

Supporting Information

3D Printing of Biocompatible Supramolecular Polymers and their Composites

Lewis R. Hart,^a Siwei Li,^b Ricky Wildman,^c Julian Jones^b and Wayne Hayes^{*a}

^a Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, U.K. e-mail: w.c.hayes@reading.ac.uk, Tel: +44 (0)118 378 6491, Fax: +44 (0)118 378 6331

^b Department of Materials, Imperial College London, South Kensington Campus, London, SW7 2BP, U.K.

^c Department of Chemical and Environmental Engineering, The University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

Contents

Experimental	S2
Figure S1. ¹ H NMR spectra of 5a	S4
Figure S2. ¹³ C NMR spectra of 5a	S4
Figure S3. ¹ H NMR spectra of 5b	S5
Figure S4. ¹³ C NMR spectra of 5b	S5
Figure S5. ¹ H NMR spectra of 5c	S6
Figure S6. ¹³ C NMR spectra of 5c	S6
Figure S7. ¹ H NMR spectra of 5d	S7
Figure S8. ¹³ C NMR spectra of 5d	S7
Figure S9. Viscosity analysis of polymers 5a-d in solution	S8
Figure S10. Drop shape analysis and surface tension of solutions of polymers 5a-d	S8
Figure S11. Image of test printing rig used to develop waveforms	S9
Figure S12. Waveforms developed using test-rig printer	S9
Figure S13. Drop watcher images of the four supramolecular polymers 5a-d	S10
Figure S14. Image of the printed samples of supramolecular polymers 5a-d	S11
Figure S15. Microscopy images of the hybrid solutions of 5c silica particles	S11
Figure S16. Drop watcher image of the hybrid containing 5c and 5% silica particles	S12
Figure S17. ESEM micrographs of printed polymer 5c and the hybrid materials	S12

Experimental

Synthesis of 4-(2-aminoethyl) morpholine terminated SPU with 2,4-TDI and poly(caprolactone) diol (**5a**)

To poly(caprolactone) diol **1** [$M_n = 2000$ Da] (4×10^{-3} M) in a molten state at 80 °C was added the 2,4-toluenediisocyanate **2** (8.4×10^{-3} M) in the bulk before stirring the mixture for three hours at 80 °C under a nitrogen atmosphere. Dry THF (80 mL) was added and the pre-polymer **3** solution was left to cool slightly before 4-(2-aminoethyl) morpholine **4a** (9.2×10^{-3} M) was added and the solution stirred for three hours at 80 °C. The volume of solvent was then reduced *in vacuo* and the crude product purified by repeated slow precipitations into methanol before drying under vacuum at 60 °C for 12 hours to afford polymer **5a** as a tacky off-white solid (8.63 g, 81%); IR (ATR) ν/cm^{-1} : 3349, 2943, 2864, 1721, 1536, 1366, 1238, 1186, 1044; ^1H NMR (400 MHz/ CDCl_3) δ ppm: 7.78 (0.3H, s), 7.58 (0.5H, s), 7.22-7.06 (2.5H, m), 6.64-6.58 (0.8H, br), 5.54 (0.5H, s), 4.17-4.08 (2.5H, m), 4.08-3.88 (18H, t, $J = 7.0$ Hz), 3.88 (2H, s), 3.60 (2.5H, t, $J = 4.5$ Hz), 3.33 (1H, q, $J = 5.5$ Hz), 2.5-2.13 (27H, m), 1.67-1.58 (40H, m), 1.49-1.29 (20H, m), 0.97 (3H, s); ^{13}C NMR (100 MHz/ CDCl_3) δ ppm: 173.5, 173.3, 156.3, 153.8, 136.8, 136.2, 130.6, 125.9, 115.5, 114.9, 69.0, 66.8, 65.1, 64.9, 64.1, 57.6, 53.3, 36.6, 34.6, 34.1, 28.6, 28.3, 25.5, 24.5, 21.7, 17.2, 17.0; GPC (THF) $M_n = 6637$ Da, $M_w = 9961$ Da, $D_m = 1.501$; DSC: $T_g = -49.10$ °C, $T_m = 37.04$ °C

Synthesis of Ureidopyrimidinone terminated SPU with 2,4-TDI and poly(caprolactone) diol (**5b**)

To poly(caprolactone) diol **1** [$M_n = 2000$ Da] (4×10^{-3} M) in a molten state at 80 °C was added the 2,4-toluenediisocyanate **2** (8.4×10^{-3} M) in the bulk before stirring the mixture for three hours at 80 °C under a nitrogen atmosphere. Dry DMAc (80 mL) was added and the pre-polymer **3** solution was left to cool slightly before 2-Amino-4-hydroxy-6-methylpyrimidine **4b** (9.2×10^{-3} M) was added and the solution stirred for three hours at 80 °C. The volume of solvent was then reduced *in vacuo* and the crude product purified by repeated slow precipitations into methanol before drying under vacuum at 60 °C for 12 hours to afford polymer **5b** as a white solid (8.06 g, 76%); IR (ATR) ν/cm^{-1} : 3346, 3018, 2942, 2865, 1724, 1624, 1536, 1455, 1227, 1160, 1028, 748; ^1H NMR (400 MHz/ CDCl_3) δ ppm: 9.55-9.29 (2.5H, m), 9.10 (0.25H, s), 8.71-8.64 (1.5H), 8.36-8.17 (48H, s), 8.17-8.10 (1H, m) 8.10-7.91 (1.0 H, m), 7.53 (1.5H, s), 7.33-6.97 (7H, m), 6.88-6.70 (0.75H, m), 6.62-6.32 (1.5H, br), 5.90-5.76 (1H, m), 5.39 (0.5H, s), 4.16-3.90 (120H, br), 3.88 (2H, s), 3.82 (10H, s), 3.73 (1H, s), 3.64 (2H, s), 3.46-3.31 (7H, br), 3.25-3.16 (100H, br), 2.95 (12H, s), 2.80 (11H, s), 2.55 (2.5H, m), 2.38-2.09 (99H, br), 1.99-1.94 (16H, m), 1.68-1.43 (168H, m), 1.44-1.23 (84H, m), 0.91 (15H, s); ^{13}C NMR (100 MHz/ CDCl_3) δ ppm: 172.5, 172.4, 169.5, 155.3, 154.2, 153.4, 146.3, 137.2, 136.4, 129.9, 125.2, 121.6, 114.8, 112.0, 105.2, 100.2, 68.3, 63.7, 63.4, 52.7, 51.4, 48.5, 39.4, 38.9, 37.3, 34.2, 33.3, 28.2, 27.8, 24.0, 21.2, 17.3, 16.6; GPC (THF) $M_n = 8310$ Da, $M_w = 15426$ Da, $D_m = 1.856$.

