Supporting Information for:

Debonding on demand with highly crosslinked photopolymers: A combination of network regulation and thermally induced gas formation

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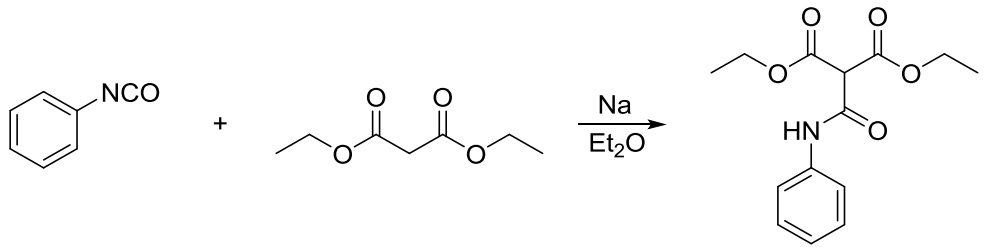
Synthesis of diethyl 2-(phenylcarbamoyl)malonate (BIC1)



DEM **BIC1**

[119.04] [160.07] [279.11]

The synthesis was performed according to literature.[1] In a 100 mL three-necked round bottom flask Na (0.36 g, 15.6 mmol) was combined with 150 mL dry diethyl ether (Et_2O) under Ar atmosphere. Over a period of approximately 30 min diethyl malonate (DEM, 2.4 g, 15 mmol) was added to the stirred solution at ambient temperature. After 24 h a white slurry was formed and phenyl isocyanate (1.77 g, 15 mmol, distilled prior to use) was added over a period of 30 min. The progress of the reaction was monitored via ATR-IR spectroscopy (NCO peak at approx. 2270 cm^{-1}) and thin layer chromatography (TLC). After about 30 minutes full conversion of the isocyanate was confirmed and the reaction was worked-up. Therefore, the white slurry was filtered off, washed with Et_2O and then dissolved in 75 mL dimethylformamide. This solution was then added to 500 mL cold HCl (2N) and the formation of a white emulsion-type precipitate was observed. The solution was then extracted four times using 100 mL ethyl acetate (EA) each. Subsequently, the organic fractions were combined and the solvent was removed using a rotary evaporator. A yellowish solid was isolated as crude product. The crude product was recrystallized using 30 mL EA. The resulting white solid was filtered off, washed with ice cold petroleum ether (PE) and dried at ambient temperature under vacuum.

Yield: 2.19 g (52% theoretical yield) white crystalline solid

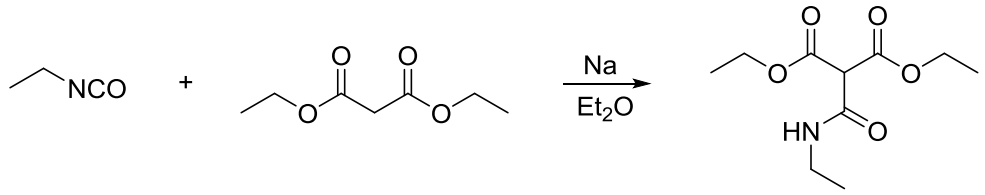
Melting point: 124 °C (Lit.: 124 °C)[2]

R_f: 0.45 (PE:EA = 3:1)

^{1}H-NMR: (200 MHz, $CDCl_3$) δ (ppm): 9.31 (s, 1H, NH), 7.59 - 7.55 (m, 2H, Ar), 7.38 - 7.30 (m, 2H, Ar), 7.17 – 7.10 (m, 1H, Ar), 4.45 (s, 1H, CH), 4.30 (q, 4H, CH_2, J = 7.0 Hz), 1.32 (t, 6H, CH_3, J = 7.0 Hz)

^{13}C-NMR: (50 MHz, $CDCl_3$) δ (ppm): 165.8 (C=O), 160.1 (C=O), 137.3 (C4), 129.1 (C3), 124.9 (C3), 120.3 (C3), 63.0 (C2), 59.7 (C3), 14.0 (C1)

Synthesis of diethyl 2-(ethylcarbamoyl)malonate (BIC2)



DEM **BIC2**

[71.04] [160.07] [231.25]

The synthesis of BIC2 was carried out in accordance to the synthesis of BIC1. Only the work-up procedure had to be adapted. Because of its good solubility in EA, the crude product was recrystallized from PE.

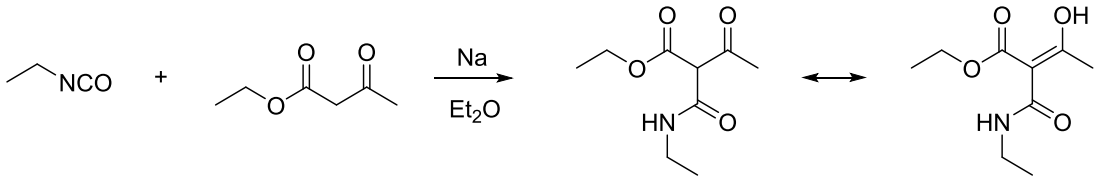
Yield: 2.16 g (62% theoretical yield) white crystalline solid

Melting point: 70-71 °C

^{1}H-NMR: (200 MHz, $CDCl_3$) δ (ppm): 7.27 (s, 1H, NH), 4.29 -4.19 (m, 5H, CH, -OCH_2), 3.40 – 3.26 (m, 2H, -NHC$\underline{H}_2$), 1.28 (t, 6H, -$OCH_2C\underline{H}_3$, J = 7.0 Hz), 1.16 (t, 3H, -$NHCH_2C\underline{H}_3$, J = 7.0 Hz)

^{13}C-NMR: (50 MHz, $CDCl_3$) δ (ppm): 165.8 (C=O), 162.1 (C=O), 62.6 (C2), 59.7 (C3), 34.8 (C2), 14.7 (C1) 14.2 (C1)

Synthesis of ethyl 2-(ethylcarbamoyl)-3-oxobutanoate (BIC3)



EAA **BIC3 keto** **BIC3 enol**

[71.04] [130.06] [201.10] [201.10]

The synthesis of BIC3 was performed according to the synthesis of BIC1. There were only minor variations in the reaction times and the purification method. The Na (40 mmol, 1.02 g) was fully dissolved after 42 h and once the ethyl isocyanate (44 mmol, 2.84 g) was added to the solution, the full conversion of the ethyl 2-acetoacetate (EAA, 40 mmol, 5.21 g) was reached after 4 h.

