Small-angle neutron scattering, reflectometry, and diffractometry using proton-polarized samples

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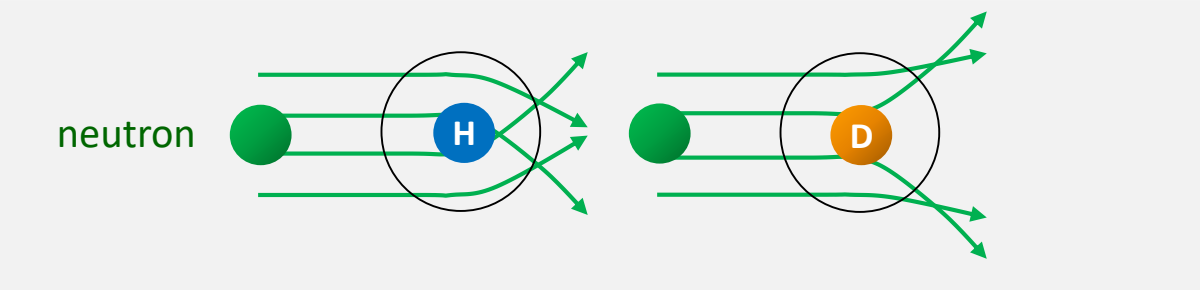
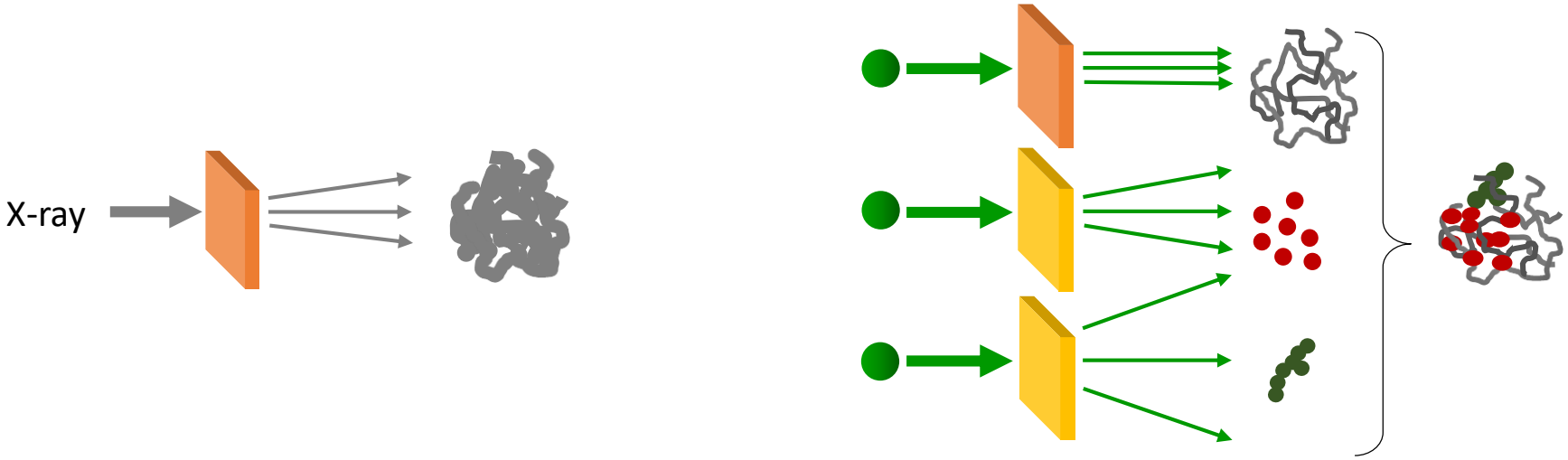
J-PARC and JRR-3 neutron facilities @JAEA

Structural study of composite materials



Partially deuterated model samples



"Monochromatic picture"

"Color picture!"

