Supporting information

Ligand Switch in Photoinduced Copper-Mediated Polymerization: Synthesis of methacrylate-acrylate block copolymers

Ya-Mi Chuang,[a,b] Benjamin Wenn,[a] Sam Gielen [a] Anitha Ethirajan,[b] and Tanja Junkers[a,c]

[a] Polymer Reaction Design Group, Institute for Materials Research (IMO-IMOMEC), Hasselt University, Agoralaan D, 3590 Diepenbeen, Belgium. E-mail: tanja.junkers@uhasselt.be; Fax: +32 (11) 26 8399; Tel: +32 (11) 26 8318
[b] Organic and (Bio-)Polymer Chemistry, Institute for Materials Research, Hasselt University, Agoralaan D, 3590 Diepenbeen, Belgium
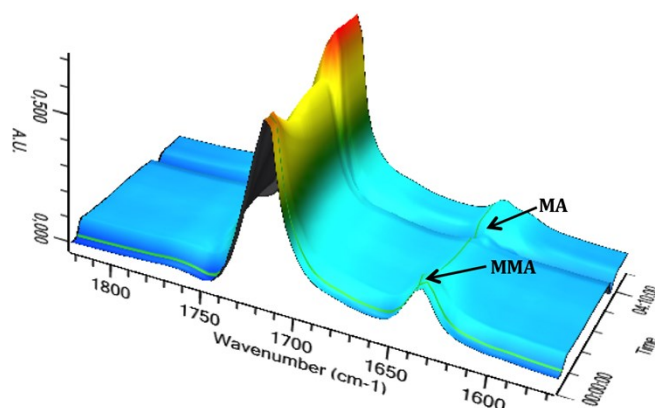[c] IMEC, Division IMOMEC, Wetenschapspark 1, 3590 Diepenbeek, Belgium
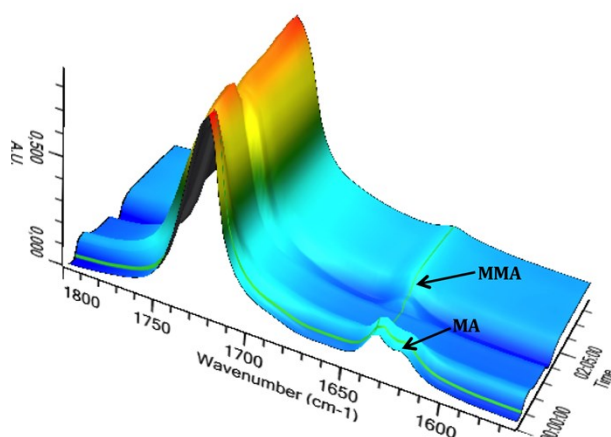
Fig. S 1 FT-IR profiles of MA photoCMP, reaching to 95 % monomer conversion, followed by addition of MMA to the reaction mixture.
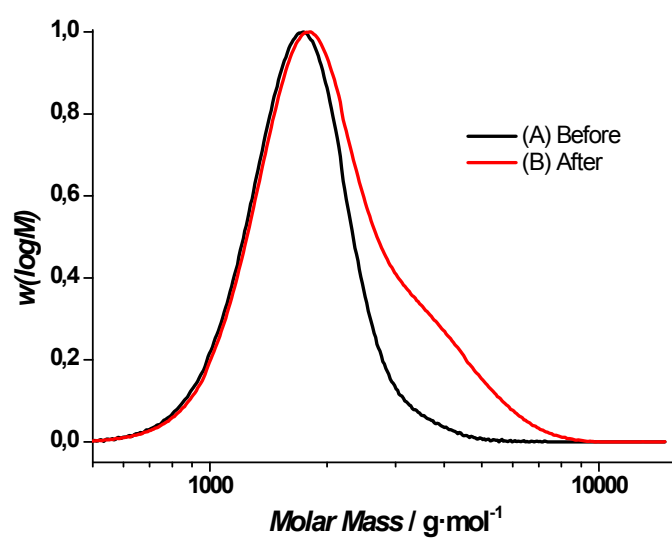
Fig. S 2 Molecular weight distributions of PMA-Br (A); and the same polymer chain extended with MMA (B). Both reactions were conducted in $Me_6TREN/CuBr_2/$ DMSO.

