Design Rules to Advance Materials Development: Double-Network Hydrogels

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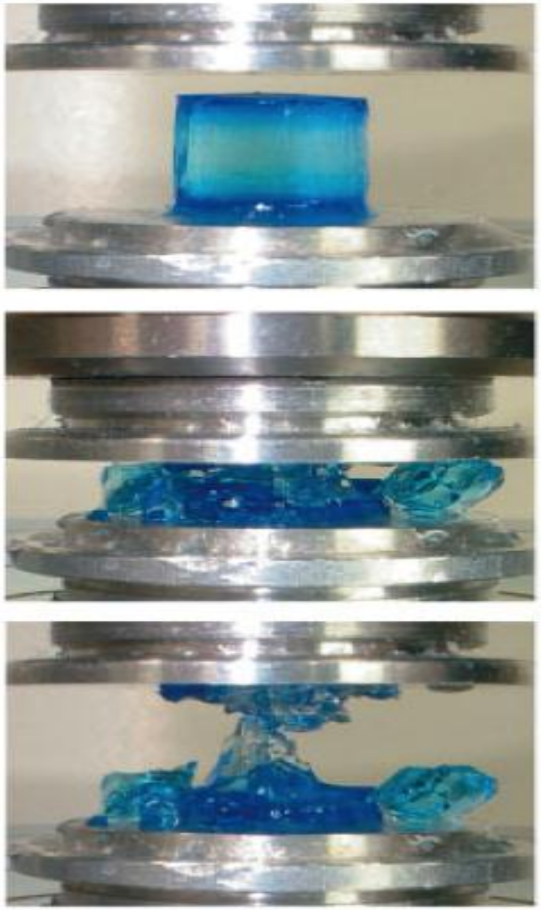
Hydrogels: Introduction

- Crosslinked polymer networks that can absorb as much as 99% water by volume.
- Are biocompatible.
- Widely used in applications
  - personal care, pharmaceutical, biomedical, controlled release, lab-on-chip analytics etc.

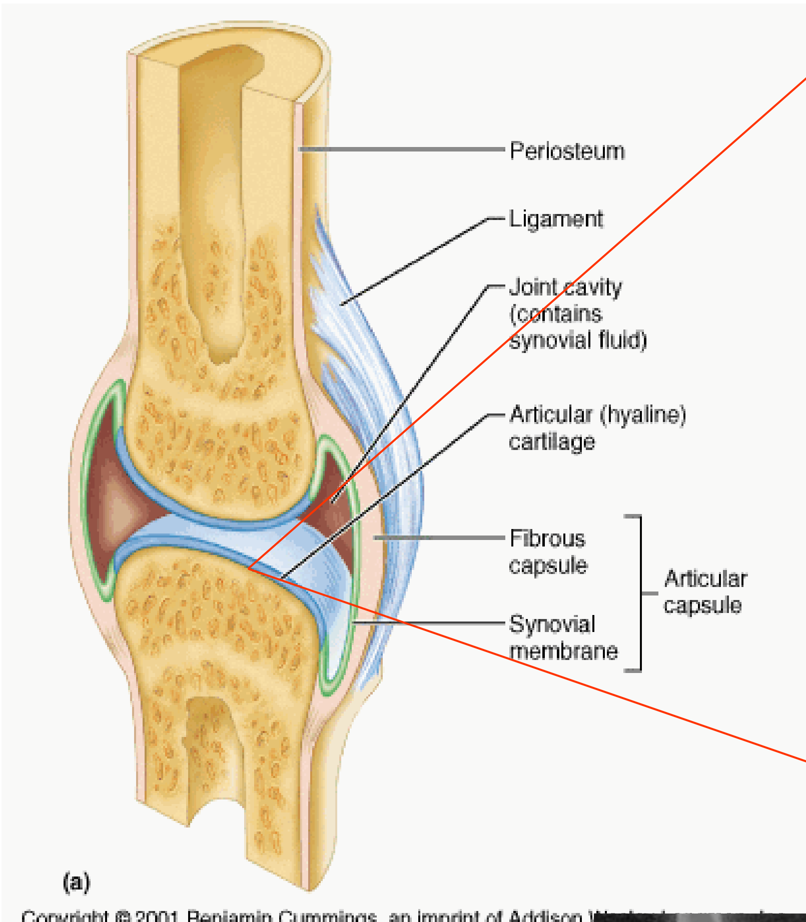
Hydrogels: Recap

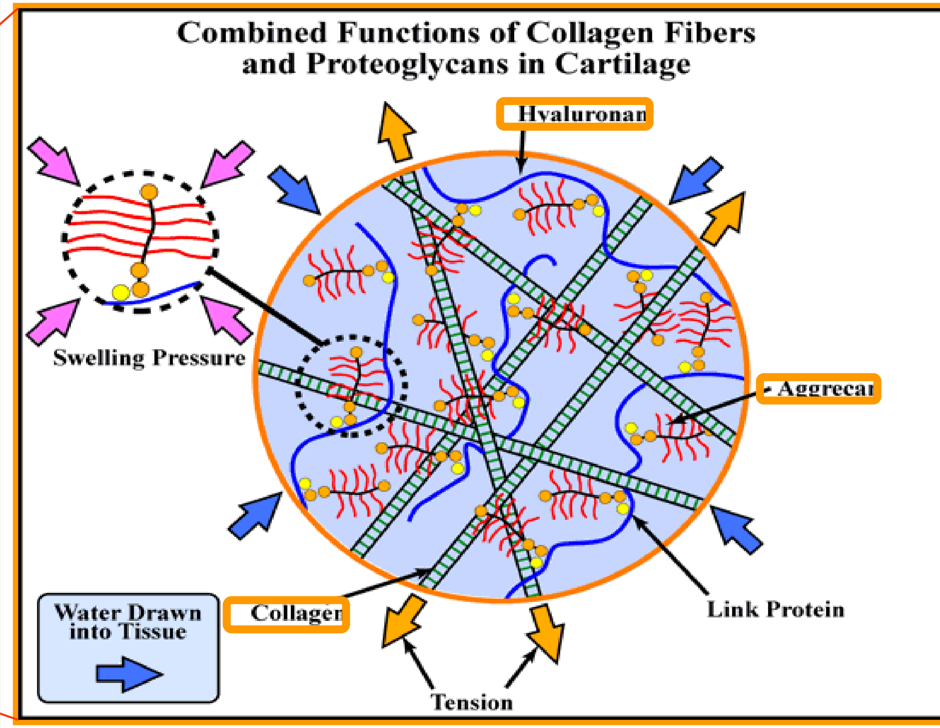
- Hydrogels can absorb and retain as much as 99% water by volume.
- Can be biocompatible.
- Widely used in applications
  - personal care, pharmaceutical, biomedical, controlled release, lab-on-chip analytics etc.
- **But are inherently weak to sustain high mechanical loads.**



Conventional hydrogels

Grand Challenge: Synthetic Cartilage





Contains 80% water by vol.

TOUGH!

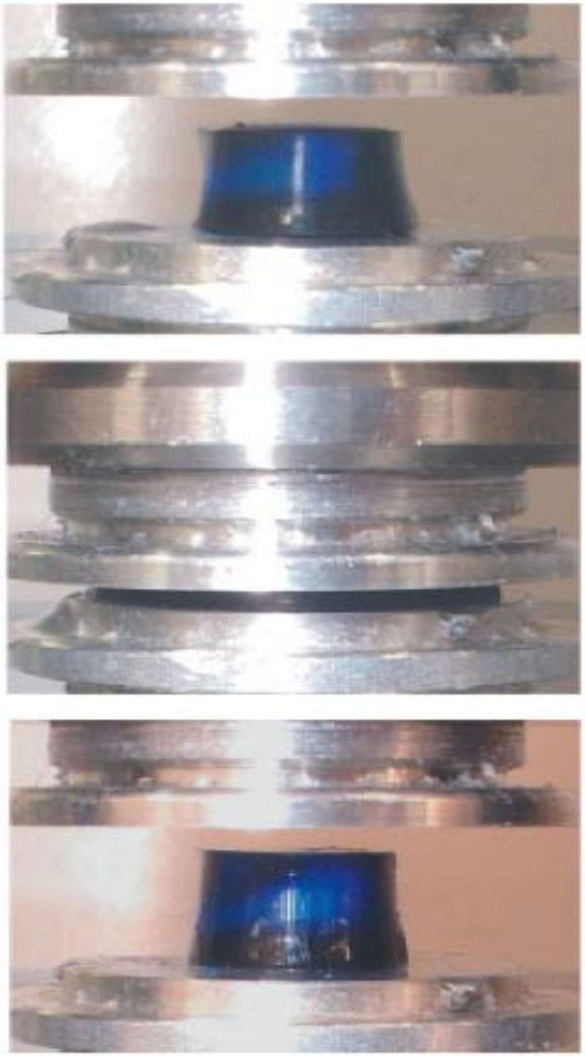
Hydrogels w/ Improved Mechanical Properties

A number of approaches are explored to improve the extensibility of hydrogels: (i) polyrotoxane crosslinks,

(ii) clay nanocomposites, etc.

