

Dithiocarbamate RAFT agents with broad applicability – the 3,5-dimethyl-1H-pyrazole-1-carbodithioates

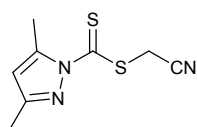
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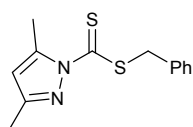
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Supporting Information

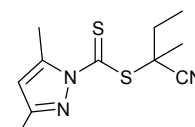
1. NMR spectra of 3,5-dimethyl-1H-pyrazole-1-carbodithioates (18-20).



18



19



20

The ¹H and ¹³C NMR characterisation data for 3,5-dimethyl-1H-pyrazole-1-carbodithioate RAFT agents (**18-20**) is presented in this section. The compound numbering corresponds to that used in the main document.

Cyanomethyl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (**18**).

^1H NMR (CDCl_3 , 400 MHz) δ 2.26 (s, 3H, CH_3), 2.68 (d, $J = 1.0\text{Hz}$, 3H, CH_3), 3.95 (s, 2H, CH_2CN); 6.12 ($\delta J = 0.8\text{Hz}$, 1H, ArH) (Figure 1S). ^{13}C NMR (CDCl_3 , 100 MHz) δ 13.8, 17.2, 21.7, 114.2, 115.5, 146.3, 153.1, 195.4 (Figure 2S).

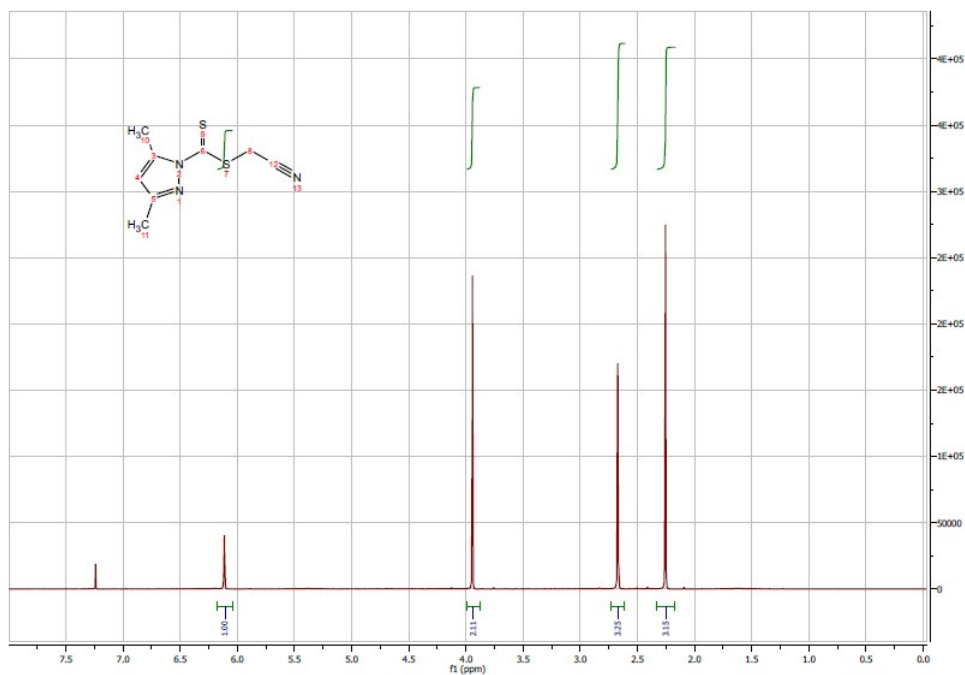


Figure 1S. ^1H NMR Spectrum of **18** (CDCl_3 , 400MHz).

