

Supporting Information

Supramolecular Polymer Networks made by Solvent-Free Copolymerization of a Liquid 2-Ureido-4[1*H*]pyrimidinone Methacrylamide

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Determination of the UPy-OPG-MAA content in the copolymers by the Fox equation.

The Fox equation (1) can be used to determine the weight fractions (w_1 and w_2) of two monomers in a copolymer from its glass transition temperature (T_g) if the glass transition temperatures of the corresponding homopolymers ($T_{g,1}$ and $T_{g,2}$) are known:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

This was applied to copolymers made from hexyl methacrylate and UPy-OPG-MAA. The glass transition temperatures of poly(UPy-OPG-MAA) ($T_{g,1} = 318$ K) and poly(hexyl methacrylate) (poly(HMA)) ($T_{g,2} = 267$ K) were both determined by DSC measurements (**Figure 2** in the manuscript). With

$$w_2 = 1 - w_1 \quad (2)$$

equation (1) can be re-formulated to:

$$\left(\frac{1}{T_g} - \frac{1-w_1}{T_{g,2}} \right) T_{g,1} = w_1 \quad (3)$$

and numerical analysis permits calculating w_1 (weight fraction of UPy-OPG-MAA) from the experimentally determined T_g , $T_{g,1}$ and $T_{g,2}$, which can be converted into mol % by:

$$n_1 = \frac{\frac{w_1}{M_1}}{\frac{w_1}{M_1} + \frac{1-w_1}{M_2}} \quad (4)$$

where n_1 is the mol-fraction of UPy-OPG-MAA and M_1 and M_2 are the molecular weights of UPy-OPG-MAA and HMA, respectively.

Table S1. Bulk (co)polymerization reactions carried out under thermal initiation with AIBN.

UPy-OPG-MAA	Comonomer ^a	Initiator ^b	Temperature	Time	Yield	Solubility ^c	Processability ^d
(mol %)	(wt %)	(mol %)	(mol %)	(°C)	(h)	(wt %)	
100	100	0	0.5	70	1.25	< 1	no
100	100	0	1	70	6	1.6	no
100	100	0	5	75	1	< 10	no
100	100	0	2.5	75	16	> 20	no
0	0	100 (BMA)	0.25	70	1.5	> 30	DMF and CHCl ₃
0	0	100 (HMA)	1	70	1.5	> 40	CHCl ₃
0	0	100 (HMA)	1	70	2	33	CHCl ₃
2.5	10	97.5 (BMA)	0.5	70	2.5	36	no
5	29	95 (MA)	0.5	80	5	< 2	hot DMF
5	16	95 (BnMA)	1	80	2	< 90	hot CHCl ₃
5	17	95 (HMA)	0.25	70	6	28	DMF and CHCl ₃
5	19	95 (BMA)	0.25	70	1	5	DMF and CHCl ₃
5	19	95 (BMA)	0.25	70	2	> 20	DMF and CHCl ₃
5	19	95 (BMA)	0.5	70	2	52	no
10	34	90 (BMA)	0.5	70	1.5	37	no
50	79	50 (HMA)	1	70	2	< 5	no
50	79	50 (HMA)	2	70	4	< 2	no
50	79	50 (HMA)	5	70	2	< 2	no

^aFour different comonomers were used: butyl methacrylate (BMA), hexyl methacrylate (HMA), benzyl methacrylate (BnMA), and methyl acrylate (MA). ^bAzobisisobutyronitrile (AIBN) was used as initiator. ^cSolubility was tested in (hot) CHCl₃ and DMF (c < 1 mg/mL). ^dMelt-processability was qualitatively explored by testing if the product could be compression-molded with a Carver® hot-press into a film upon heating up to 140 °C.

Table S2. Solution (co)polymerization reactions carried out under thermal initiation with AIBN.

UPy-OPG-MAA		Comonomer ^a	Initiator ^b	Solvent	Temperature	Time	Yield	Solubility ^d	Processability ^e
(mol %)	(wt %)	(mol %)	(mol %)	([c]) ^c	(°C)	(min)	(wt %)		
5	17	95 (HMA)	2.5	5 (DMF)	80	21.5	32	DMF and CHCl ₃	yes
10	30	90 (HMA)	2.5	5 (DMF)	80	21.5	0.6	DMF and CHCl ₃	yes
50	79	50 (HMA)	2.5	40 (DMF)	70	15.5	32	hot DMF	yes
50	79	50 (HMA)	1	21 (DMF)	80	5	4	no	no
50	79	50 (HMA)	5	21 (DMF)	80	24	18	no	no
100	100	0	1	11 (DMF)	80	5	2	no	no
100	100	0	1	17 (DMF)	80	22.5	< 1	no	no
100	100	0	2.5	5 (DMF)	80	1	0.5	no	no
5	17	95 (HMA)	2.5	22 (tol)	80	6	68	CHCl ₃	yes
50	78	50 (BnMA)	2.5	22 (tol)	70	6	1.9	no	yes
50	79	50 (HMA)	2.5	22 (tol)	80	6	44	hot DMF and CHCl ₃	yes
50	82	50 (BMA)	2.5	22 (tol)	80	5	46	hot DMF	yes
100	100	0	2.5	22 (tol)	80	8	36	hot DMF	yes

Either DMF or toluene (tol) were used as solvent. ^aThree different monomers were employed: butyl methacrylate (BMA), benzyl methacrylate (BnMA), and hexyl methacrylate (HMA). ^bAzobisisobutyronitrile (AIBN) was used as initiator. ^cTotal monomer concentration in wt %. ^dSolubility was tested in (hot) CHCl₃ and DMF (c < 1 mg/mL). ^eMelt-processability was qualitatively explored by testing if the product could be compression-molded with a Carver® hot-press into a film upon heating up to 140 °C.

Table S3. Solution (co)polymerization reactions carried out under photochemical initiation with HMPP.

UPy-OPG-MAA		Hexyl-MA	Initiator ^a	Toluene	Time	Yield	Solubility ^b	Processability ^c
(mol %)	(wt %)	(mol %)	(mol %)	([c] in wt %)	(min)	(wt %)		
10	30	90	1.5	20	45	> 28	CHCl ₃	yes
100	100	0	1.5	53	1	10	swelling in hot DMF	yes
100	100	0	1.5	53	0.5	4	swelling in hot DMF	yes
100	100	0	1.5	20	10	> 15	no	yes
100	100	0	1.5	53	3	28	no	no

^a2-Hydroxy-2-methyl-1-phenyl-propan-1-one was used as initiator. ^bSolubility was tested in (hot) DMF, and CHCl₃ (c < 1 mg/mL). ^cMelt-processability was qualitatively explored by testing if the product could be compression-molded with a Carver® hot-press into a film upon heating up to 80 °C.

