Molecular Mobility in Polyelectrolyte Multi-Layers and Heterogeneous Polymers

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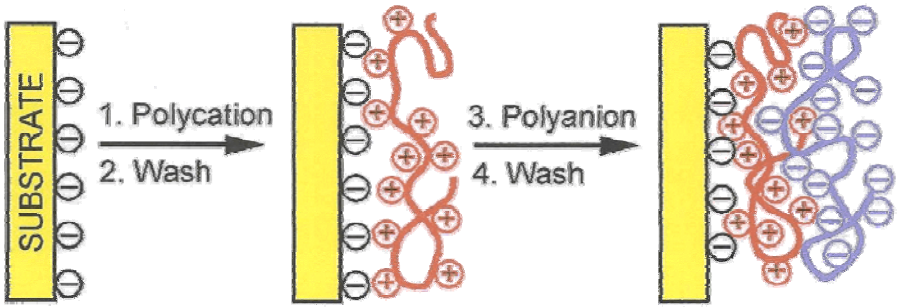
I. Polyelectrolyte multi-layers

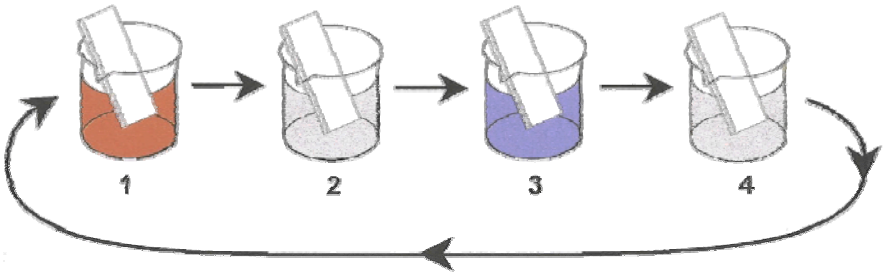
- Introduction
- Local structure of layered systems
- Polymer mobility in PEMs
- Water mobility in PEMs
- PEM Summary

II. Heterogeneous Polymers

- Poly-phenylenes with PEO sidechains
- Information from separate local field experiments
- Recoupled polarization transfer experiments
- Order-parameters from ^{1}H double quantum NMR
- Conclusions

Polyelectrolyte Multi-Layers





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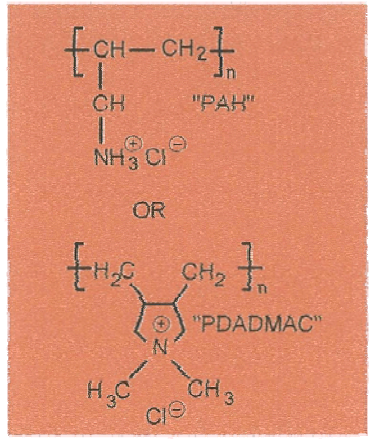

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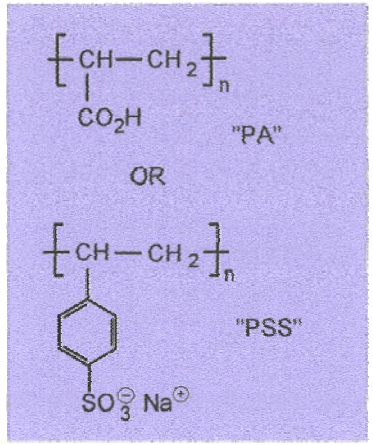
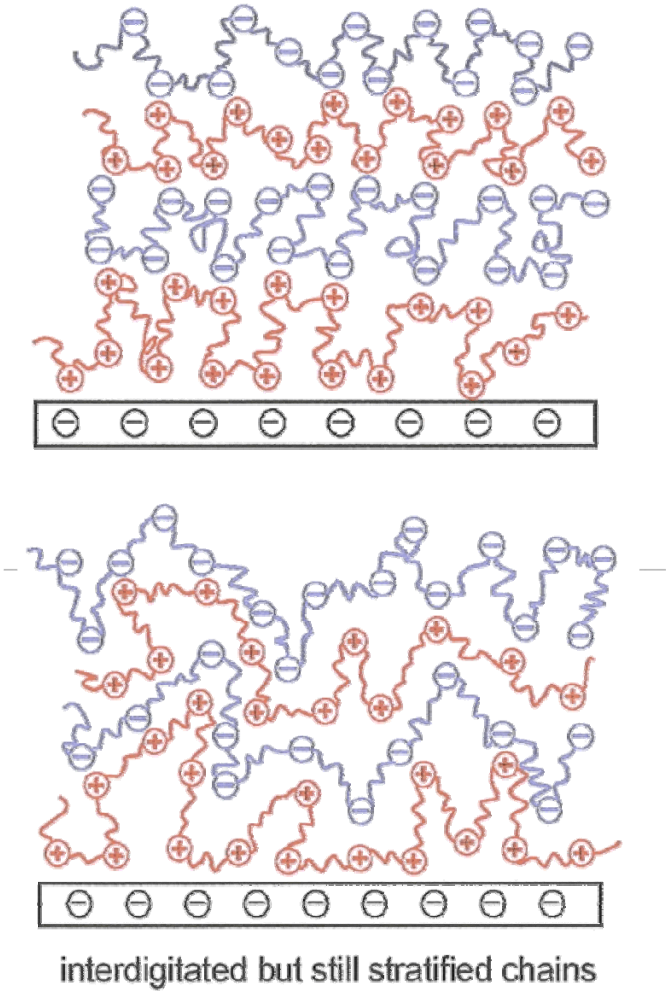
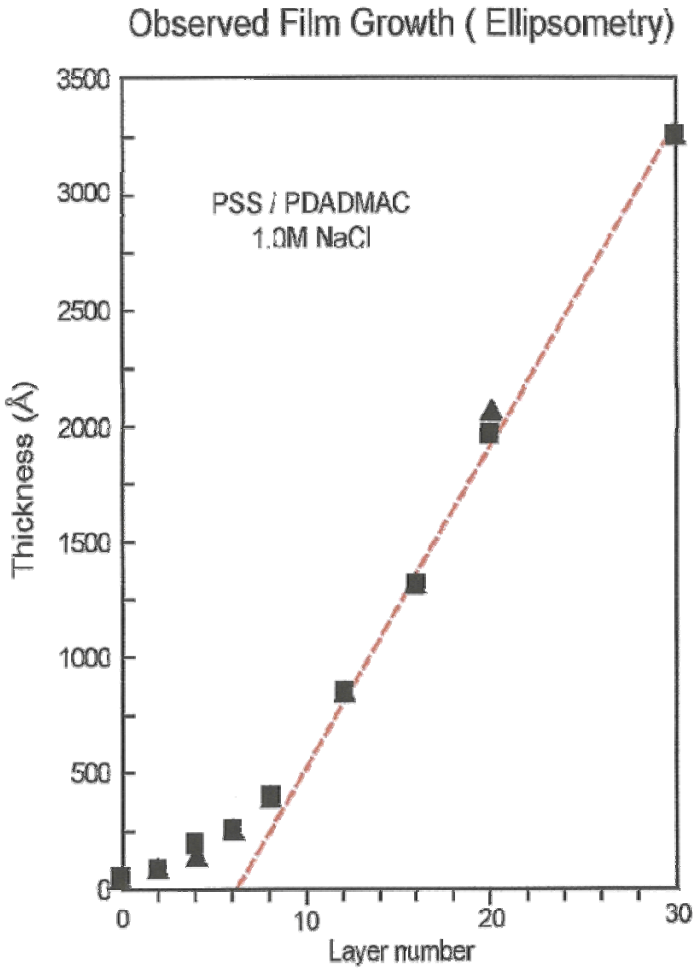


