

Supporting Information for

Photoinduced Morphology Change in Ionic Supramolecular Block Copolymer

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Dryad Data Repository

The data and methods for processing the data are described in the manuscript and SI can be found at Dryad Data Repository.

Materials and Instrumentation

Materials. Solvents and reagents were purchased from commercial vendors and used without further purification unless otherwise specified. Monovinyl-terminated PDMS 6.7 kDa (MCR-V21) was purchased from Gelest. PS- ω -SO₃H (4.1 kDa) was purchased from Polymer Source. Anhydrous dimethylformamide (DMF) was purchased from Alfa Aesar. Tetrahydrofuran (THF) and dichloromethane (DCM) were dispensed from a solvent purification system. Methanol was stored over 3 Å molecular sieves. Thin-layer chromatography (TLC) was carried out with Merck TLC plates (silica gel 60 F254 on aluminum) and visualized by exposure to UV light (254/ 366 nm). Silica gel chromatography was performed using silica gel (60 Å pore size, 40 – 63 μm particle size).

Preparation of the Photoresponsive Ionic Blends by Reactive Blending. Required amounts of PDMS- ω -DAE (10 wt% in THF) and PS- ω -SO₃H (10 wt% in THF) were mixed at a 1:1 molar ratio between DAE and SO₃H end groups for two hours at room temperature, resulting in an ion-containing blend PS- ω -SO₃⁻/PDMS- ω -DAE-H⁺ (Table 1). The final solution was equally separated into two separate vials. One of the vials was subjected to UV irradiation to convert the DAE-O to DAE-C using a low-intensity 300 nm light source (≈ 1.32 mW/cm²) for 5 minutes. Upon irradiation, the solution turned dark blue, indicating the formation of the DAE-C end group. Note that overexposing material to high-intensity UV light for a prolonged time can lead to degradation of the DAE chain-ends. The blend solution of DAE-O, and DAE-C (before and after UV irradiation) was separately cast on a PTFE film (McMaster-Carr) and dried under ambient conditions for 3 hours. Note that the thermal relaxation of DAE-C in THF solutions is ≈ 10 h, and we observed that most of the THF solvent evaporated within 20 minutes. DAE-H⁺-C remained in the closed form when the polymer chains were frozen due to the immobility of the PS block (T_g is

ca. 100 °C). The polymer films and the PTFE substrate were transferred to a high vacuum oven equipped with a turbo pump ($\sim 10^{-8}$ torr) and dried at room temperature for 12 hours, followed by another 12 hours at 60 °C. The samples were slowly cooled to room temperature and stored in an argon-filled glovebox.

Solution-State Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer using CDCl_3 as the solvent. Chemical shifts are reported relative to residual solvent peaks (δ 7.26 ppm for CDCl_3 in ^1H NMR and δ 77.05 for CDCl_3 in ^{13}C NMR). Size-exclusion chromatography (SEC) was obtained with a Waters SEC system equipped with a refractive index detector and Agilent PLgel 5 μm MiniMIX-D column at 35 °C with THF as the eluent. Molecular weight distribution was estimated by a series of polystyrene standards. Mass spectral data was collected on the Shimadzu LCMS-9030 Q-TOF Mass Spectrometer with an electrospray ionization (ESI) source.

Matrix-assisted laser desorption ionization (MALDI-TOF) mass spectrometry. MALDI-TOF experiments were performed using a Bruker Microflex MALDI-TOF mass spectrometer (Bruker Daltonics). Samples were prepared in tetrahydrofuran at 5 mg/ml. Trans-2-[3-(4-tert-Butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) (10 mg/mL) and potassium trifluoroacetic acid (KTFA) (10 mg/ml) were used as a matrix and cationization agent respectively. One microliter of sample, 1 μl of KTFA, and 20 μl of DCTB were mixed thoroughly. About 0.5 μl of this mixture was deposited on a stainless-steel sample holder.

Fourier-Transform Infrared Spectroscopy (FTIR). FTIR measurements were performed on a Thermo Nicolet iS10 spectrometer equipped with a Smart Diamond attenuated total reflectance (ATR) accessory. A background spectrum was obtained every 30 minutes, and sample spectra were taken using 64 scans in absorbance mode.

UV-Vis Spectroscopy and UV-Vis Kinetic Measurements. UV-Vis absorption spectra were recorded on Agilent 8453 UV-Vis spectrometer. The switching kinetics of PS- ω - SO_3^- / PDMS- ω -

DAE-H⁺-O ionic blend was measured on a home-built pump-probe setup, as previously reported by our group.¹ The UV pump source was generated by a Deep UV LED (Thorlabs M300F2, 300 nm), positioned to illuminate the sample directly without coupling into a multimode optical fiber (≈ 1.32 mW/cm²). The probe beam was generated by a high-power MINI Deuterium Tungsten Halogen Source w/shutter 200–2000 nm (Ocean Optics DH-MINI) coupled into a multimode fiber with an output collimator for the light delivery. The probe light was modulated by a shutter (Uniblitz CS25), which could be controlled manually or through a digital output port (National Instruments USB-6009) using LabVIEW. Pump and probe beams overlapped using steering and focusing optics at a 90° angle inside a sample holder, allowing 10×10 mm² rectangular spectrophotometer cells to be held within or cast film samples to be held to the front using metal spring clips. The solutions were continuously stirred during the measurements by a miniature stirring plate inserted into the sample holder (Starna Cells SCS 1.11). Both pump and probe beams were nearly collimated inside the cell with a diameter of about 2 mm. The pump beam was blocked after passing through the sample, and the probe beam was directed by a system of lenses into the detector (Ocean Optics Flame-S1-XR spectrometer), which acquired spectra of the probe light. The detector was connected to a PC via a USB port. The experiment was controlled by a National Instrument LabVIEW program, which collected the probe light spectra, determined sample optical absorption spectra, controlled pump, and probe light sources.

Small-angle X-ray Scattering (SAXS). Samples were loaded into aluminum washers (1 mm thickness) and sealed with Kapton tape. All experiments were performed at the National Synchrotron Light Source II (NSLS-II, beamline 11-BM, Brookhaven National Laboratory), with an X-ray energy of 13.5 keV. The sample to detector distance (3m) was calibrated using a silver behenate standard, and the isotropic 2D scattering patterns were reduced into 1D scattering intensity as a function of the wavevector $q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the X-ray wavelength. Temperature-dependent SAXS experiments were conducted on selected

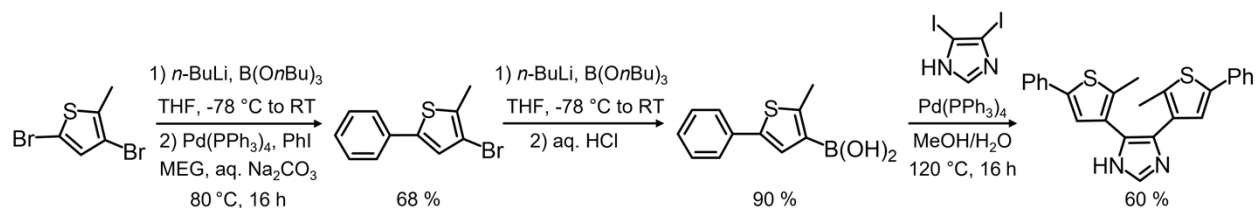
ionic polymer blends, heated incrementally to 65, 85, 95, 105, 120, and 140 °C, followed by an equilibration time of 15 min at each temperature.

Transmission Electron Microscopy (TEM). Thin sections (ca. 120 nm) for electron microscopy were obtained by cryo-microtoming at a Leica EM UC 7 at -100 °C to -80 °C and collected on 200-mesh copper grids. TEM experiments were performed on Talos™ F200X G2 TEM at an acceleration voltage of 200 keV.

