Femtosecond micromachining in polymers

Prof. Dr Cleber R. Mendonca

Daniel S. Corrêa

Prakriti Tayalia

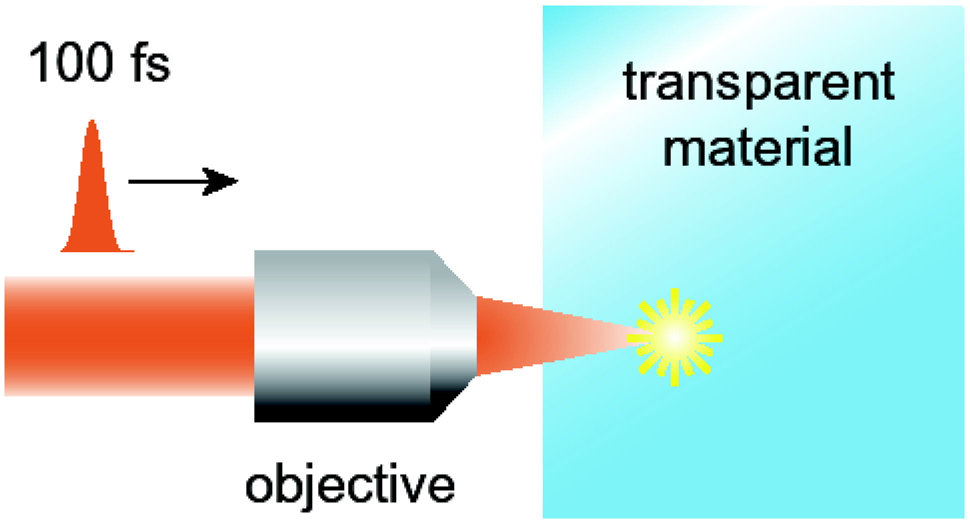
Dr. Tobias Voss

Dr. Tommaso Baldacchini

Prof. Dr. Eric Mazur

fs-micromachining

focus laser beam inside material or on its surface



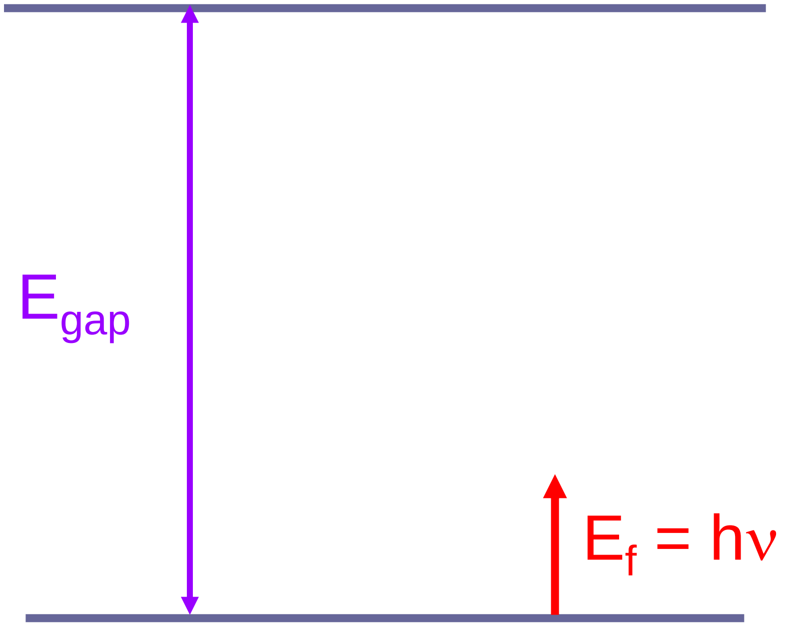
fs-micromachining

photon energy < bandgap

nonlinear interaction

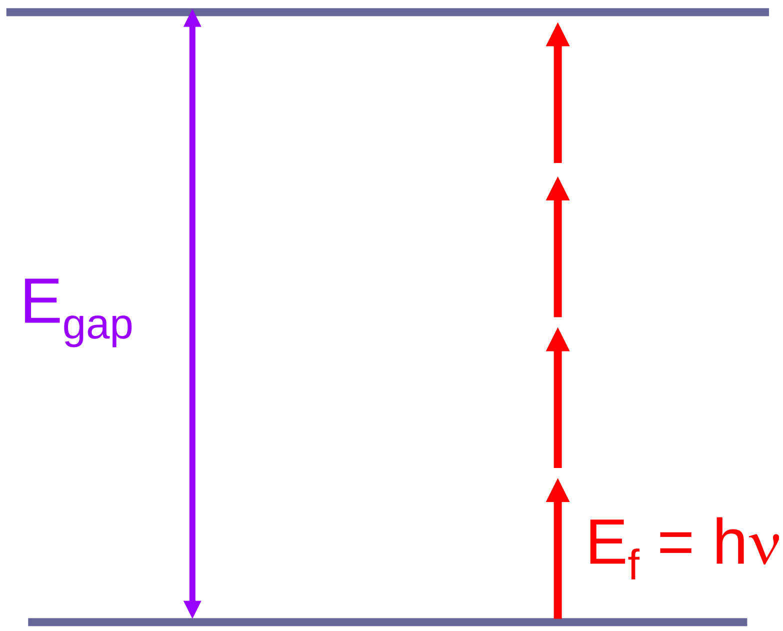
fs-micromachining

nonlinear interaction



fs-micromachining

nonlinear interaction



multiphoton absorption

fs-micromachining

it is important to understand the nonlinear interaction, as well as the nonlinear response of organic compounds and polymers

fs-micromachining

applications:

- data storage
- waveguides
- microfluidics
- biology

Polymers and organic materials

Outline

Introduction to nonlinear optics

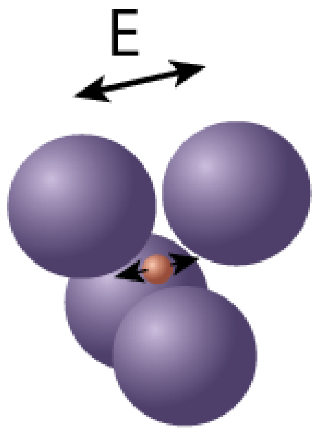
fs-micromachining

- microstructuring MEH-PPV
- waveguides in azopolymers

two-photon polymerization

- birefringent microstructures
- fluorescent microstructures
- biocompatible microstructures

