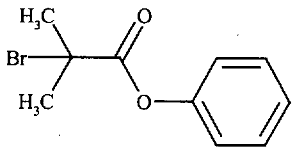
Supplementary Information

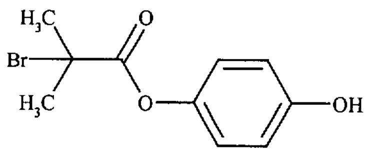
Synthesis of 2-bromo-2-methyl-propionic acid phenyl ester [1]



18.85 g (0.20 mol) of phenol was added to 400 mL of tetrahydrofuran (THF). The mixture was then stirred to allow complete dissolution of the phenol. 30.7 mL (0.22 mol) of triethylamine was added to the mixture followed by the slow addition of 27.2 mL bromoisobutyryl bromide (0.22 mol). The reaction created a exotherm and a white precipitate of triethylammonium bromide was formed. The reaction was allowed to stir at room temperature for 4 hours. Triethylammonium bromide was removed by filtration and the mixture was concentrated to give a slightly orange liquid. This was vacuum distilled at 70 °C and 0.06 Torr to give a colorless liquid. Yield = 37.7g (77.5%)

^{1}H NMR ($CDCl_3$, 298K, 250.13 MHz) δ 7.41 (t, *J* 7.6 Hz, 2 H), 7.25 (t, *J* 7.5 Hz, 1H), 7.13 (d, *J* 8.3 Hz, 2 H), 2.06 (s, 6 H) : ^{13}C {^{1}H} NMR ($CDCl_3$, 298K 100.6 MHz) δ 169.88 (C-3), 150.51 (C-4), 129.23 (C-5) , 125.88 (C-6) , 120.77 (C-7), 55.24 (C-2), 30.34 (C-1). IR (Liquid, ATR Cell,) 2977, 1749 (C=O), 1591, 1493, 1463, 1262, 1185, 1161, 1135, 1100, 1007, 938, 910, 742, 688. CI MS 263, 261, 244, 242, 151, 149, 135, 123, 121, 93. **Anal Calcd.** for $C_6H_{11}O_3$ Br: C = 49.41 , H= 4.56. **Found:** C = 49.26 , H = 4.52.
BRN 2519108
CAS 114397-50-1

Synthesis of 4-(2'-methyl-2'-bromopropanoate)phenol

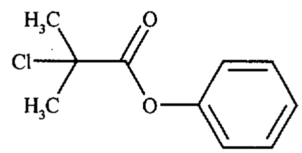


Hydroquinone 110.11 g (1.0 mol), tetrahydrofuran 800 mL and triethylamine 15.3 mL (0.11 mol) were placed in a 1 L round bottom and the flask was equipped with a pressure equilibrating dropping funnel. 2-Bromoisobutyryl bromide 12.4 mL (0.1 mol) and tetrahydrofuran 87.6 mL was placed into the dropping funnel. The 2-bromoisobut -yryl bromide solution was added dropwise over 2 hours with stirring which formed triethylammonium bromide and upon complete addition the reaction was stirred for 2 hours. The triethylammonium bromide was removed by filtration and the solvent was removed under reduced pressure. This resulted in a brown white crystalline mixture, which was placed into a round bottom flask with chloroform 600 mL and stirred overnight to separate the unreacted excess hydroquinone. The unreacted hydroquinone was removed from the solution by filtration and the filtrate was concentrated under reduced pressure to give a brown crystalline compound. The resulting brown crystalline solid was purified by column chromatography eluting with 100 % dichloromethane followed by 100 % methanol to give a pale brown crystalline solid. Yield = 18.5 g (71%), m.pt. 92.4 °C

^{1}H NMR ($CDCl_3$, 298K, 250.13 MHz) δ 6.98 (d, *J* 8.8 Hz, 2 H), 6.81 (d, *J* 9.1 Hz, 2 H), 4.84 (s, 1H), 2.04 (s, 6 H) : ^{13}C {^{1}H} NMR ($CDCl_3$, 298K 100.6 MHz) δ 171.56, 153.69, 143.85, 121.75, 116.13, 55.29, 30.49 : IR (Solid, ATR Cell) 3464 (O-H, br), 2982, 1736 (C=O), 1601, 1506, 1461, 1442, 1393, 1374, 1265, 1203, 1183, 1160, 1145, 1097, 1010, 950, 936, 879, 822, 777, 752 : Mass Spectrometry (+CI/NH_3) (m/z) 278, 276 (M+NH_3), 260, 258 (mass peaks) 199, 197, 180, 151, 135, 127, 110, 71 : Anal. Calcd for $C_{10}H_{11}BrO_3$: C = 46.36 , H = 4.28 . Found: C = 46.15, H = 4.25

Synthesis of phenyl 2'-chloro-2'-methyl propionate

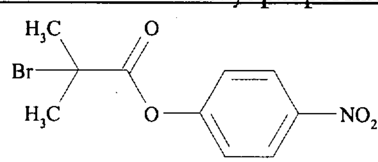
This compound had been prepared previously by Mc Elvain. [2]



Phenol 18.85 g (0.20 mol), tetrahydrofuran 400 mL and triethylamine 30.6 mL (0.22 mol) were placed in a 500 mL round bottom flask. Chloroisobutyryl chloride 26.4 mL (0.22 mol) was added slowly. The reaction was followed as in 7.2.3 and the triethylammonium chloride was removed by filtration and the solvent was removed under reduced pressure to give a slightly yellow/brown liquid. This was vacuum distilled at 58 °C and 0.2 Torr to give a colourless liquid Yield = 28.9 g (72.7 %)

