Relaxation in Polymers with Conformational Memory

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Relaxation in Polymers with Conformational Memory

Introduction • interactions in solid state NMR

Isotropization in PEMA • 1D and 2D ^{13}C NMR lineshapes, dynamic model for line narrowing, conformational exchange, length scale of isotropization process, sidechain dependence.

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Acylates vs Methacrylates • Dipolar filter, NOE, sidechain dynamics

Conclusions • Slow processes in amorphous polymers

Important NMR interactions in the solid state:

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

Zeemann Interaction :

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

Quadrupol Interaction :

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

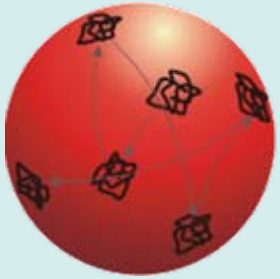
Electronic Shielding :

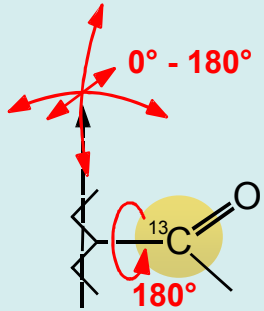
$$H_{CS} = -\sum_i \gamma_i \underline{B}_0 \underline{\underline{\boldsymbol{\sigma}}} \underline{\mathbf{I}}^i$$

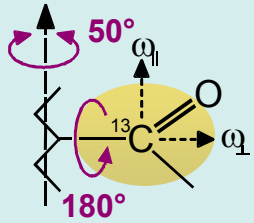
Dipol-Dipol Interaction :

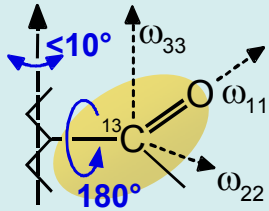
$$H_D = -\sum_{i \neq j} \frac{\mu_0 \hbar}{4\pi} \frac{\gamma_i \gamma_j}{r^3} \left[\frac{3}{r^2} (\underline{\mathbf{I}}^i \cdot \underline{r})(\underline{\mathbf{I}}^j \cdot \underline{r}) - \underline{\mathbf{I}}^i \cdot \underline{\mathbf{I}}^j \right]$$

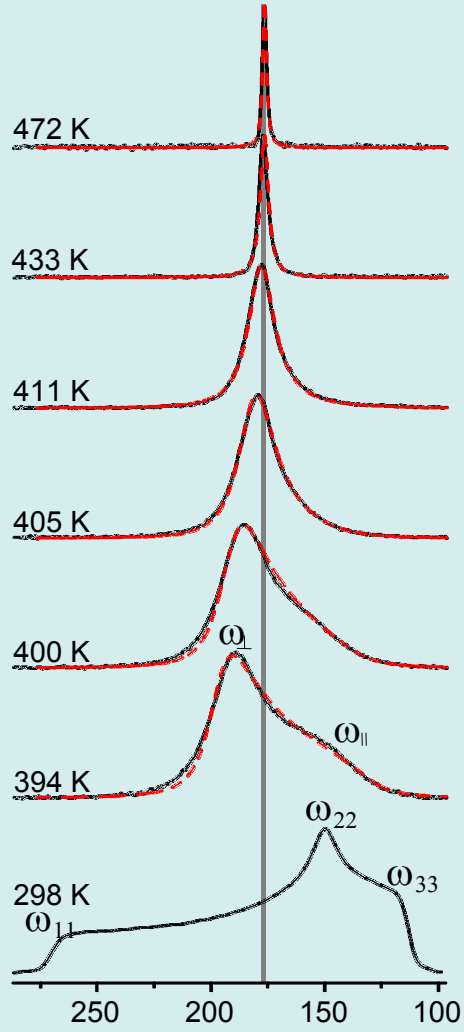
a-PEMA: Isotropisation of Chain Dynamics







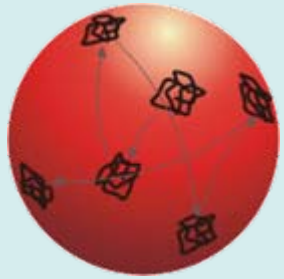


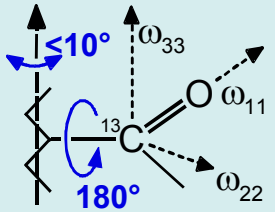


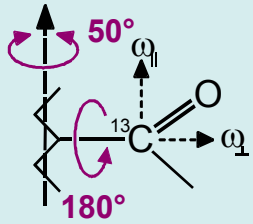
1D ^{13}C NMR: experiment, simulation

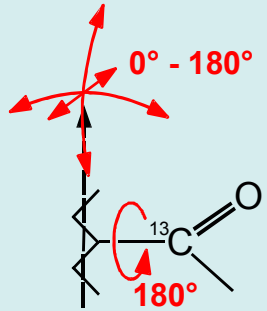
Glass T_g Melt Melt

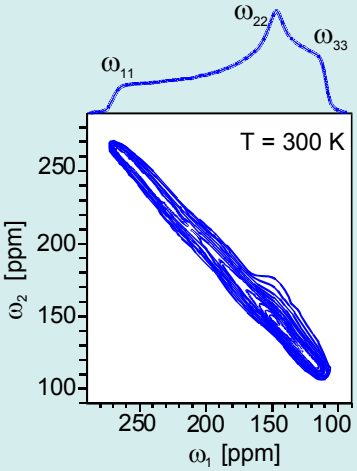
a-PEMA: Isotropisation of Chain Dynamics

