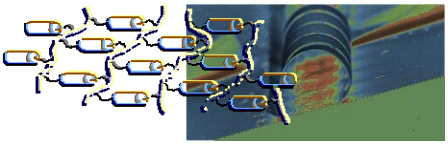
# POLYMERS IN MOTION

## on a successful interplay between DPI and a Company



**Dirk J. Broer**
**Philips Research Laboratories**
**Eindhoven University of Technology**

TU/e PHILIPS

## An interplay with many contributors:

My colleagues at TU/e Chem. Eng.
SKT (Piet Lemstra) - PICT)

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- Ko Hermans
- Carlos Sanchez
- Chris van Heesch
- Ken Harris
- Carmen Luengo
- Blanca Serrano
- Charlotte Kjellander
- Joachim Loos
- Kangbo Lu

TU/e Applied Physics
- Leo IJzendoorn
- Arthur de Jong
- Christian Leewis
- and co-workers

DPI DUTCH POLYMER INSTITUTE

TU/e Makromol. Chem & Nanoscience
- Ulrich Schubert
- Jolke Perelaer
- and co-workers

My colleagues at Philips
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Steve Klink
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Joost Vogels
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Hans Kloosterboer
Marc van Delden

TU/e Mechanical Engineering
- Han Meijer
- Jaap den Toonder
- and co-workers

TU/e PHILIPS

# Polymerization induced diffusion: a long DPI history with numerous spin-offs

PHILIPS • Mobile display reflectors

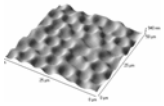
TU/e DPI • Photoembossing / basics

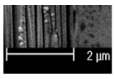
PHILIPS • Paintable displays

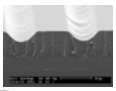
TU/e DPI • Multilayer reflectors

TU/e DPI • Enhanced photoembossing / multilayer systems

PHILIPS TU/e • Seals for Microfluidics





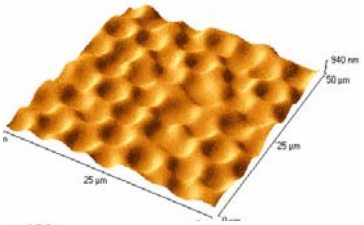
EVONIK INDUSTRIES | degussa.

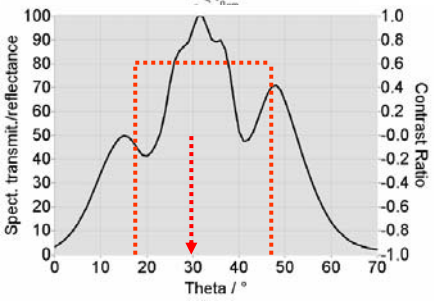
MERCK DSM

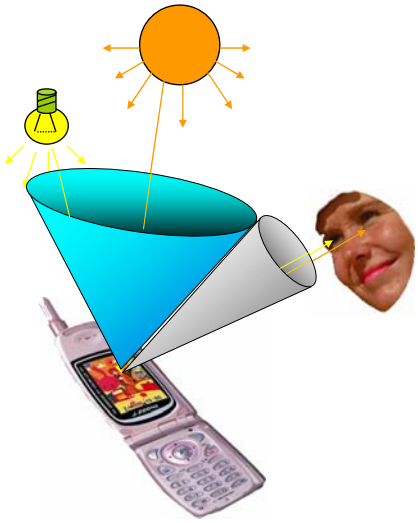
microfluidics & actuators PHILIPS



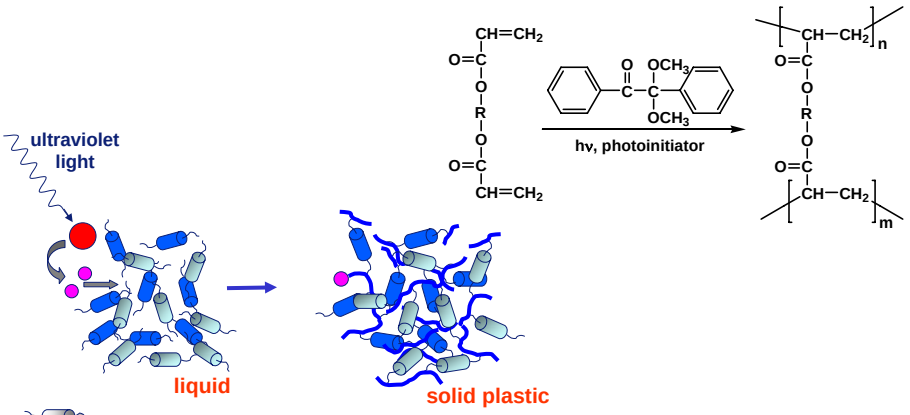
# Photo-embossed mirrors for reflective displays



# Polymerization-induced diffusion in photopolymerizing systems



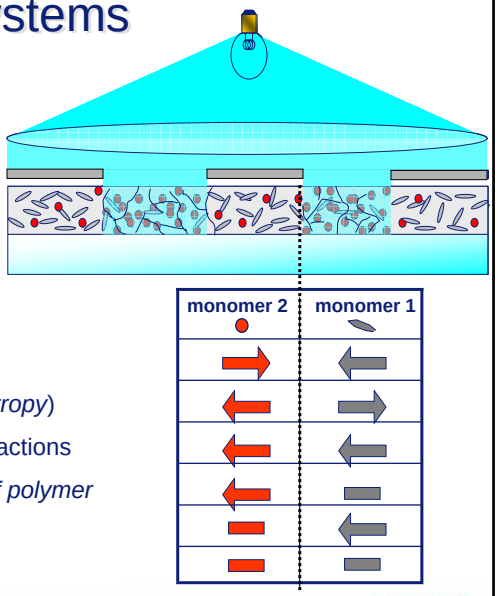

monomers or monomer+ non-reactive materials

photoinitiator

free radical or cation



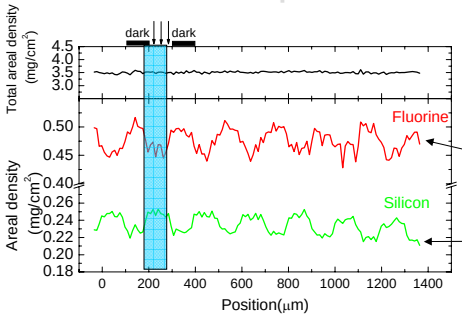
# Polymerization-induced diffusion in photopolymerizing systems



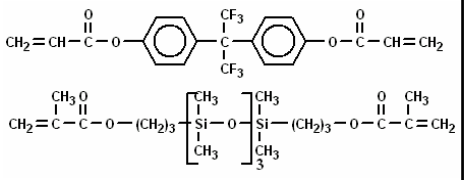

Materials transport can be described in terms of chemical potential of the reacting components:

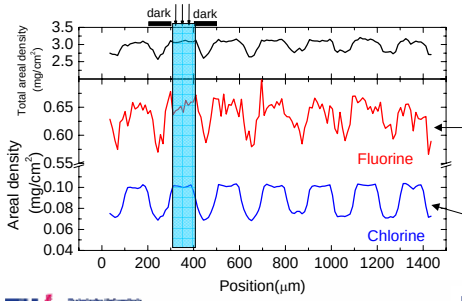
- monomer reactivity differences
- interaction parameters ($\chi$'s)
- monomer size (*diffusion, size entropy*)
- monomer and polymer volume fractions
- network elasticity (*deformation of polymer network under swelling*)
- surface energy