Synthesis of benzylamine terminated SPU with 2,4-TDI and poly(caprolactone) diol (**5c**)

To poly(caprolactone) diol **1** [$M_n = 2000$ Da] (4×10^{-3} M) in a molten state at 80 °C was added the 2,4-toluenediisocyanate **2** (8.4×10^{-3} M) in the bulk before stirring the mixture for three hours at 80 °C under a nitrogen atmosphere. Dry DMAc (80 mL) was added and the pre-polymer **3** solution was left to cool slightly before benzylamine **4c** (9.2×10^{-3} M) was added and the solution stirred for three hours at 80 °C. The volume of solvent was then reduced *in vacuo* and the crude product purified by repeated slow precipitations into methanol before drying under vacuum at 60 °C for 12 hours to afford polymer **5c** as a tacky white solid (8.77 g, 84%); IR (ATR) ν/cm^{-1} : 3353, 2942, 2865, 1727, 1536, 1220, 1159, 1096, 1065, 750; ^1H NMR (400 MHz/ CDCl_3) δ ppm: 7.77 (0.5H, s), 7.69-7.64 (2.5H, m), 7.35-7.16 (33H, br), 7.14-6.92 (5.5H, m), 6.87 (2H, s), 6.68 (0.5H, s), 6.01-5.90 (2H, br) 4.40-4.20 (5H, m), 4.18-4.00 (82H, m), 3.88 (10H, s) 3.74 (2.5H, t, $J = 8\text{Hz}$), 2.44-2.19 (89H, m), 2.18 (5H, s), 2.03 (7.5H, s), 1.77-1.49 (166H, m), 1.46-1.24 (84H, m), 0.97 (14H, s); ^{13}C NMR (100 MHz/ CDCl_3) δ ppm: 173.5, 156.2, 154.0, 139.4, 137.0, 136.6, 130.6, 128.4, 127.3, 126.9, 115.1, 114.3, 68.9, 67.8, 64.7, 64.1, 50.4, 43.9, 34.6, 34.0, 28.5, 28.3, 24.5, 21.7, 17.0; GPC (THF) $M_n = 6676$ Da, $M_w = 9508$ Da, $D_m = 1.424$; DSC: $T_g = -48.39$ °C, $T_m = 34.03$ °C.

Synthesis of *N*-(4-methoxybenzyl)-1-(4-nitrophenyl)methanamine terminated SPU with 2,4-TDI and poly(caprolactone) diol (**5d**)

To poly(caprolactone) diol **1** [$M_n = 2000$ Da] (4×10^{-3} M) in a molten state at 80 °C was added the 2,4-toluenediisocyanate **2** (8.4×10^{-3} M) in the bulk before stirring the mixture for three hours at 80 °C under a nitrogen atmosphere. Dry DMAc (80 mL) was added and the pre-polymer **3** solution was left to cool slightly before *N*-(4-methoxybenzyl)-1-(4-nitrophenyl)methanamine **4d** (9.2×10^{-3} M) was added and the solution stirred for three hours at 80 °C. The volume of solvent was then reduced *in vacuo* and the crude product purified by repeated slow precipitations into methanol before drying under vacuum at 60 °C for 12 hours to afford polymer **5d** as an orange viscous oil (8.97 g, 75 %); IR (ATR) ν/cm^{-1} : 3024, 2945, 2881, 1722, 1547, 1329, 1233, 1184, 1024, 758; ^1H NMR (400 MHz/ CDCl_3) δ ppm: 8.21-8.07 (6.5H, d, $J = 8.5$ Hz), 7.79-7.65 (4H, br), 7.56-7.35 (6H, m), 7.29-7.09 (16H, m), 7.00-6.80 (12H, m), 6.66-6.57 (1H, m), 6.40 (2H, s), 4.76 (5H, s), 4.52 (7H, s), 4.18-3.97 (79H, m), 3.88 (10H, s), 3.80 (12H, s), 2.46-2.20 (79H, m), 2.18-2.13 (3H, m), 1.90-1.50 (168H, m), 1.46-1.28 (80H, m), 0.97 (14H, s); ^{13}C NMR (100 MHz/ CDCl_3) δ ppm: 173.5, 173.3, 159.5, 153.7, 147.3, 145.7, 137.0, 136.7, 130.4, 128.0, 123.8, 123.2, 114.6, 68.9, 64.7, 64.1, 55.3, 50.8, 50.7, 34.6, 34.0, 28.3, 25.5, 24.5, 21.7, 17.0, 16.6; GPC (THF) $M_n = 8224$ Da, $M_w = 12971$ Da, $D_m = 1.577$; DSC: $T_g = -48.51$ °C.

