Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Triazine-Mediated Controlled Radical Polymerization: New Unimolecular Initiators

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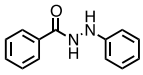
Materials and Equipment

All reactions were conducted under Argon unless noted. Benzoyl peroxide (BPO, 97%), N,N,N′,N′,N′′-pentamethyldiethylenetriamine (99%), Cu(0) (99%), and CuBr (99.999%) were purchased from Sigma Aldrich and used as received. Monomers were passed through a column of basic alumina to remove inhibitors before use. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 MHz, Varian 500 MHz, or a Varian 600 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra are reported in ppm relative to deuterated chloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. VG70 Magnetic Sector and Waters GCT Premier TOF instruments were used for low- and high-resolution mass analysis by electron ionization (EI). A Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer was used for high-resolution mass analysis using electrospray ionization (ESI). Size exclusion chromatography (SEC) was performed on a Waters 2695 separation module with a Waters 2414 refractive index detector in chloroform with 0.25% triethylamine. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards.

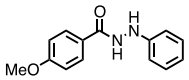
Synthesis

General procedure for the preparation of benzoyl hydrazine 1(a-c)

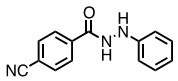
Benzoyl hydrazine was synthesized using a modified literature procedure.[1] Briefly, triethylamine (12.8 mL, 92.5 mmol) was added to a solution of phenylhydrazine (5 g, 46.3 mmol) in THF (60 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 10 min and a solution of benzoyl chloride (46.3 mmol) in THF (30 mL) was added dropwise. The reaction mixture was stirred for 18 h while allowing it to slowly warm to room temperature. The solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (150 mL), washed with water (2 x 100 mL), then dried over $MgSO_4$. The solvent was removed in vacuo. Recrystallization from a minimum amount of dichloromethane gave rise to **1a**, **1b** and **1c**.



N-phenylbenzoylhydrazide **1a**: Colorless solid, yield 60%, ^{1}H NMR (500 MHz, DMSO-d_6, δ): *δ* 10.35 (d, *J*= 2.7 Hz, NH, 1H), 7.90 (m, 2H), 7.88 (d, *J*= 2.6 Hz, NH, 1H), 7.56 (m, 1H), 7.49 (m, 2H), 7.14 (dd, *J*= 8.5, 7.2 Hz, 2H), 6.78 (m, 2H), 6.70 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 166.8, 150.0, 133.5, 132.1, 129.2, 128.9, 127.7, 119.1, 112.8. HR-ESI $C_{13}H_{12}N_2O$ $(M+Na)^+$ calcd. 235.0847, found 235.0832. IR (neat) $\tilde{\nu}$ = 3268, 3056, 1642, 1600, 1494, 1481, 1303, 1205, 901, 750 cm^{-1}.



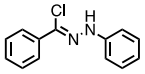
N'-(4-methoxyphenyl)benzohydrazide **1b**: Colorless solid, yield 50%, ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.91 (br, NH, 1H), 7.81 (d, *J*= 8.8 Hz, 2H), 7.24 (m, 2H), 6.96-6.91 (m, 5H), 6.34 (br, NH, 1H), 3.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): *δ* 162.7, 148.2, 129.2, 129.0, 124.4, 121.3, 114.0, 113.8, 55.4. HR-ESI $C_{14}H_{14}N_2O_2$ $(M)^+$ calcd. 242.1055, found 242.1065. IR (neat) $\tilde{\nu}$ = 3261, 1636, 1601, 1494, 1247, 1172, 1027, 903, 843, 751 cm^{-1}.



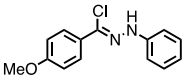
N'-(4-cyanophenyl)benzohydrazide **1c**: Yellow solid, yield 51%, ^{1}H NMR (500 MHz, DMSO-d_6, δ): 10.59 (d, *J*= 2.7 Hz, NH, 1H), 8.05 (d, *J*= 8.4 Hz, 2H), 7.98 (d, *J*= 8.3 Hz, 3H), 7.14 (dd, *J*= 8.5, 7.2 Hz, 2H), 6.78 (d, *J*= 7.3 Hz, 2H), 6.72 (dd, *J*= 7.3, 1.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 165.5, 149.6, 137.5, 133.1, 129.2, 128.6, 119.3, 118.7, 114.5, 112.8. HR-ESI $C_{14}H_{11}N_3O$ $(M+Na)^+$ calcd. 260.0794, found 260.0791. IR (neat) $\tilde{\nu}$ = 3243, 2232, 1648, 1600, 1493, 1307, 1250, 904, 862, 747 cm^{-1}.

