Electronic Supplementary Material (ESI) for Soft Matter.

EFFECTS OF CYCLIC AND ACYCLIC AMIDINE SIDE-CHAINS ON THE PROPERTIES OF POLYSILOXANE IONOMERS CONSTRUCTED *IN SITU* FROM THREE UNCHARGED COMPONENTS

*Louis Poon, Jacob R. Hum, and Richard G. Weiss**

Department of Chemistry and Institute for Soft Matter Synthesis and Metrology

Georgetown University, Washington. DC 20057-1227, USA

E-mail: weissr@georgetown.edu

Electronic supplementary information

1. EXPERIMENTAL

1.1. Materials

Carbon disulfide (Acros, ≥99%); chloroform (Fisher, HPLC-Grade, ≥99% with 0.5% ethanol as stabilizer); chloroform (Fisher, ACS-Grade and HPLC-Grade, ≥99% with 0.75% ethanol as stabilizer); chloroform-d (Cambridge Isotope Inc., ≥99%); N,N-dimethylacetamide dimethylacetal (**DMADA**, Alfa Aesar, ≥90%, 5-10% methanol as stabilizer); N,N-dimethylamine (Sigma-Aldrich, 2.0M in THF); 1-hexylamine (Alfa Aesar, ≥ 99%); 1-octadecylamine (Alfa Aesar, ≥ 97%); poly[3-aminopropylmethylsiloxane-*co*-dimethylsiloxane] copolymer with 6-7% amine-monomer content (**6-7/7 AP**, Gelest, AMS 162, M_w = 5.4-7.7 KDa, ≥ 95%, 80-120 centistokes (cst)); poly[3-aminopropylmethylsiloxane-*co*-dimethylsiloxane] copolymer with 20-25% amine-monomer content (**20-25/28 AP**, Gelest, AMS 1203, M_w = 25.2-27.5 KDa, ≥ 95%, 900-1100 cst; poly[3-(2-aminoethyl)aminopropylmethylsiloxane-*co*-dimethylsiloxane] copolymer with 18-24% amine-monomer content (**18-24/19 AEAP**, Gelest, AMS 1203, M_w = 14.4-19.1 KDa, ≥ 95%, 300-500 cst); and potassium chloride (Fisher, ≥99%). All chemicals were used as received unless specified otherwise. Molecular weight ranges for the copolymers were calculated using Barry's relationship[1] and the cst viscosities provided by Gelest. Millipore water (18.2 Ω·cm, 0.05 μS/cm) was used for all relevant ionic conductivity measurements. 1-Hexylamine (Alfa Aesar, ≥ 99%) was distilled before use (boiling point of fraction collected: 129-130 ^{o}C, 760 mmHg. lit. bp [2] 129-130 ^{o}C, 760 mmHg). 1-Octadecylamine was vacuum distilled twice [3] (boiling point of fraction collected: 142-143 ^{o}C, 0.5 mmHg; lit. [4] 183.0-183.1 ^{o}C/5 mmHg and ΔH_{vap} [5]= 76.2 KJ/mol). Prior to use, 1-octadecylamine was also melted (mp 51.6-52.1 ^{o}C; lit [3] 50-52 ^{o}C) at 90 ^{o}C and cooled to room temperature under nitrogen to ensure removal of any residual carbon dioxide. The amidine copolymers (**1**) and ionomers (**1a-6, 1-6**, and **1-18**) were synthesized and characterized according to literature (Note: compounds **1**, **1-6**, and **1-18** are listed as **1c**, **1c-6**, and **1c-18**, respectively, in literature).[6]

1.2. Spectral characterizations

FT-IR spectra of the samples were obtained on a Perkin-Elmer Spectrum 2 spectrometer and the peak frequencies are reported as cm^{-1}. The technique used was attenuated total reflectance obtained through the UATR accessory with a single reflection diamond. 16 scans per sample were obtained over a range of 400-4000 cm^{-1} and collect at an interval of 0.5 cm^{-1}. Resolution was set at 2 cm^{-1}. ^{13}C and ^{1}H NMR spectra were obtained on a Varian MR-400 MHz (100.5 MHz for ^{13}C NMR) spectrometer. Unless specified otherwise, all ^{13}C and ^{1}H NMR spectra are reported in $CDCl_3$ with the chemical shift calibrated to the residual chloroform peak at 77.16 and 7.26 ppm, respectively.

1.3. Rheology

Oscillatory and rotational rheology were performed using a stress-controlled Anton-Paar MCR 302 rheometer using a stainless-steel cone-plate (CP25-1/TG) with a 25 mm diameter and cone angle of 1^{o} and a gap of 0.052 mm. Measurements were commenced only after the vertical load was 0 N. Temperature control was achieved using an Anton-Paar Peltier PTD-200 attachment with air as the cooling gas. Samples were equilibrated for 15-30 min at their requisite temperatures before commencing measurements. Strain sweeps were from 0.08% to 100% at a fixed angular frequency of 1 rad/s; angular frequency sweeps were performed at a fixed strain in the linear portions of the viscoelastic curves, and the angular frequency ranged from 0.08 to 100 rad/s. All samples were measured three times using the same aliquot for the first two and a different one for the third run. Strain and frequency sweeps were separated by a 30 min equilibration time to allow the polymeric systems to re-equilibrate. Dynamic viscosities were obtained for shear rates from 0.01 to 300 s^{-1}.

1.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on a Q200 differential scanning calorimeter with samples in open aluminum pans. Prior to taking measurements, residual chloroform was removed from the samples by heating them for 30 min at 40 °C and then at room temperature (18-20 °C) for 72 h, both at 100 mmHg. Then, the data were recorded on samples equilibrated at 0 °C for 1 min, heated to 120 °C, and held there for 5 min before cooling to 0 °C. They were kept at 0 °C for 5 min before reheating. The cycles were repeated 3 more times. Rates of heating and cooling were 5 °C/min unless specified otherwise.

1.5. Temperature-dependent powder X-ray diffraction (PXRD)

Samples were placed inside Kapton® capillaries with 1.0 mm diameters and kept in a nitrogen stream whose temperature was controlled using an Oxford 700 Cryostream cooler. The samples were initially at 0 °C for 10-20 min before being heated at a constant rate of 5 °C /min (to mimic the DSC experiments) to each desired temperature and equilibrated there for 10-20 min before data were collected on a Bruker Apex DUO diffractometer equipped with an APEXII CCD detector using a Cu IμS source (λ = 1.542 Å). A series of 360° Φ scans was collected and data were integrated in the range of 2° to 60° in 2θ.

