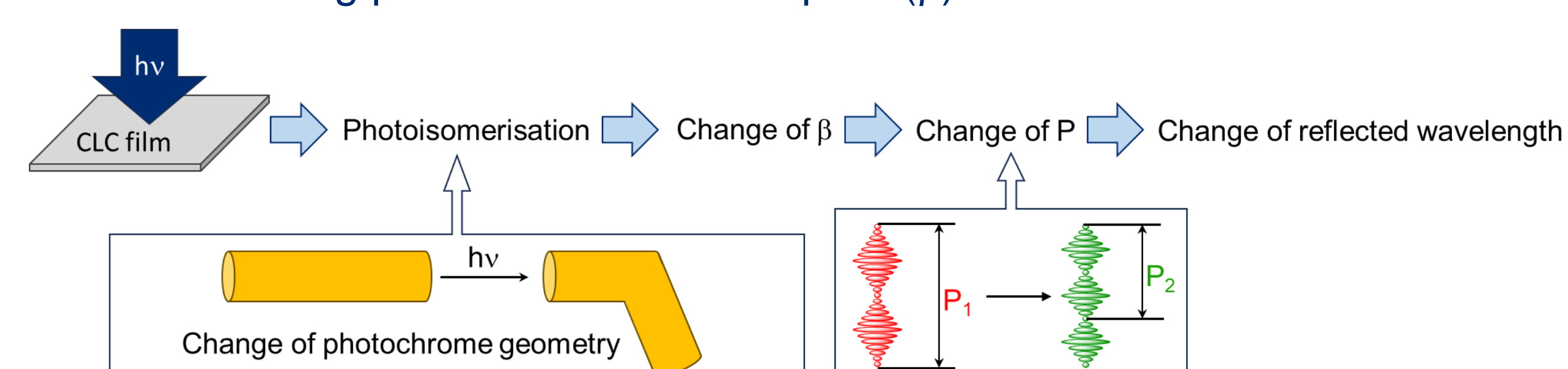


## Motivation

Chiral liquid crystalline phases can be used in different fields of optoelectronics and photonics due to their ability to show dynamic changes or switching of optical properties in response to external stimuli, such as heat, light or electrical fields. Doping cholesteric liquid crystals (CLCs) with chiral photochromic dyes makes it possible to control the pitch (P) of the helix, and so the reflected wavelength, using light. Principle is the photoinduced change of helical twisting power of the chiral dopant ( $\beta$ ).

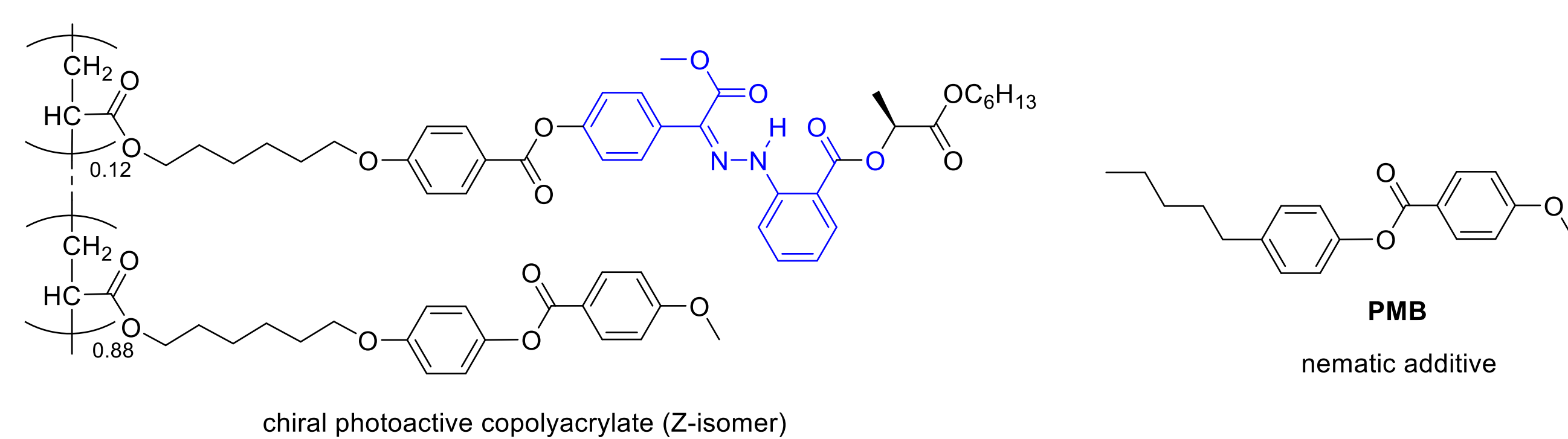


Phototuning of CLCs could be used, e.g., for the creation of materials used in tunable diffractive optics, light-tunable displays, reflectors, lasing, color filters and photoinduced gratings[1].

