Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

A Novel One-pot Approach towards Dynamically Cross-linked Hydrogels

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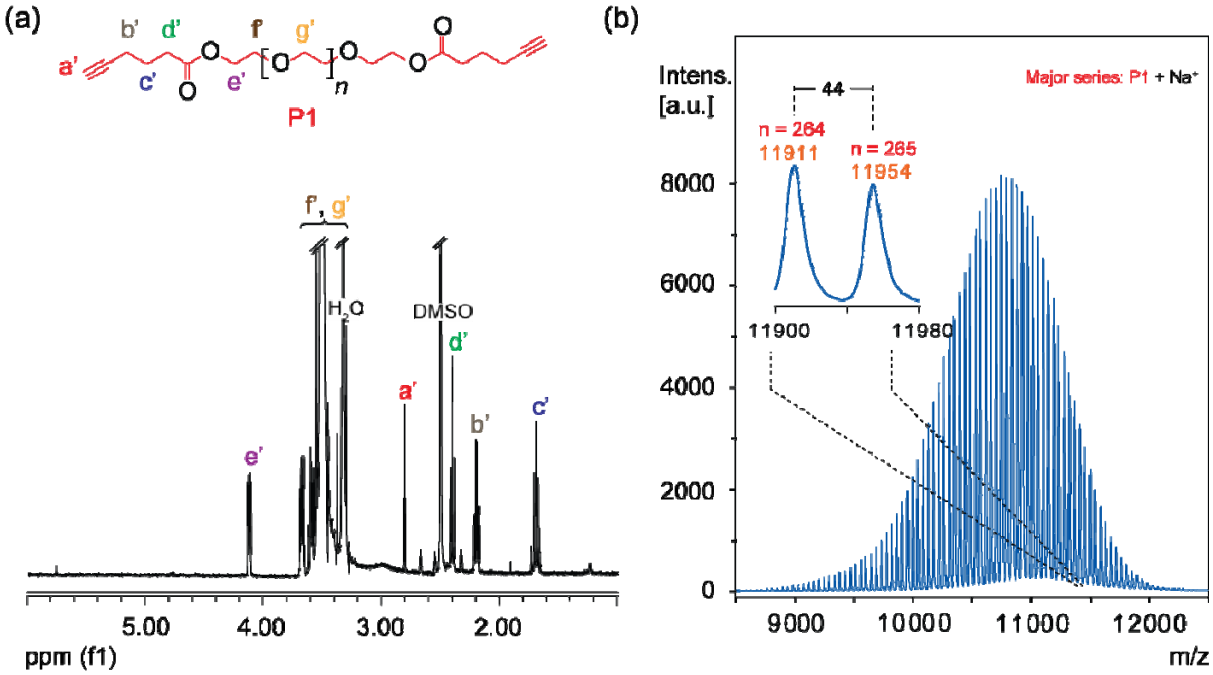


Figure S1. (a) ^{1}H NMR spectrum (d_6-DMSO, 400 MHz) and **(b)** MALDI ToF mass spectrum of α,ω–dialkyne PEG_{10K} **P1**. The mass spectrum was recorded in linear/positive mode using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix and sodium trifluroacetate (NaTFA) as the cationisation agent. The numbers on the mass spectrum denote the number of repeat units (n), the peak m/z values and mass difference. The single mass series correlates to the Na^+ salt.

