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Electronic Supplementary Information

Aziridine-Functionalized Polydimethylsiloxanes for Tailorable Polymeric Scaffolds: Aziridine as a Clickable Moiety for Structural Modification of Materials

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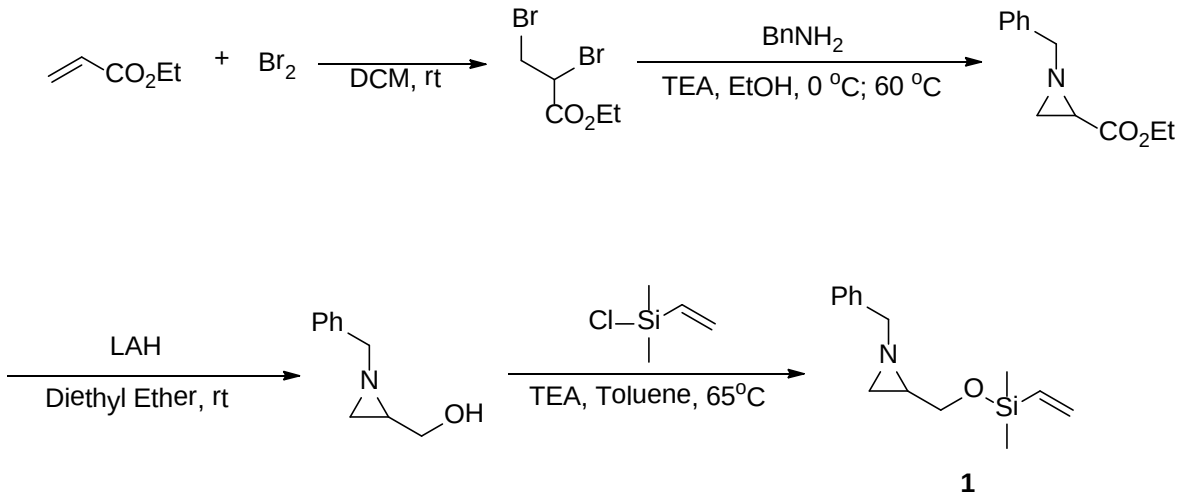
1. Experimental Details

Materials: All reagents were used as supplied unless otherwise specified. All organic solvents were purchased from Daejung while water was purified using an Aqua MAX-Basic System (deionized water, electrical resistivity of which is ~18.2 MΩ·cm). Sylgard 184 elastoemr kit from Dow Corning was used.

Characterization: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-NMR Advance-500 using $CDCl_3$ as solvent and residual solvents as an internal standard. Chemical shifts are expressed in parts per million (ppm) related to internal TMS and coupling constant (*J*) are in Hertz. MS (ESI-QTOF) measurements were recorded on a Bruker compat Q-TOF MS. All XPS measurements were carried out on a Thermo Scientific K-Alpha XPS machine with a monochromated Al K_α source. UV-vis spectra were measured using Agilent technologies-Agilent 8453 UV-Vis spectrometer. For UV-vis absorbance measurements, an intact PDMS film was used as blank. The film thickness was kept constant (~2 mm) across samples. Although we have attempted to keep the thickness of film across samples relatively constant (~2 mm), there is inevitably variation at the microscopic level to some extent, which does not affect the overall trend of λ_{max} as a function of aziridine's mass ratio. Photoluminescence spectra were recorded using a Hitachi F-7000 Fluorescence spectrophotometer. We determined the tensile strength of PDMS and aziPDMS by using a Universal Testing Machine (UTM; WL 2100).

2. Synthetic Procedures



Scheme S1. Synthetic scheme for the preparation of 1-benzyl-2-(((dimethyl(vinyl)silyl)oxy)-methyl)aziridine (**1**).