Table S4. Bulk (co)polymerization reactions carried out under photochemical initiation with HMPP and low conversion.

Entry	UPy-OPG-MAA		HMA ^a	Initiator ^b	Time	Yield	Solubility ^c	Processability ^d
	(mol %)	(wt %)	(mol %)	(mol %)	(min)	(wt %)		
34	0	0	100	1.5	15	40	THF, CHCl ₃	yes
37	5	17	95	1.5	15	49	THF, DMF, and CHCl ₃	yes
41	10	30	90	1.5	8.5	32	THF, DMF, and CHCl ₃	yes
44	20	49	80	1.5	4.5	49	THF, DMF, and CHCl ₃	yes
C198	100	100	0	1.5	2	27	swelling in CHCl ₃	yes

^aHexyl methacrylate. ^b2-Hydroxy-2-methyl-1-phenyl-propan-1-one was used as initiator. ^cSolubility was tested in (hot) THF, DMF, and CHCl₃ (c < 1 mg/mL). ^dMelt-processability was qualitatively explored by testing if the product could be compression-molded with a Carver® hot-press into a film upon heating up to 80 °C.

Table S5. Bulk (co)polymerization reactions carried out under photochemical initiation with HMPP and full conversion.

Entry	UPy-OPG-MAA		HMA ^a	Initiator ^b	Time	Yield	Solubility ^c	Processability ^d
	(mol %)	(wt %)	(mol %)	(mol %)	(min)	(wt %)		
C213	0	0	100	1.5	35	quantitative	THF, CHCl ₃	yes
C210	5	17	95	1.5	25	quantitative	swelling in hot CHCl ₃	yes
C211	10	30	90	1.5	18	quantitative	no	no
C212	20	49	80	1.5	10	quantitative	no	no
C214	100	100	0	1.5	8	quantitative	no	no

^aHexyl methacrylate. ^b2-Hydroxy-2-methyl-1-phenyl-propan-1-one was used as initiator. ^cSolubility was tested in (hot) THF, DMF, and CHCl₃ (c < 1 mg/mL). ^dMelt-processability was qualitatively explored by testing if the product could be compression-molded with a Carver® hot-press into a film upon heating up to 80 °C.

Table S6. Bulk (co)polymerization reactions carried out under photochemical initiation with HMPP between quartz glass.

Entry	UPy-OPG-MAA		HMA ^a	Initiator ^b	LHC ^c	Time
	(mol %)	(wt %)	(mol %)	(mol %)	(wt %)	(min)
C215	0	0	100	1.5	0	24
C216	5	17	95	1.5	0	15
C217	0	0	100	1.5	1	43
C219	5	17	95	1.5	1	28

^aHexyl methacrylate. ^b2-Hydroxy-2-methyl-1-phenyl-propan-1-one was used as initiator. ^cLHC = light-heat-converter, 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1'-dimethylethyl)-4-methyl-phenol.

Determination of the UPy-OPG-MAA content by elemental analysis.

Elemental analysis measurements were used to determine the UPy-OPG-MAA concentration in poly(UPy-OPG-MAA-co-HMA). UPy-OPG-MAA is the only nitrogen containing compound of the three used compounds: UPy-OPG-MAA, hexyl methacrylate (HMA) and the photoinitiator (2-Hydroxy-2-methyl-1-phenyl-propan-1-one). To calculate the nitrogen content, the following formula was used:

$$N_{calc} = \frac{x \times N_{UPy-OPG-MAA}}{(x M_{UPy-OPG-MAA} + (100 - x) M_{HMA} + 1.5 M_{Initiator})}$$

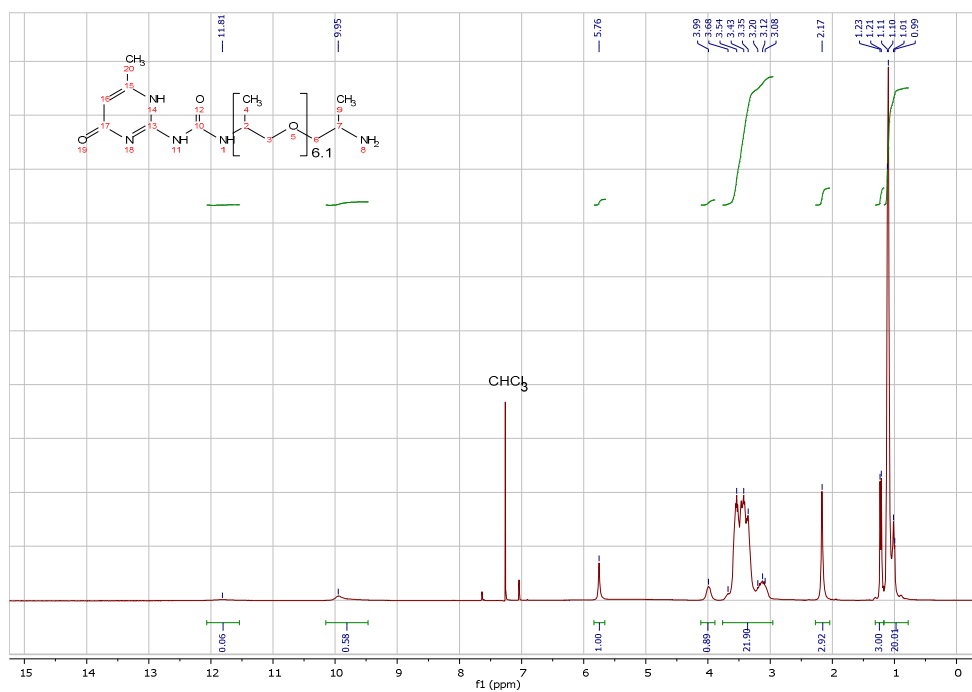
With x = mol % of UPy-OPG-MAA in the feed; $N_{UPy-OPG-MAA}$ = nitrogen content in UPy-OPG-MAA; and M_i = molecular weight of the corresponding monomers.