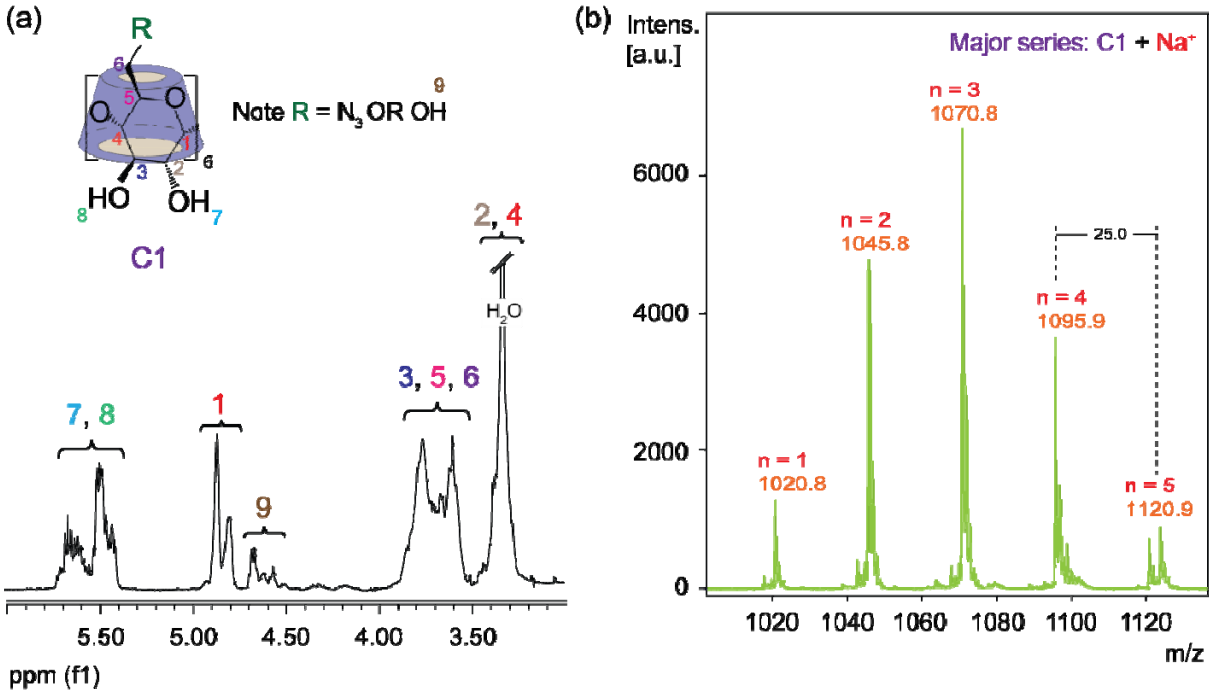
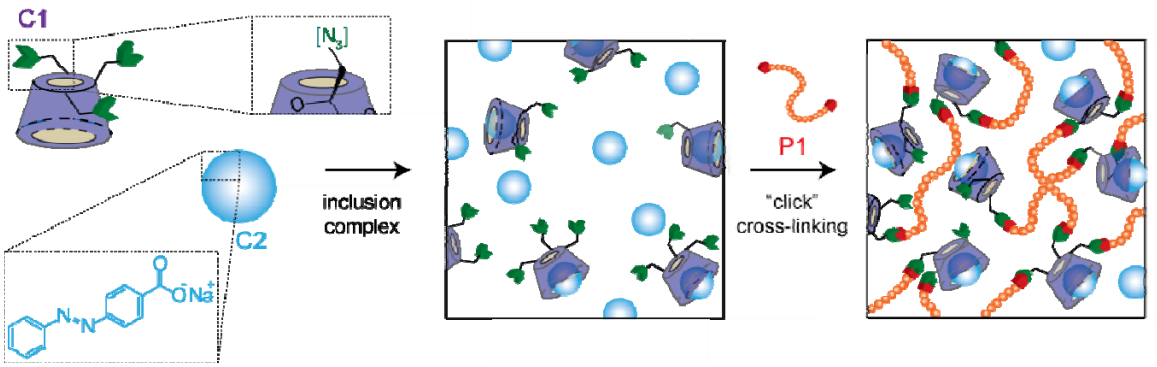


Figure S2. (a) ^{1}H NMR (d_6-DMSO, 400 MHz) spectrum and **(b)** MALDI ToF mass spectrum of **C1.** The mass spectrum was recorded in linear/positive mode using 2,5-dihydroxybenzoic acid (DHB) as the matrix and NaTFA as the cationisation agent. The numbers on the mass spectrum denote the number of repeat units (n), the peak m/z values and mass difference. The major series correlates to the Na^+ salt.



Scheme S1. Schematic representation of the one-pot approach used for the synthesis of covalent (CV) hydrogel networks.

