THE UNIVERSITY OF TOKYO

The 3rd Soft Matter Summer School : Polymer Sciences in Biology
June 21 - July 4, 2015

"Neutron and Rheology"

Mitsuhiro Shibayama,
ISSP, U. Tokyo

Part 1. Structural Analyses of Polymers by Small Angle Neutron Scattering

Part 2. Contrast Variation SANS
- The basics and applications -

Part 3. Rheo-SANS Studies on Structure Evolution in Polymer-particle Aqueous Solutions
- shear thickening -

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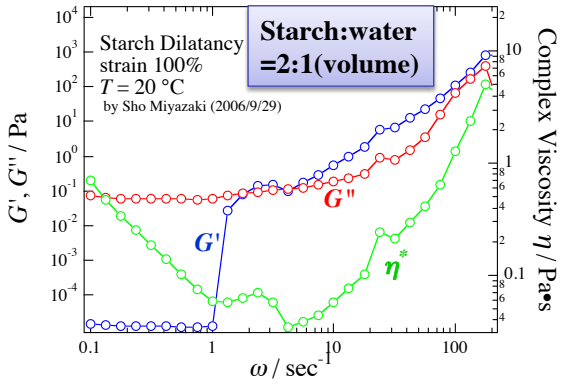
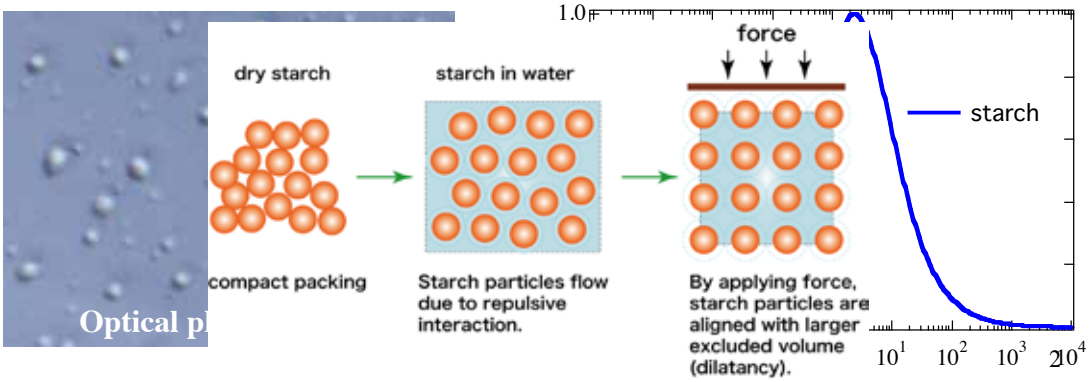
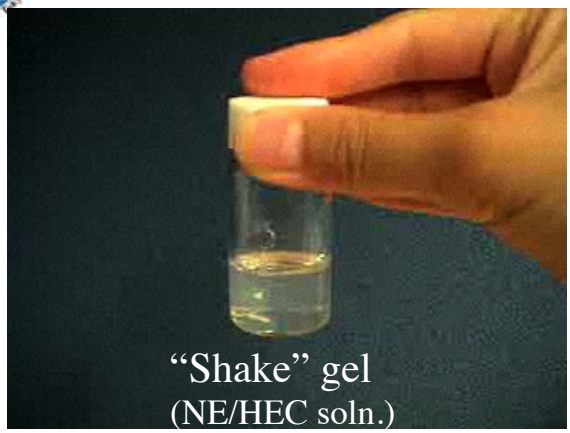
Dilatancy





dilute suspension of starch

Shake gels



Laponite (clay)-PEO

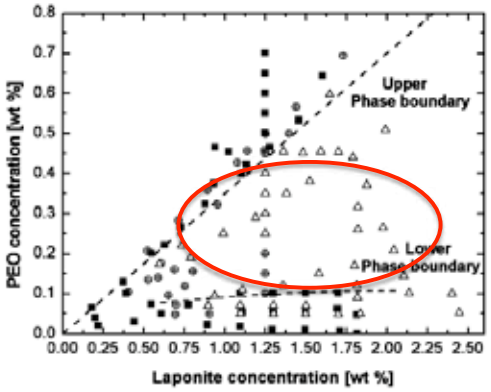


Fig. 1. Phase behavior of laponite–PEO 'shake-gels', formed by vigorous shaking. The open triangles represent mixtures that form shake-gels upon application of shear; the circles represent mixtures that shear-thicken and show an increase in viscosity but do not gel; and the solid squares represent mixtures that do not gel even when subjected to large shear. The molecular weight of PEO used is $M_w = 300\,000$ g mol^{-1}, with a radius of gyration $R_g = 32$ nm.

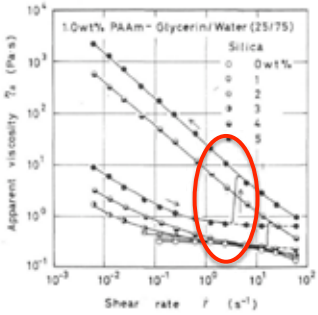


Fig. 7. Shear rate dependence of apparent viscosity for 1.0 wt % PAAm solution in glycerin/water mixture with 25/75 mixing ratio and the suspensions at different particle concentrations.

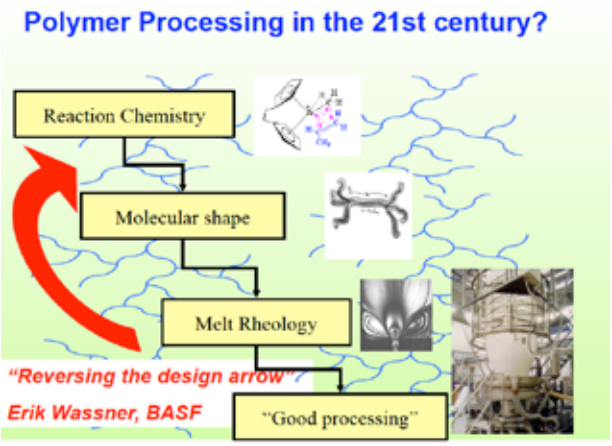
Silica-PA

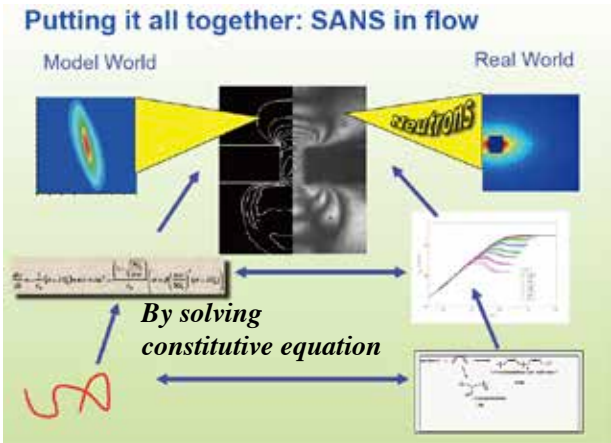
Silica suspensions in polyacrylamide solutions
Y. Otsubo, K. Umeya
J.Rheology, 1984, 28, 95-108.

Shear-induced gelation of laponite-PEO mixtures
J. Zebrowski, D. A. Weitz et al.
Colloid Surface and Interface, 213, 2003, 189.

Advances in Rheo-SANS: The structural rheology of long polymer chain branched polymers

Measuring and modelling of macromolecules in flow





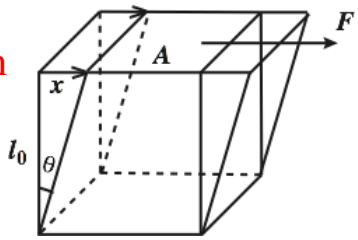
Tom McLeish (U. Durham, UK),
ISSPSoft2010, Kashiwa, U. Tokyo, 2010

Shear deformation and response

= variety of rheological behavior of polymeric systems =

Rheology; science to understand the relationship between deformation and its response

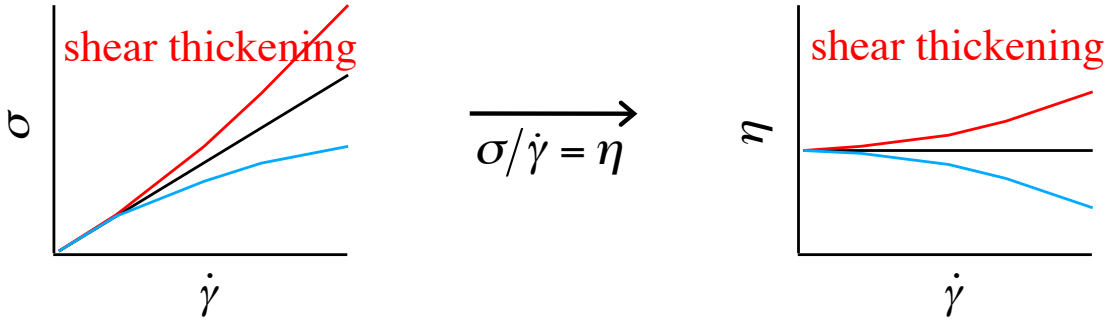
Shear deformation
shear



Stress: $\sigma = F / A_0$

Shear strain: $\gamma = l_0 / x = tan\theta$

Shear rate: $\dot{\gamma} = \frac{d\gamma}{dt}$



e.g.) Shear thinning ; ketchup, mayonnaise, cosmetics, paints
Shear thickening ; starch, sand of seashore

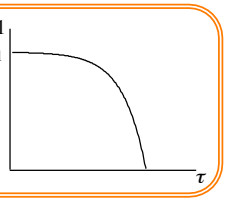
Experimental

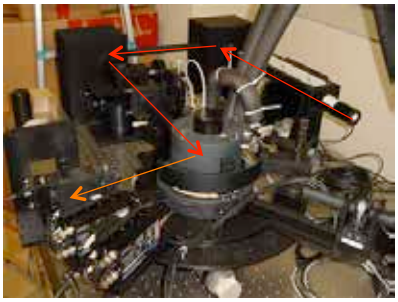
dynamics

diffusion
Translation/local motion

DLS

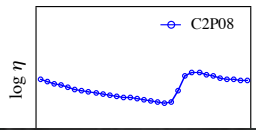
ALV-5000

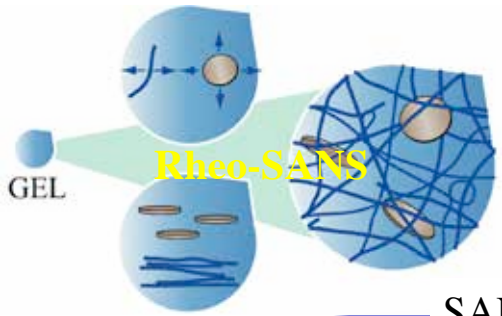




properties

viscometry

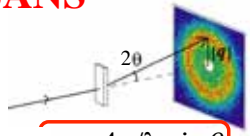




structure

Intermolecular
interaction

SANS

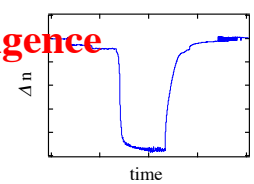


SANS-U $q = 4\pi/\lambda \sin\theta$

small q

orientation

birefringence



Rheo-SANS

SANS-U, ISSP, Univ. Tokyo

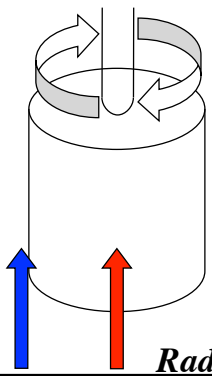
Wavelength: 7 Å
SDD: 2, 4, 8 m, 12 m
Q range: 0.002 - 0.1 $Å^{-1}$

Okabe et al., J. Appl. Cryst., 2005, 38, 1035.
Iwase et al., J. Appl. Cryst., 2011, 44, 558.

MCR 501 (Anton Paar)

Torque : 0.1 μNm - 230 mN m
Torque resolution : 0.001 μN m

Quartz cell
Cylinder
Diameter : 48 mm
Angle : 2.2 °
Beaker
Diameter : 50 mm
Gap size : 1 mm
Sample amount: 10 ml



7

Tree topics

Part I: NE/HEC Shake gel

Part II: Shear thickening of Clay/PEO

Part III: Phantom chains of CTAB/salt

Tree topics

Part I: NE/HEC Shake gel

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Self-standing nano-emulsion

Kawada, et al., Langmuir, 2010, **26, 2430.**

self-standing
Nano-emulsion

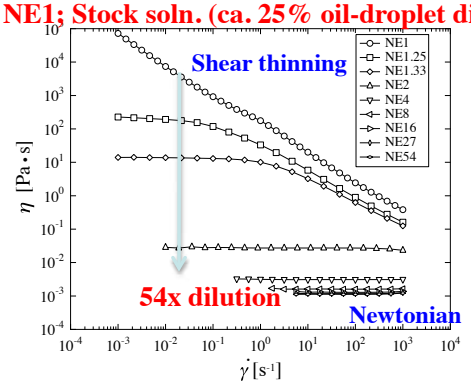
Transmission micrograph

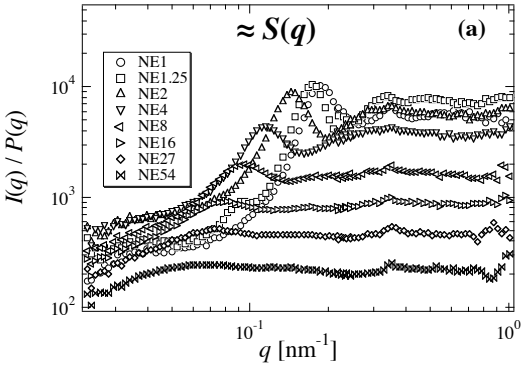
About 25% oil droplet
with small amount of anionic surfactant
obtained by high-pressure extrusion

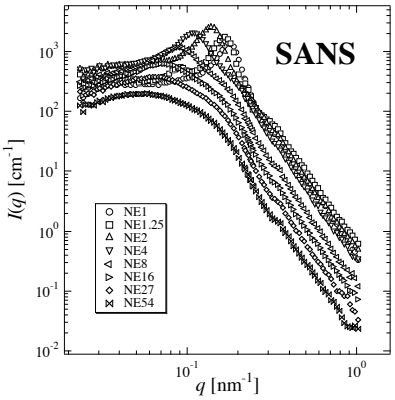
Kao Co. Ltd. kao

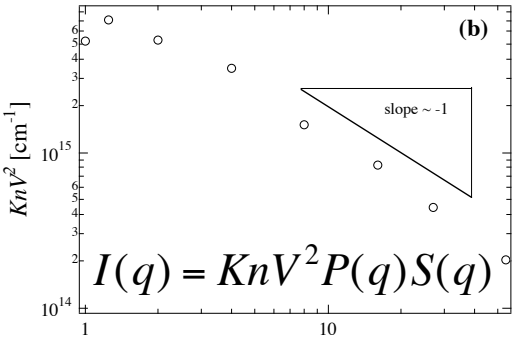
Rheological behavior

NE1; Stock soln. (ca. 25% oil-droplet dispersion)



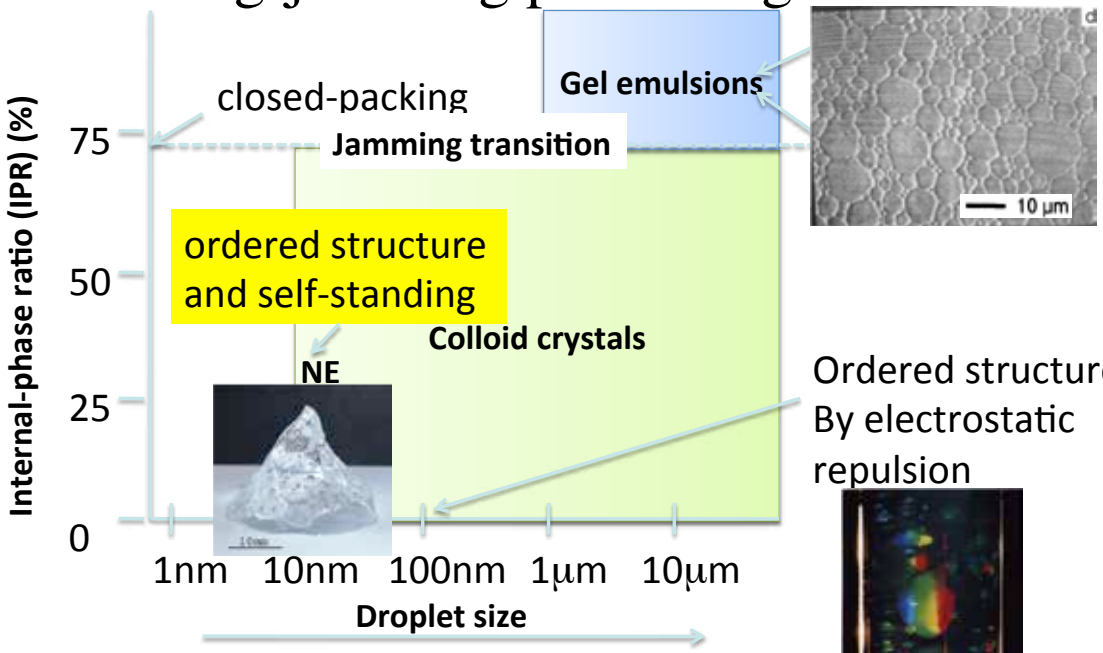






Dilution ratio, x

Ordering-jamming phase diagram



Ordered structure
By electrostatic
repulsion

Needs high purification of dispersoid to increase the Debye screening length

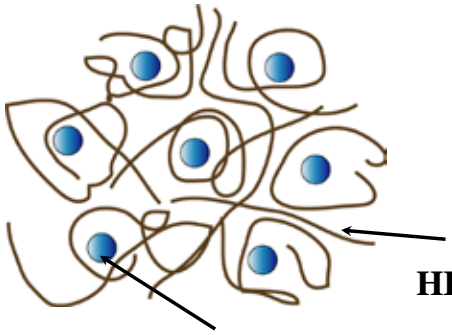
ϕ= 0.000829
d = 110nm

Kawada, et al., Langmuir, 2010, 26, 2430.