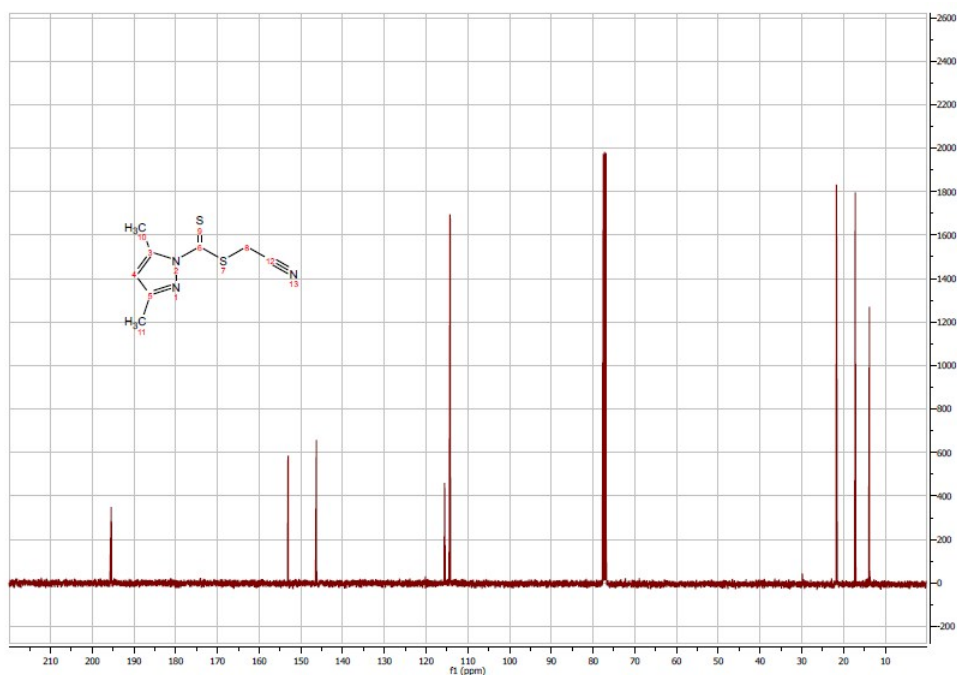


Figure 2S. ^{13}C NMR Spectrum of **18** (CDCl_3 , 100MHz)

Benzyl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (19).

^1H (CDCl_3 , 400 MHz) δ 2.22 (s, 3H, CH_3), 2.68 (d, $J = 0.9\text{Hz}$, 3H, CH_3), 4.39 (s, 2H, CH_2Ph), 6.06 (d, $J = 0.6\text{Hz}$, 1H, CH), 7.27 (m, 3H, ArH), 7.38 (m, 2H, ArH) (Figure 3S). ^{13}C NMR (CDCl_3 , 100 MHz) δ 13.8, 17.6, 41.6, 113.5, 127.7, 128.7, 129.8, 135.0, 145.7, 152.0, 200.6 (Figure 4S).

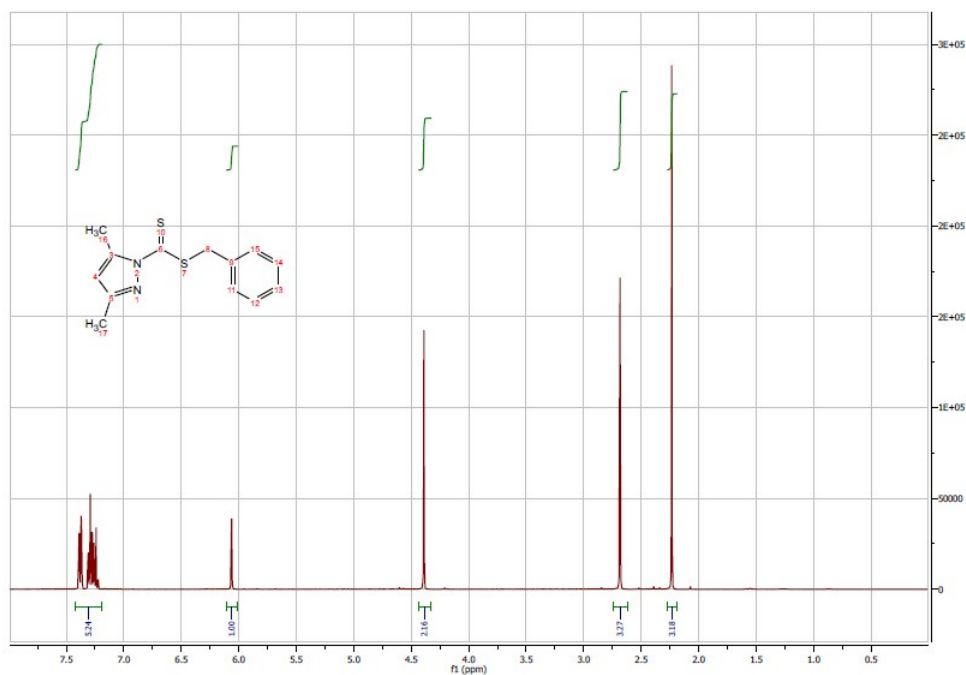


Figure 3S. ^1H NMR Spectrum of **19** (CDCl_3 , 400MHz).

