

# Thermally Induced Shape-Memory Behavior of Degradable Gelatin-Based Networks

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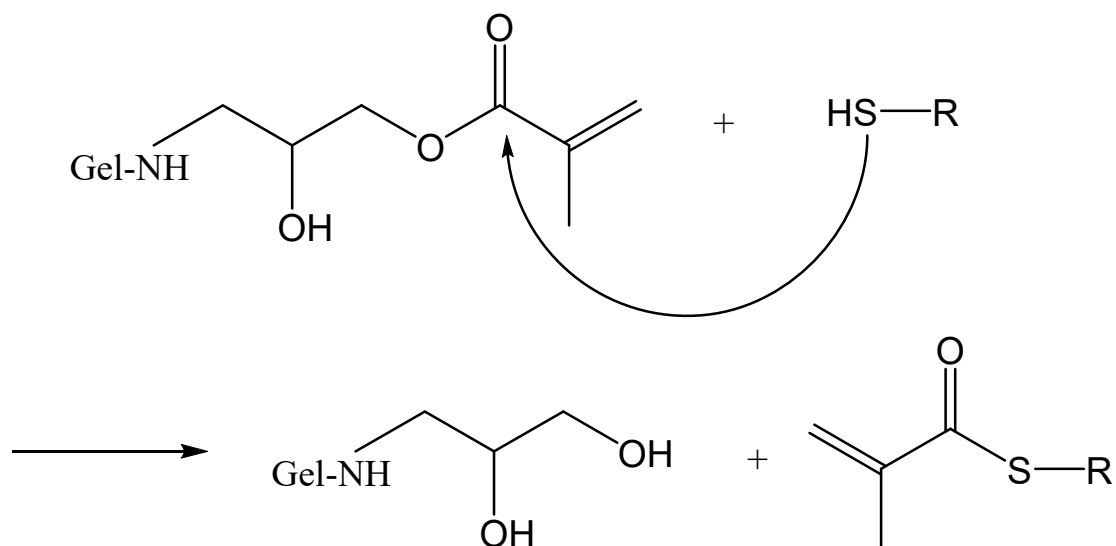
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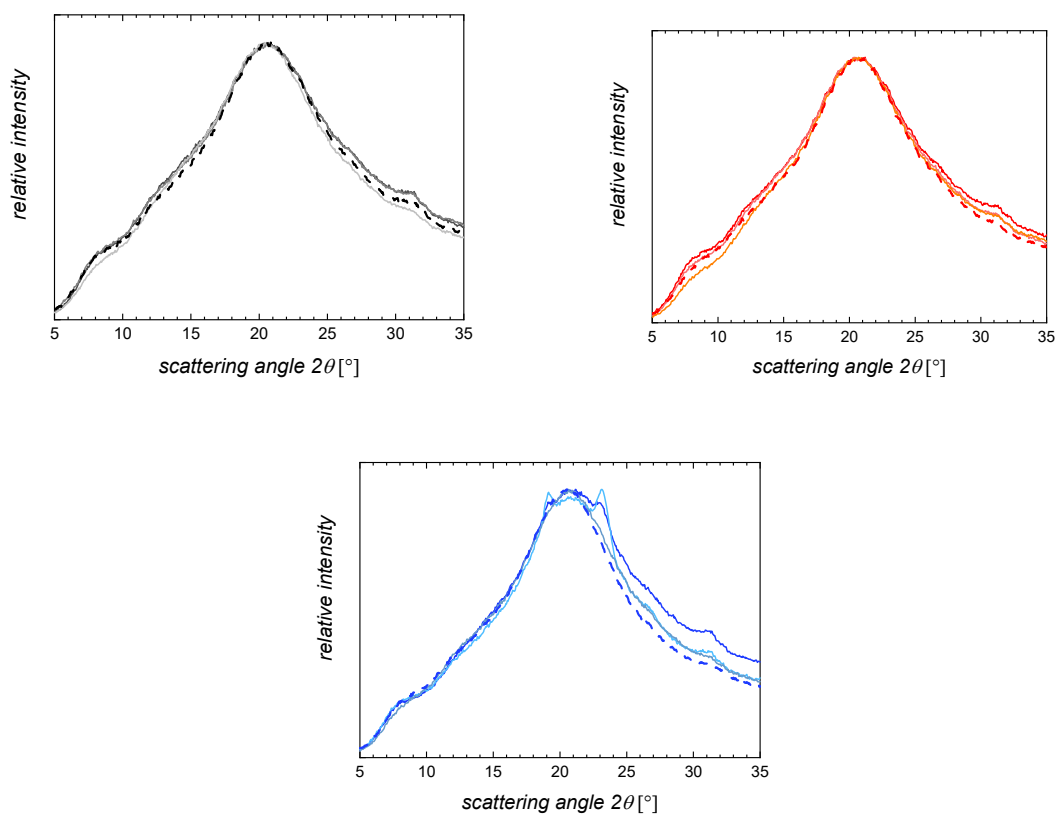
**Table S1.** Gel content (G) and volumetric degree of swelling (Q) at defined temperatures for different hydrogel compositions.

