Supplementary Information (SI) for Polymer Chemistry.

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Enhancement of the adhesion of polysiloxane-based adhesives through catechol functionalization

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Experimental section

Materials. Dimethoxydimethylsilane (DMDMS; purity: ~98.0%), 3-aminopropyldimethoxymethylsilane (APDMMS; purity: ~97.0%), lauroyl chloride (purity: ~98.0%), 1,1′-carbonyldiimidazole (CDI; purity: ~97.0%) and 3-hydroxytyramine (dopamine) hydrochloride (purity: ~98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Hydrochloric acid (HCl; purity: 35%–37%), triethylamine (Et_3N; purity: ~99.0%), chloroform ($CHCl_3$; purity: ~99.0%), dimethyl sulfoxide (DMSO; purity: ~99.0%), ethyl acetate (AcOEt; purity: ~99.5%), toluene (purity: ~99.0%), methanol (MeOH; purity: ~99.5%), *N*,*N*-dimethylformamide (DMF; purity: ~99.5%), DMSO-d_6 (d: 99.9%), chloroform-*d* ($CDCl_3$; d: 99.8%, with 0.05% TMS), potassium bromide (KBr; purity: ~99.0%) and molecular sieves 3A 1/16 were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. (Osaka, Japan). Ethanol (EtOH; purity: ~99.5%) was purchased from Japan Alcohol Trading Co., Ltd. (Tokyo, Japan). The purified water used in this study was obtained using a water purifier Elix Essential 3, Merck Millipore (Tokyo, Japan). DMSO used in the preparation of polysiloxane-based adhesives (PDMS-PS-Ph$(OH)_2$) containing polydimethylsiloxane (PDMS) and catechol-functionalized polysiloxane (PS-Ph$(OH)_2$) was simply dehydrated by adding molecular sieves 3A, which were dried in an oven at 150°C for over one day. Aluminum (A1050 1.0 × 25 × 50 (mm)) and stainless-steel (SUS304 1.0 × 25 × 50 (mm)) plates were purchased from Engineering Test Service Co., Ltd. (Osaka, Japan).

Measurements. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using an ECX 400 spectrometer (JEOL RESONANCE Inc., Tokyo, Japan). The weight-average molecular weights (M_w) and molecular weight distributions (M_w/number-average molecular weight (M_n)) of the polymers were determined via gel permeation chromatography (GPC) using polystyrene standards. The GPC analysis was performed using a SHIMADZU CTO-20AC system and a SHIMADZU RID-20A instrument (Shimadzu Corporation, Kyoto, Japan) equipped with Shodex KF-803L (bead size: 6 μm; measurable molecular weight range: 1.0×10^2–7.0×10^4) and Shodex KF-805L (bead size: 6 μm; measurable molecular weight range: 1.0×10^2–5.0×10^6) columns. $CHCl_3$ was used as the eluent at a flow rate of 1.0 mL min^{-1} and a temperature of 40°C. Fourier transform infrared (FT-IR) spectra were recorded using an IRSprit-T spectrometer (SHIMADZU CORPORATION, Kyoto, Japan). The tensile shear strength of the two plates adhered using the adhesives was evaluated using a Little Senstar LSC-1/30 instrument (Tokyo Testing Machine Co., Tokyo, Japan) at a rate of 1 mm min^{-1}. The adhesive strength (MPa) was determined by dividing the load at the time of peeling off by the adhered area. The failure mode, either interfacial peeling or cohesive fracture, was evaluated by visual observation, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). SEM and EDX were performed using a Phenom ProX (Thermo Fisher Scientific-JP Co., Tokyo, Japan). For SEM and EDX analyses, the sample surfaces were coated with platinum using an MSP-1S sputter coater (Vacuum Device Inc., Ibaraki, Japan). The adhesive properties against the impact load of the aluminum plates adhered using PDMS-PS-$Ph(OH)_2$ (x:y) ("x:y" represents the compositional ratio between the PDMS component (x) and the PS-$Ph(OH)_2$ component (y); adhered area = 125 mm^2) were evaluated by hitting perpendicular to the adhesive surface using a metal hammer (8 oz $\approx$ 0.23 kg) and monitoring the occurrence of peeling off. Furthermore, the adhesive properties were evaluated under the conditions of high temperatures or temperature fluctuations by suspending a 5 kg weight from the plates adhered using PDMS-PS-$Ph(OH)_2$ (x:y) and subsequent heating in an oven. Thermogravimetric analysis (TGA) was conducted using TGA-50 (SHIMADZU Co., Kyoto, Japan). Samples were preheated at 120°C for 30 min under nitrogen flow (100 mL min^{-1}) to remove residual solvent. After cooling to room temperature, the samples were heated to 1,000°C at a rate of 10°C min^{-1} under nitrogen flow (100 mL min^{-1}). Ultraviolet–visible (UV–Vis) spectra were measured using a JASCO V-630 spectrophotometer (JASCO Corporation, Tokyo, Japan). Differential scanning calorimetry (DSC) analysis was performed using DSC-60 Plus (SHIMADZU Co., Kyoto, Japan). Each sample was placed in an aluminum capsule and cooled to −120°C at a rate of 20°C min^{-1} under nitrogen flow (300 mL min^{-1}). It was then heated from −120°C to 150°C at the same rate. The third heating curve (from −120°C to 150°C at 20°C min^{-1}) was used to eliminate heat history effects from the samples.

Preparation of PDMS-PS-NH_3Cl (8:2) (Scheme 1). First, EtOH (5.252 g) was added to a mixture of DMDMS (2.944 g, 24.0 mmol) and APDMMS (1.010 g, 6.0 mmol). Thereafter, a mixed solution of concentrated HCl (0.591 g, 6.0 mmol) and purified water (0.709 g, 60 mmol, consideration water content in concentrated HCl) was gradually added dropwise to the aforementioned system. This mixed solution was stirred in a closed system at 60°C for approximately 12 h. Thereafter, the solution was transferred to a polypropylene disposable tray (area: 70 cm^2) and heated in an open system at ~50°C to evaporate the solvent (heating time: ~5 h). Afterward, the resulting solid was heated in an oven at 100°C for 2 h to yield 2.284 g of a viscous solid product (PDMS-PS-NH_3Cl (8:2), yield: *ca*. 81%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH_3Cl

[$CH_3SiO(CH_2)_3NH_3Cl$, FW = 153.68 g mol^{-1}] components (PDMS:PS-NH_3Cl compositional ratio = 75:25) were used for the determination. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, Fig. S1b): δ 2.82–2.63 (br, –$SiCH_2CH_2C\mathit{H}_2NH_3$), δ 1.72–1.50 (br, –$SiCH_2C\mathit{H}_2CH_2NH_3$), δ 0.63–0.40 (br, –$SiC\mathit{H}_2CH_2CH_2NH_3$), δ 0.28–−0.19 (br, $C\mathit{H}_3Si$–).

Preparation of PDMS-PS-NH_3Cl (7:3) (Scheme 1). First, EtOH (9.167 g) was added to a mixture of DMDMS (4.294 g, 35.0 mmol) and APDMMS (2.525 g, 15.0 mmol). Afterward, a mixed solution of concentrated HCl (1.478 g, 15.0 mmol) and purified water (0.870 g, 100 mmol, consideration water content in concentrated HCl) was gradually added dropwise to the aforementioned system. The subsequent procedures were similar to those used for the preparation of PDMS-PS-NH_3Cl (8:2), and 4.594 g of a viscous solid product (PDMS-PS-NH_3Cl (7:3)) was obtained (yield: ~92%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH_3Cl [$CH_3SiO(CH_2)_3NH_3Cl$, FW = 153.68 g mol^{-1}] components (PDMS:PS-NH_3Cl compositional ratio = 67:33) were used for the determination. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, Fig. S1c): δ 2.83–2.64 (br, –$SiCH_2CH_2C\mathit{H}_2NH_3$), δ 1.75–1.49 (br, –$SiCH_2C\mathit{H}_2CH_2NH_3$), δ 0.66–0.40 (br, –$SiC\mathit{H}_2CH_2CH_2NH_3$), δ 0.27–−0.15 (br, $C\mathit{H}_3Si$–).

