SUPPORTING INFORMATION

Effective Design of Supramolecular Polymer Adhesives Based on Multiple CH/π Interactions

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Methods

$^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra were recorded on a JEOL ECP-500 spectrometer in chloroform-$d_1$ (CDCl$_3$), with tetramethylsilane used as an internal standard ($\delta$ 0 ppm) for both nuclei. Mass spectra were recorded on a Bruker MicroTOF II mass spectrometer. FT-IR measurements were carried out using a JASCO FT/IR-6300 instrument. ATR measurements were performed on the FT-IR instrument equipped with a germanium prism using single-reflection ATR accessories. Transmission measurements were carried out using a fixed cell equipped with a KRS-5 aperture plate. GPC data were obtained on a Waters 2695 system equipped with a refractive index detector. DSC measurements were performed on a TA Instruments DSC Q2000 machine. X-ray photoelectron spectroscopy (XPS) data were acquired on an ULVAC-PHI PHI Quantera II instrument. XRD measurements were carried out using a Rigaku Ultima IV diffractometer. Field emission scanning electron microscopy (FE-SEM) imaging was conducted using a JEOL JSM-7401F microscope. AFM measurements were carried out using a Hitachi High-Tech Science Corporation SPA400 microscope.
Synthesis and characterization of H acceptor 1.

Synthesis of Monomer 1.

Monomer 1 was synthesized according to the reported procedure.\(^1\) Trityl chloride (25.0 g, 89.7 mmol) and triethylamine (13.6 g, 134 mmol) were added to 200 mL tetrahydrofuran (THF) in a round-bottom flask equipped with septum and stir bar. The mixture was cooled in ice bath for 30 min. Methacrylic acid (9.26 g, 108 mmol) was added slowly to the flask through a syringe dropwise at 0 °C. The reaction was allowed to proceed under room temperature overnight. THF was removed by vacuum distillation, and the residue dissolved in ethyl acetate and washed with NaHCO\(_3\) solution and brine. The solution was dried over MgSO\(_4\) and then concentrated to afford the crude product which was recrystallized from hexane to afford monomer 1 (23.0 g, 69.9 mmol, 78% yield) as a white solid.

\(^1\)H NMR (500 MHz, chloroform-\(d_1\), TMS) \(\delta\) ppm = 2.03 (s, 3H), 5.62 (s, 1H), 6.25 (s, 1H), 7.23-7.27 (m, 15H).

\(^{13}\)C NMR (125 MHz, chloroform-\(d_1\)) \(\delta\) ppm = 18.7, 90.1, 125.7, 127.3, 127.8, 128.4, 137.6, 143.5, 165.3.

HR-MS (TOF MS ESI, pos.): 351.1354 M+Na\(^+\) (calculated: 351.1356).

Synthesis of H acceptor 1.

Monomer 1 (2.00 g, 6.09 mmol), azobisisobutyronitrile (AIBN, 0.02 g, 0.12 mmol), and toluene 18 mL were added to a schlenk flask with a three-way stopcock. The reaction flask was sealed with a rubber septum and purged with nitrogen for 30 min. The reaction was allowed to proceed at 65 °C for 24 h and stopped by exposure the reaction to air. The obtained polymer was precipitated into a large amount of methanol and collected by centrifugation. The collected polymer was fractionated by precipitation from heated toluene solution by the addition of n-hexane. The obtained polymer was dried overnight at 60 °C for in vacuo.

ATR-FT-IR (Figure S4, cm\(^{-1}\)): 3080, 3052, 3017 (\(\nu\)CH, aromatic ring), 2957 (\(\nu\)CH\(_3\)), 2923 (\(\nu\)CH\(_2\)), 1731 (\(\nu\)C=O), 1490 (\(\nu\)CC, aromatic ring), 1232 (\(\nu\)sCOC), 1146 (\(\nu\)sCOC).

\(T_g\) (Figure S7, DSC): 236.88 °C.