The calculated UPy-OPG-MAA in the polymer is the ratio of N_{found} by N_{calc} and can be found in **Table S7**.

Table S7. Results from elemental analysis

Conversion	UPy-OPG-MAA (feed) (mol %)	N (calculated) (%)	N (found) (%)	UPy-OPG-MAA (calculated) (mol %)
low	0	0	0	0
low	5	1.6	0.8	2.5
low	10	3.0	1.4	4.7
low	20	5.0	2.7	10.8
full	0	0	0	0
full	5	1.7	1.5	4.4
full	10	3.0	2.7	9.0
full	20	4.9	4.8	19.6

(a)



(b)

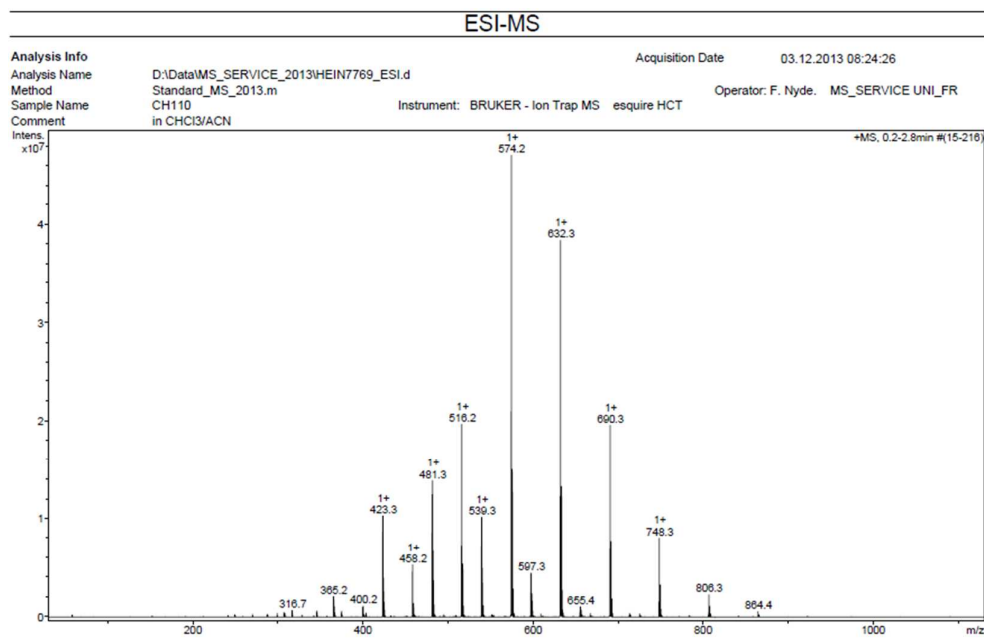
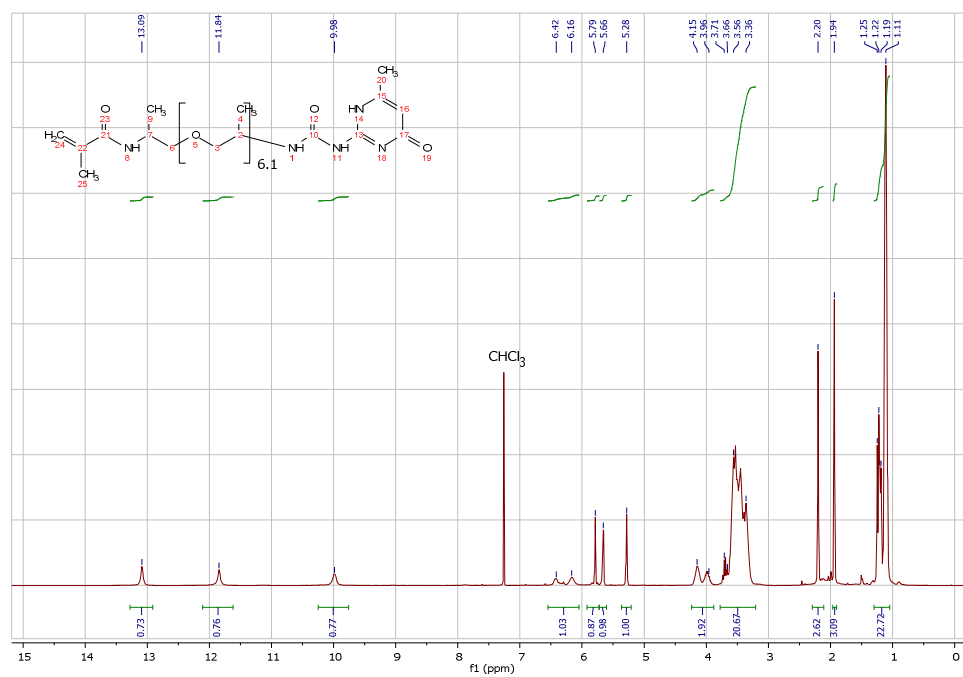


Figure S1. ¹H-NMR (a) and ESI-MS (b) spectra of UPy-OPG.

(a)



(b)

