Supporting Information

Digital Light Processing 3D Printing of Polylactone/2-hydroxylethyl acrylate Networks with Programmable Mechanical Properties towards Tissue Engineering

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1 Experimental Procedures

1.1 Methods

Nuclear Magnetic Resonance (NMR). ^{1}H and ^{1}H diffusion ordered spectroscopy (DOSY) spectra were recorded using a Bruker Avance 400 MHz spectrometer at room temperature. All chemical shifts were reported in parts per million (ppm) relative to the chloroform reference peak at δ = 7.26 ppm, while diffusion coefficients are reported in $cm^2\ s^{-1}$.

Gel Permeation Chromatography (GPC). Molecular weight distributions and polydispersity indexes were determined by a $CHCl_3$ Agilent Technologies LC 1200 Series equipped with an Agilent 1260 ISO pump, Agilent refractive index detector, and two columns. Samples were dissolved in $CHCl_3$, and their chromatograms recorded with a flow of 1.0 mL/min at 40 °C. The system was calibrated against PSS Polymer Standards Service GmbH linear poly(methyl methacrylate). All GPC samples were prepared at a concentration of 2 mg/mL and were filtered through a 0.2 μm Millipore before injection.

Differential Scanning Calorimetry. DSC measurements were performed using a TA Instruments DSC Q200 and TA Instruments RSC FC-100 immersion cooler, with 5–7 mg of the dry cross-linked material as a sample. A heating and cooling rate of 10 °C per minute was used. The second heating and cooling cycles were used to analyze the thermal properties. Each sample was measured in an aluminum Tzero pan under nitrogen flow using an empty pan as reference.

Resin Viscosity. The viscosity was measured using an Anton Paar modular compact rheometer (MCR) 301 using a Peltier hood to protect the sample from ambient light. Shear rate sweep experiments were carried out to measure the viscosity in the shear range from 0.01 s^{-1} to 100 s^{-1} using a parallel plate of 25 mm diameter with a gap length of 0.05 mm.

Photorheology. Experiments were carried out using an Anton Paar MCR 301. The machine was equipped with a Thorlabs UV LED light 405 nm (M405L3-C1) and a sample glass plate allowing the passage of light. The experiments were conducted at room temperature using a Peltier hood to protect the sample from ambient light. A parallel plate of 25 mm diameter was used with a gap length of 0.05 mm. Each time point was taken every 10 s through a time sweep experiment with constant oscillations at a fixed frequency of 10 rad/s with a strain of 0.1%. UV light 405 nm (9 mW/cm^2) was turned on after 30 s.

Fourier transform infrared (FTIR). FT-IR spectra were recorded using a spectrometer (Thermo Scientific Nicolet iS10) in the region of 500–4000 cm^{-1}. A background measurement was performed prior to the sample analysis. Eight scans were completed using a resolution of 2 cm^{-1}. Conversion of cinnamic acid from P(CL-*co*-VL)-CA/HEA after exposure at UV at 365 nm was determined from the relative decrease in the integrated peak area (after deconvolution of the absorbance spectrum) of the *C*=*C* peak, using crosslinked films of controlled and identical shape and thickness to ensure comparable sampling conditions.

Stress-relaxation. Test was carried out using an Anton Paar Modular Compact Rheometer (MCR) 301. Cylindrical samples with 7.5 mm diameter and 3 mm height were used. The test was performed by applying a constant shear strain (10%) and monitoring the decay of relaxation modulus over time (0.1-1000 seconds), with a normal force between 0.15 and 0.20 N.

Scanning Electron Microscopy (SEM). SEM images were acquired using a Zeiss EVO 50 with a tungsten source and an accelerating voltage of 15 kV. An Everhart–Thornley detector was used to form secondary electron images. No coating was applied to the sample before imaging.

Accelerated degradation. A 0.2 M NaOH aqueous solution was used as the degradation medium, and experiments were conducted at 37 °C. Samples previously irradiated at 365 nm for 24 h were used for degradation testing. Samples were prepared using a disc-shaped mold (height 3 mm, diameter 4 mm). Each disc was immersed in 4 mL of NaOH solution. At predetermined time points, samples were removed, weighed (wet mass), and subsequently freeze-dried before being weighed again to obtain the dry mass. The experiment was performed in duplicate.

