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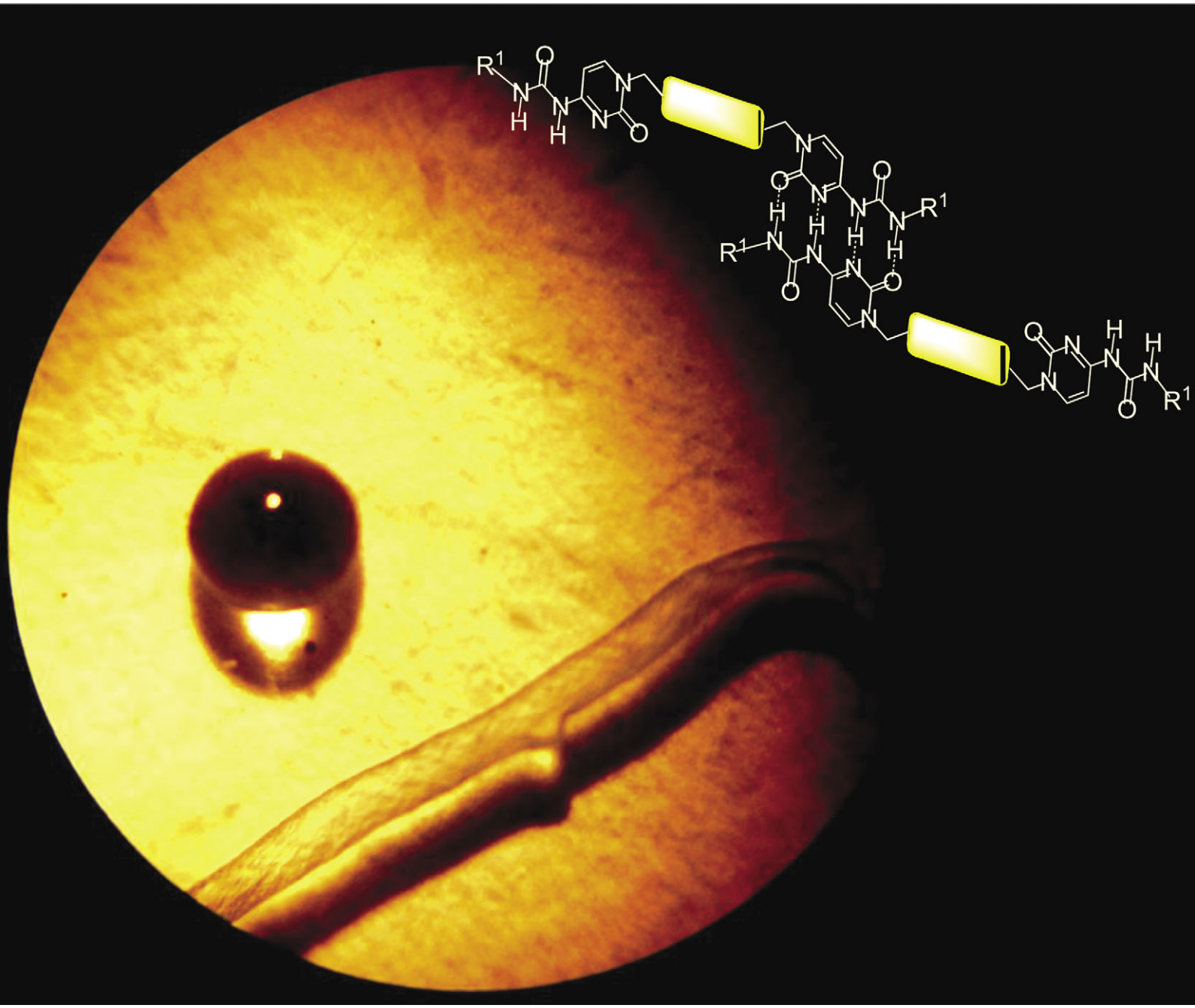

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PAPER

Quadruple hydrogen bonded cytosine modules: *N*-1 functionalised arrays†

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A ureidocytosine (UCyt) module with a pendant amine linker at *N*-1 has been prepared for applications in supramolecular quadruple hydrogen bonded array synthesis. Subsequent conjugation to four amine terminated telechelic polymers led to the formation of oligomeric DDAA arrays, as determined by NMR diffusion measurements, establishing that *N*-1 as well as *N*-9 ureidocytosine polymeric arrays can readily be accessed.

