Polydopamine (PDA) is a complex biomimetic material exhibiting advantageous properties of both melanin polymers and biological adhesives. These concomitant features have prompted an increasing interest in exploiting PDA for bioelectronics, smart coatings, and functional membranes. The ability to apply the rich biochemistry of melanins in structurally durable contexts will help accelerate their practical implementation and the design of next-generation materials. Here, this paper presents approaches for manipulating the adhesion and cohesive mechanics of PDA nanomembranes. Visual recording of PDA film delamination from SiO$_2$ substrates reveals accelerated delamination (spanning orders of magnitude from 12 h to 1 min) with increasing pH and monovalent salt concentration. Delamination is retarded for films synthesized from higher dopamine concentrations, and it is completely prevented in the presence of Ca$^{2+}$. Delaminated nanomembranes exhibit orientation-dependent underwater adhesion to polydimethylsiloxane elastomer. Elastic moduli of PDA nanomembranes are quantified by compressive thin film buckling, and the measured value of 2.0 $\pm$ 0.9 GPa supports compositional simulations of PDA. Crosslinking of primary amines within the nanomembranes by genipin is successful in increasing the modulus to 7.9 $\pm$ 2.5 GPa. These results demonstrate that the adhesive stability and elastic modulus of PDA films/nanomembranes can be controlled by synthesis and postprocessing techniques.

The catechol and amine-rich composition of adhesive mussel-foot proteins has inspired the rapid development of catecholamine coatings in the past decade.$^{[1,2]}$ Oxidative polymerization of dopamine, norepinephrine, and other catecholamines in aqueous solutions deposits conformal nanometer-scale coatings on the surfaces of many materials.$^{[1-7]}$ Catechol, quinone, and amine moieties within the films serve as anchoring points for biomolecules,$^{[8]}$ metals,$^{[9,9]}$ minerals,$^{[10]}$ or polymers.$^{[11]}$ Certain functionalities can also be included intrinsically during precursor synthesis.$^{[12,13]}$ The surface properties of numerous materials can therefore be extensively modified and functionalized via catecholamine coatings with broad prospective applications in biomaterials,$^{[14]}$ energy storage,$^{[15]}$ water purification,$^{[16-18]}$ and antifouling coatings.$^{[19,20]}$

The versatile and relatively strong underwater adhesion of catechols has been established in numerous contexts. Empirical and theoretical investigations of catechol–surface interactions have demonstrated the importance of the unoxidized, bidentate catechol moiety in forming interfacial hydrogen bonds and metal-coordination bonds in a substrate-dependent manner.$^{[21-25]}$ Primary amines also cooperate in catecholamine adhesion by displacing hydrated surface salts allowing for close approach of nearby catechol groups.$^{[26,27]}$ A more comprehensive understanding of these two adhesive mechanisms in bulk catecholamine coatings would help accelerate their practical implementation and the design of next-generation materials.

In addition to their adhesive properties, understanding the microstructure and internal cohesion of catecholamine films is important for ensuring intrinsic mechanical stability. The most commonly used catecholamine film polydopamine (PDA) is not an extended polymer in the traditional sense but likely rather a mixture of small oligomers whose bulk aggregation is sensitive to synthesis conditions.$^{[28-32]}$ Computational modeling of PDA has been successful in reproducing fundamental physical parameters of the bulk material, and has also revealed the positive role of interunit bonding in increasing the elastic modulus of PDA.$^{[33,34]}$ Increasing the internal cohesion and robustness of PDA films could improve their long-term performance in mechanically agitated environments$^{[34-37]}$ such as in the human body$^{[14]}$ or flowing liquids.$^{[16,17]}$ Here we report delamination mechanisms and cohesive properties in synthetic PDA nanomembranes. The preparation of nanomembranes from surface-deposited films, in contrast to films formed at the...
air–liquid interface, provides a new avenue for directly characterizing catecholamine surface coatings. Strategies for the synthesis and postprocessing conditions of PDA nanomembranes as a function of salt valency and chemical crosslinking are highlighted. These techniques are used to generate free standing PDA nanomembranes, the mechanical properties of which can be interrogated using a metrology technique based on thin film buckling. To further understand the structure and mechanical properties of PDA films, we performed density functional theory (DFT) calculations with van der Waals correlation on stacked dimers containing the most likely functional units among those compiled by Liebscher et al.

