Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Tunable amphiphilic graft copolymers bearing fatty chains and polyoxazoline: synthesis and self-assembly behavior in solution

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EXPERIMENTAL PART

Synthesis of 11-azido-1-undecanol (2)

In one typical experiment, sodium azide (11.6 g, 179 mmol) was dissolved in 200 mL of DMSO at 80 °C in a 1 L round-bottom flask. The resulting solution was allowed to cool to room temperature, after which another solution of 11-bromo-1-undecanol (30.0 g, 119 mmol) in 100 mL of DMSO was added. The reaction mixture was stirred for 24 h at room temperature. At the end of the reaction, 300 mL of deionized water was added and the solution was washed with diethyl ether (3 × 150 mL). The organic phase was then dried in anhydrous $MgSO_4$, filtered off and concentrated. The obtained product was a colorless liquid (22.4 g, 88%). ^{1}H NMR analysis and FTIR analyses confirmed the chemical structure of the pure product.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.53 (t, C**H₂**-OH, 2H), 3.18 (t, C**H₂**-N_3, 2H), 1.08-1.65 (m, C**H₂**, 18H).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 167.6 (**C**OO, 1C), 136.8 (CH_2=**C**CH_3, 1C), 125.4 (**C**H_2=CCH_3, 1C), 64.8 (O**C**H_2, 1C), 51.6 (-**C**H_2-N_3, 1C), 29.6-25.9 (-(**C**H_2)$_9$-, 9C), 18.5 (CH_2=C**C**H_3, 1C).

FTIR spectra revealed the appearance of azide signals at 2100 cm^{-1}.

Synthesis of α-alkyne-POx by CROP

In one typical experiment, 1.64 g (7.83 mmol) of PTS and 40.1 g (471 mmol) of MOx were dissolved in 40 mL of acetonitrile in a 250 mL round-bottom schlenk containing a magnetic stirrer. The content was heated at 80 °C for 1 h 20 under a nitrogen atmosphere. The schlenck was then immersed in liquid nitrogen to cool the reaction medium. ^{1}H NMR (300 MHz, $CDCl_3$) and SEC (RI detector, DMAc) was performed on the crude sample to determine conversion and molecular weight. In order to stop the reaction, 3.80 g (44.8 mmol) of piperidine was added to the schlenck and allowed to stir for 8 h at room temperature. The product was then precipitated in cold diethyl ether and vacuum-dried. The homopolymer P(MOx) (25.0 g, yield: 89%) generated was subsequently characterized by ^{1}H NMR (300 MHz, $CDCl_3$) and SEC (RI detector, DMAc).

Synthesis of the linear amphiphilic macromonomer AzUMA-*b*-POx$_{32}$

In a 500 mL round-bottom flask, 2.71 g (9.64 mmol) of AZuMA was dissolved in 100 mL of DMF, followed by 0.134 g (0.537 mmol) of $CuSO_4.5H_2O$ under magnetic stirring. The mixture was bubbled with nitrogen for 45 min. In a 250 mL round-bottom flask, a mixture comprising of 15.3 g (5.36 mmol) of POx ($M_{n,NMR}$= 2850 g mol^{-1}, $Đ$ = 1.23) and 0.212 g (1.07 mmol) of NaAsc in 100 mL of DMF was bubbled for 45 min with nitrogen. The two mixtures were then mixed together under a nitrogen flux. At this step (t=0), FTIR and SEC (RI detector, DMAc) were performed. The reaction medium was left to stir for 5 days at room temperature. At the end of the reaction, FTIR and SEC (RI detector, DMAc) were performed on the crude product. Cryo-distillation of the latter was performed to discard DMF. 7.03 g of eventual product was dissolved in 20 mL of chloroform and then precipitated in cold methanol. After solvent evaporation, a white powder (5.37 g, yield: 76 %) was collected. This product was characterized by FTIR, ^1H NMR (300 MHz, $CDCl_3$) and SEC (RI detector, DMAc).