General procedure for the preparation of benzohydrazonoyl chloride 2(a-c)

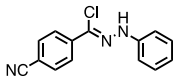
To a dried flask was added a suspension of **2a-c** (22.0 mmol), triphenylphosphine (27.2 mmol), and anhydrous carbon tetrachloride (27.2 mmol) in anhydrous acetonitrile (60 mL). The mixture was stirred overnight at room temperature. Afterwards, solvent was evaporated under reduced pressure and the crude product was purified by chromatography on silica gel (see below).



(*E/Z*)-*N*'-phenylbenzohydrazonoyl chloride **2a**: Compound **2a** was obtained according to literature procedure.[2]



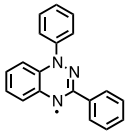
(*E/Z*)-*N*'-(4-methoxyphenyl)benzohydrazonoyl chloride **2b**: Compound **2b** was obtained as a colorless solid, yield 62% following the general procedure (EtOAC/Hexane 1/30). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.94 (br, NH, 1H), 7.86 (d, *J*= 8.9 Hz, 2H), 7.31 (m, 2H), 7.16 (d, *J*= 7.7 Hz, 2H), 6.93 (d, *J*= 8.9 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 160.5, 143.6, 132.1, 132.0, 131.9, 129.3, 128.5, 128.4, 127.9, 127.1, 124.7, 120.8, 113.8, 113.3, 55.4. HR-ESI $C_{14}H_{13}N_2OCl$ $(M)^+$ calcd. 260.0716, found. 260.0717. IR (neat) $\tilde{\nu}$ = 3314, 1600, 1500, 1434, 1259, 1109, 940, 825, 754 cm^{-1}.

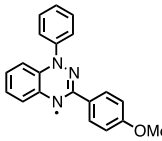


(*E/Z*)-*N*'-(4-cyanophenyl)benzohydrazonoyl chloride **2c**: Compound **2c** was obtained as a yellow solid, yield 96% following the general procedure (EtOAC/Hexane 1/30). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.21 (s, NH, 1H), 8.01 (d, *J*= 8.5 Hz, 2H), 7.68 (d, *J*= 8.6 Hz, 2H), 7.34 (dd, *J*= 8.6, 7.3 Hz, 2H), 7.24 (m, 2H), 7.01 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 142.5, 138.5, 132.2, 132.1, 132.1, 129.5, 128.6, 128.5, 126.5, 122.4, 122.1, 118.6, 113.7, 112.1. HR-ESI $C_{14}H_{10}N_3Cl$ $(M+Na)^+$ calcd. 278.0461, found 278.0454. IR (neat) $\tilde{\nu}$ = 3288, 2219, 1601, 1544, 1495, 1237, 1164, 947, 833, 736 cm^{-1}.

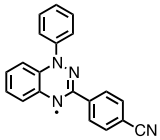
General procedure for the preparation of benzo-1,2,4-triazinyl radical 3(a-c)

Benzo-1,2,4-triazinyl radical 3(a-c) was prepared following a modified literature procedure.[3] A solution of 2a (1.50 g, 5.70 mmol), aniline (0.57 mL, 6.27 mmol) and TEA (1.20 mL, 8.65 mmol) in 25 mL benzene was refluxed overnight. The solvent was removed under reduced pressure and the mixture was diluted with CH_2Cl_2 before extracting with 50 mL cold water. The organic phase was then washed with brine and dried over $MgSO_4$ before concentration under reduced pressure. The residue was treated with Pd/C (9.5 mg, 1.6 mol%) and 1,8-Diazabicycloundec-7-ene (DBU) (0.8 mL) in CH_2Cl_2 (50 mL). The reaction mixture was stirred in air at room temperature for 3 h until TLC showed the presence of a new fast running brown compound (CH_2Cl_2/hexane 1/1). The solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (ethyl acetate/hexane 5/95) to give **3a** as a black solid.


1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl **3a**: black solid, yield 36%. HRMS $C_{19}H_{14}N_3$ $(M)^+$ calcd. 284.1188, found 284.1175.



