Supporting Information

for

Wetting-Enhanced Adhesion of Photo-polymerized Supramolecular Adhesives for both Smooth and Rough Surfaces

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1. Experimental Section

1.1 Materials.

Triethylamine (TEA, 99%, Aladdin), thymine (99%, Aladdin), *n*-butyl acrylate (*n*BA, 99%, Aladdin), 2, 6-di-*tert*-butyl-4-methylphenol (BHT, 99%, Aladdin), 1, 4-butanediol diacrylate (99%, Aladdin), *N*, *N*-dimethylformamide (DMF), dichloromethane (DCM), and 2, 2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aladdin) were all used as received. 2, 2′-Azo-bis-(isobutyronitrile) (AIBN) was obtained from Energy Chemical and recrystallized from methanol three times prior to use. 4-((3-(Thymin-l-yl)propanoyl)oxy)butyl acrylate (TAc) was prepared according to the previous publications with slight modifications.[1, 2]

1.2 Characterization

All ^{1}H NMR spectra were recorded on an Avance III HD400 spectrometer (Bruker) with CDCl$_3$ or DMSO-d_6 as the solvent. The external reference method involves placing monomer mixtures of *n*BA and TAc without any solvents in a NMR tube, and then using a sealed tube with a smaller inner diameter than the NMR tube, to which CDCl$_3$ was added. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 spectrometer (Thermo Scientific). The molecular weight and molecular weight distribution of the nucleobase-containing copolymers were measured by size exclusion chromatography (SEC), which was equipped with a PLgel column using DMF (containing 5 mM NH$_4$BF$_4$) as the eluent with a flow rate of 1 mL min^{-1} at 50 °C. The

SEC system was calibrated with PMMA standards before use. Samples were filtered through a nylon filter (pore size of 0.22 µm) before SEC characterization. Thermogravimetric analysis (TGA) was conducted on a TA Q5000IR TGA instrument under a nitrogen atmosphere to obtain the decomposition temperature (T_d) at 5% degradation of the copolymers. Warming up from 40 to 700 °C with a rate of 10 °C min^{-1} was conducted. The glass transition temperatures (T_gs) of copolymers were obtained by DSC using a PerkinElmer DSC 8500 instrument under a nitrogen atmosphere. The sample was first heated from room temperature to 70 °C at a rate of 10 °C min^{-1}, then cooled down to -70 °C at the same rate. Following this, the sample was heated to 70 °C at a rate of 10 °C min^{-1} again. The T_g value was determined from the second heating scan. The contact angle (CA) of liquids was determined by using a contact angle goniometer (CAM 200, KSV). The adhesive force was measured underwater using a high-sensitivity microelectromechanical balance system (Data Physics DCAT 25). UV-vis spectra were measured by using an UV-2802 UV-visible spectrophotometer. For the UV irradiation of the samples, a SCIENTZ03-2 crosslinker chamber, equipped with 6 × 8 W UV tubes with the maximum intensity at 365 nm was employed.

Characterization of adhesive properties of nucleobase-containing adhesives was performed on a SANS TS7104 electronic testing instrument (SANS, China) at 10 mm min^{-1}. Each polymer sample was measured at least three times to ensure repeatability. Based on the same procedures, the adhesion strengths were tested when bonding with different substrates.

1.3 Synthetic procedures

Synthesis of 4-((3-(thymin-l-yl)propanoyl)oxy)butyl acrylate (TAc).

For the synthesis of TAc, thymine (12.6 g, 100 mmol), BHT (881 mg, 4 mmol), and *N*, *N*-dimethylformamide (180 mL) were added into round-bottomed flask. Further, TEA (2.02 g, 20 mmol) was added into the mixture at room temperature. The reaction mixture was stirred under argon for 1 h before adding 1, 4-butanediol diacrylate (37.7 mL, 200 mmol) (Scheme S1). The reaction solution turned clear after stirring for 24 h at room temperature. Then the reaction mixture was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ before filtering, then concentrated in a rotary evaporator to remove the solvent. The evaporation residue was further separated using flash column chromatography with CH_2Cl_2 as the eluent. The obtained viscous liquid was dispersed in Et_2O and recrystallized to get white crystals TAc (18.0 g, 55% yield). Assigned ^1H and ^{13}C NMR spectrum of TAc was shown in Figure S3. HR-MS (m/z) found 325.1388, calc. 325.1321 $[M+H]^+$.
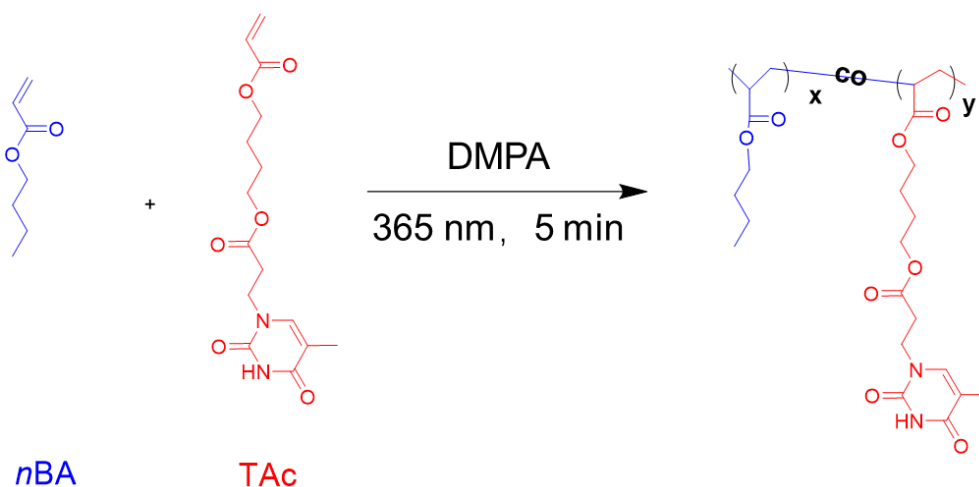
Scheme S1. Synthesis of 4-((3-(thymin-l-yl)propanoyl)oxy)butyl acrylate (TAc).
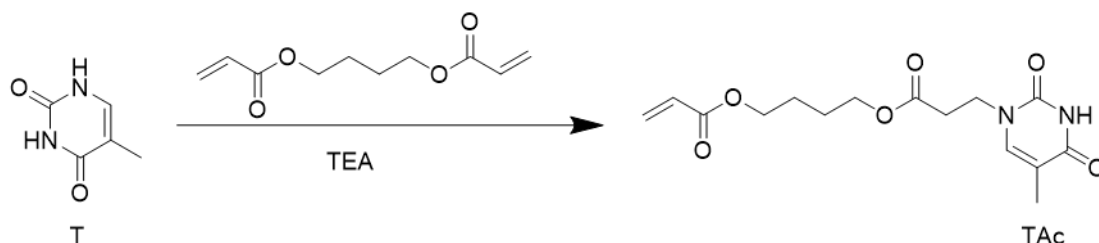
Synthesis of homopolymer P*n*BA and copolymers of *n*BA and TAc at different molar ratios through photopolymerization.

Poly(*n*-butyl acrylate-*co*-4-((3-(thymin-l-yl)propanoyl)oxy)butyl acrylate) (P(*n*BA-*co*-TAc) copolymers were prepared by using conventional bulk polymerization with DMPA as the initiator (Scheme S2). A typical synthetic procedure is as follows. For P(nBA$_{0.75}$-*co*-TAc$_{0.25}$) (PL$_{3-1}$), a dry 5 ml glass vial was charged with *n*BA (0.5 mL, 3.5 mmol), TAc (378 mg, 1.17 mmol), DMPA (8.3 mg, 0.06 mmol) and dissolved by heating with a water bath at 60 °C to form a mixed solution of colorless and transparent monomers, and the samples were coated on glass slides and subjected to a UV crosslinker at a wavelength of 365 nm to achieve the photopolymerization. The polymerization products were further characterized without further purification by using Fourier infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), respectively.

