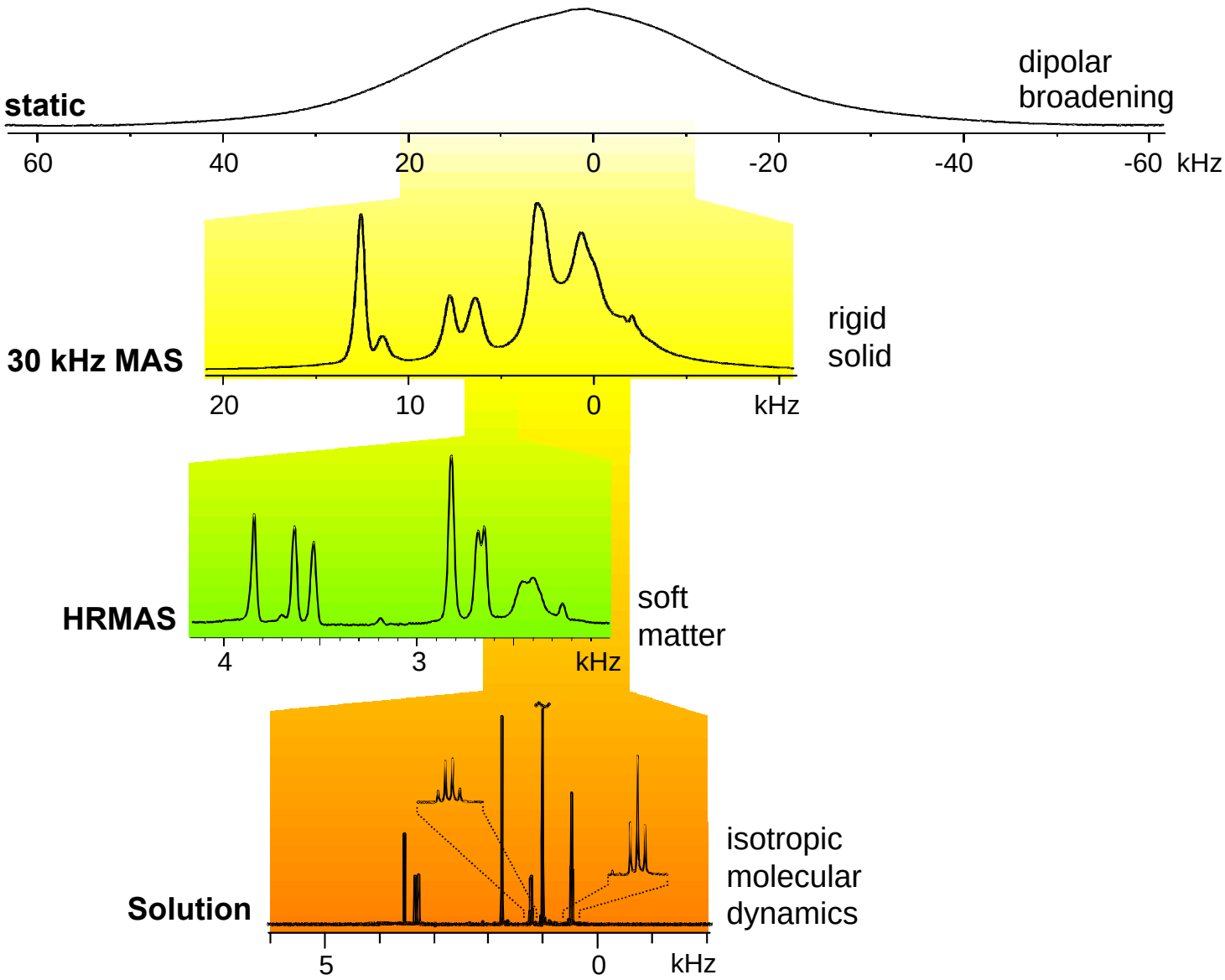
NMR Studies of Polyethylene: Towards the Organization of Semi Crystalline Polymers

Yefeng Yao, Robert Graf, Hans Wolfgang Spiess

Max-Planck-Institute for Polymer Research, Mainz, Germany

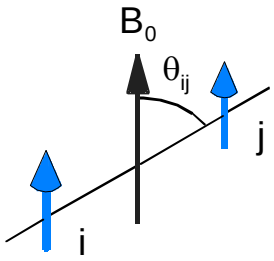
Leibniz Institut für Polymerforschung, Dresden, January 15th 2008

Line Width in ^{1}H NMR Spectra



Resolution Enhancement in NMR

dipol-dipol coupling:



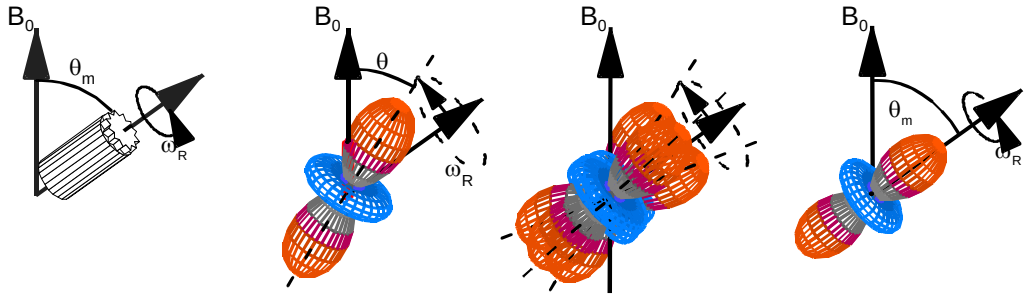
$$\hat{H} = \hat{R}_{2,0} \cdot \hat{T}_{2,0}$$

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:

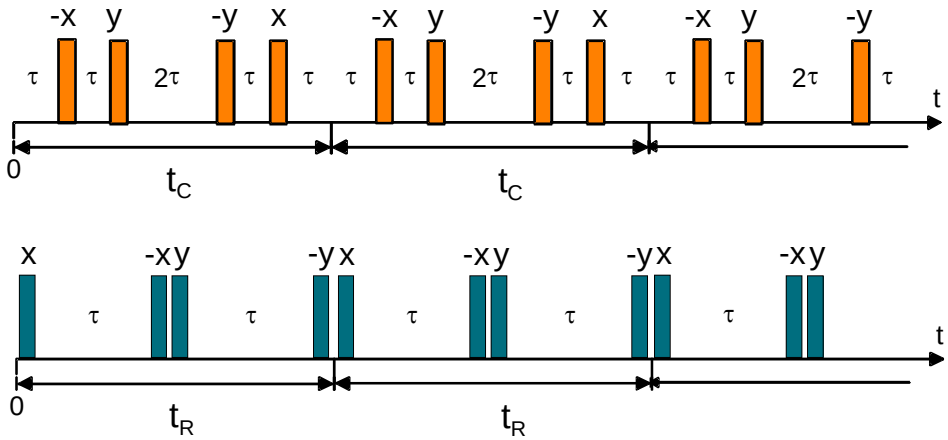
$$\overline{\hat{R}}_{2,0} \rightarrow 0$$



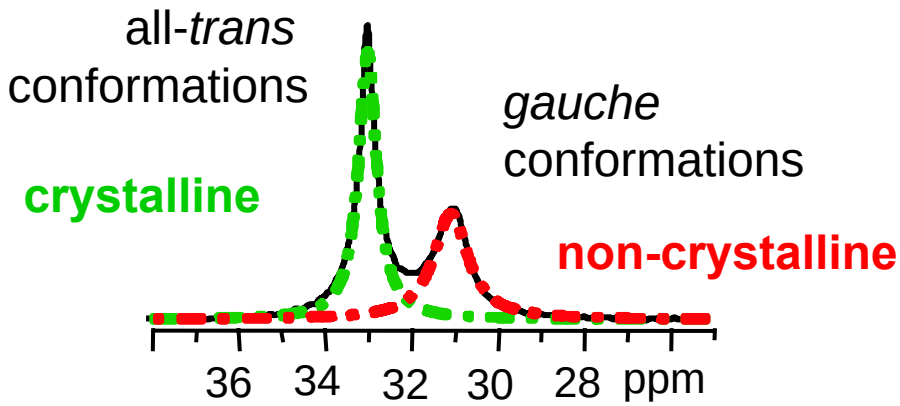
RF irradiation:

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

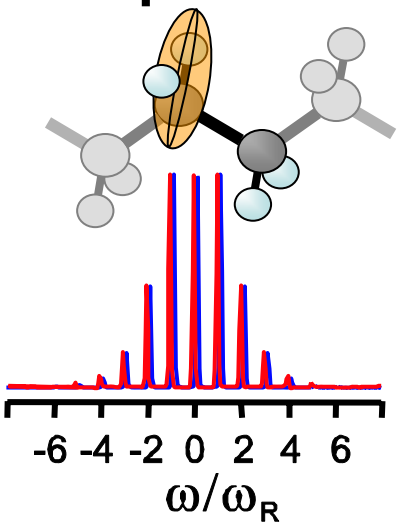
$$\overline{\hat{T}}_{2,0} \rightarrow H_{D,eff.} \ \text{(Recoupling)}$$



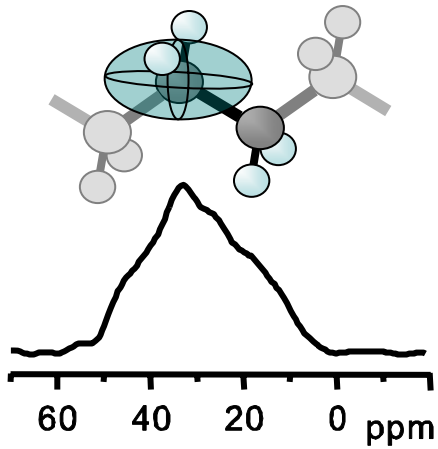
Anisotropic NMR Interactions



^{1}H-^{13}C dipolar couplings



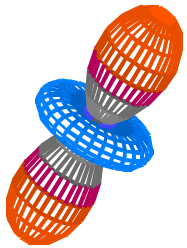
^{13}C chemical shift anisotropy



Dipolar Sideband Pattern

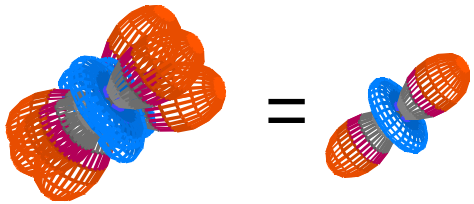
dipolar couplings:

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

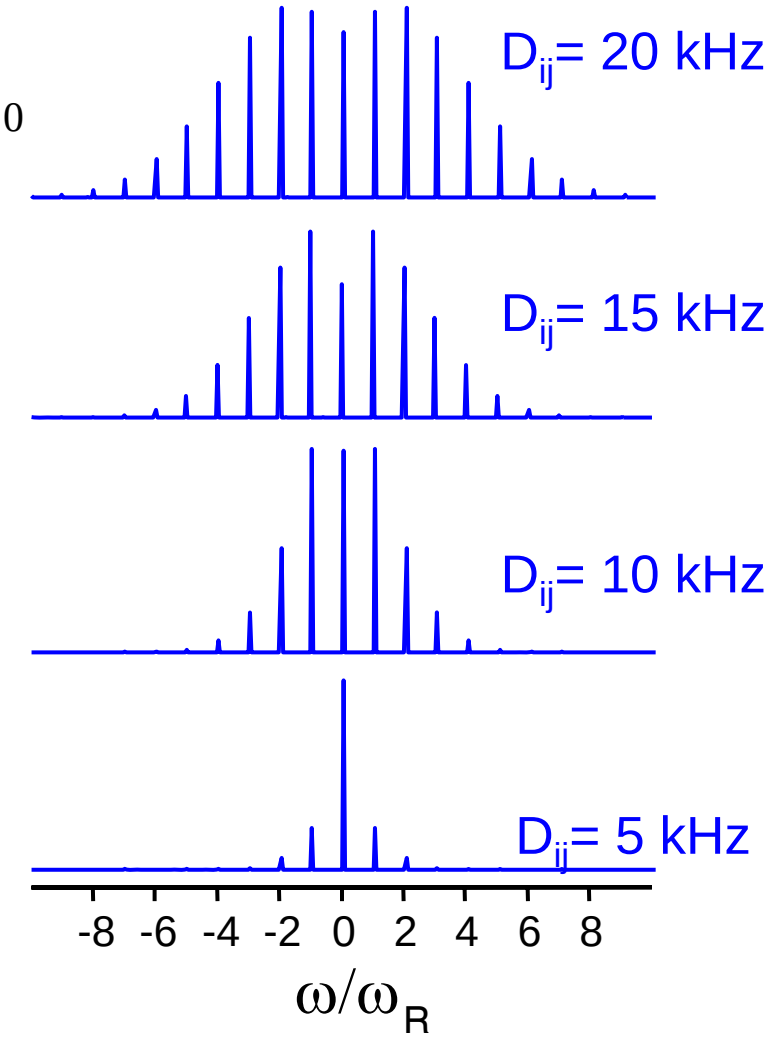


motional averaged

$$\int_t$$



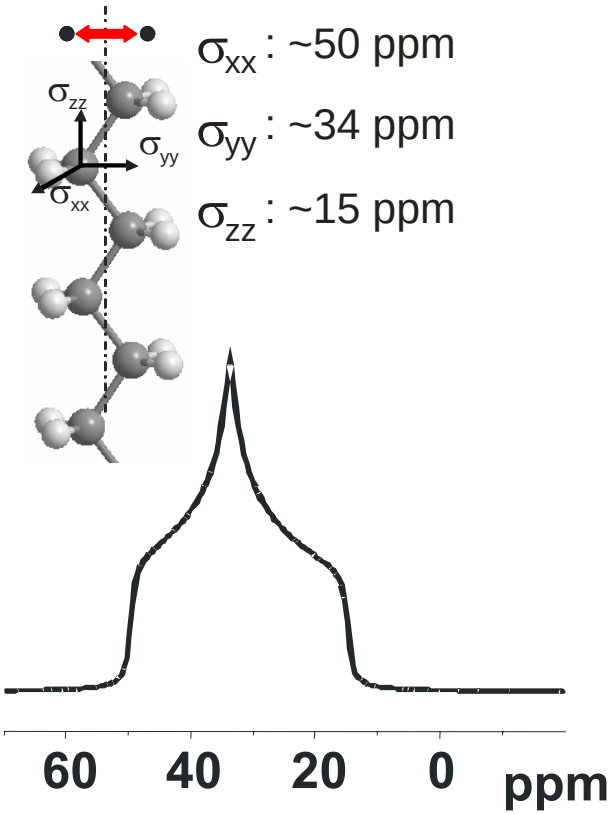
ReREDOR sideband pattern



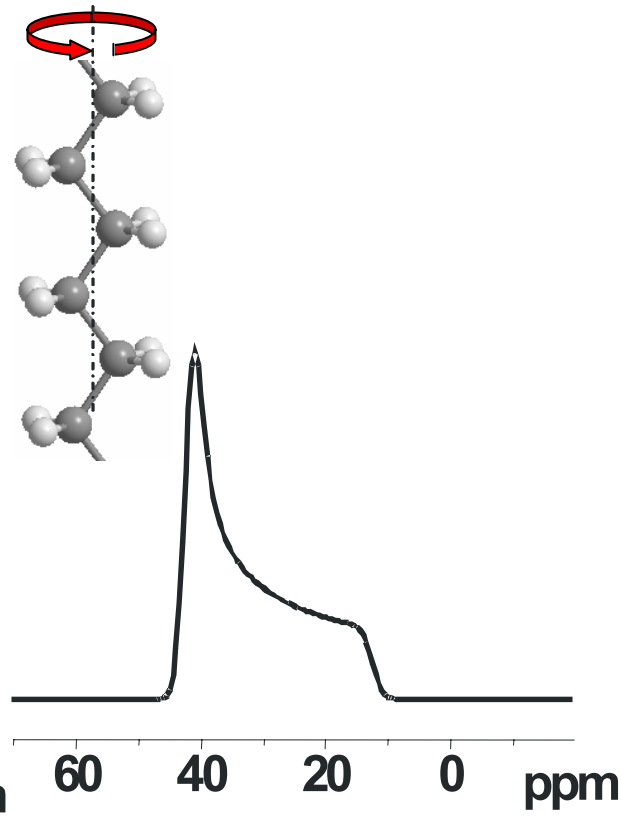
Saalwächter et al., *Solid State NMR* ,**22**, 154 (2002).