1.6. Adhesion studies

Adhesion was measured using an Instron 5965 Universal Testing System with a 5 kN instrument loading capacity. Protocols for the extension of the sample were adapted from ASTM-D1002 [7]: the rate of extension was 5.0 mm/min and the custom-built glass sample holder had a single lap joint. It consisted of 3 standard microscope slides (2.5 cm x 7.5 cm x 1.4 mm) glued together with an epoxy adhesive (ATACS, 5104/4103) to form a single lap joint with a defined shear area of 7.5 cm^2 (width 2.5 cm; length 3.0 cm) for the samples. Two of the glass slides were held by the instrument clamps. The thickness of the epoxy layer, 100 μm, constant from end-to-end, was measured by a Nikon Eclipse Ti microscope at 10x magnification. The average thickness of each ionomer layer pressed between the slides was measured from images taken with a Luminera Infinity 2-1R camera using the thickness of the glass slides (1.4 mm) as a reference.

1.7. Thermogravimetric Analyses (TGA)

Thermogravimetric analyses of the ionomer melts were conducted using a TA instrument thermogravimetric analyzer (Model Q5000). Nitrogen gas was used for purging the sample compartment during heating while compressed air was used for cooling. Samples were placed in platinum pans and equilibrated there initially at 30 °C. Then, they were heated at 5 °C/min to 600 °C (unless stated otherwise).

1.8. Detailed descriptions of syntheses of imidazoline-based ionomers and their precursors

Poly[3-(2-methyl-4,5-dihydro-1H-imidazol-1-yl)propylmethylsiloxane-co-dimethylsiloxane] copolymer with 18-24% amine content **(2)**. Under a nitrogen atmosphere, *N,N*-dimethylacetamide dimethyl acetal (8.0 g, 61 mmol) was added to a solution of 2.0 M dimethylamine (25 mL, 40 mmol) in THF and stirred for 10 min at room temperature. **18-24/19 AEAP** (10.0 g, 26 mmol of monomers with aminoethylaminopropyl substituents) was then added dropwise over a period of 1 h and then stirred in the dark for an additional18 h. Solvent and excess reactants were removed at 100 mmHg and 40 °C followed by 0.3 mmHg and 45 °C for 2 h. No noticeable change in the intensity of the residual *N,N*-dimethylacetamide impurity peaks at 2.1, 2.9, and 3.0 ppm was observed after 2 h by ^{1}H NMR; the amount of *N,N*-dimethylacetamide, calculated from the area of the 2.1 ppm peak, with reference to the peak at 0.53 ppm, was 0.3 – 0.6 wt%. The dark red liquid was filtered through a polypropylene 0.2 µm membrane pore syringe filter to yield 9.4 g (93% yield; 12% imidate ester content). ^{1}H NMR ($CDCl_3$): 0.05 (m, 25.0H, $\underline{\mathbf{CH_3}}$-Si); 0.49 (t, 2.0H, *J* = 7.2 Hz, Si-$\underline{\mathbf{CH_2}}$-$CH_2$); 1.54 (m, 2.0H, Si-$CH_2$-$\underline{\mathbf{CH_2}}$); 1.90 (s, 2.8H, $\underline{\mathbf{CH_3}}$-C=N); 3.03 (t, 2.0H, J = 6.9 Hz, $SiCH_2CH_2$-$\underline{\mathbf{CH_2}}$-N); 3.25 (t, 1.9H, *J* = 9.0 Hz, C=$NCH_2\underline{\mathbf{CH_2}}$N-); 3.64 (t, 1.9H, *J* = 9.0 Hz, C=N$\underline{\mathbf{CH_2}}CH_2$N-). ^{13}C NMR ($CDCl_3$): -0.5, 1.0, 14.2, 22.2, 49.8, 51.8, 164.5. IR: 2959 (m), 1620 (m), 1413 (m), 1256 (s), 1063 (s), 1009 (s), 794 (s).

Polysiloxane-based ionomers with 18-24% imidazolinium hexyldithiocarbamate monomeric fractions **(2-6)**. A solution of **2** (2.0 g, 3.7 mmol of imidazoline-monomer) and 1-hexylamine (0.38 g, 3.7 mmol) in $CHCl_3$ (15 mL) was cooled in an ice bath. To it was added, dropwise, an ice-cooled 1.45 M stock solution of CS_2 in HPLC-grade $CHCl_3$ (3.7 mL, 5.6 mmol). The reaction vessel was closed, warmed to room temperature, and stirred overnight. Full conversion to amidinium dithiocarbamate was indicated by the disappearance of the triplet at 2.6 ppm in the ^{1}H-NMR spectrum that is diagnostic for 1-hexylamine. The solution was dried at 100-125 mmHg and 36 °C for 1 h followed by washing with $CHCl_3$ (20 mL). The drying process was repeated to aid removal of residual CS_2. The liquid was then dried at 100-125 mmHg and 36 °C for 1 h and then at 100-125 mmHg and room temperature for 2 days before recording a ^{1}H NMR spectroscopy. If some 1-hexylamine was detected, the product was dissolved in $CHCl_3$ (10 mL) and cooled in an ice-bath. Then, CS_2 (same solution and amount as above) was added dropwise, the solution was stirred for another 24 h, and solvent was removed as above. ^{1}H NMR ($CDCl_3$): -0.02 (m, 25.4H, $\underline{\mathbf{CH_3}}$-Si); 0.38 (m, 2.0 H, Si-$\underline{\mathbf{CH_2}}$-$CH_2$); 0.78 (t, 2.6H, J = 6.4 Hz, $\underline{\mathbf{CH_3}}$-$(CH_2)_3$-); 1.19 (m, 5.4H, CH_3-($\underline{\mathbf{CH_2}}$)$_3$-); 1.47 (quint. , 1.7H, J = 7.0Hz, $(CH_2)_3$-$\underline{\mathbf{CH_2}}$-); 1.55 (m, 2.0 H, Si-$CH_2$-$\underline{\mathbf{CH_2}}$); 2.31 (m, 2.3H, $\underline{\mathbf{CH_3}}$-C=NH); 3.26 (s, 2.3H, $SiCH_2CH_2$-$\underline{\mathbf{CH_2}}$-N=C); 3.45 (m, 1.8H, and -$\underline{\mathbf{CH_2}}$-NH-$CS_2$); 3.61 (m, 0.5H, $SiCH_2CH_2$-$\underline{\mathbf{CH_2}}$-N=C); 3.77 (m, 1.7H, -N$\underline{\mathbf{CH_2}}$$CH_2$N-); 3.92 (m, 1.6H, , -N$\underline{\mathbf{CH_2}}$$CH_2$N-); 7.44 (br., 0.8H, -$CH_2$N-C=$\underline{\mathbf{NH}}$-); 7.51 (m, 0.7 H, -$CH_2$-$\underline{\mathbf{NH}}$-$CS_2$); 9.48 (m, 0.1H, -$CH_2$N-C=$\underline{\mathbf{NH}}$-). ^{13}C NMR ($CDCl_3$): 0.93, 15.51, 16.62, 23.84, 25.12, 29.47, 31.55, 33.83, 46.94, 50.85, 51.54, 166.76, 213.30. IR: 3381 (br), 3197 (w), 3133 (w), 2960 (m), 2931 (m), 2861 (w), 1617 (m), 1597 (m), 1527 (m), 1444 (w), 1400 (w), 1300 (w), 1251 (s), 1075 (s), 1067 (s), 1010 (s), 965 (shoulder), 794 (s).