Fig. S 3 FT-IR profiles of MMA photoCMP, reaching to 89 % monomer conversion, followed by addition of MA to the reaction mixture.
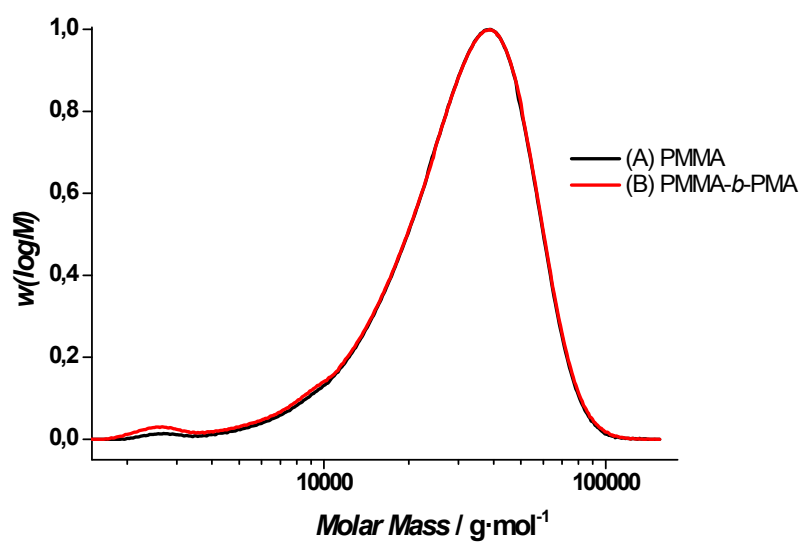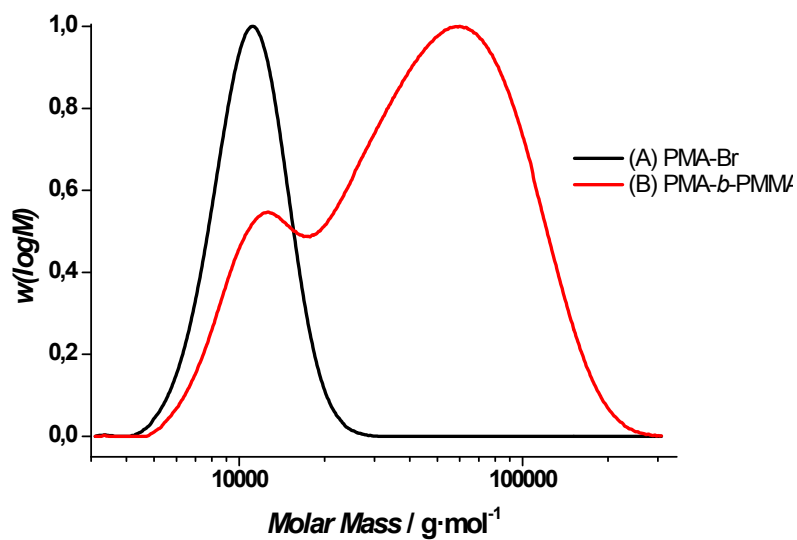
Fig. S 4 Molecular weight distributions of PMMA-Br (A); and the same polymer chain extended with MA (B). Both reactions were conducted in Me$_6$TREN/CuBr$_2$/ DMSO.

Table. S 1 Molecular weight data for polymers obtained for the PMA-Br macroinitiator and PMA-b-PMMA-Br

S/N	Polymer	[M]:[PMA-Br]:[CuI]:[PMDETA]	Time (hrs)	F.C.	Theory (M_n)	SEC (M_n)	Đ
A	PMA-Br	N/A*	1.5	0.93	2000	1900	1.11
B	PMA-*b*-PMMA-Br	179: 1: 1.45: 4.2	4	0.80	7000	3000	2.37
C	PMA-*b*-PMMA-Br	176: 1: 0.70: 4.1	4	0.79	6000	4000	2.23
D	PMA-*b*-PMMA-Br	174: 1: 0.30: 4.0	4	0.84	6000	8000	2.02

* Monomer/EBiB/CuBr$_2$/Me$_6$Tren = 22: 1: 0.03: 0.16 in molar ratio.

