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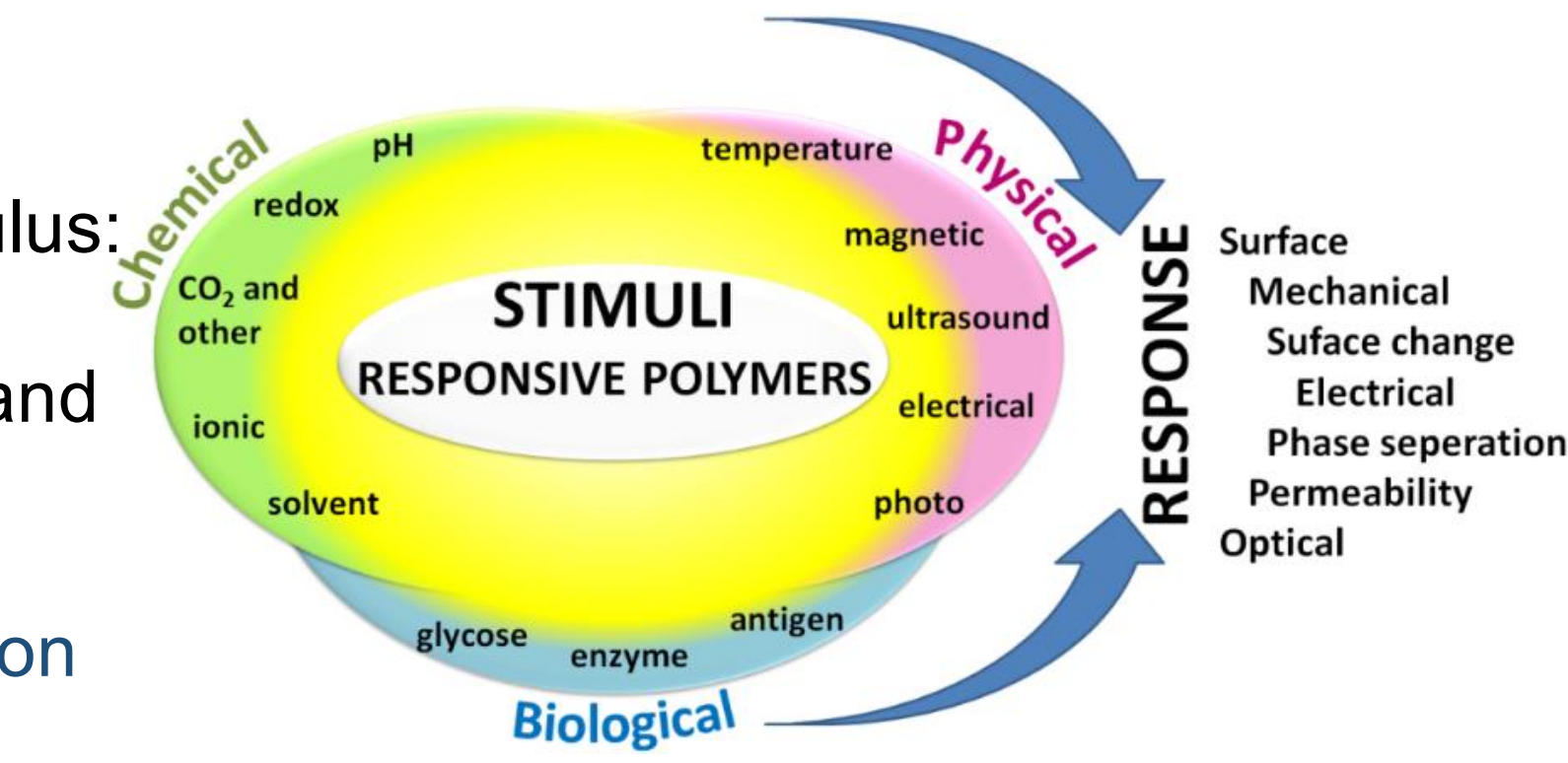
## Responsive Polymers

Response of polymer to external stimulus:

**Light, temperature**

Stimulus can cause reversible micro- and macroscopic changes in polymer

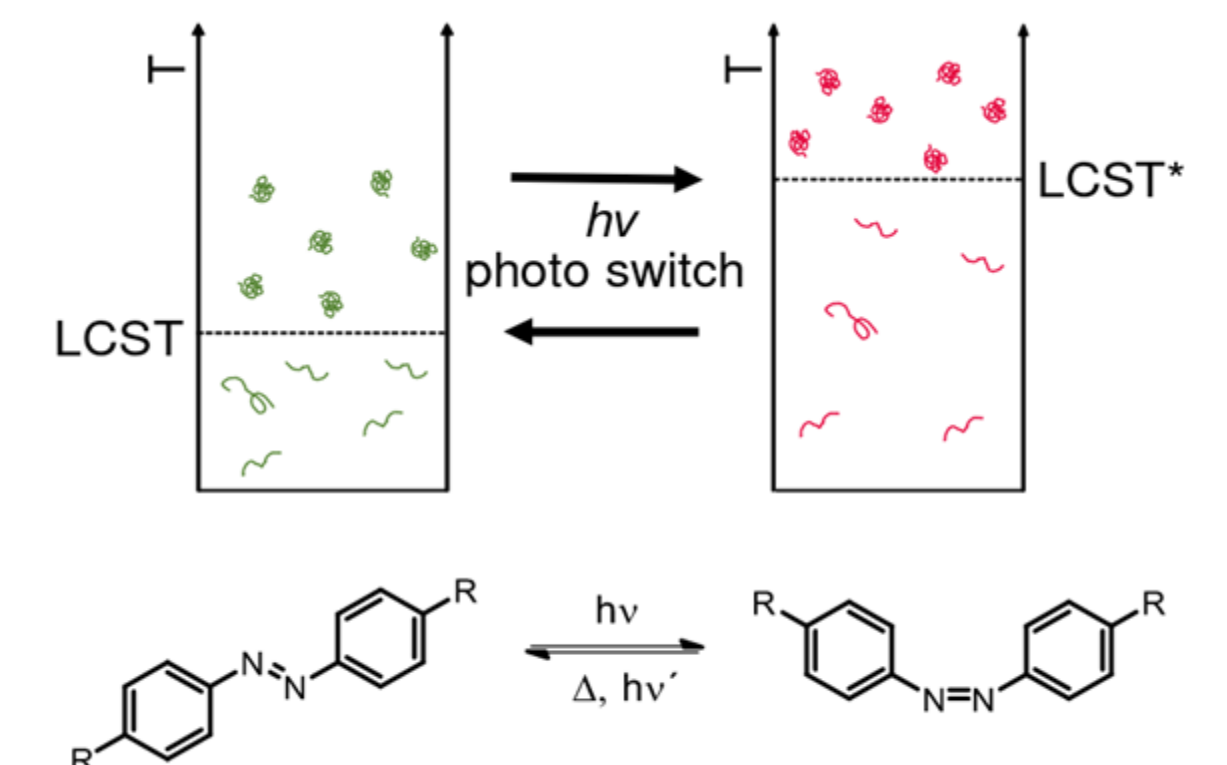
- change in **optical absorption**
- change in **polymer chain conformation**



G. Koçak, C. Tuncer, V. Büttin, HJBC 2020, 48, 527–574.

## Photoresponsive Polymers

- control of LCST with light
- use of photoactive moieties, e.g. **azobenzene** photoisomerization
- non-invasive stimulus with high temporal resolution
- application for light-sensors and drug-delivery devices



