Humidity-responsive Janus polymer–inorganic films formed by evaporation-induced vertical segregation

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1 Experimental Section

1.1 Materials

Phosphoric acid (H_3PO_4, ≥85%) and triethylamine (TEA) were purchased from Macklin Chemical Reagent Co. (China). 4,4′-Azobis(4-cyanovaleric acid) (ACVA, 98%), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPCP), *L*-serine (98.5%), and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$, 99%) were obtained from Aladdin Reagent Co. (China). Glycidyl methacrylate (GlyMA) was purchased from Shanghai Yuanye Biotechnology Co. (China) and was purified by passage through a basic aluminum oxide column to remove polymerization inhibitors. Deionized water (resistivity 18.2 MΩ·cm) was produced using a laboratory water purification system.

1.2 Synthesis of poly((2-hydroxy-3-(methacryloyloxy)propyl)serine)$_x$ via RAFT polymerization

The synthesis of poly((2-hydroxy-3-(methacryloyloxy)propyl)serine)$_{50}$ (denoted as S_{50}) is described as a representative example. GlyMA (12.0 g, 84.4 mmol) and excess *L*-serine (9.5 g, 90.4 mmol) were added to a 500 mL round-bottom flask to ensure complete ring-opening of GlyMA, followed by the addition of 200 mL of deionized water. The pH of the mixture was adjusted to approximately 8 by dropwise addition of 1 M $NaHCO_3$. The flask was equipped with a condenser and heated under reflux at 60 °C for 12 h. Upon completion of the reaction, the initial emulsion transformed into a light-yellow, clear solution.

After cooling to room temperature, the chain transfer agent CPCP (475.5 mg, 1.7 mmol) and the initiator ACVA (95.4 mg, 0.34 mmol; [CPCP]/[ACVA] = 5.0) were added to the solution corresponding to a target degree of polymerization of 50. The pH was adjusted to 7–8 by dropwise addition of 1 M $NaHCO_3$. The flask was sealed with a rubber septum and purged with nitrogen for 35 min, and then placed in a preheated oil bath at 70 °C for 5.5 h to initiate RAFT polymerization. The reaction was quenched by cooling the flask in an ice–water bath and exposing the reaction mixture to air. The resulting polymer was purified by dialysis against deionized water for one week using a dialysis membrane with a molecular weight cutoff of 3500 Da to remove unreacted monomers. The synthesis of S_{500} and S_{1000} followed an analogous procedure, with specific reaction parameters summarized in Table S1.

1.3 Synthesis of calcium phosphate oligomers (CPO)

CPO was synthesized according to the method with only minor modification by Liu et al.[1] Briefly, $CaCl_2 \cdot 2H_2O$ (5.88 g) was added to a reagent bottle and dissolved in ethanol (0.80 L) to form a clear solution at room temperature. Triethylamine (TEA, 110.9 mL) was then added, and the mixture was stirred for 30 min. Subsequently, an alcoholic solution of H_3PO_4 (2.09 mL H_3PO_4 dissolved in 40 mL ethanol) was added dropwise to the above solution using a syringe pump. After continuous stirring for 12 h, the resulting suspension was centrifuged at 6000 rpm and washed with ethanol three times to remove excess TEA, yielding a CPO gel. The obtained CPO was finally redispersed in ethanol to form a homogeneous dispersion (~10 mg mL^{-1}) and stored at 4 °C for further use.

1.4 Synthesis of S_x/CPO composite films

In a typical procedure, S_{1000} (0.6 g) was dissolved in 30 mL of deionized water, and the pH was adjusted to approximately 8 (±0.1) by dropwise addition of $NH_3 \cdot H_2O$. Separately, 10 mL of a CPO dispersion (10 mg mL^{-1}) was centrifuged at 6000 rpm for 5 min. The resulting CPO precipitate was then combined with the S_{1000} solution and homogenized by vortex mixing to obtain a uniform suspension. The mixture was allowed to react at 4 °C for 3 h. Subsequently, the suspension was cast into square Petri dishes (10 cm × 10 cm × 1.5 cm) and maintained at 25 °C until a self-supporting film formed, which could be readily peeled from the dish. Composite films based on other S_x polymers were prepared following the same procedure, with S_{1000} replaced by the corresponding S_x. S_x films were prepared following the same procedure described above, except that no CPO was added. Briefly, an aqueous S_x solution (30 mL, 2.0 wt%) was cast into square Petri dishes (10 cm × 10 cm × 1.5 cm) and dried at 25 °C until a self-supporting film formed, which could be readily peeled from the Petri dish.

