Supporting Information

Highly Robust Interfacially Polymerized PA Layer on Thermally Responsive Semi-IPN Hydrogel: Towards On-Demand Tuning of Porosity and Surface Charge

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Table S1 Summary of parameters used for GLIP to study the effect of PEI concentration and IP time on surface morphology of the PA layer.

Sample name	PEI conc. in DI water (wt.%)	PEI M_w (kDa)	pH of PEI aq. solution	TMC conc. in hexane (wt.%)	reaction time (min)
PEI-25k/pH5_0.2	0.2	25	9.5	0.1	1
					5
					15
					30
PEI-25k/pH5_2	2	25	9.5	0.1	1
					5
					15
					30

Table S2 Summary of parameters used for GLIP to study the effect of M_w and pH of the aqueous PEI solution used on surface morphology of the PA layer.

Sample name	MPD/PEI conc. in DI water (wt.%)	PEI M_w (kDa)	pH of PEI aq. solution	TMC conc. in hexane (wt.%)	reaction time (min)	Thickness as measured by FESEM (nm)*
MPD-TMC	2	-	-			163 ± 38
PEI-2k/pH5		2	5			47 ± 19
PEI-2k/pH9.5	2	2	9.5	0.1	30	618 ± 145
PEI-25k/pH5		25	5			134 ± 18
PEI-25k/pH9.5		25	9.5			342 ± 75

*Note that the thickness of the film measured is estimated based on the FESEM as it was not possible to delaminate the film and was taken as average for 10 values measured at 10 different points using ImageJ software

Table S3 Surface chemical composition of the hydrogel with and without PA layer by XPS analysis

Sample	C	O	N	O/N
PNIPAM/PSA	78.8	14.36	6.9	2.1
PEI-2k/pH5	75.0	13.72	11.3	1.2
PEI-2k/pH9.5	76.3	11.72	11.9	1.0

Table S4: XPS results from PA/hydrogel composites. Binding energy and plausible species were determined from the deconvolution of C 1s, O 1s and N 1s core level XPS spectra.

Sample	C1s			O1s			N1s		
	Energy (eV)	Species	(%)	Energy (eV)	Species	(%)	Energy (eV)	Species	(%)
PNIPAM/PSA	284.8	C-H, C-C, C=C	65.0	531.2	N-C=O	49.6	399.3	R-NH2	20.7
	285.9	C-N	20.8	532.2	O-C=O	50.4	399.7	N-C=O	78.8
	287.7	N-C=O, O-C=O	14.2				401.7	R-N+H3	0.5
PEI-2k/pH5	284.7	C-H, C-C, C=C	44.0	530.8	N-C=O	24.4	398.9	R-NH2	29.8
	285.8	C-N	46.9	532.3	O-C=O	75.6	399.5	N-C=O	41.7
	287.7	N-C=O, O-C=O	9.2				401.2	R-N+H3	28.5
PEI-2k/pH9.5	284.7	C-H, C-C, C=C	50.9	530.9	N-C=O	52.4	399.1	R-NH2	56.6
	285.6	C-N	35.1	531.7	O-C=O	47.6	399.7	N-C=O	32.7
	287.6	N-C=O, O-C=O	14.0				400.4	R-N+H3	10.7

Table S5 Summary of parameters used for GLIP to study the effect of ratio of PEI/TMC on surface charge of the PA layer.

Sample name PEI-2k/pH5	PEI conc. in DI water (wt.%)	PEI M_w (kDa)	pH of PEI aq. solution	TMC conc. in hexane (wt.%)	reaction time (min)
PEI/TMC 2/0.1	2			0.1	
PEI/TMC 2/0.5	2	2	5	0.5	30
PEI/TMC 0.2/0.5	0.2			0.5	

