Electronic Supplementary Material (ESI) for Polymer Chemistry

Organocatalytic Synthesis and Post-Polymerization Functionalization of Propargyl-Functional Poly(Carbonate)s

*Sarah Tempelaar,[a] Ian A. Barker,[a] Vinh X. Truong,[a] Daniel J. Hall,[a] Laetitia Mespouille,[b] Philippe Dubois[b] and Andrew P. Dove.[a]***

[a]Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K. [b]Laboratory of Polymeric and Composite Materials (LPCM), Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons (UMONS), 20, Place du Parc, 7000 Mons, Belgium.

Supplementary Information

Figure S1. a) MALDI-TOF MS spectra in reflectron ion-mode showing the isotope pattern of DP10 polymer chains of PMPC initiated from benzyl alcohol from polymerizations in CH_2Cl_2 (top) and $CDCl_3$ (bottom); b) Predicted isotopic distributions of DP10 polymer chains expected for PMPC with all protons retained (top), with 1, 2 and 3 protons exchanged with deuterium in a 1:1:1 ratio (middle) and with all acetylenic protons exchanged (top).

Figure S2. GPC chromatograms of block copolymers and their corresponding macro-initiator: (a) BnO-PLA_{18}-OH (M_n = 4 200 g mol^{-1}; $Đ_M$ = 1.09) and BnO-PLA_{18}-*b*-$PMPC_{20}$-OH (M_n = 8 740 g mol^{-1}; $Đ_M$ = 1.08); (b) BnO-$PMPC_{20}$-OH (M_n = 4 540 g mol^{-1}; $Đ_M$ = 1.12) and BnO-$PMPC_{20}$-*b*-PLA_{24}-OH (M_n = 10 350 g mol^{-1}; $Đ_M$ = 1.09); (c) MeO-PEO_{114}-OH (M_n = 6 790 g mol^{-1}; $Đ_M$ = 1.03) and MeO-PEO_{114}-*b*-$PMPC_{18}$-OH (M_n = 11 020 g mol^{-1}; $Đ_M$ = 1.06); (d)

BnO-PMPC$_{17}$-OH (M_n = 4 010 g mol^{-1}; $Đ_M$ = 1.11) and BnO-PMPC$_{17}$-*b*-PMAC$_{19}$-OH (M_n = 8 110 g mol^{-1}; $Đ_M$ = 1.09).

Table S1. CuAAC functionalization of BnO-PMPC$_{10}$-OH.

Figure S3. MALDI-ToF MS spectra of PMPC after CuAAC functionalization with 1-azidooctane with added NaTFA following purification with Cuprisorb^{TM} beads (top), added NaTFA before purification (middle); and no added NaTFA before purification (bottom) - key (■) Cu^+ charged and (■) Na^+ charged chains.

Figure S4. ^{1}H NMR spectra of PMPC after functionalization with benzyl azide in $CDCl_3$ (top) and of with 3-azido-7-hydroxylcoumarin in *d*-DMSO (bottom) (400 MHz, 298 K; * = residual $CDCl_3$, ** = H_2O,*** = residual *d*-DMSO).

Figure S5. MALDI-ToF MS spectrum of PMPC after CuAAC functionalization with 3-azido-7-hydroxylcoumarin (left) shows distribution with PMPC fully functionalized with 3-azido-7-hydroxylcoumarin azide (●) and polymer chains with 1 (●)or 2 (●) unfunctionalized propargyl groups.

Figure S6. DMF solutions of PMPC, 3-azido-7-hydroxylcoumarin, PMPC + 3-azido-7-hydroxylcoumarin, PMPC after functionalization with 3-azido-7-hydroxylcoumarin (A+C, from left to right) and of a further diluted solution of PMPC after functionalization (B+D) show fluorescence when irradiated at 365 nm with a UV lamp for the clicked polymer only (C+D).