Polysiloxane-based ionomers with 18-24% imidazolinium octadecyldithiocarbamate monomer fractions **(2-18)**. 1-Octadecylamine (0.95 g, 3.7 mmol) was dissolved in $CHCl_3$ (30 mL) by heating to 50 °C and cooling to room temperature before addition of **2** (2.0 g, 3.7 mmol of amidine-monomer); the solution was then cooled in an ice bath. A 1.45 M carbon disulfide in HPLC-grade chloroform (3.7 mL, 5.6 mmol) solution was added dropwise over a period of 15 mins into the ice-cooled solution. The reaction vessel was closed and the solution was warmed to room temperature and stirred overnight. Complete conversion to amidinium dithiocarbamate was indicated by the disappearance of the triplet at 2.6 ppm in the ^{1}H-NMR spectrum that is diagnostic for 1-

octadecylamine. The solution was dried at 36 °C and 100-125 mmHg for 1 h, followed by washing with $CHCl_3$ (20 mL). The drying and washing process was repeated to aid removal of residual CS_2. The liquid was then dried at 36 °C and 100-125 mmHg for 1 h, and then at room temperature and 100-125 mmHg for 2 days before being analyzed. If some 1-octadecylamine was detected by ^1H NMR spectroscopy, the product was dissolved in $CHCl_3$ (10 mL) and cooled in an ice bath. Then, CS_2 (same solution and amount as above) was added dropwise, the solution was stirred for another 24 h, and solvent was removed as above. ^1H NMR ($CDCl_3$): -0.04 (m, 25.1H); 0.46 (m, 2.0 H, Si-$\underline{\mathbf{CH_2}}$-$CH_2$); 0.84 (t, 2.7H, J = 6.9 Hz, $\underline{\mathbf{CH_3}}$-$(CH_2)_{15}$-); 1.22 (m, 35H, CH_3-$(\underline{\mathbf{CH_2}})_{15}$-); 1.54 (quint., 1.7H, J = 6.9Hz, $(CH_2)_{15}$-$\underline{\mathbf{CH_2}}$-); 1.62 (m, 2.1 H, $SiCH_2$-$\underline{\mathbf{CH_2}}$); 2.41 (2.6H, m, $\underline{\mathbf{CH_3}}$-C=N); 3.31 (s, 1.9H, $SiCH_2CH_2$-$\underline{\mathbf{CH_2}}$-N); 3.52 (q, 1.8H, J = 6.9Hz, $(CH_2)_{15}$-$\underline{\mathbf{CH_2}}$-NH-$CS_2$); 3.67 (q, 0.2H, J = 7.1 Hz, $SiCH_2CH_2$-$\underline{\mathbf{CH_2}}$-N=C); 3.79 (m, 1.8H, -N$\underline{\mathbf{CH_2}}$$CH_2$N-); 4.03 (m, 1.8H, -N$\underline{\mathbf{CH_2}}$$CH_2$N-) 7.51 (t, 0.8H, J = 4.6Hz, $(CH_2)_{15}$-CH_2-$\underline{\mathbf{NH}}$-CS_2); 8.47 (br., 0.9H, -CH_2N-C=$\underline{\mathbf{NH}}$-); 9.52 (t, 0.1H, J = 4.6Hz, -CH_2N-C=$\underline{\mathbf{NH}}$-) . ^{13}C NMR ($CDCl_3$): 3.75, 15.30, 16.77, 23.99, 25.47, 29.39-29.79 (C18-chain), 31.44, 31.66, 47.58, 47.80, 48.43, 51.73, 167.03 (broad), and 201.70. IR: 3203 (w), 3049 (w), 2957 (w), 2917 (s), 2851 (m), 1616 (m), 1591 (shoulder), 1511 (w), 1500 (w), 1456 (w), 1259 (s), 1069 (s), 1009 (s), 794 (s).

2. SPECTRAL CHARACTERIZATIONS - NMR AND FT-IR

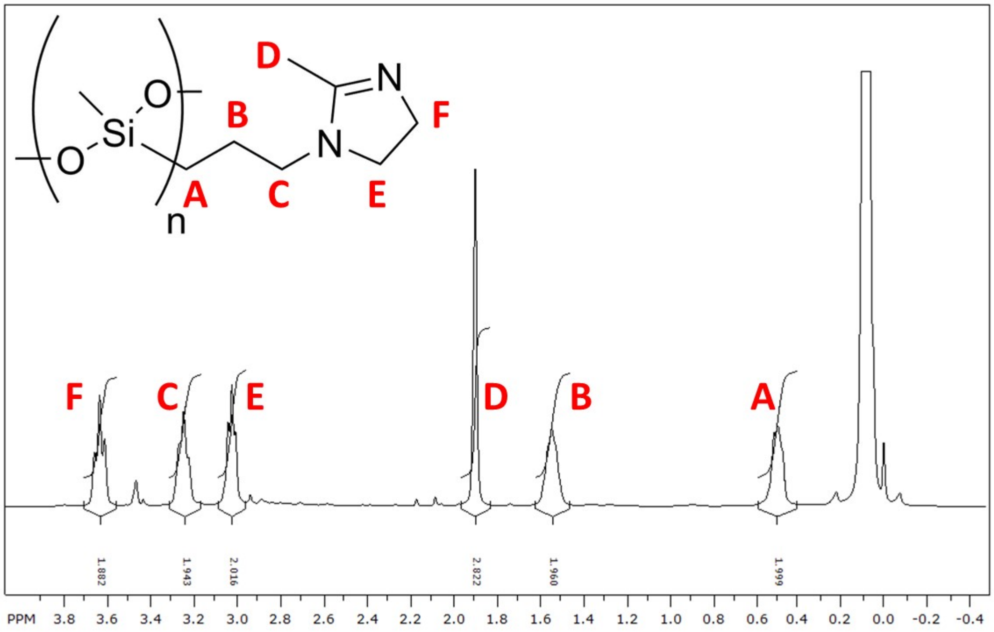

Figure S1. Assignment of ^{1}H-NMR ($CDCl_3$) peaks to **2**.