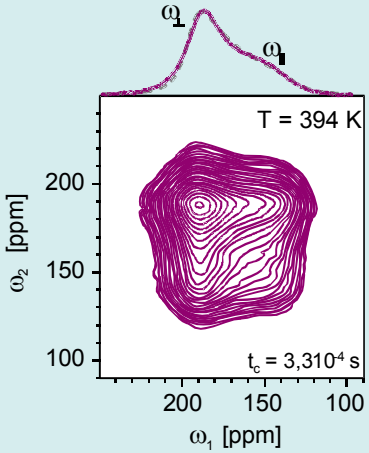


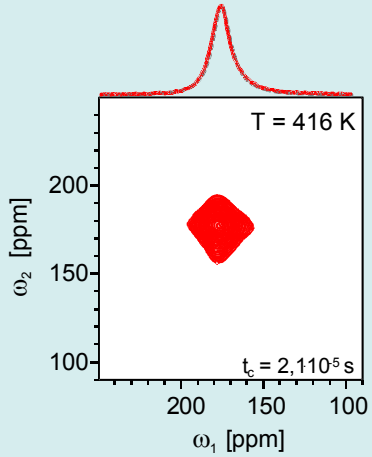




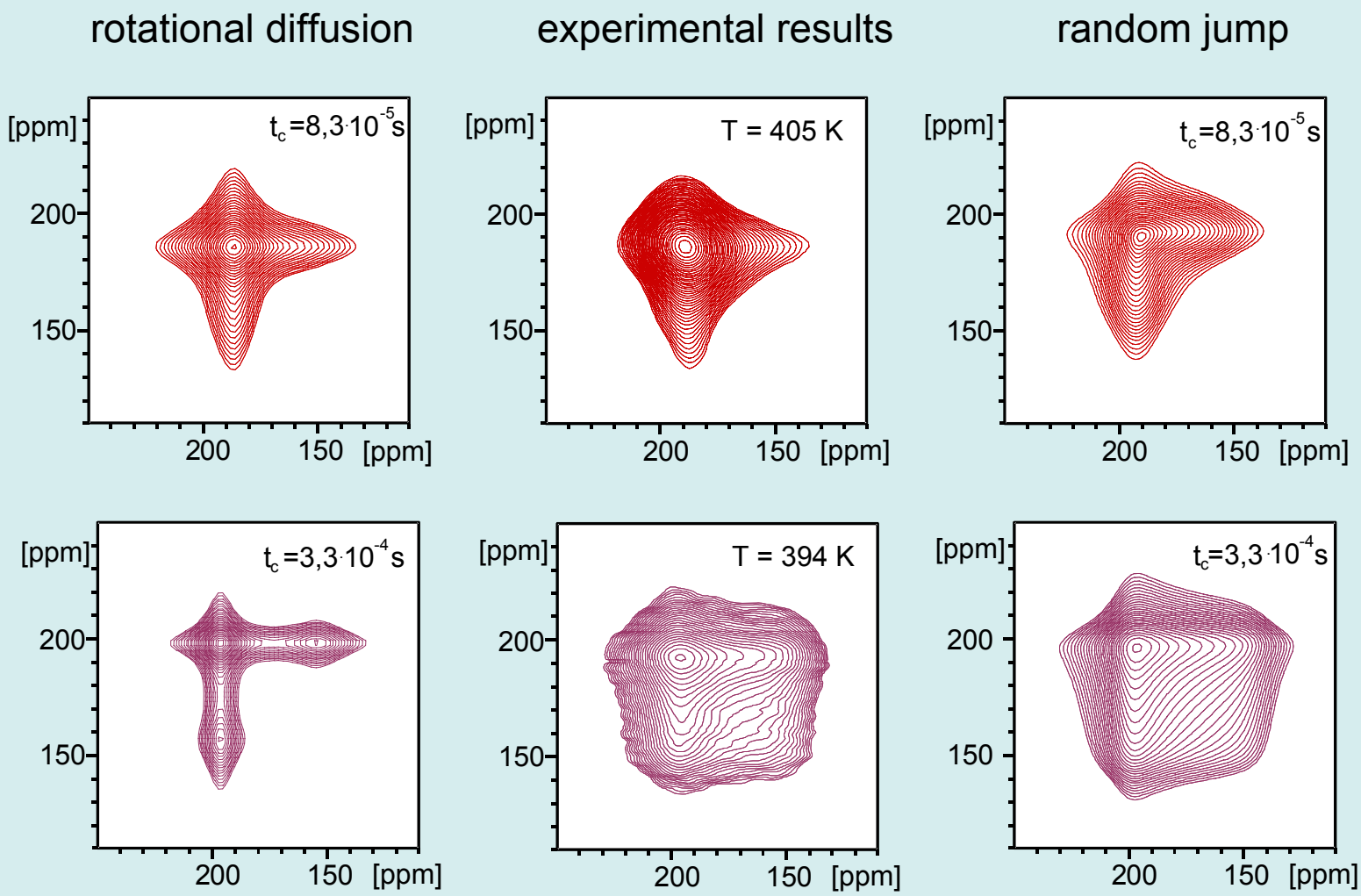




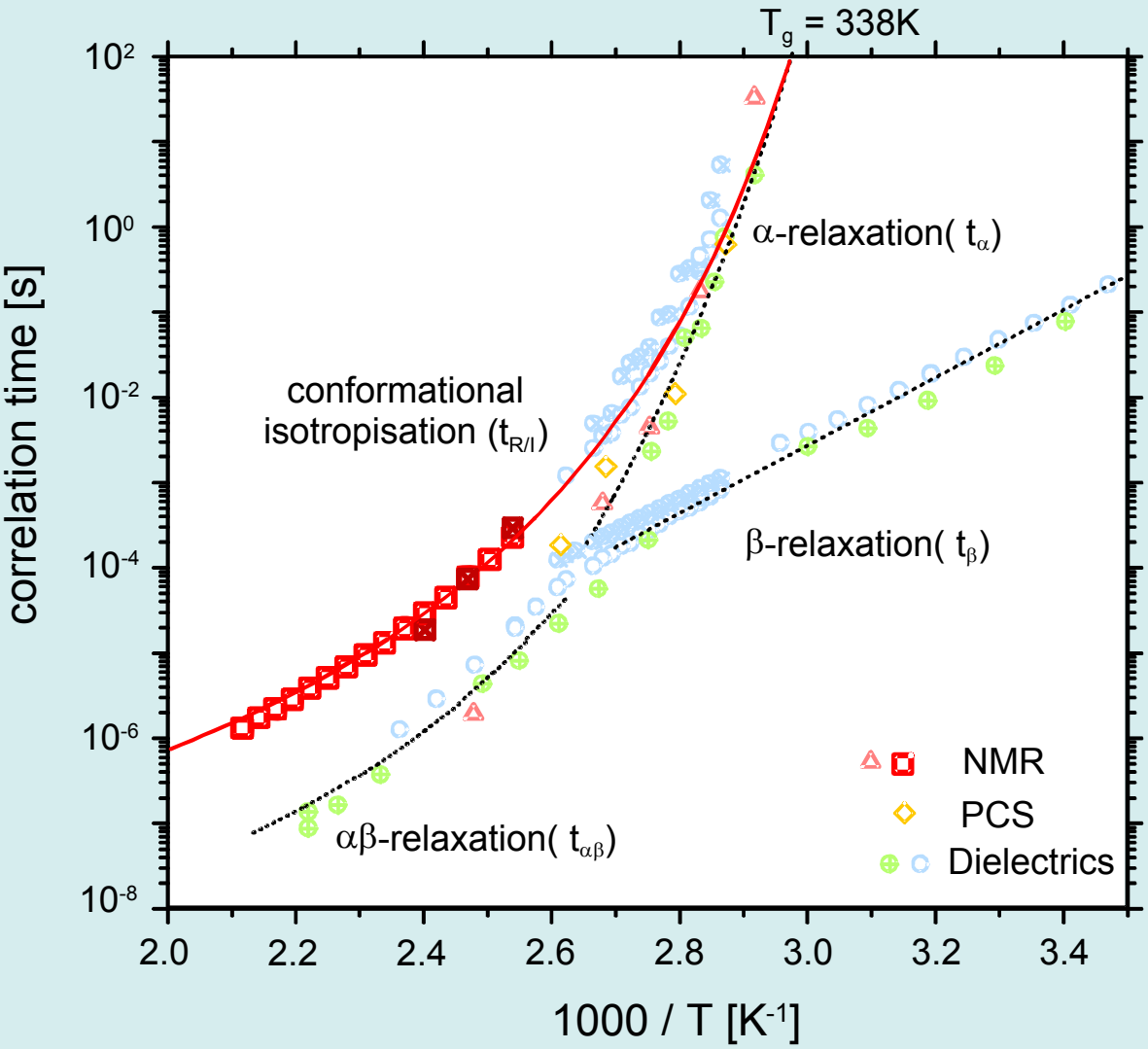




Dynamic Models: Random Jump vs. Rotational Diffusion

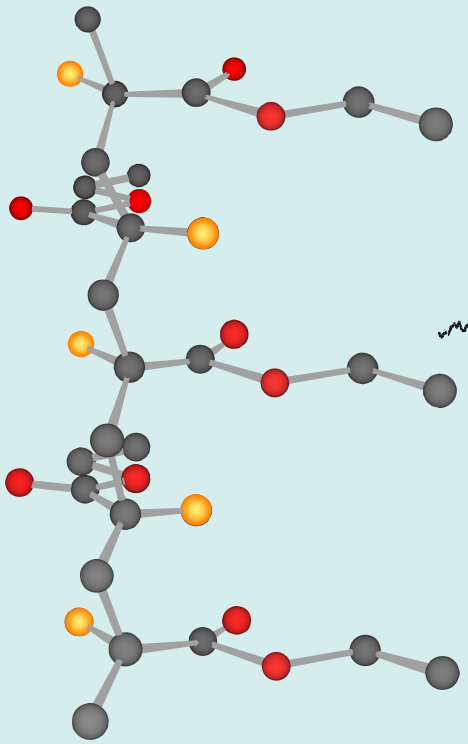


Time Sclaes of Molecular Dynamics PEMA Melts

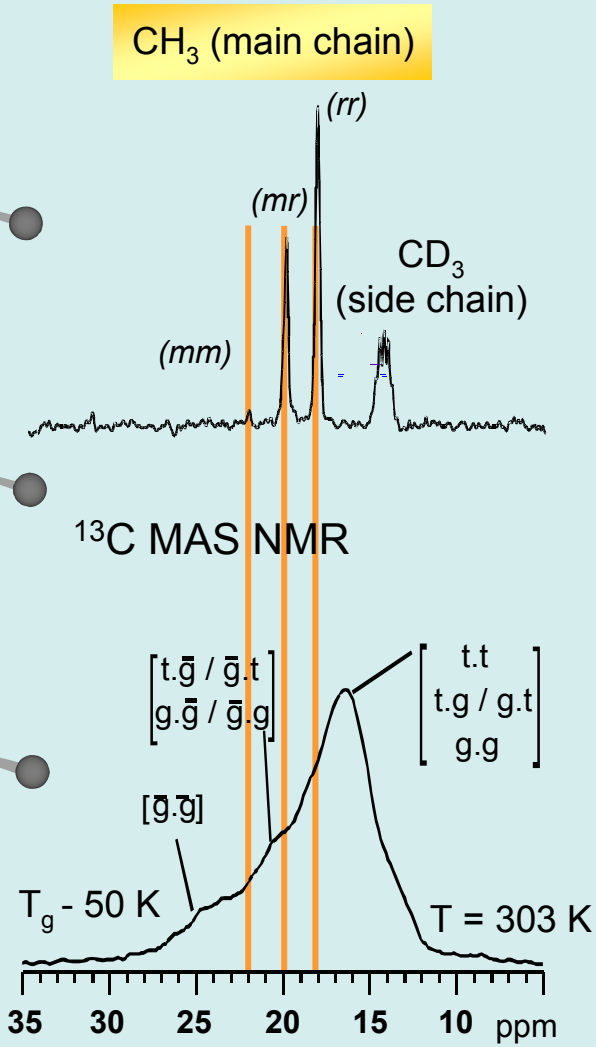


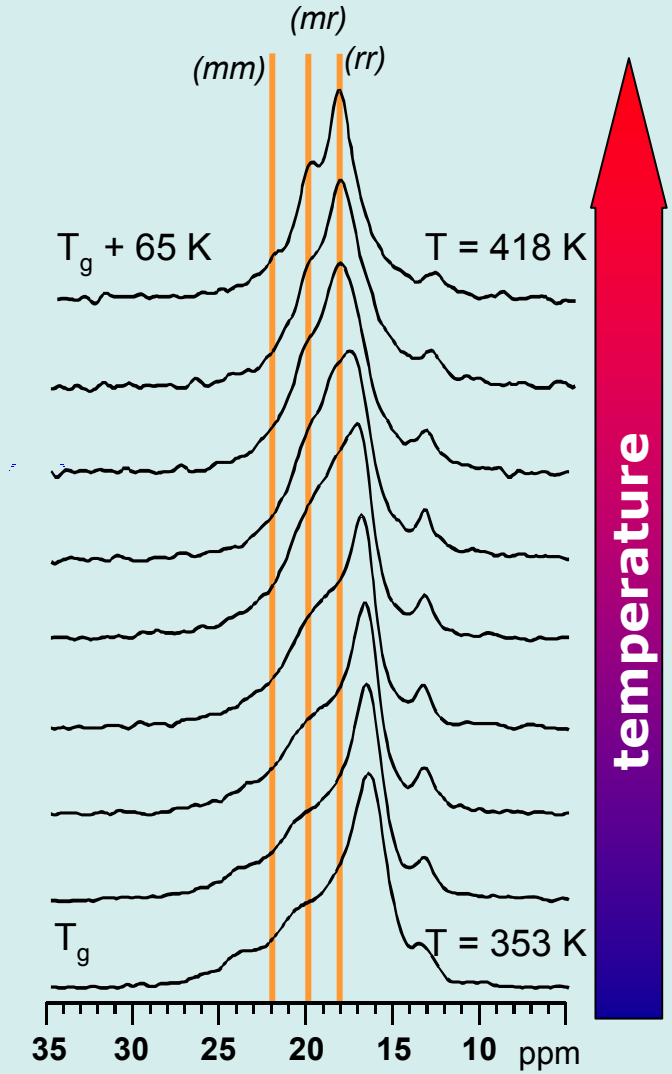
