Dimethacrylate Networks with Tunable Properties: The High Effectiveness of β-Allyl Sulfone Chain Transfer Agents

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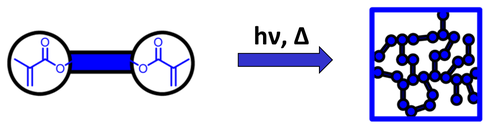
Introduction & Background

Photocured dimethacrylate networks are widely employed in dental medicine, decorative coatings and 3D-lithography. Some of their biggest drawbacks are the limited material properties (toughness, shrinkage) and incomplete conversion. By adding a chain transfer agent (CTA), e.g. thiols[1] or preferably allyl sulfones[2], more homogeneous networks with tunable and improved properties are accessible.[3,4] We synthesized mono- and difunctional β-allyl sulfones and present their high potential in regulating methacrylate networks.

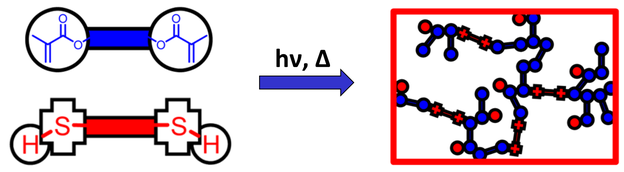
Free-Radical Polymerization

+ good photoreactivity, fast curing
+ convenient low energy processing
+ good storage stability
- no control, incomplete conversion
- **inhomogeneous** and **brittle** networks



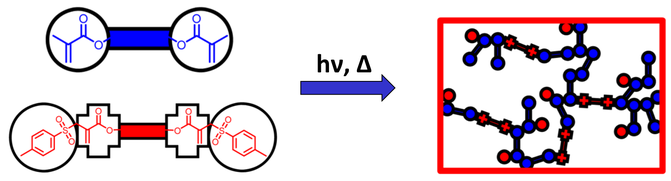
Thiol-ene chemistry[1]

+ low oxygen inhibition
+ fast and complete reaction
- bad storage stability
- strong **odor**

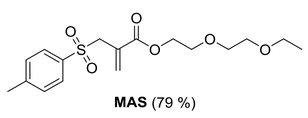


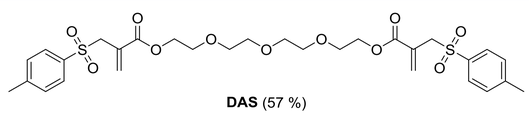
Addition-Fragmentation Chain Transfer (AFCT)[2]

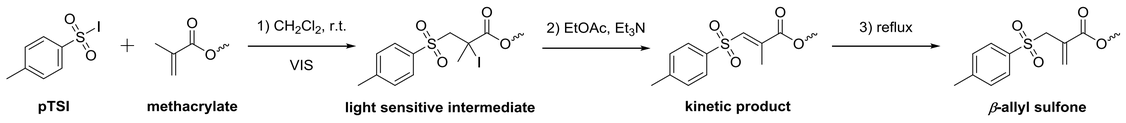
+ good photoreactivity
+ excellent storage stability
+ **tunable** and **homogeneous** networks
o hardly any studies on networks



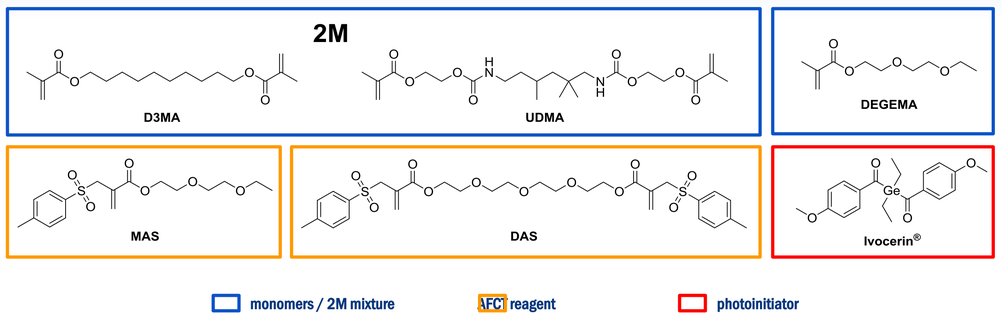
Synthesis of β-Allyl Sulfones



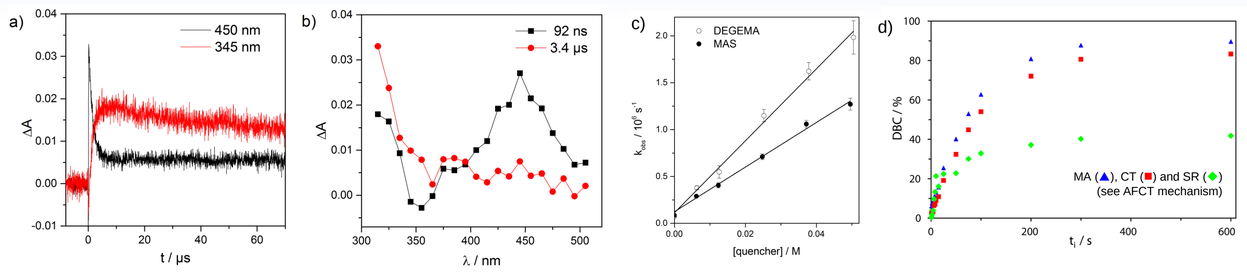




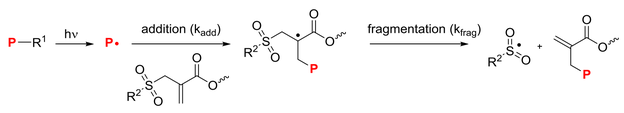
Monomers & Formulations



Mechanistic Studies



a) kinetics of the transient absorptions after laser flash b) transient absorption spectra at different delays (0.3 mM photoinitiator and 25 mM MAS in acetonitrile) c) pseudo-first-order decay rate constant (k_{obs}) of the phosphinoyl radical P• (acetonitrile at r.t.) d) evolution of the double bond conversion vs. irradiation time (^{1}H NMR; DEGEMA+25 DB MAS).*

