Hybrid covalent adaptable networks from cross-reactive poly(ε-caprolactone) and poly(ethylene-oxide) stars towards advanced shape-memory materials.

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Supporting information

Synthesis of PCL-4OH (4000g/mol)

0,63g of pentaerythritol were transferred into a washed and dried round bottom flask and three azeotropic distillation, with dry toluene, were realized. 20mL of e-caprolactone (CL), previously distillated, were added into the pentaerythritol flask under N_2. The blend is then heated to 155°C in order to dissolve the pentaerythritol into the CL. The reactive medium is cooled down to 110°C and 20mL of tin(II) 2-ethylhexanoate 0,26M were added. The monomer conversion is followed by NMR ^{1}H and after 3h, the polymer is recovered by precipitation into heptane.

^{1}H NMR (CDCl$_3$, δ): 3,97 (t, 92H, -C$\underline{H}_2$-O-C(O)-); 3,53 (t, 8H, -C$\underline{H}_2$-OH); 2,22 (t, 92H, -O-C(O)-C$\underline{H}_2$-); 1,56 (m, 190H, -C(O)-CH$_2$-C$\underline{H}_2$-CH$_2$-C$\underline{H}_2$-CH$_2$-O-); 1,30 (m, 96H, -C(O)-CH$_2$-CH$_2$-C$\underline{H}_2$-CH$_2$-CH$_2$-O-). Quantitative conversion.

Synthesis of PCL-4COOH (8000g/mol)

50 g (25 mmol of hydroxyl function) of PCL-4OH were transferred into a previously dried round bottom flask and three azeotropic distillations with anhydrous toluene were carried out. Then, 200 mL of anhydrous DMF were added to the flask through a rubber septum

with a flamed stain-less steel capillary. After complete solubilization, 2.75 g (27.5 mmol) of succinic anhydride and 3.9 mL (27.5 mmol) of triethylamine were successively added to the polymer solution. The solution was then stirred at 45°C overnight and the PCL-4COOH was successively precipitated in diethyl ether and methanol. A white powder is collected after filtration and drying under vacuum.

^{1}H NMR (CDCl$_3$,δ): 4,05 (t, 168H, H A + A'), 2,64 (s, 16H, H a + a'), 2,3 (t, 158H, H E), 1,64 (m, 316H, H B + D), 1,37 (m, 158H, H C). Functionalization: > 95%.

Synthesis of PCL-4MAL (8000g/mol)

20 g (9.5 mmol of carboxylic acid functions) of PCL-4COOH were transferred into a glass reactor previously dried. 80 ml of anhydrous CH$_2$Cl$_2$ were transferred to the reactor through a rubber septum using a flamed stainless-steel capillary. After the complete solubilization of the PCL, 2.3 g (11 mmol) of 4-(2-hydroxyethyl)-10-oxa-4-aza-tricyclo[5.2.1.0]dec-8-ene-3,5-dione, 2.27 g (11 mmol) of DCC and 0.134 g (1.1 mmol) of DMAP were transferred inside the reactor. After one night of reaction at room temperature the blend was filtrated in order to remove the DCU. The protected PCL-4MAL was recovered by precipitation in diethyl ether and in methanol, filtered and dried under vacuum. The polymer was then transferred into a glass reactor and heated at 105 ° C under vacuum for 6 h to eliminate furan and regenerate the maleimide functions. PCL-4MAL was kept at room temperature. The functionalization was determined by ^{1}H NMR. The functional PCL was also characterized by SEC.

