Electronic Supplementary Material (ESI) for Biomaterials Science.

Supporting information

Low molecular weight poly((d,l)-lactide-co-caprolactone) liquid resins for diluent-free DLP printing of cell culture platforms.

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^{1}H-NMR signal analysis of intermediate and methacrylated polymers

^{1}H NMR **2-arm-P(d,l)LA** ($CDCl_3$, 500 MHz): δ (ppm) = 1.58 (d, CH_3 PLA, 48H), δ = 3.51 (q, CH PLA, 2H), δ (ppm) = 3.65 (t, CH_2 TEG, 4H), δ = 4.33 (t, CH_2 TEG, 8H), δ = 4.97 (q, CH PLA, 14H). ^{1}H NMR **2-arm-PCL** ($CDCl_3$, 500 MHz): δ (ppm) = 1.25 (tt, CH_2 PCL, 48H), δ = 1.56 (tt, CH_2 PCL, 48H),), δ = 1.66 (tt, CH_2 PCL, 48H), δ (ppm) = 2.23 (t, CH_2 PCL, 48H), δ = 3.64 (t, CH_2 PCL, 48H), δ (ppm) = 3.65 (t, CH_2 TEG, 4H), δ = 4.33 (t, CH_2 TEG, 8H). ^{1}H NMR **2-arm-P((d,l)LA-co-CL)** ($CDCl_3$, 500 MHz): δ (ppm) = 1.25 (tt, CH_2 PCL, 36H), δ = 1.56 (tt, CH_2 PCL, 36H), δ (ppm) = 1.58 (d, CH_3 PLA, 36H), δ = 1.66 (tt, CH_2 PCL, 36H), δ (ppm) = 2.23 (t, CH_2 PCL, 36H), δ = 3.51 (q, CH PLA, 2H), δ = 3.64 (t, CH_2 PCL, 36H), δ (ppm) = 3.65 (t, CH_2 TEG, 4H), δ = 4.33 (t, CH_2 TEG, 8H), δ = 4.97 (q, CH PLA, 10H). ^{1}H NMR **3-arm-P(d,l)LA** ($CDCl_3$, 500 MHz): δ (ppm) = 0.91 (t, CH_3 TMP, 3H), δ (ppm) = 1.58 (d, CH_3 PLA, 72H), δ = 3.51 (q, CH PLA, 3H), δ = 4.02 (s, CH_2 TMP, 6H), δ = 4.97 (q, CH PLA, 21H). ^{1}H NMR **3-arm-PCL** ($CDCl_3$, 500 MHz): δ (ppm) = 0.91 (t, CH_3 TMP, 3H), δ (ppm) = 1.25 (tt, CH_2 PCL, 72H), δ = 1.56 (tt, CH_2 PCL, 72H),), δ = 1.66 (tt, CH_2 PCL, 72H), δ (ppm) = 2.23 (t, CH_2 PCL, 72H), δ = 3.64 (t, CH_2 PCL, 72H), δ = 4.02 (s, CH_2 TMP, 6H). ^{1}H NMR **3-arm-P((d,l)LA-co-CL)** ($CDCl_3$, 500 MHz): δ (ppm) = 0.91 (t, CH_3 TMP, 3H), δ (ppm) = 1.25 (tt, CH_2 PCL, 54H), δ = 1.56 (tt, CH_2 PCL, 54H), δ (ppm) = 1.58 (d, CH_3 PLA, 54H), δ = 1.66 (tt, CH_2 PCL, 54H), δ (ppm) = 2.23 (t, CH_2 PCL, 54H), δ = 3.51 (q, CH PLA, 2H), δ = 3.64 (t, CH_2 PCL, 54H), δ = 4.02 (s, CH_2 TMP, 6H), δ = 4.97 (q, CH PLA, 16H).

