UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Solid-state NMR spectroscopy of polymers

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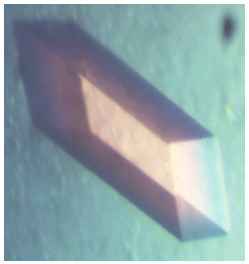
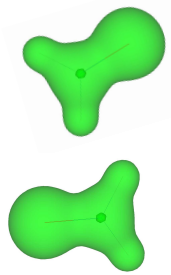
Solid-state NMR spectroscopy



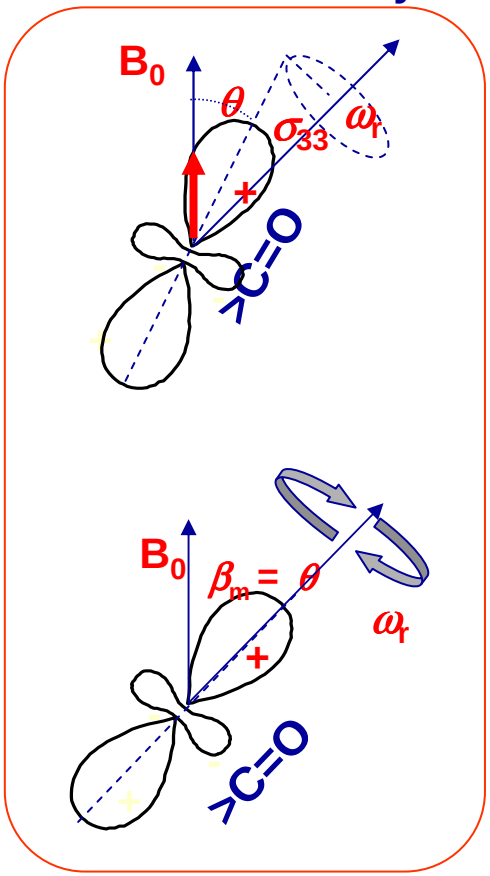


Distribution of electrons is not symmetrical and is not motionally averaged

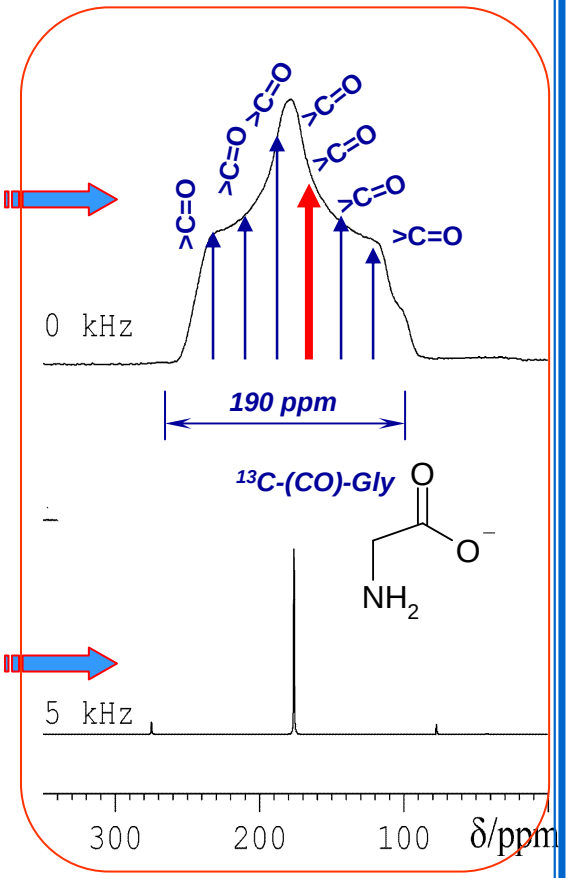
Static sample

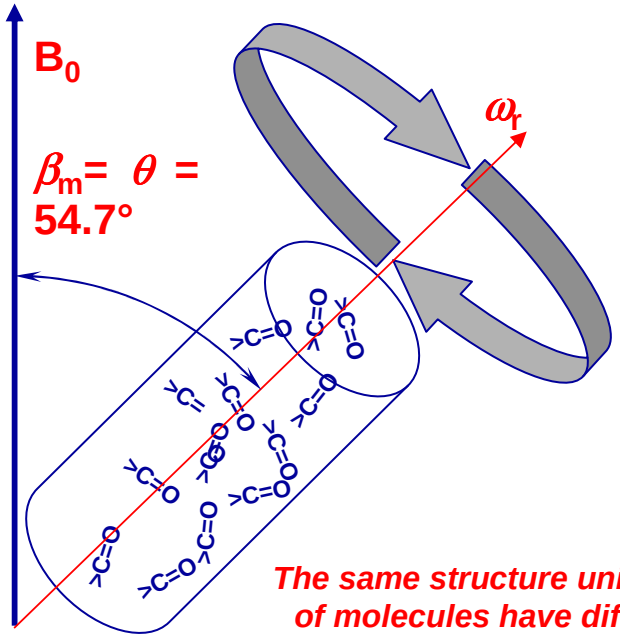
Anisotropy interactions dominate

Limited mobility



Chemical shift anisotropy



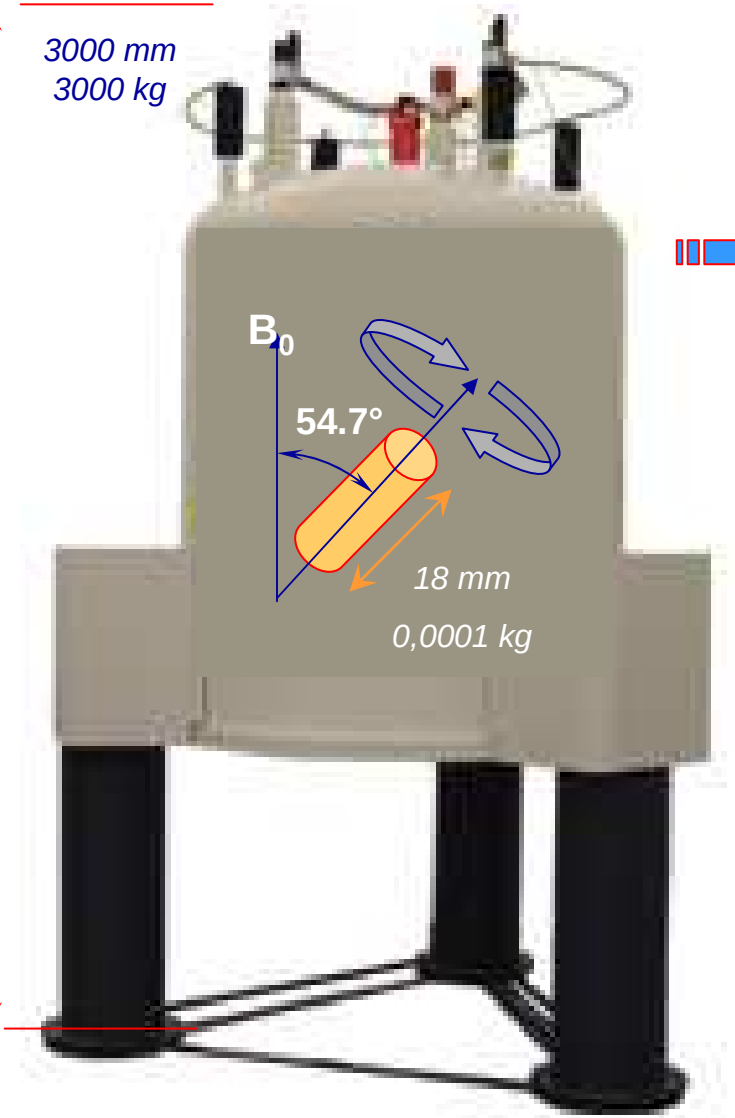


The same structure units in a collection of molecules have different chemical shifts – there is no equivalence at it was in solution.

Magic Angle Spinning (MAS)

Magic Angle Spinning (MAS)

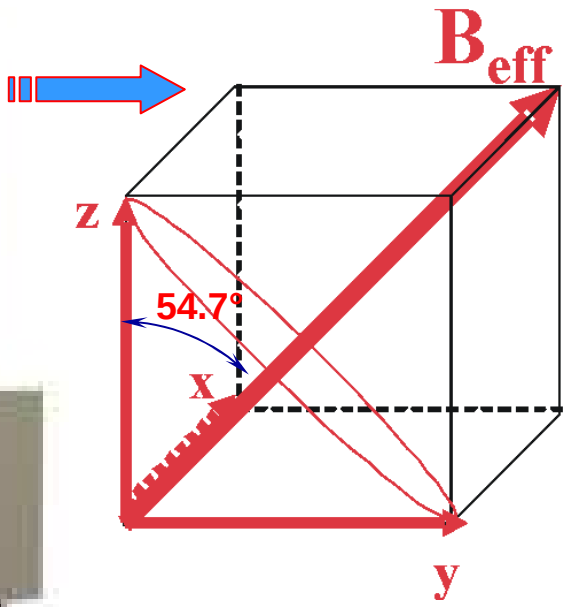
Mechanical uniaxial rotation of a sample

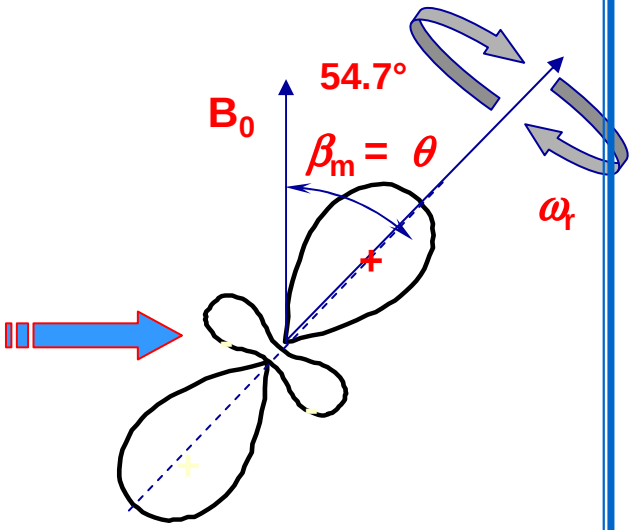


2.5 mm (<35kHz)

4mm (<20kHz)

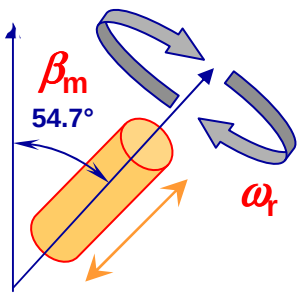
7mm (<7kHz)



