

Synthesis of Block Copolymers via Atom Transfer Radical Polymerization and ‘Click Chemistry’ grafted from Pre-functionalized Polypropylene Surfaces using Gamma Irradiation

Supporting Information*

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***Content : Figure S1-S10 and Tables 1-3.**

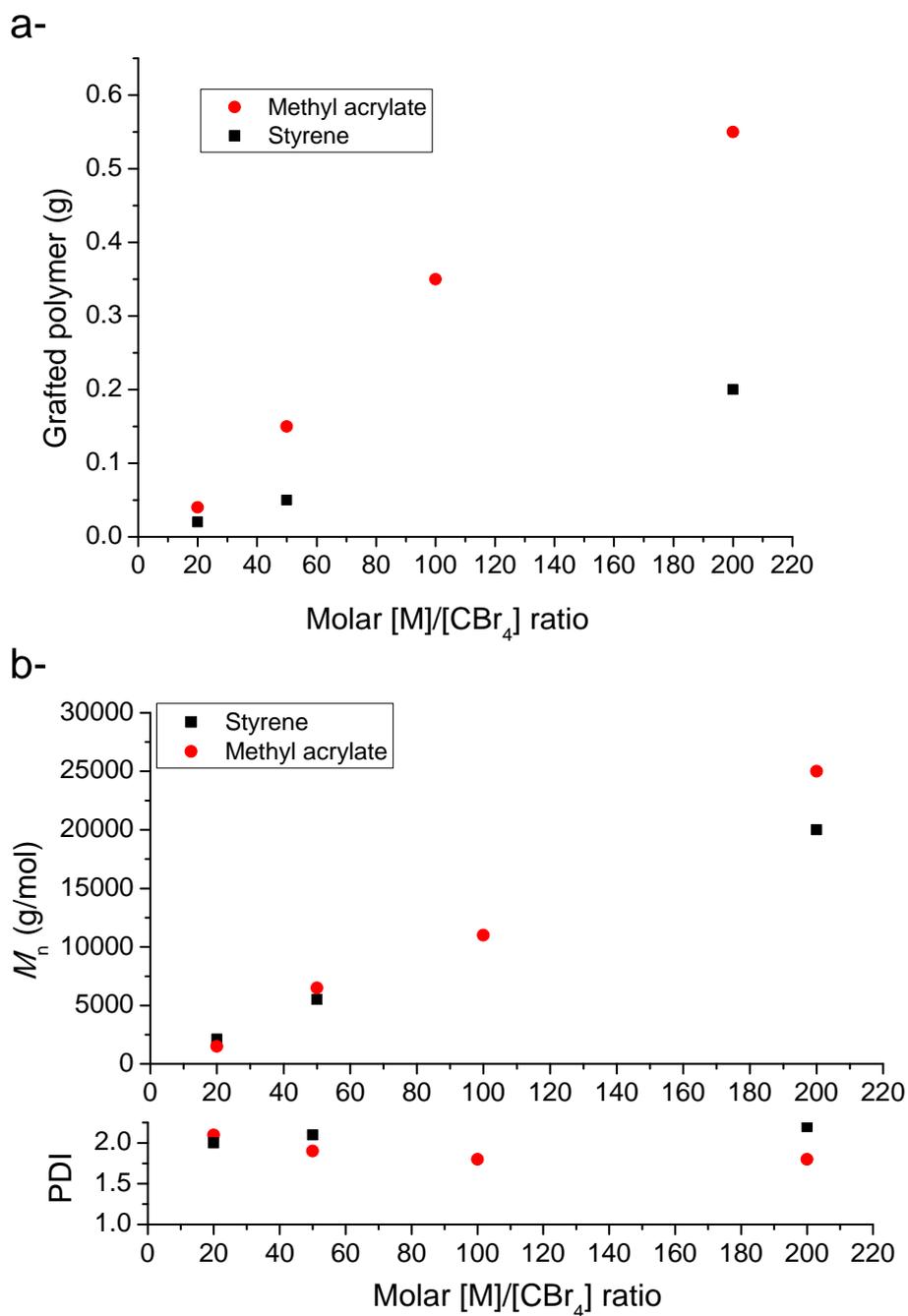


Figure S1. Grafted polymer PP surface initiated by Gamma irradiation of methyl acrylate and styrene in the presence of different $[\text{Monomer}]_0/[\text{CBr}_4]_0$ ratios: a) grafted polymer weight and b) GPC analysis of free polymer in solution.

