Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Tuning Physical Properties of Malleable and Recyclable Polyimine Thermosets: The Effect of Solvent and Monomer Concentration

*Chengpu Zhu, Cally Xi, William Doro, Tianyi Wang, Xin Zhang, Yinghua Jin, Wei Zhang**

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA

wei.zhang@colorado.edu

Contents

Materials

Reagents and solvents were purchased from commercial suppliers and used without further purification, unless otherwise indicated. Certified ACS grade 2-Propanol, methanol, ethyl acetate, methylene chloride were purchased from Fisher Chemical. Ethanol (anhydrous 200 proof) was purchased from Decon. Tetrahydrofuran (non-UV, stabilized) was purchased from EMD Millipoure Corporation. Terephthalaldehyde was purchased from Aldrich. Ethylenediamine was purchased from Alfa Aesar. 2,2',2-Triaminotriethylamine was purchased from Strem Chemicals, Inc. 4-Bromobenzaldhyde (99%) was purchased from Oakwood Chemical.

Experimental procedures for preparation of polyimine films

Polyimine preparation at low monomer concentration: To a solution of ethylene diamine (**2**, 0.268 g, 4.46 mmol) and tris(2-aminoethyl)amine (**3**, 1.02 g, 6.976 mmol) in a solvent of choice (45 mL) was added terephthalaldehyde (**1**, 2.00 g, 14.9 mmol). The mixture was vigorously stirred until the solution became translucent and yellow-to-orange in color. The solution was then poured into a tray made from silicone-coated release paper (with approximate dimensions 9 cm x 9 cm x 2 cm). The volatiles were allowed to evaporate in a fume hood overnight at room temperature. The resulting polyimine film was heat pressed at 78 °C for 3 h, at 95 °C for 1 h, and finally at 105 °C for 1 h using a top platen-heated hand-operated heat press under nominal pressure.

Polyimine preparation at high monomer concentration: The above procedure was followed but the concentrations of monomers were increased 2.5 time: ethylene diamine (**2**, 0.6721 g, 11.15 mmol), tris(2-aminoethyl)amine (**3**, 2.54 g, 17.44 mmol), terephthalaldehyde (**1**, 5.00 g, 37.25 mmol), and solvent (45 mL) were used.

