

Supporting information

**The Interplay between Phase Separation and
Gelation Controlling the Morphologies of the
Reactive Covalent Network/Polymer Blends**

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S1. Experimental procedure

1. Materials and methods

Tetrakis(4-aminophenyl)methane (TAPM) was synthesized as previously reported method with modification.¹ Hexamethylene diisocyanate (HDI) (99%, Sigma Aldrich) was freshly distilled under reduced pressure. Anhydrous grade solvents of N,N-dimethylformamide(DMF) (99.8%), N,N-dimethylacetamide(DMAc) (99.8%), Dimethyl sulfoxide(DMSO) (99.9%), propylene carbonate, and acetic acid (99.8%) were purchased from Sigma Aldrich. Tetrahydrofuran (THF)(99.9%), chloroform, acetone, acetonitrile, dichloromethane, chlorobenzene, pyridine, methanol, ethanol, water, and n-hexane were purchased from commercial sources, and used without further purification. All polymers used in this study were purchased from Sigma Aldrich and Polymer Source. Inc.. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the polymers were obtained by Gel permeation chromatography (GPC). Poly(methyl methacrylate) (PMMA) of three different molecular weights (PMMA15000: M_w =14,800 Da, M_n =9,000 Da; PMMA2700: M_w =2,700 Da, M_n =2,500 Da; PMMA50000: M_w =54,500 Da, M_n =50,000 Da), polysulfone (PSF) (PSF35000: M_w =40,700 Da, M_n =24,300 Da), polyethylene glycol (PEG) (PEG35000: M_w =31,100 Da, M_n =27,100 Da; PEG10000: M_w =10,400 Da, M_n =8,800 Da; PEG2050: M_w =2,060 Da, M_n =2,000 Da), polystyrene (PS) (PS5400: M_w =5,400 Da, M_n =4,700 Da; PS35000: M_w =35,000 Da), and polyvinyl pyrrolidone (PVP) (PVP29000: M_w =28,600 Da, M_n =11,700 Da; PVP10000: M_w =9,900 Da, M_n =4,700 Da) were used after drying at least for 24 hours in a desiccator prior to use.

2-1. Preparation of urea-bonded network (UN) sols

To prepare a 0.04 g/mL UN sol, tetrakis(4-aminophenyl) methane (TAPM) (0.200 g, 0.526 mmol) was dissolved in 5 mL of anhydrous DMF under a nitrogen atmosphere at room temperature. The solution was added to a solution of distilled hexamethylene diisocyanate (HDI) (0.175 g, 1.052 mmol) in DMF (4.4 mL) at room temperature. The reaction mixture remained in the liquid sol state until the gelation time (t_g), which was about 85 hours for a concentration of 0.04 g/mL.

2-2. Typical procedure for preparation of polymer/UN blends

In a typical UN sol preparation for blending with polymer, UN monomer solution mixture was kept for 60 hours at room temperature. To the UN sol prepared from the above was added specific amount of polymer. The weight fraction of the polymer relative to UN sol was varied in the range of W_p =0.1~0.8. The polymer/UN sol mixture was heated at 50 °C and stirred for 90 minutes. The solution was cooled to room temperature for 30 minutes under stirring after removing the heating bath. The resulting polymer/UN sol solution was cast onto a glass plate, and the solvent was evaporated by heating sequentially at the designated temperatures under nitrogen flow. The temperature increasing rate was 1°C /min. After solvent evaporation, the glass plate with the film was immersed in water to obtain free-standing polymer/UN blend film.

2-3. Preparation of PMMA/UN blend and the nanostructured PMMA/UN film

PMMA/UN blend films were prepared following the typical polymer/UN blend synthesis procedures. Heating sequence for solvent evaporation was (1) 50°C for 1 h, (2) 80°C for 8 h. After solvent evaporation, the glass plate with the film was immersed in water for 12 hours to obtain free-standing PMMA/UN blend film. PMMA was removed from the composite by stirring in acetic acid for 1 h, in water for 12 h, and in acetone for 24 h at room temperature. The film was dried in vacuum oven at 80°C for 24 h.

2-4. Preparation of PSF/UN blend and freestanding nanoporous UN film

PSF/UN blends were prepared following the typical polymer/UN blend synthesis procedures. The heating sequence for solvent evaporation was (1) 50 °C for 1 h, (2) 80°C for 8 h. After solvent evaporation, the glass plate with the film was immersed in water for 12 hours to obtain free-standing PSF/UN blend film. PSF was removed from the composite by stirring in THF for 1 week at room temperature. The film was dried in vacuum oven at 80°C for 24 h.

2-5. Preparation of PS/UN blend film and solvent treatment.

PS/UN composite films were prepared following the typical polymer/UN blend synthesis procedures. Heating sequence for solvent evaporation was (1) 50°C for 1 h, (2) 80°C for 8 h. After solvent evaporation, the glass plate with the film was immersed in water to obtain free-standing PS/UN composite film. PS was removed from the composite by stirring in THF for 1 week at room temperature. The film was dried in vacuum oven at 80°C for 24 h.

2-6. Sample preparation for investigation of polymer/UN morphologies with different polymerization time (t_p)

e-polymer/UN films were prepared following the typical procedures for each polymers, while the polymerization time was varied to 1h, 6h, 24h. The weight fraction of PS/UN and PMMA/UN was kept as 50wt%. PEG/UN blends were prepared with 60wt% polymer weight fraction following the heating sequence (1) 30°C for 2h, (2) 50°C for 2h, and (3) 60°C for 5h. Then PEG was removed from the blend by stirring in water for 1 week at room temperature. The film was dried in vacuum oven at 80°C for 24 h.

2-7. Preparation of polymer/UN sol mixture for Dynamic Light Scattering(DLS) analysis

To a 0.04 g/ml UN sol prepared by a typical procedure, each polymers were added with various weight fractions. The polymer/UN sol mixture solution was heated at 50 °C and stirred for 90 minutes. The solution was cooled to room temperature for 30 minutes under stirring, and immediately transferred to cuvette for DLS measurement.

2-8. Hansen solubility parameter estimation of UN sol

To 2 ml of various organic solvents and water, a 0.7 ml of 0.04g/ml UN sol was added dropwise and gently stirred for about 30 seconds. The solvents were classified into sol-solvent and non-solvent depending on the phase of the solvent/UN sol mixture. Based on the Hansen solubility parameter values of each solvent, optimization was performed by MATLAB[®] following the procedure reported in the literature.² (The detailed procedure is given in the following section)

2-9. Preparation of nanostructured PMMA/UN film with different solvent evaporation temperatures.

PMMA/UN blend films ($W_p = 0.5$) were prepared following a typical procedure, while the solvent temperature was each varied to 30°C or 70°C. After solvent evaporation, the PMMA/UN blend film was immersed in water for 12 hours. PMMA was removed from the blend by stirring in acetic acid for 1 h, in water for 12 h, and in acetone for 24 h at room temperature. The film was dried in vacuum oven at 80°C for 24 h.

2-10. Measurement of gelation concentration of polymer/UN sol mixtures

Each of the PEG/UN or PMMA/UN sol mixtures ($W_p = 0, 0.2, 0.4, 0.6$) was cast in a Petri dish (diameter = 5 cm). The volume of each sample was 5 mL. The weight of the dish and the sample was recorded. Then the samples were dried at 30°C under nitrogen atmosphere. Gelation point was defined as the point at which the solution did not flow even when the dish was tilted about 30 degrees from the table top surface. The weight of gelled sample on the dish was recorded. The weight loss corresponds to the amount of evaporated solvent. The composition of the resulting gelled mixture was calculated while considering the initial composition and the weight loss by drying.

