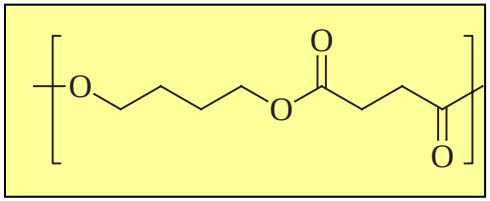
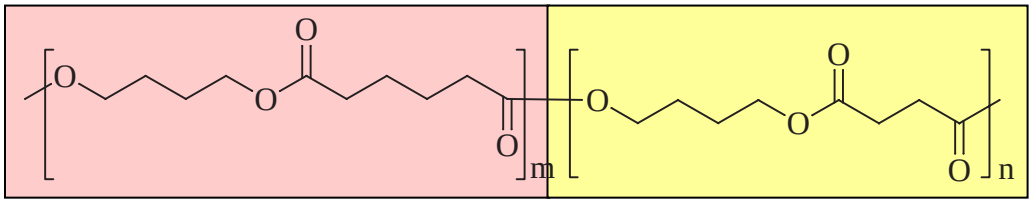
- Poly(butylene succinate) [**Bionolle 1001**] *Showa Highpolymer*

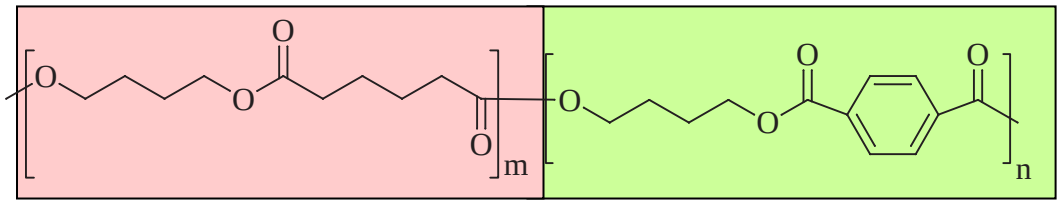


- Poly(butylene succinate-*co*-adipate) [**Bionolle 3001**] *Showa Highpolymer*



m=0.25

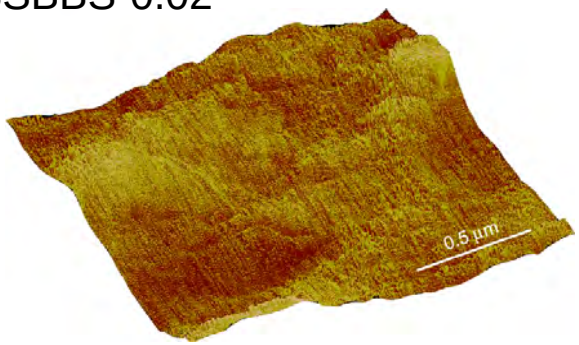
- Poly(butylene adipate-*co*-terephtalate) [**EcoFlex FBX 7011**] *BASF*