^{1}H NMR (CDCl$_3$, δ): 6,53 (s, 7,9H, H$_{MAL}$); 4,26 (t, 7,5H, H$_{MAL}$); 4,07 (t, 172H,-C$\underline{H}_2$-O-C(O)-); 3,76 (t, 7,5H, H$_{MAL}$); 2,59 (s, 16H, O-C(O)-C$\underline{H}_2$-C$\underline{H}_2$-C(O)-O-MAL); 2,3 (t, 168H, -O-C(O)-C$\underline{H}_2$-); 1,66 (m, 332H, -C(O)-CH$_2$-C$\underline{H}_2$-CH$_2$-C$\underline{H}_2$-CH$_2$-O-); 1,39 (m, 169H, -C(O)-CH$_2$-CH$_2$-C$\underline{H}_2$-CH$_2$-CH$_2$-O).
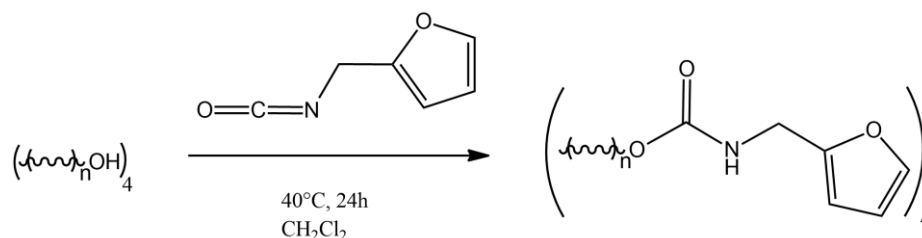
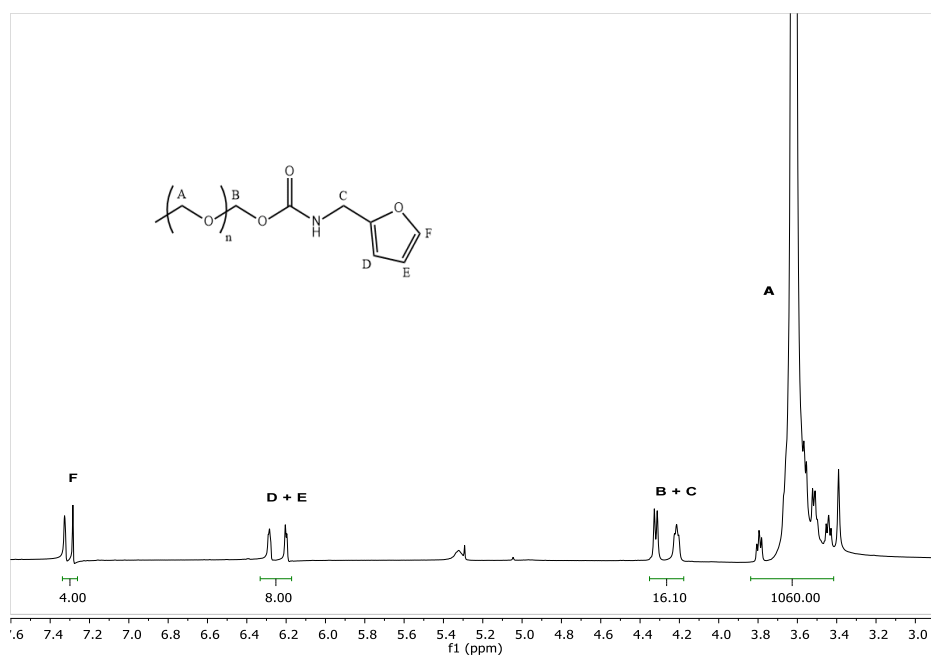Scheme S1: Synthesis of PEO-4FUR from PEO-4OH (10.000g/mol)
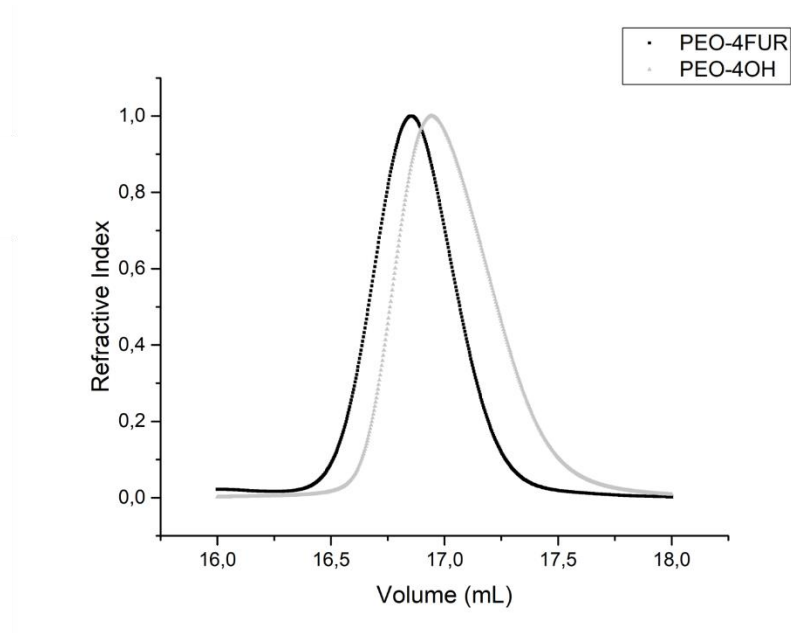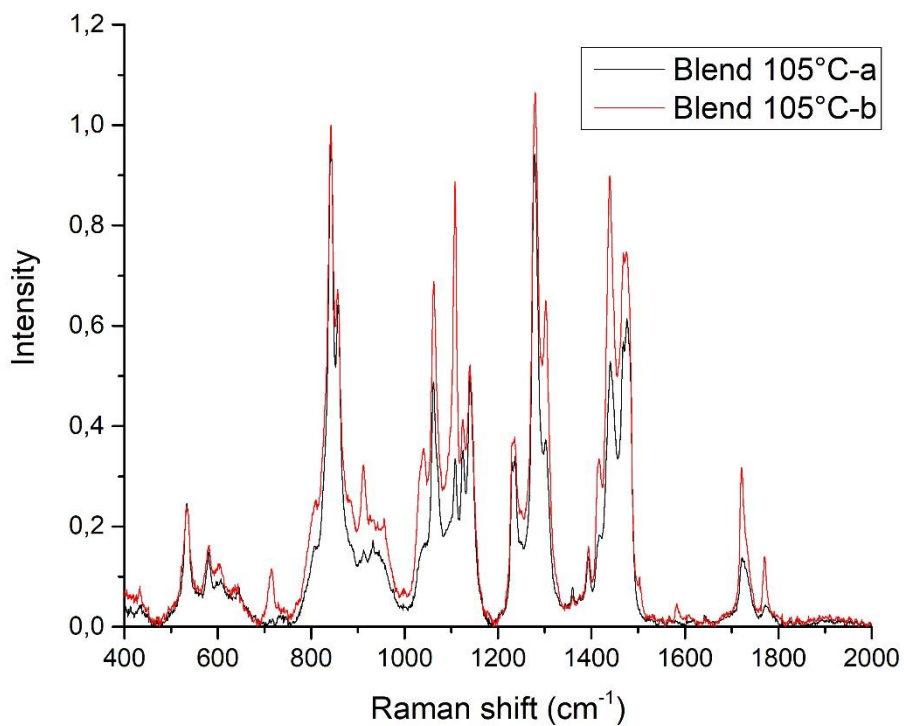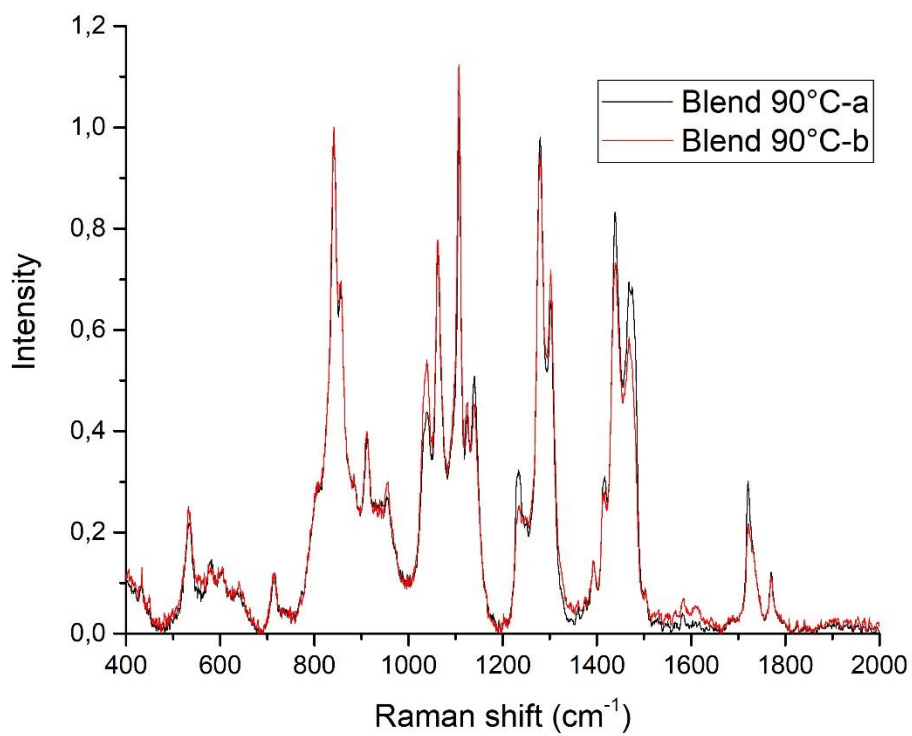
Figure S1: ¹H NMR spectrum of the PEO-4FUR

