Electronic Supporting information

Thermally Triggerable, Anchoring Block Copolymers for use in Aqueous Inkjet Printing

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Common printing technologies

In almost all cases of household and office inkjet printing, drop-on-demand (DOD) inkjet printing is used. DOD printing generates and deposits ink droplets when required on a surface. Droplet deposition is controlled *via* a generated pressure pulse¹ which forces the droplet of ink through the print head nozzle. The main advantage of this technique is the ability to create fine droplets, which provides greater resolution in the final print.² Conversely, the key limitation of this technique is the high cost and short lifetime of the printheads,³ meaning this method is not applicable for low cost, high throughput applications. On the other hand, industrial scale inkjet printing typically relies on continuous stream of ink droplets,⁴ which is ideal for fast-paced, high throughput environments. In CIJ printing, the droplets are generated using a high pressure pump whilst vibrating the nozzle using a piezoelectric crystal.⁵ The ink is then deposited at a high velocity, allowing for increased distances between the print head and substrate.⁶

Polymer Characterisation

Poly(2-hydroxyethyl acrylate), PHEA₈₀

 M_n = 22,400, D = 1.11. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.81 (br, 3H), 1.29 (br, 18 H), 1.62 (br, 2H), 1.79 (br, 6H), 2.26, (br, 1H), 2.51 (br, 2H), 3.55 (br, 2H), 4.01 (br, 2H), 4.76 (br, 1H).

FTIR assigned peaks (cm⁻¹): 3367 (O-H stretching), 2938 (C-H sp³ hybridised stretching), 1724 (C=O stretching), 1449 (C-H methyl bending), 1388 (C-H gem dimethyl bending), 1241 (C=S stretching), 1160 (C-O ester stretching), 1073 (C-O primary alcohol stretching).

Poly(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide), P(HEA₇₉-*st*-HMAA₁)

 M_n = 21,800, D = 1.12. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.84 (br, 3H), 1.29 (br, 18 H), 1.58 (br, 2H), 1.77 (br, 6H), 2.24, (br, 1H), 2.52 (br, 2H), 3.52 (br, 2H), 4.12 (br, 4H), 4.79 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3375 (O-H stretching), 2942 (C-H sp³ hybridised stretching), 1720 (C=O stretching), 1540 (N-H bending), 1452 (C-H methyl bending), 1384 (C-H gem dimethyl bending), 1245 (C=S stretching), 1157 (C-O ester stretching), 1071 (C-O primary alcohol stretching).

Poly(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide), P(HEA₇₇-*st*-HMAA₃)

 $M_{\rm n}$ = 19,600, D = 1.13. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.82 (br, 3H), 1.27 (br, 18 H), 1.60 (br, 2H), 1.78 (br, 6H), 2.22, (br, 1H), 2.53 (br, 2H), 3.54 (br, 2H), 4.14 (br, 4H), 4.80 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3470 (O-H stretching), 2948 (C-H sp³ hybridised stretching), 1723 (C=O stretching), 1536 (N-H bending), 1448 (C-H methyl bending), 1387 (C-H gem dimethyl bending), 1251 (C=S stretching), 1159 (C-O ester stretching), 1068 (C-O primary alcohol stretching).

Poly(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide), P(HEA₇₆-*st*-HMAA₄)

 M_n = 19,200, D = 1.16. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.82 (br, 3H), 1.31 (br, 18 H), 1.63 (br, 2H), 1.79 (br, 6H), 2.26, (br, 1H), 2.51 (br, 2H), 3.55 (br, 2H), 4.16 (br, 4H), 4.78 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3363 (O-H stretching), 2946 (C-H sp³ hybridised stretching), 1721 (C=O stretching), 1535 (N-H bending), 1450 (C-H methyl bending), 1385 (C-H gem dimethyl bending), 1249 (C=S stretching), 1155 (C-O ester stretching), 1070 (C-O primary alcohol stretching).

