Diffusing wave spectroscopy in elastomer fracture

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In collaboration with Luca Cipelletti (Montpellier, CNRS)

Fracture at different length scale

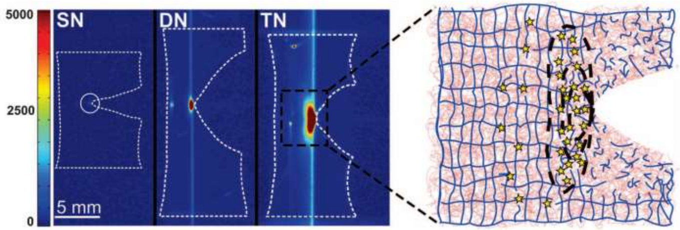
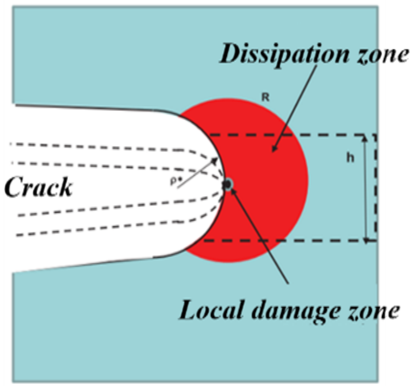


Fig. 5. Mapping of where bonds break during crack propagation. Intensity-colorized images of propagating cracks on notched samples containing dioxetane cross-linker in the first network, showing the light emission due to the breakage of bonds in SN, DN, and TN samples. The size and geometry of the sample are shown with a white dashed line. Vertical lines in the DN and TN image are due to detector artifacts; in DN and TN, spots far from the crack tip are due to reflection of the light on surface inhomogeneities and do not correspond to a local light emission. (Right) Schematic of the sacrificial bond-breaking mechanism in front of the crack tip for the DN and TN; the first network is represented in blue, and the second and third networks are in red.



Molecular scale (~10nm)

Ducrot, Etienne, et al.2014

Mesoscopic scale (0.1 ~10 μm)

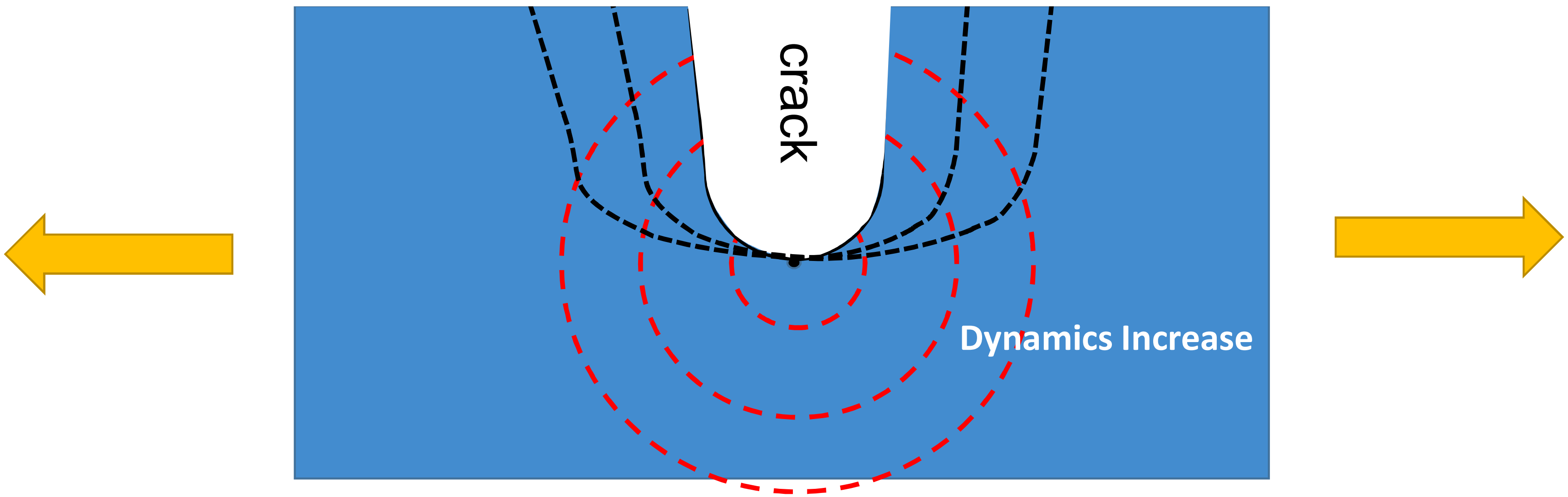
Creton, Costantino, and Matteo Ciccotti.2016

Macroscopic scale

Martínez, A. B., et al. 2017

Open question： How the network is damaged in mesoscopic scale?

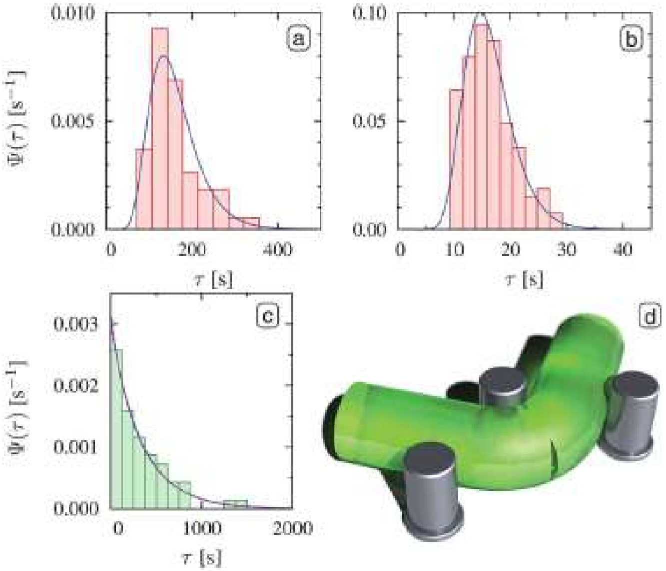
Fracture precursor



Fracture prediction?

Characterization methods?

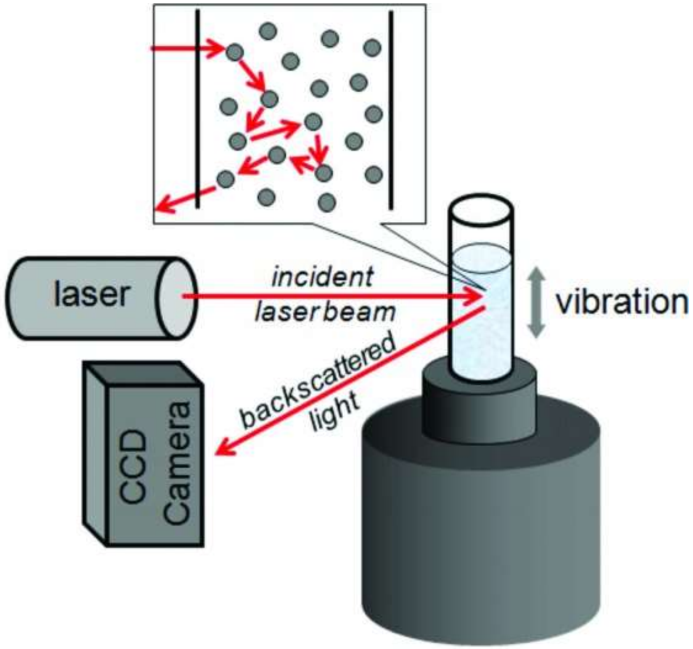
Delayed fracture

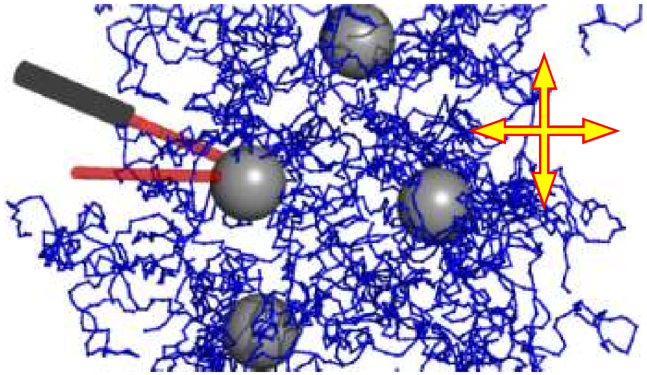


Bonn, Daniel, et al. "Delayed fracture of an inhomogeneous soft solid." *Science* 280.5361 (1998): 265-267.

Lindström, Stefan B., et al. "Structures, stresses, and fluctuations in the delayed failure of colloidal gels." *Soft Matter* 8.13 (2012): 3657-3664.

