Photoaddressable Block Copolymers as Material for Volume Holographic Data Storage

Carsten Frenz, Michael Häckel, Lothar Kador,

Hans-Werner Schmidt

Makromolecular Chemistry and Experimental Physics

Bayreuther Institut für Makromolekülforschung (BIMF)
Universität Bayreuth, Germany

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Photoaddressable block copolymers

Motivation

Fundamental aspects

- control of multi-level order on different length scales
- manipulation on nanometer scale
- photochemistry in confined geometries

Application possibilities

- holographic data storage

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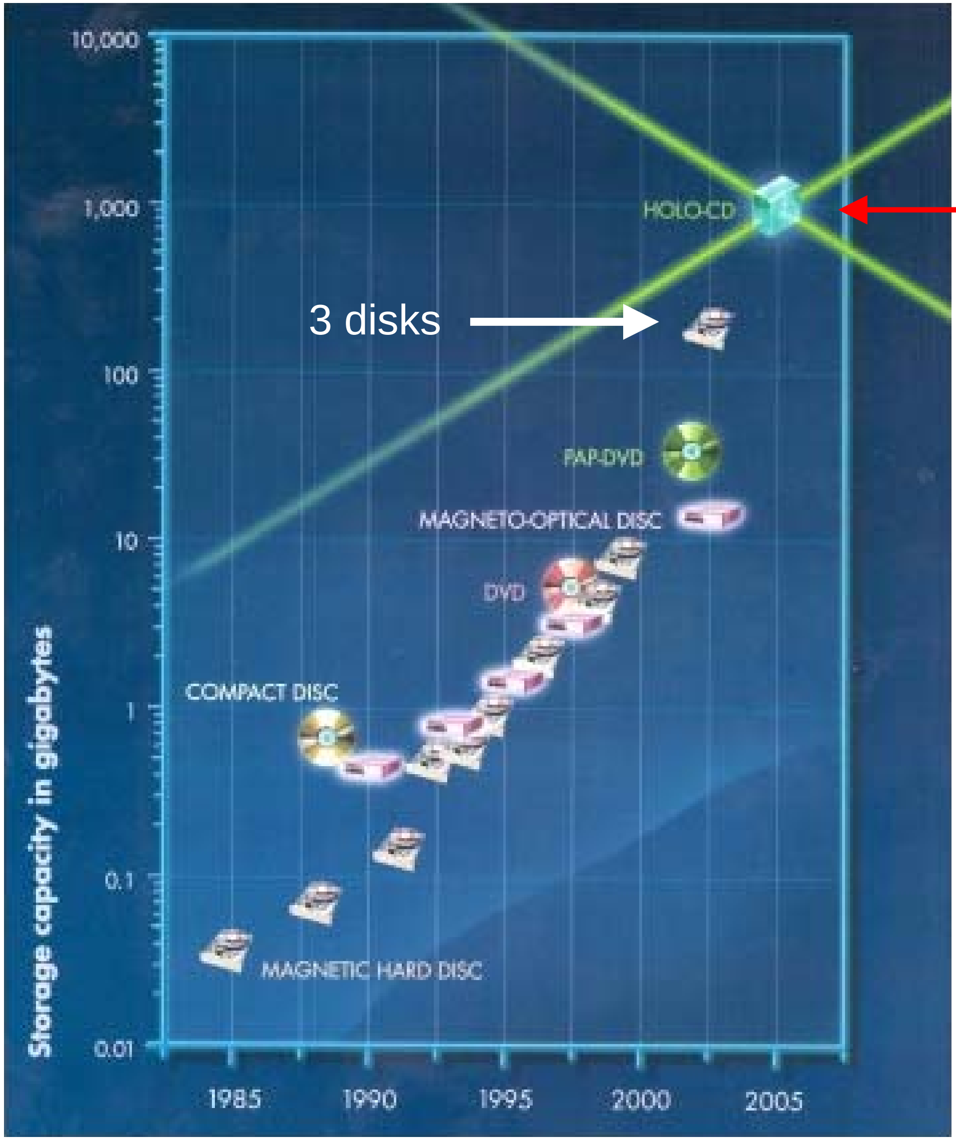
Development of storage capacity



3-dimensional
"Volume holographic storage"

2-dimensional
+ stacking

Bayer Research 10, September 1998
modified

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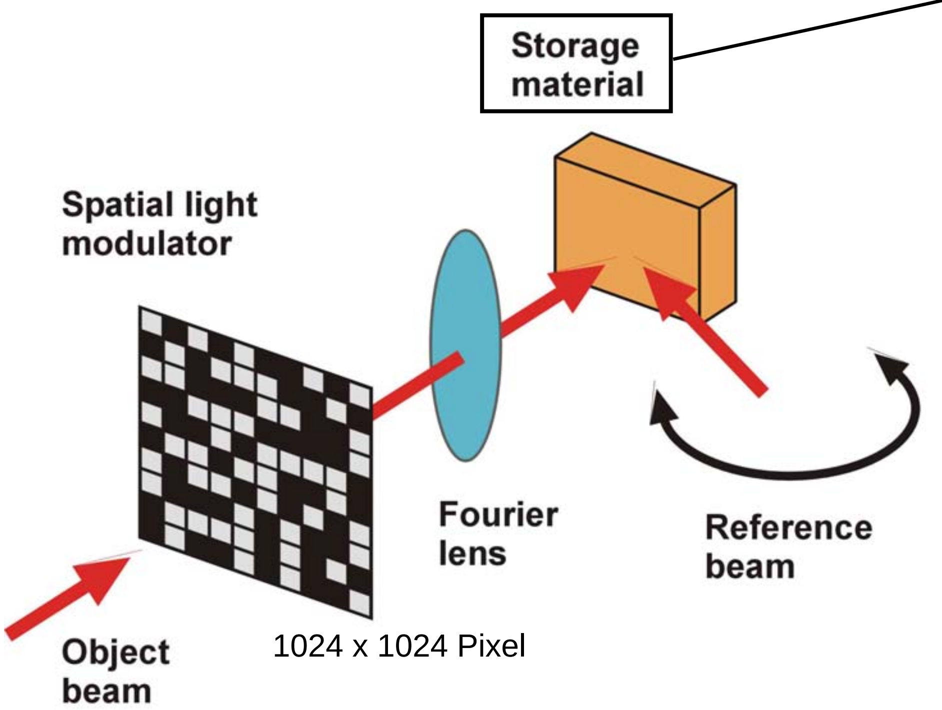
Volume holographic digital data storage

Recording principle



Irreversible materials:
- photopolymer (Polaroid)
- PQ doped PMMA

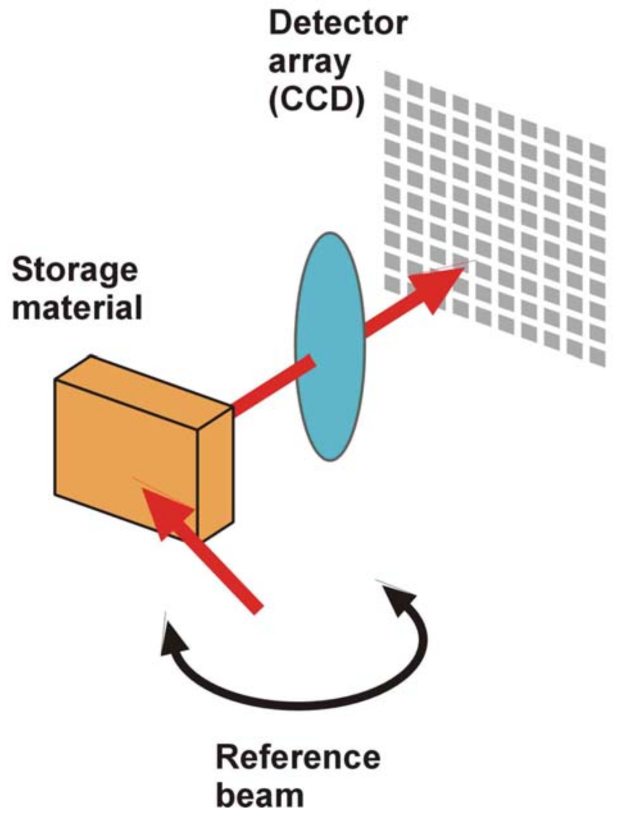
Reversible materials:
- $LiNbO_3$
- $LiNbO_3$:Fe
- photoaddressable polymers