Table S2. Radical 'thiol-yne' functionalization of BnO-PMPC$_{12}$-OH**.**

Figure S7. ^{1}H NMR spectra of PMPC after functionalization with benzyl mercaptan in $CDCl_3$ (top) and with 1-thioglycerol in *d*-DMSO (bottom) (400 MHz, 298 K; * = residual $CDCl_3$/ *d*-DMSO, ** = H_2O).

Figure S8. MALDI-ToF MS spectrum of PMPC after 'thiol-yne' functionalization with benzyl mercaptan showing a main distribution of fully functionalized polymer (●) and cross-linked, benzyl functionalized PMPC (●).

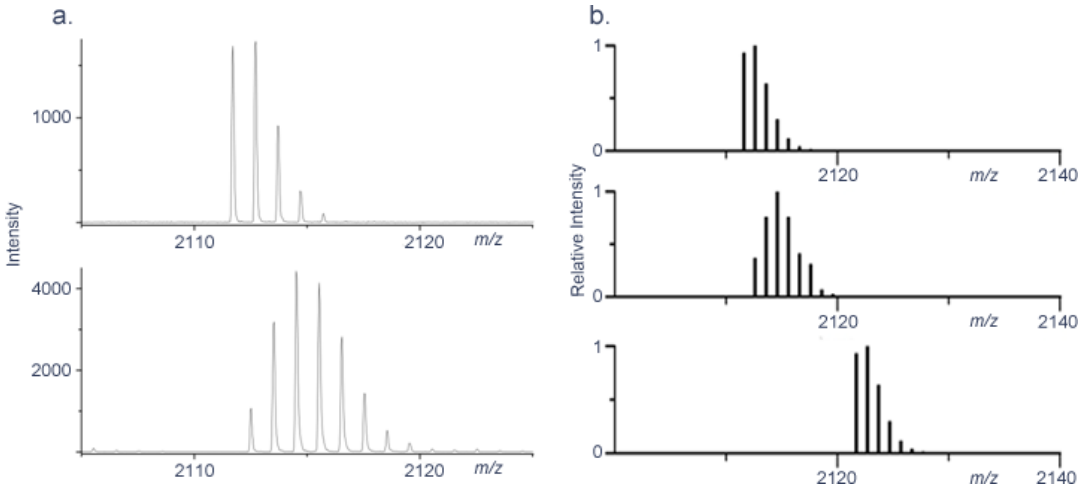

Figure S1. a) MALDI-TOF MS spectra in reflectron ion-mode showing the isotope pattern of DP10 polymer chains of PMPC initiated from benzyl alcohol from polymerizations in CH_2Cl_2 (top) and $CDCl_3$ (bottom); b) Predicted isotopic distributions of DP10 polymer chains expected for PMPC with all protons retained (top), with 1, 2 and 3 protons exchanged with deuterium in a 1:1:1 ratio (middle) and with all acetylenic protons exchanged (top).