# Nuclear microprobe analysis

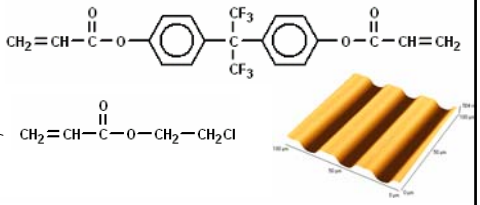



Concentration modulation





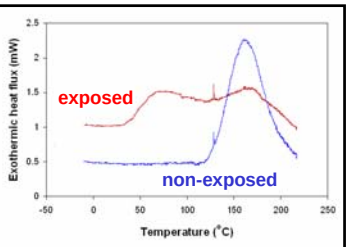

Surface modulation

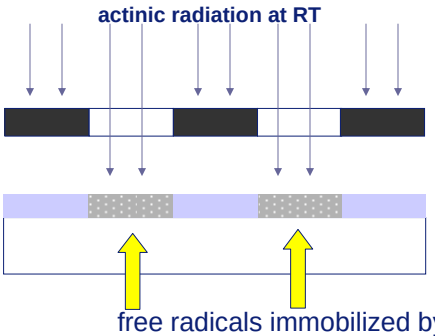




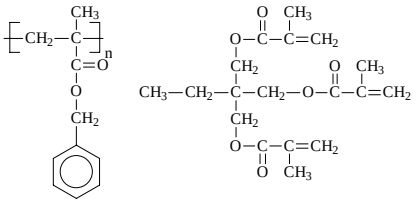
Leo van IJzendoorn, Arthur de Jong, Christian Leewis

# Photo-embossing



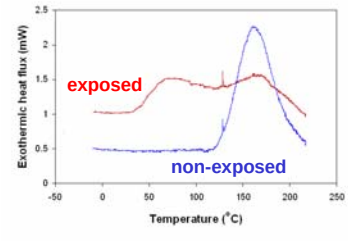



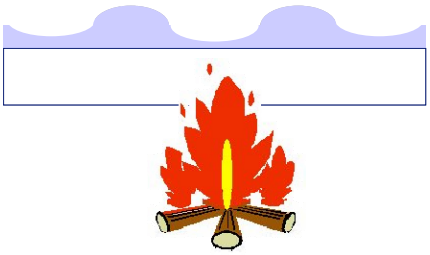

free radicals immobilized by vitrified polymer matrix



Christiane de Witz, Thijs Bel (Philips)
Ko Hermans, Carlos Sanchez, Cees Bastiaansen (TU/e)

# Heat development of the latent images



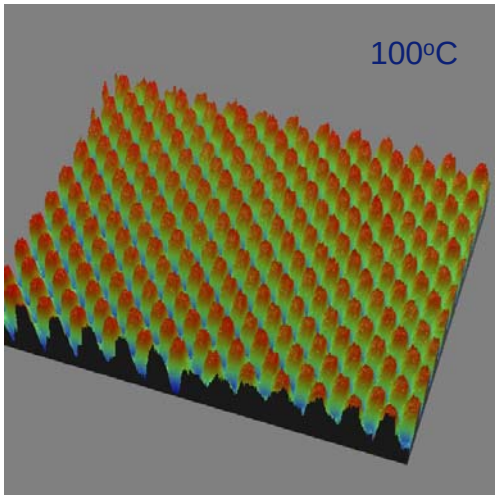



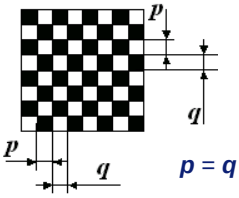

Important aspect: surface remains (almost) flat when stored at RT

**But when heated monomer diffusion is enabled**

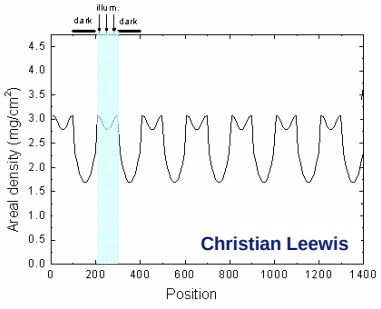
Christiane de Witz, Thijs Bel (Philips)
Ko Hermans, Carlos Sanchez, Cees Bastiaansen (TU/e)

# Heat development of the latent images



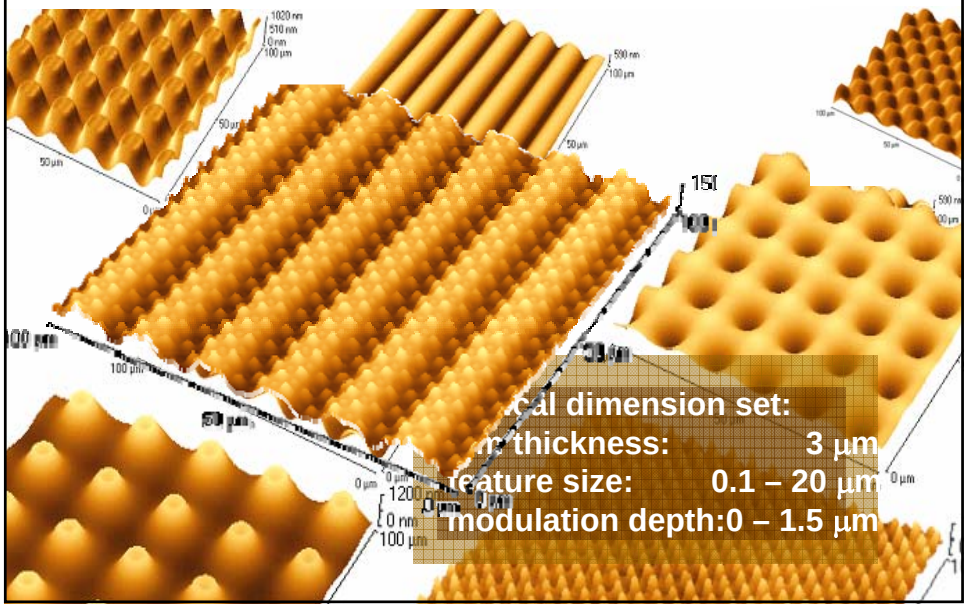




***p*** = ***q*** = 10μm

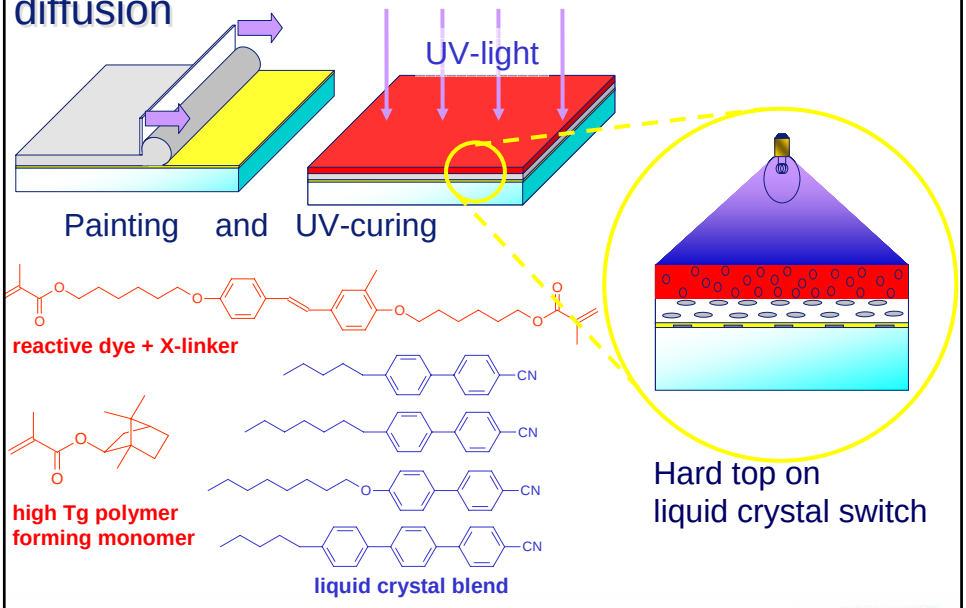



Christiane de Witz, Thijs Bel (Philips)
Ko Hermans, Carlos Sanchez, Cees Bastiaansen (TU/e)

## Relief can be adjusted by mask, exposure and heat development conditions




## Paintable displays by polymerization-induced diffusion




R.Penterman, S.Klink, J. Vogels, H.de Koning, Jacqueline van Driel, Edzer Huitema

