Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

The influence of surface grafting on the growth rate of polymer chains **

*Chengjun Kang, Rowena Crockett, and Nicholas D. Spencer **

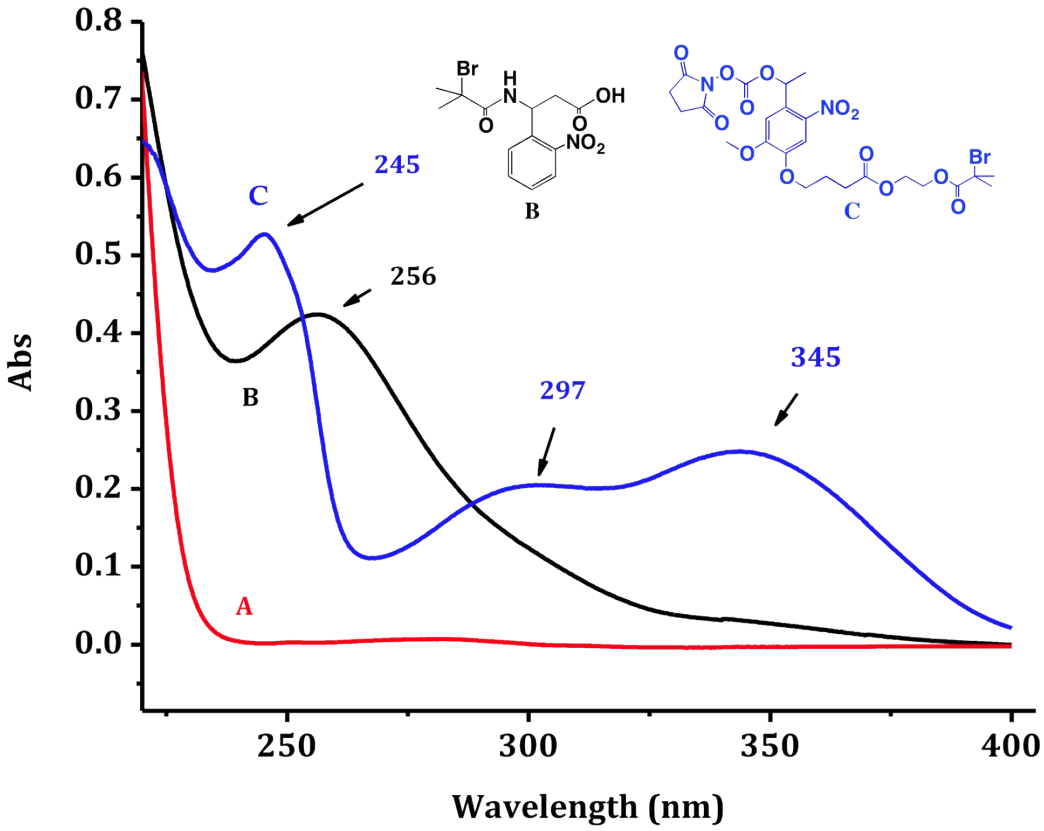

Figure S1. UV-Vis spectra of photo-cleavable initiator with THF as solvent. A is the UV-Vis spectrum of THF; B is the spectrum of the first-generation photo-cleavable initiator; C is the spectrum of the second-generation photo-cleavable initiator **7**. Compared to the first-generation initiator, two methoxyl groups have been introduced into **7** in the aromatic ring, which lead to a shift in the UV adsorption peaks from 256 nm to 345 nm.