SEM images of polyimine samples

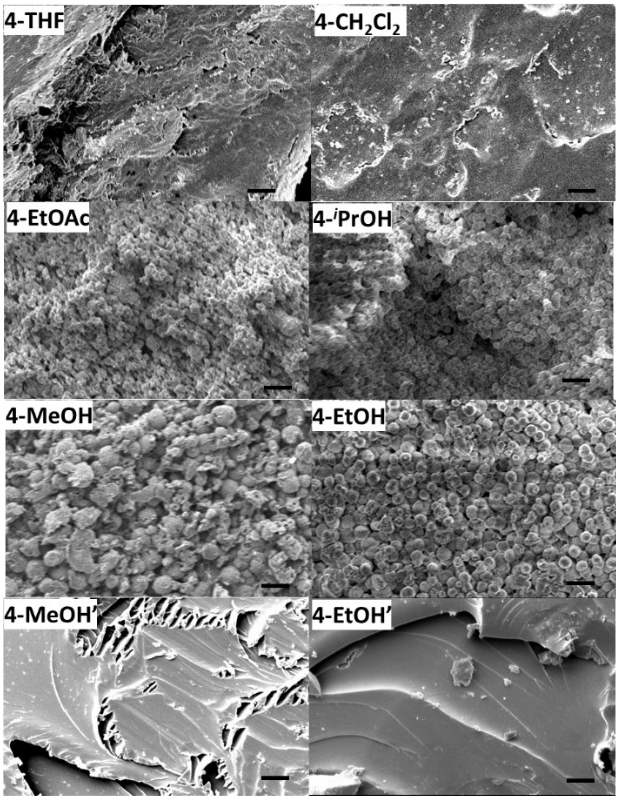


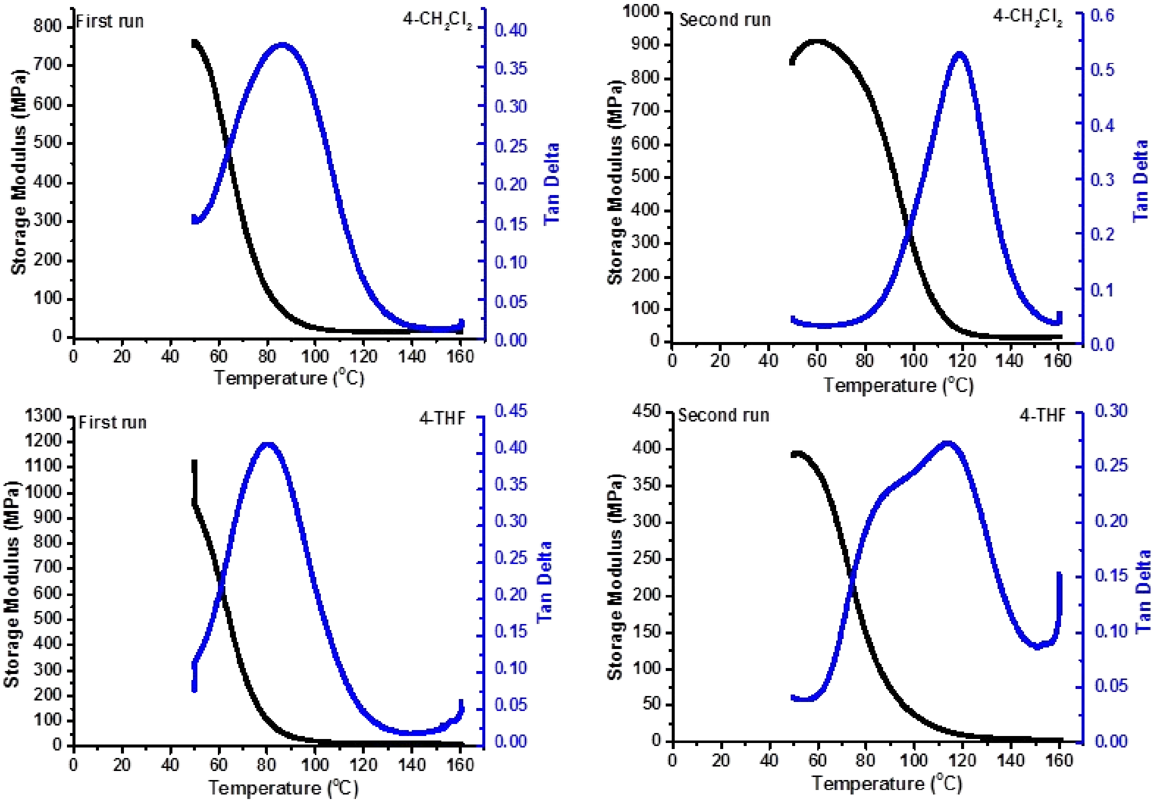
Figure S1. Cross section SEM images of the polyimine films. The scale bar is 10 μm.

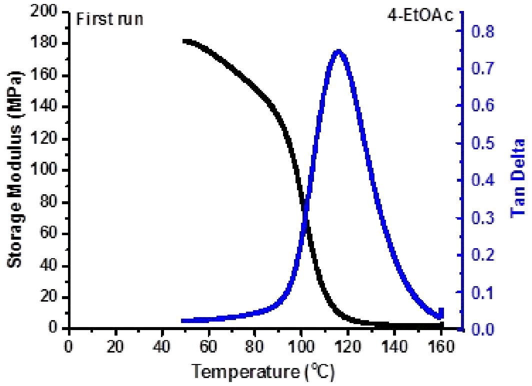
Mechanical tests of polyimine films

DMA Tension tests: A dynamic mechanical analysis (DMA) instrument (Model Q800, TA Instruments, New Castle, DE, USA) was used to carry out tension tests at room temperature (24.6 °C locally). All samples were cut into dog-bone shapes with the size of 30 mm x 4 mm (length x width), and stretched under a constant loading rate (2 MPa/min) until broken. For the wet tensile measurements, pre-cut samples in the same shape were soaked in DI water for 24 h. After being removed from the water, each sample was blotted dry with paper towel, loaded into the DMA instrument, and then tested under the same method.

Characterization of thermal properties of polyimines

Determination of glass transition temperature: Glass transition temperatures (T_g) of the samples were determined using a DMA instrument (Model Q800, TA Instruments, New Castle, DE, USA). Samples were mounted between film tension fixtures and tested under the following parameters: Test Mode DMA Multi-Frequency-Strain; Strain 0.0250 %; Preload force 0.1000 N; Force track: 125%; Equilibrate at 60 °C; Isothermal for 5.00 min; Ramp 3.00 °C /min to 160.00 °C, cooling rate 10 °C/min. We observed higher T_g in the second DMA measurement. It is likely that the samples undergo imine exchange reactions as the temperature increases, leading to higher monomer conversion and higher T_g. The data of the first measurement was used to determine the T_g.