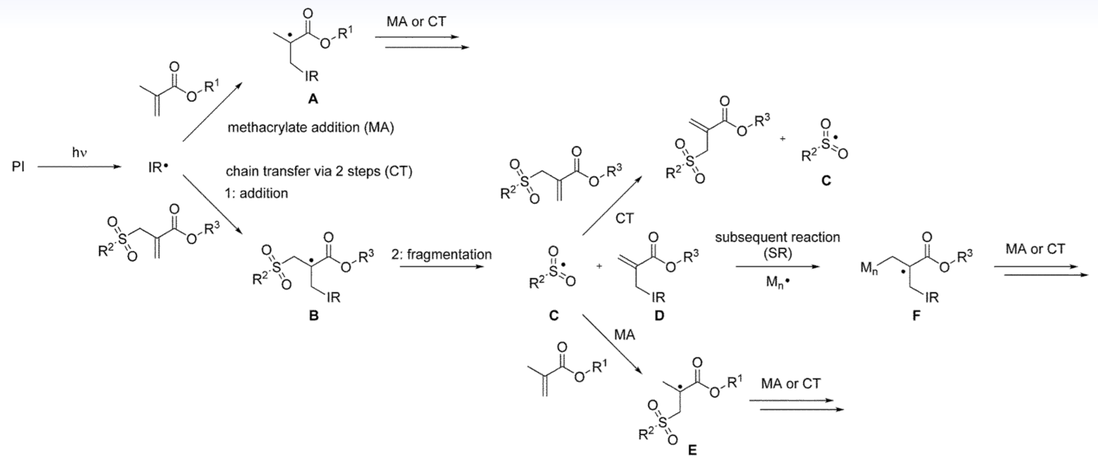


➡ **similar reactivity of methacrylate and β-allyl sulfone**

➡ **k_{add} same order of magnitude**

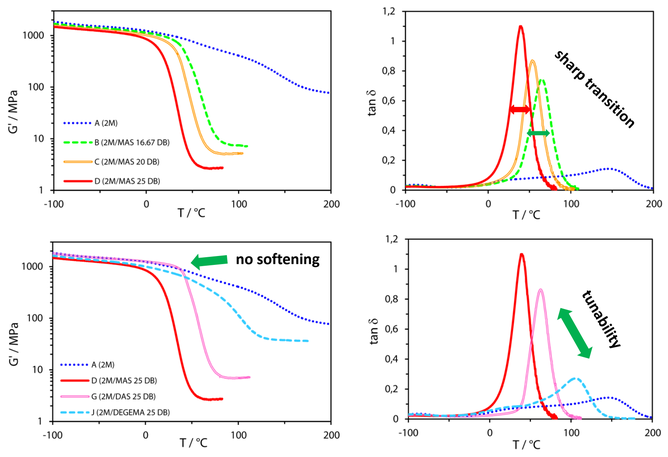
* DB = % of total double bonds in the mixture

AFCT Mechanism



Results & Discussion

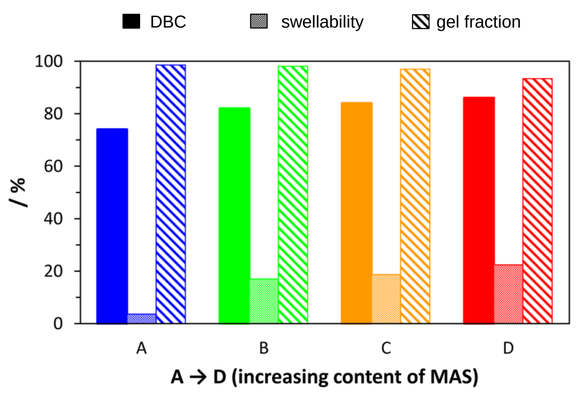
DMTA



Curve	Formulation	Color code	DBC* / %	Swellability# / wt%	Gel fraction# / wt%
A	2M	···	74	3.6	98.6
B	2M/MAS (16.67 DB)	- - -	82	17.0	98.1
C	2M/MAS (20 DB)	═	84	18.7	97.0
D	2M/MAS (25 DB)	▬	86	22.4	93.4
G	2M/DAS (25 DB)	═	86	11.4	97.5
J	2M/DEGEMA (25 DB)	- - -	-	9.8	98.5

* determined by photo-DSC; # swellability tests in EtOH at 60 °C (7 days); DB = % of total double bonds in the mixture

Photo-DSC & Swelling Experiments



➡ **sharp and tunable glass transition** ➡ **comparable modulus (difunctional AFCT)** ➡ **higher conversion** ➡ **higher swellability (maintaining high gel fraction)**

Conclusion

benefits of β-allyl sulfone chain transfer agents:

- **straightforward synthesis** from methacrylates
- good **storage stability** of the formulations
- **good coreactivity** with methacrylates
- **sufficient photoreactivity** and **higher conversion**
- **tunable** and **sharpened glass transition**
- **high gel fraction** and **tunable swelling**

References & Acknowledgements

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[2] Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer*, **2008**, *49*, 1079.
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[4] Gorsche, C.; Koch, T.; Moszner, N.; Liska, R. *Polym. Chem.*, **2015**, *6*, 2038.

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