Linear optics



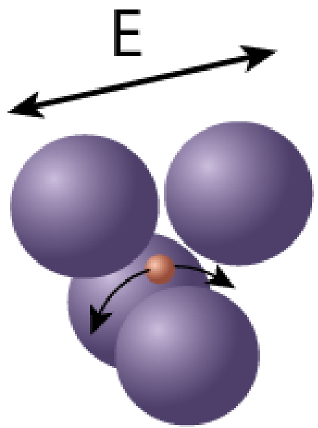
harmonic oscillator

$E_{rad.} << E_{inter.}$

linear response

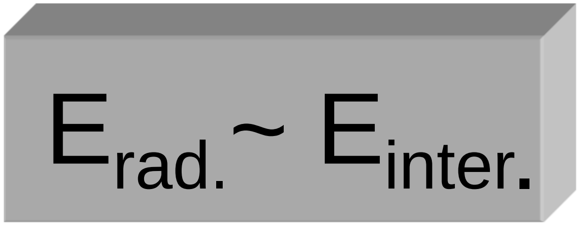
$$P = \chi E$$

Nonlinear optics



anharmonic oscillator

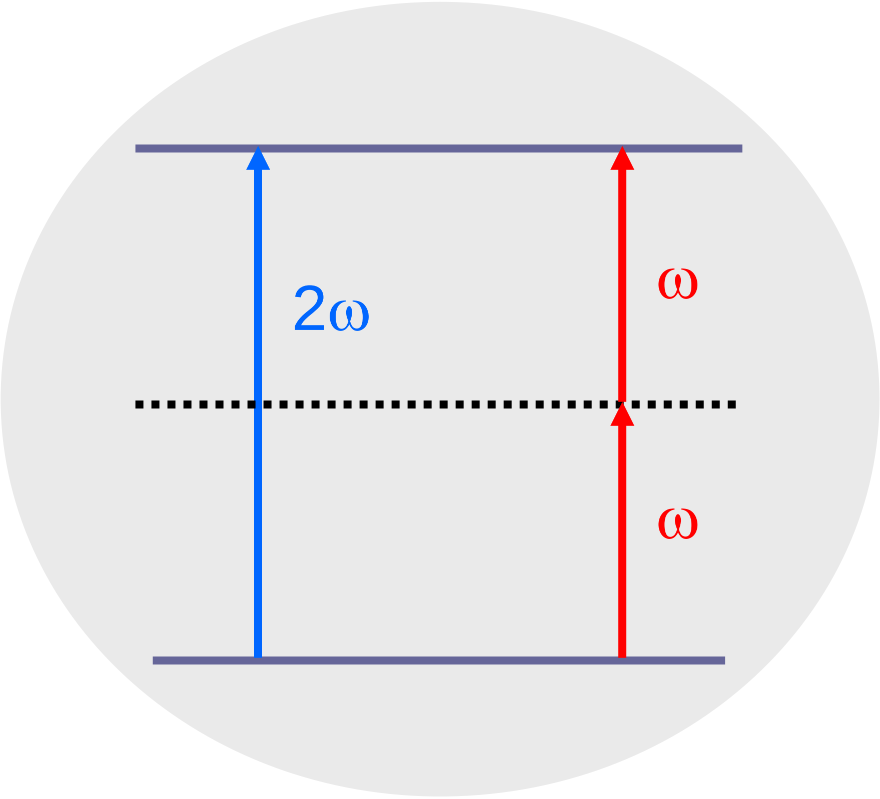
high light intensity



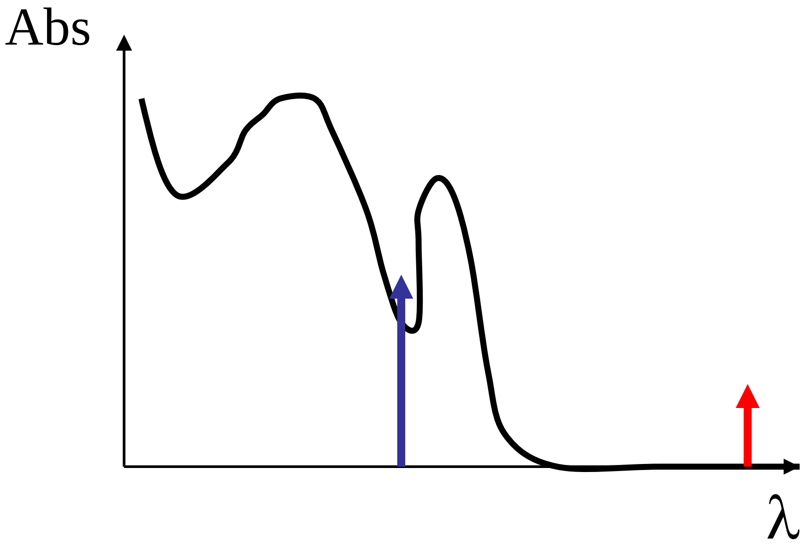
nonlinear polarization response

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

two-photon absorption



Third order processes $\chi^{(3)}$

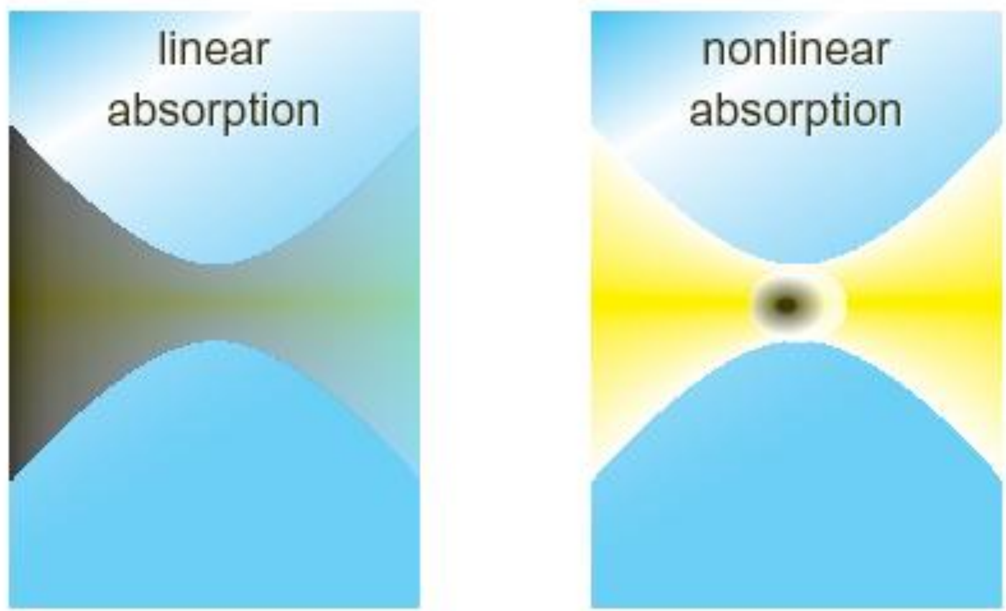


$$\alpha = \alpha_0 + \beta I$$

two-photon absorption

Nonlinear interaction provides spatial confinement of the excitation

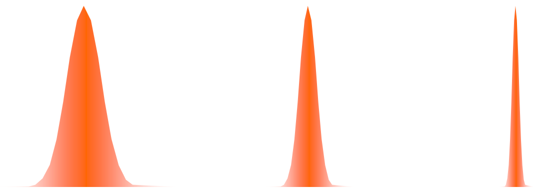
fs-microfabrication



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

femtosecond pulses

Ti:Sapphire lasers

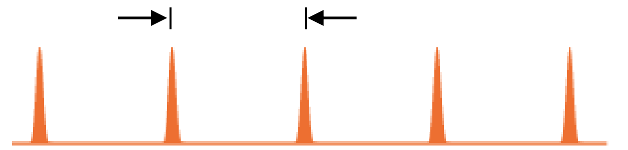


100 fs 50 fs 20 fs

Repetition rate

Energy

1 ms

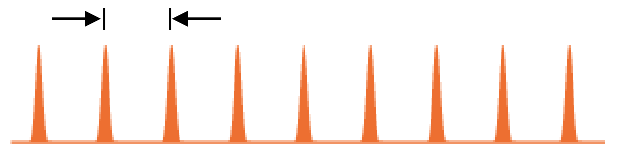


1 KHz

100 fs

mJ

12 ns



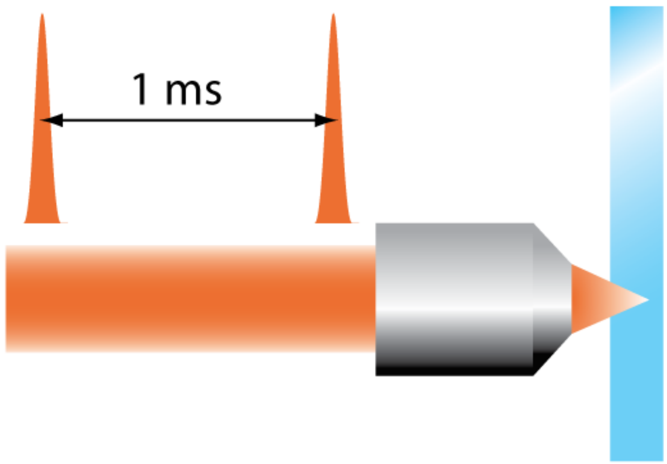
86 MHz

100 fs

nJ

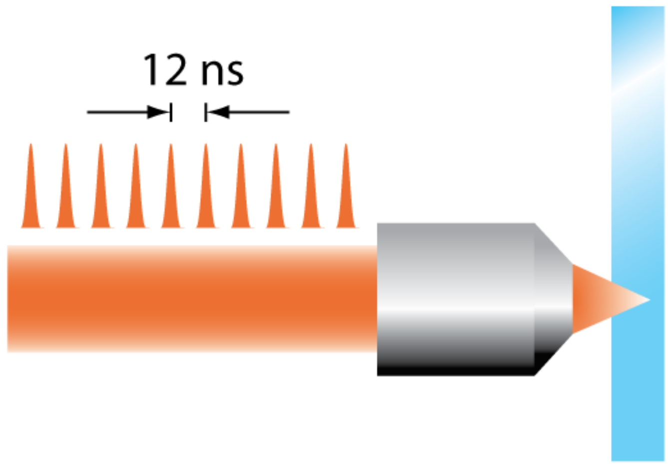
femtosecond pulses

amplified laser



repetitive

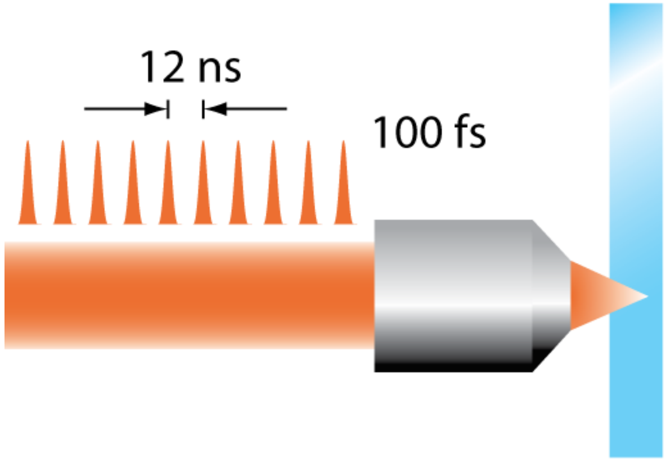
oscillator



cumulative

fs-pulses for micromachining polymers

Oscillator: 80 MHz, 5 nJ

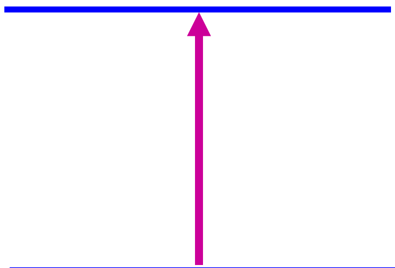


heat diffusion time: $t_{diff} \sim 1\ \mu s$

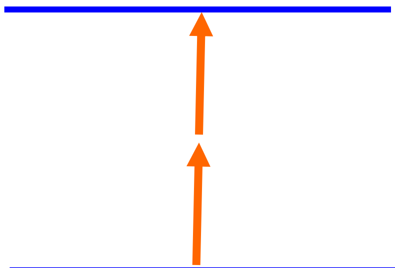
cumulative

fs-microfabrication

linear *versus* nonlinear absorption



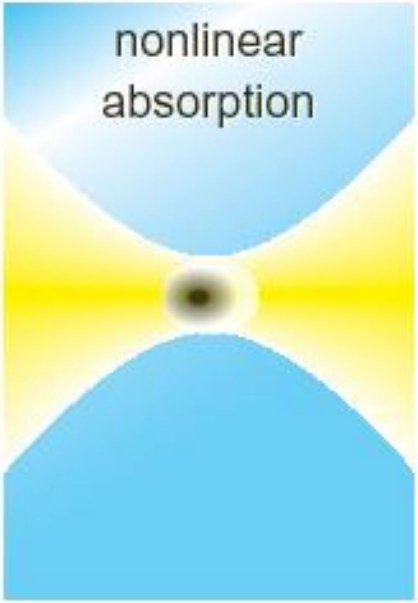
$$\alpha = \alpha_0$$



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

fs-microfabrication

Nonlinear interaction provides spatial confinement of the excitation



$$\alpha = \alpha_0$$

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

two main techniques

1

fs-laser micromachining

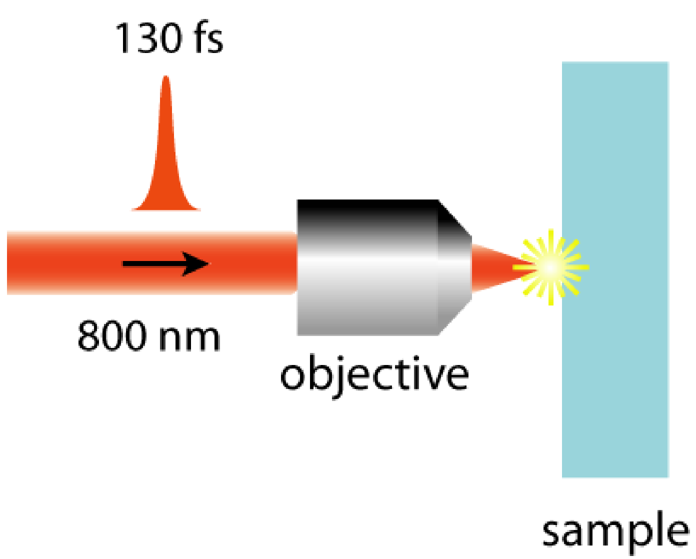
ablation
structural modification

2

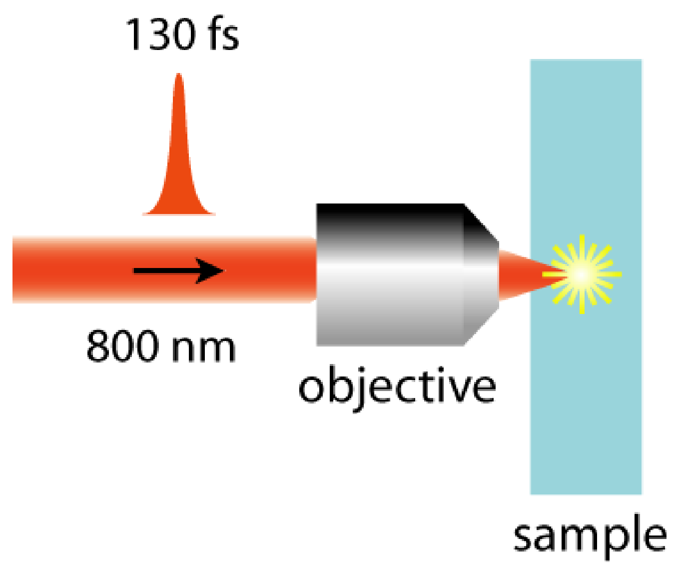
microfabrication via
two-photon polymerization

fs-laser micromaching

Surface

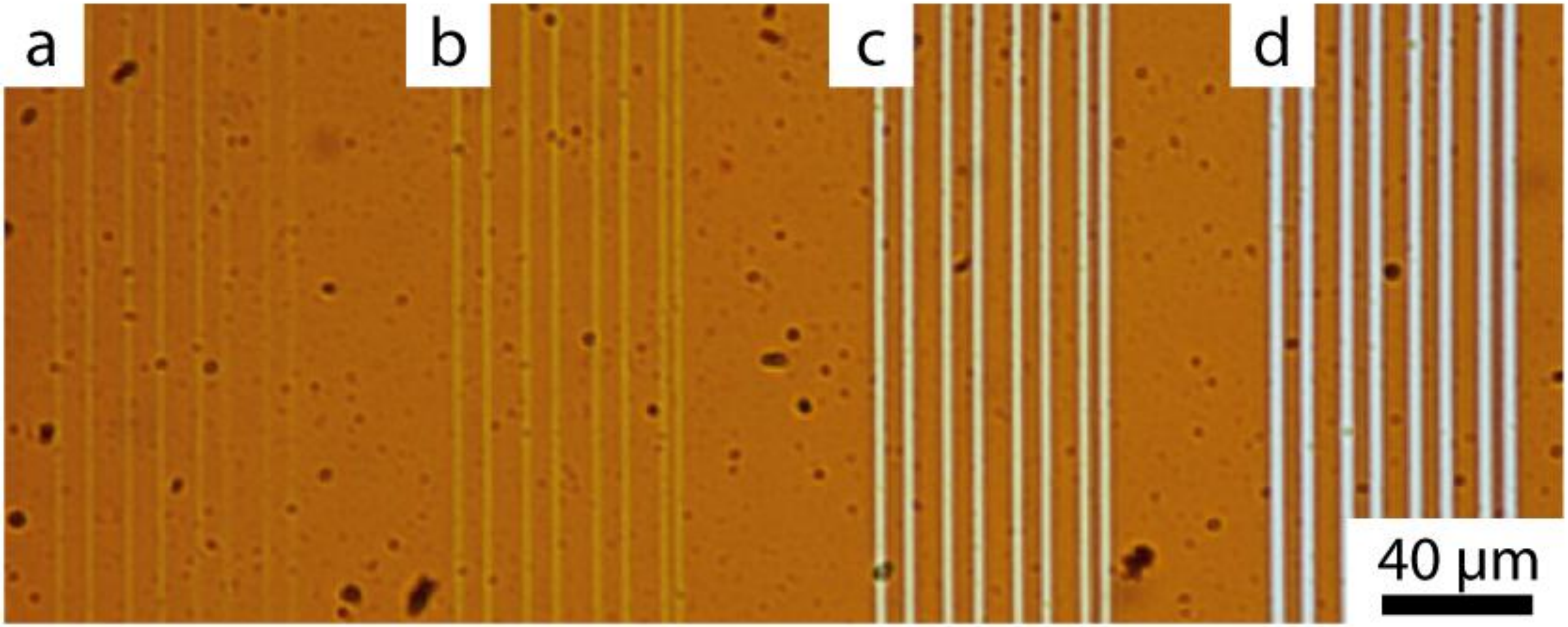


Volume



Micromachining the conductive polymer MEH-PPV

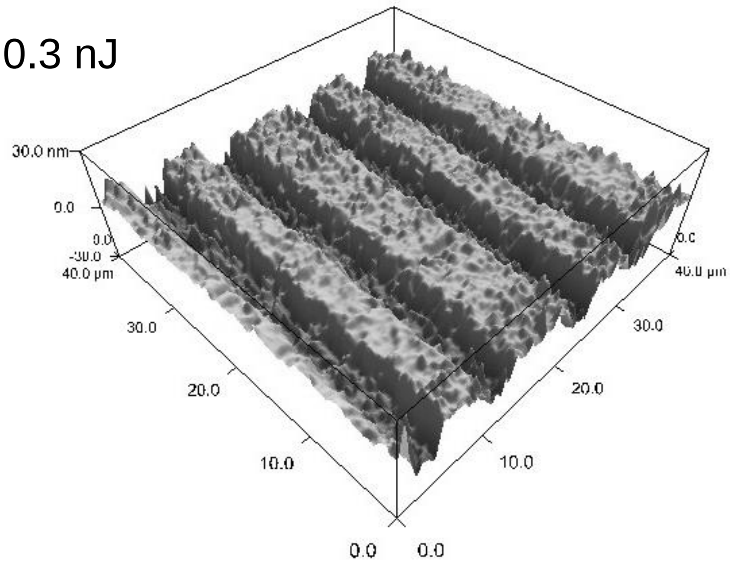
optical microscopy



a: 0.07 nJ
b: 0.14 nJ
c: 0.34 nJ
d: 0.68 nJ

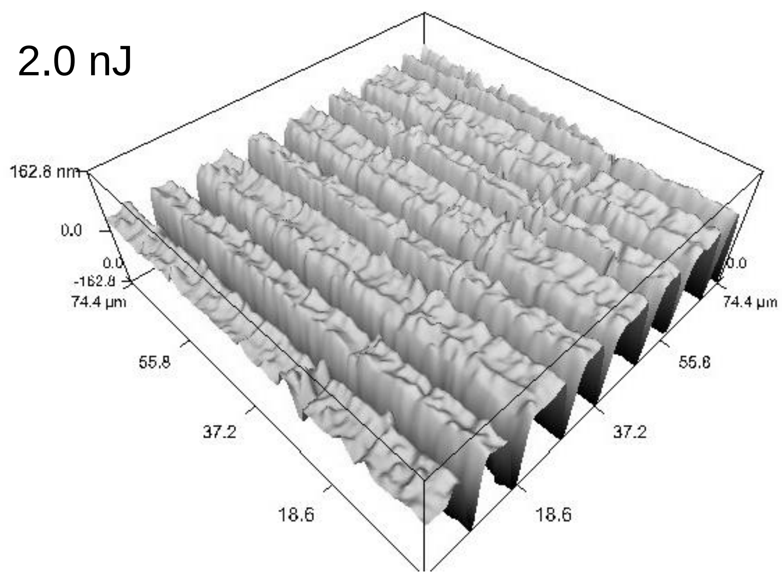
Micromachining the conductive polymer MEH-PPV

a 0.3 nJ

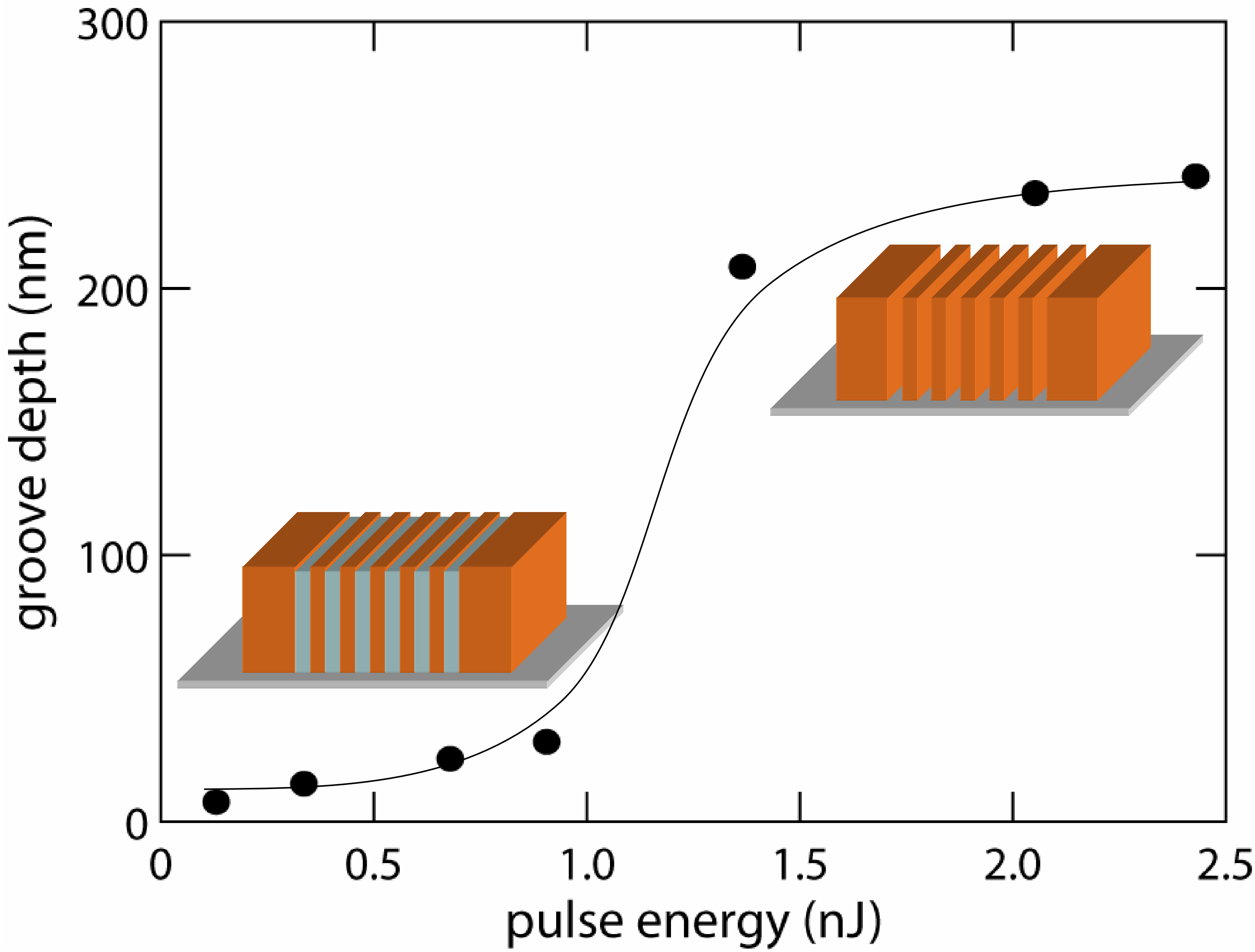


atomic force microscopy

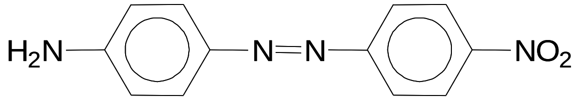
b 2.0 nJ



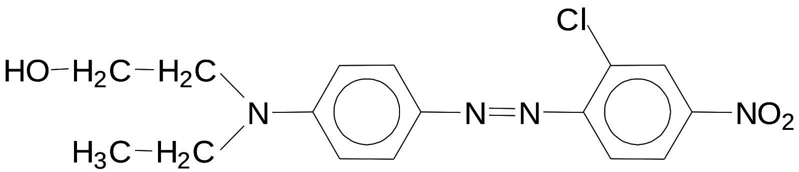
Micromachining the conductive polymer MEH-PPV



