How Unstructured are Amorphous Polymer Melts? Solid-State NMR Studies of Local Dynamic Order in Amorphous Polymer Melts

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Introduction • interactions in solid state NMR

Solid State NMR • resolution enhancement in solid state NMR, magic angle spinning, recoupling methods, double quantum NMR spectroscopy.

I. Schnell, K. Saalwächter, M. Feike, R. Graf

Polymer dynamics • Reptation model, polybutadiene, PEMA

Conclusions • How unstructured are amorphous polymers ?

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

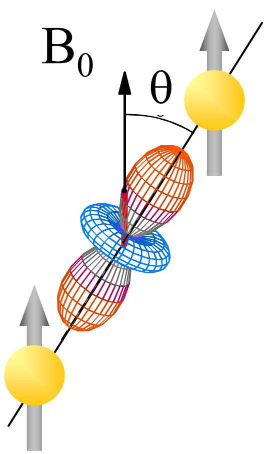
$$\mathbf{H_Q, H_D, H_{CS}, H_J}$$

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

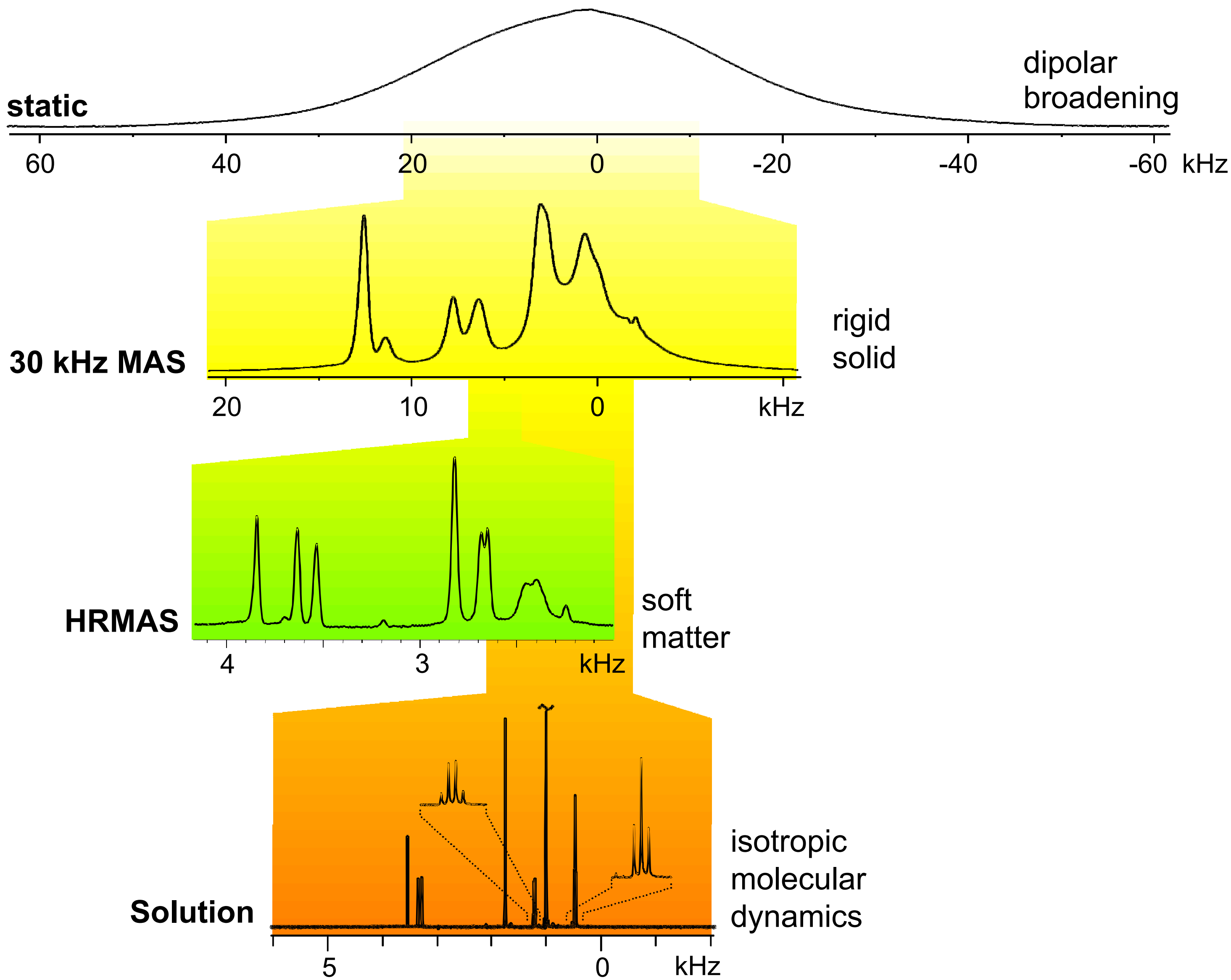
$\mathbf{H_Q}$: quadrupol

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

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

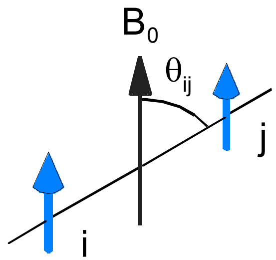
Distance ***Orientation***

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



Spectral Resolution Enhancement in Solid State NMR

dipol-dipol coupling:



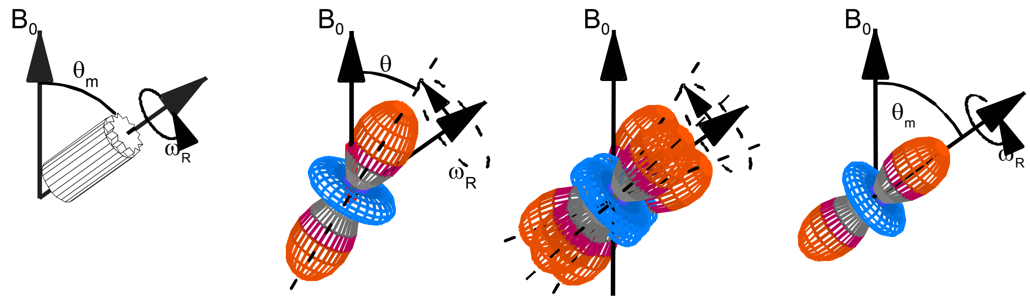
$$\hat{H} = \hat{R}_{2,0} \cdot \hat{T}_{2,0}$$

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:

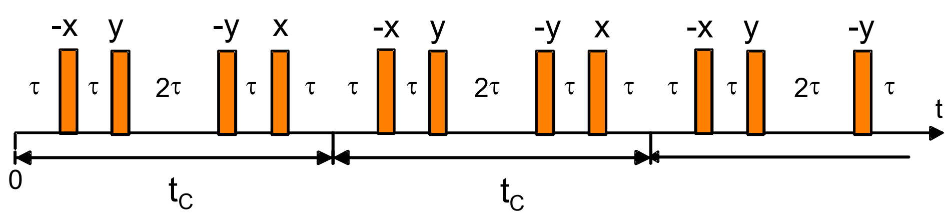
$$\overline{\hat{R}}_{2,0} \rightarrow 0$$

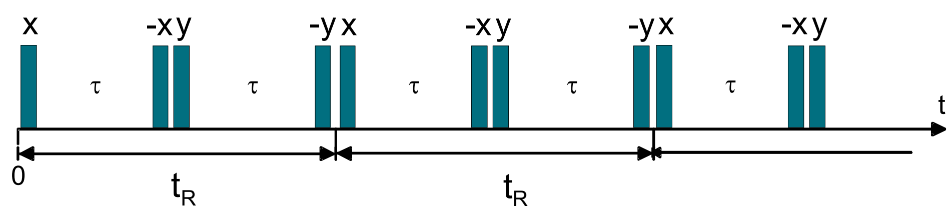


RF irradiation:

$\overline{\hat{T}}_{2,0}$ → 0 (CRAMPS)

$\overline{\hat{T}}_{2,0}$ → $H_{D,eff.}$ (Recoupling)





Double Quantum NMR Spectroscopy under MAS

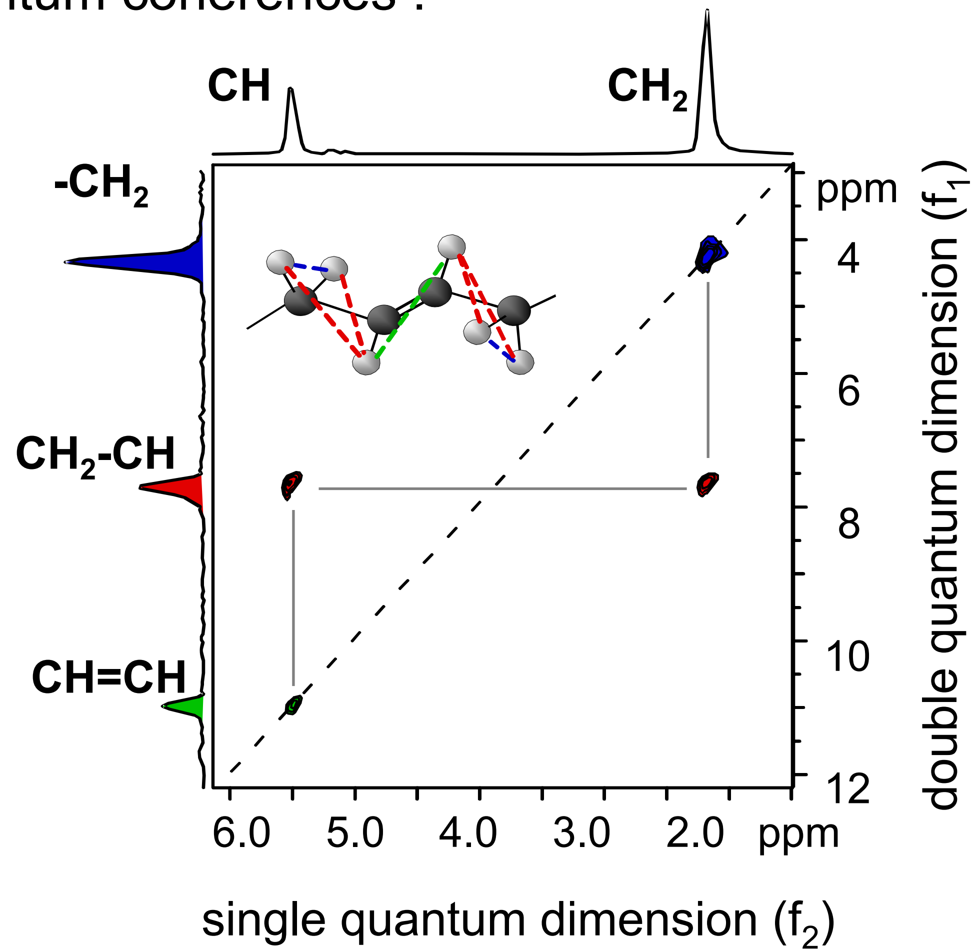
preparation | evolution t_1 | reconversion | detection t_2

properties of double quantum coherences :