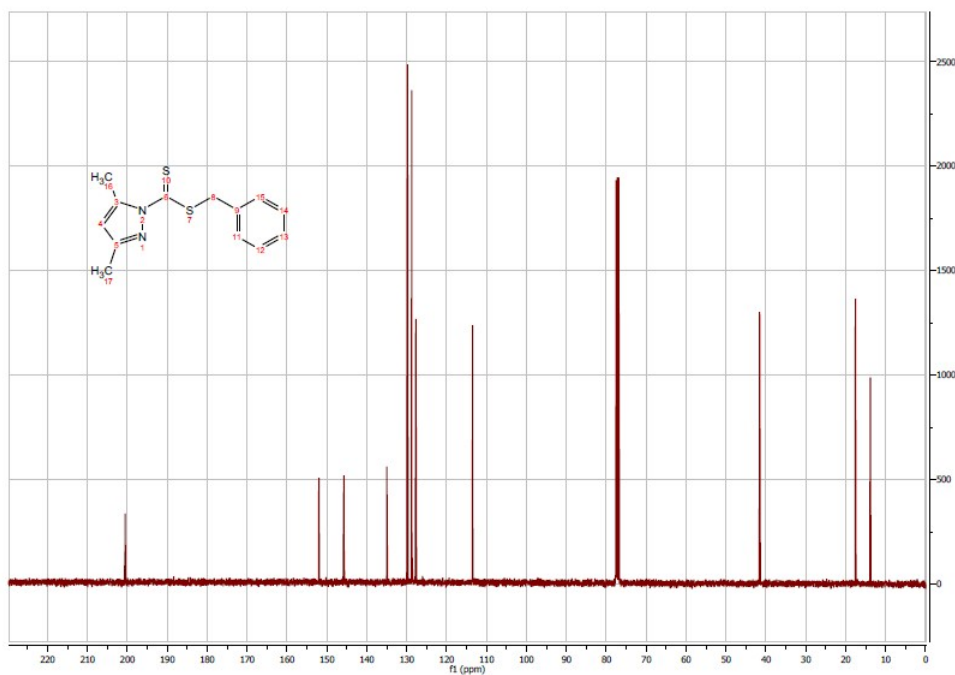


Figure 4S. ^{13}C NMR Spectrum of **19** (CDCl_3 , 100MHz)

2-Cyanobutan-2-yl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (20).

^1H NMR (CDCl_3 , 400 MHz) δ 1.20 (t $J = 7.4\text{Hz}$, 3H, CH_2CH_3), 1.86 (s, 3H, CH_3), 2.03 (m, 1H, CH_aCH_3), 2.24 (s, 3H, CH_3), 2.27 (m, 1H, CH_bCH_3), 2.67 (d $J = 0.9\text{Hz}$, 3H, CH_3), 6.08 (d $J = 0.8\text{Hz}$, 1H, ArH) (Figure 5S). ^{13}C NMR (CDCl_3 , 100 MHz) δ 9.4, 13.8, 17.5, 24.0, 32.3, 46.4, 113.9, 120.0, 145.9, 152.0, 194.6 (Figure 6S).

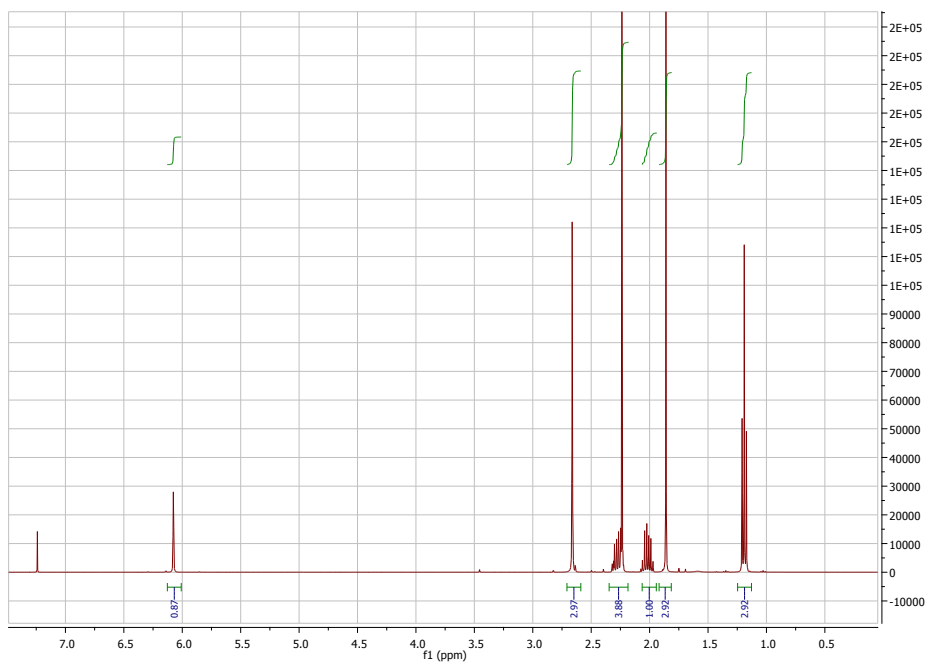


Figure 5S. ^1H NMR Spectrum of **20** (CDCl_3 , 400MHz).