Poly(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide), P(HEA₇₀-*st*-HMAA₁₀)

 M_n = 21,300, D = 1.18. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.80 (br, 3H), 1.32 (br, 18 H), 1.65 (br, 2H), 1.82 (br, 6H), 2.28, (br, 1H), 2.53 (br, 2H), 3.53 (br, 2H), 4.20 (br, 4H), 4.78 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3365 (O-H stretching), 2943 (C-H sp³ hybridised stretching), 1723 (C=O stretching), 1541 (N-H bending), 1454 (C-H methyl bending), 1385 (C-H gem dimethyl bending), 1246 (C=S stretching), 1160 (C-O ester stretching), 1068 (C-O primary alcohol stretching).

Poly(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide), P(HEA₃₆-*st*-HMAA₄)

 M_n = 10,200, D = 1.17. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.78 (br, 3H), 1.29 (br, 18 H), 1.63 (br, 2H), 1.78 (br, 6H), 2.26, (br, 1H), 2.53 (br, 2H), 3.58 (br, 2H), 4.05 (br, 4H), 4.75 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3466 (O-H stretching), 2945 (C-H sp³ hybridised stretching), 1726 (C=O stretching), 1540 (N-H bending), 1451 (C-H methyl bending), 1389 (C-H gem dimethyl bending), 1253 (C=S stretching), 1161 (C-O ester stretching), 1065 (C-O primary alcohol stretching).

Poly(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide), P(HEA₇₂-*st*-HMAA₈)

 M_n = 17,800, D = 1.18. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.81 (br, 3H), 1.32 (br, 18 H), 1.60 (br, 2H), 1.81 (br, 6H), 2.30, (br, 1H), 2.55 (br, 2H), 3.56 (br, 2H), 4.08 (br, 4H), 4.76 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3368 (O-H stretching), 2943 (C-H sp³ hybridised stretching), 1723 (C=O stretching), 1531 (N-H bending), 1448 (C-H methyl bending), 1381 (C-H gem dimethyl bending), 1250 (C=S stretching), 1154 (C-O ester stretching), 1070 (C-O primary alcohol stretching).

Poly(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide), P(HEA₁₀₈-*st*-HMAA₁₂)

 M_n = 24,700, D = 1.18. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.81 (br, 3H), 1.30 (br, 18 H), 1.62 (br, 2H), 1.83 (br, 6H), 2.26, (br, 1H), 2.53 (br, 2H), 3.52 (br, 2H), 4.12 (br, 4H), 4.72 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3468 (O-H stretching), 2950 (C-H sp³ hybridised stretching), 1724 (C=O stretching), 1545 (N-H bending), 1447 (C-H methyl bending), 1390 (C-H gem dimethyl bending), 1248 (C=S stretching), 1157 (C-O ester stretching), 1072 (C-O primary alcohol stretching).

Poly(propyl methacrylate), PPMA

 M_n = 2,700, D = 1.12. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.82 (br, 3H), 1.12 (br, 3H) 1.21 (br, 3H) 1.31 (br, 18 H), 1.58 (br, 2H), 1.81 (br, 6H), 2.24, (br, 1H), 2.55, (br, 2H), 3.55 (br, 2H), 4.01 (br, 2H)

FTIR assigned peaks (cm⁻¹): 2952 (C-H sp³ hybridised stretching), 1724 (C=O stretching), 1447 (C-H methyl bending), 1392 (C-H gem dimethyl bending), 1248 (C=S stretching), 1155 (C-O ester stretching), 1070.

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₃₆-*st*-HMAA₄)-*b*-PMA₅]

 M_n = 10,700, D = 1.21. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.83 (br, 3H), 1.11 (br, 3H), 1.23 (br, 3H), 1.31 (br, 18 H), 1.61 (br, 2H), 1.83 (br, 6H), 2.22, (br, 1H), 2.56, (br, 2H), 3.57 (br, 4H), 4.11 (br, 6H), 4.74 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3472 (O-H stretching), 2948 (C-H sp³ hybridised stretching), 1730 (C=O stretching), 1543 (N-H bending), 1452 (C-H methyl bending), 1388 (C-H gem dimethyl bending), 1251 (C=S stretching), 1154 (C-O ester stretching), 1060 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₃₆-*st*-HMAA₄)-*b*-PMA₁₀]