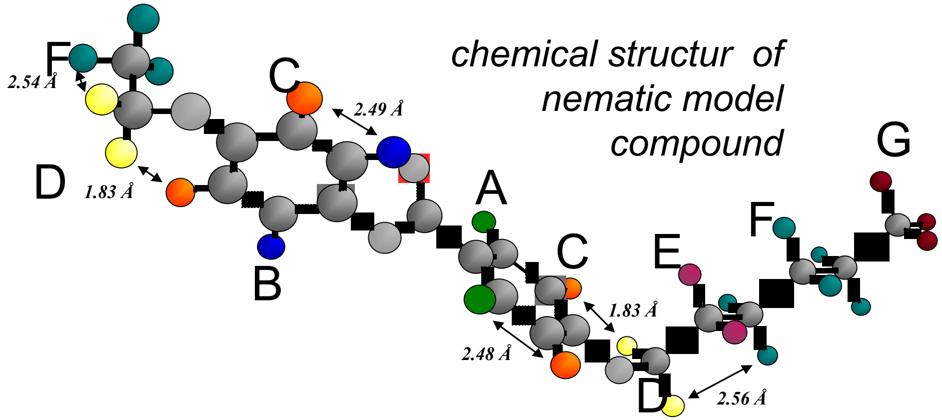
- $\omega_{DQ} = \sum_i \omega_{SQ,i}$

- $I_{DQ,ij} = f(D_{ij} \cdot t)$

- $\frac{dM}{dt} \approx 0$



Order Parameter in Liquid Crystalline Phases



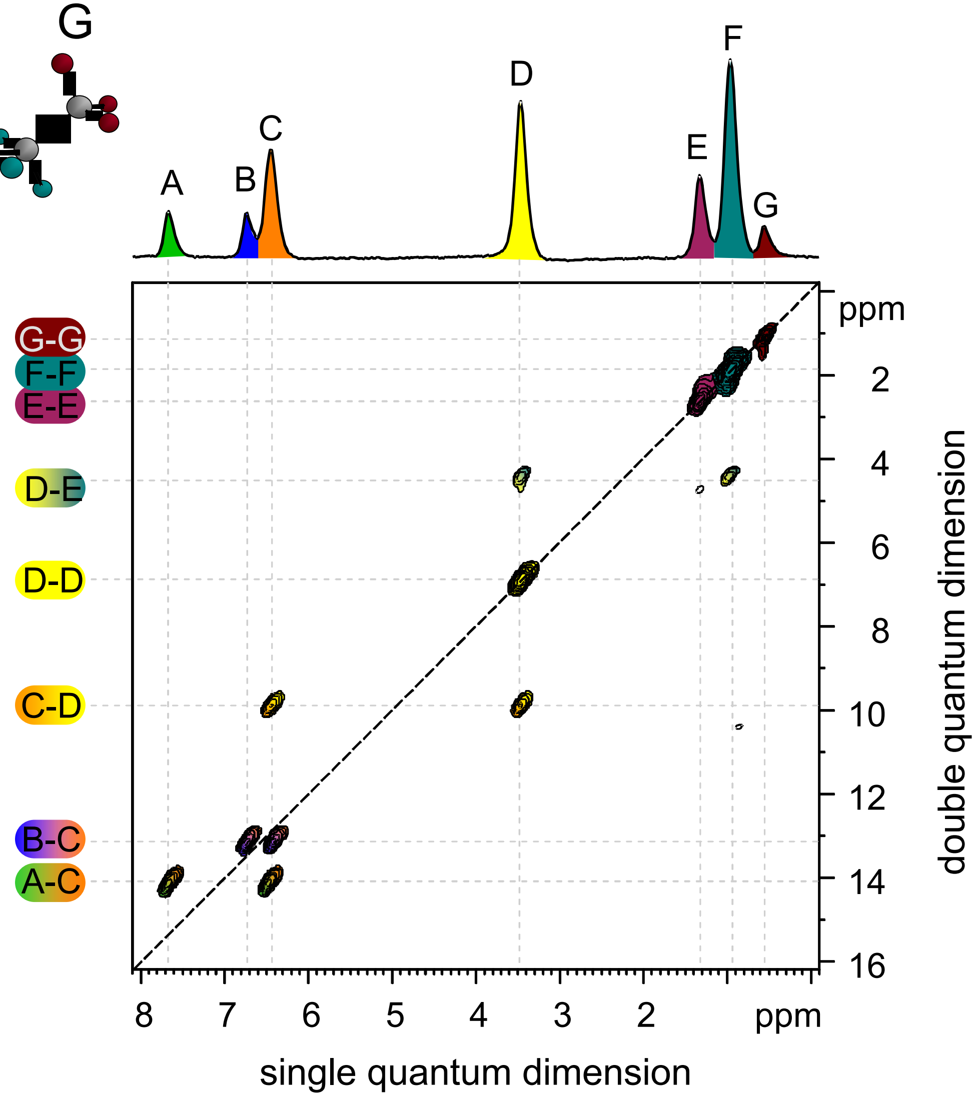
chemical structur of nematic model compound

order parameter S_{ij} :

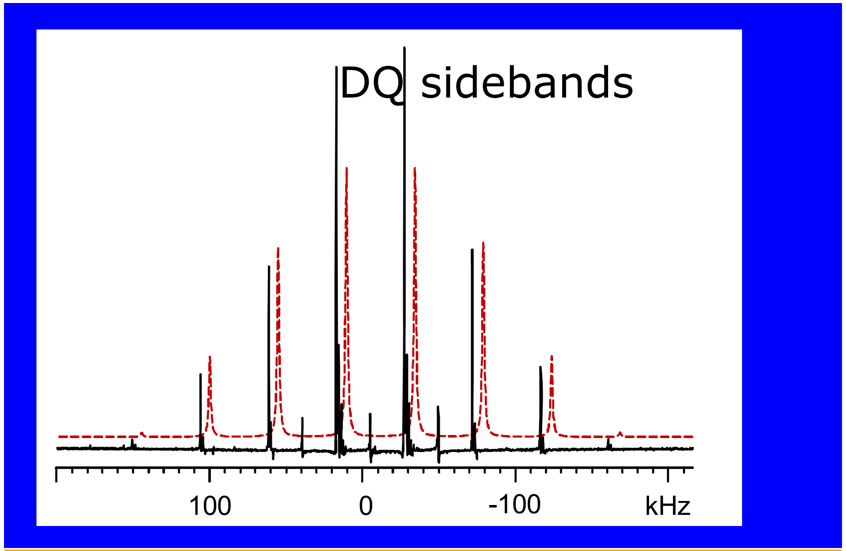
$$S_{ij} = \left\langle \tfrac{1}{2}(3\cos^2\theta - 1) \right\rangle$$

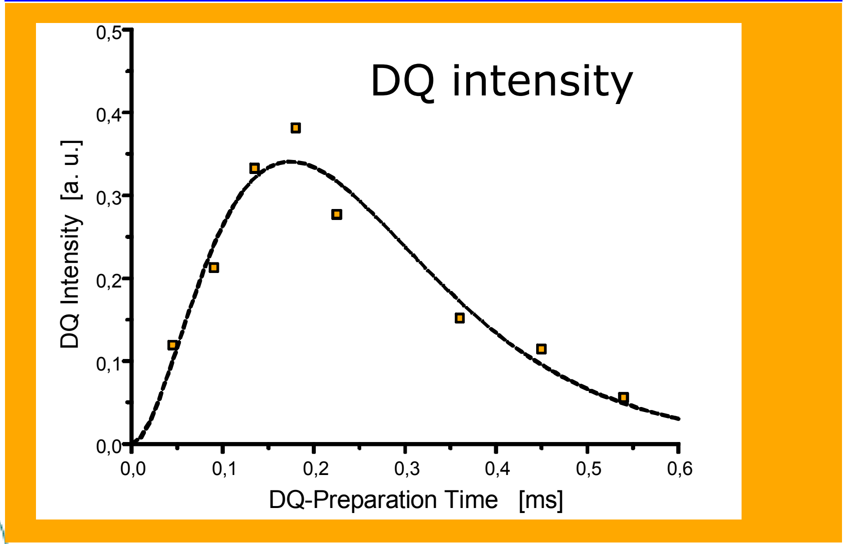
$$\Updownarrow$$

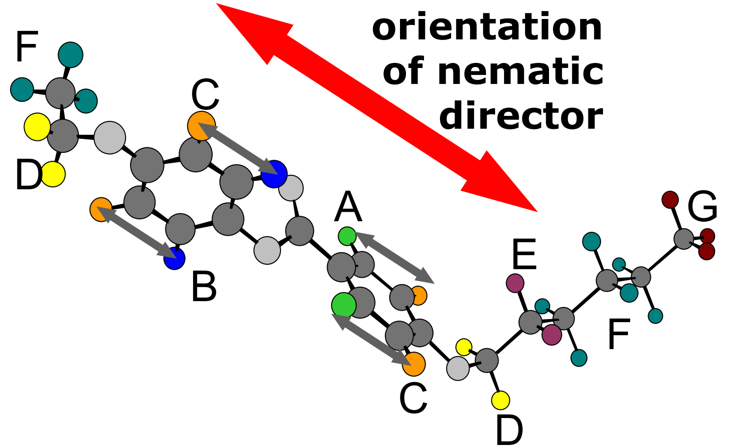
$$S_{ij} = \frac{\langle D_{ij,eff} \rangle}{D_{ij,stat}}$$