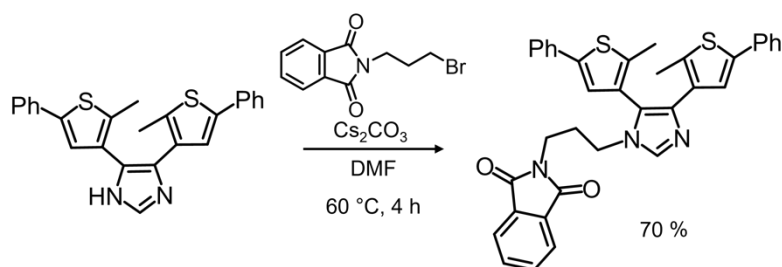
Synthesis of Small Molecules and Polymers

1. Synthesis of primary amine functionalized diarylethene (DAE-NH₂)

4,5-Bis(2-methyl-5-phenylthiophen-3-yl)-1H-imidazole (DAE) was synthesized according to the modified procedure recently reported by F. Dielmann et al.²



Synthesis of 2-(3-(4,5-bis(2-methyl-5-phenylthiophen-3-yl)-1H-imidazol-1-yl)propyl)isoindoline-1,3-dione



The target compound was synthesized according to the modified procedure reported by Nie et al.³ To a flame-dry round bottom flask equipped with a magnetic stir bar, and condenser, 4,5-Bis(2-methyl-5-phenylthiophen-3-yl)-1H-imidazole (DAE) (300 mg, 0.72 mmol, 1 eq.), *N*-3-bromopropylphthalimide (387 mg, 1.44 mmol, 2 eq.), cesium carbonate (468 mg, 1.44 mmol, 2 eq.) and 70 ml of anhydrous DMF were added. The solution was heated at 60 °C for 4 hours. Subsequently, the reaction was allowed to cool down to room temperature, and the solvent was evaporated under reduced pressure. The final mixture was purified by silica column chromatography using ethyl acetate as eluent, resulting in 300 mg of the product (70% yield). Spectral data matches the reported literature.³

¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.78 (s, 1H), 7.67 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.57 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.43 – 7.40 (m, 2H), 7.34 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.30 – 7.24 (m, 4H, overlapping with CDCl₃), 7.19 – 7.15 (m, 1H), 7.10 (s, 1H), 7.03 (s, 1H), 3.98 (dt, *J* = 14.8, 7.7 Hz, 2H), 3.66 (q, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.06 (s, 3H), 2.04 – 1.94 (m, 2H)

ppm. ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 168.20, 141.46, 139.57, 139.33, 136.91, 136.73, 135.36, 134.56, 133.96, 133.72, 131.97, 131.64, 128.89, 128.73, 127.48, 127.38, 126.80, 125.37, 125.25, 124.24, 123.93, 123.25, 123.10, 43.25, 35.08, 30.26, 14.65, 13.85. FTIR: ν_{max} 3058, 2959, 2914, 1767, 1705, 1598, 1505, 1489, 1467, 1436, 1394, 1264, 1233, 1189, 1072, 1029, 958, 843, 754, 712, 687 cm^{-1} . LC-MS (ESI) (m/z): $[\text{M}+\text{H}]^+$: 600.1804 Da.

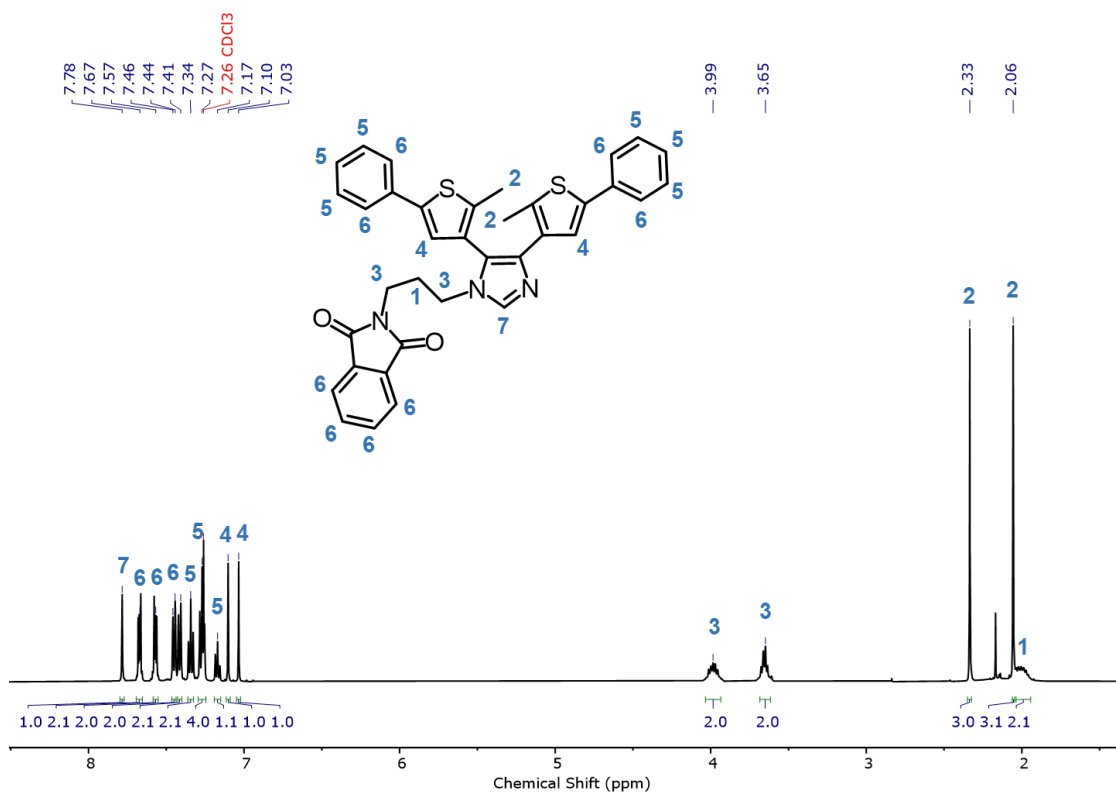


Fig. S1. ^1H NMR spectrum of 2-(3-(4,5-bis(2-methyl-5-phenylthiophen-3-yl)-1H-imidazol-1-yl)propyl)isoindoline-1,3-dione.