^{1}H NMR **2-arm-P(d,l)LA-MA** ($CDCl_3$, 500 MHz): δ (ppm) = 1.58 (d, CH_3 PLA, 48H), δ (ppm) = 1.99 (s, CH_3 MA, 6H), δ = 3.51 (q, CH PLA, 2H), δ (ppm) = 3.65 (t, CH_2 TEG, 4H), δ = 4.33 (t, CH_2 TEG, 8H), δ = 4.97 (q, CH PLA, 14H), δ = 5.58 (dd, CH_{trans}=C MA, 2H), δ = 6.15 (dd, CH_{cis}=C MA, 2H). ^{1}H NMR **2-arm-PCL-MA** ($CDCl_3$, 500 MHz): δ (ppm) = 1.25 (tt, CH_2 PCL, 48H), δ = 1.56 (tt, CH_2 PCL, 48H),), δ = 1.66 (tt, CH_2 PCL, 48H), δ (ppm) = 1.99 (s, CH_3 MA, 6H), δ (ppm) = 2.23 (t, CH_2 PCL, 48H), δ = 3.64 (t, CH_2 PCL, 48H), δ (ppm) = 3.65 (t, CH_2 TEG, 4H), δ = 4.33 (t, CH_2 TEG, 8H), δ = 5.58 (dd, CH_{trans}=C MA, 2H), δ = 6.15 (dd, CH_{cis}=C MA, 2H). ^{1}H NMR **2-arm-P((d,l)LA-co-CL)-MA** ($CDCl_3$, 500 MHz): δ (ppm) = 1.25 (tt, CH_2 PCL, 36H), δ = 1.56 (tt, CH_2 PCL, 36H), δ (ppm) = 1.58 (d, CH_3 PLA, 36H), δ = 1.66 (tt, CH_2 PCL, 36H), δ (ppm) = 1.99 (s, CH_3 MA, 6H), δ (ppm) = 2.23 (t, CH_2 PCL, 36H), δ = 3.51 (q, CH PLA, 2H), δ = 3.64 (t, CH_2 PCL, 36H), δ (ppm) = 3.65 (t, CH_2 TEG, 4H), δ = 4.33 (t, CH_2 TEG, 8H), δ = 4.97 (q, CH PLA, 10H), δ = 5.58 (dd, CH_{trans}=C MA, 2H), δ = 6.15 (dd, CH_{cis}=C MA, 2H). ^{1}H NMR **3-arm-P(d,l)LA-MA** ($CDCl_3$, 500 MHz): δ (ppm) = 0.91 (t, CH_3 TMP, 3H), δ (ppm) = 1.58 (d, CH_3 PLA, 72H), δ (ppm) = 1.99 (s, CH_3 MA, 9H), δ = 3.51 (q, CH PLA, 3H), δ = 4.02 (s, CH_2 TMP, 6H), δ = 4.97 (q, CH PLA, 21H), δ = 5.58 (dd, CH_{trans}=C MA, 3H), δ = 6.15 (dd, CH_{cis}=C MA, 3H). ^{1}H NMR **3-arm-PCL-MA** ($CDCl_3$, 500 MHz): δ (ppm) = 0.91 (t, CH_3 TMP, 3H), δ (ppm) = 1.25 (tt, CH_2 PCL, 72H), δ = 1.56 (tt, CH_2 PCL, 72H),), δ = 1.66 (tt, CH_2 PCL, 72H), δ (ppm) = 1.99 (s, CH_3 MA, 9H), δ (ppm) = 2.23 (t, CH_2 PCL, 72H), δ = 3.64 (t, CH_2 PCL, 72H), δ = 4.02 (s, CH_2 TMP, 6H), δ = 5.58 (dd, CH_{trans}=C MA, 3H), δ = 6.15 (dd, CH_{cis}=C MA, 3H). ^{1}H NMR **3-arm-P((d,l)LA-co-CL)-MA** ($CDCl_3$, 500 MHz): δ (ppm) = 0.91 (t, CH_3 TMP, 3H), δ (ppm) = 1.25 (tt, CH_2 PCL, 54H), δ = 1.56 (tt, CH_2 PCL, 54H), δ (ppm) = 1.58 (d, CH_3 PLA, 54H), δ = 1.66 (tt, CH_2 PCL, 54H), δ (ppm) = 1.99 (s, CH_3 MA, 9H), δ (ppm) = 2.23 (t, CH_2 PCL, 54H), δ = 3.51 (q, CH PLA, 2H), δ = 3.64 (t, CH_2 PCL, 54H), δ = 4.02 (s, CH_2 TMP, 6H), δ = 4.97 (q, CH PLA, 16H), δ = 5.58 (dd, CH_{trans}=C MA, 3H), δ = 6.15 (dd, CH_{cis}=C MA, 3H).