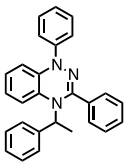
1-Phenyl-3-(4-methoxyphenyl)-1,2,4-benzotriazin-4-yl **3b**: black solid, yield 50%. HRMS $C_{20}H_{17}N_3O$ $(M+H)^+$ calcd. 315.1372, found 315.1359. IR (neat) $\tilde{\nu}$ = 1606, 1479, 1390, 1247, 1167, 1026, 837, 753.



1-Phenyl-3-(4-cyanophenyl)-1,2,4-benzotriazin-4-yl **3c**: dark green solid, yield 36%. HRMS $C_{20}H_{13}N_4$ $(M)^+$ calcd. 309.1140, found 309.1130. IR (neat) $\tilde{\nu}$ = 3044, 2227, 1592, 1482, 1385, 1207, 1079, 858, 735 cm^{-1}.

General procedure for the preparation of triazine unimolecular initiators 4(a-c)

A solution of benzene (20 mL) was sparged with argon for 30 minutes. CuBr (2.6 mmol, 0.37 g), PMDETA (5.2 mmol, 1.09 mL), and Cu(0) (2.6 mmol, 0.17 g) were placed into a schlenk flask which was subsequently evacuated and backfilled with argon three times. **3a** (1.75 mmol, 500 mg) and 1-bromoethylbenzene (1.5 equiv., 2.6 mmol, 0.36 mL) were diluted with 10 mL of degassed benzene and transferred to the schlenk flask. The reaction mixture was stirred at room temperature for 24 h. The solution was then filtered, diluted with CH_2Cl_2 (50 mL), and washed with deionized water (3 x 50 mL) to remove the copper complex. The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (ethyl acetate/hexane 5/95) to give **4a** as a yellow powder.



1,3-diphenyl-4-(1-phenylethyl)-1,4-dihydro-1,2,4-benzotriazine **4a**: yellow powder yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.91 (m, 2H), 7.40 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.24 (m, 3H), 7.19 (m, 4H), 7.13 (m, 1H), 6.84 (m, 2H), 6.75 (m, 1H), 6.52 (d, *J* = 5.0 Hz, 1H), 4.66 (q, *J* = 7.0 Hz, 1H), 1.75 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 149.4, 144.0, 143.3, 141.5, 134.5, 130.4, 129.3, 128.8, 128.4, 127.9, 127.6, 127.6, 127.5, 125.1, 124.5, 124.4, 123.3, 122.5, 111.9, 61.2, 19.7. HR-ESI: $C_{27}H_{23}N_3$ $(M)^+$ calcd. 389.1892, found 389.1900. IR (neat) $\tilde{\nu}$ = 2982, 1586, 1486, 1293, 1053, 757 cm^{-1}.