DWS technology in polymer network





Methods:
diffusing wave spectroscopy (DWS)

Measure requirement:
Polymer network + Probe particles

Krajina, Brad A., et al. 2017

Application of DWS technology on polymer network

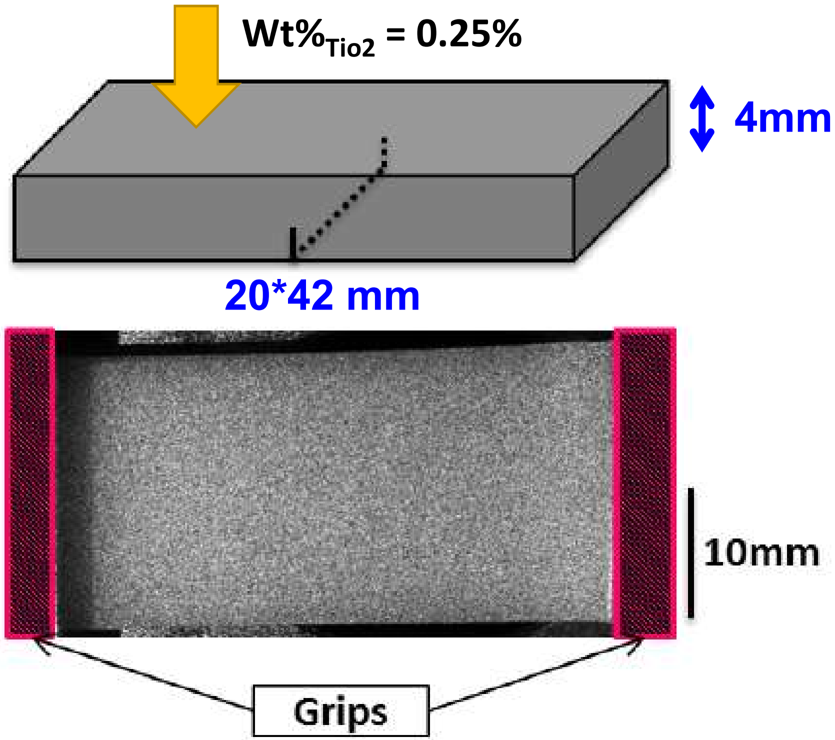
- **1. Sample preparation**

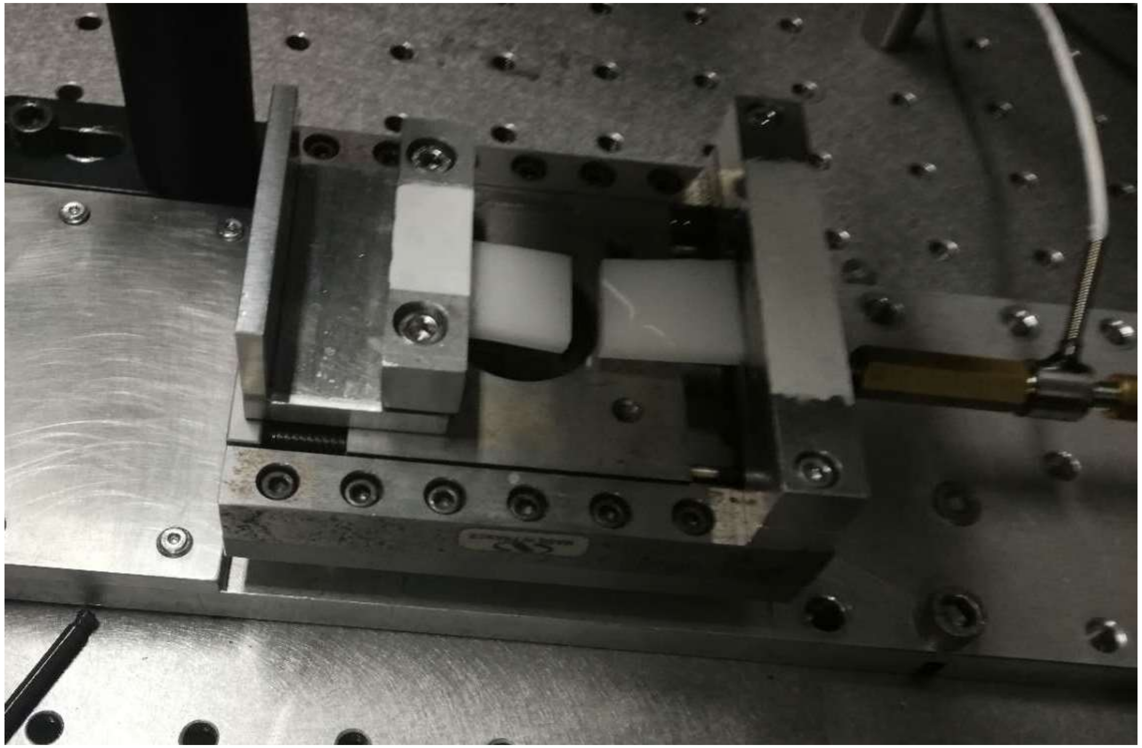
  Introduction probe particles during crosslinking

  - **1. PDMS (model sample)**
  - **2. Multiple networks from acrylates (from Labortory)**
  - **3. Double Dynamic networks (from other partners)**

- **2. Set-up development**
  - **1. optical part (DWS testing system)**
  - **2. mechanical part (Tensile machine)**

Preliminary results: fracture precursor in PDMS

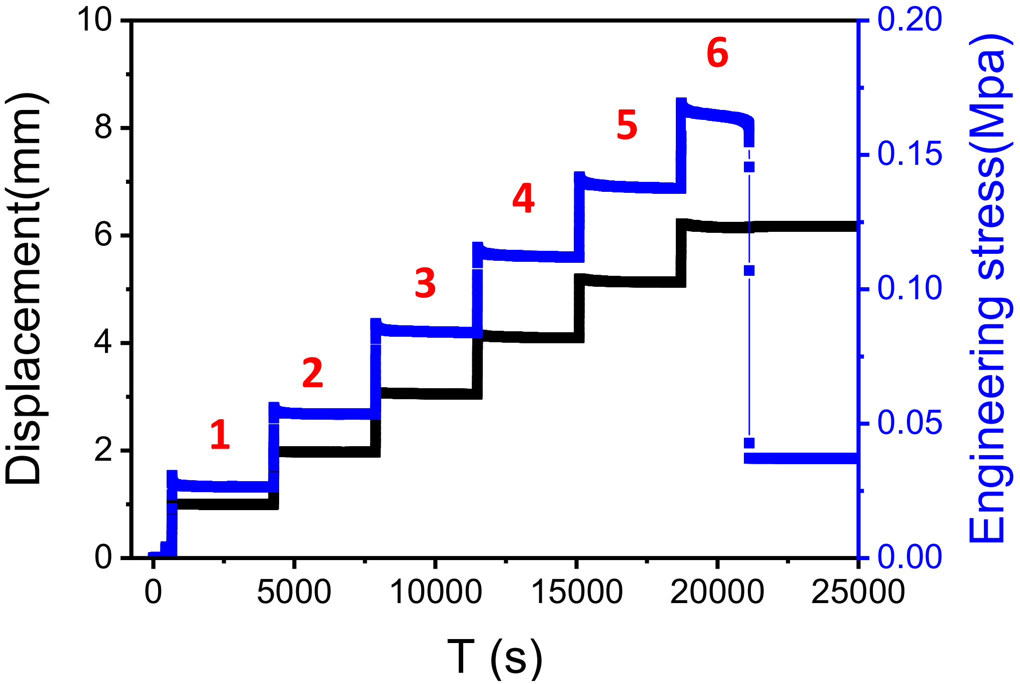


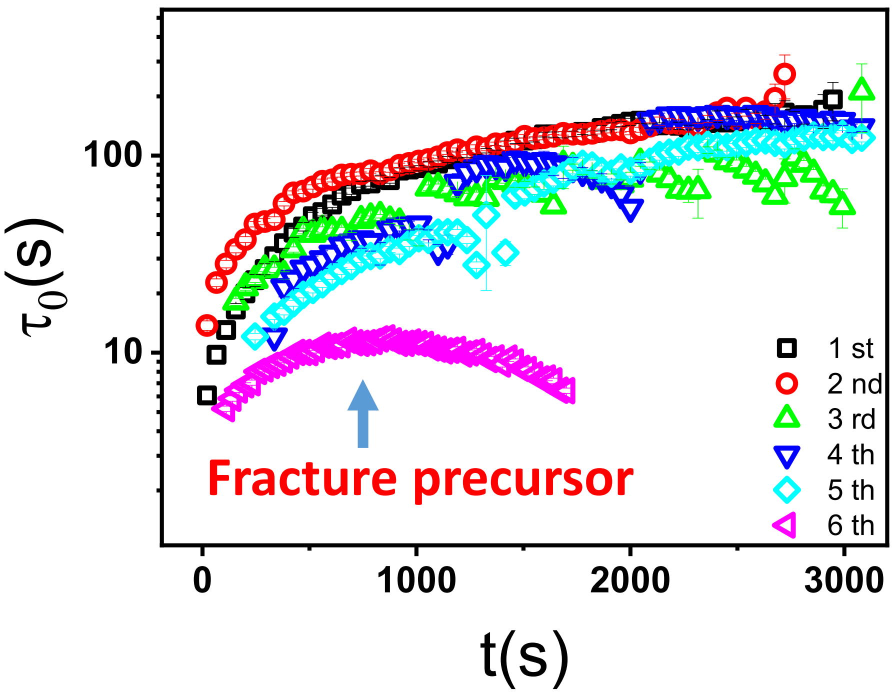


Fracture precursor

$$g_2(\tau)-1 = \frac{\langle I_P(t) I_P(t+\tau)\rangle_P}{\langle I_P(t)\rangle_P \langle I_P(t+\tau)\rangle_P} - 1$$