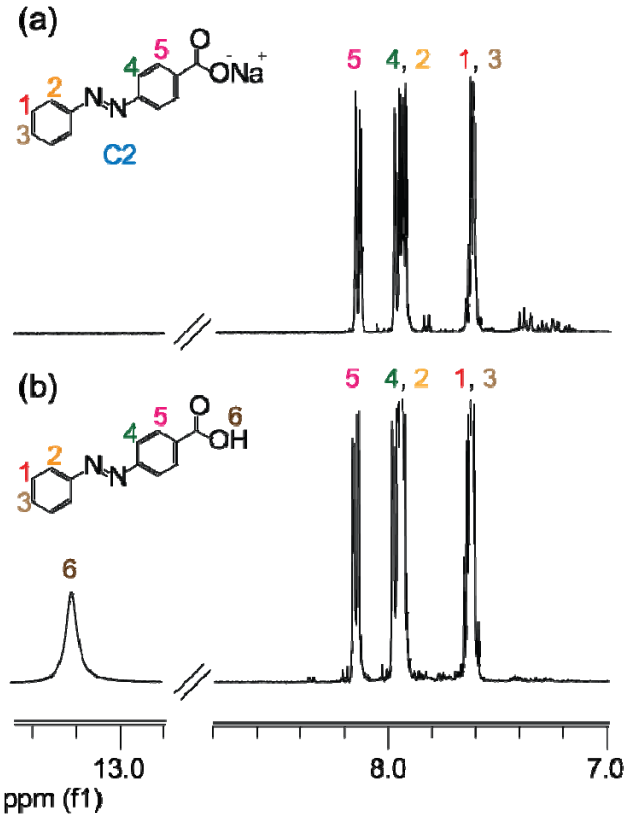


Figure S3. ^{1}H NMR (d_6-DMSO, 400 MHz) spectra of **(a)** *trans* sodium 4-(phenylazo)benzenoate **C2** and **(b)** the starting material, 4-(phenylazo)benzoic acid.

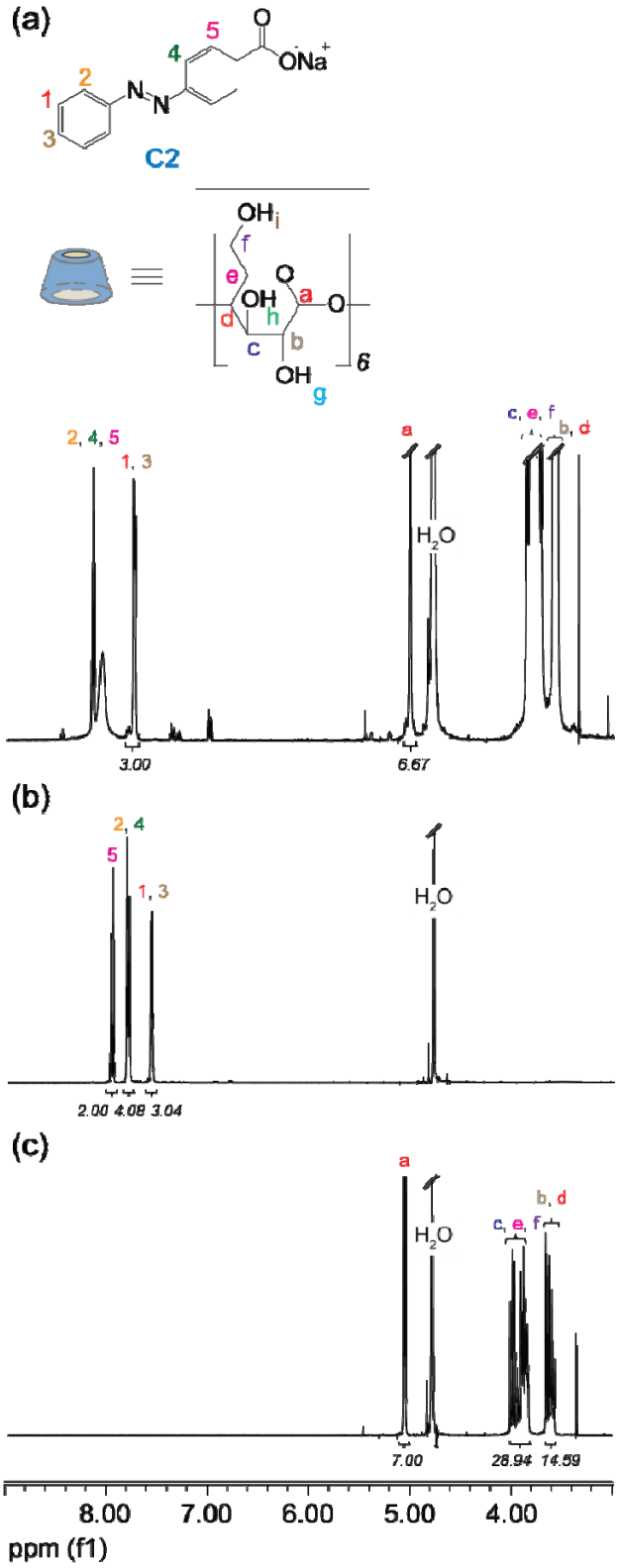


Figure S4. ^{1}H NMR (D_2O, 400 MHz) spectra of **(a)** α-CD/*trans* inclusion complex, **(b)** *trans* **C2** and **(c)** α-CD.