 M_n = 11,400, D = 1.24. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.81 (br, 3H), 1.08 (br, 3H), 1.24 (br, 3H), 1.35(br, 18 H), 1.65 (br, 2H), 1.79 (br, 6H), 2.25, (br, 1H), 2.51, (br, 2H), 3.62 (br, 4H), 4.13 (br, 6H), 4.71 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3468 (O-H stretching), 2950 (C-H sp³ hybridised stretching), 1724 (C=O stretching), 1545 (N-H bending), 1447 (C-H methyl bending), 1390 (C-H gem dimethyl bending), 1248 (C=S stretching), 1157 (C-O ester stretching), 1072 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₇₂-*st*-HMAA₈)-*b*-PMA₅]

 $M_{\rm n}$ = 17,700, D = 1.21. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.87 (br, 3H), 1.13 (br, 3H), 1.27 (br, 3H), 1.34 (br, 18 H), 1.64 (br, 2H), 1.81 (br, 6H), 2.19, (br, 1H), 2.52, (br, 2H), 3.61 (br, 4H), 4.08 (br, 6H), 4.79 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3479 (O-H stretching), 2957 (C-H sp³ hybridised stretching), 1731 (C=O stretching), 1552 (N-H bending), 1453 (C-H methyl bending), 1386 (C-H gem dimethyl bending), 1245 (C=S stretching), 1156 (C-O ester stretching), 1067 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₇₂-st-HMAA₈)-*b*-PMA₁₀]

 $M_{\rm n}$ = 18,700, D = 1.23. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.79 (br, 3H), 1.14 (br, 3H), 1.27 (br, 3H), 1.38 (br, 18 H), 1.65 (br, 2H), 1.81 (br, 6H), 2.27, (br, 1H), 2.53 (br, 2H), 3.58 (br, 4H), 4.20(br, 6H), 4.71 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3460 (O-H stretching), 2955 (C-H sp³ hybridised stretching), 1728 (C=O stretching), 1548 (N-H bending), 1449 (C-H methyl bending), 1382 (C-H gem dimethyl bending), 1249 (C=S stretching), 1158 (C-O ester stretching), 1069 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₇₂-*st*-HMAA₈)-*b*-PMA₂₀]

 M_n = 19,600, D = 1.23. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.80 (br, 3H), 1.09 (br, 3H), 1.23 (br, 3H), 1.33 (br, 18 H), 1.62 (br, 2H), 1.87 (br, 6H), 2.17, (br, 1H), 2.51, (br, 2H), 3.51 (br, 4H), 4.11 (br, 6H), 4.76 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3468 (O-H stretching), 2963 (C-H sp³ hybridised stretching), 1730 (C=O stretching), 1551 (N-H bending), 1447 (C-H methyl bending), 1378 (C-H gem dimethyl bending), 1252 (C=S stretching), 1162 (C-O ester stretching), 1062 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₇₂-*st*-HMAA₈)-*b*-PMA₄₀]

 M_n = 21,700, D = 1.25. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.79 (br, 3H), 1.14 (br, 3H), 1.26 (br, 3H), 1.40 (br, 18 H), 1.63 (br, 2H), 1.88 (br, 6H), 2.25, (br, 1H), 2.50, (br, 2H), 3.51 (br, 4H), 4.12 (br, 6H), 4.70 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3473 (O-H stretching), 2968 (C-H sp³ hybridised stretching), 1732 (C=O stretching), 1547 (N-H bending), 1454 (C-H methyl bending), 1382 (C-H gem dimethyl bending), 1247 (C=S stretching), 1165 (C-O ester stretching), 1064 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₁₀₈-st-HMAA₁₂)-*b*-PMA₅]

 M_n = 24,600, D = 1.21. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.83 (br, 3H), 1.13 (br, 3H), 1.21 (br, 3H), 1.29 (br, 18 H), 1.58 (br, 2H), 1.80 (br, 6H), 2.21, (br, 1H), 2.53, (br, 2H), 3.54 (br, 4H), 4.14 (br, 6H), 4.71 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3475 (O-H stretching), 2974 (C-H sp³ hybridised stretching), 1728 (C=O stretching), 1549 (N-H bending), 1464 (C-H methyl bending), 1386 (C-H gem dimethyl bending), 1252 (C=S stretching), 1168 (C-O ester stretching), 1059 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₁₀₈-st-HMAA₁₂)-*b*-PMA₁₀]