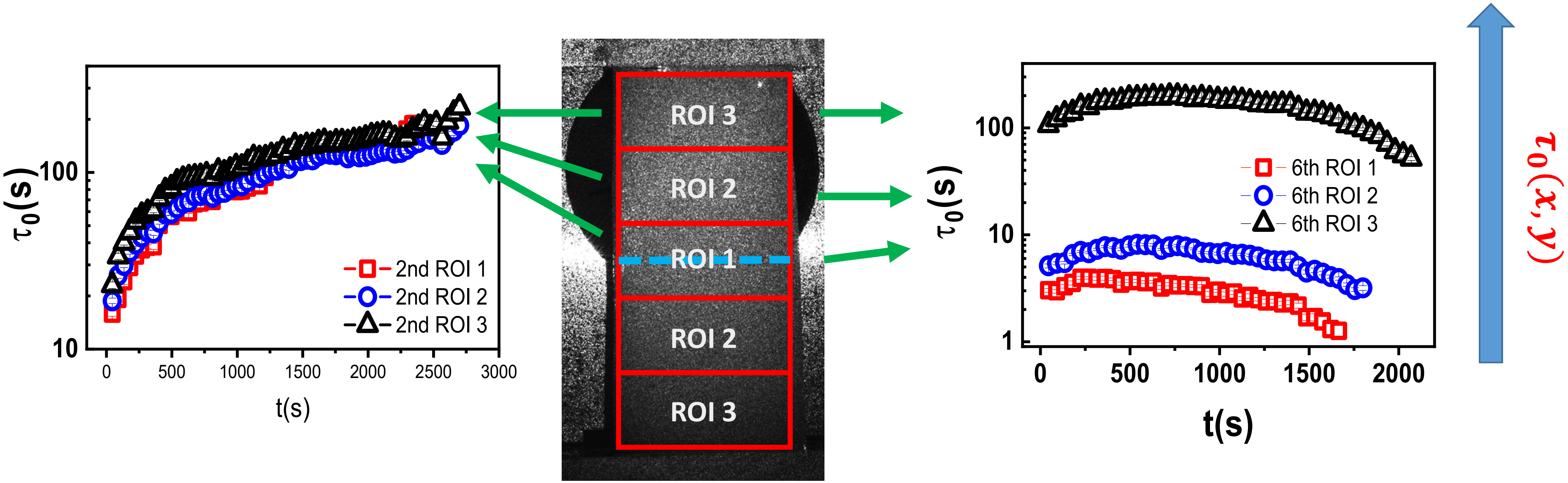
$$= Aexp\left(-\left(\frac{\tau}{\tau_0}\right)^P\right) + B$$





2nd

6th



$\tau_0(s)$
100
10
0
500
1000
1500
2000
2500
3000
t(s)
2nd ROI 1
2nd ROI 2
2nd ROI 3
ROI 3
ROI 2
ROI 1
ROI 2
ROI 3
$\tau_0(s)$
100
10
1
0
500
1000
1500
2000
t(s)
6th ROI 1
6th ROI 2
6th ROI 3
$\tau_0(x, y)$

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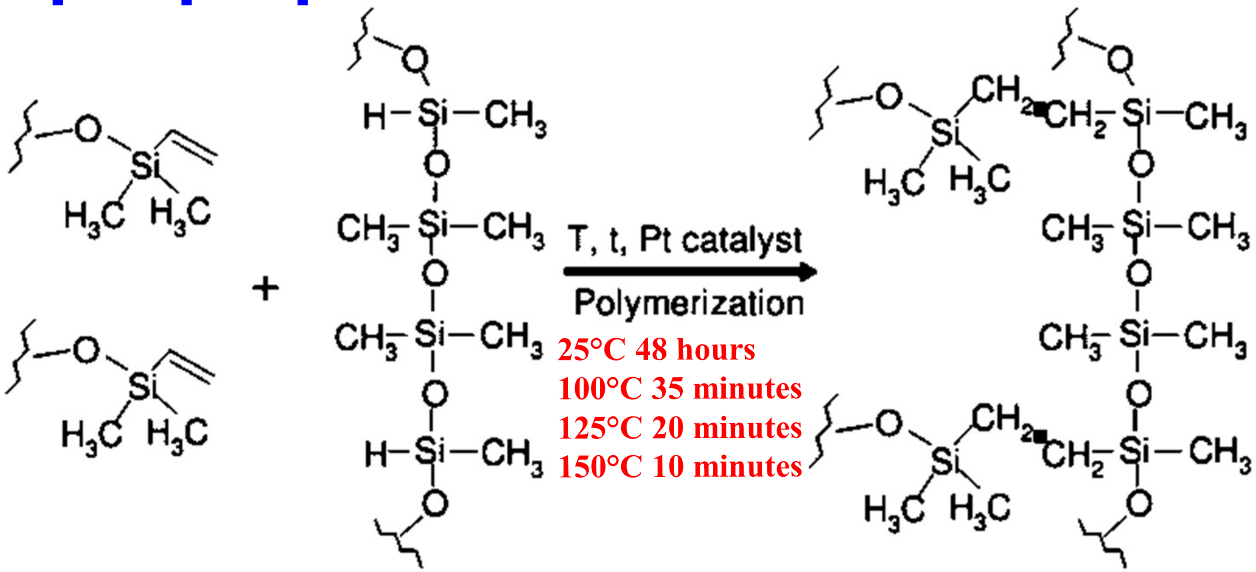
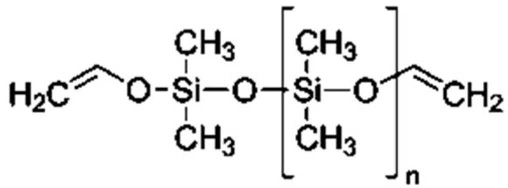
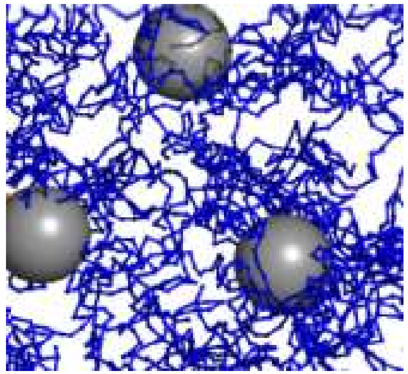
Sample preparation

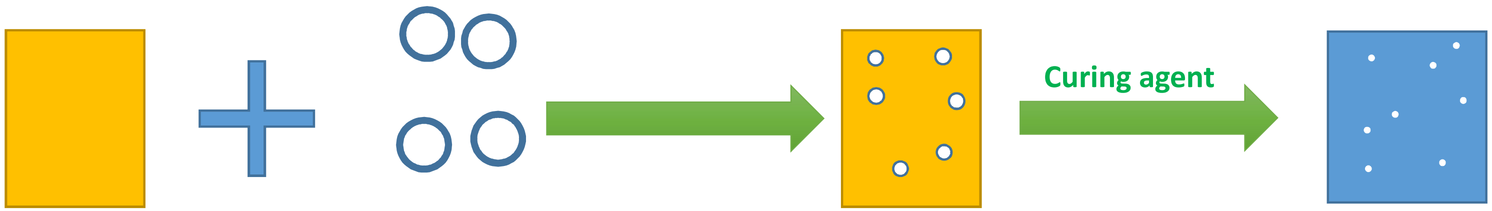


Vinyl-terminated PDMS Curing agent PDMS elastomer



Sylgard 184





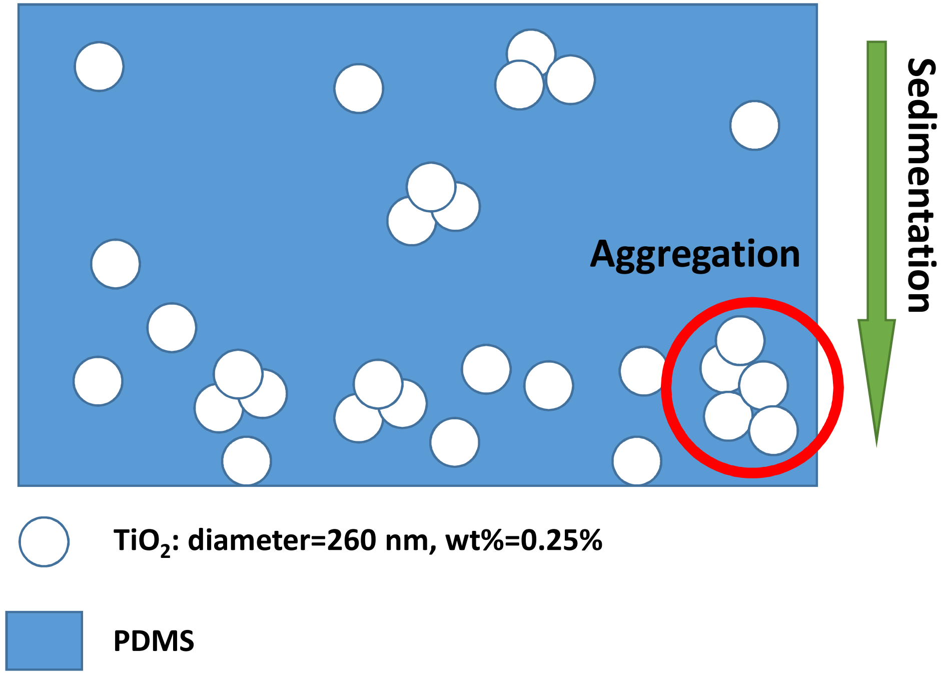
PDMS

TiO_2
d=260 nm
wt%=0.25% →very small amount

Qiu, Weiping. "PDMS based waveguides for microfluidics and EOCB." (2012).

