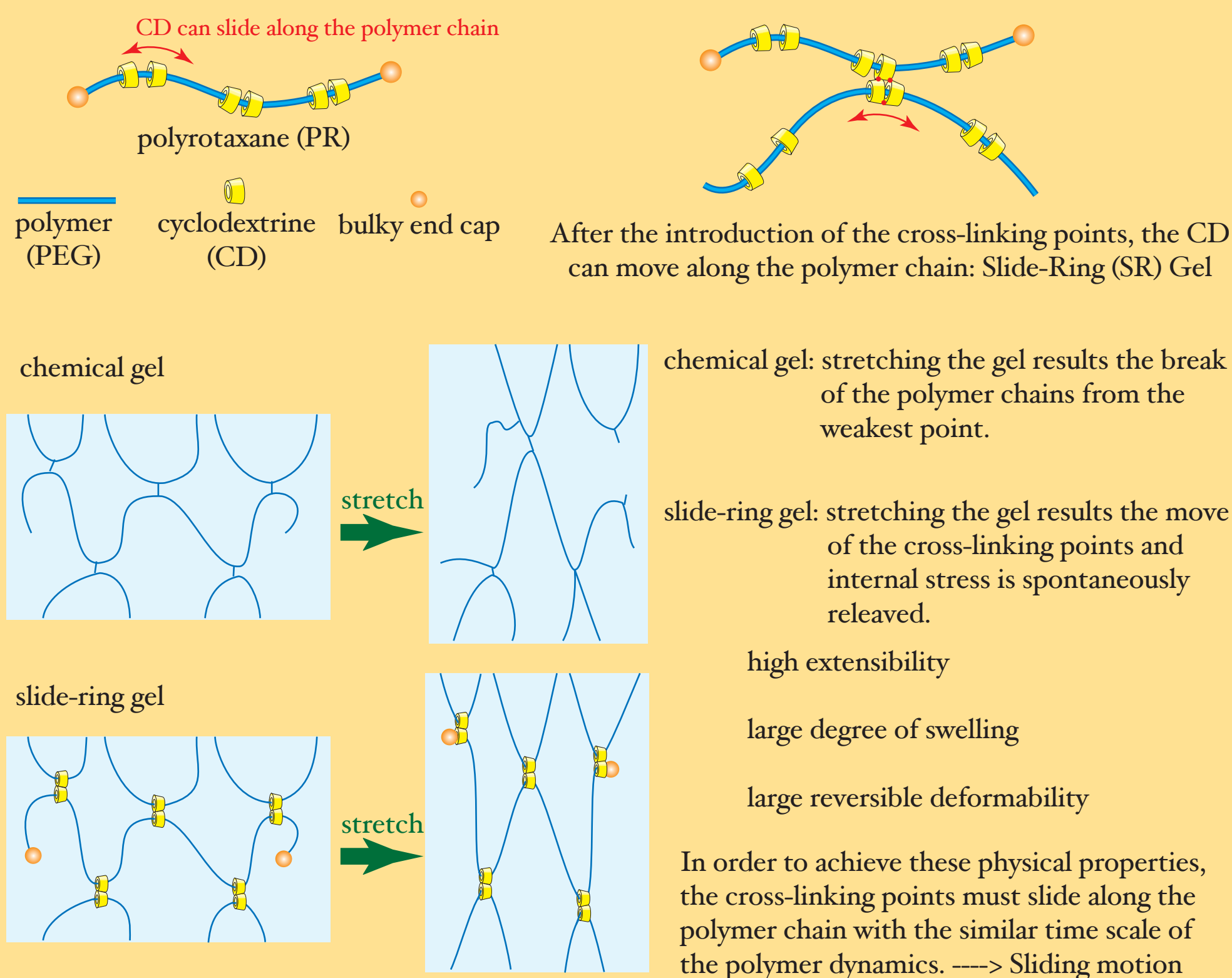


Dynamic properties of Slide-Ring Gel

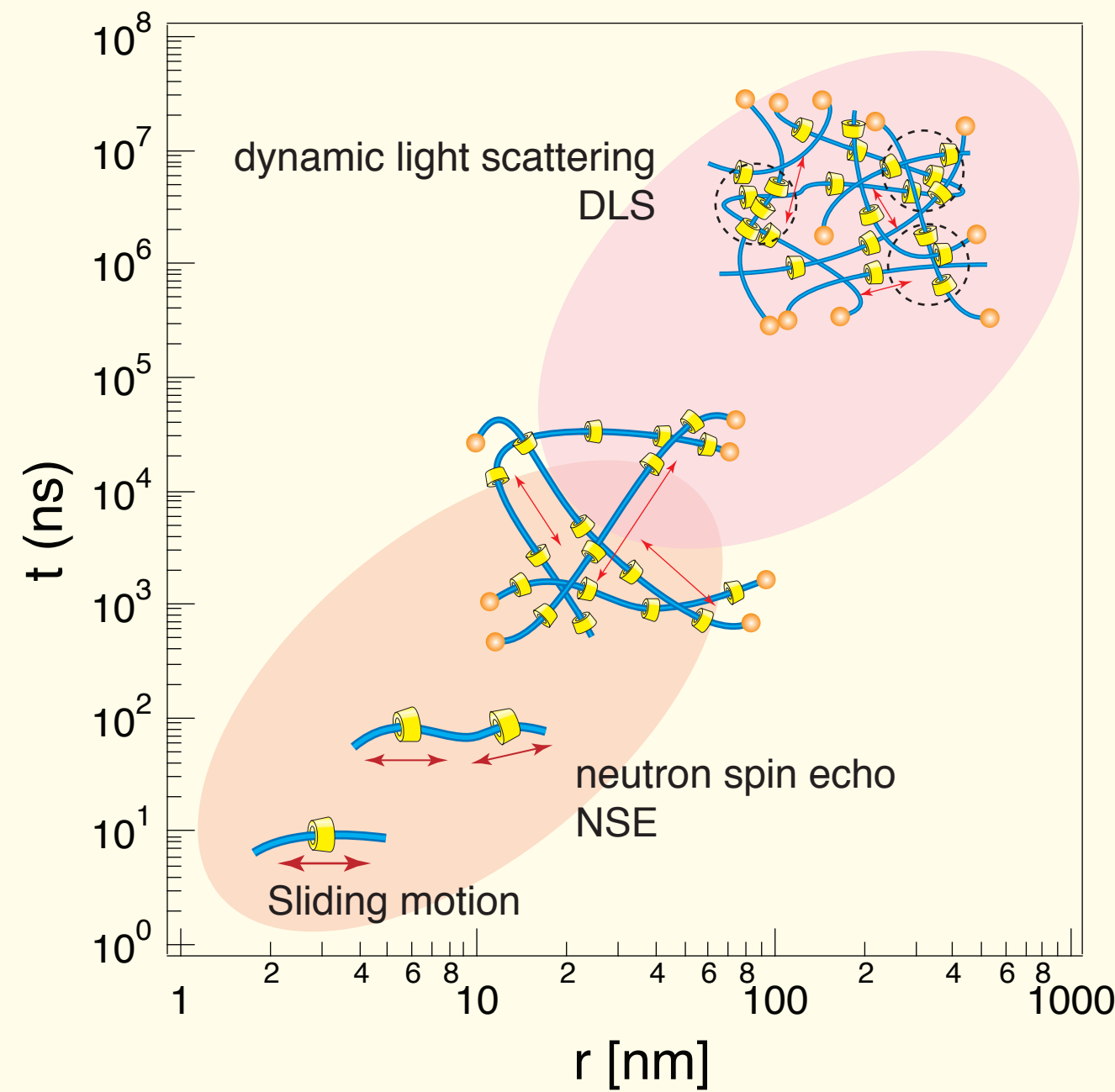
Michihiro Nagao; Cyclotron Facility, Indiana University, & Center for Neutron Research, National Institute of Standards and Technology