^{1}H NMR ($CDCl_3$, 298K, 250.13 MHz) δ (t, *J* 7.6 Hz, 2 H), 7.26 (t, *J* 6.9 Hz, 1H), 7.13 (d, *J* 8.7 Hz, 2 H), 1.93 (s, 6 H) ; ^{13}C {^{1}H} NMR ($CDCl_3$, 298K 100.6 MHz) δ 169.40, 150.38, 129.09, 125.74, 120.74, 64.14, 29.09 ; IR (Liquid, ATR Cell,) 3044, 2985, 2936, 1754, 1591, 1456, 1389, 1371, 1265, 1186, 1161, 1140, 1107, 1070, 1006, 938, 911, 859, 745, 688 ; +EI MS (m/z) 200, 198 (mass peaks) 131, 94, 77, 65, 41
Anal Calcd. for $C_{10}H_{11}O_2Cl$: C = 60.46 , H= 5.58. **Found**: C = 60.36 , H = 5.58.

Synthesis of 4-Nitrophenyl 2'-bromo-2'-methyl propionate, 8 [3]



4-Nitrophenol (0.2 moles), triethylamine, 30.6 mL (0.22 moles) and THF 400 mL were placed in a 3 neck round bottomed flask. Bromoisobutyryl bromide 27.2 mL (0.22 moles) was added slowly with stirring. A white precipitate of triethylammonium bromide was formed. The mixture was left to react for 6 hours with stirring. On completion of the reaction triethylammonium bromide was removed by filtration and the THF was removed by rotary evaporation. This gave a light brown powder, which was recrystallized from methanol. Yield = 50.6 g (88 %), m.pt. = 85.5 °C

^{1}H NMR ($CDCl_3$, 298K, 250.13 MHz) δ 8.30(d, *J* 9.5 Hz, 2 H), 7.32 (d, *J* 9.2 Hz, 2 H), 2.07 (s, 6 H) : ^{13}C {^{1}H} NMR ($CDCl_3$, 298K 100.6 MHz) δ 169.23 , 155.28 , 145.53 , 125.17 , 121.98 , 54.73 , 30.30. IR (Solid ATR Cell) 2985, 1746 (C=O) (s),1617,1595 (N-O) (s), 1522, 1485, 1457, 1345, 1265, 1210, 1192, 1157, 1131, 1100, 1006, 936, 885, 863, 829, 744, 689,. Mass Spectrometry (+EI) (m/z) : 289, 287 (M+), 151, 149, 123, 121.

Anal Calcd. for $C_{10}H_{10}NO_4$ Br,: C = 41.69 , H = 3.50 , N = 4.86. **Found**: C = 41.68 , H = 3.50 , N = 4.70

2-Bromo-2-methyl-propionic acid 4-formyl-phenyl ester, 7.

Prepared as for compound **5**. The product was recovered as a yellow oily liquid that crystallized upon standing and was recrystallized twice from diethyl ether. Yield = 18.95 g (69.9 %), m. pt. 42.6 ^{0}C

^{1}H NMR ($CDCl_3$, 298K, 250.13 MHz) δ 10.00 (s, 1 H) (C<u>H</u>O), 7.94 (d, *J* 4.6 Hz 2 H), 7.31 (d, *J* 4.8 Hz 2 H), 2.06 (s, 6H); ^{13}C {^{1}H} NMR ($CDCl_3$, 298K 100.6 MHz) δ 190.59, 169.33, 155.08, 134.07, 131.02, 121.71, 54.94, 30.25; IR (Solid, ATR Cell) 2984, 2820, 2730, 1746 $\upsilon_{C=O}$, 1693 $\upsilon_{H\text{-}C=O}$, 1590, 1500, 1374, 1262, 1207, 1153, 1132, 1099, 1009, 932, 881, 808, 658 : EI MS (m/z) 273, 271 (mass peaks), 210, 193, 163, 151, 149, 140, 123, 121, 102; Anal Calcd. for $C_{11}H_{11}O_3$Br,: C = 48.73 , H = 4.09 ; Found: C = 48.63 , H = 4.03

2-Bromo-2-methyl-propionic acid 4-benzyloxy-phenyl ester, 9.

Prepared as for compound **5**. The product was recovered as an off white in colour and crystalline. The product was recrystallized from methanol : water (90 : 10) and dried to give a white crystalline product. Yield = 28.15 g (80.6 %), m.pt. 78.5°C.

^{1}H NMR ($CDCl_3$, 298K, 250.13 MHz) δ 7.44 – 7.32 (m, 5 H), 7.04 (d, *J* 9.1 Hz, 2 H), 6.97 (d, *J* 9.1 Hz 2 H), 5.05 (s, 2 H), 2.05 (s, 6 H) ; ^{13}C {^{1}H} NMR ($CDCl_3$, 298K 100.6 MHz) δ 170.52, 156.62, 144.4, 136.68, 128.56, 127.99, 127.41, 121.79, 115.46, 70.36, 55.40, 30.60 ; IR (Solid, ATR Cell) 3063, 2979, 1742 (C=O), 1594, 1453, 1385, 1246, 1183, 1135, 1101, 1015, 941, 873, 811, 781, 738. : EI MS 349, 348 (mass peaks), 151, 149, 121, 123 Anal. Calcd. for $C_{17}H_{17}BrO_3$: C = 58.47 , H = 4.91 , Found: C = 58.45 , H = 4.78.

