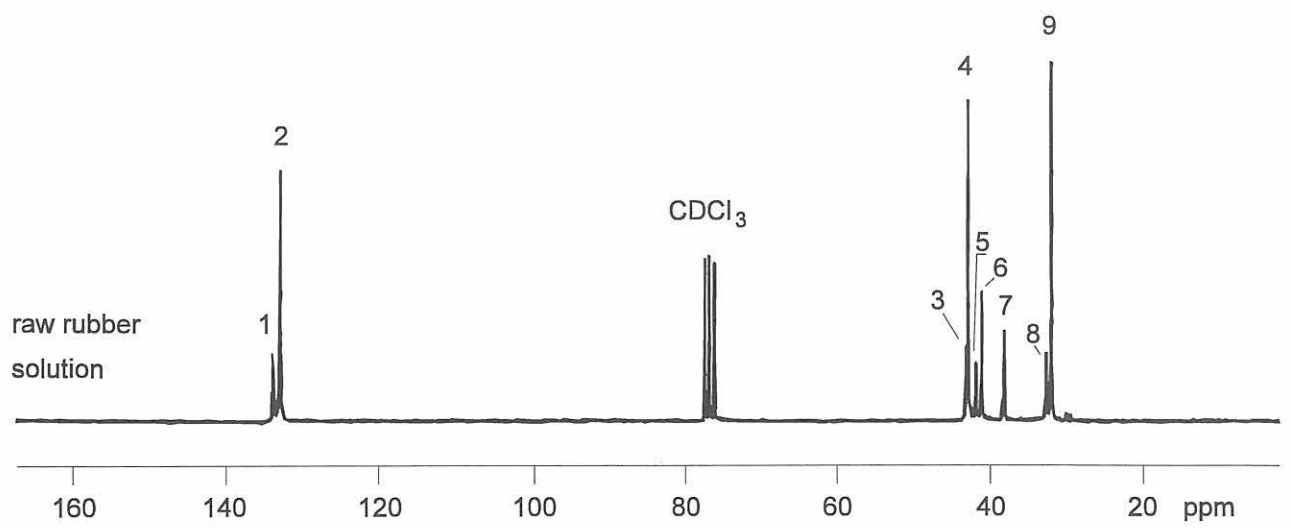
## Assignments<sup>1,2</sup>:

signal	1: $C_{\delta}(c)$	6: $C_{\gamma}(t, t)$
	2: $C_{\delta}(t)$	7: $C_{\beta}(c, t)$
	3: $C_{\beta}(t, c)$	8: $C_{\alpha}(c, t)$
	4: $C_{\beta}(t, t)$	9: $C_{\alpha}(t, t), C_{\alpha}(t, c)$
	5: $C_{\gamma}(t, c), C_{\gamma}(c, t)$	

## References:

<sup>1</sup> K. J. Ivin, D. T. Lavery and J. J. Rooney, *Makromol. Chem.* 178, 1545 (1977); *ibid.* 179, 253 (1978)

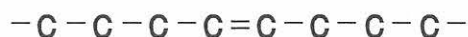
<sup>2</sup> M. F. Llauro-Darricades, J. P. Planche, A. Revillon and A. Guyot, *Polymer* 28, 1277 (1987)



# POLYOCTENAMER

## 1. Polyoctenamer, 80% trans units (according to specification)

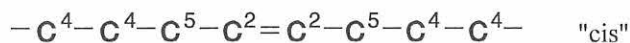
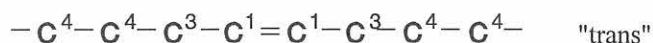
Polyoctenamer is produced by a ring-opening polymerization of cyclooctene:



The polymers can differ in the cis/trans ratio. Higher trans content means higher degree of crystallization. Another aspect of application is the low viscosity at processing temperature. Polyoctenamer is mainly used in formulations with other rubbers.

The standard type of polyoctenamer rubber has a trans content of about 80%. The different isomers can easily be distinguished. The interpretation is based on the assignments of the spectrum of polypentenamer<sup>1,2</sup>. Increment calculations can also be used. Carbons  $\beta$  and  $\gamma$  from the double bond are slightly different in both units. This explains the different chemical shifts at 30 ppm.

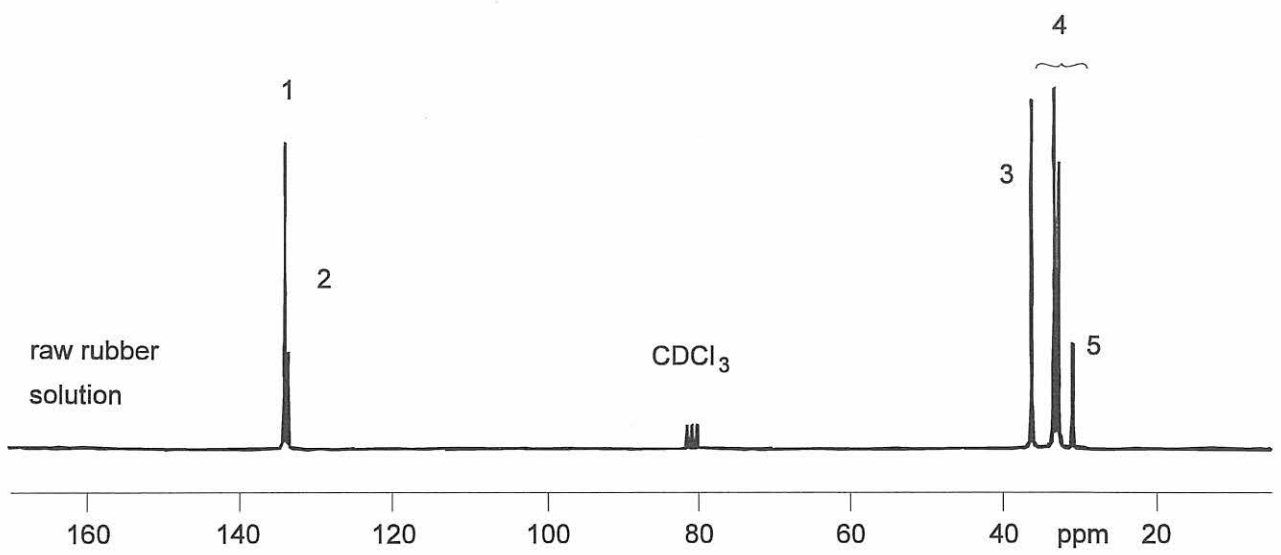
### Assignments:



### References:

<sup>1</sup> C. J. Carman and C. E. Wilkes, *Macromolecules* 7, 40 (1974)

<sup>2</sup> H. Y. Chen, *J. Polym. Sci., Polym. Lett. Ed.* 12, 85 (1974)



# POLYOCTENAMER

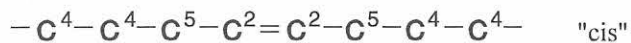
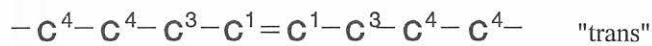
## 2. Polyoctenamer, 60% trans units (according to specification)

Polyoctenamer with a lower content of trans units has a lower degree of crystallinity. Therefore the strengthening effect in blends is smaller. The rheological properties at the temperature of processing are nearly the same.

Sometimes this type can be a better choice than the standard one.

The interpretation of the spectrum is straightforward; all cis signals have higher intensities.

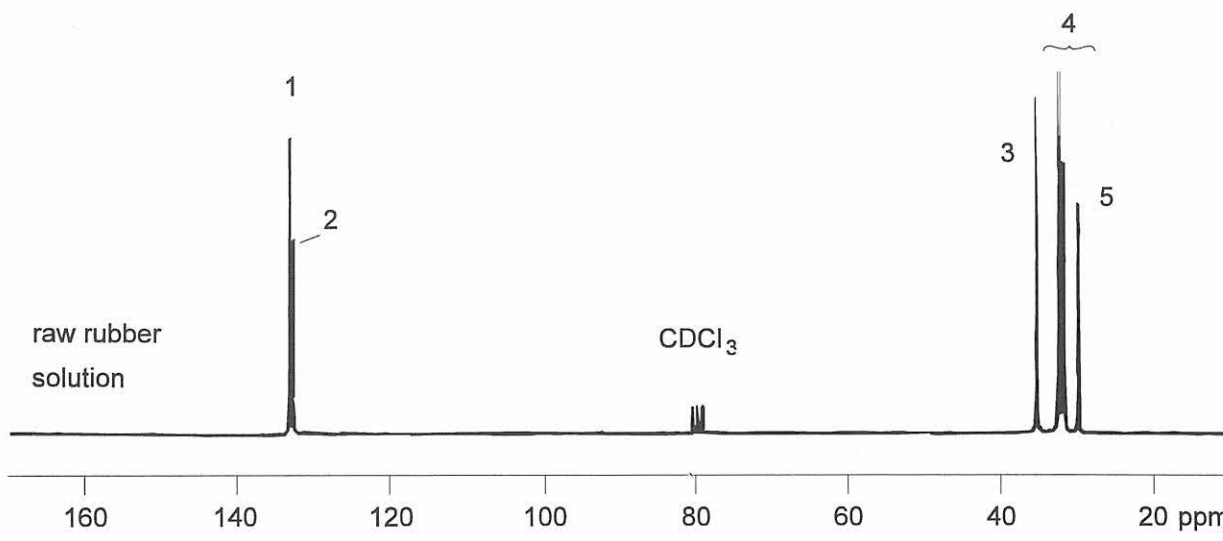
### Assignments<sup>1</sup>:



### References:

<sup>1</sup> see references of polyoctenamer, example 1



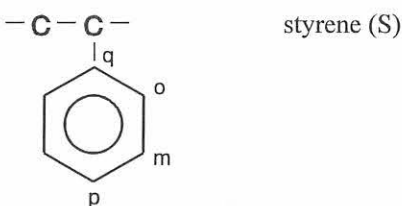
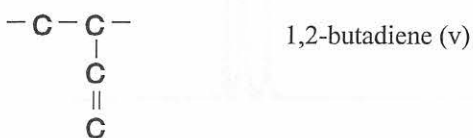
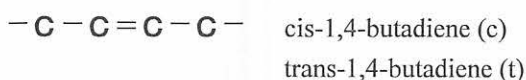


# STYRENE-BUTADIENE RUBBER (SBR)

## 1. E-SBR with 23,5% styrene (according to specification)

Styrene-butadiene rubber is a multi-purpose rubber. The applications are widely spread, but the use for tyres is most important. This is the reason why SBR is the main synthetic rubber. The copolymerization is normally performed in emulsion (E-SBR), in combination with stereo-specific catalysts, however, the solution process is also used (S-SBR).

Four structure units can be distinguished: three isomers of butadiene and styrene:



The sequence structure of SBR was first studied by Katritzky<sup>1</sup> and Segre<sup>2</sup>. Recent papers put forward some new points of view about the interpretation and give more detailed assignments<sup>3,4</sup>. According to reference 1 the spectrum is explained on the basis of different diads.

The assignments refer to the first or last atom of the underlined structure unit, adjacent to the second unit in the diad. The spectrum corresponds to the standard type of SBR, the main configuration of butadiene is trans-1,4-butadiene.

### Assignments<sup>1</sup>:

signal	1:	$\text{C}_q$ (S)	11:	$\text{CH}$ ( <u>vt</u> , <u>vc</u> )
	2:	$=\text{CH}$ (v)	12:	$\text{CH}_2$ ( <u>St</u> ), $\text{CH}$ ( <u>SS</u> , <u>sv</u> )
	3:	$=\text{CH}$ ( <u>St</u> , <u>vt</u> , <u>Sc</u> , <u>vc</u> )	13:	$\text{CH}_2$ ( <u>vt</u> )
	4:	$=\text{CH}$ ( <u>tt</u> , <u>tc</u> , <u>tt</u> , <u>ct</u> )	14:	$\text{CH}_2$ ( <u>tS</u> , <u>cS</u> )
	5:	$=\text{CH}$ ( <u>cc</u> , <u>ct</u> , <u>cc</u> , <u>tc</u> )	15:	$\text{CH}_2$ ( <u>tv</u> , <u>cv</u> )
	6, 7:	$\text{C}_o$ , $\text{C}_m$ (S), $=\text{CH}$ ( <u>tS</u> , <u>tv</u> , <u>cS</u> , <u>cv</u> )	16:	$\text{CH}_2$ ( <u>tt</u> , <u>tc</u> , <u>tt</u> , <u>ct</u> )
	8:	$\text{C}_p$ (S)	17, 18:	$\text{CH}_2$ ( <u>tS</u> , <u>tv</u> )
	9:	$=\text{CH}_2$ (v)	19:	$\text{CH}_2$ ( <u>cc</u> , <u>ct</u> , <u>cc</u> , <u>tc</u> )
	10:	$\text{CH}$ ( <u>St</u> , <u>Sc</u> )		

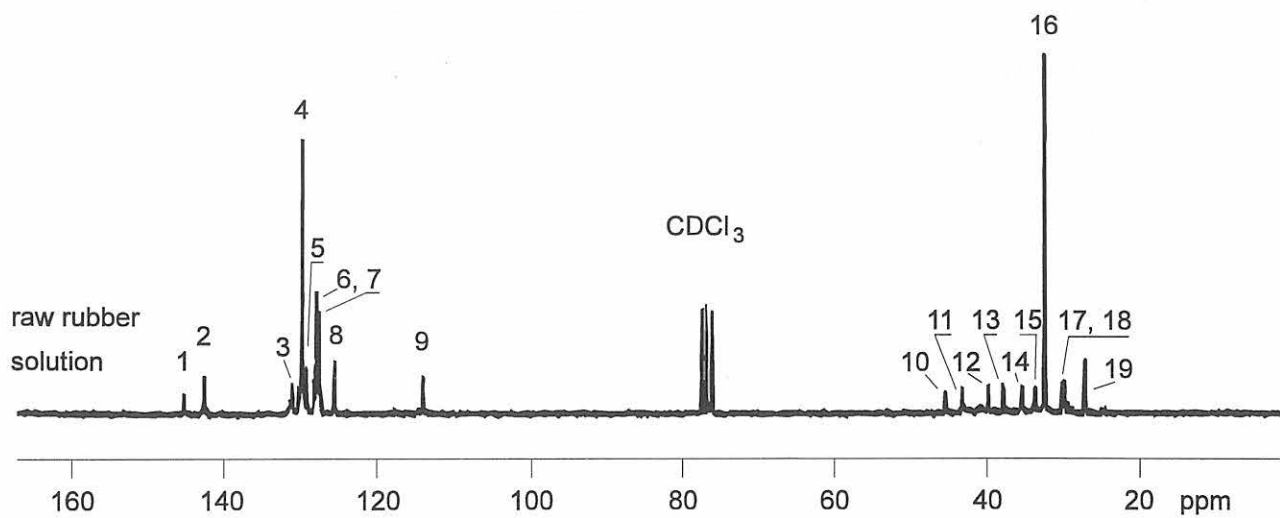
### References:

<sup>1</sup> A. R. Katritzky and D. E. Weiss, J. Chem. Soc., Perkin II 1975, 21 (1975); *ibid.* 1975, 27 (1975)

<sup>2</sup> A. L. Segre, M. Delfini, F. Conti and A. Boicelli, Polymer 16, 338 (1975)

<sup>3</sup> H. Sato, T. Ishikawa, K. Takebayashi and Y. Tanaka, Macromolecules 22, 1748 (1989)

<sup>4</sup> S. Jiao, X. Chen, L. Hu and B. Yan, Chin. J. Polym. Sci. 8, 17 (1990); *ibid.* 8, 25 (1990); *ibid.* 8, 269 (1990)



# STYRENE-BUTADIENE RUBBER (SBR)

## 2. E-SBR with 30% styrene (according to specification)

The standard SBR has a glass transition temperature of  $-50^{\circ}\text{C}$ . With increasing styrene content the temperature goes up and the elasticity decreases. But on the other hand the processing properties are improved.

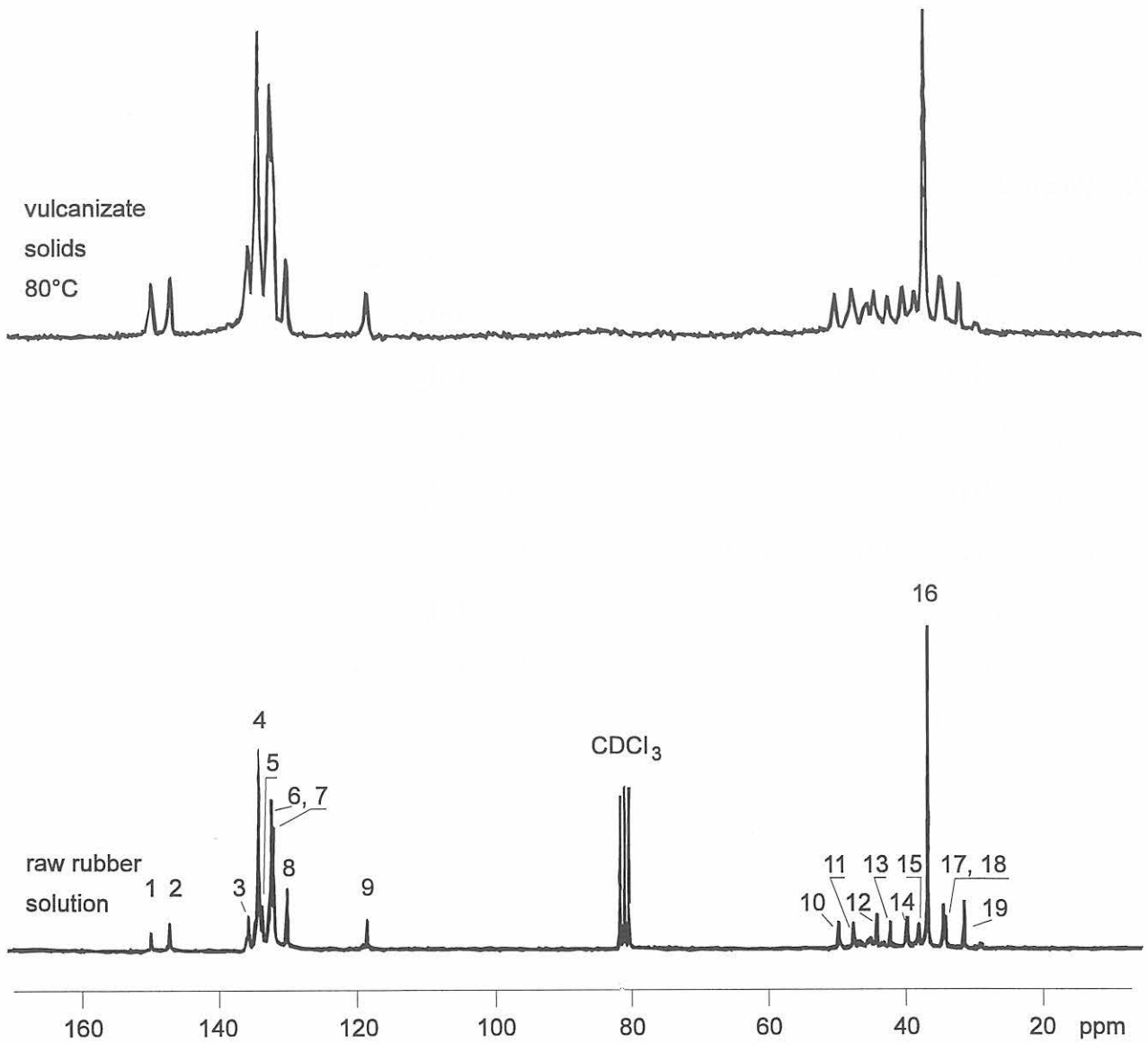
The explanation of the spectrum is the same as for example 1. The intensities of the styrene signals go up, e.g., of the signals 1, 6, 7, 8, 10, 12, 14. The configuration of butadiene seems to be same, trans units are dominating.

### Assignments<sup>1</sup>:

signal	1:	$\text{C}_q$ (S)	11:	$\text{CH}$ ( <u>vt</u> , <u>vc</u> )
	2:	$=\text{CH}$ (v)	12:	$\text{CH}_2$ (St), $\text{CH}$ ( <u>SS</u> , <u>sv</u> )
	3:	$=\text{CH}$ (St, <u>vt</u> , <u>Sc</u> , <u>vc</u> )	13:	$\text{CH}_2$ ( <u>vt</u> )
	4:	$=\text{CH}$ ( <u>tt</u> , <u>tc</u> , <u>tt</u> , <u>ct</u> )	14:	$\text{CH}_2$ ( <u>tS</u> , <u>cS</u> )
	5:	$=\text{CH}$ ( <u>cc</u> , <u>ct</u> , <u>cc</u> , <u>tc</u> )	15:	$\text{CH}_2$ ( <u>ty</u> , <u>cv</u> )
	6, 7:	$\text{C}_o$ , $\text{C}_m$ (S), $=\text{CH}$ ( <u>tS</u> , <u>tv</u> , <u>cS</u> , <u>cv</u> )	16:	$\text{CH}_2$ ( <u>tt</u> , <u>tc</u> , <u>tt</u> , <u>ct</u> )
	8:	$\text{C}_p$ (S)	17, 18:	$\text{CH}_2$ ( <u>tS</u> , <u>tv</u> )
	9:	$=\text{CH}_2$ (v)	19:	$\text{CH}_2$ ( <u>cc</u> , <u>ct</u> , <u>cc</u> , <u>tc</u> )
	10:	$\text{CH}$ ( <u>St</u> , <u>Sc</u> )		

### References:

<sup>1</sup>see references of SBR, example 1



# STYRENE-BUTADIENE RUBBER (SBR)

## 3. E-SBR with 40% styrene (according to specification)

The high styrene SBR types have styrene contents up to 40%. The change of properties is described already for example 2.

The aromatic part of styrene in the copolymer spectrum is the same as of polystyrene, the aliphatic part is different,

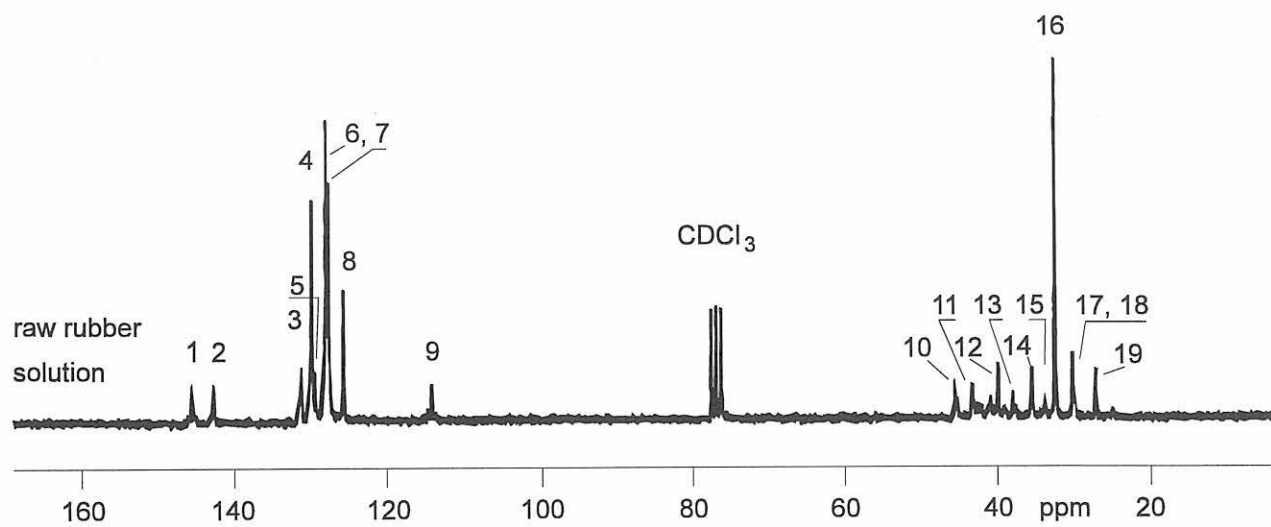
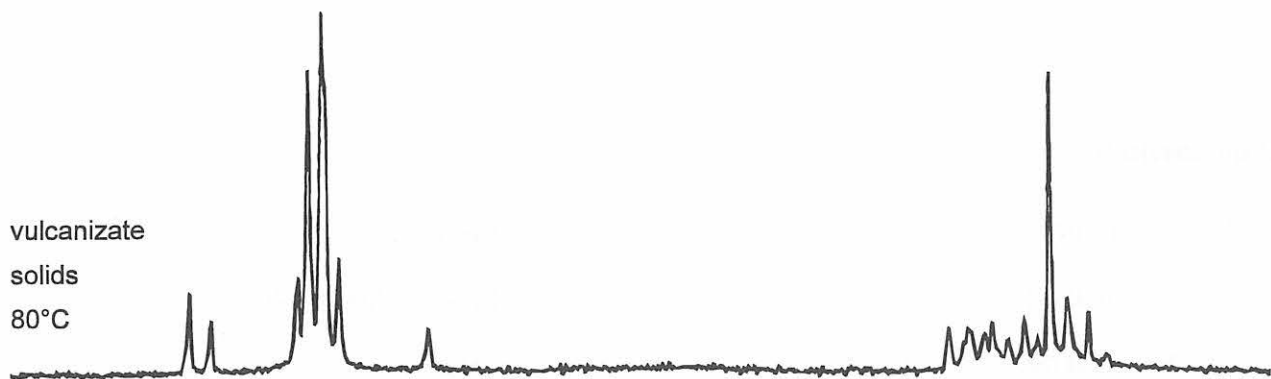
as expected. In the aliphatic region additional resonances come into play. They should be due to the stereosequences of styrene units and triad or higher sequences of the structure units.

### Assignments<sup>1</sup>:

signal	1: C <sub>q</sub> (S)	11: CH ( <u>vt</u> , <u>vc</u> )
	2: =CH (v)	12: CH <sub>2</sub> (St), CH ( <u>SS</u> , <u>Sv</u> )
	3: =CH (St, vt, Sc, vc)	13: CH <sub>2</sub> (vt)
	4: =CH (tt, tc, tt, ct)	14: CH <sub>2</sub> (tS, cS)
	5: =CH (cc, ct, cc, tc)	15: CH <sub>2</sub> (tv, cv)
6, 7:	C <sub>o</sub> , C <sub>m</sub> (S), =CH (tS, tv, cS, cv)	16: CH <sub>2</sub> (tt, tc, tt, ct)
	8: C <sub>p</sub> (S)	17, 18: CH <sub>2</sub> (tS, tv)
	9: =CH <sub>2</sub> (v)	19: CH <sub>2</sub> (cc, ct, cc, tc)
	10: CH (St, Sc)	

### References:

<sup>1</sup>see references of SBR, example 1



# STYRENE-BUTADIENE RUBBER (SBR)

## 4. S-SBR with 18% styrene (according to specification)

S-SBR is produced by using special stereospecific catalysts. Very different products can be achieved: block- and statistical copolymers, and the ratio of butadiene structure units can vary considerably.

This copolymer has a statistical distribution of monomer units. The cis content is relatively high. Except for the cis peaks 5 and 19 the spectrum is very similar to the others.

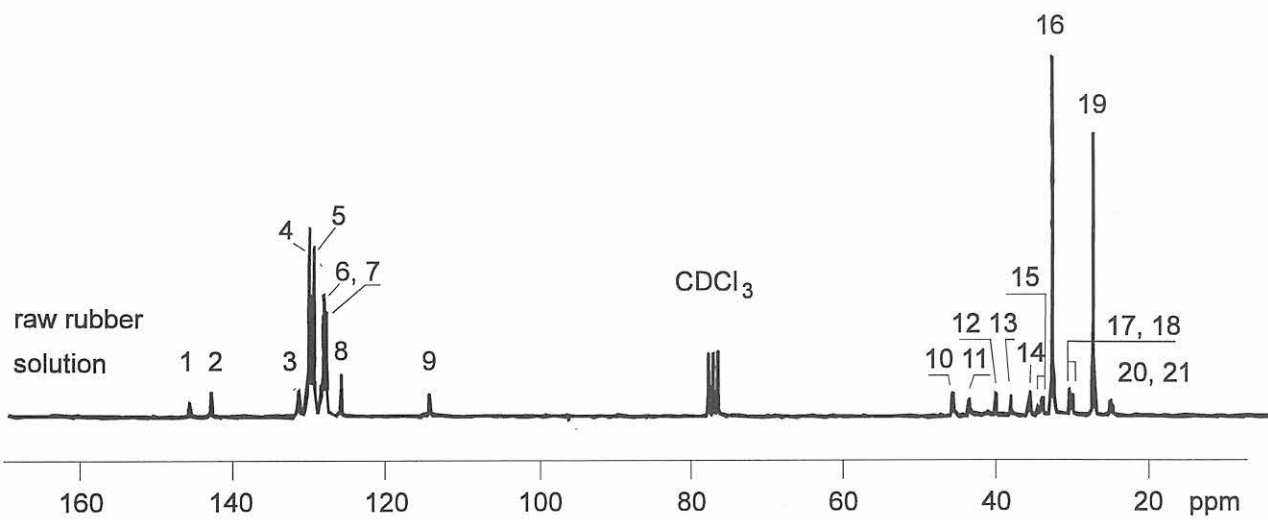
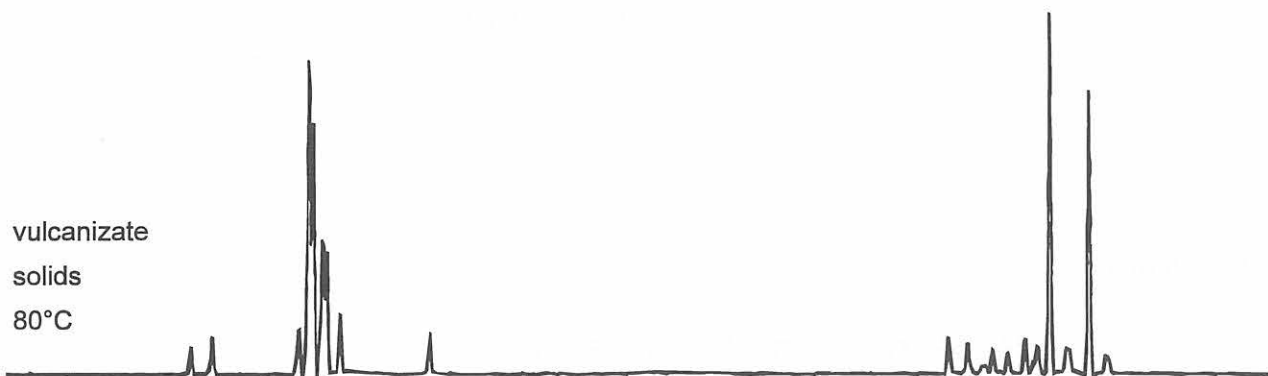
### Assignments<sup>1</sup>:

signal	1: $C_q$ (S)	11: $CH$ ( $\underline{vt}$ , $\underline{vc}$ )
	2: $=CH$ ( $\underline{v}$ )	12: $CH_2$ ( $\underline{St}$ ), $CH$ ( $\underline{SS}$ , $\underline{Sv}$ )
	3: $=CH$ ( $\underline{St}$ , $\underline{vt}$ , $\underline{Sc}$ , $\underline{vc}$ )	13: $CH_2$ ( $\underline{vt}$ )
	4: $=CH$ ( $\underline{tt}$ , $\underline{tc}$ , $\underline{tt}$ , $\underline{ct}$ )	14: $CH_2$ ( $\underline{tS}$ , $\underline{cS}$ )
	5: $=CH$ ( $\underline{cc}$ , $\underline{ct}$ , $\underline{cc}$ , $\underline{tc}$ )	15: $CH_2$ ( $\underline{tv}$ , $\underline{cv}$ )
6, 7:	$C_o$ , $C_m$ (S), $=CH$ ( $\underline{tS}$ , $\underline{tv}$ , $\underline{cS}$ , $\underline{cv}$ )	16: $CH_2$ ( $\underline{tt}$ , $\underline{tc}$ , $\underline{tt}$ , $\underline{ct}$ )
	8: $C_p$ (S)	17, 18: $CH_2$ ( $\underline{tS}$ , $\underline{tv}$ )
	9: $=CH_2$ ( $\underline{v}$ )	19: $CH_2$ ( $\underline{cc}$ , $\underline{ct}$ , $\underline{cc}$ , $\underline{tc}$ )
	10: $CH$ ( $\underline{St}$ , $\underline{Sc}$ )	20, 21: $CH_2$ ( $\underline{cS}$ , $\underline{cv}$ )

### References:

<sup>1</sup>see references of SBR, example 1

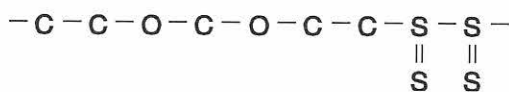




## POLYSULFIDE RUBBER (OT)

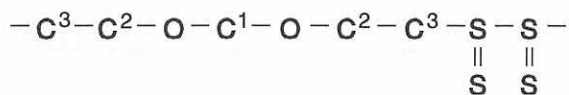
Polysulfide rubbers have an excellent resistance to swelling by aromatic hydrocarbons, ketones or chlorinated hydrocarbons. Furthermore they are resistant to weather and ozone. The mechanical properties, however, are not satisfactory<sup>1</sup>.