Figure S2: SEC chromatogram of the PEO-4FUR (black) and PEO-4OH (grey)

a)

b)

Figure S3: Raman spectra on two different spots of the PEO-PCL mixture after melt blending at a) 105°C and b) 90°C (the two spots a and b giving the highest divergences over the 15 measured spectra were selected in both cases).
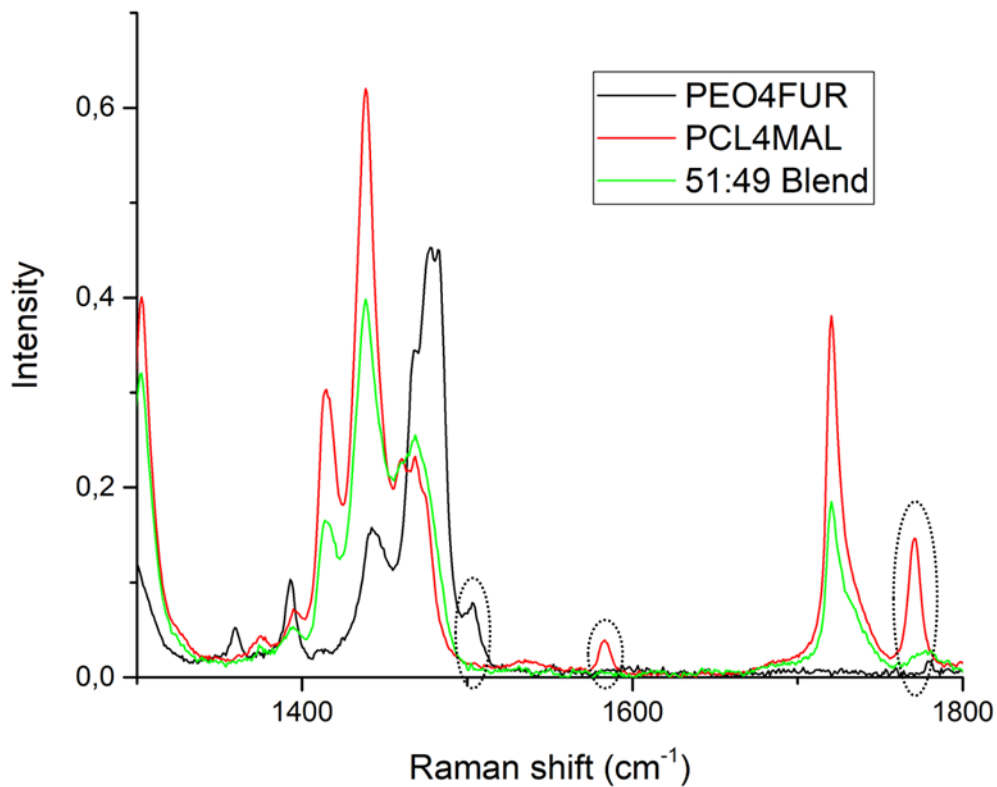