<i>Sample ID<sup>a</sup></i>	<i>G</i> [wt%]	<i>Q</i> 4 °C [vol%]	<i>Q</i> 37 °C [vol%]	<i>Q</i> 55 °C [vol%]
G20_OEG1000(0.75)	86 ± 2	1180 ± 80	1110 ± 80	1030 ± 60
G20_OEG1000(1)	89 ± 2	1080 ± 30	1010 ± 50	940 ± 50
G20_OEG1000(2)	83 ± 2	1630 ± 90	1610 ± 120	1620 ± 30
G20_OEG1000(3)	71 ± 4	3050 ± 210	3050 ± 360	2680 ± 30
G20_OEG1500(0.75)	86 ± 1	1270 ± 90	1290 ± 80	1210 ± 60
G20_OEG1500(1)	87 ± 1	1260 ± 40	1290 ± 30	1250 ± 90
G20_OEG1500(2)	82 ± 2	1690 ± 70	1730 ± 70	1700 ± 80
G20_OEG1500(3)	77 ± 3	2950 ± 70	2960 ± 60	2950 ± 80
G20_OEG3400(0.75)	86 ± 1	1340 ± 40	1280 ± 40	1290 ± 130
G20_OEG3400(1)	81 ± 1	1620 ± 70	1630 ± 120	1640 ± 170
G20_OEG3400(2)	72 ± 2	2410 ± 150	2390 ± 200	2400 ± 130
G20_OEG3400(3)	42 ± 8	2890 ± 100	2970 ± 160	2900 ± 160

a: nomenclature: G20\_OEG<sub>y</sub>(*z*), with G20 = 20 wt% concentration of gelatin in the crosslinking step, *y* = number average molar mass *M<sub>n</sub>* of the OEG crosslinkers and *z* the thiol:methacrylate molar ratio.



**Figure S1.** Thioester formation by reaction of a thiol with a glycidylmethacrylate group on GMA-gelatin as side reaction increasing in importance with increasing amount of thiols.