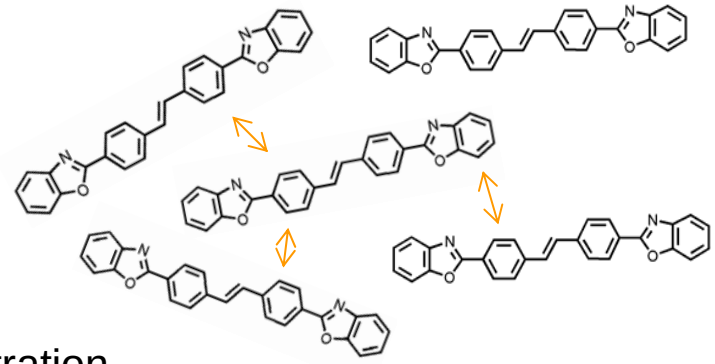


n=0.44

# Atomic force microscopy (AFM)

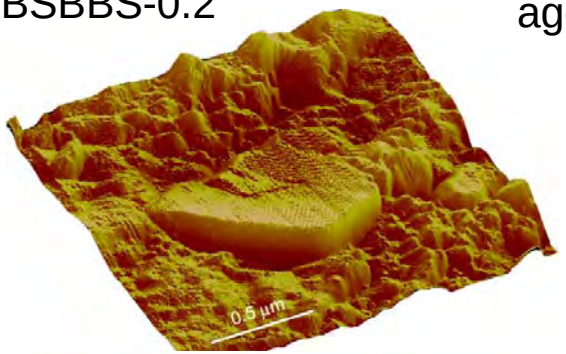
PBSBBS-0.02

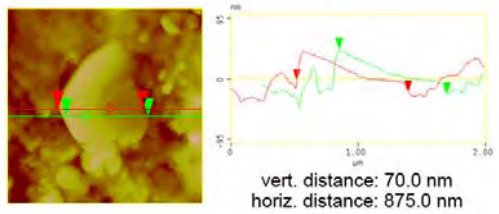


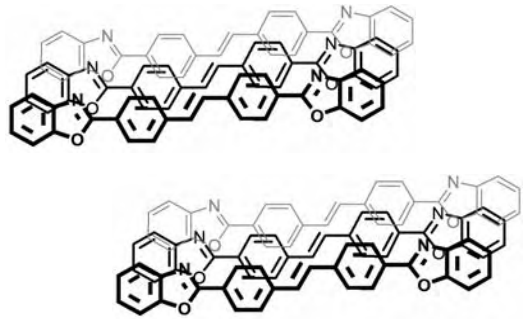



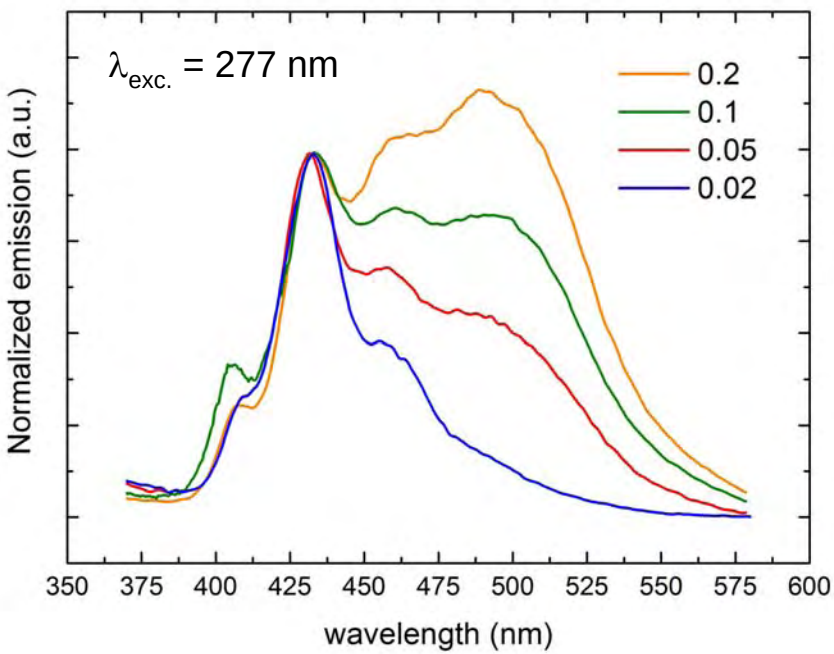
Increasing BBS concentration
aggregation π–π favoured

PBSBBS-0.2






PBSBBS-0.02: emission similar to solution. Poor red-shift.

Da 0.02 a 0.2 wt.-%: new emission in the green region (500 nm)

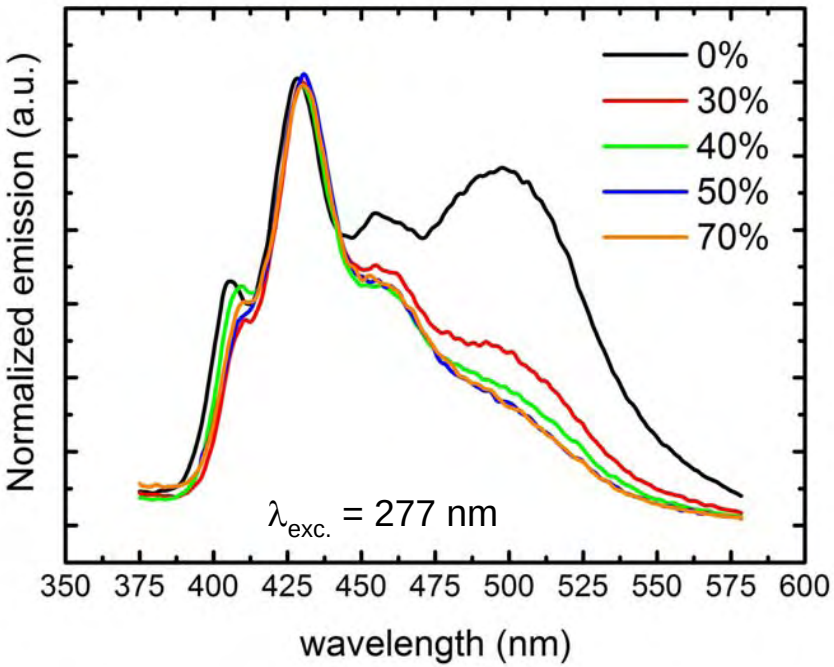
↓

formation of aggregates and/or excimers

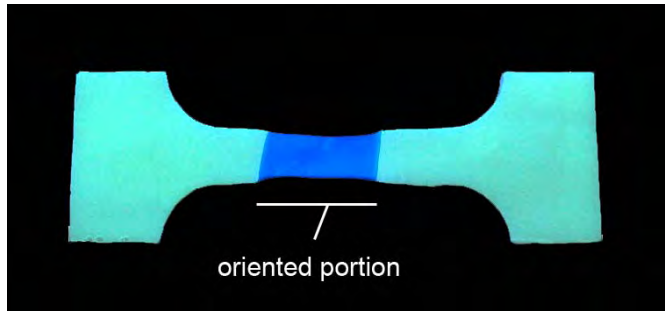
- ⇨ π–π stacking among at least 2 chromophores
- ⇨ Unstructured emission
- ⇨ Emission at lower energy

inter-planar distance = 3-4 Å

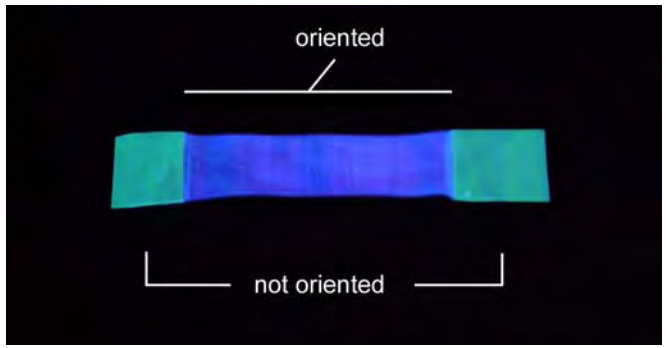
# Excimers as probes for film deformation