NE/polymer shake gel system: sample

J. Chem. Phys, 2007, 127, 144507

Shake gels, composed of a mixed solution of polymer and nano-size emulsion, show both shear thinning and shear thickening behaviors.



Nano-emulsion was made by high pressure extrusion of 30 wt % glycerol, 3 wt % ethanol, 16 wt % oil.

Nano-particles in the emulsion become cross-linkers to which polymer chains are attached.

Polymer : 2-hydroxyethyl cellulose (HEC) : M_v = 1.30 x 10^6 g/mol
Particle : nano-size emulsion (NE) : (Diameter ≈ 30 nm)
Concentrations: polymer = 0.4 %, emulsion = 12 %

C_{NE} and C_{HEC} dependence of dilatancy

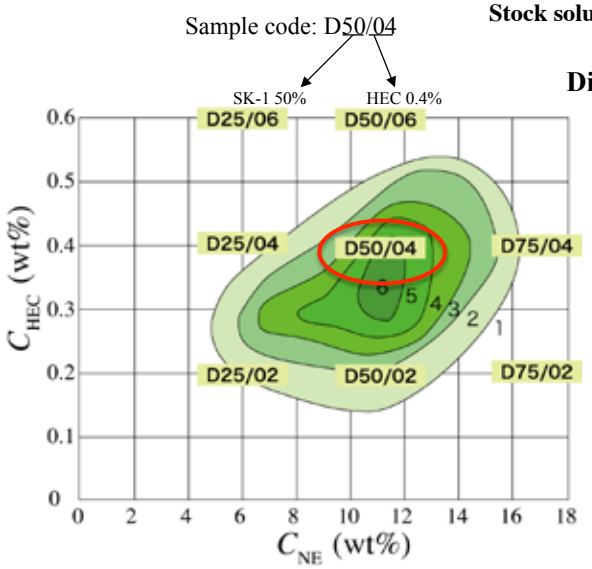
Samples

(polymer)

NE (wt%)	Conc. of HEC130 0.2%	0.4%	0.6%	dilution
25%	D25/02 (①)	D25/04 (④)	D25/06 (⑦)	·· 4x
50%	D50/02 (②)	D50/04 (⑤)	D50/06 (⑧)	·· 2x
75%	D75/02 (③)	D75/04 (⑥)	—	·· 1.33x

Stock solution : ≈ 25%

A tuning-fork vibration Viscometer (CJV5000, A&D Co. Ltd., Japan) @ 25°C, 30 Hz

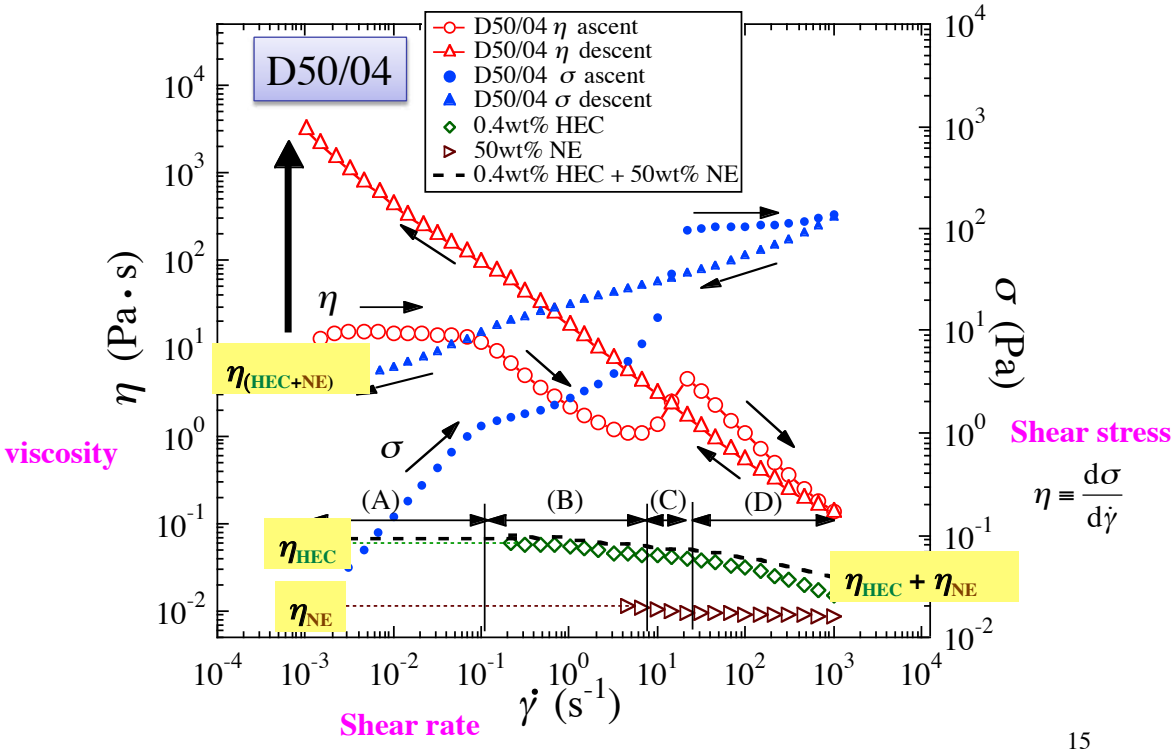


Dilatancy factor

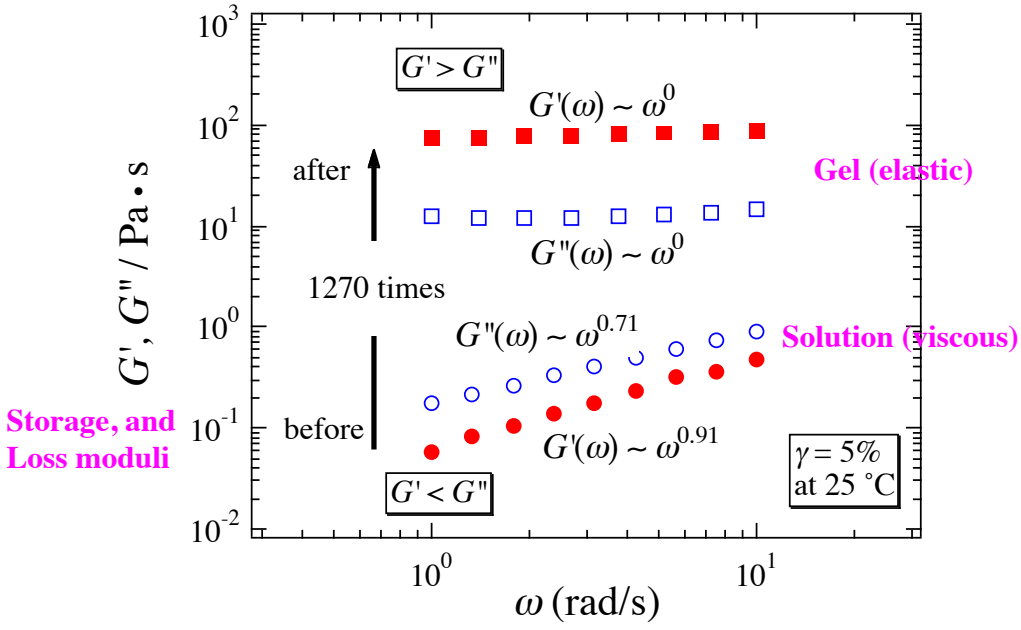
F

Def.
Dilatancy Factor = viscosity ratio after and before Shaking

Flow behavior: shear-induced transition

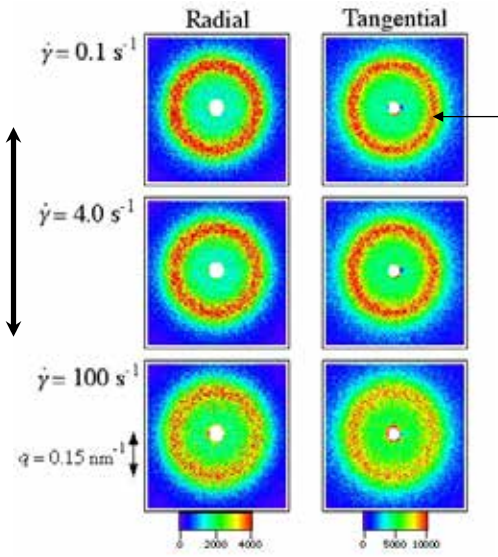


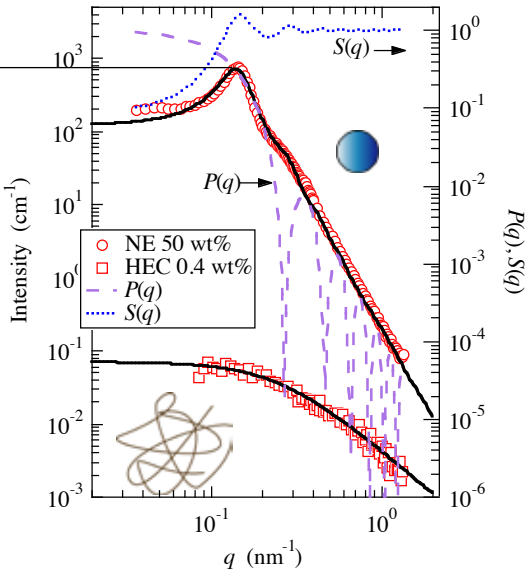
Viscoelastic transition



$G'(\omega)$ and $G''(\omega)$ were measured before and after shearing ($d\gamma/dt$ = 100 s^{-1} for 10 min)

2D SANS Patterns of Shake Gel

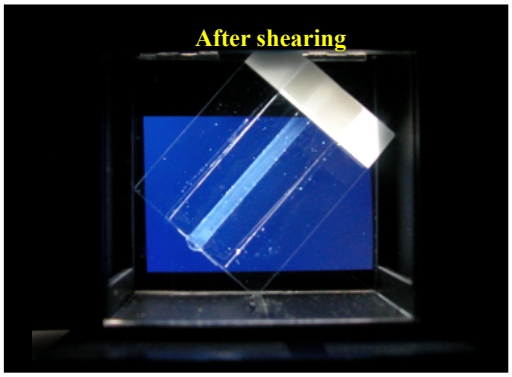


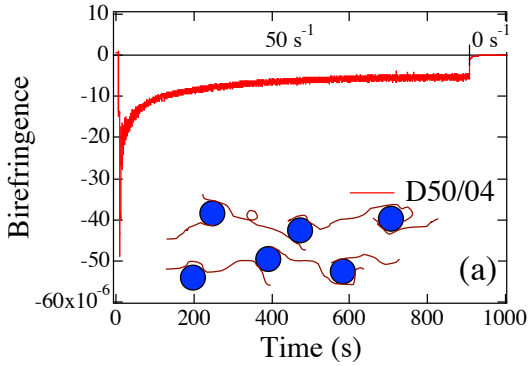


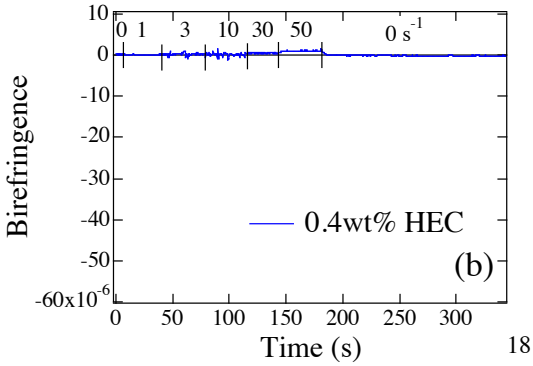
No anisotropic patterns

The shape of the NE and the inter-particle distance are preserved and only the long-range inhomogeneities increase by shearing.

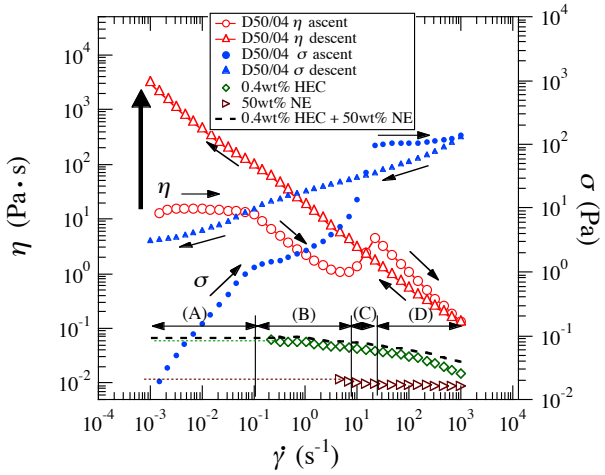
Birefringence







Discussion 1: Intuitive interpretation

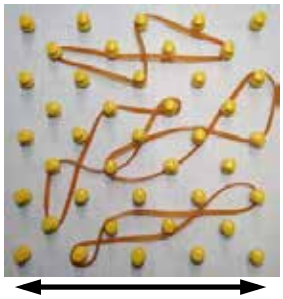


Ascent
(A) Newtonian
(B) Shear thinning
(C) Shear thickening
(D) Slipping

Descent and 2 nd run
Dilatant behavior !!
Once a high shear is applied, the structure is formed and the relaxation time becomes very long.

Percolation transition

Shear



Flow direction

From SANS, we know a does not change with shear.

Discussion 2: Estimation of shear stress at the transition

Entropy elasticity of a single Gaussian chain

$$\sigma = \frac{f}{A} = \frac{3kT}{A\langle R_0^2\rangle^{1/2}} \frac{\langle R\rangle}{\langle R_0^2\rangle^{1/2}} = E\frac{\langle R\rangle}{\langle R_0^2\rangle^{1/2}}$$

Approx.1: $A \approx a^2$

$$\sigma \approx \frac{f}{a^2} = \frac{3kT}{a^2\langle R_0^2\rangle^{1/2}} \frac{\langle R\rangle}{\langle R_0^2\rangle^{1/2}}$$

$$G = E/3, \quad \langle R\rangle/\langle R_0^2\rangle^{1/2} \to \gamma$$

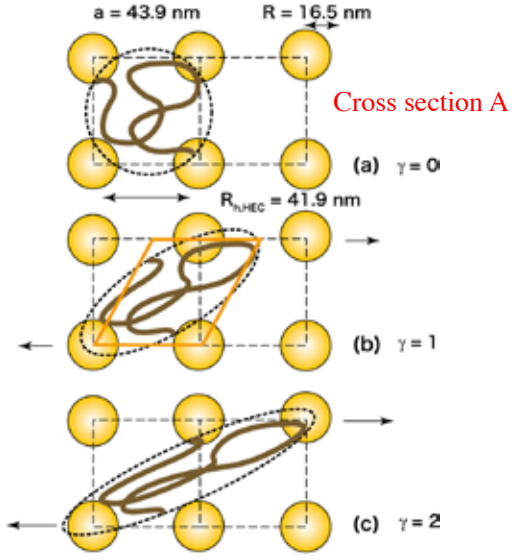
$$\sigma = G\gamma = \frac{kT}{a^2\langle R_0^2\rangle^{1/2}} \frac{\langle R\rangle}{\langle R_0^2\rangle^{1/2}} = \frac{kT}{a^2\langle R_0^2\rangle^{1/2}}\gamma$$

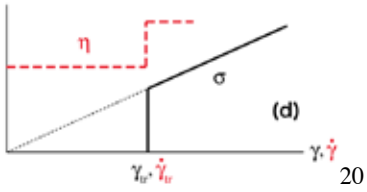
Approx.2: $\gamma \approx 1$

$$\sigma_{tr} = G\gamma \approx \frac{kT}{a^3}$$

$\sigma_{tr} = 45.7$ [J/m^3 = Pa] **Predicted by SANS data only**

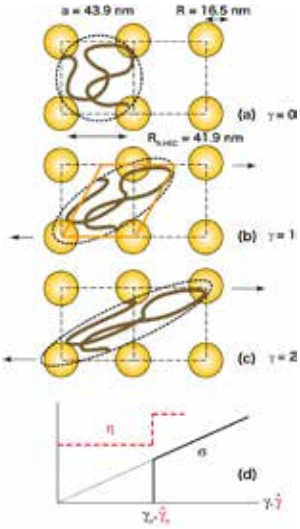
$\sigma_{tr} = 37.3$ [J/m^3 = Pa] ← **Rheology**





