Investigation of Structure and Dynamics in Polymeric Systems via Solid State NMR

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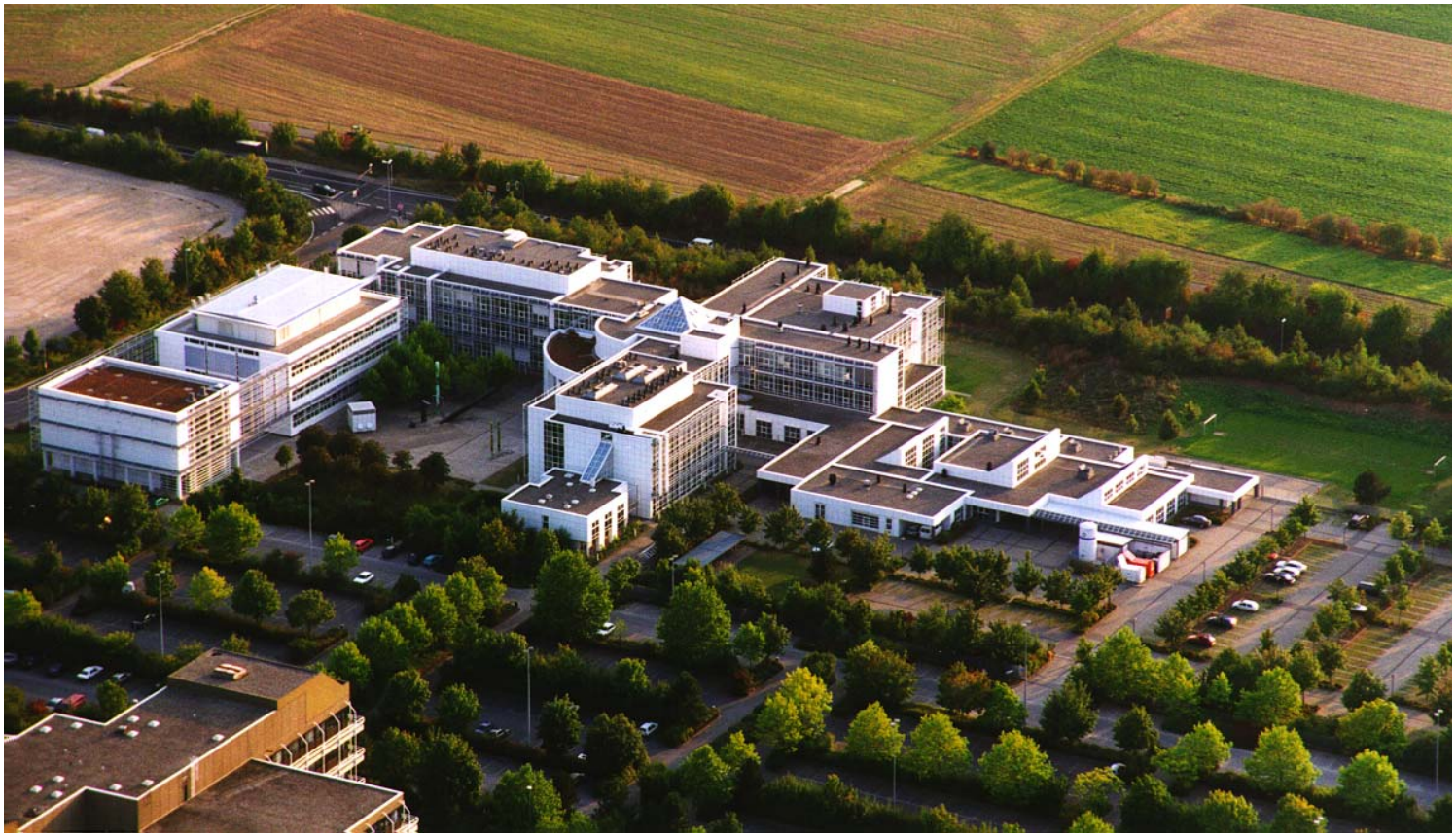
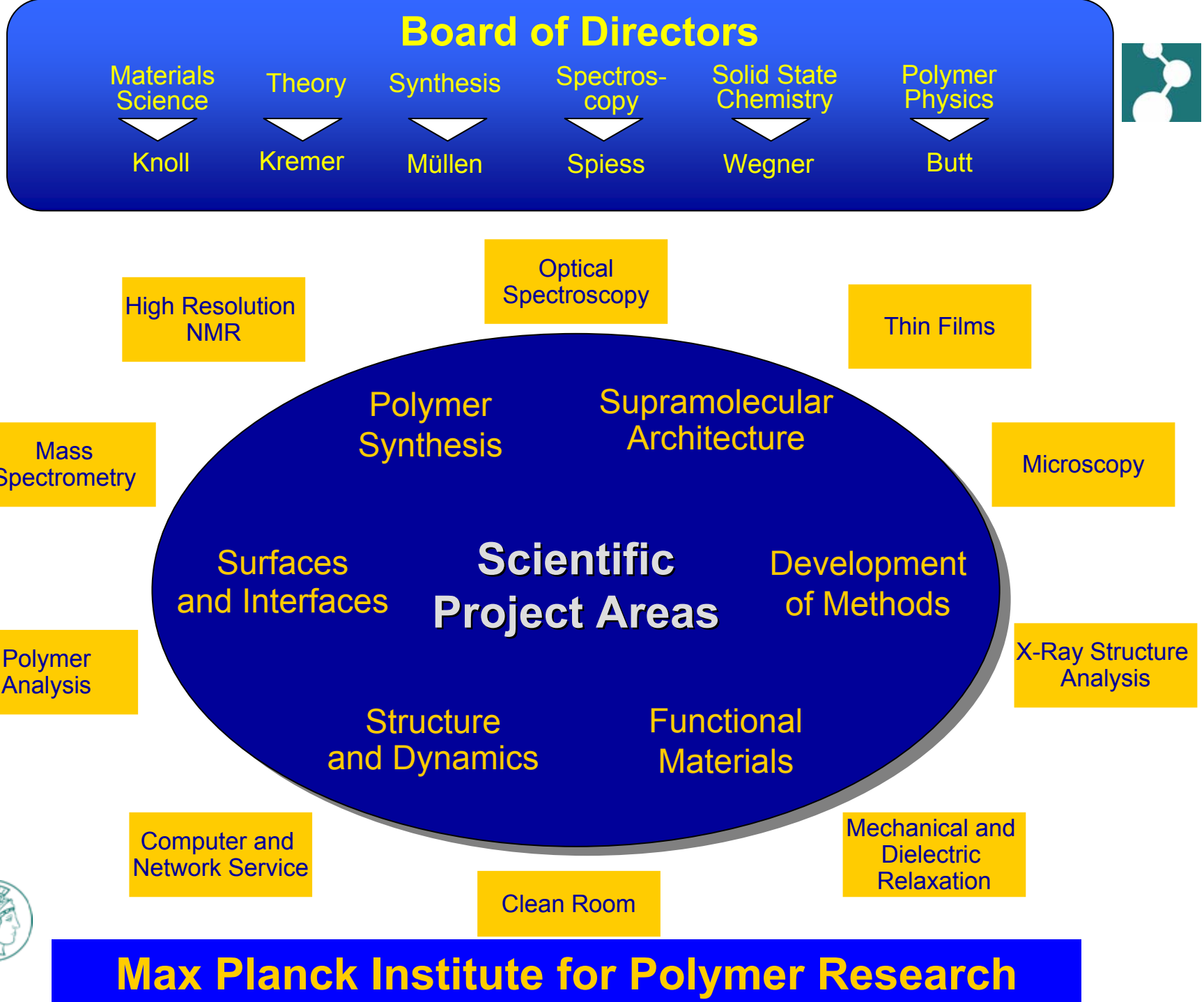
Max Planck Institute for Polymer Research



founded 1983, 450 co-workers, on campus of the University of Mainz,

interdisciplinary fundamental research of polymers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Scientific Activities of the MPI-P Spectroscopy Group

Structure and Dynamics

Polymer Chain Dynamics •
Local-Order Phenomena •

Development of Methods

- 2D Multiple Quantum MAS NMR
- Imaging of Hyperpolarized Gases
- DFT Calculations
- Pulsed and CW EPR
- Fourier-Transform Rheology

Polymer Synthesis

- Polymerization: Radical, Anionic, Emulsion, Atom-Transfer Radical
- Isotopic Labelling

Spectroscopy Group

Surfaces & Interfaces

Polyelectrolyte Multilayers •
Self Assembled Monolayers •
Surface Patterning •

Functional Materials

Photoconductors •
Protonconductors •
Shape-Persistent Macromolecules •

Supramolecular Architectures

- Columnar π-π Stacking
- Hydrogen-Bonded Structures
- Coordination Polymers

Investigation of Structure and Dynamics in Polymeric Systems via Solid State NMR

Introduction	•	interactions in solid state NMR
Solid State NMR	•	resolution enhancement in solid state NMR, magic angle spinning, recoupling methods, double quantum NMR spectroscopy
Polymer dynamics	•	Polyelectrolyte layers, polybutadiene, PEMA
Conclusions	•	Pro and Contra of Solid State NMR investigations

Molecular Structures and Dynamics via NMR

Important NMR interactions:

$$\mathbf{H} = \mathbf{H_Z} + \mathbf{H_Q} + \mathbf{H_{CS}} + \mathbf{H_D} + \mathbf{H_J}$$

Zeemann Interaction : $$H_Z = -\sum_i \gamma_i \underline{B}_0 \underline{\mathbf{I}}^i$$

Quadrupol Interaction : $$H_Q = -\sum_i \frac{eQ}{2I(2I-1)\hbar} \underline{\mathbf{I}}^i \underline{\underline{\mathbf{V}}} \underline{\mathbf{I}}^i$$

Electronic Shielding : $$H_{CS} = -\sum_i \gamma_i \underline{B}_0 \underline{\underline{\boldsymbol{\sigma}}} \underline{\mathbf{I}}^i$$

Dipol-Dipol Interaction : $$H_D = -\sum_{i \neq j} \frac{\mu_0 \hbar}{4\pi} \frac{\gamma_i \gamma_j}{r^3} \left[\frac{3}{r^2} (\underline{\mathbf{I}}^i \cdot \underline{r})(\underline{\mathbf{I}}^j \cdot \underline{r}) - \underline{\mathbf{I}}^i \cdot \underline{\mathbf{I}}^j \right]$$

Indirect Spin-Spin Interaction : $$H_J = -\sum_{i \neq j} \underline{\mathbf{I}}^i \cdot \underline{\underline{\mathbf{J}}}^{ij} \underline{\mathbf{I}}^j$$

Interactions in Solid State NMR Spectroscopy

Zeemann interaction dominates all other NMR interactions

Perturbation Theory Orientation dependence of local spin interaction on B_0

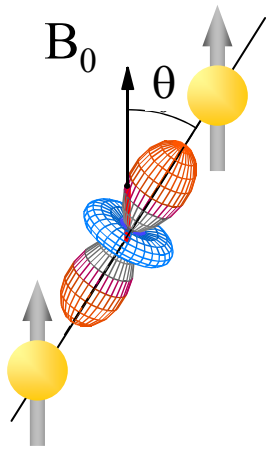
$\mathbf{H_Q}$, $\mathbf{H_D}$, $\mathbf{H_{CS}}$, $\mathbf{H_J}$

Isotropic Contributions

$\mathbf{H_{CS}}$: chemical shift

$\mathbf{H_J}$: J-couplings

Liquid state NMR



Anisotropic Contributions

Symmetric

$\mathbf{H_Q}$: quadrupol

$\mathbf{H_D}$: dipol-dipol

$\mathbf{H_{CS}}$: chemical shift

Asymmetric

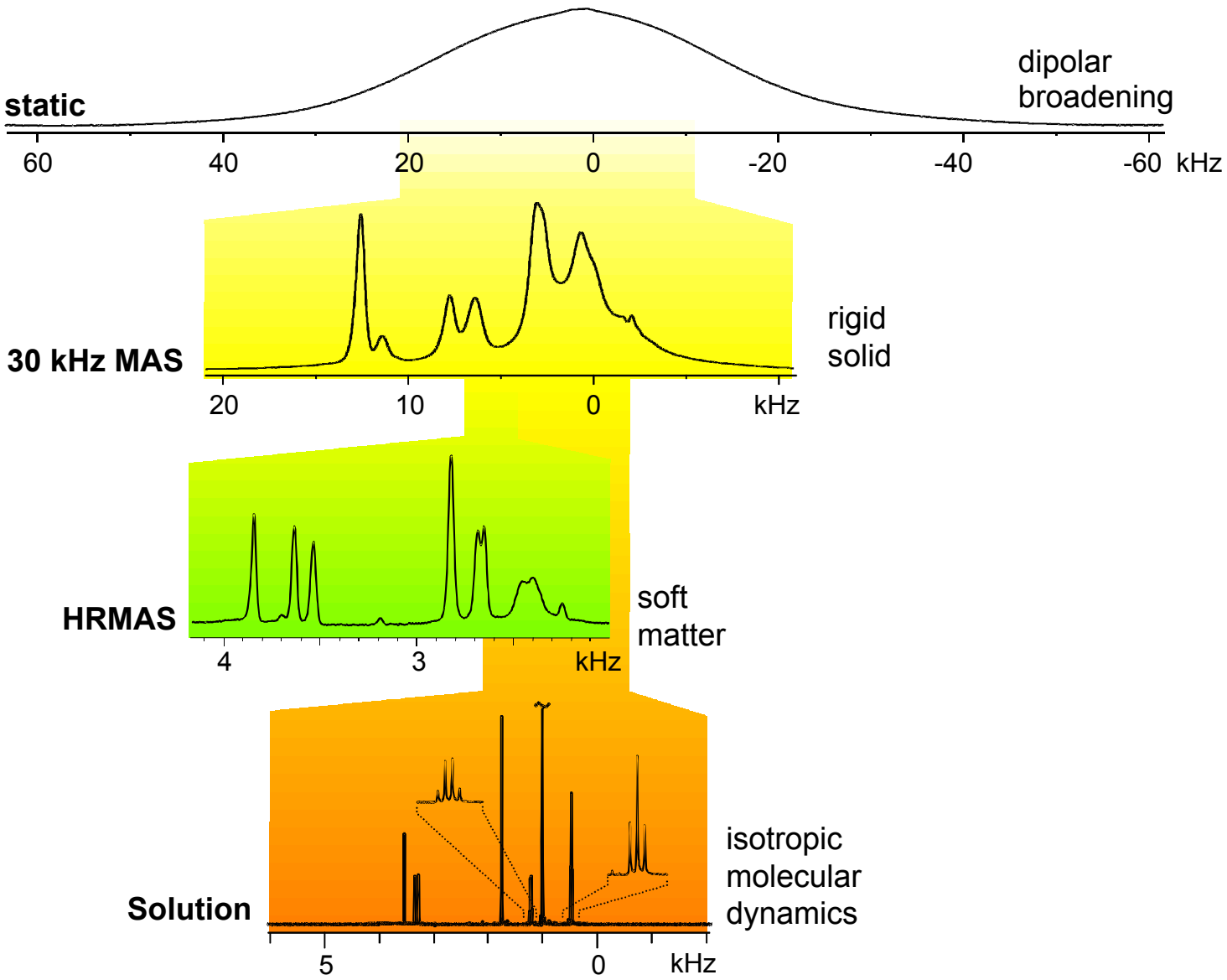
$\mathbf{H_Q}$: quadrupol

$\mathbf{H_{CS}}$: chemical shift

$$H_D = \sum_{i \neq j} \frac{\mu_0 \hbar}{4\pi} \frac{\gamma_i \gamma_j}{r_{ij}^3} \frac{1}{2}(3\cos^2\theta_{ij} - 1)\, T^{ij}_{2,0}$$

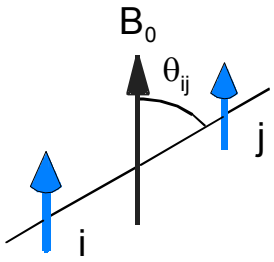
Distance ***Orientation***

^{1}H NMR Spectra in Liquid and in Solid State



Spectral Resolution Enhancement in Solid State NMR

dipol-dipol coupling:



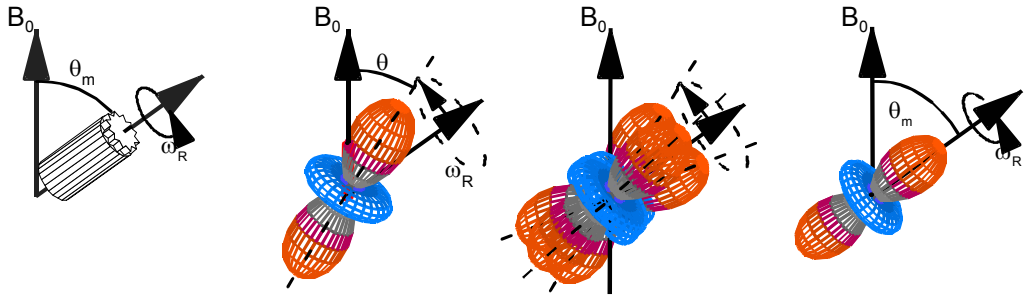
$$\hat{H} = \hat{R}_{2,0} \cdot \hat{T}_{2,0}$$

space spin

$$\hat{H} \propto \frac{1}{r_{ij}^3} \frac{1}{2}(3\cos^2\theta_{ij} - 1)\, \gamma_i \gamma_j (3\hat{I}_{Z,i}\hat{I}_{Z,j} - \hat{I}_i \cdot \hat{I}_j)$$

magic angle spinning:

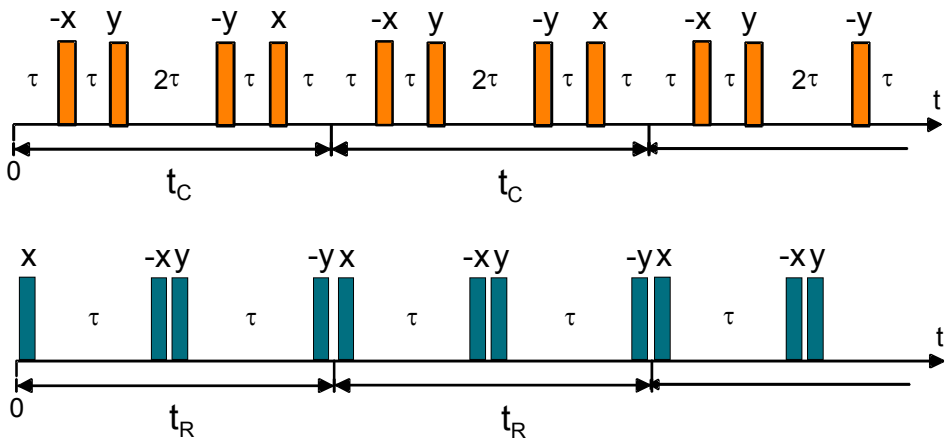
$$\bar{\hat{R}}_{2,0} \rightarrow 0$$



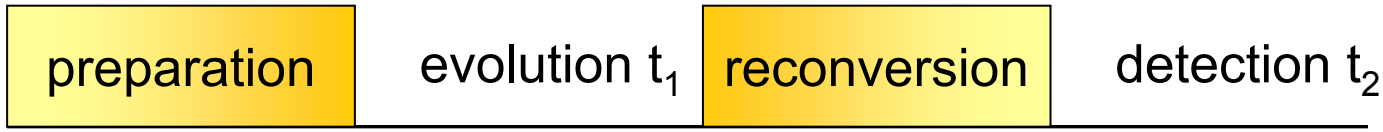
RF irradiation:

$$\bar{\hat{T}}_{2,0} \rightarrow 0 \quad \text{(CRAMPS)}$$

$$\bar{\hat{T}}_{2,0} \rightarrow H_{D,eff.} \quad \text{(Recoupling)}$$

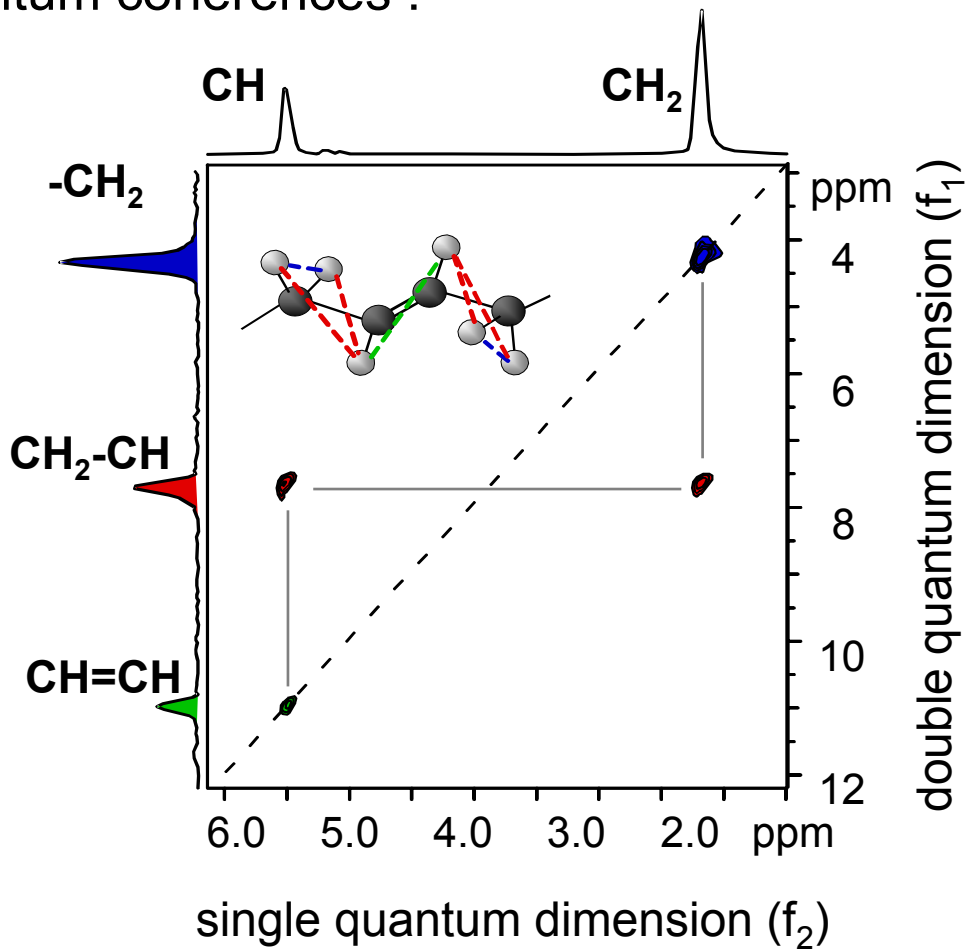


Double Quantum NMR Spectroscopy under MAS



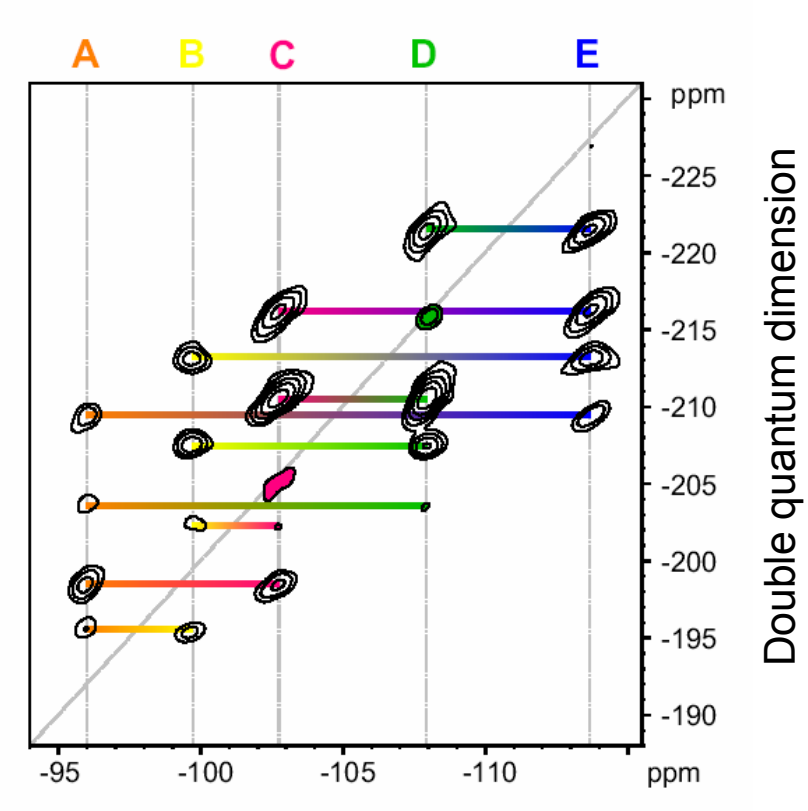
properties of double quantum coherences :

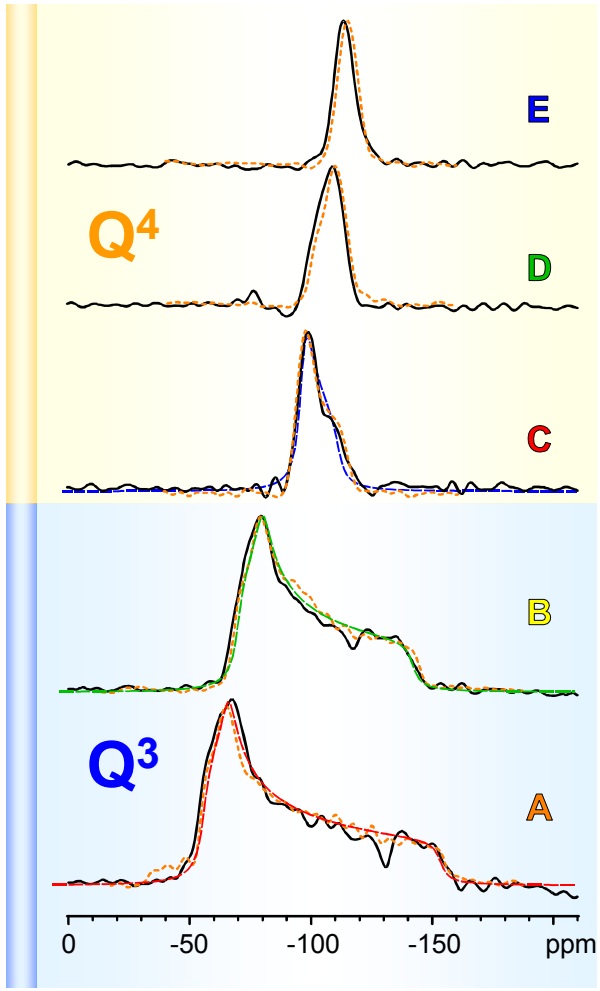
- $\omega_{DQ} = \sum_i \omega_{SQ,i}$
- $I_{DQ,ij} = f(D_{ij} \cdot t)$
- $\frac{dM}{dt} \approx 0$



Molekulare Stuktur von Silikat-Schichten

^{29}Si double quantum spectrum: DQ intensity $\propto r^{-6}$ => coordination shells

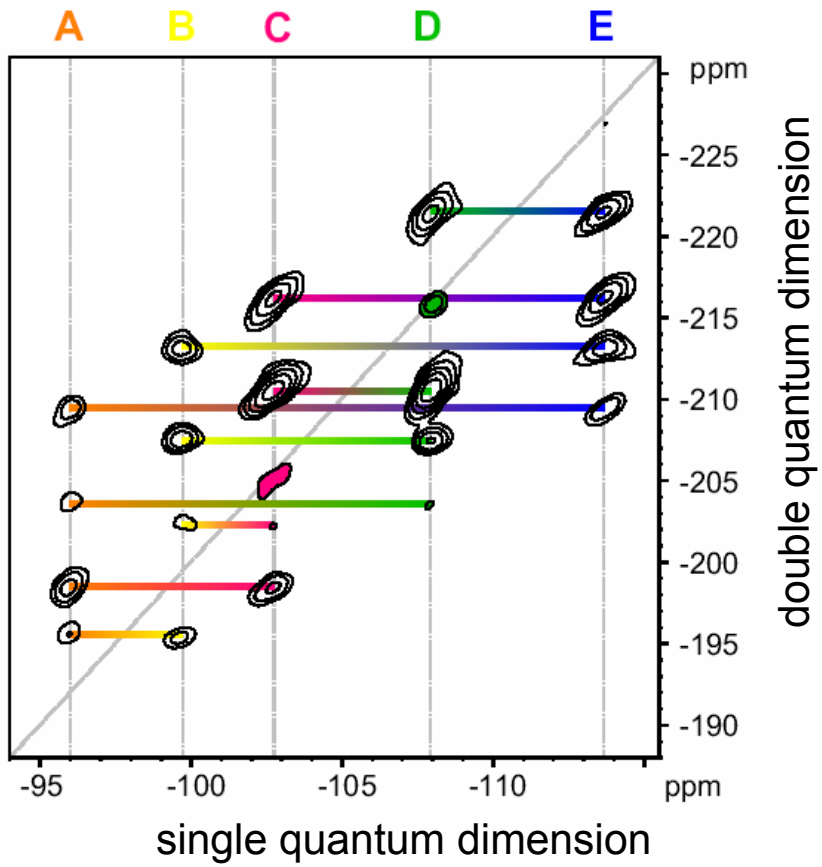


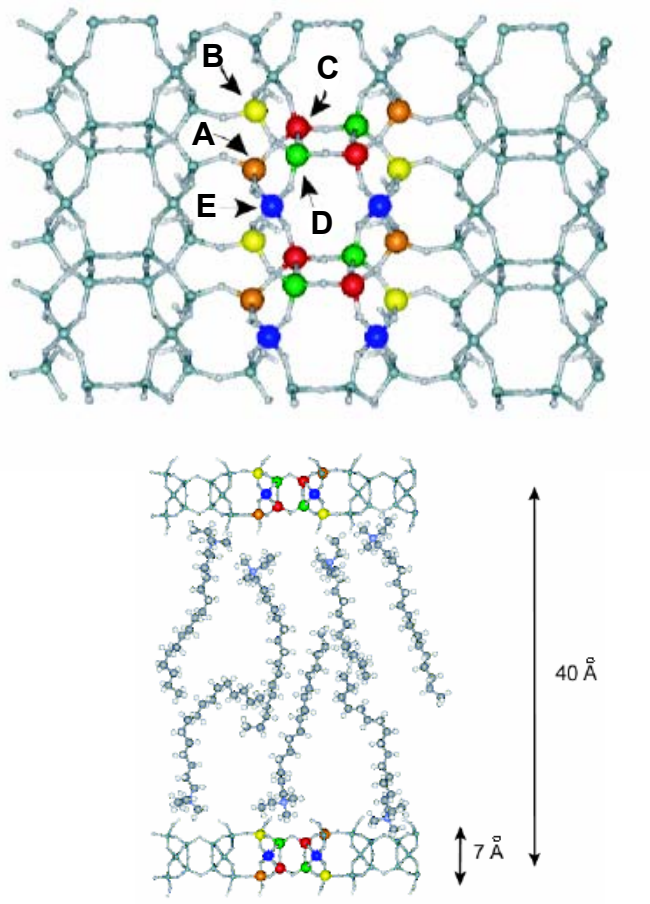


Analysis of layered silicates via next nearest neighbor relations

Molecular Structure of Layered Silicates

^{29}Si double-quantum spectrum: DQ-Intensities => coordination spheres





structure of layered silicates from analysis of spatial proximities

N. Hedin et al., *J. Am. Chem. Soc.* **126**, 9425 (2004).

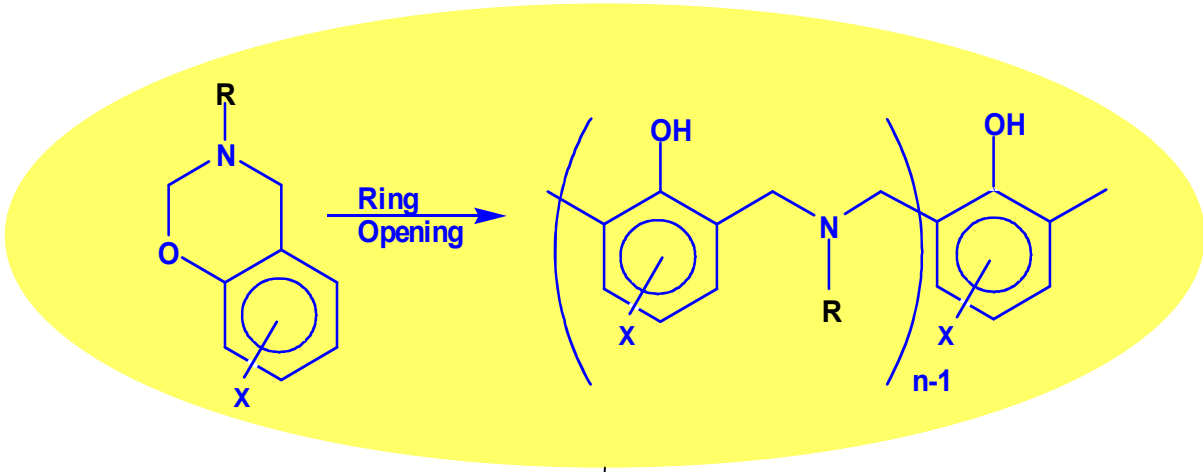
Polybenzoxazines

Useful Properties

- High T_g
- Good mechanical properties
- Excellent UV and chemical resistance

Unusual Properties

- Low water absorption
- Low volumetric expansion on curing
- High modulus

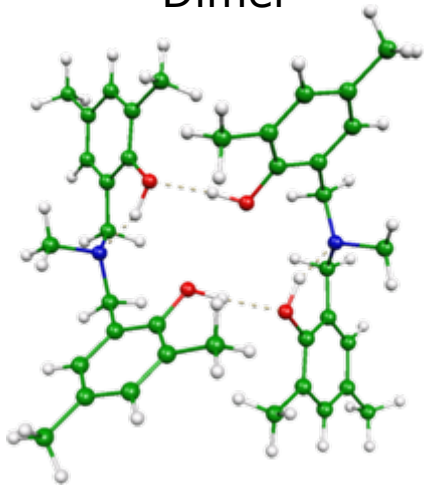


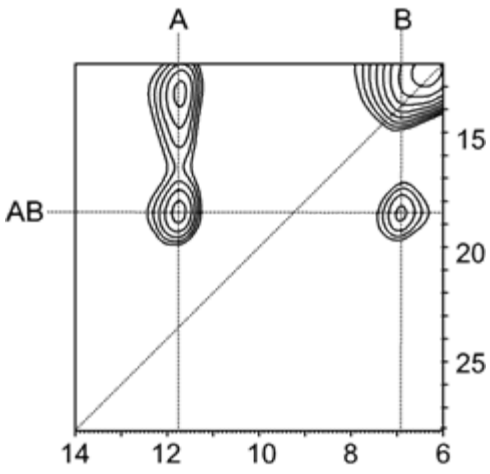
Hydrogen-bonded network

What is the nature of the network?