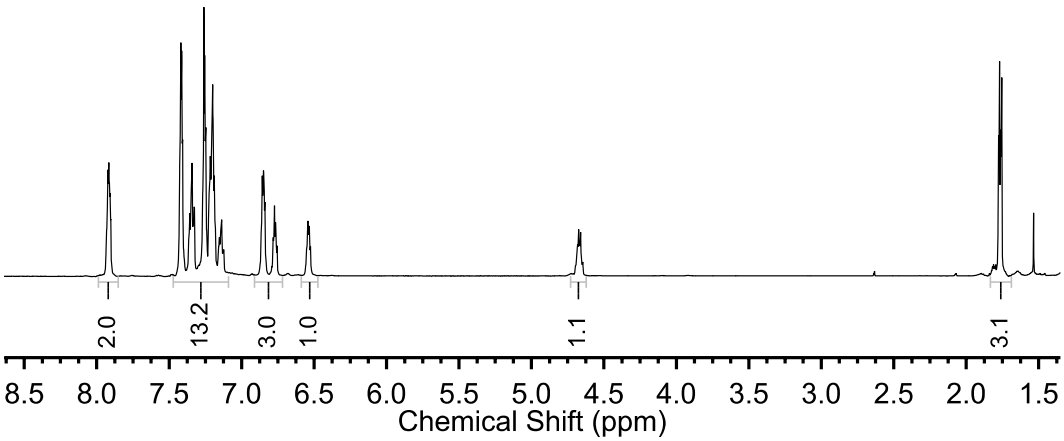


Figure S1. ^{1}H NMR spectrum of triazine unimolecular initiator **4a**

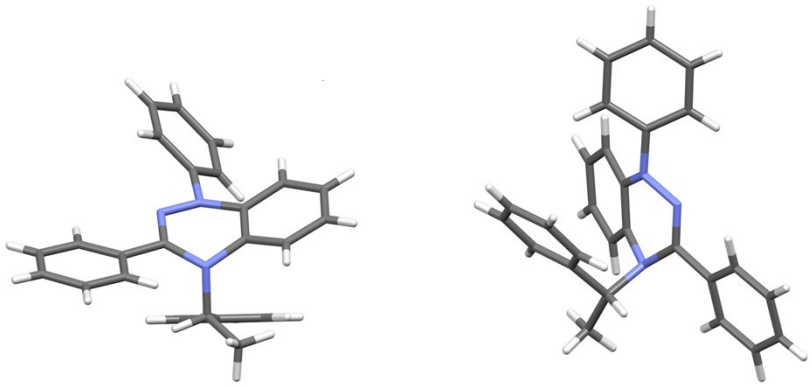
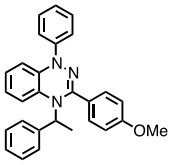


Figure S2. Crystal structure of triazine unimolecular initiator **4a** determined by X-ray crystallography.



1-Phenyl-3-(4-methoxyphenyl)-4-(1-phenylethyl)-1,4-dihydro-1,2,4-benzotriazine **4b**: yellow powder, yield 58%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.84 (d, *J* = 9.0 Hz, 2H), 7.32 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.24 (m, 3H), 7.19 (m, 4H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.94 (m, 2H), 6.83 (m, 2H), 6.74 (m, 1H), 6.53 (m, 1H), 4.68 (q, *J* = 7.1 Hz, 1H), 3.86 (s, 3H), 1.75 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 160.9, 150.2, 143.7, 143.3, 141.8, 130.9, 129.4, 129.3, 128.4, 127.9, 127.5, 126.2, 125.6, 124.7, 124.2, 123.1, 122.8, 114.5, 111.8, 60.8, 55.7, 20.4. HRMS $C_{28}H_{26}N_5O_3$ $(M+H)^+$ calcd. 420.2076, found 420.2057. IR (neat) $\tilde{\nu}$ = 2832, 1602, 1452, 1252, 1166, 1038, 841, 737 cm^{-1}.

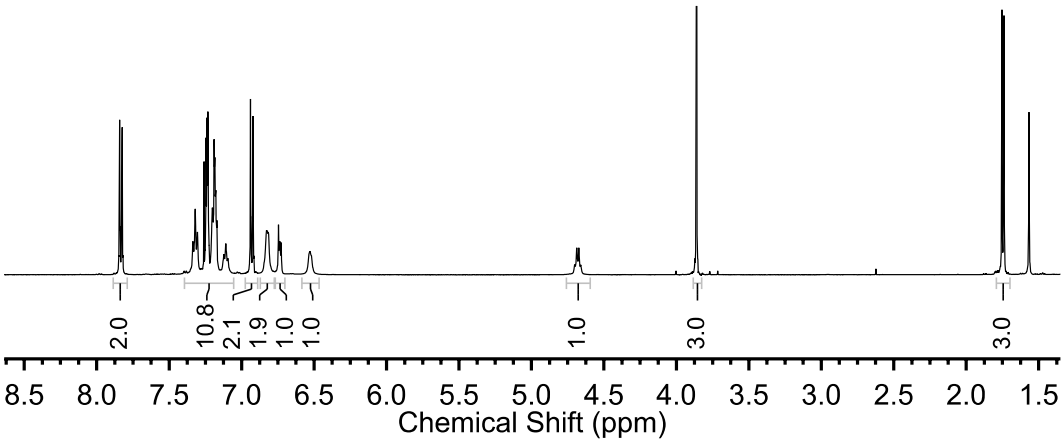
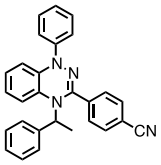