3. Characterization

Scanning electron microscopy (SEM) was performed on a JEOL JSM-7500F Field emission scanning electron microscope. Sample films for cross-section analysis were fractured in liquid nitrogen and dried for 12 h under vacuum. The samples were then coated with 3nm of platinum using sputter before SEM imaging. Dynamic Light Scattering (DLS) was carried out using a model ELS-Z of Zeta-potential & Particle analyzer (OTSUKA Electronics Co., Ltd). Each sample was analyzed three times, and then the average value was calculated. The Fourier Transform Infrared (FTIR) spectra (4,000–400 cm^{-1}) were recorded by a System 2000 FTIR spectrophotometer (Perkin Elmer). FTIR samples of polymers were prepared by the KBr pellet method, and freestanding films of polymer/UN blends were used for measurements. Reflection polarized light microscopy was conducted with BX51-P polarizing microscope (Olympus corporation).

The molecular weights (M_n and M_w) of PMMA was obtained from Gel Permeation Chromatography (GPC) by using EcoSEC HLC-8320 GPC (Tosoh) equipped with a refractive index detector. Three columns were used (two TSKgel SupermultiporeHZ-M columns [4.6×150 mm] and a TSKgel SuperHZ-2500 [4.6×150 mm]), which is connected with a Shodex HK-G guard filter. Tetrahydrofuran (THF) was used as an eluent with a flow rate of 0.35 mLmin^{-1} at 40 °C. Calibration curve was obtained using monodisperse PMMA as a standard. The molecular weights of PEGs were obtained with the three columns (two TSKgel GMPWxl, and TSKgel G2500PWxl [7.8 x 300mm]) and a Tskgel guard PWxl guard column. 0.1M NaNO_3 aqueous solution was used as an eluent with a flow rate of 1.0 mLmin^{-1} at 40 °C. Calibration curve was obtained using monodisperse PEG as a standard. For GPC analysis of PSF, PS, and PVP, we used home-made GPC system equipped with three columns (two Shodex LF-804 columns and a Shodex LF-G guard column). We analyzed PSF and PS with the elution conditions (flow rate=1.0 mLmin^{-1} at 40 °C, eluent=THF), and PVP with a flow rate=1.0 mLmin^{-1} at 50 °C, eluent=DMF(10mM LiBr). Calibration curve was obtained using monodisperse PS as a standard for THF, and PEG for DMF eluent.

S2. FTIR spectroscopy of PS/UN blends and solvent-treated films

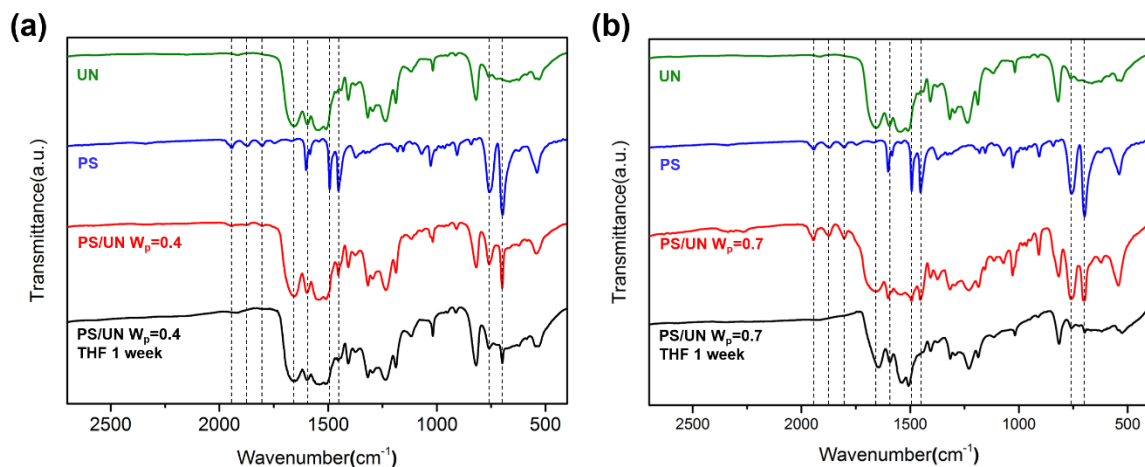


Figure S1. FTIR spectrum of PS/UN before and after solvent treatment. (a) $W_p = 0.4$, (b) $W_p = 0.7$.

Table S1. FTIR peak assignments of polymer/UN blends

Polymer/UN	Peak (cm ⁻¹)	Vibrational modes
PSF/UN ³	3450-3300	Secondary N-H stretching
	3080-3030	Aromatic C-H stretching
	1375, 1151	S=O asymmetric and symmetric stretching
	1244, 1014	C-O asymmetric stretching
PS/UN	3450-3300	Secondary N-H stretching
	3080-3030	Aromatic C-H stretching
	2000-1650	Combination vibration, overtones of aromatic hydrocarbons
	1645	CO stretching
	1600-1585	C-C stretching (in-ring)
	1500-1400	C-C stretching (in-ring)
PEG/UN ^{4,5}	900-675	C-H out of plane vibration
	3450-3300	Secondary N-H stretching
	1408	Aromatic C=C stretching
	1348	O-H bending
	1168-1049	C-O-C stretching
PMMA/UN ⁶⁻⁸	1040	O-H stretching
	3450-3300	Secondary N-H stretching
	3080-3030	Aromatic C-H stretching
	2952	O-CH ₃ stretching of PMMA
	3000-2850	Aliphatic C-H stretching
	1727-1732	C=O stretching (Ketone)
	1450	C-H bending (Alkane)
	1149	C-O-C stretching (Ether)
	1018	C-N stretching
	751-988	(CH ₂) _n with $n \geq 4$ (Alkane)

S3. DLS characterization of polymer/UN sol mixture

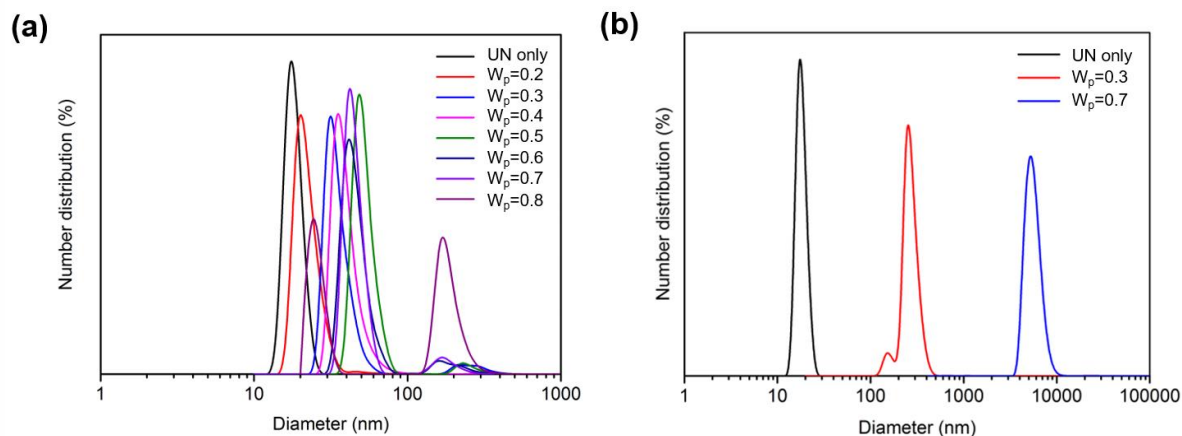


Figure S2. Particle size distribution of polymer/UN sol mixture solution obtained from dynamic light scattering (DLS) analysis. (a) PMMA/UN and (b) PS/UN.

