

Studium fázových přechodů v kapalných krystalech

Aleksej Gaj

Fakulta jaderná a fyzikálně inženýrská

České vysoké učení technické

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Podivný cholesterolbenzoát...



- 1888 – UK Praha - rakouský chemik Friedrich Reinitzer
 - zkoumá cholesterol, pozoruje jeho fáze pod mikroskopem -> krystalické změny
- autor názvu – Otto Lehmann
 - 1960...kolem 1 400 KK
 - 1984...kolem 12 900 KK
 - 1996...kolem 72 000 KK
 - 2002...více než 130 000 KK
 - 2013...více než 250 000 KK

Beiträge zur Kenntniß des Cholesterins

1888

Friedrich Reinitzer,

Assistent am k. k. pflanzenphysiologischen Institute der österreichischen Universität in Prag.

Aus dem pflanzenphys. Institute des Prof. Ad. Weiss
an der k. k. deutschen Universität in Prag.

(Vorgelegt in der Sitzung am 3. Mai 1888.)

Vor etwa 1½ Jahren theilte ich das Ergebniss einiger Untersuchungen¹ über ein in der Wurzel der Möhre vorkommendes Cholesterin mit, welches von Ang. Husemann den Namen Hydrocarotin erhalten hat. Ich führte damals aus, dass dasselbe, wenn auch nicht in der von Husemann vermuteten Art, mit dem rothen Farbstoff der Möhren, dem Carotin, in Zusammenhang zu stehen scheine und durch letzteres wieder mit dem Chlorophyllfarbstoffe. Es musste daher von Interesse sein, die nähere Natur dieses Körpers zu ergründen. Da derselbe jedoch schwierig in grösserer Menge zu beschaffen ist, anderseits aber die Cholesterine untereinander eine grosse Ähnlichkeit ihrer Eigenschaften zeigen, so beschloss ich, die diesbezüglichen Vorarbeiten erst mit dem gewöhnlichen Cholesterin vorzunehmen, welches leicht in grösserer Menge erhalten werden kann und über dessen Natur nun gleichfalls noch völlig im Unklaren ist. Erst auf Grund der hierbei gesammelten Erfahrungen soll dann das ungleich kostbarere Hydrocarotin näher untersucht werden. Im Folgenden will ich einige Ergebnisse dieser Vorarbeit mittheilen.

Pamětní deska (aneb trocha patriotismu)



- Husova 5, Praha

V této budově bývalé
Německé university v Praze
objevil v roce 1888
první kapalný krystal

**Prof. Friedrich
Reinitzer**

(*25. 2. 1857, Praha – †16. 2. 1927, Graz)

hat in diesem Gebäude
der Deutschen Universität in
Prag im Jahre 1888 den ersten
flüssigen Kristall erfunden



Co to je?

- **Kapalný krystal (KK)**
 - = stav hmoty; 4. skupenství, přechodné mezi *kapalinou* a *pevnou krystalickou látkou*
 - tekuté vlastnosti - viskozita (~ kapalina)
 - uspořádané a orientované molekuly – parametr uspořádání (~ krystal)
 - organické materiály
 - schopnost samouspořadávání (*self-assembly*)
- typy:
 - termotropní (T) a lyotropní (c)
 - s nízkou molární hmotností a makromolekulární
- lze měnit/řídit strukturní, dielektrické a optické vlastnosti vnějšími podmínkami
 - teplota, elektrické pole, magnetické pole, mech. působení, ozařování (UV a jiné λ) apod.

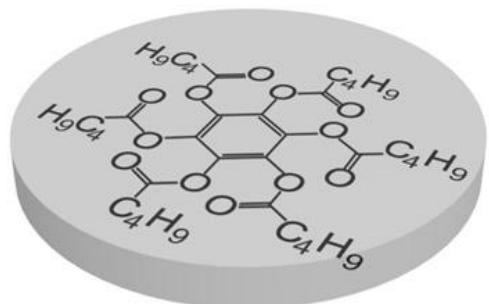
Tvary molekul



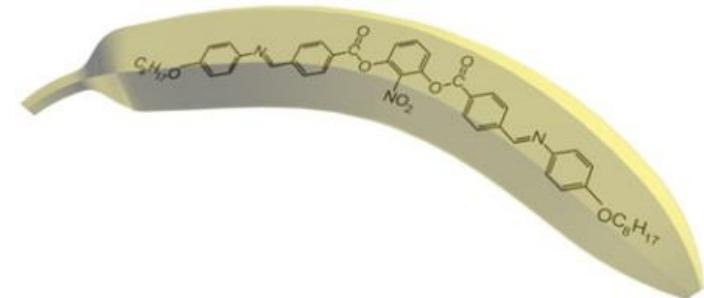
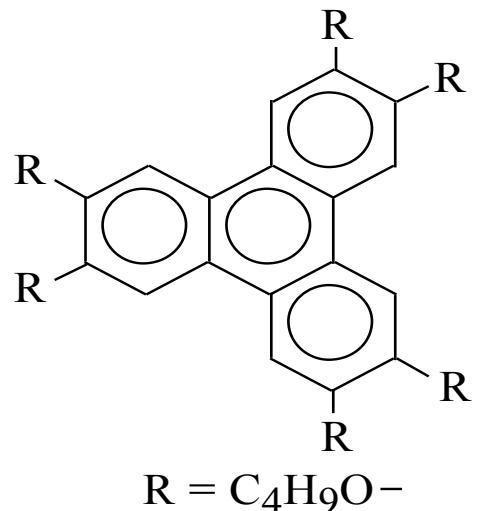
- tyčinkovité



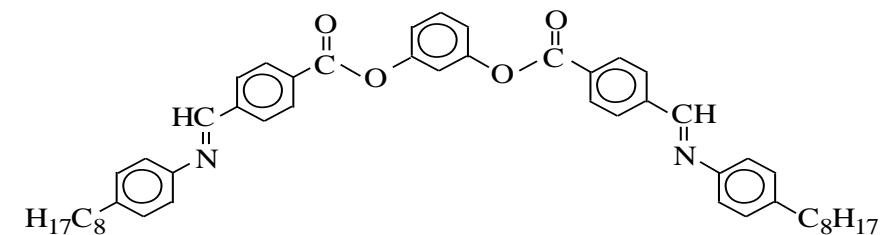
a další...



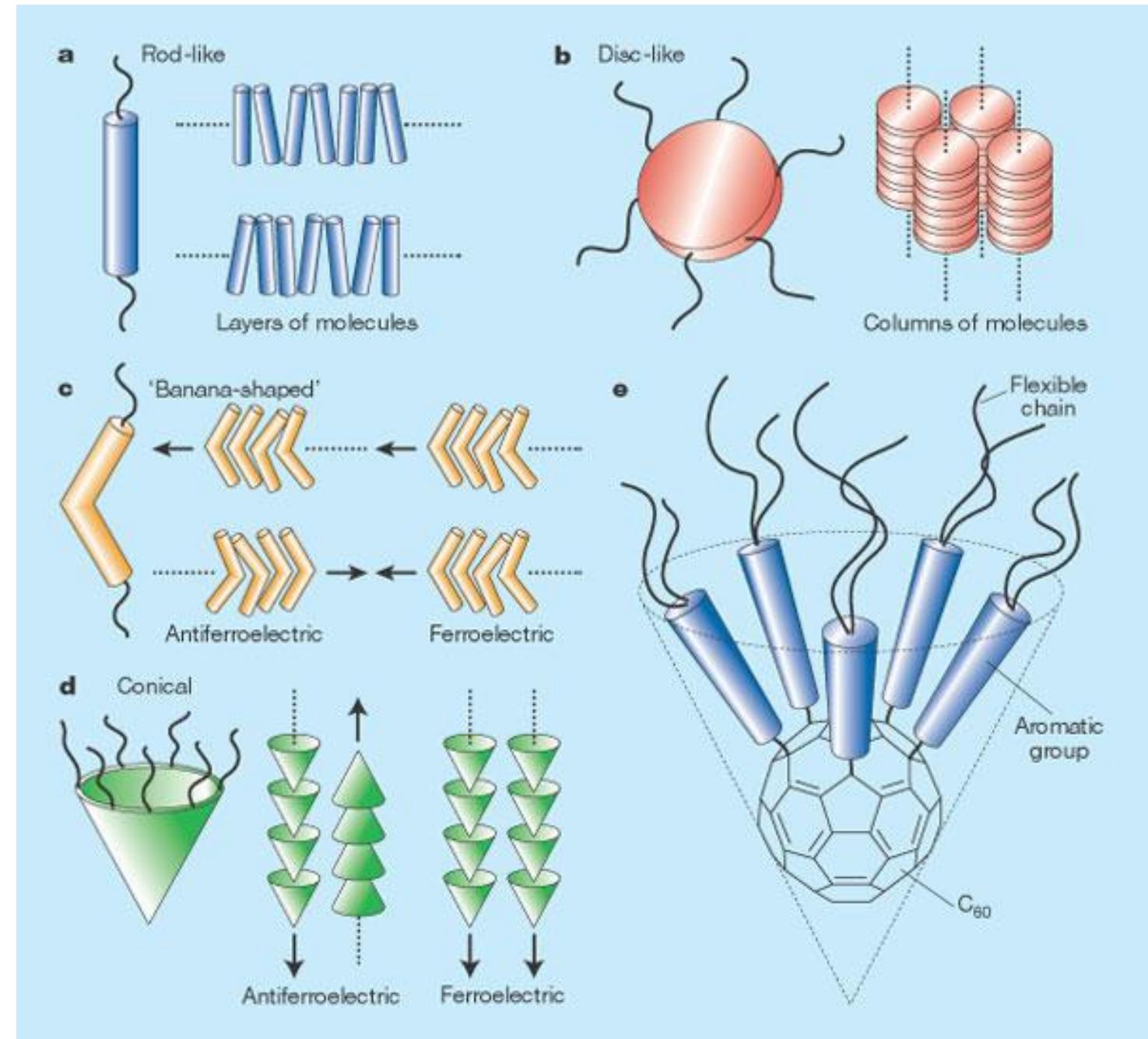
- diskotické



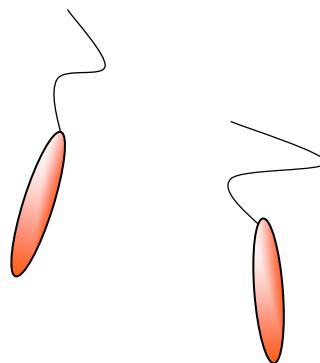
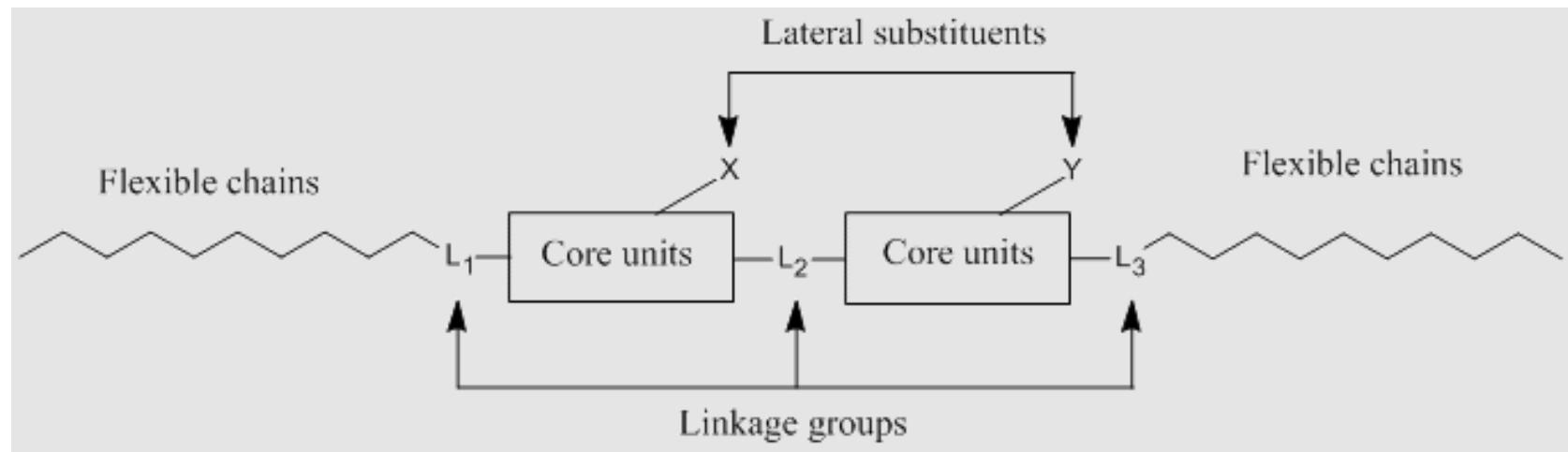
- zahnuté
(ve tvaru banánu)



