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Supplementary Materials:

Hyper-cross-linked Polymer with Controlled Multiscale Porosity via Polymerization-induced Microphase Separation within High Internal Phase Emulsion

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Materials and Methods

Supporting Tables S1-S2

Supporting Figures S1-S11

Materials and Methods

Materials. Unless noted otherwise, all the chemicals were used as received. 1,8-Diaza-bicyclo[5.4.0]undec-7-ene (DBU), potassium persulfate (KPS, > 99%), sorbitan monooleate (Span 80), 1,2-dichloroethane (anhydrous, 99.8 %), formaldehyde dimethyl acetal (FDA, 99%) and iron(III) chloride ($FeCl_3$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Information from the vendor was used to describe their hydrodynamic diameters (D_h) in aqueous solution. Sodium chloride (NaCl, 99%) and calcium chloride dihydrate ($CaCl_2$, 97%) were purchased from Daejung Chemicals (Siheung, Korea) and Yukari Pure Chemical Co., LTD (Kyoto, Japan), respectively. d,l-Lactide was kindly provided by Corbion Purac (Amsterdam, Netherlands) and stored in a glovebox after recrystallization from toluene. Styrene (S, 99%) and divinylbenzene (DVB) (technical grade, 80%) were filtered through basic alumina prior to use. HPLC grade toluene and dichloromethane (DCM) were purchased from Burdick & Jackson (Morristown, NJ, USA) and J. T. Baker (Center Valley, PA), respectively, and purified using a solvent purification system (C&T International, Suwon, Korea).

S-Dodecyl-S'-(R,R'-dimethyl-R"-acetic acid) trithiocarbonate (CTA)[1] and 2-hydroxylethyl 2-(((dodecylthio)carbonothioyl)-thio)-2-methylpropanoate) (CTA-OH)[2] were prepared by following literature procedure. Polylactide macro-chain transfer agent (PLA-CTA) was synthesized by ring opening transesterification polymerization (ROTEP) using CTA-OH as initiator and DBU as catalyst.[2] The PLA-CTAs were denoted as PLA-CTA-xx where xx represents the number averaged molar mass of the PLA-CTA (kg mol^{-1}) that was determined by end group anaylsis using ^1H nuclear magnetic resonance (NMR) spectroscopy. PLA-CTA-20 (20.5 kg mol^{-1}, $Đ = 1.06$) and PLA-CTA-40 (42.5 kg mol^{-1}, $Đ = 1.09$) were used in this study (Figure S1).

Instrumentation. ^1H nuclear magnetic resonance (NMR) signal was obtained using a

Bruker Avance 400 MHz spectrometer (Bilerica, MA, USA) using the residual NMR solvent signal as an internal reference. Size exclusion chromatography (SEC) was performed in chloroform at 40 °C with a flow rate of 1 mL min^{-1} on an Agilent 1260 infinity system (Santa Clara, CA, USA). The instrument is equipped with a 1260 refractive index detector and three PLgel 10 μm Mixed-B columns in series with a molar mass range 500 – 10,000,000 g mol^{-1}. The molar masses of the polymers were calculated relative to linear polystyrene (PS) standards from Agilent Technologies. Fourier transform infrared (FTIR) spectra were obtained on a Bruker Alpha FTIR spectrometer using a Platinum attenuation total reflection (ATR) single reflection module.

Synchrotron small-angle X-ray scattering (SAXS) experiments were performed at the 9A beamline in Pohang Accelerator Laboratory (PAL). A monochromatized X-ray radiation source of 20.01 keV with the sample-to-detector distance of 6.455 m was used. Scattering intensity was monitored by a Mar 165 mm diameter CCD detector with 2048×2048 pixels. The two-dimensional scattering pattern were azimuthally integrated to afford one-dimensional profiles presented as scattering vector (q) versus scattering intensity, where the magnitude of scattering vector is calculated with $q = 4\pi/\lambda \sin\theta$. Domain spacing ($d$) was estimated from the position of the principal peak at q^* following the relationship $d = 2/q^*$. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4900 FE-SEM (Schaumburg, IL, USA) with a 5 kV accelerating voltage and an upper secondary electron detector. Samples were coated with Os prior to imaging.

Nitrogen adsorption isotherms were obtained on a Mirae SI nanoPOROSITY-XQ analyzer (Gwangju, Korea) at the temperature of liquid nitrogen (77.3 K). Mode pore diameter (D_{N2}) was estimated by Barrett-Joyner-Halenda (BJH) analysis of the desorption branch of nitrogen sorption isotherms.[3] Specific surface area (S_{N2}) was estimated by multipoint Brunauer-Emmett-Teller (BET) analysis (between $0.05 < P/P_0 < 0.35$).[4] Pore volume (V_{N2}) was calculated from the point $P/P_0 = 0.95$. The non-local density function theory (NLDFT) pore size distribution was obtained using 3Flex program (Micromeritics Instrument Corp.). The carbon slit pores model for N_2 adsorption at 77 K on carbon was selected to characterize amorphous porous structure within hyper-crosslinked polystyrene.[5] The pore size distribution was regularized by choosing $\lambda = 0.1$ as a user-adjustable parameter.

Preparation of h-polyHIPEs. Synthesis of a hierarchically porous polymerized high internal phase emulsion (h-polyHIPE) which is derived from HIPE composed of 10 vol% oil phase containing 30 wt% of PLA-CTA-40 and 90 vol% aqueous phase with $CaCl_2$ concentration of 0.02 M is given here as an example. A polymerization mixture of S (0.2053 g, 1.97 mmol), DVB (0.0642 g, 0.49 mmol), PLA-CTA-40 (0.1158 g, 0.0027 mmol), and Span 80 (0.037 g, 0.086 mmol) was prepared in a 4-mL vial and used as an oil phase. An aqueous solution consisting of deionized water (2.7 mL), KPS (0.0015 g, 0.0055 mmol), and $CaCl_2$ (0.0081 g, 0.055 mmol) was dropwisely added to the oil phase under vigorous mixing using a vortex mixer to form the HIPE. The HIPE was further mixed for 2-3 mins after addition of the aqueous phase was completed. Then the vial was placed in an oil bath at 70 °C to polymerize the HIPE for 48 h via the polymerization-induced microphase separation (PIMS) process. Microphase-separated polyHIPE (m-polyHIPE) was produced as a white and monolithic solid, which was collected by cracking the vial, washed with deionized water and methanol several times, and dried at under vacuum at room temperature overnight (0.3442 g, 89.4% mass yield).

h-polyHIPE was obtained by etching PLA from the m-polyHIPE precursor following the literature protocol.[6] The m-polyHIPE (0.1336 g) was placed in a polypropylene vial and 20 mL of solution of 0.5 M NaOH (methanol/water = 4/6 (v/v)) was poured over the sample. The vial was sealed with electrical tape and heated in an oil bath at 70 °C for 48 h. The h-polyHIPE was collected by draining the base solution and thoroughly rinsed with water and methanol sequentially. The remaining solvents were dried at ambient condition for 1 h and then under vacuum at room temperature overnight (0.1058 g, 79.2% mass yield). The mesoprous structure of h-polyHIPE was evaluated by SAXS and nitrogen adsorption. Their domain size and pore characteristics were summarized in Table S1.

We note that h-polyHIPEs can be prepared in a wide range of composition. Meso- and macroporosity of the h-polyHIPEs were independently tunable by varying weight fraction of PLA-CTA ($w_{\text{PLA-CTA}}$) in the oil phase, and volume fraction of the aqueous phase (ϕ_{water}) in the HIPE (the Span 80 concentration may need to be adjusted accordingly. See Figure S4 for the composition window as a function of Span 80 concentration). Different electrolytes such as NaCl could be also used to prepare the aqueous phase to replace $CaCl_2$.