Koichi Mayumi, Hitoshi Endo, Mitsuhiro Shibayama, and Kozo Ito; The University of Tokyo

Slide-Ring Gel

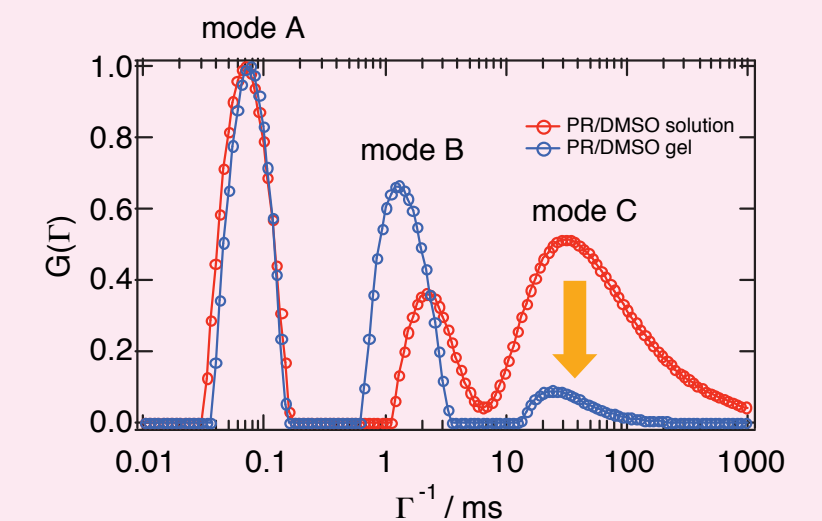
Okumura and Ito, Adv. Mater. 13, 485 (2001).
Ito, Polymer J. 39, 489 (2007).