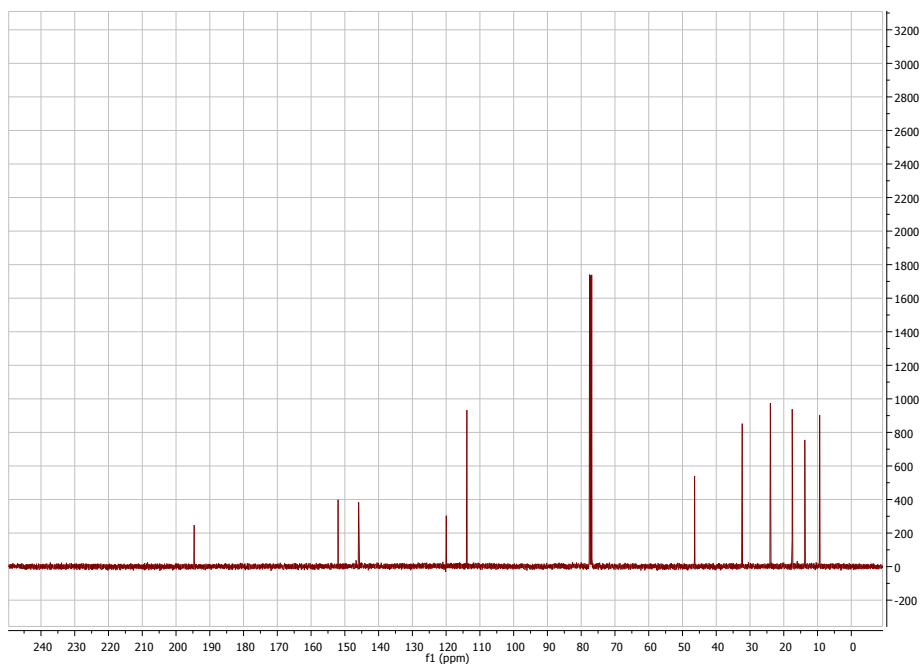


Figure 6S. ^{13}C NMR Spectrum of **20** (CDCl_3 , 100MHz).

2. Ultraviolet-visible spectra for 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates (18-20).

The UV-visible spectra of the RAFT agents **19-21** were each measured at two different concentrations for solutions in acetonitrile and are shown in Figure 7S. The absorption maxima and extinction coefficients are summarized in Table 1S. The UV-visible spectra were recorded using a Hewlett Packard 8453 UV-spectrometer scanning between 200 and 800 nm.

Table 1S. UV-vis spectral parameters for RAFT agents **18-20**.

RAFT agent	λ (nm)	absorbance (au)	concentration (mg mL ⁻¹)	concentration (M)	extinction (M ⁻¹ cm ⁻¹)
18	306	1.0017	0.010	4.73×10^{-5}	21200
19	301	0.67850	0.010	3.81×10^{-5}	17800
20	301	0.96840	0.010	3.95×10^{-5}	24500
18	439	0.39330	2.00	0.0095	41.5
19	417	0.53410	2.00	0.0076	70.1
20	425	0.66870	2.00	0.0079	84.6

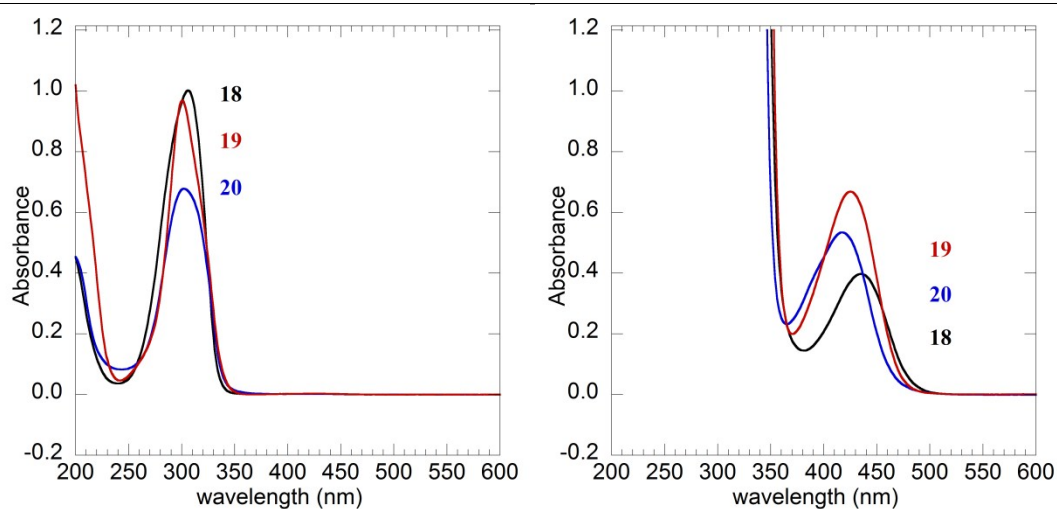


Figure 7S. UV-vis spectra of RAFT agents **18-20** with concentration (a) 2 mg mL⁻¹ (b) 0.01 mg mL⁻¹ in acetonitrile.

