

Joint Laboratory of Solid-State NMR
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(3)

Structure of multicomponent polymer systems: ¹H-¹H correlation experiments and spin diffusion

2D ¹H-¹H CRAMPS

BR24 Mixing BR24

¹H: 54° 90° 90° 54°

() 2n () 2n

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

Two-dimensional NMR spectroscopy(1971)

Transfer of magnetization through bonding electrons

Lecture on Summer School, Baska Polje, Yugoslavia, 1971
Two-dimensional NMR, COSY

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

Jean Louis Charles Jeener
*1931

90° 90°

2D COSY NMR

2D correlation experiments in solid state - 1985

Morphology of polymer blends

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

BR24 Mixing BR24

54° 90° 100-300µs 90° 54°

¹H:

Relayed coherence transfer
¹H-¹H correlation of chemical shifts

PS OCH₃ OCH₃ PVME

arom. aliph.

Non-miscible

Miscible

¹H-¹H spin exchange (diffusion)

Selective excitation

Glycine

10 ms NH₃⁺ CH₂

50 ms

100 ms

200 ms

Selection and transfer of magnetization

Spin diffusion:

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

Size of dispersed component A in matrix B:

$$d_A = 2 \frac{\epsilon}{f_B} \left(\frac{1}{\pi} D t_n^2 \right)^{1/2}$$

Relations of spin-diffusion coefficients and segmental dynamics:

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

$$D_{mob} = 8.2 \times 10^{-6} T_2^{-1} + 0.007 \quad D_{mob} = 4.4 \times 10^{-3} T_2^{-1} + 0.26$$

¹H-¹H spin exchange (diffusion)

Selection and transfer of magnetization

Spin diffusion:

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Solid-state NMR - 2D spin-diffusion experiments

2D ¹H MAS NMR pulse sequence

BR24 Mixing BR24

54° 90° 100-300µs 90° 54°

¹H:

A general two-component system in 1D spectra

Spatially separated

A general two-component system in 2D spectra

Well mixed

diagonal a b ppm

diagonal a b ppm

diagonal a b ppm

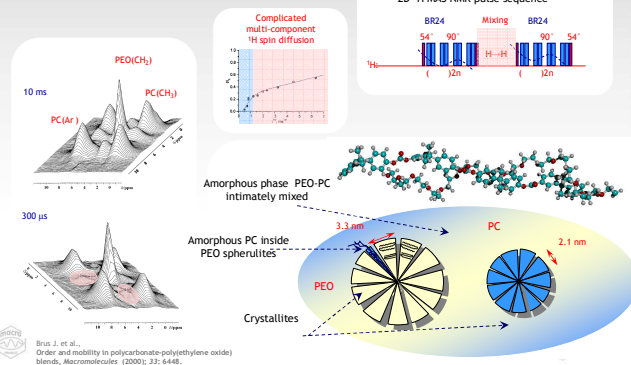
Only diagonal signals are detected - no polarization transfer occurs

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

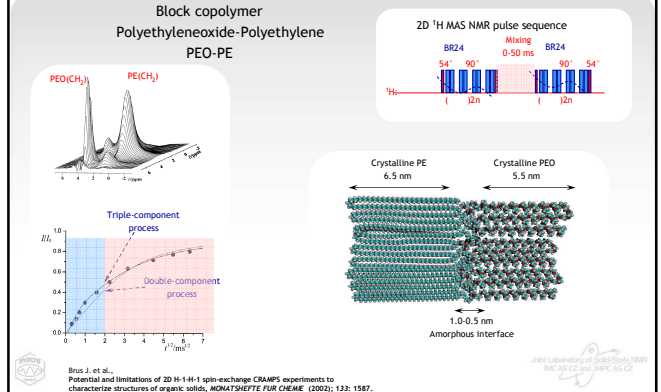
Polymer blends

Polycarbonate - Polyethyleneoxide (PC-PEO)



