Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Templated polymerizations on solid supports mediated by complementary nucleoside interactions

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Materials and Instrumentation

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The synthesis of 5'-methacryloyluridine **1**,[1] 5'-methacryloyladenosine **2**,[1] 5'-methacryloylcytidine **5**,[1] methacryloylacetone oxime,[1] Wang resin initiator **11**[2] and the ligand *N*-(*n*-pentyl)-2-pyridylmethanimine[3] were synthesized as previously reported and stored under anhydrous conditions prior to use. Copper(I) bromide (Aldrich, 98 %) was purified according to the method of Keller and Wrcoff.[4] All other reagents were purchased from Aldrich or Lancaster Synthesis at the highest purity available and used without further purification unless otherwise stated. Solvents were of the highest grade available and were used as supplied. DSC was carried out on a Perkin Elmer Pyris 1 differential scanning calorimeter. TGA were recorded on a Perkin Elmer TGA 7 apparatus. Temperatures reported are T_{onset}. IR spectra were recorded on an Avatar 320 FT-IR fitted with a "Golden gate" attenuated total reflection (ATR) cell attachment. NMR spectra were recorded with a Bruker DPX 300. Chemical shifts (δ) are quoted in ppm using residual non-deuterated solvents as internal standard [d_6-DMSO (^{1}H, δ: 2.50 ppm; ^{13}C, δ: 39.5 ppm)]. Coupling constants (*J*) are quoted in Hz. Molar mass distributions with PMMA standards in the range (200 to 6.85 x 10^5 g mol^{-1}) used for specific calibration were measured using size exclusion chromatography (SEC) at ambient temperature, on a system equipped with a guard column and on 2 x mixed-C columns (Agilent) with differential refractive index detection using DMF as eluent, at a flow rate of 0.5 ml min^{-1}. Sample solutions were prepared by adding 2.0 ml of solvent to 4.0 mg of sample; leaving 72 h at 60 ºC to dissolve. Molar mass distributions with PEO/PEG standards were carried out at RAPRA Polymer Laboratories. They were measured using size exclusion chromatography (SEC) at 80 ºC, on a system equipped with a PLgel 2 x mixed bed-B 30 cm and 10 μm columns with differential refractive index detection using DMF with 1 % of lithium bromide as eluent, at a flow rate of 1.0 ml min^{-1}. Sample solutions were prepared by adding 10 ml of solvent to 20 mg of sample, leaving overnight and warming, if necessary, at 80 ºC for 20 minutes to dissolve. After thorough mixing, the solutions were filtered through a 0.2 μm PTFE membrane prior to chromatography. Nomenclature of the compounds refers to a mixture of systematic and trivial nomenclature, which is in accordance with that used by other authors.

Monomer Synthesis

5'-*O*-Methacryloylcytidine

To a stirred suspension of cytidine (2.00 g, 8.2 mmol) in dioxane (80 ml) was added a catalytic amount of 2,6-di-*tert*-butyl-4-methylphenol (radical inhibitor), methacryloylacetone oxime[5] (3.48 g, 24.7 mmol) and the immobilized enzyme *C. antartica* lipase (Novozyme 435®, 11.0 g). The reaction mixture was then stirred at 60 °C for 22 h, the enzyme filtered and silica gel added. The solvent was removed under reduced pressure and the solid residue purified by column chromatography [SiO_2, ethyl acetate/methanol (8:2)] by dry loading to give the product 5'-*O*-methacryloylcytidine as a white solid (1.20 g, 47 %); m.p. 82-83 ºC; R_f = 0.26 [TLC, SiO_2, ethyl acetate/methanol (7:3)]; n_{max} / cm^{-1} (solid): 3380 (O-H *st*), 3206 (N-H *st*), 2980 (C-H and $=CH_2$ *st*), 1716 (C=O *st* ester), 1645 (C=O and C=C *st*), 1480 (NH d and N-C=O *sym st*), 1284 (N-H δ *ip*), 1102 (C-O-C *as st*), 1033 ($C=CH_2$ δ *oop*); d_H (*d_6*-DMSO, 300 MHz) 7.53 [1H, d, *J* = 7.5, H(6)], 7.27 (2H, bs, N*H*$_2$), 6.04 [1H, s, 1H(9)], 5.73-5.70 [3H, m, H(1'), H(5) and 1H(9)], 5.51 (1H, bs, O*H*), 5.30 (1H, bs, O*H*), 4.39-4.22 [2H, m, 2H(5')], 3.96 [3H, m, H(2'-4')], 1.88 [3H, s, *CH*$_3$*(*10)] ppm; d_C (*d_6*-DMSO, 75 MHz) 166.7 [1C, C=O(7)], 165.9 [1C, C=O(2)], 155.4 [1C, C(4)], 141.5 [1C, C(6)], 136.0 [1C, C(8)], 126.5 [1C, C(9)], 94.5 [1C, C(5)], 90.5 [1C, C(1')], 80.6 [1C, C(4')], 73.8 [1C, C(2'-3')], 69.9 [1C, C(2'-3')], 64.4 [1C, C(5')], 18.4 [1C, C(10)] ppm; MS-ESI, *m/z* (%): 645.2([2M+Na]$^+$, 100), 334.1 ([M+Na]$^+$, 37); HRMS (ESI) for $C_{13}H_{17}N_3O_6$ [(M+Na)$^+$]: calcd. 334.1015; found 334.1011.

2',3'-*O*-Isopropylidene-5-*O*-methacryloylcytidine (3)

To a stirred suspension of *p*-toluenesulfonic acid (1.65 g, 6.1 mmol), dried over P_2O_5 *in vacuo*, in acetone (80 ml) in a 3-necked round bottom flask under nitrogen was added 5'-*O*-methacryloylcytidine **5** (540 mg, 1.81 mmol) previously dried over P_2O_5 *in vacuo*. Triethylorthoformate (3.47 g, 3.9 ml, 23.4 mmol; distilled, b.p. = 146 °C) was added dropwise over 15 min. Further 5'-*O*-methacryloylcytidine **5** (1.11 g, 3.7 mmol) was added and the reaction was left with stirring 43 h at ambient temperature. The solvent was removed under reduced pressure and the product was dissolved in ethyl acetate. The organic phase was washed with saturated hydrogencarbonate (x 3) and water (x 3), dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford the 2',3'-*O*-isopropylidene-5-*O*-methacryloylcytidine **3** as a white-yellow pale solid (1.00 g, 55 %); m.p. 78-80 ºC; R_f = 0.15 [TLC, SiO_2, ethyl acetate/methanol (95:5)]; n_{max} / cm^{-1} (solid): 3350 (N-H *st*), 3280 (NH_2 *st*),