Synthesis of ethyl 2,3-dibromopropanoate[1]

To a solution of ethyl acrylate (16.3 mL, 150 mmol) in DCM (75 mL), bromine (7.7 mL, 150 mmol) was added dropwise at 0 °C during 20 min under an inert atmosphere. The reaction mixture was allowed to stir at 0 °C for 1 h and then at r.t for 3 h. After completion of the reaction, the mixture was quenched with saturated $Na_2S_2O_3$ aqueous solution followed by extraction of the mixture with DCM and water and then separation of the organic layer gave the dibromo compound in 97% yield (37.6 g).The analytical data for this compound were in excellent agreement with the reported data.[2]

Synthesis of ethyl 1-benzylaziridine-2-carboxylate

Ethyl 2,3-dibromopropanoate (8 g, 30.8 mmol) and trimethylamine (8.5 mL, 69.6 mmol) were sequentially added to a solution of benzylamine (3.4 mL, 30.8 mmol) in anhydrous ethanol (60 mL) at 0 °C under N_2 atmosphere. The mixture was stirred at 60 °C for 1 hour. The solvent of mixture was evaporated and the reaction crude was extracted with dichloromethane. The organic phase was dried with magnesium sulfate, and the solvent was removed under reduced pressure at room temperature. The resulting crude was purified by flash column chromatography to obtain the corresponding product in 80% yield (6.2 g) as a white solid. The analytical data for this compound were in excellent agreement with the reported data.[3]

Synthesis of (1-benzylaziridin-2-yl)methanol

Lithium aluminum hydride (2.29 g, 60.4 mmol)) was slowly added to a solution of ethyl 1-benzylaziridine-2-carboxylate (6.2 g, 30.2 mmol) in diethylether (130 ml). The mixture was stirred at room temperature for 3 hours. The reaction mixture was quenched with water (2.3 mL) and 15% NaOH aqueous solution (2.3 mL), then water (6.9 mL) After the filteration of the mixture, the crude compound was extracted with ethyl acetate. The organic phase was dried with magnesium sulfate, and the solvent was removed under reduced pressure. The product was obtained in 87% yield (4.31 g) as a yellowish powder. The analytical data for this compound were in excellent agreement with the reported data.[4]

Synthesis of 1-benzyl-2-(((dimethyl(vinyl)silyl)oxy)methyl)aziridine (**1**)

(1-benzylaziridin-2-yl)methanol (5.5 g, 33.7 mmol) and triethylamine (5.0 mL, 36.1 mmol) was added in distilled toluene (50 mL) under N_2 atmosphere at room temperature followed by slowly adding chlorodimethyl(vinyl)silane(5.1 mL, 35.4 mmol). The mixture was warmed to 60 °C and stirred overnight, then extracted three times with ethyl acetate. The ethyl acetate layers were combined, washed with distilled water, dried over anhydrous sodium sulfate and filtered. The solvent was evaporated under reduced pressure on a rotary evaporator. The product was obtained in 92% yield (7.7 g) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.21 - 7.40 (m, 5H), 6.05 - 6.16 (m, 1H), 5.97 - 6.05 (m, 1H), 5.75 (dd, *J*=20.1, 4.0 Hz, 1H), 3.62 (dd, *J*=11.1, 5.6 Hz, 1H), 3.53 (dd, *J*=11.1, 5.6 Hz, 1H), 3.45 (s, 2H), 1.72 - 1.82 (m, 1H), 1.69 (s, 1H), 1.45 (d, *J*=6.1 Hz, 1H), 0.18 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 139.1, 137.2, 133.3, 128.3, 129.9, 65.3, 64.3, 40.5, 31.2, -2.2, -2.3; MS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{22}NOSi$: 248.1465; found: 248.1429.

PDMS preparation: Sylgard 184 from Dow Corning Silicone elastomer kit contains base, and curing agent. The conventional synthetic route to PDMS involves Pt-catalyzed addition of vinyl to Si-H. Briefly i) the two reagents 10:1 weight ratio (base:curing agent=10:1) are blended, ii) the blend leaves under reduced pressure for 2 h to remove bubbles trapped in it, and iii) it is cured at 80 °C for 2 h.