Summary 1: NE/HEC mixture

- **Shear-induced gelation in a mixture of NE and HEC was investigated by Rheo-SANS.**
- **The mixture exhibits a distinct viscosity-jump (dilatancy) at the shear rate of 4 s^{-1}, which corresponds to a steep upturn of SANS intensity at the low *q*-region.**
- **No anisotropy was observed even at the shear rate of 100 s^{-1}.**
- **The dilatancy effect becomes largest when $a \approx R_h$.**
- **The shear stress at the transition can be simply estimated only with the structure parameters.**
- **The dilatancy behavior is due not to non-Gaussian chains, but to percolation transition of the system.**



Shibayama, et al., J. Chem. Phys, 2007, **127, 144507.**

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Tree topics

Part I: NE/HEC Shake gel

Part II: Shear thickening of Clay/PEO

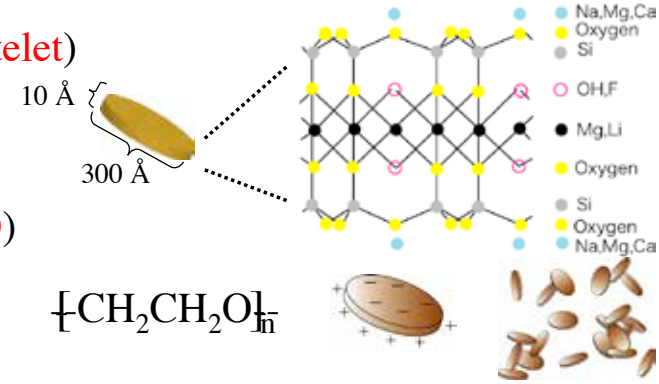
Part III: Phantom chains of CTAB/salt

shake gel composed of clay-PEO mixture

Takeda, et al., Macromolecules, 2010, 43, 7793.

samples

•Laponite (XLG) (clay platelet)



•poly(ethylene oxide) (PEO)

$M_w = 400{,}000$

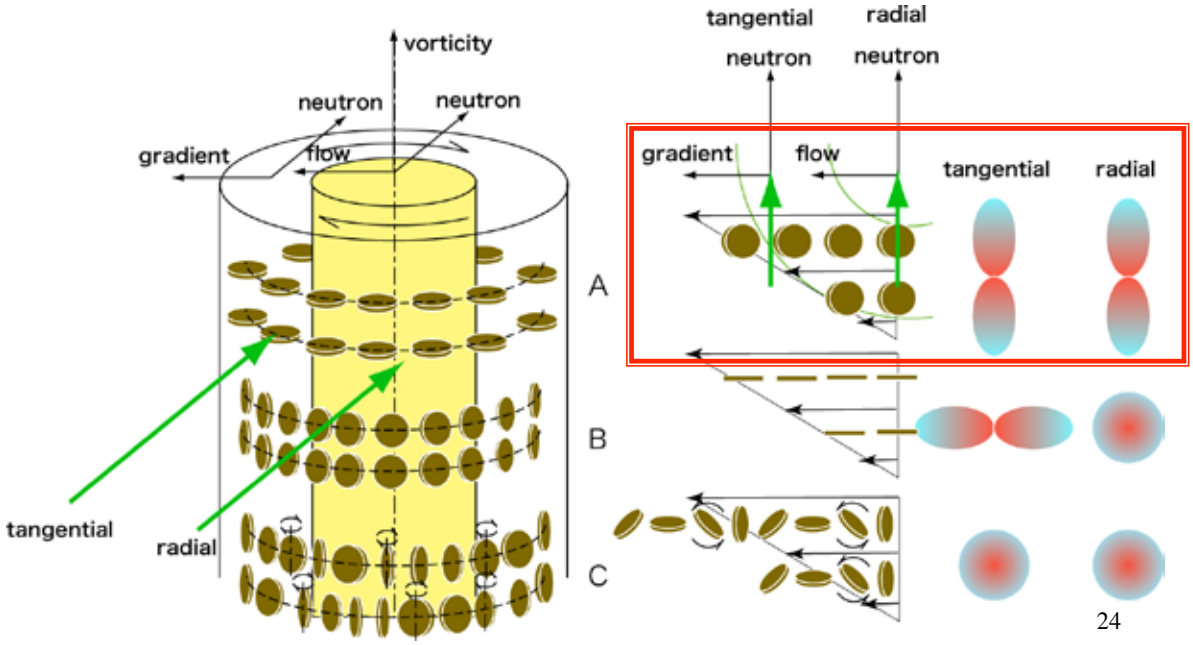
$+CH_2CH_2O+_n$

•water H_2O and D_2O mixtures for SANS
(contrast variation SANS)

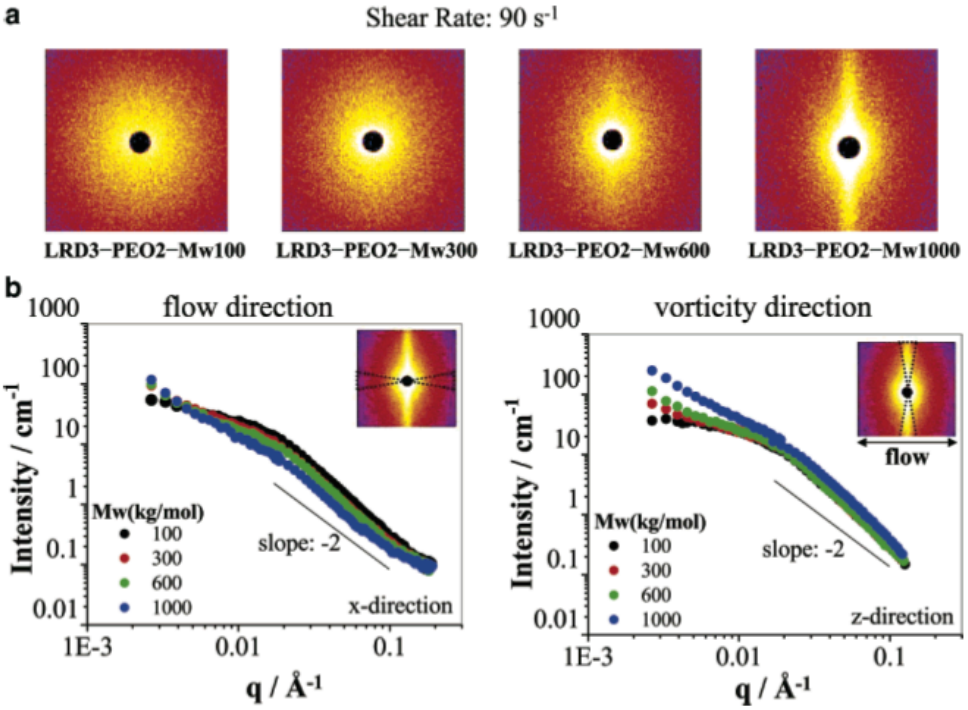
Clay Orientation in a flow field

"Gedankenexperiment"

Schematic illustration showing the relationship between the anisotropy of scattering intensity and clay's orientation.



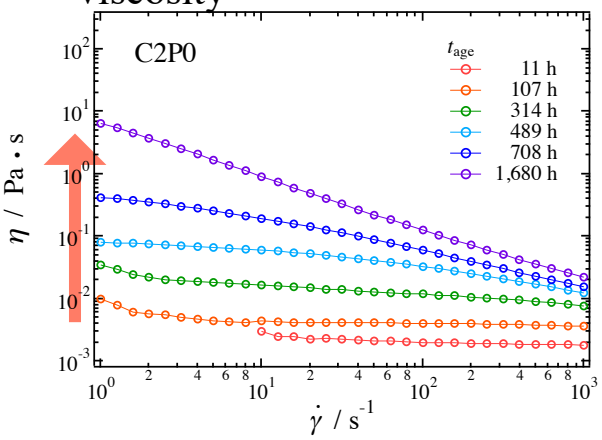
Rheo-SANS of clay/PEO



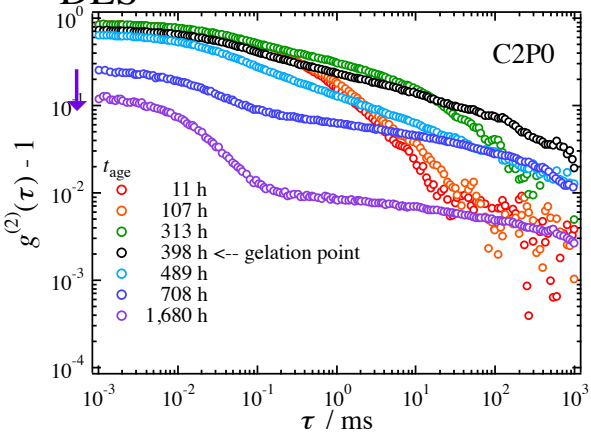
Schmidt et al., *Macromolecules*, 2005

Aging of clay 2 wt%

viscosity

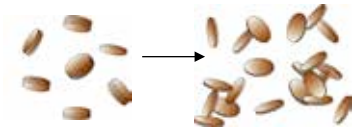


DLS



$\eta\ (\dot{\gamma} \to 0)$

Gelation at stationary state



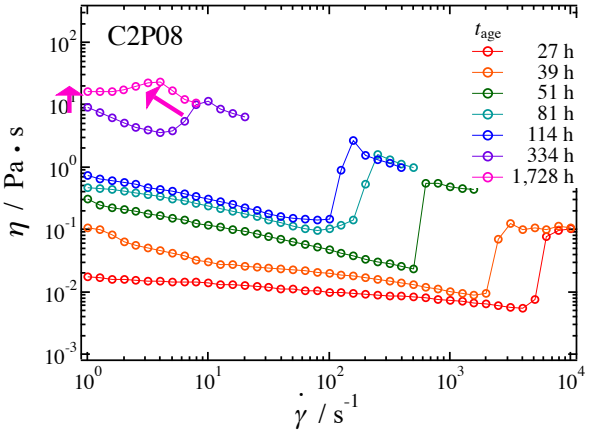
solution; $g^{(2)}(0) = 1$

Gel point; power law with τ
→ self-similar cluster formation

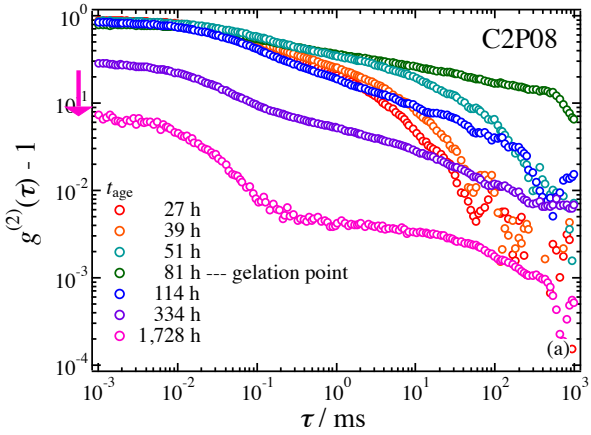
gel; suppression of $g^{(2)}(0)$
→ gel mode, nonergodicity

Evolution of clay-PEO mixture

viscosity



DLS



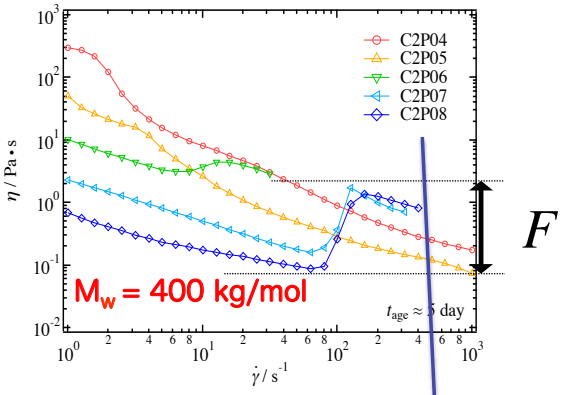
1. η ($\dot{\gamma}\rightarrow 0$) increase
2. Lowering of $\dot{\gamma}$ at shear thickening
3. Gelation at stationary state

Origin of structural evolution

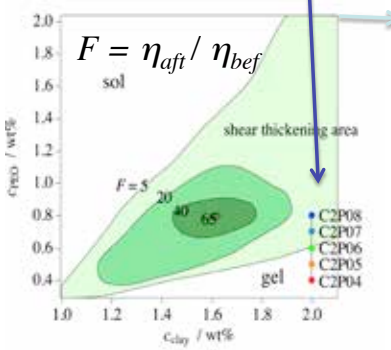
⇒ gelation of card-house structure of clay

Rheological behaviors

shear thickening system



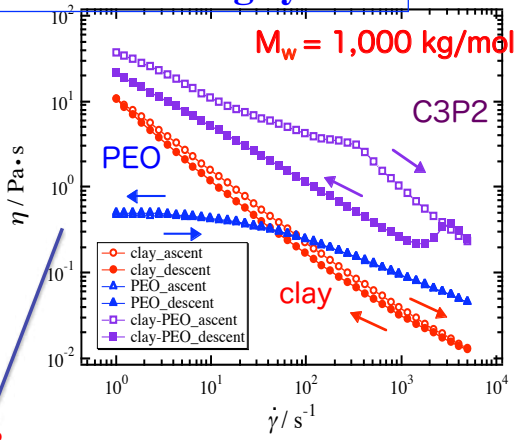
F



C3P2

3.0%

shear thinning system

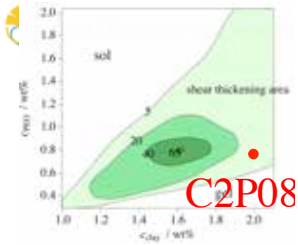


Matsunaga et al., Macromolecules, 2010, 43, 5075.

Sample code:
C2P04 ; clay:2 wt%-PEO:0.4 wt%

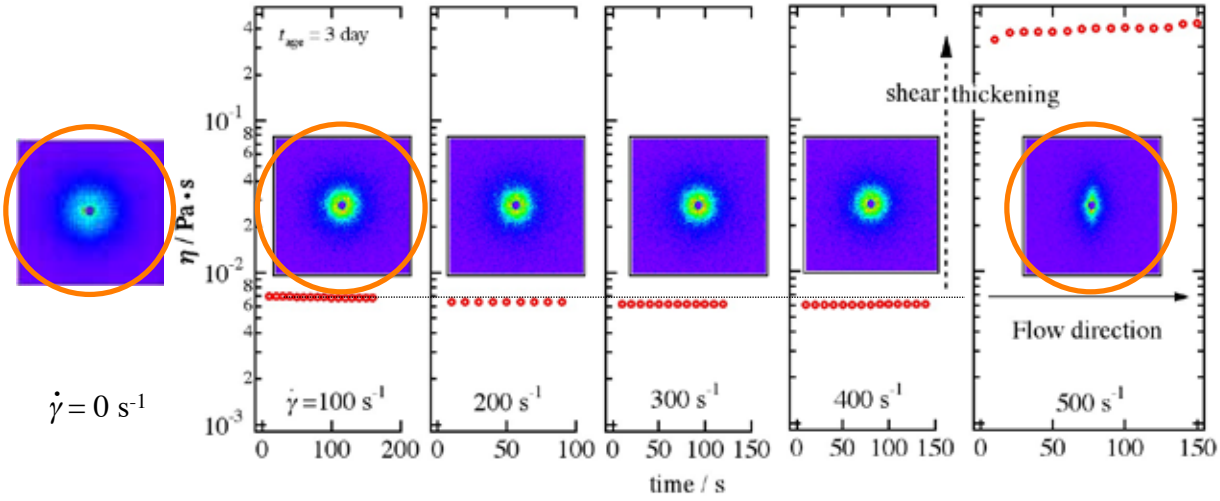
Phase diagram of shear thickening behavior with contour lines of F.

Rheology and SANS measurements



C2P08 ϕ_{D2O}=1 t_{age} = 3 day

SDD = 8 m, 4m



The scattering pattern changed to anisotropic at 500 s^{-1}.

To investigate $\dot{\gamma}$ = 0, 100, 500 s^{-1} more precisely, CV-SANS was applied.

