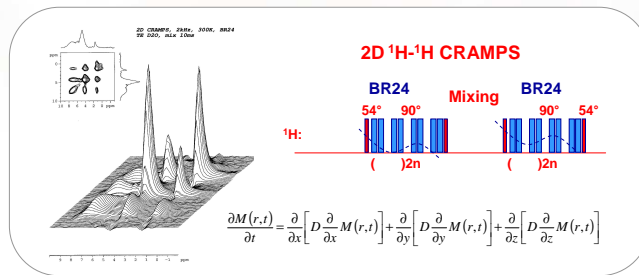


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Chemistry AS CR
Heyrovský Sq. 2
162 06 Praha 6
Czech Republ.

Homonukleární ¹H-¹H korelační experimenty



Objev více-rozměrné NMR spektroskopie (1971)

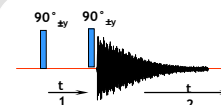
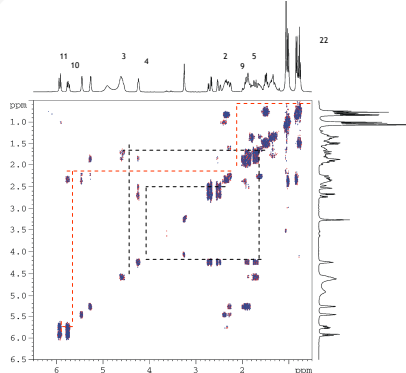
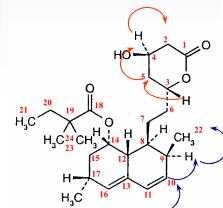


Jean Luis Charles Jeener
*1931

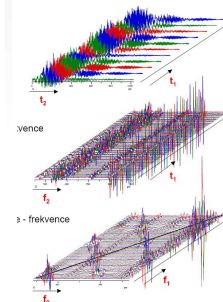
Přenos magnetizace přes vazebné elektrony (konektivita řetězce)

Přednáška na letní škole v Basko Polje, Jugoslávie, 1971
Dvoudimenzionální NMR, COSY

Aue W.P., Bartholdi E., Ernst R.R.
2D Spectroscopy. Application to NMR, *J. Chem. Phys.* (1976); 64: 229.



2D COSY NMR

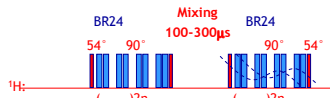


2D korelační NMR v pevné fázi - 1985

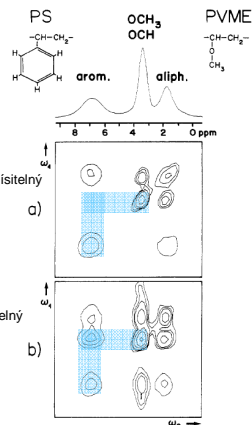
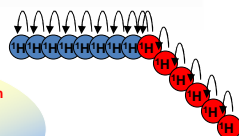
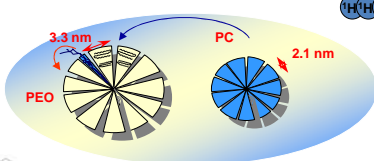
Morfologie polymerních směsí

Caravatti P., Neuschwander P., Ernst R.R.
 Characterization of Heterogeneous Polymer Blends by 2D ¹H Spin Diffusion Spectroscopy,
Macromolecules. (1985); 18: 119.

2D ¹H MAS NMR pulse sequence

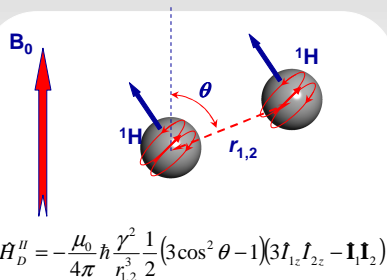


Štafetový přenos polarizace
 Korelace ¹H-¹H chemických posunů

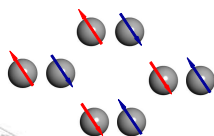
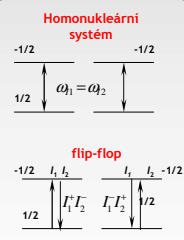
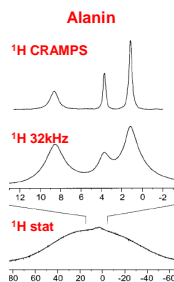