AziPDMS preparation: Sylgard 184 was used as a model elastomer. A mixture of base and curing agent, and 1-benzyl-2-(((dimethyl(vinyl)silyl)oxy)methyl)aziridine (10:1:*x* ratio by weight,

where *x* ranged from 0.025 to 0.2) was poured in a polytetrafluoroethylene (PTFE) mold, and degassed by placing in a vacuum desiccator for 20 min to remove bubbles trapped inside. Thermal curing of the mixture at 80 ^{o}C for 2 h yielded aziPDMS film.

Preparation of ring-opened aziPDMS using carboxylic acid: AziPDMS films having different amounts of aziridine were incubated in a 2.5 mM solution (typically, methanol:CH_2Cl_2=1:1; v/v) of 5(6)-carboxyfluorescein at room temperature for ~18 h (or at slightly elevated temperature (e.g., ~50 ^{o}C) for ~12 h). Samples were thoroughly rinsed with pure methanol and CH_2Cl_2 to remove unreacted 5(6)-carboxyfluorescein, and dried in a hot oven and under vacuum.

Preparation of ring-opened aziPDMS using fluorinated carboxylic acid (3,5-bis(trifluoromethyl)benzoic acid), phenol (2,3,4,5,6-pentafluorophenol), thiophenol (2,3,4,5,6-pentafluorobenzenethiol), and amine derivatives: AziPDMS films were post-modified by the various fluorinated nucleophiles following the similar procedure as that for 5(6)-carboxyfluorescein. AziPDMS was incubated in 20 mM THF solution of each fluorinated compound. For the amine derivative (4-trifluoromethyl)aniline), Lewis acid (10 mM of $BF_3{\cdot}OEt_2$) was added for post-modification. The Lewis acid-assisted post-modification of aziPDMS for the amine was attributed to the decreased nucleophilicity of amine by fluorination.

3. Additional Discussions

^{1}H NMR Study for determining the reaction of vinylaziridine (1) with silyl hydride prepolymer (curing agent B in Figure 1a), and the ring opening reaction with benzoic acid: We studied if the vinyl group of compound **1** in Figure 1a could be coupled with silyl hydride in the presence of Pt catalyst through ^{1}H NMR spectroscopic study. Compound **1** (120 mg, 0.48 mmol) was added to the part B (600 mg) under neat condition at room temperature. This starting mixture was characterized by ^{1}H NMR spectroscopy (black line in Figure S2). Pt catalyst (Karstedt's catalyst, 1 mg, 0.001 mmol) was then added, and the resulting mixture was stirred for 1.5 h at 80 ℃. The hydrosilylation reaction between compound **1** and the part B was confirmed through ^{1}H NMR (red line in Figure S2). Chemical shifts at 5.75, 6.01 and 6.10 ppm corresponding to the vinyl protons of compound **1** completely disappeared in 1.5 h, which indicates that the desired coupling reaction was highly efficient. The aziridine ring structure was retained after the reaction: chemical shifts (1.45, 1.69 and 1.77 ppm) corresponding to the aziridine moiety remained unchanged after the reaction.

Next, we determined whether the covalently attached aziridine can undergo efficient ring-opening reaction with carboxylic acid derivative. Structurally simple compound, benzoic acid, was used for this experiment. Benzoic acid (67.0 mg, 0.55 mmol) in dichloromethane (3 mL) was added to the aziridine-functionalized prepolymer for 13 h at room temperature. The ring-opening reaction of aziridine was confirmed through ^{1}H NMR (blue line in Figure S2). Chemical shifts at 1.45, 1.69 and 1.77 ppm corresponding to the covalently linked aziridine's protons completely disappeared, which indicates that the desired ring-opening reaction was quantitatively completed.

XPS analysis: For structural analysis using X-ray photoelectron spectroscopy (XPS), aziPDMS was thoroughly rinsed by immersing in pure hexane and dichloromethane for 6 h, respectively. Survey scans of aziPDMS showed Si2p (~102 eV) and O1s (~532 eV) signals corresponding to the PDMS backbone, and C1s (~284eV) and N1s (~398 eV) corresponding the aziridine pendants (Figure 1d). The calculated and experimental atomic concentrations (atom%) agreed well for both PDMS and aziPDMS (see Table S1). The depth profile XPS scans were achieved *via* in situ etching (etching speed: ~5 nm/min) of aziPDMS surfaces (Figure 1e). The depth profile of aziPDMS showed the highest atom% of Si and O, and the lowest atom% of C during etching. Interestingly, the atom% for N1s was consistent throughout the measurements for aziPDMS, indicating that aziridines are present equivalently from surface to bulk.