Scheme S2. Synthesis of P(*n*BA-*co*-TAc) copolymers of *n*BA and TAc at different molar ratios through photopolymerization.

Synthesis of copolymers of *n*BA and TAc at different molar ratios through thermal polymerization.

Poly(*n*-butyl acrylate-*co*-4-((3-(thymin-l-yl)propanoyl)oxy)butyl acrylate) (P(*n*BA-*co*-TAc) copolymers were prepared by using conventional free radical polymerization with AIBN as the thermal initiator (Scheme S3). A typical synthetic procedure is as follows. For P(*n*BA$_{0.75}$-*co*-TAc$_{0.25}$) (PT$_{3-1}$), a dried ampoule was charged with *n*BA (0.5 mL, 3.5 mmol), TAc (378 mg, 1.17 mmol), AIBN (8.3 mg, 0.05 mmol), and anhydrous DMF (0.881 mL). The reaction mixture was degassed through 4 freeze-pump-thaw cycles, then put in an oil bath at 75 °C for 2 h with constant stirring. After polymerization, an aliquot of the reaction mixture was taken and analyzed by ^{1}H NMR spectroscopy and size exclusion chromatography (SEC) to calculate the conversion. The residual solution was precipitated three times from cold CH$_3$OH. The purified polymer was dried in a vacuum oven overnight at room temperature and further characterized by ^{1}H NMR spectroscopy, SEC, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), respectively.

Scheme S3. Synthesis of P(*n*BA-*co*-TAc) copolymers of *n*BA and TAc at different molar ratios through thermal polymerization.
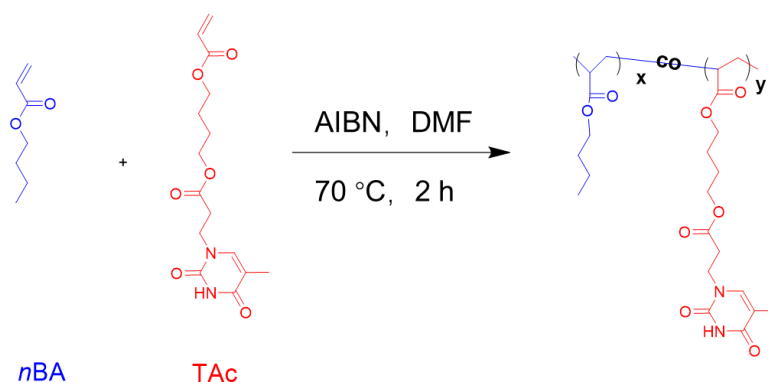
Preparation of nucleobase-containing supramolecular adhesives

The nucleobase-containing supramolecular adhesives were fabricated via either in situ photopolymerization or the thermal polymerization. The typical procedures are as follows. For PL_{x-y}, 50 µL of the mixed monomer solution was applied to 1.0 cm^2 of plasma-cleaned glass slides, covered with another untreated glass sheet and clamped with dovetail clips, and placed in a water-filled dish for 5 min of photopolymerization, and then subjected to pull-up experiments. For PT_{x-y}, the obtained polymers were firstly dissolved in DCM to make a 5 wt% solution. Then 80 µL of the 5 wt% solution was applied to plasma-cleaned glass slides with a coating area of 1.0 cm^2 and dried at room temperature under vacuum for 24 h. Another untreated glass sheet was covered with the above-mentioned polymer-coated glass sheet with 20 N loading for 10 s underwater before testing of adhesion strengths.

