Supplementary Information for

Direct Observation of the Interplay of Catechol Binding and Polymer Hydrophobicity in a Mussel-Inspired Elastomeric Adhesive

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Experimental section

Materials

Sebacic acid (98+%), was purchased from Alfa Aesar. Deuterium oxide (D, 99.8%) was bought from Acros Organics. N,N′-Diisopropylcarbodiimide (DIC, 99.5%), was received from Chem-Impex Int’l Inc. Trifluoroacetic acid (TFA, 99%) and triisopropylsilane (TIPS, 98%) were purchased from Oakwood Chemical. Spectroscopy grade toluene and sodium periodate (99.8%) was purchased from Sigma Aldrich. Dichloromethane (Sigma-Aldrich, 99.5%) was dried by distilling over anhydrous CaH₂. Other solvents were used as it was received. Acetone-d₆ (D, 99.85%) was purchased from Cambridge Isotope Lab. Catechol (99%) was purchased from BeanTown chemical. Hydrochloric acid (37 % HCl in water, Fisher chemical) and sodium hydroxide (NaOH, 98%, VWR) were used for making solutions with different pH. 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS) and the N-functionalized diol monomers aliphatic diol (S), 3-(2,2-dimethylbenzo[d][1,3]dioxol-5-yl)-N,N-bis(2-hydroxyethyl)propenamide (D) and N,N-bis(2-hydroxyethyl)-4-((4-methyl-2-oxo-2H-chromen-7-
yl)oxy)butanamide (C) were prepared as per reported procedures with some modifications.\textsuperscript{1-3} Vinyl terminated polydimethylsiloxane (PDMS), tetrafunctional crosslinker, Platinum based catalyst were bought from Gelest Inc. PDMS sheets and lenses (Young’s modulus ~ 2 MPa) were made from these using the method defined in the literature.\textsuperscript{4} No unexpected or unusual experimental hazards were encountered during the study.

Instrumentation

\textsuperscript{1}H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. FT-IR absorption spectra of the polymers were recorded on a Shimadzu MIRacle 10 ATR-FTIR. UV-Vis absorption spectrums of the polymer films (coated over quartz) were recorded on a Shimadzu UV-1800 spectrophotometer. The molar mass ($M_{n,GPC}$) and dispersity ($D$) of the polymers were calculated using a TOSOH EcoSec HLC-8320 GPC equipped with refractive index (RI) and UV detectors. Molar masses were obtained relative to polystyrene standards ($D < 1.05$). The thermal analysis was performed on a TA Q2000 differential scanning calorimeter (DSC) with a liquid N\textsubscript{2} cooling unit at a heating/cooling rate of 10 °C/min. The water contact angles were measured by Rame-Hart instrument on a 4.3 % polymer solution (wt/wt, in toluene) spin coated silicon wafer (200-300 nm film thickness), with 9 water droplets. Rheological measurements were performed on a TA ARES-G2 rheometer with 8.0 mm stainless steel parallel plates. The crosslinked polymers were placed directly on the bottom plate which was preheated to 60 °C. Initially, a strain sweep at angular frequency of 1 rad/s was performed to find the linear viscoelastic region, from which an appropriate strain value was selected for the further sweeps. The time sweep was then carried out to evaluate the equilibrium state of the material. Later, the frequency sweep was done using a predetermined strain value in a frequency range of 0.1 to 100 rad/s at 25 °C. The rest of the instrumentations are described in their respective sections.
Scheme S1. The synthesis of protected polymer using DIC/DPTS mediated polyesterification reaction and the acetonide deprotection using trifluoroacetic acid to derive deprotected polymer.