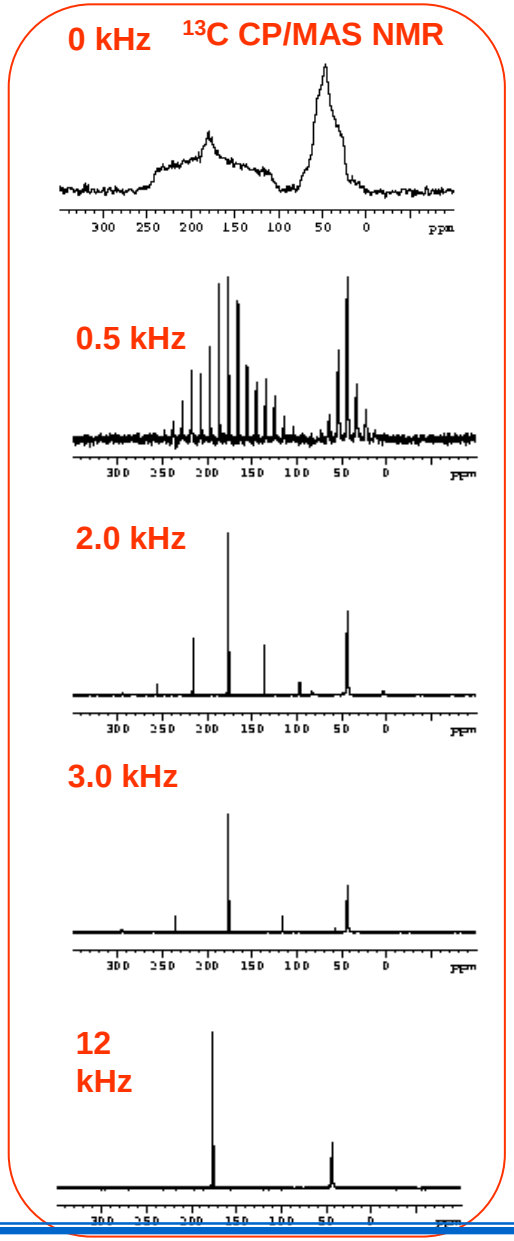


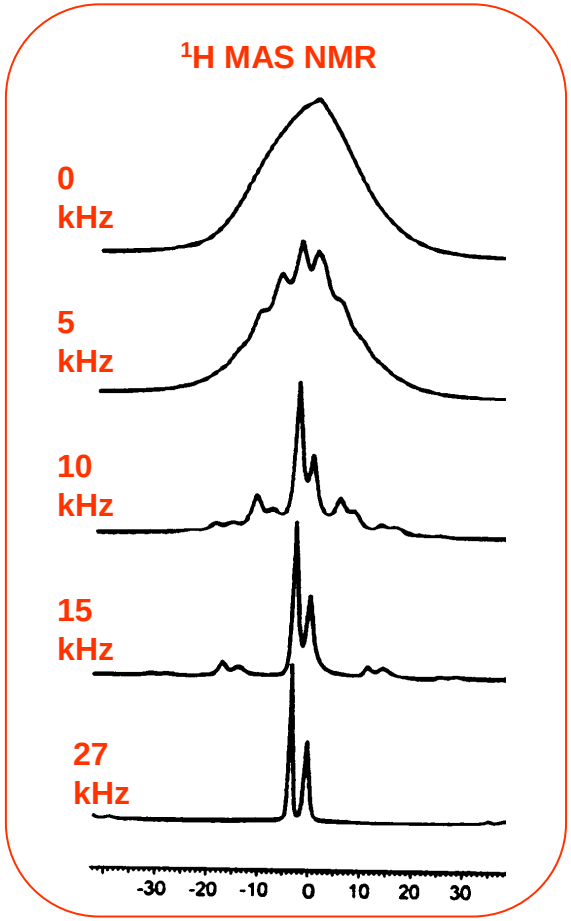
Implementation of cubic symmetry to a molecular system