Arrhenius-diagram of dynamic processes in PEMA

a-PEMA: Conformation and Conformational Dynamics



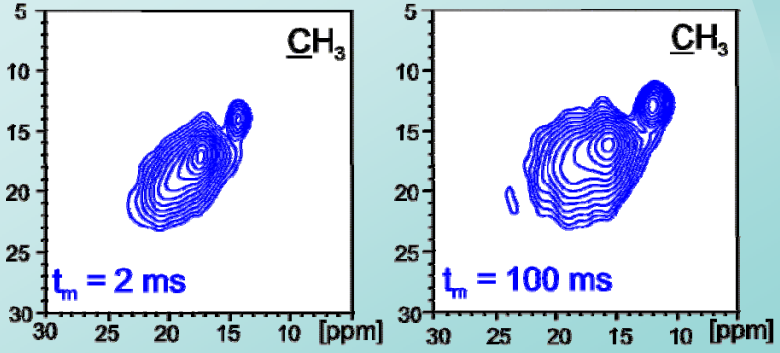
s-PEMA





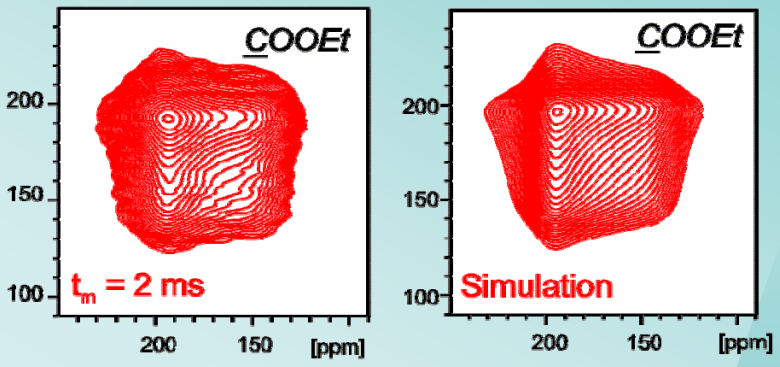
Separation of Dynamic Timescales in PEMA-Melts

Conformational Dynamics from ^{13}C MAS NMR (T = 385 K)



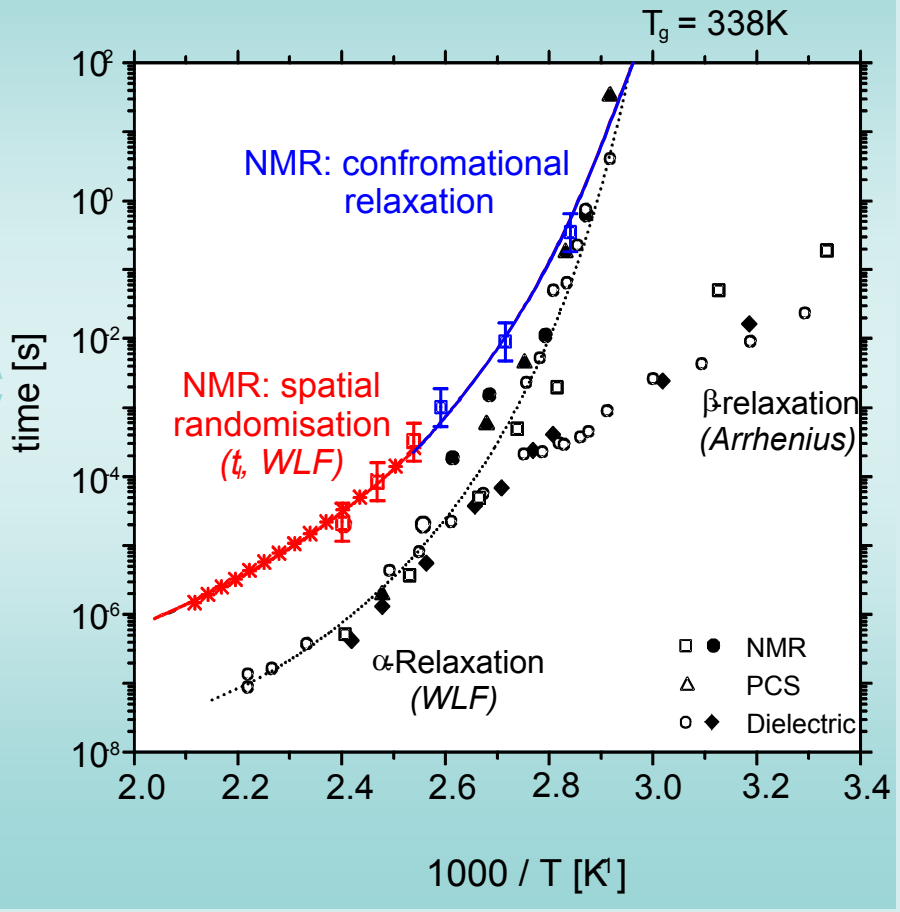
t_c = 120 ms

Randomisation from ^{13}C 2D Exchange NMR (T = 385 K)