Red-shift of λ_{max} in photoluminescence spectra for ring-opened aziPDMSs by 5(6)-carboxyfluorescein: The photoluminescence spectrum of aziPDMS showed a λ_{max} of ~531 nm (Figure S3). This emission band was slightly red-shifted ($\Delta\lambda_{max}$ = ~10 nm) relative to free 5(6)-carboxyfluorescein in a solution phase (λ_{max} = ~521 nm in methanol). This red-shift of λ_{max} was indicative of covalently attached 5(6)-carboxyfluorescein to the backbone of aziPDMS: the interaction between 5(6)-carboxyfluorescein molecules linked to PDMS leads to the change in λ_{max}.[5]

4. Image Analysis using a Thresholding Method

To determine the surface depth of post-modification, we functionalized aziPDMSs with two different photoluminescent ring opening reagents in polar and non-polar solutions. Photoluminescent images of multi-functionalized aziPDMS films were obtained, and these images were converted into the corresponding grayscale images using a software (ImageJ). These grayscale images enabled us to analyze them based on a single intensity value. The gray-level intensity at each pixel is calculated as the average of the color values for red, green, and blue components in a color image. Maximum entropy thresholding[6] was then applied to create a binary (black and white) image from a grayscale image. This method made it possible to classify all the image pixels as a foreground (here, the region where aziridines are ring-opened by 5(6)-carboxyfluorescein) or a background pixel. The percentage of the surface depth of the first post-modification was estimated by determining the ratio of width of white pixels (corresponding to the surface post-modification) to the half of the width of the film on a line and averaged over 10 parts each sample.

Figure S1. Reaction scheme for Pt(0)-catalyzed hydrosilylation between vinyl-terminated aziridine **1** and PDMS prepolymers (base and curing agents, denoted as parts **A** and **B** of the Sylgard 184 Silicone elastomer kit).

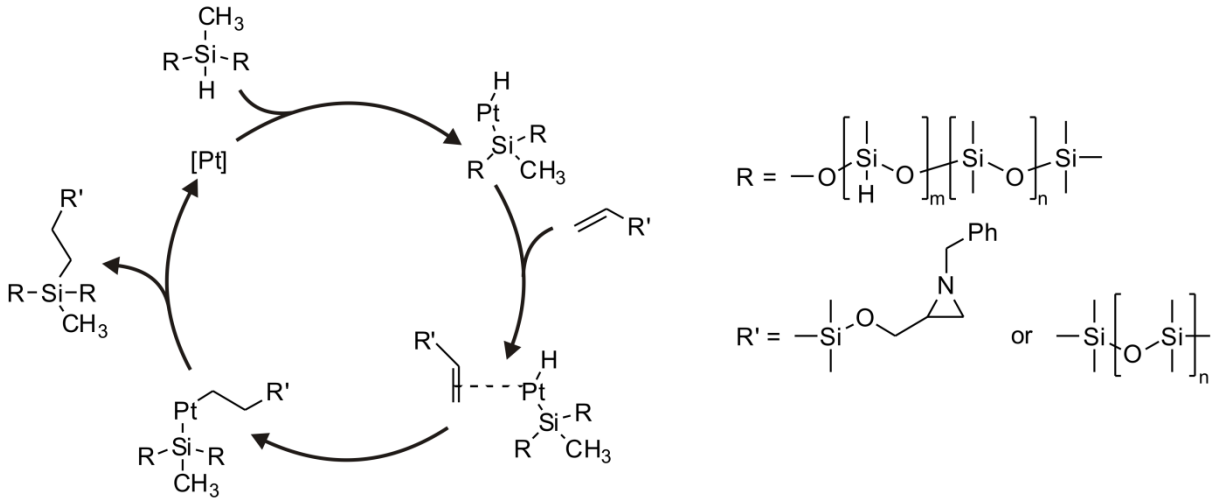


Figure S2. ^{1}H NMR spectroscopic study of Pt(0)-catalyzed hydrosilylation between silyl hydride (the curing agent B) and vinyl-terminated aziridine (**1**), and the ring-opening reaction of aziridine and benzoic acid. (Note that the commercial curing agent B contains some additive.)