Preparation of h^2-polyHIPE. Hyper-cross-linking reaction of h-polyHIPE was conducted following literature procedure.[7] In a 5-mL one-necked round bottomed flask (RBF), h-polyHIPE (0.0930 g) was placed and swollen with 1,2-dichloroethane (4 mL) for 22 h. FDA (0.2785 g, 3.66 mmol) was added to the RBF followed by $FeCl_3$ (0.5863 g, 3.66 mmol) at room temperature. After stirring for 10 min, temperature was raised to 45 °C for 4 h and then 80 °C for 13 h under N_2 condition. After cooling to ambient temperature, the resulting material was collected by filtration, washed several times with concentrated hydrochloric acid and methanol, and dried under vacuum at room temperature overnight (0.1006 g). The pore characteristics of h^2-polyHIPE was evaluated by SEM, SAXS and nitrogen adsorption, and summarized in Table S1.

Preparation of RMP, polyHIPE, hyper-cross-linked RMP and hyper-cross-linked

polyHIPE. Reticulated mesoporous polymer (RMP) as cross-linked and mesoporous P(S-co-DVB) reported in the previous publication,[6] and polyHIPE containing only macropores in the P(S-co-DVB) framework without the mesopores were synthesized as references. RMP, polyHIPE, and their hyper-cross-linked polymers were used in sorption experiments in comparison with h-polyHIPE and h^2-polyHIPE. Their nitrogen sorption isotherms are shown in Figure S7, and the pore characteristics is summarized in Table S1.

RMP was prepared by conducting copolymerization of S and DVB ([S]:[DVB] = 4:1 molar ratio) in the presence of 30 wt% PLA-CTA-20, without Span 80. A mixture of S, DVB and PLA-CTA-20 (10 vol %) was placed in a 20-ml vial containing 20 mM of KPS aqueous solution (90 vol%), and stirred for 48 h at 70 °C. The resulting monolithic pieces were subjected to PLA etching to produce RMP.

PolyHIPE was obtained from the HIPE composed of 10 vol% oil phase and 90 vol% aqueous phase. While the composition of the aqueous phase was identical with the h-polyHIPE synthesis, the oil phase consisted of S, DVB ([S]:[DVB] = 4:1 molar ratio), and Span 80. The HIPE was polymerized at 70 °C for 48 h, washed and dried to yield polyHIPE.

Hyper-cross-linking reaction of RMP and polyHIPE were conducted following the hyper-cross-linking procedure described above.

Interfacial tension measurement. Interfacial tension between oil and aqueous phases was measured by using a customized pendent drop method.[8] The oil solution was transferred to a quartz cuvette (Sigma-Aldrich, 3.5 mL volume), and a microsyringe (Hamilton, 710SNR, 100 μL) containing the aqueous solution was then immersed in the oil phase. Then a pendent drop was formed at the end of the syringe needle, and the drop were recorded for 15-30 minutes through the side of the cuvette. Finally, the interfacial tension was calculated from a shape analysis of each pendent drop using a customized Matlab code.

Determination of adsorption capacity (*Q*). To investigate sorption kinetics of Rhodamine B, fluorescence intensity of aqueous solutions containing the dye solution was monitored using a Tecan Infinite Pro M200 microplate spectrofluorometer (Männedorf, Switzerland) at room temperature. Excitation wavelengths of 460 nm was used for Rhodamine B.

To determine maximum adsorption capacitance (Q_{max}), a piece of polyHIPE, h-polyHIPE, h^2-polyHIPE, RMP, hyper-cross-linked RMP, and hyper-cross-linked polyHIPE (2 mg) was prewetted with methanol for 1 h and placed in 20-ml vials. 2 mL of Rhodamine B aqueous solution (1000 μg mL^{-1}) was added to each vial. The solutions were gently stirred at room temperature. After 48 h. fluorescence intensity of the solutions were measured to determine their concentration based on the predetermined calibration curve. From the extent of the concentration decrease, the amount of Rhodamine B adsorbed on the polymer was estimated and normalized by the weight of the polymer to yield Q_{max}.

For kinetics experiment of dye adsorption, a piece of polyHIPE, h-polyHIPE, h^2-polyHIPE, RMP, hyper-cross-linked RMP, and hyper-cross-linked polyHIPE (10 mg) was prewetted with methanol for 1 h and placed in 20-ml vials. 10 mL of Rhodamine B aqueous solution (100 μg mL^{-1}) was added to each vial. The solutions were gently stirred at room temperature, and fluorescence intensity of the solutions was measured over time to determine their concentration based on the predetermined calibration curve. From the extent of the concentration decrease, the amount of Rhodamine B adsorbed on the polymer was estimated and normalized by the weight of the polymer to yield *Q*.

Table S1. Pore characteristics of porous polymers

Entry	Micropore characteristics		Mesopore characteristics				Whole	
	S_{micro} (m^{2} g^{-1})[a]	V_{mciro} (mL g^{-1})[a]	d (nm)[b]	S_{ext} (m^{2} g^{-1})[c]	V_{BJH} (mL g^{-1})[d]	D_{N2} (nm)[d]	S_{BET} (m^{2} g^{-1})[e]	V_{N2} (mL g^{-1})[f]
m-polyHIPE[g]	-	-	-	-		-[i]	10	0.02
h-polyHIPE[g]	-	-	34	-	0.26	10.8	79	0.21
h^{2}-polyHIPE[g]	84	0.033	30	267	0.41	11.6	328	0.44
polyHIPE	-	-	-	-	-	-[i]	16	0.03
h-polyHIPE[h]	-	-	25	-	0.27	10.2	102	0.23
h^{2}-polyHIPE[h]	235	0.101	31	264	0.46	12.2	448	0.50
RMP[h]	-	-	24	-	0.50	8.6	196	0.44
hyper-cross-linked RMP[h]	165	0.067	28	406	0.71	8.5	529	0.67
hyper-cross-linked polyHIPE	182	0.081	-	143	0.19	-	290	0.24

[a] Micropore surface area and pore volume estimated by t-plot analysis from the range between $0.2 < P/P_0 < 0.45$

[b] Domain spacing determined by SAXS

[c] External surface area estimated by t-plot analysis

[d] Pore volume and mean pore diameter determined by BJH analysis of the desorption branch

[e] Surface area determined by BET analysis from the range between $0.05 < P/P_0 < 0.35$

[f] Pore volume calculated near the point $P/P_0 = 0.95$

[g] Porous polymers prepared by using PLA-CTA-40

[h] Porous polymers prepared by using PLA-CTA-20

[i] Capillary condensation was not observed

Table S2. BET surface area vs maximum dye adsorption capacity (Q_{max}) of porous polymers synthesized with PLA-CTA-20

Entry	S_{BET} (m^{2} g^{-1})[a]	Q_{max} (μg mg^{-1})
polyHIPE[b]	16	26
h-polyHIPE[b]	102	65
h^{2}-polyHIPE[b]	448	99
RMP[b]	196	57
hyper-cross-linked RMP[b]	529	118
hyper-cross-linked polyHIPE[b]	290	66