2 Characterisation of polymers

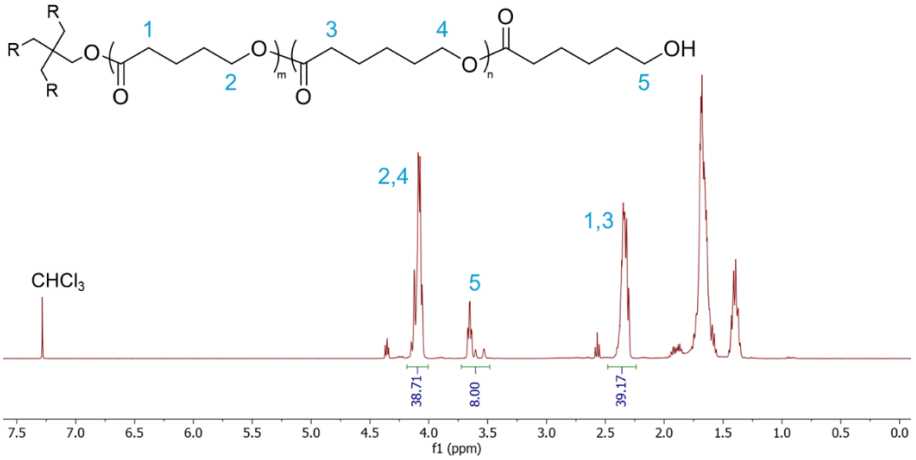

Figure S1. ^{1}H NMR spectrum of P(CL-*co*-VL) ($CDCl_3$).

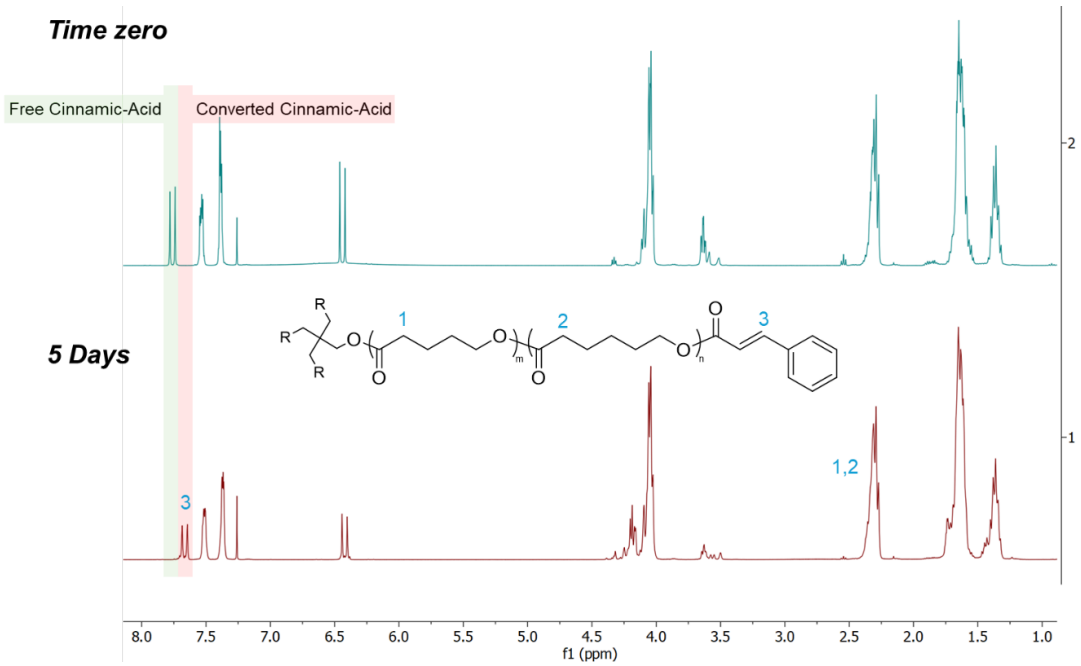

Figure S2. ^{1}H NMR spectra of the reaction between P(CL-*co*-VL) and Cinnamic Acid at time zero and after 5 days ($CDCl_3$).