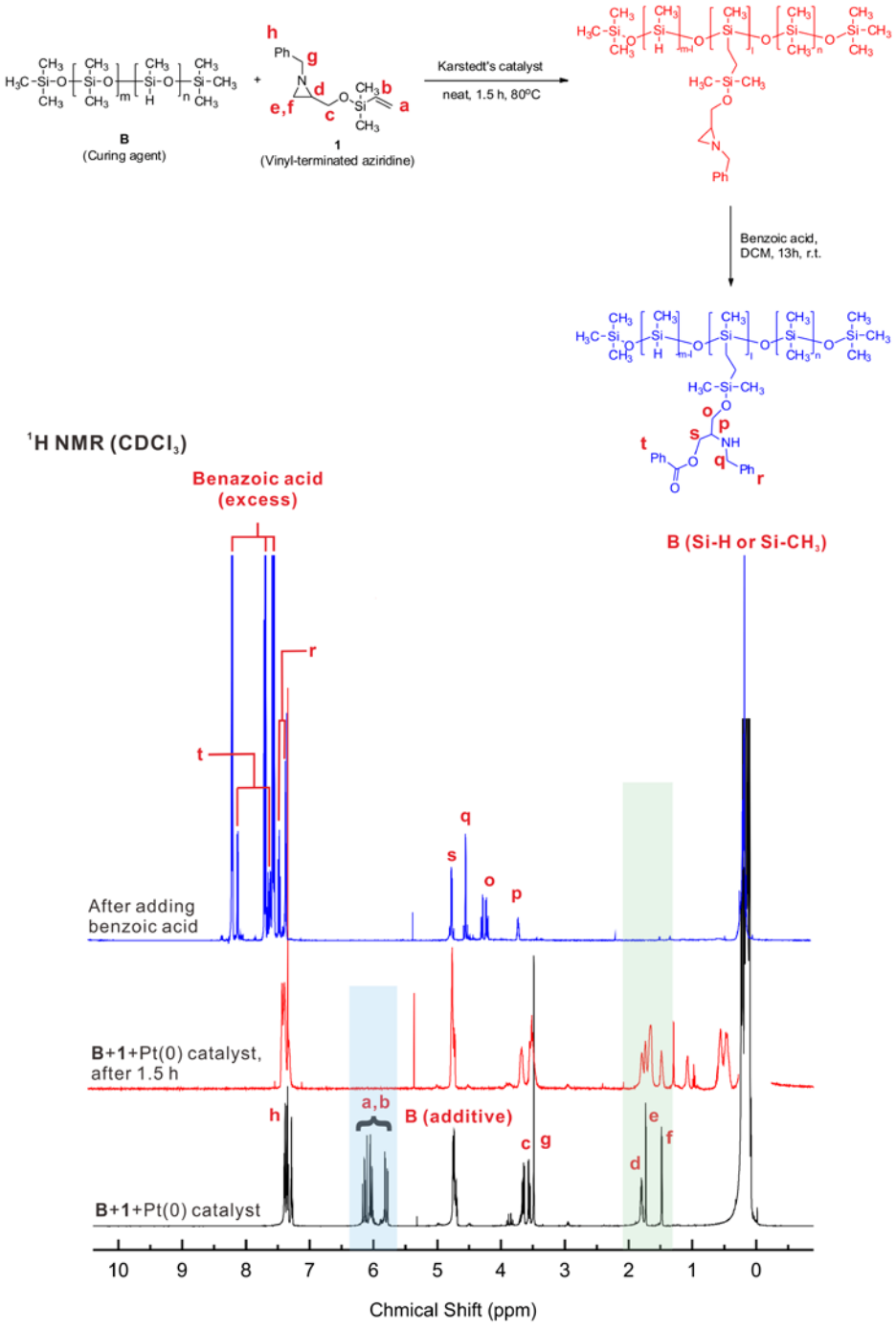


Table S1. XPS confirmed uniform distribution of aziridines in PDMS, and aziPDMS

		atom %			
		Si	C	O	N
PDMS	calcd[b]	25.0	50.0	25.0	0.0
	exptl[c]	29.4	43.9	26.7	0.0
aziPDMS[a]	Calcd[d]	24.6	50.7	24.6	0.1
	exptl[c]	27.3	47.6	24.6	0.5

[a] 10:1:0.2 mass ratio of base, curing agent and vinyl-terminated aziridine **1** films

[b] Atom % was calculated using ($SiOC_2$) as the repeat unit.