Preparation of PDMS-PS-NH_3Cl (6:4) (Scheme 1). First, EtOH (9.578 g) was added to a mixture of DMDMS (3.680 g, 30.0 mmol) and APDMMS (3.367 g, 20.0 mmol). Thereafter, a mixed solution of concentrated HCl (1.971 g, 20.0 mmol) and purified water (0.560 g, 100 mmol, consideration water content in concentrated HCl) was gradually added dropwise to the aforementioned system. Subsequent procedures were similar to those used for the preparation of PDMS-PS-NH_3Cl (8:2), and 5.316 g of a viscous solid product (PDMS-PS-NH_3Cl (6:4)) was obtained (yield: ~100%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH_3Cl [$CH_3SiO(CH_2)_3NH_3Cl$, FW = 153.68 g mol^{-1}] components (PDMS:PS-NH_3Cl compositional ratio = 59:41) were used for the determination. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, Fig. S1d): δ 2.83–2.63 (br, –$SiCH_2CH_2C\mathit{H}_2NH_3$), δ 1.72–1.50 (br, –$SiCH_2C\mathit{H}_2CH_2NH_3$), δ 0.65–0.42 (br, –$SiC\mathit{H}_2CH_2CH_2NH_3$), δ 0.27–−0.13 (br, $C\mathit{H}_3Si$–).

Preparation of PDMS-PS-NH_3Cl (5:5) (Scheme 1). First, EtOH (9.988 g) was added to a mixture of DMDMS (3.067 g, 25.0 mmol) and APDMMS (4.209 g, 25.0 mmol). Afterward, a mixed solution of concentrated HCl (2.464 g, 25.0 mmol) and purified water (0.250 g, 100 mmol, consideration water content in concentrated HCl) was gradually added dropwise to the aforementioned system. Subsequent procedures were similar to those used for the preparation of PDMS-PS-NH_3Cl (8:2), and 5.889 g of a viscous solid product (PDMS-PS-NH_3Cl (5:5)) was obtained (yield: ~103%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH_3Cl [$CH_3SiO(CH_2)_3NH_3Cl$, FW = 153.68 g mol^{-1}] components (PDMS:PS-NH_3Cl compositional ratio = 49:51) were used for the determination. ^1H NMR (400 MHz, DMSO-d_6, Fig. S1e): δ 2.83–2.64 (br, $-SiCH_2CH_2C\mathit{H}_2NH_3$), δ 1.75–1.49 (br, $-SiCH_2C\mathit{H}_2CH_2NH_3$), δ 0.67–0.41 (br, $-SiC\mathit{H}_2CH_2CH_2NH_3$), δ 0.28–−0.12 (br, $C\mathit{H}_3Si-$).

Preparation of PDMS-PS-NH_3Cl (9:1) (Scheme 1). First, EtOH (3.973 g) was added to a mixture of DMDMS (2.699 g, 22.0 mmol) and APDMMS (0.337 g, 2.0 mmol). Thereafter, a mixed solution of concentrated HCl (0.197 g, 2.0 mmol) and purified water (0.741 g, 48.0 mmol, consideration water content in concentrated HCl) was gradually added dropwise to the aforementioned system. Thereafter, this mixed solution was stirred in a closed system at 60°C for 12 h. The solution was subsequently transferred to a glass sample vial (volume: 10 mL, liquid–gas interface area: ~5 cm^2 when filled with liquid), and the solvent was gradually removed for approximately 24 h. Thereafter, the resulting solid was heated in an oven at 100°C for 2 h to obtain 1.793 g of a liquid product (PDMS-PS-NH_3Cl (9:1), yield: ~91%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH_3Cl [$CH_3SiO(CH_2)_3NH_3Cl$, FW = 153.68 g mol^{-1}] components (PDMS:PS-NH_3Cl compositional ratio = 90:10) were used for the determination. ^1H NMR (400 MHz, $CDCl_3$, Fig. S1a): δ 3.12–2.81 (br, $-SiCH_2CH_2C\mathit{H}_2NH_3$), δ 1.95–1.63 (br, $-SiCH_2C\mathit{H}_2CH_2NH_3$), δ 0.77–0.50 (br, $-SiC\mathit{H}_2CH_2CH_2NH_3$), δ 0.30–−0.09 (br, $C\mathit{H}_3Si-$).

Protection of the primary ammonium groups on the side chains of PDMS-PS-NH_3Cl (8:2) with lauroyl chloride (Scheme S1). First, PDMS-PS-NH_3Cl (8:2) (0.141 g, 1.5 mmol unit) was dissolved in MeOH (1.0 mL). Subsequently, a solution of Et_3N (0.379 g, 3.71 mmol) in DMF (1.0 mL) and a solution of lauroyl chloride (0.828 g, 3.71 mmol) in DMF (1.0 mL) were successively added under vigorous stirring at room temperature, and the mixture was stirred for an additional 30 min. After allowing the mixture to stand for several minutes, the insoluble fraction was collected via decantation. The insoluble fraction was subsequently washed by adding MeOH (2 mL), stirred with a spatula, and decanted. This washing procedure was repeated six times. Finally, the material was dried under reduced pressure to yield 0.0713 g of the product (yield: ~37%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH-lauroyl [$CH_3SiO(CH_2)_3NHC(=O)(CH_2)_{10}CH_3$, FW = 299.52 g mol^{-1}] components (PDMS:PS-NH-lauroyl compositional ratio = 76:24) were used for the determination. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, Fig. S2b): δ 3.27–3.13 (br, $-\mathrm{SiCH_2CH_2C}\mathit{H}_2\mathrm{NHC(=O)}-$), δ 2.23–2.09 (br, $-\mathrm{NHC(=O)C}\mathit{H}_2-$), δ 1.66–1.48 (br, $-\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_2NHC(=O)}-$ and $-\mathrm{NHC(=O)CH_2C}\mathit{H}_2\mathrm{(CH_2)CH_3}$), δ 1.34–1.19 (br, $-\mathrm{NHC(=O)CH_2CH_2(C}\mathit{H}_2\mathrm{)CH_3}$), δ 0.88 (t, J = 6.91, $-\mathrm{NHC(=O)CH_2CH_2(CH_2)C}\mathit{H}_3$), δ 0.50 (t, J = 8.48, $-\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2NHC(=O)}-$), δ 0.13–0.02 (br, $\mathrm{C}\mathit{H}_3\mathrm{Si}-$). GPC analysis revealed the M_w and $M_\mathrm{w}/M_\mathrm{n}$ values of the product as 3.18 × 10^4 and 1.39, respectively (Fig. S3b).

Protection of the primary ammonium groups on the side chains of PDMS-PS-$\mathbf{NH_3Cl}$ (7:3) with lauroyl chloride (Scheme S1). PDMS-PS-$\mathrm{NH_3Cl}$ (7:3) (0.100 g, 1.0 mmol unit) was dissolved in a mixed solvent of DMF (2.0 mL) and purified water (3.0 mL). Subsequently, a solution of $\mathrm{Et_3N}$ (0.169 g, 1.65 mmol) in DMF (0.5 mL) and a solution of lauroyl chloride (0.295 g, 1.32 mmol) in DMF (0.5 mL) were successively added under vigorous stirring at room temperature, and the mixture was stirred for an additional 30 min. MeOH (10 mL) was subsequently added to the mixture, which was stirred at room temperature for a few minutes and left to stand for several minutes. The insoluble fraction was collected via decantation. Next, MeOH (2 mL) was added to the insoluble fraction, stirred using a spatula, and washed via decantation. This washing procedure was repeated 10 times. Finally, the material was dried under reduced pressure to obtain 0.0536 g of the product (yield: ~37%). The ideal chemical formulas of the repeating units of the PDMS [$\mathrm{SiO(CH_3)_2}$, FW = 74.16 g mol^{-1}] and PS-NH-lauroyl [$\mathrm{CH_3SiO(CH_2)_3NHC(=O)(CH_2)_{10}CH_3}$, FW = 299.52 g mol^{-1}] components (PDMS:PS-NH-lauroyl compositional ratio = 68:32) were used for the determination. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, Fig. S2c): δ 3.24–3.15 (br, $-\mathrm{SiCH_2CH_2C}\mathit{H}_2\mathrm{NHC(=O)}-$), δ 2.21–2.12 (br, $-\mathrm{NHC(=O)C}\mathit{H}_2-$), δ 1.66–1.48 (br, $-\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_2NHC(=O)}-$ and $-\mathrm{NHC(=O)CH_2C}\mathit{H}_2\mathrm{(CH_2)CH_3}$), δ 1.34–1.20 (br, $-\mathrm{NHC(=O)CH_2CH_2(C}\mathit{H}_2\mathrm{)CH_3}$), δ 0.88 (t, J = 6.91, $-\mathrm{NHC(=O)CH_2CH_2(CH_2)C}\mathit{H}_3$), δ 0.50 (t, J = 8.32, $-\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2NHC(=O)}-$), δ 0.12–0.02 (br, $\mathrm{C}\mathit{H}_3\mathrm{Si}-$). GPC analysis revealed the M_w and $M_\mathrm{w}/M_\mathrm{n}$ values of the product as 2.97 × 10^4 and 1.35, respectively (Fig. S3c).

