

Synthesis and characterisation of photo-responsive hydrogels

Stephane Louisia¹, Bartosz Ziolkowski¹, Michele Zaroni¹ and Dermot Diamond¹.

¹ CLARITY Centre for Sensor Web Technologies, NCSR, Dublin City University, Dublin 9, Dublin, Ireland.

Contact: Prof. Dermot Diamond (Dermot.Diamond@dcu.ie)

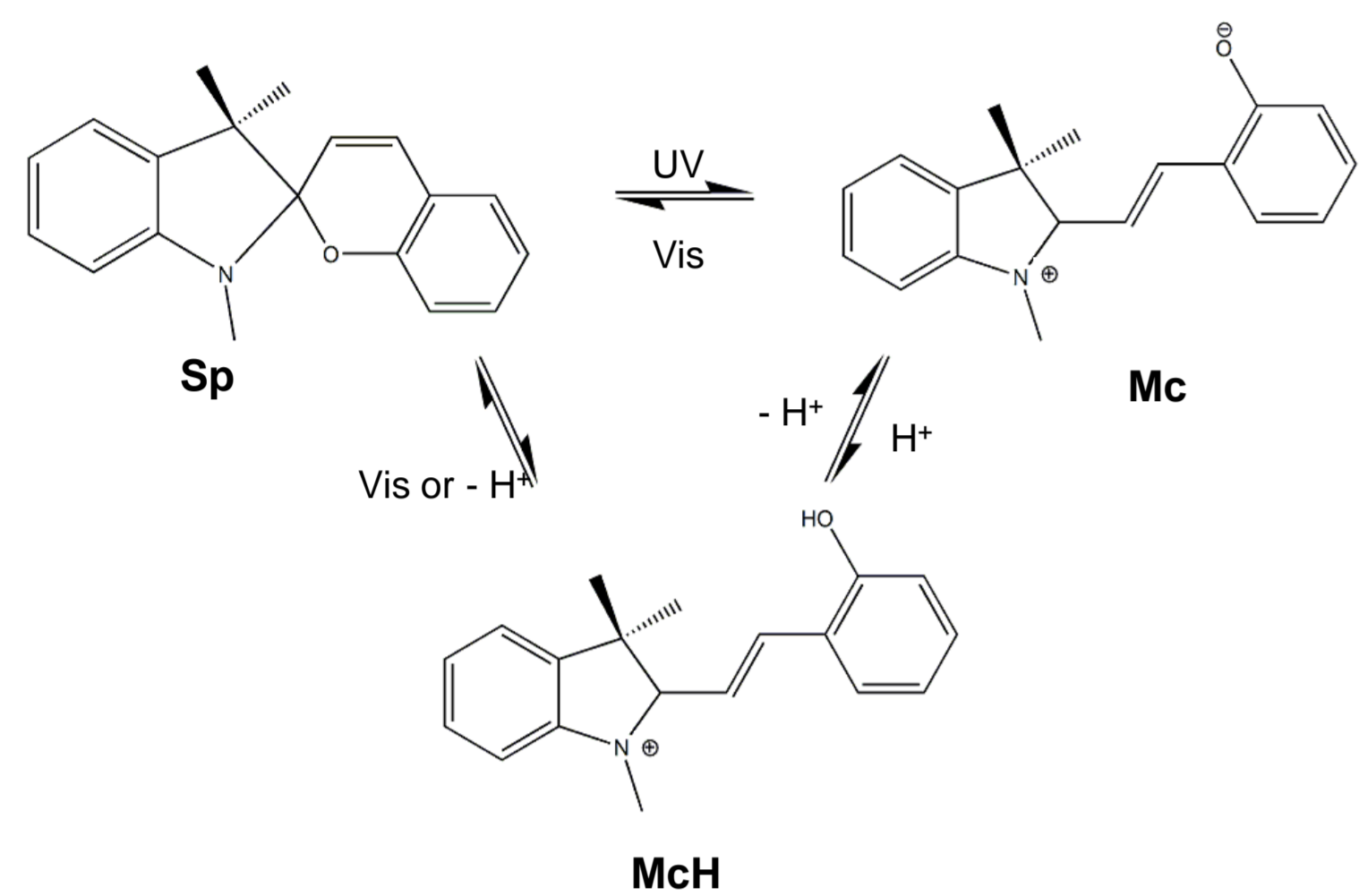


OBJECTIVES

- Synthesis of spiropyran monomers and preparation of photo-responsive linear polymers
- UV-vis analysis and protonation/deprotonation kinetic study of polymer aqueous solution