2970 (=CH_2 *st*), 1722 (C=O *st*), 1645 (C=O and C=C *st*), 1489 (N-C=O *sym st*), 1374 (C-N *st*), 1294 (N-H δ *ip*), 1157 (C-C-N *bending*), 1063 (C-O-C *as st*), 863 (-C=CH_2 δ *oop*); d_H (*d_6*-DMSO, 300 MHz) 7.63 [1H, d, *J* = 7.5, H(6)], 7.35 (2H, bs, N*H_2*), 6.02 [1H, s, 1H(9)], 5.70-5.68 [3H, m, H(1'), H(5) and 1H(9)], 4.99 [1H, dd, *J* = 6.4 and 1.5, H(2')], 4.84 [1H, dd, *J* = 6.4 and 3.3, H(3')], 4.36-4.29 [2H, m, 2H(5')], 4.27-4.22 [1H, m, H(4')], 1.86 [3H, s, C*H_3*(10)], 1.47 [3H, s, C*H_3*(12)], 1.28 [3H, s, 3H, C*H_3*(12)] ppm; d_C (*d_6*-DMSO, 75 MHz) 166.6 [1C, C=O(7)], 166.1 [1C, C=O(2)], 154.8 [1C, C(4)], 144.3 [1C, C(6)], 135.9 [1C, C(8)], 126.5 [1C, C(9)], 113.2 [1C, C(11)], 94.8 [1C, C(5)], 94.4 [1C, C(1')], 85.1 [1C, C(4')], 84.7 [1C, C(2')], 81.6 [1C, C(3')], 65.2 [1C, C(5')], 27.3 [1C, C(12)], 27.3 [1C, C(12)], 18.4 [1C, C(10)] ppm; MS-ESI, *m/z* (%): 725.2 [$(2M+Na)^+$, 100], 374.1 [$(M+Na)^+$, 49]; HRMS (ESI) for $C_{16}H_{21}N_3O_6$ ($(M+Na)^+$): calcd. 374.1328; found 374.1334.

5'-*O*-*tert*-Butyldimethylsilyl-2',3'-*O*-isopropylideneguanosine (7)

2',3'-*O*-Ispropylideneguanosine **6** (10.18 g, 31.5 mmol) in dichloromethane (200 ml) was added triethylamine (4.78 g, 47.2 mmol) and dimethylaminopyridine (769 mg, 6.3 mmol), followed by *tert*-butyldimethylsilylchloride (10.75 g, 62.9 mmol) and the mixture was stirred at ambient temperature 72 h. The organic phase was washed with saturated sodium hydrogencarbonate (x 2), water (x 2), dried ($MgSO_4$) and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography [SiO_2, gradient from ethyl acetate to ethyl acetate/methanol (95:5)] to give the 5'-*O*-*tert*-butyldimethylsilyl-2',3'-*O*-isopropylideneguanosine **7** (12.13 g, 88 %) as a white solid; m.p. 289.2 ºC by DSC; R_f = 0.29 [TLC, SiO_2, ethyl acetate/methanol (9:1)]; $n_{max\ /}$ cm^{-1} (solid): 3300 (NH_2 *st*), 3100 (N-H *st*), 2931 (C-H *st*), 1683 C=O *st*), 1532 (N-H δ and N-C=O *sym st*), 1374 (C-N *st*), 1254 (Si-CH_3 δ *sym*), 1063 (C-O-C *as st* and Si-O *st*), 832 and 777 (Si-CH_3 γ), 690 (N-H δ *oop*) cm^{-1}; d_H (*d_6*-DMSO, 300 MHz) 10.70 (1H, s, N*H*), 7.83 [1H, s, H(8)], 6.55 (2H, bs, N*H_2*), 5.95 [1H, d, *J* = 2.2, H(1')], 5.21 [1H, dd, *J* = 6.2 and 2.2, H(2')], 4.96 [1H, dd, *J* = 6.2 and 3.2, H(3')], 4.13-4.08 [1H, m, H(4')], 3.69 [2H, d, *J* = 5.5, H(5')], 1.49 [3H, s, C*H_3*(11)], 1.30 [3H, s, C*H_3*(11)], 0.80 [9H, s, C*H_3*(14)], -0.05 [3H, s, C*H_3*(12)], -0.06 [3H, s, C*H_3*(12)] ppm; d_C (*d_6*-DMSO, 75 MHz) 157.1 [1C, C=O(6)], 154.0 [1C, C(2)], 150.9 [1C, C(4)], 136.2 [1C, C(8)], 117.2 [1C, C(5)], 113.4 [1C, C(10)], 88.7 [1C, C(1')], 87.3 [1C, C(4')], 84.0 [1C, C(2')], 81.3 [1C, C(3')], 63.8 [1C, C(5')], 27.3 [1C, *C*H_3(11)], 26.1 [3C, *C*H_3(14)], 25.6 [1C, *C*H_3(11)], 18.3 [1C, C(13)], -5.5 [1C, *C*H_3(12)], -5.6 [1C, *C*H_3(12)] ppm; MS-ESI, *m/z* (%):

897.4 [$(2M+Na)^+$,19]; 460.2 [$(M+Na)^+$,100]; HRMS (ESI) for $C_{19}H_{31}N_5O_5Si$ [$(M+Na)^+$]: calcd. 460.1992; found 460.1980.