In situ polymerization of AzUMA-*b*-POx$_{32}$

In a 10 mm diameter cylindrical cell, AzUMA-*b*-POx$_{32}$ was dissolved in Milli-Q water at a concentration of 1 mg mL^{-1} and let under stirring for 3 h 30 at room temperature. The self-organization was verified by DLS-measurements. After addition of 5 %mol of AIBN, the solution was deoxygenated by thoroughly bubbling argon through the solution. The polymerization was then performed at 80 °C overnight.

FIGURES

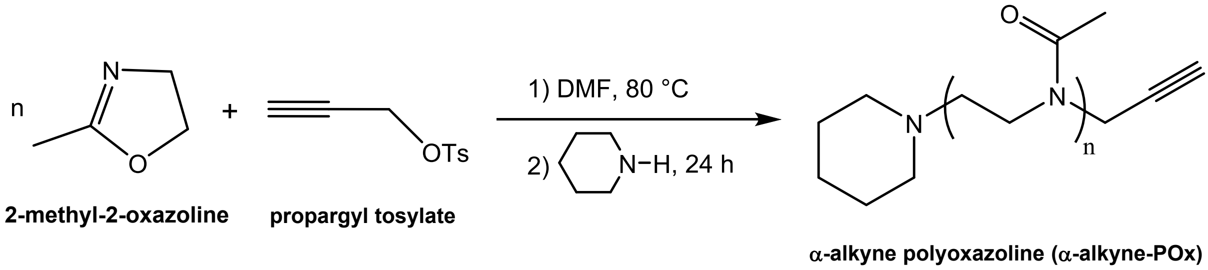

Fig. S1 Synthesis of α-alkyne-polyoxazoline (α-alkyne-POx) by cationic ring-opening polymerization (CROP).

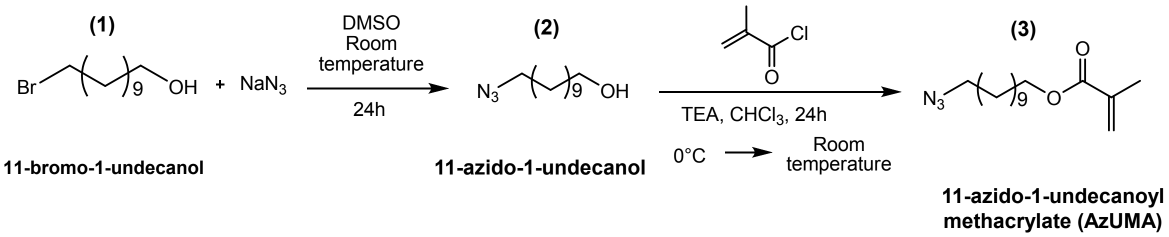

Fig. S2 Synthesis of the monomer 11-azido-1-undecanoyl methacrylate (AzUMA).