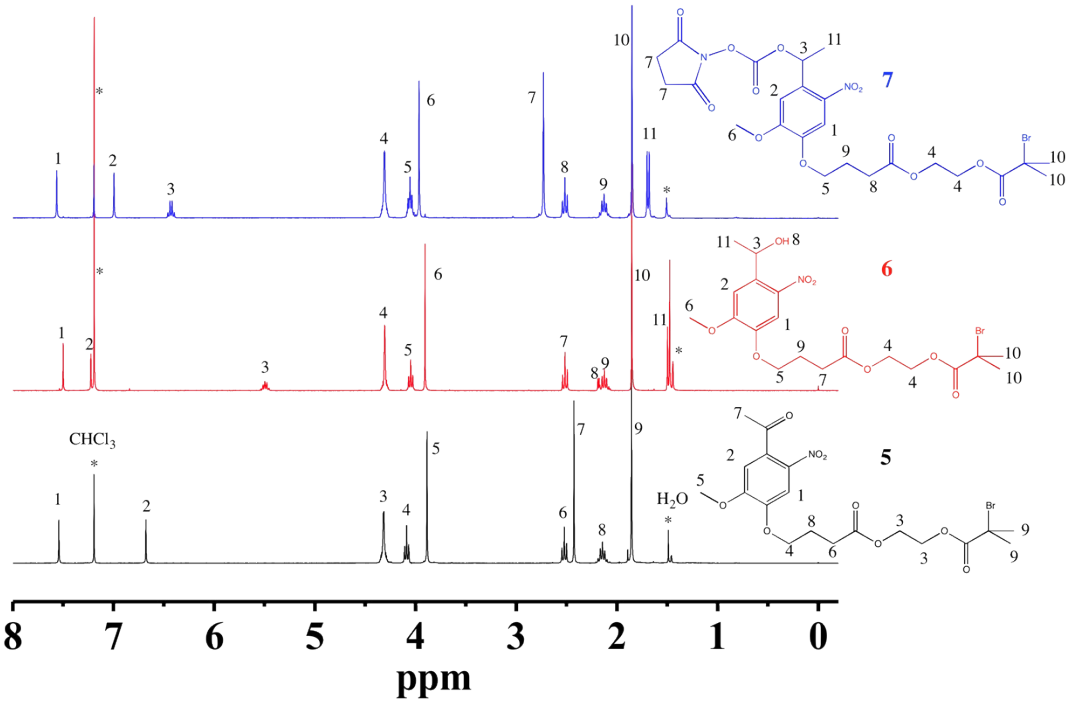

Figure S2 ^{1}H NMR spectra of newly synthesized compounds **5**, **6**, **7** corresponding to Scheme 1 in the manuscript.

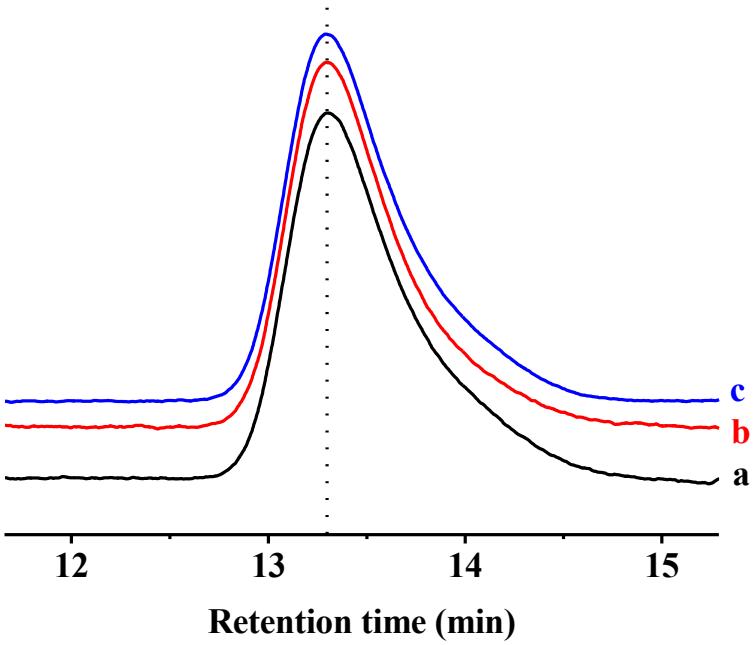

Figure S3 SEC measurements of PMMA in $CHCl_3$ with a concentration of 0.5 mg/ml: a: without UV illumination, b: after illumination at 366 nm for 3h, and c: ground powder of PMMA after illumination at 366 nm for 3h. There is no change in the molecular weight of the polymer following UV irradiation at 366 nm.

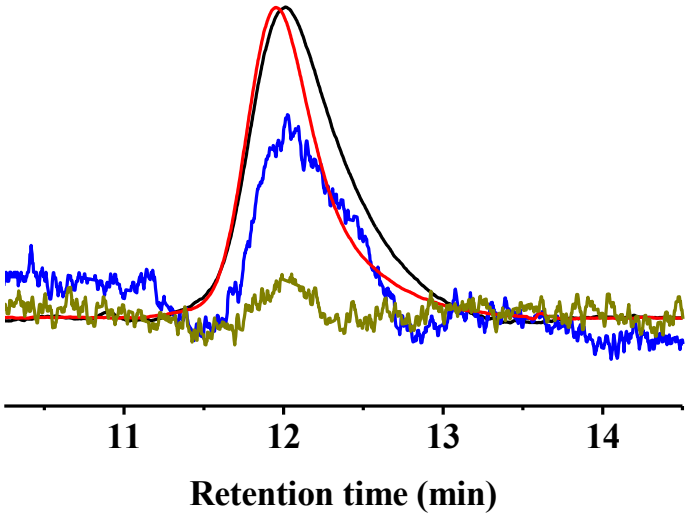

Figure S4

— RI signal of PMMA cleaved from substrates with a calculated concentration of 0.23mg/ml for SEC measurement.