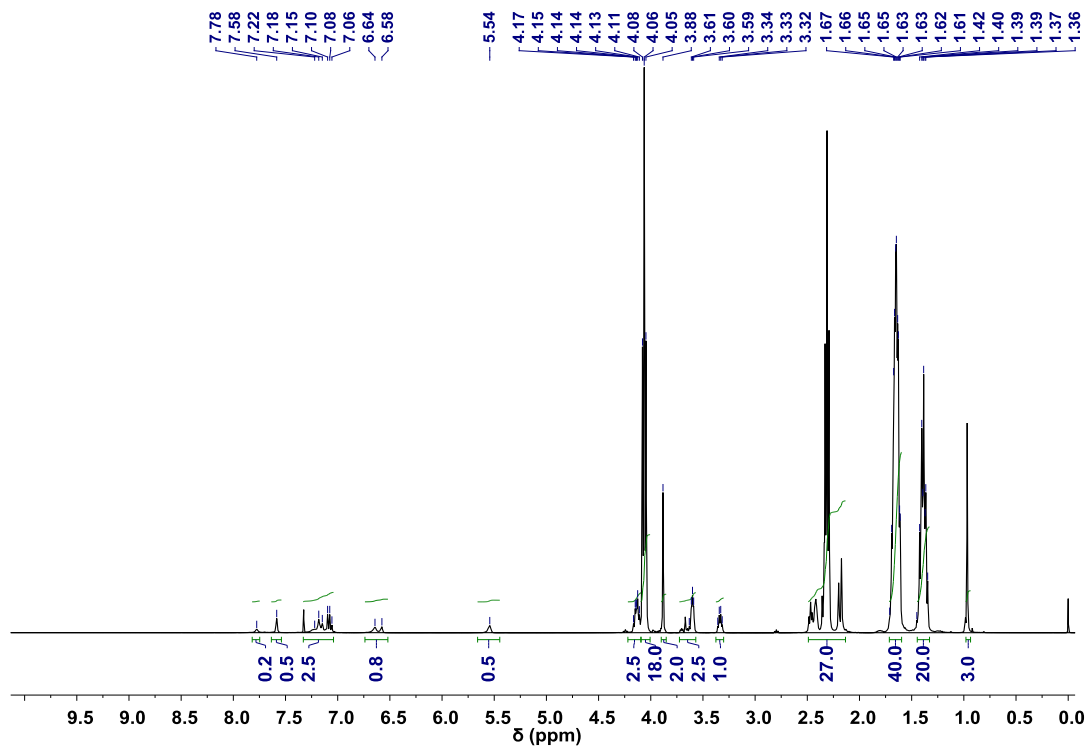


Figure S1. ¹H NMR spectra of 5a

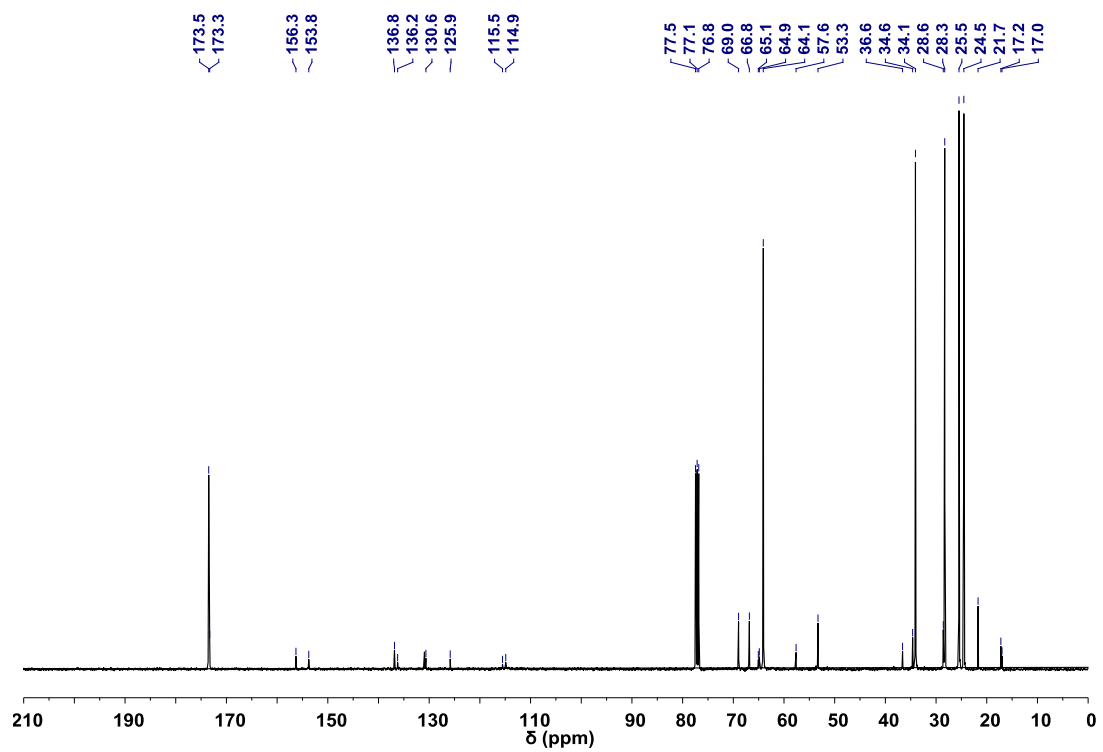


Figure S2. ¹³C NMR spectra of 5a

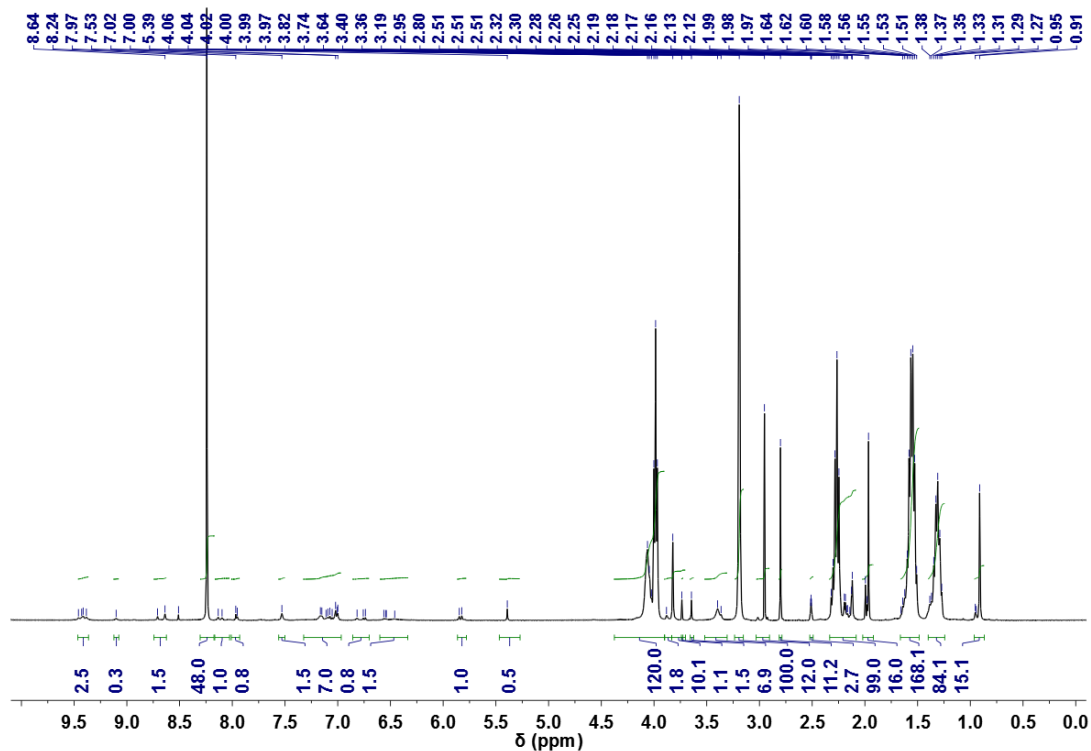


Figure S3. ¹H NMR spectra of 5b

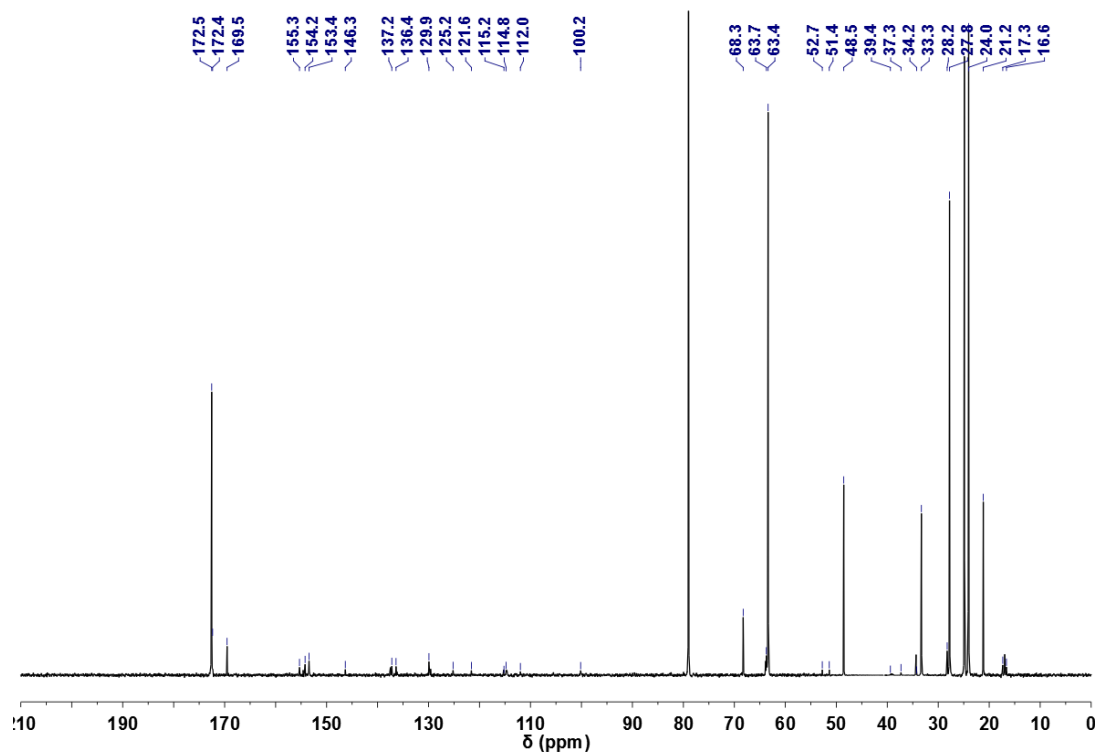


