

Spiropyran based responsive polymers

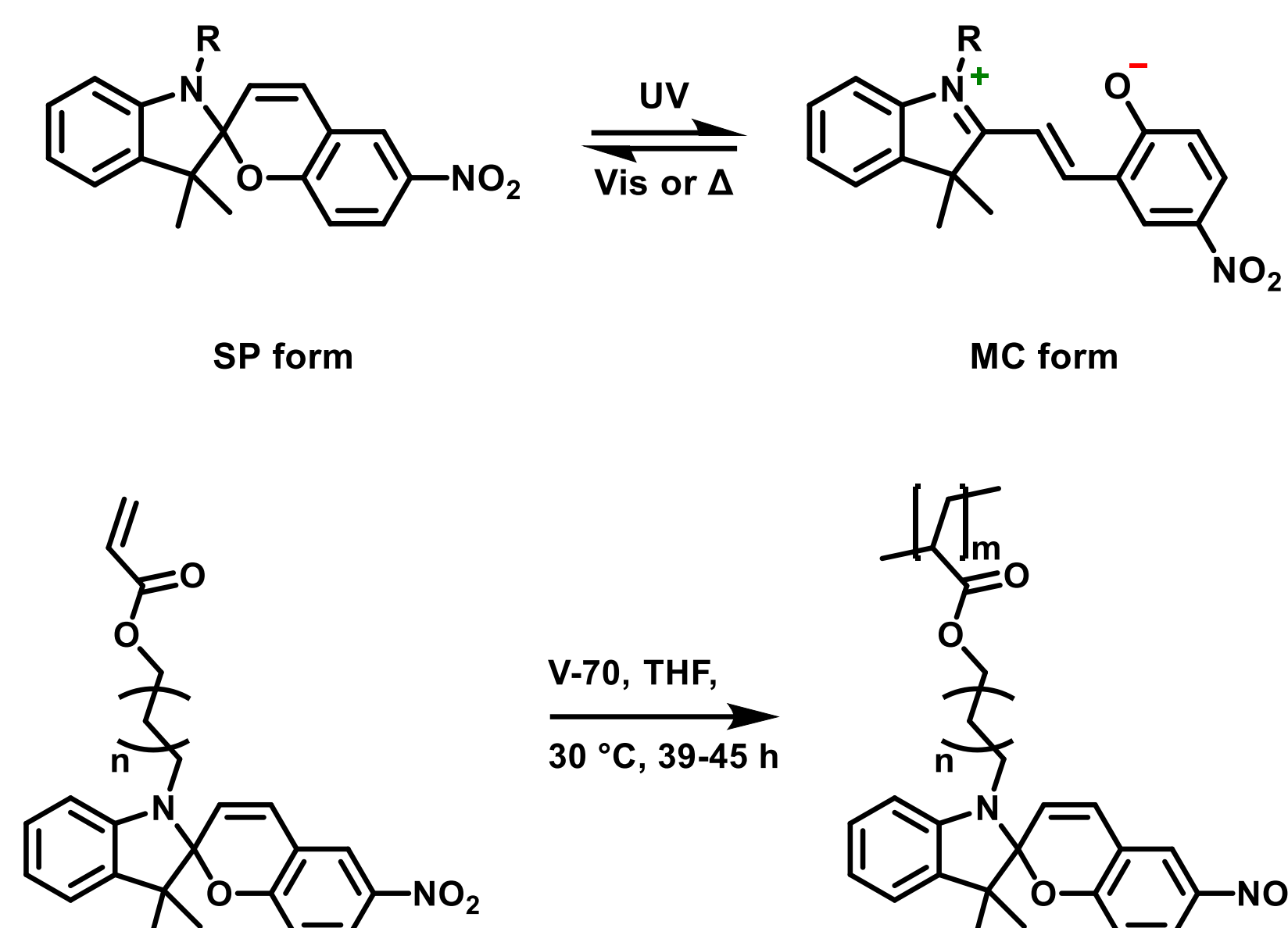
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1 Switchable spiropyran polymers

The production of smart materials responsive to external stimuli has gained increasing interest recently for its application in various fields. These materials for example include molecular switches in the main chain, side chain and crosslinks of polymer networks which are responsible for the responsiveness. With the use of responsive units such as spiropyran incorporated into materials, macroscopic properties can be altered through external stimuli. This work presents a design which incorporates a spiropyran (SP) derivative in the side chain of polymers recently published in literature.¹ Current research aims towards the effect of functionalized spiropyran side chain moieties on coating properties before and after switching to the merocyanine (MC) form.