Synthesis

Synthesis of the protected polymer

The protected polymer was synthesized using a similar procedure reported by Gokhale et al. (Scheme S1). To a 100 mL one neck round bottom flask pre-equipped with magnetic spin bar, we added aliphatic diol (S, 1021.6 mg, 2.77 mmol), coumarin diol (C, 74.64 mg, 0.21 mmol), acetonide protected catechol diol (D<sub>pr</sub>, 396.84 mg, 1.28 mmol), sebacic acid (864.8 mg, 4.27 mmol) and DPTS (503.46 mg, 1.71 mmol). The sealed round bottom flask was then connected to a Schlenk line and dried under vacuum and backfilled with dry N<sub>2</sub> alternatively for three times. 5.0 mL of dry DCM was then added to the reaction vessel under N<sub>2</sub>. After 20 min of homogenization at room temperature, the reaction vessel was kept under ice-water bath. DIC (2.70 mL, 17.10 mmol) was added dropwise and allowed to react for 48 h. Upon completion of the reaction period, DCM (~ 50 mL) was added to the mixture and kept at -10 °C overnight. The urea formed during polymerization was then filtered and the concentrated reaction mixture was
precipitated from DCM in cold methanol for 5 times. The obtained light-yellow liquid polymer was then dried under high vacuum for 24 h. The purified polymer (protected polymer) was then characterized by GPC, DSC (Table S1), $^1$H NMR (Figure S1A) and FT-IR spectroscopy (Figure S2).

Acetonide deprotection

A two-neck round bottom flask equipped with addition funnel was connected to Schlenk line and dried using three vacuum-N$_2$ alternate cycles. Protected polymer (500 mg) was dissolved in dry DCM (10 mL) and added to the reaction vessel and the solution was bubbled with N$_2$ for 15 min. The solution was then cooled to -15 °C (ice-methanol bath) and TFA (5 mL) and TIPS (100 µL) were added slowly using the addition funnel, sequentially. Half an hour after adding the reagents, the reaction mixture was warmed to room temperature and reacted for 2 h. The reaction was quenched using slow addition of methanol and the volatiles were removed under reduced pressure. The concentrated solution was then precipitated from DCM to methanol three times. The obtained yellow liquid, deprotected polymer, was then dried under high vacuum for 24 h and characterized using DSC (Table S1), $^1$H NMR (Figure S1B) and FT-IR spectroscopy (Figure S2).

Table S1. The calculated monomer ratios, molar masses ($M_{n,GPC}$ obtained from GPC and $M_{n,\text{theo}}$ theoretically calculated), dispersity ($D$), glass transition temperature ($T_g$) and static water contact angle of the protected and deprotected polymers.

| Polymer    | S:C:D$_{pr}$/D | $M_{n,GPC/\text{theo}}$ ($D$)$^a$ | $T_g$ (°C) | Static contact angle (°) |
|------------|----------------|----------------------------------|------------|--------------------------|
| protected  | 63:5:32        | 11.3 kDa ($1.6$)                 | -47        | 96 ± 2                   |
| deprotected| 63:5:32        | 11.1 kDa ($1.6$)                 | -43        | 99 ± 1                   |

$^a$protected polymer molar mass was obtained from GPC and the deprotected polymer molar mass was calculated theoretically by deducting the protection group molar mass from $M_{n,GPC}$ of protected polymer
Characterization

**Figure S1.** $^1$H NMR of the (A) protected and (B) deprotected polymers in acetone-$d_6$. The integers in blue and red are chemical shifts of the protons and integral values, respectively. The molecular composition of the polymer was found from the ratio of characteristic chemical shift integration of the corresponding monomers. For example, in (A) the integration ratio of peaks 8:14:10 normalized to respective number of protons is 0.63:0.32:0.05, which is the ratio of S:C:D$_{pr}$. The deprotection of acetonide group is proven by the disappearance of acetonide (11, –(CH$_3$)$_2$) at 1.63 ppm. When the integration values from 1.51 to 1.71 ppm of (A) and (B) are compared,
there is a loss of ~ 6 proton, which is due to the loss of two methyl groups whereas other integral values across the $^1$H NMR spectra remain similar.