Protection of the primary ammonium groups on the side chains of PDMS-PS-$\mathbf{NH_3Cl}$ (6:4) with lauroyl chloride (Scheme S1). PDMS-PS-$\mathrm{NH_3Cl}$ (6:4) (0.107 g, 1.0 mmol unit) was dissolved in a mixed solvent of DMF (2.0 mL) and purified water (3.0 mL). Subsequently, a solution of $\mathrm{Et_3N}$ (0.210 g, 2.05 mmol) in DMF (0.5 mL) and a solution of lauroyl chloride (0.366 g, 1.64 mmol) in DMF (0.5 mL) were successively added under vigorous stirring at room temperature, and the mixture was stirred for an additional 30 min. The insoluble fraction was collected via decantation. Next, MeOH (10 mL) was added to the insoluble fraction, stirred using a spatula, and washed via decantation. This washing procedure was repeated five times. Finally, the material was dried under reduced pressure to obtain 0.0773 g of the product (yield: ~46%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH-lauroyl [$CH_3SiO(CH_2)_3NHC(=O)(CH_2)_{10}CH_3$, FW = 299.52 g mol^{-1}] components (PDMS:PS-NH-lauroyl compositional ratio = 59:41) were used for the determination. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S2d): δ 3.25–3.13 (br, –$SiCH_2CH_2C\mathit{H}_2NHC(=O)$–), δ 2.23–2.12 (br, –$NHC(=O)C\mathit{H}_2$–), δ 1.67–1.46 (br, –$SiCH_2C\mathit{H}_2CH_2NHC(=O)$– and –$NHC(=O)CH_2C\mathit{H}_2(CH_2)CH_3$), δ 1.35–1.20 (br, –$NHC(=O)CH_2CH_2(C\mathit{H}_2)CH_3$), δ 0.88 (t, J = 6.91, –$NHC(=O)CH_2CH_2(CH_2)C\mathit{H}_3$), δ 0.55–0.45 (br, –$SiC\mathit{H}_2CH_2CH_2NHC(=O)$–), δ 0.14–0.02 (br, $C\mathit{H}_3Si$–). GPC analysis revealed the M_w and M_w/M_n values of the product as 3.39×10^4 and 1.54, respectively (Fig. S3d).

Protection of the primary ammonium groups on the side chains of PDMS-PS-NH_3Cl (5:5) with lauroyl chloride (Scheme S1). PDMS-PS-NH_3Cl (5:5) (0.115 g, 1.0 mmol unit) was dissolved in a mixed solvent of DMF (2.0 mL) and purified water (4.0 mL). Subsequently, a solution of Et_3N (0.261 g, 2.55 mmol) in DMF (0.5 mL) and a solution of lauroyl chloride (0.455 g, 2.04 mmol) in DMF (0.5 mL) were successively added under vigorous stirring at room temperature, and the mixture was stirred for an additional 30 min. The subsequent washing via decantation was performed using the same method as that employed for PDMS-PS-NH_3Cl (6:4), yielding 0.0998 g of the product (yield: ~52%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH-lauroyl [$CH_3SiO(CH_2)_3NHC(=O)(CH_2)_{10}CH_3$, FW = 299.52 g mol^{-1}] components (PDMS:PS-NH-lauroyl compositional ratio = 47:53) were used for the determination. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S2e): δ 3.24–3.12 (br, –$SiCH_2CH_2C\mathit{H}_2NHC(=O)$–), δ 2.23–2.12 (br, –$NHC(=O)C\mathit{H}_2$–), δ 1.66–1.48 (br, –$SiCH_2C\mathit{H}_2CH_2NHC(=O)$– and –$NHC(=O)CH_2C\mathit{H}_2(CH_2)CH_3$), δ 1.35–1.20 (br, –$NHC(=O)CH_2CH_2(C\mathit{H}_2)CH_3$), δ 0.88 (t, J = 6.91, –$NHC(=O)CH_2CH_2(CH_2)C\mathit{H}_3$), δ 0.55–0.45 (br, –$SiC\mathit{H}_2CH_2CH_2NHC(=O)$–), δ 0.12–0.02 (br, $C\mathit{H}_3Si$–). GPC analysis revealed the M_w and M_w/M_n values of the product as 4.00×10^4 and 1.76, respectively (Fig. S3e).

Protection of the primary ammonium groups on the side chains of PDMS-PS-NH_3Cl (9:1) with lauroyl chloride (Scheme S1). PDMS-PS-NH_3Cl (9:1) (0.128 g, 1.5 mmol unit) was dissolved in MeOH (1.0 mL). Subsequently, a solution of Et_3N (0.435 g, 4.26 mmol) in DMF (1.0 mL) and a solution of lauroyl chloride (0.828 g, 4.26 mmol) in DMF (1.0 mL) were successively added under vigorous stirring at room temperature, and the mixture was stirred for an additional 30 min. MeOH (5.0 mL) was subsequently added to the mixture, stirred at room temperature for a few minutes, and left to stand for several more minutes. The insoluble fraction was collected via decantation. Thereafter, the insoluble fraction was then washed by adding MeOH (2 mL), stirred using a spatula, and decanted. This washing procedure was repeated six times. Finally, the material was dried under reduced pressure to obtain 0.0680 g of the product (yield: ~45%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-NH-lauroyl [$CH_3SiO(CH_2)_3NHC(=O)(CH_2)_{10}CH_3$, FW = 299.52 g mol^{-1}] components (PDMS:PS-NH-lauroyl compositional ratio = 88:12) were used for the determination. ^1H NMR (400 MHz, $CDCl_3$, Fig. S2a): δ 3.27–3.16 (br, $–SiCH_2CH_2CH_2NHC(=O)–$), δ 2.19–2.10 (br, $–NHC(=O)CH_2–$), δ 1.66–1.48 (br, $–SiCH_2CH_2CH_2NHC(=O)–$ and $–NHC(=O)CH_2CH_2(CH_2)CH_3$), δ 1.35–1.20 (br, $–NHC(=O)CH_2CH_2(CH_2)CH_3$), δ 0.88 (t, J = 6.91, $–NHC(=O)CH_2CH_2(CH_2)CH_3$), δ 0.50 (t, J = 8.48, $–SiCH_2CH_2CH_2NHC(=O)–$), δ 0.13–0.01 (br, $CH_3Si–$). GPC analysis revealed the M_w and M_w/M_n values of the product as 2.30×10^4 and 1.32, respectively (Fig. S3a).