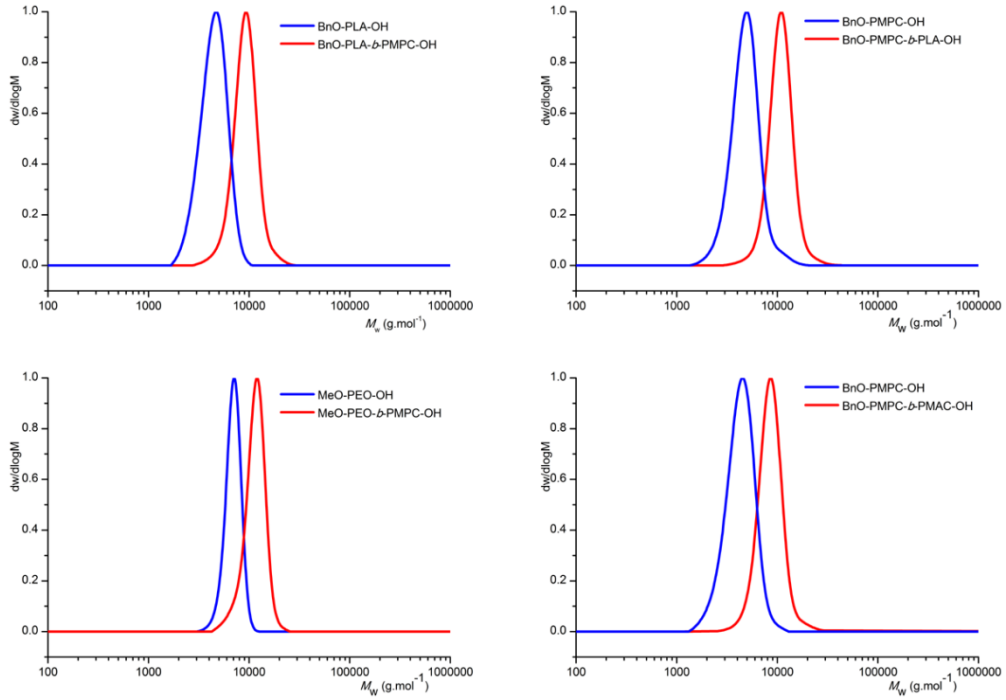

Figure S2. GPC chromatograms of block copolymers and their corresponding macro-initiator: (a) BnO-PLA_{18}-OH (M_n = 4 200 g mol^{-1}; $Đ_M$ = 1.09) and BnO-PLA_{18}-*b*-$PMPC_{20}$-OH (M_n = 8 740 g mol^{-1}; $Đ_M$ = 1.08); (b) BnO-$PMPC_{20}$-OH (M_n = 4 540 g mol^{-1}; $Đ_M$ = 1.12) and BnO-$PMPC_{20}$-*b*-PLA_{24}-OH (M_n = 10 350 g mol^{-1}; $Đ_M$ = 1.09); (c) MeO-PEO_{114}-OH (M_n = 6 790 g mol^{-1}; $Đ_M$ = 1.03) and MeO-PEO_{114}-*b*-$PMPC_{18}$-OH (M_n = 11 020 g mol^{-1}; $Đ_M$ = 1.06); (d) BnO-$PMPC_{17}$-OH (M_n = 4 010 g mol^{-1}; $Đ_M$ = 1.11) and BnO-$PMPC_{17}$-*b*-$PMAC_{19}$-OH (M_n = 8 110 g mol^{-1}; $Đ_M$ = 1.09).

Table S1. CuAAC functionalization of BnO-PMPC$_{10}$-OH.[a]

Azide	M_n[b] (g mol^{-1})	M_w/M_n[b]
-	2,240[c]/ 4,600[d]	1.33[c]/ 1.18[d]
1-azidooctane	5,560[c]	1.16[c]
benzyl azide	2,670[c]	1.33[c]
TEG azide	2,480[c]	1.28[c]
3-azido-7-hydroxylcoumarin	8,610[d]	1.23[d]

[a] $[PMPC]_0$ = *ca.* 0.34 M in THF or DMF, 1.05 eq. azide, 25 ºC, 24 h. [b] Measured by GPC analysis using. [c] THF or [d] DMF as eluent.