Figure S4. ¹³C NMR spectra of 5b

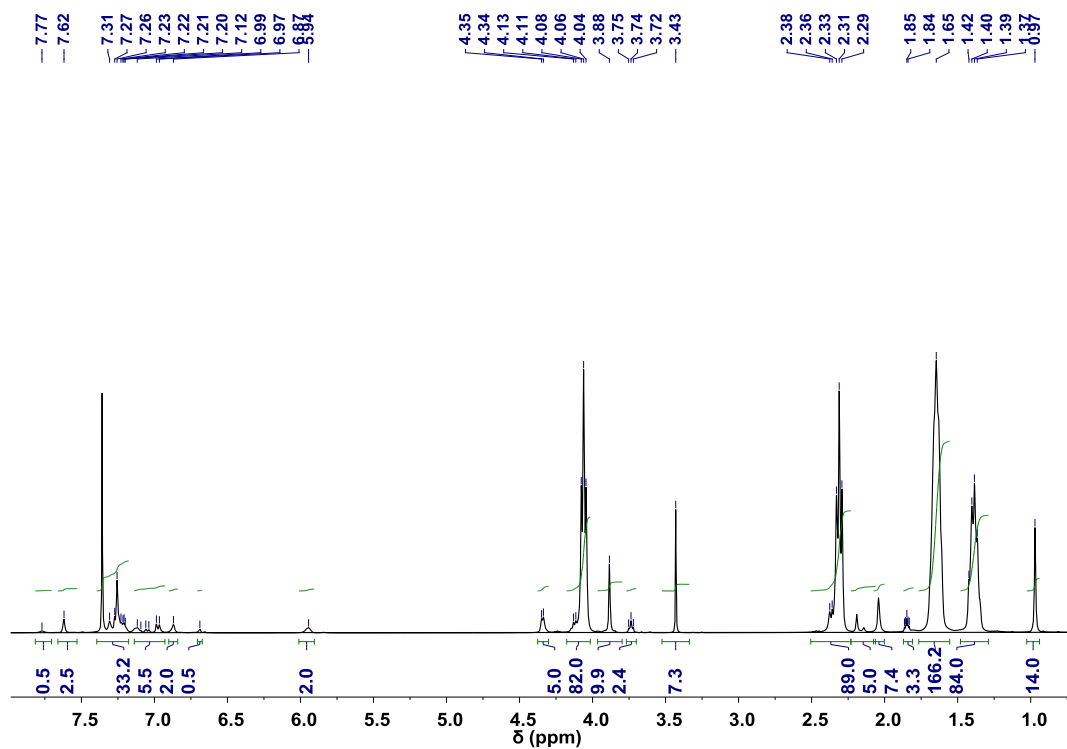


Figure S5. ^1H NMR spectra of **5c**

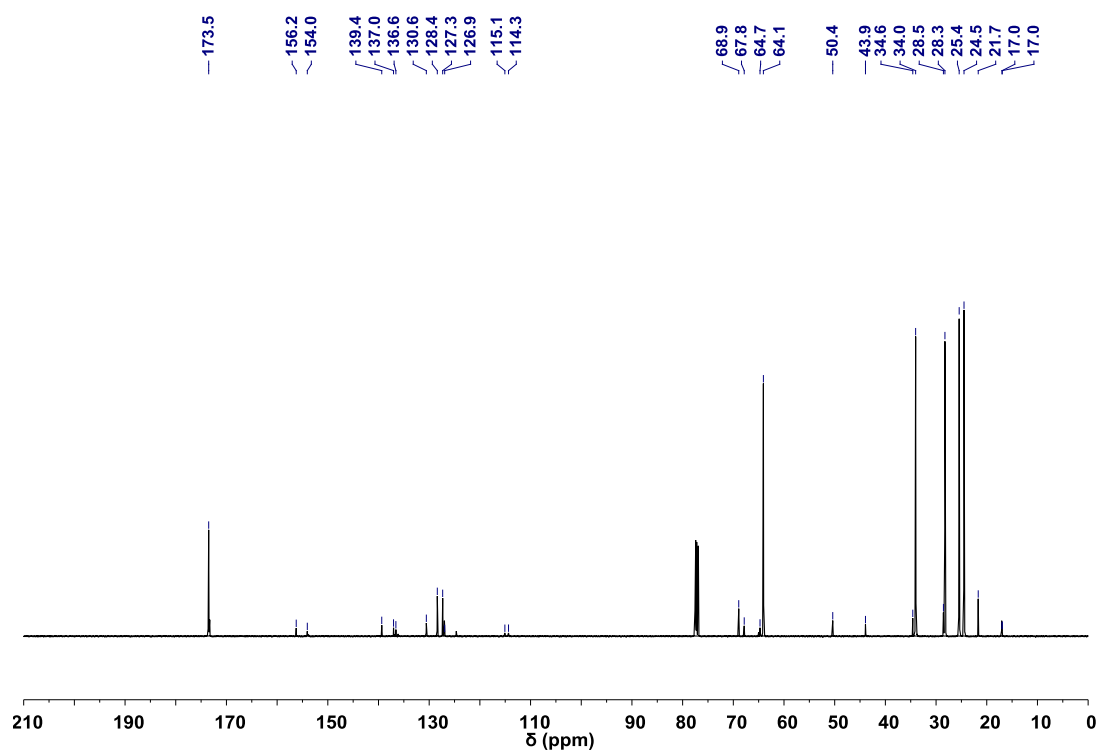


Figure S6. ^{13}C NMR spectra of **5c**

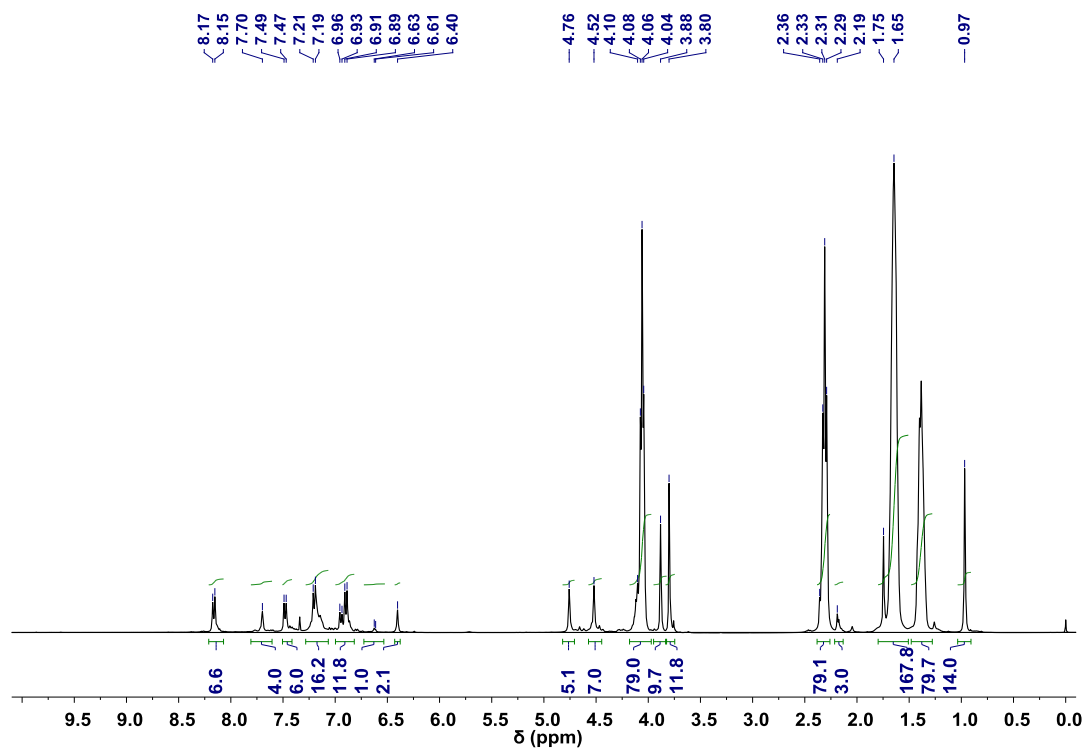


Figure S7. ^1H NMR spectra of **5d**

