

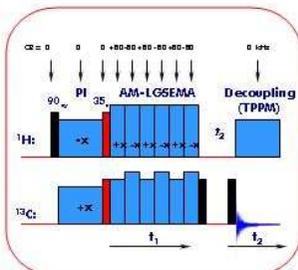
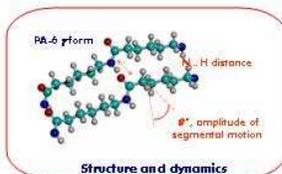
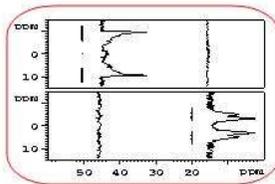
NMR spectroscopy of polymers



Joint Laboratory of Solid-State NMR
IMC AS CR and JHPC AS CR

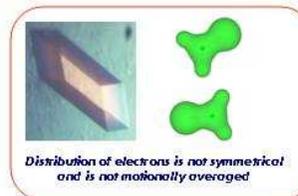


UNESCO/IUPAC Course 2005/2006
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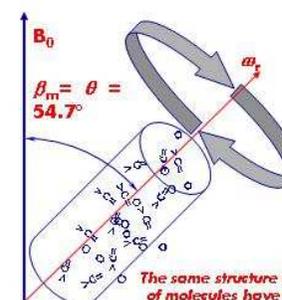
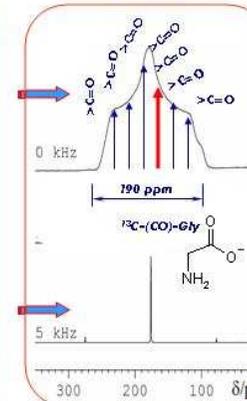
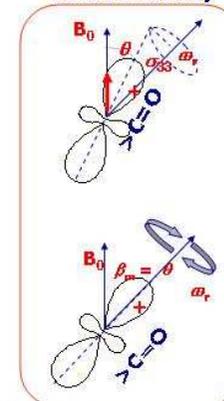


Solid-state NMR spectroscopy

Joint Laboratory of Solid-State NMR
IMC AS CR and JHPC AS CR



Static sample
Anisotropy interactions dominate
Limited mobility



The same structure units in a collection of molecules have different chemical shifts - there is no equivalence of it was in solution.

Magic Angle Spinning (MAS)