Figure UV and DRI SEC chromatograms of PMMA initiated using, **2**

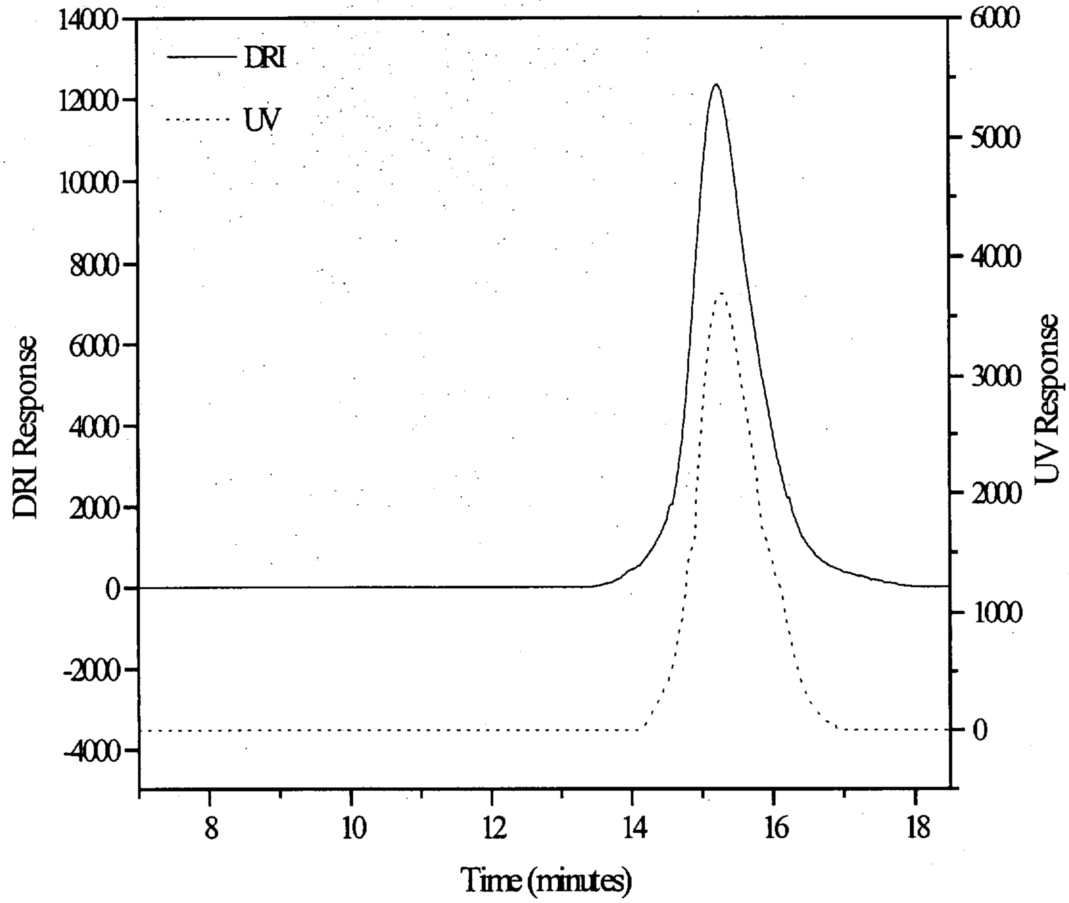
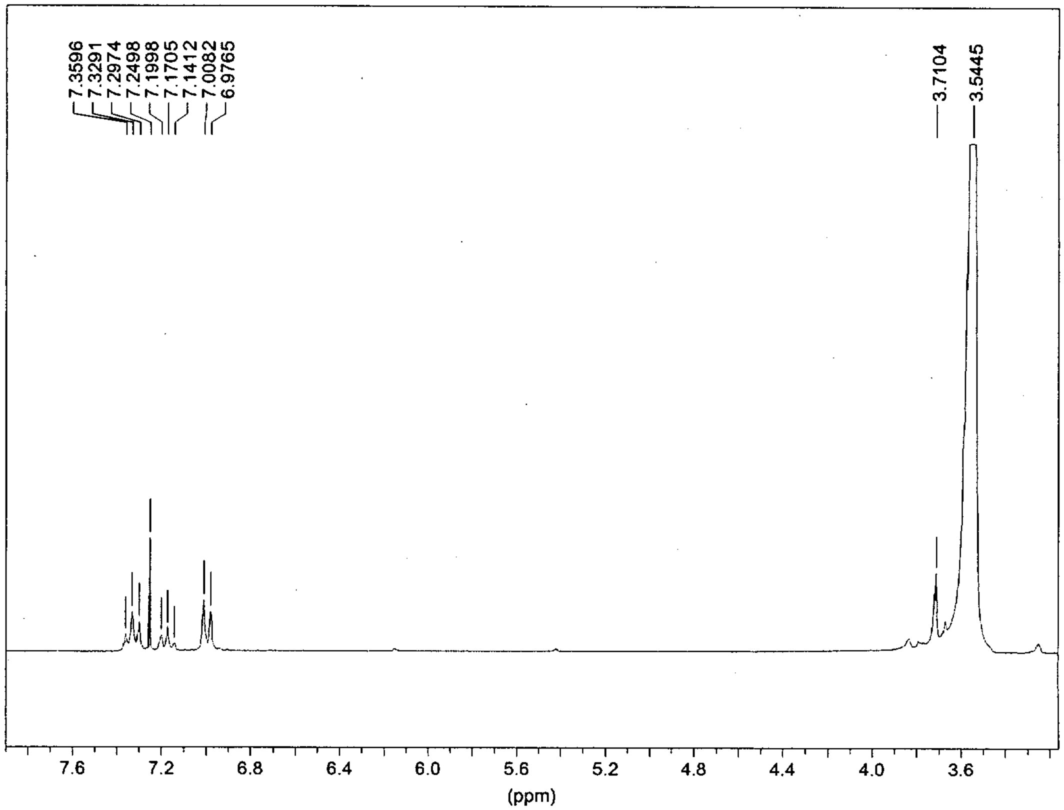


