

Supporting Information

Regulated acrylate networks as tough photocurable materials for 3D structuring

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RT-NIR Photorheology

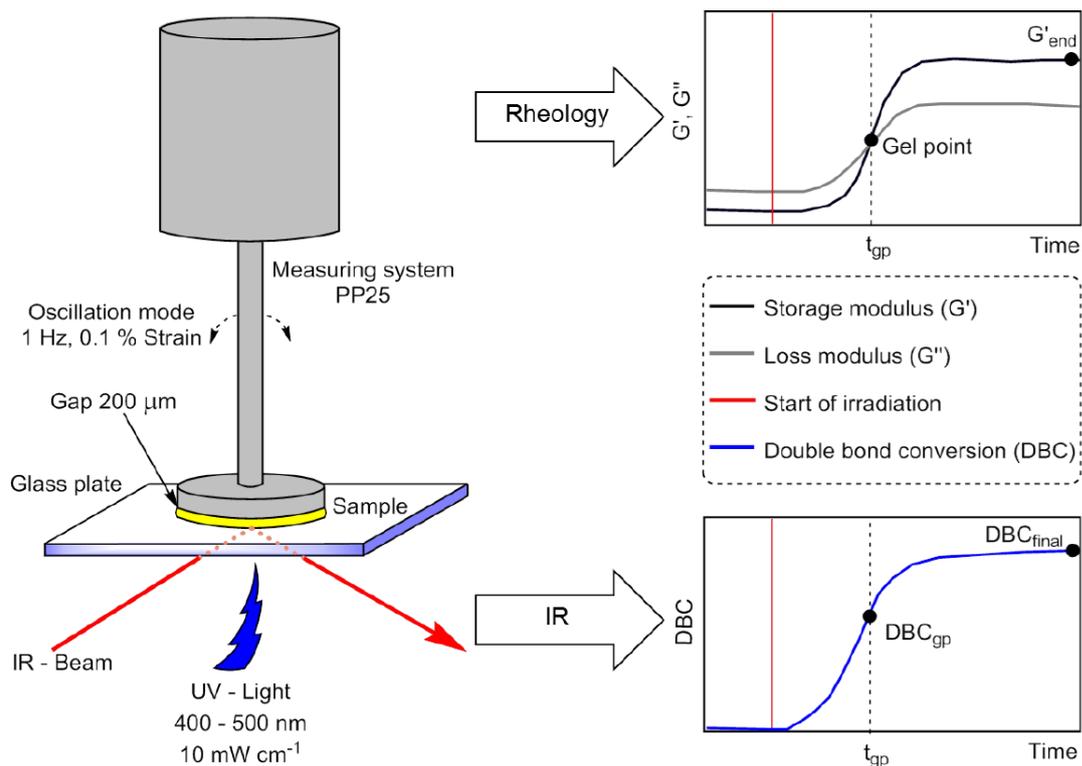


FIGURE S1: Setup of RT-NIR photorheology

FIGURE S1 shows a general set up of a photorheometer with real-time NIR tracking ability and its recorded data. Irradiation of the sample formulation can be conducted through a glass plate to initiate curing of a photopolymerizable formulation subjected to rheological and NIR measurement simultaneously. The gel point can be extracted from the recorded rheology data as the intersection of G' and G'' with $G'/G'' < 1$ describing liquid and $G'/G'' > 1$ describing solid (gel) behavior of the cured material. Hence, the time until gelation (t_{gp}) can be determined. The combination of rheology and IR data reveals DBC at the gel point (DBC_{gp}). Moreover, values for the final storage modulus (G'_{end}), and the final DBC (DBC_{final}) can be extracted. Another parameter of interest, which was gained from rheology data, was the development of the normal force (F_N), which is the force necessary to maintain the gap of 200 μm between glass and steel plate, as a measure for shrinkage stress during photopolymerization.

Visualization of all samples measured by this method can be found in Figures S2 – S4.