INTRODUCTION

Poly-(N-isopropylacrylamide) (pNIPAM) is a well-known thermo-responsive material. The rise of the temperature above 32° C leads to the reversible Low Critical Solution Temperature (LCST)¹, which is a phase transition from the hydrophilic state to the shrunken hydrophobic state. One possible way to trigger the response of this material is the functionalization of pNIPAM gels with spirobenzopyran to transform the polymer into a photo-responsive polymer.



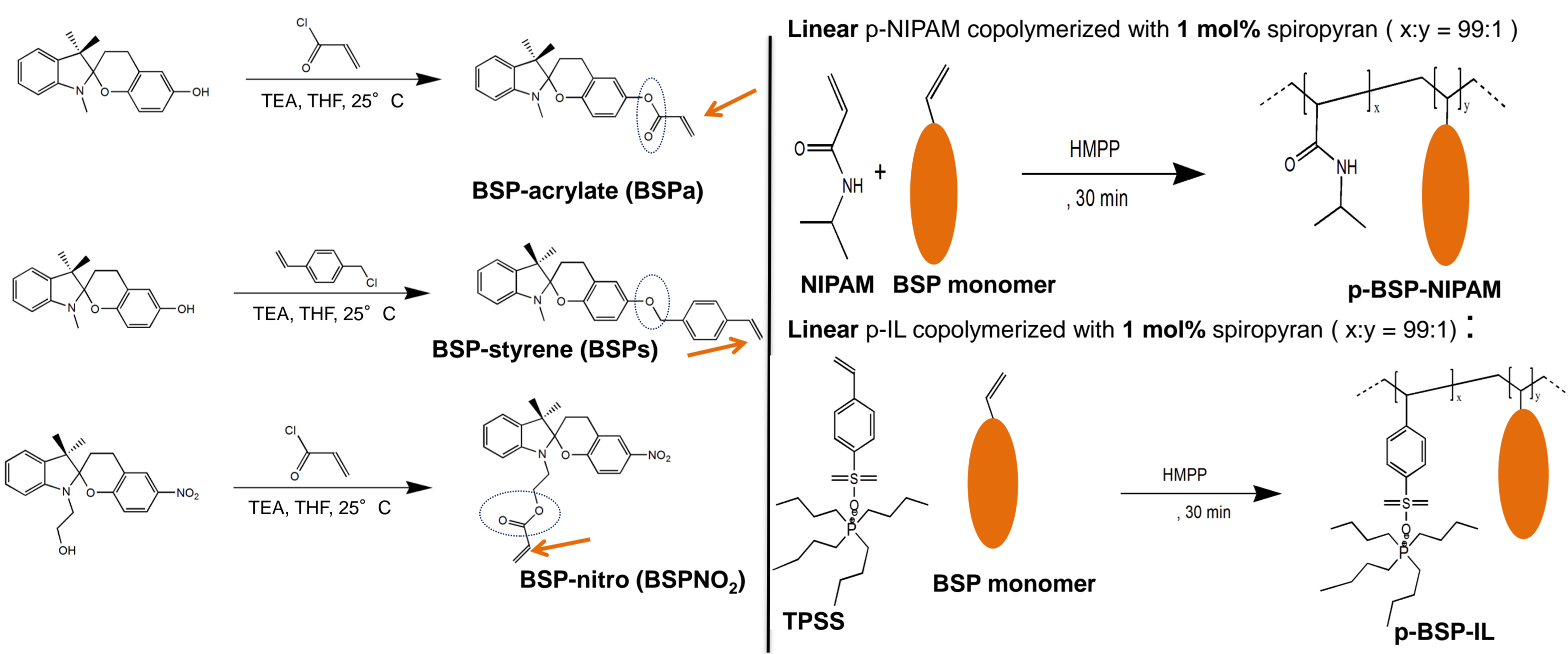
Spirobenzopyrans are photo chromic organic compounds. UV light induces the opening of the spiropyran (Sp) leading to formation of the Merocyanine (Mc). White light induces a reverse reaction. In acidic solution, there is a third form of the spirobenzopyran, the protonated merocyanine form (MCh)², which exist in the dark but it closes to Sp form with white light.