2. Supplementary Figures and Table
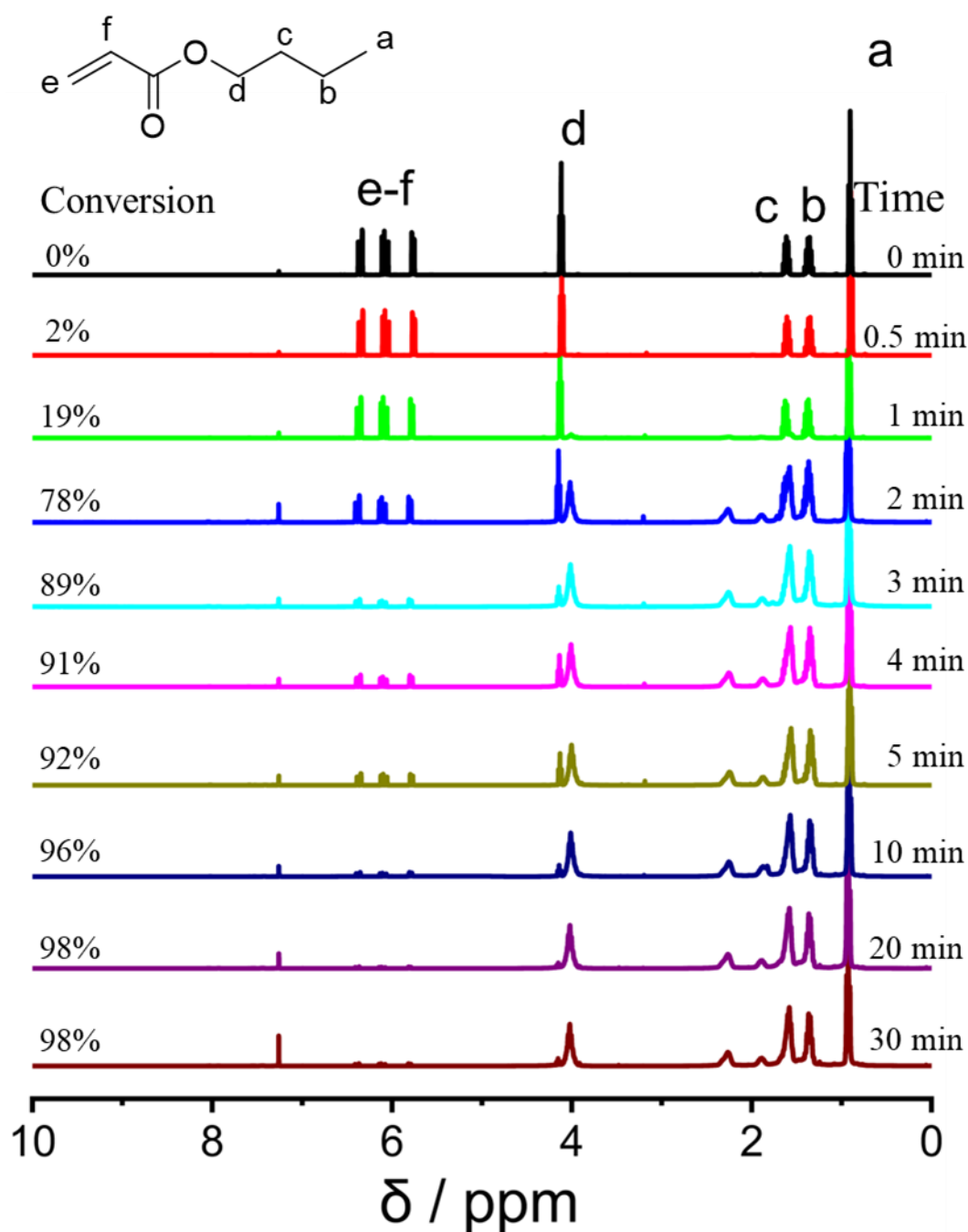
Figure S1. In situ photopolymerization kinetics of *n*BA monitored by ^{1}H NMR spectroscopy.
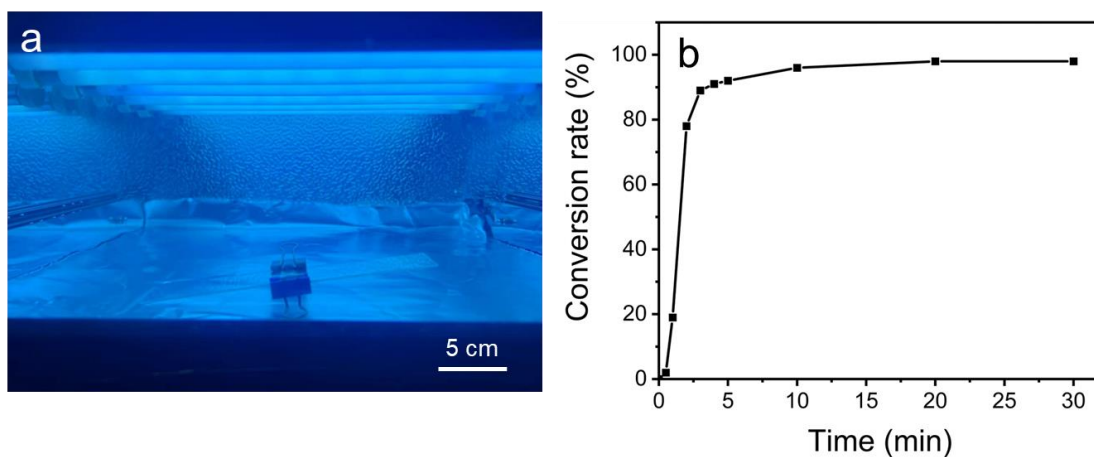
Figure S2. (a) Photo of the photopolymerization illumination setup; (b) Conversion of *n*BA at different photopolymerization time obtained from ^{1}H NMR analyses.
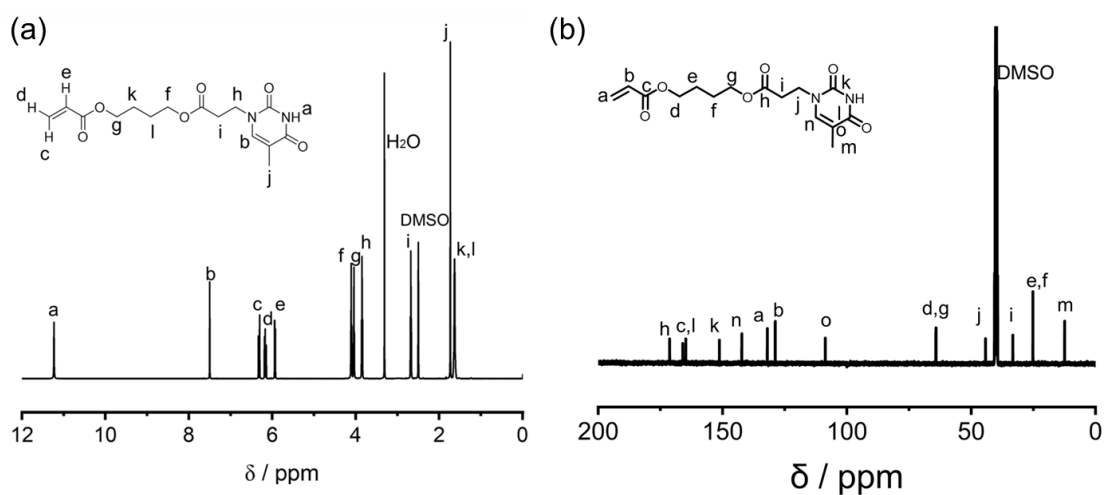
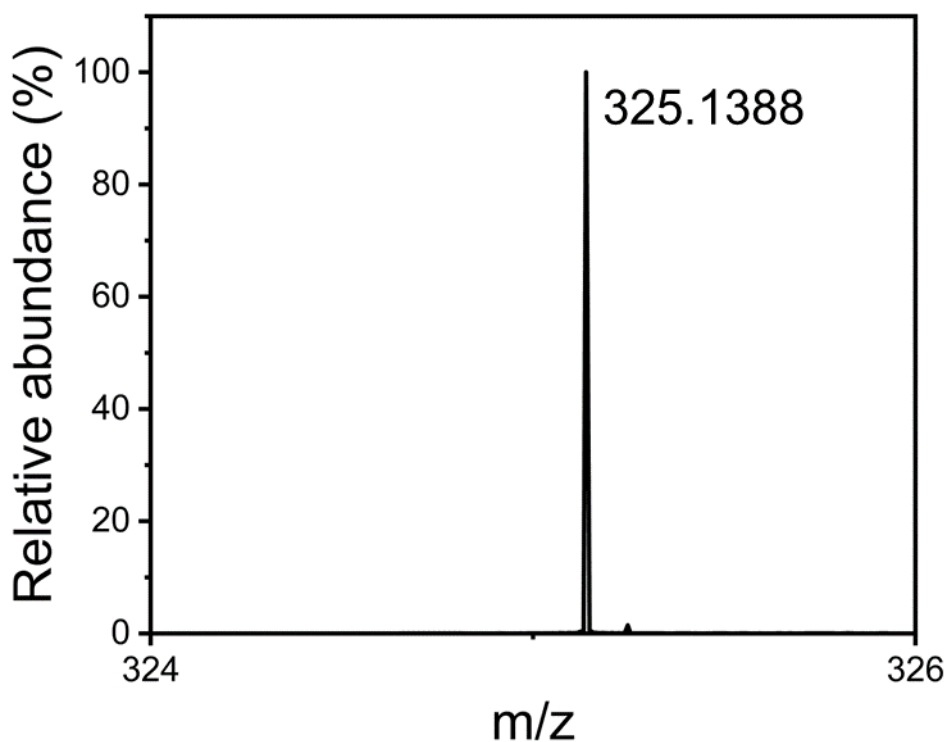**Figure S3.** Assigned (a) ^{1}H and (b) ^{13}C NMR spectra of 4-((3-(thymin-l-yl)propanoyl)oxy)butyl acrylate (TAc) in DMSO-d_6.