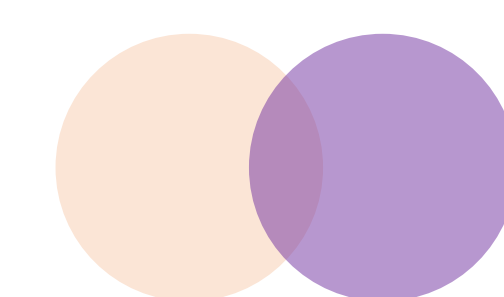
Literature¹



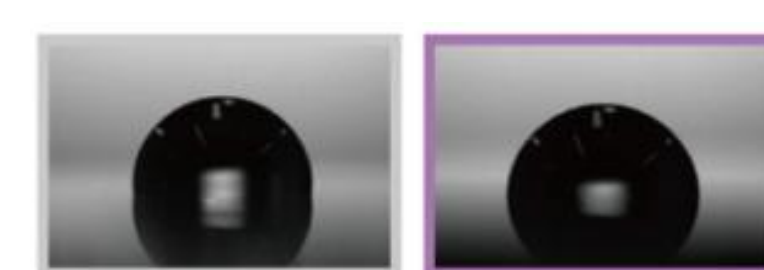
Change in:



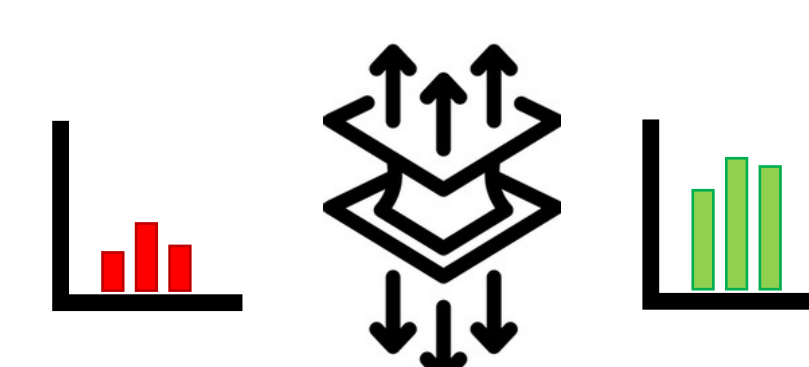
Color



Contact angle



Adhesion



2 Project goal

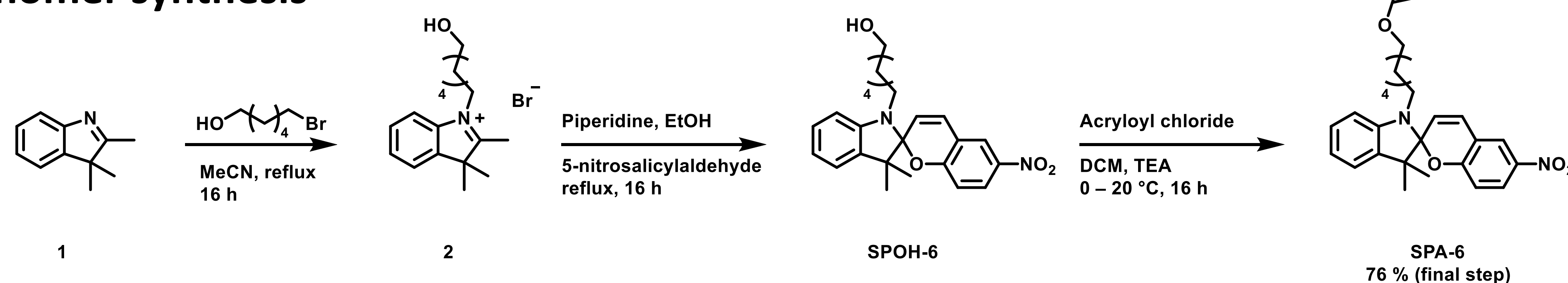


Switchable coating properties with
spiropyran based copolymers

Criteria:

- ❖ Observable change in macroscopic coating properties
- ❖ Minimal spiropyran loading in copolymers for feasibility in applications

3 Monomer synthesis¹



- ✓ Synthesized on gram scale
- ✓ Intermediate compound 2 used without further purification

4 Copolymerization and optical properties

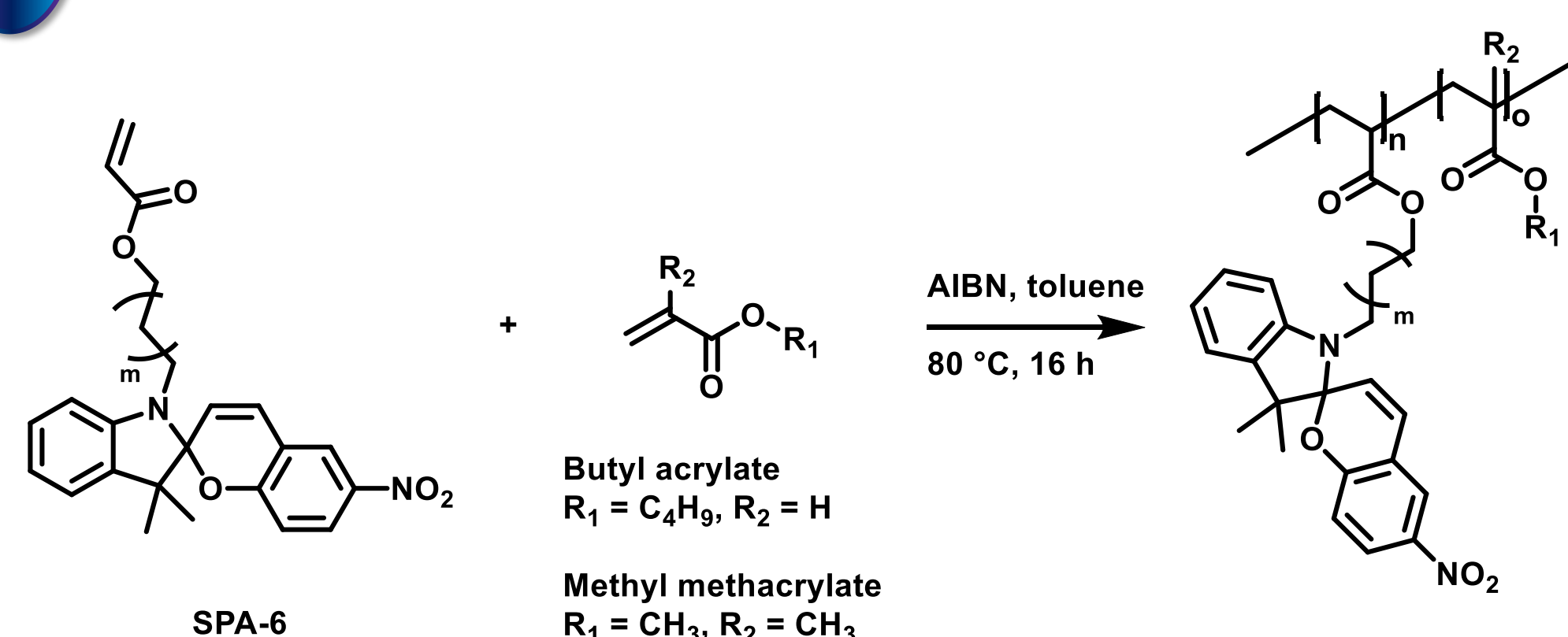


Figure 1. Copolymerization of SPA-6 with butyl acrylate or methyl methacrylate.

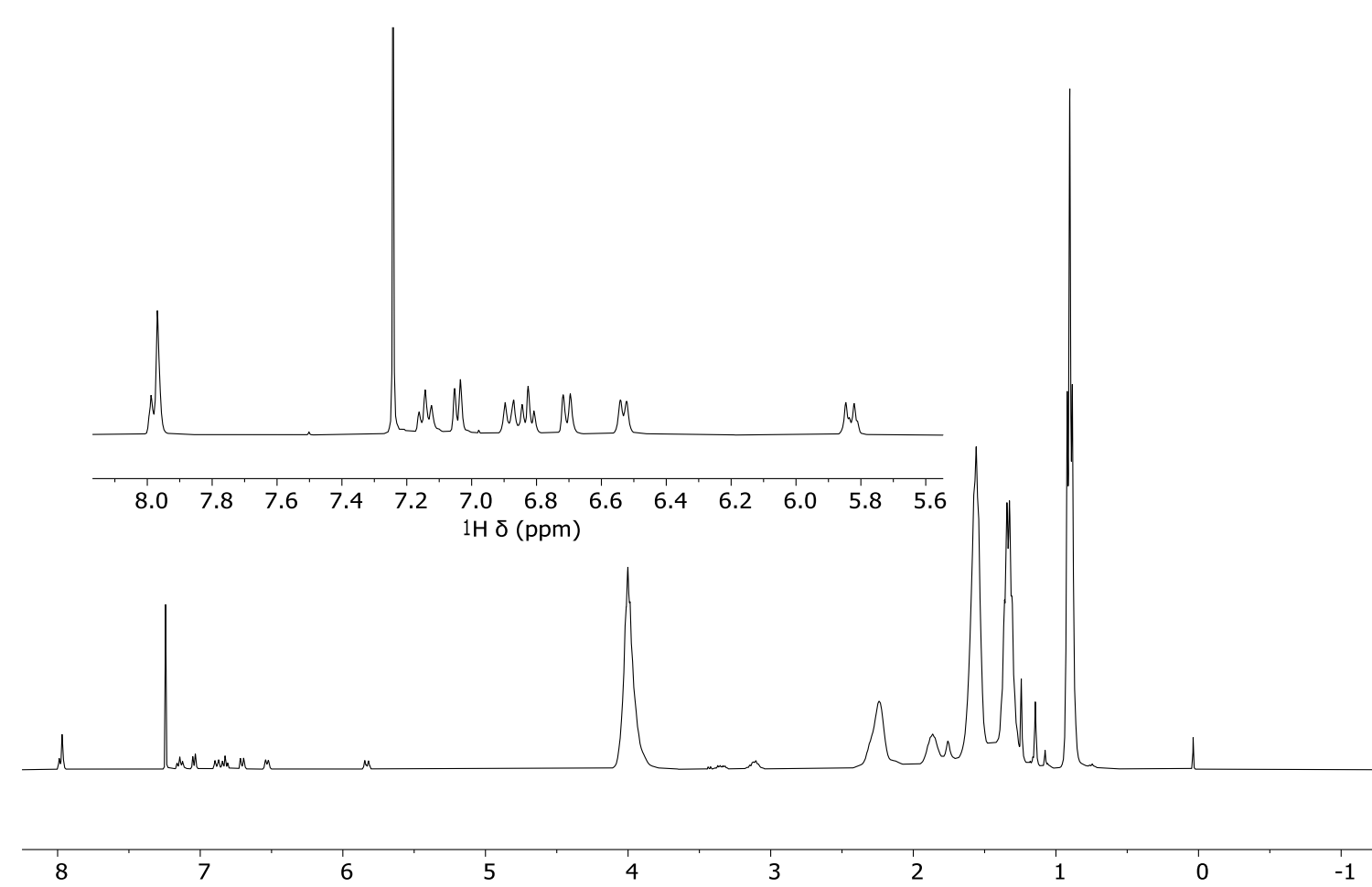


Figure 2. ¹H NMR of poly[(SPA-6)-co-(butyl acrylate)] after workup (400 MHz, chloroform-d).

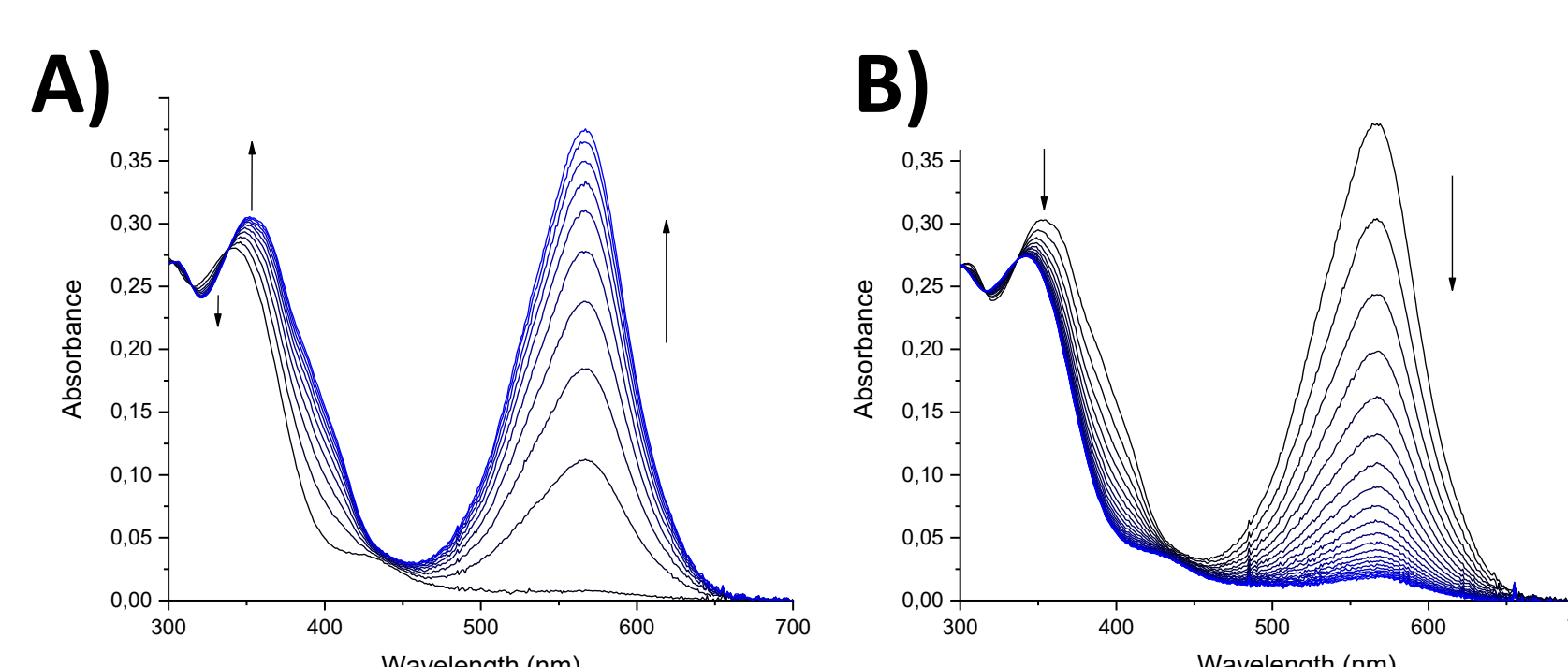


Figure 3. UV-Vis spectrum of 0.5 mg/mL poly[(SPA-6)-co-(butyl acrylate)] in MeCN upon irradiation with 365 nm for 225 s (A) and thermal relaxation in the dark over a time period of 1300 s (B). The black-blue gradients indicate $t_0 - t_{end}$ respectively.

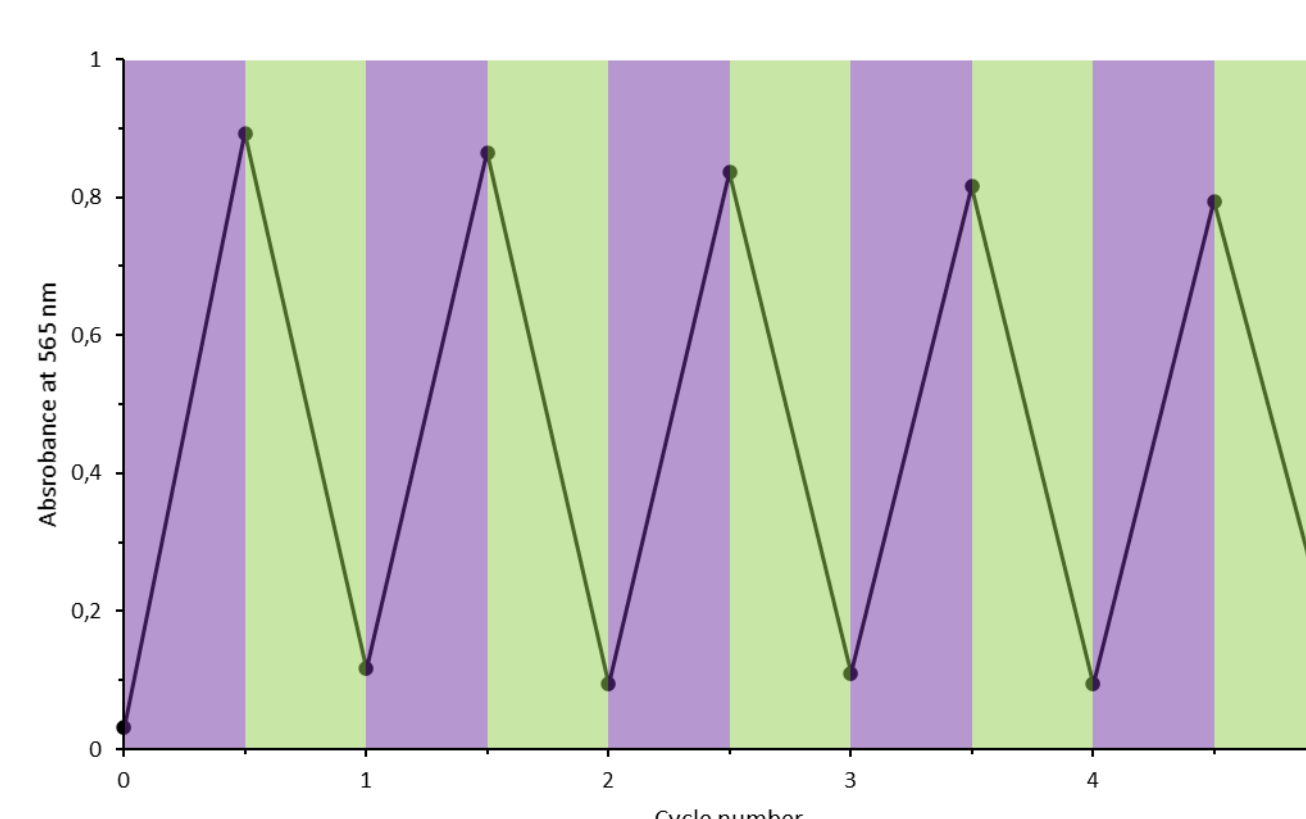


Figure 4. Repeated photoisomerization of 0.5 mg/mL poly[(SPA-6)-co-(butyl acrylate)] in MeCN with alternating irradiation of 365 nm for 600 s (purple area) and 535 nm for 600 s (green area).

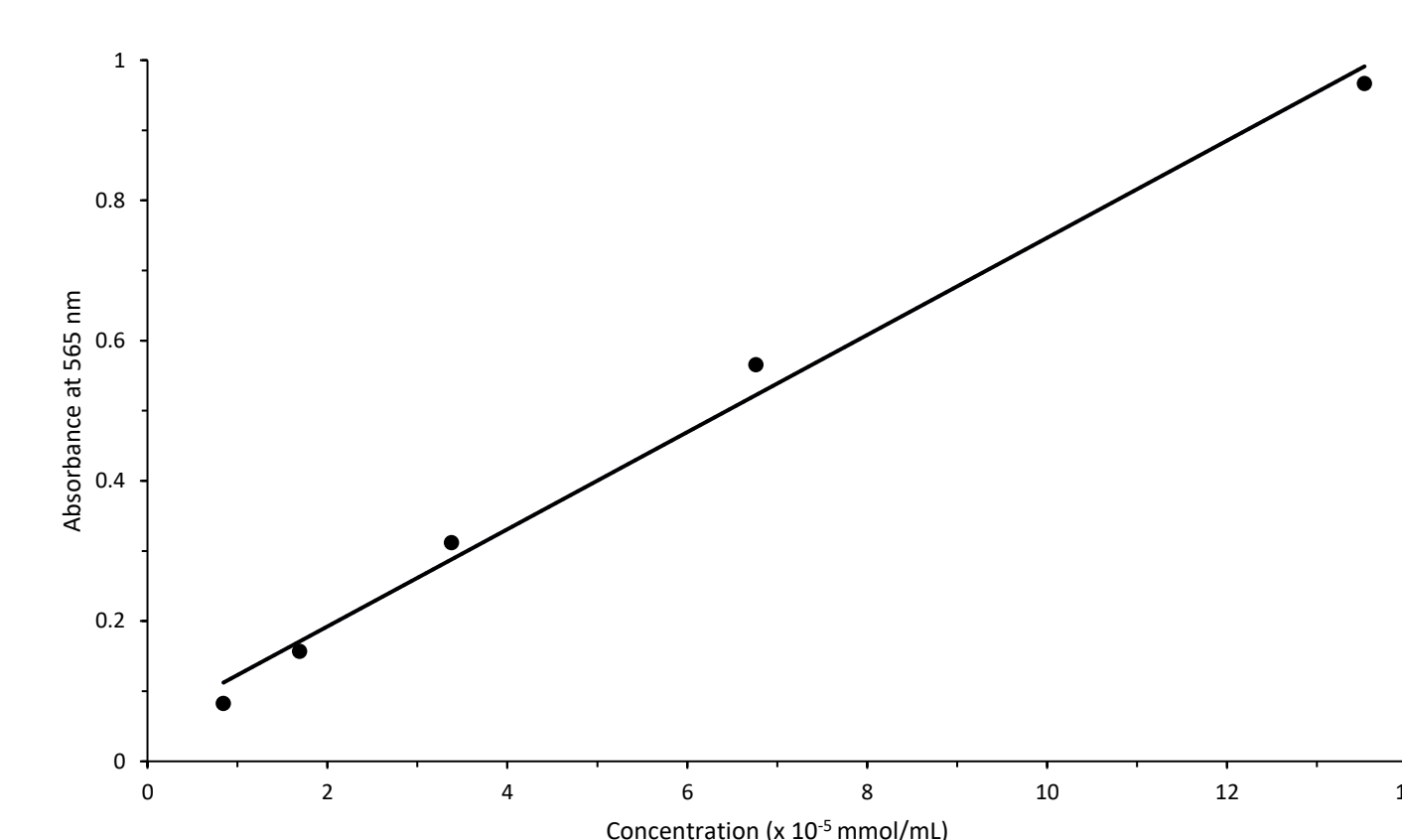


Figure 5. Calibration curve of solutions of SPA-6 irradiated to the photo stationary state (PSS) with 365 nm. The SP:BA ratio in poly[(SPA-6)-co-(butyl acrylate)] was determined to be 1 : 29 by irradiating a known concentration of polymer to the PSS and measuring the absorbance at 565 nm ($9.44 \pm 0.93 \cdot 10^3 \text{ cm}^{-1} \text{ M}^{-1}$). $y = 0.0693x + 0.0538$. $R^2 = 0.992$.

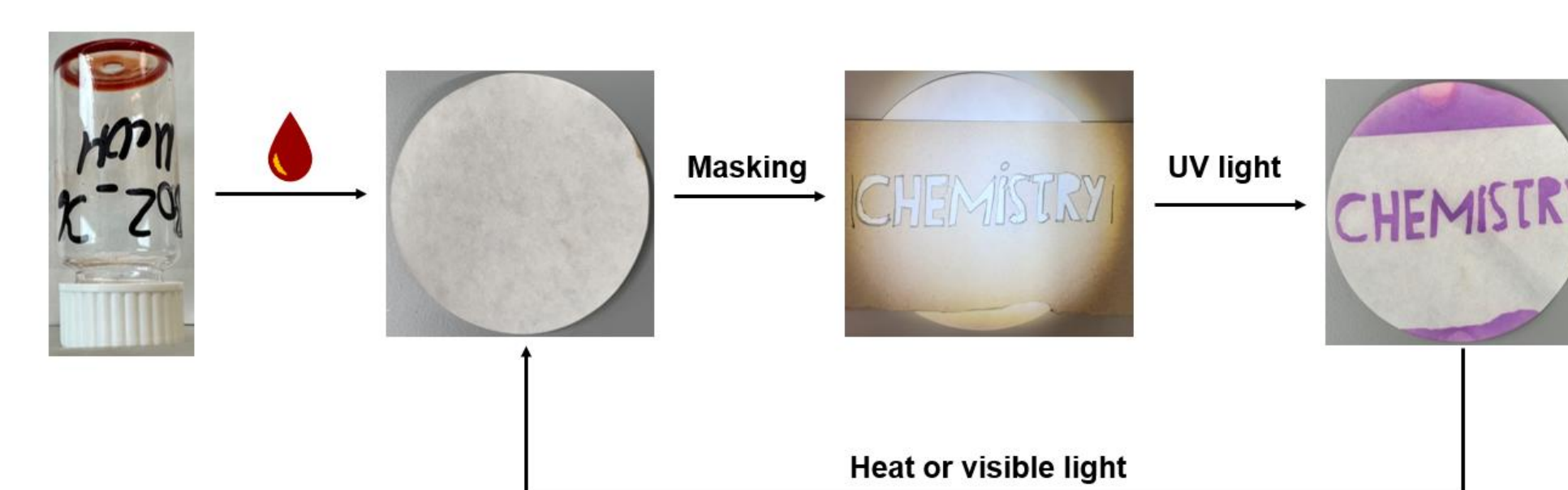


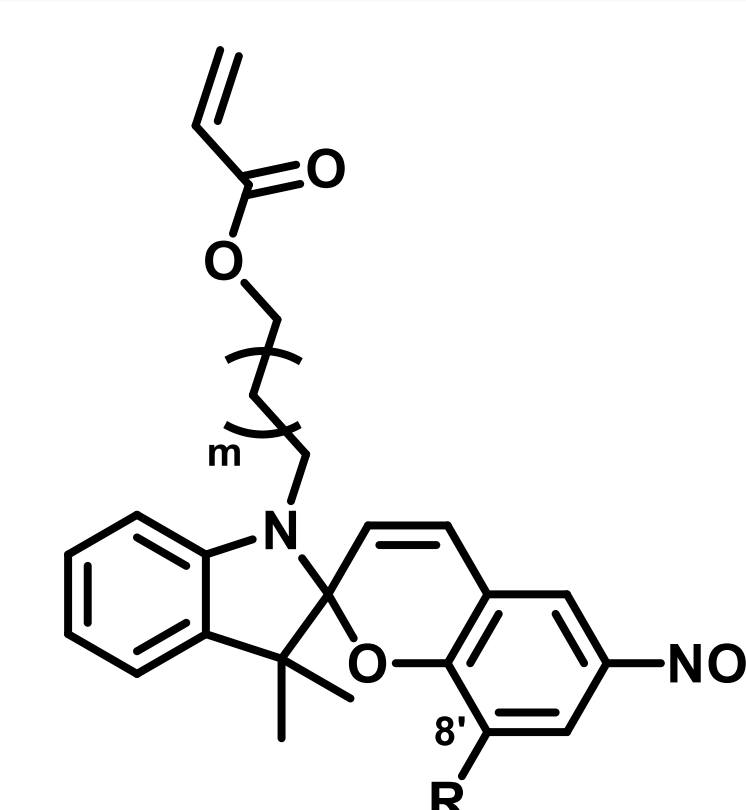
Figure 6. Photopatterning of poly[(SPA-6)-co-(butyl acrylate)] coated on filter paper.

5 Conclusion

A spiropyran functionalized acrylate was synthesized according to literature procedures and copolymerized with butyl acrylate (BA) and methyl methacrylate (MMA). The synthesized copolymers showed reversible changes in optical properties.

6 Outlook

Further research will focus on synthesizing spiropyran acrylates with various functional groups on the 8' position in which the effects of these functional groups on coating properties are of main interest.



References

1. *Chem. Mater.* **2022**, 34 (18), 8289-8296.

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Confidential information



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