Supporting Information

Imine and Metal-Ligand Dynamic Bonds in Soft Polymers for Autonomous Self-Healing Capacitive-Based Pressure Sensors

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General Procedure and Materials

Materials: Commercial reactants were used without further purification unless stated otherwise. All the solvents used in these reactions were distilled prior to use. Aminopropyl-terminated polydimethylsiloxane with molecular weight of 1000 Da, and dispersity of 1.33 was purchased from Gelest (Pennsylvania, USA). Pyridine-2-carboxaldehyde and Iron (II) tetrafluoroborate hexahydrate were purchased from Sigma-Aldrich and used as received.

Measurements and Characterization: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz spectrometer. The spectra for all polymers were obtained in deuterated chloroform at room temperature. Chemical shifts are given in parts per million (ppm). Number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity index (PDI) were evaluated by high-temperature size-exclusion chromatography (SEC) using 1,2,4-trichlorobenzene at 180°C and performed on an EcoSEC HLC-8321GPC/HT (Tosoh Bioscience) equipped with a single TSKgel GPC column ($\text{GMH}_{HR}$-H; 300 mm $\times$ 7.8 mm) calibrated with monodisperse polystyrene standards. UV-Visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. The surface structure of polymer film was obtained using a Multimode atomic force microscope (AFM, Digital Instruments) operated in the tapping mode at room temperature. Images were collected using Nanoscope 6 software and
Sample Preparation: The pre-polymer was solubilized in dichloromethane, filtered on 0.45 µm filter, crosslinked with Fe(II) and casted into 3-cavities PTFE mold with cavity dimensions of 37.6mm L x 13.8mm W x 3mm D (Ted Pella). Once a gel was formed, the samples were placed in a vacuum oven at 50 °C and left to dry for 48 hours. Structuring of the dielectrics was performed by using an inverse PDMS-based mold prepared from commercially-available safety tape ribbons following a previously reported procedure. The mold was cured with UV-ozone for 5 minutes and was used as a stamp to produce the nanostructure on the desired materials. The polymer was then left for 24 hours in vacuum at 50 °C to dry. Once dried, the sample was slowly peeled off and directly used for the fabrication of the devices.

Evans method for determining effective magnetic moment: A previously reported procedure was followed. Briefly, samples of known concentration (0.9 mM) were prepared. An NMR tube made of concentric tubes was filled with pure solvent (CDCl₃, inner tube) and sample (outer tube). The magnetic susceptibility ($\chi_{mass}$) was determined by using the formula $\chi_{mass} = \frac{3\Delta f}{4\pi fm} + \chi_0 + \frac{\chi_0(d_0- d_s)}{m}$, where $\chi_{mass}$ is mass susceptibility (cm$^3$·g$^{-1}$), $\Delta f$ is the observed frequency difference (Hz), $f$ is spectrometer frequency (Hz), $m$ is the mass of paramagnetic substance (g·cm$^{-3}$), $\chi_0$ is the mass susceptibility of solvent (cm$^3$·g$^{-1}$), $d_0$ is the density of solvent (g·cm$^{-3}$), and $d_s$ is the density of solution (g·cm$^{-3}$). The magnetic susceptibility was further converted to the effective magnetic moment ($\mu_{eff}$) following a previously reported procedure.
Device Fabrication and Characterization: Devices were fabricated by lamination of the structured dielectrics (self-healing polymer) with copper tape. Note that an overhanging end was left to be connected and tested using Agilent E4980A 2MHz Precision LCR meter for capacitance measurements. Sensitivity upon pressure was evaluated using a home-made force linear actuator and force sensor connected to the device. The range of pressure evaluated was from 0 to 32 kPa. The devices were tested at various pressures within this range in order to construct a sensitivity curve. Stretched samples were subjected to 30% strain for 100 cycles using a custom-built stretching station. Healed samples were cut in half with a blade and pressed back together for intrinsic self-healing before being used as a dielectric.

Evaluation of self-healing properties: Self-healing was evaluated by tensile strain analysis as well as by device signal sensitivity before and after healing. For the tensile strain analysis, a flat molded sample was simply cut in half with a blade, pressed back together and left to heal for 24 or 48 hours before being characterized. Tensile-strain analysis was performed on an Instron Tensile Strain instrument with a test rate of 100 mm/min. Self-healing ability of the pressure sensing devices was characterized by testing the device before and after a healing period of 48 hours. For evaluation of the self-healing properties by atomic force microscopy, a sample was frozen in liquid nitrogen and carefully cut with a scalpel. The films analyzed were spin coated on a cleaned glass substrate, at 2000 rpm for 1 min. It is important to mention that several attempts were required to make a cut small enough to properly self-heal, but large enough that the full capability of the material is demonstrated. The cut sample was then left on the AFM stage on day 0 and measured after 24, 48 and 72 hours.
Evaluation of degradability: A small piece of the self-healing material was characterized in terms of degradability by placing a solid piece of the polymer in solution with ~ 1 M acetic acid and left to stir until fully dissolved (2 days). The resulting solution was then directly characterized without further treatments.