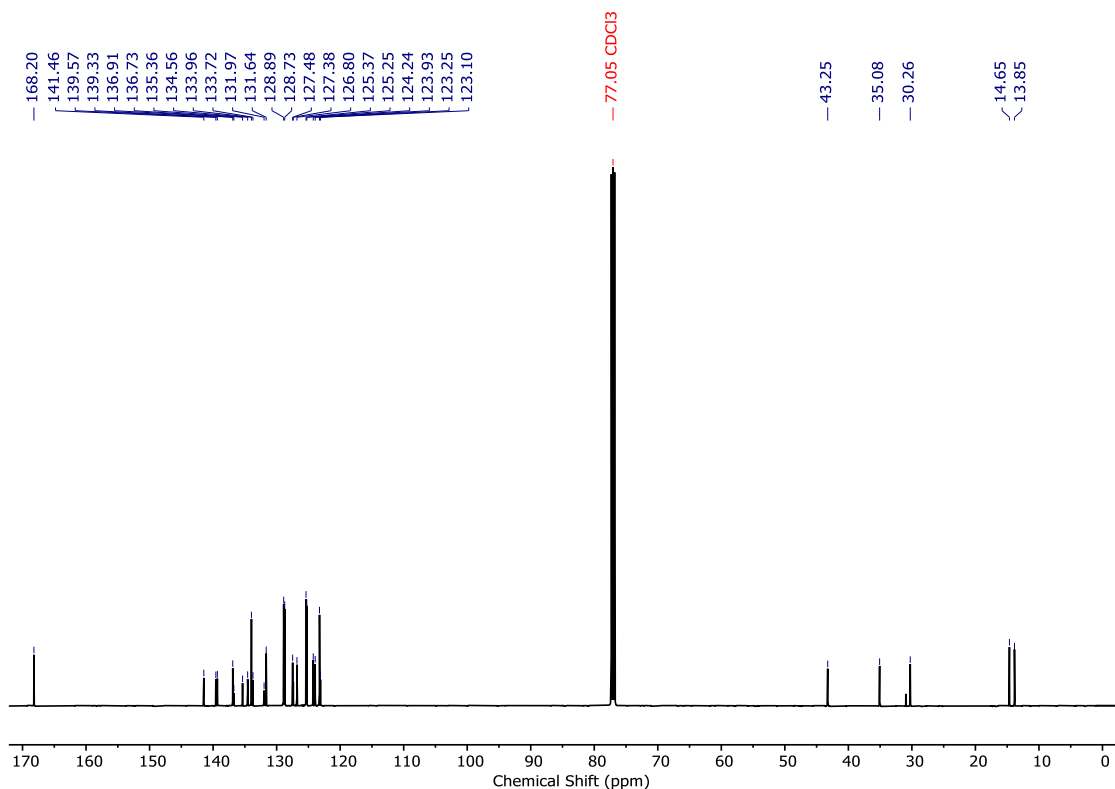
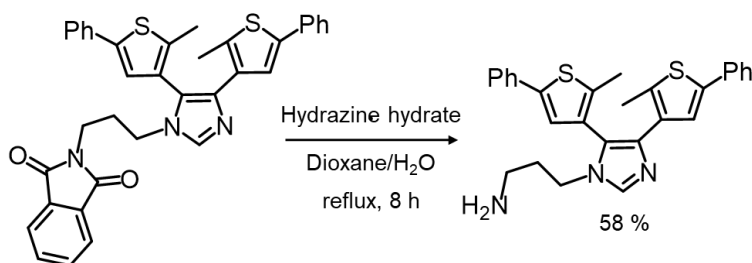


Fig. S2. ^1H NMR spectrum of 2-(3-(4,5-bis(2-methyl-5-phenylthiophen-3-yl)-1*H*-imidazol-1-yl)propyl)isoindoline-1,3-dione.

*3-(4,5-bis(2-methyl-5-phenylthiophen-3-yl)-1*H*-imidazol-1-yl)propan-1-amine (DAE-NH₂)*



The target compound was synthesized according to the modified procedure reported by Nie et al.³ Phthalimide-protected diarylethene (300 mg, 0.5 mmol, 1 eq.) was dissolved in a dioxane/water mixture (6 ml, 3/1). Hydrazine hydrate (0.17 ml, 3.45 mmol) was then added to the solution, and the mixture was refluxed overnight. The reaction was cooled to room temperature, and concentrated hydrochloric acid (0.53 ml) was added. The mixture was refluxed for 6 hours. Subsequently, the reaction was cooled to room temperature and filtered. The filtrate was

evaporated, resulting in a pale yellow solid, which was diluted with deionized water. The aqueous solution was washed three times with DCM, followed by the addition of an aqueous solution of 6 M sodium hydroxide until pH 12 was reached. The solution was washed with dichloromethane three times and evaporated under reduced pressure to obtain the final product. (140 mg, 58% yield).

¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.69 (s, 1H), 7.60 – 7.56 (m, 2H), 7.45 – 7.42 (m, 2H), 7.39 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.29 (td, *J* = 7.7, 6.1 Hz, 3H), 7.21 – 7.14 (m, 2H), 7.08 (s, 1H), 4.01 (dt, *J* = 13.4, 7.1 Hz, 2H), 2.65 (t, *J* = 6.7 Hz, 2H), 2.35 (s, 3H), 2.07 (s, 3H), 1.77 (p, *J* = 6.9 Hz, 2H), 1.57 (s, 2H, overlapping with H₂O). **¹³C NMR (126 MHz, CDCl₃) δ (ppm):** 141.41, 139.29, 139.24, 137.03, 136.71, 135.13, 134.60, 133.96, 132.41, 129.01, 128.74, 127.91, 127.61, 126.80, 125.49, 125.23, 124.35, 124.32, 123.38, 42.88, 38.72, 34.18, 14.64, 13.94. **FTIR:** ν_{\max} 3312 (broad) 3061 2913, 1704, 1597, 1489, 1467, 1442, 1394, 1333, 1264, 1193, 1030, 958, 841, 802, 754, 688 cm⁻¹. **LC-MS (ESI) (m/z):** [M+H]⁺: 470.1738 Da.

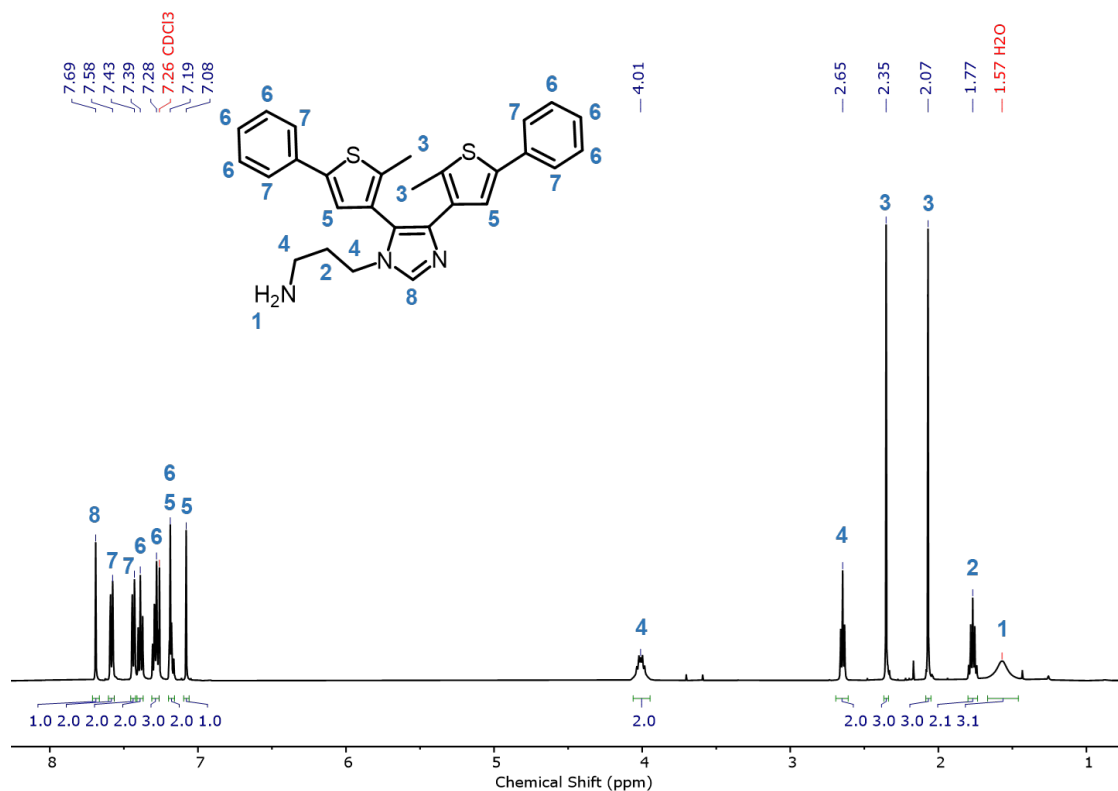


Fig. S3. ¹H NMR spectrum of 3-(4,5-bis(2-methyl-5-phenylthiophen-3-yl)-1H-imidazol-1-yl)propan-1-amine (DAE-NH₂).