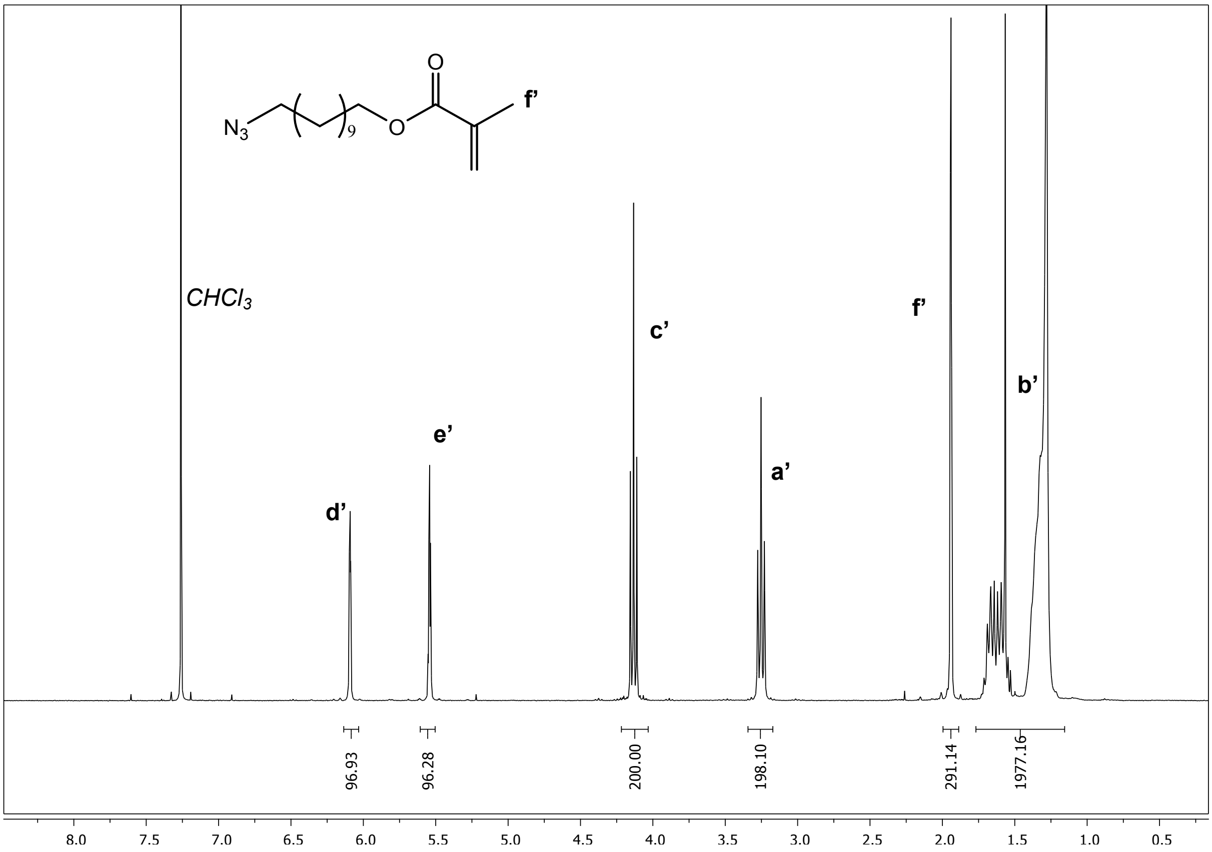

Fig. S3 ^{1}H NMR spectrum (CDCl$_3$; 300MHz) of AzUMA.

^{1}H NMR analysis confirms the formation of the azido methacrylate-based monomer as the signal of the methylene protons in α-position of the azide group was observed at $\delta = 3.26$ ppm (Figure S3) together with the signal at $\delta = 4.14$ ppm corresponding to the -CH$_2$- in α-position of the carboxyl group and the three singlets at $\delta = 1.94$, 5.54 and 6.09 ppm corresponding to the protons of the methacylate group.