Fig. S 5 Molecular weight distributions of PMA-Br (A); and the same polymer chain extended with MMA (B). The chain extension was conducted without purification but with a higher amount of PMDETA in the reaction. The molar ratio of Me$_6$TREN to PMDETA is 1:17.
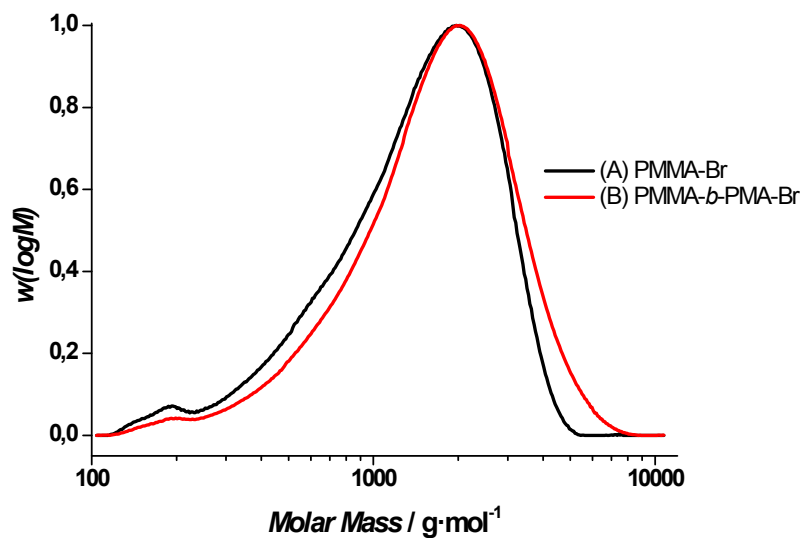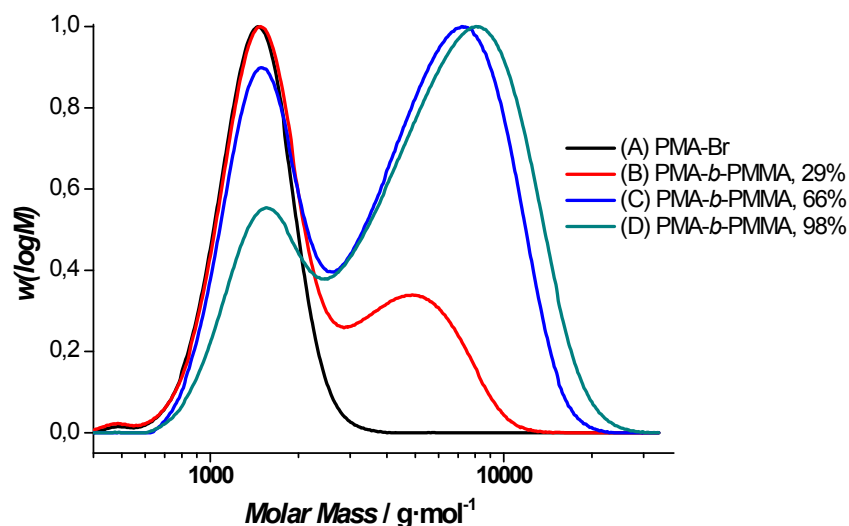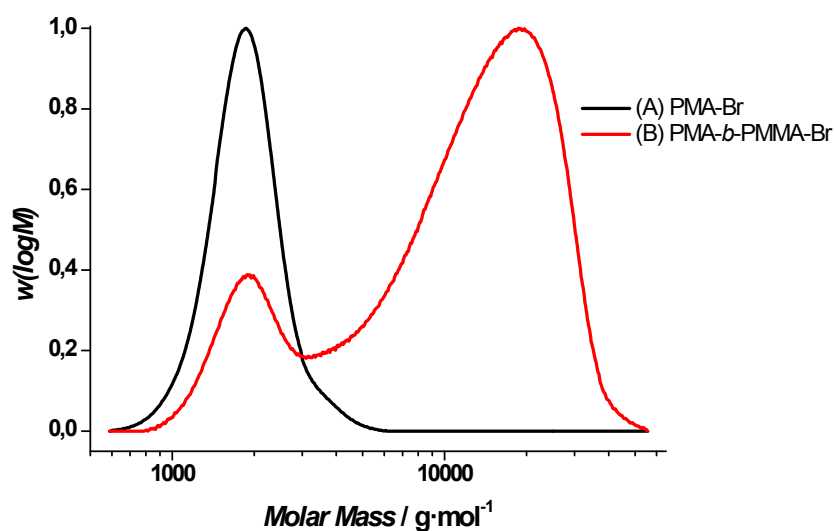

Fig. S 6 Molecular weight distributions of PMMA-Br (A); and the same polymer chain extended with MA (B). The chain extension was conducted without purification. The reaction used DMSO as solvent.

PMA-Br macroinitiator (Fig. S 6 (A)) was synthesized as in the above experiments and the polymerization was stopped (by turning off the UV lamp) when a monomer conversion of 93% or above was reached. Fig. S 6 depicts an example for the PMA molecular weight distribution. Synthesis of the PMA-Br is uncomplicated and for the present case, a polymer with $M_n = 1400$ g·mol^{-1} and a dispersity of 1.2 is obtained. Without any further treatment, MMA (137 eq to PMA-Br) and PMDETA (8 eq. to Me$_6$TREN) is added into the reaction mixture and then exposed to UV. Samples at different time intervals were then collected and studied by SEC (covering reaction times allowing for almost quantitative MMA polymerization). All the samples appear to feature bimodal distributions (Fig. S 6 (B-D)). Closer analysis reveals that re-initiation of PMA-Br has not efficiently occurred and that MMA had polymerized independently, most likely in an uncontrolled polymerization since the high molecular weight distribution hardly grows in size with increasing conversion.

Fig. S 7 Molecular weight distributions of PMA-Br macroinitiator (A); and its chain extension with MMA at monomer conversion of 29% (B), 66%(C) and 98% (D).

PMA-Br (Fig. S 8 (A)) is prepared and when the monomer conversion reached 90%, the reaction was stopped and all volatiles were removed in vacuo. After such isolation of the polymer, PMA-Br, MMA, PMDETA and $CuBr_2$ were dissolved in DMF/MeOH, followed by UV exposure. Molecular weight distributions of PMA-Br and its chain extended products are shown in Fig. S 8. Again, bimodal molecular weight distributions are obtained. The observed bimodality is similar to what is observed for the copolymer that is prepared from non-purified method, even if respective amounts of material seem to be somewhat different.

Fig. S 8 Molecular weight distributions of PMA-Br (A); and PMA-*b*-PMMA-Br prepared after isolation of the macroinitiator (B).