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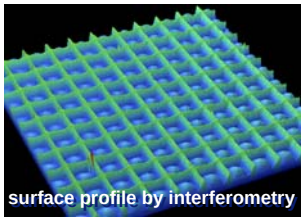
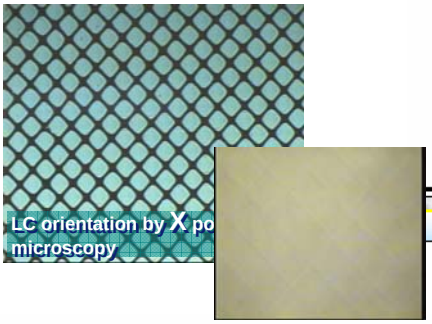
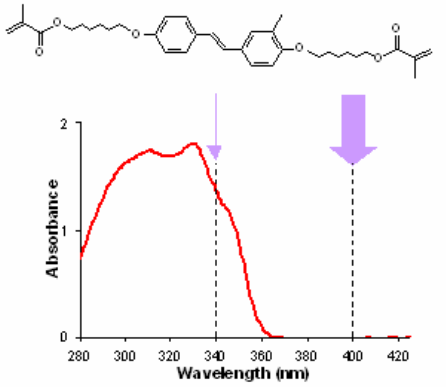
# Two sequential diffusion processes provide the mechanical integrity

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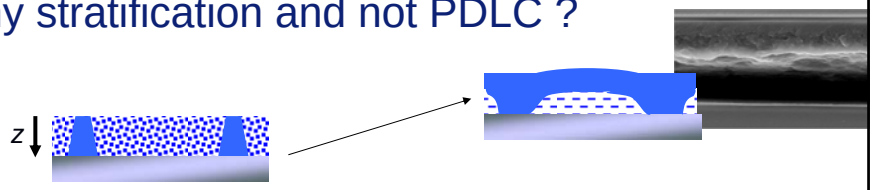
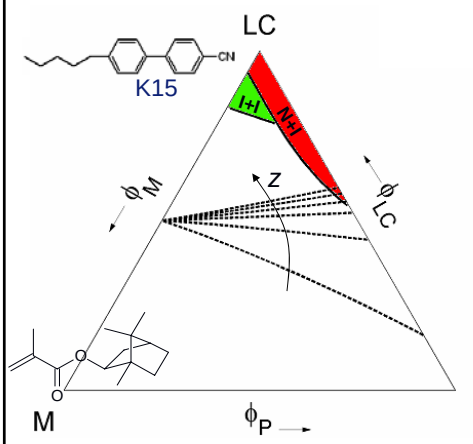
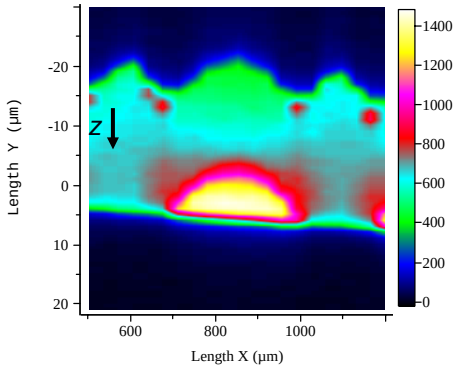
# Why stratification and not PDLC ?




K15 profile by confocal Raman:




R.Penterman (TU/e thesis), S.Klink, Joris Vorselaars, Hans Kloosterboer

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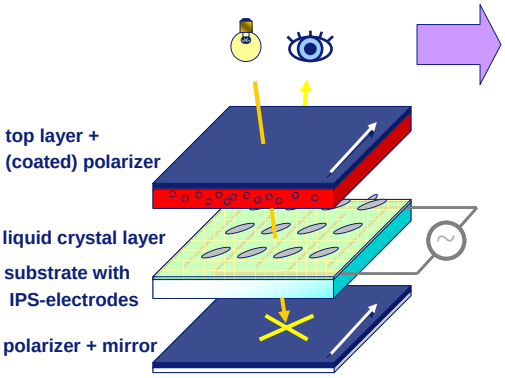
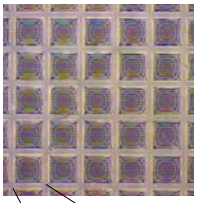
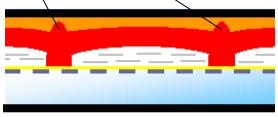
# Interdigitated electrodes for in-plane switching of liquid crystals



Polarization microscopy



- Stratified layer: 20-30 μm
- LC thickness: 10 μm
- Pixel size: 400 μm

R.Penterman, S.Klink, J. Vogels, H.de Koning, Jacqueline van Driel, Edzer Huitema

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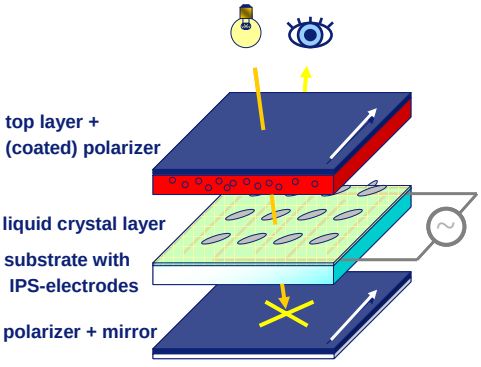
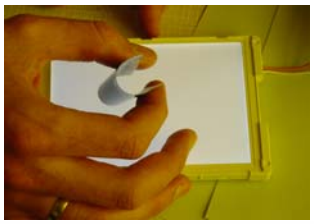
# Interdigitated electrodes for in-plane switching (IPS)



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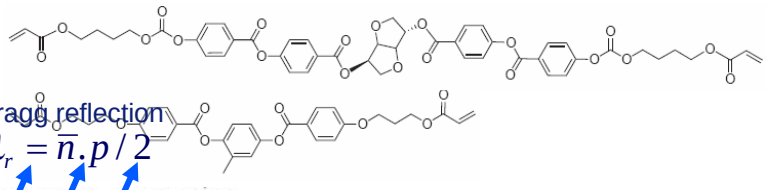
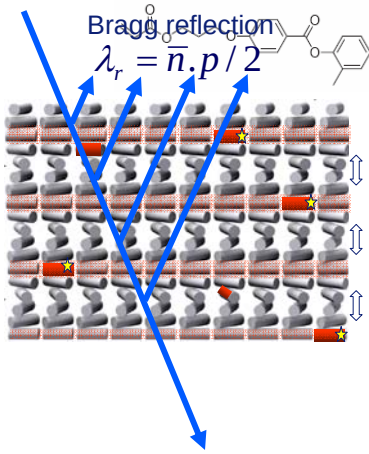
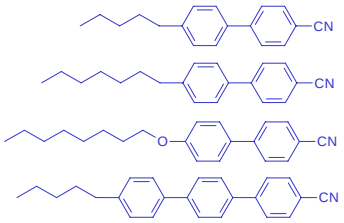
# Multilayer stratification using cholesteric LC



