Electronic Supplementary Materials

Strong, tough, and repeatable adhesion of an alternating peptide comprising phenyl glycine as a repeating unit

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General Methods

Materials

Trifluoromethanesulfonic acid (TfOH; Kanto Chemical Co., Ltd., Tokyo, Japan), isobutyraldehyde (Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan), benzaldehyde (Nacalai Tesque, Inc., Kyoto, Japan), phenylacetaldehyde (Alfa Aesar, Massachusetts, USA), butylamine (Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan), i-propyl alcohol (Taiyo Chemicals, Co., Ltd., Wakayama, Japan), and chloroform (Kanto Chemical Co., Ltd., Tokyo, Japan) were used as obtained. Potassium isocyanoacetate was synthesized according to the literature.

Measurements

The $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker Avance II 400 spectrometer (Bruker, Fällanden, Switzerland), using CDCl$_3$ as a solvent, and calibrated using residual undeuterated solvent and tetramethylsilane as internal standards. DOSY measurements were recorded using 2.0 mg of the alternating peptide in 600 µL of CDCl$_3$ to estimate the diffusion coefficients. DOSY spectra were obtained on a Bruker Avance II 400 spectrometer. Experiments were run without spinning to avoid convection. The standard Bruker pulse program ledpgp2s was used, which employs simulated echo and longitudinal eddy delay with bipolar gradients and two spoil gradients. The obtained DOSY spectra were processed with TopSpin 3.2 software. The diffusion coefficients of a selected narrow chemical shift in the spectra of the compounds were determined using Dynamics Center software (ver. 2.4.8; Bruker, Fällanden, Switzerland). Fourier transform infrared (FT-IR) spectra were recorded via an attenuated total reflection (ATR) method using a PerkinElmer spectrum 100 spectrometer (PerkinElmer, Shelton, USA). Size exclusion column chromatography (SEC) analyses were performed using a chromatographic system comprising a Shimadzu LC-20AT pump (Shimadzu Co. Ltd., Kyoto, Japan) with a Shimadzu SPD-20A UV detector equipped with two consecutive linear polystyrene gel columns (TSKgel GMHHR-H and TSKgel G3000HHR; Tosoh Co. Ltd., Tokyo, Japan) at room temperature using polystyrene standards with tetrahydrofuran (THF) as an eluent (flow rate: 1.0 mL/min). Differential scanning calorimetry (DSC) was performed using a DSC-60 plus instrument (Shimadzu Co., Ltd., Kyoto, Japan) for P1, P2, and P3 under a N$_2$ atmosphere (flow rate: 50 mL/min). The lap-shear adhesive test was performed with an EZ-SX tensile machine (Shimadzu Co., Ltd., Kyoto, Japan) at a different shear velocity. Fiber formation and alignment on a glass plate after lap-shear testing were precisely observed by SEM with a field emission gun (S-4000; Hitachi Co., Ltd., Tokyo, Japan) after sputter-coating the specimen’s surface with a thin layer of gold (thickness: 5 nm). The glass plate after the repeated lap-shear tests were directly used for the SEM measurements of stretched samples. The SEM sample for the macroscopic fiber was prepared by attaching the fiber generated during the lap-shear test to a new glass plate. Wide angle X-ray diffraction (XRD) profiles were recorded on a benchtop powder X-ray diffraction (XRD) instrument.
Rheological measurements were performed using a high performance, fully self-contained, rotational rheometer (Merlin VR; Rheosys LLC, Trenton, USA) with 30 mm 2° cone (shear stress constant: 141471, shear rate constant: 28.647). UV–Vis spectra were recorded on a JASCO V-630 spectrophotometer (JASCO Co. Ltd., Tokyo, Japan) using a 1.0 mm path quartz cuvette maintained at 25 °C with a temperature controller (CTU-100, JASCO Co. Ltd., Tokyo, Japan). The thin films for the UV–Vis measurements were prepared inside a UV cell via a casting method using THF.