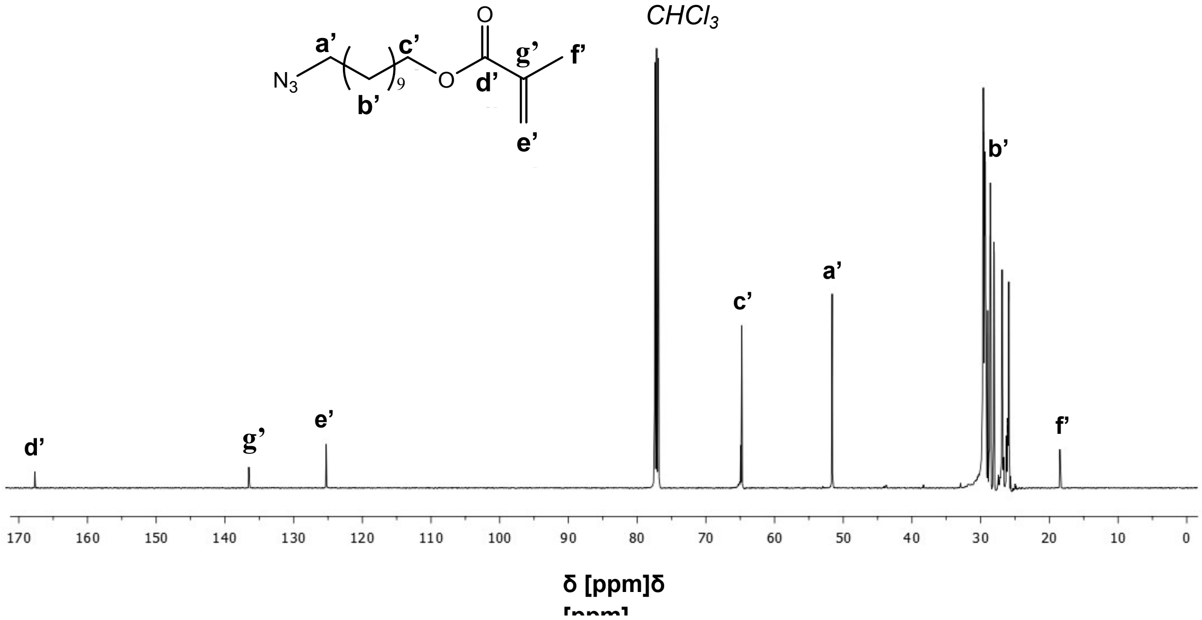

Fig. S4 ^{13} C NMR spectrum ($CDCl_3$; 500MHz) of AzUMA.

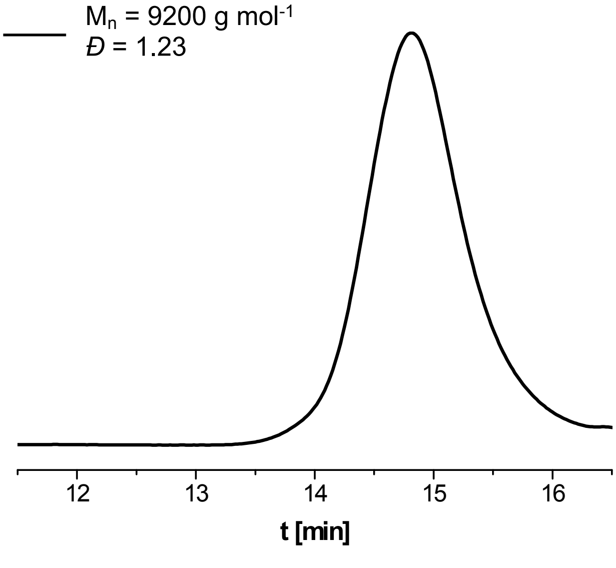

Fig. S5 SEC trace (in THF) of poly(11-azido-undecanoyl methacrylate) ($P(AzUMA)_{23}$) synthesized by RAFT polymerization.

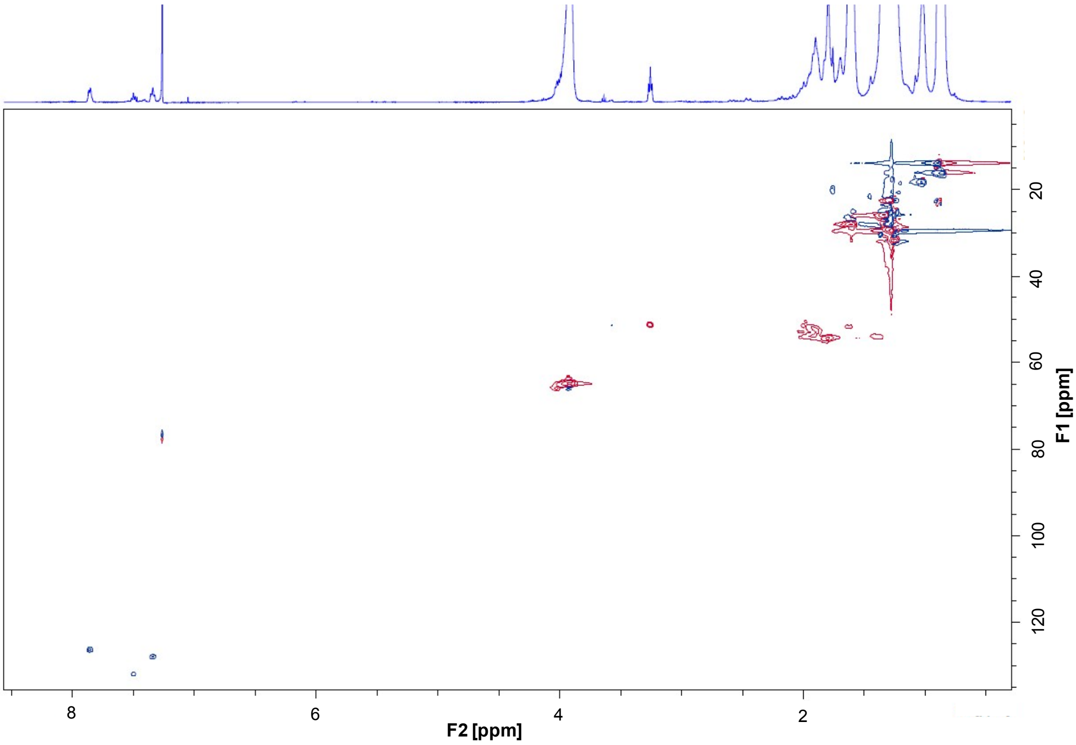

Fig. S6 Phase sensitive HSQC spectrum ($CDCl_3$; 500 MHz,) of P($AzUMA_2$-*stat*-LM_{28}) synthesized by RAFT (red: CH_2, blue: CH/CH_3).

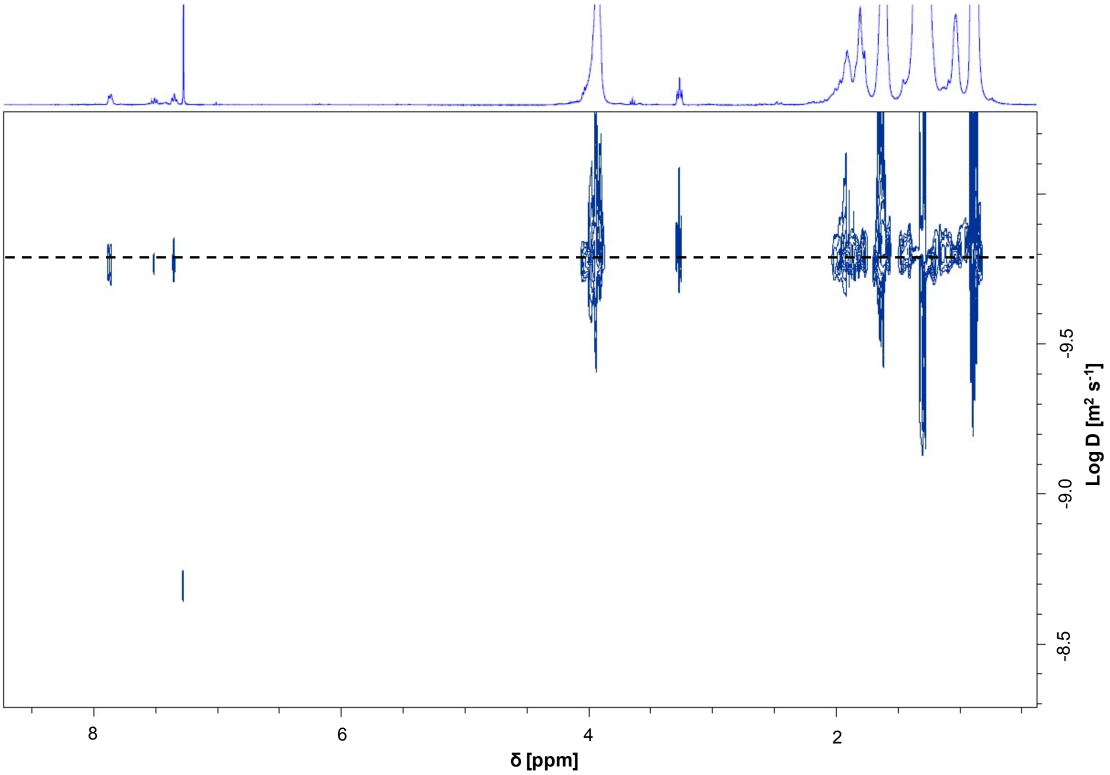

Fig S7. ^1H DOSY NMR spectrum ($CDCl_3$; 600 MHz) of P($AzUMA_2$-*stat*-LM_{28}) synthesized by RAFT.