3. Estimation of transfer coefficients for 3,5-dimethyl-1H-pyrazole-1-carbodithioates (18-20).

The expression for dispersity for polymerization with degenerative chain transfer (eqn. 1)¹ can be rearranged to provide a qualitative estimate of the transfer constant (C_{tr}) (eqn. 2).

$$D = 1 + \frac{1}{X_n} + \left(\frac{2-x}{x}\right) \frac{1}{C_{tr}} \quad (1)$$

$$C_{tr} = \left(\frac{2-x}{x}\right) \left(D - 1 - \frac{1}{X_n}\right)^{-1} \quad (2)$$

where x is the fractional monomer conversion and X_n is the degree of polymerization. Note that the derivation of expression is based on termination and other side reactions being absent. For DMA polymerization with RAFT agent **19** the estimated transfer constant can be seen to reduce with the molecular weight of the polymer formed. This might be attributed to the contribution of initiator derived chains to the molecular weight distribution, which is greater when low concentrations of RAFT agent are used. The values for C_{tr} will also be lowered by SEC band broadening and can be strongly influenced by SEC baseline selection.

The values of C_{tr} obtained are not very sensitive to the precision of X_n , nonetheless, as absolute molecular weights are not available, we also explored using the calculated M_n rather than the experimental M_n . The results shown in Table 2S confirm that the molecular weight term is only important for very low molecular weights.

1. A. Goto and T. Fukuda, *Prog. Polym. Sci.*, 2004, 29, 329-385.

Table 2S. Estimated transfer coefficients for 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates (**18-20**)^a

RAFT agent	monomer	Conversion (%)	$M_n(\text{exp})$ (PMMA equivalents)	\bar{D}	M_{monomer}	$M_n(\text{calc})$ (g mol ⁻¹)	C_{tr}^b	C_{tr}^c
18	DMA	99	12100	1.07	99	9641	17	17
18	DMA	99	11800	1.06	99	9830	20	20
18	DMA	99	2600	1.07	99	2098	32	45
18	DMA	96	11500	1.05	99	9690	26	27
18	DMA	86	24000	1.11	99	25479	13	12
18	DMA	87	40800	1.14	99	42471	9	9
19	DMA	99	10400	1.07	99	9690	17	17
20	DMA	99	11000	1.07	99	9681	17	17
20	DMA	99	11200	1.08	99	9870	14	15
6	DMA	99	12800	1.65	99	9650	2	2
21	DMA	98	10700	1.07	99	9697	17	17
22	DMA	99	12700	1.09	99	9746	12	13
18	MA	77	8600	1.12	86	6581	15	15
18	MA	71	6800	1.10	86	6203	21	21
18	MA	47	5700	1.15	86	4242	24	25
19	MA	79	7100	1.12	86	6796	14	14
20	MA	83	7200	1.08	86	7118	21	21
6	MA	88	13400	1.96	86	7500	1	1
21	MA	81	6400	1.06	86	7064	32	31
18	St	52	5200	1.10	104	3584	36	40
20	St	63	5500	1.07	104	4337	43	47
18	MMA	53	441900	2.71	100	7184	-	-
20	MMA	74	17400	1.44	100	9987	4	4
18	VAc	62	5000	1.29	86	3059	8	8
18	VAc	47	5900	1.27	86	3880	13	13
18	VAc	64	7300	1.51	86	5576	4	4
18	VAc	87	24700	1.56	86	22453	2	2
19	VAc	49	3300	1.07	86	2506	70	86
20	VAc	57	4600	1.17	86	2864	17	18
6	VAc	85	6200	1.18	86	4429	8	8

^a All experiments were conducted with microwave heating at 100 °C unless indicated. Control experiments with dithiocarbamate **6** and trithiocarbonates **21** or **22** are shown greyed. All concentrations are based on the mass or volume of material used at 22 °C and do not take into account volume of mixing effects. For further detail refer to Table 1 of main text. ^b C_{tr} estimated using the measured M_n in PMMA equivalents. ^c C_{tr} estimated using the calculated M_n .