Possible dynamics in the Slide-Ring Gel



dynamic light scattering (DLS)

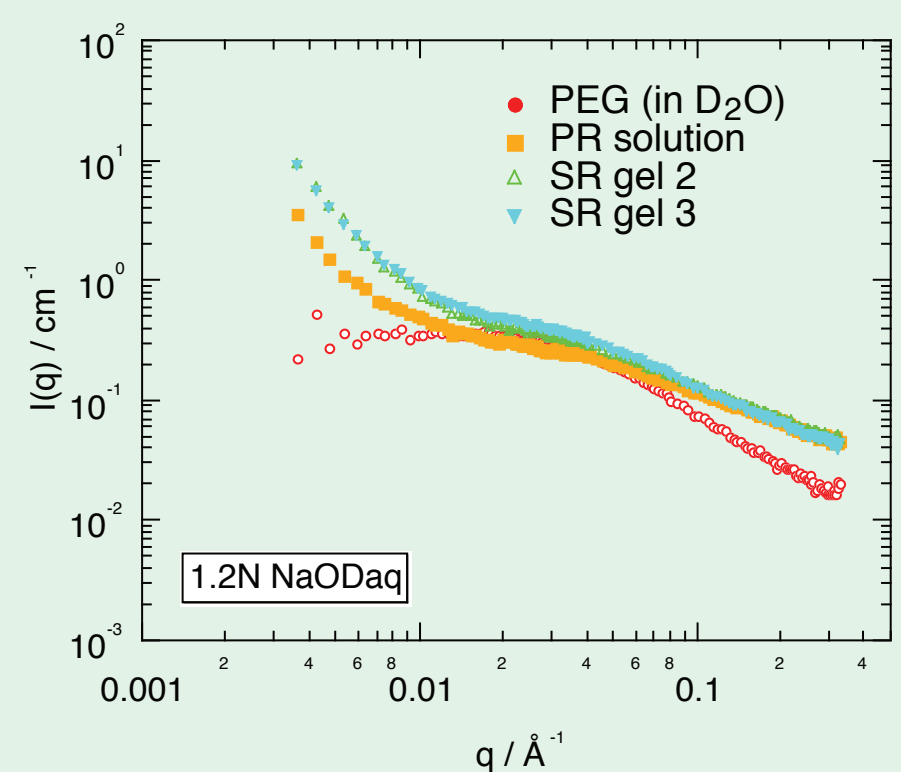


mode A & B: existing both in solution and gel
mode C : disappeared in the gel

mode assignment
mode A: due to the collective dynamics of the PEG chain
mode B: sliding along the PEG chain?
mode C: self-diffusion of CD cluster along the PEG chain

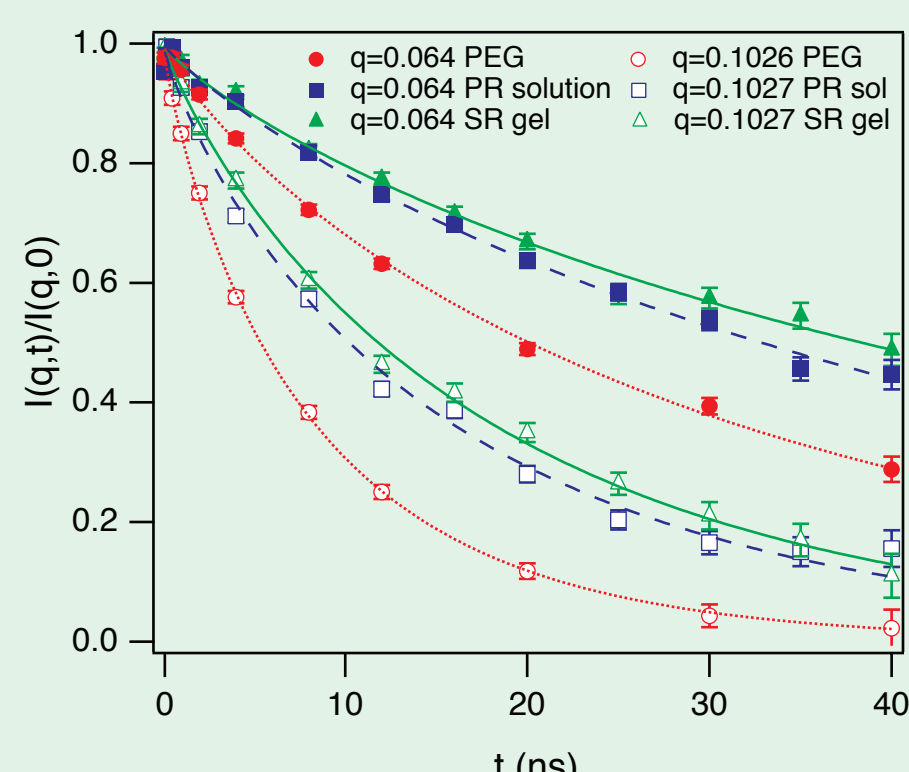
to define local dynamics of the CD molecule
NSE measurement is necessary

Polyrotaxane in NaOD aqueous solution and gel



Comparison of the SANS profiles obtained from the PEG in D₂O, polyrotaxane in NaOD aqueous solution, and slide-ring gel with the solvent of NaOD and water.

