Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Exploiting the network architecture of thiol-ene photo-crosslinked poly(ε-caprolactone) towards tailorable materials for light-based 3D-printing

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Chemical characterization via ^{1}H-NMR spectroscopy

1. Determination of the molar mass for E-PCL precursors, via ^{1}H-NMR spectroscopy

Table S1. The molar mass (M_n) is represented for each E-PCL precursor, obtained through ^{1}H-NMR spectroscopy. The molar mass was calculated based on the H_e (next to the urethane bonds) to PCL (repeating unit) ratio, as listed in the table.

	Integration H_e next to urethane (3.78 ppm)	Integration PCL (4.1 ppm)	Number of repeating units	Molar mass (g.mol^{-1})
E-PCL(2)	4	139.09	67	8000
E-PCL(3)	6	136.04	68	7900
E-PCL(4)	8	132.57	66	7700

2. Determination of the alkene content and degree of substitution for E-PCL precursors, via ^{1}H-NMR spectroscopy with dimethyl terephthalate (DMT) as internal standard

	Molar mass (g.mol^{-1})	E-PCL mass (mg)	DMT mass (mg)	Integration at 5.8 ppm	Integration at 5.2 ppm	Alkene content (mol.g^{-1})	Degree of substitution (%)
E-PCL(2)	8000	10.4	9.8	11.95	22.93	$2.26*10^{-4}$	91
E-PCL(3)	7900	10.4	10.1	19.65	36.98	$3.78*10^{-4}$	99
E-PCL(4)	7700	10.92	10.11	26.82	50.11	$4.89*10^{-4}$	94

Table S2. The alkene content and degree of substitution values are represented, for each E-PCL precursor, obtained through ^{1}H-NMR spectroscopy with DMT as an internal standard.

3. Demonstrating successful synthesis of the E-PCL precursors

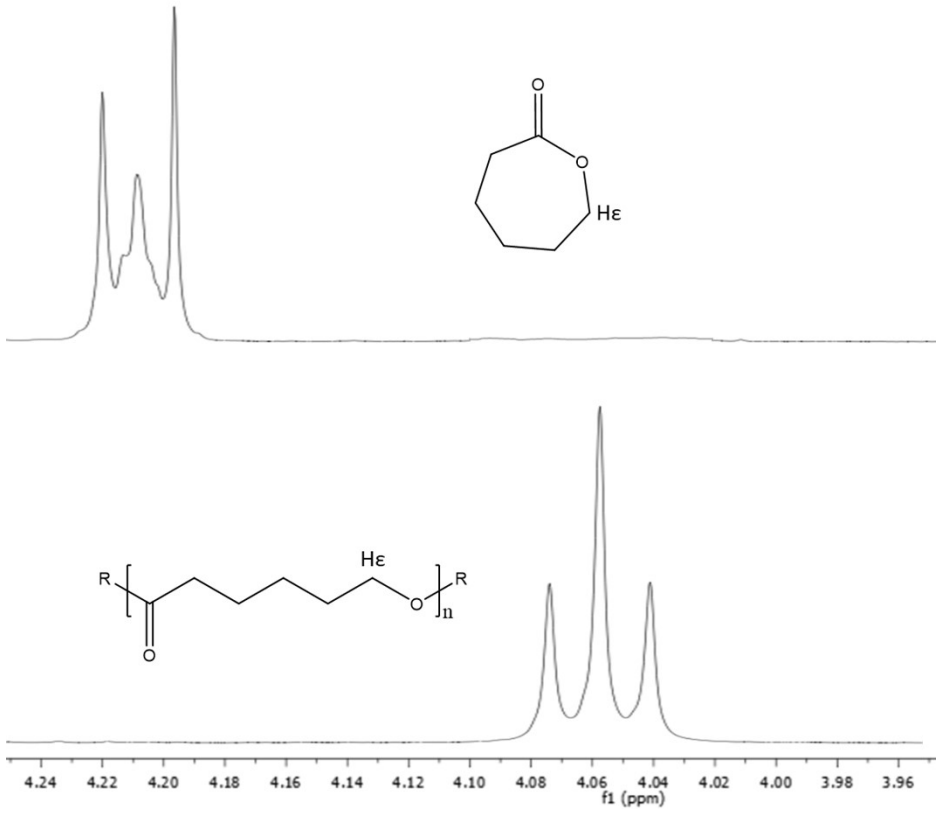


Figure S1. ^{1}H-NMR spectrum displaying the conversion of the H_e protons from ε-caprolactone monomers (4.21 ppm) into those of the synthesized PCL polymer (4.06 ppm).