Figure S4. Mass spectrum of 4-((3-(thymin-1-yl)propanoyl)oxy)butyl acrylate (TAc).
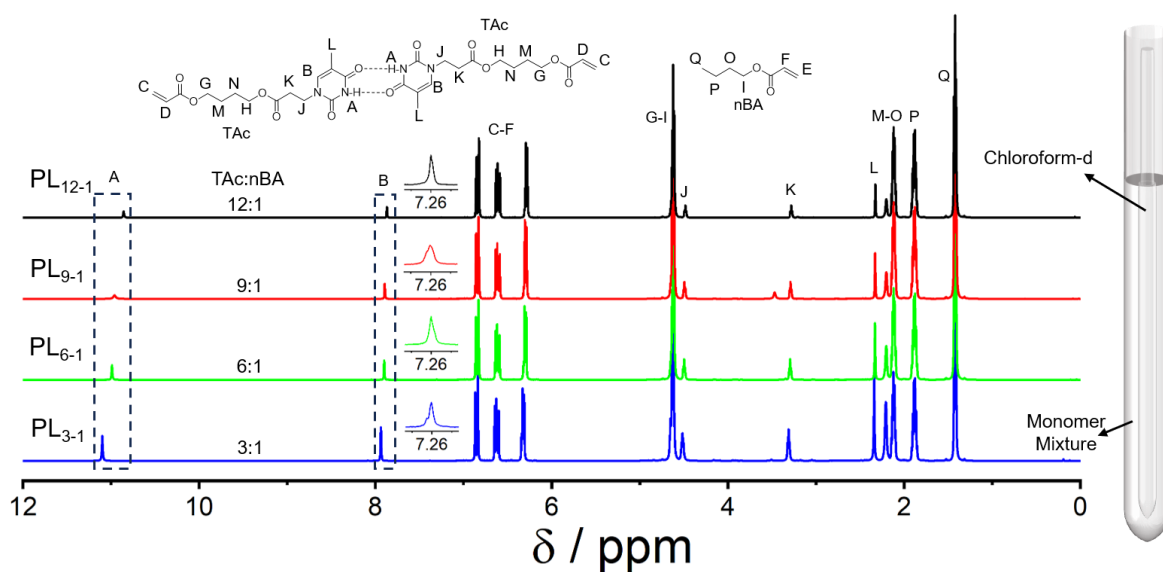
Figure S5. Full ^{1}H NMR spectra of *n*BA and TAc monomer mixtures at different molar ratios with CDCl$_3$ in the interior tube.
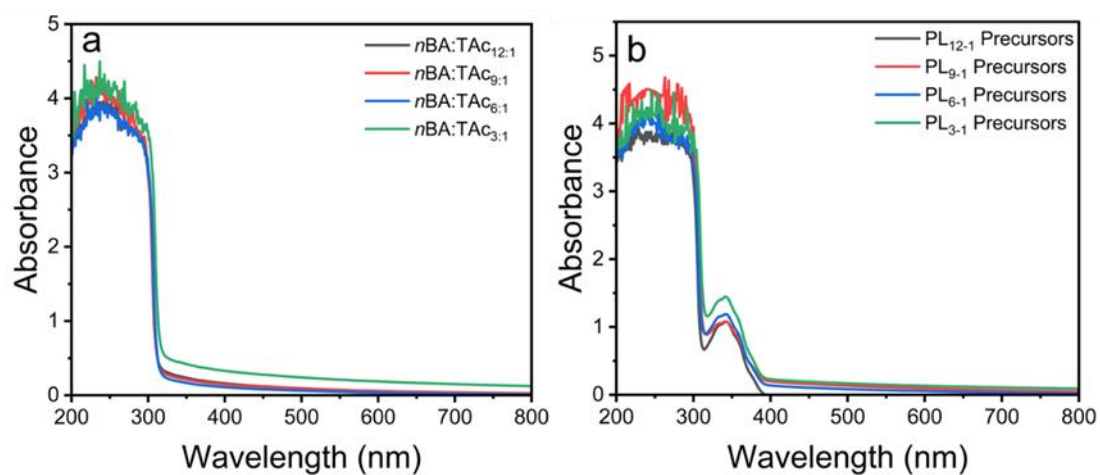
Figure S6. UV-vis spectra of the supramolecular mixtures containing different proportions of monomers (a) without and (b) with the photoinitiator.
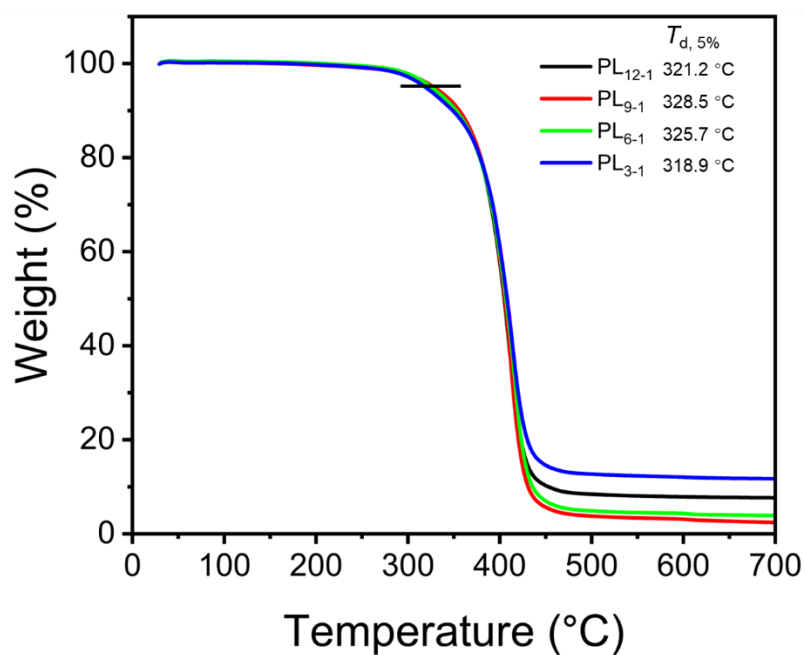
Figure S7. TGA curves of P(nBA-*co*-TAc) copolymers with different monomer compositions obtained from photopolymerization.
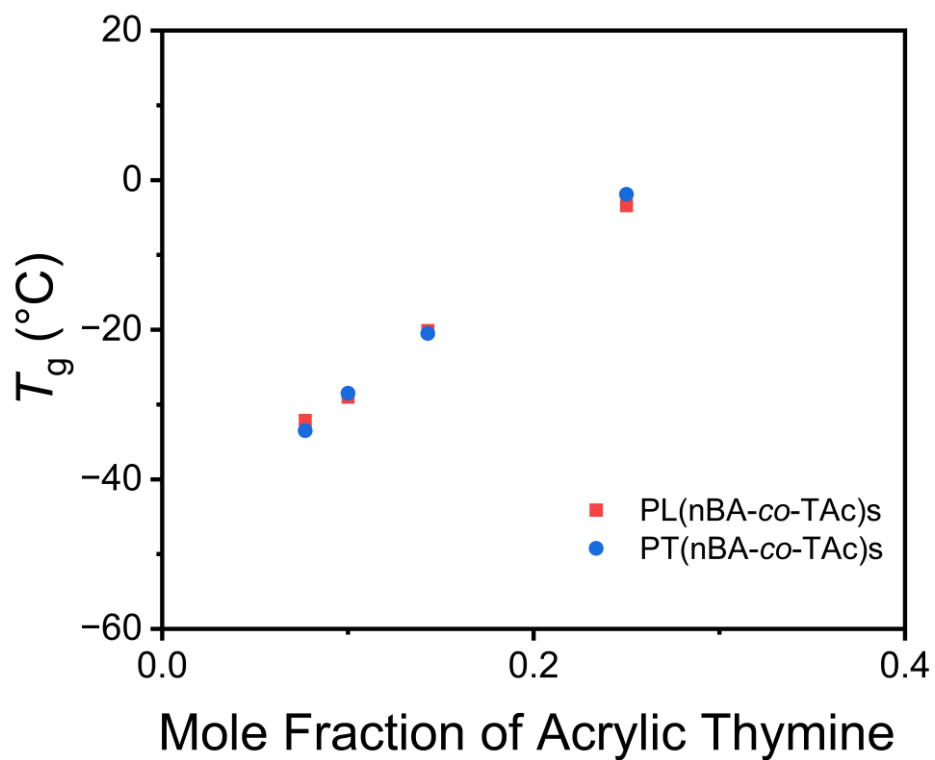
Figure S8. Relationship between acrylic thymine monomer contents and glass transition temperature (T_g) of P(nBA-co-TAc) copolymers.
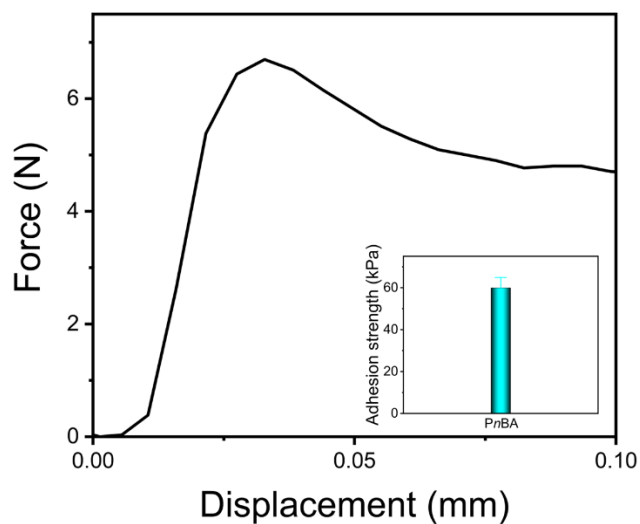
Figure S9. Shear test curve for PnBA with the inset showing the adhesion strength.
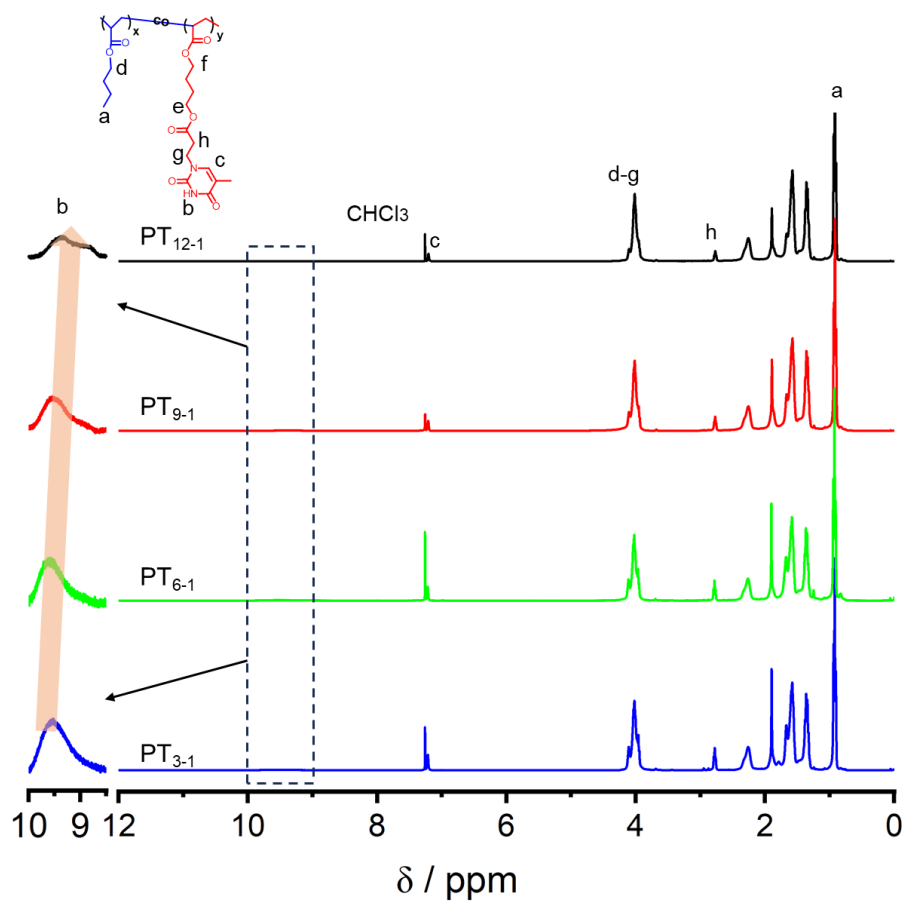
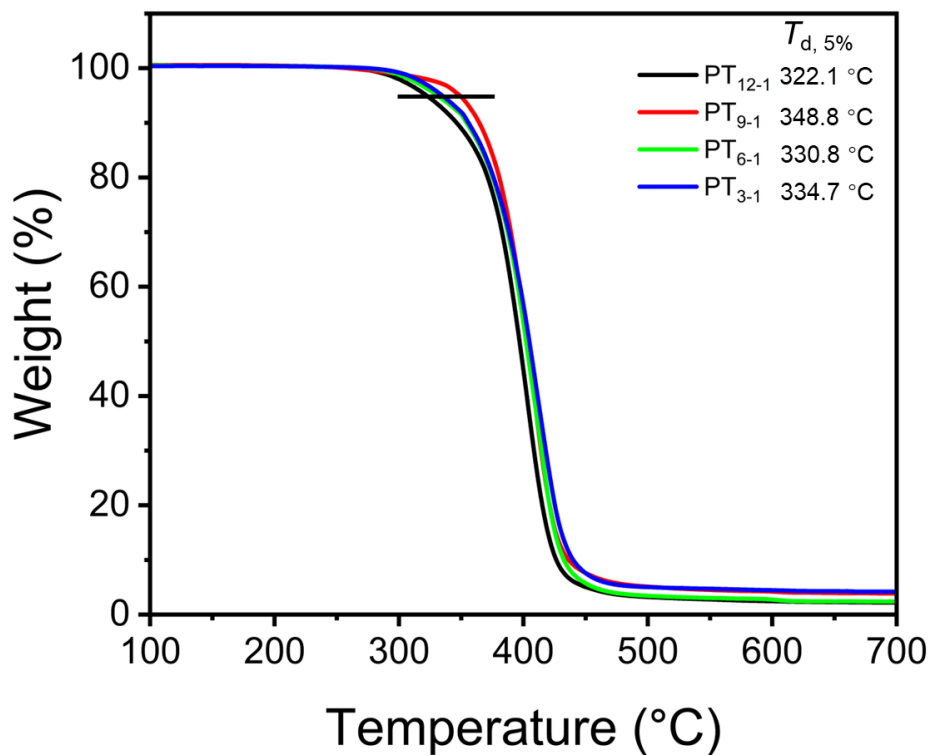**Figure S10.** ^{1}H NMR spectra of P(nBA-co-TAc) copolymers through thermal polymerization.