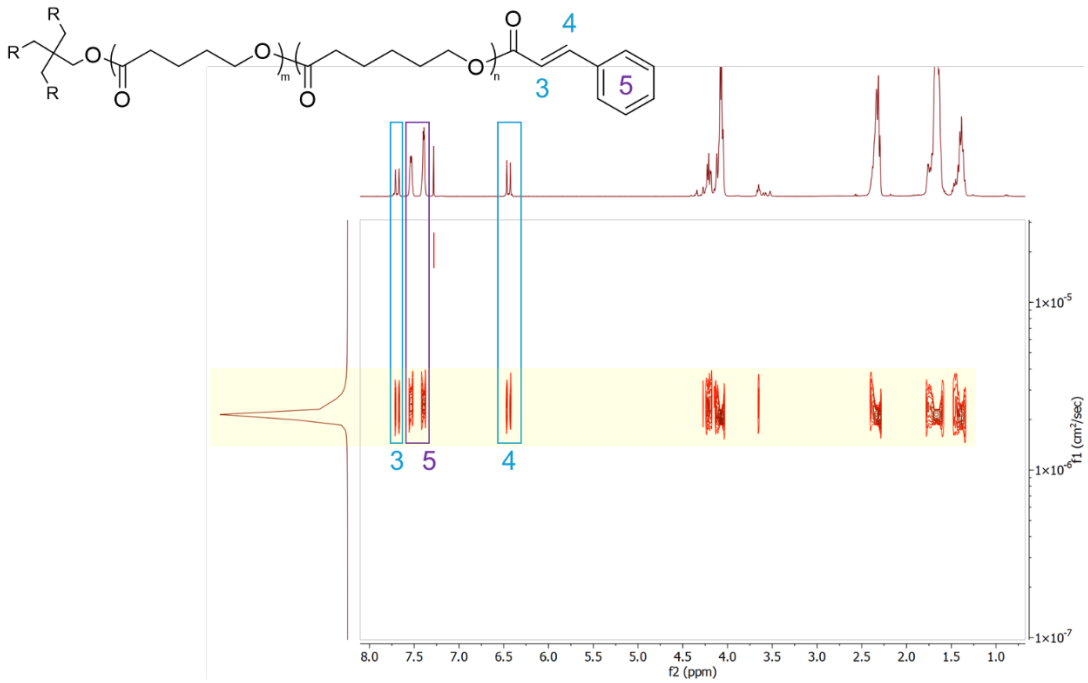

Figure S3. DOSY NMR spectrum of P(CL-*co*-VL)-CA ($CDCl_3$).

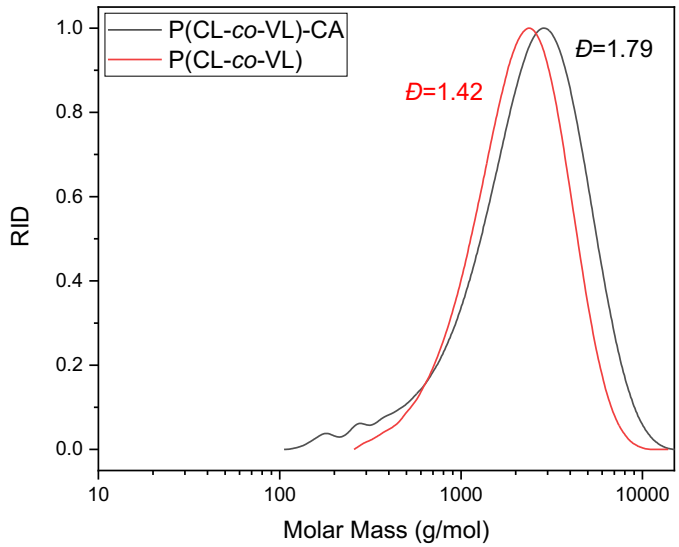

Figure S4. Overlayed SEC of poly(valerolactone-*co*-caprolactone) and poly(valerolactone-*co*-caprolactone)-cinnamic acid in $CHCl_3$.