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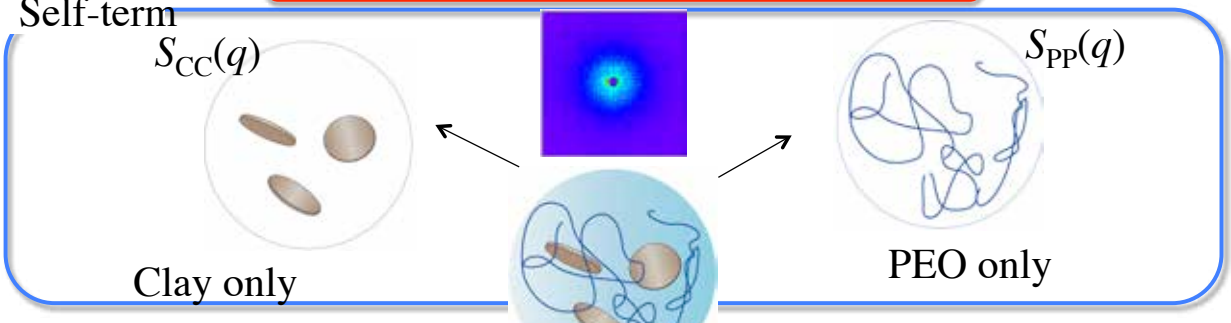
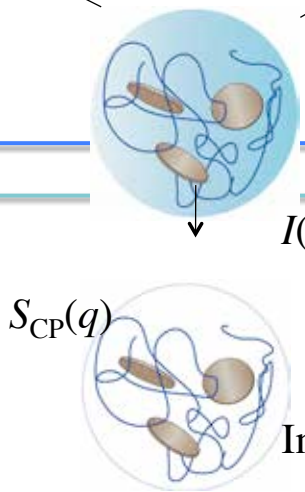
Scattering from three-component systems

$$I(q) \approx \Delta\rho_C{}^2 S_{CC}(q) + 2\Delta\rho_C\Delta\rho_P S_{CP}(q) + \Delta\rho_P{}^2 S_{PP}(q)$$

Self-term

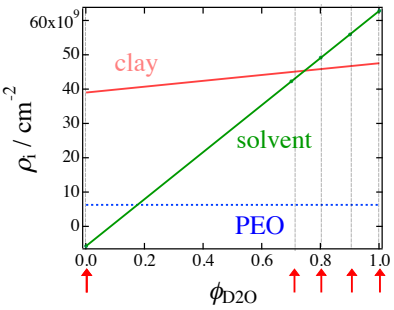


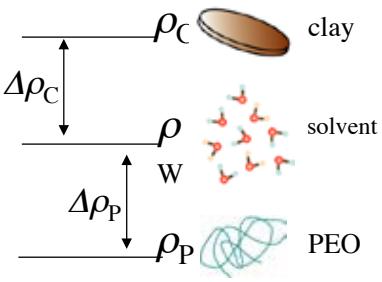
Cross-term

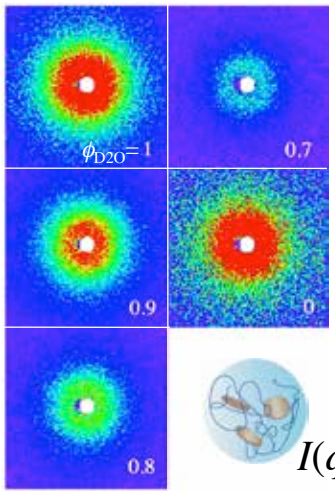


Contrast Variation SANS

$$I(q) \approx \Delta\rho_C^{\,2} S_{CC}(q) + 2\Delta\rho_C\Delta\rho_P S_{CP}(q) + \Delta\rho_P^{\,2} S_{PP}(q)$$

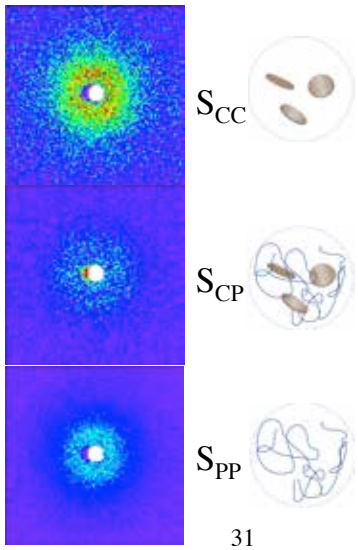






singular value decomposition

$$I_1(q) \approx {}^1\Delta\rho_C^{\,2} S_{CC}(q) + 2\,{}^1\Delta\rho_C\,{}^1\Delta\rho_P S_{CP}(q) + {}^1\Delta\rho_P^{\,2} S_{PP}(q)$$
$$I_2(q) \approx {}^2\Delta\rho_C^{\,2} S_{CC}(q) + 2\,{}^2\Delta\rho_C\,{}^2\Delta\rho_P S_{CP}(q) + {}^2\Delta\rho_P^{\,2} S_{PP}(q)$$
$$I_3(q) \approx {}^3\Delta\rho_C^{\,2} S_{CC}(q) + 2\,{}^3\Delta\rho_C\,{}^3\Delta\rho_P S_{CP}(q) + {}^3\Delta\rho_P^{\,2} S_{PP}(q)$$
$$\vdots$$



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$I(q)$ measurements

Partial scatt. fun.

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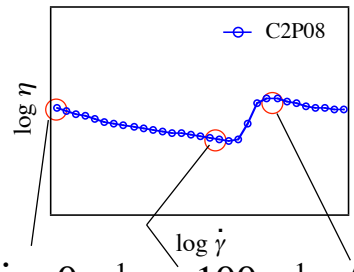
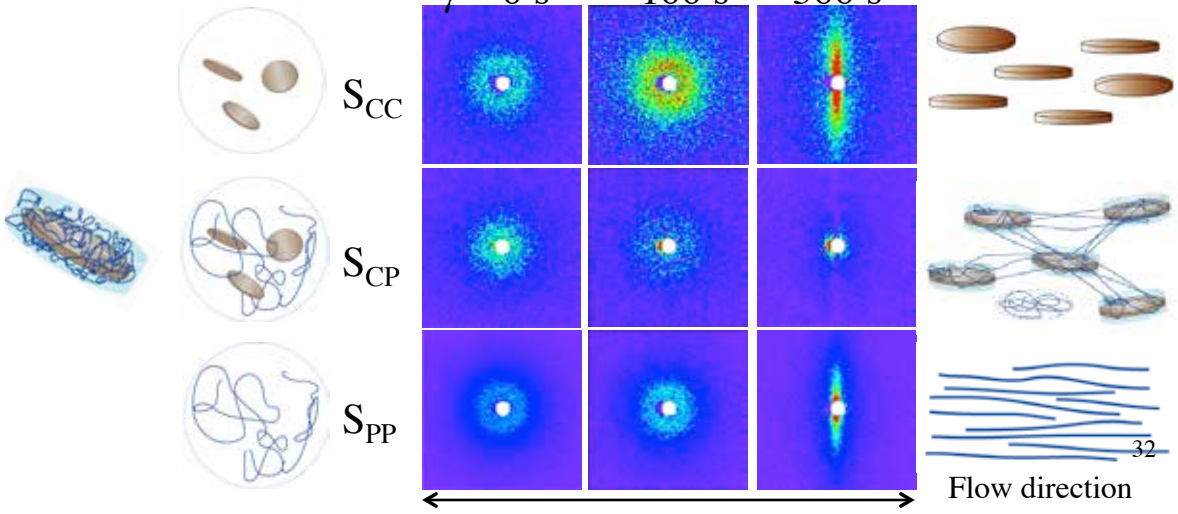
2D scattering Functions for C2P08



Col/SDD=8 m/8 m

$\dot{\gamma} = 0$ s^{-1} 100 s^{-1} 500 s^{-1}



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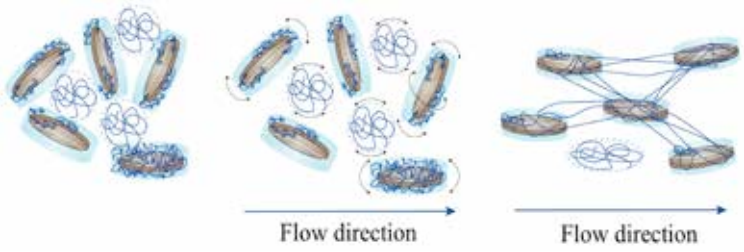
Flow direction

Conclusion 2: Clay/PEO

- Structural analyses were conducted on a clay/PEO mixture C2P08 undergoing shear thickening.
- **Orientation of clay and polymer chains in C2P08 with shear thickening was observed by means of Rheo-SANS and Rheo-BF.**
- **CV-Rheo-SANS result revealed the origin of orientation at shear thickening threshold.**
- **Both of clay and PEO were orientated parallel to the flow direction.**
- **CV-Rheo-SANS data gave not only the information of orientation but also that of clay-PEO interaction.**
- **PEO chains adsorbed on clay surfaces are peeled off with shear thickening and bridge clay platelets, resulted in percolation transition.**

Mechanism of shear thickening



stationary **Shear thinning** **Shear thickening**

Takeda, et al., Macromolecules, 2010, 43, 7793.

Tree topics

Part I: NE/HEC Shake gel

Part II: Shear thickening of Clay/PEO

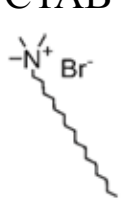
Part III: Phantom chains of CTAB/salt

CTAB/Na*p*TS

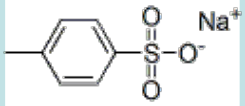
Takeda et al., Langmuir, 2011, 27, 1731.

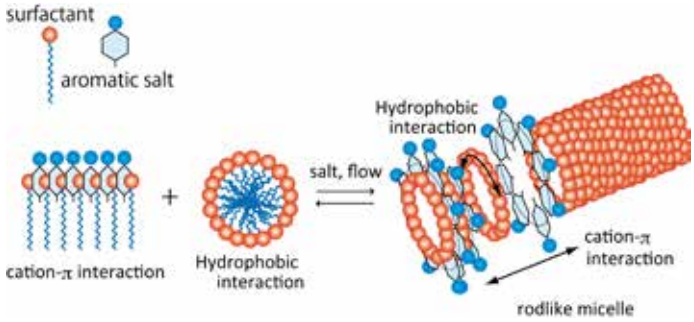
Cetyltrimethylammonium bromide (CTAB) transforms to a rodlike structure by adding sodium *p*-toluene sulfonate (Na*p*TS)

CTAB



Na*p*TS





Rheological properties

1. Maxwell model with a single relaxation at high micelle *C*.
2. shear thinning at high micelle *C*
3. shear thickening at low micelle *C*

Critical chain length (rod radius)

$$l_c \le l_{\max} \approx (0.154 + 0.1265n)$$

l_c : critical chain length

$l_{\max}$: extended chain length

n : number of carbon

Tanford, C,(1973,1980) *The Hydrophobic Effect*, Wiley, New York.

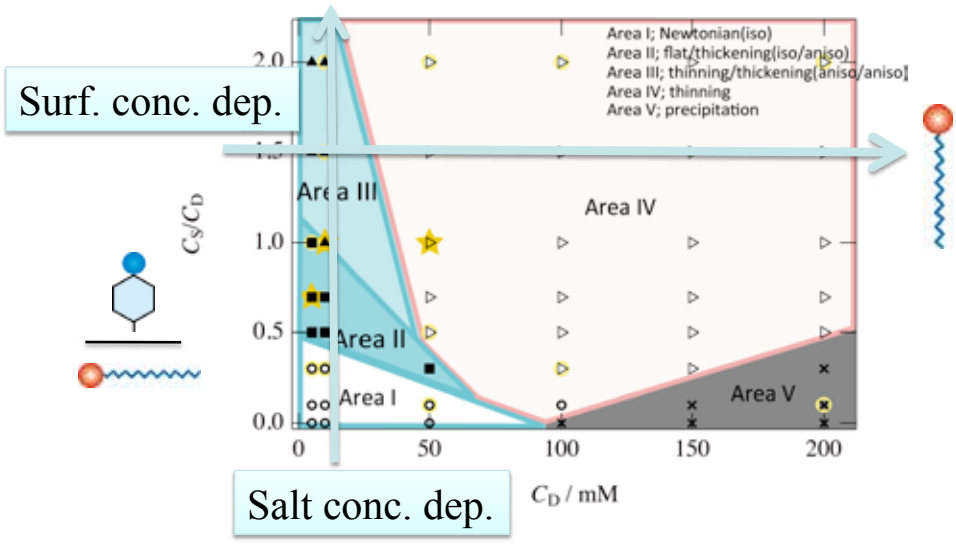
CTAB ⟹ $l_{\max} = 21.78 Å$

Fitting result $R \approx 23 Å$

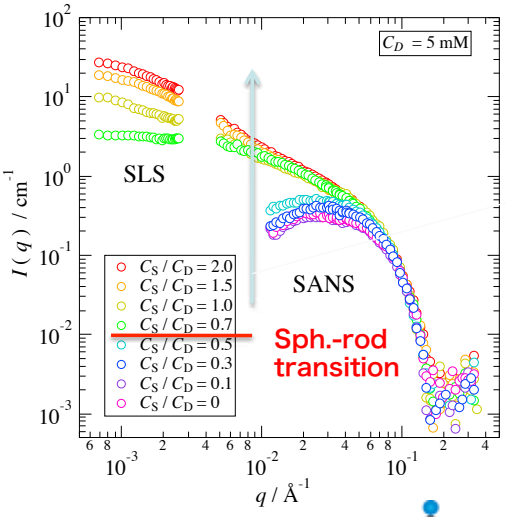
SANS at stationary state

Measuring condition

CTAB conc. (C_D); 5～200 mM
Salt conc. (C_S) /CTAB conc.(C_D) ratio; 0～2.0
Room temp. (25 °C)

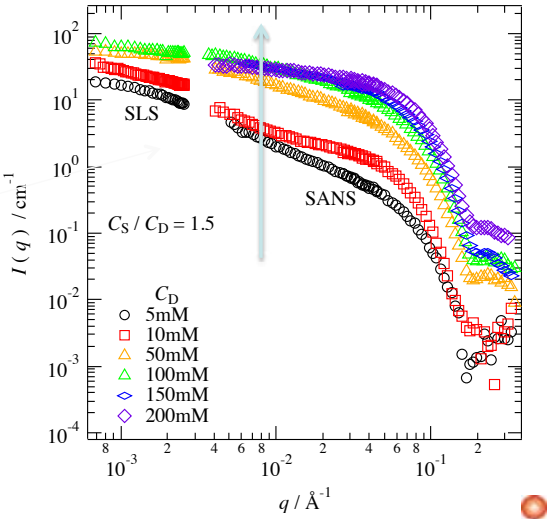


SANS at stationary state



Salt conc. dep.

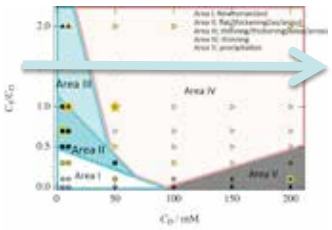
sph.-rod transition

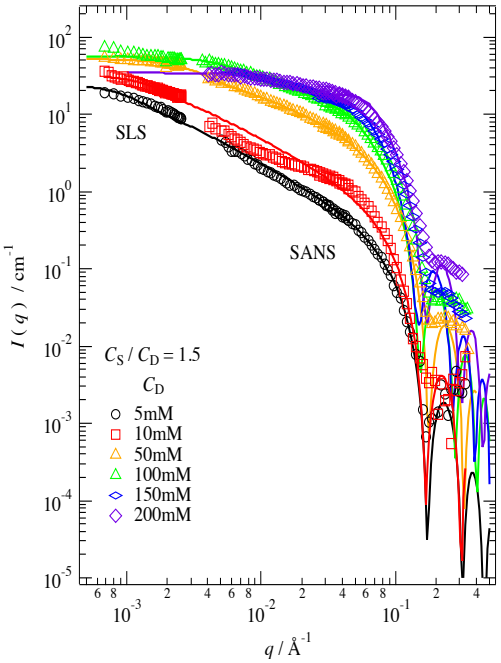


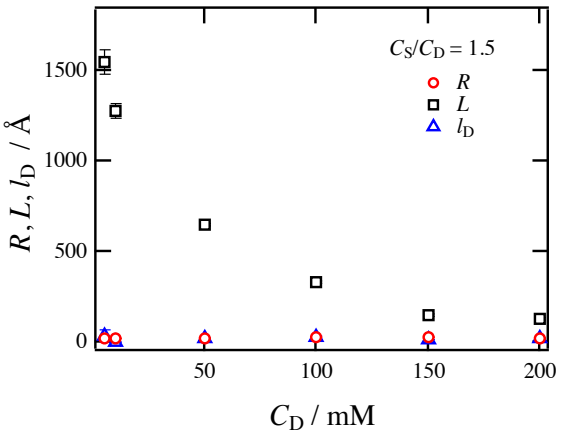
Surfactant conc. dep.

Inter-rod interference

Surfactant conc. Dep.

