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Supporting Information

Design rationale for stimuli responsive semi-IPN hydrogel – A quantitative approach

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I. Materials

N-isopropylacrylamide (NIPAM) (Wako Pure Chemical Industries Ltd.) was recrystallized from n-hexane before use. N, N'-methylene-bis-acrylamide (MBA) as crosslinker, ammonium peroxydisulfate (APS) as initiator, N,N,N',N'-tetramethyl ethylenediamine (TEMED) as accelerator were purchased from Sigma-Aldrich and used as received. Linear poly (sodium acrylate) (PSA) polymers with different molecular weight (MW) of 6000, 170000, 800000 g mol⁻¹ were used as obtained.

II. Semi-IPN hydrogel synthesis

Typically, NIPAM, MBA and PSA were first dissolved in DI water under constant stirring at room temperature. The mixture was then purged with nitrogen for 20 minutes and allowed to cool down to polymerization temperature. Keeping the mixture under nitrogen atmosphere and cold, freshly prepared TEMED and APS solutions were added. The mixture

was allowed to gel without stirring at ice-bath temperature for 15 minutes, before allowing for low-temperature polymerization at 10 °C for 24 h. The semi-IPN hydrogels were washed thoroughly by immersion in DI water for 3 days with periodic water change before drying at 60 °C.

III. Characterization Methods

The chemical compositions of the hydrogels were analysed by FTIR (Perkin Elmer Frontier) using attenuated total reflection (ATR) mode. Field emission scanning electron microscopy (FESEM) (JSM-7600, JEOL) was employed to study the microstructures of lyophilized hydrogels. Determination of volume phase transition temperature (VPPT) was done by differential scanning calorimeter (TA Q10, TA Instruments). 5-10 mg of equilibrium swollen hydrogel was sealed into hermetic aluminium pan, equilibrated at 10 °C, and heated to 80 °C at 3 °C/min. VPTT is identified as the endothermic peak around 35-40 °C.

a. Swelling ratio

The equilibrium swelling ratio (ESR) of fully swollen PNIPAM/PSA semi-IPN hydrogel in DI water was measured gravimetrically:

$$\text{Equilibrium Swelling Ratio (ESR)} = \frac{(W_t - W_d)}{W_d} \quad \text{Equation (S1)}$$

where w_t is the weight of the swollen hydrogel and w_d is the dry weight of the hydrogel obtained after heating to constant weight at 60 °C. Specific effects of pH on the swelling ratio noted elsewhere^[1], does not apply here in which the swelling medium is DI water. The ESR at 40 and 50 °C were also determined after 1 hour immersion in water at the respective temperatures.

b. Evaluation of swelling behaviour

To investigate the swelling kinetic of the dried PNIPAM/PSA semi-IPN hydrogel, the rate parameter k_s was empirically determined using the first and second order rate kinetic model. According to the first order kinetics, rate of swelling is directly proportional to time before the ESR has been reached. If M_t is the mass of the water absorbed at any given time t and M_{Inf} is

the amount of water absorbed at infinite time, then the proportionality kinetic rate constant k_s is given by the slope of the curve^[2]

$$-\ln\left(1 - \frac{M}{M_{\text{Inf}}}\right) = k_{s1}t \quad \text{Equation (S2)}$$

The Schott's second order equation for swelling is given by^[3]

$$\frac{t}{S} = A + Bt \quad \text{Equation (S3)}$$

Where S is the swelling at time t , $A = 1/k_{s2}S_{\text{eq}}^2$ is the reciprocal of the initial swelling rate and k_{s2} is the swelling rate constant, $B = 1/S_{\text{eq}}$ is the inverse of the equilibrium swelling

c. Diffusion mechanism of water in Semi-IPN hydrogels

Following equation was used to determine the diffusion mechanism of water into hydrogels

$$F = \frac{M_t}{M_{\infty}} = kt^n \quad \text{Equation (S4)}$$

Where M_t and M_{inf} is the water uptake at a given time t and at equilibrium respectively, k is the characteristic constant of the polymeric gel related to the structure of the network. The n is the diffusional exponent that elucidates the transport mechanism. For $n=0.5$, it indicates Fickian diffusion; for $1 > n > 0.5$, it indicates anomalous diffusion. Above equation is only applied to the initial 60% of the normalized water absorption of the swelling curve.^[4] The n and k values are calculated from the slopes and intercepts of the plots of $\ln F$ versus $\ln t$ respectively.

d. Evaluation of deswelling behaviour

The deswelling behaviour of the PNIPAM/PSA semi-IPN hydrogel was determined by heating fully swollen hydrogel, with the assumption of first order kinetics and the Arrhenius equation defined as below:

$$K = A \exp\left(-\frac{E_a}{RT}\right) \quad \text{Equation (S5)}$$

K is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. The activation energy was determined from the slope of the plot of $\ln K$ vs. $1/T$, where K is the first order deswelling rate constant at 40, 50 and 60 °C as deswelling temperatures.

e. Determination of PSA retention

Freshly synthesized hydrogel (4 g with a known PSA wt.%) was cut into 1-5 mm pieces and immersed into 80 mL of 0.9 wt.% NaCl solution. The solution was stirred at 500 rpm for 16 h. The solution was filtered, and 20 mL filtrate was titrated with 0.1 N NaOH until pH 10 ([NaOH] mL), subsequently with 0.1 N HCl until pH 2.7 ([HCl] mL). Blank 0.9 wt.% NaCl solution was titrated to obtain [bNaOH] mL and [bHCl] mL as calibration. The residual PSA can then be determined.

Detailed procedure of PSA retention determination

The procedure involved in determination of PSA leaching is as follows: 4 g of a hydrogel cut into pieces of approximately 1 mm to 5 mm square (PSA weight: $4 \text{ g} \times 1.9\text{wt}\% = 0.076 \text{ g}$) and 80 mL of a 0.9 wt.% sodium chloride aqueous solution were placed in a 250 mL plastic container with a lid, and stirred with a cylindrical stirrer of 3.5 cm in length and 6 mm diameter at 500 rpm for 16 hours, so that water soluble component can be extracted from the semi-IPN hydrogel. The extracted solution was filtered by use of a sheet of filter paper (retained particle diameter 5 μm), and 40 g of a filtrate thus obtained was employed as a measurement solution.

Subsequently, the measurement solution was titrated with a 0.1 N NaOH aqueous solution until the measurement solution had pH of 10, and then titrated with a 0.1 N HCl aqueous solution until the measurement solution had pH of 2.7. Then, titrators ([NaOH] mL, [HCl] mL) were obtained. Furthermore, the same operation was carried out only with respect to a 0.9 wt. % sodium chloride aqueous solution, and blank titrators ([bNaOH] mL, [bHCl] mL) were obtained. From an average molecular weight of the monomers of the hydrogel and the titrator obtained as a result of the above operation, Ext (water soluble component) was calculated based on the following Equation (1):

PSA elution (wt%)

$$= 0.1 * (\text{avg. Mw. of monomer}) * 80 * 100 * \frac{\frac{[\text{HCL}] - [\text{bHCL}]}{1000}}{\frac{0.076}{40}} \quad \text{Equation (S6)}$$

Residual PSA(mol%)

$$= 0.01 * (100 - \text{PSA elution}(\text{wt}\%)) * \frac{\text{Initial PSA} \left(\frac{\text{mol}}{\text{L}} \right)}{\text{Initial PSA} \left(\frac{\text{mol}}{\text{L}} \right) + \text{NIPAM} \left(\frac{\text{mol}}{\text{L}} \right)} \quad \text{Equation (S7)}$$

The measurement of PSA 0.9 wt.% sodium chloride aqueous solution was carried out in the same manner in order to prepare a calibration curve.

f. Cyclic test for FO performance and dewatering

To investigate the performance of the synthesised semi-IPNs as FO draw solute, customised FO setup was used for the measurement for water flux as illustrated in Figure S4. For each test, FO membrane (FTS, FSB-CTA) was cut into desirable shape (30 mm diameter circular with 25 mm diameter for active FO membrane area) and secured (with a flat silicone O-ring beneath) in between top and bottom part of the FO setup. The active layer of the membrane is facing the draw solution (referred as ALDS). After that, 0.3 g of the hydrogel powder (ball-milled until size <50 µm) is put on the active layer side of the FO membrane. Feed solution (2000 ppm NaCl unless otherwise stated) is slowly filled into the indicator syringe by syringe. After that, the water level at the indicator syringe is read and recorded at fixed time intervals, used for calculation of the water flux in litre per m² per hour (LMH). The feed solution is stirred at 500 rpm throughout the measurement. The deswelling of the gel sample is done similar to the method described previously^[5]. Apparent water flux (J_{app}) of representative samples are calculated based on the method of Hu et al.^[6]

$$J_{\text{app}} = \frac{m_{\text{water}}}{(T_{\text{FO}} + T_{\text{des}}) \cdot A} \quad \text{Equation (S8)}$$

Based on the SR, optimal T_{FO} and T_{des} can be calculated; giving rise to optimal J_{app} . The cyclic swelling and deswelling study at room temperature and 40°C respectively was done for two repeated cycles see Figure S5.

g. Curve fitting for J_{app}

As proposed by Hu et al. an ‘apparent water flux’ (J_{app}) can be deduced from the experimental conditions for the universal quantification of FO technologies of various types of configurations and materials (**Error! Reference source not found.11**). An optimal cycle can be deduced to maximize the performance of the FO and dewater process so to generate the largest amount of purified water output (or highest feed concentration).

Apparent water flux (J_{app}) as proposed by Hu et al. which serve as a universal approach to quantify FO system performance of different technologies. Figure taken from ^[6].

Table S1. Synthesis compositions for PNIPAM/PSA semi-IPN hydrogel

Sample	NIPAM (M)	PSA		MBA (mol%/monomer)	APS ^a (mM)	TEMED ^b (mM)
		Mw. (g mol ⁻¹)	(M)			
SI-0.2/2-6	0.8	6000	0.2	2	8	8
SI-0.2/2-170		170000	0.2	2		
SI-0.3/2-170		170000	0.3	2		
SI-0.2/0.5-170		170000	0.2	0.5		
SI-0.4/0.5-170		170000	0.4	0.5		
SI-0.2/4-800		800000	0.2	4		
SI-0.2/2-800		800000	0.2	2		
SI-0.3/2-800		800000	0.3	2		
SI-0.2/0.5-800		800000	0.2	0.5		
SI-0.4/0.5-800		800000	0.4	0.5		

Initiator and accelerator are 1 mol% with respect to monomer (NIPAM for all semi-IPNs)

a. In 10% (w/v) aqueous solution

b. In 5% (v/v) aqueous solution.

Table S2: Effect of polymerization temperature: Swelling ratio and the PSA retention factor of

SI-0.2/2-800 semi-IPN hydrogel synthesized at 10 and 25 °C respectively

Temperature (°C)	SR	C _{Residual PSA} /C _{Initial PSA}
10	56	0.59
25	33	0.06

Table S3: Determination of PSA retention and swelling ratio. Swelling ratio and PSA retention

for a series of PNIPAM/PSA semi-IPN hydrogel synthesized at 10 °C.

Sample	Initial PSA ^c	Residual PSA ^d	Percentage leached ^e	Swelling ratio ^f	C _{Residual PSA} / C _{Initial PSA}
	mol%	mol%	%	SR	
SI-0.2/2-6	20	<1	>99	14	<0.05
SI-0.2/2-170	20	11	45	35	0.55
SI-0.3/2-170	27	15	44	49	0.55
SI-0.2/0.5-170	20	10	50	110	0.5
SI-0.4/0.5-170	33	13	61	140	0.39
SI-0.2/4-800	20	14	57	32	0.70
SI-0.2/2-800	20	15	25	53	0.75
SI-0.3/2-800	27	20	26	70	0.74

SI-0.2/0.5-800	20	15	25	160	0.75
SI-0.4/0.5-800	33	22	33	260	0.67

- c. Initial mol% of PSA during synthesis
d. Residual mol% of PSA after leaching study
e. Amount of PSA leached out after synthesis
f. Equilibrium swelling ratio measured at room temperature after equilibrating the sample in DI water for 3 days.

Table S4: Determination of Volume phase transition temperature of semi-IPN hydrogels

Sample	VPTT (°C)
SI-0.3/2-170	37.05
SI-0.2/0.5-170	35.78
SI-0.4/0.5-170	36.96
SI-0.2/2-800	39.26
SI-0.3/2-800	38.97
SI-0.2/0.5-800	37.58
SI-0.4/0.5-800	37.66

As the deswelling is not discontinuous, it is not easy to assign an exact value for VPTT, instead the derivative of temperature was used to determine the exact VPTT for each semi-IPN hydrogels.

Table S5: Determination of diffusional exponents of PNIPAM/PSA semi-IPN hydrogels

Semi-IPN hydrogel	ESR (g g ⁻¹)	Diffusion parameters					
		t<10 min			t>10 min		
		n	k	R ²	n	k	R ²
SI-0.2/4-800	32	0.7334	0.1584	0.9951	0.2378	0.4831	0.9738
SI-0.2/2-800	53	0.9613	0.0733	0.9958	0.4145	0.2502	0.9933
SI-0.2/0.5-800	160	1.1154*	0.0469	0.9899	0.3871	0.2368	0.9971
SI-0.3/2-800	70	0.9218	0.0946	0.9938	0.3019	0.3831	0.9532
SI-0.4/0.5-800	260	1.7088*	0.0116	0.9964	0.5562	0.1609	0.9307

If R_{diffuion} and $R_{\text{relaxation}}$ refers to the rate of diffusion and polymer chain relaxation ^[3]

Fickian diffusion ($n=0.5$, $R_{\text{diffuion}} \ll R_{\text{relaxation}}$)

Non-Fickian diffusion ($n>0.5$, $R_{\text{diffuion}} \gg R_{\text{relaxation}}$ Case II transport, $R_{\text{diffuion}} \sim R_{\text{relaxation}}$ anomalous diffusion)

*the values of $n > 1$ was observed indicates anomalous diffusion mechanism where rate of diffusion and rate of polymer chain relaxation is comparable.

Table S6: Diffusion parameters of pure PNIPAM hydrogel

Pure PNIPAM		Diffusion parameters		
hydrogel	ESR (g g^{-1})	n	k	R^2
PNIPAM-0.5	20	0.4079	0.0916	0.9949
PNIPAM-2	13	0.4046	0.1181	0.9975
PNIPAM-4	8	0.3793	0.1439	0.9988

Here, PNIPAM-0.5 means 0.5 wt.% crosslinker with respect to NIPAM monomer. Higher swelling and deswelling rate for pure PNIPAM was observed with increasing crosslinking density.

Figure S1: FTIR spectra show the absorption peaks of pure PNIPAM, PSA, and the semi-IPNs. The FTIR is used to evaluate the functional groups of carboxyl and amide present in the semi-IPNs. Among the characteristic absorption bands, the amide (1665 cm^{-1}) and carboxyl (1560 cm^{-1}). The amide peaks of the semi-IPN SI-0.2/0.5-800, SI-0.3/2-800, SI-0.4/0.5-800 were similar to that of pure PNIPAM, suggesting that the linear PSA within the PNIPAM network do not have major structural transformations in comparison to the pure PNIPAM network.

Figure S2 Swelling/deswelling behaviour of pure PNIPAM hydrogels with different crosslinking density. (a) & (b) shows time dependent swelling ratio (SR) and normalized swelling ratio (SR/ESR) during free swelling of dried PNIPAM hydrogel particles $\sim 200 \mu\text{m}$ in DI water at room temperature (c) logarithmic plot of water absorbed as function of time for determination of kinetic rate constant, assuming first order rate equation (d) & (e) shows time dependent SR and normalized SR during deswelling of PNIPAM particles $\sim 200 \mu\text{m}$ at constant 50°C (f) Arrhenius plot for determination of activation energy. Here K is the first order rate constant at 40, 50 and 60°C . All the values reported are the average values of three repeated measurements.

Figure S3: Plot of $\ln F$ vs $\ln t$ for the diffusional constant determination for semi-IPN hydrogels and pure PNIPAM hydrogels. The diffusional coefficient n was determined from the slope of the curve. Our study suggests swelling of semi-IPN takes place in different diffusion stages, i.e. a fast-initial stage followed by slow water uptake (see Table S5 supporting information). But unlike pure PNIPAM, swelling mechanism of semi-IPN is more complex due to the presence of PSA chains.

Figure S4: Illustration of the steps used for the cyclic FO/dewater test.

Figure S5: Cyclic study of the FO water flux for a swelling/deswelling cycle duration of 60 minutes. Feed for FO 2000 ppm NaCl solution. 0.3 g of hydrogel used as draw solute with active layer facing the draw solute. FO was performed at room temperature and dewatering at 40 °C. The dried PSA/PNIPAM semi-IPN hydrogels particles were able to extract water from the 2000 ppm NaCl solution when placed in contact with the FTS membrane (see Figure S4 and S5 supporting information). As compared to free swelling of the hydrogel in DI water, rate

of hydrogel swelling in contact with the membrane decreased when used for FO due to reduction in osmotic swelling pressure.

Table S7: Parameters obtained for a cyclic swelling and deswelling study of semi-IPN hydrogels as draw solute for FO.

Sample	SR ₀	SR ₁	T _{FO} (min)	T _{DES} (min)	m _{water} (mg)	J _{aap.} (LMH)	Range of experiment	
							SR _{min}	SR _{MAX}
SI-0.2/2-800	0.84	1.33	48	12	145	0.296	0.12	2.37
SI-0.3/2-800	0.91	1.43	49	11	156	0.319	0.01	2.63

List of Abbreviations

Semi-IPN	Semi-interpenetrating polymeric network
NIPAM	N-isopropylacrylamide
PSA	Poly (sodium acrylate)
MBA	N, N'-methylene-bis-acrylamide
TEMED	N,N,N',N'-tetramethyl ethylenediamine
APS	ammonium peroxydisulfate
VPTT	Volume phase transition temperature
MW	Molecular weight
SA	Sodium acrylate
SR	Swelling ratio
ESR	Equilibrium swelling ratio

References

- [1] H. Chen, Y.-L. Hsieh, *Journal of Polymer Science Part A: Polymer Chemistry* **2004**, *42*, 3293.
- [2] J. M. Varghese, Y. A. Ismail, C. K. Lee, K. M. Shin, M. K. Shin, S. I. Kim, I. So, S. J. Kim, *Sensors and Actuators B: Chemical* **2008**, *135*, 336.
- [3] F. Ganji, S. Vasheghani Farahani, E. Vasheghani-Farahani, *Iranian Polymer Journal* **2010**, *19*, 375.
- [4] N. Sahiner, W. T. Godbey, G. L. McPherson, V. T. John, *Colloid and Polymer Science* **2006**, *284*, 1121.
- [5] Y. Cai, W. Shen, S. L. Loo, W. B. Krantz, R. Wang, A. G. Fane, X. Hu, *Water Research* **2013**, *47*, 3773.
- [6] Y. Cai, R. Wang, W. B. Krantz, A. G. Fane, X. M. Hu, *RSC Advances* **2015**, *5*, 97143.