— RI signal of PMMA generated in solution by free initiator ethyl 2-bromo-2-methylpropanoate with a concentration of 0.49mg/ml for SEC measurement.

— UV detector signal corresponding to surface-detached polymer.

— UV detector signal corresponding to solution-generated polymer.

From this figure, it is evident that the polymers detached from the surface have a much stronger UV adsorption signal than those generated in solution, although the surface detached polymer has a lower concentration. This indicates that the aromatic ring from the UV labile linker is attached at the end of surface-cleaved polymer.

The UV detector of the SEC is not as sensitive as the RI detector, therefore only the RI signal was used to calculated Mn and PDI.

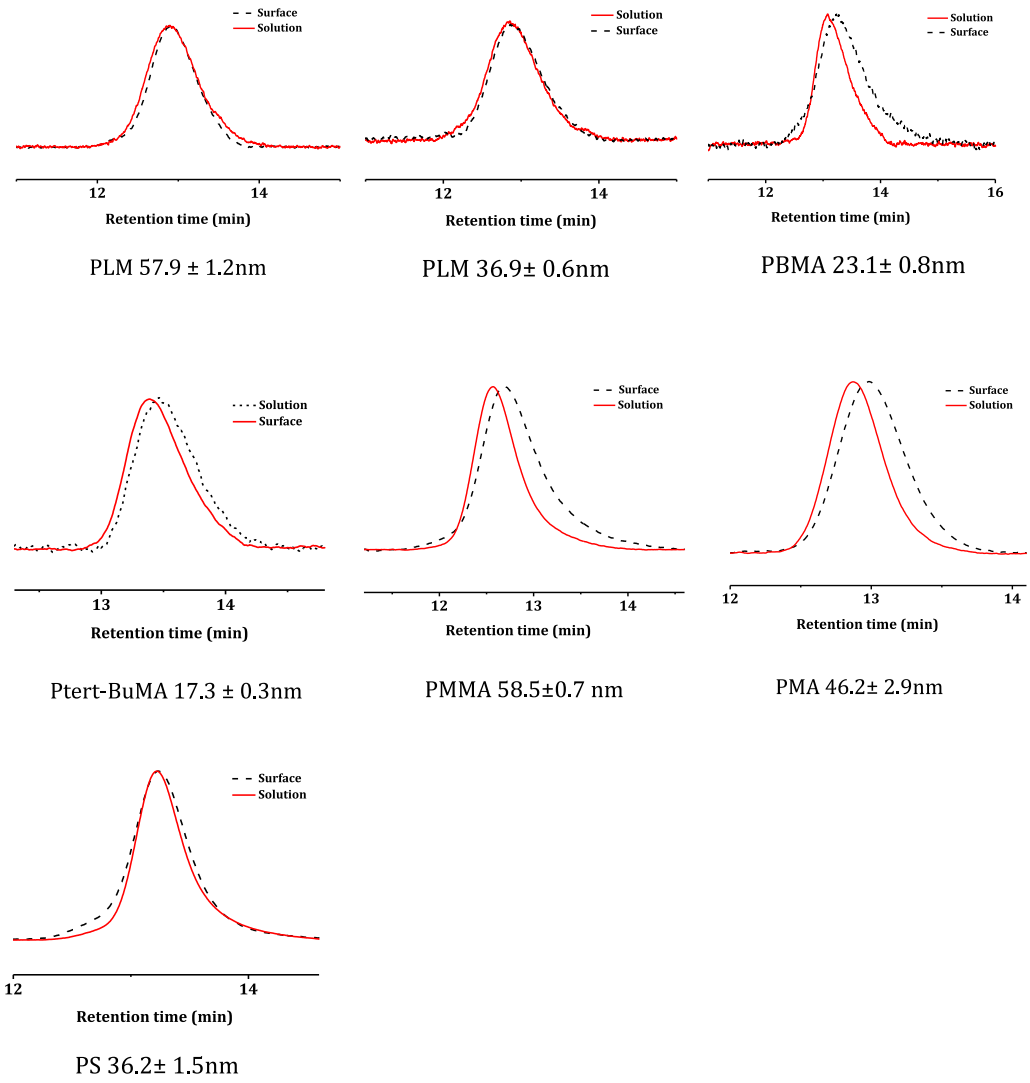

Figure S5. Typical SEC traces of different polymers generated both on the surface and in solution, showing the excellent S/N ratio obtainable, even from small-surface-area samples.

