Flüssigkristalle

Arne Thomas / Jens Weber

MPI of Colloids and Interfaces

Outline:

1. The liquid crystalline state

1.1. Terminology of liquid crystals

1.2. History of liquid crystals

1.3. Mesogens – the subunits of liquid crystals

2. Mesophases

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2.2. Mesophases of calamitic mesogens

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2.4. The order parameter S

2.5. Why do LC phases form?

2.6 Characterisation of mesophases

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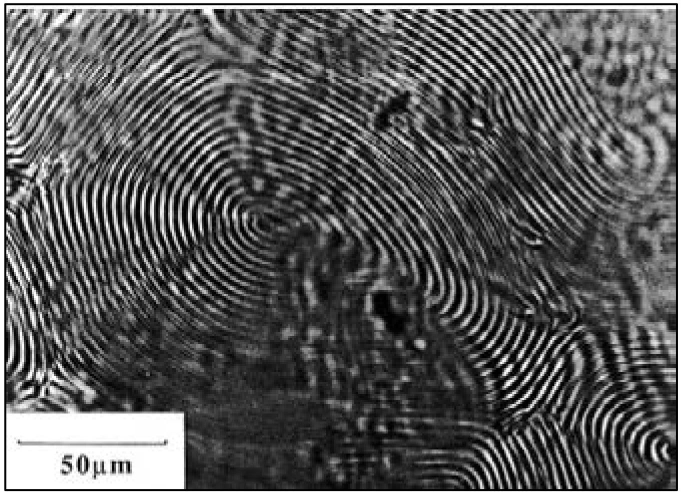
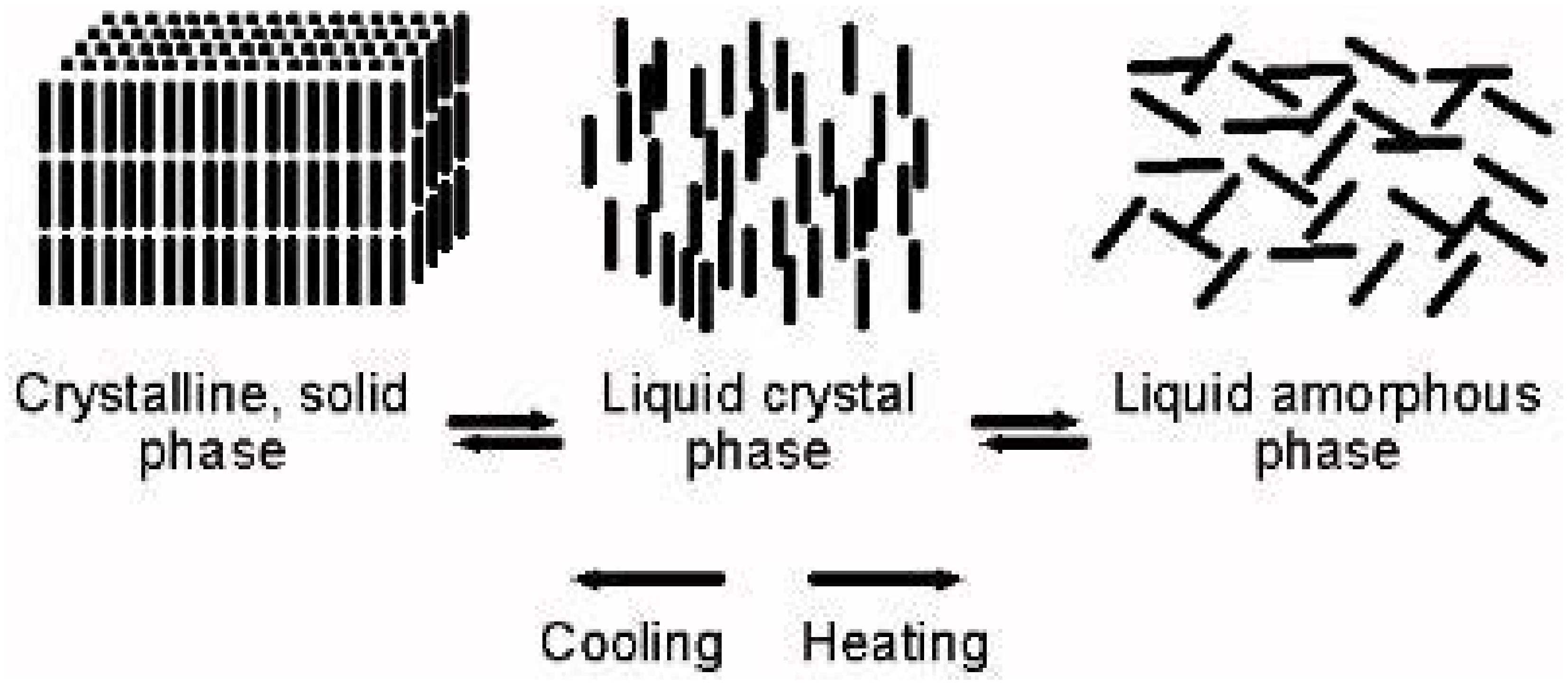
4. **Application of Liquid Crystals**

5. Literature



1. The liquid crystalline state



Crystals:
3D long range order
(∞ position- and orientational order)

Mesophases / liquid crystalline phases:
orientational order,
translational long range order
in 1 or 2 dimensions

Liquids:
No long range order,
Statistical arrangements of molecules

1. The liquid crystalline state

Properties of condensed phases:

- Solids:

  # crystalline state: 3D long range order!
  (∞ position- and orientation order)

  # glasses: just short range order, positions of molecules statistically distributed, kinetically frozen molecular motion

- Liquids: fluid states: no long range order, just short range order, positions of molecules statistically distributed

- Mesophases (mesomorphic phases) (meso (*gr.)*: middle; morphe: shape): long range (but not perfect) order in respect to the position and/or orientation of molecules; anisotropic (like crystals) but fluid properties (like liquids)

1.1 Terminology of Liquid Crystals:

Description of liquid crystals (LC´s):

Formation of the mesophase:

Thermotropic LC: temperature induced formation of the LC phases
*Lyotropic LC***:** formation of LC phase upon solvation

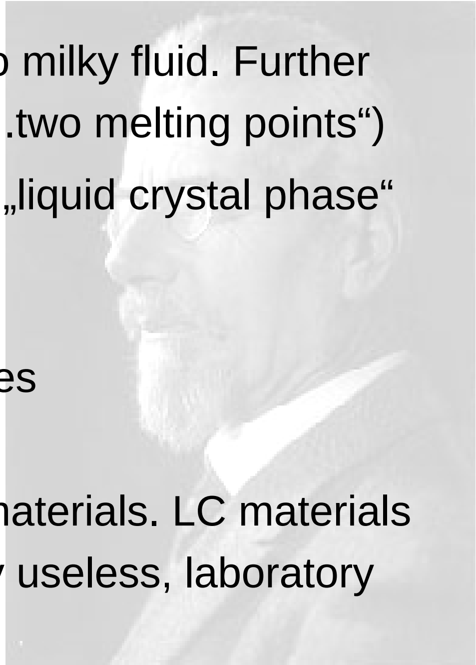
Structure of the mesophase:

Friedelian classes: Nematic, smectic, cholesteric LC´s

Structure of the mesogens:

Calamitic, discotic, banana shape LC´s, LC-polymers

1.2 History of Liquid Crystals



1888 *Friedrich Reinitzer**: Derivates of cholesterole melt at 145.5°C to milky fluid. Further heating up to 178.5°C makes the liquid clear and transparent. („..two melting points“)

1890 *Otto Lehmann* identifies a „new and distinct state of matter“, the „liquid crystal phase“

1904 First commercially available Liquid-crystals (**Merck-AG**)

1922 *Friedel* establishes the names of the three liquid crystalline phases (*nematic, smectic and cholesteric*).

Next 30 yrs. The scientific community gradually losses interest in LC materials. LC materials were widely considered as an interesting, but essentially useless, laboratory curiosity.

End of 1960s Suggestion of cholesteric LC´s as temperature indicators, analytical metrology, cancer diagnostics and non-destructive testing of materials

1968 ***George Heilmeier*** first prototype of LCD‘s

1970-71 *Fergason, Schadt, Helfrich**:* Invention of the twisted nematic (TN) cell → extensive R&D efforts in LC materials and LCD´s all over the world

1980s-1990s LCDs replace conventional display devices in many applications → portable PC´s, mobile telephones, electronic toys

Today: broad applications in display technology, high modulus fibres and opto-electronic devices

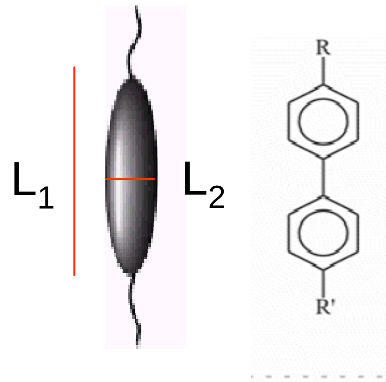
*F. Reinitzer, *Phys. Chem*., 4, 462, (1889)

1.3 Mesogens – the subunits of liquid crystals

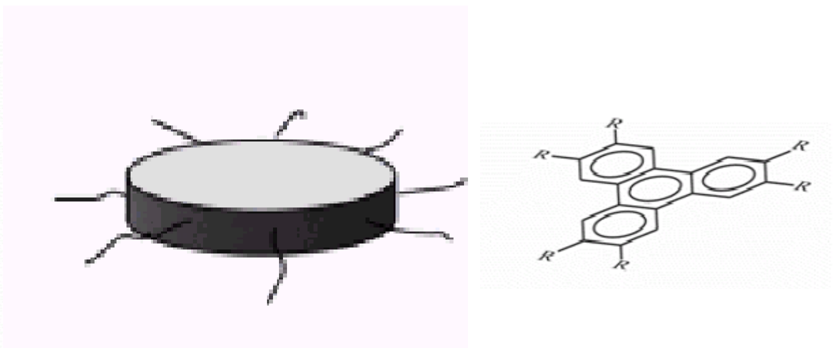
Requirement: Geometrical anisotropic units (mesogens)

Mesogens (Definition): Rigid molecule or molecule segment with anisometric (geometrical anisotropic) architecture

$L_{krit} = L_1/L_2$



calamitic



discotic

Aspect ratio of calamitic mesogens:

$L_{krit.} \geq 6.4$

for $L < 6.4$ e.g. $L_{Sphere} = 1$ ➔ Mesophase formation impossible

Requirement: Geometrical anisotropic units (mesogens)

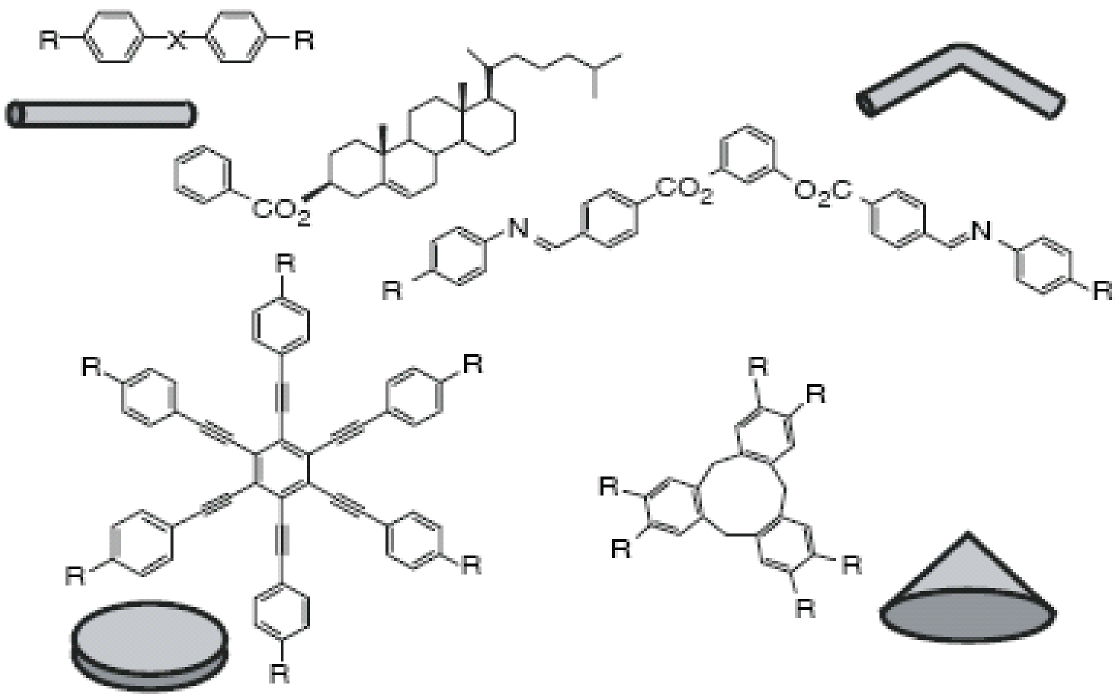
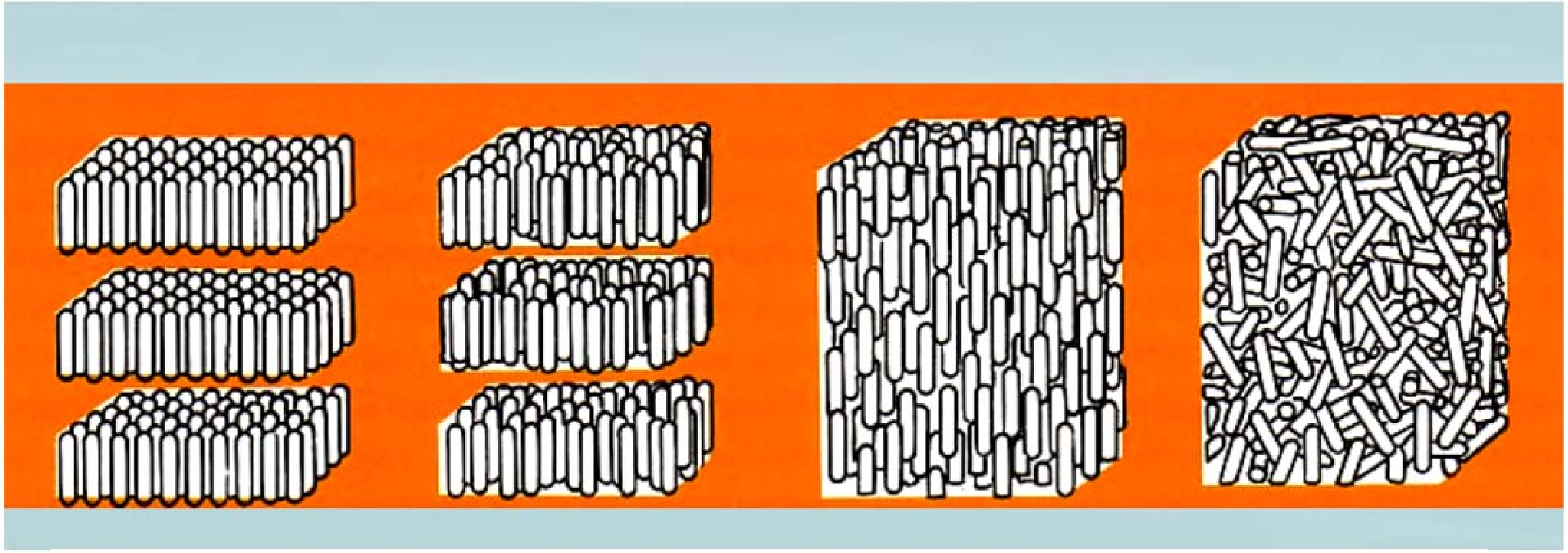