PQ: phenantrenequinone

J. Ashley et.al., IBM J. Research Development 44(3) 2000, modified

Volume holographic digital data storage

Reading principle



J. Ashley et.al., IBM J. Research Development 44(3) 2000, modified

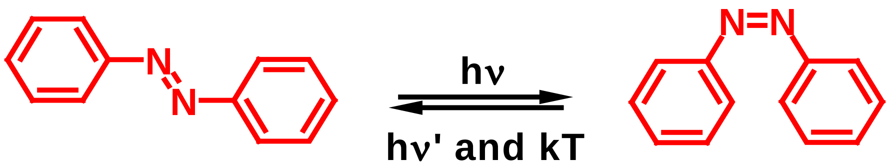
Optical data storage

Material requirements for volume holographic storage

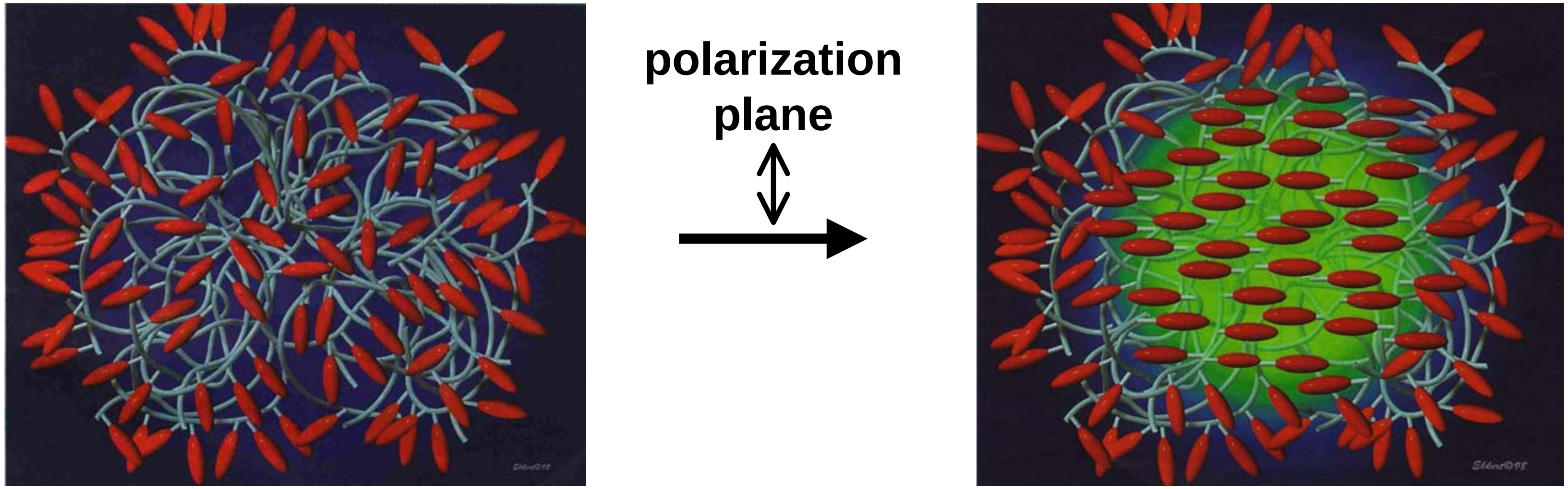
- photoeffect (local modulation of refractive index)
- sufficient high Δn
- excellent optical quality throughout the sample
- sample thickness of 1–2 mm (hologram multiplexing)
- optical density 0.5 - 0.7 (utilizing of total volume)
- low response time (milliseconds)
- long-term stability of the stored information

Photoaddressable polymers

Light-induced isomerization



Azo-dye containing side-group polymers

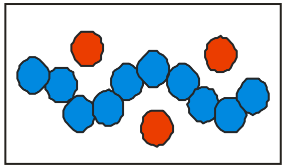


source: BAYER AG

⇨ chromophores orient perpendicular to the polarization plane

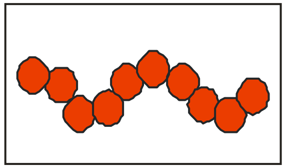
M. Eich, J.H. Wendorff, H. Ringsdorf, H.-W. Schmidt, Makromol.Chem. **186**, 2639 (1985). BAYER-research, 36 (1999).
R.H. Berg, S. Hvilsted, et al., Nature **383**, 505 (1996). X. Meng, A. Natansohn, et al., Polymer **38** (11), 2677 (1997). And others.

Polymer systems for holographic storage



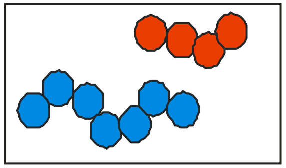
- **Doped polymers**

  migration, macrophase separation, stability



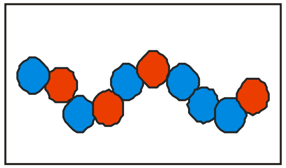
- **Homopolymers**

  too high optical density, formation of surface gratings



- **Polymer blends**

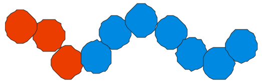
  macrophase separation results in bulk scattering



- **Statistical copolymers**

  loss of cooperative effect

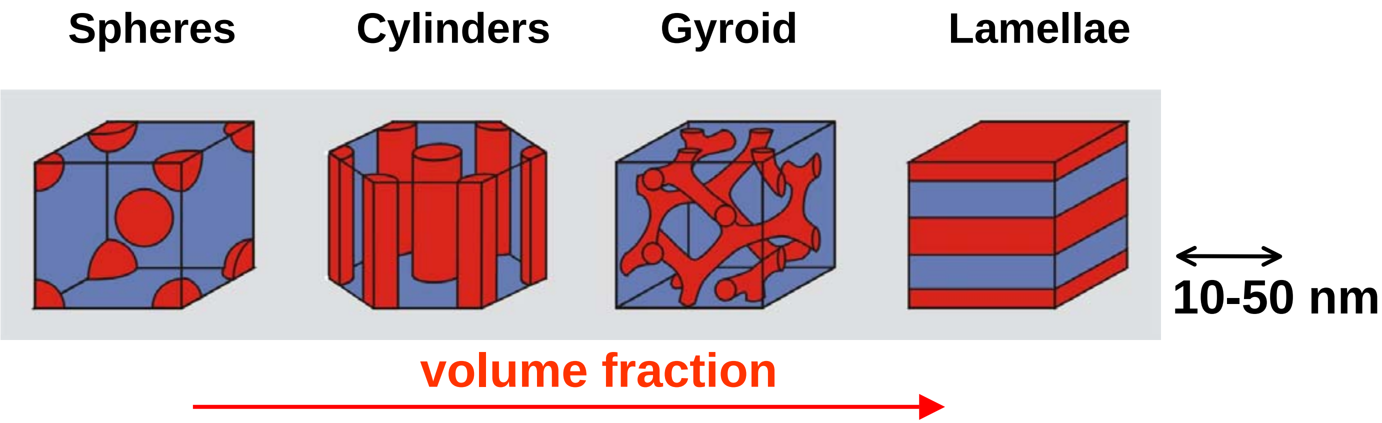
Block copolymers



Photoaddressable block copolymers

Block copolymers

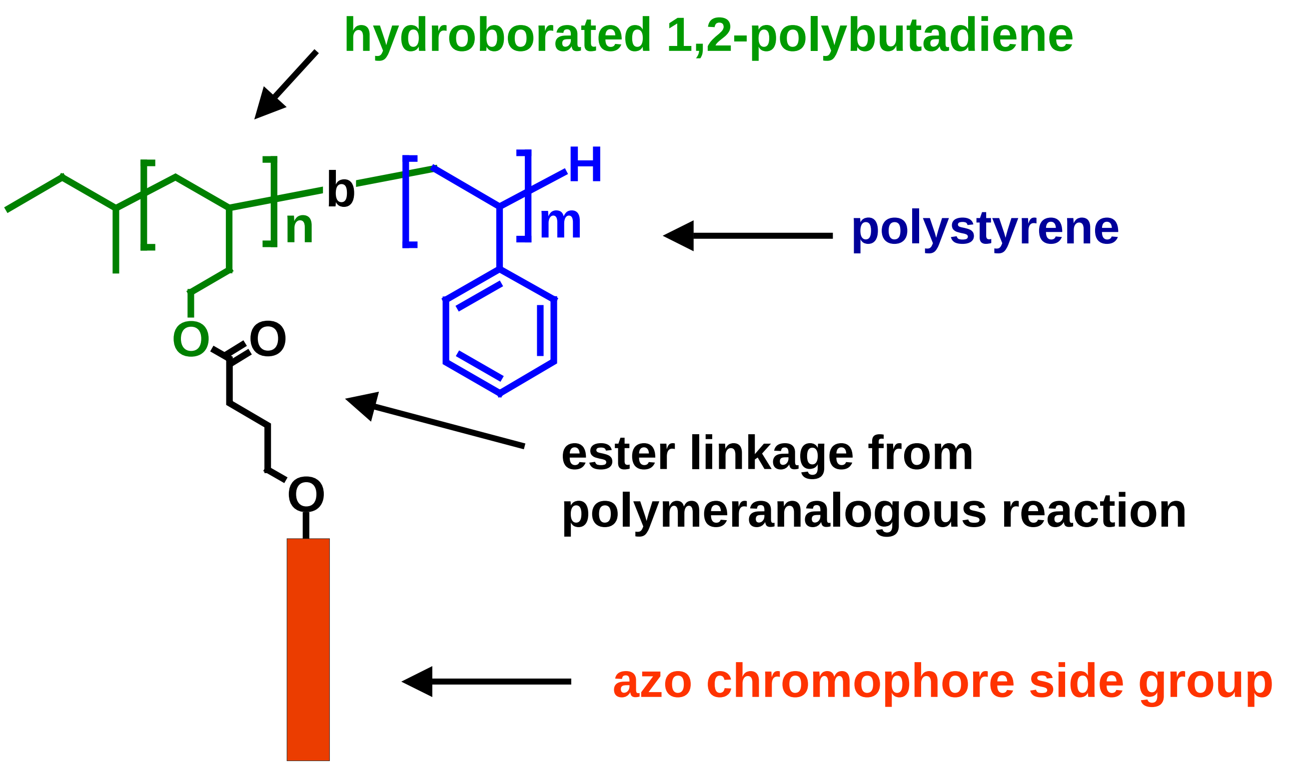
- Self organization into *ordered nanophase separated morphologies*