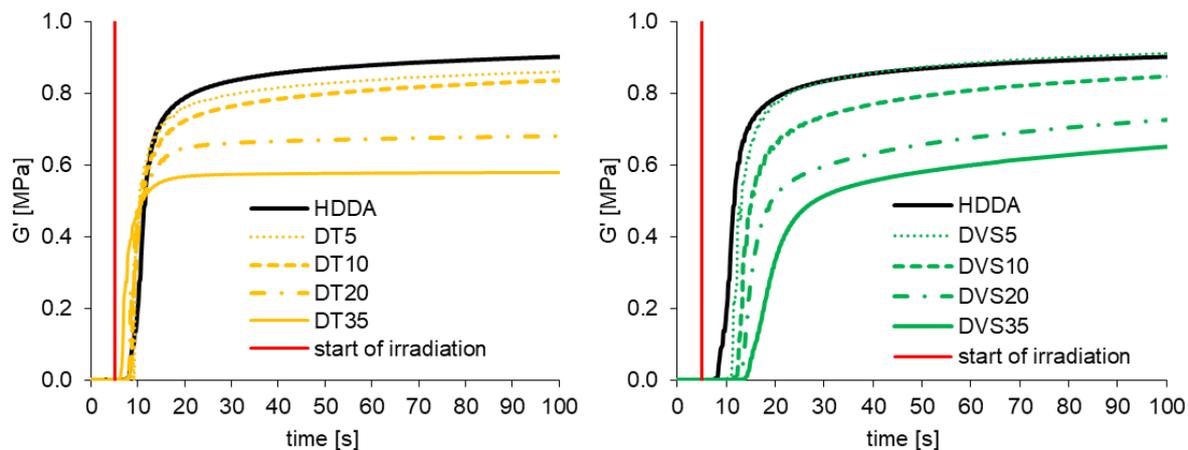


FIGURE S2: Obtained storage moduli (G') during curing for all formulations measured by photorheology: pure hexanediol diacrylate and its mixtures with 5, 10, 20, or 35 mol% either dithiol (DT, left) or difunctional vinyl sulfonate (DVS, right)

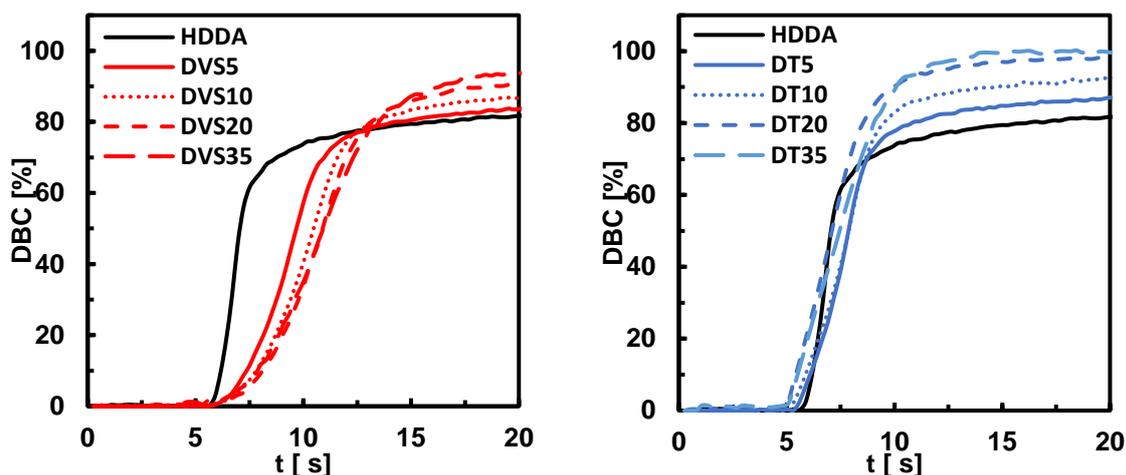


FIGURE S3: Double bond conversion (DBC) during curing for all formulations measured by photorheology: pure hexanediol diacrylate and its mixtures with 5, 10, 20, or 35 mol% either dithiol (DT) or difunctional vinyl sulfonate (DVS)