NONE, however, improve the toughness.

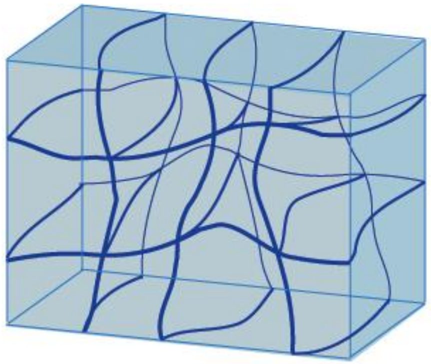
Double-Network Hydrogels (J.P. Gong *et al.*, *Adv. Mater.* **2003**,*15*,1155.)



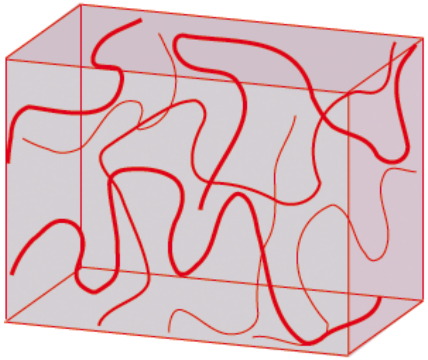
Tough but elastic!

> 85% water by vol.

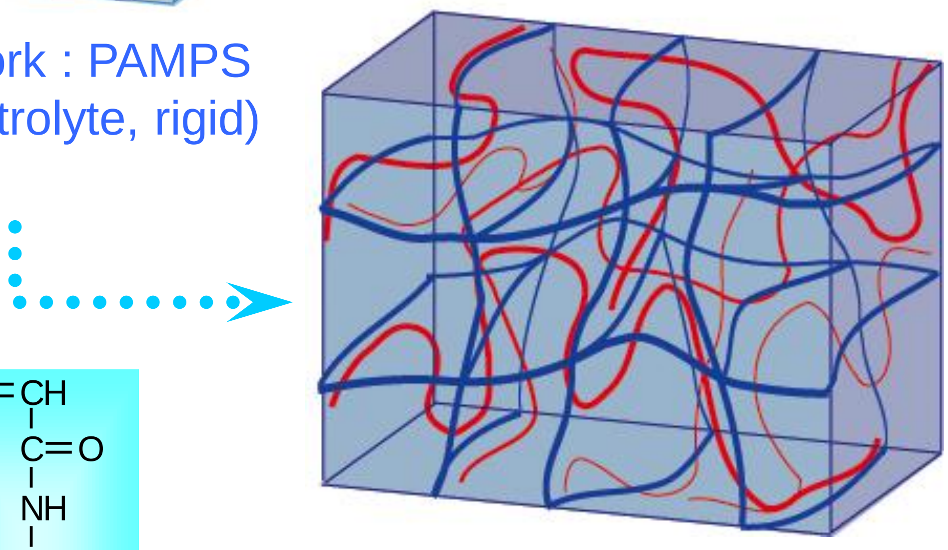
DN-gels

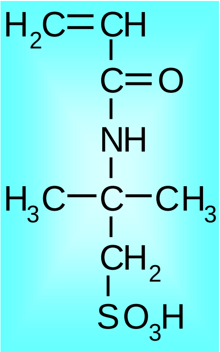


1st network : PAMPS
(polyelectrolyte, rigid)

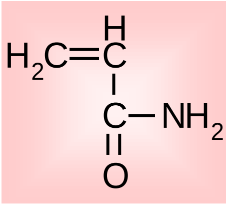


2nd network:PAAm
(neutral, soft)





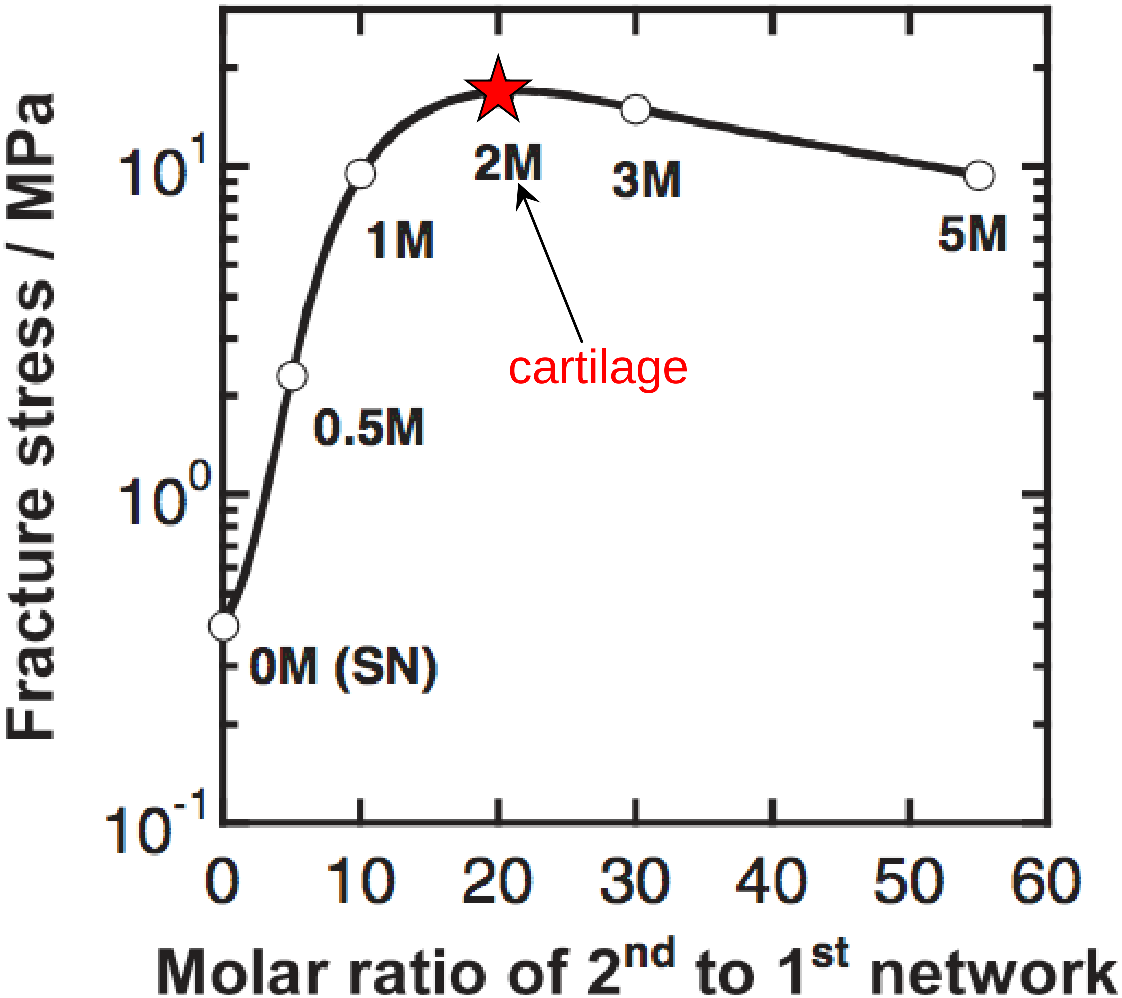
2-acrylamido, 2-methyl
propane sulfonic acid (AMPS)



Acrylamide (AAm)

DN-gels: PAMPS/PAAm

(J.P. Gong *et al.*, *Adv. Mater.* **2003**,*15*,1155.)



Synthetic alternative to tissue cartilage.

A fairly general approach

Table 1. Compressive properties of hydrogels at room temperature.

First network	Second network	Water content [wt.-%]	Fracture stress σ_{max} [MPa]	Fracture strain λ_{max} [%]	$\sigma_{max}^{DN}/\sigma_{max}^{SN}$
PAMPS-1-4 [a]	–	92	0.4	41	–
	PAMPS-2.2-0.1	93	3.0	80	7.5
	PAA-1-0.1	92	2.3	75	5.8
	PAAm-2-0.1	90	17.2	92	43
PAMPS-1-8	–	98	0.006 [b]	0.13 [b]	–
	TFEA-1-0.1	52	1.6 [b]	4.9 [b]	267
PAA-1					
PAAm-1-1	–	93	0.7	98	–
	PAAm-1-0.1	92	5.4	92	7.7
P(AMPS-*co*-TFEA)-1-4	–	98	0.03	73	–
	AAm-1-0.1	93	21.0	97	700
Collagen [c]	–	93	0.26	52	–
	PDMAAm-1-0.1	87	2.9	53	11
Agarose [c]	–	96	0.02	20	–
	HEMA-2.5-0.1	66	2.4	87	120
Bacteria cellulose	–	–	–	–	–
	Gelatin	78	3.7	37	31 [d]

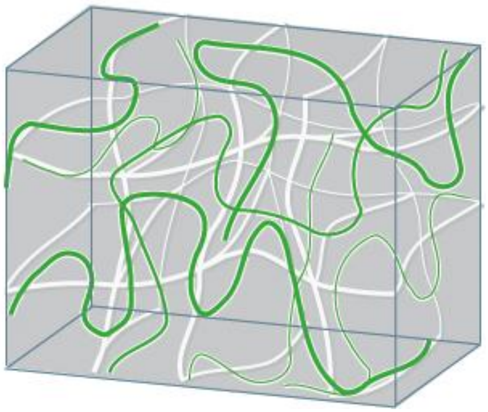
How do flexible polymer chains reinforce a brittle primary network?