The crude product was purified by flash chromatography using a 1:3 mixture of PE:EA as eluent.

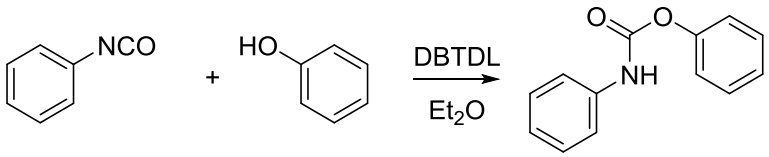
Yield: 2.57 g (32% theoretical yield.) yellowish oily liquid

R_f: 0.6 (PE:EA = 1:3)

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm): 18.56 (s, 1H, OH), 9.18 (s, 1H, NH), 4.21 (q, 2H, CH_3-C$\underline{H}_2$-O-, J = 7.2 Hz), 3.38 – 3.31 (m, 2H, CH_3-C$\underline{H}_2$-NH-), 2.41 (s, 3H, C$\underline{H}_3$-C-OH), 1.33 (t, 3H, C$\underline{H}_3$-CH_2-O-, J = 7.2 Hz), 1.19 (t, 3H, C$\underline{H}_3$-CH_2-NH-, J = 7.3 Hz) (enol-form is favored in $CDCl_3$)

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm): 191.8 (C4), 172.3 (C=O), 169.0 (C=O), 94.1 (C4), 60.4 (C2), 34.2 (C2), 26.4 (C1), 14.5 (C1), 14.3 (C1) (enol-form is favored in $CDCl_3$)

Synthesis of phenyl N-phenylcarbamate (BIC4)



BIC4

[119.04] [94.04] [213.08]

In a 100 mL three-necked round bottom flask phenol (75 mmol, 7.05 g) was dissolved in 500 mL dry Et_2O and dibutyltin dilaurate (0.06 g) was added. Phenyl isocyanate (75 mmol, 8.85 g, distilled prior to use) was added over a period of 30 min. After 18 h the conversion of the isocyanate was complete and the solvent was removed on the rotary evaporator.

The crude product was purified by recrystallization in 200 mL of a 3:1 mixture of PE:EA. (35 °C respectively -20 °C). After about 5 h a fine crystalline solid was filtered off and dried at room temperature under high vacuum.

Yield: 15 g (94% theoretical yield) white crystalline solid

Melting point: 125 - 127 °C (Lit.: 125 - 127 °C)[3]

^{1}H-NMR: (400 MHz, DMSO) δ (ppm): 10.26 (s, 1H, NH), 7.58 – 7.56 (m, 2H, CH), 7.45 – 7.41 (m, 2H, CH), 7.35 – 7.31 (m, 2H, CH) 7.27 – 7.23 (m, 3H, CH), 7.07 – 7.03 (m, 1H, CH)

^{13}C-NMR: (100 MHz, DMSO) δ (ppm): 152.2 (C4), 151.0 (C=O), 139.1 (C4), 129.9 (C3), 129.8 (C3), 129.4 (C3), 129.3 (C3), 125.9 (C3), 123.4 (C3), 122.4 (C3), 119.3 (C3), 119.0 (C3), 115.73 (C3)

Simultaneous thermal analysis (TGA and DSC) of BICs (BIC1-4) neat

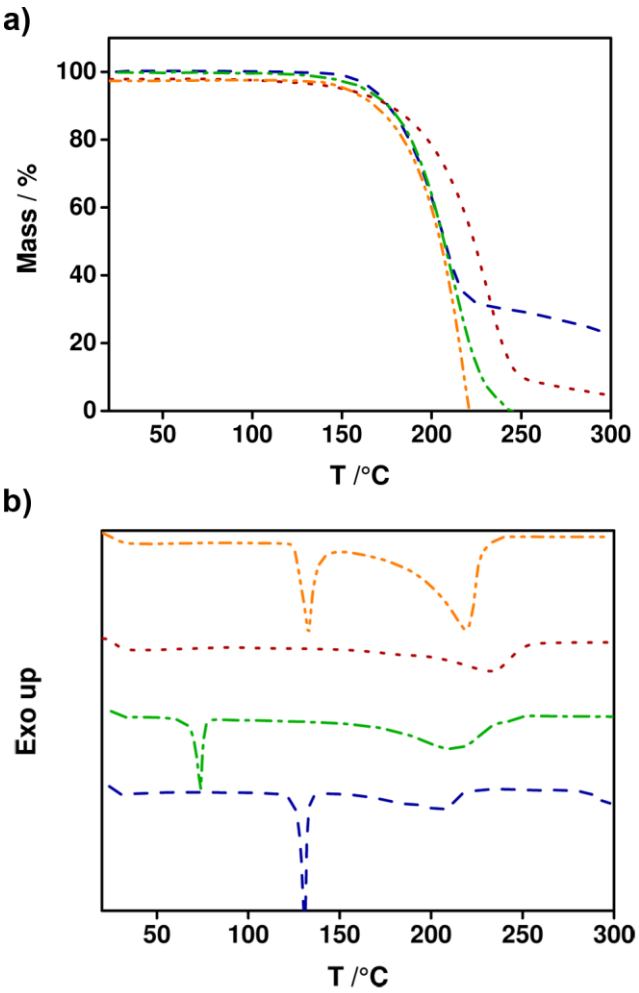


Figure S1. a) TGA and b) DSC plots of BIC1 (---), BIC2 (-•-), BIC3 (•••), and BIC4 (-••).