T rubbers have carbon, oxygen and sulfur in the chain<sup>2</sup>:



Alternative T rubbers have ethylene groups between the sulfur bridges additionally (EOT). The main signals of the spectrum can be explained readily. The small peaks may be partly due to end groups.

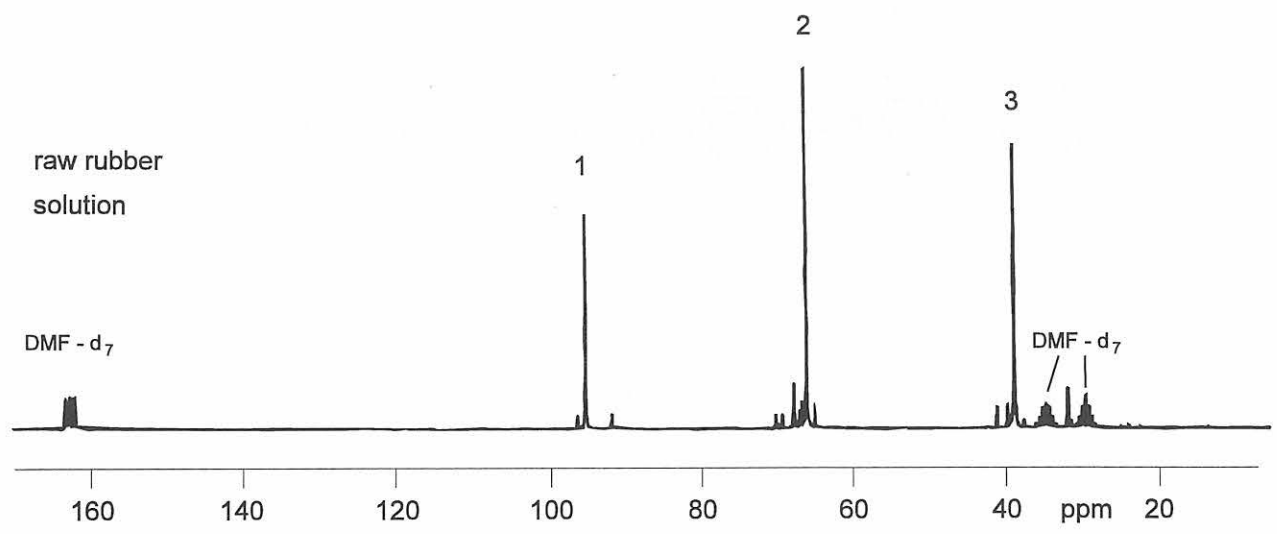
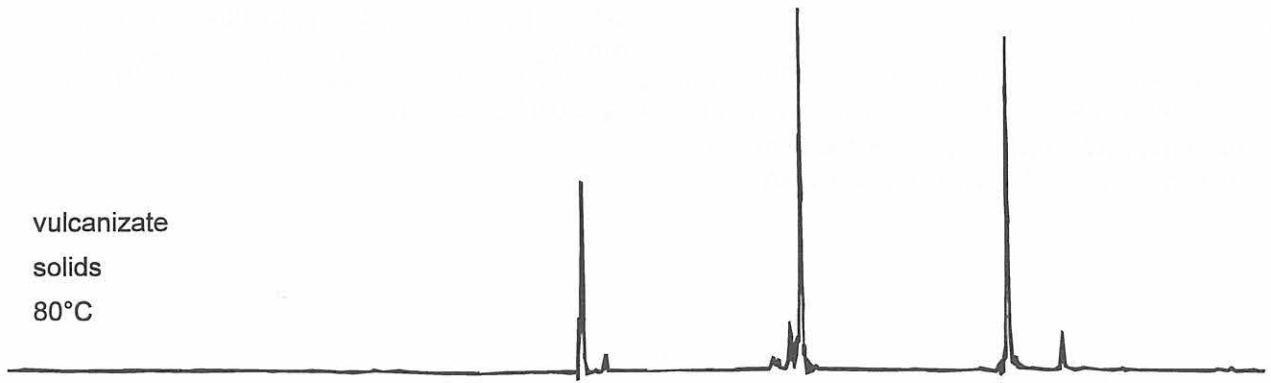
### Assignments:



### References:

<sup>1</sup> W. Hofmann, "Kautschuk-Technologie", Gentner-Verlag, Stuttgart, 1980

<sup>2</sup> D. Hummel, "Kunststoff-, Lack- und Gummi-Analyse, Textband", Carl-Hanser-Verlag, München, 1958



# URETHANE RUBBER (U)

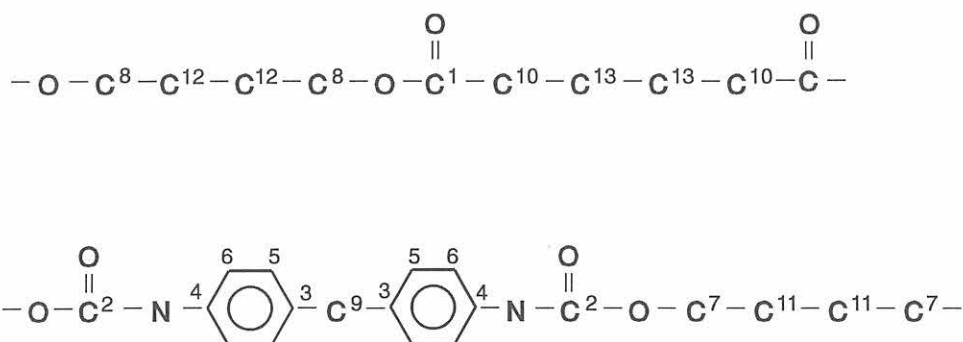
## 1. Polyester urethane rubber (AU)

Urethane rubbers are polyurethanes based on polyesters or polyethers (AU, EU). In these elastomers polyester or polyether chains are linked together by urethane units repeatedly. According to the variety of starting materials, polyurethanes behave very different. They can be thermoplastic polymers, thermoplastic elastomers, elastomers or duroplastic polymers<sup>1</sup>.

Urethane rubbers can be prepared by the reaction of a diisocyanate with either a hydroxyterminated polyester or polyether to produce a prepolymer, followed by reaction of the prepolymer with a diamine or diol chain extender.

In this example diphenylmethane diisocyanate, polytetramethylene adipate and butanediol are used. The polyesters form the soft, flexible phase, the diisocyanate and the chain extender butanediol the hard phase. The spectra correspond to each other, but the intensities of the hard phase signals are very much reduced in the solid state spectrum. The CH<sub>2</sub> resonance of the diisocyanate appears completely suppressed. In the solution spectrum it is hidden under the solvent resonance. By the DEPT experiment it can be revealed.

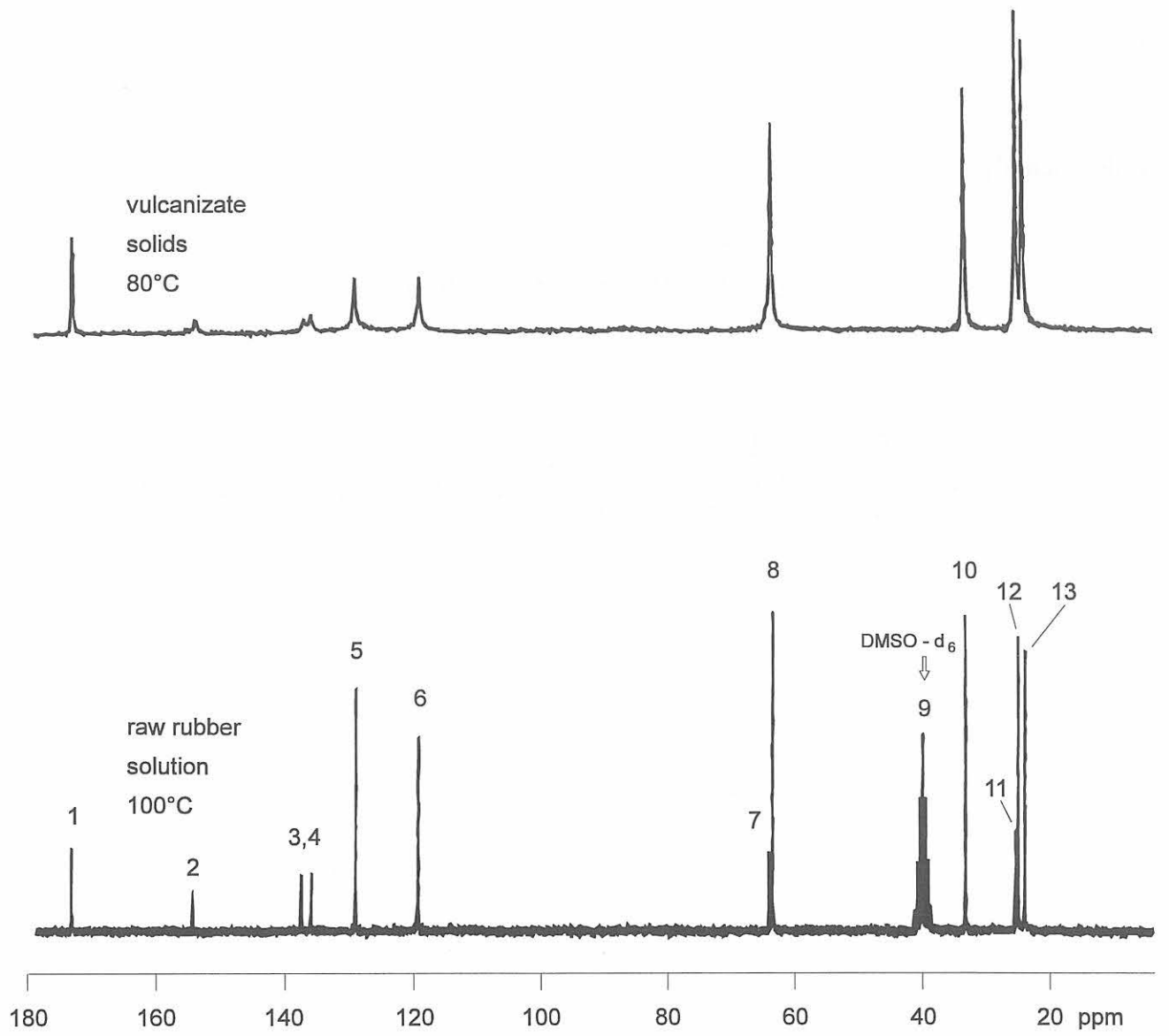
### Assignments<sup>2,3</sup>:



### References:

- <sup>1</sup> T. Timm, *Kautsch., Gummi, Kunstst.* 35, 568 (1982)  
<sup>2</sup> C. Delides, R. A. Pethrick, A. V. Cunliffe, P. G. Klein, *Polymer* 22, 1205 (1981)

- <sup>3</sup> K. H. Matthews, I. McLennaghan and R. A. Pethrick, *Brit. Polym. J.* 19, 165 (1987)



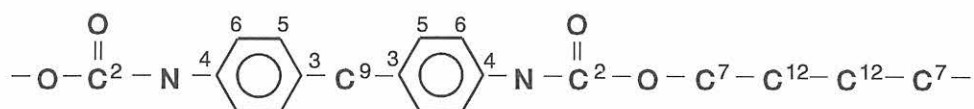
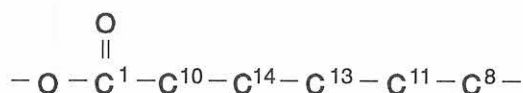
# URETHANE RUBBER (U)

## 2. Polyester urethane rubber (AU)

This urethane rubber consists of polycaprolactone, diphenylmethane, diisocyanate, butanediol and additional components. Polycaprolactone forms the soft phase - as for example 1 - the diisocyanate and butanediol the hard

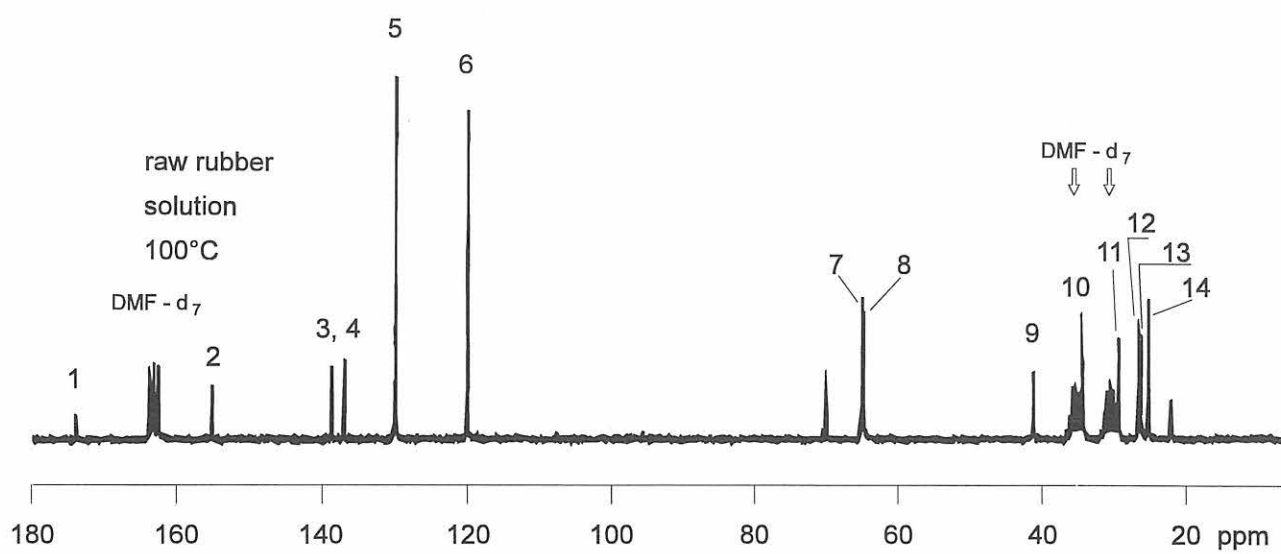
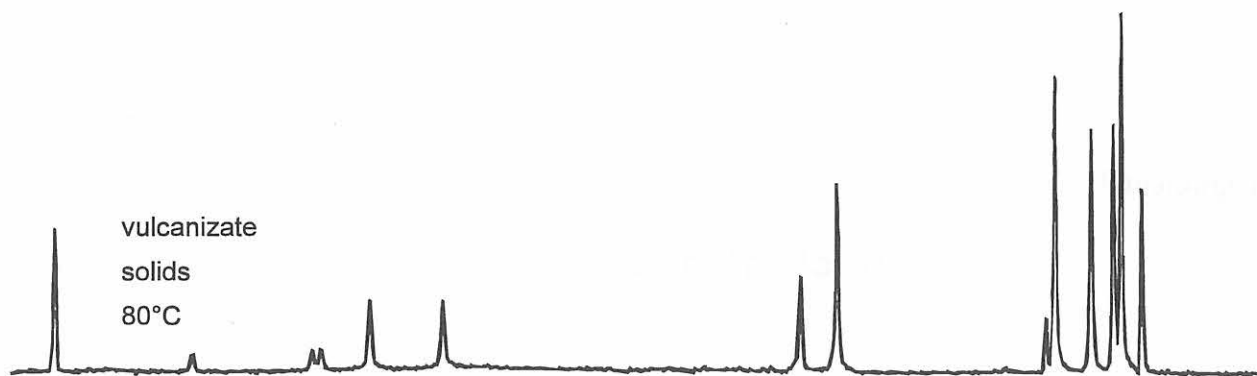
phase. Due to the different solvent the CH<sub>2</sub> resonance of the diisocyanate is free from overlapping. As in the foregoing example the hard phase signals have reduced intensities in the solid state spectrum.

### Assignments<sup>1</sup>:



### References:

<sup>1</sup> see references of AU, example 1



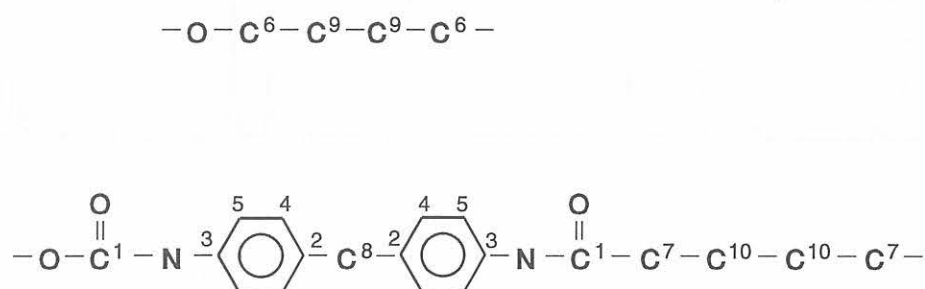
# URETHANE RUBBER (U)

## 3. Polyether urethane rubber (EU)

The polyester can be replaced by a polyether. In this example polytetramethylene oxide is used. The hard phase is again formed by diphenylmethane diisocyanate and butanediol. As for example 1 the CH<sub>2</sub> resonance of the

diisocyanate is hidden under the solvent peak. The intensity decrease of the hard phase signals in the solid state spectrum is even more pronounced than for the AU examples.

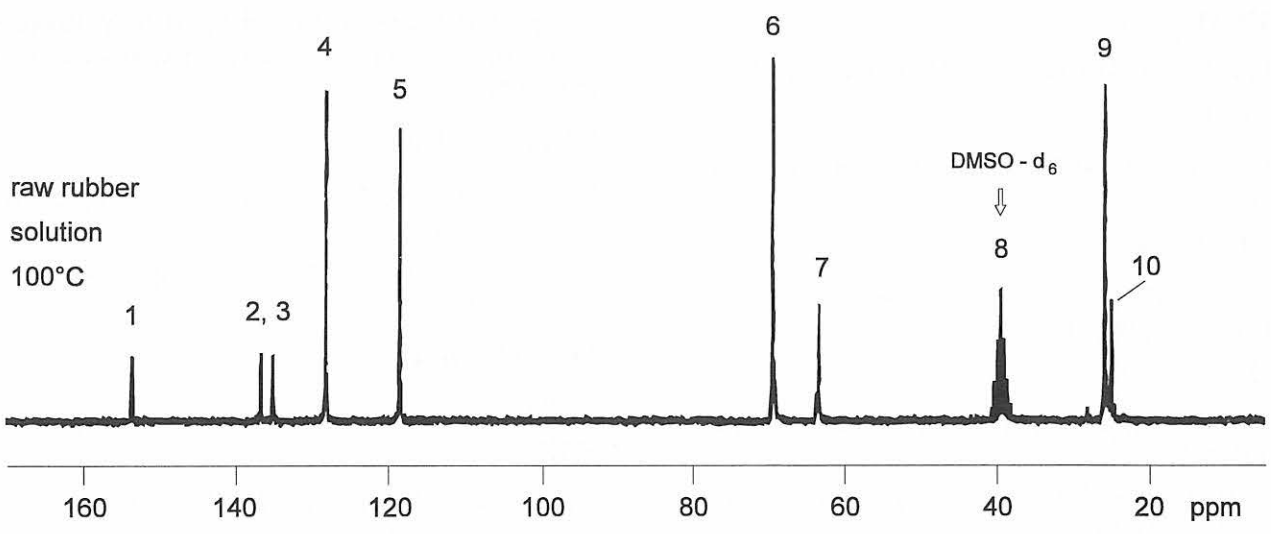
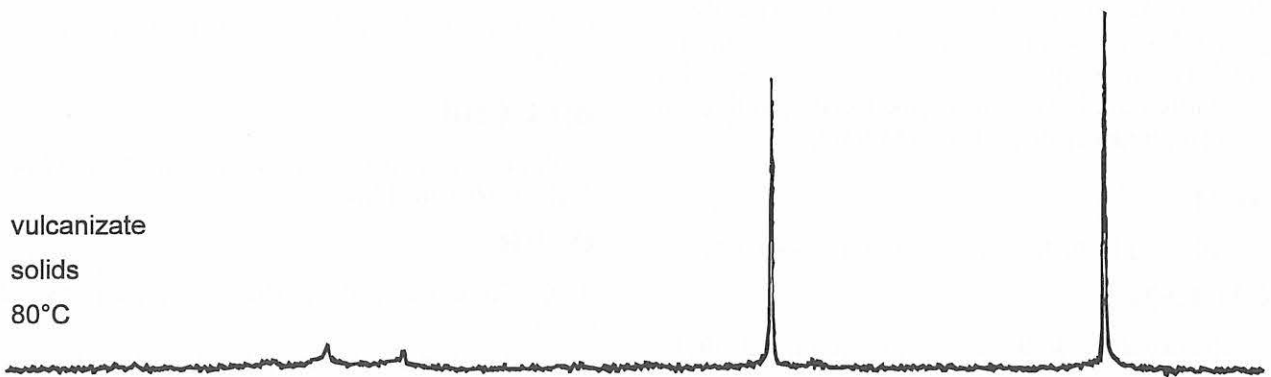
### Assignments<sup>1</sup>:



### References

<sup>1</sup> see references of AU, example 1





## 5. <sup>1</sup>H-NMR Spectra of Raw Rubbers

The spectra catalogue is completed by <sup>1</sup>H-NMR spectra. For the measurements the same samples were used as for the carbon spectra described in the main part. No effort has been undertaken to make small differences visible, as for , e.g., IIR, CIIR and BIIR or EPM and EPDM. The spectra only represent the main structures of the polymer. An interpretation is not given explicitly as proton NMR spectra are not the main aim of this brochure. In many cases the assignments are rather straightforward. Nevertheless some literature is listed as an aid for interpretation, whenever known.

### ACM

F. Keller and H. Roth, *Plaste Kautsch.* 19, 566 (1972)

### CM, CSM

W. Heintke and F. Keller, *Plaste Kautsch.* 18, 732 (1971)

### EPM

C. J. Carman and K. C. Baranwal, *Rubber Chem. Technol.* 48, 705 (1975)

### EPDM

A. G. Altenau, L. M. Headley, C. O. Jones and H. C. Ransaw, *Anal.Chem.* 42, 1280 (1970)

### EVM

F. Keller, *Plaste Kautsch.* 18, 657 (1971)

### FPM

E. G. Brame and F. W. Yeager, *Anal. Chem.* 48, 709 (1976)

### CO, ECO

K.-J.Liu, *Makromol. Chem.* 116, 146 (1968)

F. F.-L. Ho, *Polym.Lett. Ed.* 9, 491 (1971)

### Q

G. Engelhardt and H. Jancke, *J. Organomet. Chem.* 28, 293 (1971)

X. H. Zhang and R. West, *J. Polym. Sci., Polym. Lett. Ed.* 23, 479 (1985)

F. C.Schilling, F. A. Bovey and J. M. Zeigler, *Polym. Mater. Sci. Eng.* 54, 475 (1986)

### BR

Y. Tanaka, Y. Takeuchi, M. Kobayashi and H. Tadokoro, *J. Polym. Sci., Polym. Phys. Ed.* 9, 43 (1971)

### CR

R. C. Ferguson, *J. Polym. Sci., Polym. Chem. Ed.* 2, 4735 (1964)

T. Okada and T. Ikushige, *J. Polym. Sci., Polym. Chem. Ed.* 14, 2059 (1976)

### IIR

H. Y.Chen and J. E. Field, *Rubber Chem. Technol.* 42, 392 (1969)

C. Y. Chu and R. Vukow, *Macromolecules* 18, 1423 (1985)

### BIIR, CIIR

C. Y. Chu, K. N. Watson and R. Vukow, *Rubber Chem. Technol.* 60, 636 (1987)

### IR, NR

R .C. Ferguson, *Kautsch. Gummi, Kunstst.* 18, 723 (1965)

Y. Tanaka, Y. Takeuchi, M. Kobayshi and H. Tadokoro, *J. Polym. Sci., Polym. Phys. Ed.* 9, 43 (1971)

F. A. Bovey: "High Resolution NMR of Macromolecules", Academic Press, New York and London, 1972

### NBR, HNBR

N. A. Mohammadi and G. L. Rempel, *Macromolecules* 20, 2362 (1987)

A. Kondo, H. Ohtani, Y. Kosugi, S. Tsuge, Y. Kubo, N. Asada, H. Inaki and A. Yoshioka, *Macromolecules* 21, 2918 (1988)

### NR, epoxidized

D. R. Burfield, K.-L. Lim, K.-S. Law and S. Ng, *Polymer* 25, 995 (1984)

J. H. Bradbury and M. C. S. Perera, *J. Appl. Polym. Sci.* 30, 3347 (1985)

### Polyoctenamer

see BR

### SBR

W. L. Senn, *Anal. Chim. Acta* 29, 505 (1963)

V. D. Mochel, *Rubber Chem. Technol.* 40, 1200 (1967)

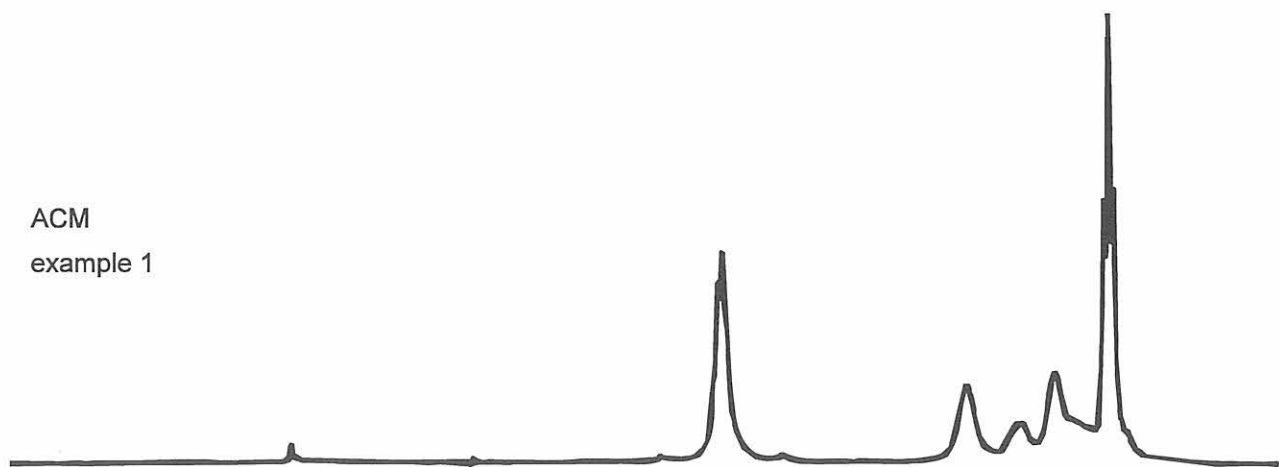
### AU, EU

E. G. Brame, R. C. Ferguson and G. J. Thomas, *Anal. Chem.* 39, 517 (1967)

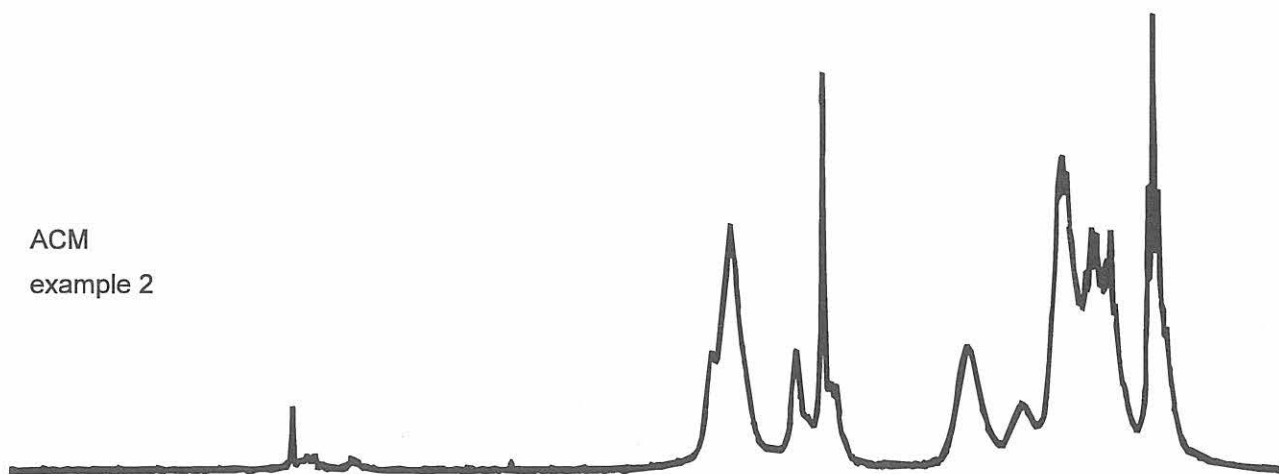
Y. Chokki, M. Nakabayashi and M. Sumi, *Makromol. Chem.* 153, 189 (1972)