[a] BET surface area (S_{BET}) was estimated from nitrogen sorption isotherm

[b] Same data shown as porous polymers prepared by using PLA-CTA-20 in Table S1

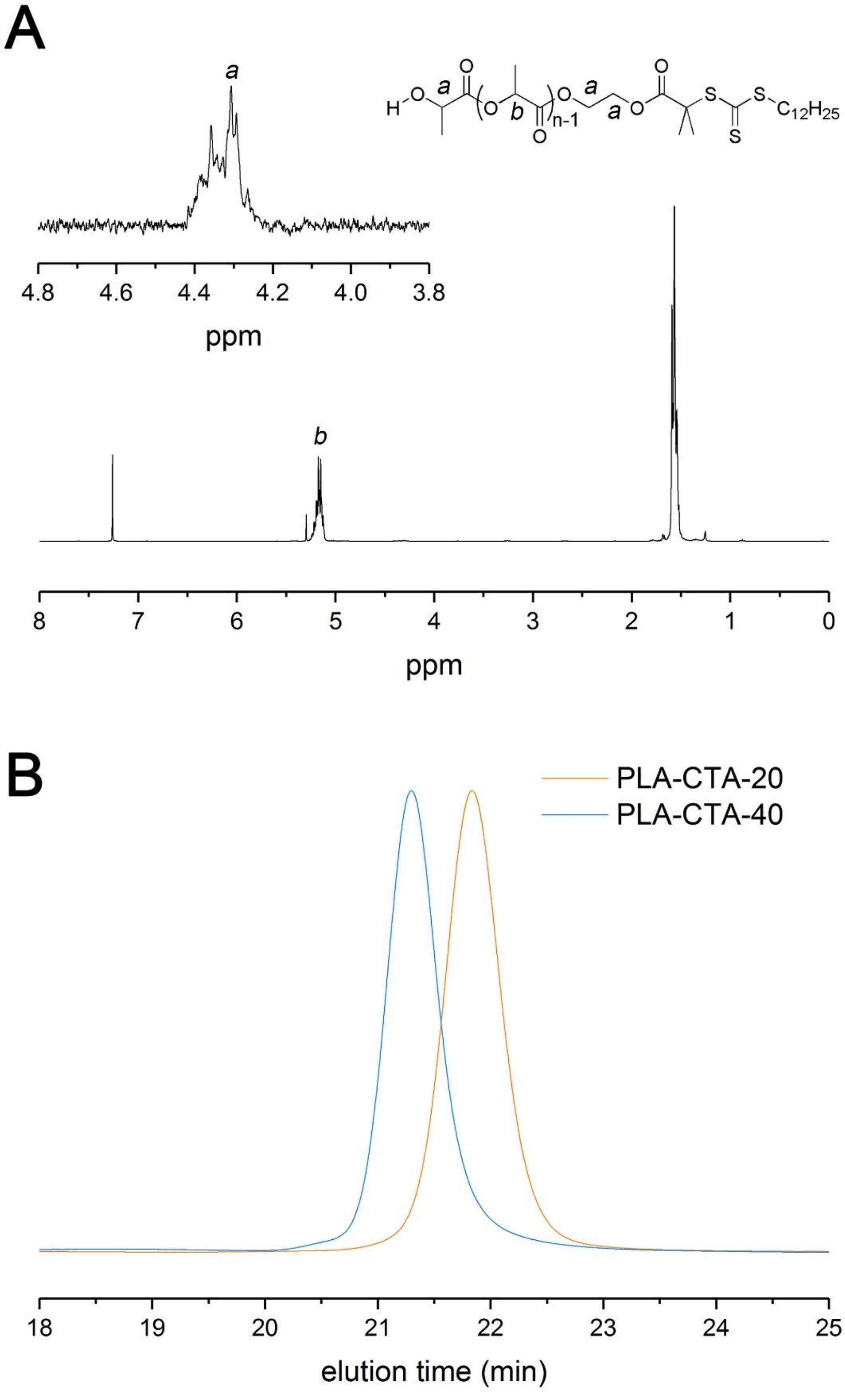

Figure S1. PLA-CTA-xx samples with different molecular mass. (A) Chemical structure and representative ^{1}H NMR spectra of PLA-CTA (400 MHz, $CDCl_3$, 20 °C). (C) SEC traces of PLA-CTAs used in this study (1 mL min^{-1}, chloroform, 40 °C).

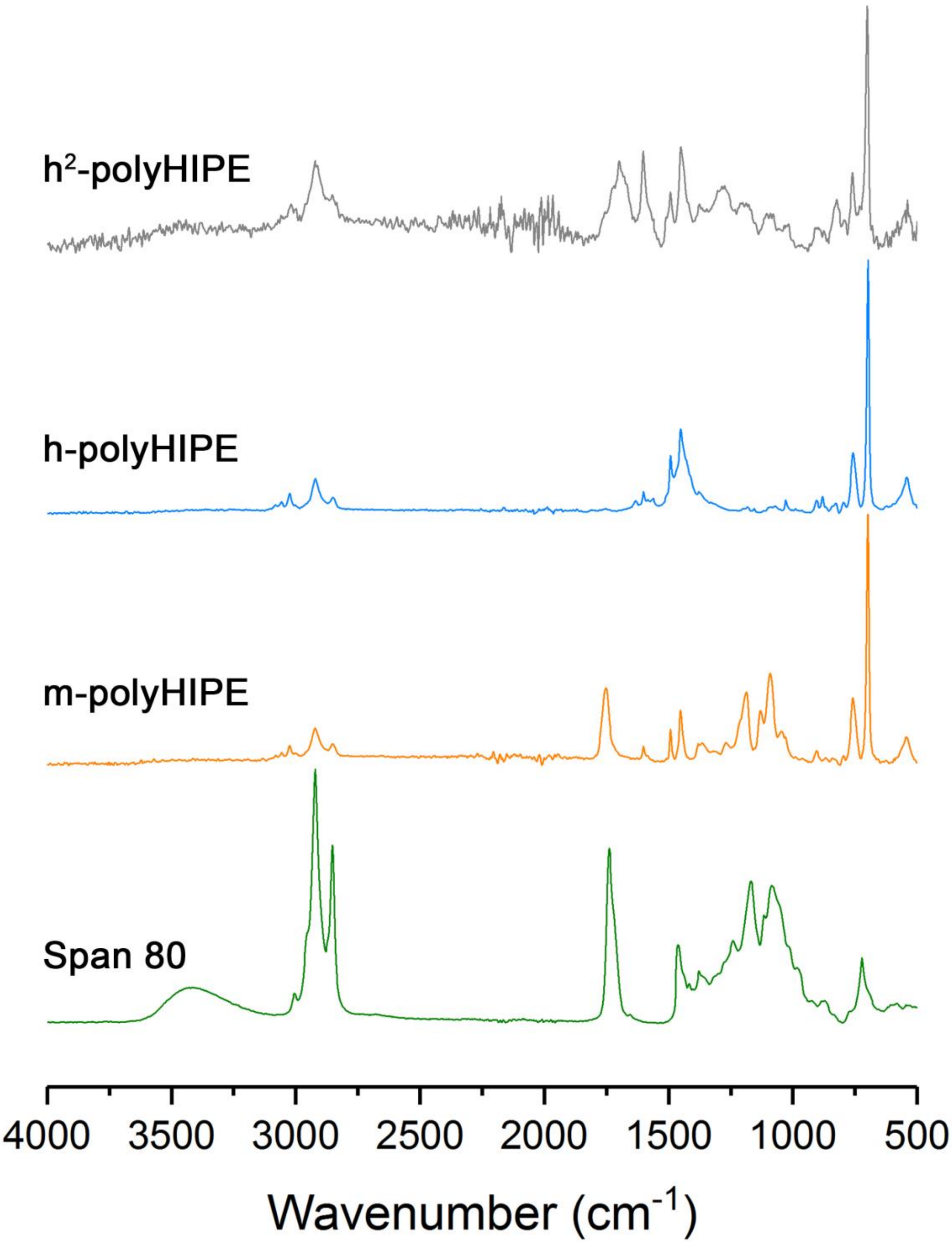

Figure S2. FTIR spectra of Span 80 (green), m-polyHIPE (blue), h-polyHIPE (orange) and h^2-polyHIPE (gray).