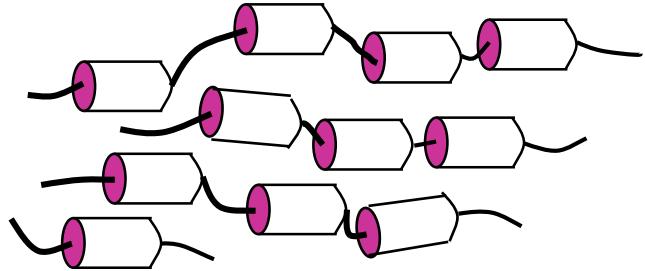
Tvary molekul



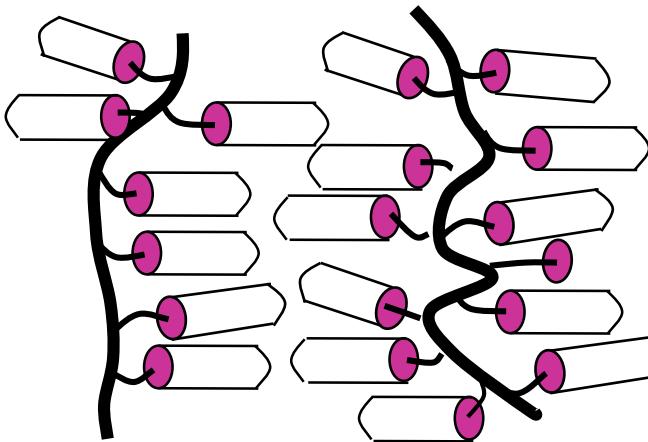
Stavba molekuly



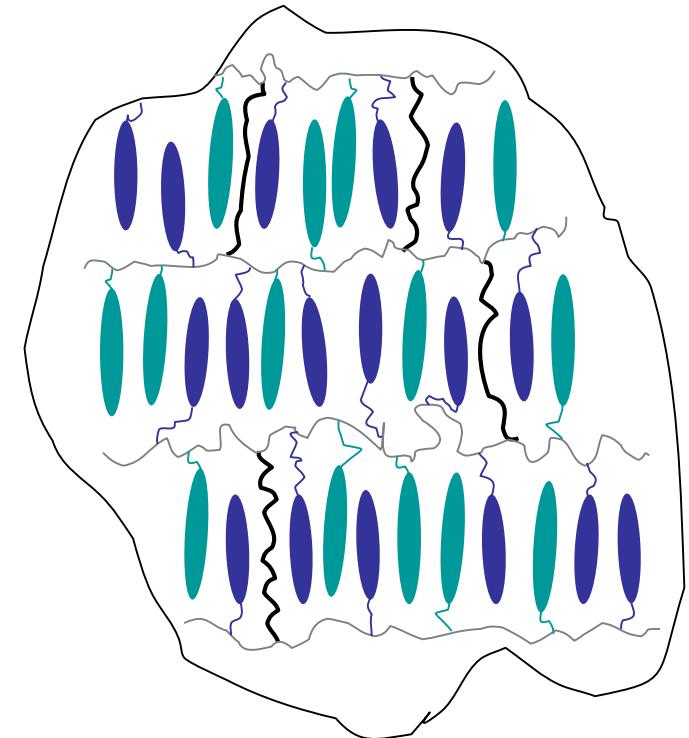
Makromolekulární KK



Main-chain polymer

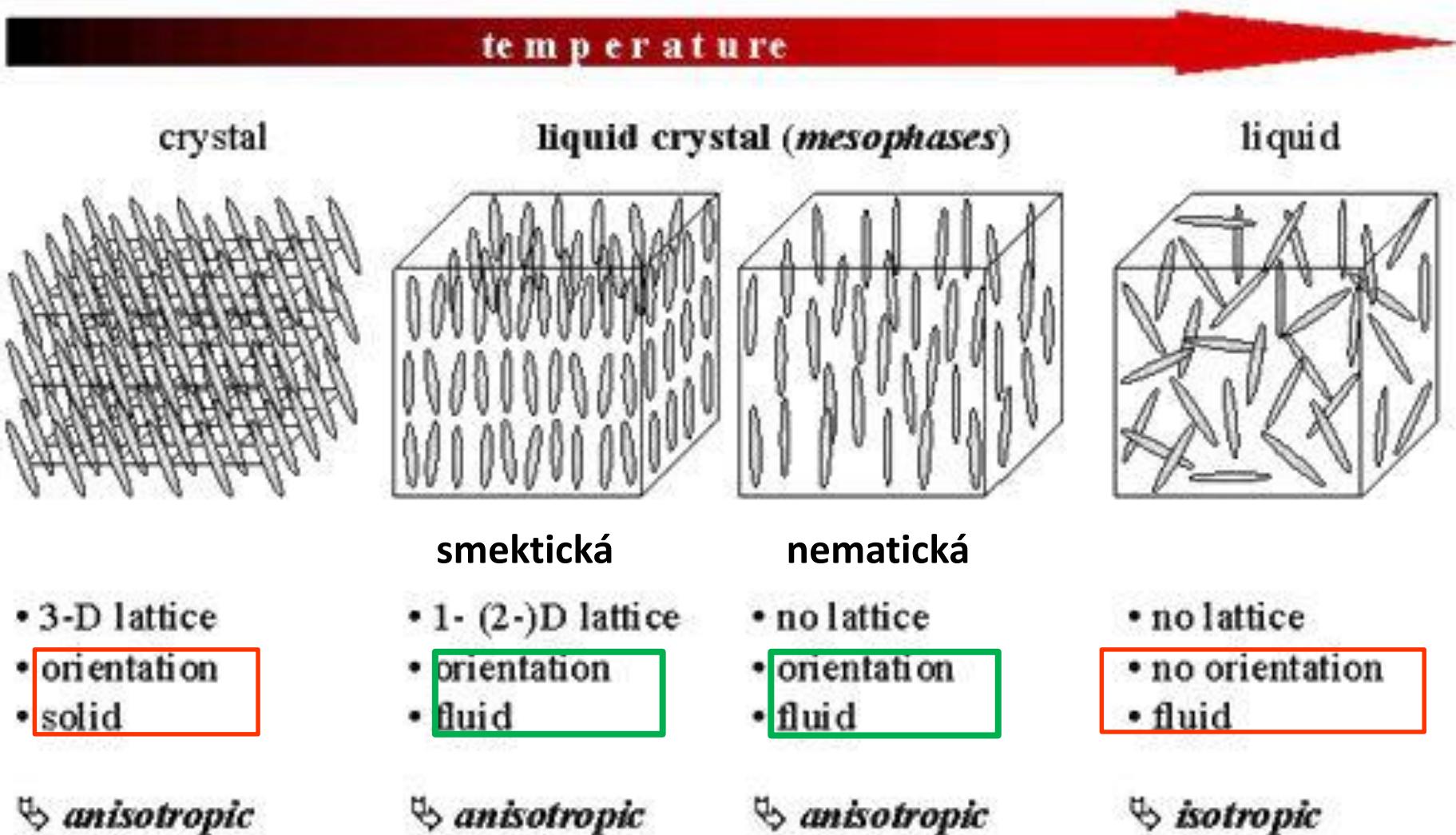


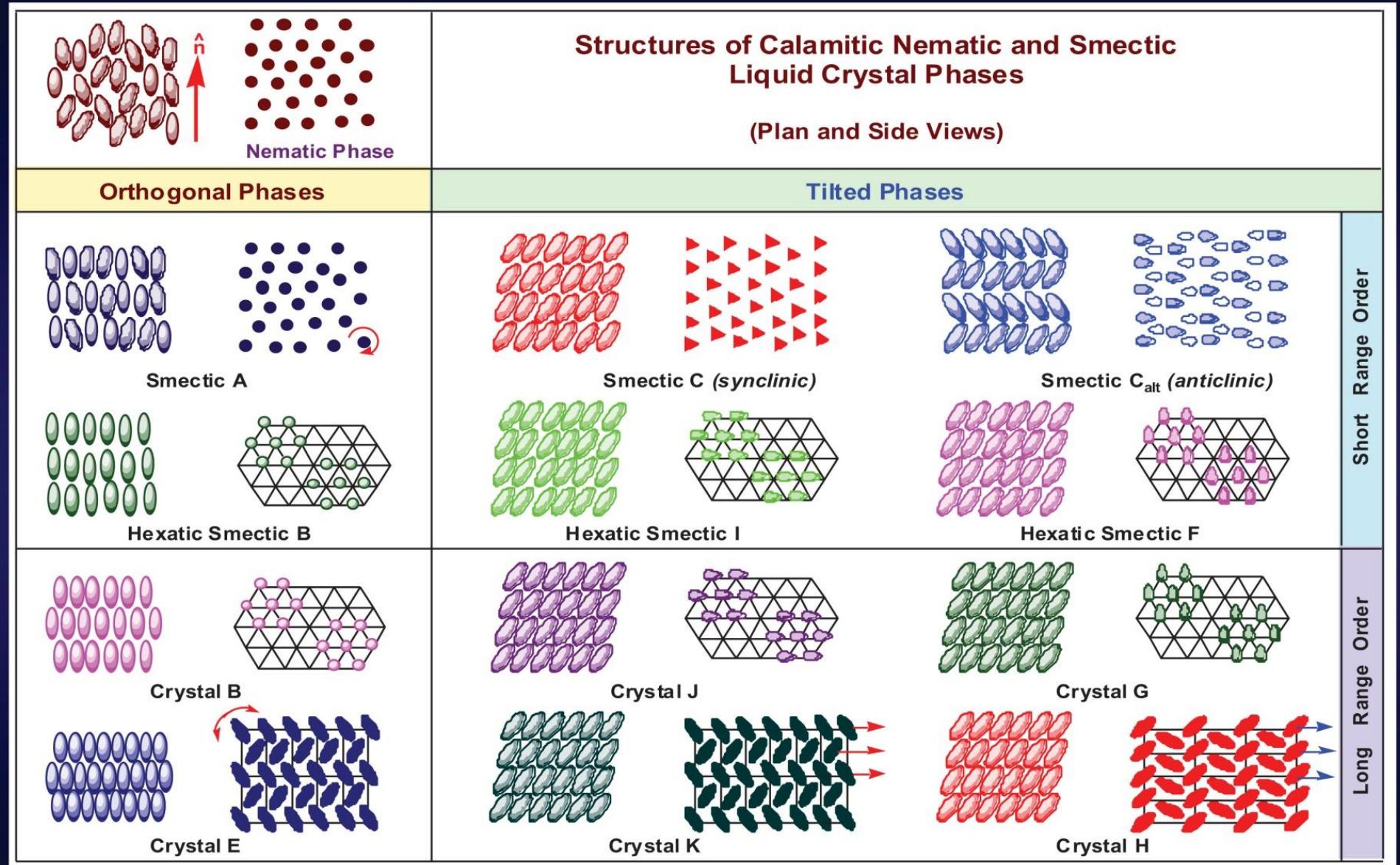
Side-chain polymers



Side-chain elastomers

Termotropní KK





Proč a nač?

Syntéza nového KK materiálu



Vlastnosti nového KK materiálu?