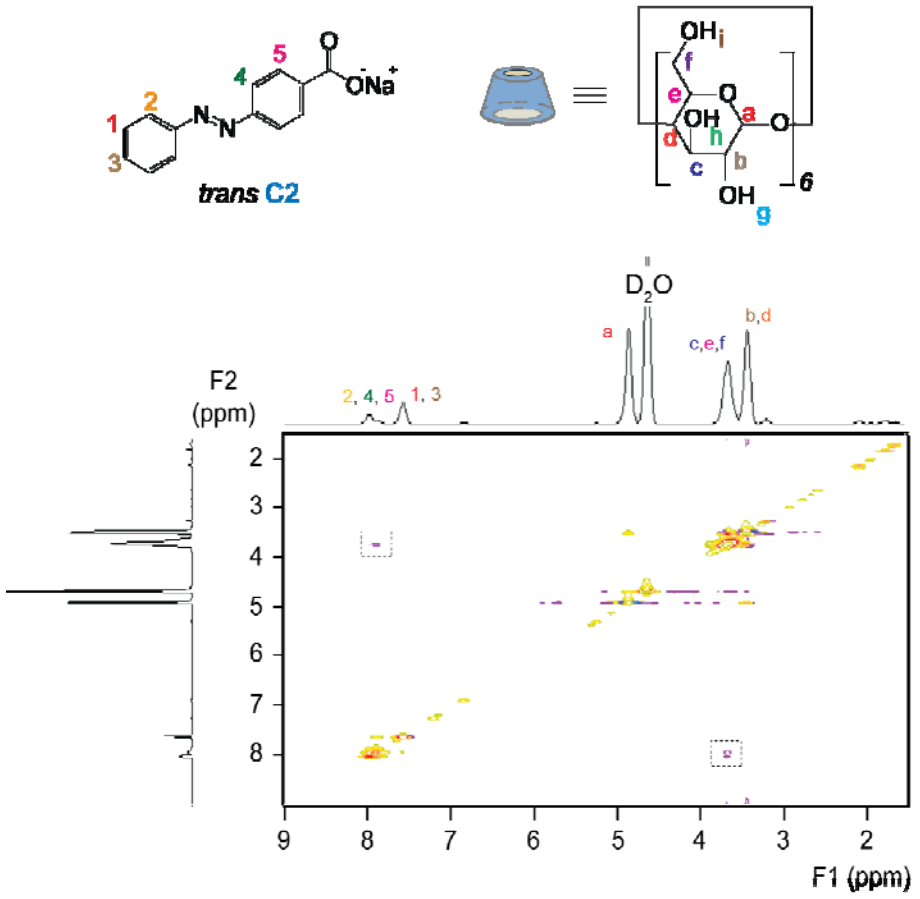


Figure S5. ^{1}H NMR NOESY (D_2O, 400 MHz) spectra of **(a)** *trans* **C2**/CD inclusion complex.

Table S1. Summary of the conditions used to synthesise the SR and CV hydrogels and their physical properties.

Hydrogel[a]	T_c[b] (ºC)	Molar excess of **C2**	ESR[c]	E_v[d] (MPa)	E_e[e] (MPa)
SR-15wt%	20	-	32.50	0.022	0.010
	60	-	20.84	0.191	0.027
SR-21wt%	20	-	19.15	0.081	0.011
	60	-	17.25	0.666	0.041
SR-28wt%	20	-	11.61	0.128	0.020
	60	-	14.21	1.292	0.075
CV-15wt%	20	2	24.75	0.023	0.021
	60	5	18.26	0.728	0.032
CV-21wt%	20	2	19.15	0.102	0.035
	60	5	13.35	1.253	0.051
CV-28wt%	20	2	12.27	0.263	0.046
	60	5	7.13	1.612	0.111

[a] SR refers to sliding-ring networks, CV refers to covalent networks and wt% refers to the weight percent of reagents used in the total reaction mixture

[b] T_c refers to the curing temperature.

[c] Equilibrium swelling ratio (ESR) = $((W_s-W_r)/W_r)$, where W_s refers to the weights of the swollen hydrogel and W_r refers the weight of the reagents used.

[d] Compressive stress required to achieve 0.3 mm/mm deformation on ‘as-prepared' hydrogels. Determined using an Instron Microtester 4858.

