Optical Storage and Surface Relief Gratings in Azo-Compounds

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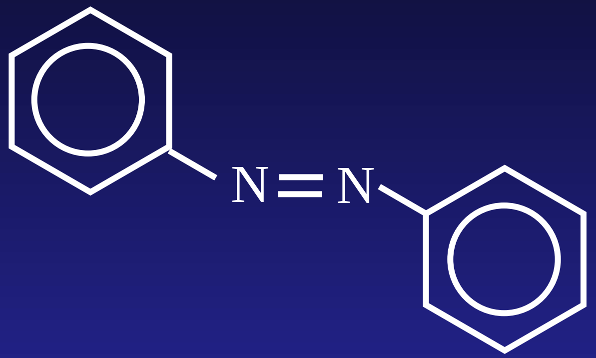
Azoaromatic compounds



- photo-isomerization

- polymers
  - guest host
  - functionalized

Motivation

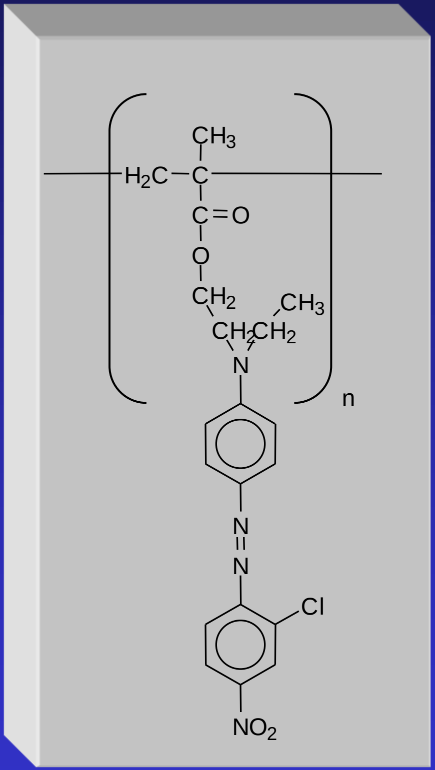
- **Optical Devices**
  - Second Harmonic Generation
  - Electro-Optic Effect
  - Optical Storage
  - Holographic Relief Gratings
  - Slow Optical Modulators

} Photo-isomerization

- **Study of the physical and chemical properties**

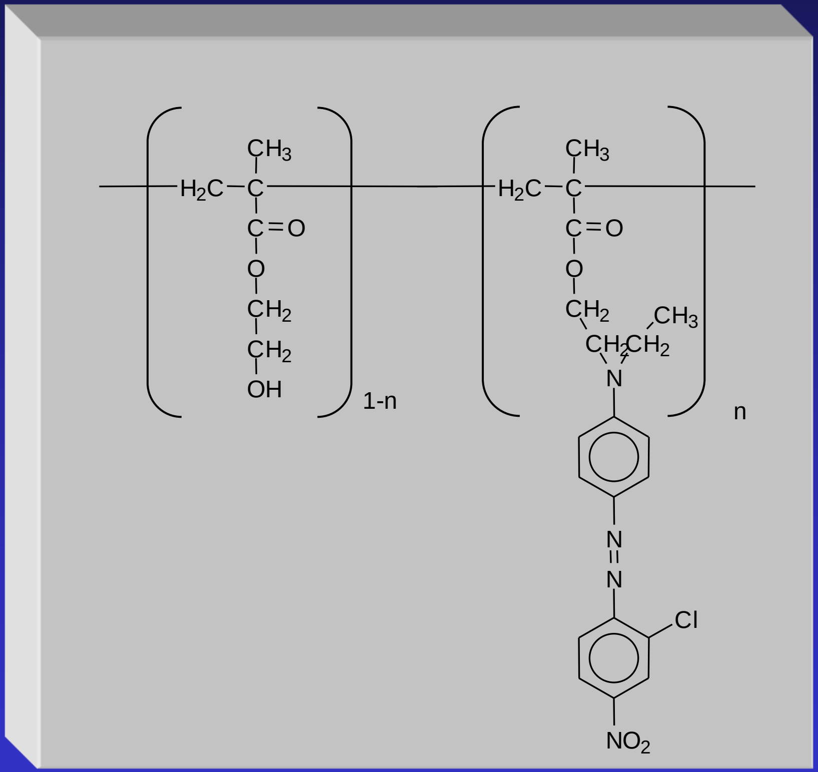
Studied materials

HPDR13

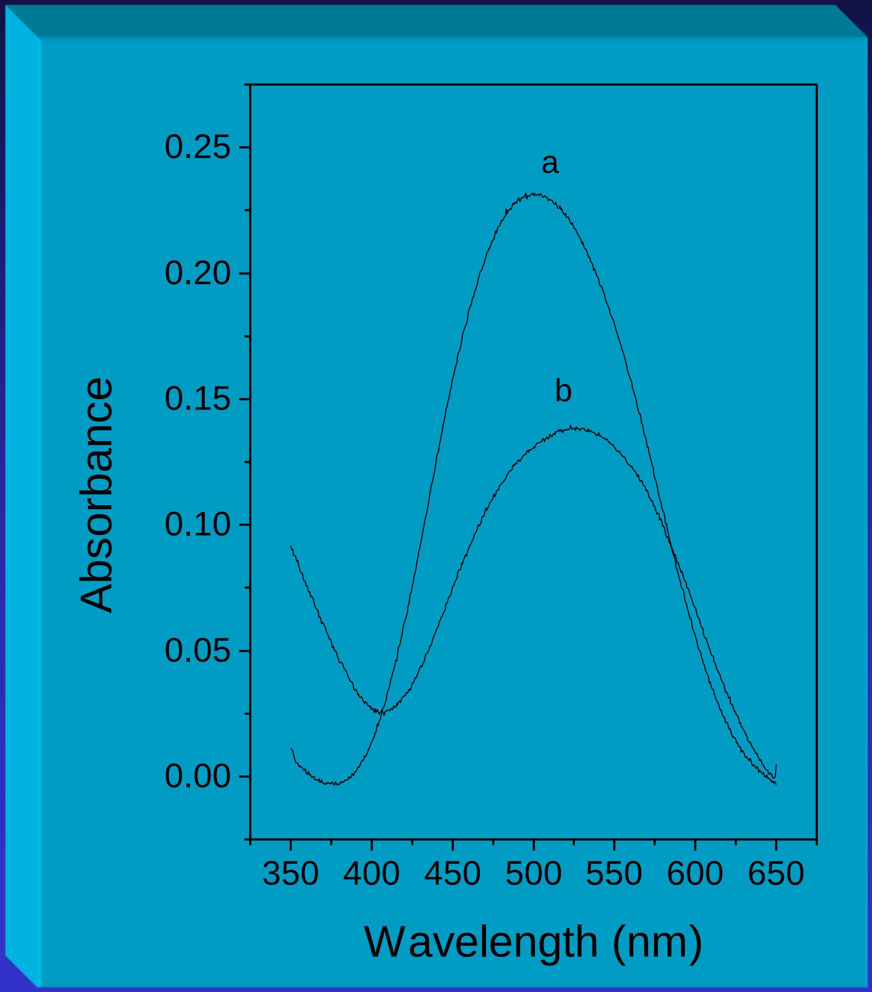


LB films

DR13 Copolymers



Absorption spectra HPDR13

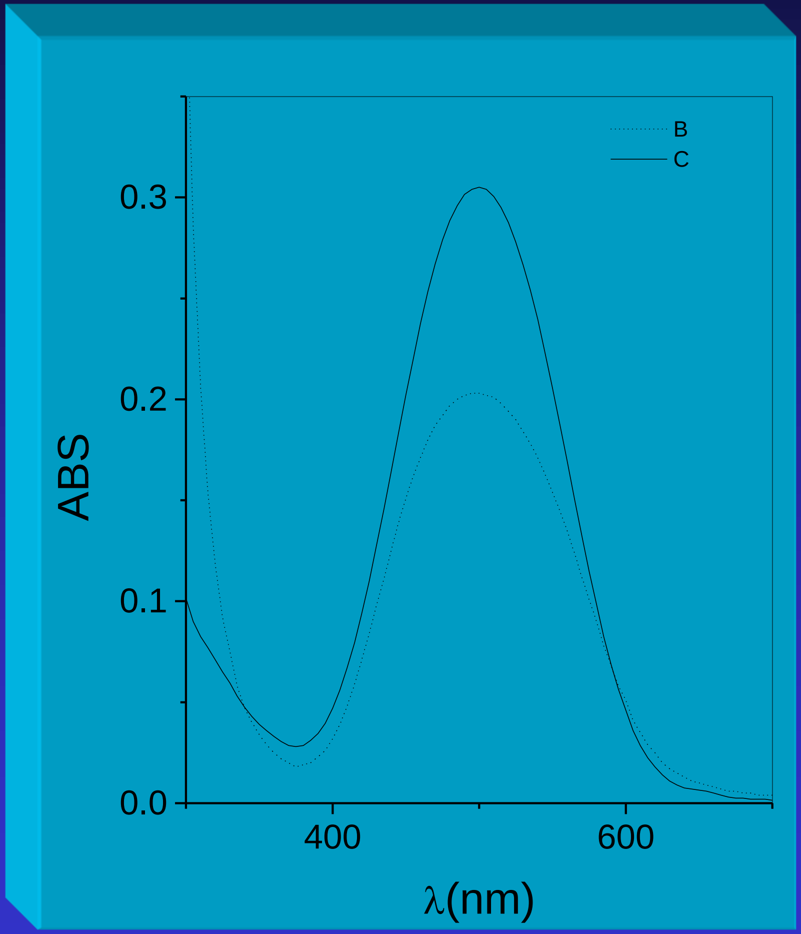


Absorption around 500nm

(a) $CHCl_3$ Solution
(b) LB film

Red Shift: J-type aggregation anti-parallel aggregation.

Absorption spectra DR13 copolymer



Absorption around 500nm

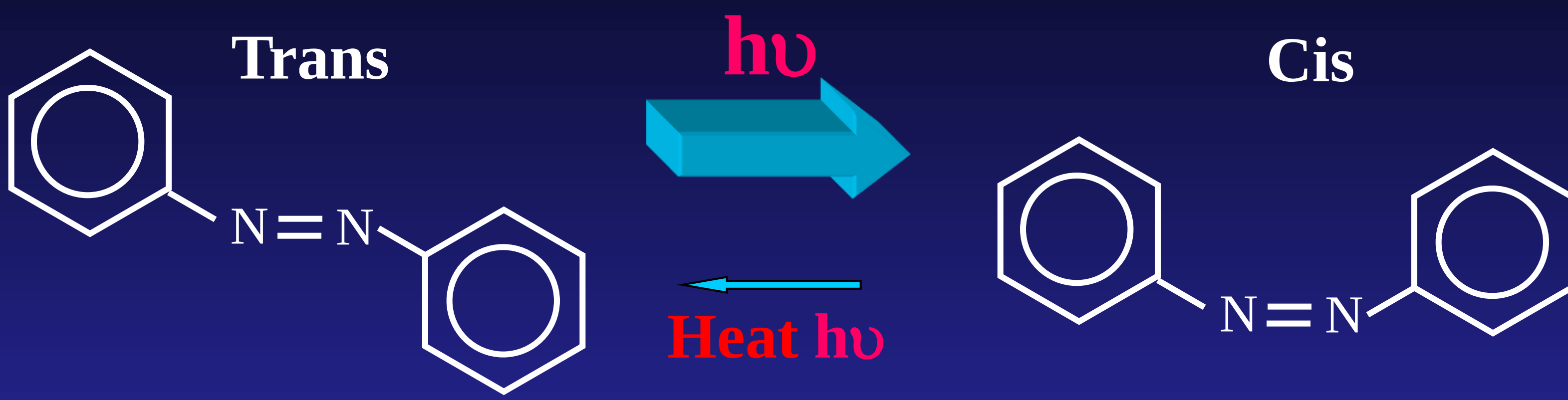
J-type aggregation

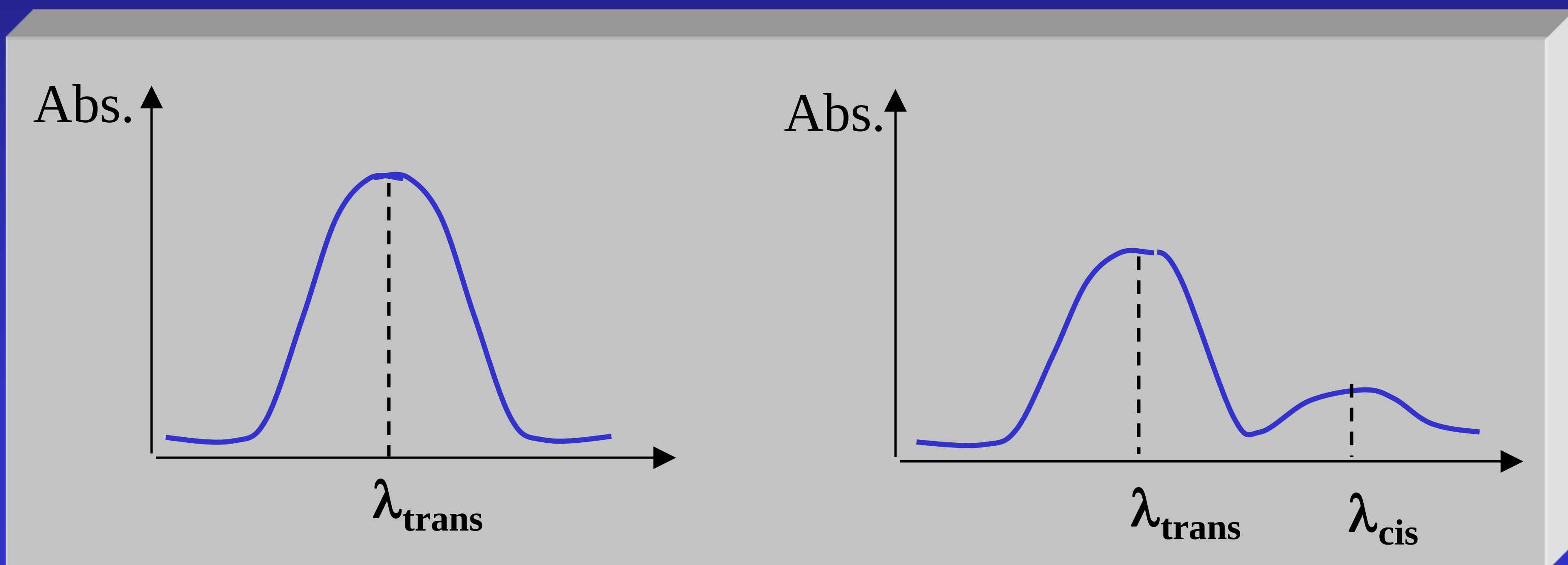
(B) $CHCl_3$ Solution
(C) LB film

Studied properties

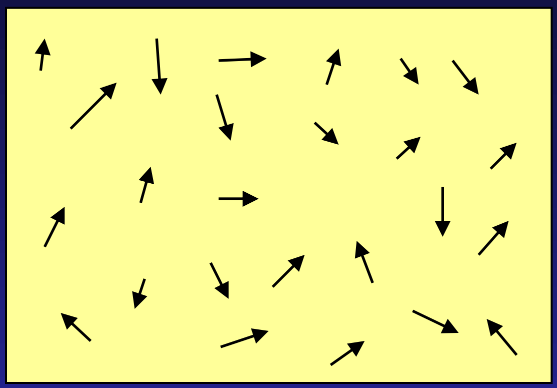
- Trans-Cis-Trans Photisomerization
- Optical Storage
- Holographic Relief Gratings