Pictures from thermomicroscopy experiments

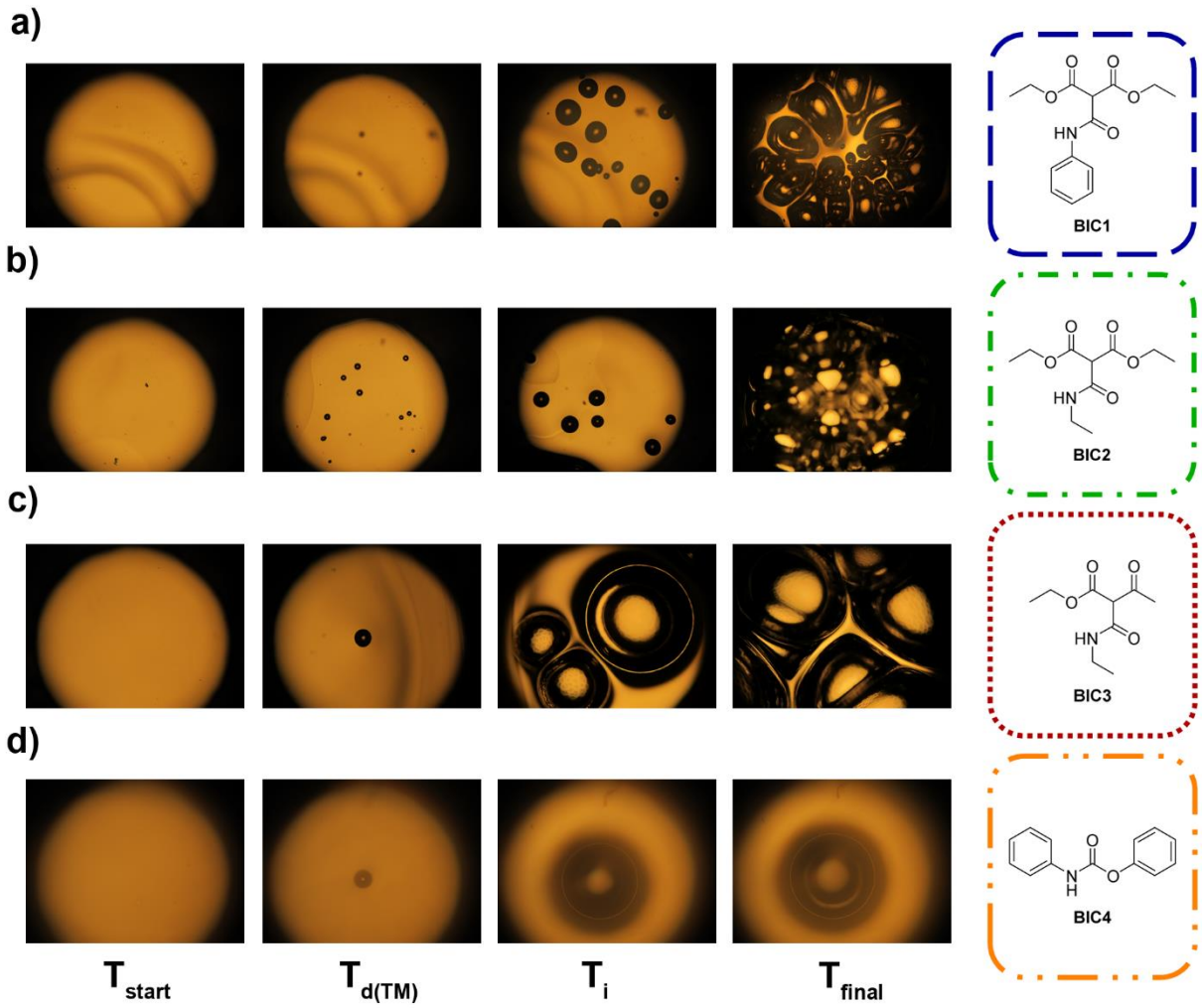


Figure S2. Picture series for thermomicroscopy experiments, a) polyNAM/BIC1, b) polyNAM/BIC2, c) polyNAM/BIC3, d) polyNAM/BIC4.