Abbildung 2.2: Bekannte formanisotrope Moleküle, die thermotrope Flüssigkristalle bilden. Links Beispiele für stab- und scheibenförmige Moleküle, rechts ihre gewinkelten Analoga: Oben Bananen-, unten Hutform. Die Reste R können Alkyl-, Alkoxy- oder komplexere, auch chirale Ketten, einzeln auch polare Gruppen wie CN oder NO_2 sein. Die Brückengruppe X kann z. B. eine Esterfunktion, eine Methylengruppe, eine Schiffsche Base oder eine Phenylgruppe sein.

2. Mesophases

crystalline phases	mesophases	amorphous phases
3D-order	2D-, 1D-order	no long-range order



crystalline | smectic | nematic | liquid

„liquid crystalline“ (smectic, nematic)

3D | **2D** | **1D** | **0D**

2.2 Mesophases of calamitic mesogens

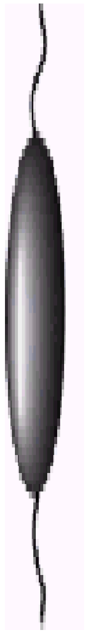
Smectic mesophase: (gr.: soapy)

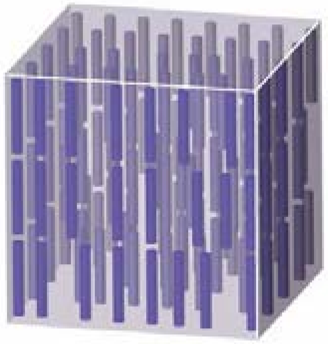
layer structures (2D-Order)

parallel molecular axes

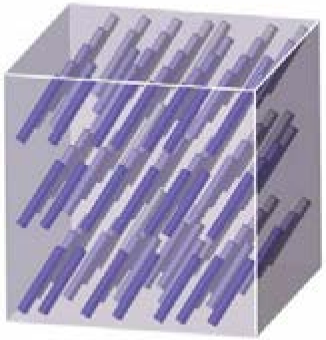
molecule centers are orientated in the layers

→ molecular packing within the layers is liquid-like and has no long range positional order!





(c) Smectic A liquid crystal



(d) Smectic C liquid crystal

Other smectic variants and sub-variants: ~ 26 polymorphs

In general mesogenic molecules with terminal alkyl or alkoxy chains will tend to favor smectic phases, and the longer the terminal chains the more the smectic phases will be stabilized with respect to other liquid crystalline structures

2.2 Mesophases of calamitic mesogens

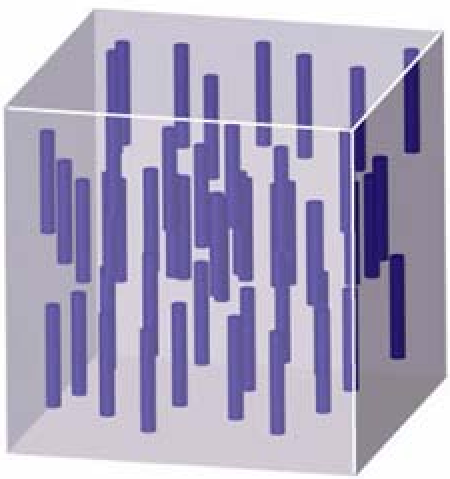
Nematic mesophase: (gr.: „thread“; threaded textures in the light microscope)

1D-order

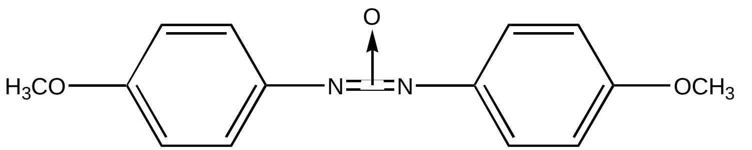
parallel molecular axes

molecule centers are not orientated

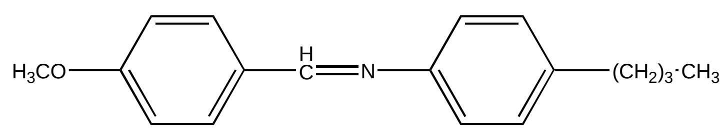
long-range orientational order / short range positional order



(b) Nematic liquid crystal



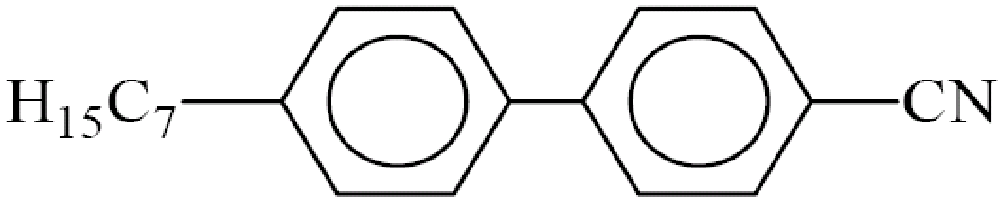
PAA: p-azoxyanisole



MBBA: n-(p-methoxybenzyidene)-
p-butylaniline

2.2 Mesophases of calamitic mesogens

One Example:

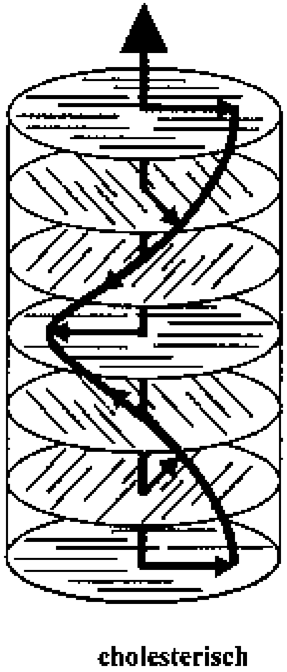


Increasing the length of the alkyl tail increases the order (CH2)x
x = 3-7 nematic , 7-11 smectic, >12 crystalline

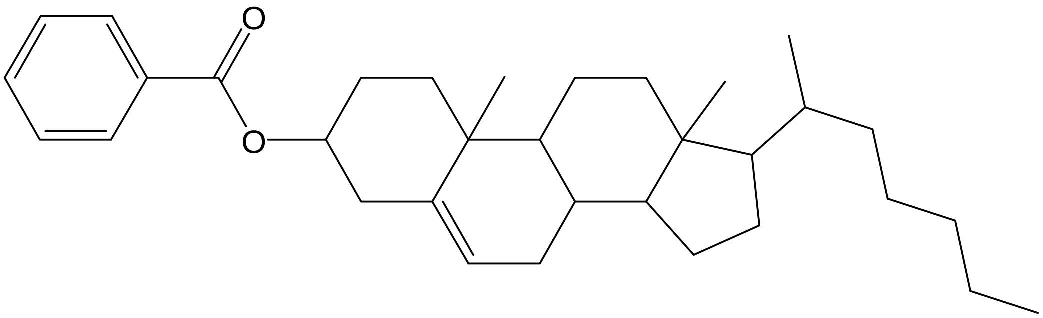
2.2 Mesophases of calamitic mesogens

Cholesteric mesophase: equivalent to nematic, which has been twisted periodically about an axis perpendicular to the director → („chiral nematic“)

formed from chiral mesogenic molecules or after doping of a nematic phase with a chiral molecule



Chiral nematic

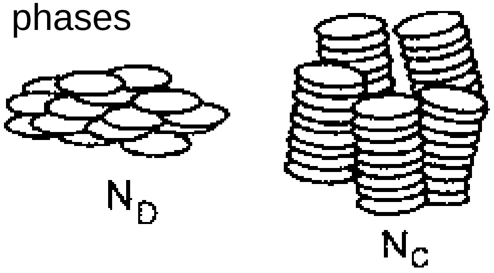


First identified mesophase from cholesterol benzoate
(Reinitzer 1888)

2.3 Mesophases of discotic mesogens

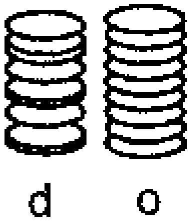
<u>Nematic-discotic phase</u> (N_D):
- discs nearly parallel
- statistical distribution of centers of molecules

<u>Nematic-columnar phase</u> (N_C):
- discs columnar orientated
- no positional order



<u>Intercolumnar order</u>

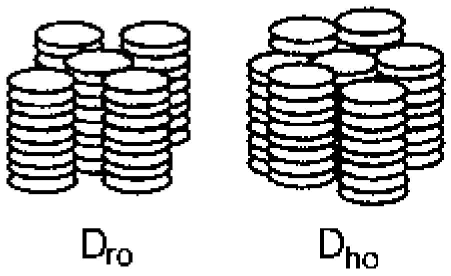
ordered (o): ◆ positional short range order
disordered (d): ◆ weak positional short range order

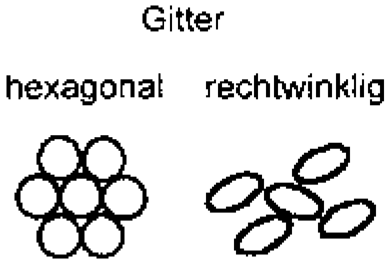


<u>Higher ordered columnar phases</u>

Discotic columnar right-angled (D_{ro}):
- columns are parallel alligned
- on right angled 2D-lattice

Discotic columnar hexagonal (D_{ho}):
- columns are parallel alligned
- hexagonal 2D lattice

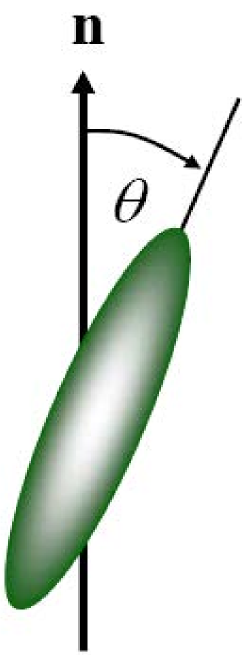




2.4 The order parameter S

Def.: Quantitative Description of the orientation of th mesogens in the LC-Phase

$$S = (3\cos^2\theta - 1)/2$$



Anisotropy is defined by the symmetry axis of the orientation distribution, i.e. the director n

θ = Average deviation angle of the mesogen axes from the director

All molecules aligned parallel to the director: S = 1
Statistical distribution: S = 0

LC-Polymere mit smektischen Phasen: $0.85 < S < 0.95$

nematischen Phasen: $0.45 < S < 0.65$

→ Order parameter can be determined using diffraction measurements!

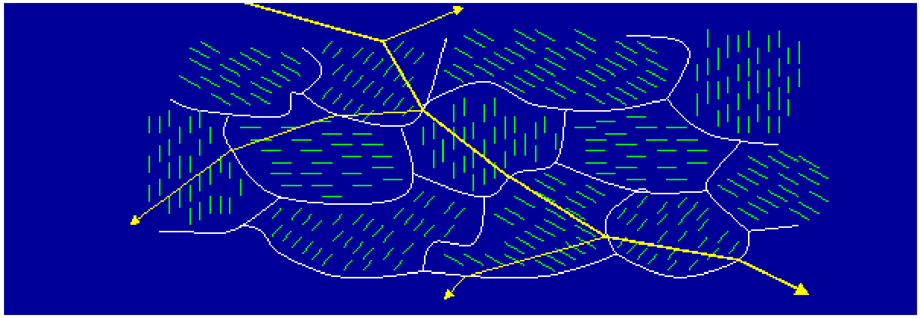
2.4 The order parameter S

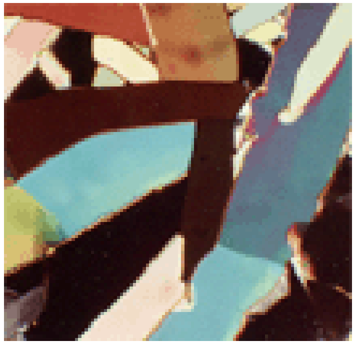
Hierarchy of Orientation:

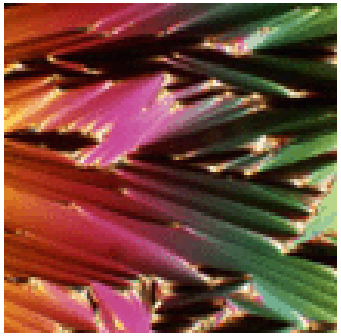
1.) Orientation of mesogens in domains
(domain sizes: µm-range).