Figure S2. FT-IR absorption spectra of the \textbf{protected} (green) and \textbf{deprotected} (red) polymers. Disappearance of acetonide $-\text{(CH}_3\text{)}$ bend signal at 1498 cm$^-1$, and appearance of broad band from catechol O-H at 3100-3650 cm$^-1$ in the \textbf{deprotected} polymer FT-IR absorption spectrum.
**Figure S3.** The storage ($G'$) and loss ($G''$) moduli response to the increase of angular frequency of the **protected** and **deprotected** polymers at 25 °C.

**Adhesion Measurements**

A home built JKR system was used to measure the adhesion force between glass lens and flat substrate as shown in **Figure 3A**. A hemispherical glass lens (2.5 mm diameter; Changchun worldhawk optoelectronics co. ltd) is mounted on the zigzag arm attached to 1 N load cell (Futek, LSB) connected to the XY translating stage. The substrate is mounted on the plate that has controlled movement in Z-direction controlled by high-resolution picometer® motor. For underwater measurements, the substrate is placed in a small container filled with water (Millipore, pH = 6.5) and the lens is brought in contact from top. For the adhesion measurements in different pH solution, HCl (for acidic) and NaOH (for basic) were diluted with Millipore water to obtain solutions with pH 3 and 9. Prior to measurements, all the glass wares were cleaned by soaking them in a base bath followed by thorough rinsing with water and drying at higher temperature overnight and an air-plasma treatment for 5 min.

The substrates were prepared by coating the polymers on PDMS elastomer. To prepare the film, a 40 μL of the polymer solution (4.3 % w/w in toluene) was drop casted over a corona treated PDMS elastomer of ~ 70 mm$^2$ area. After allowing the toluene to evaporate at room temperature, the films were kept under vacuum for 12 h (theoretical thickness of polymer coating ~ 20 μm). The dried polymer films were then crosslinked under Dymax UV lamp (λ ~ 340 - 420 nm, intensity at the substrate 50 mW/cm$^2$) for 10 min. The homogeneity of films was ensured by fluorescence microscopy (**Figure 2A**) and the presence of polymers on the surface of PDMS was characterized using ATR/FT-IR spectroscopy (**Figure 2C**).
Pull-off force measurement

For adhesion measurements, the loading and unloading were done at a rate of ~ 0.4 μm/sec and the system was given an equilibration time of 3 min before unloading. A typical plot for loading and unloading is shown in Figure 3B. Force value become negative when the lens is in contact with the film and after reaching a preload of ~ 1 mN, the system is left for equilibration. Since the substrate is adhesive in nature, the force values become positive and later the lens detaches from the surface. The maximum force required to separate these surfaces apart is recorded as the pull-off force \( F \), which is then used to calculate the theoretical work of adhesion \( W \) using JKR model, \( W = F/(1.5 \times \pi \times R) \) where \( R \) is the radius of the glass lens.
Figure S4. Pull-off forces in wet environment for protected and deprotected polymer films loaded to 1 mN force and unloaded at a rate of 0.4 μm/s at (A) different pH after 3 min equilibration time and after the periodate treatment of the films at pH 6.5. (B) different equilibration time at pH 6.5 along with the dry adhesion. (C) Pull-off forces of the PDMS sheet in dry and wet conditions. The data represented here is in terms of mean ± standard deviation (SD) and ‘*’ represents the statistical significance among the samples using Tukey mean comparison test (p < 0.05). Error bars (SD) are evaluated from at least 3 readings for each condition.
Mode of failure

Figure S5 show the area of contact during unloading in the dry condition. For protected elastomer, we see that the area of the contact remained circular as the lens is being retracted. However, in case of deprotected elastomer, we see the distortion in the shape of the contact region with some circular imprint left on the region where lens was in contact with the film before. In case of wet condition, because of poor contrast between glass and water, we cannot comment on the mode of failure.