Table S1. Temperatures from thermomicroscopy experiments (T_{start} … starting temperature; $T_{d(TM)}$ … temperature, at which first gas bubbles appeared; T_i … temperature, at which the rate of gas evolution increased; T_{final} … final temperature, at which gas evolution slowed down).

polymer	T_{start} / °C	$T_{d(TM)}$ / °C	T_i / °C	T_{final} / °C
polyNAM/BIC1	100	116 ± 1	124 ± 4	131 ± 3
polyNAM/BIC2	100	113 ± 2	121 ± 5	129 ± 6
polyNAM/BIC3	100	136 ± 5	149 ± 4	161 ± 7
polyNAM/BIC4	100	174 ± 4	190 ± 1	203 ± 3

DMTA of polyNAM without and with BICs (BIC1-4)

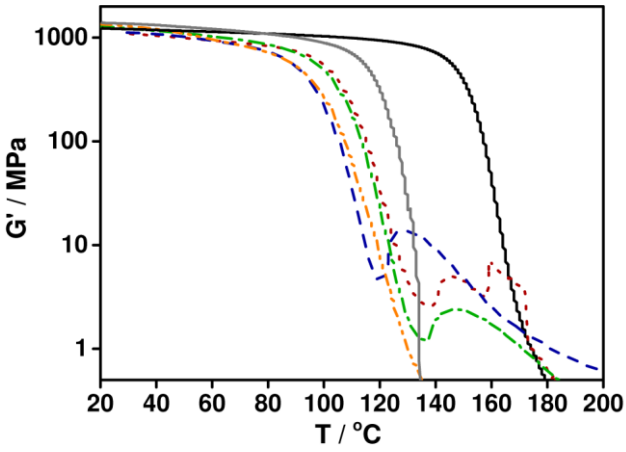


Figure S3. Storage modulus (G') plots of polyNAM (—) and polyNAM with added DEP (—), BIC1 (---), BIC2 (-•-), BIC3 (•••), and BIC4 (-••), respectively.

Cleavage mechanism of β-ketoester-blocked BIC3

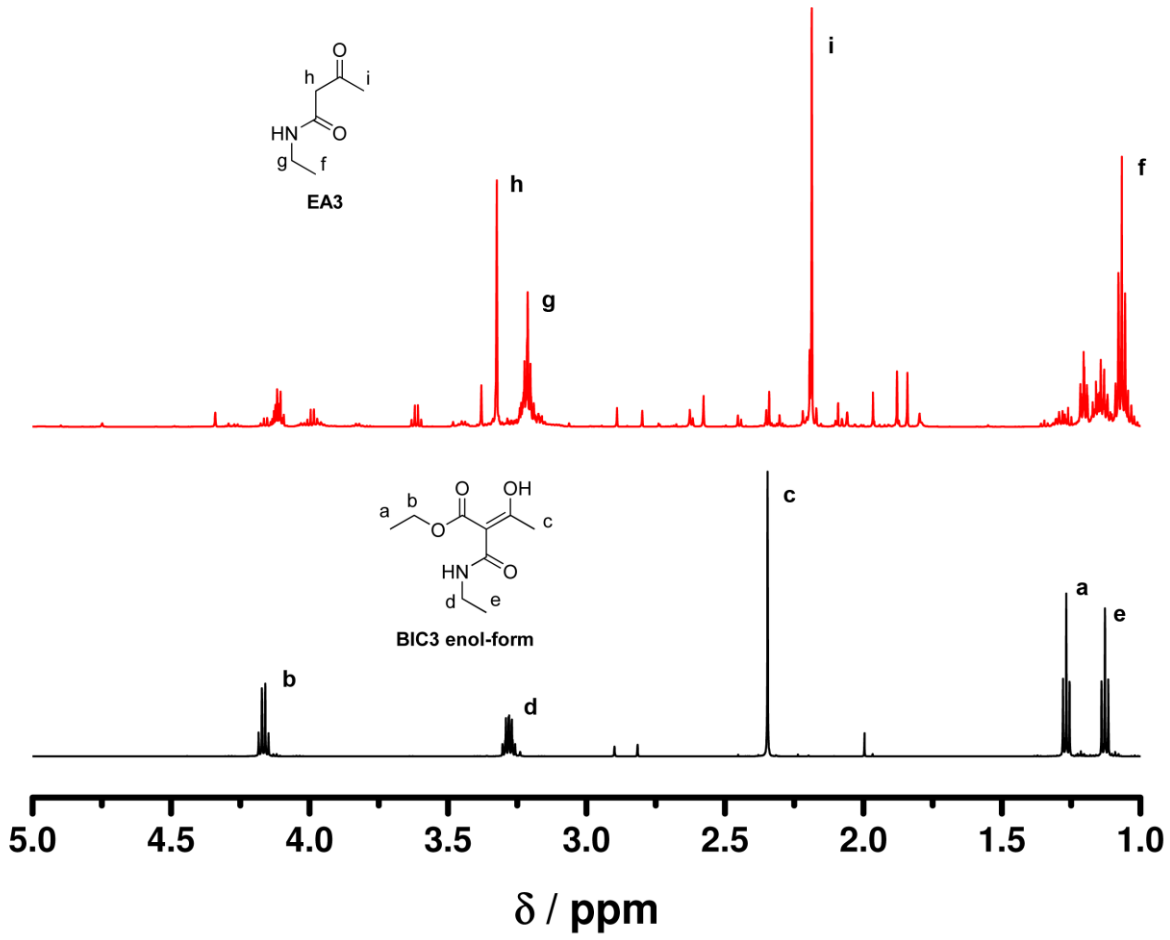


Figure S4. ^{1}H-NMR spectra of BIC3 before (bottom, black) and after thermal treatment (top, red).