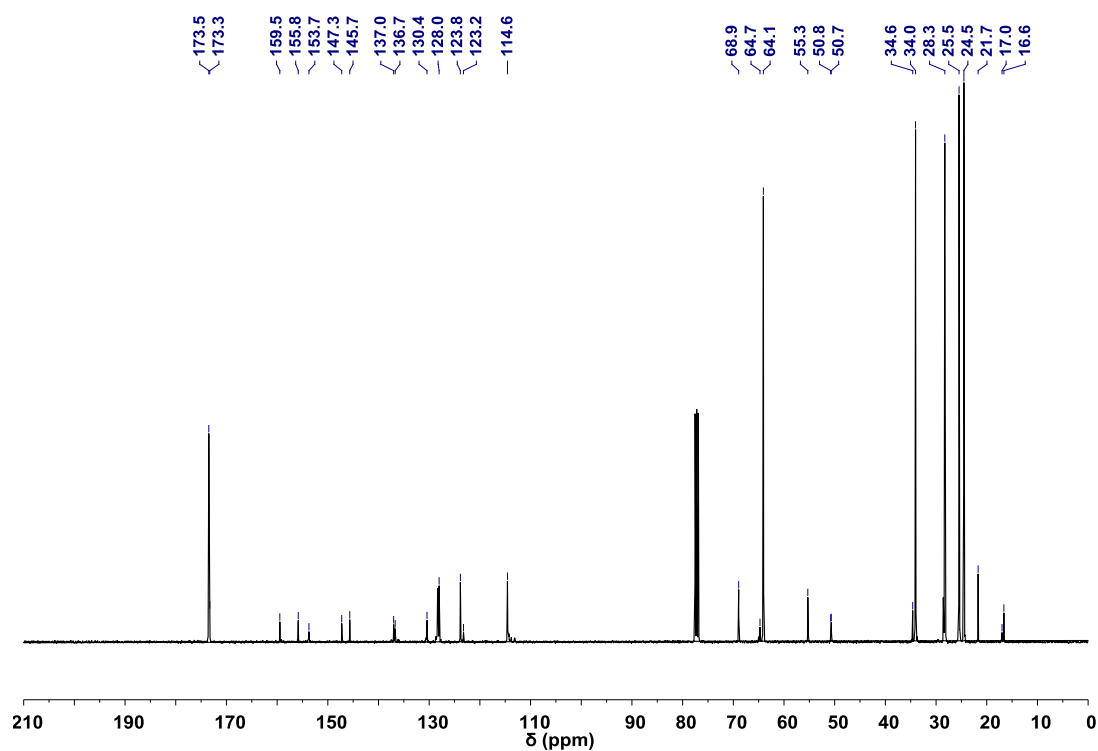


Figure S8. ^{13}C NMR spectra of **5d**

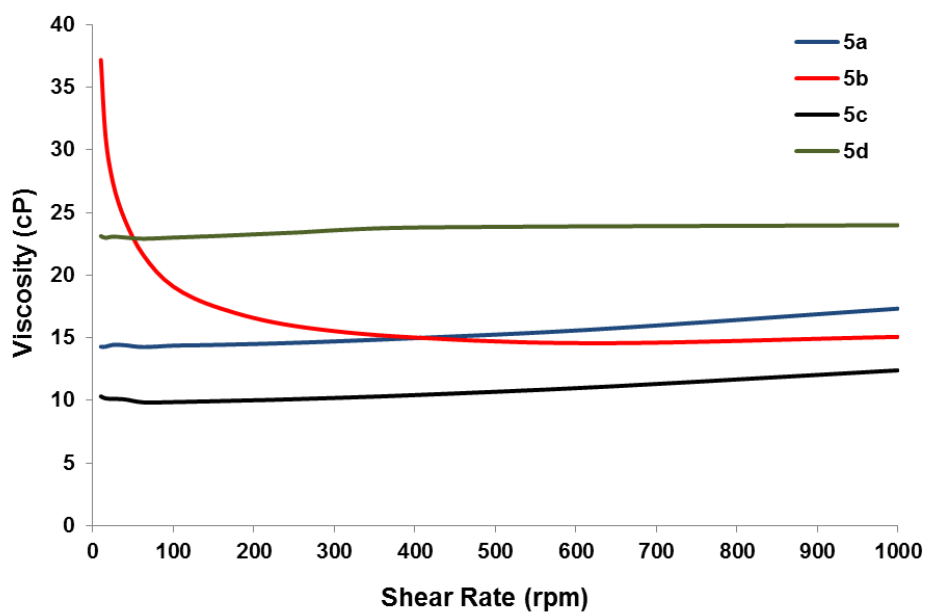


Figure S9. Viscosity analysis at 20 °C of the supramolecular polymers **5a-d** at 150 mM in DMAc/Chloroform (2:1, v/v).