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Dipolární interakce v homonukleárním systému



Flip-flop přechody



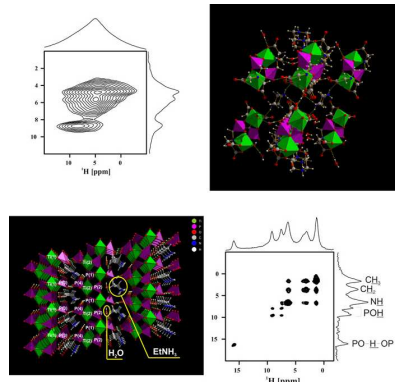
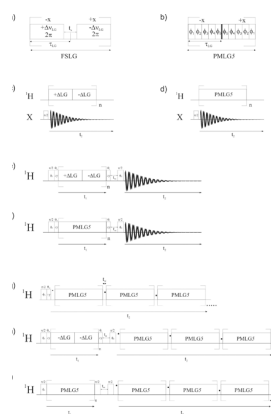
$$\mathbf{I}_1\mathbf{I}_2 = (I_{1x}I_{2x} + I_{1y}I_{2y} + I_{1z}I_{2z})$$

$$I^+ = I_x + iI_y; I^- = I_x - iI_y$$

$$\hat{H}_D'' = -\frac{\mu_0}{4\pi} \hbar \frac{\gamma^2}{r_{1,2}^3} \frac{1}{2} (3\cos^2\theta - 1)(2I_{1z}I_{2z} - 1/2(I_1^+I_2^- + I_1^-I_2^+))$$

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Kontinuální homodekaplink při vysokých rotacích




<http://dx.doi.org/10.1016/j.cplett.2008.10.029>
<http://dx.doi.org/10.1016/j.jmr.2008.07.019>

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Kontinuální homodekaplink

Fázově modulovaný Lee-Goldburgův experiment

Fázová modulace

$$\phi(t) = \omega_{PMLG} t$$

$$|\omega_{PMLG}| = \omega_1 / \sqrt{2}$$

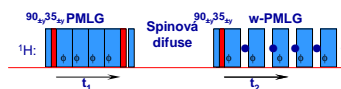
Doba trvání LG cyklu

$$t_{LG} = \sqrt{(2/3)} (2\pi / \omega_1)$$

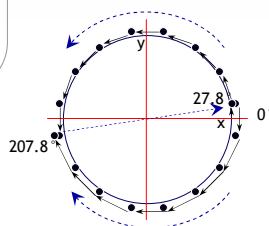
Celková fázová změna během jednoho LG cyklu

$$\alpha_{LG} = |\omega_{PMLG}| t_{LG} = 207.8^\circ$$

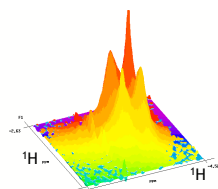
„On-resonance“ experiment



Trajektorie rf pole během cyklu PMLG-9



¹H-¹H PMLG w-PMLG

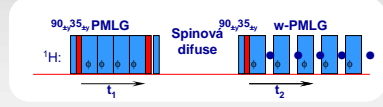
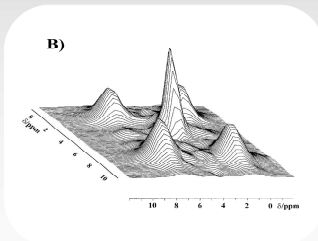




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¹H-¹H Spinová výměna (difuze)

Výběr a přenos magnetizace



Rychlost spinové výměny: $\frac{\partial M(r,t)}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial M(r,t)}{\partial x} \right] + \frac{\partial}{\partial y} \left[D \frac{\partial M(r,t)}{\partial y} \right] + \frac{\partial}{\partial z} \left[D \frac{\partial M(r,t)}{\partial z} \right]$