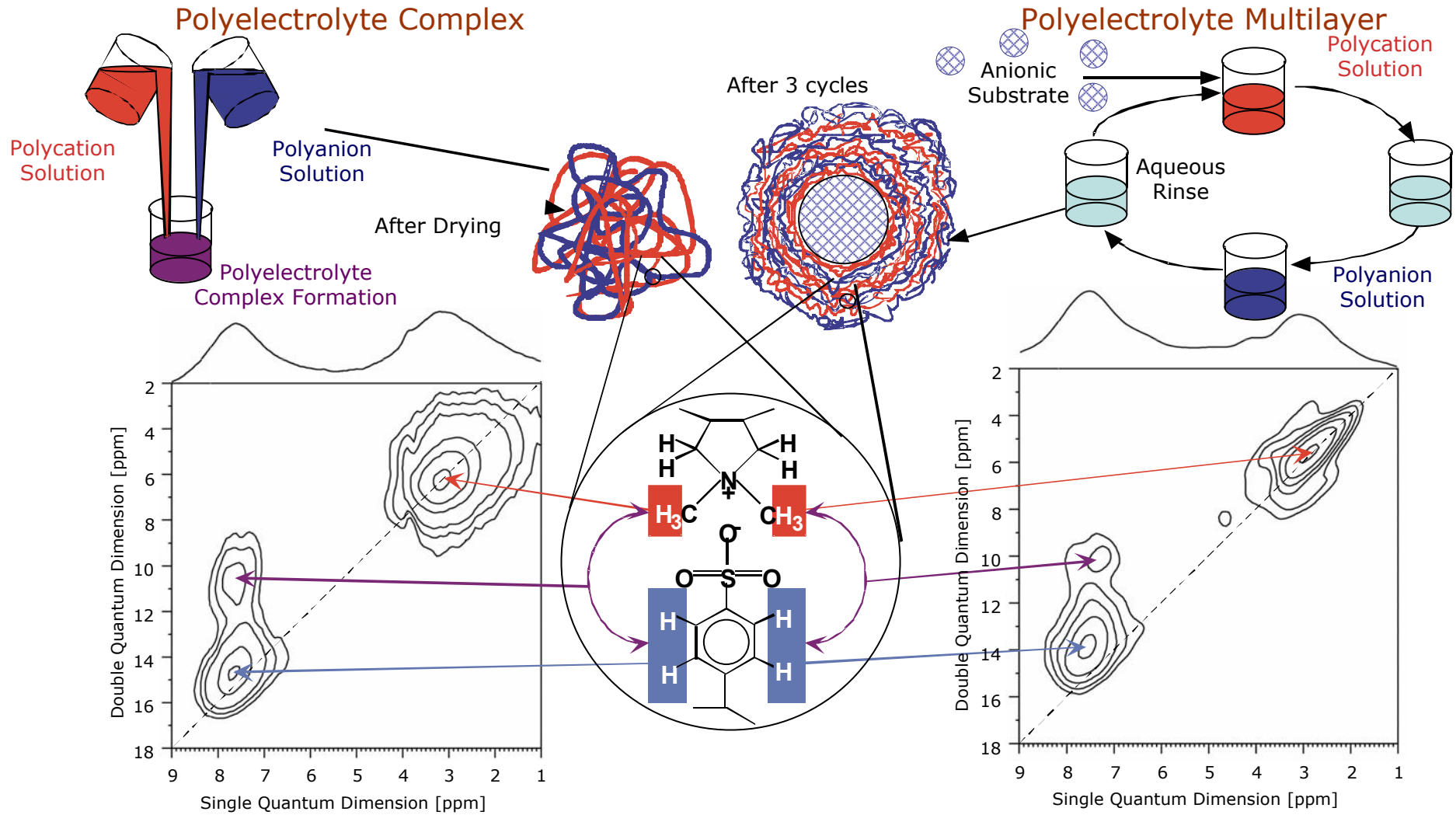
Structure of Polyelectrolyte Layers



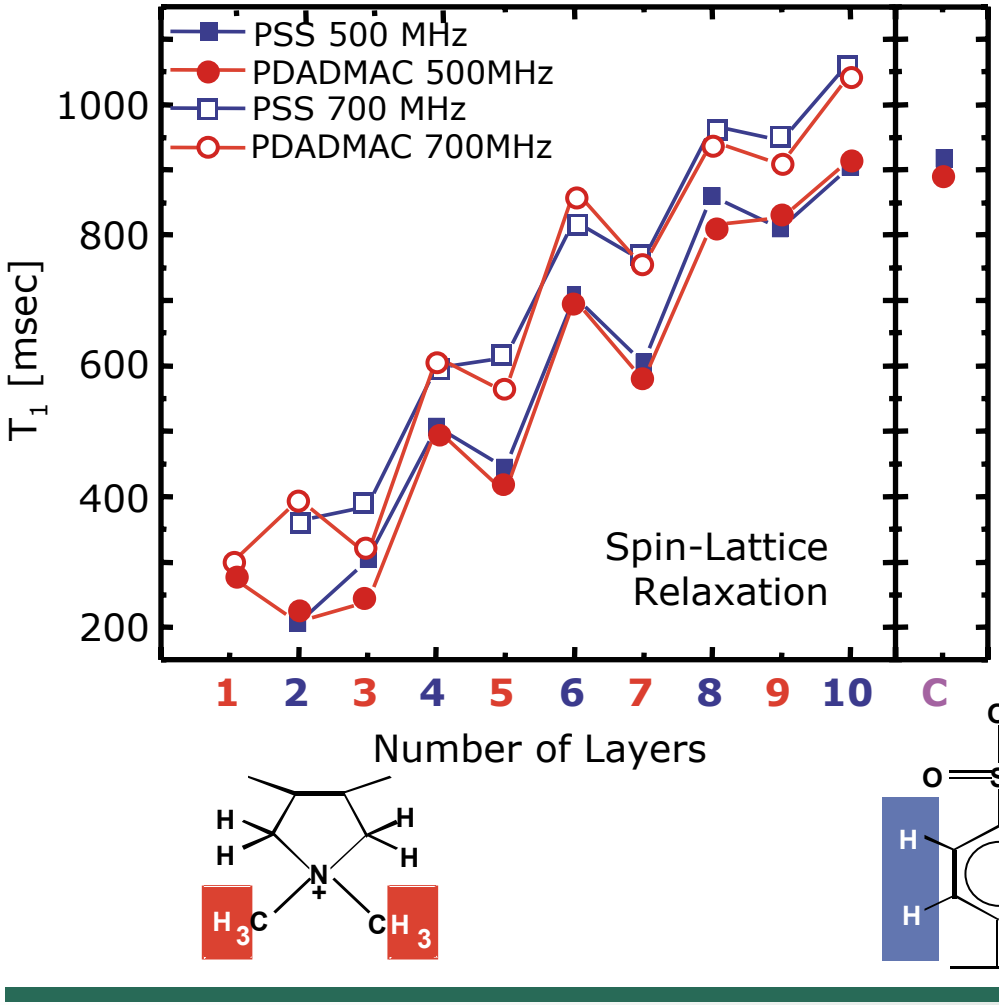
interdigitated but still stratified chains



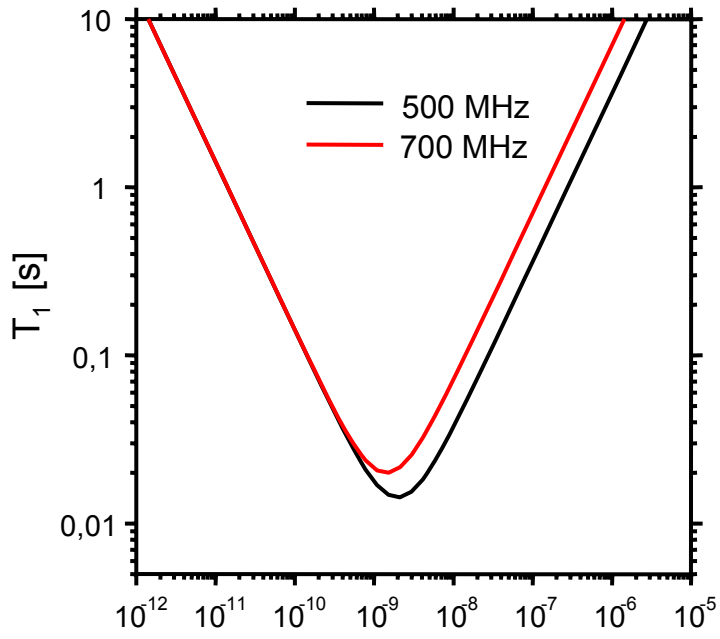