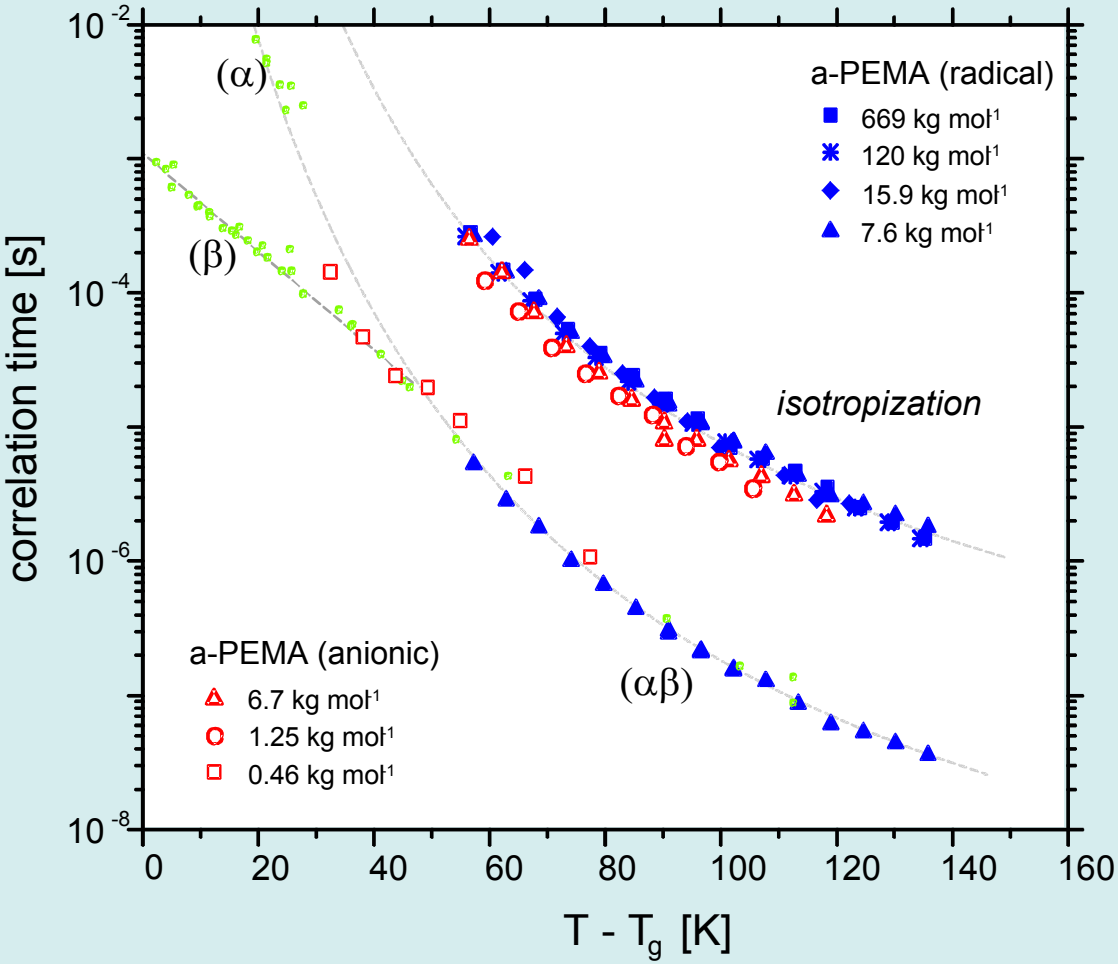


t_c = 0.33 ms

Correlation Times from NMR, PCS, Dielectrics

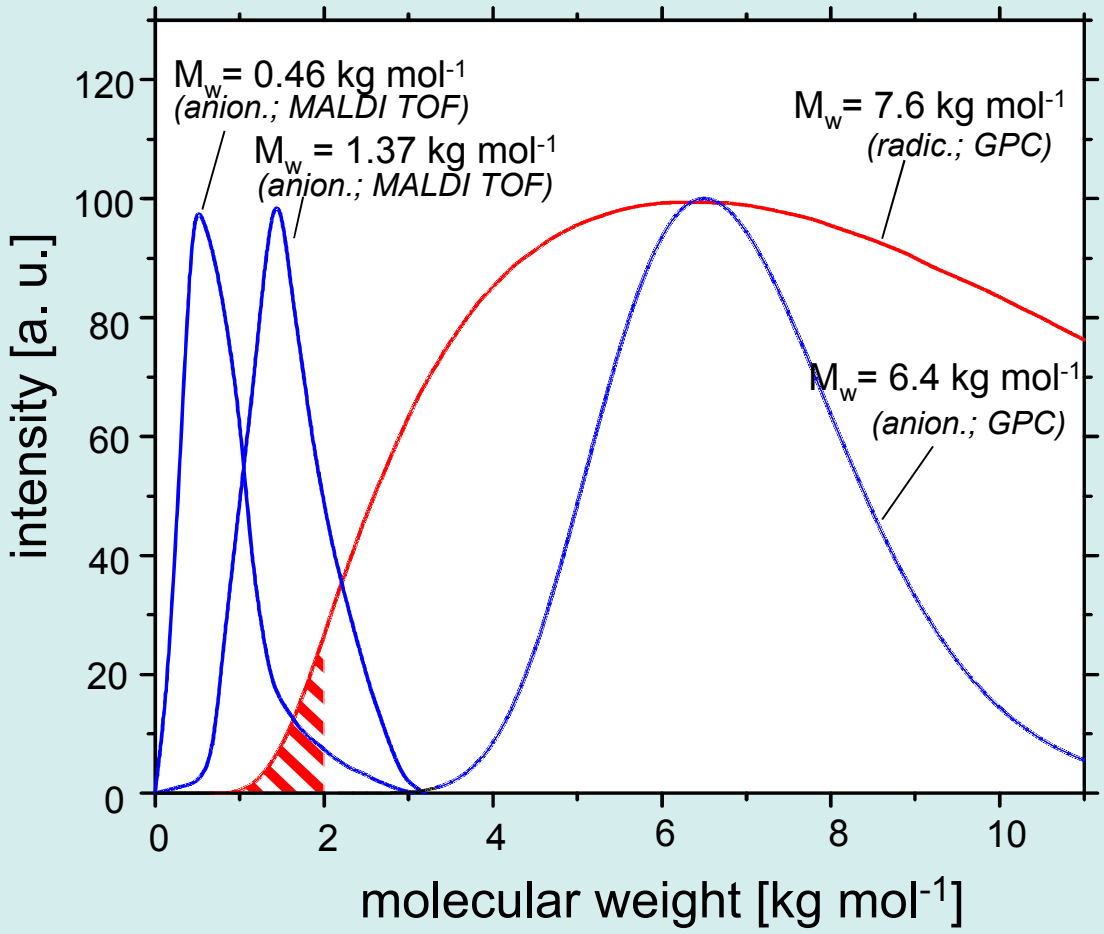


M_w Dependence of the Isotropization Process

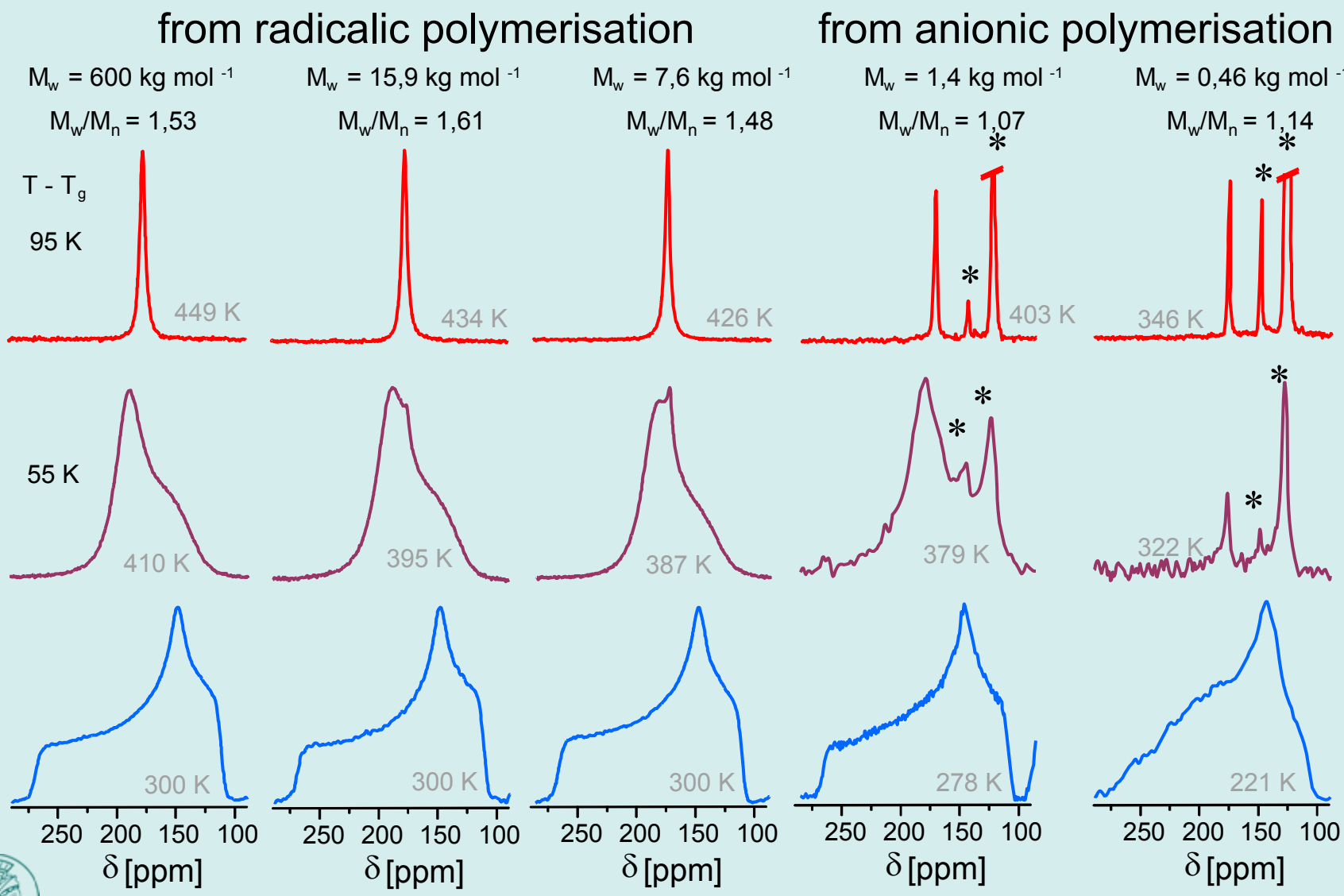


The break down of the isotropization process is determined by the polydispersity of the polymers.