Introduction

Linear hydrogen bonded supramolecular polymers have emerged in the last decade as a new class of materials whose unique properties can respond to external stimuli such as temperature or solvent.[1] In order to generate high molecular weight polymers, a strong association between the repeating units is a prerequisite. In this regard, multiple hydrogen bonding units have been intensively studied and continue to be of significant interest.[1–3] Meijer's quadruple hydrogen bonded unit based on Ureidopyrimidinones (Upys) **1** containing two donors (D) and two acceptors (A) have shown great potential in this field.[3] With a high dimerization constant (K_{dim} 6 × 10^7 M^{-1} in $CHCl_3$) the DDAA quadruple hydrogen bonded unit has been extensively used in the synthesis of supramolecular polymers. Despite several advantages, the Upy module can exhibit up to three tautomeric forms depending on the environment and substituents attached, which can increase the number of species present.[3] Several other modules have been described that can generate complementary DDAA arrays, including, ureidonaphthyridine (UN),[2b] ureidoimidazo-[1,2-*a*]pyrimidines (Ulmp),[2f] and our ureidocytosine based module (UCyt) **2** which forms DDAA dimers with a high K_{dim} (>9 × 10^6 M^{-1} in benzene and >2.5 × 10^5 M^{-1} in $CDCl_3$) (Fig. 1).[4] However, compared to the Upy unit, the UCyt module lacks an intramolecular N–H···O hydrogen bond resulting in some conformational flexibility in the ureido fragment between unfolded **2** and **2′** folded forms.[4]

The folded conformer can dimerize *via* two hydrogen bonds and in apolar solvents such as toluene or benzene, the unfolded form **2** was found exclusively, while in very polar solvents such as DMSO the folded form **2′** alone was detected.[4] In $CDCl_3$ at room temperature it was observed that the linear DDAA array was in fast exchange with approximately 5% of the folded form **2′**. More recently, the influence of an alkyl chain at *N*-1 and *N*-9 was investigated and longer alkyl chains were found to give rise to more of the unfolded rotamer, with the chain length and degree of unsaturation at *N*-1 having the major affect.[5]

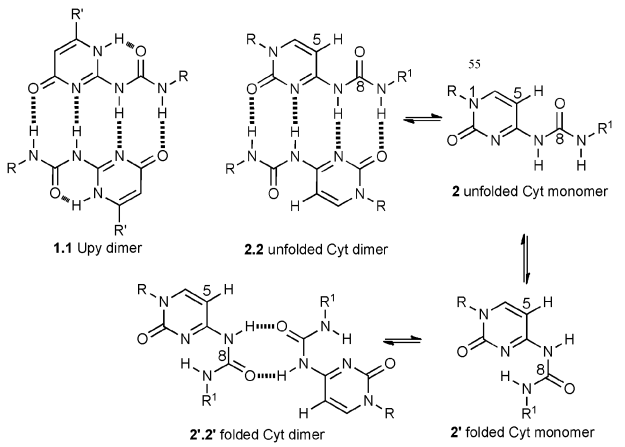

Fig. 1 Upy **1.1** dimer and unfolded (**2**) and folded (**2′**) monomer and dimer forms of the UCyt module.

Despite this methyl cytosine modules were prepared and readily used in polymer synthesis with attachment of the polymer at *N*-9.[5] Studies investigating heterodimeric arrays between **1** and **2** also suggested that the *N*-1 methyl and hexyl UCyt DDAA units competed well with the Upy module.[4,5]

One advantage of modules such as the ureidocytosines is that they can in principle readily be functionalised at *N*-1 and *N*-9, enabling the introduction of alternative moieties such as polymers or fluorescent groups at different positions in the arrays. In previous work the capacity of the UCyt modules to

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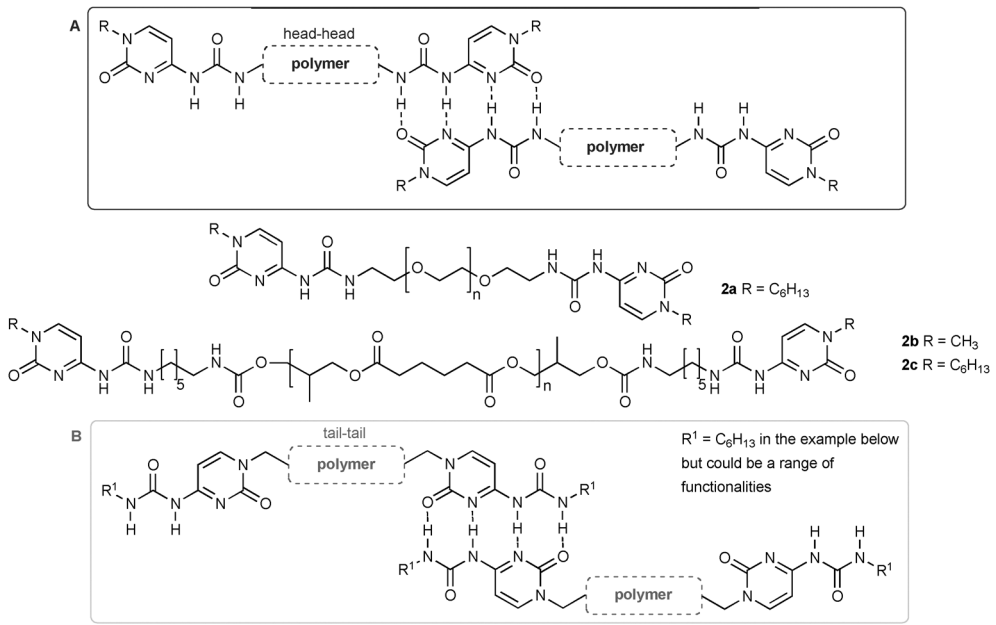
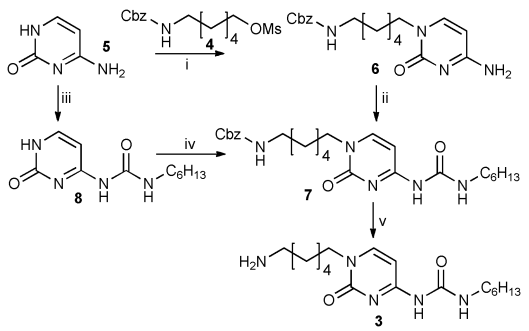


