



Solid State NMR Studies of Complex Two Dimensional Structures: Polyelectrolyte Multilayers and Layered Silicates



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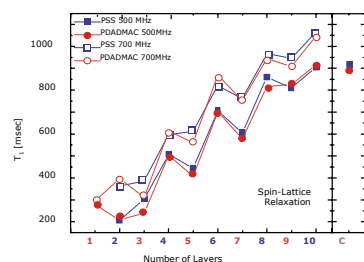
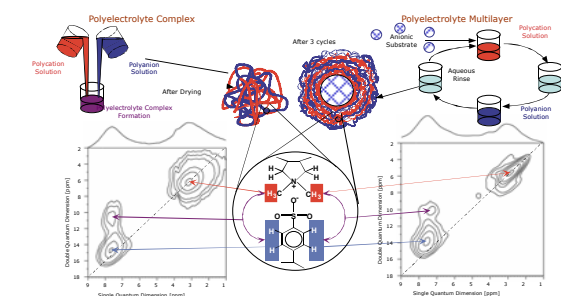
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Introduction

The inherently low sensitivity of NMR hampers in many cases studies of low dimensional entities such as films or molecular layers. However, fast MAS in combination with advanced recoupling techniques are able to increase the signal to noise ratio sufficiently such that structure and dynamics of polyelectrolyte multilayers (PEM) [1] or surfactant controlled silicate layers can be investigated.

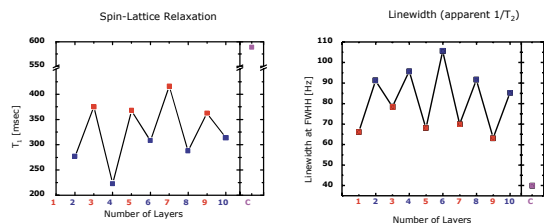
Due to the complex structure of the samples, the most robust recoupling sequences available had to be chosen to obtain artefact free results. The double-quantum NMR experiments have been recorded using the Back-to-Back sequence [2] in the fast MAS limit, whereas the SUPER-NMR scheme [4] has been applied for chemical shift anisotropy recoupling.

NMR Investigations of Polyelectrolyte Multi-Layers

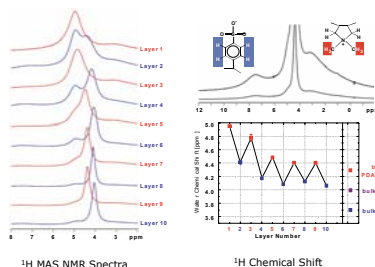


T_1 relaxation measurements of PDADMAC-PSS multilayers find the polymers to move in the slow motion regime and exhibit an oscillatory behavior the relaxation times approaching the value of the polyelectrolyte complex.

¹H double quantum NMR indicates that the layered structure of PDADMAC-PSS multi-layers is strongly interdigitating and resembles the polyelectrolyte complex.



Water adsorbed in PEMs, shows oscillatory relaxation times and chemical shifts depending on the material of the last layer. Its T_1 relaxation is in the fast motion limit.



i. Complexation:

- Polycation-polyanion complexation of polyelectrolyte multi-layers (PEM) is similar to that in the bulk polyelectrolyte complex (PEC).
- Water-polymer association in PEMs is much stronger than in PEC.

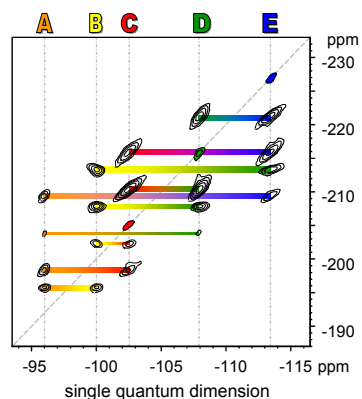
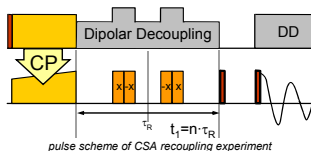
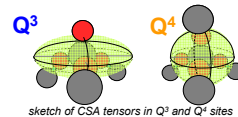
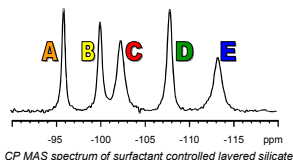
ii. Polymer Dynamics:

- Addition of water increases the polymer mobility in PEMs but not in the PEC.
- Enhanced polymer mobility is observed for hydrated PDADMAC-capped films relative to PSS capped films.
- 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.

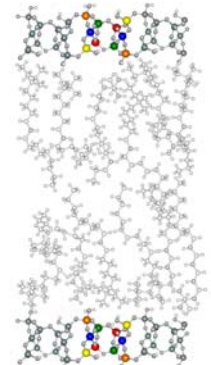
iii. Adsorbed Water:

- Mobility of adsorbed water is more restricted in PEMs than in the PEC.
- Water mobility is lower and water content is higher in PSS capped films as compared to PDADMAC capped PEMs.
- ¹H NMR peak intensity increases monotonically and its chemical shift oscillates between the PEC bulk and the bulk PDADMAC value.

Structure of Surfactant Controlled Silicate Layers



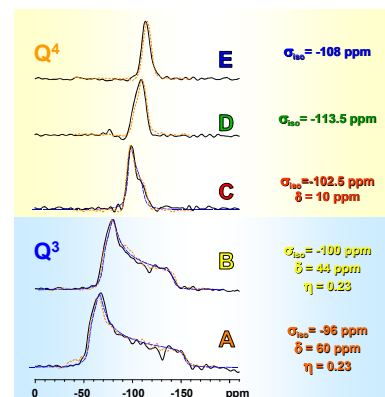
Si site	direct neighbor	Next nearest neighbor.
A	B C E	D
B	A D E	C
C	A D D E	B C
D	B C C E	A D
E	A B C D	E



Combining short range spatial information from NMR methods with MD simulations and QC computations can unravel low dimensional structures yet inaccessible to common scattering methods.

The ²⁹Si CP MAS spectrum of the layered silicate sample exhibits five different sites (left). The chemical bonded network was investigated using INADEQUATE measurements [3]. Exploring the CSA of these sites provides a direct method to distinguish the Q³ and Q⁴ sites present in the sample.

Overlapping peaks and weak signal intensities hamper the acquisition of static powder spectra. CSA recoupling pulse program [4] (shown at the left hand side) provides access to the static line shapes of the individual sites, and thus to the complete set of CSA parameters.



²⁹Si double quantum spectra, recorded with various DQ recoupling times, provide the nearest and next nearest neighbor relation (given in the table) between the sites of the sample, leading to a proposed structure shown right. MD simulation and quantum chemical (QC) computations have been used to verify the structure.

References

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