Advantages as holographic storage material

- localized concentration and confinement of addressable units
- cooperative effect
- no bulk scattering
- control of optical density
- no formation of surface gratings
- low shrinkage

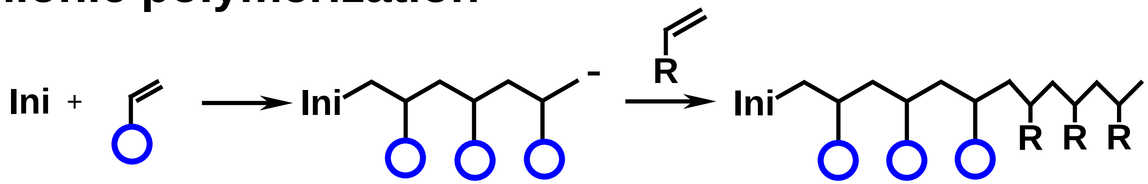
Block copolymers with PS matrix



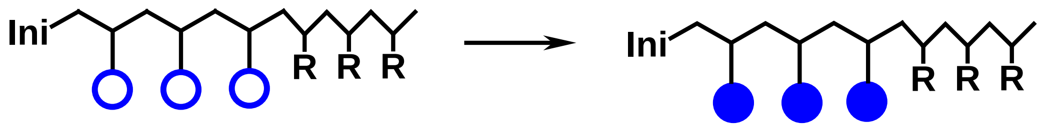
Block copolymer composition: polystyrene as matrix

Synthesis of functionalized block copolymers

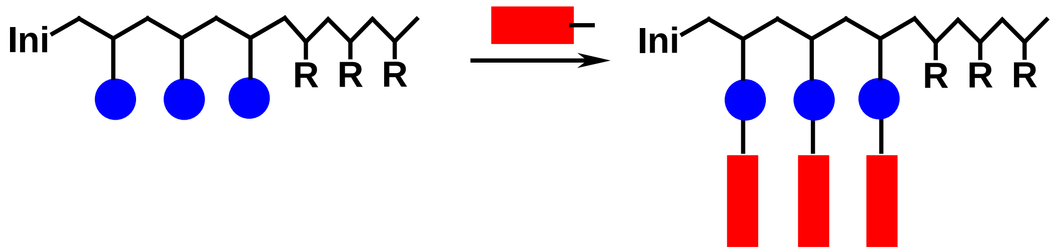
Sequential anionic polymerization



Conversion to hydroxy function



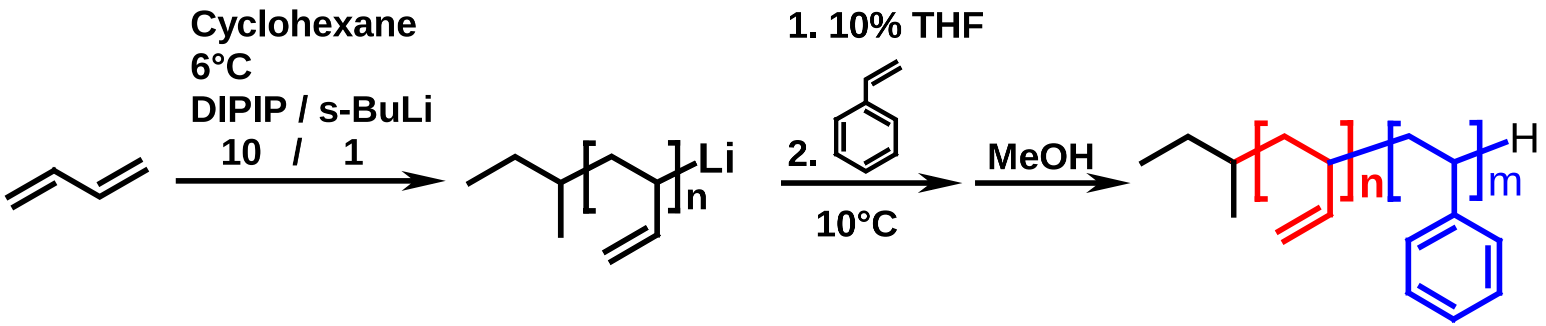
Polymeranalogous reaction with functional side groups



Synthetic advantages:
- easy purification of monomers
- activation of low molecular functional side groups
- polymeranalog. reaction allows variation of side groups

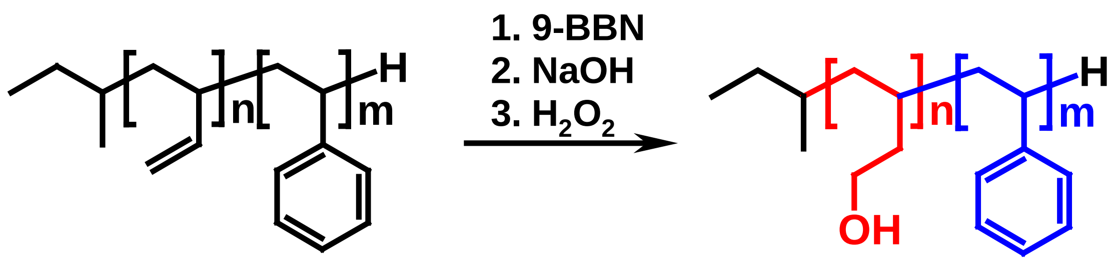
G. Mao et al. *Macromolecules*, 1997, 30, 2556-2567. J. Adams et al. *Makromol. Chem., Rapid Commun.* 1989, 10(10), 553-557

Sequential anionic polymerization



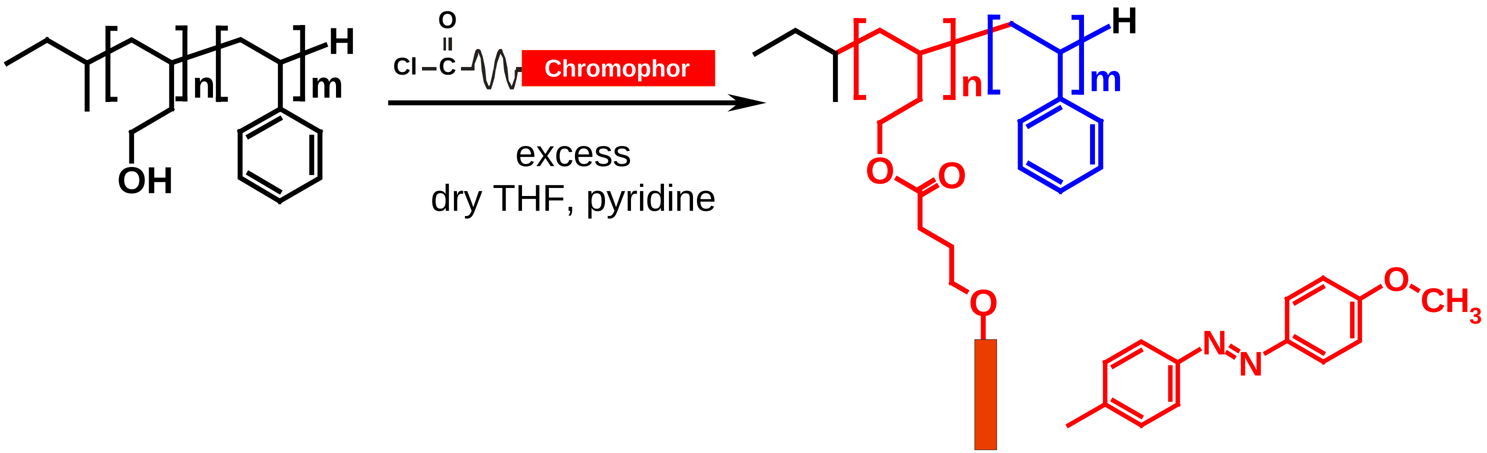
DIPIP: Dipiperidinoethane

Halasa et al.