Fig. 2 Head–head A and tail–tail B arrangement of quadruple H-bonding array and compounds **2a–c**.



Scheme 1 Synthesis of amine terminated analogue **3**. *Reagents and conditions*: (i) K_2CO_3, DMF, 80 °C, 15%; (ii) $C_6H_{13}NCO$, pyridine, 110 °C, 50%; (iii) $C_6H_{13}NCO$, pyridine, 110 °C, 93%; (iv) **4**, K_2CO_3, DMF, 80 °C, 49%; (v) H_2, Pd/C, MeOH, 84%.

form linear supramolecular polymers was assessed following substitution at *N*-9 to give rise to a head–head arrangement A (Fig. 2), directly incorporating a telechelic PEG (3400 g mol^{-1}) (**2a**) and *via* a hydrophobic spacer and carbamate poly-(2-methyl-1,3-propylene adipate) (2000 g mol^{-1}) (**2b** and **2c**).[4,5]

Diffusion experiments showed slow diffusion coefficients (*D*) indicative of the formation of high molecular weight supramolecular polymers. Cytosine has been widely substituted at *N*-1, but bis-cytosines incorporating a linker at *N*-1 have received little attention. With a view to expanding the diversity of UCyt polymer architectures, in current work we have investigated incorporating a polymer *via* a linker at *N*-1, to generate a tail–tail arrangement B (Fig. 2) to establish whether they readily assemble into DDAA arrays.

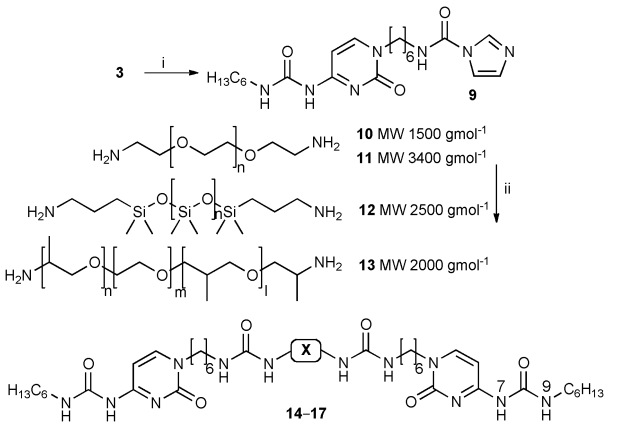
Results and discussion

To prepare polymers at *N*-1 the amine terminated cytosine **3** was prepared (Scheme 1). 6-Aminohexanol was Cbz protected then activated as the mesylate **4** as previously described.[6,7] Compound **4** was then used to alkylate cytosine **5** at *N*-1 and the reaction was examined using different bases, including potassium carbonate, caesium carbonate and sodium carbonate. In all cases, the coupled product **6** was obtained in low yields of typically 15%. Reaction of **6** with hexylisocyanate in pyridine then gave **7** in a 50% yield. Problems have been reported when alkylating cytosine at *N*-1 due to competing *O*-2 alkylation and this is normally alleviated to some degree by using *N*-4 acetylcytosine rather than cytosine.[5,8] To improve the yield for the alkylation step, rather than *N*-4 acetylation and deprotection, instead cytosine **5** was reacted with hexylisocyanate in pyridine to form the urea **8** in 93% yield. Alkylation was then performed at *N*-1 as before using mesylate **4**, which gave **7** in 49% yield after purification. Removal of the Cbz group under standard conditions readily gave the *N*-1 terminal amine **3** in high yield, and no reduction of the heterocyclic ring was observed.