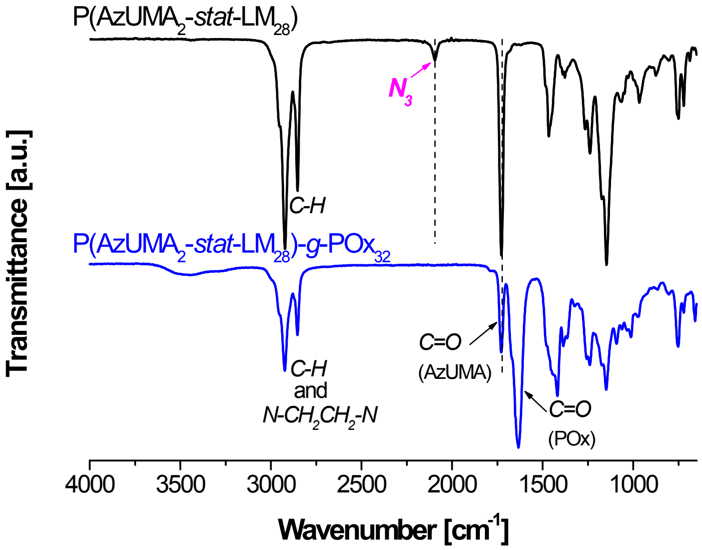

Fig. S8 IR spectra of P(AzUMA$_2$-*stat*-LM$_{28}$) and P(AzUMA$_2$-*stat*-LM$_{28}$)-*g*-POx$_{32}$.