X-ray studies

Mezomorfni vlastnosti

Sequence of phases

Phase transition temperatures

Transition enthalpies

Spontaneous quantities

Tilt angle

Polarization

Helix pitch

Další vlastnosti

Dielectric permittivity

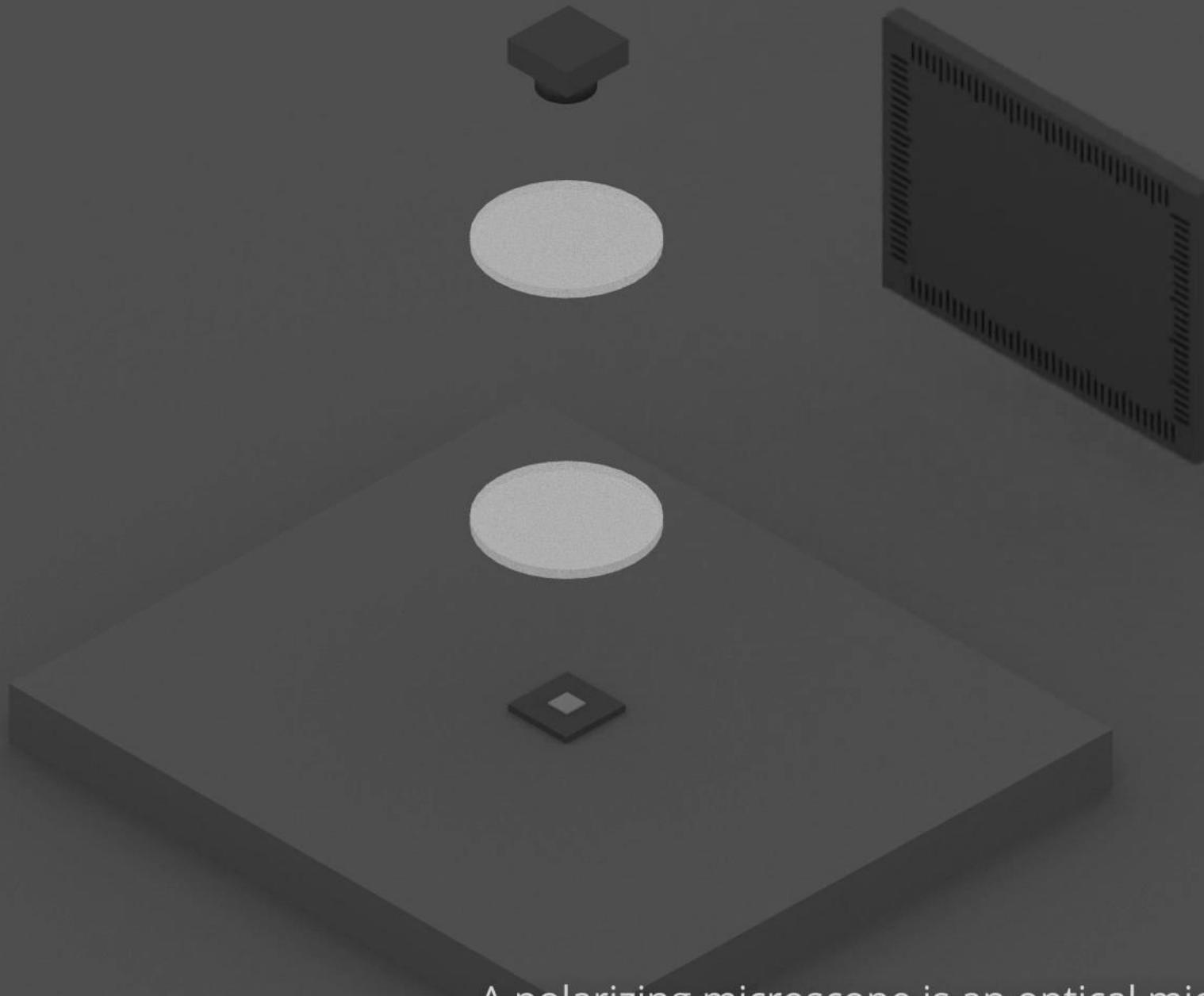
Rotational viscosity

Electro-optical coefficient

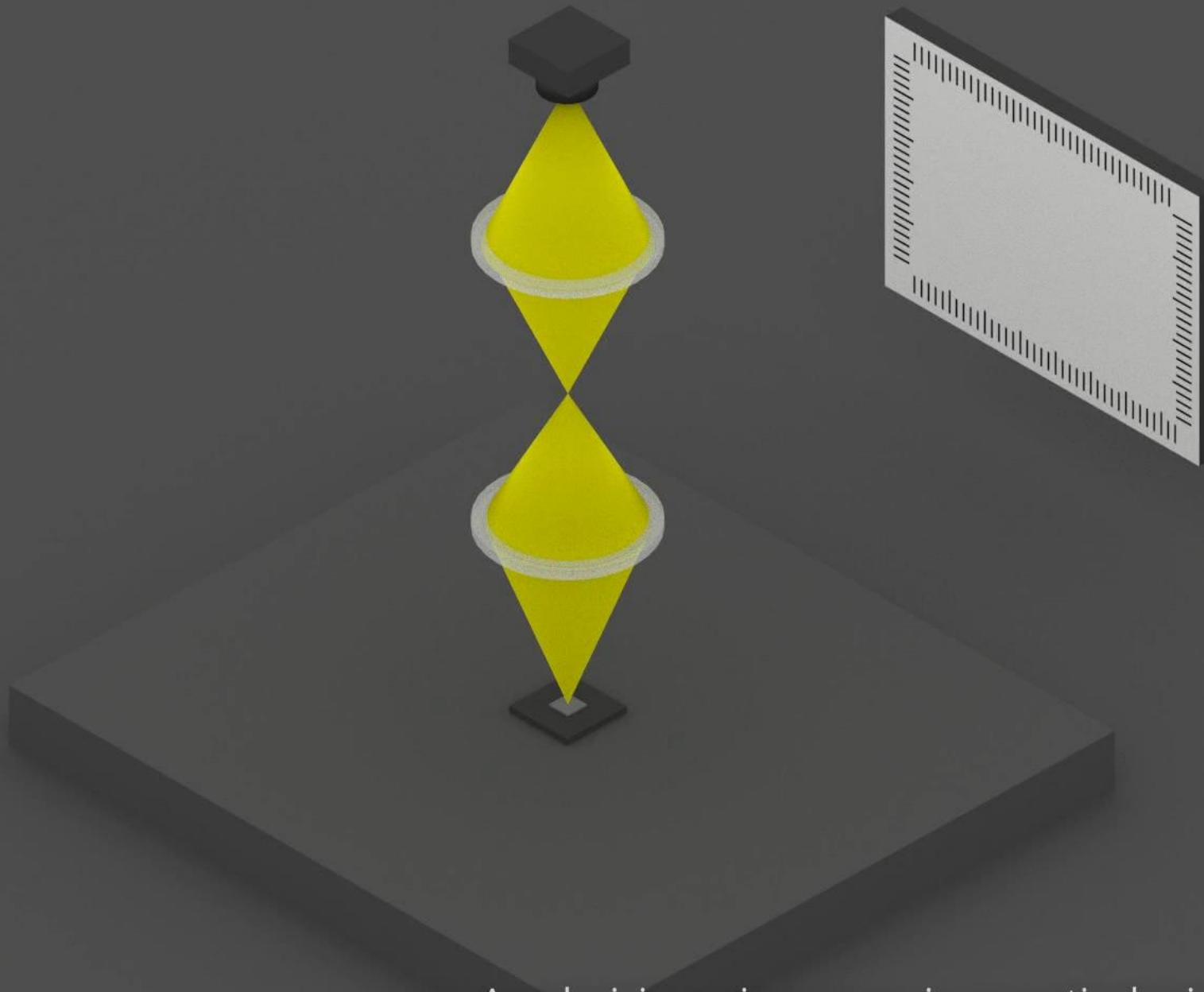
cíl: struktura → vlastnosti (+ verifikace)

Polarizační optický mikroskop

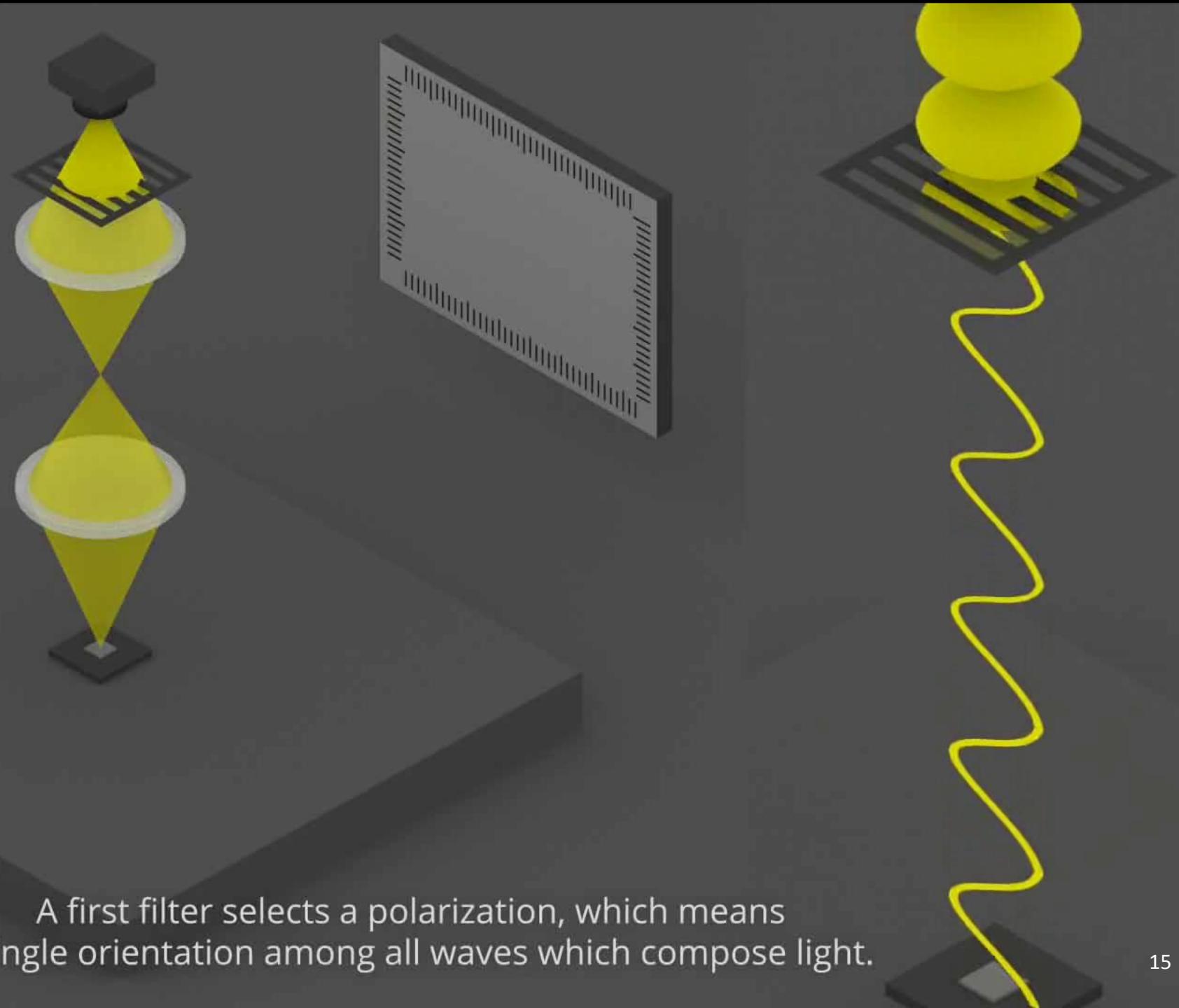




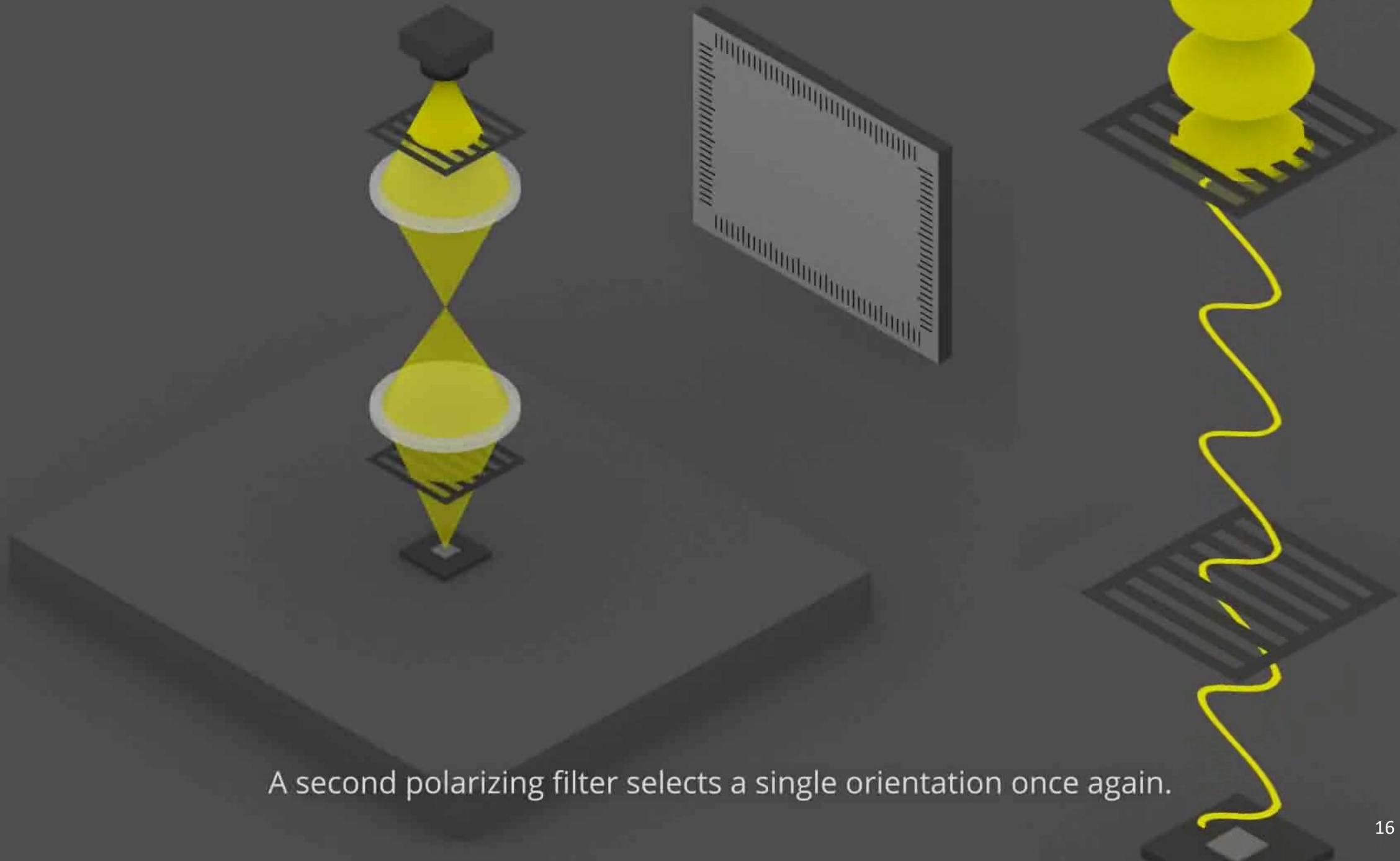
A polarizing microscope is an optical microscope composed of a detector, lenses and polarizing filters.

