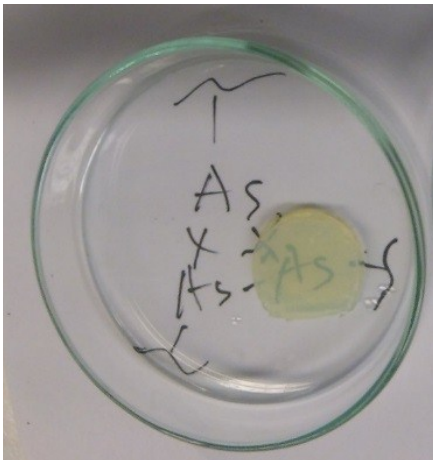
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Polymeric arsenicals as scaffolds for functional and responsive hydrogels



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Reverse Phase High performance liquid chromatography (RP-HPLC)

The gradient of the mobile phase varied in each analysis and purification. The standard analysis method is as followed:

Time (min)	A (%)	B (%)
0.00	90.0	10.0
15.00	50.0	50.0
25.00	0.0	100.0
27.00	90.0	10.0
35.00	90.0	10.0

Calculation of AsAm content with respect to DMA by ^{1}H-NMR

Method 1

$$\frac{\int [2[M]_{AsAm} + 2[M]_{DMA}]_{1.0\,-\,1.8\,ppm} - \int 4[[M]_{AsAm}]_{7.2\,-\,7.8\,ppm} \Big/ 2}{2} = [M]_{DMA}$$

Method 2

$$\frac{\int [[M]_{AsAm} + 7[M]_{DMA}]_{2.1\,-\,3.0\,ppm} - \int 4[[M]_{AsAm}]_{7.2\,-\,7.8\,ppm} \Big/ 4}{7} = [M]_{DMA}$$

The value from each method was averaged.

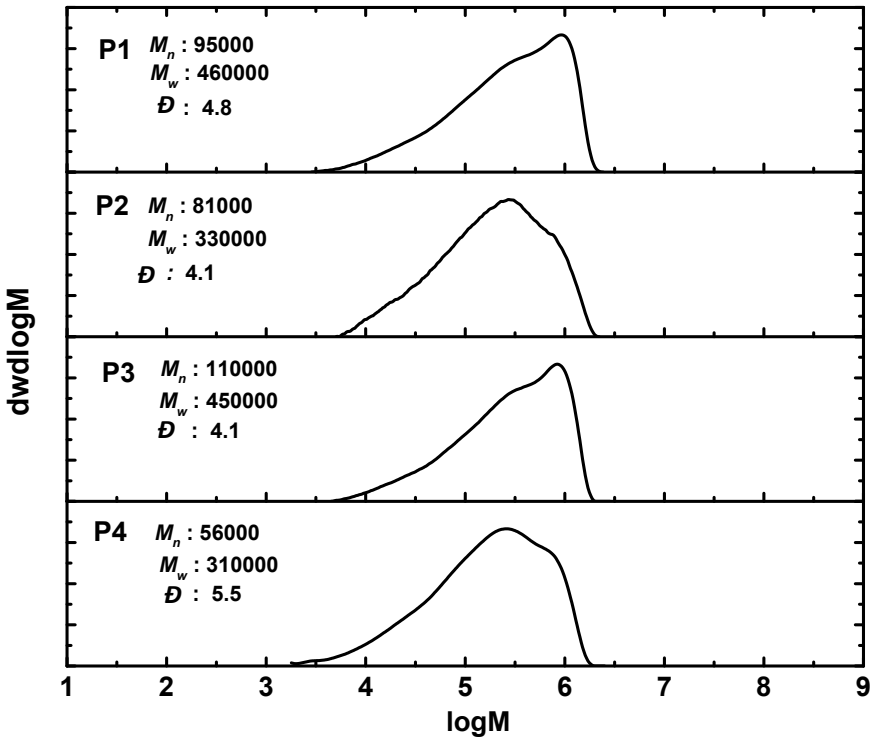

Figure S1. Molecular weight data for polymeric arsenical scaffolds **P1 – P4** obtained from aqueous SEC

Table S1. Composition and molecular weight data for the polymeric arsenical scaffolds **P1 – P4**

	Composition*	M_n**	M_w**	Đ**
P1	**P(DMAm$_{0.98}$-AsAm$_{0.02}$)**	**95000**	**460000**	**4.8**
P2	**P(DMAm$_{0.96}$-AsAm$_{0.04}$)**	**81000**	**330000**	**4.1**
P3	**P(DMAm$_{0.94}$-AsAm$_{0.06}$)**	**110000**	**450000**	**4.1**
P4	**P(DMAm$_{0.92}$-AsAm$_{0.08}$)**	**56000**	**310000**	**5.5**

*** from ^{1}H NMR (*vide supra*) ** from aqueous SEC**

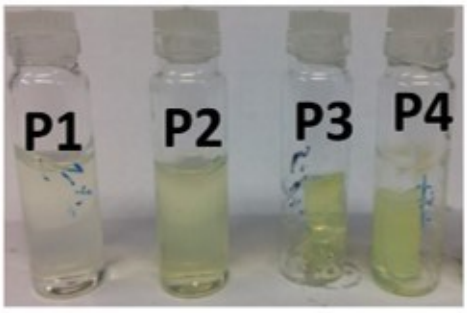

Figure S2: Image of 2.5 wt % arsenohydrogels **P1 – P4** in which **P1** and **P2** formed stable gels while **P3** and **P4** undergo syneresis, expelling up to 40% of the aqueous solution after 2 hours.