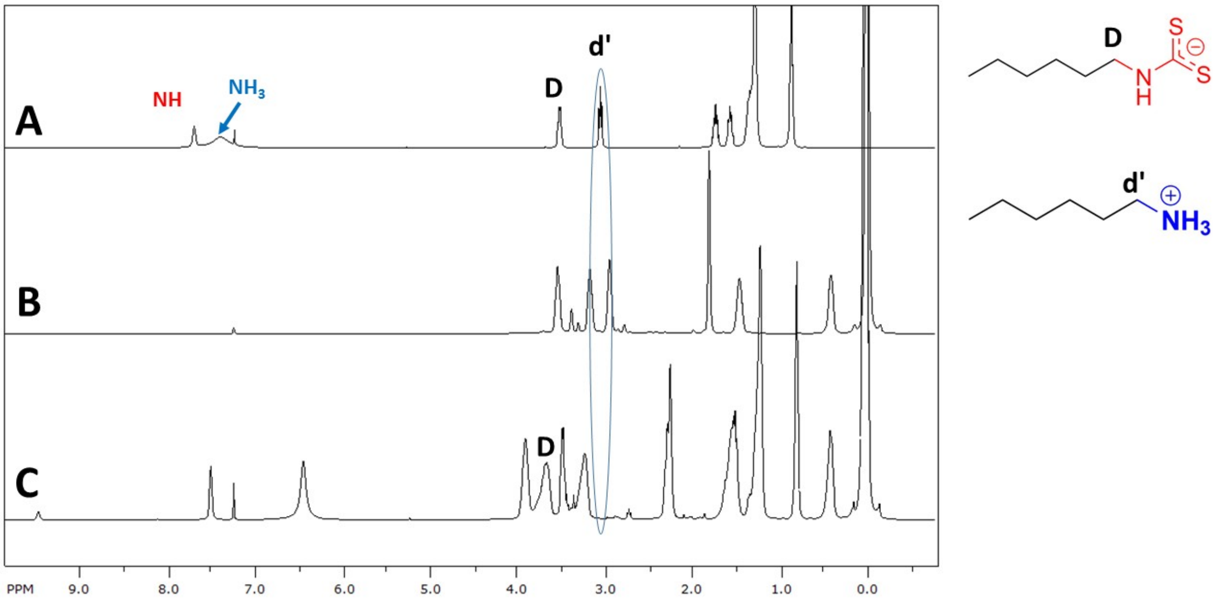

Figure S2. ^{1}H NMR spectra ($CDCl_3$) associated with the conversion of **2** to **2-6**. A) Hexylammonium N-hexyldithiocarbamate from the addition of CS_2 to 1-hexylamine; B) compound **2**; and C) Reaction of equimolar amount of imidazoline groups in **2** and hexylammonium N-hexyldithiocarbamate after 24 h. The small triplet at 2.8 ppm is from the imidate ester side product.

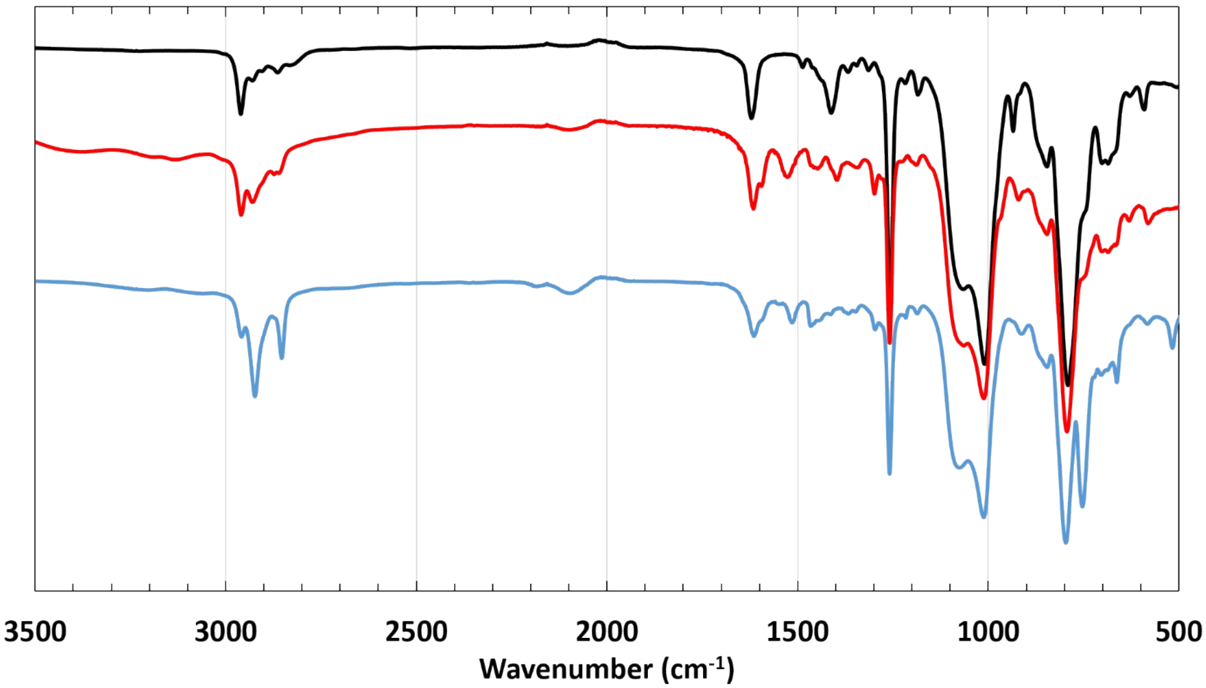

Figure S3. Y-axis offset FT-IR spectra of **2** (black), **2-6** (red), and **2-18** (blue).