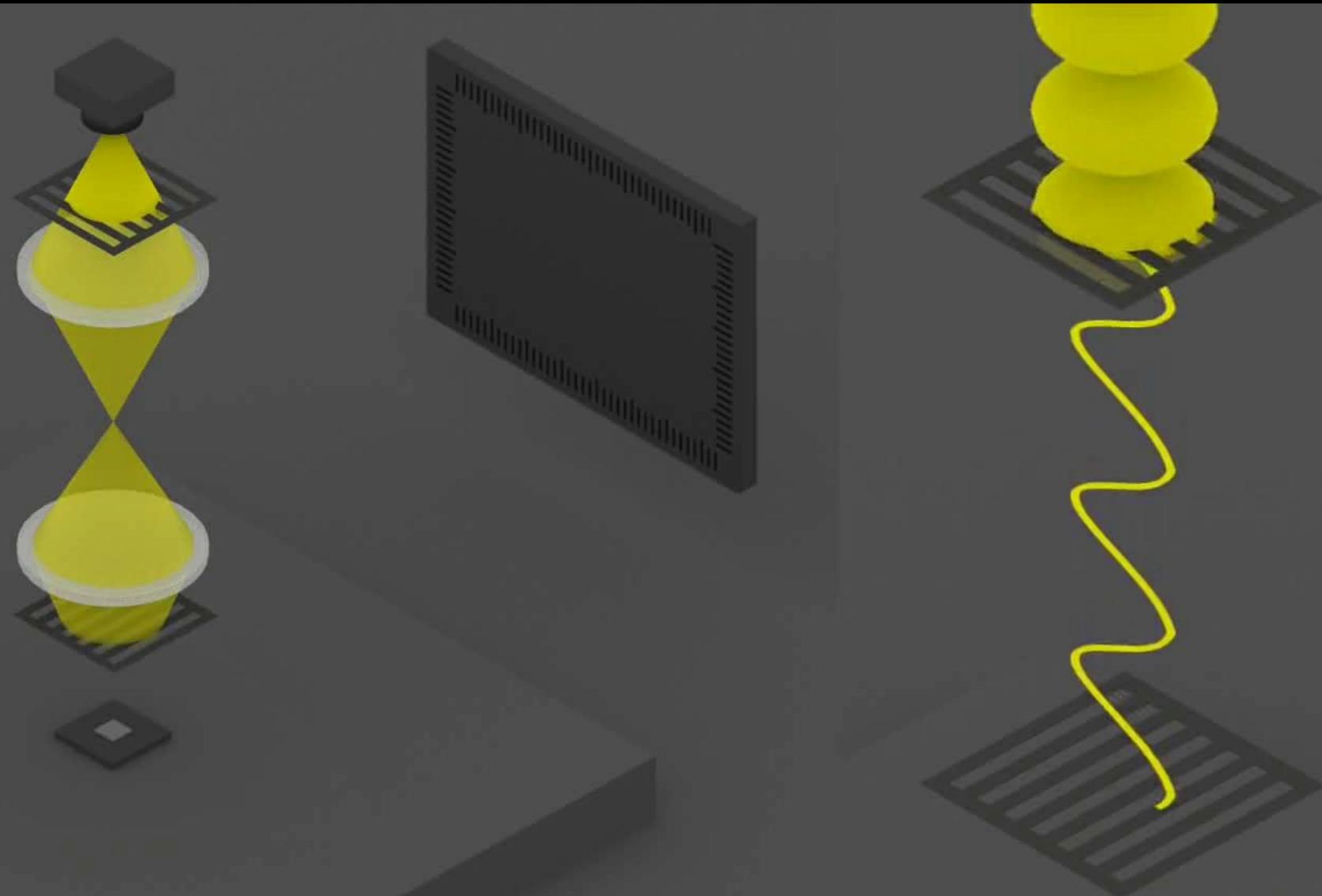


A polarizing microscope is an optical microscope composed of a detector, lenses and polarizing filters.



A first filter selects a polarization, which means a single orientation among all waves which compose light.

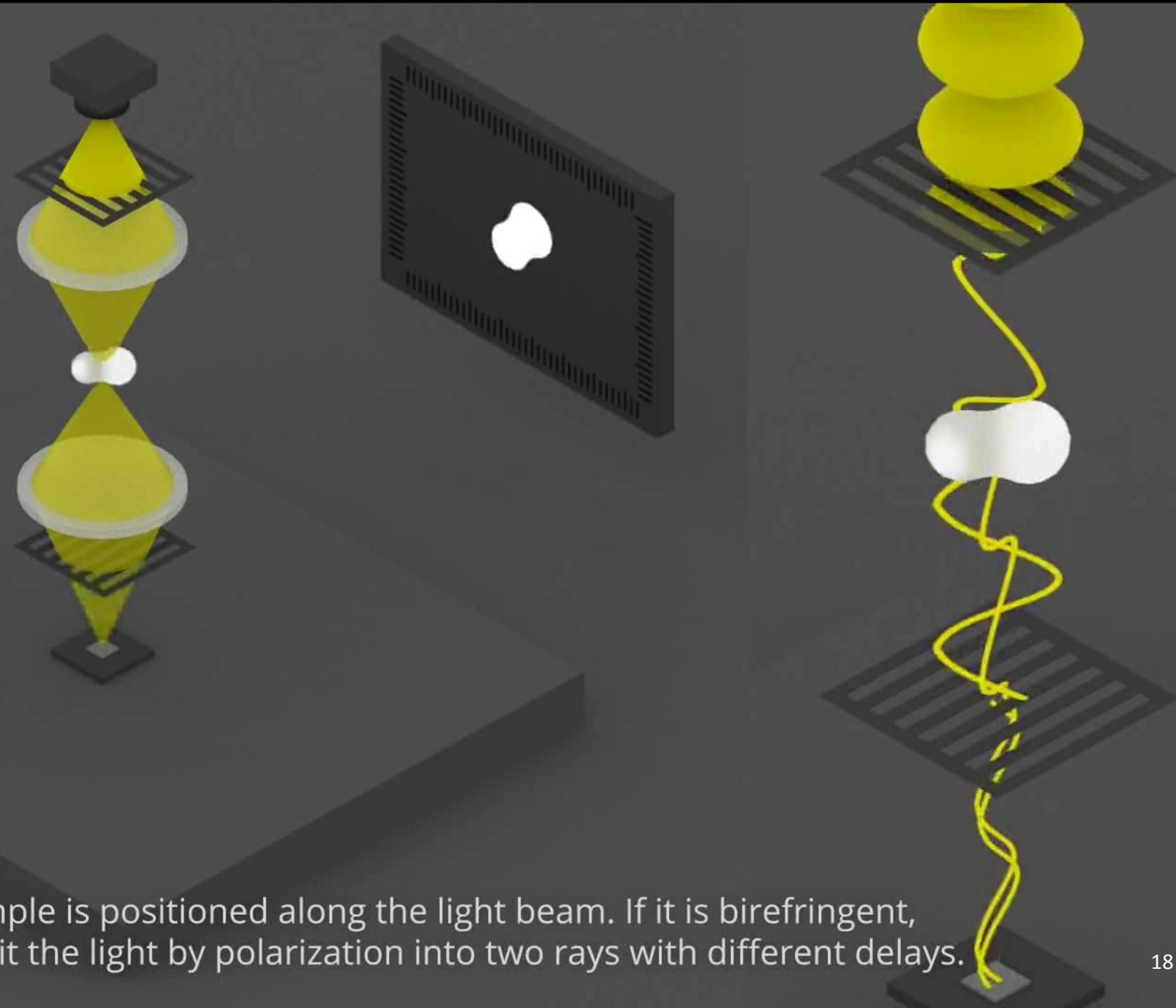


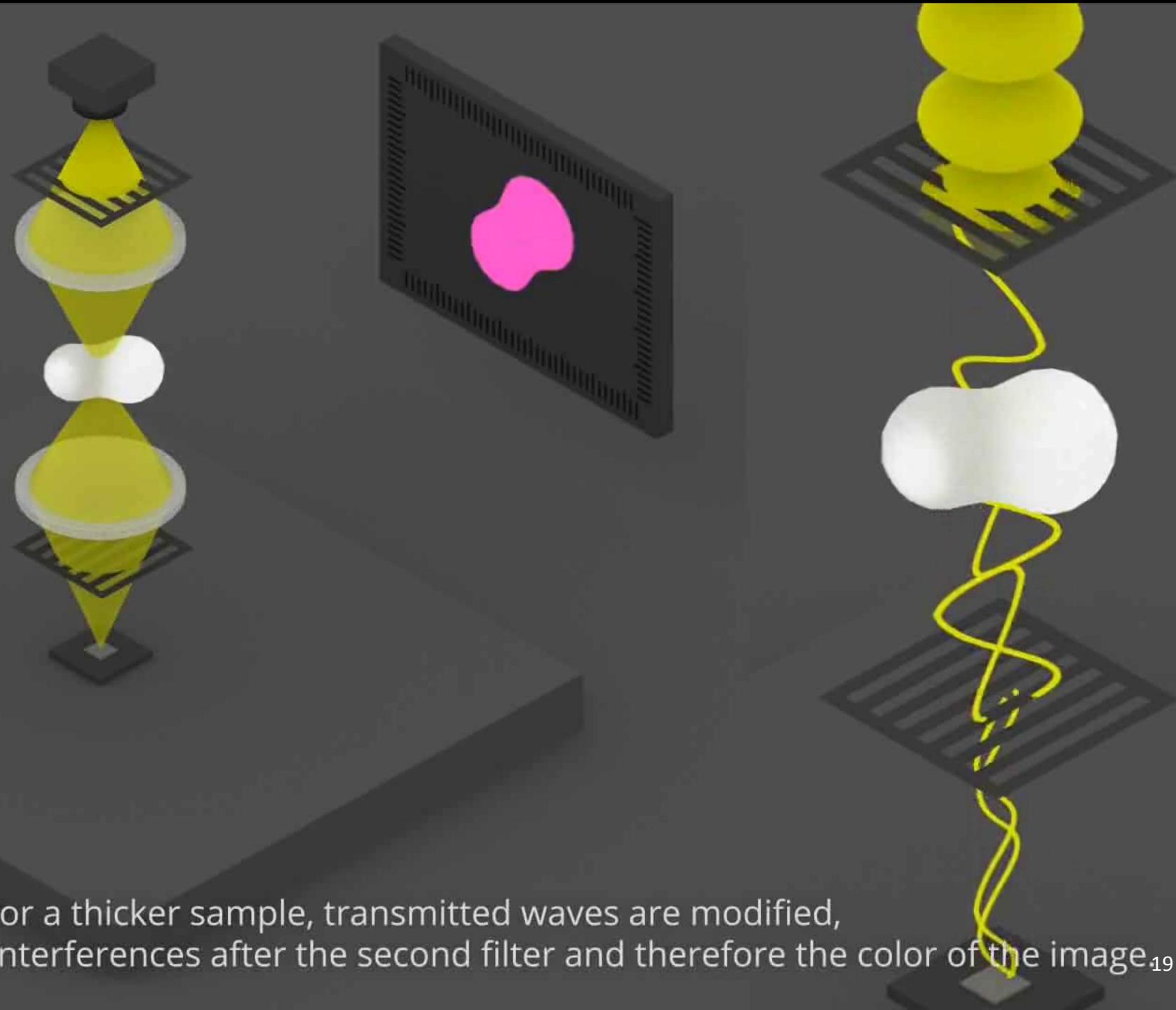


When the two filters are perpendicular, no wave can go through anymore.