9-BBN: 9-Borabicyclo[3.3.1]nonan

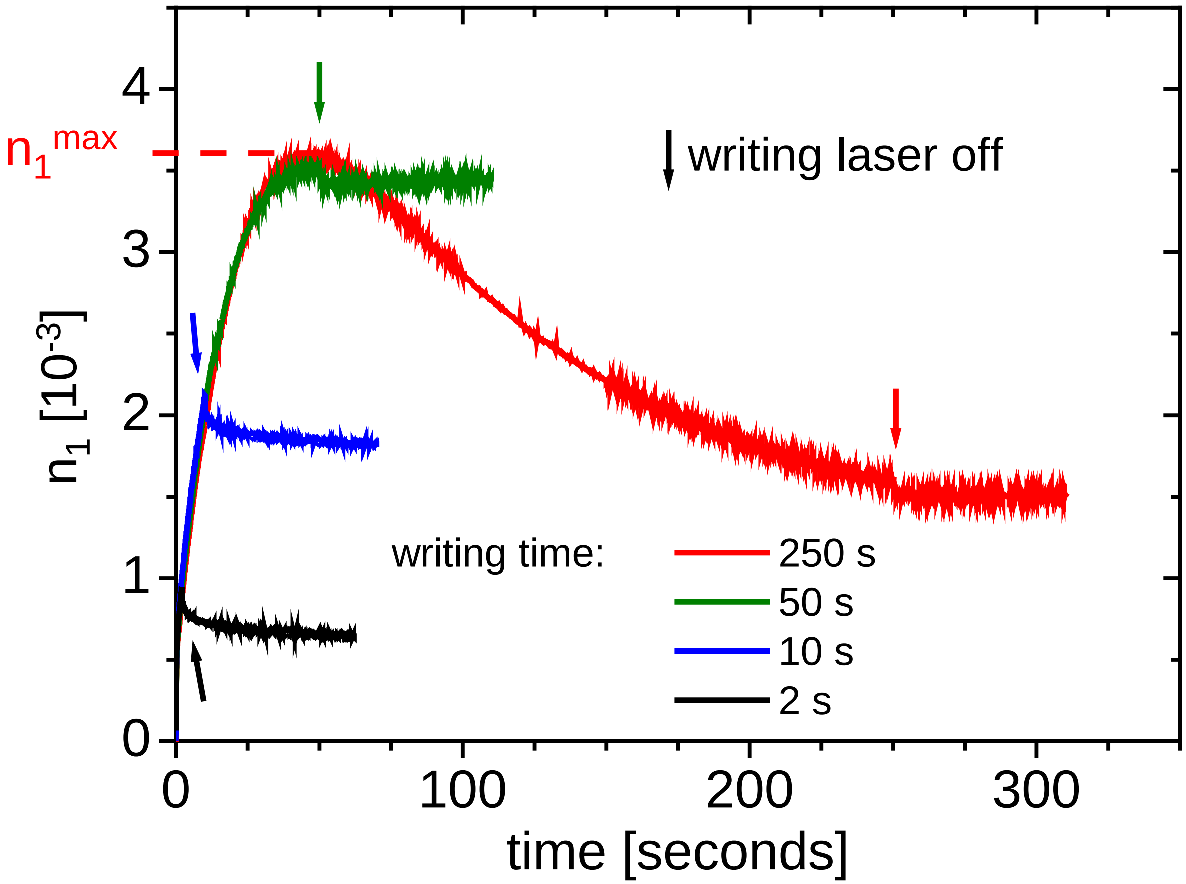
Block copolymers with methoxyazo chromophore



Block copolymer	Weight fraction PS / methoxyazo (wt.-%)	M_n (g/mol)	M_w/M_n	Glass transitions T_{g1}(°C)	T_{g2}(°C)	
OMe-1	75 / 25	68100	1.07	104	66	cylinder
OMe-2	82 / 18	59000	1.04	101	n.d.	cylinder
OMe-3	89 / 11	56000	1.03	97	n.d.	sphere
OMe-4	98 / 2	52000	1.02	101	n.d.	miscible

(C. Frenz)

Holographic writing curve



Block copolymer azo content: 25 wt. %

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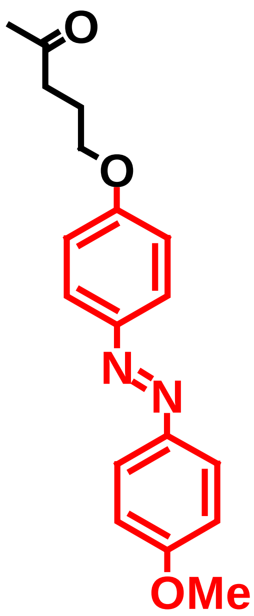
Azo-dye containing side-chain polymers

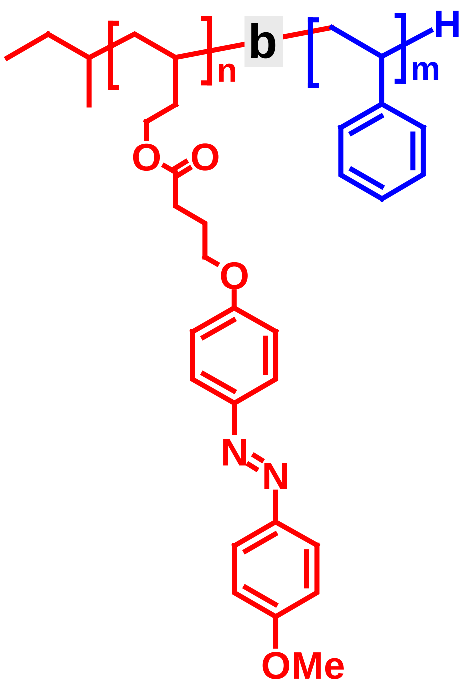


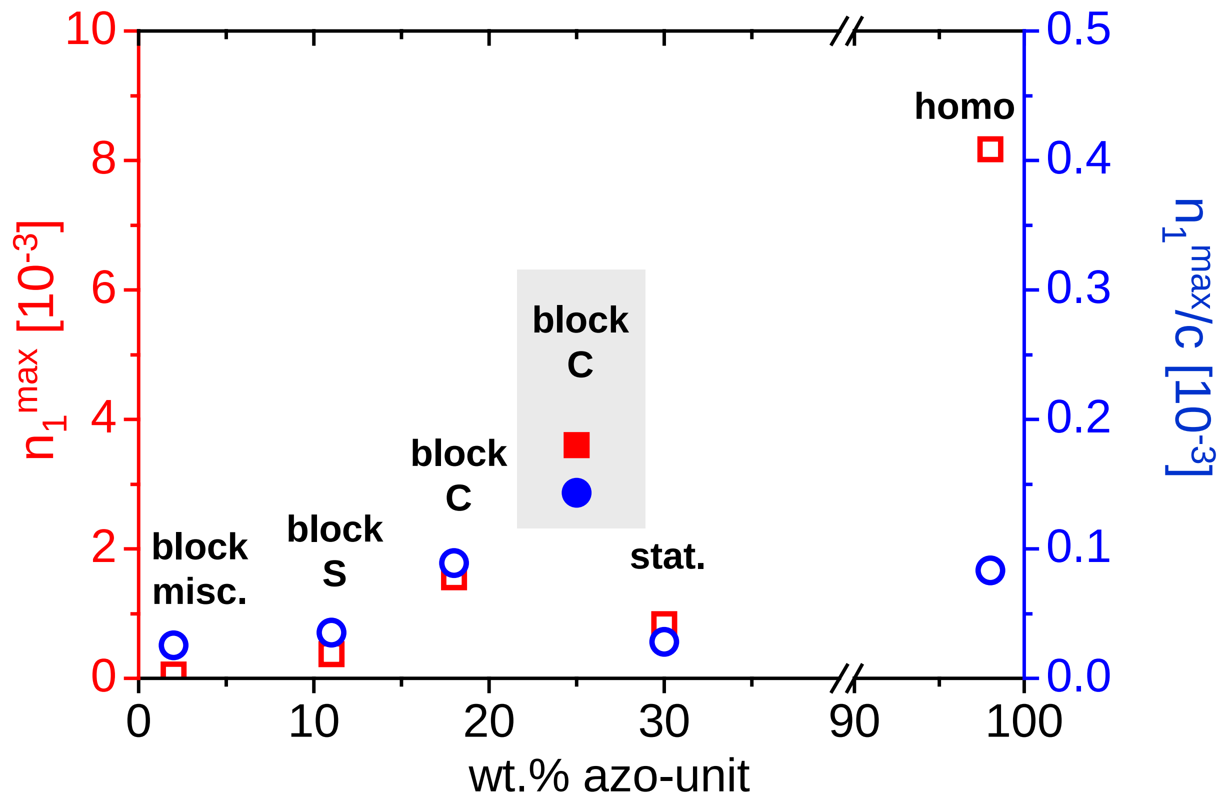
- homopolymer
- statistical copolymer
- block copolymer miscible
- block copolymer with spherical and cylindrical morphology