[c] Data averaged from three measurements.

[d] The M_w for the siloxane repeating units with and without aziridine pendant was 74.

Figure S3. Photoluminescence spectra of 5(6)-carboxyfluoroscein in MeOH (red) and aziPDMS after incubation in a 2.5 mM solution of 5(6)-carboxyfluoroscein (black).

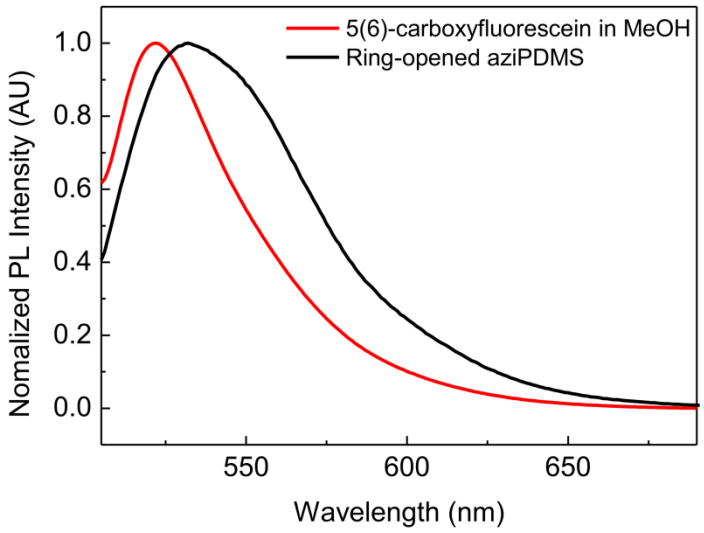


Figure S4. The application of the thresholding techniques for the sliced aziPDMS films in Figure 4b.