C

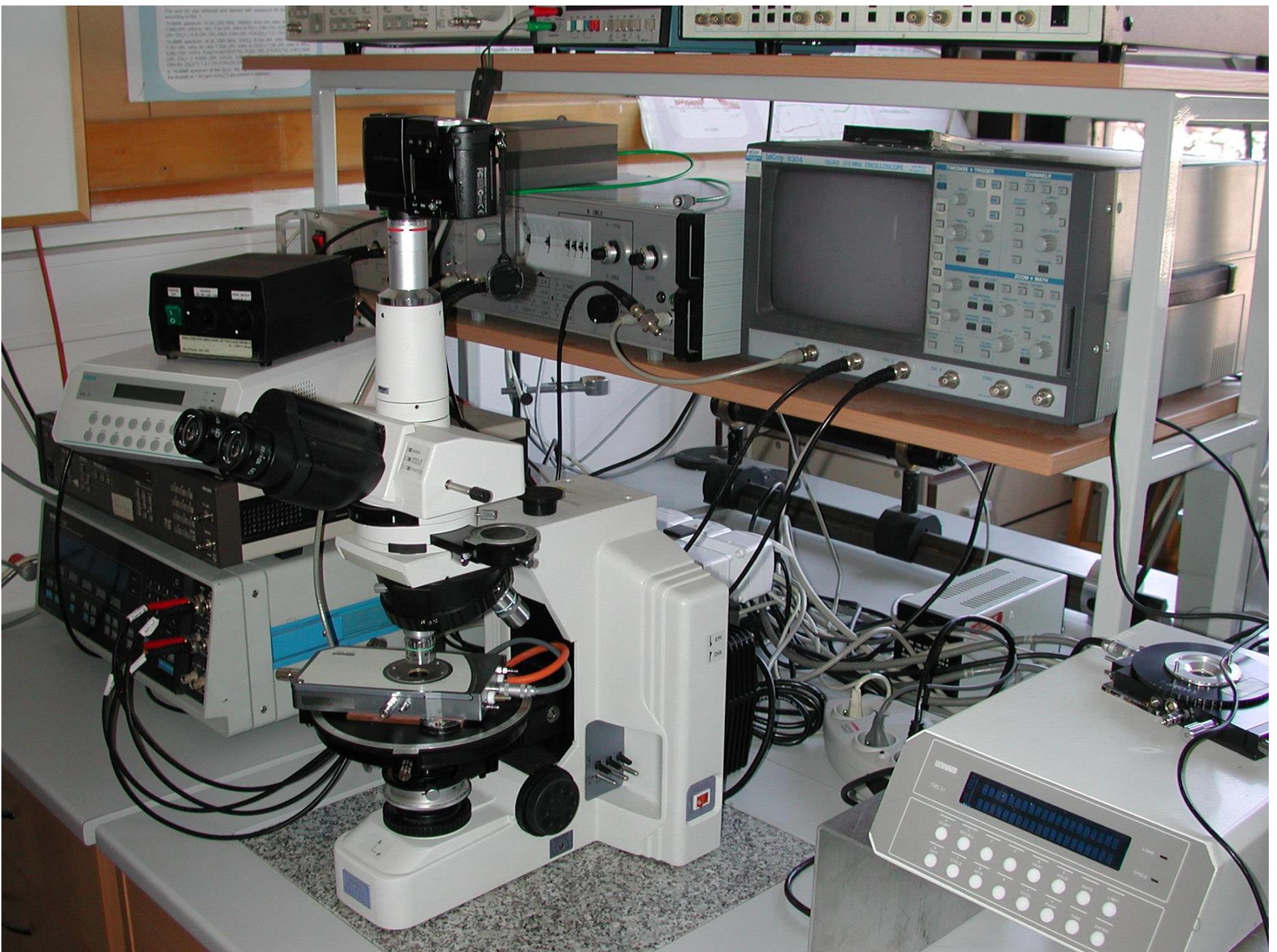
A sample is positioned along the light beam. If it is birefringent, it will split the light by polarization into two rays with different delays.





For a thicker sample, transmitted waves are modified, hence changing the interferences after the second filter and therefore the color of the image.¹⁹

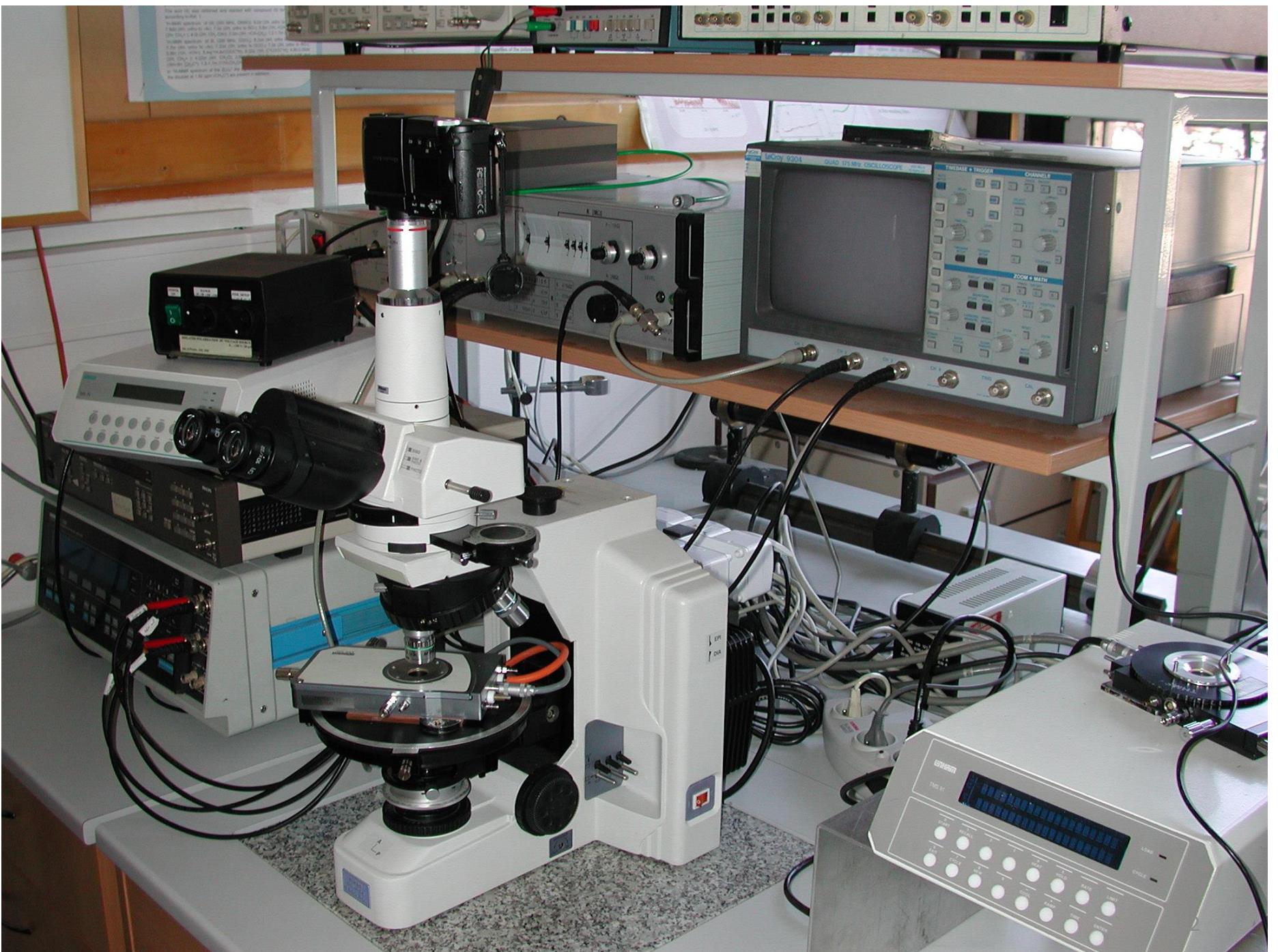
Setup



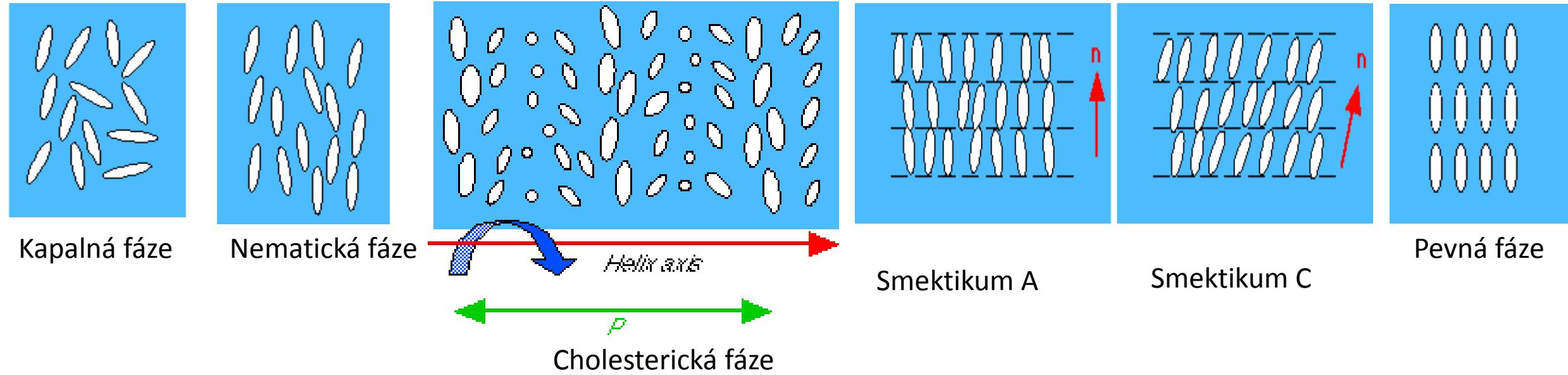
Napouštění KK
do cely



Setup



KK fáze jak je (ne)vidíme..

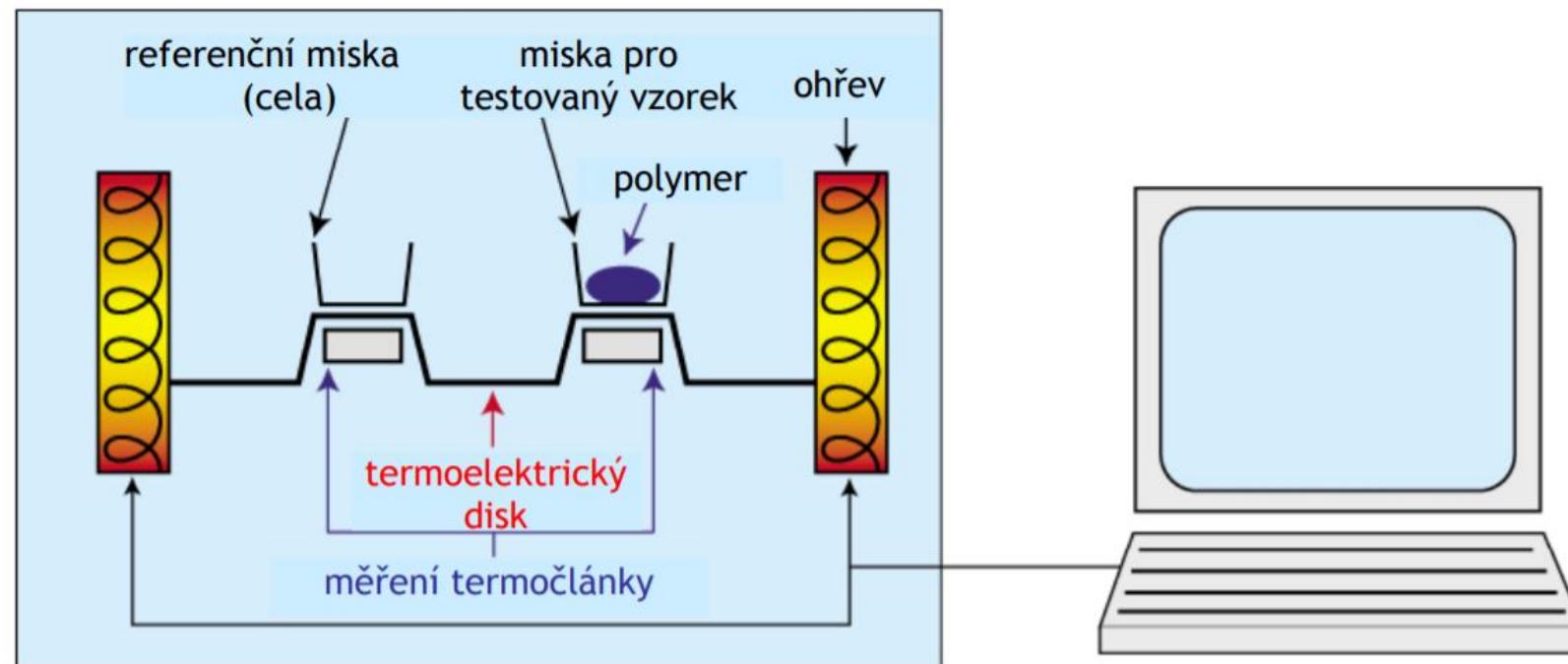


KK fáze jak je vidíme v polarizačním optickém mikroskopu



Diferenciální skenovací kalorimetrie (DSC)