Photo-isomerization

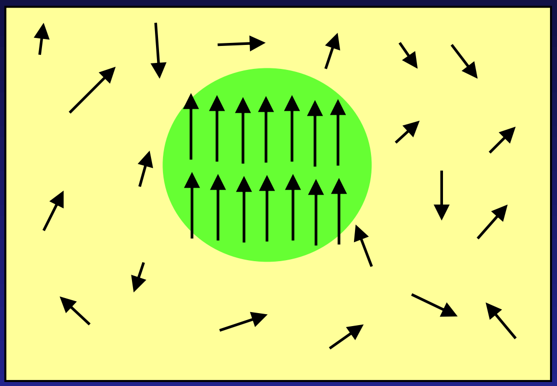




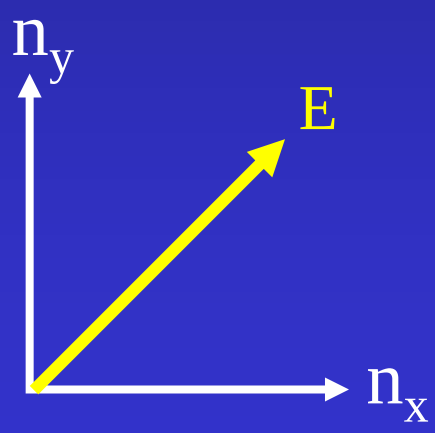
Birefringence and Dichroism



Isotropic Sample



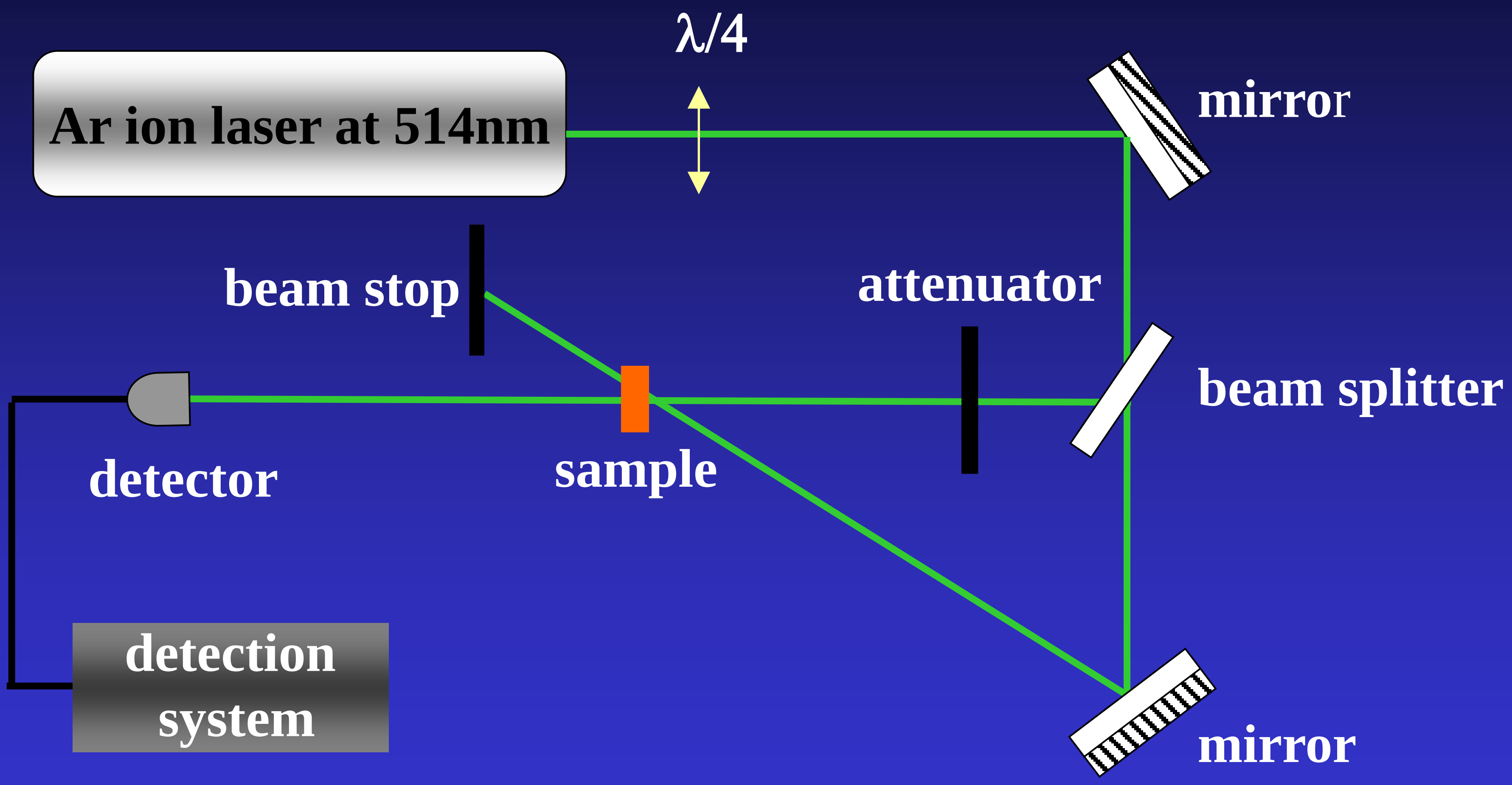
Anisotropic Sample



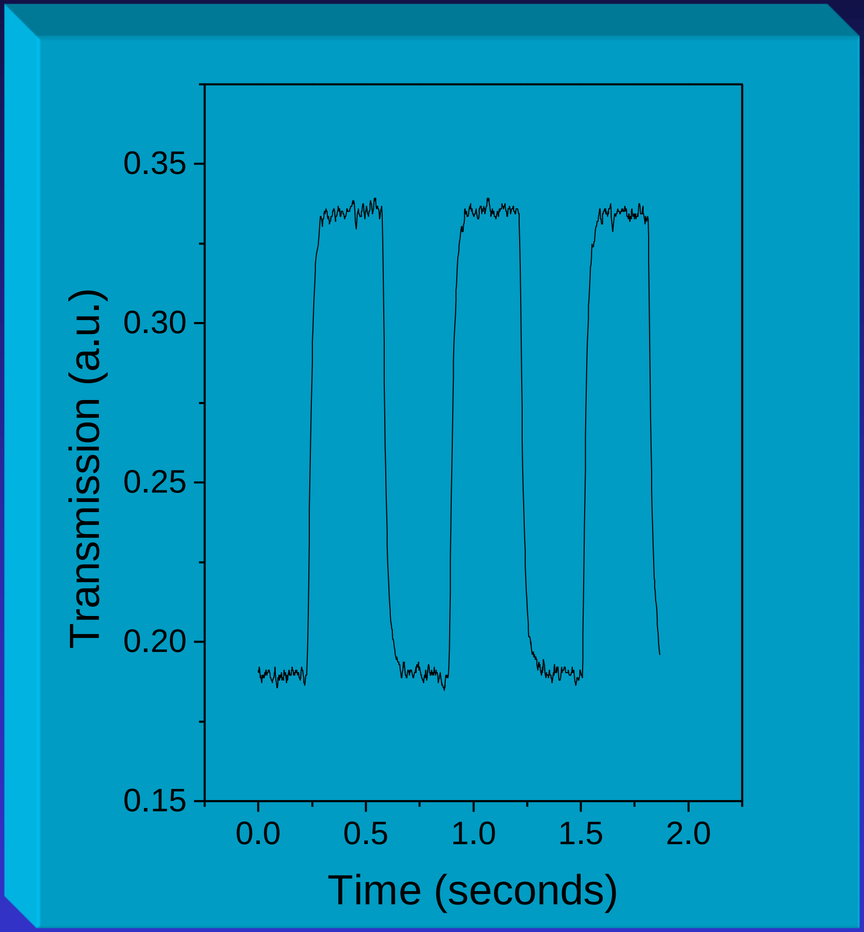
Linearly

Elipticaly

Experimental Setup



HPDR13 Results



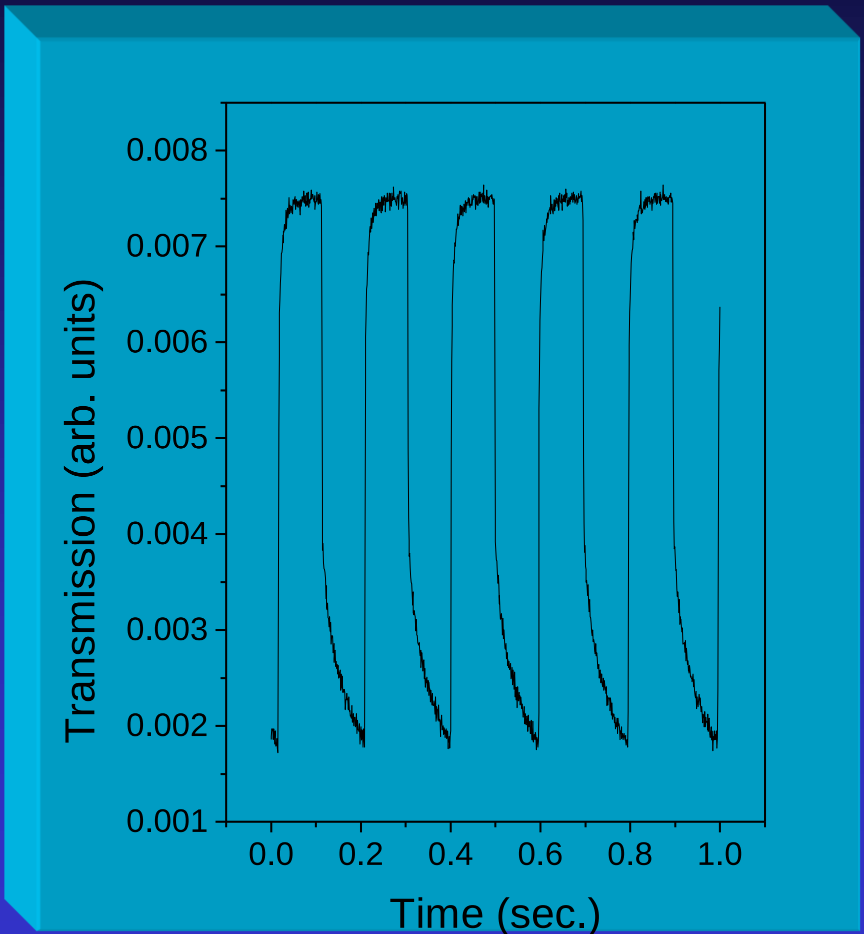
HPDR13 in $CHCl_3$ Solution

P=80mW

trans-cis: 30ms

cis-trans: 18ms

HPDR13 Results



LB film:

HPDR13 and Cd St

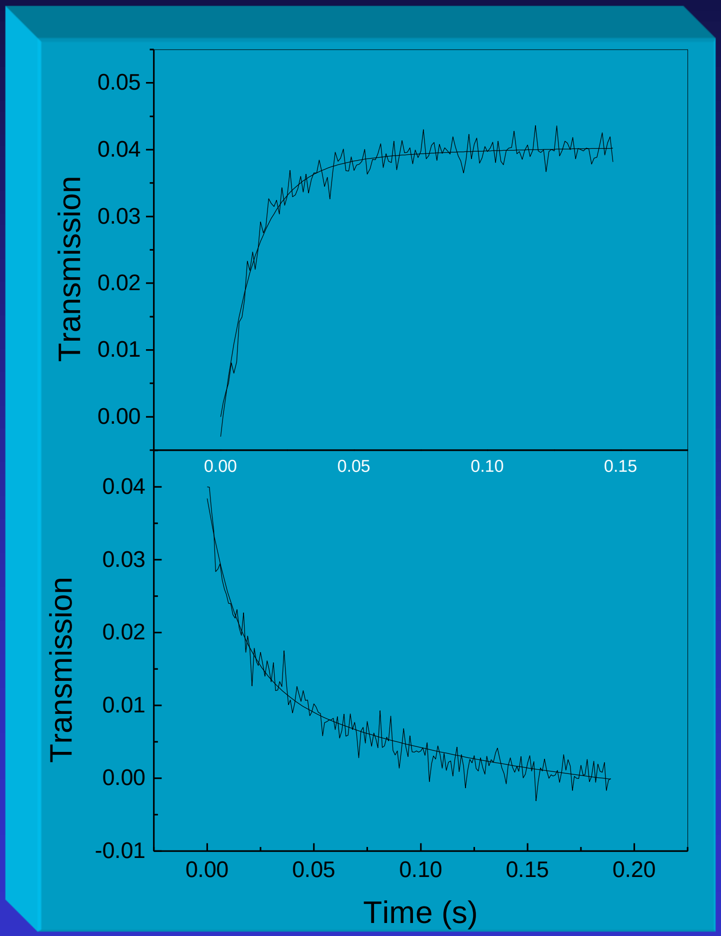
(75:25 w/w, 41 layers)