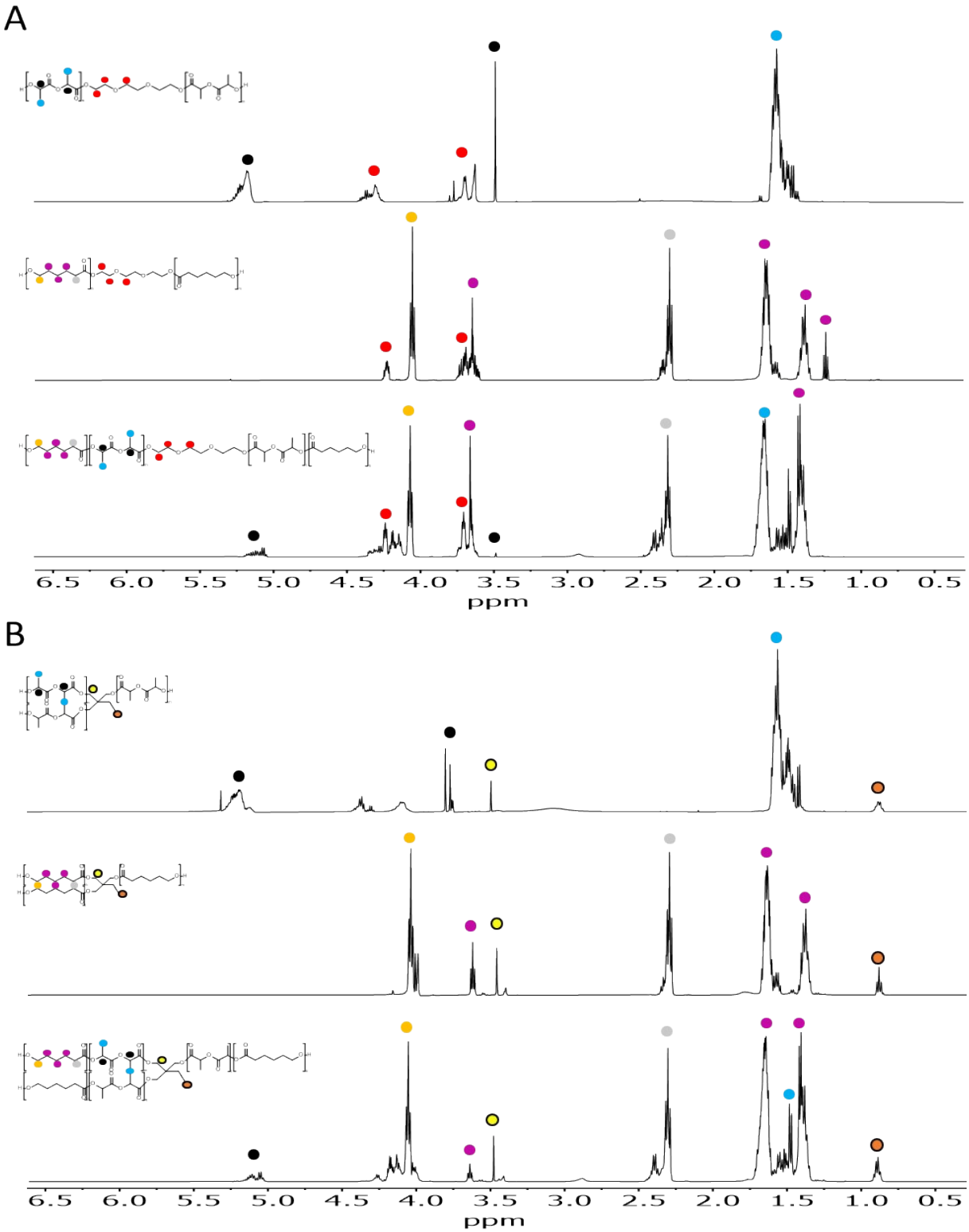

Fig. S1 ^{1}H-NMR spectrum analysis of 2- *(A)* and 3-arm *(B)* intermediate polymers in $CDCl_3$: *(top)* P(d,l)LA, *(middle)* PCL and *(bottom)* P((d,l)LA-co-CL). The specific proton signals are related to the molecule ones using colour dots.