Bragg reflection

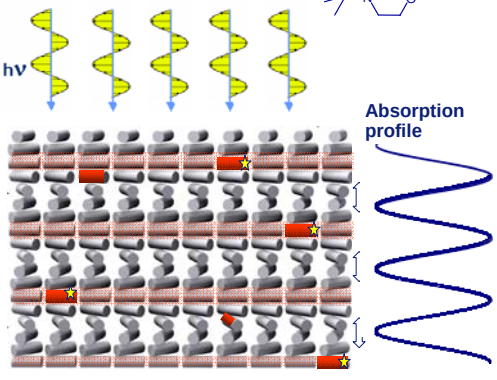
$\lambda_r = \bar{n}.p/2$

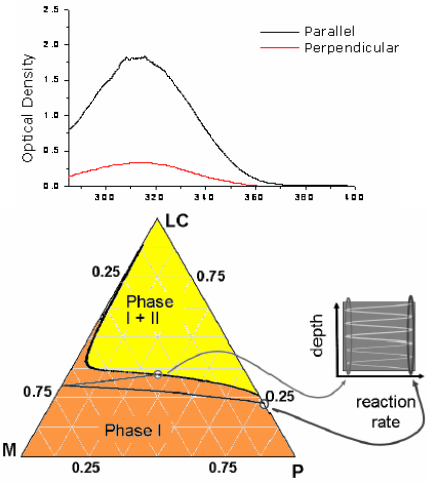




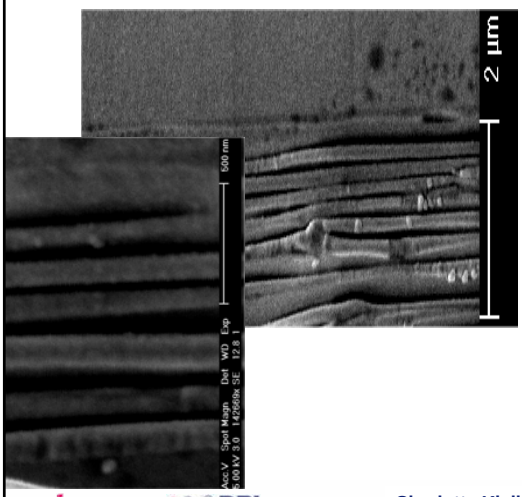


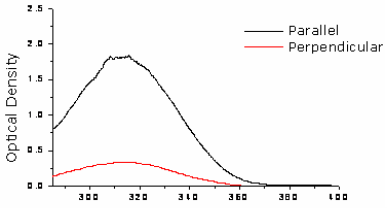

# Multilayer stratification using cholesteric LC + dichroic photoinitiator

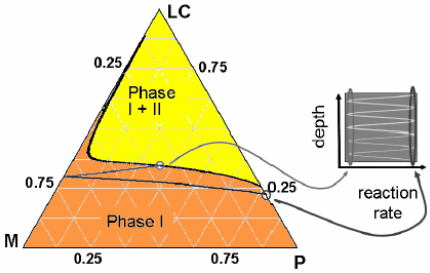


# Multilayer stratification

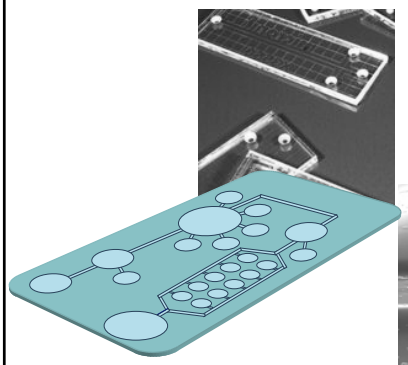


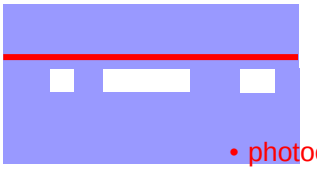



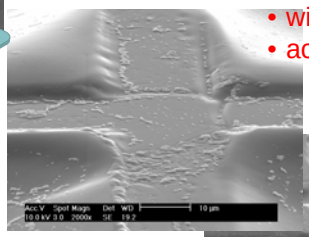

Charlotte Kjellander, Shabnam Zakerhamidi, Cees Bastiaansen

# Sealing of microfluidic devices by photoembossing

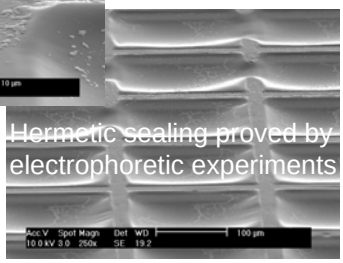




- photoembossing film
- with latent pattern
- activated by heating

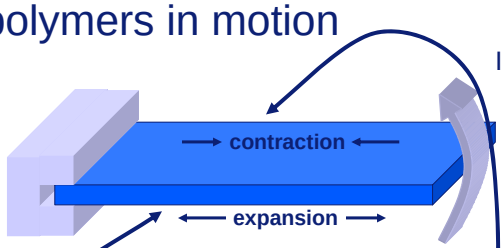


- bio-analytical applications
  - lab-on-a-chip assays
  - cell sorting & analysis
- micro-reactors

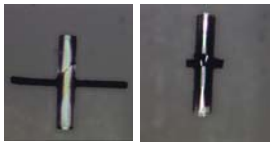


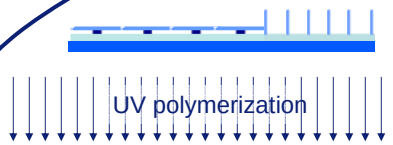

Ko Hermans, Cees Bastiaansen (TU/e), Marc van Delden (Philips)

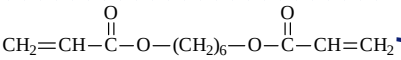
# Polymerization-induced diffusion brings polymers in motion



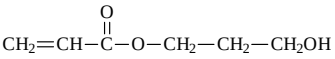

In water:



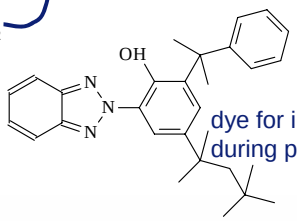


hydrophobic monomer



hydrophilic monomer




dye for intensity gradient during polymerization

Christiane de Witz, Thijs Bel

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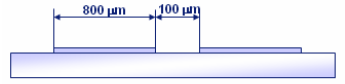
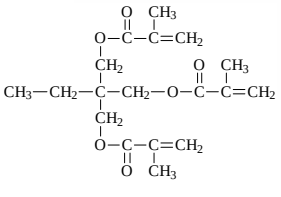
# Polymerization-induced diffusion brings polymers in motion

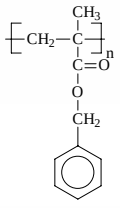



glass (embedded electrodes not shown) + patterned Al (100 nm)

add 10 nm chromium layer

add 10 µm acrylate mix photopolymerized through mask



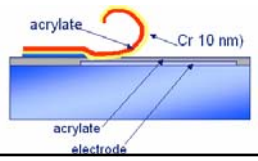


develop acrylate in alkaline solution

etch Cr in cerium ammonium nitrate

etch Al in phosphoric acid

induced stresses make the elements curl




Christiane de Witz, Thijs Bel, Jaap den Toonder

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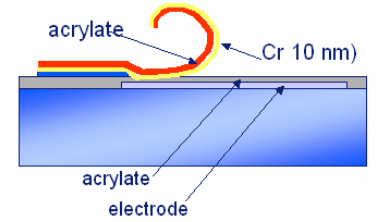
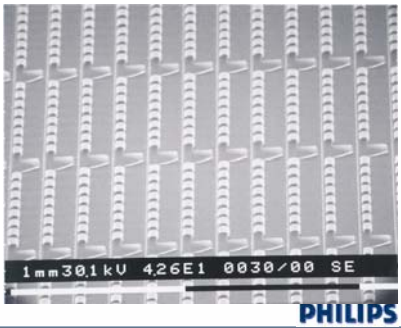
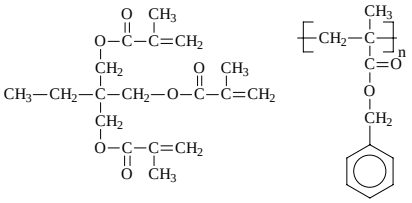
# Polymerization-induced diffusion brings polymers in motion







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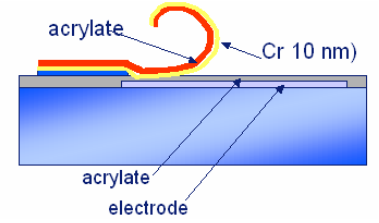
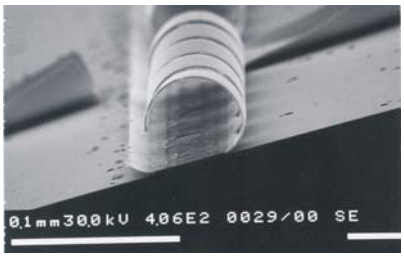
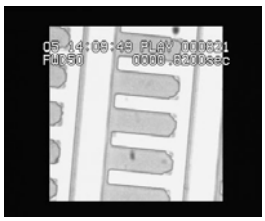
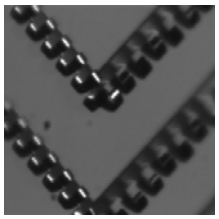
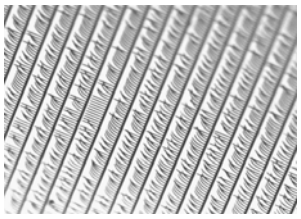
# Polymerization-induced diffusion brings polymers in motion