Figure S3. ^{1}H NMR spectrum of triazine unimolecular initiator **4b**



1-Phenyl-3-(4-cyanophenyl)-4-(1-phenylethyl)-1,4-dihydro-1,2,4-benzotriazine **4b**: orange powder, yield 71%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.99 (d, *J*= 8.4 Hz, 2H), 7.65 (d, *J*= 8.4 Hz, 2H), 7.33 (m, 2H), 7.28-7.14 (m, 4H), 7.12-7.04 (m, 4H), 6.96-6.81 (m, 3H), 6.48 (dd, *J*= 8.0, 1.4 Hz, 1H), 4.47 (q, *J*= 7.1 Hz, 1H), 1.73 (d, *J*= 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 146.2, 143.8, 142.7, 140.8, 139.6, 132.2, 129.5, 129.0, 128.0, 127.9, 127.6, 127.6, 125.6, 125.3, 125.3, 123.8, 123.3, 118.9, 112.2, 112.1, 62.4, 19.7. HRMS $C_{28}H_{22}N_4$ $(M+H)^+$ calcd. 415.1923, found 415.1906. IR (neat) $\tilde{\nu}$ = 2930, 2224, 1588, 1485, 1293, 846, 755 cm^{-1}.

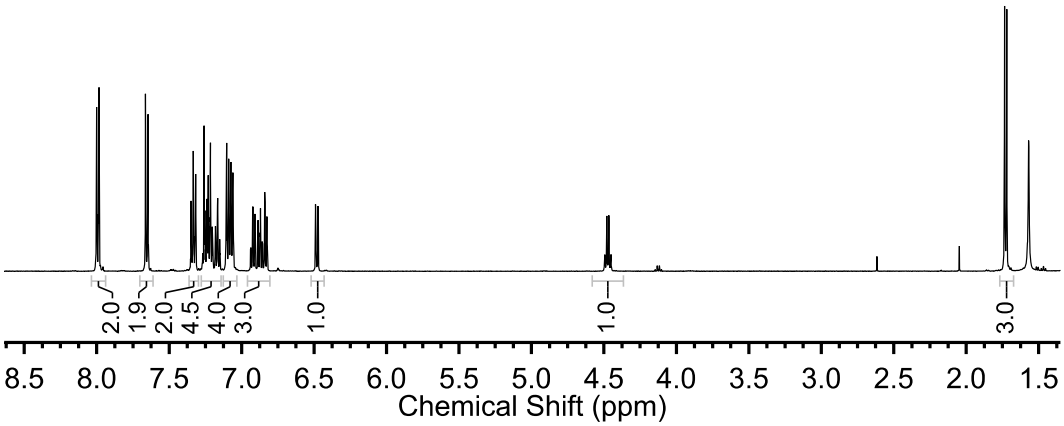


Figure S4. ^{1}H NMR spectrum of triazine unimolecular initiator **4c**

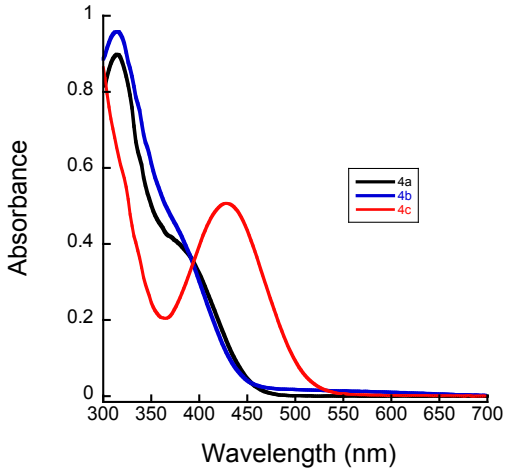


Figure S5. UV-vis spectra of triazine unimolecular initiators **4a-c** in CH_2Cl_2.

Polymerization

General procedure for styrene polymerization

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with desired triazine unimolecular initiator **4** (10 mg, 0.025 mmol, 1 equiv.) and styrene (0.74 mL, 6.4 mmol, 250 equiv.). The solution was degassed using three freeze-pump-thaw cycles. The vial was then backfilled with argon and stirred at 125 °C for 6 h. The reaction mixture was dissolved in dichloromethane (1 mL) and precipitated in MeOH. The resulting solid was dried, redissolved, and precipitated a second time into MeOH. After drying, the polymers were analyzed by SEC to give the number average M_n, M_w and dispersity (M_w/M_n) of the polymer.