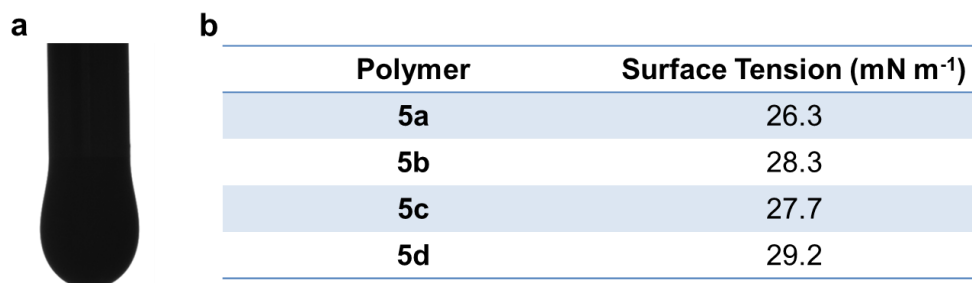


Figure S10. a: Typical drop shape produced by supramolecular polymers **5a-d** and b: their respective surface tensions.

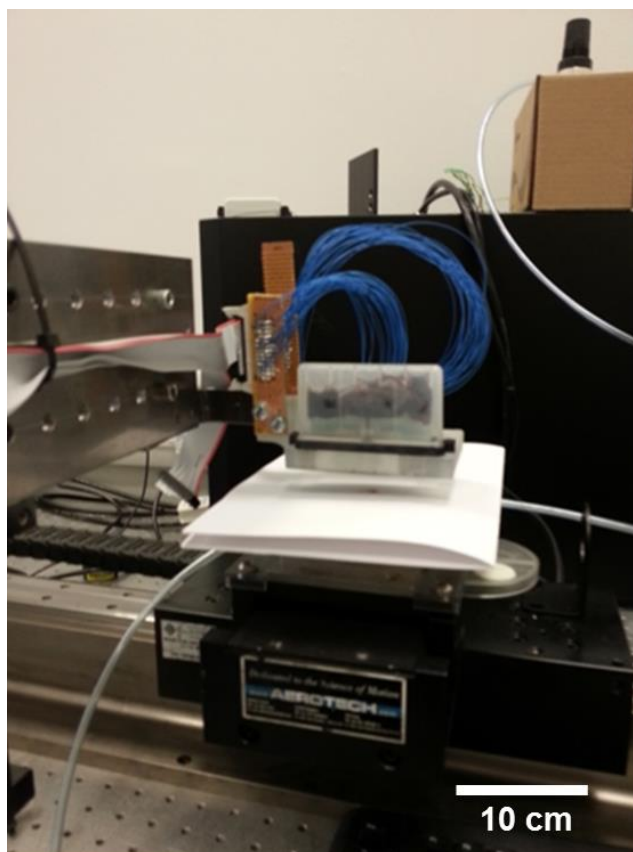


Figure S11. Image of test printing rig used to develop waveforms.