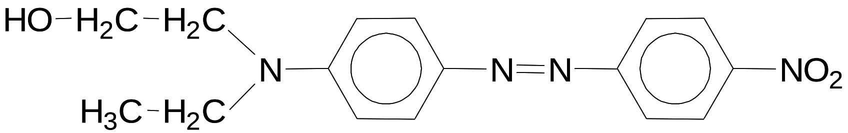
Waveguides in azo-polymers



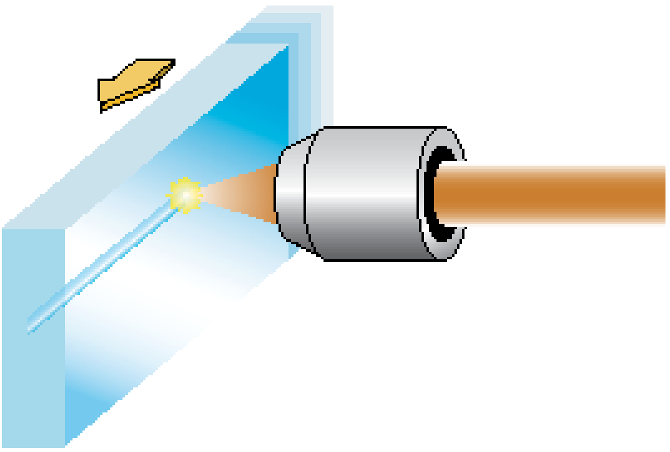
DO3



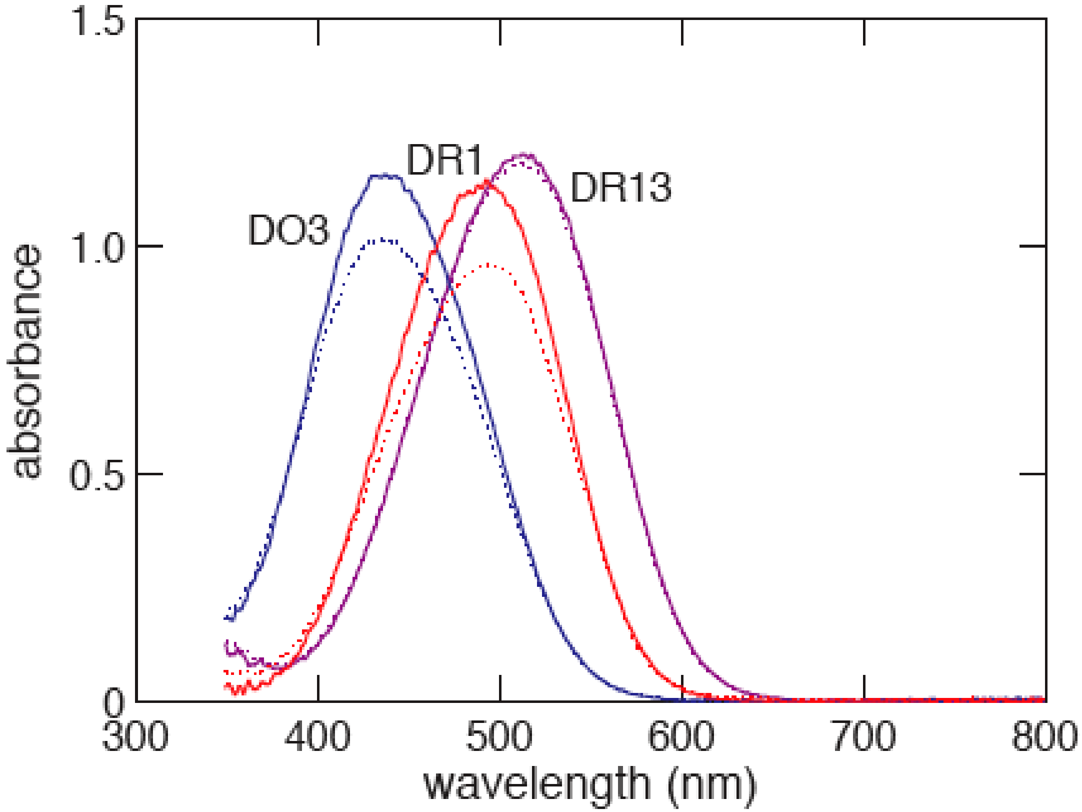
DR13



DR1

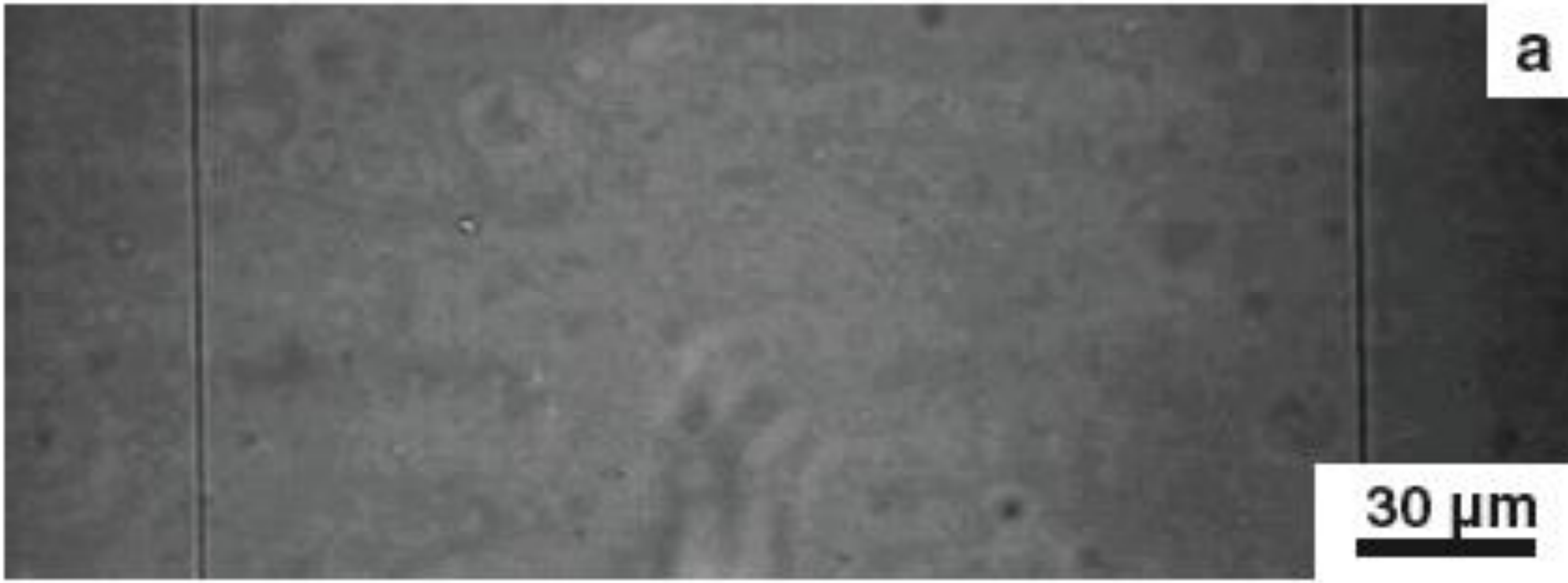


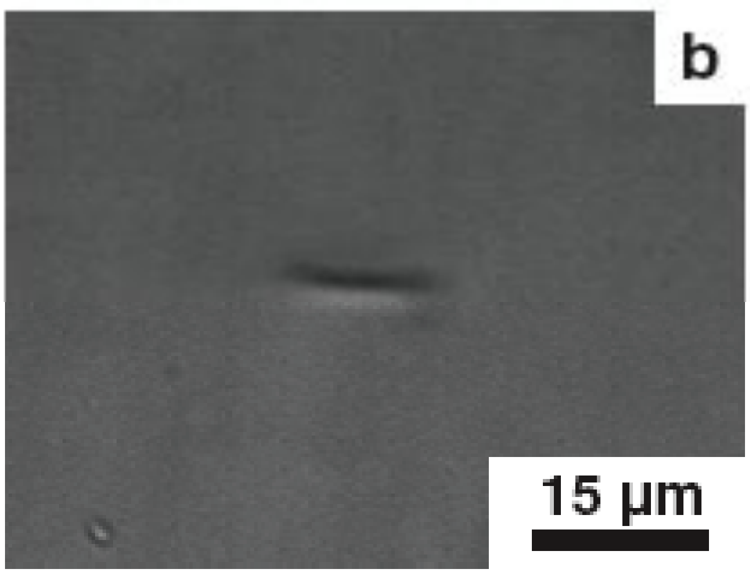
Waveguides in azo-polymers - photobleaching



Absorbance spectrum of PMMA films containing 3.5% by weight of (a) DO3, (b) DR1, and (c) DR13. The dashed lines show the absorbance after micromachining the films.

Waveguides in azo-polymers

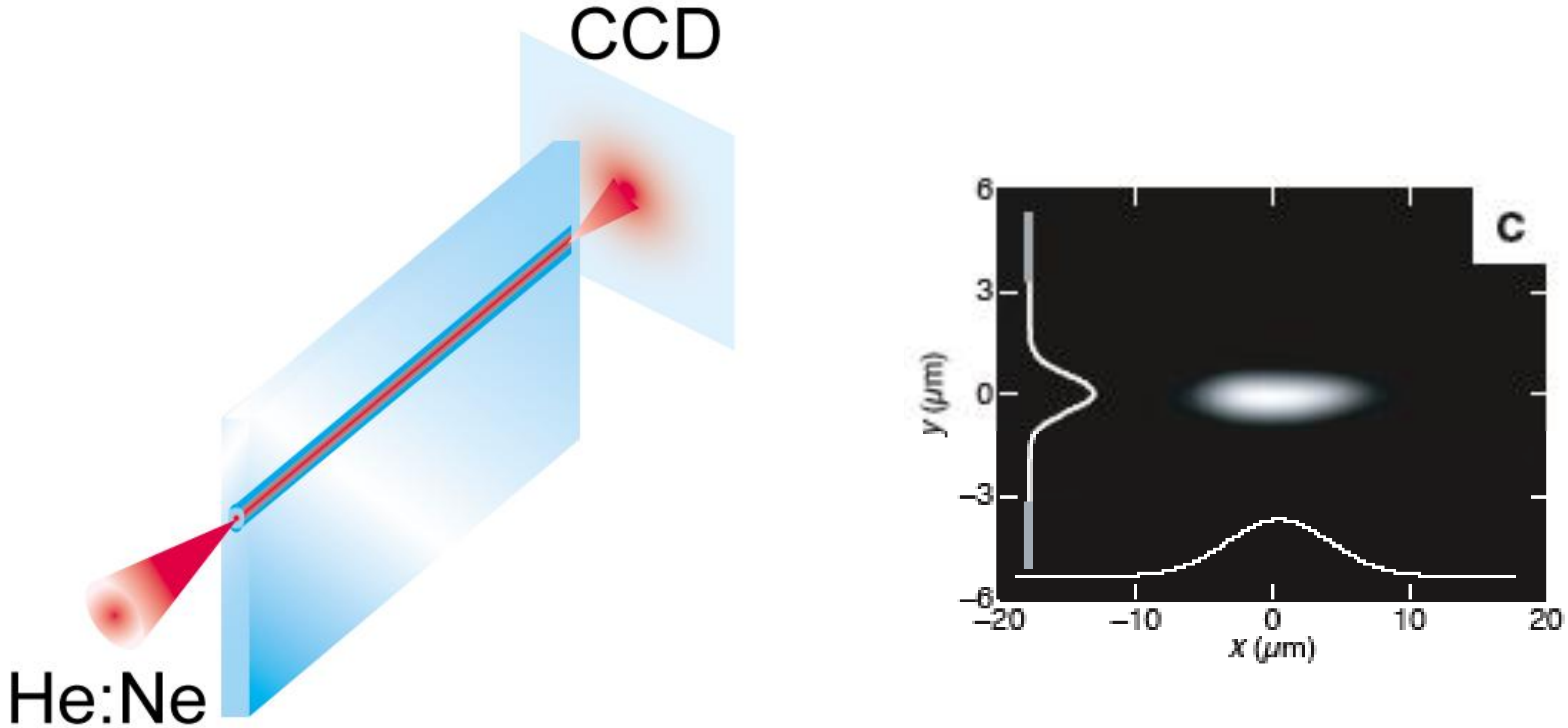




(a) Optical microscope image of the waveguides micromachined (PMMA/DR1)

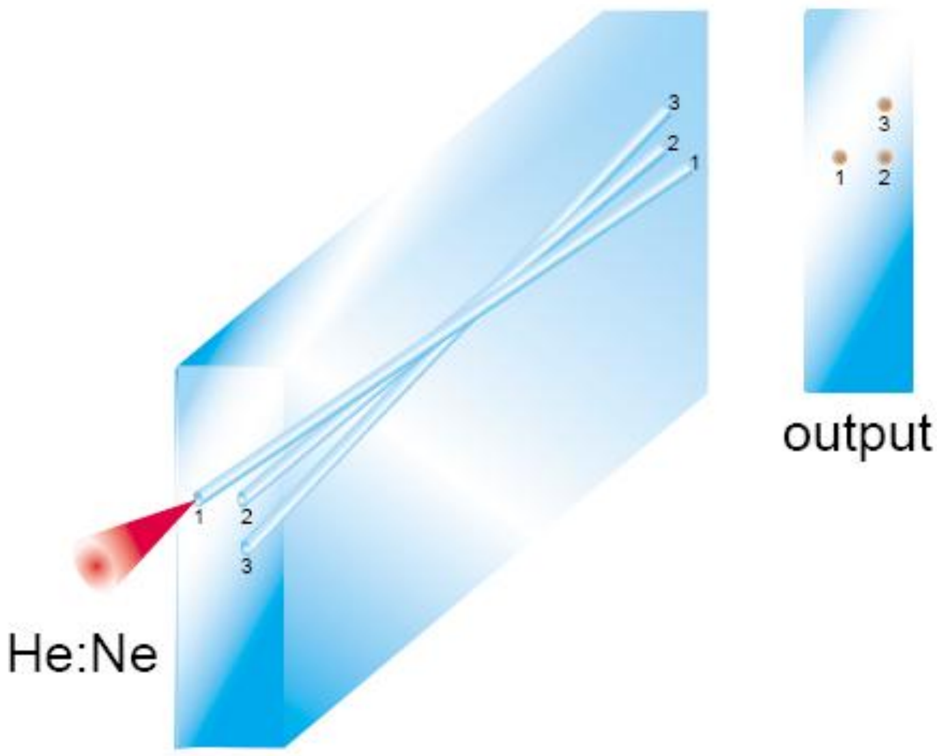
(b) Cross-sectional view of the waveguides

waveguides in azo-polymers

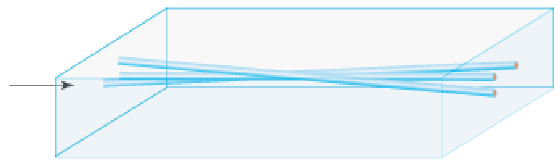


(c) Output image of the mode profile of 632.8-nm light coupled through the waveguide *photonic devices - wiring optoelectronics circuits of the future*