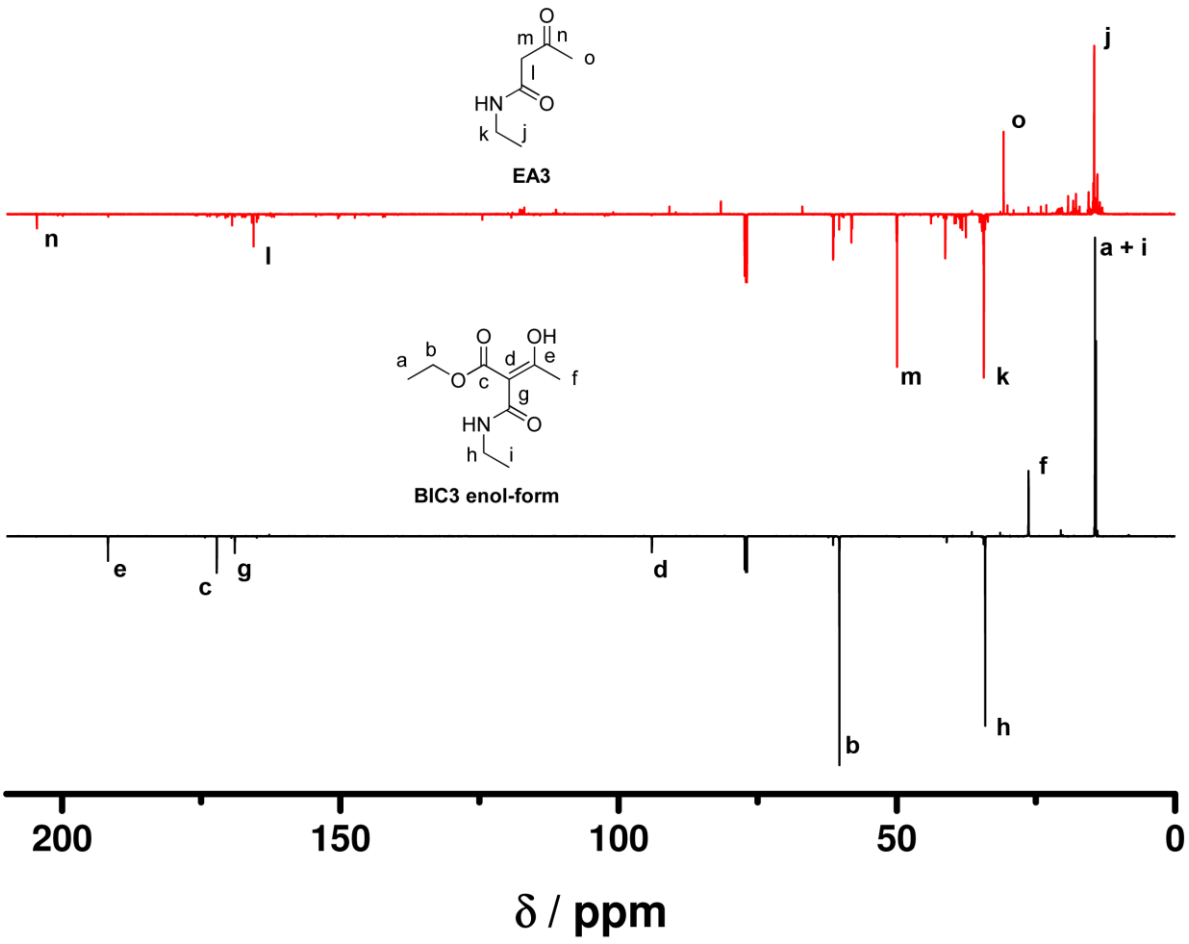
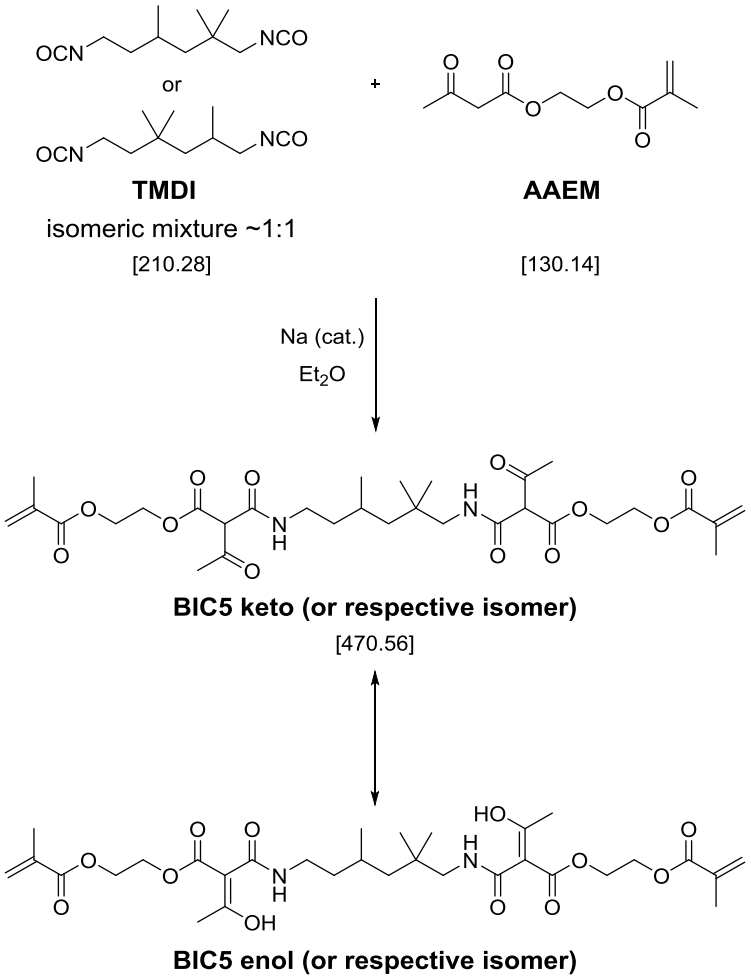


Figure S5. ^{13}C-NMR spectra of BIC3 before (bottom, black) and after thermal treatment (top, red).