P=60mW

trans-cis: 30ms

cis-trans: slower

DR13 copolymer results



(trans-cis) Photoisomerization

biexponential behavior

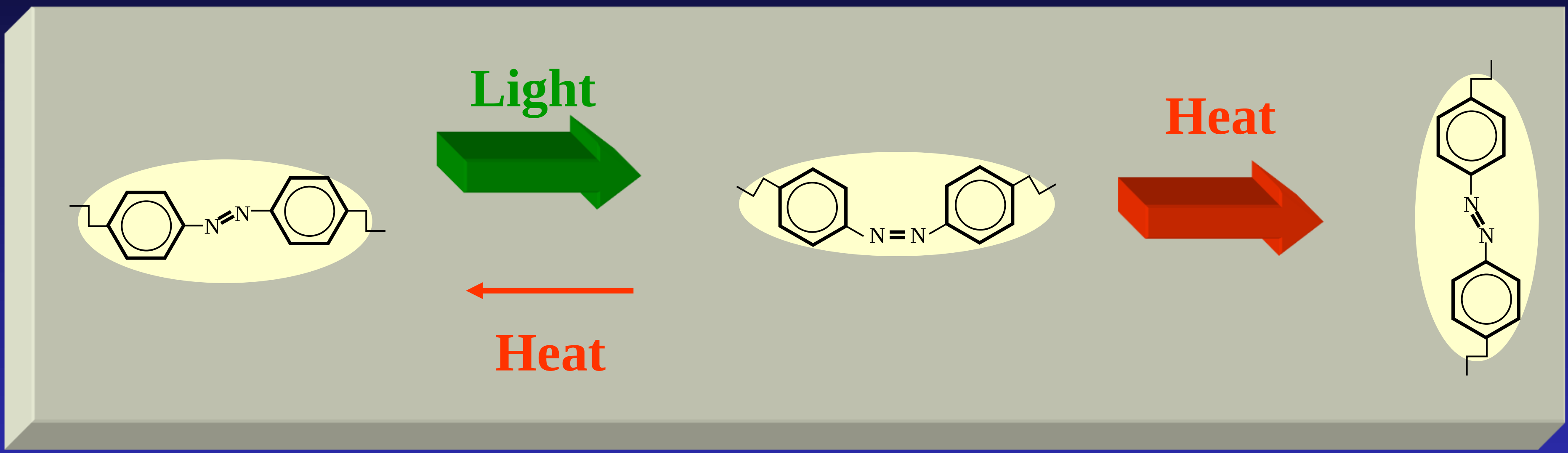
$t_{fast} \approx 20ms$

(*cis-trans*) Thermal relaxation

biexponential behavior

Orientation mechanism

Photochemical trans-cis rate: $R = I\cos^2(\phi)$



E_{Light}

P_{dye}

$\phi = 0^0$

P_{dye}

E_{Light}

$\phi = 90^0$

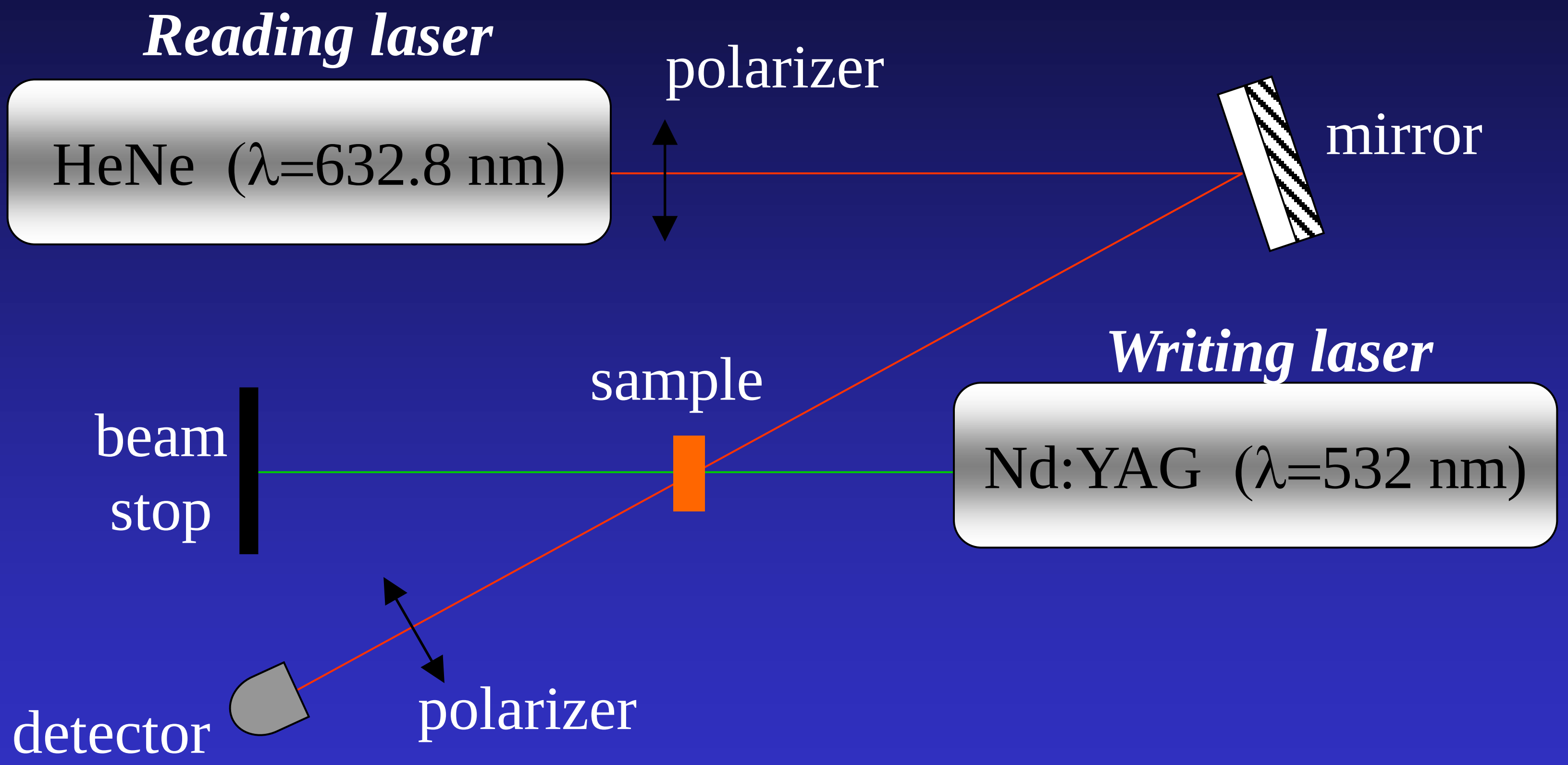
R=I

R=0

Induces mobility

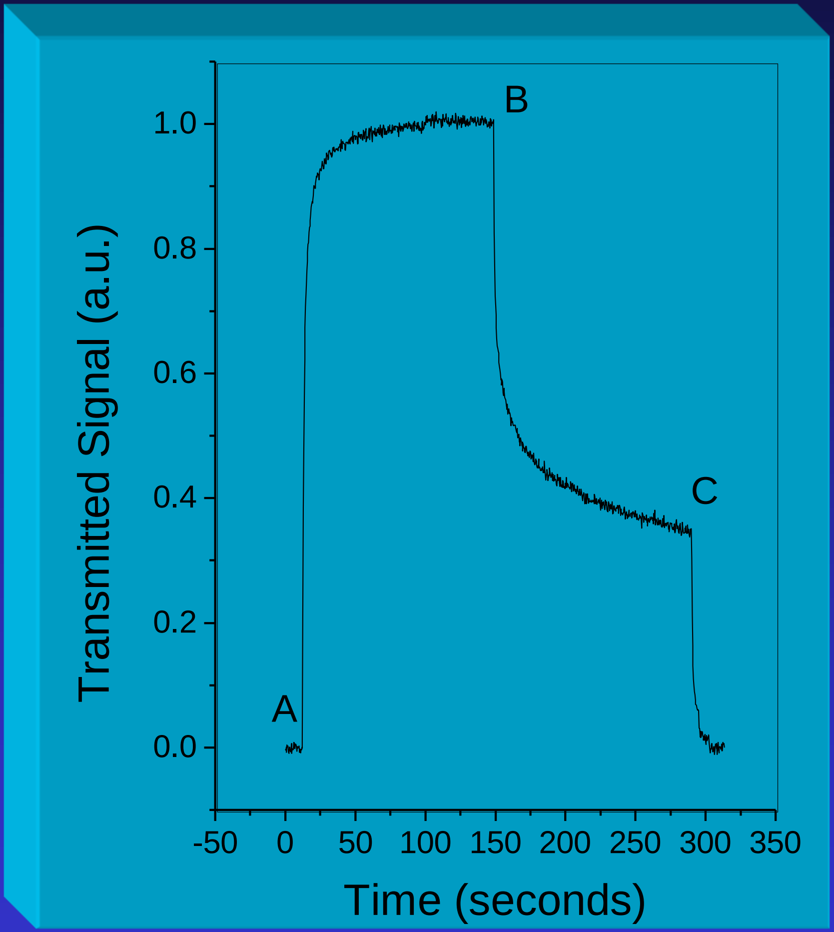
Mobility not induced

Experimental setup



$$\Delta n = \frac{\lambda}{\pi d} \sin^{-1} \sqrt{\frac{I}{I_0}}$$

HPDR13 results



writing/erasing sequence

LB film:

HPDR13 and Cd St

(50:50 w/w, 100 layers)

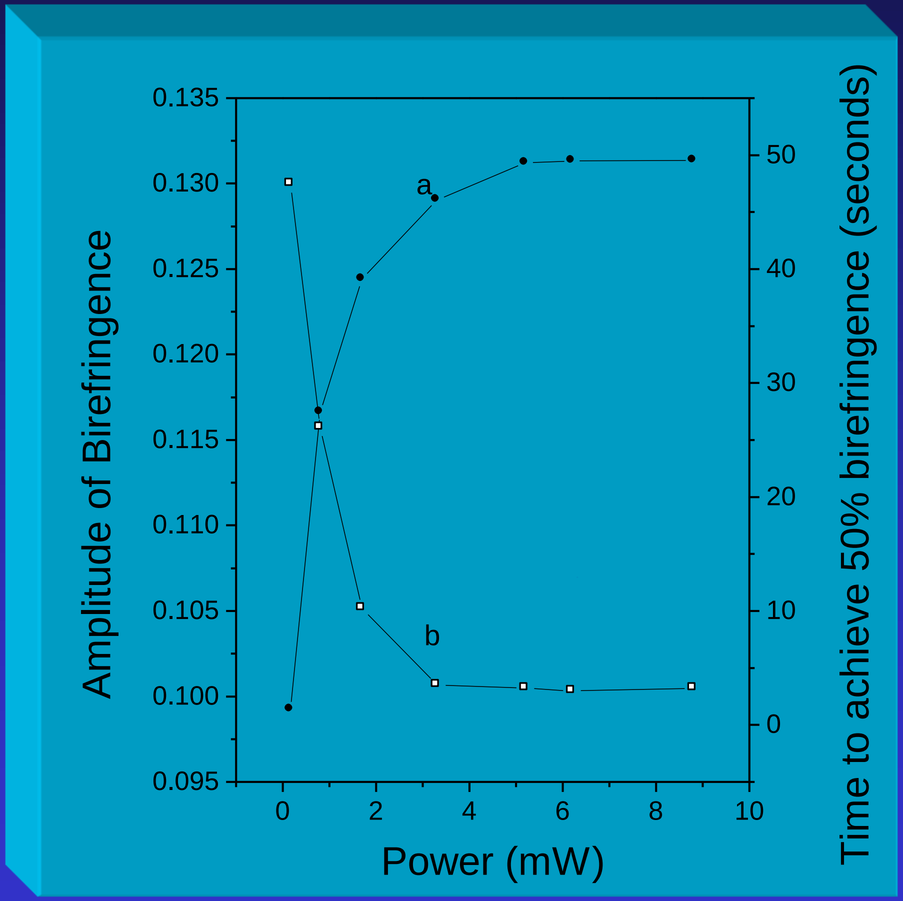
A: writing beam switched ON

B: writing beam switched OFF

C: erasing beam switched ON

HPDR13 results

Dependence of Optical Storage Characteristics on the laser Power



LB film:

HPDR13 and Cd St

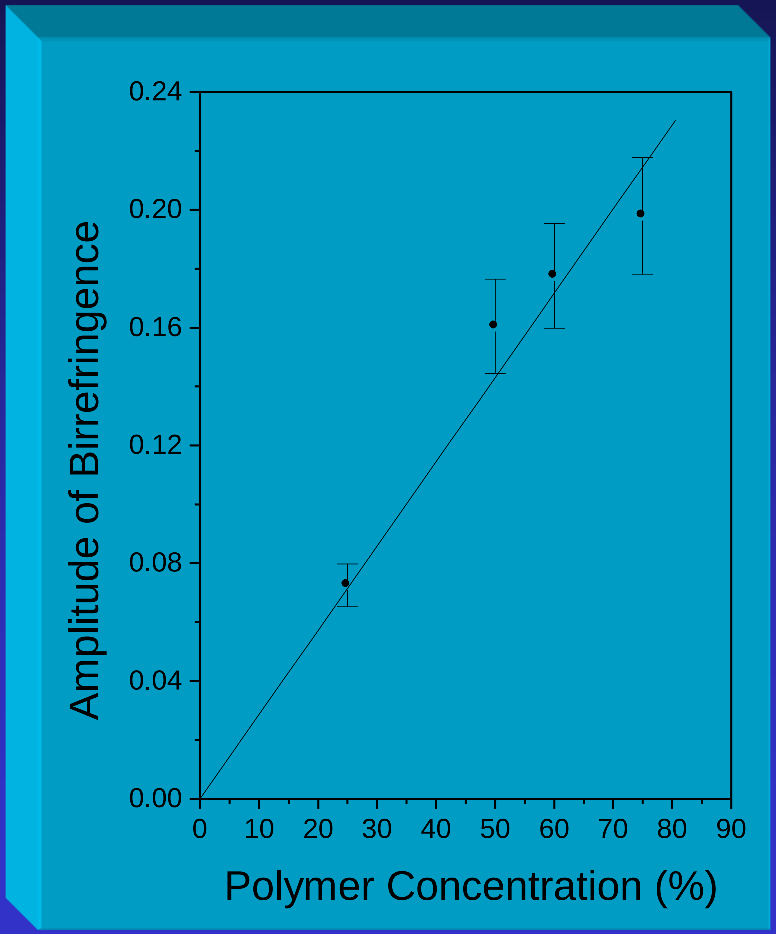
(50:50 w/w, 100 layers)

a: Amplitude of Optical Storage Saturation Behavior (2mW)

b: Time to write 50% decrease dramatically (2mW)

HPDR13 results

Dependence of the amplitude on the weight percentage of HPDR13



LB film:

HPDR13 and Cd St

(41 layers)

a: Amplitude of birefringence increases linearly with the weight percentage of HPDR13