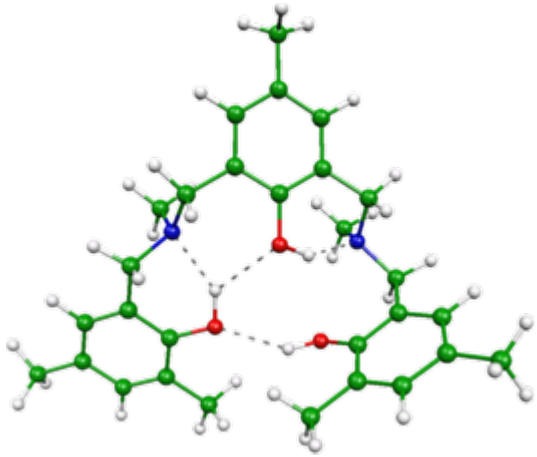
Benzoxazine Oligomers Studied by ^{1}H DQ NMR

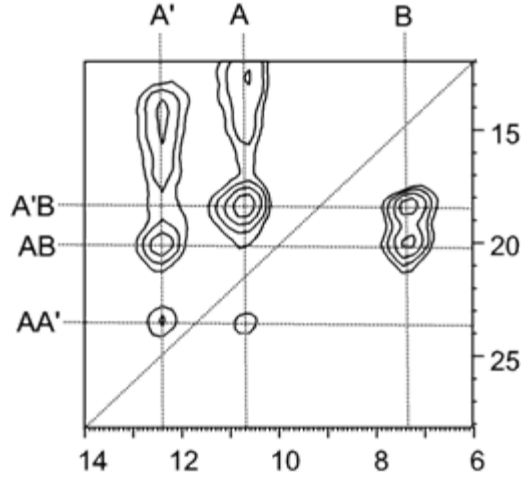
Dimer



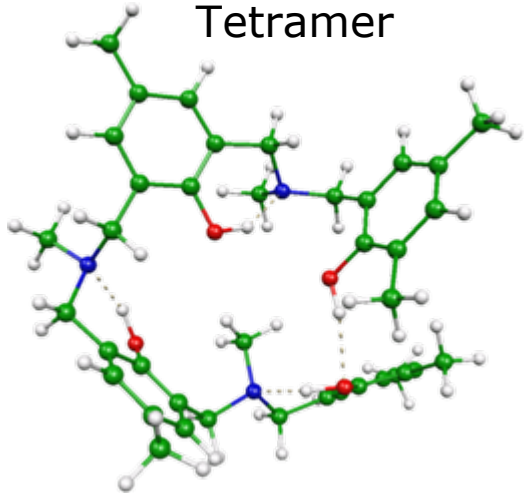


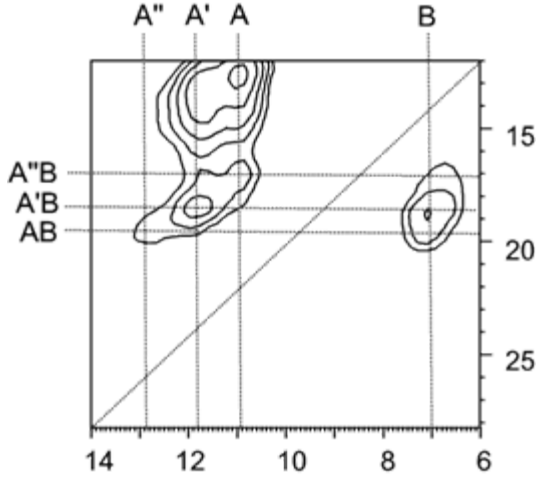
Trimer





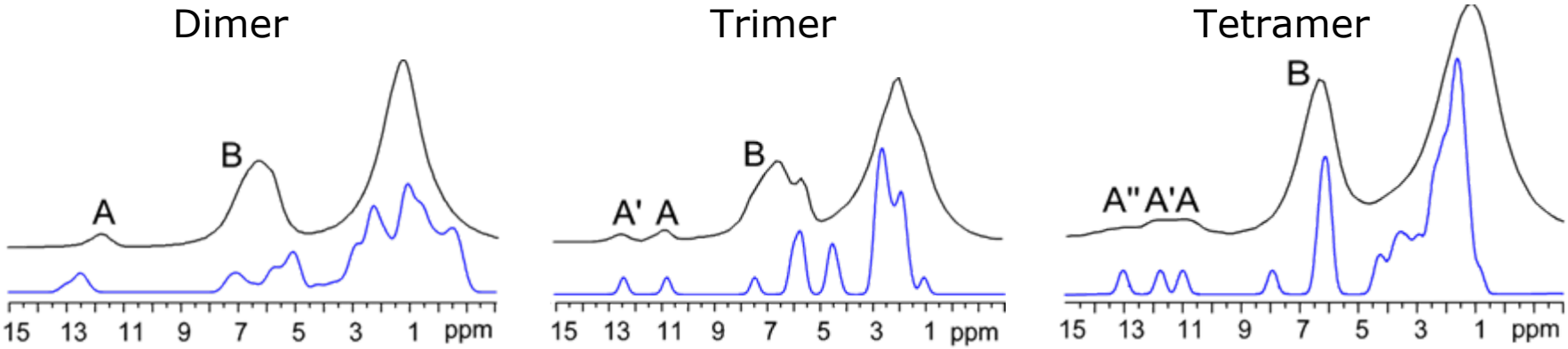
Tetramer



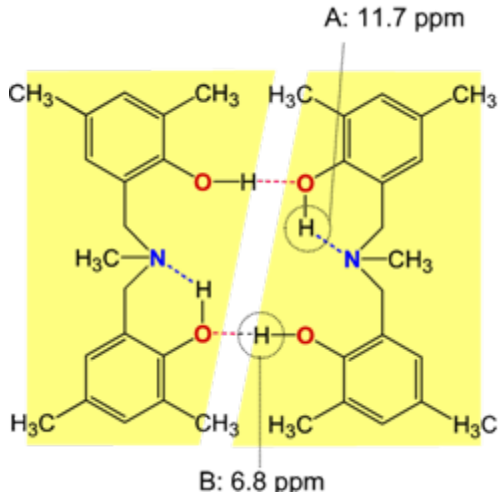


Changes in hydrogen bonding structure evident from changing ^{1}H resonances and DQ contacts

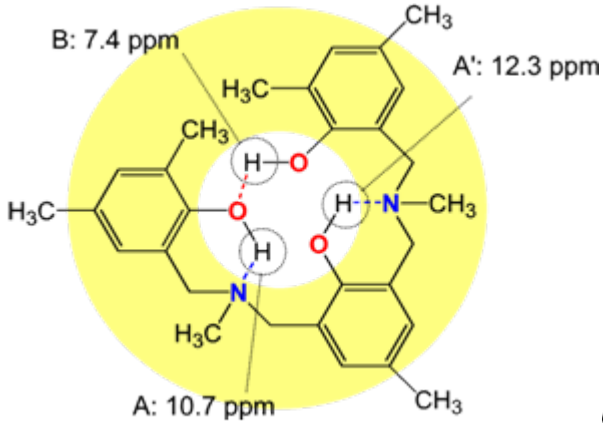
Hydrogen Bonds Assigned *via* DFT-Based Chemical Shift Calculations



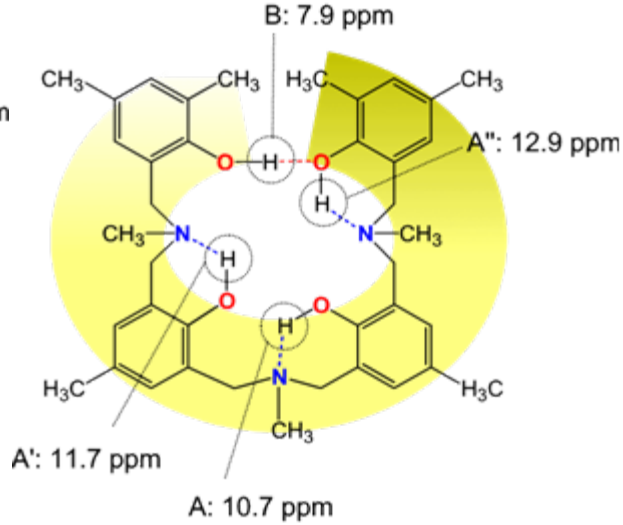
Calculated and **experimental ^{1}H NMR** spectra agree, particularly in hydrogen-bonding region.



Isolated Dimer Pair - X-ray Structure
Intra:Inter = 1:1



Trimer forms Planar Ring
Intra:Inter = 2:1

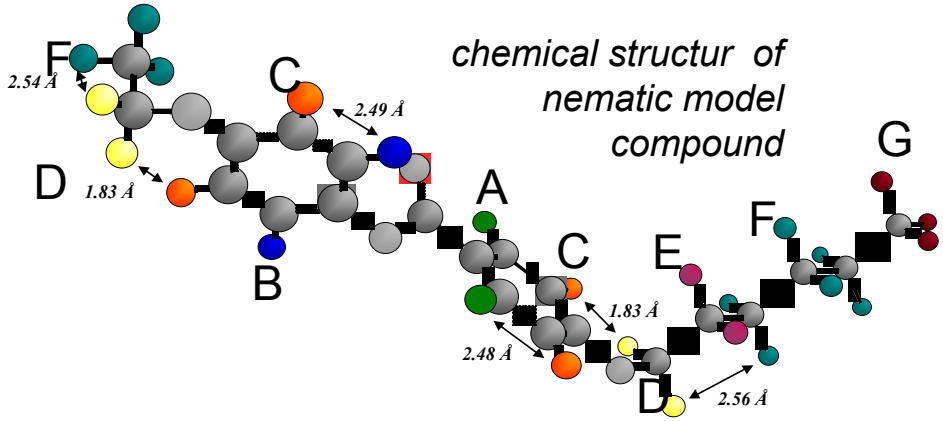


Tetramer forms Overlapping Loop
Intra:Inter = 3:1

^{1}H chemical shifts influenced by proximity to oxygen. Helical structure predicted for polymer.

G. R. Goward et al., *J. Am. Chem. Soc.* **125**, 5792 (2003).

Order Parameter in Liquid Crystalline Phases



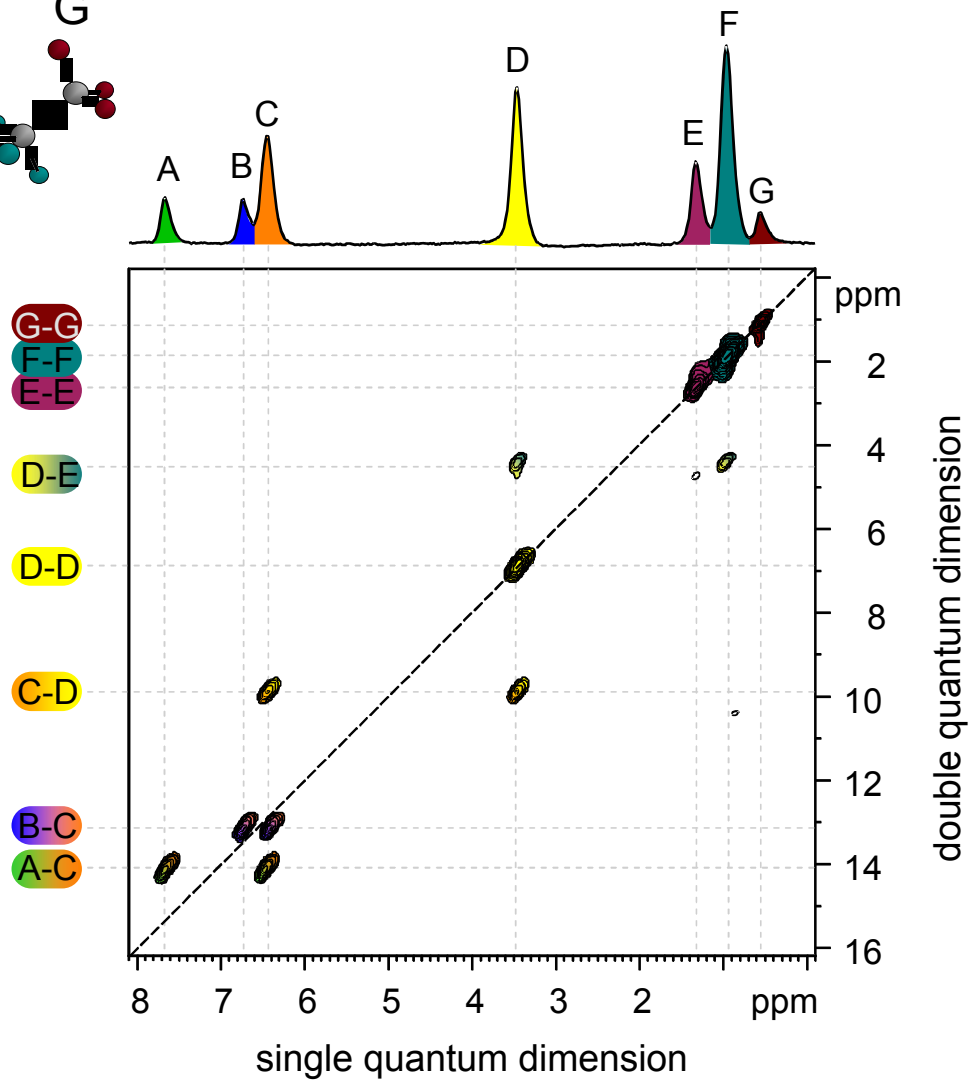
chemical structur of nematic model compound

order parameter S_{ij} :