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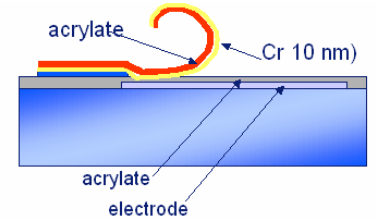
# Polymerization-induced diffusion brings polymers in motion





Applications:

- Electro-optical switches (e.g. large area displays)
- Microfluidic elements
  - Micro-pumps
  - Mixers
  - Solvatizers

TU/e Technische Universiteit Eindhoven University of Technology

DPI DUTCH POLYMER INSTITUTE

**New project on responsive materials with other driving mechanisms**

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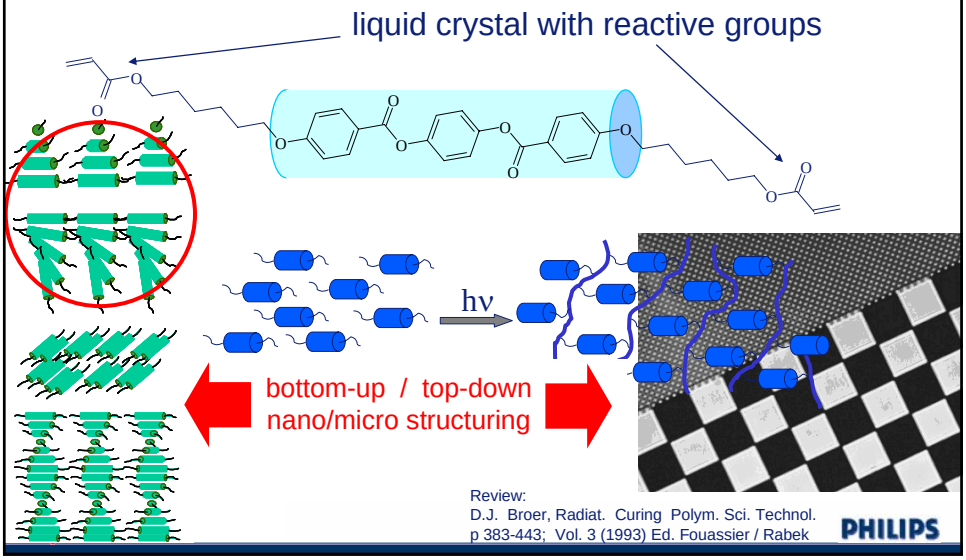
# Formation of LC networks by photopolymerization of LC monomers




Review:
D.J. Broer, Radiat. Curing Polym. Sci. Technol. p 383-443; Vol. 3 (1993) Ed. Fouassier / Rabek

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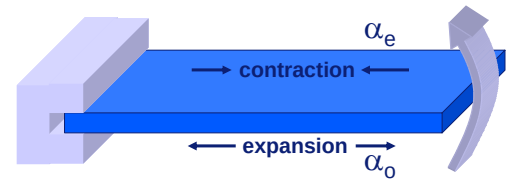
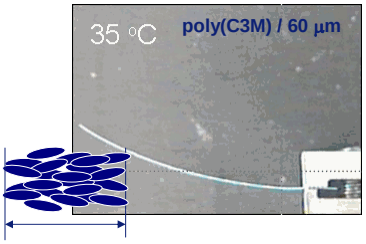
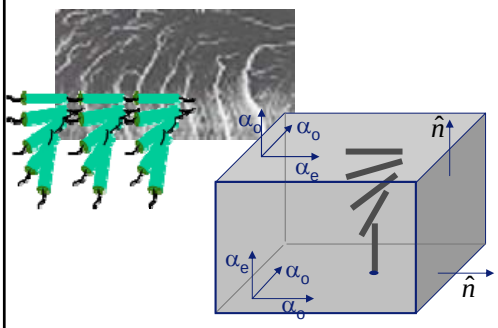
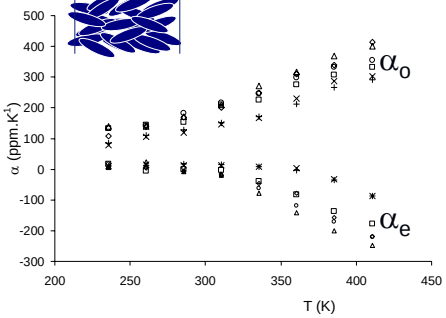
# Controlled thermal actuation in splayed LC networks



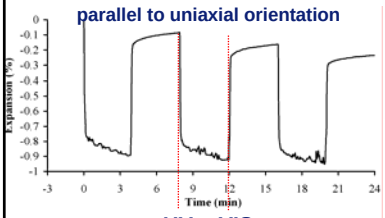



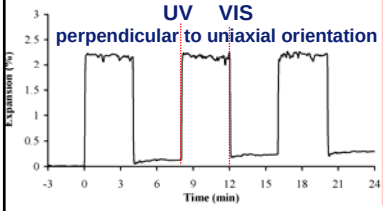



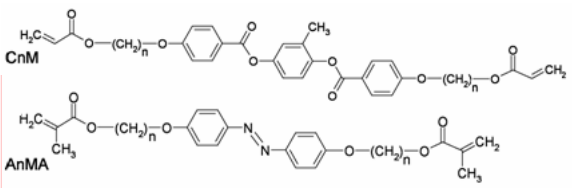



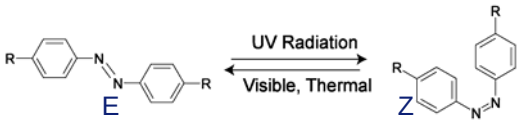

K. Harris, C. van Oosten, C. Bastiaansen (TU/e) G.N. Mol (Philips)

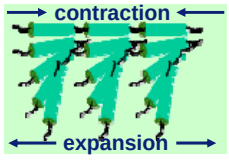
# UV light driven

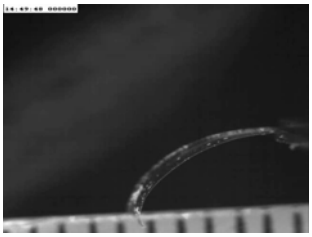


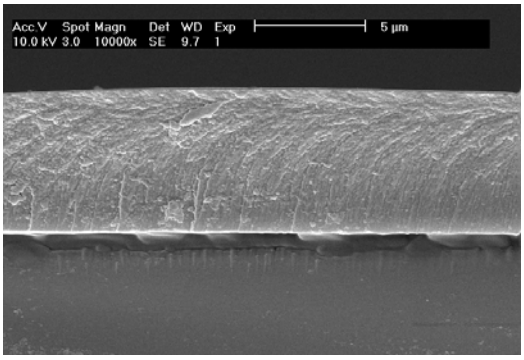



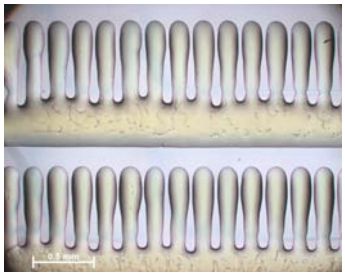



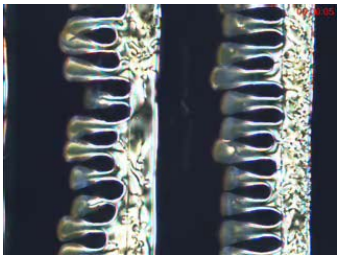



K. Harris, C. van Oosten, C. Bastiaansen (TU/e), J. Lub, R.Cuypers (Philips)

# UV light driven



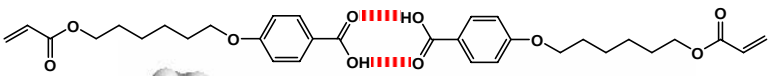



Casper van Oosten, Cees Bastiaansen (TU/e)