Figure S11. TGA curves of P(*n*BA-*co*-TAc) copolymers with different monomer compositions obtained from thermal polymerization.
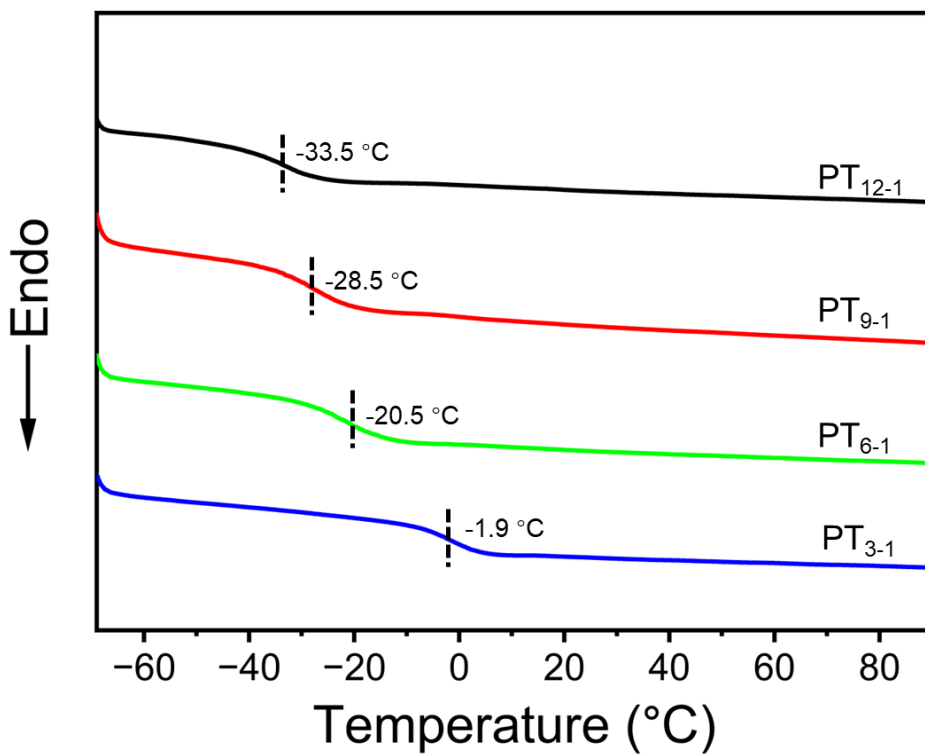