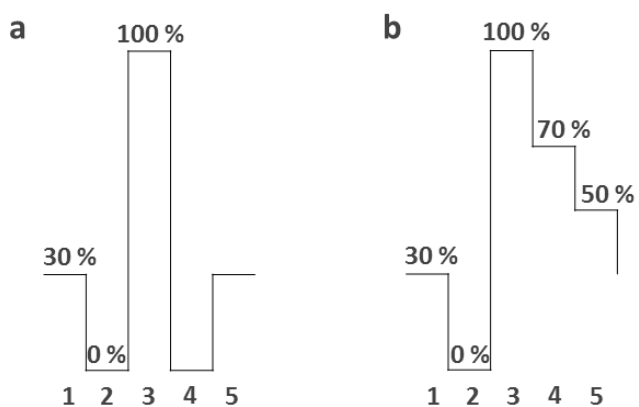


Figure S12. Waveforms developed using test-rig printer. Waveform 'a' where 100% corresponds to 27 V and each time interval represents 3 μ s. and waveform 'b' where intervals 1-4 represent 3.5 μ s and interval 5 represents 0.8 μ s.

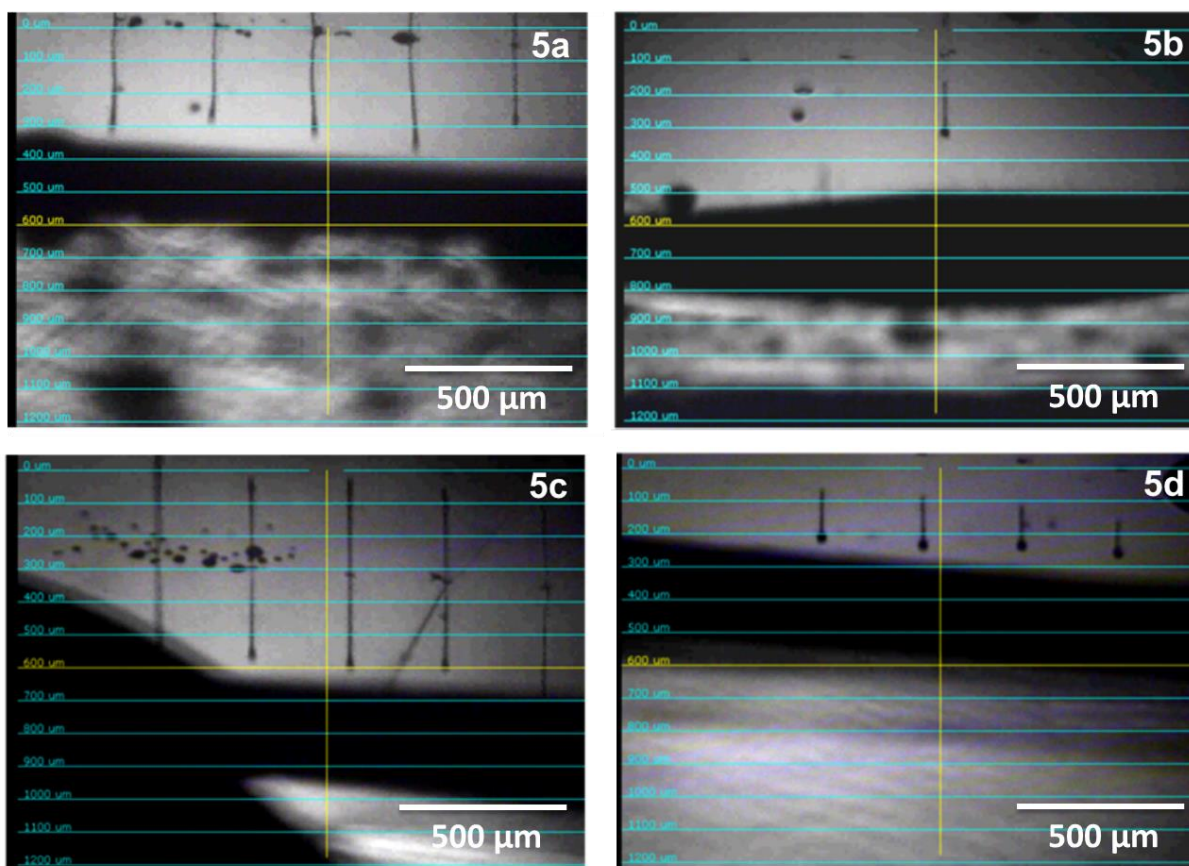


Figure S13. Drop watcher images of the four supramolecular polymers **5a-d** using waveform ‘a’ (**5a**, **5b**, and **5c**) or waveform ‘b’ (**5d**)

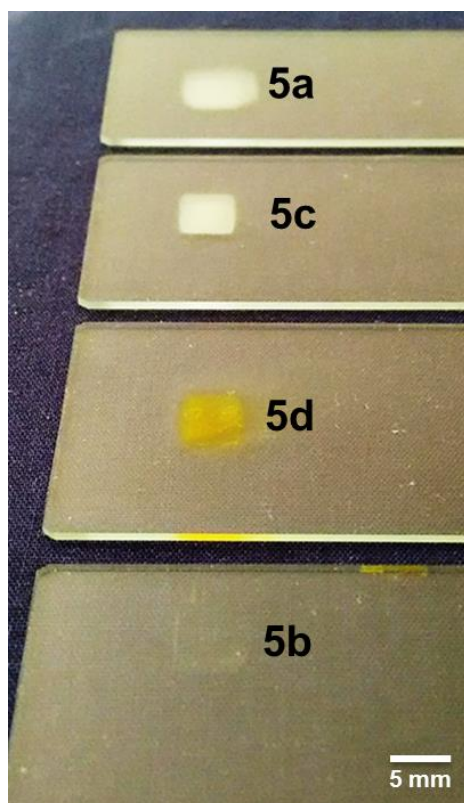


Figure S14. Image of the printed samples of supramolecular polymers **5a**, **5b**, **5c**, and **5d** deposited onto clean glass slides. Each feature is 300 layers in thickness – *ca.* >1 μm .

