

Supporting Information

Core hyper-cross-linked star polymers from block polymer micelle precursors

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This information includes:

Experimental Section

Figures S1-S12

Tables S1-S5

Experimental Section

Materials. Without specific descriptions, the chemicals were used as purchased. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CTA, 97%), α,α' -dichloro-*p*-xylene (DCX, 98%) acetonitrile (MeCN, anhydrous 99.8%), and FeCl₃, (97%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Nile red was purchased from TCI (Tokyo, Japan). Hydrochloric acid (HCl, 35%) and methanol (MeOH, 99 %) were purchased from Daejung chemicals (Siheung, Korea). Styrene (S, 99%) and methyl methacrylate (MMA, 99%) were purchased from Sigma-Aldrich and filtered through basic alumina prior to use. HPLC grade DMF and toluene were purchased from Daejung chemicals and Burdick & Jackson (Morristown, NJ, USA). Those solvents were purified using solvent purification system (C&T International, Suwon, Korea). Azobisisobutyronitrile (AIBN, 98%) was purchased from Junsei (Tokyo, Japan) and purified by recrystallization in methanol.

Methods. ¹H nuclear magnetic resonance (NMR) spectra was obtained using a Bruker Advance 400 MHz spectrometer (Billerica, 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 an Optilab T-rEX refractive index detector purchased from Wyatt technology (Santa Barbara, CA, USA) and three PLgel 10 μ m Mixed-B columns in series with a molar mass range 500 – 10,000,000 g mol⁻¹. The molar masses and dispersities (\bar{D}) of the polymers were calculated relative to linear polystyrene standards (EasiVial) purchased from Agilent Technologies. Weight-average absolute molecular masses ($M_{w,MALLS}$) were determined by using a Wyatt DAWN8+ multi-angle laser light scattering (MALLS) detector (Santa Barbara, CA) equipped to SEC. dn/dc values were determined as a slope of refractive index change as a function of the concentration. Thermogravimetric analysis (TGA)

was performed on a TA Instruments TGA Q500. Dynamic light scattering (DLS) measurements were performed on a Brookhaven 90Plus/BI-MAS particle size analyzer (Holtville, NY, USA) at wavelength of 658 nm with scattering angle of 90°. Samples were prepared at a concentration of 2 mg mL⁻¹ and filtered through 0.2 mm PTFE syringe filters prior to the measurements. Transmission electron microscopy (TEM) was performed on a Jeol JEM-2100F field-emission transmission electron microscope (Tokyo, Japan) with acceleration voltage of 200 kV. Samples were prepared on 300 mesh carbon-coated copper grids by dropping solution (2 mg mL⁻¹) followed by solvent evaporation in ambient condition. Synchrotron small-angle X-ray scattering (SAXS) experiments on MS and CHS film samples were performed at 9A U-SAXS beam line in Pohang Accelerator Laboratory (PAL). A monochromatized X-ray radiation source of 11.07 keV with the sample-to-detector distance of 6.441 m was used. Scattering intensity was monitored by a Mar 165 mm diameter CCD detector with 2048×2048 pixels. The two-dimensional scattering patterns were azimuthally integrated to afford one-dimensional profiles presented as scattering vector (q) versus scattering intensity, where the magnitude of scattering vector is given by $q=(4\pi/\lambda)\sin\theta$. The solution SAXS experiments were conducted in the Australian Synchrotron, Victoria, Australia. Samples were prepared by dissolving each polymer in MeCN (2 mg.ml⁻¹), which was then transferred to 1.0 mm quartz capillaries and sealed with wax to prevent evaporation. Scattering intensity was collected in replicate using a Dectris Pilatus 2M SAXS detector housed in a high vacuum, variable camera length enclosure. Two camera lengths 1338 mm and 7668 mm were used to extend the collected q range (0.00022 – 0.2 Å⁻¹). For MS(72.4, 0.42) and CHS(72.4, 0.42), the scattering intensity profile was fitted by the hard sphere model using the following equation:

$$I = A \times \left(\frac{3}{x^3}\right)^2 (\sin x - x \cos x)^2 + B \times q^{-4} + C, \text{ where } x = q \times R_g, \text{ and } A, B, \text{ and } C \text{ are fitting constants. We fitted the data using OriginPro 2019 by non-linear function fitting, and}$$

summarized the results in Table S1. The scattering intensity was assumed to mostly originate from the electron density difference between the solvophobic core with the surrounding, including the corona and the solvent. Gas adsorption isotherms for carbon dioxide (CO₂, 273 K) and nitrogen (N₂, 77 K) were obtained using a Micromeritics 3 Flex. Samples were activated overnight at 80 °C prior to measurement. UV-vis spectra were obtained by using a Shimadzu UV-2600 UV-Vis spectrophotometer (Kyoto, Japan) at room temperature.

Table S1. The constants obtained from solution SAXS fitting using the hard sphere model

Entry	A	B	C	R_g (nm)	χ^2
CHS(72.4, 0.42)	0.76697	0.00161	5.795×10^{-9}	17.7	0.9999
MS(72.4, 0.42)	0.44986	0.0253	3.731×10^{-9}	17.3	0.9999

Synthesis of PMMA. A polymerization mixture containing MMA (3.0022 g, 29.9860 mmol), CTA (0.0157 g, 0.0389 mmol) AIBN (0.0006 g, 0.0037 mmol) and toluene (3 mL) was prepared in ampoule. After three cycle of freeze pump thaw, the ampoule was flame sealed under vacuum and then immersed in an oil bath preset to 70 °C. After 16 h, the ampoule was cooled to RT and then opened to stop the polymerization. The reaction mixture was precipitated in MeOH to obtain the polymer product by filtration. The resulting polymer was collected and dried under vacuum at 40 °C overnight prior to ¹H NMR and SEC analyses.

Synthesis of PMMA-*b*-PS. Polymerization of MS(72.4, 0.42) is given as an example. A polymerization mixture containing PMMA (0.5995 g, 0.0136 mmol), S (1.4160 g, 13.5958 mmol), DMF (6 mL) was prepared in ampoule. After three cycle of freeze pump thaw, the ampoule was flame sealed under vacuum and then immersed in an oil bath preset to 120 °C. After 24 h, the ampoule was cooled to RT and then opened to stop the polymerization. The

reaction mixture was precipitated in MeOH to obtain the polymer product by filtration. The resulting polymer was collected and dried under vacuum at 40 °C overnight.

Following the protocol described above, other PMMA-b-PSs were synthesized by varying the [PMMA]:[S] ratio.