Synthesis of a thermolabile photopolymerizable crosslinker (BIC5)

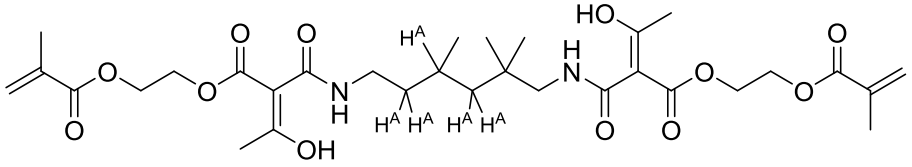


For the synthesis of bis(2-(methacryloyloxy)ethyl) 2,2'-(((2,2,4-trimethylhexane-1,6-diyl) bis(azanediyl)) bis(carbonyl))bis(3-oxobutanoate) (BIC5, or respective 2,4,4-trimethyl-isomer) a 500 mL three-necked round bottom flask was purged with Ar and charged with Na (0.5 g, 2.2 mmol) and 400 mL of dry Et_2O. The methacrylate AAEM (85.69 g, 0.4 mol) was slowly added and the mixture was stirred at ambient temperature until all Na was dissolved. Then the reaction mixture was cooled to -5 °C with a NaCl ice bath and TMDI (42.06 g, 0.2 mol, distilled prior to use) was added dropwise over the course of approximately 1 h. The reaction was monitored via TLC and ATR-IR spectroscopy. After full conversion of the isocyanate (no NCO-Peak observed in the ATR-IR spectrum, approx. 3 d), the reaction mixture was worked up. First the solution was washed with HCl (1 N, 2 x 100 mL) and

deionized water (100 mL). The collected washing solutions were extracted with Et_2O (100 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was evaporated and the crude product was purified via column chromatography (PE:EA = 1:1).

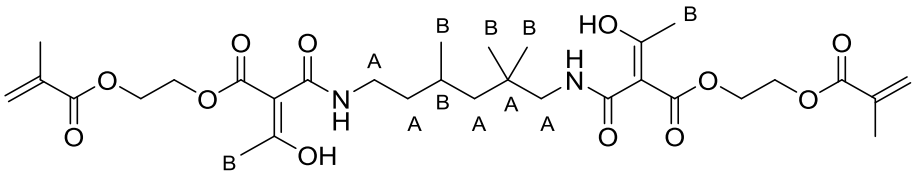
Yield: 105.42 g (83% theoretical yield) viscous liquid

R_f: 0.82 (PE:EA = 1:1)



BIC5 enol-form

^{1}H-NMR: (200 MHz, $CDCl_3$) δ (ppm): 18.69 (bs, 1H; =C(OH)CH_3), 18.67 (bs, 1H; =C(OH)CH_3), 9.31 (m, 1H; -NH-), 9.09 (m, 1H; -NH-), 6.11 (s, 2H; =CH_2), 5.59 (m, 2H; =CH_2), 4.41 (s, 8H; -OCH_2CH_2O-), 3.39-2.95 (m, 4H; -$NHCH_2$-), 2.39 (s, 6H; =C(OH)CH_3), 1.94 (s, 6H; =C-CH_3), 1.88-1.38 (m, 3H; H^A), 1.36-1.04 (m, 2H; H^A), 1.02-0.95 (m, 3H; -CH_3), 0.93 (s, 6H; -CH_3). (enol-form is favored in $CDCl_3$)



BIC5 enol-form

^{13}C-NMR: (50 MHz, $CDCl_3$) δ (ppm): 192.9-192.5 (m, C4), 172.5-172.1 (m, C=O), 169.1-168.5 (m, C=O), 167.0 (C=O), 135.8 (C4), 126.1 (C2), 93.7-93.5 (m, C4), 62.3 (C2), 62.1 (C2), 49.4 (C^A), 46.8 (C^A), 46.7 (C^A), 46.4 (C^A), 41.4 (C^A), 38.5 (C^A), 37.4 (C^A), 35.6 (C^A), 34.8 (C^A), 33.0 (C^A), 29.0 (C^B), 27.2 (C^B), 27.1 (C^B), 26.7 (C^B), 26.6 (C^B), 26.5 (C^B), 26.5 (C^B), 25.5 (C^B), 22.3 (C^B), 20.7 (C^B), 18.2 (C1). (enol-form is favored in $CDCl_3$)

Elemental analysis: Anal. calcd. for $C_{31}H_{46}N_2O_{12}$: C 58.30, H 7.26, N 4.39, O 30.06; found: C 58.51, H 7.50, N 4.50, O 30.05.