Table S2. Estimated polymer overlap concentration of the polymers studied in this work

Polymer	average M_w (g/mol)	polymer overlap concentration, C^* (g/ml) ^[a]	W_p at C^*	reference
PEG	31,100	0.0369	0.470	10
PMMA	14,800	0.0966	0.707	11
PSF	40,700	0.0325	0.448	12
PS	35,000	0.0987	0.712	13

[a] The polymer overlap concentration of each polymers was calculated from the data provided in the above references.

S4. Morphology characterization of polymer/UN blends and e-polymer/UNs

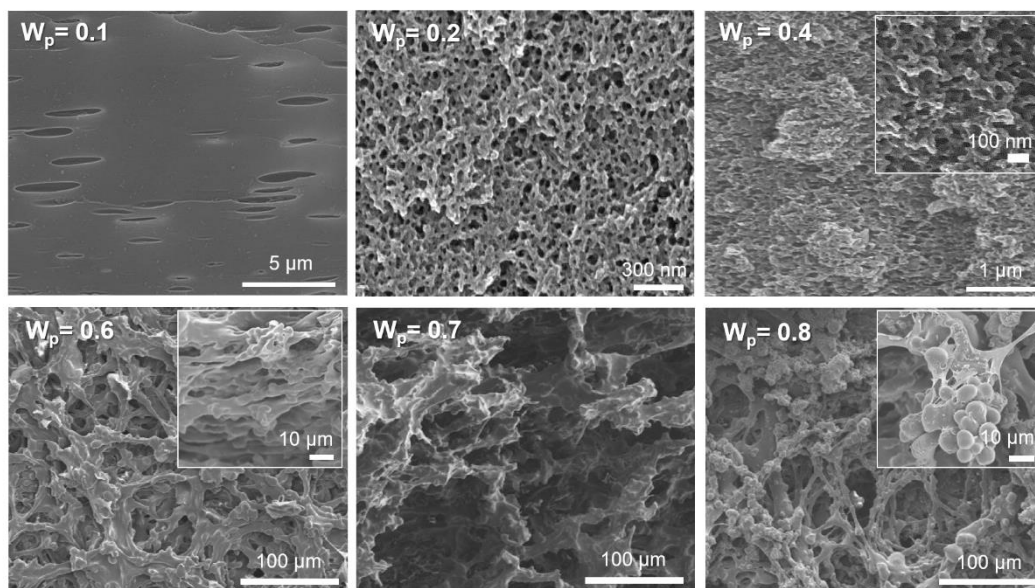


Figure S3. Cross-sectional SEM images of e-PSF/UN ($W_p=0.1\sim0.8$) obtained after treatment of PSF/UN blend in THF. The blend film was dipped in THF under stirring for 1 week, and dried in vacuum at 80°C for 24 h.

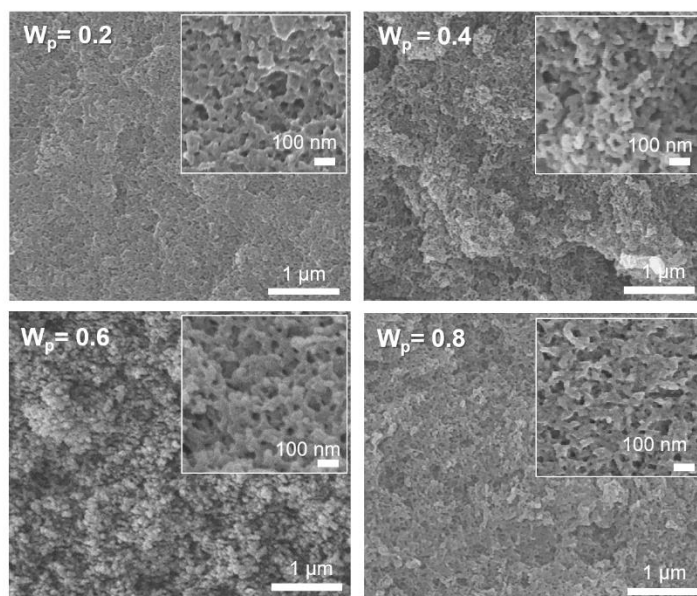


Figure S4. Cross-sectional SEM images of e-PEG/UN ($W_p=0.2\sim0.8$) obtained after treatment of PEG/UN blend in deionized water. The blend film was dipped in deionized water under stirring for 1 week, and dried in vacuum at 80°C for 24 h.

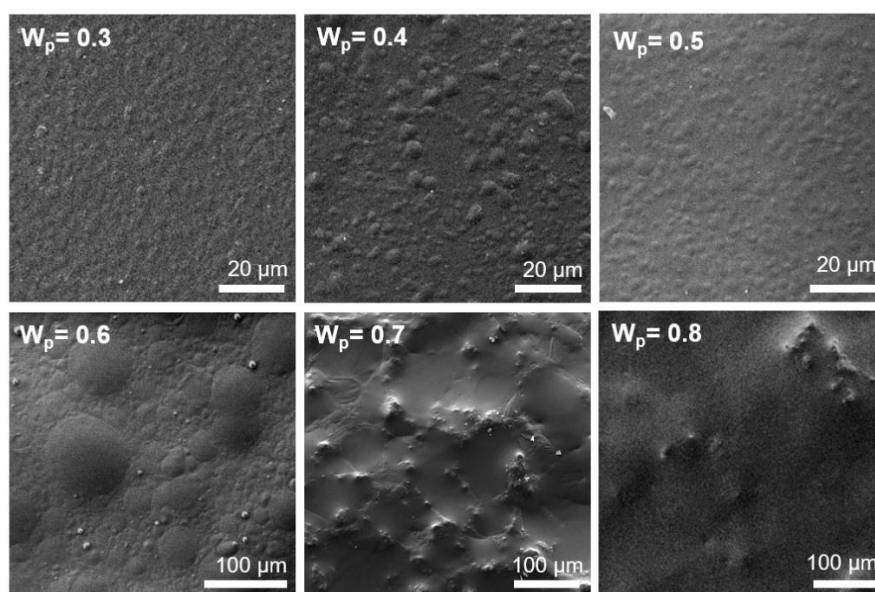


Figure S5. Top surface SEM images of PS/UN blend films with various PS compositions ($W_p=0.3\sim0.8$)

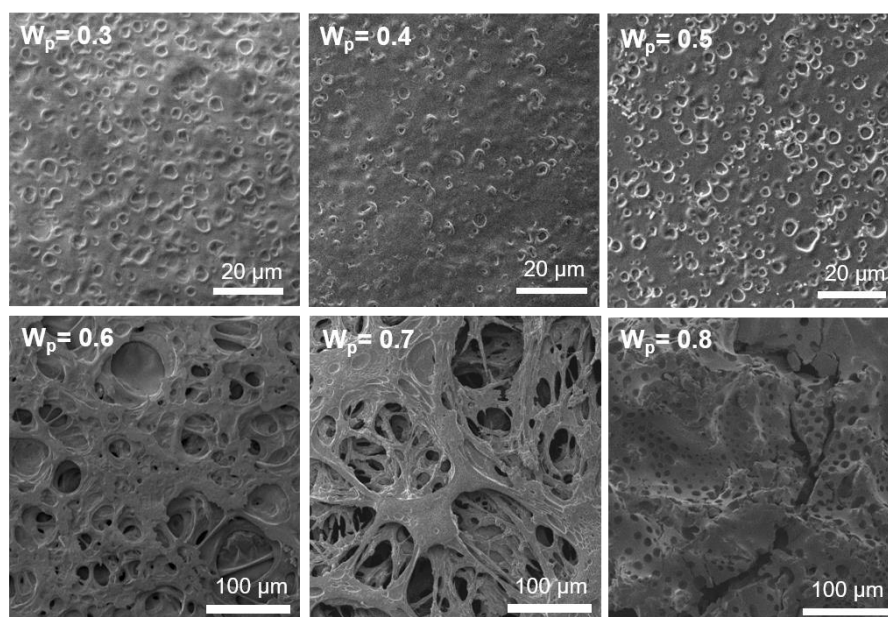


Figure S6. Top surface SEM images of PS/UN blends ($W_p=0.3\sim0.8$) after THF treatment(e-PS/UN). PS/UN blend films were dipped in THF under stirring for 1 week, and dried in vacuum at 80°C for 24 hours.