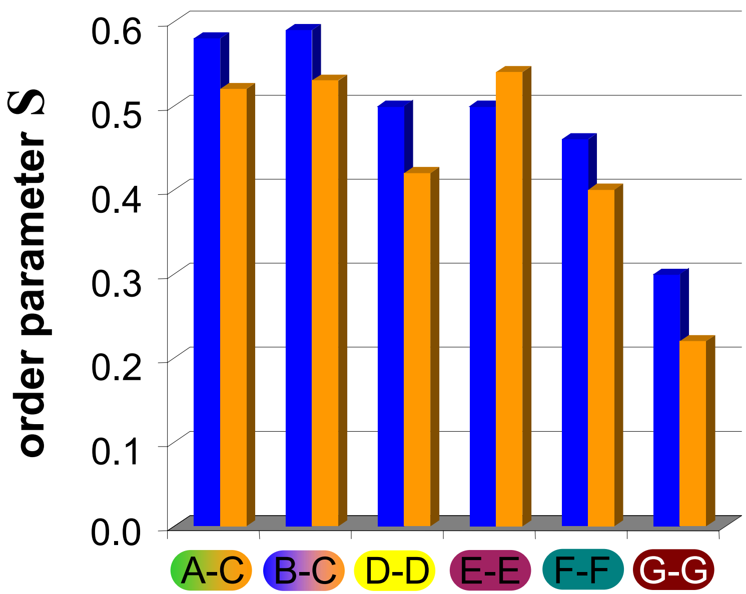


Order Parameters in Liquid Crystalline Systems





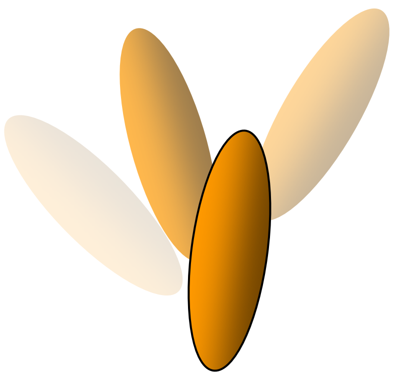




Local Order Parameter in Liquid Crystals and Polymers

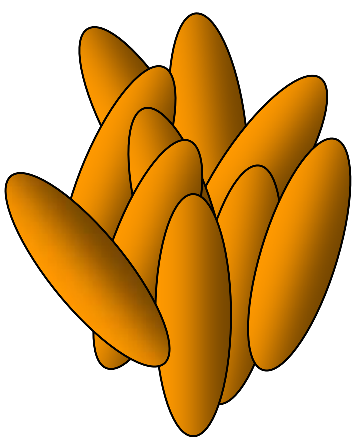
Nematic Systems

time



$$\langle S \rangle_t = \langle S \rangle_n$$

ensemble



Polymers

$$\langle S \rangle_t > 0, \langle S \rangle_N = 0,$$

$$\text{but } \langle S \rangle_{n \subseteq N} > 0$$

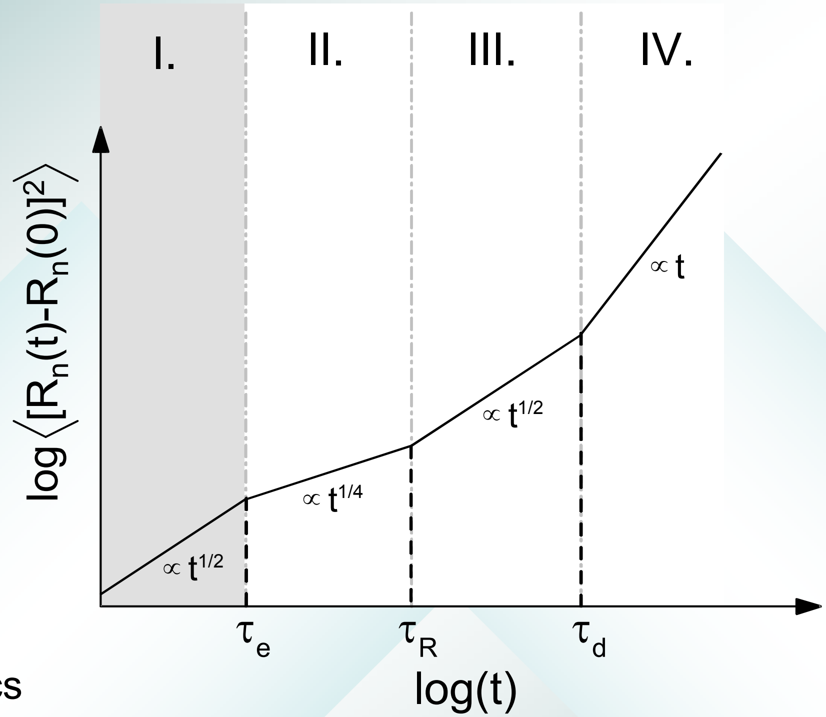
?

How Unstructured are Amorphous Polymer Melts? Solid-State NMR Studies of Local Dynamic Order in Amorphous Polymer Melts

Introduction	• Interaction in solid state NMR
Solid State NMR	• MAS, recoupling, double-quantum NMR
Polymer Dynamics	• Reptations-model, scaling laws in polymer dynamics, influence of rigid confinements, conformational stability in PEMA melts. *T. Dollase, M. Neidhöfer, M. Wind, A. Heuer, R. Graf*
Conclusions	• How unstructured are amorphous polymers ?

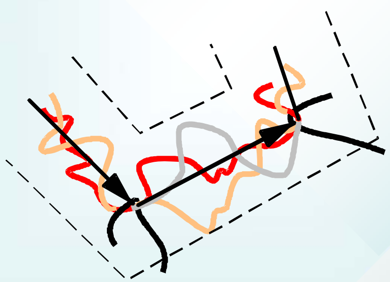
Length- and Time Scales in Polymer Dynamics

dynamic regimes of the Reptation model :



$t < \tau_e$

fast, local dynamics



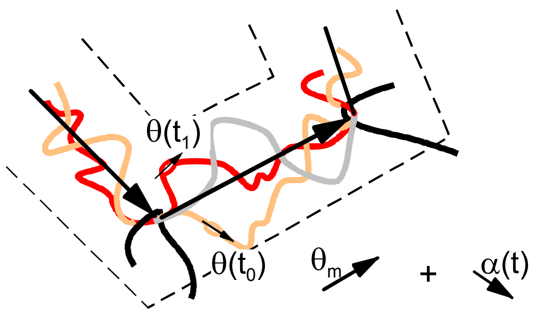
$t > \tau_e$

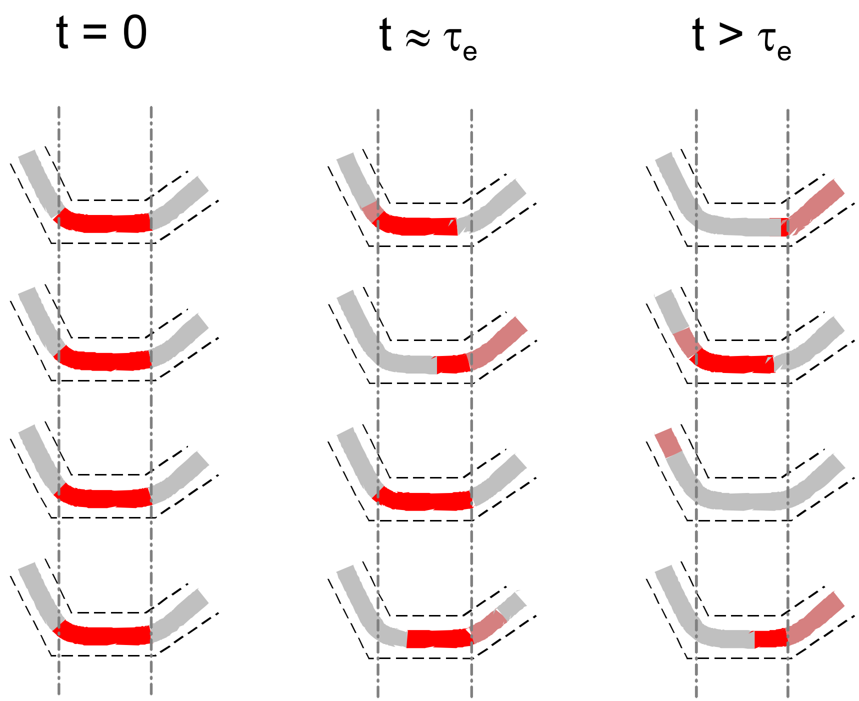
slow, collective Reptation dynamics

separation of time scales!

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

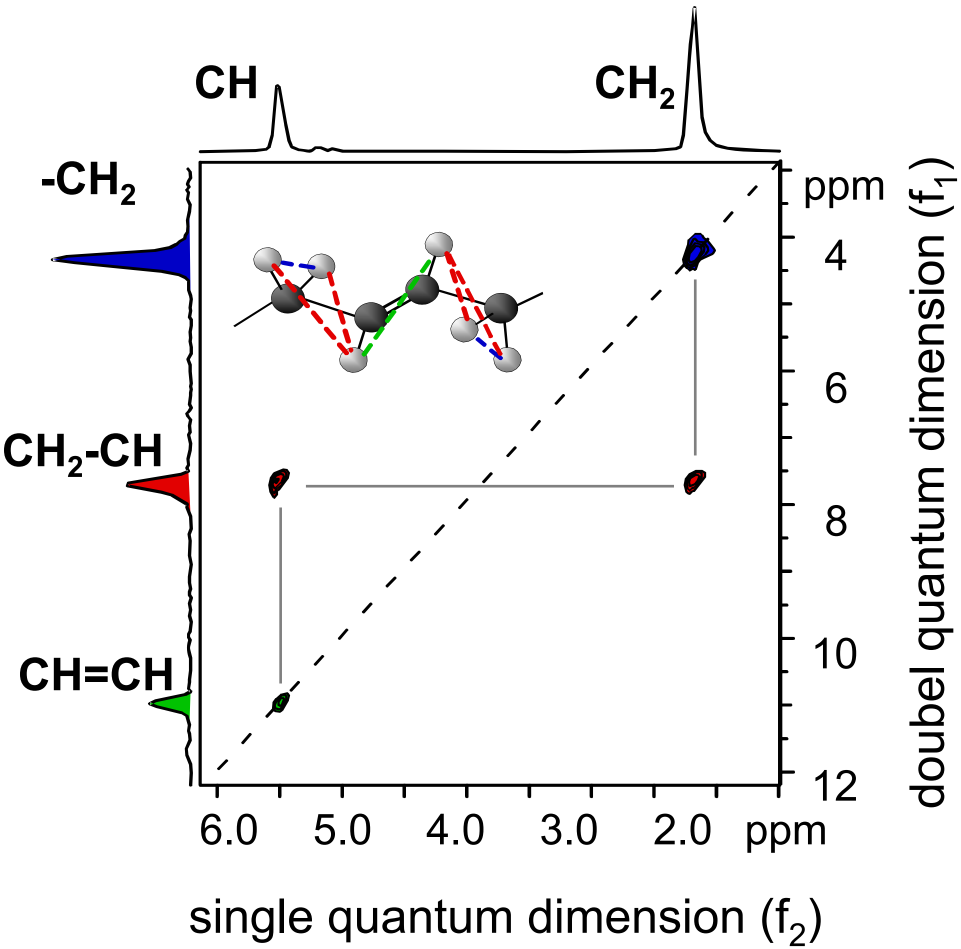
Polybutadien : $S \approx \frac{3}{5} \frac{M_{Kuhn}}{M_e} \approx 0.03$

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

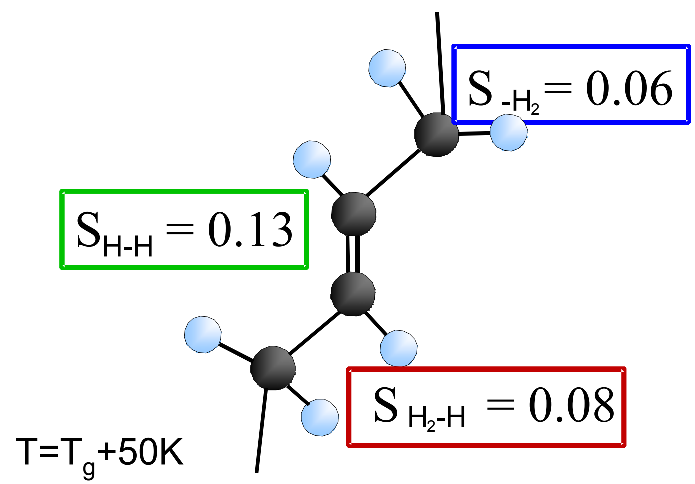
return-to-origin probability C (t)