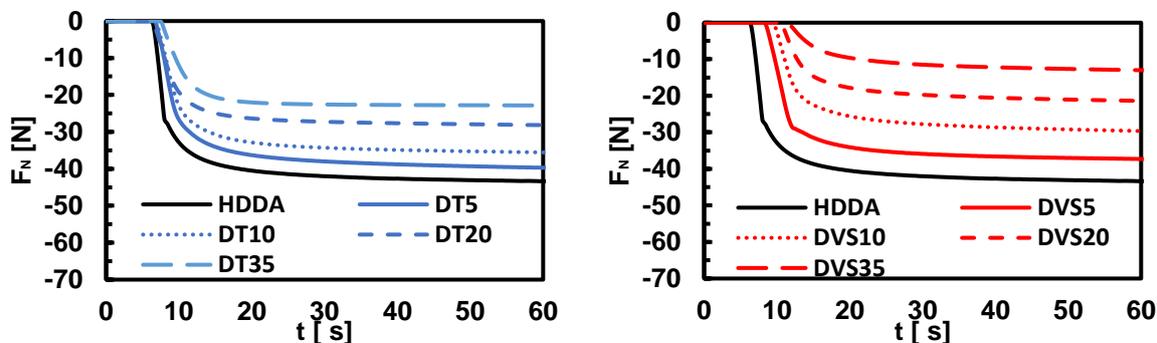


FIGURE S4: Normal force (F_N) development during photopolymerization reactions as a measure for the formed shrinkage stress for all formulations measured by photorheology: pure hexanediol diacrylate and its mixtures with 5, 10, 20, or 35 mol% either dithiol (DT) or difunctional vinyl sulfonate (DVS)

Dynamic Mechanical Thermal Analysis

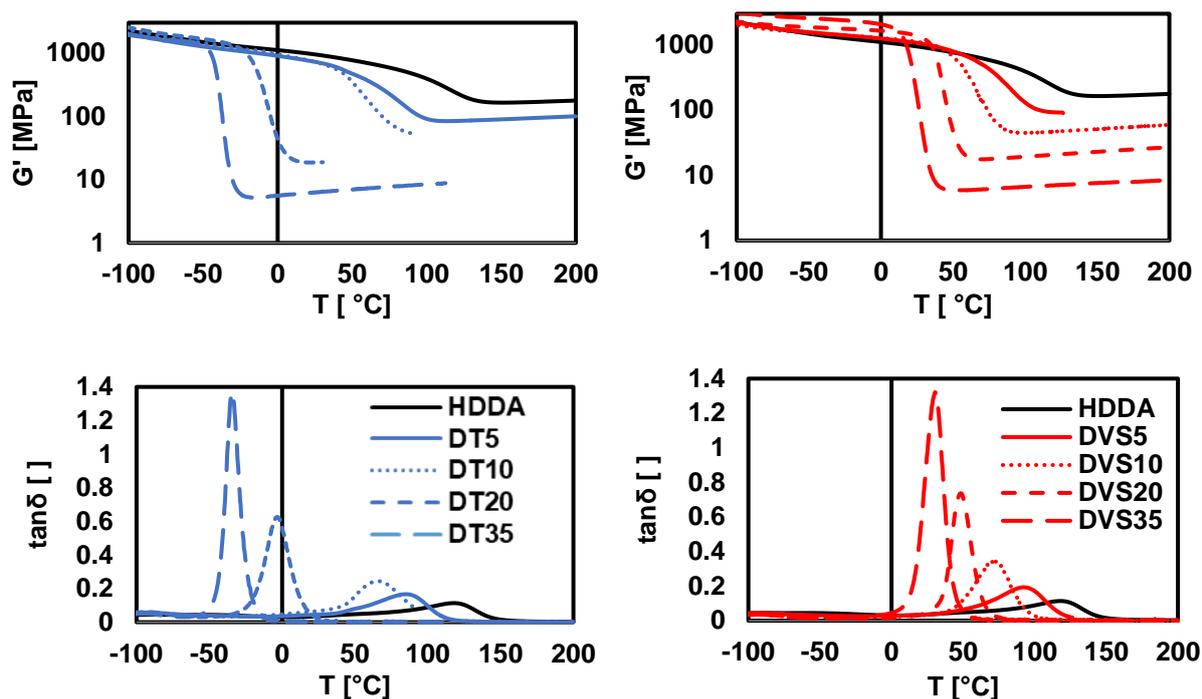


FIGURE S5: DMTA curves for all (a) dithiol (DT) and (b) divinyl sulfonate ester (DVS) regulated photopolymers (5, 10, 20, 35 mol% regulator in HDDA) with pure hexanediol diacrylate (HDDA) as reference

Remark: In some cases the modulus curves for samples (DT10, DT20, DT35, and DVS5) only arrive to 100 °C or less. This is because the samples broke or slipped out of the measuring device when they were in the rubbery state.