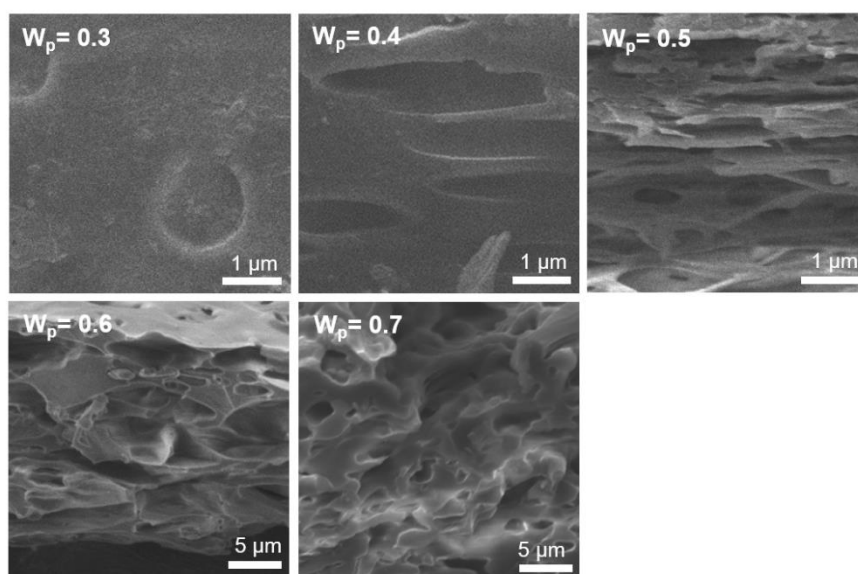


Figure S7. Cross-sectional SEM images of e-PS/UN ($W_p=0.3\sim0.7$) obtained after treatment of PS/UN blend in THF. The blend film was dipped in THF under stirring for 1 week, and dried in vacuum at 80°C for 24 h.

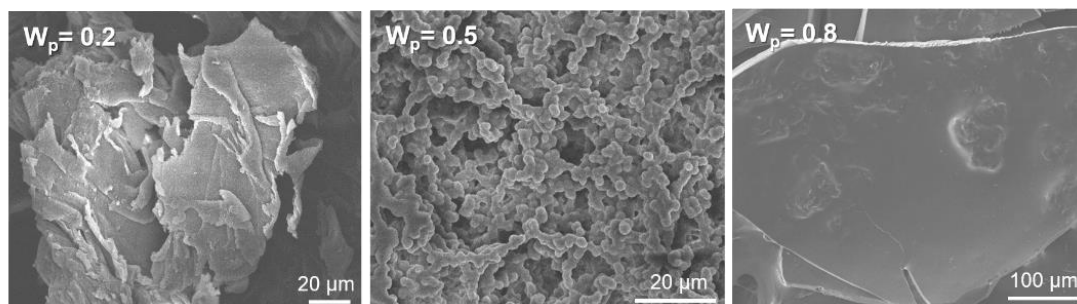


Figure S8. SEM images of e-PVP/UN ($W_p=0.2, 0.5, \text{ and } 0.8$) derived from PVP/UN. The membranes were prepared by immersing PVP/UN blend film or powder in deionized water for 1 week and then dried in a vacuum oven at 100 °C for 12 h.

S5. Effect of polymer molecular weight on the morphology of polymer/UNs

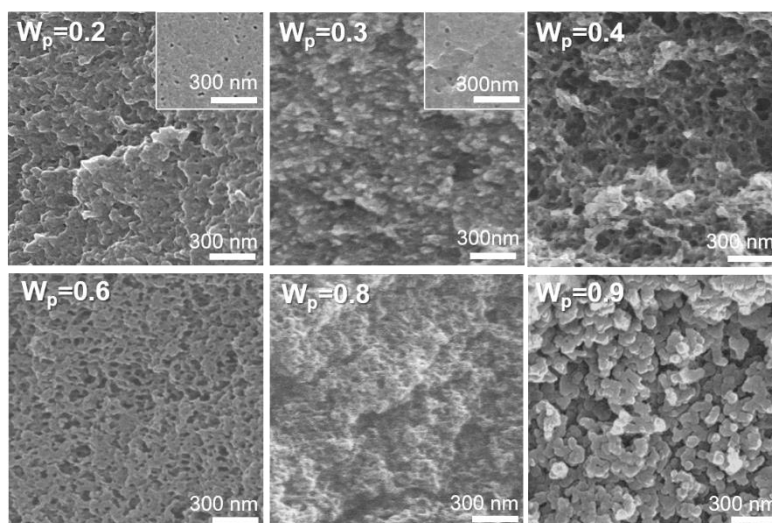


Figure S9. Cross-sectional SEM images of e-PEG/UN samples obtained after solvent treatment of PEG/UN blends (PEG10000, $W_p=0.2\sim0.9$). The blend film was dipped in deionized water under stirring for 1 week, and dried in vacuum at 80°C for 24 h.

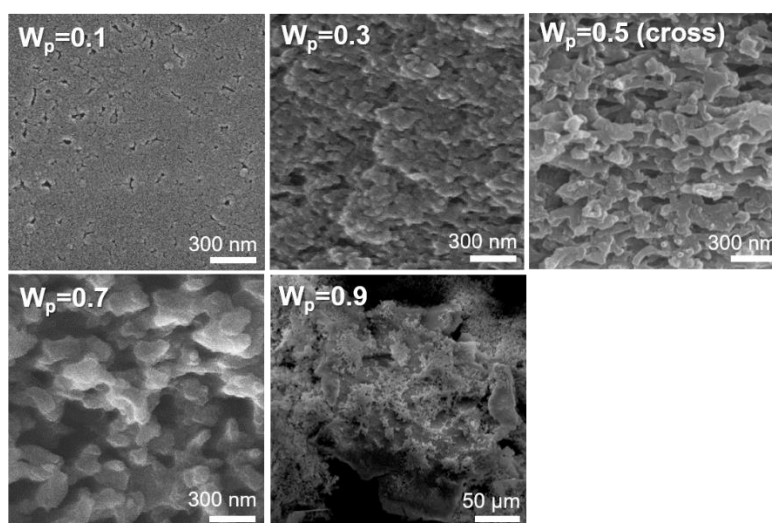


Figure S10. Cross-sectional SEM images of e-PMMA/UN obtained after solvent treatment of PMMA/UN blends (PMMA2700, $W_p=0.1\sim0.9$). The blend film was dipped consecutively in acetic acid, deionized water, and acetone, then dried in vacuum at 80°C for 24 h.

