

Supplementary information

Preparation of poly(*N*-vinylcarbazole) using RAFT agents 3-8 at 60 °C. – target molar mass 13750

A stock solution containing a RAFT agent (**3-8**) (0.154 mmol, see Table S1 for amounts), NVC (2.12 g, 10.94 mmol), AIBN (8.3 mg, 0.051 mmol) and 1,4-dioxane to a volume of 5 mL was prepared in a volumetric flask. The reaction mixture was divided in four and transferred to ampules which were degassed by three repeated freeze–evacuate–thaw cycles and sealed. The ampules were heated at 60 °C for 2, 4, 6, or 16 h (see entries 1-6, Table S2)

Table S1. Amount (mg) of RAFT agent used in NVC polymerization

RAFT agent	Z	R	Amount (mg)
3	SC ₁₂ H ₂₅	CH ₂ CN	48.9
4	SC ₁₂ H ₂₅	CH(CH ₃)Ph	58.9
5	N-(4-Py)(4-CNPh)	CH ₂ CN	47.8
6	N(4-Py)(CH ₃)	CH ₂ CN	34.4
7	OC ₂ H ₅	CH ₂ CN	24.8
8	OC ₂ H ₅	CH(CH ₃)Ph	34.8

Preparation of poly(*N*-vinylcarbazole) using RAFT agent 9 at 60 °C. – target molar mass 27000

A stock solution containing RAFT agent (**9**) (16.2 mg, 0.077 mmol), NVC (2.12 g, 10.94 mmol), AIBN (8.3 mg, 0.051 mmol) and 1,4-dioxane to a volume of 5 mL was prepared in a volumetric flask. The reaction mixture was divided in three and transferred to ampules which were degassed by three repeated freeze–evacuate–thaw cycles and sealed. The ampules were heated at 60 °C for 2, 6 or 20 h (see entry 7, Table S2)

Table S2. Details of PNVC polymerization^a

Entry	RAFT agent	Time (h)	Conversion (%)	M_n^a	M_n (calc) ^b	M_w/M_n^a
1	3	2	6	2390	1140	1.05
		4	37	6360	5350	1.08
		6	60	8900	8450	1.09
		16	92	11500	12600	1.11
2	4	2	0	1060	380	1.00
		4	1	1110	520	1.00 ^f
		6	1	1100	520	1.00
		16	61	9420	8500	1.10
3	5	2	1	1540	450	1.02
		4	2	1790	580	1.03
		6	8	2890	1400	1.08
		16	74	11200	10200	1.10
4	6	2	6	3320	1040	1.17
		4	37	6240	5260	1.20
		6	67	9070	9300	1.16
		16	99	10990	13400	1.15
5	7	2	11	3780	1670	1.21
		4	48	6920	6690	1.24
		6	75	9060	10320	1.21
		16	99	10700	13300	1.20
6	8	2	1	2280	360	1.15
		4	2	2610	500	1.22
		6	5	2670	900	1.22
		16	99	9630	13400	1.28
7	9	2	0	700	190	1.03
		6	0	710	190	1.05
		20	7	8940	1980	1.33

^aGPC DMAc eluent, PSt equivalents ^b M_n (calc) = $\frac{([M]_0 - [M]_t)}{([RAFT]_0 + df([I]_0(1 - e^{k_d t})))} \times MW_{\text{monomer}} + MW_{\text{RAFT}}$, (where d is number of chains formed by radical-radical termination (= 1), f is the initiator efficiency (= 0.23), $k_d = 9.6 \times 10^6 \text{ s}^{-1}$ and t = time in s)

Preparation of poly(*n*-butyl acrylate)

A stock solution containing cyanomethyl dodecyltrithiocarbonate **3** (60.0 mg), BA (1.79 g, 2.0 mL), AIBN (3.3 mg) and toluene to a volume of 5 mL was prepared in a volumetric flask. The reaction mixture was divided in two and transferred to ampules which were degassed by three repeated freeze–evacuate–thaw cycles and sealed. The ampules were heated at 70 °C for either 2 or 6 h (see Table S3).

Table S3. Molar mass and conversion data for PBA using **3** at 70 °C

Entry	time/h	M_n	M_n theory	M_w/M_n	Conversion (%)
1	2	8260	8080	1.14	85
2	6	9000	9120	1.20	96

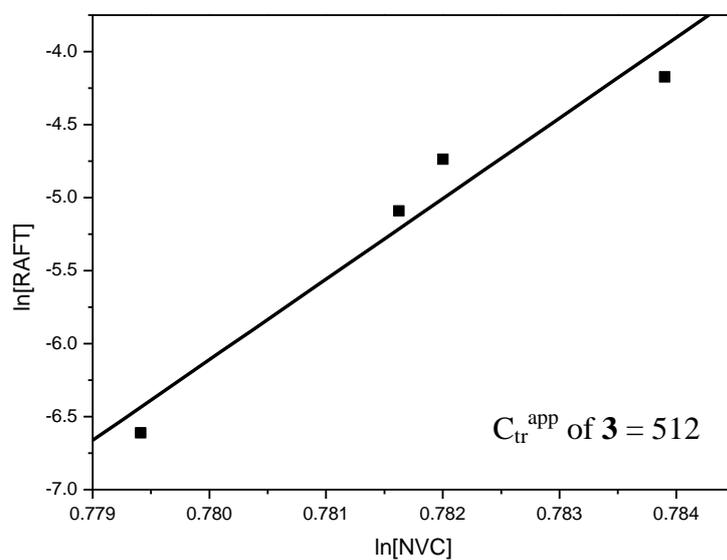
Preparation of polystyrene

A stock solution containing cyanomethyl dodecyltrithiocarbonate **3** (72.0 mg) and St (4.54 g, 5.0 mL), were prepared in a volumetric flask. The reaction mixture was divided in two and transferred to ampules which were degassed by three repeated freeze–evacuate–thaw cycles and sealed. The ampules were heated at 110 °C for either 6 or 16 h (see Table S4).