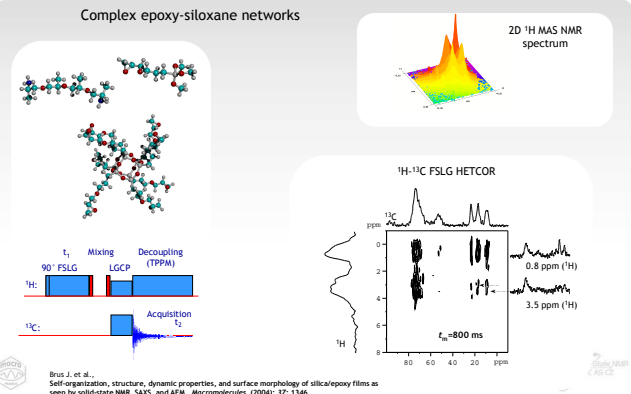
Block copolymers

Block copolymer Polyethyleneoxide-Polyethylene PEO-PE



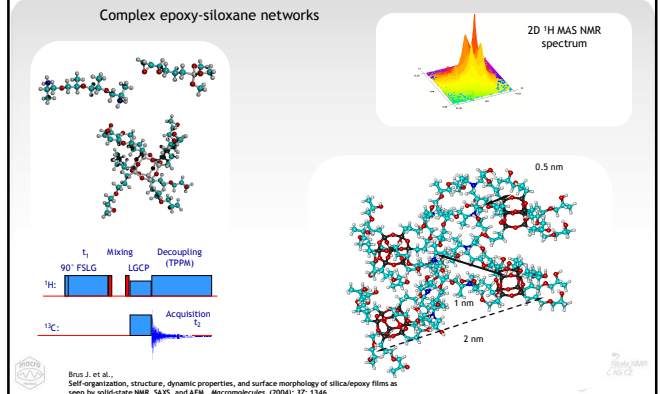
Polymer networks

Complex epoxy-siloxane networks



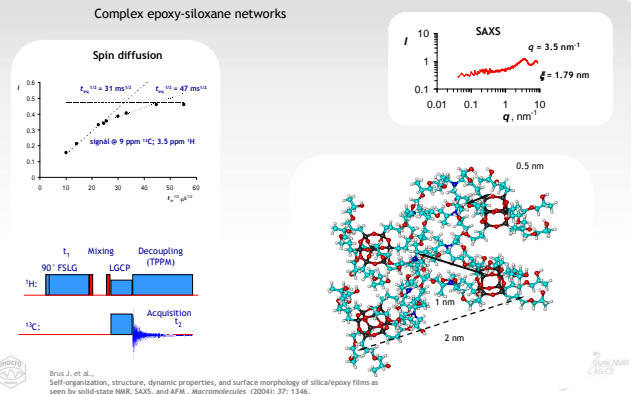
Polymer networks

Complex epoxy-siloxane networks



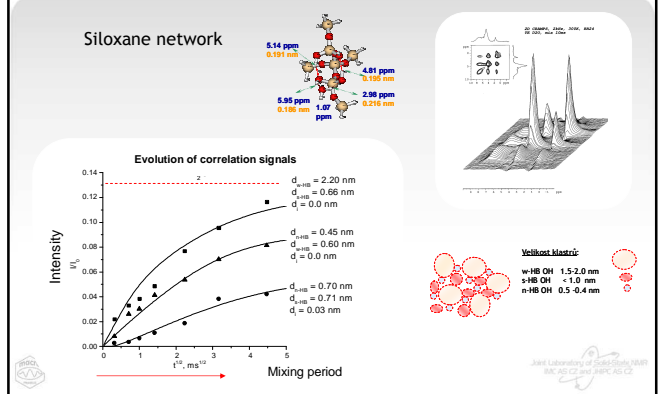
Nano-heterogeneous polymer networks

Complex epoxy-siloxane networks



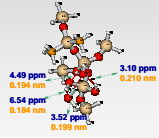
Surface hydroxyls on amorphous silica

Siloxane network

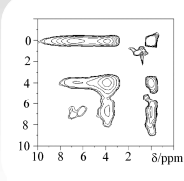
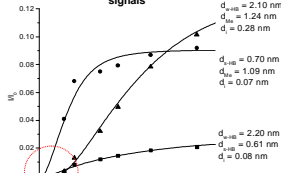