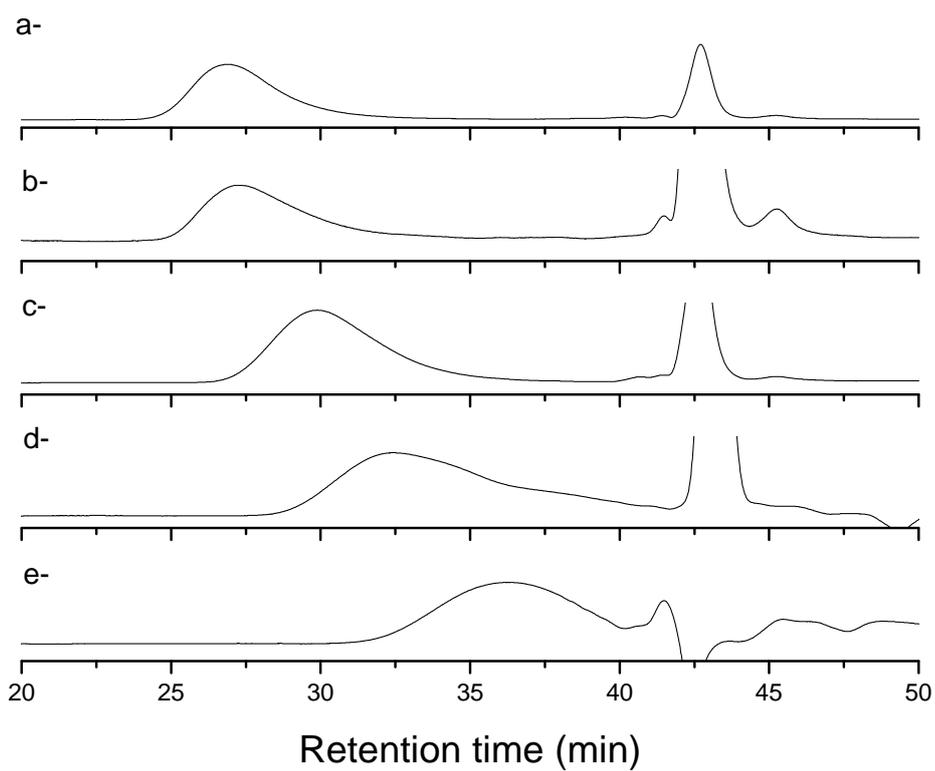


Figure S2. GPC traces of poly(methyl acrylate) in solution obtained using gamma irradiation of PP in the presence of methyl acrylate(MA) and transfer agent (CBr_4). $[\text{MA}]/[\text{CBr}_4]$ ratio corresponds to 300/1 (a), 200/1 (b), 100/1 (c), 50/1, and 20/1 (d).