***N-tert*-Butylcarbonate-5'-*O-tert*-butyldimethylsilyl-2',3'-*O*-isopropylideneguanosine (8)**

To a stirred suspension of 5'-*O-tert*-butyldimethylsilyl-2',3'-*O*-isopropylideneguanosine **7** (2.55 g, 5.8 mmol) in anhydrous DMF (25 ml) under an atmosphere of N_2 was added dimethylaminopyridine (713.2 mg, 5.8 mmol) dissolved in anhydrous V (2.0 ml),. Di-*tert*-butyldicarbonate (2.54 g, 11.7 mmol) dissolved in anhydrous V (2.0 ml) was added dropwise. The mixture was stirred at 60 ºC for 48 h, and then the solvent was removed under reduced pressure to dryness. The compound was purified by column chromatography [SiO_2, gradient from ethyl acetate/petroleum ether (8:2) to ethyl acetate/methanol (9:1)] to give the *N-tert*-butylcarbonate-5'-*O-tert*-butyldimethylsilyl-2',3'-*O*-isopropylideneguanosine **8** (1.43 g, 46 %) as a white-pale yellow solid; m.p. 92-94 ºC; R_f = 0.66 [TLC, SiO_2, ethyl acetate/methanol (9:1)]; n_{max} / cm^{-1} (solid): 3360 (N-H *st*), 2932 (C-H *st*), 1682 (C=O *st*), 1607 (C=N *st*), 1563 (N-H δ and N-C=O *sym st*), 1369 (C-N *st*), 1248 (Si-CH_3 δ *sym*), 1151 (C-C-N *bending*), 1077 (C-O-C *as st* and Si-O *st*), 833 and 778 (Si-CH_3 γ), 649 (NH δ *oop*); d_H (d_6-DMSO, 300 MHz) 11.35 (1H, bs, N*H*), 11.17 (1H, bs, N*H*), 8.08 [1H, s, H(8)], 6.11 [1H, d, *J* = 1.3, H(1')], 5.29 [1H, dd, *J* = 6.2 and 1.3, H(2')], 5.19 [1H, dd, *J* = 6.2 and 3.4, H(3')], 4.13-4.08 [1H, m, H(4')], 3.65 [2H, d, *J* = 5.8, H(5')], 1.50 [12H, s, 3CH_3(17) and 1CH_3(11)], 1.32 [3H, s, CH_3(11)], 0.77 [9H, s, CH_3(14)], -0.09 [3H, s, CH_3(12)], -0.13 [3H, s, CH_3(12)] ppm; d_C (d_6-DMSO, 75 MHz) 155.3 [1C, C=O(6)], 153.9 [1C, C=O(15)], 148.5 [1C, C(2)], 147.8 [1C, C(4)], 139.1 [1C, C(8)], 120.5 [1C, C(5), 113.2 [1C, C(10)], 89.2 [1C, C(1')], 88.2 [1C, C(2')], 84.0 [1C, C(3')], 83.1 [1C, C(16)], 81.3 [1C, C(4')], 64.0 [1C, C(5')], 28.1 [3C, C(17)], 27.3 [1C, CH_3(11)], 26.1 [3C, CH_3(14)], 25.6 [3C, CH_3(11)], 18.3 [1C, C(13)], -5.12 [1C, CH_3(12)], -5.31 [1C, CH_3(12)] ppm; MS-FAB, *m/z* (%): 538 [$(M+1)^+$, 100], 482 (17), 438 (68), 287 (26), 234 (37), 196 (30), 152 (72); HRMS (ESI) for $C_{24}H_{39}N_5O_7Si$ [$(M+Na)^+$]: calcd. 560.2516; found 560.2501.

***N-tert*-Butylcarbonate -2',3'-*O*-isopropylideneguanosine (9)**

To a stirred solution of *N-tert*-butylcarbonate-5'-*O-tert*-butyldimethylsilyl-2',3'-*O*-isopropylideneguanosine **8** (1.98 g, 3.7 mmol) in THF (20 ml) was added a solution of tetrabutylammonium fluoride (1 M) in THF (2.01 g, 7.7 ml, 7.7 mmol). The solution was stirred for 2 h at ambient temperature and the solvent was removed under reduced pressure.

Ethyl acetate and saturated ammonium chloride were added and the organic phase was washed with more saturated ammonium chloride (x 2), water (x 2), dried ($MgSO_4$) and the organic phase was removed under reduced pressure. The resulting solid was purified by column chromatography (SiO_2, gradient from ethyl acetate/petroleum ether (7:3) to ethyl acetate) to give *N-tert*-butylcarbonate-2',3'-*O*-isopropylideneguanosine **9** (1.55, 99 %) as a pale yellow solid; m.p. 278.3 ºC by DSC; R_f = 0.31 [TLC, SiO_2, ethyl acetate/methanol (9:1)]; n_{max} / cm^{-1} (solid): 3400-3100 (N-H and O-H *st*), 2990 (C-H *st*), 1681 (C=O *st*), 1605 (C=N *st*), 1564 (N-H δ and N-C=O *sym st*), 1398 (C-N *st*), 1245 (N-H δ *ip*), 1149 (C-C-N *bending*), 1071 (C-O-C *as st*); d_H (d_6-DMSO, 300 MHz) 11.38 (1H, bs, N*H*), 11.18 (1H, bs, N*H*), 8.14 [1H, s, H(8)], 6.06 [1H, d, *J* = 2.1, H(1')], 5.25 [1H, dd, *J* = 6.2 and 2.1, H(2')], 5.16 [1H, dd, *J* = 6.2 and 3.4, H(3')], 4.95 [1H, t, *J* = 5.1, O*H*(5')], 4.11-4.08 [1H, m, H(4')], 3.52-3.46 [2H, m, H(5')], 1.52 [12H, s, 3CH_3(14) and 1 CH_3(11)], 1.32 [3H, s, CH_3(11)] ppm; d_C (d_6-DMSO, 75 MHz) 155.3 [1C, C=O(6)], 154.1 [1C, C=O(12)], 148.5 [1C, C(2)], 147.8 [1C, C(4)], 138.9 [1C, C(8)], 120.5 [1C, C(5)], 113.2 [1C, C(10)], 89.1 [1C, C(1')], 87.9 [1C, C(2')], 84.0 [1C, C(3')], 83.1 [1C, C(13)], 81.5 [1C, C(4')], 62.1 [1C, C(5')], 28.1 ([C, *C*H_3(14)], 27.3 [1C, *C*H_3(11)], 25.6 [1C, *C*H_3(11)] ppm; MS-EI, *m/z* (%): 423 (M^+, 38), 409 (20), 367 (51), 293 (39), 280 (21), 279 (100), 234 (31), 217 (58), 208 (20); HRMS (ESI) for $C_{18}H_{25}N_5O_7$ [$(M+Na)^+$]: calcd. 446.1652; found 446.1667.

***N-tert*-Butylcarbonate–2',3'-*O*-isopropylidene-5'-*O*-methacryloylguanosine (10)**

To a suspension of *N-tert*-butylcarbonate-2',3'-*O*-isopropylideneguanosine **9** (1.23 g, 2.91 mmol) in dioxane (70 ml) was added a catalytic amount of 2,6-di-*tert*-butyl-4-methylphenol (radical inhibitor), methacryloylacetone oxime (3.18 g, 22.53 mmol) and the enzyme *C. antarctica* lipase (Novozyme 435®,.30 g). The reaction mixture was stirred at 60 °C for 24 h, then more methacryloylacetone oxime was added (1.50 g, 10.63 mmol) and the reaction mixture was stirred at 60 ºC for further 21 h. The enzyme was filtered and silica gel added to the filtrate. The solvent was removed under reduced pressure and the solid residue purified by column chromatography [SiO_2, gradient from ethyl acetate/petroleum ether (8:2) to ethyl acetate/ methanol (9:1)] by dry loading to give *N-tert*-butylcarbonate-2',3'-*O*-isopropylidene-5'-*O*-methacryloylguanosine **10** (1.08 g, 78 %) as a white solid; m.p. 97-98 ºC; R_f = 0.42 [TLC, SiO_2, ethyl acetate/methanol (9:1)]; n_{max} / cm^{-1} (solid): 3300-3100 (N-H *st*), 2990 and 2910 (=CH_2 *st*), 1681 (C=O and C=C *st*), 1605 (C=N *st*), 1564 (N-H δ and N-C=O *sym st*), 1395 (C-N *st*), 1246 (N-H δ *ip*), 1149 (C-C-N *bending*), 1074 (C-O-C *as st*), 868 (C-H δ