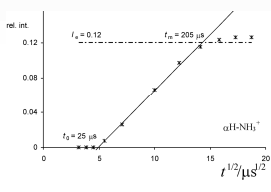
Velikost domény dispergované složky A :

$$d_A = 2 \frac{\mathcal{E}}{f_B} \left(\frac{1}{\pi} D t_m^s \right)^{1/2}$$

Stanovení spin-difusního koeficientu z pološířky:

$$D_{rig} = \frac{1}{12} \sqrt{\frac{\pi}{2 \ln 2}} \langle r^2 \rangle \Delta v_{1/2} \quad D_{mob} = \frac{1}{6} \langle r^2 \rangle [\alpha \Delta v_{1/2}]^{1/2}$$

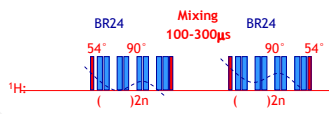
$$D_{mob} = 8.2 \times 10^{-6} T_2^{-1} + 0.007 \quad D_{mob} = 4.4 \times 10^{-5} T_2^{-1} + 0.26$$



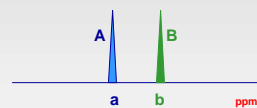
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Spinová difuze - koherentní přenos magnetizace

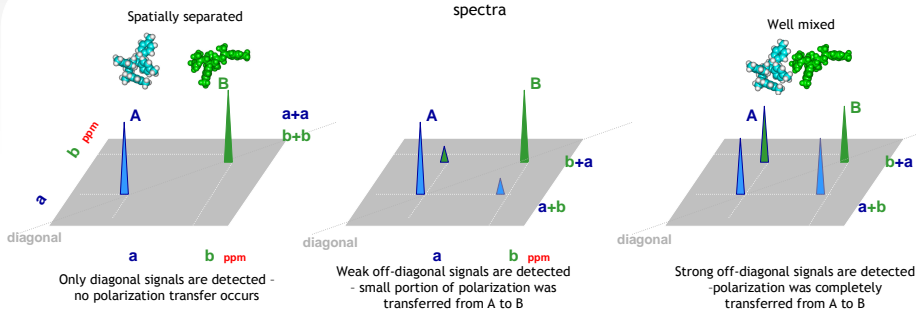
2D ¹H MAS NMR pulse sequence



A general two-component system in 1D spectra



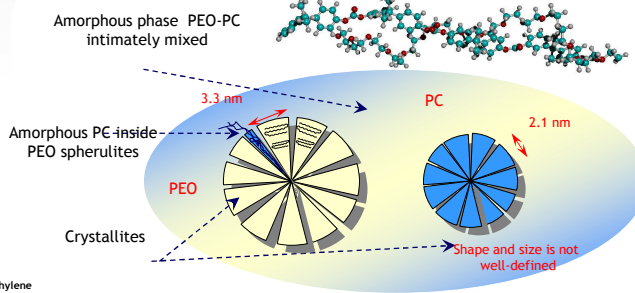
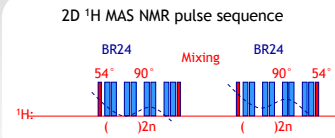
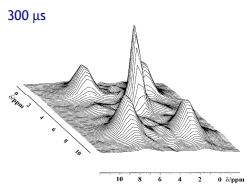
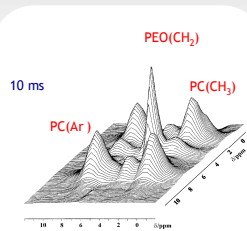
A general two-component system in 2D spectra



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ss NMR - 2D spin-difuzní experimenty

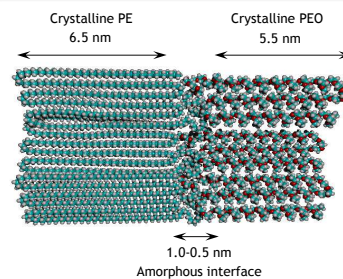
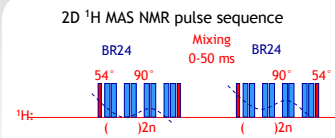
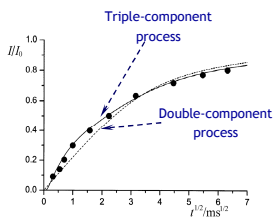
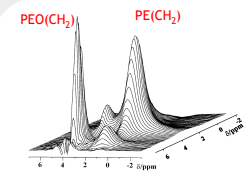
Polymer blend Polycarbonate - Polyethyleneoxide (PC-PEO)