HPDR13 results

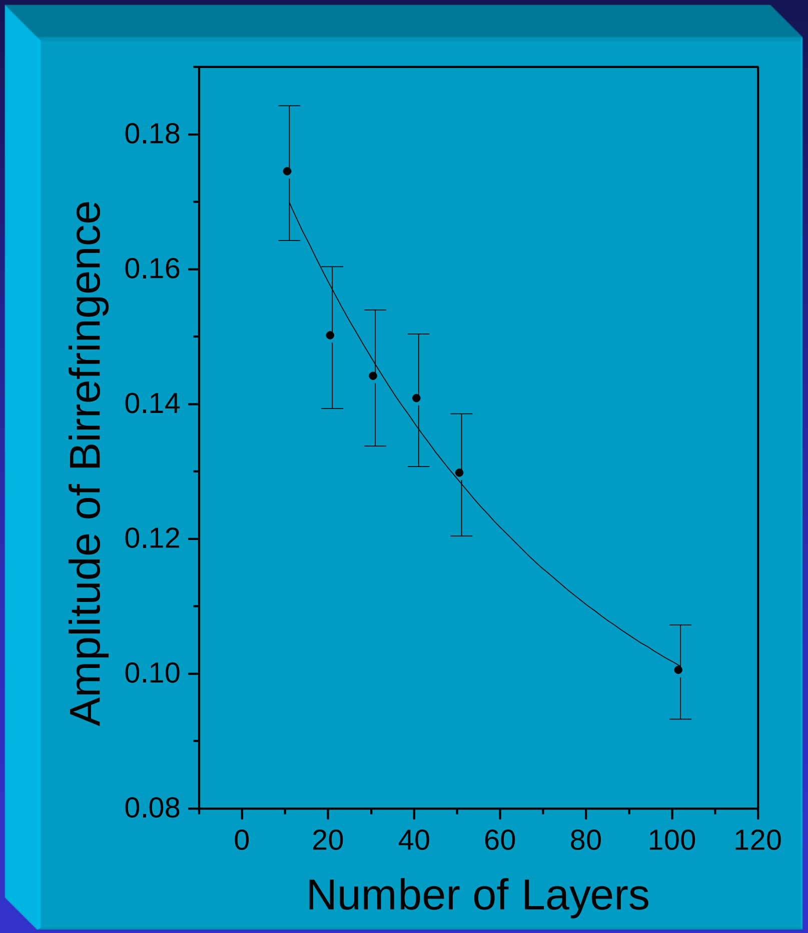
Comparison with casting/spin coating films

LB film	Spin coating
HPDR13 and Cd St	PDR13a
41 layers 75% of HPDR13	(similar to ourpolymer)
$\Delta n=0.19$	$\Delta n=0.08$

Ordering in the packing contributes to the optical induced birefringence

HPDR13 Results

Dependence of the amplitude on the number of layers



LB film:

HPDR13 and Cd St

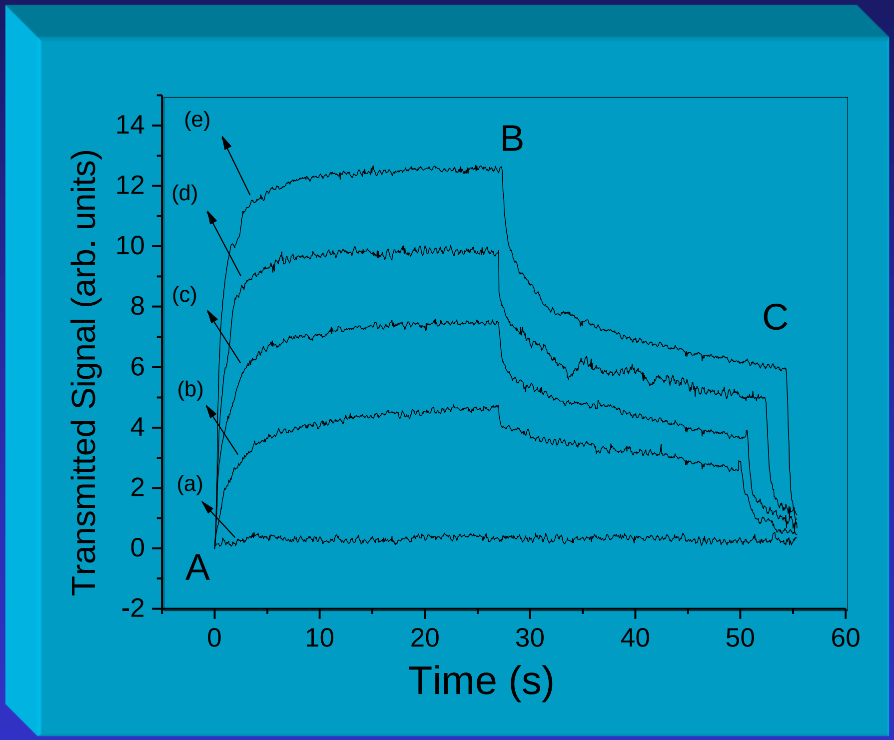
(50:50 w/w)

The maximum birefringence decreases with the number of layers

Related to the decrease in the ordering in the LB film

DR13 copolymer results

writing/erasing sequence

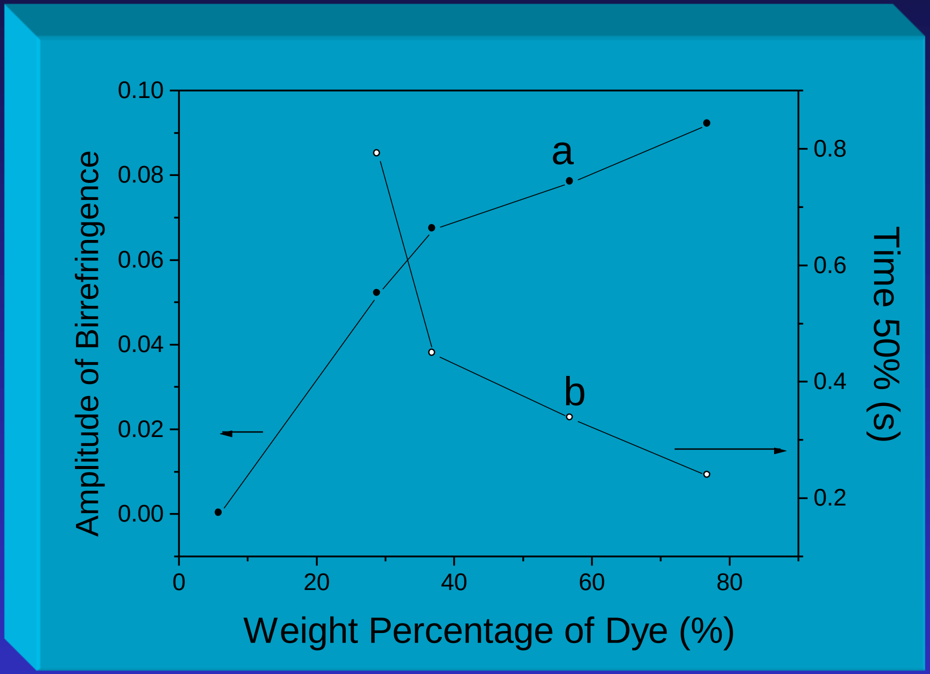


Copolymer LB films (15 layers) with different dye contents. (weight percentage)

(a) CoDR6 : 6% DR13
(b) CoDR29 : 29% DR13
(c) CoDR37 : 37% DR13
(d) CoDR57 : 57% DR13
(e) CoDR77 : 77% DR13

DR13 copolymer results

Dependence of the amplitude on the DR13 weight percentage



a: Amplitude of Optical Storage :
nonlinear behavior
- thermal effect

b: Time to write 50%
decrease almost exponentially
- cooperative effect

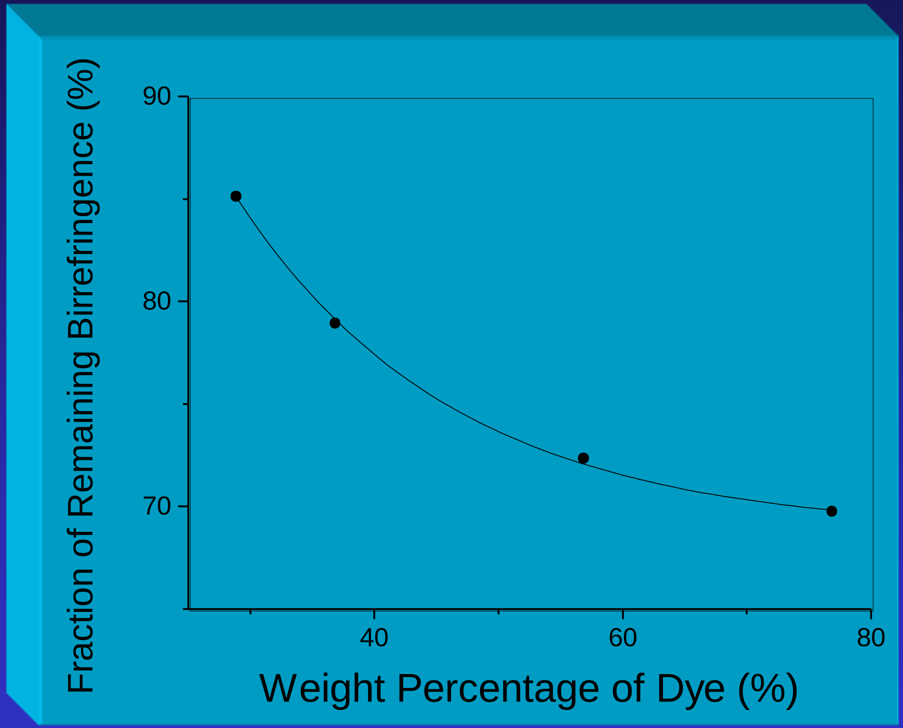
Thermal Effect

X

Cooperative Effect

DR13 copolymer results

Remaining birefringence as a function of DR13 weight percentage

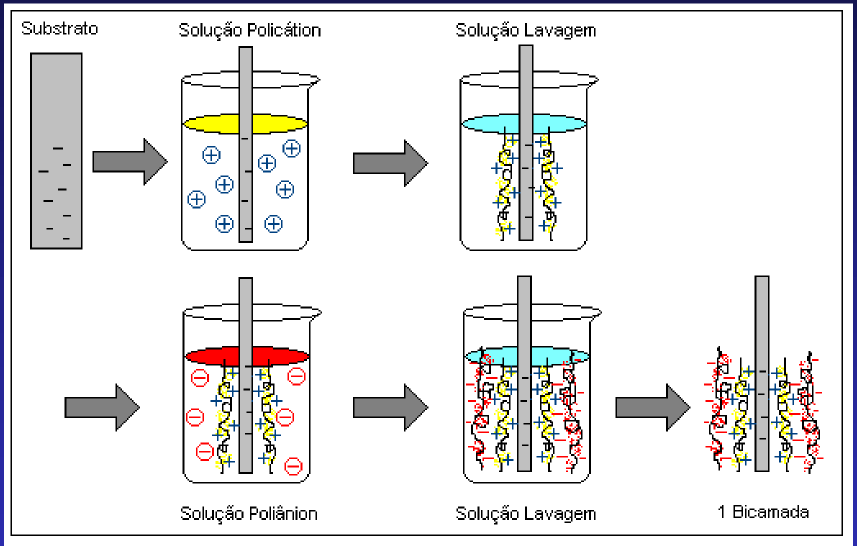


Exponential decay with the dye content:

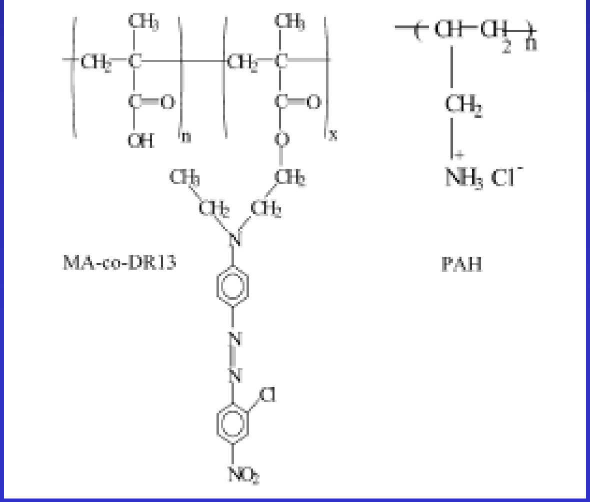
- cooperative motion

Optical storage in LBL

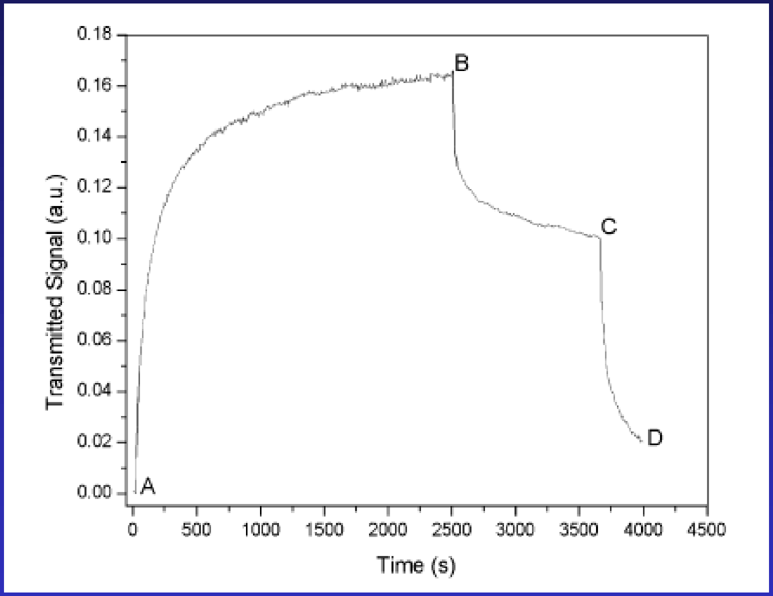
Layer-by-layer (LBL)