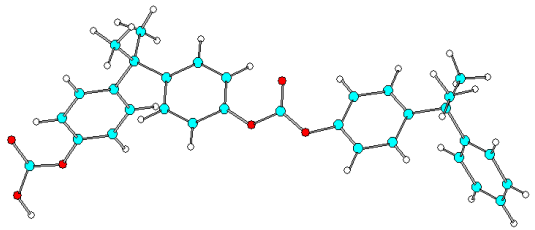
Solid state NMR spectra



Increasing frequency of MAS



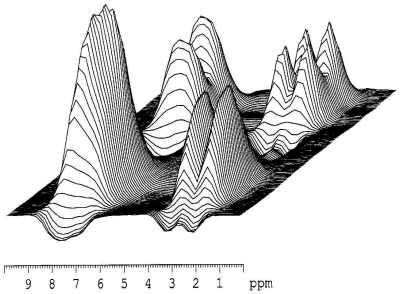




Solid state NMR spectroscopy

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

^{1}H-^{1}H correlation spectrum

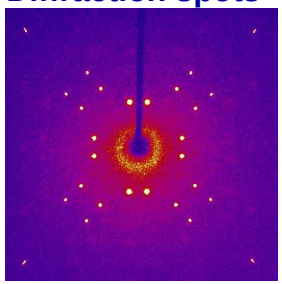


NMR

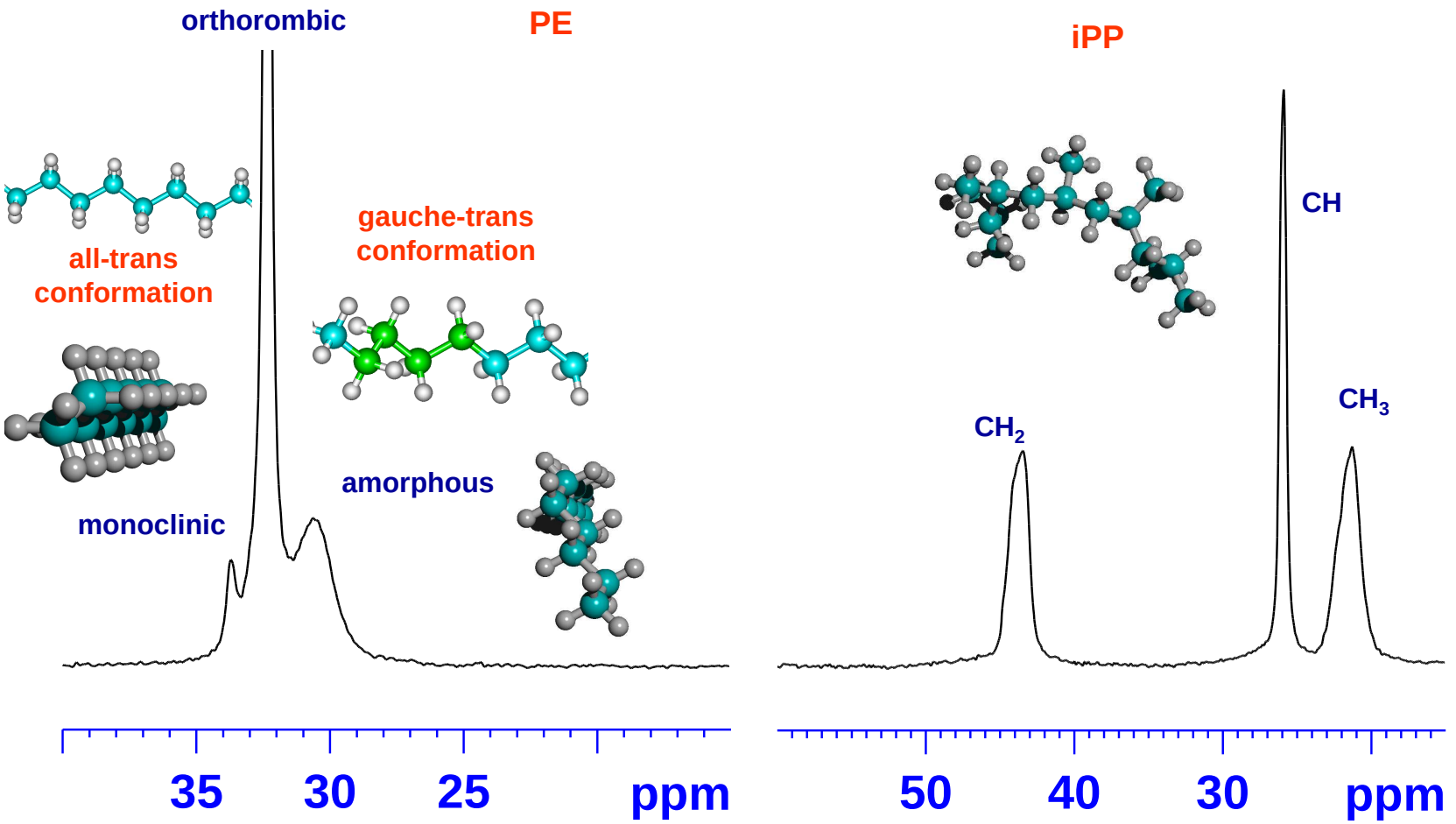
XRD

Interatomic distances

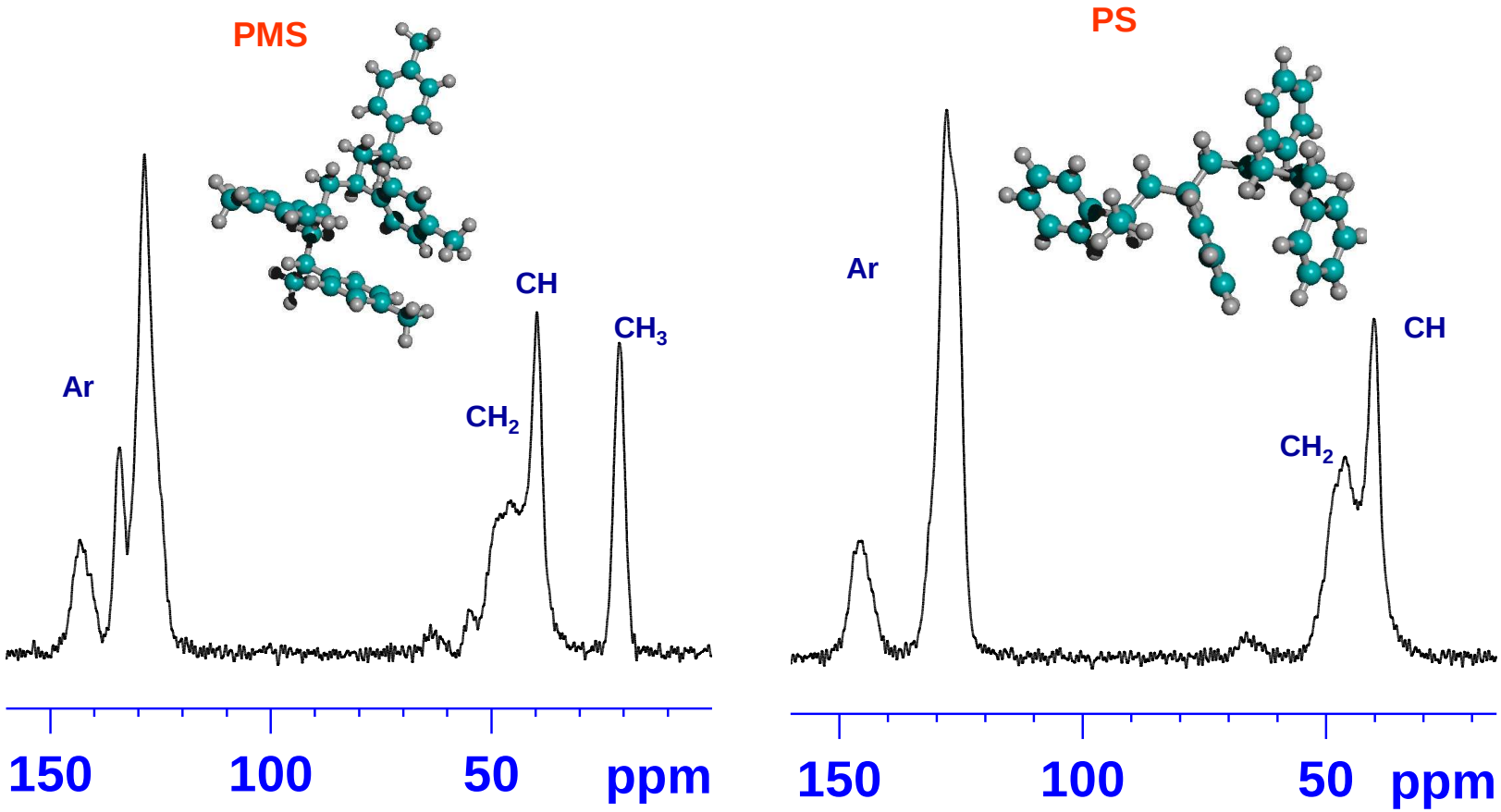
Diffraction spots



Solid state NMR spectra



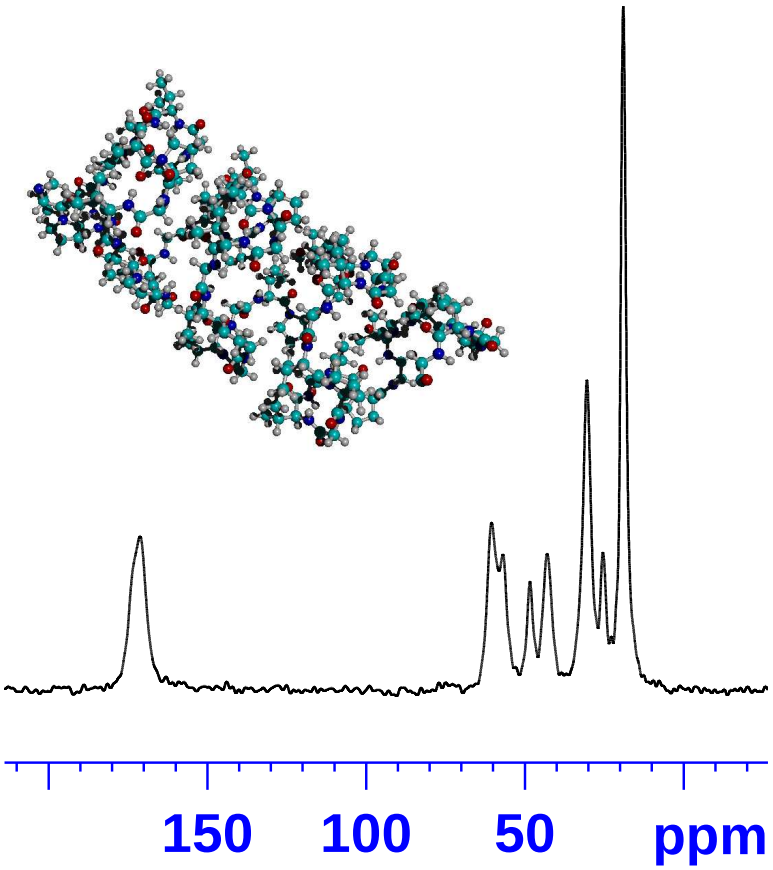
Solid state NMR spectra



Solid state NMR spectra

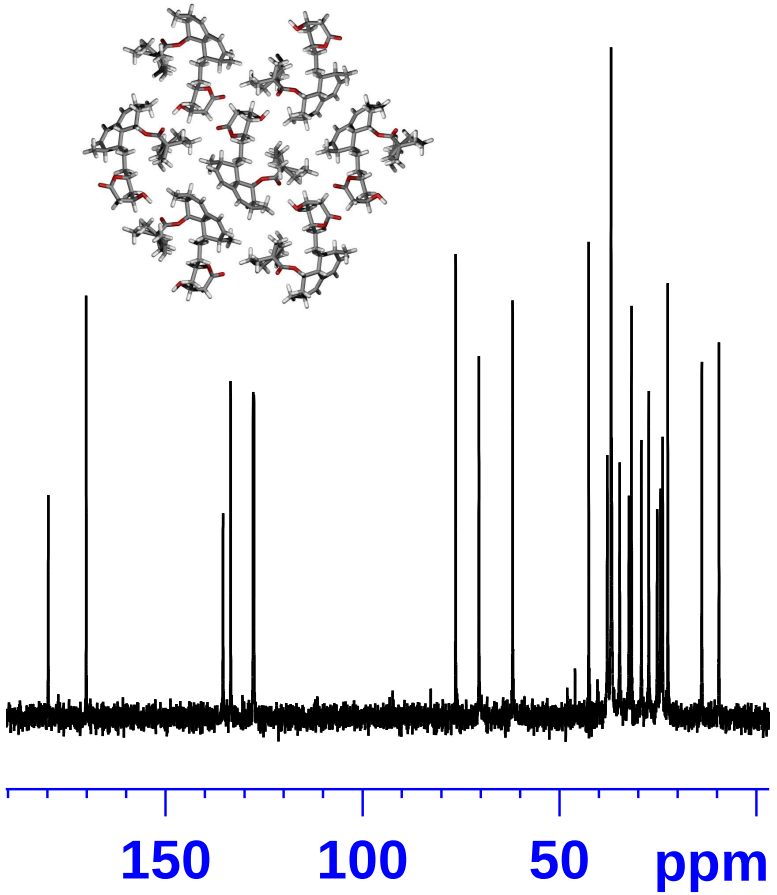
Elastin

amorphous



Simvastatin

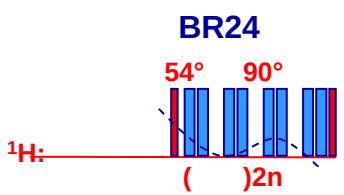
crystalline

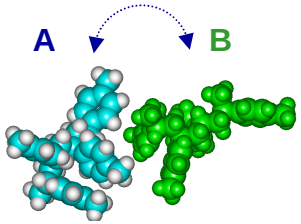


Two-dimensional spectroscopy

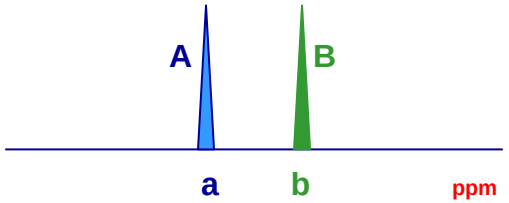
A two-component system

1D ^{1}H MAS NMR pulse sequence

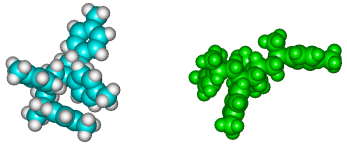




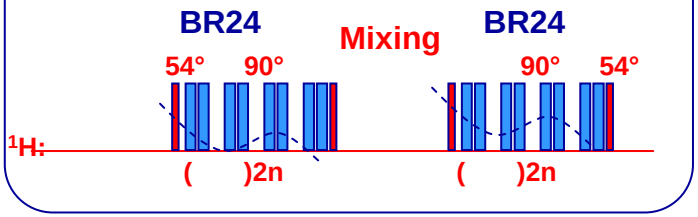
1D ^{1}H MAS NMR spectrum



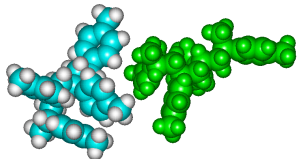
Spatially separated with distance larger than 5 A

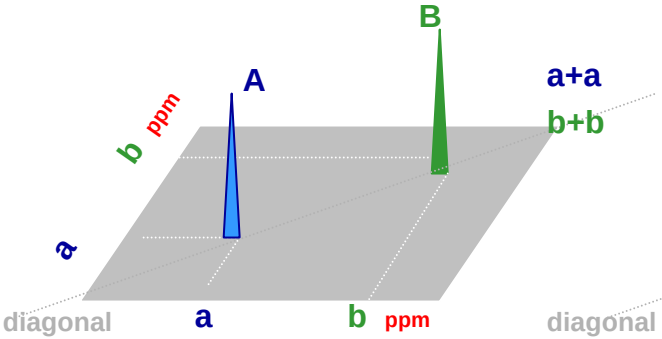


2D ^{1}H MAS NMR pulse sequence

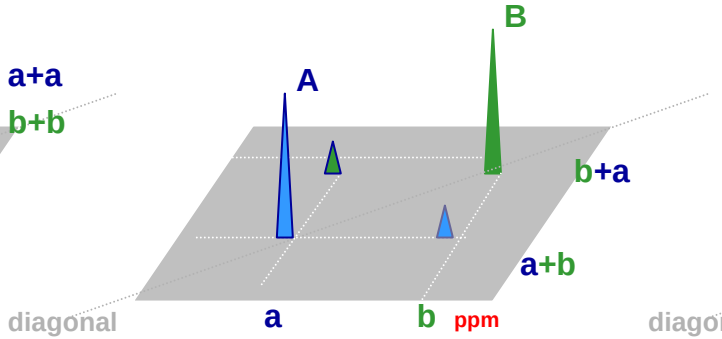


Both components well mixed

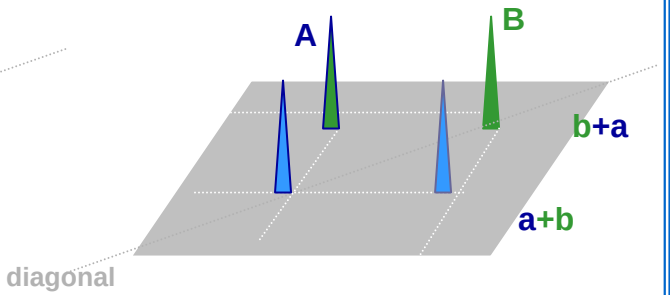




Only diagonal signals are detected – no polarization transfer occurs



Weak off-diagonal signals are detected – small portion of polarization was transferred from A to B

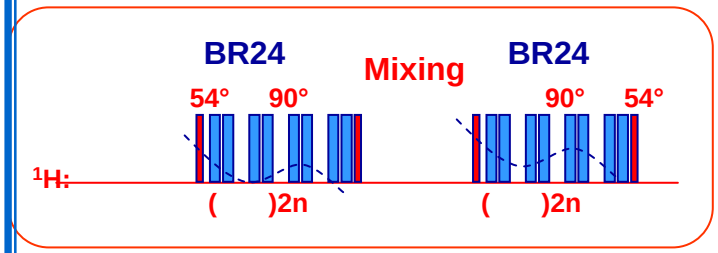


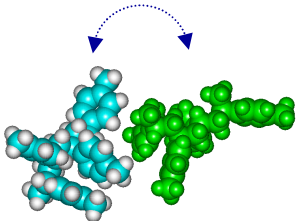
Strong off-diagonal signals are detected –polarization was completely transferred from A to B

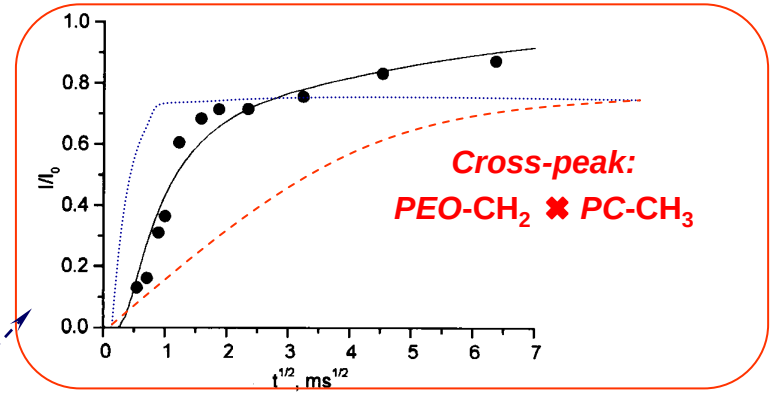
Determination of the Domain Size

Polymer blend

Polycarbonate – Polyethyleneoxide (PC-PEO)







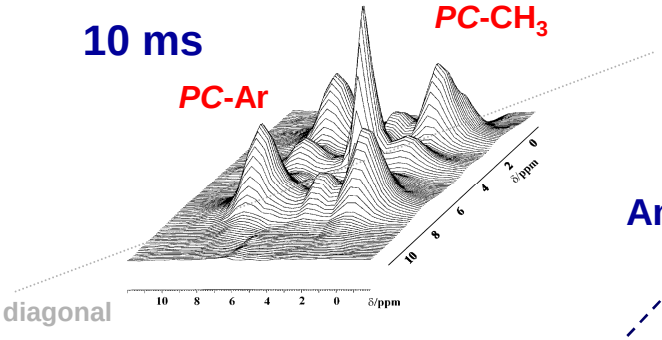
Fast process, nm				Slow process, nm		
d_{PEO}	d_{PC}	d_{int}	d_{long}	d_{PEO}	d_{PC}	d_{long}
0.2	0.4	0.8	1.4	3.3	2.1	5.4