Aggregation and Sedimentation

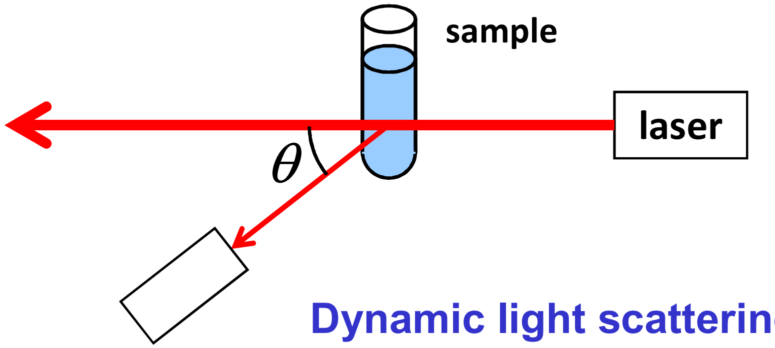
Elastomer after curing (RT)



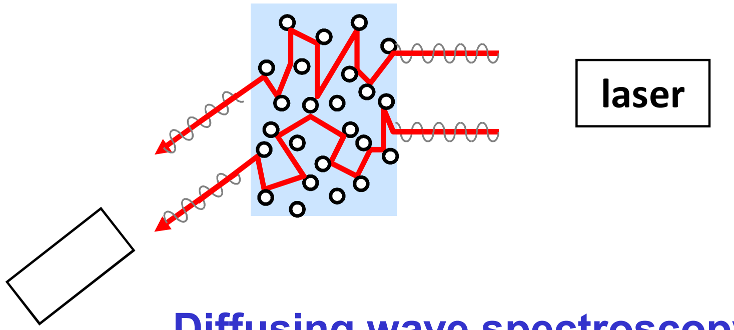
1. Aggregation → sonication

2. Sedimentation → heating

Characterization in PDMS base: DLS and DWS



Dynamic light scattering (DLS)



Diffusing wave spectroscopy (DWS)

DLS:

$$g_2(t) = \frac{\langle I(t') \cdot I(t'+t) \rangle}{\langle I(t') \rangle^2}$$

$$= 1 + \beta [g_1(t)]^2$$

$$g_1(q,t) = \exp\left[- \frac{< \Delta r^2(t) > \cdot q^2}{6} \right]$$

DWS:

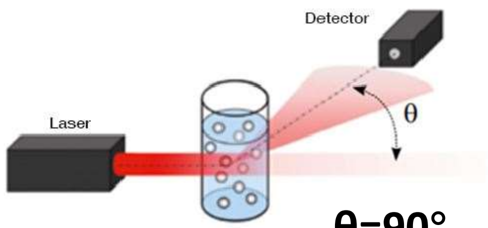
$$g_2(t) = \frac{\langle I(t') \cdot I(t'+t) \rangle}{\langle I(t') \rangle^2}$$

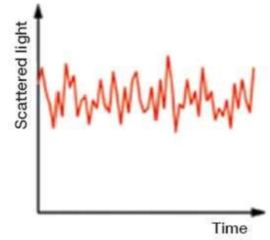
$$= 1 + \beta [g_1(t)]^2$$

$$g_1(t) = \frac{\dfrac{L/l^* + 4/3}{5/3} \sinh\left(\sqrt{k_0^2 \langle \Delta r^2(t) \rangle} \right) + \dfrac{2}{3} \sqrt{k_0^2 \langle \Delta r^2(t) \rangle} \cosh\left(\sqrt{k_0^2 \langle \Delta r^2(t) \rangle} \right)}{\left(1 + \dfrac{4}{9} k_0^2 \langle \Delta r^2(t) \rangle \right) \sinh\left(\dfrac{L}{l^*} \sqrt{k_0^2 \langle \Delta r^2(t) \rangle} \right) + \dfrac{4}{3} \sqrt{x} \cosh\left(\dfrac{L}{l^*} \sqrt{k_0^2 \langle \Delta r^2(t) \rangle} \right)}$$

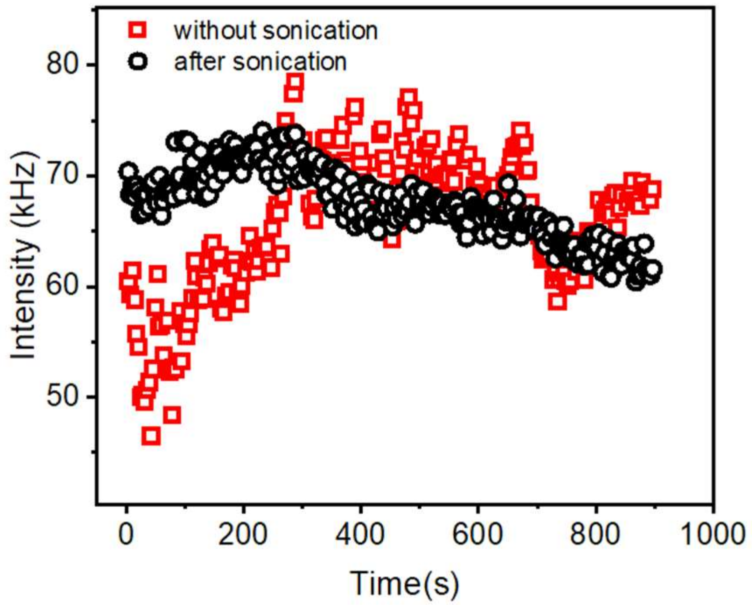
$\langle r^2 \rangle$: Mean square displacement (MSD)

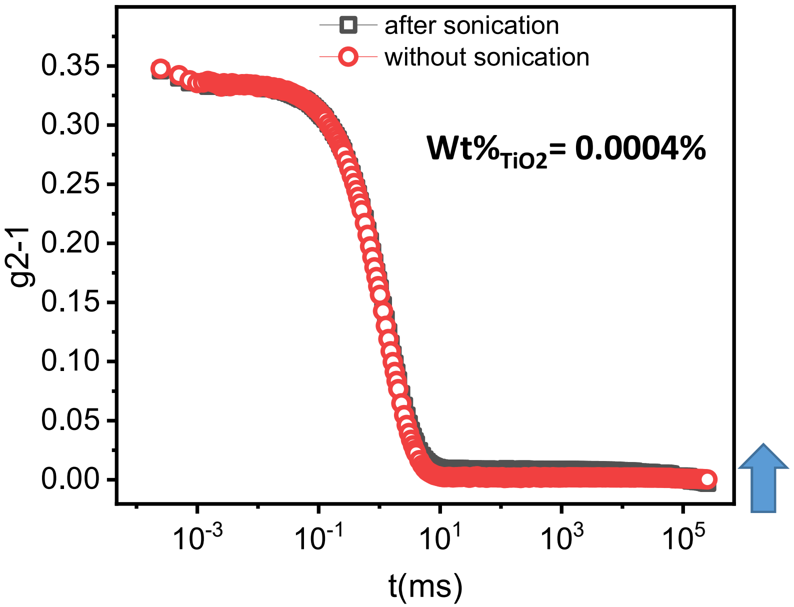
Size measurement in water (DLS)





θ=90°





D_{TiO2}= 260 nm

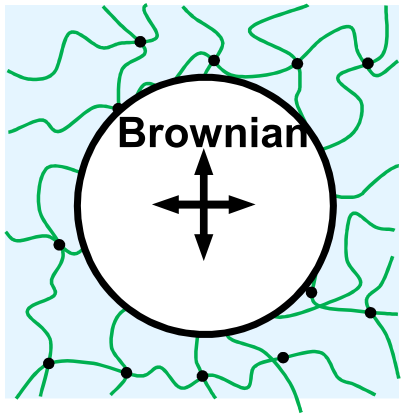
In dilute suspension, aggregation can be observed, but negligible.

Sedimentation in PDMS (time-averaged DWS)

Brownian movement

$$\langle r^2 \rangle = 6Dt = \frac{kT}{\pi r \eta} t$$

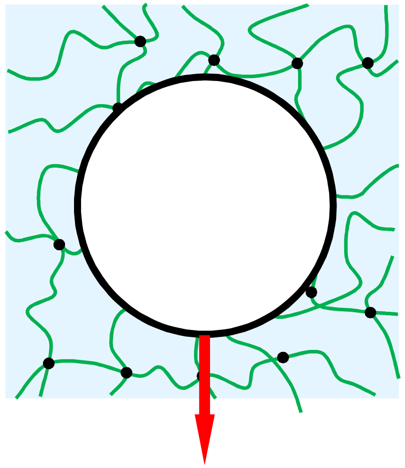
$$\frac{d\ln\langle r^2 \rangle}{d\ln t} = 1$$