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Jiri Brus

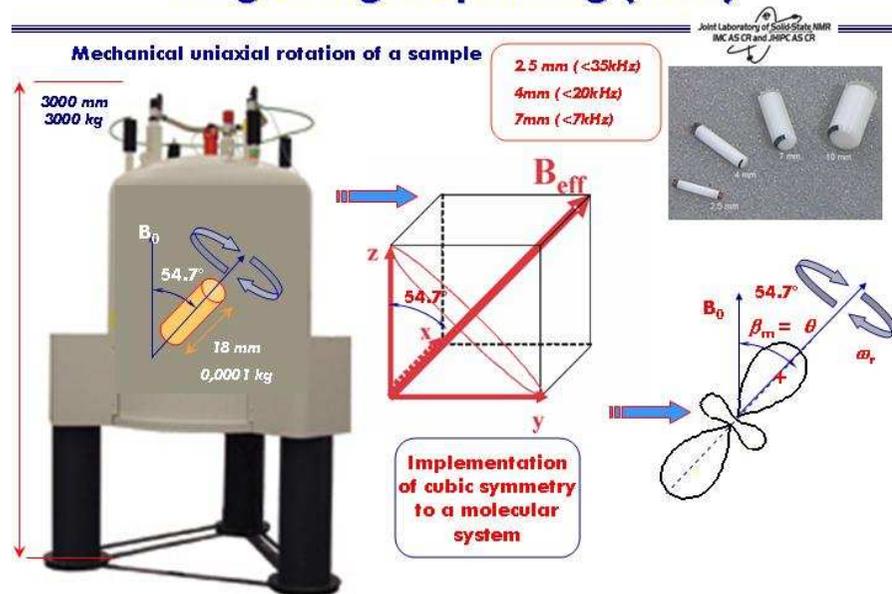
NMR Spectroscopy of Polymers

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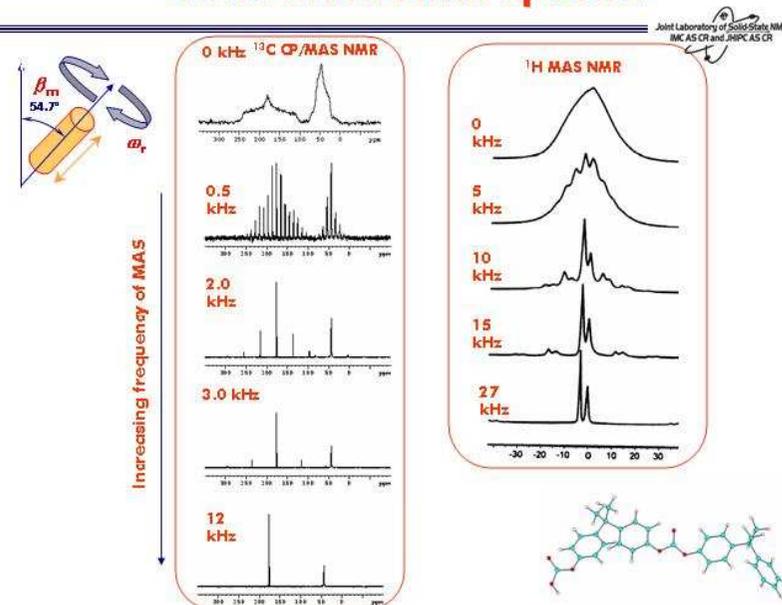
In solid state the situation is a bit complicated because missing isotropic molecular tumbling causes that anisotropy of nuclear interaction now plays dominant role in the appearance of NMR spectra. Frankly speaking the NMR signals are very broad and spectra become featureless. In general missing isotropic tumbling leads to severe broadening of the detected signals. The lack of resolution, however, does not mean the absence of structure information, it rather reflects its overcrowding in such extent that we are not able to read out and understand it. Due to this fact various techniques have been proposed to increase spectral resolution.

Magic Angle Spinning (MAS)



One possible way how to compensate missing molecular motion is mechanical uniaxial rotation. Anisotropic interactions such as chemical shift anisotropy have an orientation dependence that can be described by the second rank tensor. In such case physical rotation of the sample around the axis, containing angle 54.7° with direction of static magnetic field leads to averaging of anisotropy broadening to zero.

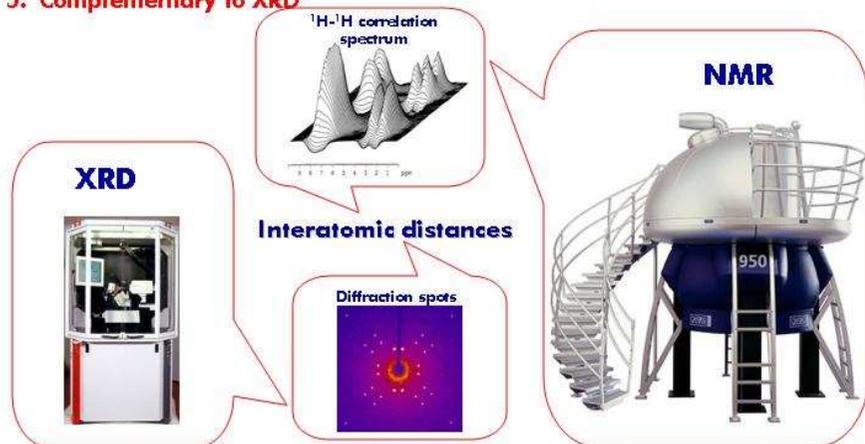
Solid state NMR spectra



In other words, if anisotropic interaction is refocused at the end of each rotor period the originally broad NMR signal is easily broken up into series of spinning sidebands. It is quite clear that with increasing spinning frequency resolution of NMR spectra significantly improves. However, in the case of a dense network of strongly dipolar-coupled spins like ^1H the line-widths of NMR signals are frequency dependent and all signals are still broad. Even at moderately fast spinning speeds ^1H NMR spectra remain featureless. Sufficient resolution is provided by rotation frequencies larger than 35 kHz.

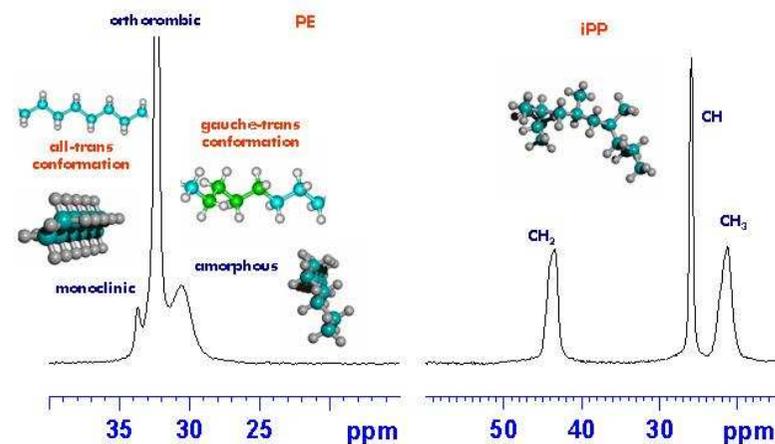
Solid state NMR spectroscopy

1. NMR – a probe to electronic surrounding of specific nucleus
2. High selectivity
3. Structure and dynamics (distances 0.1-0.7 nm)
4. Crystalline, microcrystalline and amorphous substances
5. Complementary to XRD