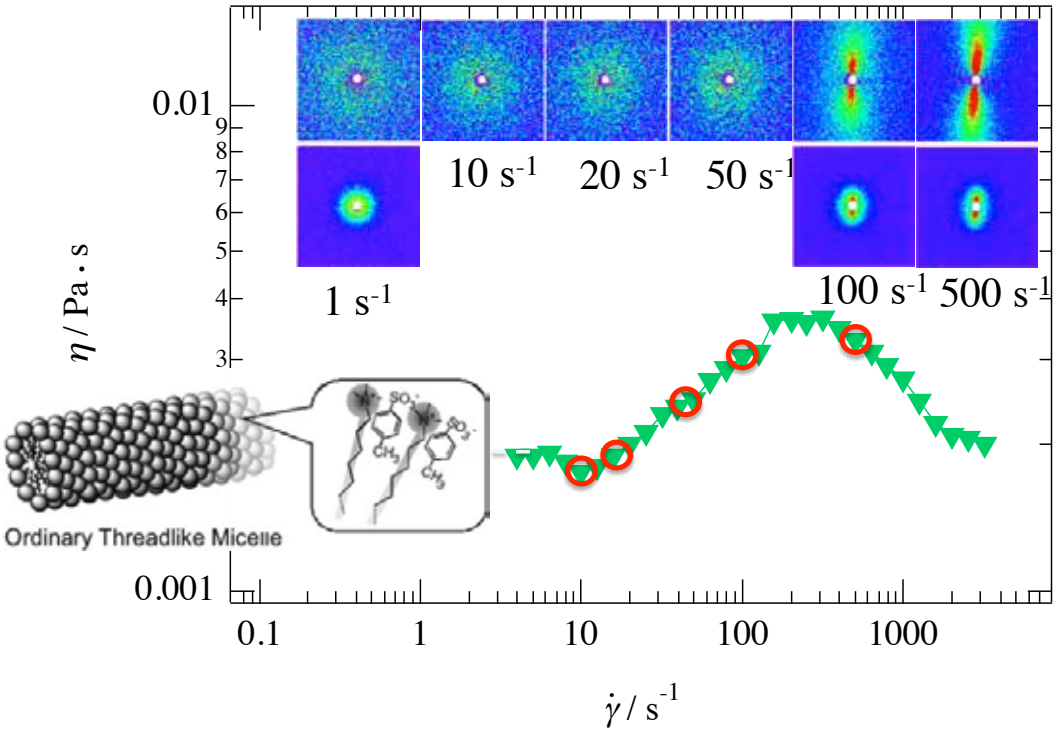




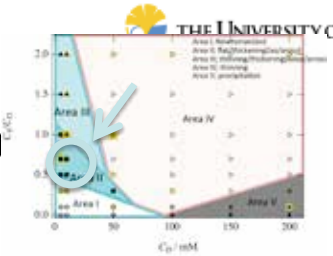


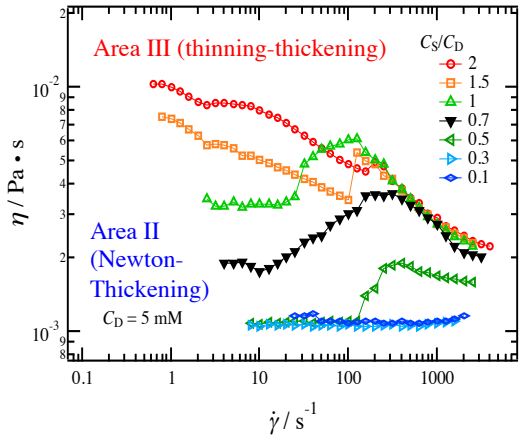
With increasing C_D, L decreases, l_D; constant
→NO., no shortening, but inter-rod entanglements

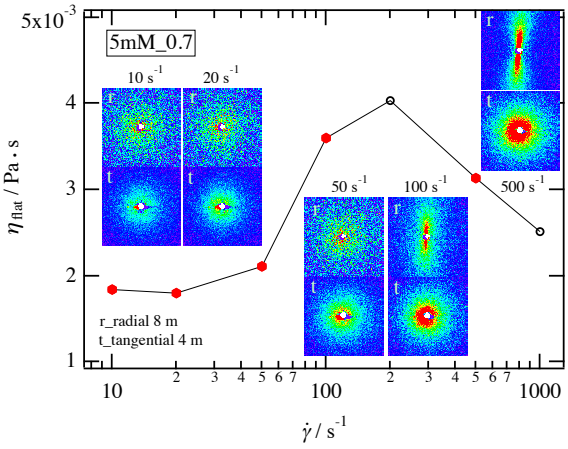
Viscosity and 2D scattering pattern on 5 mM_0.7



Shear thickening (low micelle conc.) Area II, III

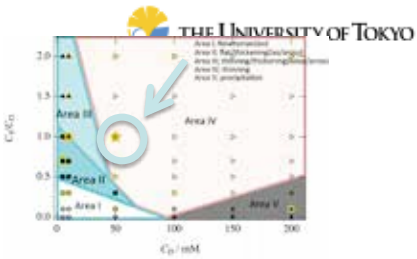


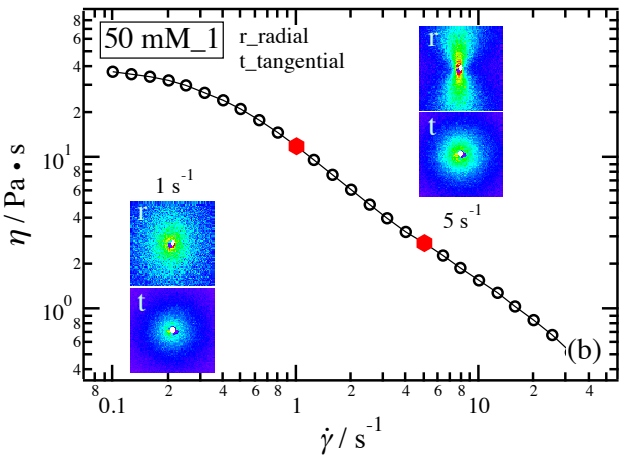


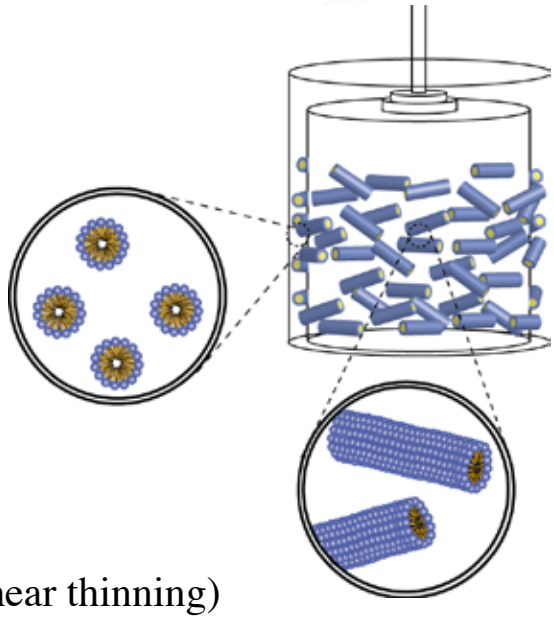


5mM; too low conc. for entanglement formation.
Micelle orientation occurs with thickening.

Shear thinning (high micelle conc. region) Area IV

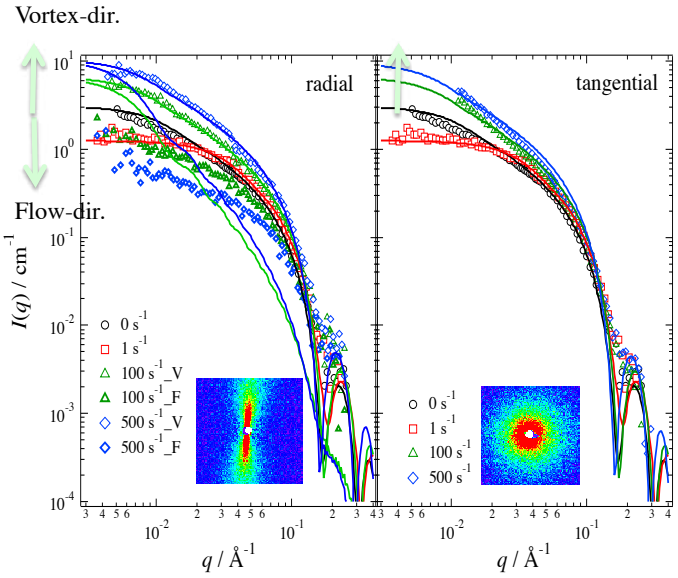


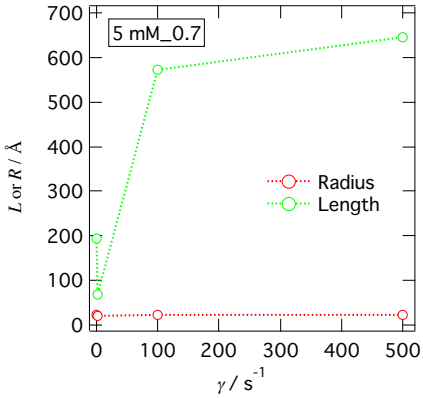


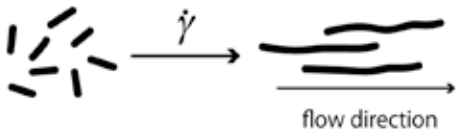


Orientation of rodlike micelle
at high micelle conc. Region (Shear thinning)

Rheo-SANS and fitting



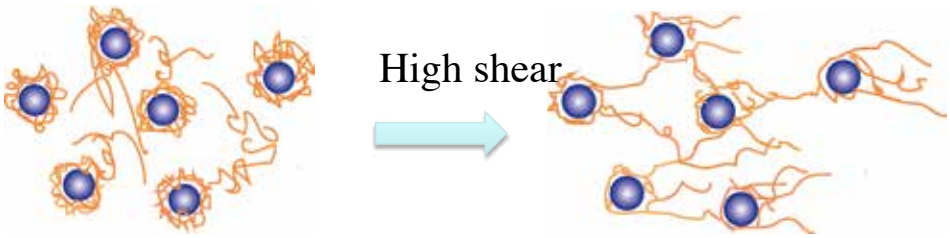




Comparison of Shear thickening mechanisms

Particle-polymer

Bridging of particles by polymer chains

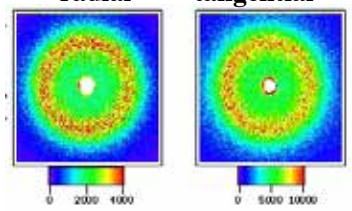
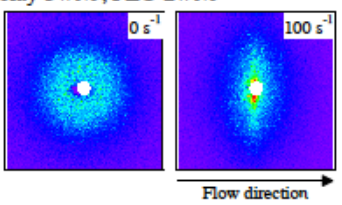
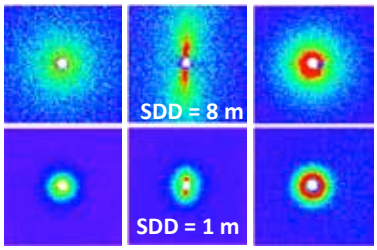
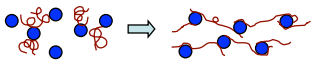
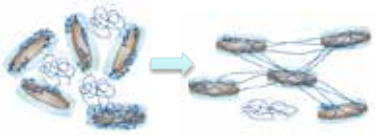
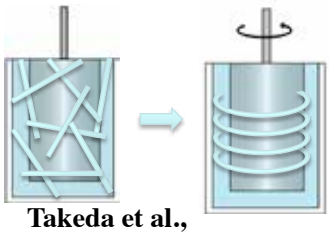


Surfactant-salt

Connection-extension

"parcolation" transition

Summary:
Rheo-SANS of Shear thickening

NE/HEC Nanoemulsion/polymer	clay/PEO Clay/polymer	CTAB/Na*p*TS micelle
$\gamma = 100\ s^{-1}$ radial tangential	(c) clay 3wt%, PEO 2wt%	0 s^{-1} 100 s^{-1} radial tangential
		
		
Shibayama et al., JCP, 2007, 127, 144507.	Takeda et al., Macromolecules, 2010, 43, 7793.	Takeda et al., Langmuir, 2011, 27, 1731.

Percolation transition

Conclusion

Shear-thickening phenomena were investigated by Rheo-SANS for complex systems, i.e., nano-emulsion/polymer, clay/polymer, and surfactant/salt aqueous systems.

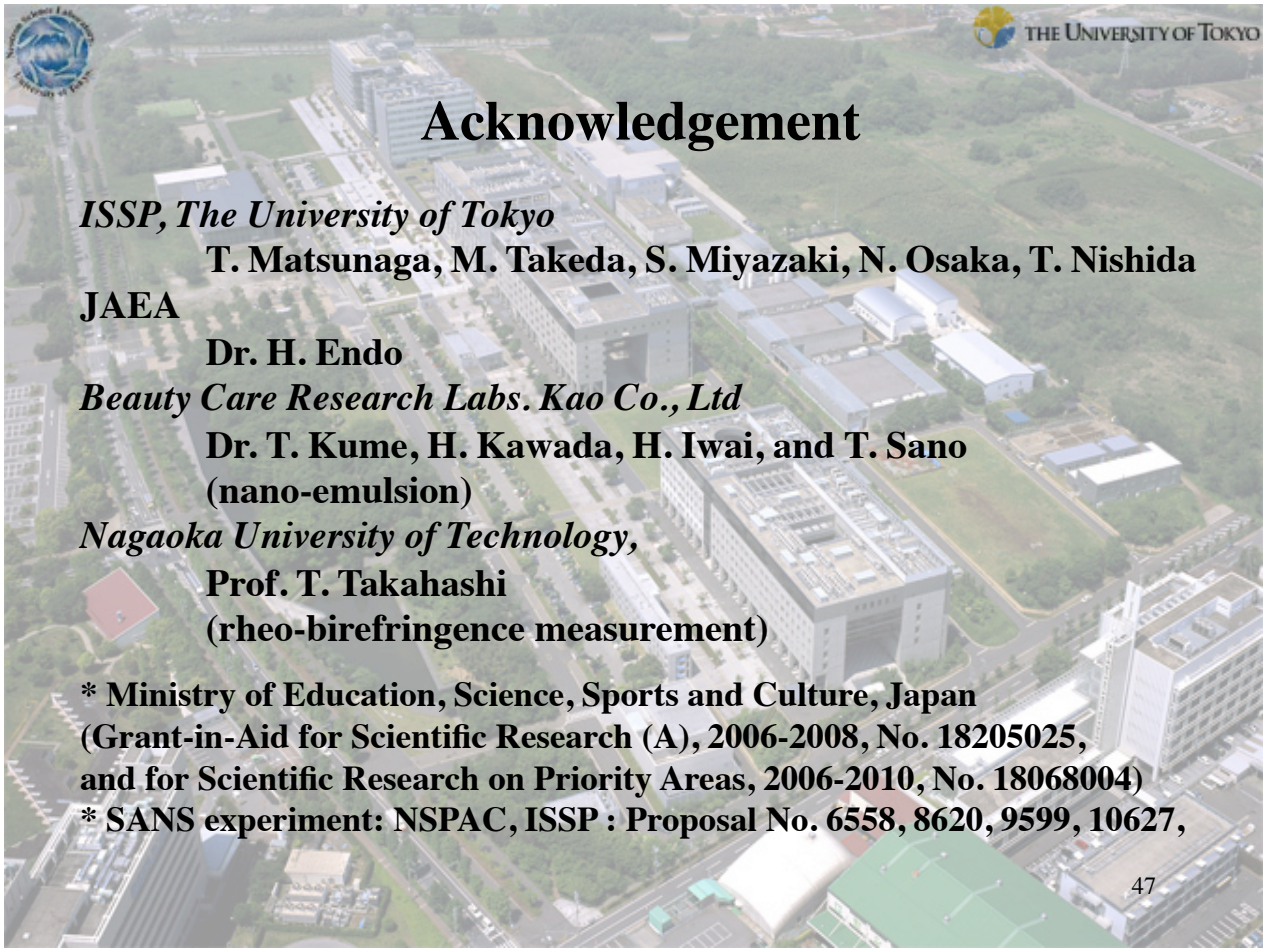
It was found that

(1)shear-thickening occurred in a small window of particle/polymer concentrations, where the inter-particle distance is close to the polymer size.

(2) Anisotropic patterns are observed by Rheo-SANS when the particles have anisotropic shape.

(3) The transition is explained as a percolation transition in which polymer chains bridge neighboring particles.

(4) In the case of CTAB/salt, a continuity transition is responsible for the shear-thickening behavior.



