Supplementary Material (ESI) for Soft Matter

Supporting data

Experimental

Synthesis of Highly-branched (15:1) N-pyrrole chain-end functionalized poly-N-isopropyl acrylamide

For example, N-isopropylacrylamide (1.757g,15.53mmol) and 4-vinylbenzyl-pyrrolecarbodithioate (0.4022g, 1.553mmol) was dissolved in dioxane (6.0ml). Azobis(isobutyronitrile) (0.2519g, 1.553mmol) was dissolved in the solution which was transferred to a glass ampoule. The ampoule was sealed and freeze-pump-thaw cycles were carried out thrice at 10^{-4} mbar. It was then heated at 60^0C for 48 h and quenched with liquid nitrogen. The polymer solution was precipitated by dropwise addition to diethylether (100ml).The ether was decanted off , the solids further washed with ether then vacuum-oven dried *in vacuo* at room temperature for 16h. The procedure was repeated twice more to give1.34g (62%) of a yellow solid.
^{1}H NMR ($CDCl_3$, ca. 5% CD_3OD, RT, 400MHz): δ/ppm 1.0 (s, br, -N($C\underline{H}_3$)$_2$), 1.45-1.60 (m, br, 2H, -$C\underline{H}_2$-CH-C_6H_4-) and (m, br, 1H, -CH_2-$C\underline{H}$-C_6H_4-), 1.75-2.05 (m, br, 1H, -$C\underline{H}_2$-CH-CO-NH-) and (m, br, 1H, -CH_2-$C\underline{H}$-CO-NH-), 3.32 (s, br, $\underline{H}_2$O-polymer bound), 3.98 (s, br,1H, $(CH_3)_2C\underline{H}$-), 4.50 (m, br, 1H, $CH_2C\underline{H}$-S-C(=S)-N-pyrrole), 6.30 (s, br, 2H, N-pyrrole-H_b), 7.62 (d, br, 2H, N-pyrrole-H_a)

Synthesis of highly-branched Carboxylic-acid chain-end functionalized Poly-N-isopropylacrylamides

For example, the highly-branched N-pyrroledithioate chain-ended polymer (0.500g) was dissolved in DMF (25ml) (degassed with nitrogen/30min) and stirred at 60^0C under a nitrogen atmosphere. The 4,4'-azobis-(4-cyanopentanoic acid) (1.7356g, 0.6192mmol, 20eq-relative to the no.of pyrrole chain-end groups) was added to the reaction mixture as a solution in DMF(5.0ml) and heated at 60^0C for 16h. This procedure was repeated twice more so that a total of 60eq of the reagent were added. The DMF was removed under high vacuum at 40-50^0C and the resultant oil was ultrafiltered using a blend of acetone/ethanol (10:1, vol:vol) through a 3,000 MWCO cellulose filter. The resultant concentrate was evaporated under reduced pressure and vacuum-oven dried at room temperature to yield 0.3477g of a buff coloured solid.
^{1}H NMR ($CDCl_3$, ca. 5% CD_3OD, RT, 400MHz): δ/ppm 1.0 (s, br, -N($C\underline{H}_3$)$_2$), 1.45-1.60 (m, br, 2H, -$C\underline{H}_2$-CH-C_6H_4-) and (m, br, 1H, -CH_2-$C\underline{H}$-C_6H_4-), 1.75-2.05 (m, br, 1H,-$C\underline{H}_2$-CH-CO-NH-) and (m, br, 1H, -CH_2-$C\underline{H}$-CO-NH-), 3.32 (s, br, $\underline{H}_2$O-polymer bound), 4.05 (s, br, 1H, $(CH_3)_2C\underline{H}$-), 6.60-7.40 (m, br, 4H, -$C_6\underline{H}_4$-), 7.65 (s, br, -N$\underline{H}$-CO-).

Synthesis of highly-branched RGD-peptide chain-end functionalized Poly-N-isopropylacrylamides

For example, the highly-branched carboxylic-acid chain-end functionalized poly-N-isopropylacrylamide (0.070g) was dissolved in DMF (1.0ml) and a solution of dicyclohexylurea (0.017g, 0.0825 mmol) and N-hydroxysuccinimide (0.095 g, 0.0825mmol) in DMF(2.0 ml) was added. The solution was stirred at room

temperature under a nitrogen atmosphere for 16h then precipitated dropwise into rapidly stirring diethylether (80ml). The ether was decanted from the solids and the solids dried in *vacuo* at room temperature. The procedure was repeated to give a buff-coloured solid.