Compound **3** was then activated using excess carbonyldiimidazole to give the intermediate **9** which was directly reacted with a series of commercially available linear and branched NH_2-terminated telechelic polymers **10–13** to give materials **14–17** in 45 to 60% yield (Scheme 2, Table 1).

Purification of these polymers was performed using silica gel chromatography and a gradient column with ethyl acetate/methanol (3 : 1) and then chloroform/methanol (7 : 1). Removal of the remaining traces of the carbonyldiimidazole was not straightforward. However, it was carefully removed as even small quantities can decrease the degree of polymerisation in the final polymer.

Analysis of the ^{1}H NMR spectra of polymers **14** to **17** indicated that the materials had formed quadruple hydrogen-bonded arrays, with proton signals at δ 10.9 ppm and 8.9 ppm corresponding to the unfolded urea protons at 7-H and 9-H (Fig. 2B and Fig. 3). Previous studies on model cytosine DDAA array systems have established that 7-H is observed at approximately δ 10.9 ppm while the urea 9-H is at δ 9.0 ppm.



Scheme 2 Synthesis of polymers **14–17** (**X** = polymers **10–13**). *Reagents and conditions*: (i) carbonyldiimidazole, Et_3N; (ii) polymers **10–13**, Et_3N, 45–60% over 2 steps.

For the folded conformer these are both normally observed at about 9.6 ppm. Furthermore, the N–H chemical shifts for the new polymer urea bond were observed at approximately δ 5.2 ppm. Proton integrations were also in accordance with formation of the desired bifunctional polymers.

The telechelic polymers **10** to **13** and supramolecular polymers **14** to **17** were then studied using NMR diffusion measurements in order to evaluate the diffusion coefficients (D) and to estimate the average molecular weight (M). Two concentrations were chosen for the diffusion experiments, 6 mM and 22 mM. From the data, the diffusion coefficients for 22 mM solutions of the telechelic polymers in $CDCl_3$ varied from 14.8×10^{-11} m^2 s^{-1} for the largest polymer (**11**, PEG 3400 g mol^{-1}) to 30.8×10^{-11} m^2 s^{-1} for the smallest one (**10**, PEG 1500 g mol^{-1}). The polymers **13** (PPG-PEG-PPG 2000 g mol^{-1}) and polysiloxanes **12** (2500 g mol^{-1}) had intermediate diffusion coefficients of approximately 22×10^{-11} m^2 s^{-1}. For the supramolecular polymers **14** to **17** there was a clear decrease in the diffusion coefficient at a concentration of 22 mM in $CDCl_3$, compared to the telechelic polymers before functionalisation. For example polymer **15** showed a decrease from 14.8×10^{-11} m^2 s^{-1} to 3.8×10^{-11} m^2 s^{-1} consistent with the presence of high molecular weight species in solution in $CDCl_3$, as a consequence of the self-assembly. This diffusion coefficient was comparable to that observed for polymer **2a**, previously prepared using polymer **11** conjugated *via* a head–head quadruple array (A, Fig. 2) where D was measured as 1.9×10^{-11} m^2 s^{-1} at a concentration of 37 mM in $CDCl_3$. A decrease in D was also observed for **14**, when incorporating the lower molecular weight telechelic polymer **10**. Decreased diffusion coefficients were similarly observed for

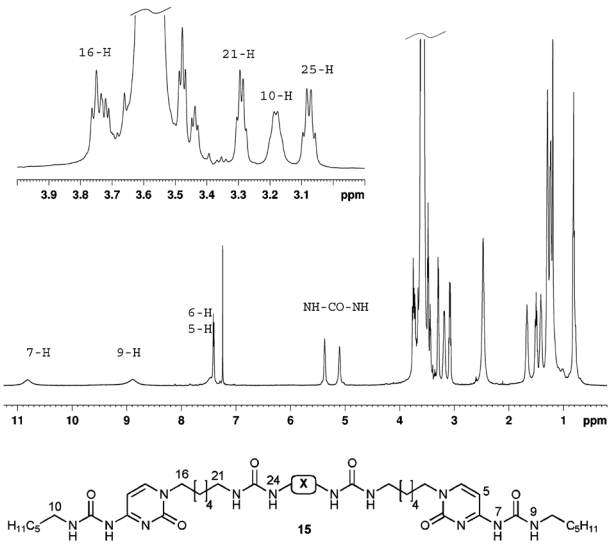


Fig. 3 ^{1}H NMR spectrum of polymer **15**.

polymers **16** and **17**, although the decrease was less pronounced, perhaps due to methyl side-groups in the telechelic materials resulting in slightly weaker hydrogen-bonding and polymerisation levels. Dilution of the materials **14–17** from 22 mM down to a concentration of 6 mM in $CDCl_3$, resulted in an increase in the diffusion as expected, but it was still consistent with the formation of oligomeric species.