Polydispersity of Low Molecular Weight PEMAs

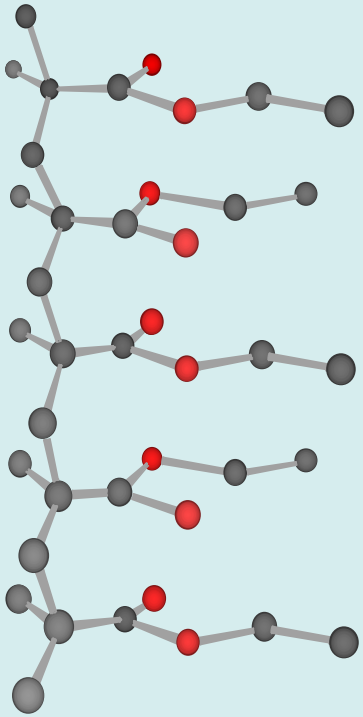


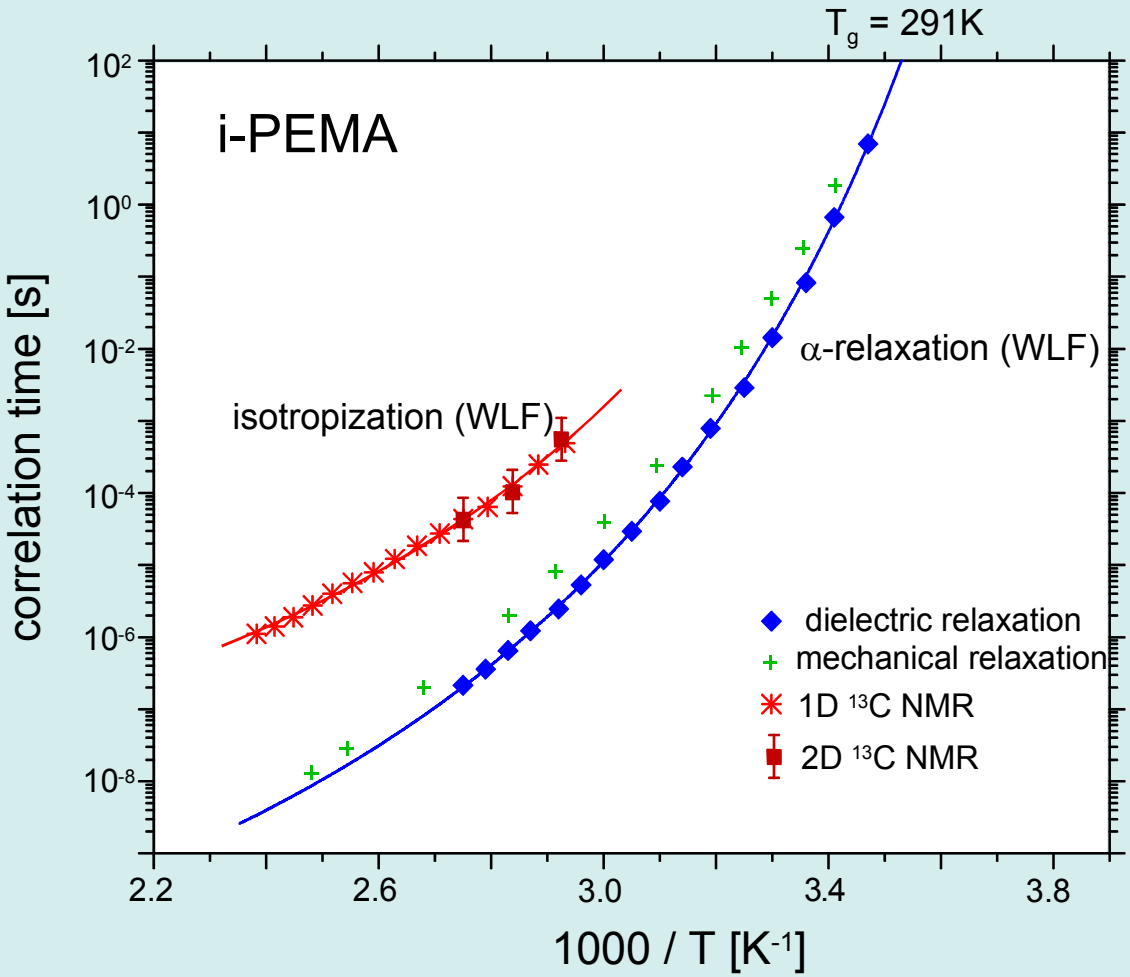
Length Scale of Isotropisation Process



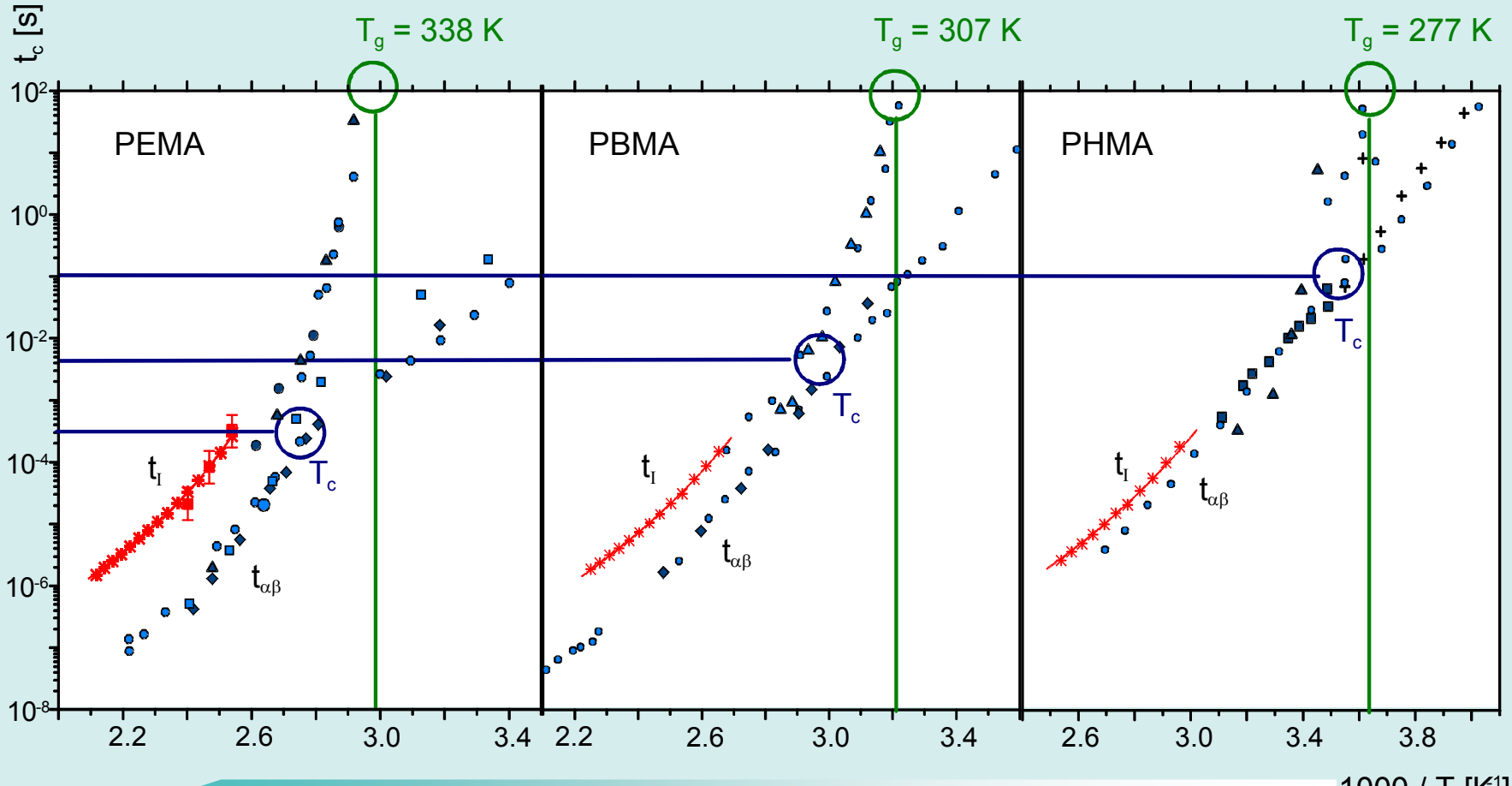
Influence of Tacticity on the Insotropization of PEMA

isotactic PEMA
(mm = 0.92)





Poly(Methacrylates): Separation of Time Scales of Chain Randomization and α/β-Prozess



increasing separation of t_I and $t_{\alpha\beta}$

decreasing T_g (internal plastification)

β-relaxation with constant activation

T_c at lower temperature T and longer t_c

Relaxation in Polymers with Conformational Memory