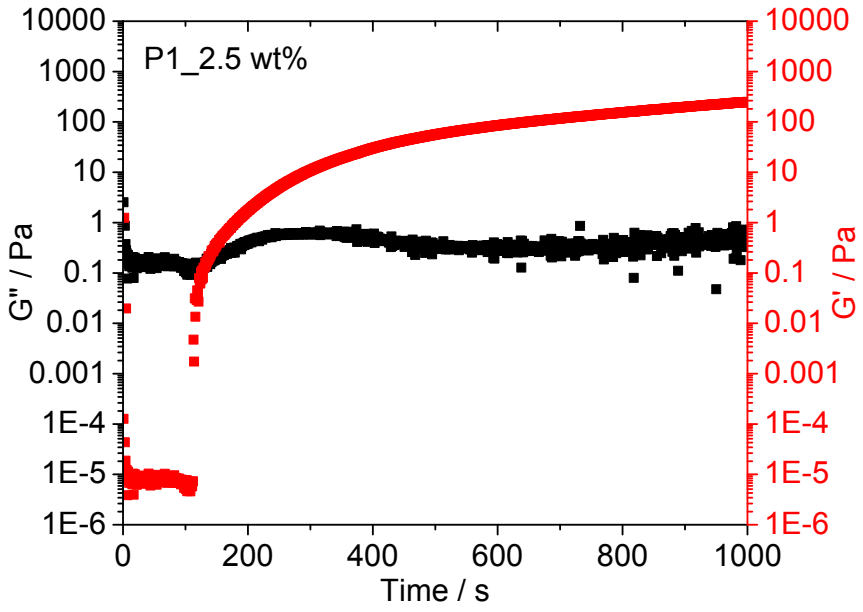

Figure S3: Rheology of the arsenohydrogel formation of **P1** (2.5 wt %, strain = 1.0 %, frequency = 10 rad.s^{-1}, temperature = 60 °C) in the presence of H_3PO_2 and KI

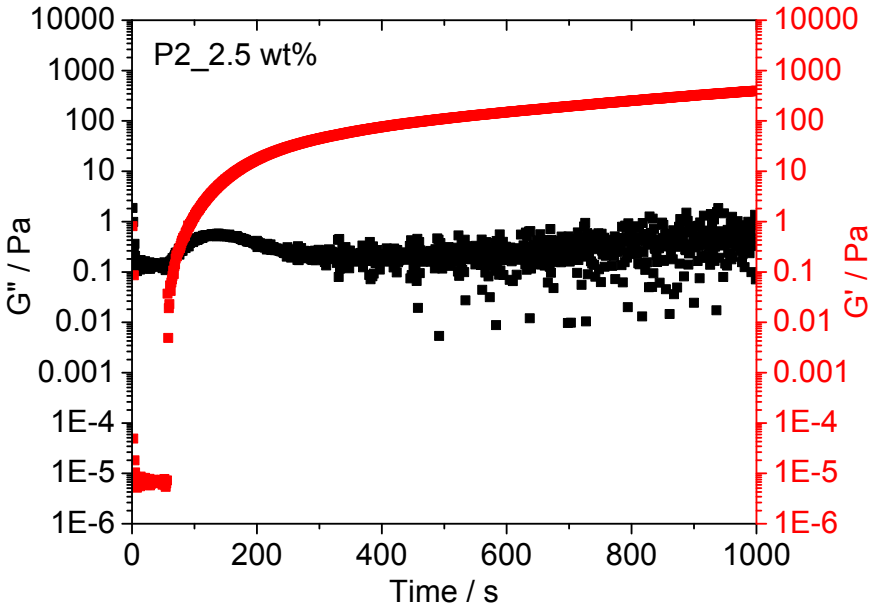

Figure S4: Rheology of the arsenohydrogel formation of **P2** (2.5 wt %, strain = 1.0 %, frequency = 10 rad.s^{-1}, temperature = 60 °C) in the presence of H_3PO_2 and KI

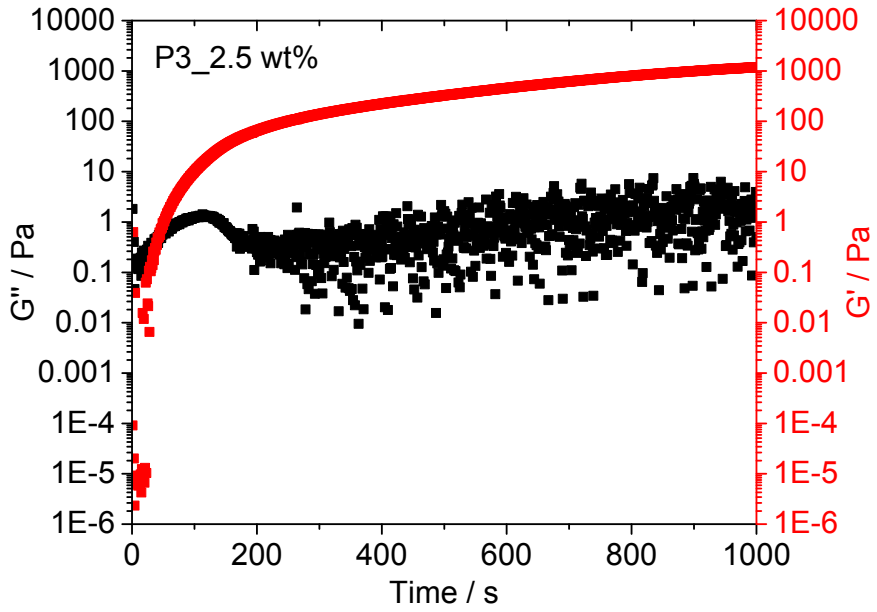

Figure S5: Rheology of the arsenohydrogel formation of **P3** (2.5 wt %, strain = 1.0 %, frequency = 10 rad.s^{-1}, temperature = 60 °C) in the presence of H_3PO_2 and KI