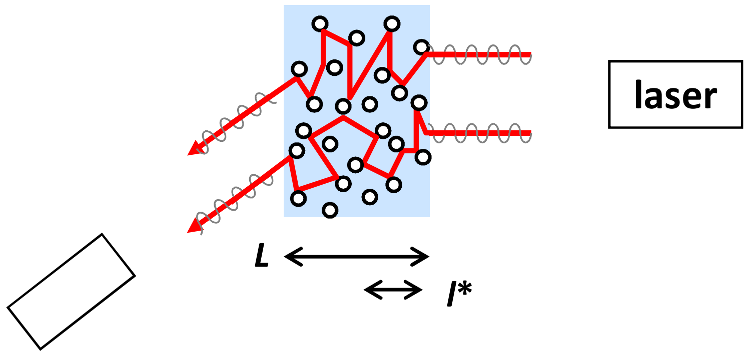


Equilibrium sedimentation velocity v_e

$$\langle r^2 \rangle = (v_e t)^2$$

$$\frac{d\ln\langle r^2 \rangle}{d\ln t} = 2$$



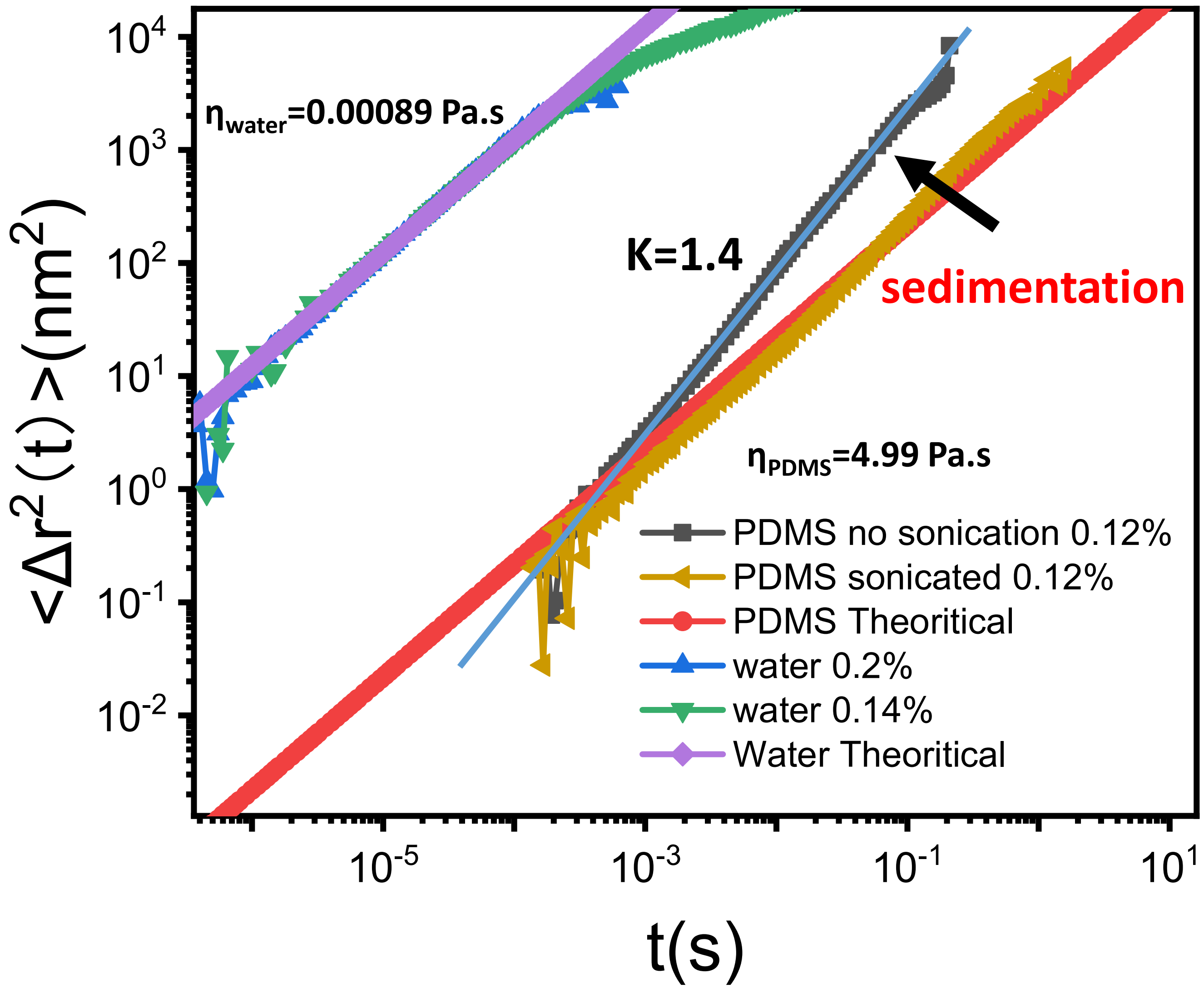


Theoretical value （only consider Brownian movement）：

$$\langle r^2 \rangle = 6Dt = \frac{kT}{\pi r \eta} t$$

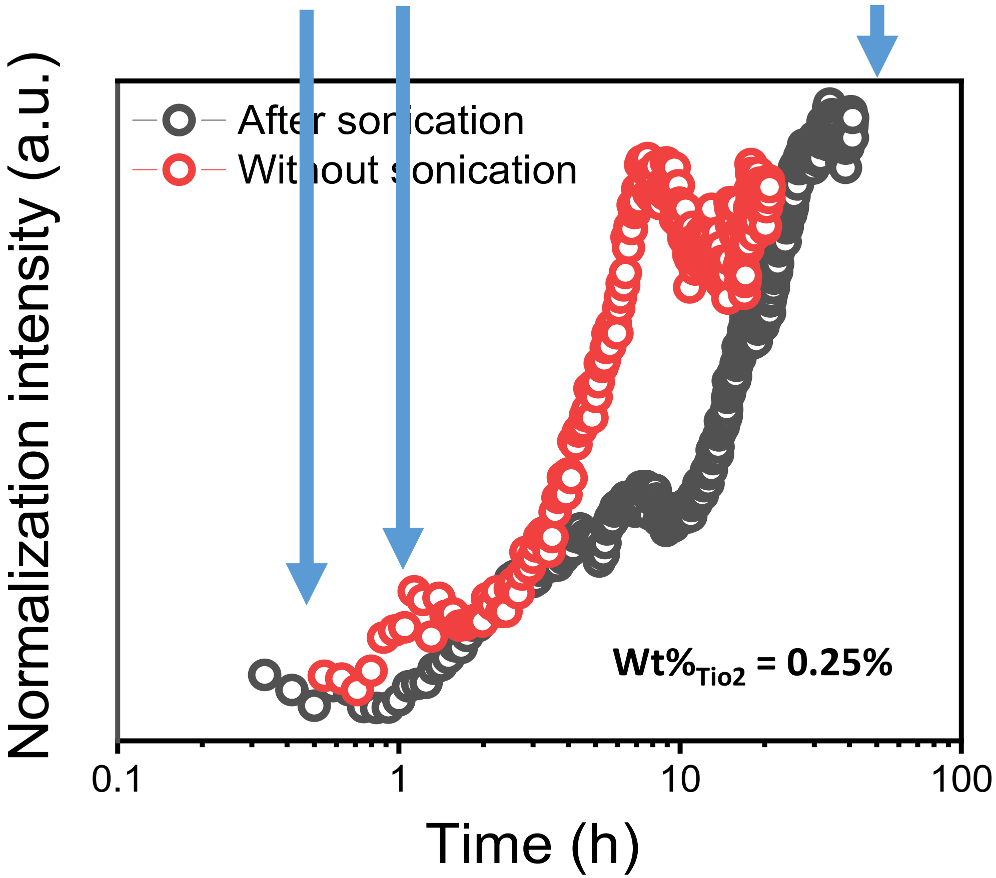
$$\frac{d\ln\langle r^2 \rangle}{d\ln t} = 1$$

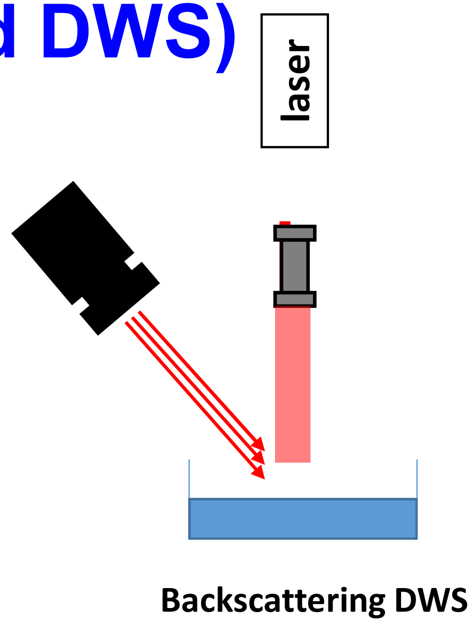
Slope after sonication is almost 1.



Sedimentation in PDMS (ensemble averaged DWS)

curing temperature: 100 ℃ 90 ℃ RT





No sonication, cured at room temperature

After sonication, cure at 90 °

Summary

1. Sedimentation and aggregation of PDMS are characterized by DWS.

2. Aggregation can be effectively reduced by sonication.

3. Influence of sedimentation can be reduced by curing at higher temperature.

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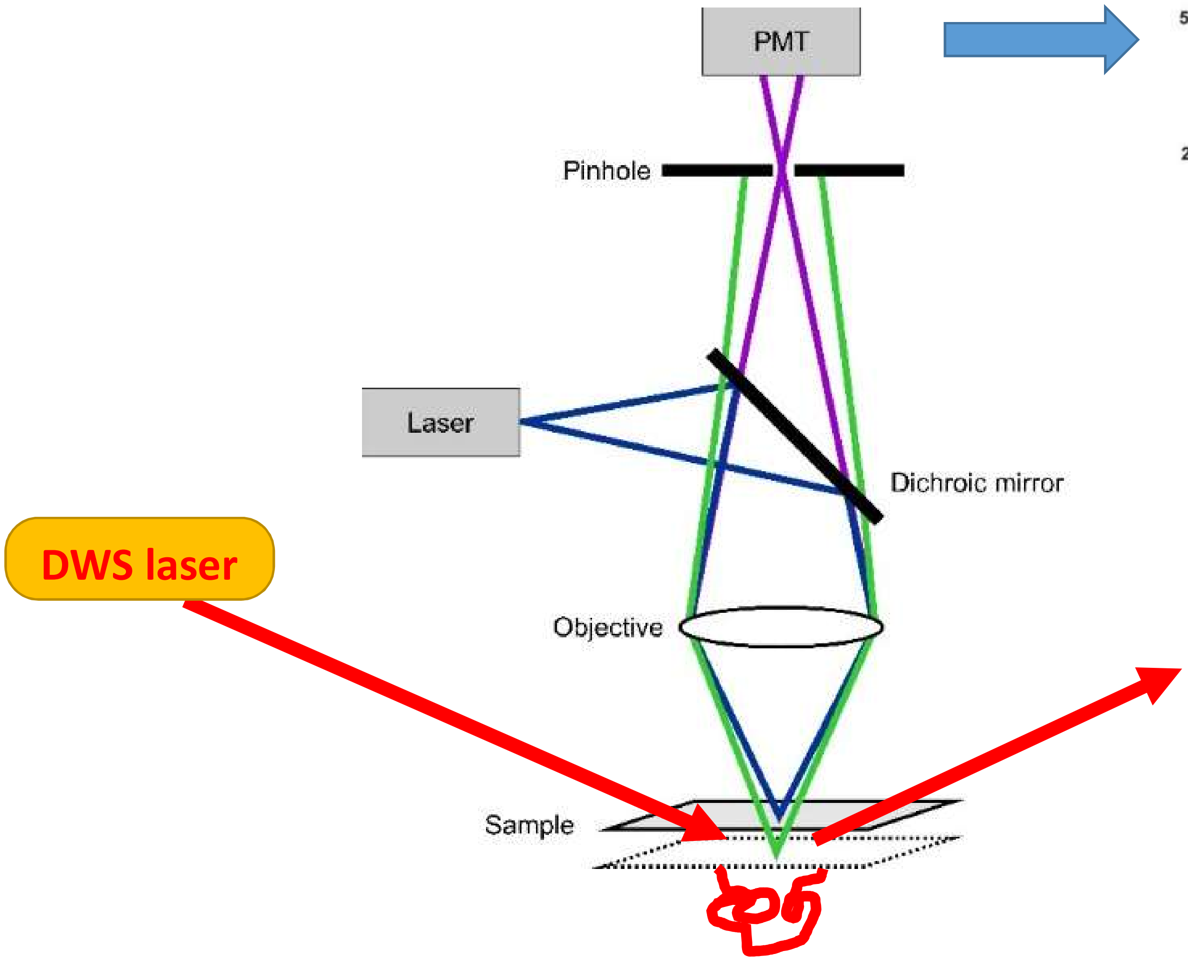
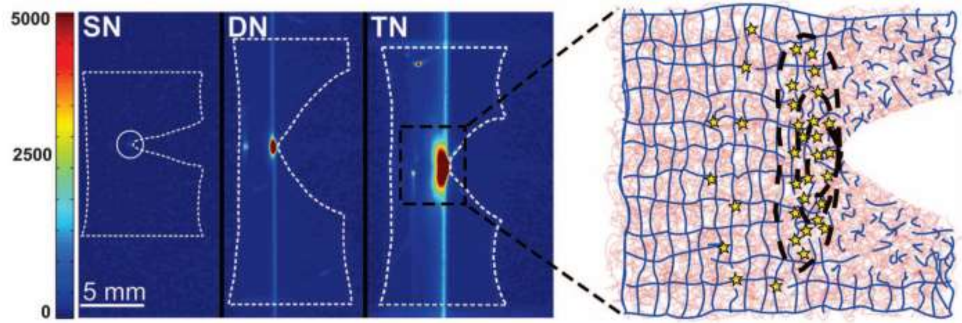
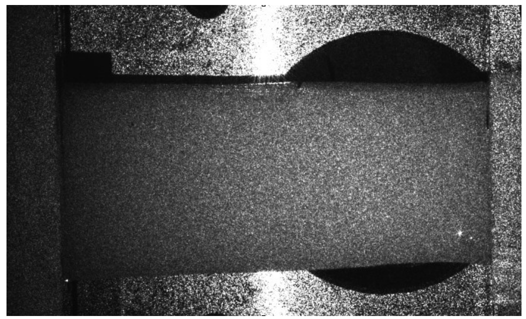
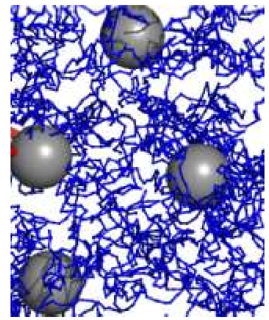
Goal: DWS & confocal microscopy