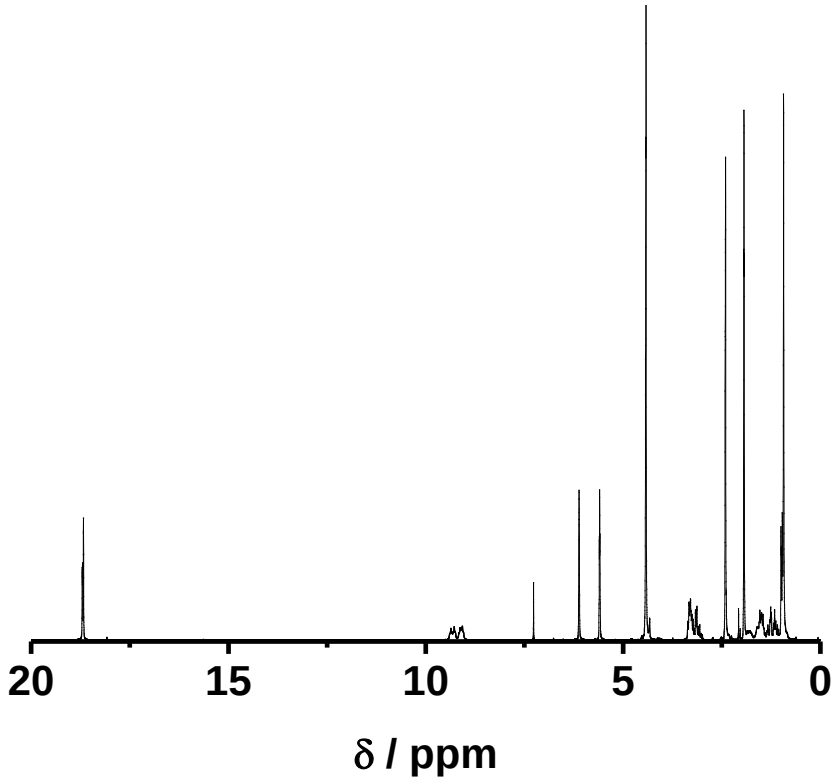


Figure S6. ^{1}H-NMR spectrum of BIC5.

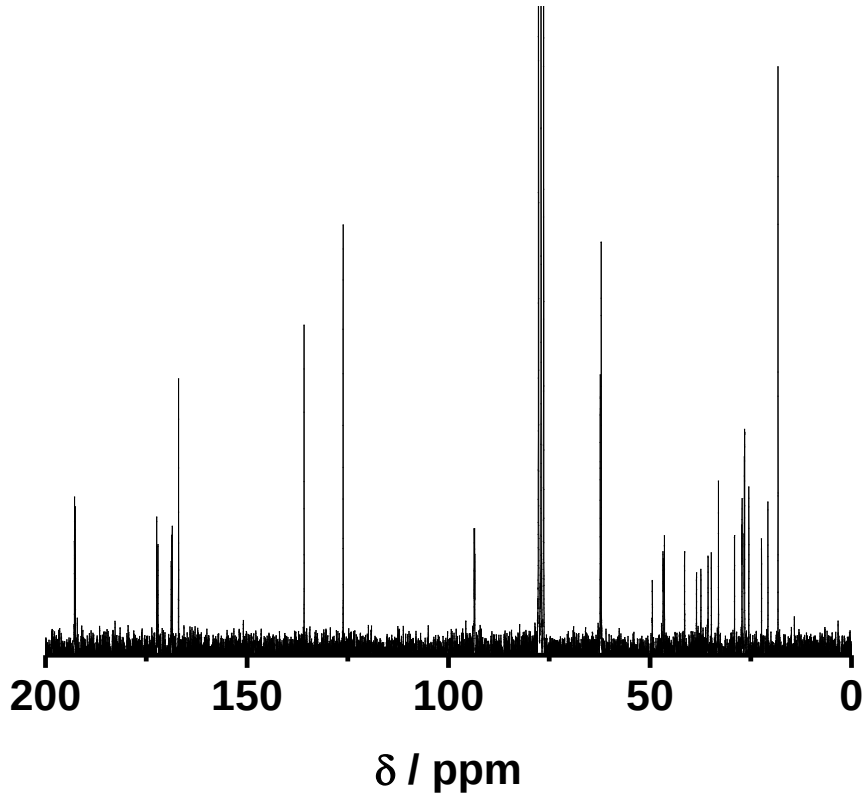


Figure S7. ^{13}C-NMR spectrum of BIC5.

Simultaneous thermal analysis (TGA and DSC) of polyBIC5

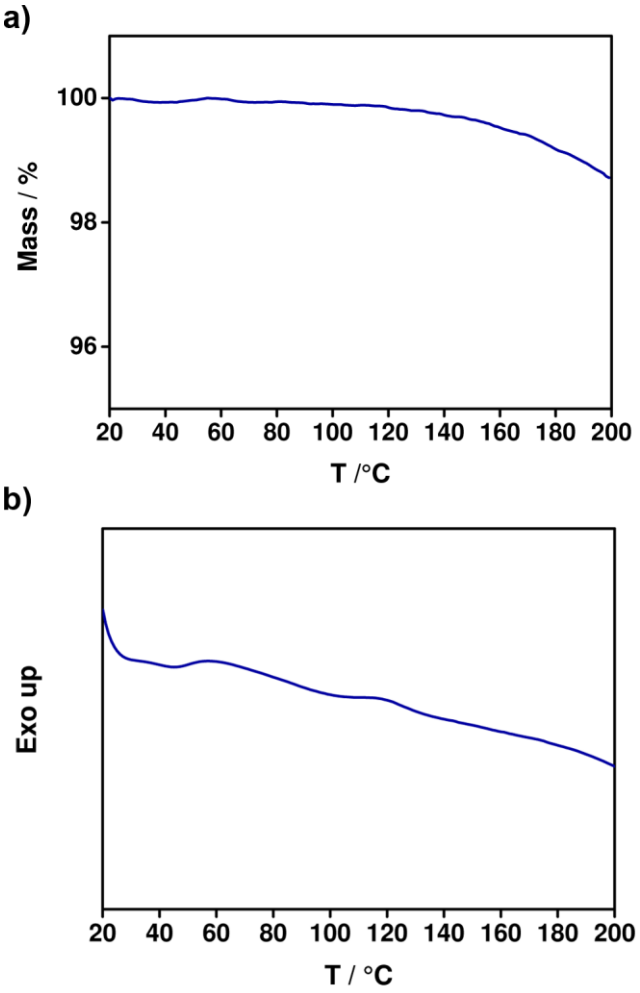


Figure S8. a) TGA and b) DSC plot of polyBIC5 (—).