Chemical Shift Anisotropy Pattern

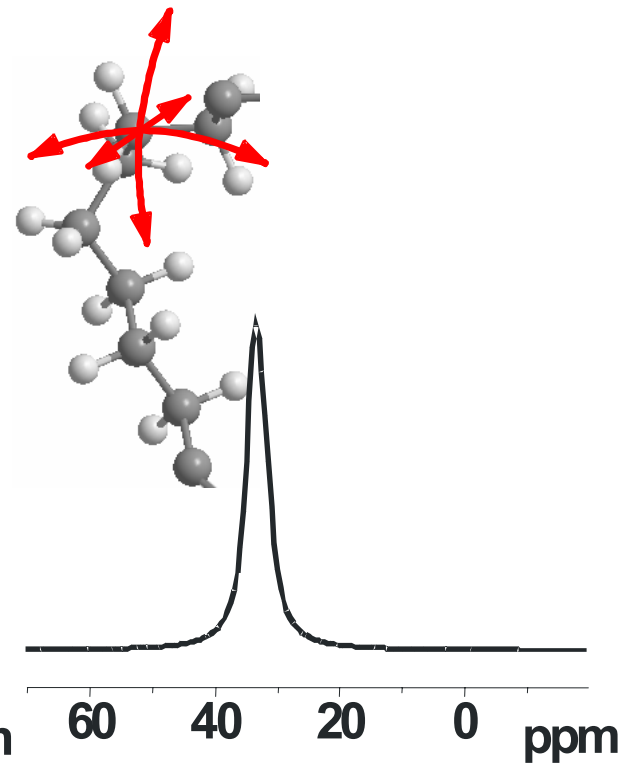
180° hopping



axial rotation



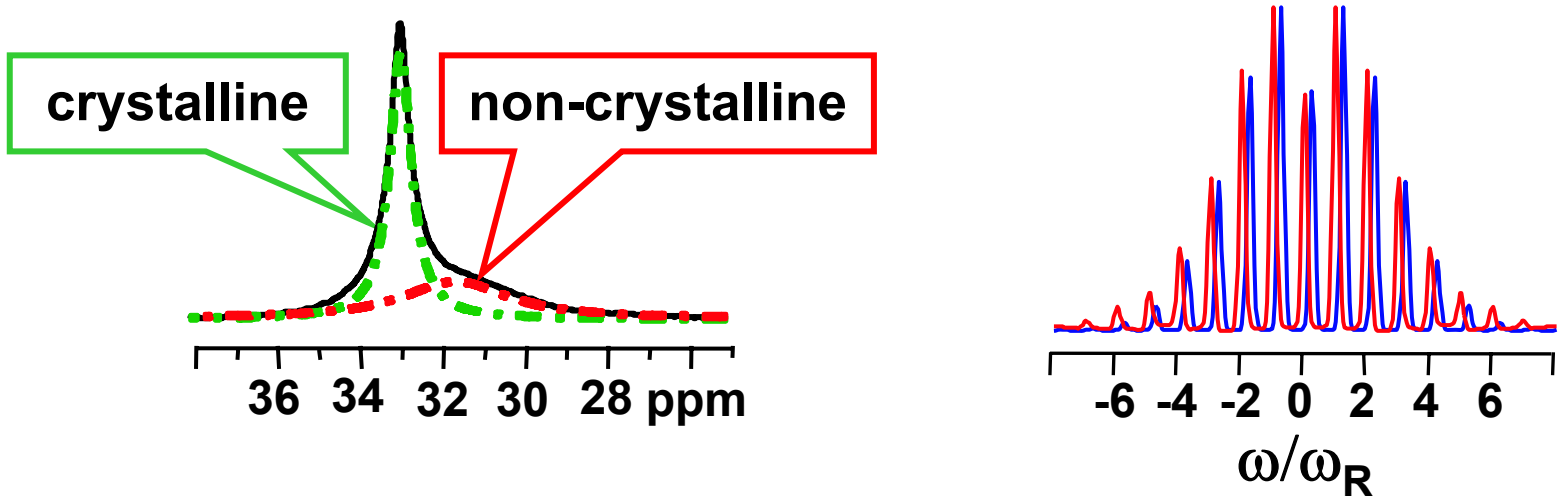
isotropic motion



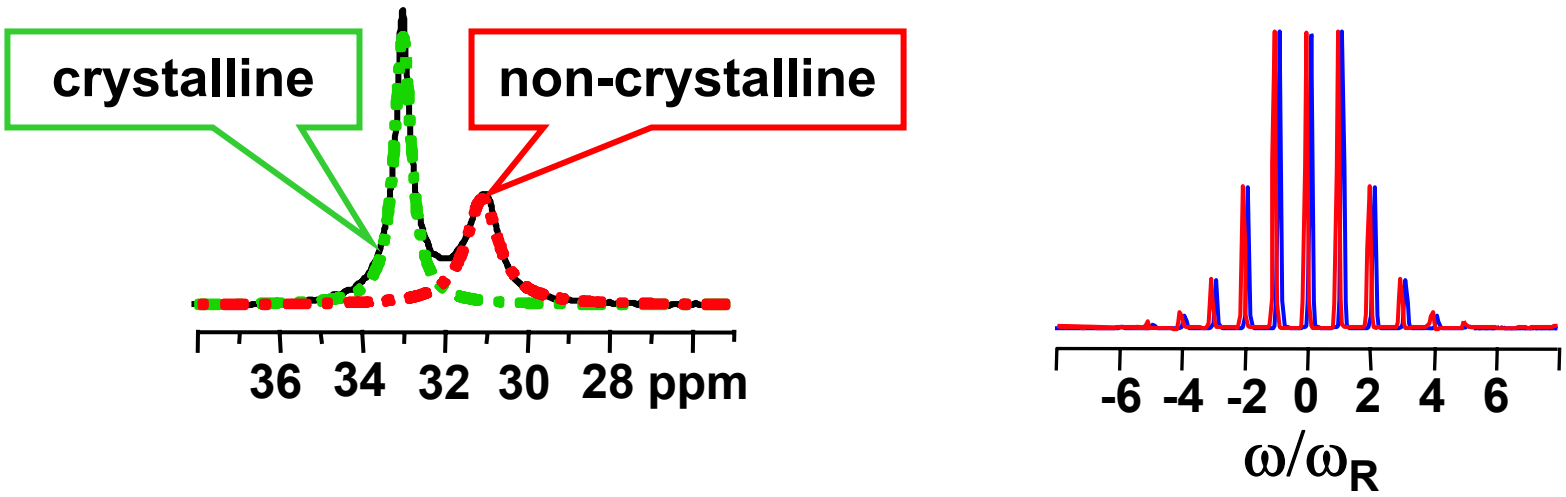
Liu et al., *J. Magn. Reson.* ,**155**, 15 (2002).

Morphology and Chain Dynamics in PE

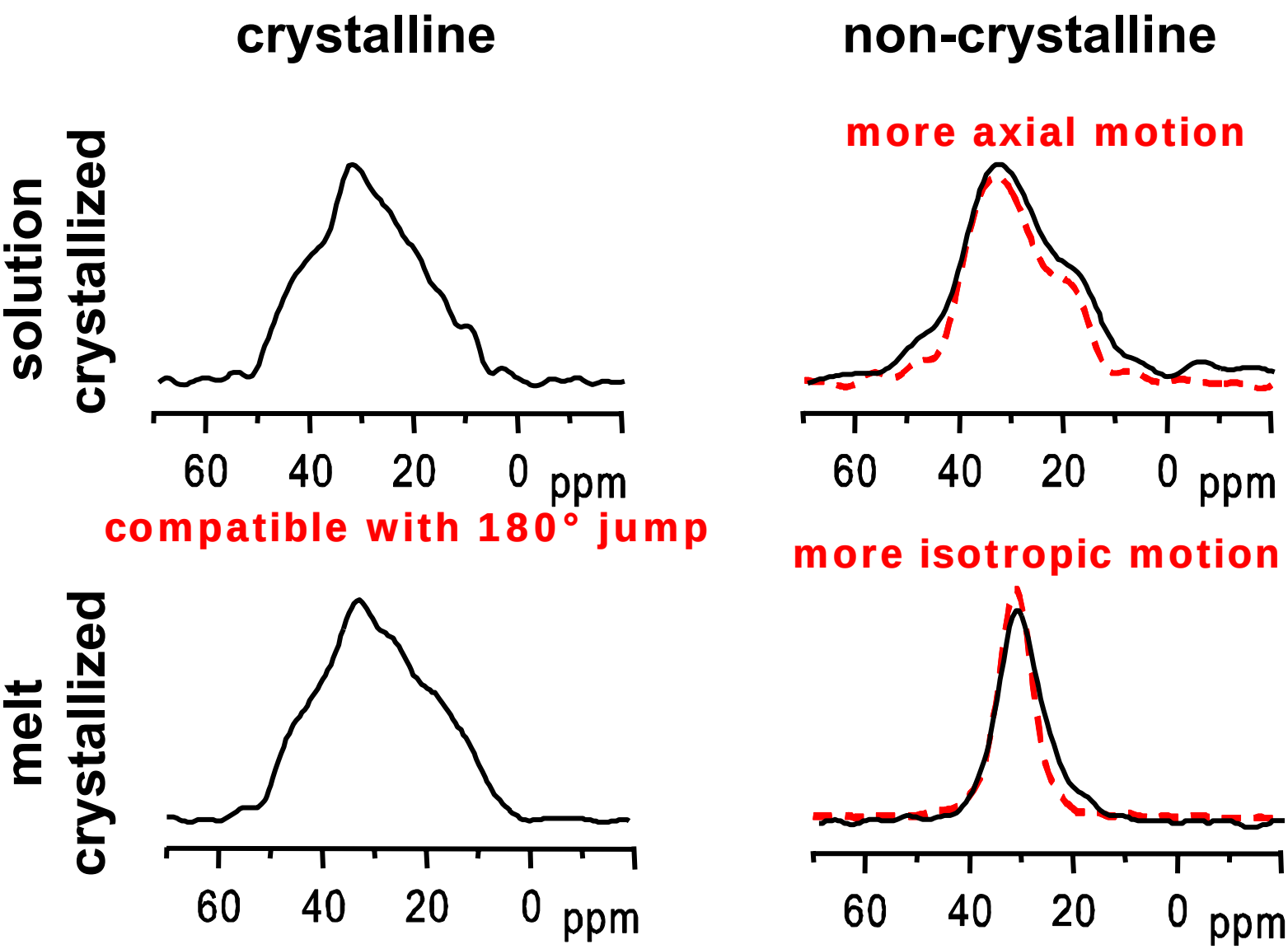
solution crystallized ultra high molecular weight PE



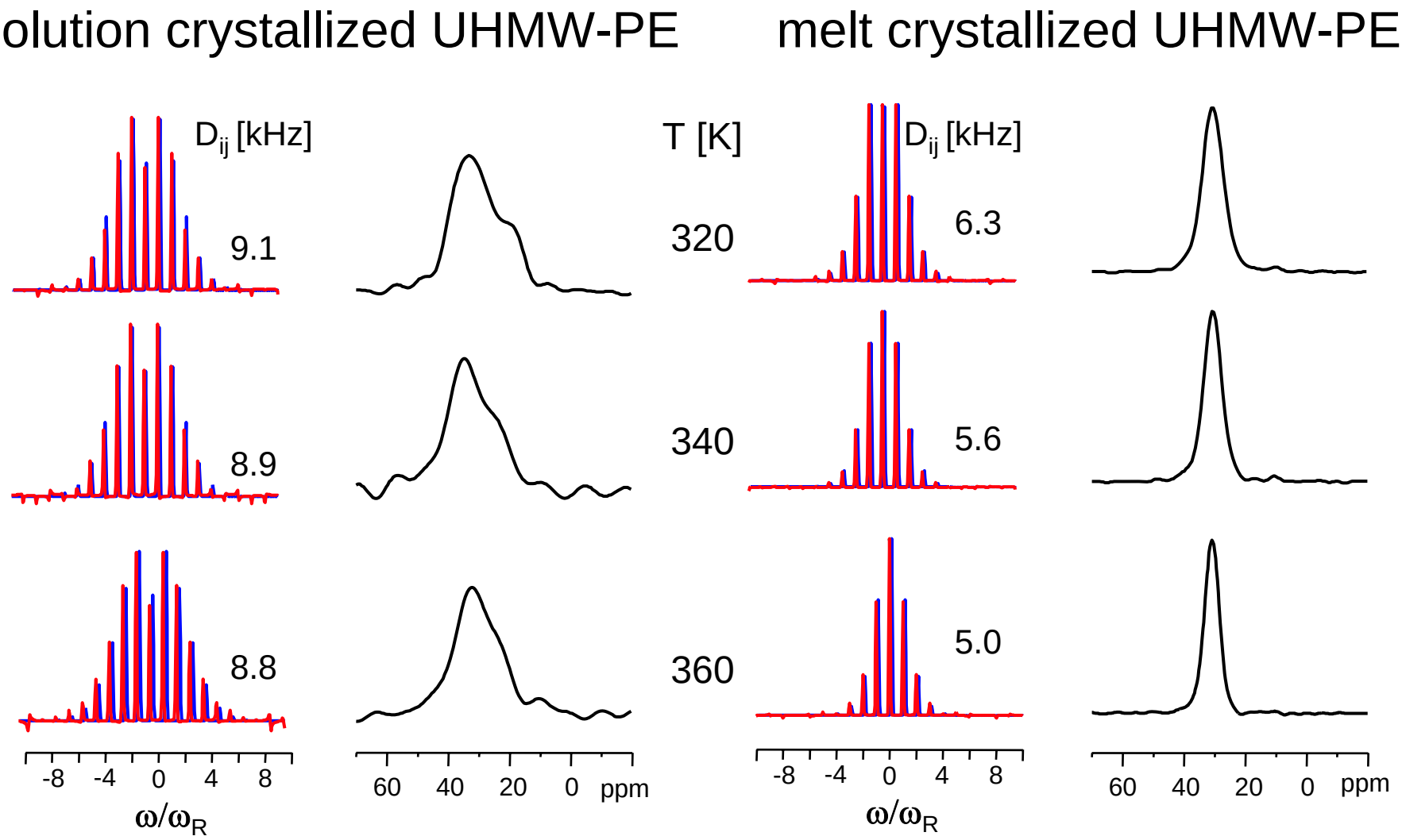
melt crystallized ultra high molecular weight PE