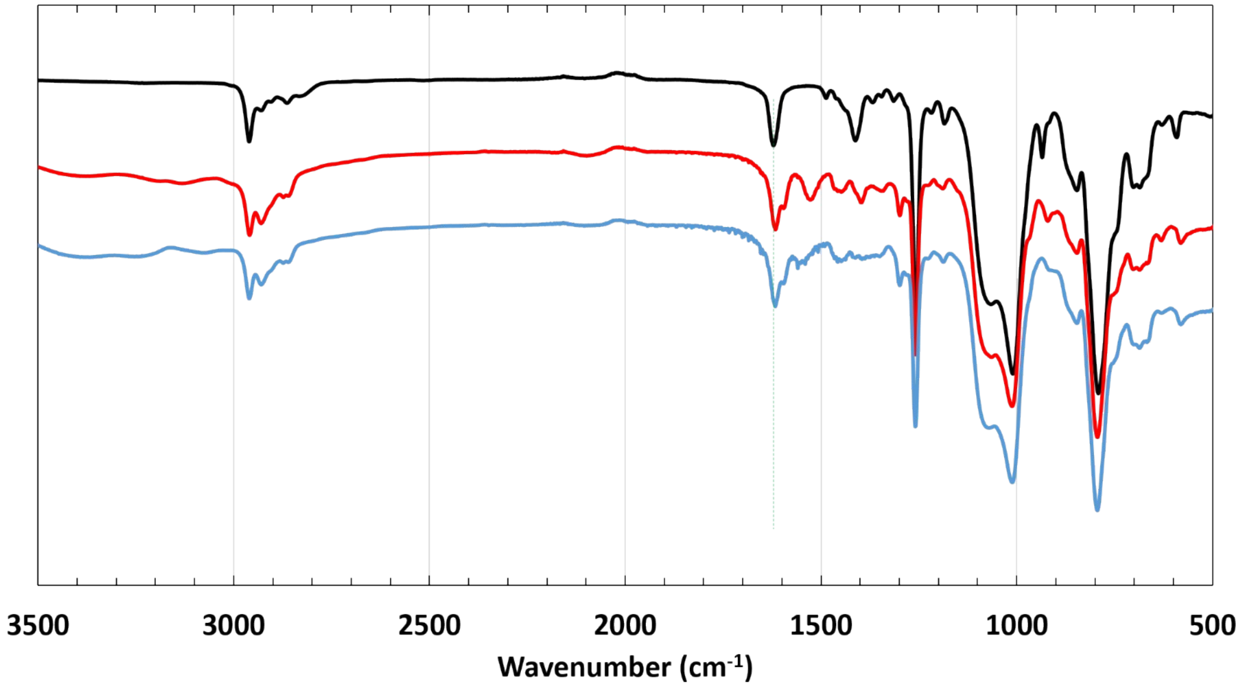

Figure S4. FT-IR spectra of **2** (black), **2-6** before (red) and after (blue) DSC measurements (see above). The measurements included 4 cycles of heating and cooling from 0-120 °C.

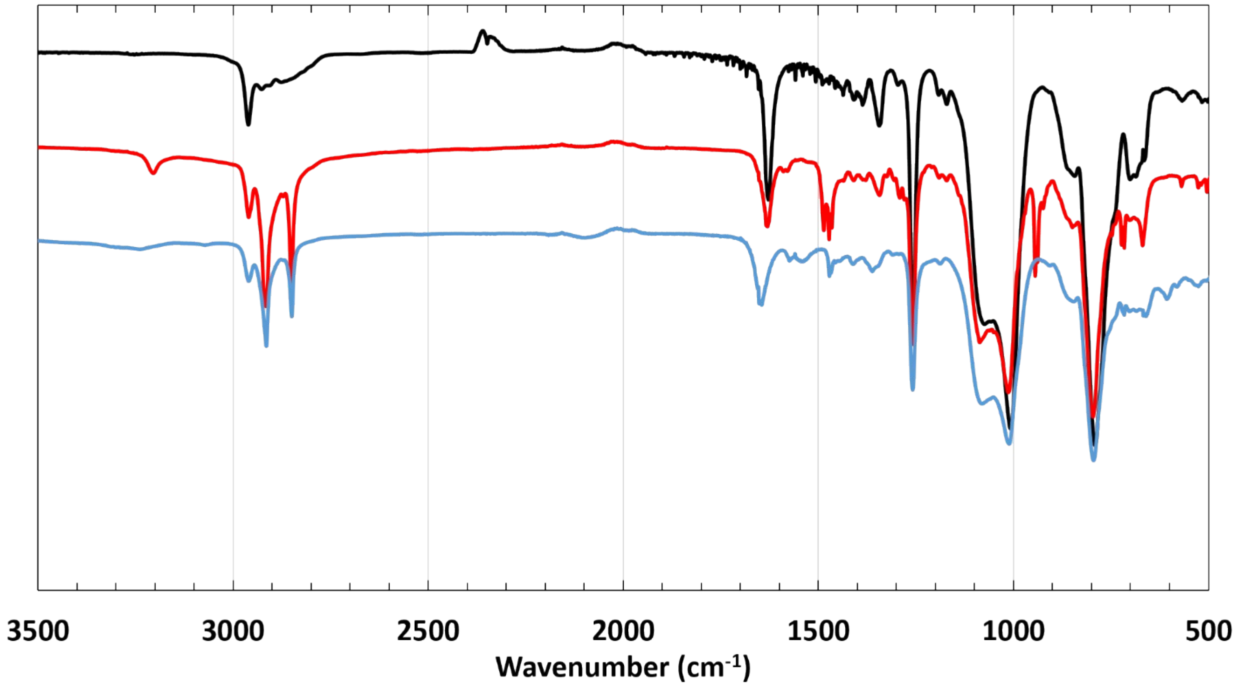

Figure S5. FT-IR spectra of **2** (black) and **2-18** before (red) and after (blue) DSC measurements (see above). The DSC measurements included 4 cycles of heating and cooling from 0-120 ^{o}C.