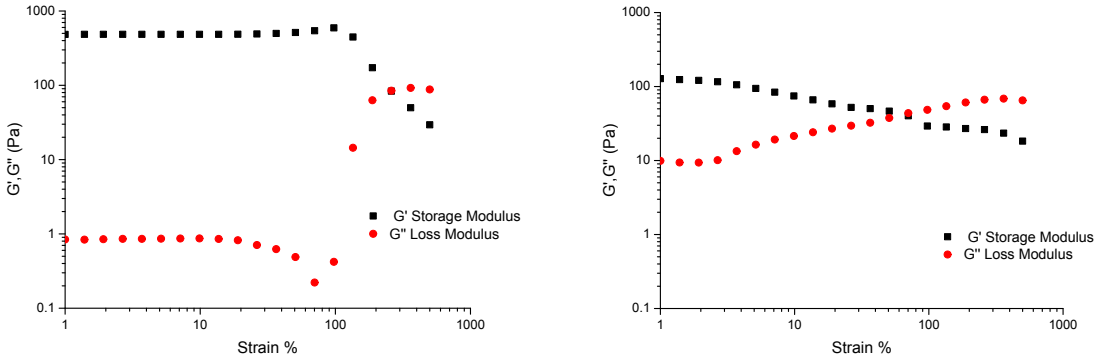

Figure S6: Amplitude sweep of arsenohydrogel of **P1** at 30 °C and frequency of 1 rad s^{-1} 1st cycle (left) and 2nd (right)

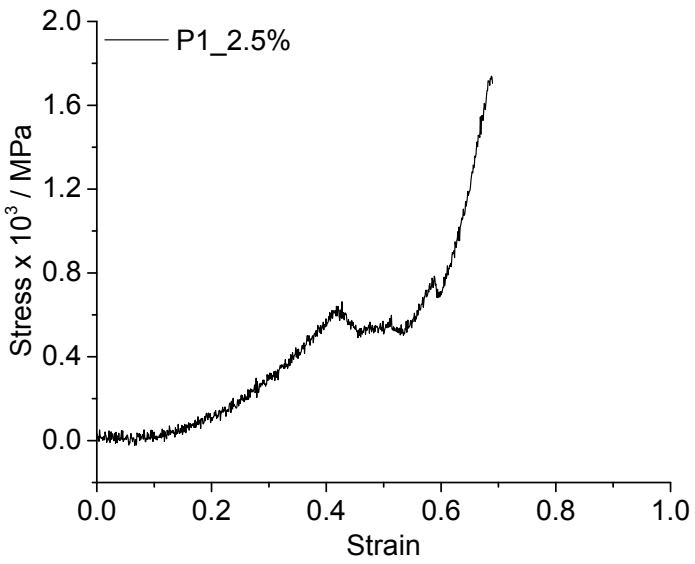

Figure S7: Representative stress/strain curve for arsenohydrogel of **P1** (2.5 wt%).

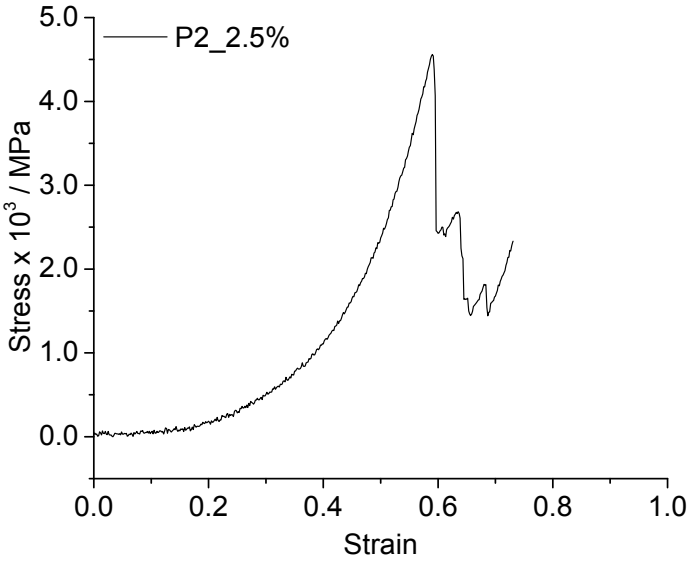

Figure S8: Representative stress/strain curve for arsenohydrogel of **P2** (2.5 wt%).