K. H. Matthews, I. McLennaghan and R. A. Pethrick, *Brit. Polym. J.* 19, 165 (1987)

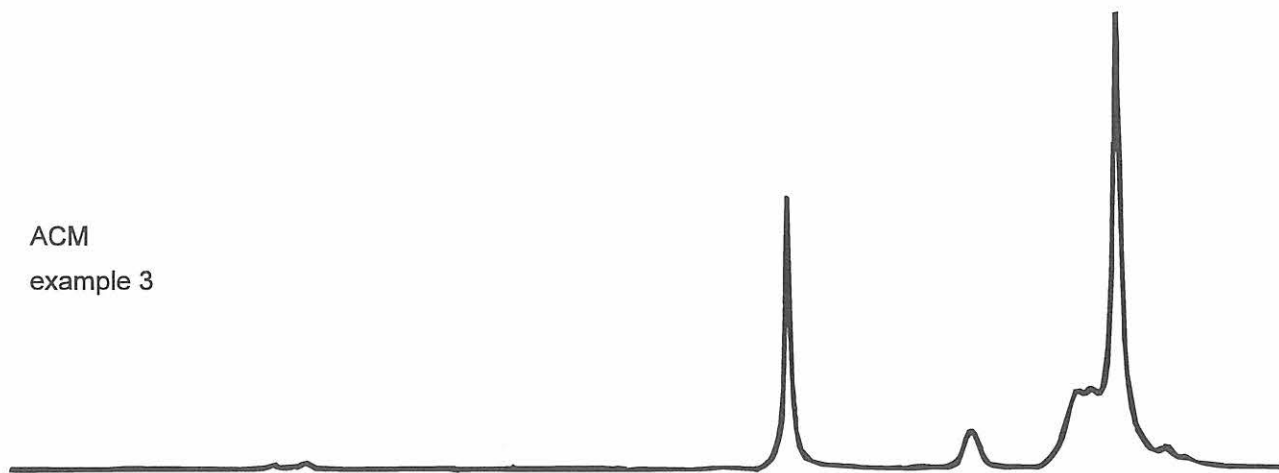
ACM  
example 1



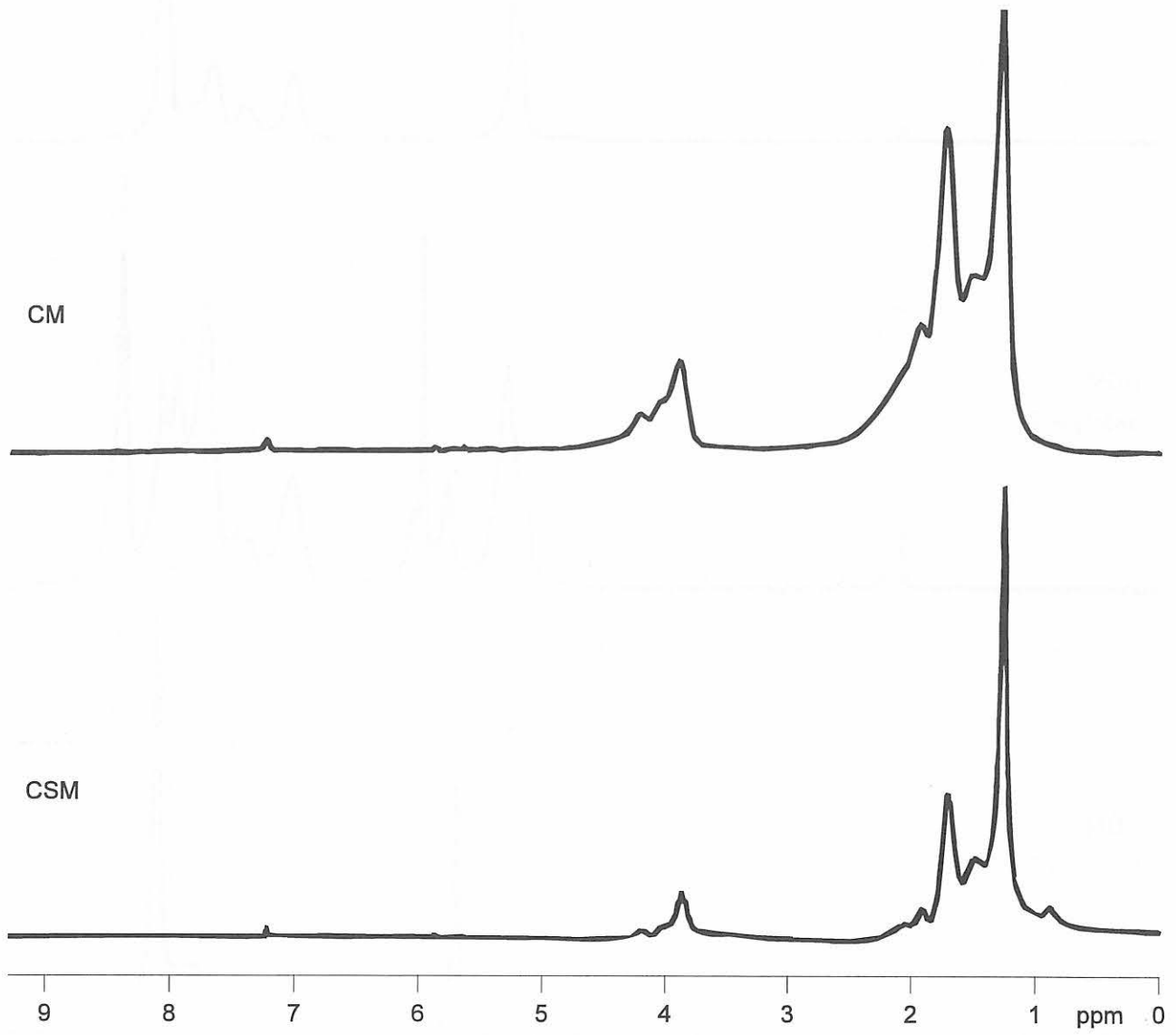
ACM  
example 2

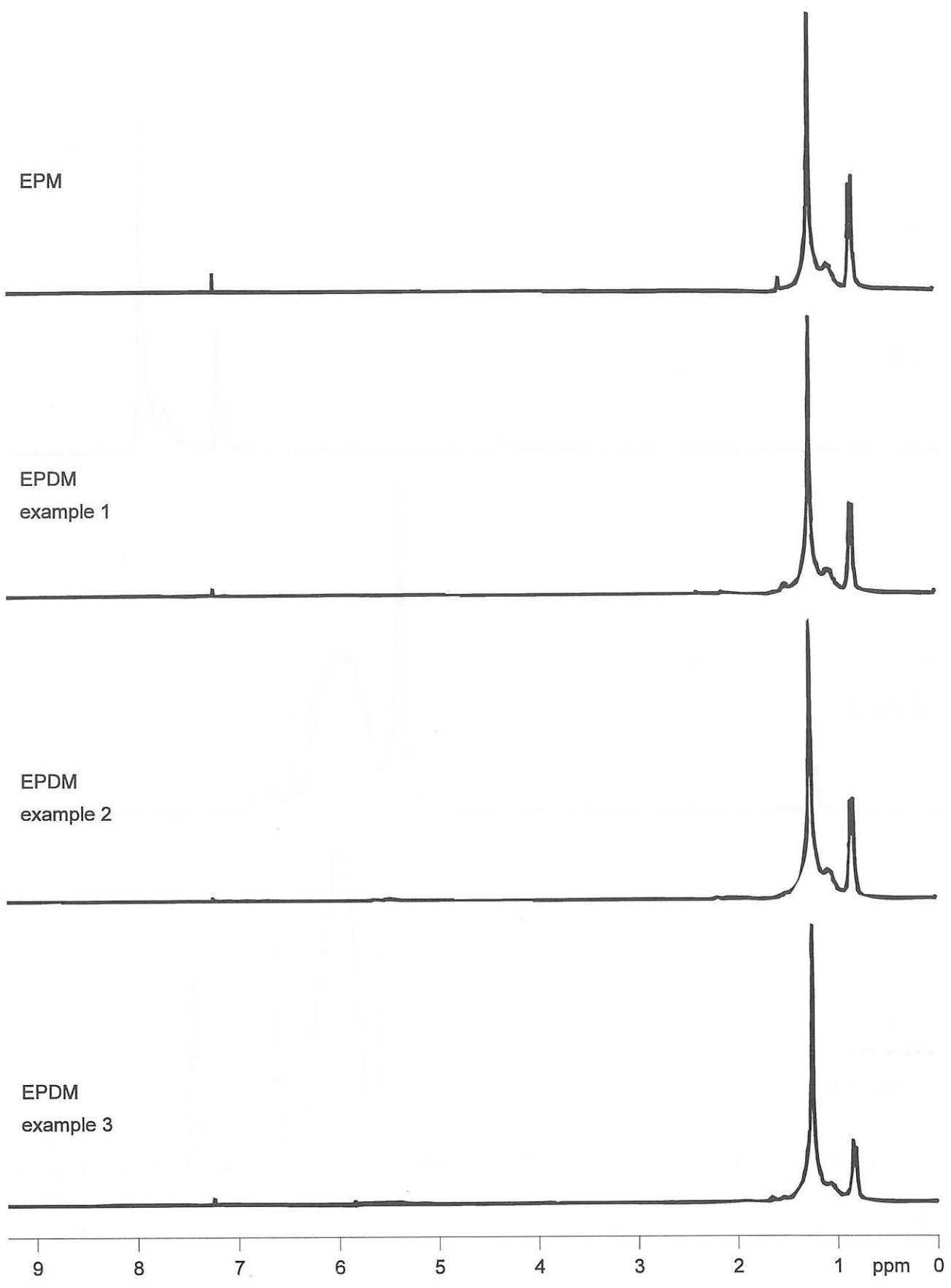


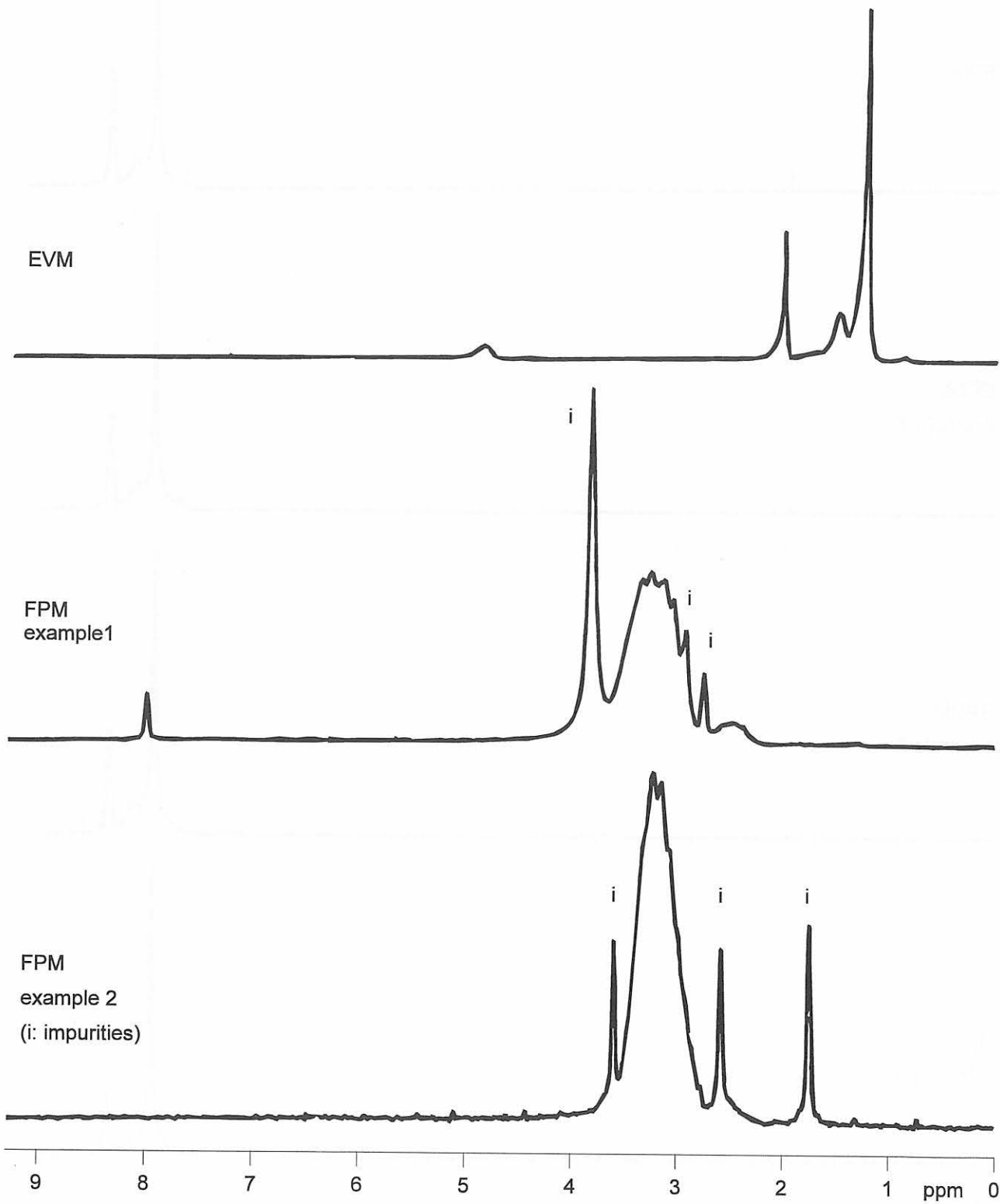
ACM  
example 3

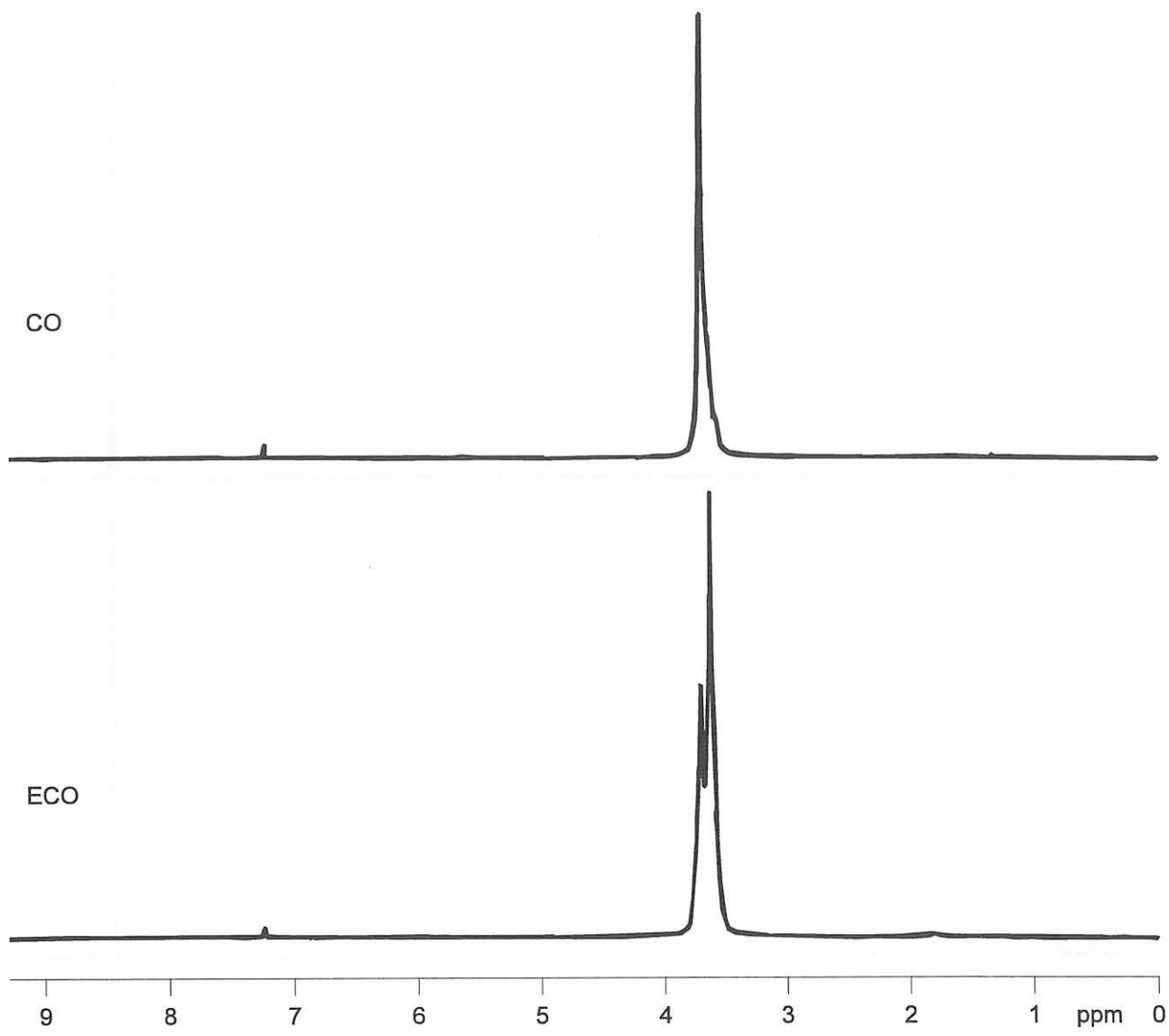


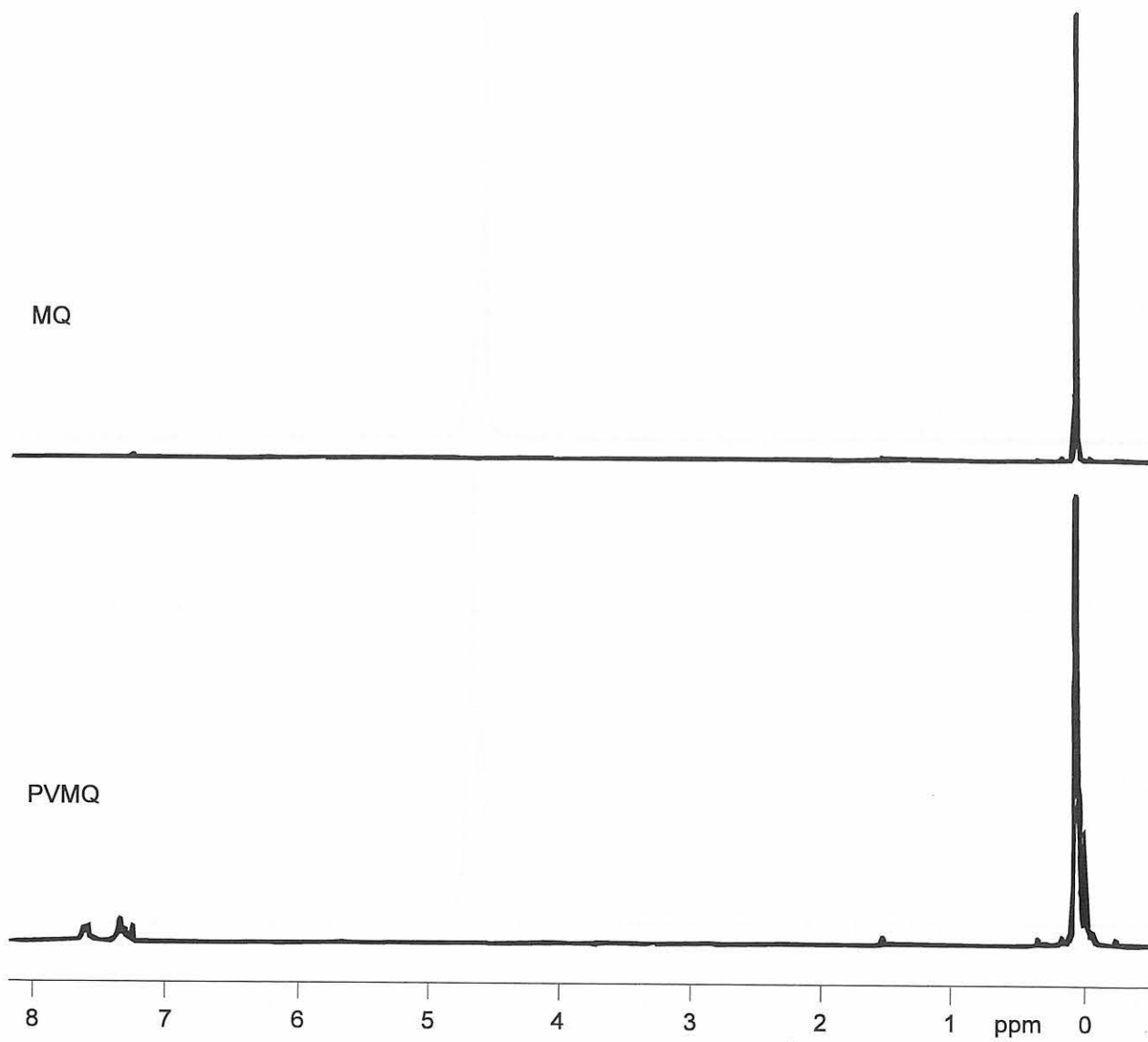
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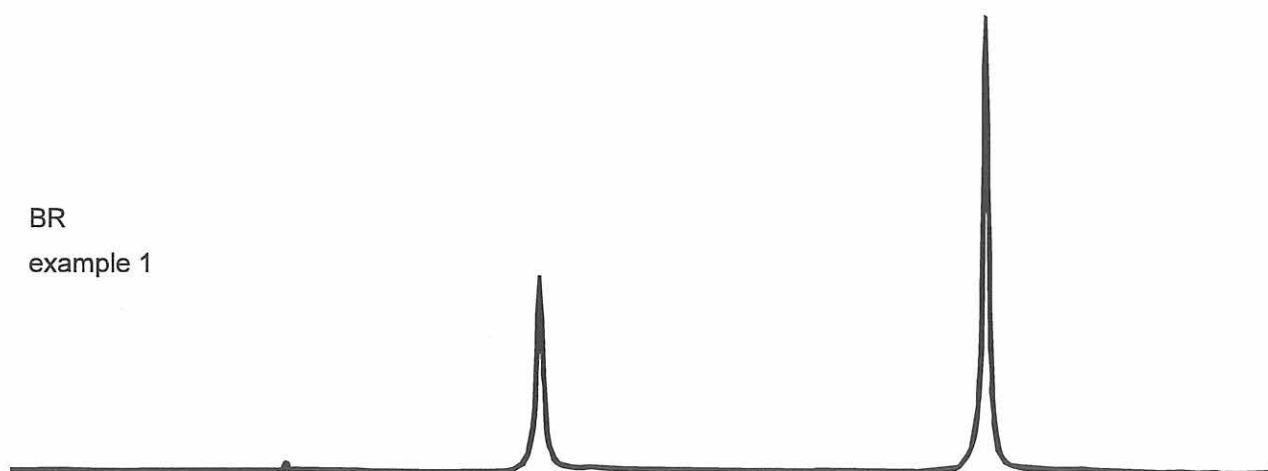