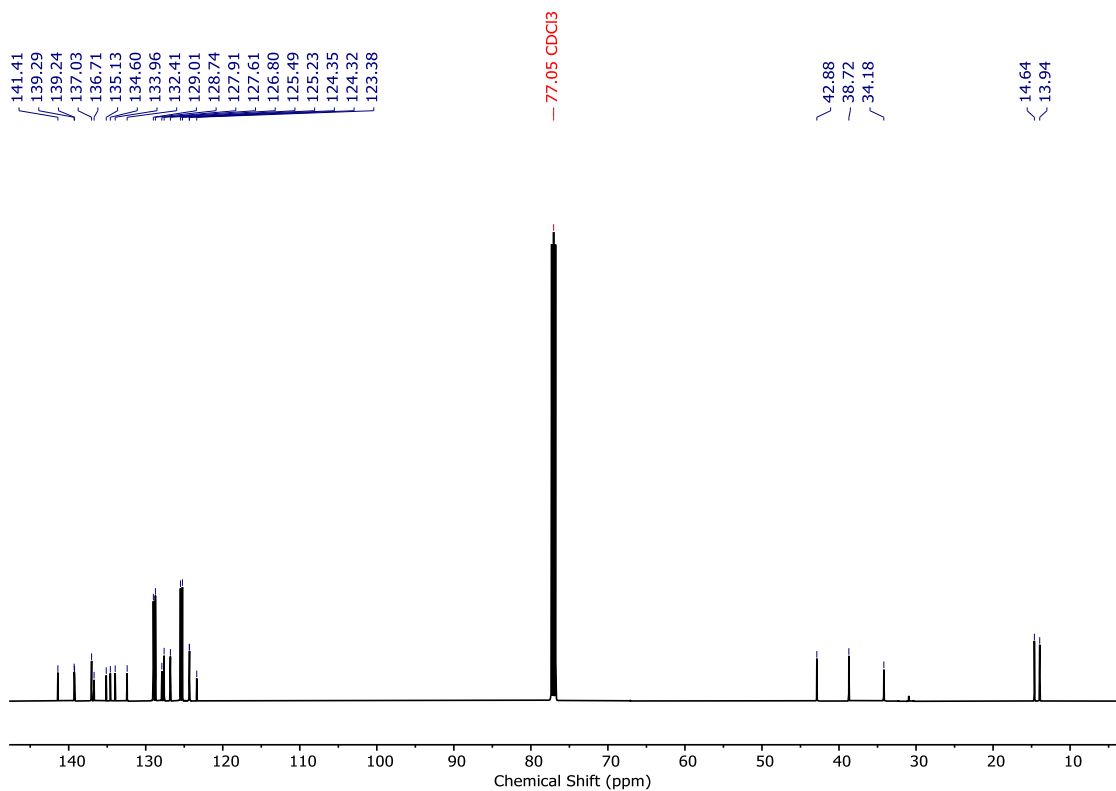
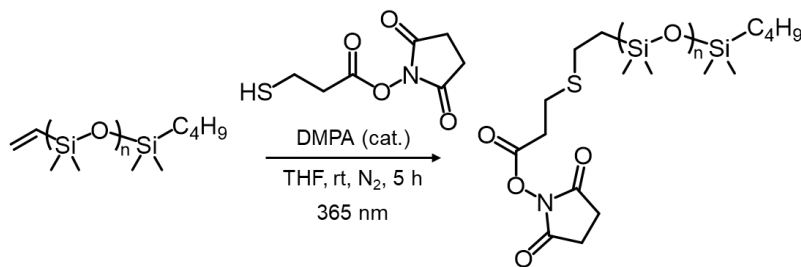


Fig. S4. ^{13}C NMR spectrum of 3-(4,5-bis(2-methyl-5-phenylthiophen-3-yl)-1*H*-imidazol-1-yl)propan-1-amine (DAE-NH₂).

2. Synthesis of polydimethylsiloxane chain-end functionalized with diarylethene unit (PDMS-*ω*-DAE)

Synthesis of 3-mercaptopropanyl-*N*-hydroxysuccinimide ester chain-end functionalized PDMS



To a flame-dry round bottom flask equipped with a magnetic stir bar, monovinyl-terminated PDMS (1.4 g, 0.21 mmol, 1 eq., $M_n = 6.7$ kDa, $D = 1.09$), 3-mercaptopropanyl-*N*-hydroxysuccinimide ester (85 mg, 0.42 mmol, 2 eq.), photoinitiator 2,2-dimethoxy-2-

phenylacetophenone (10.7 mg, 0.042 mmol, 0.2 eq.), and 10 ml of deoxygenated absolute THF were added. The solution was bubbled with nitrogen for 30 minutes, after which the reaction proceeded under 365 nm lamp irradiation (15 Watt) for 5 hours. Upon completion, the product was purified by precipitation in cold methanol and dried under a high vacuum. The final product was stored in the freezer. $M_n(\text{NMR}) = 6.9 \text{ kDa}$.

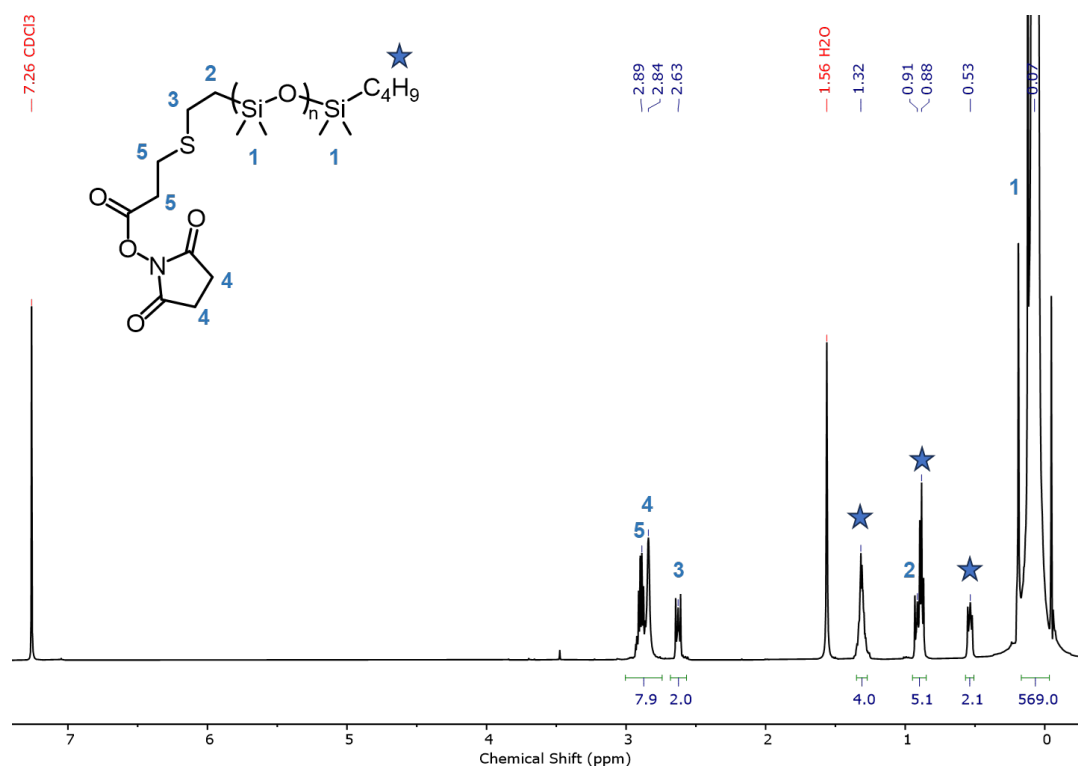
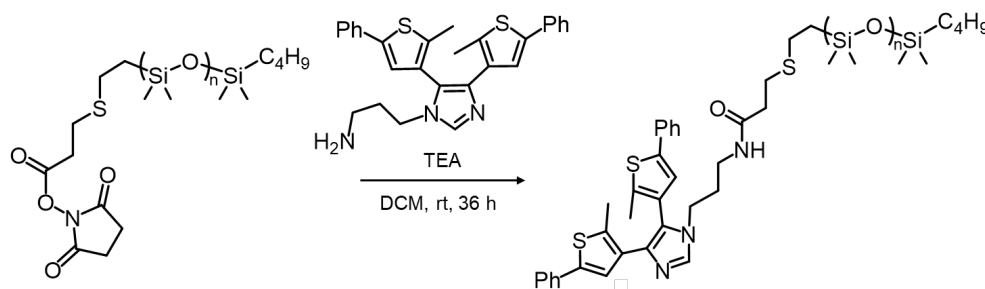