Figure S5. The microscopic images of the change in area of contact during the unloading (L-R) of glass lens from deprotected (top) and protected (bottom) elastomers in dry conditions. The cohesive failure of the deprotected elastomer (circular imprint other than the contact area) can be observed during their unloading in dry condition.
Pull-off force measurements on a sapphire plate

Due to the inadequate control over polymer coating thickness on the curvature of PDMS lens and unavailability of sapphire lens, the adhesion and SFG measurements were carried out on polymer contacts against glass sheets and sapphire prisms, respectively. To check the possible variations in the results due this substrate difference, we performed adhesion measurements of the polymer coated PDMS lens to sapphire sheets in dry and wet environment. PDMS lens of radius ~ 1.1 mm was coated with ~ 10 \( \mu \text{L} \) of polymer solution (4.3 % wt/wt, in toluene) and was dried overnight. The polymer coated lenses were then crosslinked using photoirradiation and the pull-off force measurements were done as described before.

![Figure S6](image)

**Figure S6.** The work of adhesion in dry and wet environment for *protected* and *deprotected* polymer coated PDMS lenses with sapphire substrate loaded to 1 mN force and unloaded at 0.4 \( \mu \text{m/s} \) rate after equilibrating for 3 min. The trend in adhesion strength is identical to the previous geometry using a glass lens against a polymer film. Higher adhesion was observed for *deprotected* polymer in dry and wet environments, and reduced adhesion was observed underwater for both polymers.
**Sum frequency generation (SFG) spectroscopy**

SFG is a surface specific non-linear optical technique which can be used to obtain information about the molecular groups present at the interface and their orientation. According to dipole approximation, the signal is generated when there is a breakdown in centrosymmetry of the system, which generally happens at the interface that is surrounded by two centrosymmetric media. When two beams of different frequencies are overlapped spatially and temporally at the interface, they generate the third beam of frequency (SFG), which is sum of the frequencies of incident beams. To probe the molecular groups at the interface, generally tunable infrared (IR) is overlapped with the visible beam and the SFG intensity is enhanced when the IR frequency match with the molecular vibration energy of the functional groups. To obtain detailed information about the orientation of the molecular groups present at the interface, different polarization combinations of the three beams are used. The SFG intensity is proportional to the number of molecular groups present at the interface and their orientation.

Polymer coated PDMS lenses were made by drop casting the 10 µL polymer solution (same solution used for adhesion measurements) on the corona treated PDMS lens and then dried under vacuum for overnight. Later, the polymer coating was crosslinked using photoirradiation. Depending upon the experiment, these lenses were brought into contact with the sapphire prisms in dry or wet (D₂O) environment using a plunger system whose design is discussed in detail elsewhere.⁵

SFG spectra were collected at room temperature using a picosecond Spectra Physics laser system with a tunable IR beam (2000 - 3800 cm⁻¹, 1 ps pulse width, 1 KHz repetition rate) and an 800 nm wavelength visible beam (1 ps pulse width, 1 KHz repetition rate). The spot area where the beams are overlapped is approximated to be ~ 0.2 mm². The spectra were collected in both
SSP and PPP polarization combinations. The resulting spectra were fitted according to Lorentzian fitting equation:

\[
\text{Intensity (SFG)} = \left| x_{\text{eff}, NR} + \sum A_q e^{i\phi} \right|
\]

(2)

where \(x_{\text{eff}, NR}\) is the non-resonant signal, \(A_q\) is the amplitude of the molecular vibration, \(\tau_q\) is the damping constant and \(\omega_q\) is the angular frequency.

SFG spectra were collected in SSP and PPP polarizations (polarization combination for three beams SFG, visible and IR, respectively). Depending upon the polarization, the molecular groups orientation information can be obtained.6-7

**PPP spectra of wet polymer sapphire contact**

![Figure S7](image)

Figure S7. SFG spectra (PPP polarization) of the **protected** and **deprotected** polymers in contact with the sapphire under wet (D2O) condition. (A) SFG spectra of **protected** polymer, and **deprotected** polymer in contact with the sapphire in wet (D2O) conditions in the O-D stretch region. Features in region from 2200 - 2800 cm\(^{-1}\) indicate the presence of D2O in the contact region. (B) Spectra were collected in two regions 2700 - 3200 cm\(^{-1}\) and 3100 - 3800 cm\(^{-1}\) separately and overlapped later. These spectra show the hydrocarbon signature from the polymer and sapphire hydroxyl groups.
First moment peak analysis