DQ NMR Investigation of Structure: PEM vs. PEC

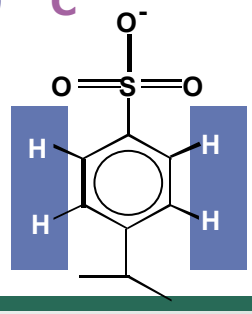


Molecular Dynamics in Polyelectrolyte Multi Layers



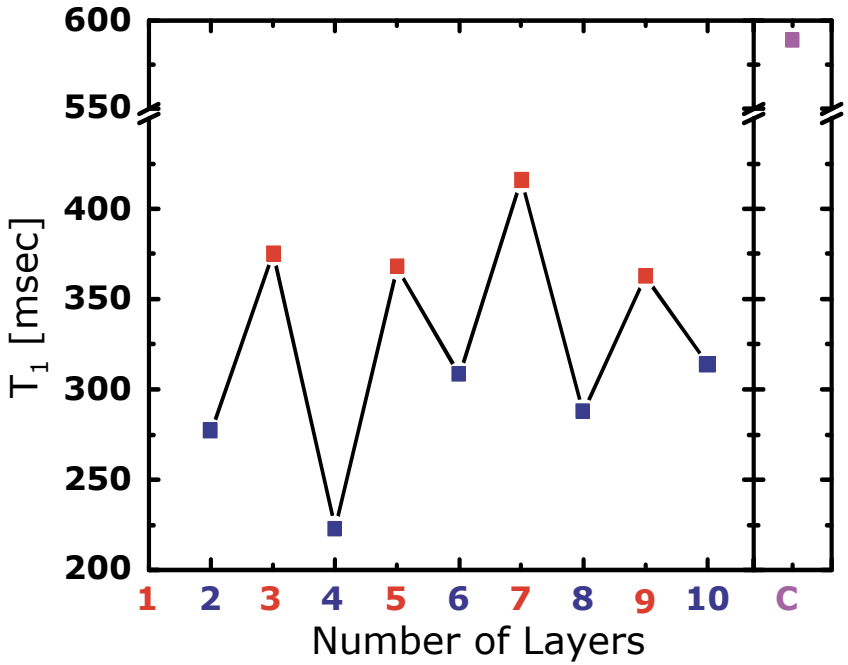
theoretical T_1 relaxation behavior:



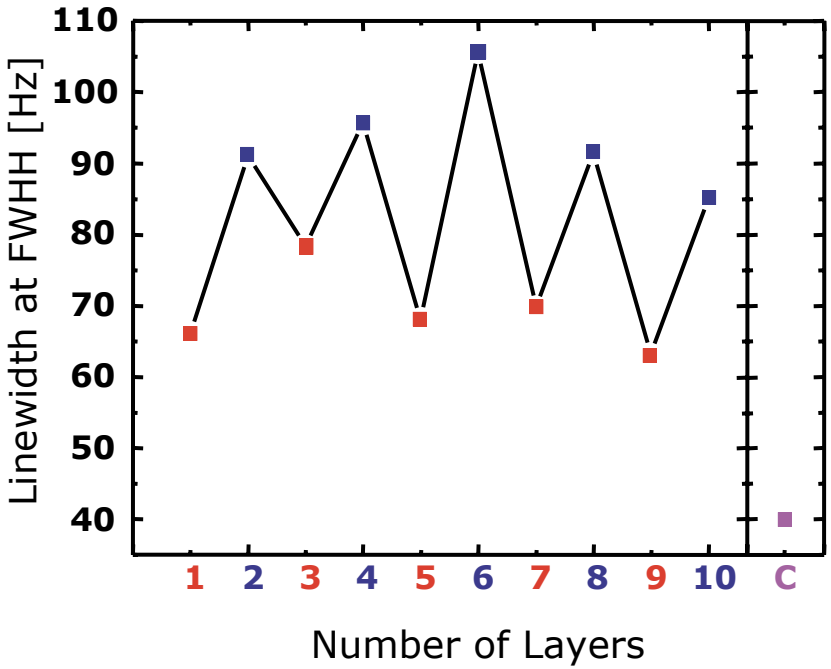


Water Mobility in Polyelectrolyte Multilayers

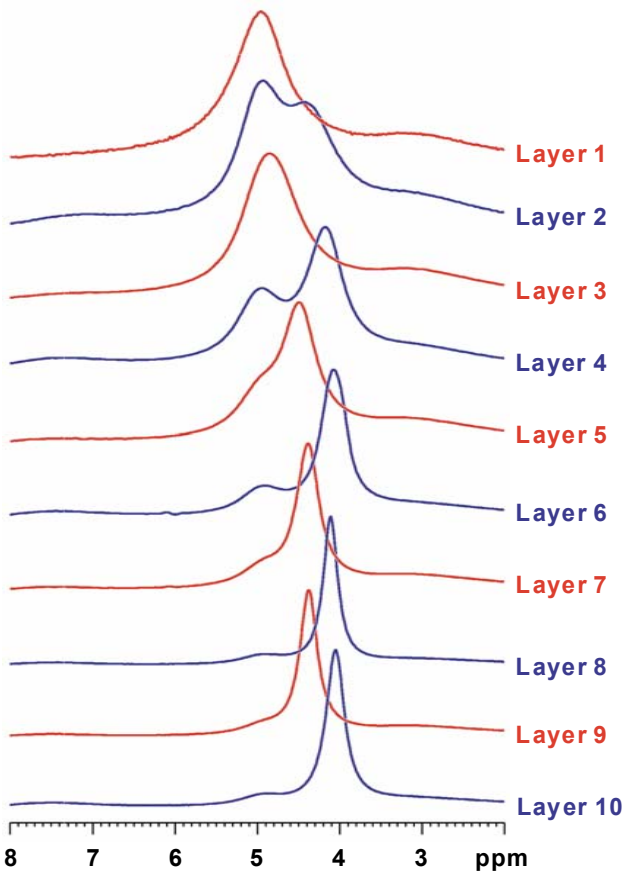
Spin-Lattice Relaxation



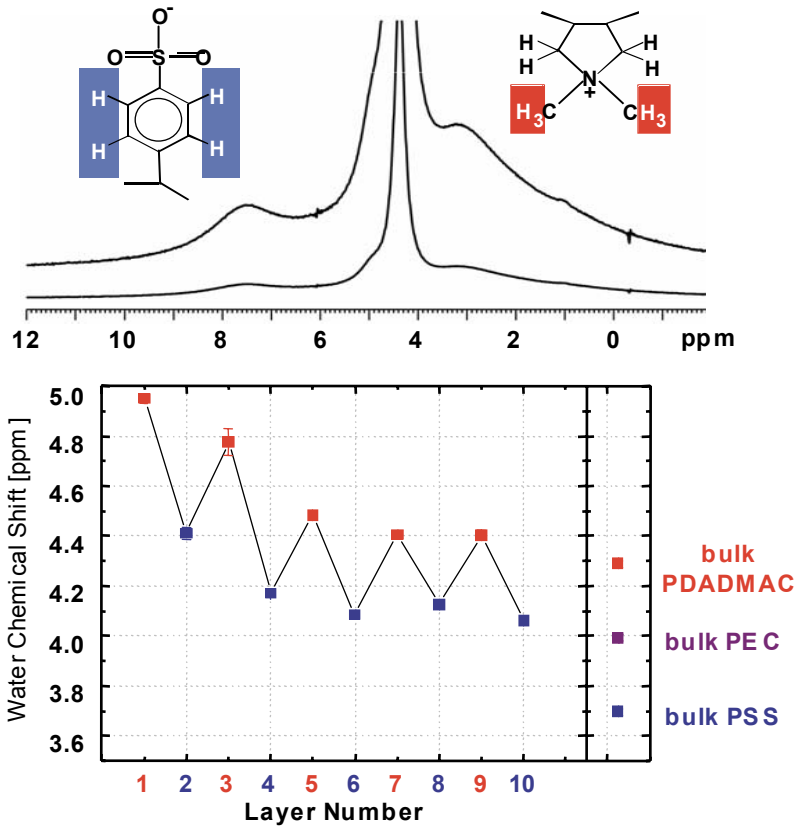
Linewidth (apparent T_2)



Localization of Water in Polyelectrolyte Multilayers



^{1}H MAS NMR Spectra



^{1}H Chemical Shift

Polyelectrolyte Multi-Layer Summary

I. Complexation:

(i) Polycation-polyanion complexation of polyelectrolyte multi-layers (PEM) is similar to that in the bulk polyelectrolyte complex (PEC).