\(M_n\) and PDI (GPC): 47.0×10\(^3\) and 1.29.
Synthesis and characterization of H acceptor 2.

**Synthesis of intermediate 2.**

Intermediate 2 was synthesized according to the reported procedure. 3,3,3-Triphenylpropionic acid (10.0 g, 33.1 mmol) was added to THF 35 mL in a round-bottom flask equipped with septum and stir bar. The mixture was cooled in ice bath for 30 min. Lithium aluminum hydride (10% LiAlH₄ in THF, ca. 2.5mol/L) 20 mL was added slowly to the flask through a syringe dropwise at 0 °C. The reaction was allowed to proceed under room temperature overnight and excess LiAlH₄ was decomposed by slow addition of water. THF was removed by vacuum distillation, and the residue dissolved in ethyl acetate and washed with water. The solution was dried over MgSO₄ and then concentrated to afford the crude product which was purified using column chromatograph on silica gel (silica gel 60, 63-200 mesh) with toluene:ethyl acetate (10:1 v/v) as the mobile phase. The solvent was removed and the product dried in vacuum to afford intermediate 1 (5.82 g, 20.2 mmol, 61% yield) as a white solid.

**1H NMR** (500 MHz, chloroform-d₁, TMS) δ ppm = 2.93 (t, J = 7.0, 2H), 3.48 (t, J = 7.0 Hz, 2H), 7.17-7.34 (m, 15H).

**13C NMR** (125 MHz, chloroform-d₁) δ ppm = 45.8, 55.3, 60.7, 126.2, 128.0, 128.1, 147.0.

**HR-MS** (TOF MS ESI, pos.): 311.1405 M+Na⁺ (calculated: 311.1406).

**Synthesis of Monomer 2.**

Intermediate 2 (5.00 g, 17.3 mmol) and triethylamine (3.51 g, 34.7 mmol) were added to 45 mL THF in a round-bottom flask equipped with septum and stir bar. The mixture was cooled in ice bath for 30 min. Methacryloyl chloride (2.72 g, 26.1 mmol) was added slowly to the flask through a syringe dropwise at 0 °C. The reaction was allowed to proceed under room temperature overnight. THF was removed by vacuum distillation, and the residue dissolved in ethyl acetate and washed with 1M HCl solution, NaHCO₃ solution and brine. The solution was dried over MgSO₄ and then concentrated to afford the crude product which was purified using column chromatograph on silica gel (silica gel 60, 63-200 mesh) with ethyl acetate:hexane (1.25 v/v) as the
mobile phase. The solvent was removed and the product dried in vacuum to afford monomer 2 (5.01 g, 14.0 mmol, 81% yield) as colorless oil.

$^1$H NMR (500 MHz, chloroform-$d_1$, TMS) $\delta$ ppm = 2.04 (s, 3H), 2.99 (t, $J = 7.7$ Hz, 2H), 3.96 (t, $J = 7.7$, 2H), 5.52 (s, 1H), 6.03 (s, 1H), 7.19-7.32 (m, 15H).

$^{13}$C NMR (125 MHz, chloroform-$d_1$) $\delta$ ppm = 18.4, 38.7, 55.2, 62.9, 125.5, 126.3, 128.2, 129.0, 136.4, 146.7, 167.5.

HR-MS (TOF MS ESI, pos.): 379.1692 M+Na$^+$ (calculated: 379.1669).

Synthesis of H acceptor 2.

Monomer 2 (2.00 g, 5.61 mmol), AIBN (2.30 mg, 0.001 mmol), and toluene 18 mL were added to a schlenk flask with a three-way stopcock. The reaction flask was sealed with a rubber septum and purged with nitrogen for 30 min. The reaction was allowed to proceed at 65 °C for 24 h and stopped by exposure the reaction to air. The obtained polymer was precipitated into a large amount of methanol and collected by centrifugation. The collected polymer was fractionated by gel permeation chromatography (GPC). The obtained polymer was dried overnight at 60 °C in vacuo.