The adhesive stability of PDA films was characterized by their time to delamination in static basic salt solutions (Figure 1a,b). Concentrated aqueous solutions of NaOH are known to remove PDA from various substrates. We separated the concomitant variables of pH and metal salt concentration using an organic amine buffer and independent addition of metal salts. Macroscopic delamination was inferred by gross light scattering at the deformed interfaces that originate due to loss of conformal contact between the PDA film and the SiO₂ substrate (Figure 1b; Figures S1 and S2, Supporting Information). Two types of delamination centers were observed: large interfacial defects (edges and scratches; labeled by arrows 1 and 2 in Figure 1b) and points in the bulk of the film (arrow 3). A typical delamination process results in radial propagation from each origin, eventually leading to delamination and formation of a free-standing PDA nanomembrane with morphologically distinguishable basal and apical sides (Figure 1c,d).

Delamination of conformal PDA films is accelerated by solutions containing group I cations (Figure 2a), requiring $t > 12$ h for complete delamination in the absence of NaCl to $t = 1$ min in $200 \times 10^{-3}$ M NaCl (pH = 10). This phenomenon may be explained in light of the catecholate adhesion mode to SiO₂. Simulations of catechol interaction with silica surfaces showed direct hydrogen bonding between the catecholic hydroxyls and silica surfaces underwater. Metal cations such as sodium may competitively adsorb to the silica surface and disrupt interfacial hydrogen bonds. Raising the pH of the NaCl solution from pH = 9 to 10 deprotonates catechols thereby compromising bidentate hydrogen bonding and accelerating film delamination (Figure 2b). In support of this observation, increasing the pH of PDA precursor solutions inhibits PDA deposition on SiO₂.

The cooperative adhesive action of primary amines in the PDA film is supported by the slower delamination of films that had been synthesized from more highly concentrated precursor solutions (Figure 2c). PDA films prepared from low aqueous concentrations of dopamine (e.g., $0.5 \times 10^{-3}$ M dopamine) contain lower concentrations of primary amines compared to PDA films synthesized from highly concentrated solutions (e.g., $10 \times 10^{-3}$ M dopamine). A higher concentration of primary amines in PDA films may inhibit metal cation adsorption at the SiO₂ interface via a similar mechanism to that observed for catecholamine adsorption to mica. Characteristic delamination rates were independent of PDA film thickness (Figure 2d). This observation is attributed to structural defects in the film (Figure 1b) and the persistence of

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**Figure 1.** a) Schematic of polydopamine (PDA) film delamination process in alkaline monovalent salt solutions (right) or with the addition of multivalent cations (left). b) Time lapse of PDA film delamination in $200 \times 10^{-3}$ M NaCl + $50 \times 10^{-3}$ M tris(hydroxymethyl) aminomethane (Tris) buffer at pH = 9.5. Arrows indicate delamination centers. c) Image of a delaminated PDA nanomembrane ($h = 59 \pm 4$ nm) along with a SiO₂ wafer from which the PDA film had been delaminated. d) Atomic force microscopy (AFM) images of the two surfaces of the delaminated PDA film that formed at the two labeled interfaces.
permeable pathways for monovalent cations in bulk PDA films of different thickness.\cite{51}

The simultaneous presence of the divalent cation Ca\(^{2+}\) in NaCl solutions prevented delamination of PDA films (Figure 2a; Figure S3, Supporting Information). This enhanced stability persisted upon subsequently removing the Ca\(^{2+}\) component of the salt solution (Figure S4, Supporting Information). We speculate that Ca\(^{2+}\)-enhanced adhesion may be related to attractive electrostatic interactions between negatively charged ionized catechols and divalent Ca\(^{2+}\) cations adsorbed at the SiO\(_2\) surface.\cite{47,52} Possible electrostatic attractions of ionized catechols with adsorbed monovalent Na\(^+\) cations may, by contrast, be neutralized by the ionized silanol groups at the surface. Both direct adsorption of catechols\cite{23,24,26,27} and electrostatic attraction would be suppressed in such case. The positive charges presented by Ca\(^{2+}\) cations absorbed in the film may also retard transport and adsorption of Na\(^+\) to the PDA–SiO\(_2\) interface.\cite{51,53} Fe\(^{3+}\) cations enhance PDA film stability in strongly alkaline solutions, which corroborates observations reported here.\cite{48} Delamination processes were consistently observed in