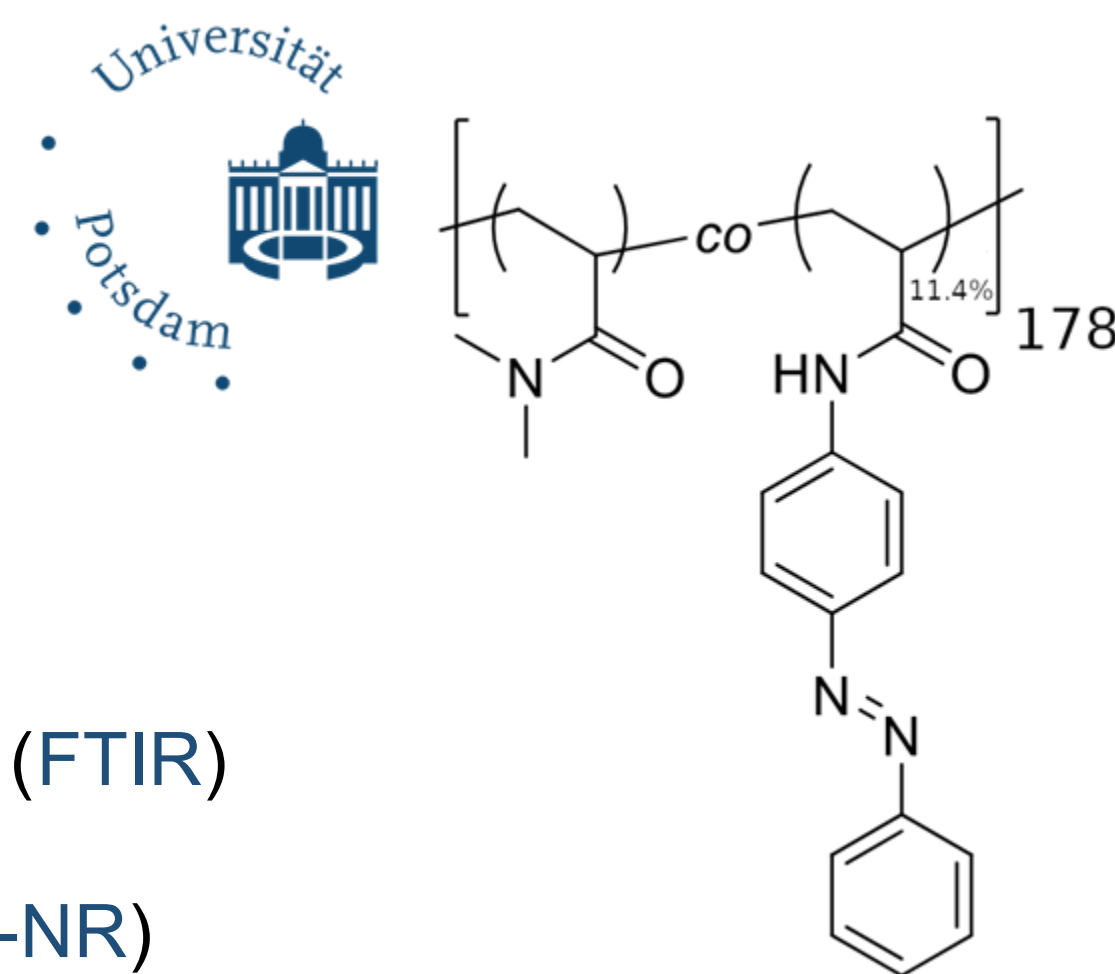
## Azobenzene-Modified pDMAm

**p(DMAm-co-AzAm11.4%)**

- statistical copolymer of dimethyl-acrylamide (DMAm) and azobenzene-acrylamide (AzAm)
- cloud point shift upon UV-irradiation in solution

behavior in thin films unknown:

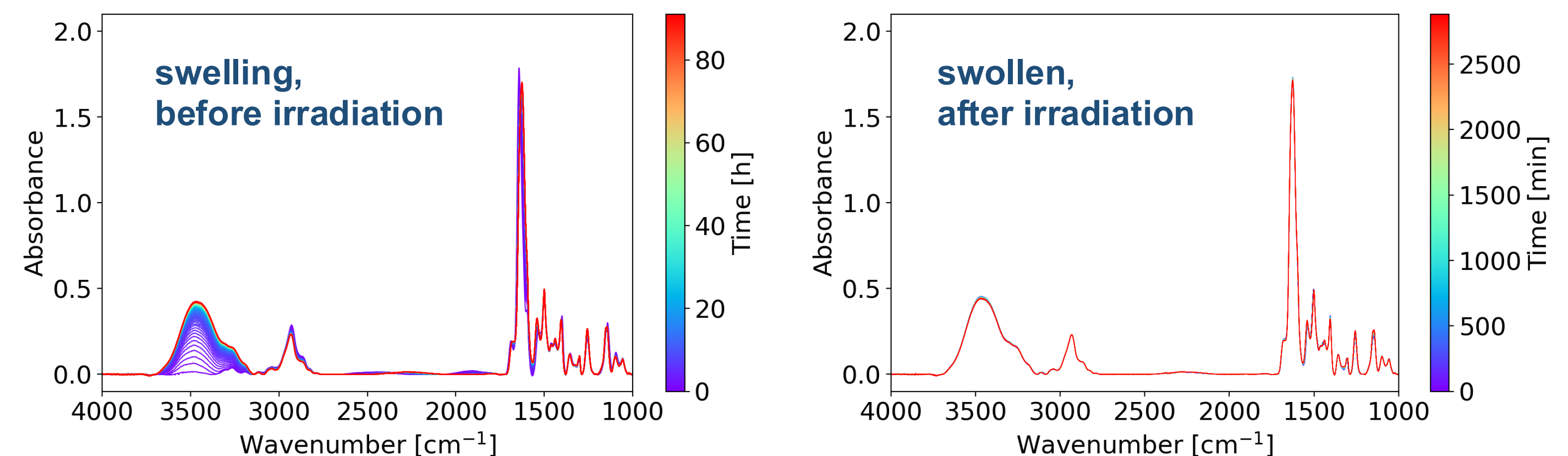
- **swelling** of polymer films in water vapor?
- behavior upon **irradiation** with UV light?
- kinetic Fourier-transform infrared spectroscopy (FTIR) during irradiation
- kinetic time-of-flight neutron reflectometry (ToF-NR) during irradiation