Figure Partial (3.2-7.9 ppm) 250MHz, ^{1}H NMR in $CDCl_3$ of PMMA initiated with, **2**



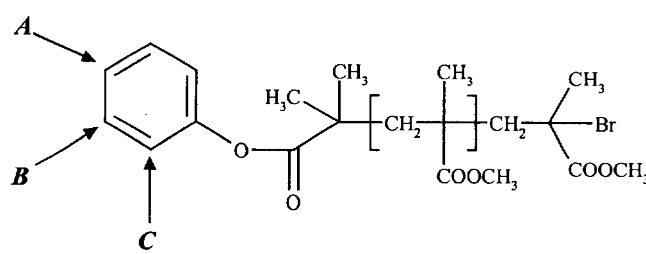
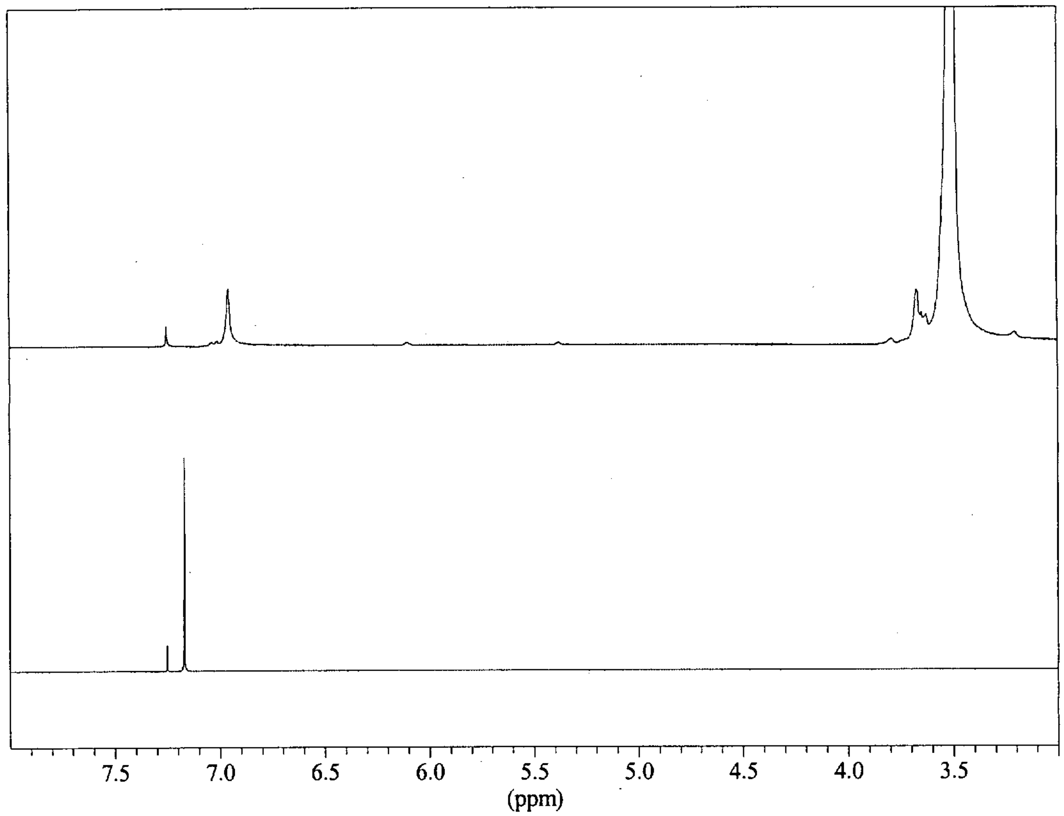


Figure Partial 250 MHz ^{1}H NMR (3.0-8.0 ppm) in $CDCl_3$ of PMMA initiated with **10**(top) and initiator **10** (bottom), small peak due to solvent.



MMA was polymerized under the conditions outlined in table 3-1 but the polymerization was terminated at 3600 s to produce a low M_n polymer to investigate if both initiator sites had reacted. The reaction was precipitated into petroleum ether and gave the NMR of the resulting polymer was obtained in $CDCl_3$. If the polymer was propagating from one site on some initiator molecules then it would be expected that the aromatic region should contain two doublets shifted slightly upfield as the protons on the aromatic ring are inequivalent. If however, initiation is taking place on both sites the signal pattern obtained should be one singlet-shifted upfield from its original position in initiator **10**.

From the above figure it is noted that the singlet in the initiator at 7.16 ppm has shifted upfield to 6.95 ppm in the polymer. This demonstrates that the polymerization occurs on both sites as any partial initiation would have resulted in the presence of two doublets, which are not observed.

Full polymerisation data sets

Table 1 Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**2**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2250	1.14	23.5	0.267
3600	3670	1.13	42.3	0.550
5400	4470	1.12	53.9	0.775
7200	5170	1.12	63.2	0.999
9000	5650	1.12	68.6	1.160
10800	6110	1.12	73.5	1.327
14400	6620	1.11	84.2	1.846
k_p [pol *] = 1.298 x 10^{-4} s^{-1}				

Table 2 Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**1**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	3030	1.14	15.9	0.174
3600	4080	1.16	27.9	0.327
5400	4660	1.18	38.1	0.480
7200	5260	1.17	47.7	0.649
9000	6000	1.17	56.1	0.822
10800	6650	1.17	64.7	1.041
14400	7290	1.18	76.9	1.466
k_p [pol *] = 9.66 x 10^{-5} s^{-1}				

Table 3. Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**3**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	1400	1.15	11.1	0.118
3600	2000	1.29	17.6	0.193
5400	2500	1.30	23.2	0.264
7200	3240	1.31	29.3	0.347
9000	3670	1.32	34.3	0.420
10800	4150	1.32	39.4	0.500
14400	5120	1.34	48.7	0.667
k_p [pol *] = 4.7 x 10^{-5} s^{-1}				