Fig. S5. $^1\text{H NMR}$ spectrum of 3-mercaptopropanyl-*N*-hydroxysuccinimide ester chain-end functionalized PDMS.

Synthesis of diarylethene chain-end functionalized PDMS (PDMS- ω -DAE)



To a flame-dry round bottom flask equipped with a magnetic stir bar, DAE-NH₂ (102 mg, 0.22 mmol, 3 eq.), triethylamine (167 μL), 10 ml of dry dichloromethane were added. Subsequently, 3-mercaptopropanyl-*N*-hydroxysuccinimide ester chain-end functionalized PDMS (500 mg, 0.072 mmol, 1 eq., $M_n = 6.9$ kDa) was added in 4 ml of dry dichloromethane. The solution was stirred at room temperature for 36 hours, then concentrated under reduced pressure, purified by precipitation in cold methanol, and dried under a vacuum atmosphere. The final product was stored in the freezer. $M_n(\text{NMR}) = 7.3$ kDa.

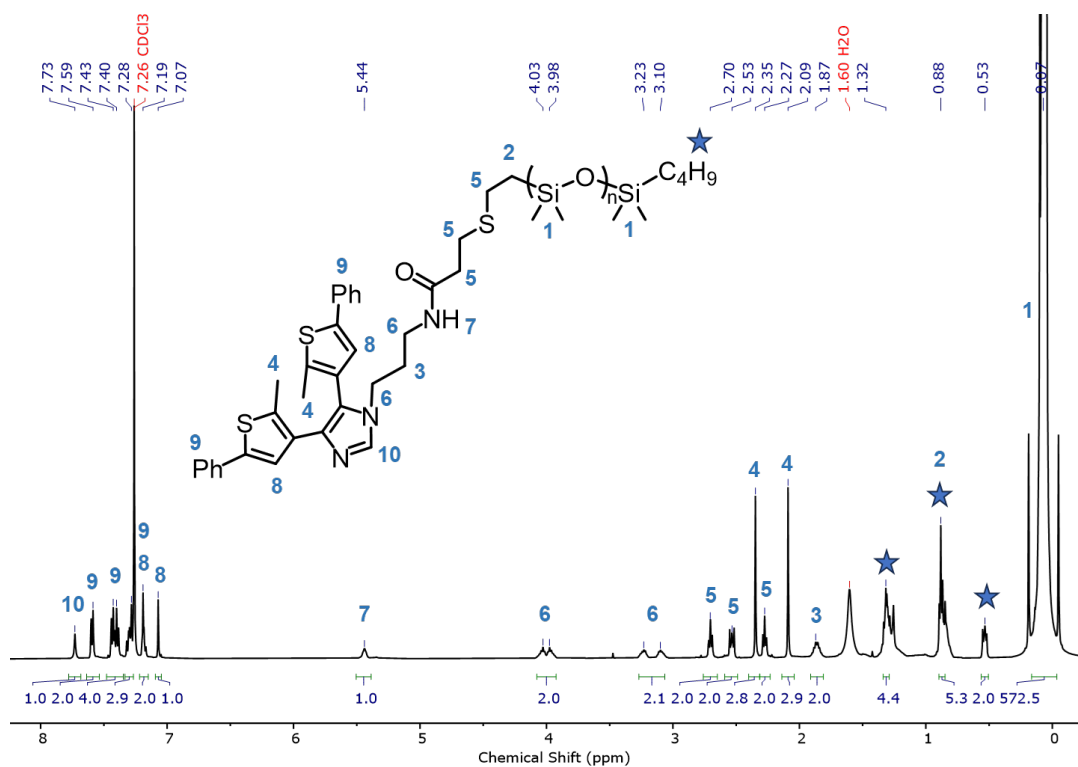
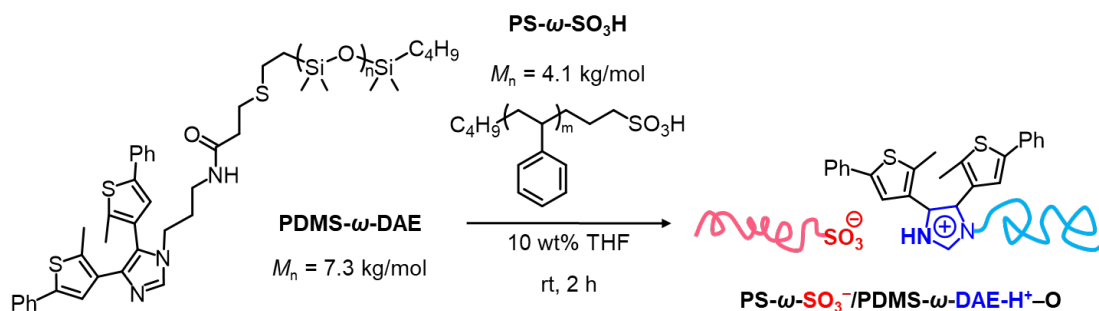
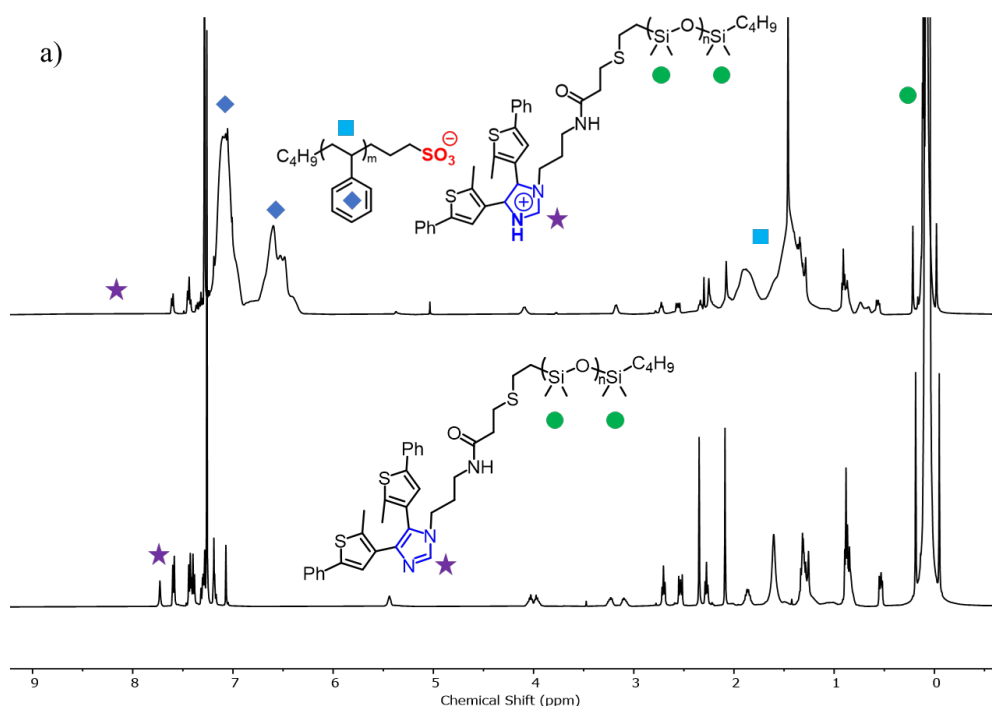