PEO-CH_2

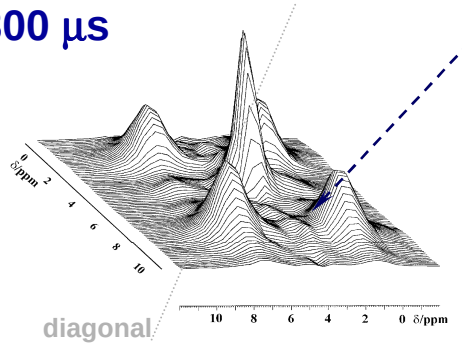
PC-CH_3

10 ms

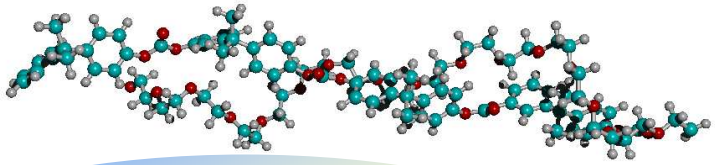
PC-Ar



300 μs

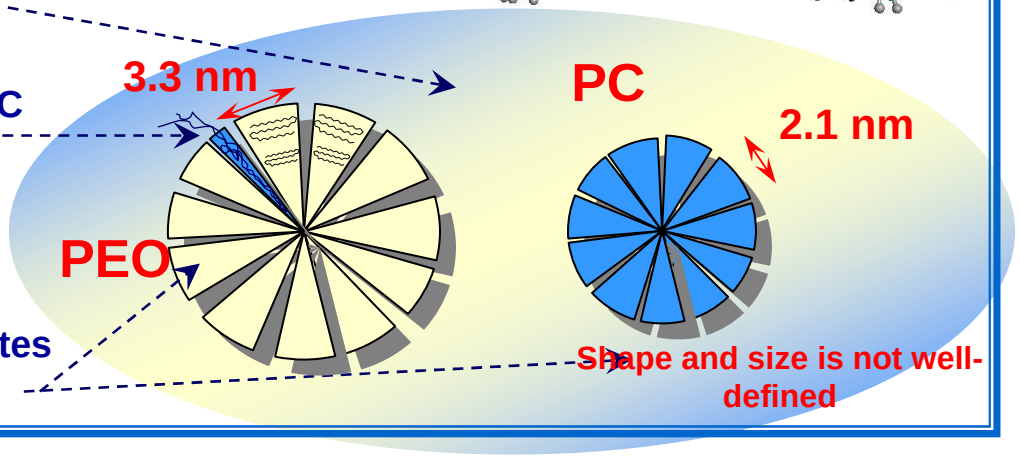


Amorphous phase PEO-PC intimately mixed



Amorphous PC inside PEO spherulites

Crystallites

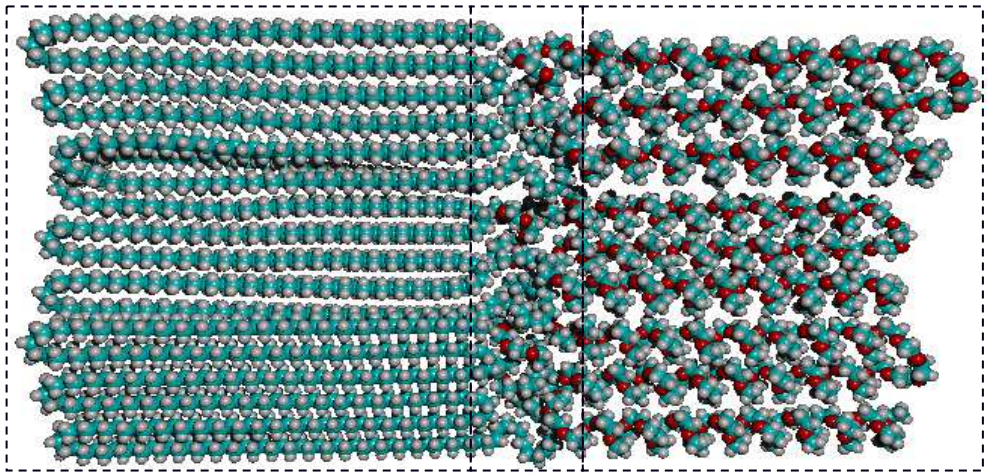


Determination of the Domain Size

Block copolymer
Polyethyleneoxide-Polyethylene
PEO-PE

X_n = 170 X_n = 110

6.5 nm 5.5 nm

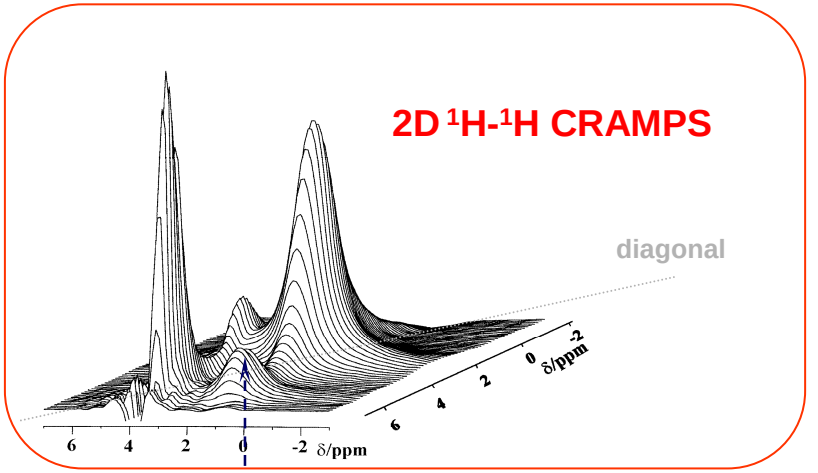


Crystalline PE

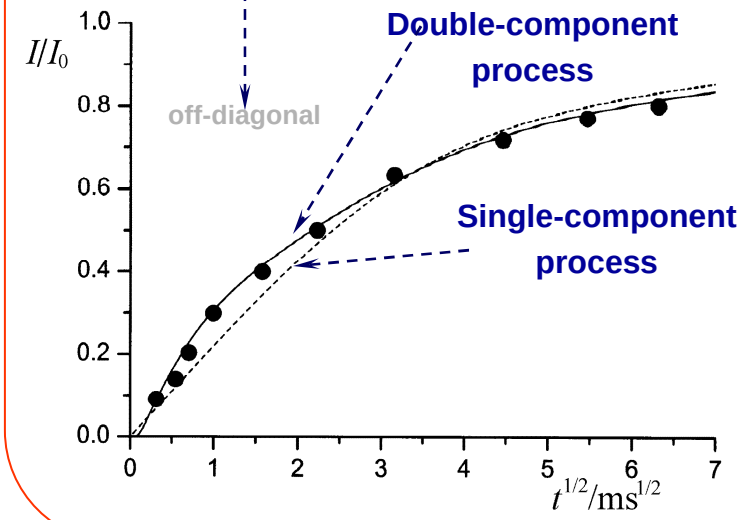
1.0-0.5 nm

Crystalline PEO

Amorphous interface of PE-PEO

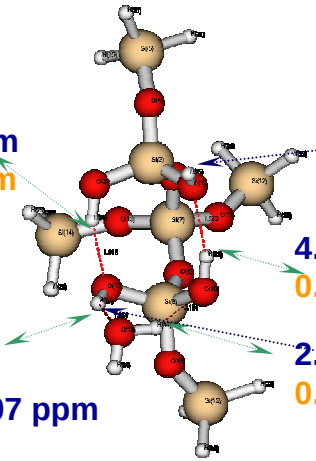


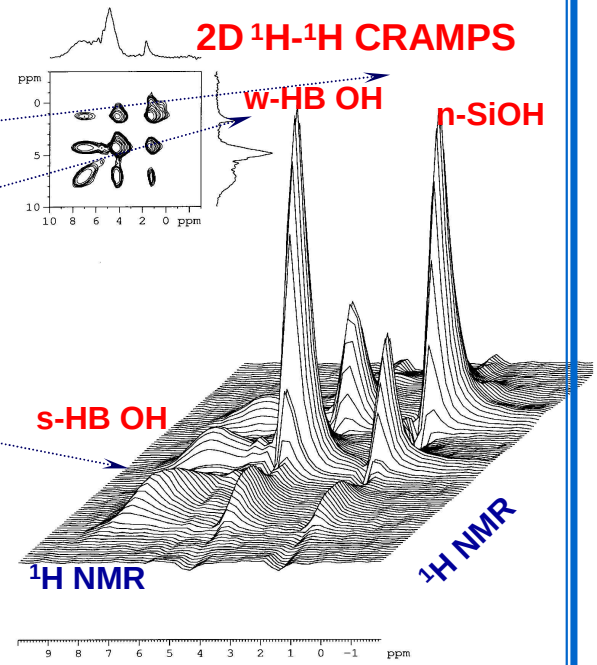
Cross-peak: PEO-CH_2 ✖ *PE*-CH_2

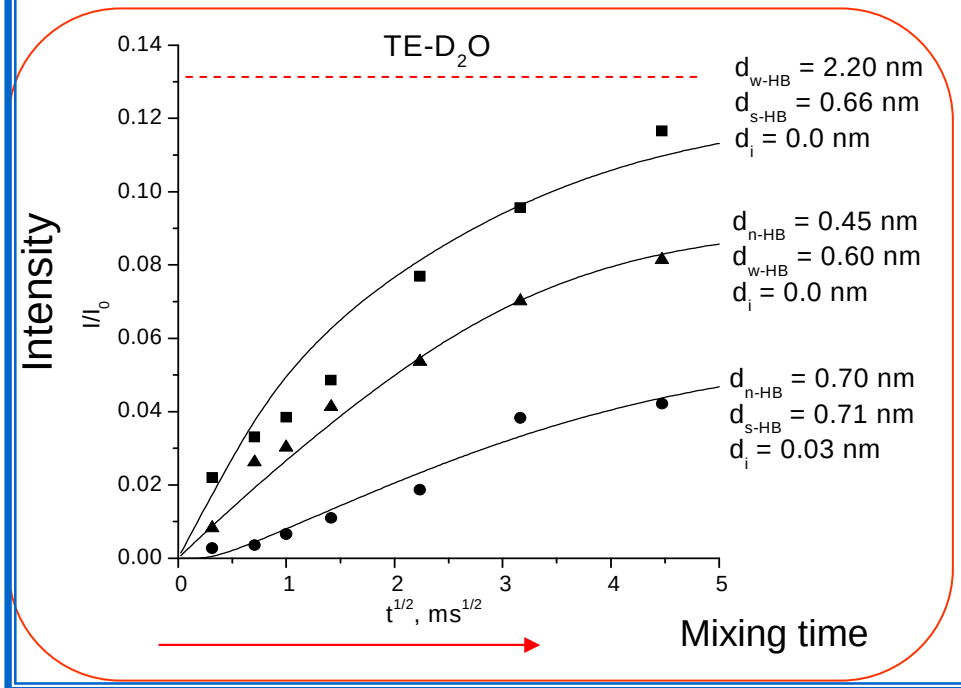


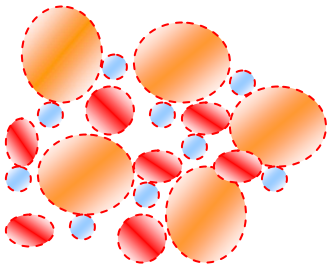
Clustering of Surface Hydroxyls

Siloxane network (silica)





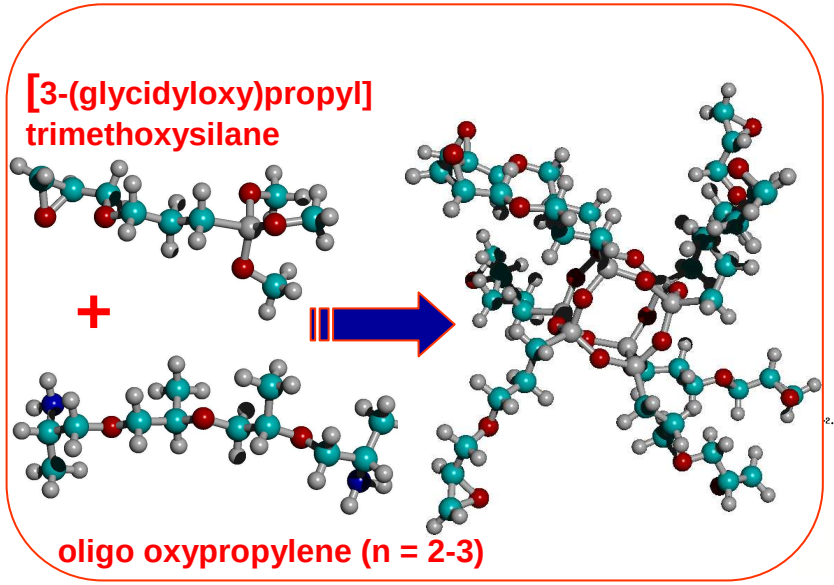


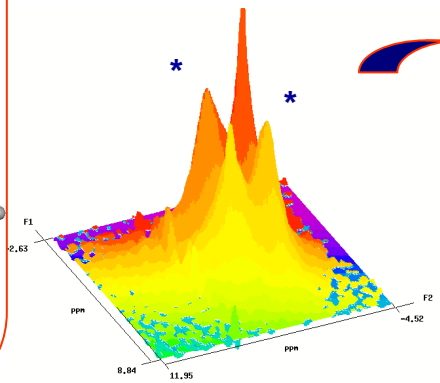


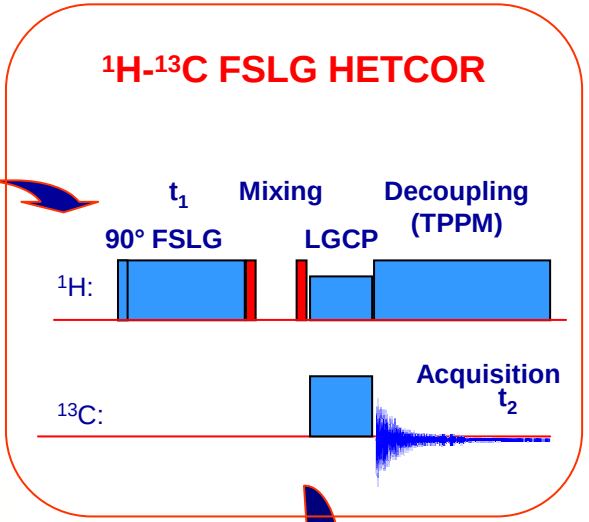
Size of the clusters:

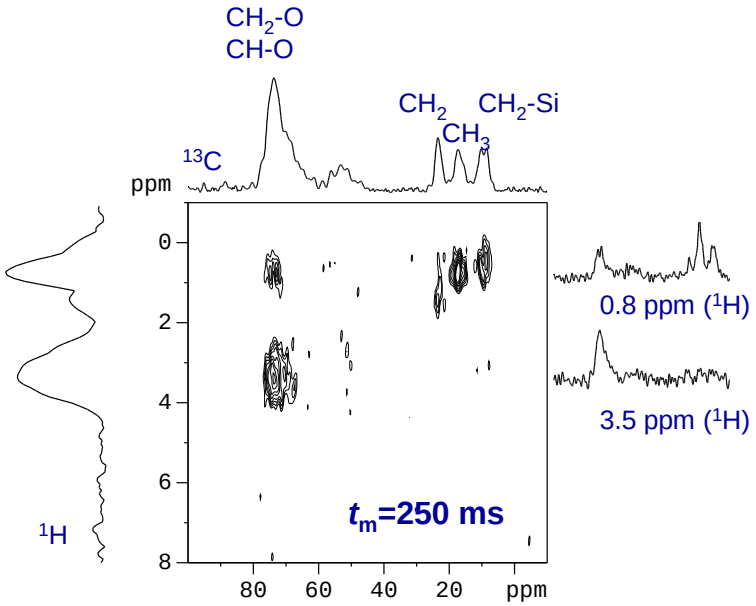
w-HB OH 1.5-2.0 nm
s-HB OH < 1.0 nm
n-HB OH 0.5 -0.4 nm

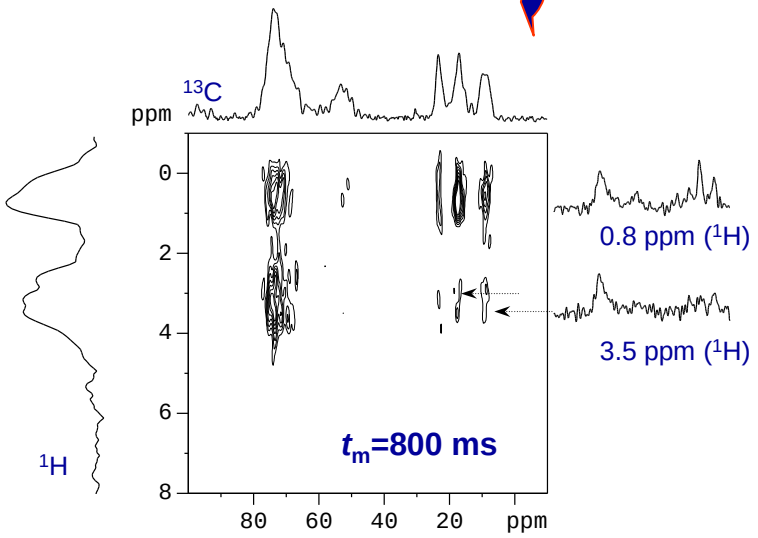
Self-organization in Epoxy-Siloxanes







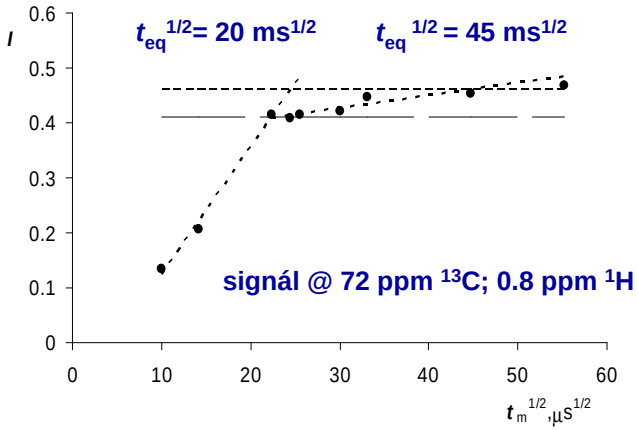




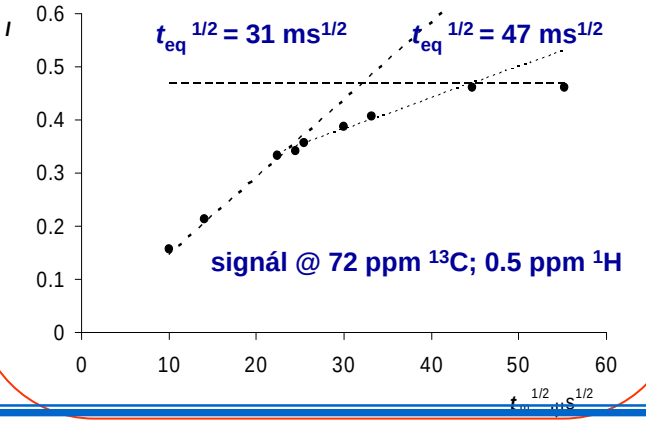
Self-organization in Epoxy-Siloxanes

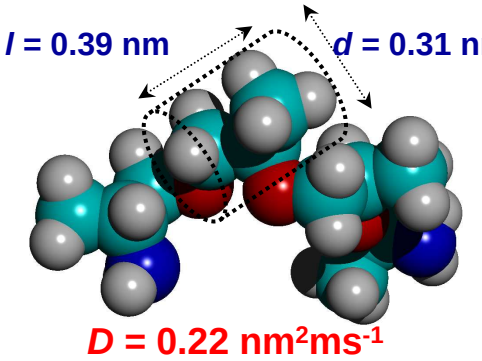
^{1}H-^{13}C FSLG HETCOR

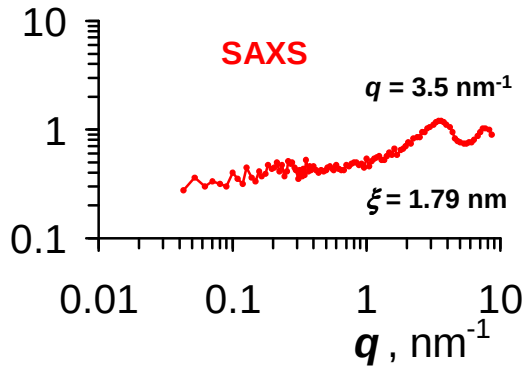
Correlation signal: H (CH_3) x C (CH_2-O)

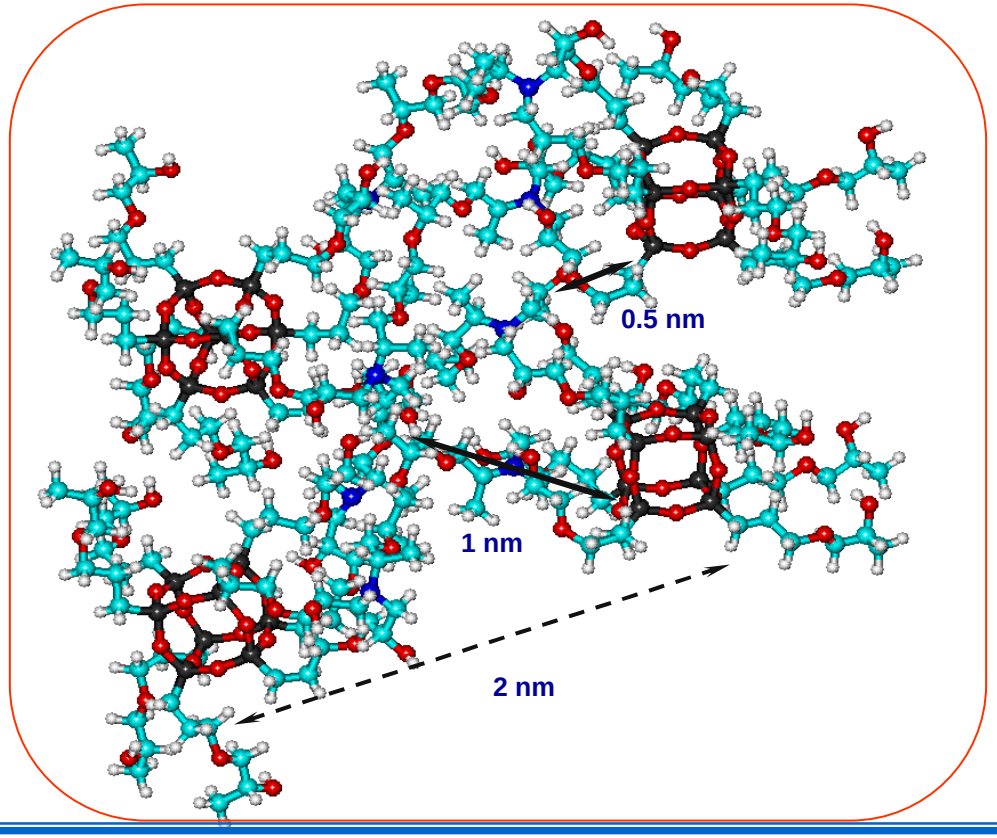


Correlation signal: C (CH_2-O) x H (CH_2-Si)



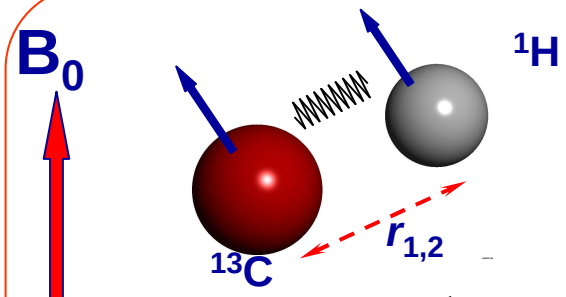






^{1}H-X interatomic distance

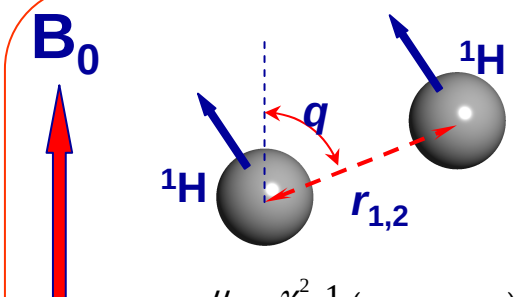
At natural isotopic abundance information about interatomic distance can be derived from ^{1}H-^{1}H a ^{1}H-^{13}C dipolar couplings



$$\hat{H}_D^{IS} = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma_I\gamma_S}{r_{I,S}^3}\frac{1}{2}\left(3\cos^2\theta - 1\right)2\hat{I}_z\hat{S}_z$$

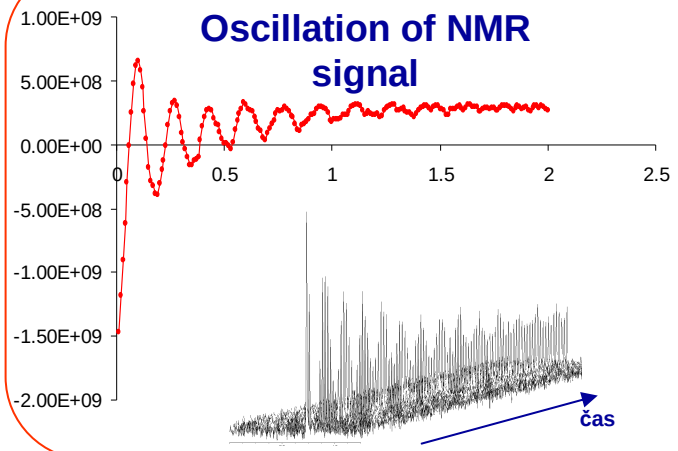
^{1}H-^{13}C dipolar interaction

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



$$\hat{H}_D^{II} = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma^2}{r_{1,2}^3}\frac{1}{2}\left(3\cos^2\theta - 1\right)\left(3\hat{I}_{1z}\hat{I}_{2z} - \hat{\mathbf{I}}_1\hat{\mathbf{I}}_2\right)$$