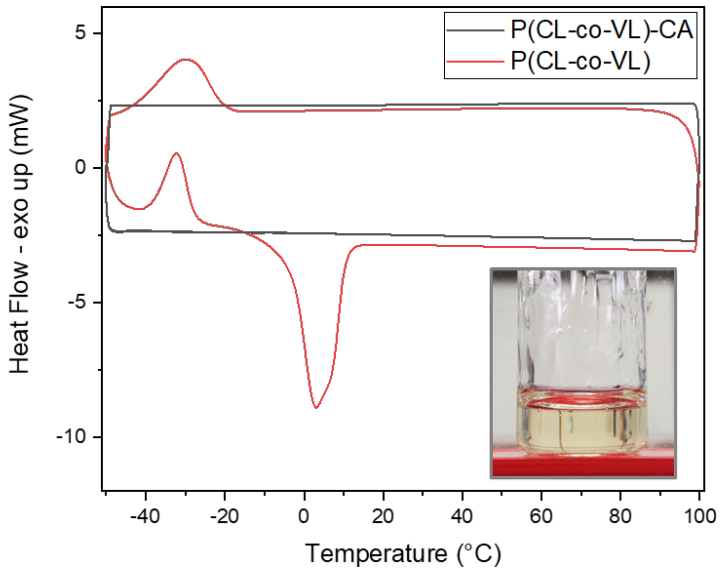

Figure S5. Overlayed DSC curves of poly(valerolactone-*co*-caprolactone) and poly(valerolactone-*co*-caprolactone)-cinnamic acid. The photo illustrates the P(CL-*co*-VL)-CA copolymer.

3 Photocurable resins

Table S1. Photoreactive resins composition.

Resin	***P(CL-co-VL)-CA (wt%)***	***HEA (wt%)***	***Pentaerythritol tetraacrylate (PETA) (wt%)***	***BAPO (wt%)***
PCVL-CA	99	0	0	1
HEA	0	98	1	1
PCVL-CA+HEA	49	49	1	1

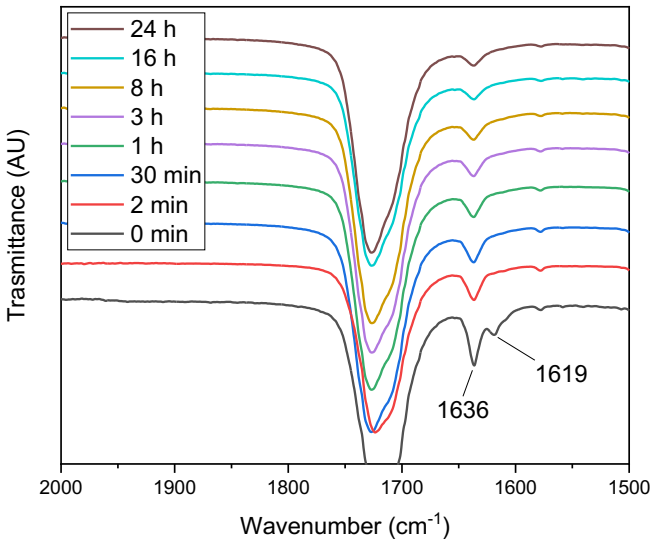

Figure S6. FT-IR spectra of P(CL-*co*-VL)-CA/HEA networks after different exposure times of UV at 365 nm. HEA *C=C* at 1619 cm^{-1} and Cinnamic acid *C=C* at 1636 cm^{-1}.

Table S2. Mechanical properties of networks irradiated for different time derives from the resin P(CL-*co*-VL)-CA/HEA. The entry 1 corresponds to irradiation time of 2 min at 405 nm, the successive time points to 365 nm.

Entry	***Exposure Time (h)***	***Elongation at Break (%)***	***Young's Modulus (MPa)***	***Ultimate Strength (MPa)***
1	0.03	45.5 ± 6.7	0.29 ± 0.03	0.15 ± 0.03
2	0.5	53.4 ± 6.0	0.70 ± 0.12	0.35 ± 0.05
3	1	59.6 ± 0.8	0.82 ± 0.05	0.47 ± 0.01
4	3	67.7 ± 27.2	1.08 ± 0.27	0.69 ± 0.37
5	8	62.4 ± 11.1	1.08 ± 0.10	0.61 ± 0.12
6	16	82.9 ± 15.1	1.46 ± 0.08	1.00 ± 0.24
7	24	109.2 ± 11.0	1.80 ± 0.16	1.39 ± 0.16