3. TGA and DSC data

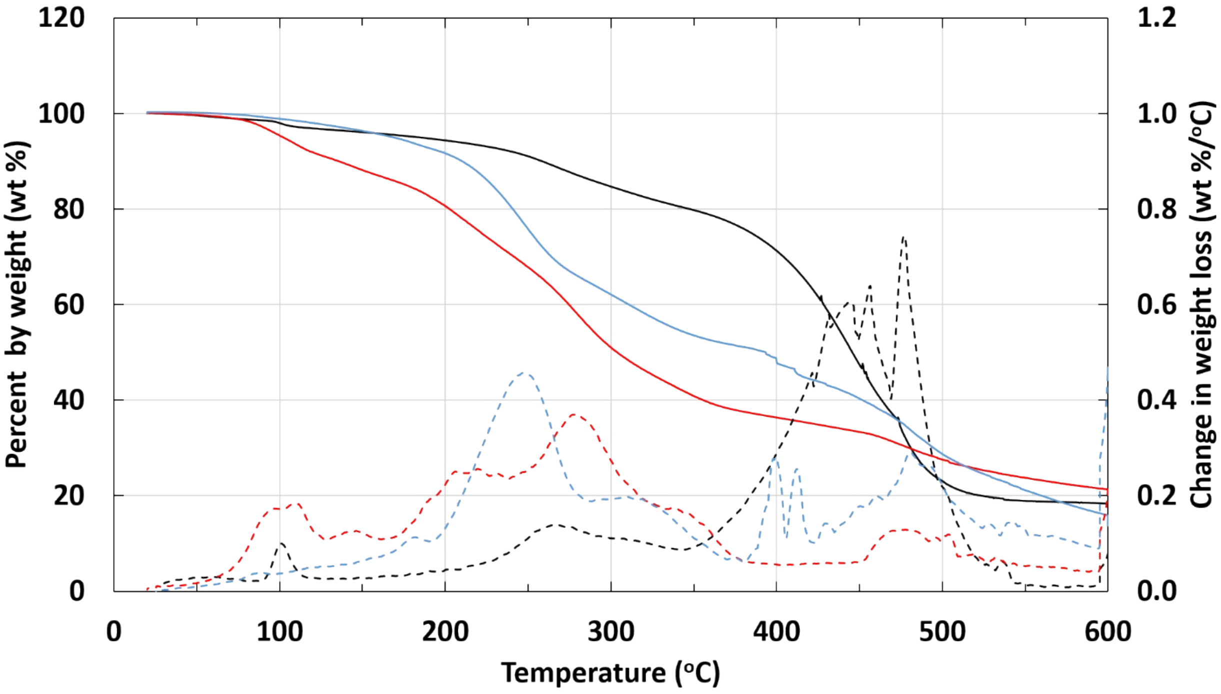

Figure S6. TGA thermograms of **2** (solid black line), **2-6** (solid red line), and **2-18**(8KD) (solid blue line). The rate of change in weight loss as a function of temperature is also plotted on the right side of the y-axis: **2** (dashed black line), **2-6** (dashed red line), and **2-18** (38KD) (dashed blue line).

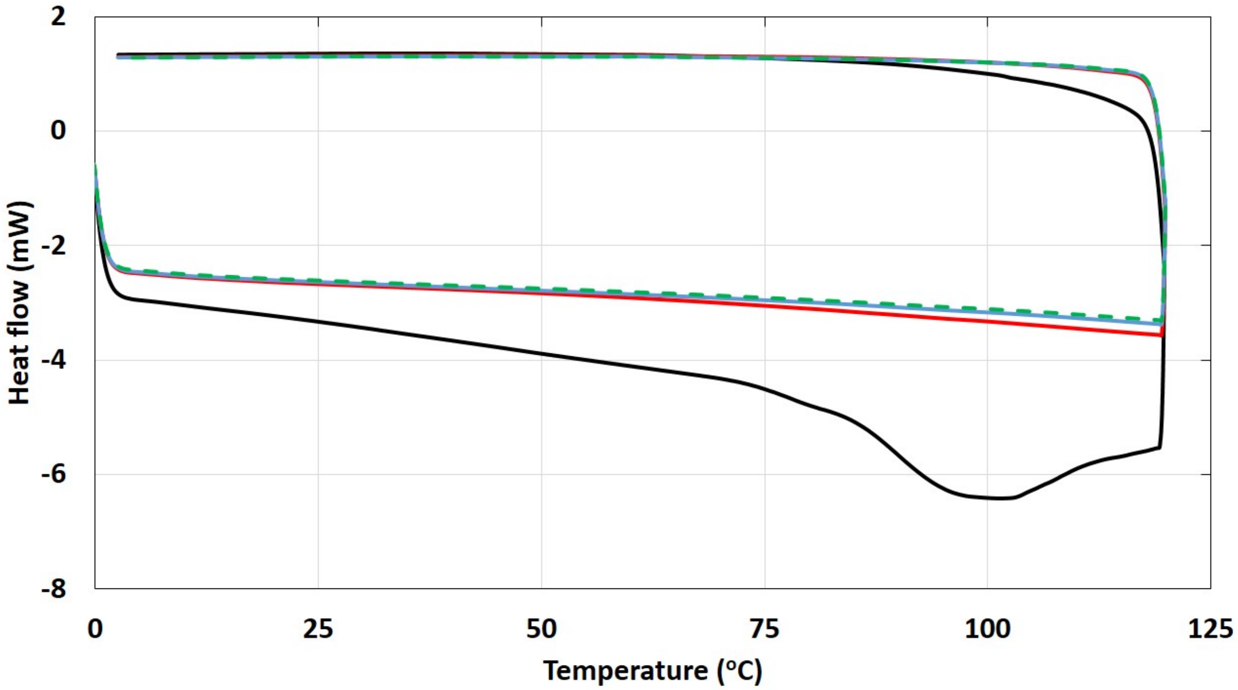

Figure S7. DSC data for **2-6**: heating-cooling cycle 1 (black), cycle 2 (red), cycle 3 (blue), and cycle 4 (green dashed).