4. Size Exclusion Chromatography for Selected Copolymers

Molar mass distributions were derived from SEC traces by applying the appropriate calibration polynomial from the time the SEC trace was obtained. Those for copolymer and block copolymers are provided in Figures 3, 7 and 8 of the main document and in Figure 8S-Figure 12S below. Refer to Tables 2,3 in the main text for further details.. Excerpts of the relevant Table entries are also provided below as Table 3S - Table 7S. A large peak with apparent molar mass $< 10^3$ poly(MMA) equivalents (>38 minutes in the corresponding SEC trace) appears in all traces. This is a “salt peak” associated with the LiBr/DMAc SEC eluent and may vary in size and appear as a positive or a negative peak dependent on the water content of the eluent. Where the distribution is truncated by this salt peak, the quoted molar mass will be an overestimate and the dispersity will be an underestimate.

Table 3S. RAFT copolymerizations in presence of 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates.

monomer 1	monomer 2	[monomer] (M)	RAFT agent	[RAFT] (M)	[ACHN] ^b (M)	solvent ^b	time (h)	conv (%)	M_n^c	M_n (calcd) ^d	\mathcal{D}	L^e
VAc		1.5	18	0.048	0.012	EtOAc	12	62	7600	4245	1.18	0.85
	DMA	1.5						99				
VAc		1.5	20	0.03	0.003	CH ₃ CN	12	45	7900	6650	1.18	0.94
	DMA	1.5						99				

For meanings of footnotes refer to Table 3 of main text.

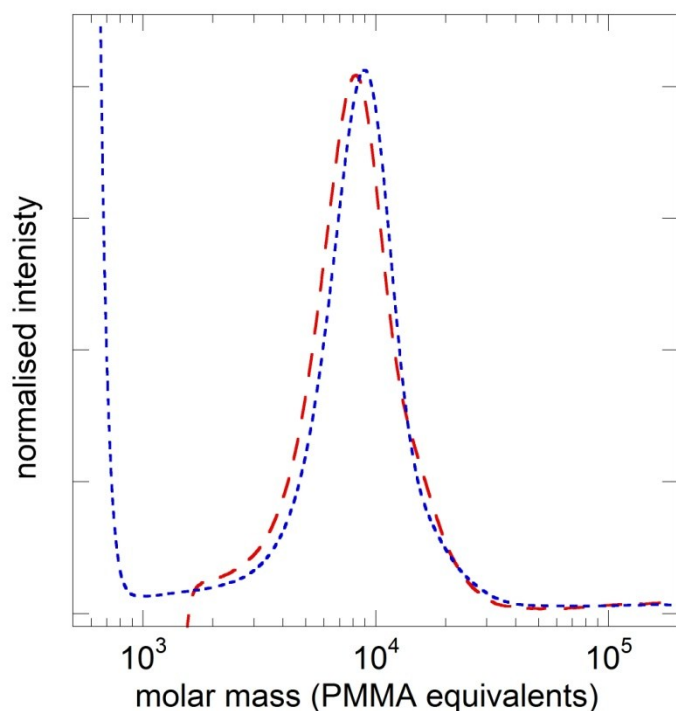


Figure 8S. Molar mass distributions for poly(*N,N*-dimethylacrylamide-co-vinyl acetate) macro-RAFT agent prepared with RAFT agent **18** (---) or RAFT agent **20** (----). Refer to Table 3S. The large peak with apparent molar mass $< 10^3$ poly(MMA) equivalents is a “salt peak” associated with the LiBr/DMAc SEC eluent.

Table 4S. RAFT copolymerizations in presence of 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates.

monomer 1	monomer 2	[monomer] (M)	RAFT agent	[RAFT] (M)	[ACHN] ^b (M)	solvent ^b	time (h)	conv (%)	M_n^c	M_n (calcd) ^d	\bar{D}	L^e
DMA		1.5	18	0.03	0.003	CH ₃ CN	2	98	9600	8929	1.18	0.97
	MA	1.5						97				
DMA		1.5	20	0.03	0.003	CH ₃ CN	2	97	9200	8967	1.13	0.97
	MA	1.5						98				

For meanings of footnotes refer to Table 3 of main text.

