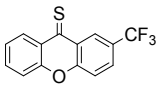
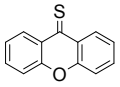
Supporting Information for

Aromatic Thioketones-Mediated Radical Polymerization of Methacrylates and the Preparation of Amphiphilic Quasi-Block Copolymer



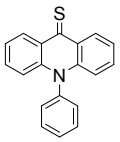
2-Trifluoromethyl-9*H*-xanthene-9-thione (TfXT)

Dark brown crystal. ^{1}H NMR (Acetone-d_6/TMS, 600 MHz): δ = 8.89 (s, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.7 Hz, 1H), 7.94 (dd, J = 8.5, 7.2 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.50-7.46 (m, 1H). ^{13}C NMR (Acetone-d_6/TMS, 151 MHz): δ = 204.88, 153.21, 151.16, 137.07, 131.91, 130.10, 129.65, 128.90, 127.6 (q), 126.60, 125.76, 123.96, 121.26, 119.47; IR (KBr): 3033, 1604, 1455, 1298, 1211, 1178, 1146, 1117, 831, 656 cm^{-1}. ESI-MS m/z of $[M+H]^+$ calculated for $C_{14}H_7F_3OS$: 281.0242; Found: 281.0259. UV-Vis ($CHCl_3$) absorption peaks: 239, 308, 405 nm.



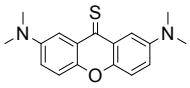
9*H*-xanthene-9-thione (XT)

XT: Dark brown crystal. ^{1}H NMR (Acetone-d_6/TMS, 600 MHz): δ = 8.69 (d, J= 8.2 Hz, 2H), 7.92 (dd, J = 8.3, 7.1 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.47 (dd, J = 8.2, 7.1 Hz, 2H); ^{13}C NMR (Acetone-d_6/TMS, 151 MHz): δ = 205.84, 151.43, 136.42, 130.24, 129.66, 125.92, 119.41; IR (KBr): 3061, 1593, 1445, 1319, 1240, 1214, 763, 744 cm^{-1}; ESI-MS m/z of $[M+H]^+$ calculated for $C_{13}H_8OS$: 213.0369; Found: 213.0376. UV-Vis ($CHCl_3$) absorption peaks: 236, 304, 406 nm.



10-Phenylacridine-9(10H)-thione (*N*-PhAT)

Dark reddish brown crystal. ^{1}H NMR (Acetone-d_6/TMS, 400 MHz): δ = 9.13 (d, J = 8.4 Hz, 2H), 7.89-7.76 (m, 3H), 7.67 (dd, J = 8.6, 6.9 Hz, 2H), 7.62 (d, J = 7.3 Hz, 2H), 7.38 (dd, J = 8.6, 6.6 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H). ^{13}C NMR (Acetone-d_6/TMS, 101 MHz): δ = 206.12, 139.77, 139.21, 134.55, 132.14, 131.69, 131.13, 130.95, 130.68, 123.90, 118.91. ESI-MS m/z of $[M+H]^+$ calculated for $C_{19}H_{13}NS$: 288.0841; Found: 288.0858. UV-Vis ($CHCl_3$) absorption peaks: 292, 457, 486 nm.



2,7-Bis(dimethylamino)-9*H*-xanthene-9-thione (BDMAXT)

Dark reddish brown crystal. ^{1}H NMR (Acetone-d_6/TMS, 600 MHz): δ = 7.88 (m, 2H), 7.50-7.49 (m, 4H), 3.05 (s, 12H). ^{13}C NMR (Acetone-d_6/TMS, 151 MHz): δ = 202.37, 148.85, 144.21, 129.68, 123.31, 119.79, 109.40, 40.94. IR (KBr): 3068, 2891, 2798, 1608, 1489, 1439, 1217, 926, 669 cm^{-1}. ESI-MS m/z of $[M+H]^+$ calculated for $C_{17}H_{18}N_2OS$: 299.1213; Found: 299.1219. UV-Vis ($CHCl_3$) absorption peaks: 251, 284, 309, 372, 452, 532 nm.