Isomerisation of spirobenzopyran isomers

Another way to obtain a photo-responsive polymer is to replace pNIPAM by the **poly-(tetrabutylphosphonium-4-styrenesulfonate)** (pTPSS), which is a poly ionic liquid known to show a LCST that depends on the concentration of the polymer and the ionic strength³.

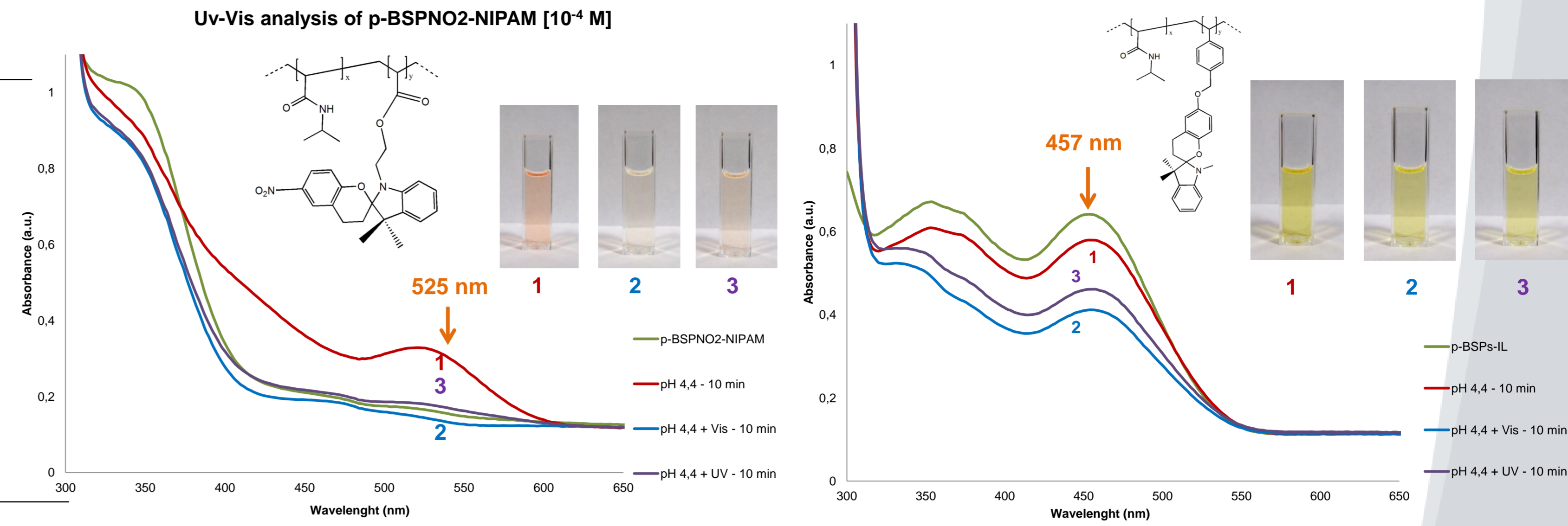
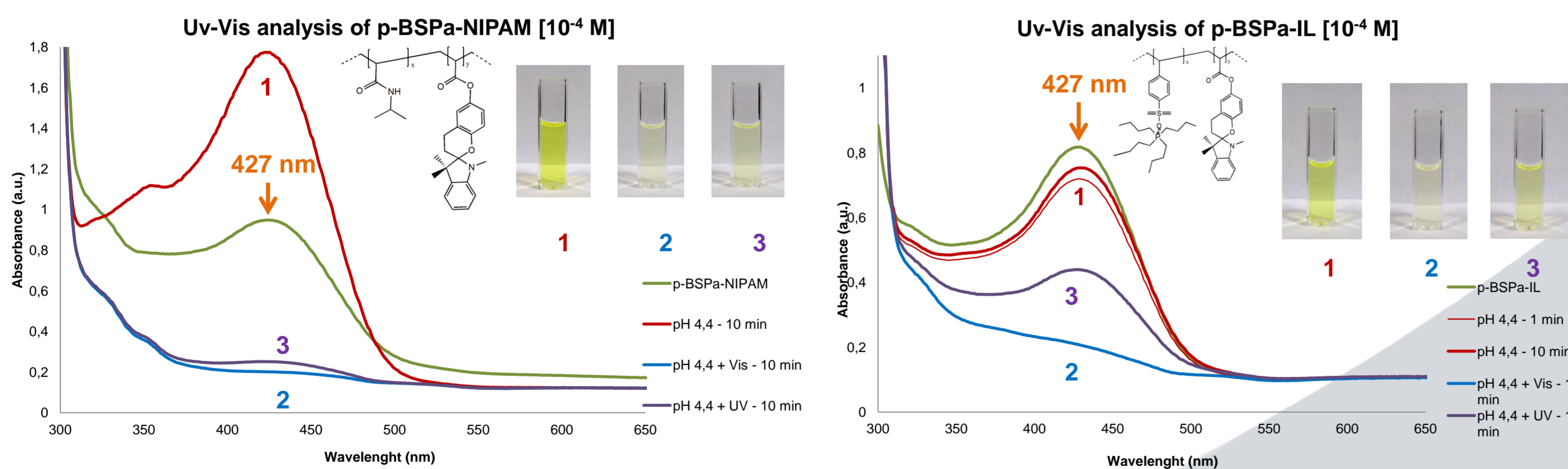
SYNTHESIS

Preparation of spiropyran monomers by addition of vinyl groups (nucleophilic substitution of chloride derivatives) and linear polymer to the UV-vis study:



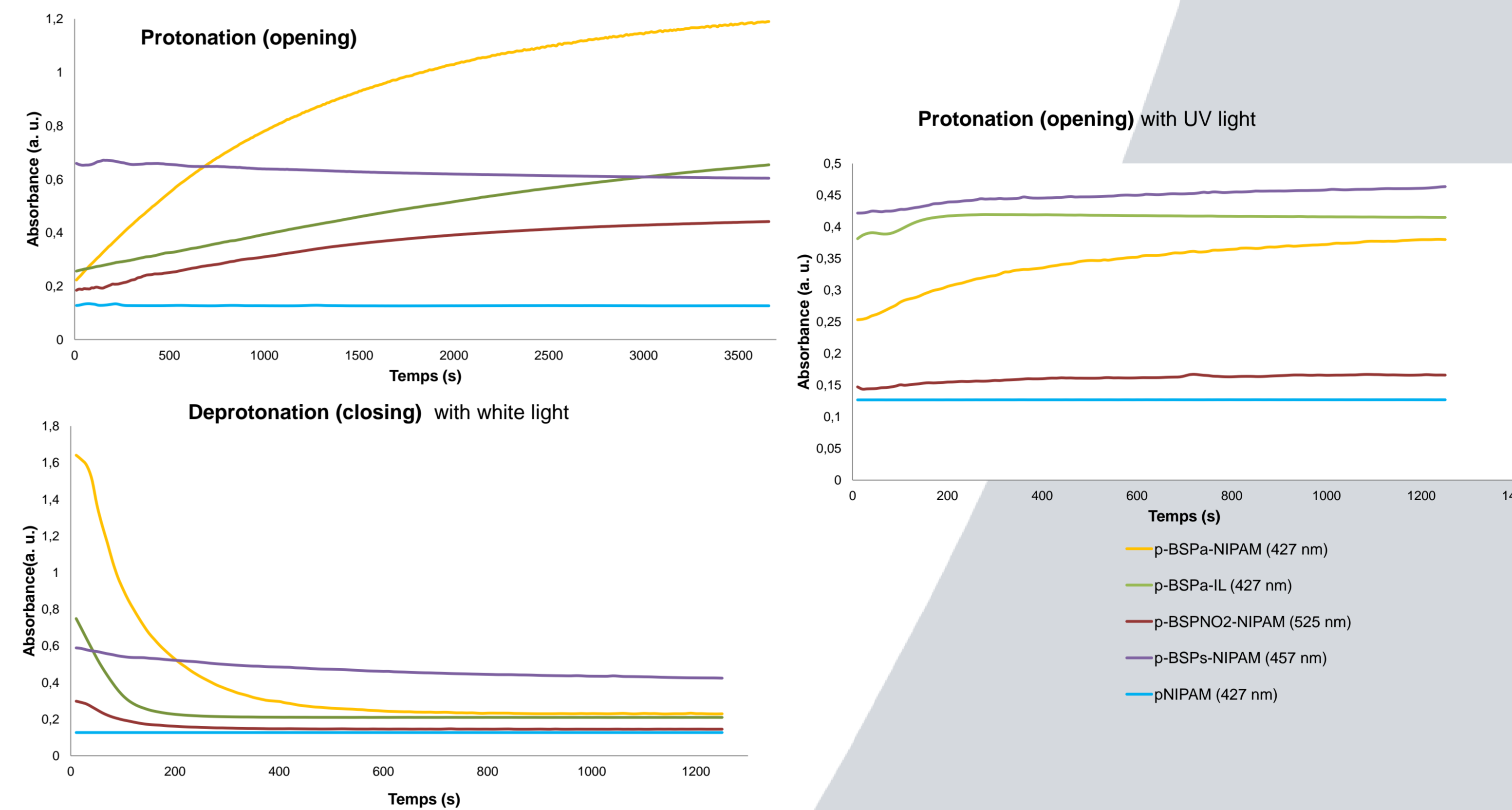
UV-Vis ANALYSIS

- UV-vis analysis of 10⁻⁴ M of spiropyran linear BSP copolymers:



- **p-BSP-co-NIPAM:** Increasing intensity at 427 nm after addition of acidic buffer solution that shows the switch from the Sp to the MCh form.
- **p-BSP-co-IL:** the addition of the acidic buffer solution did not give the same result because of the electrical environment of the spiropyran in the IL
- **p-BSPNO₂-co-NIPAM:** Increasing peak intensity at 525 nm with the acidic buffer solution and also a decrease between 300 and 400 nm because of the precipitation of the Sp
- **p-BSPs-co-NIPAM:** the addition of the buffer solution causes a decrease of absorbtion at 457 nm, the spiropyran is already protonated in aqueous solution

KINETIC STUDY



The opening and the closing of the spiropyran are first order kinetic⁴. Rate of each phenomenon has been found using an exponential model study:

	Protonation	Protonation (UV-light)	Deprotonation (White light)
	k (s ⁻¹)		
p-BSPa-NIPAM	7,28E-04	3,16E-03	8,59E-03
p-BSPa-IL	3,15E-04	2,01E-02	1,66E-02
p-BSPNO2-NIPAM	6,79E-04	4,59E-03	1,36E-02
p-BSPs-NIPAM	4,79E-04	3,18E-03	2,65E-03

First-order ring opening/closing rate

- p-BSPa-NIPAM has the fastest protonation in the dark
- p-BSPa-IL has a rate ten more important with UV-light than other sample ???