Pictures from thermomicroscopy experiments

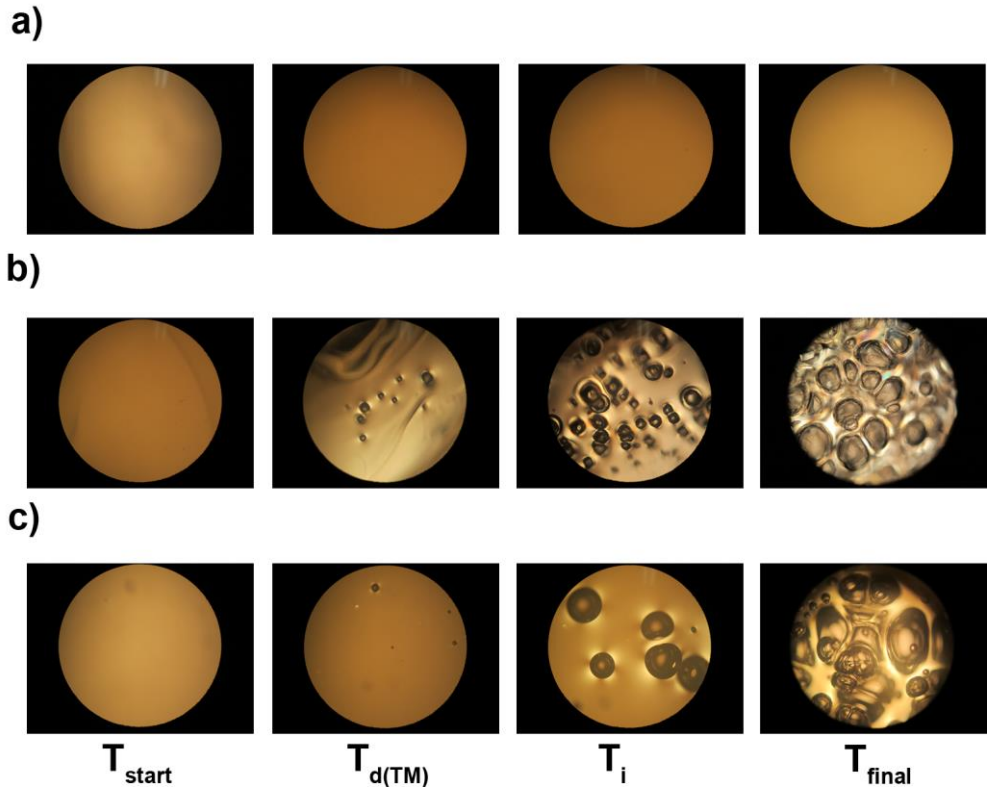


Figure S9. Picture series for thermomicroscopy experiments, a) polyBIC5, b) polyNAM/BIC5, c) poly(BIC5-co-DAS).

Table S2. Temperatures from thermomicroscopy experiments (T_{start} … starting temperature; $T_{d(TM)}$ … temperature, at which first gas bubbles appeared; T_i … temperature, at which the rate of gas evolution increased; T_{final} … final temperature, at which gas evolution slowed down).

polymer	T_{start} / °C	$T_{d(TM)}$ / °C	T_i / °C	T_{final} / °C
polyBIC5	100	-	-	-
polyNAM/BIC5	100	138 ± 3	171 ± 2	185 ± 3
poly(BIC5-co-DAS)	100	138 ± 1	150 ± 3	160 ± 3

Table S3. Results for tensile (σ_{max} … maximum stress; ε_{break} … strain at break) and Dynstat tests (a … impact resistance).

polymer	before thermal treatment			after thermal treatment		
	σ_{max} / N mm^{-2}	ε_{break} / %	a / kJ m^{-2}	σ_{max} / N mm^{-2}	ε_{break} / %	a / kJ m^{-2}
polyUDMA	78 ± 18	7.3 ± 1.8	5.3 ± 1.1	59 ± 14	4.4 ± 1.6	3.6 ± 0.6
polyBIC5	68 ± 7	5.0 ± 1.1	2.5 ± 0.7	61 ± 2	7.6 ± 0.9	2.5 ± 0.8
poly(UDMA-co-DAS)	88 ± 3	9.7 ± 2.4	6.3 ± 0.4	67 ± 3	4.7 ± 0.4	4.7 ± 1.8
poly(BIC5-co-DAS)	69 ± 10	5.6 ± 1.8	4.5 ± 0.9	27 ± 7	5.1 ± 1.5	0.3 ± 0.1

DoD test

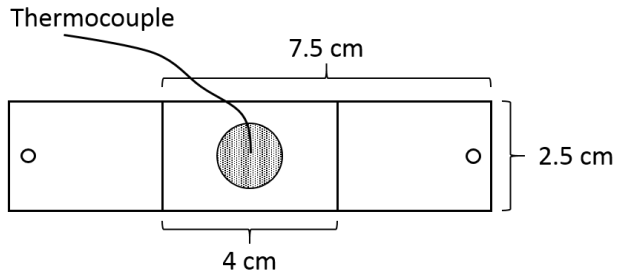


Figure S10. Schematic illustration of the fabricated DoD test specimens.

Link to DoD video

References

1. Meyrick, T. J.; Parry, E. G.; Watts, J. T. Adhesives. US2826526, 1958.
2. Dieckmann, W.; Hoppe, J.; Stein, R., Over the Behavior of 1,3-Dicarbonyl Compounds Against Phenylisocyanate. [machine translation]. *Ber. Dtsch. chem. Ges.* **1904,** 37, 4627-38.
3. Ho, B. T.; An, R.; Noel, M. B.; Tansey, L. W., Central nervous system depressive activity of some amides of tryptamine. *Journal of Medicinal Chemistry* **1971,** 14, (6), 553-554.