^{1}H-^{1}H dipolar interaction

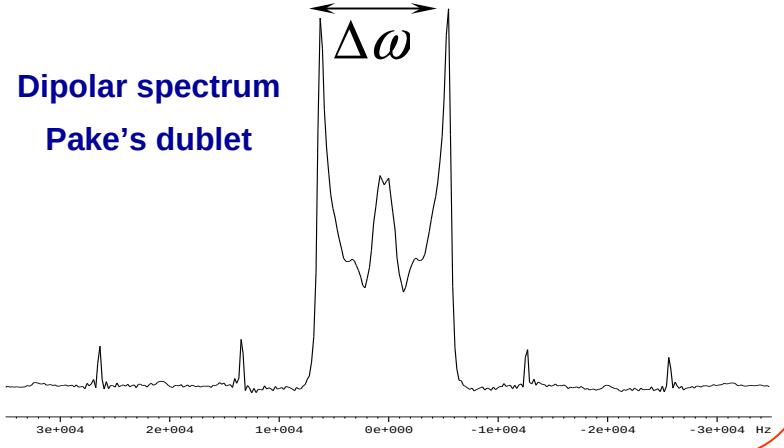


FT

^{1}H-^{1}H
^{1}H-^{13}C
^{1}H-^{15}N
^{1}H-^{19}F
^{1}H-^{29}Si
^{1}H-^{31}P
^{1}H-^{119}Sn

Dipolar spectrum

Pake's dublet



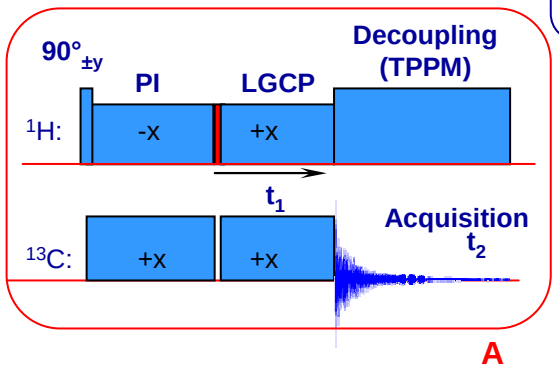
Refinement of position of hydrogen atoms

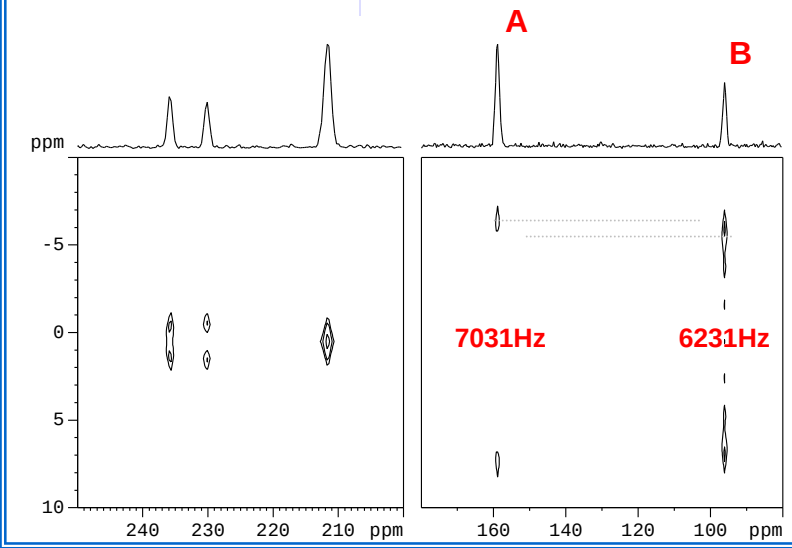
Measurement of ^{1}H-^{15}N dipolar couplings

Selective only for one-bond interaction

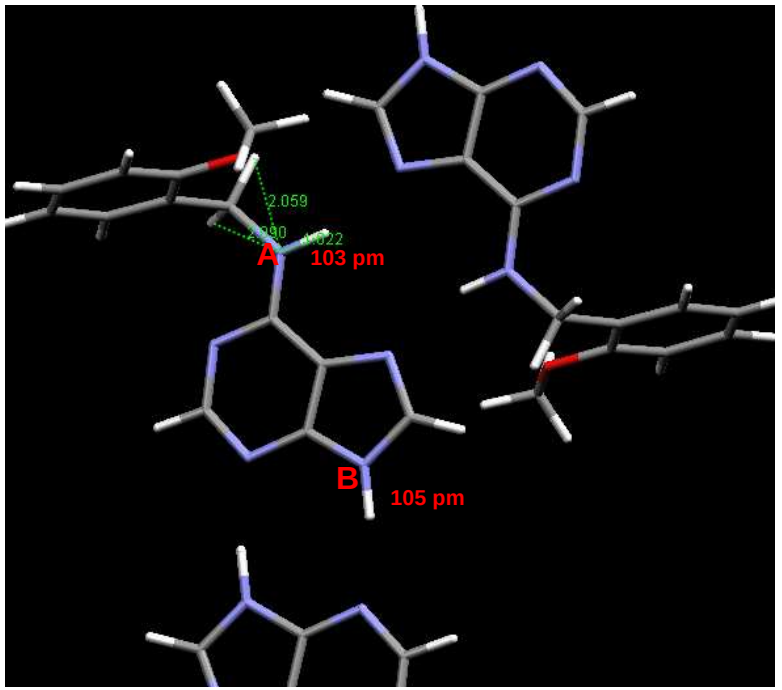
Suitable for measurement of N…H distances in hydrogen bonds

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





DFT optimized structure

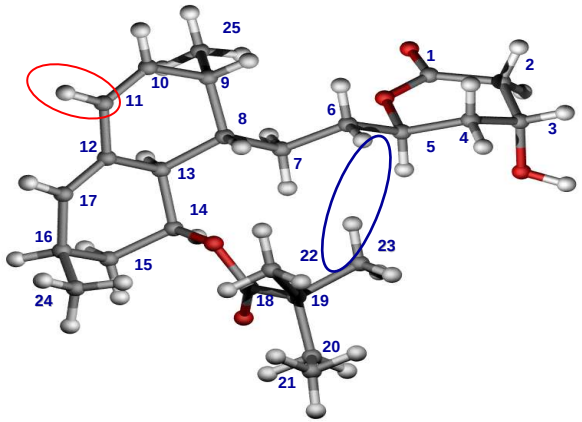


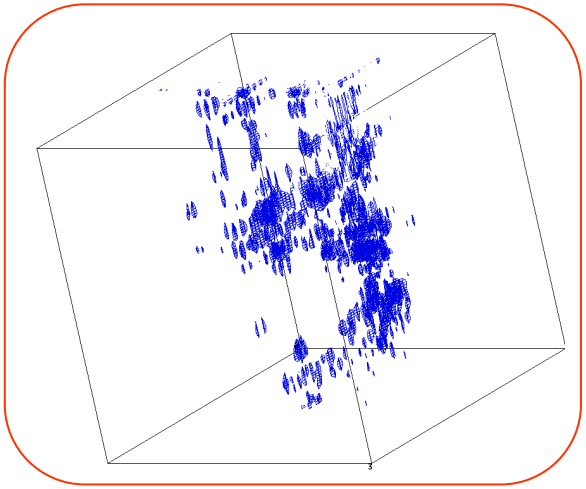
Method	NH(A)	NH(B)
DFT calculation	103 pm	105 pm
NMR experiment	101±1 pm	106 ±1 pm

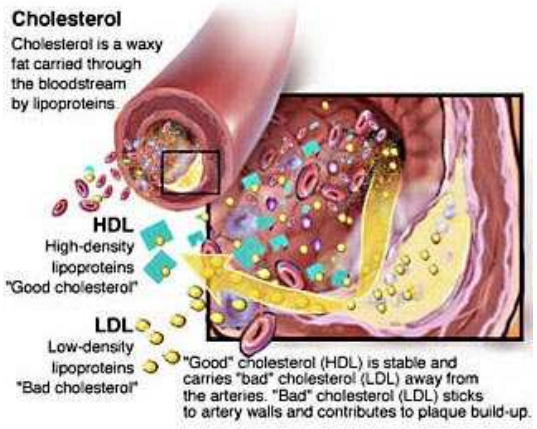
3D structure: ^{1}H-^{13}C interatomic distance

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

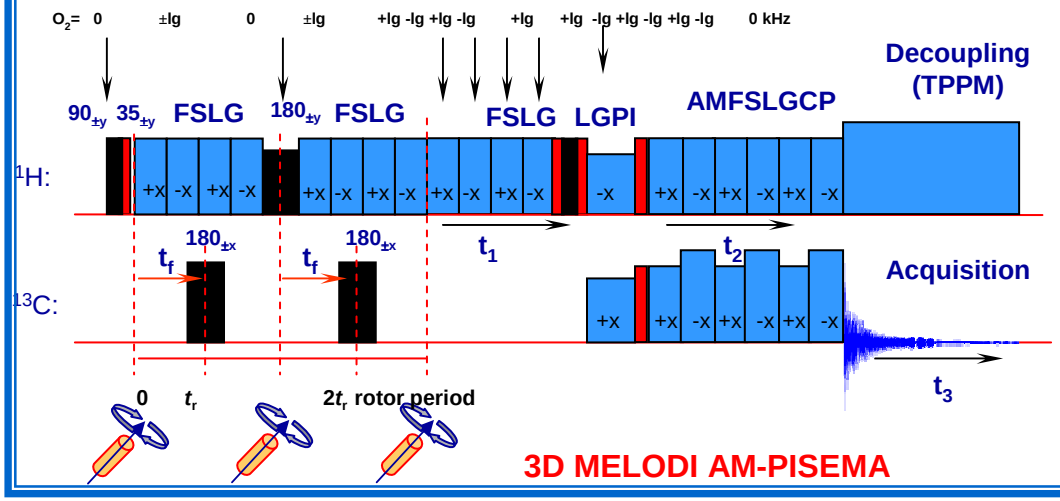
Simvastatin





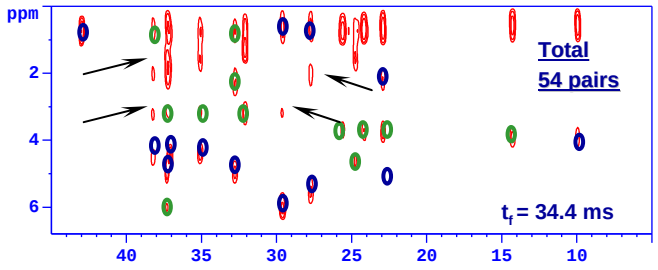


$$r_{CH} = a\left(\frac{\Delta\omega}{2\pi}\right)^{-\frac{1}{3}}$$



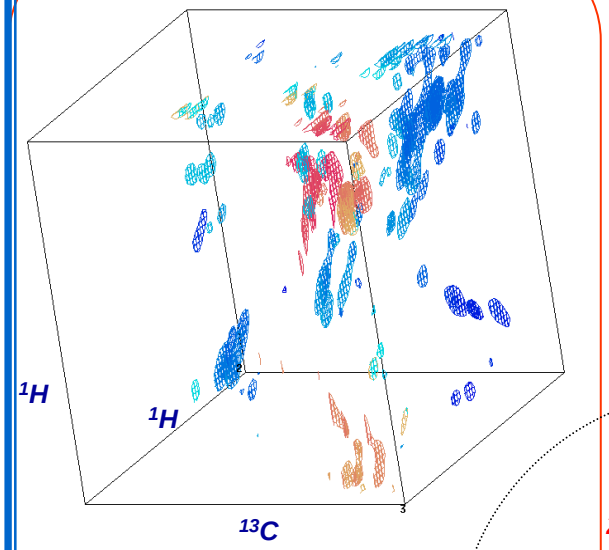
3D MELODI AM-PISEMA

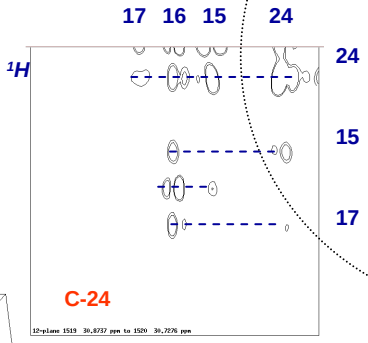
Detection of long-range ^{1}H-^{13}C coherences