Preparation of model imine compounds. The synthesis of the \((E)\)-N-butyl-1-(pyridin-2-yl)methanimine has been performed according to a previously reported procedure. Following its preparation, the compound (1 eq.) was reacted with 6-aminohexan-1-ol (1.2 eq.) in tetrahydrofuran (2 M). The reaction mixture was stirred for 72 h at 30 °C. The product was used without any further purification for LC-MS analysis.

Experimental Procedure

Pre-polymer 1. A round bottom flask equipped with a magnetic stir bar was charged with aminopropyl-terminated PDMS (20 g, 0.020 mol), pyrimidine-2-carboxaldehyde (4.28 g, 0.042 mol) and CHCl₃ (20 mL). The reaction was left stirring for 48 hours at room temperature and

Scheme S1. Synthesis of pre-polymer 1 followed by chemical crosslinking with Fe(II)-based salts.
CH$_3$Cl was removed under reduced pressure. The resulting materials was diluted in hexanes and was extracted with MeCN to remove unreacted monomer and dried under vacuum to afford pre-polymer 1 as a viscous thick oil. $^1$H NMR (300MHz, CDCl$_3$, 298 K): 8.62 (d, J= 4.2 Hz, 2H), 8.35 (s, 2H), 7.98 (dd, 7.8 Hz, 2H), 7.72 (t, 2H), 7.29 (t, J= 15.3 , 2H), 3.67 (t, J= 14.1, 4H), 2.29 (m, 12H), 1.79 (m, 4H), 0.584 (t, 7.5 Hz, 4H). Molecular weight estimated from high temperature GPC (1,2,4-trichlorobenzene, 200°C): $M_n = 839$ Da, $M_w = 2286$ Da, PDI = 2.737

$^1$H NMR spectrum of pre-polymer 1 in CDCl$_3$ after purification by liquid extraction with hexanes/MeCN.
**General procedure for the preparation of Fe-coordinated polymer:** The crosslinking of pre-polymer 1 was performed by dissolving a selected amount of materials in dichloromethane and stirring for 5 minutes. A selected amount of iron(II) tetrafluoroborate hexahydrate dissolved in a minimal amount of methanol was then added to the mixture. The reaction was left to stir at room temperature for 30 minutes and the resulting materials was directly molded for further analysis. Molecular weight for a 1:3 pre-polymer/Fe(II) ratio sample was estimated from high temperature GPC (1,2,4-trichlorobenzene, 200°C): $M_n = 1140$ Da, $M_w = 3407$ Da, PDI = 2.989

![Image of 1H NMR spectrum](image-url)

$^1$H NMR spectrum of pre-polymer 1 crosslinked with Fe(II) in CDCl$_3$
$^{19}$F NMR spectrum of pre-polymer 1 crosslinked with Fe(II) in CDCl$_3$
Material Characterization:

Figure S1. FT-IR spectra of pre-polymer 1 before and after crosslinking with 0.25 eq. of Fe(BF₄)₂.
Figure S2. Energy-dispersive x-ray spectroscopy (EDX) analysis map; a) scanning electron Micrograph of EDX scanning area cumulative elemental overlay (yellow = Si, red = Fe), and b) independent elemental overlay of Fe atoms. Scale bar is 2 µm.

Figure S3. Atomic force microscopy (AFM) a) height image, and b) 3d image of pre-polymer 1 after Fe(II) coordination. Scale bar is 2.0 µm.
Figure S4. Stress-strain curves of pre-polymer 1 crosslinked with 0.33 equivalent of Fe(BF$_4$)$_2$ a) before; b) after self-healing for 24 hours, and c) after self-healing for 48 hours at room temperature. Measurements were recorded on two samples from two different batches of materials.
Figure S5. Atomic force microscopy (AFM) height images of pre-polymer 1 after Fe(II) coordination a) after being cut with a razor blade; b) after 24 hours of self-healing; c) after 72 hours of self-healing, and d) depth profile of the damaged zone and its evolution upon self-healing. Scale bar is 20 µm. No more cut at the nanoscale was observed by AFM after more than 72 hours.
**Figure S6.** Preparation of compound $(E)$-N-butyl-1-(pyridin-2-yl)methanimine and investigation of the dynamic behaviour of the imine bond by mass spectrometry. Measurements were completed in ASAP(+) sensitivity mode using the crude samples.

**Figure S7.** UV-Vis spectra of pre-polymer 1 pristine, after Fe(II) coordination, and after being stirred in a 1.0 M solution of hydrochloric acid for 4 hours.
Figure S8. Degradation of Fe(II)-crosslinked soft polymer at various pH (aqueous HCl solutions) upon a) initial time; b) 24 hours, and c) 72 hours of stirring.
**Figure S9.** a) 2-D Optical Microscope image of dielectric structures and b) 3D image of dielectric structures.

**Figure S10.** a) Standard deviation between devices sensitivity: Pristine, 100 cycles at 30% strain, healed for 24 hours, and healed after 100 cycles at 30% strain. Sensitivity averaged over 4 devices.
References