Inside each domain:
Orientation of the molecular axes in respect to the director

2.) The directors of the domains are statistically distributed







3.) Alignement of the domains possible *via* rubbing,
aligned substrates, electric/ magnetic fields……

2.5 Why do LC phases form?

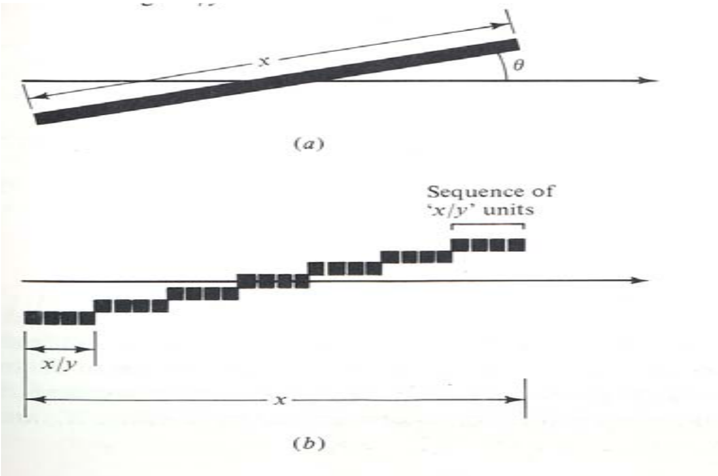
Steric theory of liquid crystals (Onsager / Flory)

→ Mesogens are modelled as rigid rods: no interpenetration,
i.e. no possibility for two molecules to occupy the same region of space

→attractive intermolecular forces are not taken into account in any specific way!

Central objective → determine the number of ways of arranging a population of rods at a particular concentration in a given volume

$S = k \ln Z$ Z =partition function → number of arrangements

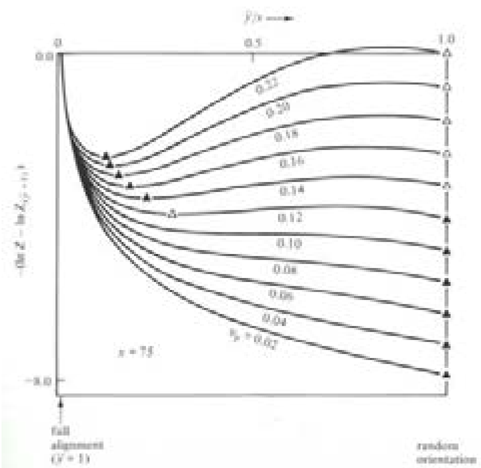


2.5 Why do LC phases form?

$S = k \ln Z$

Z =partition function → number of arrangements

$Z = Z_{comb} Z_{orient}$



Z_{comb}= combinatory partition function

Describes the number of ways of arranging the positions of n_p identical rod molecules on the lattice, when the orientation of each rod (with respect to the director) is fixed

Z_{orient}= oriental partition function

Accounts for the additional arrangements which are possible when a range of orientational options are assigned to each rods

Z_{comb} decreases / Z_{orient} increases when misalignement increases!

- Small axis ratios and / or concentrations Z is dominated by Z_{orient} → stability of phases increase with misorientation, isotropic state is the equilibrium state
- Higher axis ratios and / or concentrations Z_{orient} and Z_{comb} are evenly balanced → maximum in Z, i.e. phase stability optimal at some intermediate value of orientational disorder

2.5 Why do LC phases form?

Driving force: pure geometrical aspects!

Better packing of anisomeric mesogens in a LC phase

with $S = k \ln Z$ → LC formation is entropy driven !

- Decrease of rotational entropy, but
- Increase of the translation entropy

(*Example: matches in a box*)

Maier-Saupe-Theory (1960): Introduction of an orientation dependent interaction (dispersion forces) of the rod like molecules into the lattice model

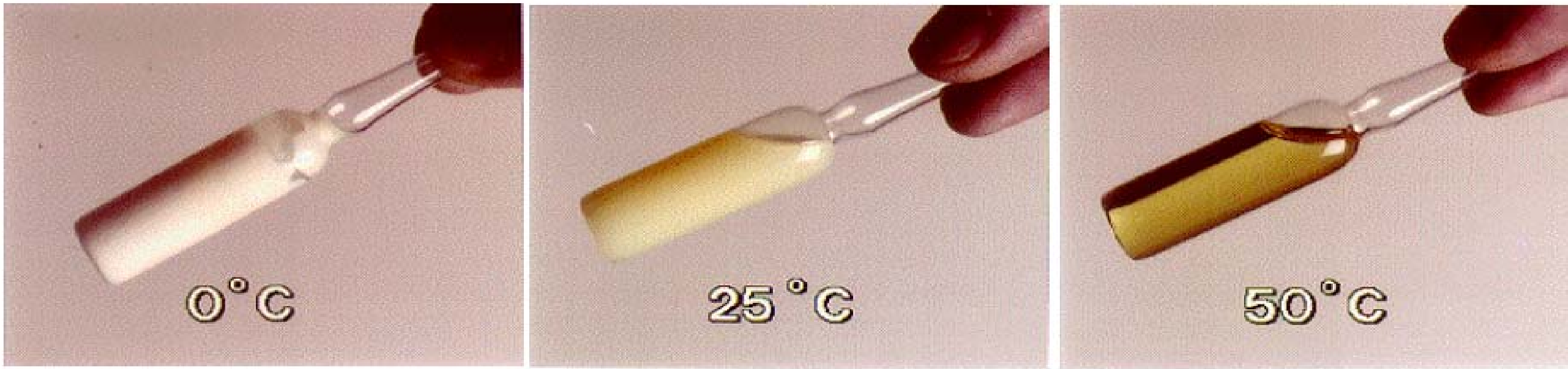
Mesogen-Mesogen interaction: stabilizes LC Phases

but

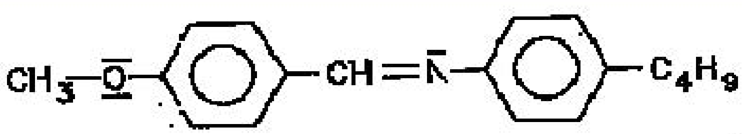
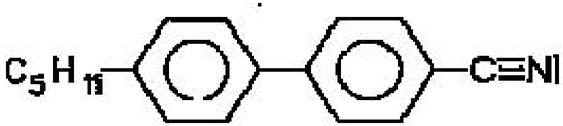
→ is not the driving force for the formation of th LC phase!

2.6 Characterization of LC phases

Erstarrungs- und Klärpunkt

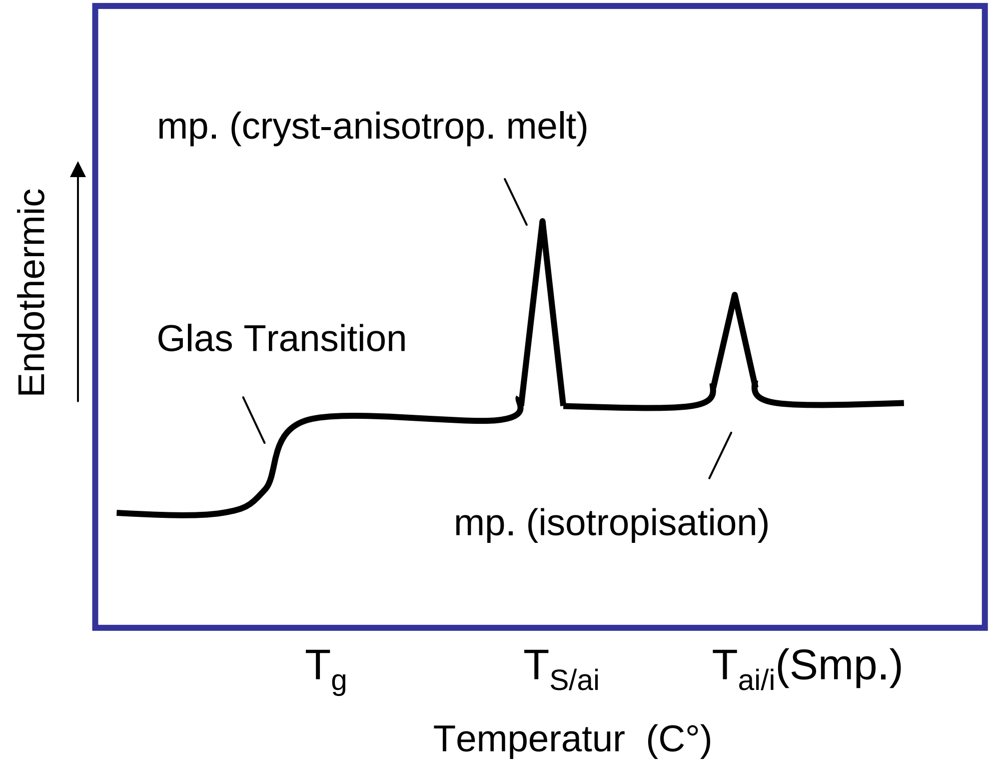


erstarrt (Eis) — milchig trüb — klar (Flüssigkeit)

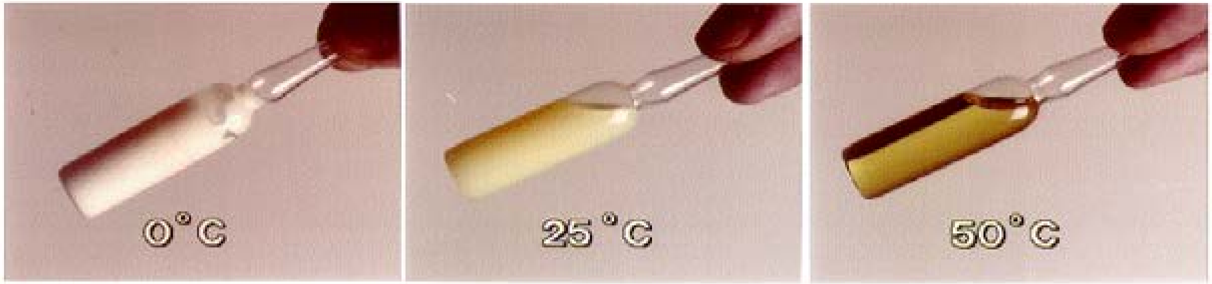
		T_{sol}	$T_{klär}$
	MBBA	22°C	47°C
	5CB	23°C	35°C

2.6 Characterization of LC phases

DSC (Differential Scanning Calometry):



DSC measurement of a LC polymer

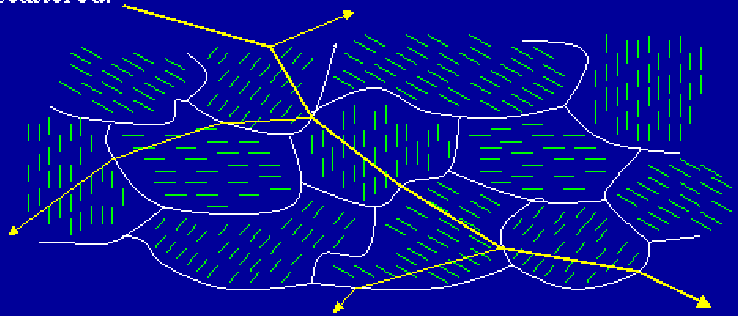


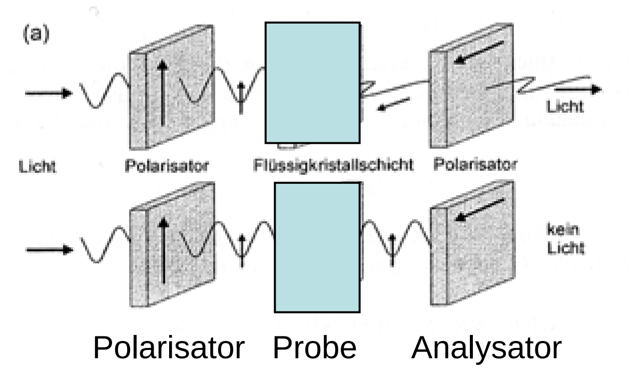
erstarrt (Eis) milchig trüb klar (Flüssigkeit)

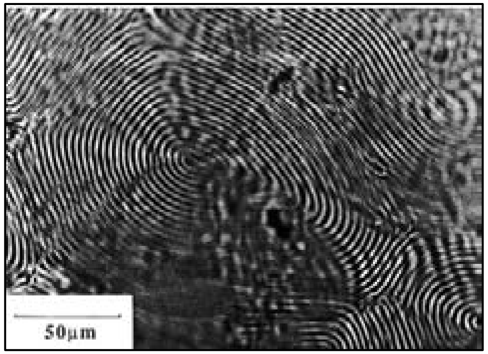
2.6 Characterization of LC phases

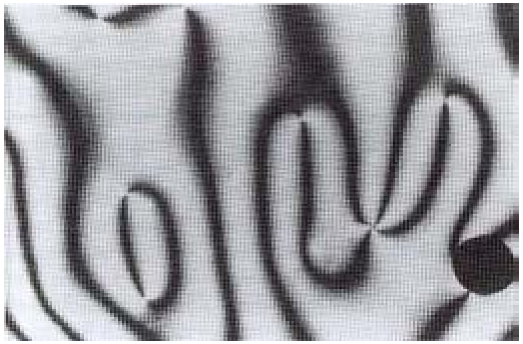
Polarisation microscopy

Liquid crystals organize locally into *domains* with the same orientation. Light coming into a domain from most directions will be bent because of the change in refractive index. Light coming into a liquid crystal with many domains will be scattered.