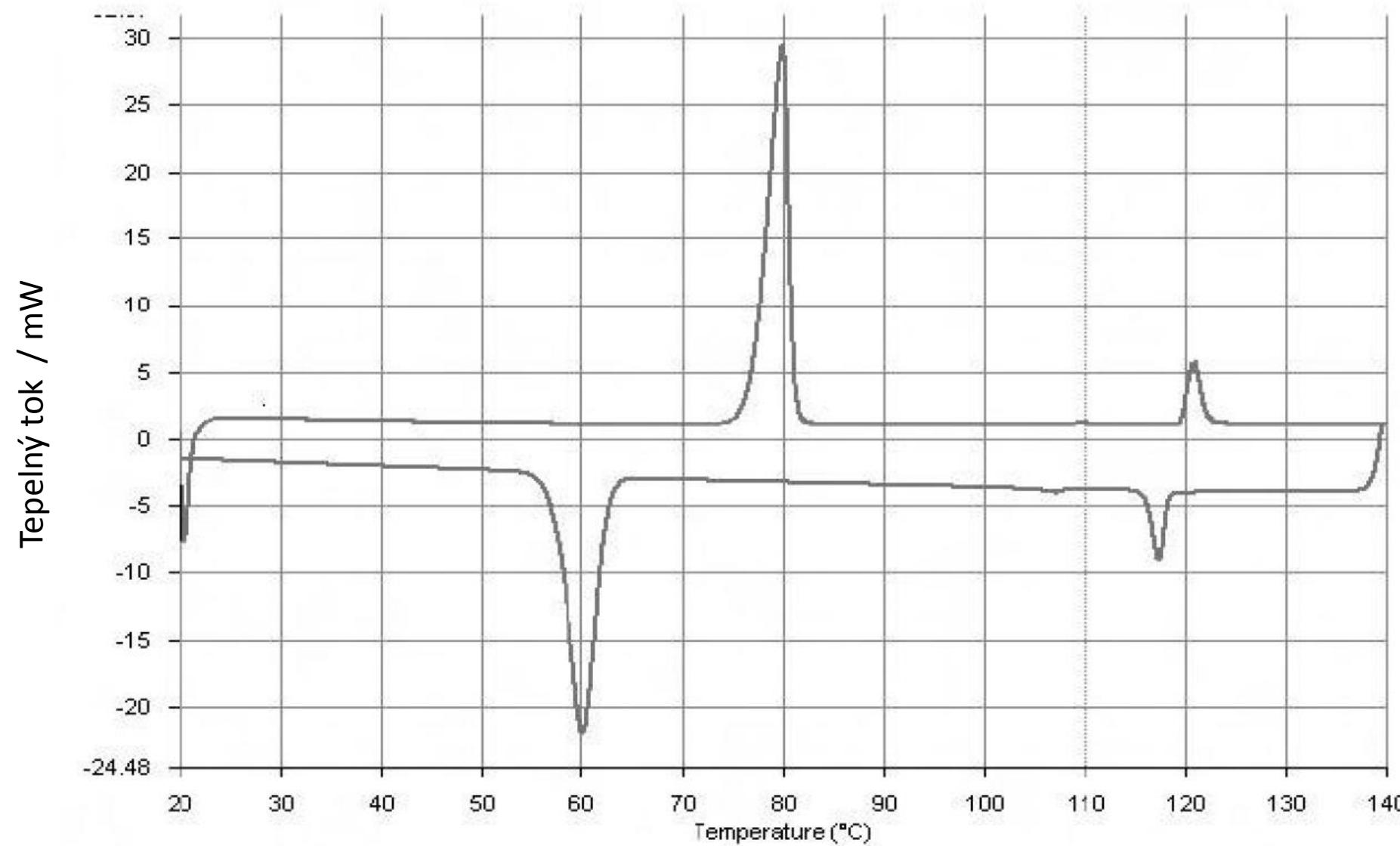
- metoda termické analýzy
- pozorování změn vlastností látek při ohřevu a chlazení
- princip: měření přísunu tepelné E tak, aby T_{VZORKU} a $T_{REFEREN.VZORKU}$ byly stejné



Setup

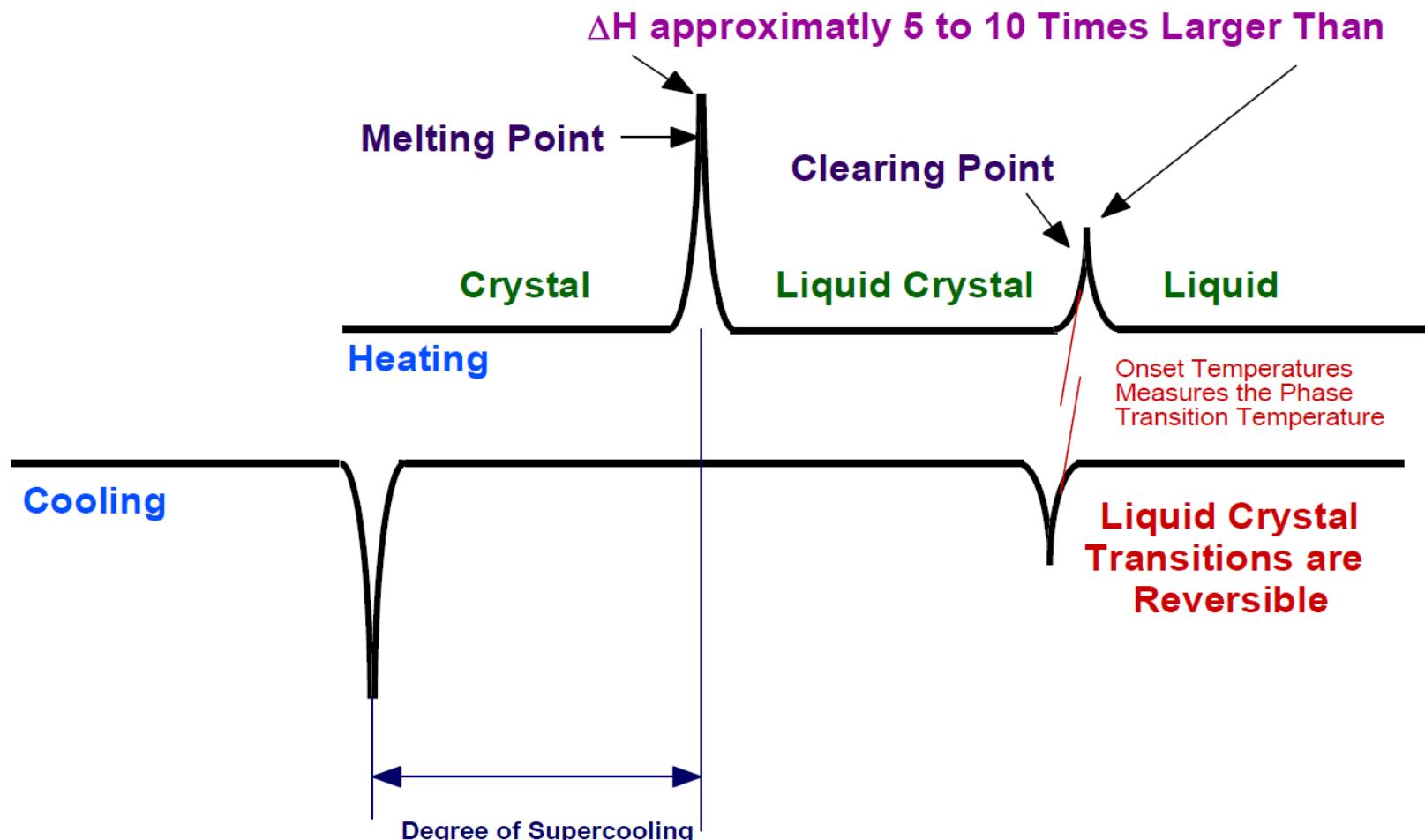


Fázové přechody – detekce pomocí DSC



Fázové přechody – detekce pomocí DSC

Typical DSC of a Liquid Crystalline Material





Comb-shaped LC Stereoregular Cyclolinear Methylsiloxane Copolymers with Chiral Mesogenic Lactate Side Groups



Irina Petrova¹, Aleksej Gaj², Alexej Bubnov³, Nataliya Makarova^{1*}

¹Nesmeyanov Institute of Organoelement compounds, RAS, Moscow, Russia

²Gymnázium Christiana Dopplera, 150 00 Prague, Czech Republic

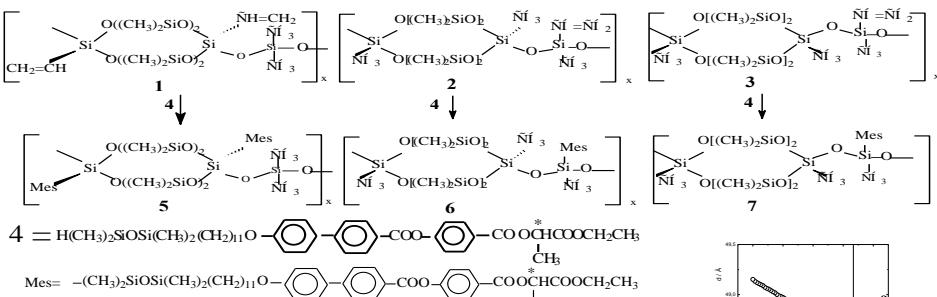
³Institute of Physics, The Czech Academy of Sciences, Prague, Czech Republic



Recently first liquid crystalline (LC) comb-like stereoregular cyclolinear (CL) methylsiloxane copolymers (MSCP) with a certain position and quantity of side mesogenic groups with the terminal lactate derivative have been obtained. It has also been stated that the cycle of the main chain causes a change of the inter-chain distance and an increase of the order in the syndiotactic copolymer

THE AIM OF WORK is to determine the critical distance between the mesogenes providing the layer order formation, CL MSCP with a different position and quantity of $\text{CH}_2\text{-CH}$ groups in the copolymer link and the hydrosilylation reaction with mesogene **4** in the presence of Karstedt catalyst have been synthesized.

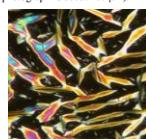
Preparation of cyclolinear organosiloxane copolymers: LC comb-like stereoregular CL MSSP (**5-7**) with mesogenic groups in $\text{Me}(\text{Mes})\text{SiO}$ and MesSiO groupings have been obtained according to the scheme:



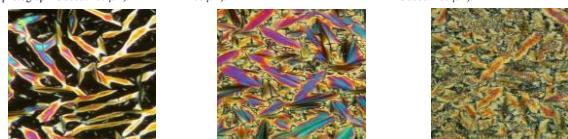
Mesomorphic behaviour of stereoregular CL organosiloxane copolymers **5-7** in the bulk



The texture of the Iso-SmA* phase transition on cooling at about 155°C. (Planar alignment; cell thickness is 2 μm ; width of the microphotograph is about 200 μm).



The texture of the SmA* phase on cooling at about 148°C. (Planar alignment; cell thickness is 2 μm ; width of the microphotograph is about 200 μm).



The texture of the SmC* phase on cooling taken at about 110°C. (Planar alignment; cell thickness is 2 μm ; width of the microphotograph is about 200 μm).

The texture of the SmC* phase on cooling taken at about 75°C. (Planar alignment; cell thickness is 5 μm ; width of the microphotograph is about 200 μm).

Fig.1. Textures of the LC copolymer **5**

Data on the temperature and enthalpies of transitions of the copolymers **5-7**

Polymer	No	m.p. [+3.1]	c.p. [+1.6]	Cr		SmC*		SmA*		Iso
5	2.4	161.2		•	0.8 [-3.5]	•	124.2 [-0.2]	•	154.6 [-3.1]	•
6	33.9	*)		•	-15.0	•	60.7 [-0.9]	•	116.5 [-0.04]	•
7	*)	144.9		•	-14.3 [-1.4]	•	69.5 [-0.4]	•	136.9 [-1.5]	•

*) measured by DSC

Conclusions:

1. A decrease in the content of mesogenic groups in the link from three [1] to one cyclolinear copolymer **6,7** leads to a decrease in the phase transition temperatures.