40 bilayers films



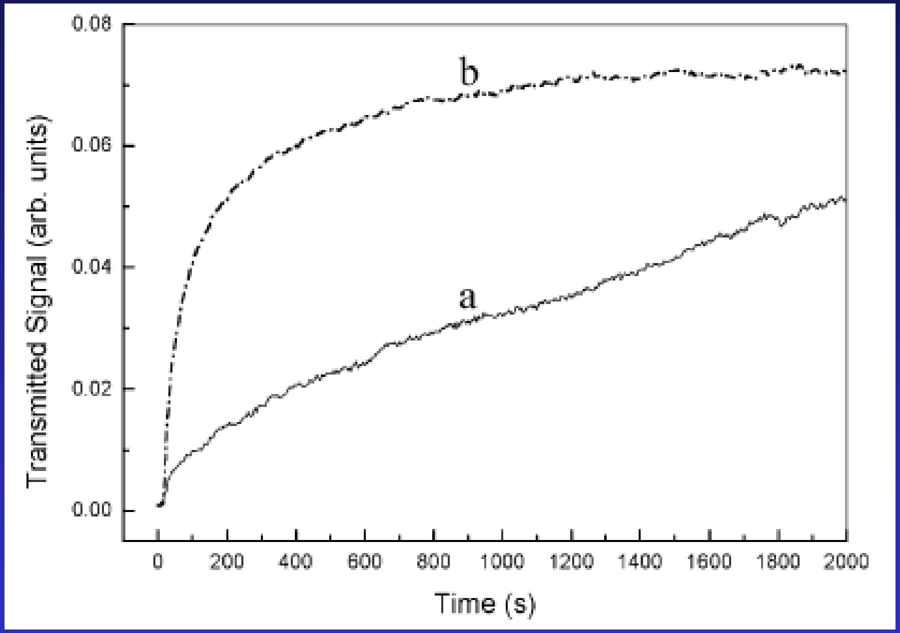
Optical storage in LBL



slower process

electrostatic interaction hampers molecular movement

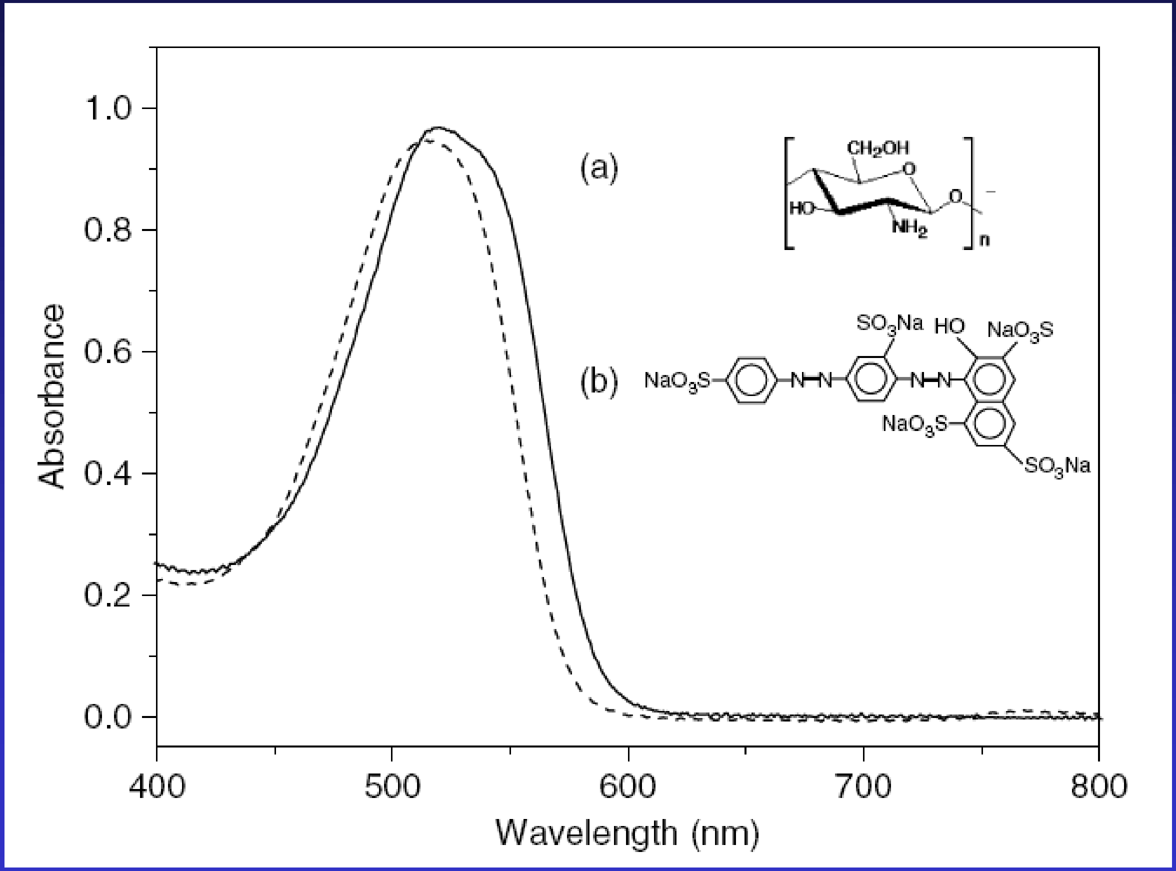
Optical storage in LBL water effect



a: **as deposited**
b: **blowing water vapor few seconds**

Entrapped water decrease the interaction between the sample components

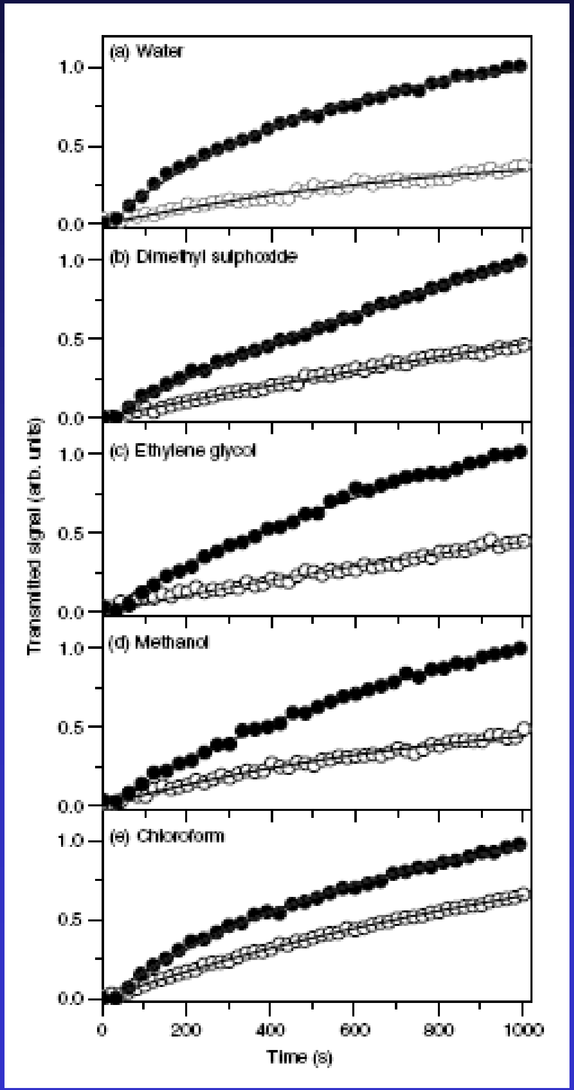
Biocompatible samples



a: chitosan
b: Ponceau-S

Film prepared in a LBL approach

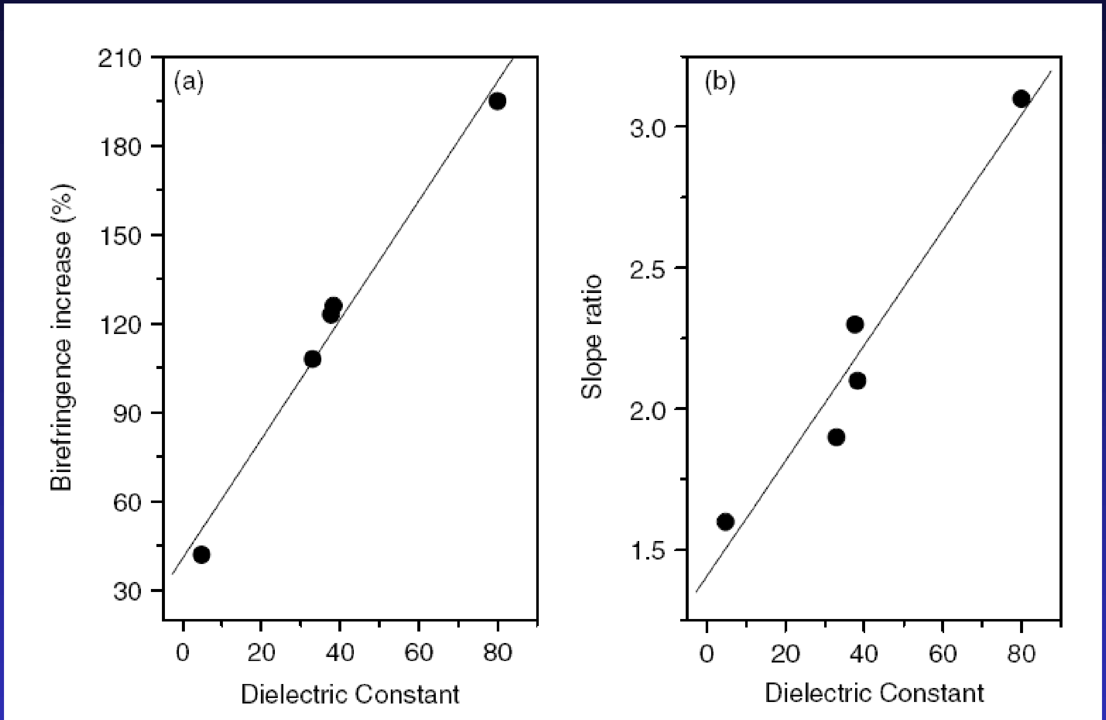
Optical storage : solvent effect



Samples immersed in solvent for 20 s and then dried with N_2

- **increase in birefringence amplitude**
- **decrease in writing time**

Optical storage: solvent effect



Optical storage features change can be used as a sensor

Table 1. Solvent effect on the birefringence

Solvent	Dielectric constant	Birefringence increase (%)	Slope ratio
Water	80	195	3.1
Dimethylsulfoxide	38.3	126	2.1
Ethylene glycol	37.7	123	2.3
Methanol	33	108	1.9
Chloroform	4.8	42	1.6

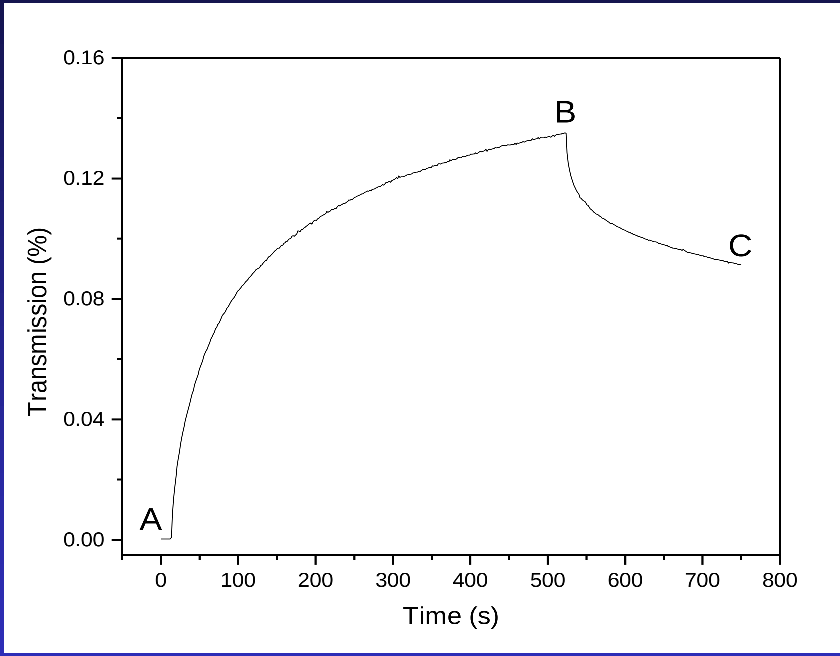
Optical storage: solvent effect

Influence of the polymer rigidity on the optical storage

Table 1
Optical storage characteristics of 61-layer LB films from the azopolymers HPDR13, DR19-IPDI, DR19-MDI and 15-layer LB films from copolymers HEMA-DR13 with four distinct dye concentrations

	Chromophore content (%w/w)	Maximum Δn	$T_{50\%}^{\mathrm{write}}$ (s)	Residual signal	$T_{50\%}^{\mathrm{relax}}$ (s)	Tg (°C)
HEMA-DR13	18	0.04	1.6	0.73	0.8	82
HEMA-DR13	24	0.05	0.9	0.64	0.7	79
HEMA-DR13	42	0.06	0.7	0.52	1.3	72
HEMA-DR13	64	0.07	0.5	0.48	1.6	64
HPDR13	83	0.12	1.0	0.35	3.0	56
DR19-IPDI	59	0.013	0.8	0.70	0.6	138
DR19-MDI	56	0.026	2.8	0.80	0.9	145

2D Optical storage



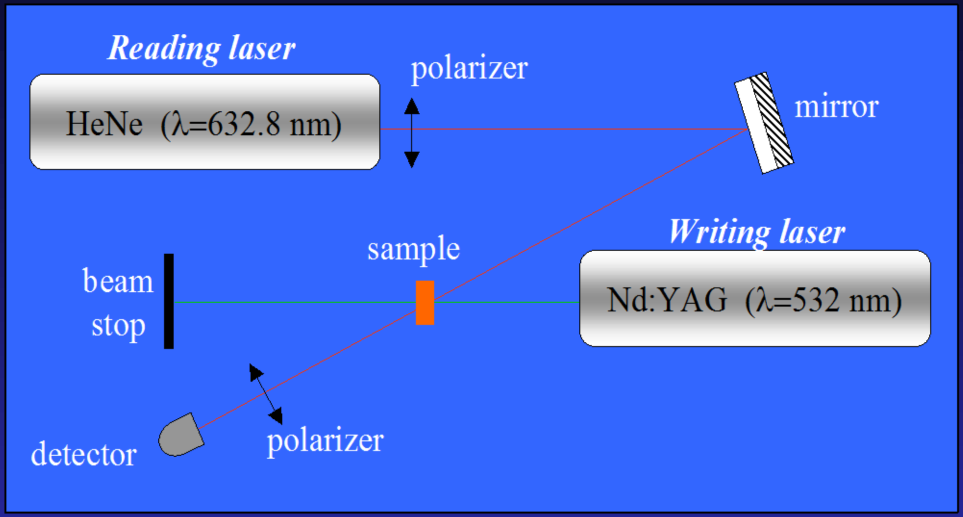
We selected MDI (cast film)