Table 4 Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**4**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2450	1.19	17.0	0.187
3600	3270	1.17	25.5	0.294
5400	3730	1.16	36.2	0.449
7200	4190	1.16	44.3	0.585
9000	4650	1.15	51.7	0.729
10800	4960	1.14	57.5	0.856
14400	5427	1.14	66.9	1.104
k_p [pol *] = 7.91 x 10^{-5} s^{-1}				

Table 5 Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**5**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2360	1.22	25.9	0.300
3600	3830	1.14	46.0	0.615
5400	4700	1.14	56.7	0.837
7200	5130	1.14	64.7	1.050
9000	5640	1.13	71.1	1.240
10800	5960	1.13	75.6	1.412
14400	6580	1.12	85.1	1.907
k_p [pol *] = 1.367 x 10^{-4} s^{-1}				

Table 6 Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**6**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2680	1.22	18.6	0.206
3600	4030	1.24	33.2	0.403
5400	5250	1.26	45.4	0.604
7200	6220	1.23	60.7	0.935
9000	7150	1.22	67.9	1.138
10800	8060	1.19	77.5	1.494
14400	9340	1.19	86.6	2.014
k_p [pol *] = 1.338 x 10^{-4} s^{-1}				

Table 7 Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**7**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	1940	1.09	20.3	0.227
3600	2656	1.10	30.8	0.368
5400	3589	1.09	40.0	0.512
7200	4525	1.07	52.0	0.733
9000	5429	1.08	61.0	0.942
10800	5948	1.08	68.1	1.142
14400	6436	1.10	76.7	1.456
k_p [pol *] = 1.027 x 10^{-4} s^{-1}				

Table 8 Polymerisation of MMA in xylene at 90 °C , [MMA]/[Cu(I)Br]/[**18**]/[**8**] = 100 : 1: 2 : 1

secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	1990	1.11	25.4	0.280
3600	3500	1.09	43.4	0.570
5400	4450	1.09	55.4	0.807
7200	4990	1.09	64.2	1.027
9000	5530	1.09	70.6	1.223
10800	5780	1.09	75.4	1.404
14400	6530	1.09	85.2	1.911
k_p [pol *] = 1.354 x 10^{-4} s^{-1}				

Table 9 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**][**9**] = 100 : 1: 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2280	1.14	26.7	0.311
3600	3660	1.11	44.7	0.592
5400	4590	1.10	56.3	0.828
7200	5110	1.10	64.0	1.022
9000	5650	1.10	69..0	1.170
10800	5850	1.10	74.6	1.372
14400	6710	1.10	82.2	1.729
k_p [pol *] = 1.290 x 10^{-4} s^{-1}				

Table 10 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**]/[**10**] = 100 : 1 : 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	3206	1.17	27.5	0.320
3600	4827	1.13	45.7	0.611
5400	5850	1.11	57.7	0.861
7200	6511	1.11	66.9	1.105
9000	7013	1.10	75.6	1.410
10800	7394	1.10	79.8	1.598
14400	7900	1.09	85.8	1.949
k_p [pol *] = 1.46 x 10^{-4} s^{-1}				

Table 11 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**]/[**10**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	3640	1.11	44.2	0.584
3600	4920	1.10	61.1	0.945
5400	5790	1.09	73.8	1.338
7200	6380	1.09	82.1	1.721
9000	6830	1.08	87.6	2.087
10800	7050	1.08	92.2	2.555
14400	7500	1.08	98.1	3.952
k_p [pol *] = 2.54 x 10^{-4} s^{-1}				

Table 12 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**]/[**10**] = 100 : 2 : 4 : 2

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2550	1.14	51.7	0.728
3600	3170	1.16	73.5	1.328
5400	3780	1.15	88.4	2.158
7200	4170	1.12	94.4	2.885
9000	4390	1.12	96.6	3.380
10800	4590	1.13	98.5	4.203
14400	4740	1.13	99.7	5.752
k_p [pol *] = 3.92 x 10^{-4} s^{-1}				

Table 13 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**]/[**11**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	4190	1.20	42.5	0.553
3600	5480	1.14	58.0	0.867
5400	6520	1.14	72.9	1.305
7200	7290	1.12	81.1	1.665
9000	7813	1.11	89.8	2.284
10800	8144	1.10	93.6	2.755
14400	8600	1.09	97.8	3.823
k_p [pol *] = 2.56 x 10^{-4} s^{-1}				

Table 14 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**]/[**12**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	3660	1.18	39.3	0.499
3600	5120	1.16	54.5	0.788
5400	6426	1.14	71.1	1.241
7200	7443	1.13	78.9	1.555
9000	7865	1.13	85.6	1.936
10800	8578	1.12	91.3	2.439
14400	8974	1.10	96.1	3.242
k_p [pol *] = 2.23 x 10^{-4} s^{-1}				

Table 15 Polymerisation of EMA in xylene at 90 °C, [EMA]/[Cu(I)Br]/[**18**]/[**10**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	3740	1.10	39.0	0.494
3600	5510	1.09	58.3	0.875
5400	6530	1.09	70.1	1.207
7200	7170	1.09	77.9	1.512
9000	7630	1.09	82.9	1.768
10800	8050	1.09	87.6	2.091
14400	8460	1.10	93.6	2.743
k_p [pol *] = 1.98 x 10^{-4} s^{-1}				