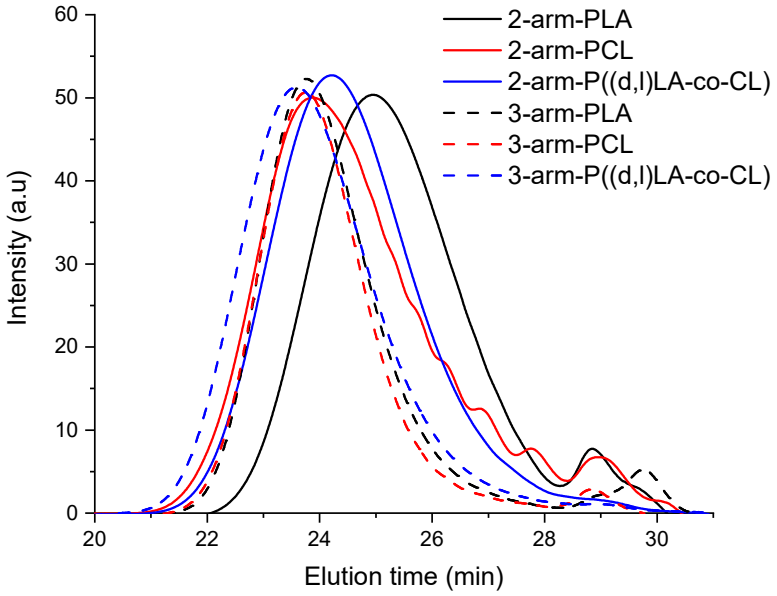

Fig. S2 GPC chromatogram of synthesized polymers.

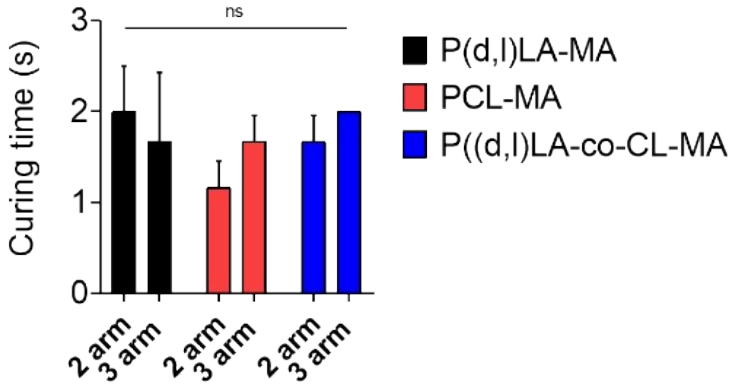

Fig. S3 Curing time of the methacrylated resins during photorheological experiments. Error bars denote standard deviation.