Schlierentextur (nematic phase N)

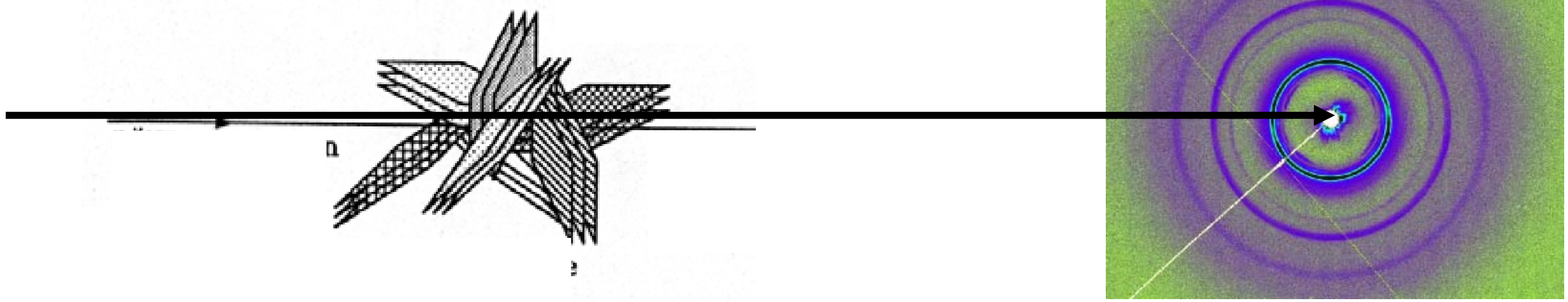
Fingerprint texture cholesteric phase (N*)

Fokal-conic texture (smectic phase S_A)

2.6 Characterization of LC phases

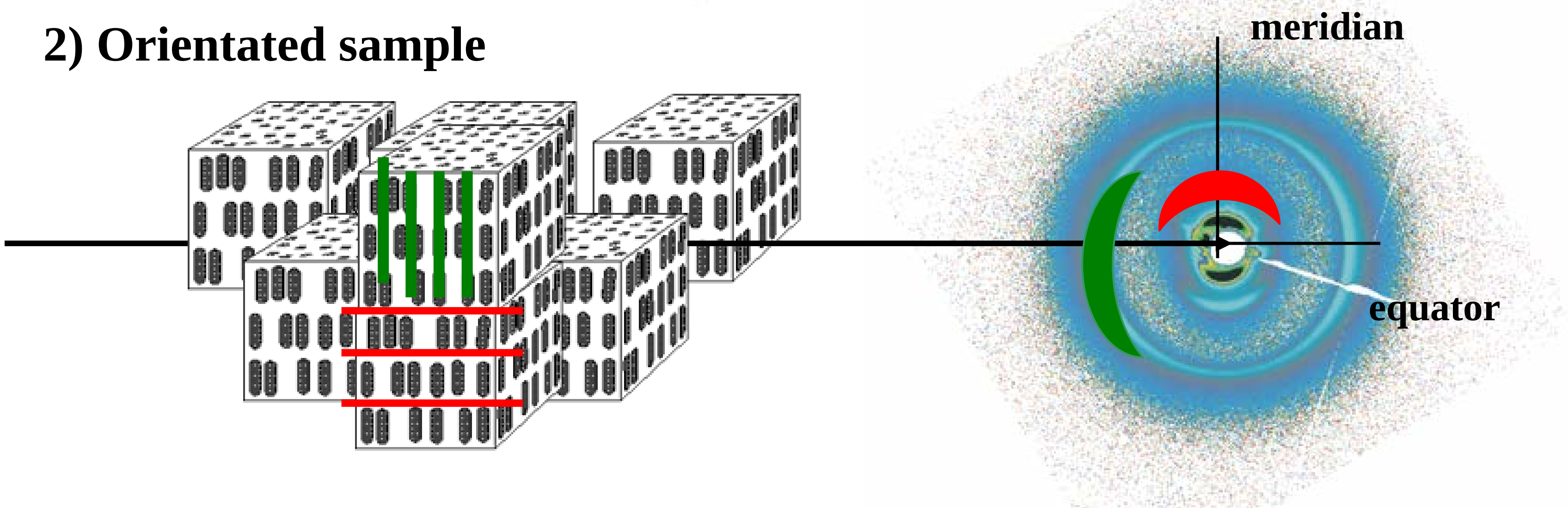
<u>Diffraction</u>

1) Randomly orientated



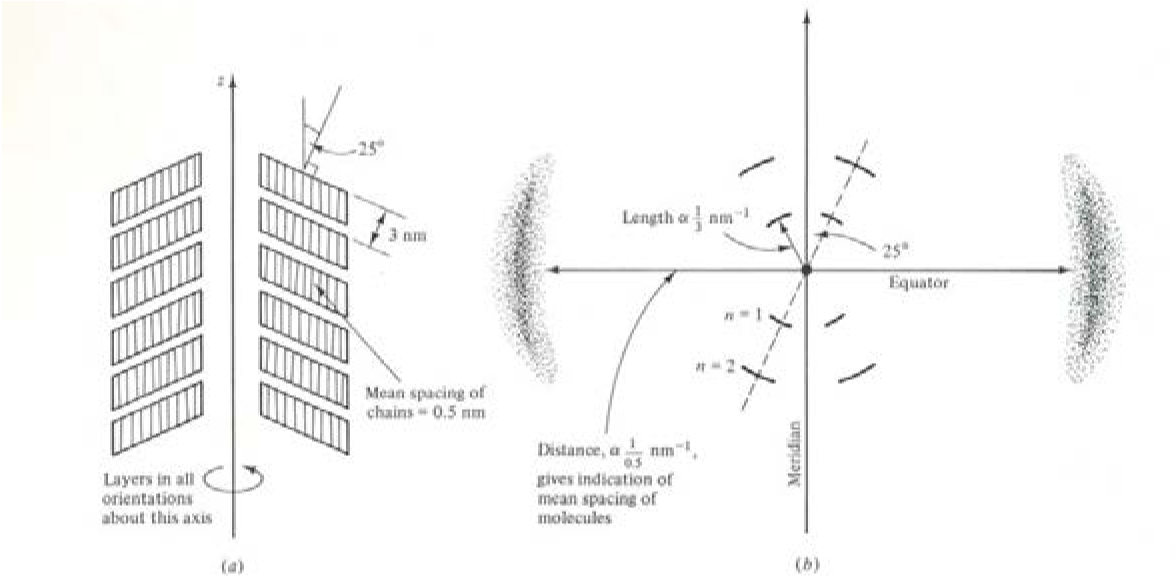
Isotropic "Debye-Scherrer" pattern

2) Orientated sample

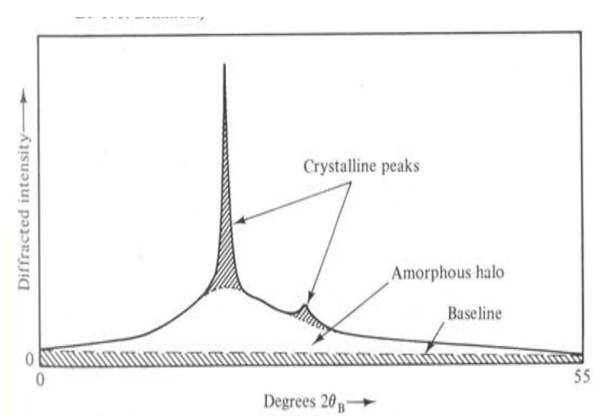


Anisotropic pattern

Diffraction



Relationship between a smectic C structure and various features of the resulting diffraction pattern



Powder XRD of a thermotropic liquid crystalline polymer with partial crystalline order (20%)

2.6 Characterization of LC phases

Spectroscopy → Polarized absorption/emission from aligned chromophores!

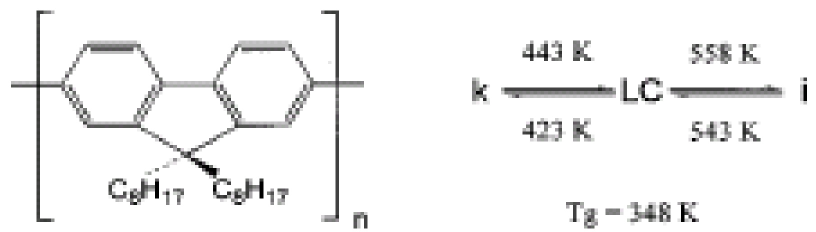


FIG. 1. Structure of PFO and phase behavior of PFO.

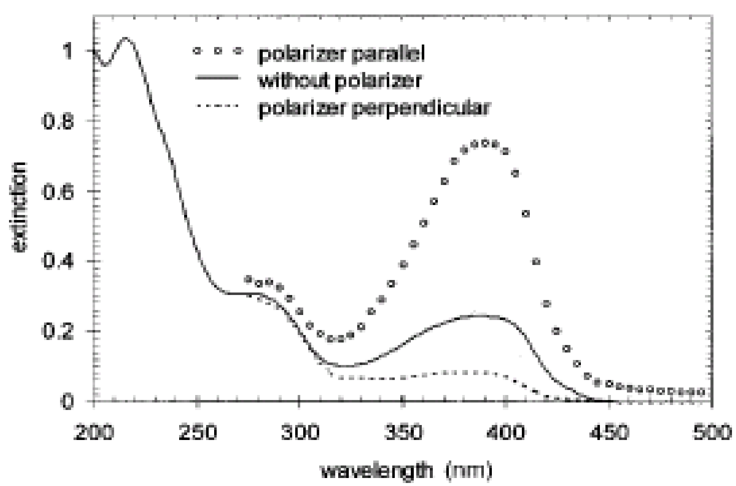


FIG. 3. Polarized UV/VIS absorption spectra for sample II. The low wavelength cutoff for the polarized spectra arises from the transmission cutoff of the polarizer.

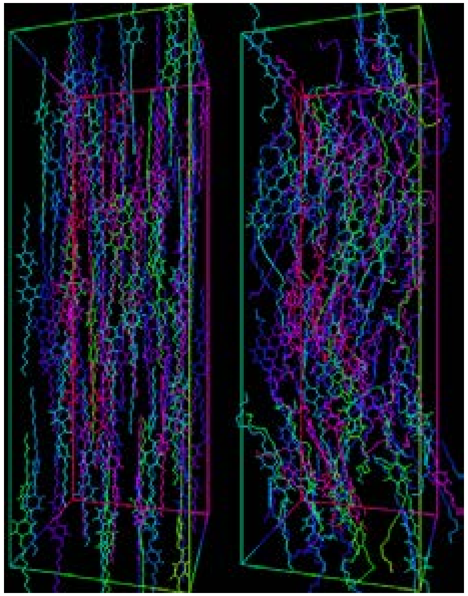
$$\langle P_2\rangle^{UV}=\left(1-\frac{3}{2}p\right)^{-1}\frac{E_\parallel-E_\perp}{E_\parallel+2E_\perp}.$$

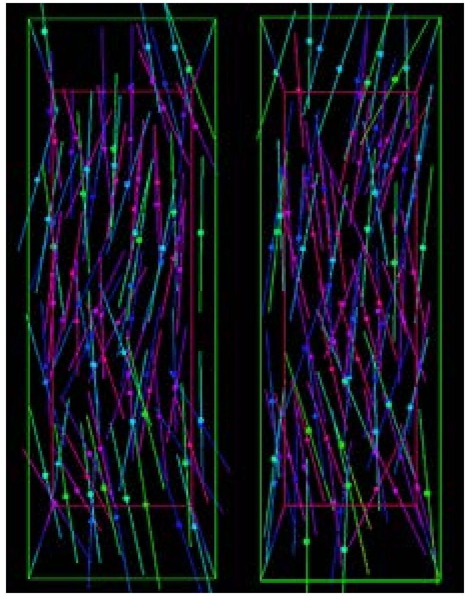
$$\langle P_2\rangle^{UV}=0.82\pm0.01.$$

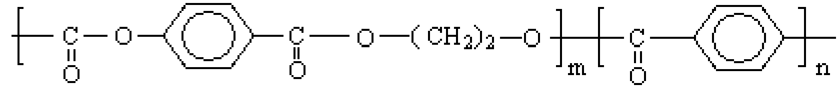
P_2 = Orientation function (= order parameter)

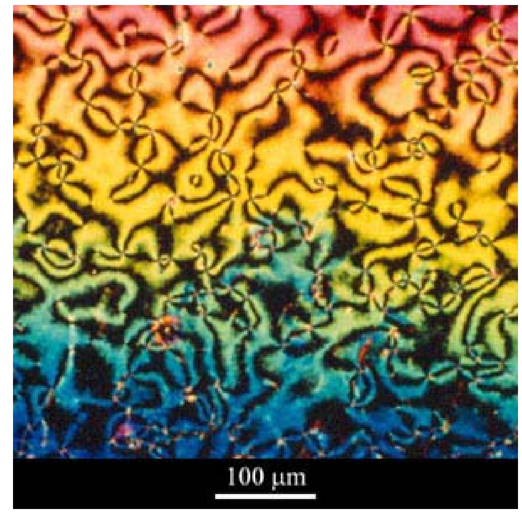
Schartel et al., *Phys. Rev. B* **1999**, *60*, 277