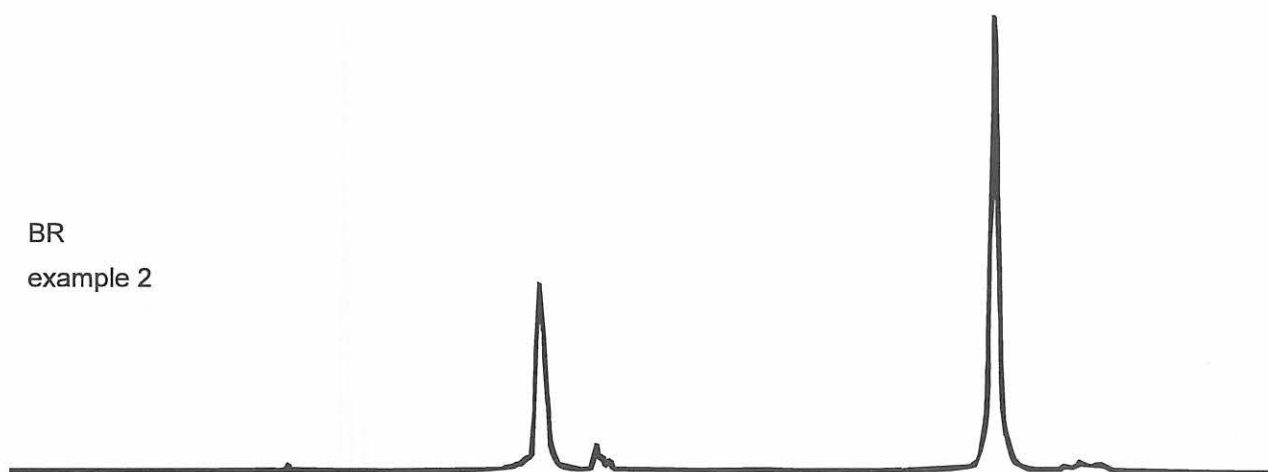




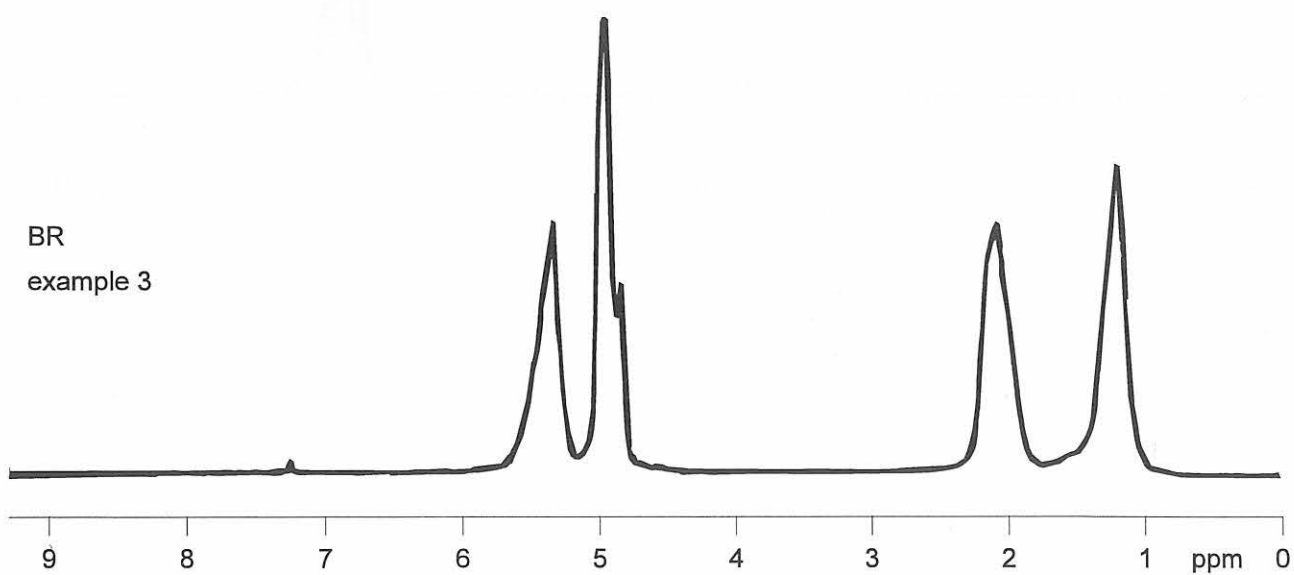
BR  
example 1

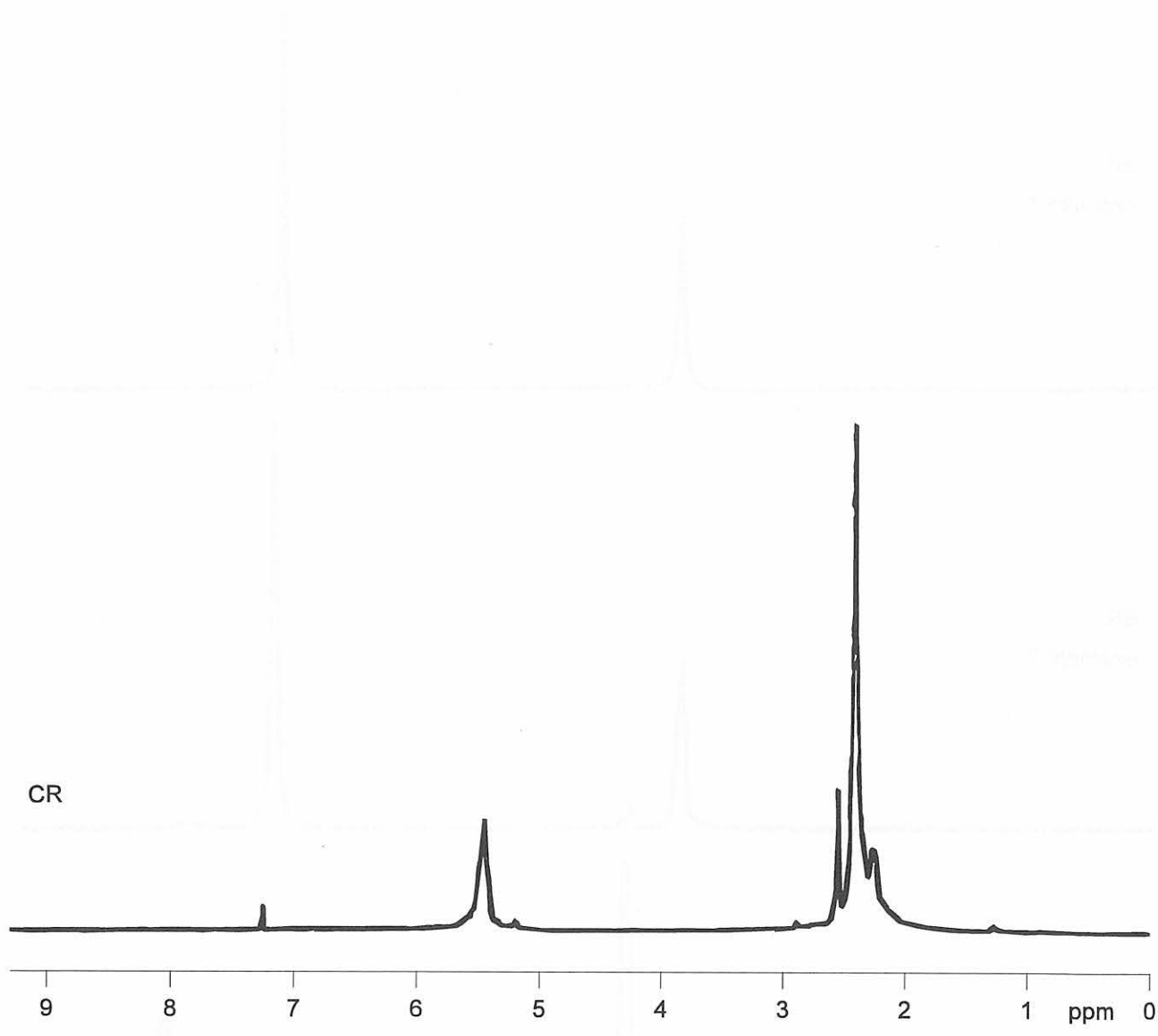


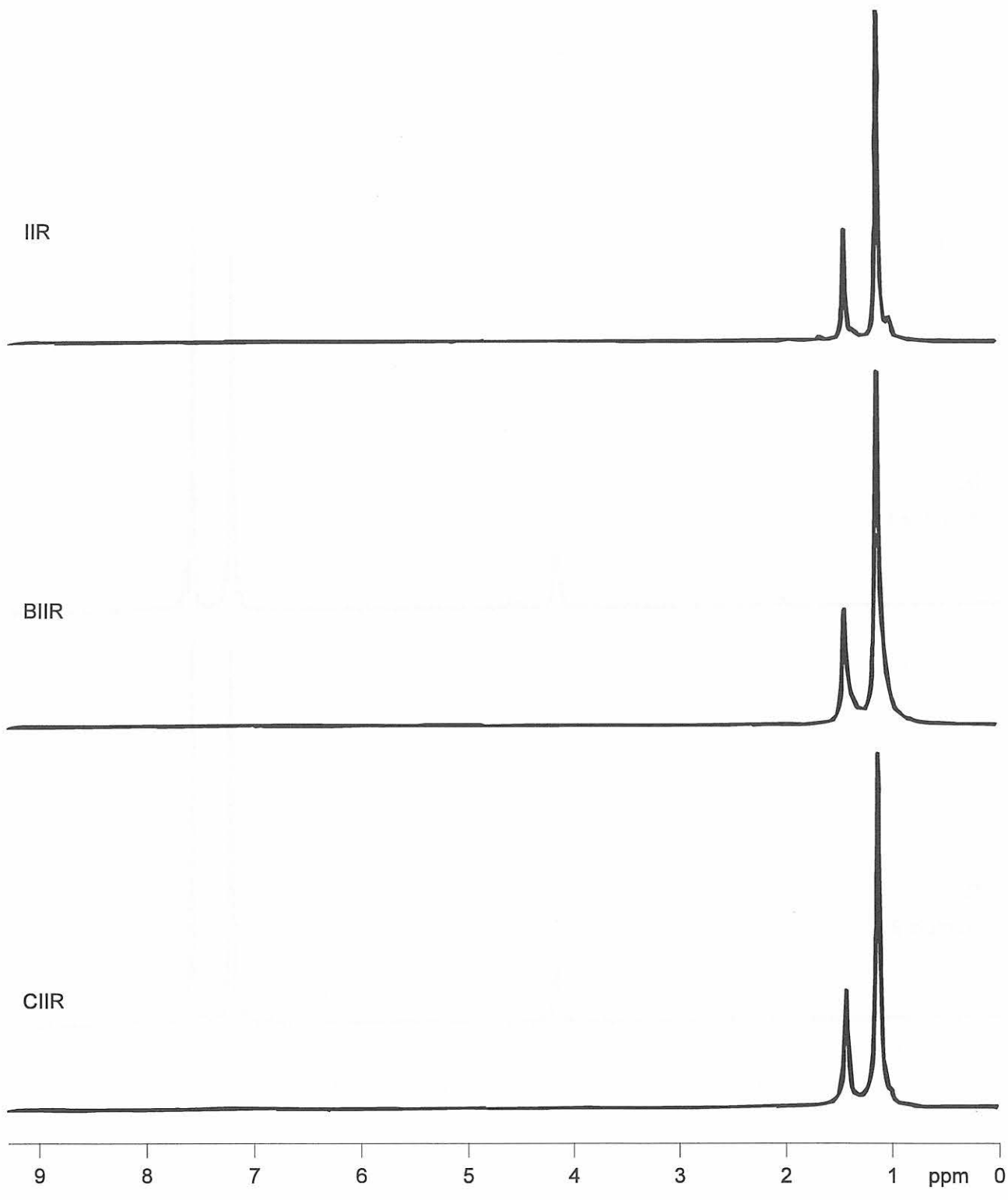
BR  
example 2



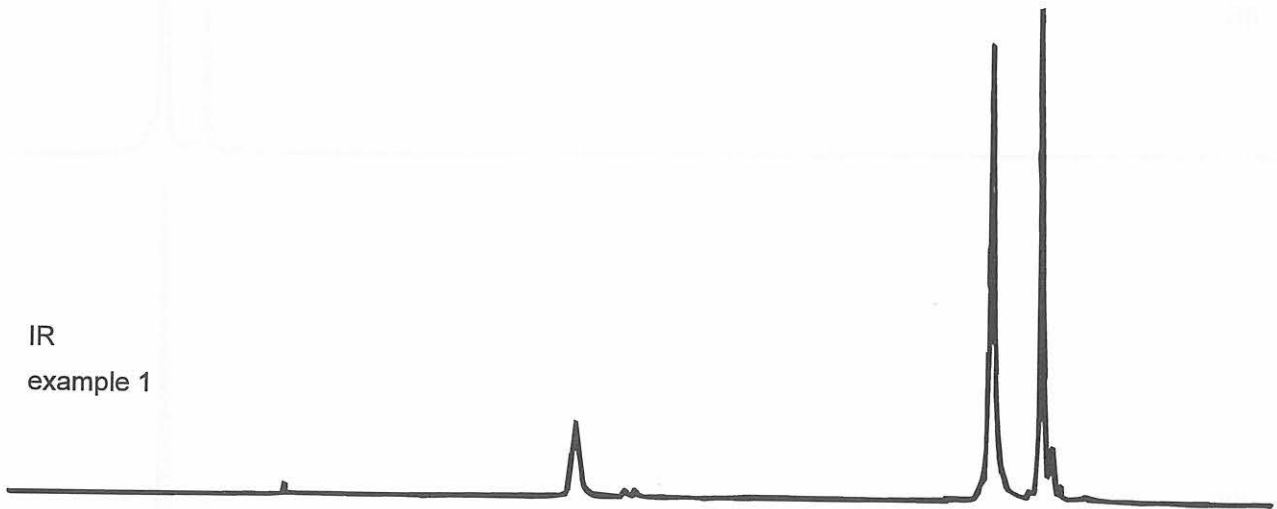
BR  
example 3



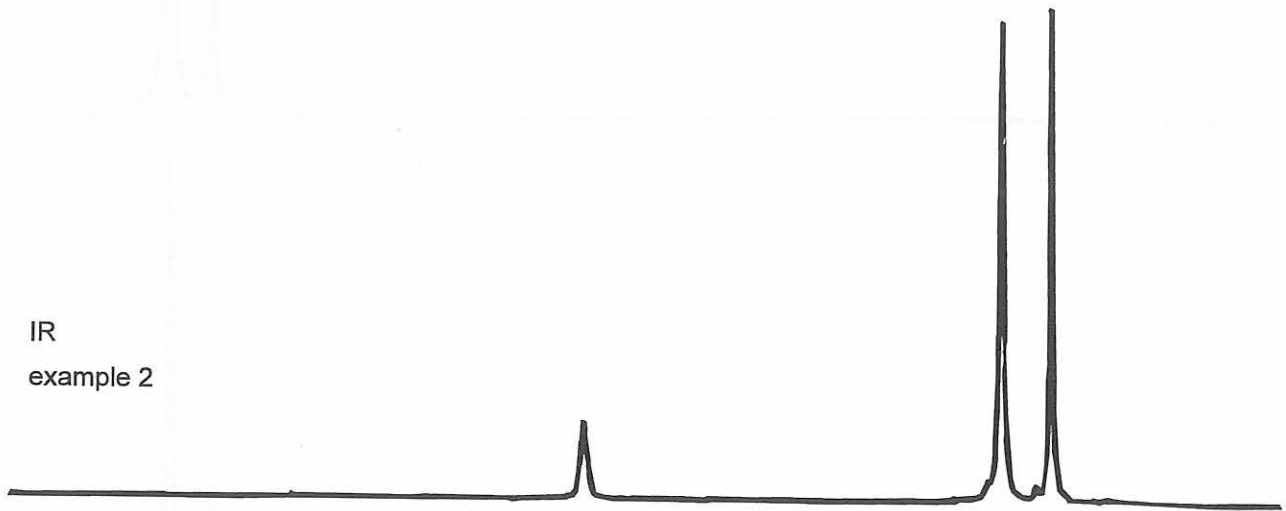




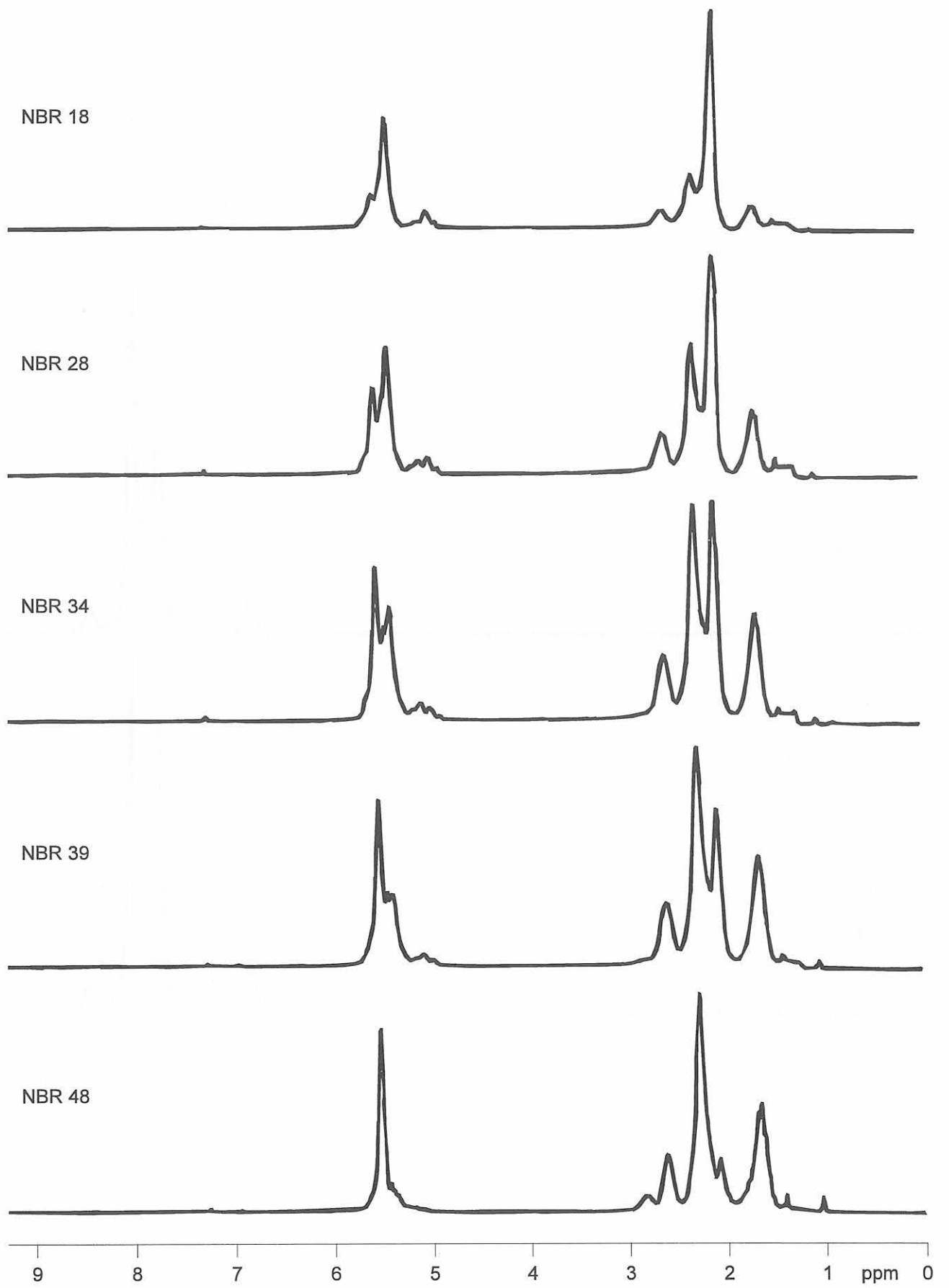
IR  
example 1



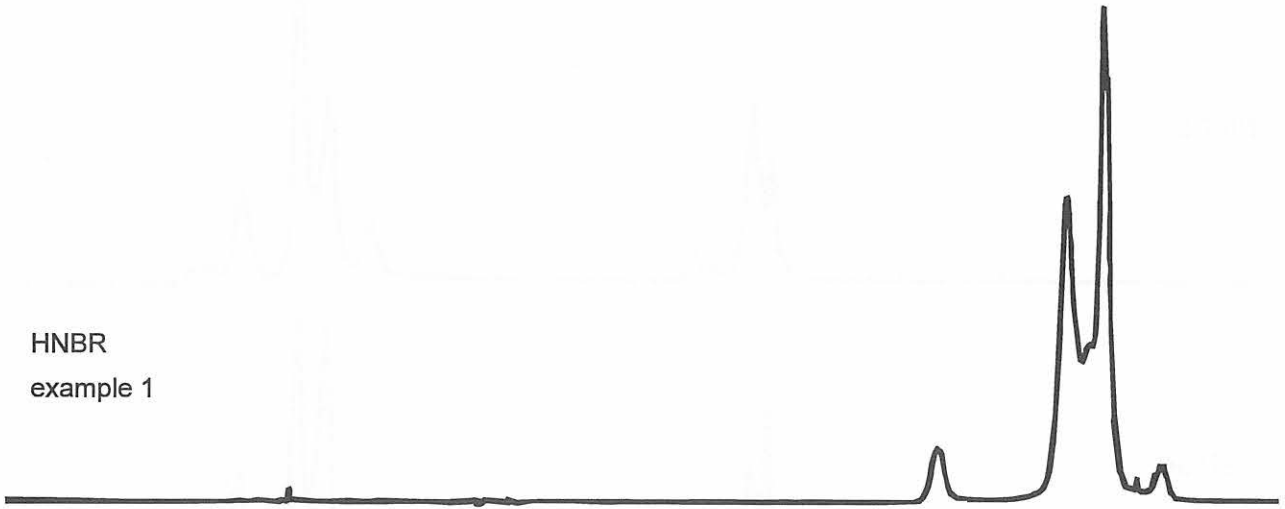
IR  
example 2



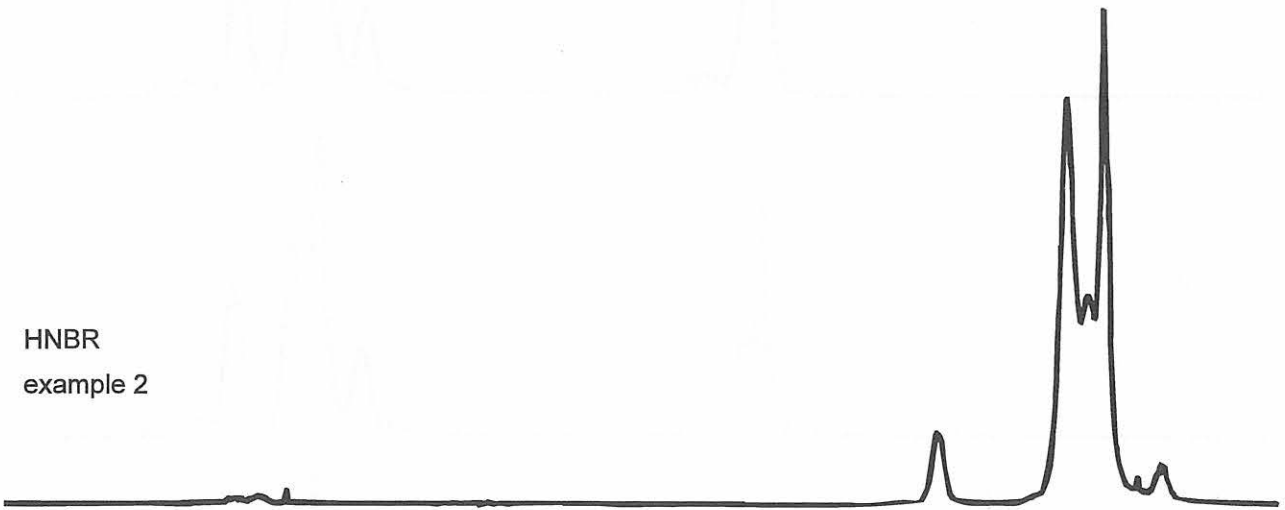
9 8 7 6 5 4 3 2 1 ppm 0



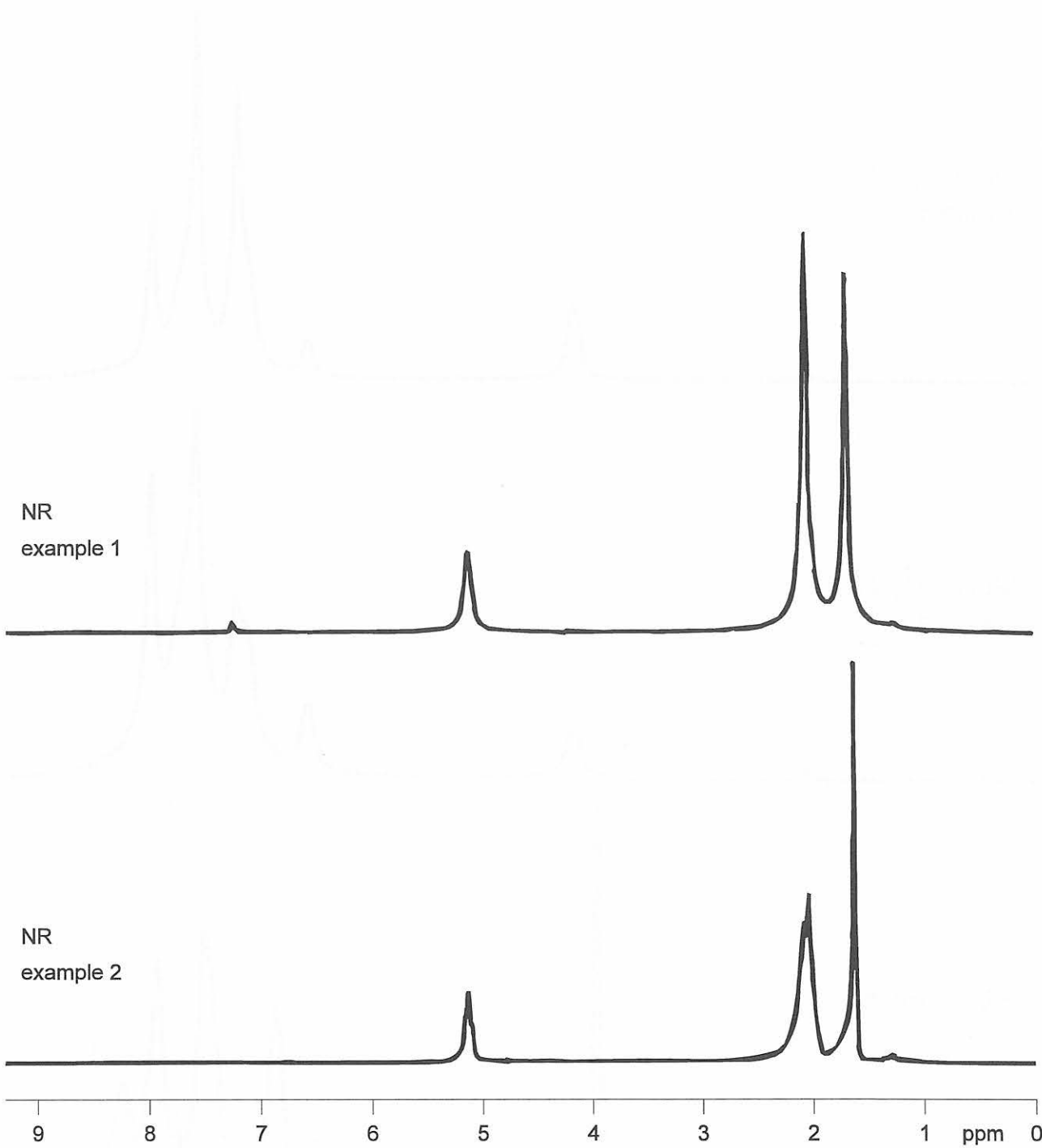
HNBR  
example 1



HNBR  
example 2



9 8 7 6 5 4 3 2 1 ppm 0

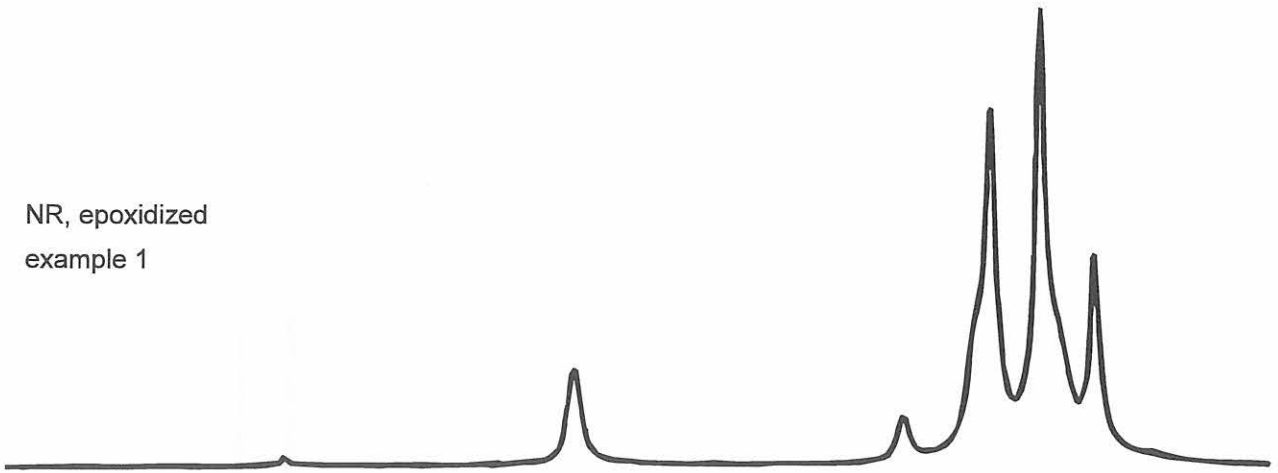


NR  
example 1

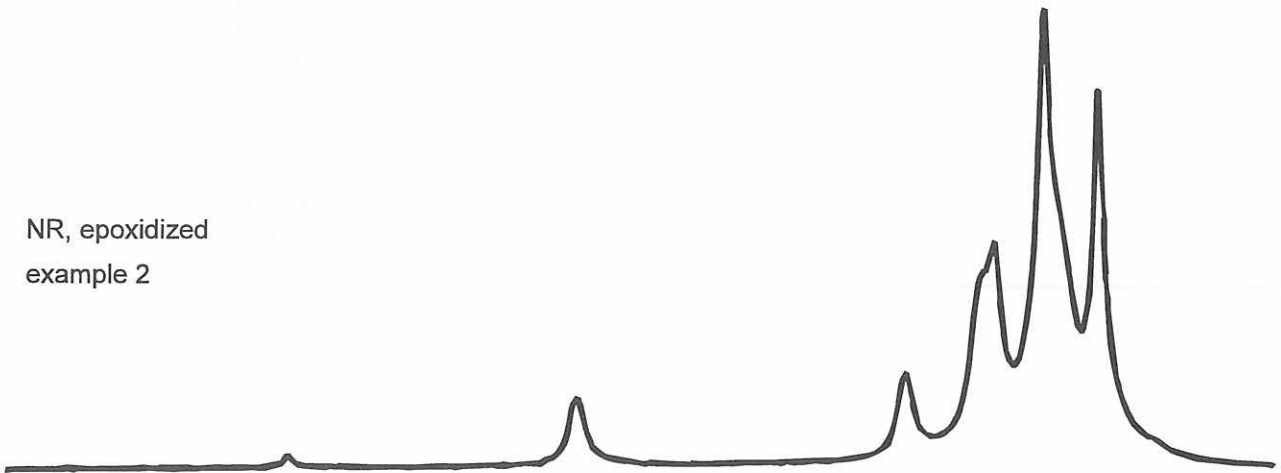
NR  
example 2

9 8 7 6 5 4 3 2 1 ppm 0

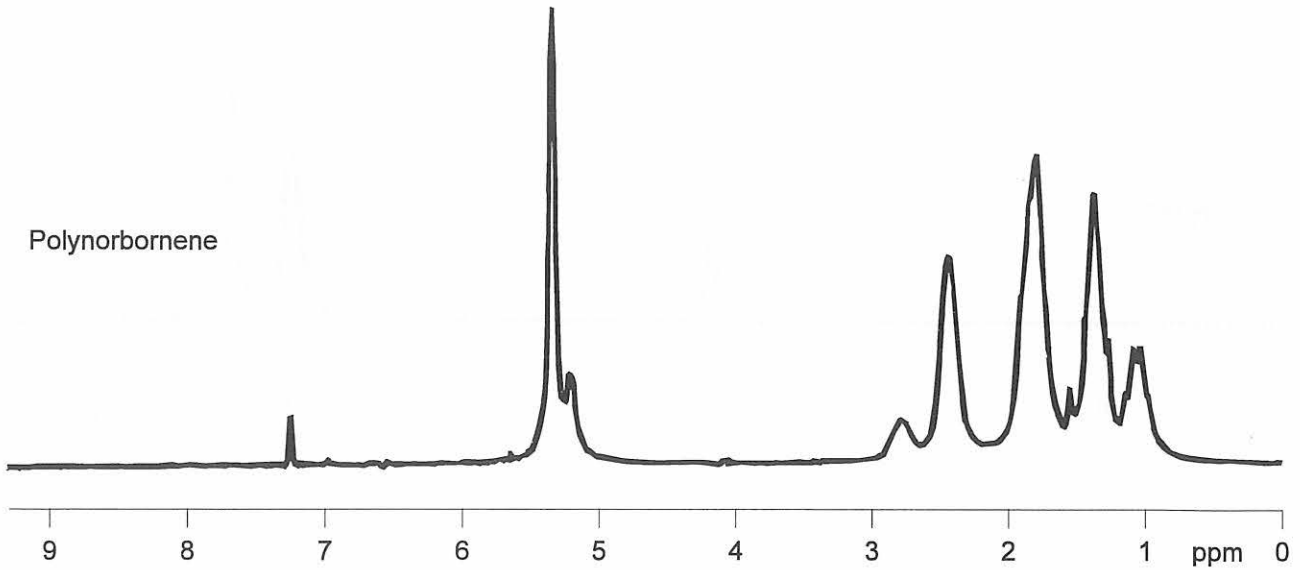
NR, epoxidized  
example 1



NR, epoxidized  
example 2

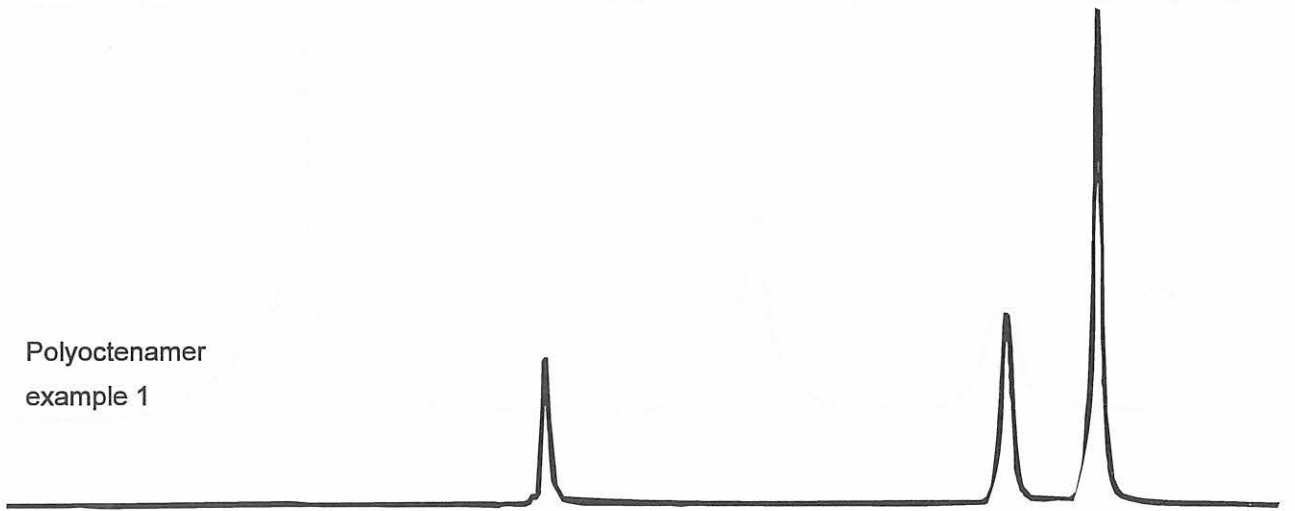


Polynorbornene

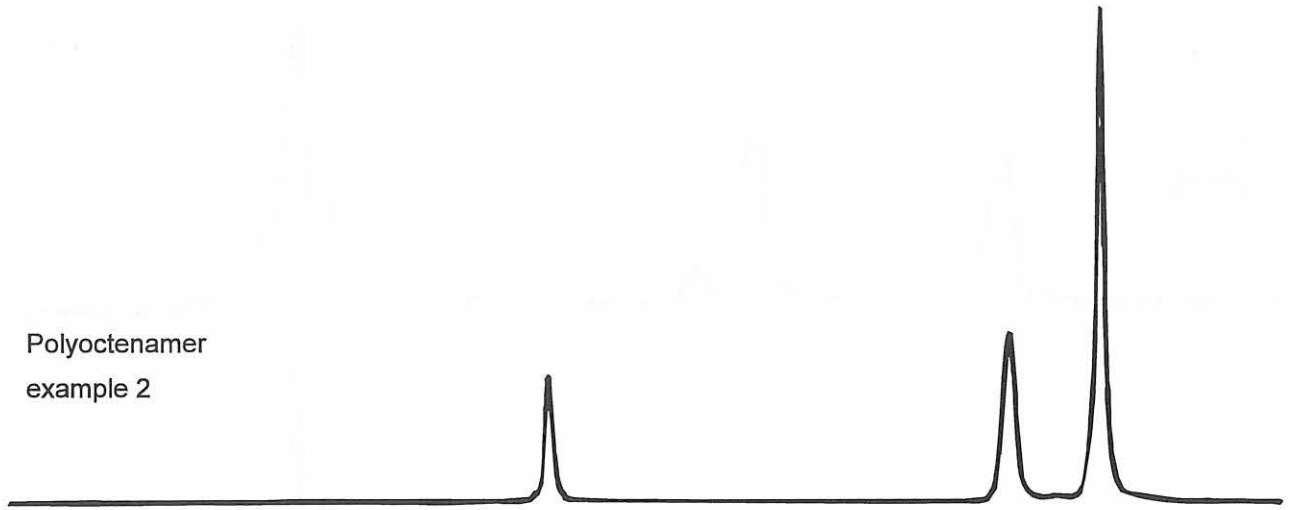




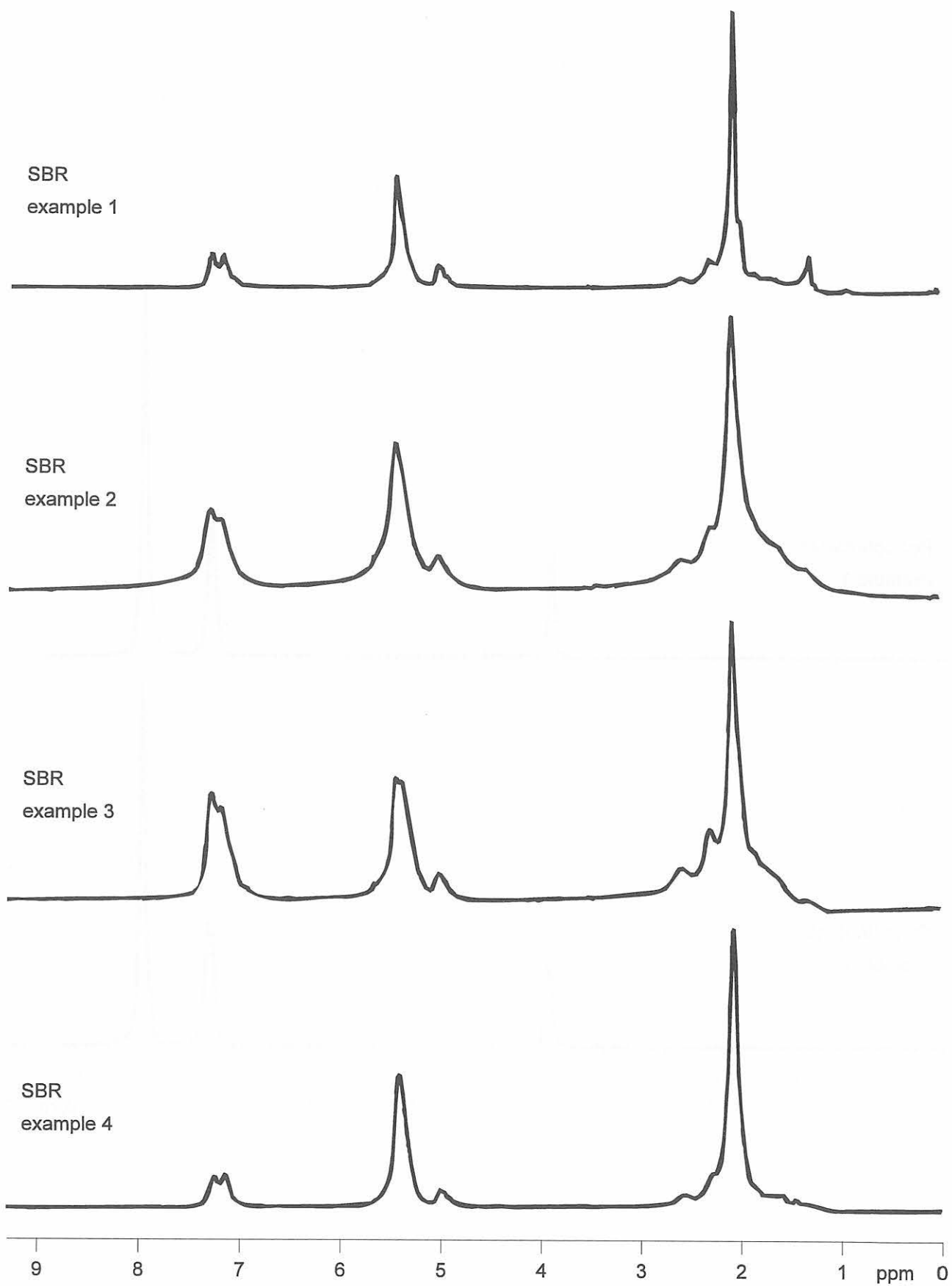
Polyoctenamer  
example 1

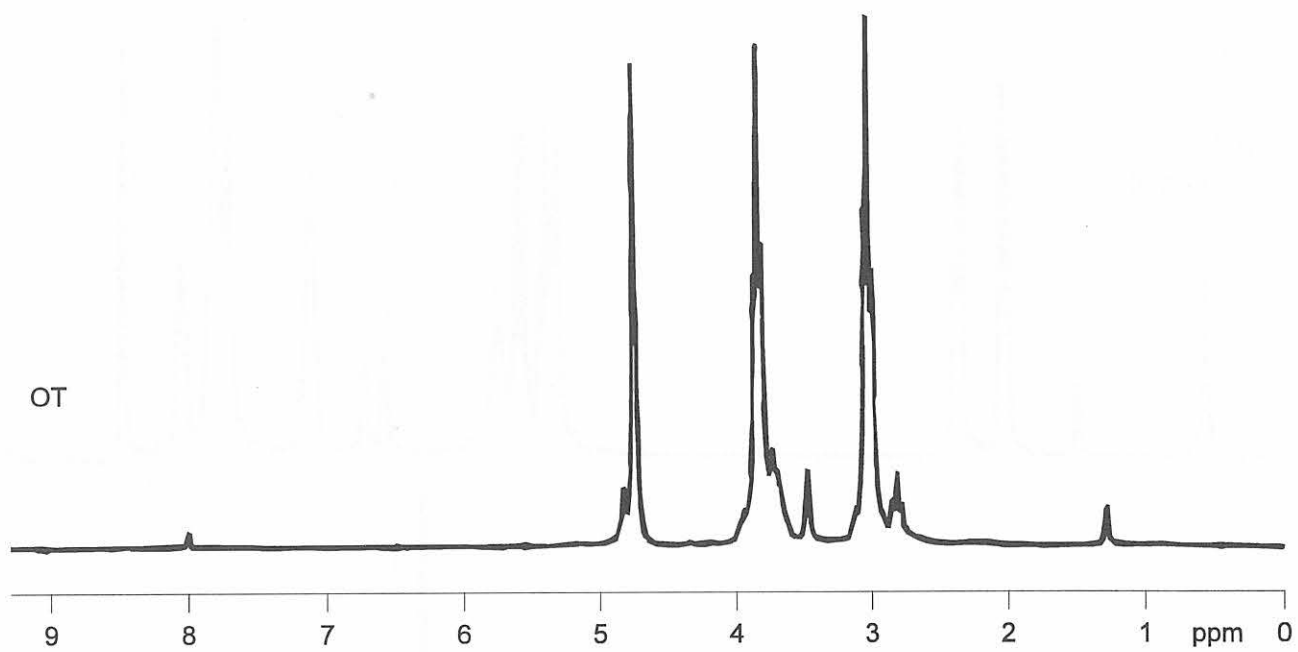


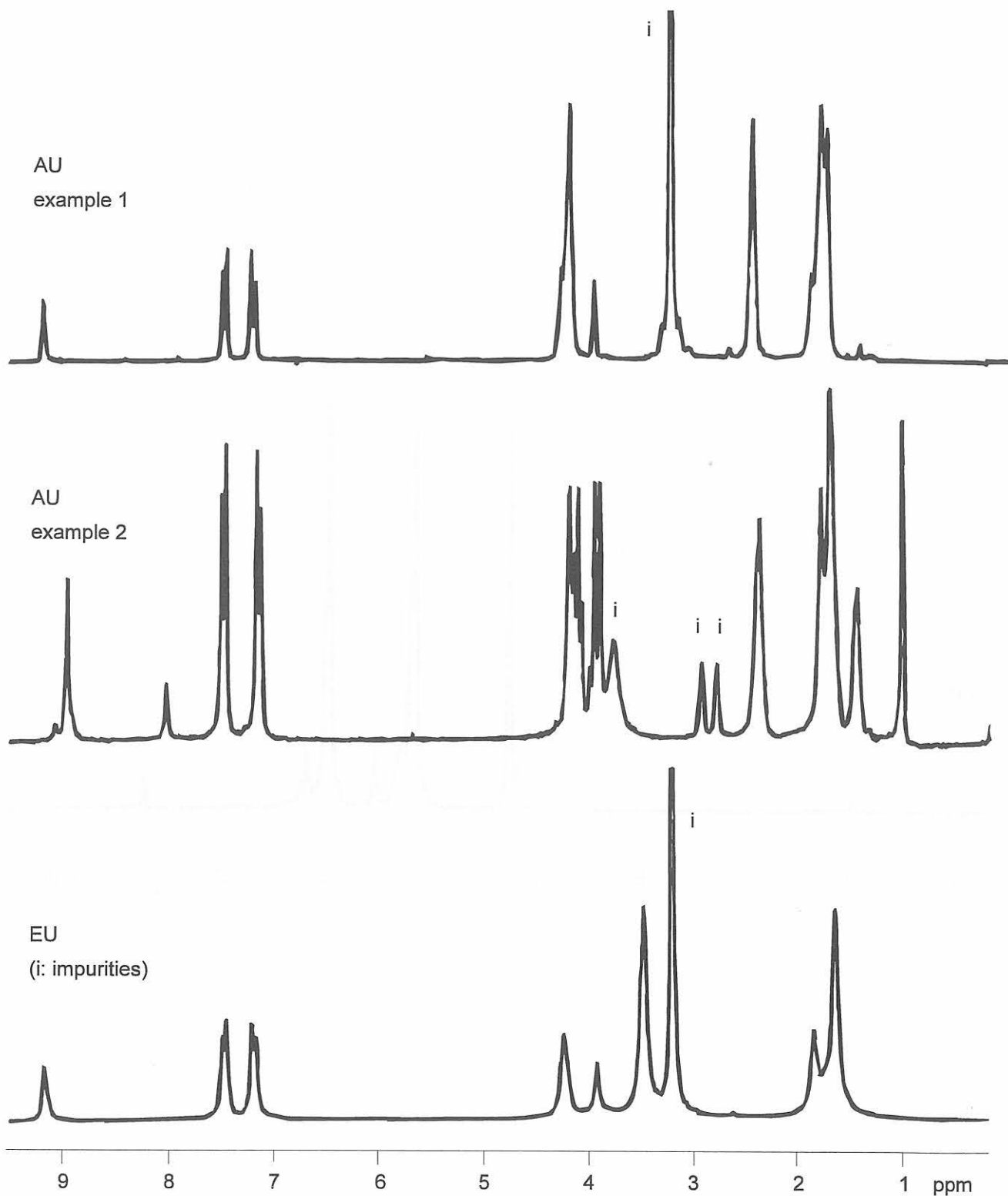
Polyoctenamer  
example 2



9 8 7 6 5 4 3 2 1 ppm 0