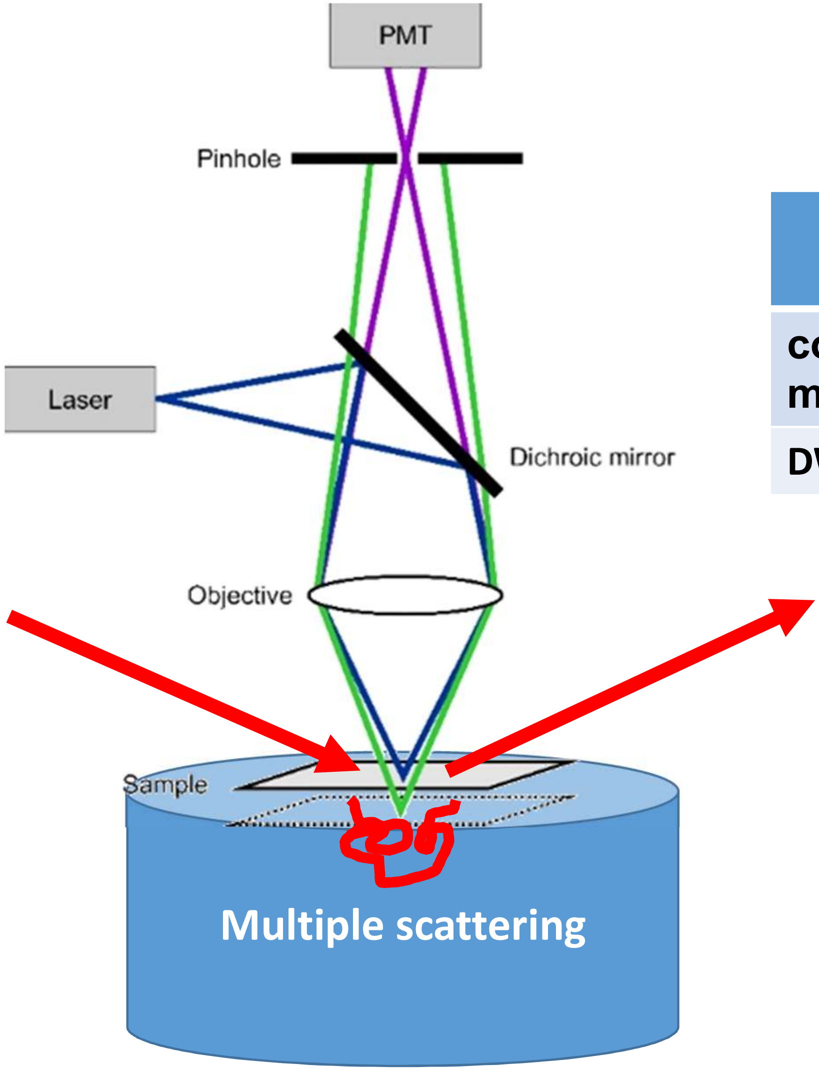


Molecular scale (~10nm)





Mesoscopic scale (0,1 ~10 μm)



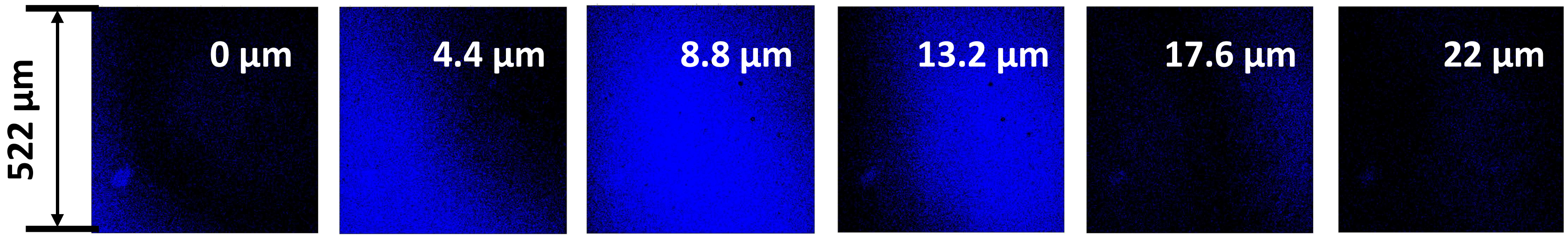
	Material requirement	Depth Limitation
confocal microscopy	Mechanofluorochromic materials	~100 µm
DWS	Probe particles	l*~100 µm

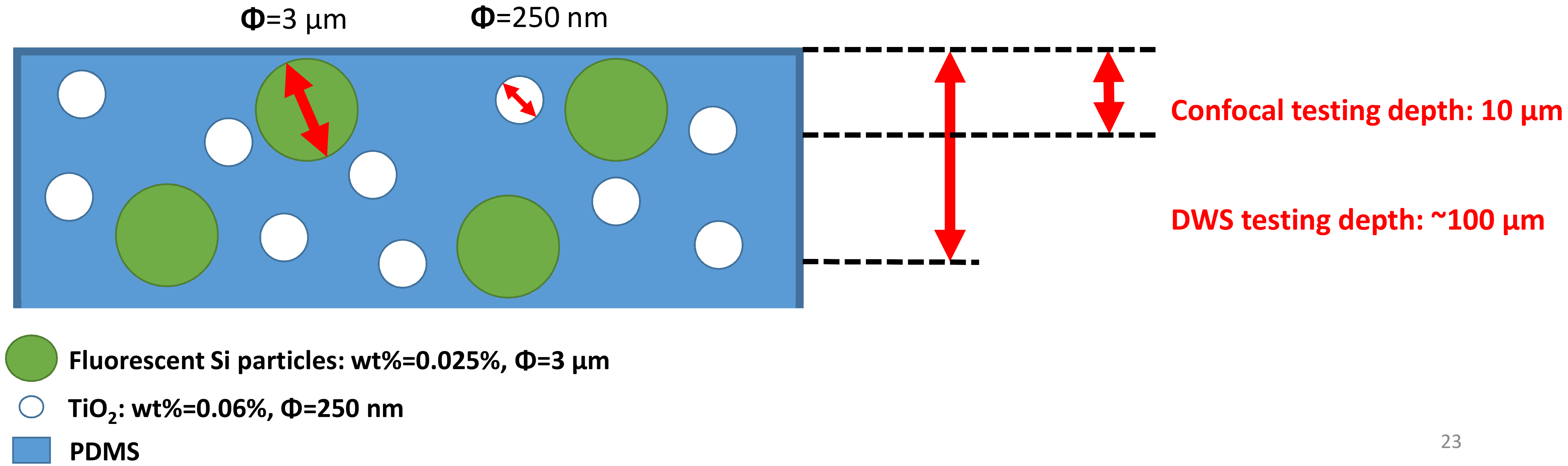
transparent

white

Trade off between multiple scattering and confocal measure depth

Probe particles influence in confocal microscopy (PDMS)