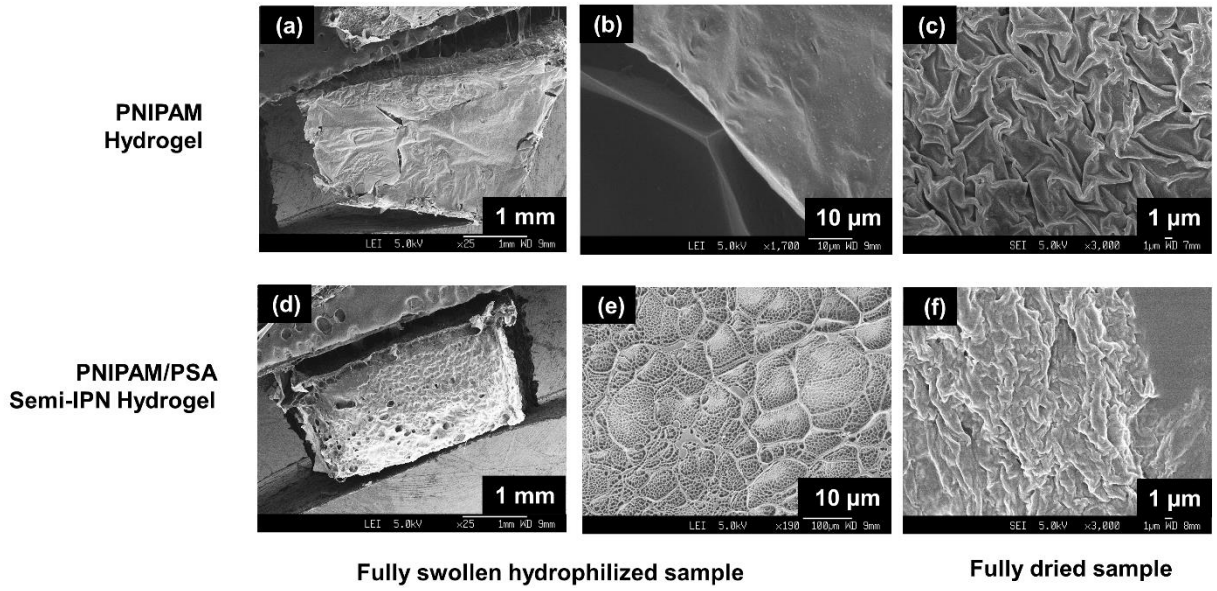

Figure S1: FESEM micrographs of top view of the PA skin layer on PNIPAM/PSA semi-IPN hydrogel formed by reaction of 2 wt% branched PEI (M_w 25 kDa) adjusted to pH 9.5 and 0.1 wt% TMC. The immersion time of fully swollen hydrogel in aq. PEI solution was 30 min followed by 30 min polymerization time for IP layer formation. (a, b) lyophilized swollen PA/hydrogel composite formed using pure PNIPAM hydrogel and (d, e) for PNIPAM/PSA hydrogel. (c) (f) oven dried PA/hydrogel sample for PNIPAM and PNIPAM/PSA hydrogel system, respectively.

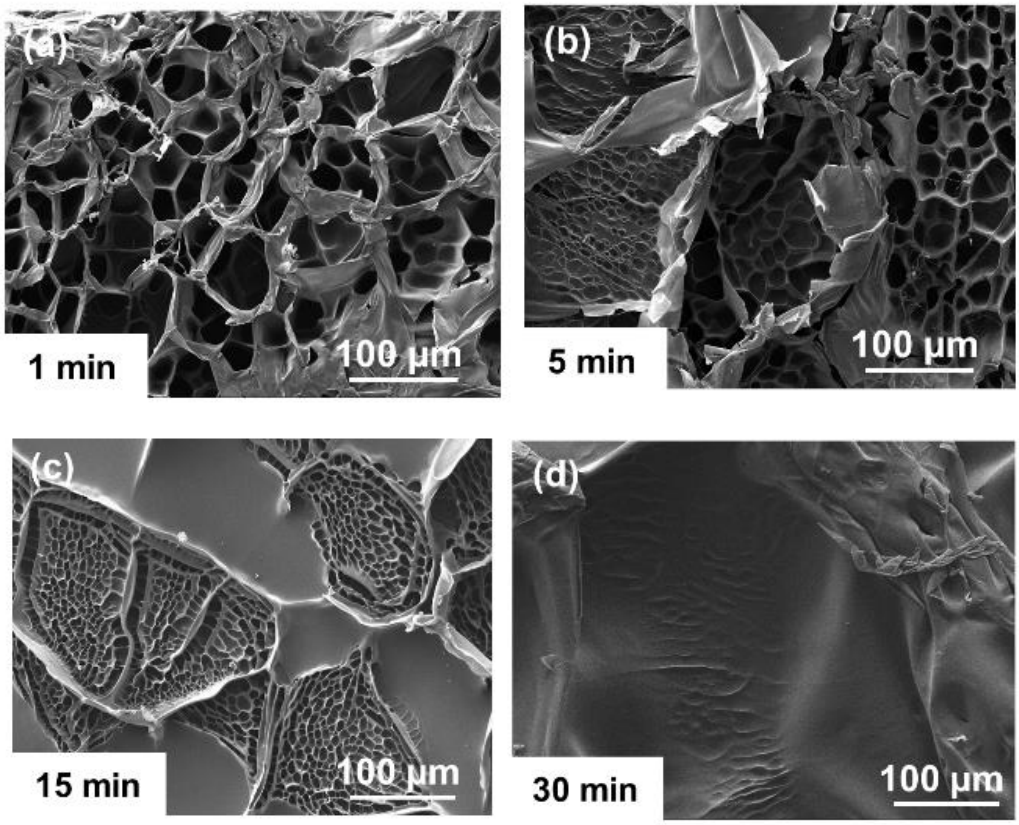

Figure S2 (a-d) FESEM micrographs of top view of the PA skin layer on PNIPAM/PSA semi-IPN hydrogel formed by reaction of 0.2 wt% PEI (M_w 25 kDa), pH of the solution adjusted to 9.5, and 0.1 wt% TMC system at different polymerization time i.e., 1, 5, 15 and 30 min respectively.