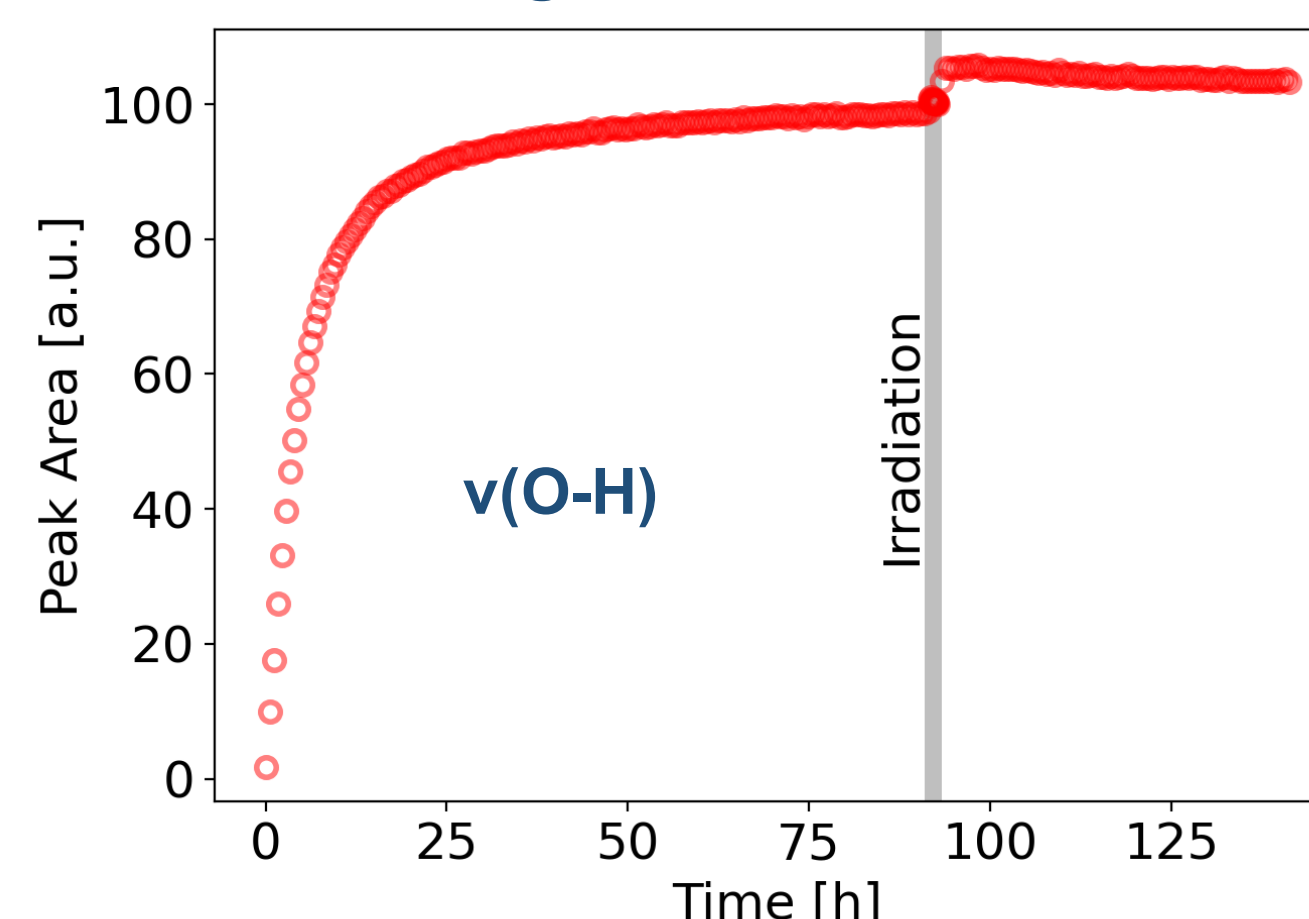
## Kinetic FTIR

**Time-resolved FTIR measurements**

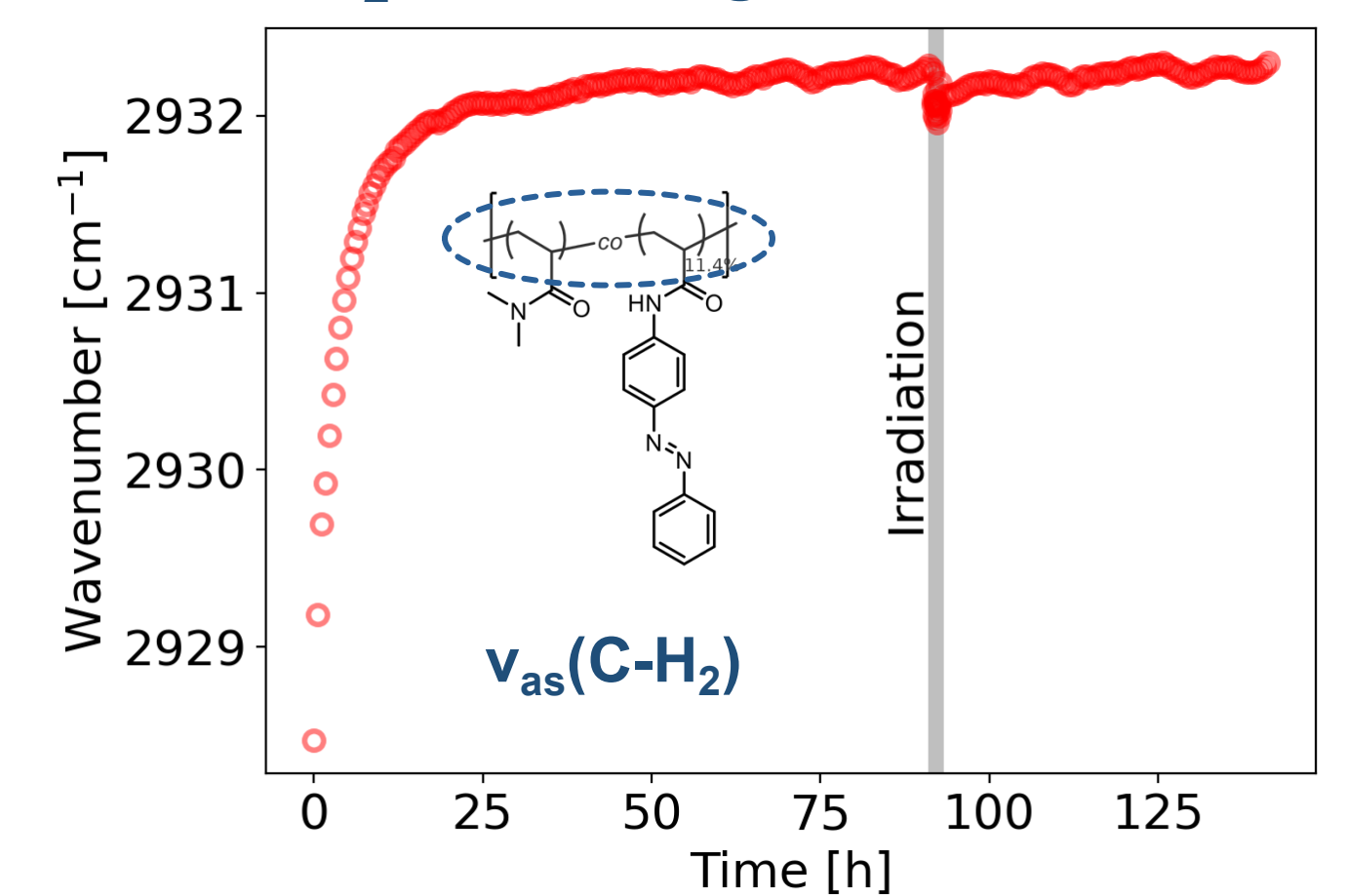
- polymer films on silicon substrate
- swelling in H<sub>2</sub>O vapor and irradiation with UV-lamp
- examine changes in group vibrations as result of swelling and irradiation