**Synthetic Procedures to Obtain Alternating Peptides**

**Synthesis of P1**

TfOH (88.5 μL, 1.00 mmol) was added to a mixture of butylamine (98.8 μL, 1.00 mmol) and i-PrOH (0.5 mL) at 0 °C, followed by adding potassium isocyanate (123.2 mg, 1.00 mmol). After dissolving potassium isocyanate, isobutylaldehyde (91.3 μL, 1.00 mmol) was added at the same temperature. The mixture was then warmed to room temperature, stirred for 5 d, and concentrated under vacuum. The resulting crude mixture was stirred for a further 6 d at room temperature and diluted with CHCl3 for purification. The reaction was quenched by adding water, and the products were extracted with CHCl3. The combined organic layer was dried over MgSO4, filtered, and concentrated under vacuum to give P1 (145.5 mg, 69%) as a colorless viscous polymer: $M_w$ 5,300 Da (estimated by NMR); $M_w/M_n$ 1.2 (estimated by SEC based on polystyrene standards); $T_g$ −23.4 °C; $^1$H NMR (400 MHz, 293 K, CDCl3) δ 8.82 (brd, NH), 7.96 (brd, NH), 7.71 (brd, NH), 7.53 (brd, NH), 7.51 (brd, NH), 6.99 (brd, NH), 4.46–3.84 (m, CH, CH2), 3.31–2.53 (m, CH2), 2.16 (brd, CH, CH2), 1.50–0.88 (m, CH2, CH3) ppm; $^{13}$C NMR (100 MHz, 293 K, CDCl3) δ174.5–165.6 (C=O), 68.5–66.1 (CH), 50.0–39.3 (CH2), 31.9–27.3 (CH), 22.0–13.8 (CH2, CH3) ppm; IR (ATR) ν 3300 (NH), 3073, 2958, 2903, 2872, 1713, 1644 (C=O), 1527, 1465, 1371, 1334, 1261, 1228, 1182, 1133, 1105, 1029, 981, 962, 897, 783, 735 cm$^{-1}$.

**Synthesis of P2**

TfOH (88.5 μL, 1.00 mmol) was added to a mixture of butylamine (98.8 μL, 1.00 mmol) and i-PrOH (0.5 mL) at 0 °C, followed by adding potassium isocyanate (123.2 mg, 1.00 mmol). After dissolving potassium isocyanate, benzaldehyde (101.7 μL, 1.00 mmol) was added at the same temperature. The mixture was then warmed to room temperature, stirred for 5 d, and concentrated under vacuum. The resulting crude mixture was stirred for a further 6 d at room temperature and diluted with CHCl3 for purification. The reaction was quenched by adding water. The products were extracted with CHCl3. The combined organic layer was dried over MgSO4, filtered, and concentrated under vacuum to afford P2 (199.7 mg, 81%) as a yellow viscous polymer: $M_w$ 5,600 Da (estimated by
NMR; $M_w/M_n 1.6$ (estimated by SEC based on polystyrene standards); $T_g ^-9.9$ °C; $^1$H NMR (400 MHz, 293 K, CDCl$_3$) δ 8.80 (brd, NH), 8.32–6.67 (m, Ar), 4.99–4.21 (m, CH, CH$_2$), 4.03–2.63 (m, CH$_2$), 2.61 (brd, CH), 1.46–0.76 (m, CH$_2$, CH$_3$) ppm; $^{13}$C NMR (100 MHz, 293 K, CDCl$_3$) δ171.8–164.1 (C=O), 139.4–119.2 (Ar), 68.8–63.7 (CH), 48.7–19.6 (CH$_2$), 14.0–13.9 (CH$_3$) ppm; IR (ATR) $\nu$ 3286 (NH), 3062, 3030, 2958, 2930, 2871, 1651 (C=O), 1627, 1533, 1492, 1478, 1465, 1451, 1376, 1336, 1282, 1225, 1206, 1181, 1154, 1145, 1123, 1075, 1030, 924, 853, 834, 731, 720, 691 cm$^{-1}$.