Synthesis of core hyper-cross-linked star (CHS) polymer. Synthesis of CHS(72.4, 0.42) is given as an example. A reaction mixture containing MS(72.4, 0.42) (0.1998 g, 0.7490 mmol of styrene repeating unit), DCX(0.5238 g, 2.992 mmol, 4 equiv. to styrene repeating units), and MeCN (5 mL) was prepared in a 10 mL-round bottomed flask. Under N₂ condition, the reaction mixture was immersed in an oil bath preset to 80 °C. After 30 min, FeCl₃ (0.4841 g, 3.0218 mmol) was added and the mixture was stirred for 18 h. After cooling to ambient temperature, the reaction mixture was precipitated in the mixture of MeOH and HCl. The resulting polymer was collected, purified by soxhlet extraction using MeOH for 24 h, and finally dried under vacuum at 40 °C.

Determination of adsorption capacity (Q). A solution of MS and CHS (4 mg) was prepared in MeCN (0.5 mL) and stirred for 3 h at room temperature. A Nile red solution in MeCN (0.5 mL, 200 $\mu\text{g mL}^{-1}$ concentration) was added to make initial concentration as 100 $\mu\text{g mL}^{-1}$. The solutions were gently stirred at room temperature for 48 h. The absorbance spectra were obtained after diluting the solutions by 10 times, and the amount of Nile red in solution was determined based on the predetermined calibration curve. From the extent of the concentration decrease, the amount of Nile red adsorbed in the polymer was estimated and normalized by the weight of the polymer to yield Q .

When the experiments were conducted in THF, the polymers were removed before obtaining the UV-vis spectra by adding methanol (950% (v/v) to the MeCN solution) to

precipitate and filtering through a 0.2 μm syringe filter. Then the Nile red concentration was determined based on the calibration curve that was generated at MeCN/MeOH = 5/95 composition.

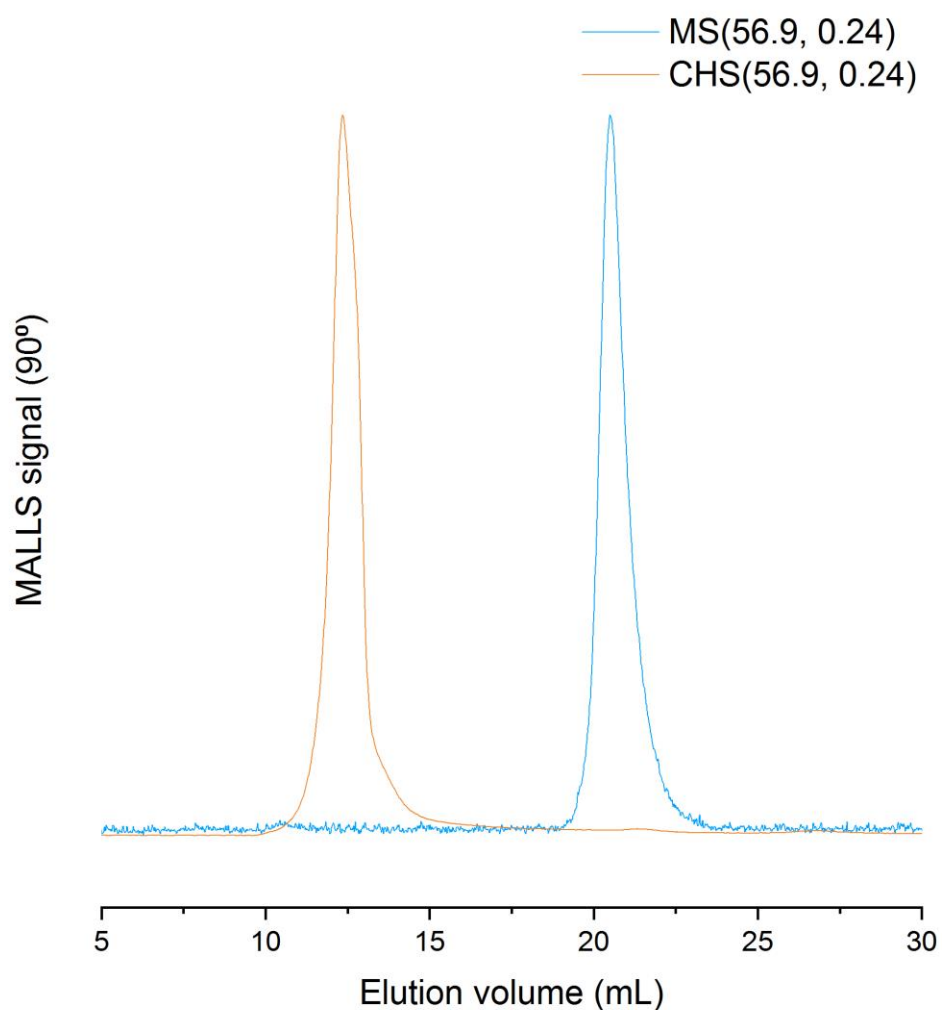


Figure S1. SEC traces of MS(56.9, 0.24) and CHS(56.9, 0.24) recorded with a MALLS detector (CHCl_3 , $40\text{ }^\circ\text{C}$, 1 mL min^{-1}).

Table S2. Molar mass information of MS(56.9, 0.24) and CHS(56.9, 0.24)

Entry	$M_{n,\text{NMR}}$ (kg mol^{-1})	$M_{n,\text{SEC}}$ (kg mol^{-1})	\mathcal{D}	dn/dc	$M_{w,\text{MALLS}}$ (kg mol^{-1})	\mathcal{D}
MS(56.9, 0.24)	56.9	50.3	1.66	0.1201	102.9	1.52
CHS(56.9, 0.24)	-	65700	2.35	0.1097	5972	3.81