solid-state with <u>no</u> liquid crystalline order

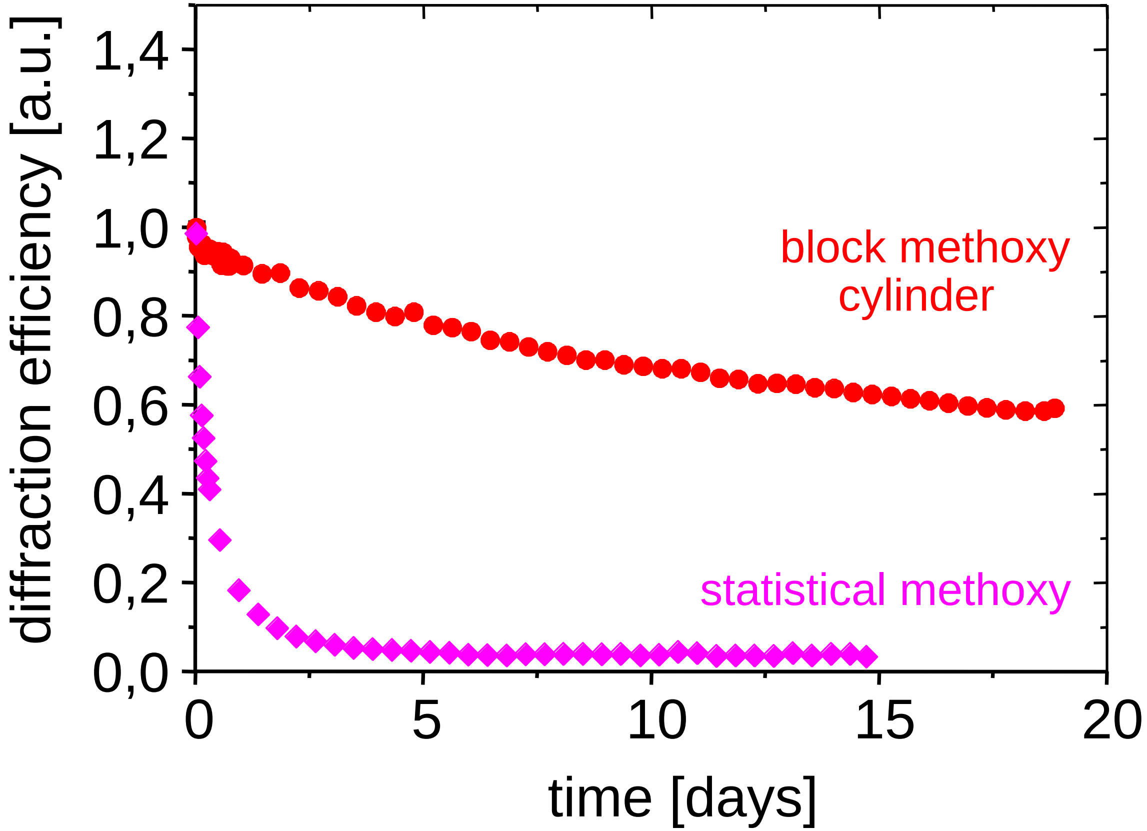
Influence of block copolymer morphology

Block copolymer series





Long-term stability



η: diffraction efficiency

$$= \frac{I_1(t)}{I_0(t_0)}$$

$I_1(t)$ – 1st order diffracted beam

$I_0(t_0)$ – transmitted beam

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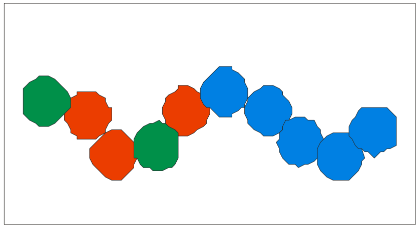
Materials

▪ **Partial replacement of azo-units with non-absorbing mesogens**

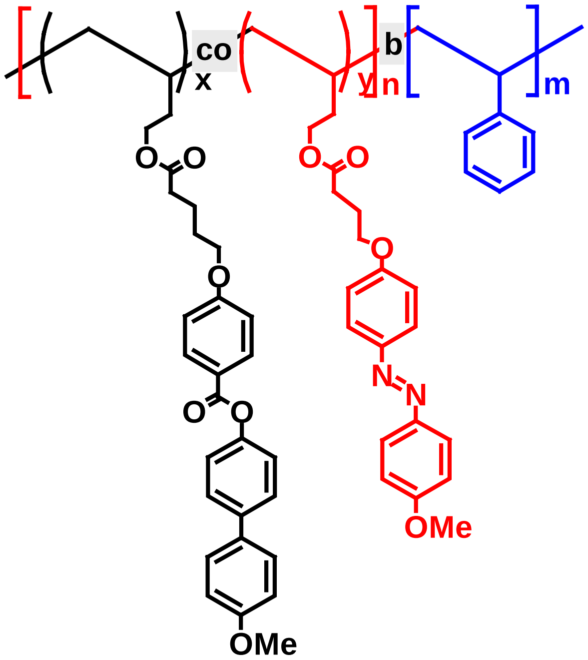


⇨ **Concepts to decrease the optical density and maintaining sufficiently high n_1 values**

⇨ **Introduction of liquid crystalline order and increase long term stability**

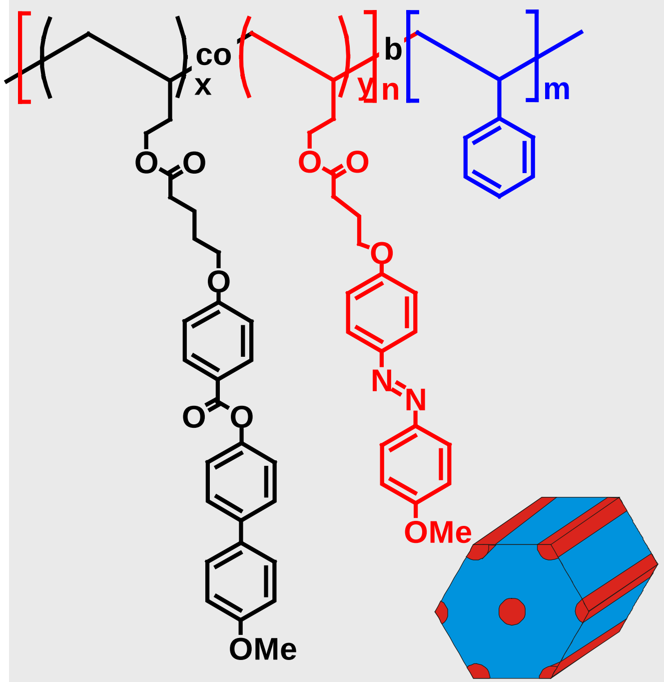
Photoaddressable materials

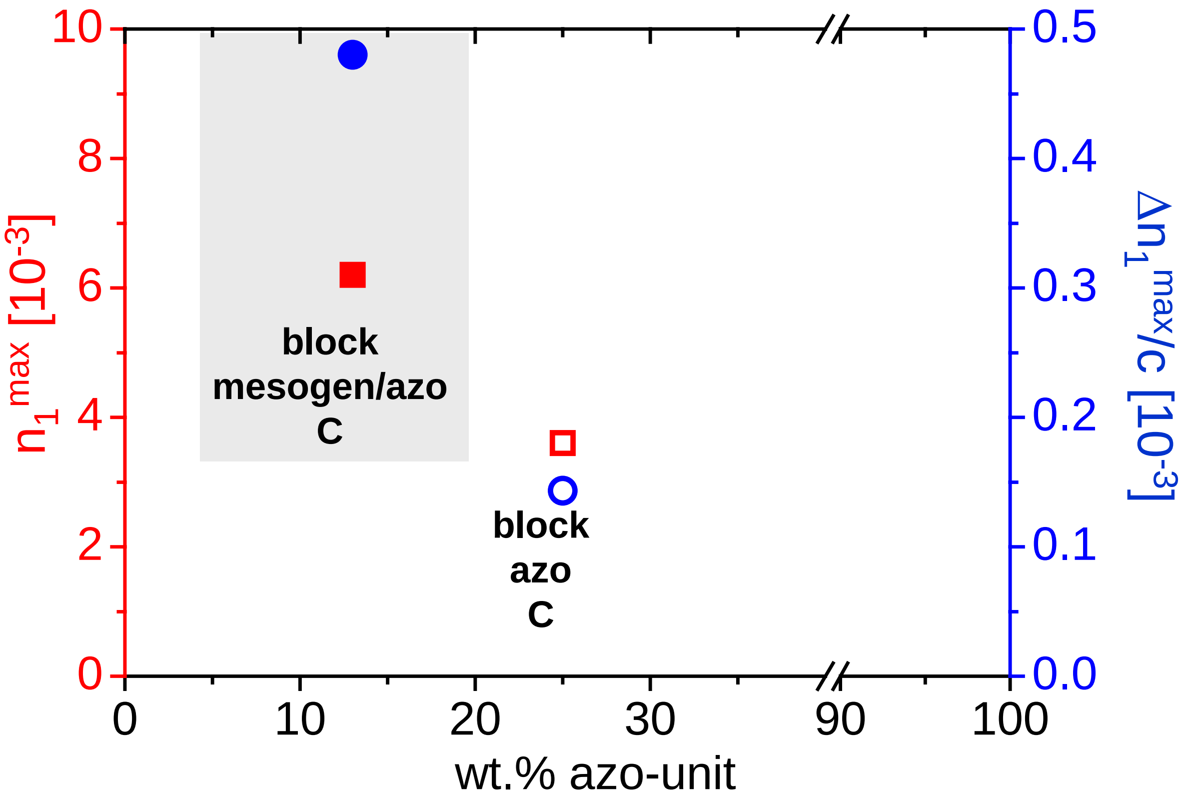
Block copolymers with azo side-groups and mesogenic units in the photoaddressable segment