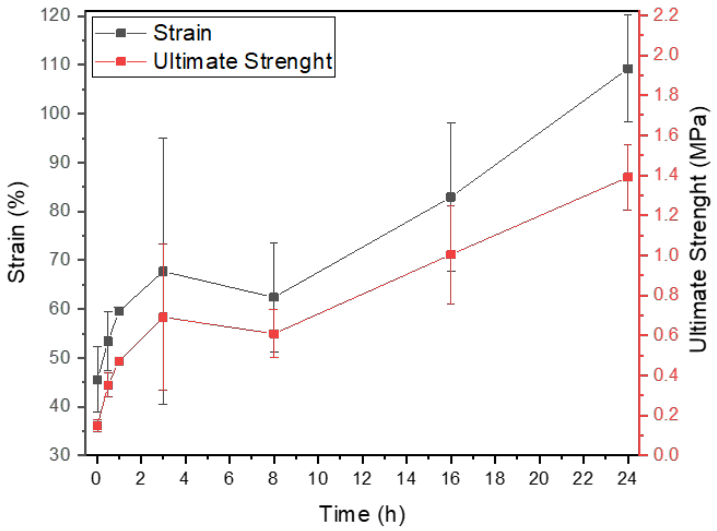

Figure S7. Elongation and Stress at break of P(CL-*co*-VL)-CA/HEA networks as a function of irradiation time.

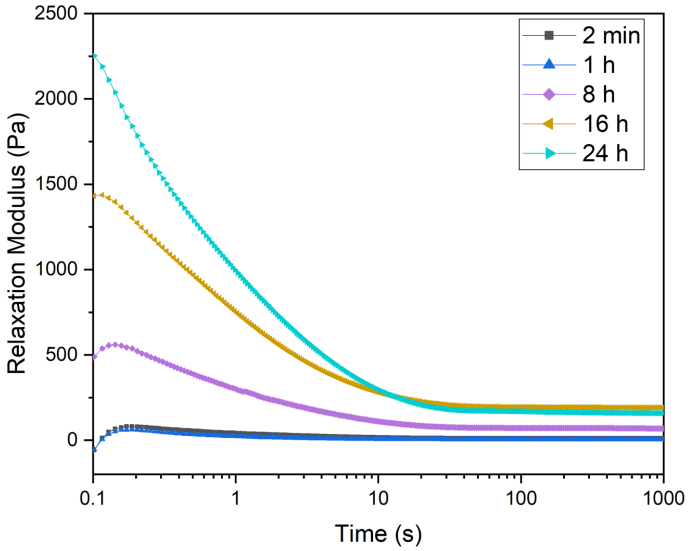

Figure S8. Stress relaxation of P(CL-co-VL)-CA/HEA networks at different irradiation times obtained from cylinder shaped samples. Light at 405 nm was used for the sample at 2 min; all successive samples were irradiated at 365 nm.

Table S3. Swelling ratio and gel fraction of single and double cured networks derived from the resin P(CL-*co*-VL)-CA/HEA (in acetone, 48 h).

Entry	***Exposure Time (h)***	***Swelling ratio***	***Gel fraction (%)***
1 (single)	0.03	1.35 ± 0.04	51.4 ± 0.8
7 (double)	24	0.69 ± 0.01	81.4 ± 0.6

Table S4. Mechanical properties of P(CL-co-VL)-CA/HEA networks irradiated for different durations. Entry 1 corresponds to an irradiation time of 2 minutes at 405 nm, while the subsequent entries correspond to irradiation at 365 nm for increasing time intervals.

Entry	**Exposure Time (h)**	**Compressive Modulus (MPa)**	**Stress at 50% strain**
1	0.03	374.7 ± 10.0	202.6 ± 8.3
2	0.5	759.0 ± 227.8	260.9 ± 53.1
3	1	943.7 ± 106.1	396.9 ± 33.7
4	3	1237.0 ± 35.4	545.6 ± 30.6
5	8	1271.0 ± 157.6	520.0 ± 38.1
6	16	1418.0 ± 162.9	665.4 ± 115.0
7	24	1446.5 ± 9.2	597.7 ± 36.4