**Synthesis of P3**

TfOH (88.5 μL, 1.00 mmol) was added to a mixture of butylamine (98.8 μL, 1.00 mmol) and $i$-PrOH (0.5 mL) at 0 °C, followed by adding potassium isocyanate (123.2 mg, 1.00 mmol). After dissolving potassium isocyanate, phenylacetaldehyde (117.1 μL, 1.00 mmol) was added at the same temperature. The mixture was warmed to room temperature, stirred for 5 d, and concentrated under vacuum. The resulting crude mixture was stirred for a further 6 d at room temperature and diluted with CHCl$_3$ for purification. The reaction was quenched by adding water, and the products were extracted with CHCl$_3$. The combined organic layer was dried over MgSO$_4$, filtered, and concentrated under vacuum to afford P3 (189.9 mg, 73%) as a pale yellow viscous polymer: $M_w$ 6,300 Da (estimated by NMR); $M_w/M_n 1.2$ (estimated by SEC based on polystyrene standards); $T_g ^-16.5$ °C; $^1$H NMR (400 MHz, 293 K, CDCl$_3$) δ 8.24 (brd, NH), 7.91 (brd, NH), 7.31–6.92 (m, Ar), 4.94–4.27 (m, CH, CH$_2$), 3.94–2.41 (m, CH$_2$), 1.49–0.80 (m, CH$_2$, CH$_3$) ppm; $^{13}$C NMR (100 MHz, 293 K, CDCl$_3$) δ 174.5–162.1 (C=O), 138.9–126.2 (Ar), 64.7–63.5 (CH), 48.1–38.6 (CH$_2$), 31.5–20.1 (CH$_2$), 13.8 (CH$_3$) ppm; IR (ATR) $\nu$ 3302 (NH), 3085, 3062, 3028, 3003, 2957, 2929, 2871, 1647 (C=O), 1520, 1495, 1454, 1413, 1377, 1334, 1246, 1181, 1125, 1078, 1030, 1001, 982, 911, 843,744, 698 cm$^{-1}$.

**Lap-Shear Sample Preparation and Testing**

Lap-shear joints were prepared as shown in Fig. 1(a), according to a process that is frequently used to measure the adhesive strength of adhesive materials. Two glass plates (length × width = 75 mm × 25 mm) were brought into contact with a fixed quantity (20 mg) of polymers, which formed a junction contact area of 5.0 cm$^2$ ($l_0 \times w = 20$ mm × 25 mm). The lap joint was slightly pressurized with a finger for 30 s before clamping the two ends of the glass plate to a tensile machine (EZ-SX; Shimadzu Co., Ltd.). Shear adhesive tests were performed at a different shear velocity ($v$). $S_{Adh}$, defined as the strength of the lap-shear sample immediately before the interface of the two adhered surfaces begins to separate, was estimated from the measured maximum adhesive force ($F_{\text{max}}$) according to the following expression: $S_{Adh} = F_{\text{max}}$/surface ($l_0 \times w$), where $l_0 \times w = 20$ mm × 25 mm. $G$ was obtained by dividing $S_{Adh}$ by the strain: $G = S_{Adh}/(ll_0)$. The area and thickness of glue at the lap joint were constant during the re-adhesion experiments.
Figure S1: $^1$H NMR spectrum of P1 (400 MHz, CDCl$_3$, 298 K).

Figure S2: $^{13}$C NMR spectrum of P1 (100 MHz, CDCl$_3$, 298 K).
Figure S3: DOSY correlations of P1 (400 MHz, CDCl₃, 298 K) with the attenuation curve.
Figure S4: $^1$H NMR spectrum of P2 (400 MHz, CDCl$_3$, 298 K).

Figure S5: $^{13}$C NMR spectrum of P2 (100 MHz, CDCl$_3$, 298 K).
Figure S6: DOSY correlations of P2 (400 MHz, CDCl₃, 298 K) with the attenuation curve.
Figure S7: $^1$H NMR spectrum of P3 (400 MHz, CDCl₃, 298 K).

Figure S8: $^{13}$C NMR spectrum of P3 (100 MHz, CDCl₃, 298 K).
Figure S9: DOSY correlations of P3 (400 MHz, CDCl₃, 298 K) with the attenuation curve.
Figure S10: IR spectrum of P1 (ATR).