**O-H stretching of water molecules**

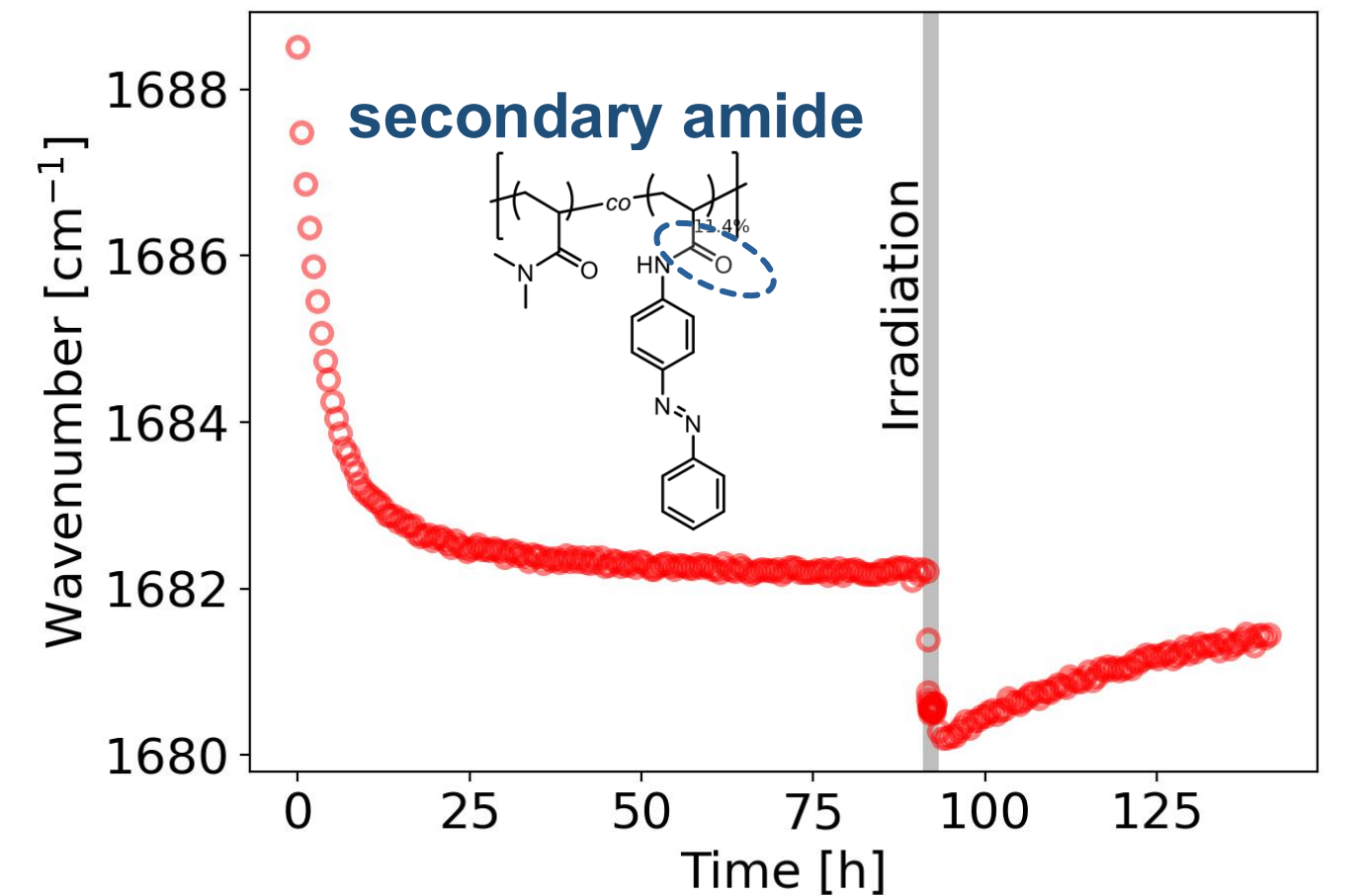
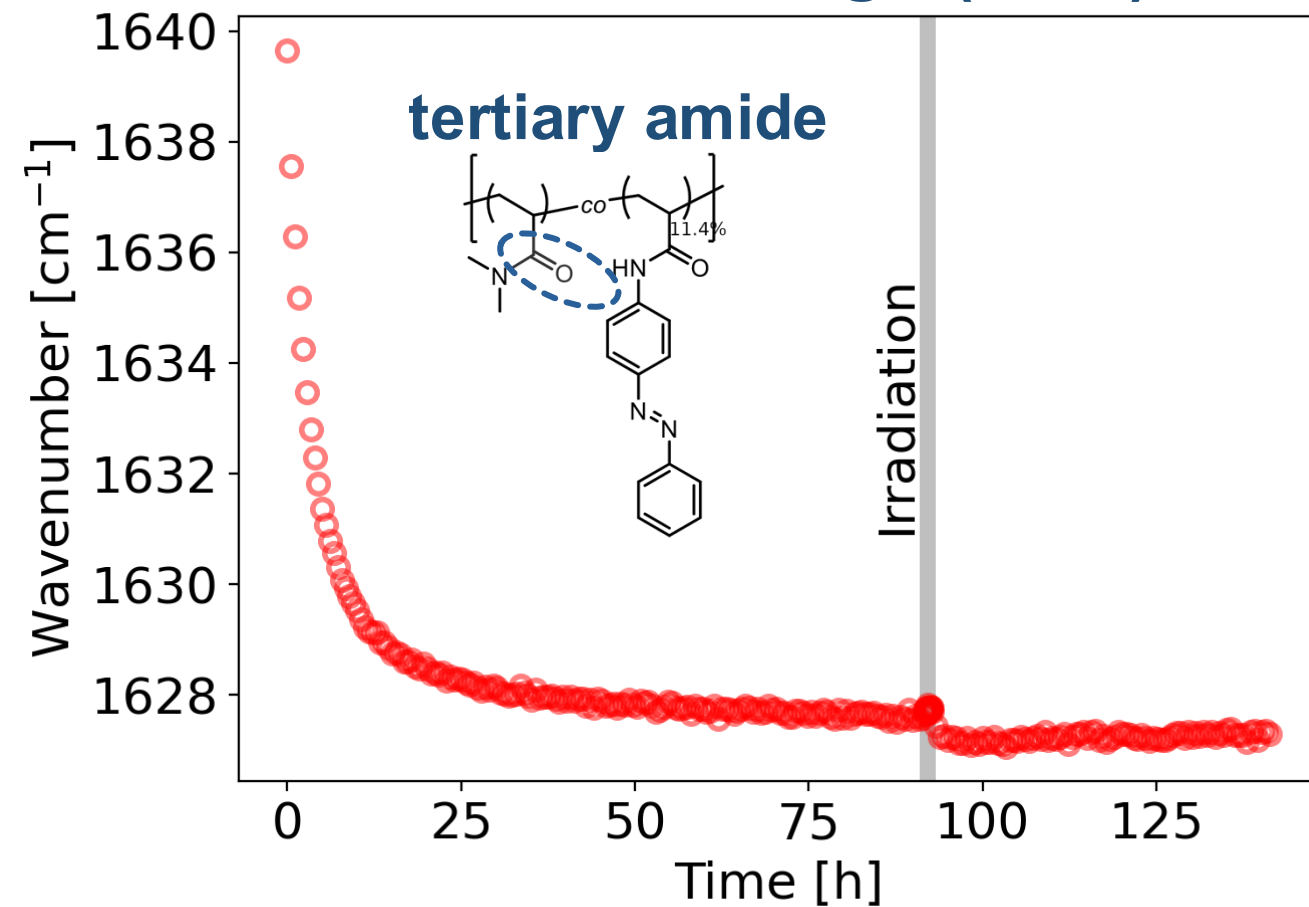