Holographic experiments

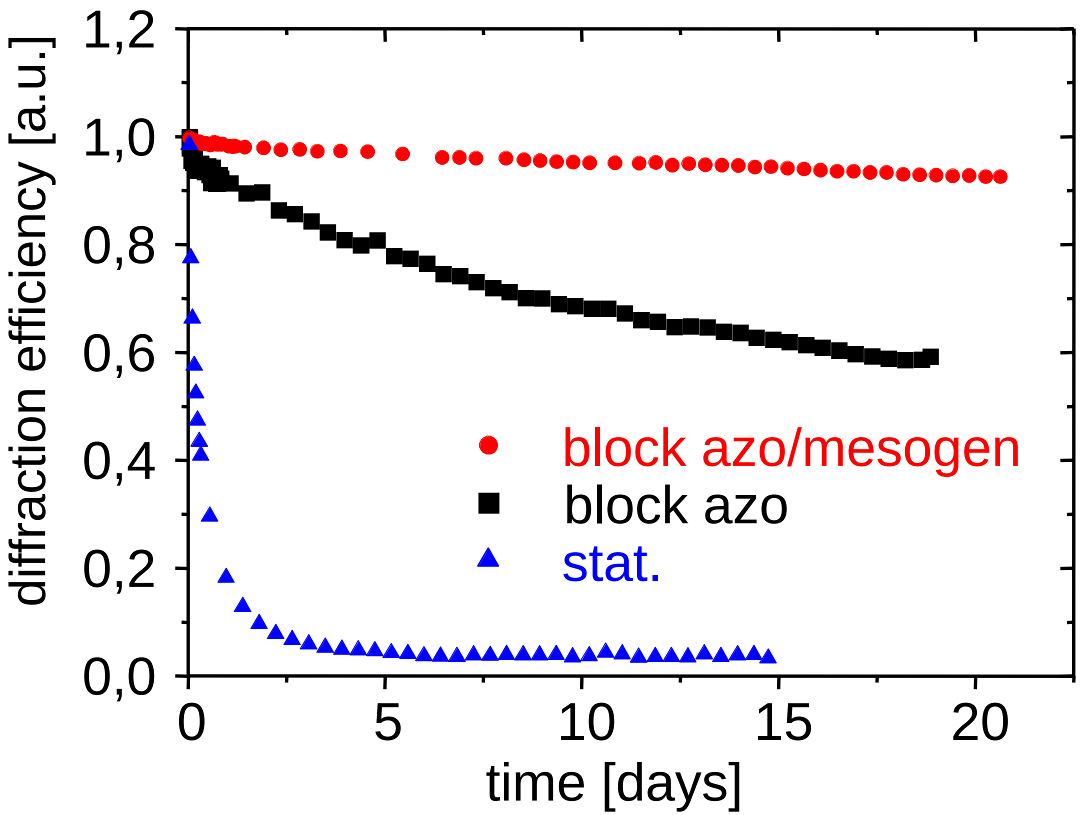
Block copolymer

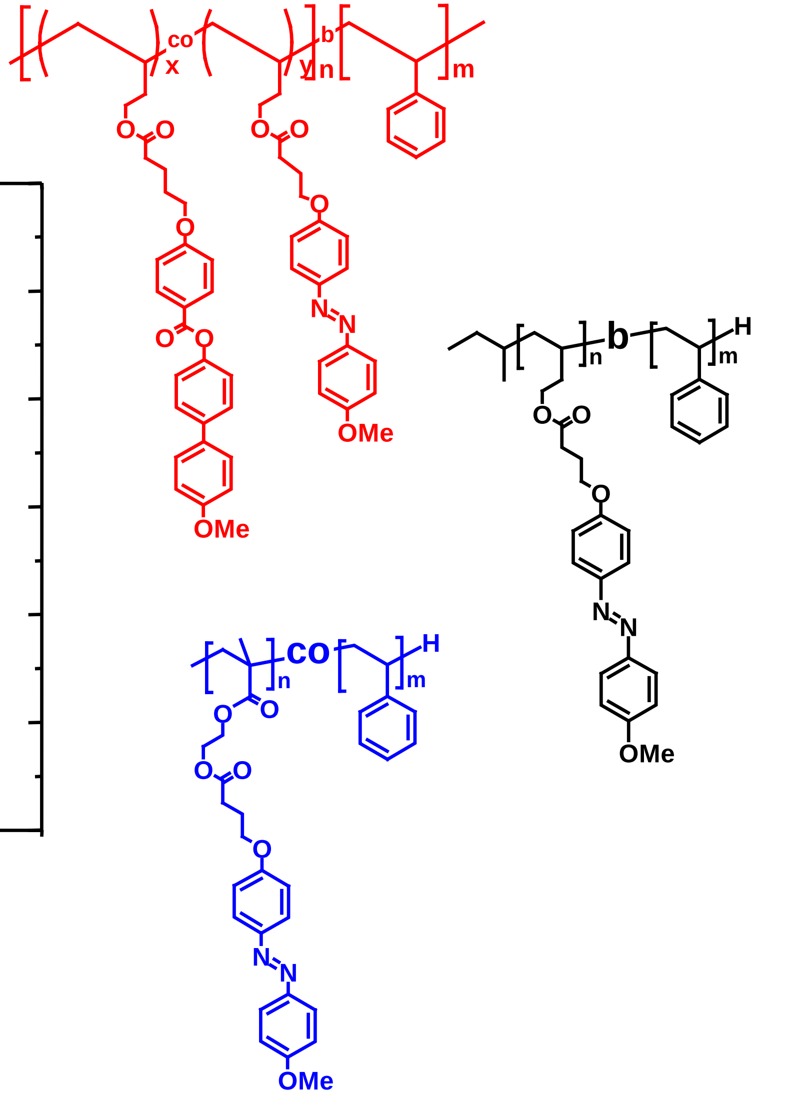




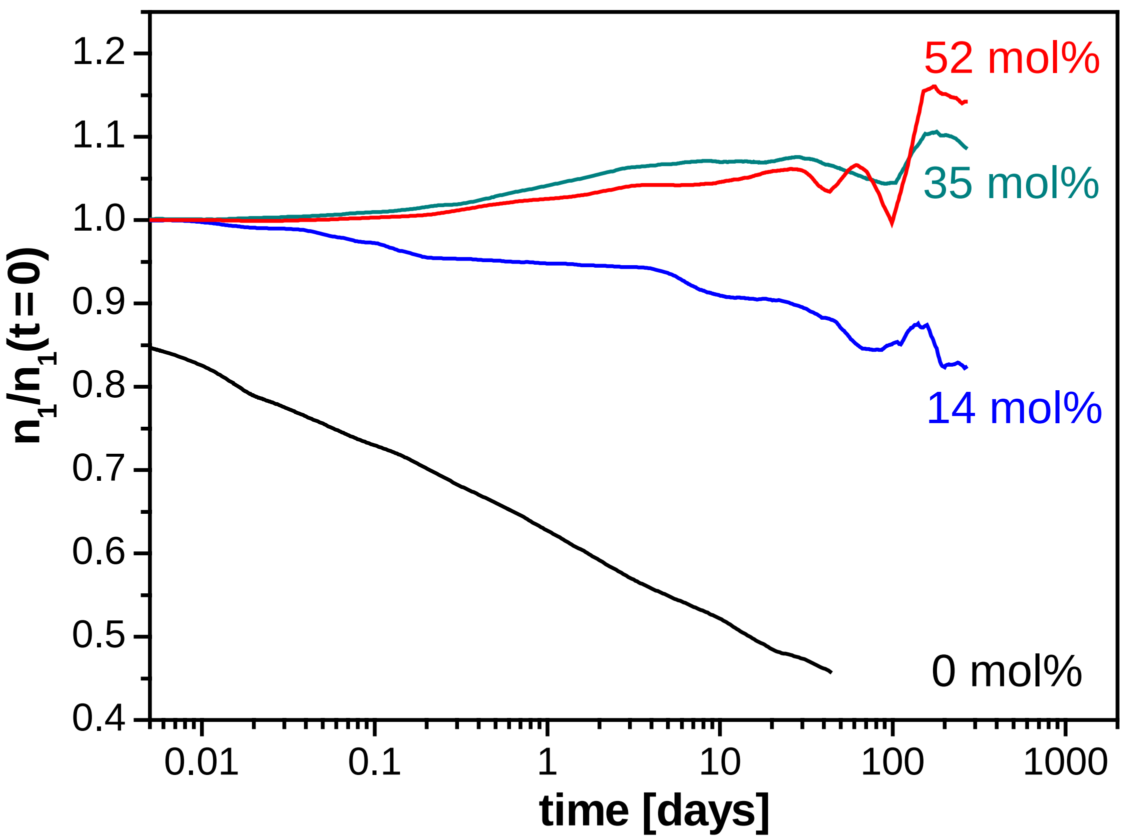
Azo content: 13 wt.%
Repeating units: PS = 445; Azo = 24; Mesogen = 24
Molecular weight: M_n 66000 g/mol
Glass transition: T_{g1} = 39 °C; T_{g2} = 99 °C