Calculation of crosslinking density:

The crosslinking density (ρ) in the cured photopolymers was determined as followed:

$$\rho = \frac{G'_{rubber}}{\phi R T_{g+30}}$$

G'_{rubber} representing the storage modulus measured 30 °C above the T_g , R representing the gas constant, T_{g+30} describing the temperature 30 °C higher than the T_g , and ϕ representing the front factor (approximated to 1 in Flory theory^{1,2,3}).

Polymer	G'_{rubber} [MPa]	T_g [°C]	T_{g+30} [K]	ρ [mol L ⁻¹]
HDDA	164	118	421	46.9
DT5	84	85	388	26.0
DT10	52	65	368	17.0
DT20	19	-3	300	7.6
DT35	5	-34	269	2.2
DVS5	90	92	395	27.4
DVS10	45	71	374	14.5
DVS20	17	48	351	5.8
DVS35	5	35	338	1.8

Tensile Tests

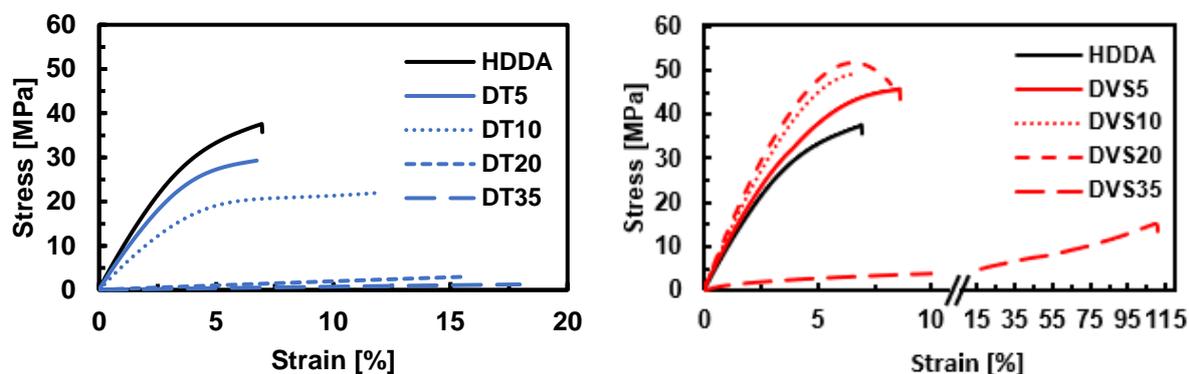


FIGURE S6: Tensile curves for all (a) dithiol (DT) and (b) divinyl sulfonate ester (DVS) regulated photopolymers (5, 10, 20, or 35 mol% regulator in HDDA) with pure hexanediol diacrylate (HDDA) as reference

Swelling Tests

The swellability (S) and gel fraction (G) can be calculated by means of the following equations:

$$S = m_{\text{swollen}}/m_{\text{dry}}$$

$$G = m_{\text{dry}}/m_{\text{start}}$$

m_{start} mass before placing the

m_{swollen} Mass in the swollen state after 14 days of being submerged in EtOH

m_{dry} dried until constant weight was reached in a vacuum oven

TABLE S1: Overview over swellability (S) and gel fraction (G) values for pure hexanediol diacrylate and its mixtures with 5, 10, 20, or 35 mol% dithiol (DT) or difunctional vinyl sulfonate (DVS)

Polymer	Swellability	
	S [w%]	G [w%]
HDDA	3.3 ± 0.1	99.8 ± 0.2
DT5	5.2 ± 0.7	99.8 ± 0.2
DT10	6.7 ± 0.3	99.5 ± 0.3
DT20	9.8 ± 0.3	99.1 ± 0.1
DT35	14.5 ± 0.1	95.7 ± 0.2
DVS5	2.5 ± 0.2	99.5 ± 0.2
DVS10	3.2 ± 0.4	99.3 ± 0.2
DVS20	8.2 ± 0.8	99.2 ± 0.2
DVS35	15.3 ± 0.3	96.3 ± 0.1