3D wave splitter

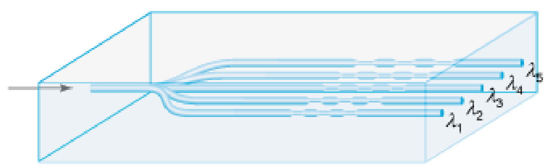


photonic devices - wiring optoelectronics circuits of the future



3D splitter

Bragg grating

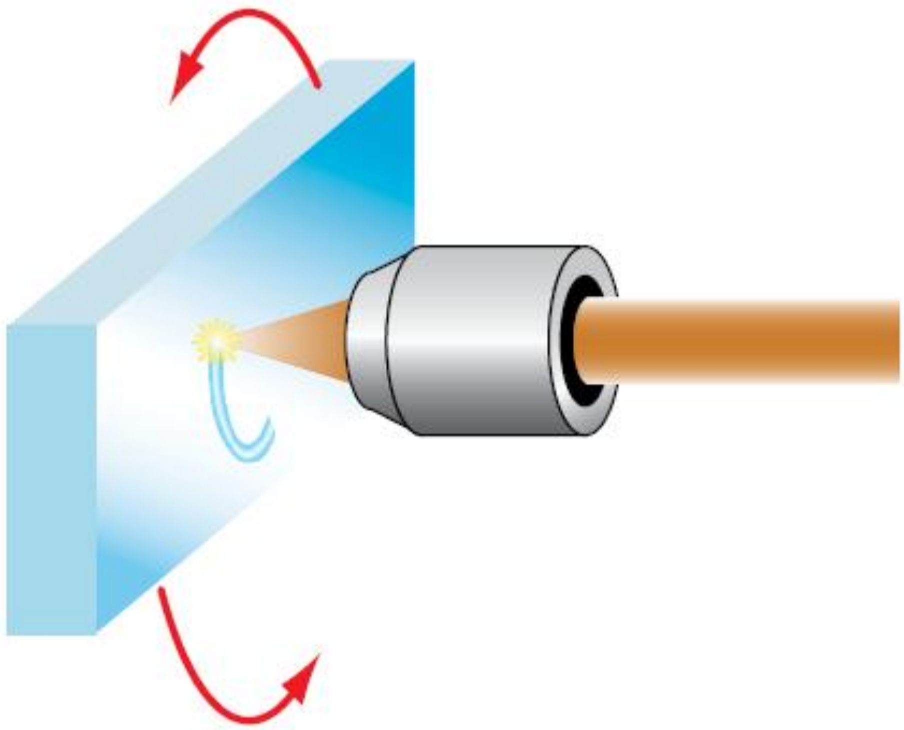


demultiplexer

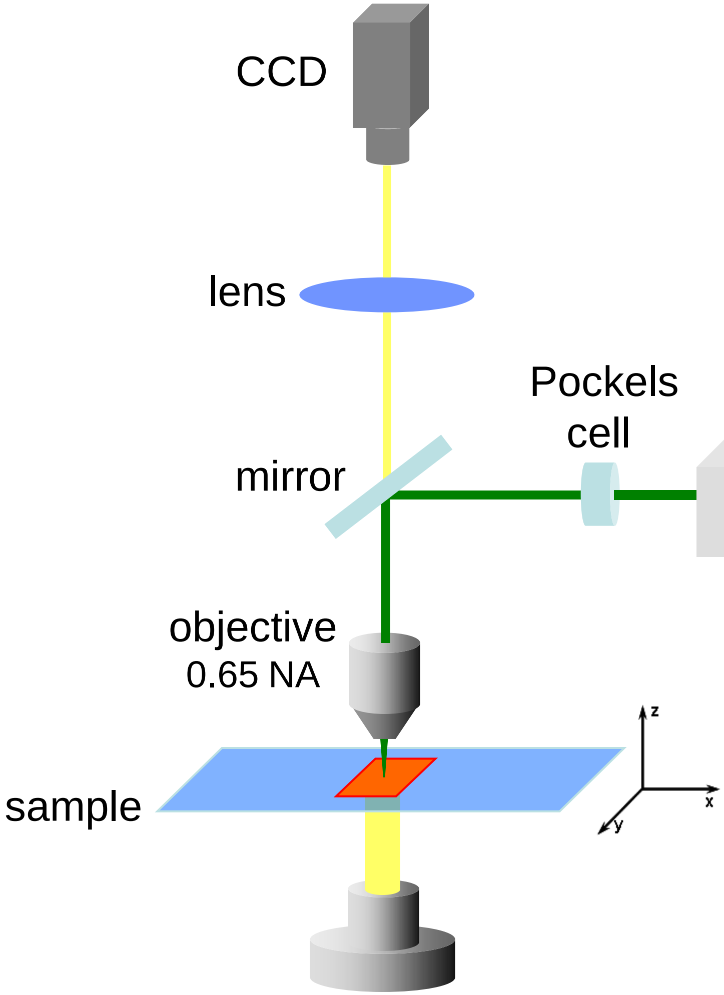
amplifier

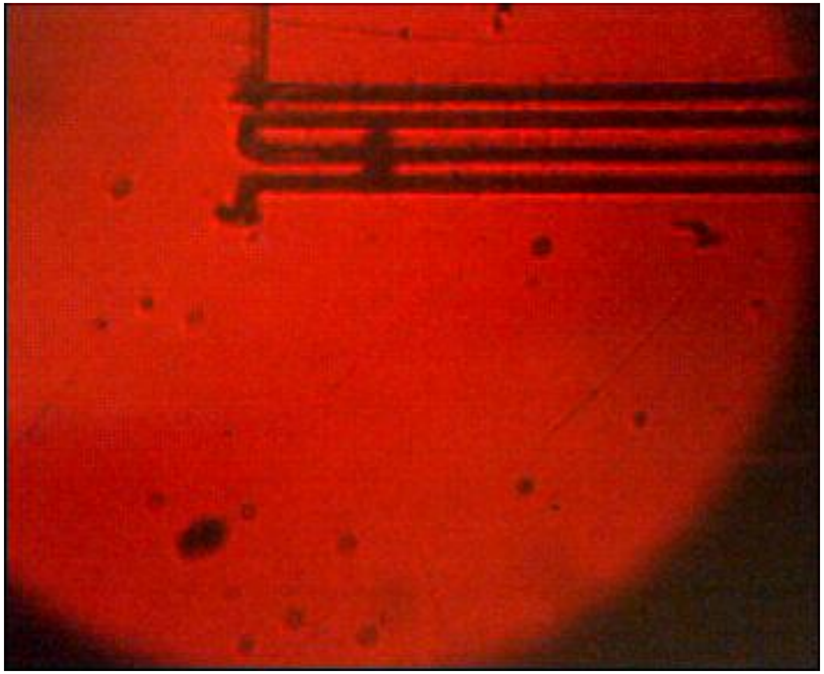
interferometer

Curved waveguides



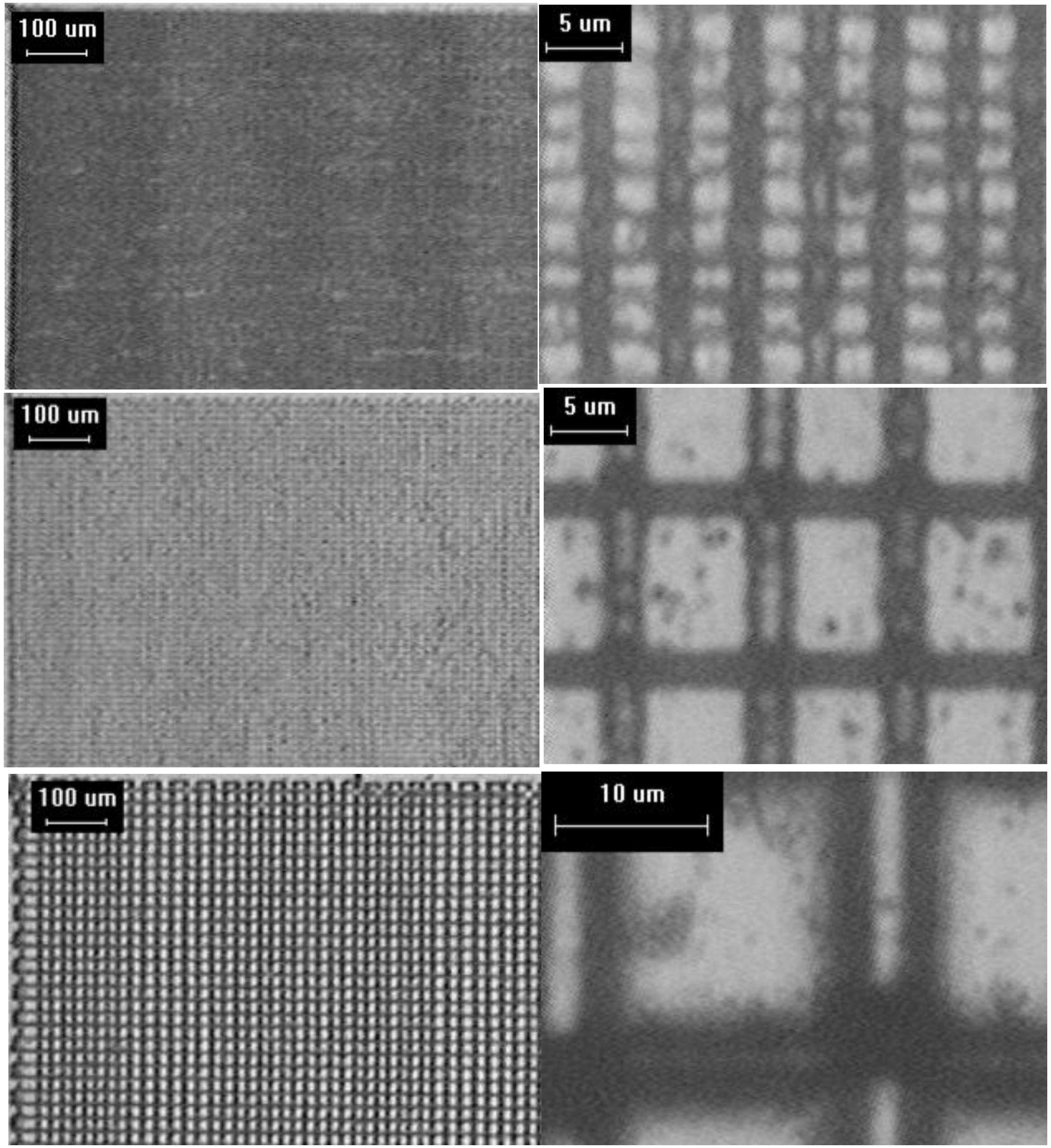
microstructuring polymer: super hydrophobic surface



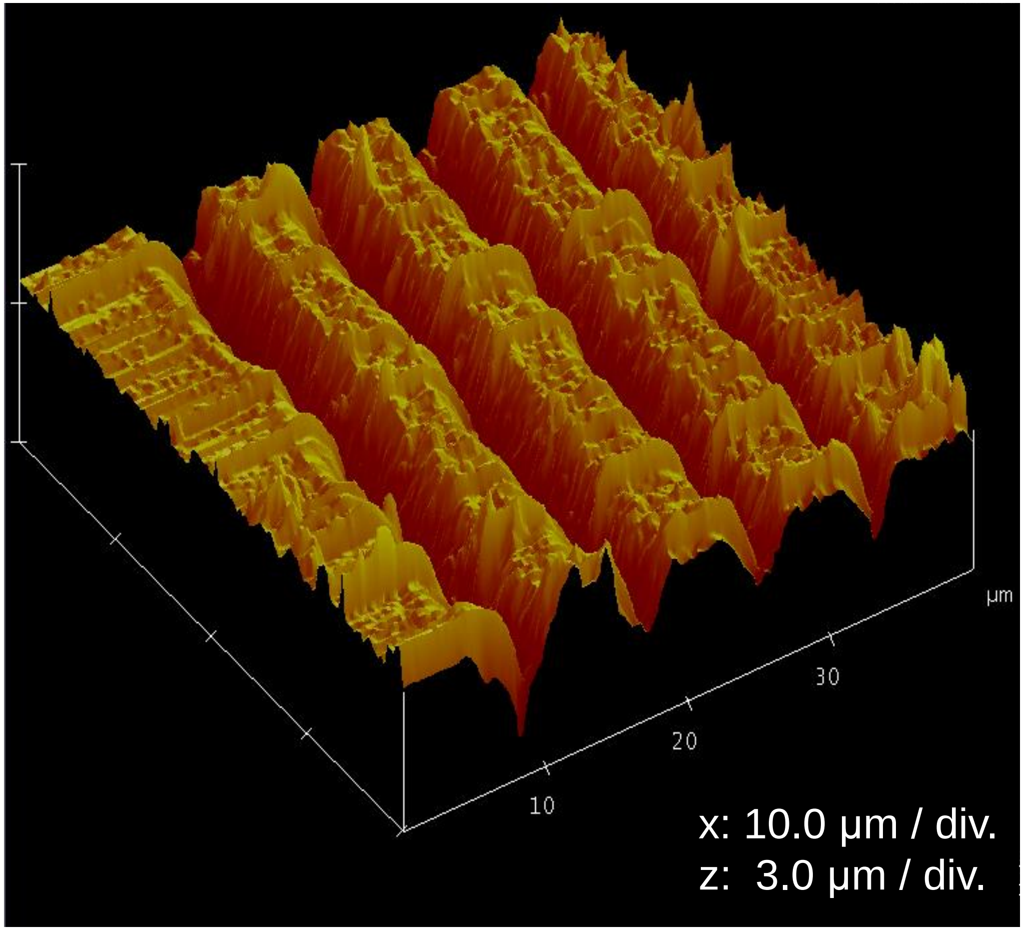


M.R. Cardoso and C. R. Mendonca

microstructuring polymer

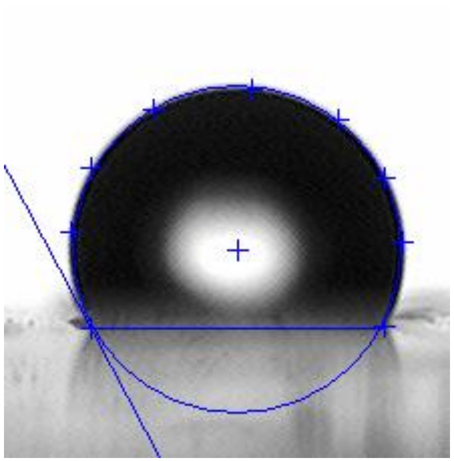


microstructuring polymer



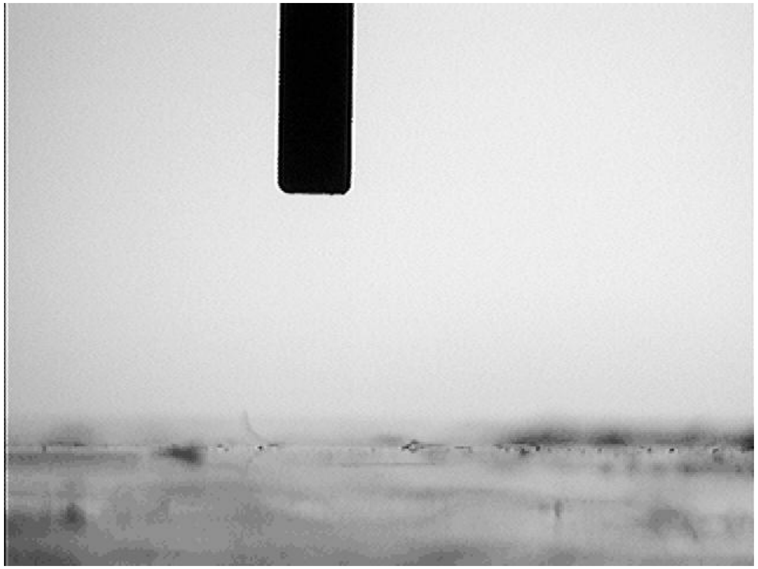
width and depth control

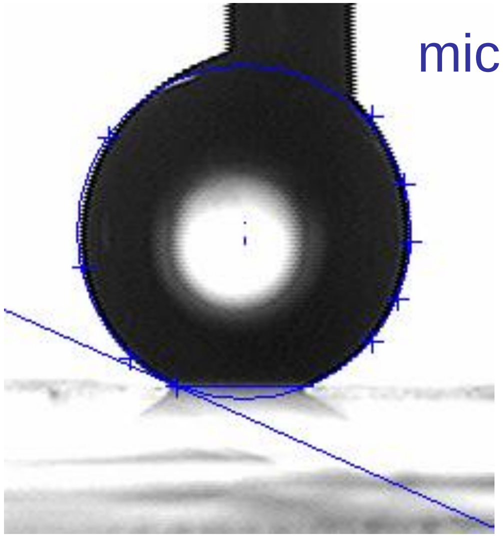
microstructuring polymer



flat surface

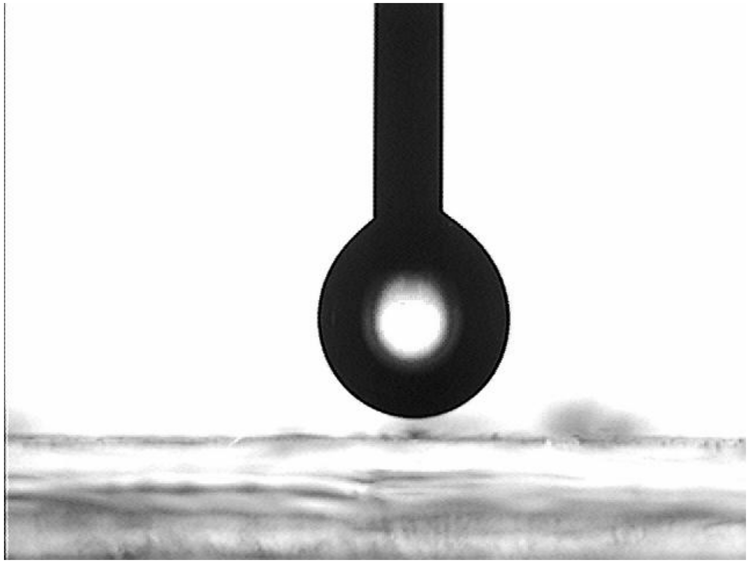
$\theta = 118^o$





microstructured surface

$\theta = 160^o$



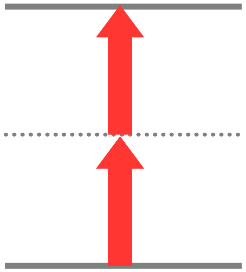
2

Two-photon polymerization

Monomer + Photoinitiator $\rightarrow$ *Polymer*

light

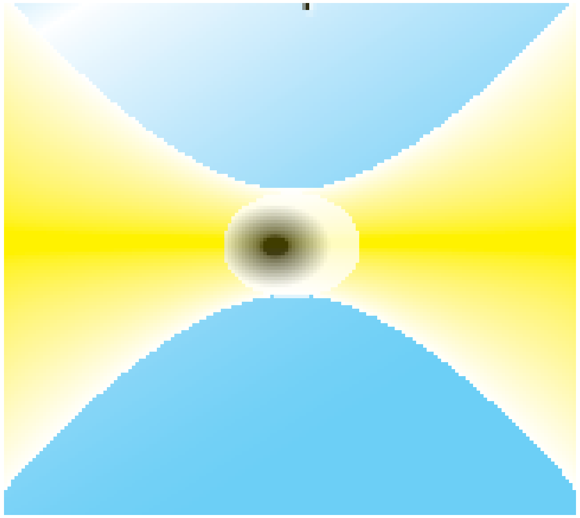
Photoinitiator is excited by ***two-photon absorption***



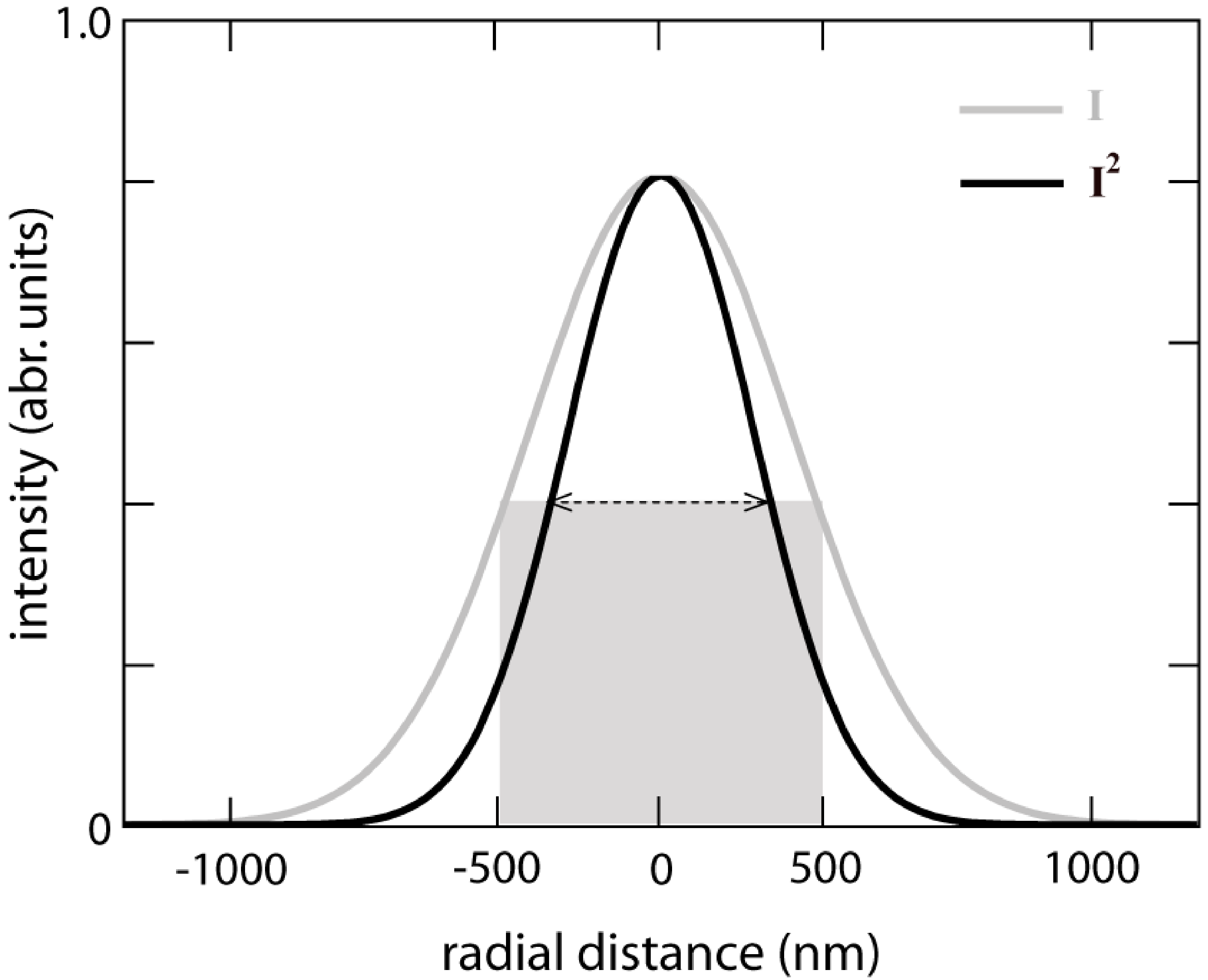
$$R_{2PA} \propto I^2$$

The polymerization is confined to the focal volume.