The degree of polymerisation (DP) for **14** to **17** in 22 mM $CDCl_3$ solutions was approximately 5–19 monomeric units for the supramolecular polymers generated (Table 1) (DPs of approximately 2–4 were estimated at concentrations of 6 mM). Differential scanning calorimetry (DSC) of the polymers indicated glass transition temperatures T_g of just above -50 °C for **15** and **17** although for **16** the T_g was not detectable in the range -50 to 200 °C (not determined for **14**). Overall the data indicated that quadruple hydrogen-bonding arrays could be prepared *via* the incorporation of polymers at *N*-1.

Conclusions

In summary, supramolecular polymers have been generated *via* the addition of a linker at *N*-1 in ureidocytosines, and conjugation of this to telechelic polymers led to the formation of oligomeric species, as determined by NMR diffusion measurements. Since it has now been established that DDAA-based UCyt polymers can be prepared *via* the attachment of polymeric species at *N*-1 and *N*-9, bis-functionalised polymeric assemblies can now be constructed.

Table 1 Polymers prepared (**14–17**), diffusion coefficients (D) and estimated degrees of polymerisation (DP)

Polymer **X** incorporated	MW **X** g mol^{-1}	Diffusion[a] (D) m^2 s^{-1}	Polymer	Diffusion[b] (D) m^2 s^{-1}	Diffusion[a] (D) m^2 s^{-1}	DP[a]
10	1500	30.8×10^{-11}	**14**	24.0×10^{-11}	12.8×10^{-11}	5
11	3400	14.8×10^{-11}	**15**	10.7×10^{-11}	3.8×10^{-11}	19
12	2500	22.6×10^{-11}	**16**	14.7×10^{-11}	8.5×10^{-11}	7
13	2000	21.5×10^{-11}	**17**	18.6×10^{-11}	10.6×10^{-11}	6

[a] Concentration 22 mM. [b] Concentration 6 mM.

Experimental

General methods

Unless otherwise noted, solvents and reagents were reagent grade from commercial suppliers and used without further purification. Anhydrous solvents were obtained using anhydrous alumina columns.[9] All moisture-sensitive reactions were performed under a nitrogen atmosphere using oven-dried glassware. Reactions were monitored by TLC on Kieselgel 60 F_{254} plates with detection by UV, or permanganate, and phosphomolybdic acid stains. Flash column chromatography was carried out using silica gel (particle size 40–63 μm). Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at the field indicated. *J* values are given in Hz. Cbz protected aminohexanol and compound **4** were prepared as previously described.[5,6] Full details of methods for NMR diffusion measurements (all at 298 K) were previously described.[10] Assuming that supramolecular polymers **14–17** are monodisperse, a relationship between D^w in water and molecular weight *M* of a polymer was used to estimate *M* of **14–17**.[11] First, an estimate of diffusion coefficients in water (D^w) was made by dividing the *D* values measured in $CDCl_3$ (Table 1) by the ratio of the solvent viscosities ($\eta(H_2O)/\eta(CHCl_3)$ = 1.75) based on the Einstein–Smoluchowski relation. Then using the relationship between D^w and *M* ($D^w = 10^{-7.62}\ M^{-0.62}$, with D^w in units of $m^2\ s^{-1}$)[11] approximate values of degrees of polymerisation (DP) were estimated as M/M_{mono}, where M_{mono} is the molecular weight of the monomeric unit.

6-[(4-Amino-2-oxo-2*H*-pyrimidin-1-yl)-hexyl]-carbamic acid benzyl ester 6

To a solution of cytosine **5** (0.258 g, 2.33 mmol) in DMF (30 ml) was added mesylate **4** (1.00 g, 3.03 mmol) and anhydrous potassium carbonate (0.385 g, 2.79 mmol). The solution was heated at 80 °C for 18 h, then cooled, filtered and the solvent evaporated under vacuum. The residue was recrystallised from ethyl acetate affording **6** (0.120 g, 15%) as a white solid. Mp 160–162 °C (ethyl acetate); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.30 (5H, m, Ph), 7.19 (1H, d, *J* 7.1 Hz, 6-H), 5.63 (1H, d, *J* 7.1 Hz, 5-H), 5.1 (2H, s, CH_2Ph), 4.92 (1H, broad s, NHCOO), 3.72 (2H, t, *J* 7.2 Hz, CH_2N), 3.15 (2H, q, *J* 6.7 Hz, CH_2NHCOO), 1.76 (2H, broad s, NH_2), 1.68 (2H, m, CH_2CH_2N), 1.48 (2H, m, $OCONHCH_2CH_2$), 1.25 (4H, m, 2 × CH_2); ^{13}C NMR (100 MHz; $CDCl_3$) δ 165.3 (C-2), 156.5 (C-4), 145.8 (C-6), 136.6 (C-Ph), 128.4 (signals superimposed), 93.7 (C-5), 66.9 (CH_2OCONH), 50.3 (CH_2N), 41.1 (CH_2NHCOO), 30.0, 29.1, 26.5 (signals superimposed); HRMS (+CI) calculated for $C_{18}H_{25}N_4O_3$ (MH^+) 345.19267, measured 345.19272.