ATR-FT-IR (Figure S5, cm$^{-1}$): 3090, 3059, 3031 ($\nu$CH, aromatic ring), 2979 ($\nu$CH$_3$), 2953 ($\nu$aCH$_2$), 1733 ($\nu$C=O), 1497 ($\nu$CC, aromatic ring), 1231 ($\nu$aCOC), 1142 ($\nu$COC).

$T_g$ (Figure S8, DSC): 120.01 °C.

$M_n$ and PDI (GPC): 44.2×10$^3$ and 1.27.
Synthesis and characterization of H acceptor 3.

Monomer 3                         H acceptor 3

Synthesis of intermediate 3.

Triphenylmethane (10.00 g, 40.9 mmol) was added to 290 mL THF in a round-bottom flask equipped with septum and stir bar. The mixture was cooled in ice bath for 30 min. n-Butyl lithium (15% nBuLi in hexane, ca. 1.6 mol/L) 30 mL was added slowly to the flask through a dropping funnel dropwise at 0 °C. (3-Bromopropoxy)-tert-butyldimethylsilane (12.4 g, 49.1 mmol) in THF 100 mL was added slowly to the flask through a dropping funnel dropwise at 0 °C. The reaction was allowed to proceed under 0-10 °C, 2 h and devitalized by slow addition of water. THF was removed by vacuum distillation, and the residue dissolved in ethyl acetate and washed with water. The solution was dried over MgSO₄ and then concentrated to afford the crude product which was purified using column chromatograph on silica gel (silica gel 60, 63-200 mesh) with ethyl acetate:hexane (1:40 v/v) as the mobile phase. The solvent was removed and the product dried in vacuum to afford intermediate 3 (15.35 g, 36.8 mmol, 90% yield) as a white solid.

1H NMR (500 MHz, chloroform-d₆, TMS) δ ppm = 0.06 (s, 6H), 0.94 (s, 9H), 1.27 (m, 2H), 2.66 (m, 2H), 3.57 (t, 5.9 Hz, 2H), 7.07-7.32 (m, 15H).

13C NMR (125 MHz, chloroform-d₆) δ ppm = -5.2, 18.4, 26.1, 29.3, 36.7, 56.3, 63.3, 125.6, 127.8, 129.3, 147.6.

HR-MS (TOF MS ESI, pos.): 439.2449 M+Na⁺ (calculated: 439.2428).

Synthesis of intermediate 3'.

Intermediate 3 (10.0 g, 24.0 mmol) and tetrabutylammonium chloride (50.2 g, 192 mmol) was added to 250 mL THF in a round-bottom flask equipped with septum and stir bar. The reaction was allowed to proceed under room temperature overnight. 1M HClaq. 100 mL was added to solution and the solution stirred for 30min. THF was removed by vacuum distillation, and the residue dissolved in ethyl acetate and washed with water. The solution was dried over MgSO₄ and then concentrated to afford the crude product which was purified using column chromatograph on silica gel (silica gel 60, 63-200 mesh) with toluene:ethyl acetate (10:1 v/v) as the mobile phase. The solvent was removed and the product dried in vacuum to afford intermediate 3’ (6.39, 21.1 mmol, 88% yield) as a white solid.

1H NMR (500 MHz, chloroform-d₆, TMS) δ ppm = 1.25 (s, 1H), 1.36 (m, 2H), 2.65 (m, 2H), 3.62 (m, 2H), 7.15-7.31 (m, 15H).
\(^{13}\text{C NMR}\) (125 MHz, chloroform-\(d_1\)) \(\delta\) ppm = 29.2, 36.5, 56.4, 63.4, 125.9, 127.9, 129.3, 147.4.

\(\text{HR-MS}\) (TOF MS ESI, pos.): 393.1854 M\(^+\)Na\(^+\) (calculated: 393.1825).