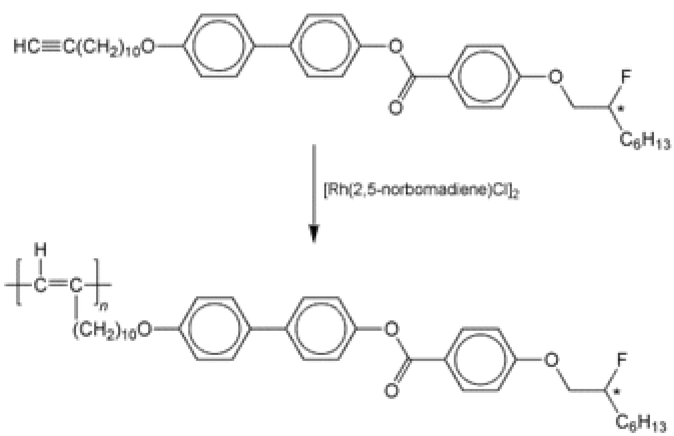
3. LC polymers





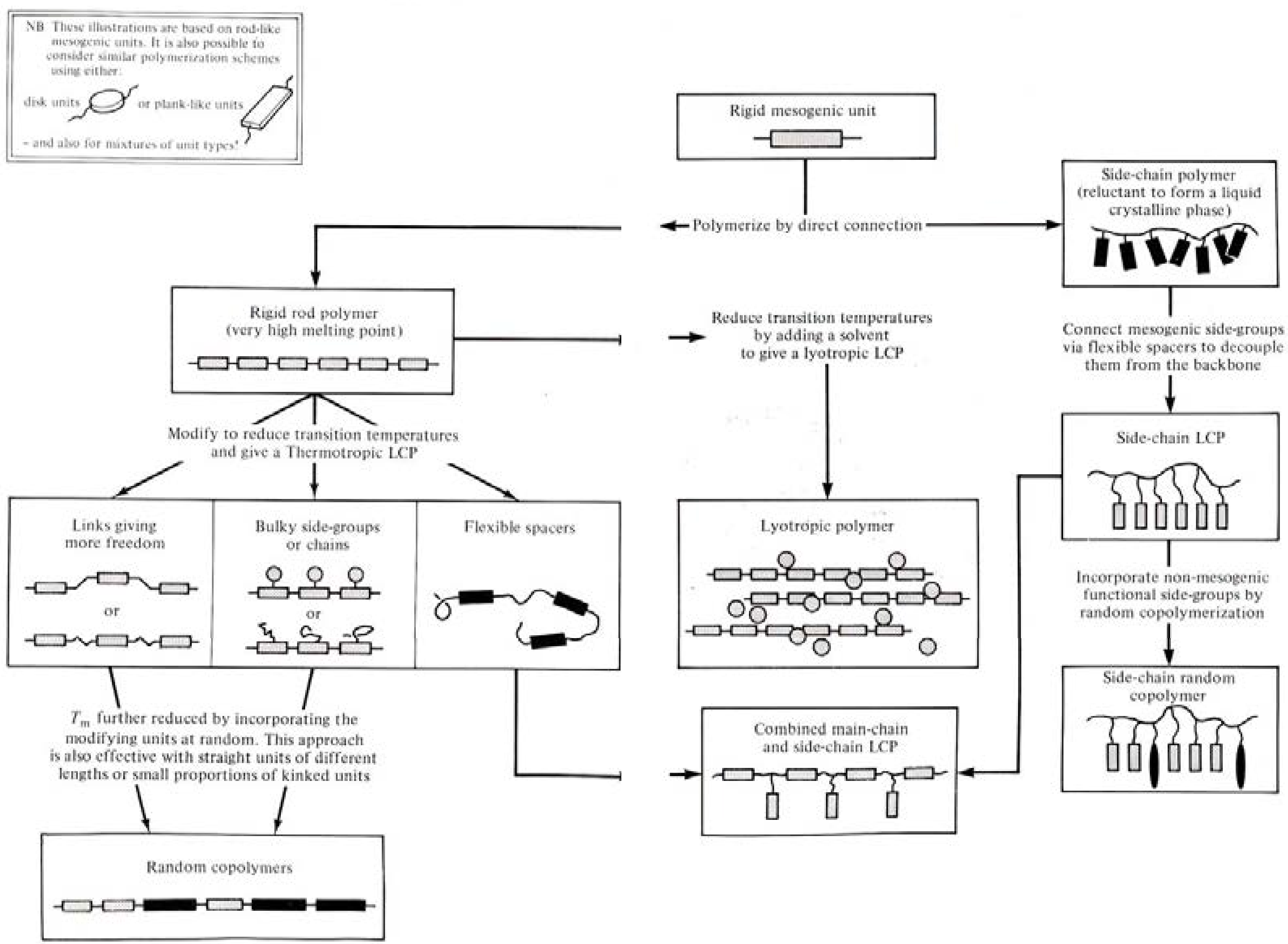






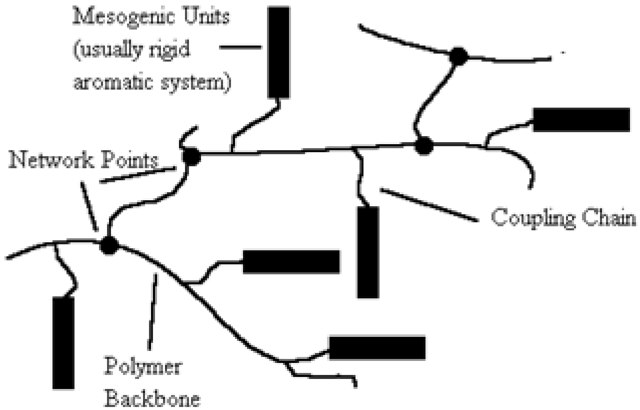
3. Structure of LC polymers

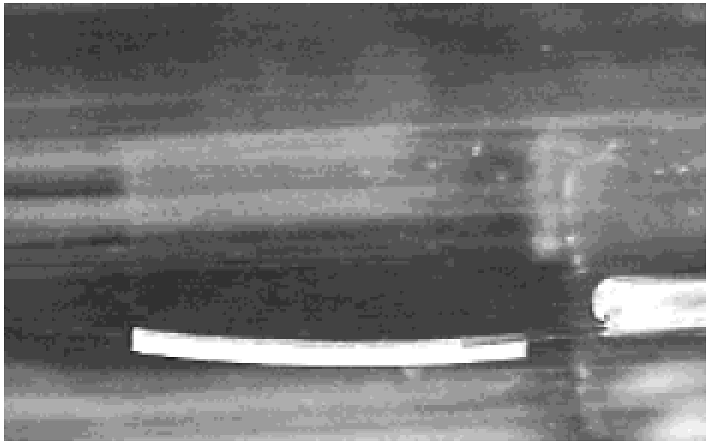
Various types of liquid crystalline polymers

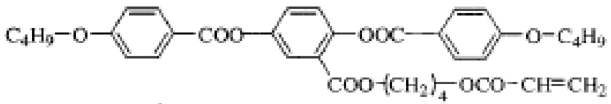


3. Structure of LC polymers

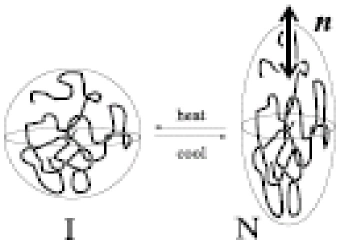
Liquid crystalline elastomers







4a



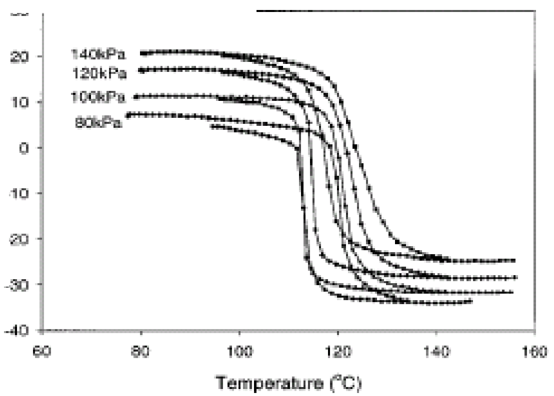
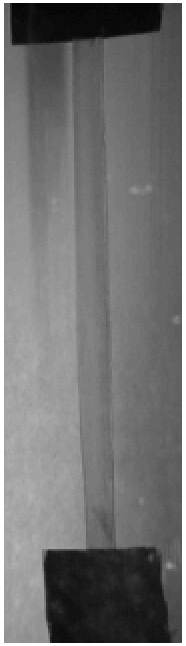


Figure 3. Thermoelastic measurements of aligned LCE 1 at 3 °C/min heating and cooling.

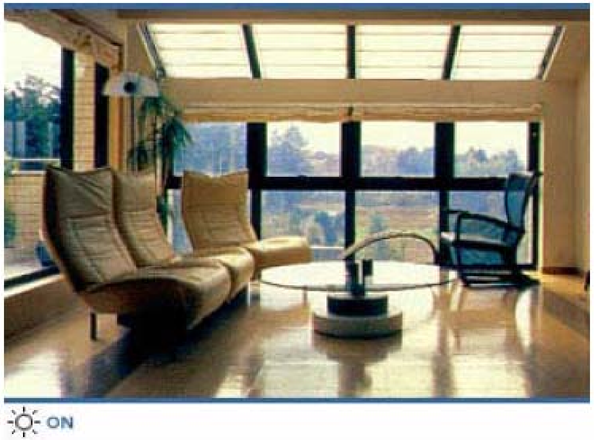


Artificial muscles!

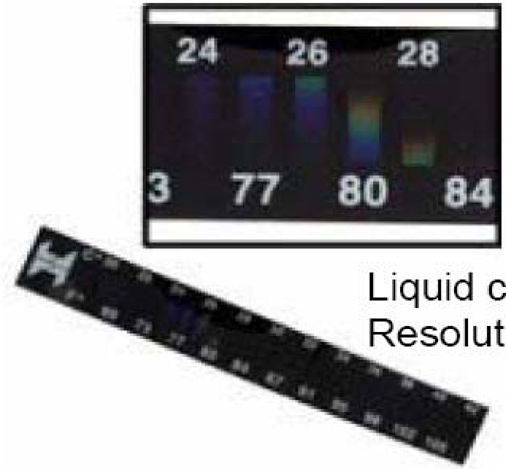
Thomsen et al. *Macromolecules* **2001,** *34,* 5868

4. Application of Liquid Crystals

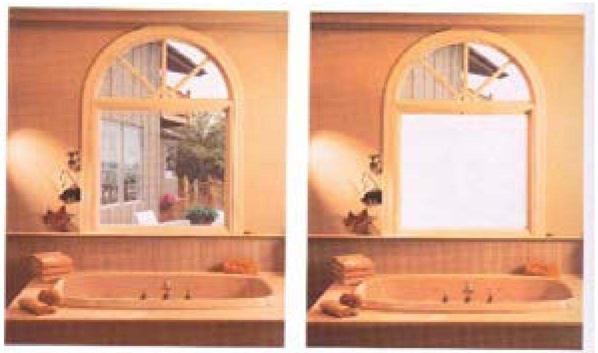
LC displays (phones, monitors, TVs, GPS, etc.)



Switchable windows (Polymer dispersed liquid crystals, PDLC) [see www.switchlite.com]



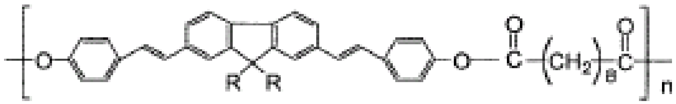
Liquid crystal thermometer.
Resolutions are in the 0.1°C range.



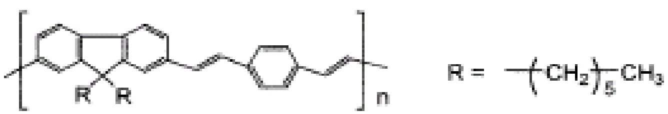
LC´s as opto-electronic materials

Lasing

Low-Threshold Amplified Spontaneous Emission in a Fluorene-Based Liquid Crystalline Polymer Blend



1



2

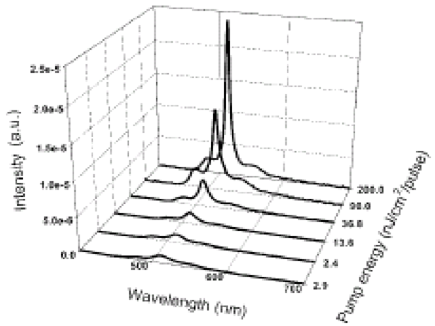
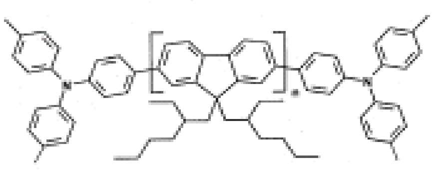


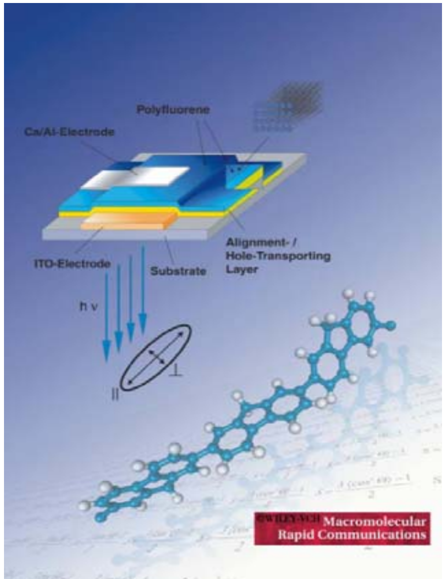
Fig. 3. Evolution of the PL spectrum of the polymer 1/polymer 2 (98:2) blend waveguide near the threshold for gain narrowing. The specimen was photo-pumped with 1 Hz, 800 ps pulses at 337.1 nm generated by a nitrogen laser.