Brus J. et al.,
Order and mobility in polycarbonate-poly(ethylene oxide) blends, *Macromolecules* (2000); 33: 6448.

ss NMR - 2D spin-difuzní experimenty

Blokový kopolymer Polyethyleneoxide-Polyethylene PEO-PE

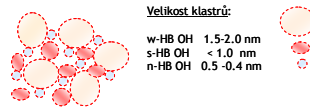
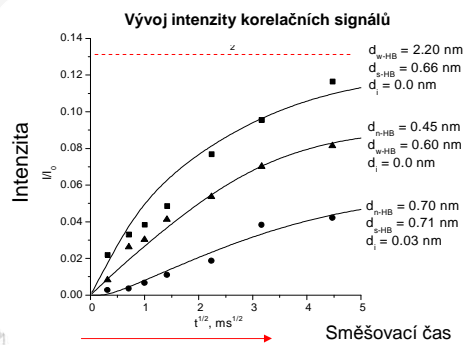
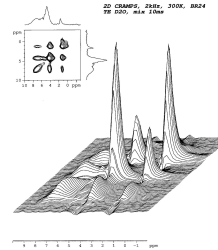
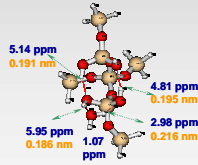


Brus J. et al.,
Potential and limitations of 2D H-1-H-1 spin-exchange CRAMPS experiments to characterize structures of organic solids, *MONATSHFTE FÜR CHEMIE* (2002); 133: 1587.

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ss NMR - 2D spin-difuzní experimenty

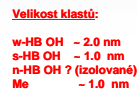
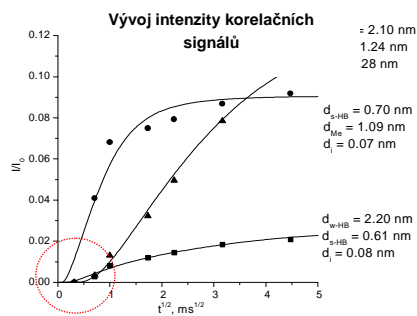
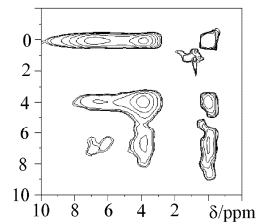
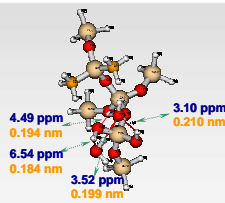
Siloxanová síť



Jiří Labárek, Laboratory of Solid State NMR
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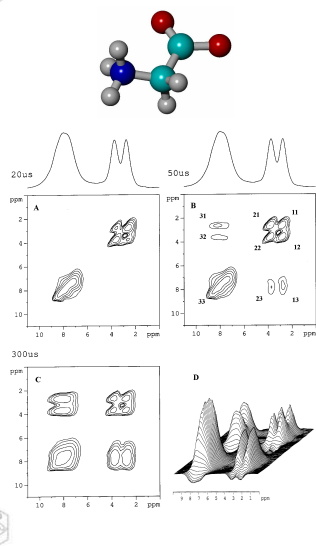
ss NMR - 2D spin-difuzní experimenty

Modifikovaná siloxanová síť



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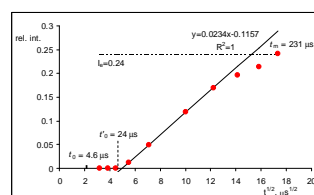
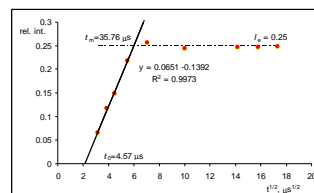
Měření meziatomových vzdáleností