2 Characterization

2.1 ^{1}H NMR spectroscopy

^{1}H NMR spectra were recorded on a Bruker Ascend 400 spectrometer equipped with an AVANCE NEO console (Bruker Corporation, Switzerland), operating at 400 MHz, using D_2O as the solvent.

2.2 Scanning electron microscopy (SEM)

The cross-sectional morphologies of the composite film samples were examined by SEM (SU1000, Hitachi, Japan). Prior to observation, the samples were sputter-coated with a thin layer of gold at 8 mA for 20 s to ensure adequate conductivity.

2.3 Tensile test

Mechanical tensile properties were measured using a universal testing machine (AGS-X, Shimadzu, Japan) equipped with a 10 kN load cell. All tests were conducted at room temperature and a relative humidity of 40–50%, with a constant crosshead speed of 5 mm min^{-1}. Specimens were cut into rectangular strips with dimensions of 2 mm × 20 mm × d mm, where d denotes the sample thickness. The reported mechanical properties represent the average values obtained from five independently tested specimens.

2.4 Humidity response test

Humidity-responsive behavior was evaluated using a custom-designed humidity chamber. The device consisted of a transparent acrylic box equipped with two sliding top covers for convenient opening and sealing. Saturated salt solution and anhydrous calcium chloride were placed on opposite sides of the chamber to establish distinct humidity environments. A saturated NaCl solution was used to maintain the relative humidity at 45% ± 5% in the enclosed space, while anhydrous calcium chloride fixed the relative humidity on the opposite side at 20% ± 4%. The relative humidity was monitored using a high-precision hygrometer. A square opening (3 cm × 2 cm) was fabricated at the center of the partition separating the two humidity zones, into which the film sample was tightly mounted. The bending and straightening behavior of the film in response to the humidity gradient was recorded using a camera.

2.5 Other measurements

Fourier transform infrared (FTIR) spectra were collected using an FTIR spectrometer (Spectrum Two, PerkinElmer, USA) equipped with an attenuated total reflection (ATR) accessory. Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku MiniFlex 600, Japan) using Ni-filtered Cu Kα radiation ($\lambda = 1.542$ Å), operated at an accelerating voltage of 30 kV and a tube current of 10 mA. Energy-dispersive X-ray (EDX) elemental mappings were obtained using a field-emission scanning electron microscope (SU1000, Hitachi, Japan). Film transmittance was measured using a UV–vis spectrophotometer (UV-3600i Plus, Shimadzu, Japan).

Table S1. Summary of the synthetic recipes for various S_x polymers with different degrees of polymerization.

Entry	**GlyMA**		***L*-Serine**		**CPCP**		**ACVA**		**Water**	
	Mass (g)	**Moles (mmol)**	**Mass (g)**	**Moles (mmol)**	**Mass (mg)**	**Moles (mmol)**	**Mass (mg)**	**Moles (mmol)**	**Mass (mL)**	**Solid content % w/w**
S_{50}	12.0	84.4	9.5	90.4	475.5	1.7	95.4	0.34	200	10
S_{500}	12.0	84.4	9.5	90.4	47.5	0.17	9.5	0.034	194	10
S_{1000}	12.0	84.4	9.5	90.4	23.5	0.08	4.8	0.017	194	10

Table S2. Time-dependent bending angles of the S_{500}/CPO and S_{1000}/CPO films measured at various response times.

Response time (s)		**0**	**1**	**2**	**3**	**5**	**7**	**10**	**14**	**20**	**25**	**30**	**36**	**40**	**45**	**50**
Bending angle (°)	**S_{500}/CPO**	**0**	**16**	**24**	**31**	**38**	**44**	**50**	**56**	**64**	**70**	**74**	**79**	**82**	**85**	**89**
	S_{1000}/CPO	**0**	**30**	**45**	**60**	**75**	**88**	**103**	**120**	**137**	**148**	**157**	**166**	**170**	**176**	**180**

Table S3. Time-dependent bending angles of the S_{500}/CPO and S_{1000}/CPO films measured during the recovery process.