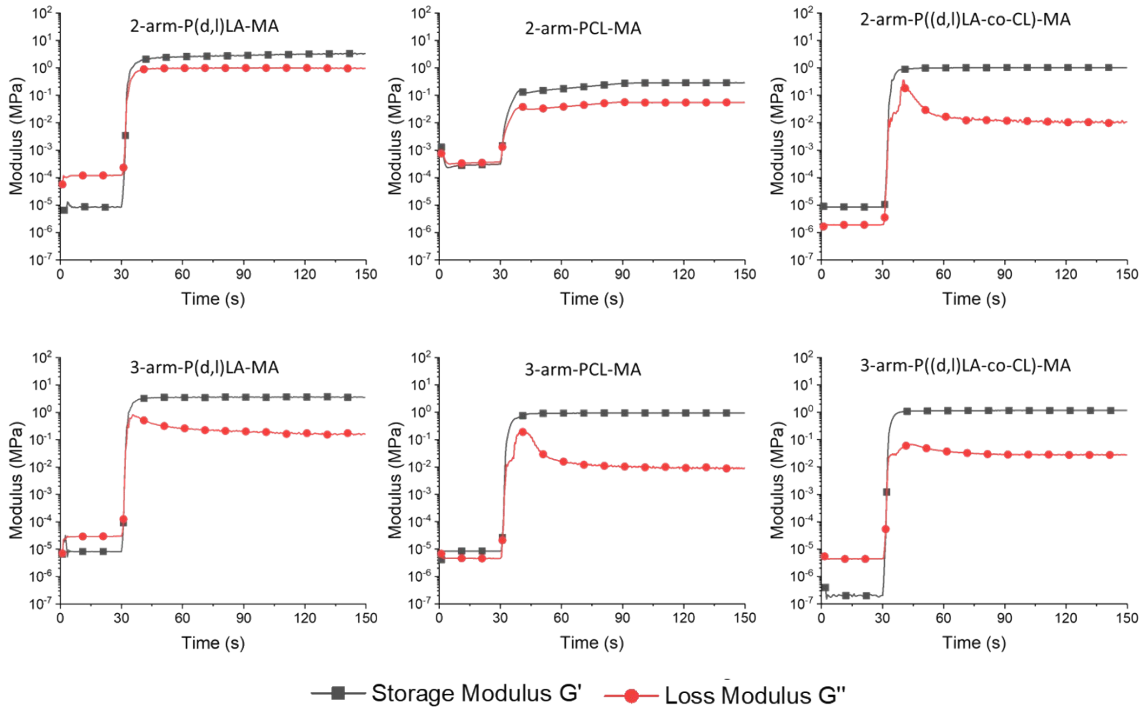

Fig. S4 Storage and Loss moduli before and after UV exposure of 2-arm (top row) and 3-arm (bottom row) P((d,l)LA-co-CL)-MA (left), PCL-MA (middle) and P((d,)-LA-MA (left).