The succinimide chain-end functionalized polymer was dissolved in deionized water (3.5ml) at 0-1^{0}C and stirred at room temperature under a nitrogen atmosphere. The RGD-peptide was dissolved in water (1.0ml) then added to the stirring solution followed by 0.1M sodium phosphate buffer, pH 8.5 (0.5ml). The solution was stirred at room temperature for 16h then ultrafiltered with water (2x300ml-50ml). The solution was then freeze-dried to yield 0.050g (ca.70%) of a buff-coloured solid.
^{1}H NMR ($CDCl_3$, ca. 5% CD_3OD, RT, 400MHz): δ/ppm 1.0 (s, br, -N($C\underline{H}_3$)$_2$), 1.45-1.60 (m, br, 2H, -$C\underline{H}_2$-CH-C_6H_4-) and (m, br, 1H, -CH_2-$C\underline{H}$-C_6H_4-), 1.75-2.05 (m, br, 1H, -$C\underline{H}_2$-CH-CO-NH-) and (m, br, 1H, -CH_2-$C\underline{H}$-CO-NH-), 3.26 (s, br, 2H, -CH_2-NH-C(NH)-NH_2; from arginine residue), 3.60 (s, br, $\underline{H}_2$O-polymer bound), 3.90 (s, br, 1H, $(CH_3)_2C\underline{H}$-), 6.60-7.35 (m, br, 4H, -$C_6\underline{H}_4$-), 7.60 (s, br, -CO-N$\underline{H}$-).

Particle size Measurements (Carboxylic acid and RGD ended polymers)
The polymer (0.030g) was dissolved in deionized water (3.0ml) at 0-1^{0}C to give a solution of 10.0mg.ml^{-1} as the high concentration sample and then further diluted to 3mg.ml^{-1} with deionized water to give the low concentration sample. The solutions were filtered through 0.2μm filter units into plastic cuvettes (3.0ml) and the particle size analysis carried out to give five readings from which a final average reading was obtained. Measurements were carried out in duplicate and obtained at a suitable temperature (35^{0}C) which was above the cloud-point of each of the samples.

SEC data

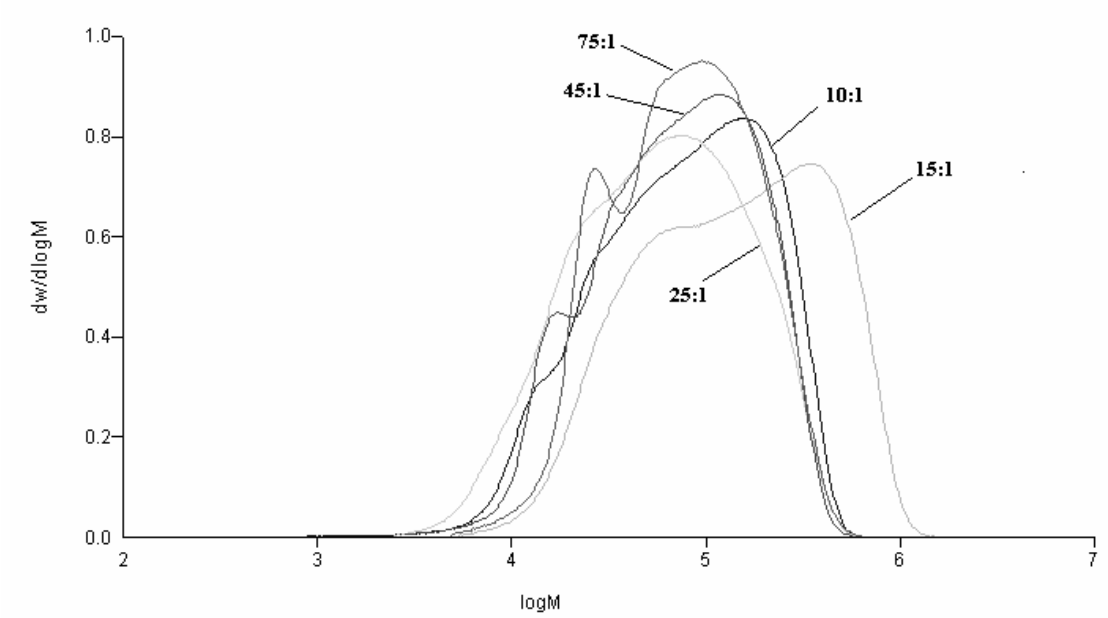

Figure S1: SEC data for highly-branched polymers formed from polymerizations of NIPAM with **1.** Multimodal profiles characteristic of highly-branched PNIPAM (Eluant:THF(0.1%TBAB). Labels are mole ratios of NIPAM:**1**