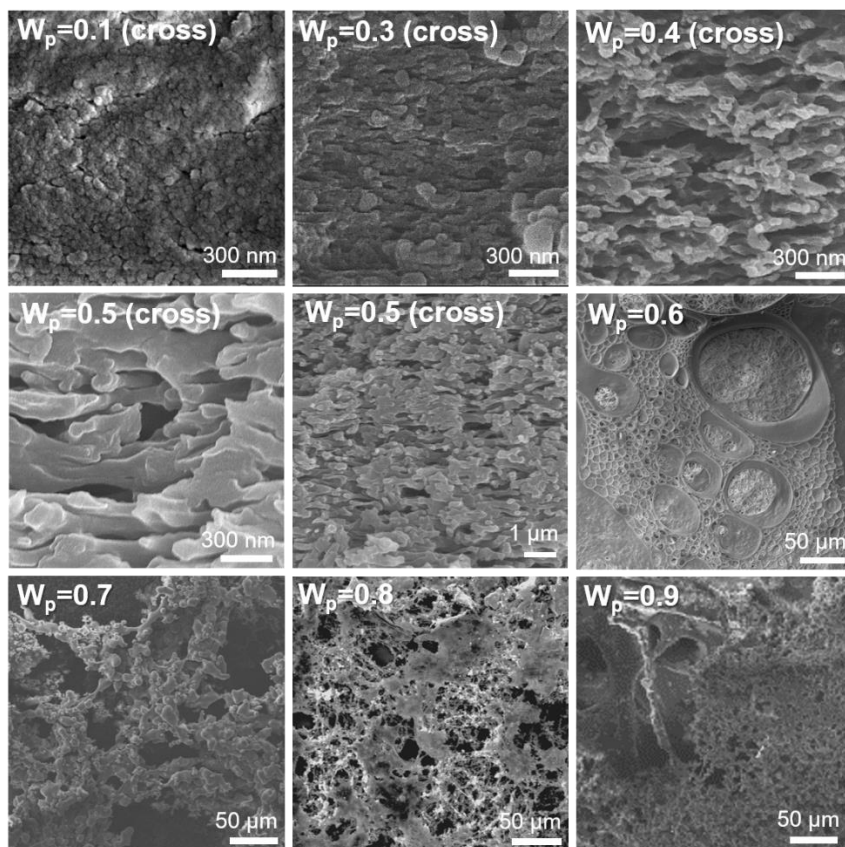


Figure S11. Cross-sectional SEM images of e-PMMA/UN obtained after solvent treatment of PMMA/UN blends (PMMA50000, $W_p=0.1\sim0.9$). The blend film was dipped consecutively in acetic acid, deionized water, and acetone, then dried in vacuum at 80°C for 24 h.

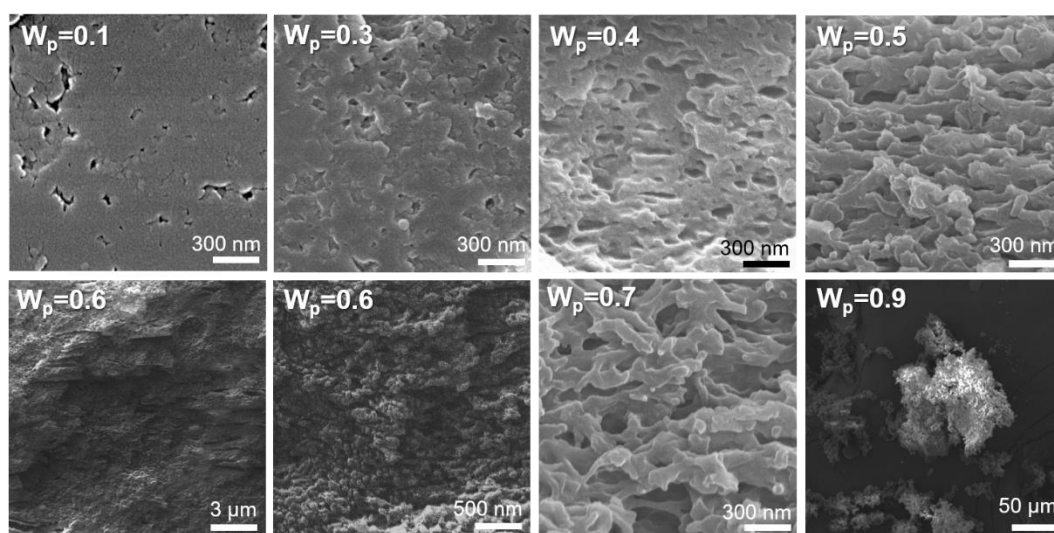


Figure S12. Cross-sectional SEM images of e-PS/UN samples obtained after solvent treatment of PS/UN blends (PS4700, $W_p=0.1\sim0.9$). The blend film was dipped in THF under stirring for 1 week, and dried in vacuum at 80°C for 24 h.

S6. Estimation of Hansen solubility parameter of UN sol

The estimation of HSP values of UN sol includes the following 3 steps.

- 1) 3-D plotting of the solvents using HSP values as coordinates,
- 2) searching a sphere whose origin is HSP values of UN sol and that embraces sol-solvents inside but excludes non-solvents,
- 3) optimization of the sphere's position and size by comparing its goodness-of-fit.

1) The solvents were classified into two categories (sol-solvent or non-solvent) based on the result of UN sol addition test (**Table S3 and Figure S11**). Using the HSP values of the solvents as coordinates ($2\delta_d$, δ_p , δ_h), we plotted the dots in 3-D space, which is often called Hansen space.

2) We can think of a sphere whose origin is HSP values of UN sol. According to the characteristics of HSP values, the sphere should encompass sol-solvents (good solvents) inside but excludes non-solvents (poor solvents). The size or radius of the sphere, and its location (determined by its origin, HSP values of UN sol) are the two variables to be optimized. We used a MATLAB program to find the optimal location and size of the sphere that satisfied the above criterion. The algorithm and fitting procedure was based on the reference,² and the MATLAB code was written and modified for our calculation.

3) For optimization of the two variables, we first make an initial guess for the location and the radius based on the HSP values of the solvents. We took the arithmetic mean (average) of each HSP components and used them as initial coordinates. To find the optimized position, a desirability function (DF) was employed to determine the goodness-of-fit for this radius and origin. Nelder-Mead algorithm available in the Optimization Toolbox of MATLAB was used for the optimization, with the objective function (OF) defined for the process. The optimization of the location and size of the sphere was iterated until the DF was maximized, or OF was minimized.

Table S3. Physical properties of various solvents tested in this study and the result of UN sol addition test

Solvent	UN sol addition test (Sol-solvent : S / Non-solvent : N)	Solubility parameter(MPa) ^{$\frac{1}{2}$} [a]				note
		δ_d	δ_p	δ_h	δ_t	
N,N-dimethylformamide(DMF)	S	17.4	13.7	11.3	24.8	
Dimethyl sulfoxide(DMSO)	S	18.4	16.4	10.2	26.68	
N-methyl-2-pyrrolidone(NMP)	S	18	12.3	7.2	22.96	
N,N-dimethylacetamide(DMAc)	S	16.8	11.5	10.2	22.77	
Tetrahydrofuran(THF)	N	16.8	5.7	8	18.43	
Acetone	N	15.5	10.4	7	19.94	
Acetonitrile(MeCN)	N	15.3	18	6.1	24.4	
Chloroform(CF)	N	17.8	3.1	5.7	19.95	
Dichloromethane(DCM)	N	18.2	6.3	6.1	20.2	
Chlorobenzene(CB)	N	19	4.3	2	19.58	
Pyridine	N	19	8.8	5.9	21.75	
Methanol(MeOH)	N	15.1	12.3	22.3	29.61	

Ethanol(EtOH)	N	15.8	8.8	19.4	26.52	
Water	N	15.5	16	42.3	47.81	
n-hexane	N	14.9	0	0	14.9	
1,2-dichloroethane	N	19.0	7.4	4.1	20.8	
Diethyl ether	N	14.5	2.9	5.1	15.65	
Propylene carbonate	N	20.0	18.0	4.1	27.22	14
Ethyl acetate	N	15.8	5.3	7.2	18.15	

[a] : Solubility parameter values were obtained from ref. ¹⁵⁻¹⁷.

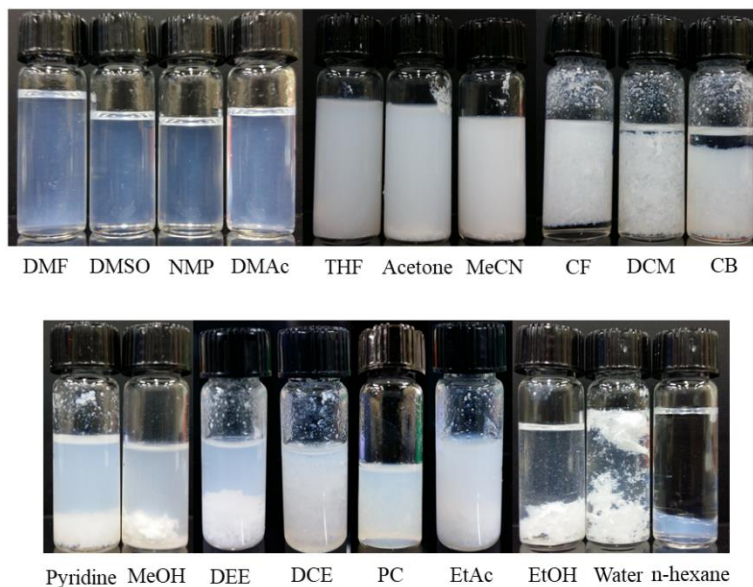


Figure S13. Optical image of the various solvents after UN sol (0.04g/ml, $t_p = 60$ h) was added dropwise.

Table S4. Estimated Hansen solubility parameters of UN sol

	$\delta_d (MPa)^{\frac{1}{2}}$	$\delta_p (MPa)^{\frac{1}{2}}$	$\delta_h (MPa)^{\frac{1}{2}}$	$\delta_t (MPa)^{\frac{1}{2}}$
UN sol	18.4496	13.4352	8.5432	24.37

To graphically express the relative contribution of each HSP component to the total HSP, a set of fractional parameters (Ξ_d , Ξ_p , Ξ_h) were derived from the HSP values of the solvents and polymers using the formulas¹⁸

$$\Xi_d = \delta_d / (\delta_d + \delta_p + \delta_h) \quad (2),$$

$$\Xi_p = \delta_p / (\delta_d + \delta_p + \delta_h) \quad (3),$$

$$\Xi_h = \delta_h / (\delta_d + \delta_p + \delta_h) \quad (4).$$

The fractional parameters were plotted on a triangular graph, also known as a Teas graph, with sol-solvents, non-solvents, and polymers marked in different colors (**Figure S12**).

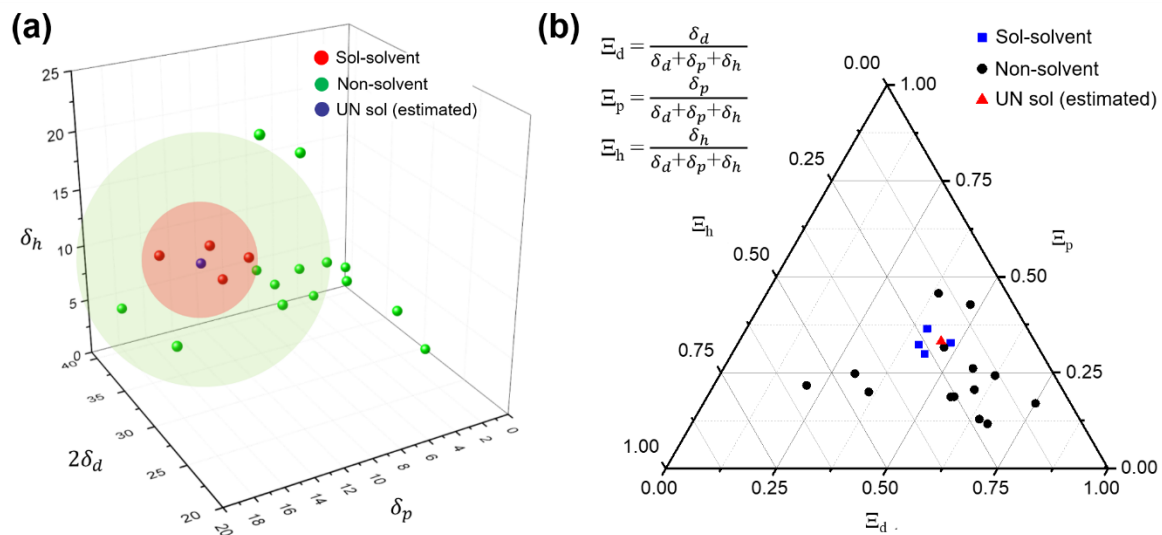


Figure S14. Hansen solubility parameter estimation of UN sol. (a) Solubility parameter space (b) Teas plot

S7. Calculation of interaction parameters between polymers and UN sol

Interaction parameter between polymer and UN sol ($\chi_{\text{polymer-UN}}$) was calculated using the following expression.(ref)

$$\chi_{\text{polymer-UN}} = (v_{\text{seg}}/kT)(\delta_{\text{polymer}} - \delta_{\text{UN}})^2$$

, where v_{seg} is a segmental volume, k is Boltzmann constant, T is absolute temperature (K), and δ_{polymer} and δ_{UN} are solubility parameters of polymer and UN sol, respectively. We used a molar volume of DMF (77 cm³/mol) for the segmental volume, $k = 1.3806 \times 10^{-23}$ m² kg s⁻² K⁻¹ and $T = 303\text{K}$ for the calculation.

Table S5. Estimated interaction parameters between polymers and UN sol

species	solubility parameter (MPa ^{1/2})	$\chi_{\text{polymer-UN}}$
UN sol	24.4	-
DMF	24.8	-
PEG	19.9	0.61
PMMA	21.1	0.33
PSF	22.9	0.066
PS	19.3	0.80
PVP	24.3	0.00015

Table S6. Calculation of segregation strength between polymer and UN sol

Polymer	$\chi_{\text{polymer-UN}}$	average M_w (g/mol)	R_g (nm) ^{[a][b]}	$R_{g, \text{polymer}}/R_{h, \text{UN}}$ ^[c]	$\chi_{\text{polymer-UN}}(R_{g, \text{polymer}}/R_{h, \text{UN}})$
PEG	0.951	31,100	5.24	0.887	0.844
		10,400	2.52	0.427	0.406
PMMA	0.667	14,800	2.92	0.492	0.328
		2,700	1.14	0.193	0.129
		54,500	5.7	0.966	0.644
PSF	0.406	40,700	6	1.02	0.413
PS	1.14	35,000	5.2	0.881	1.003
		5,400	2.78	0.471	0.536
PVP	0.00015	28,600	5.58	0.947	0.000142
		9,900	3.1	0.528	7.91×10^{-5}

[a] Radius of gyration (R_g) values of the polymers were estimated from the references using their molecular weights.

[b] For PVP, R_g values were obtained from the scaling relationship between R_g and hydrodynamic radius as used in the reference.¹⁹

[c] Hydrodynamic radius of UN sol was obtained from DLS measurement of UN sol solution (0.04 g/ml, polymerization time = 60 h)

S8. Effect of polymerization time on the morphology of e-polymer/UN films

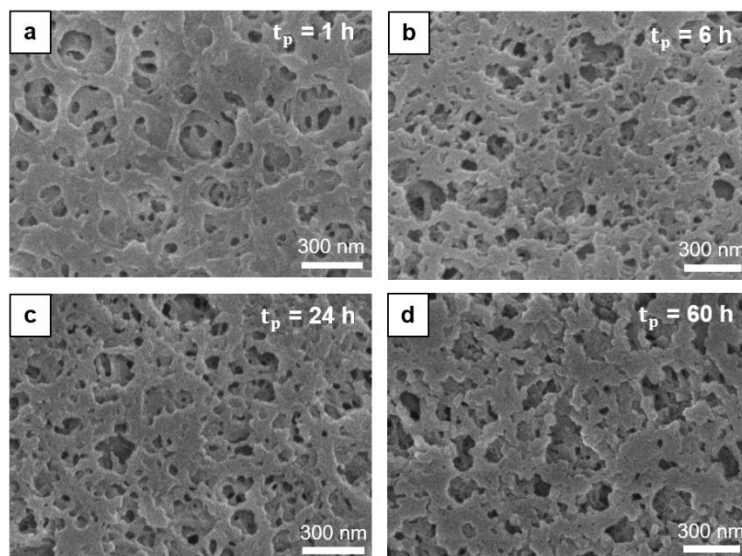


Figure S15. Top-surface SEM images of e-PMMA/UN (PMMA15000, $W_p=0.5$) films with different polymerization times. (a) $t_p=1$ h, (b) $t_p=6$ h, (c) $t_p=24$ h, and (d) $t_p=60$ h.

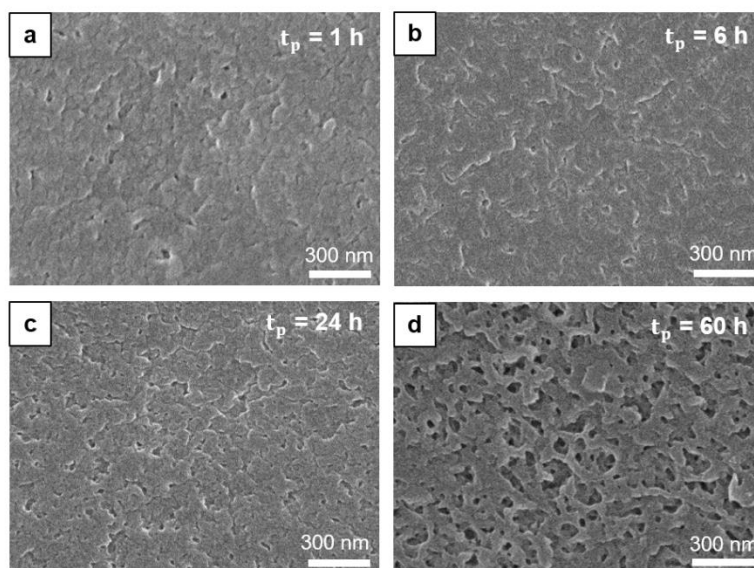


Figure S16. Top-surface SEM images of e-PEG/UN (PEG35000, $W_p=0.6$) films with different polymerization times. (a) $t_p=1$ h, (b) $t_p=6$ h, (c) $t_p=24$ h, and (d) $t_p=60$ h.

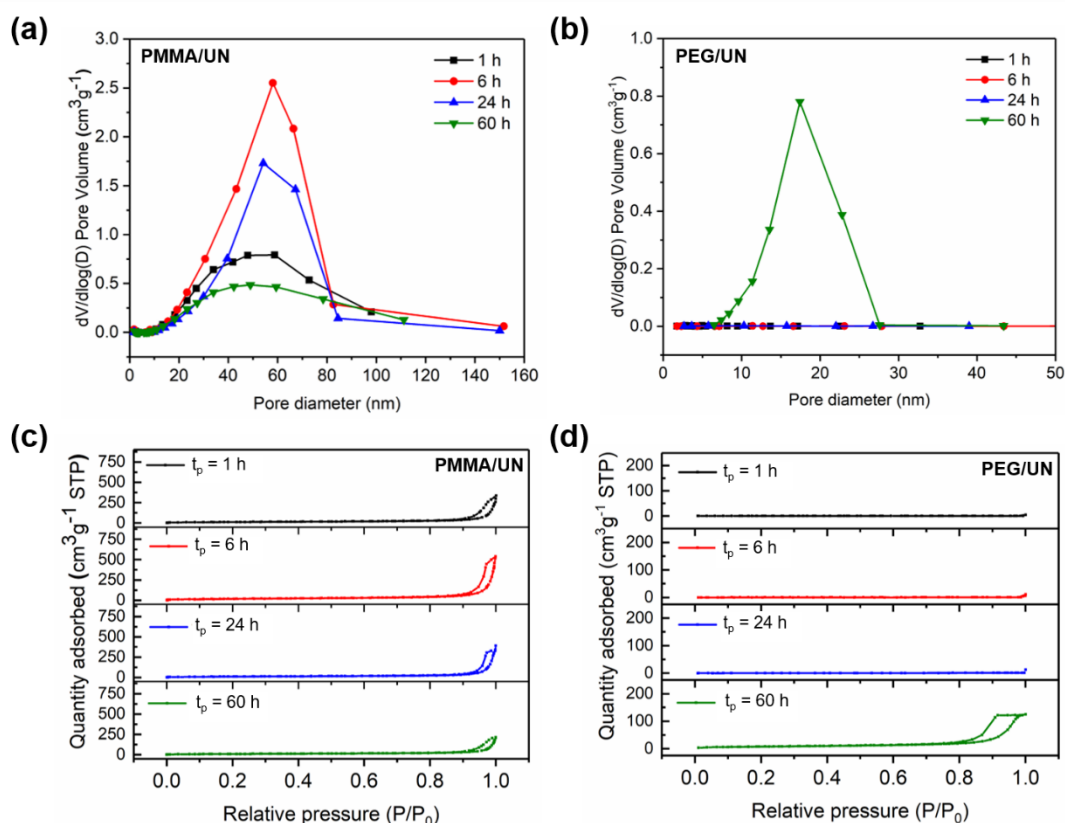


Figure S17. Porosity of e-PMMA/UN and e-PEG/UN films prepared with different polymerization time (t_p). BJH pore size distribution curves of (a) e-PMMA/UN and (b) e-PEG/UN. Nitrogen sorption isotherms of (c) e-PMMA/UN and (d) e-PEG/UN.

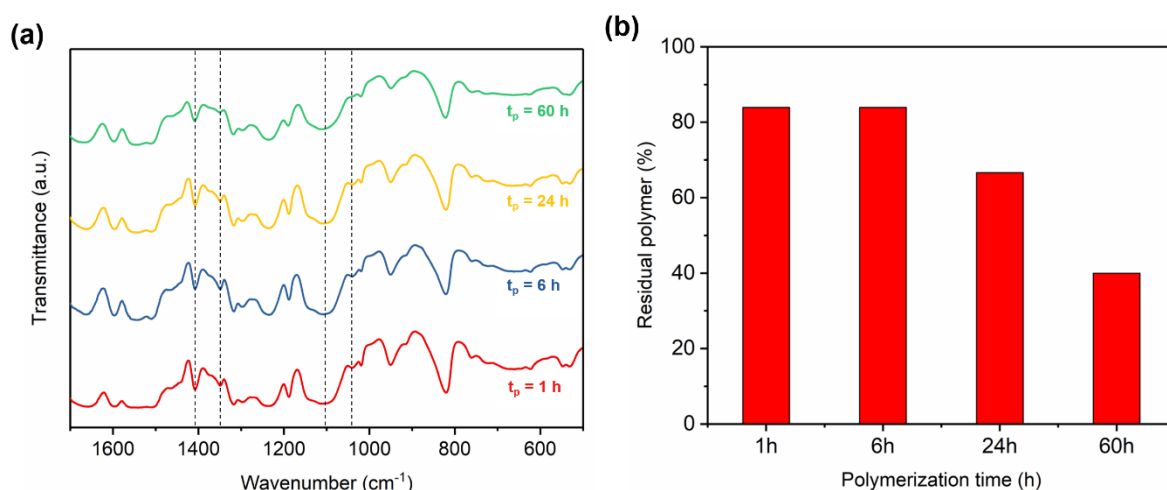


Figure S18. Effect of polymerization time of UN sol. (a) FTIR spectrum of e-PEG/UN prepared from PEG/UN blend (PEG35000, $W_p=0.5$) with different polymerization time (t_p) of 1, 6, 24, and 60 h. Characteristic peaks of PEG used for the calculation of the remaining PEG in e-PEG/UN are denoted by the dotted lines. (b) The residual amount of PEG relative to the initial amount after solvent extraction of the PEG/UN blends prepared with various polymerization time.

Table S7. Porous characteristics of solvent-extracted PMMA/UN and PEG/UN films (e-PMMA/UN and PEG/UN) prepared with different polymerization time (t_p)

e-polymer/UN	Polymerization time (t_p , hour)	Porosity		
		BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume* ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter* (nm)
e-PMMA/UN ($W_p=0.5$)	1	44.7	0.44	35.6
	6	66.3	0.83	41.5
	24	39.8	0.52	44.0
	60	36.1	0.31	34.6
e-PEG/UN ($W_p=0.5$)	1	0.621	0.000584	5.70
	6	0.500	0.000761	9.43
	24	1.28	0.00154	7.74
	60	28.8	0.189	15.7

* Pore volume and average pore diameter were calculated by BJH method from the desorption branch of the nitrogen sorption isotherm.

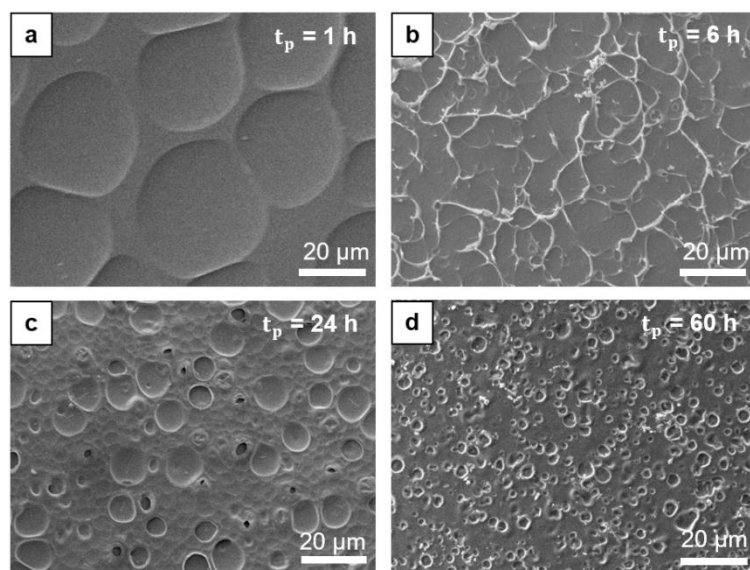


Figure S19. Top-surface SEM images of e-PS/UN (PS35000, $W_p=0.5$) films with different polymerization times. (a) $t_p=1\text{h}$, (b) $t_p=6\text{h}$, (c) $t_p=24\text{h}$, and (d) $t_p=60\text{h}$.

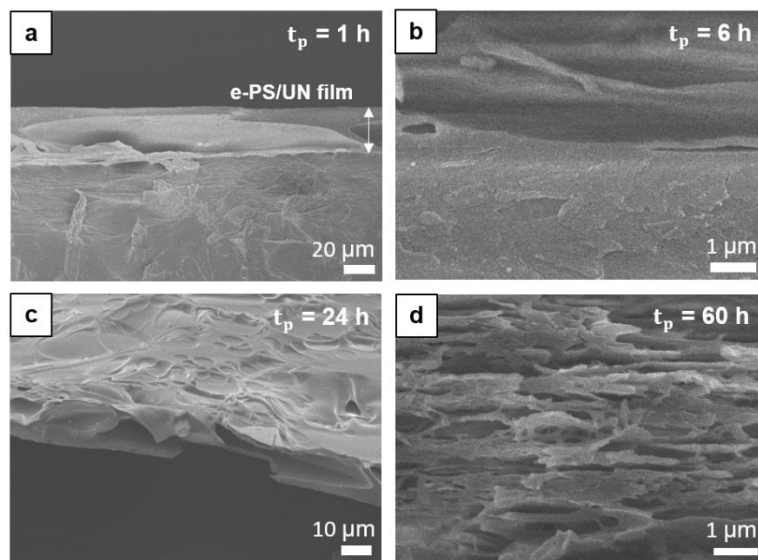


Figure S20. Cross-sectional SEM images of e-PS/UN (PS35000, $W_p=0.5$) films with different polymerization times. (a) $t_p=1\text{h}$, (b) $t_p=6\text{h}$, (c) $t_p=24\text{h}$, and (d) $t_p=60\text{h}$.

S9. Effect of solvent evaporation temperature on the morphology of e-PMMA/UN films

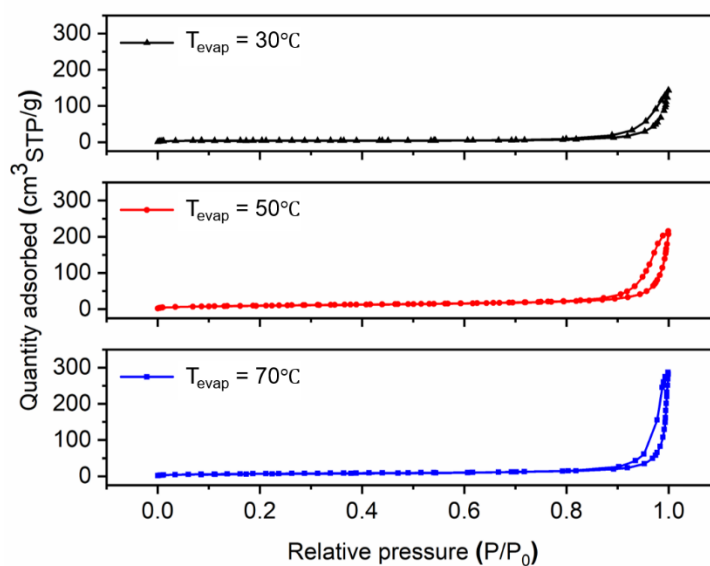


Figure S21. Nitrogen sorption isotherms of e-PMMA/UN films prepared with different solvent evaporation temperature (T_{evap}).

Table S8. Porous characteristics of solvent-extracted PMMA/UN and PEG/UN films prepared with different solvent evaporation temperature (T_{evap})

Polymer/UN	Solvent evaporation temperature (T_{evap} , °C)	Porosity		
		BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume* ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter* (nm)
PMMA/UN ($W_p=0.5$)	30	14.6	0.20	36.0
	50	36.1	0.33	36.6
	70	24.4	0.43	53.3

* Pore volume and average pore diameter were calculated by BJH method from the desorption branch of the nitrogen sorption isotherm.

S10. Supplementary references

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