Supporting Information

Synthesis of functionalized poly(vinyl acetate) mediated by alkyne-terminated RAFT agents

Joana R. Góis,[a] Anatoliy V. Popov,[b] Tamaz Guliashvili,[c] Arménio C. Serra,[a] Jorge F. J. Coelho[a]*

[a] *CEMUC, Department of Chemical Engineering, University of Coimbra, Polo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal. Fax: +351 239 798 703; Tel:+351 239 798 764; E-mail: jcoelho@eq.uc.pt*

[b] *Department of Radiology, University of Pennsylvania, Philadelphia, PA19104, United States.*

[c] *Home Address: 1761 Foster Street, F5B, Philadelphia PA 191116, United States. E-mail: tamazguliasvili@yahoo.com*

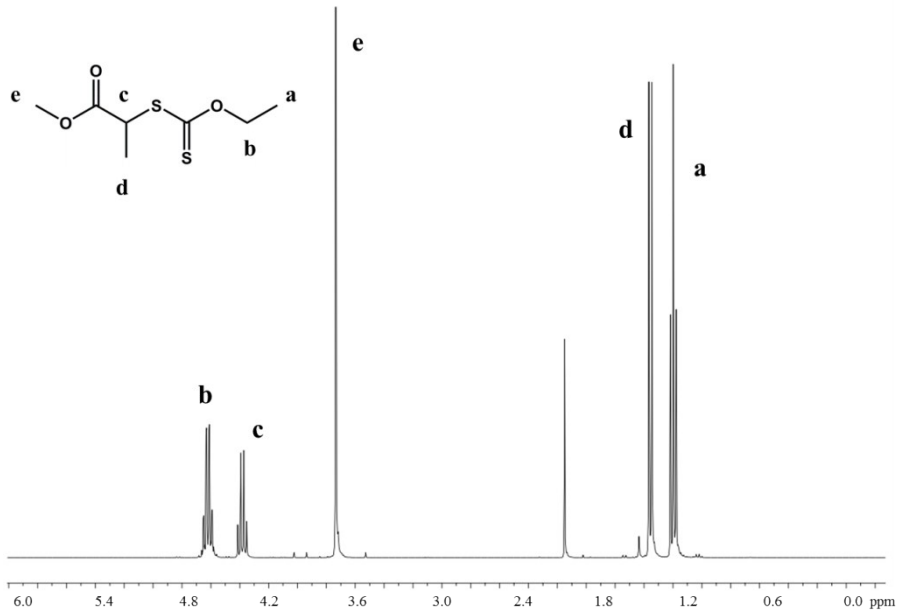

Fig. S1: ^{1}H NMR spectrum of X1 in $CDCl_3$.

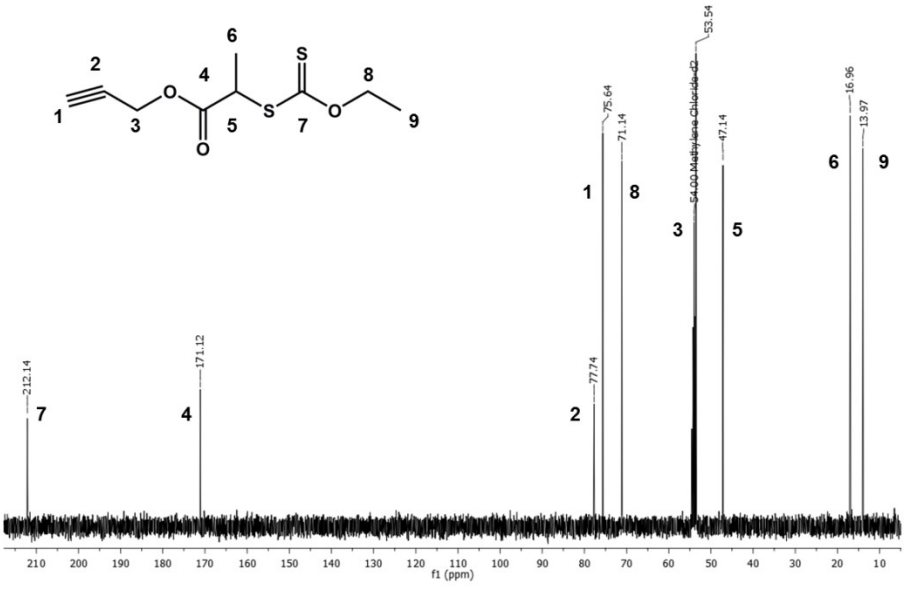

Fig. S2: ^{13}C NMR spectrum of AT-X_1 in CD_2Cl_2.