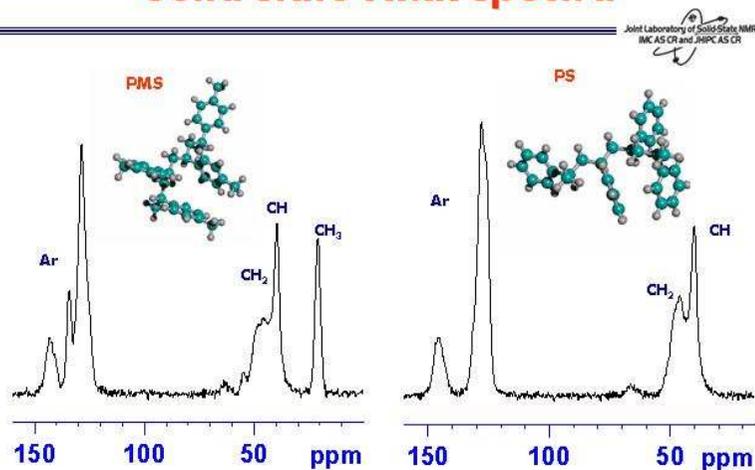
Nevertheless we can say that recent methodology and hardware development significantly increases resolution and selectivity of solid-state NMR experiment that can now provide detailed information about the structure and segmental dynamics of wide range of materials. It has to be mentioned that quite recently full three dimensional structures of several proteins in solid microcrystalline state have been successfully determined by solid-state NMR.

Solid state NMR spectra



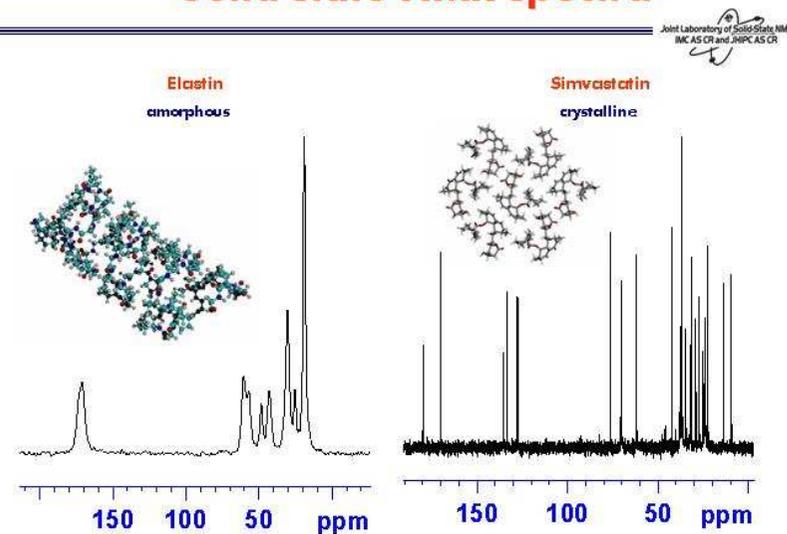
Typical examples of solid state ^{13}C NMR spectra of several systems: Due to the significant differences in conformation of polymer chains we can easily resolve amorphous and crystalline fractions. This is a typical spectrum of polyethylene and polypropylene. Two crystal modification as well as amorphous phase of PE can be clearly distinguished.

Solid state NMR spectra



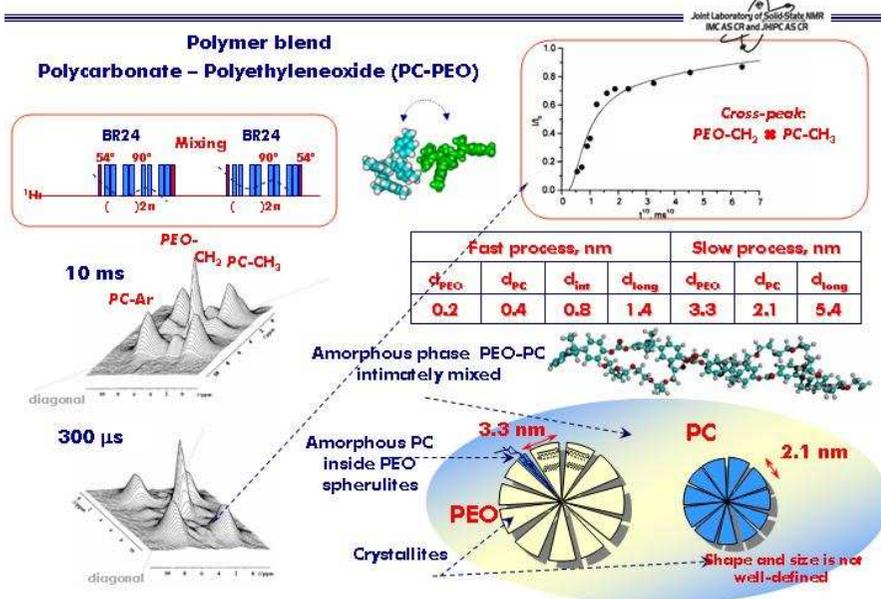
The signal of methyl then clearly distinguishes polymethylstyrene from polystyrene.