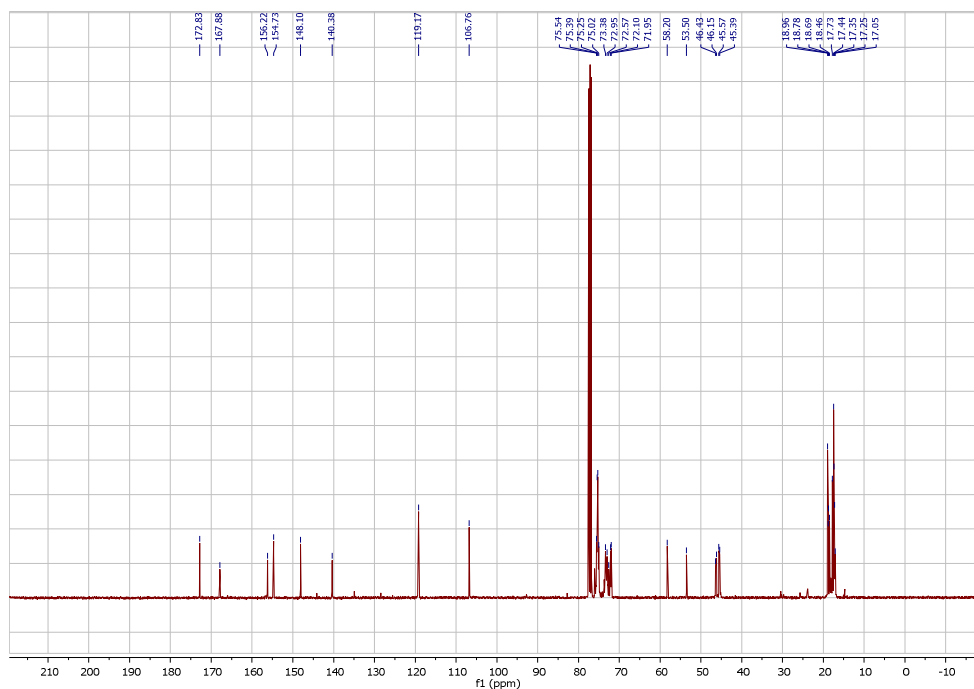
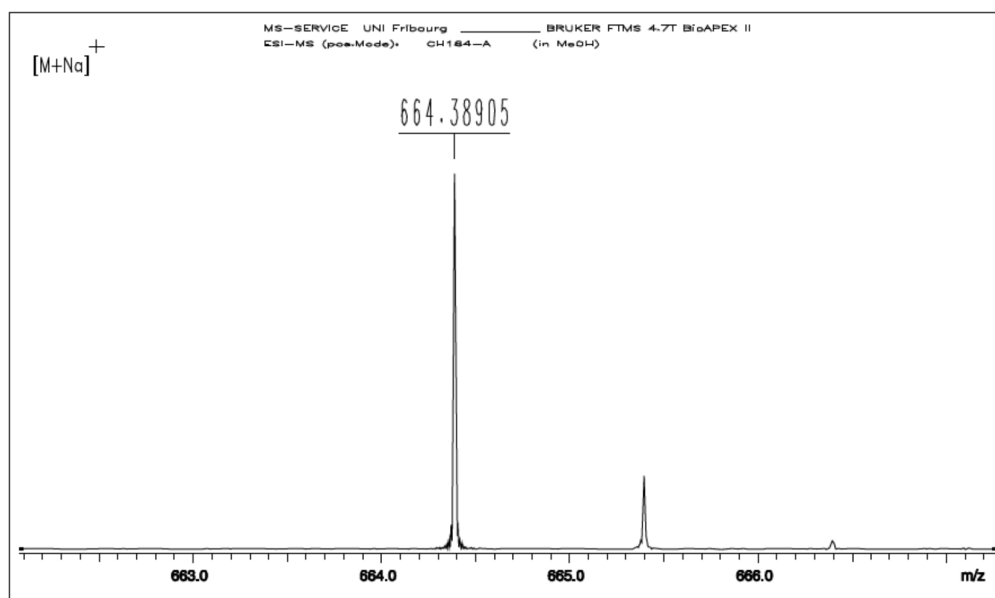


Figure S2. ¹H-NMR (a) and ¹³C-NMR (b) spectra of UPy-OPG-MAA.

(a)



(b)

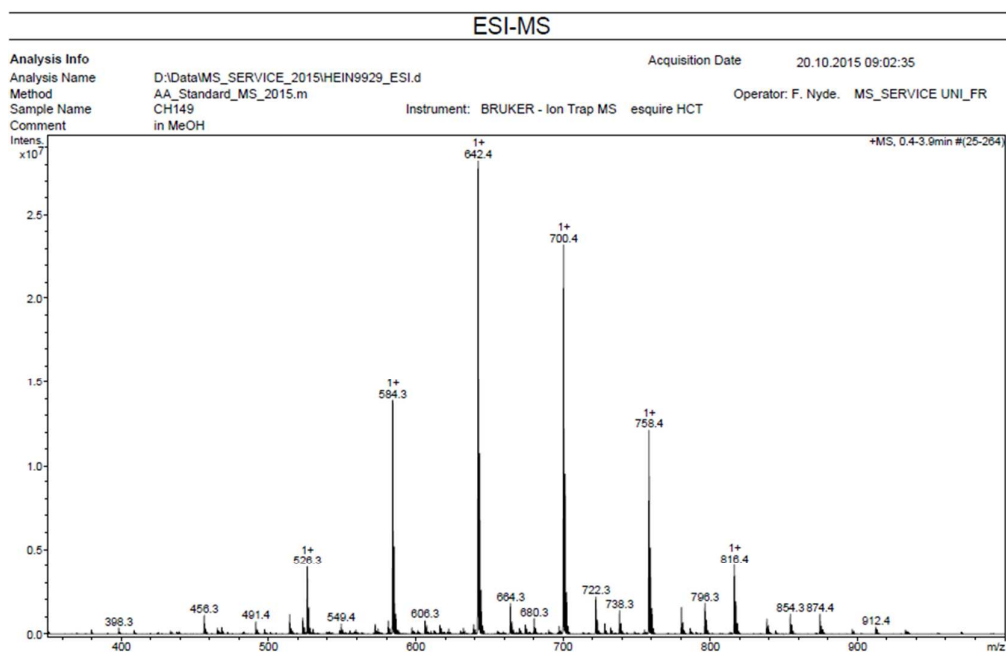


Figure S3. HR-MS (a) and ESI-MS (b) spectra of UPy-OPG-MAA.