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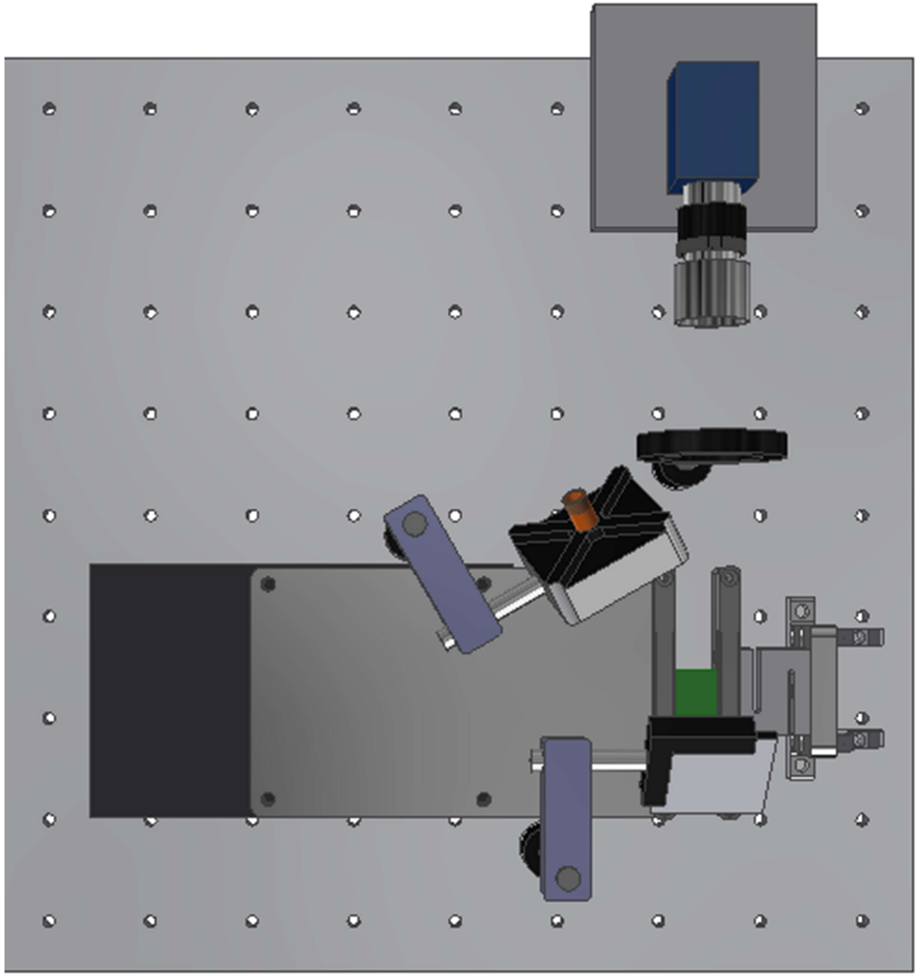
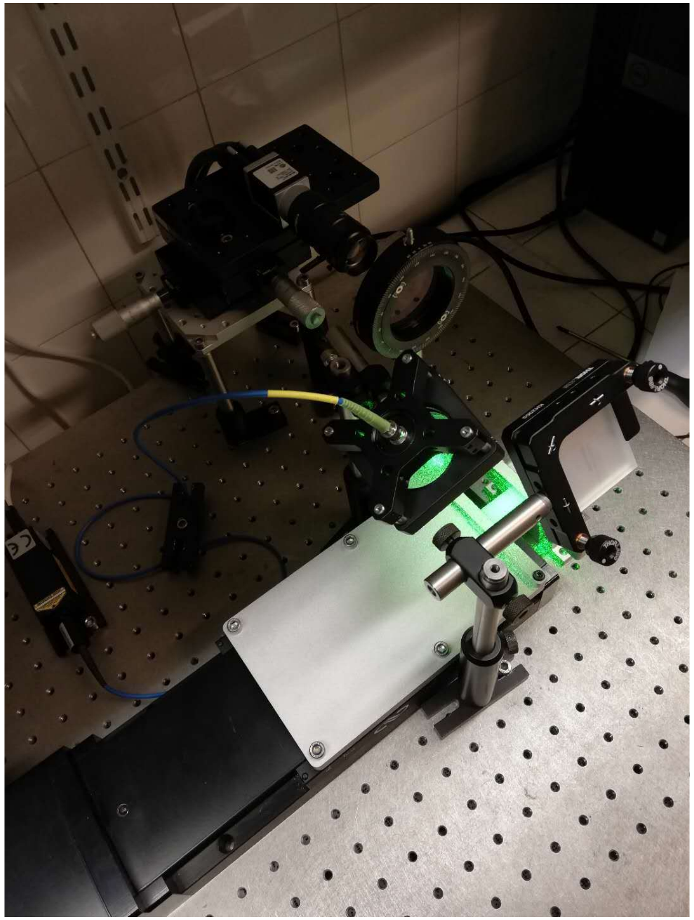
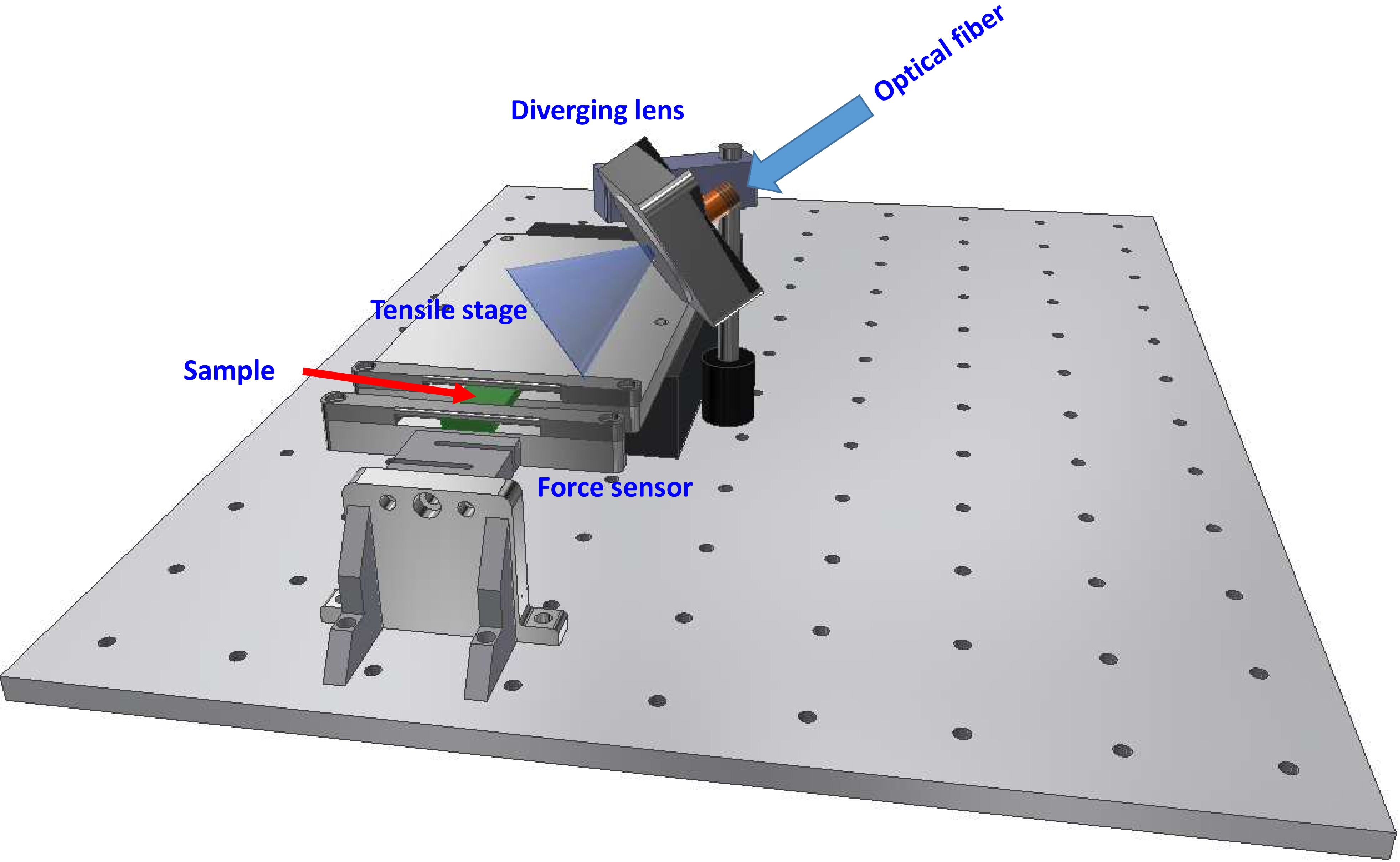
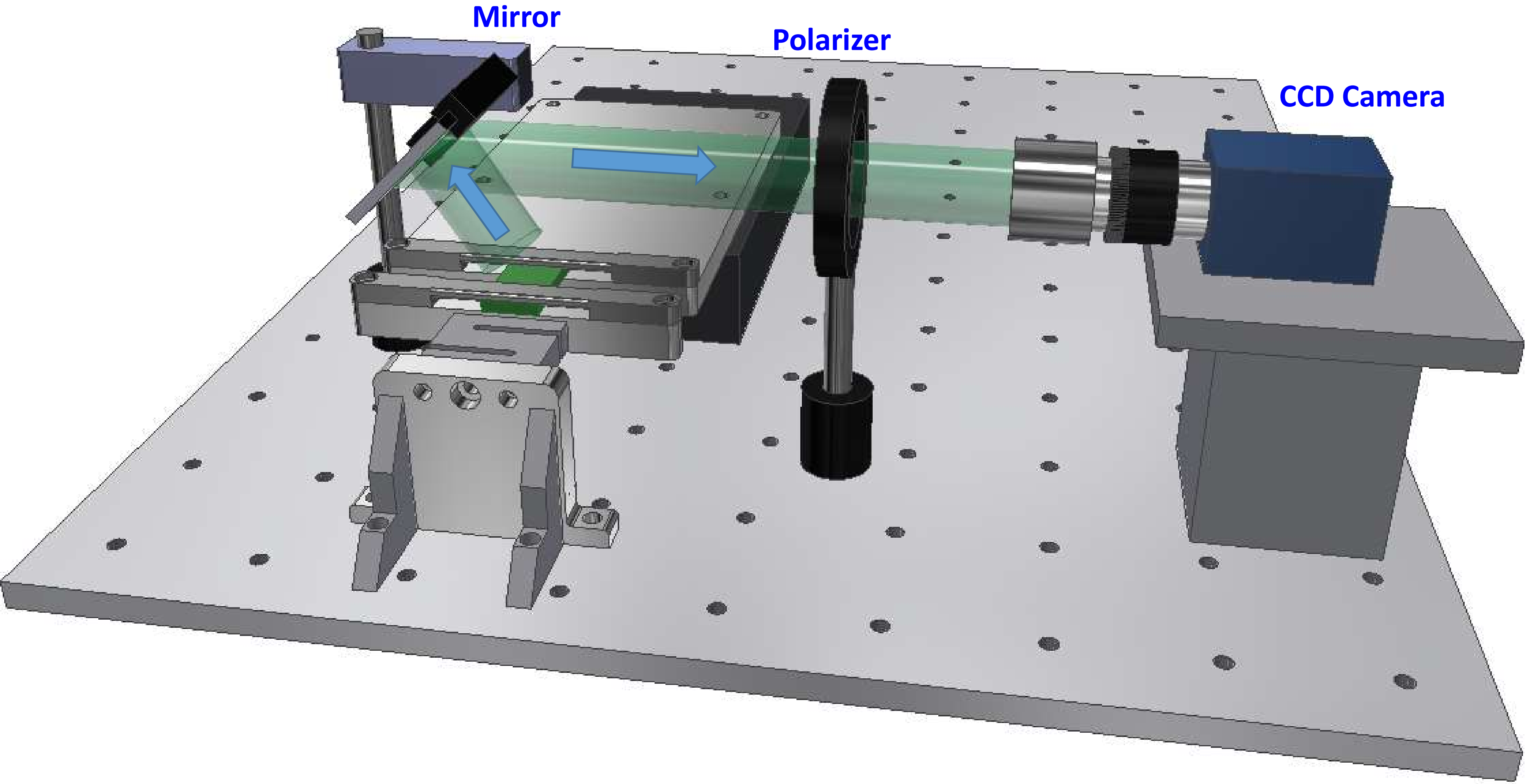
Fabrication of DWS testing Set-up in lab