Local Order Parameters in 1,4 Polybutadien Melts

^{1}H double quantum NMR spectrum



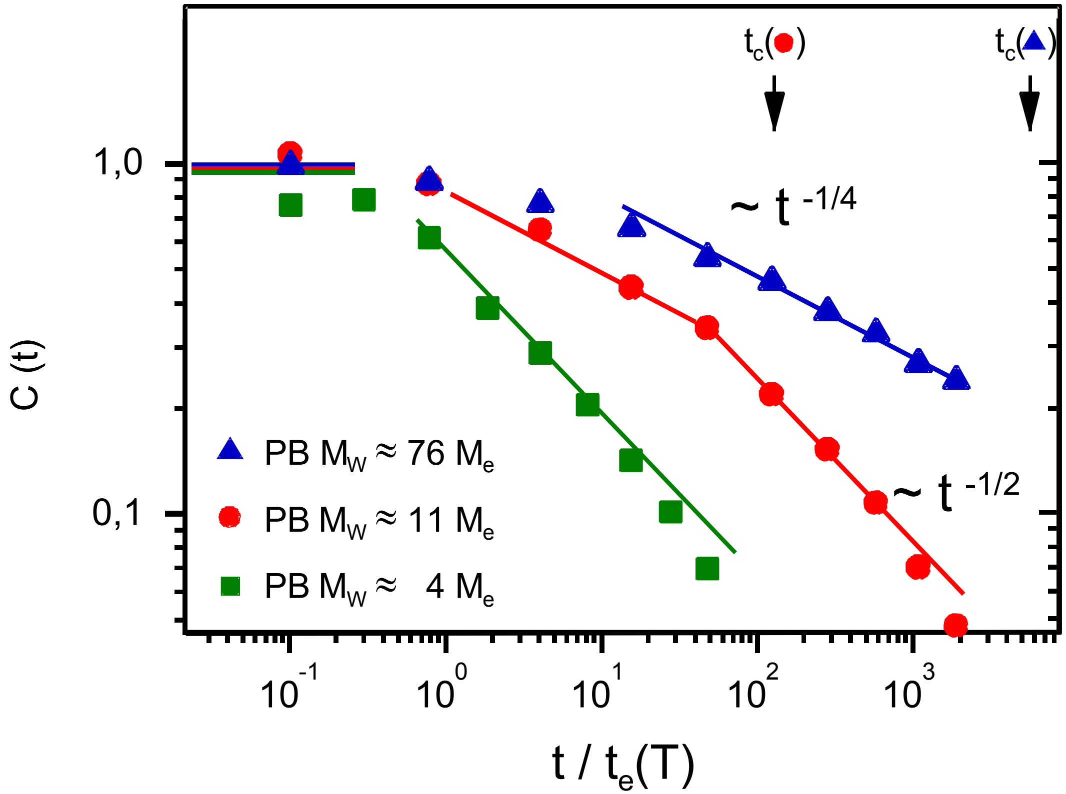
Dynamic order parameter **S**
via residual dipolar couplings



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

Time Dependence of Local Order Parameter

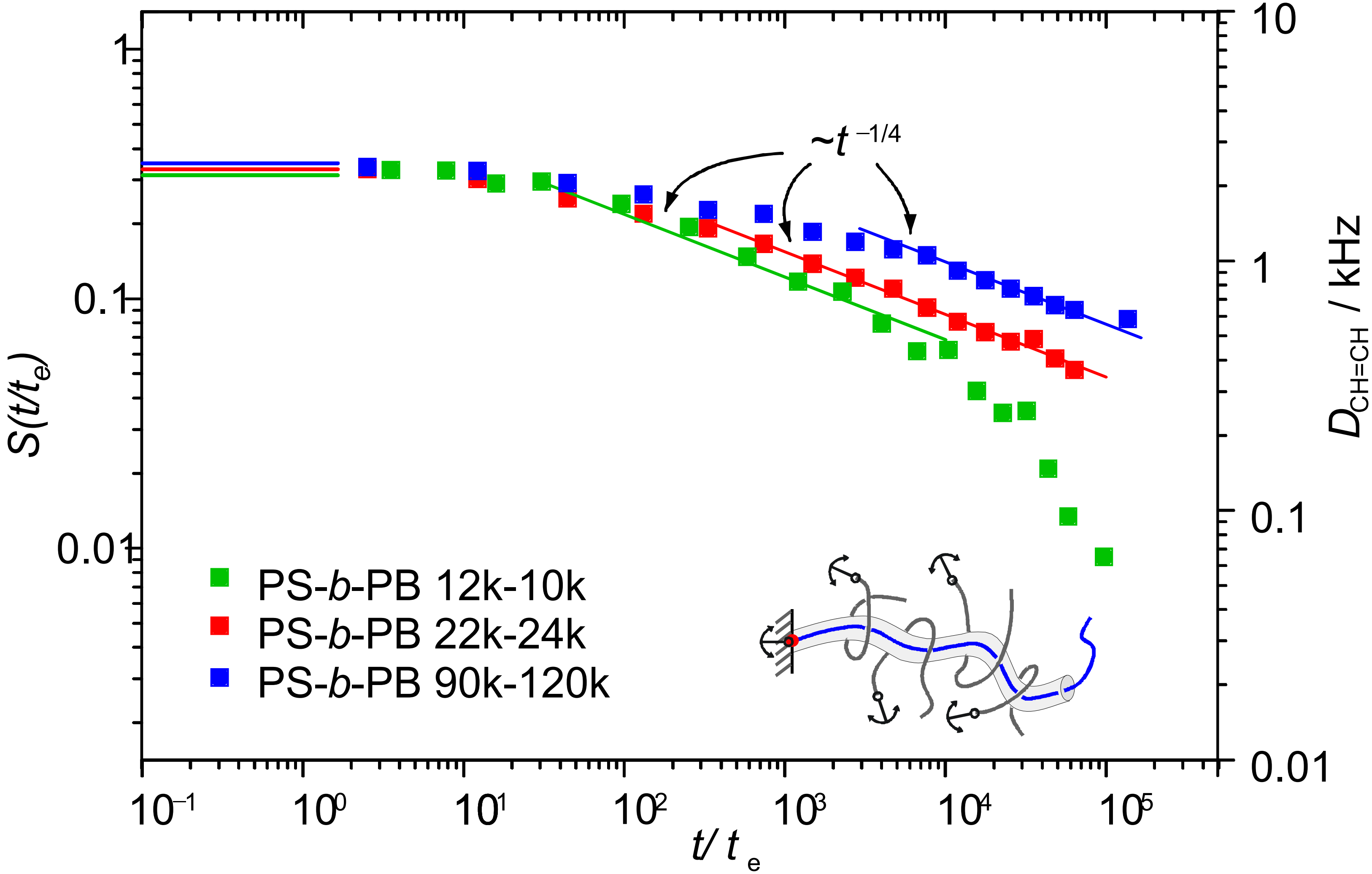
double-quantum filtered experiments on 1,4 poly-butadien



Reptation-model predicts two scaling laws:

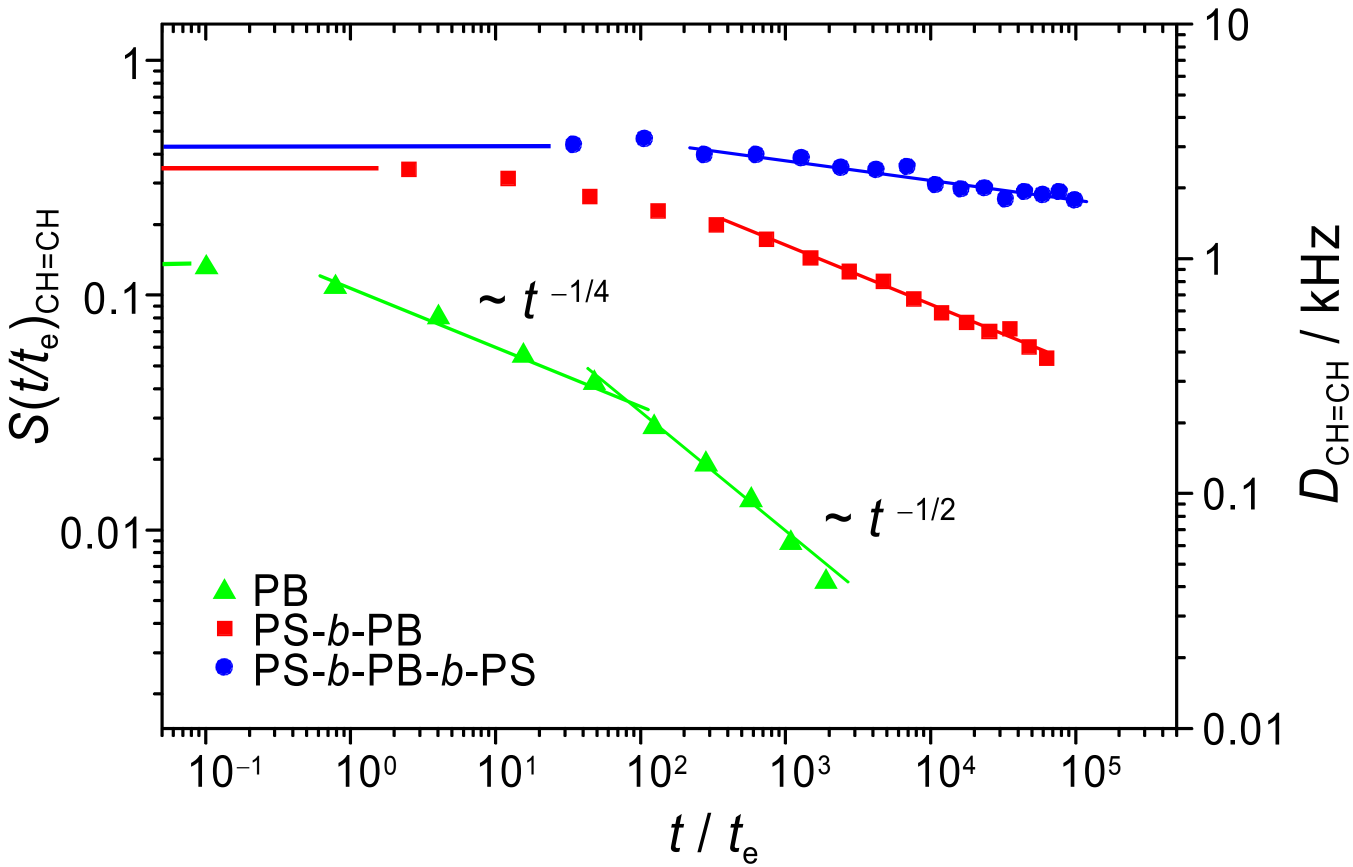
$S \sim t^{-1/4}$ and $S \sim t^{-1/2}$

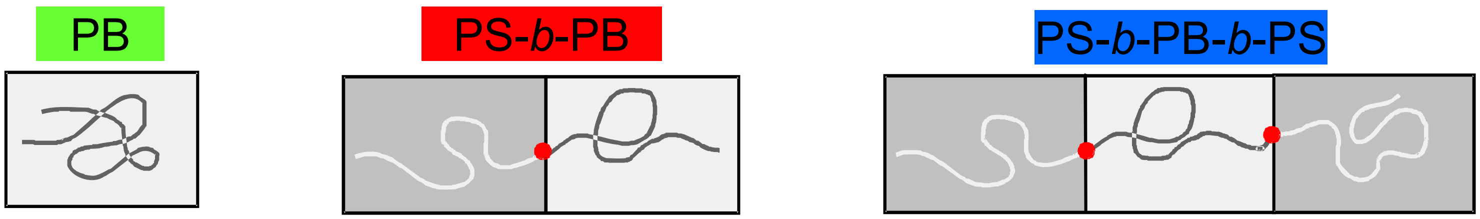
Molecular Weight Dependent Dynamics of PB Melts in PS-PB



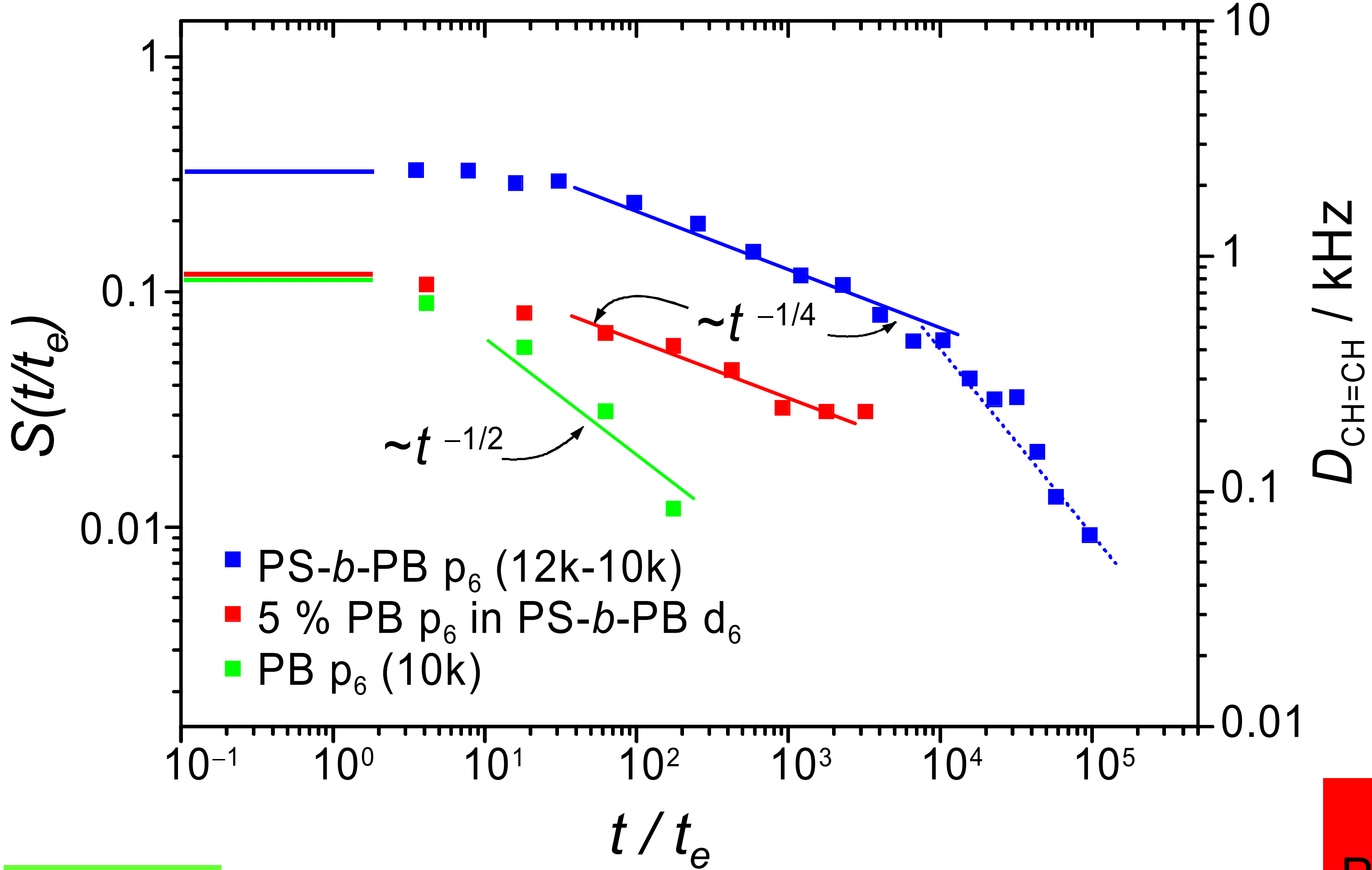
Tethering a PB chain end to a rigid PS block stabilizes the $t^{-1/4}$-regime

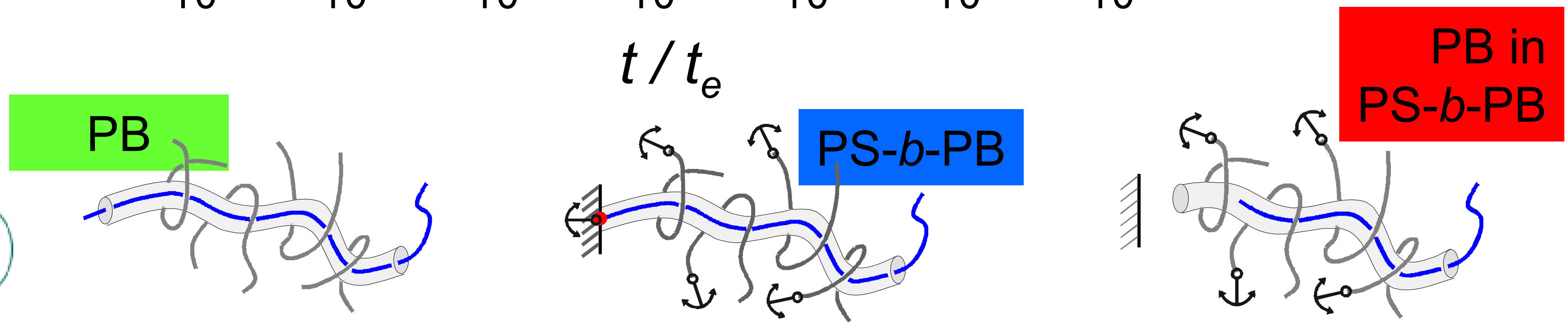
Influence of Rigid Confinements on Polymer Dynamics