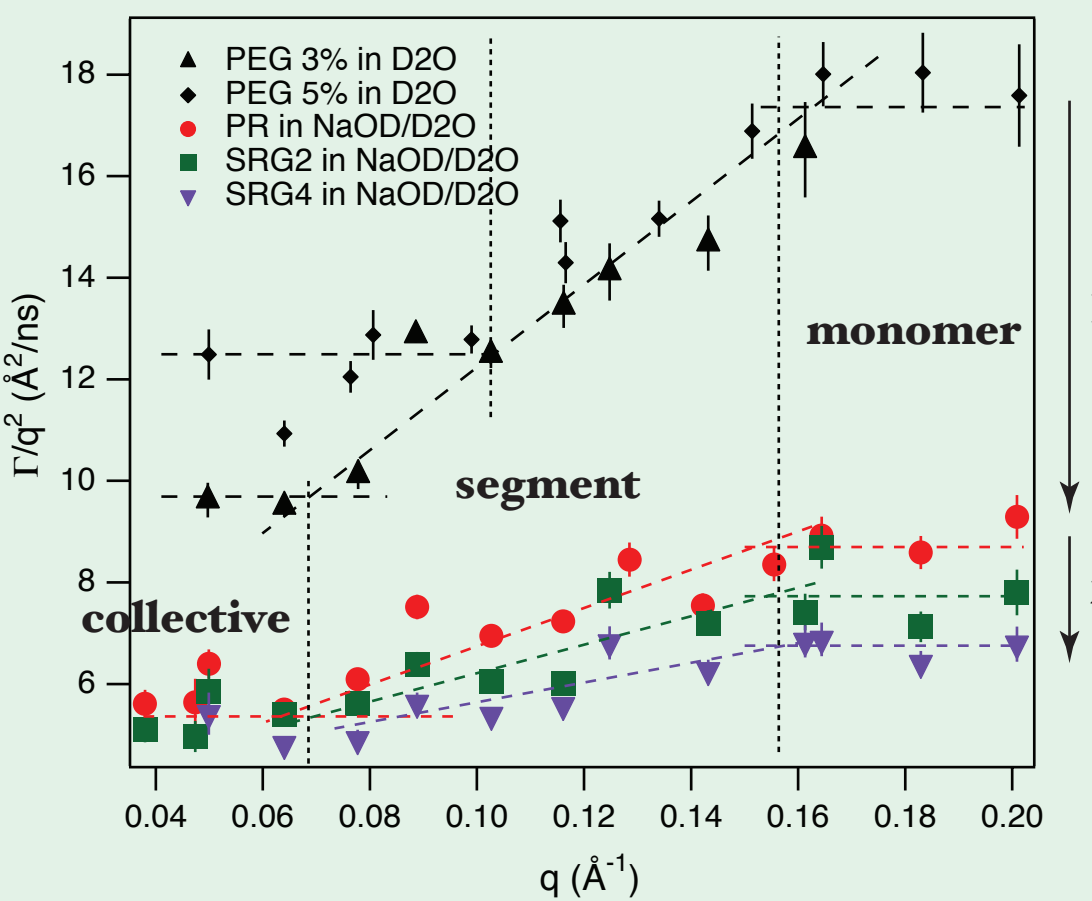
Upturn at low-q for PR solution and SR gel is due to the inhomogeneity of the system. The higher intensity at high-q for PR solution and SR gel is ascribed to be the existence of CD molecules.



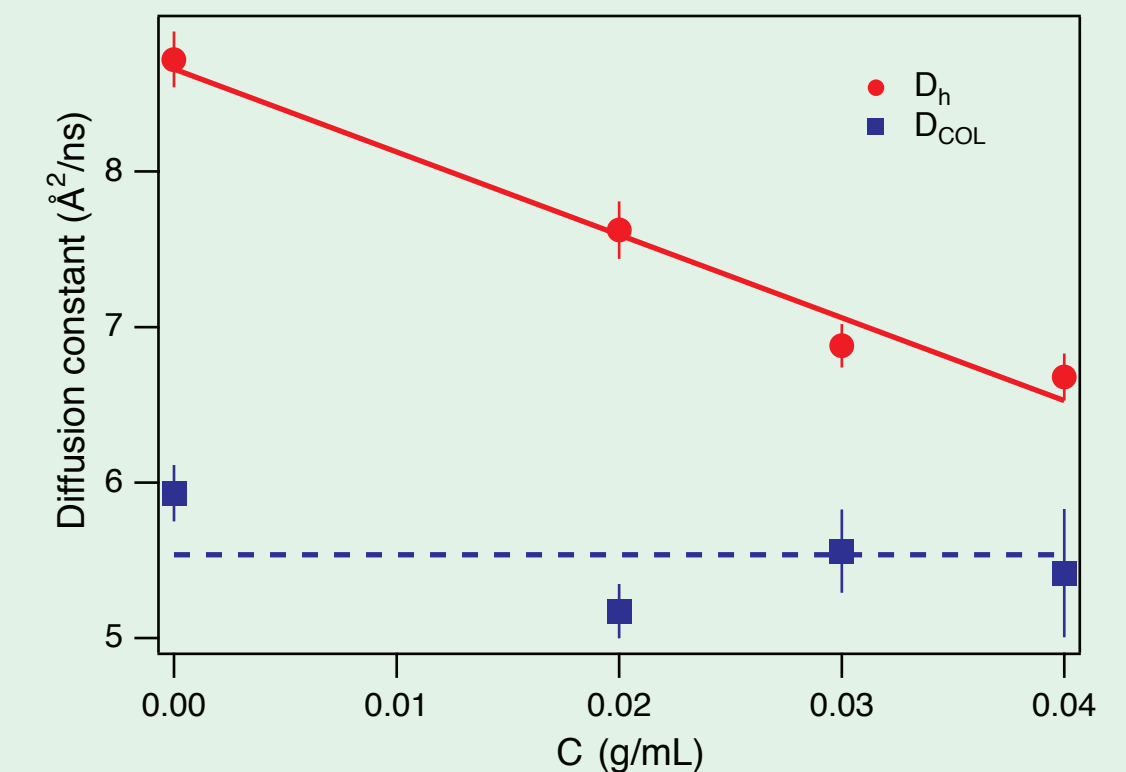
Comparison of the I(q,t)/I(q,0) obtained from the PEG in D₂O, polyrotaxane in NaOD aqueous solution, and slide-ring gel with the solvent of NaOD and water.