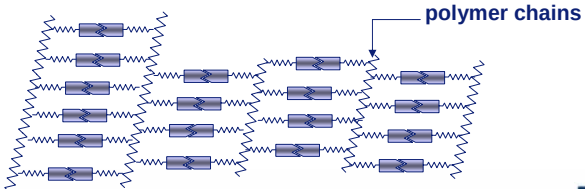
# Hydrogen-bridged LC (H-bLC) networks

**H-bLC polymers in literature:**

**L. Strezelecki, L. Liebert, Bull. Soc. Chim. France, 597 (1973) & 605 (1973)**




Cr 92 SmA 110 I

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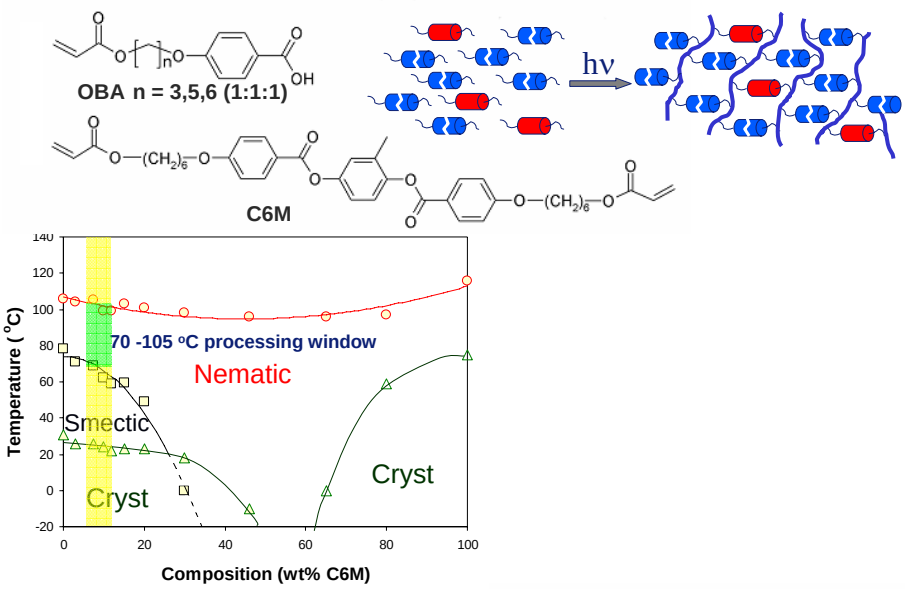
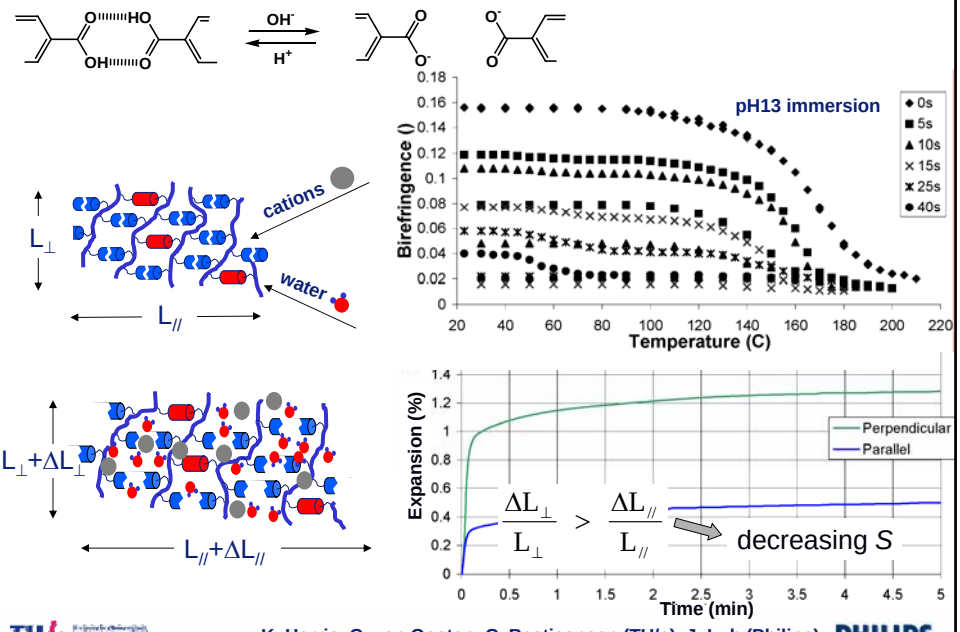
# Covalently X-linked nematic H-bLC networks