Fig. S6. ¹H NMR spectrum of PDMS- ω -DAE.

3. Synthesis of PS- ω -SO₃⁻/PDMS- ω -DAE-H⁺-O ionic copolymer



To form an ionic copolymer PS- ω -SO₃⁻/PDMS- ω -DAE-H⁺-O, desired amounts of PDMS- ω -DAE (10 wt% in dry THF) and PS- ω -SO₃H (10 wt% in dry THF) solutions were mixed at a 1:1 molar ratio between DAE and SO₃H end groups for two hours at room temperature. The proton transfer process can be observed by ¹H NMR through the disappearance of the characteristic imidazole signal at 7.73 ppm and the appearance of a new broad imidazolium signal at 8.68 ppm upon blending.



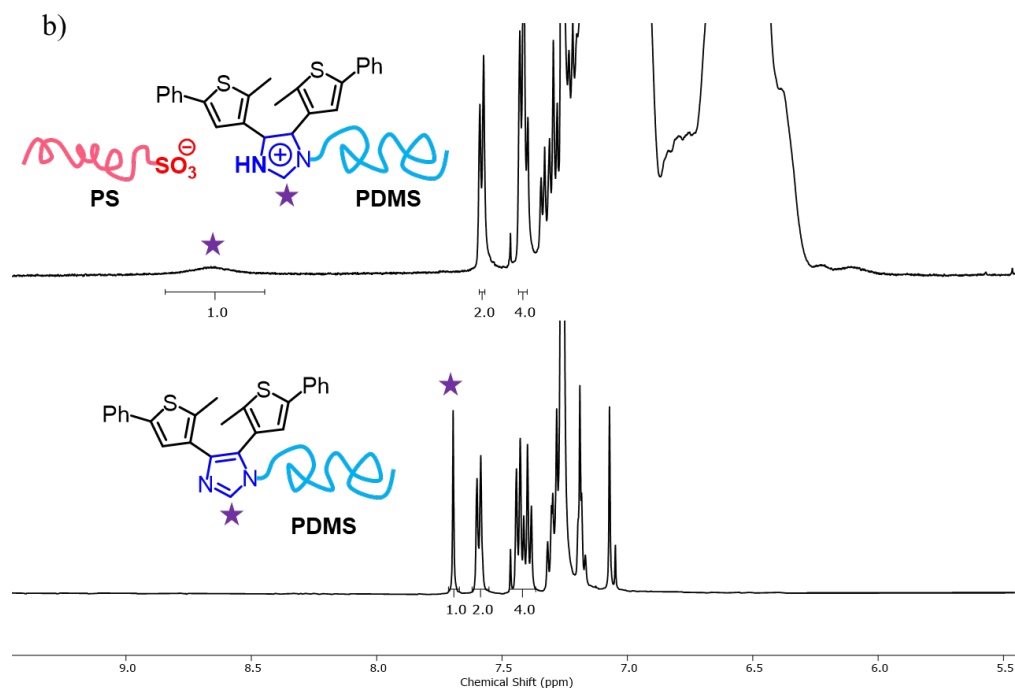
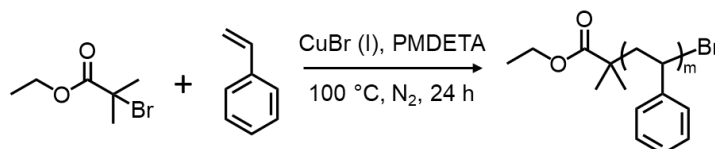


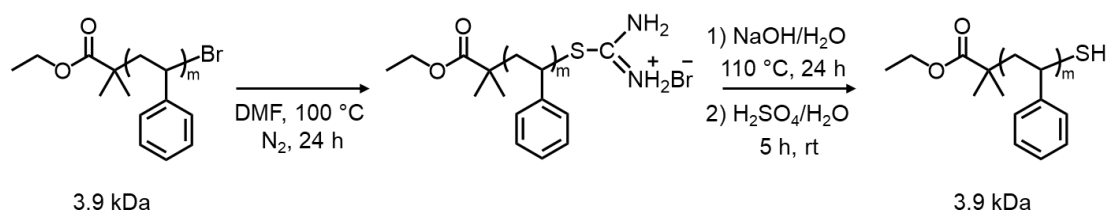
Fig. S7. a) Comparison of ^1H NMR spectra of PDMS- ω -DAE and PS- ω -SO $_3^-$ /PDMS- ω -DAE- H^+ -O ionic copolymer b) selected area 5.5 – 9.4 ppm in CDCl_3 .

4. Synthesis of bromine-terminated polystyrene (PS-Br)



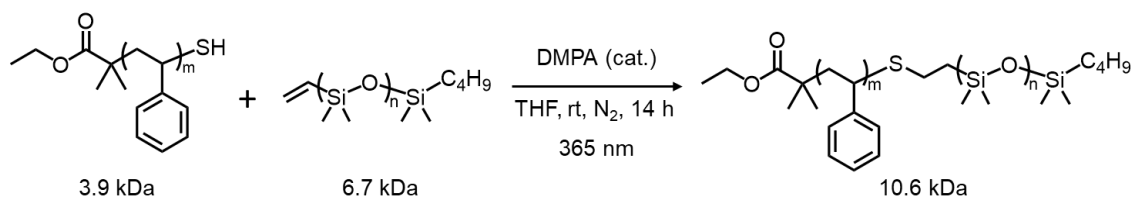
The synthesis was adapted from Segalman et. al.⁴ Ethyl- α -bromoisobutyrate (EBiB) (146 μL , 1 eq.), N,N,N',N'',N'' -pentamethyldiethyltri-amine PMDETA (42 μL , 0.2 eq.), and styrene (4 g, 36 eq.) were combined in a Schlenk flask. The solution was purged with nitrogen for 30 min before adding copper (I) bromide (29 mg, 0.2 eq.). The mixture was further degassed with three freeze-pump-thaw cycles and then stirred under a nitrogen atmosphere at $100\text{ }^\circ\text{C}$. After 24 h, the solid was dissolved in THF, filtered through alumina to remove copper compounds, and then precipitated into 1 L of methanol. The filtered polymer was dried *in vacuo* overnight. The molecular weight was determined by SEC against PS standards to be $M_n = 3.9\text{ kg/mol}$, $D = 1.10$.