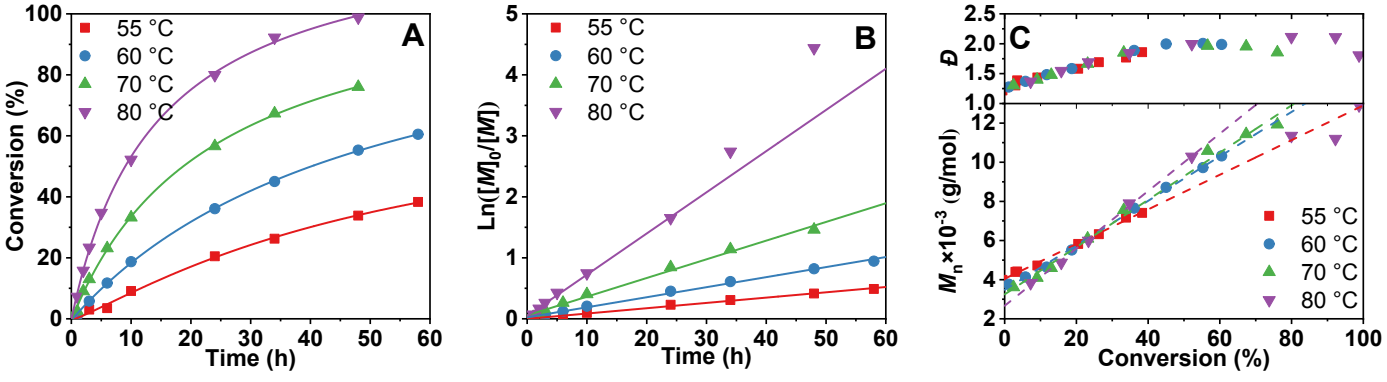


Fig. S1. Results of the polymerization of MMA mediated by TfXT with ABVN/TfXT = 1/2 in toluene at different temperatures: Plots of MMA conversion *vs.* time (A), polymerization kinetics (B), and plots of M_n & $Đ$ *vs.* conversion of MMA. Concentration of MMA: 30 wt%; MMA/ABVN = 100/1.

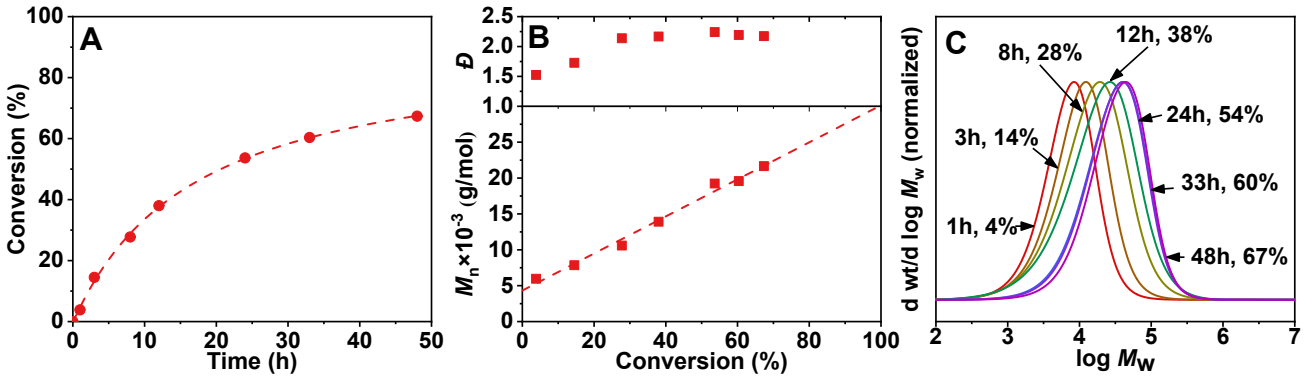


Fig. S2. Results of the polymerization of *t*BMA mediated by TfXT in toluene at 65 °C: plots of conversion of *t*BMA *vs.* time (A), plots of M_n & $Đ$ *vs.* conversion of *t*BMA (B) and GPC-derived differential molecular weight distribution curves (C). Concentration of *t*BMA: 30 wt%; *t*BMA/ABVN/TfXT = 200/1/5.

