Supplementary Information

for

Synthesis of modifiable photo-responsive polypeptides bearing allyloxylated azobenzene side-chains

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Instrumentation: ^{1}H NMR spectra were recorded using an AVANCE 400 spectrometer (Bruker Biospin, Switzerland). Deuterium chloride solution (DCl), Trifluoroacetic Acid-d (TFA-*d*), Dimethyl sulfoxide-d_6 (DMSO-d_6), or deuterated chloroform ($CDCl_3$) were used as the solvent for ^{1}H NMR measurements. Fourier transform infrared spectroscopy (FT-IR) was recorded using a Bruker Tensor 27 FT-IR spectrometer (Bruker, Bremen, Germany) in the range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1} and 32 scans. Thermal gravimetric analysis (TGA) was performed on a TA Instrument Q600 analyzer. Samples were heated from ambient temperatures to 400 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument DSC822 calorimeter with a heating rate of 10 °C/min. Tandem gel permeation chromatography (GPC) experiments were performed on a system equipped with an isocratic pump (Model 1100, Agilent Technology, Santa Clara, CA), and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA). The temperature of the refractive index detectors was 25 °C. Separations were performed using serially connected size exclusion columns (500, 10^3, 10^4 and 10^5 Å Phenogel columns, 5 μm, 7.8 × 300 mm, Phenomenex, Torrance, CA) at 50 °C using DMF containing 0.1 M LiBr as the mobile phase. The molecular weights of all polymers were determined using the *dn/dc* values calculated from internal calibration system provided by Wyatt Technology. Circular dichroism (CD) spectroscopy was carried out on a Bio–Logic MOS 450 CD spectrometer. The polymer solution was placed in a quartz cell with a light path of 1.0 cm. The mean residue molar ellipticity was calculated by the formula: [θ] in $deg \cdot cm^2 \cdot dmol^{-1}$

= (millidegrees × mean residue weight)/(pathlength in millimeters × concentration of polypeptide in mg/mL). The α-helix contents of polypeptides were calculated using the following equation: % α-helix = $(-[\theta_{222}] + 3{,}000)/39{,}000$.[1]

References

1. H. Lu, J. Wang, Y. Bai, J. W. Lang, S. Liu, Y. Lin and J. Cheng, *Nat Commun*, 2011, **2**, 206.

Supplementary Figures

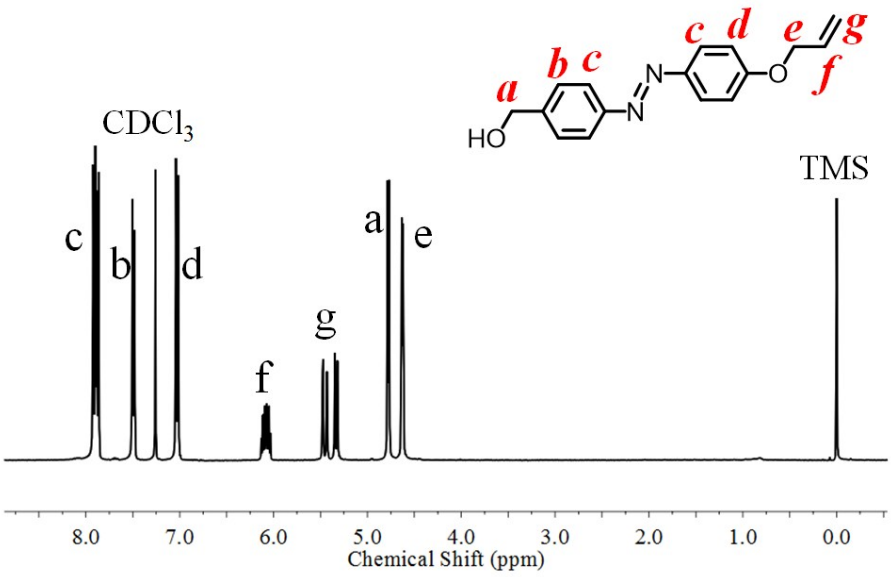

Figure S1. ^{1}H NMR spectrum of Azoene-OH in $CDCl_3$.