Residual fraction 80 %

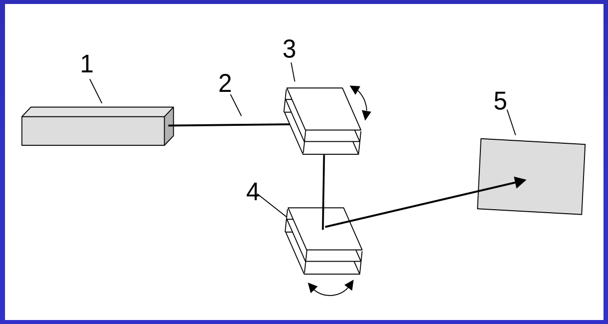
$\Delta n = 0.03$

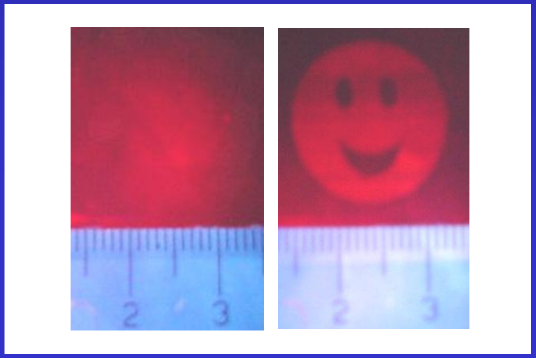
Not the best Δn, but an interesting residual rate

2D Optical storage



bi-dimensional optical storage

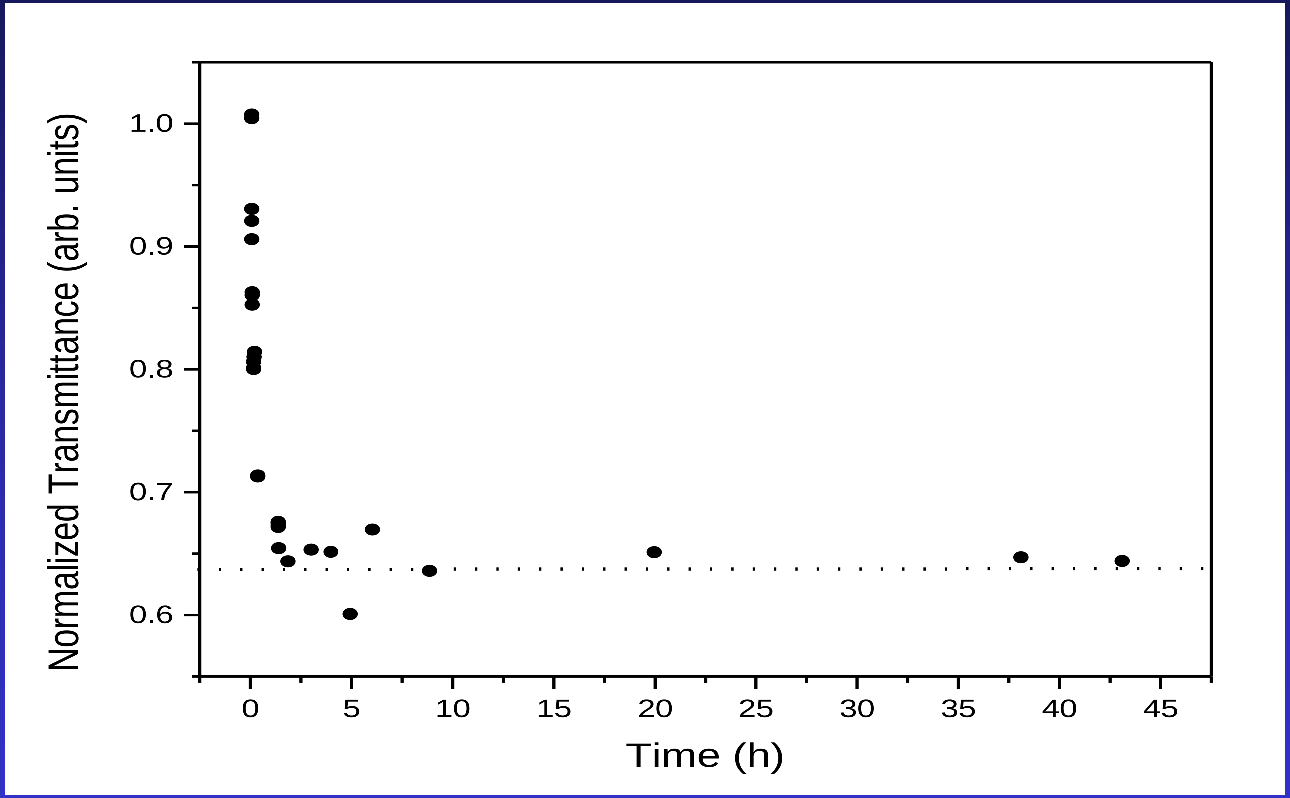




MDI

2D Optical storage

long-term memory

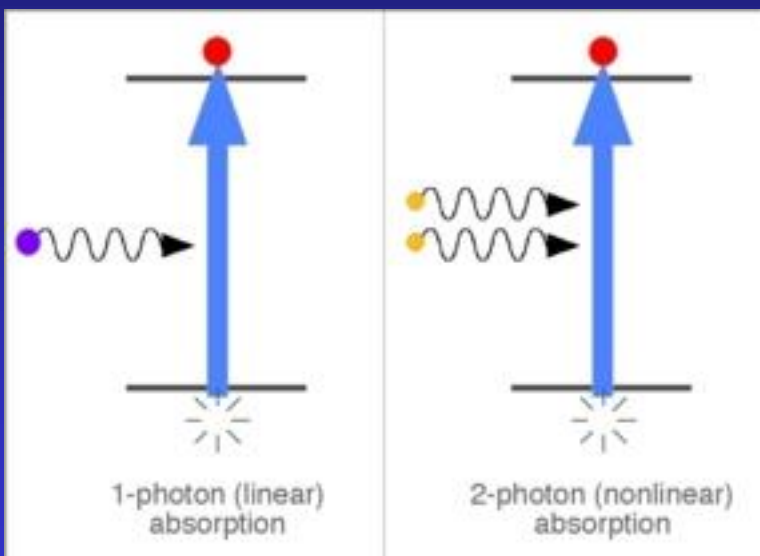


3D optical storage

$$\vec{P} = \chi^{(1)}.\vec{E} + \chi^{(2)} : \vec{E}\vec{E} + \chi^{(3)} \vdots \vec{E}\vec{E}\vec{E} + \ldots$$

$$Im\left[\chi^{(3)}\right]$$

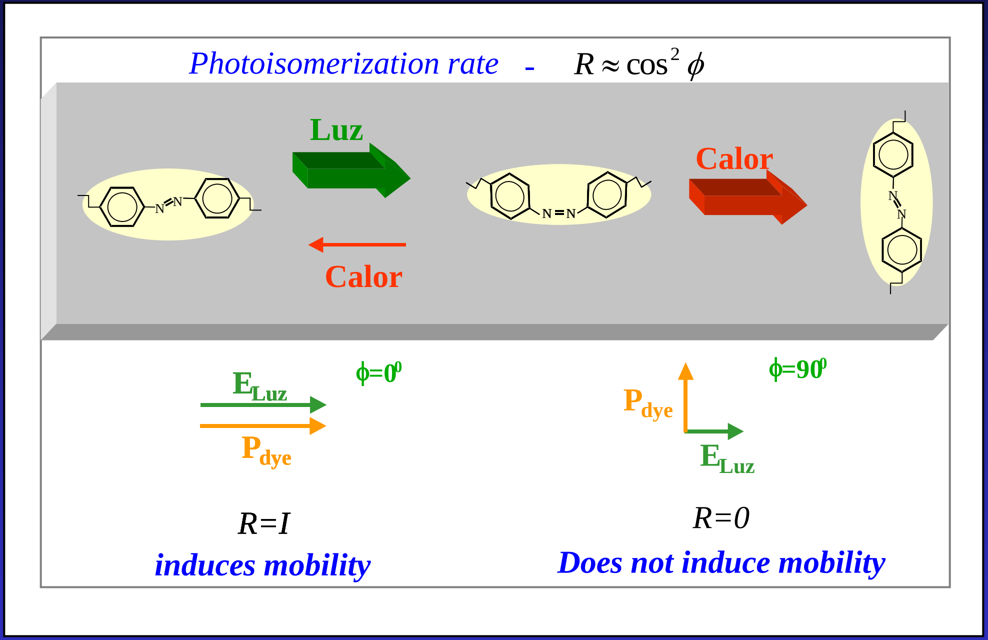
Two-photon absorption

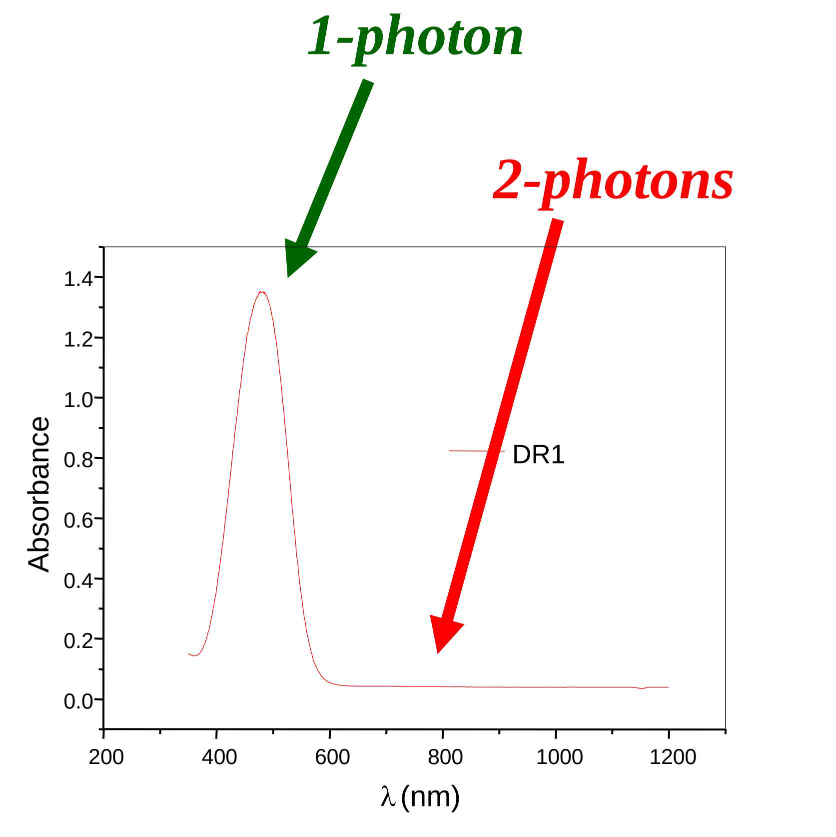


$$\alpha = \alpha_0 + \beta\, I$$

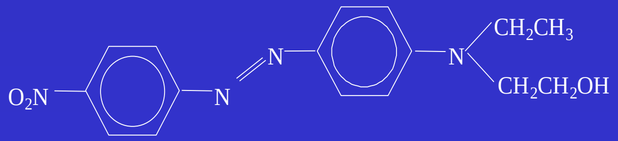
β: two-photon absorption coefficient

two-photon induced birefringence: 3D optical storage



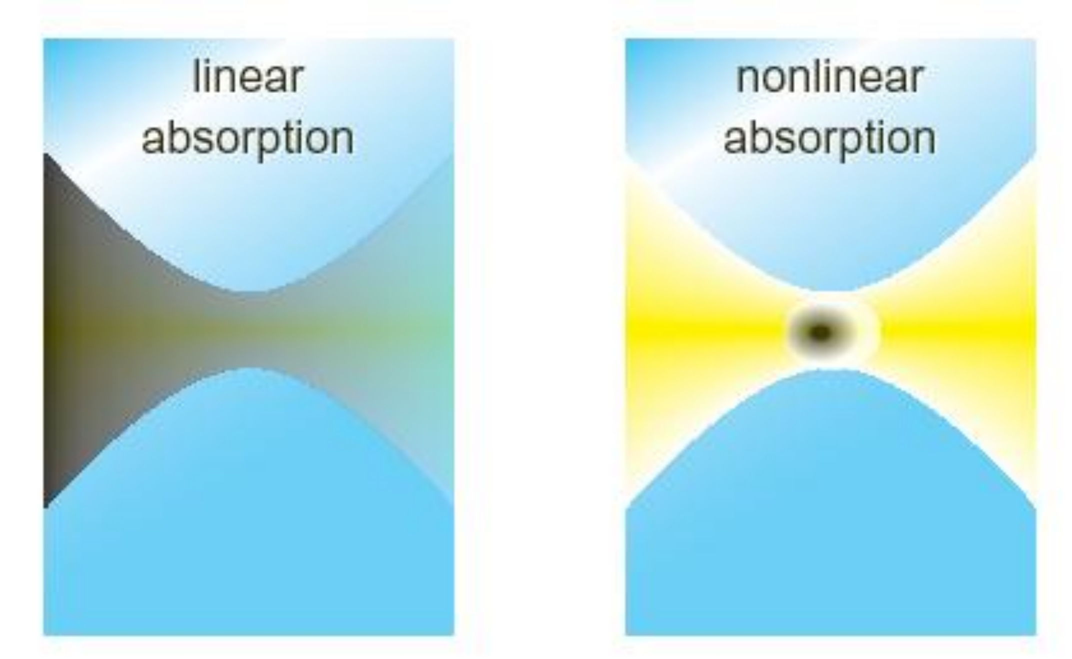


DR1



Two-photon absorption

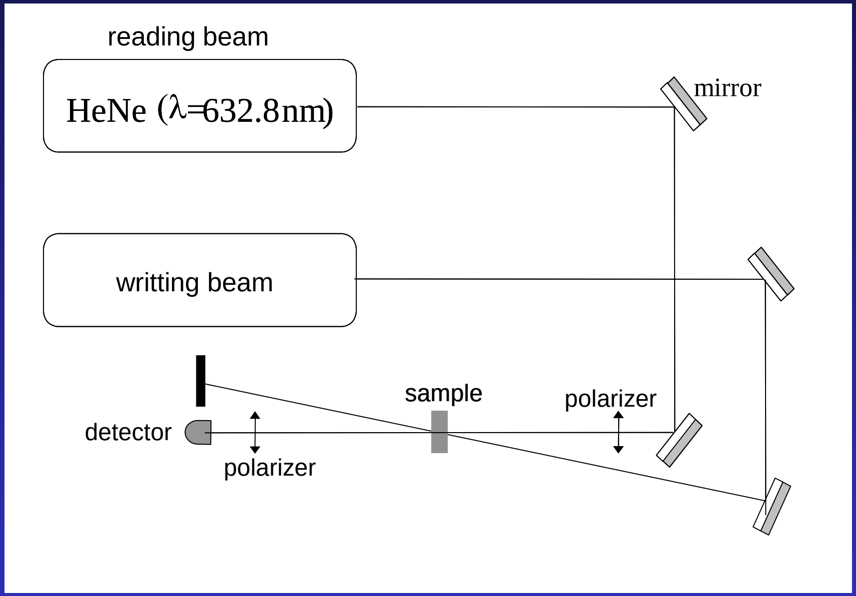
Nonlinear interaction provides spatial confinement of the excitation