## 6. Solid State Spectra of Blends

Instead of a single rubber a rubber blend is used for many applications. The reason is to improve the processing characteristics and to achieve new properties fitting to the special demand. Blends can be studied by the solid state method successfully<sup>1</sup>. Peak overlapping will not be a serious problem because of the good resolution and the large spectral width. The spectra give information about the overall composition and often the microstructure of the polymer can be revealed additionally.

Blends can be determined quantitatively, as well. NMR has decided advantages for such measurements because, under suitable experimental conditions, integrated signal

intensities are accurately proportional to the concentration. Of course, there are - as for solutions - various problems, such as differential saturation, varying nuclear Overhauser enhancements, overlapping lines and inadequate digitization, but these are generally well understood and solutions to the difficulties are well known<sup>2</sup>. Different from other methods the concentrations of the components are not changed during the preparation as the samples have not to be decomposed but are only exposed to relatively mild procedures.

The following spectra of diblends show the possibilities and limits representatively.

### References:

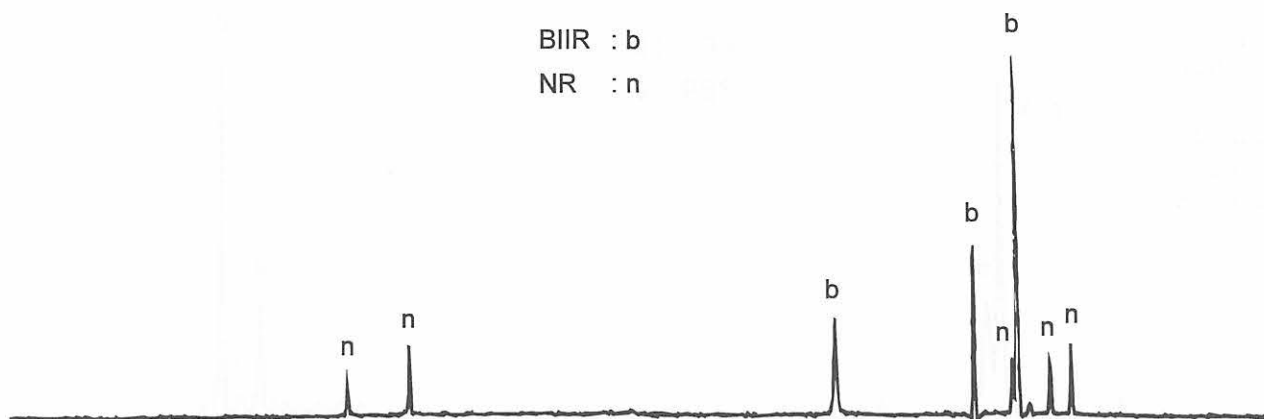
<sup>1</sup> J. Kelm and D. Groß, *Kautsch. Gummi, Kunstst.* 42, 3 88 (1989)

<sup>2</sup> R. K. Harris, *Analyst* 110, 649 (1985)