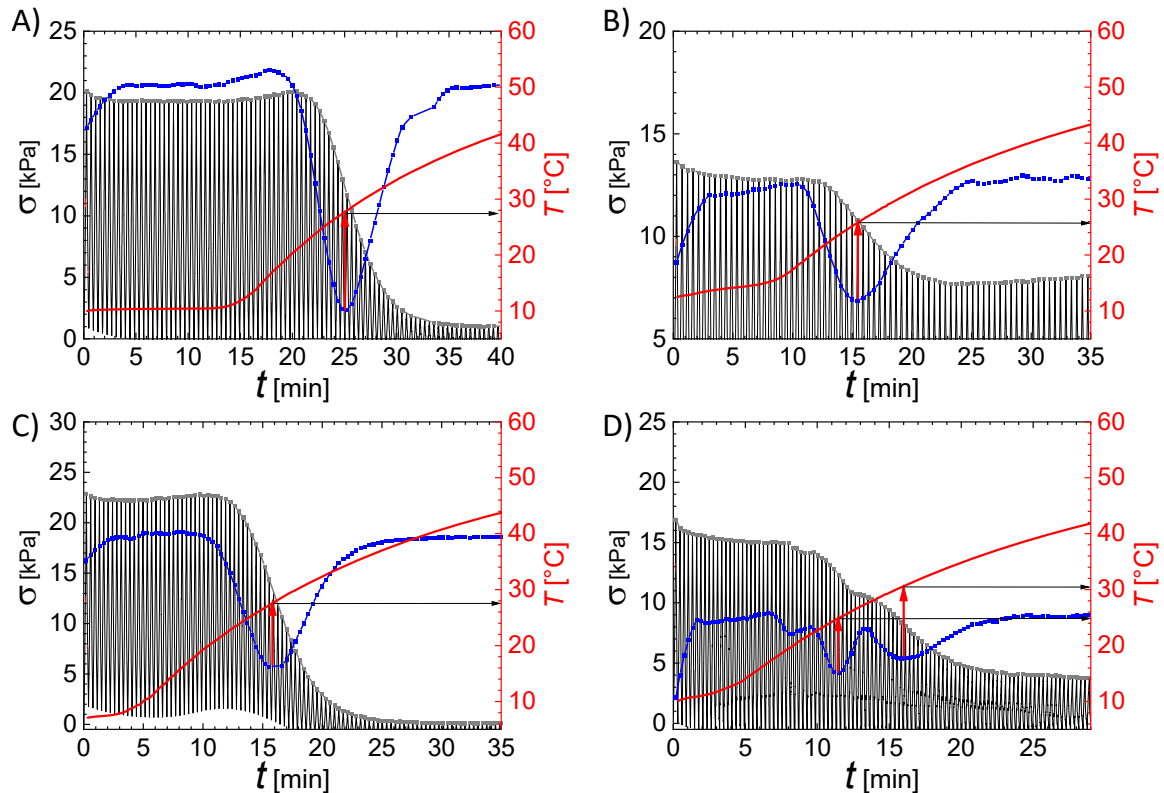


**Figure S2.** WAXS spectra of (A) G20\_OEG1000( $z$ ), (B) G20\_OEG1500( $z$ ), and (C) G20\_OEG3400( $z$ ) networks.  $z = 0.75$  (— — —), 1 (— — —), 2 (— — —), and 3 (— — —).

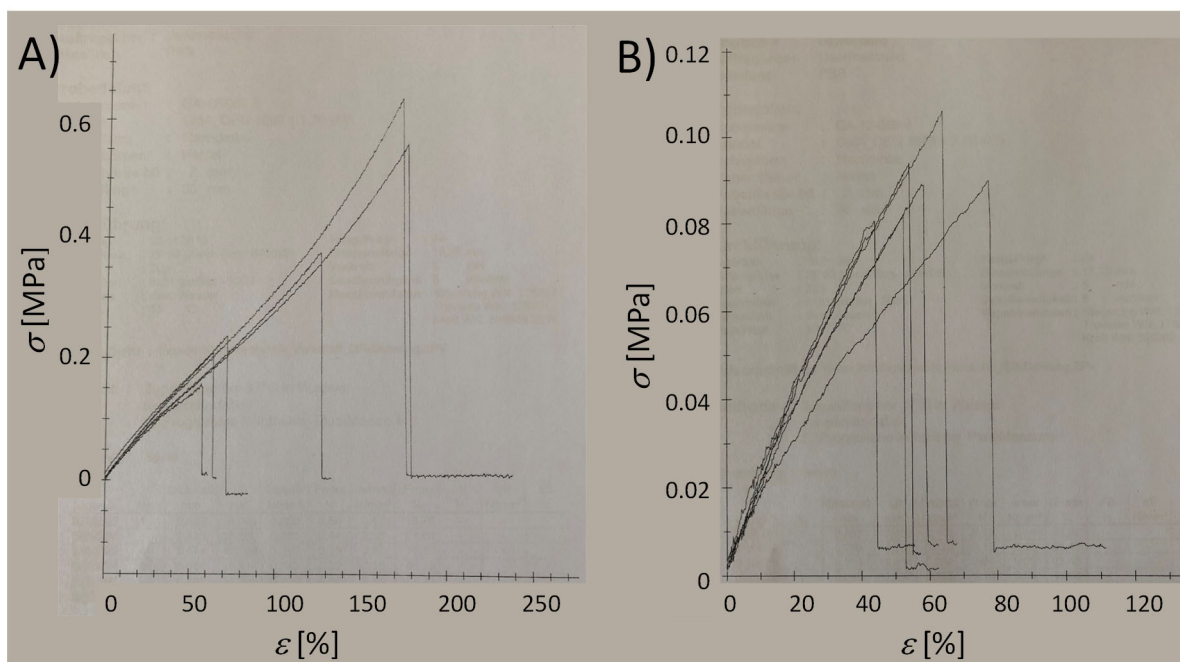
**Table S2.** Calculated values for relative triple helix content ( $X_{TH}$ ) and relative single helix content ( $X_{SH}$ ), as determined by means of WAXS measurements.