**C-H<sub>2</sub> stretching of backbone**



- fitting of the FTIR spectra shows that global water content in polymer increases after irradiation
- however, loss of water in vicinity of polymer backbone

**Amide I C=O stretching  $\nu(C=O)$**



- decrease in wavenumber during swelling, due to hydrogen bond formation
- further decrease after irradiation, however much stronger for secondary amide
- increase in global water content accounted for by side chains
- increased water uptake mostly limited to photoactive side chain

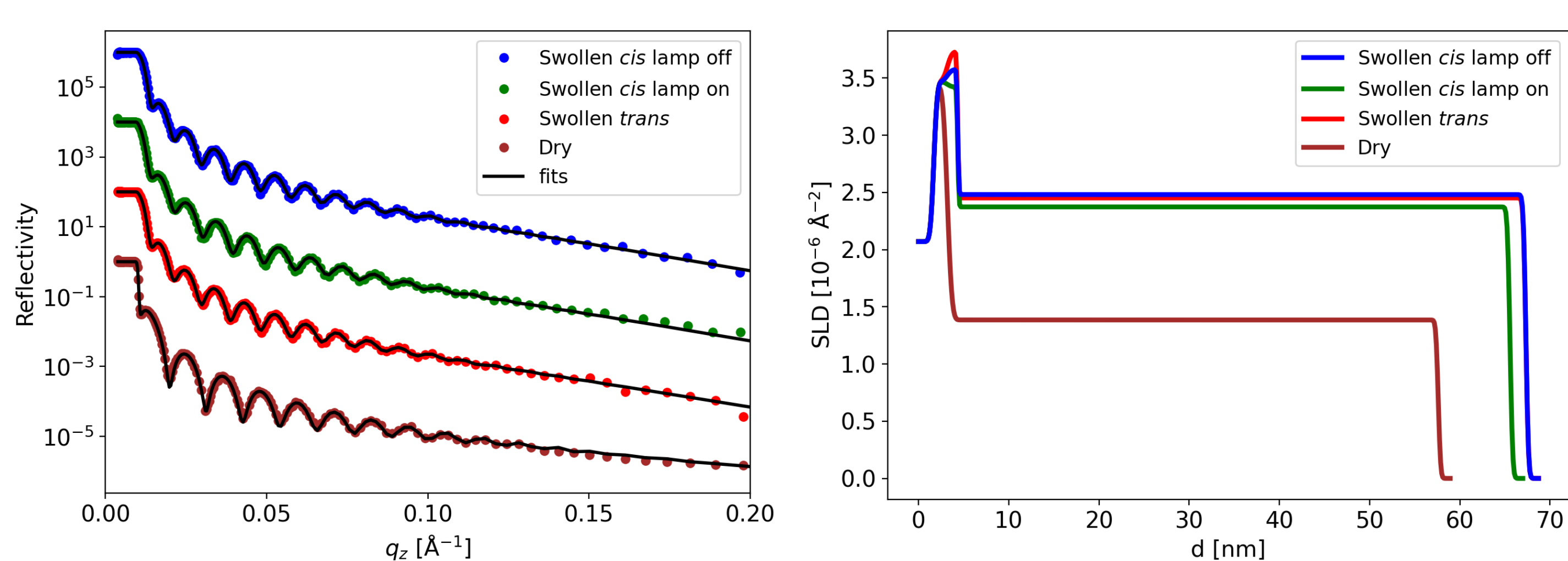
## ToF-NR

**ToF-NR measurements at the D17 instrument of Institute Laue-Langevin**

- drying with N<sub>2</sub>, swelling in D<sub>2</sub>O vapor and irradiation with UV-lamp at 30 °C
- investigate changes in film thickness and SLD as result of UV light