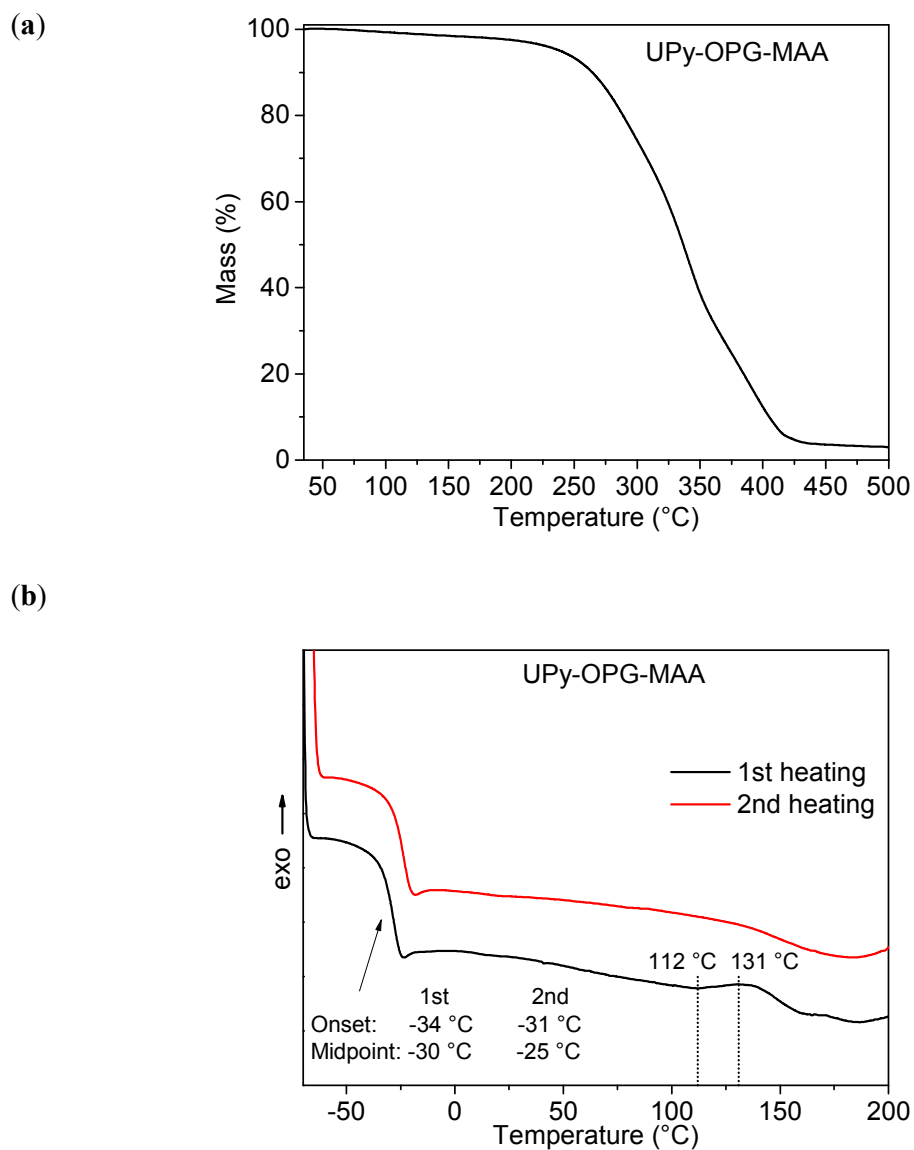


Figure S4. TGA (a) and DSC (b) traces of UPy-OPG-MAA.

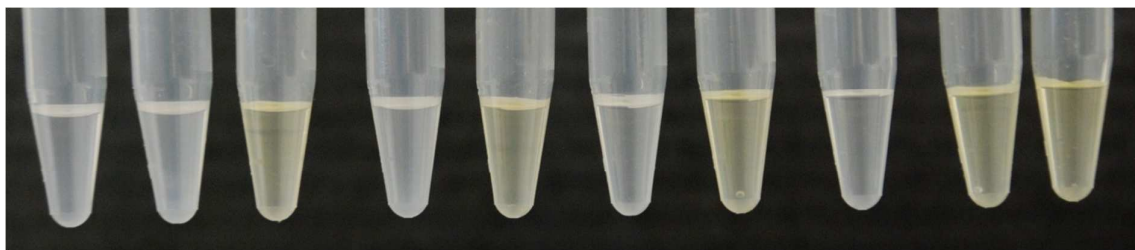


Figure S5. Picture of miscibility test of UPy-OPG-MAA with methacrylic monomers in Eppendorf tubes. From left to right: butyl methacrylate (BMA); hexyl methacrylate (HMA) : UPy-OPG-MAA, 10:1; HMA : UPy-OPG-MAA, 1:10; BMA : UPy-OPG-MAA, 10:1; BMA : UPy-OPG-MAA, 1:10; benzyl methacrylate (BnMA) : UPy-OPG-MAA, 10:1; BnMA : UPy-OPG-MAA, 1:10; 2-hydroxyethyl methacrylate (HEMA) : UPy-OPG-MAA, 10:1; HEMA : UPy-OPG-MAA, 1:10; UPy-OPG-MAA. It can be concluded from these data points, that UPy-OPG-MAA is fully miscible in all the tested monomers at any ratio.



Figure S6. Pictures of a poly(tetrafluoro ethylene) (PTFE) mold with sample cavities (30 mm x 5 mm x 0.4 mm) (large picture) and a polymer sample made with this mold (inset).

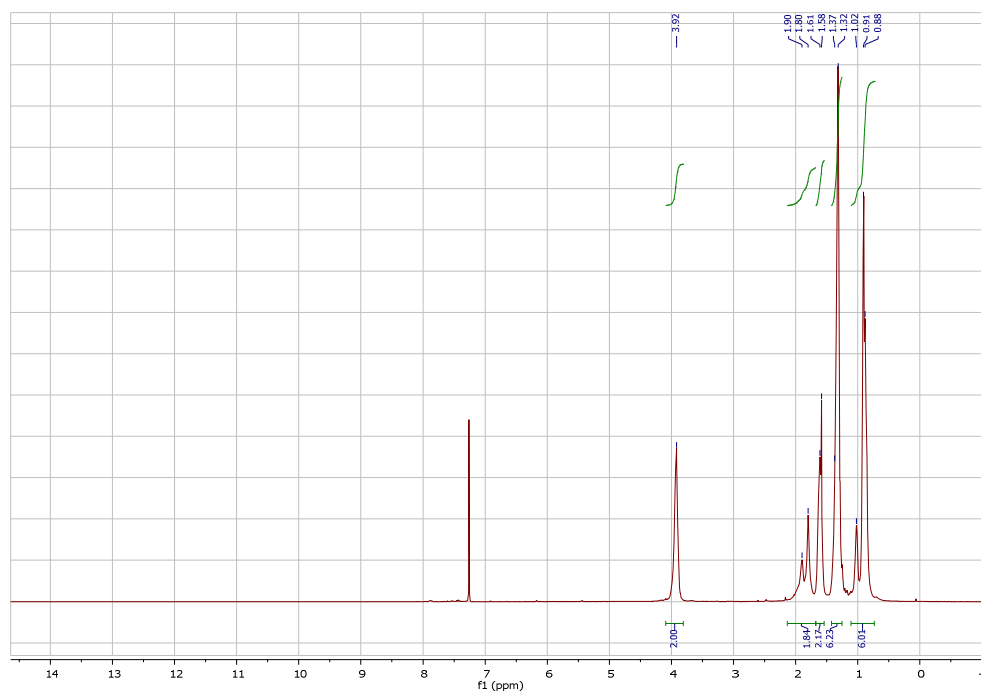


Figure S7. ^1H -NMR spectrum of poly(hexyl methacrylate) in CDCl_3 (from Table S4).