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(nano-emulsion)

Nagaoka University of Technology,

Prof. T. Takahashi

(rheo-birefringence measurement)

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(Grant-in-Aid for Scientific Research (A), 2006-2008, No. 18205025,
and for Scientific Research on Priority Areas, 2006-2010, No. 18068004)
*** SANS experiment: NSPAC, ISSP : Proposal No. 6558, 8620, 9599, 10627,**

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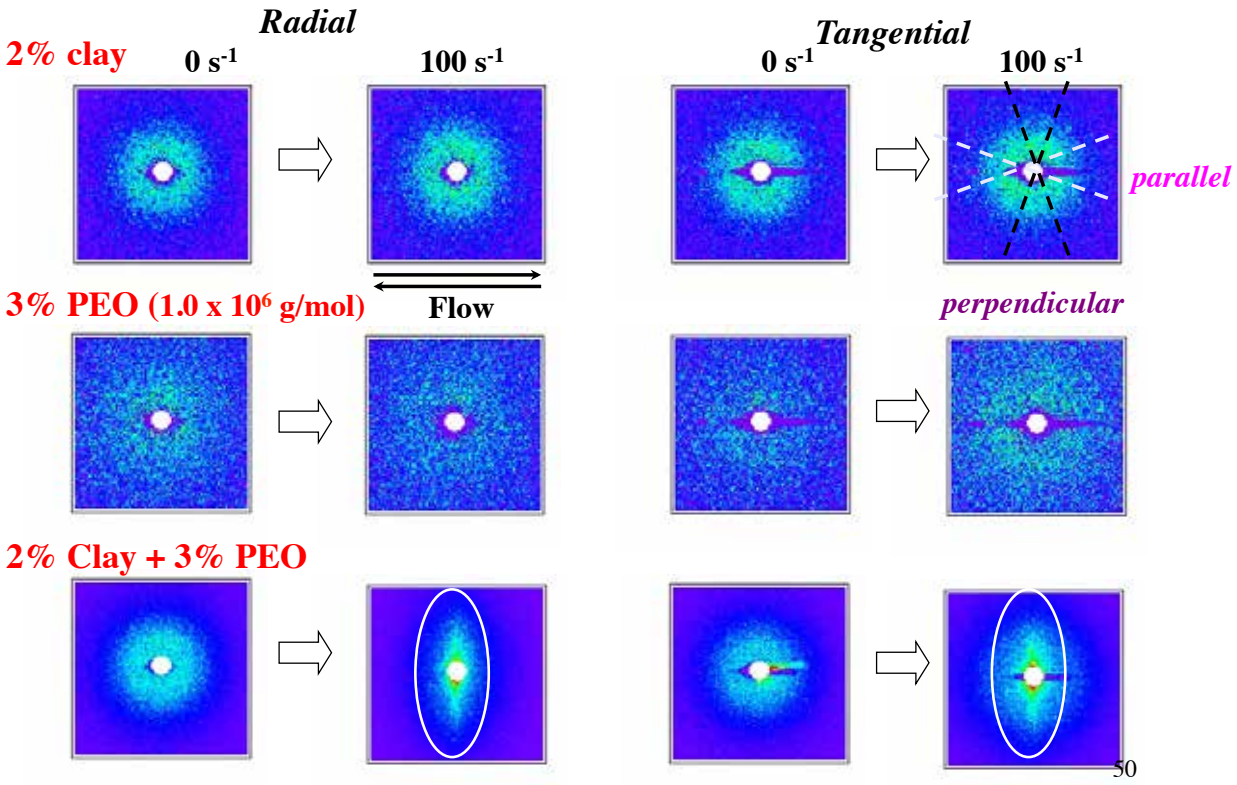
Fitting parameter

low ⟷ PEO conc ⟷ high

	C2P04	C2P05	C2P06	C2P07	C2P08
R_C/ Å			150		
D_C/ Å			10		
ϕ_{clay}			0.00763		
R_{PY}/ Å	91.1	72.1	75.9	76.0	108
R_{pl}/ Å	150	150	150	150	193
D_{pl}/ Å	17.5	20.8	20.6	21.5	24.3
ϕ_{pl}	0.235	0.388	0.378	0.298	0.206
S^0_{PP}	0.0824	0.119	0.137	0.194	0.255
ξ/ Å	113	117	121	127	181

Gel phase | shear thickening phase

Comparison: Clay-PEO



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SANS experiment: NSPAC, ISSP, Atomic Energy Initiative, MEXT, 2008-2010

まとめ

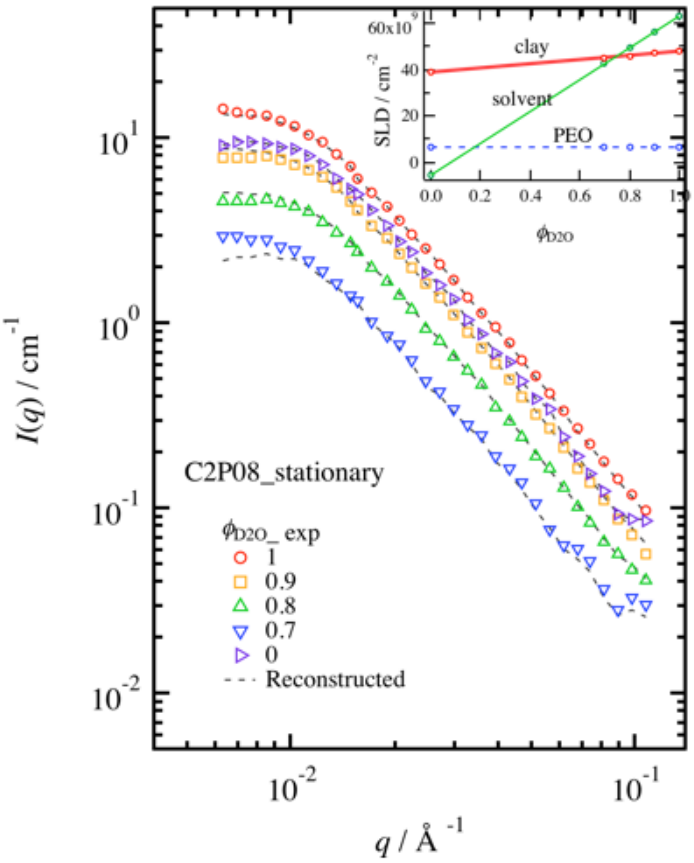
クレイーPEO高分子溶液系

- クレイーPEO高分子溶液系においてshear thickening挙動が観察された。この時の構造変化をcontrast variation SANSにより研究し、クレイへの高分子鎖の吸着、shear thickeningはパーコレーション転移であることを解明した。

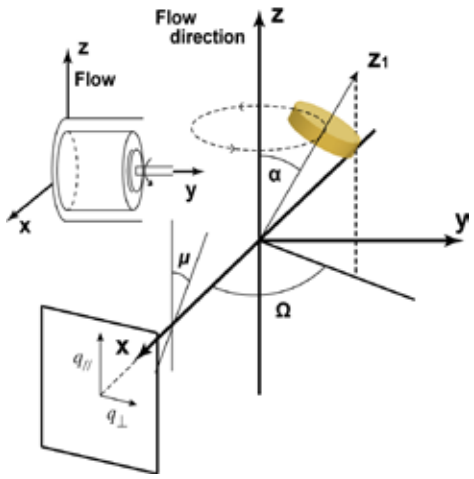
CTAB-塩混合系

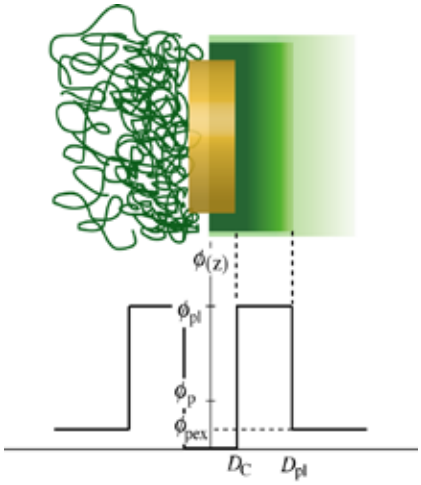
- CTAB-塩混合系は粒子–高分子混合系と同様、特定濃度領域においてshear thickening挙動を示し、剪断による構造転移をすることが分かった。

- shear thickeningに伴う配向と、ミセルの伸長が確認された。この系のshear thickeningは、半径が変化していないことから紐状ミセルが剪断により流動方向に配向、連結し、より長い紐状ミセルへと転移したことで粘度増大するために起きる現象であると考えられる。


C2P08_stationary
ϕ_{D2O}_ exp
1
0.9
0.8
0.7
0
Reconstructed
$I(q)$ / cm^{-1}
q / Å^{-1}
SLD / cm^{-2}
clay
solvent
PEO
ϕ_{D2O}

Coordinate system and Scattering functions





$$S_{CC} = \int_{\alpha=0}^{\pi/2} F_{cyl}(R_C, D_C, \alpha)^2 \sin\alpha \mathrm{d}\alpha$$

☆Structure factor : Percus-Yevick equation

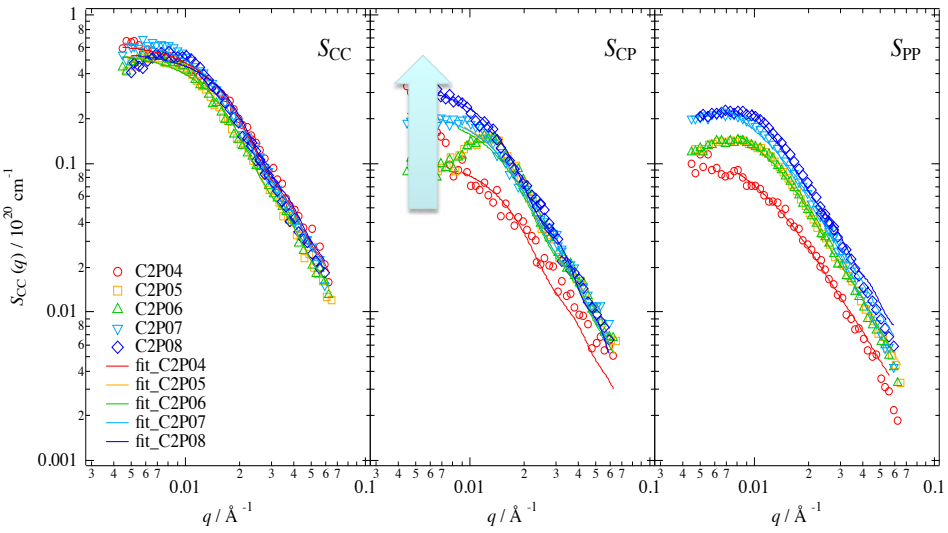
$$F_{cyl}(R, D, \alpha) = 2V \frac{\sin(qD\cos\alpha)}{qD\cos\alpha} \frac{J_1(qR\sin\alpha)}{qR\sin\alpha}$$

$$S_{CP} = \frac{n_C}{2}\left\{(\phi_{pl} - \phi_{pex}) \int_{\alpha=0}^{\pi/2} F_{cyl}(R_C, D_C, \alpha) F_{cyl}(R_{pl}, D_{pl}, \alpha) \sin\alpha \mathrm{d}\alpha - \phi_{pl} \int_{\alpha=0}^{\pi/2} F_{cyl}{}^2(R_{pl}, D_{pl}, \alpha) \sin\alpha \mathrm{d}\alpha\right\}$$

$$S_{PP} = \frac{n_C}{2}\left\{\int_{\alpha=0}^{\pi/2}\left[(\phi_{pl} - \phi_{pex}) F_{cyl}(R_{pl}, D_{pl}, \alpha) - \phi_{pl} F_{cyl}(R_C, D_C, \alpha)\right]^2 \sin\alpha \mathrm{d}\alpha + \frac{S^0{}_{PP}(0)}{1 + \xi^2 q^2}\right.$$

Partial Scattering Functions at 0 s^{-1}

$S_{ij}(q)$s at various concentrations with fitting functions



- **At all conditions, S_{CC} curves show the same function.**
- **S_{CP} values are positive. → There are polymer condensed layer on a clay surface.**
- **As increasing polymer concentration, S_{CP} values increase.**

Fitting Parameters

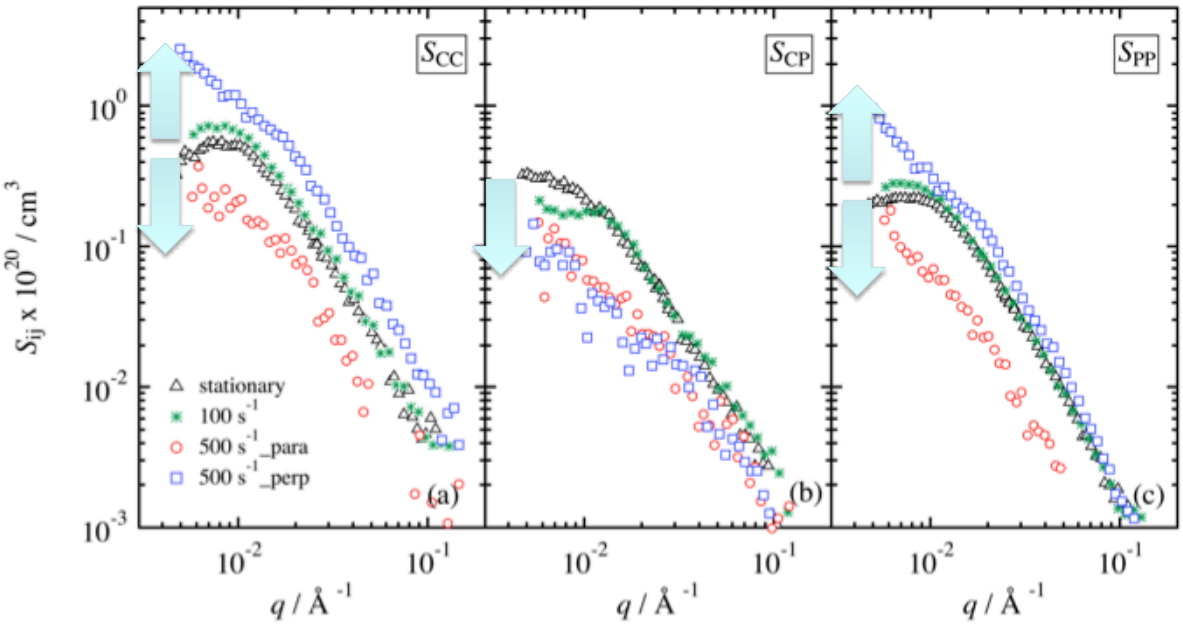
fitting parameter

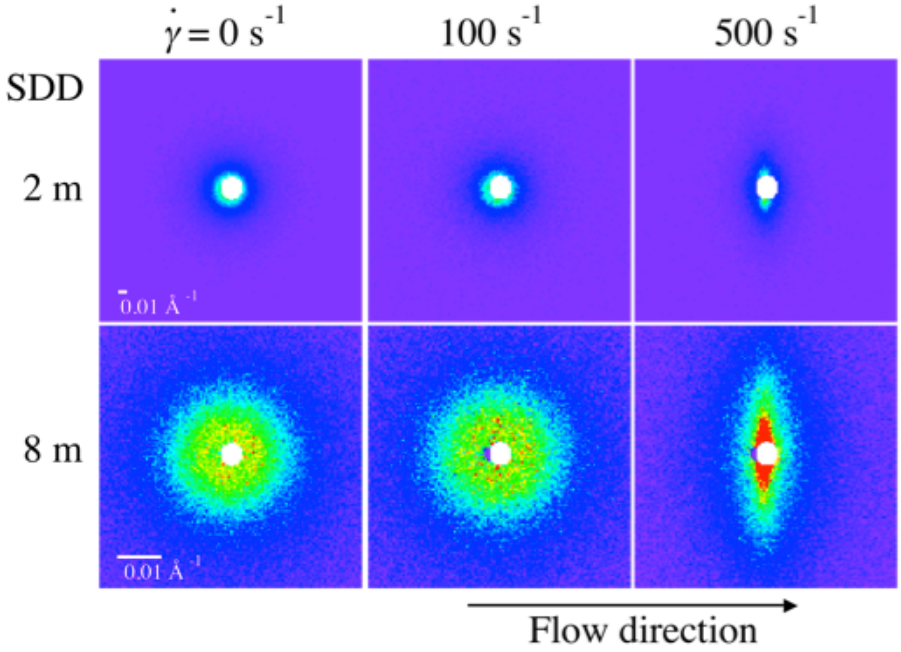
low — PEO concentration — high

	C2P04	C2P05	C2P06	C2P07	C2P08
R_C/ Å			150		
D_C/ Å			10		
ϕ_{clay}			0.00763		
R_{PY}/ Å	91.1	72.1	75.9	76.0	108
R_{pl}/ Å	150	150	150	150	193
D_{pl}/ Å	17.5	20.8	20.6	21.5	24.3
ϕ_{pl}	0.235	0.388	0.378	0.298	0.206
S^0_{PP}	0.0824	0.119	0.137	0.194	0.255
ξ/ Å	113	117	121	127	181

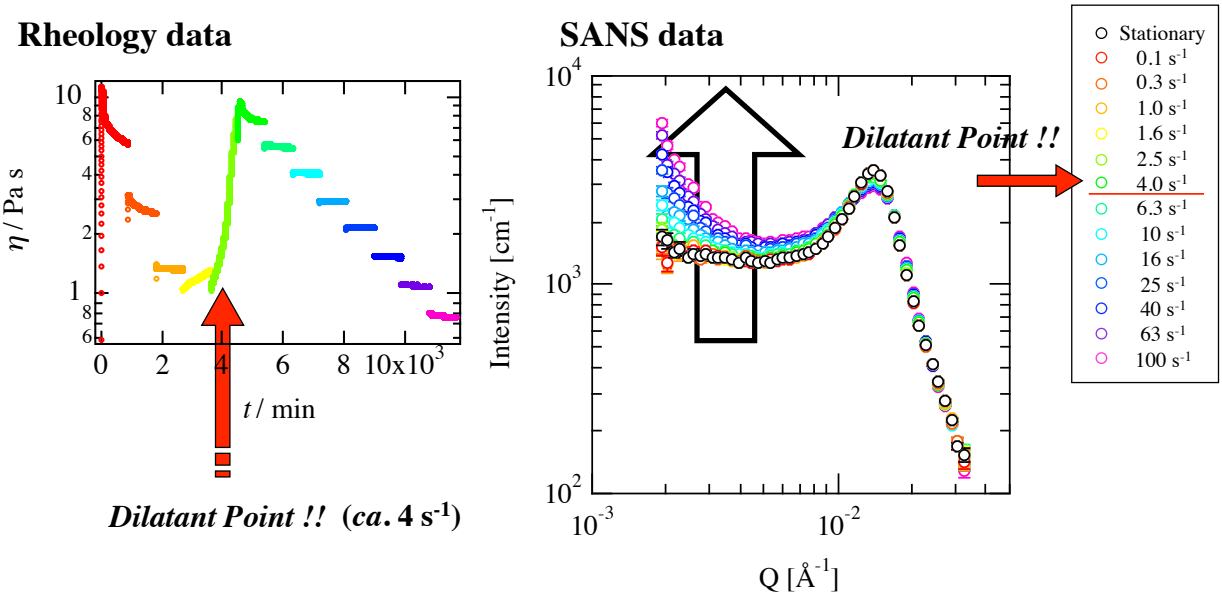
gel area — shear thickening area

There is no significant structure change on these concentrations.