[e] Compressive stress required to achieve 0.5 mm/mm deformation on fully swollen hydrogels at 0.5 mm/mm strain. Determined using an Instron Microtester 4858.

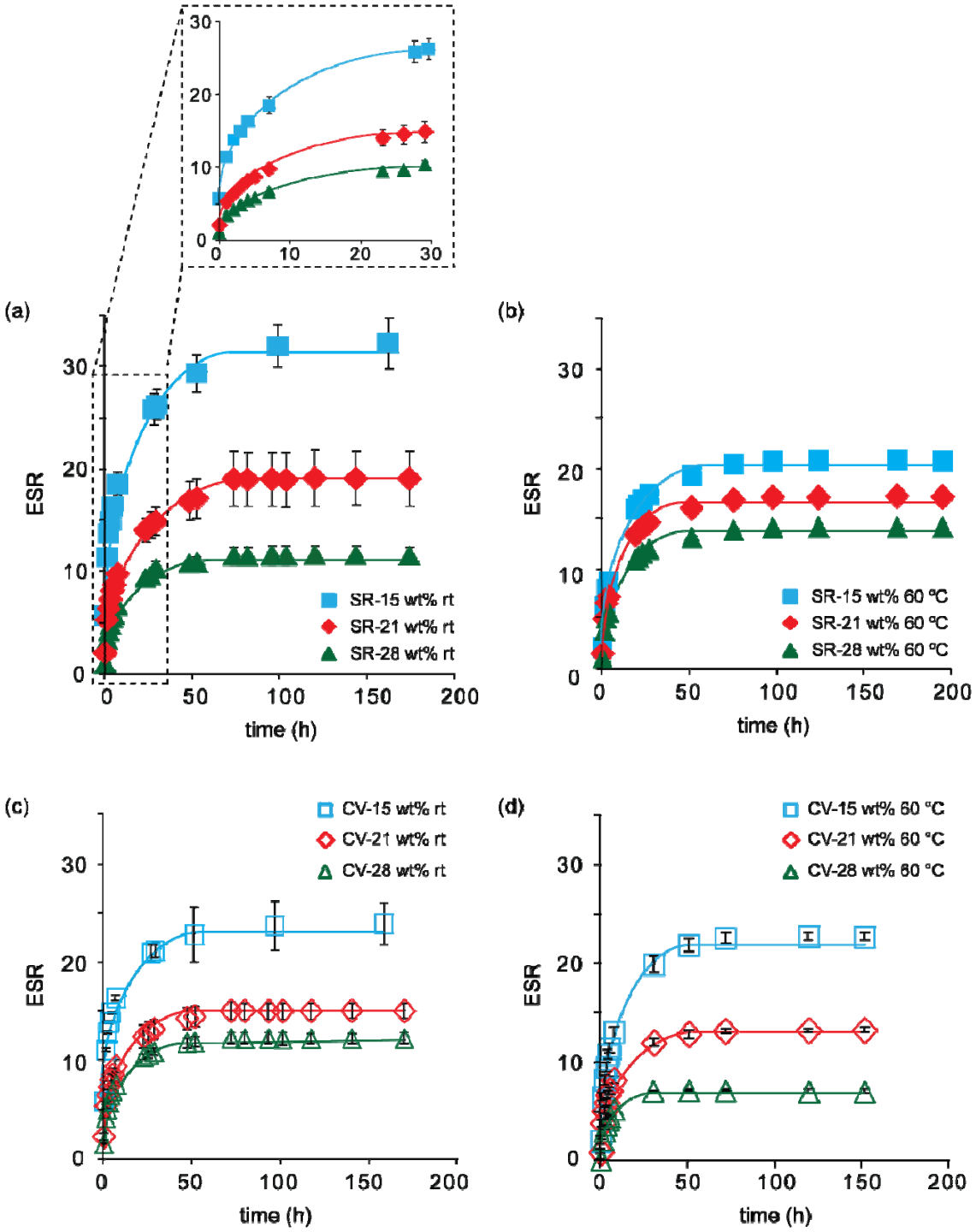


Figure S6. Equilibrium swelling ratio (ESR) of sliding-ring (SR) hydrogels cured at **(a)** 20 °C and **(b)** 60 °C, and covalent (CV) hydrogels cured at **(c)** 20 °C and **(d)** 60 °C. All ESR experiments were conducted in distilled water.