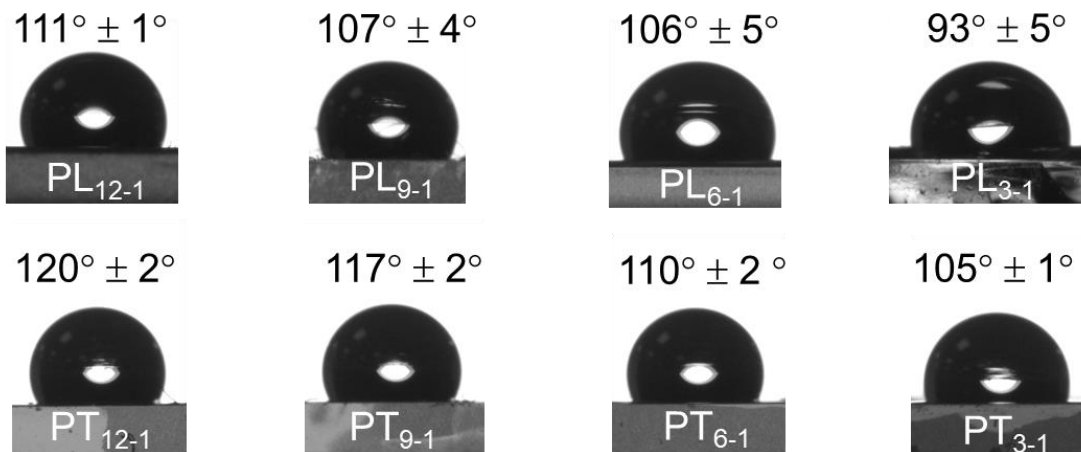**Figure S12.** DSC curves of P(*n*BA-*co*-TAc) copolymers through thermal polymerization.

Figure S13. Water contact angles (WCA) on surfaces coated with P(*n*BA-*co*-TAc) copolymers through photopolymerization or thermal polymerization.
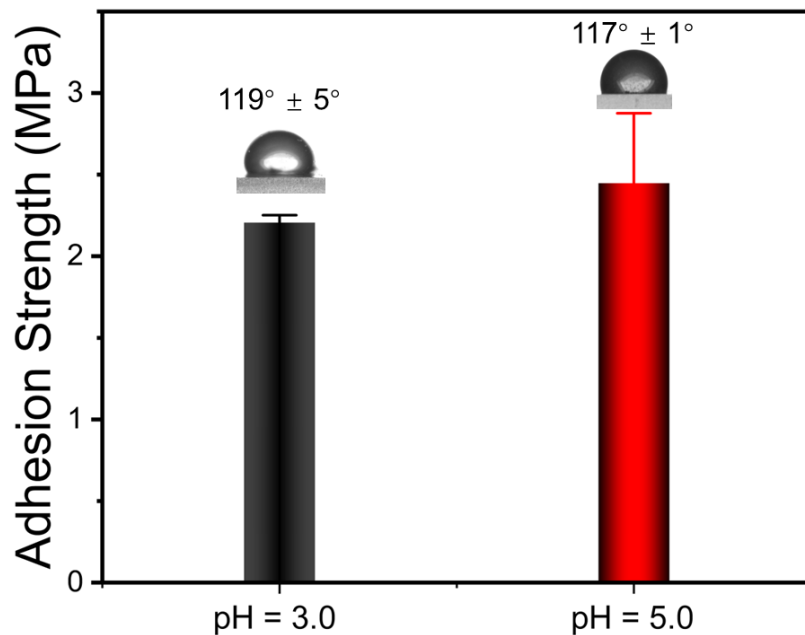

Figure S14. Adhesion strength of PL$_{3-1}$ in underwater environments at pH of 3.0 and 5.0 with the insets showing the contact angles of PL$_{3-1}$ precursors on glass.
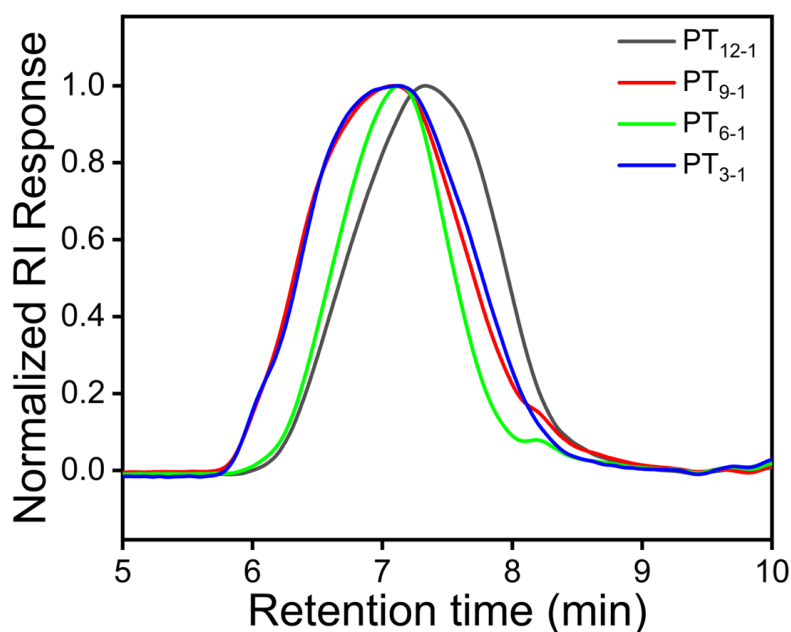
Figure S15. SEC traces of nucleobase-containing copolymers from PT_{12-1} to PT_{3-1} with DMF SEC with a flow rate of 1 mL min^{-1} at 50 °C.

Table S1. Molecular characterization data of P(nBA-co-TAc) copolymers with various nucleobase contents through thermal polymerization.

Polymer	Structure	M_n (kDa)[a]	$Đ_M$[a]	T_g (°C)[b]	$T_{d,5\%}$ (°C)[c]
PT_{12-1}	P(nBA$_{0.96}$-co-TAc$_{0.08}$)	62.2	2.92	-1.9	322.1
PT_{9-1}	P(nBA$_{0.9}$-co-TAc$_{0.1}$)	89.4	2.83	-20.5	348.8
PT_{6-1}	P(nBA$_{0.84}$-co-TAc$_{0.14}$)	95.2	3.83	-28.5	330.8
PT_{3-1}	P(nBA$_{0.75}$-co-TAc$_{0.25}$)	104.3	3.45	-33.5	334.7

[a]Determined by DMF SEC with poly(methyl methacrylate) (PMMA) standards.

[b]Measured by DSC from the second scan from −70 to 70 °C at a rate of 10 °C min^{-1}.