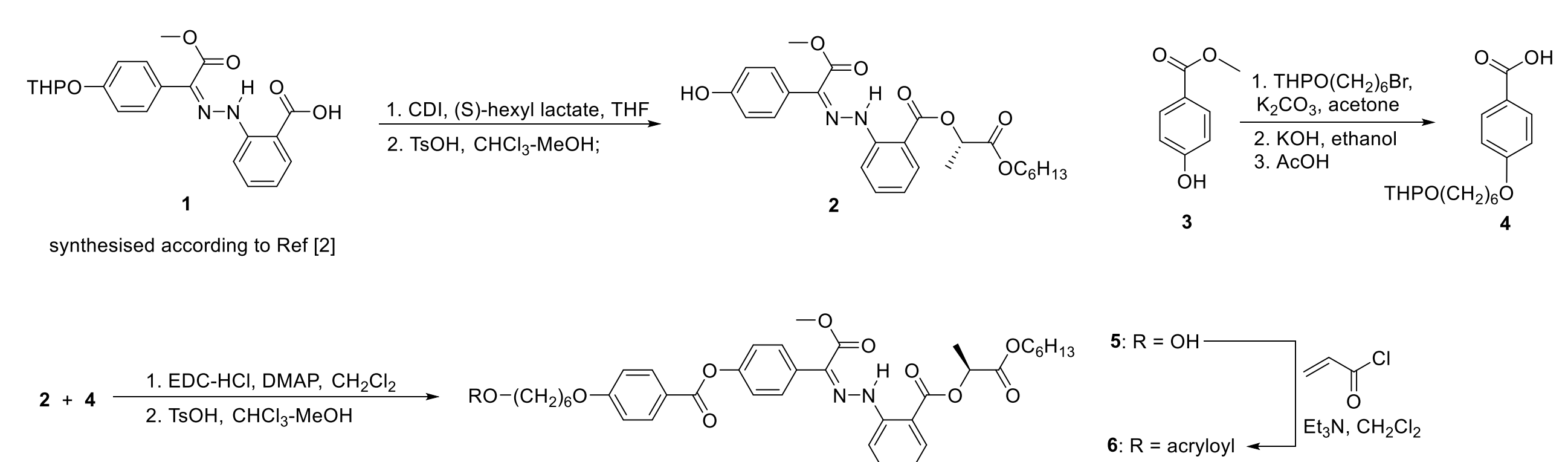
Hydrazone functional group (C=N–NH) has imine double bond that could be photoisomerized under the action of light and acidic NH proton. The one of the most important structural features of such systems is the presence of an acidic NH proton with specific hydrogen bonding allowing to enhance the kinetic stability of both hydrazone isomers. The kinetic stability of switchable isomers is necessary for bistable switching in photochromic systems, but it is found in a very few photochromes.

## Materials and methods

New comb-shaped chiral liquid crystalline hydrazone-containing copolyacrylate and its mixture with LC (nematic additive PMB, 10 wt%) have been synthesized and formulated for the purposes of our study. The synthetic methodology for the new chiral photochromic hydrazone monomer has been developed.



### Synthesis of photoactive monomer



### Polymerisation

- Radical copolymerisation of hydrazone monomer (12 mol%) with phenyl benzoate nematogenic monomer in toluene solution in the presence of AIBN thermoinitiator (2 wt % to monomer) under argon atmosphere at 65°C for 3 days in a sealed tube.
- Purification by washing several times with boiling ethanol. Yield of polymerization was 88% for copolymer.
- Thin films (100-200 nm) were obtained by spin-coating technique on quartz substrates without special pretreatment.