Figure 2. Delamination kinetics of PDA films under different conditions along with graphical summaries of proposed explanatory phenomena. a) Time to complete delamination in different salt solutions in 50 \(\times\) 10\(^{-3}\) \(\text{m}\) Tris buffer at pH = 10. All PDA films were 59 \(\pm\) 4 nm thick and synthesized from 1 mg mL\(^{-1}\) dopamine solutions. Films in 200 \(\times\) 10\(^{-3}\) \(\text{m}\) NaCl + 200 \(\times\) 10\(^{-3}\) \(\text{m}\) CaCl\(_2\) solutions showed no evidence of delamination initiation over the course of 12 h. Associated graphic illustrates proposed disruption of catechol-SiO\(_2\) hydrogen bonding by adsorption of cations. b) Time to complete delamination at different pH in 200 \(\times\) 10\(^{-3}\) \(\text{m}\) NaCl + 50 \(\times\) 10\(^{-3}\) \(\text{m}\) Tris buffer. All PDA films were 59 \(\pm\) 4 nm thick and synthesized from 1 mg mL\(^{-1}\) dopamine solutions. Associated graphic illustrates ionization of catechol groups and deprotonation of primary amines on dopamine within the PDA film. c) Time to complete delamination for films that had been synthesized from solutions of varying dopamine concentration. All solutions were 200 \(\times\) 10\(^{-3}\) \(\text{m}\) NaCl + 50 \(\times\) 10\(^{-3}\) \(\text{m}\) Tris buffer at pH = 10. Associated graphic illustrates the greater proportion of uncyclized dopamine and primary amines in the 2.5 and 4 mg mL\(^{-1}\) films. d) Time to complete delamination for different film thicknesses. All solutions were 200 \(\times\) 10\(^{-3}\) \(\text{m}\) NaCl + 50 \(\times\) 10\(^{-3}\) \(\text{m}\) Tris buffer at pH = 10. The associated graphic illustrates the independence of cation transport with respect to PDA film thickness. All data presented as mean \(\pm\) SD.
the presence of multivalent anions (e.g., present in Na₂CO₃ and Na₂SO₄ solutions; data not shown).

PDA films on indium tin oxide (ITO) substrates did not spontaneously delaminate in alkaline salt solution (Figure S5, Supporting Information). However, electrically oxidizing the films at +0.9 V (vs Ag/AgCl) for 20 min did result in delamination, which is attributed to the oxidation of catechols into o-quinones (see voltammogram in Figure S6, Supporting Information).[21,54,55] This contrast of PDA film stability between SiO₂ and ITO substrate underscores the multimodal interactions between catechol networks at interfaces.[25] For example, catechols participate in strong complexes with TiO₂ surfaces[56] in contrast to weaker hydrogen bonds with mica, and a similar contrast may account for the greater stability of PDA films prepared on ITO versus SiO₂ substrates.[22] A summary of the influence of different factors on PDA film delamination is presented in Table 1.

Free-standing PDA nanomembranes (Figure 1c) are stable under gentle mechanical manipulation and can be relaminated to polydimethylsiloxane (PDMS) elastomer underwater in an orientation-dependent manner. The basal sides of PDA nanomembranes readily adhere to PDMS in underwater environments, whereas apical sides do not (see Video S1, Supporting Information). Atomic force microscopy (AFM) images of the nanomembranes on melanin materials.[62,63] PDA films delaminated in NaCl CaCl₂ Na₂CO₃ Na₂SO₄ Increasing pHb) High precursor concentrationc) Film thickness Ambient Electrochemical oxidation

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a)Measured at pH = 10 in Tris buffer; b)Measured in 200 × 10⁻³ M NaCl; c)Refers to the dopamine concentration in the solution used for film synthesis where “high” concentration means 2.5–4 mg mL⁻¹ in contrast to 1 mg mL⁻¹ (low); d)Measured in pH = 10 solutions containing 200 × 10⁻³ M Na⁺ with an applied oxidizing potential bias (as labeled) or without (ambient).
a direction and 0.33–0.80 GPa along the b direction. The lower value in the b direction may result from compressive stabilization via hydrogen bondings, which results in an overall gentler energy landscape (see Figure S7, Supporting Information). The c-direction is not expected to contribute significantly to the Young’s modulus in the model since the stacked dimers are bound by weaker van der Waals forces along this direction. The greater empirical and molecular dynamic modeling values