(ii) Water-polymer association in PEMs is much stronger than in PEC.

II. Polymer Dynamics:

(i) Addition of water increases the polymer mobility in PEMs but not in the PEC.

(ii) Enhanced polymer mobility is observed for hydrated PDADMAC-capped films relative to PSS capped films.

(iii) This oscillation in the polymer mobility dampens and is superimposed on a gradient of decreasing mobility with film thickness. No changes with layer number are observed for dry films.

II. Adsorbed Water:

(i) Mobility of adsorbed water is more restricted in PEMs than in the PEC.

(ii) Water mobility is lower and water content is higher in PSS capped films as compared to PDADMAC capped PEMs.

(iii) ^{1}H NMR peak intensity increases monotonically and its chemical shift oscillates between the PEC bulk and the bulk PDADMAC value.

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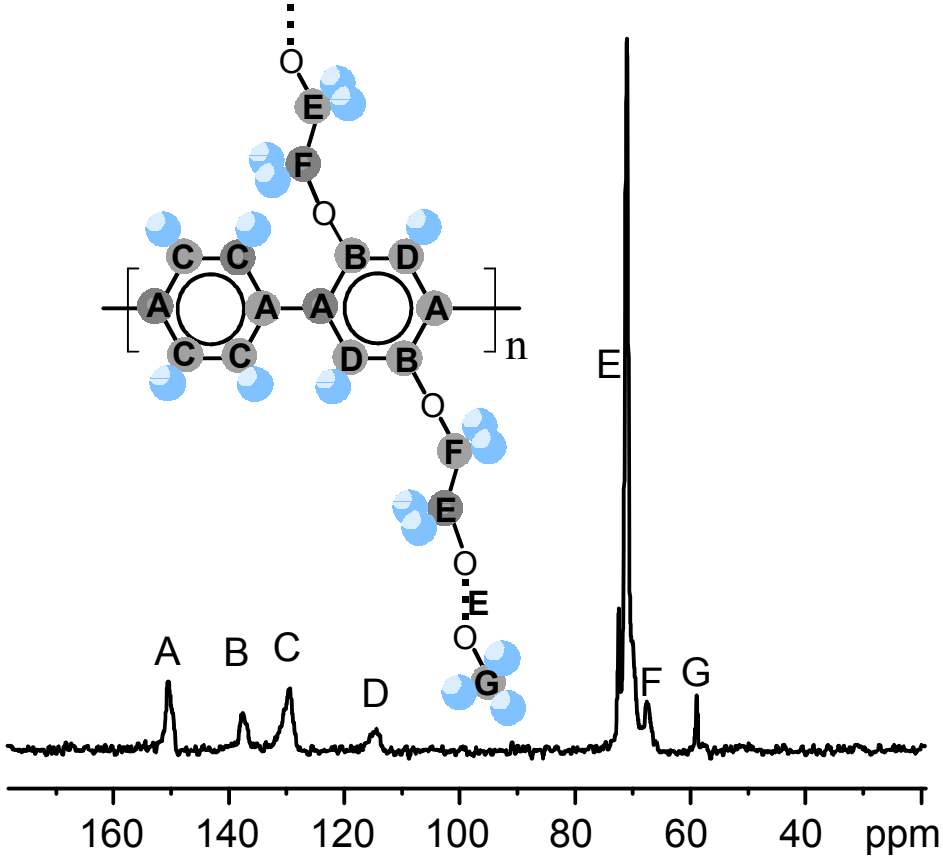
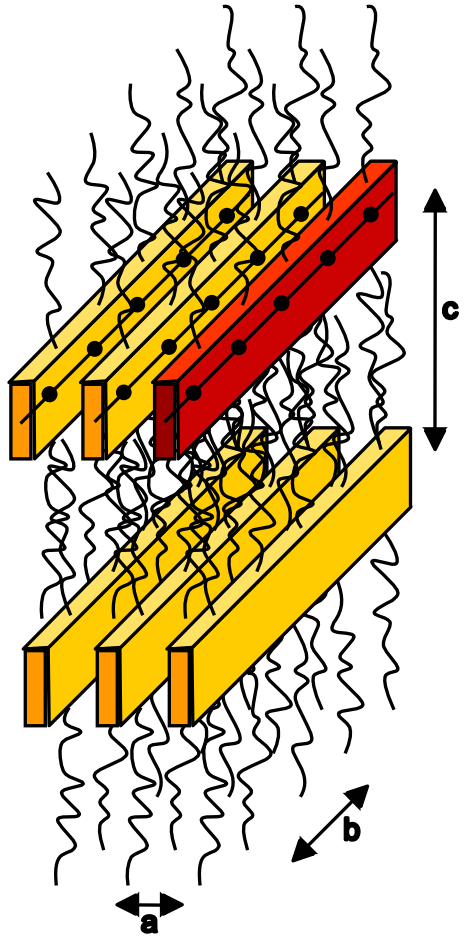
- *Introduction*
- *Local structure of layered systems*
- *Polymer mobility in PEMs*
- *Water mobility in PEMs*
- *PEM Summary*

II. Heterogeneous Polymers

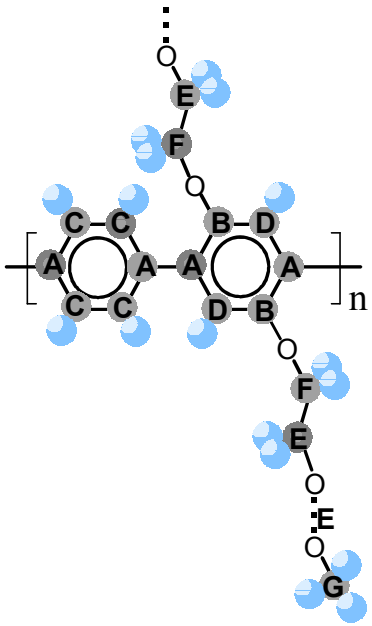
- ***Poly-phenylenes with PEO sidechains***
- ***Information from separate local field experiments***
- ***Recoupled polarization transfer experiments***
- ***Order-parameters from ^{1}H double quantum NMR***
- ***PP-PEO Summary***