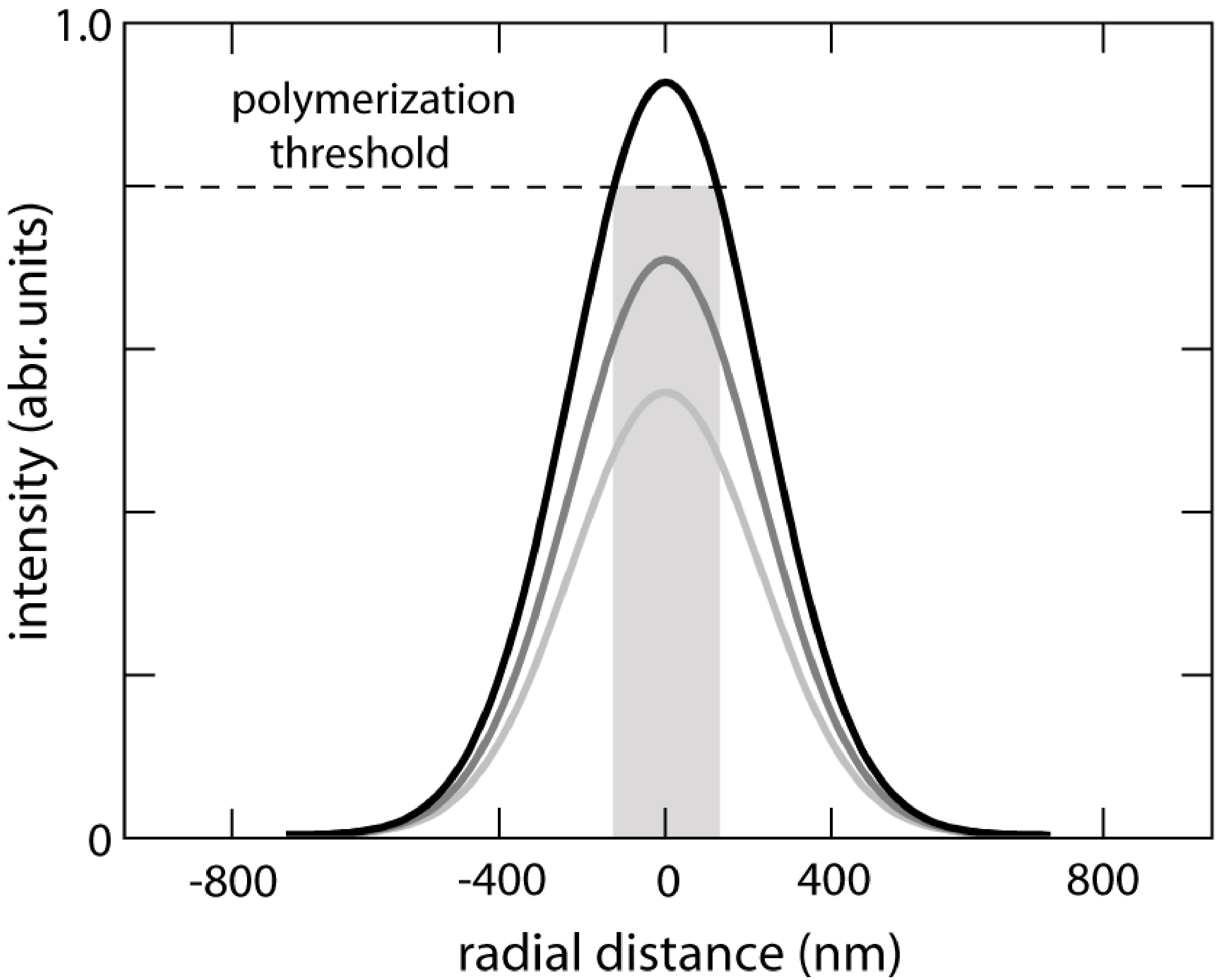
High spatial resolution



Two-photon polymerization

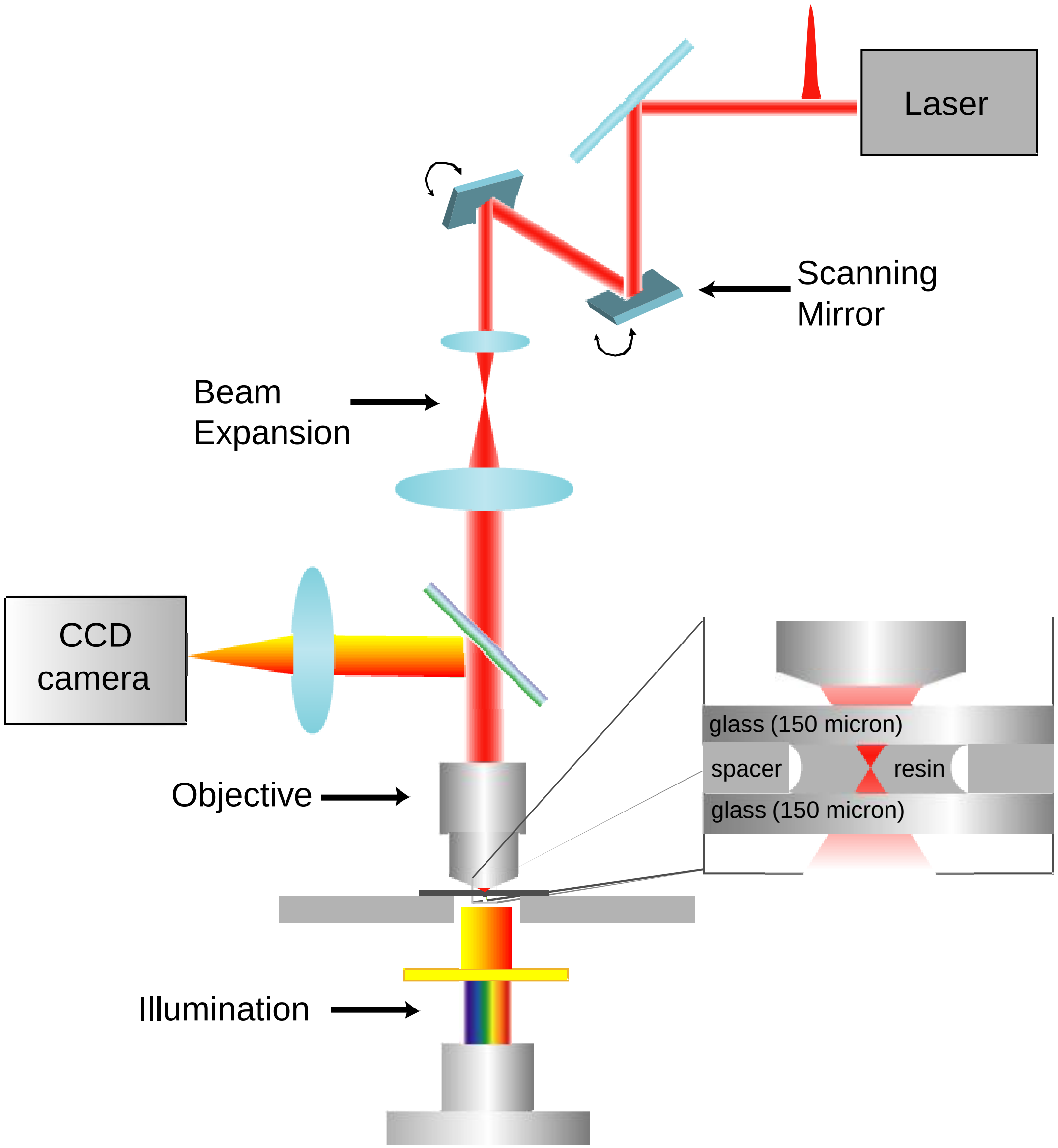


Two-photon polymerization



even higher spatial resolution

Two-photon polymerization setup



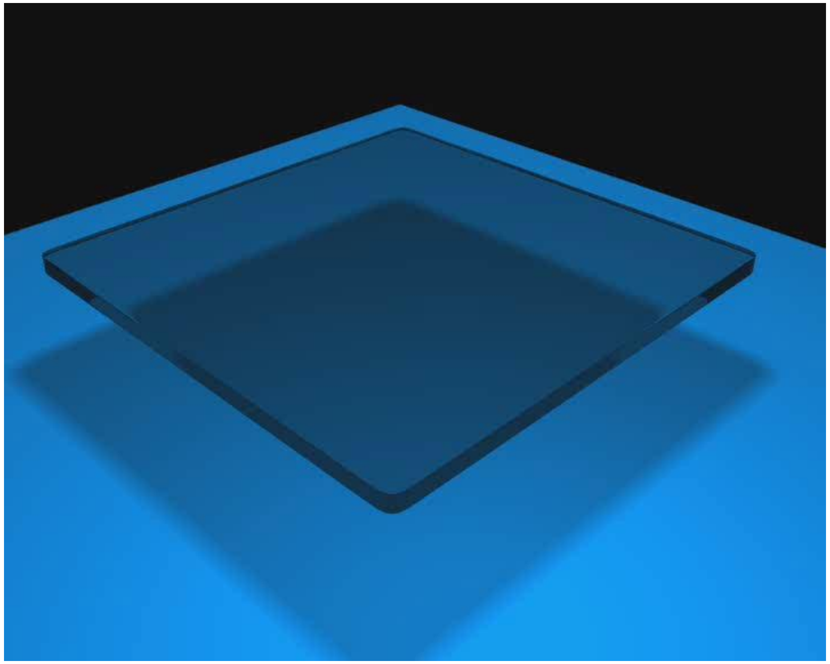
Ti:sapphire laser oscillator

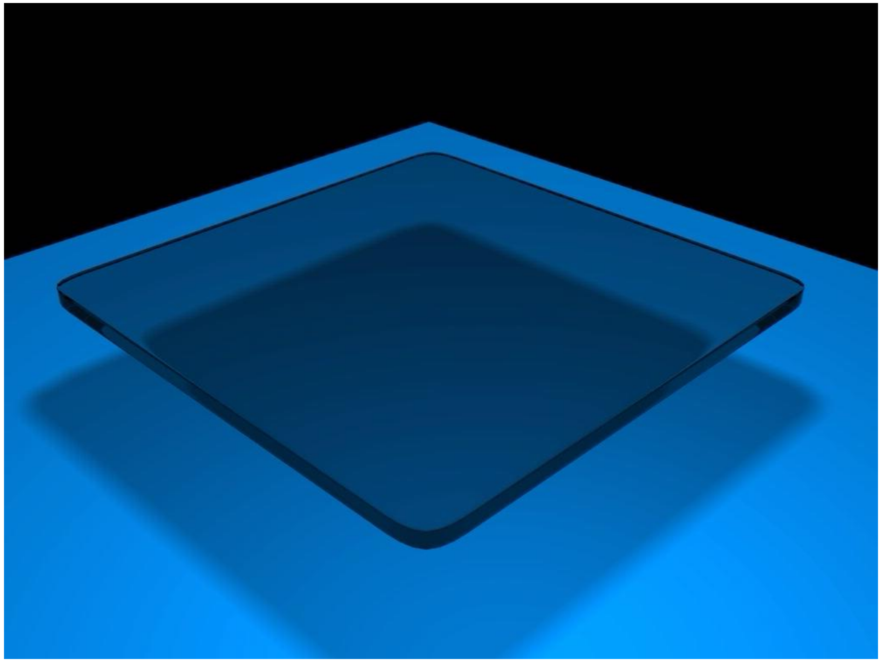
- 130 fs
- 800 nm
- 76 MHz
- 20 mW

Objective

40 x
0.65 NA

Two-photon polymerization

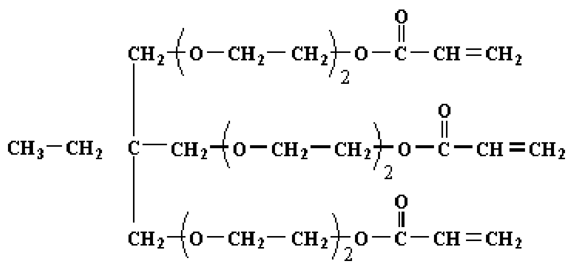




Resin Preparation

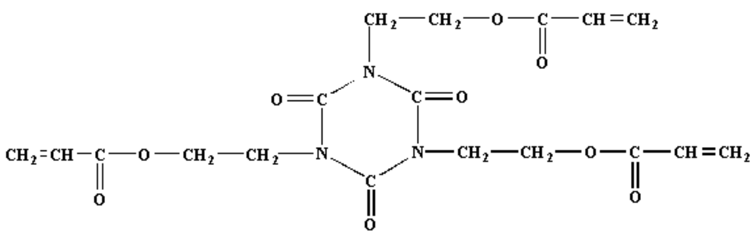
Monomers

SR499



reduces the shrinkage upon polymerization

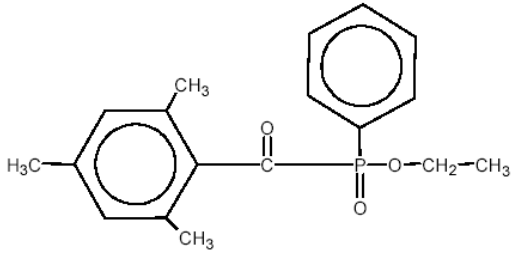
SR368



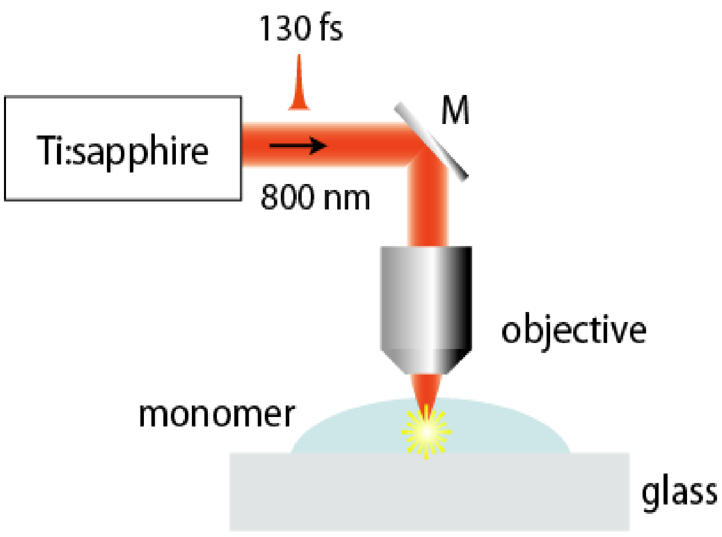
gives hardness to the polymeric structure