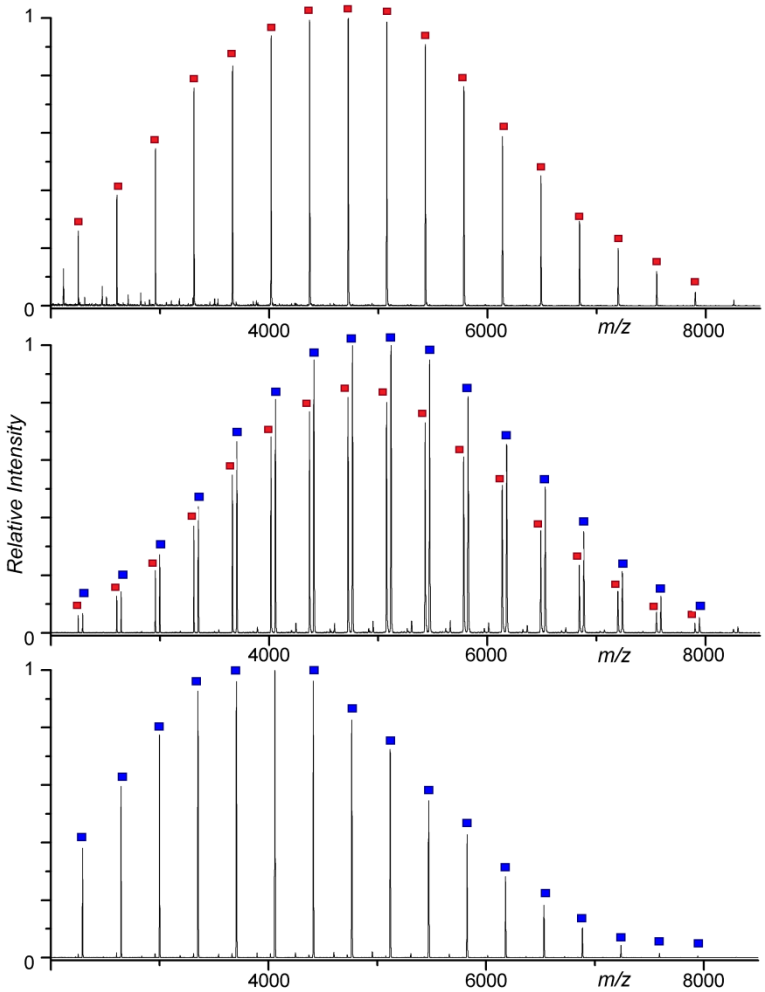

Figure S3. MALDI-ToF MS spectra of PMPC after CuAAC functionalization with 1-azidooctane with added NaTFA following purification with Cuprisorb^{TM} beads (top), added NaTFA before purification (middle); and no added NaTFA before purification (bottom) - key (■) Cu^+ charged and (■) Na^+ charged chains.