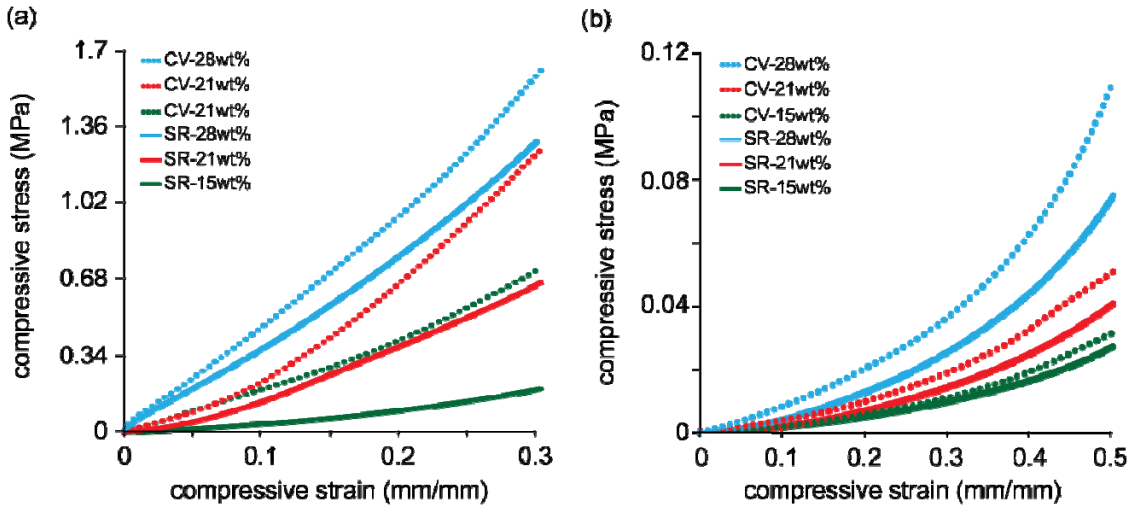
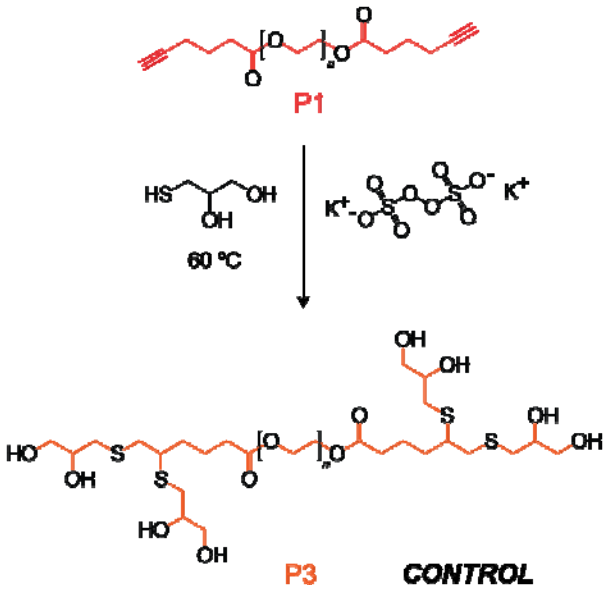


Figure S7. Stress-strain curves of the sliding-ring (SR) and covalent (CV) hydrogels cured at 60 °C at **(a)** no volume change ('as-prepared') and **(b)** equilibrium.



Scheme S2. Synthesis of the control, thioglycerol end-functionalised PEG_{10K} **P3**, via thiolyne click chemistry.