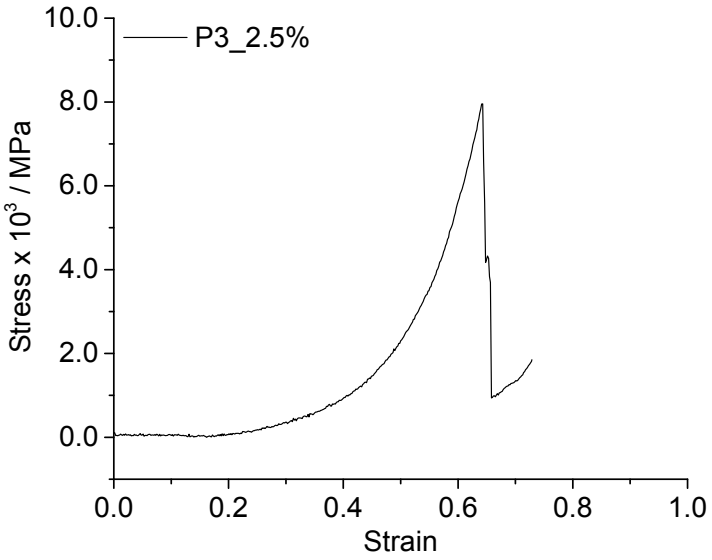

Figure S9: Representative stress/strain curve for arsenohydrogel of **P3** (2.5 wt%).

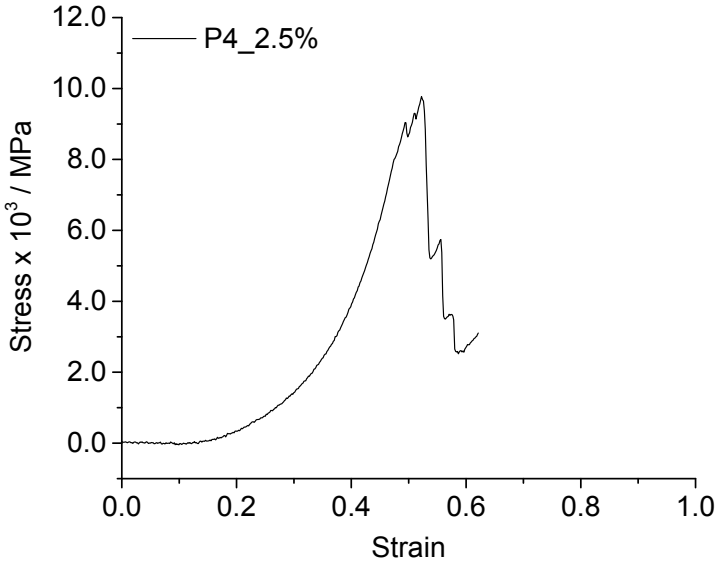

Figure S10: Representative stress/strain curve for arsenohydrogel of **P4** (2.5 wt%).

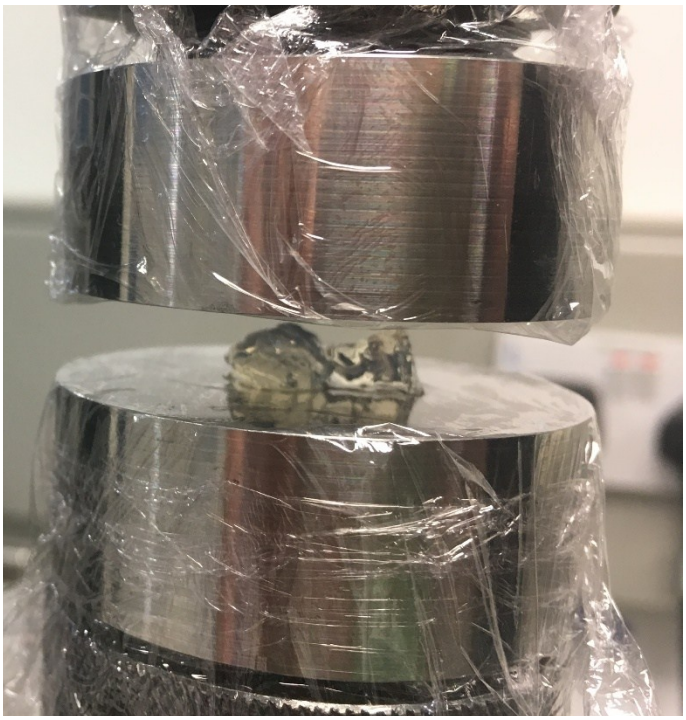

Figure S11: Image of the arsenohydrogel **P1** showing catastrophic failure after the first cycle of compression testing.

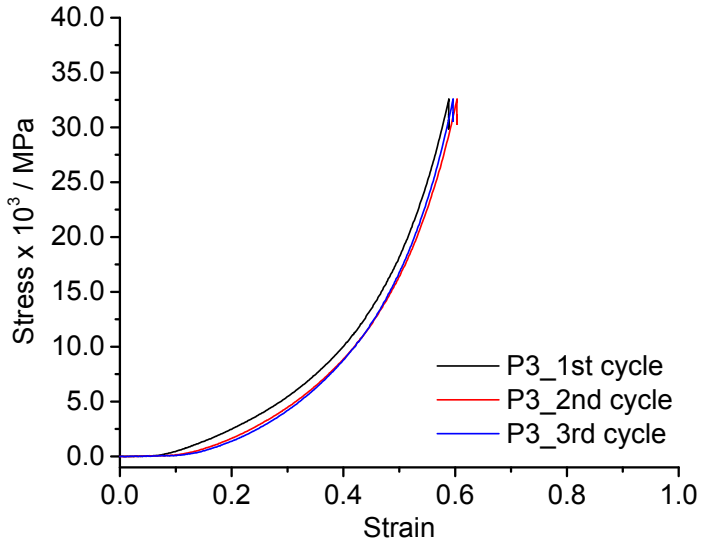

Figure S12: Overlay of the stress/strain curves of arsenohydrogel **P3** through 3 cycles of compression tests (load 5 N, hold 30 secs).

