

Willkommen
Welcome
Bienvenue



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

Annual Review Meeting 2024

Empa: Vitor Vlnieska, Jakob Heier, Yaroslav Romanyuk

ETHZ: Mark Tibbit, Morris Wolf

EPFL: Yves Letterier, Alper Balkan

Motivation: Industry needs

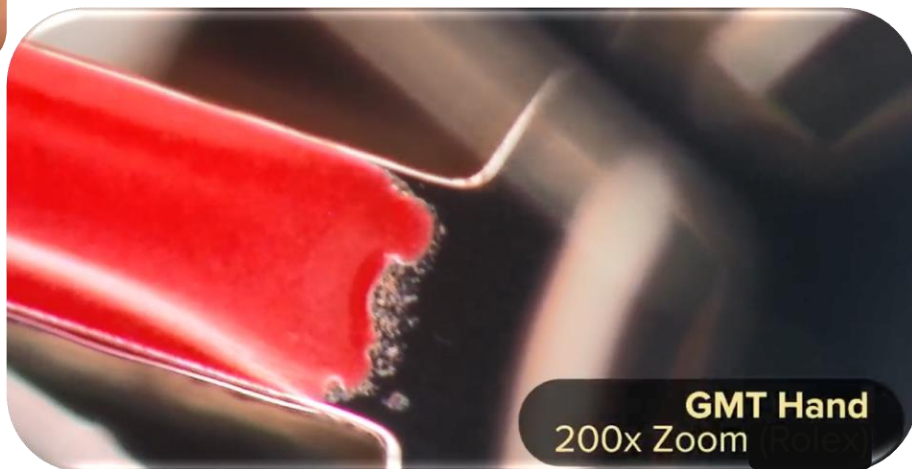
ASRH

RECHERCHE HORLOGERE COMMUNAUTAIRE
Swiss Association for Horological Research

Replace manual coating



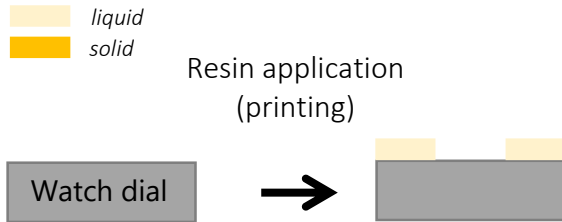
Increase coating precision



Challenges

■ How to print photopolymers?

■ How to remove (non-contact)?



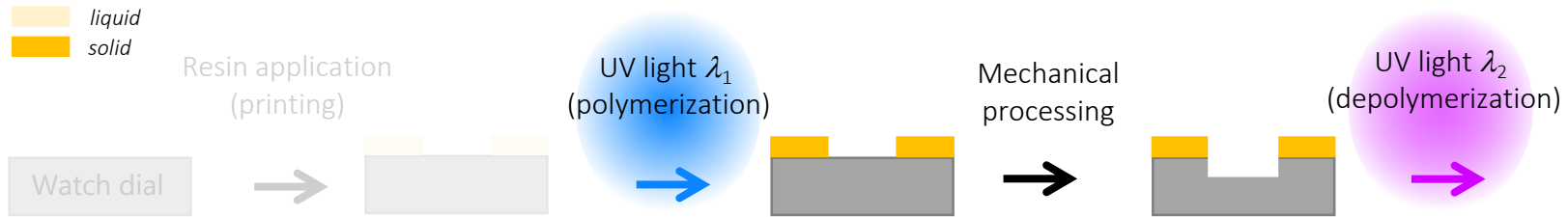
1. Digital printing:

- *High resolution, precision, and throughput*
- *Maskless printing*

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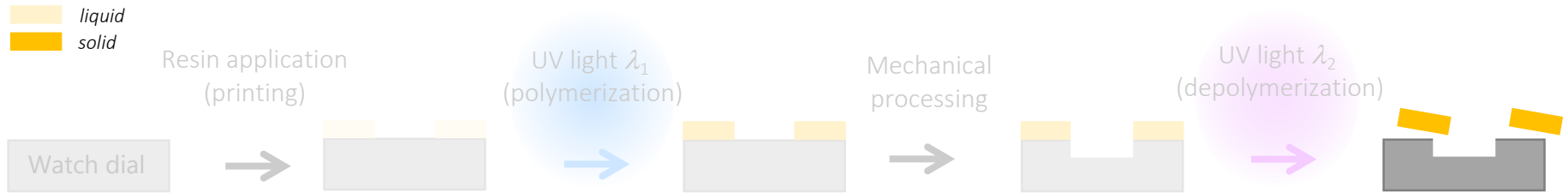
2. Photo-reversible polymers as inks:

- Polymerization for hardening and adhesion
- Depolymerization for peeling of

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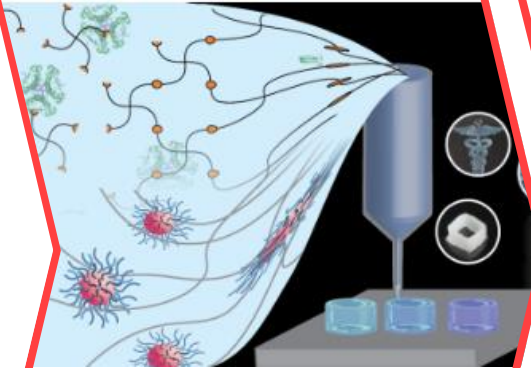
- Polymerization for hardening and adhesion
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3. Non-contact removal:

- Thermal release
- Flash lamp annealing

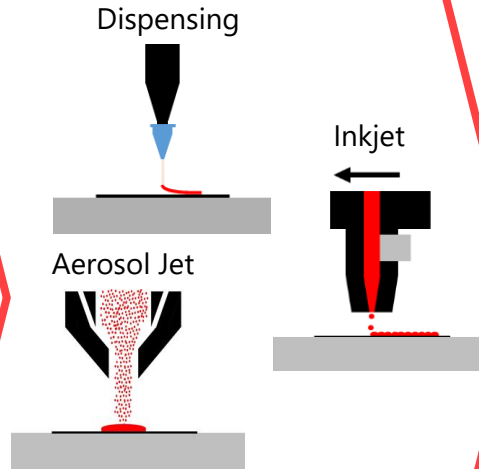
DiPrintProtect - Overview

Photopolymers



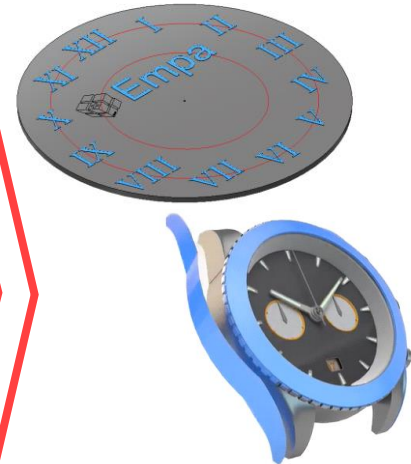
- Photocurable and photo-reversible polymers and resins
- Sacrificial layers for coating