Recovery time (s)		**0**	**2**	**5**	**8**	**10**	**14**	**20**	**25**	**30**	**35**	**40**
Bending angle (°)	**S_{500}/CPO**	**90**	**72**	**59**	**50**	**46**	**36**	**26**	**20**	**13**	**7**	**0**
	S_{1000}/CPO	**90**	**69**	**57**	**45**	**41**	**26**	**18**	**10**	**6**	**2**	**-2**

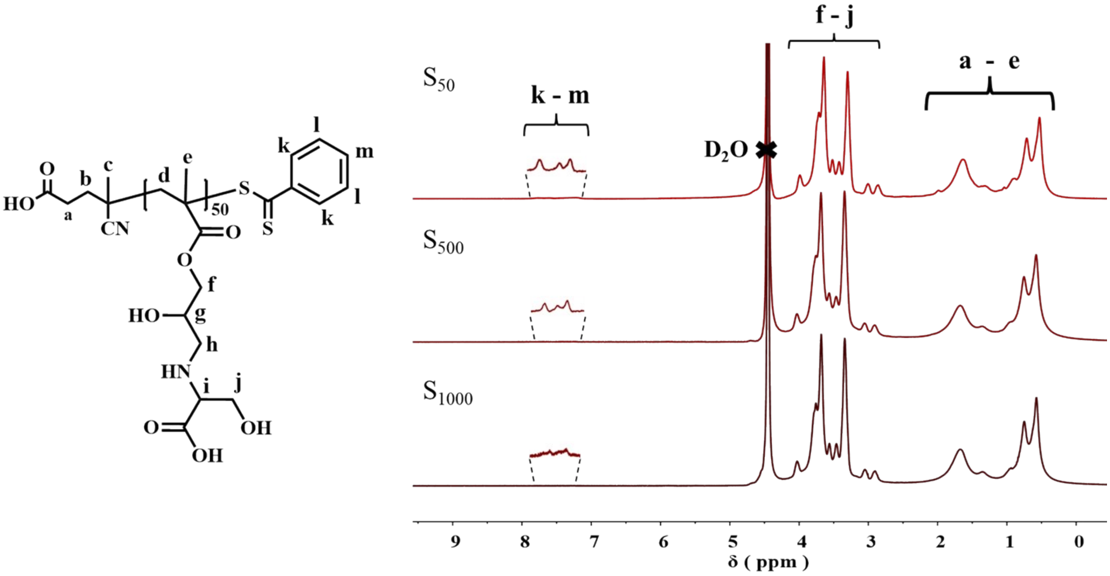

Figure S1. ^{1}H NMR spectra (D_2O) recorded for various S_x macro-CTAs.

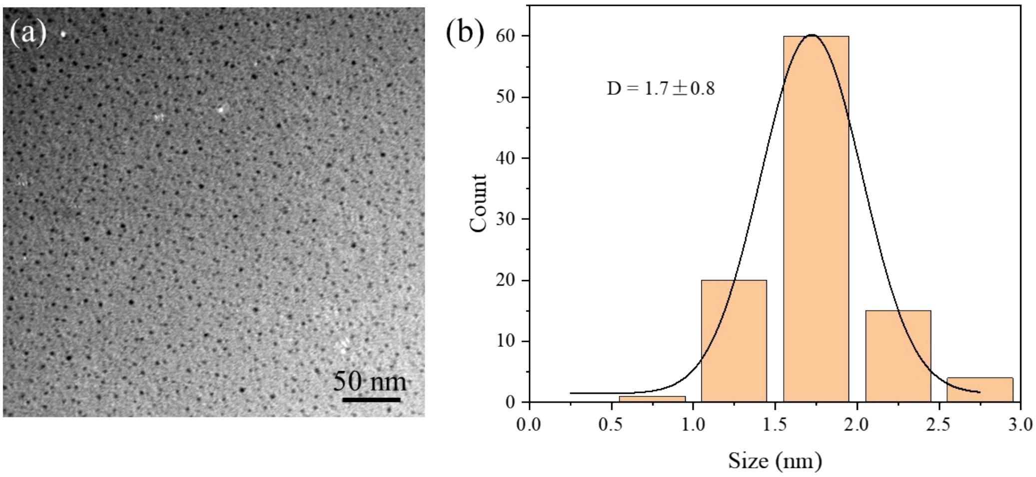

Figure S2. (a) TEM image of CPO. (b) The particle size distribution of the CPO nanoparticles was determined by statistical analysis of 100 individual particles, giving an average diameter of approximately 1.7 nm.