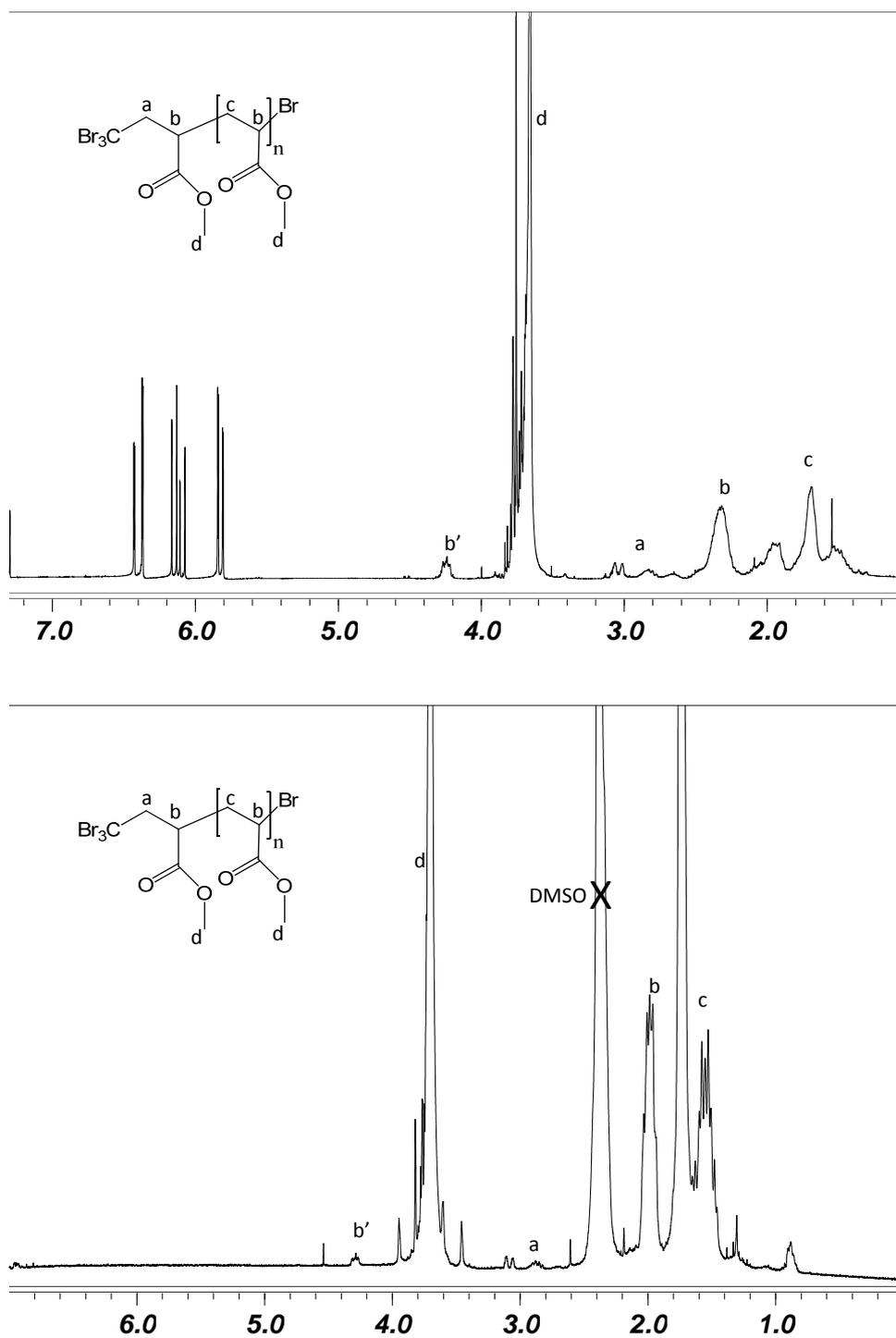


Figure S3. Examples of ¹H NMR spectra of poly(methyl acrylate) obtained using gamma irradiation of PP in the presence of methyl acrylate (MA) and transfer agent (CBr₄). [MA]/[CBr₄] ratio equals to 100/1 (up) and 50/1 (bottom): up- poly(methyl acrylate) in the presence of methyl acrylate monomer; bottom- purified poly(methyl acrylate).

Note: CH in adjacent of bromine (b') appears at 4.3 ppm.

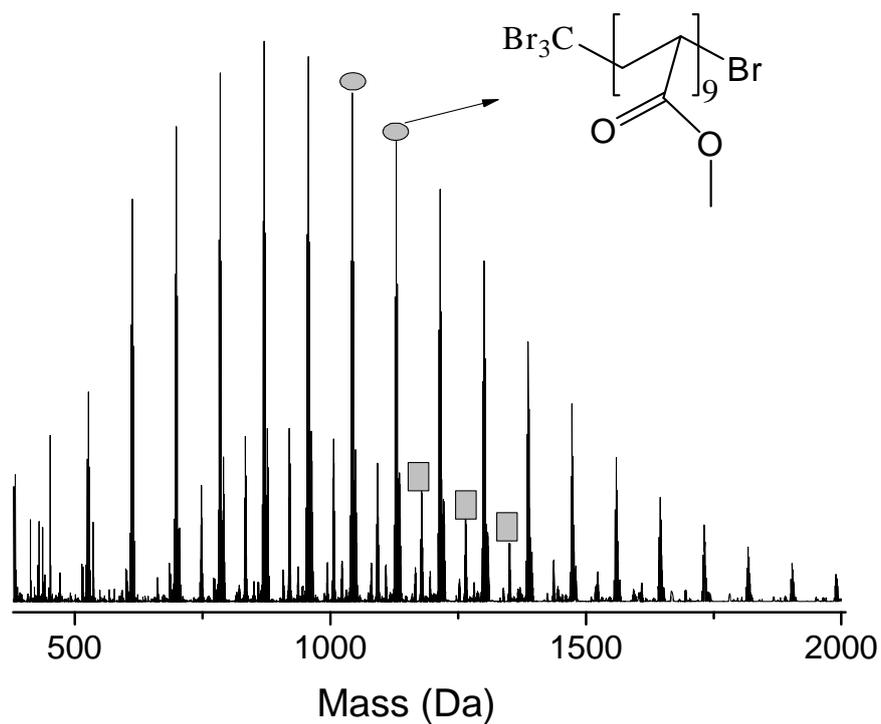


Figure S4. ESI-MS of poly(methyl acrylate) in solution obtained using gamma irradiation of PP in the presence of methyl acrylate (MA) and transfer agent (CBr_4). $[\text{MA}]/[\text{CBr}_4]$ ratio corresponds 20/1.

Note: ESI-MS shows the distribution of expected populations, i.e. $\text{CBr}_3\text{-PMA-Br}$ charged with sodium (Na^+) (circle in Figure S4). Additional populations can be observed and are attributed to double charge species indicated by squares.

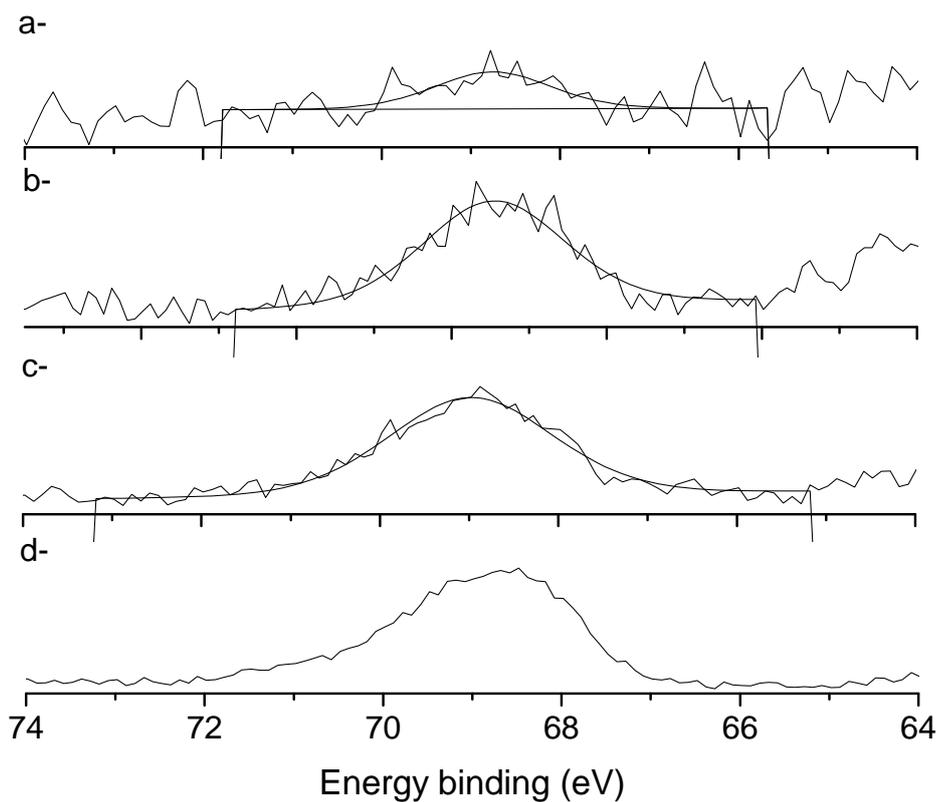


Figure S5. High resolution XPS spectra of Br(3d) regions of purified PP films obtained after gamma irradiation in the presence of CBr_4 and methyl acrylate. a- sample 1 ($[\text{M}]/[\text{CBr}_4]$ molar ratio = 200/1), b- sample 2 ($[\text{M}]/[\text{CBr}_4]$ molar ratio = 100/1), c- sample 3 ($[\text{M}]/[\text{CBr}_4]$ molar ratio = 50/1) and d- sample 4 ($[\text{M}]/[\text{CBr}_4]$ molar ratio = 20/1) of **Table 1**.

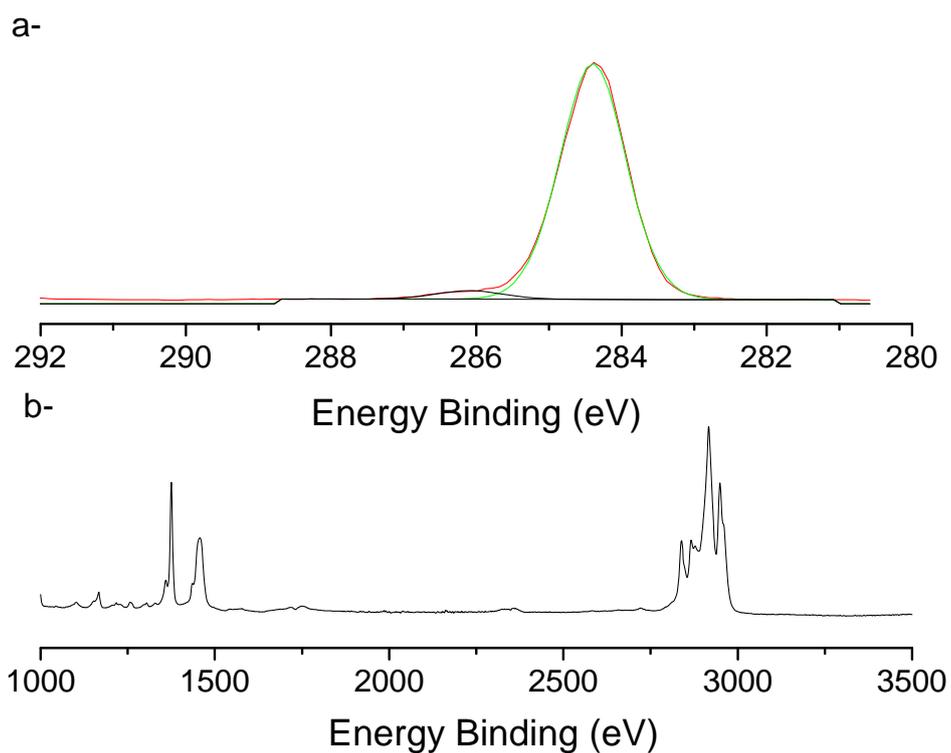


Figure S6. Analysis of purified PP surface after ATRP of MA in the presence of non functional PP: a- high resolution XPS spectrum of C(1s), b- ATR-FTIR spectrum of purified PP-*g*-PMA.

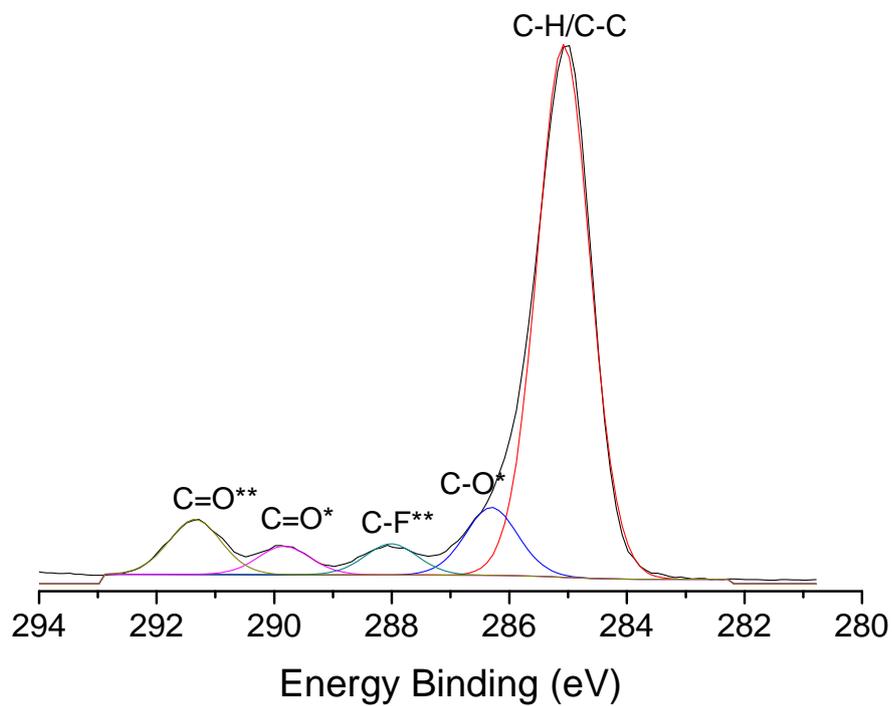


Figure S7. Deconvolution of high resolution XPS of purified PP-*g*-[PS-*b*-PMA-*b*-PFA] surface after ATRP of MA and then, chain extension with FA.

Note: C=O** and C-F** are attributed to PFA block, while C=O* and C-O* correspond to MA block.

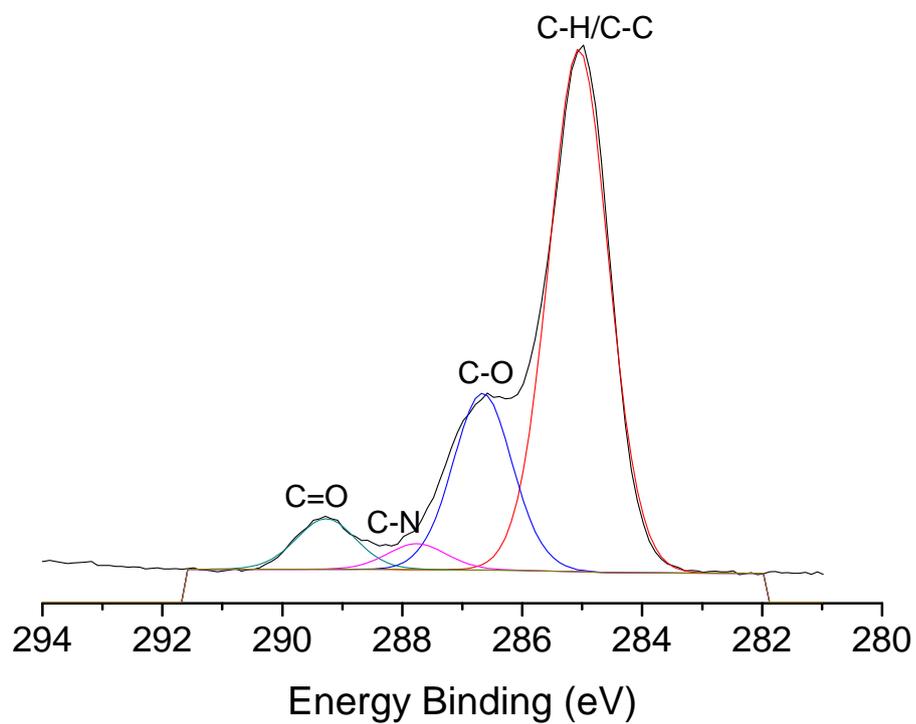


Figure S8. Deconvolution of C1(s) high resolution XPS of purified PP-*g*-[PS-*b*-PMA-*b*-PDMAEA] surface after ATRP of MA, and then, chain extension with DMAEA.

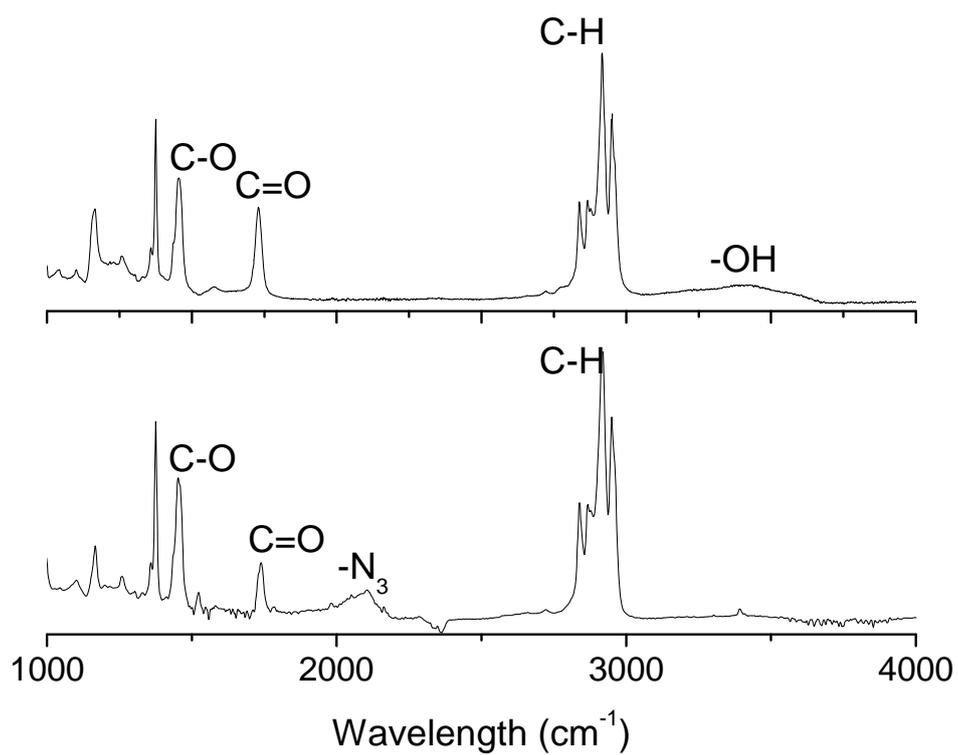


Figure S9. ATR-FTIR spectra of (up) purified PP-g-PMA-N₃ after click chemistry in the presence of propargyl alcohol and (bottom) purified PP-g-PMA-N₃ before click chemistry.