BLEND

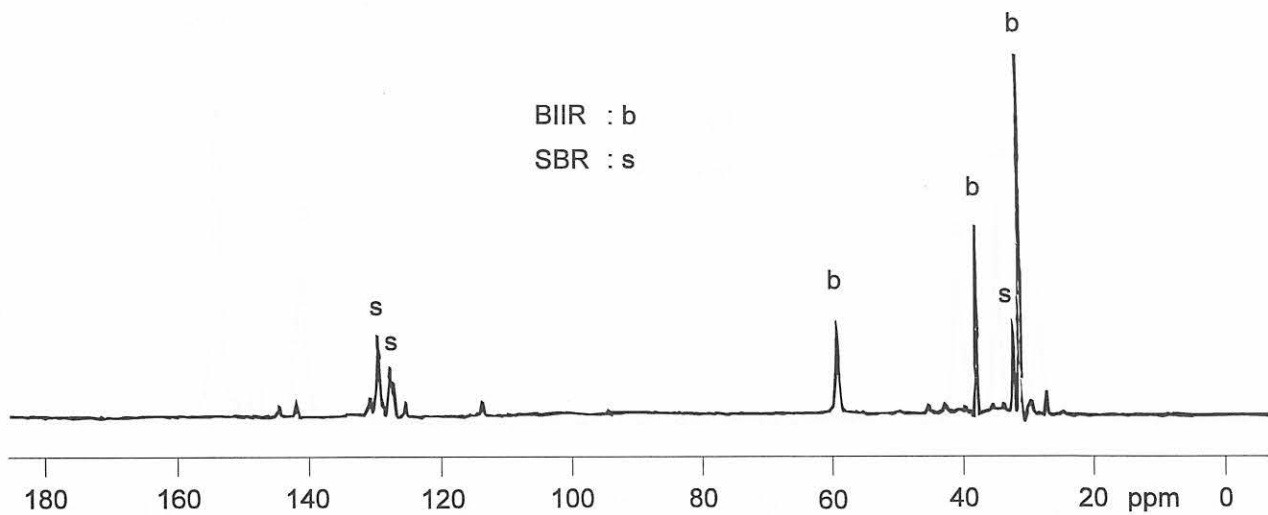
BIIR : b

NR : n



BIIR : b

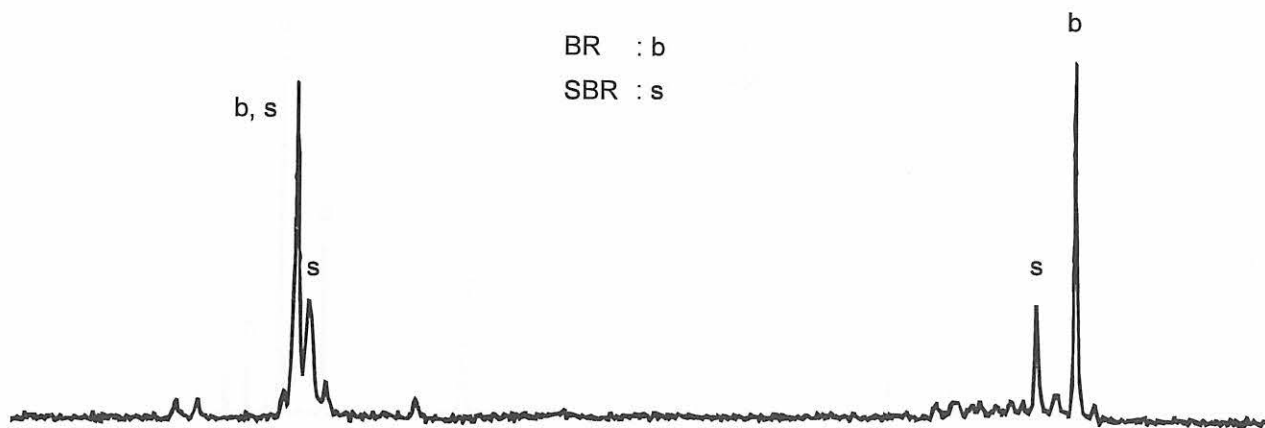
SBR : s



BLEND

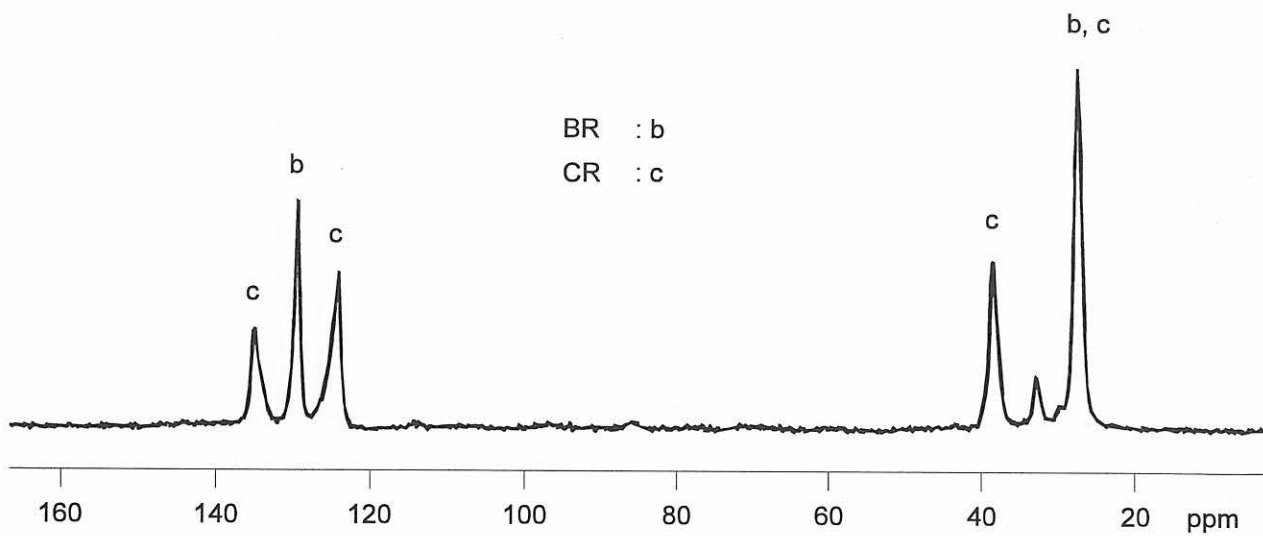
BR : b

SBR : s



BR : b

CR : c

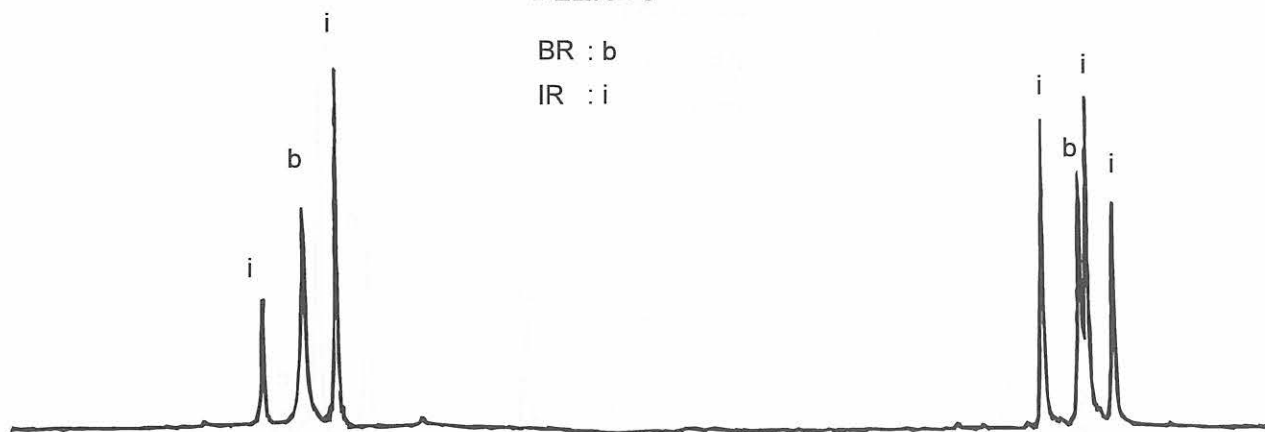




BLENDS

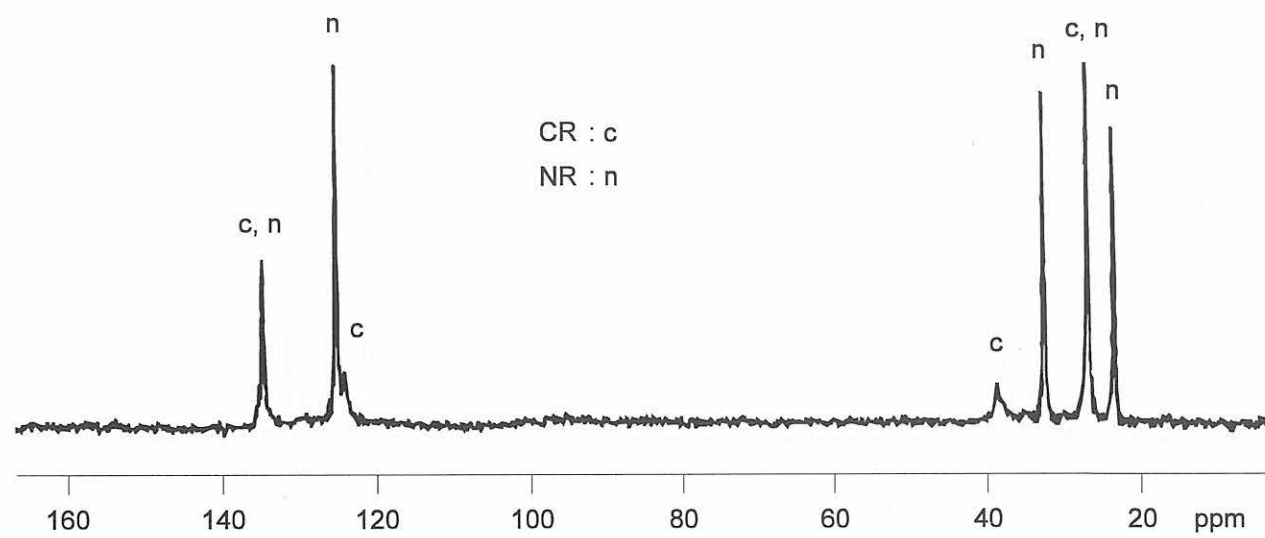
BR : b

IR : i



CR : c

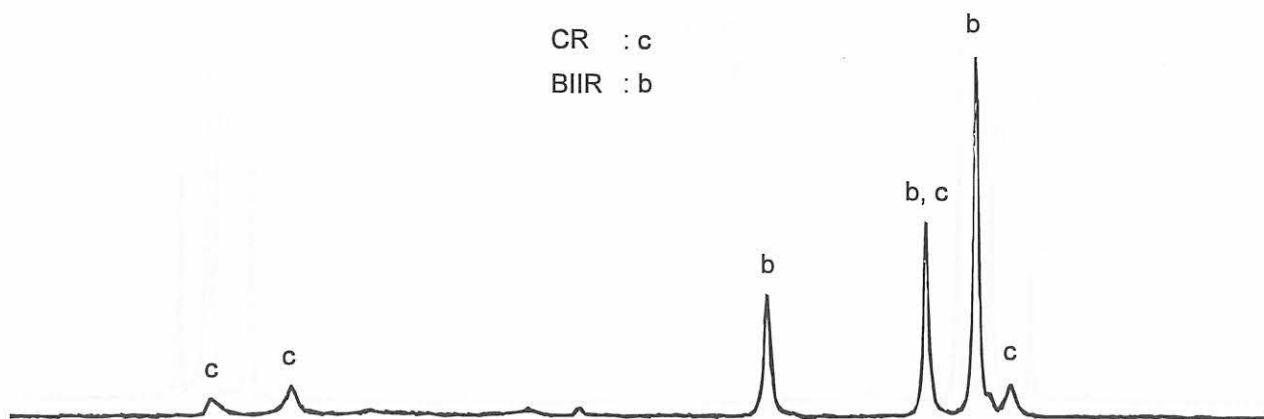
NR : n



BLEND

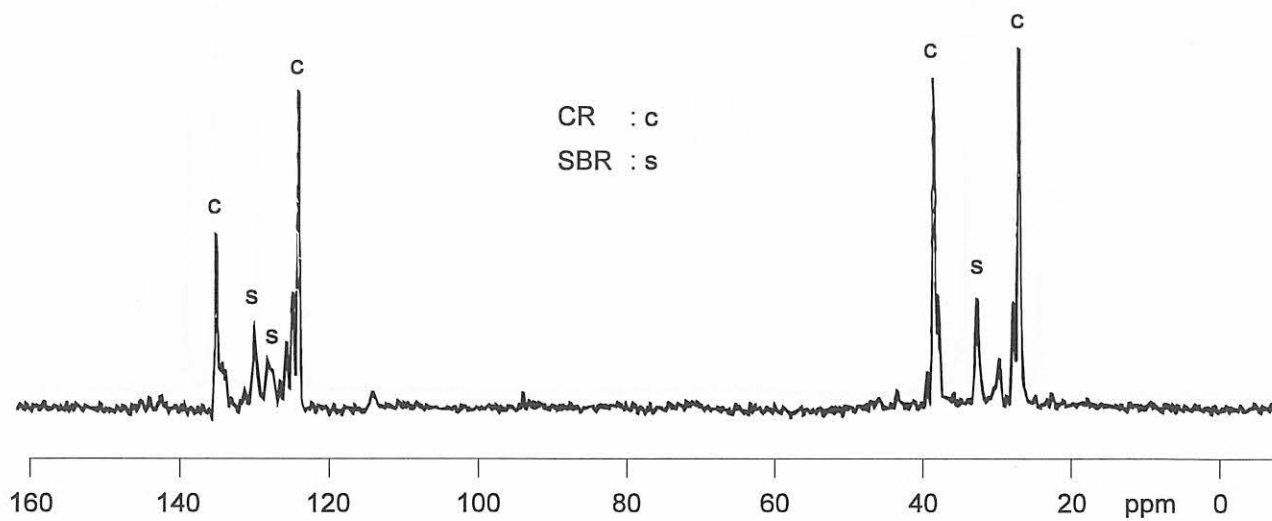
CR : c

BIIR : b



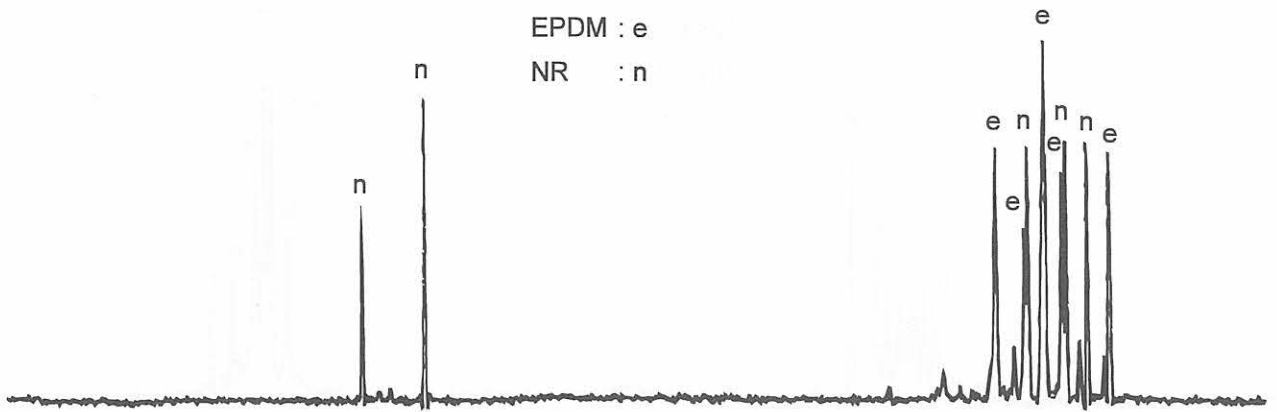
CR : c

SBR : s

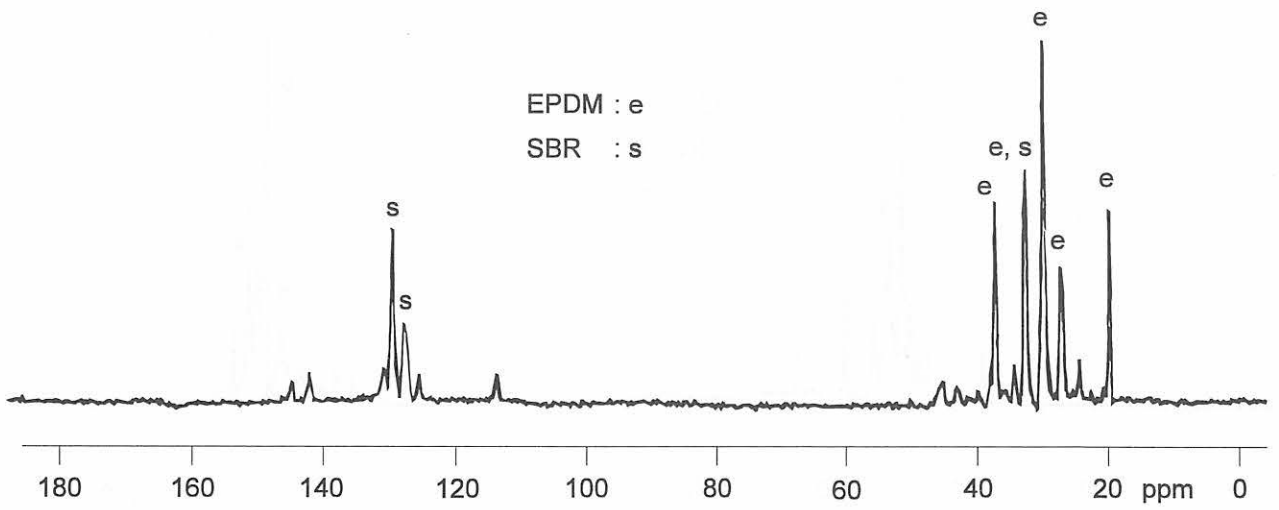


BLENDS

EPDM : e  
NR : n



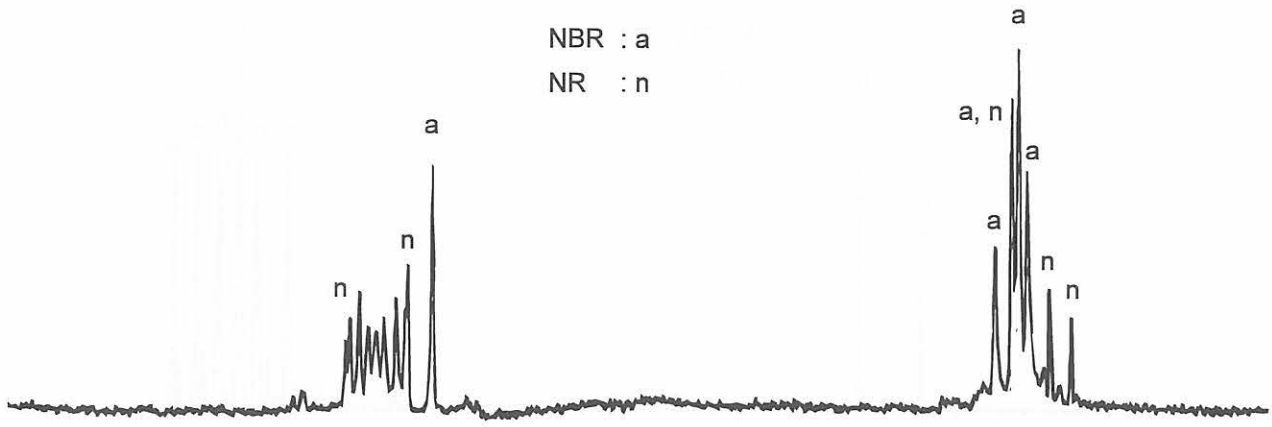
EPDM : e  
SBR : s



BLEND

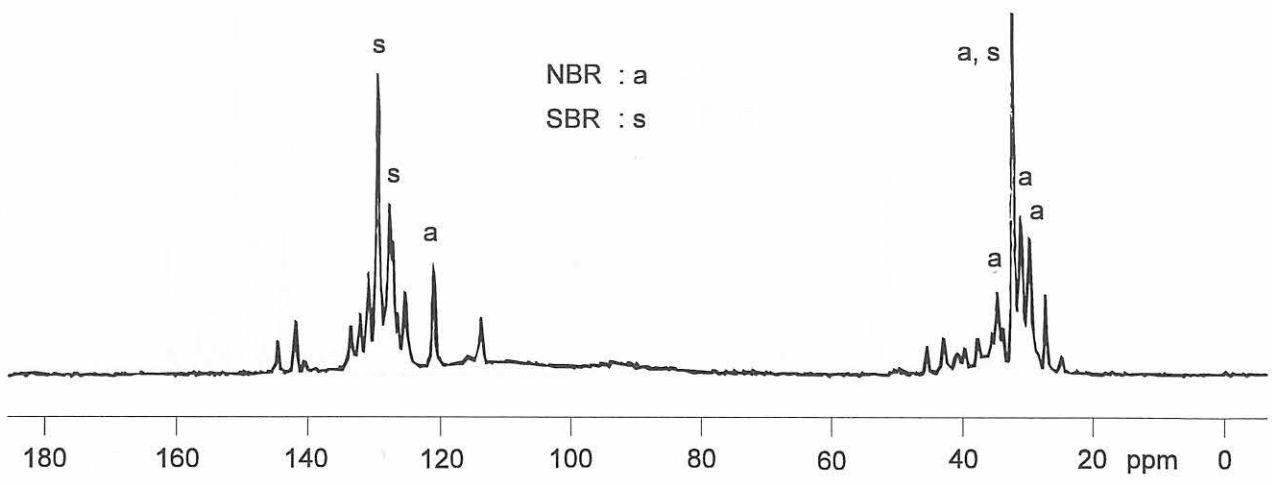
NBR : a

NR : n



NBR : a

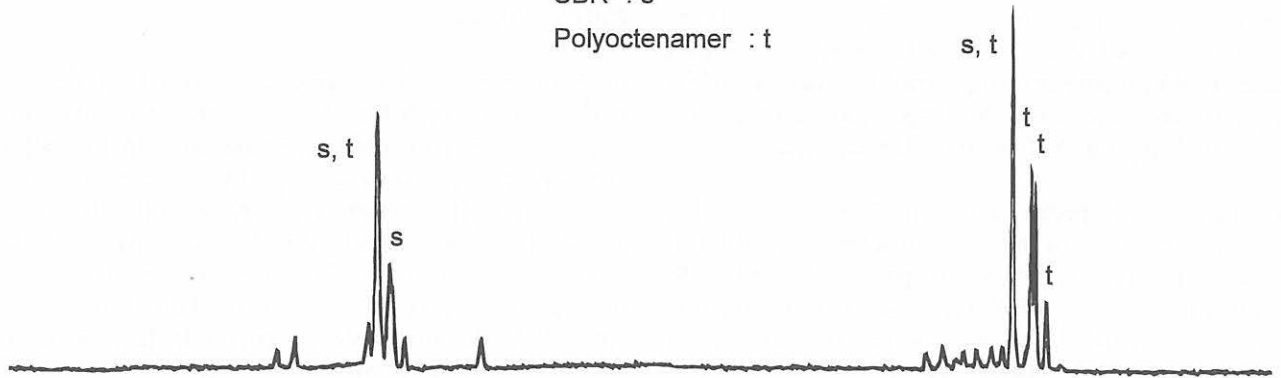
SBR : s



BLEND

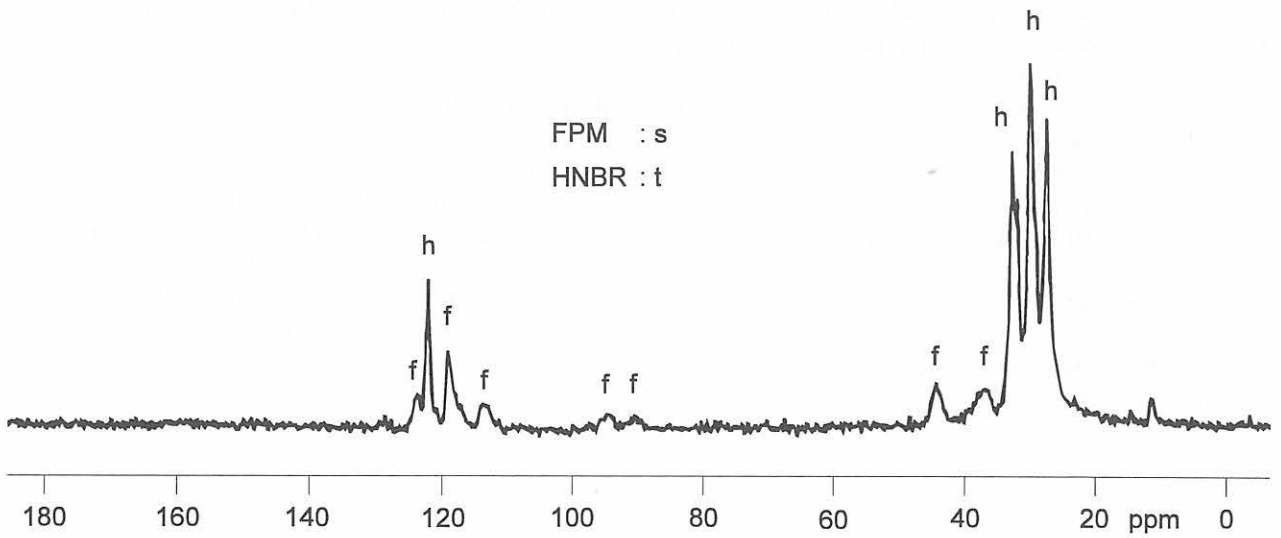
SBR : s

Polyoctenamer : t



FPM : s

HNBR : t



## 7. Thermoplastic Elastomers

Thermoplastic elastomers have been described in the chapter „Fundamentals“ already. They have become more and more important in recent years, but, still play only a minor part in the entire elastomer market. As mentioned already, commercial types mainly belong to five basic classes: styrene block copolymers, polyolefin blends, polyurethanes, polyetherester and polyetheramides. In this field the CP experiment becomes important as it gives complementary results to the SPE measurement. The hard phases require CP operation with relatively short contact times at or near ambient temperature whereas the mobile segments are accentuated by longer contact times or - most efficiently - by SPE at higher temperature.

A collection of spectra is presented on the following pages in order to show the differentiating power of solids NMR. The representation compares CP and SPE measurements and - whenever possible - the solution spectra are included. An explicit interpretation is not given. But partly the interpretations of the main part of this paper may be used. The appearance of intense anisotropy bands has to be taken into account.

### *Styrene block copolymers*

Styrene block copolymers consist of styrene blocks connected by rubbery segments. They can take the form of linear, branched or radial block copolymers. In the case of linear polymers it is a triple block structure consisting of a rubber central block and polystyrene terminal blocks. The styrene blocks form a physical, reversible network. For the rubbery, soft domains it is common to use polybutadiene (SBS), polyisoprene (SIS) or a copolymer of ethylene and butylene (SEBS, not included) because of better stability against oxidation.

### *Polyolefin blends*

Polyolefin thermoplastic elastomers constitute a broad family of materials with many possibilities of changing

properties and processing characteristics through formulation and compounding. They are obtained by blending thermoplastic polymers and elastomers, in most cases polypropylene and EPDM. EPDM can have an amorphous or partially-crystalline structure as becomes clear in the first two examples. The other five examples show the variety of this class.

### *Polyurethanes*

In thermoplastic polyurethane elastomers long flexible polyester (AU) or polyether (EU) chains are linked together by the more polar urethane units in the polymer. The latter associate together by hydrogen bonding and thus form the reversible crosslinks at or below service temperature. The examples chosen are the same as in the chapter on conventional elastomers. The hard phase is formed in all cases by diphenylmethane diisocyanate and butanediol, the soft phase by poly (butylene adipate), polycaprolactone or poly(butylene glycol).

### *Polyetheresters*

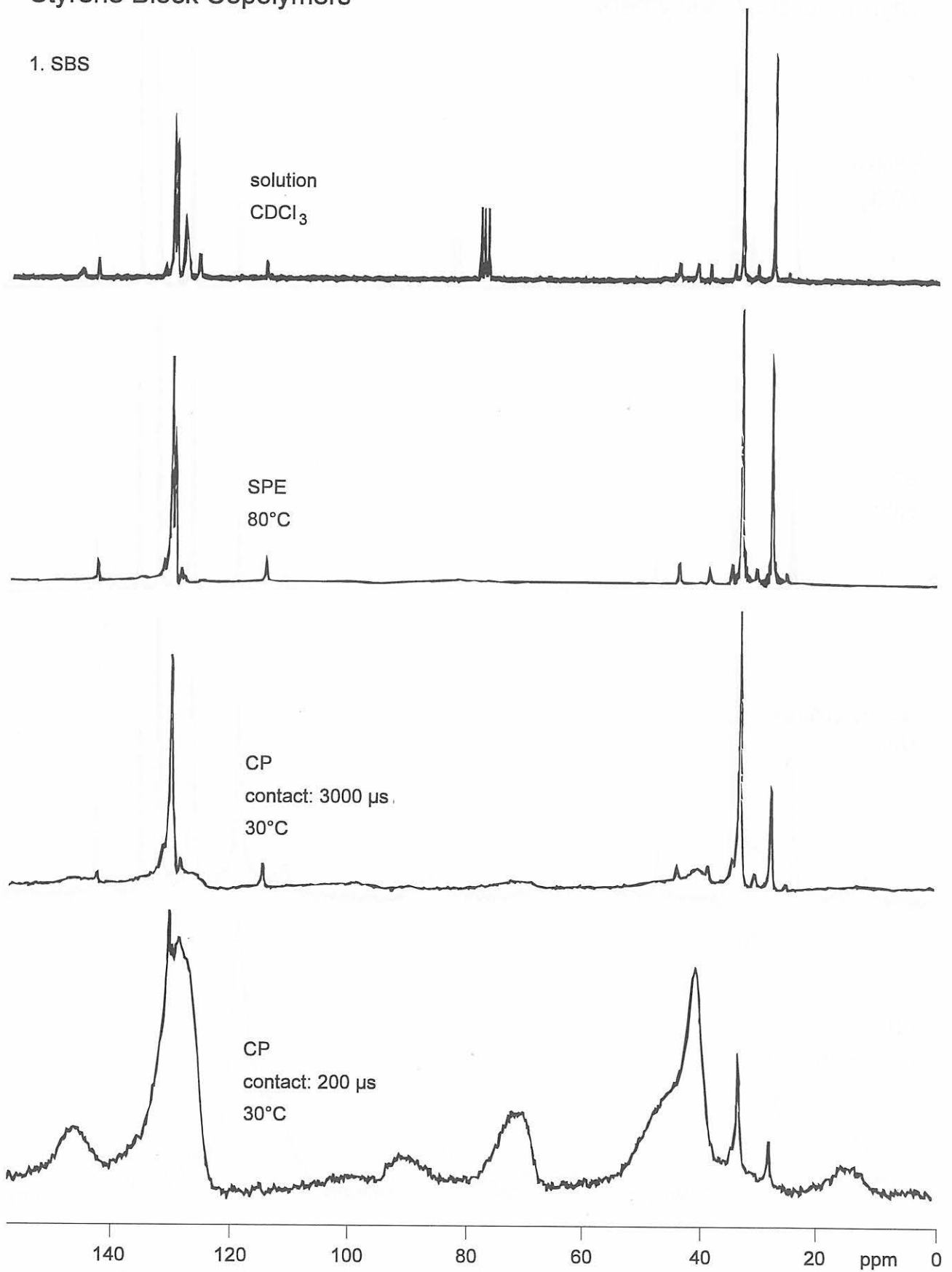
Polyether-ester copolymers consist of flexible polyether chains and polyester groups which function as the inter-chain links. The polyesters are mainly based on poly (butylene terephthalate). For the soft domains poly (ethylene glycol), poly(propylene glycol) or poly(butylene glycol) are in use.

### *Polyetheramides*

Polyetheramides are block copolymers containing polyether and polyamide segments. As for polyetheresters the polyether chain segments form the flexible part of the molecule. The polyamide segments are held together by hydrogen bonding. Different polyamides are used commercially: PA 12, PA 6 or PA 6 12.