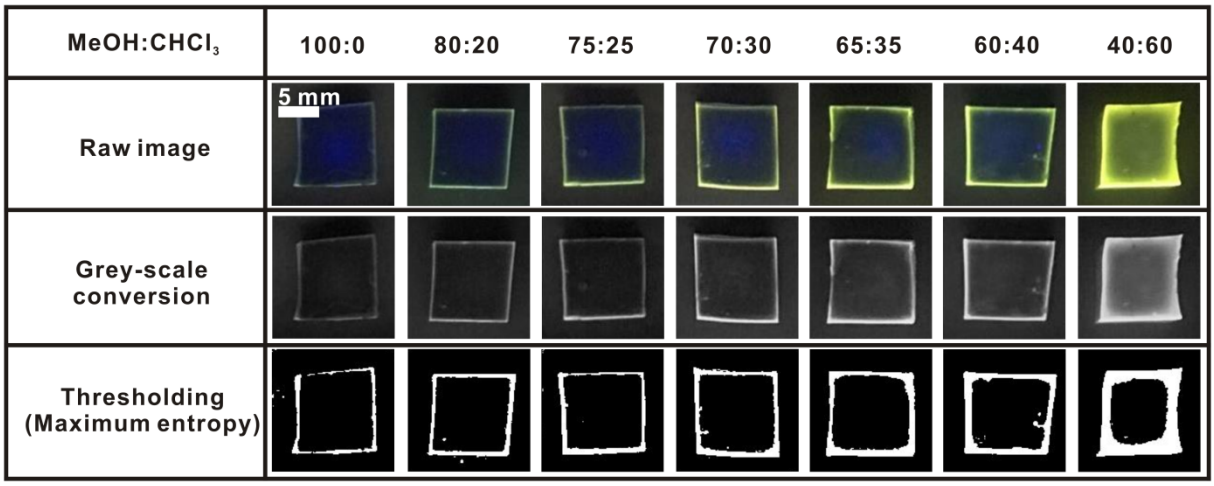
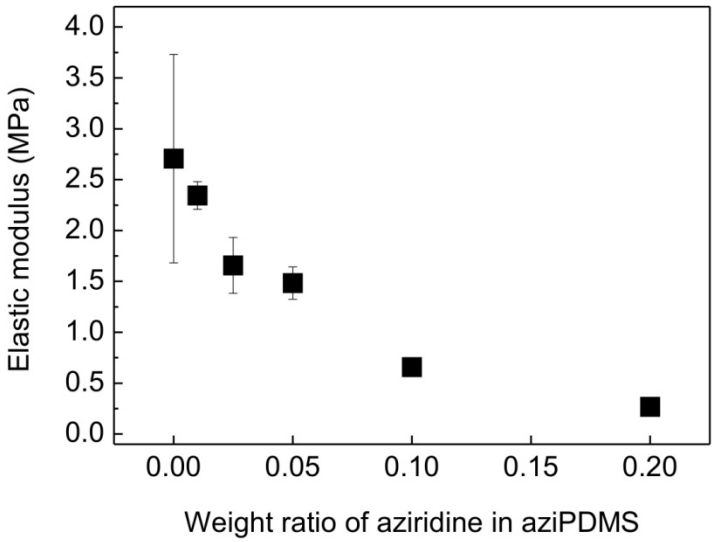
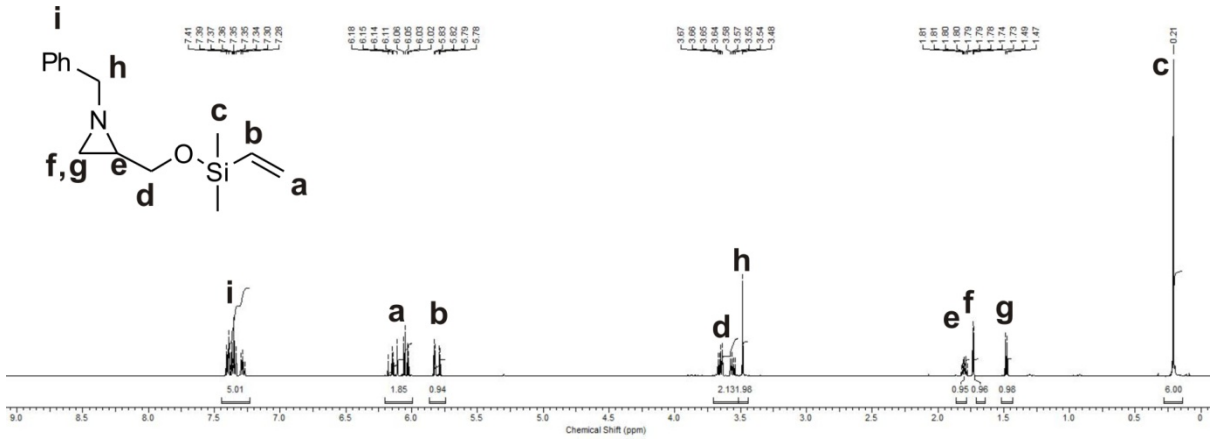


Figure S5. Elastic modulus of aziPDMSs having different amounts of aziridine (base:curing agent:**1**=10:1:*x*, where *x* ranged from 0.00 to 0.20).