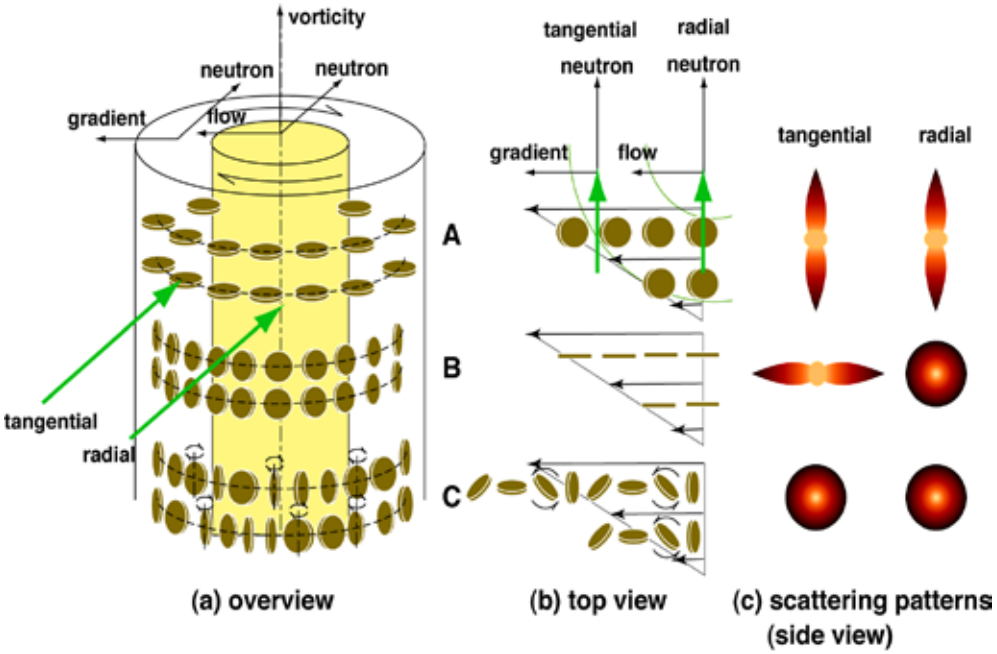


Rheo-SANS 1



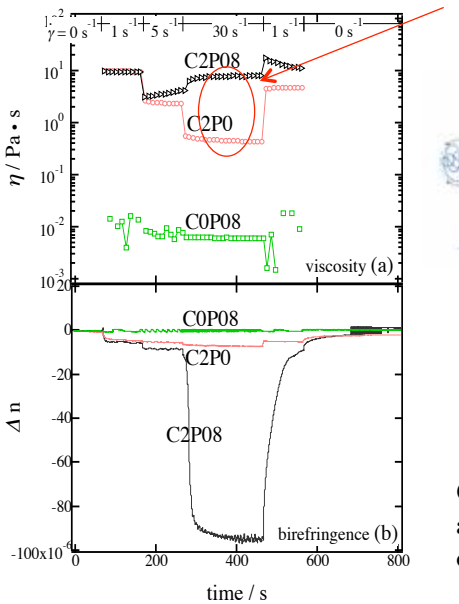
At the shear rate above the dilatant point, a steep increase of the scattering intensity was observed in the low-Q region.

Schematic images of clay orientation



Birefringence Measurements

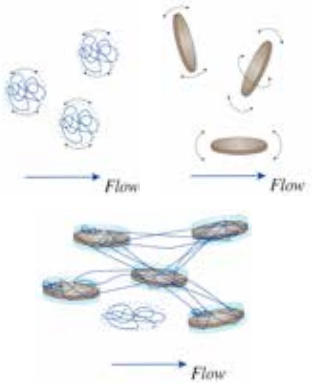
Viscosity η and birefringence Δn at various shear rates



Shear thickening

$\dot{\gamma} = 30\ s^{-1}$

t_{age} ~ 840 h



Only C2P08 with shear thickening shows optical anisotropy. The changes in Δn come from clay orientation coupled with PEO.

Schmidtの例

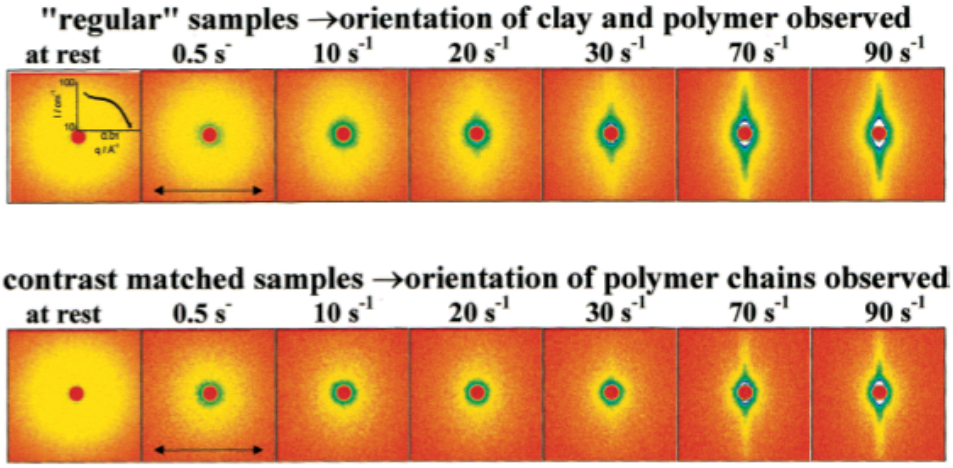
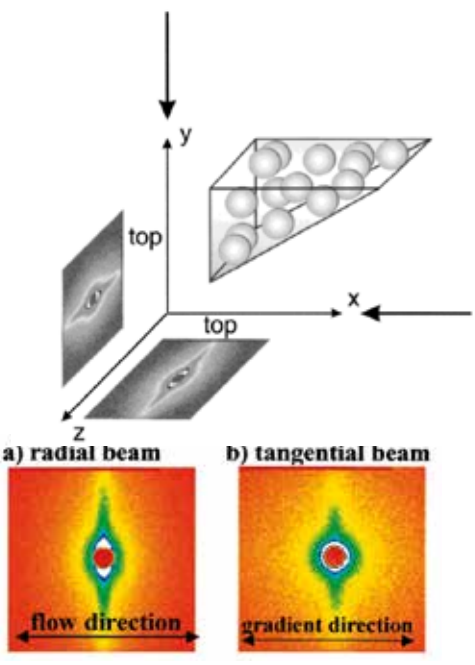


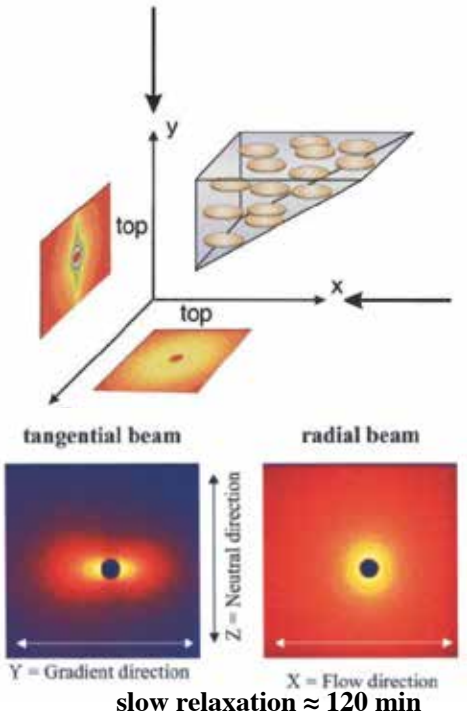
Figure 4. Radial beam configuration: two-dimensional SANS profiles obtained from LRD2 samples in D_2O (first series, same scaling) and LRD2 contrast matched samples (second series, same scaling).

Schmidt et al. *Macromolecules*, 2002

NIST: Two different orientations



fast relaxation < 50 s



slow relaxation ≈ 120 min

Schmidt et al., Macromolecules, 2000, 2002.

JPS, 2004

Discussion 3: Effects of non-Gaussianity

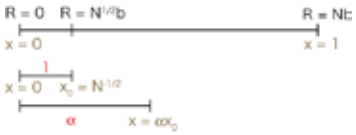
3. Effects of non-Gaussianity

For highly-stretched polymer chains, the restoring force can be expressed by the inverse-Langevin chains, $L^{-1}(x)$,

$$f = \frac{kT}{b} L^{-1}\left(\frac{< R >}{Nb}\right)$$

Hence, the shear stress is given by,

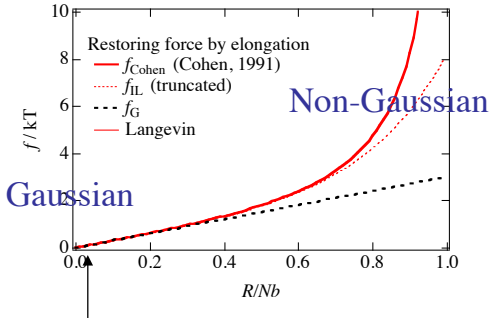
$$\sigma = G\gamma = \frac{4}{3} N^{1/2} \frac{kT}{a^2} L^{-1}\left(\frac{\gamma}{N^{1/2}}\right)$$



$$L^{-1}(x) = 3x + \frac{9}{5}x^3 + \frac{297}{175}x^5 + O\left(x^7\right)$$

$$\cong x\frac{3-(36/35)x^2}{1-(33/35)x^2} + O\left(x^6\right) \quad \text{(Padé approximation)}$$

Since $N = 2848$, $N^{1/2}$ is order of 50 for HEC. Thus, $x \approx \gamma / N^{1/2} \approx 0.02$, where the restoring force is given by Gaussian chain statistics.

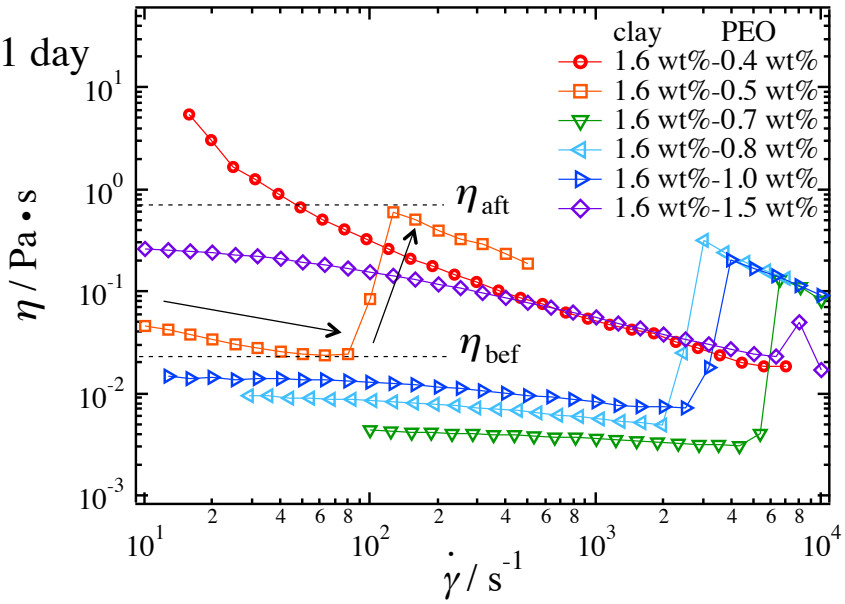


$x \approx \gamma / N^{1/2} \approx 0.02$

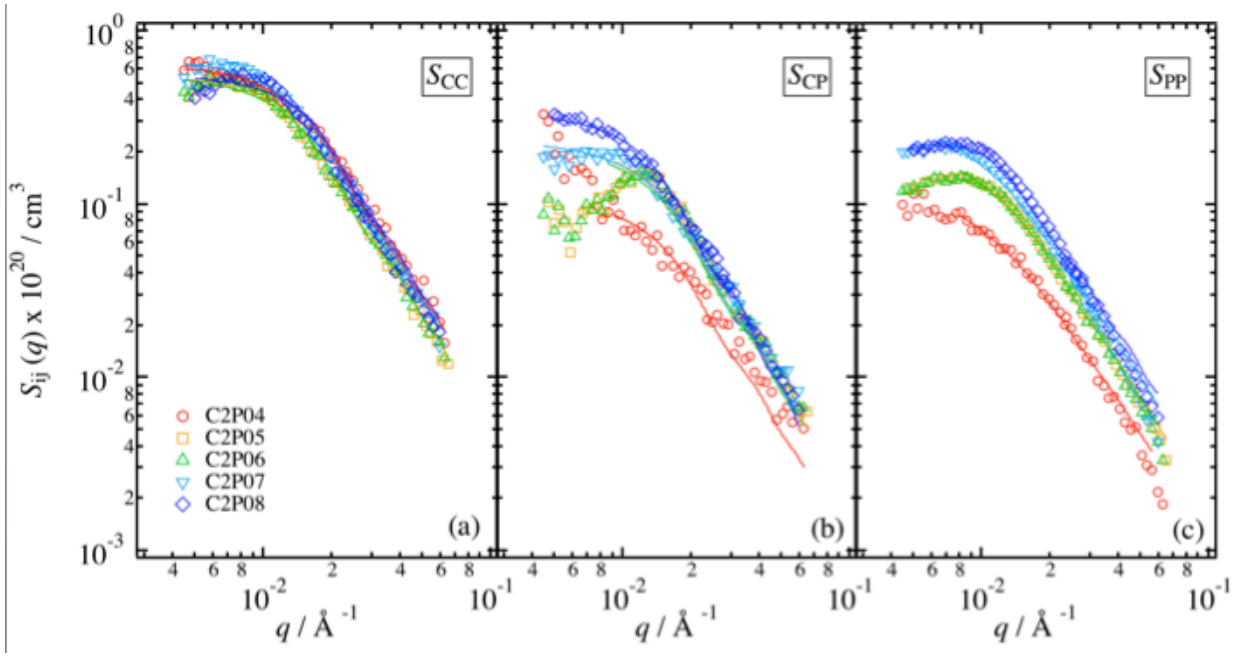
The effects of non-Gaussianity is NOT significant at all in this case.