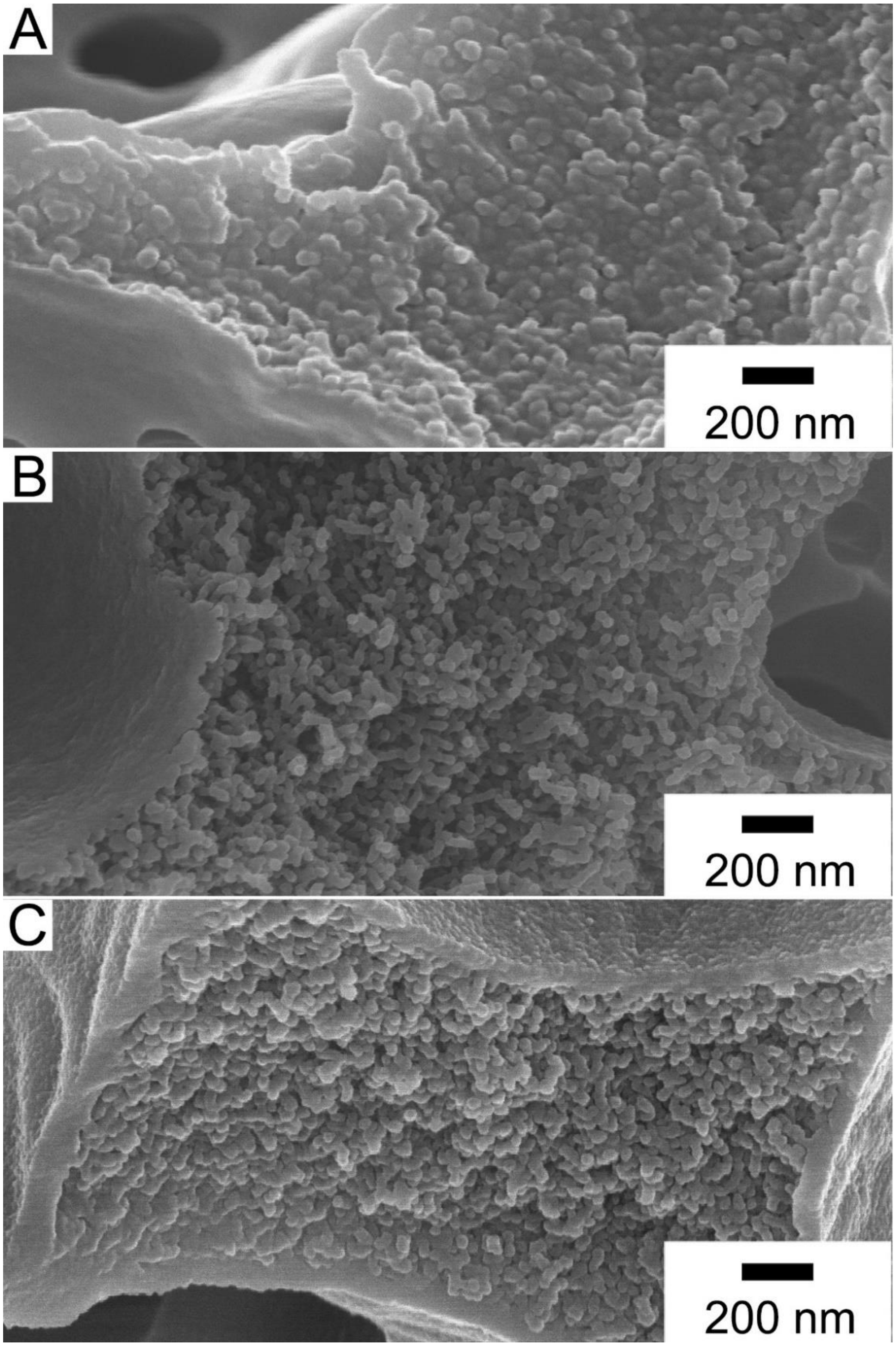

Figure S3. SEM Images of m-polyHIPE (A), h-polyHIPE (B) and h^2-polyHIPE (C) at high magnification. We note surface of the h-polyHIPE framework was relatively less porous than the cross-section presumably due to influence of the water/oil interface on the RAFT polymerization.

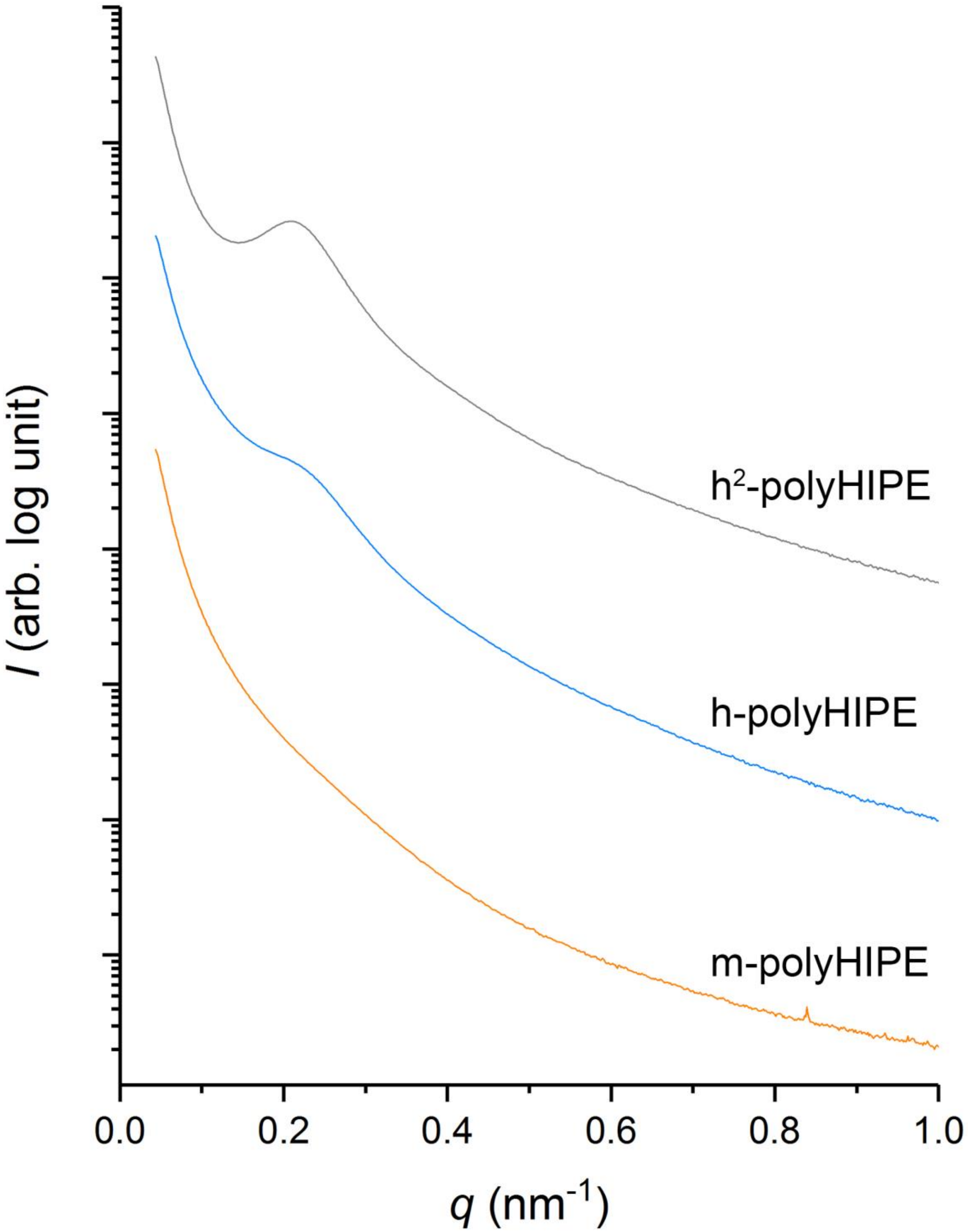

Figure S4. One-dimensional SAXS profiles of m-polyHIPE (orange), h-polyHIPE (blue) and h^2-polyHIPE (gray) synthesized with PLA-CTA-40.