$$\langle r^2 \rangle = 3 D_{\text{eff}} t_m$$

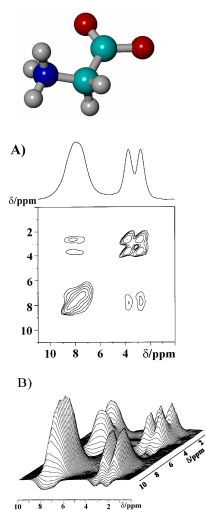
$$r_{12} = 0.178 \text{ nm}$$

$$r_{12} = 0.247 \text{ nm}$$



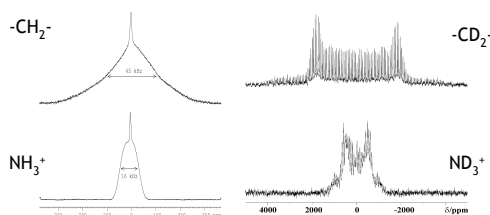
W GC NMR

Měření meziatomových vzdáleností



¹H NMR

²H NMR



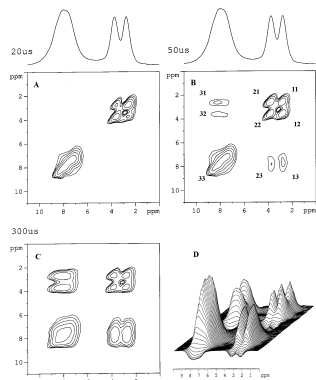
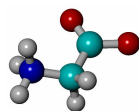
$$\frac{D_{\text{eff}}^*}{D_{\text{eff}}} \cong \frac{\Delta \nu_{1/2}(\text{NH}_3^+)}{\Delta \nu_{1/2}(\text{CH}_2)} \cong \frac{\delta_Q(\text{NH}_3^+)}{\delta_Q(\text{CH}_2)} \cong \frac{1}{3}$$

Spinová výměna je ovlivněna segmentálním pohybem, rozsah ovlivnění lze odhadnout z kvadrupolových interakčních konstant.

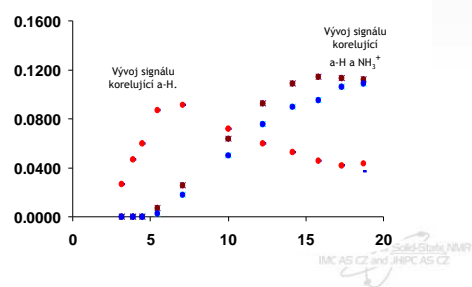
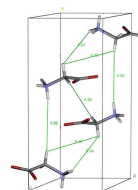


W GC NMR

Měření meziatomových vzdáleností



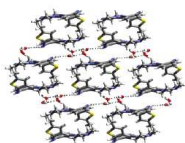
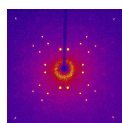
Mezimolekulární vzdálenosti mohou být teoreticky získány z vývoje spinové difuze.



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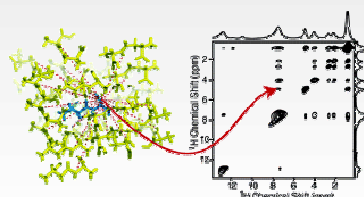
NMR krystalografie - 2006...

XRD



Reutzel-Edens S. et al. *Crystal Growth & Design* 3, 897 (2003)

ss-NMR

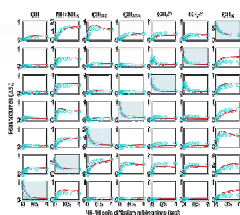
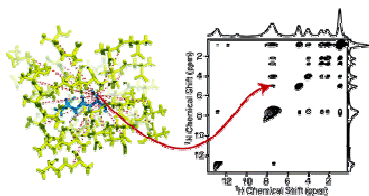


Elena B. et al. *J. Am. Chem. Soc.* (2006); 128, 9555.



Joint Laboratory of Solid-State NMR
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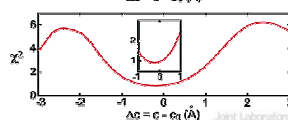
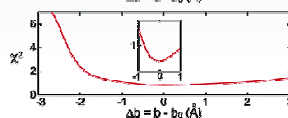
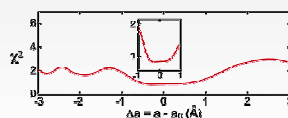
NMR krystalografie - parametry krystalové buňky



$$\frac{d\mathbf{M}}{dt} = -\mathbf{K}(\mathbf{M} - \mathbf{M}_0) \quad k_{ij} = \sum_{\lambda} \left(\frac{\mu_0 \gamma^2 \hbar}{4\pi} \right)^2 \frac{A}{(r_{ij}^{\lambda})^3} \quad k_{ii} = -\sum_j k_{ij}$$