PP/BBS-0.5: uniaxially drawn at different strain




50%




700%

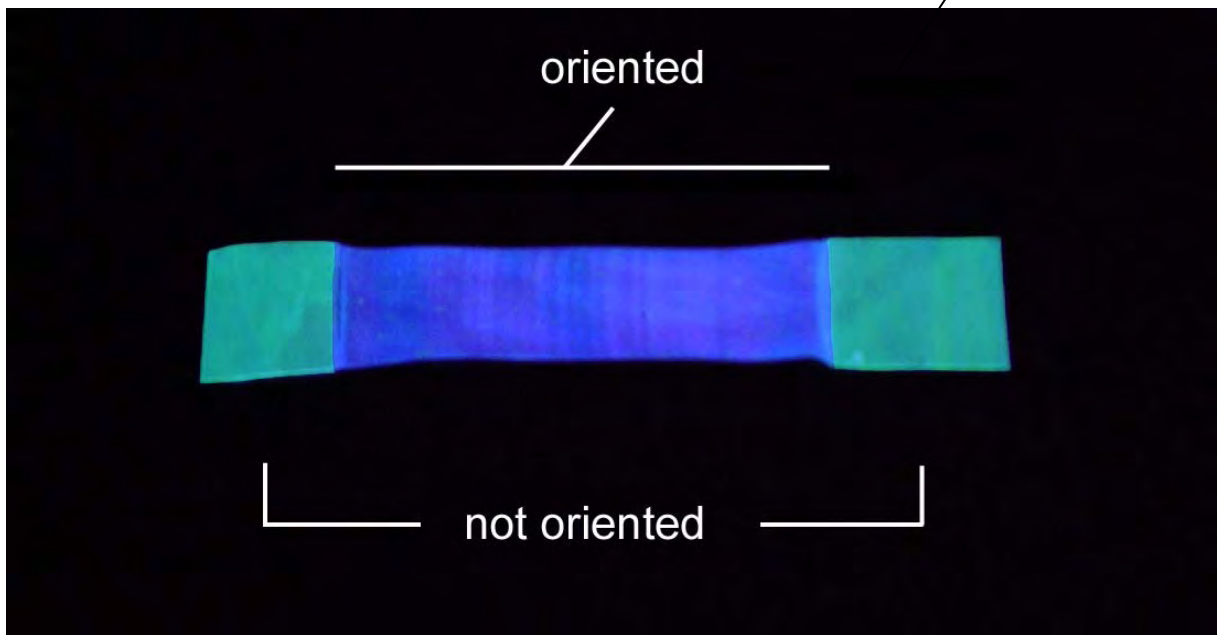
$\lambda_{exc}$ = 366 nm

- ⇨ Suppression of the excimer band
- ⇨ Emission from green to blue: **from excimer to “monomer” fluorescence**

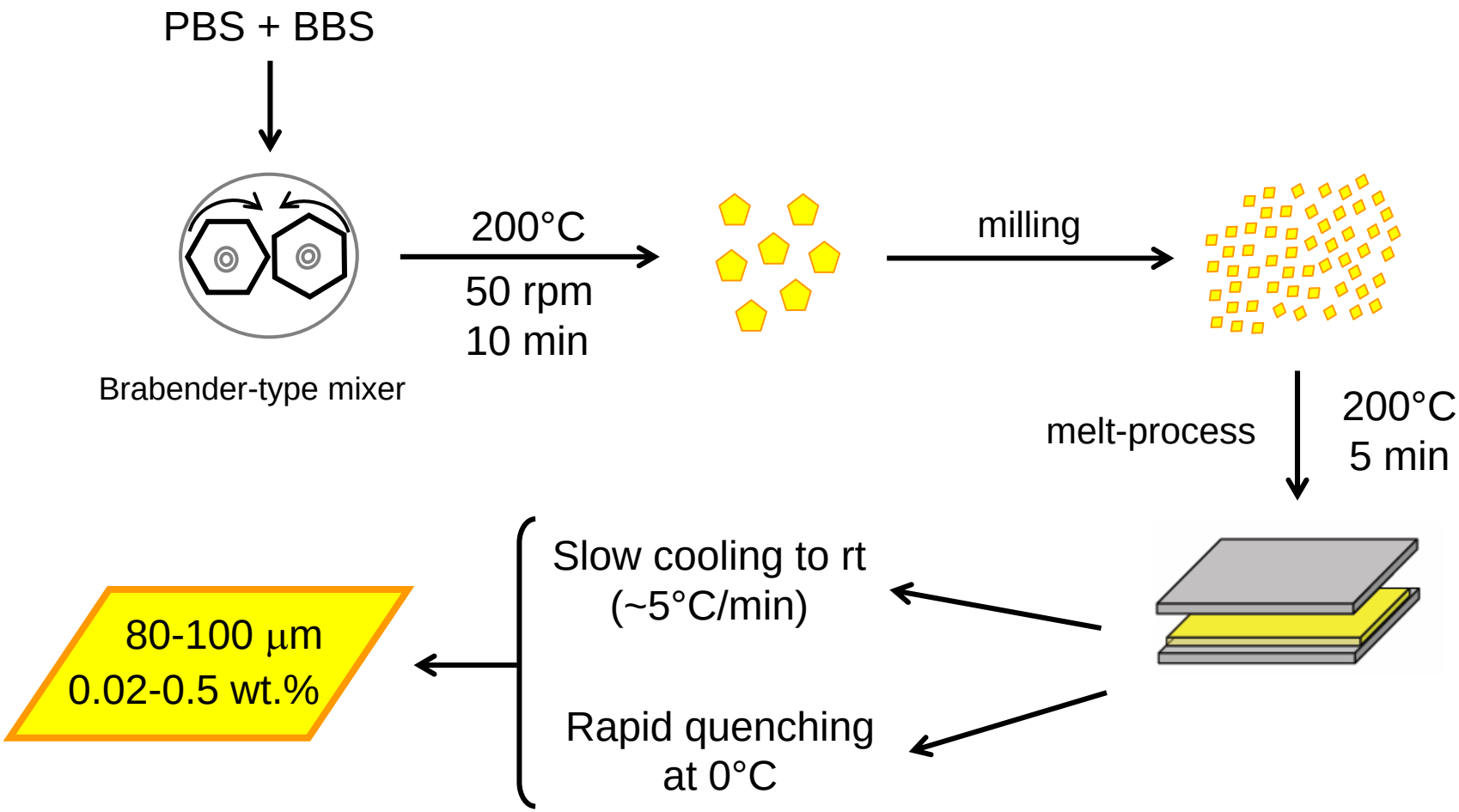
# Stilbene derivative/polypropylene: Fluorescence