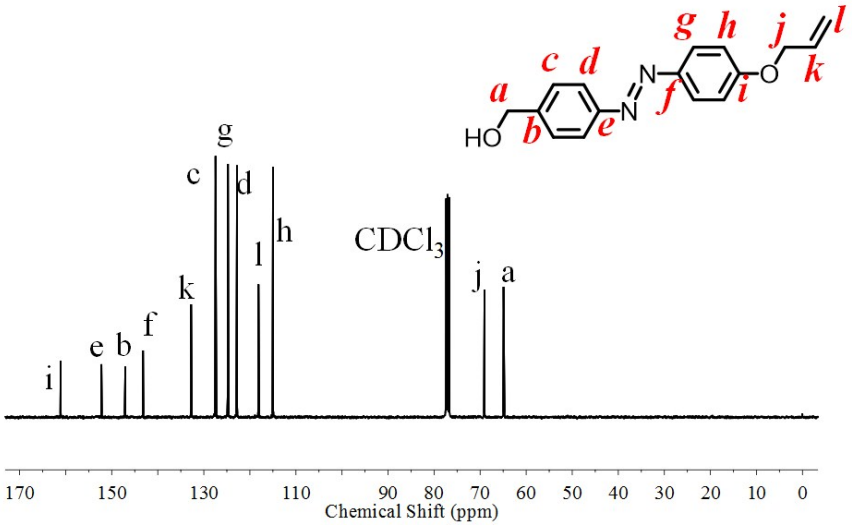

Figure S2. ^{13}C NMR spectrum of Azoene-OH in $CDCl_3$.

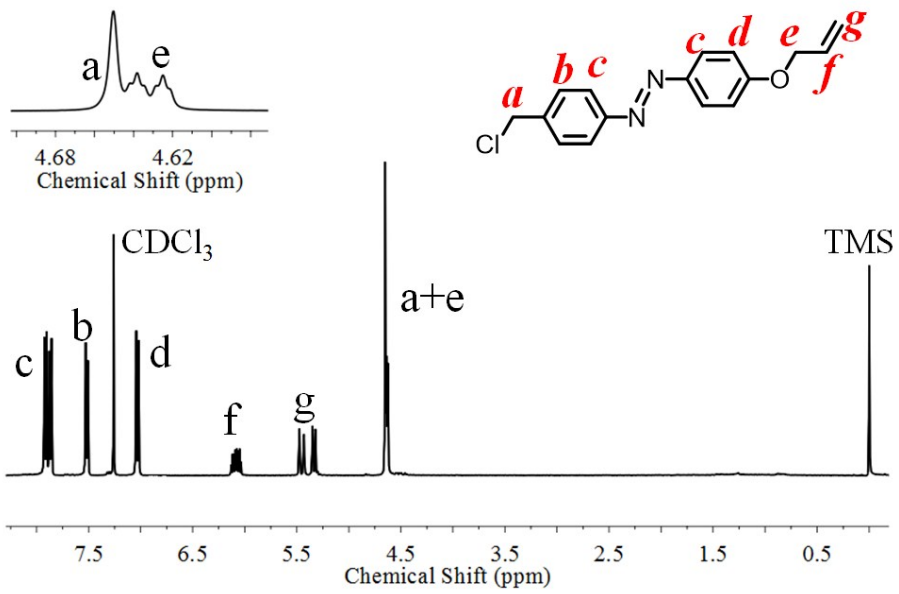

Figure S3. ^{1}H NMR spectrum of Azoene-Cl in $CDCl_3$.