 M_n = 25,700, D = 1.23. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.84 (br, 3H), 1.17 (br, 3H), 1.27 (br, 3H), 1.33 (br, 18 H), 1.62 (br, 2H), 1.83 (br, 6H), 2.30, (br, 1H), 2.51 (br, 2H), 3.60 (br, 4H), 4.22 (br, 6H), 4.69 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3472 (O-H stretching), 2973 (C-H sp³ hybridised stretching), 1732 (C=O stretching), 1547 (N-H bending), 1466 (C-H methyl bending), 1390 (C-H gem dimethyl bending), 1251 (C=S stretching), 1170 (C-O ester stretching), 1061 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₁₀₈-st-HMAA₁₂)-*b*-PMA₂₀]

 M_n = 26,700, D = 1.24. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.85 (br, 3H), 1.15 (br, 3H), 1.26 (br, 3H), 1.32 (br, 18 H), 1.58 (br, 2H), 1.81 (br, 6H), 2.23, (br, 1H), 2.52, (br, 2H), 3.60 (br, 4H), 4.19 (br, 6H), 4.71 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3475 (O-H stretching), 2969 (C-H sp³ hybridised stretching), 1733 (C=O stretching), 1555 (N-H bending), 1464 (C-H methyl bending), 1387 (C-H gem dimethyl bending), 1253 (C=S stretching), 1168 (C-O ester stretching), 1058 (C-O primary alcohol stretching).

Poly[(2-hydroxyethyl acrylate-*stat-N*-hydroxymethyl acrylamide)-*b*-propyl methacrylate], P[(HEA₁₀₈-st-HMAA₁₂)-*b*-PMA₄₀]

 M_n = 28,600, D = 1.25. ¹H NMR (300 MHz, d₆-DMSO, δ ppm from TMS): 0.84 (br, 3H), 1.12(br, 3H), 1.21 (br, 3H), 1.33 (br, 18 H), 1.61 (br, 2H), 1.81 (br, 6H), 2.22, (br, 1H), 2.57, (br, 2H), 3.63 (br, 4H), 4.12 (br, 6H), 4.69 (br, 2H)

FTIR assigned peaks (cm⁻¹): 3478 (O-H stretching), 2964 (C-H sp³ hybridised stretching), 1731 (C=O stretching), 1561 (N-H bending), 1458 (C-H methyl bending), 1382 (C-H gem dimethyl bending), 1252 (C=S stretching), 1171 (C-O ester stretching), 1054 (C-O primary alcohol stretching).

Reaction	СТА	solvent	Time [h]	Monomer conv.ª [%]	M _{nth} [g mol⁻¹] ^b	<i>M</i> [g mol⁻¹] ^c	Ð (<i>M</i> _w / <i>M</i> _n) °
1	CPDT	DMF	5	98	9448	20,300	1.13
2	CPDT	Methanol	3	90	8706	18,400	1.15
3	DCMP	DMF	5	97	9375	22,500	1.12
4	DCMP	Methanol	4	98	9468	22,400	1.11

Table S1. Molar Mass data for the RAFT polymerisation of HEA (Target D_p =80)

(a) Determined by ¹H NMR spectroscopy

(b) Theoretical molecular mass: Calculated using Equation S1

(c) Determined by DMF GPC using poly(methyl methacrylate) standards

Theoretical molecular mass $(M_{n, th})$ calculation for PHEA

 $\frac{\% \text{ monomer conversion}}{100}$

 $M_{n, th (PHEA)} = (target D_p \times Equation S1)$

 $\times M_{r(HEA)}) + M_{r(CTA)}$

where target D_p = moles of monomer/moles of CTA



Figure S1. Kinetic data; molar mass evolution with time using (a) CPDT and (b) DCMP, Monomer conversion during the RAFT polymerisation of HEA using (c) CPDT and (d) DCMP and GPC traces of PHEA synthesised using (e) CPDT and (f) DCMP.



Figure S2. GPC kinetic traces for polymerisations is (a) CPDT and (b) DCMP, where the arrow shows polymer evolution with time.



Figure S3. Plots of molar mass (M_n) and dispersity *versus* monomer conversion for the RAFT polymerisation of HEA using CPDT and DCMP in DMF or methanol.