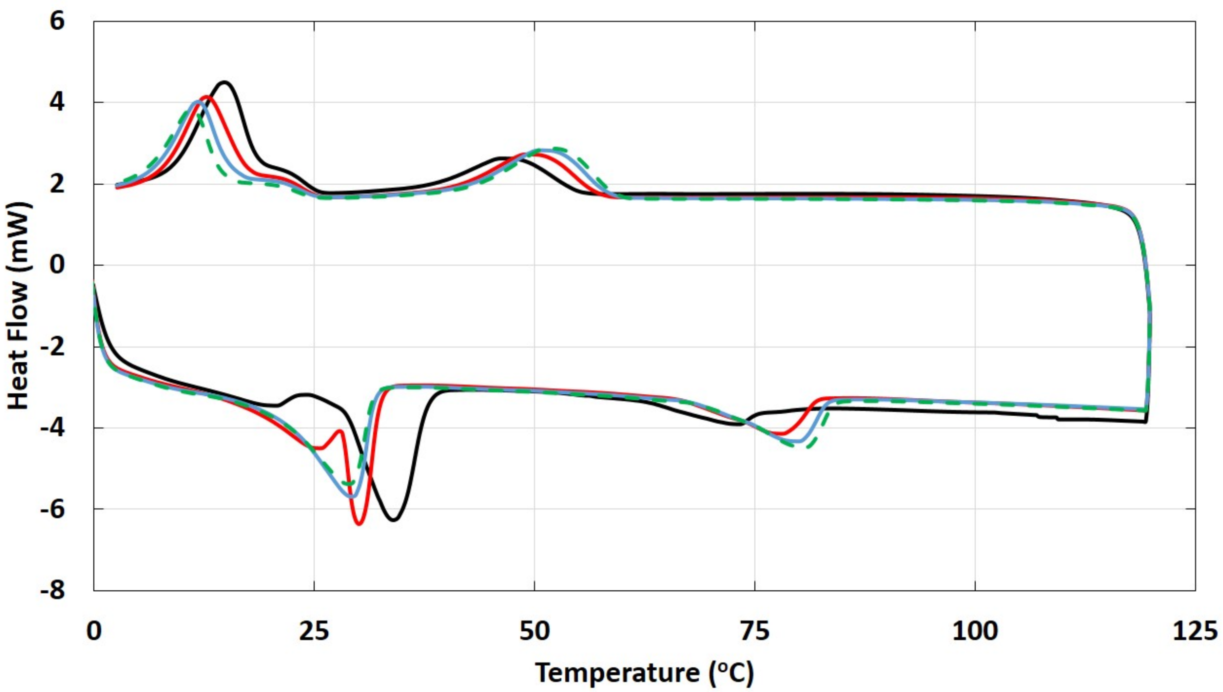

Figure S8. DSC data for **2-18**: heating-cooling cycle 1 (black), cycle 2 (red), cycle 3 (blue), and cycle 4 (green dashed).

Table S1. Onset temperatures (T_{on}, °C), peak temperatures (T_p, °C), and phase transition enthalpies (ΔH, J/g) of **2-18** during the heating and cooling parts of each cycle.

	2-18 (heating)			**2-18 (cooling)**		
	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
Cycle 1	21.5	20.5	19.8	26.1	20.5	20.6
	63.6	72.0	6.78	59.0	46.4	10.2
Cycle 2	20.0	21.3	20.7	28.0	20.3	18.3
	65.7	77.1	12.6	60.4	49.2	12.3
Cycle 3	20.0	29.2	24.8	27.3	20.3	15.5
	69.2	79.0	14.5	60.6	50.8	13.7
Cycle 4	20.0	28.8	25.5	29.2	20.3	13.5
	69.7	79.9	16.4	60.5	51.6	14.5

4. Powder x-ray diffraction data

Table S2. PXRD peaks for 2-18 from heating: Phase A (< 25 ^{o}C) and Phase B (> 50 ^{o}C).

Phase A			Phase B		
2θ (deg)	d (Å)	(h k l)	2θ (deg)	d (Å)	(h k l)
4.08	21.66	(0 0 3) α and γ state	4.12	21.45	(0 0 3) γ state
5.44	16.25	(0 0 4) α and γ state	5.52	16.01	(0 0 4) γ state
5.72	15.45	Kapton[a]	6.94	12.74	(0 0 5) γ state
6.82	12.96	(0 0 5) α and γ state	9.74	9.08	(0 1 0)
8.3	10.65	(0 0 6) α and γ state	12.26	7.22	siloxane[b]
11.8	7.50	siloxane[b]	12.50	7.08	siloxane[b]
12.66	6.99	siloxane[b]	14.54	6.09	(0 0 10) γ state

[a] Peak from Kapton® tube that was the sample holder. [b] Peaks from the broad amorphous siloxane chains in the polymer backbone.

.

Table S2. (Cont.)

Phase A			Phase B		
2θ (deg)	d (Å)	(h k l)	2θ (deg)	d (Å)	(h k l)
15.22	5.82	(0 0 9)	19.08	4.65	(2 0 0) γ-state
19.26	4.61	(2 0 0) γ-state	21.38	4.16	(0 1 0) γ state
21.56	4.12	(1 1 0) or (2 0 0) α-state	23.60	3.77	(1 1 0) γ-state
21.64	4.11	(1 1 0) or (2 0 0) α-state	37.72	2.38	(3 1 0) γ state
			39.60	2.28	(4 0 0) γ state

[a] Peak from Kapton® tube that was the sample holder. [b] Peaks from the broad amorphous siloxane chains in the polymer backbone.

5. Adhesion

Shear moduli were determined specifically in the linear elastic region of the stress-strain curve before the yield stress occurred. These can be observed in Figure S9. A linear regression fit using equation 1 on the stress-strain curves (where F is the shearing force (in Newtons), A is the shear area (m^2), Δx is the displacement (m), and L is the length of the shear area (m)) was used to calculate the shear modulus and the results are summarized in Table S3. Due to how the instrument initialized the experiment, there is a small amount of force that was applied at the beginning of the stress-strain curve, resulting in the linear fits having non-zero y-intercepts. All shear moduli are reported in GPa and coefficients of determination (R^2) were used to assess the goodness-of-fits using linear regressions (see Table S4).

$$Shear\ Modulus\ (Pa) = \frac{Shear\ Stress}{Shear\ Strain} = \frac{F/A}{\Delta x/L} \quad (1)$$