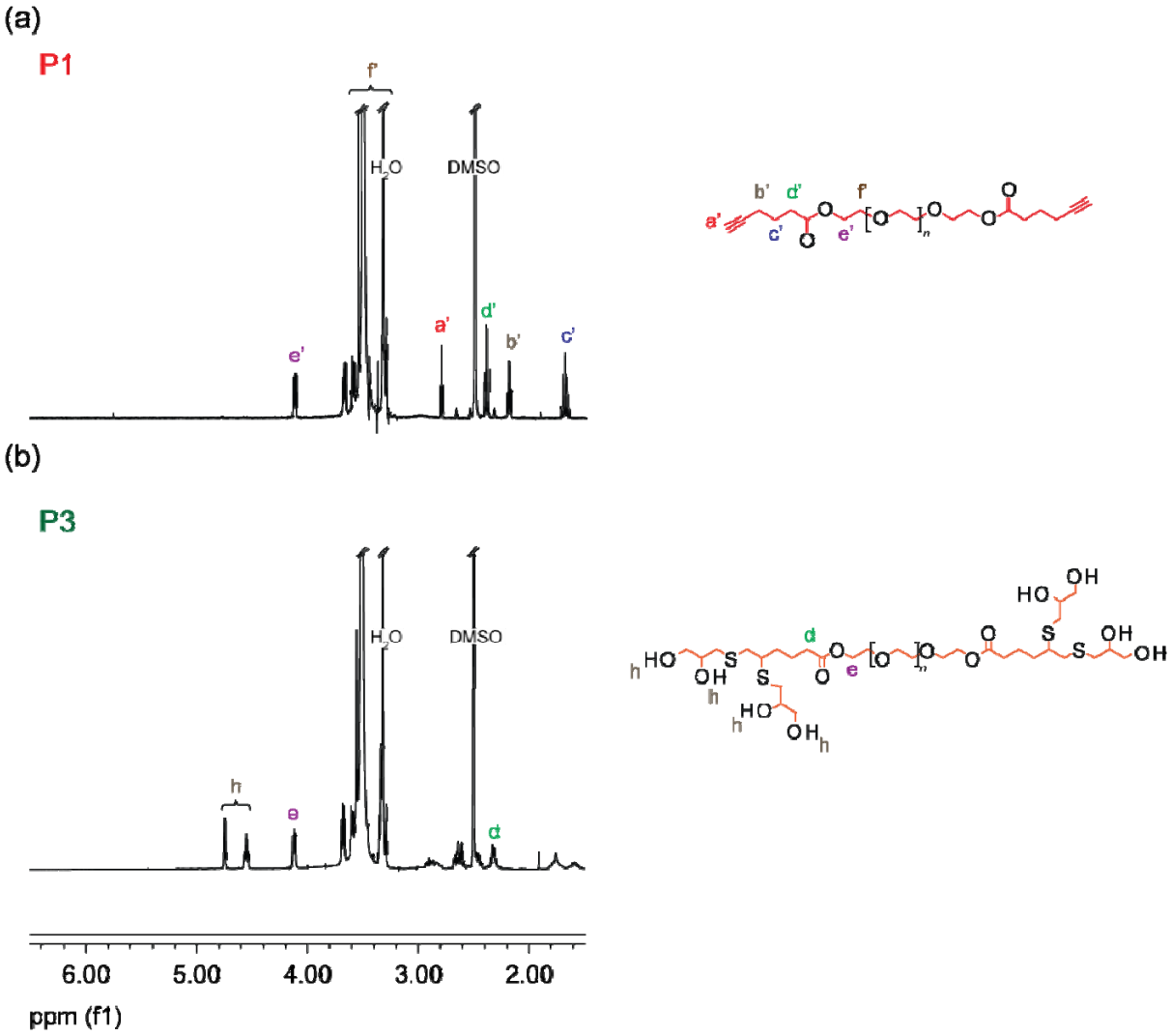


Figure S8. ^{1}H NMR (d_6-DMSO, 400 MHz) spectra of **(a)** the starting material α,ω-dialkyne PEG_{10K} **P1** and **(b)** the control, thioglycerol end-functionalised PEG_{10K} **P3**.