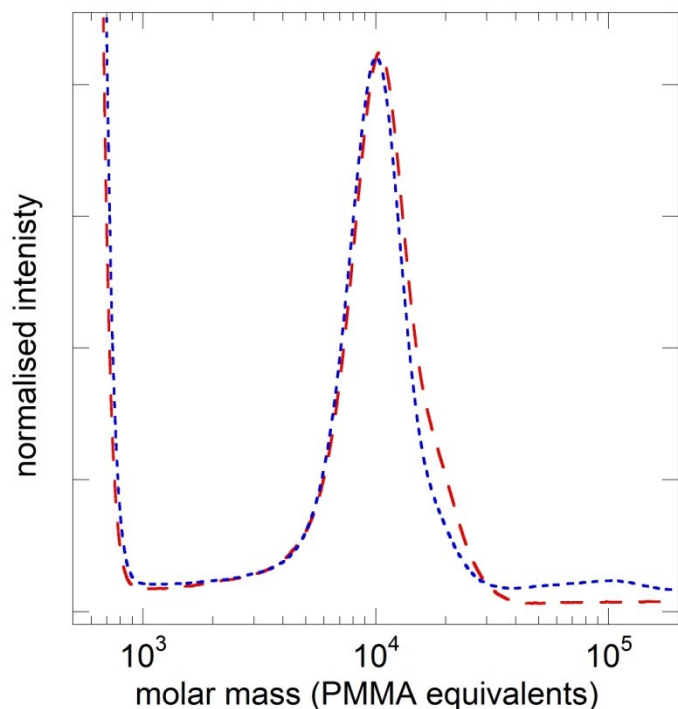


Figure 9S. Molar mass distributions for poly(*N,N*-dimethylacrylamide-co-methyl acrylate) macro-RAFT agent prepared with RAFT agent **18** (---) or RAFT agent **20** (- - -). Refer to Table 4S. The large peak with apparent molar mass $< 10^3$ poly(MMA) equivalents is a “salt peak” associated with the LiBr/DMAc SEC eluent. The value of dispersity for poly(MMA-co-St) is likely to be effected by intrusion of salt peak.

Table 5S. RAFT copolymerizations in presence of 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates.

monomer 1	monomer 2	[monomer] (M)	RAFT agent	[RAFT] (M)	[ACHN] ^b (M)	solvent ^b	time (h)	conv (%)	M_n^c	M_n (calcd) ^d	\bar{D}	L^e
MMA	DMA	3.5 0.0263	20	0.0263	0.0053	CH ₃ CN	4	68 99	12000	8529	1.45	0.90
MMA	DMA	1.75 1.75	20	0.0263	0.0053	CH ₃ CN	4	91 99	13600	11631	1.18	0.90
MMA	St	1.5 1.5	20	0.03	0.006	Toluene	12	50 36	5100	4098	1.15	0.88

For meaning of footnotes refer to Table 3 of main text.

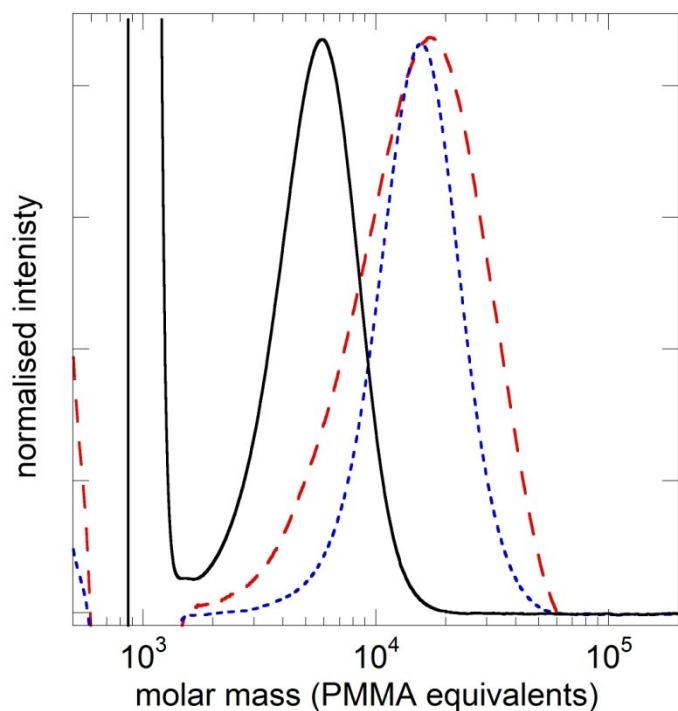


Figure 10S. Molar mass distributions for poly(*N,N*-dimethylacrylamide-*co*-methyl methacrylate) macro-RAFT agent prepared with RAFT agent **20** with DMA:MMA 93:7 (---) or 1:1 (---) and for poly(styrene-*co*-methyl methacrylate) and St:MMA 1:1. Refer to Table 5S. The large peak with apparent molar mass < 10³ poly(MMA) equivalents is a “salt peak” associated with the LiBr/DMAc SEC eluent.

Table 6S. Block copolymer prepared with 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates.

monomer Block 1	monomer Block 2	[M] (M)	RAFT agent	[RAFT] (M)	[ACHN] ^b (M)	solvent	time (h)	conv (%)	M_n^c	M_n (calcd) ^d	\mathcal{D}	L^e
DMA*		1.5	20	0.03	0.003	CH ₃ CN	0.75	92	5400	4771	1.07	0.98
	VAc (1:1) ^f	1.5			0.003		12	60	8200	7734	1.25	0.88

For meaning of footnotes refer to Table 3 of main text.