Kim et al. *Adv. Mater*. **2001**, *13*, 646

Polarized OLEDs



PF2/6amX



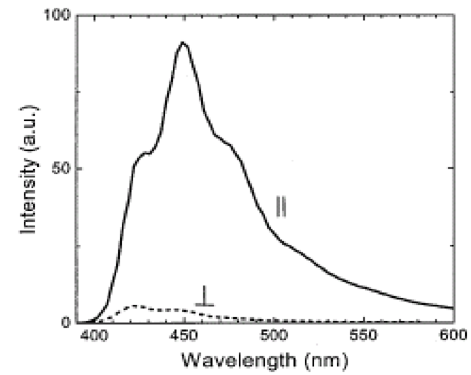
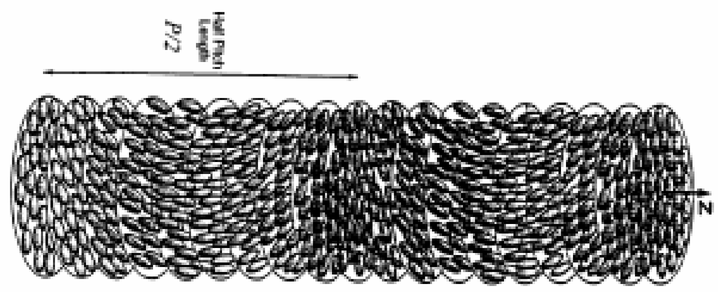


Figure 12. EL spectra of a device based on monodomain-aligned PF26am9 measured parallel (——) or orthogonal (- - - -) to the rubbing direction of the alignment layer.[58]

D. Neher, *Macromol. Rapid Commun*. **2001**, *22*, 1365

4. Application of Liquid Crystals

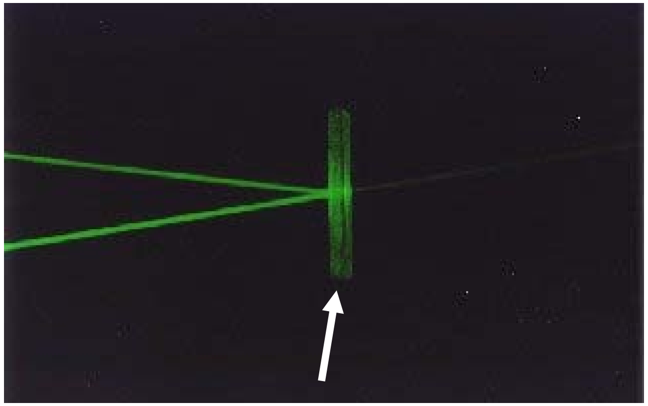
“Guidance” of elliptically polarized light



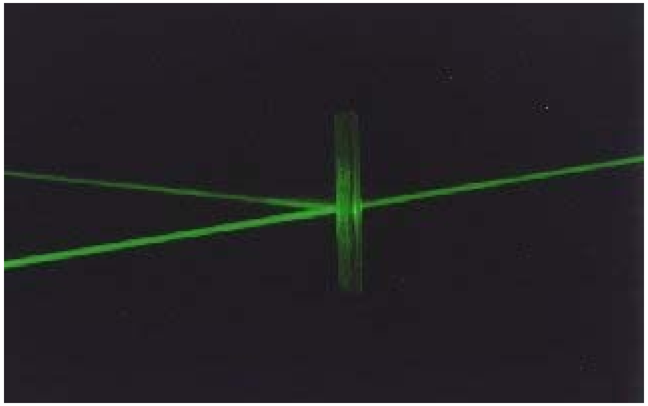
Left handed chiral cholesteric phase

Circular polarized light

Right-handed



left-handed

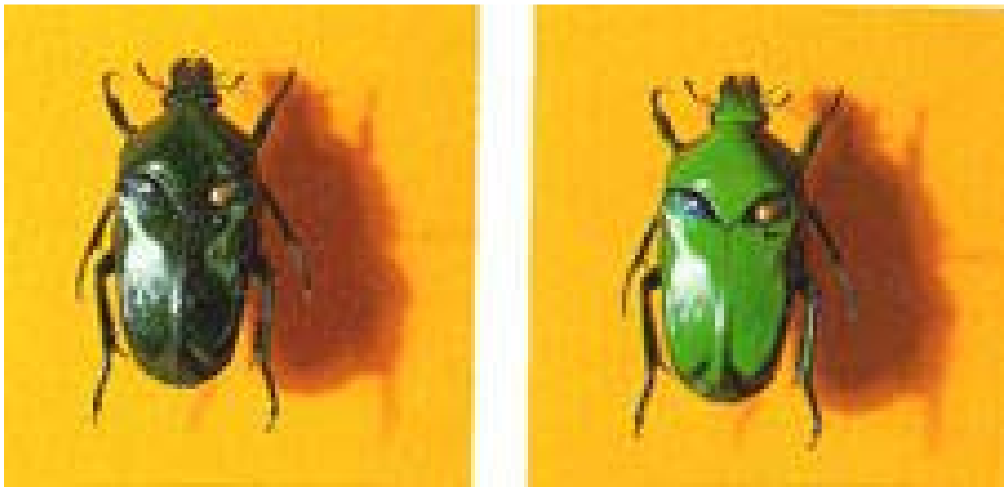


LC

LCs “guide” polarized light!

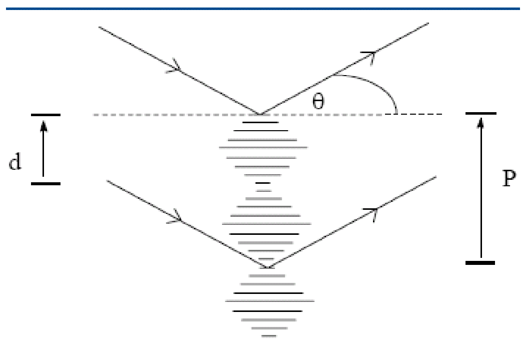
4. Application of Liquid Crystals

Cholesteric (Chiral nematic) phases as optical materials



The Exocuticles of Beetles contain Layers of **Chitin**, a naturally occurring polysaccaride that possesses a cholesteric liquid crystal Structure

The scarab beetle *plusiotis woodi* viewed under both a left and right circular polarizer



A supra-molecular helical structure defined by twiting sense (right or left) and pitch length leads to selective reflection

λ_{max} = 2d sin θ as 2d = P
λ_{max} = nP sin θ and at 90o
λ_{max} = nP

LC´s as opto-electronic materials

Cholesteric Liquid crystals are 1D (chiral) photonic crystals→ circular polarized light from dyes incorporated into CLCs

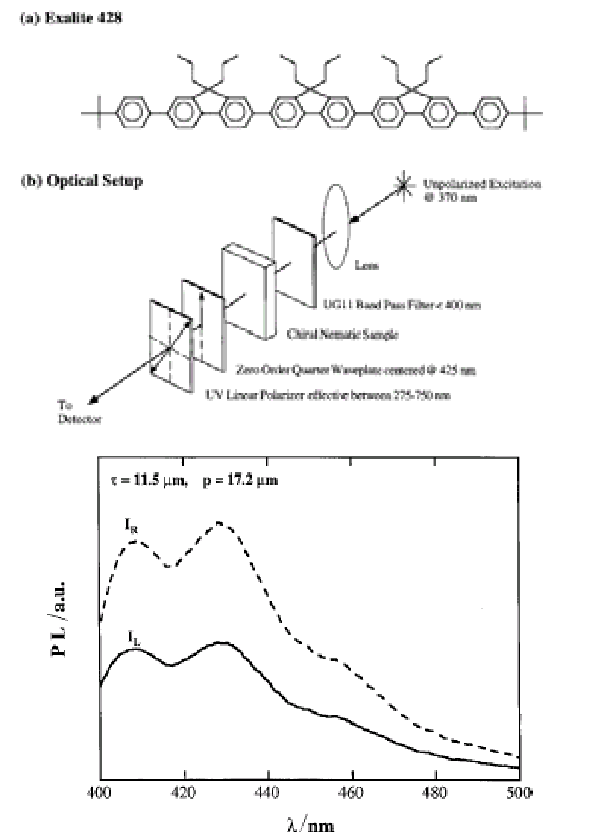
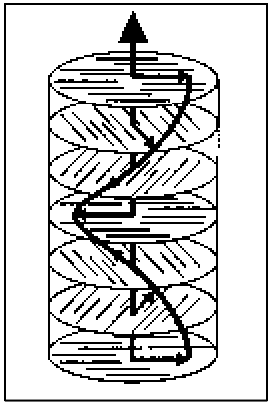
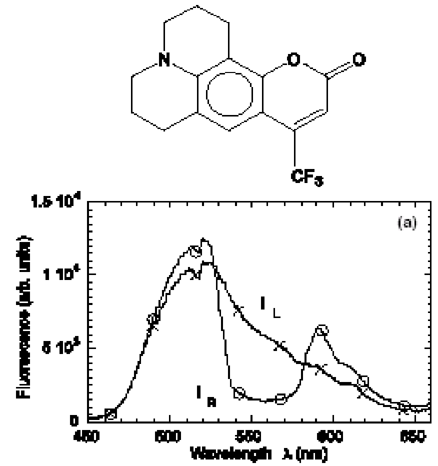


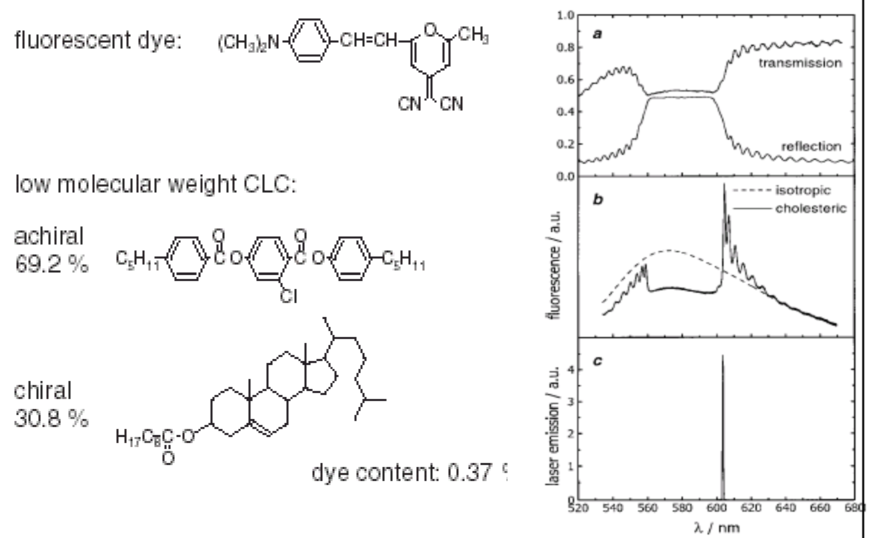
Figure 2. CPPL spectra resulting from an unpolarized excitation at 370 nm of a chiral-nematic film with $\tau = 11.5\,\mu m$, $p = 17.2\,\mu m$ and containing Exalite 428 at 0.52 wt %.

Dimitris Katsis , Ansgar W. Schmidt, Shaw H. Chen, *Liquid Crystals* **1999**, *26*, 181





M.Voigt, M. Chambers, M. Grell, *Chem. Phys. Lett.* **2001**, *347*, 173

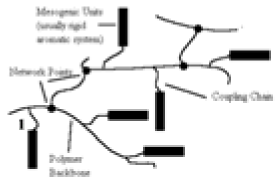


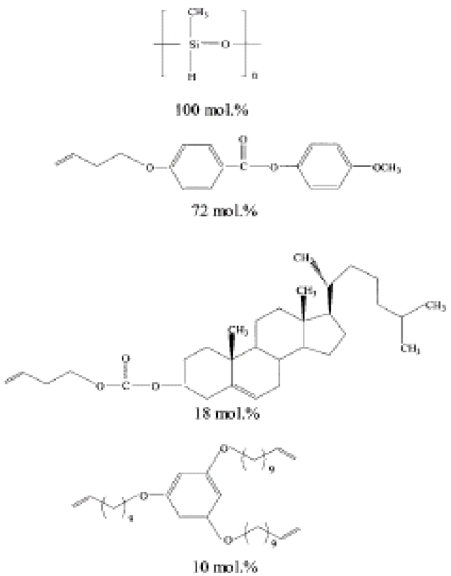
J. Schmidtke, W. Stille, H. Finkelmann, S.T. Kim, *Adv. Mater*. **2002**, *14*, 746

4. Application of Liquid Crystals

LCP´s as opto-electronic materials

"Tunable Mirrorless Lasing in Cholesteric Liquid Crystalline Elastomers"



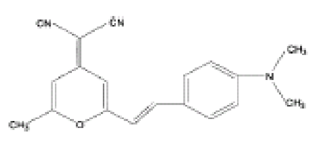


1

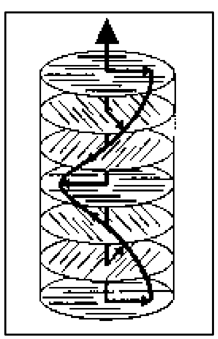
2

3

4



DCM



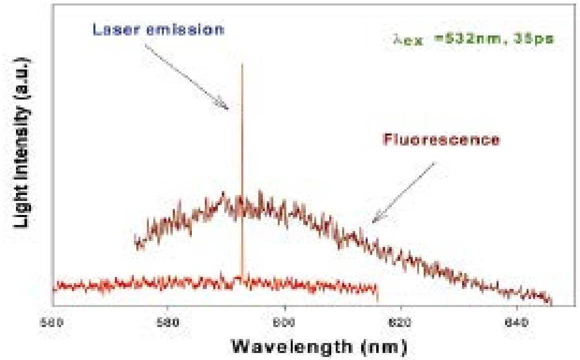


Fig. 4. Fluorescence spectrum of the DCM dye and laser line in a dye-doped LSCE sample.

