Master of Science HES-SO in Life Sciences

Photo-degradable polymers for temporary coatings

Michelangelo Maccanelli

CHEMICAL DEVELOPMENT & PRODUCTION

HEIA-FR

Advisor: Prof. Dr. O. Mamula Steiner & Drs R. Hofmann (Psinex AG)

DESCRIPTION

A protective film that is easy to remove without damaging the initially protected layer is a growing demand in the manufacturing industry. Currently, this process is performed by means of a thermal polymerisation process and then removed manually by stripping. Such processes are inefficient both economically and technically, as automation is impossible, resulting in a lack of precision. Photo-reversible or photo-degradable polymers can play a key role in meeting this demand, thanks to their photo-cycloaddition [2p+2p] mechanism[1], whereby under the influence of a light stimulus, they allow a covalent bond to be formed or cleaved. This process involves first depositing the monomer material, which is then polymerised by photo-reversible polymerisation at a wavelength of λ_1. The parts not protected by the polymerised film can then be modified. Subsequently, the protective film can be photodepolymerised by exposure to a more energetic λ_2 light ($\lambda_2 < \lambda_1$), resulting in softening and removal simply by washing with solvent (Figure 1).

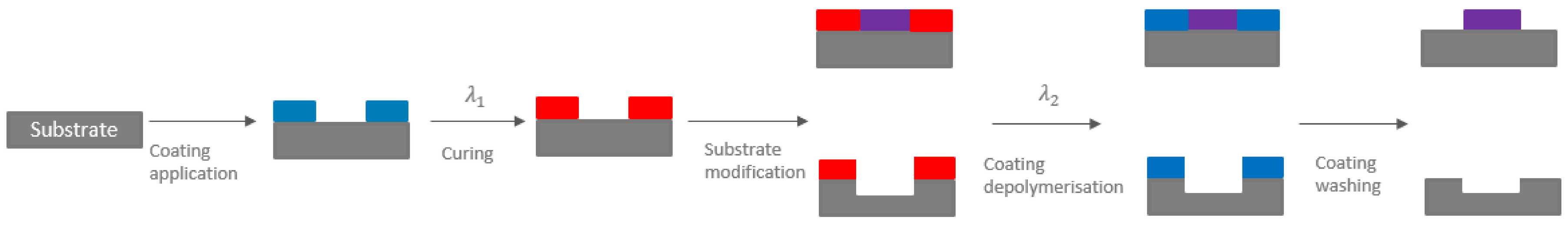


Figure 1 : Illustration of the concept of photo-reversible protective coating

Research has been conducted on these photoreversible polymers, finding four very promising systems using thymine or coumarin as photoresponsive elements (Figure 2).The photopolymerisation and photodepolymerisation reactions will be studied under a variety of conditions, using a multi-wavelength device based on a Psinex AG instrument.

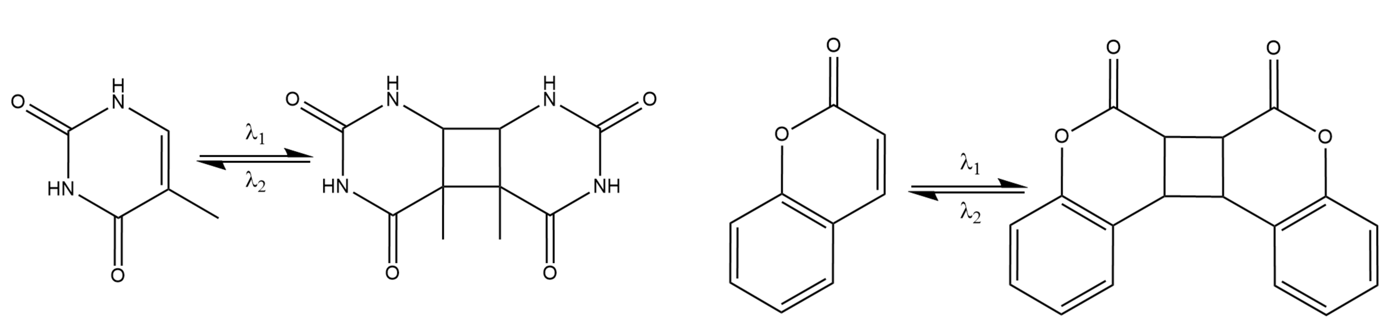
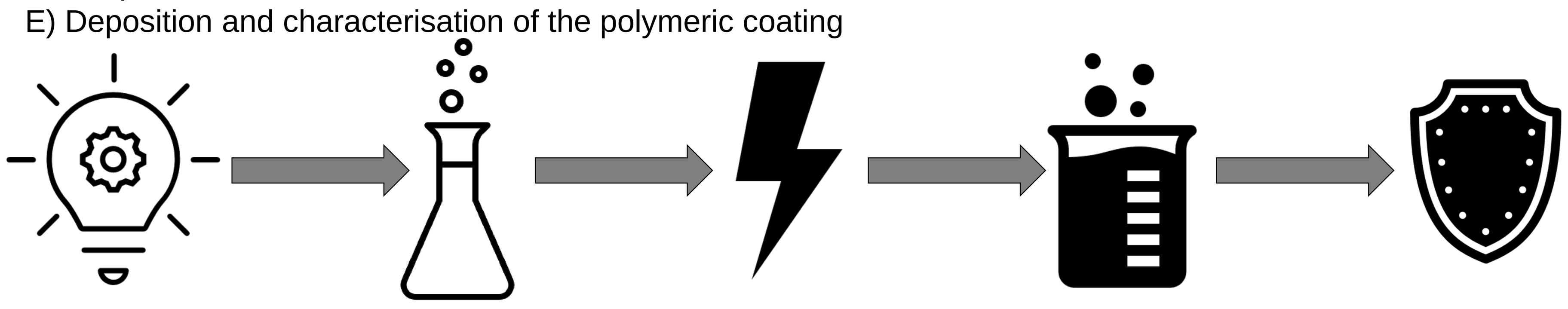


Figure 2 : Illustration of the [2p+2p] cycloaddition of thymine (left) and coumarin (right)

OBJECTIFS

A) Construction of a multi-wavelength device and determination of the emission parameters for the various wavelengths emitters (diodes)
B) Synthesis of the monomers /oligomers
C) Perform polymerisation / depolymerisation tests and determine the best system
D) Perform preliminary resins formulations and their coating properties in collaboration with our partners.
E) Deposition and characterisation of the polymeric coating



A) B) C) D) E)

[1] Sicignano *et al.*, Eur. J. Org. Chem., 2021, 2, 3303-3321
[2] Saito *et al.* , Chem. Sci. 2012, 3, 2301-2306
[3] Chimichi *et al.* , Tetrahedron 2002, 58, 4851
[4] Love *et al.*, Macromol Chem Phys, 2004, 205, 715-723
[5] Joy *et al.*, Macromolecules, 2013, 46, 13, 5133-5140
[6] Sumerlin *et al.*, ACS Appl. Mater. Interfaces 2018, 10, 19, 16793–16801

RESULTS

Multi-wavelength emission device – Artemisia

The multi-wavelength emission device, called Artemisia, features 6 LEDs with different wavelengths that are mounted in duplicate. The system is equipped with an air cooling system for the electrical components and a liquid cooling systems for the samples.

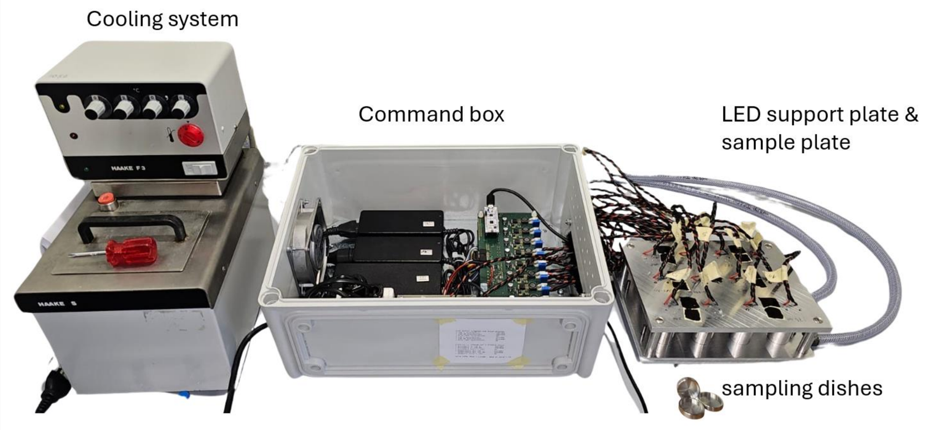
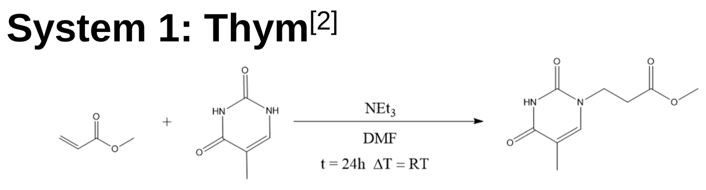


Figure 3 : Set up of the multi-wavelength device Artemisia

Table 1 : LED emission parameters

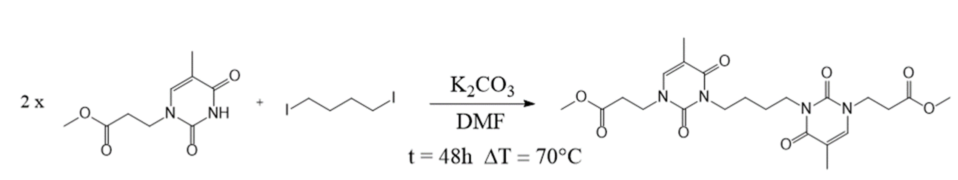
LED wavelength [nm]	Measured wavelength [nm]	Power density [mW/cm2]
275	277	3.48
310	313	0.05
365	367	226.74
365-370	368	128.70
385	381	54.57
405	407	36.30

System 1: Thym[2]



Scheme 1 : First step of the synthesis and results

Sample	Yield	Purity
Thy-01-01	94%	96%
Thy-01-02	97%	98%

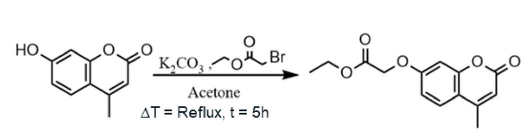


Scheme 2 : Second step of the synthesis and results

Sample	Yield	Purity
Thy-02-01	4%[a]	95%
Thy-02-02	8%[a]	91%
Thy-02-03	40%[b]	95%

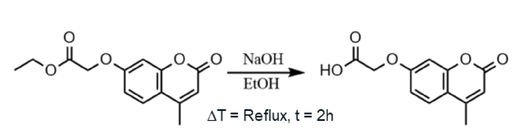
[a]Reaction carried out with DMF; [b] Reaction carried out with dry DMF (0.05%$_{wt}$ H_2O) in Schlenk line

System 2: CoumSilox [3-4]



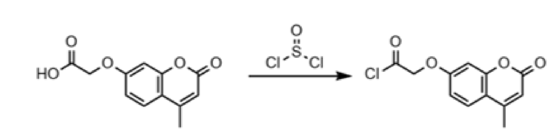
Scheme 3: First step and results

Sample	Yield	Masse [g]	Purity
Csil-01-01	72%	1.80	99%
Csil-01-02	96%	0.91	98%
Csil-01-03	91%	15.90	95%



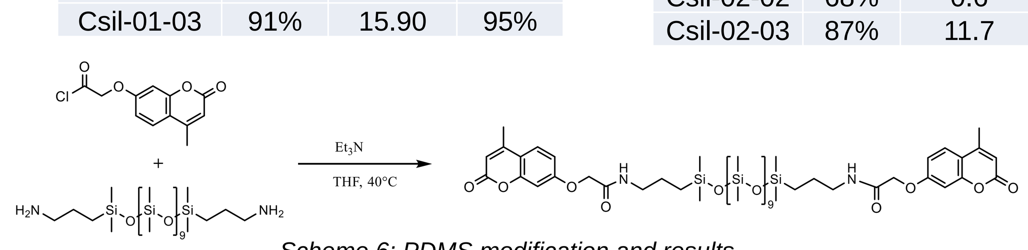
Scheme 4 : Second step and results

Sample	Yield	Masse [g]	Purity
Csil-02-01	64%	0.86	100%
Csil-02-02	68%	0.6	72%
Csil-02-03	87%	11.7	94%



Scheme 5 : Third step and results

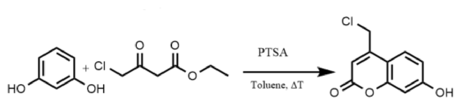
Sample	Yield	Purity	Masse [g]
Csil-03-03	100%	92%	1.97
Csil-03-04	100%	86%	2.04



Scheme 6: PDMS modification and results

Sample	Yield	Masse
Csil-04-01	24%	0.278 g
Csil-04-02	53%	0.597 g
Csil-04-03	76%	1.169 g
Csil-04-04	85%	2.761 g

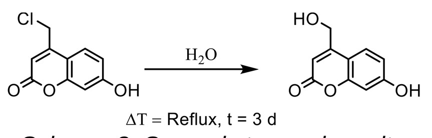
System 3: CoumEster [5].



Scheme 7: First step and results

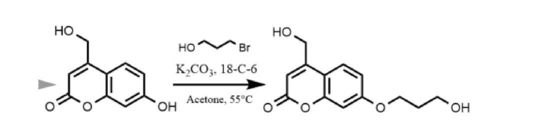
Sample	Yield	Purity	M [g]
Cest-01-01	58%[a]	>95%	7.71
Cest-01-03	53%[b]	>95%	4.20

[a] Theoretical value since purification was carried out on a portion of the raw product (from 69% of the raw product was obtained 7.71g)
[b] Purification carried out using CombiFlash



Scheme 8: Second step and results

Sample	Yield	M [g]
Cest-02-01	84%	4.2g (99%)
Cest-02-02	85%	1.95g (99%)
Cest-02-03	84%	3.08g (99%)

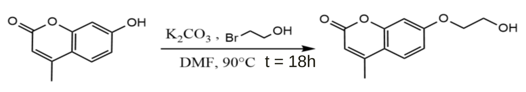


Scheme 9: Third step and results

Sample	Yield	Masse [mg]	Reaction parameters
Cest-03-06	27%	272	Filling half volume, P = 1 bar
Cest-03-10	39%	399	Filling half volume, T = 95°C
Cest-03-11	48%	484	Filling half volume, T = 90°C
Cest-03-12	36%	370	Filling half volume, T = 80°C

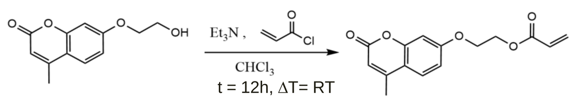
System 4: CoumGel[6].

Scheme 10: First step



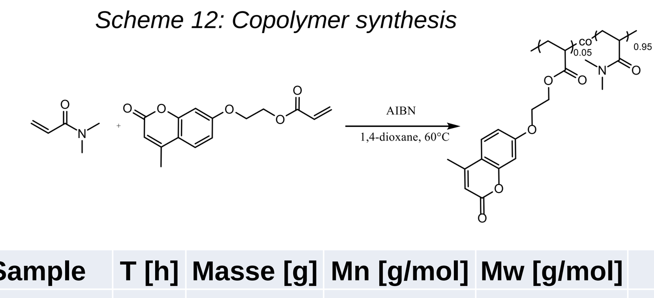
Sample	Yield	Masse	Purity
Cgel-01-01	83%	7.47	78%
Cgel-01-02	80%	31.26	93%

Scheme 11: Second step

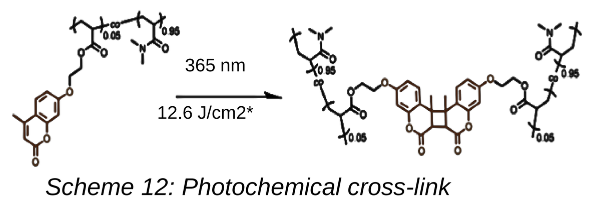


Sample	Yield	Masse	Purity
Cgel-02-01	81%	2.85	67%
Cgel-02-02	30%	6.83	70%

Scheme 12: Copolymer synthesis



Sample	T [h]	Masse [g]	Mn [g/mol]	Mw [g/mol]	D
CGel-03-09	4	5.227	34000	101000	2.98

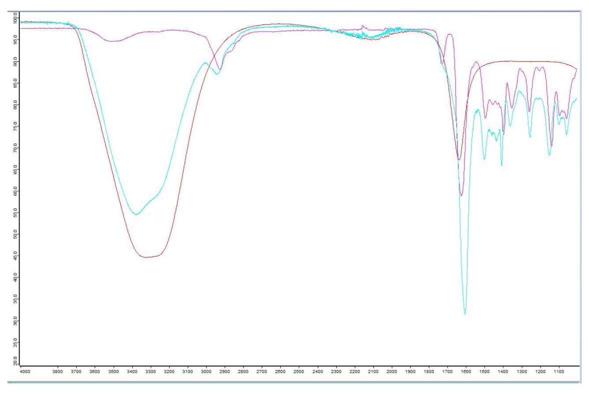


Scheme 12: Photochemical cross-link

Sample	M sol. [mg][a]	Wavelength [nm]	time [min]	Energy [J/cm2]
Cgel-05-01.01	245.6	365	0.93	11.98
Cgel-05-01.02	243.1	365	5.00	71.61
Cgel-05-02.01	243.3	365-370	1.63	12.29
Cgel-05-02.02	233.1	365-370	8.17	64.55
Cgel-05-03.01	237	385	3.85	12.05
Cgel-05-03.02	238.8	385	19.25	65.78
Cgel-05-03.03	239.4	385	39.25	122.87

[a] Solution 10wt% in dem. water

Table 12 : Result of the of the photochemical cross-link Water (red), starting copolymer P(Coum-co-DMA) (pink) and cross-linked copolymer (blue)



CONCLUSION

From the preliminary results obtained so far, producing a reversible light-cured protective film for the manufacturing industry is possible. The first tests are indicating that the CoumGel system seems to be the most promising because the starting copolymer is water-soluble, opening the possibility to formulate an environmentally friendly, printable ink. Moreover, the photo-device built during this project (Artemisia) is very versatile. In fact, the LEDs can be easily replaced with different ones possessing other emission wavelengths and powers, adapted to other chemical systems showing the photo - polymerisation / depolymerisation behaviour.

Hes·so Haute Ecole Spécialisée de Suisse occidentale
Fachhochschule Westschweiz
University of Applied Sciences and Arts Western Switzerland

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