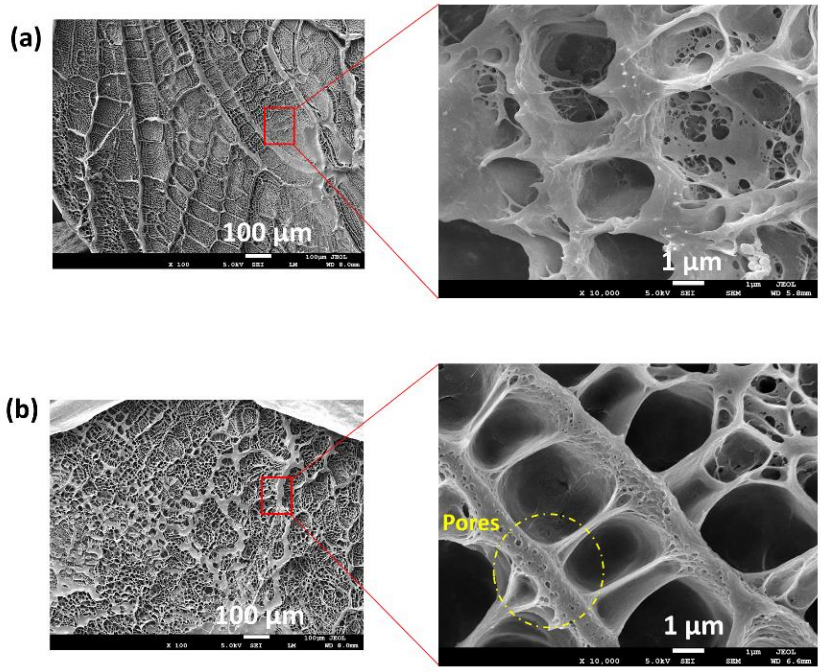

Figure S3 FESEM micrograph of top view of PA/hydrogel composite formed by interfacial reaction of 2 wt% branched PEI (pH adjusted to 9.5) with 0.1 wt% TMC for 30 min using (a) PEI M_w 2 kDa and (b) PEI M_w 25 kDa

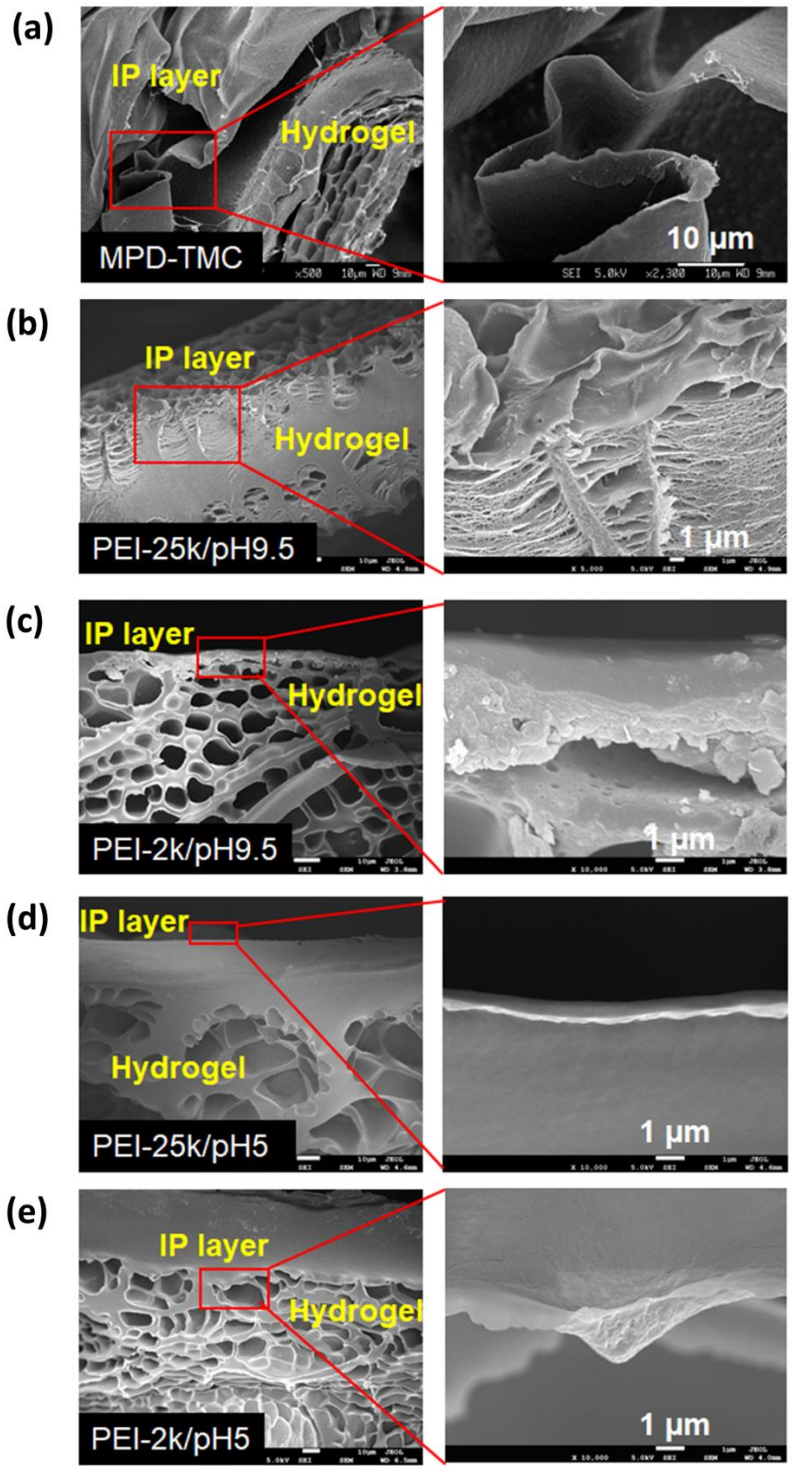

Figure S4: FESEM micrograph of cross section morphology of (a) MPD-TMC (b) PEI M_w 25 kDa, pH adjusted to 9.5 (c) PEI M_w 2 kDa, pH adjusted to 9.5 (d) PEI M_w 25 kDa, pH adjusted to 5 (e) PEI M_w 2 kDa, pH adjusted to 5, PA/hydrogel composite formed by reacting 2 wt% of different amine monomers with 0.1 wt% TMC for 30 min.

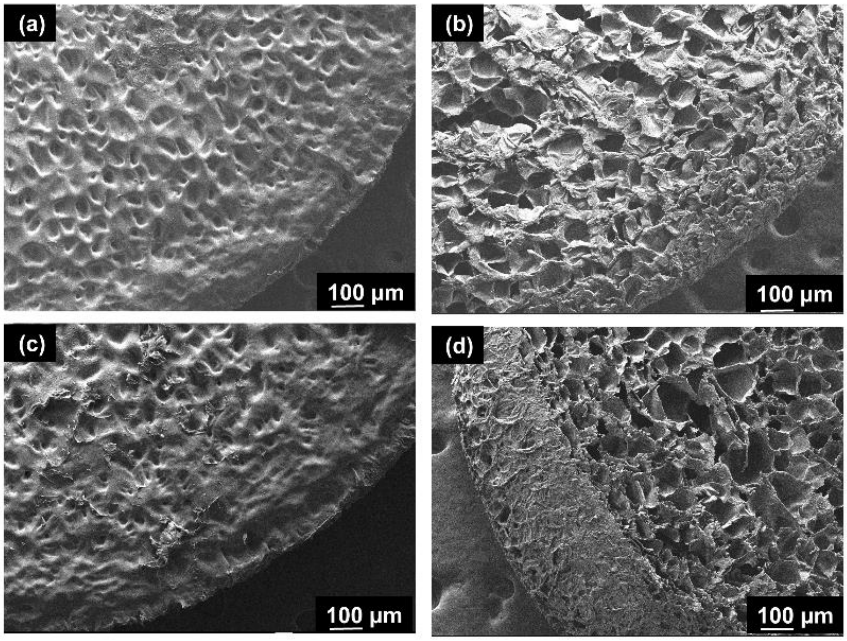

Figure S5: FESEM micrograph of top view and cross section morphology of semi-IPN hydrogel immersed in 2 wt% branched PEI (pH adjusted to 5) (a-b) PEI M_w 25 kDa and (c-d) PEI M_w 2 kDa after 24 h.

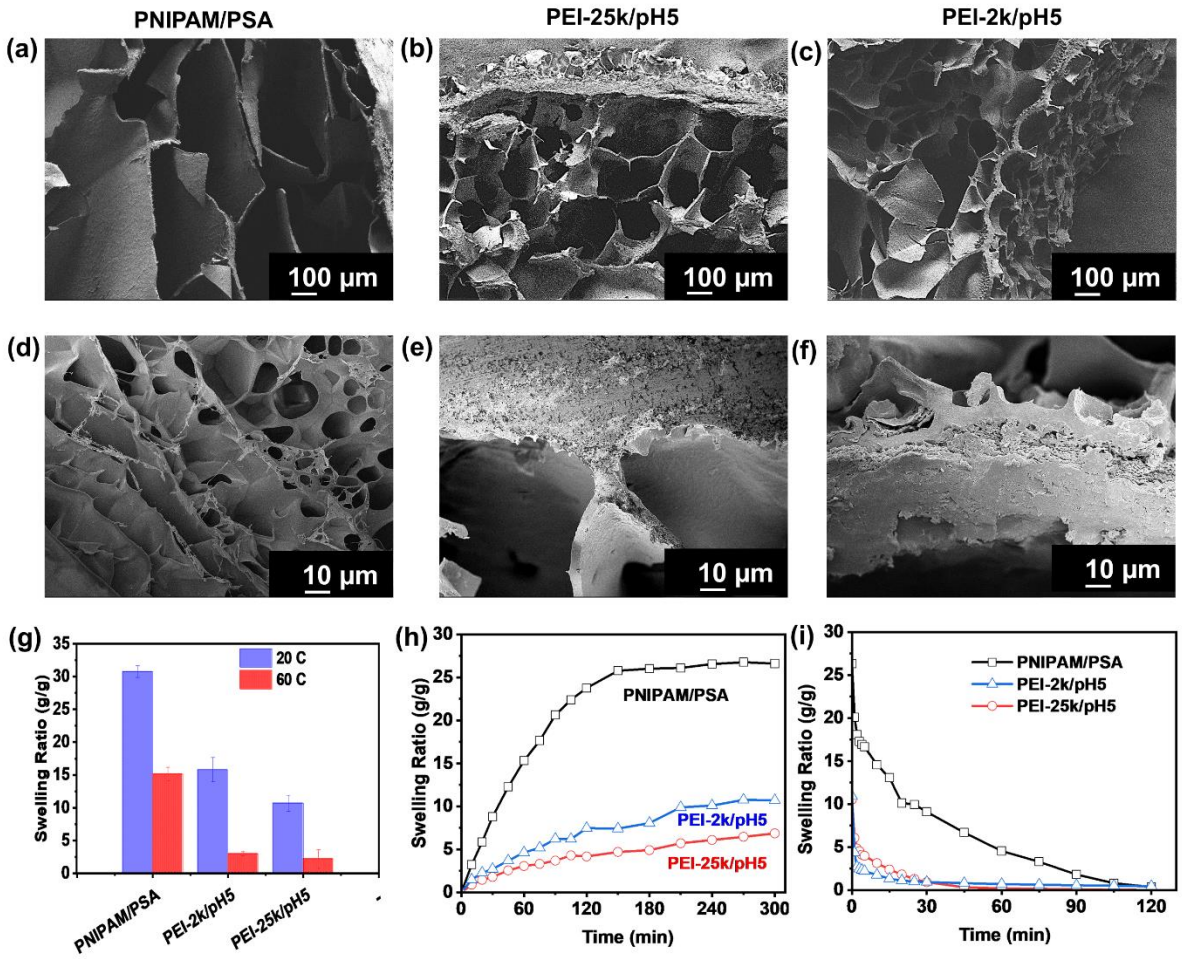

Figure S6: (a, b, c) FESEM micrograph of cross-section of PNIPAM/PSA semi-IPN hydrogel beads and PEI-25k/pH5, PEI-2k/pH5 PA/hydrogel composites respectively (d, e, f) are magnified images of hydrogel beads and PEI-25k/pH5, PEI-2k/pH5 PA/hydrogel composites respectively (g) ESR of PNIPAM/PSA hydrogel beads measured without and with IP layer at 20 and 60 °C (h) Swelling kinetics of the hydrogel with and without IP layer at room temperature as time dependent function of swelling ratio (i) Deswelling kinetics of the hydrogel with and without IP layer at 60 °C as time dependent function of swelling ratio.

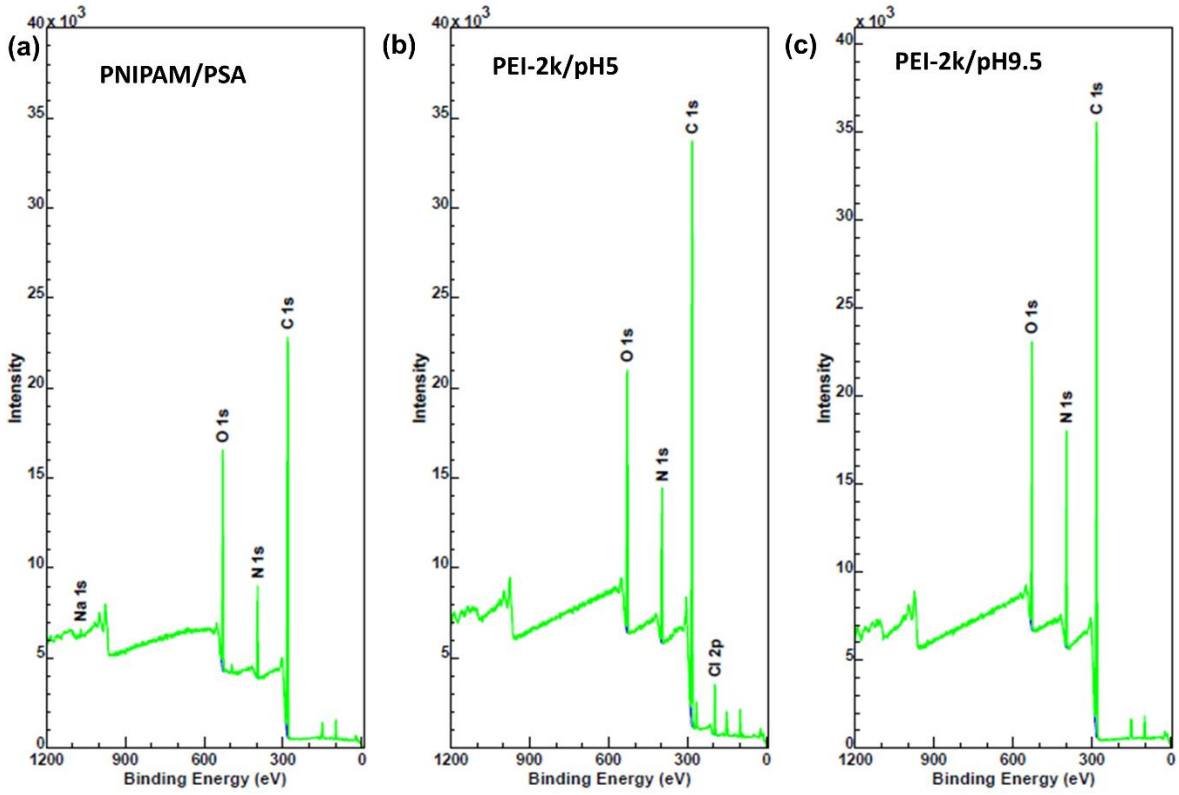

Figure S7: XPS survey spectra of hydrogel and PA/hydrogel composites (a) PNIPAM/PSA, (b) PEI-2k/pH5, (c) PEI-2k/pH9.5. As an indication of polyamide layer formation three major peaks of carbon, nitrogen and oxygen were observed. The chemical composition and atomic percentage of the hydrogel composites were calculated from XPS and are listed in Table S3. The observed peak for Na 1s for PP sample is not observed after PA layer formation in PEI-2k/pH5 and PEI-2k/pH9.5 indicating uniform PA thickness over hydrogel surface. The presence of Cl 2p for PEI-2k/pH5 indicates presence of unreacted acyl groups.