Solid state NMR spectra



And here we can see the basic difference between NMR spectra of amorphous and highly crystalline systems. Highly organized and ordered molecular systems produce the spectra with very narrow signals while disordered systems are reflected by signals which are more or less broad depending on the degree of organization and assembling of the molecules.

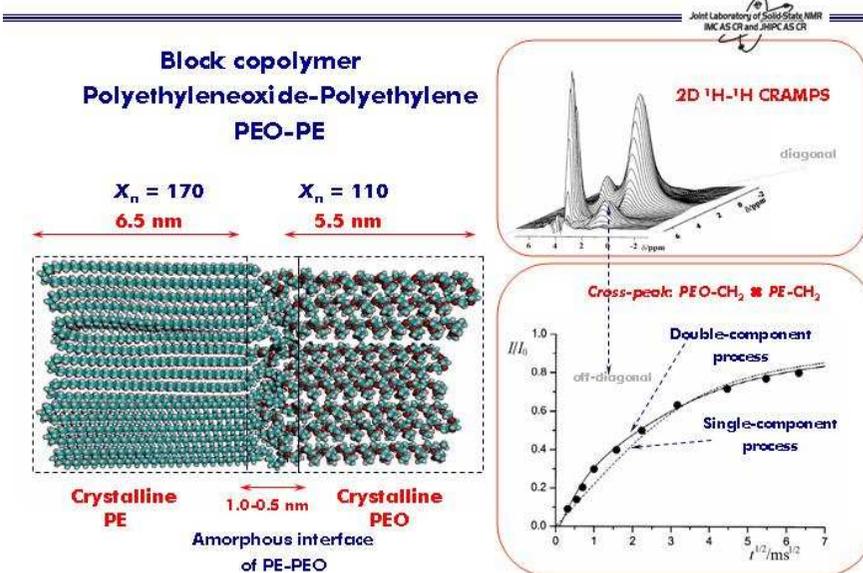
Determination of the Domain Size



To obtain detail information it is very often necessary to record two or multidimensional dimensional spectra.

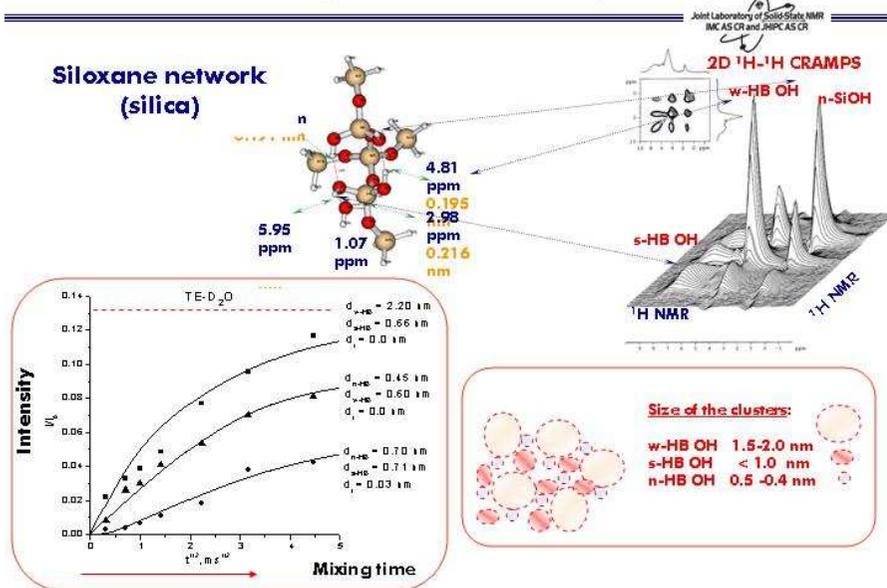
Here we can see a typical example of interpretation of the so called spin-exchange experiment. This can be demonstrated on the investigation of the extent of mixing in polymer blends based on semicrystalline PEO and polycarbonate. In these spectra the presence of off-diagonal signals indicates polarization transfer between spatially close polymer components and from the time dependence of the signal intensity we can estimate size of these domains. The first cross-signals indicating contact of both components are detected after 300 us of mixing time. This reflects an intimate almost molecular mixing of both components in the amorphous phase. Full equilibration is however achieved within 70 ms, which reflects complicate polarization transfer between crystallites which size can be exactly determined. The slow process, predominantly corresponds to polarization transfer from crystalline PEO to PC located within interlamellar space of spherulites of PEO.