Surface hydroxyls on amorphous silica

Modified siloxane network



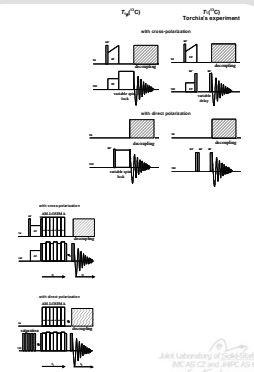
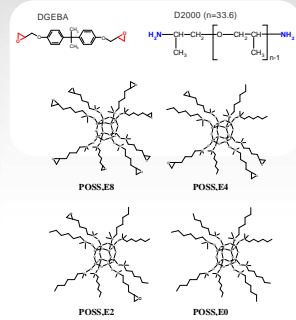
Evolution of correlation signals



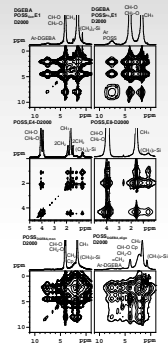
Yellowst Menti:
w-HB OH - 1.0 nm
s-HB OH - 1.0 nm
n-HB OH ? (coloured) - 1.0 nm
Me - 1.0 nm

Structure and dynamics in polymer nanocomposites

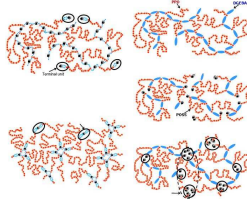
POSS-reinforced DGEBA-epoxy networks



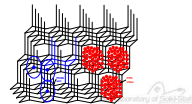
Structure and dynamics in polymer nanocomposites



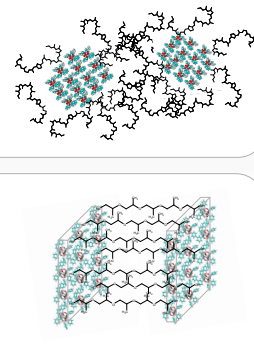
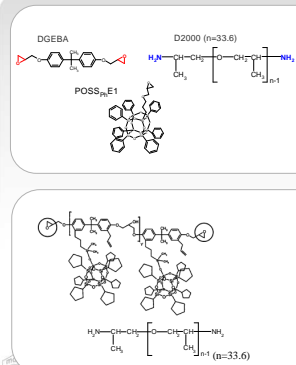
Structural variability of the networks ...



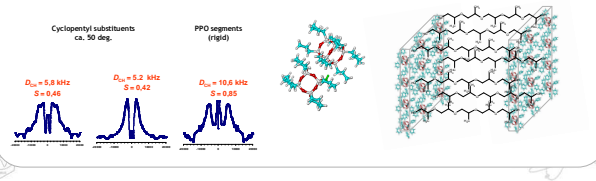
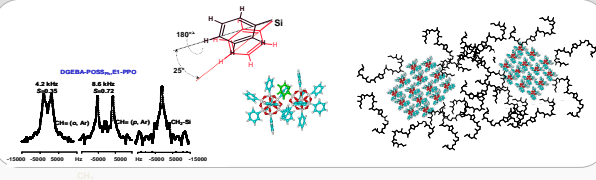
... and idealized structure



Structure and dynamics in polymer nanocomposites



Structure and dynamics in polymer nanocomposites



Summary

Segmental dynamics in nanocomposites

2D experiments and spin diffusion

Global architecture of polymer networks

Miscibility of polymer blends

Morphology of copolymers

Solid-state NMR and polymers