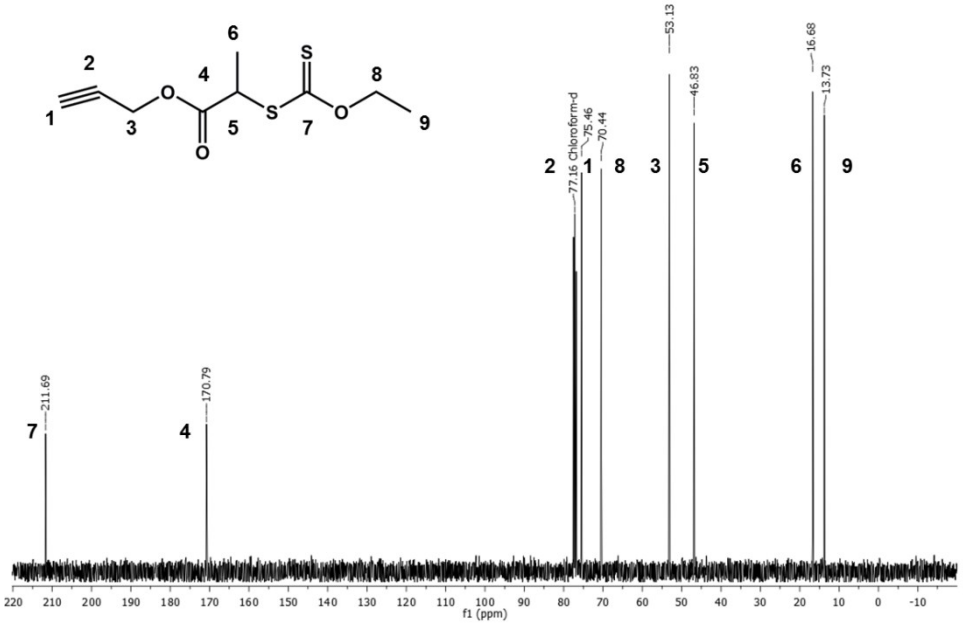

Fig. S3: ^{13}C NMR spectrum of AT-X_1 in $CDCl_3$.

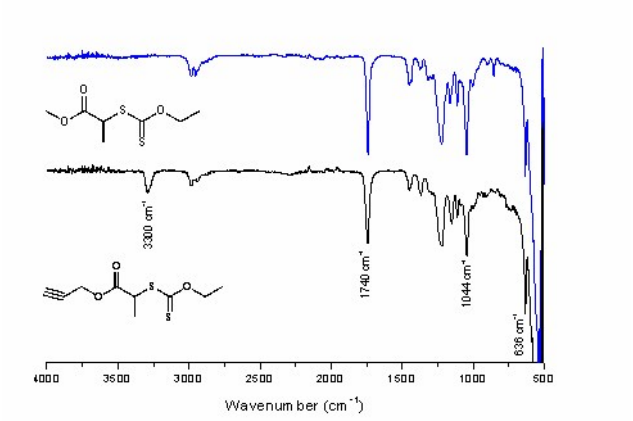

Fig. S4: FTIR-ATR spectra of the X_1 and AT- X_1.

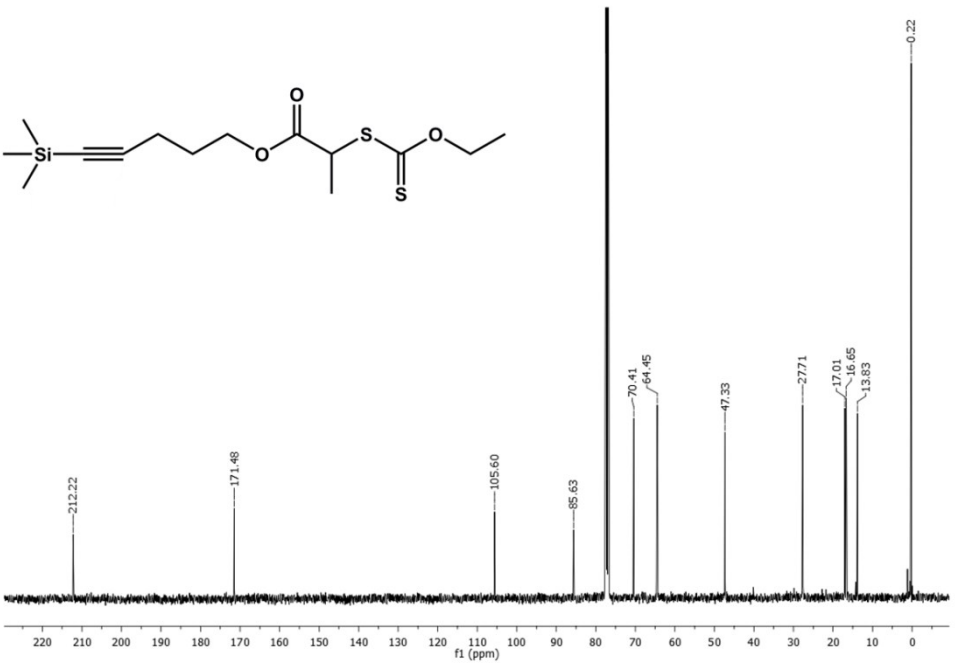

Fig. S5: ^{13}C NMR spectrum of PAT- X_1 in $CDCl_3$.