oop), 650 (N-H δ *oop*); d_H (*d*$_6$-DMSO, 300 MHz) 11.37 (1H, bs, N*H*), 11.19 (1H, bs, N*H*), 8.08 [1H, s, H(8)], 6.18 [1H, s, H(1')], 5.95 [1H, s, H(17)], 5.62 [1H, s, H(17)], 5.46-5.42 [1H, m, H(3')], 5.25 [1H, d, *J* = 6.2, H(2')], 4.36-4.25 [2H, m, H(4') and 1H(5')], 4.22-4.14 [1H, m, 1H(5')], 1.81 [3H, s, C*H*$_3$(18)], 1.50 [12H, s, 3C*H*$_3$(14) and 1C*H*$_3$(11)], 1.31 [3H, s, C*H*$_3$(11)] ppm; d_C (*d*$_6$-DMSO, 75 MHz) 170.6 [1C, C=O(15)], 155.3 [1C, C=O(6)], 154.0 [1C, C=O(12)], 148.4 [1C, C(2)], 147.9 [1C, C(4)], 139.3 [1C, C(8)], 135.8 [1C, C(16)], 126.3 [1C, C(17)], 120.6 [1C, C(5)], 113.5 [1C, C(10)], 89.0 [1C, C(1')], 85.4 [1C, C(4')], 84.2 [1C, C(2')], 83.2 [1C, C(13)], 81.1 [1C, C(3')], 64.9 [1C, C(5')], 28.0 [3C, *C*H$_3$(14)], 27.2 [1C, *C*H$_3$(11)], 25.6 [1C, *C*H$_3$(11)], 18.3 [1C, *C*H$_3$(18)] ppm; MS-FAB, *m/z* (%): 492 [$(M+1)^+$, 88], 436 (16), 414 (21), 392 (66), 241 (100), 196 (20), 152 (51), 136 (14); HRMS (ESI) for $C_{22}H_{29}N_5O_8$ [$(M+Na)^+$]: calcd. 514.1914; found 514.1924.

2',3'-*O*-Isopropylidene-5'-methacryloylguanosine (4)

N-*tert*-butylcarbonate-2',3'-*O*-isopropylidene-5'-*O*-methacryloyl-guanosine **10** (1.40 g, 2.95 mmol) was dissolved in trifluoroacetic acid/dichloromethane (1:1, 50 ml) and stirred at ambient temperature for 2 h. The solvent was removed under reduced pressure and more dichloromethane was added (x 6) and removed under reduced pressure to eliminate the last traces of trifluoroacetic acid. The product was purified by column chromatography [SiO_2, chloroform/methanol (9:1)] to give 2',3'-*O*-isopropylidene-5'-methacryloylguanosine **4** (668 mg, 58 %) as a white solid; m.p. 127-128 ºC; R_f = 0.22 [TLC, SiO_2, ethyl acetate/methanol (95:5)]; ν_{max} / cm^{-1} (solid): 3330 (N-H *st*), 3119 (NH_2 *st*), 2980 and 2925 (=CH_2 *st*), 1682 (C=O and C=C *st*), 1605 (C=N *st*), 1534 (N-H δ and N-C=O *sym st*), 1377 (C-N *st*), 1176, 1134 (C-C-N *bending*), 1069 (C-O-C *as st*), 800 (C-H δ *oop*), 650 (N-H δ *oop*) cm^{-1}; d_H (*d*$_6$-DMSO, 300 MHz) 10.83 (1H, bs, N*H*), 7.83 [1H, s, H(8)], 6.64 (2H, s, N*H*$_2$), 6.10 [2H, s, H1' and 1H(14)], 5.67 [1H, s, H(14)], 5.27-5.23 [1H, m, H(2')], 5.18-5.11 [1H, m, H(3')], 4.36-4.06 [3H, m, H(4') and 2H(5')], 1.98 [3H, s, C*H*$_3$(15)], 1.50 [3H, s, C*H*$_3$(11)], 1.31 [3H, s, C*H*$_3$(11)] ppm; d_C (*d*$_6$-DMSO, 75 MHz) 169.1 [1C, C=O(12)], 166.6 [1C, C=O(6)], 157.1 [1C, C(2)], 154.1 [1C, C(4)], 140.0 [1C, C(8)], 135.8 [1C, C(13)], 126.6 [1C, C(14)], 120.6 [1C, C(5)], 113.7 [1C, C(10)], 88.6 [1C, C(1')], 84.5 [1C, C(4')], 84.1 [1C, C(2')], 81.3 [1C, C(3')], 70.1 [1C, C(5')], 27.3 [1C, *C*H$_3$(11)], 25.6 [1C, *C*H$_3$(11)], 18.3 [1C, *C*H$_3$(15)] ppm; MS-ESI, *m/z* (%): 805.2 [$(2M + Na)^+$, 16], 414.1 [$(M + Na)^+$, 100]; HRMS (ESI) for $C_{17}H_{27}O_8N_5$ [$(M + Na)^+$]: calcd. 414.1390; found 414.1395.

Template polymerizations/reactions

Resin initiated polymerization of 2

Following the general procedure with Wang initiator-resin **11** (264.0 mg, 0.26 mmol), 5'-*O*-methacryloyl-2',3'-*O*-*tert*-butyldimethylsilyladenosine **2** (1.49 g, 2.64 mmol), copper (I) bromide (37.9 mg, 0.26 mmol), the ligand *N*-(*n*-pentyl)-2-pyridylmethanimine (93.3 mg, 0.53 mmol) and stirring at 110 °C for 19 h to give the *title product* **13** (836 mg, 220 % weight increase) as a brown solid; T_g 381.3 and 389.0 ºC by DSC; TGA 66.2, 336.1, 399.9 and 551.1 ºC; T_{onset} 292.9 ºC; n_{max} / cm^{-1} (solid): 3350 (NH_2 *st*), 2929 (C-H *st*), 1729 (C=O *st*), 1633 (C=N *st*), 1471 (N-C=O *sym st* and NH *amide II*), 1252 (C-C-N *bending*), 1154 and 1076 (C-O *as st*), 835 (Si-CH_3), 776 (Si-C *st*), 698 (C-Br *st*); d_H (*d_6*-DMSO, gel phase, 300 MHz) 8.37 [1H, bs, H(2)], 8.18 [1H, bs, H(8)], 7.31 (2H, bs, N*H_2*), 5.92-5.89 [1H, m, H(1')], 5.03-4.98 [1H, m, H(2')], 4.57-4.11 [3H, m, H(3'-5')], 1.88 (2H, bs, CH_2), 0.89 [9H, bs, Si(CH_3)$_2$C(C*H_3*)$_3$], 0.71 [9H, bs, Si(CH_3)$_2$C(C*H_3*)$_3$], 0.12 (3H, bs, C*H_3*), -0.08 [6H, bs, Si(C*H_3*)$_2$C(CH_3)$_3$], -0.39 [6H, bs, Si(C*H_3*)$_2$C(CH_3)$_3$] ppm.