# Styrene Block Copolymers

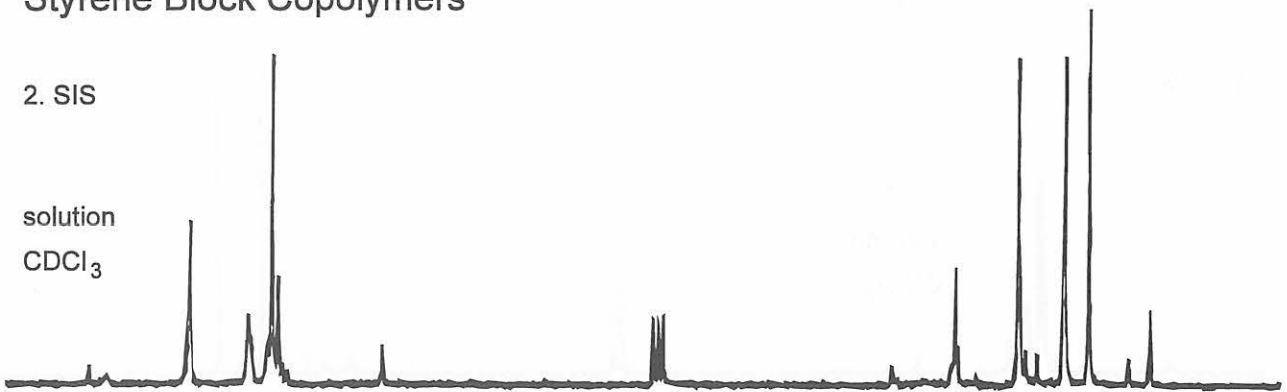
## 1. SBS



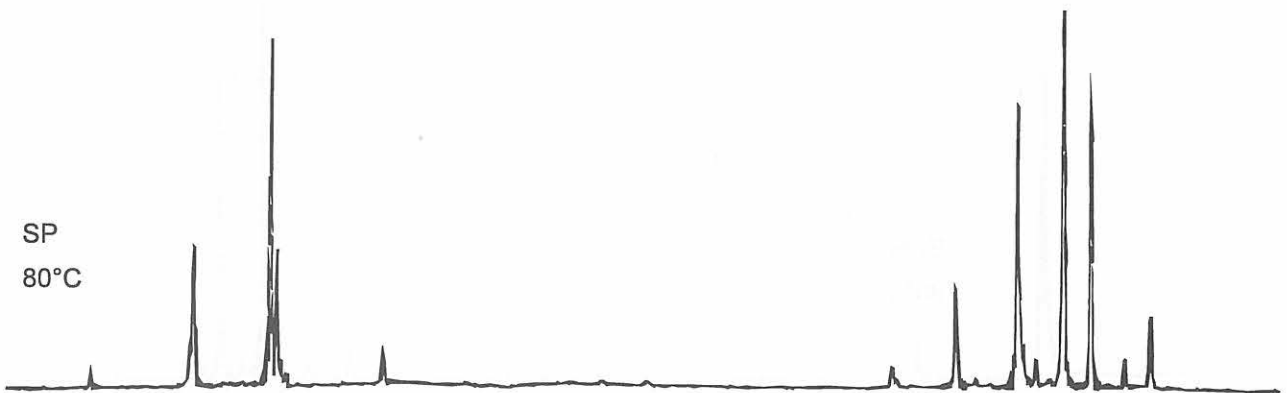
# Styrene Block Copolymers

2. SIS

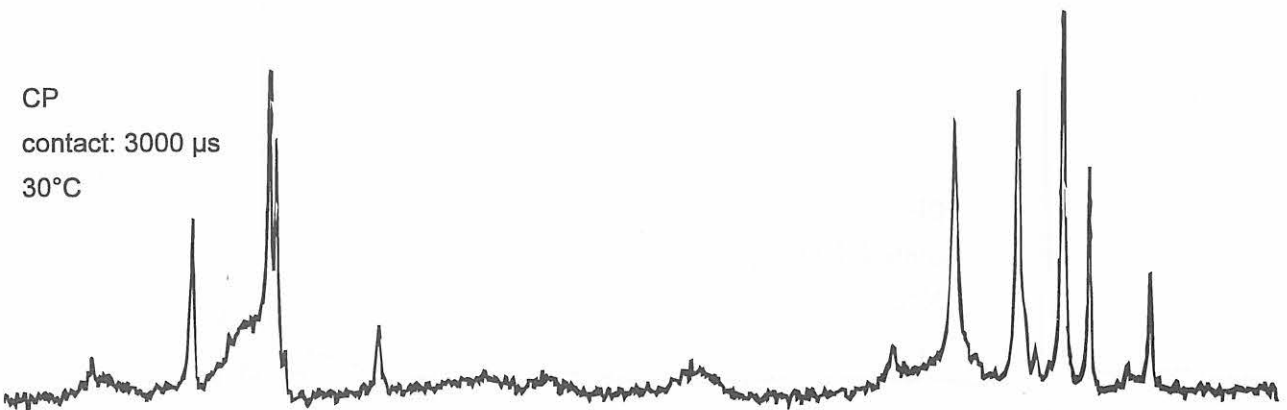
solution  
 $\text{CDCl}_3$



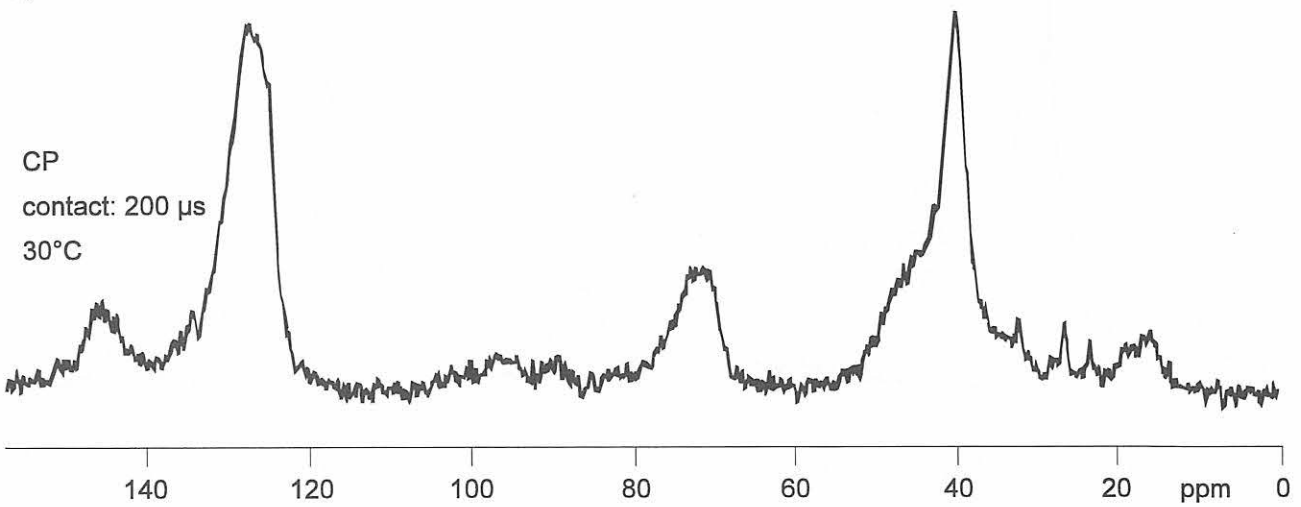
SP  
80°C



CP  
contact: 3000  $\mu\text{s}$   
30°C



CP  
contact: 200  $\mu\text{s}$   
30°C

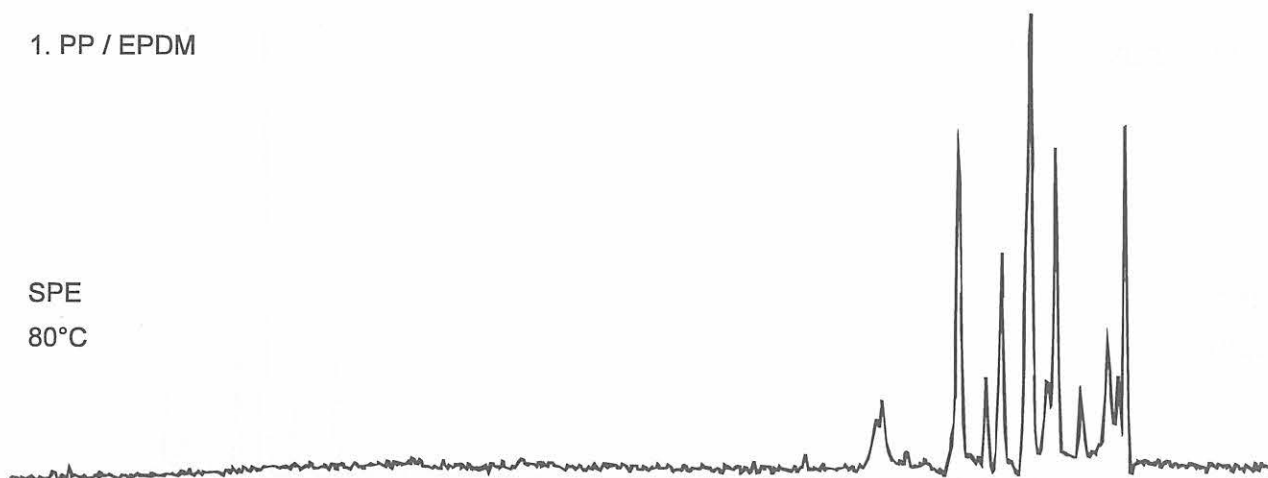




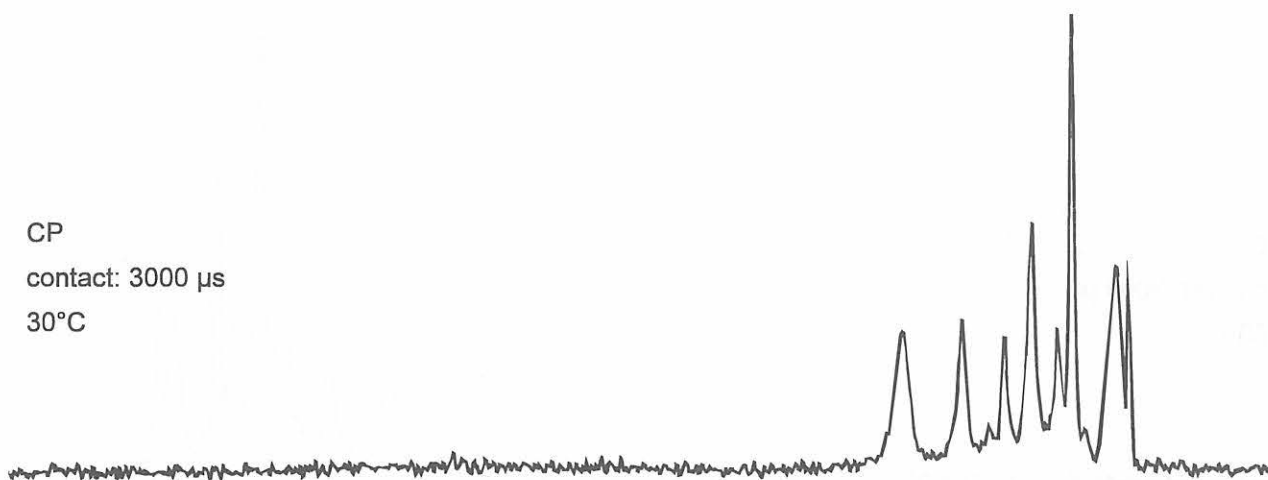
# Polyolefin Blends

## 1. PP / EPDM

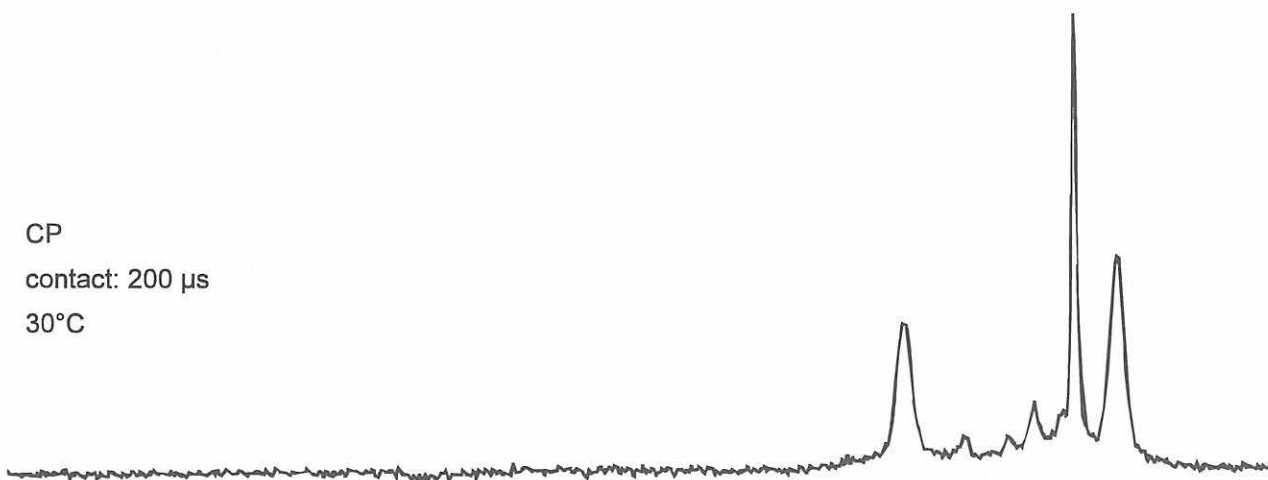
SPE  
80°C



CP  
contact: 3000  $\mu$ s  
30°C



CP  
contact: 200  $\mu$ s  
30°C



120

100

80

60

40

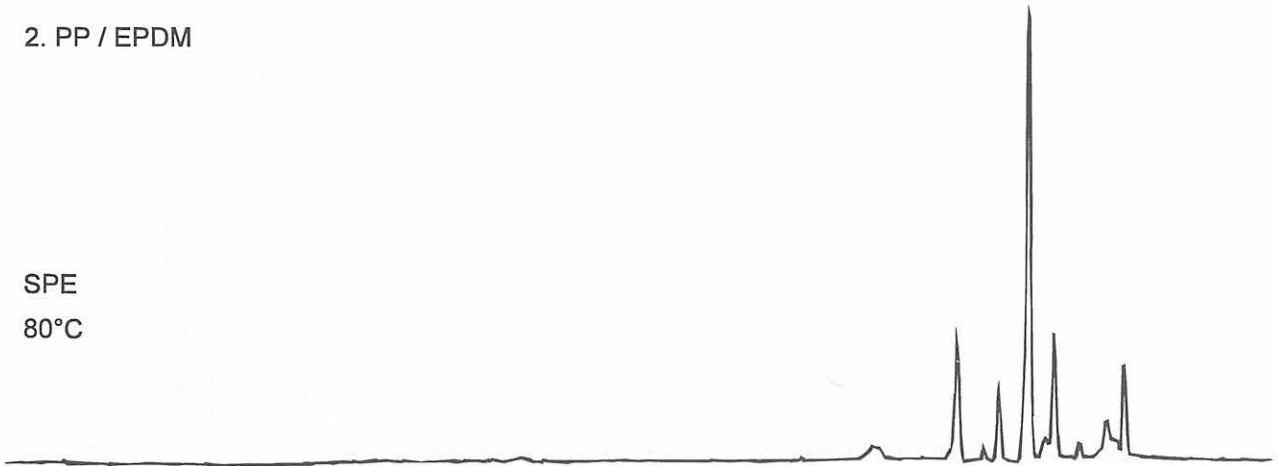
20

ppm

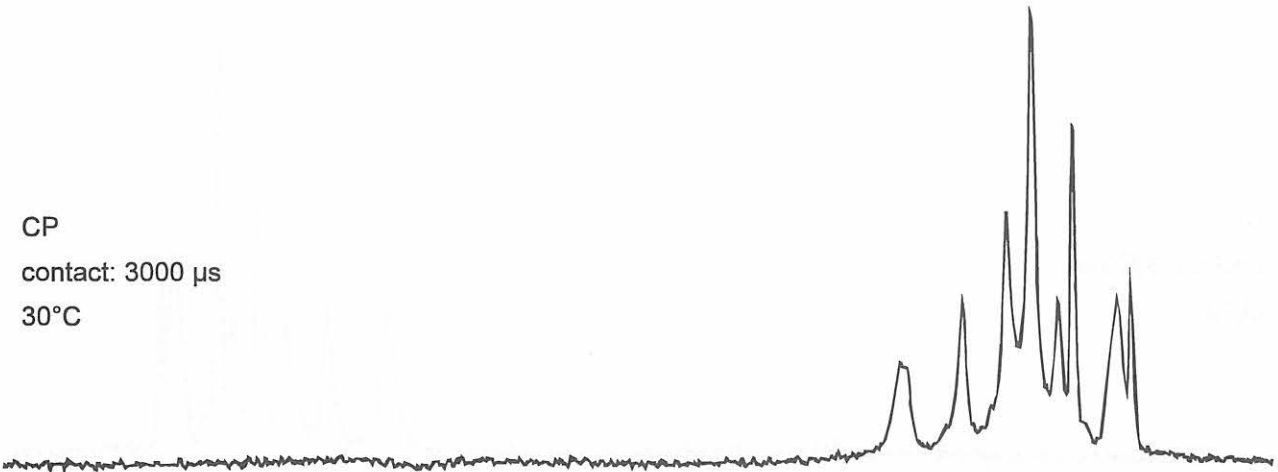
# Polyolefin Blends

2. PP / EPDM

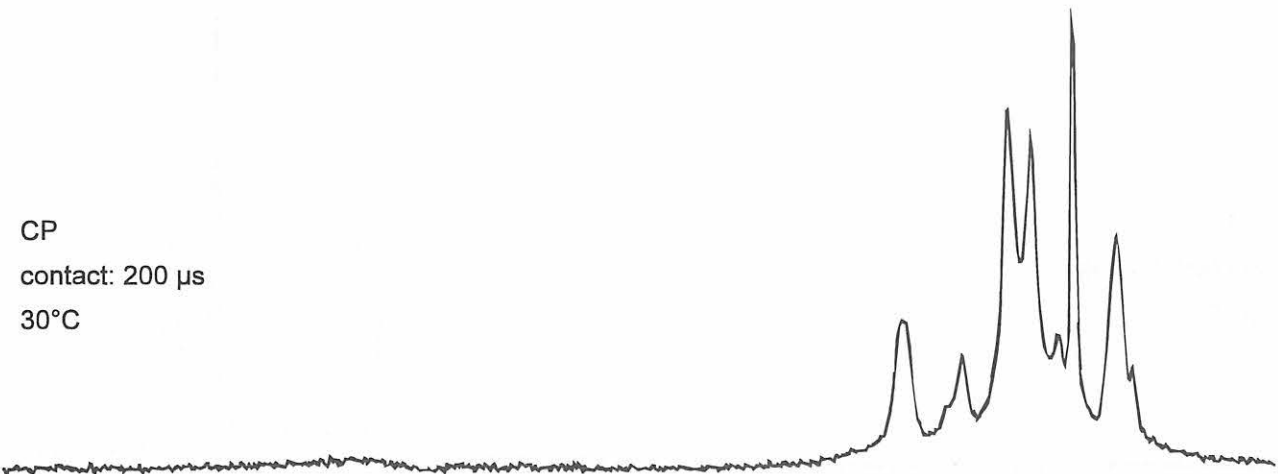
SPE  
80°C



CP  
contact: 3000 μs  
30°C



CP  
contact: 200 μs  
30°C

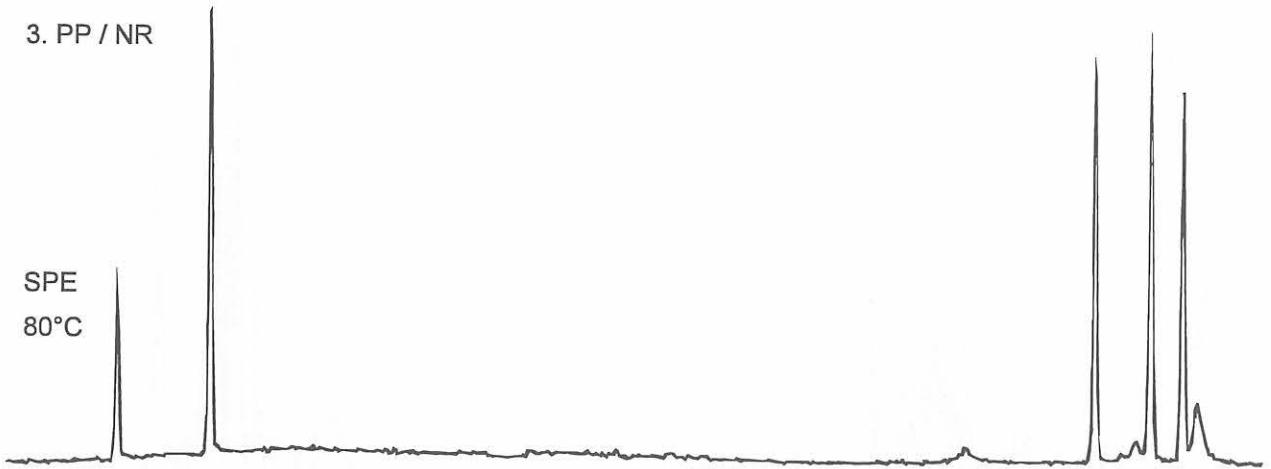


120 100 80 60 40 20 ppm

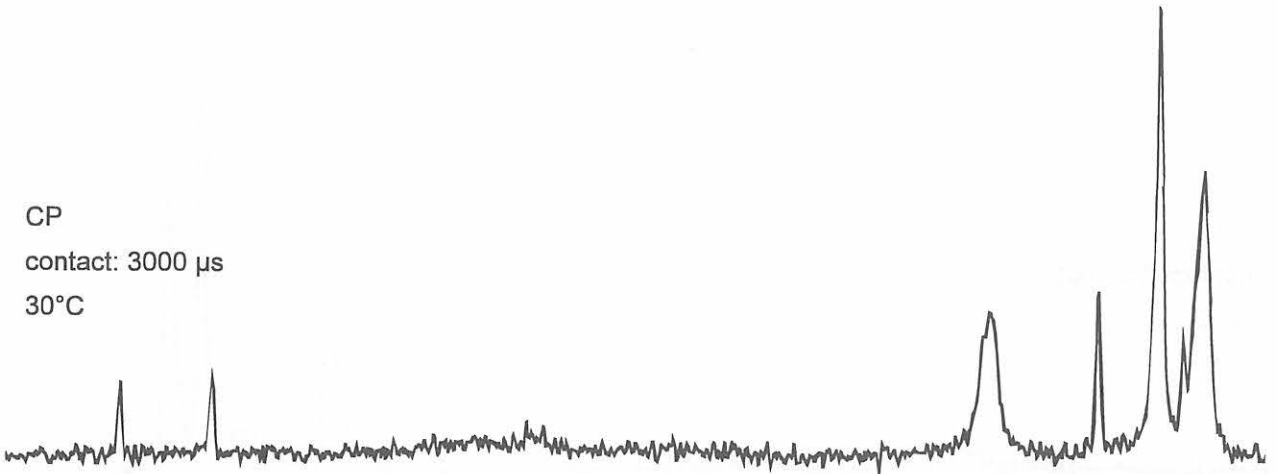
# Polyolefin Blends

3. PP / NR

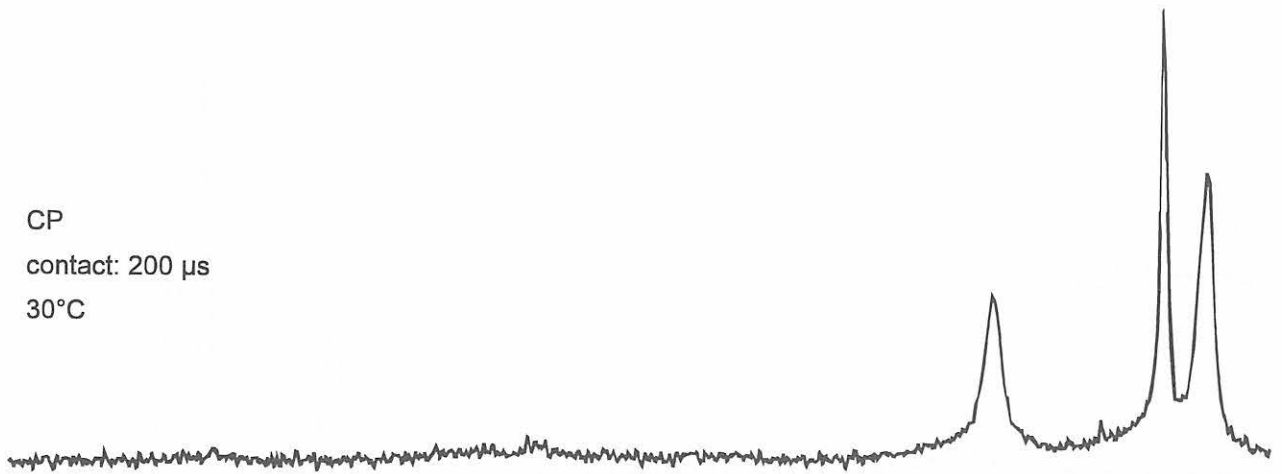
SPE  
80°C



CP  
contact: 3000  $\mu$ s  
30°C



CP  
contact: 200  $\mu$ s  
30°C



140

120

100

80

60

40

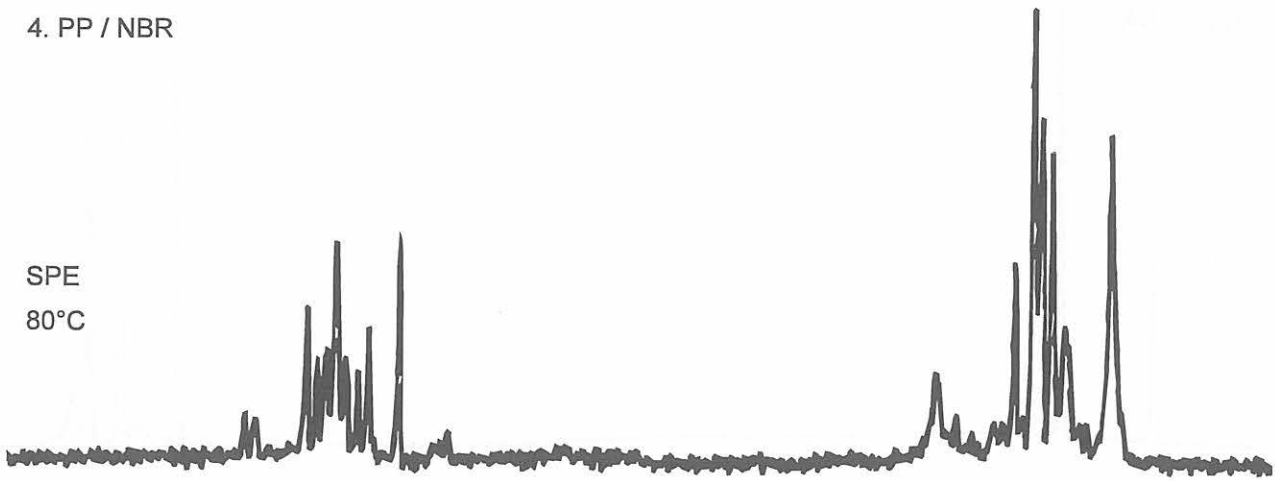
ppm

20

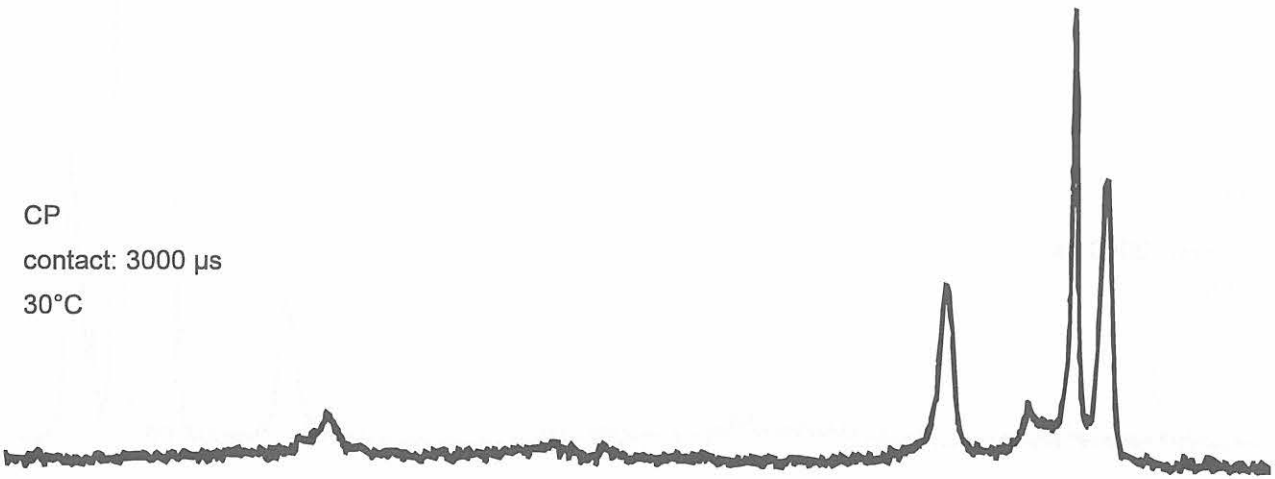
# Polyolefin Blends

## 4. PP / NBR

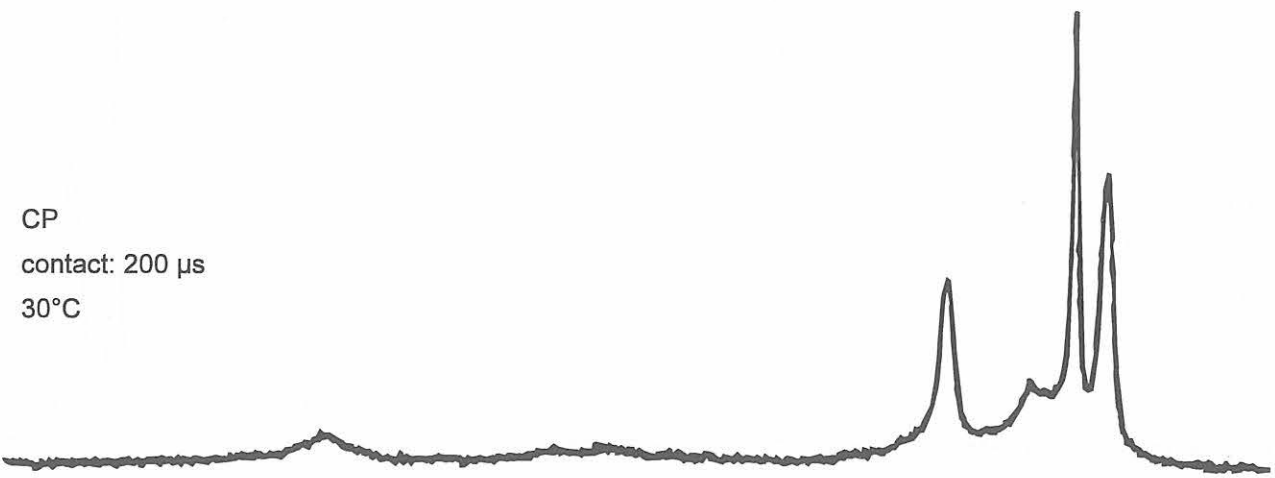
SPE  
80°C



CP  
contact: 3000  $\mu$ s  
30°C



CP  
contact: 200  $\mu$ s  
30°C

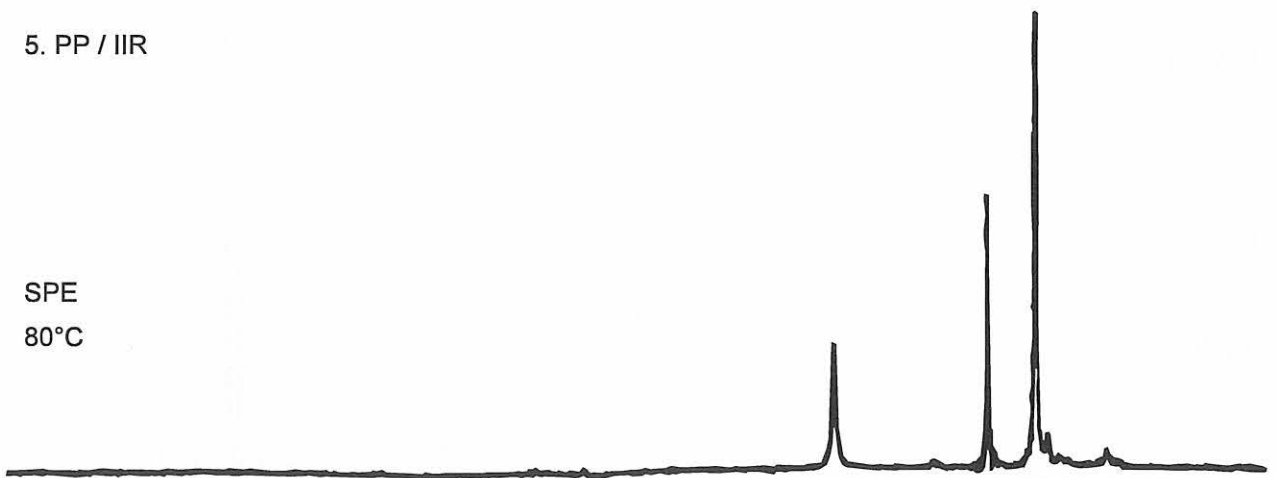


160 140 120 100 80 60 40 20 ppm 0

# Polyolefin Blends

5. PP / IIR

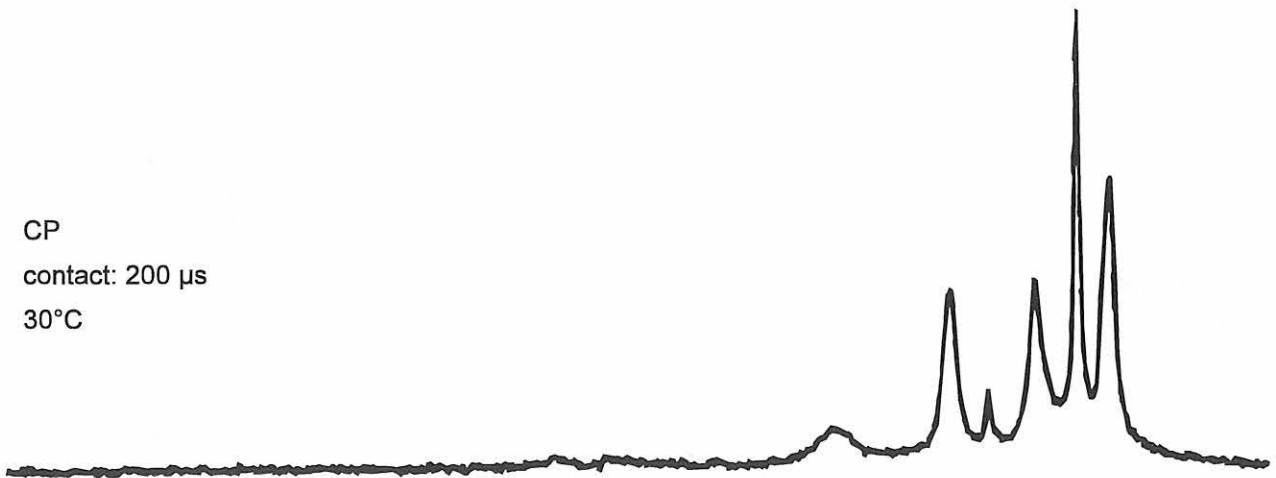
SPE  
80°C



CP  
contact: 3000  $\mu$ s  
30°C



CP  
contact: 200  $\mu$ s  
30°C

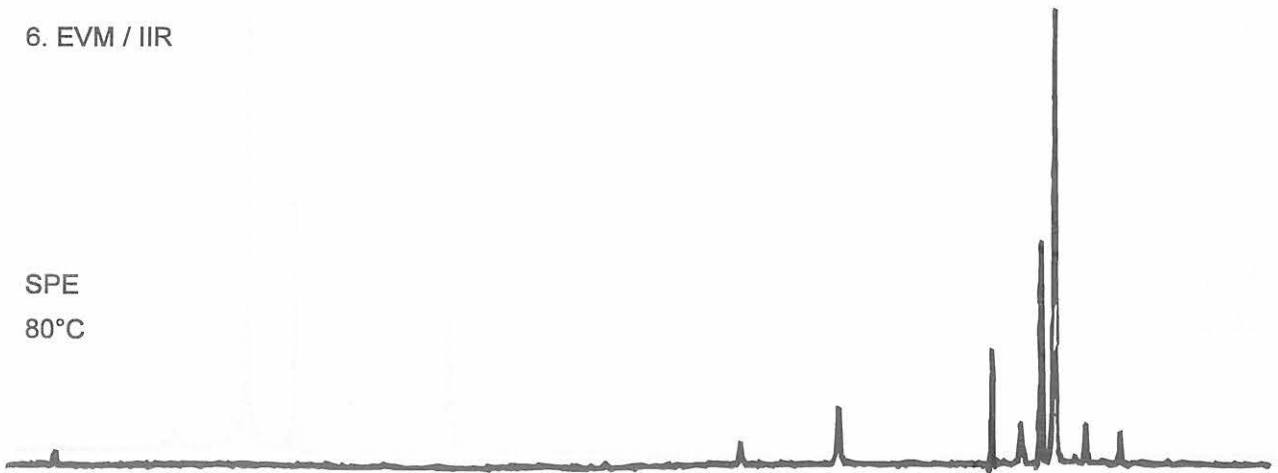


160 140 120 100 80 60 40 20 ppm

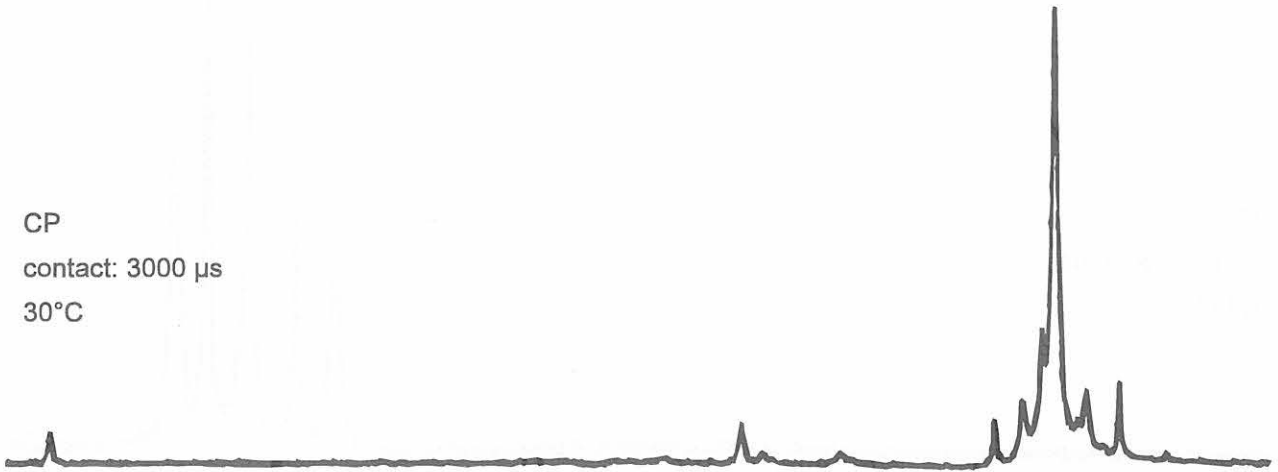