Linear amphiphilic macromonomer AzUMA-*b*-POx$_{32}$

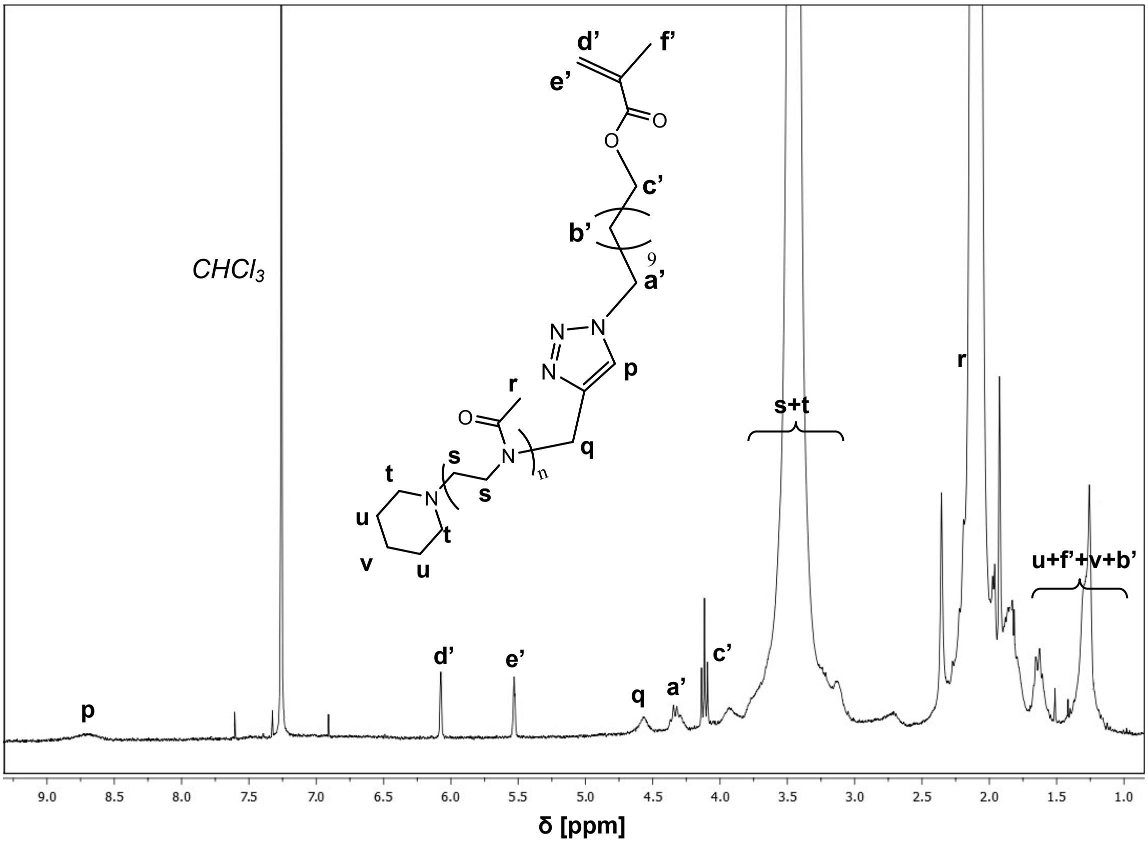

Fig. S9 ^{1}H NMR spectrum (CDCl$_3$; 300 MHz) of AzUMA-*b*-POx$_{32}$ synthesized by click chemistry.

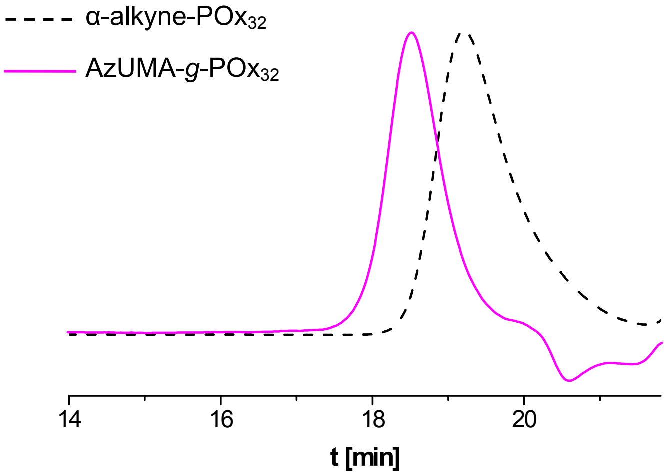

Fig. S10 SEC traces (in DMAc) of α-alkyne-POx$_{32}$ and AzUMA-*b*-POx$_{32}$.

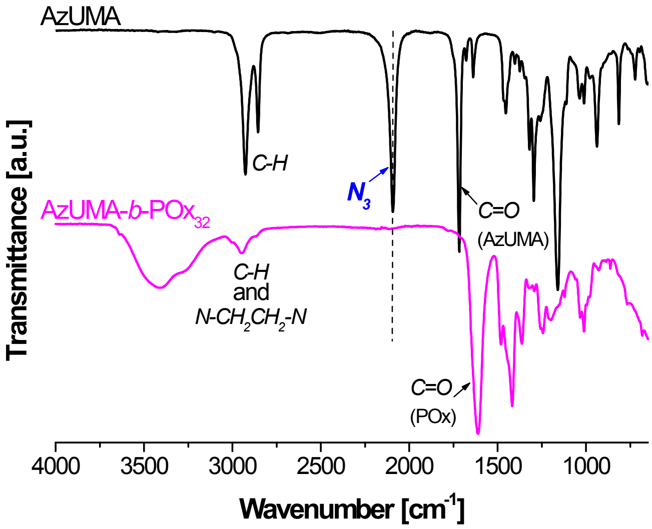

Fig. S11 IR spectra of AzUMA and AzUMA-*b*-POx$_{32}$.