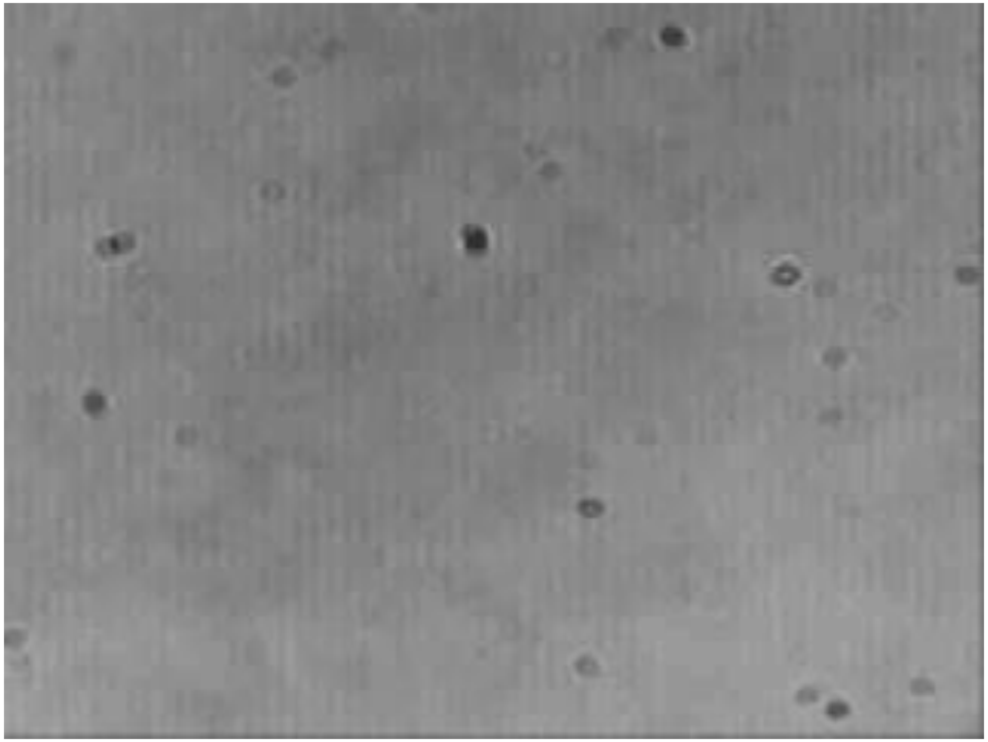
Photoinitiator

Lucirin TPO-L

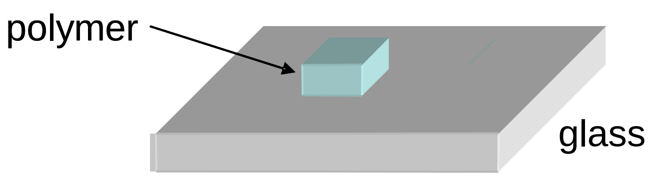


Two-photon polymerization

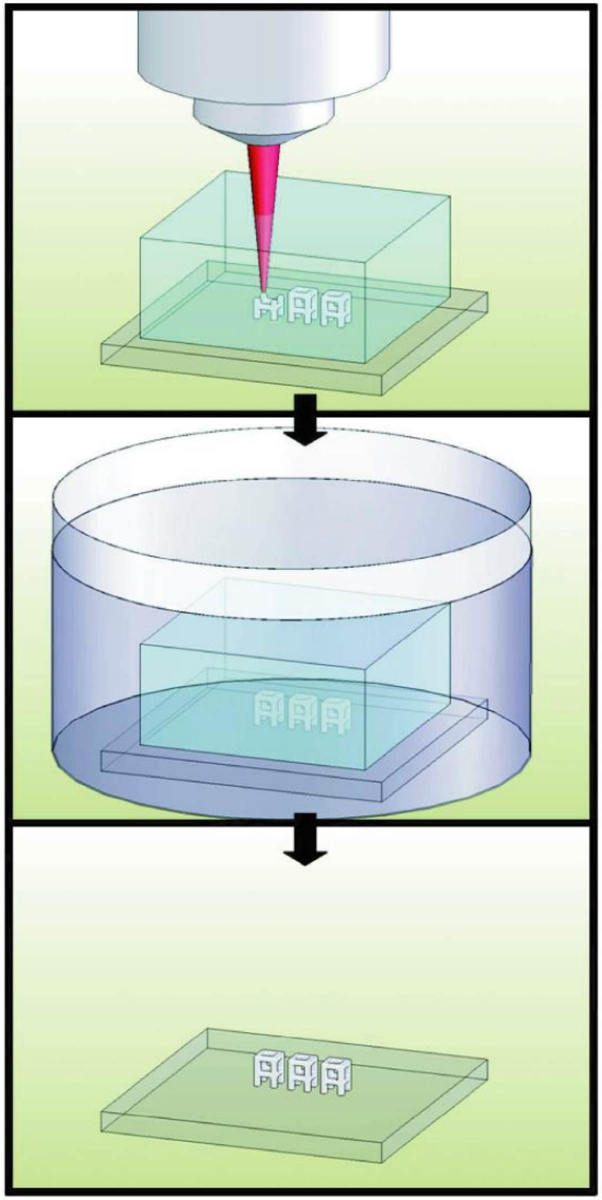




30 µm x 30 µm x 12 µm cube

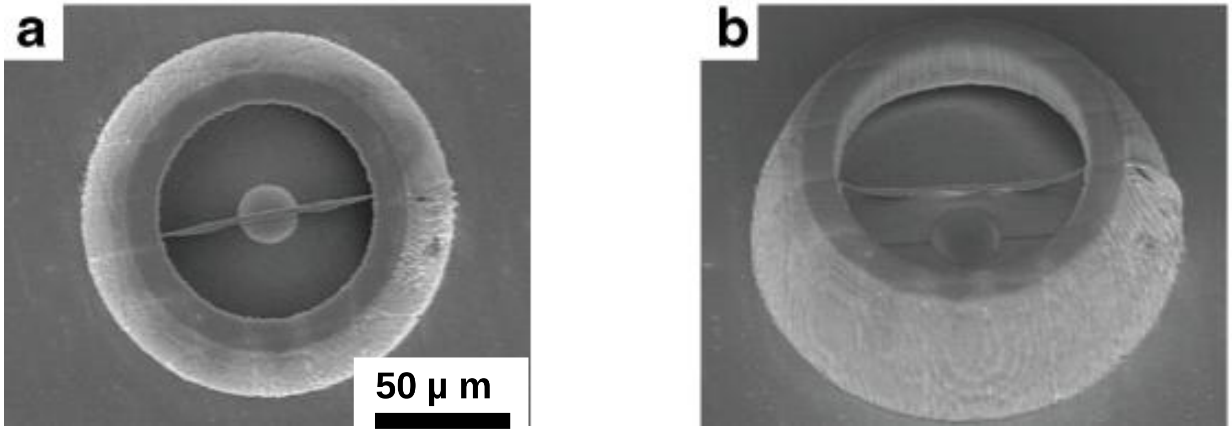


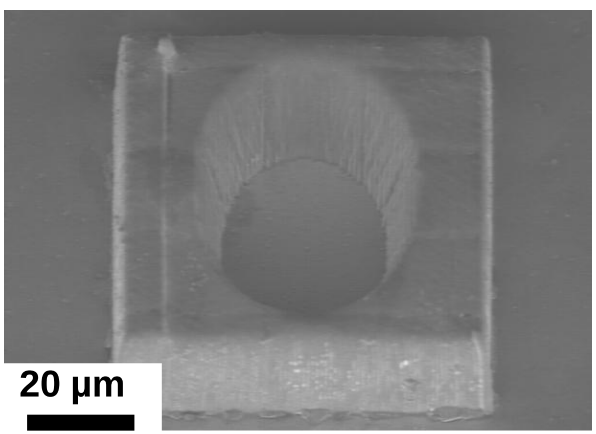
Two-photon polymerization

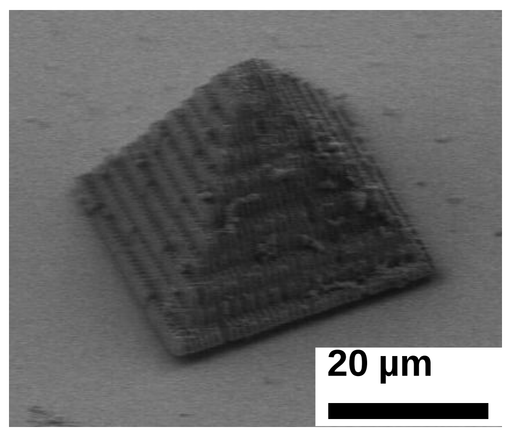


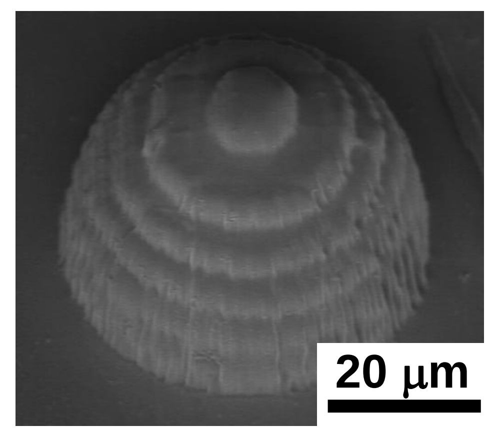
After the fabrication, the sample is immersed in ethanol to wash away any unsolidified resin and then dried

Microstructures fabricated by two-photon polymerization

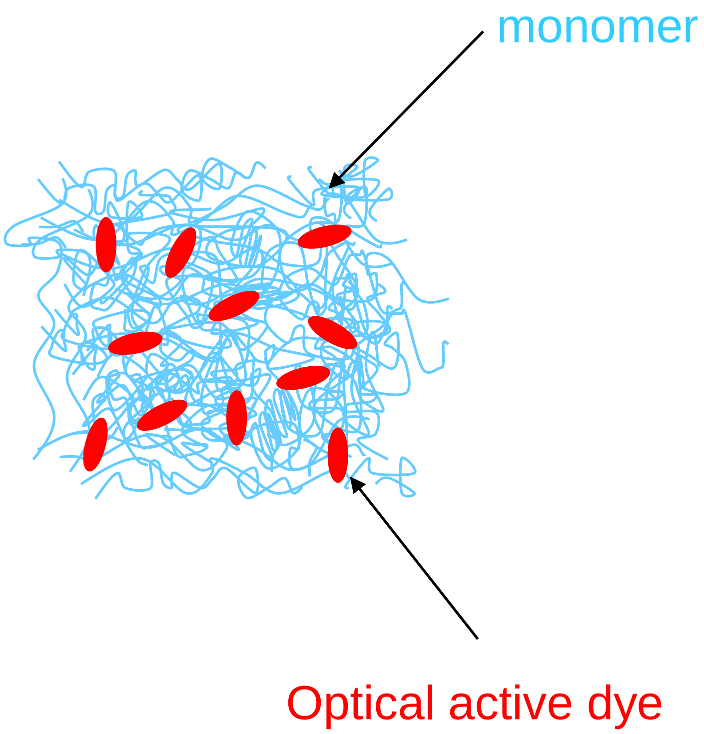


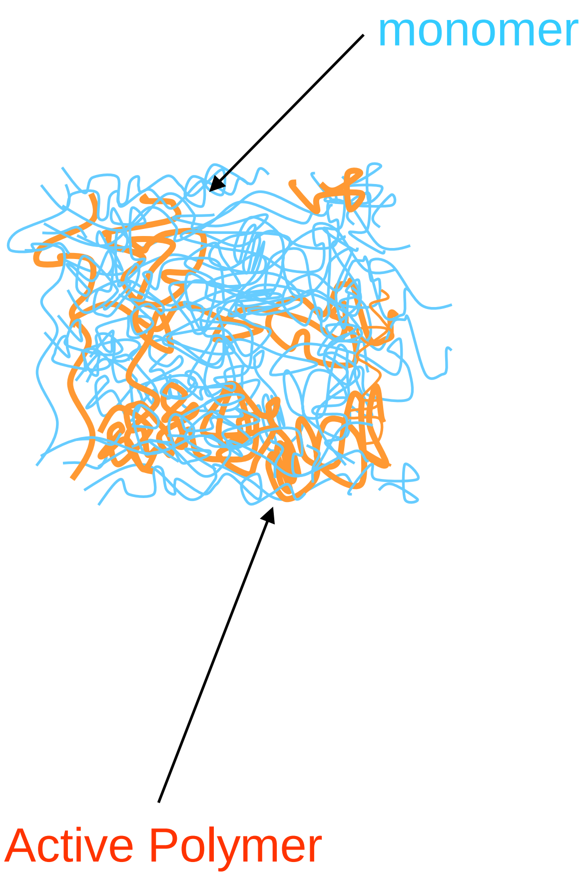






Microstructures containing active compounds





Applications of two-photon polymerization

Optics and Photonics

Doping microstructures with organic molecules and metals

- fluorescence
- birefringence
- conductivity

Bio-applications

Fabrication using bio-compatible resins to biological applications

- tissue engineering scaffolds
- fabrication of microneedle
- cell study

Applications

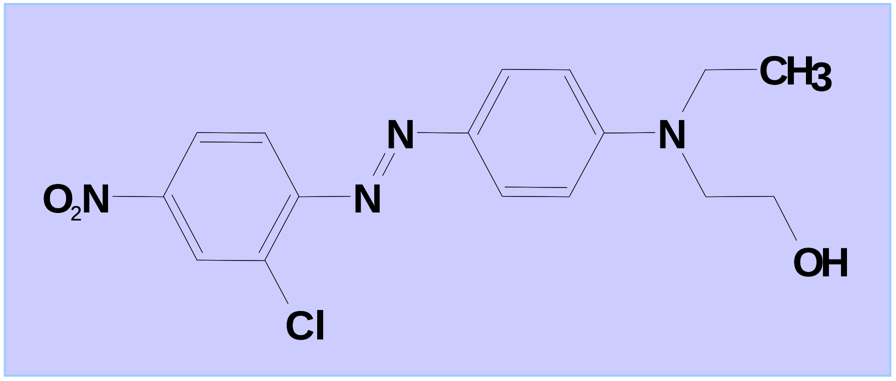
1) Optically induced birefringence

2) Emission and conduction

3) Biocompatible microstructure

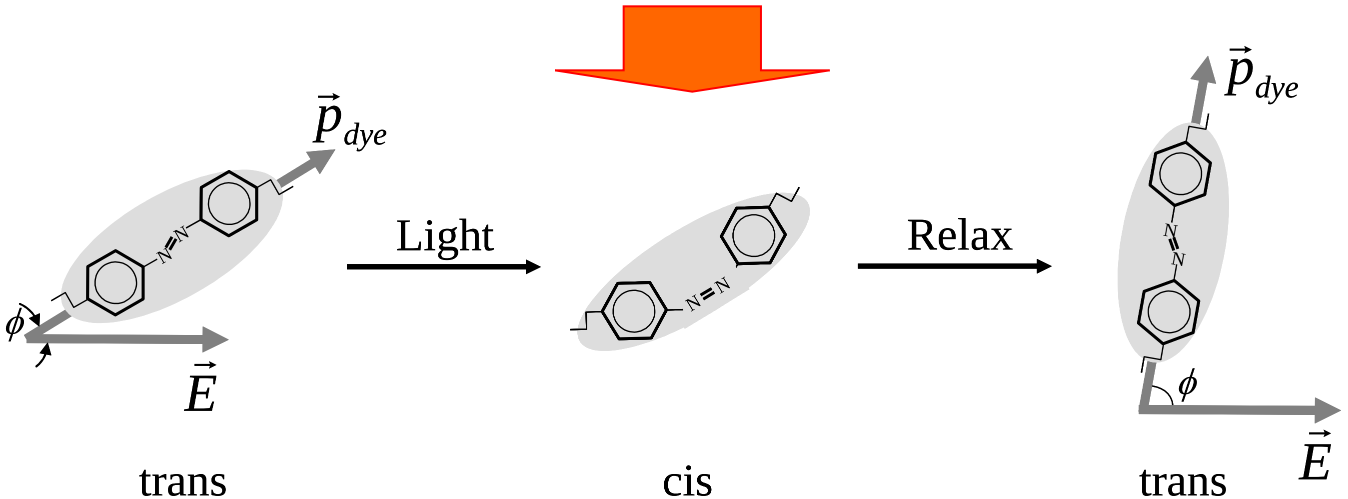
Birefringent microstructures

Incorporating the azodye DR13 into the microstructure

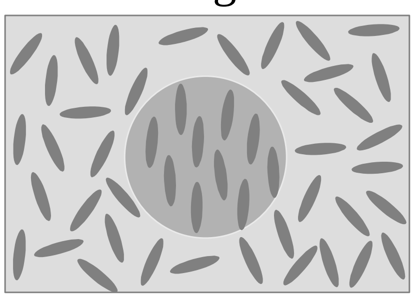


Birefringent microstructures

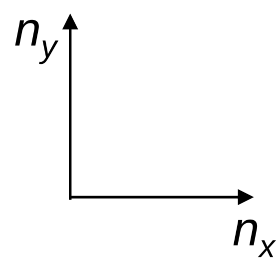
Molecular orientation by excitation with linearly polarized light