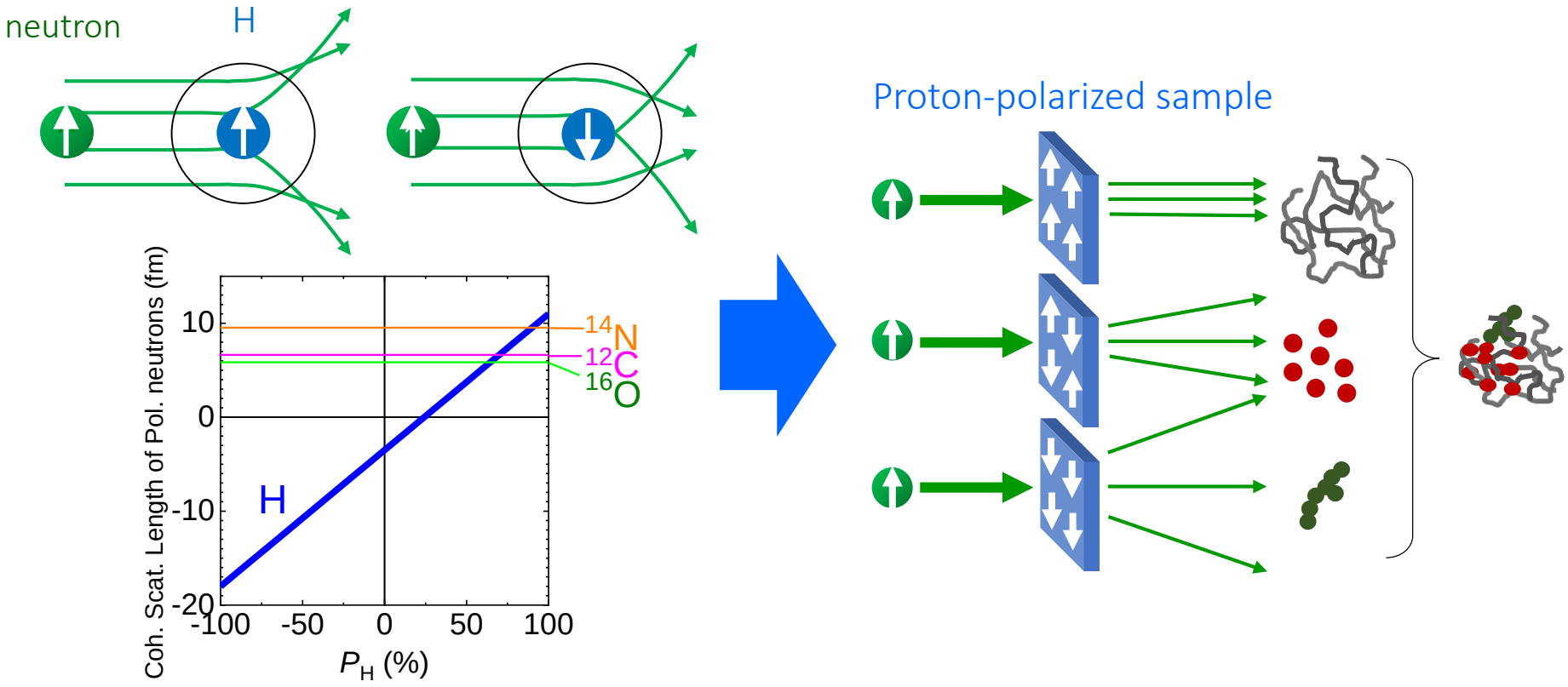
Deuterated model samples! No way, we go home!

☹ Tough

☹Are structures of real product and model samples the same?

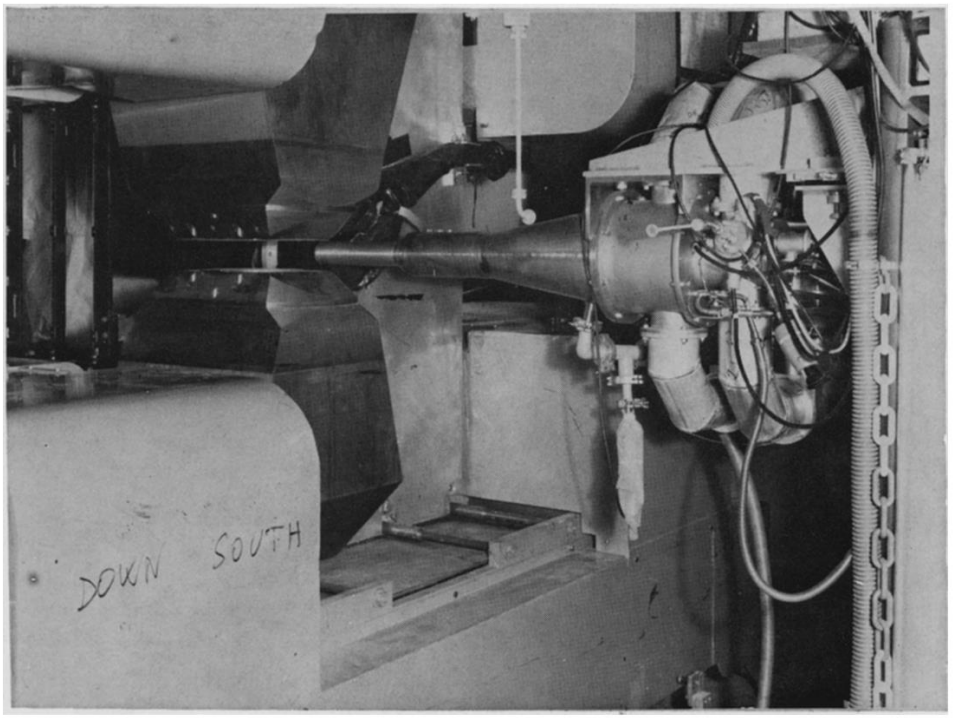
Spin contrast variation (SCV)

Stuhrmann et al. J. Appl. Cryst. (1989)



- Not just a labor saving technique.
- To extract new information that conventional technique cannot access.

SCV was very tough previously…

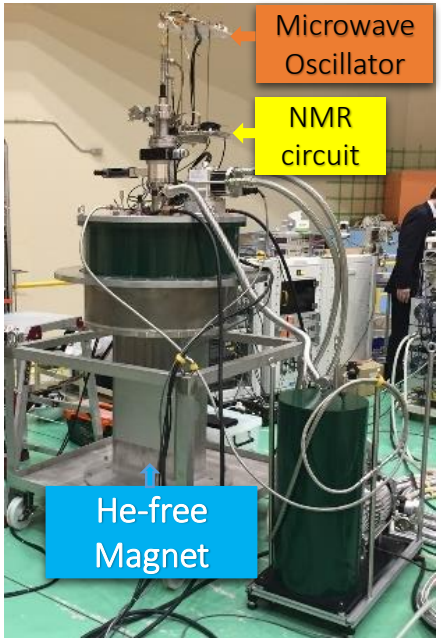


Unrealistic!

- The magnet was too heavy to move out for next experiments.
- 2w for sample change is too long. We measure several samples per day.

Thanks to modern DNP tech., SCV is no longer unrealistic!

Special thanks to Dr. B. van den Brandt and Dr. P. Hautle in PSI



	1st (2007)	2nd (2016)	3rd (Constructing)
H, T	3.3 T, 1 K	3.3 T, 2.2 K (He-free)	6.7 T, 2.2 K (He-free)
P_H	20-40%	10-20%	70% ??

☺ 3 h for installation to beamline, ☺ 1-3 h for sample change

Small-angle

Reflectometry

Crystallography

Small-angle neutron scattering (SANS)

$$2d \sin\theta = n\lambda$$

1-100 nm 0.01-10° 2-9 A

SCV-SANS has a history.

It is technically established.

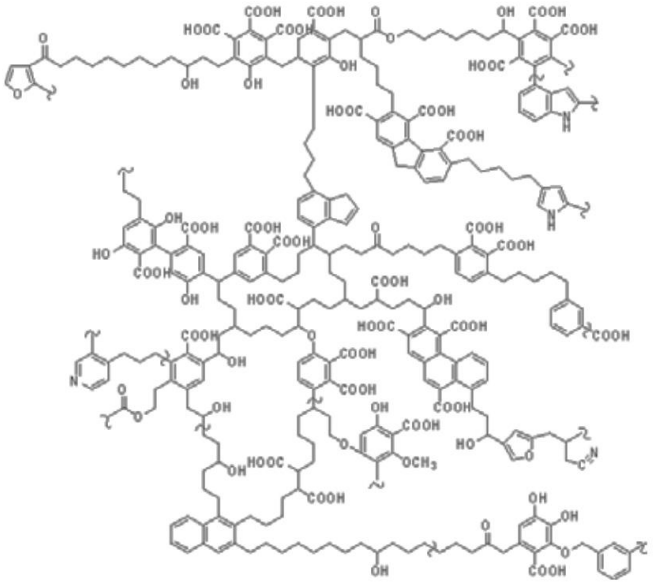
What we have to do now is

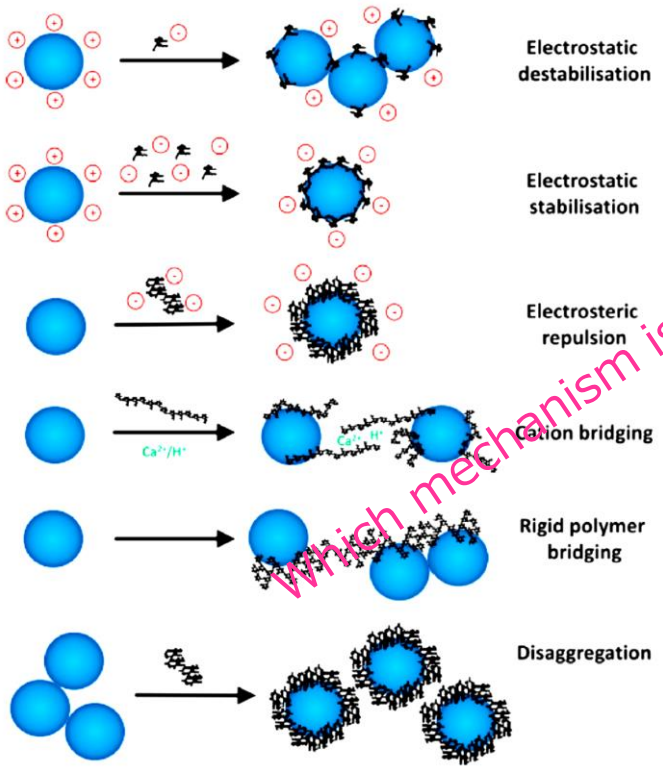
to show GOOD EXAMPLES.

How do organics bind inorganics to form soils?

Elasticity, air permeability, water holding, and whether resistance

Proposed structure of
Soil organics (Humic acid)



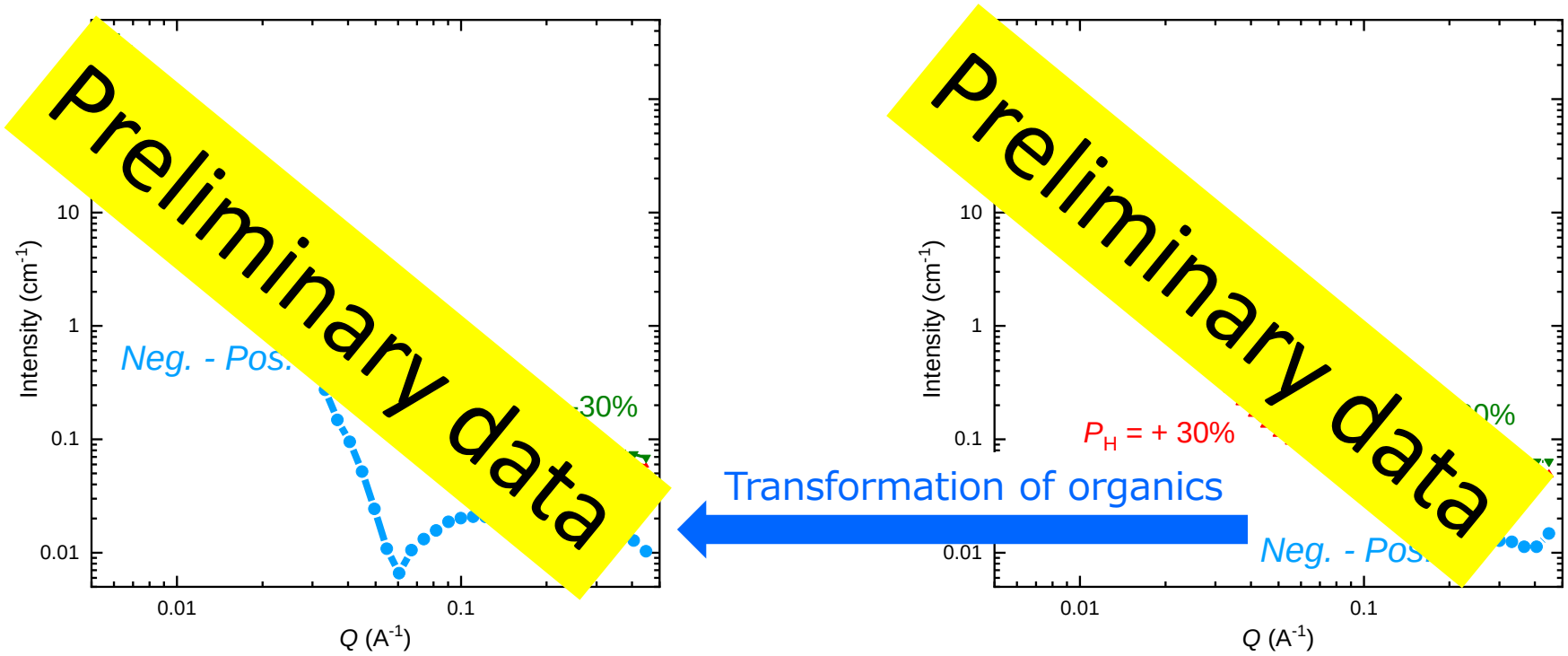


A. Philippe and
G. E. Schaumann
Environ. Sci. Technol.
2014 (REVIEW)

Aggregated nanostructure of organics clarify the binding mechanism.

Organics & Al_2O_3 (1:10) in D_2O/*d*Gly.

Organics in D_2O/*d*Gly.

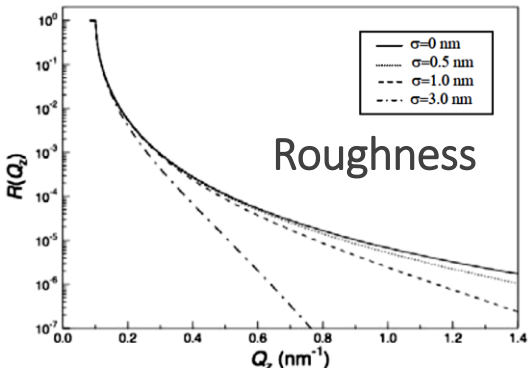


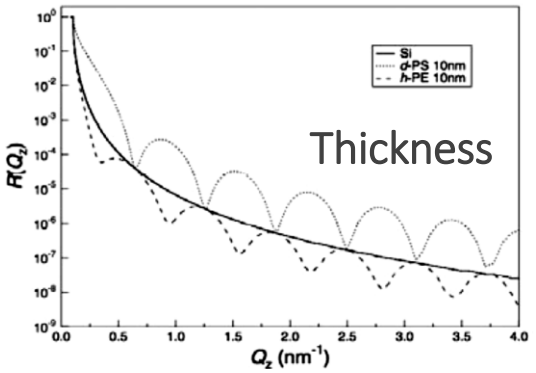
- Raw data: Scattering from organics is hidden by intense scattering from Al_2O_3.
- Subtracted: Scattering from organics is extracted by cancelling out Al_2O_3 signal.

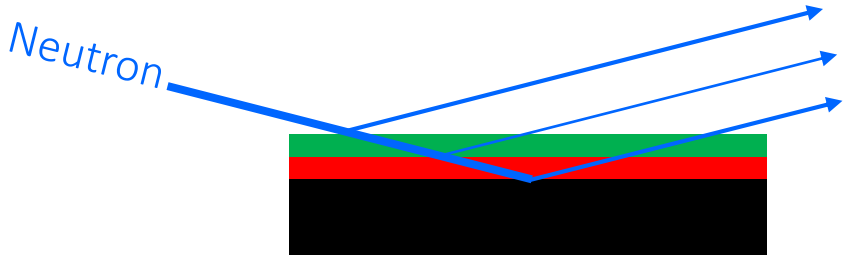
Small-angle

Reflectometry

Crystallography



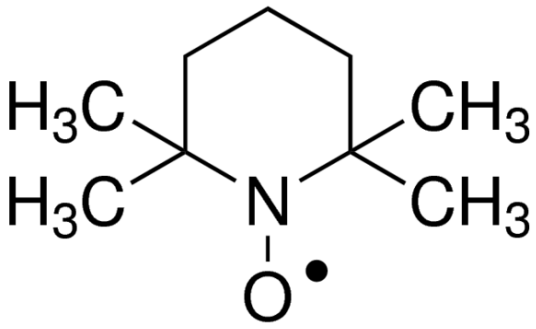


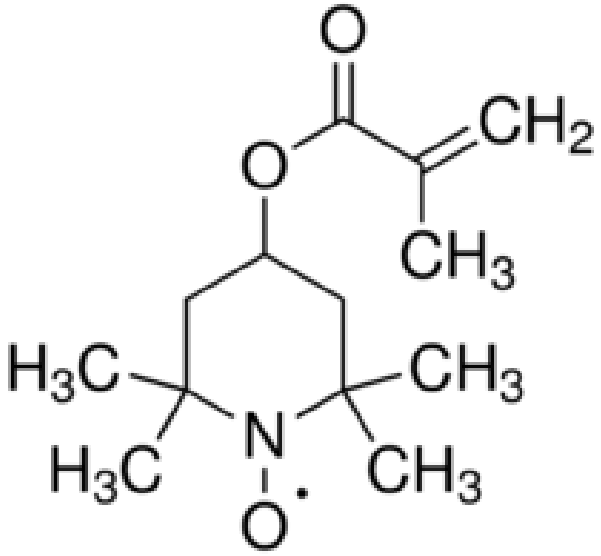


☹ Tough to distinguish reflections in multilayer.

Let's develop SCV neutron reflectometry!

TEMPO methacrylate for nm-thick films





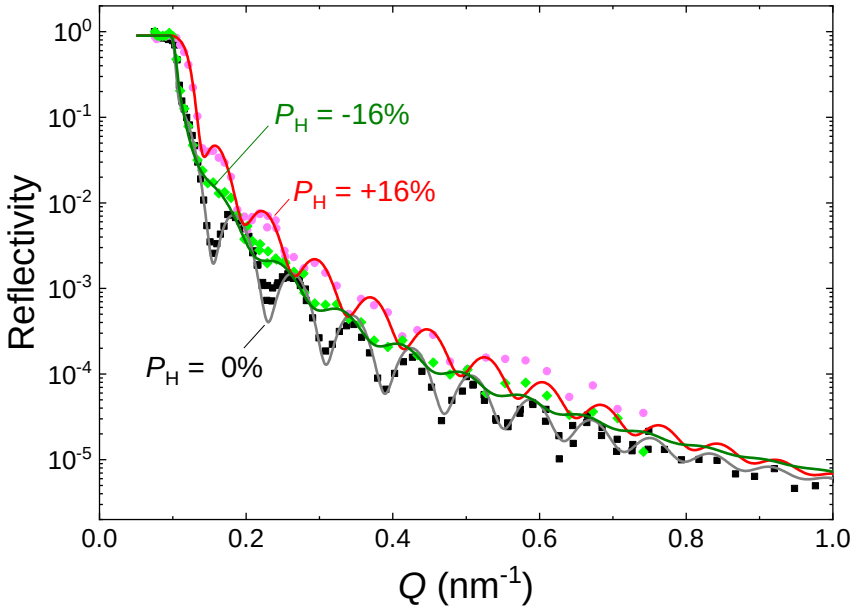
Easily evaporates from surfaces

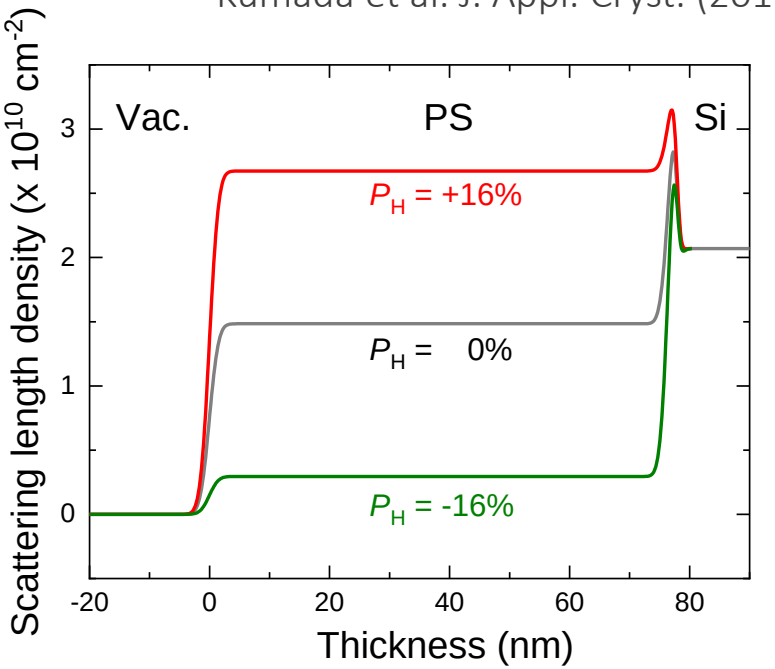
Never evaporates even at RT

@J-PARC MLF BL17

Demonstration using PS monolayer film

Kumada et al. J. Appl. Cryst. (2019)





Homogeneously polarized including surface and interface

→ SCV-neutron reflectometry can be used for structural study.

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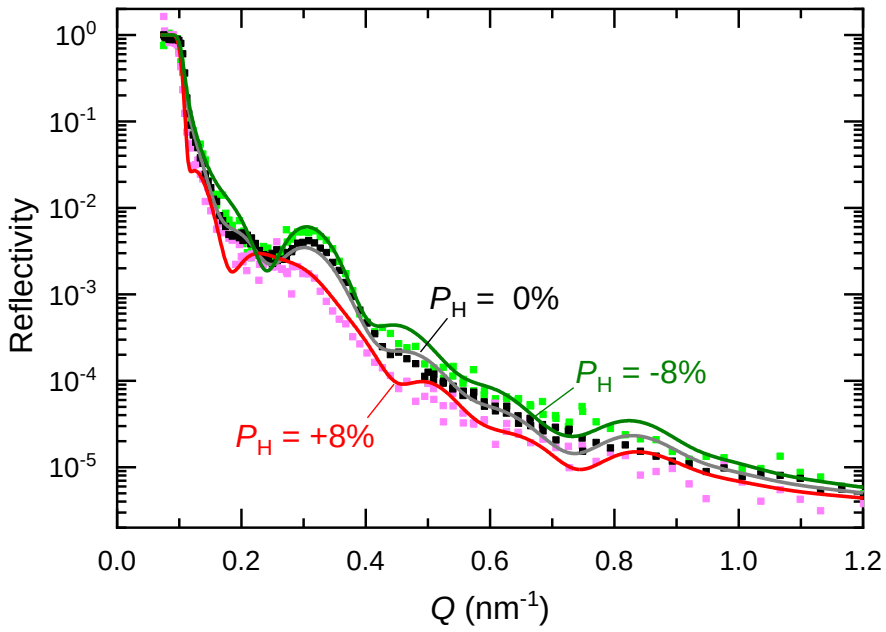
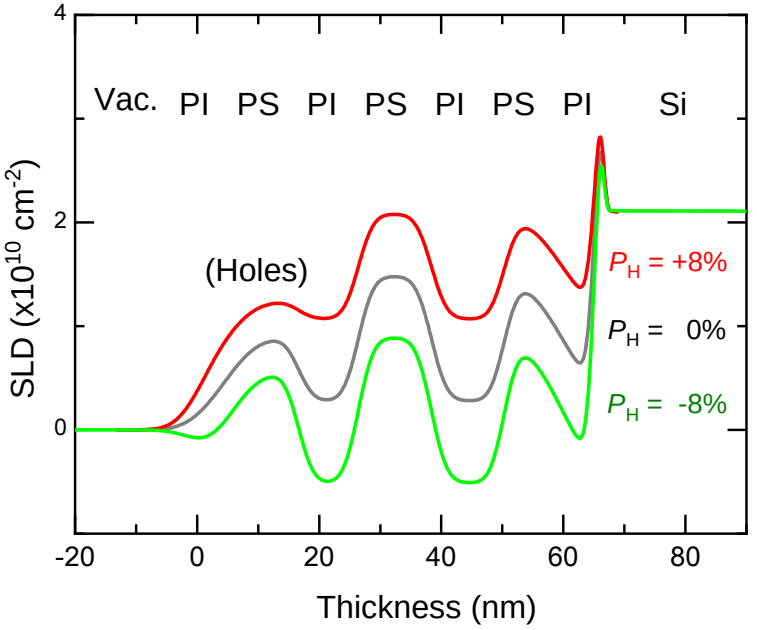
poly(styrene-*b*-isoprene)

Kumada et al. J. Appl. Cryst. (2019)

Microphase-separated PS and PI lamellae are stacked on Si

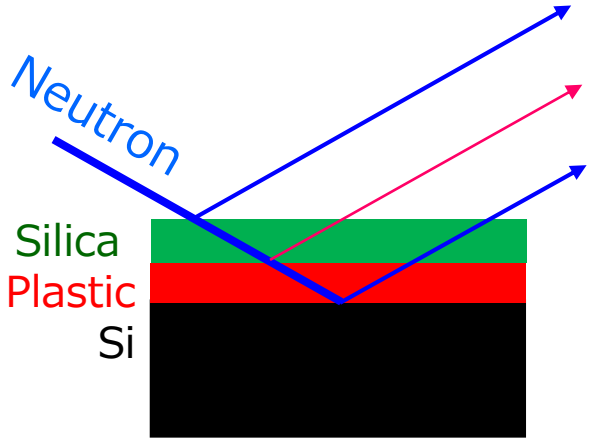




Whereas a lot of structure models can reproduce the P_H = 0% curve only,

the model is strictly specified by fitting the P_H-dependent 3 curves.

On-going: Silica coating for plastic tablewares



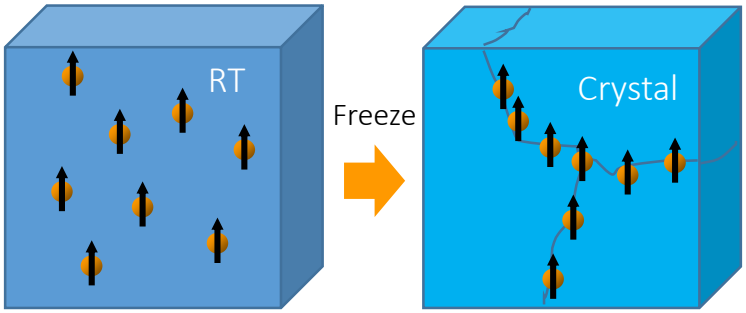
Silica should stick to polymer surface,

Otherwise it will peer off.

Small-angle

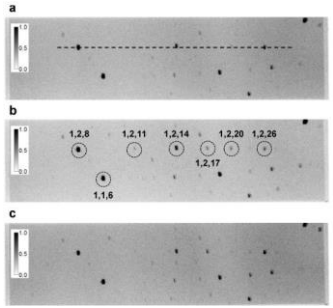
Reflectometry

Crystallography

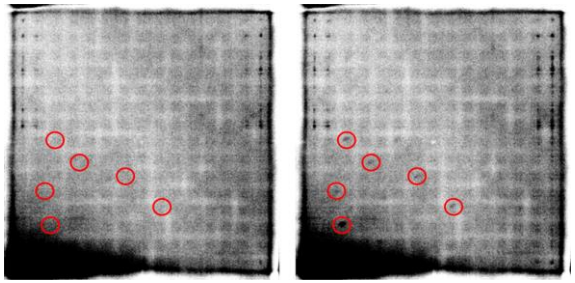


"SCV cannot be used for crystallography!"

LMN:Nd Piegsa et al. (2013)



Protein Pierce et al. (2019)

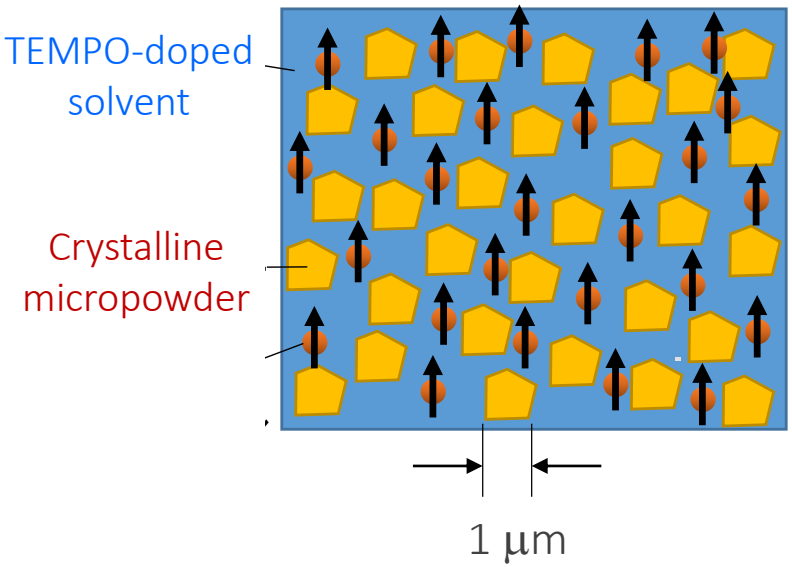


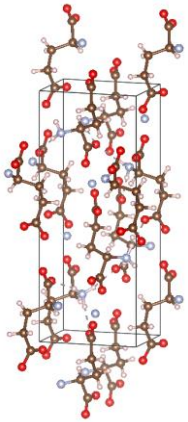
"They are excellent, but not VERSATILE."

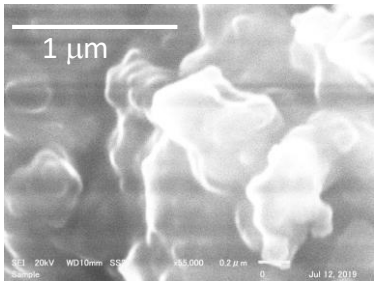
Yamagata's group broke through the difficulty!

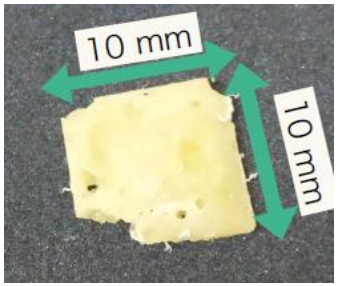
Mechanical Doping for polarization of crystals

Miura, Iwata, *et. al.* PTEP (2017).





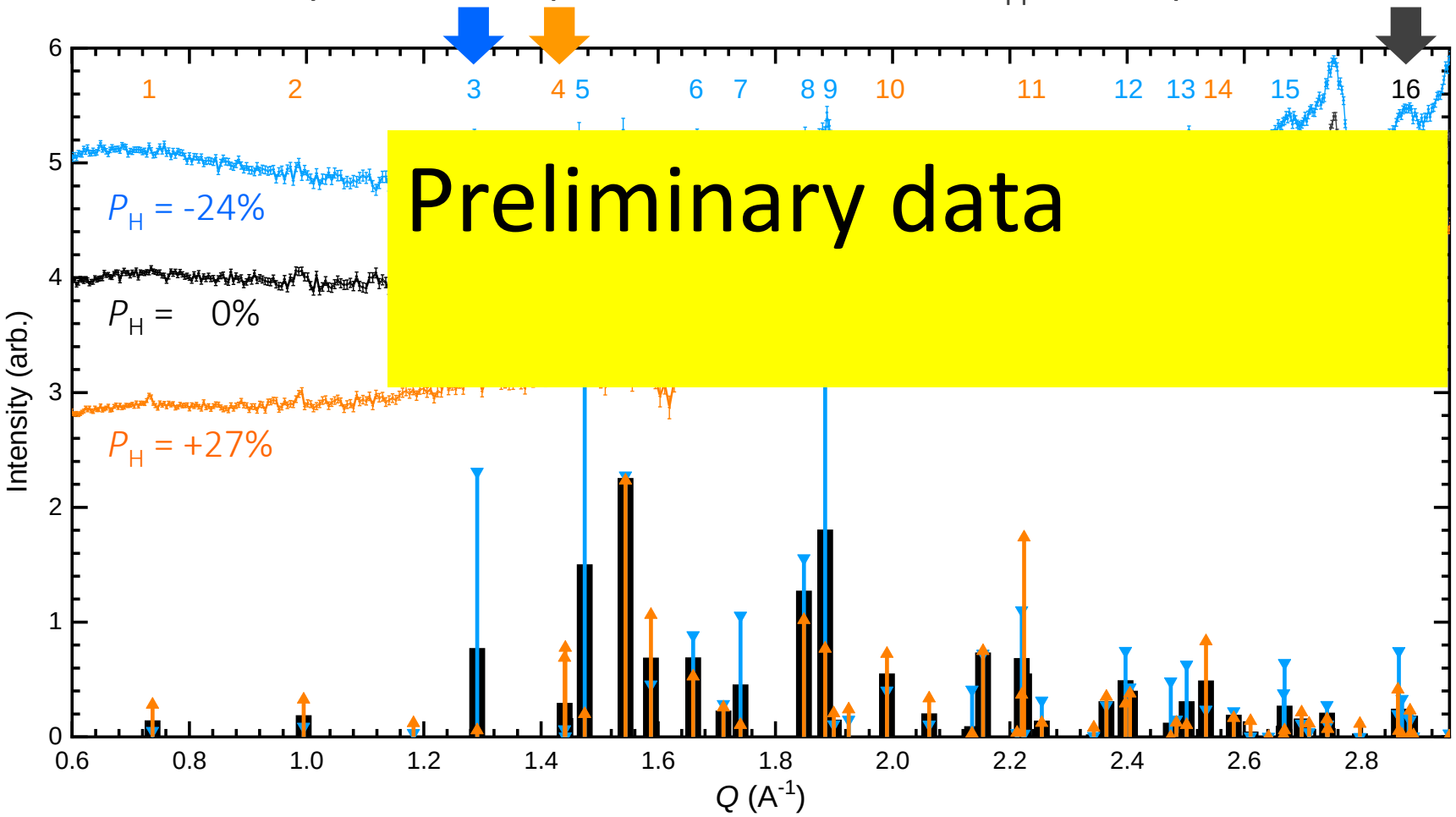




Glutamine micropowder in TEMPO-doped PS

Let's develop **VERSATILE** SCV-crystallography using mechanical doping!

Intensity of each peak varies with P_H as expected.



→ Separation of overlapped peaks, Assignment of unknown peaks, etc.

Acknowledgment

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Summary

- ✓ SCV determines structures using P_H-dependent polarized neutron scattering.
- ✓ Now, we can do SCV experiments conveniently using modern DNP techniques.
  - Structure of subcomponent was extracted from NEG. - POS..
  - We developed SCV reflectometry that determines structure of multilayer films.
  - We developed versatile SCV crystallography using mechanical doping.

Goal: SCV as non-special and versatile technique for structural study