Determination of the Domain Size



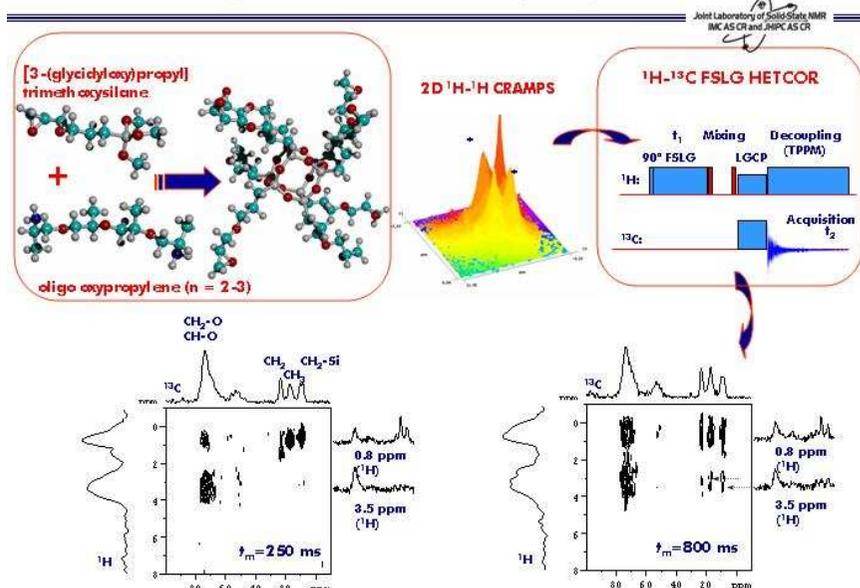
Another example of polymer system with complicated morphology provides diblock copolymer PE-PEO. The deviation of the experimental dependence from the model of a simple two-phase system reflects complicated morphology in interface region. Amorphous interface is not uniform nor homogeneous but rather both components form relatively small domains with diameter ca. 1.0 and 0.5 nm. Magnetization exchange between them is apparent at the beginning of spin diffusion. The slow spin-diffusion process corresponds to the magnetization transfer involving substantially larger crystallites of both polymers and simulation of spin exchange process revealed that crystallites are substantially larger, ca. 6.0 nm. From the known number-average polymerization degree of both polymer chains it is clear that lamellae consist of folded polymer chains.

Clustering of Surface Hydroxyls



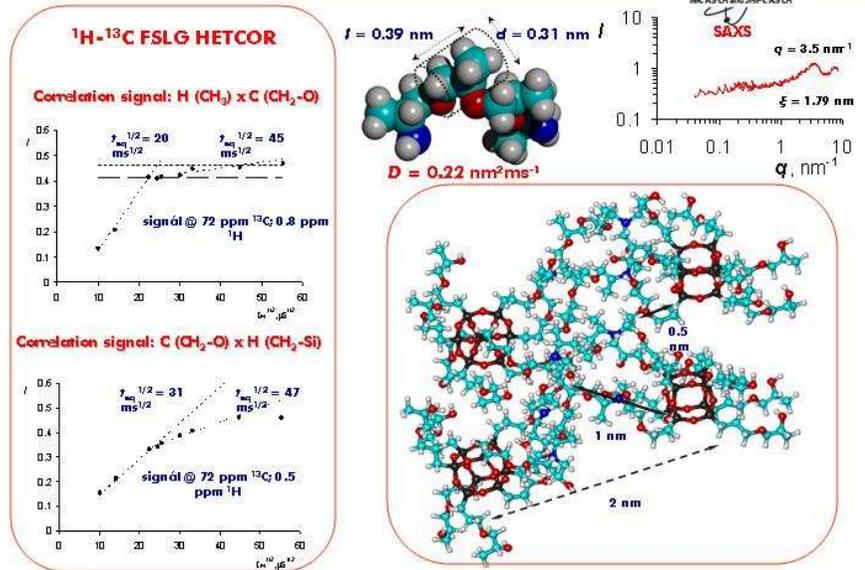
This spin-exchange experiments can be extended also to study formation and size of hydroxyl clusters at the surface of polysiloxane networks which are short-range-ordered materials. We can clearly resolve three basic types of surface hydroxyls: strongly hydrogen-bonded (s -HB OH) and weakly hydrogen-bonded hydroxyl groups (w -HB OH), and non-hydrogen-bonded silanols (n -HB OH). The distribution of these hydroxyl groups can be successfully probed by a series of 2D ^1H - ^1H correlation experiments. In fact we observe relatively slow spin-exchange indicating that the clusters of strongly and weakly hydrogen-bonded OH form relatively large regions. From the best fits, average size of hydroxyl clusters can be estimated.