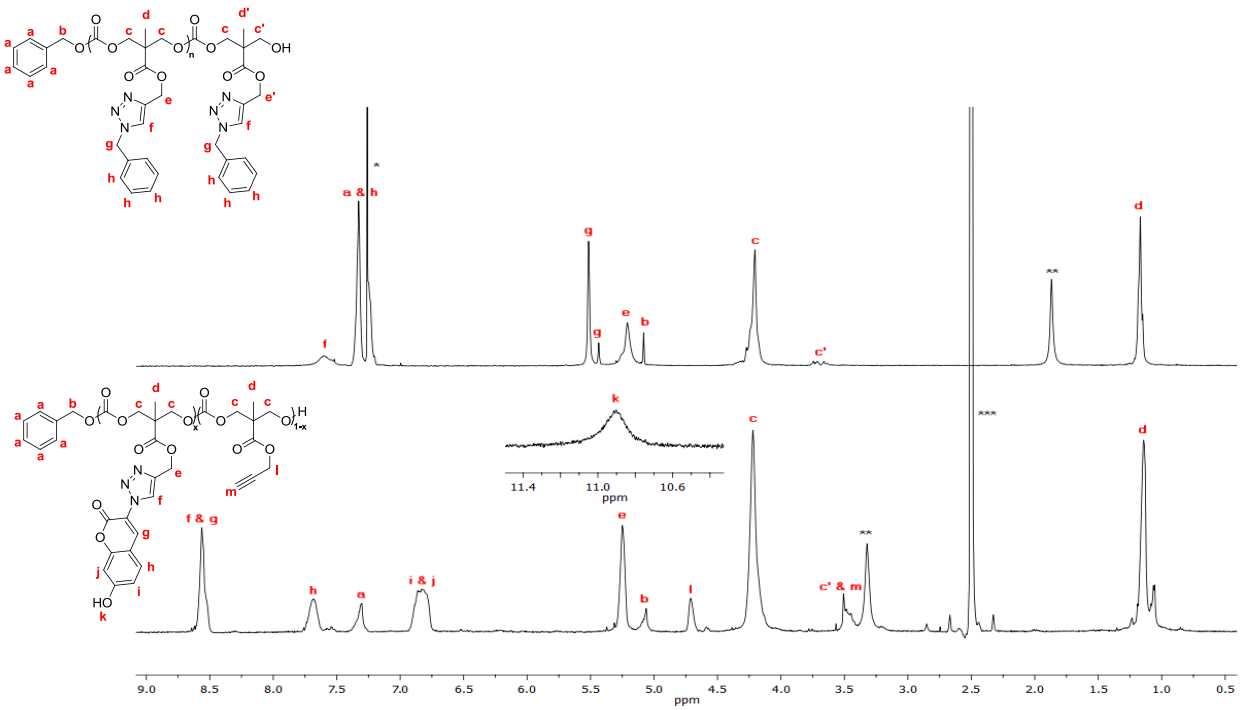

Figure S4. ^{1}H NMR spectra of PMPC after functionalization with benzyl azide in $CDCl_3$ (top) and of with 3-azido-7-hydroxylcoumarin in *d*-DMSO (bottom) (400 MHz, 298 K; * = residual $CDCl_3$, ** = H_2O,*** = residual *d*-DMSO).

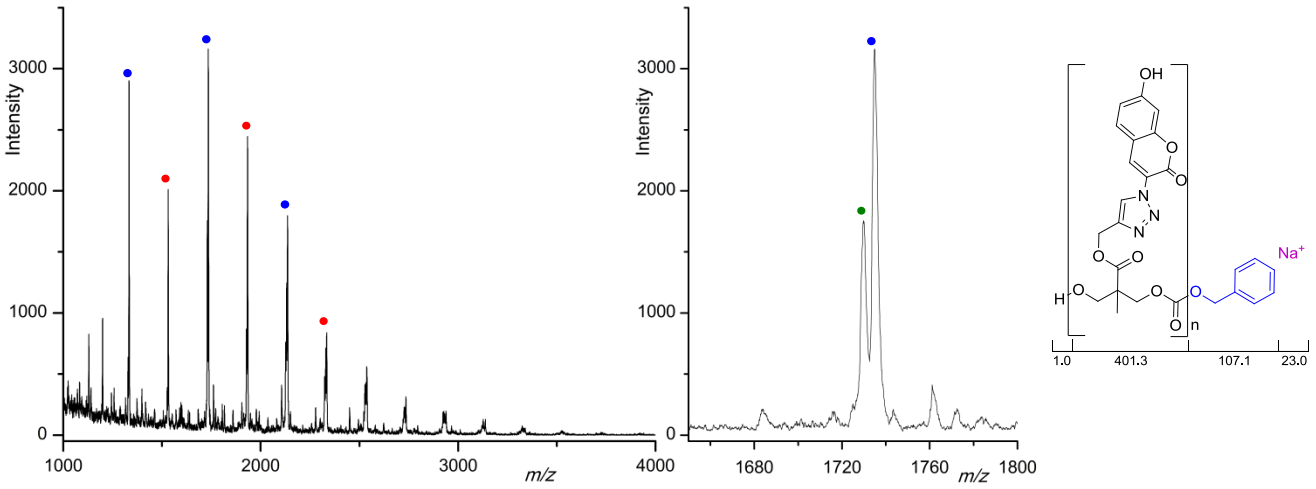

Figure S5. MALDI-ToF MS spectrum of PMPC after CuAAC functionalization with 3-azido-7-hydroxylcoumarin (left) shows distribution with PMPC fully functionalized with 3-azido-7-hydroxylcoumarin azide (●) and polymer chains with 1 (●)or 2 (●) unfunctionalized propargyl groups.