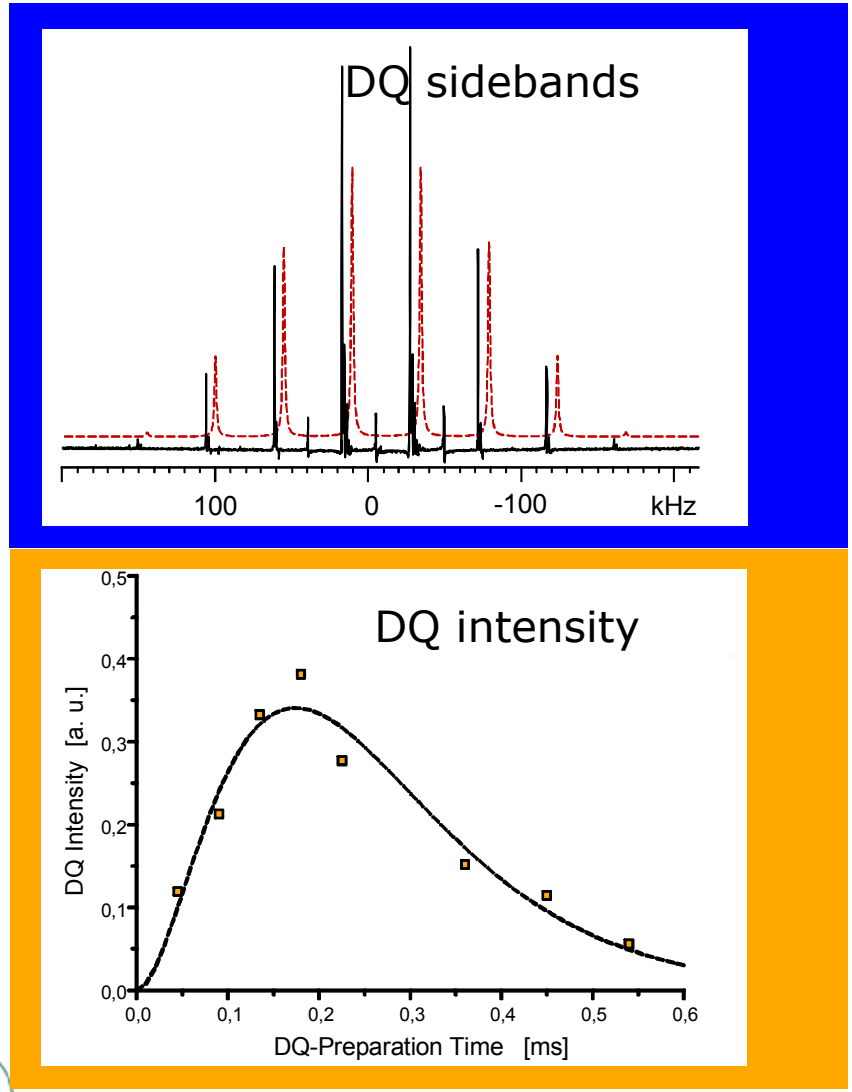
$$S_{ij} = \left\langle \frac{1}{2}(3\cos^2\theta - 1) \right\rangle$$

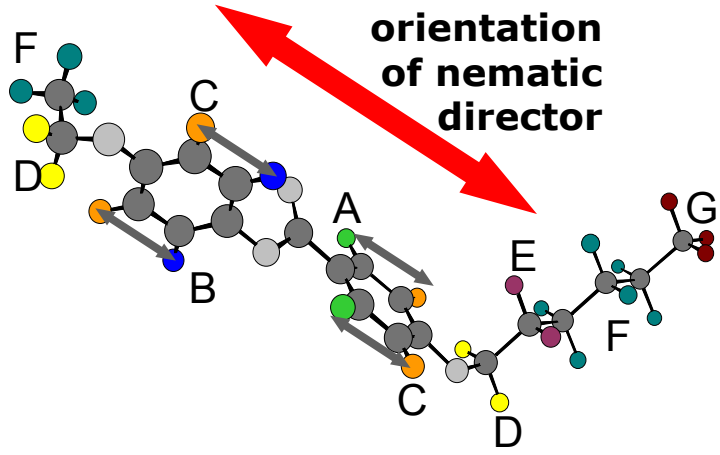
$$\Updownarrow$$

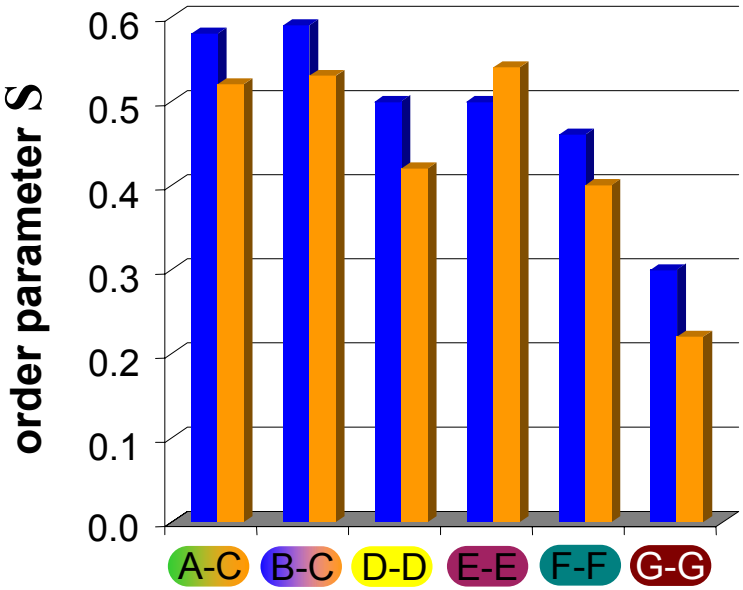
$$S_{ij} = \frac{\left\langle D_{ij,eff} \right\rangle}{D_{ij,stat}}$$



Order Parameters in Liquid Crystalline Systems



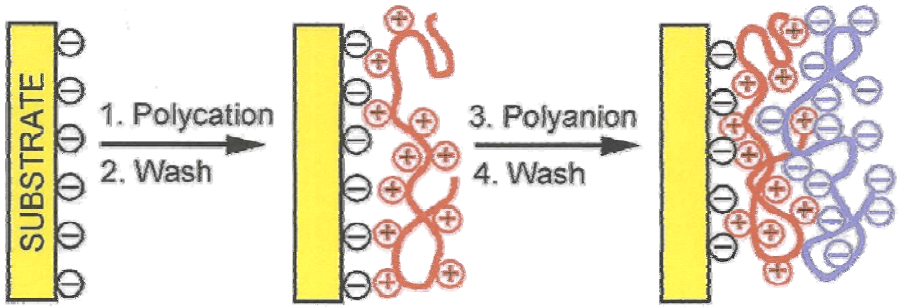


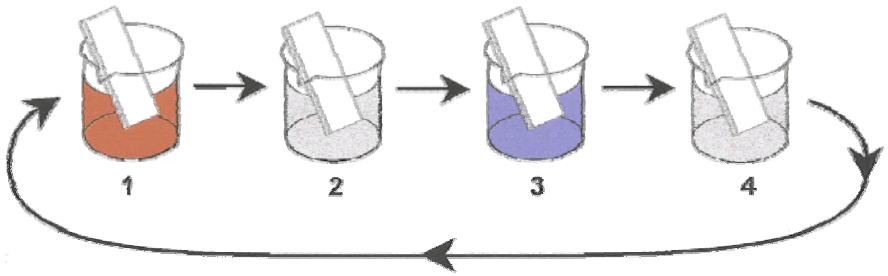


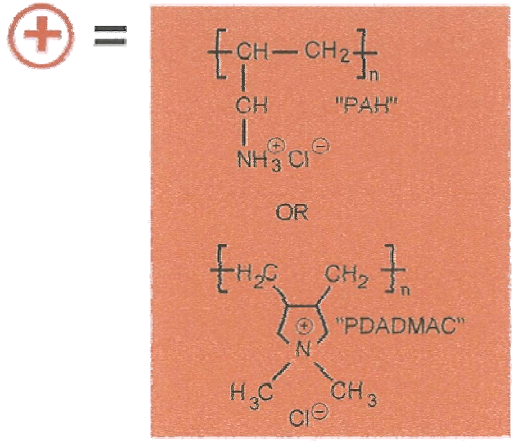
Investigation of Structure and Dynamics in Polymeric Systems via Solid State NMR

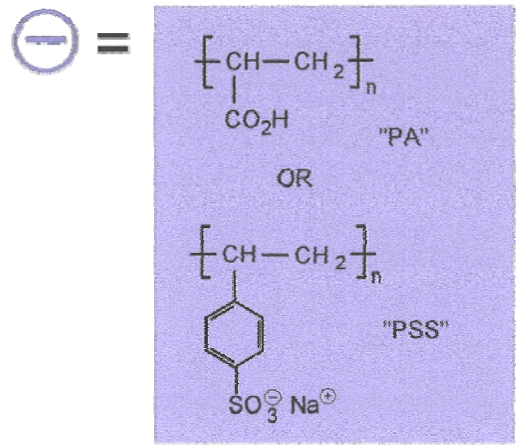
Introduction	• Interaction in solid state NMR
Solid State NMR	• MAS, recoupling, double-quantum NMR
Polymer Dynamics	• Polyelectrolyte multi layers,reptations-model, scaling laws in polymer dynamics, influence of rigid confinements, conformational stability in PEMA melts.
Conclusions	• Pro and Contra Solid State NMR investigations