Table 16 Polymerisation of IPMA in xylene at 90 °C, [IPMA]/[Cu(I)Br]/[**18**]/[**10**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	2880	1.12	18.4	0.204
3600	3590	1.10	29.8	0.354
5400	4250	1.10	36.9	0.461
7200	4910	1.10	48.4	0.661
9000	5420	1.10	53.4	0.764
10800	5740	1.11	57.4	0.853
14400	6320	1.12	67.8	1.133
k_p [pol *] = 8.22 x 10^{-5} s^{-1}				

Table 17 Polymerisation of *t*-BMA in xylene at 90 °C, [*t*-BMA]/[Cu(I)Br]/[**18**]/[**10**] = 100 : 2 : 4 : 1

t/hrs	M_n	PDi	Conv %	ln([M]$_0$/[M])
0.5	4838	1.12	38.5	0.4859
1	6358	1.15	49.9	0.6929
1.5	6864	1.21	53.9	0.7764
2	7021	1.25	54.9	0.7959
2.5	7117	1.28	56.8	0.8402
3	7170	1.30	56.9	0.8409
4	7130	1.31	57.5	0.8557

Table 18 Polymerisation of n-BMA in xylene at 90 °C, [n-BMA]/[Cu(I)Br]/[**18**][**10**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	5770	1.14	56.5	0.833
3600	8050	1.12	79.3	1.576
5400	9170	1.12	89.7	2.269
7200	9930	1.12	95.8	3.168
9000	10210	1.13	97.8	3.818
10800	10420	1.14	99.0	4.654
14400	10790	1.15	99.8	6.250
k_p [pol *] = 4.32 x 10^{-4} s^{-1}				

Table 19 Polymerisation of *i*-BMA in xylene at 90 °C, [*i*-BMA]/[Cu(I)Br]/[**18**][**10**] = 100 : 2 : 4 : 1

t/hrs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	5360	1.13	53.6	0.768
3600	7550	1.13	75.8	1.417
5400	8600	1.12	86.4	1.998
7200	9220	1.13	92.8	2.631
9000	9810	1.13	96.6	3.393
10800	9870	1.12	98.6	4.234
14400	10370	1.13	99.7	5.730
k_p [pol *] = 3.88 x 10^{-4} s^{-1}				

Table 20 Polymerisation of BzMA in xylene at 90 °C, [BzMA]/[Cu(I)Br]/[**18**][**10**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	9590	1.21	87.1	2.048
3600	11440	1.13	98.6	4.251
5400	12780	1.11	99.8	6.336
k_p [pol *] = 1.17 x 10^{-3} s^{-1}				

Table 21 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Cl]/[**18**]/[**15**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	4010	1.37	21.3	0.240
3600	4640	1.45	33.3	0.405
5400	5610	1.42	46.9	0.634
7200	6290	1.38	57.0	0.845
9000	7089	1.36	68.1	1.144
10800	7540	1.30	75.5	1.405
14400	8350	1.21	84.6	1.869
k_p [pol *] = 1.270 x 10^{-4} s^{-1}				

Table 22. Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**]/[**13**] = 100 : 1 : 2 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	2710	1.10	22.1	0.250
3600	3700	1.13	34.9	0.429
5400	4770	1.11	47.0	0.635
7200	5670	1.10	58.5	0.879
9000	6230	1.09	64.9	1.048
10800	6750	1.10	71.8	1.266
14400	7220	1.09	80.6	1.642
k_p [pol *] = 1.165 x 10^{-4} s^{-1}				

Table 23 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Cl]/[**18**]/[**14**] = 100 : 1 : 2 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	3260	1.23	8.4	0.087
3600	4190	1.27	20.8	0.233
5400	5070	1.29	29.2	0.345
7200	5820	1.28	38.2	0.481
9000	6410	1.29	48.8	0.669
10800	6820	1.29	56.1	0.823
14400	7415	1.23	64.6	1.039
k_p [pol *] = 7.21 x 10^{-5} s^{-1}				

Table 24 Polymerisation of styrene in xylene 50% (v/v) at 110 °C, [STY]/[Cu(I)Br] /[**18**]/[**16**] = 100 : 3 : 6 : 1

t/secs	M_n	PDi	Conv %	ln([M]$_0$/[M])
1800	2180	1.09	21.5	0.242
3600	3090	1.11	33.8	0.413
5400	3680	1.11	39.3	0.499
7200	4500	1.14	45.2	0.602
10800	5850	1.15	56.5	0.833
14400	7054	1.15	68.2	1.146
18800	8340	1.17	78.9	1.558
21600	9710	1.17	82.8	1.761
25200	10350	1.24	89.8	2.280
28800	11000	1.28	91.7	2.490
k_p [pol *] = 8.58 x 10^{-5} s^{-1}				

Table 25 Polymerisation of styrene in xylene 50% (v/v) at 110 °C, [STY]/[Cu(I)Cl] /[**18**]/[**17**] = 100 : 3 : 6 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	3720	1.32	30.6	0.366
3600	4370	1.33	36.3	0.452
5400	4900	1.33	41.7	0.540
7200	5380	1.33	47.2	0.638
10800	6300	1.34	57.0	0.844
14400	7080	1.35	65.6	1.066
18800	7990	1.35	74.6	1.369
21600	8570	1.35	84.7	1.877
25200	9450	1.35	88.8	2.193
28800	9680	1.37	91.2	2.549
k_p [pol *] = 8.52 x 10^{-5} s^{-1}				

Table 26 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[**18**]/[**16**] = 100 : 3 : 6 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	5460	1.18	55.0	0.798
3600	7460	1.18	77.6	1.495
5400	8640	1.17	88.0	2.120
7200	8980	1.11	95.0	2.991
9000	9250	1.12	97.2	3.564
10800	9600	1.12	98.8	4.452
k_p [pol *] = 4.068 x 10^{-4} s^{-1}				