Digital printing



- Process automation
- Fine features down to 10 μm

Demonstrators



- Temporary protective coatings
- Peelable films

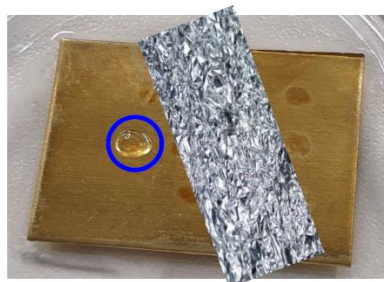
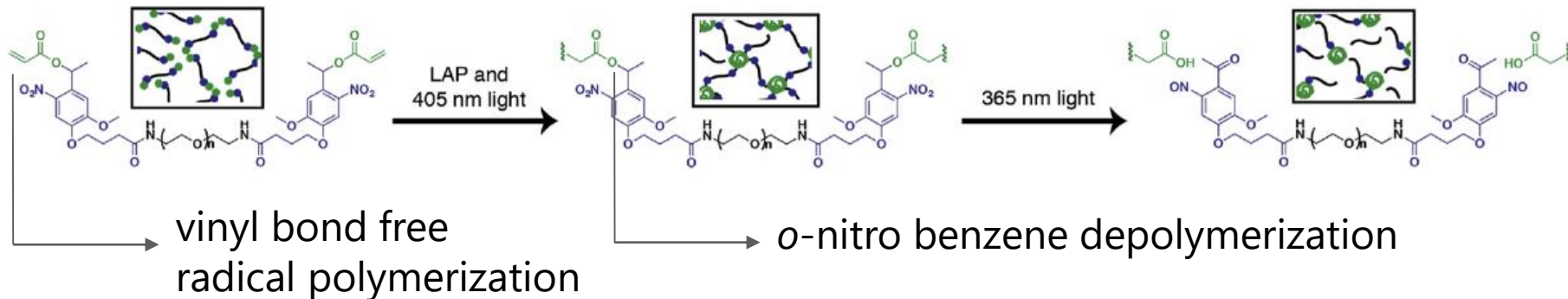
Photo-reversible polymer 1:



Prof. Dr. Mark Tibbitt
Morris Wolf

ETH zürich

PEGdiPDA hydrogel (water based)



365 nm
➔
~10 min



Non-toxic chemistry

Depolymerization works in minutes

Adhesion to metallic substrates is an issue

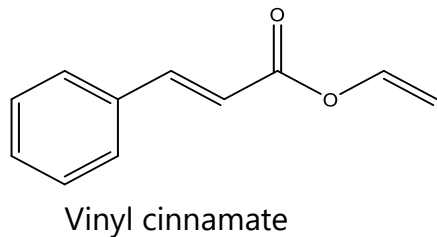
Photo-reversible polymer 2:



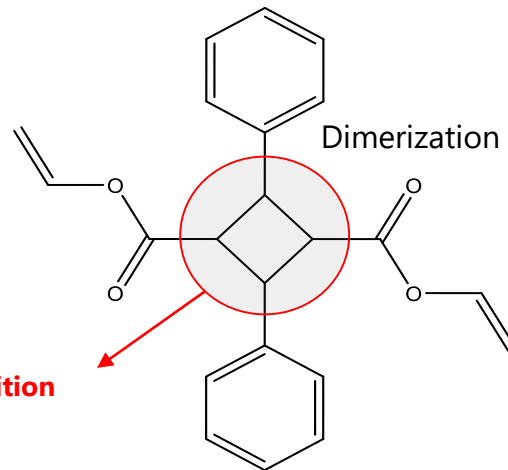
Dr. Yves Letierrier



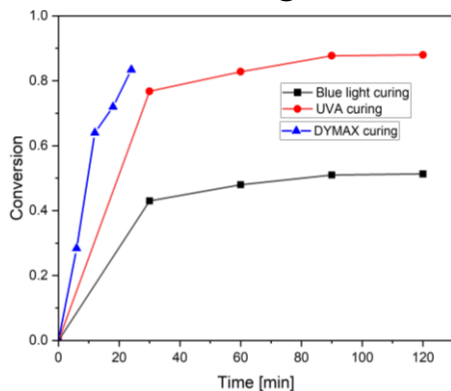
Alper Balkan



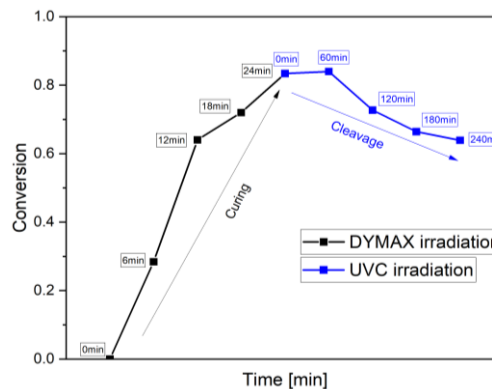
> 300 nm
UV lamp
< 300 nm
[2+2] Photocycloaddition