Emission sensitive to drawing

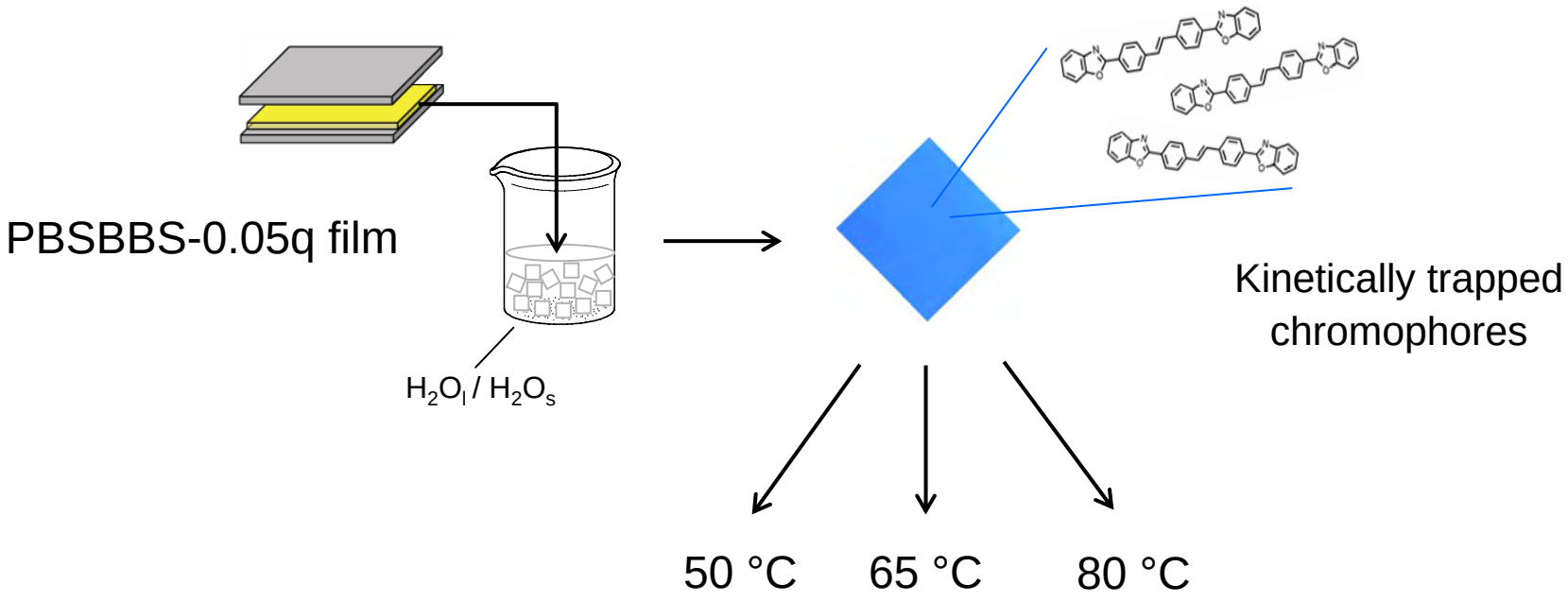
Taken under irradiation of a long-range source (366 nm)

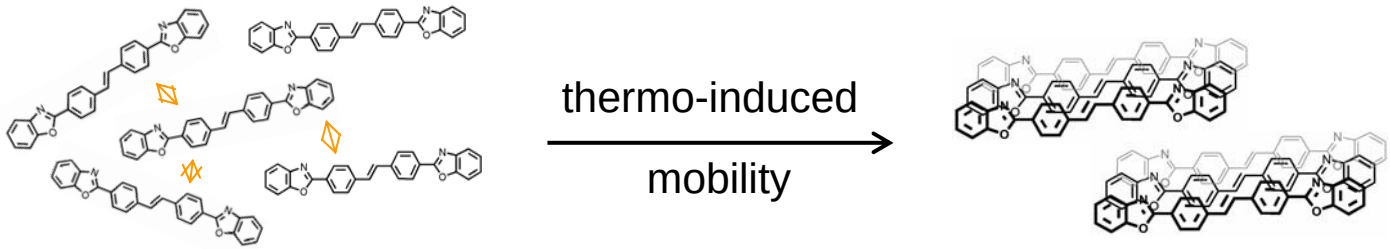



Stilbene derivative as stress-strain sensors for PP matrix: potential application for intelligent and smart polymer object in packaging materials


PBS + BBS
200°C
50 rpm
10 min
Brabender-type mixer
milling
melt-process
200°C
5 min
Slow cooling to rt
(~5°C/min)
Rapid quenching
at 0°C
80-100 µm
0.02-0.5 wt.%