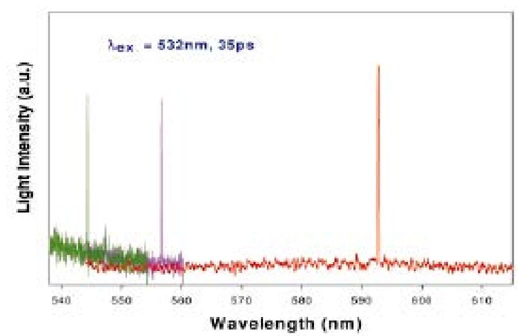


Fig. 5. Laser emission from the DCM-doped LSCE sample.

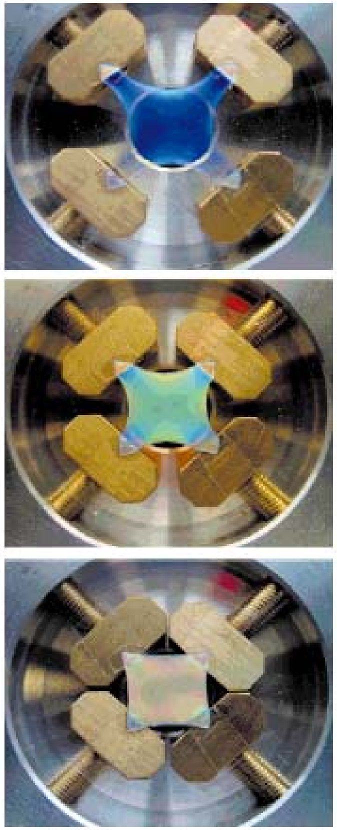


Fig. 1. Appearance of the cholesteric LSCE sample under white light illumination as a function of mechanical strain. The diameter of the large circular sample chamber is 3.5 cm; the thickness of the unstrained sample is 0.25 mm.

Finkelmann et al. *Adv. Mater.* **2001**, *13*, 1069

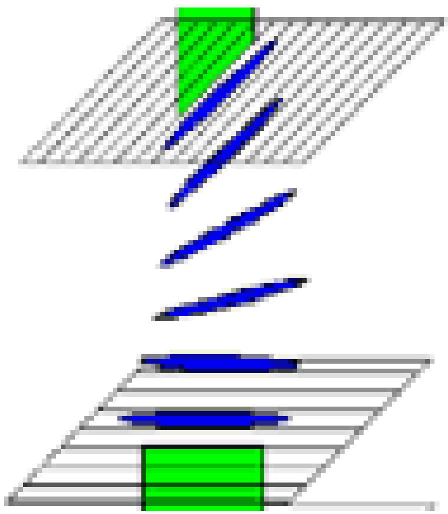
4. Application of Liquid Crystals

Flüssigkristallanzeige
Liquid Crystal Displays (LCDs)

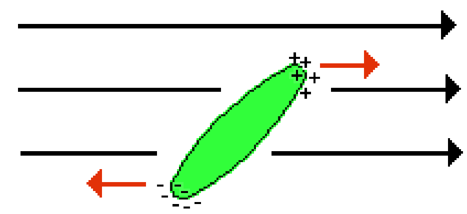
4. Application of Liquid Crystals

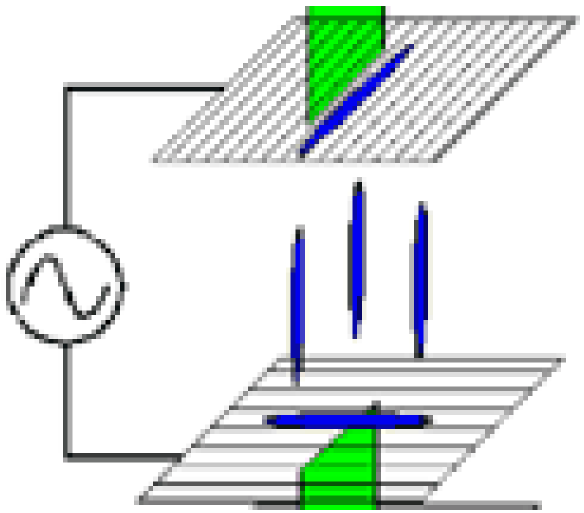
Two independent observations:

1.



2.





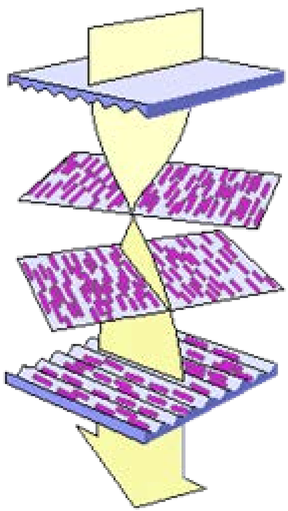
- *Liquid crystals could be aligned when placing them in contact with a crystal surface / if a liquid crystalline compound is placed between to aligning surfaces of different orientations, the director of the liquid crystalline compound smoothly follows the transition, rotating from one surface to the other*

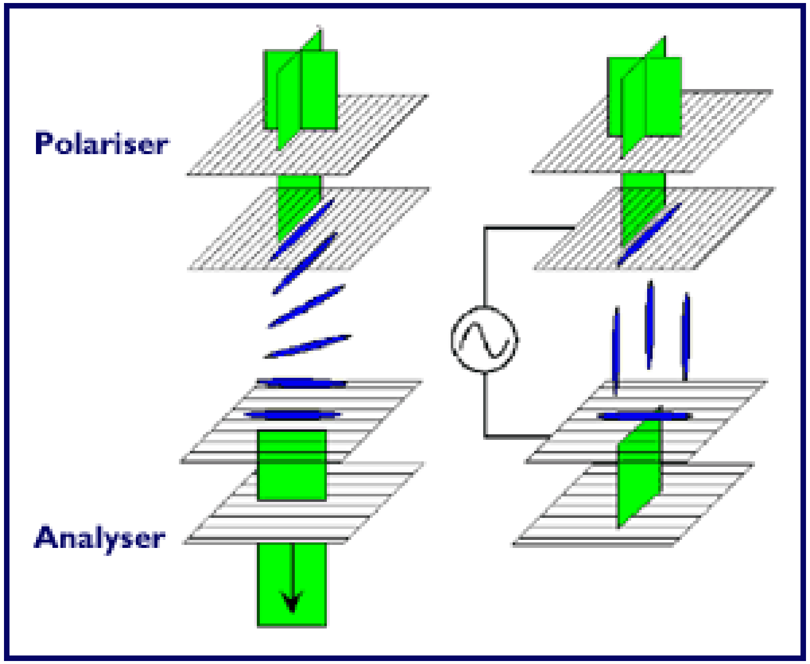
- *The orientation of liquid crystal molecules could be influenced by application of an electric field. The liquid crystal molecules would orient themselves with their dipoles (permanent or induced) parallel to the field, abonding their previous orientation*

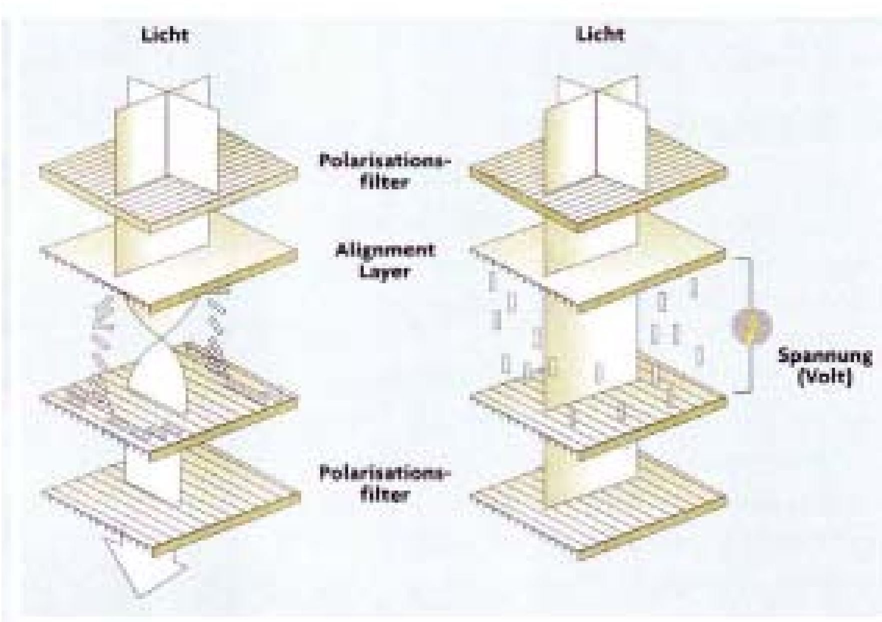
→ **Freedericksz Transition**

4. Application of Liquid Crystals

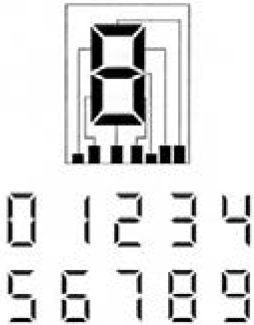
Standard LCD (twisted nematic)







An applied electric field change the orientation of the mesogens → Absorption of light on the second polarization filter

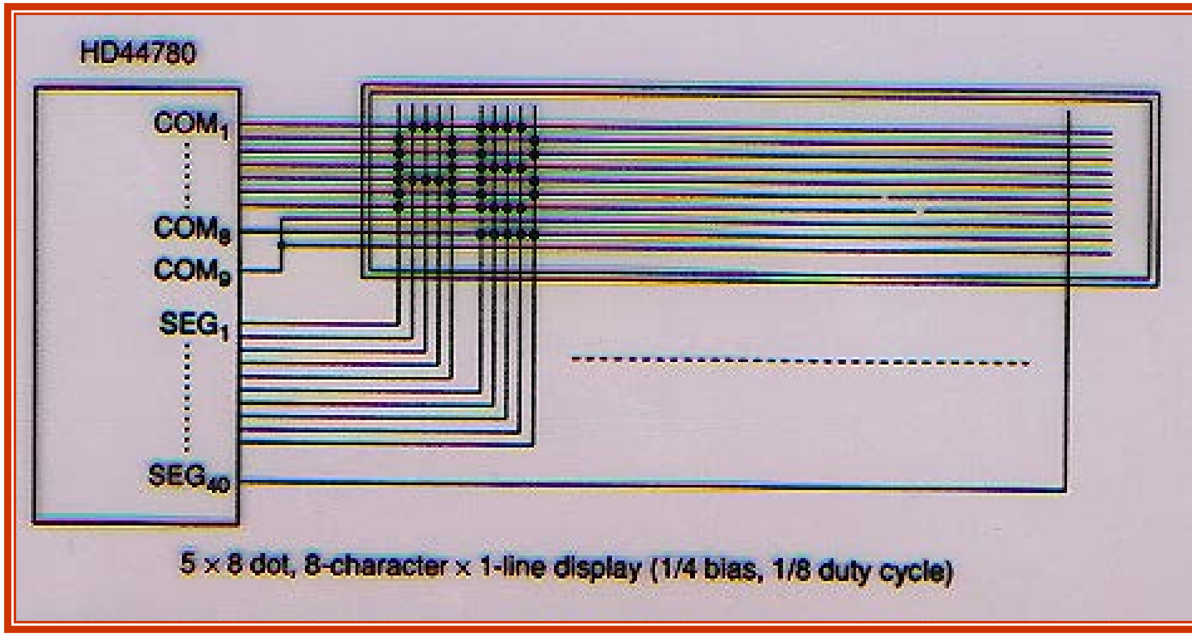


Direct driven image elements

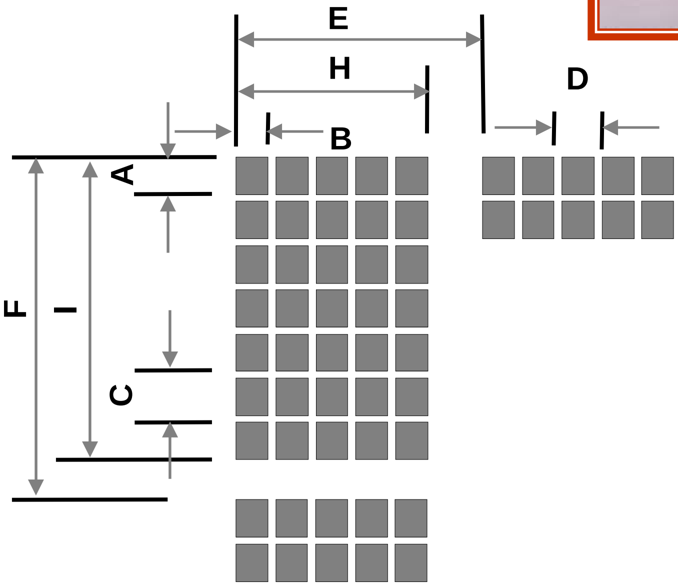
4. Application of Liquid Crystals

Addressing in Liquid Crystal Displays (LCDs)