5. Synthesis of thiol end-functional polystyrene (PS-SH)



Synthesis was adapted from Hilborn et al.⁵ A mixture of 1 g of polystyrene (PS-Br, $M_n = 3.9$ kg/mol), thiourea (0.20 g, 2.6 mmol), and 30 ml of DMF was heated at 100 °C under nitrogen flow for 24 h. Then, NaOH (0.1 g, 2.6 mmol) was dissolved in 0.8 ml of water and added to the mixture, which was heated at 110 °C for 24 h. Two drops of 95% sulfuric acid in 0.5 ml of water were added, and the mixture was stirred at room temperature for an additional 5 h. DMF was evaporated and the functionalized polymer was dissolved in 10 mL THF and precipitated from methanol twice.

6. Synthesis of PS-*b*-PDMS



PS-*b*-PDMS was synthesized by thiol-ene. A mixture of Monovinyl-PDMS (0.2 g, 0.03 mmol, 1 eq), PS-SH (0.168 g, 0.043 mmol, 1.4 eq), and DMPA (1.53 mg, 0.006 mmol, 0.2 eq) was dissolved in THF and purged with nitrogen gas for 15 min, after which the reaction proceeded under 365 nm UV irradiation (15 Watt) for 14 hours. The polymer was precipitated in pentane

several times to remove excess PS-SH, and Biotage Selekt flash chromatography equipped with a light-scattering detector was used to remove unreacted polymers with hexane/ethyl acetate gradient 95/5.

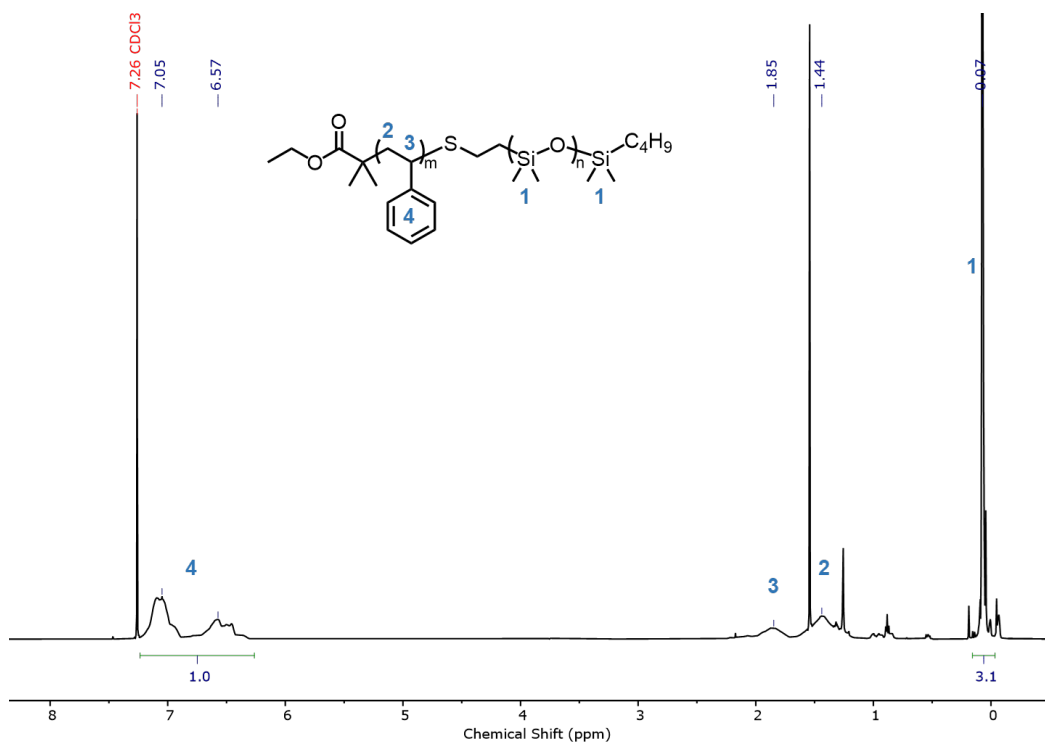


Fig. S8. ¹H NMR spectrum of PS-*b*-PDMS.

Polymer Characterization

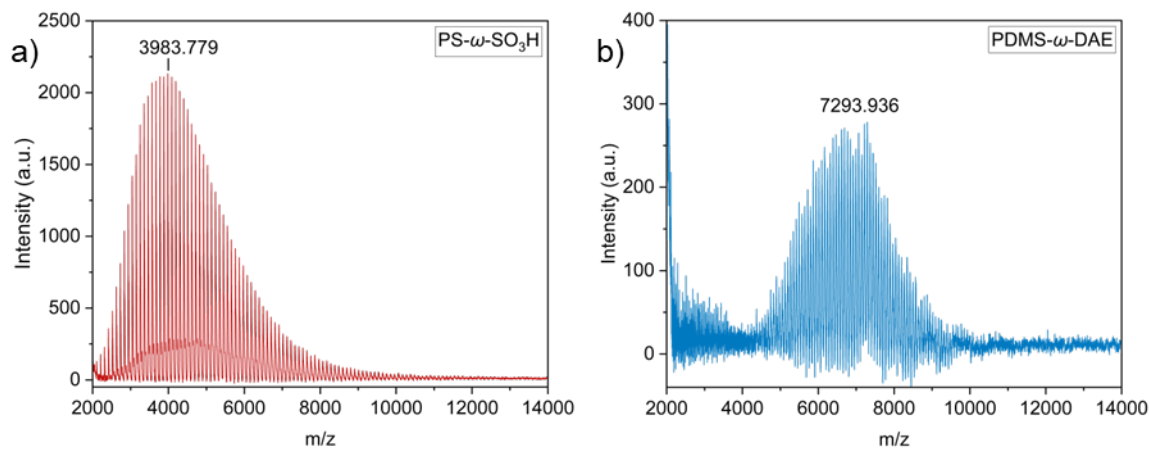


Fig. S9. MALDI spectrum of (a) PS- ω -SO₃H, $m/z = 3944.681 + K$ (b) PDMS- ω -DAE, $m/z = 7254.838 + K$.

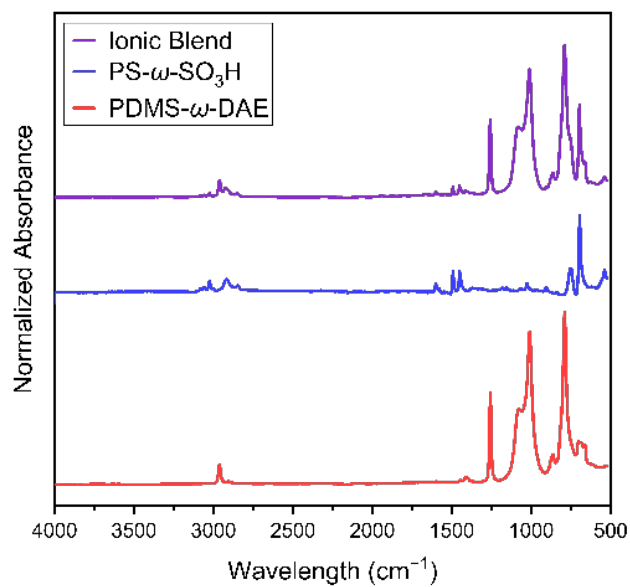


Fig. S10. Stacked Fourier-transform infrared spectra of PS- ω -SO₃⁻/PDMS- ω -DAE-H⁺ ionic blend, PS- ω -SO₃H, and PDMS- ω -DAE.