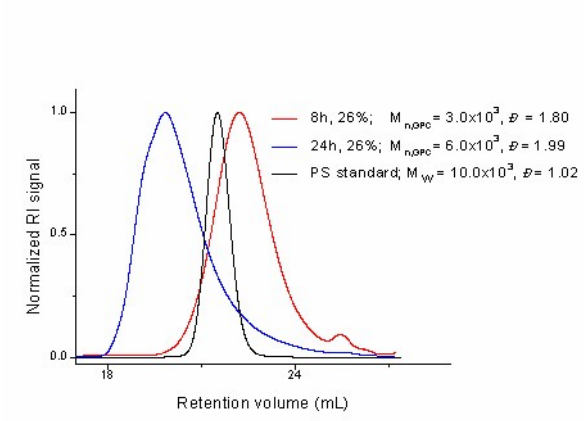

Fig. S6: GPC traces of poly(styrene) (PS) standard (M_p = 10 050 $gmol^{-1}$; $Đ$ = 1.02) and PVAc samples taken at different times of reaction. Conditions: $[VAc]_0/[1,4\text{-dioxane}]_0$ = 1/1 (m/m); $[VAc]_0/[AT\text{-}X_1]_0/[AIBN]_0$ =100/1/0.2, T=60 °C.

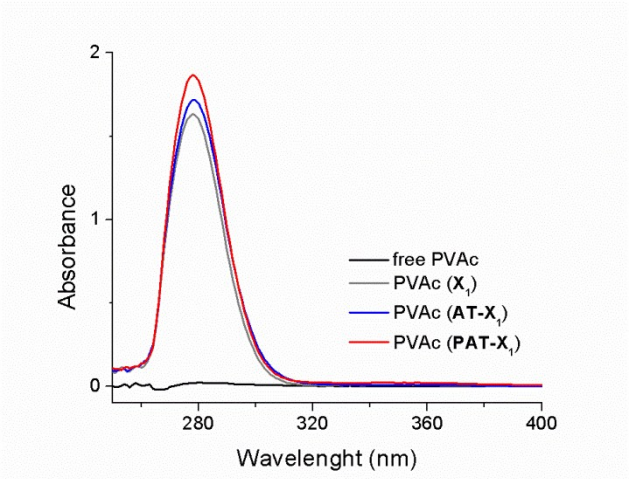

Fig. S7: UV-vis spectra of free-PVAc and PVAc synthesised through RAFT polymerization using the different RAFT agents: X_1, AT- X_1 and PAT- X_1 respectively. Samples with 1.5 $mg.mL^{-1}$ concentration in $CHCl_3$.

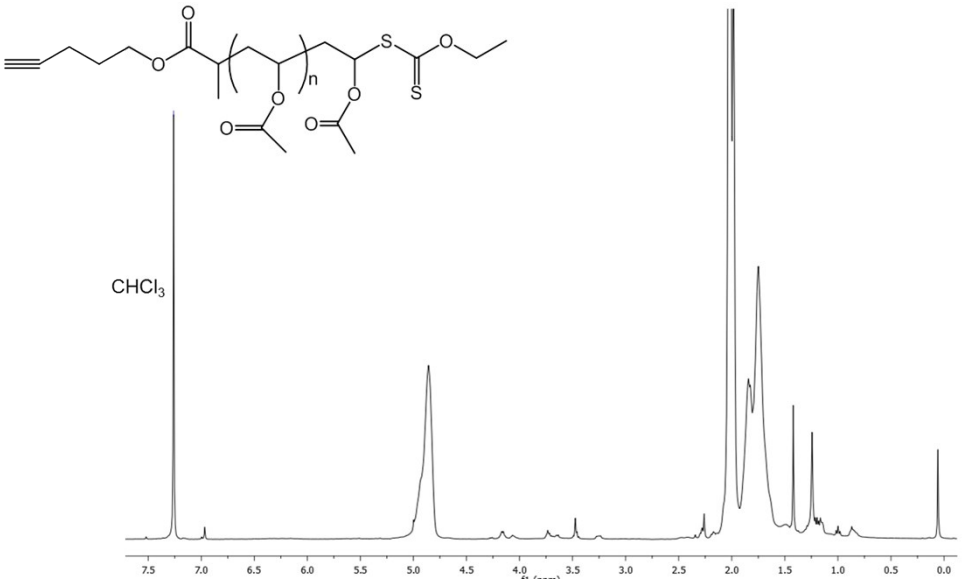

Fig. S8: ^1H NMR spectrum of PVAc after the deprotection of the alkyne moiety in $CDCl_3$.