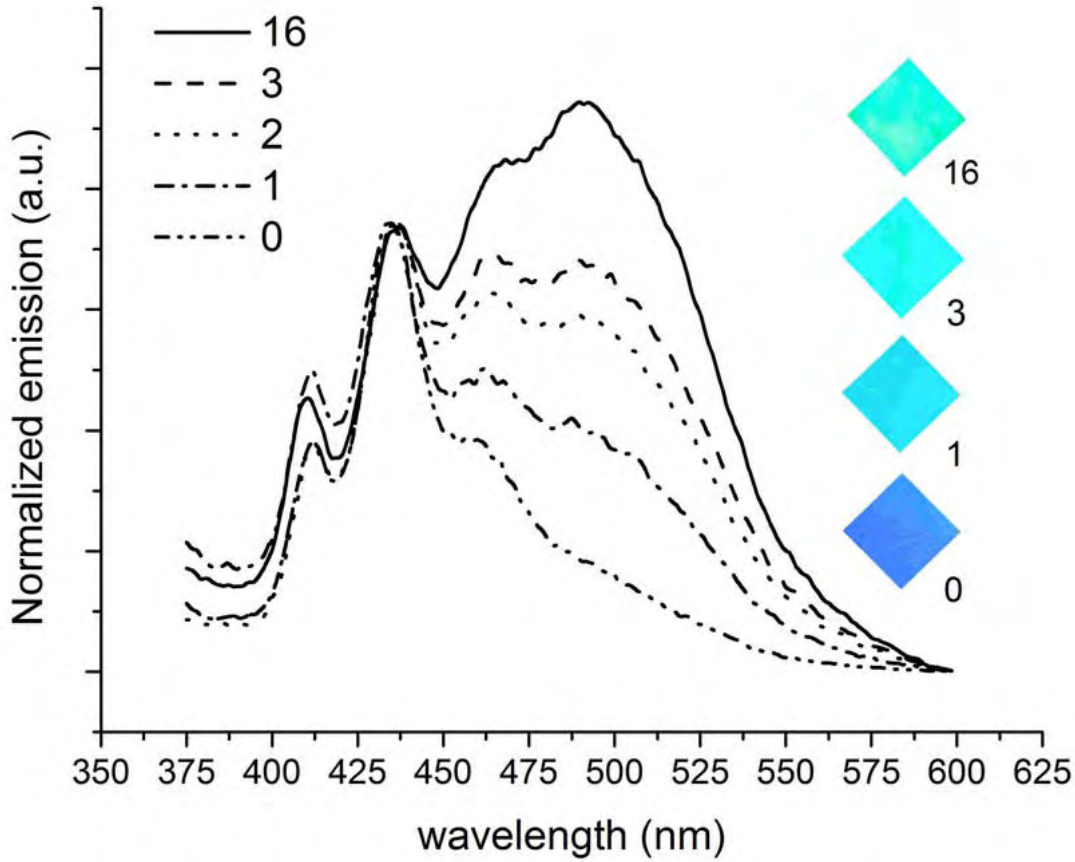
Rapid quenching at 0°C



# BBS as thermal sensors in PBS

PBSBBS-0.05q film: 65 °C



# Comments

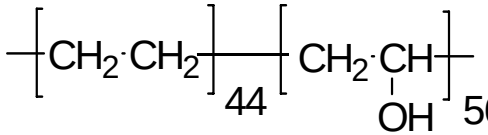
The optimized preparation procedure of PBSBBS composites allows the control of the supramolecular structure of Bis(benzoxazolyl)stilbene (BBS) dyes into Poly(1,4-butylene succinate) matrix:

Slow cooling → **Stress-strain molecular sensors**

Rapid quenching → **Thermal molecular sensors**

**Applications:** smart and intelligent packaging films starting from thermoplastic polymer matrices based on polyolefins and polyesters