		[g mol ⁻¹] ^a	20,200	20,200	19,800	20,000	15,400	15,900
Table S2. Molar mass data 1 P[l	c	Extension	18	10	16	8	109	119
	Timo		120	120	120	120	175	175
		Target M _n	20,360	21,460	20,360	21,460	11,860	11,210
		Solvent	МеОН	МеОН	DMF	DMF	DMF	DMF
		Monomer	РМА	РМА	PMA	PMA	HEA- HMAA	HEA- HMAA
		E $[M_w/M_n]^a$	1.18	1.19	1.18	1.19	1.12	1.27
	٨	M _n a [g mol ⁻¹]	17,800	18,900	17,800	18,900	2,700	2,100
	Macro-CT	Base CTA	CPDT	DCMP	CPDT	DCMP	CPDT	DCMP
		Name	P(HEA-st-HMAA)	P(HEA-st-HMAA)	P(HEA-st-HMAA)	P(HEA- <i>st</i> -HMAA)	РРМА	РРМА



Figure S4. GPC traces of macro-CTAs and block copolymers where [P(HEA-*st*-HMAA)-*b*-PMA)] is synthesised using (a) CPDT-based P(HEA-*st*-HMAA) macro-CTA and (b) DCMP-based P(HEA-*st*-HMAA) macro-CTA in methanol and DMF, and P[PMA-*b*-(HEA-*st*-HMAA)] is synthesised using (c) CPDT-based PPMA macro-CTA and (d) DCMP-based PPMA macro-CTA in DMF.

Figure S4 shows that all synthetic routes provided unimodal chain extension. DCMPbased PPMA macro CTAs yielded block copolymers with large dispersites due to the poor control of the first step. DCMP-based P(HEA-*st*-HMAA) macro-CTAs also yielded polymers with large dispersities, and thus DCMP was deemed to be an unsuitable CTA for the synthesis of these block copolymers. Syntheses conducted in DMF also resulted in slightly larger dispersities compared to those in methanol when using DCMP-based P(HEA-*st*-HMAA) macro-CTAs.

Theoretical molecular mass $(M_{n, th})$ calculation for P(HEA-st-HMAA)



where target D_p = moles of monomer/moles of CTA



Figure S5. DMF GPC traces of copolymers with different target HMAA loading.

Table S3. Time required to crosslink hydrophilic P(HEA-st-HMAA) copolymers containing varying HMAA contents in the bulk at 150 °C, where S denotes soluble in methanol and IS indicates insoluble. The dark line is a guide for the eye to show the 'border' between soluble (non-crosslinked) and insoluble (crosslinked).

Time [min]	P(HEA-st-HMAA) target D _p								
	80 - 0	79 - 1	77 - 3	76 - 4	72 - 8	70 - 10			
0	S	S	S	S	S	S			
5	S	S	S	S	S	S			
10	S	S	S	S	IS	IS			
15	S	S	S	S	IS	IS			
20	S	S	S	IS	IS	IS			
30	S	S	S	IS	IS	IS			
60	S	S	S	IS	IS	IS			
90	S	S	IS	IS	IS	IS			
120	S	S	IS	IS	IS	IS			
150	S	S	IS	IS	IS	IS			
180	S	IS	IS	IS	IS	IS			

$P(HEA_st-HMAA)$ target D

Table S4. Time required to crosslink hydrophilic P(HEA-st-HMAA) copolymers containing varying HMAA contents in thin-film at 150 °C, where S denotes soluble in methanol and IS indicates insoluble. The dark line is a guide for the eye to show the 'border' between soluble (non-crosslinked) and insoluble (crosslinked).

Time [mins]		P(HEA- <i>st</i> -HMAA) target <i>D</i> _p								
	80 - 0	79 - 1	77 - 3	76 - 4	72 - 8	70 - 10				
0	S	S	S	S	S	S				
30	S	S	S	S	S	S				
60	S	S	S	S	S	S				
70	S	S	S	S	S	IS				
80	S	S	S	S	IS	IS				
90	S	S	S	S	IS	IS				
120	S	S	S	IS	IS	IS				
150	S	S	S	IS	IS	IS				
180	S	S	IS	IS	IS	IS				
210	S	S	IS	IS	IS	IS				
240	S	IS	IS	IS	IS	IS				

P(HEA-st-HMAA) target D_n

Table S5. Time required to crosslink bulk and thin-film $P(HEA_{36}-st-HMAA_4)$, $P(HEA_{72}-st-HMAA_8)$ and $P(HEA_{108}-st-HMAA_{12})$ copolymers at 150 °C, where S denotes soluble in methanol and IS indicates insoluble. The dark line is a guide for the eye to show the 'border' between soluble (non-crosslinked) and insoluble (crosslinked).