1-Hexyl-3-(2-oxo-1,2-dihydro-pyrimidin-4-yl)-urea 8

The reaction was carried out under anhydrous conditions. To a solution of cytosine (0.100 g, 0.900 mmol) in pyridine (5 ml) was added hexylisocyanate (0.140 ml, 0.960 mmol). The reaction was heated at 110 °C for 16 h, then cooled to rt and hexane was added, which led to the formation of a white precipitate, which was collected by filtration. The product was dried under vacuum to give **8** (0.200 g, 93%) as a white solid, which was used without further purification. Mp 178–180 °C (hexane); ν_{max}/cm^{-1} (solid) 3414, 3362, 3232, 3136, 2927, 2858, 1728, 1701, 1633, 1598; ^{1}H NMR (400 MHz; DMSO-d_6) δ 11.26 (1H, broad s, 1-H), 9.83 (1H, broad s, 7-H), 9.13 (1H, broad, 9-H), 7.65 (1H, d, *J* 7.0 Hz, 6-H), 6.16 (1H, broad d, 5-H), 3.15 (2H, app. q, *J* 6.6 Hz, $NHCONHCH_2$), 1.45 (2H, m, CH_2), 1.26 (6H, m, 3 × CH_2), 0.85 (3H, t, *J* 6.6 Hz, CH_3); ^{13}C NMR (125 MHz; DMSO-d_6) δ 163.5 (C-4), 155.1 (NHCONH), 153.3 (C-2), 145.3 (C-6), 93.8 (C-5), 39.0 (CH_2N), 30.9, 29.3, 26.1, 22.1 (CH_2CH_3), 13.9 (CH_3); HRMS (+CI) calculated for $C_{11}H_{19}N_4O_2$ (MH^+) 239.15079, measured 239.15105.

{6-[4-(3-Hexyl-ureido)-2-oxo-2*H*-pyrimidin-1-yl]-hexyl}-carbamic acid benzyl ester 7

Method 1. The reaction was carried out under anhydrous conditions. To a solution of compound **6** (0.700 g, 2.03 mmol) in dry pyridine (9 ml) was added hexylisocyanate (0.336 g, 2.64 mmol) and the mixture was stirred at 110 °C for 15 h. The reaction was cooled to rt and hexane was added that led to the formation of a white precipitate, which was collected by filtration. The product was washed with hexane, dried under vacuum and recrystallised from ethyl acetate to give **7** (0.478 g, 50%) as a white solid, and the characterisation data was identical to that given for **7** below.

Method 2. The reaction was carried out under anhydrous conditions. To a solution of compound **8** (1.00 g, 4.20 mmol) in dry DMF (100 ml) was added potassium carbonate (0.640 g, 4.64 mmol) and mesylate **4** (1.73 g, 5.26 mmol). The mixture was stirred under nitrogen at 80 °C for 20 h. The solution was then filtered and the solvent was evaporated under vacuum. The residue was recrystallised using ethyl acetate to give **7** as a white solid (0.966 g, 49%). Mp 270 °C decomp. (hexane); ν_{max}/cm^{-1} 3327, 3217, 3059, 2860, 1700, 1660, 1620, 1554, 1514; ^{1}H NMR (500 MHz; $CDCl_3$) δ 10.88 (1H, s, 7-H), 8.94 (1H, s, 9-H), 7.53 (1H, broad, 5-H), 7.37 (1H, d, *J* 7.1 Hz, 6-H), 7.30 (5H, m, Ph), 5.06 (2H, s, CH_2Ph), 4.73 (1H, s, NHCOO), 3.77 (2H, t, *J* 7.2 Hz, CH_2N), 3.21 (2H, broad q, $NHCONHCH_2$), 3.18 (2H, q, *J* 6.7 Hz, CH_2NHCOO), 1.71 (2H, quint, *J* 6.9 Hz, CH_2CH_2N), 1.56 (2H, broad quint, $NHCONHCH_2CH_2$), 1.50 (2H, m, CH_2CH_2NHCOO), 1.33 (6H, m, 3 × CH_2), 1.29 (4H, m, 2 × CH_2), 0.84 (3H, t, *J* 7.3 Hz, CH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 164.9 (C-4), 157.2 (C-2), 156.4 ($NHCOOCH_2$), 154.3 (NHCONH), 146.6 (C-6), 136.6 (C-Ph), 128.5 (C-Ph), 128.1 (C-Ph), 97.4 (C-5), 66.6 (CH_2OCONH), 50.6 (CH_2N), 40.8 (CH_2NHCOO), 40.1 ($CH_2NHCONH$), 31.5, 29.8, 29.4, 28.8, 26.6, 26.2, 26.1, 22.6 (CH_2CH_3), 14.1 (CH_3); HRMS (+CI) calculated for $C_{25}H_{38}N_5O_4$ (MH^+) 472.29183, found 472.29041.