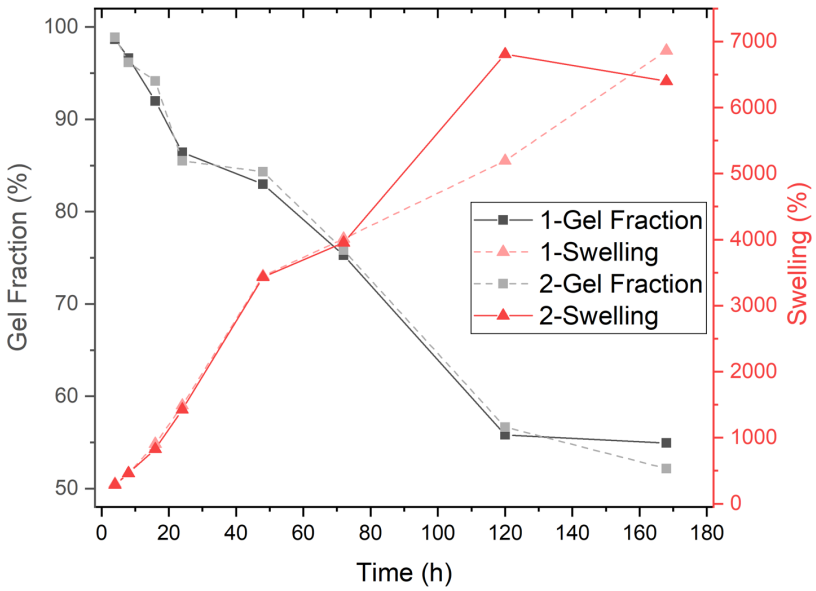

Figure S9. Influence of network degradation (duplicate) of samples irradiated at 365 nm for 24 h in 0.2 M NaOH aqueous solution at 37 °C on swelling and gel fraction. Samples were prepared using a disc-shaped mold (height 3 mm, diameter 4 mm). Each disc was immersed in 4 mL of NaOH solution.

4 3D printing

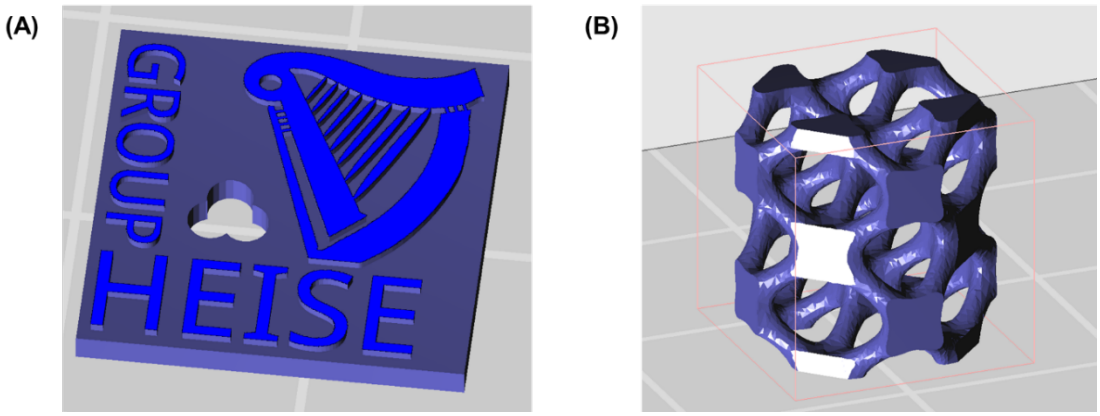

Figure S10. CAD 3D models of (A) HEISE GROUP and (B) scaffold.

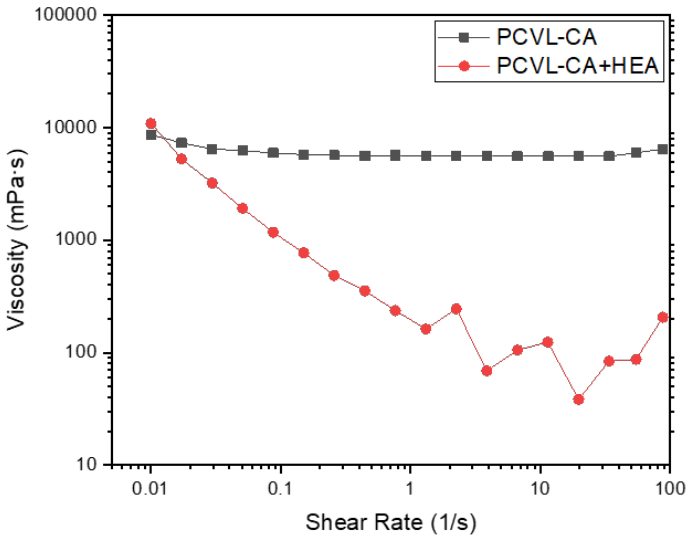

Figure S11. Viscosity at room temperature of the resin P(CL-*co*-VL)-CA/HEA and the polymer P(CL-*co*-VL)-CA.