Figure S4: Raman spectra of the PEO-4FUR (black curve), PCL-4MAL (red curve) and the 51:49 blend after melt blending at 90°C and curing at 65°C for 72h (green curve). The dotted ovals highlight some bands characteristic of the furan (1503cm^{-1}) and maleimide (1587 and 1770cm^{-1}) end groups.
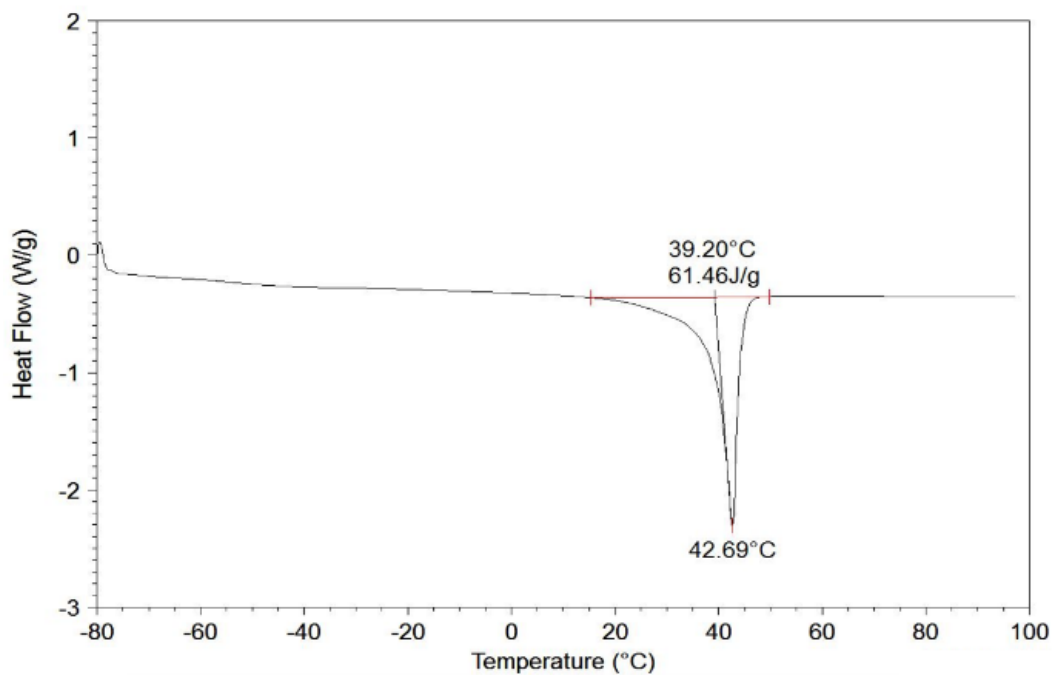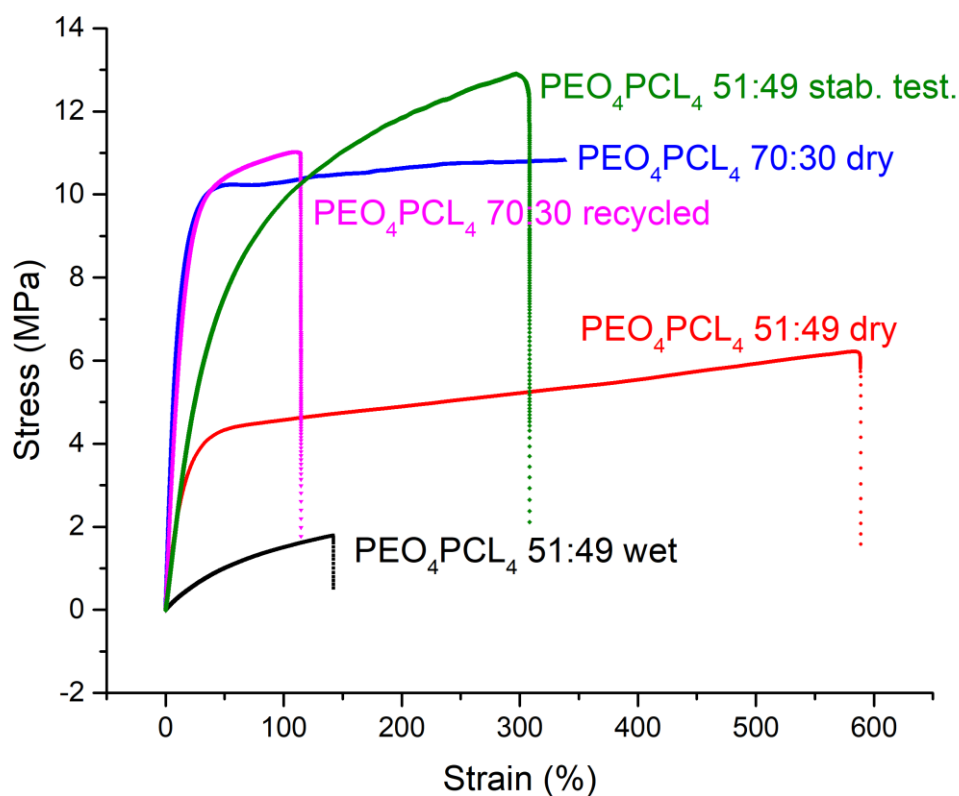