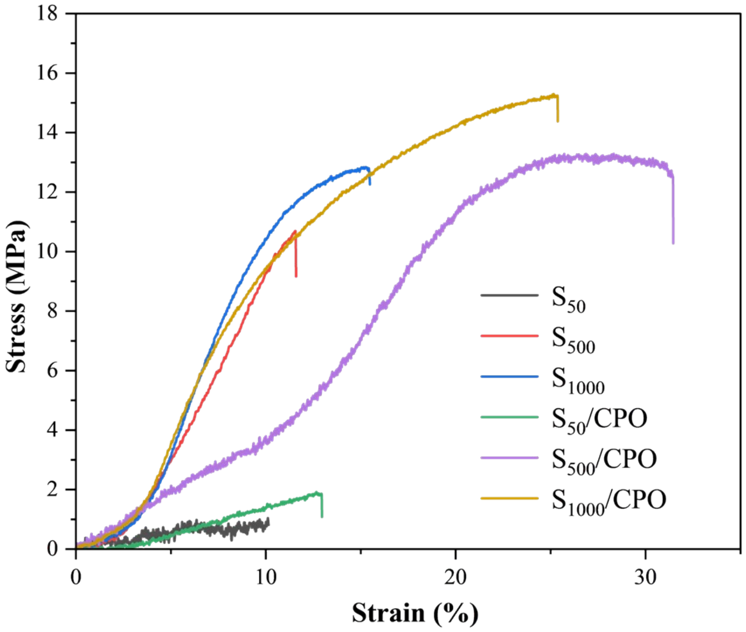

Figure S3 Tensile stress-strain curves of various S_x films and their corresponding S_x/CPO composite films.

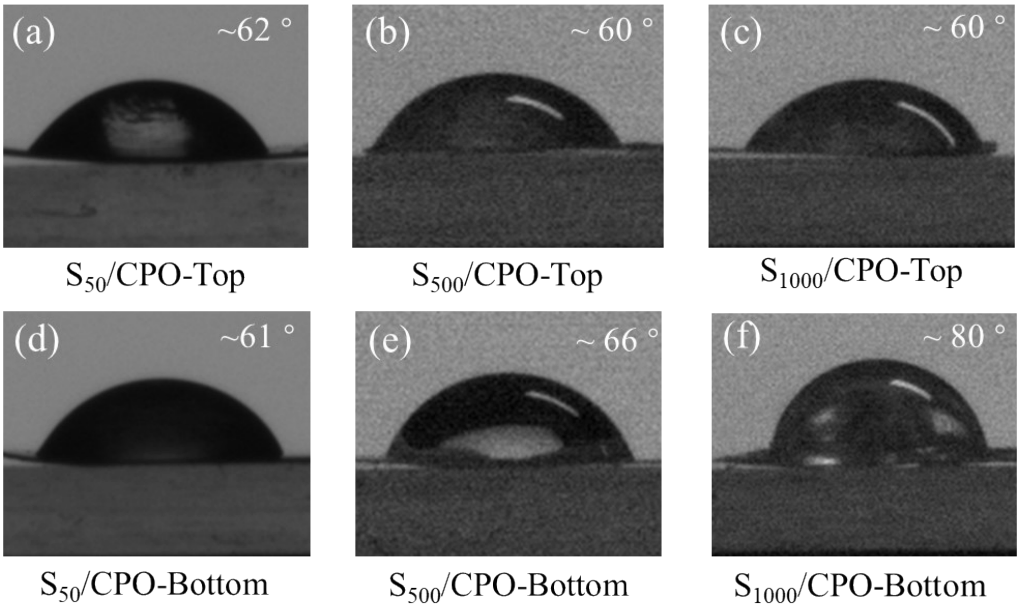

Figure S4. Water contact angles measured on the top and bottom surfaces of S_{50}/CPO (a, d), S_{500}/CPO (b, e), and S_{1000}/CPO (c, f) composite films, respectively.

Reference

[1] Y. Yu, Z. Liu, Q. Zhao, *Adv. Funct. Mater.* **2023**, *33*, 2213699.