[c]Measured by TGA from 40 to 700 °C at a rate of 10 °C min^{-1}; the values represent the 5% degradation point of the copolymers.
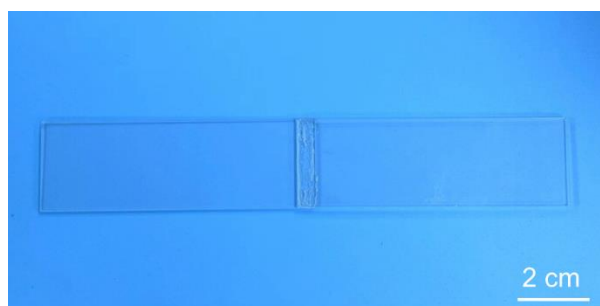
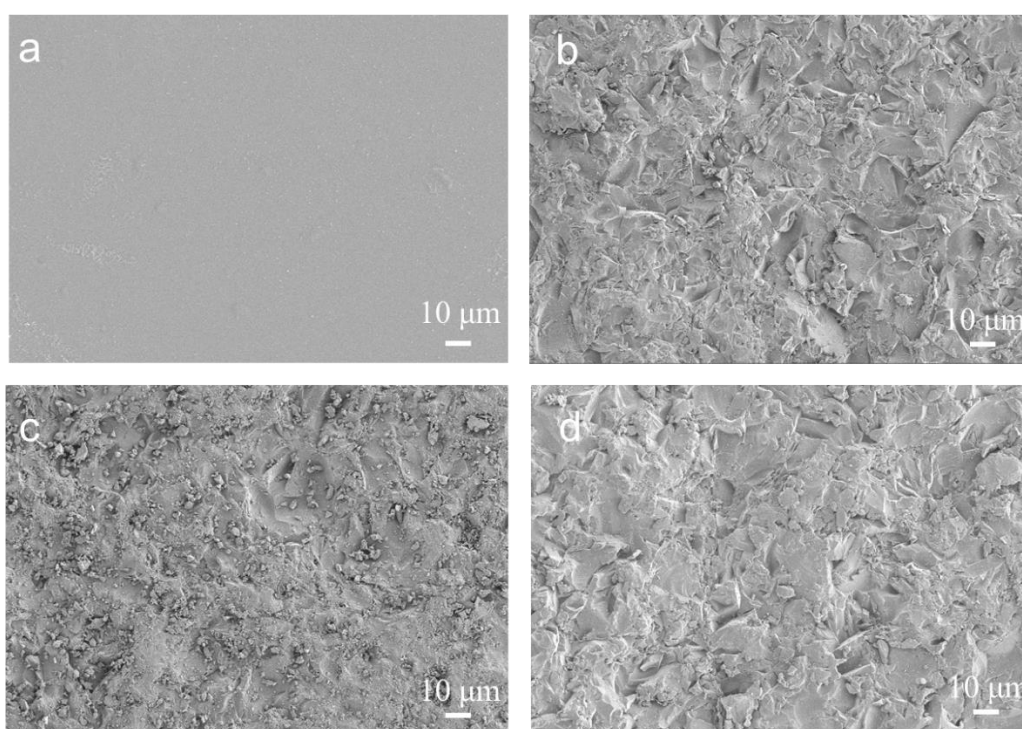**Figure S16.** Photograph of two glass slides bonded with PT$_{3\text{-}1}$.

Figure S17. SEM images of rough glass substrates with different average surface roughness (a) smooth, (b) 0.93 μm, (c) 1.06 μm, (d) 1.37 μm.
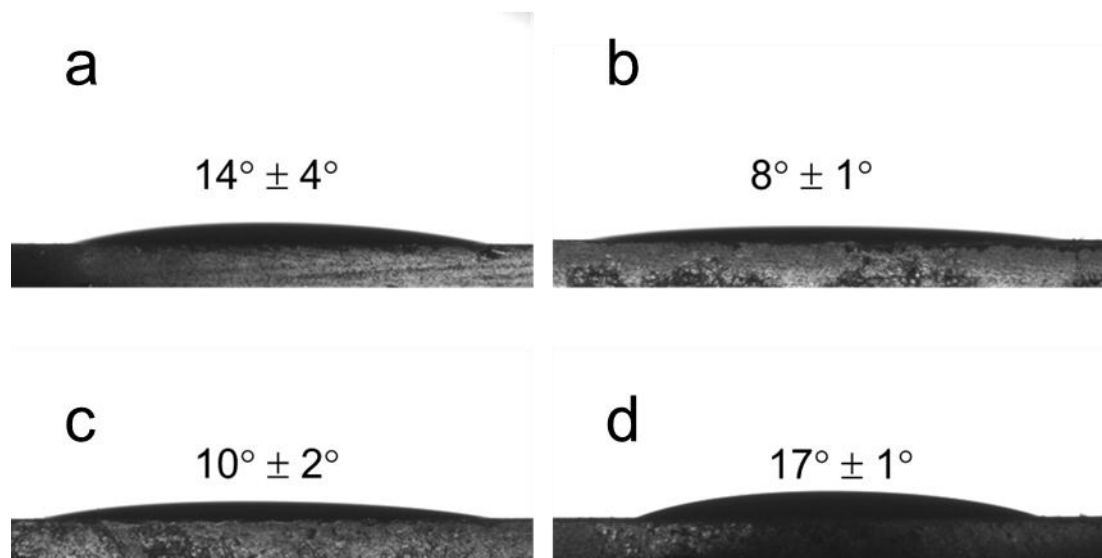
Figure S18. Contact angles of PL$_{3\text{-}1}$ precursor on rough glass substrates with different average surface roughness (a) 0.93 μm, (b) 1.06 μm, (c) 1.37 μm, (d) 1.64 μm.
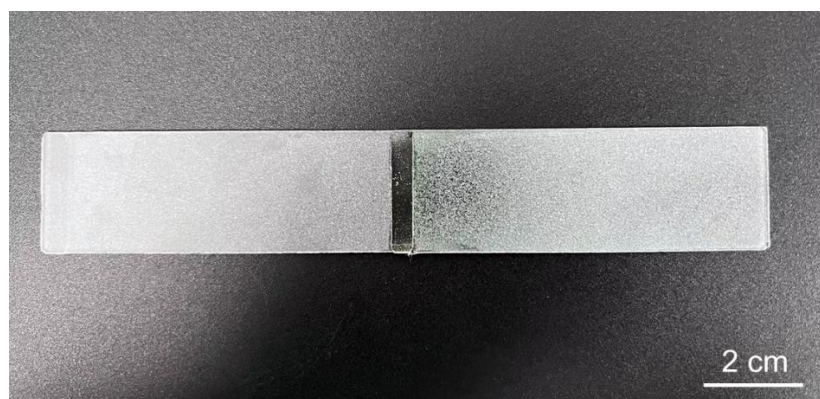