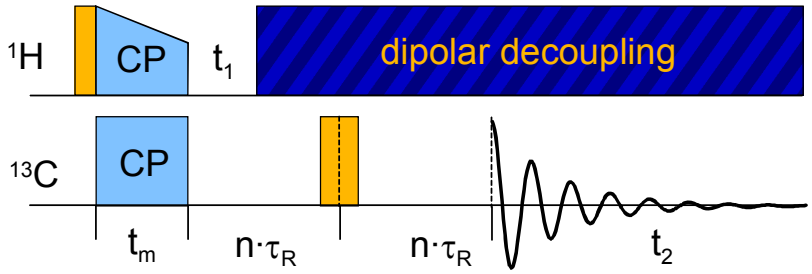
NMR Investigation of Moelcular Dyamics in $PPPEO_4$

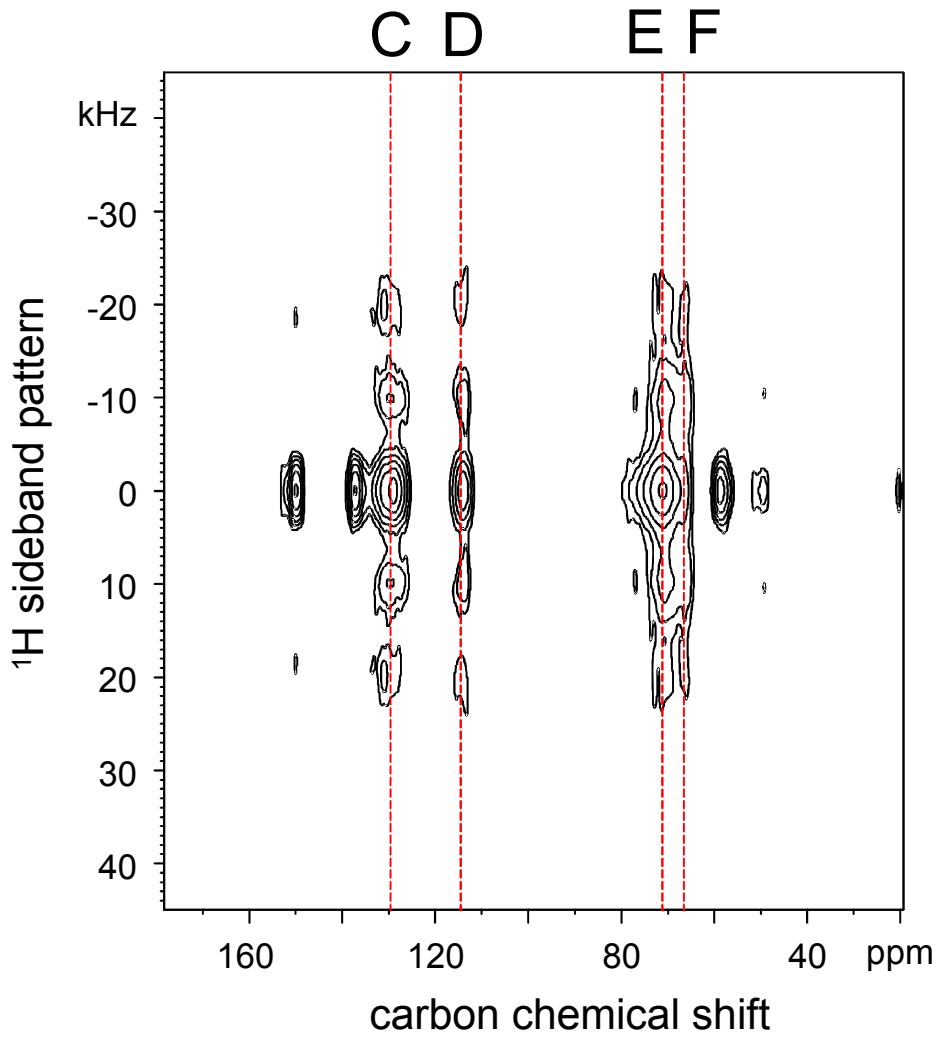




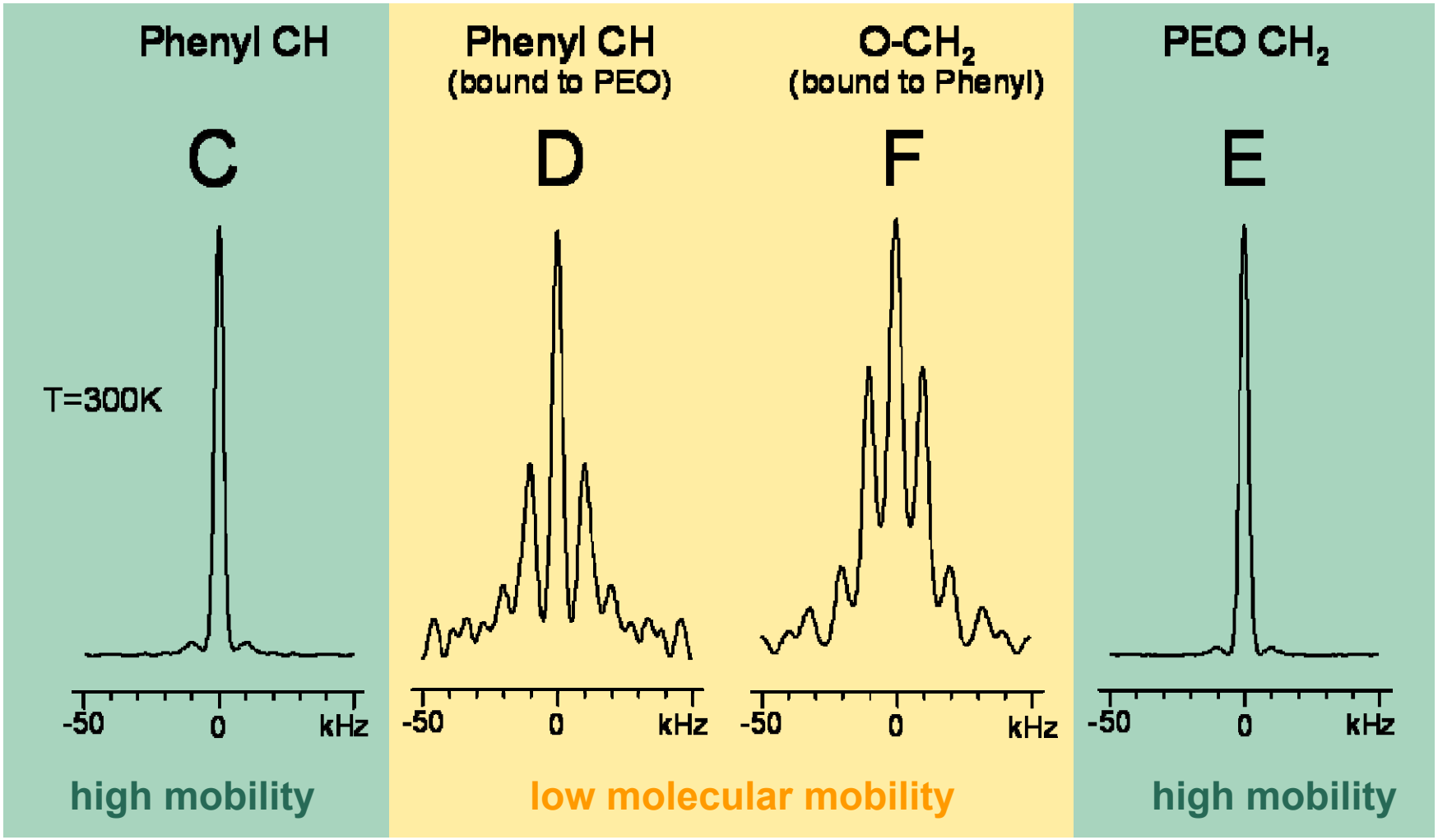
Molecular Dynmiacs via Separate Local Field NMR