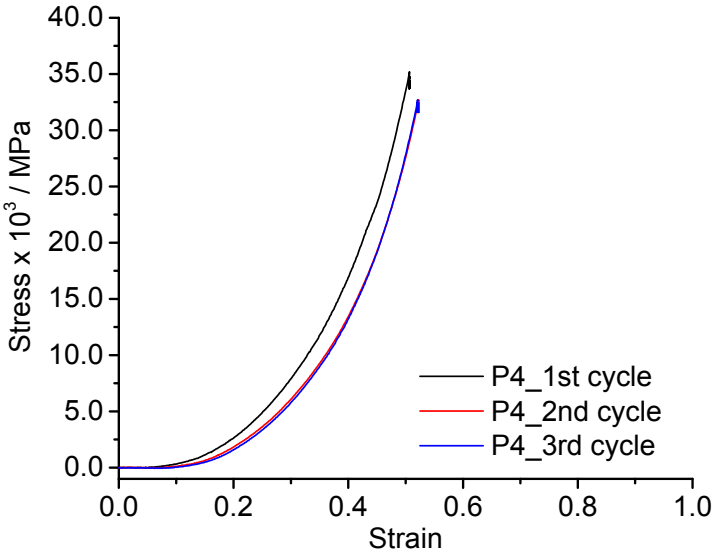

Figure S13: Overlay of the stress/strain curves of arsenohydrogel **P4** through 3 cycles of compression tests (load 5 N, hold 30 secs).

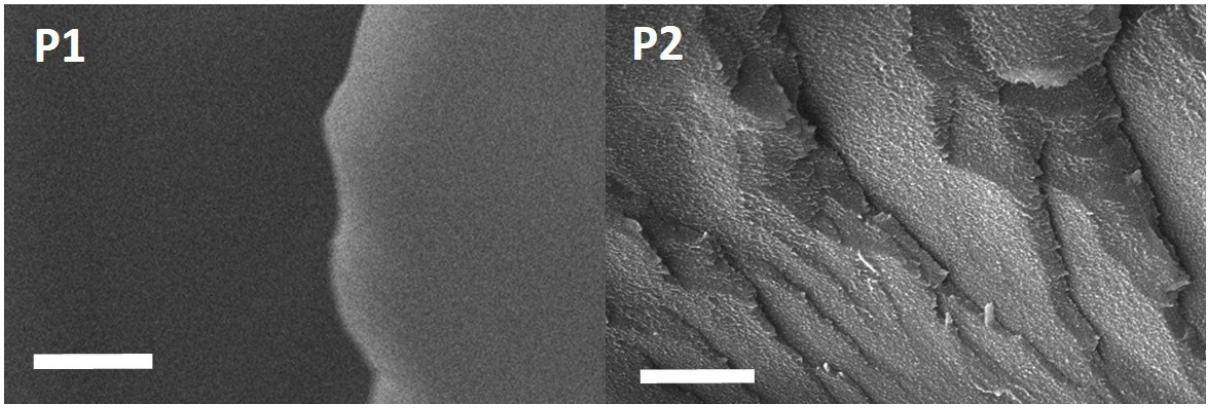

Figure S14: Scanning electron microscopy of dry 10 wt % arsenohydrogels after dialysis and lyophilisation. **P1** = 2 mol% AsAm; **P2** = 4 mol% AsAm (Scale bar = 2 µm).

Table S2: Elemental analysis summary from EDX of the arsenohydrogels.

	Wt %[a]			
	C	N	O	As
P1	41.41	9.46	46.52	2.61
P2	35.67	9.89	51.24	3.20
P3	37.24	9.73	48.15	4.89
P4	39.45	11.09	43.06	6.41

[a]Other elements such as potassium, iodide and phosphorous is not taken into account.

Table S3: Degree of swelling (W_s-W_0/W_0) x 100 for **P1-P4** in PBS (pH 7.4)

	Time / hrs				
	24	48	72	96	120
P1	175	385	900	1610	2040
P2	50	195	400	615	880
P3	25	80	140	250	360
P4	5	25	60	115	160