**Synthesis of Monomer 3.**

Intermediate 3\(^{'}\) (5.00 g, 16.5 mmol) and triethylamine (3.35 g, 33.1 mmol) were added to 100 mL THF in a round-bottom flask equipped with septum and stir bar. The mixture was cooled in ice bath for 30 min. Methacryloyl chloride (2.59 g, 24.8 mmol) was added slowly to the flask through a syringe dropwise at 0 °C. The reaction was allowed to proceed under room temperature overnight. THF was removed by vacuum distillation, and the residue dissolved in ethyl acetate and washed with 1M HCl solution, NaHCO\(_3\) solution and brine. The solution was dried over MgSO\(_4\) and then concentrated to afford the crude product which was purified using column chromatograph on silica gel (silica gel 60, 63-200 mesh) with ethyl acetate:hexane (1:25 v/v) as the mobile phase. The solvent was removed and the product dried in vacuum to afford monomer 3 (4.90 g, 13.2 mmol, 80% yield) as colorless oil.

\(^1\text{H NMR}\) (500 MHz, chloroform-\(d_1\), TMS) \(\delta\) ppm = 1.47 (m, 2H), 1.98 (s, 3H), 2.68 (m, 2H), 4.12 (t, \(J = 5.6\) Hz, 2H), 5.58 (s, 1H), 6.13 (s, 1H), 7.16-7.29 (m, 15H).

\(^{13}\text{C NMR}\) (125 MHz, chloroform-\(d_1\)) \(\delta\) ppm = 18.5, 25.3, 36.8, 56.3, 65.1, 125.5, 126.1, 128.0, 129.2, 136.5, 147.2, 167.6.

\(\text{HR-MS}\) (TOF MS ESI, pos.): 393.1854 M\(^+\)Na\(^+\) (calculated: 393.1825).

**Synthesis of H acceptor 3.**

Monomer 3 (2.00 g, 5.40 mmol), AIBN (2.22 mg, 0.001 mmol), and toluene 18 mL were added to a schlenk flask with a three-way stopcock. The reaction flask was sealed with a rubber septum and purged with nitrogen for 30 min. The reaction was allowed to proceed at 65 °C for 24 h and stopped by exposure the reaction to air. The obtained polymer was precipitated into a large amount of methanol and collected by centrifugation. The collected polymer was fractionated by gel permeation chromatography (GPC). The obtained polymer was dried overnight at 60 °C for in vacuo.

\(\text{ATR-FT-IR (Figure S6, cm}^{-1}\): 3068, 3048, 3019 (\(\nu\)CH, aromatic ring), 2973 (\(\nu\)CH\(_3\)), 2940 (\(\nu\)aCH\(_2\)), 1719 (\(\nu\)C=O), 1491 (\(\nu\)CC, aromatic ring), 1236 (\(\nu\)aCOC), 1149 (\(\nu\)sCOC).

\(T_g\) (Figure S9, DSC): 110.52 °C.

\(M_n\) and \(\text{PDI (GPC): 45.9}\times10^3 \text{ and 1.21.}\)
Figure S1 | $^1$H NMR spectrum (500 MHz, r.t., chloroform-$d_1$) of H acceptor 1.
Figure S2 | $^1$H NMR spectrum (500 MHz, r.t., chloroform-$d_1$) of H acceptor 2.
Figure S3 | $^1$H NMR spectrum (500 MHz, r.t., Chloroform-$d_1$) of H acceptor 3.
**Figure S4** | FT-IR (ATR) spectrum of H acceptor 1.

**Figure S5** | FT-IR (ATR) spectrum of H acceptor 2.
Figure S6 | FT-IR (ATR) spectrum of H acceptor 3.
Figure S7 | DSC thermogram of H acceptor 1.
Figure S8 | DSC thermogram of H acceptor 2.
Figure S9 | DSC thermogram of H acceptor 3.
Figure S10 | FT-IR (ATR) spectrum of PE.

Figure S11 | XRD pattern of PE.
Figure S12 | AFM images of the PE.