Figure S5: DSC trace for the 70:30 network.

Figure S6: Stress-strain curves at room temperature of the PEO-4FUR/PCL-4MAL8k (51:49) material at the dry state (red), in the hydrated state (black) and after 2 months in PBS solution and dried (green), of PEO-4FUR/PCL-4MAL4k (70:30) material at dry state (blue) and of PEO-4FUR/PCL-4MAL recycled (pink).
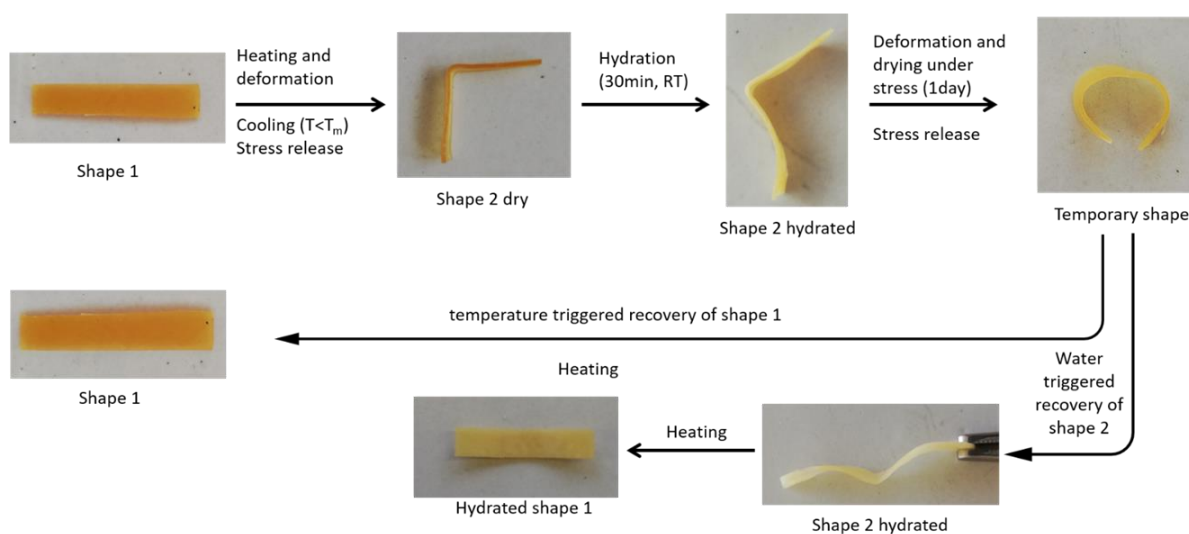