2. Two mesogenic groups in the unit of copolymer **5** create conditions for the formation of the LC state and $\text{Sma}^*\rightarrow\text{SmC}^*$ transition with the layer order.

References:

1. I.M. Petrova, M.A. Shcherbina, A.V. Bakirov, S.N. Chvalun, N.N. Makarova. *Mendeleev Commun.* **23**, 347 (2013).

Fig.2. Temperature dependences of the interchain distance d_i for LC copolymer **5** (a) and **7** (b).

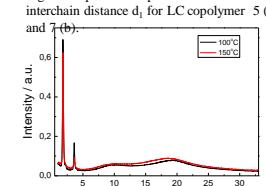


Fig.3 X-ray diffraction pattern of LC copolymer **5** at 100°C and 150°C.

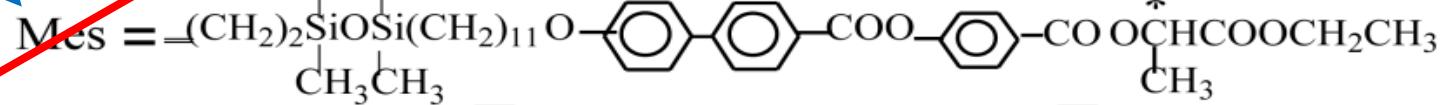
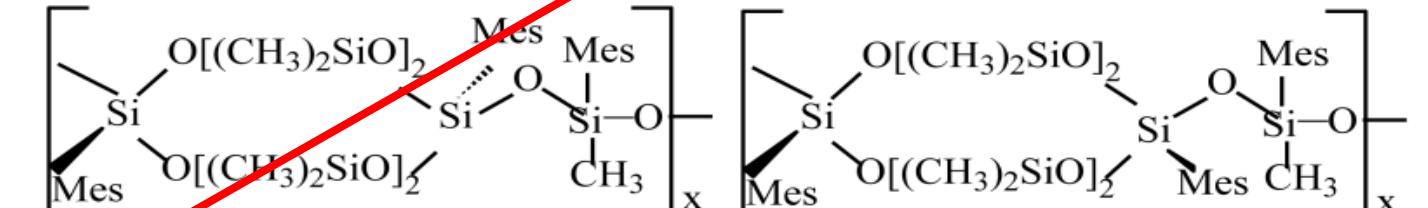
Experimental:

Mesomorphic behavior: With all studied materials, sequence of phases and phase transition temperatures were determined on cooling from characteristic textures and their changes observed in polarizing optical microscopy. The LINKAM LTS E100 heating stage with TMS-93 software was used for temperature control, which enabled temperature stabilization within 0.1 K. The phase transition temperatures were checked by DSC (Pyris Diamond Perkin-Elmer 7) on cooling/heating runs at a rate of 5 K/min-1 in a nitrogen atmosphere.

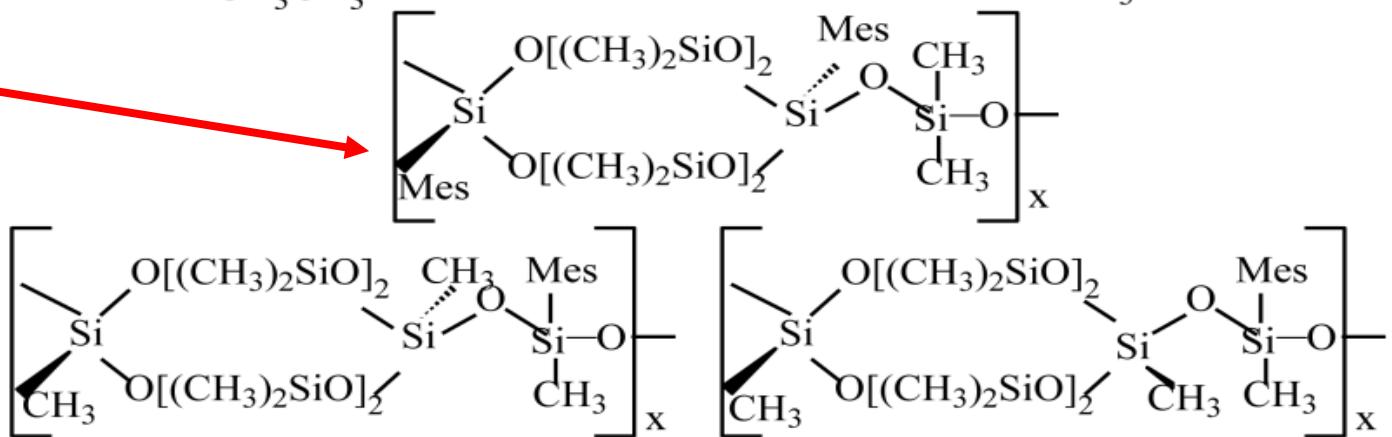
X-ray temperature dependence of smectic layer thickness was determined from small-angle X-ray diffraction experiments performed with Bruker D8 Discover system (CuK α line, Goebel mirror, Antara Plus DCS350 heating stage, scintillation counter) working in the angle range from 5 to 30°. The samples were prepared as thin film on a silicon wafer. Wide angle X-ray diffractograms were obtained with Bruker D8 GADOS system (CuK α line, Goebel mirror, point beam collimator, Vantec2000 area detector). Samples were prepared as droplets on heated surface.

Syntéza

- mesogen (KK)



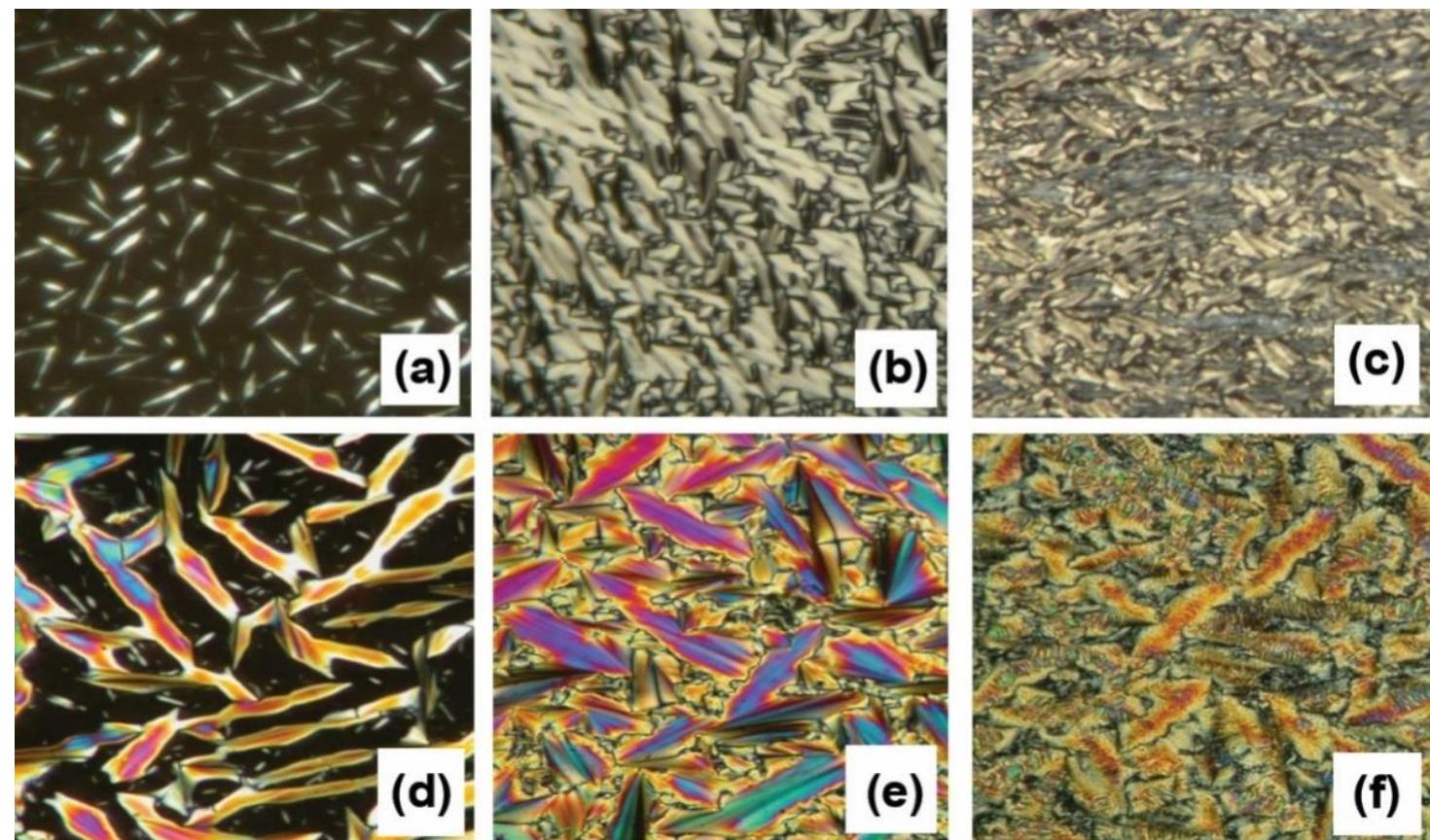
- polysiloxanový řetězec



katalyzátor - Pt

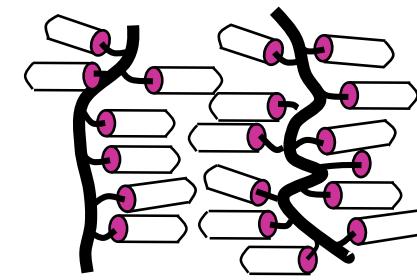
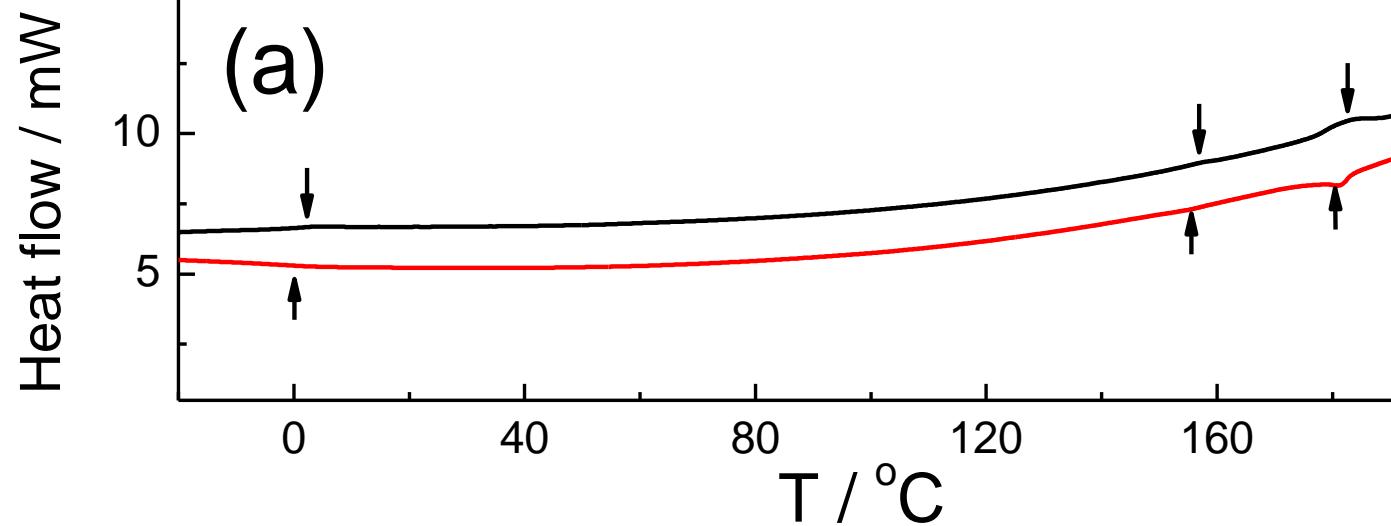
Určení mezofází pomocí POM

Fáze \ Tloušťka	2μm	5μm
Iso-SmA	$\approx 155^{\circ}\text{C}$ (a)	$\approx 155^{\circ}\text{C}$ (d)
SmA	$\approx 148^{\circ}\text{C}$ (b)	$\approx 135^{\circ}\text{C}$ (e)
SmC	$\approx 110^{\circ}\text{C}$ (c)	$\approx 75^{\circ}\text{C}$ (f)