[a] *P-x-y*: *P*, *x*, and *y* denote the abbreviated polymer name, molar monomer concentration, and the crosslinker concentration in mol-% with respect to the monomer, respectively. [b] Stretching properties. [c] Physically cross-linked gel prepared from 2 wt.-% solution. [d] Relative to gelatin SN gel.

J.P. Gong *et al.*, *Adv, Matter.* **2003**,*15*,1155.

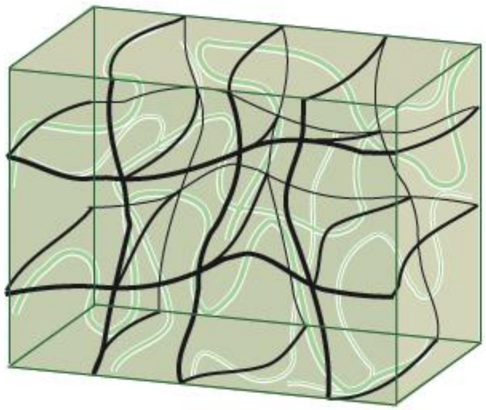
Advantage of Neutron Scattering: Contrast Variation

PAAm linear chains alone



AMPS/d_3-AAm in H_2O

PAMPS network alone

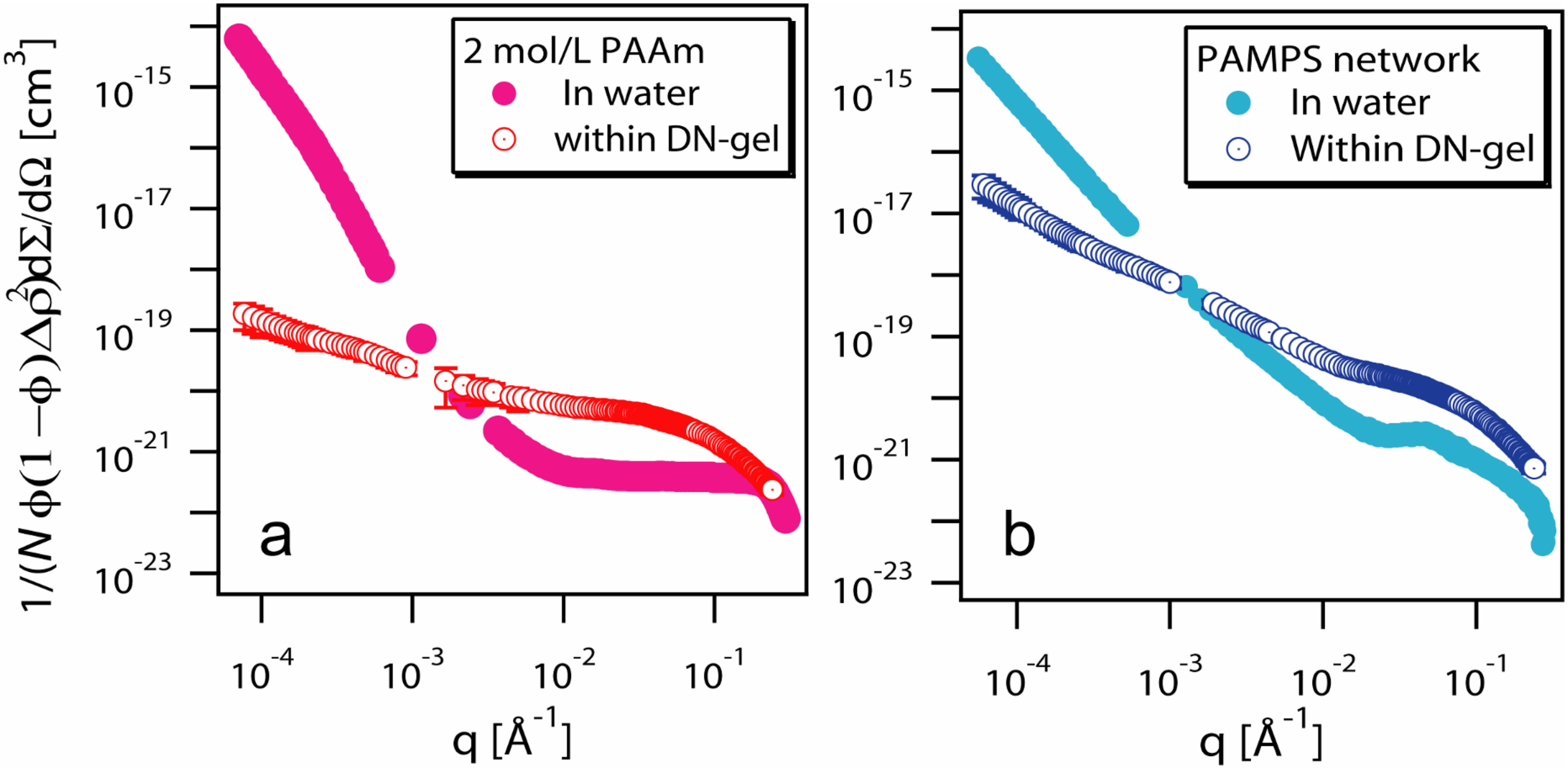


AMPS/d_3-AAm in D_2O/H_2O

$$2nm < \xi < 12\mu m \quad (\xi = \frac{2\pi}{q})$$

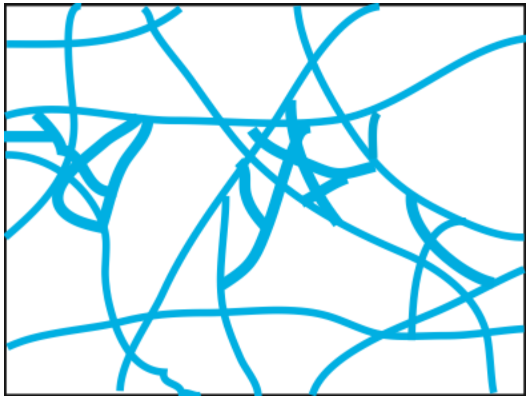
$$(5 \times 10^{-5}\,\mathring{A} < q < 0.3\,\mathring{A})$$

PAMPS and PAAm: In water and in DN-gels



Tominaga, Tirumala *et al. Polymer* **2007**.

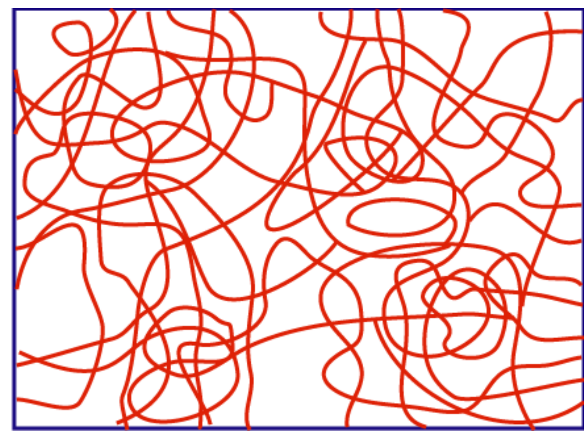
Schematic for structure of PAMPS (blue) and PAAm (red) in DN-gels