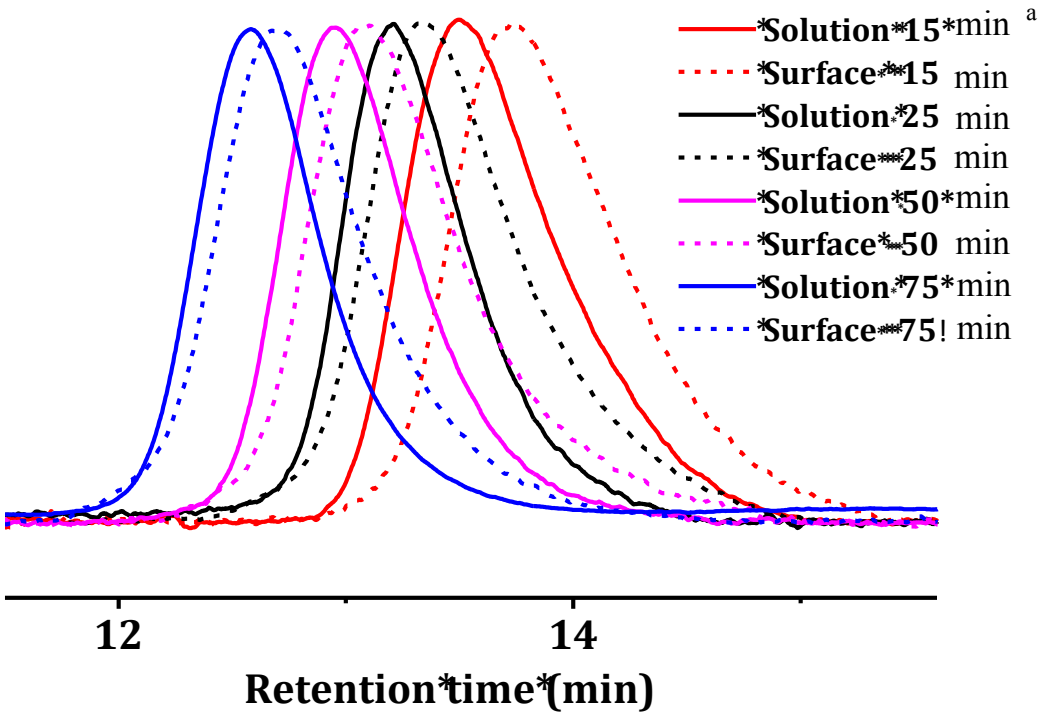

Figure S6. Typical SEC traces of PMMA generated both on the surface and in solution with different polymerization times. [a] the number in the graph indicates the polymerization time for each sample.

Table S1. Data for polymers of monomers shown in Figures 1 and 5.

Sample	Thickness (nm)	Mn Solution (Da)	Mn Surface (Da)	Grafting density (chain/nm^2)	PDI solution	PDI surface
P-tert-BMA	17.8±0.3	65000	56000	0.2	1.1	1.19
P-tert-BMA	16.9±0.2	61000	51000	0.2	1.06	1.13
P-tert-BMA	17.3±0.3	74000	61000	0.18	1.11	1.17
PBMA	19.8±0.5	99000	83000	0.16	1.25	1.38
PBMA	22.3±0.7	105000	86000	0.16	1.3	1.44
PBMA	23.1±0.8	127000	91000	0.17	1.34	1.46
PLM	34.7±0.9	228000	219000	0.09	1.23	1.28
PLM	36.9±0.6	223000	206000	0.1	1.3	1.29
PLM	33.5±0.7	211000	194000	0.09	1.34	1.32
PLM	55.3±1.5	216000	197000	0.15	1.35	1.31
PLM	52.8±0.9	209000	186000	0.15	1.32	1.27
PLM	57.9±1.2	227000	201000	0.16	1.29	1.29
PMA	43.3±1.1	101000	72000	0.44	1.04	1.29
PMA	46.2±2.9	122000	79000	0.43	1.09	1.28
PMA	45.3±2.5	118000	73000	0.46	1.08	1.3
PS	36.2±1.5	70000	68000	0.32	1.16	1.19
PS	33.7±1.3	72000	69000	0.31	1.14	1.18
PS	35.1±1.9	69000	64000	0.35	1.17	1.21
PMMA	15.1±0.3	134200	120100	0.083	1.1	1.120
PMMA	14.8±0.5	130300	128900	0.076	1.12	1.150
PMMA	16.3±0.5	138400	127600	0.085	1.090	1.130
PMMA	60.5±1.1	140100	111200	0.360	1.13	1.230
PMMA	56.9±0.6	136900	103400	0.360	1.11	1.240
PMMA	58.1±0.7	139800	109800	0.350	1.120	1.220