Preparation of PDMS-PS-Ph(OH)$_2$ (8:2) (Scheme 2). Et_3N (0.153 g, 1.50 mmol) dissolved in DMSO (1.5 mL) and CDI (0.251 g, 1.50 mmol) dissolved in DMSO (1.5 mL) were successively added to a PDMS-PS-NH_3Cl (8:2) solution (0.470 g, 5.0 mmol unit) in DMSO (5 mL), and the mixture was stirred at room temperature for 15 min. Subsequently, dopamine hydrochloride (0.484 g, 2.5 mmol) dissolved in DMSO (2.5 mL) and Et_3N (0.256 g, 2.5 mmol) dissolved in DMSO (2.5 mL) were mixed and added to the reaction mixture, which was subsequently stirred at 50°C for 2 h. The reaction solution was poured into AcOEt (450 mL), and the precipitated white solid was collected via suction filtration. Thereafter, the crude product was washed with purified water (20 mL), and the insoluble portion was recovered via decantation. The product was dissolved in EtOH (~1.5 mL) and poured into purified water. The precipitated product was recovered via decantation (repeated twice) to yield the product PDMS-PS-Ph(OH)$_2$ (8:2). The water content was calculated as ~45% using the weights before and after lyophilization. The yield was calculated considering the water content (0.4799 g containing 45% water; yield: ~43%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-Ph(OH)$_2$ [$CH_3SiO(CH_2)_3NHC(=O)NH(CH_2)_2C_6H_3(OH)_2$, FW = 296.39 g mol^{-1}] components

(PDMS:PS-Ph(OH)$_2$ compositional ratio = 78:22) were used for the determination. FT-IR (KBr, Fig. 1b): 1628 and 1577 cm^{-1} (urea bond). ^{1}H NMR (400 MHz, DMSO-d_6, Fig. 2b): δ 8.83–8.55 (br, –NHC(=O)NHCH$_2$CH$_2$C$_6$H$_3$(O*H*)$_2$), δ 6.64–6.53 and δ 6.43–6.34 (br, –NHC(=O)NHCH$_2$CH$_2$C$_6$*H*$_3$(OH)$_2$), δ 6.01–5.84 and δ 5.84–5.68 (br, –N*H*C(=O)N*H*–), δ 3.14–3.05 (br, –NHC(=O)NHC*H*$_2$CH$_2$C$_6$H$_3$(OH)$_2$), δ 3.00–2.86 (br, –SiCH$_2$CH$_2$C*H*$_2$NHC(=O)NH–), δ 2.49–2.40 (br, –NHC(=O)NHCH$_2$C*H*$_2$C$_6$H$_3$(OH)$_2$, overlapping with solvent), δ 1.43–1.29 (br, –SiCH$_2$C*H*$_2$CH$_2$NHC(=O)NH–), δ 0.52–0.32 (br, –SiC*H*$_2$CH$_2$CH$_2$NHC(=O)NH–), δ 0.20–−0.20 (br, C*H*$_3$Si–).

Owing to partial insolubility upon drying, the product was stored as an EtOH solution (~30 mL). When using as an adhesive, it was concentrated using a rotary evaporator (to 5 mL at 40°C) and subsequently poured into purified water (~100 mL), and the precipitated solid was applied to the substrates.

Preparation of PDMS-PS-Ph(OH)$_2$ (7:3) (Scheme 2). Et$_3$N (0.202 g, 1.98 mmol) dissolved in DMSO (2 mL) and CDI (0.332 g, 1.98 mmol) dissolved in DMSO (2 mL) were successively added to a solution of PDMS-PS-NH$_3$Cl (7:3) (0.502 g, 5.0 mmol unit) in DMSO (5 mL), and the mixture was stirred at room temperature for 15 min. Subsequently, dopamine hydrochloride (0.639 g, 3.3 mmol) dissolved in DMSO (3 mL) and Et$_3$N (0.337 g, 3.3 mmol) dissolved in DMSO (3 mL) were mixed and added to the reaction mixture, followed by stirring at 50°C for 2 h. The subsequent procedures were almost identical to those used for the preparation of PDMS-PS-Ph(OH)$_2$ (8:2), obtaining a viscous solid product (PDMS-PS-Ph(OH)$_2$ (7:3)). The water content was calculated as ~46% using the weights before and after lyophilization. The yield was calculated considering the water content (0.545 g containing 46% water; yield: ~42%). The ideal chemical formulas of the repeating units of the PDMS [SiO(CH$_3$)$_2$, FW = 74.16 g mol^{-1}] and PS-Ph(OH)$_2$ [CH$_3$SiO(CH$_2$)$_3$NHC(=O)NH(CH$_2$)$_2$C$_6$H$_3$(OH)$_2$, FW = 296.39 g mol^{-1}] components (PDMS:PS-Ph(OH)$_2$ compositional ratio = 70:30) were used for the determination. FT-IR (KBr, Fig. 1c): 1628 and 1581 cm^{-1} (urea bond). ^{1}H NMR (400 MHz, DMSO-d_6, Fig. 2c): δ 8.82–8.58 (br, –NHC(=O)NHCH$_2$CH$_2$C$_6$H$_3$(O*H*)$_2$), δ 6.66–6.52 and δ 6.44–6.34 (br, –NHC(=O)NHCH$_2$CH$_2$C$_6$*H*$_3$(OH)$_2$), δ 6.06–5.66 (br, –N*H*C(=O)N*H*–), δ 3.15–3.06 (br, –NHC(=O)NHC*H*$_2$CH$_2$C$_6$H$_3$(OH)$_2$), δ 3.01–2.86 (br, –SiCH$_2$CH$_2$C*H*$_2$NHC(=O)NH–), δ 2.48–2.41 (br, –NHC(=O)NHCH$_2$C*H*$_2$C$_6$H$_3$(OH)$_2$, overlapping with solvent), δ 1.43–1.29 (br, –SiCH$_2$C*H*$_2$CH$_2$NHC(=O)NH–), δ 0.53–0.34 (br, –SiC*H*$_2$CH$_2$CH$_2$NHC(=O)NH–), δ 0.20–−0.17 (br, C*H*$_3$Si–).

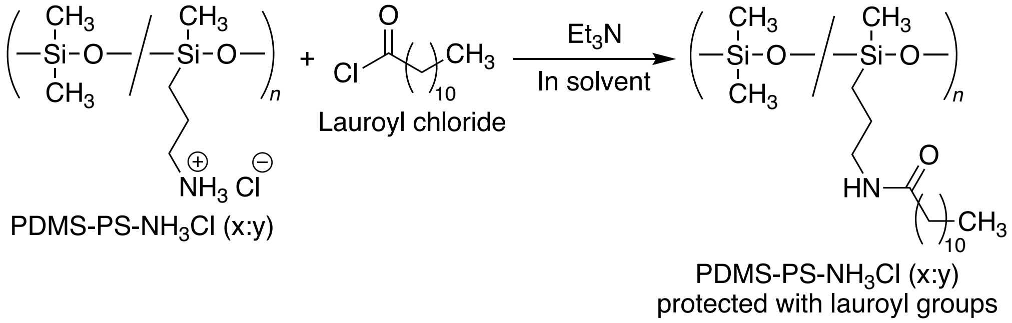
Preparation of PDMS-PS-Ph(OH)$_2$ (6:4) (Scheme 2). Et_3N (0.251 g, 2.46 mmol) dissolved in DMSO (2.5 mL) and CDI (0.412 g, 2.46 mmol) dissolved in DMSO (2.5 mL) were successively added to a solution of PDMS-PS-NH_3Cl (6:4) (0.534 g, 5.0 mmol unit) in DMSO (5 mL), and the mixture was stirred at room temperature for 15 min. Subsequently, dopamine hydrochloride (0.793 g, 4.1 mmol) dissolved in DMSO (4.0 mL) and Et_3N (0.419 g, 4.1 mmol) dissolved in DMSO (4.0 mL) were mixed and added to the reaction mixture, followed by stirring at 50°C for 2 h. The subsequent procedures were similar to those used for the preparation of PDMS-PS-Ph(OH)$_2$ (8:2), yielding a powdery product (PDMS-PS-Ph(OH)$_2$ (6:4)). The water content was calculated as ~46% using the weights before and after lyophilization. The yield was calculated considering the water content (0.698 g containing 46% water; yield: ~49%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-Ph(OH)$_2$ [$CH_3SiO(CH_2)_3NHC(=O)NH(CH_2)_2C_6H_3(OH)_2$, FW = 296.39 g mol^{-1}] components (PDMS:PS-Ph(OH)$_2$ compositional ratio = 65:35) were used for the determination. FT-IR (KBr, Fig. 1d): 1632 and 1575 cm^{-1} (urea bond). ^{1}H NMR (400 MHz, DMSO-d_6, Fig. 2d): δ 9.05–8.37 (br, $–NHC(=O)NHCH_2CH_2C_6H_3(OH)_2$), δ 6.66–6.51 and δ 6.44–6.34 (br, $–NHC(=O)NHCH_2CH_2C_6H_3(OH)_2$), δ 6.12–5.63 (br, $–NHC(=O)NH–$), δ 3.17–3.04 (br, $–NHC(=O)NHCH_2CH_2C_6H_3(OH)_2$), δ 3.03–2.86 (br, $–SiCH_2CH_2CH_2NHC(=O)NH–$), δ 2.48–2.41 (br, $–NHC(=O)NHCH_2CH_2C_6H_3(OH)_2$, overlapping with solvent), δ 1.45–1.29 (br, $–SiCH_2CH_2CH_2NHC(=O)NH–$), δ 0.53–0.32 (br, $–SiCH_2CH_2CH_2NHC(=O)NH–$), δ 0.21–−0.16 (br, $CH_3Si–$).