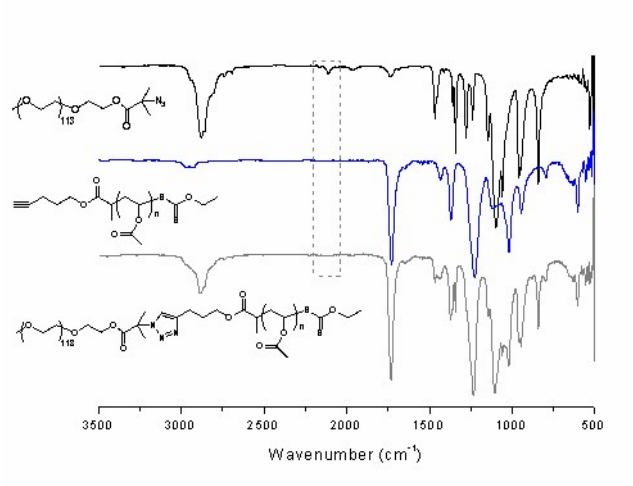

Fig. S9: FTIR-ATR spectra of the azido terminated-poly(ethylene glycol) ($mPEG_{113}$-N_3), alkyne terminated PVAc and the copolymer $mPEG_{113}$-*b*-PVAc after the coupling reaction.

Synthesis of azido terminated-poly(ethylene glycol) ($mPEG_{113}$-N_3)

$mPEG_{113}$-N_3 was synthesized from poly(ethylene glycol) methyl ether bromoisobutyrate (PEG_{113}-BiB) by a nucleophilic substitution with sodium azide (NaN_3). NaN_3 (2.04 g, 31.43 mmol) was added to a solution of $mPEG_{113}$-BiB (4.00 g, 0.79 mmol) in DMF (60 mL) and the reaction proceeded for 24h at 85 °C. The final reaction mixture was dialyzed against deionized water, and the polymer was isolated after freeze drying. ^{1}H NMR (400 MHz, $CDCl_3$) (Figure S10): δ (ppm) 4.32 (t, 2H, -O-C**H$_2$**-), 3.4 (m, 454H, (-O-C**H$_2$**-C**H$_2$**-)$_{113}$), 3.37 (s, 3H, -C**H$_3$**), 1.48 (s, 6H, -(C**H$_3$**)$_2$$N_3$).

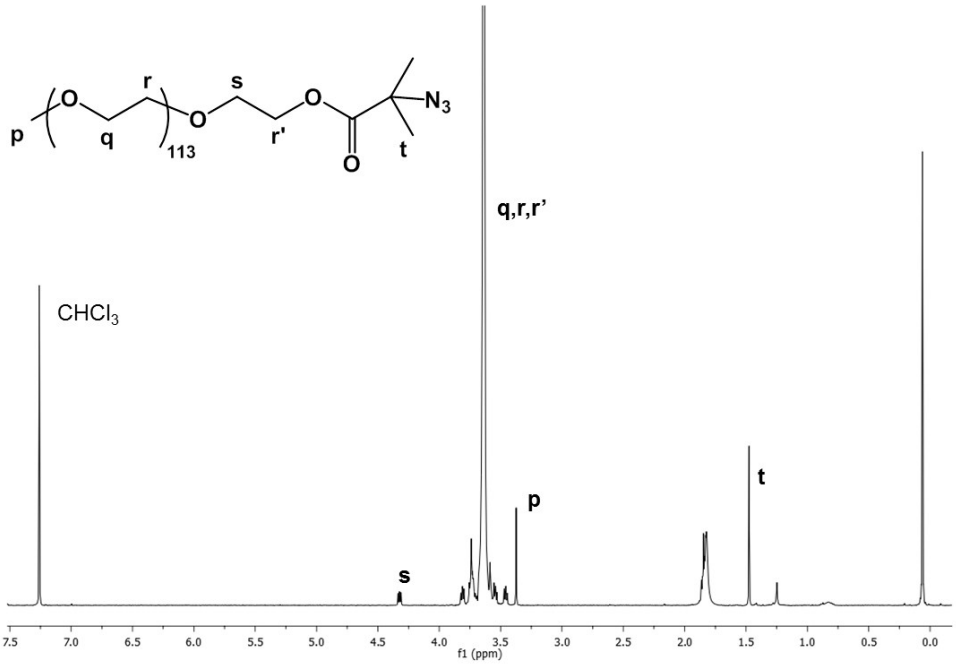

Fig. S10: ^{1}H NMR spectrum of azido terminated-poly(ethylene glycol) ($mPEG_{113}$-N_3) in $CDCl_3$.