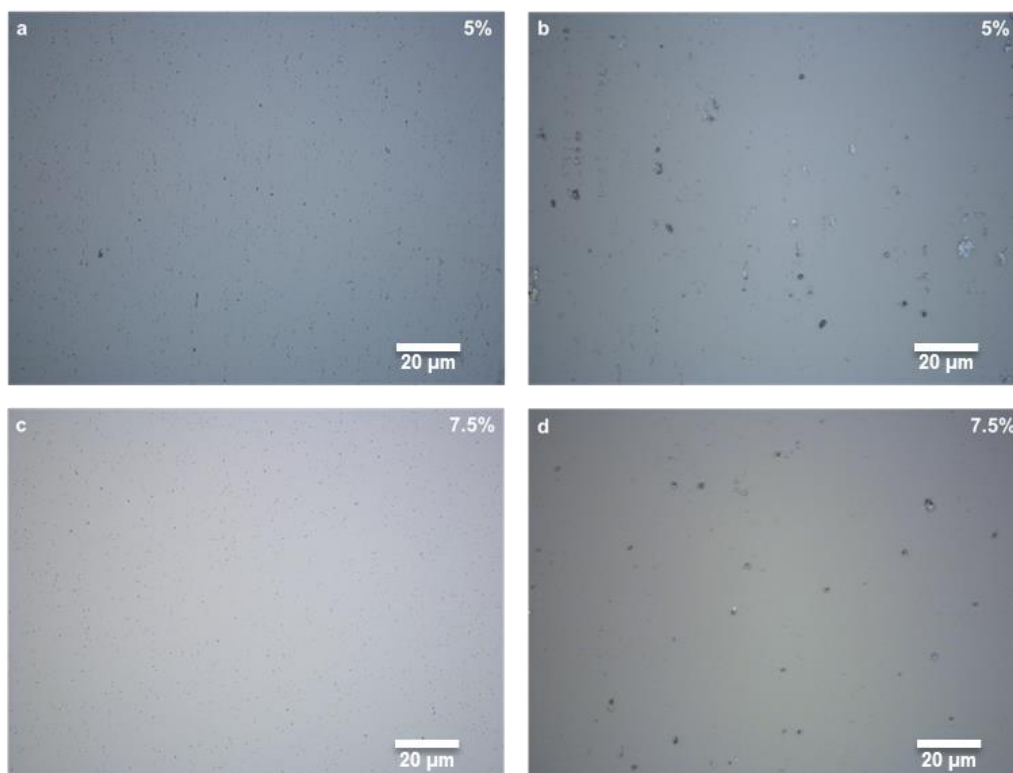


Figure S15. Microscopy images of the hybrid solutions of **5c** with 5% or 7.5% silica particles at 10 (a & c) and 100 times (b & d) magnification.

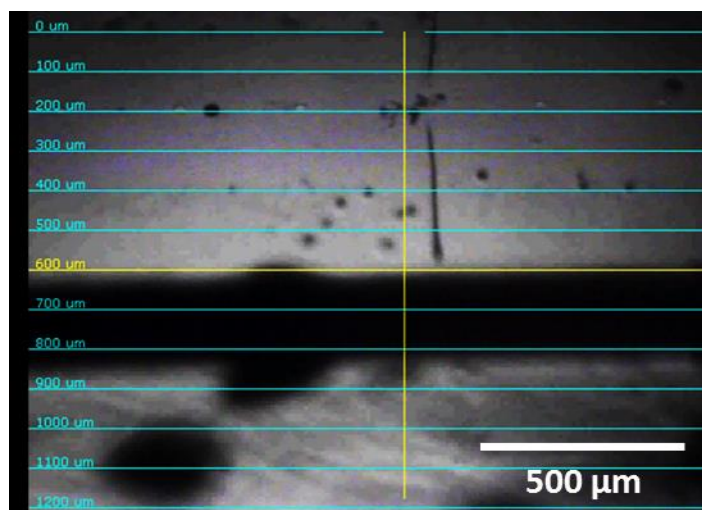


Figure S16. Drop watcher image of the hybrid containing **5c** and 5% silica particles showing slight deflection of the drop from the vertical.

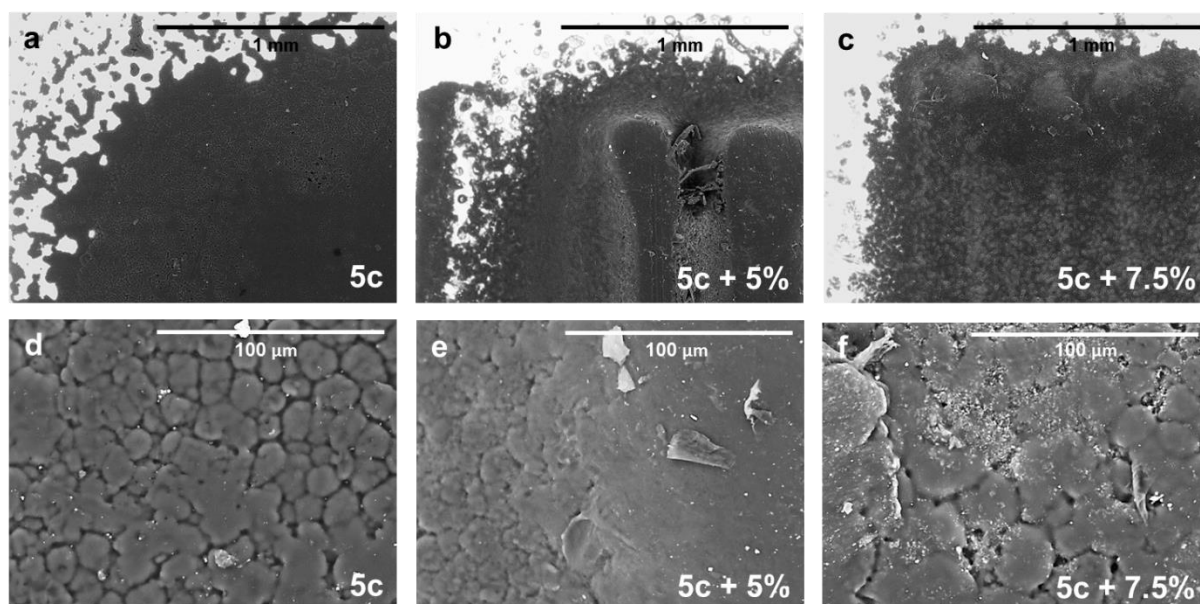


Figure S17. ESEM micrographs of printed samples of the polymer **5c** (**a**), and the hybrid material with silica particles loaded at 5% (**b**) and 7.5% (**c**) at 1 mm and the same samples at increased magnification (**d-f**)