Introduction • interactions in solid state NMR

Isotropization in PEMA • line narrowing, length scale, sidechain length

Acylates vs Methacrylates • Dipolar filter NMR experiments, NOE polarization transfer, poly(n-alkyl methacrylates), poly(n-alkyl acrylates).

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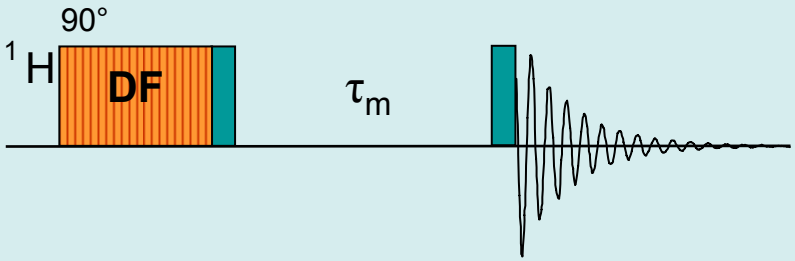
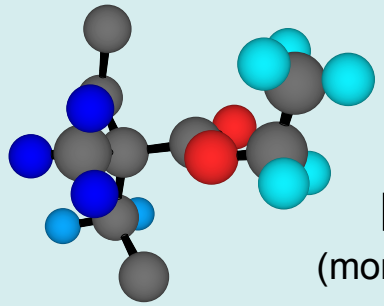
Conclusions • Slow processes in amorphous polymers

Correlation Times from Dipolar Filter Experiments

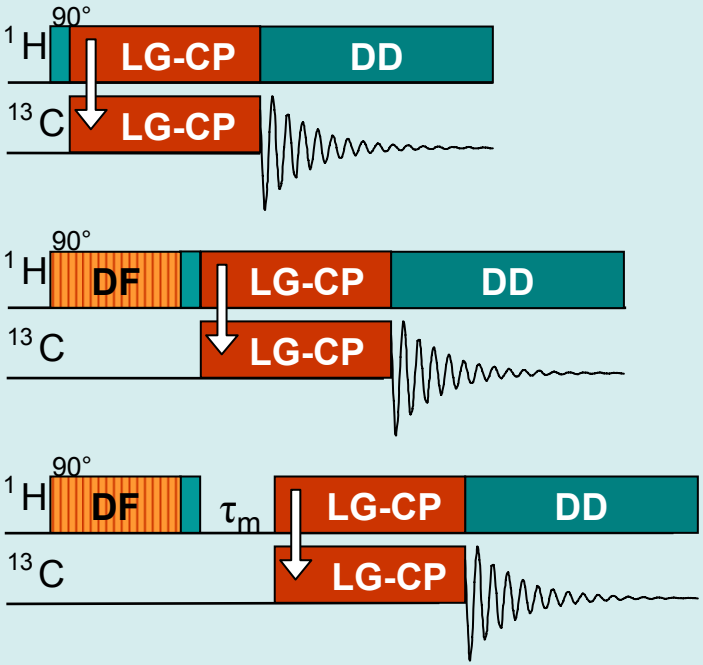
Scheme of dipolar filter experiment

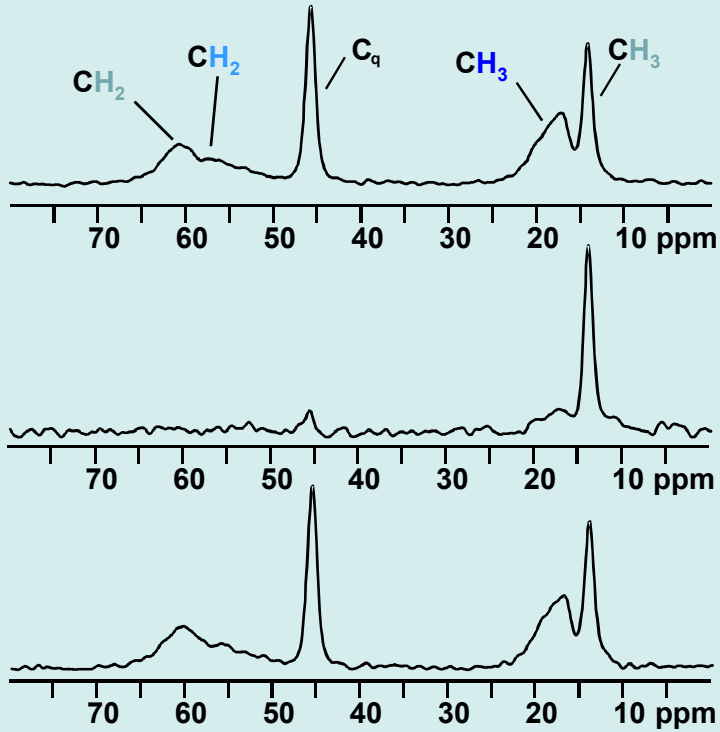




PEMA
(monomeric unit)