^{13}C Chemical Shift Anisotropy



Temperature Dependence

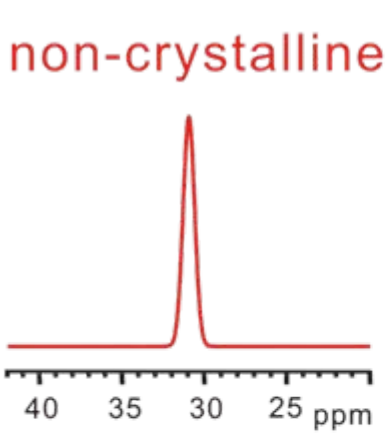


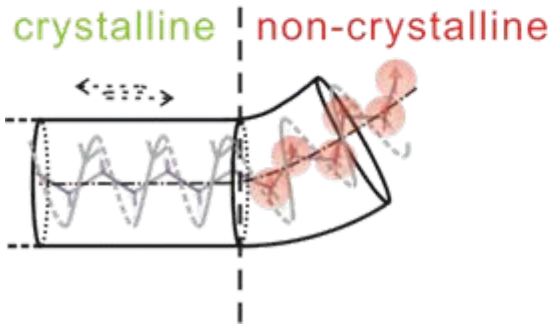
Observation and Analysis of Chain Translation Motion with ^{13}C NMR Experiments

Observation of Chain Translation

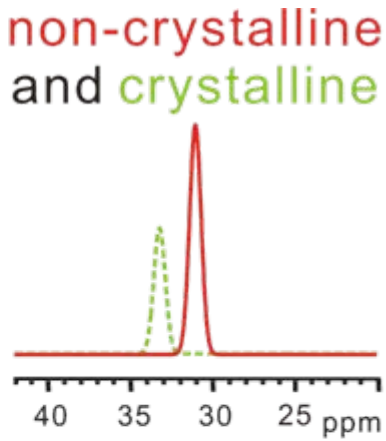
saturate ^{13}C	^{13}C relaxation / chain diffusion	acquisition