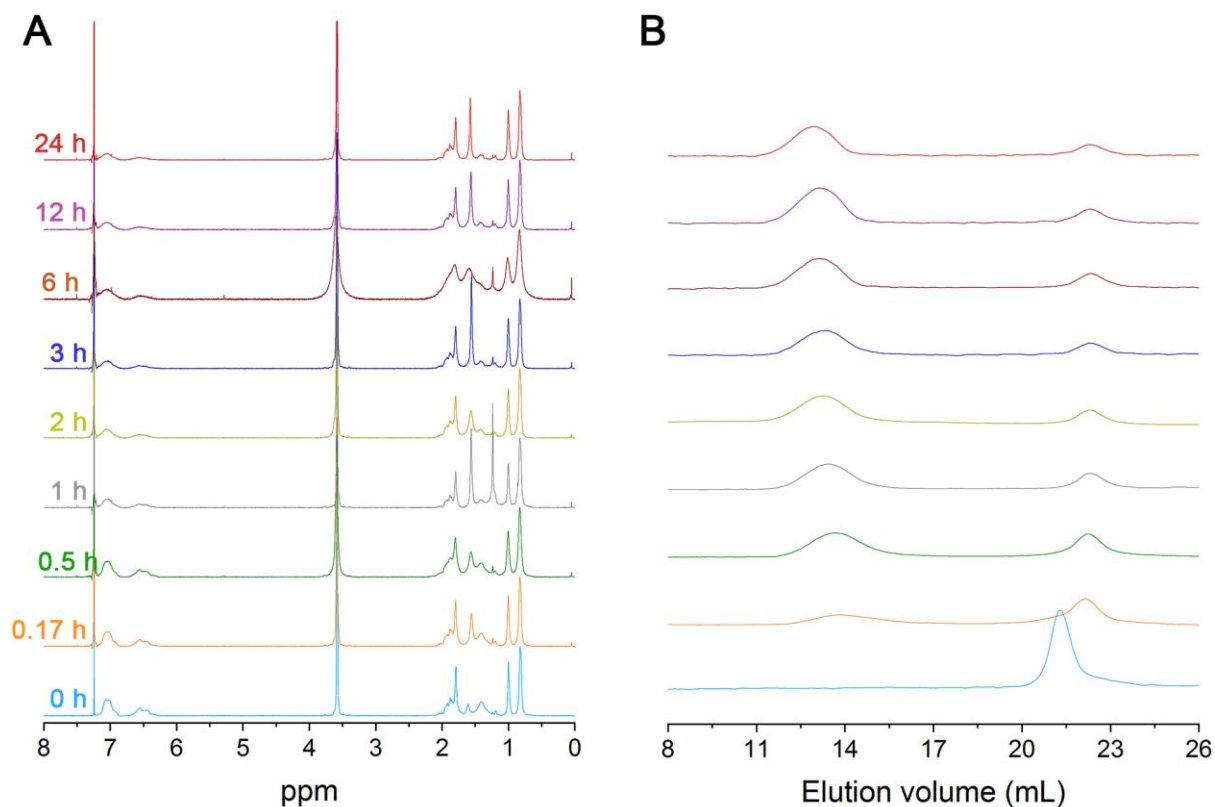


Figure S2. (A) ^1H NMR spectra (400 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) and (B) SEC traces (CHCl_3 , $40\text{ }^\circ\text{C}$, 1 ml min^{-1}) of CHS from MS(69.2, 0.36) as a function of reaction time.

Table S3. Kinetics of hyper-cross-linking of MS(69.2, 0.36)

Reaction time (h)	Conv. (%)	$M_{n,\text{SEC}}(\text{kg mol}^{-1})$	D	$D_{h,\text{MeCN}}(\text{nm})$	$D_{h,\text{CHCl}_3}(\text{nm})$
0	0	39.5	1.4	75.9	0
0.17	65.0	19360	2.4	52.4	127.8
0.5	66.4	24430	2.5	65.7	98.6
1	73.2	43380	1.8	71.6	86.7
2	80.1	51510	1.9	57	86.4
3	75.9	55570	1.6	58.6	84.1
6	72.1	73650	1.5	58.6	84.8
12	82.9	67780	1.5	55.5	82.1
24	83.5	89710	1.4	55.8	82.3

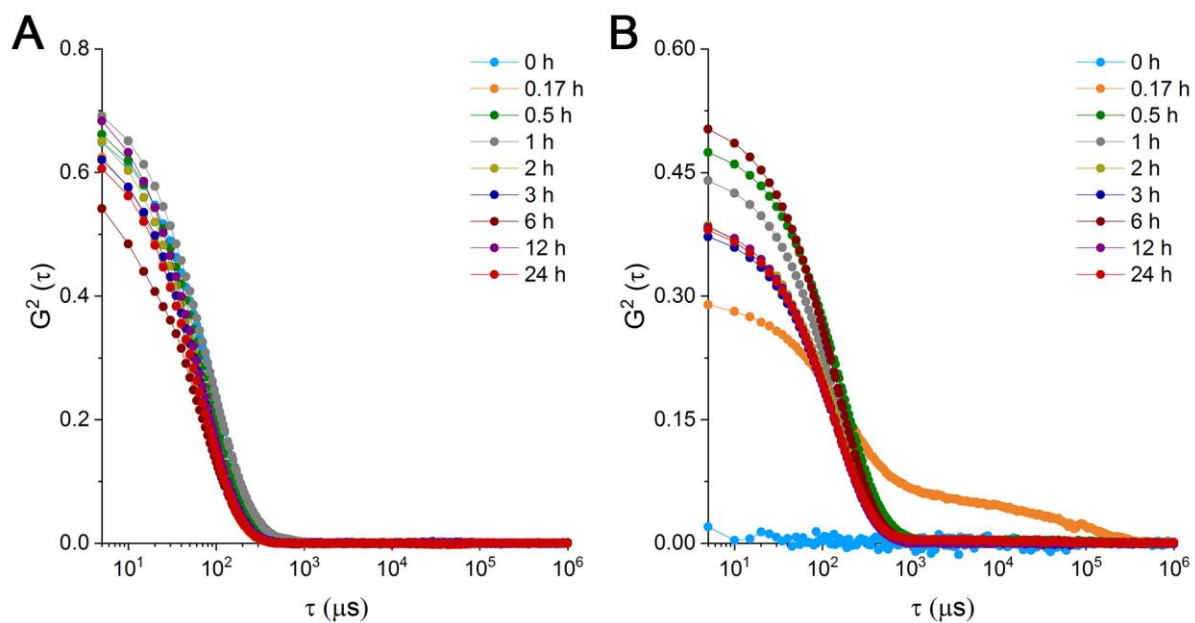


Figure S3. DLS autocorrelation functions of CHS from MS(69.2, 0.36) as a function of reaction time. Solutions of purified polymers were prepared in MeCN (A) and CHCl_3 (B) at 2 mg mL^{-1} , and analyzed at $20 \text{ }^\circ\text{C}$.