Figure S19. Photograph of two rough glass slides bonded with PL$_{3\text{-}1}$.
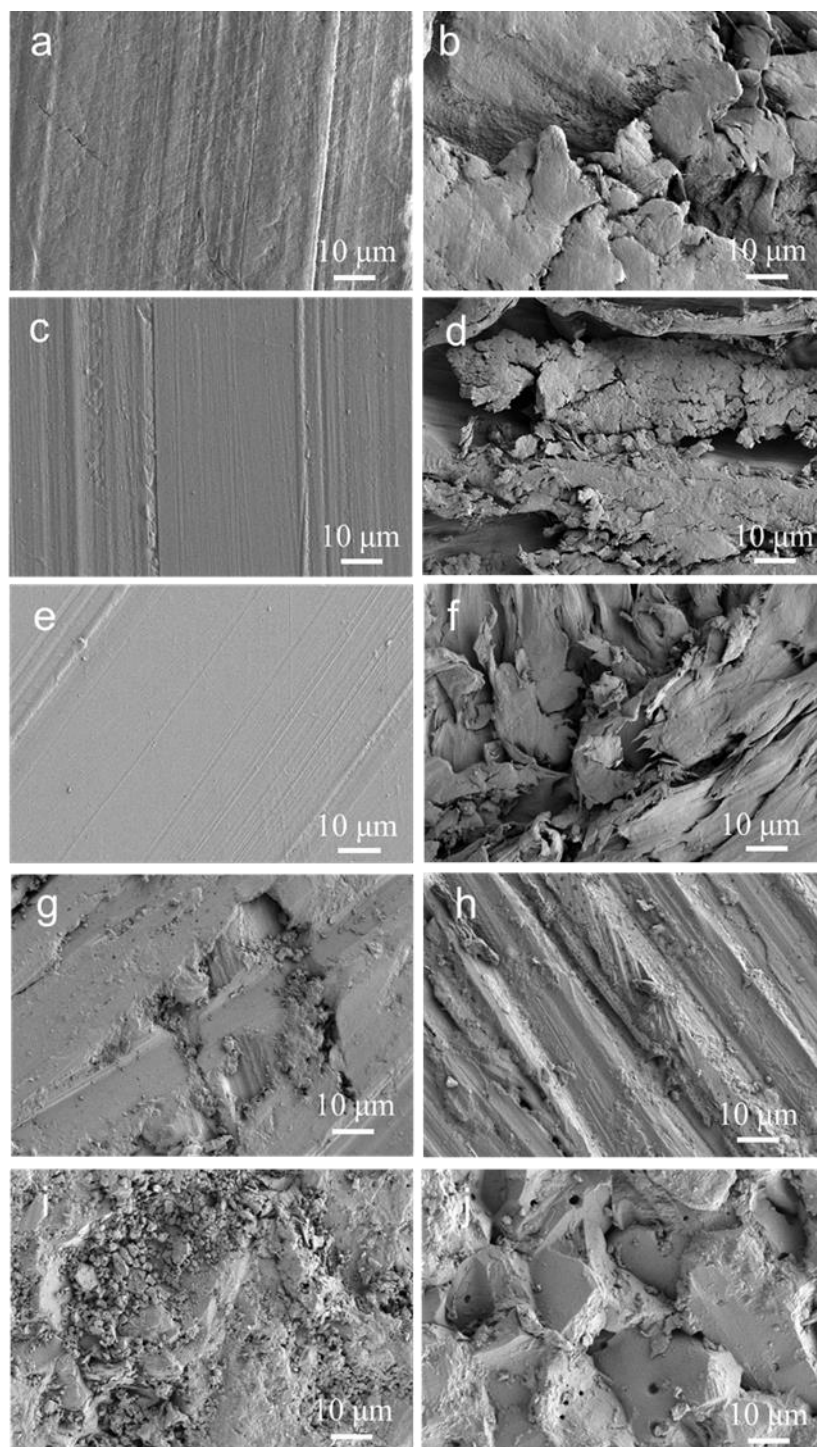
Figure S20. SEM images of distinct smooth and rough substrates. (a) smooth and (b) rough PTFE surfaces; (c) smooth and (d) rough PMMA surfaces; (e) smooth and (f) rough PET surfaces; (g) smooth and (h) rough steel surfaces; (i) smooth and (j) rough ceramics surfaces.
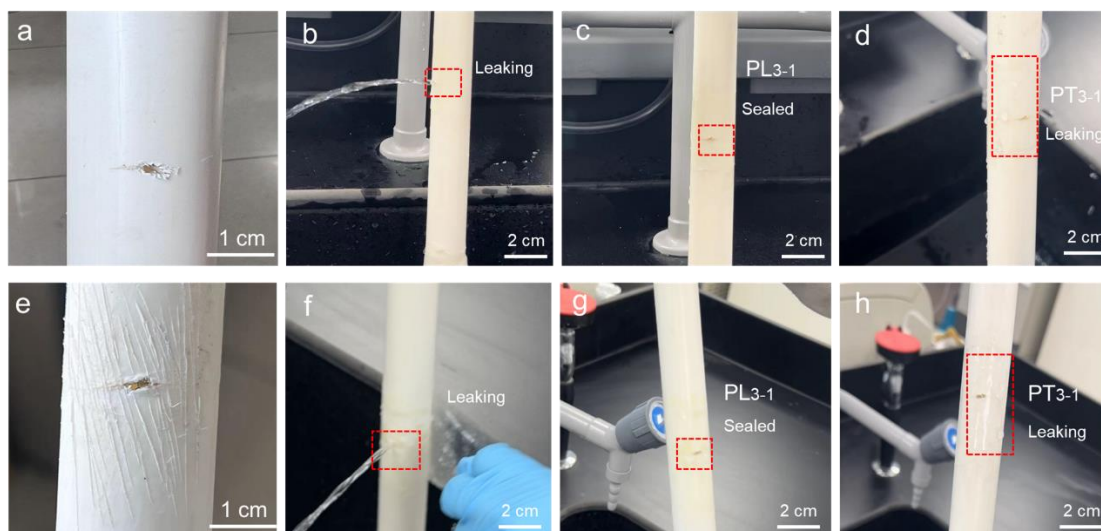
Figure S21. Demonstration of the use of PL$_{3-1}$ and PT$_{3-1}$ for *in situ* repair of a leaking water pipeline with (a-d) smooth and (e-h) rough surfaces.
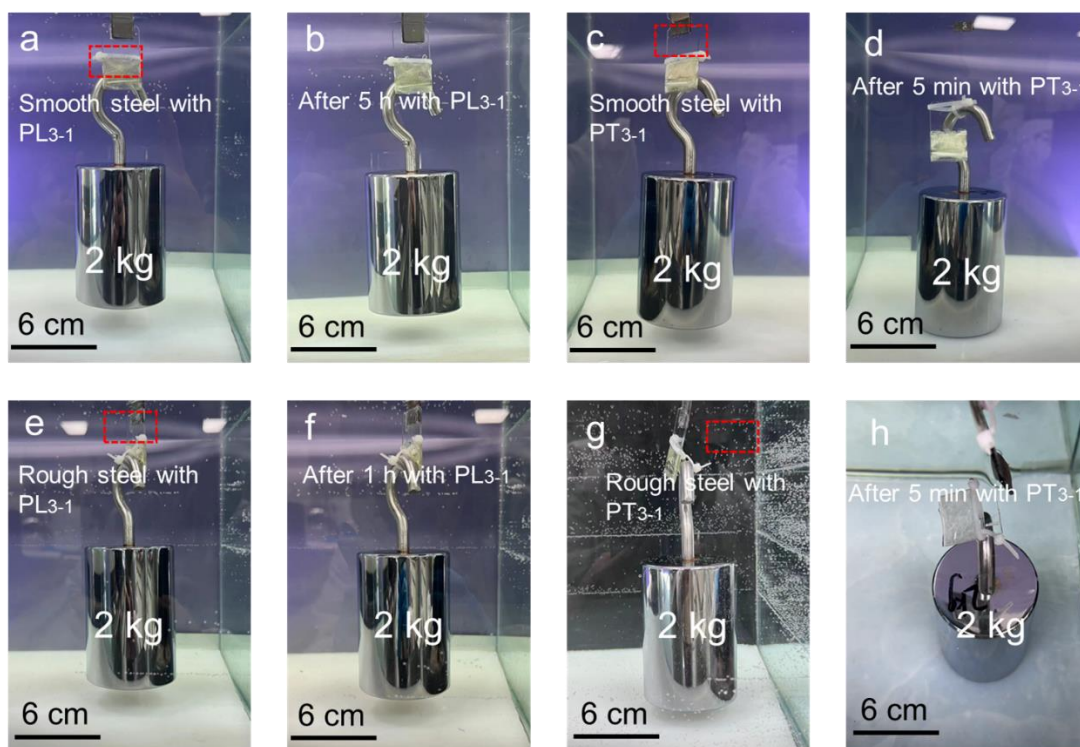

Figure S22. Photo showing that PL$_{3-1}$ and PT$_{3-1}$ bonded substrates can sustain a weight of 2 kg with (a-d) smooth and (e-h) rough surfaces.

3. References

(1) Cheng S.; Zhang M.; Dixit N.; Moore R.B.; Long T.E. Nucleobase Self-Assembly in Supramolecular Adhesives. *Macromolecules* **2012**, *45*, 805-812.

(2) Wu J.; Lei H.; Fang X.; Wang B.; Yang G.; O'Reilly R.K.; Wang Z.; Hua Z.; Liu G. Instant Strong and Responsive Underwater Adhesion Manifested by Bioinspired Supramolecular Polymeric Adhesives. *Macromolecules* **2022**, *55*, 2003-2013.