Self-organization in Epoxy-Siloxanes



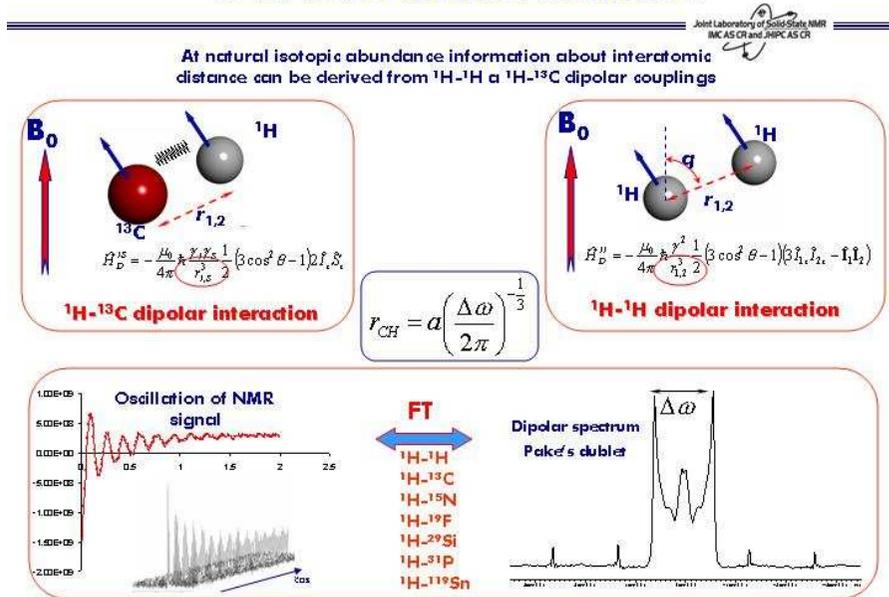
It is quite clear that in many cases the spectral resolution in 2D spin exchange experiments is not sufficient to provide required data, especially for complicated polymer networks. For instance for this system we can resolve only two signals. To increase the spectral resolution we must use heteronuclear correlation experiment. This is the experiment which correlates proton and carbon chemical shift and which is based on polarization transfer from protons to carbon atoms. Due to this correlation significantly better resolution is afforded by ^{13}C chemical shift dispersion. Consequently ordering and arrangement of various segments in this complex polymer networks can be probed.

Self-organization in Epoxy-Siloxanes



Due to the improved resolution we can resolve protons located at the surface of siloxane clusters and consequently we can observe polarization transfer to polypropylene segments. In this way, from the obtained build-up curves we can determine the largest distance between center of propyleneoxide phase and the surface of siloxane clusters. It is approximately 1nm which means that corresponding distance between these clusters is not larger that 2 nm. In addition the observed strictly two-step process indicates that that clusters are regularly dispersed in the bulk of network and random distribution can be nearly excluded. This regular distribution was finally confirmed by SAXS.

¹H-X interatomic distance



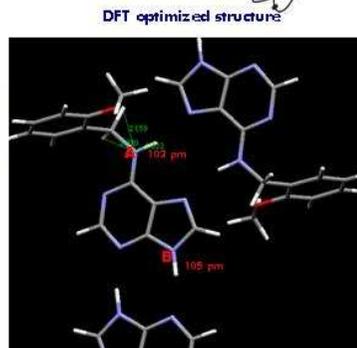
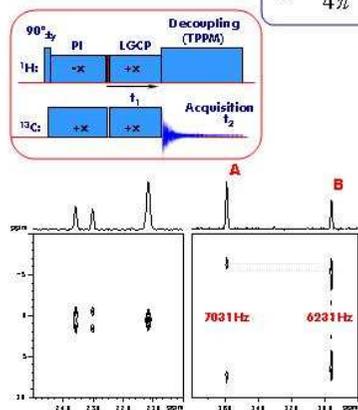
However solid state NMR spectroscopy provides much more precise measurement of interatomic distances. Simply speaking under special experimental conditions called as recoupling conditions, dipole-dipole interactions between two spins produces oscillation of the detected NMR signal and FT of this oscillation leads to a dipolar spectrum which is known as Pake's doublet. Splitting of this doublet is related to dipolar coupling constant. And from this splitting, from the dipolar coupling constant, we can easily extract interatomic distance.

Refinement of position of hydrogen atoms

Measurement of ^1H - ^{15}N dipolar couplings

Selective only for one-bond interaction
Suitable for measurement of N...H distances in hydrogen bonds

$$\omega_d = \frac{\mu_0 \gamma_{1\text{H}} \gamma_{15\text{N}}}{4\pi} \frac{1}{r_{1,2}^3}$$



| Method | NH(A) | NH(B) |
|-----------------|------------|------------|
| DFT calculation | 103 pm | 105 pm |
| NMR experiment | 101 ± 1 pm | 106 ± 1 pm |

This is very advantageous especially for refinement of position of protons involved in hydrogen bonding because in contrast to x-ray crystallography NMR spectroscopy is highly sensitive to the presence and position of hydrogen atoms.

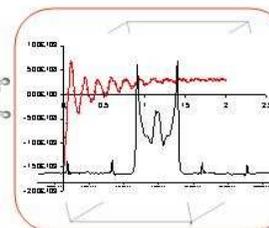
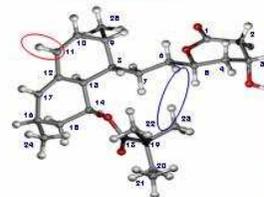
For instance we can measure proton – nitrogen distances in purine bases. Applying the relatively simple LG-CP experiment, we obtain 2D spectra in which splitting between the cross-peaks (the frequency difference) is directly related to interatomic distances.