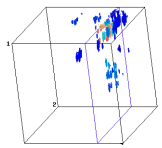


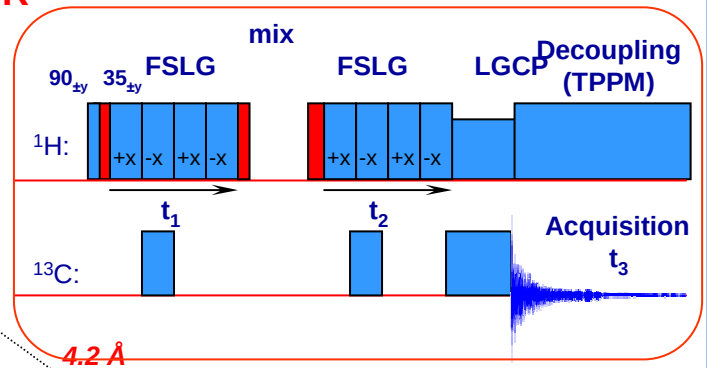
3D structure: ^{1}H-^{1}H interatomic distance

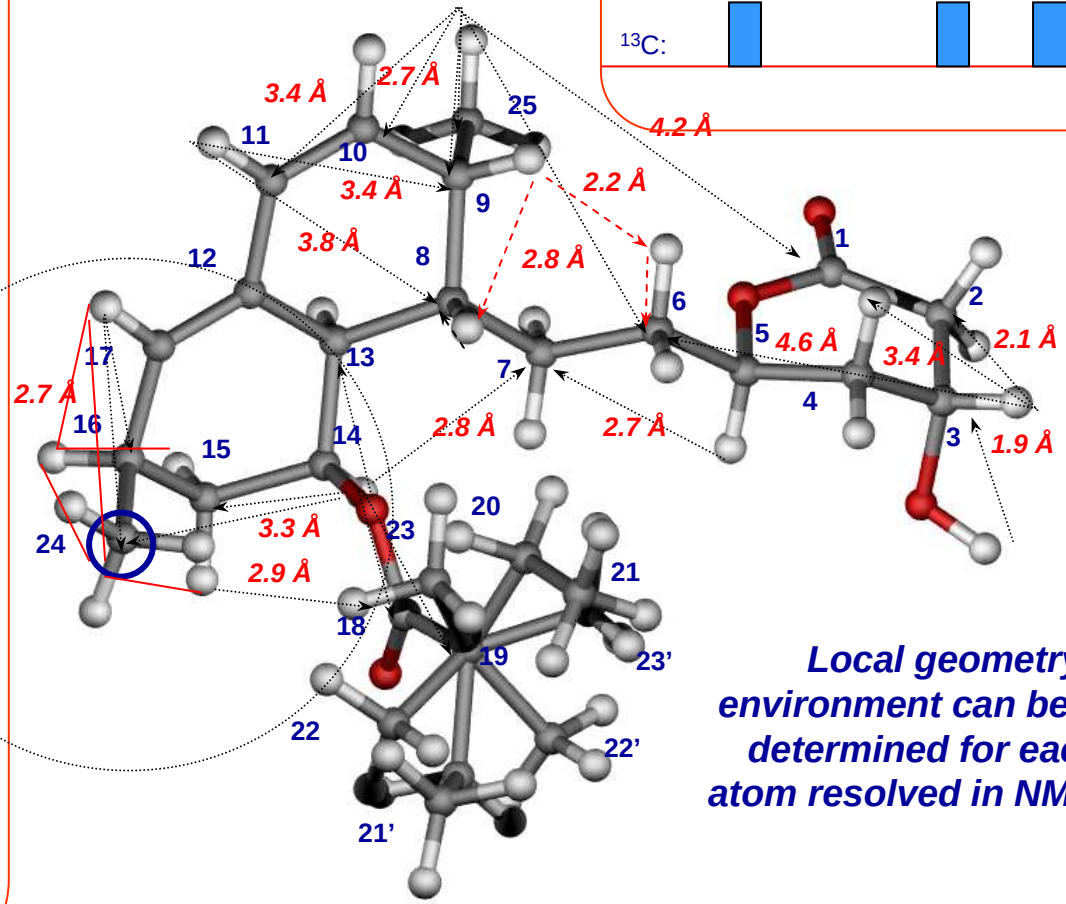
Simvastatin – 3D ^{1}H-^{1}H-^{13}C CP/MAS NMR







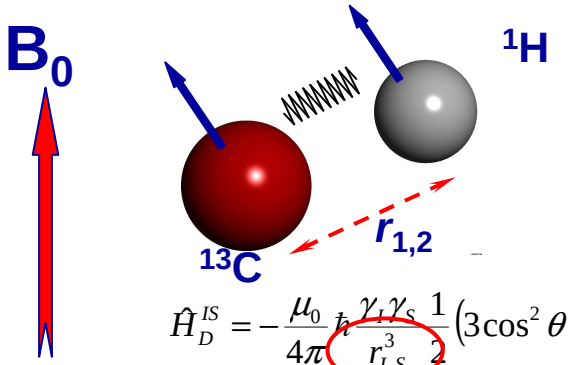




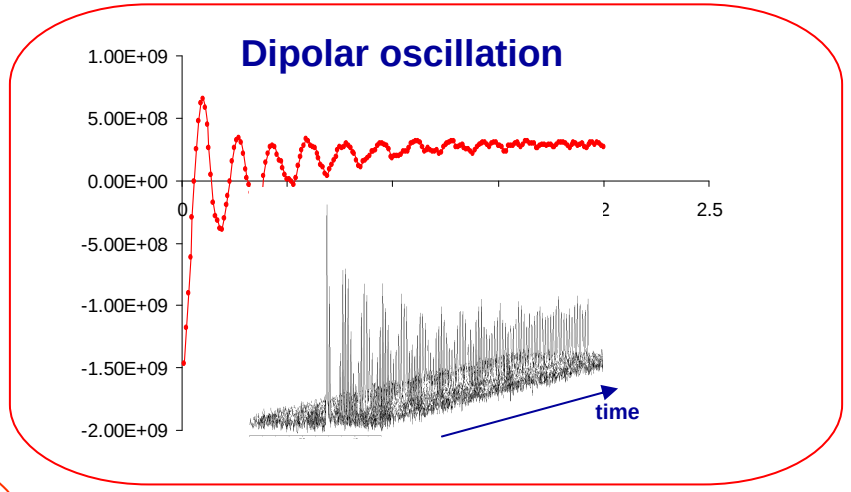
Local geometry of ^{1}H environment can be selectively determined for each carbon atom resolved in NMR spectrum

(1*S*,3*R*,7*S*,8*S*,8a*R*)-8-{2-[(2*R*,4*R*)-4-hydroxy-oxo-3,4,5,6-tetrahydro-2*H*-pyran-2-yl]ethyl}-3,7-dimethyl-1,2,3,7,8,8a-hexahydronapthalen-1-yl 2,2-dimethybutanoate

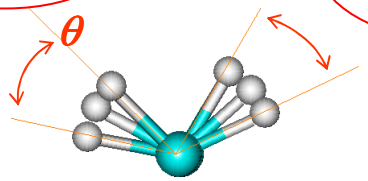
^{1}H-^{13}C dipolar couplings (motional averaging)



$$\hat{H}_D^{IS} = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma_I\gamma_S}{r_{I,S}^3}\frac{1}{2}\left(3\cos^2\theta - 1\right)2\hat{I}_z\hat{S}_z$$

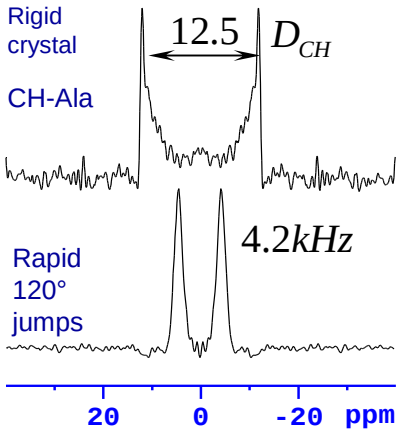


Amplitude of segmental (C-H) reorientation



FT

Dipolar spectrum (Pake's doublet)



Motion on the cone

$$S_{CH} = \left[\cos\theta\left(\frac{1+\cos\theta}{2}\right)\right]$$

Uniaxial rotational diffusion motion

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

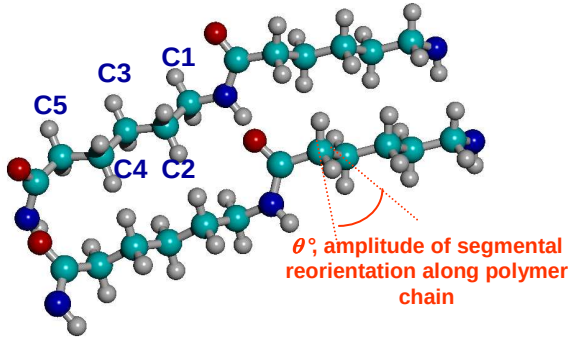
Order parameter

$$S_{CH} = \frac{D_{\mathrm{CH}}}{D_{\mathrm{CH}}^{\mathrm{rig}}} = \frac{D_{\mathrm{CH}}}{12.5(\mathrm{kHz})}$$

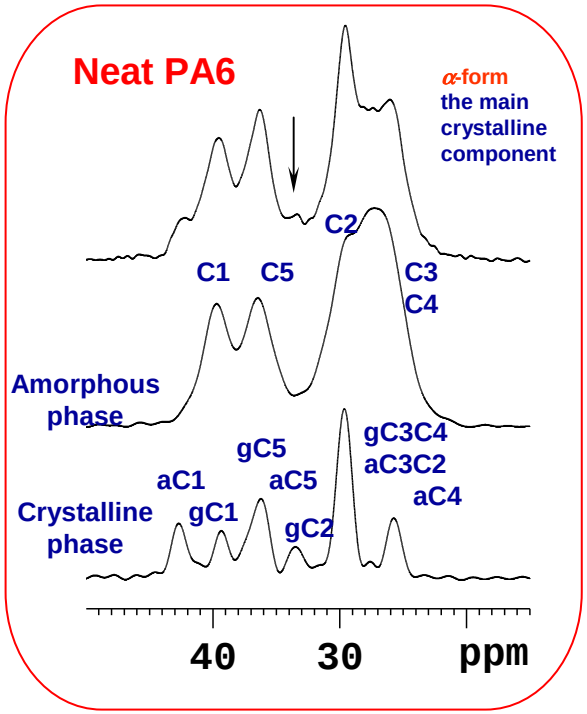
Amplitudes of segmental reorientations

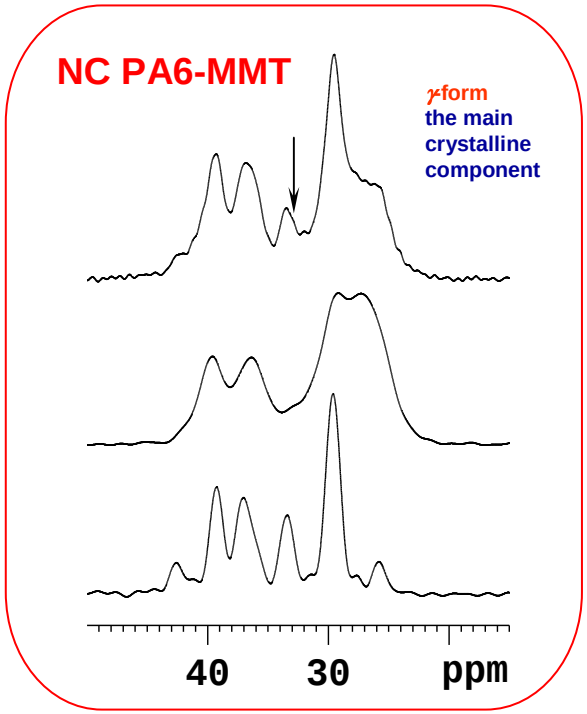
1) Semicrystalline system
2) *a*-form, *g*-form and amorphous phase
3) Segmental dynamics in amorphous phase
4) Phase-selective experiments