Mechanism

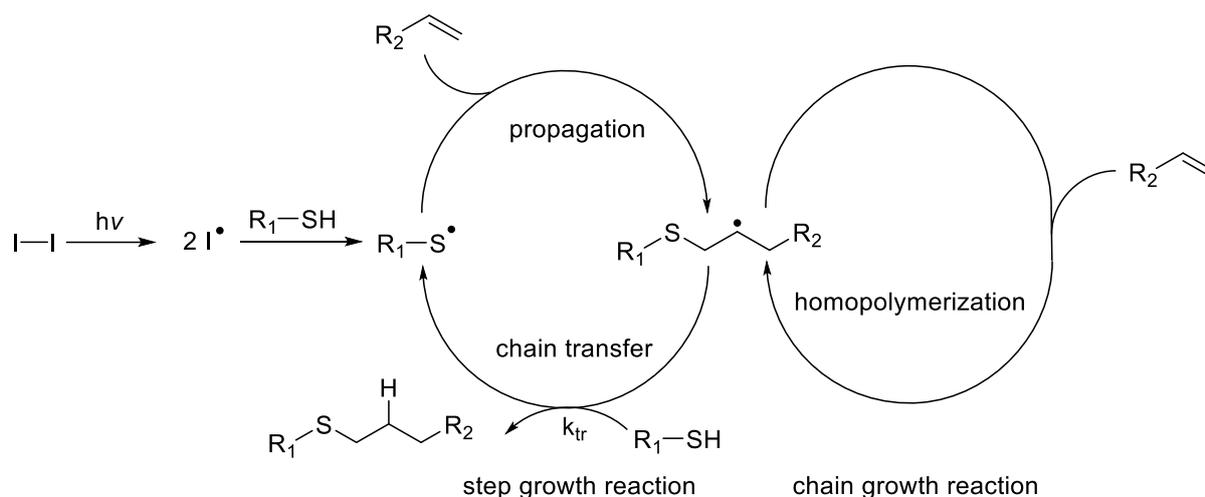


FIGURE S 7: Regulation mechanism* of mixed chain growth/step growth reaction of thiol-acrylate systems⁴

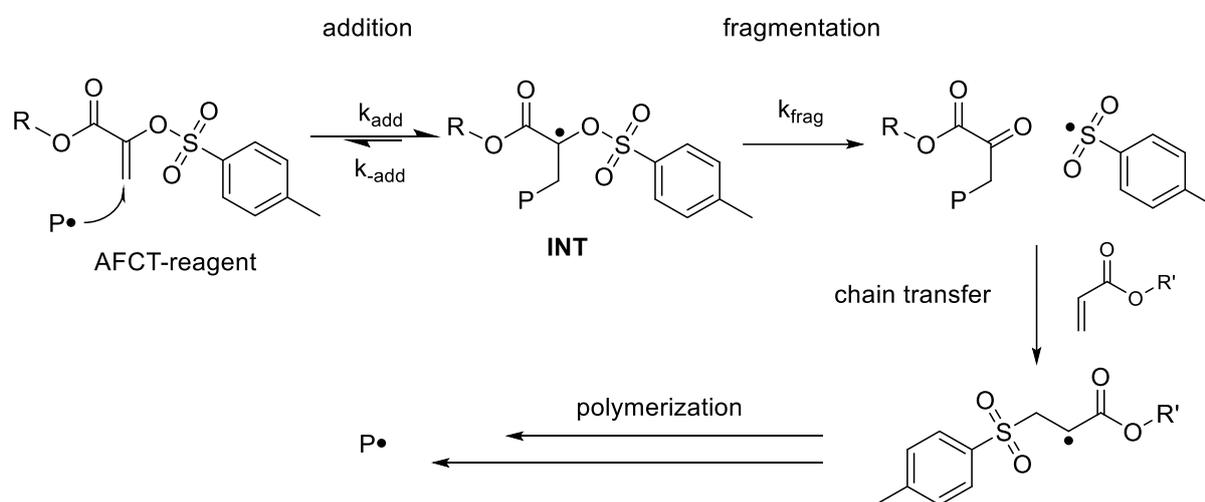


FIGURE S 8: Regulation mechanism* of a vinyl sulfonate ester AFCT reagent

*Please note that there are multiple reaction pathways possible in FIGURE S7 and FIGURE S8

References

- 1 P. J. Flory, *Polymer* **20**:1317-1320 (1979).
- 2 S. Zhao and M. M. Abu-Omar, *ACS Sustainable Chemistry & Engineering* **4**:6082-6089 (2016).
- 3 H. Nouailhas, C. Aouf, C. Le Guerneve, S. Caillol, B. Boutevin and H. Fulcrand, *Journal of Polymer Science Part A: Polymer Chemistry* **49**:2261-2270 (2011).
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