PAMPS in D_2O

PAAm in D_2O

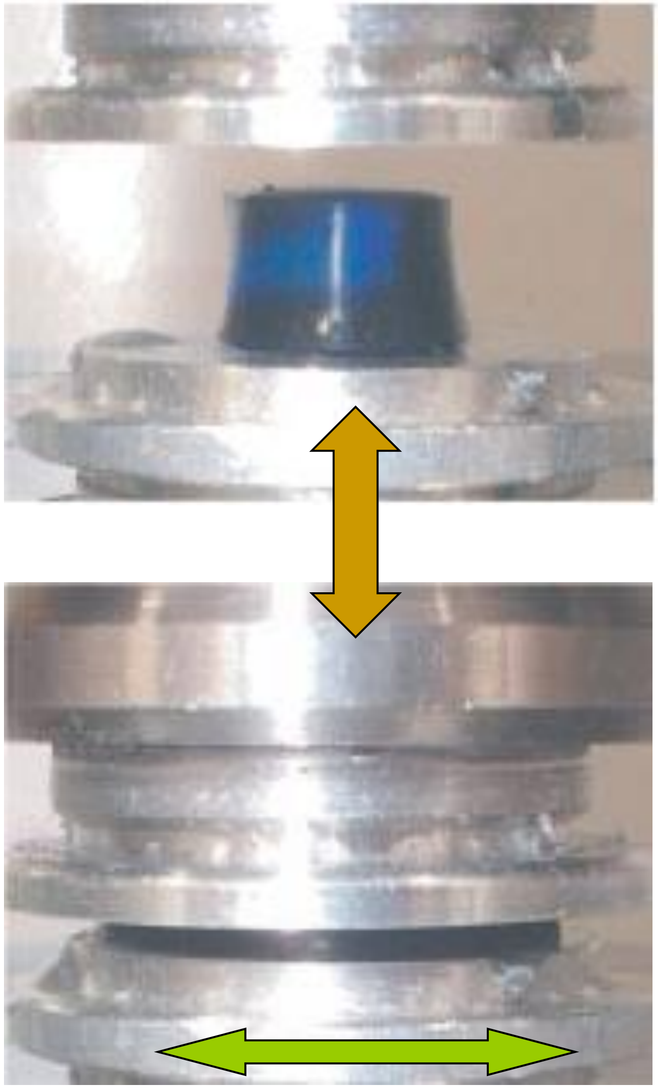
PAMPS in DN



PAAm in DN

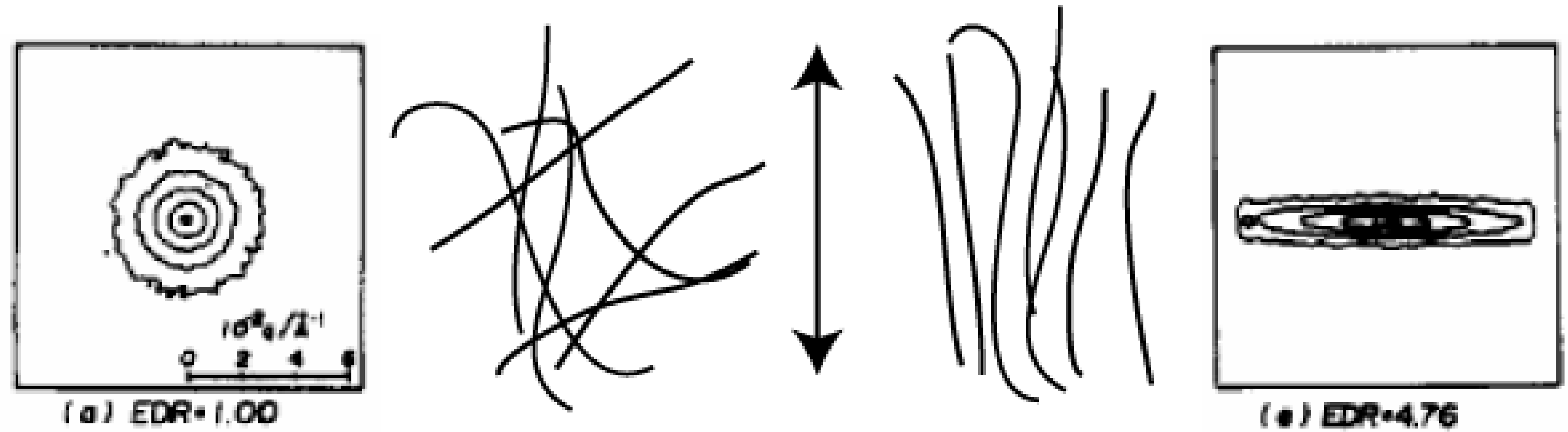
PAMPS and PAAm dissolve better in water when in presence of the other.

Response to Compression?



Uniaxial Deformation of Neutral Polymers

Solvent-cast and uniaxially extruded poly (vinyl alcohol) films.



Shibayama, M.; Wu, W.-L, *et al*. *Macromol*., **1990**, *23*, 1438.

Scattering Intensity lower in stretching direction: $I_{\perp} > I_{||}$

Affine deformation → Polymer chains readily deform along the extension axis.

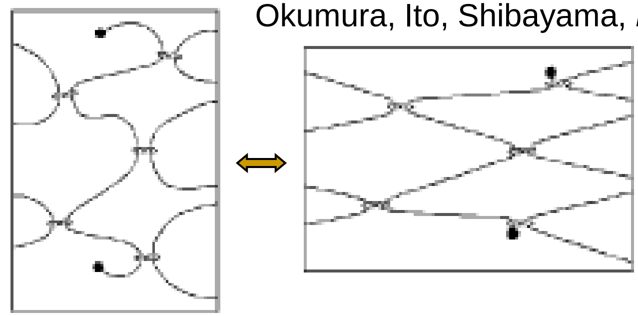
Uniaxial Deformation of Extensible Gels

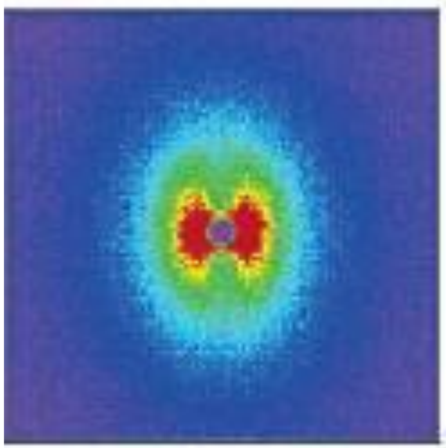
Haraguchi and Takehisa, *Adv. Mater.* **2002**.

Shibayama, Takehisa, Haraguchi, *Macromol.* **2005**.

Okumura and Ito, *Adv. Mater.* **2001**.

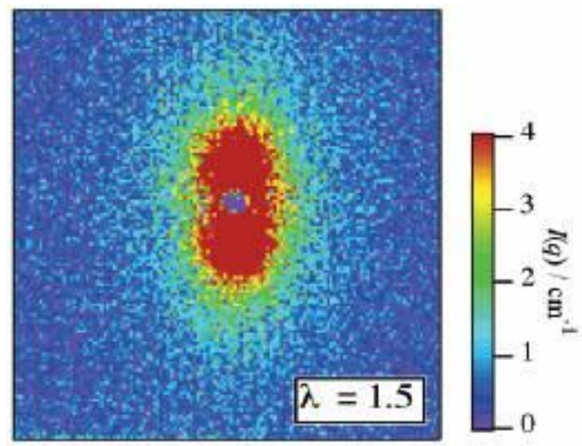
Okumura, Ito, Shibayama, *Macromol.* **2005**.





Clay-PNIPAm Nanocomposite

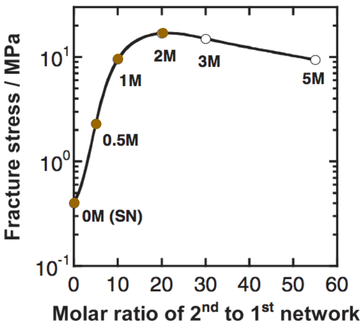
SDD ~ 8 m.



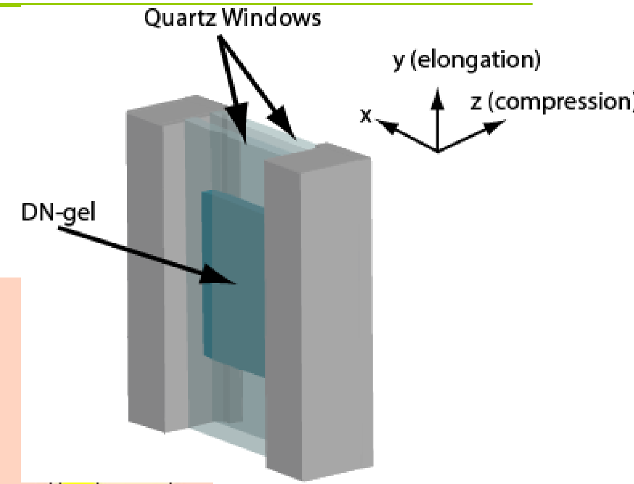
Side-ring gels w/ polyrotaxane

Deformation in extensible hydrogels propagates down to molecular scale.