Polymer nanocomposite PA6-MMT

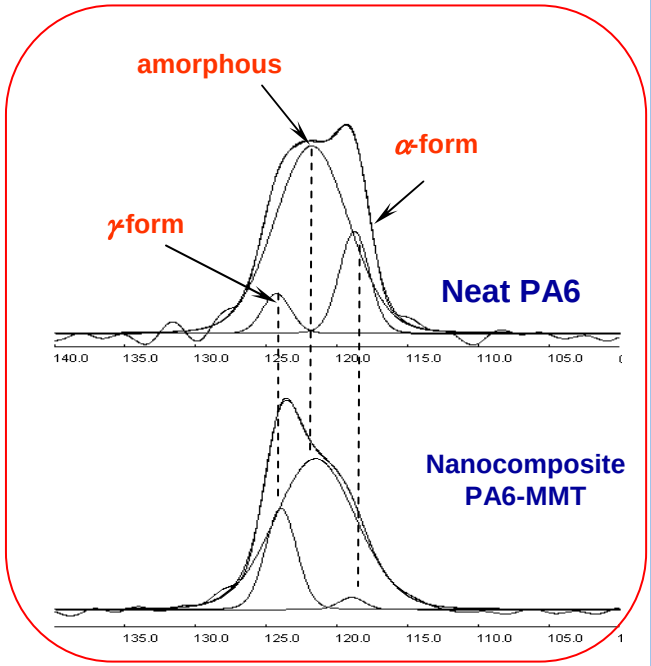


Standard ^{13}C CP/MAS NMR spectrum

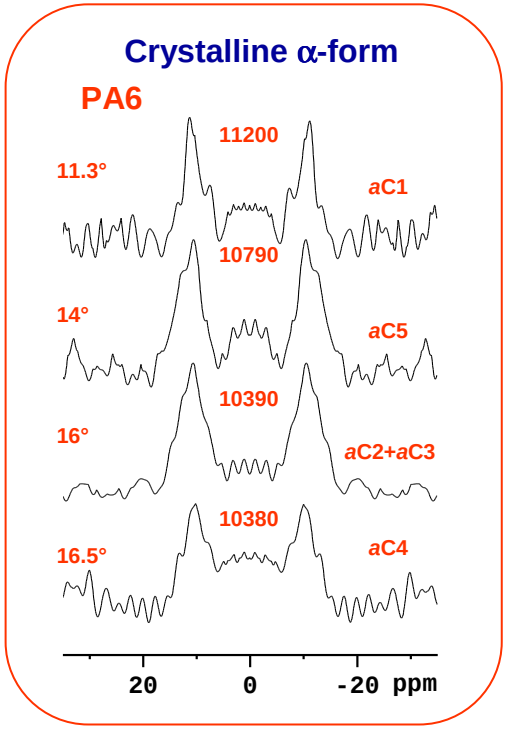


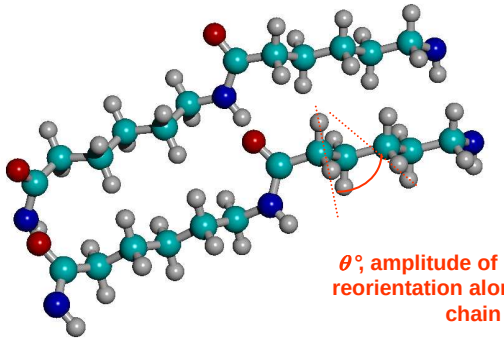


Standard ^{15}N CP/MAS NMR spectrum



Amplitudes of segmental reorientations

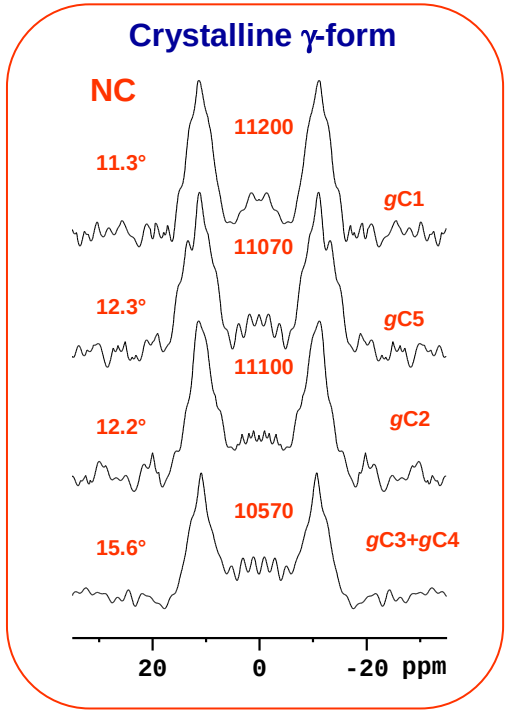




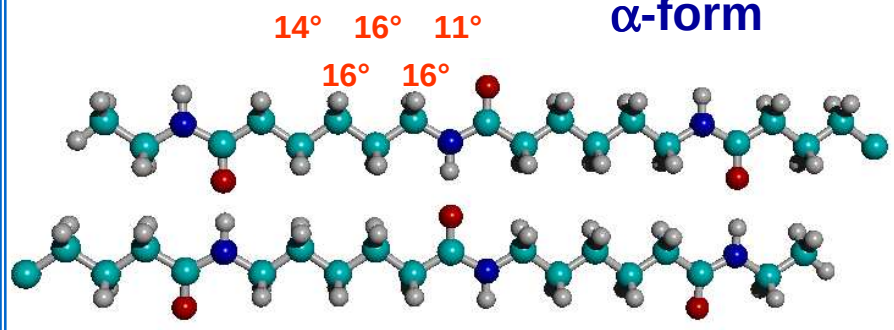
θ°, amplitude of segmental reorientation along polymer chain

Relation between order parameter and amplitude of uniaxial rotation motion

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

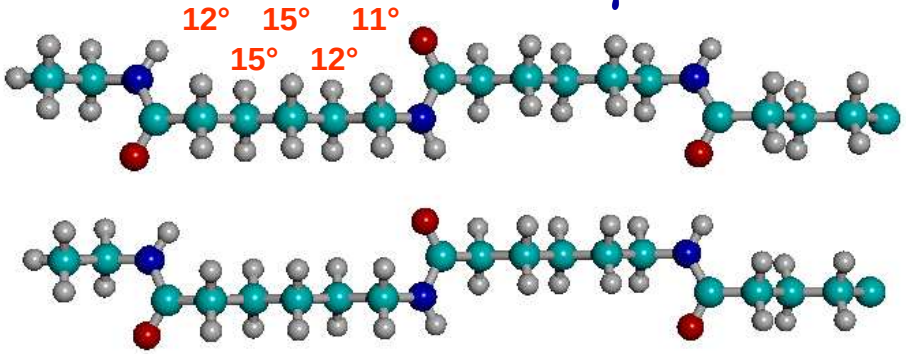


α-form



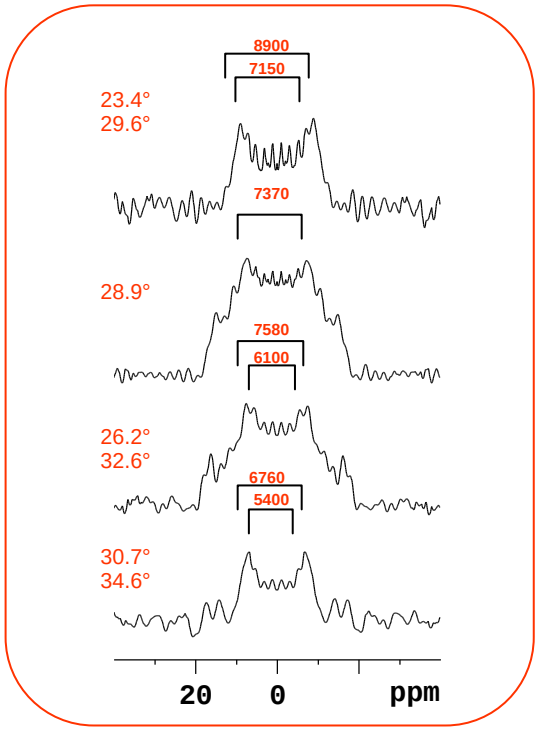
Crystalline α-form, antiparallel orientation

γ-form

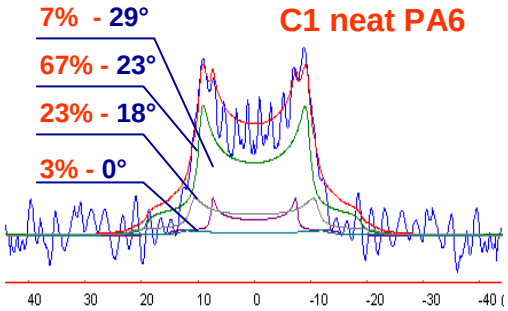


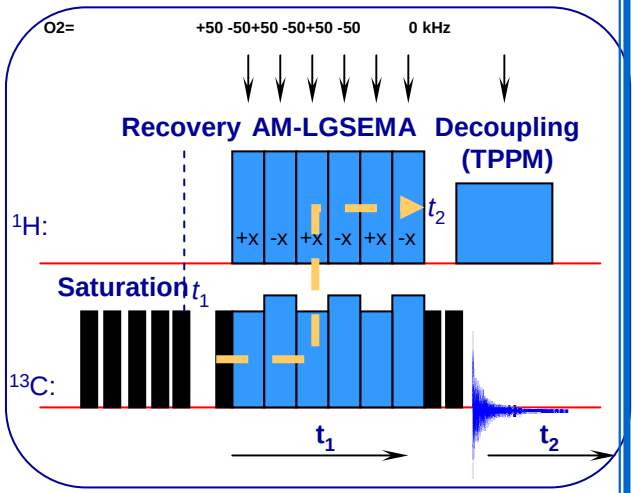
crystalline γ-form, parallel orientation

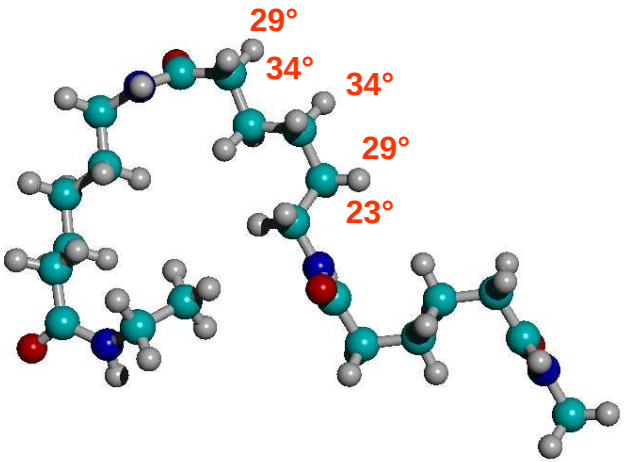
Amplitudes of segmental reorientations



Determination of fractions of polymer chains with variable motional amplitudes.

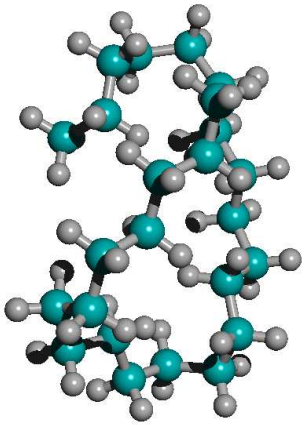




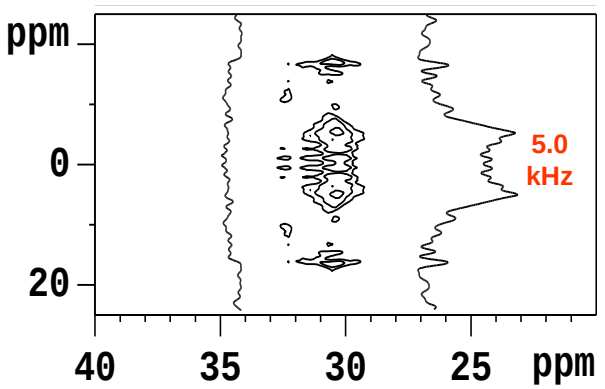


36°- rotational diffusion

58°- motion on the cone



Polyethylen



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