Cleavage of poly(methacryloyl adenosine) from Wang resin

Following the general procedure with poly(methacryloyl adenosine) substituted Wang resin **13** (197.8 mg) in a mixture of trifluoroacetic acid/dichloromethane (1:1) (6.0 ml) and stirring at ambient temperature for 23 h. The ether solution was evaporated under reduced pressure to afford **17**. The polymer **17** was dissolved in methanol and purified through an activated basic alumina pad to afford the poly-2',3'-*O*-*tert*-butyldimethylsilyl-5'-*O*-methacryloyladenosine **17** (63 mg, 32 %) as a brown solid; TGA 89.0, 336.1 and 551.1 ºC by DSC; T_{onset} 306.7; n_{max} / cm^{-1} (solid): 3330 (N*H_2 st*), 2931 (C-H *st*), 1694 (C=O *st*), 1636 (C=N *st*), 1472 (N-C=O *sym st* and N-H *amide II*), 1251 (C-C-N *bending*), 1155 and 1078 (C-O *as st*), 834 (Si-CH_3), 776 (Si-C *st*), 692 (C-Br *st*); d_H (*d_6*-DMSO, 300 MHz): 8.67-8.32 [2H, m, H(2) and H(8)], 6.20-6.03 (2H, bs, N*H_2*), 5.92-5.89 [1H, m, H(1')], 4.70-3.85 [5H, m, H(2'-5')], 1.30-(-0.6) [35H, m, 2Si(C*H_3*)$_2$C(C*H_3*)$_3$, C*H_3* and C*H_2*] ppm.

Debromination of poly(methacryloyl adenosine) substituted Wang resin

Following the general procedure with poly(methacryloyl adenosine) substituted Wang resin **13** (600.0 mg, 410.5 mg polymer, 0.72 mmol polymer), tri-*n*-butyltin hydride (263.3 mg, 1.09 mmol), AIBN (18.0 mg) in de-aerated toluene (6.0 ml) and stirring at 100 ºC for 20 h and the

resin was filtered, washed with water, methanol and acetone and dried *in vacuo* to give the debrominated poly-2',3'-*O*-*tert*-butyldimethylsilyl-5'-*O*-methacryloyladenosine substituted Wang resin **21** (578 mg) as a brown solid. The product did not swell properly in any solvent, so no data for ^{1}H NMR (gel phase) was obtained; TGA 359.4 and 417.3 ºC; T_{onset} 328.8 ºC; n_{max} / cm^{-1} (solid): 3330 (NH_2 *st*), 2929 (C-H *st*), 1690 (C=O *st*), 1633 (C=N *st*), 1471 (N-H δ *ip*), 1252 (C-N *st*), 1155 and 1079 (C-O *as st*), 834 (Si-CH_3), 776 (Si-C *st*).

Cleavage of debrominated poly(methacryloyl adenosine) from Wang resin

Following the general procedure with the debrominated poly(methacryl adenosine) substituted Wang resin **21** (100.0 mg) in a mixture of trifluoroacetic acid/dichloromethane (1:1) (2.0 ml) and stirring the solution The solvent was removed under reduced pressure to afford the debrominated poly-2',3'-*O*-*tert*-butyldimethylsilyl-5'-*O*-methacryloyladenosine **25**. The polymer was dissolved in methanol and purified through an activated basic alumina pad to afford the *title product* **25** (47 mg, 47 %) as a brown solid; TGA 342.3 and 478.7 ºC; T_{onset} 288.7; M_n = 28,700, Đ = 2.01 (SEC-DMF, PMMA calibrated); $n_{max\ /}$ cm^{-1} (solid): 3333 (NH_2 *st*), 2927 (C-H *st*), 1695 (C=O *st*), 1634 (C=N *st*), 1471 (N-C=O *sym st* and N-H *amide II*), 1253 (C-C-N *bending*), 1157 and 1077 (C-O *as st*), 831 (Si-CH_3), 779 (Si-C *st*); d_H (*d_6*-DMSO, 300 MHz): 8.73-8.34 [2H, m, H(2) and H(8)], 6.19-6.03 (2H, bs, N*H_2*), 5.91-5.89 [1H, m, H(1')], 4.73-3.85 [5H, m, H(2'-5')], 1.32-(-0.6) [35H, m, 2Si(C*H_3*)$_2$C(C*H_3*)$_3$, C*H_3* and C*H_2*] ppm.

Polymerization of 1 using immobilized template of poly(methacryloyl adenosine) 21

Following the general procedure with a solution of AIBN (0.3 ml of a 30.0 mg in 3.0 ml methanol solution), 5'-*O*-methacryloyl-2',3'-*O*-trimethylsilyluridine **1** (110.8 mg, 0.24 mmol), the immobilized template of poly(methacryloyl adenosine) **21** (200.0 mg, 136.8 mg polymer, 0.24 mmol polymer), ethyl acetate (2.0 ml), de-aerated toluene (1.0 ml) were added and stirring at 60 ºC for 44 h. It was then filtered and washed with toluene and dried *in vacuo* to give the complex **29** (301.0 mg, 97 %) as a cream colored solid. d_H (*d_6*-DMSO) of this complex **29** did not allow the ratio of uridine to adenosine to be determined; TGA 348.1 and 411.0 ºC; T_{onset} 292.1 ºC; n_{max} / cm^{-1} (solid): 3461, 3346 and 3190 (N-H *hydrogen bonded*), 2928 and 2856 (C-H *st*), 1698 (C=O *st*), 1633 (C=O and C=C *st*), 1471 (N-H δ *ip*), 1250 (C-O-C *as st*), 1153 and 1075 (C-O *as st*), 836 (Si-CH_3), 777 (Si-C *st*); d_H (*d_6*-DMSO, gel phase, 300 MHz): 11.40 (1H, bs, N*H*), 7.61-7.48 [2H, m, H(2A) and H(8A)], 7.20-7.09 [3H, m, N*H_2*

and H(6)], 5.82-5.50 [3H, m, H(5U) and 2H(1')], 4.52-3.48 [10H, m, 2H(2'-5')], 2.00-(-0.60) [58, m, $2Si(CH_3)_3$, $2Si(CH_3)_2C(CH_3)_3$, $2CH_3$ and $2CH_2$] ppm.