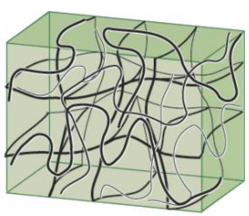
Uniaxial Extension of DN-Gel

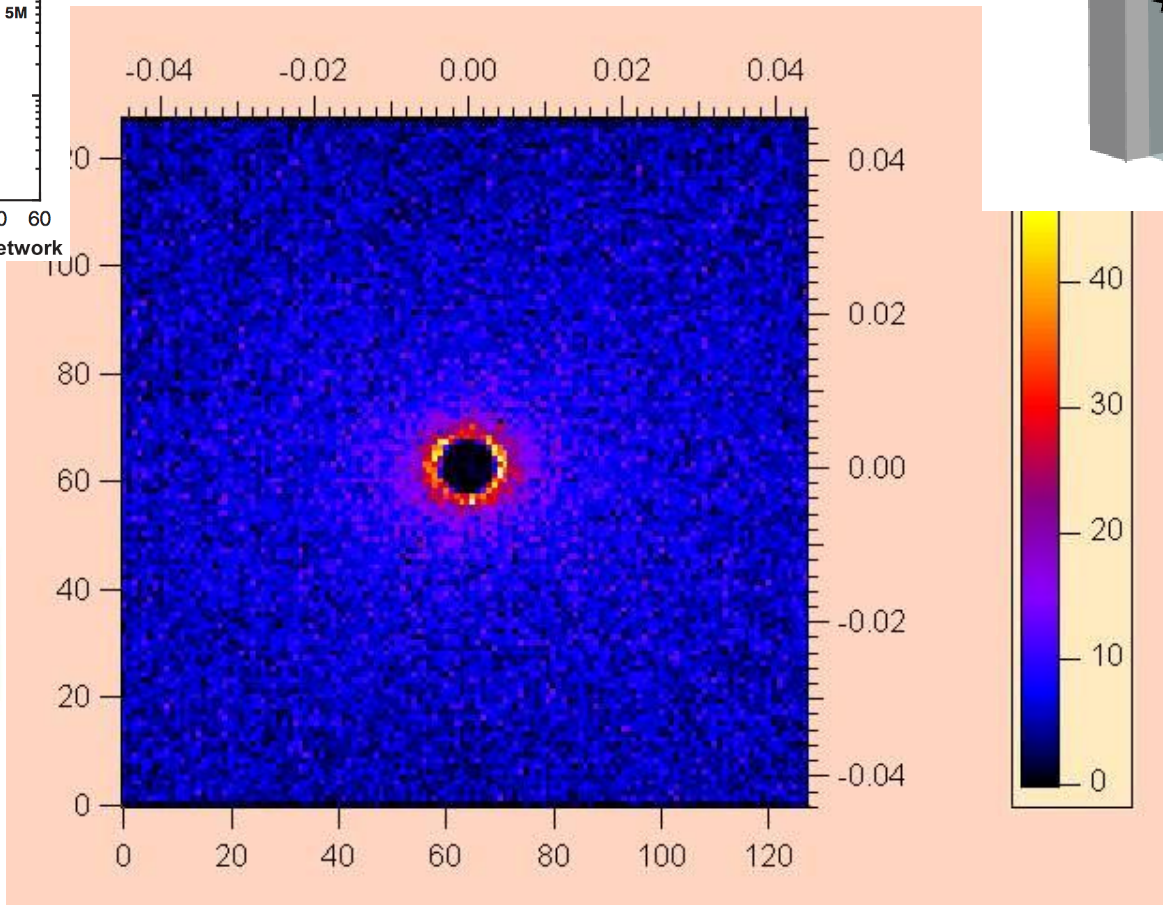


SDD = 4.5 m



100% uniaxial extension





Total DN-gel:

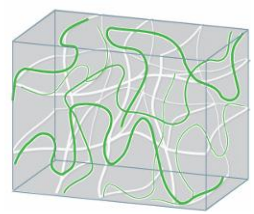
PAMPS + PAAm

0.006 < *q* (Å^{-1}) < 0.1

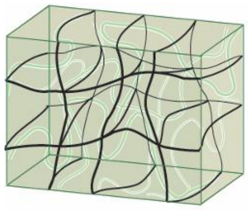
No anisotropy in small-angle scattering.