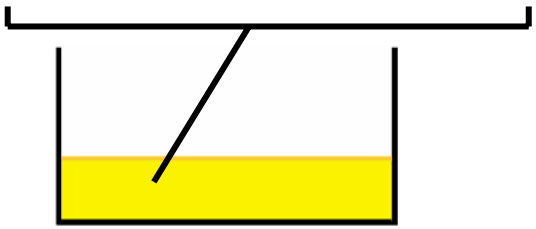
# METAL NANOPARTICLES




# : EVOH-nanoparticelle di oro

3 wt.-% $HAuCl_4$ + $H_2O$/DMSO

$HOCH_2CH_2OH_{cat}$ + EVOH

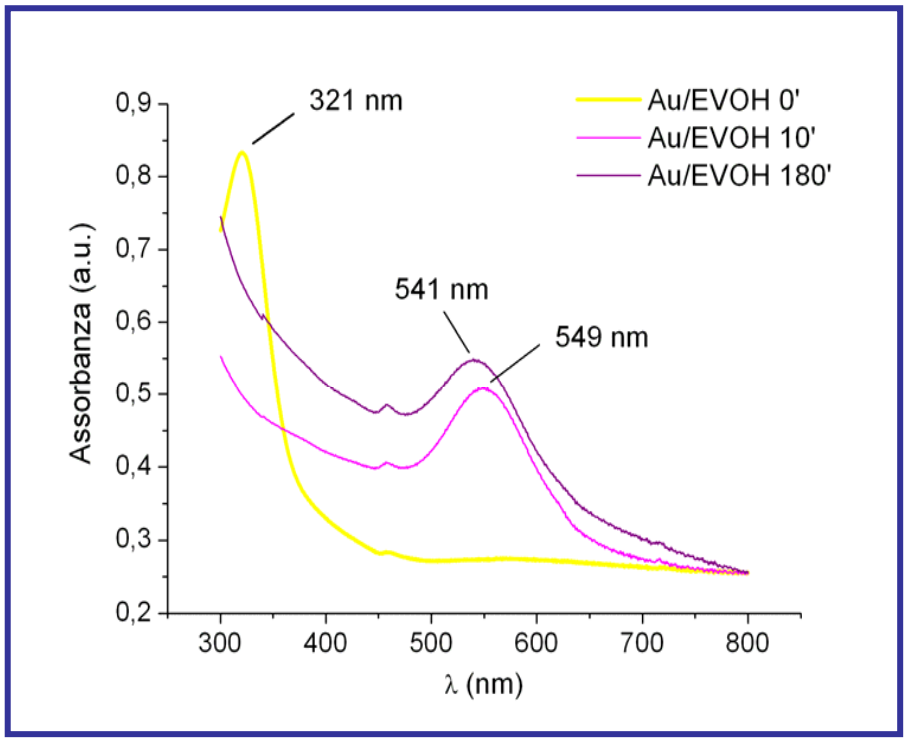


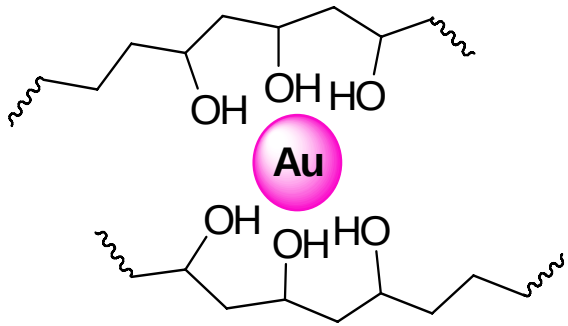
evaporazione solvente

Polymer 400 Helios Italquarz

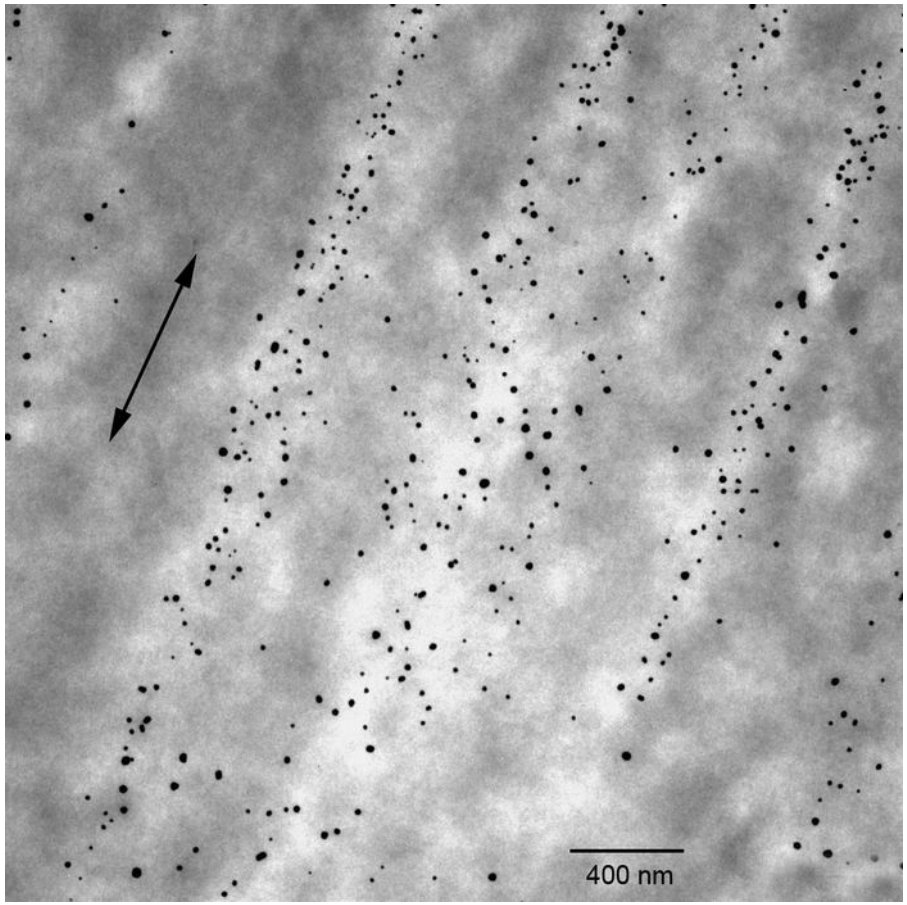
400 W (2170 mW/cm$^2$ a 365 nm)