Root-mean-square (RMS) roughness value is 0.515 nm.
Figure S13 | a) Schematic diagram showing the adhesion of H-acceptor polymers to PE and b) photograph of samples fabricated H acceptor layers on PE.
**Figure S14** | FT-IR (ATR) spectrum of H acceptor 1 layer on PE.

**Figure S15** | FT-IR (ATR) spectrum of H acceptor 2 layer on PE.
Figure S16 | FT-IR (ATR) spectrum of H acceptor 3 layer on PE.
**Figure S17** | The C1s peak in the XPS spectrum of H acceptor 1 layer on PE.

**Figure S18** | The C1s peak in the XPS spectrum of H acceptor 2 layer on PE.
Figure S19 | The C1s peak in the XPS spectrum of H acceptor 3 layer on PE.
Figure S20 | FE-SEM image of H acceptor 1 layer on PE. Thickness of H acceptor 1 layer is 258 nm.

Figure S21 | FE-SEM image of H acceptor 2 layer on PE. Thickness of H acceptor 2 layer is 254 nm.
Figure S22 | FE-SEM image of H acceptor 3 layer on PE. Thickness of H acceptor 3 layer is 239 nm.
Figure S23 | a) Schematic diagram of a lap-shear test sample, b) photograph of lap-shear test samples, c) schematic diagram of a loaded lap-shear test sample, d) photograph of lap-shear testing, and e) schematic diagram of the adhesion failure mechanism.
Figure S24 | FT-IR (ATR) spectrum of PE after lap-shear test of H acceptor 1 layer and PE.

Figure S25 | FT-IR (ATR) spectrum of PE after lap-shear test of H acceptor 2 layer and PE.
Figure S26 | FT-IR (ATR) spectrum of PE after lap-shear test of H acceptor 3 layer and PE.
Figure S27 | The C1s peak in the XPS spectrum of PE after lap-shear test of H acceptor 1 and PE.

Figure S28 | The C1s peak in the XPS spectrum of PE after lap-shear test of H acceptor 2 and PE.
Figure S29 | The C1s peak in the XPS spectrum of PE after lap-shear test of H acceptor 3 and PE.
Comparisons to commercially available adhesives.

Two different commercially available adhesives (urethane (05139, Konishi Co., Ltd.) and silicone (9078, 3M Japan Limited)) were evaluated for their adhesion strength to PE substrate using lap-shear tests. Samples were fabricated according to the recommended procedure. A PE substrate sample (2.0 × 5.0 × 0.2 cm) and poly(ethylene terephthalate) film (TOYOBO Co., Ltd., COSMOSHINE®, A4300, 20 × 100 × 0.188 mm) were jointed over a 2.0 × 2.0 cm contact area using adhesives. Lap-shear tests were carried out using similar conditions to the ones applied to H-acceptor 1. Adhesion strength to PE is summarized in Table S1.

Table S1 | Adhesion strength of commercially available adhesives to PE by lap-shear test.

<table>
<thead>
<tr>
<th>Adhesives</th>
<th>Adhesion Strength (MPa)</th>
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<tr>
<td>Urethane</td>
<td>0.55 ± 0.06</td>
</tr>
<tr>
<td>Silicone</td>
<td>0.43 ± 0.05</td>
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</table>

Standard tape test method (ASTM D3359).

The strength of H-acceptor layer adhesion to PE was tested using the ASTM D3359B-02 tape test, which was performed using a cross-cut tester (BYK Additives & Instruments, PE-5123). A multi-cut blade comprising 11 blades spaced 1 mm apart was used to cut lattice patterns in samples measuring 20 × 20 mm. A tape (adhesive tape for ASTM IPG 51596) was then applied to the crosshatched area and subsequently pulled off. Adhesion was qualitatively assessed on a 0–5 scale according to ASTM guidelines. The adhesion strength of each H acceptor to PE was rated from 0B (lowest level) to 5B (highest level), according to failure area: 5B denotes no failure area, while 4B–0B indicate failure areas of < 5%, 5–15%, 15–35%, 35–65%, and > 65%, respectively.