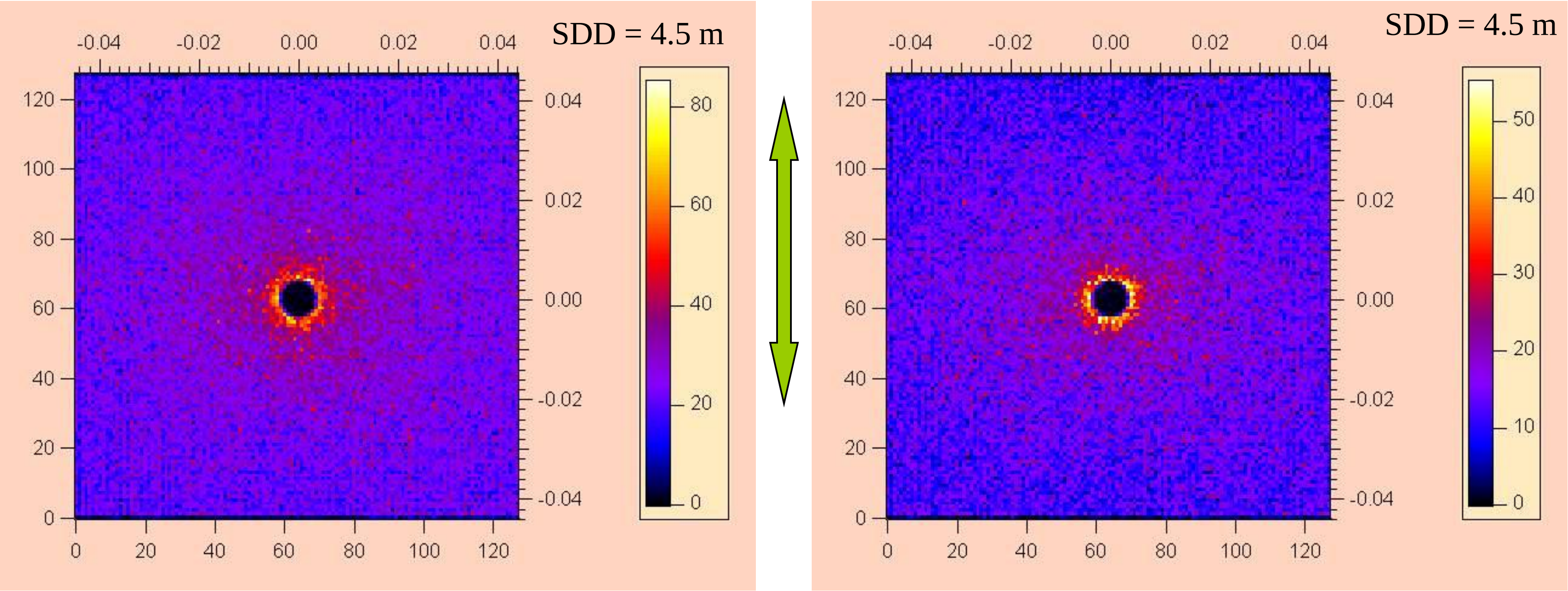
Uniaxial Extension of DN-Gel

*d*PAAm chains in PAMPS network



Contrast-matched *d*PAAm chains in PAMPS network

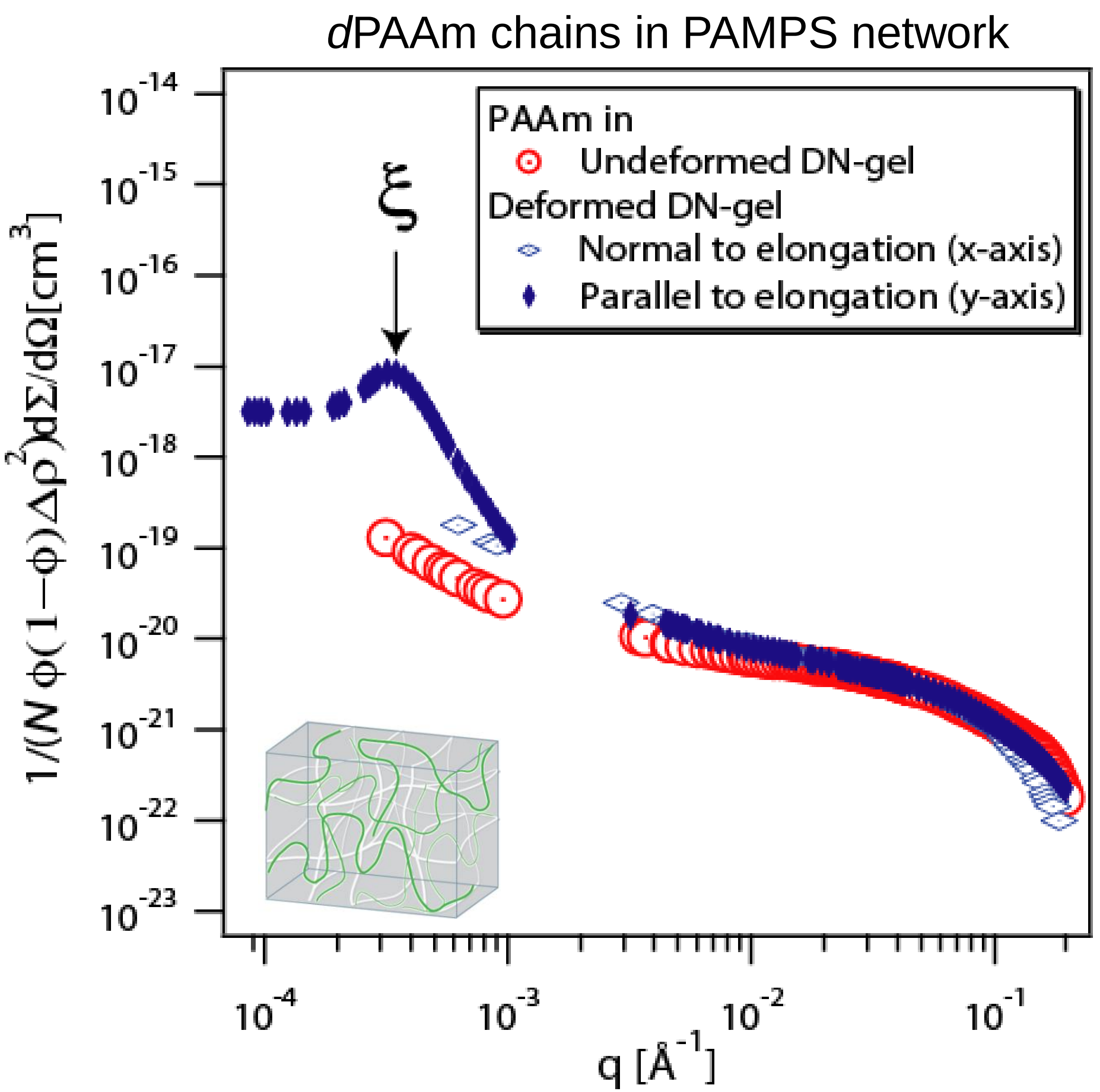




No anisotropy in the small-angle region, $0.002 \leq q$ (Å^{-1}) ≤ 0.2.

Uniaxial stress is effectively relaxed at small length scales.

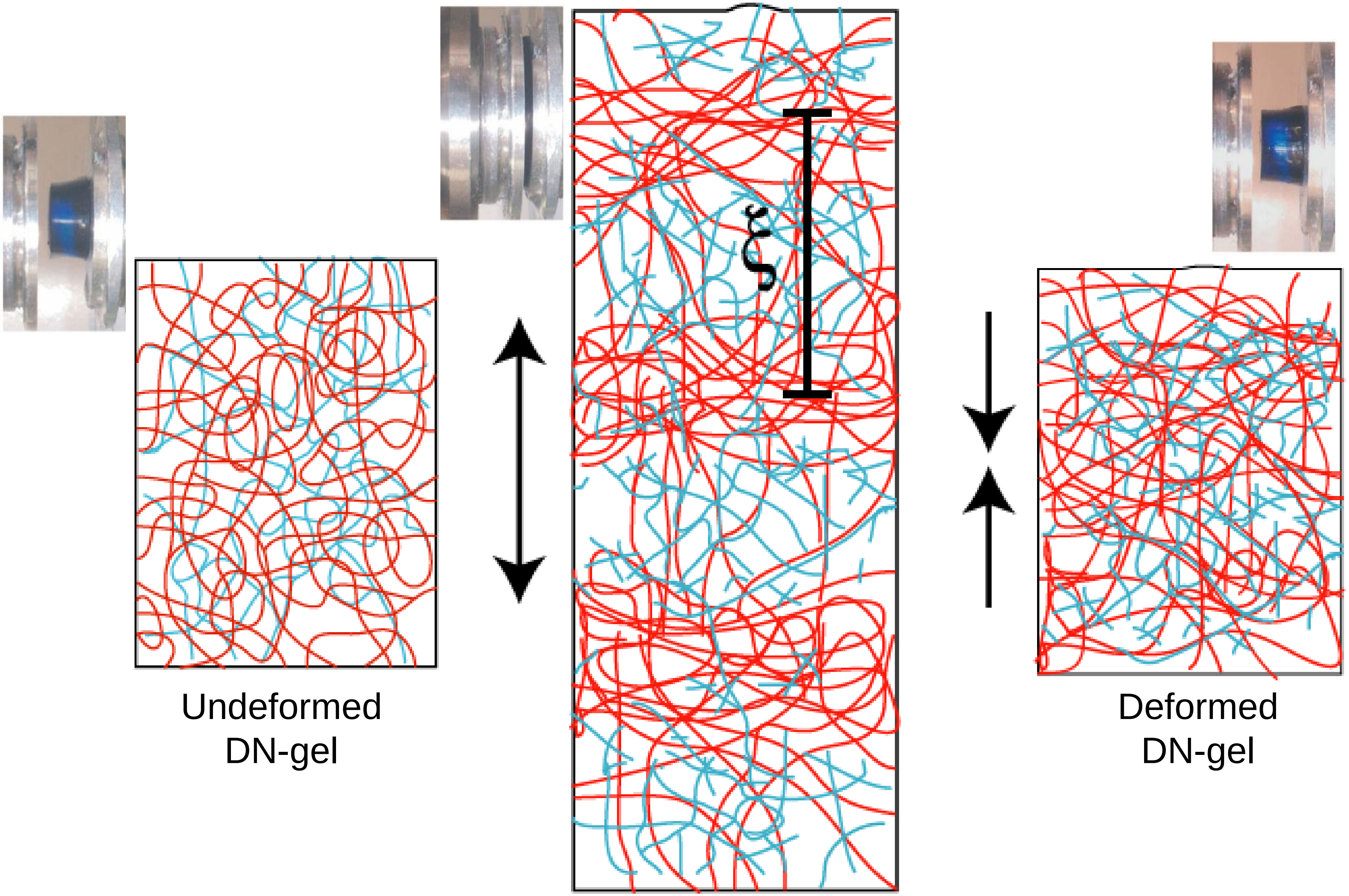
Toughest DN-gel under pure shear



Tominaga, Tirumala *et al. J. Phys. Chem.* **2008**.

Strong low *q* anisotropy.

Structural Response to Deformation in DN-gels



Undeformed DN-gel

100% extension

Deformed DN-gel

Tominaga, Tirumala *et al. J. Phys. Chem.* **2008**.

SANS Data Anaysis: Theory

Static scattering from mixtures of polyelectrolytes and neutral chains :

Benmouna and Vilgis Macromolecues, 1991, 24, 3866.
Benmouna, Vilgis, Hakem and Negadi, 1991, 24, 6418.

$$S^{-1}(q) = S_o^{-1}(q) + V$$

$S(q)$ Total Structure Matrix

$S_o(q)$ Bare Structure Matrix

V Interaction Matrix

q $4\pi/\lambda(\sin\theta)$

Tominaga, Tirumala *et al. J. Phys. Chem.* **2008**.

Theoretical Model – Contd…

3-component system of **polyelectrolyte, neutral polymer and solvent**

2 X 2 Matrices are needed. (Incompressible system.)

PE : Polyelectrolyte (PAMPS), NP : Neutral Polymer (PAAm), S : Solvent (water)

$$S_o(q) = \begin{pmatrix} S^o_{PE} & 0 \\ 0 & S^o_{NP} \end{pmatrix}$$

$$V = \begin{pmatrix} \upsilon_{PE-PE} & \upsilon_{PE-NP} \\ \upsilon_{PE-NP} & \upsilon_{NP-NP} \end{pmatrix}$$

$$\upsilon_{PE-PE} = \frac{1}{\varphi_S} - 2\chi_{PE-S} + \frac{4\pi l_b}{q^2 + \kappa^2}$$

$$\upsilon_{NP-NP} = \frac{1}{\varphi_S} - 2\chi_{NP-S}$$

$$\upsilon_{PE-NP} = \frac{1}{\varphi_S} - \chi_{PE-S} - \chi_{NP-S} + \chi_{PE-NP}$$

φ_S : Volume fraction of the solvent

l_b : Bjerrum length

κ^{-1} : Debye length

Tominaga, Tirumala *et al. J. Phys. Chem.* **2008**.

Theoretical Model – Contd…

$$\frac{1}{S_{AA}} = \frac{1}{S_A^o} + \upsilon_{AB} - \frac{\upsilon_{AB}^2 S_B^o}{1 + \upsilon_{BB} S_B^o}$$