Accuracy of this measurement is very good. Usually the interatomic distances are determined with precision plus minus five picometers.

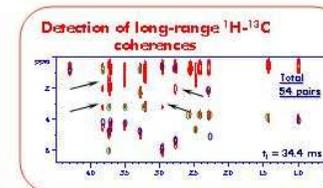
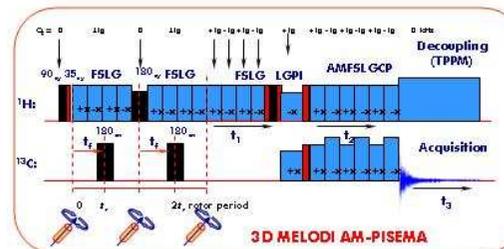
3D structure: ^1H - ^{13}C interatomic distance

Inhibitor of 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase

Simvastatin



$$r_{\text{CH}} = a \left(\frac{\Delta\omega}{2\pi} \right)^{\frac{1}{3}}$$



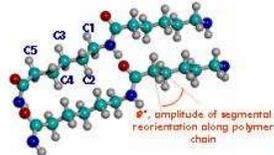
Using a similar but significantly extended approach we can determine full three-dimensional structure of organic crystalline compounds.

In the 2D spectrum obtained by the 3D ^1H - ^{13}C correlation experiment every hydrogen-carbon spin pair is reflected by the correlation signal and the interatomic distance can be derived from the intensity. In fact applying this technique we obtain series of the 2D correlation spectra in which intensities of these signals oscillate. This oscillation can be transformed by the third FT to the dipolar spectrum in which splitting directly reflects interatomic distance according to this relation. It is very simple. Consequently we obtain a set of hydrogen-carbon interatomic distances.

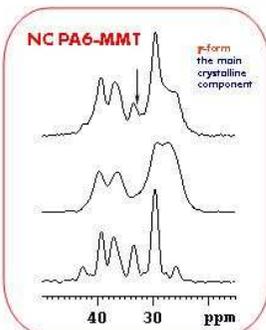
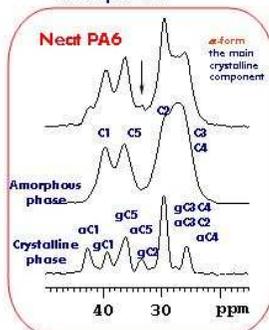
Amplitudes of segmental reorientations

- 1) Semicrystalline system
- 2) α -form, γ -form and amorphous phase
- 3) Segmental dynamics in amorphous phase
- 4) Phase-selective experiments

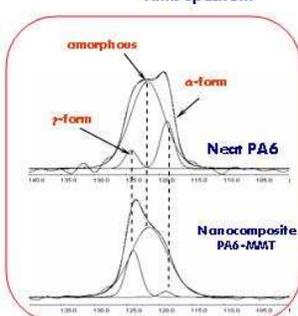
Polymer nanocomposite PA6-MMT



Standard ^{13}C CP/MAS NMR spectrum



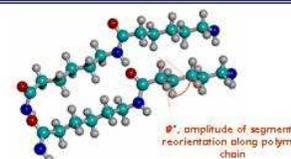
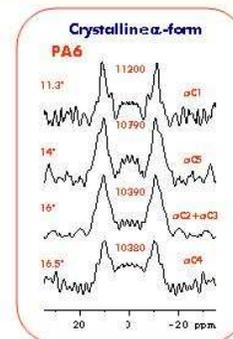
Standard ^{15}N CP/MAS NMR spectrum



This technique is very useful especially for polymer materials because a lot of mechanical properties can be directly related to the segmental dynamics and the measurements of motion-averaged dipolar couplings can provide required data.

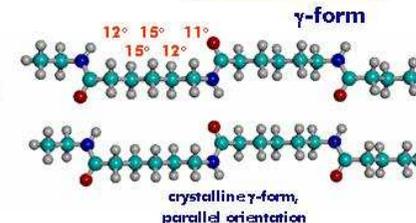
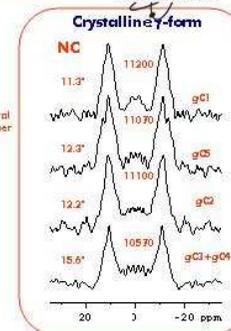
However, situation is much complicated in heterogeneous systems like semicrystalline polymers for instance in nanocomposites of polyamide – 6 containing layered silicate minerals. Polymer matrix is composed by two crystalline forms α and γ and dominating amorphous phase. That is why the resulting NMR spectra are strongly overlapped and complicated. From this follows that precise description of amplitudes of reorientations of polymer segments can be achieved only by the techniques which can detect dipolar spectra separately in crystalline and amorphous phase.