Mark-Houwink-Sakarada plots

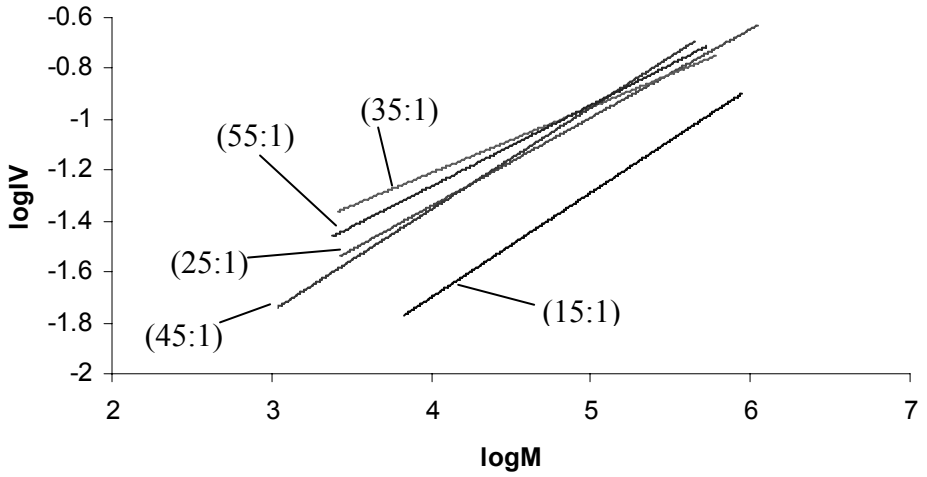

Figure S2: Plots of logM vs logIV for the range of highly-branched N-pyrrole dithioate chain-ended polymers analysed at varying NIPAM:**1** feed ratios (numbers in brackets refer to these ratios)

NMR data

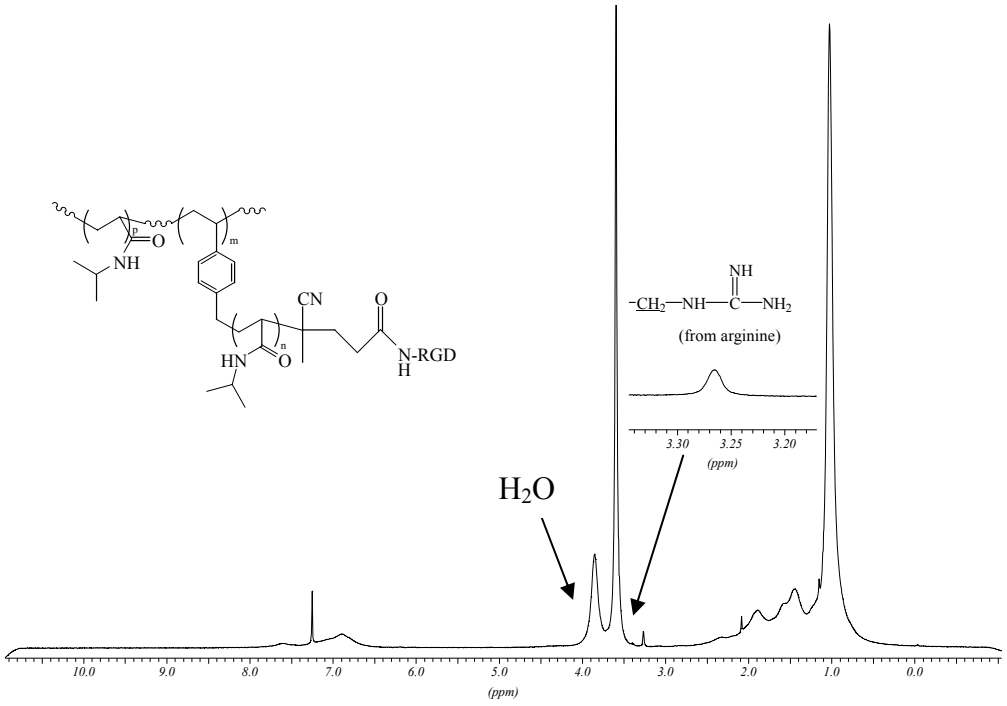

Figure S3: Example of 400MHz ^{1}H nmr spectrum of a highly branched PNIPAM with RGD peptide chain ends