SR gel < PR solution < PEG in D₂O
faster dynamics

q-dependence of the initial decay rate Γ of the $I(q,t)/I(q,0)$



collective mode → segment mode → monomer diffusion
suppression of dynamic mode
1. Strong suppression due to the association with CD
2. Slight suppression due to the introduction of cross-linking points



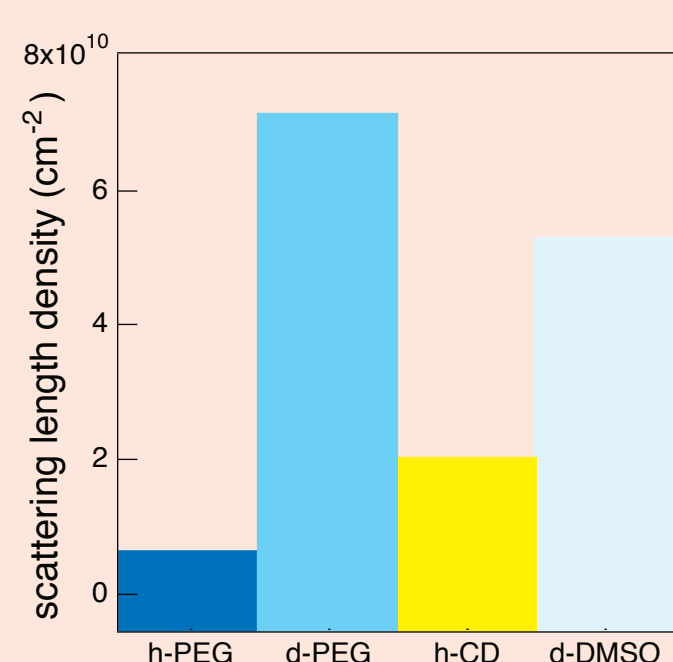
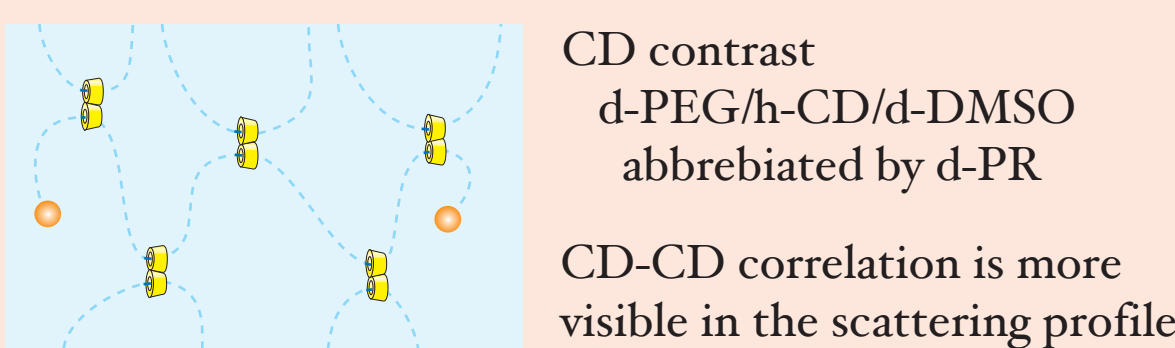
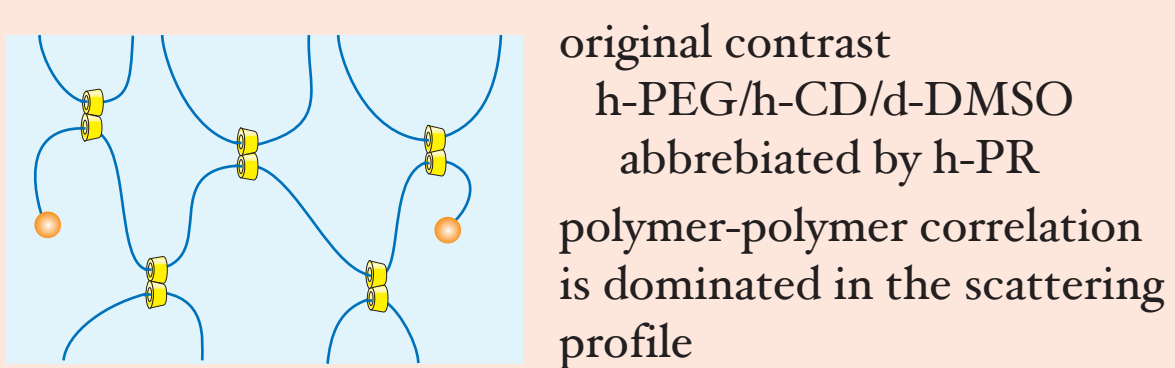
Diffusion constant at low-q: collective mode, D_{COL}, almost constant with cross-linker concentration, C.