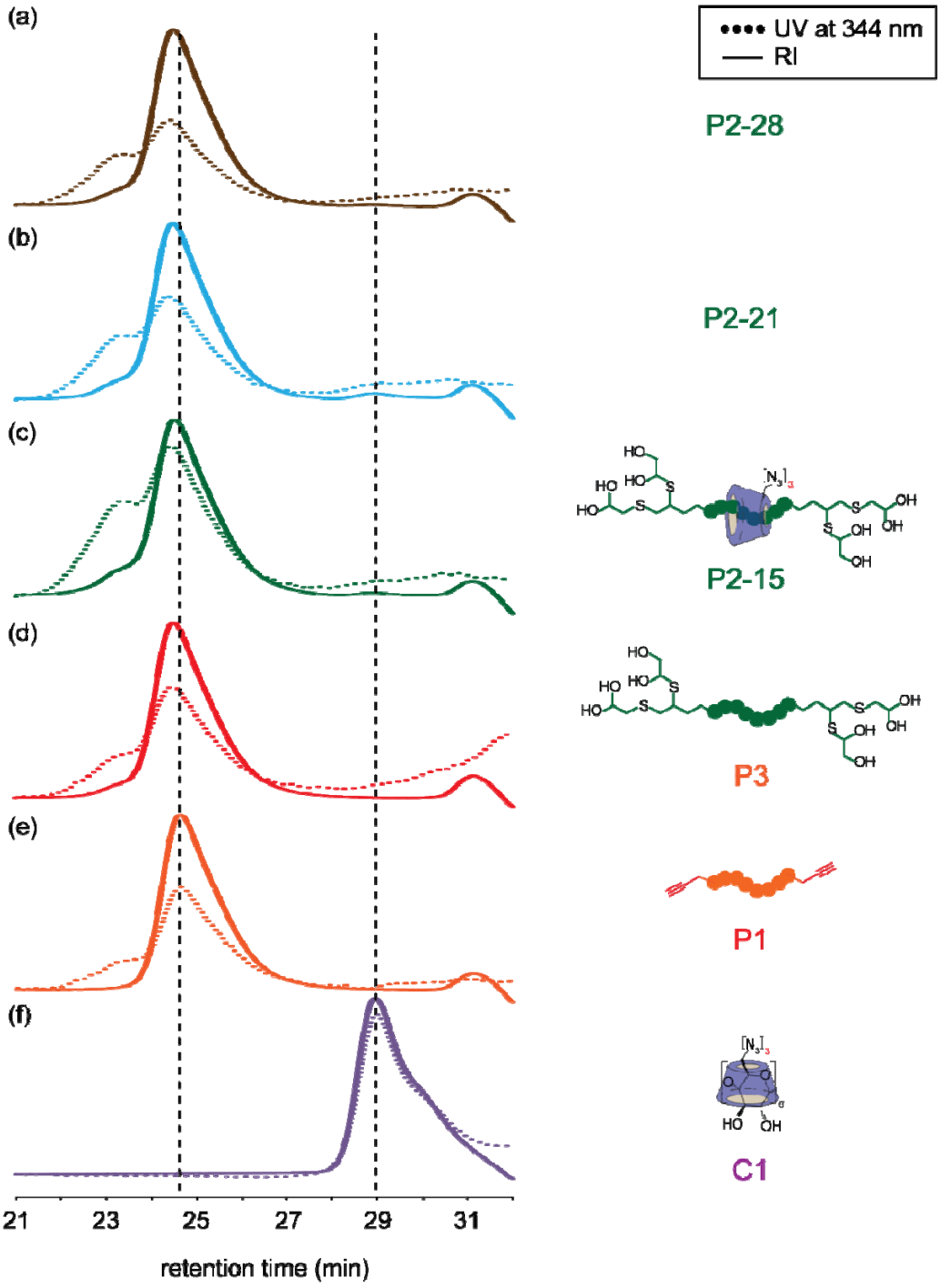


Figure S9. DRI (solid) and UV (dotted) (λ = 344 nm) chromatograms of the rotaxanes **(a) P2-28**, **(b) P2-21** and **(c) P2-15** cured with 28, 21 and 15 wt % of reagents, respectively, **(d)** the control **P3**, **(e)** the starting material **P1** and **(d)** the azido functionalised *α*-CD **C1**.

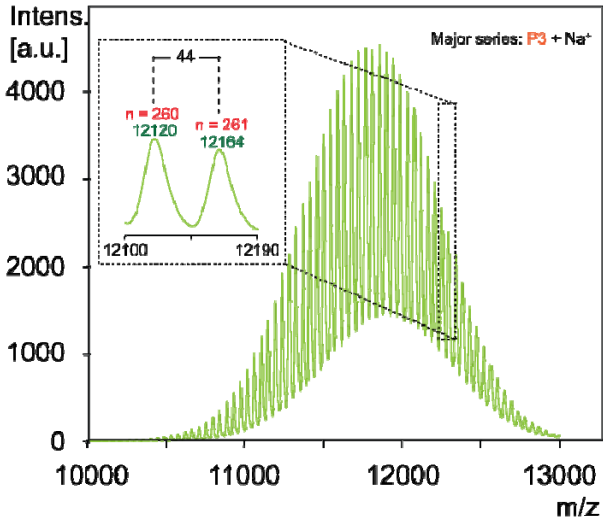


Figure S10. MALDI ToF mass spectrum of **P3.** The mass spectrum was recorded in linear/positive mode using 2,5-dihydroxybenzoic acid (DHB) as the matrix and NaTFA as the cationisation agent. The numbers on the mass spectrum denote the number of repeat units (n), the peak m/z values and mass difference. The major series correlates to the Na^+ salt.

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