Probing the selection of the dipolar filter:





Correlation Times from Dipolar Filter Experiments

NOE magnetization decay in a CH_2-CH_3 moiety:

$$I(\tau_m) = \tfrac{3}{5} I_0 + \tfrac{2}{5} I_0 \cdot \exp\left(-5 \cdot q_{AB} \cdot \tau_C^{AB} \cdot \tau_m\right)$$

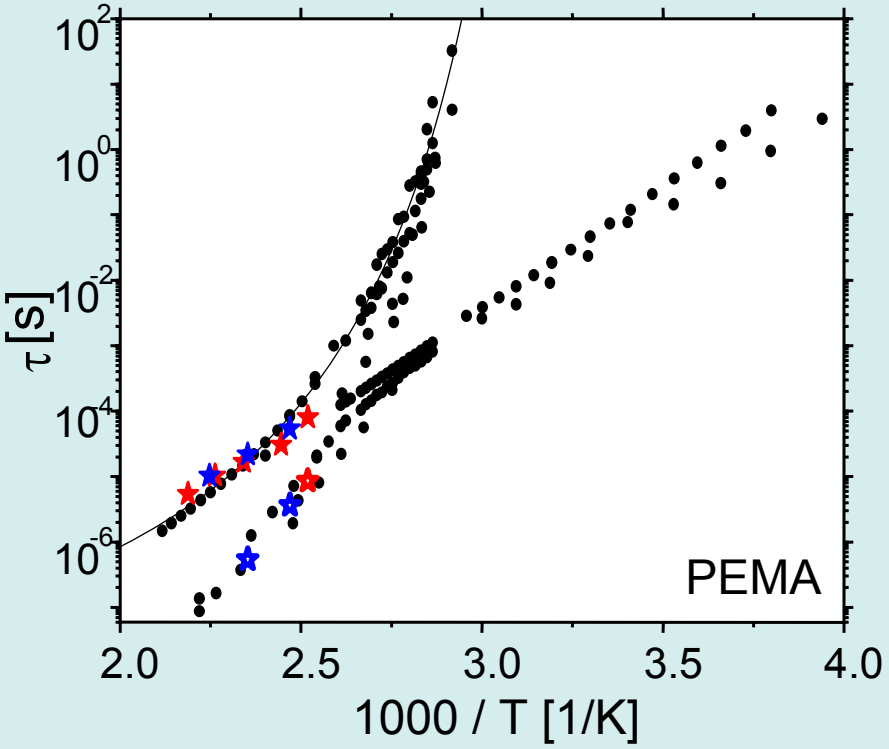
q_{AB} : static dipolar coupling parameter,determined via M_2 measurements .