Polyelectrolyte Multi-Layers

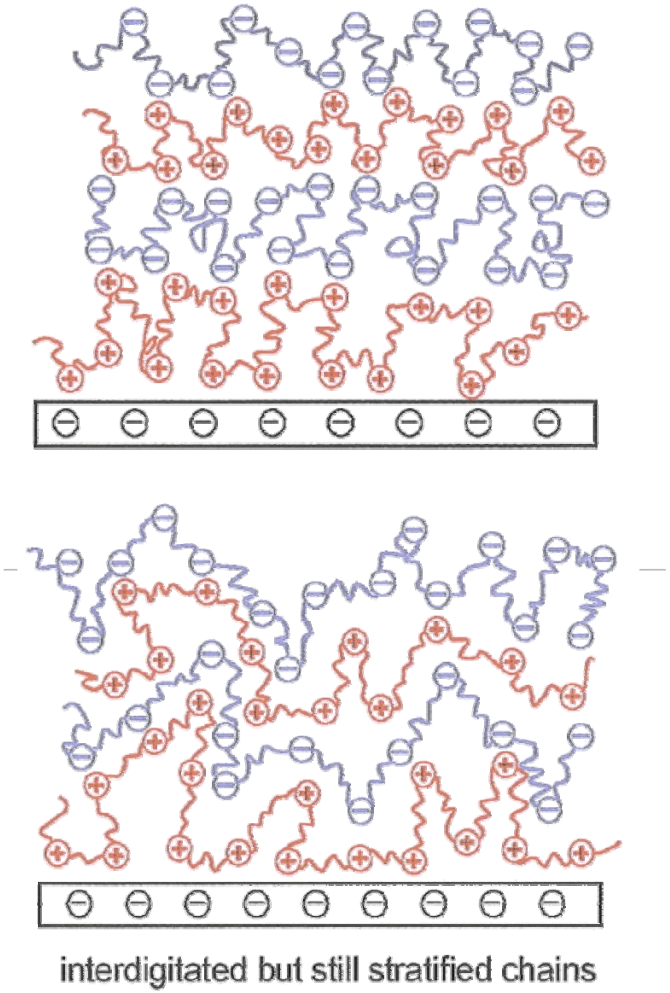




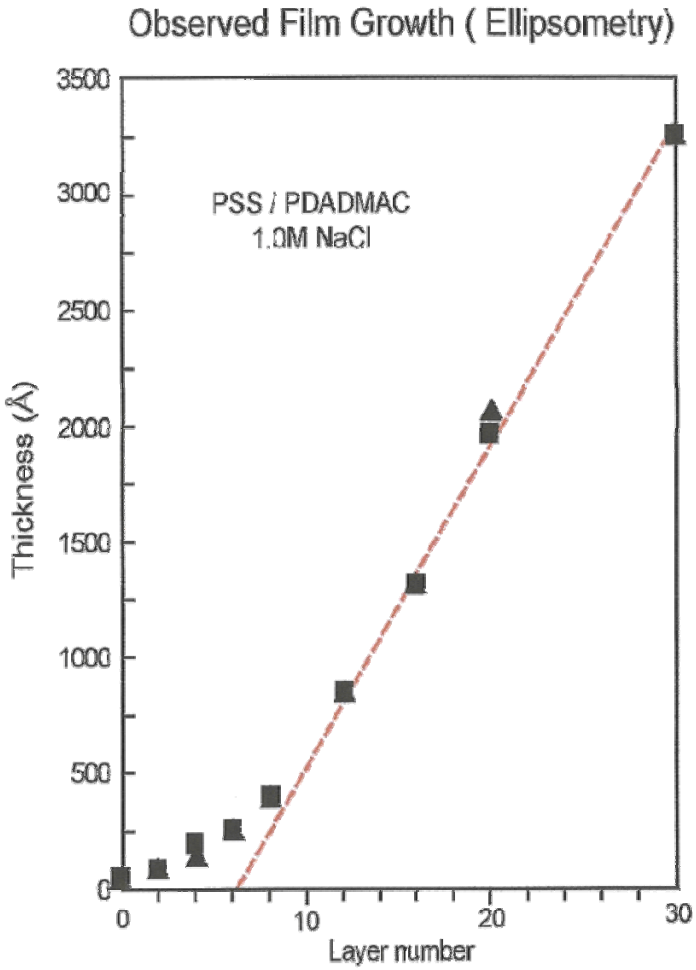




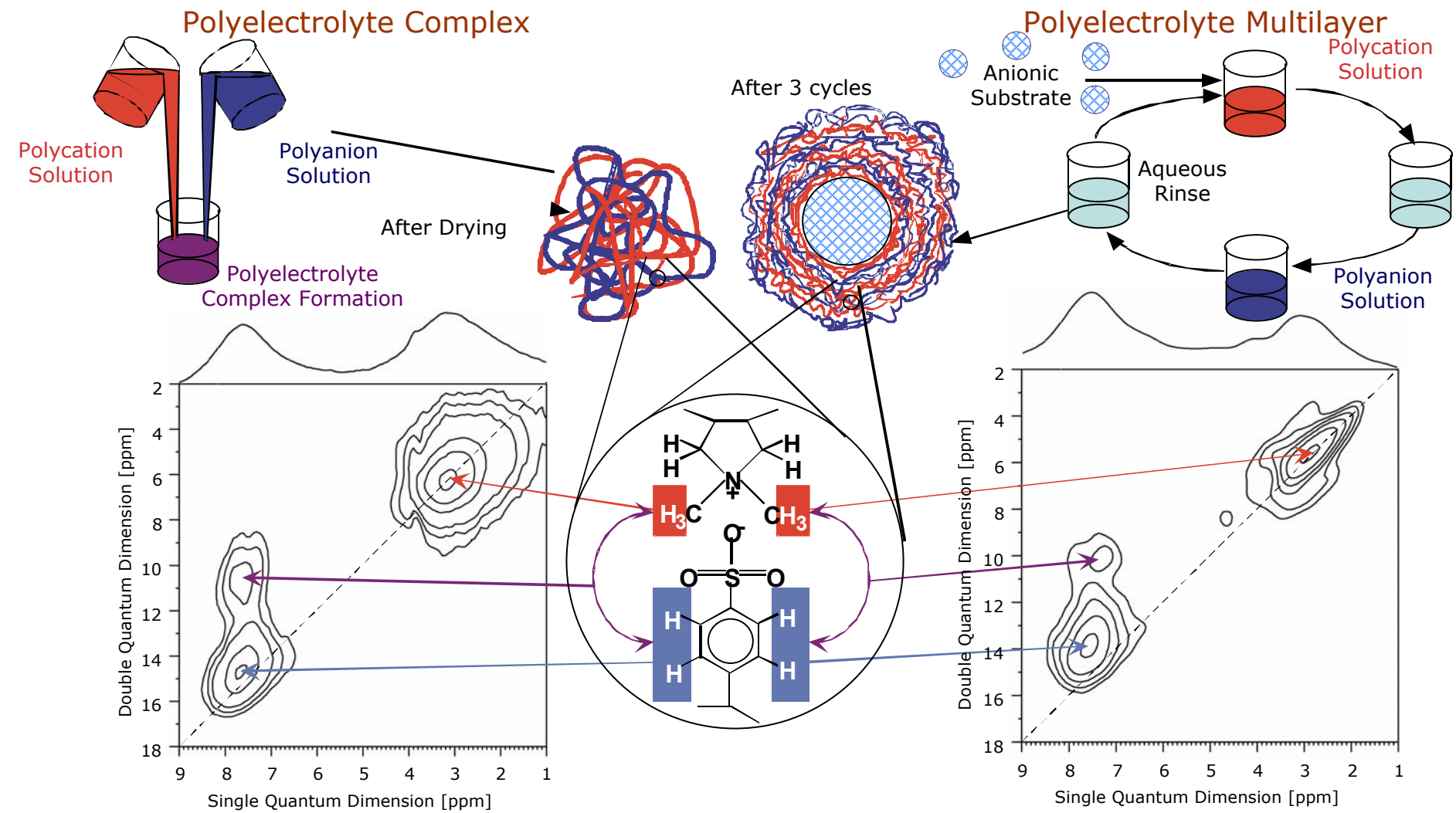
Structure of Polyelectrolyte Layers



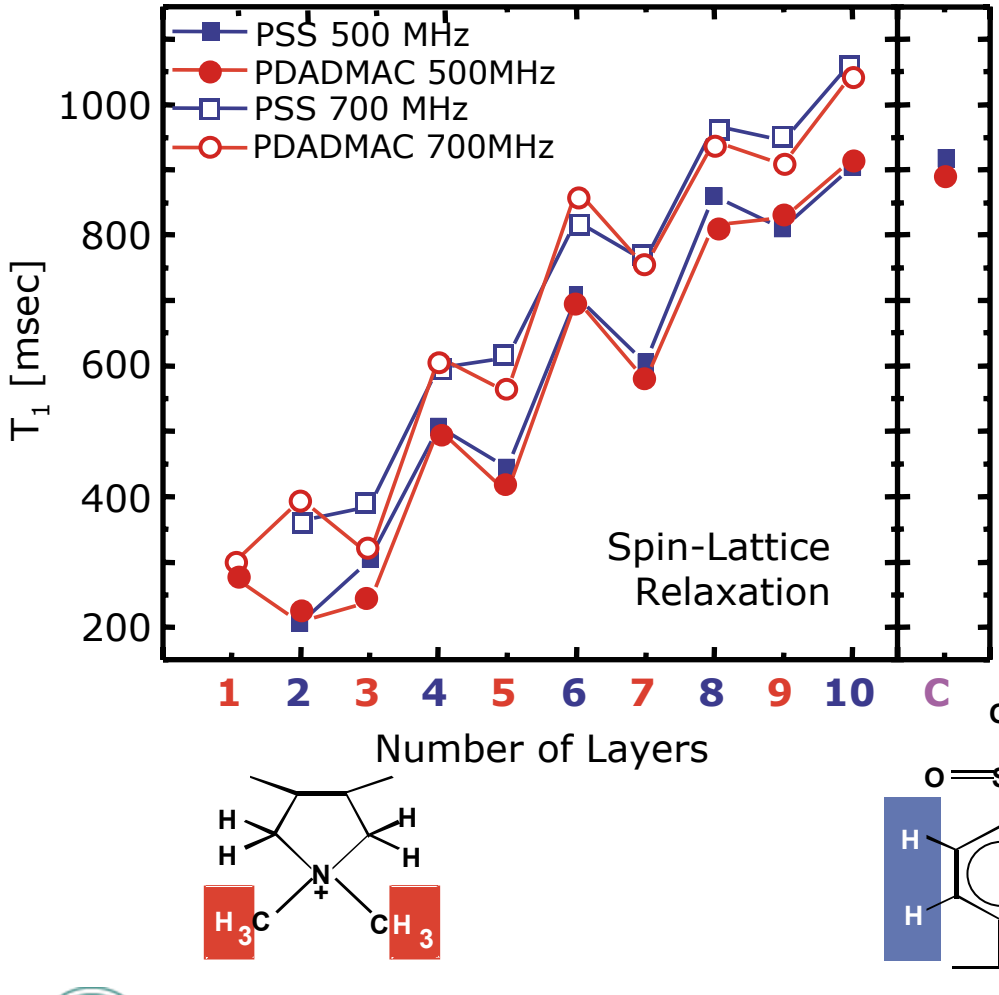
interdigitated but still stratified chains



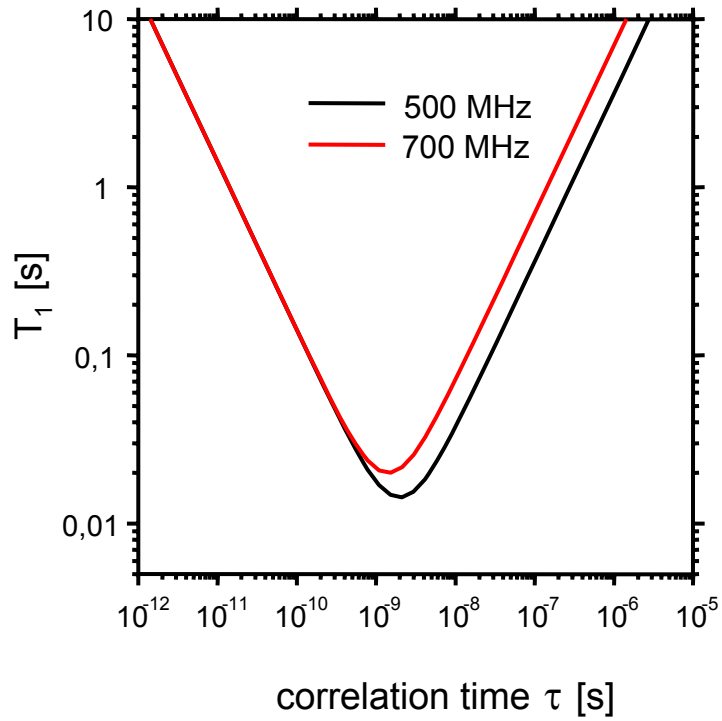
DQ NMR Investigation of Structure: PEM vs. PEC

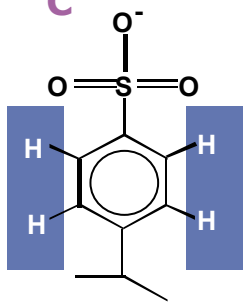


Molecular Dynamics in Polyelectrolyte Multi Layers

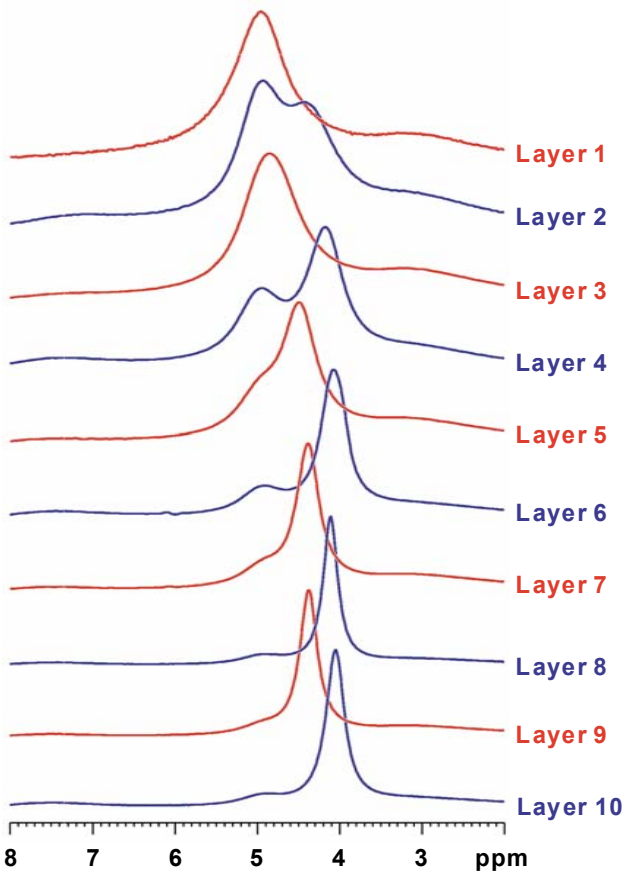


theoretical T_1 relaxation behavior:

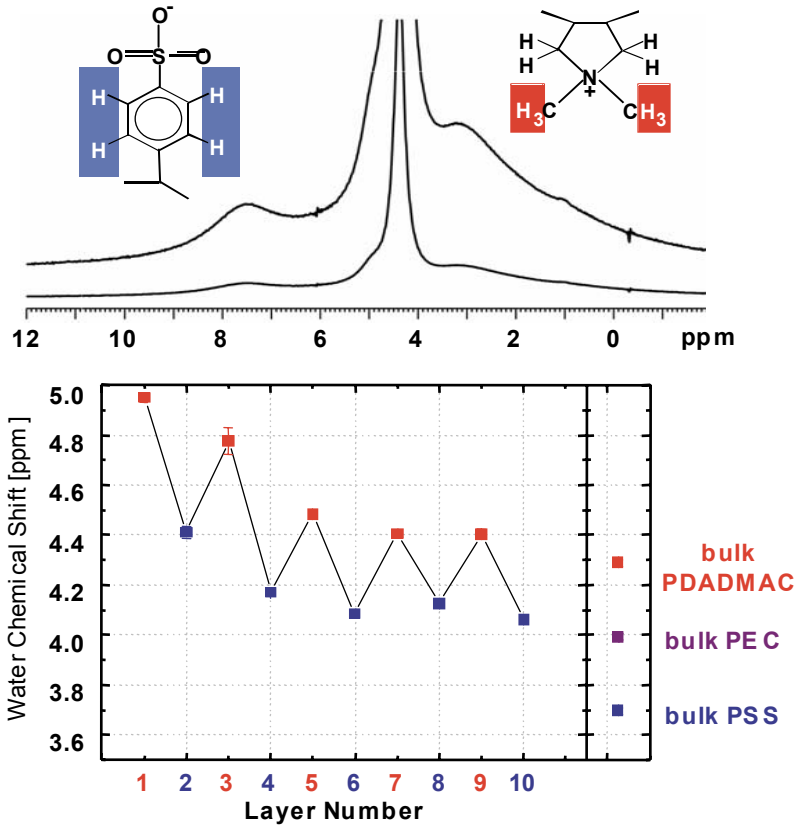




Localization of Water in Polyelectrolyte Multilayers



^{1}H MAS NMR Spectra



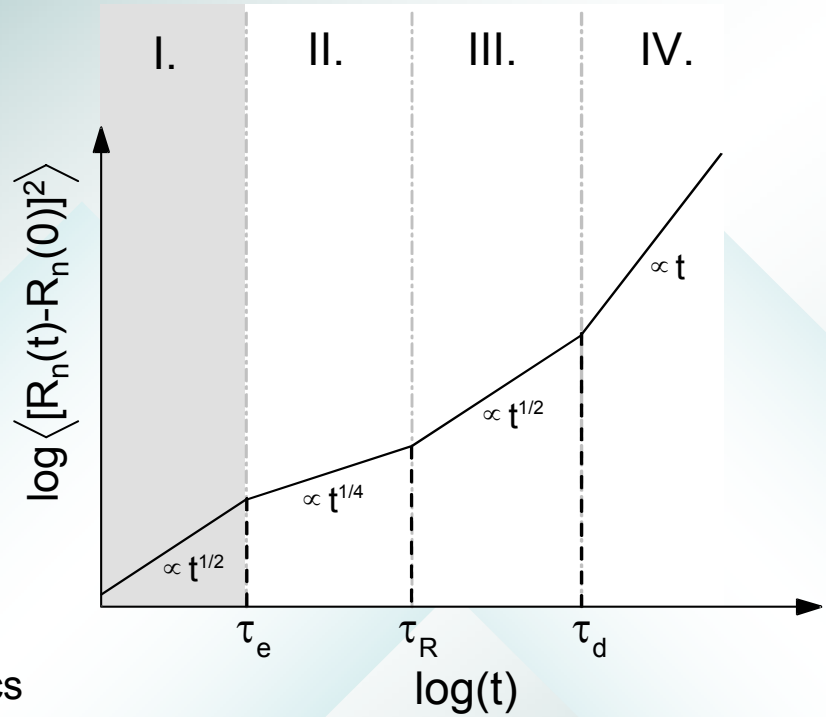
^{1}H Chemical Shift

M. McCormick et al., *Macromolecules* **36**, 3616 (2003).

S. Pawsey et al., *J. Am Chem. Soc.* **125**, 4174 (2003).

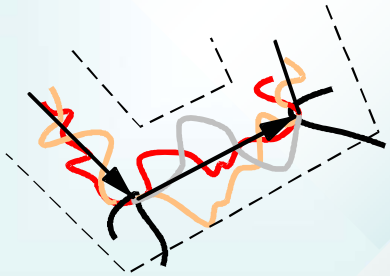
Length- and Time Scales in Polymer Dynamics

dynamic regimes of the Reptation model :



$t < \tau_e$

fast, local dynamics



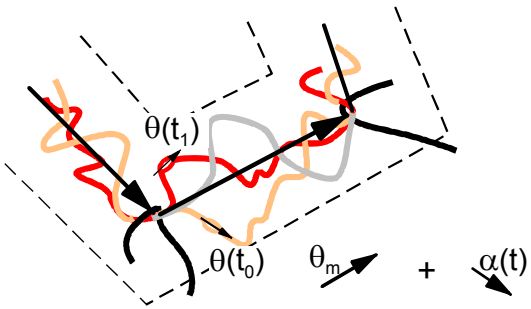
separation of time scales!

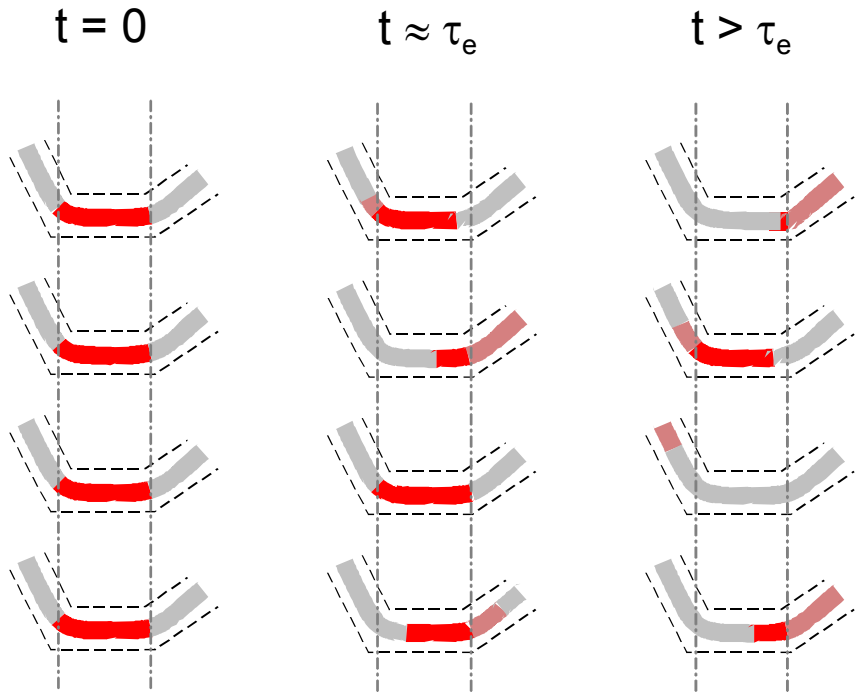
$t > \tau_e$

slow, collective Reptation dynamics

DQ Measurements of Dynamics on Different Time Scales

$$I_{DQ} \propto \left\langle \int_0^t dt' \int_{t+t_1}^{2t+t_1} dt'' \left\langle D_{ij,eff} \right\rangle^2 \cdot d^{(2)}_{2,-m}(t') d^{(2)}_{2,m}(t'') \right\rangle$$





local order parameter : $S_{ij} = \left\langle D_{ij,eff} \right\rangle / D_{ij}$

static systems : $S_{ij}(t)=1$

isotropic motion : $S_{ij}(t)=0$

polymer network theory : $S \approx \frac{3}{5} N_e^{-1}$

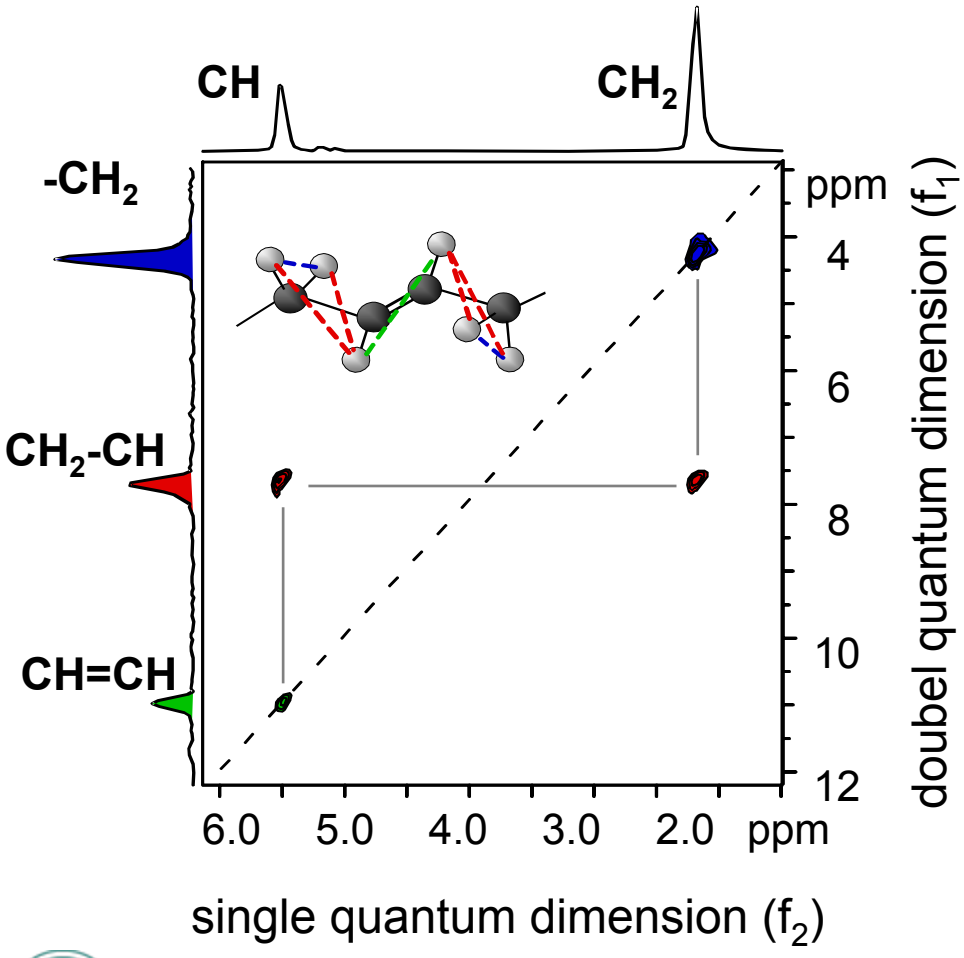
Polybutadien : $S \approx \frac{3}{5} \frac{M_{Kuhn}}{M_e} \approx 0.03$

$\left\langle d^{(2)}_{2,-m}(t'_{exc.}) \cdot d^{(2)}_{2,m}(t''_{rec.}) \right\rangle_t$ corresponds to

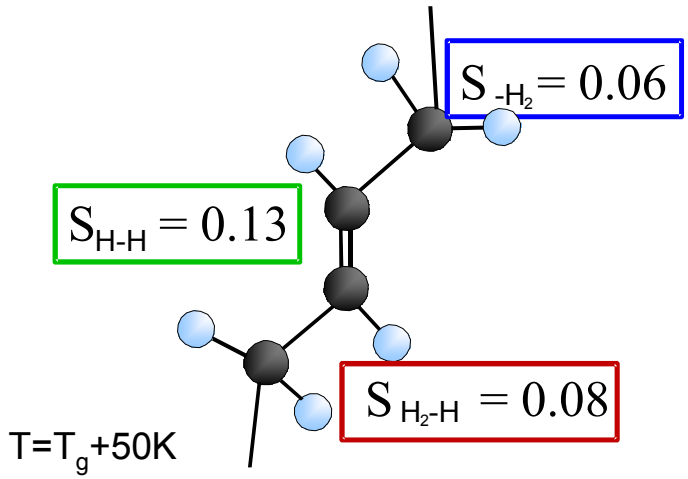
return-to-origin probability C (t)

Local Order Parameters in 1,4 Polybutadien Melts

^{1}H double quantum NMR spectrum



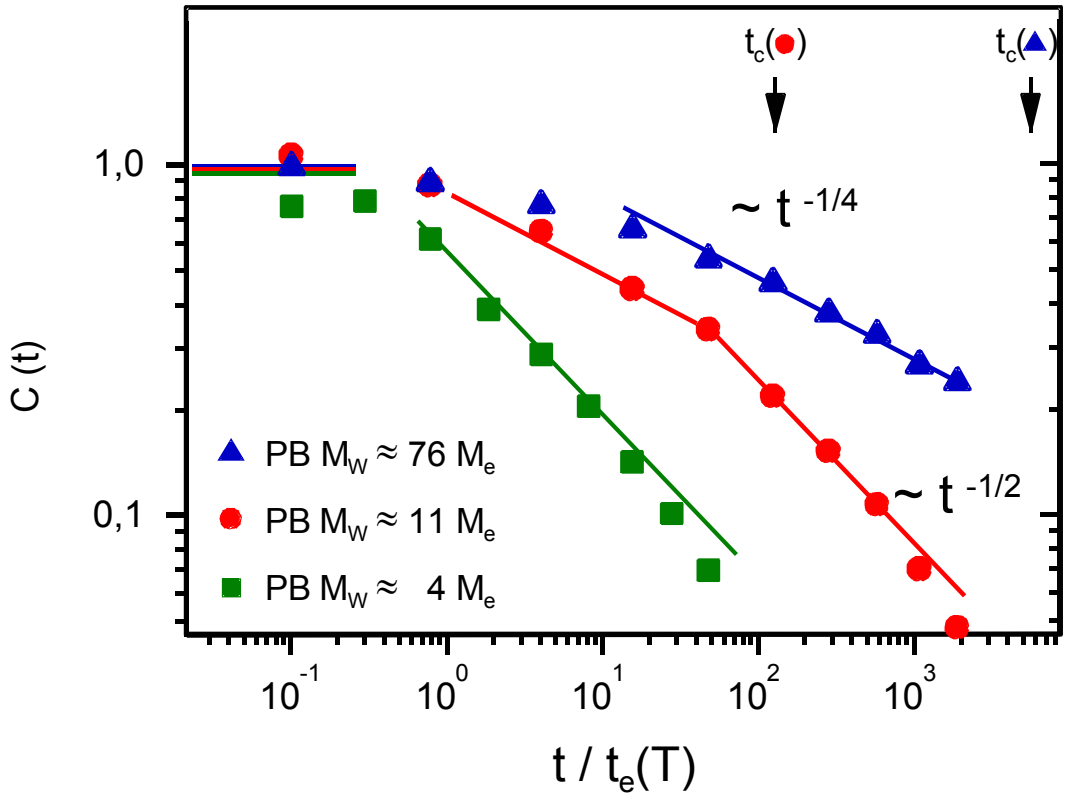
Dynamic order parameter S
via residual dipolar couplings



$\Rightarrow \quad S_{C=C} = 0.20 \pm 0.05$

Time Dependence of Local Order Parameter

double-quantum filtered experiments on 1,4 poly-butadien

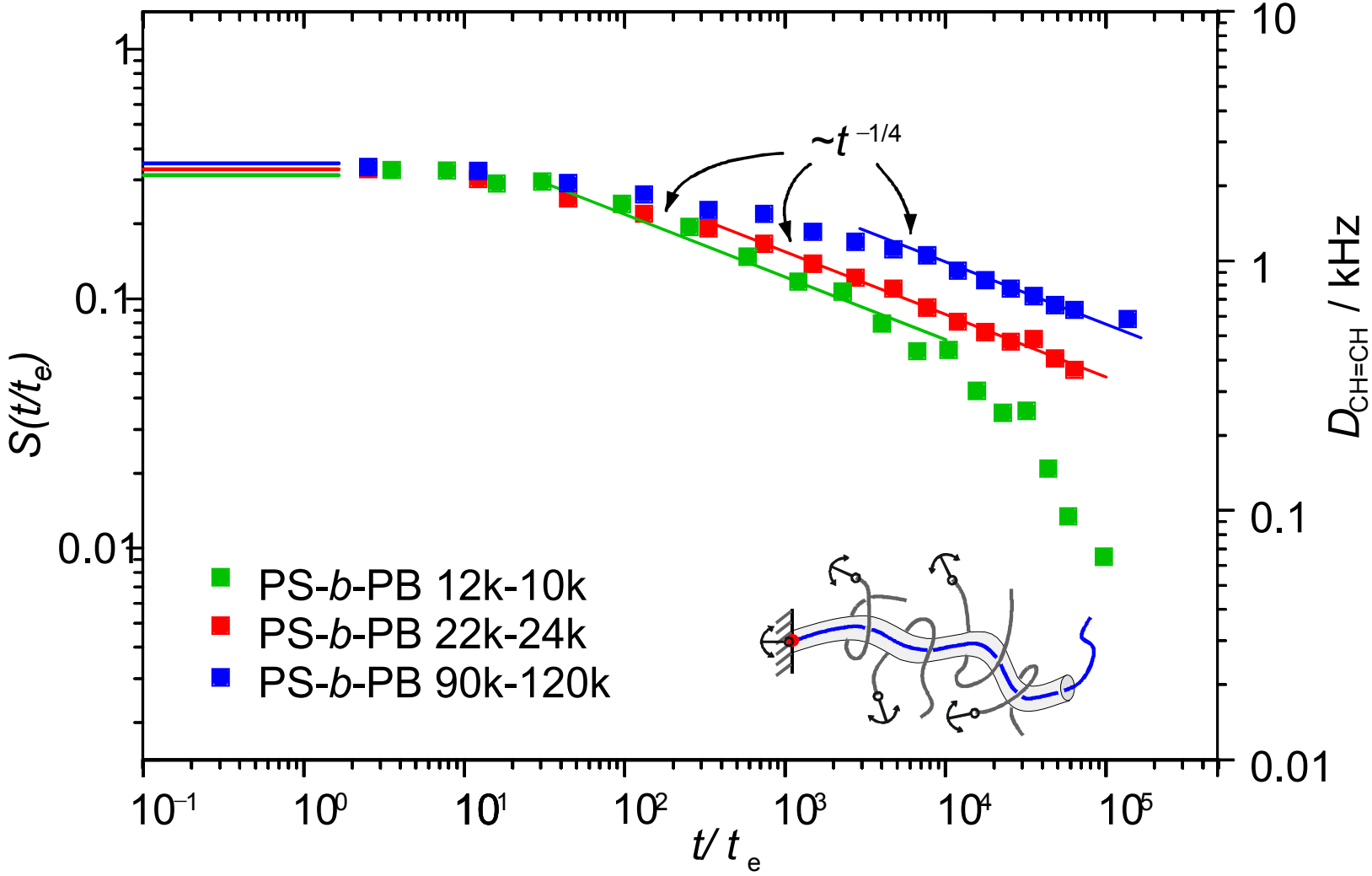


Reptation-model predicts two scaling laws:

$S \sim t^{-1/4}$ and $S \sim t^{-1/2}$

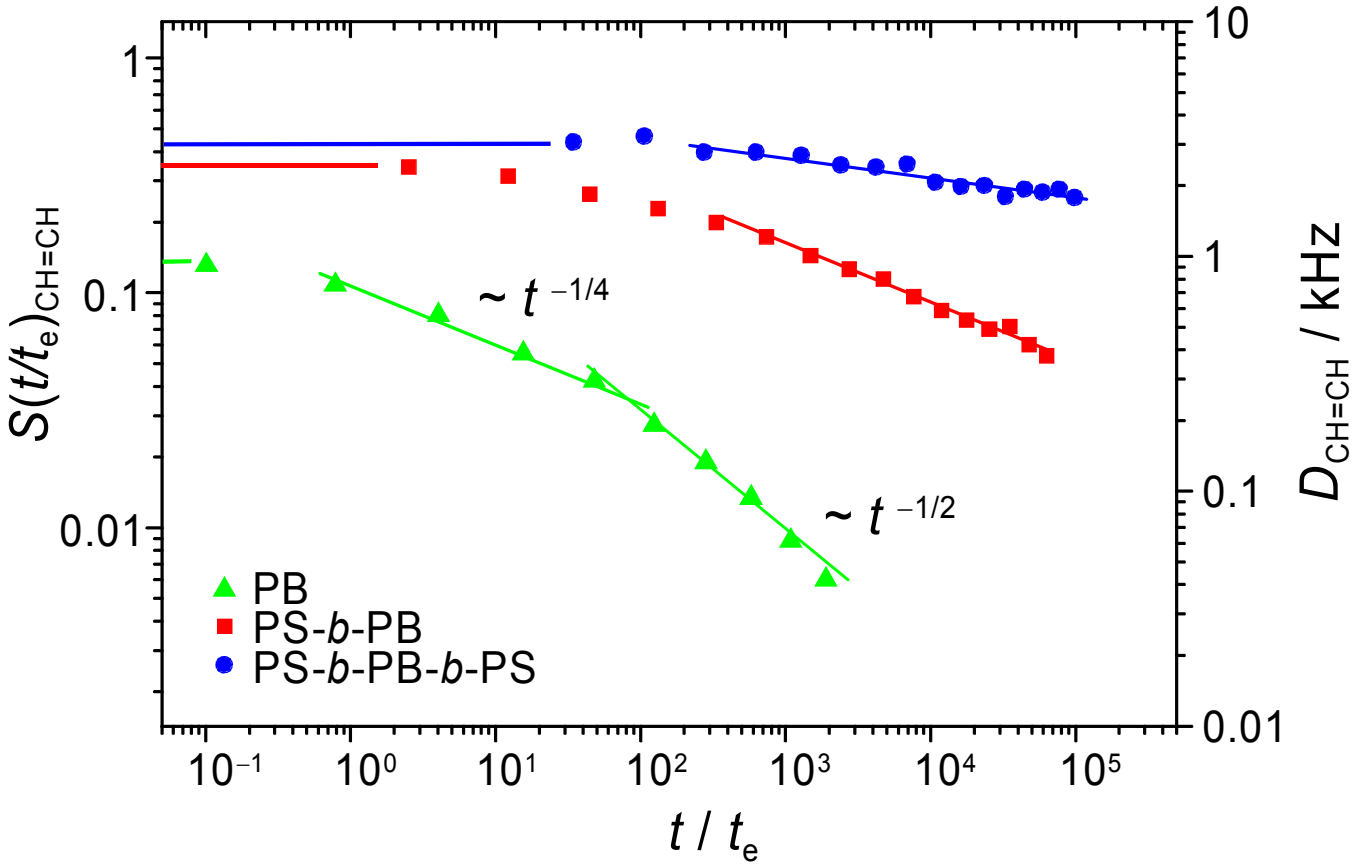
R. Graf et al., *Phys. Rev. Lett.* **80**, 5738 (1998).

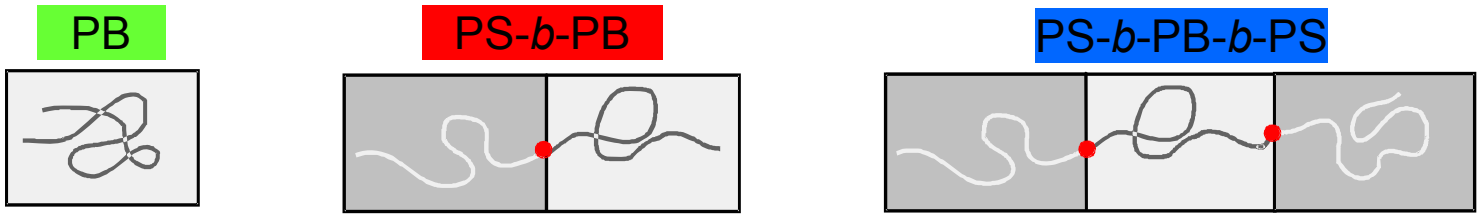
Molecular Weight Dependent Dynamics of PB Melts in PS-PB



Tethering a PB chain end to a rigid PS block stabilizes the $t^{-1/4}$-regime

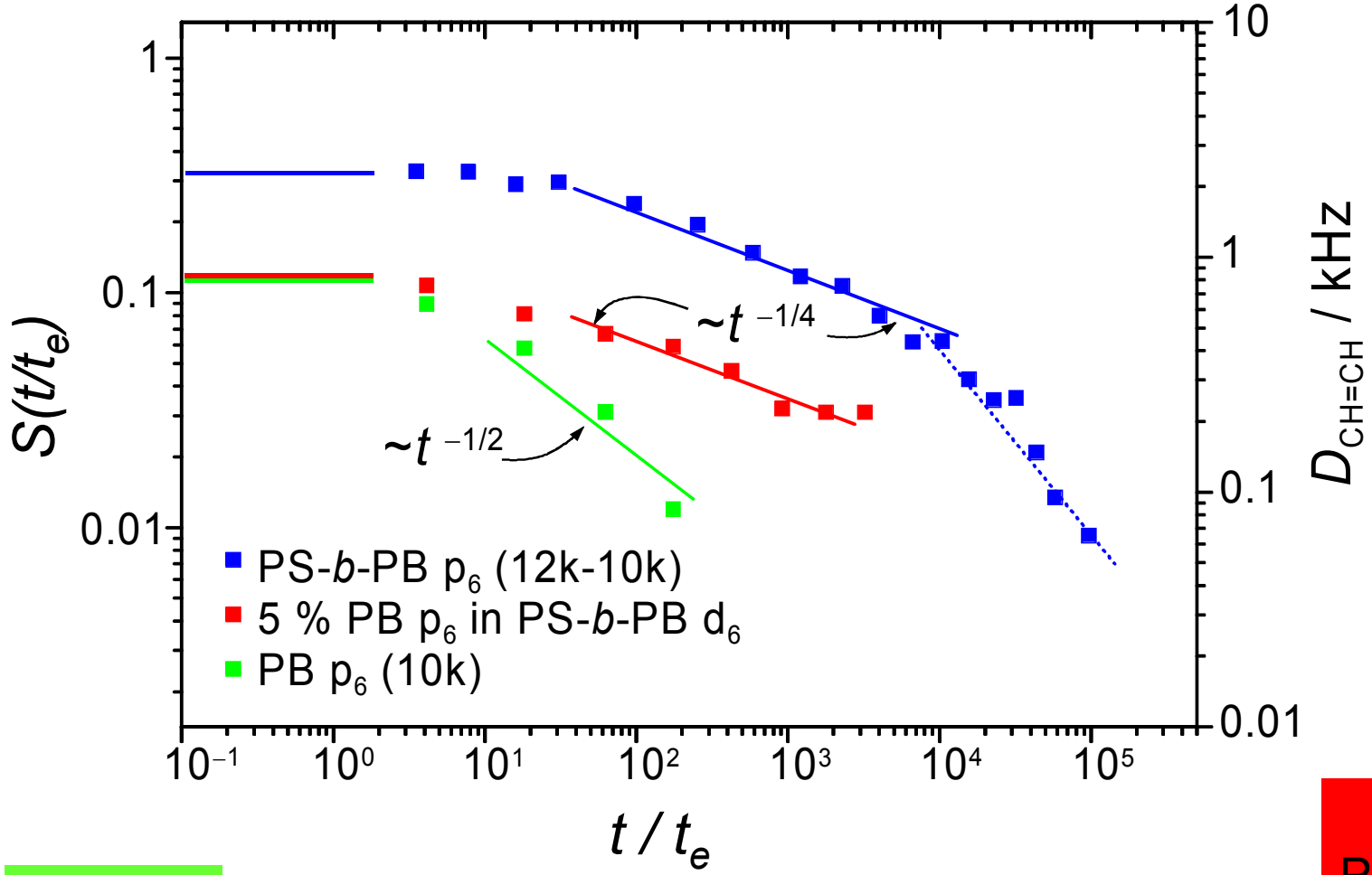
Influence of Rigid Confinements on Polymer Dynamics

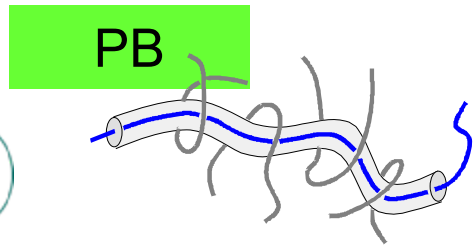


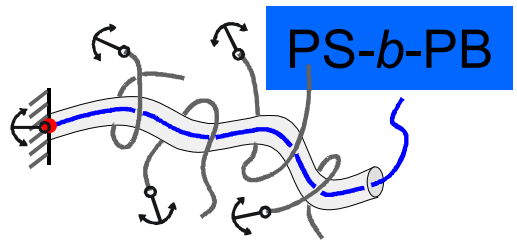


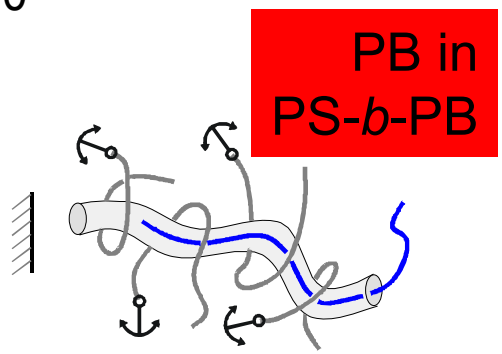
T. Dollase et al., *Macromolecules* **34**, 298 (2001).

Polymer Dynamics in heterogeneous Polymer Melts

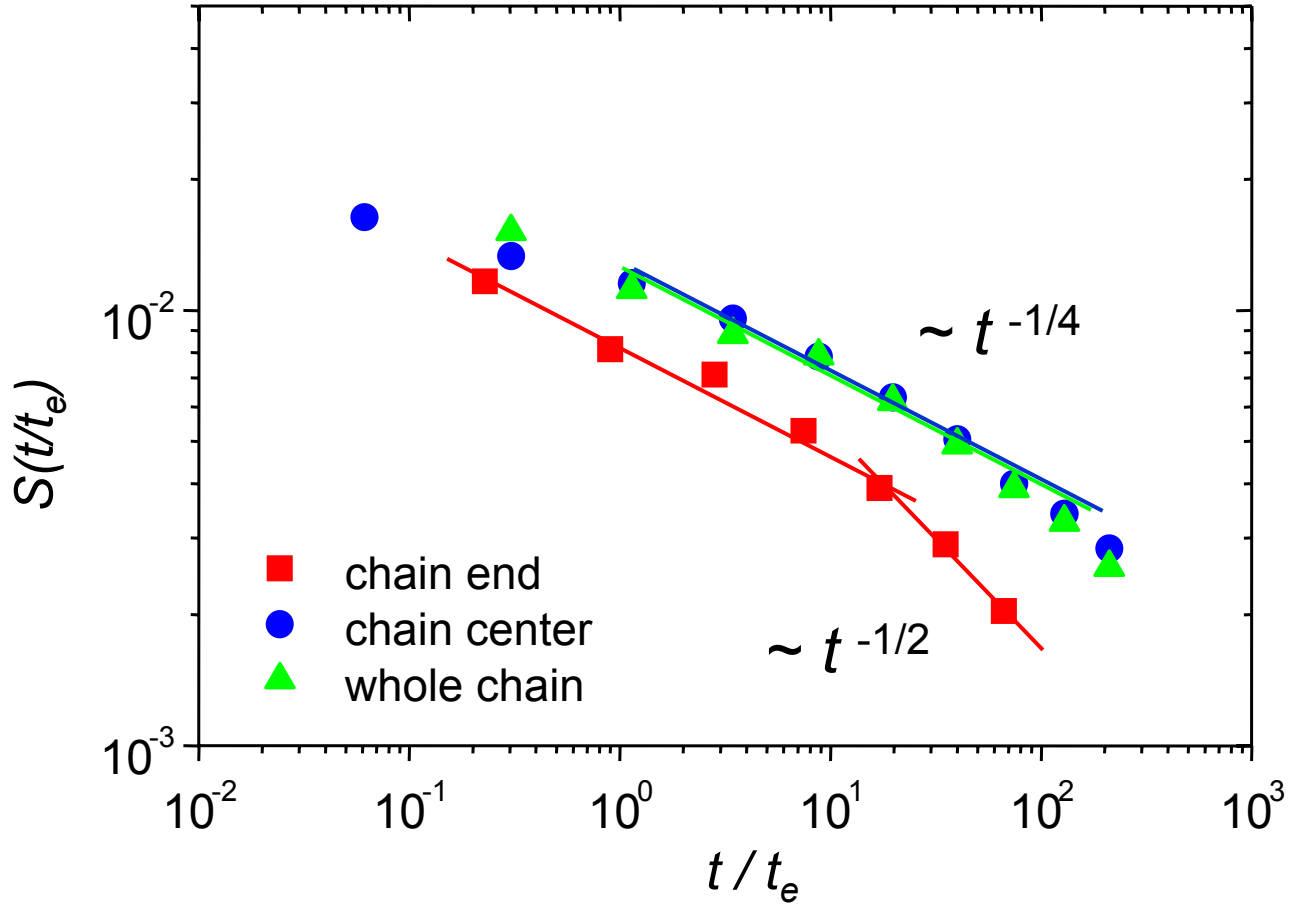




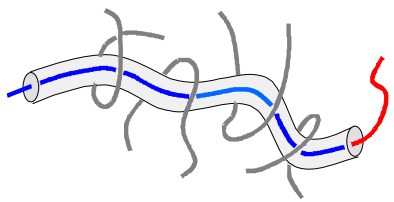




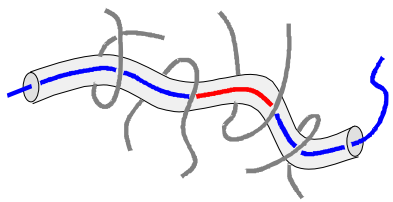
Variation of Dynamic Order Along the Polymer Chain



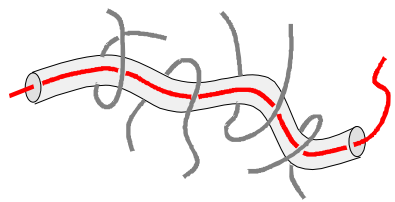
PB(d_6)-PB



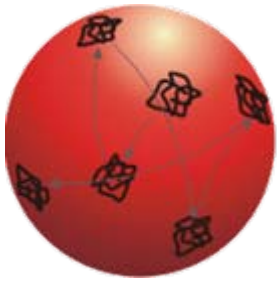
PB(d_6)-PB-PB(d_6)

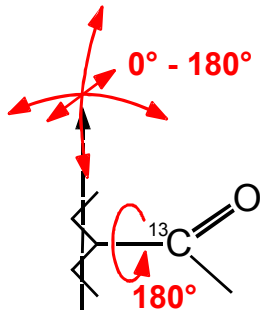


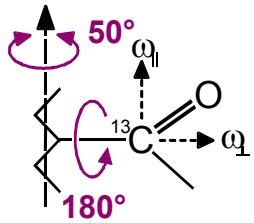
PB

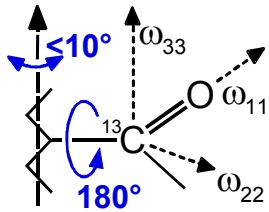


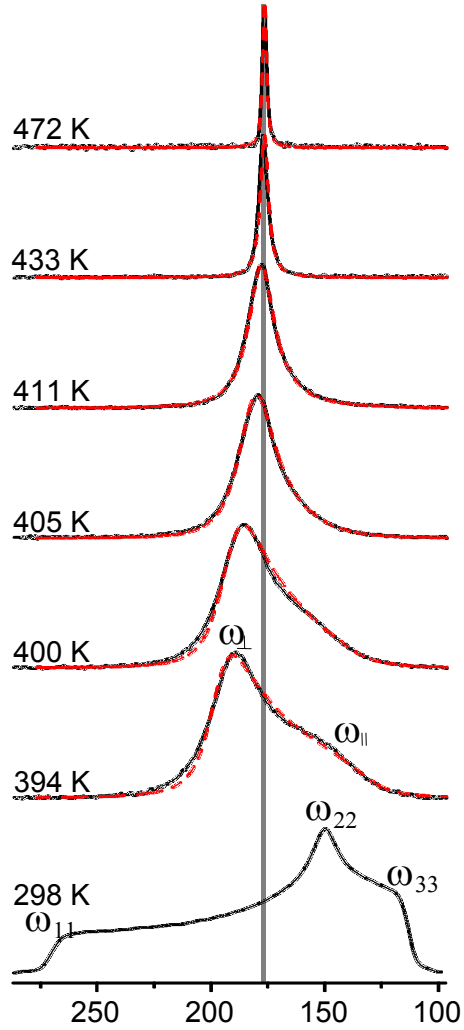
a-PEMA: Isotropisation of Chain Dynamics







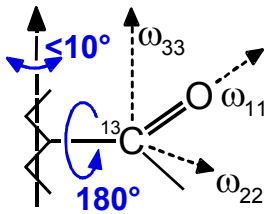


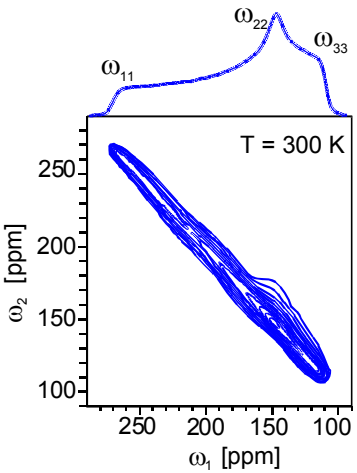


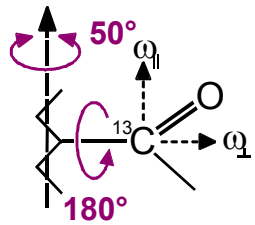
1D ^{13}C NMR: experiment, simulation

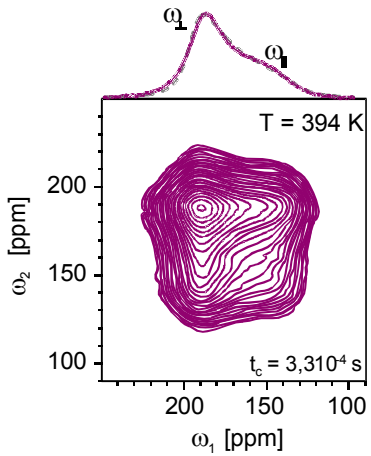
Glass T_g Melt Melt

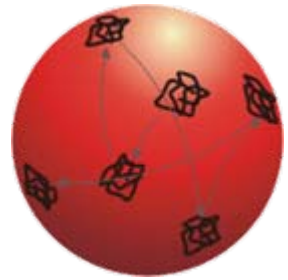
a-PEMA: Isotropisation of Chain Dynamics