1-[1-(6-Amino-hexyl)-2-oxo-1,2-dihydro-pyrimidin-4-yl]-3-hexyl-urea 3

To compound **7** (0.700 g, 1.48 mmol) in methanol (25 ml), Pd/C (10% Degussa wet; 0.070 g) was added. The reaction was stirred for 18 h under a hydrogen atmosphere. The reaction was then filtered through Celite, and the residual solvent evaporated under vacuum giving compound **3** (0.420, 84%)

as a white solid. Mp 169–171 °C (methanol); ν_{max}/cm^{-1} 3365, 3217, 3058, 2923, 2852, 1708, 1660, 1620, 1566, 1562; ^{1}H NMR (500 MHz; DMSO-d_6) δ 8.98 (1H, s, 7-H), 8.94 (1H, s, 9-H), 7.90 (1H, d, J 7.1 Hz, 6-H), 6.24 (1H, d, J 7.1 Hz, 5-H), 3.70 (2H, t, J 7.2 Hz, CH_2N), 3.15 (2H, q, J 6.4 Hz, NHCONHCH_2), 1.57 (2H, m, CH_2), 1.43 (2H, m, CH_2), 1.30 (12H, m, 6 × CH_2), 0.84 (3H, t, J 7.3 Hz, CH_3); ^{13}C NMR (125 MHz; DMSO-d_6) δ 162.3 (C-4), 154.1 (C-2), 153.6 (NHCONH), 148.4 (C-6), 94.2 (C-5), 49.2 (CH_2N), 41.4 (CH_2NH_2), 39.5 (CH_2NHCONH), 33.5, 31.3, 29.7, 28.8, 26.4, 26.2, 22.4 (CH_2CH_3), 14.2 (CH_3); HRMS (+CI) calculated for $C_{17}H_{32}N_5O_2$ 338.25505 (MH^+), measured 338.25484.

General polymer synthesis

1,1′-Carbonyldiimidazole (0.166 g, 1.02 mmol) and amine **3** (0.300 g, 0.890 mmol) were stirred in chloroform (10 ml) for 18 h at rt. Hexane (40 ml) was added and the precipitate **9** (0.366 g, 95%) collected by filtration, then used directly in the next step. To a solution of the polymer (*e.g.* PEG 3400) (0.350 g, 1.04 mmol) in dry THF (15 ml) was added the imidazolide **9** (0.180 g, 4.17 mmol). The solution was heated at reflux for 16 h, then evaporated to dryness and the residue redissolved in chloroform. The organic phase was washed with water (10 ml) and brine (20 ml), then dried ($MgSO_4$). The solvent was evaporated under vacuo and the product purified using flash silica chromatography (methanol/ethyl acetate, 1 : 2 then chloroform/methanol, 7 : 1) to give polymers **14** to **17** in approximately 45–60% yield.

Polymer 14 incorporating 10 (MW 1500)

Mp 169 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 10.84 (2H, broad s, 7-H), 8.89 (2H, broad s, 9-H), 7.47 (2H, broad s, 5-H), 7.43 (2H, d, J 7.1 Hz, 6-H), 5.20 (2H, broad s, 23-H), 4.95 (2H, broad s, 22-H), 3.76 (4H, m, 16-H), 3.50 (130H, m, 65 × CH_2O), 3.21 (8H, m, 24-H and 10-H), 3.10 (4H, m, 21-H), 1.69 (8H, m, 4 × CH_2), 1.55–1.24 (28H, m, 14 × CH_2), 0.83 (6H, t, J 6.6 Hz, 2 × CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 164.7 (C-4), 158.8 ($CH_2NHCONHCH_2$), 157.1 (C-2), 154.3 (C-8), 146.8 (C-6), 97.1 (C-5), 70.5 (CH_2O signals superimposed), 69.8 (NHCH_2CH_2O), 69.6 (NHCH_2CH_2O), 50.6 (CH_2N), 40.0 (OCH$_2CH_2$NH), 40.0 (CH_2NHCONHCH$_2CH_2O$), 38.5 (CH_2NH), 31.5, 30.7, 29.3, 28.8, 26.6, 26.4, 26.1, 22.6, 14.1 (CH_3).