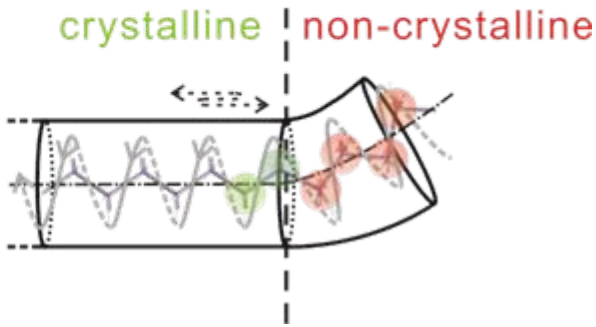
t ≈ 0



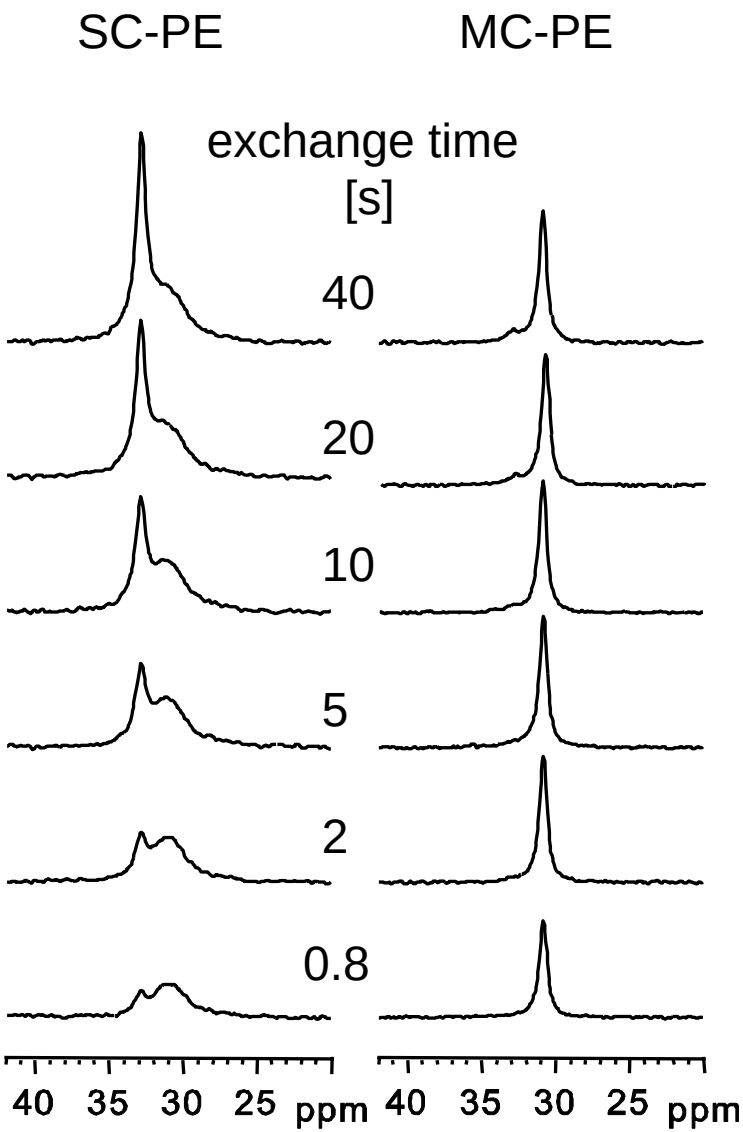


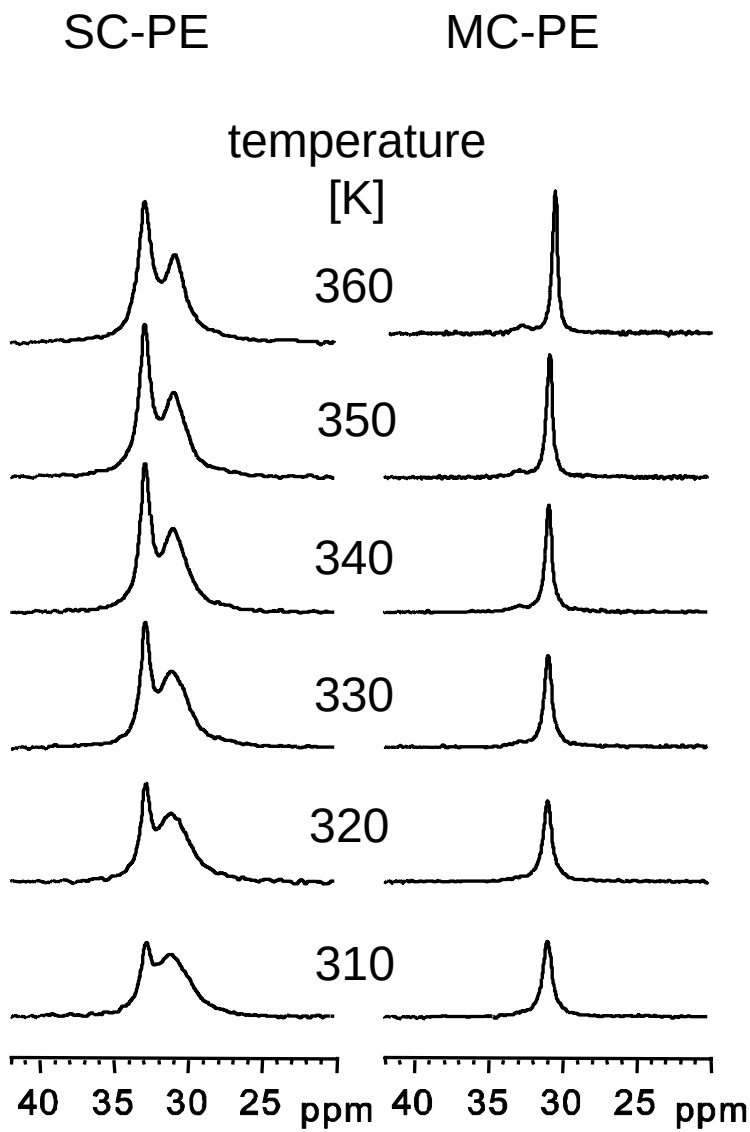
t < 0





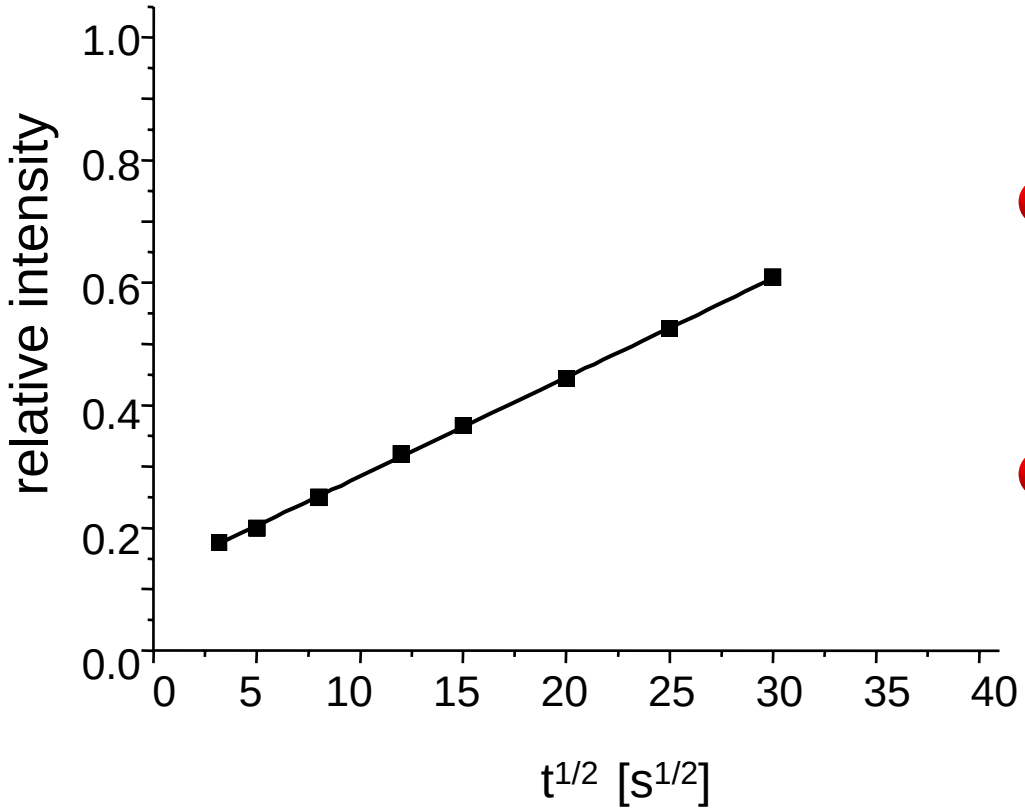
Time and Temperature Dependence





Quantification of Chain Translation

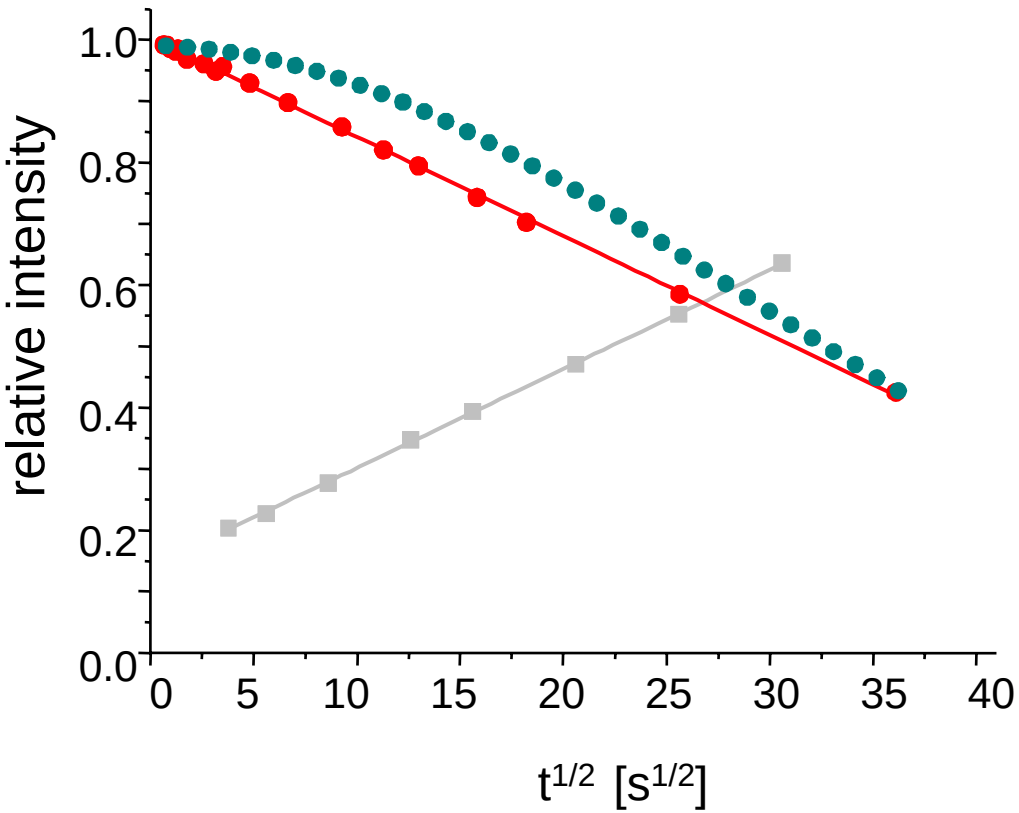
saturate ^{13}C	^{13}C relaxation / chain diffusion	acquisition



- Intensities at short times are affected by T_1 relaxation
- Normalization needs the Intensity at infinit diffusion time.

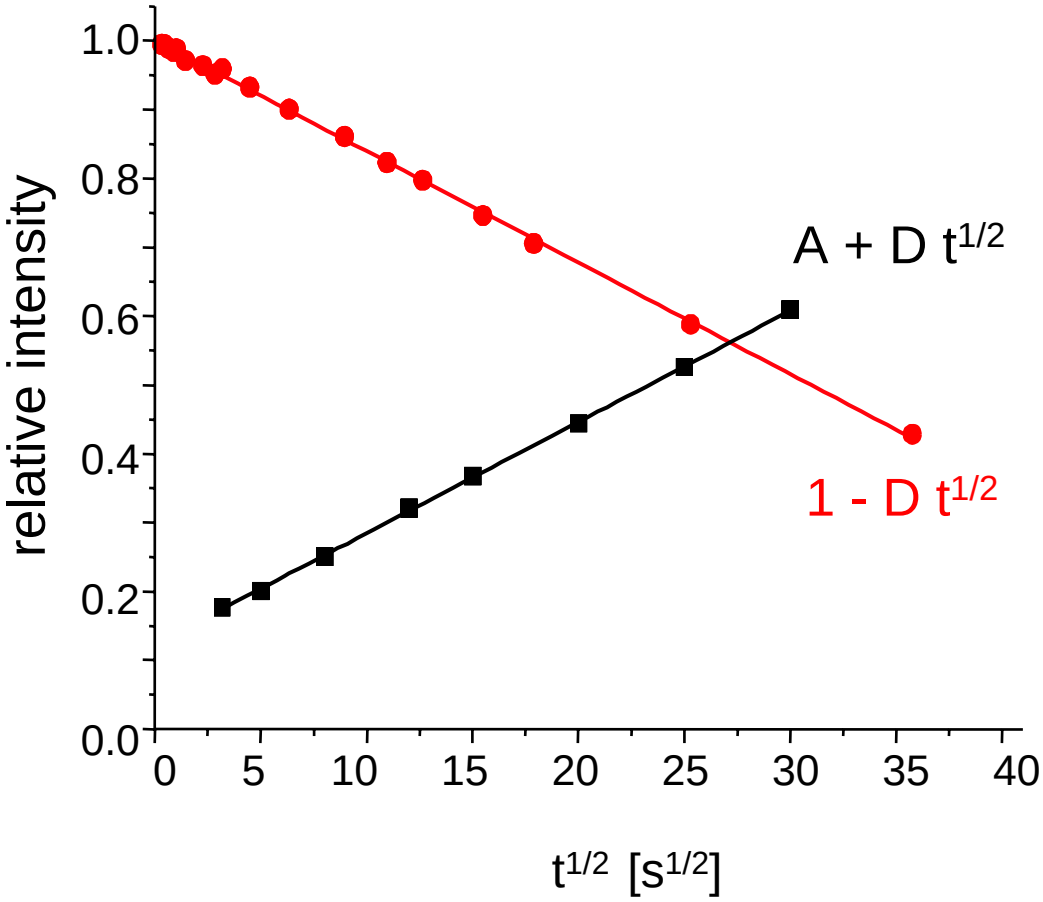
Quantification of Chain Translation

selective ^{13}C polarization	chain diffusion	acquisition



- ~~Intensities at short times are affected by T_1 relaxation~~
- ~~Normalization needs the Intensity at infinit diffusion time~~
- Non-exponential signal decay does not originate from T1 relxation