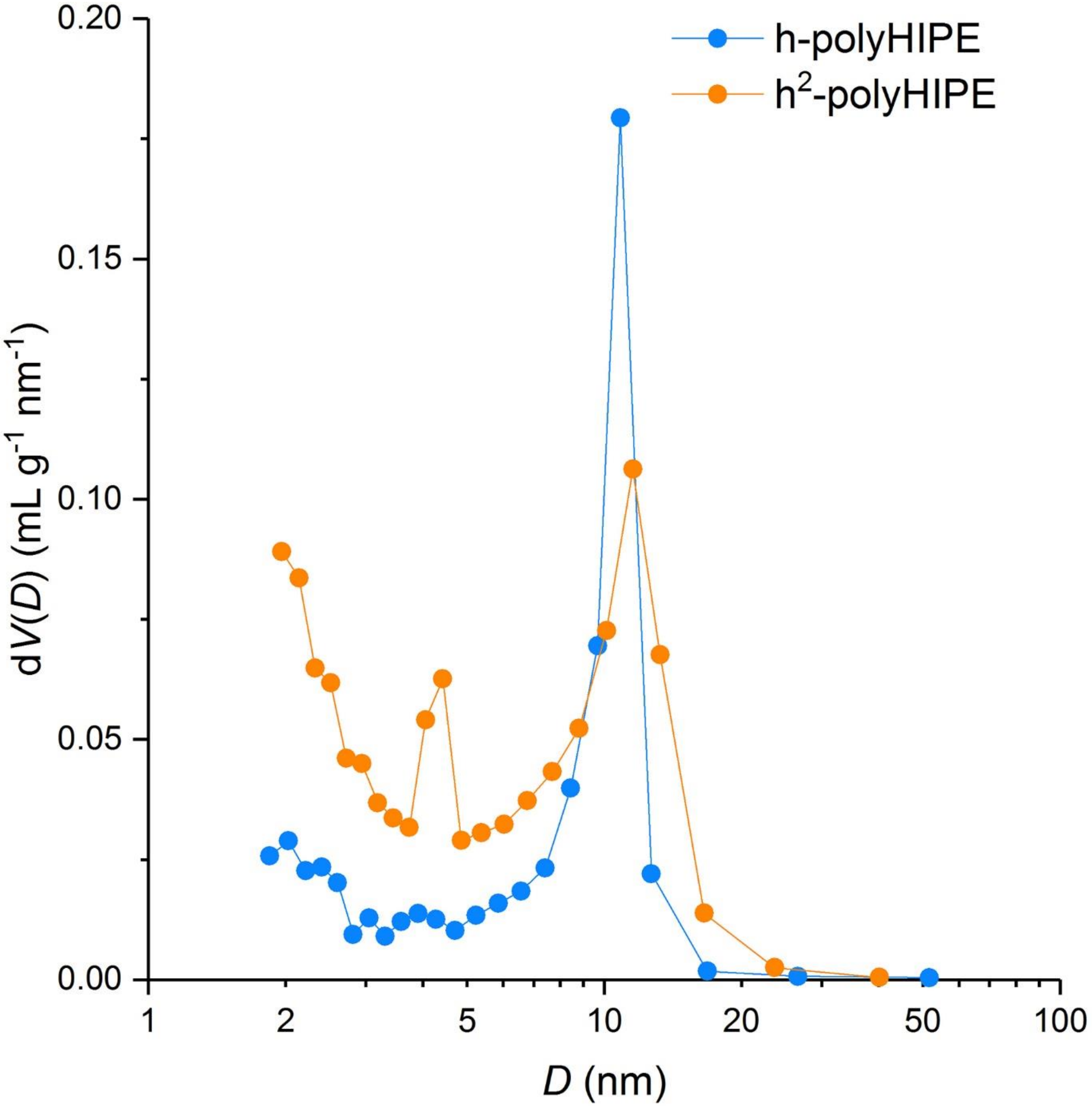

Figure S5. Pore size distributions of h-polyHIPE (blue) and h^2-polyHIPE (orange) estimated by Barrett-Joyner-Halenda (BJH) analysis of the desorption branch of the nitrogen sorption isotherms.