Polymer 15 incorporating 11 (MW 3400)

Mp 40 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 10.89 (2H, broad s, 7-H), 8.88 (2H, broad s, 9-H), 7.51 (2H, broad s, 5-H), 7.44 (2H, d, J 7.3 Hz, 6-H), 5.28 (2H, broad s, 24-H), 5.10 (2H, broad s, 22-H), 3.80 (4H, m, 16-H), 3.50 (150H, m, 75 × CH_2O), 3.33 (4H, q, J 5.1 Hz, 25-H), 3.23 (4H, br q, J 6.0 Hz, 10-H), 3.12 (4H, m, 21-H), 1.72 (4H, m, 2 × CH_2), 1.55–1.24 (28H, m, 14 × CH_2), 0.86 (6H, t, J 6.6 Hz, 2 × CH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 164.7 (C-4), 158.7 ($CH_2NHCONHCH_2$), 156.2 (C-2), 154.2 (C-8), 146.7 (C-6), 97.0 (C-5), 70.4 (CH_2O, signals superimposed), 70.2, 69.8 (NHCH_2CH_2O), 50.5 (CH_2N), 40.1 (OCH$_2CH_2$NH), 40.0 (CH_2NHCONHCH$_2CH_2O$), 39.9 (CH_2NH), 31.4, 30.1, 29.6, 29.3, 28.7, 26.5, 26.3, 26.1, 22.6, 13.9 (CH_3).

Polymer 16 incorporating 12 (MW 2500)

^{1}H NMR (500 MHz; $CDCl_3$) δ 10.88 (2H, broad s, 7-H), 8.92 (2H, broad s, 9-H), 7.49 (2H, broad s, 5-H), 7.42 (2H, d, J 7.1 Hz, 6-H), 4.45 (4H, broad s, NHCONH), 3.78 (4H, m, 16-H), 3.22 (4H, m, 10-H), 3.10 (8H, m, CH_2CH_2NHCONH-$CH_2CH_2CH_2Si$+ NHCONHC$H_2CH_2CH_2Si$), 1.55–1.24 (36H, m, 18 × CH_2), 0.83 (6H, t, J 6.6 Hz, 2 × CH_3), 0.50 (4H, m, 2 × CH_2Si), 0.08 (250H, s, 125 × CH_3Si); ^{13}C NMR (125 MHz; $CDCl_3$) δ 164.6 (C-4), 158.2 ($CH_2NHCONHCH_2$), 157.1 (C-2), 154.3 (C-8), 146.7 (C-6), 97.1 (C-5), 50.5 (CH_2N), 43.3 (OSi$CH_2CH_2CH_2NH$), 40.1 (C-10+CH_2NHCONH$(CH_2)_3$ SiO), 33.0 ($CH_2NHCH_2CH_2Si$), 31.5, 30.0, 29.4, 28.8, 26.6, 26.3, 26.0, 24.1, 22.6, 15.3 (CH_2Si), 14.0 (CH_3), 0.7 (CH_3Si).

Polymer 17 incorporating 13 (MW 2000)

Mp 40 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 10.85 (2H, broad s, 7-H), 8.92 (2H, broad s, 9-H), 7.49 (2H, broad s, 5-H), 7.42 (2H, d, J 7.1 Hz, 6-H), 5.08 (4H, broad s, NHCONH), 3.76 (4H, m, 16-H), 3.50 (216H, m, CH_2O+$CHCH_3$), 3.20 (4H, m, 10-H), 3.10 (4H, m, 21-H), 1.69 (4H, m, 2 × CH_2), 1.55–1.24 (28H, m, 14 × CH_2), 1.08 (23H, m, CH_3), 0.83 (6H, t, J 6.6 Hz, 2 × CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 164.7 (C-4), 158.4 ($CH_2NHCONHCH(CH_3)$), 157.1 (C-2), 154.2 (C-8), 146.8 (C-6), 97.1 (C-5), 75.1 (OCHCH$_3$), 70.5 (CH_2O, signals superimposed), 50.5 (CH_2N), 46.2 (NHCONHCH(CH_3)), 40.0 (CH_2NHCONHCH$_2$CH(CH_3)O+C-10), 31.4, 30.2, 29.3 (CH_2), 28.8 (CH_2), 26.6, 26.4, 26.1, 22.5, 18.4 (OCH(CH_3), 17.0 (NHCHCH_3), 13.0 (CH_2CH_3).

Differential Scanning Calorimetry (DSC) thermograms were obtained using a TA instrument Q100 DSC. Samples were analysed in a pierced lid pan. An initial melt run was carried out from room temperature (18 °C) to 300 °C at 20 °C min^{-1}. The sample was then equilibrated at −90 °C, heated to 300 °C at a rate of 10 °C min^{-1} and stabilised again at 300 °C then cooled to 90 °C at the same rate. Samples were analysed in triplicate.

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Notes and references

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