# Polyolefin Blends

6. EVM / IIR

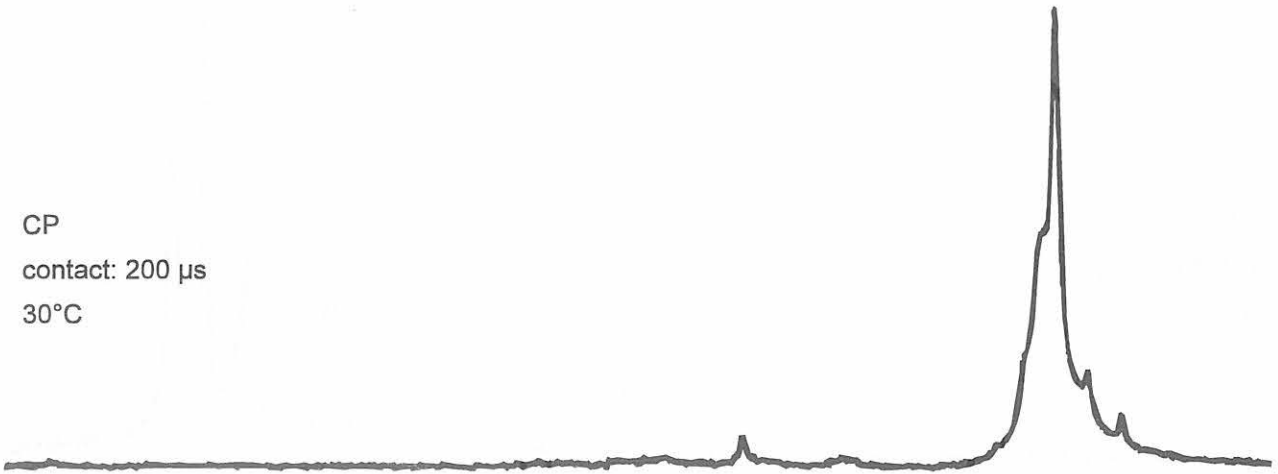
SPE  
80°C



CP  
contact: 3000 μs  
30°C



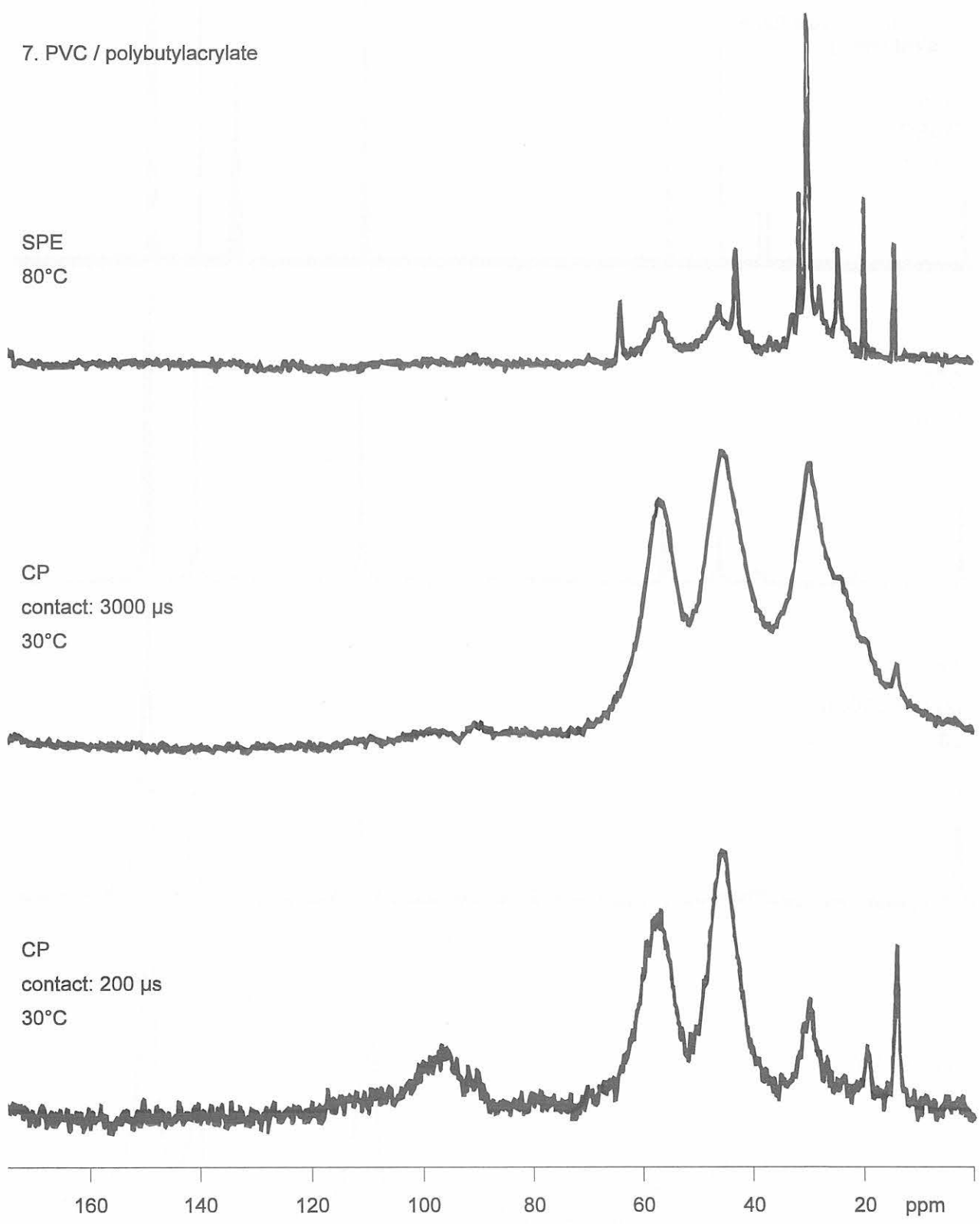
CP  
contact: 200 μs  
30°C



160 140 120 100 80 60 40 20 ppm

# Blends

7. PVC / polybutylacrylate



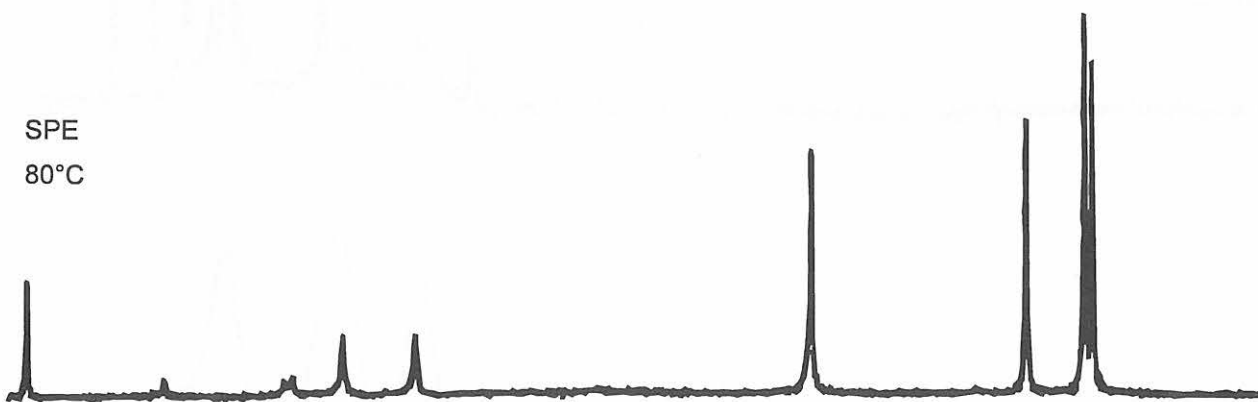
# Polyurethanes

1. AU (see polyurethane elastomers)

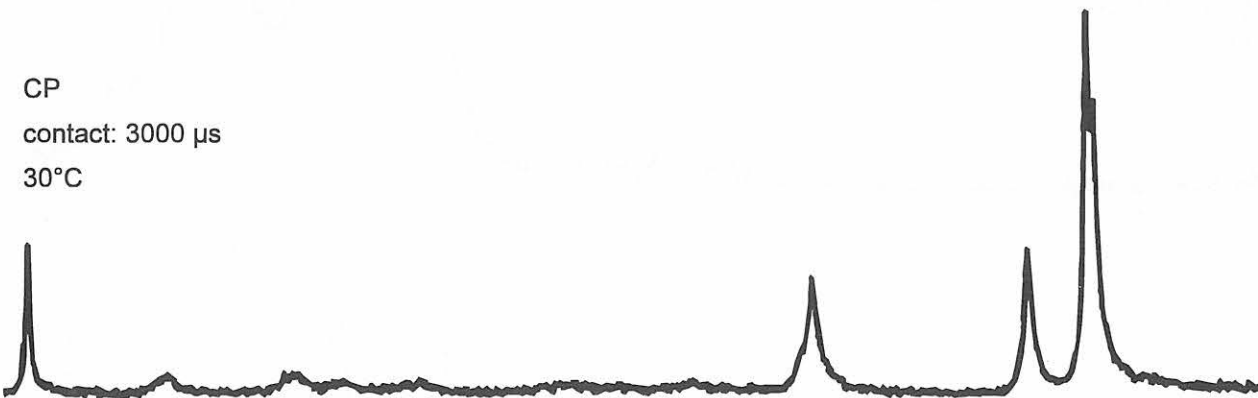
solution  
DMSO — d<sub>6</sub>  
100°C



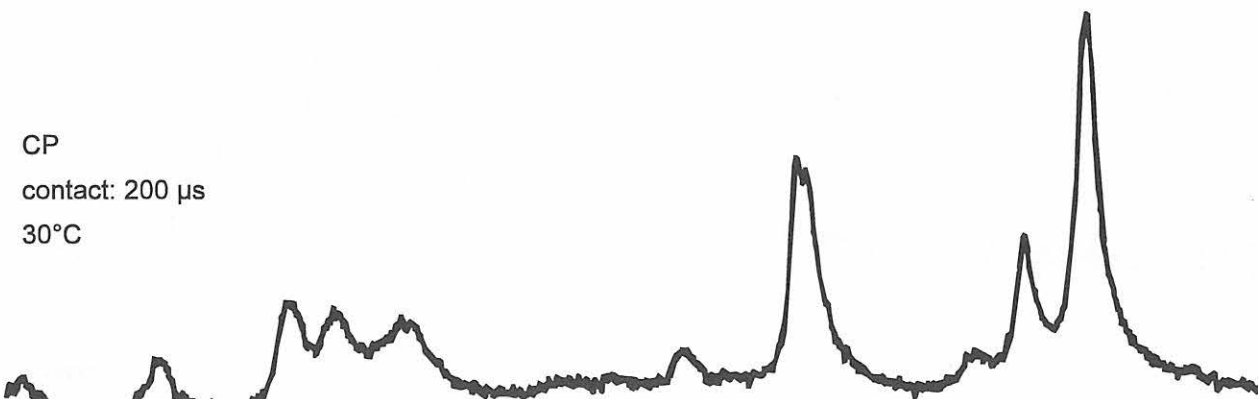
SPE  
80°C



CP  
contact: 3000 μs  
30°C



CP  
contact: 200 μs  
30°C



160 140 120 100 80 60 40 20 ppm 0



# Polyurethanes

2. AU (see polyurethane elastomers)

solution

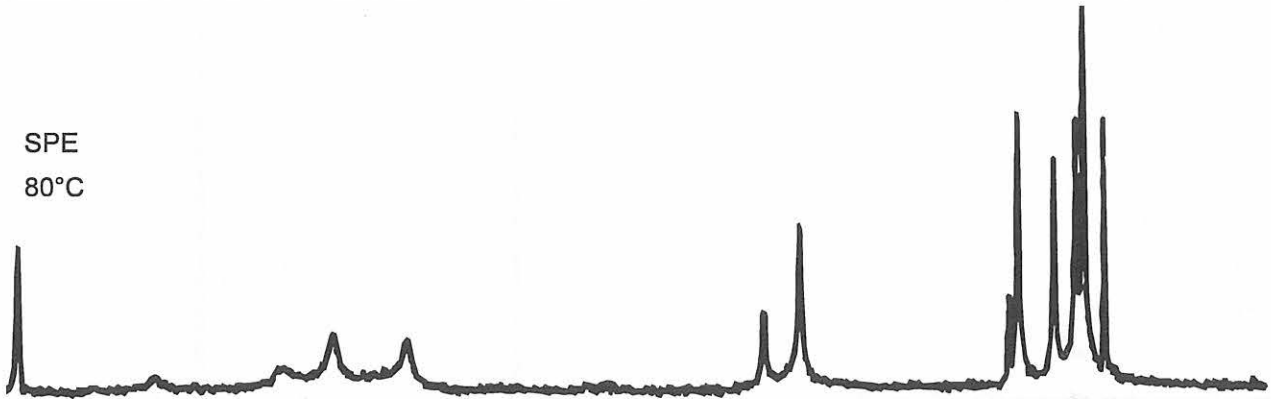
DMF - d<sub>7</sub>

100°C



SPE

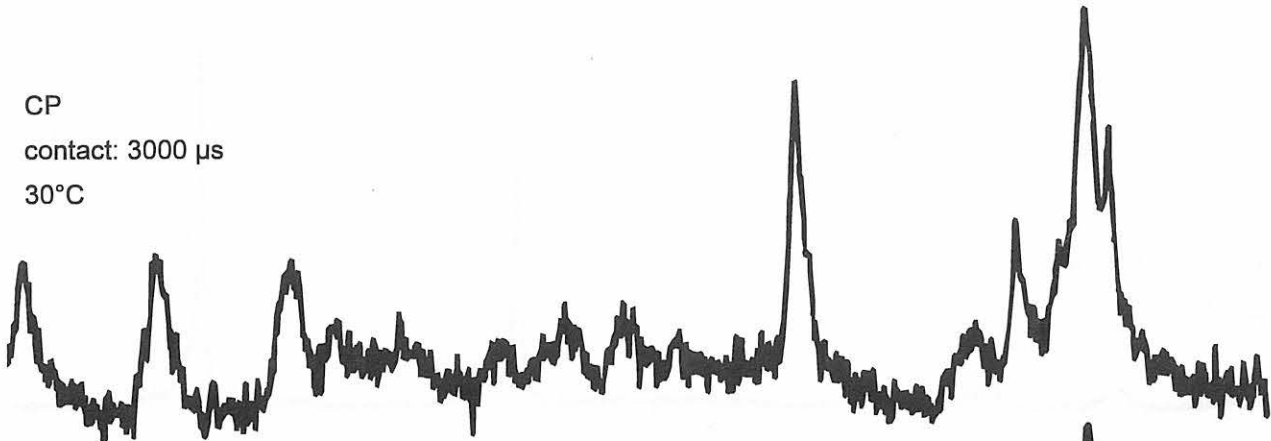
80°C



CP

contact: 3000 μs

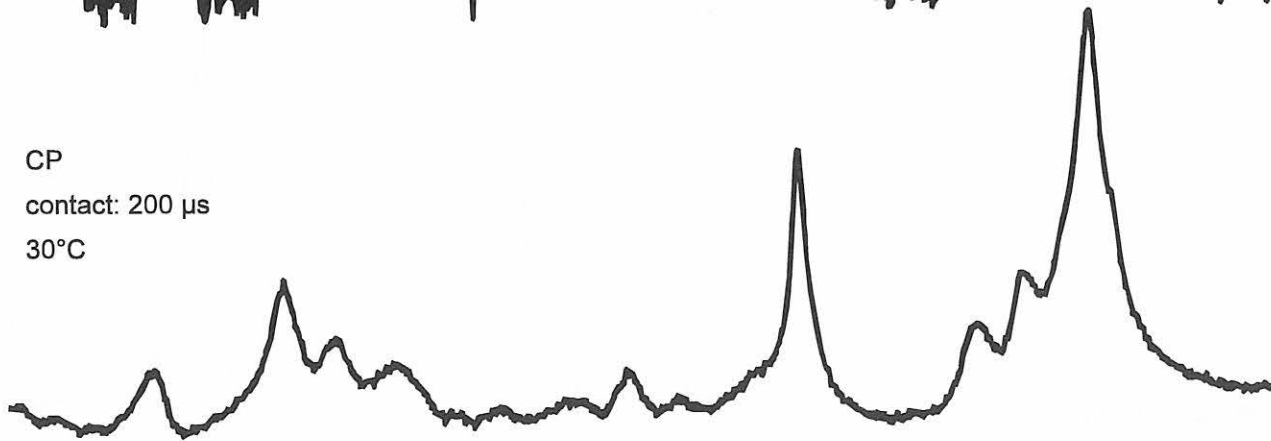
30°C



CP

contact: 200 μs

30°C

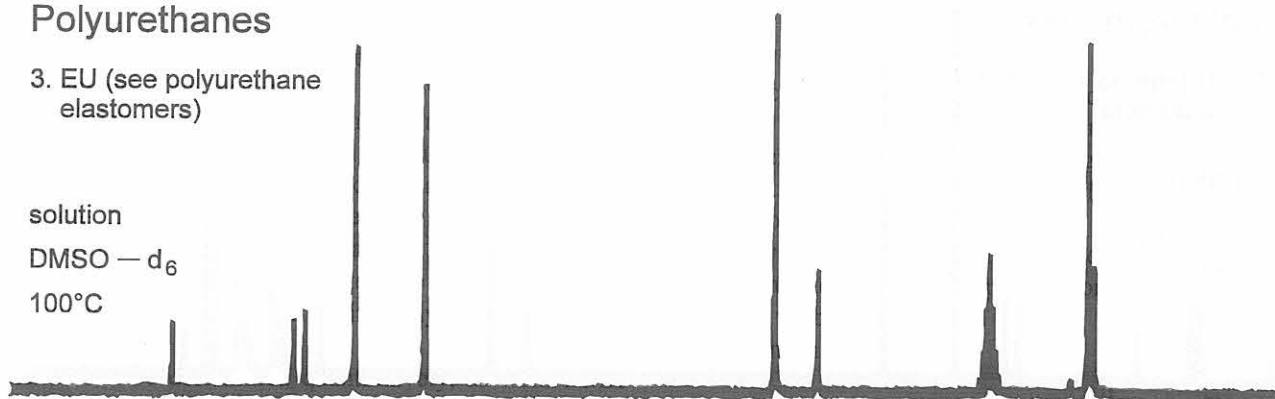


160 140 120 100 80 60 40 20 ppm

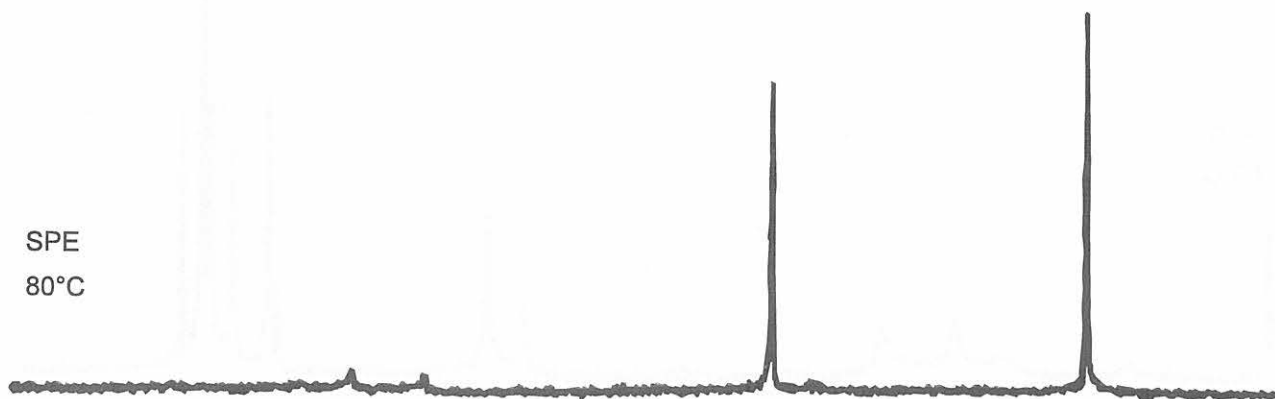
# Polyurethanes

3. EU (see polyurethane elastomers)

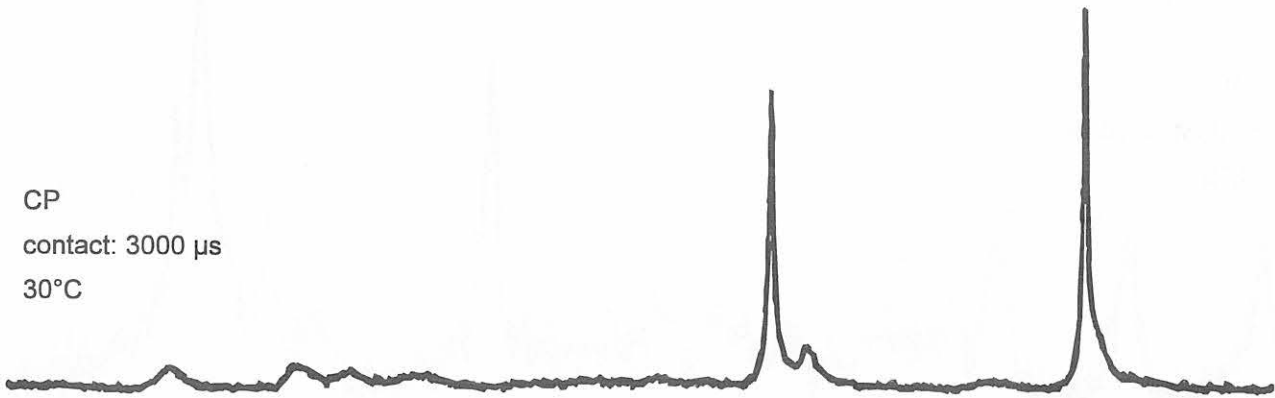
solution  
DMSO - d<sub>6</sub>  
100°C



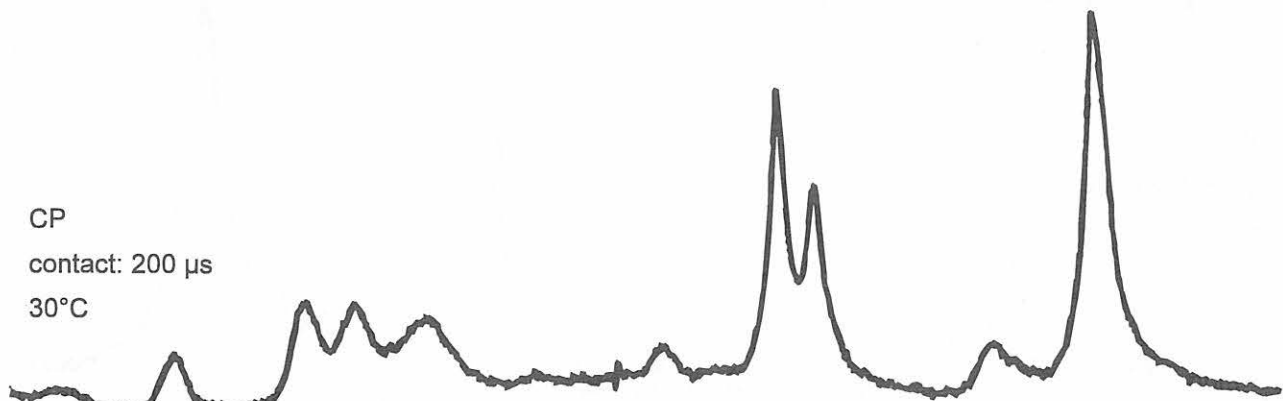
SPE  
80°C



CP  
contact: 3000 μs  
30°C



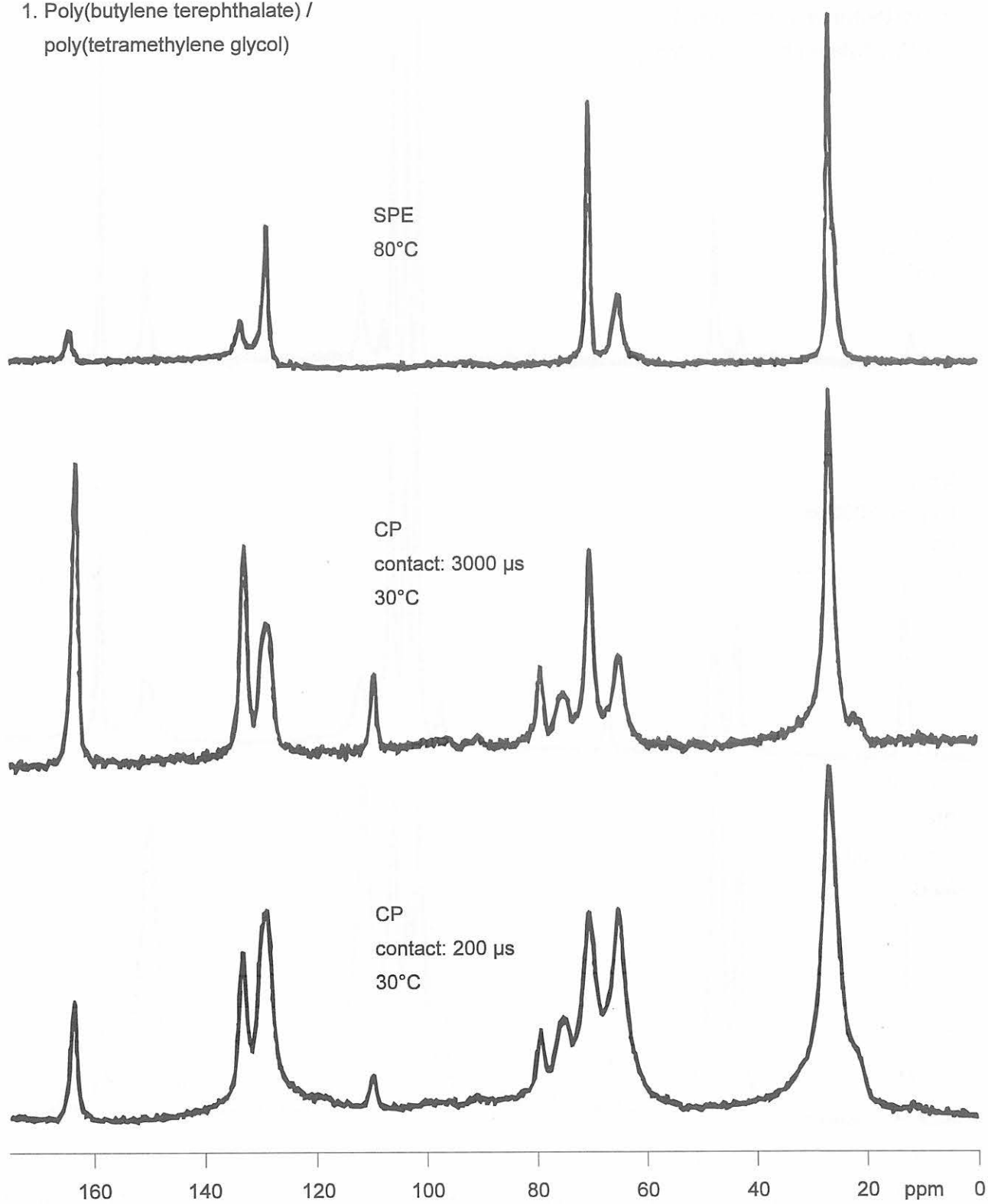
CP  
contact: 200 μs  
30°C



160 140 120 100 80 60 40 20 ppm 0

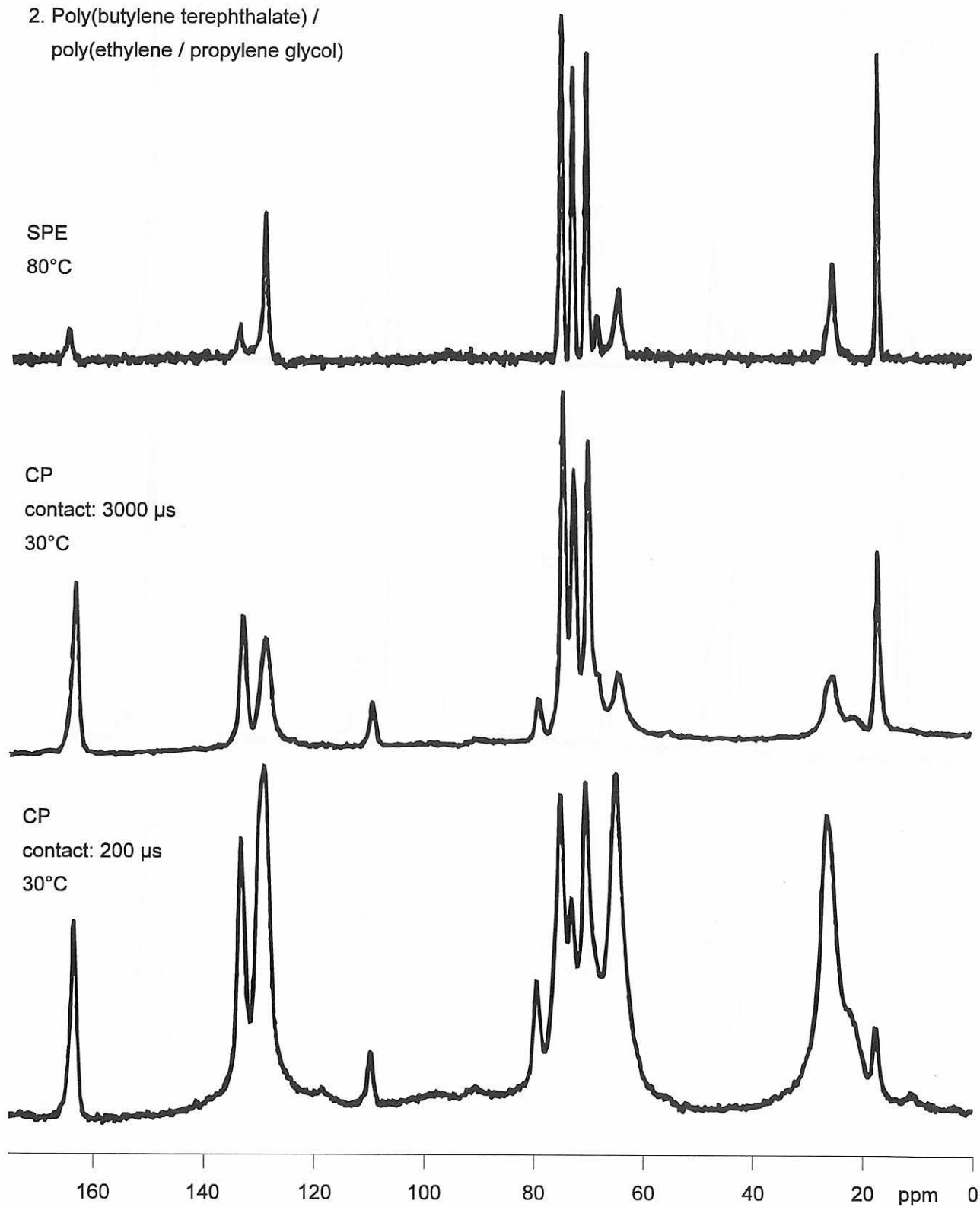
# Polyetheresters

1. Poly(butylene terephthalate) /  
poly(tetramethylene glycol)

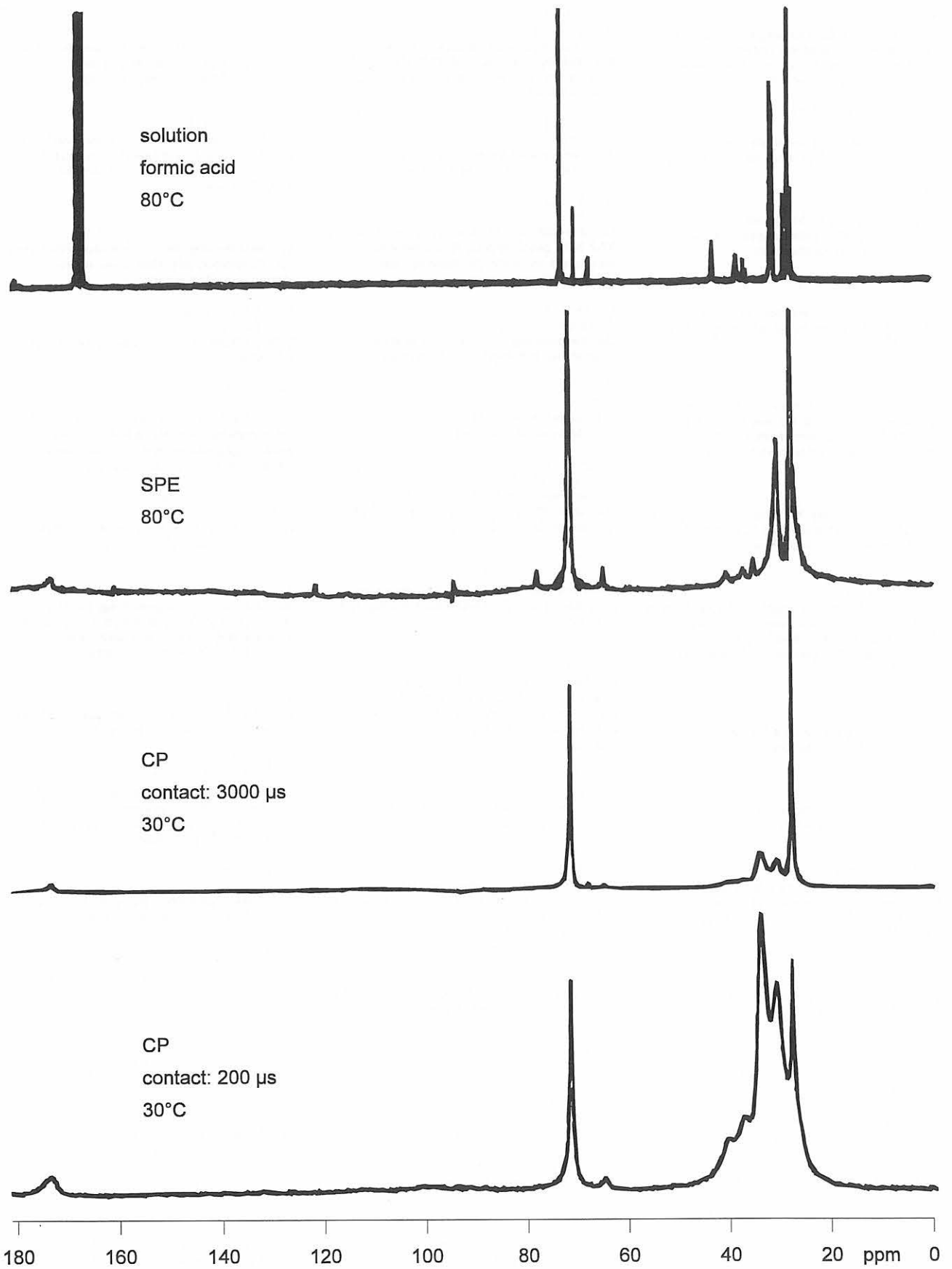


# Polyetheresters

2. Poly(butylene terephthalate) /  
poly(ethylene / propylene glycol)



# Polyetheramide



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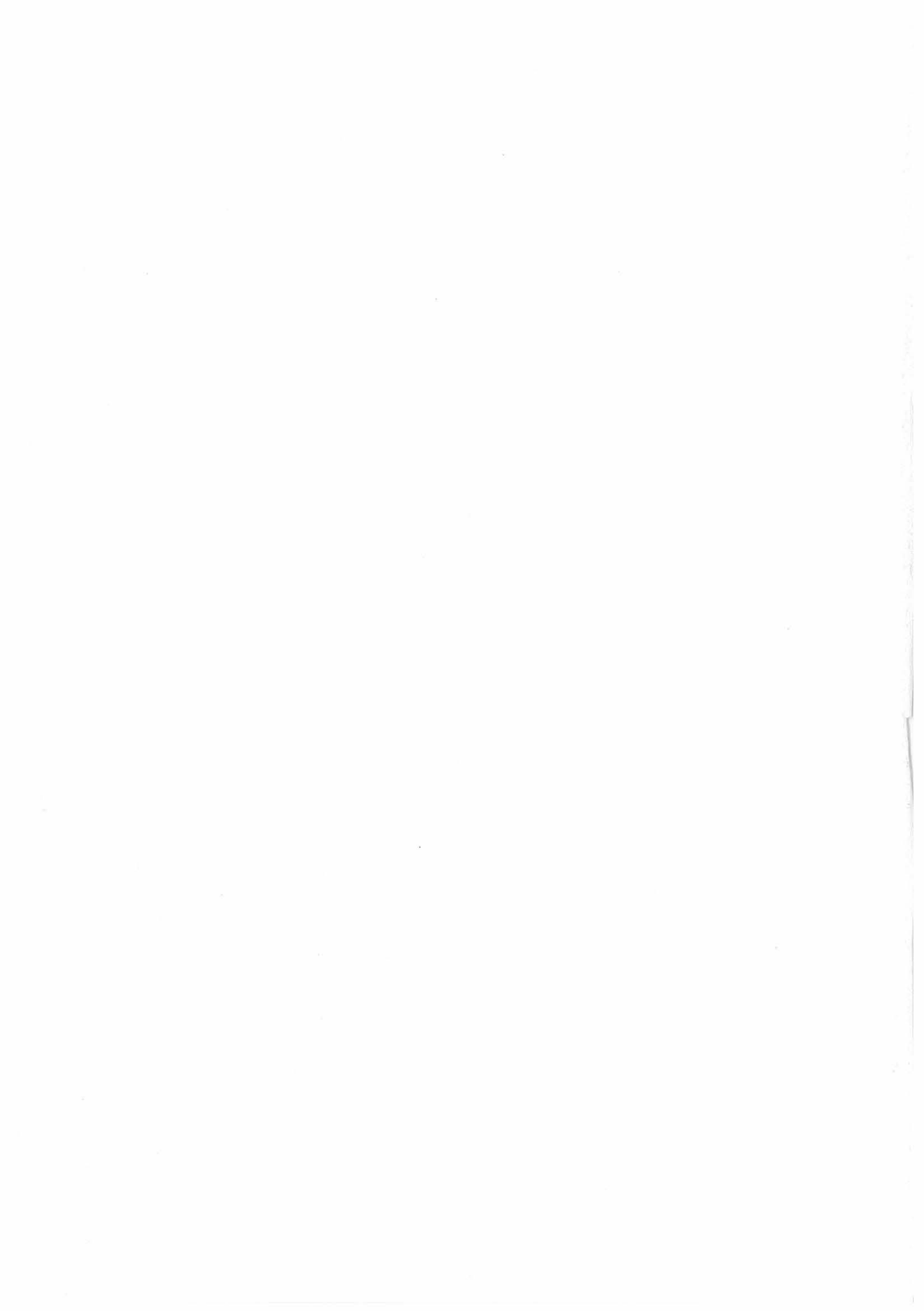
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