Preparation of PDMS-PS-Ph(OH)$_2$ (5:5) (Scheme 2). Et_3N (0.313 g, 3.06 mmol) dissolved in DMSO (3.0 mL) and CDI (0.513 g, 3.06 mmol) dissolved in DMSO (3.0 mL) were successively added to a solution of PDMS-PS-NH3Cl (5:5) (0.574 g, 5.0 mmol unit) in DMSO (5.0 mL), and the mixture was stirred at room temperature for 15 min. Subsequently, dopamine hydrochloride (0.987 g, 5.1 mmol) dissolved in DMSO (5.0 mL) and Et_3N (0.521 g, 5.1 mmol) dissolved in DMSO (5.0 mL) were mixed and added to the reaction mixture, followed by stirring at 50°C for 2 h. The subsequent procedures were similar to those used for the preparation of PDMS-PS-Ph(OH)$_2$ (8:2), yielding a viscous solid product (PDMS-PS-Ph(OH)$_2$ (5:5)). The water content was calculated as ~37% using the weights before and after lyophilization. The yield was calculated considering the water content (0.911 g containing 37% water; yield: ~64%). The ideal chemical formulas of the repeating units of the PDMS [$SiO(CH_3)_2$, FW = 74.16 g mol^{-1}] and PS-Ph(OH)$_2$

[$\mathrm{CH_3SiO(CH_2)_3NHC(=O)NH(CH_2)_2C_6H_3(OH)_2}$, FW = 296.39 g mol^{-1}] components (PDMS:PS-Ph$\mathrm{(OH)_2}$ compositional ratio = 52:48) were used for the determination. FT-IR (KBr, Fig. 1e): 1626 and 1575 cm^{-1} (urea bond). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, Fig. 2e): δ 8.81–8.56 (br, $\mathrm{–NHC(=O)NHCH_2CH_2C_6H_3(O}\mathit{H}\mathrm{)_2}$), δ 6.65–6.52 and δ 6.44–6.35 (br, $\mathrm{–NHC(=O)NHCH_2CH_2C_6}\mathit{H}\mathrm{_3(OH)_2}$), δ 6.10–5.66 (br, $\mathrm{–N}\mathit{H}\mathrm{C(=O)N}\mathit{H}\mathrm{–}$), δ 3.15–3.06 (br, $\mathrm{–NHC(=O)NHC}\mathit{H}\mathrm{_2CH_2C_6H_3(OH)_2}$), δ 3.01–2.87 (br, $\mathrm{–SiCH_2CH_2C}\mathit{H}\mathrm{_2NHC(=O)NH–}$), δ 2.48–2.40 (br, $\mathrm{–NHC(=O)NHCH_2C}\mathit{H}\mathrm{_2C_6H_3(OH)_2}$, overlapping with solvent), δ 1.43–1.29 (br, $\mathrm{–SiCH_2C}\mathit{H}\mathrm{_2CH_2NHC(=O)NH–}$), δ 0.56–0.33 (br, $\mathrm{–SiC}\mathit{H}\mathrm{_2CH_2CH_2NHC(=O)NH–}$), δ 0.22–−0.16 (br, $\mathrm{C}\mathit{H}\mathrm{_3Si–}$).

Preparation of PDMS-PS-Ph(OH)$_2$ (9:1) (Scheme 2). $\mathrm{Et_3N}$ (0.061 g, 0.60 mmol) dissolved in a mixture of DMSO (0.36 mL) and toluene (0.24 mL), and CDI (0.101 g, 0.60 mmol) dissolved in the same solvents (DMSO (0.36 mL) and toluene (0.24 mL)) were successively added to a solution of PDMS-PS-$\mathrm{NH_3Cl}$ (9:1) (0.411 g, 5.0 mmol unit) in a mixture of DMSO (3.0 mL) and toluene (2.0 mL). The mixture was stirred at room temperature for 15 min. Subsequently, dopamine hydrochloride (0.194 g, 1.0 mmol) dissolved in a mixture of DMSO (0.6 mL) and toluene (0.4 mL) along with $\mathrm{Et_3N}$ (0.102 g, 1.0 mmol) dissolved in the same solvents (DMSO (0.6 mL) and toluene (0.4 mL)) were added to the reaction mixture and stirred at 50°C for 2 h. The reaction solution was subsequently poured into AcOEt (300 mL). The precipitated salts were removed via suction filtration, and AcOEt was evaporated. Finally, the product was washed with purified water (300 mL), and the insoluble portion was separated via decantation. The product was dissolved in EtOH and poured into purified water. The precipitated product was recovered via decantation (repeated twice) to yield the product PDMS-PS-Ph$\mathrm{(OH)_2}$ (9:1). The water content was calculated as ~25% using the weights before and after lyophilization. The yield was calculated considering the water content (0.243 g containing 25% water; yield: ~40%). The ideal chemical formulas of the repeating units of the PDMS [$\mathrm{SiO(CH_3)_2}$, FW = 74.16 g mol^{-1}] and PS-Ph$\mathrm{(OH)_2}$ [$\mathrm{CH_3SiO(CH_2)_3NHC(=O)NH(CH_2)_2C_6H_3(OH)_2}$, FW = 296.39 g mol^{-1}] components (PDMS:PS-Ph$\mathrm{(OH)_2}$ compositional ratio = 92:8) were used for the determination. FT-IR (KBr, Fig. 1a): 1638 and 1557 cm^{-1} (urea bond). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, Fig. 2a): δ 8.85–8.49 (br, $\mathrm{–NHC(=O)NHCH_2CH_2C_6H_3(O}\mathit{H}\mathrm{)_2}$), δ 6.67–6.51 and δ 6.47–6.32 (br, $\mathrm{–NHC(=O)NHCH_2CH_2C_6}\mathit{H}\mathrm{_3(OH)_2}$), δ 5.93–5.81 and δ 5.75– 5.64 (br, $\mathrm{–N}\mathit{H}\mathrm{C(=O)N}\mathit{H}\mathrm{–}$), δ 3.15–3.06 (br, $\mathrm{–NHC(=O)NHC}\mathit{H}\mathrm{_2CH_2C_6H_3(OH)_2}$), δ 2.97–2.87 (br, $\mathrm{–SiCH_2CH_2C}\mathit{H}\mathrm{_2NHC(=O)NH–}$), δ 2.48–2.40 (br, $\mathrm{–NHC(=O)NHCH_2C}\mathit{H}\mathrm{_2C_6H_3(OH)_2}$, overlapping with solvent), δ 1.43–1.29 (br,

–$\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_2NHC(=O)NH}$–), δ 0.52–0.34 (br, –$\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2NHC(=O)NH}$–), δ 0.16–−0.15 (br, $\mathrm{C}\mathit{H}_3\mathrm{Si}$–).



Scheme S1 Protection of the primary ammonium groups on the side chains of PDMS-PS-NH_3Cl (x:y) using lauroyl chloride.