Time	P(HEA- <i>st</i> -HMAA) target <i>D</i> _p									
[min]		Bulk			Thin film					
	36-4	72-8	108-12	36-4	72-8	108-12				
0	S	S	S	S	S	S				
5	S	S	IS	S	S	S				
10	S	IS	IS	S	S	S				
15	S	IS	IS	S	S	S				
20	IS	IS	IS	S	S	S				
30	IS	IS	IS	S	S	S				
40	IS	IS	IS	S	S	S				
50	IS	IS	IS	S	S	S				
60	IS	IS	IS	S	s	S				
70	IS	IS	IS	S	S	IS				
80	IS	IS	IS	S	IS	IS				
90	IS	IS	IS	IS	IS	IS				

Table S6. RAFT copolymerisation of HEA and HMAA targeting different molecular weights.

PHEA	PHMAA	Total	0T1	Monomer	$M_{ m n}^{ m th}$	Mn	Ð	HMAA
target	target	target	CIA	conv ^a [%]	[a mol-1] b	[a mol ⁻¹] c	(M/M) °	mol% ^d
$D_{ m p}$	D_{p}	Dp		001111 [70]	[9]	[9]	(
36	4	40	CPDT	98	4,827	10,200	1.17	10.8
72	8	80	CPDT	97	9,220	17,800	1.18	11.3
108	12	120	CPDT	98	13,803	24,700	1.18	11.6
36	4	40	DCMP	97	4,795	11,500	1.18	10.7
72	8	80	DCMP	96	9,143	18,900	1.19	11.6
108	12	120	DCMP	98	13,822	26,200	1.19	11.9

(a) Determined by ¹H NMR

(b) Calculated using Equation S2

(c) Determined by DMF GPC using poly(methyl methacrylate) standards

(d) Estimated by FTIR

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CPDT = cyano-2-propyl dodecyl trithiocarbonate

DCMP = 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid



Figure S6. GPC traces of copolymers of HEA and HMAA targeting different total degrees of polymerisation using (a) CPDT and (b) DCMP as CTAs. The HEA:HMAA target molar ratio is fixed at 9:1 in each case.



Figure S7. Ratio of sp³ C-H and N-H bands for polymers with different molar masses, but with 10 mol% target loading of HMAA. The calibration curve from Figure 2(b) included (polymer series target D_p 80 with varying HMAA content). Data added is highlighted with a red box.

Table S7. RAFT polymerisation of PMA (in DMF) molar mass data.

СТА	Monomer conv.ª [%]	M _n th [g mol⁻¹] ^b	<i>M</i> _n [g mol⁻¹] ^c	Ð [<i>M</i> _w / <i>M</i> _n] ^c	Time [h]
CPDT	93	2,701	2,700	1.12	30
DCMP	76	2,222	2,050	1.27	30

(a) Determined by ¹H NMR

(b) Target degree of polymerisation D_p = 20. Calculated using Equation S3

(c) Determined by DMF GPC using poly(methyl methacrylate) standards

Theoretical molecular mass $(M_{n, th})$ calculation for PPMA

	% monomer conversion		Equation S3
$M_{n, th (PPMA)} = (target D_p \times$	100	$\times M_{r (PMA)}) + M_{r}$	
(CTA)			

where target D_p = moles of monomer/moles of CTA



Figure S8. (a) molar mass (M_n) evolution with time, (b) molar mass and dispersity *versus* monomer conversion and (c) semi-logarithmic kinetic plots of the RAFT polymerisation of PMA using both CPDT and DCMP in DMF.



Figure S9. DMF GPC traces of PPMA synthesised with CPDT and DCMP in DMF.