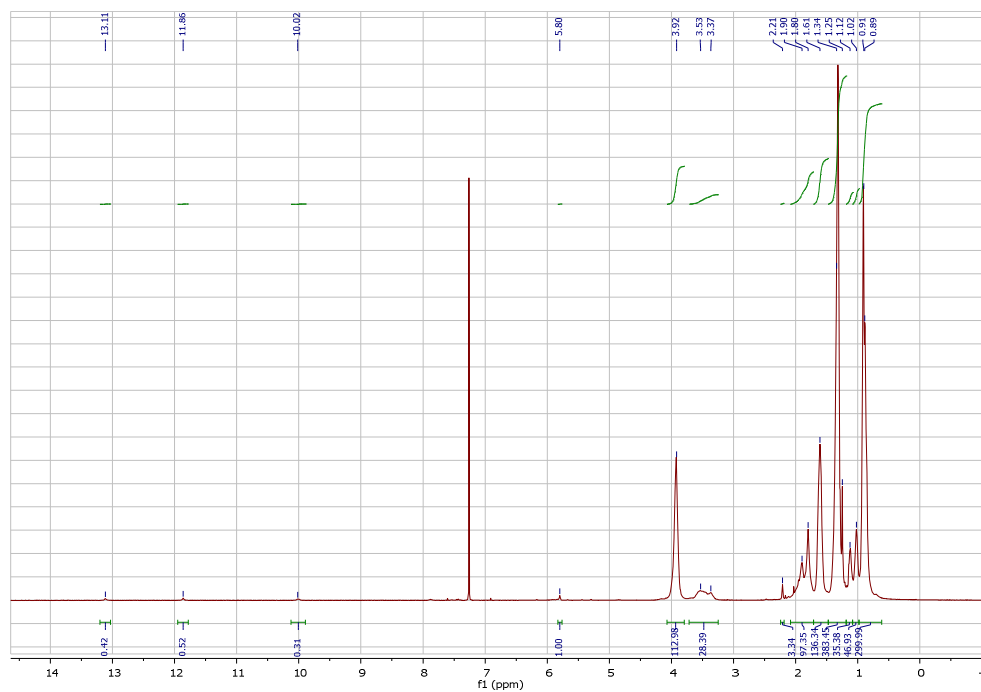


Figure S8. ^1H -NMR spectrum of 5 mol % UPy poly(UPy-OPG-MAA-co-HMA) in CDCl_3 (from Table S4).

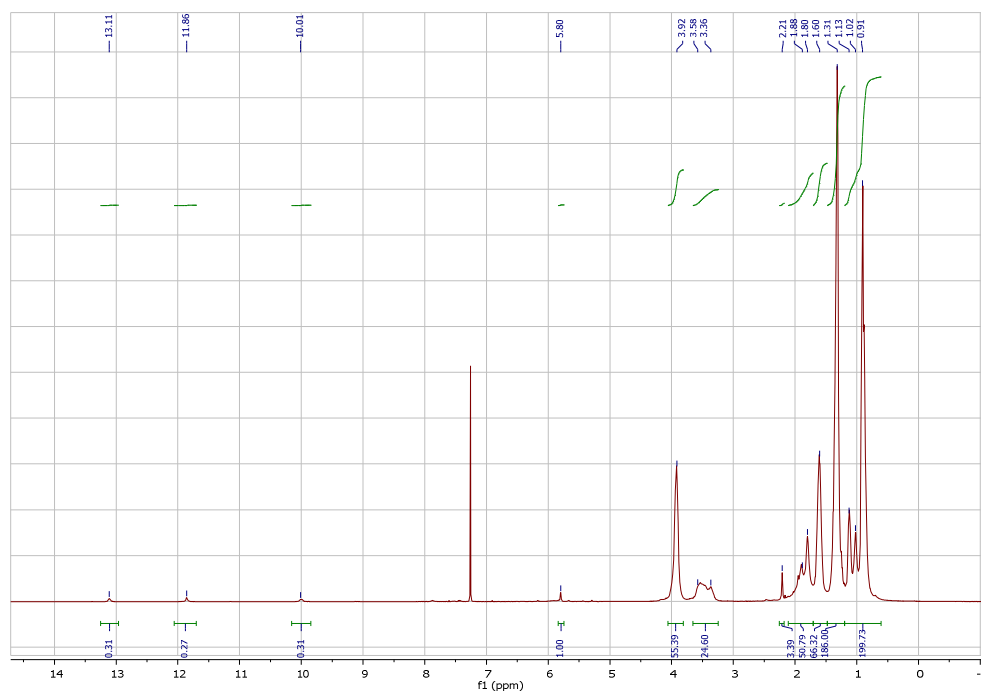


Figure S9. ¹H-NMR spectrum of 10 mol % UPy poly(UPy-OPG-MAA-co-HMA) in CDCl₃ (from Table S4).