Separation of the daughter polymer poly(methacryloyl uridine) 33 from its parent polymer immobilized poly(methacryloyl adenosine) 25

Following the general procedure with the previous complex **29** (254.9 mg) in trifluoroethanol (5.0 ml) and stirring at ambient temperature for 1 h to give the *title product* **33** (38 mg, 34 %) as a white solid. Analytical data for the solid-supported parent polymer was identical to the parent polymer **25** synthesized above. Analytical data for the daughter polymer **33** is shown below; TGA 337.2; T_{onset} 223.7 ºC; M_n = 2,100, Đ = 1.67 (SEC-THF, PMMA calibrated); n_{max} / cm^{-1} (solid): 3250 (N-H *st*), 2958 (C-H *st*), 1693 (C=O *st*), 1432 (N-C=O *sym st* and NH *amide II*), 1251 (C-C-N *bending*), 1155 and 1078 (C-O *as st*), 839 ($Si-CH_3$); d_H (d_6-DMSO, 300 MHz): 11.42 (1H, bs, N*H*), 7.66 [1H, bs, H(6)], 5.99-5.64 [2H, m, H(1') and H(5)], 4.33-3.93 [5H, m, H(2'-5')], 1.45-(-0.12) [23H, m, $2Si(CH_3)_3$, CH_3 and CH_2] ppm.

Resin initiated polymerization of 3

Following the general procedure with Wang initiator-resin **11** (300.0 mg, 0.30 mmol), 2',3'-*O*-isopropylidene-5'-*O*-methacryloylcytidine **3** (1.05 g, 3.00 mmol), copper(I) bromide (42.8 mg, 0.30 mmol), the ligand *N*-(*n*-pentyl)-2-pyridylmethanimine (105.3 mg, 0.60 mmol), de-aerated toluene (8 ml) and stirring at 110 ^oC for 20 h to give the *title product* **14** (1.02 g, 240 % weight increase) as a brown solid. The product did not swell properly in any solvent, thus no data for ^1H-NMR (gel phase) was obtained; TGA 58.0, 320.8, 458.5 and 623.7 ºC; T_{onset} 281.2 ºC; n_{max} / cm^{-1} (solid): 3441 and 3396 (NH_2 *st*), 3184 (N-H *st*), 2982 and 2935 (C-H *st*), 1725 (C=O *st*), 1645 (C=O and C=C *st*), 1487 (N-C=O *sym st* and CH_3 δ *as*), 1374 (C-N *st* and CH_3 δ *sym*), 1155 (C-C-N *bending*), 1065 (C-O-C *as st*) cm^{-1}.

Cleavage of poly(methacryloyl cytidine) from the Wang resin

Following the general procedure with poly(methacryloyl cytidine) substituted Wang resin **14** (98.7 mg) in a mixture of trifluoroacetic acid/dichloromethane (1:1) (4.0 ml) and stirring the solution at ambient temperature for 20 h, to afford the *title product* **18** (64 mg, 65 %) as a pale brown solid; TGA 179.5, 254.4, 309.1 and 701.6 ºC; T_{onset} 197.8 ºC; M_n = 14,600, Đ = 1.14 (SEC-DMF, PMMA calibrated); n_{max} / cm^{-1} (solid): 3477-3188 (NH_2 and N-H *st*), 3099 and 2972 (CH *st*), 1722 (C=O *st*), 1667 (C=O and C=C *st*), 1488 (N-C=O *sym st* and

CH_3 δ *as*), 1275 (N-H δ *ip*), 1128 (C-C-N *bending*) cm^{-1}; d_H (*d_6*-DMSO, 300 MHz): 8.03-7.64 [1H, bs, H(6)], 6.19 (2H, bs, N*H_2*), 5.88-5.61 [2H, m, H(1') and H(5)], 4.45-3.48 [5H, m, H(2'-5')], 1.53-0.65 [11H, m, C(C*H_3*)$_2$, C*H_3* and C*H_2*] ppm.

Debromination of poly(methacryloyl cytidine) substituted Wang resin

Following the general procedure with poly-2',3'-*O*-isopropylidene-5'-*O*-methacryloylcytidine substituted Wang resin **14** (600.0 mg, 418.9 mg polymer, 1.19 mmol polymer), tri-*n*-butyltin hydride (431.6 mg, 1.79 mmol), AIBN (18.0 mg), de-aerated toluene (6.0 ml) and stirring at 100 ºC for 17 h, to give the debrominated *title product* **22** (525 mg) as a brown solid. The product did not swell properly in any solvent, so no data for ^{1}H-NMR (gel phase) was obtained; TGA 339.0 and 460.3 ºC; T_{onset} 297.9 ºC; n_{max} / cm^{-1} (solid): 3547 and 3349 (NH_2 *st*), 3194 (N-H *st*), 2987 and 2937 (CH *st*), 1727 (C=O *st*), 1644 (C=O and C=C *st*), 1486 (N-C=O *sym st* and CH_3 δ *as*), 1373 (C-N *st* and CH_3 δ *sym*), 1154 (C-C-N *bending*), 1064 (C-O-C *as st*).

Cleavage of debrominated poly(methacryloyl cytidine) from Wang resin

Following the general procedure with the debrominated poly(methacryloyl cytidine) substituted Wang resin **22** (77.4 mg) in a mixture of trifluoroacetic acid/dichloromethane (1:1, 4.0 ml) and stirring the solution at ambient temperature for 20 h, to give the debrominated poly-2',3'-*O*-isopropylidene-5'-*O*-methacryloylcytidine **26** (27 mg, 35 %) as a white solid; TGA 258.1 and 320.2 ºC; T_{onset} 217.0 ºC; M_n = 15,700, Đ = 1.29 (SEC-DMF, PMMA calibrated); n_{max} (solid): 3444-3132 (NH_2 and N-H *st*), 2920 (C-H *st*), 1720 (C=O *st*), 1674 (C=O and C=C *st*), 1138 (C-C-N *bending*), 1078 (C-O-C *as st*) cm^{-1}; d_H (*d_6*-DMSO, 300 MHz): 8.11-7.67 [1H, bs, H(6)], 6.11 (2H, bs, N*H_2*), 5.87-5.57 [2H, m, H(1') and H(5)], 4.49-3.78 [5H, m, H(2'-5')], 1.44-0.52 [11H, m, C(C*H_3*)$_2$, C*H_3* and C*H_2*] ppm.