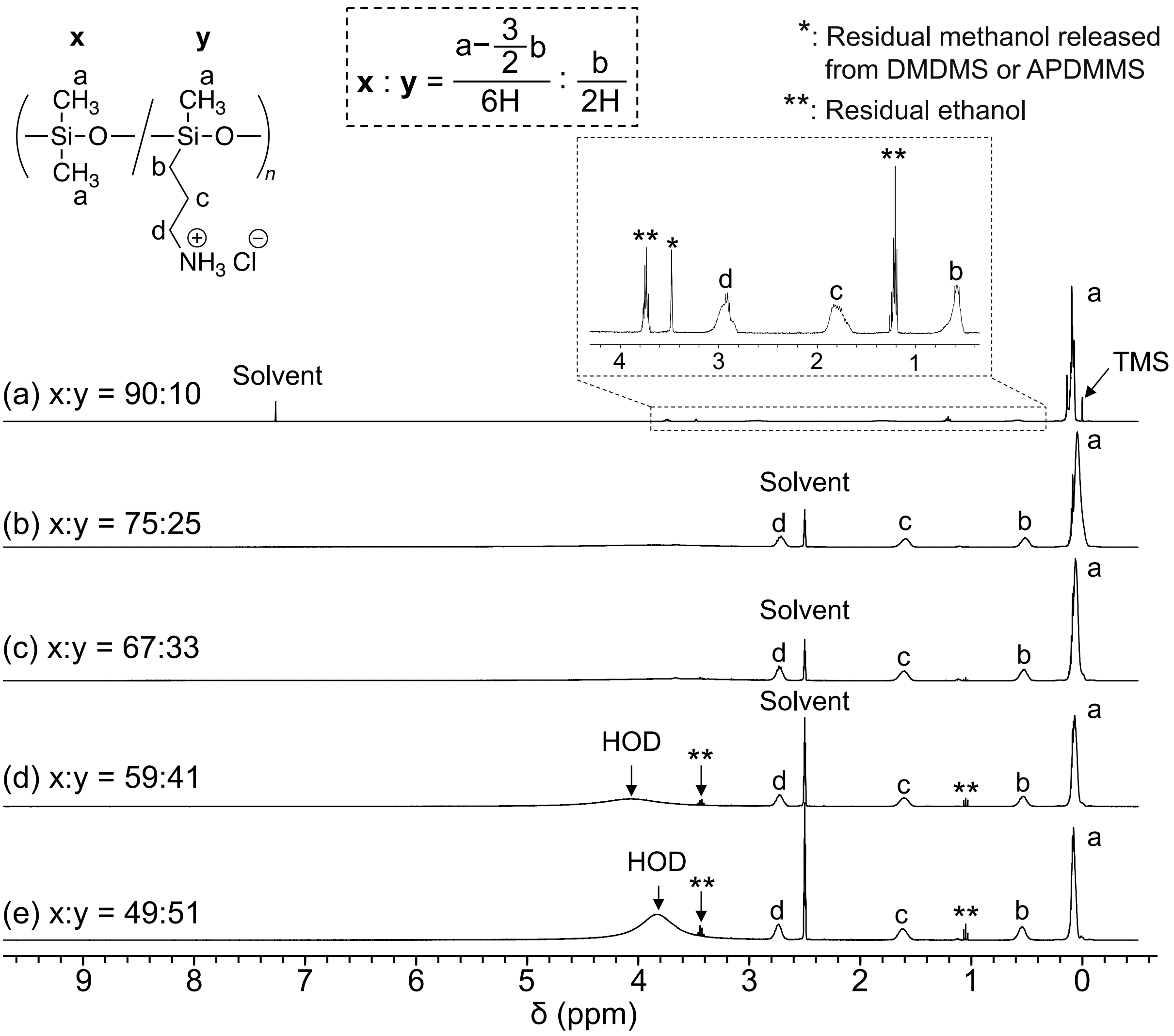


Fig. S1 ^{1}H NMR spectra in DMSO-d_6 of PDMS-PS-NH$_3$Cl (x:y); x:y = (a) 9:1, (b) 8:2, (c) 7:3, (d) 6:4 and (e) 5:5. Chemical shifts were referenced to DMSO-d_6 (δ 2.5).

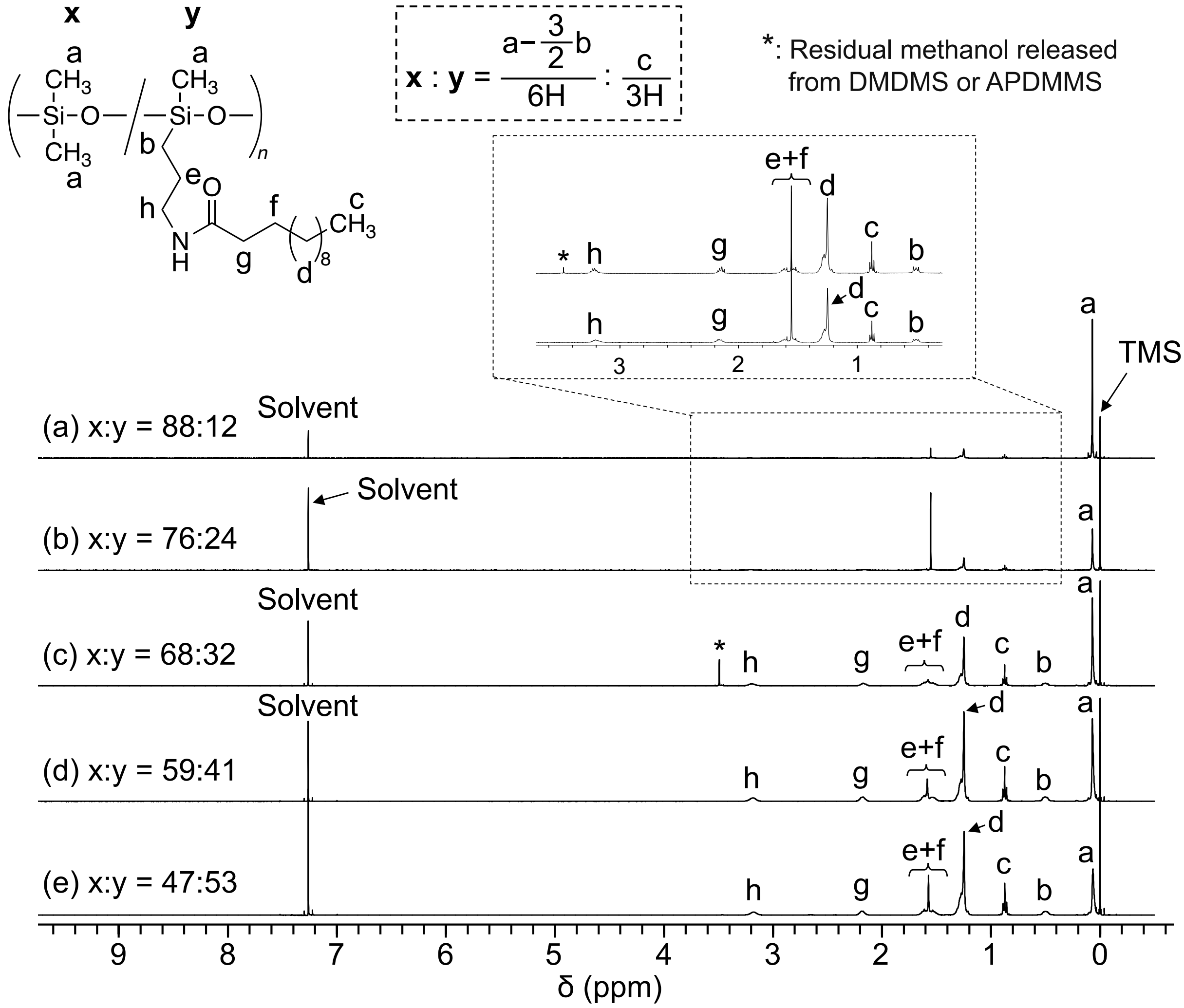


Fig. S2 ^{1}H NMR spectra in $CDCl_3$ of the products obtained by reacting the primary ammonium group in PDMS-PS-NH_3Cl (x:y); x:y = (a) 9:1, (b) 8:2, (c) 7:3, (d) 6:4 and (e) 5:5 with lauroyl chloride. Chemical shifts were referenced to DMSO-d_6 (δ 2.5).