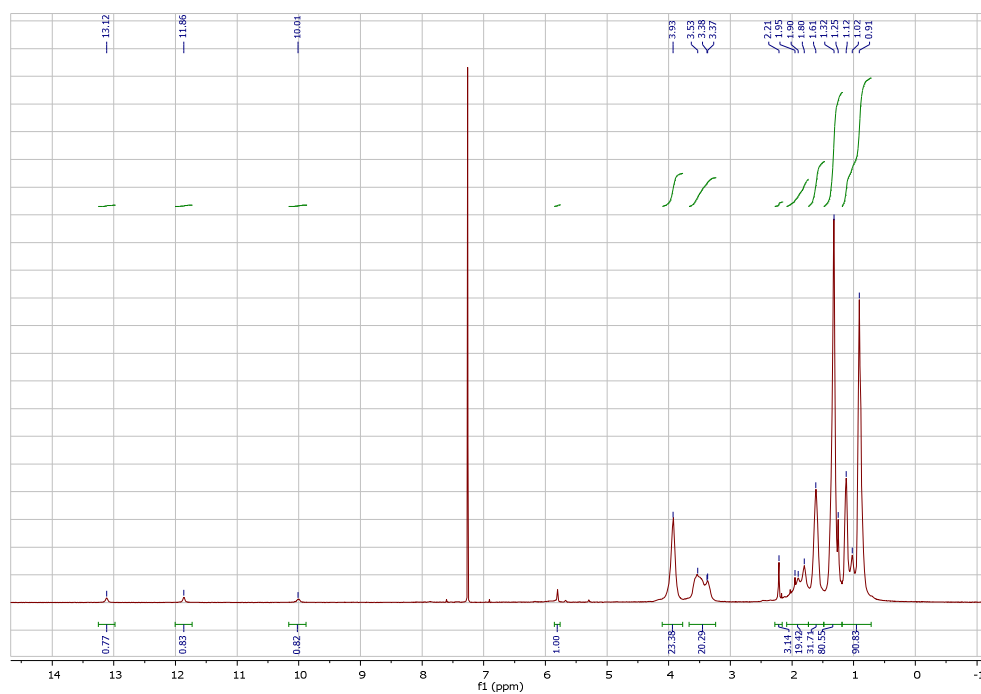
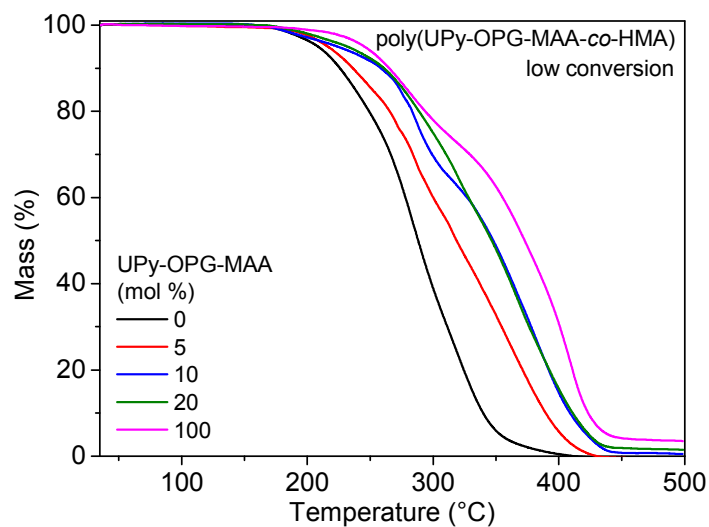


Figure S10. ¹H-NMR spectrum of 20 mol % UPy poly(UPy-OPG-MAA-co-HMA) in CDCl₃ (from Table S4).

(a)



(b)

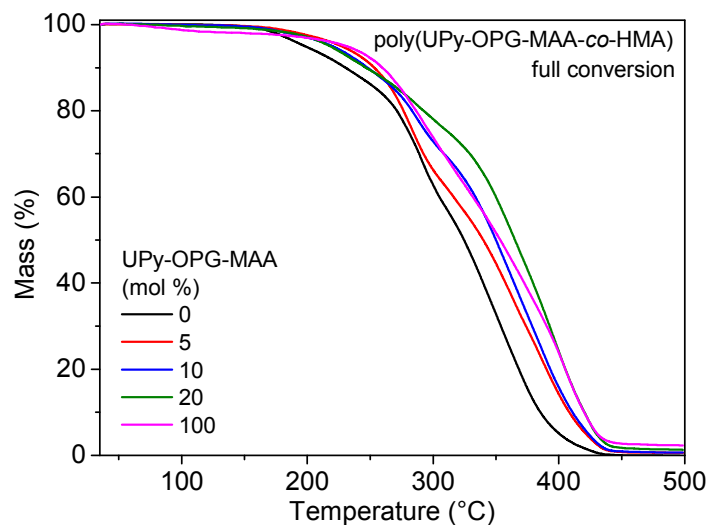


Figure S11. TGA traces of poly(UPy-OPG-MAA-co-HMA) at low conversion ((a); see **Table S4**) and full conversion ((b); see **Table S5**). The temperatures at 5 % mass loss are 208 °C (0 mol % UPy-OPG-MAA), 216 °C (5 mol %), 224 °C (10 mol %), 231 °C (20 mol %), and 245 °C (100 mol %) for the low conversion and 198 °C (0 mol %), 227 °C (5 mol %), 220 °C (10 mol %), 218 °C (20 mol %), and 231 °C (100 mol %) for the full conversion.

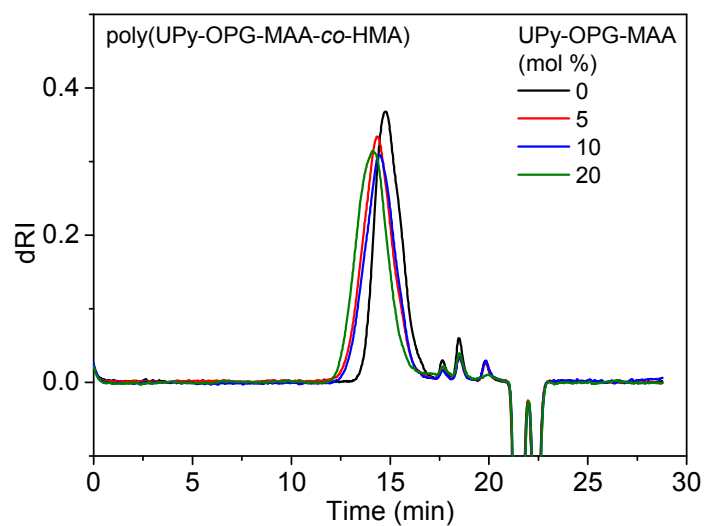


Figure S12. Size exclusion chromatography (SEC) measurements of poly(UPy-OPG-MAA-*co*-HMA) (from **Table S4**) in THF. Shown is the differential refractive index (dRI) signal against elution time at a temperature of 40 °C after injecting sample solutions with a concentration of 1 mg/mL.