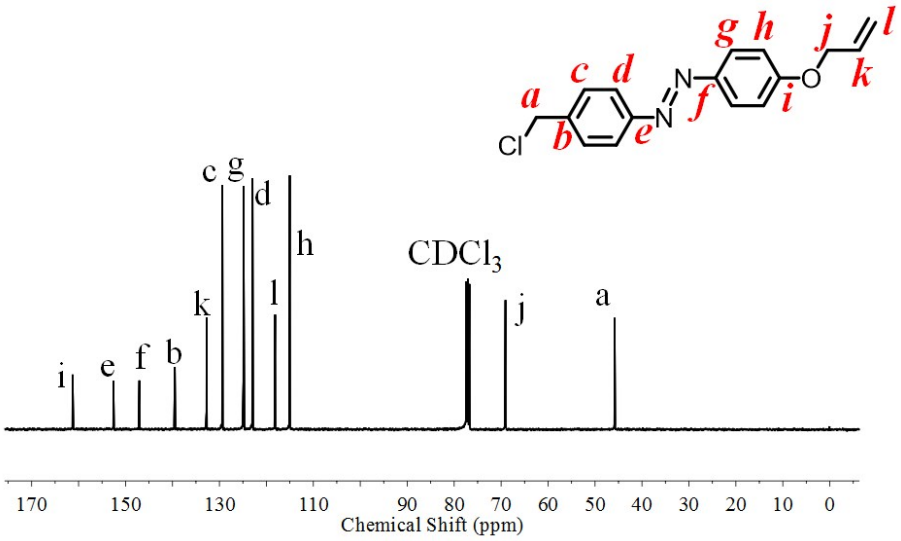

Figure S4. ^{13}C NMR spectrum of Azoene-Cl in $CDCl_3$.

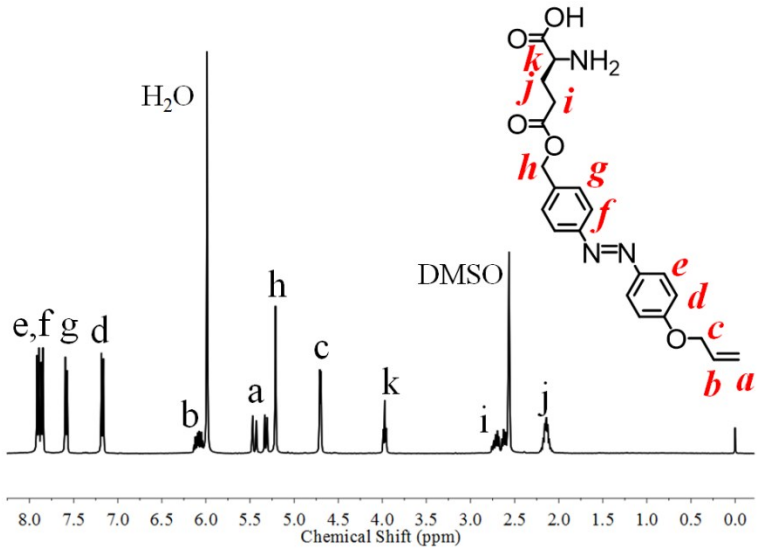

Figure S5. ^{1}H NMR spectrum of $_{L}$-Azoene-Glu-AA in DMSO-d_6: DCl = 9:1, v/v.

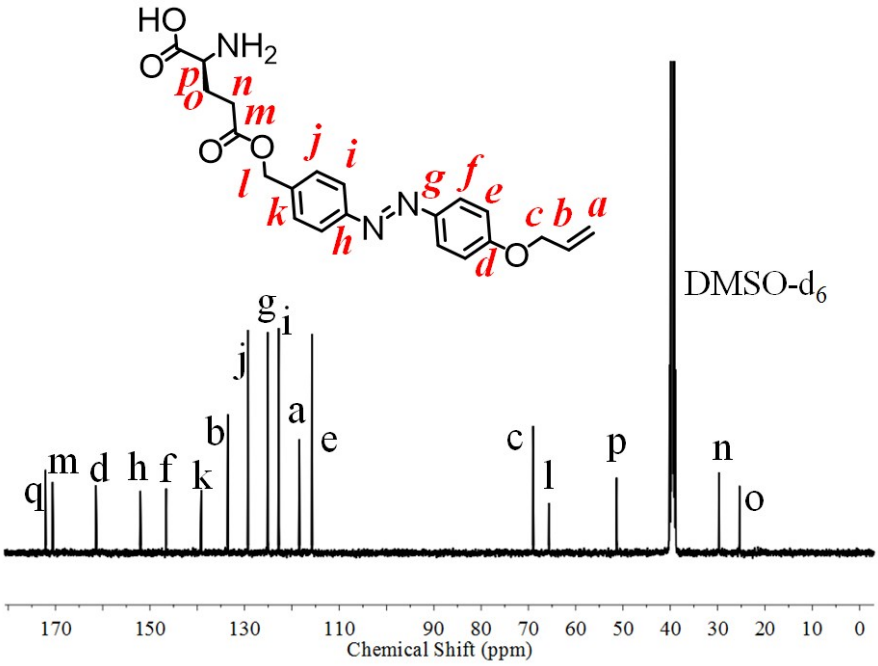

Figure S6. ^{13}C NMR spectrum of $_{L}$-Azoene-Glu-AA in DMSO-d_6: DCl = 9:1, v/v.

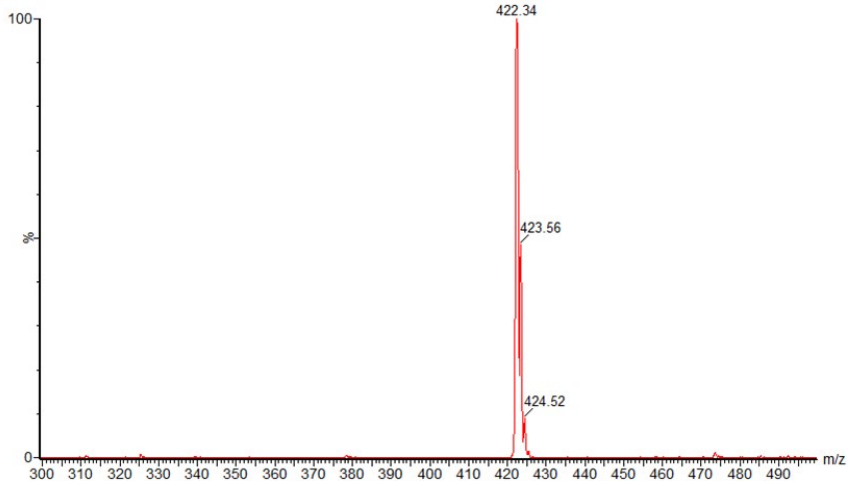

Figure S7. ESI-MS spectrum of Azoene-Glu-NCA. Calculated $[M - H]^+/Z$ = 422.14 Da; Obtained $[M - H]^+/Z$ = 422.34 Da:

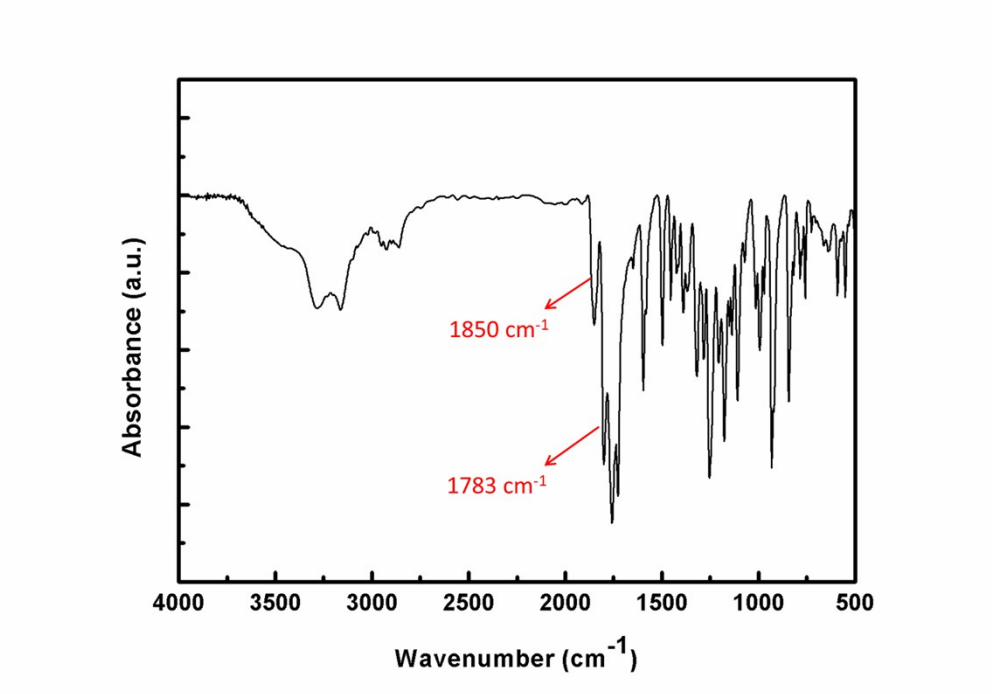

Figure S8. FTIR spectrum of AzoEne-GluNCA.

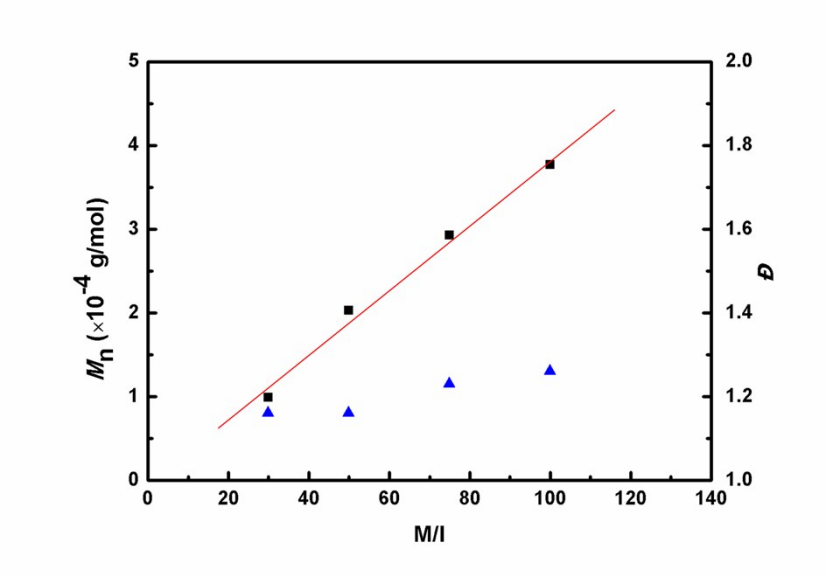

Figure S9. Plots of M_n and $Đ$ of **P(AzoEne-Glu)**s as a function of monomer/initiator (M/I) ratio in the HMDS mediated ROP of **AzoEne-GluNCA**.

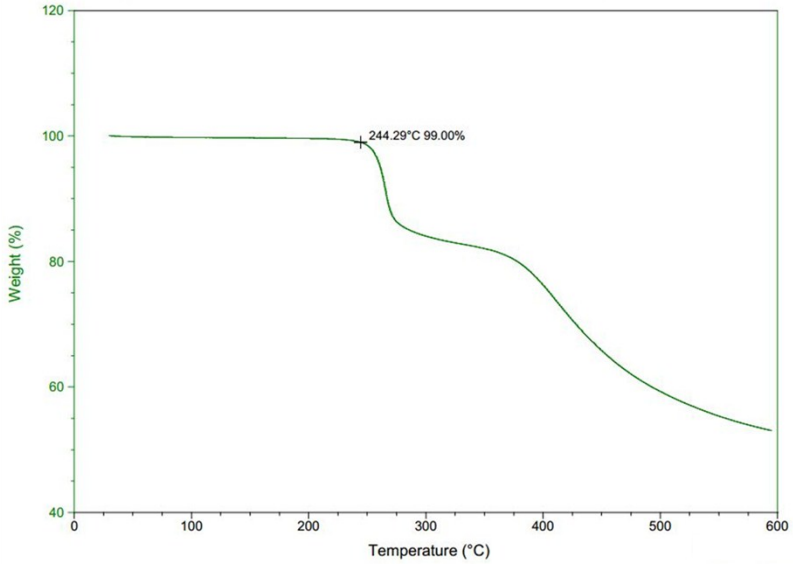

Figure S10. TGA curve of **P(AzoEne-Glu)$_{50}$**.

Table S1. SAXS data for the sample P(AzoEne-Glu)$_{50}$ at different temperatures

20 °C		150 °C	
d (nm)	*hkl*[a]	*d* (nm)	*hkl*[a]
Low-angle region			
2.43	200	2.48	200
1.22	400	1.35	310
1.06	410	1.22	400
0.82	600	1.07	410
		0.82	600

[a]Indices are calculated using the unit cells proposed. The low-angle scatterings result from P(AzoEne-Glu)$_{50}$ at 20 and 150 °C.

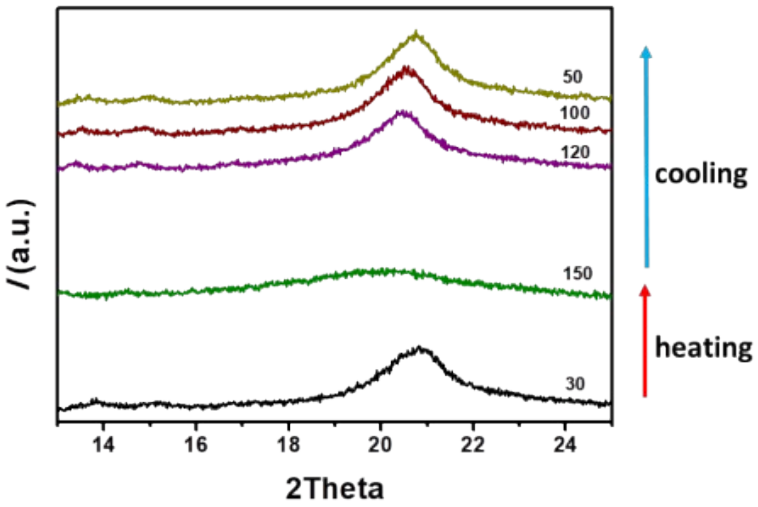

Figure S11. 1D WAXD curves of **P(AzoEne-Glu)$_{50}$**.

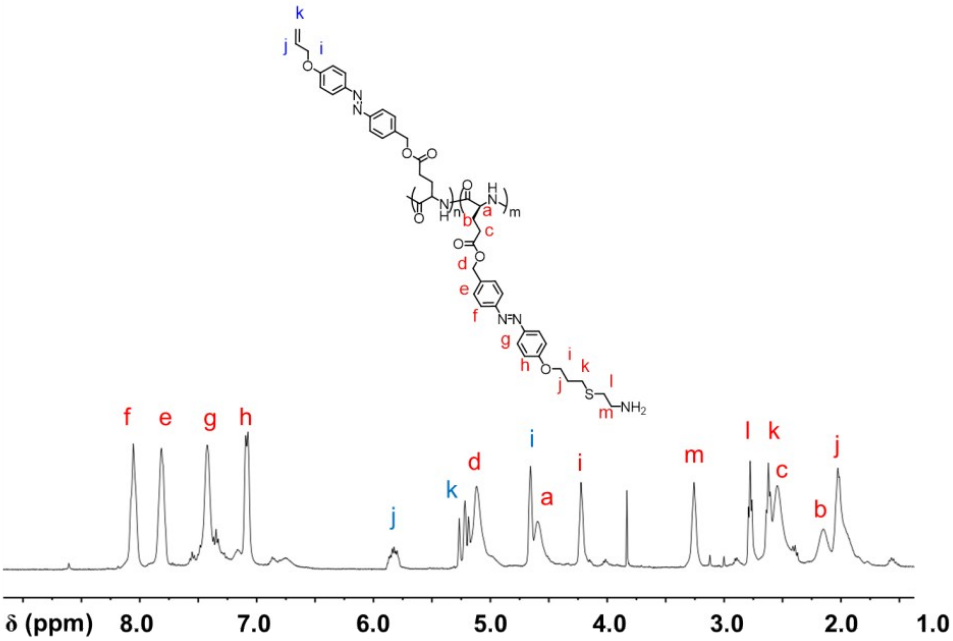

Figure S12. ^{1}H NMR of **P(AzoNH$_2$-Glu)$_{100}$** in TFA-*d*.

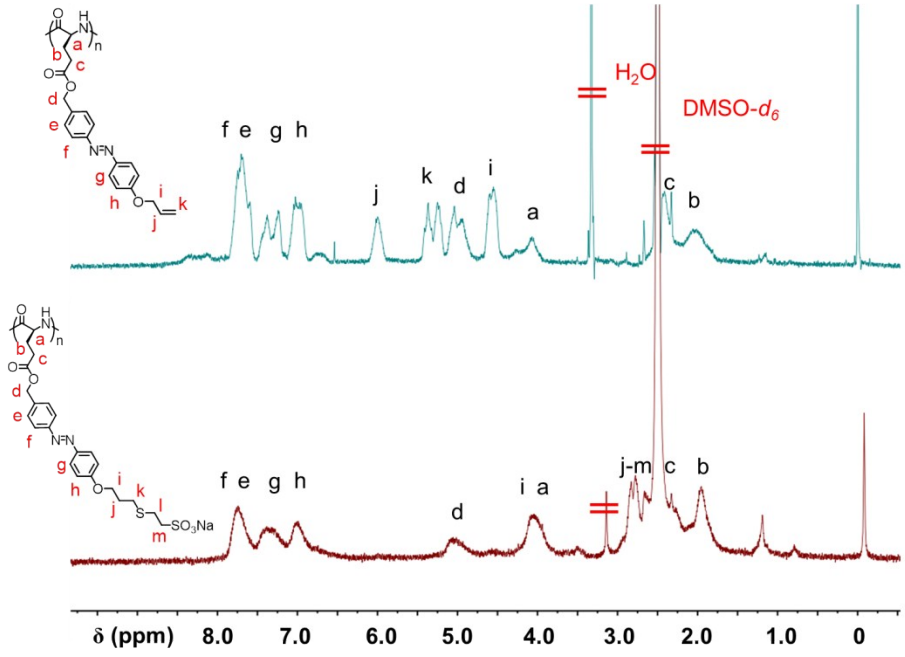

Figure S13. ^{1}H NMR of **P(AzoSO$_3$Na-Glu)$_{100}$** in DMSO-d_6: TFA-d = 9:1, v/v.

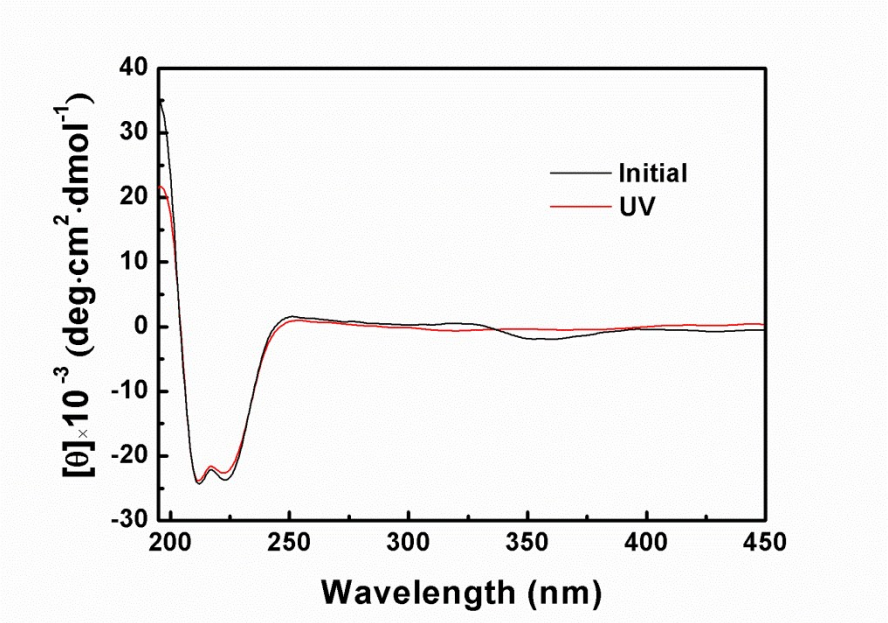

Figure S14. CD spectra of **P(AzoSO$_3$Na-Glu)$_{100}$** in H_2O.

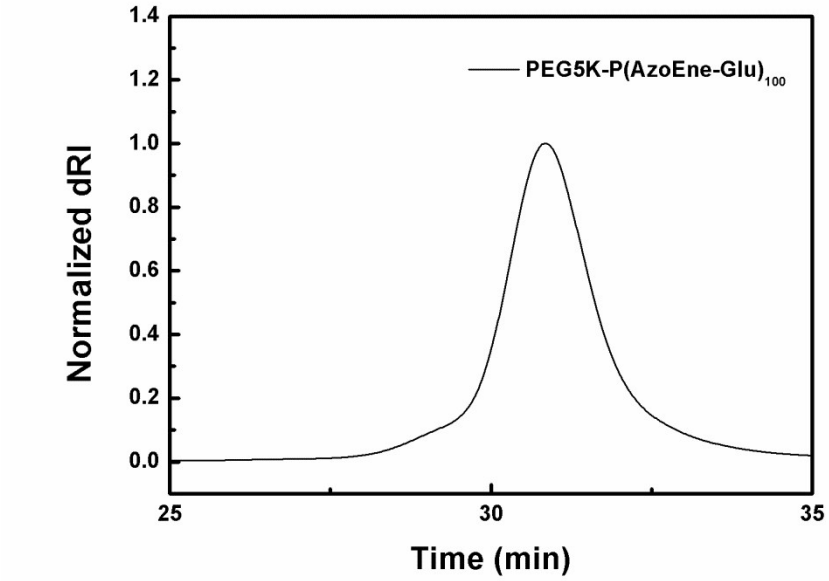

Figure S15. SEC curve of **PEG5K-P(AzoEne-Glu)$_{100}$**.

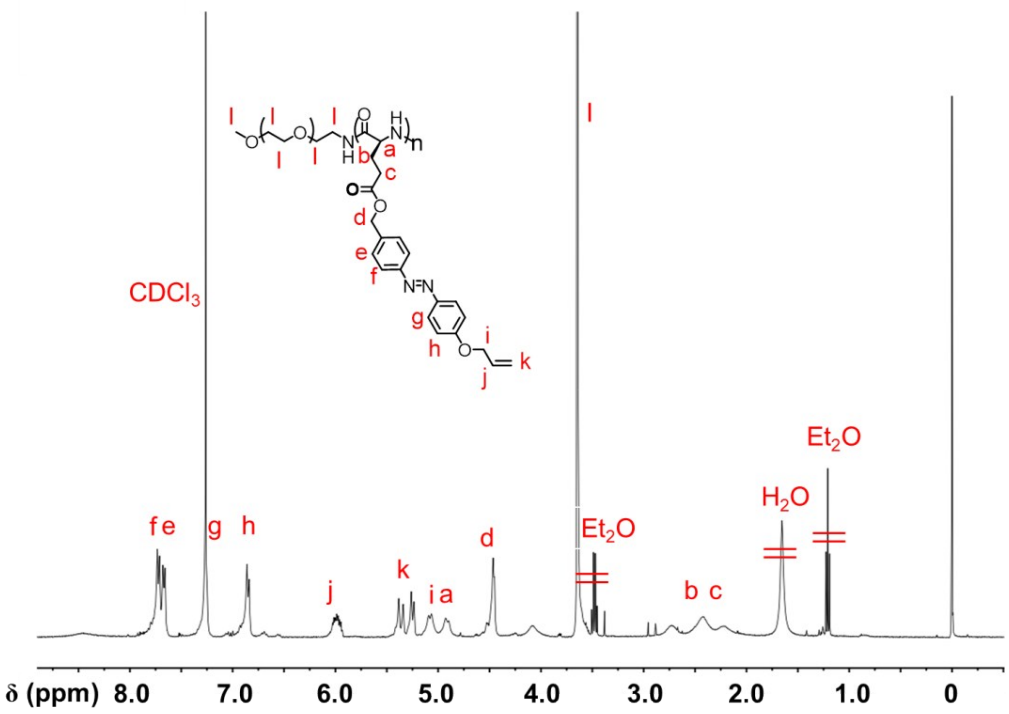

Figure S16. ^{1}H NMR of **PEG5K-P(AzoNH$_2$-Glu)$_{100}$** in $CDCl_3$.

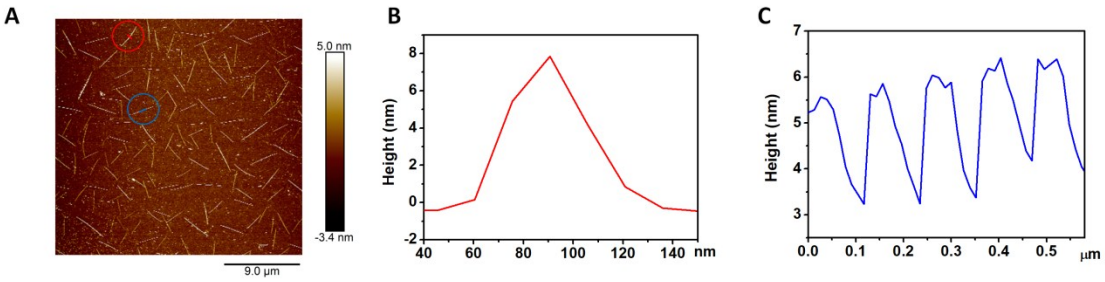

Figure S17. (A) AFM image of diblock co-polymer **PEG5K-P(AzoNH$_2$-Glu)$_{100}$** self-assembled with scale bar of 9.0 µm. (B) Height profile of the helical nanowires with a diameter of ~60 nm. (C) Height profile of the helical nanowires with helical pitches of ~110 nm.