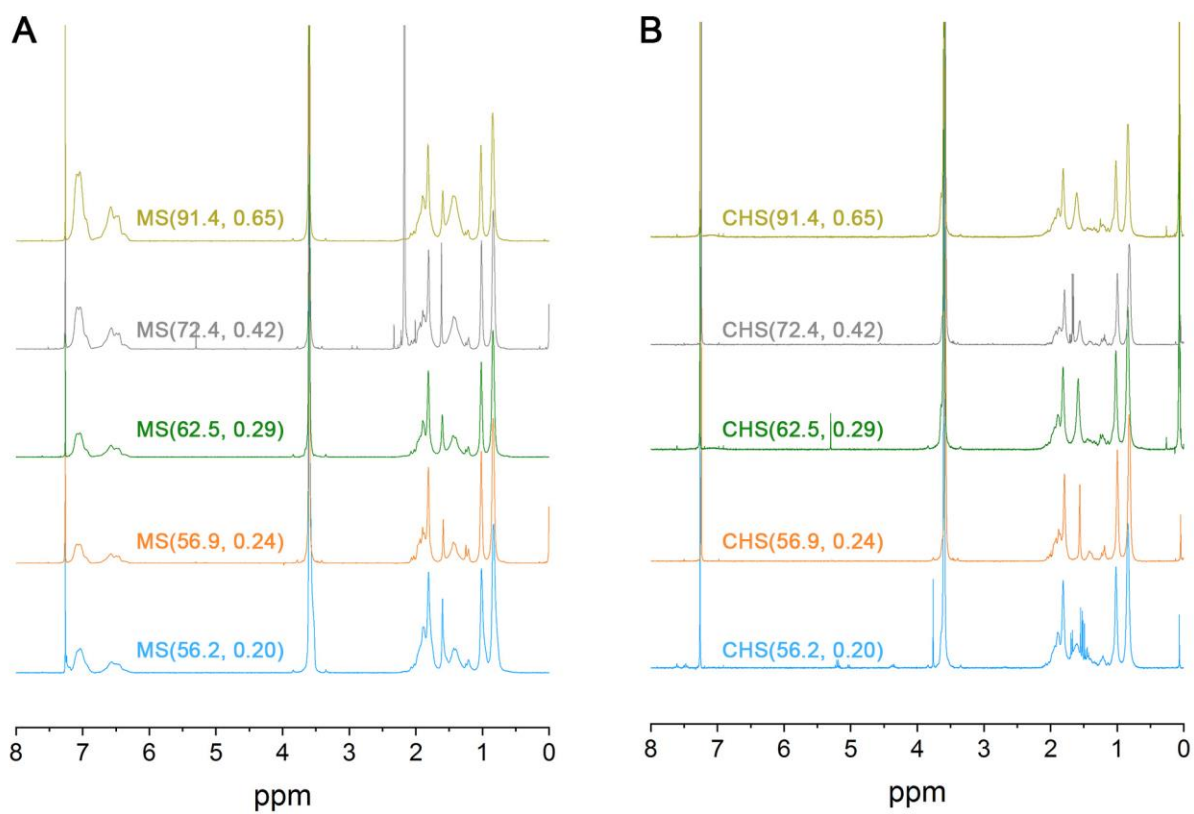


Figure S4. ^1H NMR spectra of (A) MS and (B) CHS polymers with varying f_{PS} (400 MHz, CDCl_3 , 20 $^\circ\text{C}$).

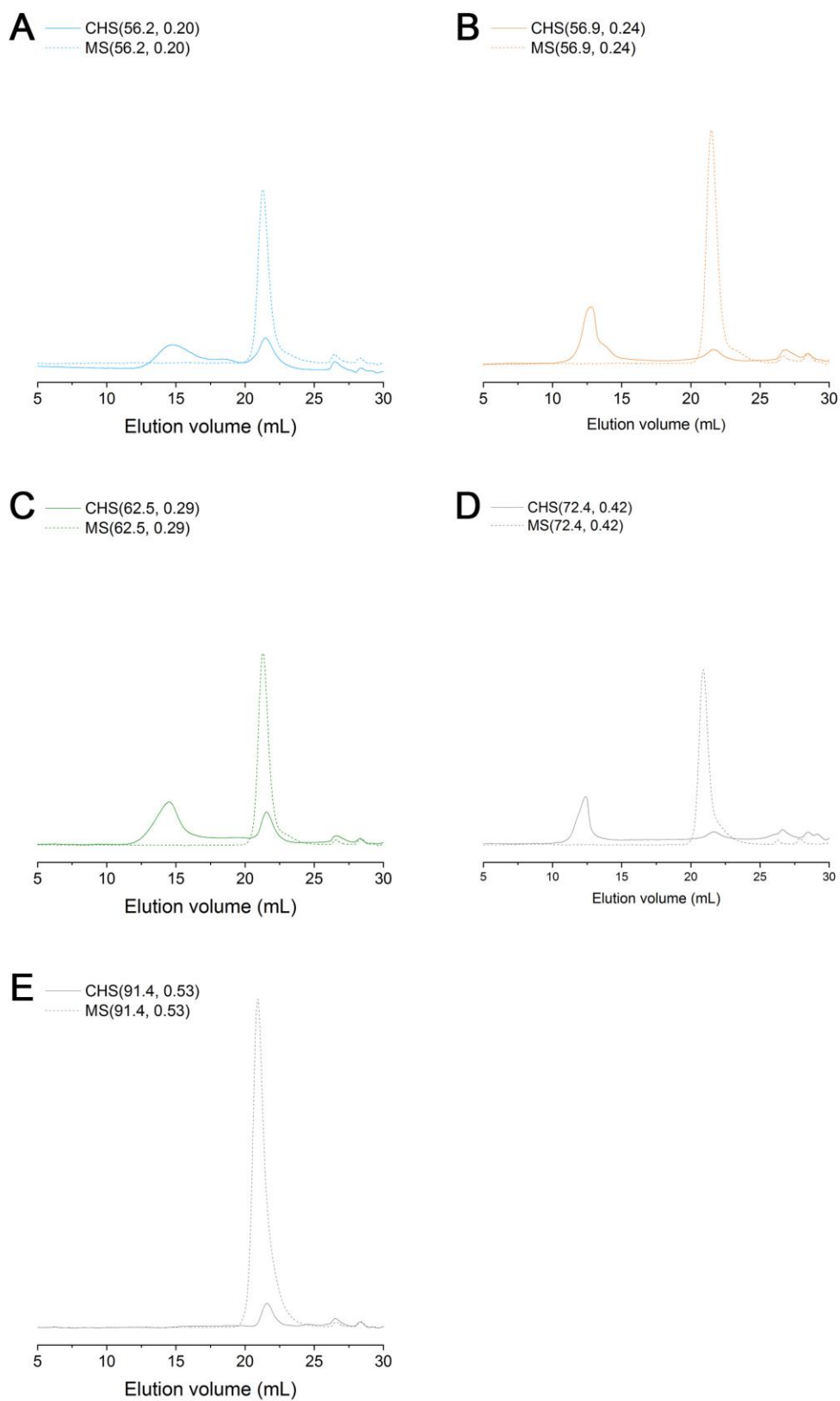


Figure S5. SEC traces of MS and CHS polymers with varying f_{PS} (1 mL min^{-1} , CHCl_3 , $40 \text{ }^\circ\text{C}$).

The signals were recorded with dRI detector.