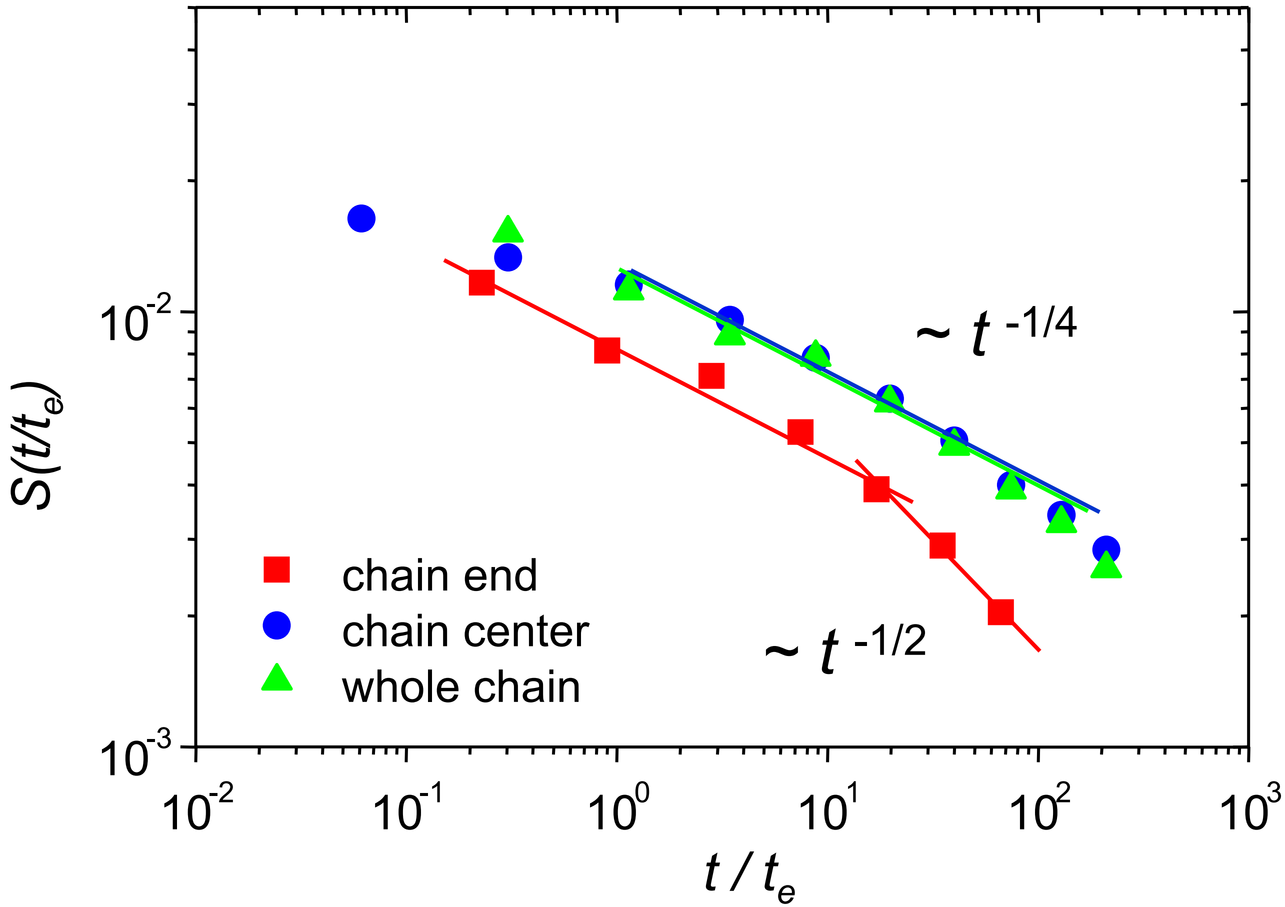


Polymer Dynamics in heterogeneous Polymer Melts

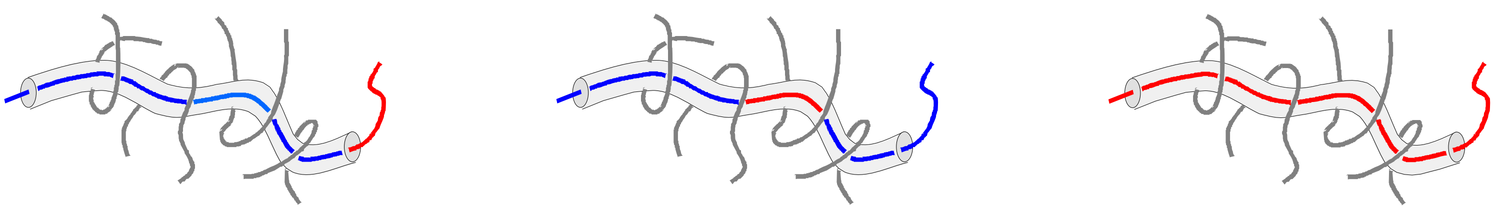




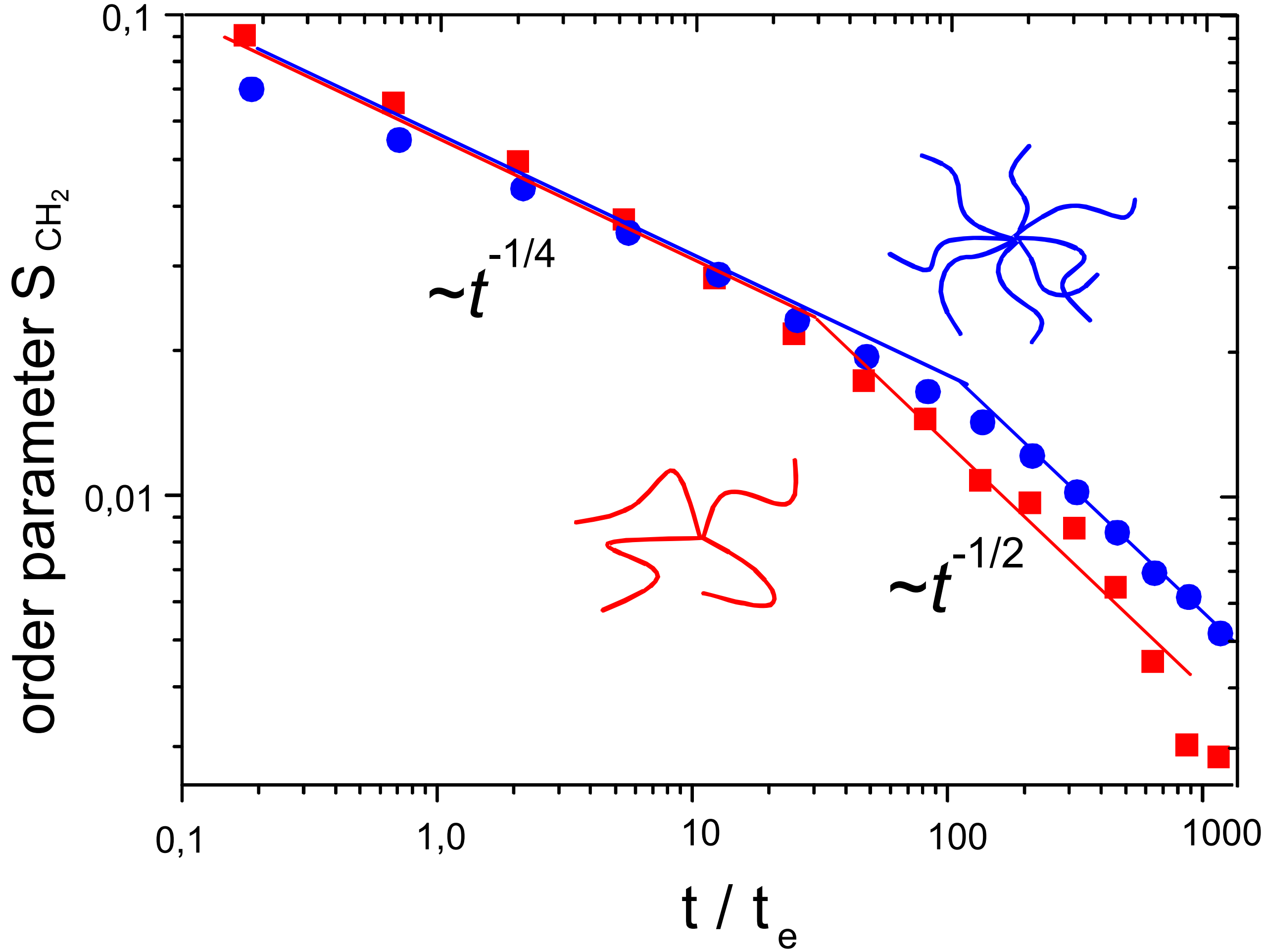
Variation of Dynamic Order Along the Polymer Chain



PB(d_6)-PB | PB(d_6)-PB-PB(d_6) | PB

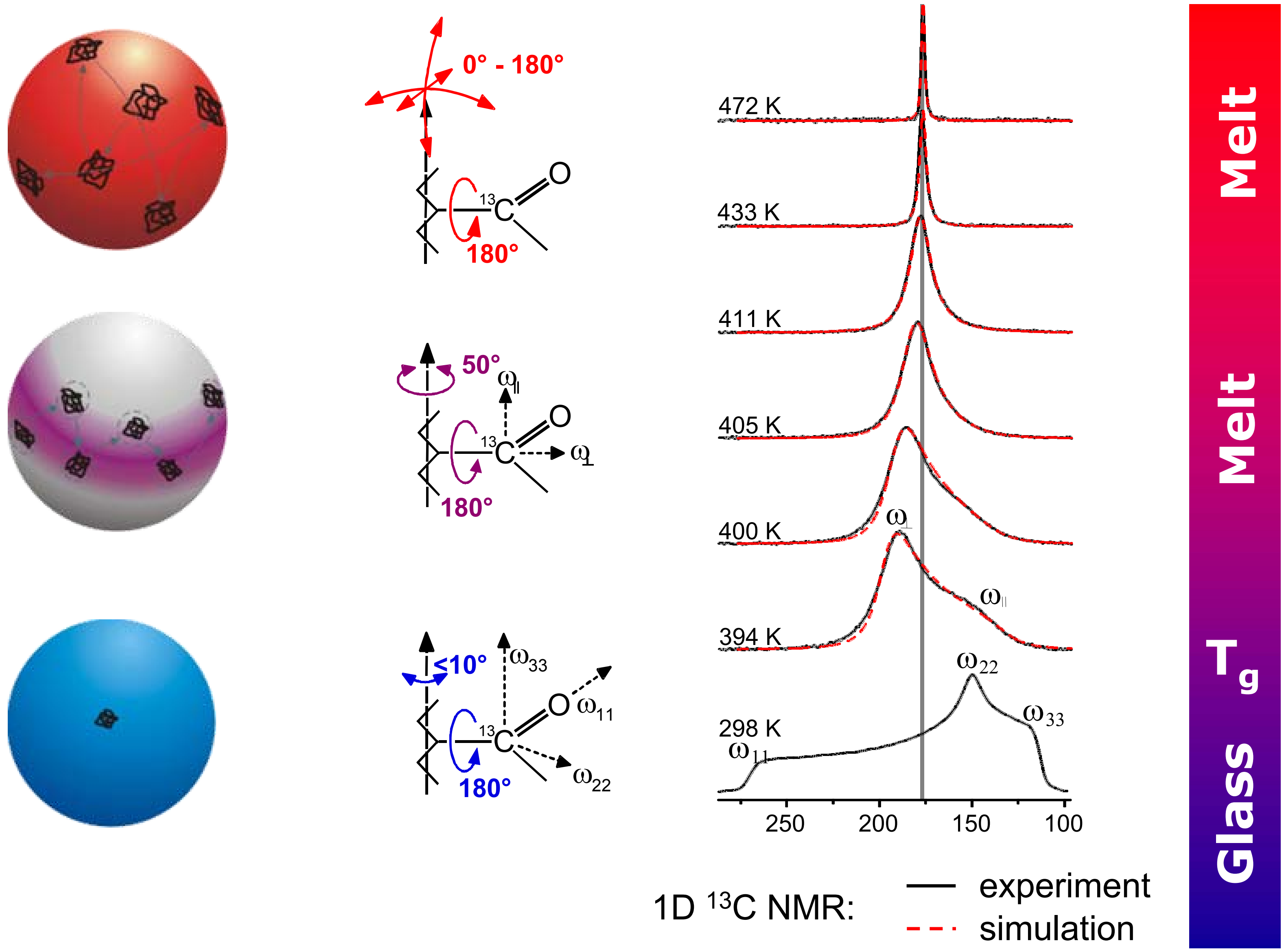


Local Order Parameters in Star Shaped Polymers



cooperation with Prof. Hadjichristidis / Athen.