Determination of NMR Crystallinity

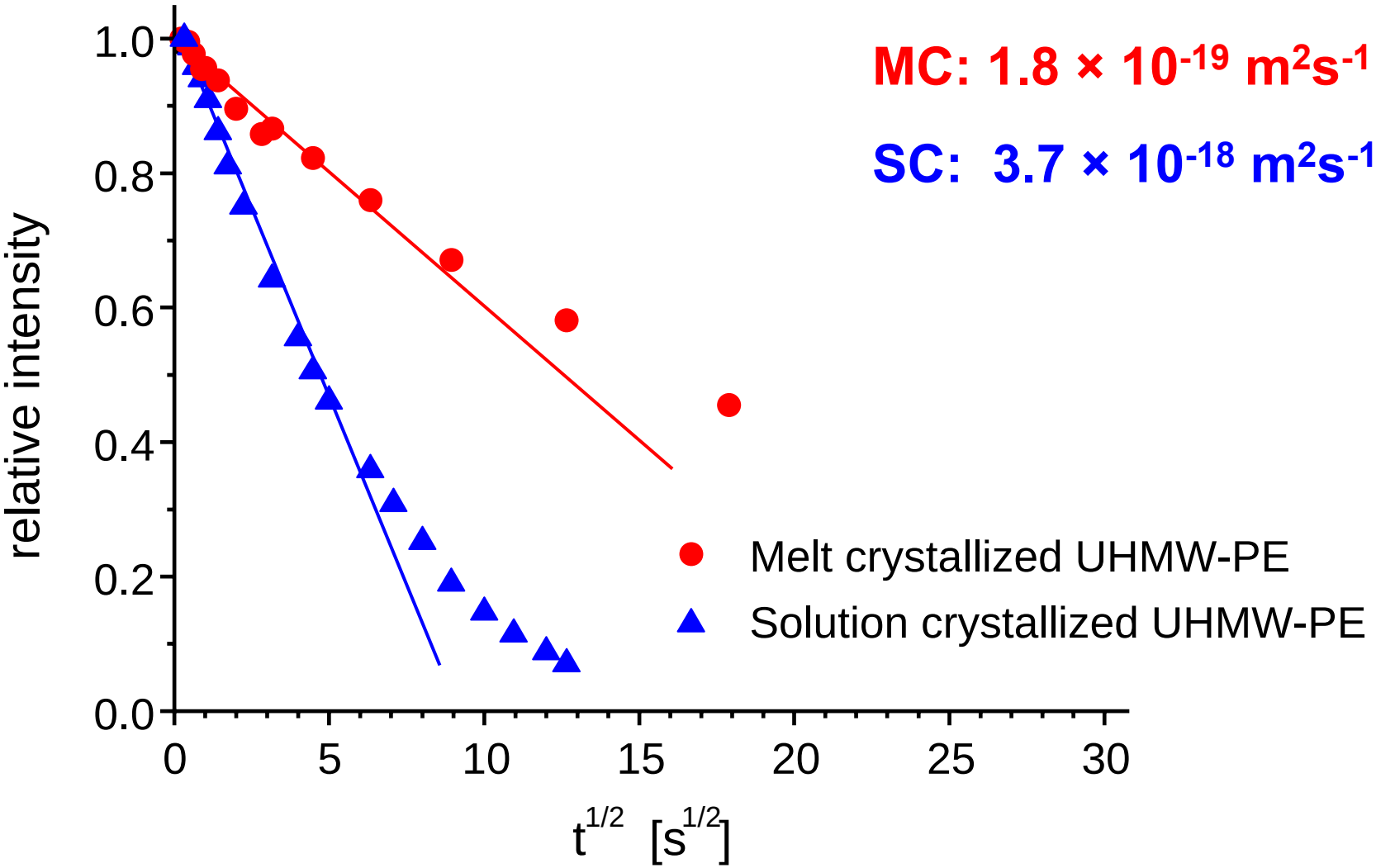


crystallinity C:

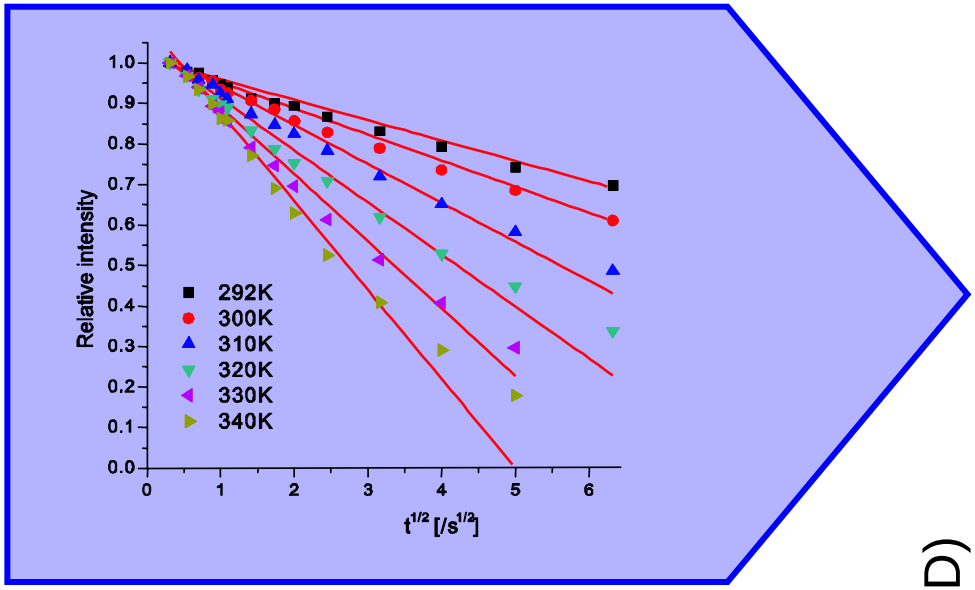
$C = 1 / (A+1)$

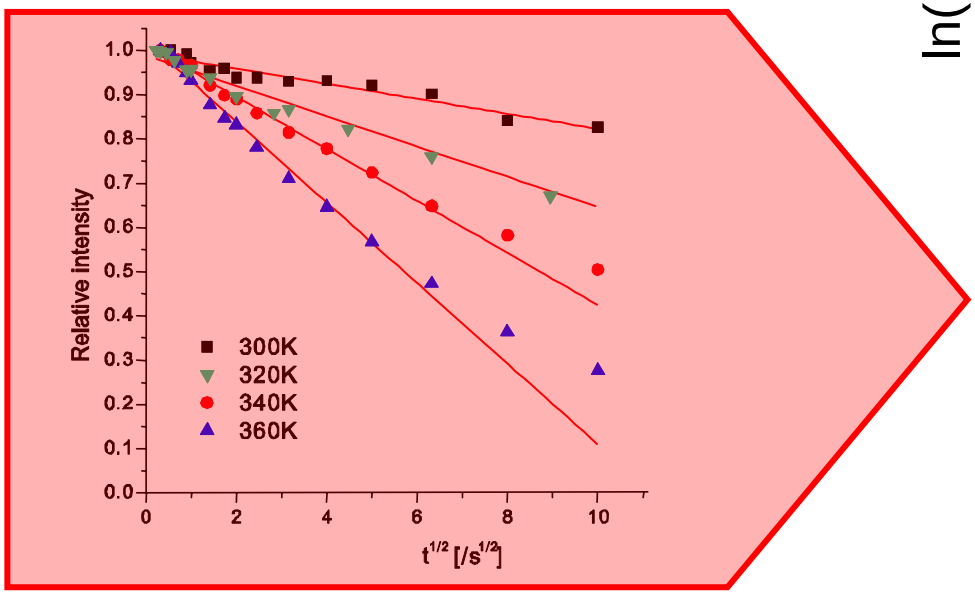
	x-ray	NMR
MC	39%	46%
SC	74%	75%
fiber	95%	90%