Rheological properties of clay-PEO soln.

t_{age} = 1 day



Shear-thickening transition took place at a finite concentration window.
The strength of thickening was defined by $F = \eta_{aft}/\eta_{bef}$


S_{CC}
S_{CP}
S_{PP}
S_{ij} (q) x 10^{20} / cm^3
C2P04
C2P05
C2P06
C2P07
C2P08
(a)
(b)
(c)
q / Å $^{-1}$

67

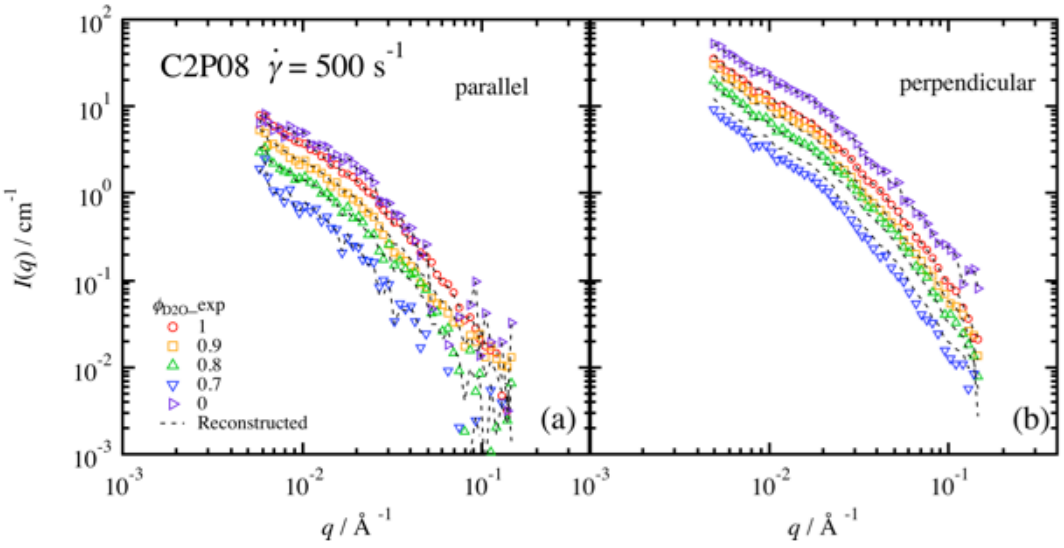

C2P08 $\dot{\gamma}$ = 500 s^{-1}
parallel
perpendicular
I(q) / cm^{-1}
ϕ_{D2O_exp}
1
0.9
0.8
0.7
0
Reconstructed
(a)
(b)
q / Å $^{-1}$

Fig.11

68

Table 2 stationary fitting parameter

	C2P04	C2P05	C2P06	C2P07	C2P08
R_C / Å	150				
D_C / Å	10				
ϕ_{cyl}	0.0076				
R_{PY}/ Å	91	72	76	76	110
prefactor	1.6	1.2	1.2	1.5	1.6
R_{pl} / Å	150	150	150	150	190
D_{pl} / Å	17	21	21	21	24
ϕ_{pl}	0.23	0.39	0.38	0.30	0.21
S^0_{PP}	0.082	0.12	0.14	0.19	0.25
ξ / Å	110	120	120	130	180

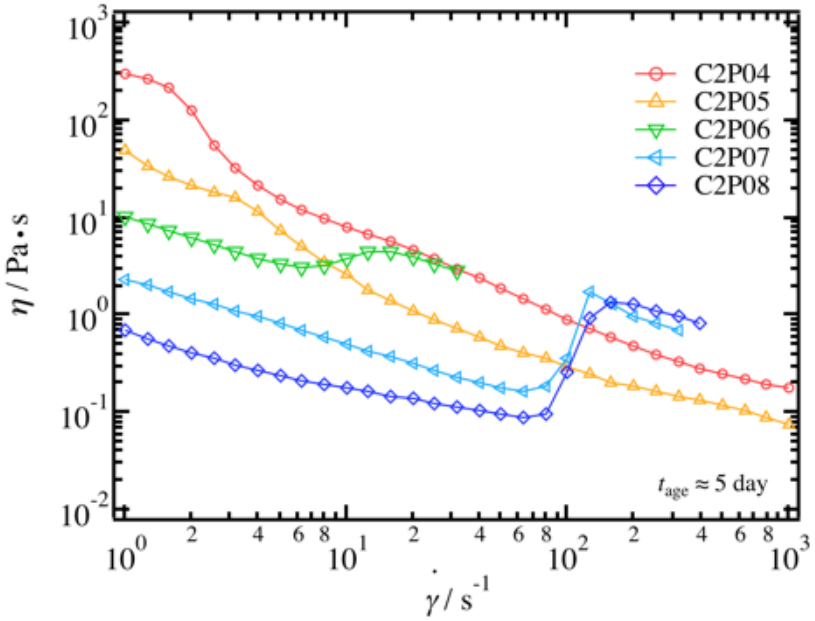


Fig.1

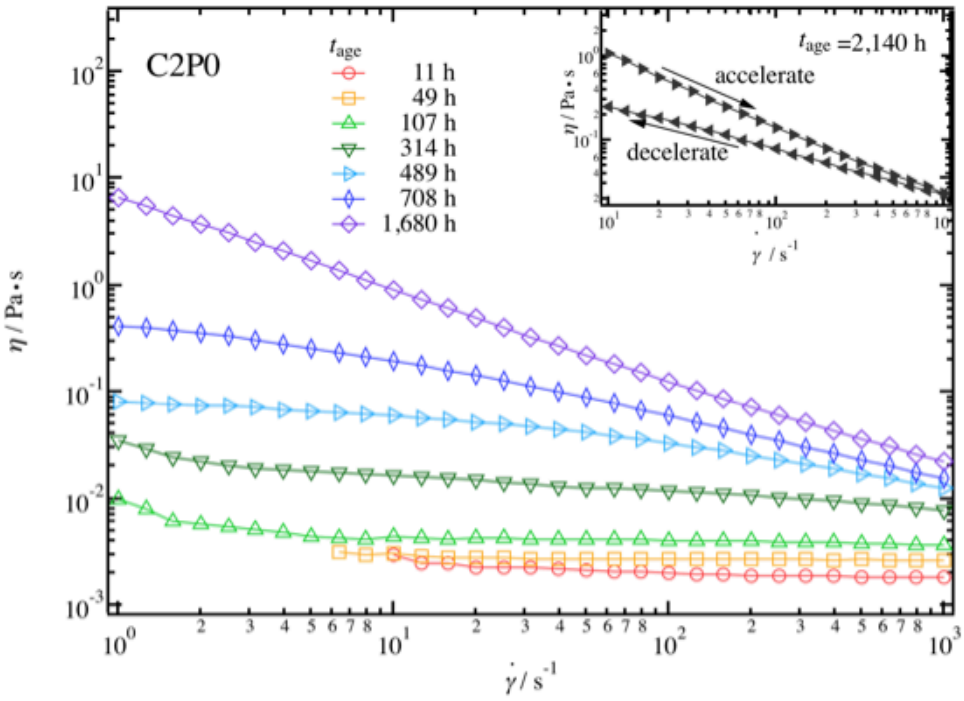

C2P0
t_{age}
11 h
49 h
107 h
314 h
489 h
708 h
1,680 h
t_{age} =2,140 h
accelerate
decelerate
η / Pa • s
$\dot{\gamma}$ / s^{-1}

Fig.3

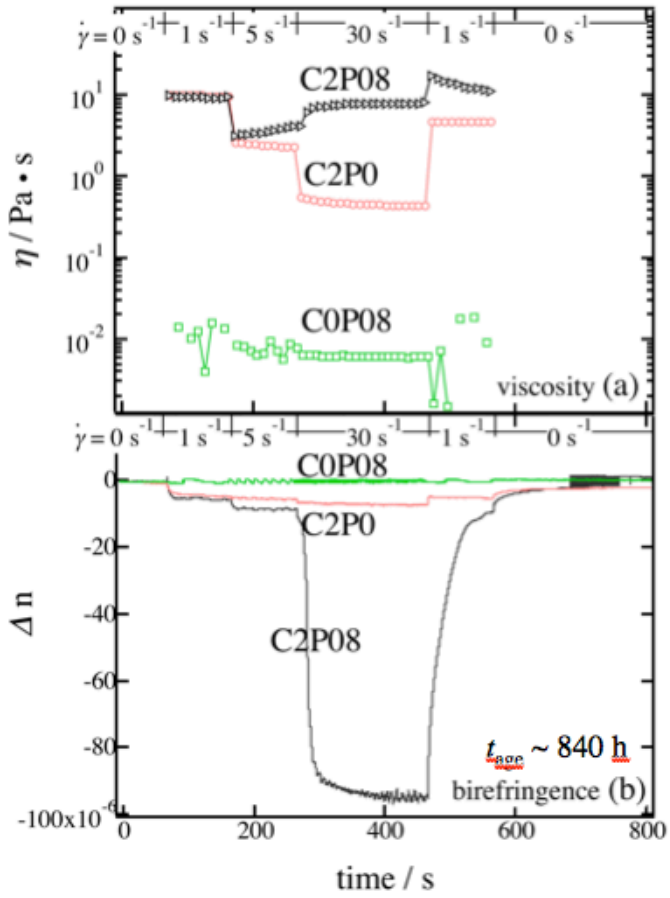
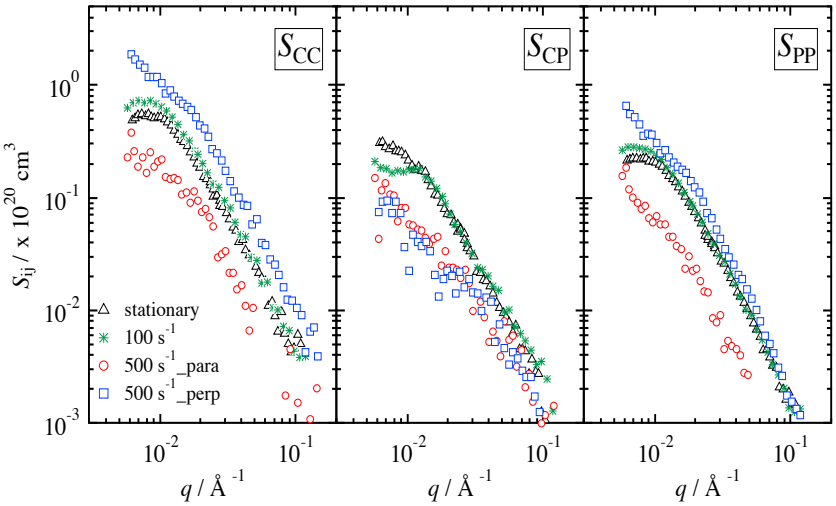

$\dot{\gamma}$ = 0 s^{-1} 1 s^{-1} 5 s^{-1} 30 s^{-1} 1 s^{-1} 0 s^{-1}
C2P08
C2P0
C0P08
viscosity (a)
η / Pa • s
Δ n
t_{age} ~ 840 h
birefringence (b)
time / s

Fig.13

Partial Scattering Functions in a flow

1D partial scattering functions (SDD = 2, 8 m)



- Partial scattering functions at 100 s^{-1} show same patterns with 0 s^{-1}.
- There are PEO layers adsorbed on clay at each shear rate, but the layers were peeled off by shear thickening.
- Clay and PEO orient to parallel to the flow direction at 500 s^{-1}.

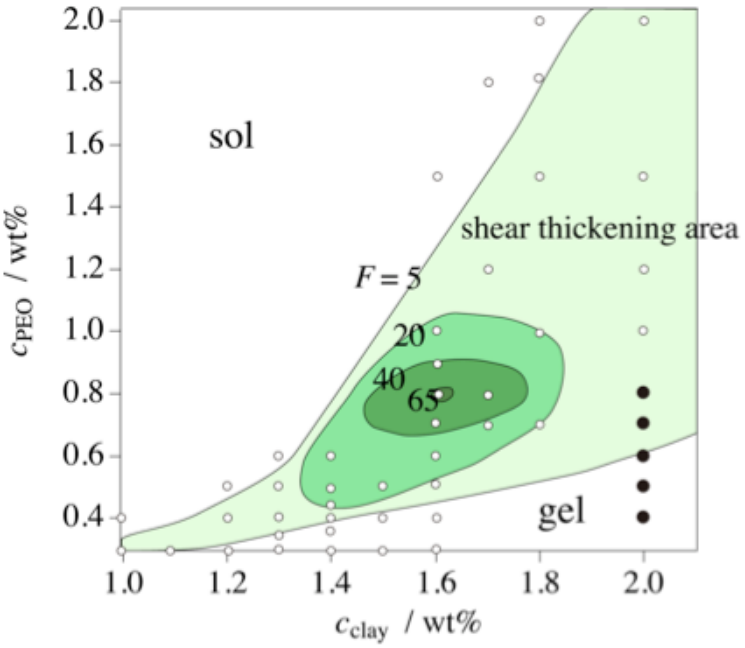


Fig.2

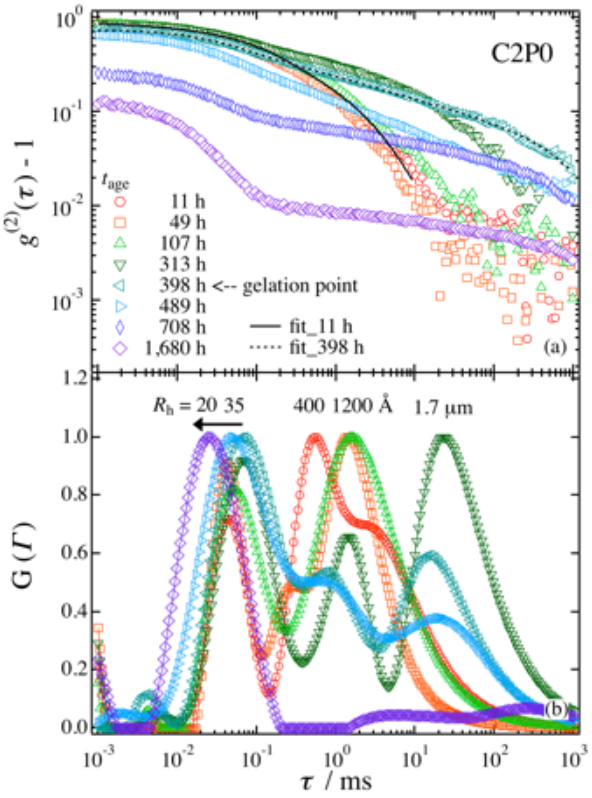

C2P0
t_{age}
11 h
49 h
107 h
313 h
398 h <-- gelation point
489 h
708 h
1,680 h
fit_11 h
fit_398 h
(a)
R_h = 20 35
400 1200 Å
1.7 μm
(b)
$g^{(2)}(\tau)$ - 1
G (Γ)
τ / ms

Fig.4

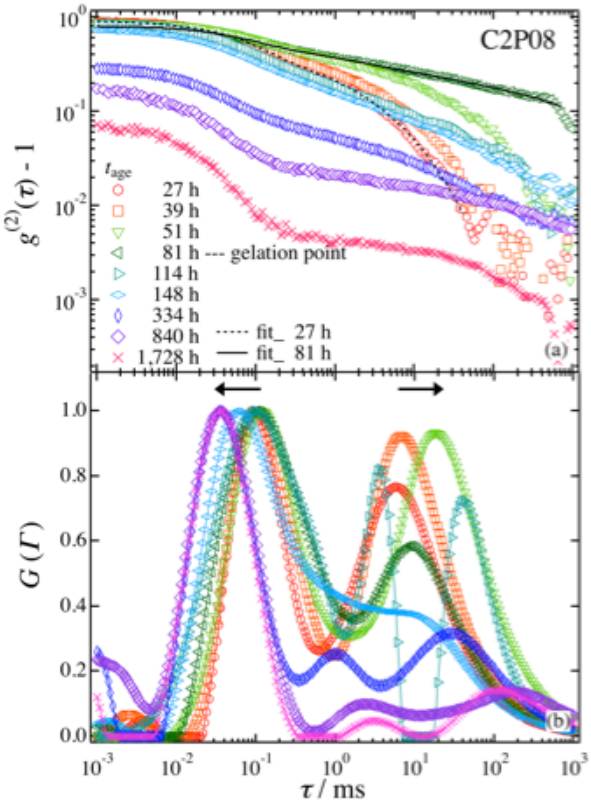

C2P08
t_{age}
27 h
39 h
51 h
81 h --- gelation point
114 h
148 h
334 h
840 h
1,728 h
fit_ 27 h
fit_ 81 h
(a)
(b)
$g^{(2)}(\tau)$ - 1
G (Γ)
τ / ms

Fig.6

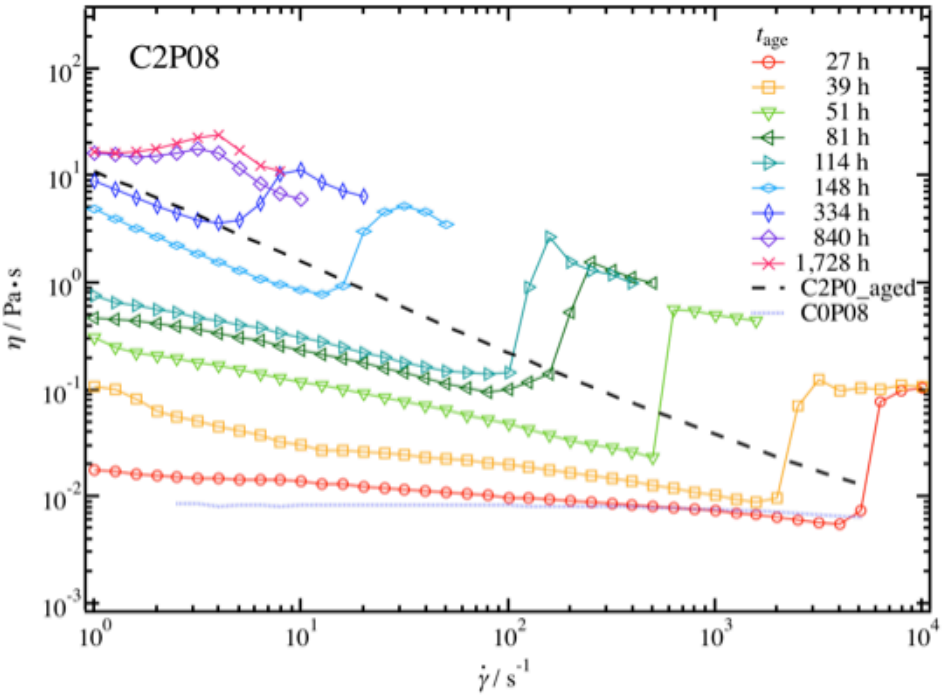

C2P08
t_{age}
27 h
39 h
51 h
81 h
114 h
148 h
334 h
840 h
1,728 h
C2P0_aged
C0P08
η / Pa·s
$\dot{\gamma}$ / s^{-1}

Fig.5