Table S1. *Polymerization of styrene (250 equiv.) at 125 °C in bulk, and mediated by triazinyl radical* ***3(a-c)****.*

Entry	Time (h)	Conversion[c] (%)	M_n[a] (kg·mol^{-1})	M_{nth}[b] (kg·mol^{-1})	M_w/M_n
1) **3a**	5	< 5	nd	nd	nd
2) **3a**, **BPO (0.5 equiv.)**	1	-	-	-	-
	2	-	-	-	-
	3	14	4.2	3.6	1.16
	4	17	9.2	4.4	1.24
	5	23	11.2	5.9	1.35
	7	29	15.1	7.6	1.53
	9	31	16.0	8.0	1.65
	12	36	16.3	9.5	1.68
3) **3b**	5	< 5	nd	nd	nd
4) **3b, BPO (0.5 equiv.)**	7	19	11.8	7.1	1.44
2) **3c**	1	-	-	-	-
	3	-	-	-	-
	5	3	2.6		1.08
	7	12	5.4	0.8	1.14
	9	20	7.8	3.0	1.33
	11	22	7.7	5.3	1.42
	13	22	7.9	5.8	1.53
				5.8	
3) **3c**, **BPO (0.5 equiv.)**	1	-	-	-	-
	2	-	-	-	-
	3	-	-	-	-
	5	7	5.4	1.8	1.17
	7	12	8.3	3.1	1.44
	10	15	9.1	4.0	1.54
	12	20	10.0	5.2	1.61

a) Determined by SEC analysis, b) theoretical molecular weight calculated on the basis of monomer conversion, c) conversion determined by ^{1}H NMR, nd = not determined.