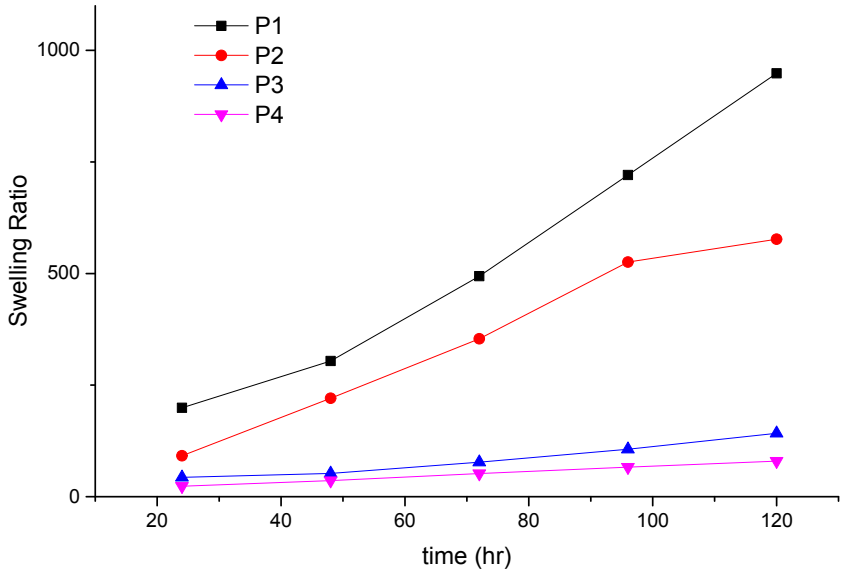

Figure S15: Swelling ratio of the arsenohydrogels derived from **P1-P4** calculated as $(W_s\text{-}W_0)/W_0$ x 100 where W_0 is the weight of the hydrogel after drying in the oven and W_s is the weight of the swollen hydrogel at a definite time interval (**Table S4**). Swelling was performed in GSH (5 mM).

Table S4: Degree of swelling $(W_s\text{-}W_0/W_0)$ x 100 for **P1-P4** in GSH (5 mM)

	Time / hrs				
	24	48	72	96	120
P1	200	305	495	720	950
P2	90	220	355	525	580
P3	45	50	80	110	140
P4	25	35	50	65	80

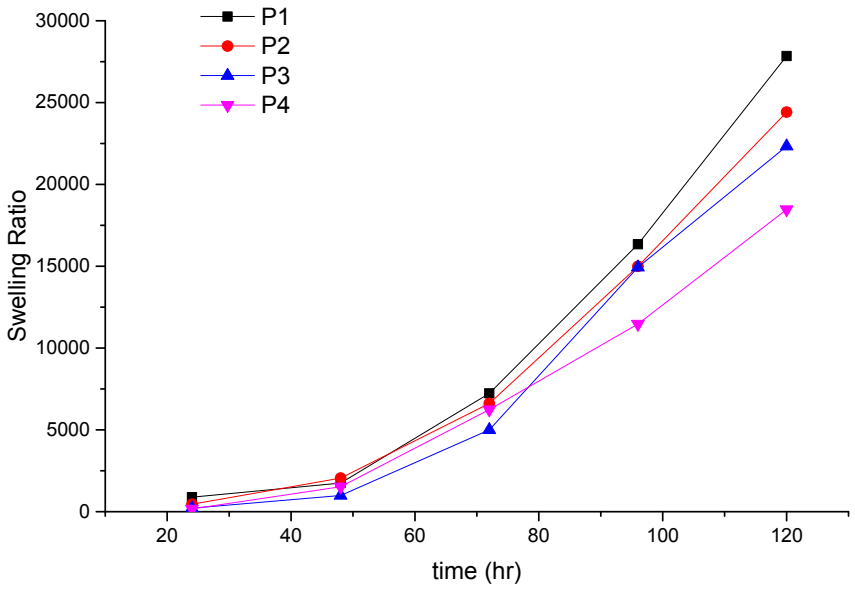

Figure S16: Swelling ratio of the arsenohydrogels derived from **P1-P4** calculated as $(W_s\text{-}W_0)/W_0$ x 100 where W_0 is the weight of the hydrogel after drying in the oven and W_s is the weight of the swollen hydrogel at a definite time interval (**Table S5**). Swelling was performed in H_2O_2 (5 mM).

Table S5: Degree of swelling $(W_s\text{-}W_0/W_0)$ x 100 for **P1-P4** in H_2O_2 (5 mM)

	Time / hrs				
	24	48	72	96	120
P1	885	1750	7230	16350	27850
P2	460	2050	6620	15000	24400
P3	215	990	5000	14900	22300
P4	170	1525	6240	11500	18500