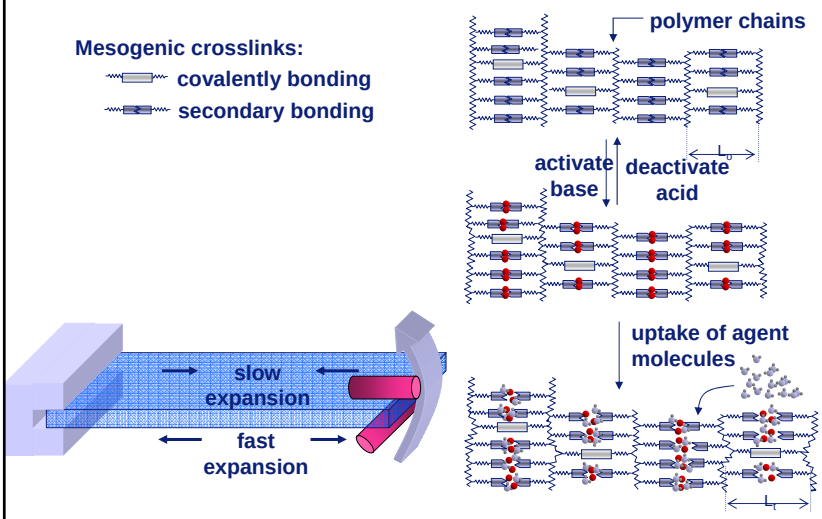





# Anisotropic swelling in alkaline buffer solution

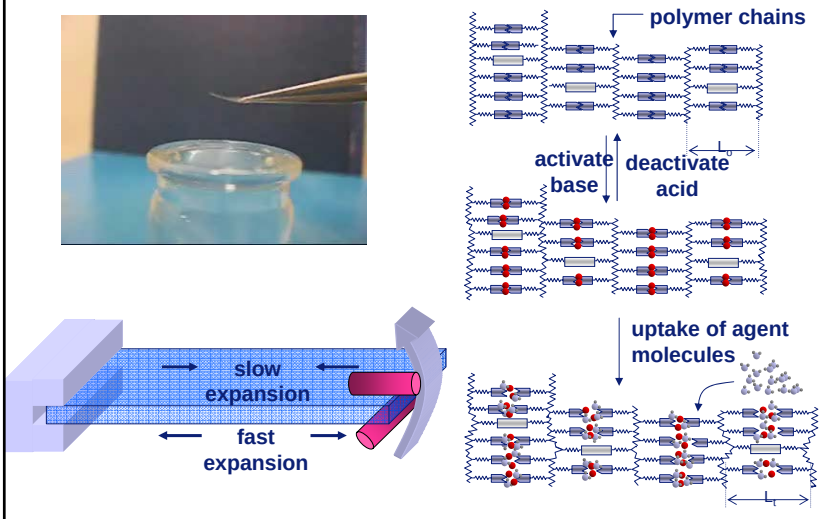


# Activate by KOH dip – deactivate in acetic acid



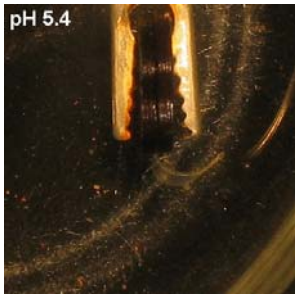


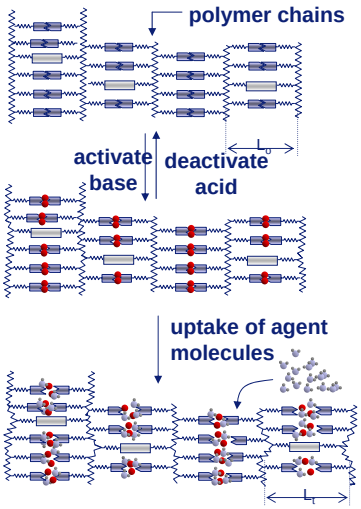

# Activate by KOH dip – deactivate in acetic acid

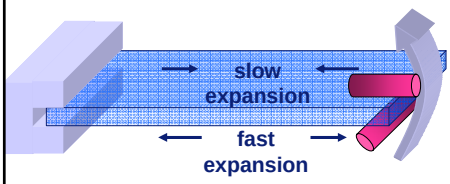



K. Harris, C. van Oosten, C. Bastiaansen (TU/e), J. Lub (Philips)

## Or activate dynamically by changing pH of buffer



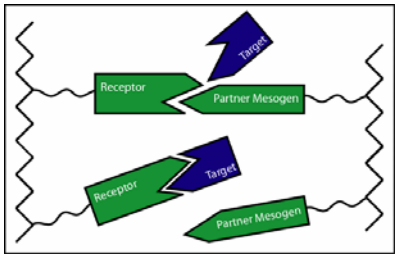



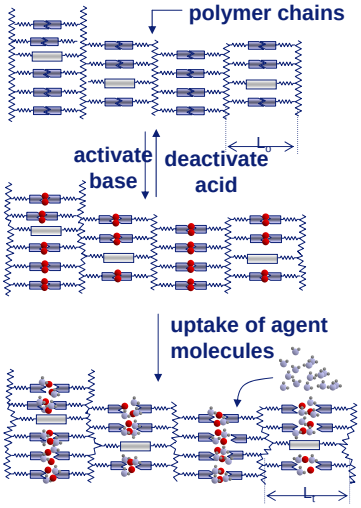





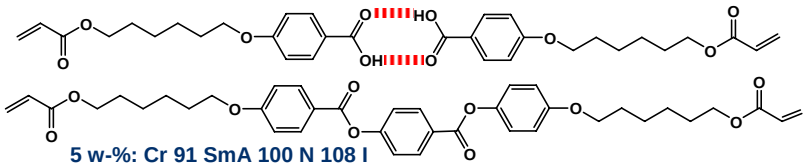

## Challenges

- integrate the elements into devices
- create sensors (new DPI project)
- create bio-responsive devices



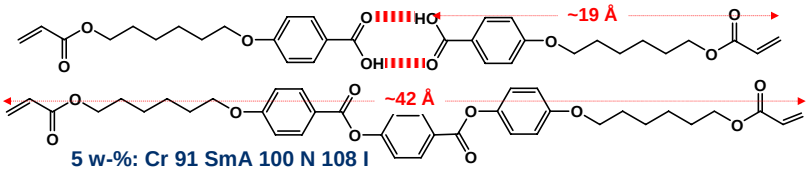
# Smectic responsive networks



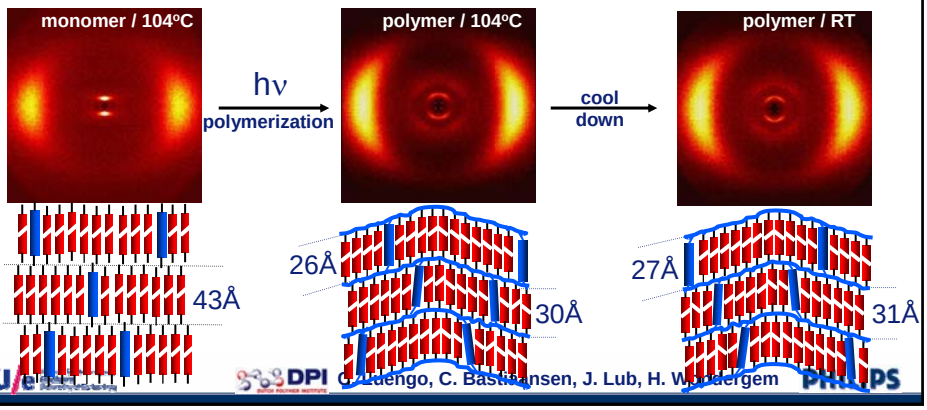
5 w-%: Cr 91 SmA 100 N 108 I
10 w-%: Cr 91 SmA 110 N 134 I
100 w-%: Cr 76 SmA 138 N 150 I



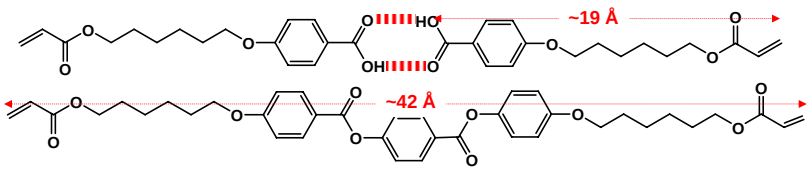
# Covalently X-linked smectic H-bLC networks

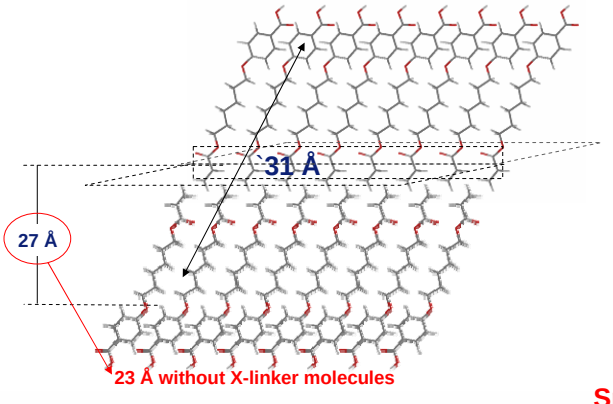


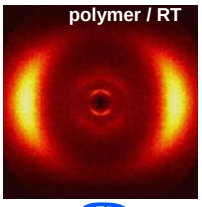

5 w-%: Cr 91 SmA 100 N 108 I
10 w-%: Cr 91 SmA 110 N 134 I
100 w-%: Cr 76 SmA 138 N 150 I