Table S8 M	lolar mass data t	for P(HFA-	st-HMAA) to b	be used as	macro-CTAs

PHEA D _p	PHMAA D _p	Monomer conv. ^a [%]	<i>M</i> n th [g mol⁻¹] ^b	<i>M</i> n [g mol⁻¹] ^c	Ð (<i>M</i> _w / <i>M</i> _n) ^c	HMAA mol% ^d
36	4	98	4,827	9,900	1.20	9.8
72	8	97	9,220	17,200	1.21	10.2
108	12	98	13,803	24,000	1.21	10.7

(a) Determined by ¹H NMR

(b) Calculated using Equation S2 with CPDT as CTA

(c) Determined by DMF GPC using poly(methyl methacrylate) standards

(d) Estimated by FTIR

Table S9. Required crosslinking via different routes. The dark lin soluble (non-crosslinked) and in			EA-st-HMAA)]	EA-st-HMAA)] MF		20-72-8	S	S	S	S	S	S	SI	S	
			P[PMA- <i>b</i> -(H		CPDT	20-72-8	S	S	S	S	S	IS	IS	IS	ed en
		target $D_{ m p}$	(A)]	ΛF	DCMP	72-8-20	S	ა	S	IS	S	S	S	เร	1
	Polymer ta			IAA)- <i>b</i> -PI	CPDT	72-8-20	S	S	S	S	S	<u>N</u>	S	ิง	15
			MA-st-HN	anol	DCMP	72-8-20	S	S	S	SI	S	S	S	<u>N</u>	12
			P[(H	Meth	CPDT	72-8-20	S	S	S	S	S	S	S	S	
		_	(AMMA)	anol	DCMP	72-8	S	S	S	<u>N</u>	<u>N</u>	<u>N</u>	<u>N</u>	<u>N</u>	
50:50.	scosity measurement	s of	HEA-90	Meth	CPDT 0	yme	rs a ທ	at 5 ທ	ഗ ഗ	<u>S</u>	n et <u>ທ</u>	nar ഗ	<u>v/ام</u>	vate <u>v</u>	۶r
	Macro-CTA			<u> </u>		fmP	a.sl		fa	nol-	1]				2
-			20			3.	7		19	,600)				
P(HEA ₇₂ - <i>st</i> -HMAA ₈) P(HEA ₁₀₈ - <i>st</i> -HMAA ₁₂)			40			3.	8		21	,700	C				
)	20 20 40	[min]		4. 5.	7 ⁰ 6	2.5	12 6 28	, 7 00 ,600) - 2 -2	20	25	30	
		I				-			-	,					



Figure S10. Dynamic light scattering (DLS) traces for (a) $P[(HEA_{72}-st-HMAA_8)-b-PMA_{20}]$, (b) $P[(HEA_{72}-st-HMAA_8)-b-PMA_{40}]$, (c) $P[(HEA_{108}-st-HMAA_{12})-b-PMA_{20}]$ and (d) $P[(HEA_{108}-st-HMAA_{12})-b-PMA_{40}]$.

Table S11. Dynamic Light Scattering measurements of 5% w/w block copolymer solutions in 50:50 ethanol/water.

Macro-CTA	РРМА <i>D</i> ₀	Z-average diameter, nm	PDI
	20	424	0.238
$P(\Pi E A_{72}$ -St- $\Pi W A A_8)$	40	330	0.312
	20	480	0.232
$\Gamma(\Pi \Box A_{108} - St - \Pi V A A_{12})$	40	425	0.330



Figure S11. Chemical structure of the dye '*Brilliant Blue*' provided by Domino Printing UK.

Table S12. Ink formulation compositions for inkjet printing studies.

Formulation code:	CF1	CF2	CF3	CF4	CF8
Component [% w/w]					
Brilliant Blue	1	1	1	1	1
P[(HEA ₇₂ -st-HMAA ₈)-b-PMA ₂₀]		5			
P[(HEA ₇₂ -st-HMAA ₈)-b-PMA ₄₀]			5		
P[(HEA ₁₀₈ -s <i>t</i> -HMAA ₁₂)- <i>b</i> -PMA ₂₀]	5				
P[(HEA ₁₀₈ -s <i>t</i> -HMAA ₁₂)- <i>b</i> -PMA ₄₀]				5	
Ethanol	47	47	47	47	49.5
Water	47	47	47	47	49.5

Table S13. Physical properties and dimensionless numbers for ink formulations containing polymer and commercially available inks.