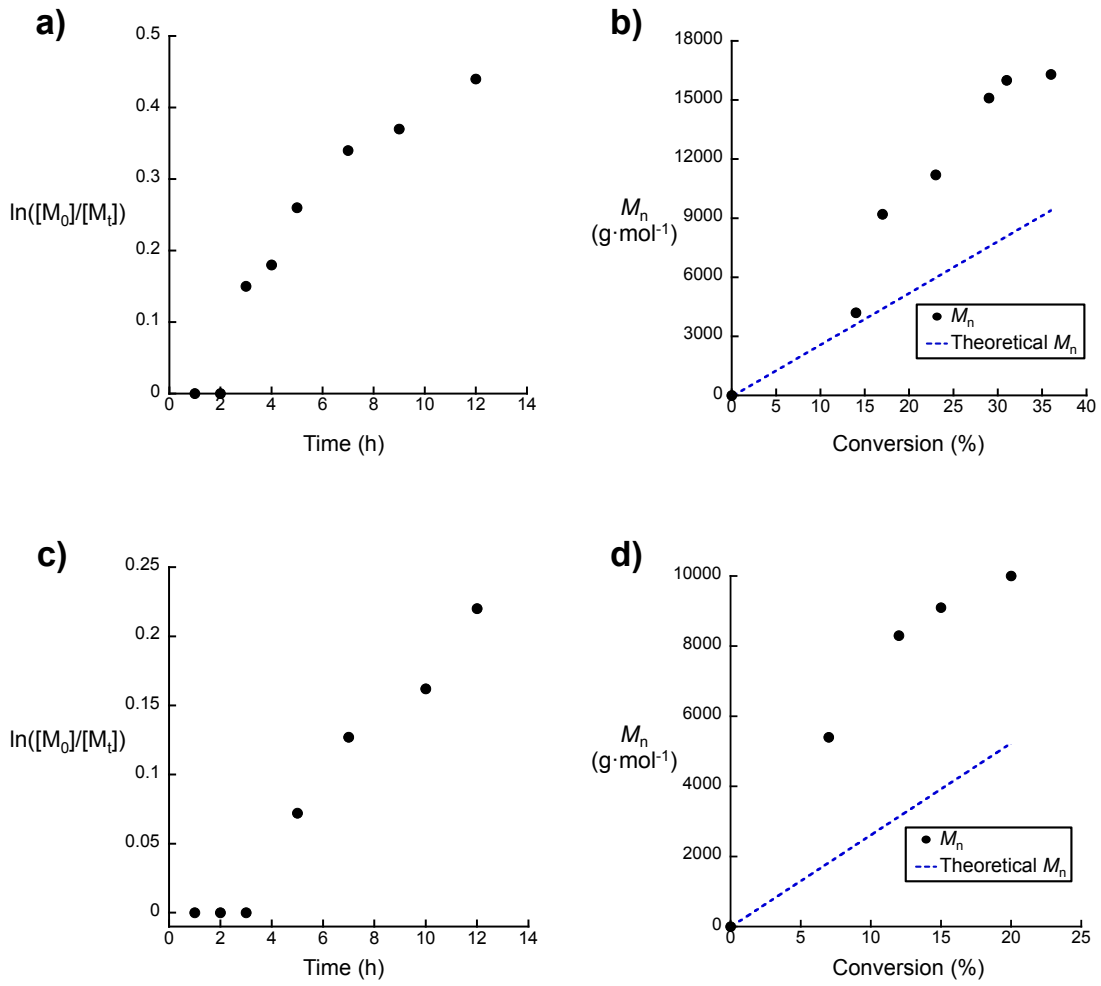


Figure S6. a) Kinetic plot $\ln([M_0]/[M_t])$ vs. time for bulk polymerization of styrene at 125 °C with triazinyl radical **3a** (●) and BPO (0.5 equiv.). b) Evolution of molecular weight (M_n) **3a** (●) versus conversion for triazine mediated polymerization. c) Kinetic plot $\ln([M_0]/[M_t])$ vs. time for bulk polymerization of styrene at 125 °C in the presence of triazinyl radical **3c** and BPO (0.5 equiv.) (●); d) Evolution of molecular weight (M_n) **3c** (●) versus conversion for triazine mediated polymerization.

Table S2. *Bulk polymerization of styrene (250 equiv.) at 125 °C, and mediated by triazine unimolecular initiator* ***4(a-c)****.*

Entry	Time (h)	Conversion[c] (%)	M_n[a] (kg·mol^{-1})	M_{nth}[b] (kg·mol^{-1})	M_w/M_n
1) **4a**	1	23	5.4	6.0	1.15
	2	33	8.3	8.7	1.15
	4	50	14.8	13.0	1.18
	8	67	20.4	17.4	1.23
2) **4b**	2	15	2.3	3.9	1.20
	4	27	6.3	7.0	1.14
	6	49	10.8	12.8	1.17
	8	58	13.4	15.1	1.21
3) **4c**	2	21	5.3	5.6	1.15
	4	39	8.0	10.1	1.16
	6	47	10.0	12.2	1.21
	8	52	11.1	13.5	1.28
4) **4a**[d]	6	21	5.4	5.3	1.25

a) Determined by SEC analysis, b) theoretical molecular weight calculated on the basis of monomer conversion, c) conversion determined by ^{1}H NMR d) reaction run at 110 °C using 240 equiv. of styrene to **4a**.

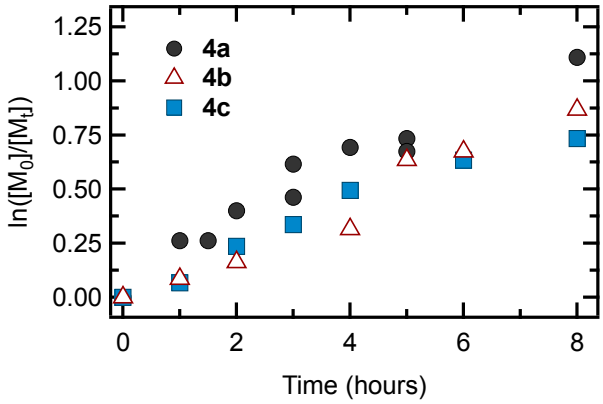


Figure S7. Kinetic plot ln([M_0]/[M_t]) versus time for the bulk polymerization of styrene at 125 °C with triazine unimolecular initiators 4a, 4b, and 4c.

Table S3. *Polymerization of Styrene targeted at different molecular weights, 125 °C, 8 h, mediated by triazine unimolecular initiator* ***4a.***

Entry	$[Sty]_0/[\mathbf{4a}]_0$	Conversion[c] (%)	M_n[a] (kg·mol^{-1})	M_{nth}[b] (kg·mol^{-1})	M_w/M_n
1	25/1	54	1.5	1.4	1.24
2	50/1	65	3.1	3.4	1.18
3	100/1	67	5.3	7.0	1.17
4	250/1	67	17.4	20.4	1.23
5	400/1	67	20.5	28.5	1.19
3	600/1	67	35.1	42.3	1.20
4	1000/1*	50	49.5	52.0	1.40

a) Determined by SEC analysis, b) theoretical molecular weight calculated on the basis of monomer conversion, c) conversion determined by ^{1}H NMR (* in 50% v/v NMP)