Figure S7: Multiple shape-memory of PEO/PCL network with the 51:49 composition. The temporary shape is obtained by bending the shape 2 by about 270°.
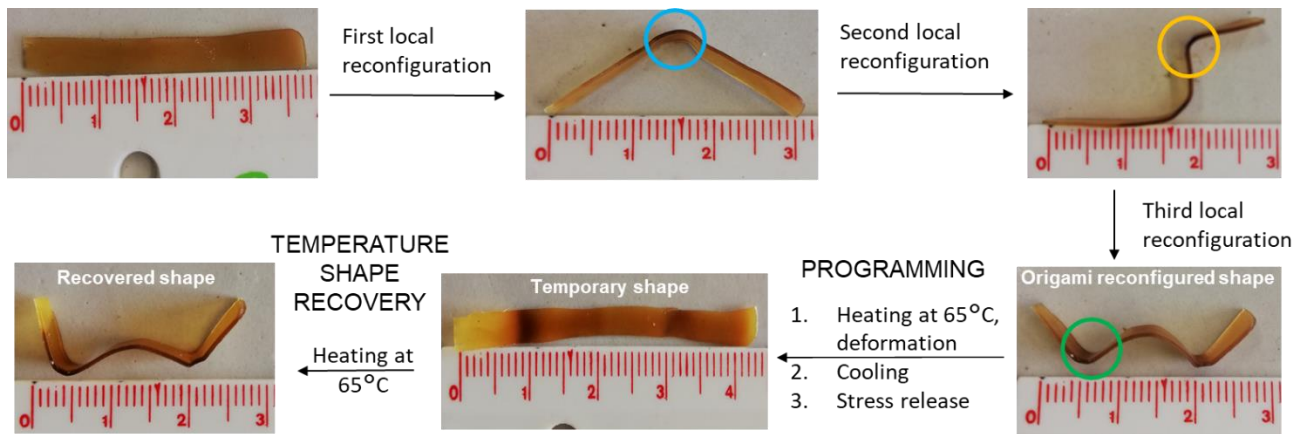
Figure S8: Origami reconfiguration by local heating of the 51:49 network followed by thermal induced shape memory cycle.
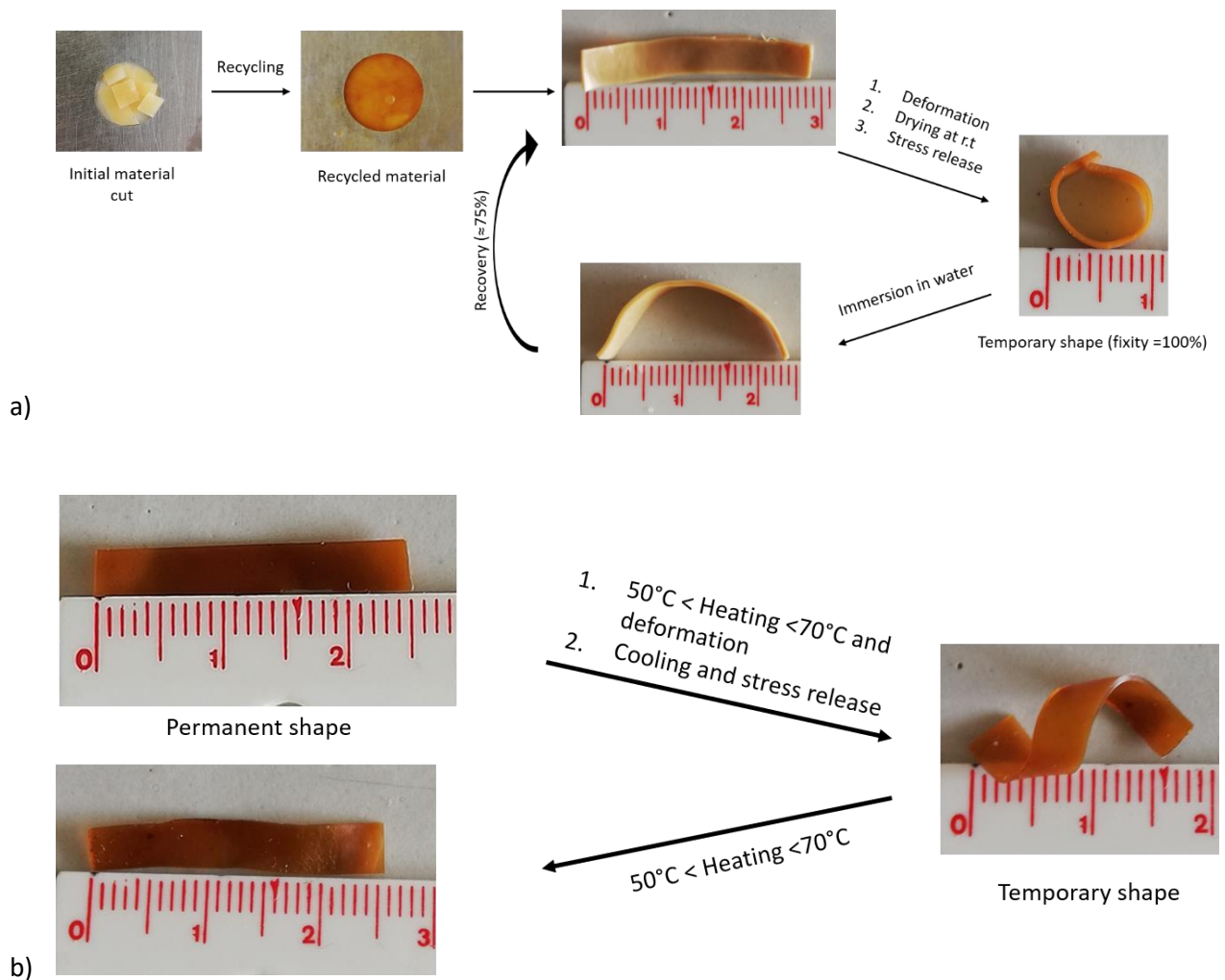