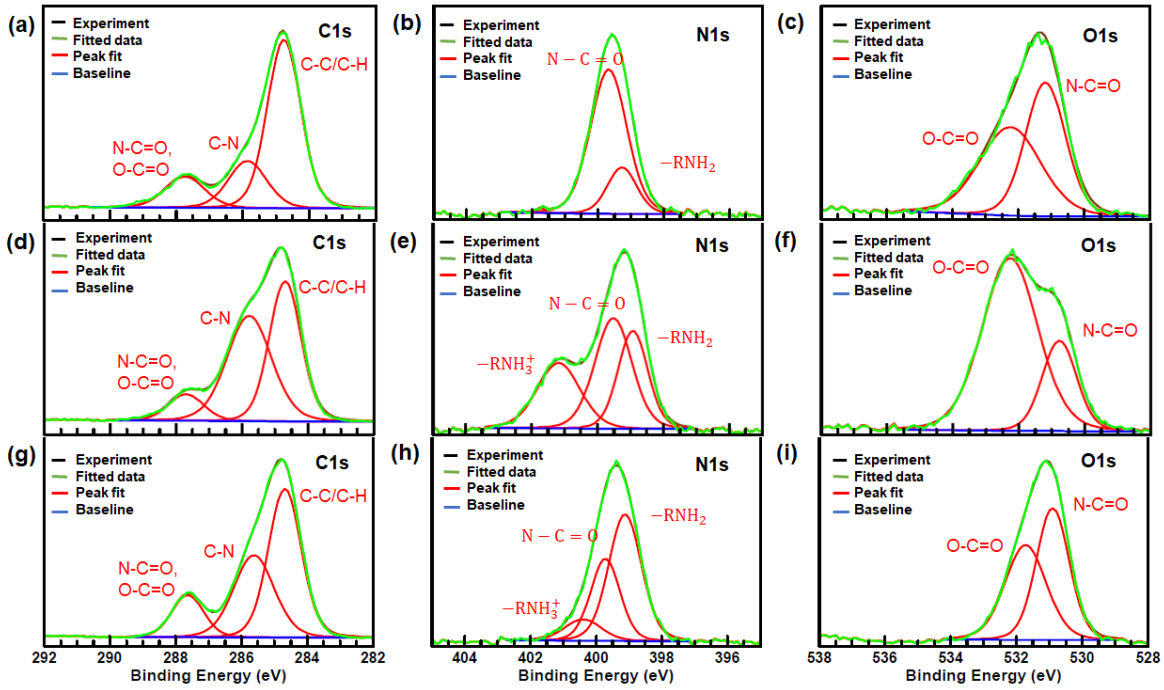

Figure S8: Narrow scan results of x-ray photoelectron spectra of hydrogel (PNIPAM/PSA) and PA/hydrogel composite (PEI-2k/pH5, PEI-2k/pH9.5). The PA/hydrogel composites were prepared using 2 wt% PEI (M_w 2kDa) and 0.1 wt% TMC reacted for 30 minutes at two different pH of the PEI solution i.e., pH 5 and 9.5 for LP2b sample. (a-c) PNIPAM/PSA hydrogel, (d-f) PEI-2k/pH5 and (g-i) PEI-2k/pH9.5.

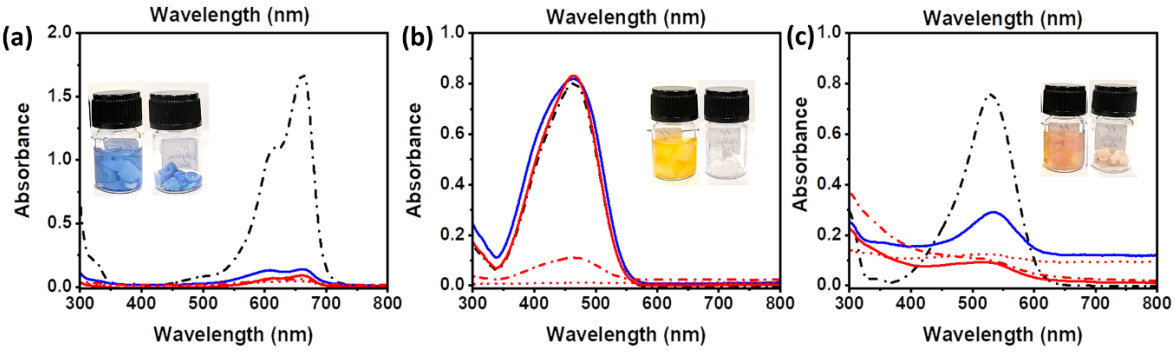

Figure S9: (a-c) UV-Vis absorption spectra for rejection and deswelling performance for MB, MO, NR dye solution respectively. The inset of the graphs shows the optical image of the samples after rejection and 2nd washing

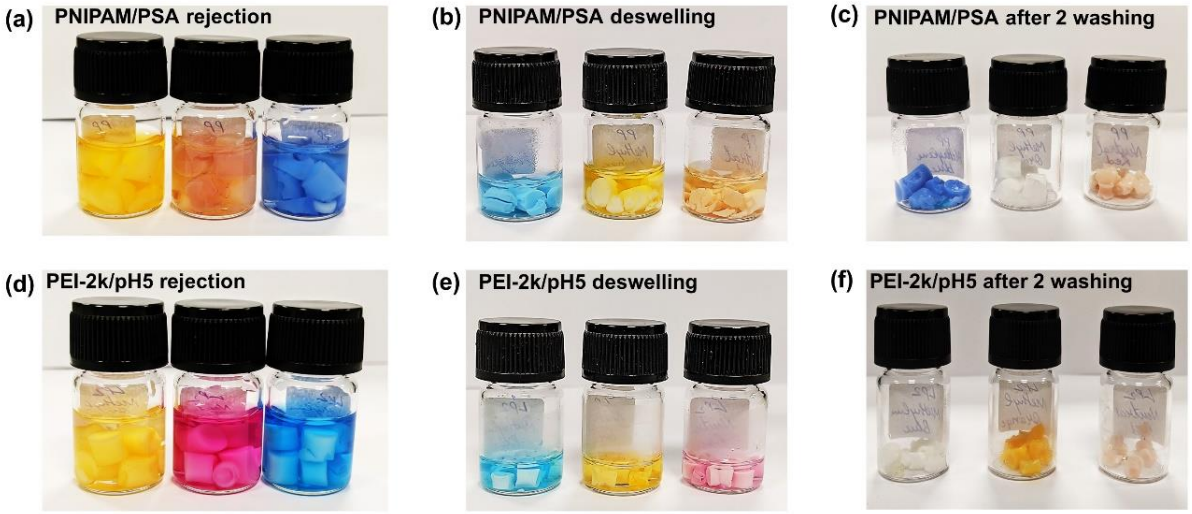

Figure S10: Optical images for rejection and deswelling performance for MB, MO, NR dye solution using (a-c) PNIPAM/PSA hydrogel beads and (d-f) PEI-2k/pH5 PA/hydrogel composite

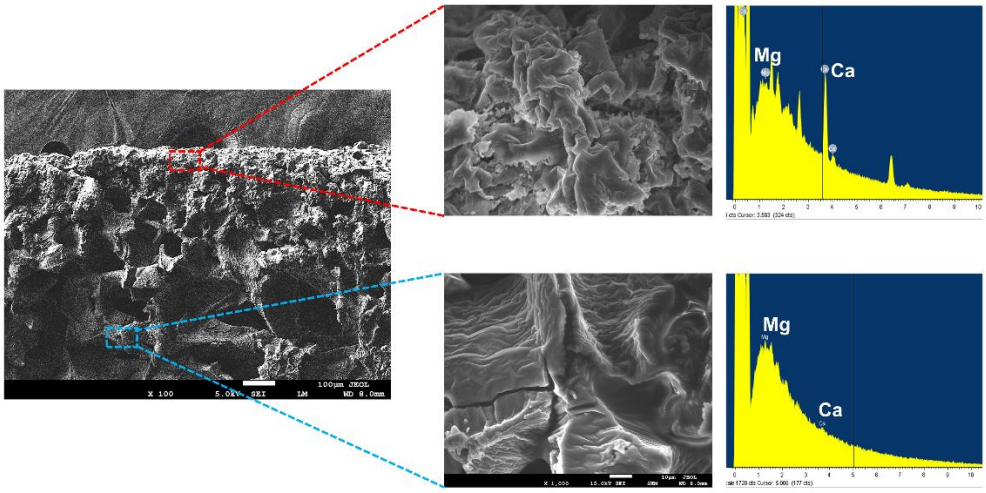

Figure S11: FESEM micrograph of cross-section of lyophilized PEI-2k/pH5 bead after rejection test for a mixture containing 10 ppm Li^{+}, Ca^{2+}, and Mg^{2+}. The EDX mapping was done for a region on the surface and within the hydrogel. Red box shows the EDX spectrum on the surface and blue box shows the EDX spectrum of a region within the hydrogel for the $Ca^{2+}$and Mg^{2+}.

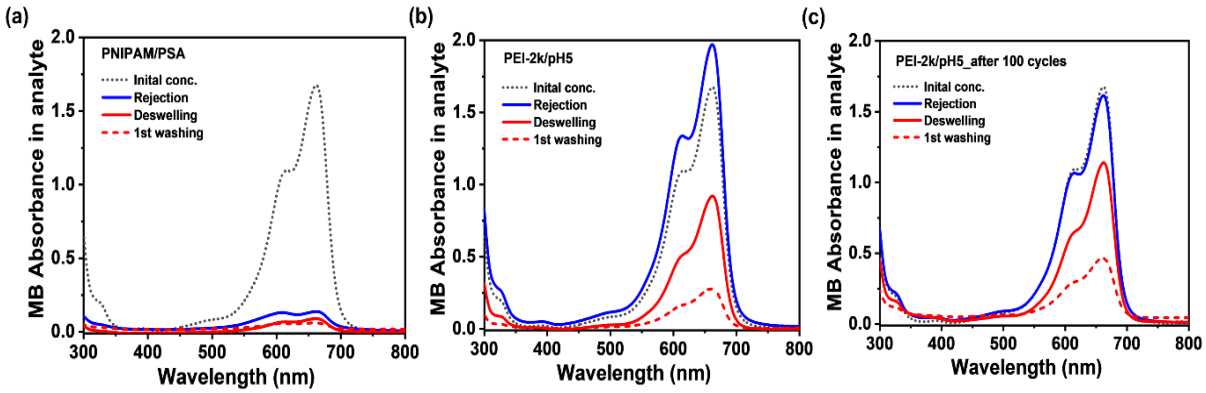

Figure S12: UV-Vis absorption spectra for rejection and deswelling performance for MB dye solution using (a) PNIPAM/PSA hydrogel bead, (b) PEI-2k/pH5 PA/hydrogel bead before and (c) PEI-2k/pH5 PA/hydrogel bead after 100 swelling/deswelling cycles. Blue line shows the concentration of the dye in non-absorbed water. While red line shows the concentration of dye in the water released after deswelling the swollen hydrogel beads.