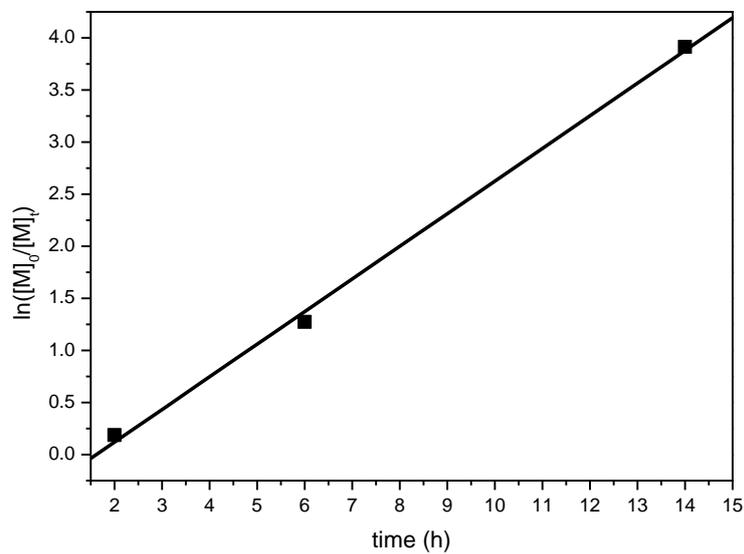
Table S4. Molar mass and conversion data for PSt using **3** at 110 °C

Entry	time/h	M_n	M_n theory	M_w/M_n	Conversion (%)
1	6	5040	4200	1.12	25
2	16	10600	9400	1.09	47

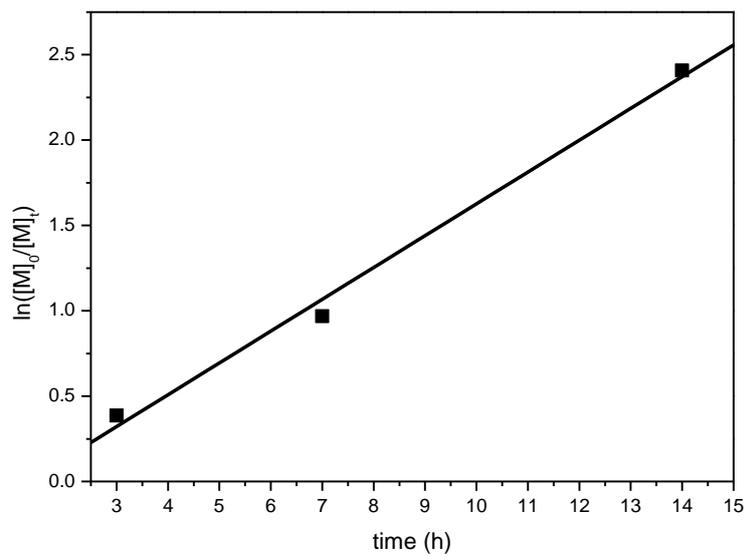
Figure S1: Apparent transfer coefficient plot of 3 in NVC polymerization



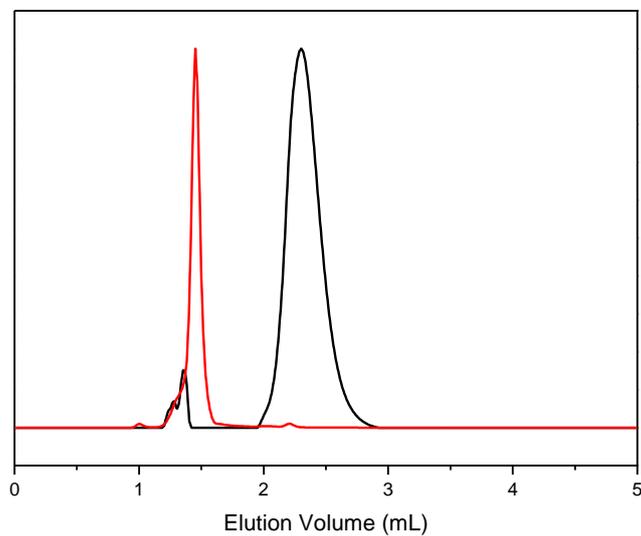
**Figure S2: Pseudo-first order kinetic analysis of NVC conversion with respect to time
for block extension of 3-PBA**



**Figure S3: Pseudo-first order kinetic analysis of NVC conversion with respect to time
for block extension of 3-PSt**



**Figure S4: LCCC analysis of 3-PSt (black) and 3-PNVC (red) near critical conditions
for PSt on a reversed phase column (18% THF/82%DMF)**



**Figure S5: LCCC analysis of 3-PBA (black) and 3-PNVC (red) near critical conditions
for PBA on a normal phase column (13% MeCN/87%DCM)**