Figure S9: a) Sample before and after recycling process (method B) (left) and water shape-memory properties of the recycled 70:30 material (right). b) Thermal shape-memory properties of the recycled 70:30 material.
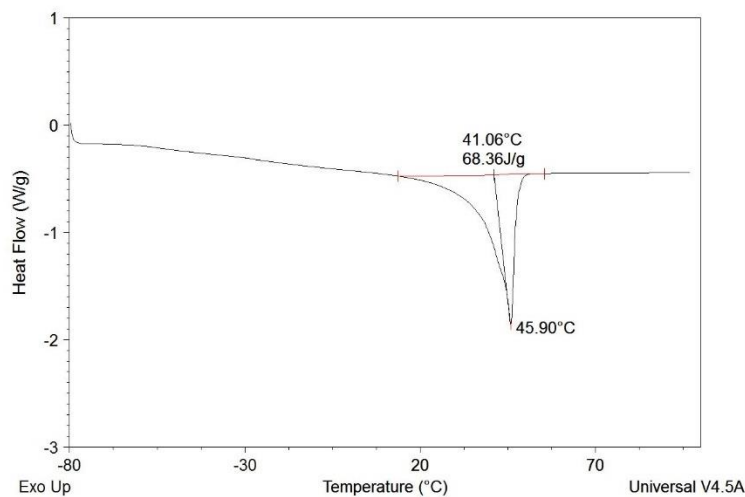
Figure S10: DSC traces for the recycled 70:30 network

Table S1: Temperature shape-memory properties of the 51:49 hybrid network as determined by DMA in the dry state.

Cycle number	1	2	3	4
Fixity ratio (%)	98	98	98	98
Recovery ratio (%)	85	97	97	97

Table S2: Temperature shape-memory properties of the 51:49 network after immersion in PBS

	Fixity ratio (%)				Recovery ratio (%)			
Immersion time \ *Cycle number*	*1*	*2*	*3*	*4*	*1*	*2*	*3*	*4*
2 weeks	97	98	98	98	75	96	99	99
1 month	98	98	98	98	79	97	97	97

Table S3: Mechanical properties at room temperature of the dry 51:49 material before and after hydrolytic test of 2 months

Material	E (MPa)	σ (MPa)	ε (%)
51 : 49 before hydrolytic test	31	6.2	600
51 : 49 after hydrolytic test	43	12.9	310