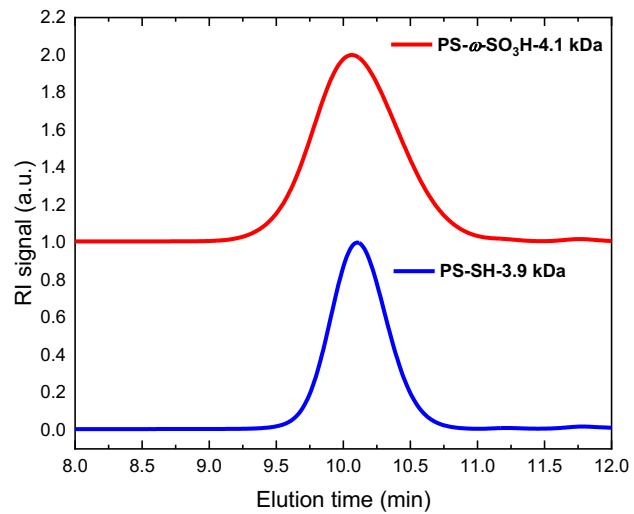


Fig. S11. SEC traces of PS-SH and PS- ω -SO₃H.

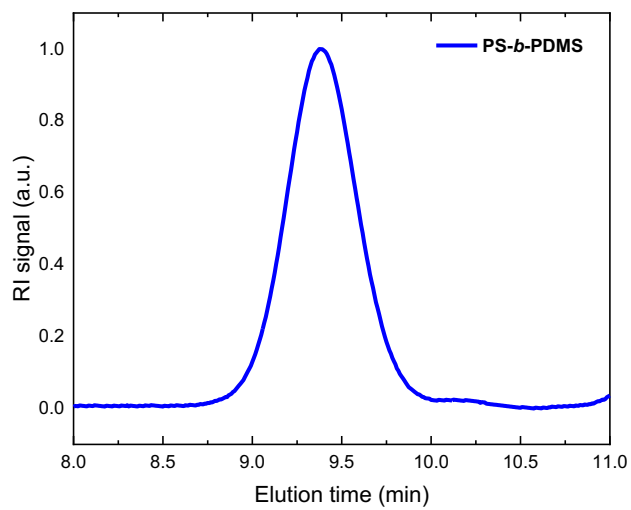


Fig. S12. SEC trace of PS-*b*-PDMS synthesized by thiol-ene click reaction.

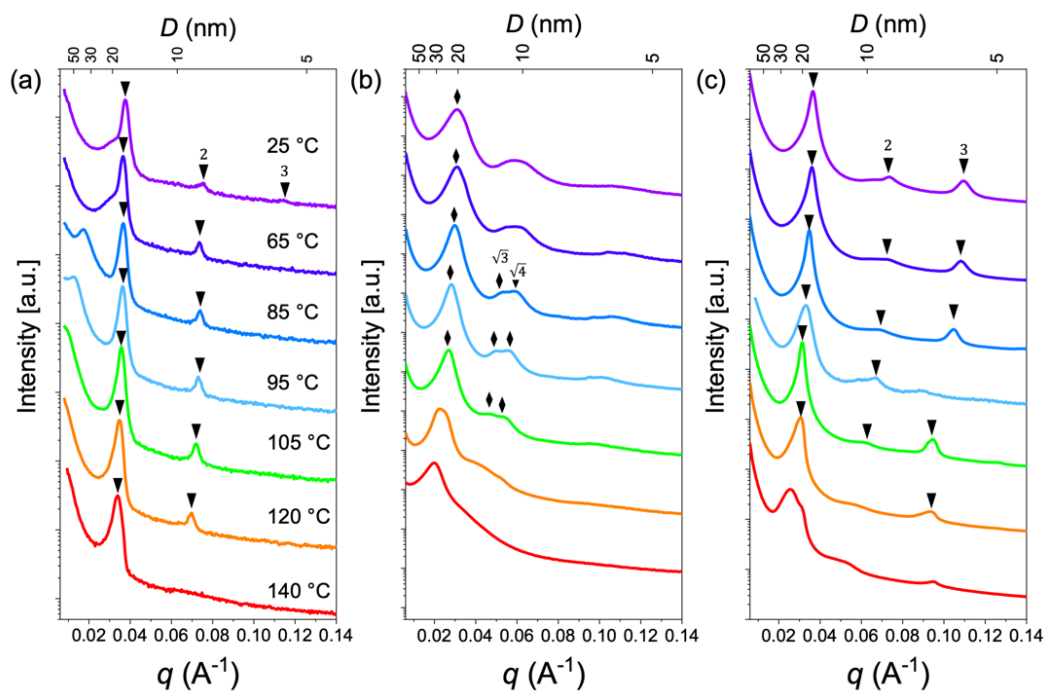


Fig. S13. SAXS profiles of (a) PS-*b*-PDMS, (b) PS- ω -SO $_3^-$ / PDMS- ω -DAE-H $^+$ -O, and (c) PS- ω -SO $_3^-$ / PDMS- ω -DAE-H $^+$ -C blends. Higher order peaks are marked with the inverted triangles at $2q^*$ and $3q^*$ for LAM, and diamonds at $\sqrt{3}q^*$ and $\sqrt{4}q^*$ for HEX.

Calculation of Interfacial Area.

The microstructure of the DAE-H⁺-O blend is illustrated in Fig. 4 in the main text.

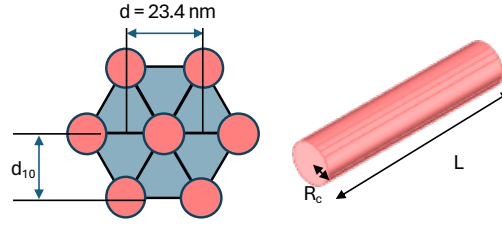


Fig. S14. Schematic of ideal HEX. Blue domains correspond to PDMS, while pink cylinders are formed by PDMS.

Assuming each unit cell has cylinders (PS) with a length of L . Then the number of (PS-*b*-PDMS) chains per unit cell is:

$$\frac{\#chains}{unitcell} = \frac{\frac{\sqrt{3}}{2} d^2 L}{V_0}$$

where V_0 is the volume of one PS-*b*-PDMS copolymer chain.

Assuming incompressibility,

$$V_0 = \frac{M / N_{av}}{\rho} = \frac{M / N_{av}}{f_c \rho_{PS} + (1 - f_c) \rho_{PDMS}}$$

where M is the molar mass of one PS-*b*-PDMS chain, N_{av} is the Avogadro constant, ρ is the density, f_c is the volume fraction of the cylinders (0.34). Thus, the volume of a cylinder is:

$$f_c \frac{\sqrt{3}}{2} d^2 L = \pi R_c^2 L$$

where R_c is the radius of the cylinder, reducing to:

$$R_c = 0.525 f_c^{1/2} d$$

The surface area per unit cell is:

$$\Sigma_{cell} = 2\pi R_c L$$

Thus, the surface area per chain is:

$$\Sigma_{chain,HEX} = \frac{2\pi R_c L}{\frac{\sqrt{3}}{2} d^2 L} = 3.809 \frac{f_c^{1/2} V_0}{d} = 1.76 \text{ nm}^2$$

The microstructure of the DAE-H⁺-C blend is illustrated in Fig. 4 in the main text.

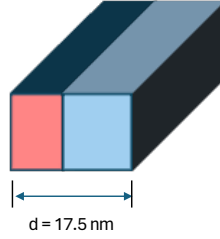


Fig. S15. Schematic of ideal LAM. Blue and pink domains correspond to PDMS and PS, respectively.

Similarly, the surface area per chain is:

$$\Sigma_{chain,LAM} = \frac{2V_0}{d} = 2.10 \text{ nm}^2$$

For the conventional PS-*b*-PDMS block copolymer linked by a -S- bond:

$$\Sigma_{chain,LAM} = \frac{2V_0}{d} = 2.11 \text{ nm}^2$$

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