Figure 3. a) Schematic of PDA film buckling achieved by relaminating a PDA nanomembrane on a prestrained polydimethylsiloxane (PDMS) substrate, then releasing the strain to buckle the film via compression. b) AFM scan of a buckled PDA nanomembrane delaminated in 200 × 10^{-3} M NaCl + 50 × 10^{-3} M Tris buffer at pH = 10. c) AFM image of a buckled genipin-crosslinked PDA nanomembrane. d) Illustration of the two crosslinking schemes investigated. Top: catechol crosslinking via Fe^{3+} cations. Bottom: proposed amine crosslinking via genipin. Note that the structure of genipin shown is modified upon crosslinking (see Figure 4b). e) Young’s modulus of PDA films as determined from the buckling wavelengths (n = 5). Different delamination conditions did not have a statistically significant effect on the modulus (one-way ANOVA, F = 1.146, p > 0.05). All data presented as mean ± SD.

Figure 4. a) Structure of PDA dimer considered for density functional theory (DFT) simulations. The structure is stacked dimer containing units of dopamine, dopaminochrome, and 5,6-dihydroxyindole. b) Proposed structure of genipin-crosslinked dimer containing two stacked dimers and genipin molecules as the linker. c) DFT-converged structure of PDA dimer. The figure was created using VESTA package. d) DFT-converged structure of crosslinked PDA. Crosslinking interactions are expected to increase the Young’s modulus of PDA.
for $E_t$ compared to values obtained from DFT must be attributed to higher order interactions not accessible from the simple dimer model. However, the same order of magnitude for the maximum value supports the general compositional model of PDA as units of dopamine and its cyclization products.

The mechanical robustness of PDA nanomembranes may be enhanced through crosslinking of aggregated oligomers and potentially serve to improve the long term stability of PDA coatings in mechanically agitated environments.

This work evaluated two types of PDA crosslinking motifs: metal cation crosslinking via catechols and chemical crosslinking via primary amines (Figure 3d). Fe$^{3+}$ cations were chosen as a catechol crosslinking agent based on their known ability to enhance the mechanical robustness of other catecholic materials.

Iron chelation in the PDA films was confirmed via Raman spectroscopy (Figure S8, Supporting Information). Genipin was chosen as an amine crosslinking agent based on its relatively low cytotoxicity which is an important property for PDA's many potential biomedical applications.

The results shown in Figure 3e (and Table S1, Supporting Information) indicate that amine crosslinking through genipin complexation is a more viable crosslinking scheme for PDA films compared to coordination bond formation via Fe$^{3+}$. The elastic modulus in both pristine PDA and iron chelated PDA nanomembranes were comparable. This observation may be attributed to limited permeation of Fe$^{3+}$ throughout the films. The $5 \times 10^{-3} \, \text{mol} \, \text{dm}^{-3}$ FeCl$_3$ solution used for crosslinking was at pH $= 2.6$, and the positive surface charge of PDA at this pH would inhibit the complete permeation of the Fe$^{3+}$ cations throughout the film, limiting the extent of crosslinking. By contrast, PDA films incubated in genipin solution exhibited a $>5x$ increase in modulus over the control: $E_t = 7.9 \pm 1.7$ versus $1.5 \pm 0.4 \, \text{GPa}$ (mean $\pm \text{SD}$; unpaired $t$-test, $p < 0.001$). Increased interunit bonding of PDA monomers in silico increases the elastic modulus of PDA. Therefore, the greater modulus of the PDA nanomembranes incubated in genipin compared to the control is evidence that genipin is an effective crosslinking agent for PDA films. DFT simulations of crosslinked PDA consist of the same stacked dimer units with genipin molecule as the linker (Figure 4b). The converged geometry is shown in Figure 4d. Besides crosslinking effects due to the addition of new bonds, the Young's modulus is also expected to increase due to hydrogen bonding which is evident in Figure 4d. Due to the enormous computational cost of van der Waals DFT for large systems (>100 atoms), mapping out a complete energy landscape for the Young's modulus is beyond the scope of the present work.