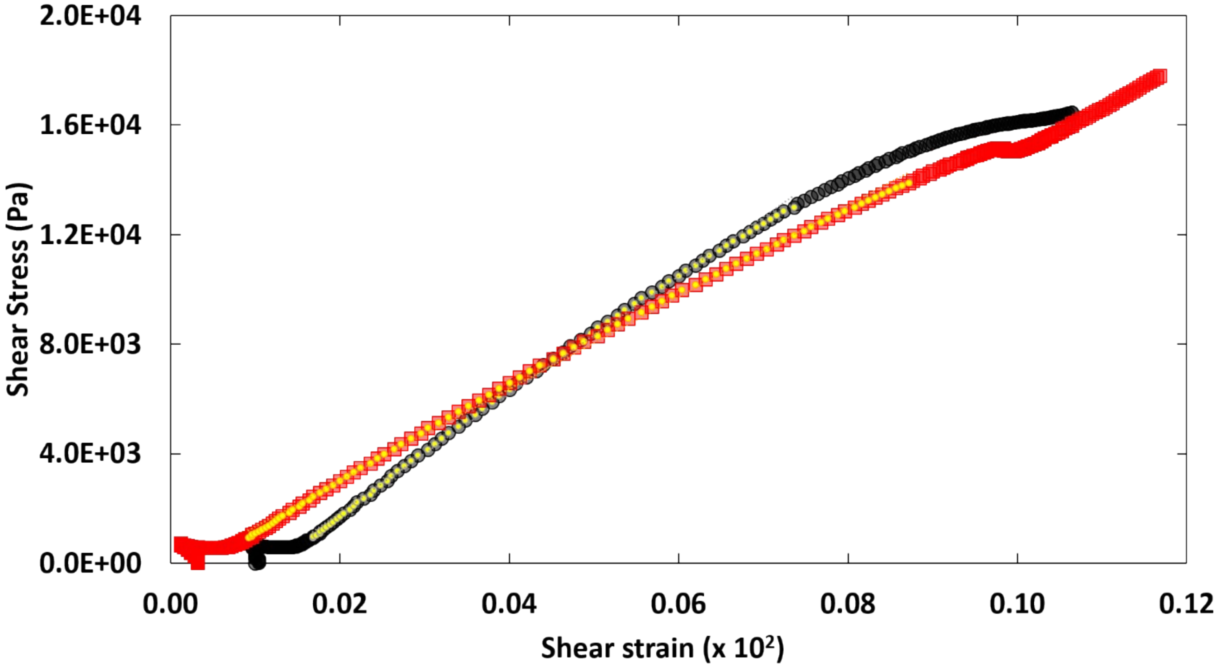

Figure S9. Magnification of the stress-strain curves for **2-18** to highlight the elastic region (the region highlighted in yellow and with the larger data points for each trial) where the shear modulus was approximated using linear regressions.

Table S3. Shear moduli and ultimate shear strength of ionomers calculated from the lap shear strengths and displacements of **2-18**.

	Shear modulus (GPa)	Ultimate shear strength (KPa)
Trial 1	0.022	120.8
Trial 2	0.017	131.7
Average	0.020	126.3

Table S4. Linear regression results and coefficients of determination (R^2) for data in Figure 3.1.

	2-18
Trial 1	$y = 215827x - 2469.6$ $R^2 = 0.9983$
Trial 2	$y = 167610x - 333.85$ $R^2 = 0.9982$

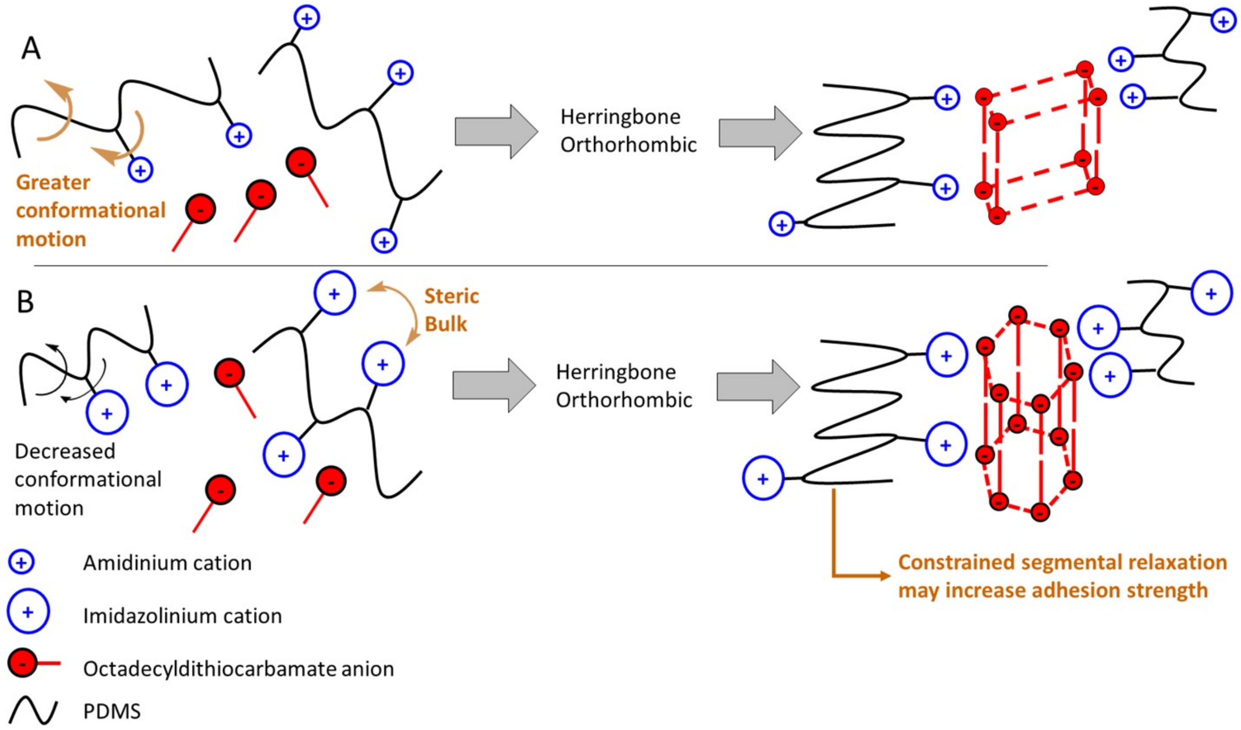

Fig. S10. Cartoon describing the possible consequences of cooling (A) **1-18** and (B) **2-18** from their isotropic phases (left) to room temperature (right) on their adhesion.

6. References Cited

1 A. J. Barry, *J. Appl. Phys.*, 1946, **17**, 1020–1024.

2 K. C. Prakasha, M. Sindhumol, A. R. Baba and D. C. Gowda, *J. Chem. Res.*, 2007, 284–286.

3 M. George and R. G. Weiss, *Langmuir*, 2003, **19**, 1017–1025.

4 W. L. F. Armarego and C. L. L. Chai, in *Purification of laboratory chemicals*, Elsevier, 7th edn., 2013, p. 191.

5 National Institute of Standards and Technology Chemistry WebBook, 1-Octadecanamine, https://webbook.nist.gov/cgi/inchi?ID=C124301&Mask=4#, (accessed 19 July 2019).

6 L. Poon and R. G. Weiss, *J. Polym. Sci.*, 2021, **59**, 2345–2354.

7 ASTM (American Society for Testing and Materials), *Standard test method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal - to - Metal), D 1002-99*, ASTM, West Conshocken, PA, 1999.