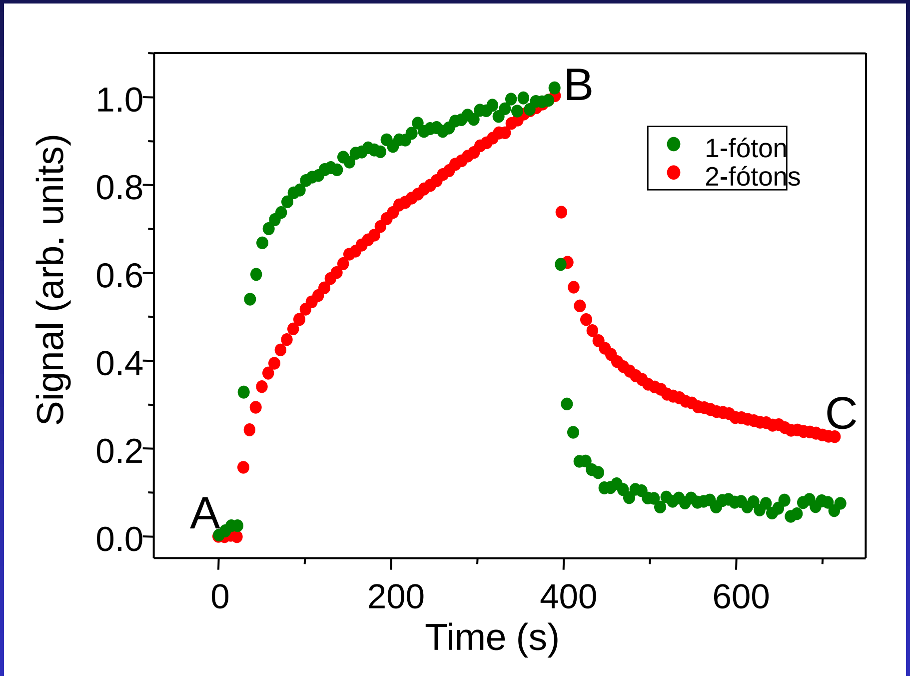


$$\alpha = \alpha_0$$

$$\alpha = \alpha_0 + \beta I$$

3D optical storage





λ= 532 nm I= 0.1 W/cm^2

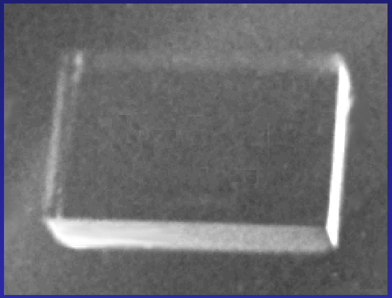
λ= 775 nm I= 25 GW/cm^2

3D optical storage

Thick samples PMMA/DR13
(1x2x0.5 cm^3)

Use two-photon excitation to induce molecular orientation

(a)

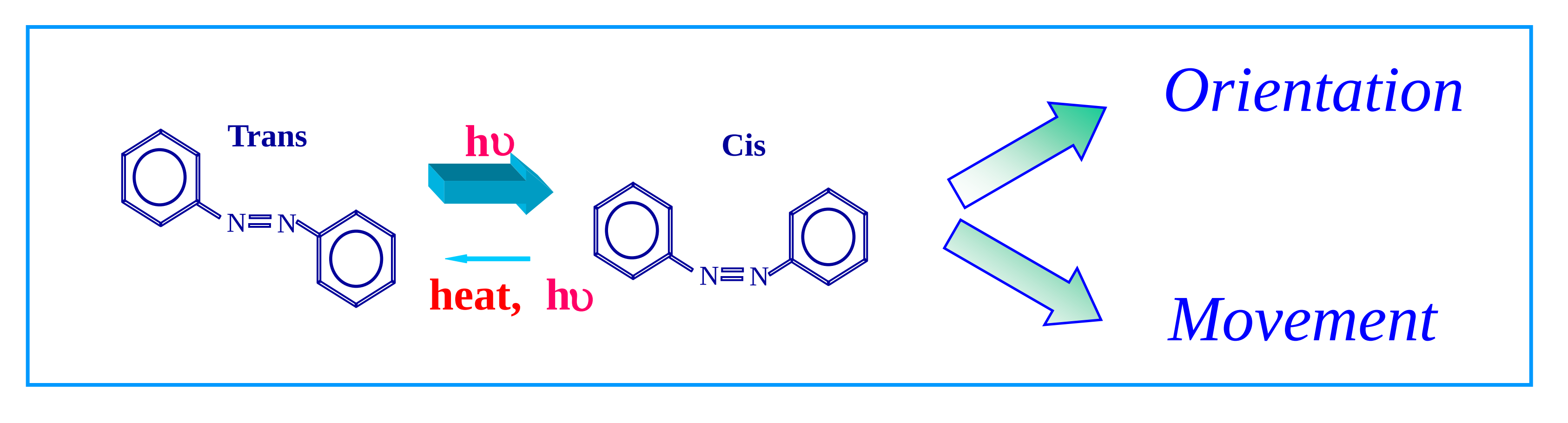


(b)

Taking advantage of the spatial localization of excitation

Optical storage and surface relief gratings

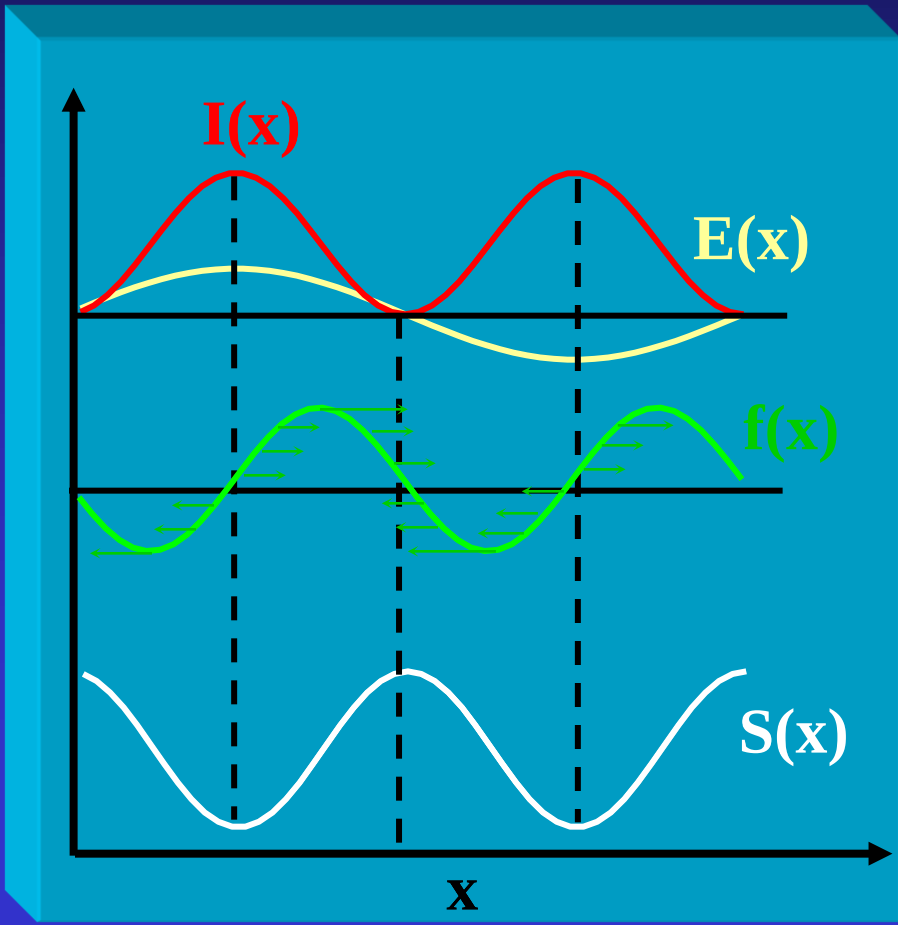
- *Study of optically induced birefringence (molecular orientation) in azopolymers*



Grating formation mechanism

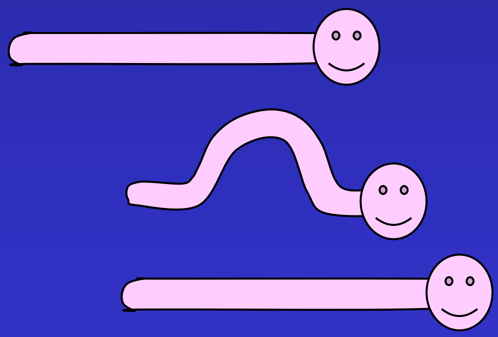
The force density exerted on the dipole molecule is:

$$\mathbf{f} = \langle (\mathbf{P}(\mathbf{r},t).\nabla)\mathbf{E}(\mathbf{r},t) \rangle$$

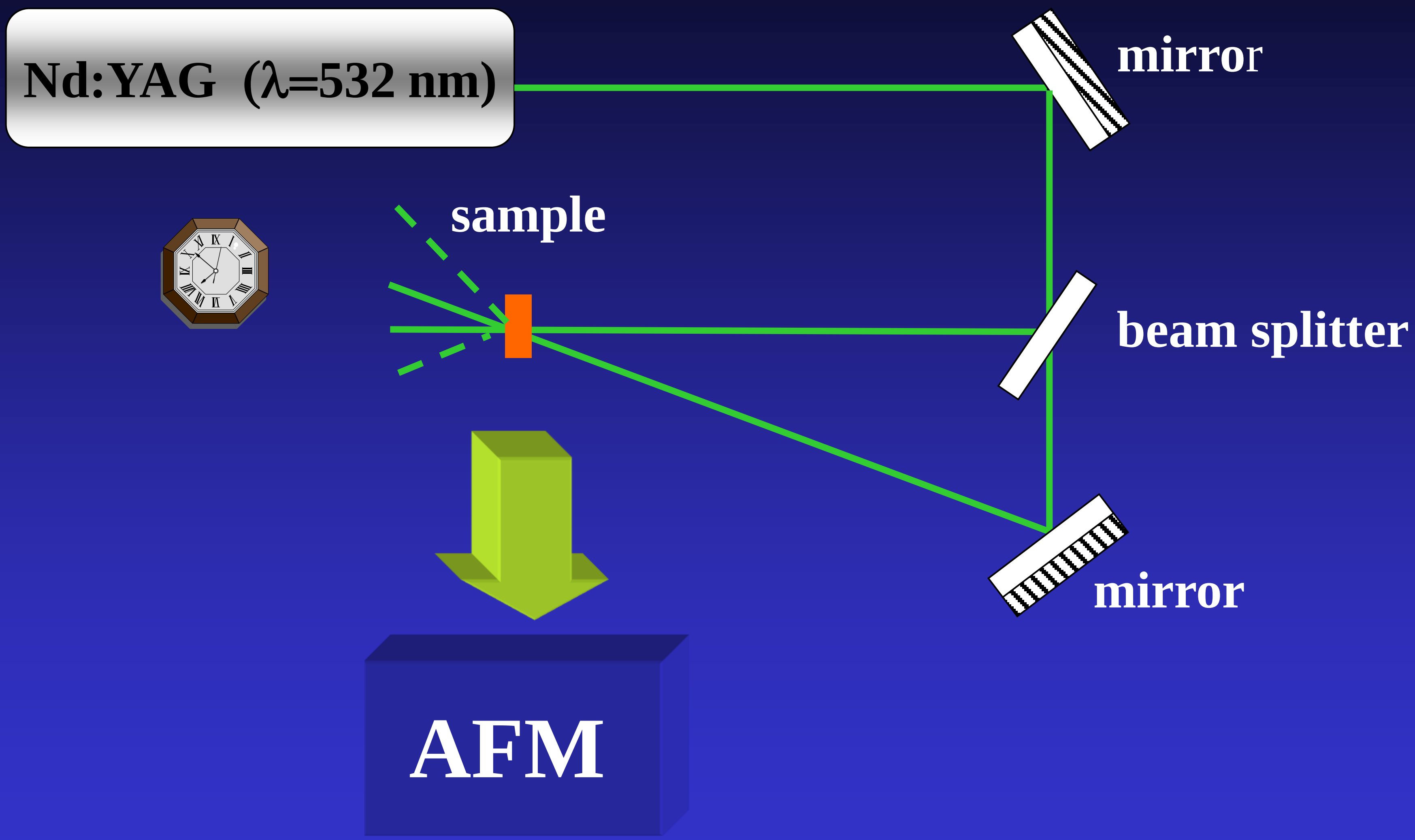


Facilitated by the photoisomerization

Worm like movement

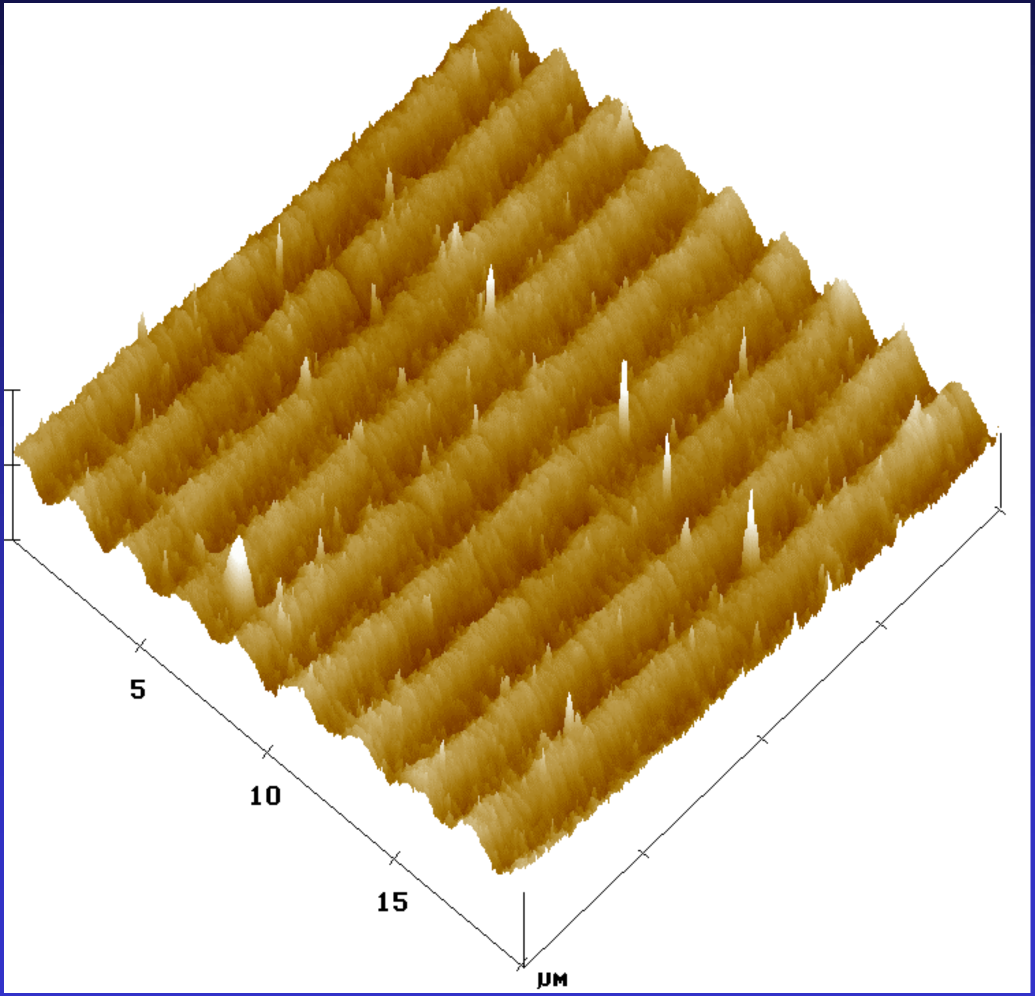


Experimental setup



HPDR13 results

AFM 3D- topography image



LB film:

HPDR13 and Cd St

(100 layers 50:50 w/w)

P=180mW/cm^2

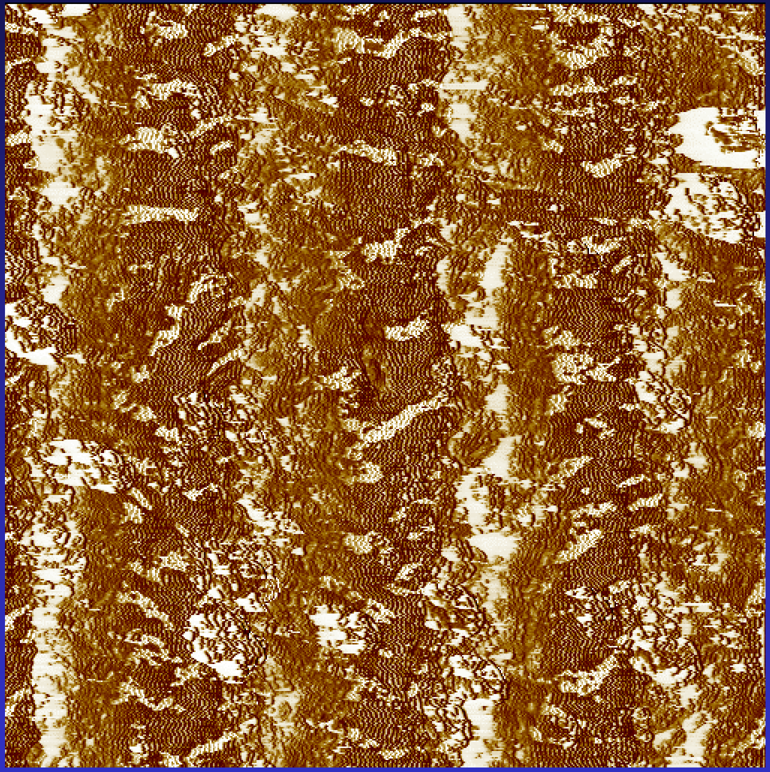
p-polarized

grating spacing: 2.6µm

peak-valey height: 50-60nm

HPDR13 results

AFM phase image

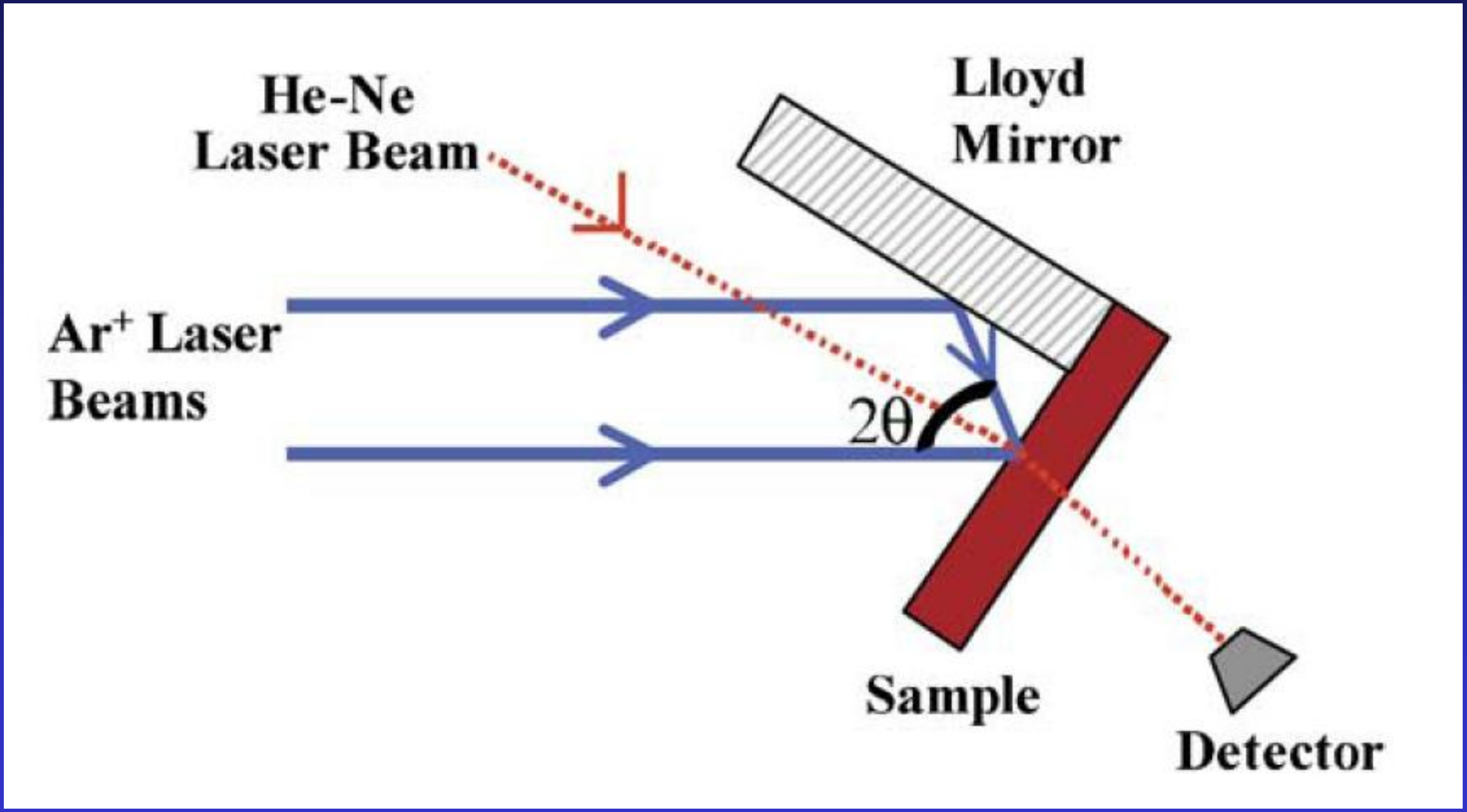


The CdSt domains have moved along with HPDR13 molecules

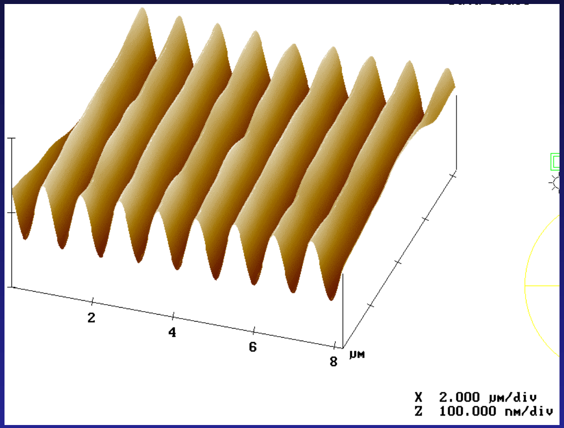
Two types of material with different viscoelasticity.

Surface relief gratings

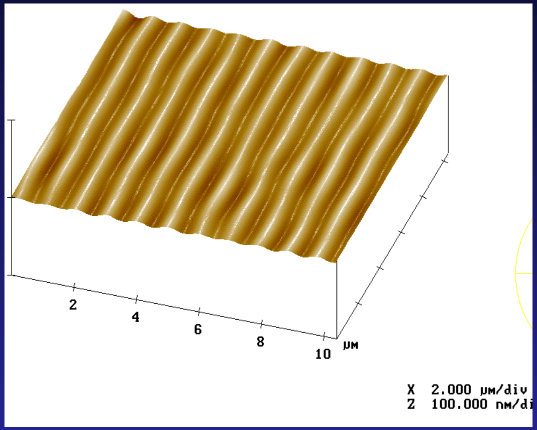
Experimental setup



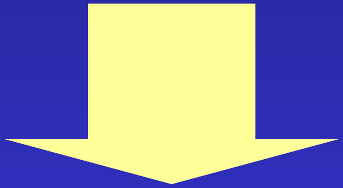
Surface relief gratings



p - polarized

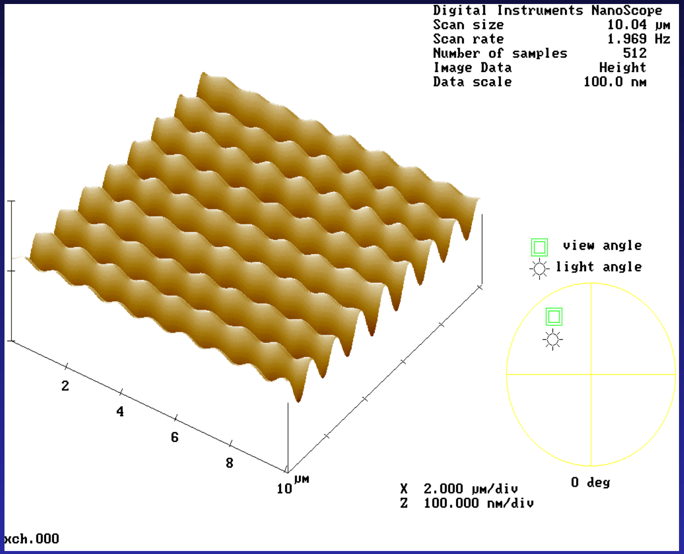


s - polarized



Polarization in the direction of the intensity gradient

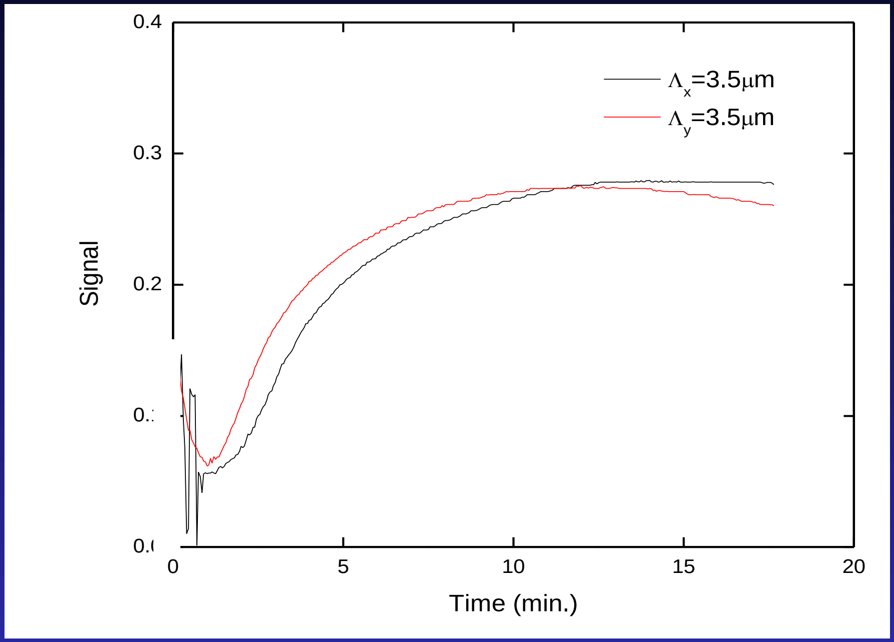
Surface relief gratings



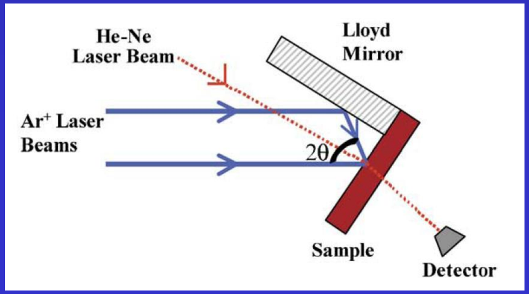
Surface relief grating in LBL films

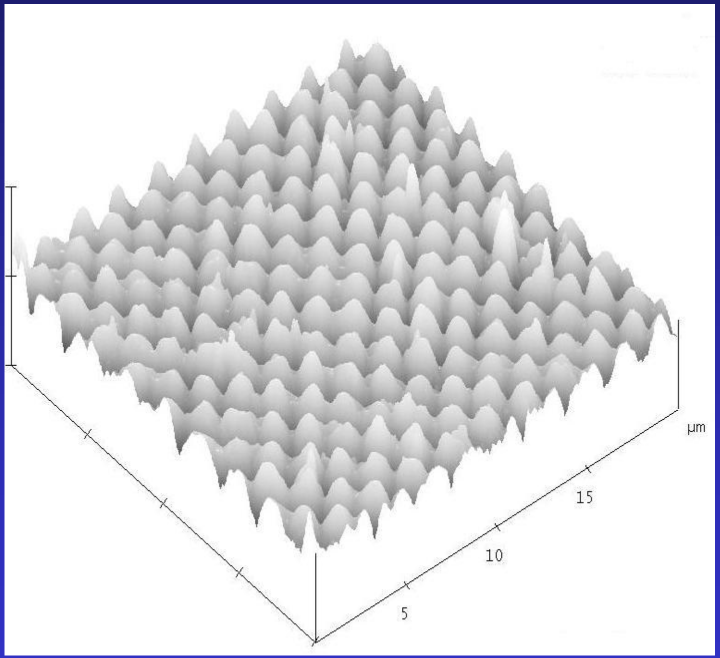
both polymers move together

Surface relief gratings



Diffraction of a probe beam to monitor the grating formation





We are able to microstructure the polymer surface using only cw lasers

Conclusion

- Possible to control the optical storage
  - using different polymeric matrix
  - using different azodyes
  - using distinct fabrication methods
  - application in sensors
  - 2D optical storage with long-term
  - 3D optical storage using two-photon absorption

- Surface relief gratings using low-power cw laser