The use of amine groups for crosslinking is advantageous over iron-catechol crosslinking since it preserves the adhesive functionality of catechols within the films and does not face the sensitive complexation versus precipitation obstacle of iron-catechol crosslinking. Aminic crosslinking is similarly advantageous over proposed oxidative crosslinking of PDA because oxidation could lower the catechol population in favor of less adhesive quinones or degrade the film composition.

The quantitative impact that a crosslinking modality has on the modulus of PDA will likely depend on the composition and available sites for crosslinking as determined by synthesis and processing conditions on the PDA material. Lower dopamine precursor concentrations during synthesis, for example, may result in a greater fraction of cyclization products of dopamine and therefore fewer crosslinking sites available for genipin.

In summary, we have investigated bulk delamination and cohesive mechanisms of PDA nanomembranes and post-processing techniques to control them. The adhesion of PDA films to metal oxides during synthesis is multimodal and practical implementation of this material must account for the surface-specific bonding mode between the catechol and metal oxide substrates. In particular, hydrogen-bonding of PDA films to SiO$_2$ is disrupted in monovalent salt solutions, but adhesion may be stabilized by increased precursor concentration during film synthesis or the addition of multivalent cations in the delamination buffer. The underwater adhesion of PDA nanomembranes is orientation dependent with basal interfaces exhibiting qualitatively more adhesion than apical interfaces. This observation emphasizes the fact that the presence of catechol groups within a PDA network is necessary, but not sufficient for underwater adhesion. Rather, surface morphology and likely catechol density and orientation at the adhering interface are also critical. Surface-buckling measurements of the elastic modulus of PDA support the oligomeric aggregate model of PDA. Genipin is an effective crosslinking modality for PDA and presents certain advantages over iron or oxidative crosslinking.

**Experimental Section**

**Materials:** Dopamine hydrochloride (>98%), sodium chloride (>99%), and iron(III) chloride hexahydrate (>99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Sodium bicarbonate (>99%), sodium carbonate (>99%), tris(hydroxymethyl)aminomethane (Tris), sodium sulfate (>99%), and sodium phosphate dibasic (99.2%) were purchased from Fisher Scientific (Hampton, NH, USA) and used as received. Calcium chloride dihydrate (>99%) was purchased from BDH VWR International (Radnor, PA USA). Water was purified (18.2 MΩ cm) using Direct-Q 3 UV-R system (EMD Millipore, Billerica, MA USA). Silicon wafers with 1 µm thermal oxide were purchased from Silicon Quest International (San Jose, CA USA; 4” diameter, phosphorus doped). ITO pieces were purchased from University Wafer (Boston, MA, USA; 20 Ω sq$^{-1}$; ITO on glass).

**PDA Film Preparation:** Silicon and ITO substrates were cleaned by sonication in acetone, followed by isopropl alcohol and then rinsed with deionized water (ddH$_2$O). Substrates were then cleaned by UV-ozone (30 mW cm$^{-2}$; 5 min: Jelight, Irvine, CA, USA). PDA films were prepared by dissolving 1, 2.5, or 4 mg ml$^{-1}$ dopamine hydrochloride in 200 ml of 50 $\times$ 10$^{-3}$ M bicarbonate buffer at pH = 8.5. Precleaned substrates were incubated in dopamine solutions in ambient air and rotational agitation (65 rpm). After 24 h the substrates were rinsed and incubated in a refreshed deposition solution. This process was repeated as necessary to achieve a desired film thickness (24, 48, or 72 h). The substrates were then rinsed and placed in ddH$_2$O for 24 h then dried under a stream of N$_2$. The pH values of all sample solutions were measured using an Ag/AgCl pH electrode (Hach, model 5014T; Loveland, CO, USA).

**Delamination of PDA Films:** Individual square (1 $\times$ 1 cm$^2$) PDA films were cut from a larger parent sample and placed in ddH$_2$O for 12 h prior to delamination. Samples were then placed in petri dishes, the desired delamination buffer was poured in, and the process was observed visually using a Canon EOS Rebel T3i camera. Buffers were periodically refreshed during long tests (>30 min) to maintain the specified pH. The times until complete delamination were recorded.