Conversion in different wavelengths



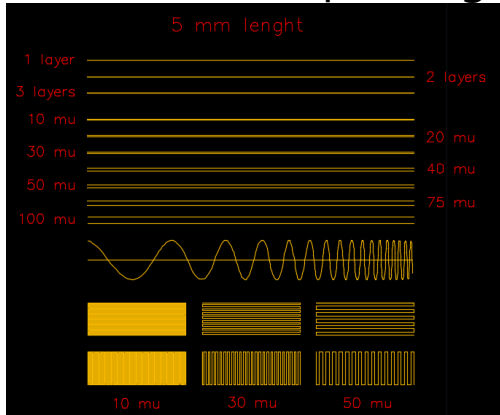
Reversibility



Only partial depolymerization achieved after ~4h

Digital Printing

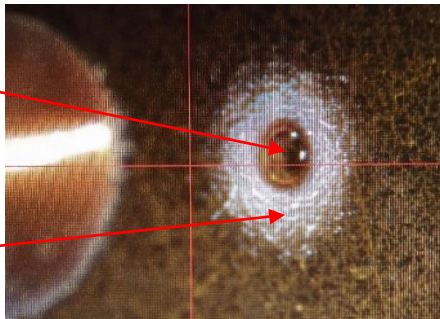
Standard test printing



AJP – satellite droplet

Liquid phase
(coating region)

Solid phase
(satellite droplets)



	AJP	Inkjet	Dispensing	Spraying
Ink				
Bitumen	X	✓	✓	✓
Berlacryl	X	✓	✓	✓
Zappon	✓	✓	✓	✓
Polyolefin	✓	✓	✓	✓
PVA	✓	✓	✓	✓
Aryl epoxy photopolymer	✓	✓	✓	✓

Most of the chemical formulations are printable

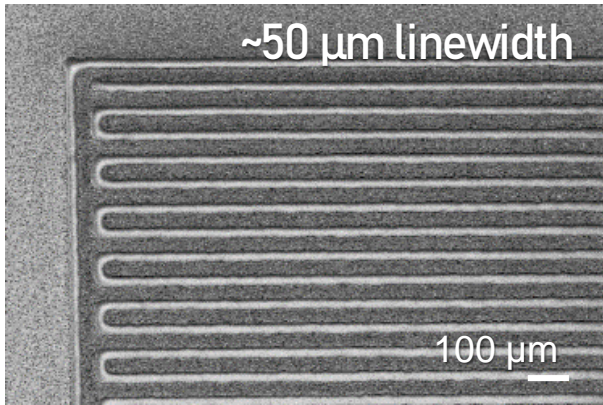
AJP present satellite droplets

Examples Aerosol Jet Printing (AJP)

Watch dial demonstrator

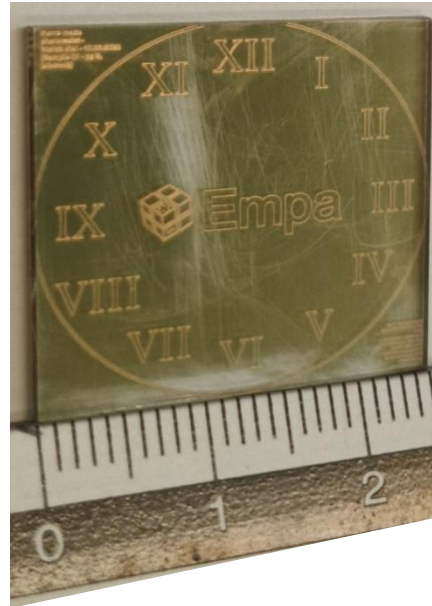
Line printing test

~50 μm linewidth



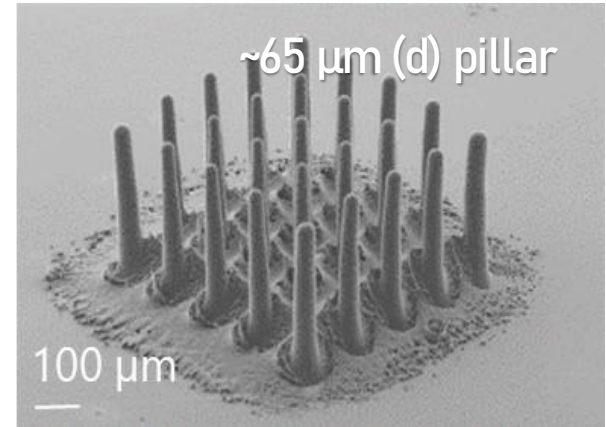
100 μm

Aryl epoxy photopolymer
printed with AJP



AJ-3D printing of photopolymer

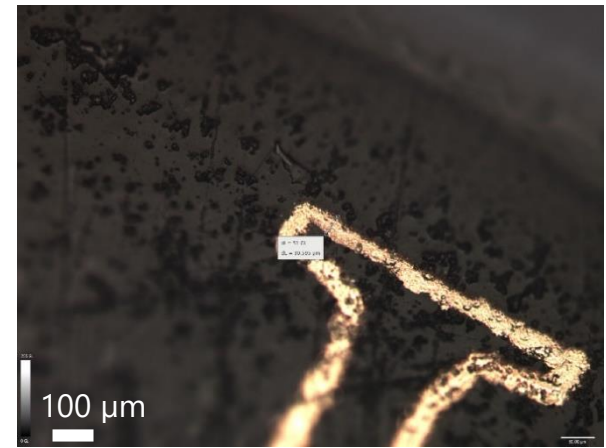
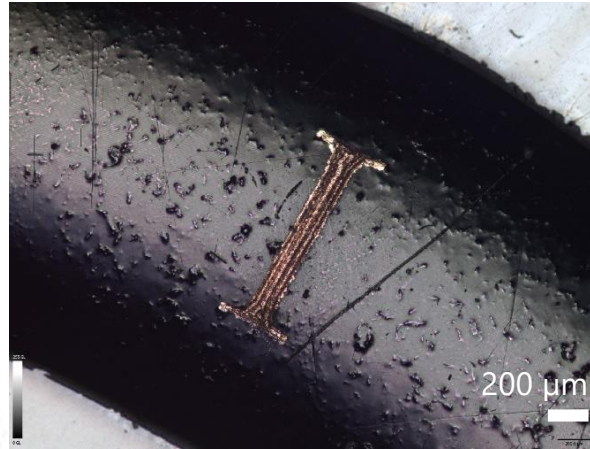
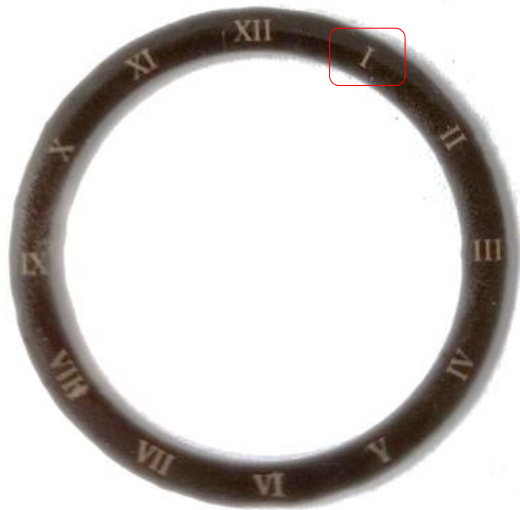
~65 μm (d) pillar



100 μm

Vnieska, V., et al. *Polymers* **2022**, 14, 3411.

Combination AJP + dispensing



-	Dispensing	AJP
Printing time (min)	2.1	3.4
Line width (μm)	300	35
Thickness (μm)	250	8

Lessons learned

- How to print Photopolymers:
 - Digital printing possible w/ linewidth down to 30 microns
 - Wide selection of commercial & in-house polymers tested
 - Flat and curved substrates
- Photo-reversible polymers:
 - PEGdiPDA hydrogels: de-polymerization ~10 min
 - Cinnamates: incomplete de-polymerization after 4 hours
- Non-contact removal:
 - Not achieved yet
 - Flash lamp annealing (FLA) decomposes most polymers before delamination
 - Thermally-induced release – ongoing