Templated polymerization of 4 using an immobilized template of poly(methacryloyl cytidine) 26

Following the general procedure with a solution of AIBN (0.6 ml of a 30.0 mg in 3.0 ml methanol solution), 2',3'-*O*-isopropylidene-5'-*O*-methacryloylguanosine **4** (155.5 mg, 0.40 mmol), the immobilized template of poly(methacryloyl cytidine) **26** (200.0 mg, 139.6 mg polymer, 0.40 mmol polymer), ethyl acetate (4.0 ml), de-aerated toluene (2.0 ml) were added and stirring at 60 ºC for 23 h, to give the complex **34** as a cream colored solid (321 mg,

yield). ^{1}H NMR showed only methacryloyl guanosine monomer **4** and no parent polymer; TGA 342.0 and 462.0 ºC; T_{onset} 291.4 ºC; n_{max} / cm^{-1} (solid): 3440, 3301 and 3155 (N-H *hydrogen bonded*), 2978, 2926 and 2729 (C-H *st*), 1697, 1638 and 1603 (C=O *st*), 1485 (N-C=O *sym st* and CH_3 δ *as*), 1375 (C-N *st* and CH_3 δ *sym*), 1174 (C-C-N *bending*), 1077 (C-O-C *as st*); d_H (*d_6*-DMSO, gel phase, 300 MHz): 10.1 (1H, bs, N*H*), 7.83 [1H, s, H(8)], 6.54 (2H, s, N*H_2*), 6.02 [2H, bs, H(1') and 1H(14)], 5.68 [1H, s, 1H(14)], 5.26-5.23 [1H, m, H(2')], 5.18-5.15 [1H, m, H(3')], 4.37-4.19 [3H, m, H(4') and 2H(5')], 1.84 [3H, s, CH_3(15)], 1.51 [3H, s, CH_3(11)], 1.32 [3H, s, CH_3(11)] ppm.

Resin initiated polymerization of 4

Following the general procedure Wang initiator-resin **11** (179.5 mg, 0.18 mmol), 2',3'-*O*-isopropylidene-5'-*O*-methacryloylguanosine **4** (701.8 mg, 1.80 mmol), copper (I) bromide (25.1 mg, 0.18 mmol), the ligand *N*-(*n*-pentyl)-2-pyridylmethanimine (63.3 mg, 0.36 mmol), de-aerated toluene (3.0 ml) and stirring at 110 ^{o}C for 17 h to afford the poly(methacryloyl guanosine) substituted Wang resin **15** as a dark brown solid (392 mg, 120 % weight increase); n_{max} / cm^{-1} (solid): 3392-3111 (NH_2 and N-H *st*), 2987 and 2924 (C-H *st*), 1682 (C=O and C=C *st*), 1627 (C=N *st*), 1593 (N-C=O *sym st*, CH_3 δ *as* and N-H δ), 1373 (C-N *st* and CH_3 δ *sym*), 1154 (C-C-N *bending*), 1071 (C-O-C *as st*); d_H (*d_6*-DMSO, gel phase, 300 MHz): 10.72 (1H, bs, N*H*), 7.88 [1H, bs, H(8)], 6.55 (2H, bs, N*H_2*), 6.02 [1H, bs, H(1')], 5.27-5.14 [2H, m, H(2'-3')], 4.38-4.02 [3H, m, H(4'-5')], 1.99 (3H, bs, C*H_3*), 1.84 (2H, bs, C*H_2*), 1.51 [3H, bs, C(CH_3)], 1.32 [3H, bs, C(C*H_3*)] ppm.

Cleavage of poly(methacryloyl guanosine) from Wang resin

Following the general procedure with the poly(methacryloyl guanosine) substituted Wang resin **15** (48.1 mg) in a mixture of trifluoroacetic acid/dichloromethane (1:1, 1.0 ml) and stirring the solution at ambient temperature for 18 h, to afford the poly-2',3'-*O*-isopropylidene-5'-*O*-methacryloylguanosine **19** (18 mg, 37 %); TGA 293.3 and 315.1 ºC; T_{onset} 329 ºC; M_n = 12,400, Đ = 1.26 (SEC-DMF, PMMA calibrated); n_{max} / cm^{-1} (solid): 3352-3131 (NH_2 and N-H *st*), 2977 and 2904 (C-H *st*), 1684 (C=O and C=C *st*), 1626 (C=C *st*), 1594 (N-C=O *sym st*, CH_3 δ *as* and N-H δ), 1373 (C-N *st* and CH_3 δ *sym*), 1154 (C-C-N *bending*), 1073 (C-O-C *as st*); d_H (*d_6*-DMSO, 300 MHz): 10.81 (1H, bs, N*H*), 7.97 [1H, bs, H(8)], 6.58 (2H, bs, N*H_2*), 5.82-5.62 [1H, m, H(1')], 4.63-3.87 [5H, m, H(2'-5')], 1.91-0.59 [11H, m, C(CH_3)$_2$, CH_3 and CH_2] ppm.

Debromination of poly(methacryloyl guanosine) substituted Wang resin

Following the general procedure with poly-2',3'-*O*-isopropylidene-5'-*O*-methacryloyl-guanosine substituted Wang resin **19** (264.9 mg, 97.5 mg polymer, 0.25 mmol polymer), tri-*n*-butyltin hydride (90.2 mg, 0.37 mmol), AIBN (8.0 mg), de-aerated toluene (2.6 ml) and stirring at 100 ºC for 24 h to give the debrominated polymer bound to the resin **23** (217.4 mg) as a brown solid; TGA 296.3, 322.4 and 519.1 ºC; T_{onset} 359.1 ºC; n_{max} / cm^{-1} (solid): 2987 and 2917 (CH *st*), 1683 (C=O and C=C *st*), 1645 (C=C *st*), 1598 (N-C=O *sym st* and CH_3 δ *as*), 1489 (NH δ *ip*), 1373 (C-N *st* and CH_3 δ *sym*), 1153 (C-C-N *bending*), 1073 (C-O-C *as st*); d_H (*d_6*-DMSO, gel phase, 300 MHz): 10.81 (1H, bs, N*H*), 7.97 [1H, bs, H(8)], 6.58 (2H, bs, N*H_2*), 5.82-5.62 [1H, m, H(1')], 4.63-3.87 [5H, m, H(2'-5')], 1.63-0.63 [11H, m, C(C*H_3*)$_2$, C*H_3* and C*H_2*] ppm.