After alignment

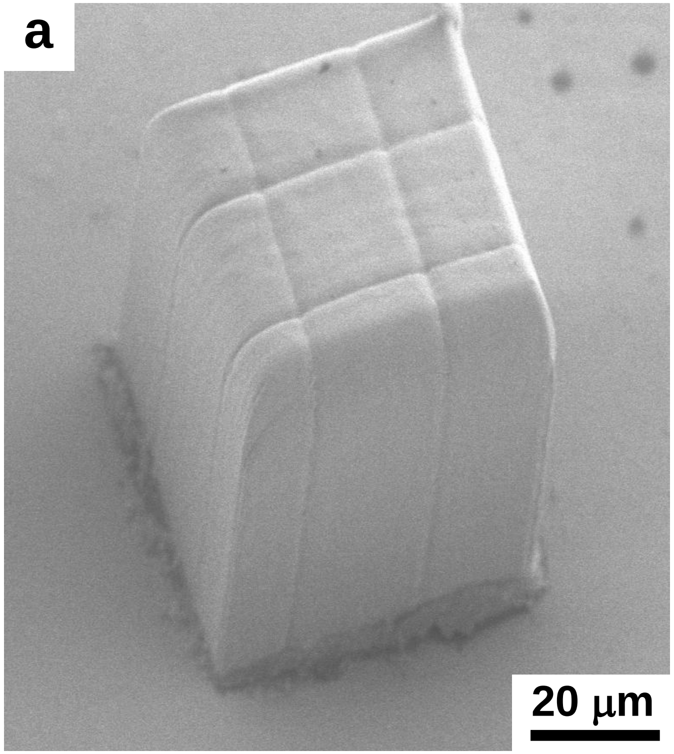


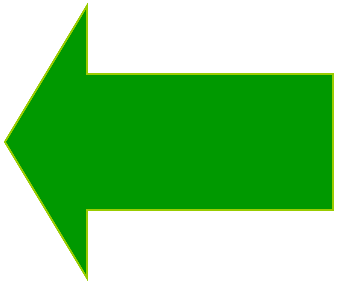
Optically Induced birefringence



$$n_y > n_x$$

Birefringent microstructures



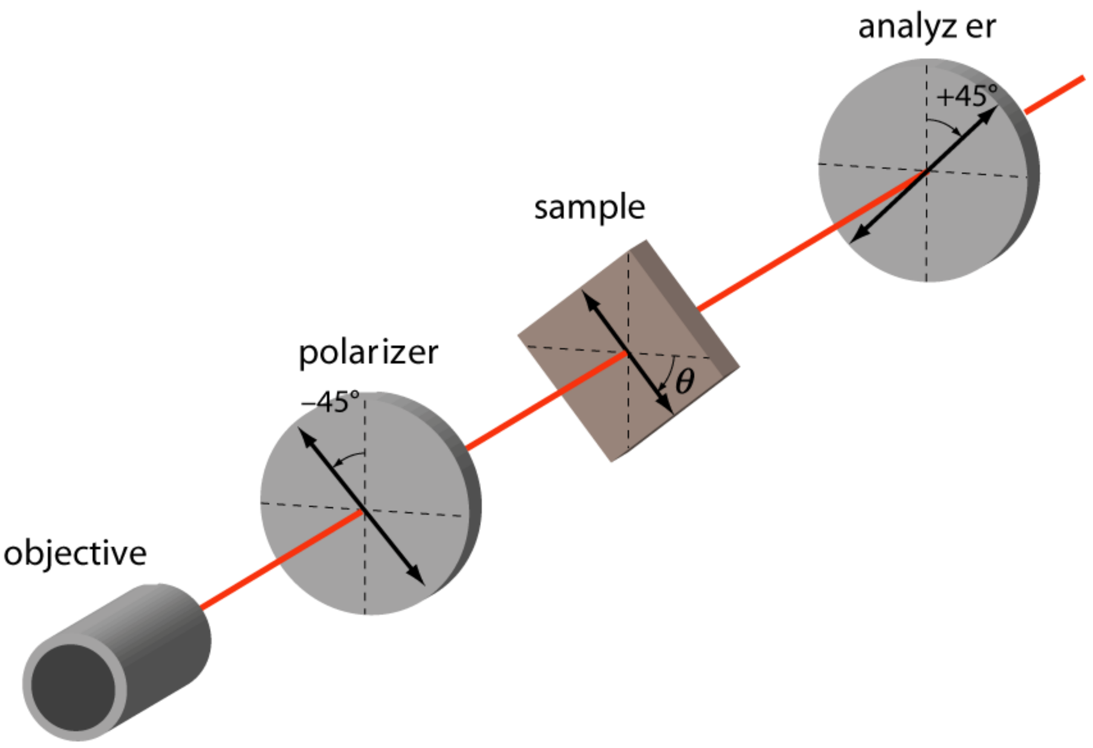


Ar+ ion laser irradiation

- 514.5 nm
- one minute
- intensity of 600 mW/cm^2

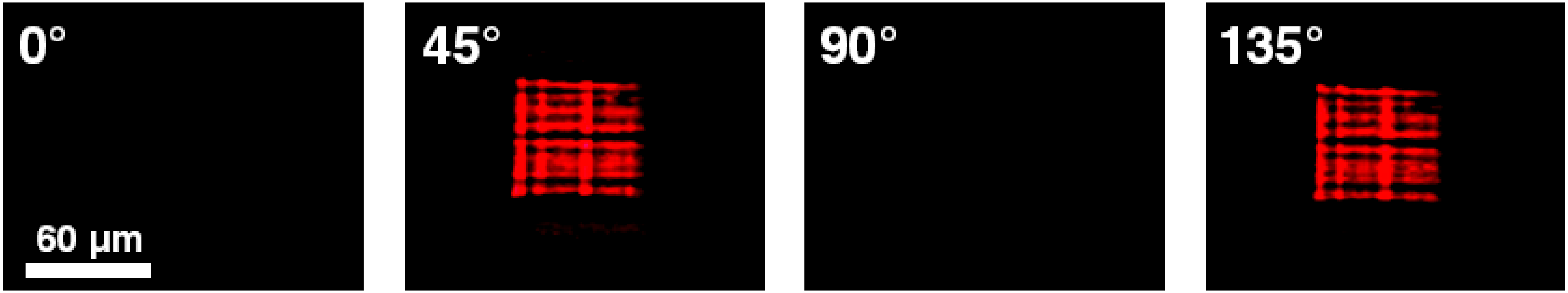
Birefringent microstructures

The sample was placed under an optical microscope between crossed polarizers and its angle was varied with respect to the polarizer angle



Birefringent microstructures

The structure is visible when the angle between the birefringence axis and the polarizer is an odd multiple of 45°

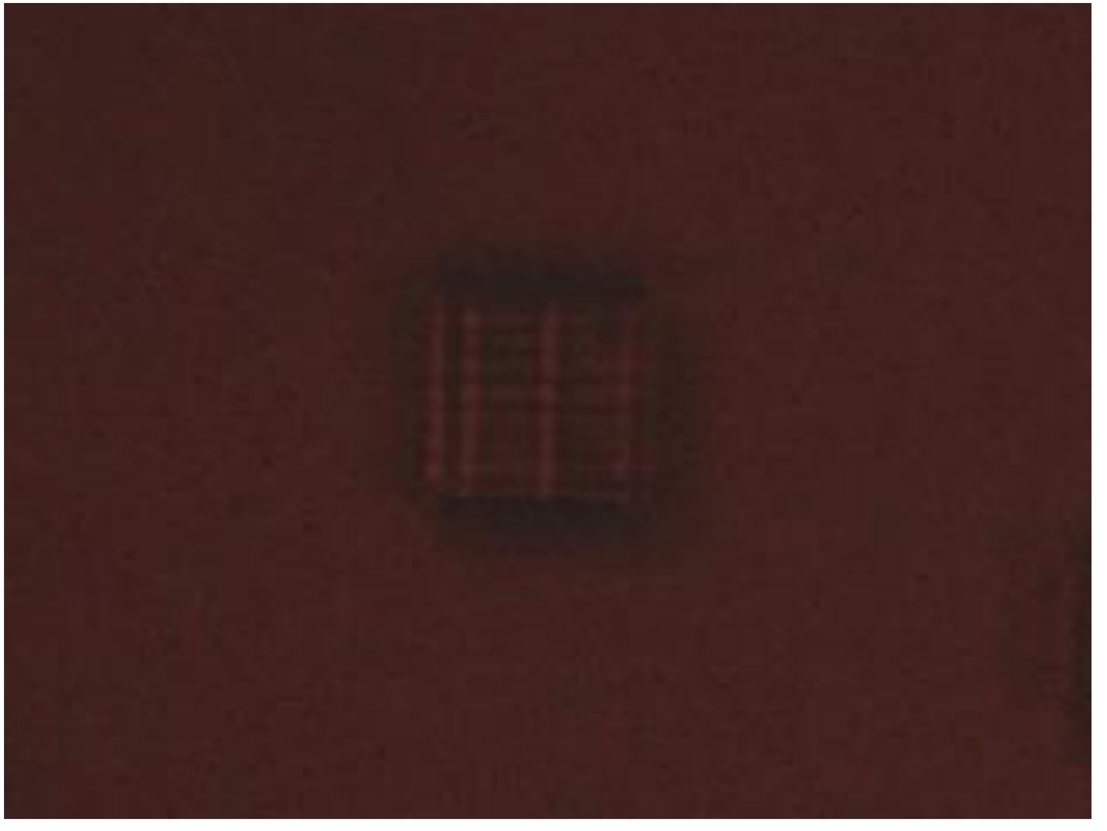


$\Delta n = 5x10^{-5}$

This birefringence can be completely erased by irradiating the sample with circularly polarized light.

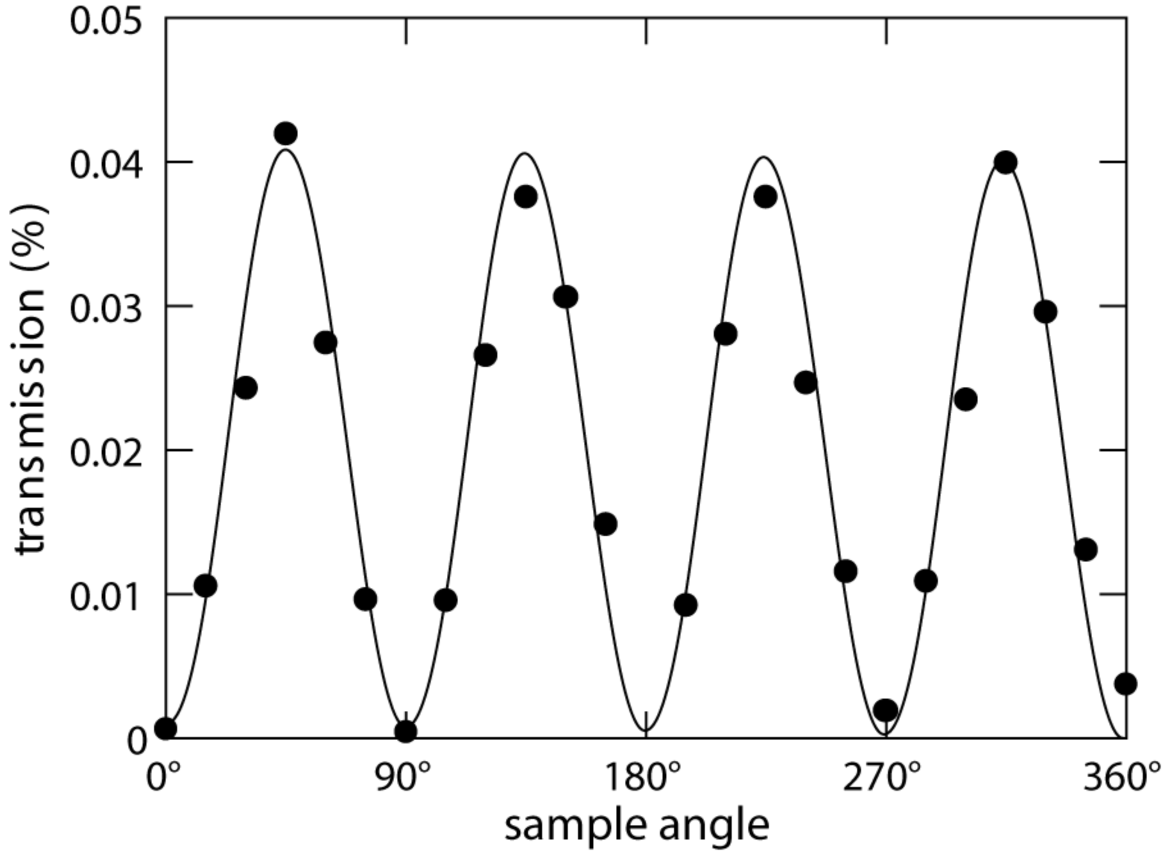
Applications: micro-optical switch, micro-optical storage

Birefringent microstructures



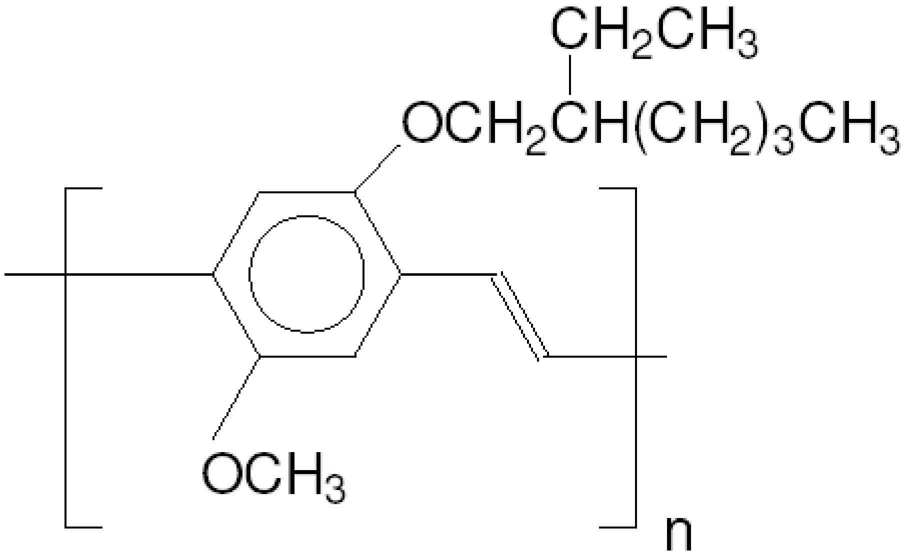
Birefringent microstructures

The structure is visible when the angle between the birefringence axis and the polarizer is an odd multiple of 45°



This birefringence can be completely erased by irradiating the sample with circularly polarized light.

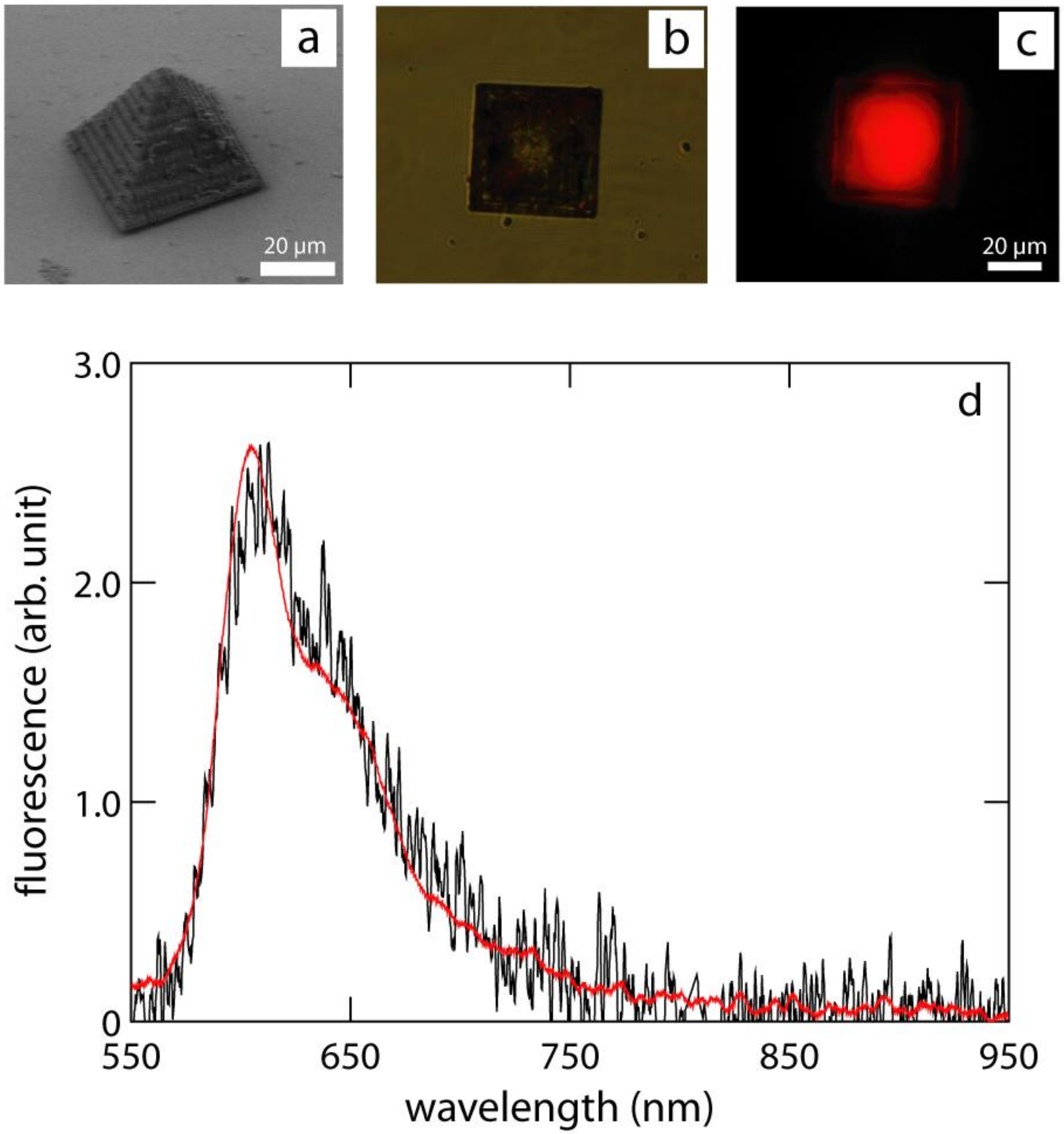
microstructure containing MEH-PPV



MEH-PPV

Fluorescence
Electro Luminescent
Conductive

microstructure containing MEH-PPV

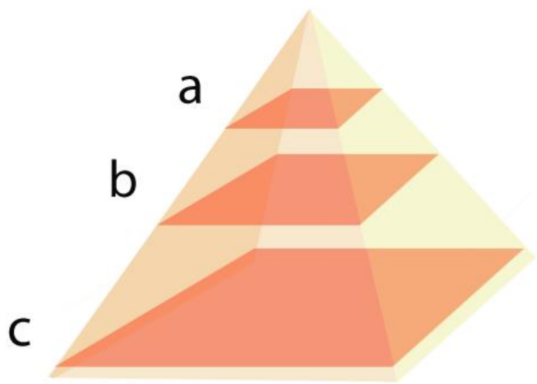


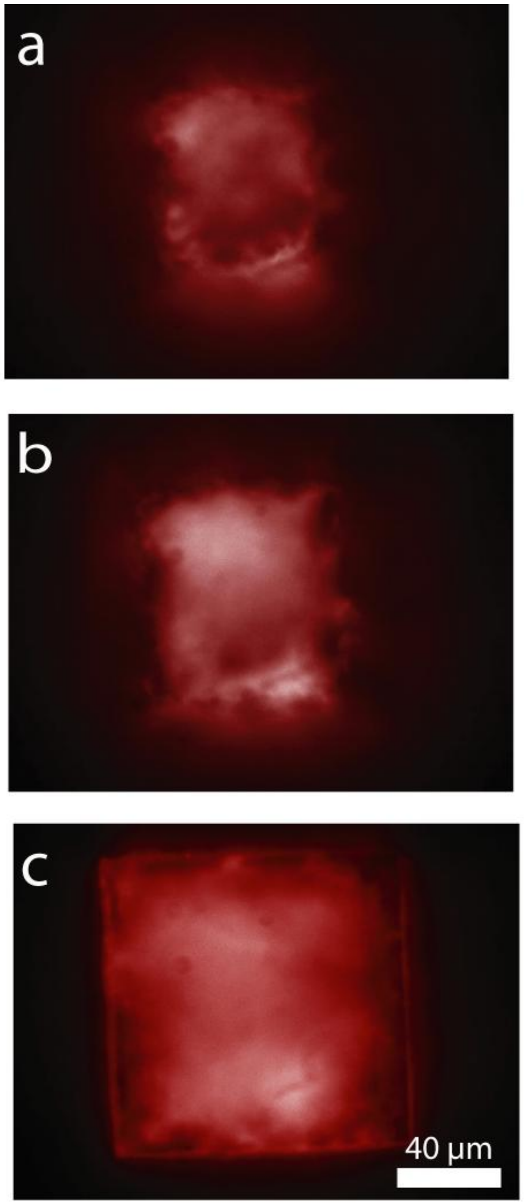
(a) Scanning electron microscopy

(b,c) Fluorescence microscopy of the microstructure with the excitation OFF (b) and ON (c)