fotoriduzione

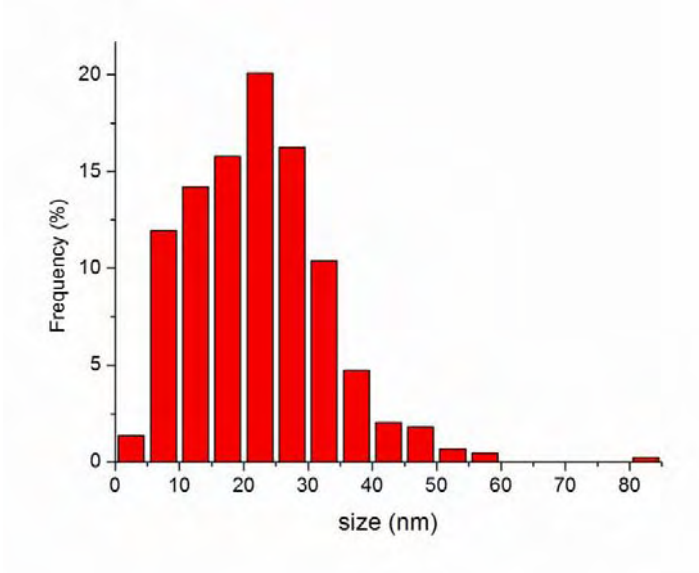


# TEM micrographs of EVOH/Au oriented nanocomposites

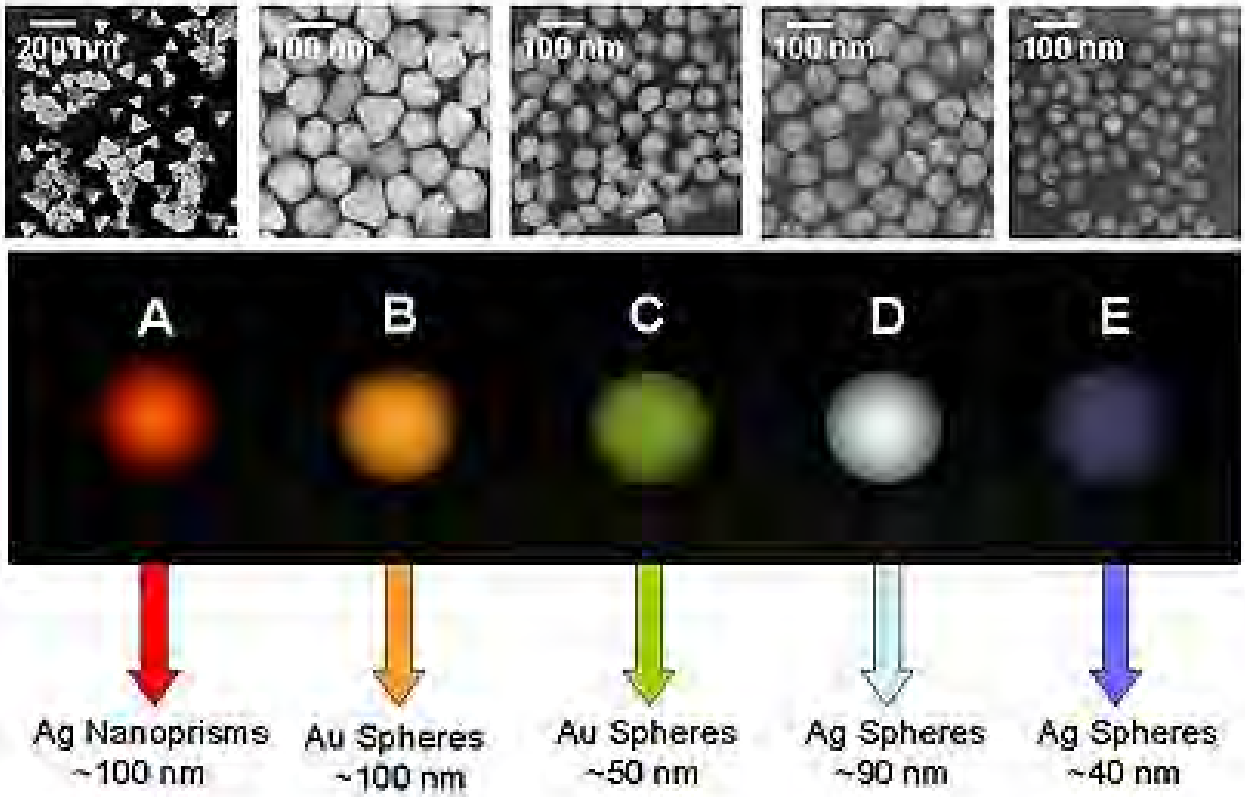



5 min of irradiation, Draw ratio = 6

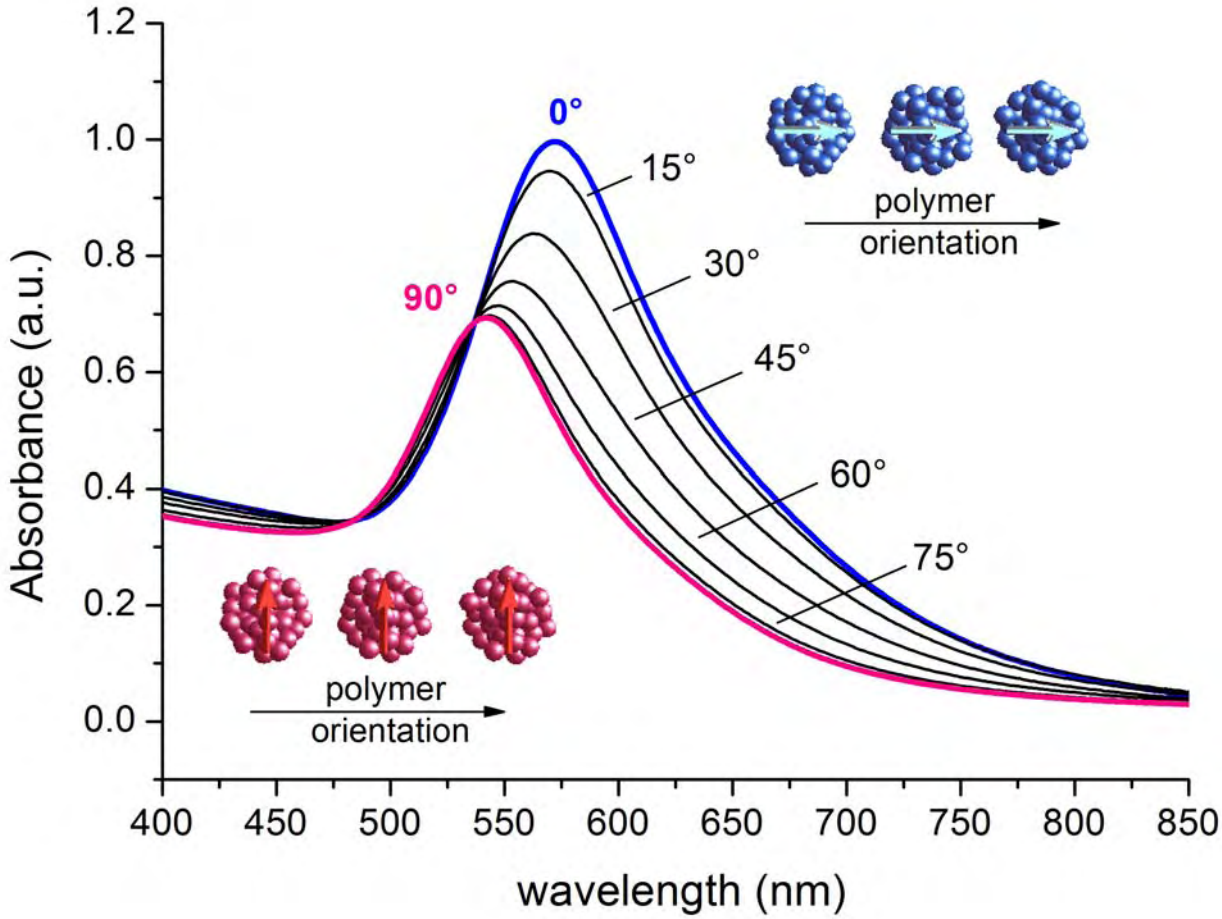



Wide distribution due to the photoreduction in the solid state

# Composition, Size, and Shape Matter

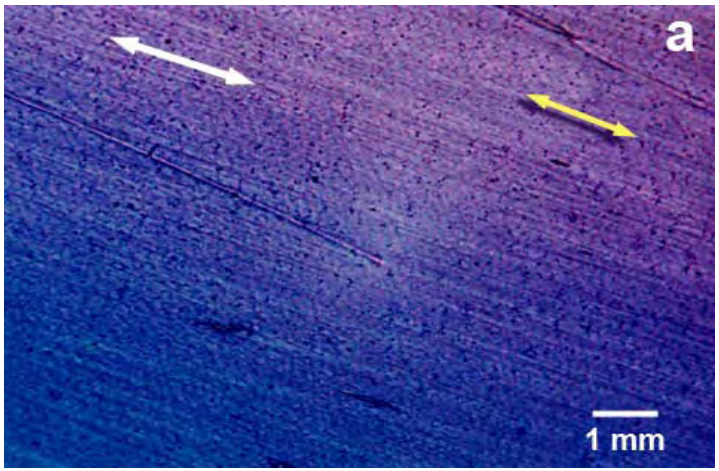


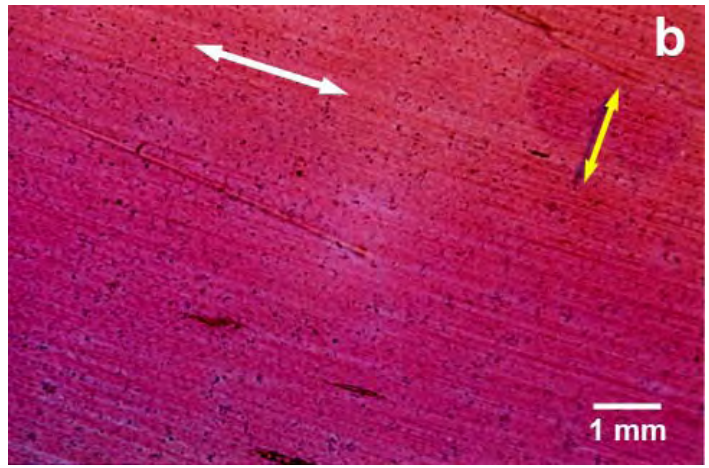
# EVOH/Au oriented films: UV-Vis in PL




Draw ratio = 6

# EVOH/Au oriented films: microscopy in PL




Draw ratio = 6

# Contributions

1. Valter Castelvetro, Francesco Ciardelli, Andrea Pucci, Giacomo Ruggeri, *Dipartimento Chimica e Chimica Industriale, Università di Pisa and PolyLab-INFM*