Měření metodou DSC

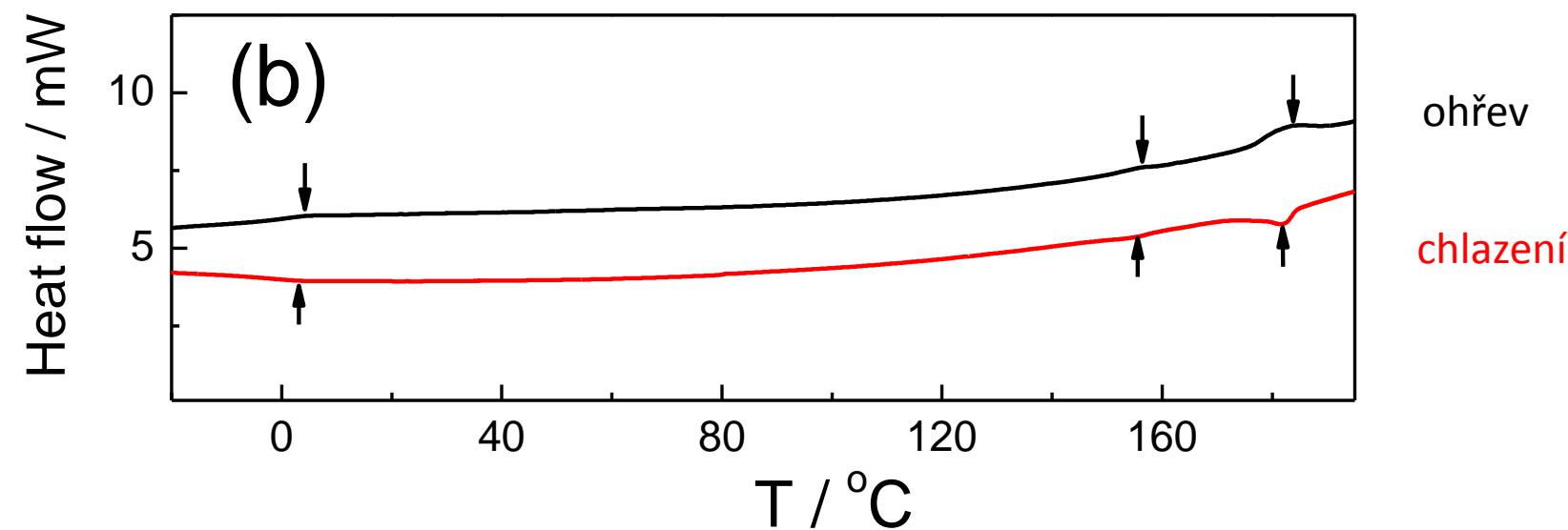
- copolymer
7



ohřev

chlazení

- copolymer
8



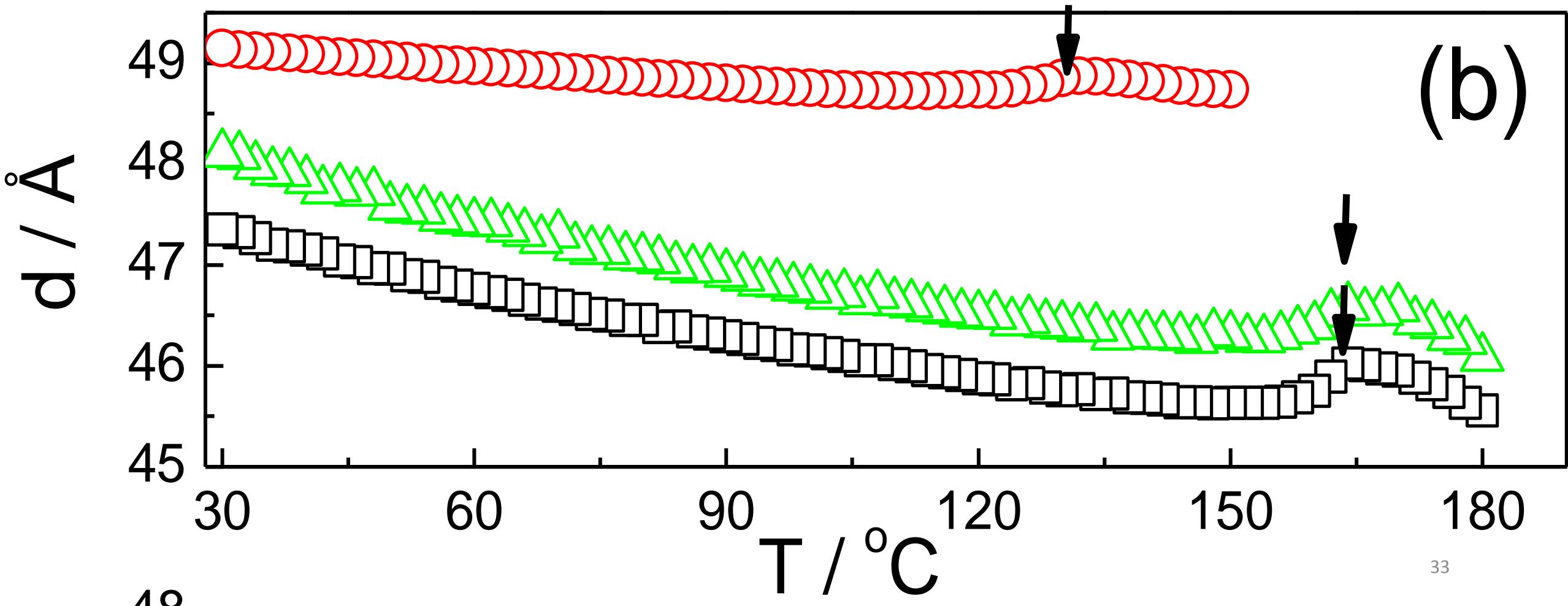
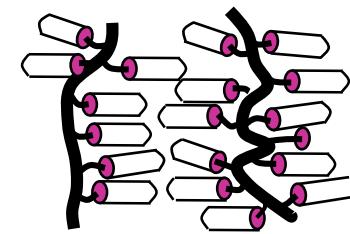
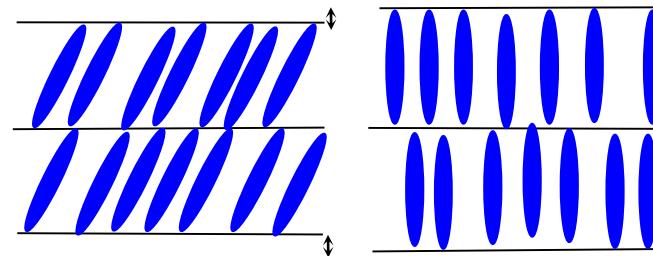
ohřev

chlazení

Měření metodou DSC

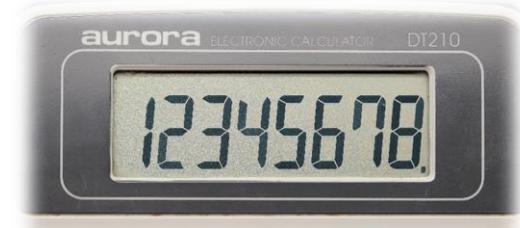
Name	T _g		SmC*		SmA*		Iso
NN-1	•	+5.5	•	+155.1 [-1.7]	•	+181.3 [-5.0]	•
NN-2	•	+4.9	•	+154.7 [-0.8]	•	+181.9 [-5.1]	•
NN-3	•	+0.8	•	+124.2 [-0.2]	•	+154.6 [-3.1]	•
NN-4	•	-15.0	•	+60.7 [-0.9]	•	+116.5 [-0.04]	•
NN-5	•	-14.3	•	+69.5 [-0.4]	•	+136.9 [-1.5]	•

Měření metodou RTG

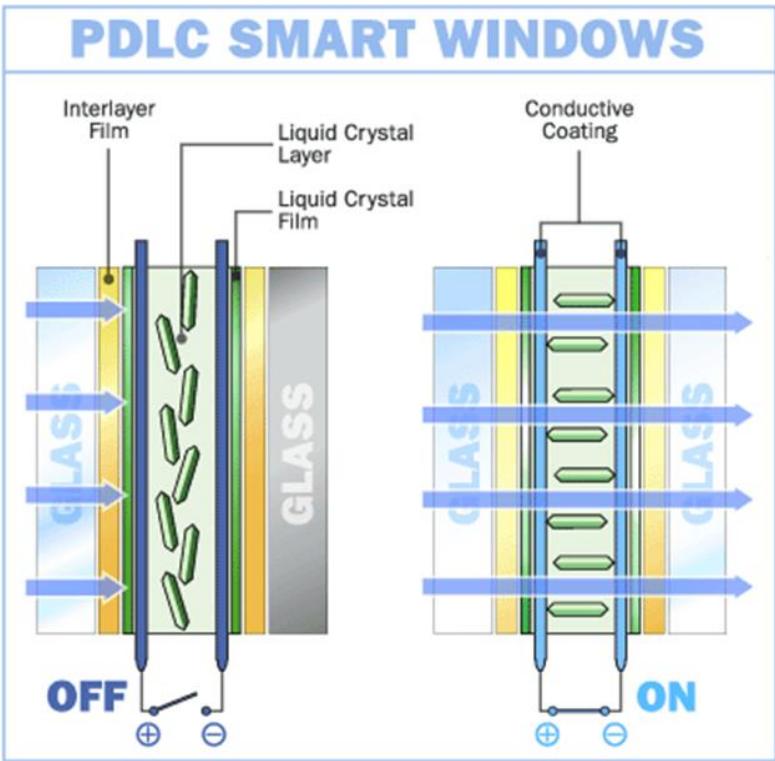


K čemu je to dobré? (aneb aplikace)

- zobrazovače různých typů
- lékařství – diagnostika nádorů
- regulace světelné propustnosti (ochranné helmy, okna...)
- teploměry
- ... a mnoho dalšího ...



Okna





LCD helma pro absorpci světelného záření



Smart cards s LCD zobrazovačem



Dóza na léky s LCD zobrazovačem a alarmem



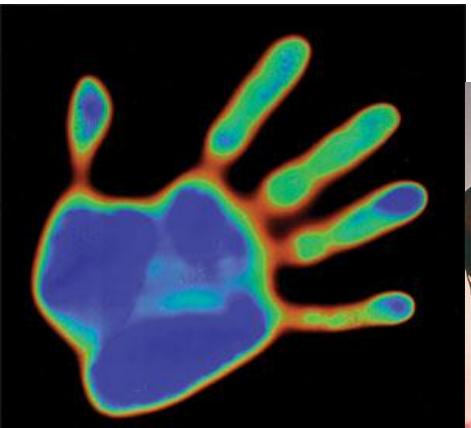
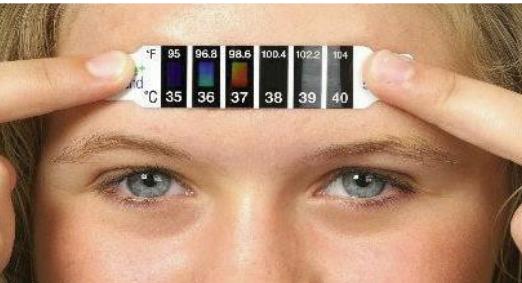
KK v přírodě: perlorodky a brouci



LC-based thermometer showing the temperature of the wine



LC thermometers



Liquid crystal thermography used for diagnostics in medicine



Textile materials with liquid crystals causing color change



HUD (heads-up display)



v automobilu (nikoliv LCD, ale projekce LED)



v plaveckých brýlích pro zobrazení času



v letadle

Zdroje

- výsledky, prezentované na European Conference on LC (2017)
- I. Petrova, A. Gaj, D. Pochiecha, M. Shcherbina, N. N. Makarova, A. Bubnov
Design and self-assembling behaviour of comb-like stereoregular cyclolinear methylsiloxane copolymers with chiral lactate groups
(odesláno do časopisu Liquid Crystals)
- prezentace - prof. J. Goodby, Velká Británie
- prezentace - prof. R. Zentel, Německo
- https://en.wikipedia.org/wiki/File:Polarizing_microscope.ogv
- https://en.wikipedia.org/wiki/Polarized_light_microscopy
- http://www.wikiskripta.eu/w/Soubor:Cholesterol_Crystals_Synovial_Fluid_Polarized_Light.jpg
- <http://www.chempoint.cz/kucerik-2>

A microscopic image showing a cross-section of plant tissue. The image is dominated by large, elongated, light-colored cells with distinct boundaries. In the upper right quadrant, there is a cluster of smaller, more densely packed cells. A prominent feature is a large, irregularly shaped cavity or air space containing several small, clear, spherical structures, possibly pollen grains or starch granules. The overall texture is somewhat fibrous and layered.

Děkuji za pozornost!