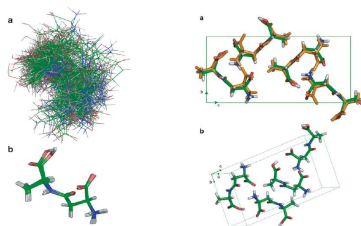
$$\mathbf{M}(t, \tau_{SD}) = \exp(-\mathbf{K} \tau_{SD}) \mathbf{M}_z(t, 0) \quad \mathbf{P}(\tau_{SD}) = \exp(-\mathbf{K} \tau_{SD}) \mathbf{M}_z^a$$

n ... Functional dependence on internuclear distance



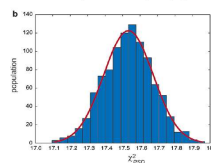
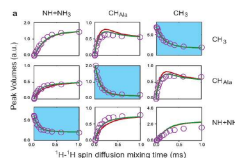
Jaroslav Labárek, Institute of Solid State NMR, IBC, AS CZ and JNEPC AS CZ

NMR krystalografie



Elena B. et al. Solid-state 1H NMR crystallography, *J. Am. Chem. Soc.* (2005); 127(25), 9140.

Elena B. et al. Molecular Structure Determination in Powders by NMR Crystallography from Proton Spin Diffusion, *J. Am. Chem. Soc.* (2006); 128, 9555.



$$\frac{d\mathbf{M}}{dt} = -\mathbf{K}(\mathbf{M} - \mathbf{M}_0) \quad k_{ij} = \sum_{\lambda} \left(\frac{\mu_0 \gamma^2 \hbar}{4\pi} \right)^2 \frac{A}{(r_{ij}^{\lambda})^3} \quad k_{ii} = -\sum_j k_{ij}$$

$$\mathbf{M}(t, \tau_{SD}) = \exp(-\mathbf{K} \tau_{SD}) \mathbf{M}_z(t, 0) \quad \mathbf{P}(\tau_{SD}) = \exp(-\mathbf{K} \tau_{SD}) \mathbf{M}_z^a$$

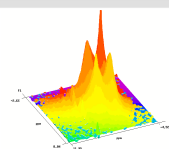
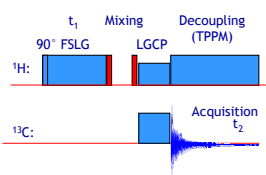
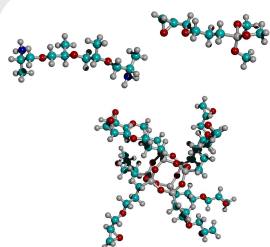
n ... Functional dependence on internuclear distance

$$\chi^2 = \sum \frac{(\text{calc}_i - t_i)^2}{\sigma_i^2}$$

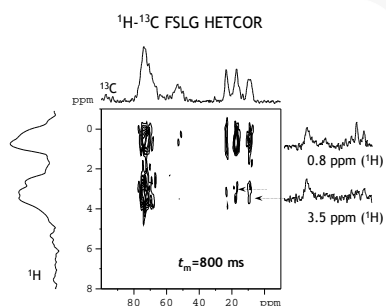
NMR-GZ

ss NMR - 2D spin-difuzní experimenty

Složité epoxy-siloxanová síť



2D ^1H MAS NMR spectrum



^1H - ^{13}C FSLG HETCOR

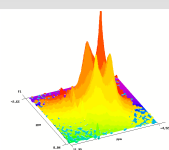
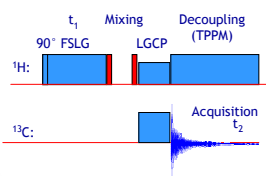
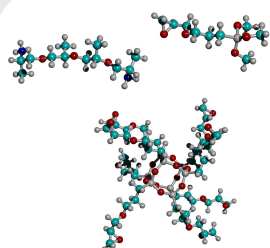


Brus J. et al., Self-organization, structure, dynamic properties, and surface morphology of silica/epoxy films as seen by solid-state NMR, SAXS, and AFM, *Macromolecules* (2004); 37: 1346.