2. Monica Bertoldo, Simona Bronco, *PolyLab-INFM, Pisa*

3. Elisa Passaglia, *CNR-ICCOM, Firenze/Pisa*

4. Pierangelo Rolla, *Dipartimento di Fisica, Università di Pisa, and PolyLab-INFM*

5. Leonardo Andreotti, Marion Sterner, Giorgio Trani, *CIP, VEGA, Mestre*

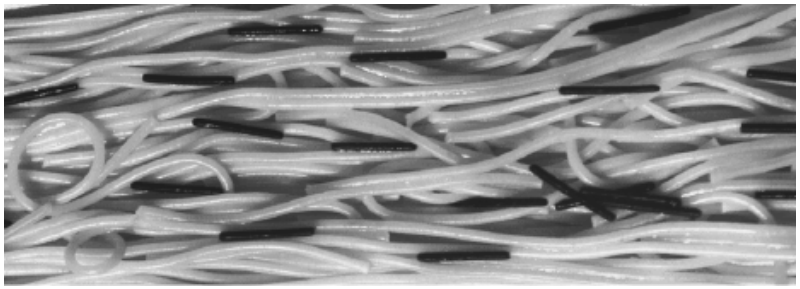
# *Grazie*

*Department of Chemistry*
*and Industrial Chemistry*
*University of Pisa*
*Italy*

nano/micro-structured dispersion of aggregates

Images from Prof. Weder homepage: http://macromolecules.case.edu/

mechanical deformation



- Thermodynamic stability
- Lower thermal stability by decreasing concentration (higher solubility)

Induced dispersion by shear stress:

- Aggregates mechanically broken
- Uniaxial orientation of the dye

P.J. Phillips, *Chem. Rev.***1990**, *90*, 425.
N.Tirelli et al., *Macromolecules* **2001**, *34*, 2129

Elongation = $(d - d_0)/d_0$

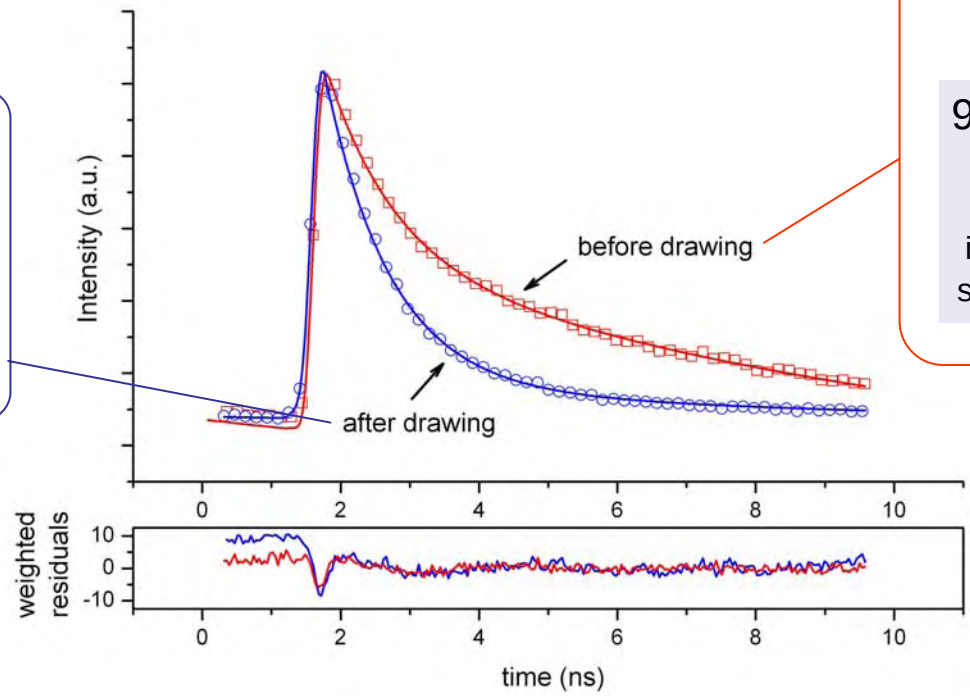
Photoluminescence decay lifetime at 500 nm

PBSBBS-0.1 film

1 component

↓

1040 ps




2 components

↙ ↘

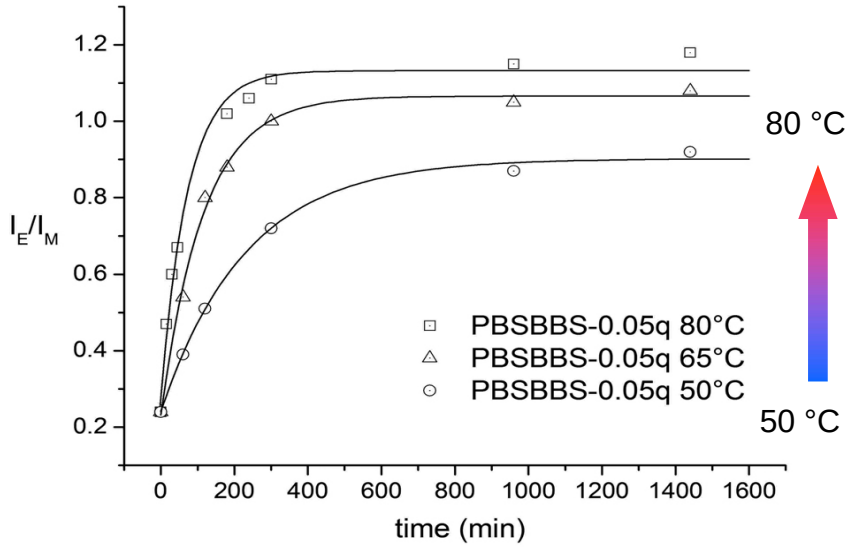
980 ps → isolated stilbenes

10430 ps → stilbenes in a rigid environment

**After deformation:** strongly reduced contribution of the long lived component

# BBS as thermal sensors

Kinetic aspects




$I_E/I_M = A + B \cdot \exp(-t/\tau)$