$$S_A^o = \varphi_A N_A P_A(q)$$

φ_A : Volume fraction of A

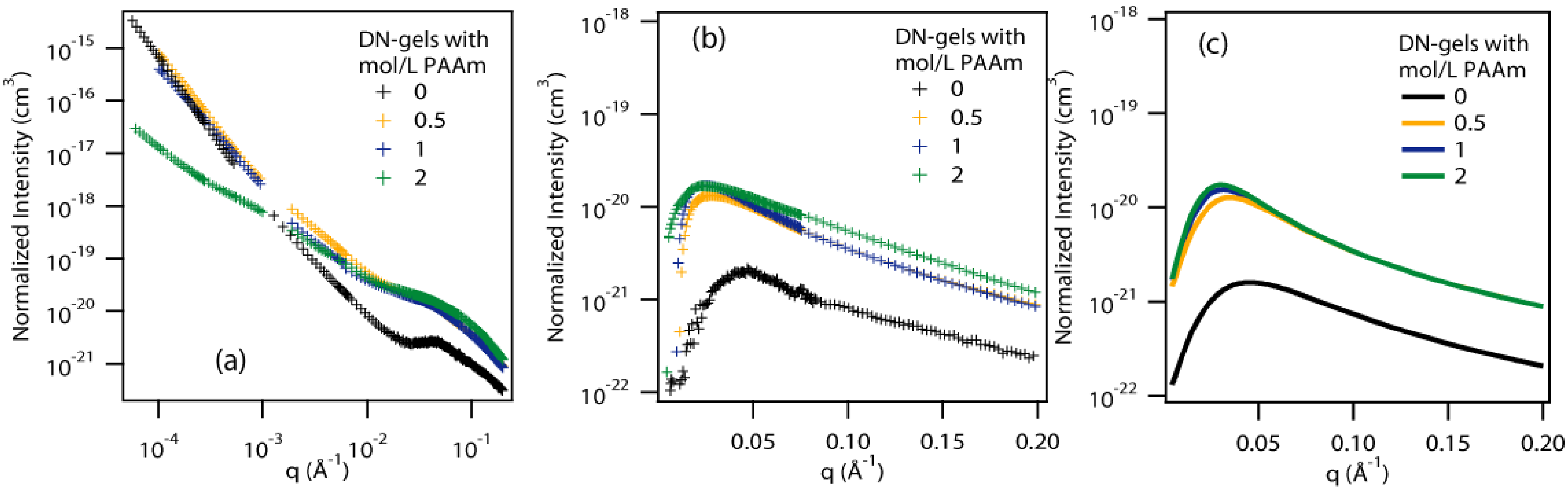
N_A : Degree of polymerization of A

$P_A(q)$: Form factor of A (Debye function)

$$P_A(q) = \frac{2}{\alpha^2}\left[e^{-\alpha} + \alpha - 1\right]; \qquad \alpha = q^2 R_g^2$$

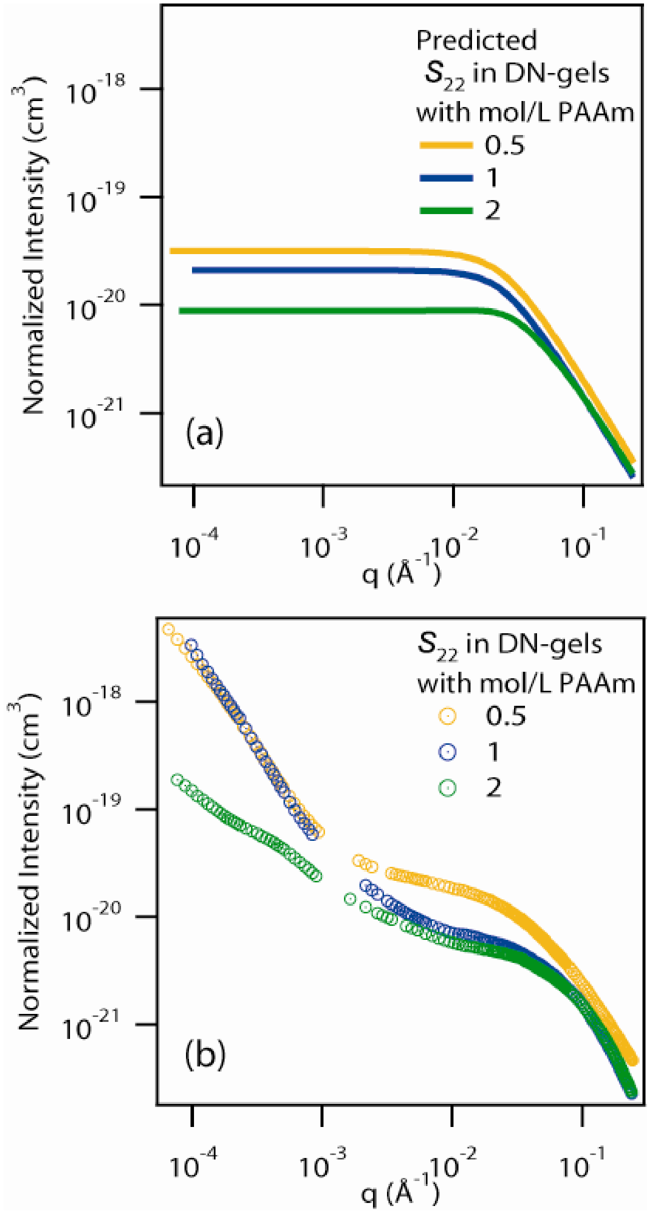
Tominaga, Tirumala *et al. J. Phys. Chem.* **2008**.

Fitting Results: PAMPS

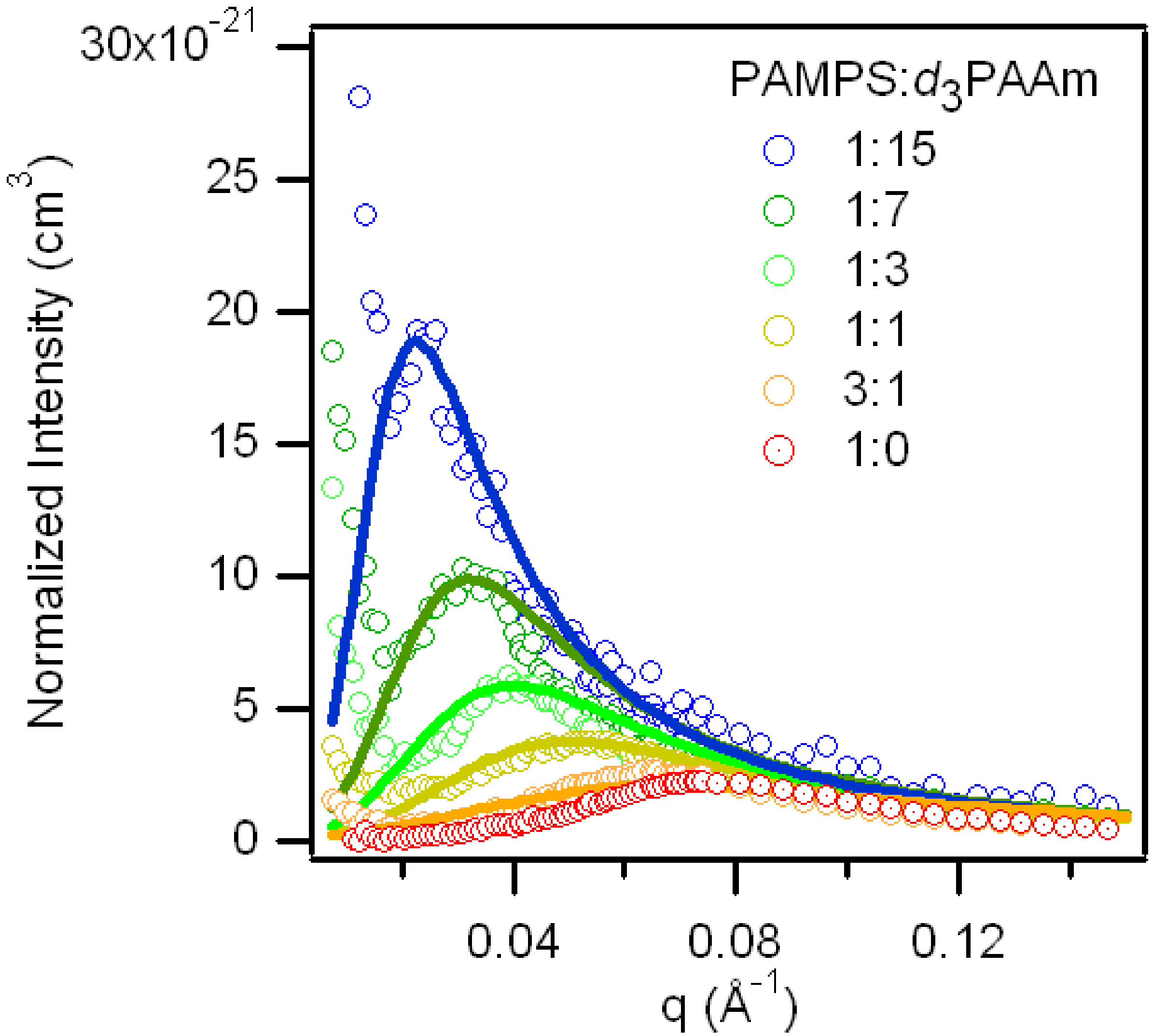


Tominaga, Tirumala *et al. J. Phys. Chem.* **2008**.

