

Willkommen  
Welcome  
Bienvenue



# DiPrintProtect - Digitally printed temporary protective films for application in the watch industry

Annual Review Meeting 2022

# Motivation

## ASRH

RECHERCHE HORLOGERE COMMUNAUTAIRE  
Swiss Association for Horological Research

- Manual process



A – Masking of selected areas for mechanical processing

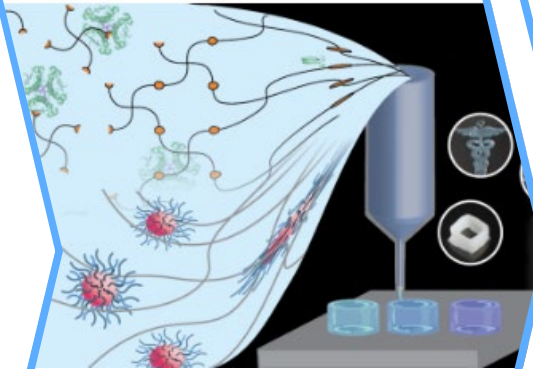
B – Protection of finished watch parts for storage purposes

C – Protection of a complete watch for manipulation in the boutique

[www.metalem.ch](http://www.metalem.ch)

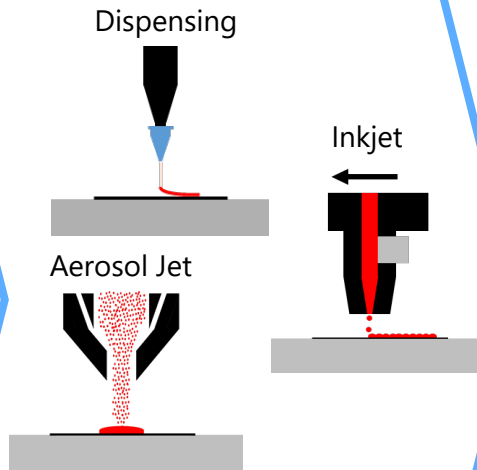
# DiPrintProtect - Overview

## Photochemistry



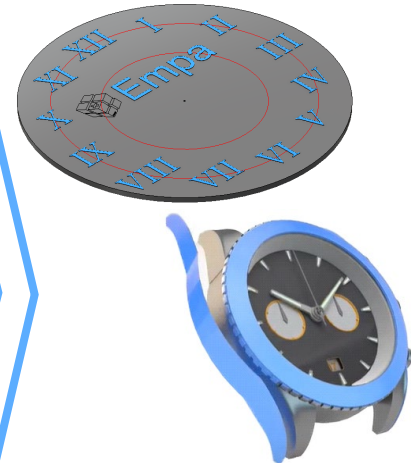
- Photocurable and photo-reversible polymers and resins
- Sacrificial layers for coating

## Digital printing



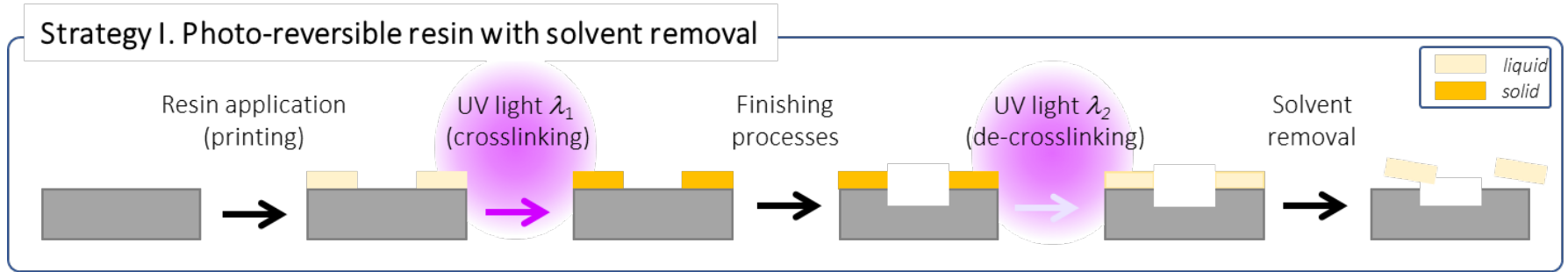
- Process automation
- Fine features down to 10  $\mu\text{m}$

## Demonstrators



- Temporary protective coatings
- Peelable films

# Approach

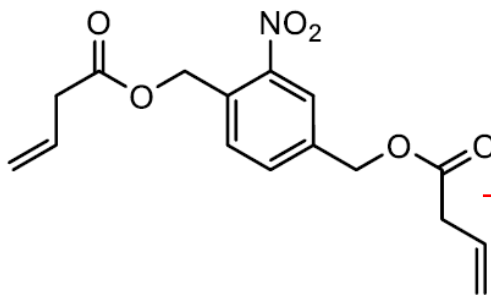




Prof. Dr. Mark Tibbitt    Morris Wolf

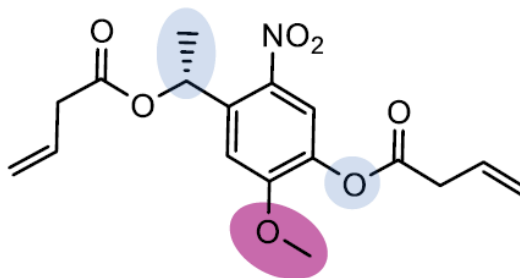


- First crosslinker (based on Radl et al. 2015)



→ No cleavage was observed in reasonable time frames

- New crosslinker in development



Added methoxy group could

- red-shift absorption
- increase quantum yield
- stabilize cleaving



Prof. Dr. Mark Tibbitt  
Morris Wolf

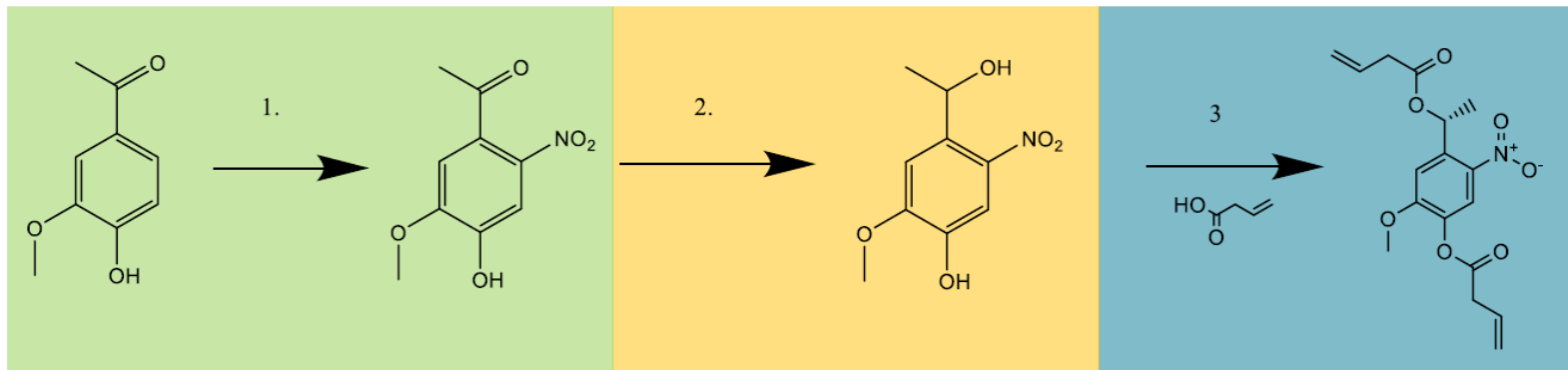


## New Crosslinker – Reaction Path

Successful

Troubleshooting

To be tried



**Nitration of Acetovanilone:**  
Potassium nitrate, acetic acid  
at 60°C overnight

**Reduction of Ketone:**  
Sodium borohydride in  
Ethanol, at RT overnight  
under Argon

**Coupling of functional ends:**  
3-Butenoic acid with DCC and  
DMAP in DCM at RT for 2h

# Traceless removal (EPFL)



Dr. Yves Leterrier



Alper Balkan

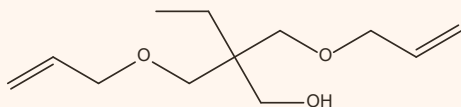
**EPFL**

**LPAC**

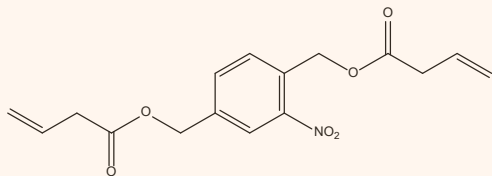
Laboratory for Processing of Advanced Composites

## Ene monomers

TMPDE

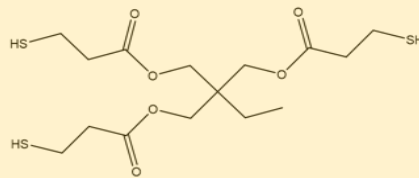


ONB diallyl ester

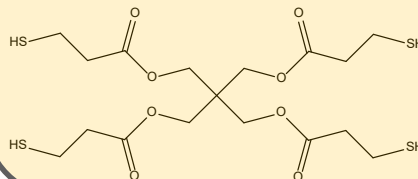


## Thiol monomers

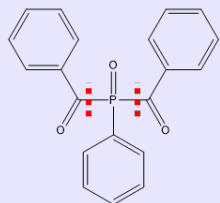
TMPTMP



PETMP

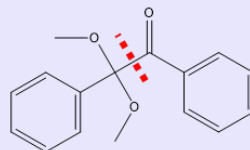


## Photoinitiators



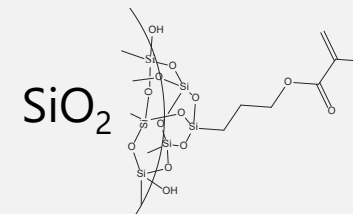
VIS: BAPO  
(Irgacure 819)

UV: DMPA  
(Irgacure 651)

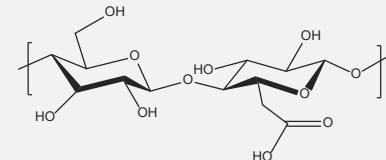


## Nanofillers

Methacrylated silica: AerosilR7200



TEMPO-oxidized cellulose nanofibrils (TOCNF)



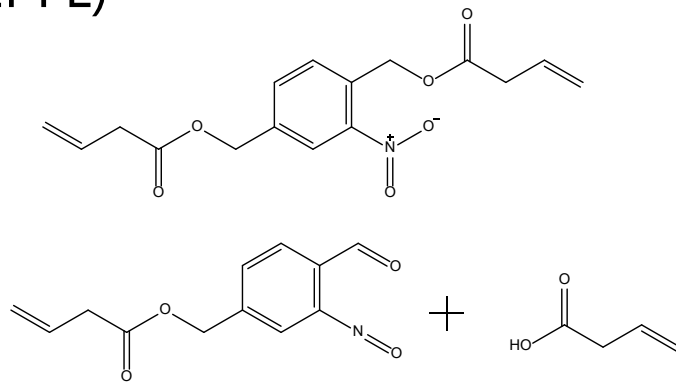
# Traceless removal (EPFL)



Dr. Yves Leterrier



Alper Balkan

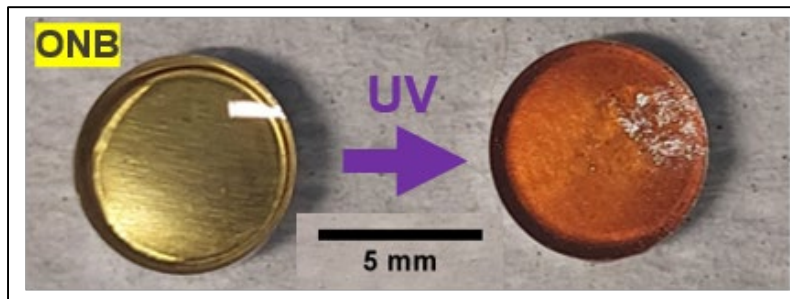


S. V. Radl et al., *Polym. Chem.*, 8 (2017) 1562–1572.

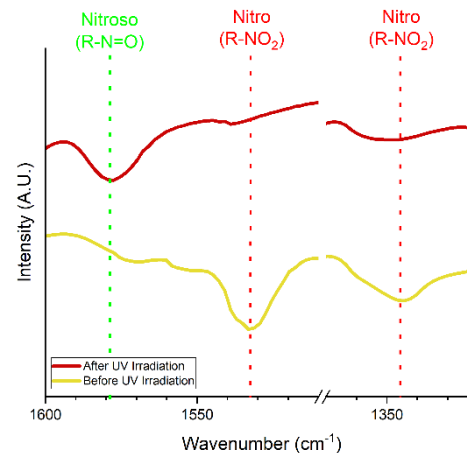
**EPFL**

**LPAC**

Laboratory for Processing  
of Advanced Composites



**Gelation on surface:** 1) Radicals from cleavage  
2) Photoinitiator less polym.





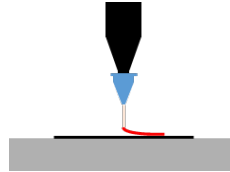
# Printing/coating methods

Technical specifications

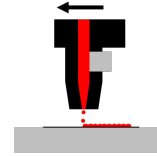
## Spray coating



## Dispensing



## Inkjet printing



## Aerosol Jet



Min. linewidth	Large areas	40 $\mu\text{m}$	40 $\mu\text{m}$	25 $\mu\text{m}$
Thickness (app.)	1 – 500 $\mu\text{m}$	3 $\mu\text{m}$ – 60 mm	3 – 6 $\mu\text{m}$	4 – 50 $\mu\text{m}$
Lacquer viscosity	< 50 cP	1...100'000 cP	8 – 12 cP	< 10 – 500 cP
Substrate shape	flat	curved	flat	any
Nr of motion axes	3	2	2	5

Equipment images



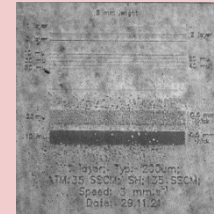
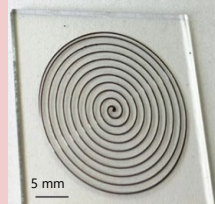
# Printability vs printing technique

Lacquer /  
photopolymer

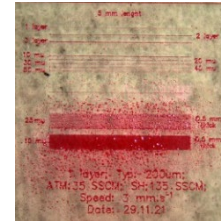
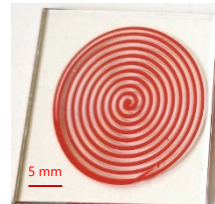
Dispensing

Aerosol Jet

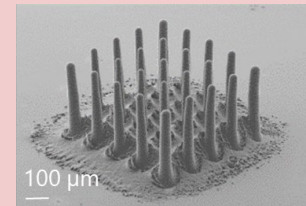
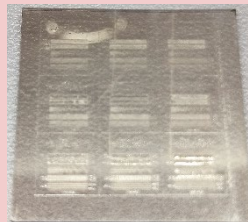
Bitumen (Berlac)



BerlacrylRed (Berlac)



Aryl epoxy  
photopolymer

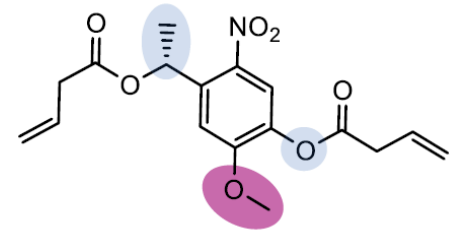


# Summary

## ETHZ-ME

- Two crosslinkers studied (vinyl-and epoxy-NBE),
- No photocleavage observed in reasonable timeframe in 235 nm and 365 nm UV irradiation.

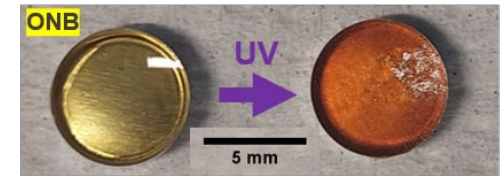
*Outlook: new photochemistry under investigation*



## EPFL – LPAC

- Non-cleavable resins, surface-modified nanosilica, nanocellulose fibers and crystals were formulated, photocured and analyzed via thermal and mechanical methods.
- Spray and spin coating techniques explored with composite resins.

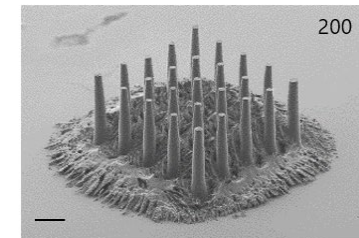
*Outlook: Photo-reversible rheology characterization setup is in development.*



## EMPA – TFPV-FP

- Three different digital printing techniques (aerosol jet, inkjet, and pneumatic dispensing) were explored.
- In house developed photopolymer and commercial lacquers were printable.
- Aerosol jet of aryl epoxy photoresin was realized, obtaining linewidth resolution of 25  $\mu\text{m}$ , however, satellite droplets could not be avoided.

*Outlook: first demonstrators to be prepared.*



DiPrintProtect

Digitally printed temporary protective films for application in the watch industry



**ETH** zürich



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RECHERCHE HORLOGERE COMMUNAUTAIRE

Thank you for  
your attention