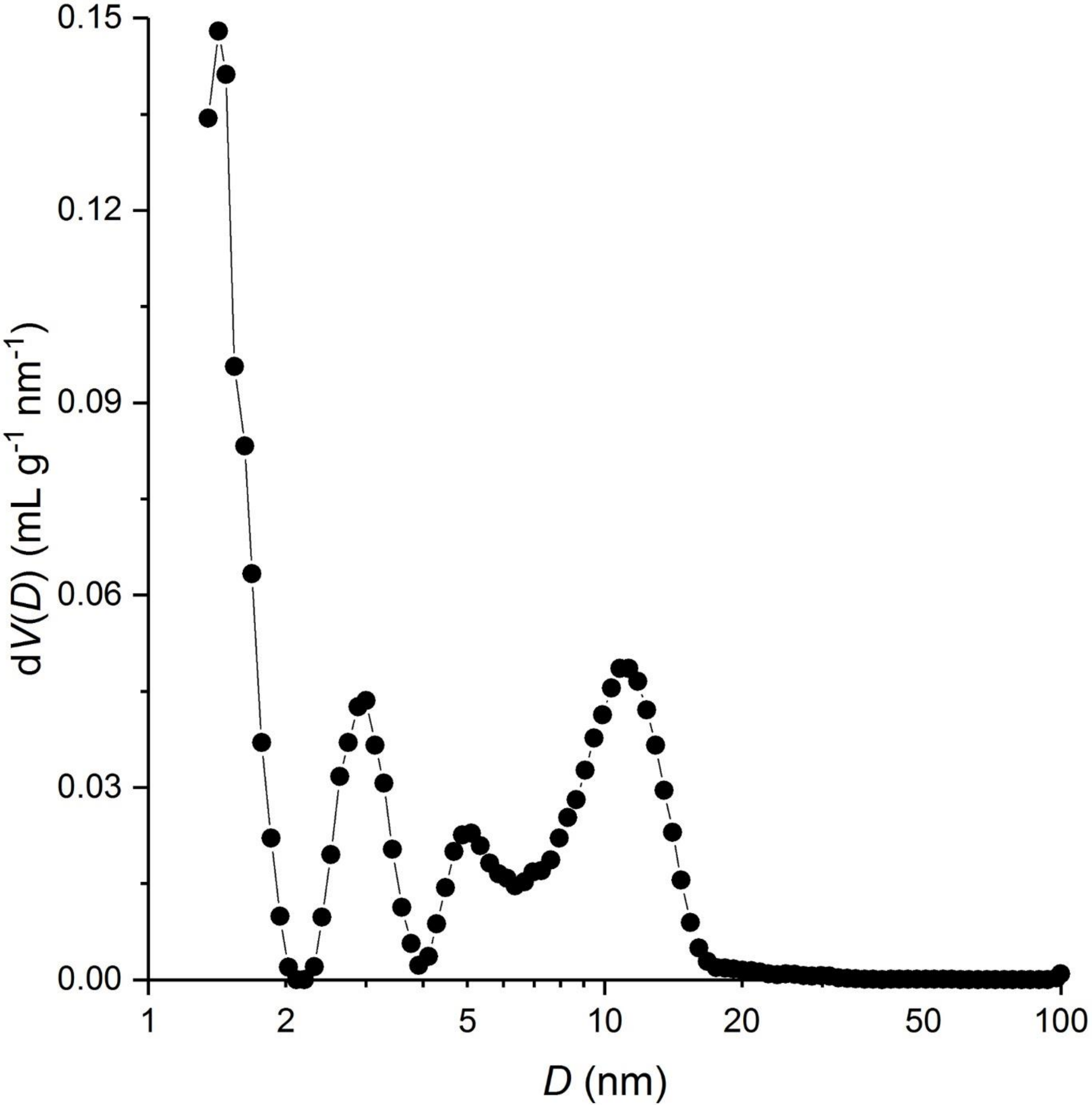

Figure S6. Pore size distribution of h^2-polyHIPE estimated by non-local density function theory (NLDFT) analysis of the adsorption branch of the nitrogen sorption isotherm.

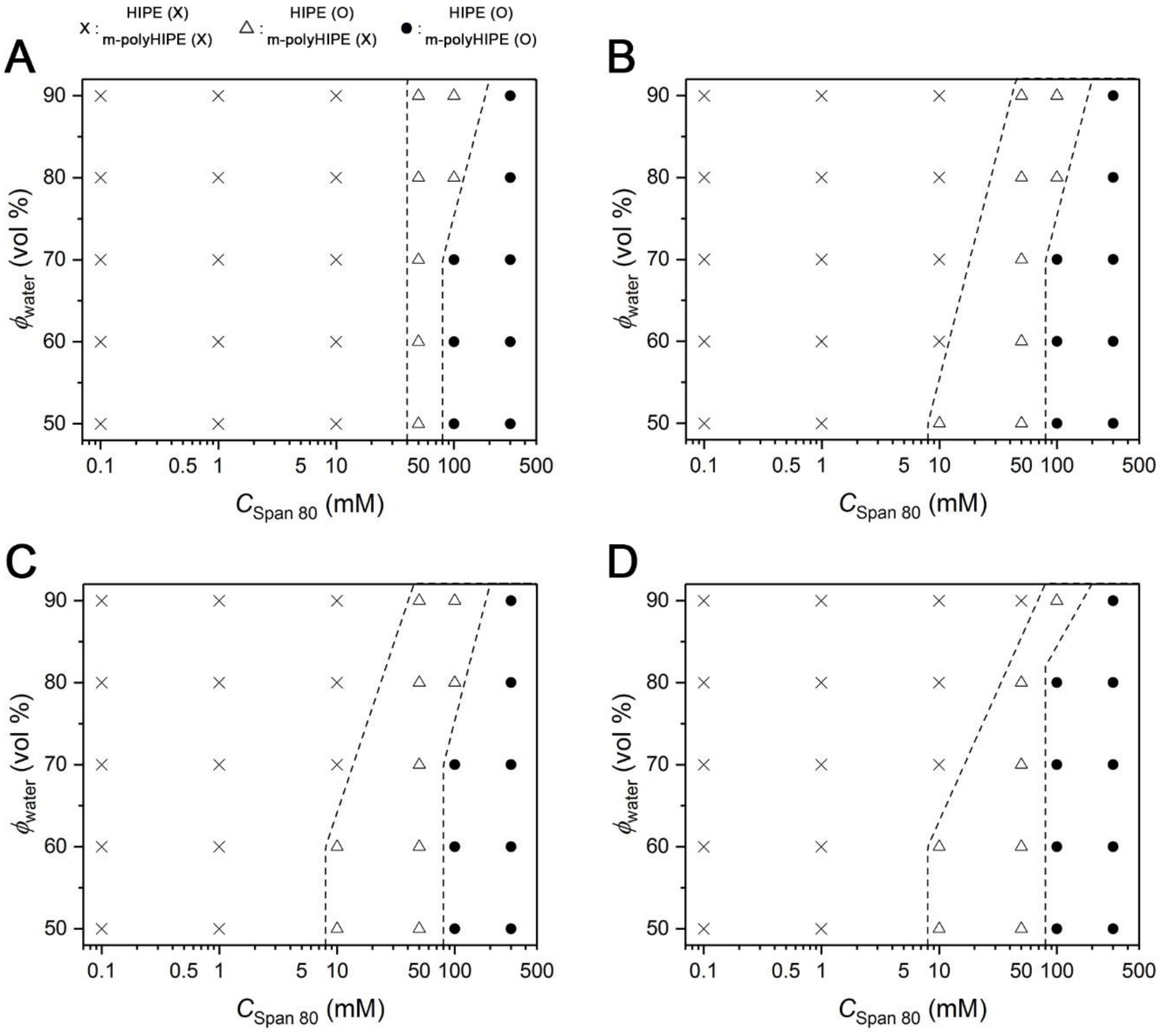

Figure S7. Phase diagram for stable HIPE and m-polyHIPE formation at different weight fraction of PLA-CTA in oil phase ($w_{PLA\text{-}CTA}$) as a function of concentration of Span 80 ($C_{Span\ 80}$) and volume fraction of internal phase (ϕ_{water}). $w_{PLA\text{-}CTA}$ was varied from 0, 3, and 10 to 30%. We note that $C_{Span\ 80} > 500$ mM often led to macroscopic collapse during conversion of m-polyHIPE into h-polyHIPE. This is probably because the macropore framework was too thin to retain the pore structure as PLA etching decreases Young's modulus of the material.[5]