"Matrix" method



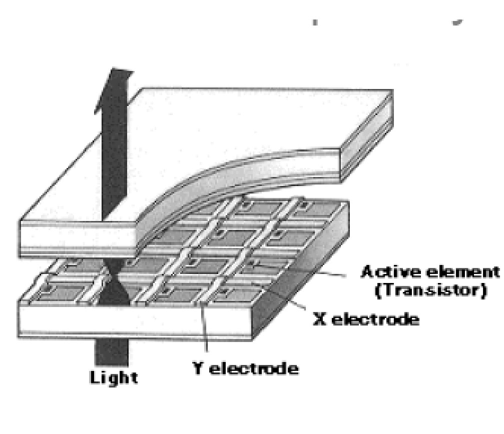
Character Type



Dot Size = A x B

Character pitch = E

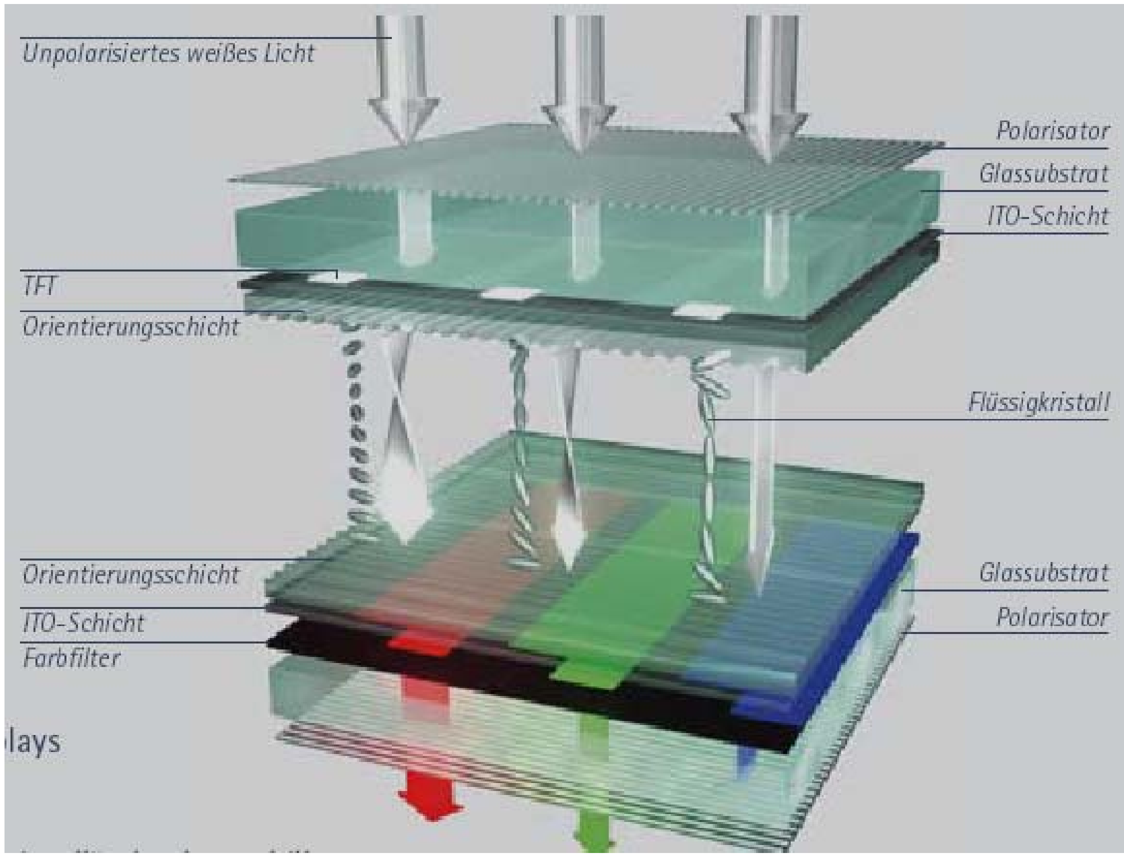
Character size = H x I



4. Application of Liquid Crystals

TFT Displays (twisted nematic)

TFT – Thin Film Transistor



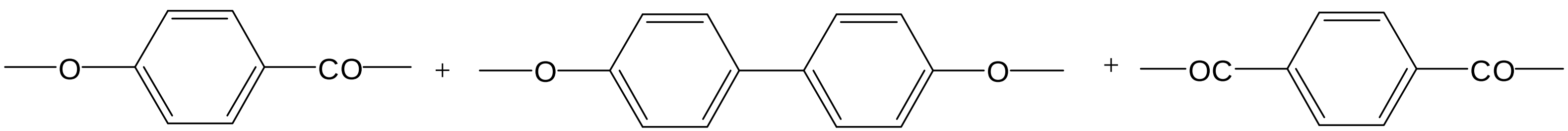
Colored LCDs are achieved by suitable light filters

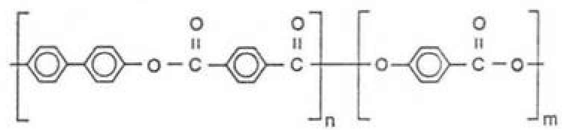
TFT: Pixels are addresses in rows and columns → reduction of the connection count from millions to thousands.

4.1 Application of LC polymers

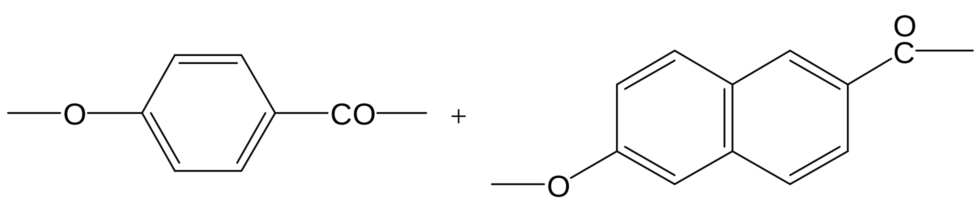
LCP´s as structural materials

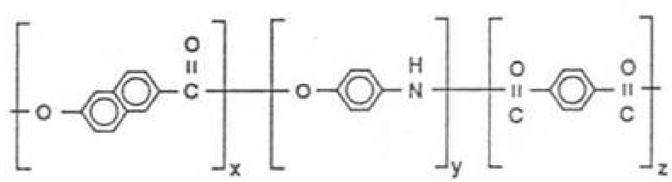
Technical important thermotropic main chain LCP´s





Xydar





<u>Vectra® LCP</u>

4.1 Application of LC polymers

LCP´s as structural materials

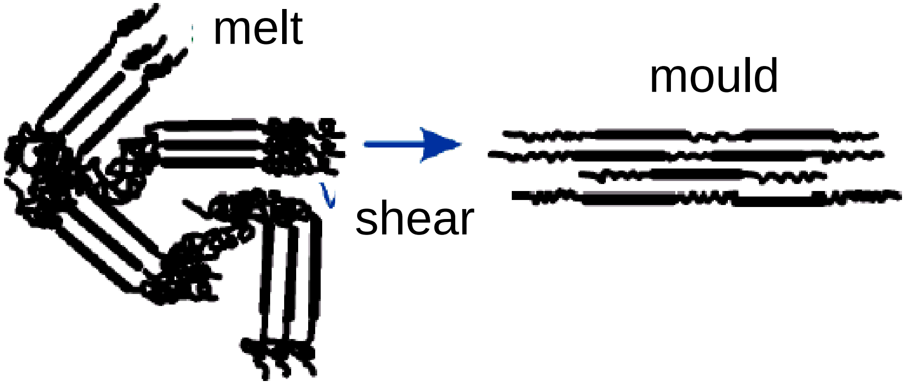
Thermotropic LCP‘s:

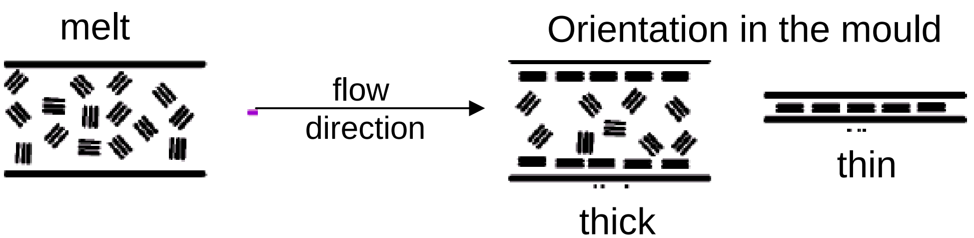
Excellent mouldability

→ Viscosity of mesogenic melts lower than that of conventional polymers

shear thinning (T < $T_{isotrop}$)
(↑ shear force
→ ↑ Fluidity ↓ shear viscosity)
(Alignment of anisometric parts in shear direction)

injection molding or extrusion
➔ flow-oriented domains in moulds (**self-reinforcement**)





4.1 Application of LC polymers

LCP´s as structural materials

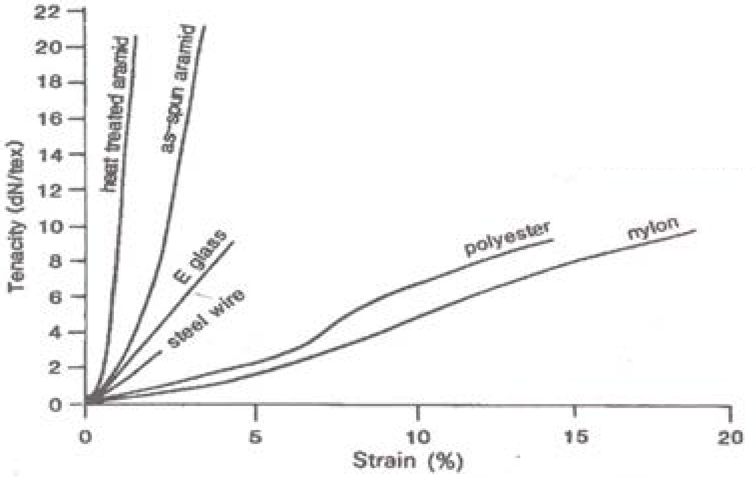
Properties of aligned LCP´s:

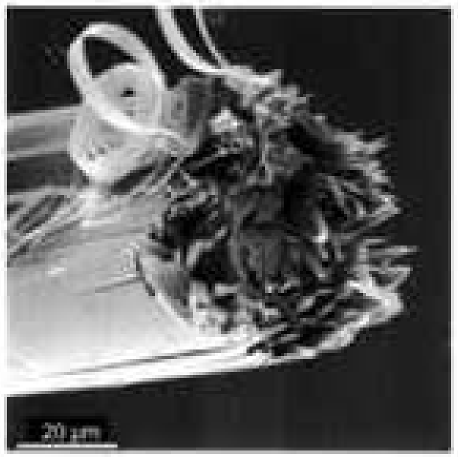
(→ aligned, i.e. direction dependent)

High tensile strength, e-moduli
(up to 10x higher than for non-LCP‘s)

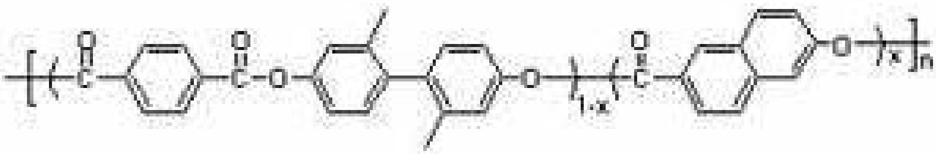
Low thermal extension coefficient
(sometimes < 0)

High working temperatures (>250 °C)





Thermotropic Main Chain Polyesters

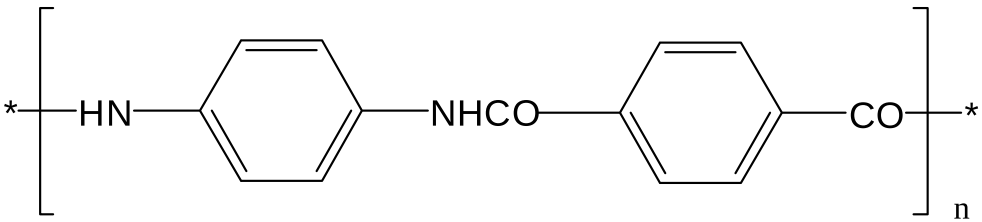


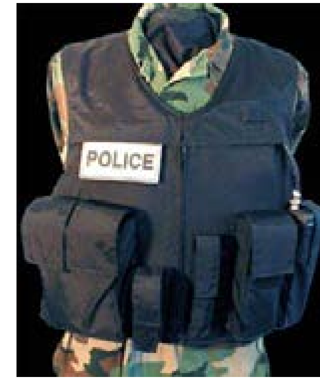
☛ High Modulus Fibers

4.1 Application of LC polymers

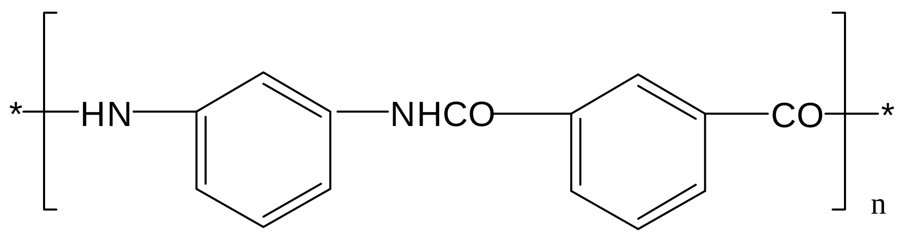
LCP´s as structural materials

Technical important lyotropic main chain LCP´s





Kevlar, 1965 DuPont



Nomex, 1965 DuPont

Anisotropic solutions show decrease of viscosity during shearing

→ Spinning of solutions above $C_{krit\ i/ai}$ to high modulus fibers

heavy duty ropes, bulletproof vests, puncture resistant bicycle tires

5. Literature

Books:

1. Handbook of Liquid crystals, Vol. 1-3, Wiley VCH 1998

2. Liquid Crystalline Polymers, Cambridge University Press 1992

Reviews:

1. M. Schadt, Liquid crystal materials and liquid crystal displays, Ann. Rev. Mater. Sci. **1997**, *27*, 305