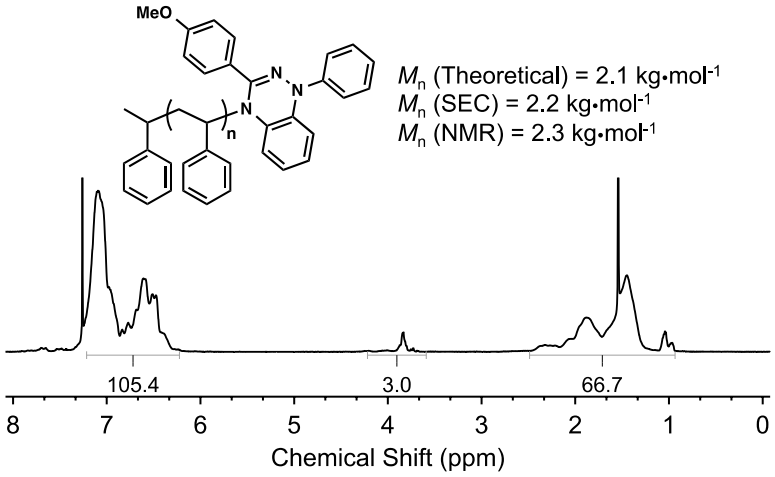


Figure S8. ^{1}H NMR spectrum of polystyrene synthesized with triazine unimolecular initiator **4b**.

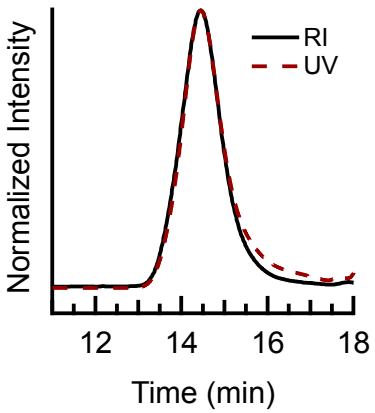


Figure S9. Overlaid refractive index (solid black line) and UV detector (350 nm, dashed red line) SEC traces of polystyrene terminated with triazine unimolecular initiator **4a**, M_n = 5.5 kg·mol^{-1}, M_w/M_n = 1.13. Please note the UV trace has been shifted by 14 seconds to account for the detector offset.

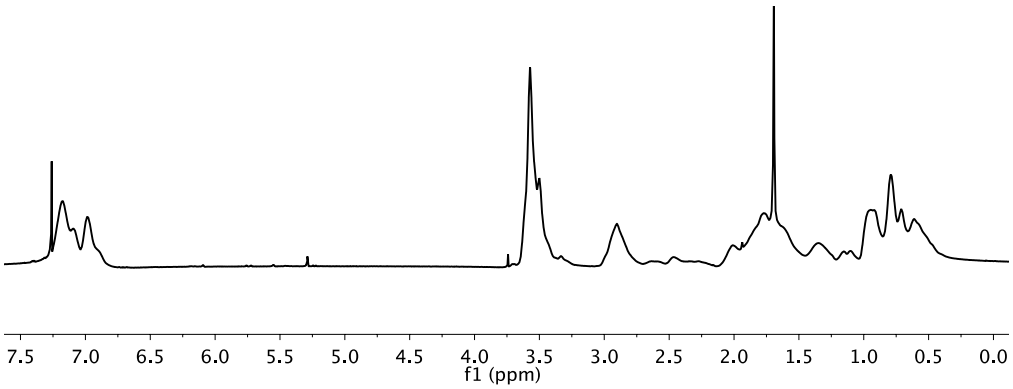


Figure S10. ^{1}H NMR spectrum of PS-*r*-PMMA (monomer ratio = 20:80 styrene:methyl methacrylate).

References

1 L. Li, L. Zhu, D. Chen, X. Hu and R. Wang, *Eur. J. Org. Chem.*, **2011**, *14*, 2692–2696.
2 C.-Y. Zhang, X.-H. Liu, B.-L. Wang, S.-H. Wang and Z.-M. Li, *Chem. Biol. Drug Des.*, **2010**, *75*, 489–493.
3 P. Koutentis and D. Lo Re, *Synthesis*, **2010**, 2075–2079.