Optical fiber
Diverging lens
Tensile stage
Sample
Force sensor


Mirror
Polarizer
CCD Camera

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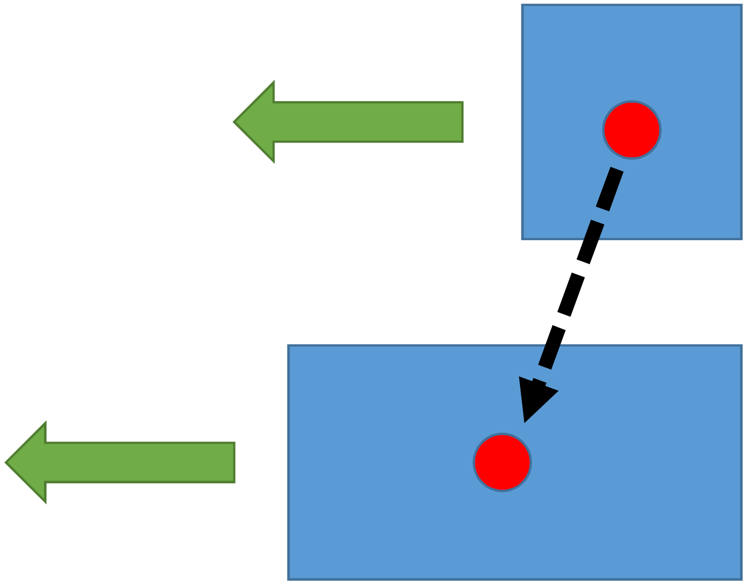
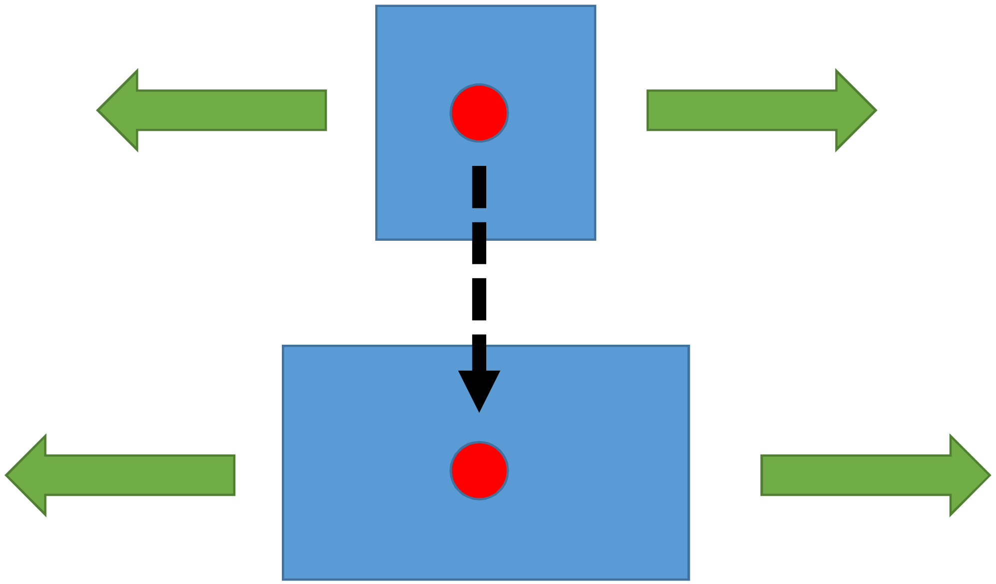
unidirectional tensile



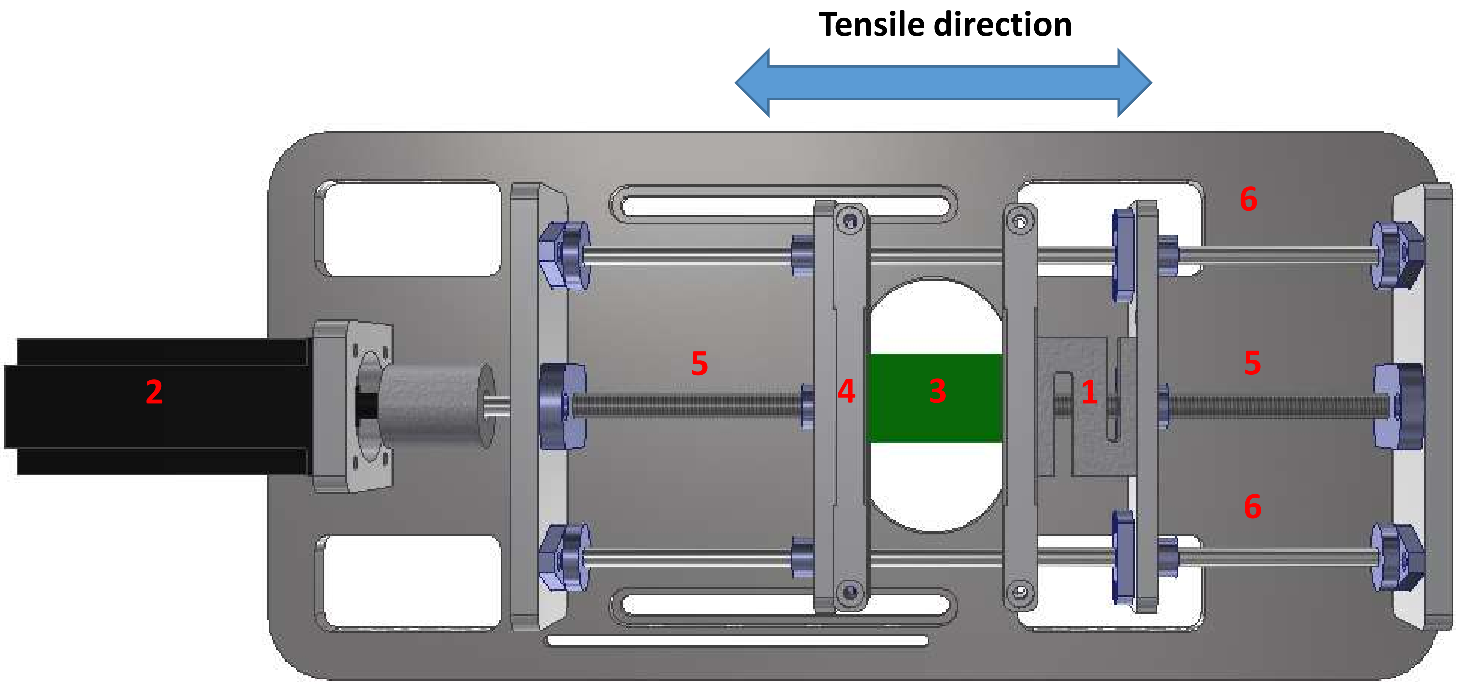
bidirectional tensile



Combination of different measurement → **constant detection position**

DWS spatial resolution limitation → **big enough sample size**

Fabrication of bidirectional tensile stage



1. Force Sensor
2. Motor
3. Sample
4. Clamps
5. Bidirectional ball screw
6. Slides shaft

Chosen sample size: 2mm x 20mm x 50mm
Calculated Strength range: 0-12.5 MPa
Moving distance: 0~150 mm
Sample width: 0~100 mm

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  On the way

Thank you!