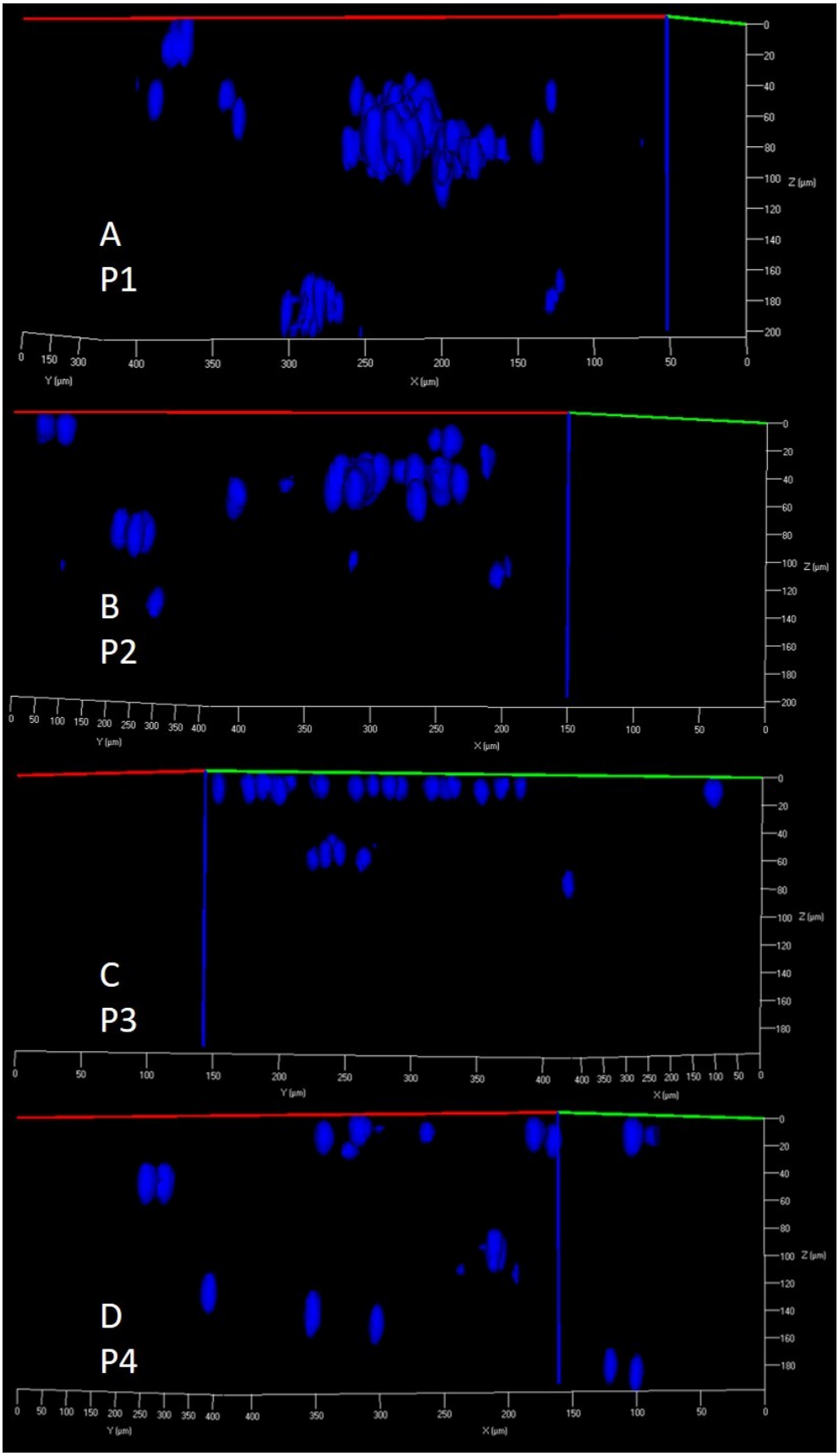

Figure S17: z-Stack tomography of NIH/3T3 cells encapsulated within arsenohydrogel matrices (10 wt%) derived from (A) **P1**; (B) **P2**; (C) **P3**; (D) **P4**, imaged with Hoechst dye.