In addition to Lorentzian peak fitting, the region between 3300 - 3800 cm\(^{-1}\) were also analyzed using first moment analysis method. The sapphire O-H peak shift (\(\omega\)) for the dry contact was also calculated using the following equation where \(I_i\) is the SFG intensity at frequency \(\omega_i\).

\[
\omega = \frac{\sum I_i \cdot \omega_i}{\sum I_i}
\]  

The shifted peak for the protected and deprotected polymers obtained by this method was similar in position with the peaks obtained by Lorentzian fit using equation 2. We did not find any significant difference in the peak shift for both the polymers.

Molecular adsorption of catechol-d\(_2\)

The deuterated catechol was prepared by reacting catechol with degassed D\(_2\)O (0.01 % w/w) in a vial stirred on a hot plate at 25 °C for 72 h. The excess D\(_2\)O was then removed under high vacuum for 24 h to obtain a white powder, catechol-d\(_2\) (> 60%, D).

The catechol-d\(_2\) solution (0.07 M, in chloroform-d) was exposed to a sapphire prism in a closed chamber for SFG measurements. SFG spectra were collected for pure chloroform-d and the solution of catechol-d\(_2\) in chloroform-d. Catechol solution showed peak at ~ 3070 cm\(^{-1}\) corresponding to aromatic C-H vibration. There are two distributions of -OH groups in the spectrum recorded for the solution of catechol-d\(_2\) in CHCl\(_3\)-d one corresponding to the chloroform interacting with sapphire -OH and the other represents the interaction of catechol to sapphire. Since the distribution of chloroform interacting with sapphire -OH does not change its peak position in the presence of catechol in comparison to the spectrum recorded for only chloroform, we do not
expect changes of catechol interacting with sapphire to be significantly different across the solution and polymer form. The interaction of catechol with sapphire O-H causes the shift of O-H to ~ 3590 ± 2 cm\(^{-1}\) which corresponds to an adhesion energy of 5.5 ± 0.2 kJ/(mole of O-H groups). Assuming 9 O-H groups per nm\(^2\) for a sapphire surface and all O-H are interacting with catechol, the interaction strength for the catechol can contribute to 0.8 J/m\(^2\) adhesion energy.

**Figure S8.** SFG spectra in SSP polarization for chloroform-\(d\) and solution of catechol-\(d_2\) in chloroform-\(d\) showing the interaction of catechol with sapphire causes the shift of sapphire O-H peak to ~ 3590 cm\(^{-1}\).

**Effective bulk modulus measurement**

To find the effective bulk modulus, a glass lens was brought in contact with the polymer film at the slowest rate possible using the JKR instrumentation (0.04 μm/s). Loading was done in a step-wise manner and the sample was equilibrated for 1 min at each step. The area of contact as a function of load was determined from the pictures taken using an optical microscope. Details of this method are mentioned elsewhere.\(^5\) After loading the sample to ~ 1 mN, the lens is then retracted back at the similar rate of approach and the areas were recorded at predetermined forces.
Both the polymers showed similar behavior during loading and the effective bulk modulus \( K \) of the substrates were calculated using the following JKR equation:

\[
a^3 = \frac{R}{K} \left[ P + 3\pi RG + \sqrt{6\pi RGP + (3\pi RG)^2} \right]
\]  \( (1) \)

where \( a \) is the radius of contact area, \( R \) is the radius of lens, \( P \) is the load value and \( G \) is the strain energy release rate. The \( K \) values were similar for both polymers (~ 1.9 MPa for **protected** polymer and ~ 1.5 MPa for **deprotected** polymer).

![Contact area vs load plot](image)

**Figure S9.** The contact area vs load plot of **protected** and **deprotected** polymers during loading and unloading of the sample at a rate of 0.04 \( \mu \text{m/s} \).

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