- p-BSPa-IL also has the fastest deprotonation rate with white light

CONCLUSION

- Synthesis of spiropyran derivatives and preparation of photo-responsive linear polymer possible
- Study of responses with UV and white light stimuli in buffer solution pH 4,4 shows reversible spiropyran opening-closing and protonation/deprotonation.
- Kinetic study of the protonation (opening) and deprotonation (closing) is an efficient way to compare our samples

REFERENCES

[1] T. Satoh, K. Sumaru, T. Takagi, et T. Kanamori, « Fast-reversible light-driven hydrogels consisting of spirobenzopyran-functionalized poly(N-isopropylacrylamide) », *Soft Matter*, vol. 7, n°. 18, p. 8030-8034, sept. 2011. [2] Szilágyi, K. Sumaru, S. Sugiura, T. Takagi, T. Shinbo, M. Zrínyi, et T. Kanamori, « Rewritable Microrelief Formation on Photoresponsive Hydrogel Layers », *Chem. Mater.*, vol. 19, n°. 11, p. 2730-2732, 2007. [3] Szilágyi, K. Sumaru, S. Sugiura, T. Takagi, T. Shinbo, M. Zrínyi, et T. Kanamori, « Rewritable Microrelief Formation on Photoresponsive Hydrogel Layers », *Chem. Mater.*, vol. 19, n°. 11, p. 2730-2732, 2007. [4] M. Zaroni, S. Coleman, K. J. Fraser, R. Byrne, K. Wagner, S. Gambhir, D. L. Officer, G. G. Wallace, et D. Diamond, « Physicochemical study of spiropyran-terthiophene derivatives: photochemistry and thermodynamics », *Phys Chem Chem Phys*, vol. 14, n°. 25, p. 9112-9120, 2012.

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