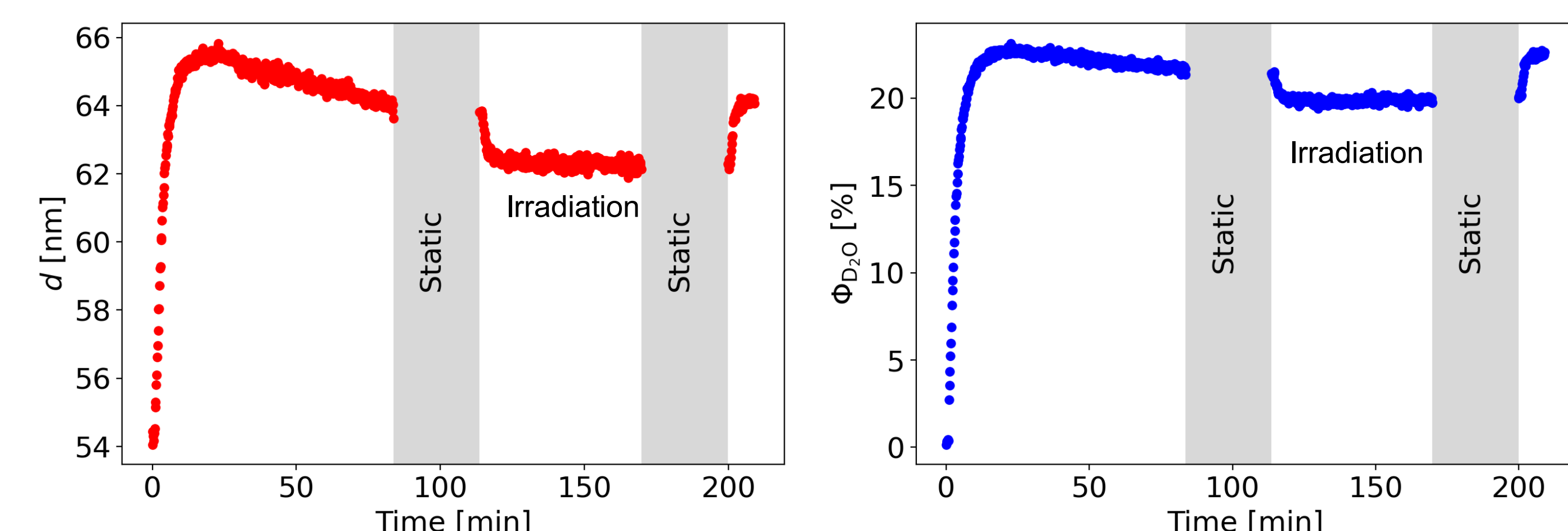
**Static measurements**



- Increase of film thickness and SLD due to incorporation of D<sub>2</sub>O
- Small change after irradiation with UV-lamp for 1 h

**Time-resolved measurements**

- Investigate kinetics of water uptake in polymer and response to UV-light
- Evolution of thickness and D<sub>2</sub>O volume fraction over time



- loss of D<sub>2</sub>O during irradiation from heat
- return to previous thickness and D<sub>2</sub>O content after heat from lamp is removed
- heat from lamp dominates water expulsion due to isomerization
- only small changes after lamp is switched off

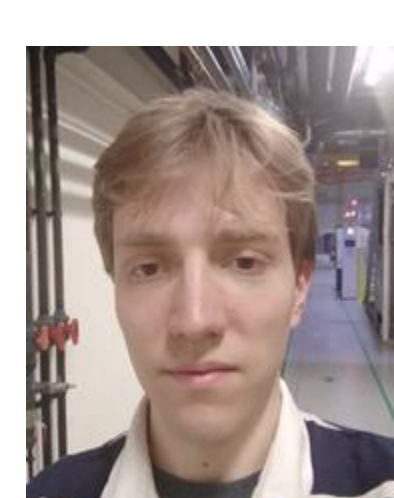
## Conclusions

**FTIR**

- increase in hydration due to isomerization of azobenzene
- mainly located around photoactive sites

**ToF-NR**

- small increase in D<sub>2</sub>O content after irradiation
- light responsive effect weaker compared to FTIR
- likely due to lower film thickness (more interface effects)



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