Sample ID <sup>a</sup>	$X_{TH}$ [%]	$X_{SH}$ [%]
G20_OEG1000(0.75)	$4.6 \pm 0.2$	$1.0 \pm 0.1$
G20_OEG1000(1)	$3.9 \pm 0.1$	$0.9 \pm 0.1$
G20_OEG1000(2)	$4.4 \pm 0.2$	$1.0 \pm 0.1$
G20_OEG1000(3)	$4.3 \pm 0.2$	$1.0 \pm 0.1$
G20_OEG1500(0.75)	$4.5 \pm 0.2$	$1.1 \pm 0.1$
G20_OEG1500(1)	$4.0 \pm 0.3$	$0.9 \pm 0.1$
G20_OEG1500(2)	$4.4 \pm 0.1$	$1.1 \pm 0.1$
G20_OEG1500(3)	$4.5 \pm 0.1$	$1.1 \pm 0.1$
G20_OEG3400(0.75)	$6.1 \pm 0.2$	$1.5 \pm 0.1$
G20_OEG3400(1)	$5.6 \pm 0.3$	$1.4 \pm 0.1$
G20_OEG3400(2)	$5.8 \pm 0.3$	$1.4 \pm 0.1$
G20_OEG3400(3)	$6.0 \pm 0.5$	$1.5 \pm 0.1$

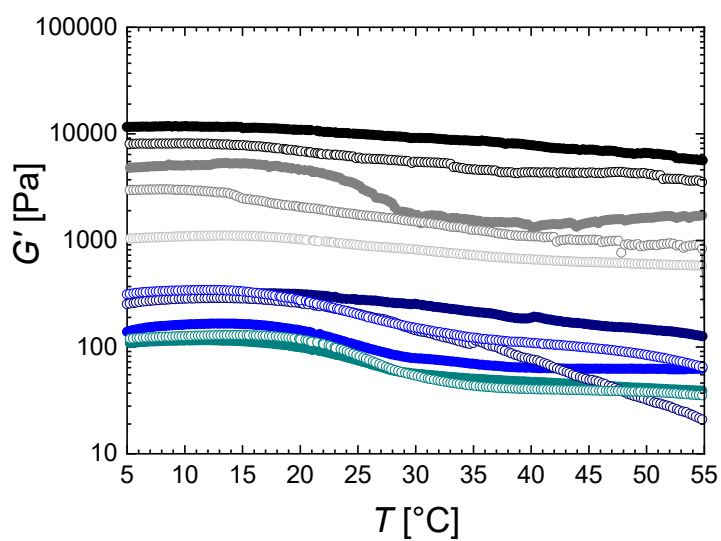
a: nomenclature: G20\_OEG $y(z)$ , with G20 = 20 wt% concentration of gelatin in the crosslinking step,  $y$  = number average molar mass  $M_n$  of the OEG crosslinkers and  $z$  the thiol:methacrylate molar ratio.



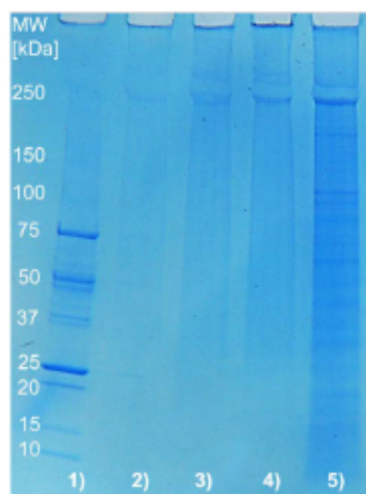
**Figure S3.** Determination of the transition temperature by rheological compression tests. A) G20\_OEG1000(1), B) G20\_OEG1000(2), C) G20\_OEG3400(1), D) G20\_OEG3400(2).