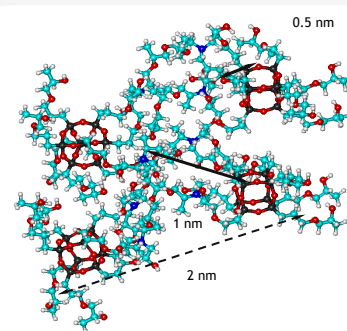


ss NMR - 2D spin-difuzní experimenty

Složité epoxy-siloxanová síť



2D ^1H MAS NMR spectrum

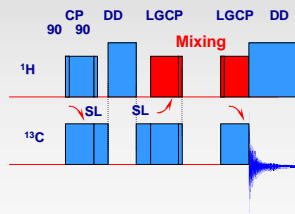
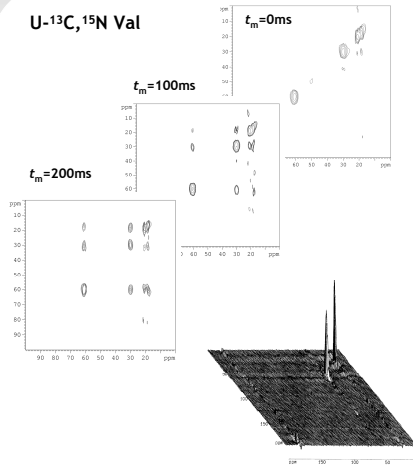


Brus J. et al., Self-organization, structure, dynamic properties, and surface morphology of silica/epoxy films as seen by solid-state NMR, SAXS, and AFM, *Macromolecules* (2004); 37: 1346.

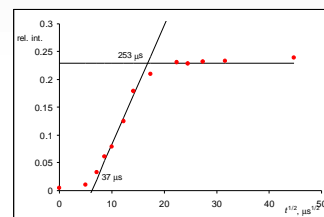


2D ^{13}C - ^{13}C korelace - ^1H - ^1H spinová difuze

U- ^{13}C , ^{15}N Val

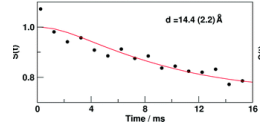
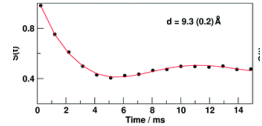
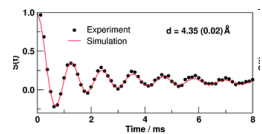
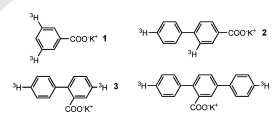
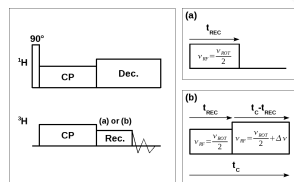
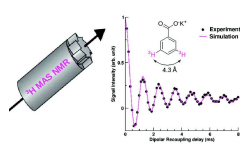


$t_m = 0\mu\text{s}$;
 CP1=500 μs ;
 CP2=100 μs ;
 CP3=100 μs



Joint Laboratory of Solid State NMR
 IMC AS CZ and JHPC AS CZ

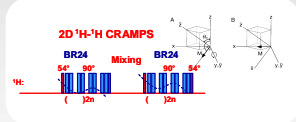
2D ^3H - ^3H korelace - dosah až 13 Å



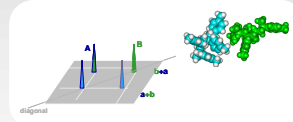
Joint Laboratory of Solid State NMR
 CZ and JHPC AS CZ

Souhrn

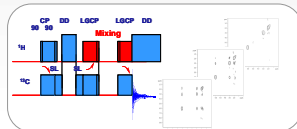
Homodekaplink: BR24, FSLG, PMLG



2D spinová difuze

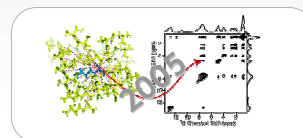


Nepřímá detekce přes ^{13}C

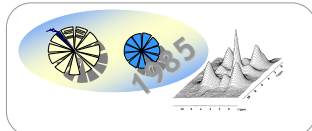


Solid-state NMR
and

NMR krystalografie



Spinová difuze a morfologie polymerů



3D korelace měření H-H vzdáleností