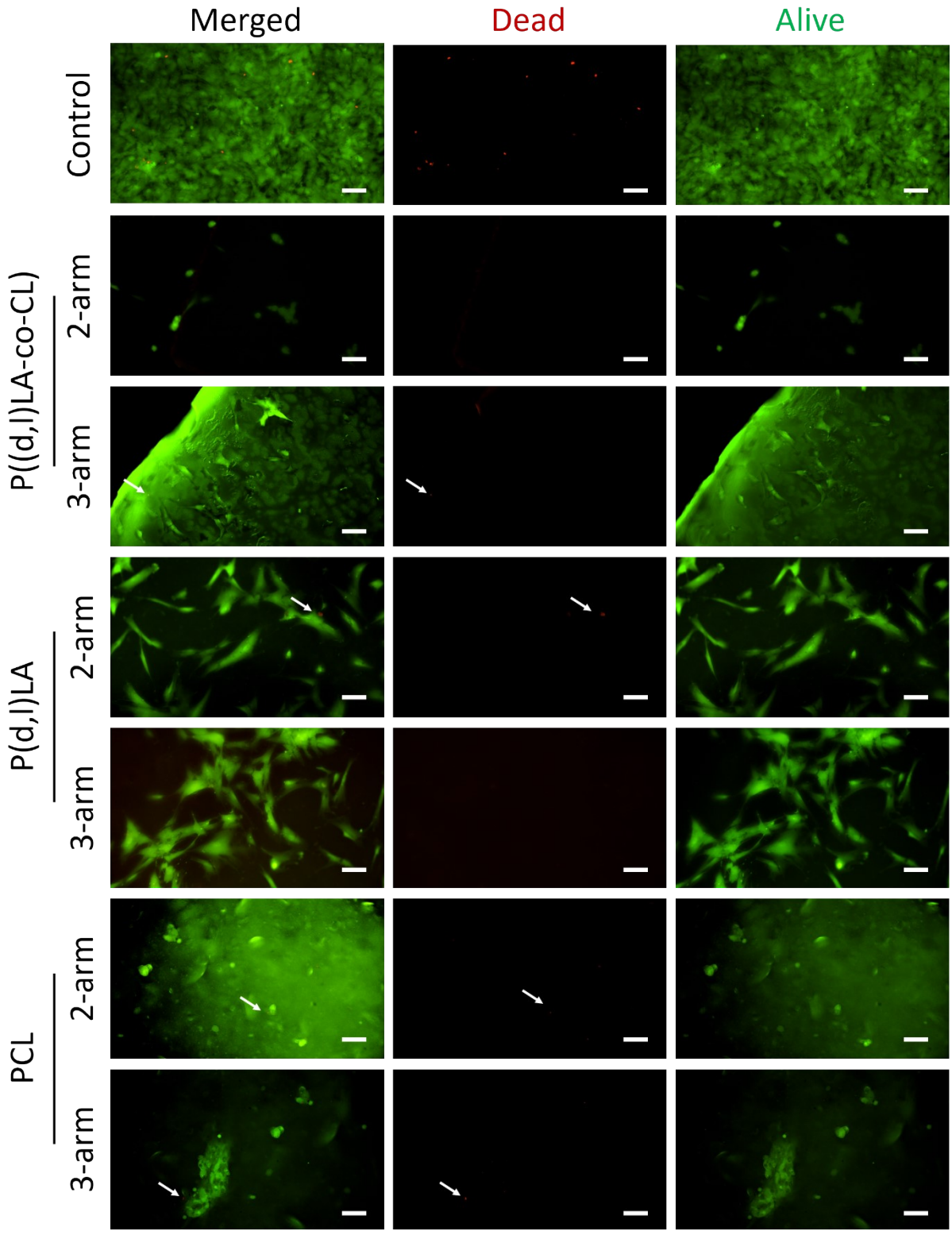

Fig. S5 Split channels and merged images for the *LIVE/DEAD assay of hMSCs after 24 hours seeded onto the films of the different (2- and 3-arms) homo- and copolymers. Dead cells are stained red (ethidium homodimer) and alive cells appear stained with calcein (green). Scale bars are 100 µm.*

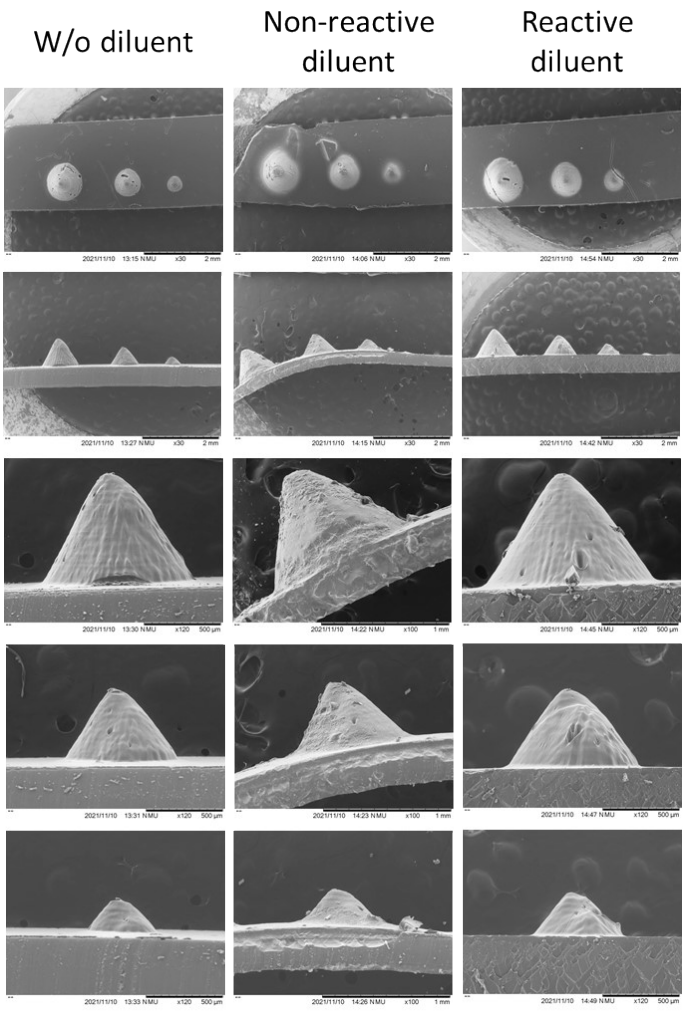

Fig. S6 SEM images of the models with a gradient of cones in the surface using the copolymer P((d,l)LA-co-CL) of 2 arms without diluent (left), with non-reactive diluent (middle) and reactive diluent (right). Higher magnification of the cones with different sizes are shown from the bigger one to the smallest at the bottom.

Table S1 Micro-topography printing error of the gradients of cubes. Average error in the diameter (εø) and the average error in height (εh). The theoretical dimensions of the 3 cones respectively was (Diameter x height): 1 mm x 1 mm, 0.75 mm x 0.75 mm and 0.5 mm x 0.5 mm.

		2-arm-P((d,l)LA-co-CL)-MA		
	Cone position	**W/o diluent**	**W/ non-reactive diluent**	**W/ reactive diluent**
$\varepsilon_{ø}$ (%) ± SD	1	2 ± 0.7	10 ± 2	3 ± 2
	2	5 ± 0.7	1 ± 0.5	7 ± 0.2
	3	19 ± 7	24 ± 3	11 ± 3
ε_{h} (%) ± SD	1	35 ± 0.4	33 ± 2	37 ± 2
	2	57 ± 1	39 ± 2	42 ± 2
	3	126 ± 3	71 ± 11	79 ± 1