Amplitudes of segmental reorientations



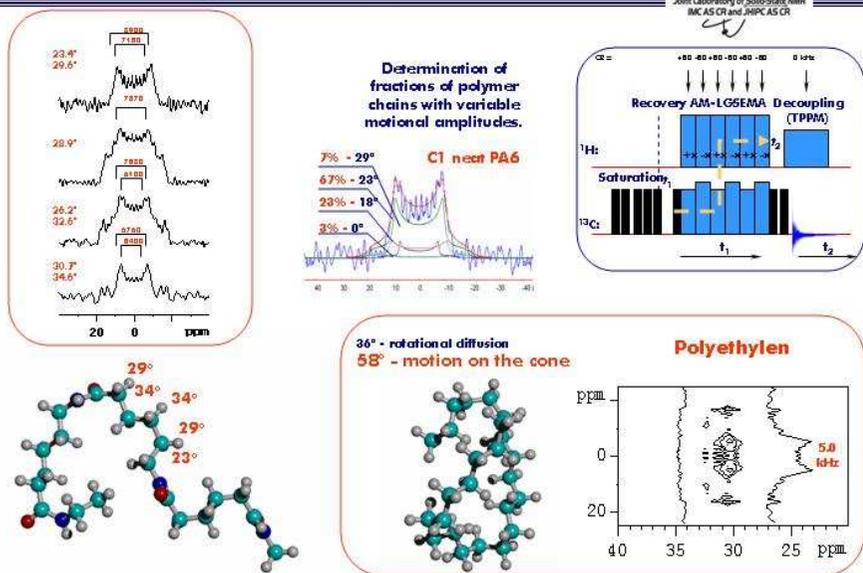
Relation between order parameter and amplitude of uniaxial rotation motion

$$S_{CH} = 1 - \frac{3}{2} \langle \theta^2 \rangle$$



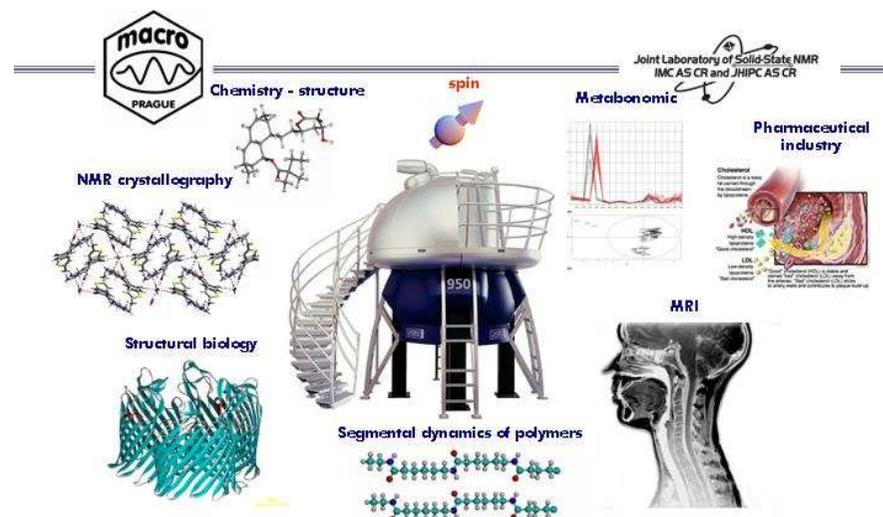
At first we can selectively measure dipolar coupling constant in crystalline phase. Comparing segmental dynamics of both crystalline forms we can say that amplitude of reorientation increases from amide groups toward the center of repeat unit and the average amplitude is about 14 degrees. This is significantly larger amplitude comparing with rigid organic crystals with amplitude smaller than 2-6 degrees. On the other hand it is comparable with motional amplitudes found in crystallites of PE and PP.

Amplitudes of segmental reorientations



In amorphous phase the situation is a bit complicated. Average amplitude is significantly larger around 30 degrees. In addition the dipolar spectra can be considered rather as superposition of several motion modes with variable amplitude. From the simulation of these spectra we can estimate fraction of polymer chains in amorphous phase adopting particular amplitude. For instance comparing neat PA6 and NC it is clear that distribution of these motional modes increases in the presence of silicate layers and in addition, probably a bit surprisingly, formation of significant fraction of polymer chains with much released segmental motions is observed. Shortly speaking in nanocomposites there are polymer chains with higher mobility compared with neat PA6.

NMR spectroscopy: applications in chemistry, biology and medicine



NMR spectroscopy as a method of structure analysis is very powerful tool to investigate structure and dynamics of wide range of materials starting from dilute solution through, liquid like gels, soft polymers up to rigid and hard glasses, crystals and in some cases living organisms. Among all NMR techniques predominantly solid-state NMR spectroscopy is nowadays rapidly developing field of structure analysis and in a near future we can expect that determination of protein structures and other complex structures in highly organized microcrystalline state will be routine procedure.