**Figure S4.** Tensile tests of G20\_OEG1000(1) samples at 4 °C (A) and 55 °C (B).  $\sigma$ = stress,  $\varepsilon$ = strain.



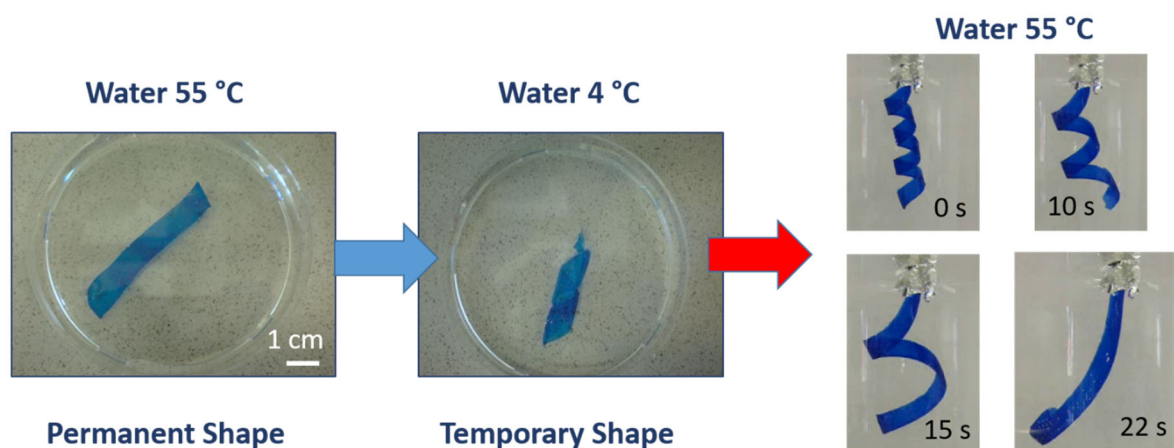
**Figure S5.** Rheological behavior of G20\_OEG1500(1) hydrogels after 1(-●-), 1.5(-○-), 2(-●-), 2.5(-○-), 3.5 (-○-), 4 (-●-), 4.5 (-○-), 5 (-●-), 5.5 (-○-), 6.5 (-●-), and 6.5 (-○-) days of hydrolytic degradation at 37 °C at pH = 7.4.



**Figure S6.** SDS-PAGE of the molar masses of the degradation products at  $t = 8$  d: 1) standard, 2) G20\_OEG1000(1), 3) G20\_OEG1500(1), 4) G20\_OEG3400(1). No larger gelatin fragments are observed, which suggests that hydrolysis primarily starts at the attached ester groups.

#### Method S1: SDS-PAGE

The determination of molar mass distribution of gelatin samples was carried out by SDS-PAGE in a Mini-Protean system (Bio-Rad, Feldkirchen, Germany), using 4-20% Ready Gels (Bio-Rad Laboratories, Feldkirchen, Germany). For the determination of the molar mass, a pre-stained SDS-PAGE standard was used. Gelatin samples were dissolved in distilled water at a concentration of 2 or 3 mg/mL. All samples were diluted 1:1 with a Laemmli sample buffer, containing 62.5 mM Tris-HCl, pH 6.8, 25% (w/v) glycerol, 2% SDS, 0.01% bromophenol blue, and 5% (w/v) 2-mercaptoethanol, followed by a heating to 90 °C for 5 min. Afterwards the samples were immediately cooled down to 25 °C. Then, 15  $\mu$ L of each sample were loaded onto their respective lane in the gel and a current of 120 V was applied for approximately 45 min in running buffer (1L 10X buffer prepared with: 30.2 g Tris base, 144 g glycine, 10 g SDS). The protein bands were visualized after a 60 min staining (0.1 wt% comassie blue, 10 vol% acetic acid and 40 vol% methanol in water) and 60 min treatment in a destaining solution (10 vol% glacial acetic acid, 20 vol% methanol in water). The molar mass of the gelatin fragments was approximated by measuring the relative mobility of the standard protein molecular weight markers.



**Figure S7.** Programming results in a helix as temporary shape; the original shape was recovered at 55 °C. For better visualization of the effect, the hydrogel stripes were stained with Coomassie blue, as original hydrogel appear to be transparent.

**Video S1.** Shape recovery of a sample at 55 °C programmed as helix (compare Fig. S5).