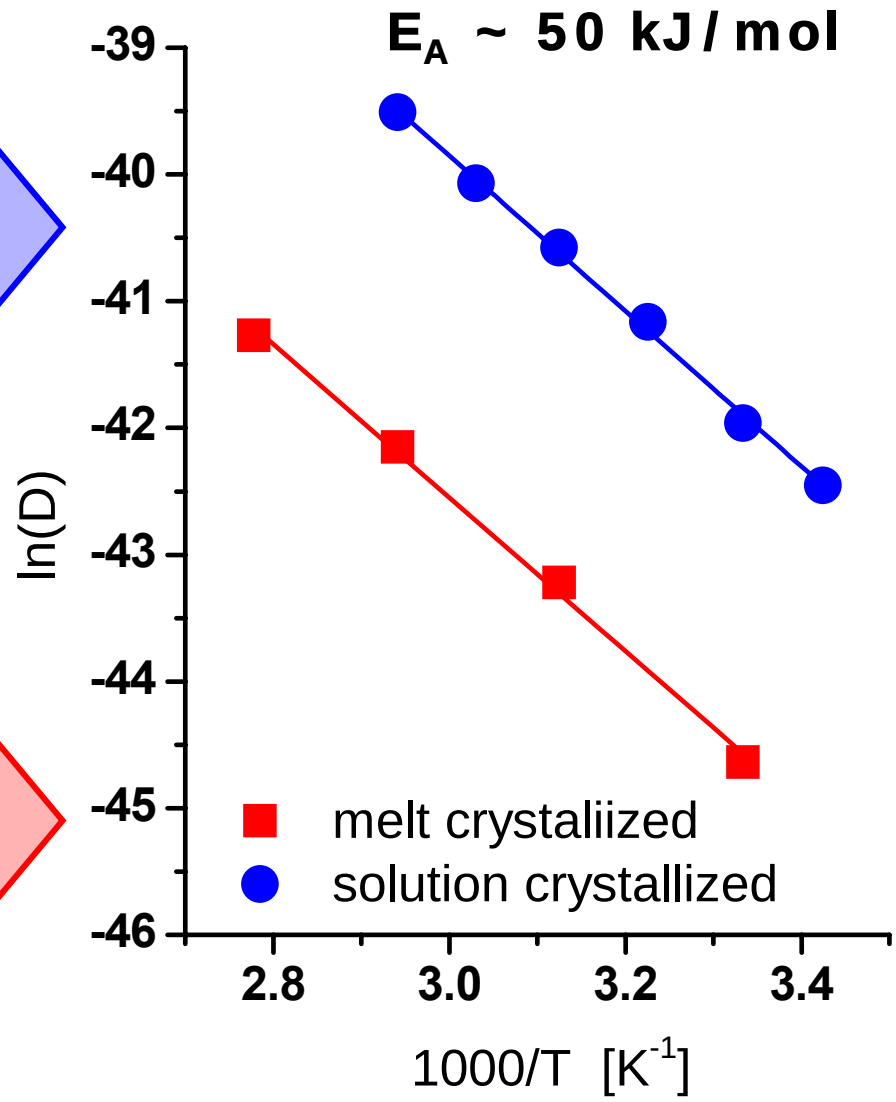
Chain Diffusion in Polyethylene



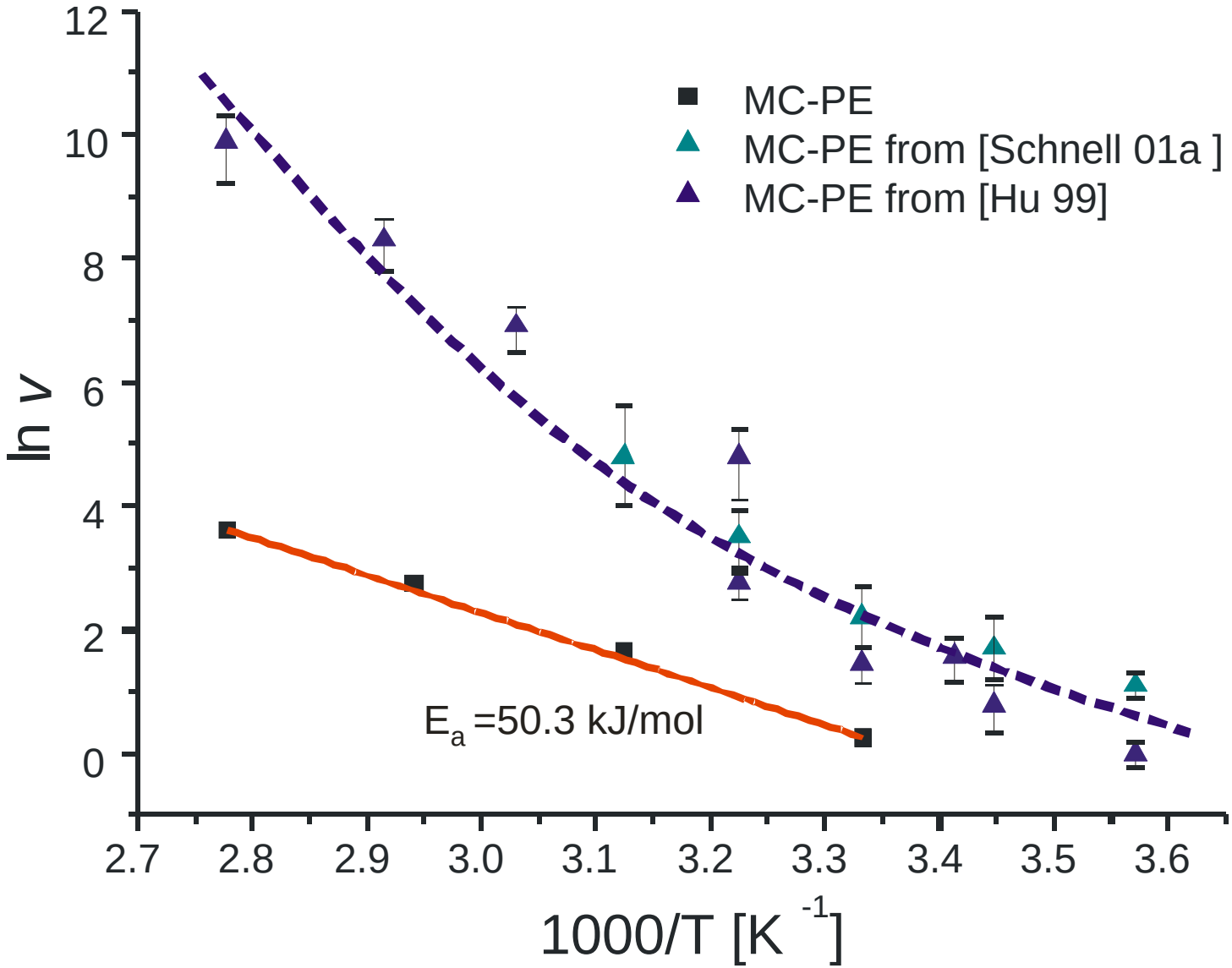
Activation Energy of Chain Motion



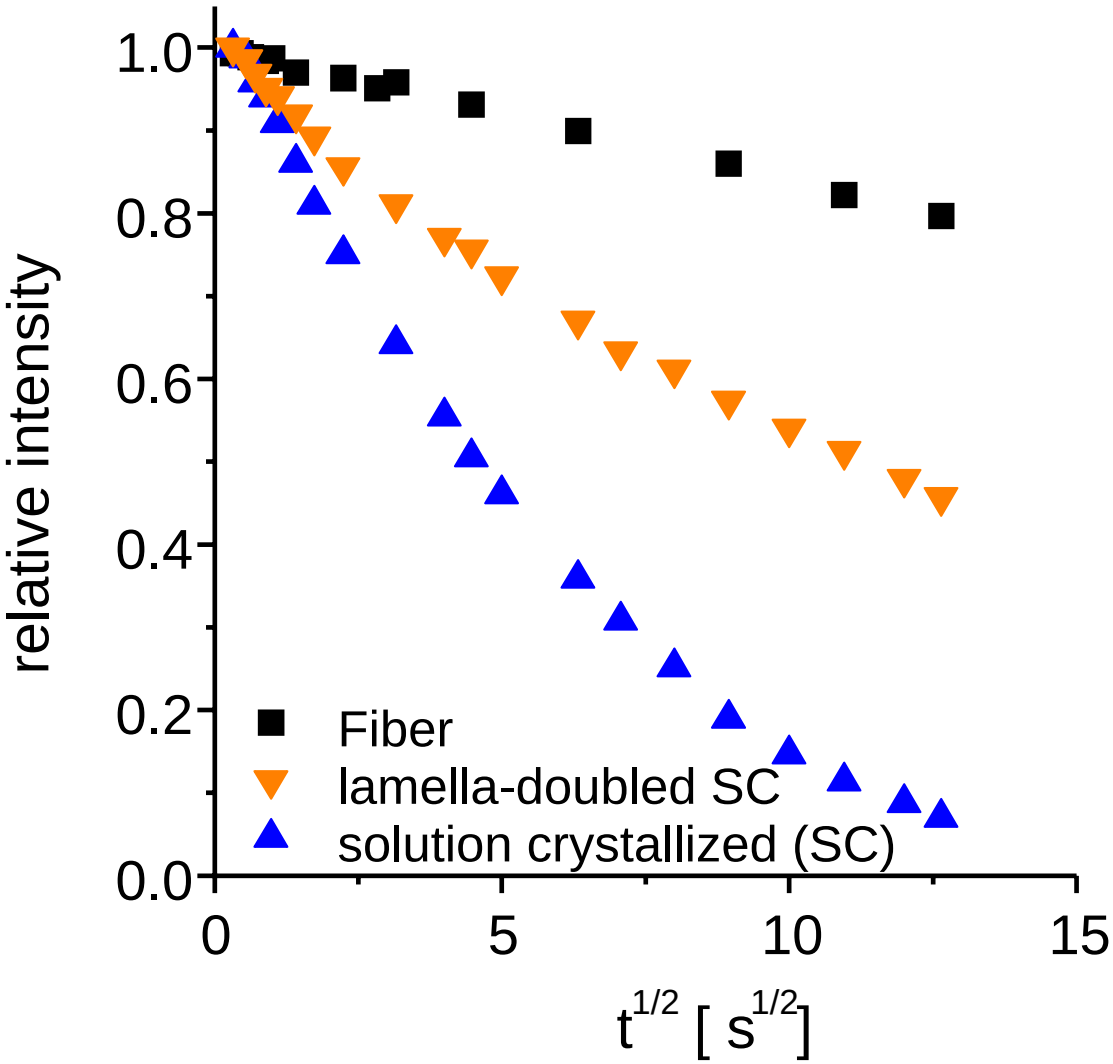




Chain Diffusion vs Local Jump Rate



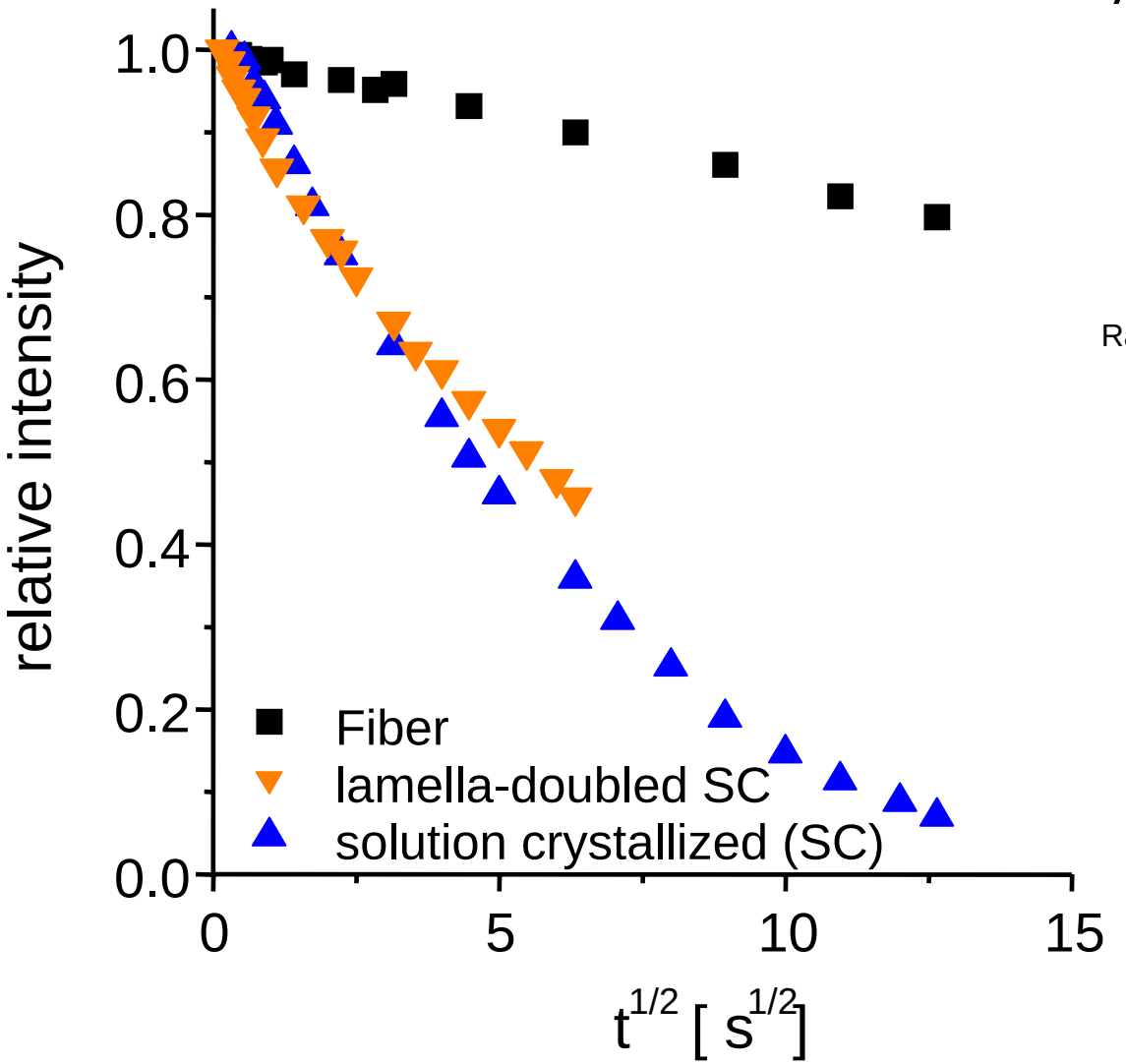
Variation of Lamellar Thickness



Annealing lamellar, solution crystallized polyethylene close to the melting point leads to lamellar doubling.