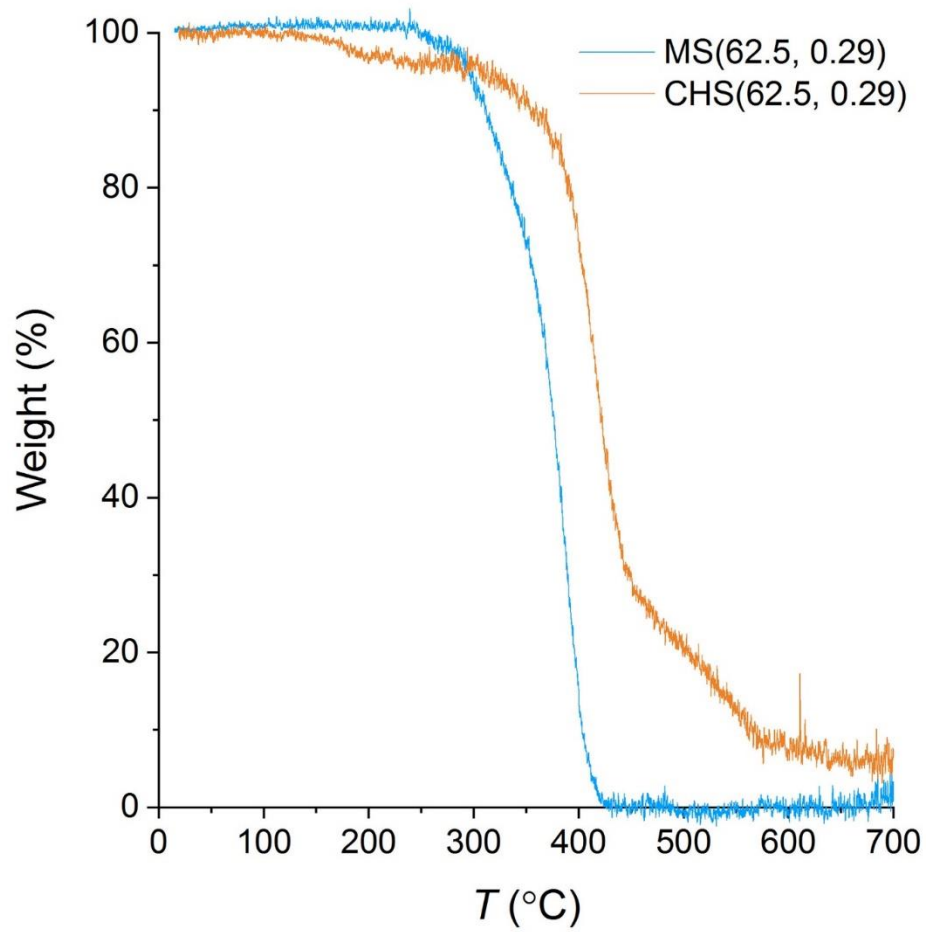


Figure S6. TGA thermograms of MS(62.5, 0.29) and CHS(62.5, 0.29).

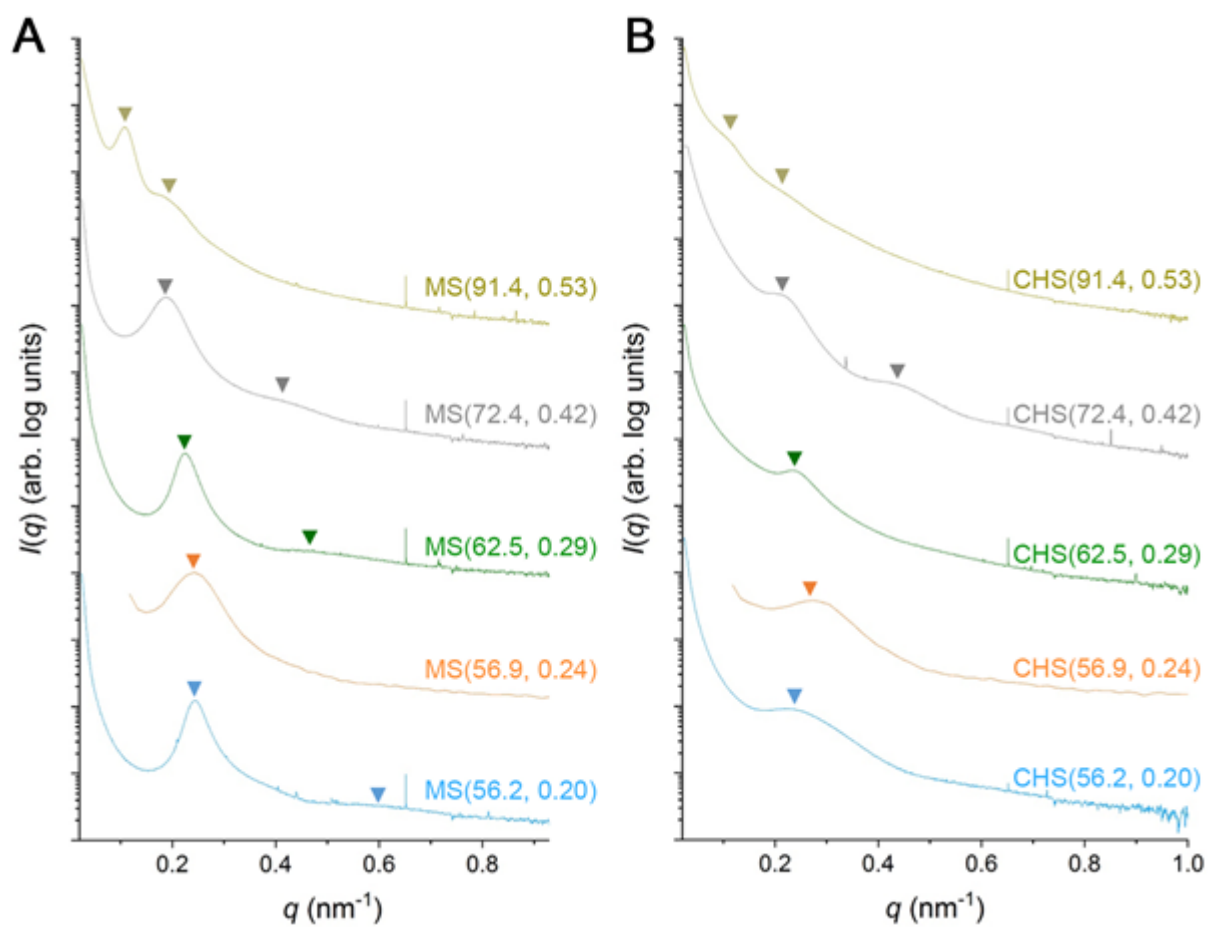


Figure S7. One-dimensional SAXS profiles of MS (A) and CHS (B) polymers obtained by casting of MeCN solutions.