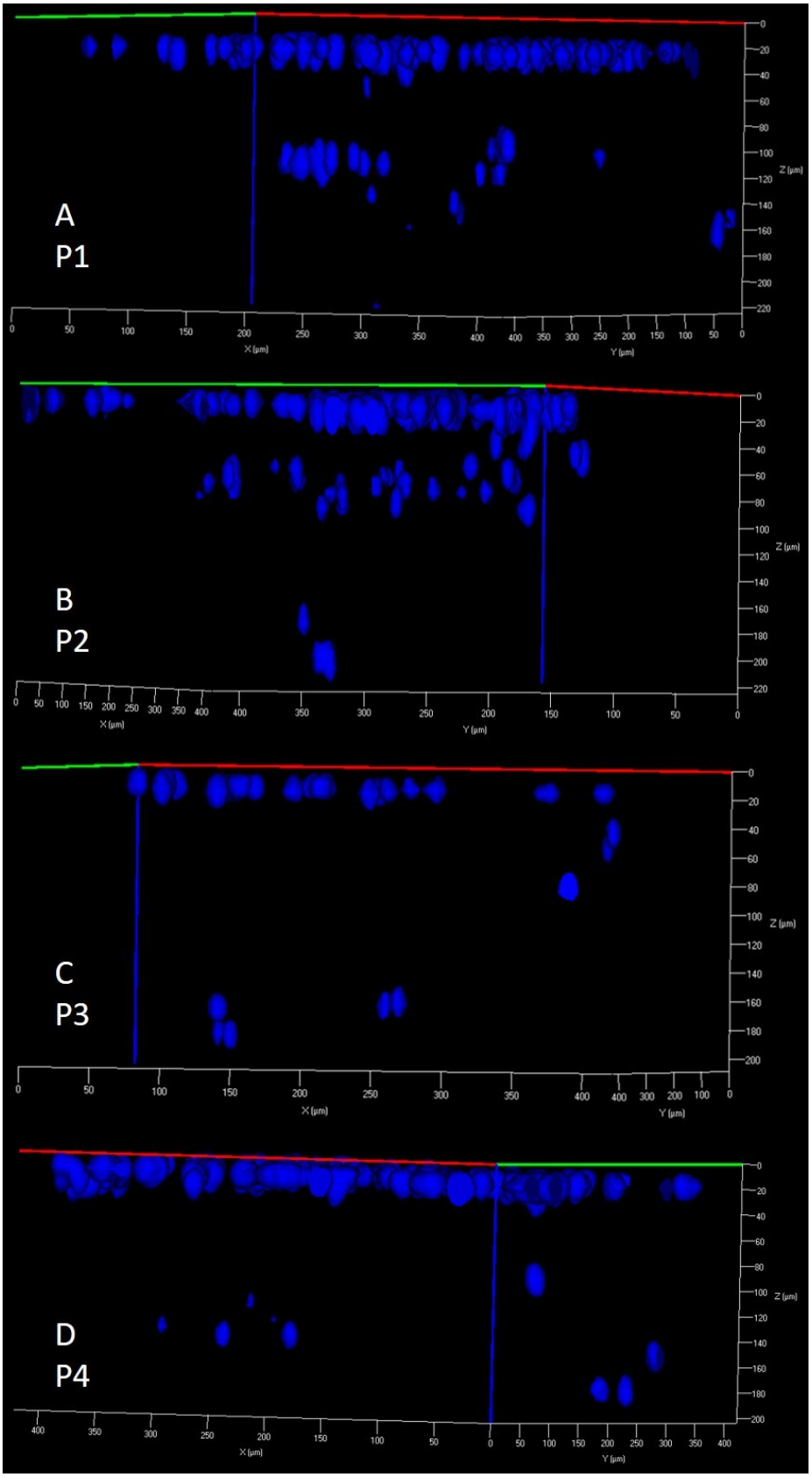

Figure S18: z-Stack tomography of PC3 cells encapsulated within arsenohydrogel matrices (10 wt%) derived from (A) **P1**; (B) **P2**; (C) **P3**; (D) **P4**, imaged with Hoechst dye.

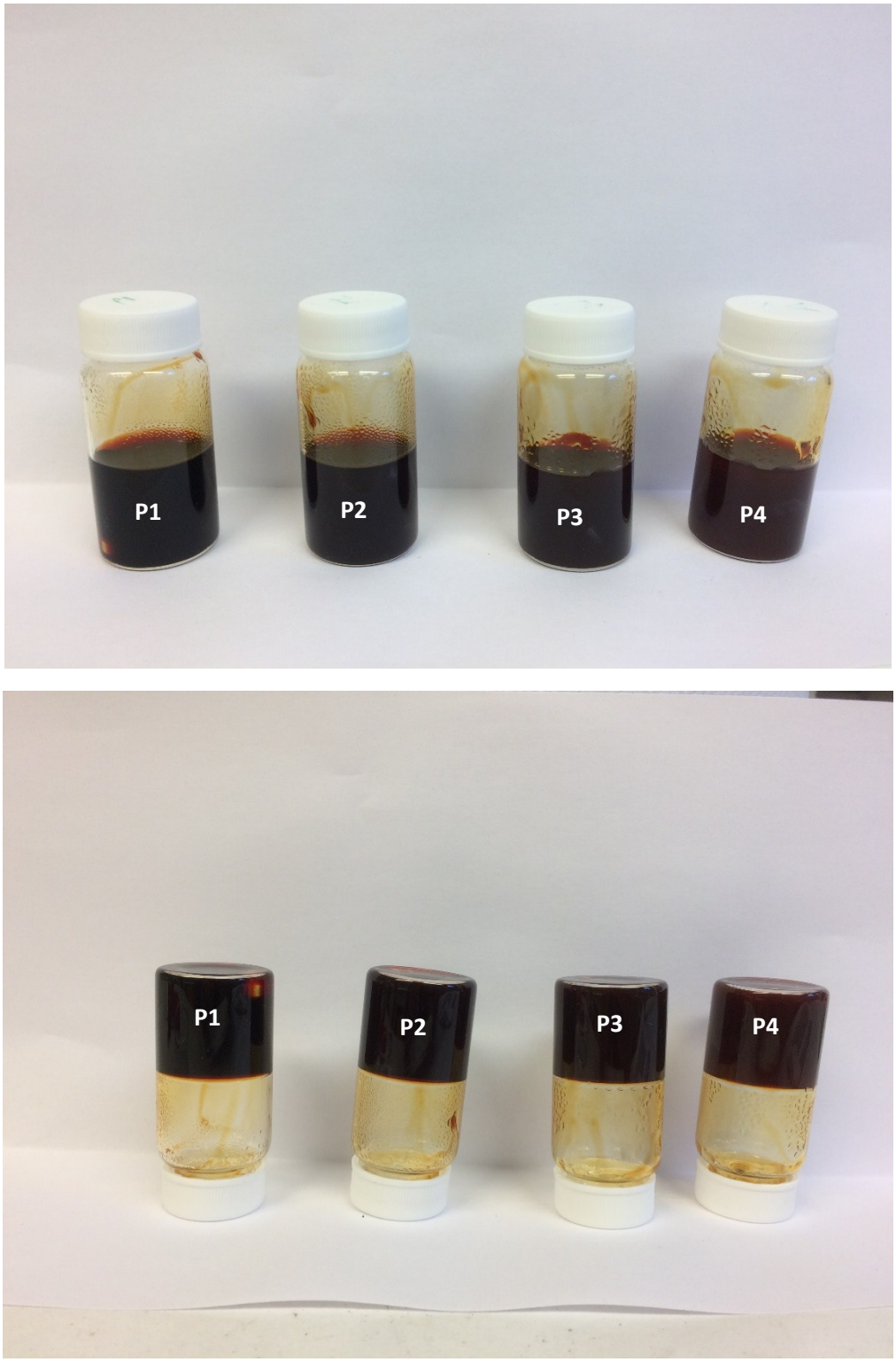

Figure S19: Inverse test qualitatively demonstrating gelation of **P1-P4** at 2.5 wt% in the presence of *p*-arsanilic acid (3.8 wt%).