Formulation	Density [kg/m ³]	Viscosity [mPa.s]	Surface tension [mN/m]	Velocity [m/s]	Length scale [µm]	Re	We	Oh	Z
CF1	906.5	4.7	38.7	21	120	486	1240	0.072	13.8
CF2	932	3.7	37.9	21	120	635	1301	0.057	17.6
CF3	938.7	3.7	36.9	21	120	639	1346	0.056	17.4

CF4	936.9	5.6	38.0	21	120	422	1305	0.086	11.7
291BK*	865.5	4.2	32.5	21	120	522	1409	0.072	13.9
299BK*	863.9	4.0	31.2	21	120	539	1465	0.071	14.0
433BL*	872.3	5.3	44.1	21	120	416	1047	0.078	12.8
1BK111*	873.1	4.2	31.9	21	120	521	1448	0.073	13.7

* 291BK, 299BK, 433BL and 1BK111 are standard ink (non-disclosed) formulations produced by Domino Science UK.

The behaviour of liquid droplets can be characterised by a grouping of dimensionless physical constants, the most useful of which are the Reynolds (Re), Weber (We), and Ohnesorge (Oh) numbers. The Reynolds number gives the ratio of fluid inertia and viscous forces, the Weber number the ratio of inertia to surface tension and the Ohnesorge number relates the viscous forces to inertial surface tension forces.^{7,8} The Reynolds, Weber and Ohnesorge numbers are expressed in Equations S4, S5 and S6, respectively.

Reynolds number
S4 $Re = \frac{\rho vL}{\mu}$ EquationWeber number
S5 $We = \frac{\rho v2L}{\sigma}$ EquationOhnesorge number
S6 $Oh = \frac{\sqrt{We}}{Re}$ Equation

Where ρ = density in kg m⁻³; v = velocity in m s⁻¹; L = characteristic length scale in μ m; μ = viscosity in Pa.s and σ = surface tension in N m⁻¹.

Dimensionless numbers were calculated using the following constants for CIJ printing: Characteristic length = 120×10^{-6} m (expected drop diameter of 120μ m from a 60 μ m nozzle) and characteristic velocity = 21 m s^{-1} (average jet velocity).

Viscosity, density and surface tension measurements were calculated at 25 °C and for surface tension the value at the shortest bubble lifetime (15 ms) was used for the calculation. Ideally these measurements would be carried out at 42 °C to be more representative of CIJ jetting.

The parameter Z is defined as Z = 1/Oh. Briefly, at high Oh values, viscous dissipation prevents droplet ejection, whereas at low values the primary drop is accompanied by a large number of satellite droplets. From a simple model of fluid flow in a drop generator of simplified geometry, Oh < 0.5 should deliver stable drop generation.⁹

It should be noted that this section describes jetting using continuous inkjet printing and the printable threshold will vary from drop-on-demand systems. From previous studies carried out at Domino, it is generally accepted that formulations with a Reynolds number between 200 and 1000 and Ohnesorge number between 0.04 and 0.2 would be expected to produce droplets reliably.

Table S14. Drop size measurements and prints for ink formulations containing block copolymers.

Formulation	Measurements	First Broken Drop	Print Sample
F1	70.6 nm 18.4 nm 108.7 nm 114.4 nm 176.5 nm		HEA108_HMA12_PMA20 01.05
F2	9.6 nm 5.4 nm 153.7 nm 94.7 nm 160.6 nm	0	HEA72_HMA8_PMA20 01.05



Table S15. Drop size measurements and prints for ink formulations containing commercial inks.

Formulation	Measurements	First Broken Drop	Print Sample
1BK111	108.3 nm 17.8 nm 115.6 nm 113.9 nm 222.7 nm		18K111 03.05.2018
2BK106- 291BK	103.7 nm 21.2 nm 115.6 nm 109.7 nm 226.5 nm		28K106_2918K 03.05.2018





Figure S12. Images showing jetting break-up of formulations containing block copolymers and commercially available inks.



Figure S13. Diagram showing the six measurements used to describe drop size.

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