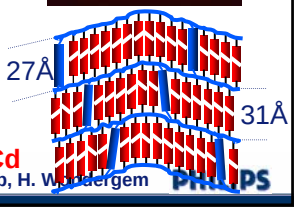


# Covalently X-linked smectic H-bLC networks



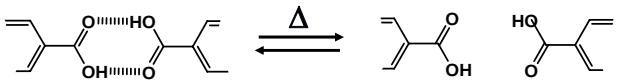



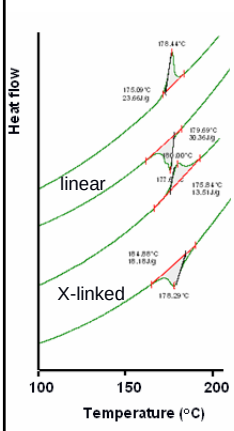



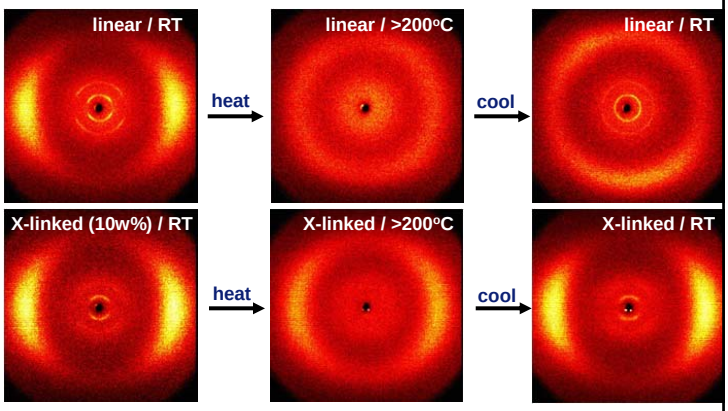

SmCd



# Covalent X-link bridges conserve order during heat cycling

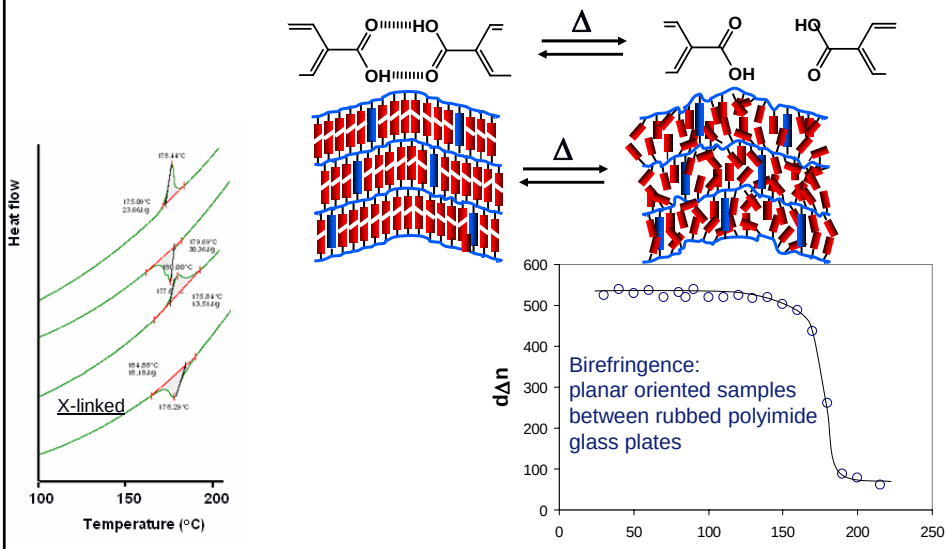


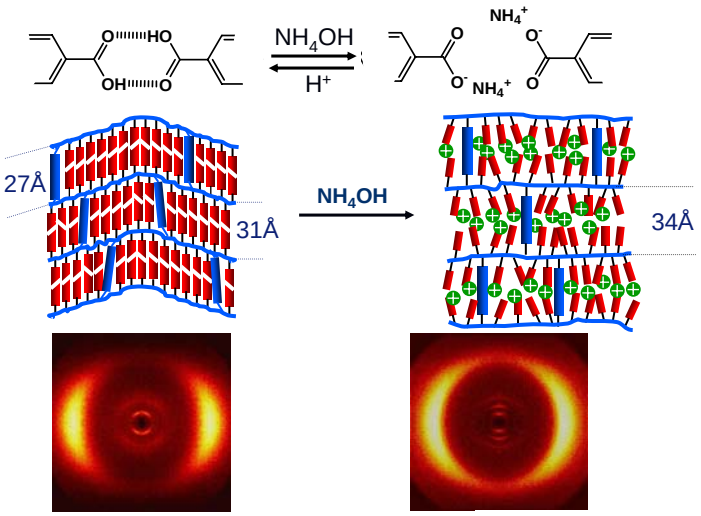

Alignment is recovered by presence of covalent X-links

# Covalent X-link bridges conserve order during heat cycling



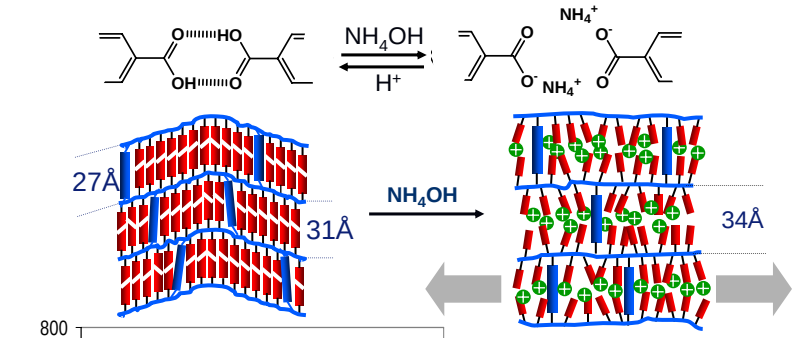


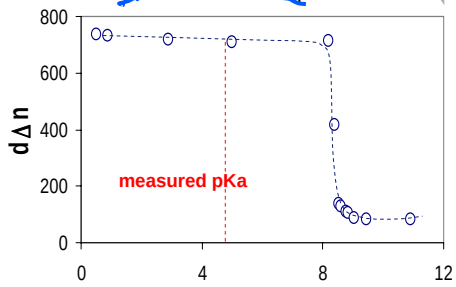

# Opening of the network at high pH




- High order of the layers
- Low order within the layer

# Opening of the network at high pH

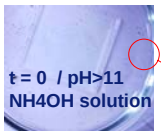


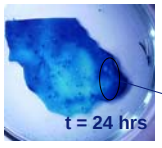




- Well-spaced porous polymer layer structure with ionic interior
- Estimated pore size ~ 1 nm when molecular rods adapt random order
- Compares with zeolites
- Anisotropic 'in-plane' pore dimensions
- Upon electrolyte/water uptake: in-plane swelling

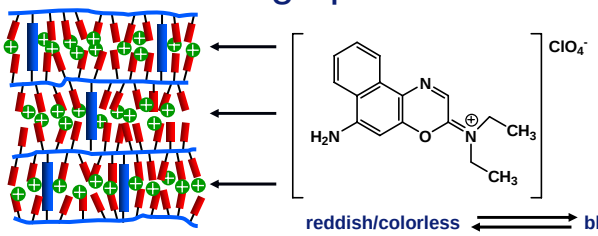


# Opening of the network at high pH

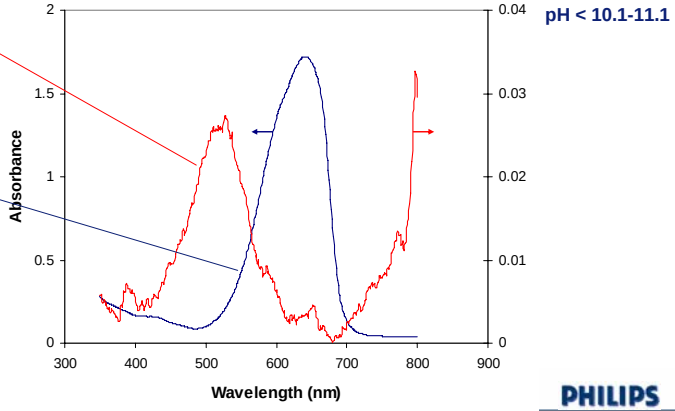





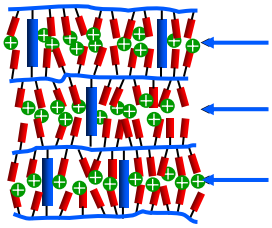


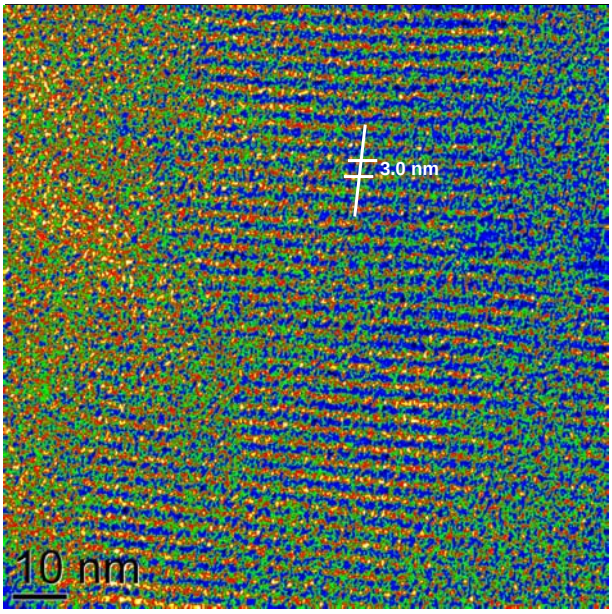

reddish/colorless ⇌ blue

pH < 10.1-11.1



## Filling the ion channels with $Ba^{2+}$



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## Conclusions

- demonstration of a successful interplay between DPI and a company
- plurality of products, but also source of inspiration for new projects
- and there are more examples:
  - project on holography ➔LCD backlights ➔E/O switches ➔ outcoupling for LED lighting➔➔ new biosensor principles
  - maskless lithography ➔3D structuring ➔E/O switches ➔➔nano-channel membranes and ionic filters

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