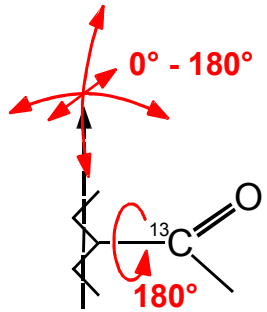


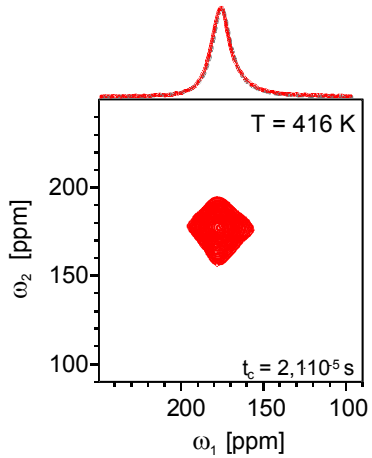




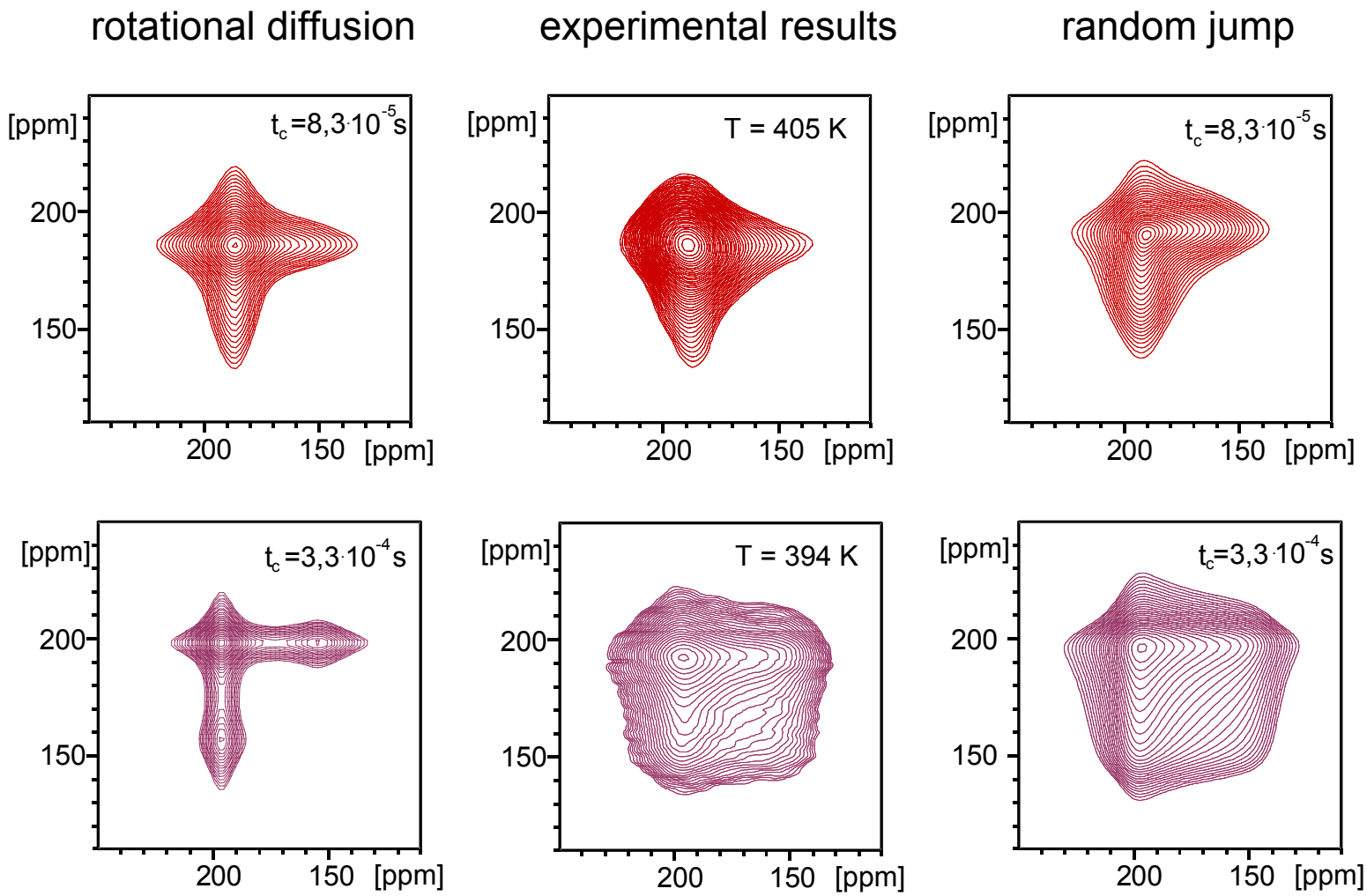






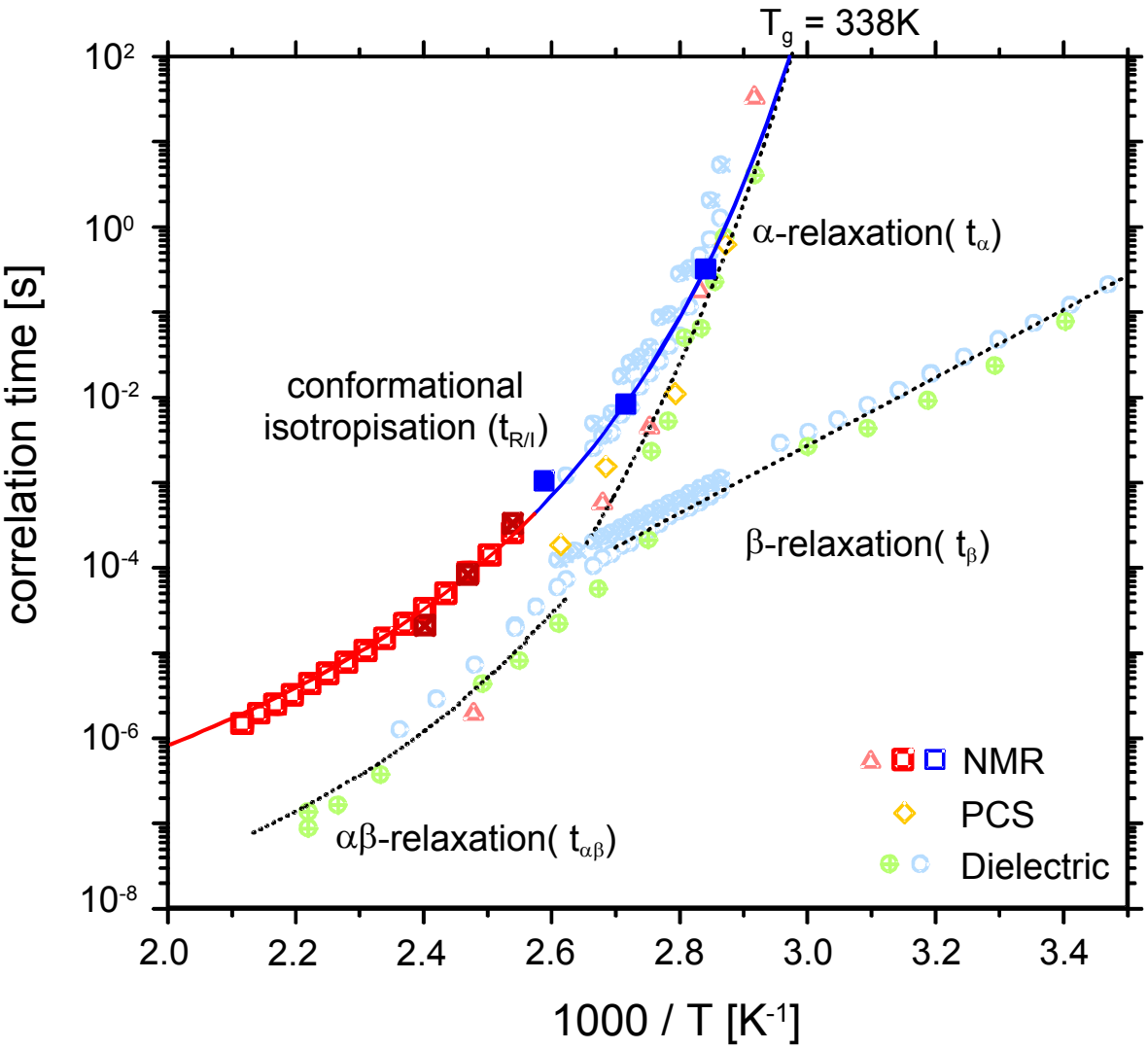


Dynamic Models: Random Jump vs. Rotational Diffusion



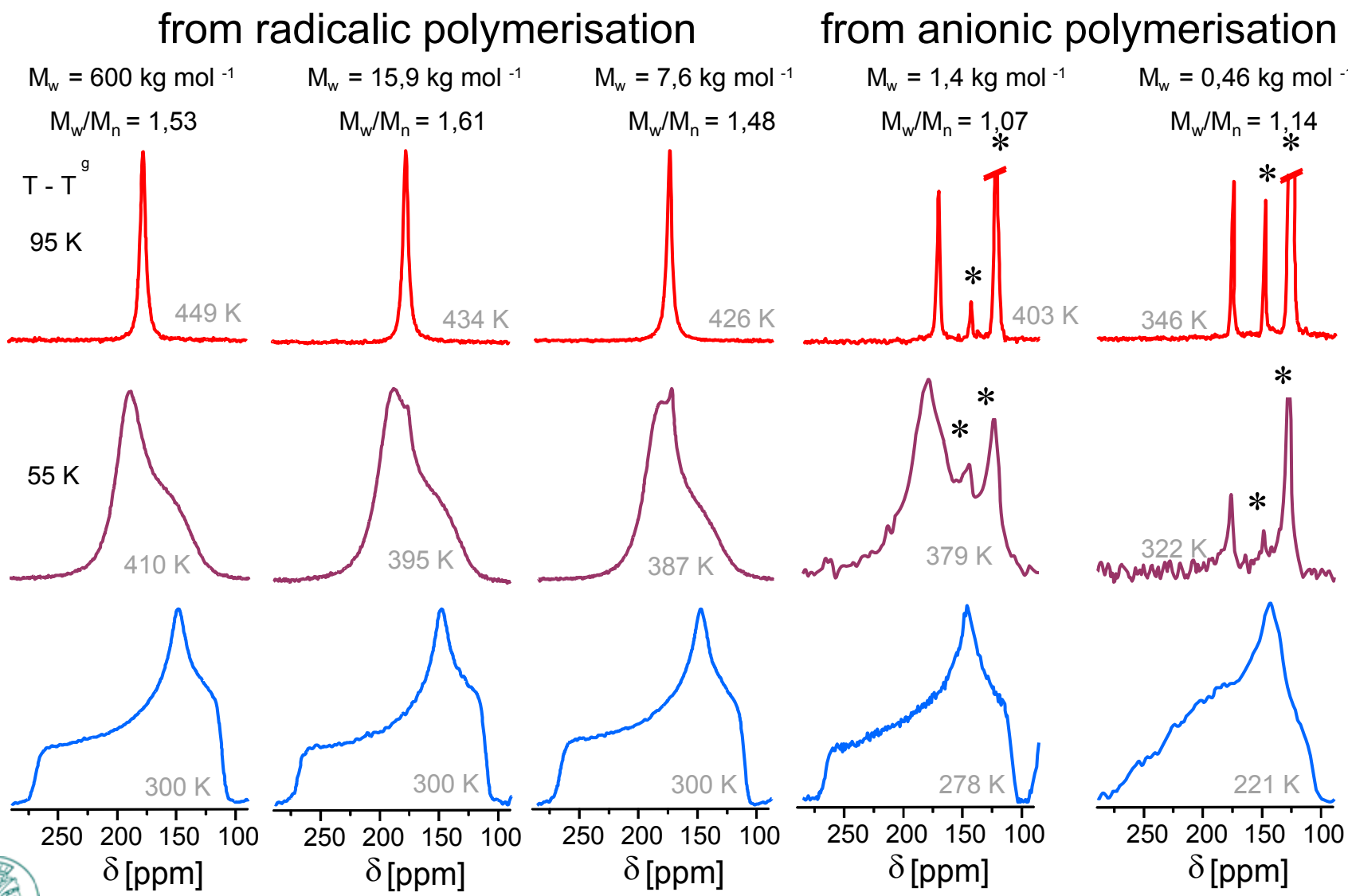
M. Wind et al., *Solid State NMR* **27**, 132-139 (2005).

Time Sclaes of Molecular Dynamics PEMA Melts



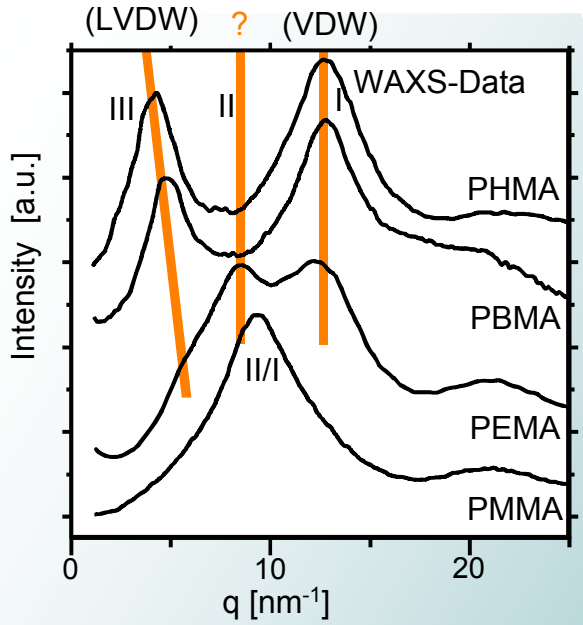
Arrhenius-diagram of dynamic processes in PEMA

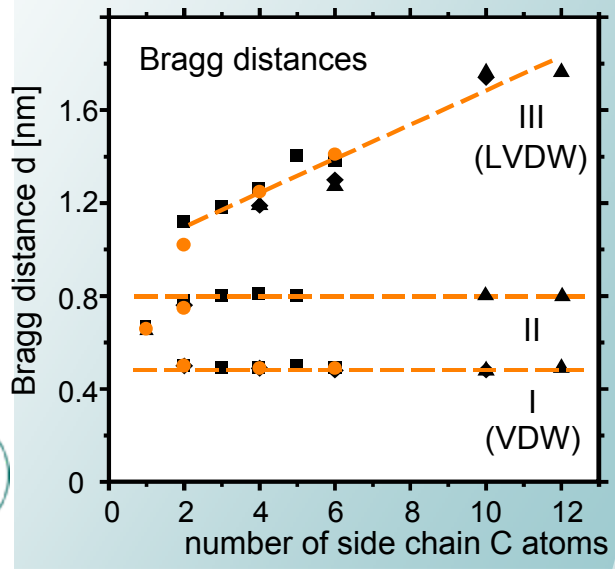
Length Scale of Isotropisation Process

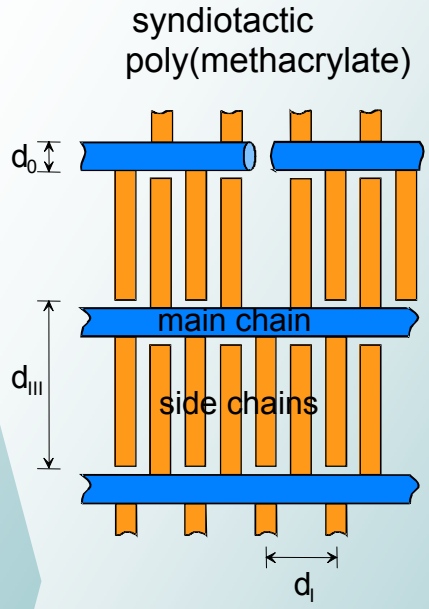


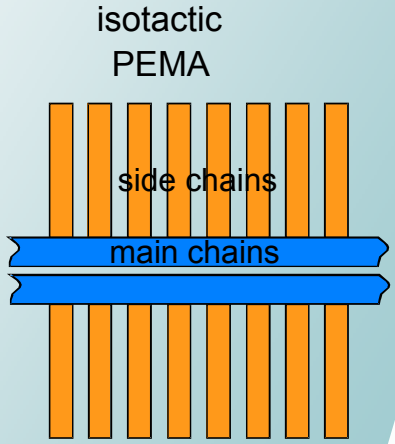
M. Wind et al., *Macromol. Chem. Phys.* **206**, 142 (2005).

Organisation in Poly(Methacrylats): WAXS



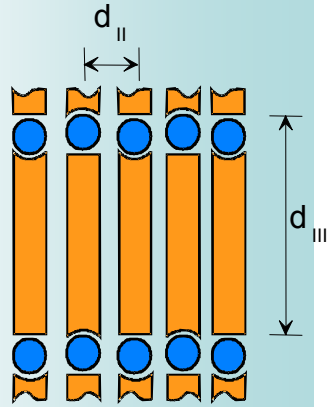






extrapolated lokal structur:

"Nano Layers"

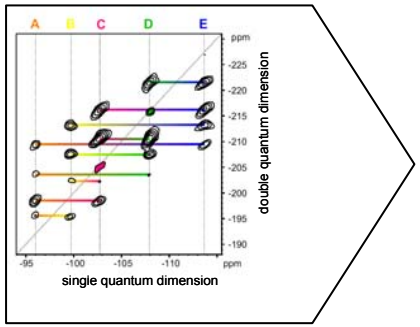


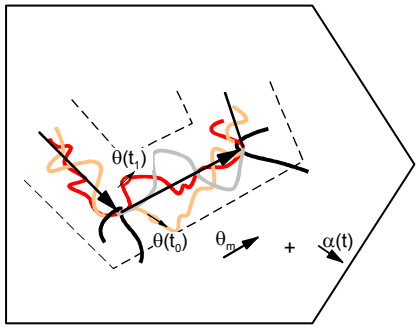
M. Wind et al., *J. Chem. Phys.* **122**, 14906 (2005).

Investigation of Structure and Dynamics in Polymeric Systems via Solid State NMR

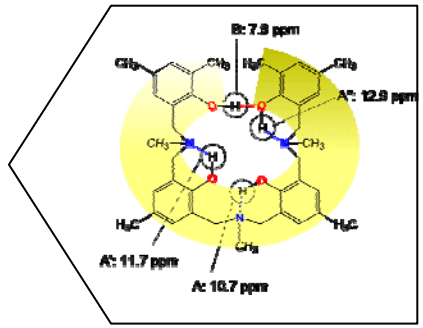
Introduction	• Interaction in solid state NMR
Solid State NMR	• MAS, recoupling, double-quantum NMR
Polymer Dynamics	• polyelectrolyte layers, polybutadiene, PEMA
Conclusions	• solid state NMR investigations

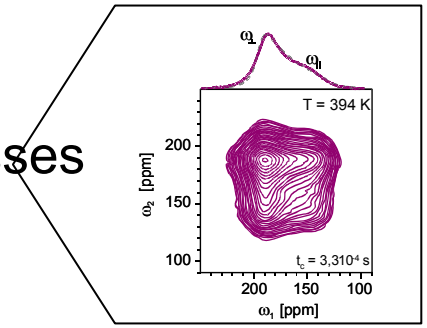
Pro and Contra of Solid State NMR Investigation





- elucidation local structures in partially disordered systems
- supra-molecular structures in hydrogen bonded systems
- local molecular dynamics
- correlation of dynamic processes and chemical structure





- needs expertise
- expensive
- ...

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Prof. K. Ishida, Dr. D. Sebastiani (polybenzoxazines)

Prof. L. Reven, Dr. M. McCormick (polyelectrolytes)

Prof. A. Heuer (polymer theory, …)

Dr. T. Dollase, Dr. M. Neidhöfer (polybutadiene)

Dr. M. Wind, Dr. W. Steffen, Prof. Do Yoon (PEMA)