Adhesion to other polyolefin materials.

H-acceptors 1-3 were evaluated for their adhesion strength to five different polyolefin materials (polypropylene (PP, WAKO Pure Chemical Industries Ltd., 2.0 × 5.0 × 0.2 cm), cyclic olefin polymer (COP, ZEON, ZEONEX790R, 2.0 × 5.0 × 0.2 cm), cyclic olefin copolymer (COC, Mitsui Chemicals, Inc., APEL APL6015T, 2.0 × 5.0 × 0.2 cm), polybutadiene rubber (PBR, Standard Test Piece, Inc.), and polymethylpentene (PMP, Mitsui Chemicals, Inc., TPX RT18, 2.0 × 5.0 × 0.2 cm)) by the standard tape test method (ASTM D3359). Samples were fabricated using conditions similar to what PE experienced. The thicknesses of the H-acceptor layers were in the range of 250-300 nm, as determined by FE-SEM. These results are summarized in Table S2.

Table S2 | Adhesion strength of H-acceptors 1-3 to other polyolefin materials by ASTM D3359.

<table>
<thead>
<tr>
<th>H acceptor</th>
<th>PP</th>
<th>COP</th>
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<th>PB</th>
<th>PMP</th>
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<td>5B</td>
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<td>5B</td>
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<tr>
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<td>2B</td>
<td>4B</td>
<td>4B</td>
<td>2B</td>
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<td>1B</td>
<td>3B</td>
<td>4B</td>
<td>1B</td>
<td>2B</td>
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**Tacticity of H acceptors 1-3.**

Each H acceptor were converted to poly(methacrylic acid) by refluxing in methanol containing hydrochloric acid overnight. These poly(methacrylic acid)s were methylated with trimethylsilyldiazomethane to poly(methyl methacrylate)s (PMMA)s. These obtained PMMAs were collected by centrifugation, repeatedly washed with methanol, and dried *in vacuo* at 60°C. The tacticity of H acceptors was determined from the $^1$H NMR spectra of the PMMAs derived from each H acceptor.

<table>
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<tr>
<th>H acceptors</th>
<th>Tacticity (mm/mr/rr)</th>
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<tr>
<td>1</td>
<td>64.56/24.66/10.78</td>
</tr>
<tr>
<td>2</td>
<td>3.12/36.23/60.65</td>
</tr>
<tr>
<td>3</td>
<td>3.66/36.78/59.56</td>
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</table>
Thermal vibration calculation using the MM method at the UFF level of theory.

We calculated the enthalpies and entropies of 1–3 at temperatures of 0, 25, 50, 75, and 100 °C, and determined the temperature dependences of these quantities. Since comparison of individual enthalpies and entropies is not possible in view of their dependence on total atomic composition, we also calculated the ratio of entropy to enthalpy (TS/H) to compare the thermodynamic parameters of various H acceptors (Table S4). The T•S/H of 1 showed lowest value among the examined three H acceptors over the whole temperature range. This result shows that 1 is lowest dynamics among three H acceptors. In addition, 2 showed lower T•S/H value than 3. These results showed that the dynamics of H acceptor is increased with increasing the length of introduced alkyl spacer.

Table S4 | Total energy, total energy, temperature, enthalpy corr., Gibbs corr., H, G, T • S, S and T • S/H of stable structure of H acceptors 1-3 obtained from thermal vibrational calculation.

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Figure S30 | Mean-Square Displacement (MSD) of H acceptors on PE obtained from MD simulation.
Figure S31 | FE-SEM image of H acceptor 1 layer on PE. Thickness of 1 layer is 80 nm.

Figure S32 | FE-SEM image of H acceptor 2 layer on PE. Thickness of 2 layer is 75 nm.
Figure S33 | FE-SEM image of H acceptor 3 layer on PE. 
Thickness of 3 layer is 89 nm.
Reference: