Supporting Information

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

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**Fig. S1:** $^1$H NMR spectrum of X1 in CDCl$_3$.

**Fig. S2:** $^{13}$C NMR spectrum of AT-X$_1$ in CD$_2$Cl$_2$. 
**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 ($M_p = 10\ 050\ \text{g mol}^{-1}$; $D = 1.02$) and PVAc samples taken at different times of reaction. Conditions: [VAc]$_0$/[1,4-dioxane]$_0 = 1/1$ (m/m); [VAc]$_0$/[AT- $X_1$]$_0$/[AIBN]$_0 = 100/1/0.2$, $T=60{^\circ}\text{C}$. 
**Fig. S7:** UV-vis spectra of free-PVAc and PVAc synthesised through RAFT polymerization using the different RAFT agents: X₁, AT- X₁ and PAT- X₁ respectively. Samples with 1.5 mg.mL⁻¹ concentration in CHCl₃.

**Fig. S8:** ¹H NMR spectrum of PVAc after the deprotection of the alkyne moiety in CDCl₃.
Synthesis of azido terminated-poly(ethylene glycol) (mPEG\textsubscript{113-N\textsubscript{3}})

mPEG\textsubscript{113-N\textsubscript{3}} was synthesized from poly(ethylene glycol) methyl ether bromoisobutyrate (PEG\textsubscript{113-BiB}) by a nucleophilic substitution with sodium azide (NaN\textsubscript{3}). NaN\textsubscript{3} (2.04 g, 31.43 mmol) was added to a solution of mPEG\textsubscript{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. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) (Figure S10): \(\delta\) (ppm) 4.32 (t, 2H, -O-C\textsubscript{2}H\textsubscript{2}-), 3.4 (m, 454H, (-O-C\textsubscript{2}H\textsubscript{2}-C\textsubscript{2}H\textsubscript{2}-)\textsubscript{113}), 3.37 (s, 3H, -C\textsubscript{2}H\textsubscript{3}), 1.48 (s, 6H, -(C\textsubscript{2}H\textsubscript{3})\textsubscript{2}N\textsubscript{3}).

Fig. S10: \textsuperscript{1}H NMR spectrum of azido terminated-poly(ethylene glycol) (mPEG\textsubscript{113-N\textsubscript{3}}) in CDCl\textsubscript{3}. 