Supporting Information

Poly(Boc-acryloyl hydrazide): The importance of temperature and RAFT agent degradation on its preparation

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Figure S1. A) Plot of fractional concentration of monomer ln(M₀/Mₜ) vs time for polymerisations of N'-1-(tert-butoxycarbonyl)acryloyl hydrazide (1) performed at different temperatures. Conditions: [M]=0.9M, [M]/[CTA]/[In]=100/1/0.2. 4,4'-Azobis(4-cyanovaleric acid) (V-501) - circles, 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65) - squares, and 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) - triangles. Adapted with permission from Crisan, D. N.; Creese, O.; Ball, R.; Brioso, J. L.; Martyn, B.; Montenegro, J.; Fernandez-Trillo, F. Polym. Chem. 2017, 8 (31), 4576–4584 - Published by The Royal Society of Chemistry. B) For polymerisations carried out in S1A, effect of temperature on the time at which deviation from linearity for the plot of ln[M₀]/[Mₜ] vs time is observed (tₜead), and the fractional concentration of monomer ln(M₀/Mₜ) at this point.
Figure S2. Plot of $\ln(M_0/M_t)$ vs time for the polymerisation of N’-(tert-butoxycarbonyl)acryloyl hydrazide (1) at 30 °C. Conditions: [M]=0.9M, [M]/[CTA]/[VA-044]=50/1/0.2.

**Small molecule analogue of a DP= 1 of N’-(tert-butoxycarbonyl)acryloyl hydrazide (1).**

![Scheme S1. Attempted route for the synthesis of a DP= 1 analogue of N’-(tert-butoxycarbonyl)acryloyl hydrazide (1).](image)

**tert-butyl 2-(2-bromopropanoyl)hydrazine-1-carboxylate (3):** 2-Bromopropionic acid (2) (10 g, 59.9 mmol) and tert-butyl carbazate (6.56 g, 49.6 mmol) were dissolved in a 2:1 mixture of water/THF (180 ml). N-(3-Dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (13.3 g, 69.5 mmol) was added in portions to the solution over 15 minutes and the mixture was left stirring for 3h at room temperature. The solution was extracted into EtOAc (3 x 60 ml) and a basic work-up performed with NaCO$_3$ (3 X 60 ml). The organic layer was further washed with water (2 x 60 ml), dried with Na$_2$SO$_4$, filtered and the solvent removed under reduced pressure to leave a white solid. This solid was then recrystallised using ethyl acetate to afford white crystalline material which was
washed with ice cold diethyl ether and dried under reduced pressure (8.9 g, 64 %): $^1$H NMR (300MHz, DMSO-$_d_6$) $\delta$ (ppm) 9.9 (s, 1H), 9.0-8.3 (s, 1H), 4.45 (q, 1H), 1.65 (d, 3H), 1.38 (s, 9H).

Figure S3. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of tert-butyl 2-(2-bromopropanoyl)hydrazine-1-carboxylate (3).

tert-butyl 2-((ethylthio)carbonothioyl)thio)propanoyl)hydrazine-1-carboxylate (4) (not isolated): Ethanethiol (0.49 ml, 6.59 mmol) was added to a suspension of K$_3$PO$_4$ (1.4 g, 6.59 mmol) in acetone (20 ml) and was left stirring at room temperature for 10 minutes. CS$_2$ (1.09 ml, 6.59 mmol) was then added and the reaction mixture was left for a further 10 minutes. tert-butyl 2-(2-bromopropanoyl)hydrazine-1-carboxylate (1) (1.6 g, 5.99 mmol) was added in one portion and the mixture left to react for 13 hours. The solvent was then removed under reduced pressure and HCl (100 ml, 1 M) was added to the crude of the reaction. The resulting mixture extracted into DCM (2 x 100 ml). The organic layer was then washed with water (2 x 100 ml) and brine (2 x 100 ml), dried with Na$_2$SO$_4$, filtered and the solvent removed under reduced pressure. The resulting orange oil was purified by column chromatography using a 7:3 ratio of diethyl ether and hexane, then dried under reduced pressure to leave a viscous orange liquid (0.12 g, 7 %) which consisted of two compounds, none of which is the title compound. a; $^1$H NMR (300MHz, CDCl$_3$) $\delta$ (ppm) 10.3-9.7 (1H, s, NH), 4.66 (q, 1H), 1.58 (d, 3H), 1.44 (s, 9H) and b; $^1$H NMR (300MHz, CDCl$_3$) $\delta$ (ppm) 10.3-9.7 (1H, s, NH), 4.73 (q, 1H), 1.59 (d, 3H), 1.44 (s, 9H).
Figure S4. A) $^1$H NMR (300 MHz, DMSO) spectrum of 2-((ethylthio)carbonothioyl)thio-2-methylpropanoic acid (CTA). B) $^1$H NMR (300 MHz, CDCl3) spectrum of tert-butyl 2-(2-bromopropanoyl)hydrazine-1-carboxylate (3). C) $^1$H NMR (300 MHz, CDCl3) spectrum of the reaction of ethanethiol with carbon disulfide and tert-butyl 2-(2-bromopropanoyl)hydrazine-1-carboxylate (3).
Figure S5. \(^1\)H NMR (300 MHz, CDCl\(_3\)) spectrum of the main fraction isolated following the reaction of ethanethiol with carbon disulfide and \textit{tert}-butyl 2-(2-bromopropanoyl)hydrazine-1-carboxylate (3).
Figure S7. GPC traces (DMF LiBr 0.05M) of isolated “living” Boc-P\textsubscript{x} after (t=30 min) after further heating (60 °C t=90 min), and subsequent inability to chain extend with (1) (t=30+60 min).
Figure S8. Top: $^1$H NMR (300 MHz, CDCl$_3$) of “living” Boc-$\text{P}_x$ after polymerisation reaction was stopped after 30 minutes, before full conversion (47%). Bottom: $^1$H NMR (300 MHz, CDCl$_3$) of “dead” Boc-$\text{P}_x$ after polymerisation for 120 minutes to maximum conversion (85%).
Figure S9. Plot of $\ln(M_0/M_t)$ vs time (A) and conversion ($\rho$) vs time (B) for the polymerisation of N'-(tert-butoxycarbonyl)acryloyl hydrazide (1) at 150 °C. Conditions: [M]=0.9M, [M]/[CTA]/[VA-044]=50/1/0.2.

Figure S10. $^1$H NMR (300 MHz, CDCl$_3$) spectrum showing vinyl region at varying time points in the polymerisation of N'-(tert-butoxycarbonyl)acryloyl hydrazide (1) at 150 °C. Conditions: [M]=0.9M, [M]/[CTA]/[VA-044]=50/1/0.2. New vinyl protons can be observed from 7 minutes, suggestive of $\beta$-elimination products.