(d) Emission of the microstructure (black line) and of a film with the same composition (red line)

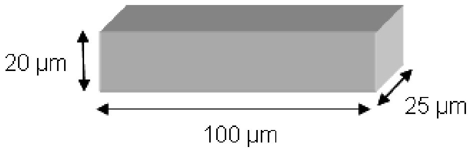
microstructure containing MEH-PPV

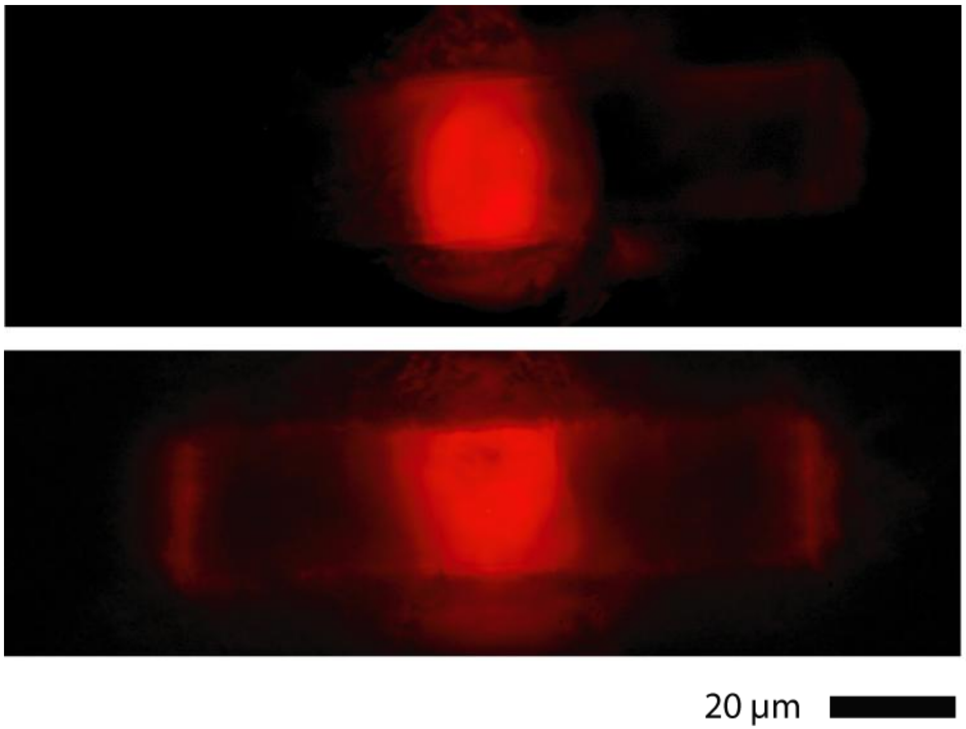


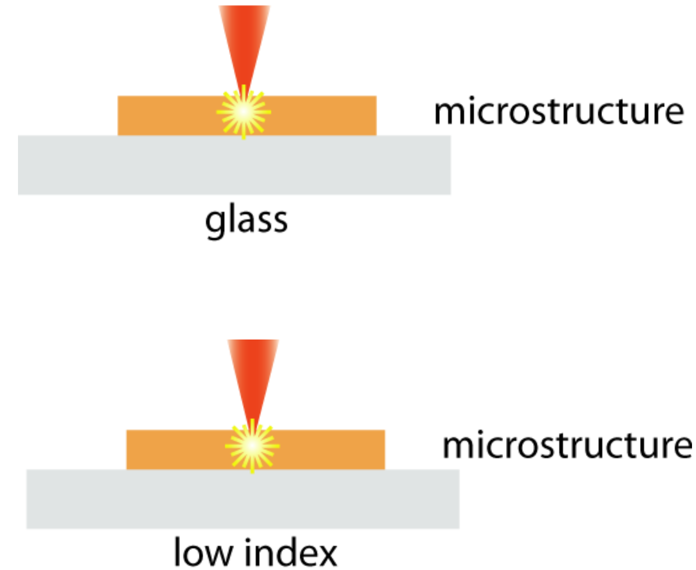


Fluorescent confocal microscopy images in planes separated by 16 μm in the pyramidal microstructure.

microstructure containing MEH-PPV



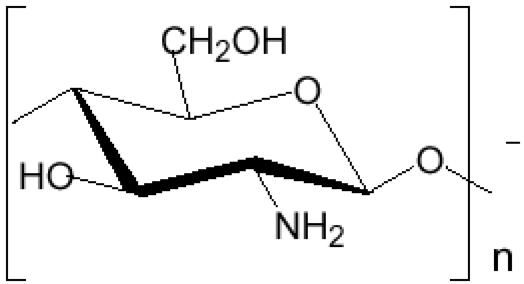




waveguiding of the microstructure fabricated on porous silica substrate (n= 1.185)

Applications: micro-laser; fluorescent microstructures; conductive microstructures

microstructures containing chitosan



Applications

biodegradability

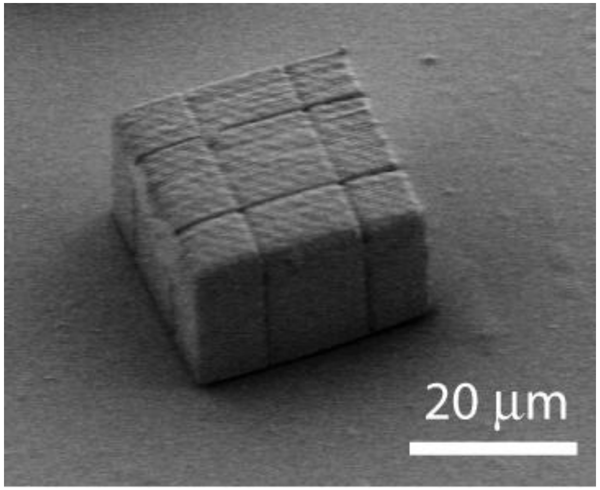
biocompatibility

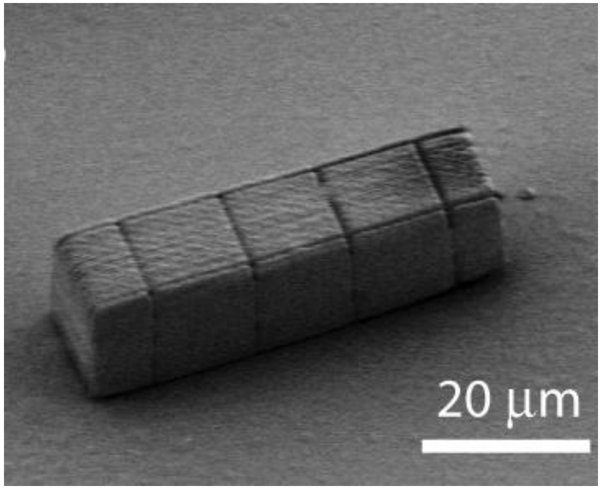
bone regeneration

drug-delivery

bactericide action

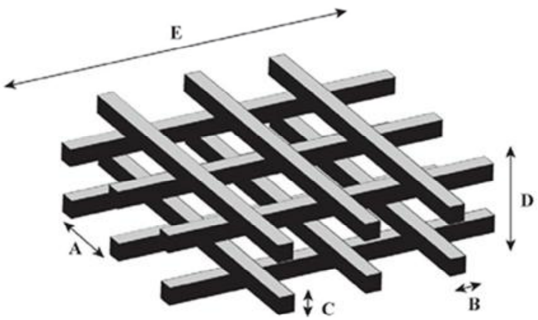
blood coagulation



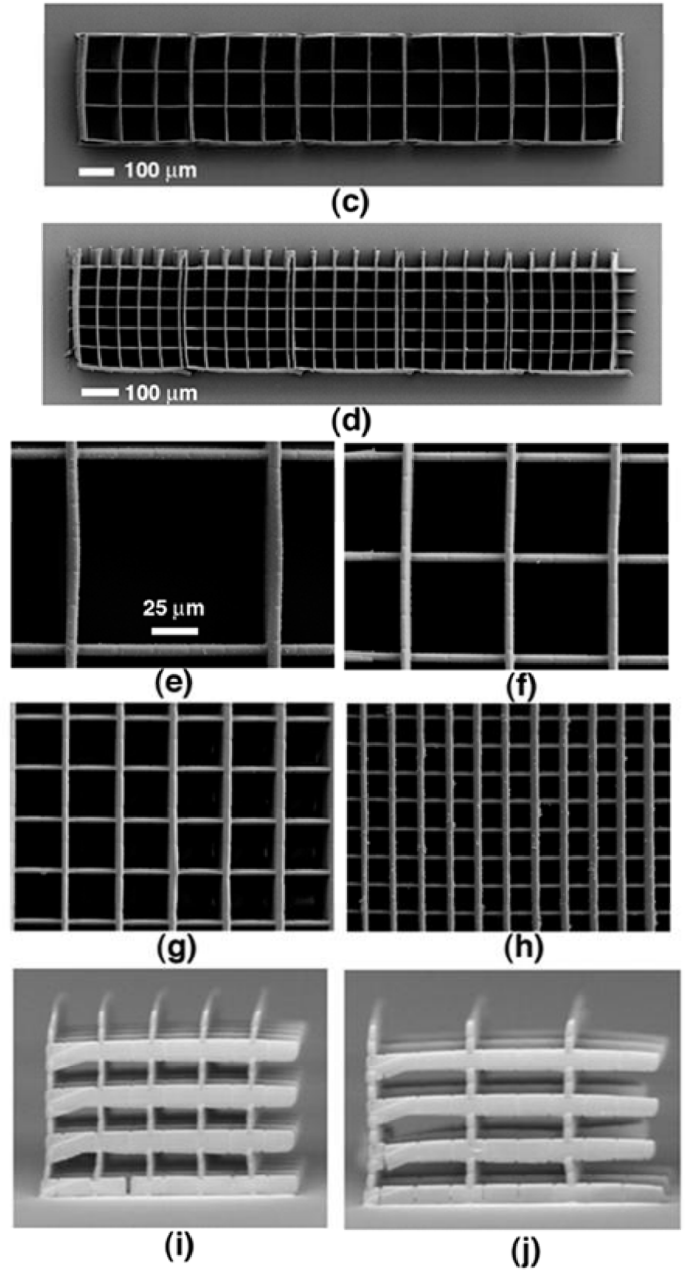


Microstructures show excellent integrity and good definition

3D cell migration studies in micro-scaffolds



schematic of the scaffold



SEM of the scaffolds

110 µm pore size

52 µm pore size

Top view

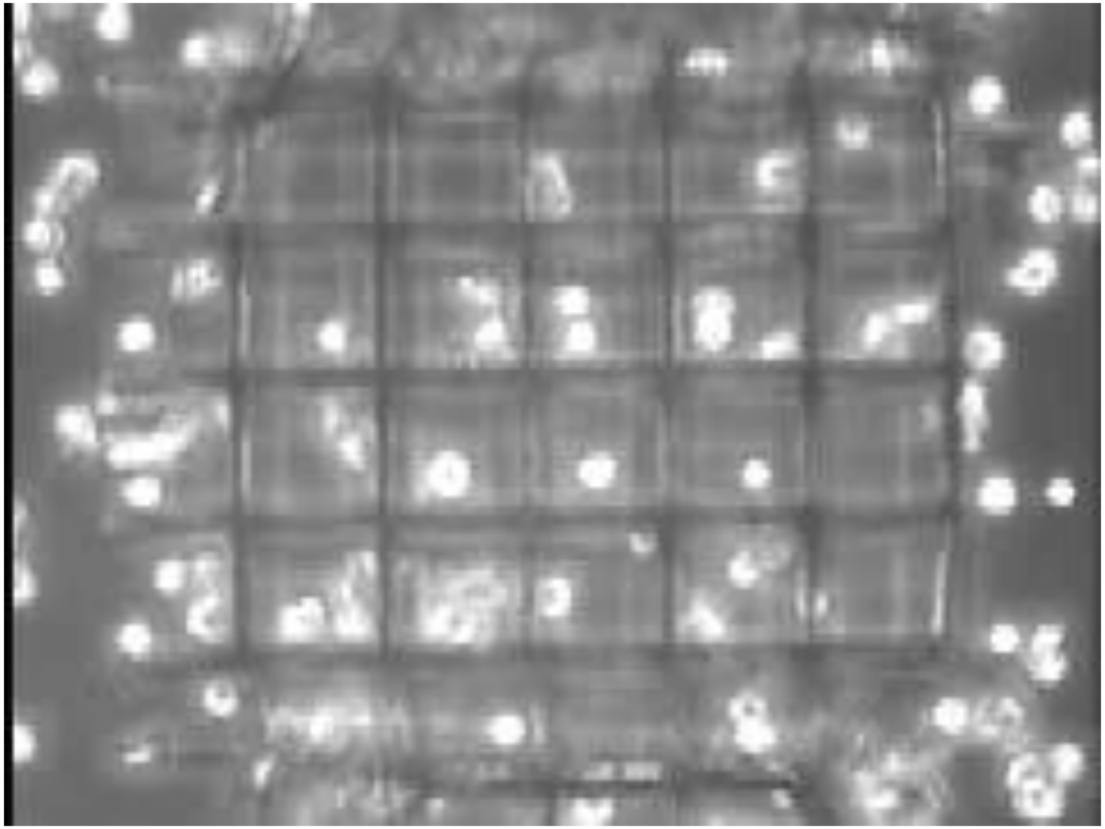
110, 52, 25, 12 µm pore size

Side view

25, 52 µm pore size

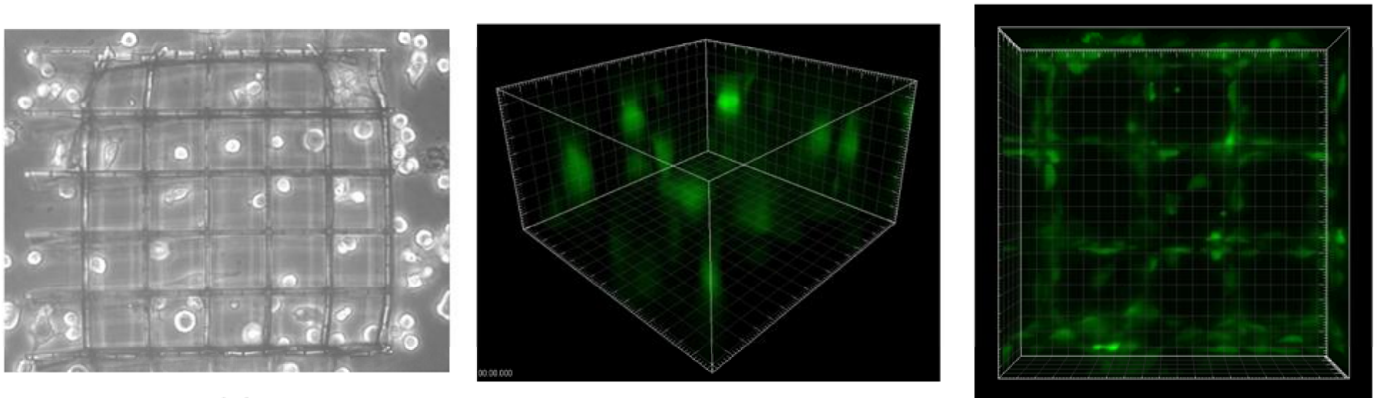
cell migration

50 μm pore size

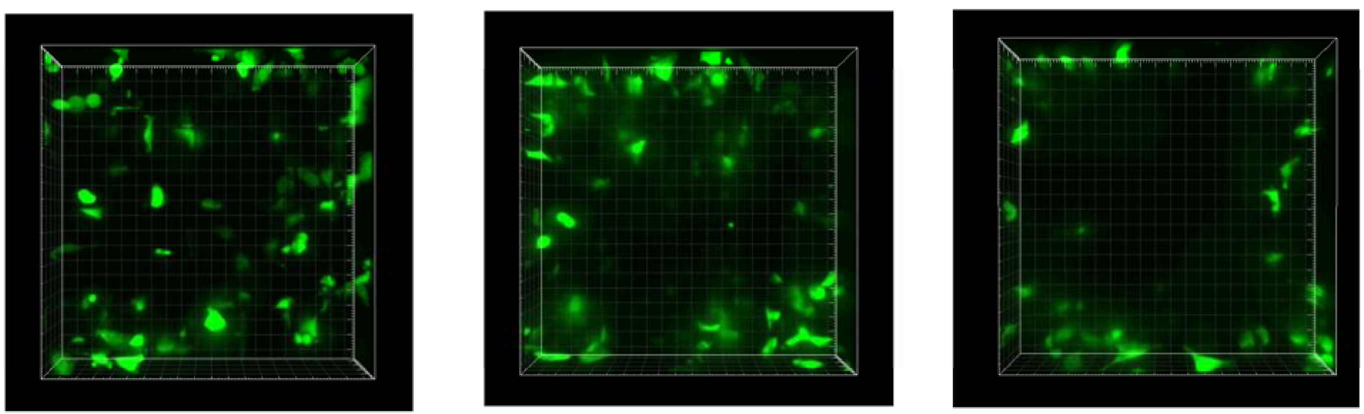


cell migration

50 μm pore size after 5 hours



(a) (b) (c)



(d) (e) (f)

c-d: 110, 52, 25 and 12 μm

Message

fs-microfabrication is a great tool for designing polymer-based devices

http://www.fotonica.ifsc.usp.br

http://www.photonics.ifsc.usp.br

Acknowledgments

National Science Foundation
Army Research Office
FAPESP, CNPq and CAPES

http://www.fotonica.ifsc.usp.br

http://www.photonics.ifsc.usp.br

Thank you !

http://www.fotonica.ifsc.usp.br

http://www.photonics.ifsc.usp.br