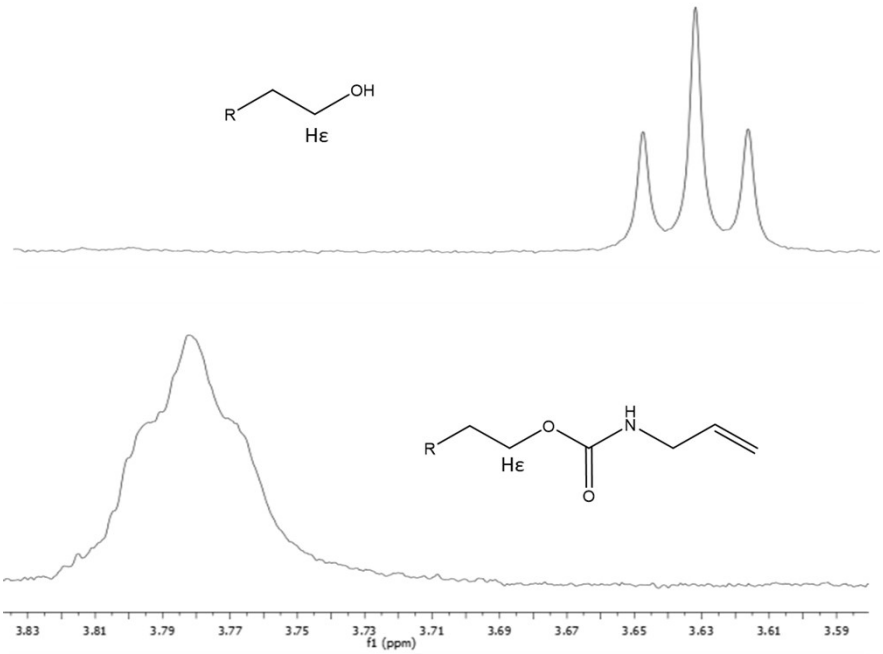
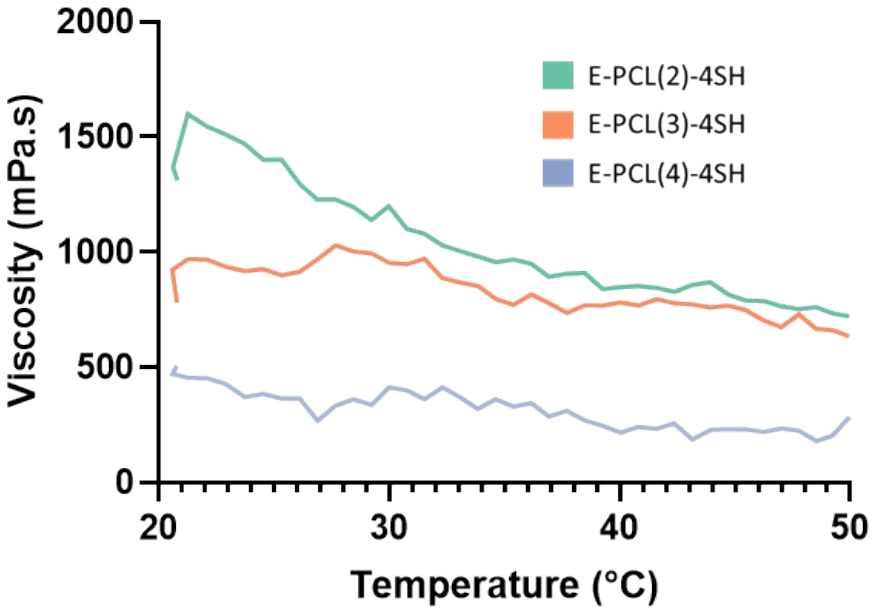


Figure S2. ^{1}H-NMR spectrum displaying the conversion of H_e protons next to a hydroxyl group (3.64 ppm) into those next to a urethane bond (3.78 ppm).



Optimization of photo-crosslinkable E-PCL resins for DLP printing

Figure S3. Viscosity measurements in function of temperature for E-PCL(2)-4SH, E-PCL(3)-4SH and E-PCL(4)-4SH photo-crosslinkable resins in NMP, with a concentration of 40, 50 and 50 w/w%, respectively.

Stability tests on photo-crosslinkable E-PCL resins to determine shelf life

Table S3. Stability tests performed on E-PCL(2)-4SH, E-PCL(3)-4SH and E-PCL(4)-4SH photo-crosslinkable resins in NMP, with a concentration of 40, 50 and 50 w/w%, respectively. The resins were stored under argon, in the dark and at different temperatures (i.e., 4°C, 20°C and 40°C) in parallel. During 7 days, the alkene content was determined for each resin, through ^{1}H-NMR spectroscopy with DMT as internal standard.

	Day	**Stored at 4°C (mol.g^{-1})**	**Stored at 20°C (mol.g^{-1})**	**Stored at 40°C (mol.g^{-1})**
E-PCL(2)-4SH	Start	$2.26*10^{-4}$	$2.26*10^{-4}$	$2.26*10^{-4}$
	1	$2.28*10^{-4}$	$2.27*10^{-4}$	$2.26*10^{-4}$
	3	$2.27*10^{-4}$	$2.25*10^{-4}$	$2.26*10^{-4}$
	5	$2.24*10^{-4}$	$2.25*10^{-4}$	$2.24*10^{-4}$
	7	$2.21*10^{-4}$	$2.21*10^{-4}$	$2.20*10^{-4}$
E-PCL(3)-4SH	Start	$3.78*10^{-4}$	$3.78*10^{-4}$	$3.78*10^{-4}$
	1	$3.80*10^{-4}$	$3.77*10^{-4}$	$3.75*10^{-4}$
	3	$3.81*10^{-4}$	$3.74*10^{-4}$	$3.75*10^{-4}$
	5	$3.73*10^{-4}$	$3.72*10^{-4}$	$3.71*10^{-4}$
	7	$3.71*10^{-4}$	$3.72*10^{-4}$	$3.70*10^{-4}$
E-PCL(4)-4SH	Start	$4.89*10^{-4}$	$4.89*10^{-4}$	$4.89*10^{-4}$
	1	$4.80*10^{-4}$	$4.79*10^{-4}$	$4.77*10^{-4}$
	3	$4.49*10^{-4}$	$4.39*10^{-4}$	$4.31*10^{-4}$
	5	$4.37*10^{-4}$	$4.29*10^{-4}$	$4.25*10^{-4}$
	7	$4.25*10^{-4}$	$4.08*10^{-4}$	$3.98*10^{-4}$