Experimental results in PEMA

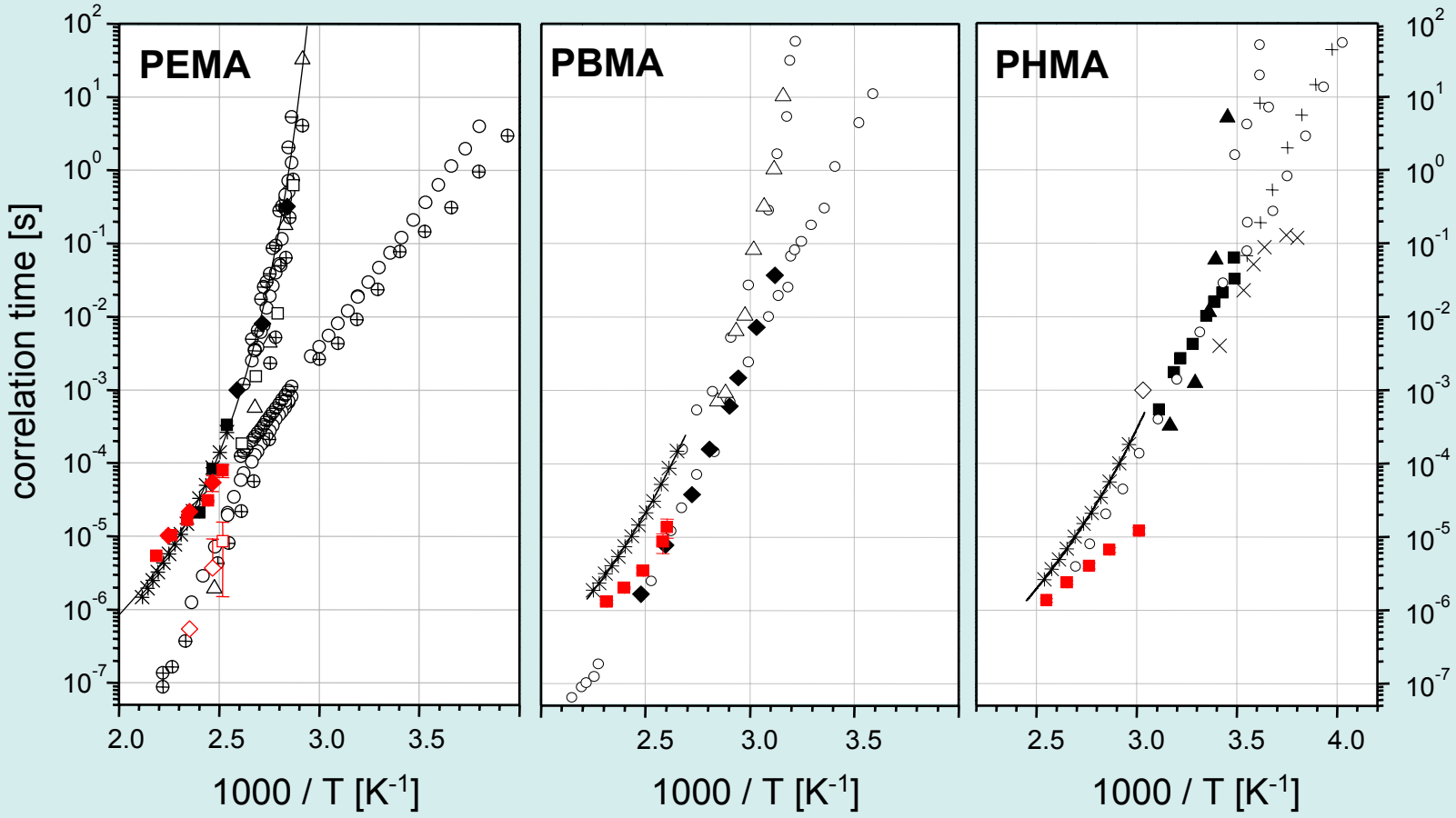
$T > T_g$: pure exponential decay

$T \sim T_g$: biexponential decay

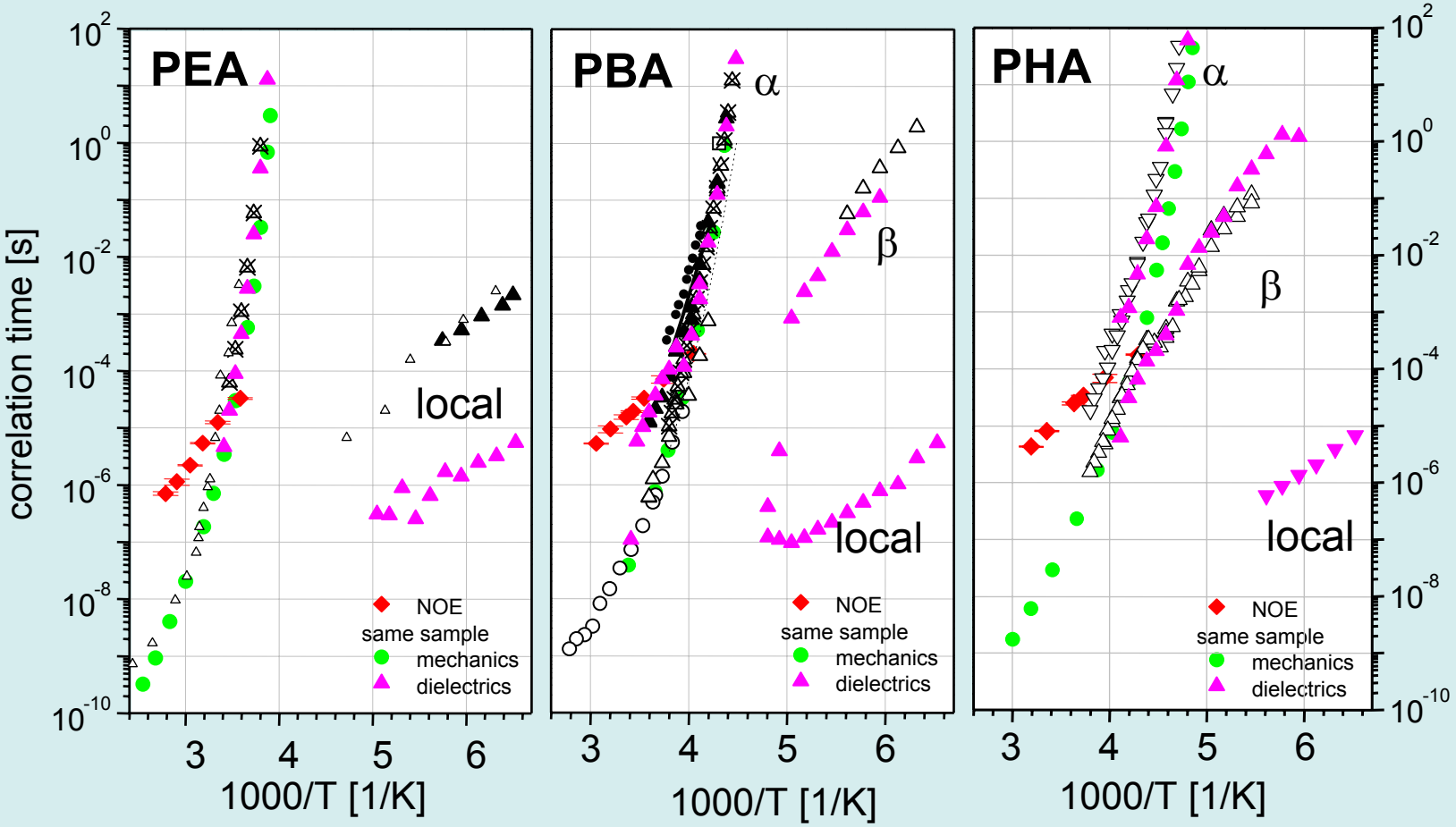
Correlation times from dipolar filter experiments



NOE Relaxation Times in PnAMA samples



Relaxation Times of Poly(n-alkyl acrylates)



Literature data (dielectrics):

- McCrum
- Gomez,Ribelles
- Reissig et al.
- Beiner
- Fioretto
- Fitzgerald
- Gomez Ribelles
- Hayakawa
- Jourdan
- Reissig
- Beiner

Local Dynamics in PnAA from NOE Analysis

apparent activation energies E_a [kJ·mol^{-1}] :

	PEA	*PBA*	*PHA*
β relaxation	-	18	ca 15-25
local relaxation	8-14	10	10
slow process (NOE)	18	13	12

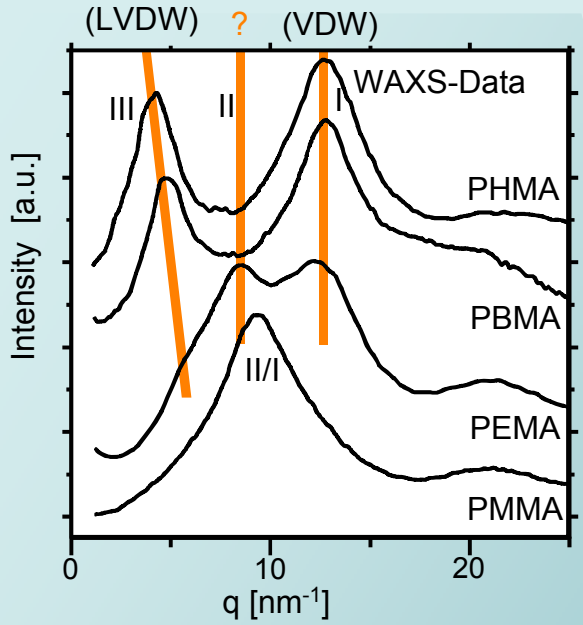
Quantified processes in PnAA samples, correspond to a superposition of β- and local processes in the side chain.

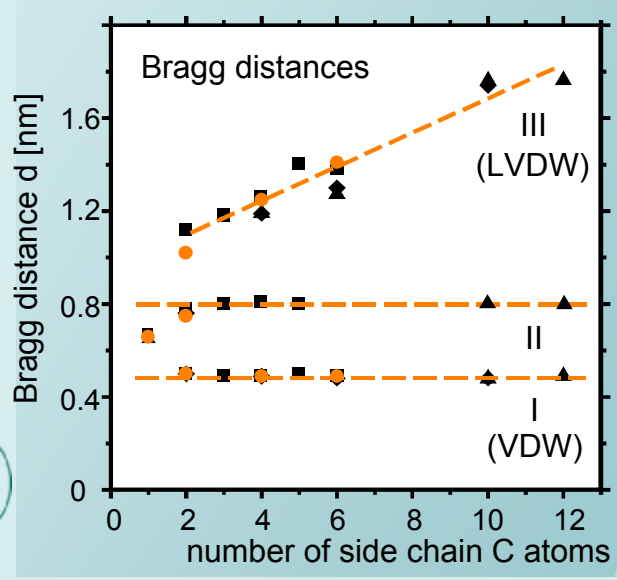
Non-isotropic side chain modes indicate organization on time scales significantly longer than the α-process

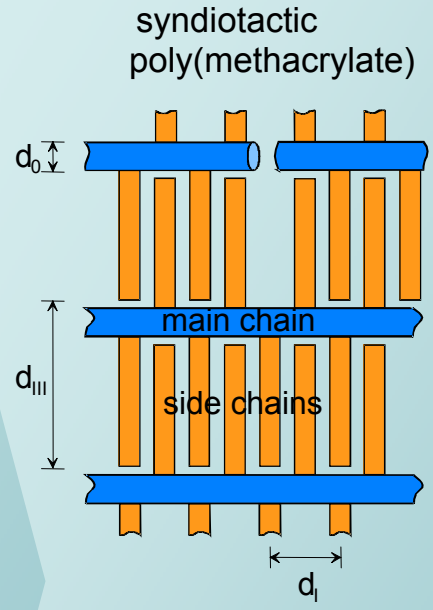
Relaxation in Polymers with Conformational Memory

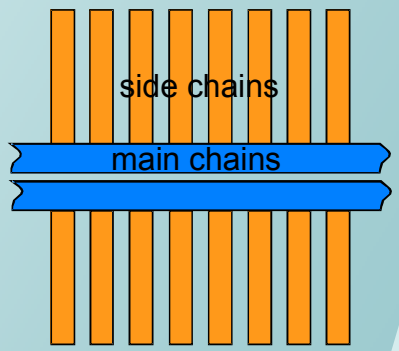
Introduction	•	interactions in solid state NMR
Isotropization in PEMA	•	line narrowing, length scale, sidechain length
Acylates vs Methacrylates	•	Dipolar filter, NOE, sidechain dynamics
Conclusions	•	Slow processes in amorphous polymers

Organisation in Poly(Methacrylats): WAXS



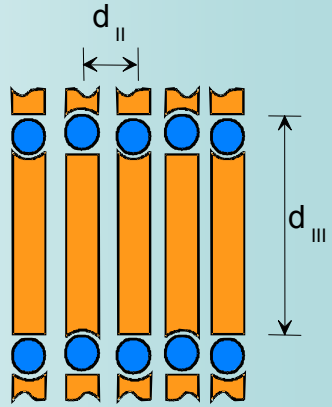






extrapolated
lokal structur:

"Nano Layers"



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	• Reptation-model, polybutadiene, PEMA
Conclusions	• How unstructured are amorphous polymers ?

Acknowledgements

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