a-PEMA: Isotropisation of Chain Dynamics



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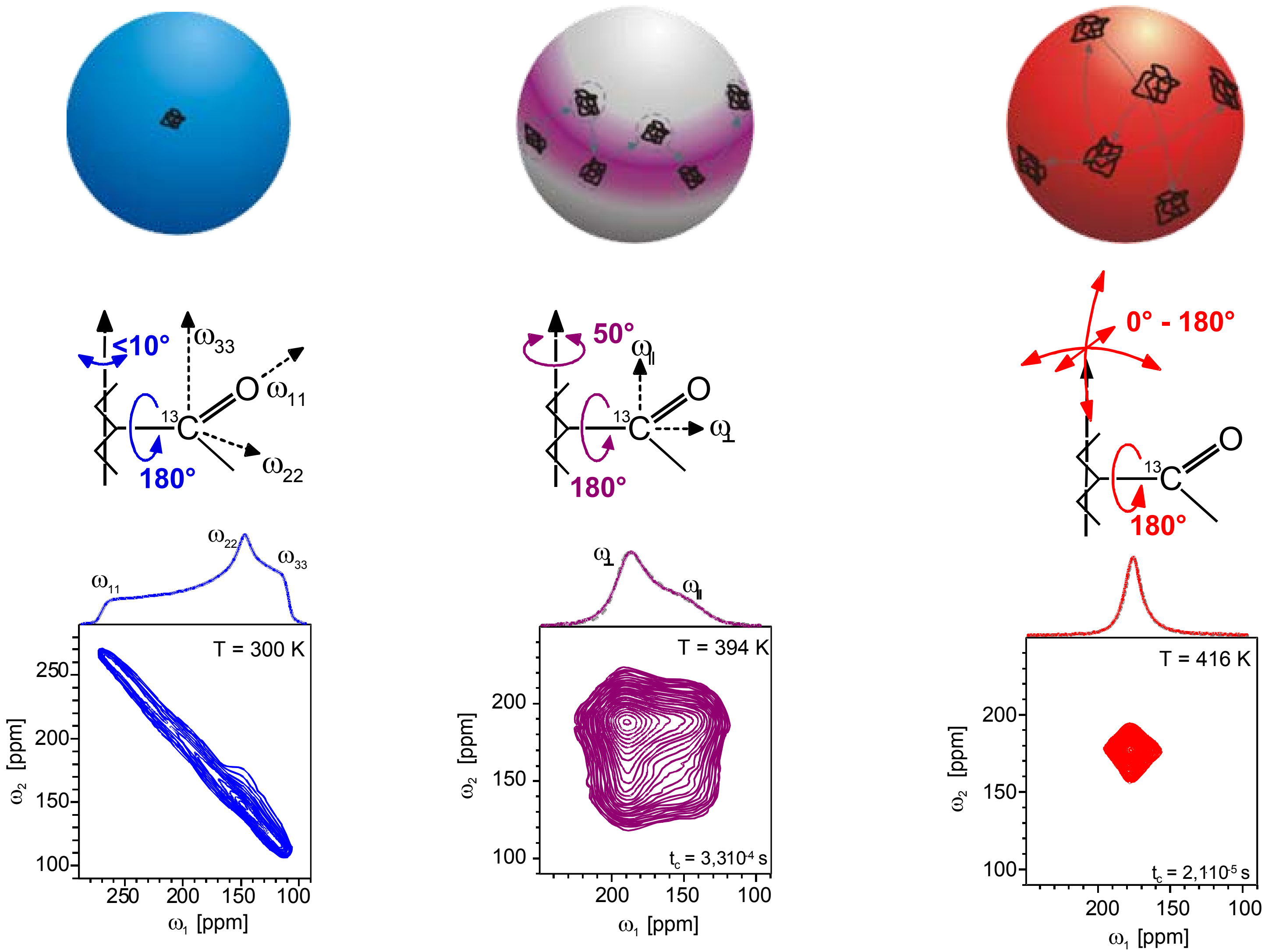
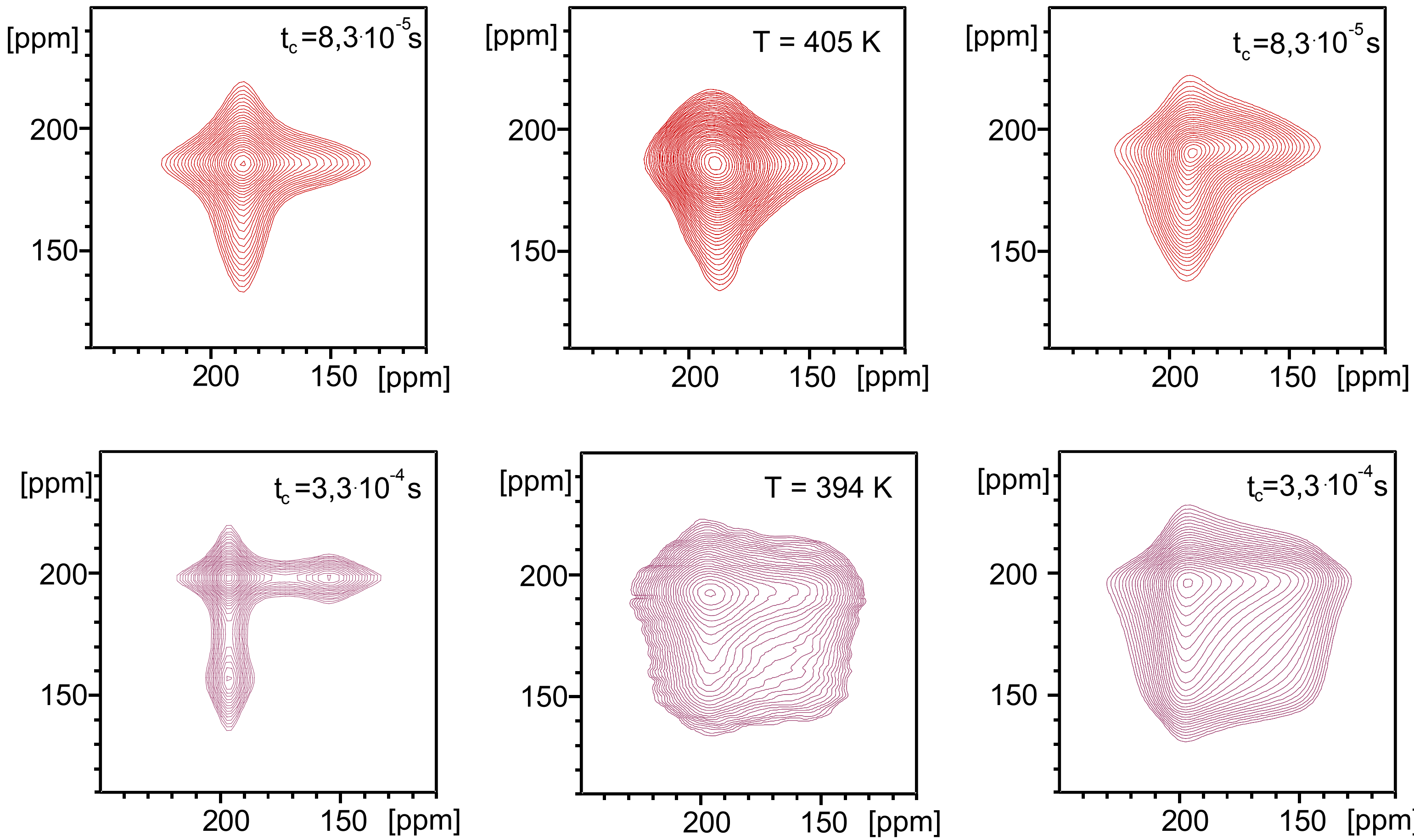
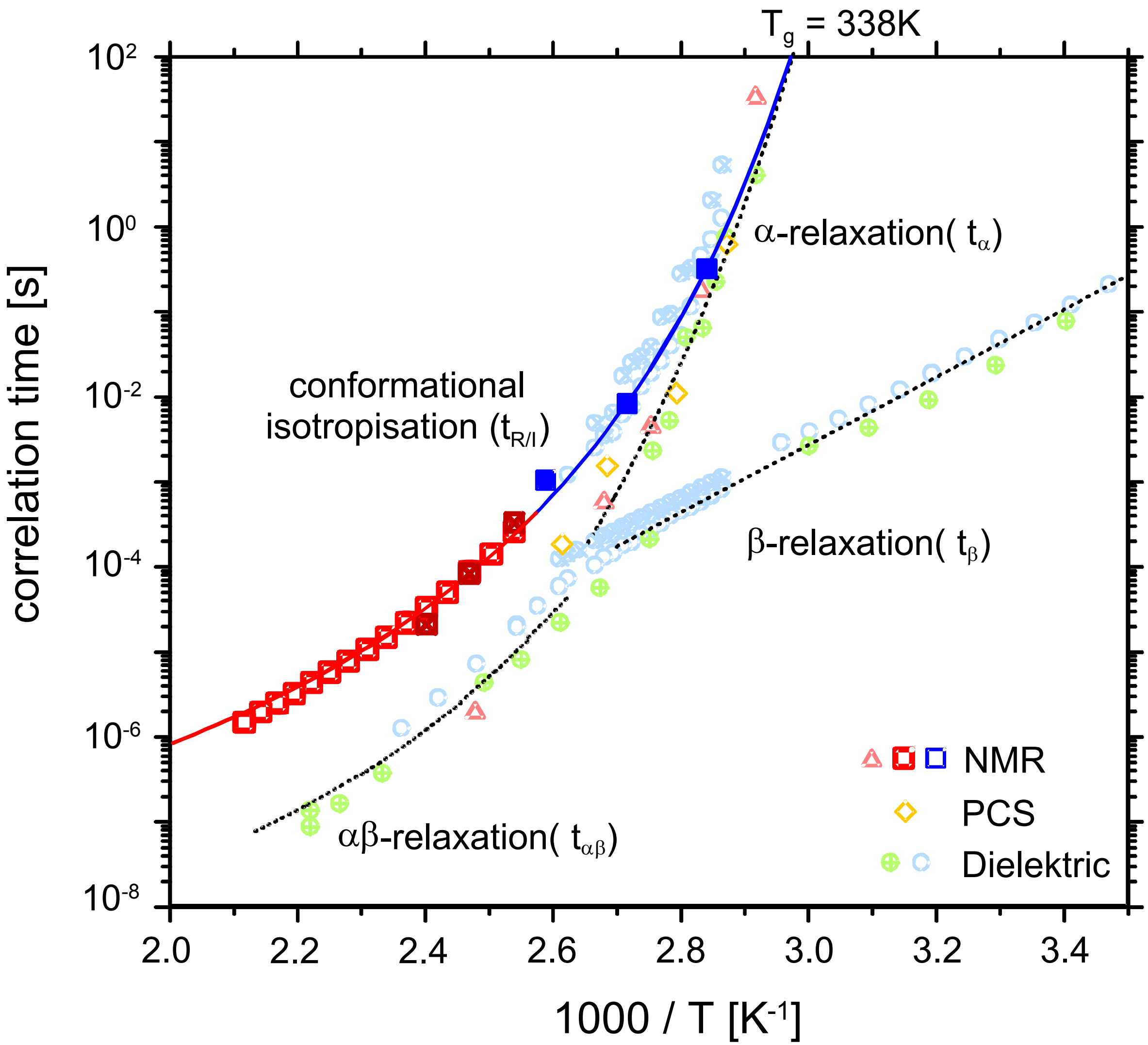