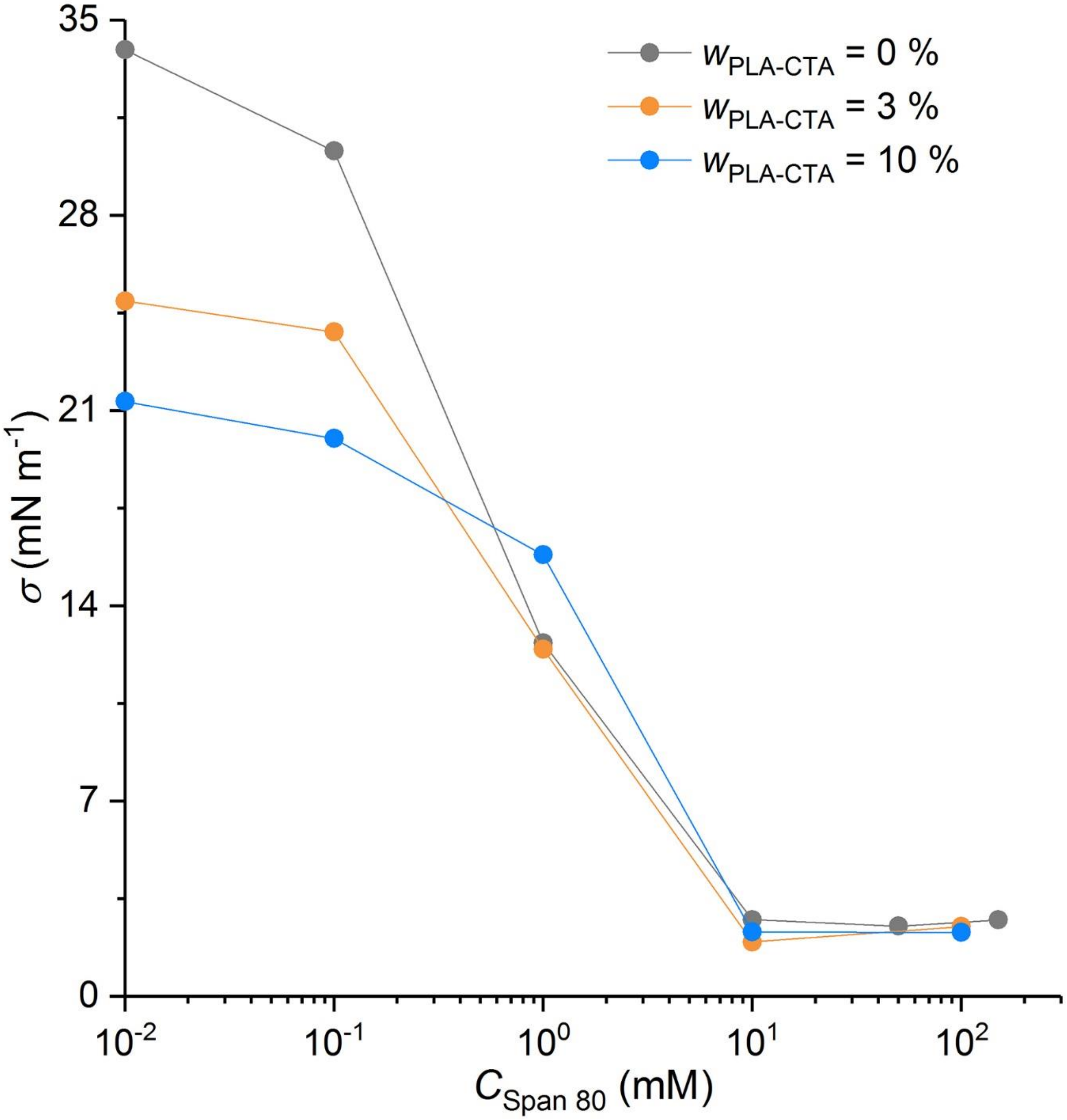

Figure S8. Interfacial tension (σ) between the aqueous phase and the polymerization mixture at different $w_{\text{PLA-CTA}}$s as a function of Span 80 concentration (C_{Span80}).

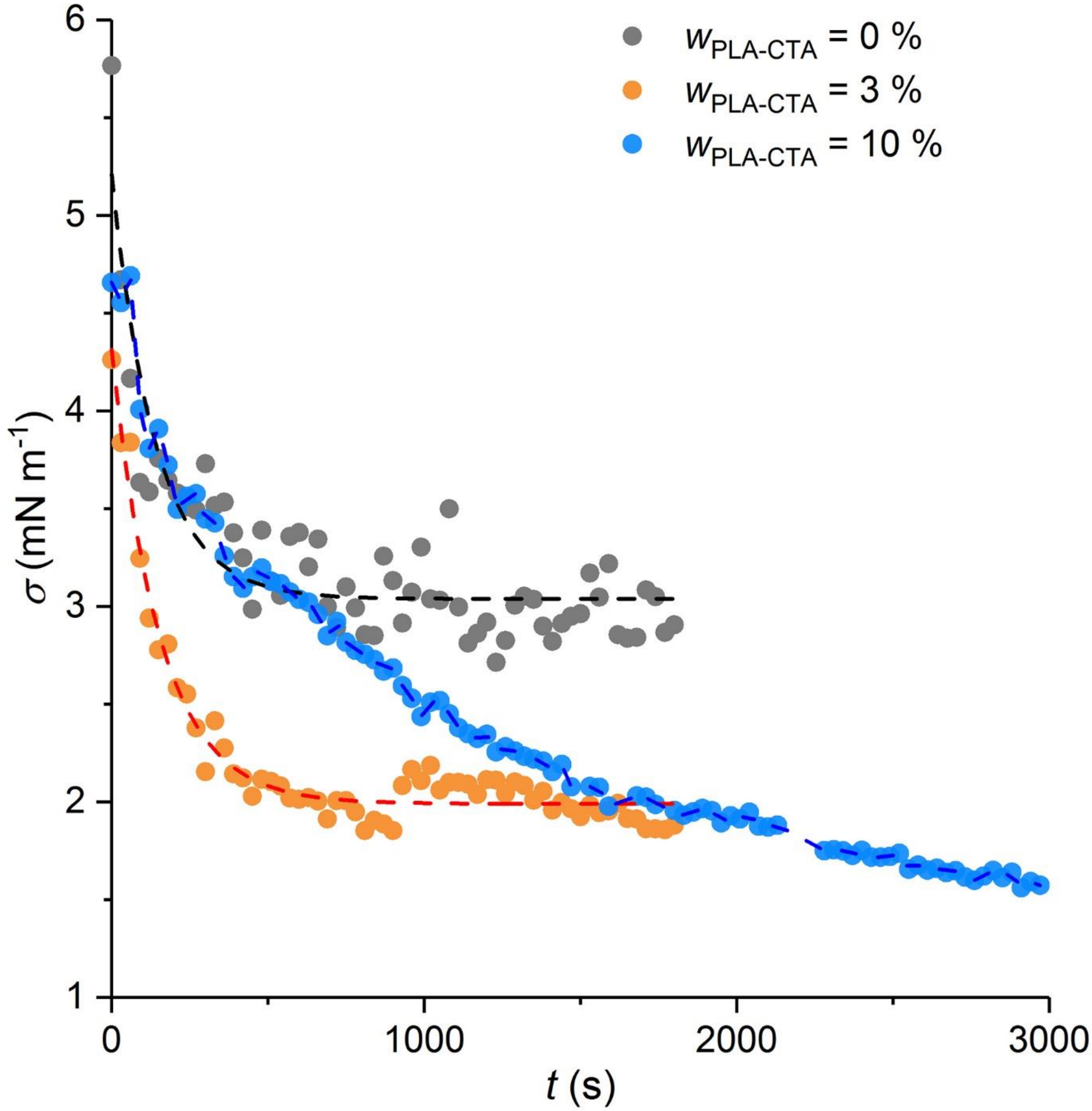

Figure S9. Interfacial tension (σ) between the aqueous phase and the polymerization mixture at different $w_{PLA\text{-}CTA}$s as a function of time with $C_{span\ 80}$ = 10 mM.