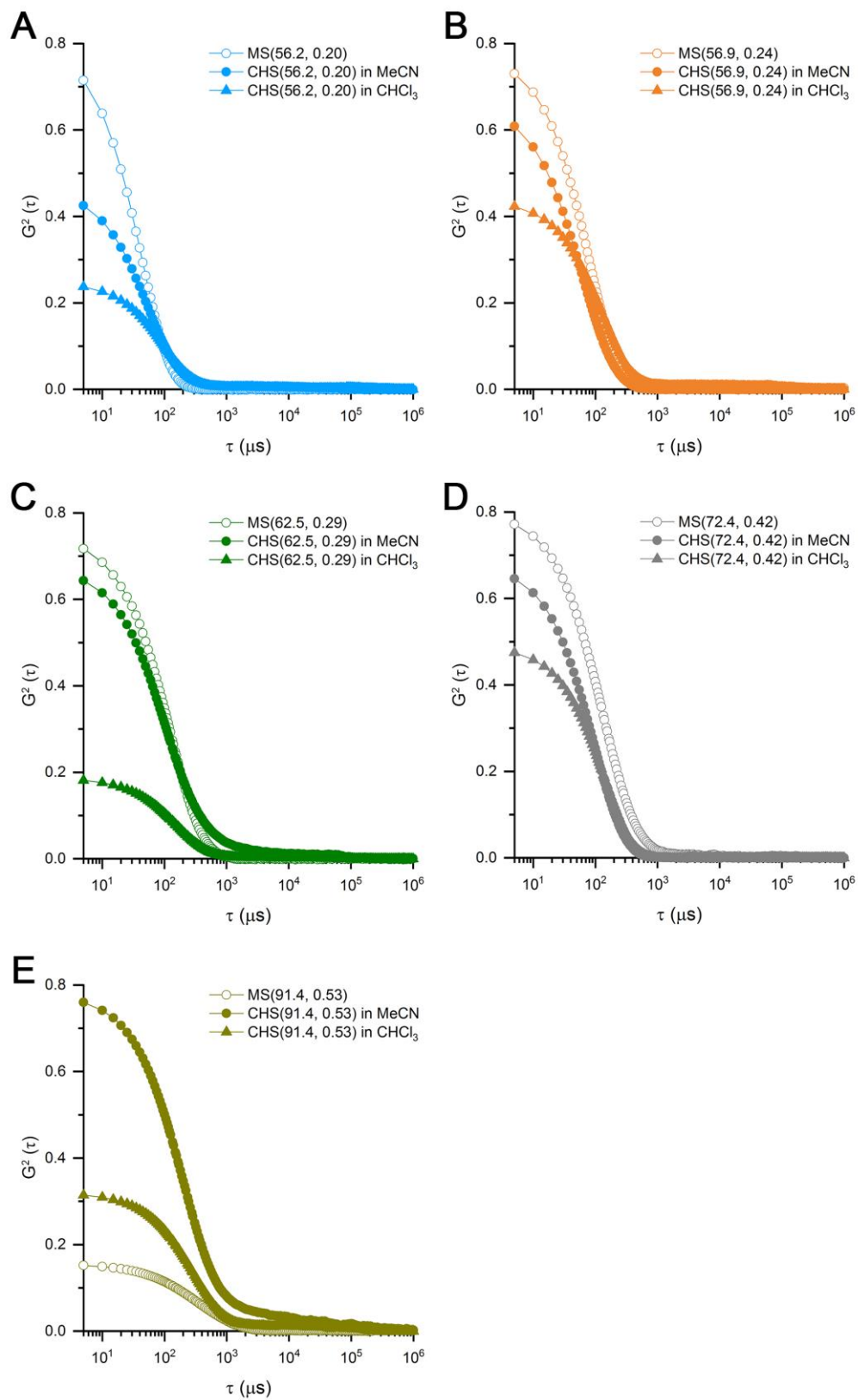


Figure S8. DLS autocorrelation functions of MS and CHS polymers (MeCN or CHCl₃, 2 mg mL⁻¹, 20 °C).

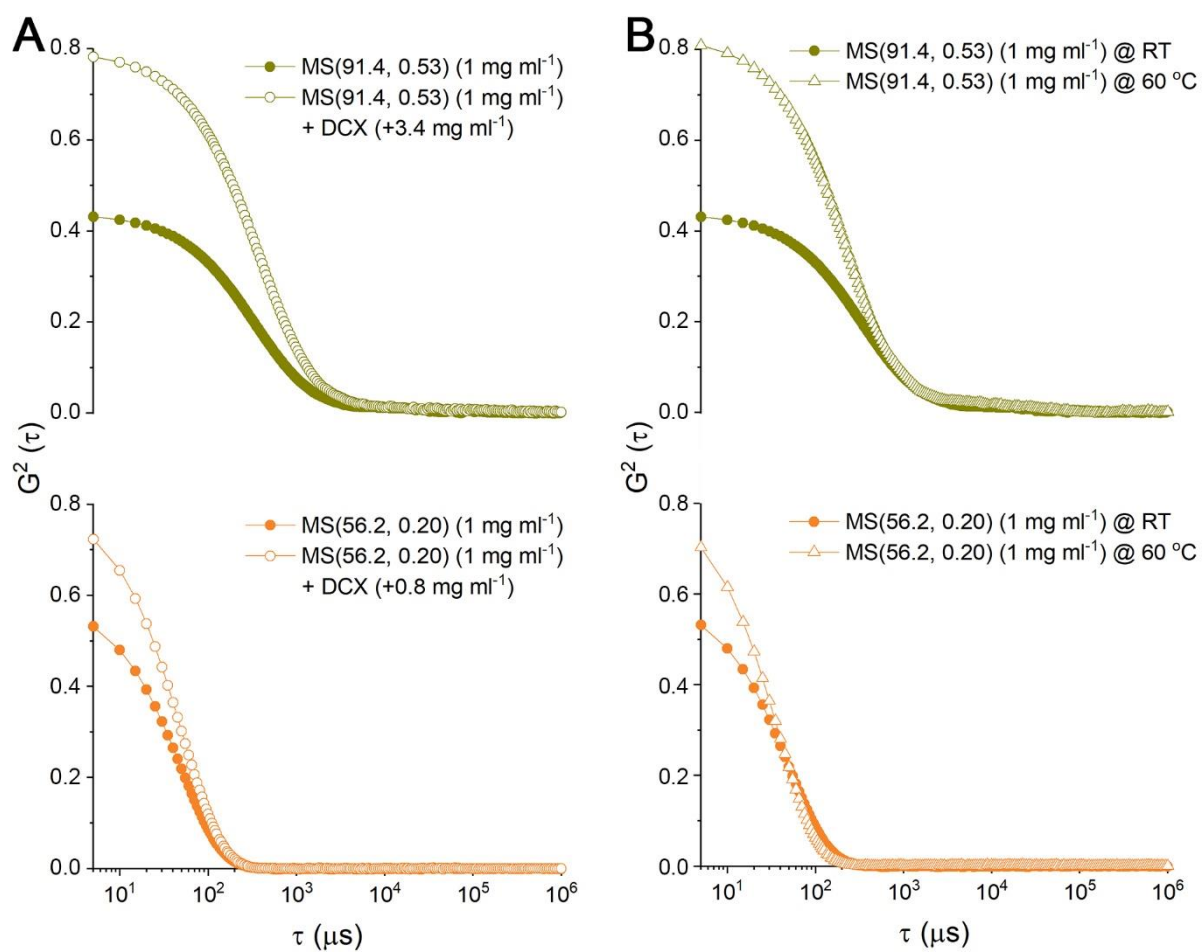


Figure S9. DLS autocorrelation functions of MS polymers with (A) adding *p*-DCX and (B) varying temperature.