Dynamic Models: Random Jump vs. Rotational Diffusion

rotational diffusion | experimental results | random jump

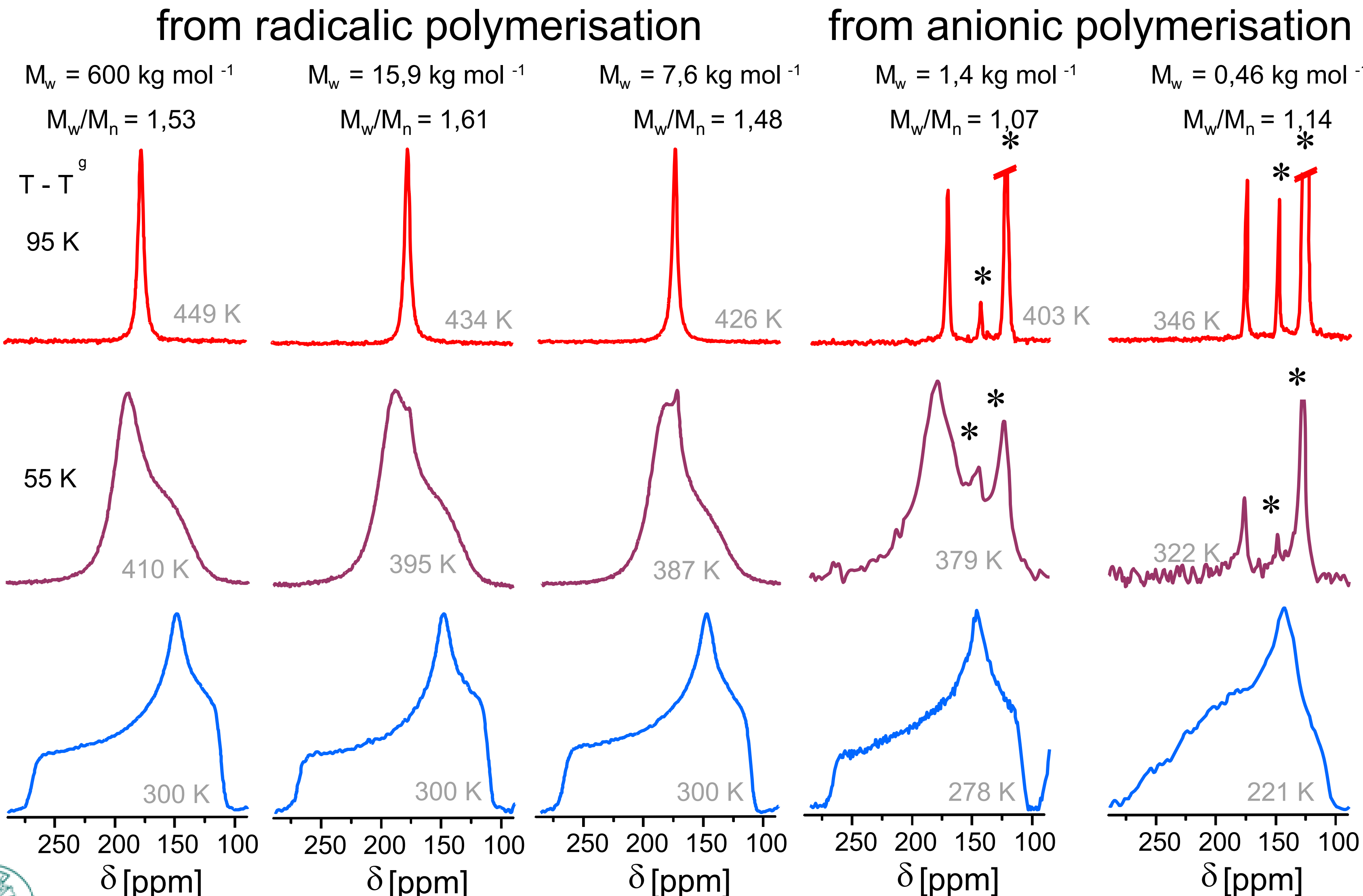


Time Sclaes of Molecular Dynamics PEMA Melts

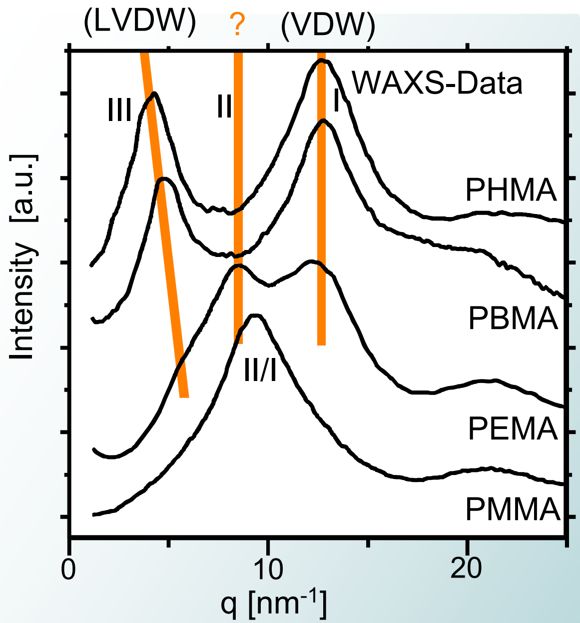


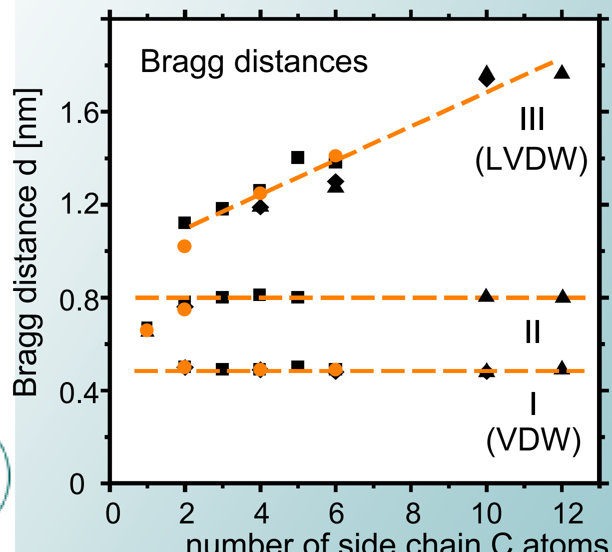
Arrhenius-diagram of dynamic processes in PEMA

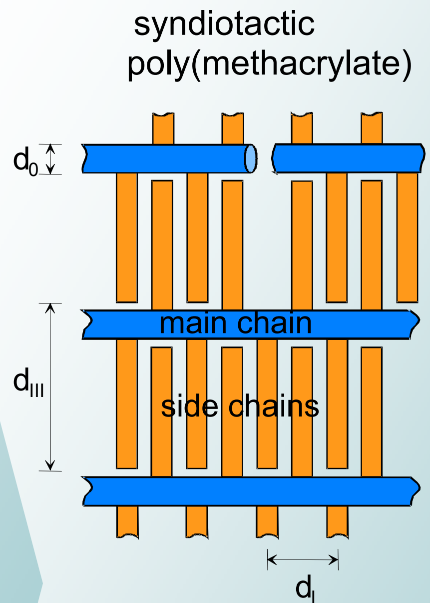
Length Scale of Isotropisation Process

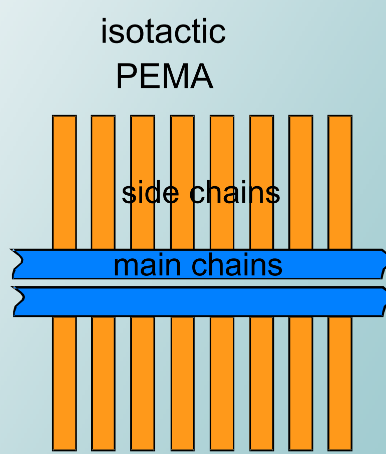


Organisation in Poly(Methacrylats): WAXS



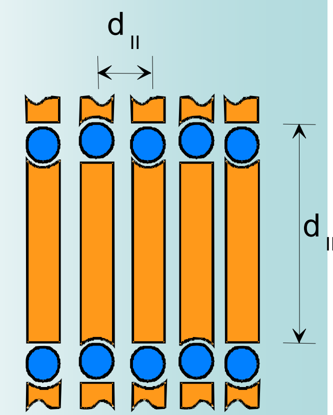






extrapolated
lokal structur:

"Nano Layers"



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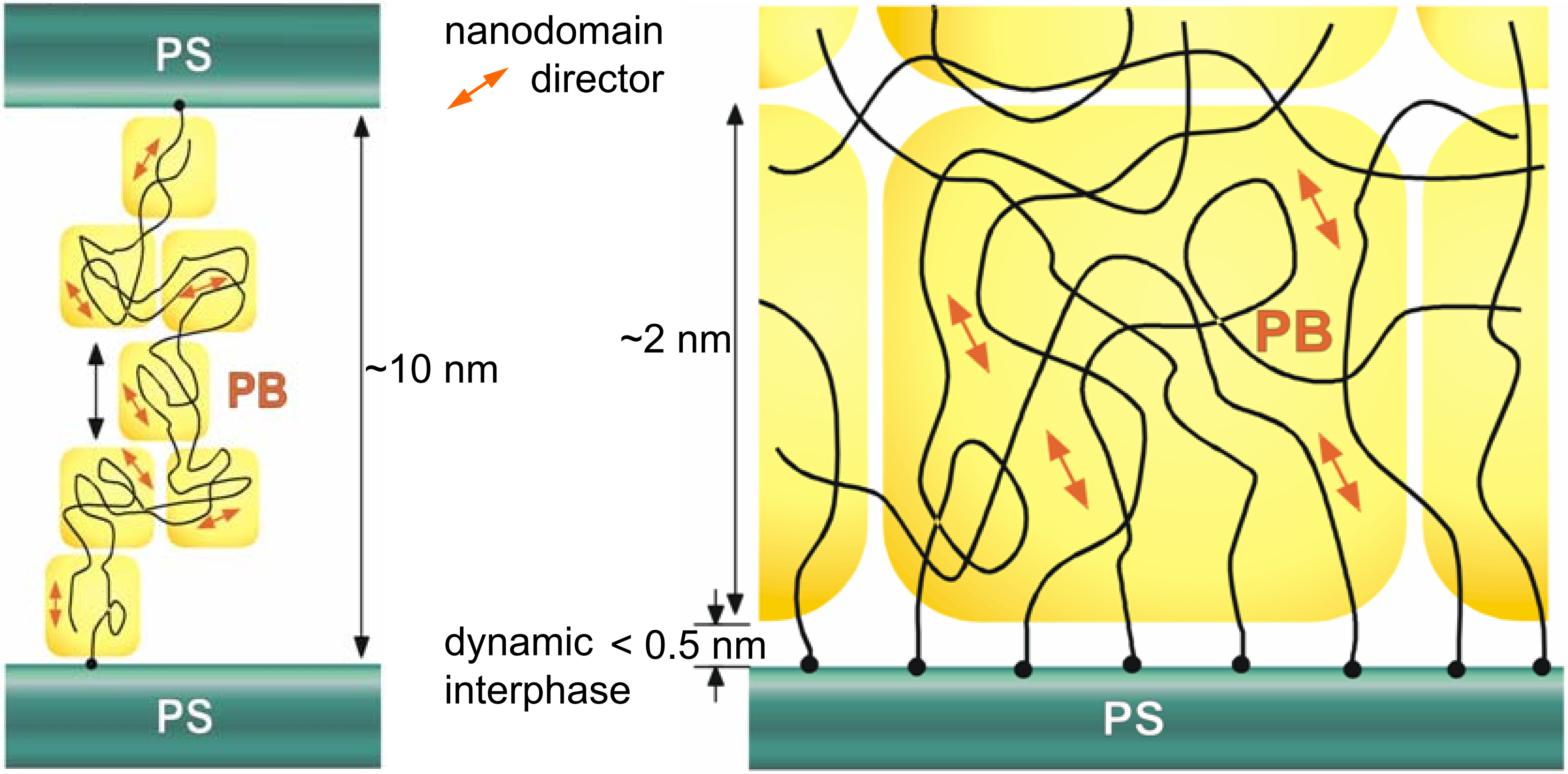
Längenskalen lokaler Ordnung in Polymerschmelzen



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