Rastogi et al, *Macromolecules* **30**, 7880 (1997).

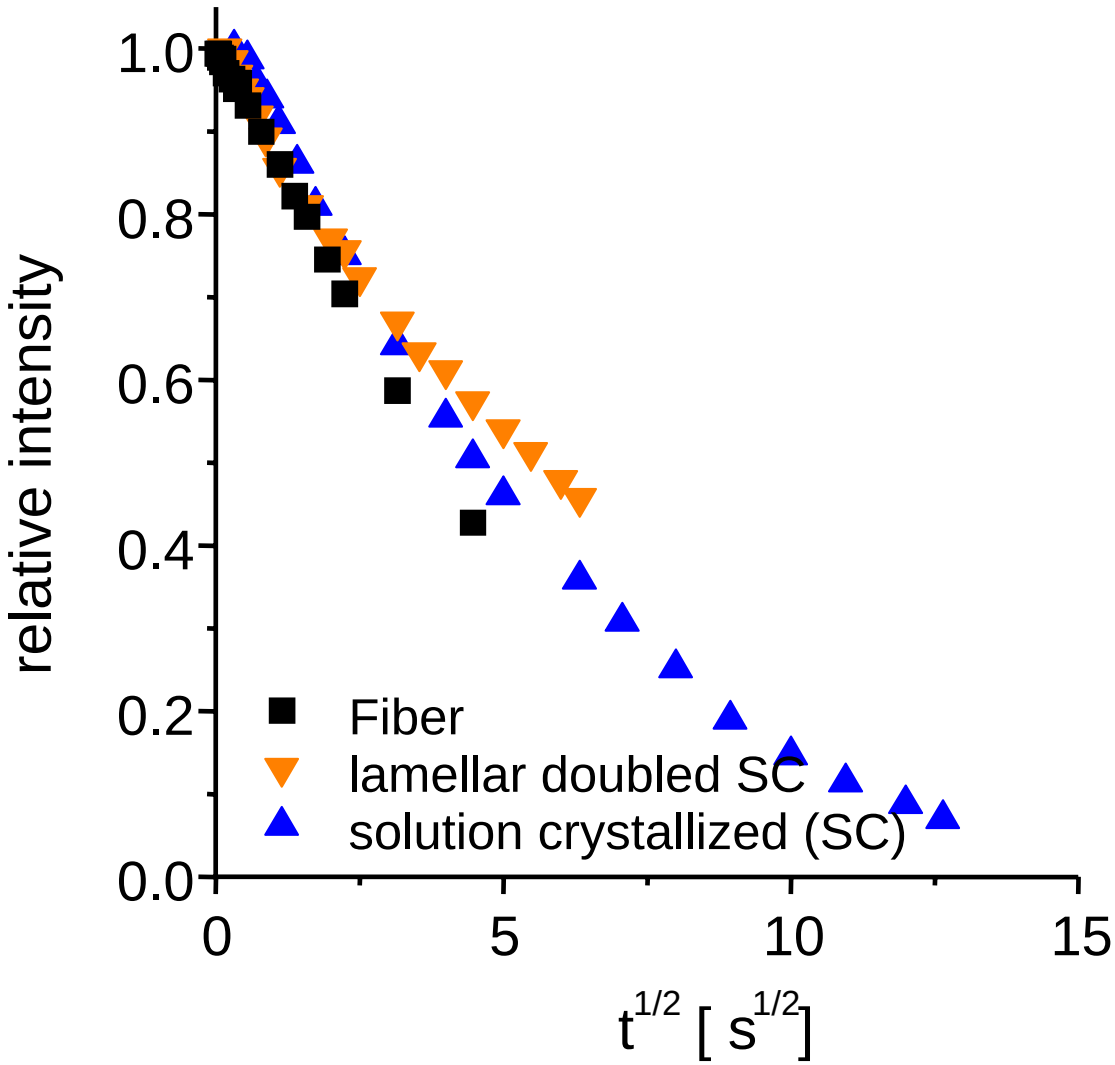
Variation of Lamellar Thickness



Annealing lamellar, solution crystallized polyethylene close to the melting point leads to lamellar doubling.

Rastogi et al, *Macromolecules* **30**, 7880 (1997).

Variation of Lamellar Thickness



Annealing lamellar, solution crystallized polyethylene close to the melting point leads to lamellar doubling.

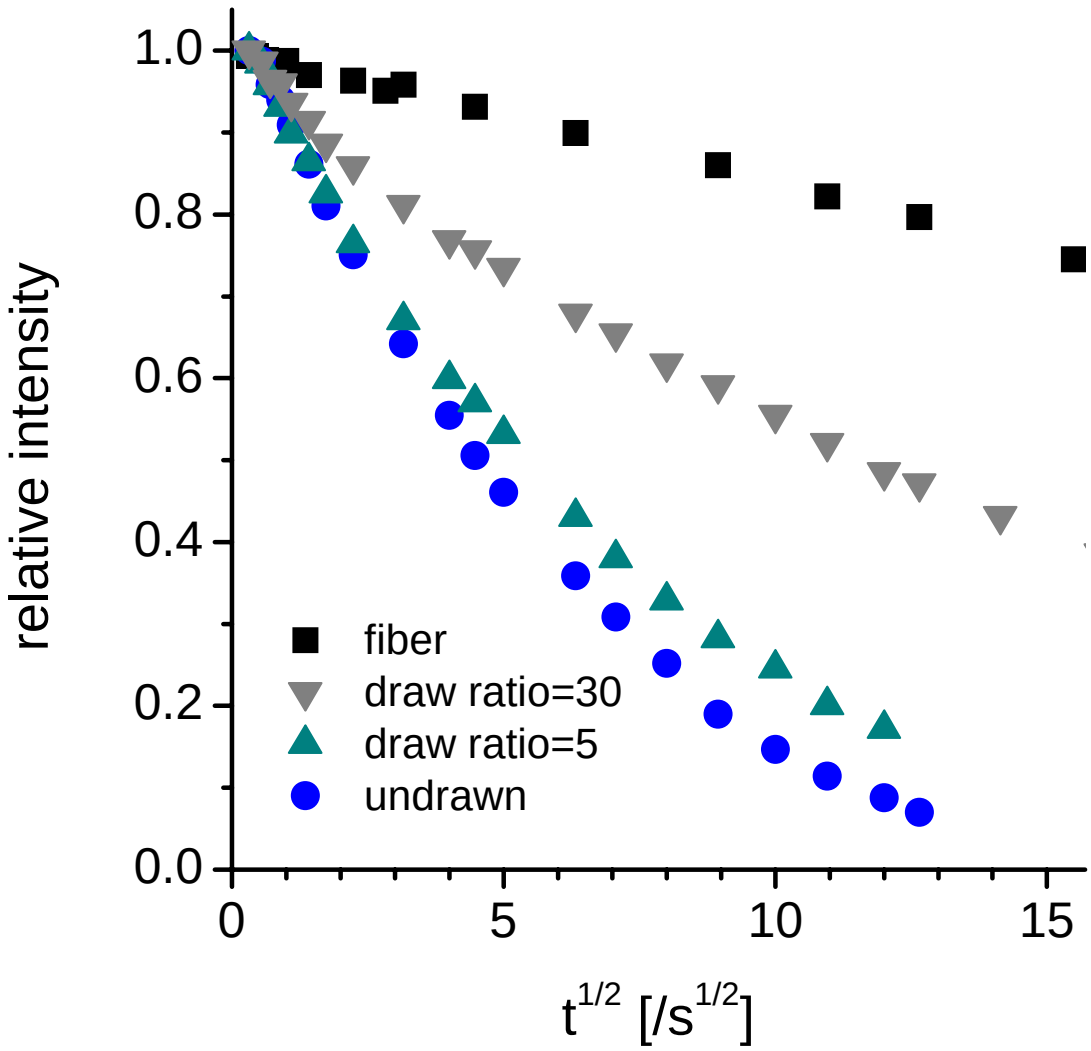
Rastogi et al, *Macromolecules* **30**, 7880 (1997).

time dependence of chain diffusion in the fiber sample

~ 100 nm

lamellar thickness.

Chain Diffusion in Drawn Samples



- Weak deformations do not change the local morphology
- Stronger deformations change the thickeness of crystalline layers

Conclusions

Anisotropic NMR Interactions in SC-PE

- highly restricted dynamics
- almost temperature independent

Observation of Chain Translation

- local chain diffusion can be observed
- (NMR) crystallinity can be determined
- studies of local structure de/formation

Acknowledgements

Max-Planck-Institut für Polymerforschung

Dr. Yefeng Yao

Prof. Dr. H.W. Spiess

University of Eindhoven

Prof. Dr. S. Rastogi

Dr. D.R. Lippits