Figure S11: IR spectrum of P2 (ATR).
Figure S12: IR spectrum of P3 (ATR).
Figure S13: Force–displacement curves from a lap-shear test to measure the adhesion of alternating peptides to glass plates (Cycle 1).
Figure S14: Adhesive behaviors of P1. (a) Repeated lap-shear tests of P1 at a stretching velocity ($v$) of 10 mm/min using the same sample on glass, (b) dependence of adhesive strength ($S_{\text{adh}}$) on the number of cycles, (c) force–displacement curves from the lap-shear test to measure the adhesion of alternating peptides to glass at different stretching velocities, and (d) dependence of $v$ on the modulus ($G$).
Figure S15: Dependence of adhesive force (N) on the stretching velocity (ν) using P2: (a) force–displacement curves from the lap-shear test to measure the adhesion of alternating peptides to glass at different stretching velocities and (b) dependence of ν on the modulus (G).
Figure S16: Adhesive behaviors of P3. (a) Repeated lap-shear tests of P3 at a stretching velocity (v) of 10 mm/min using the same sample on glass, (b) dependence of adhesive strength (S_{Adh}) on the number of cycles, (c) force–displacement curves from the lap-shear test to measure the adhesion of alternating peptides to glass at different stretching velocities, and (d) dependence of v on the modulus (G).
**Table S1:** Polymerization results and mechanical properties of alternating peptides$^a$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ (kDa)$^b$</th>
<th>$M_w/M_n$</th>
<th>$S_{adh}$ (kPa)$^d$</th>
<th>$G$ (Pa) $^e$</th>
</tr>
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<tbody>
<tr>
<td>P1–10</td>
<td>5.3</td>
<td>1.2</td>
<td>4.78</td>
<td>5.0</td>
</tr>
<tr>
<td>P1–100</td>
<td>31.96</td>
<td></td>
<td>275.28</td>
<td></td>
</tr>
<tr>
<td>P1–200</td>
<td>31.06</td>
<td></td>
<td>389.29</td>
<td></td>
</tr>
<tr>
<td>P2–10</td>
<td>50.43</td>
<td></td>
<td>3,802.88</td>
<td></td>
</tr>
<tr>
<td>P2–100</td>
<td>169.82</td>
<td></td>
<td>11,509.44</td>
<td></td>
</tr>
<tr>
<td>P2–200</td>
<td>424.71</td>
<td></td>
<td>34,452.14</td>
<td></td>
</tr>
<tr>
<td>P3–10</td>
<td>20.30</td>
<td></td>
<td>86.93</td>
<td></td>
</tr>
<tr>
<td>P3–100</td>
<td>66.63</td>
<td></td>
<td>1,183.17</td>
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<tr>
<td>P3–200</td>
<td>68.01</td>
<td></td>
<td>1,075.50</td>
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</tr>
</tbody>
</table>

$^a$Polymers are coded as P-$v$, where $v$ denotes the stretching velocity. $S_{adh}$ and $G$ were obtained after repeated tests. $^b$Estimated by NMR. $^c$Estimated by SEC. $^dS_{adh} = F_{max}/(l_0 \times w)$. $^eG = S_{adh}/(U/l_0)$. 
Thermal Properties

**Figure S17**: DSC profiles of alternating peptides (10 °C/min from −40 °C to 80 °C).

**Figure S18**: Dependence of the $S_{\text{Adh}}$ values on the glass transition temperatures ($T_g$).
SEM Observations

Figure S19: SEM observation of (a) P1 and (b) P3 after repeated lap-shear tests and (c) P2 as a virgin sample before the lap-shear test. These SEM images indicated that no fibrous structures were formed.
XRD Profiles

![XRD Profiles](image)

**Figure S20:** XRD profiles of polymeric adhesives. While the XRD profiles of P1 and P3 consist of a broad peak attributed to an amorphous halo at around 20°, the profile of P2 includes the additional signal at around 6°, which is ascribed to the nanoscale orientation of elongated polymer chains.
Rheological Studies

**Figure S21:** The frequency dependence of polymers on viscosity.

**Figure S22:** The frequency dependence of polymers on shear stress.
Figure S23: UV–Vis spectra of alternating peptides (P1, P2, and P3) in THF (100 \( \mu \)mol L\(^{-1} \) per repeating unit) at 25 °C.

Figure S24: UV–Vis spectra of alternating peptides (P1, P2, and P3) at a thin film. The slight difference of spectral pattern compared to the solution state might indicate the possibility of contribution of \( \pi \)-\( \pi \) stacking on physical cross-linking points.

References
1) A. B. Ihsan and Y. Koyama, Polymer, 2019, 161, 197.