Electrochemical tests were performed in a conventional three-electrode setup with saturated Ag/AgCl reference electrodes (Koslow Scientific; Englewood, NJ, USA) and platinum mesh as counter...
electrode. Tests were performed in 50 × 10⁻³ M bicarbonate/carbonate buffer (pH = 10) with 122 × 10⁻⁵ M NaCl supporting electrolyte (to attain [Na⁺] = 200 × 10⁻³ M) and in ambient atmosphere. PDA films on ITO were delaminated by applying +0.9 V for 20 min. Cyclic voltammetry scans were swept between −0.4 and 0.9 V at 30 mV s⁻¹ using an Interface 1000 potentiostat (Gamry Instruments; Warminster, PA, USA).

PDA Nanomembrane Buckling and Crosslinking: Elastomeric substrates were prepared using PDMS (Sylgard 184, Dow Corning, Midland, MI, USA) cured in a 10:1 ratio at 75 °C for 5 h. Rectangular PDMS coupons (W × L × H = 1.3 × 4 × 0.1 cm²) were mounted in a custom fixation device and strained by 8% on the long axis. Drops of ddH₂O were placed on the strained PDMS and free-floating PDA nanomembranes were transferred into the drops and laminated onto the PDMS using applied pressure. The excess ddH₂O was removed under an N₂ stream. After 10 min the strain on the PDMS was slowly released (≈0.5 mm s⁻¹) in order to induce buckling of PDA nanomembranes.

Iron crosslinking was performed by first incubating PDA nanomembranes in 100 × 10⁻³ M CaCl₂ (50 × 10⁻⁵ M Tris buffer, pH = 10) for 100 min. This initial step acts to promote iron chelation and was necessary to observe the diagnostic iron chelation signature in the Raman spectrum.[24] Nanomembranes were then primed in ddH₂O and incubated in 5 × 10⁻⁴ M FeCl₃ solution for 100 min. Nanomembranes were incubated in Tris buffer (pH = 10) for 20 min so that pH > 5 to ensure bis-coordination of catechols with Fe⁺.[65,75] Raman spectra of the pristine and iron-chelated nanomembranes (NTegra Spectra; Tempe, AZ, USA) were recorded with a 532 nm laser. Each measurement was performed at unique single point of spot size ~1 μm diameter at 1 mW power for 30 s.

Genipin crosslinking was performed by placing PDA nanomembranes in solutions of 3 mg mL⁻¹ genipin (pH = 7; 50 × 10⁻³ M phosphate buffer) for 24 h at 40 °C (control sample solutions did not contain genipin). Both experimental and control samples were then primed in ddH₂O and incubated in ddH₂O for 12 h before compressive buckling tests.

All PDA film samples used for buckling measurements were prepared in 1 mg mL⁻¹ dopamine solution for a 24 + 24 h deposition resulting in 59 ± 4 nm thickness. PDA films used for crosslinking were delaminated from SiO₂ in 200 × 10⁻¹⁰ M NaCl at pH = 10 (50 × 10⁻³ M Tris buffer).

Uniaxial tensile tests (n = 4) on PDMS were conducted using a 10 N load cell at strain rates of 2 mm min⁻¹ (Instron 5943 equipped with Bluehill 3 software, Norwood, MA, USA).

Morphological Characterization of PDA Film: Film thicknesses and morphology were measured using atomic force microscopy (NT-MDT NTegra AFM; Tempe, AZ, USA) in tapping mode. Scans for buckling measurements were performed with tips of radius = 35 nm and k = 25–95 N m⁻¹ (NT-MDT NTegra AFM; Tempe, AZ, USA). Buckling wavelengths were quantified by fast Fourier transform of the transverse height profile (Figure S9, Supporting Information). Small scale morphology scans were performed with tips of radius <1 nm and k = 5 N m⁻¹ (Budget Sensors; Sofia, Bulgaria). Imaging of the basal side of a PDA nanomembrane was accomplished by draping a free-floating nanomembrane over a small flat glass puck that was then lifted out of the liquid and subsequently dried in ambient atmosphere. Film thicknesses were determined by scratching the as-synthesized films and measuring the height profile with AFM.[50]

Density Functional Theory Calculations: DFT simulations were performed using the van der Waals functional BEEF-vdW[48] on a stacked dimer model of PDA. The starting structures for DFT were obtained from the converged geometries of Liebscher et al.[49] The curvature of the energy landscape at the equilibrium geometry of the structure was used to obtain the Young’s modulus (details in Supporting Information).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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