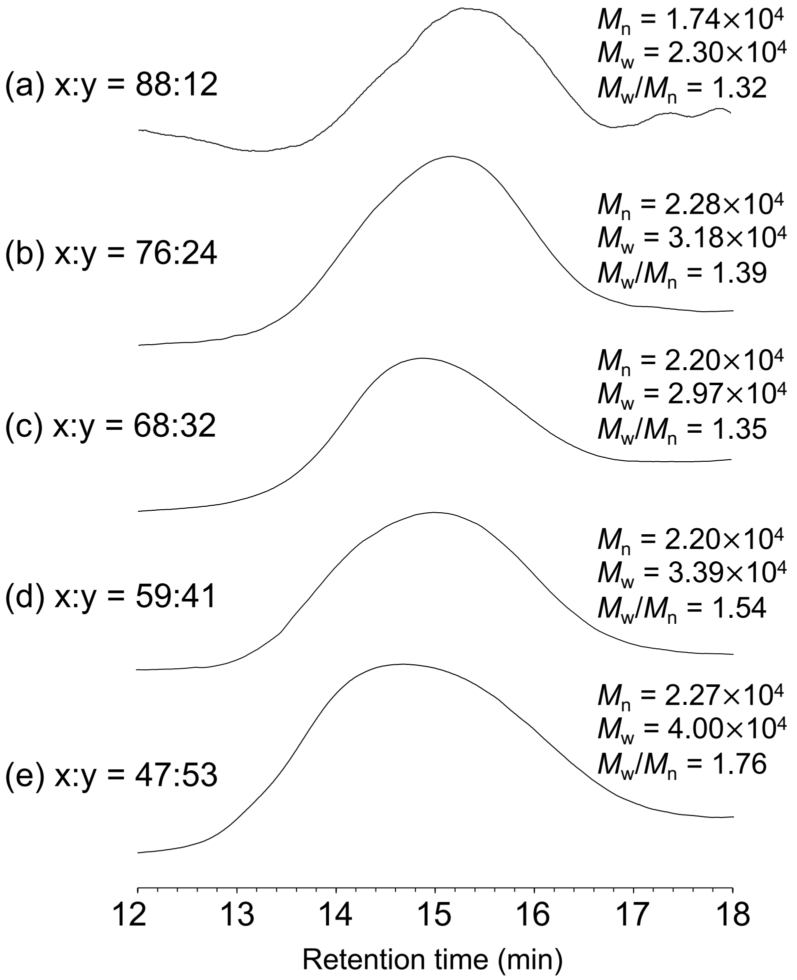


Fig. S3 GPC curves of the products obtained by reacting the primary ammonium group in PDMS-PS-NH_3Cl (x:y); x:y = (a) 9:1, (b) 8:2, (c) 7:3, (d) 6:4 and (e) 5:5 with lauroyl chloride. Chloroform and polystyrene were used as the eluent and standard, respectively.

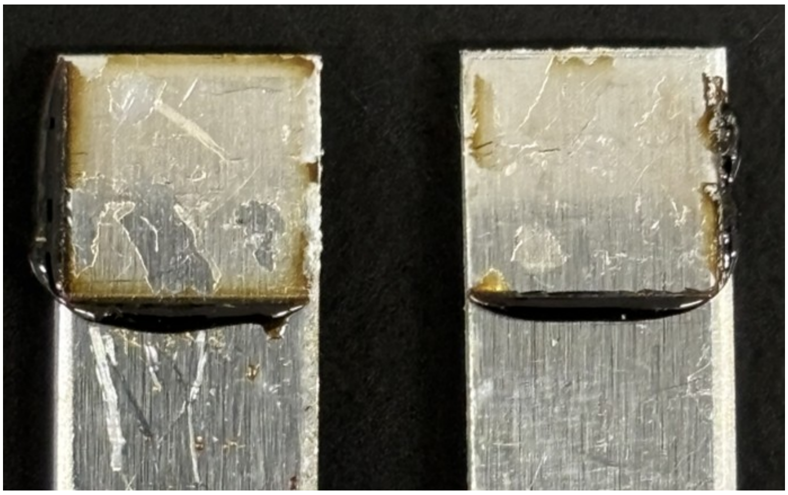


Fig. S4 Fracture surfaces of aluminum plates adhered using PDMS-PS-Ph$(OH)_2$ (7:3).

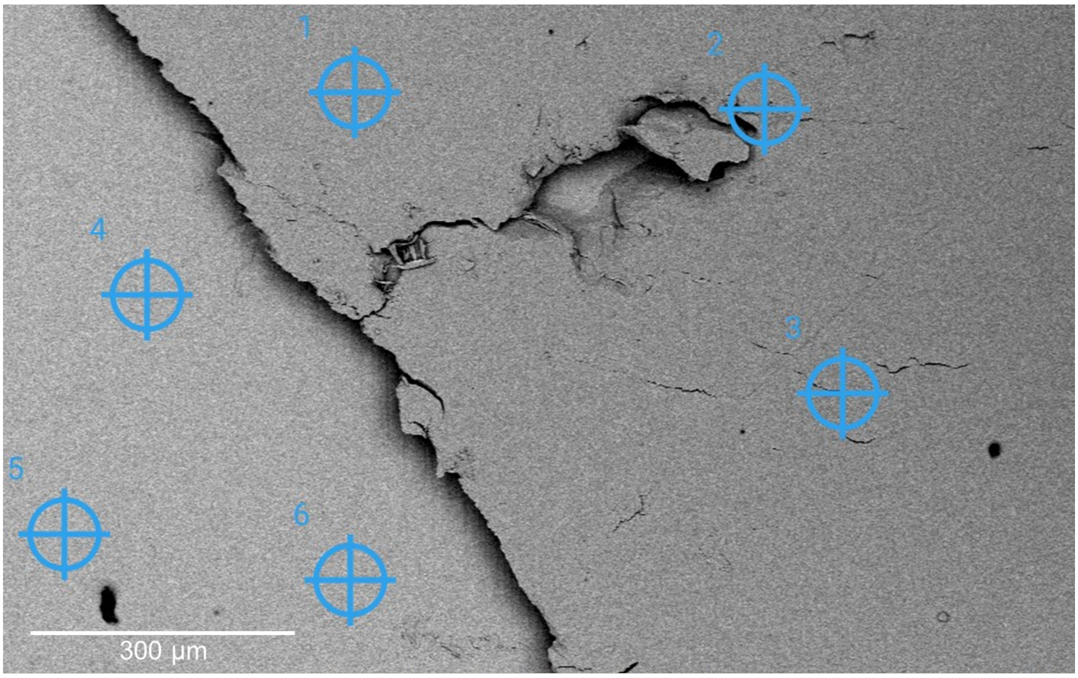
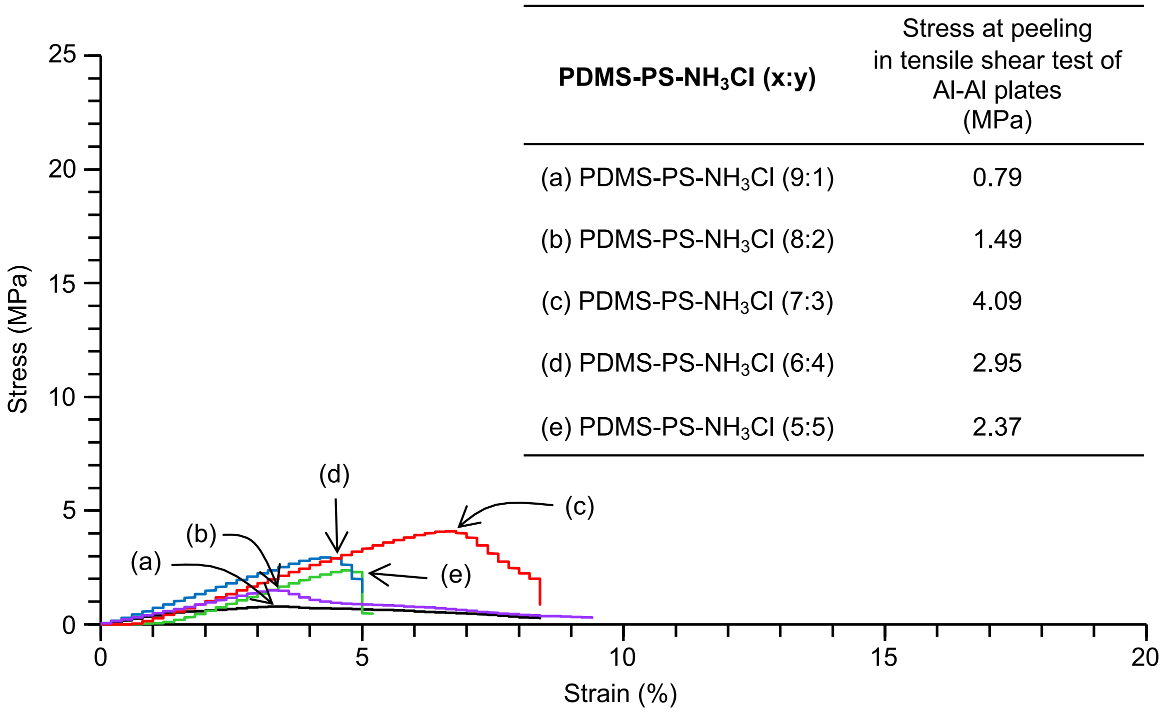


Fig. S5 SEM image of fracture surface (after platinum coating) of an aluminum plate adhered using PDMS-PS-Ph$(OH)_2$ (7:3). The six blue spots indicate the locations where EDX analysis, summarized in Table S1, was performed.