Diffusion constant at high-q: sliding mode?, D_h, linear decrease with cross-linker concentration, C.

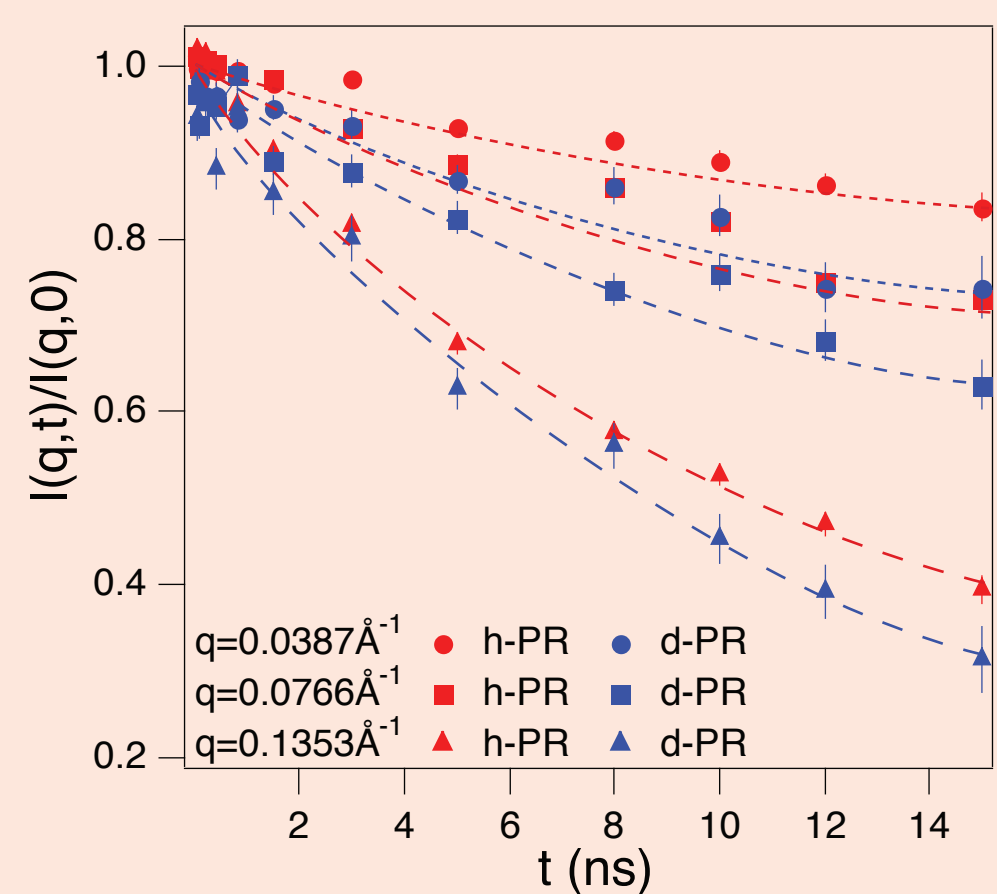
Necessary to decouple contributions between polymer chain and CD molecules since the time scale of the motion of polymer and CD is close to each other

Polyrotaxane in d-DMSO solution and gel

contrast variation technique in the SR gel systems



contrast variation NSE allows us to define more detailed dynamics in the complex polymer gel systems

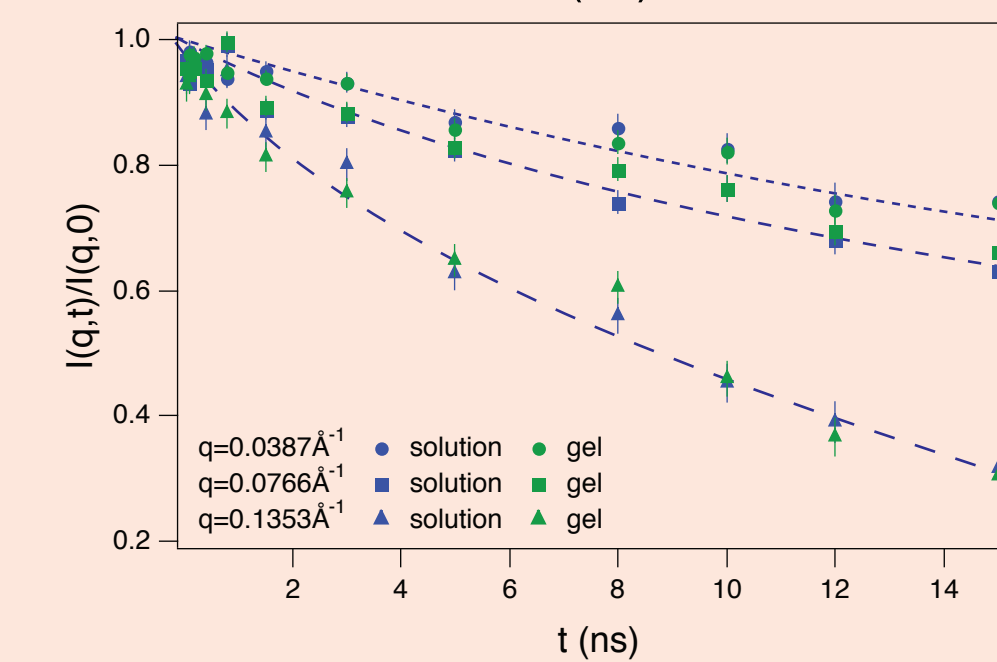


change from h-PEG to d-PEG makes the dynamics faster

excess motion due to the CD-CD correlation
→ local motion of the CD molecules?
→ Sliding motion of the CD along PEG?
→ corrective motion due to the association of the CD?

Still not the evidence of the sliding motion

One more scattering contrast data is needed to clarify the origin of the upturn



introducing the crosslinking point seems not to make any change of the decay rate.

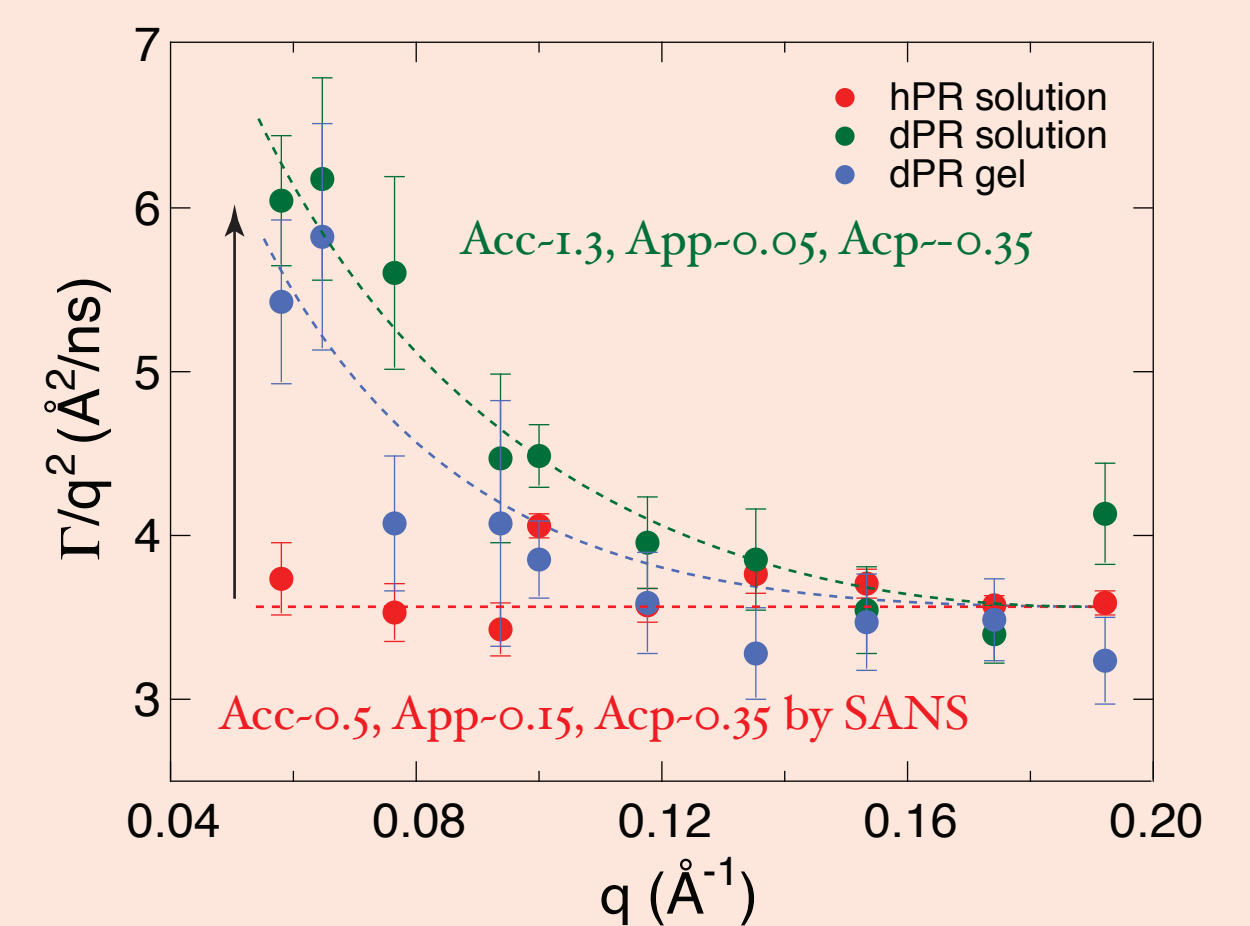
Different trend from the case of the solvent of NaOD and D₂O mixture

However, the first Cumulant analysis shows a slightly slower motion in the case of the SR gel than that of the PR solution

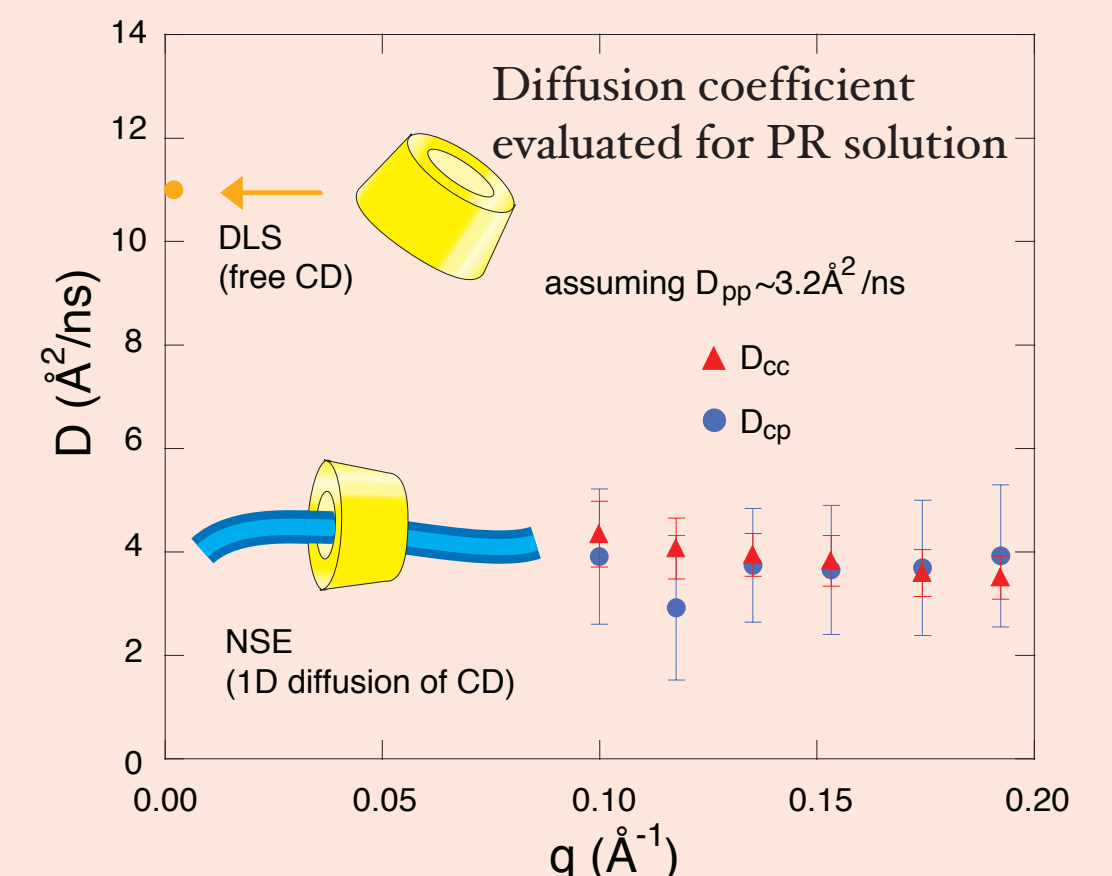
$$\Gamma(q) = \frac{-d\{\ln[I(q,t)/I(q,0)]\}}{dt}$$

$$\frac{I(q,t)}{I(q,0)} = \frac{\Delta Q_{cc}^2 S_{cc}(q) \exp(-\Gamma_{cc}t) + \Delta Q_{pp}^2 S_{pp}(q) \exp(-\Gamma_{pp}t) + 2\Delta Q_c \Delta Q_p S_{cp}(q) \exp(-\Gamma_{cp}t)}{\Delta Q_{cc}^2 S_{cc}(q) + \Delta Q_{pp}^2 S_{pp}(q) + 2\Delta Q_c \Delta Q_p S_{cp}(q)}$$

$$= A_{cc}(q) \exp(-\Gamma_{cc}t) + A_{pp}(q) \exp(-\Gamma_{pp}t) + 2A_{cp}(q) \exp(-\Gamma_{cp}t)$$



$$\Gamma(q) = A_{cc}(q)\Gamma_{cc}(q) + A_{pp}(q)\Gamma_{pp}(q) + A_{cp}(q)\Gamma_{cp}(q)$$



Summary

Dynamics of slide-ring gel has been investigated using neutron spin echo spectroscopy.

Clear slow down of the dynamics when PEG is associated with CD molecules. And also when cross-linking points are introduced.

The cross-linking points and polymer segment dynamics are realized within the same time scale, which naturally explains the high extensibility of the slide-ring gel

Contrast variation NSE experiment has been performed for the polyrotaxane in DMSO. It allows us to decouple contributions of the polymer and CD dynamics.

About 1/3 of the diffusion coefficient of the CD molecules when it is threaded with PEG chain was evaluated, comparing to the diffusion coefficient of the free CD molecules in DMSO.

More precise contrast variation NSE measurement will give us better understanding of the system, and it is now under progress.