Table S1. Comparison of Theoretical to experimental *m/z* values with *m/z* errors of peaks Series I in Fig. 3A

n	m/z_{exp}	m/z_{theo}	Molecular formula	m/z_{exp}-m/z_{theo}
0	518.2415	518.2447	$C_{28}H_{31}F_3N_2OS \cdot NH_4^+$	-0.0032
1	618.2976	618.2972	$C_{33}H_{39}F_3N_2O_3S \cdot NH_4^+$	0.0004
2	718.3506	718.3496	$C_{38}H_{49}F_3N_2O_5S \cdot NH_4^+$	0.0010
3	818.4042	818.4020	$C_{43}H_{45}F_3N_2O_7S \cdot NH_4^+$	0.0022
4	918.4582	918.4545	$C_{48}H_{63}F_3N_2O_9S \cdot NH_4^+$	0.0037
5	1018.5142	1018.5069	$C_{53}H_{71}F_3N_2O_{11}S \cdot NH_4^+$	0.0073
6	1118.5662	1118.5593	$C_{58}H_{79}F_3N_2O_{13}S \cdot NH_4^+$	0.0069
7	1218.6157	1218.6118	$C_{63}H_{87}F_3N_2O_{15}S \cdot NH_4^+$	0.0039
8	1318.6844	1318.6642	$C_{68}H_{95}F_3N_2O_{17}S \cdot NH_4^+$	0.0202
9	1418.7417	1418.7166	$C_{73}H_{103}F_3N_2O_{19}S \cdot NH_4^+$	0.0251
10	1518.7953	1518.7690	$C_{78}H_{110}F_3N_2O_{21}S \cdot NH_4^+$	0.0263
11	1618.8470	1618.8215	$C_{83}H_{119}F_3N_2O_{23}S \cdot NH_4^+$	0.0255
12	1718.8984	1718.8739	$C_{88}H_{127}F_3N_2O_{25}S \cdot NH_4^+$	0.0245
13	1818.9503	1818.9263	$C_{93}H_{135}F_3N_2O_{27}S \cdot NH_4^+$	0.0240
14	1918.9984	1918.9788	$C_{98}H_{143}F_3N_2OS \cdot NH_4^+$	0.0196

Table S2. Comparison of Theoretical to experimental *m/z* values with *m/z* errors of peaks Series II in Fig. 3A

n	m/z_{exp}	m/z_{theo}	Molecular formula	m/z_{exp}-m/z_{theo}
0	358.1421	358.1413	$C_{21}H_{19}F_3NO_1^+$	0.0008
1	458.1948	458.1938	$C_{26}H_{27}F_3NO_3^+$	0.0010
2	558.2478	558.2462	$C_{31}H_{35}F_3NO_5^+$	0.0016
3	658.3011	658.2986	$C_{36}H_{43}F_3NO_7^+$	0.0025
4	758.3521	758.3510	$C_{41}H_{51}F_3NO_9^+$	0.0011
5	858.4042	858.4035	$C_{46}H_{59}F_3NO_{11}^+$	0.0007
6	958.4600	958.4559	$C_{51}H_{67}F_3NO_{13}^+$	0.0041
7	1058.5151	1058.5083	$C_{56}H_{75}F_3NO_{15}^+$	0.0068
8	1158.5618	1158.5608	$C_{61}H_{83}F_3NO_{17}^+$	0.0010
9	1258.6168	1258.6132	$C_{66}H_{91}F_3NO_{19}^+$	0.0036
10	1358.6807	1358.6656	$C_{71}H_{99}F_3NO_{21}^+$	0.0151
11	1458.7357	1458.7180	$C_{76}H_{107}F_3NO_{23}^+$	0.0177
12	1558.7733	1558.7705	$C_{81}H_{115}F_3NO_{25}^+$	0.0028