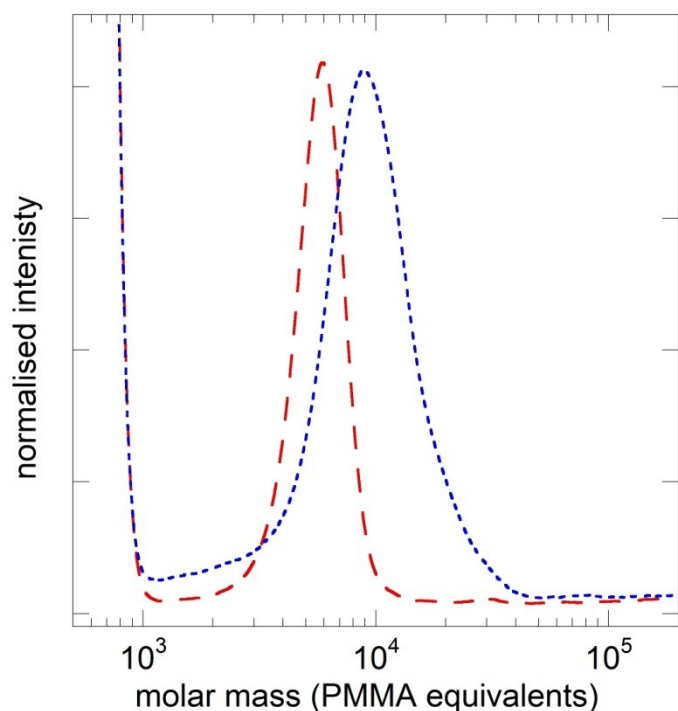


Figure 11S. Molar mass distributions for poly(*N,N*-dimethylacrylamide macro-RAFT agent prepared with RAFT agent **20** (---) and the derived poly(*N,N*-dimethylacrylamide)-block-poly(vinyl acetate) (----). Refer to entry 6 and Table 3. The large peak with apparent molar mass < 10³ poly(MMA) equivalents is a “salt peak” associated with the LiBr/DMAc SEC eluent.

Table 7S. Block copolymer prepared with 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates.

monomer Block 1	monomer Block 2	[M] (M)	RAFT agent	[RAFT] (M)	[ACHN] ^b (M)	solvent	time (h)	conv (%)	M_n^c	M_n (calcd) ^d	\mathcal{D}	L^e
DMA*		1.5	18	0.03	0.003	CH ₃ CN	1	98	5800	5168	1.05	0.98
	VAc (1:1) ^f	1.5			0.003		24	55	8500	7535	1.24	0.88

For meaning of footnotes refer to Table 3 of main text.

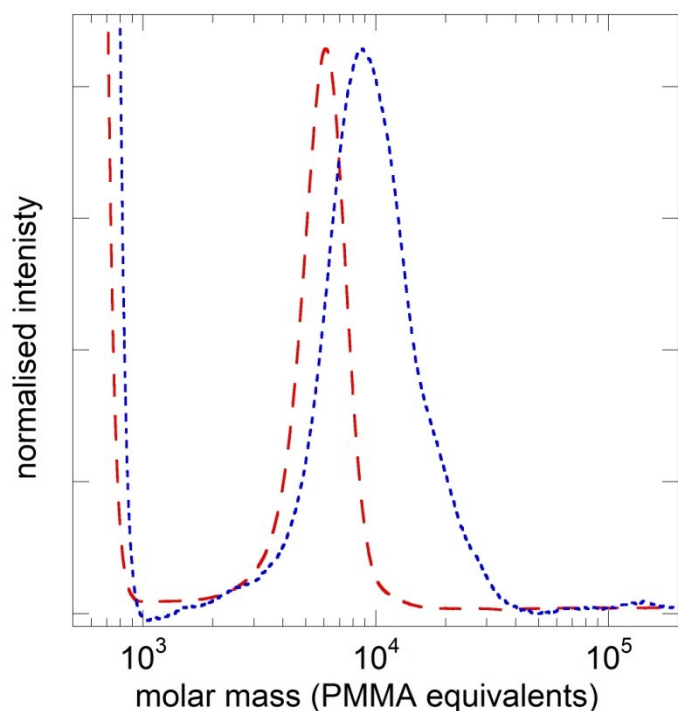


Figure 12S. Molar mass distributions for poly(*N,N*-dimethylacrylamide macro-RAFT agent prepared with RAFT agent **18** (---) and the derived poly(*N,N*-dimethylacrylamide)-block-poly(vinyl acetate) (---). Refer to entry 3 of Table 3. The large peak with apparent molar mass $< 10^3$ poly(MMA) equivalents is a “salt peak” associated with the LiBr/DMAc SEC eluent.