Long-term stability



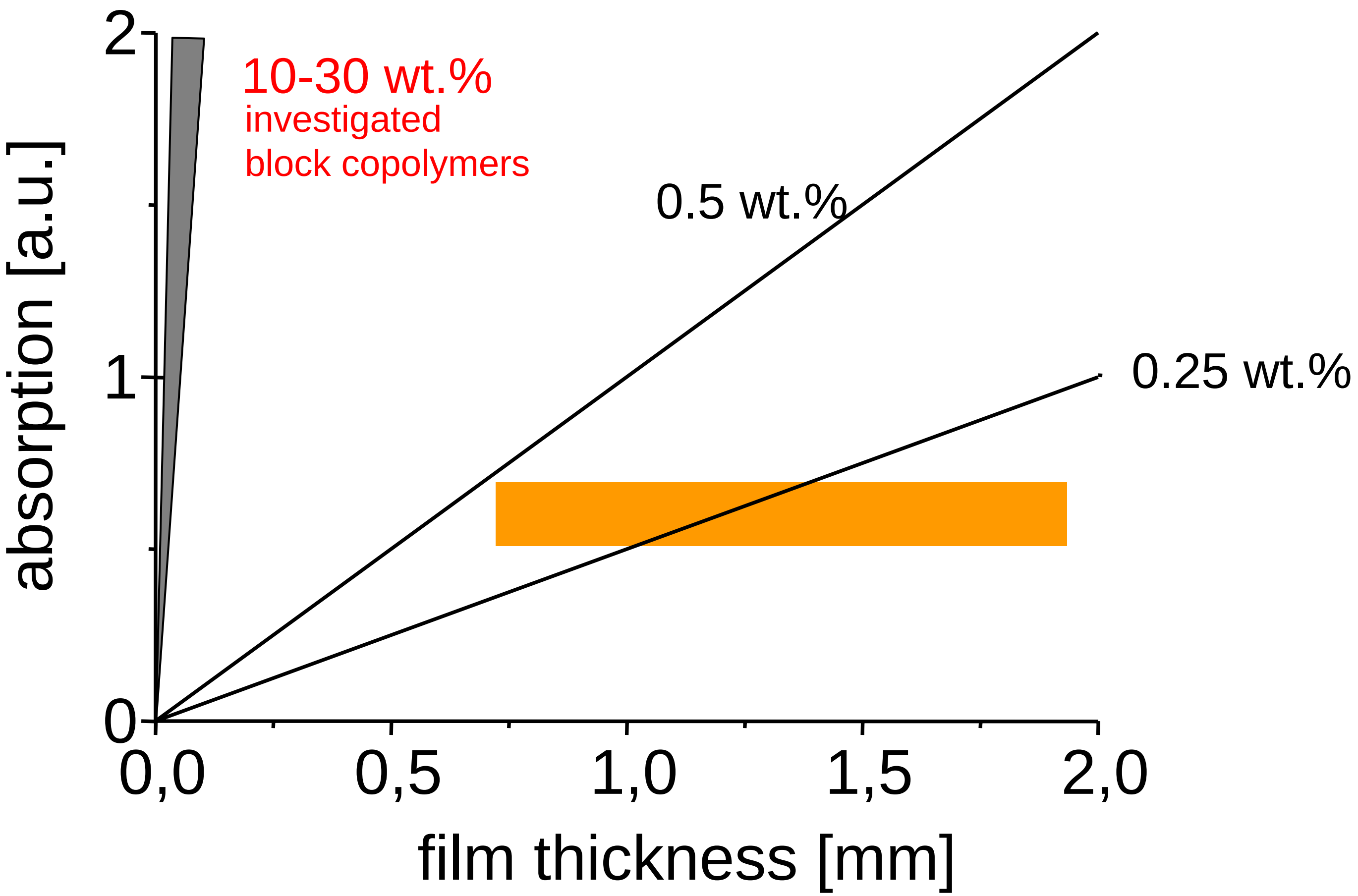


Long-term stability



Stability of the written gratings for different mesogen concentrations

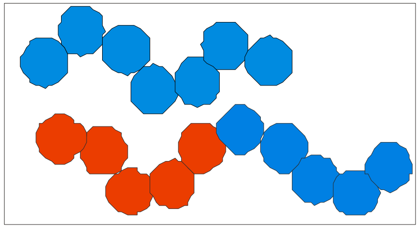
Sample thickness vs. optical density



$\varepsilon_{488} = 751\ l \cdot cm^{-1} \cdot mol^{-1}$

Materials

- Blends of block copolymer with homopolymer



⇨ Concepts to decrease the optical densityto obtain thick samples for volume holographic data storage

⇨ Thermoplastic material → injection molding

Injection molded samples

Blend of homopolymer with polystyrene

Blend of block copolymer with polystyrene

thickness: 1.1 mm

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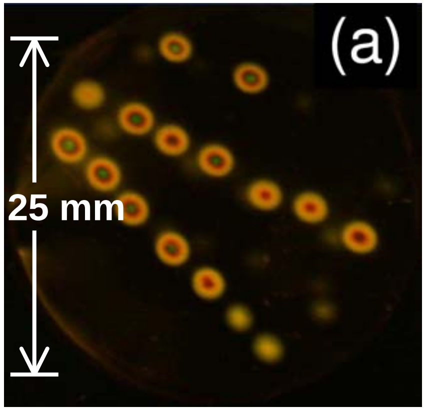
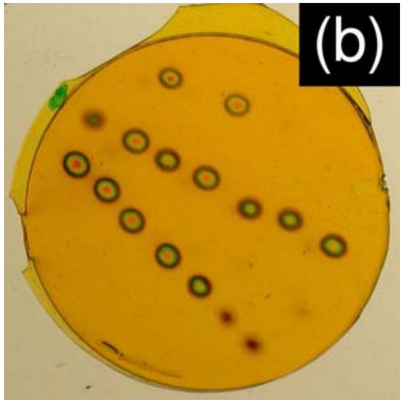
Injection molded samples

Blend of block copolymer (10 wt%) with polystyrene homopolymer (90 wt%)

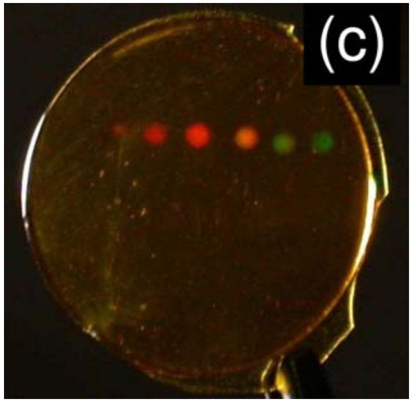
Optical light microscopy between crossed polarizers