Table S4. DLS analysis of MS polymer with varying conditions

Entry	Polymer (1 mg ml ⁻¹)	<i>T</i> (°C)	<i>p</i> -DCX (mg ml ⁻¹)	<i>D</i> _h (nm)
1	MS(56.2, 0.20)	RT	0	42.7
2	MS(56.2, 0.20)	60	0	36.0
3	MS(56.2, 0.20)	RT	0.8	43.5
4	MS(91.4, 0.53)	RT	0	342.6
5	MS(91.4, 0.53)	60	0	241.3
6	MS(91.4, 0.53)	RT	3.4	368.1

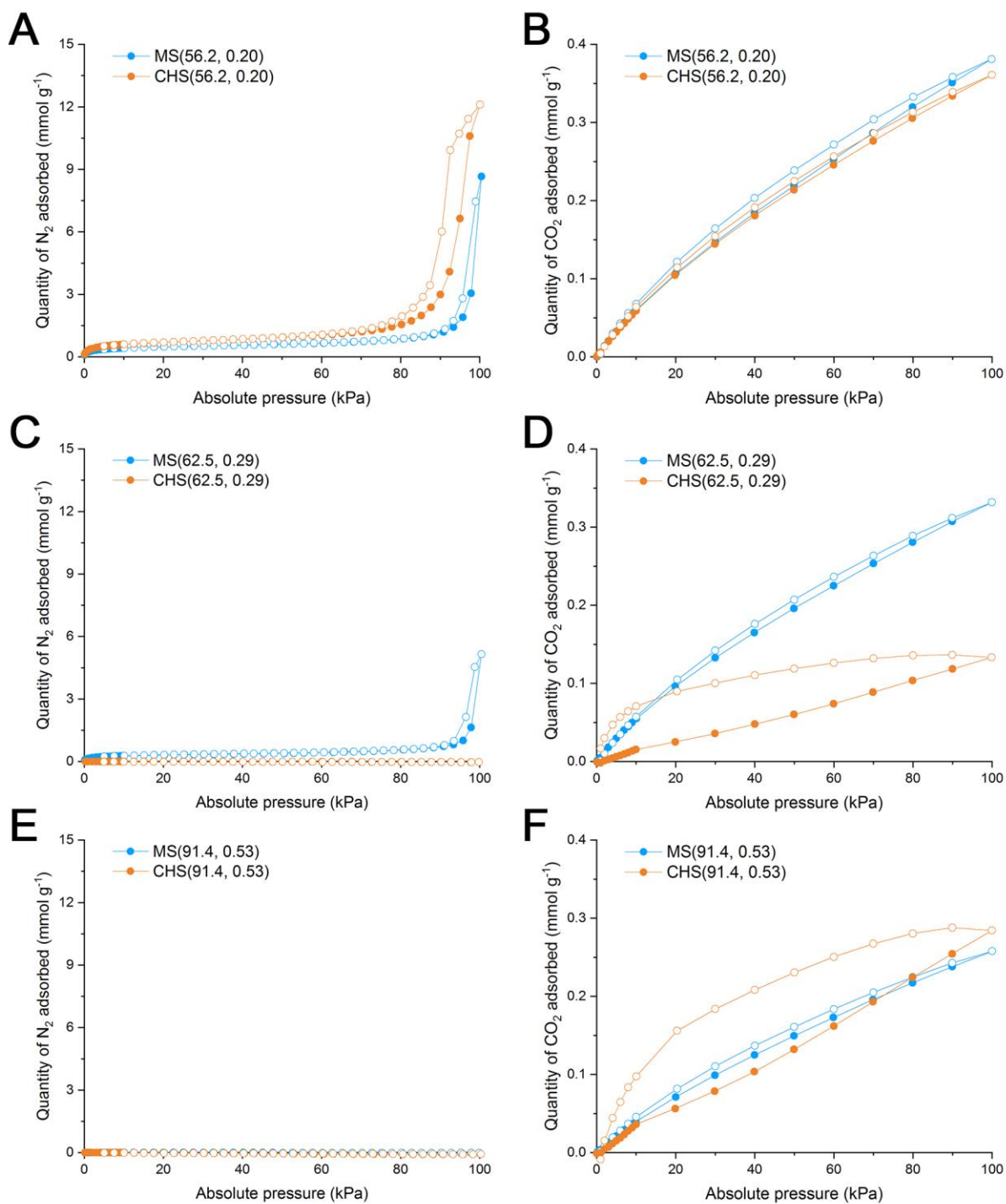


Figure S10. N_2 (A, C, E) and CO_2 (B, D, F) adsorption isotherms for representative MS and CHS polymers.