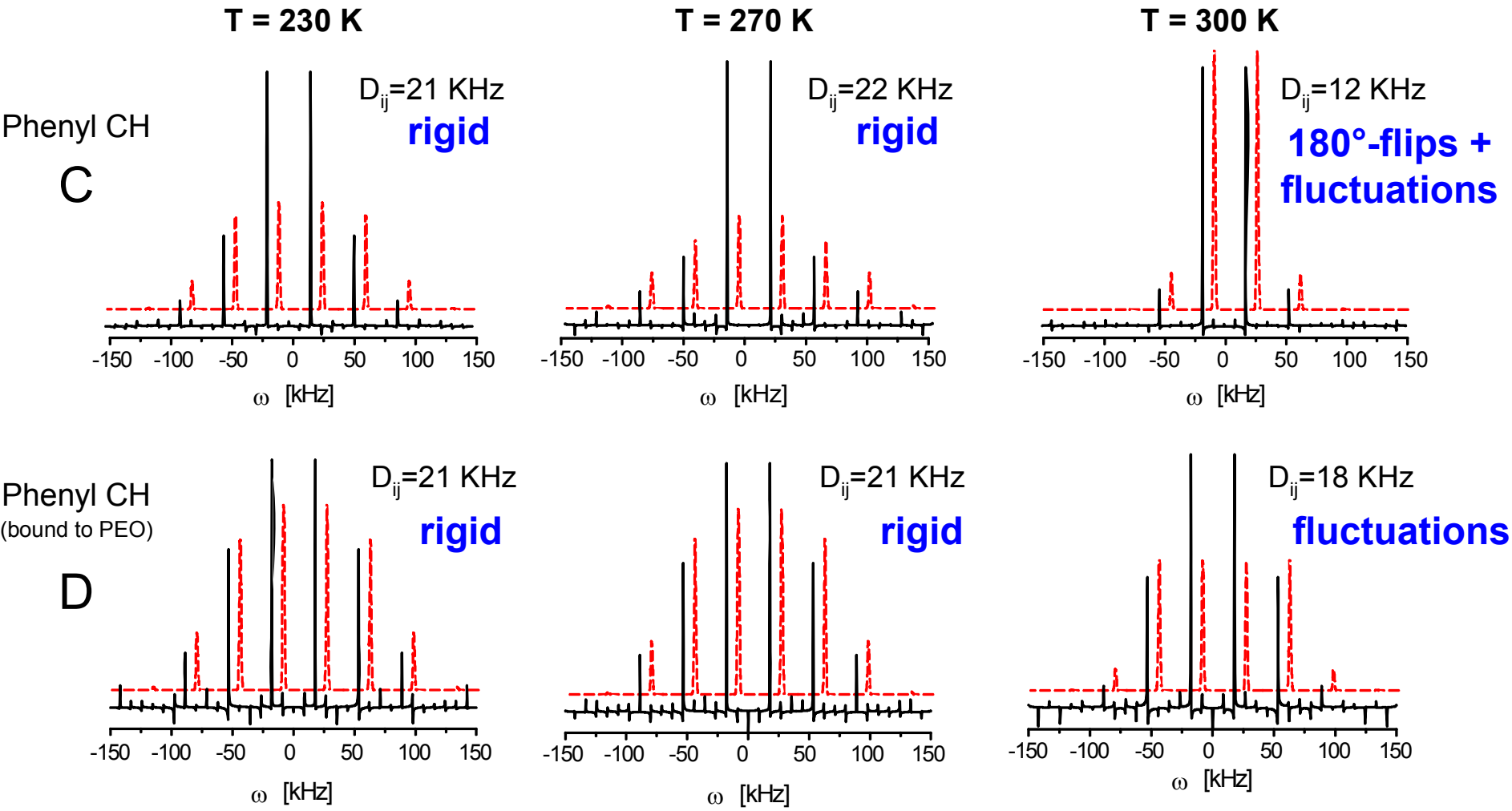




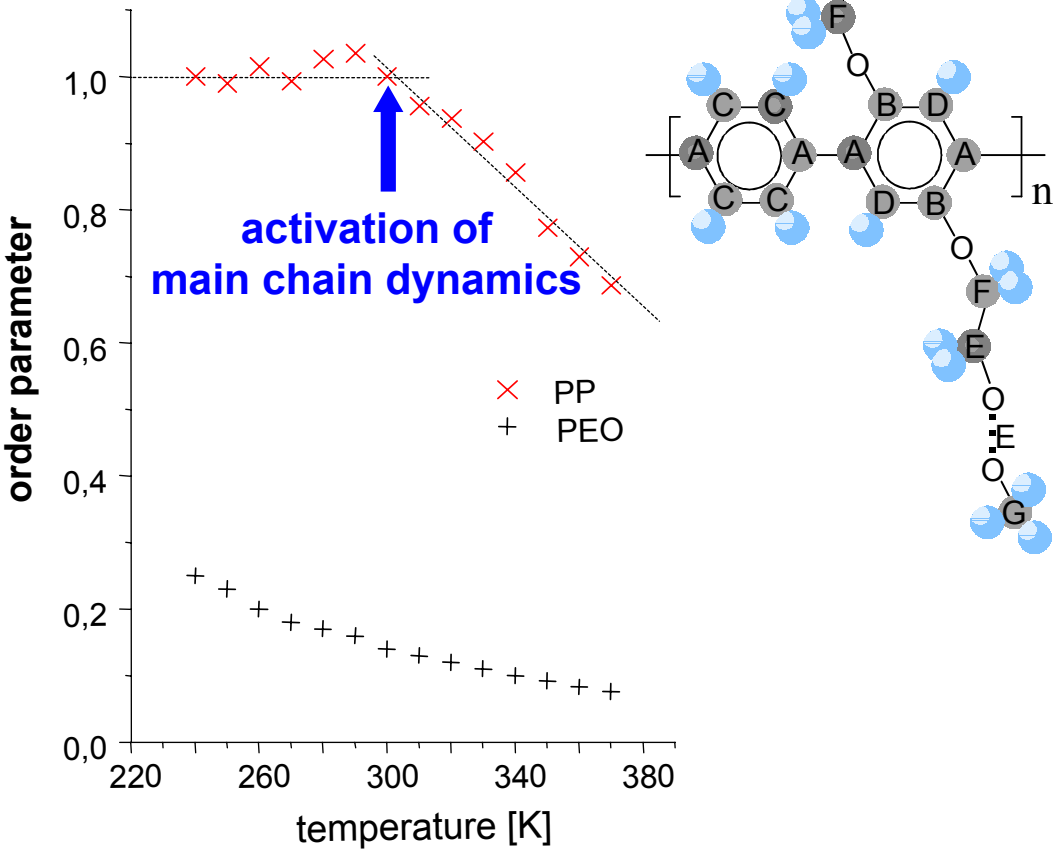
^1H sideband pattern from SLF NMR Experiments

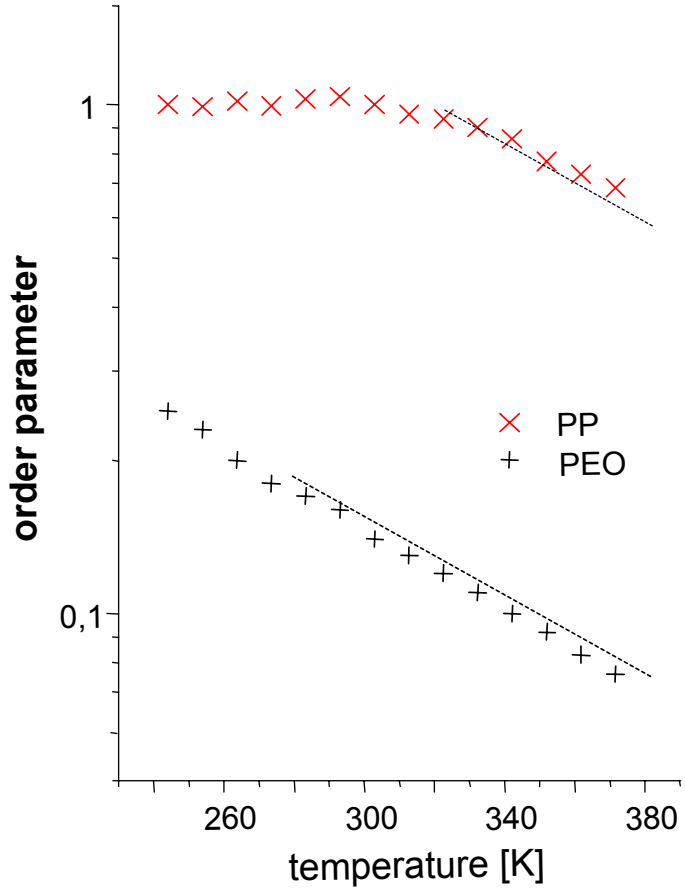


Local Dynamics via RePT-HDOR Sideband Pattern



Molecular Dynamics of PPPEO via ^{1}H DQ NMR





Polyphenylene - Polyethylenoxide Summary

I. Qualitative information about dynamics via separate local field experiments :

(i) At room temperature, the Poly-(Ethylene oxide) (PEO) chains and unsubstituted phenyl rings of the polymer backbone are highly mobile.

(ii) The first CH_2 group of the PEO side chains bound to phenyl rings of the Poly-Phenylene (PP) backbone and these phenyl rings are less mobile.

II. Identification of dynamic processes via recoupled polarization transfer NMR experiments :

(i) For temperatures below 300K, the PP backbone is rigid.

(ii) For T > 290K substituted phenyl groups, bound to PEO side chains, show substantial fluctuations.

(iii) Unsubstituted phenyl groups undergo additional phenyl flips around the chain axis.

II. Bending dynamics of the poly-phenylene main chain via ^{1}H double quantum NMR:

(i) For T > 300 K bending fluctuations of the PP backbone are observed.

(ii) The loss of dynamic anisotropy with increasing temperature is more pronounced for the PEO side chains the for the PP backbone of the polymer.

Acknowledgements

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PP-PEO Dynamics:

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