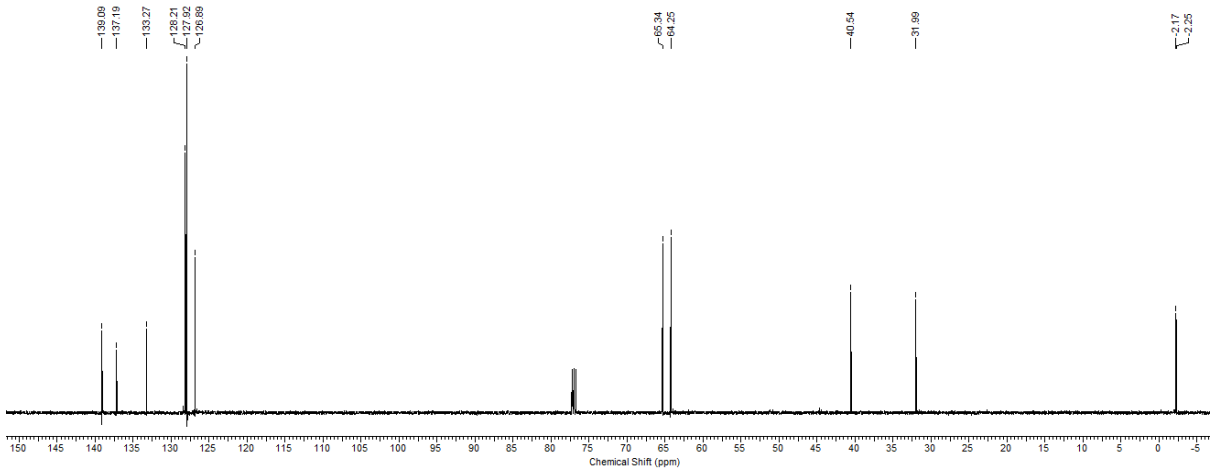


3. ^{1}H and ^{13}C NMR, and HRMS Spectra of 1-Benzyl-2-(((dimethyl(vinyl)silyl)oxy)-methyl)aziridine (1).

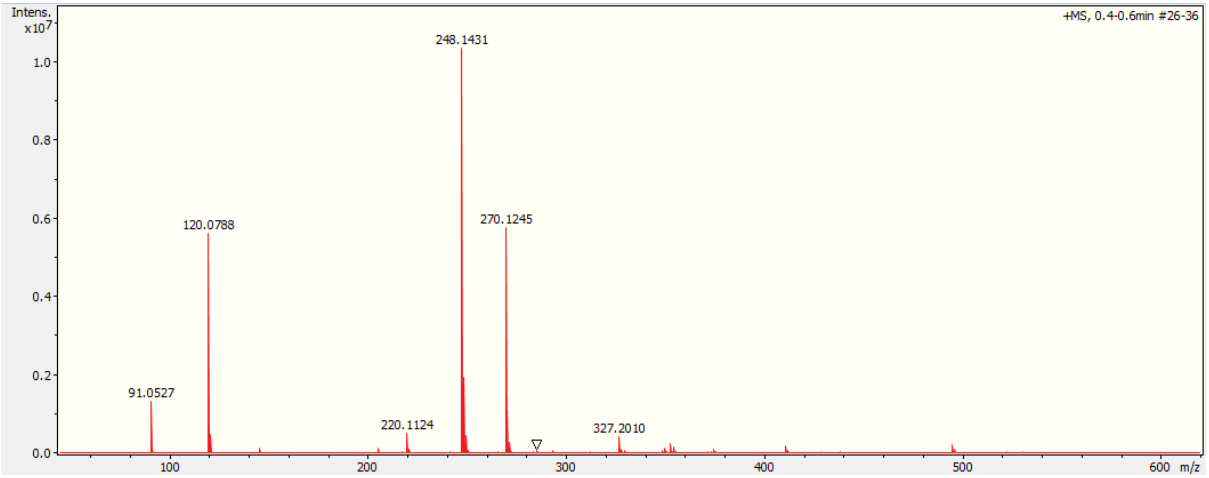
^{1}H NMR spectrum



^{13}C NMR spectrum



MS spectrum



4. References

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