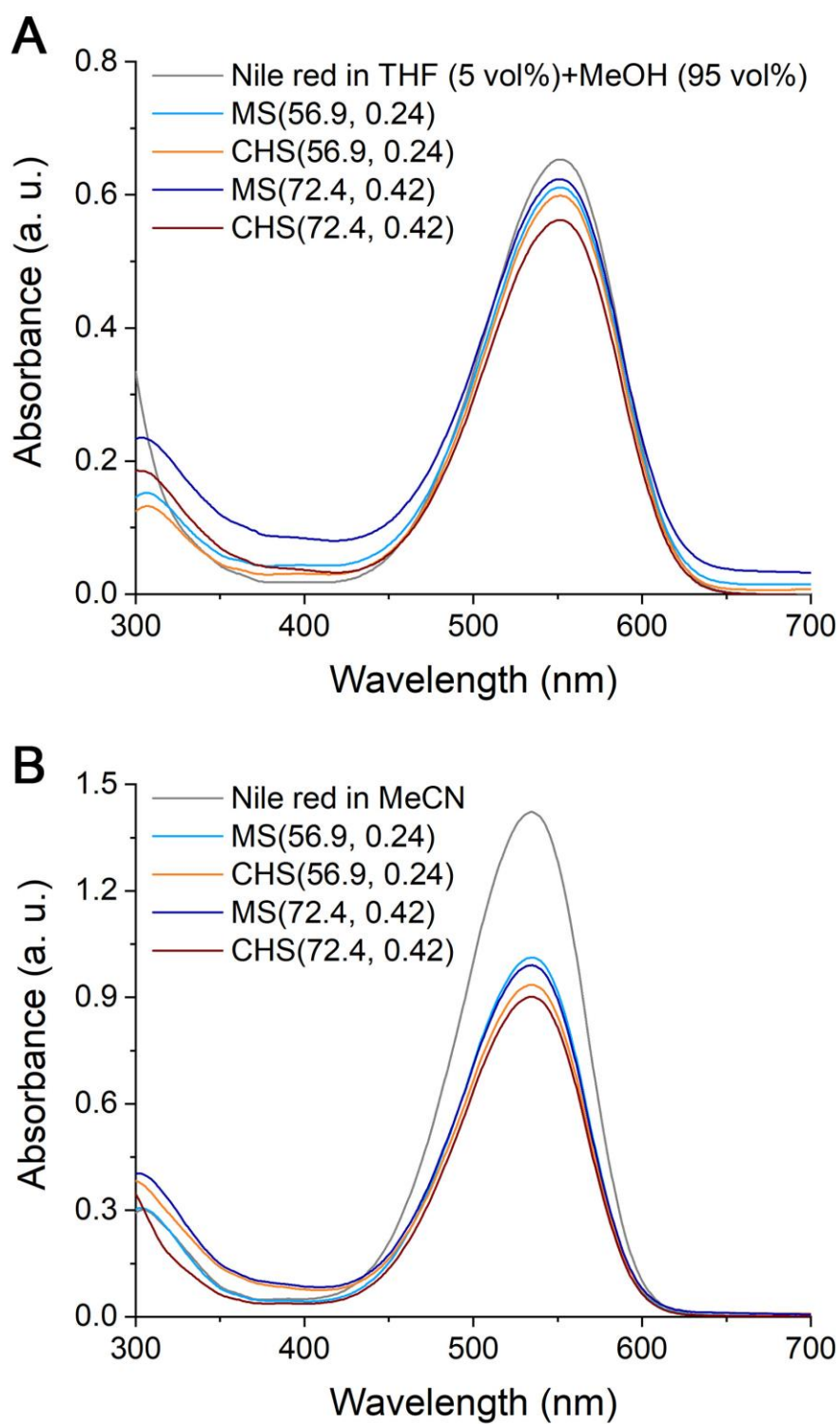


Figure S11. UV-vis spectra for the Nile red uptake experiments. (A) In THF. (B) In MeCN. Blue: MS(56.9, 0.24); Royal: MS(72.4, 0.42); Orange: CHS(56.9, 0.24); Wine: CHS(72.4, 0.42).

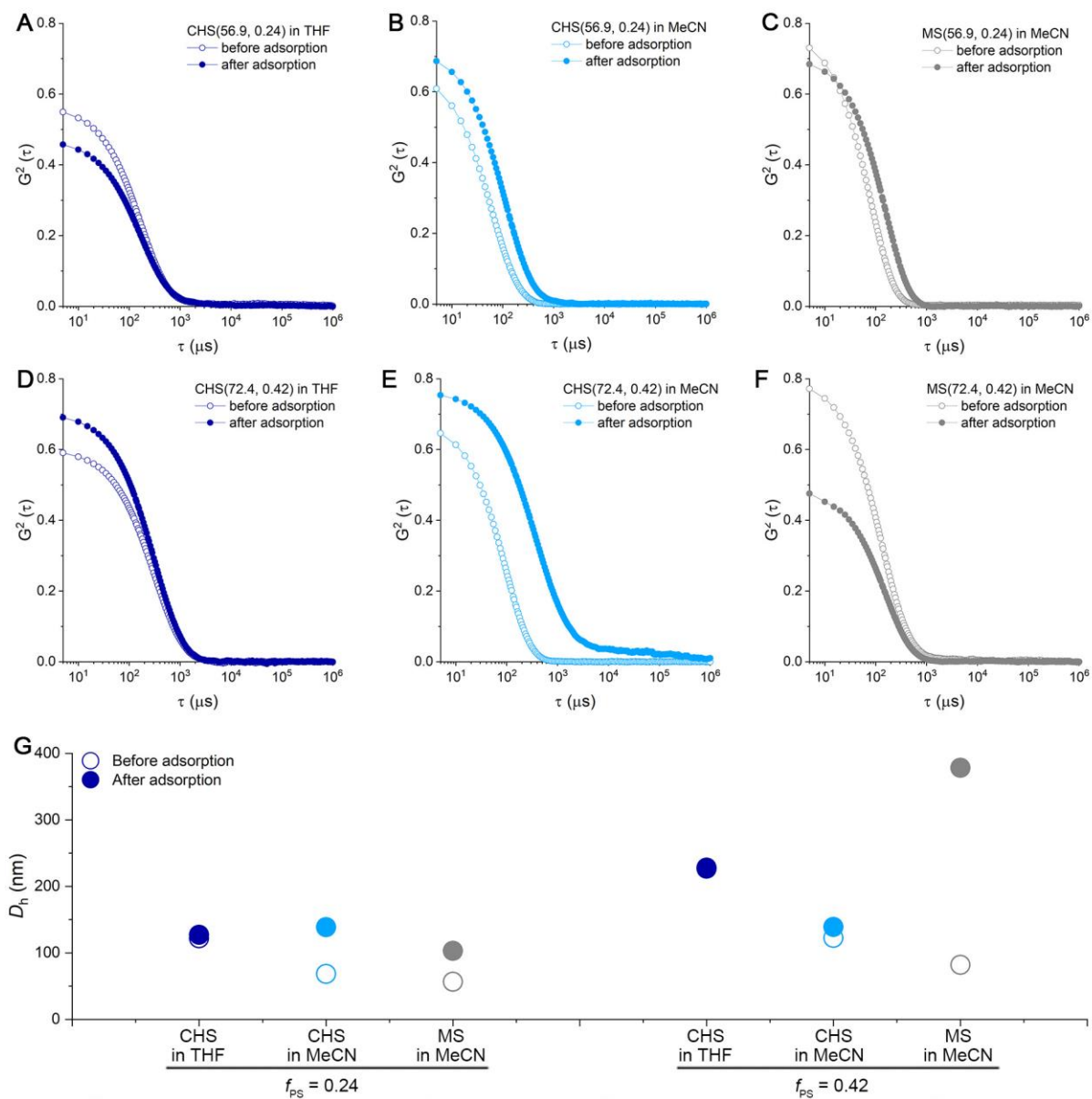


Figure S12. DLS analysis of MS and CHS polymers before and after Nile red uptake. Open circle: before uptake. Filled circle: after uptake. (A-F) DLS autocorrelation functions obtained in THF (A, D) and MeCN (B, C, E, F) solutions. (G) Change in D_h .

Table S5. Q values and change in D_h for Nile red adsorption

Entry	In THF			In MeCN		
	D_h (nm) before adsorption	D_h (nm) after adsorption	Q ($\mu\text{g mg}^{-1}$)	D_h (nm) before adsorption	D_h (nm) after adsorption	Q ($\mu\text{g mg}^{-1}$)
MS(56.9, 0.24)	-	-	-	68.3	138.5	7.2
CHS(56.9, 0.24)	121.9	127.2	2.0	56.6	103	8.5
MS(72.4, 0.42)	-	-	-	122.5	139.0	7.5
CHS(72.4, 0.42)	228.1	226.7	3.4	81.9	378.3	9.1