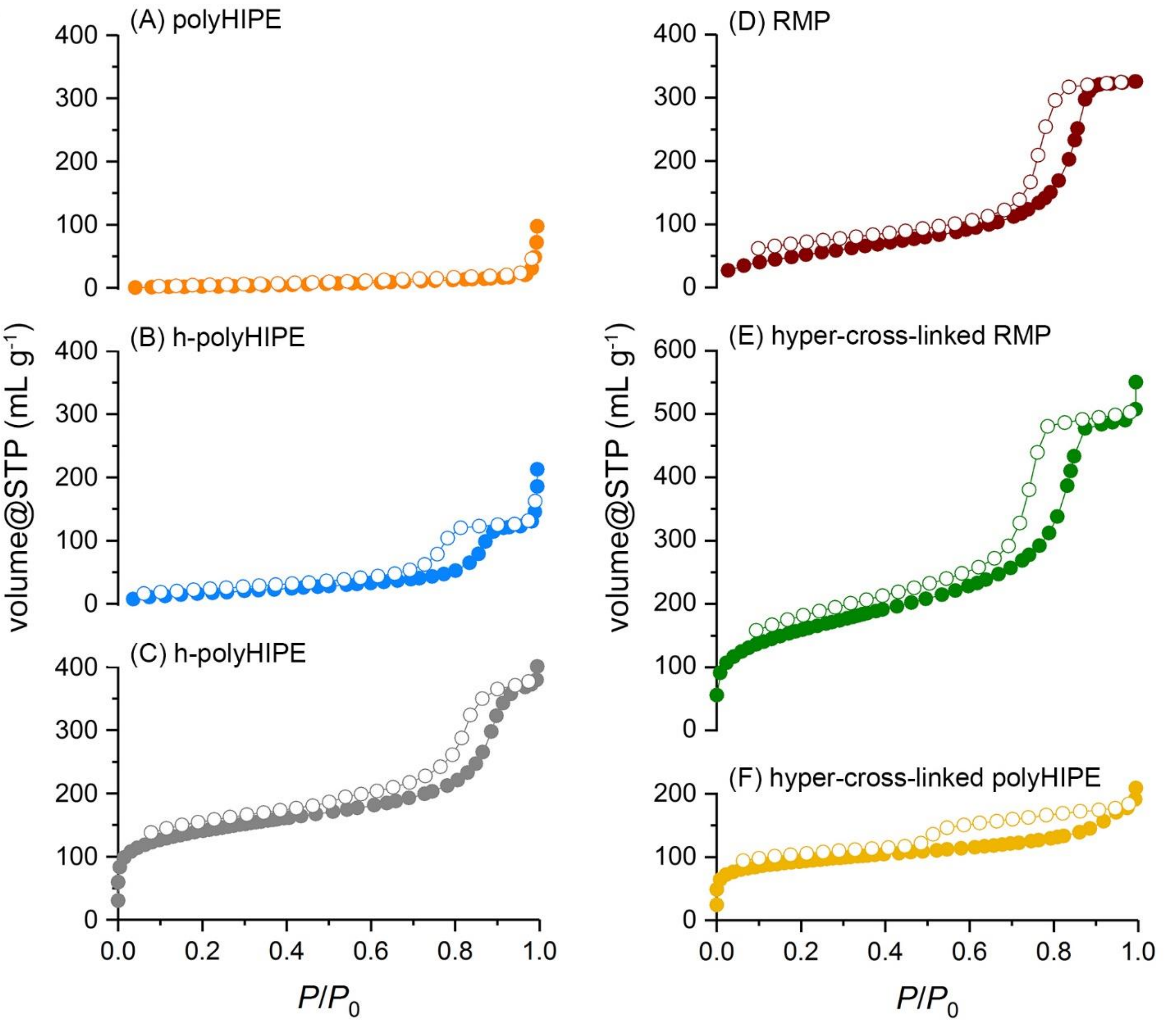

Figure S10. Nitrogen sorption isotherms of (A) polyHIPE, (B) h-polyHIPE, (C) h^2-polyHIPE, (D) RMP, (E) hyper-cross-linked RMP and (F) hyper-cross-linked polyHIPE. The porous polymers were synthesized with PLA-CTA-20. Filled circle: adsorption branch; Open circle: desorption branch.

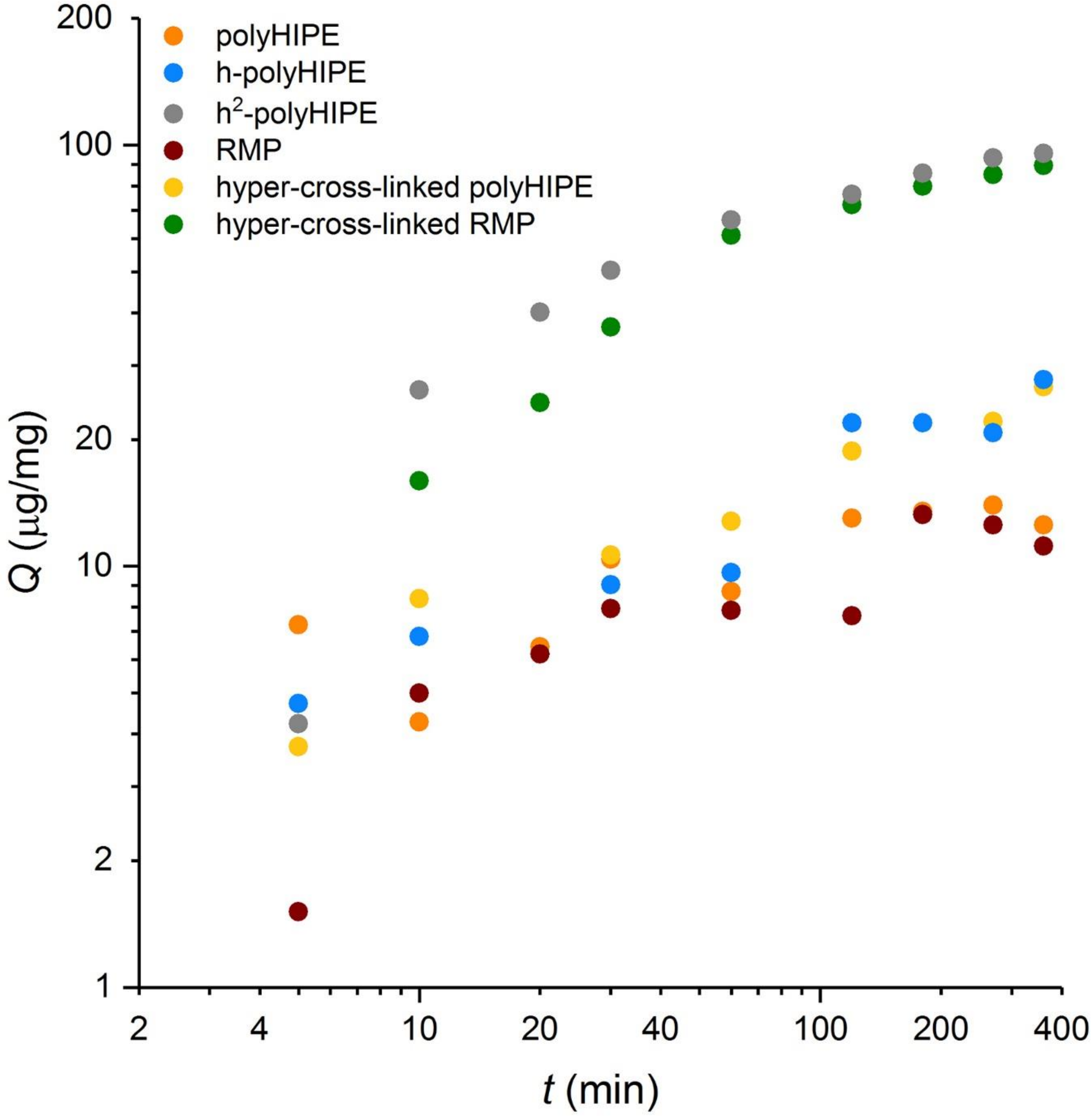

Figure S11. Adsorption kinetics of porous polymers Rhodamine B aqueous solutions at 100 μg mL^{-1} concentration at room temperature in log scale.

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