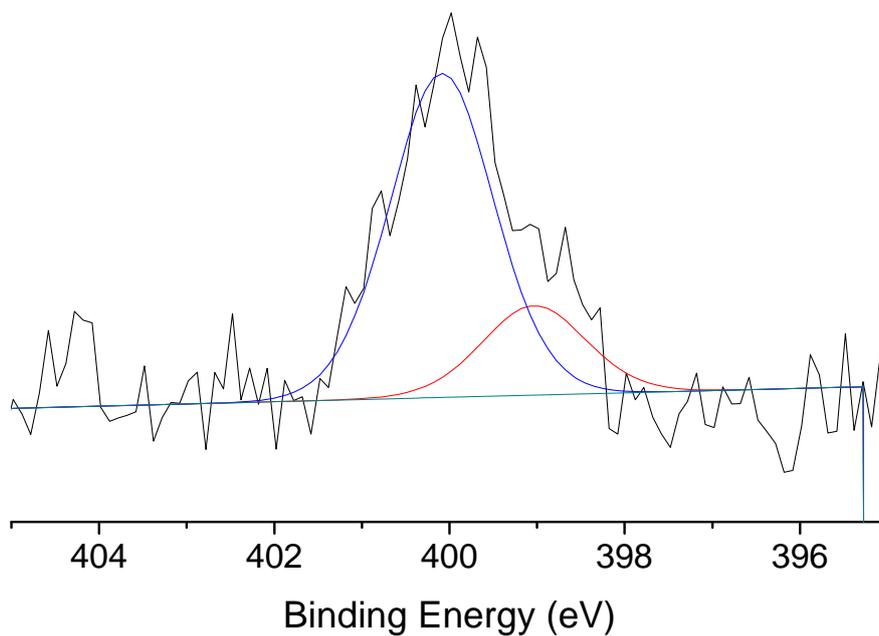


Figure S10. High resolution XPS spectrum of N1(s) after nucleophilic substitution of PP-g-PMA-Br with sodium azide.

Note: Before reaction, Nitrogen signal was not detectable.

Samples #	Transfer agents (TA)	Monomers	Composition by XPS				
			C	O	Br	I	Other elements
PP	-	-	75	20	0	0	5
1	CBr ₄	MA	55	45	0.07	0	0
2	CBr ₄	MA	62	36	0.21	0	2
3	CBr ₄	MA	68	31	0.49	0	1
4	CBr ₄	MA	69	29	0.89	0	1
5	CBr ₄	ST	88	09*	0.12	0	2
6	CBr ₄	ST	90	07*	0.24	0	3
7	CBr ₄	ST	90	09*	0.46	0	1
8	CBr ₄	MMA	62	35	0.84	0	3

Table S1. Elemental analysis obtained by XPS for different PP films after gamma irradiation in the presence of monomers and carbon tetrabromide (CBr₄).

Note * oxygen was detected on PP-g-PST attributed to the physio-sorption of O₂.

Samples #	Transfer agents (TA)	Monomers	Composition by XPS				
			C	O	Br	I	Other elements
PP	-	-	75	20	0	0	5
9	CuBr ₂	MA	70	24	1.22	0	5
10	CuBr ₂	MA	71	25	1.23	0	4
11	CuBr ₂	ST	81	19	0.83	0	2
12	CuBr ₂	ST	nd	nd	nd	nd	nd
13	CuBr ₂	MMA	73	25	0.95	0	1
14	CuBr ₂	MMA	71	28	0.89	0	3
15	I ₂	MA	79	19	0	0.91	1
16	I ₂	MA	72	24	0	0.88	1
17	I ₂	ST	78	20	0	1.12	1

Table S2. Elemental analysis obtained by XPS for different PP films after gamma irradiation in the presence of monomers and copper bromide or iodine.

Note * oxygen was detected on PP-g-PST attributed to the physio-sorption of O₂.

Samples #	Click chemistry	Composition by XPS							
		C	O	Br	I	Si	N	S	Other elements
PP-g-PMA-Br	-	68	31	0.49	0	0	0	0	1
PP-g-PMA-Br	POSS-thiol	65	30	0	0	3.85	0	0.35	1
PP-g-PMA-Br	2-AET/HCl	67	30	0	0	0	0.35	0.43	1
PP-g-PMA-Br	Sodium Azide	68	30	0	0	0	0.94	0	1
PP-g-PMA-N ₃	Propargyl alcohol	67	30	0	0	0	0.88	0	2

Table S3. Elemental analysis obtained by XPS after different click chemistry reactions.