Table 27 Polymerisation of MMA in xylene at 90 °C, [MMA]/[Cu(I)Cl]/[**18**]/[**17**] = 100 : 3 : 6 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	5320	1.34	34.6	0.425
3600	7400	1.42	57.8	0.863
5400	7980	1.41	70.4	1.216
7200	8020	1.24	76.8	1.460
9000	8440	1.21	83.6	1.807
10800	8570	1.21	87.6	2.089
k_p [pol *] =2.028 x 10^{-4} s^{-1}				

Table 28 Polymerisation of styrene in xylene 50% (v/v) at 110 °C, [STY]/[Cu(I)Br]/[**18**]/[**1**] = 100 : 1 : 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	690	1.06	8.3	0.087
3600	880	1.07	10.3	0.109
5400	1040	1.09	12.3	0.132
7200	1230	1.10	15.3	0.166
10800	1570	1.10	23.2	0.264
14400	1950	1.10	29.5	0.350
18000	2380	1.10	32.1	0.387
21600	2510	1.10	36.4	0.452
25200	2840	1.11	41.4	0.534
28800	2870	1.12	44.2	0.584
k_p [pol *] = 2.14 x 10^{-5} s^{-1}				

Table 29 Polymerisation of styrene in xylene 50% (v/v) at 110 °C, [STY]/[Cu(I)Br]/[**18**]/[**10**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	1770	1.10	10.6	0.112
3600	2360	1.10	19.1	0.211
5400	2910	1.09	25.3	0.292
7200	3480	1.10	31.8	0.383
10800	4290	1.10	41.8	0.540
14400	4950	1.11	48.6	0.666
18800	5770	1.11	54.5	0.788
21600	6420	1.12	60.1	0.918
25200	6880	1.15	67.1	1.113
28800	7460	1.17	71.6	1.258
k_p [pol *] = 4.45 x 10^{-5} s^{-1}				

Table 30 Polymerisation of styrene in xylene 50% (v/v) at 110 °C, [STY]/[Cu(I)Cl] /[**17**]/[**14**] = 100 : 2 : 4 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	3040	1.47	18.2	0.200
3600	3430	1.47	24.5	0.280
5400	3760	1.48	33.7	0.411
7200	4080	1.47	37.4	0.469
10800	4690	1.46	48.3	0.660
14400	5360	1.45	55.8	0.816
18800	5850	1.44	62.9	0.991
21600	6320	1.44	70.0	1.203
25200	6890	1.44	76.3	1.441
28800	7150	1.44	81.9	1.709
k_p [pol *] = 5.80 x 10^{-5} s^{-1}				

Table 31 Polymerisation of styrene in xylene 50% (v/v) at 110 °C, [STY]/[Cu(I)Br] /[**18**]/[**16**] = 100 : 3 : 6 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2180	1.09	21.5	0.242
3600	3090	1.11	33.8	0.413
5400	3680	1.11	39.3	0.499
7200	4500	1.14	45.2	0.602
10800	5850	1.15	56.5	0.833
14400	7054	1.15	68.2	1.146
18800	8340	1.17	78.9	1.558
21600	9710	1.17	82.8	1.761
25200	10350	1.24	89.8	2.280
28800	11000	1.28	91.7	2.490
k_p [pol *] = 8.58 x 10^{-5} s^{-1}				

Table 32 Polymerisation of styrene in xylene 50% (v/v) at 110 °C, [STY]/[Cu(I)Cl] /[**18**]/[**17**] = 100 : 3 : 6 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	3720	1.32	30.6	0.366
3600	4370	1.33	36.3	0.452
5400	4900	1.33	41.7	0.540
7200	5380	1.33	47.2	0.638
10800	6300	1.34	57.0	0.844
14400	7080	1.35	65.6	1.066
18800	7990	1.35	74.6	1.369
21600	8570	1.35	84.7	1.877
25200	9450	1.35	88.8	2.193
28800	9680	1.37	91.2	2.549
k_p [pol *] = 8.52 x 10^{-5} s^{-1}				

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Table. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **10**.

	x	y	z	U(eq)
Br(1)	-5876.5(7)	5665.5(5)	-3143.7(3)	35(1)
C(11)	1167(8)	5865(5)	-682(3)	35(1)
C(12)	-719(7)	5349(5)	-943(3)	30(1)
C(13)	-1909(8)	4493(6)	-280(3)	37(1)
O(14)	-1500(6)	5794(3)	-1911(2)	33(1)
C(15)	-1549(6)	4777(4)	-2472(3)	24(1)
O(16)	-789(6)	3561(3)	-2212(2)	35(1)
C(17)	-2642(6)	5384(4)	-3460(3)	24(1)
C(18)	-1975(8)	6826(5)	-3914(3)	33(1)
C(19)	-2319(8)	4296(5)	-4120(3)	38(1)
Br(2)	5452.9(7)	-1176.4(5)	8323.4(4)	38(1)
C(21)	2175(7)	-502(4)	5333(3)	28(1)
C(22)	599(7)	59(4)	5934(3)	26(1)
C(23)	-1556(7)	555(4)	5614(3)	27(1)
O(24)	1124(5)	38(4)	6919(2)	33(1)
C(25)	2659(6)	874(4)	7110(3)	25(1)
O(26)	3428(5)	1720(3)	6501(2)	33(1)
C(27)	3290(6)	591(4)	8196(3)	26(1)
C(28)	1357(7)	274(5)	8867(3)	34(1)
C(29)	4485(8)	1777(5)	8452(3)	35(1)

Table. Selected bond lengths [A] and angles [deg] for **10**.

Br(1)-C(17)	1.997(4)
Br(2)-C(27)	1.994(4)
C(19)-C(17)-Br(1)	108.0(3)
C(18)-C(17)-Br(1)	107.7(3)
C(15)-C(17)-Br(1)	102.9(2)
C(29)-C(27)-Br(2)	108.7(3)
C(28)-C(27)-Br(2)	108.1(3)
C(25)-C(27)-Br(2)	102.2(3)

Table. Bond lengths [A] and angles [deg] for **10**.

Br(1)-C(17)	1.997(4)
C(11)-C(12)	1.373(6)
C(11)-C(13)#1	1.385(6)
C(12)-C(13)	1.382(6)
C(12)-O(14)	1.405(5)
C(13)-C(11)#1	1.385(6)
O(14)-C(15)	1.361(5)
C(15)-O(16)	1.194(5)
C(15)-C(17)	1.515(5)
C(17)-C(19)	1.507(6)
C(17)-C(18)	1.517(6)
Br(2)-C(27)	1.994(4)
C(21)-C(22)	1.388(6)
C(21)-C(23)#2	1.384(6)
C(22)-C(23)	1.378(6)
C(22)-O(24)	1.407(5)
C(23)-C(21)#2	1.384(6)
O(24)-C(25)	1.356(5)
C(25)-O(26)	1.198(5)
C(25)-C(27)	1.531(5)
C(27)-C(29)	1.516(6)
C(27)-C(28)	1.517(6)
C(12)-C(11)-C(13)#1	118.8(4)
C(11)-C(12)-C(13)	122.4(4)
C(11)-C(12)-O(14)	117.4(4)
C(13)-C(12)-O(14)	120.1(4)
C(12)-C(13)-C(11)#1	118.9(4)
C(15)-O(14)-C(12)	117.5(3)
O(16)-C(15)-O(14)	123.4(4)
O(16)-C(15)-C(17)	124.9(4)
O(14)-C(15)-C(17)	111.8(3)
C(19)-C(17)-C(18)	113.8(4)
C(19)-C(17)-C(15)	110.2(3)
C(18)-C(17)-C(15)	113.6(3)
C(19)-C(17)-Br(1)	108.0(3)
C(18)-C(17)-Br(1)	107.7(3)
C(15)-C(17)-Br(1)	102.9(2)
C(22)-C(21)-C(23)#2	118.8(4)
C(23)-C(22)-C(21)	121.8(4)
C(23)-C(22)-O(24)	117.8(4)
C(21)-C(22)-O(24)	120.3(4)
C(22)-C(23)-C(21)#2	119.4(4)
C(25)-O(24)-C(22)	117.4(3)
O(26)-C(25)-O(24)	124.0(4)
O(26)-C(25)-C(27)	124.5(4)
O(24)-C(25)-C(27)	111.4(3)
C(29)-C(27)-C(28)	112.3(4)
C(29)-C(27)-C(25)	111.1(3)
C(28)-C(27)-C(25)	113.9(3)
C(29)-C(27)-Br(2)	108.7(3)
C(28)-C(27)-Br(2)	108.1(3)
C(25)-C(27)-Br(2)	102.2(3)

Table. Anisotropic displacement parameters (A^2 x 10^3) for **10**.

	U11	U22	U33	U23	U13	U12
Br(1)	22(1)	50(1)	32(1)	-6(1)	0(1)	6(1)
C(11)	38(2)	41(2)	29(2)	-6(2)	0(2)	4(2)
C(12)	33(2)	31(2)	24(2)	-6(2)	-5(2)	1(2)
C(13)	35(2)	52(3)	26(2)	-6(2)	-6(2)	4(2)
O(14)	49(2)	29(2)	19(1)	-4(1)	-11(1)	2(1)
C(15)	22(2)	28(2)	21(2)	-3(1)	-2(1)	4(1)
O(16)	45(2)	26(2)	29(2)	-2(1)	-6(1)	6(1)
C(17)	21(2)	30(2)	22(2)	-4(2)	-2(1)	3(1)
C(18)	35(2)	35(2)	25(2)	6(2)	0(2)	8(2)
C(19)	42(3)	43(3)	30(2)	-16(2)	-2(2)	2(2)
Br(2)	32(1)	35(1)	44(1)	-6(1)	-2(1)	2(1)
C(21)	23(2)	28(2)	32(2)	-2(2)	-4(2)	8(2)
C(22)	30(2)	26(2)	23(2)	-3(2)	-1(2)	2(2)
C(23)	24(2)	30(2)	28(2)	-5(2)	2(2)	6(2)
O(24)	32(2)	47(2)	24(1)	-4(1)	0(1)	4(1)
C(25)	23(2)	30(2)	23(2)	-4(2)	0(1)	8(2)
O(26)	38(2)	38(2)	26(2)	0(1)	1(1)	8(1)
C(27)	21(2)	29(2)	27(2)	-5(2)	0(1)	2(2)
C(28)	28(2)	49(3)	22(2)	2(2)	3(2)	4(2)
C(29)	41(2)	34(2)	34(2)	-6(2)	-8(2)	3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for arm2.

	x	y	z	U(eq)
H(11A)	1948	6457	-1152	42
H(13A)	-3215	4155	-481	45
H(18A)	-365	6734	-4025	49
H(18B)	-2353	7503	-3472	49
H(18C)	-2776	7173	-4537	49
H(19A)	-720	4014	-4191	56
H(19B)	-2994	4709	-4762	56
H(19C)	-3031	3456	-3835	56
H(21A)	3651	-844	5567	33
H(23A)	-2607	930	6040	32
H(28A)	204	1100	8769	51
H(28B)	1888	77	9547	51
H(28C)	730	-558	8718	51
H(29A)	3450	2659	8374	53
H(29B)	5750	1921	8017	53
H(29C)	5028	1518	9130	53