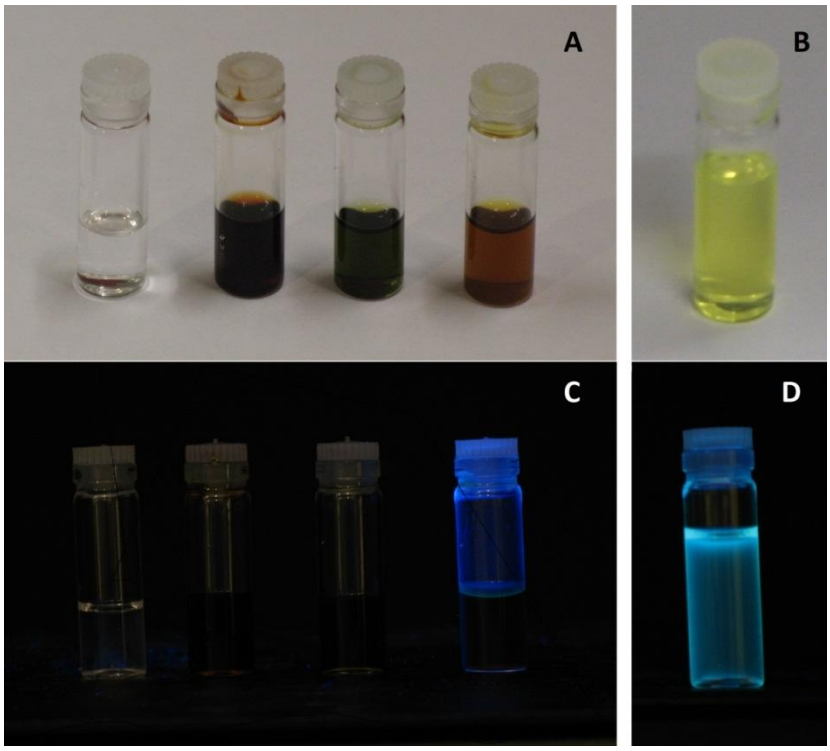

Figure S6. DMF solutions of PMPC, 3-azido-7-hydroxylcoumarin, PMPC + 3-azido-7-hydroxylcoumarin, PMPC after functionalization with 3-azido-7-hydroxylcoumarin (A+C, from left to right) and of a further diluted solution of PMPC after functionalization (B+D) show fluorescence when irradiated at 365 nm with a UV lamp for the clicked polymer only (C+D).

Table S2. Radical 'thiol-yne' functionalization of BnO-PMPC$_{12}$-OH.[a]

Thiol	M_n[b] (g mol^{-1})	M_w/M_n[b]
-	2,370[c]/ 5,810[d]	1.29[c]/ 1.17[d]
1-dodecanethiol	5,700[c]	1.80[c]
benzyl mercaptan	3,570[c]	1.36[c]
1-thioglycerol	7,830[c]	1.22[c]
mercaptoethanol	7,830[d]	1.36[d]

[a] $[PMPC]_0$ = *ca*. 0.15 M in dioxane, 10 eq. thiol, 25 ºC, 24 h. [b] Measured by GPC analysis using. [c] THF or [d] DMF as eluent.