Fitting Results: PAAm



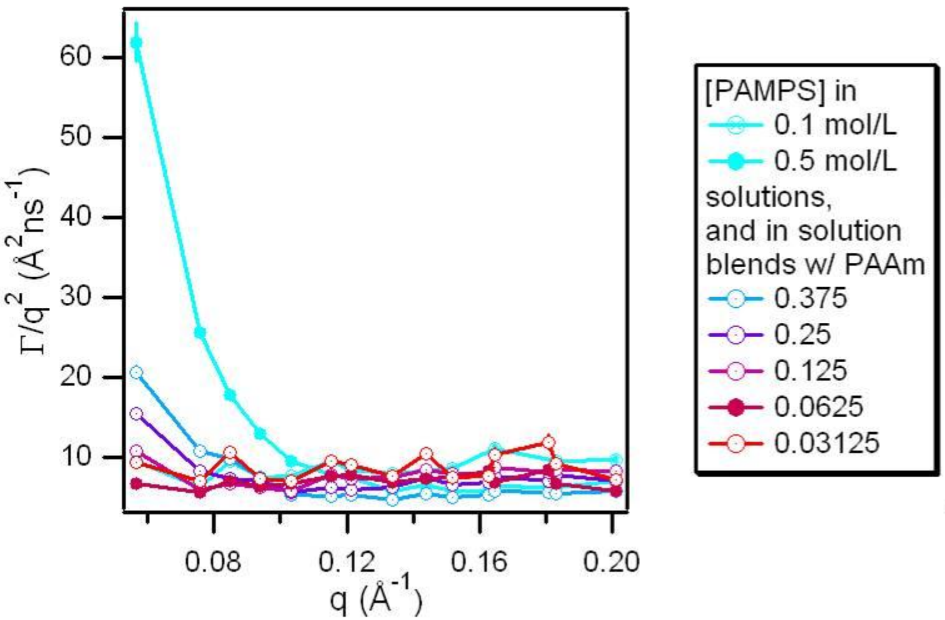
Fitting Results: PAMPS/PAAm solution blends

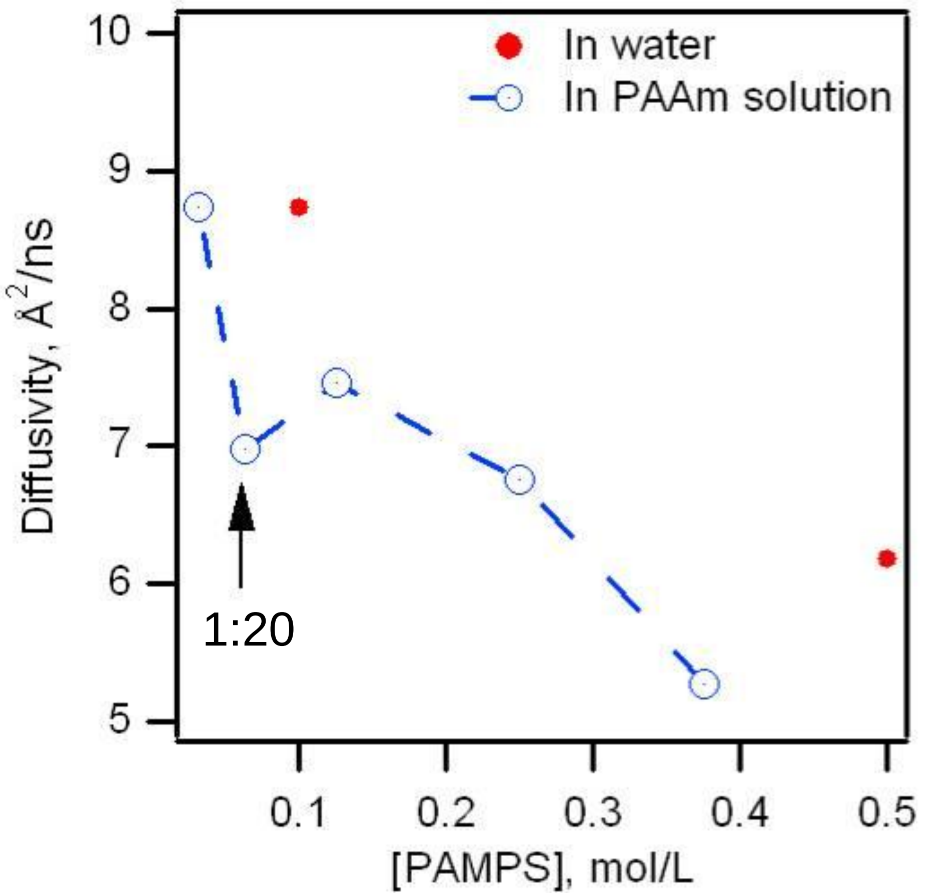


Best Fit Parameters

	χ_{PE-S}	χ_{NP-S}	χ_{PE-NP}	Mesh length (Å)
Pure PE (PAMPS)	0.2	-	-	140
0.5 M DN	0.2	0.45	0.03	545
1M DN	0.2	0.44	0.03	771
2M DN	0.2	0.48	0.03	860

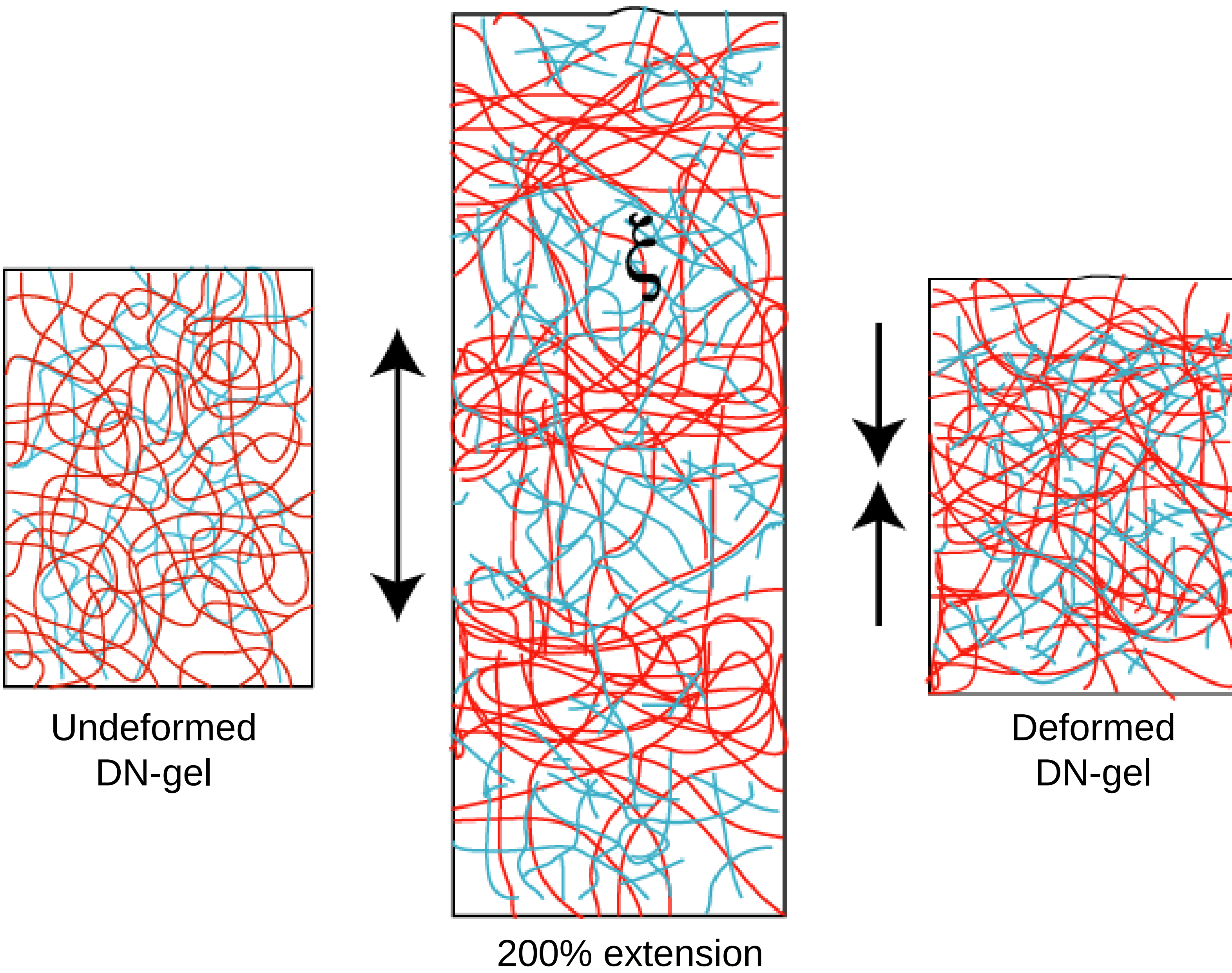
Anomalous Fluctuations in PAMPS/PAAm Solution Mixtures: Neutron Spin-Echo





Reduced diffusivity of PAMPS backbone at a critical PAMPS/PAAm molar ratio indicates complexation between the DN-gel constituents.

Deformation Mechanism in DN-gels



Summary

- ❑ Enthalpic association between the constituents allows for energy dissipation and stress-transfer from first network to the second.

- ❑ PAAm linear chains undergo dynamic reorganization under an applied load.

- ❑Linear polyacrylamide chains *reinforce* the DN-gels to sustain large deformations.

Thanks to…

Jeff Kryzwon, Bryan Greenwald, Dr. John Barker

If I could solve all the problems myself, I would. – *Thomas Edison*