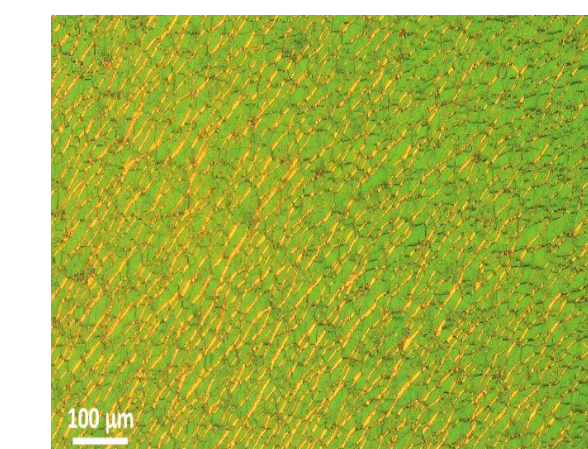
## References

- [1] See references in: A. Boychuk, V. Shibaev, M. Cigl, V. Hamplová, V. Novotná, A. Bobrovsky ChemPhysChem 24, e202300011, (2023).  
[2]. Shao, I. Aprahamian, Chem 6, 2162–2173 (2020).

## Results

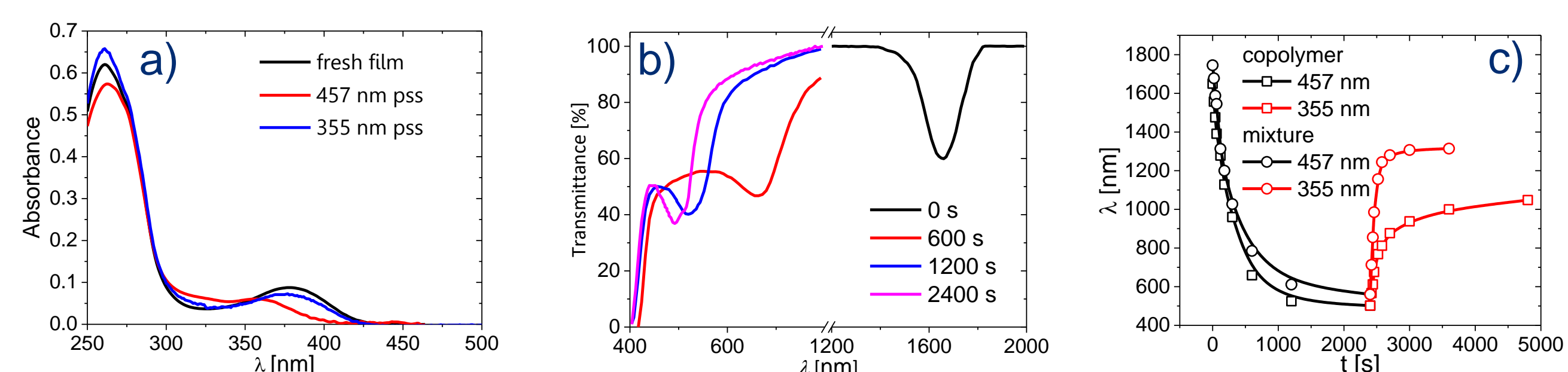
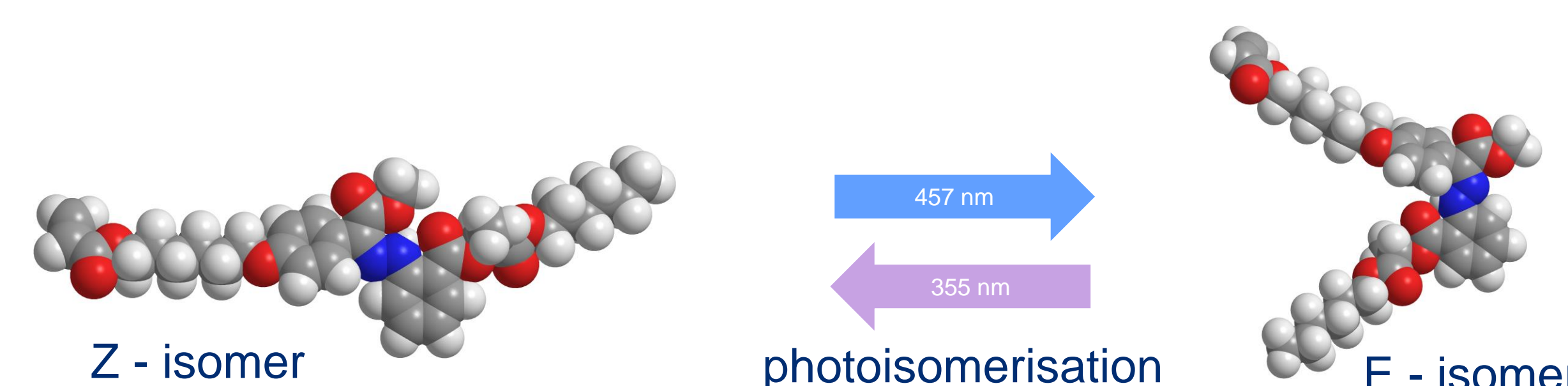
- The mesomorphic behavior (glass transition and isotropisation temperatures) of the copolymer and its mixture with nematic additive PMB obtained by POM and DSC
- Copolymer and mixture possess selective light reflection.