Table S1 Atomic concentration at the six spots on the adhered surface of the aluminum plate in the SEM image shown in Fig. S5, as determined by EDX analysis.

Element symbol	Atomic concentration [%]					
	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
C	23.36	34.66	28.45	12.03	11.37	6.27
N	7.67	7.59	8.25	2.44	3.16	0.00
O	13.43	17.16	17.27	1.66	2.08	0.26
Al	0.00	0.00	0.00	75.96	76.09	83.61
Si	32.72	25.70	28.08	0.00	0.00	0.45
Pt	22.82	14.89	17.95	7.91	7.30	9.41



PDMS-PS-NH_3Cl (x:y)	Stress at peeling in tensile shear test of Al-Al plates (MPa)
(a) PDMS-PS-NH_3Cl (9:1)	0.79
(b) PDMS-PS-NH_3Cl (8:2)	1.49
(c) PDMS-PS-NH_3Cl (7:3)	4.09
(d) PDMS-PS-NH_3Cl (6:4)	2.95
(e) PDMS-PS-NH_3Cl (5:5)	2.37

Fig. S6 Stress–strain curves evaluated via the tensile shear tests of the aluminum plates adhered using PDMS-NH_3Cl (x:y); x:y = (a) 9:1, (b) 8:2, (c) 7:3, (d) 6:4 and (e) 5:5.

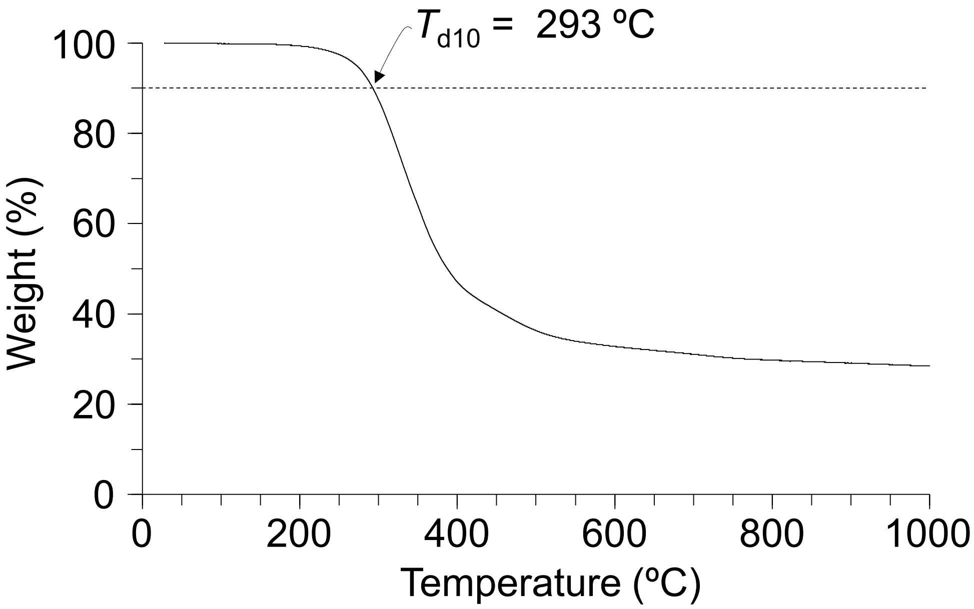


Fig. S7 TGA thermogram of the cured PDMS-PS-Ph(OH)$_2$ (7:3) sample (heat-treated at 150°C for 12 h) under a nitrogen flow of 100 mL min^{-1}.

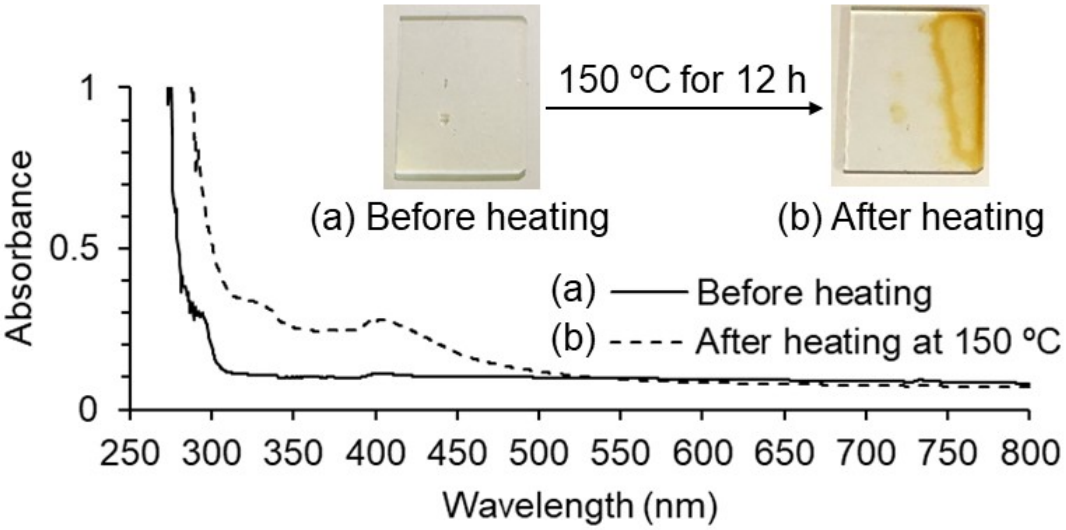


Fig. S8 UV–Vis absorption spectra of the PDMS-PS-Ph(OH)$_2$ (7:3) coating on a glass plate: (a) before and (b) after heating at 120°C for 12 h.

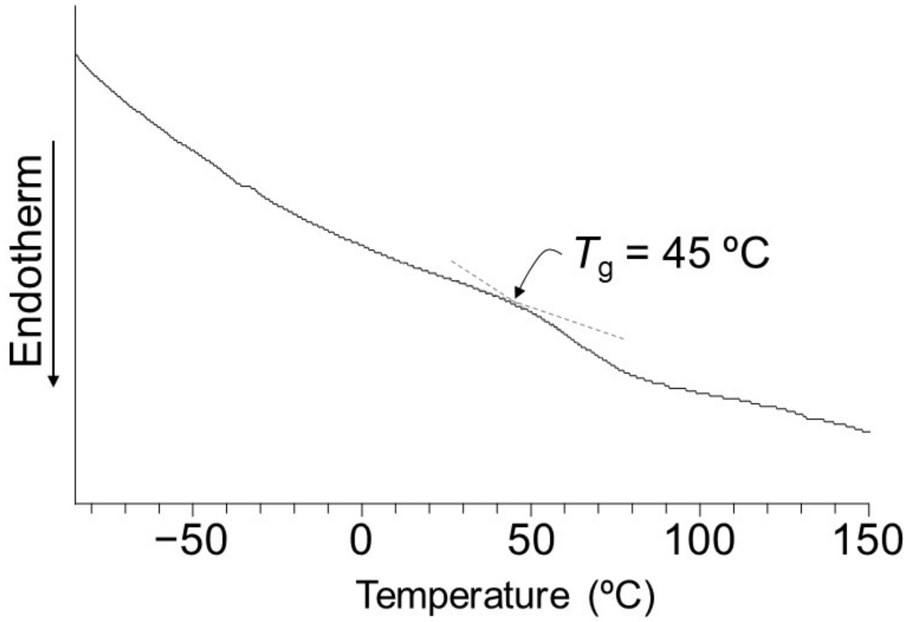


Fig. S9 DSC curve of the cured PDMS-PS-Ph(OH)$_2$ (7:3) sample (heat-treated at 150°C for 12 h) under a nitrogen flow of 300 mL min^{-1}.