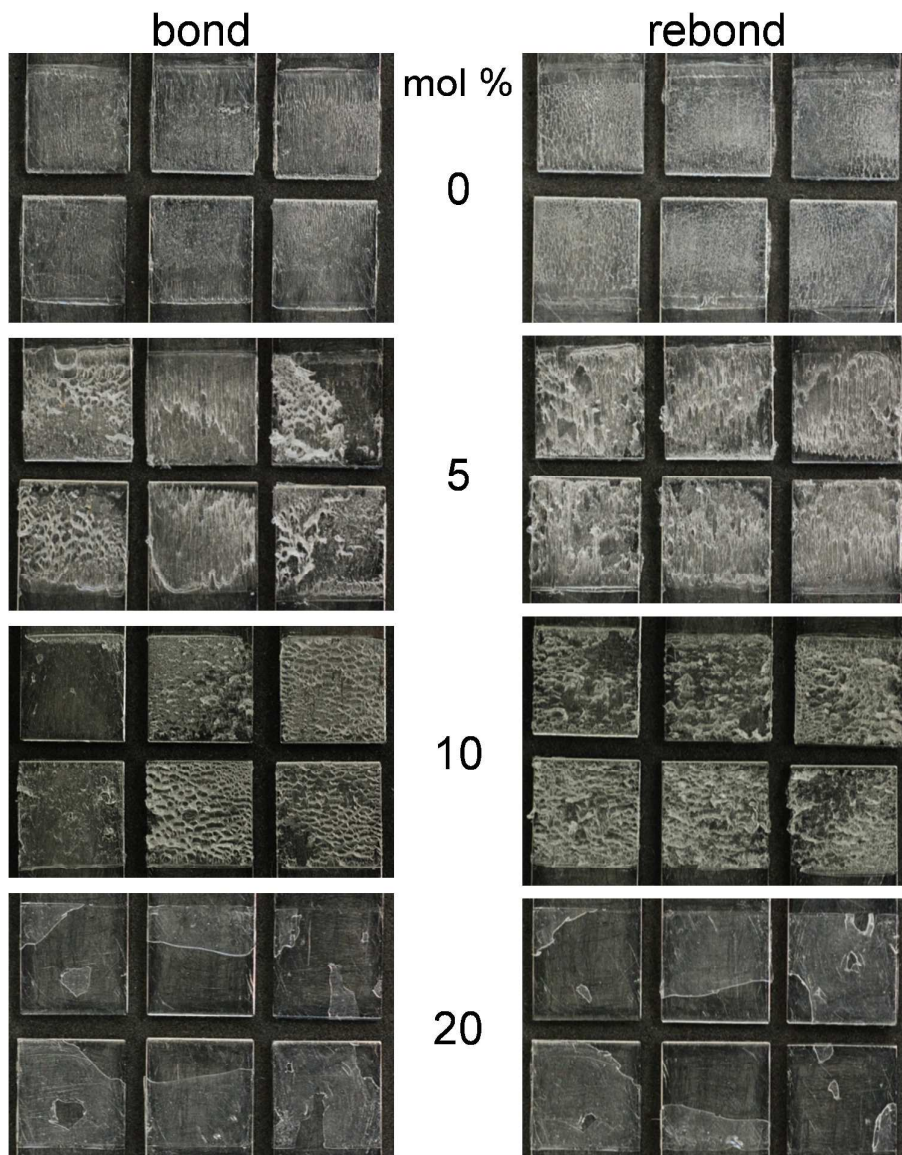
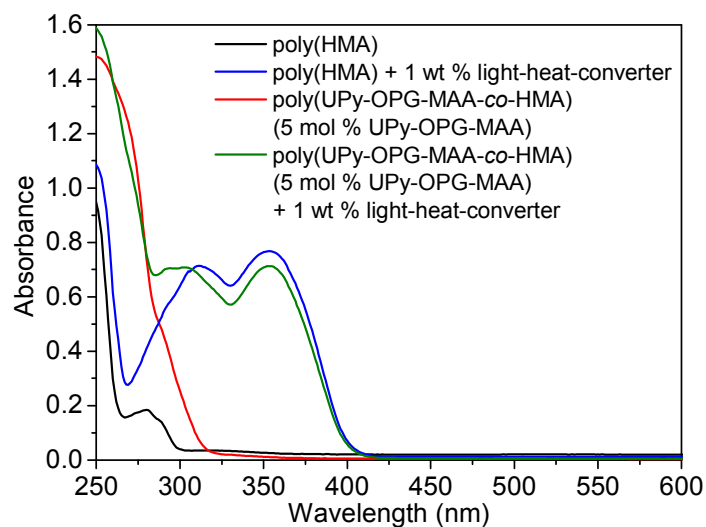


Figure S13. Pictures of lap joints bonded with poly(UPy-OPG-MAA-*co*-HMA) (**Table S4**) after shear testing original samples (bond) and samples that had been rebonded after a first shear test with the same bonding conditions (80 °C, 3 min in a preheated oven) (rebond). The UPy-OPG-MAA concentration in mol % is given in the figure.

(a)



(b)

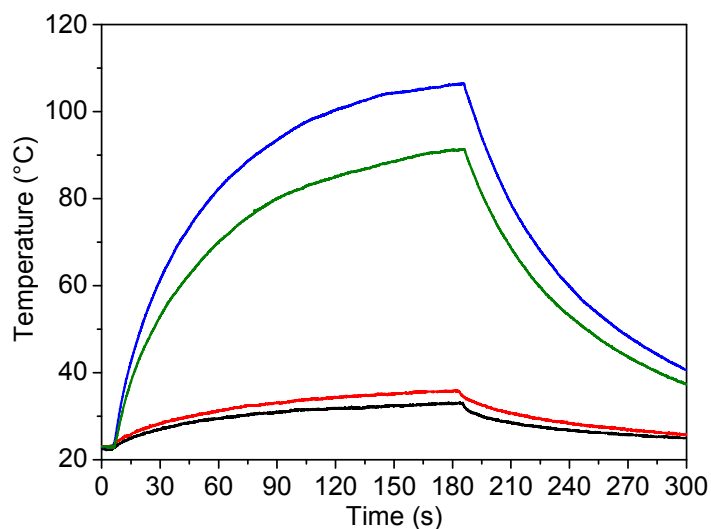


Figure S14. a) UV-Vis absorbance spectra of the polymers used for the debond on demand experiments with the polymers from **Table S6** between quartz glass lap joints. b) Temperature-time diagram of the lap joints irradiated with UV light for 3 min ($\lambda = 320\text{-}390$ nm; 900 mW/cm^2). The polymer composition for a) and b) is given in a).