Homopolymerisations

Homopolymerisation of 1 (general procedure)

A solution of AIBN (0.6 mL of a solution of 20 mg in 4.0 ml methanol) was placed in a Schlenk tube and the solvent removed *in vacuo*. 5'-*O*-methacryloyl-2',3'-*O*-trimethylsilyluridine **1** (100.0 mg, 0.22 mmol) and de-aerated toluene (1.0 ml) were added. The reaction mixture was de-aerated four times using freeze-pump-thaw cycle, then heated at 60 ^{o}C for 28 h. The solvent was removed *in vacuo* and the solid washed with petroleum ether/dichloromethane (1:4) to give the pure poly-5'-*O*-methacryloyl-2',3'-*O*-trimethylsilyluridine **36** (74 mg, 74 %) as a white solid; TGA 285.3 ºC; T_{onset} 229.1 ºC; M_n = 14,400, Đ = 1.51 (GPC-DMF, PMMA calibrated); n_{max} / cm^{-1} (solid): 3230 (N-H *st*), 2959 and 2947 (C-H *st*), 1672 (C=O *st*), 1457 (N-H δ *ip*), 1248 (C-C-N *bending*), 1124 and 1047 (C-O *as st*); d_H (*d_6*-DMSO, 300 MHz): 11.77 (1H, bs, N*H*), 7.79 [1H, bs, H(6)], 7.43 (2H, bs, N*H_2*), 5.85-5.70 [2H, m, H(5) and H(1')], 4.27-3.58 (5H, m, H(2'-5')), 1.78-0.72 (32H, m, 2SiC(CH_3)$_3$, CH_3 and CH_2) ppm.

Homopolymerisation of 2

Following the general procedure with a solution of AIBN (175.0 µl of a solution of 24.4 mg in 4.0 ml methanol), 2',3'-*O*-*tert*-Butyldimethylsilyl-5'-*O*-methacryloyladenosine **2** (53.4 mg, 0.12 mmol), de-aerated toluene (1.0 ml) and stirring at 90 ^{o}C for 64 h to give the pure poly-2',3'-*O*-*tert*-butyldimethylsilyl-5'-*O*-methacryloyladenosine **37** (53 mg, 100 %) as a white solid; T_g 388 ºC by DSC; TGA 355.2 ºC; T_{onset} 323.4 ºC; M_n = 21,200, Đ = 1.71 (GPC-THF, PMMA calibrated); n_{max} / cm^{-1} (solid): 2955 and 2940 (C-H *st*), 1690 (C=O *st*), 1610 (C=N *st*), 1435 (N-C=O *sym st* and N-H *amide II*), 1230 (C-C-N *bending*), 1138 and 1047 (C-O and C-N *st*), 817 (N-H δ *oop*); d_H (*d_6*-DMSO, 300 MHz): 8.45 [1H, bs, H(2)], 8.15 [1H, bs, H(8)], 7.30 (2H, bs, N*H_2*), 5.95 [1H, m, H(1')], 4.55-3.86 [5H, m, H(2'-5')], 2.00-(-0.5) (35 H, m, 2Si(CH_3)$_2$C(CH_3)$_3$, CH_3 and CH_2) ppm.

Homopolymerisation of 3

Following the general procedure with a solution of AIBN (0.8 ml of a solution of 20.0 mg in 4.0 ml methanol), 2',3'-*O*-isopropylidene-5'-*O*-methacryloylcytidine **3** (100.0 mg, 0.28 mmol), de-aerated toluene (1.0 ml) were added and stirring at 60 °C for 42 h to give the pure

poly-2',3'-*O*-isopropylidene-5'-*O*-methacryloylcytidine **38** (61 mg, 61 %) as a white solid; TGA 317.2 and 446.8 ºC; T_{onset} 280.1 ºC; n_{max} / cm^{-1} (solid): 2955 and 2940 (C-H *st*), 1690 (C=O *st*), 1610 (C=N *st*), 1435 (N-C=O *sym st* and N-H *amide II*), 1230 (C-C-N *bending*), 1138 and 1047 (C-O and C-N *st*), 817 (NH δ *oop*); d_H (d_6-DMSO, 300 MHz): 7.70 [1H, bs, H(6)], 7.45 (2H, bs, NH_2), 5.84-5.70 [2H, m, H(5) and H(1')], 5.15-5.05 [1H, m, H(2')], 4.98-4.84 [1H, m, H(3')], 4.27-3.98 [3H, m, H(4'-5')], 1.88 (3H, bs, CH_3), 1.47 [3H, bs, C(CH_3)$_2$], 1.29 [3H, bs, C(CH_3)$_2$], 0.85-0.62 (2H, m, CH_2) ppm.

Homopolymerisation of 4

Following the general procedure with a solution of AIBN (2.4 ml of a solution of 36.0 mg in 30 ml methanol), 2',3'-*O*-isopropylidene-5'-*O*-methacryloylguanosine **4** (96.4 mg, 0.20 mmol), ethyl acetate (2.0 ml), de-aerated toluene (1.0 ml) and stirring 18 h. The solvent was removed under reduced pressure and the solid washed with petroleum ether to give the pure poly-2',3'-*O*-isopropylidene-5'-*O*-methacryloylguanosine **39** (65.2 mg, 68 %) as a white solid; m.p. 82.3 ºC by DSC; TGA 255.6, 307.6 and 575.5 ºC; T_{onset} 326.1 ºC; M_n = 18,700, M_w = 30,500, Đ = 1.64 (GPC-DMF, PMMA calibrated); n_{max} / cm^{-1} (solid): 3420 (N-H *st*), 3122 (NH_2 *st*), 2982 (C-H *st*), 1682 (C=O *st*), 1534 (N-C=O *sym st*, amide II), 1375 (C-N and C-O *as st*), 1152 (C-C-N *bending*), 1177 and 1075 (C-O *st* and C-O-C *as st*), 781 (N-H δ *oop*); d_H (d_6-DMSO, 300 MHz), 10.76 (1H, bs, N*H*), 7.85 [1H, bs, H(8)], 6.59 (2H, bs, NH_2), 6.03-6.00 [1H, m, H(1'))] 5.27-5.16 [2H, bs, H(2'-3')], 4.32-4.07 [3H, m, H(4'-5')], 1.84 (3H, bs, CH_3), 1.51 [3H, m, C(CH_3)$_2$], 1.29 [3H, m, C(CH_3)$_2$], 1.00-0.70 (2H, m, CH_2) ppm.

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6. *Based on the amount recovered from the resin*.

7. *Based on the amount of complex obtained and the amount of template and complementary monomer used*.
8. *Based on the amount of daughter polymer recovered and the amount of daughter monomer used for the templating process*.