(a) sample with inscribed gratings between crossed polarizers



(b) between parallel polarizers

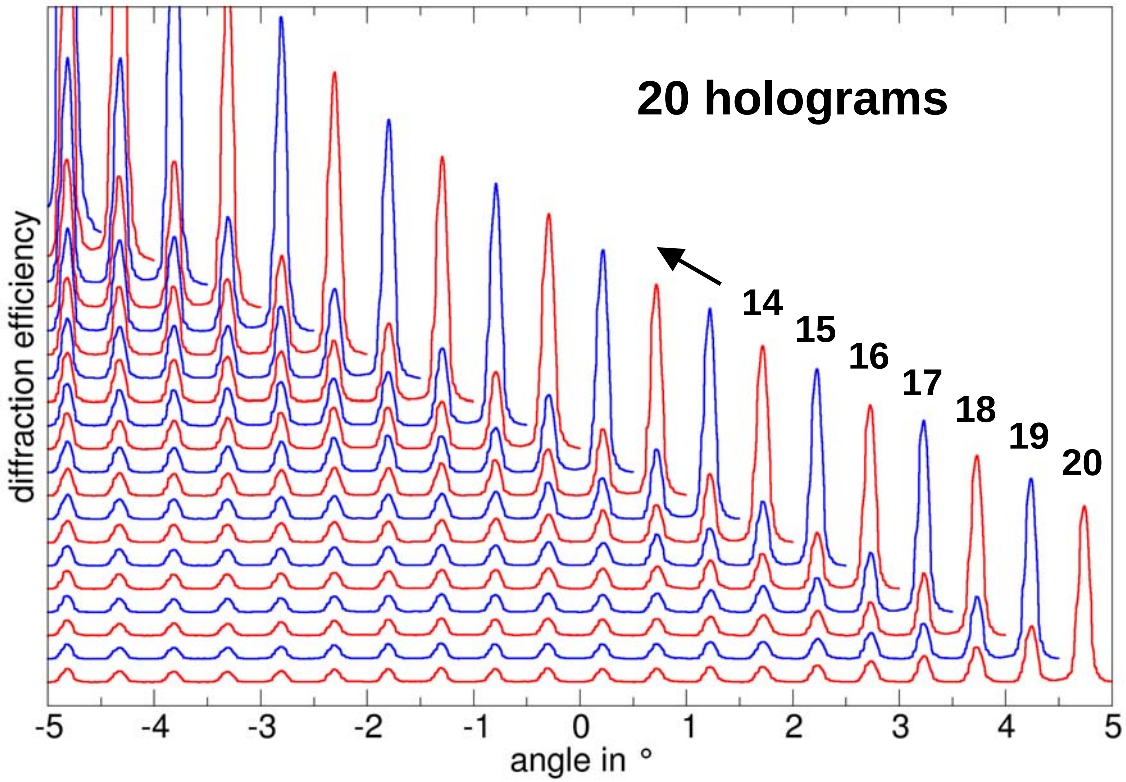


(c) first diffraction order

transmission: 69.1
haze: 3.7
clarity: 98.9

thickness: 1.1 mm

Injection molded samples



writing:
λ 514 nm

writing time:
0.5 s @ 2 W/cm^2

writing energy:
1 J/cm^2

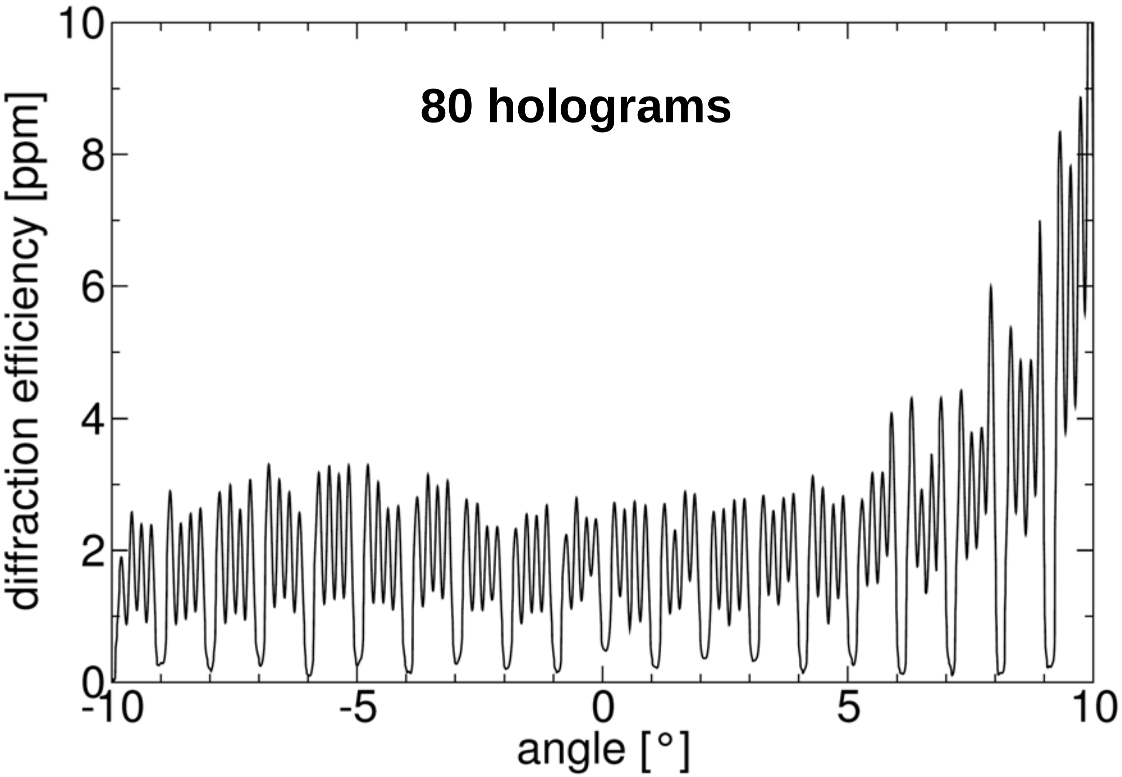
reading:
λ 685 nm

Blend composition:

10 wt% block copolymer
90 wt% polystyrene homopolymer
thickness: 1.1 mm

Block copolymer: CF110
Azo dye: methoxyazobenzene; content: 17.5 wt.%
Repeating units: PS = 467; Azo = 28
Molecular weight: M_n 59000 g/mol

Injection molded samples



writing: λ 514 nm

writing time: 1 s @ 1 W/cm²

writing energy: 1 J/cm²

reading: λ 685 nm

Blend composition:

11 wt% block copolymer
89 wt% polystyrene homopolymer
thickness: 1.1 mm

Block copolymer: DK25
Azo dye: methoxyazobenzene; content: ≈ 5 wt.%
Molecular weight: M_n 60000 g/mol

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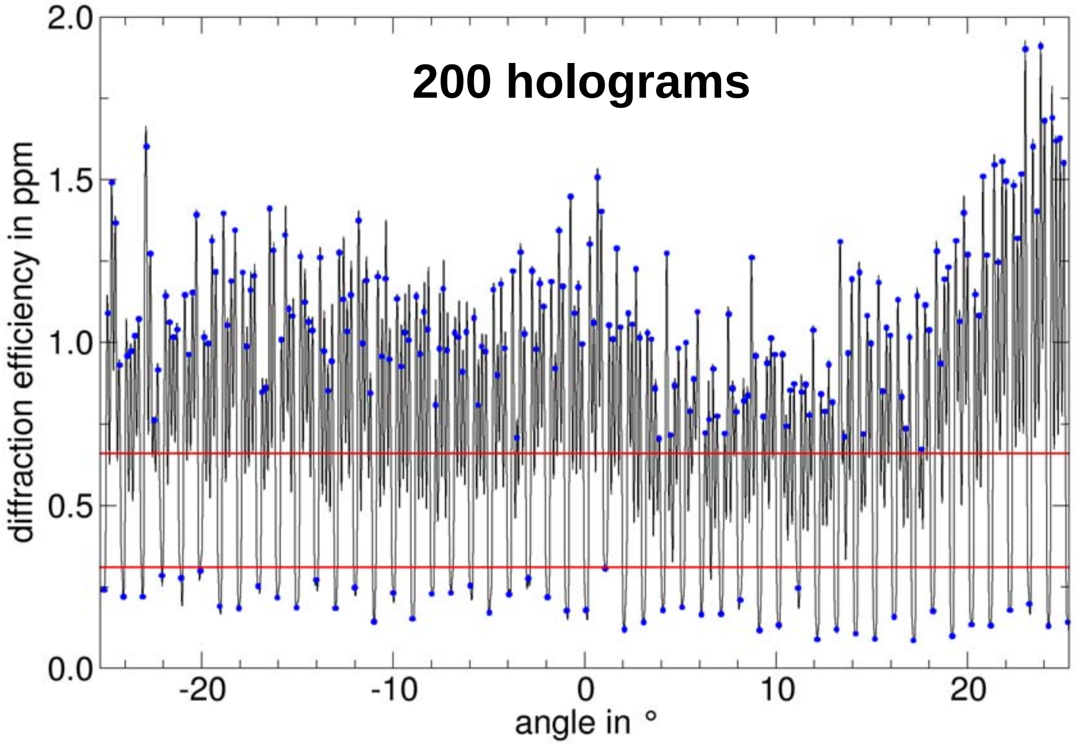
Injection molded samples



writing: λ 514 nm

writing time: 0.3 s @ 1 W/cm²

writing energy: 300 mJ/cm²

reading: λ 685 nm

Blend composition:

11 wt% block copolymer
89 wt% polystyrene homopolymer
thickness: 1.1 mm

Block copolymer: DK25
Azo dye: methoxyazobenzene; content: ≈5 wt.%
Molecular weight: M_n 60000 g/mol

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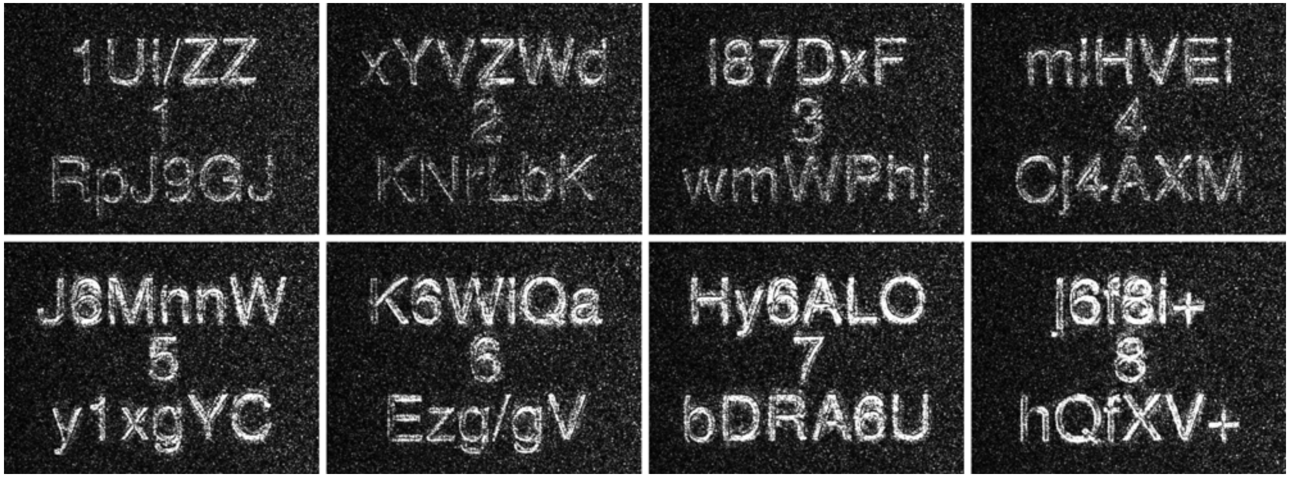
Angular multiplexing of images

Blend of block copolymer (10 wt%) with polystyrene homopolymer (90 wt%)

Eight reconstructed holographic images, written at the same location



angular distances 1
wavelength 514 nm
s:s-polarization
2 J/cm2 per hologram

thickness: 1.1 mm

Acknowledgement

Coworkers and collaboration partners

Dietrich Haarer and Daniela Kropp

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BAYER AG

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