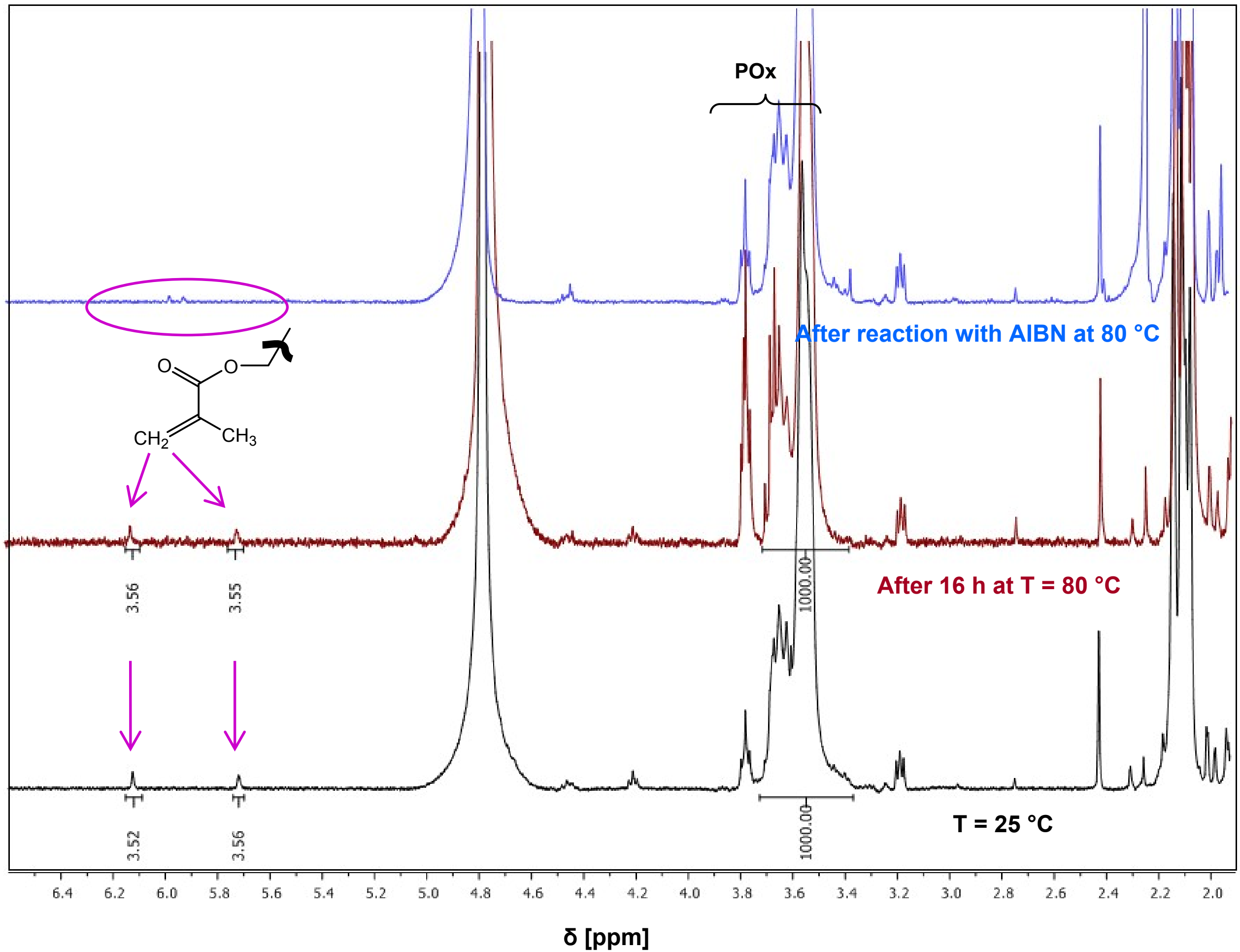

Fig. S12 ^{1}H NMR spectra (D$_2$O; 300 MHz) of AzUMA-*b*-POx$_{32}$ at different temperatures, before and after addition of AIBN.