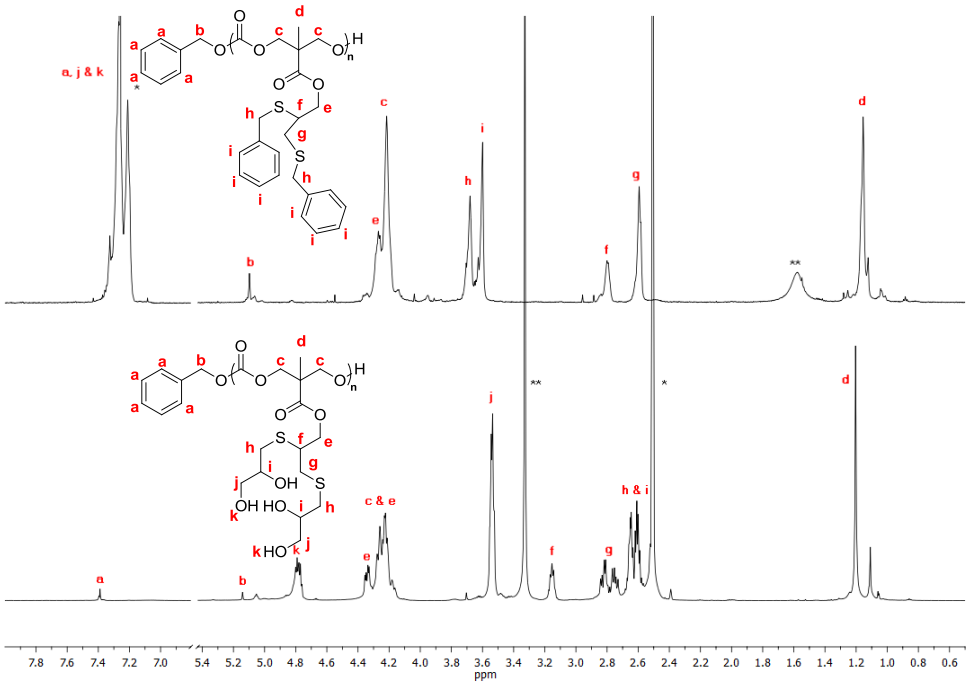

Figure S7. ^{1}H NMR spectra of PMPC after functionalization with benzyl mercaptan in $CDCl_3$ (top) and with 1-thioglycerol in *d*-DMSO (bottom) (400 MHz, 298 K; * = residual $CDCl_3$/ *d*-DMSO, ** = H_2O).

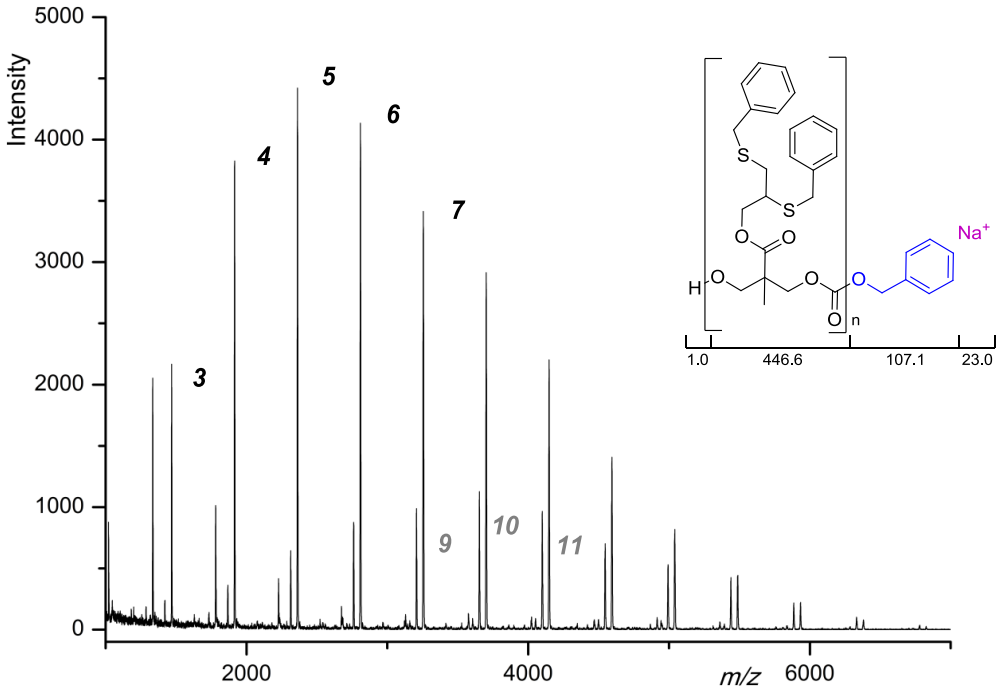

Figure S8. MALDI-ToF MS spectrum of PMPC after 'thiol-yne' functionalization with benzyl mercaptan showing a main distribution of fully functionalized polymer (●) and cross-linked, benzyl functionalized PMPC (●).