Polymer	Phase transitions / °C	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
copolymer	g 22 N* 90-92 Iso	8470	2.04
mixture	g 9 N* 80-82 Iso	-	-

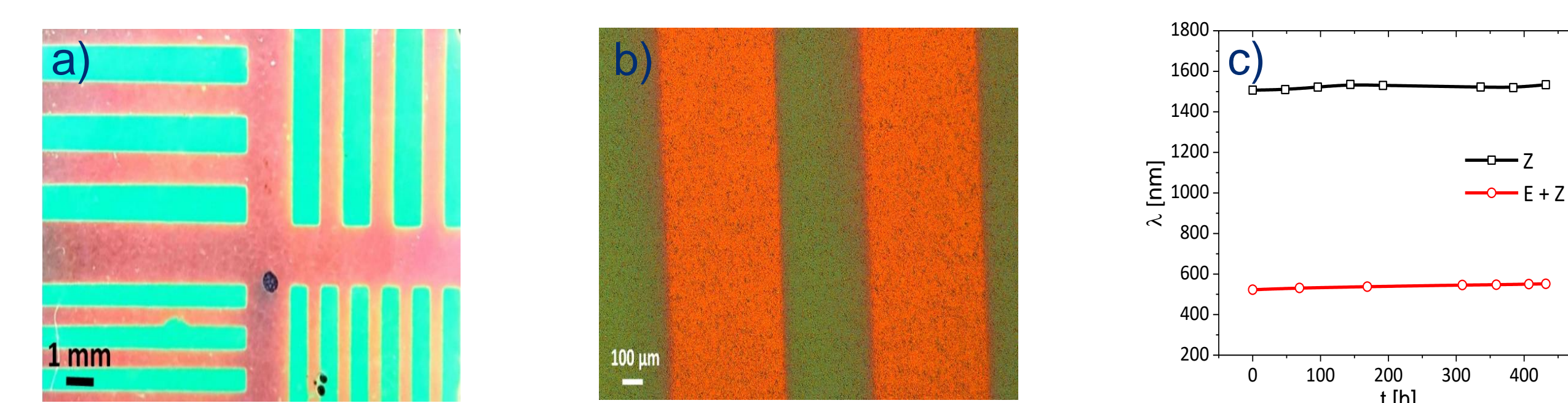


N\* - cholesteric phase; I - isotropic phase; g - glassy state, M<sub>w</sub> – weight average molar mass, M<sub>w</sub>/M<sub>n</sub> – polydispersity - determined by GPC chromatography using instrument "Knauer"

Planar texture of the copolymer N\* phase in POM



- Absorbance spectra of the copolymer film after blue (457 nm, 160 mW/cm<sup>2</sup>) and UV light (355 nm, 24 mW/cm<sup>2</sup>) irradiation in photo-stationary states (pss).
- The transmittance spectra of the planarly oriented film of the copolymer depending on the blue light (457 nm) irradiation time.
- Changes of the selective reflection peak position of the copolymer and mixture during blue (457 nm) and UV light (355 nm) irradiation.



Photos of sample of the mixture irradiated with a blue light (457 nm for 10 min, then 428 nm for 20 min) through the mask.

- Digital photo (irradiated by 428 nm light zones have green color)
- POM image of the same sample
- Thermal stability of reflection states (Z = original, E+Z = photostationary)

## Conclusions

- Large thermally irreversible photoinduced shift of selective light reflection in hydrazone-containing cholesteric polymer was demonstrated.
- Original selective light reflection (1650 nm) can be shifted by blue light (428 or 457 nm) to shorter wavelengths and is reversibly tunable in the region 500 - 1050 nm.
- Doping of copolymer with low-molar mass nematic LCs leads to the improved photooptical response and increased rate of the helix pitch changing.
- It has been shown that both E and Z hydrazone isomers are thermally kinetically stable that enables to achieve a pure photoinduced switch without any thermal relaxation in the dark at any temperatures.

## Acknowledgement

Financial support from the Czech Science Foundation (20-22615J) and by the Russian Science Foundation (19-13-00029) is gratefully acknowledged.