Table S2. Data for polymerization of MMA shown in Figures 2, 3 and 4

Sample	Time (min)	Thickness on surface (nm)	Mn Solution (Da)	Mn Surface (Da)	Grafting density (chain/nm^2)	PDI solution	PDI surface
PMMA 1.2 mM/90°C							
PMMA	15	17.1±0.5	51700	39100	0.311	1.19	1.26
PMMA	15	16.9±0.3	51300	37900	0.317	1.18	1.28
PMMA	15	17.3±0.6	48900	38600	0.318	1.2	1.25
PMMA	25	24.4±0.8	78300	58800	0.295	1.18	1.32
PMMA	25	26.3±0.9	80400	59000	0.317	1.16	1.33
PMMA	25	25.8±0.7	79200	60300	0.304	1.18	1.3
PMMA	50	36.3±1.0	110900	82600	0.312	1.16	1.37
PMMA	50	38.5±0.9	114200	82800	0.330	1.17	1.39
PMMA	50	39.9±1.2	120700	87500	0.324	1.15	1.4
PMMA	75	48.5±1.6	170800	125600	0.274	1.14	1.57
PMMA	75	49.1±1.4	178500	133200	0.262	1.16	1.6
PMMA	75	50.2±1.2	170800	127200	0.280	1.15	1.58
PMMA	130	59.1±0.8	201100	146300	0.287	1.14	1.62
PMMA	130	61.2±1.1	182200	160200	0.271	1.1	1.55
PMMA	130	58.5±0.7	191200	142400	0.292	1.18	1.63
PMMA 0.59 mM/90°C							
PMMA	30	32.1±0.2	73800	66200	0.345	1.14	1.21
PMMA	30	29.9±0.5	84900	60500	0.351	1.15	1.24
PMMA	30	31.3±0.4	78300	63700	0.349	1.15	1.22
PMMA	60	53.4±0.1	146800	119500	0.318	1.12	1.23
PMMA	60	56.4±0.6	145700	113600	0.353	1.13	1.22
PMMA	60	51.9±0.9	139600	109200	0.338	1.14	1.24
PMMA	100	62.7±1.2	179100	137800	0.323	1.13	1.18
PMMA	100	61.3±0.9	177900	138700	0.314	1.12	1.18
PMMA	100	64.2±1.4	170400	132300	0.345	1.12	1.22
PMMA	180	79.1±0.6	246000	177900	0.316	1.18	1.2
PMMA	180	80.0±1.1	240200	175800	0.323	1.15	1.22
PMMA	180	77.2±0.8	243700	180100	0.305	1.17	1.26

PMMA	260	91.6±1.4	286600	224200	0.290	1.18	1.22
PMMA	260	99.2±1.3	280800	219700	0.321	1.19	1.25
PMMA	260	93.6±1.1	289500	225200	0.295	1.17	1.3
PMMA 0.59 mM/60°C							
PMMA	80	30.8±0.6	66800	59200	0.370	1.12	1.17
PMMA	80	31.4±0.4	68300	57500	0.388	1.14	1.18
PMMA	80	31.1±0.3	67100	58600	0.377	1.12	1.18
PMMA	120	45.4±0.4	100400	90800	0.355	1.1	1.15
PMMA	120	44.9±0.7	105800	89200	0.358	1.11	1.16
PMMA	120	46.2±0.5	106700	91100	0.360	1.12	1.15
PMMA	180	60.7±0.8	139500	126200	0.342	1.1	1.15
PMMA	180	61.5±0.8	137800	128100	0.341	1.08	1.15
PMMA	180	60.9±1.1	140000	123500	0.350	1.09	1.14
PMMA	300	86.7±1.2	236300	184600	0.334	1.11	1.16
PMMA	300	87.0±1.1	230500	191300	0.323	1.11	1.17
PMMA	300	85.2±0.9	231900	190700	0.317	1.08	1.15
PMMA	360	94.1±1.5	242200	204500	0.327	1.12	1.19
PMMA	360	95.3±1.2	239500	209300	0.324	1.09	1.21
PMMA	360	96.6±1.3	240700	205200	0.335	1.13	1.18