

Disulfide-containing monomers for dynamic UV-cured networks

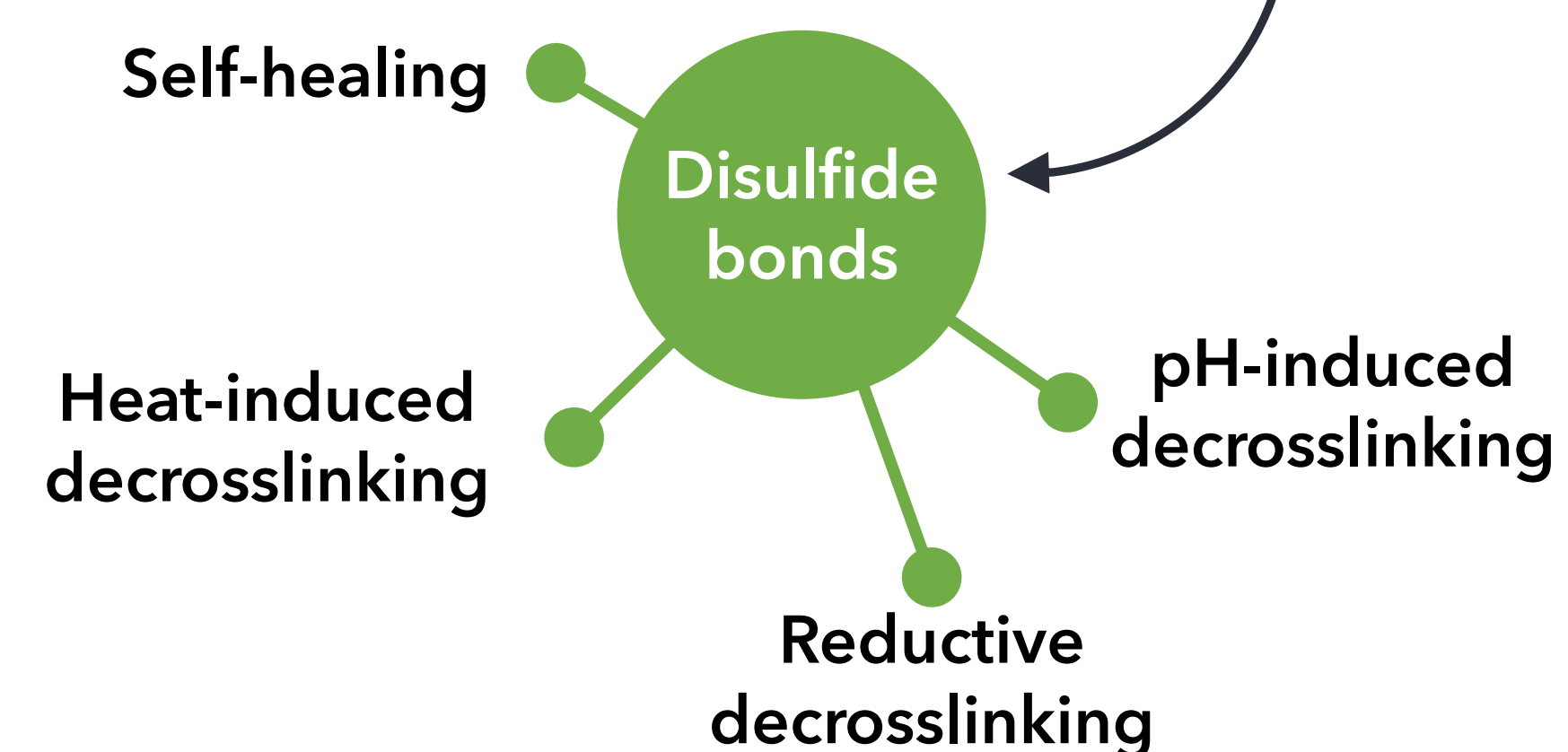
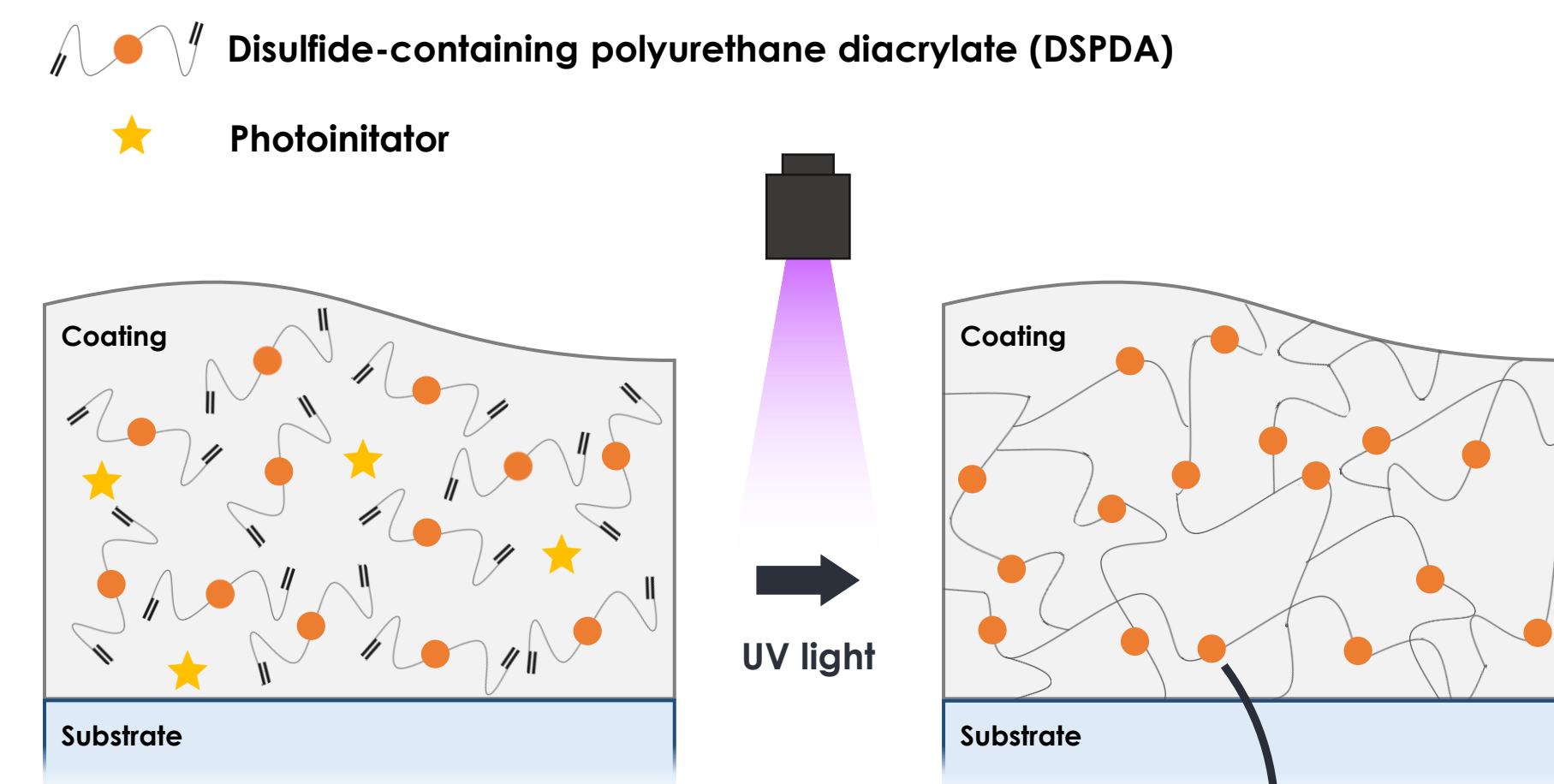
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Introduction

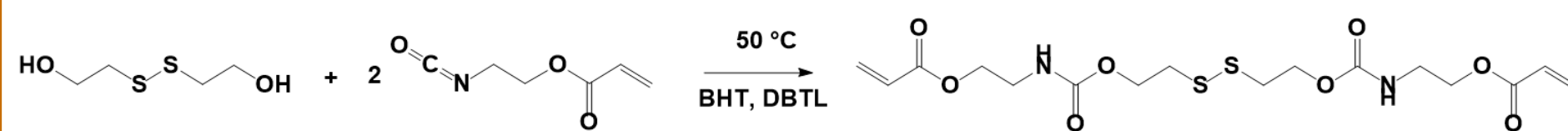
- **Disulfide-containing vitrimers** have gained importance over the past years thanks to the high responsiveness of disulfide bonds to plenty of external stimuli, like pH, light, temperature, and redox conditions^[1].
- Due to these outstanding properties, dynamically crosslinked networks containing linear disulfide have attracted a lot of interest in sectors like self-healing and **targeting applications**^[2].
- In this work, a **disulfide-containing polyurethane diacrylate (DSPDA)** was synthesized and used as a monomer for the design of dynamic acrylate networks which could find application as a coating in the packaging sector for **deinking** purposes^[3,4].
- **Self-initiated photopolymerization** was also investigated as a possible way of avoiding the use of a photoinitiator, by exploiting the photocleavage of disulfide bonds present in the main chain when DSPDA was irradiated with UV light.
- Preliminary results were obtained for **self-healing applications** of DSPDA.



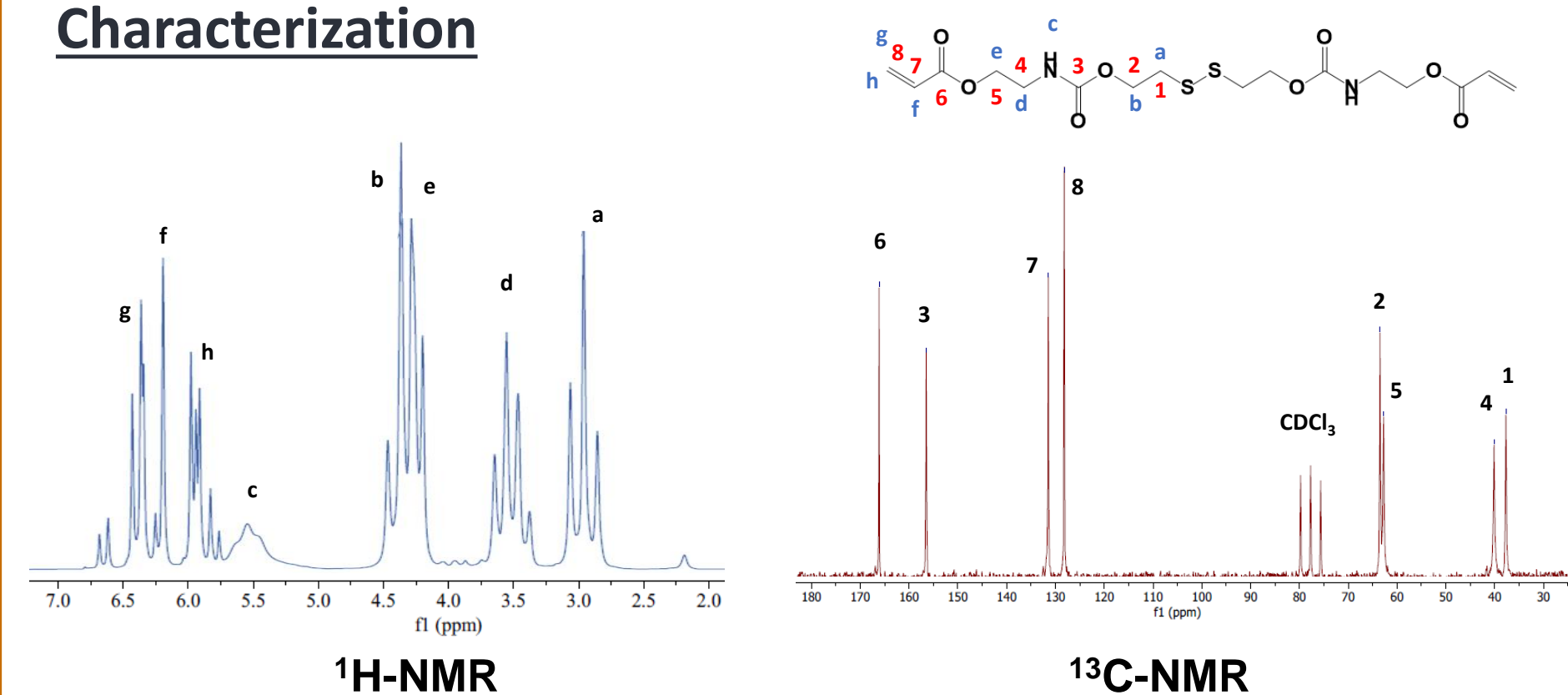
Monomer synthesis

Synthesis of DSPDA

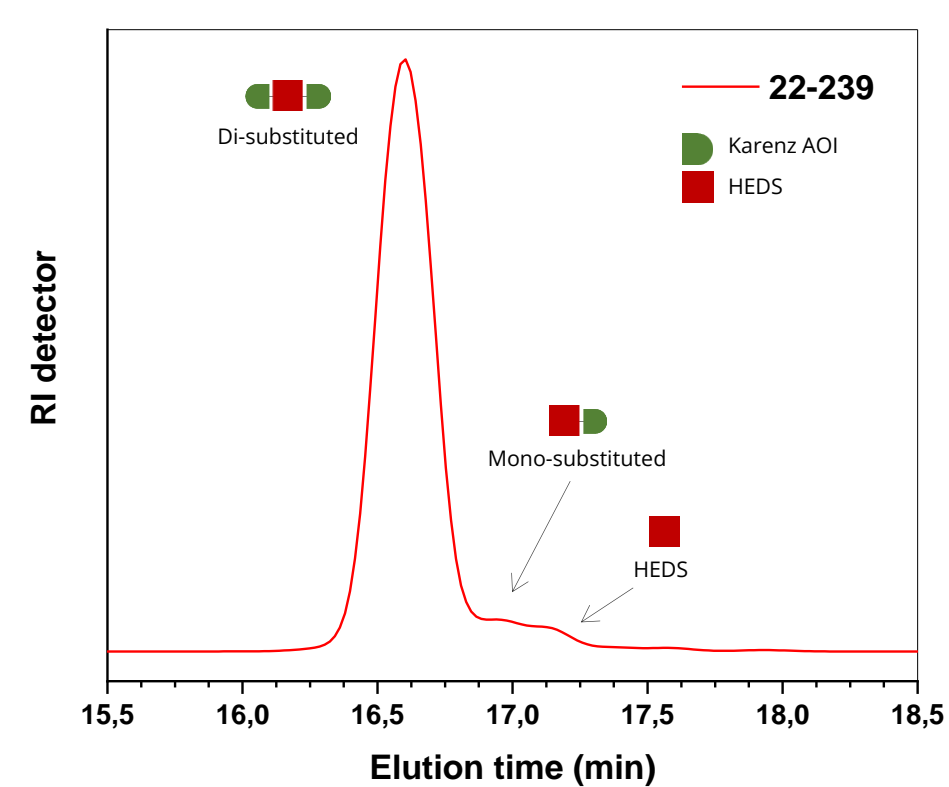
- The DSPDA was obtained through an addition reaction between 2-hydroxyethyl disulfide (HEDS) and 2-acryloyloxyethyl isocyanate (AOI)
- Reaction was performed at 50°C to avoid disulfide cleavage



Characterization



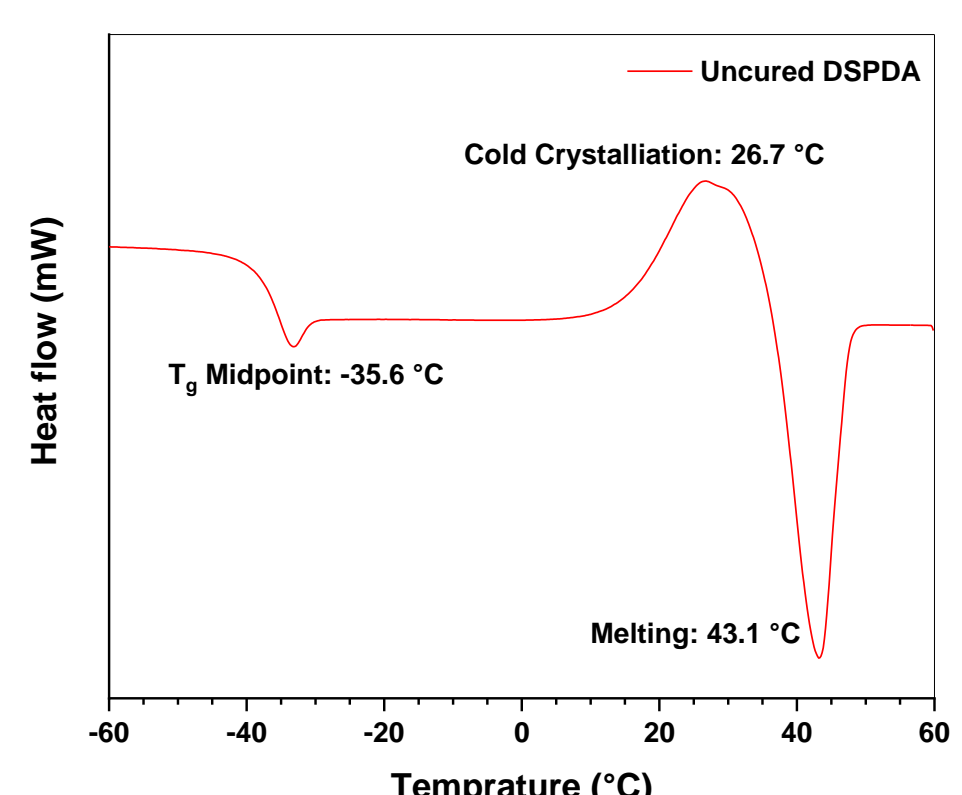
Species	% wt
Di-substituted	95.5
Mono-substituted	1.4
Unreacted HEDS	3.1



- NMR and GPC analysis confirmed the successful synthesis of DSPDA with high yield

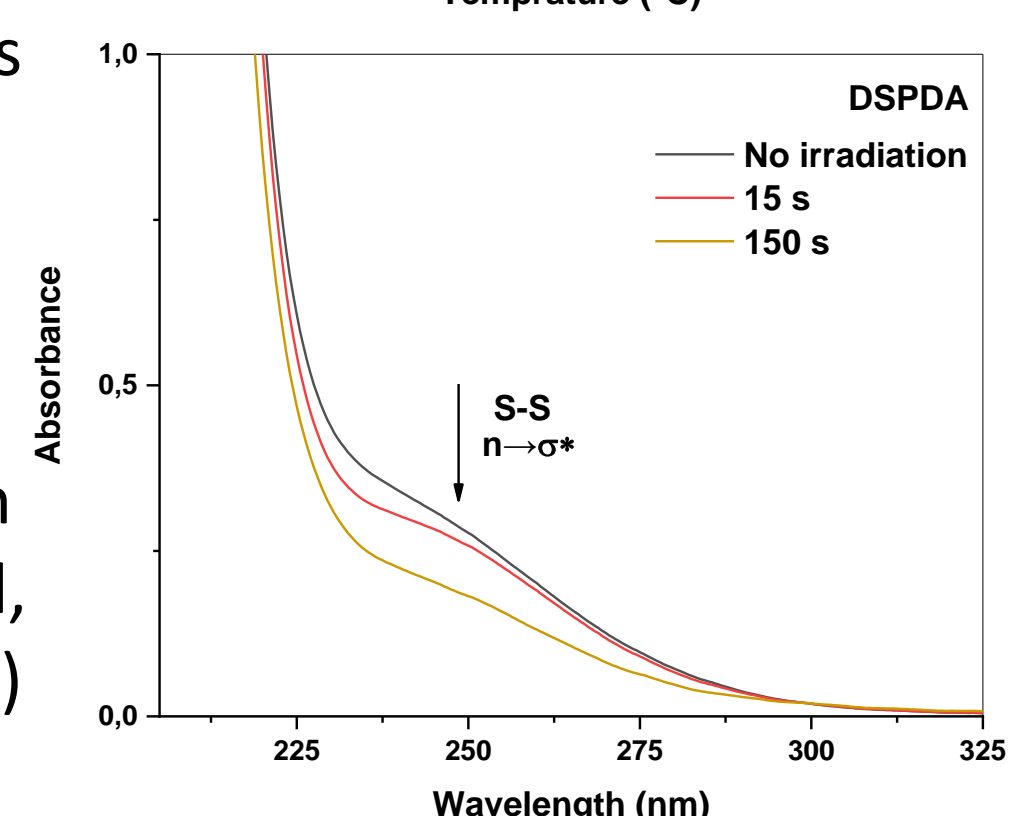
DSC

- Cold crystallization occurred between urethane groups at room temperature



Photocleavage

- UV-Vis spectroscopy was used to study the photocleavage of disulfide bonds under UV light
- When DSPDA solution in methanol was irradiated, a decrease in n→σ* (S-S) peak occurred

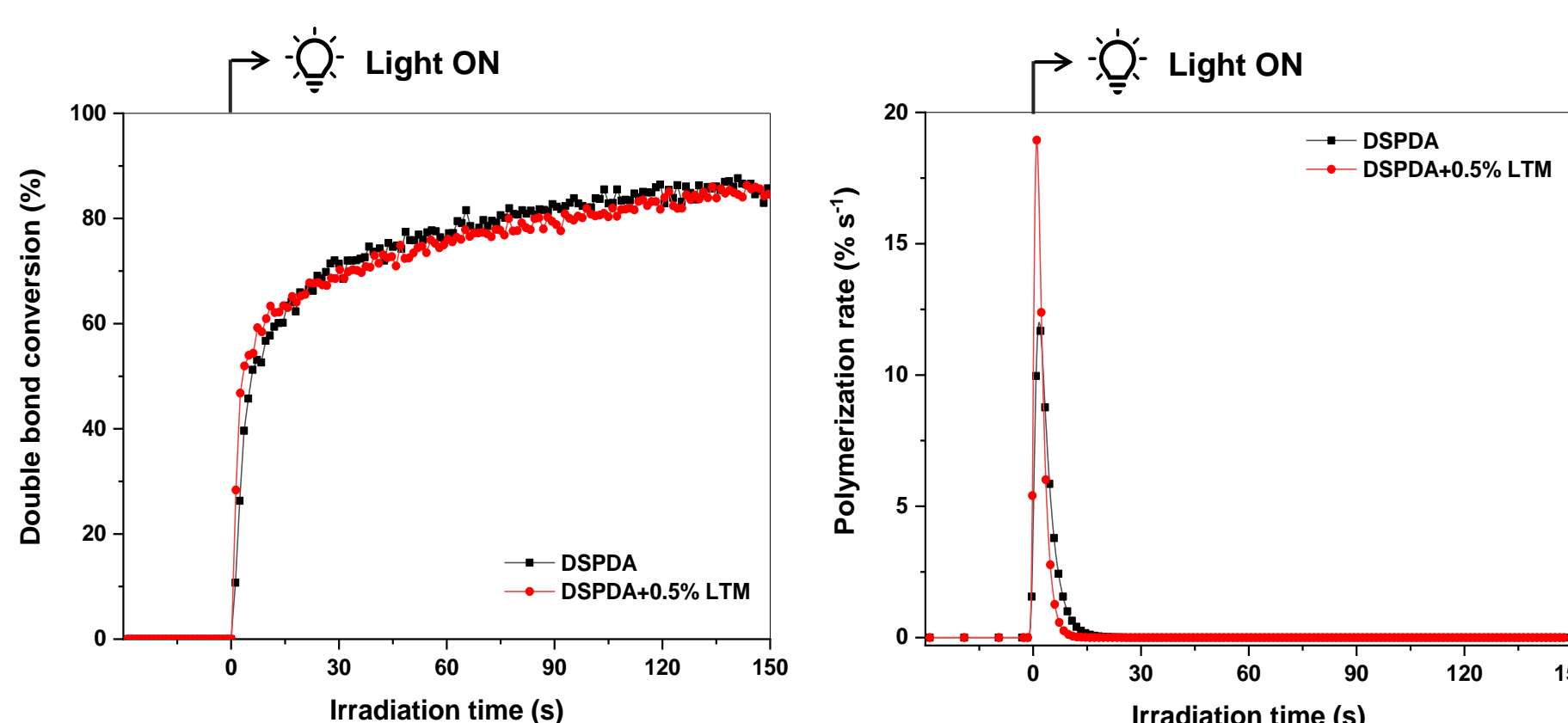


Photocuring

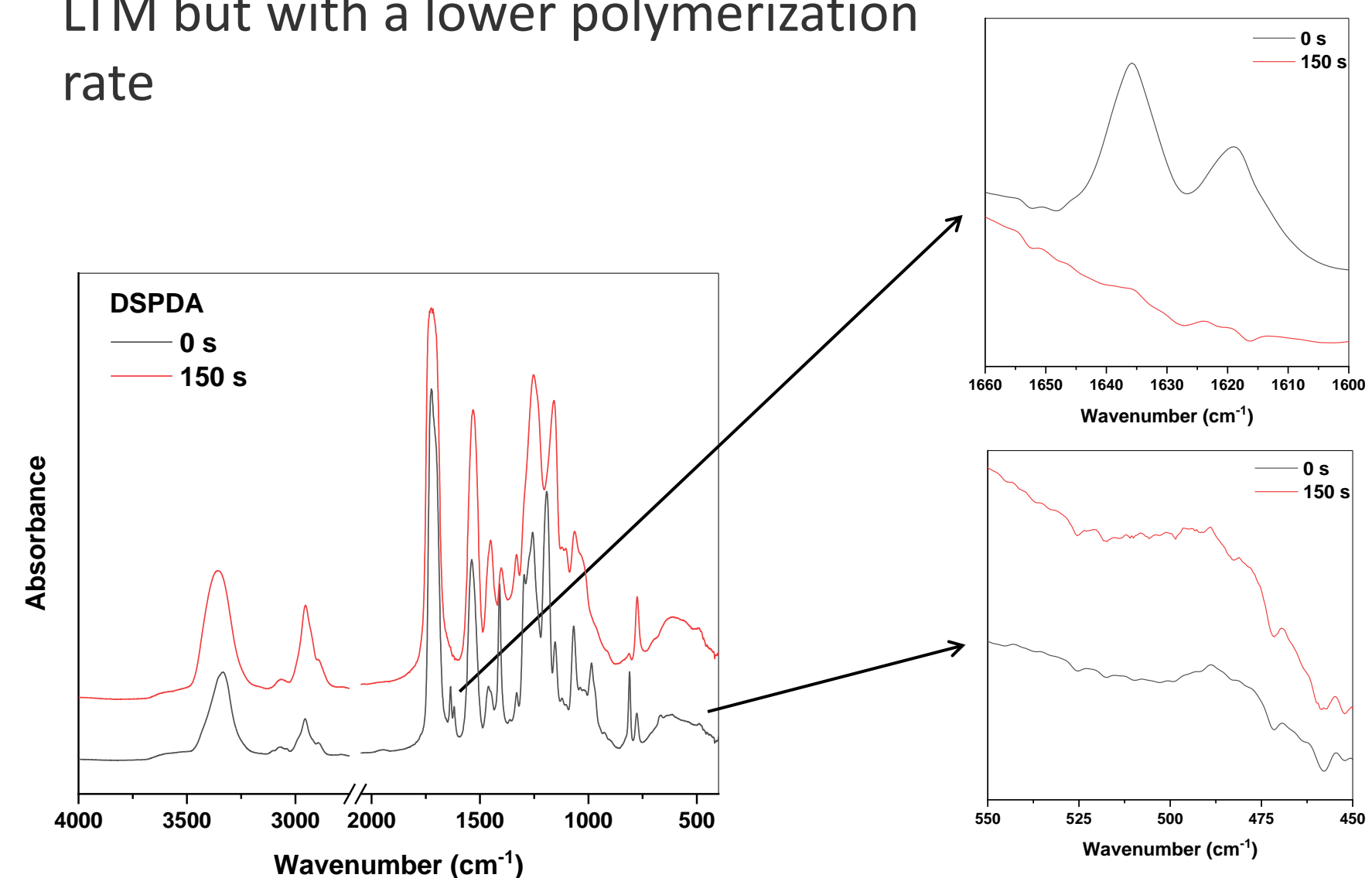
- Genocure® LTM was used as a photoinitiator for the photocuring reaction

Curing conditions

- 90 mW/cm²
- N₂ atmosphere



- Self-initiating photopolymerization due to photocleavage of disulfide bonds and production of thiyl radicals
- High degree of conversion even without LTM but with a lower polymerization rate



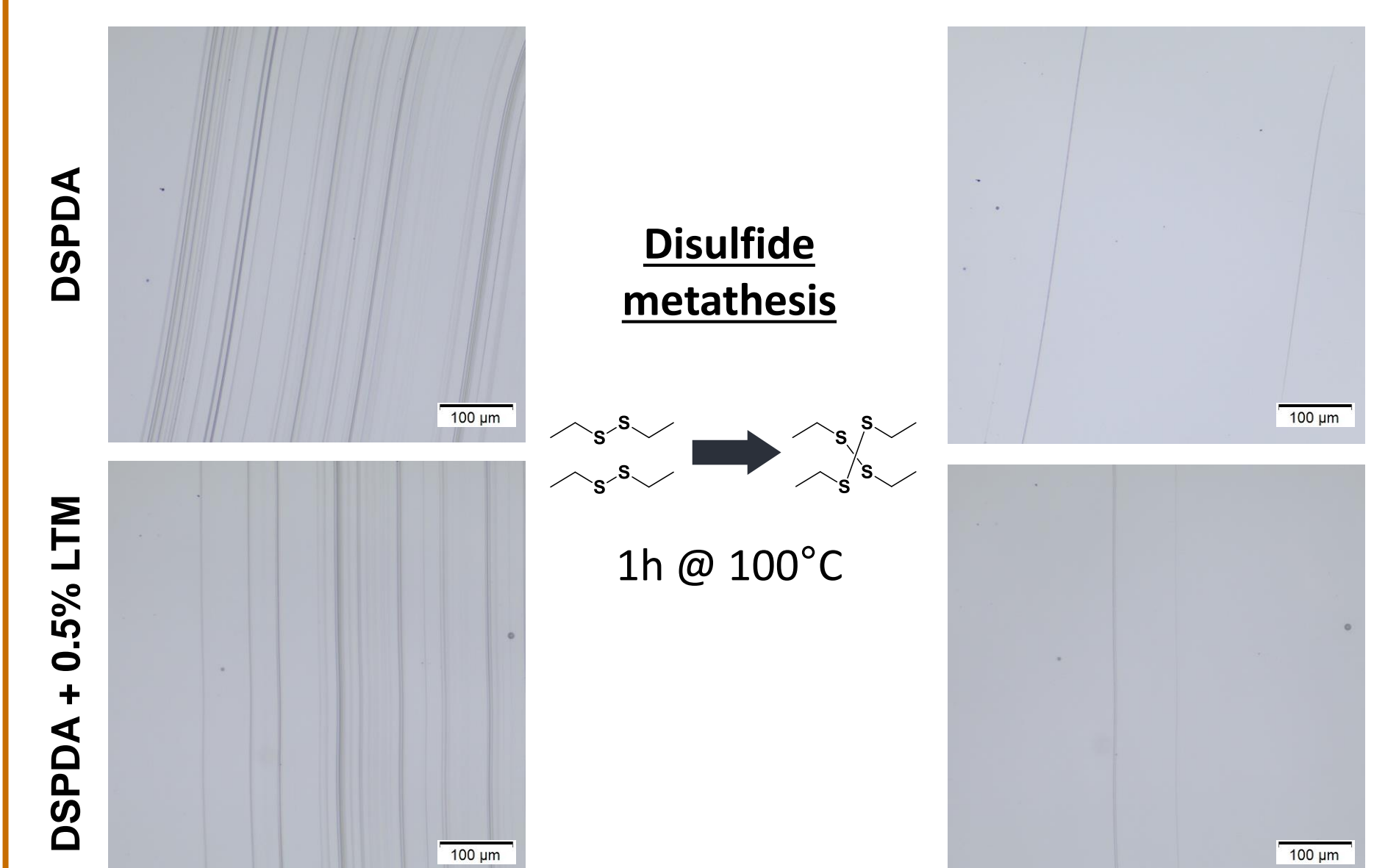
- Disulfide bonds were still present in the network after crosslinking of acrylates groups
- Crystallization of DSPDA affected chains mobility and reduced conversion degree in the final product
- Heating samples at 50°C during photocuring produced an increase the conversion of acrylate groups

Samples	Conversion @RT [%]	Conversion @50°C [%]	Gel Fraction [%]	T _g [°C]
DSPDA	86	92	95	72.6
DSPDA+0.5% LTM	85	94	97	84.2

Application

Self-healable coating

- Transparent coating was obtained after curing
- Healing of scratches performed on the surface of a coated glass slide by heating the samples at 100°C for 1h



Conclusions

- Synthesis of disulfide-containing diacrylate monomer which can initiate photopolymerization without the presence of photoinitiator
- High conversion of acrylate groups in the cured polymeric coating
- Production of a clear coating, self-healable through a metathesis-mediated mechanism

References

- [1] Canadell J. et al., Self healing materials based on disulfide links, *Macromolecules*, 2011, 44, 2536-2541.
- [2] Beaupre D.M., Weiss R.G., Thiol- and Disulfide-Based Stimulus-Responsive Soft Materials and Self-Assembling Systems, *Molecules*, 2021, 26(11), 3332.
- [3] Zhang M. et al., Design of a disulfide bond-containing photoresist with extremely low volume shrinkage and excellent degradation ability for UV-nanoimprinting lithography *Chem. Eng. J.*, 2020, 390, 124625.
- [4] Saiz L.M. et al., Self-healing materials based on disulfide bond-containing acrylate networks, *Polymer testing*, 2023, 107832.

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