First run
4-EtOAc
Storage Modulus (MPa)
0 20 40 60 80 100 120 140 160 180 200
Tan Delta
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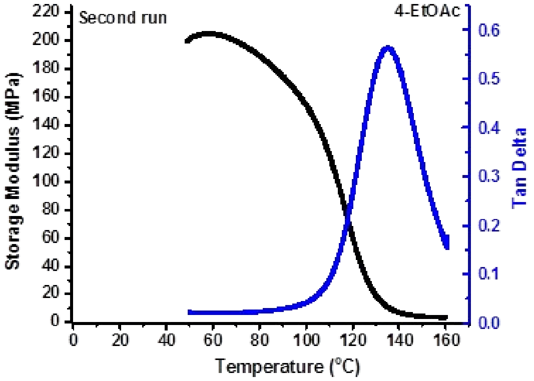
Temperature (°C)
0 20 40 60 80 100 120 140 160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4-EtOAc
Storage Modulus (MPa)
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Tan Delta
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Temperature (°C)
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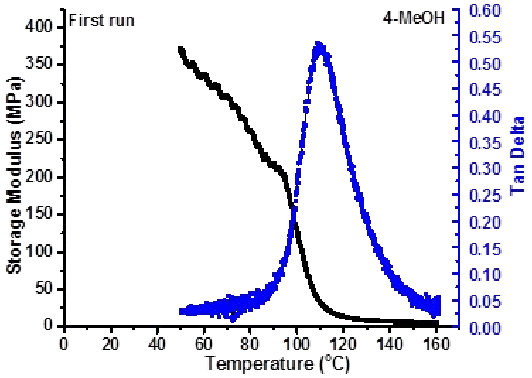
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Storage Modulus (MPa)
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Tan Delta
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Temperature (°C)
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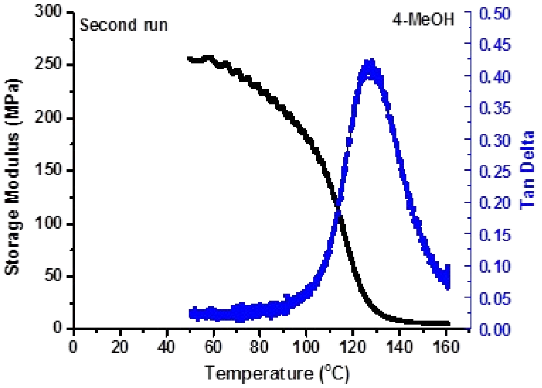
Second run
4-MeOH
Storage Modulus (MPa)
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Tan Delta
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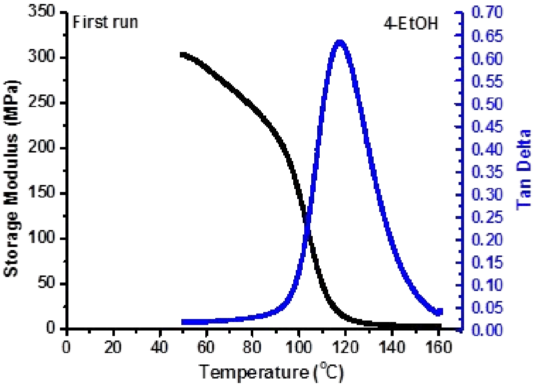
Temperature (°C)
0 20 40 60 80 100 120 140 160


First run
4-EtOH
Storage Modulus (MPa)
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Tan Delta
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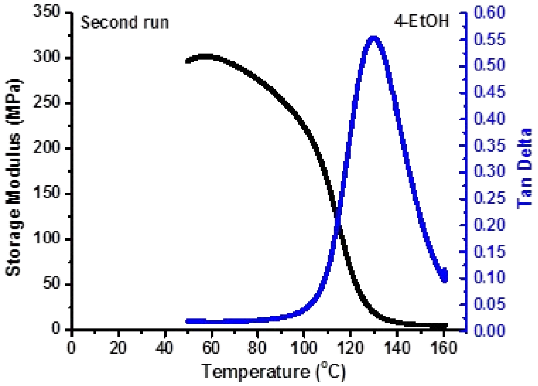
Second run
4-EtOH
Storage Modulus (MPa)
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Tan Delta
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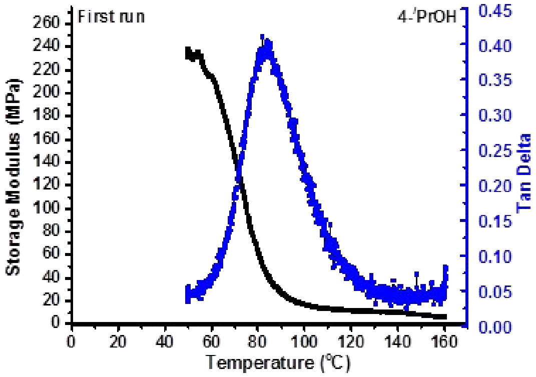
Temperature (°C)
0 20 40 60 80 100 120 140 160


First run
4-^{i}PrOH
Storage Modulus (MPa)
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Tan Delta
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Temperature (°C)
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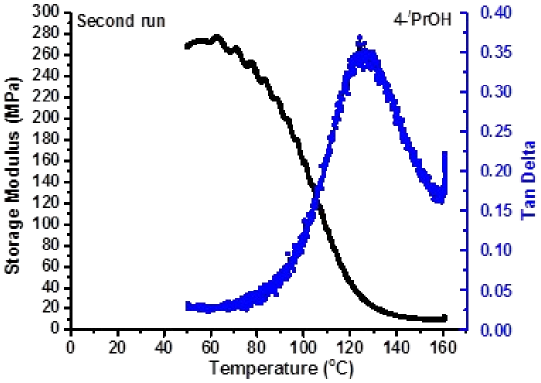
Second run
4-^{i}PrOH
Storage Modulus (MPa)
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Tan Delta
0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40
Temperature (°C)
0 20 40 60 80 100 120 140 160

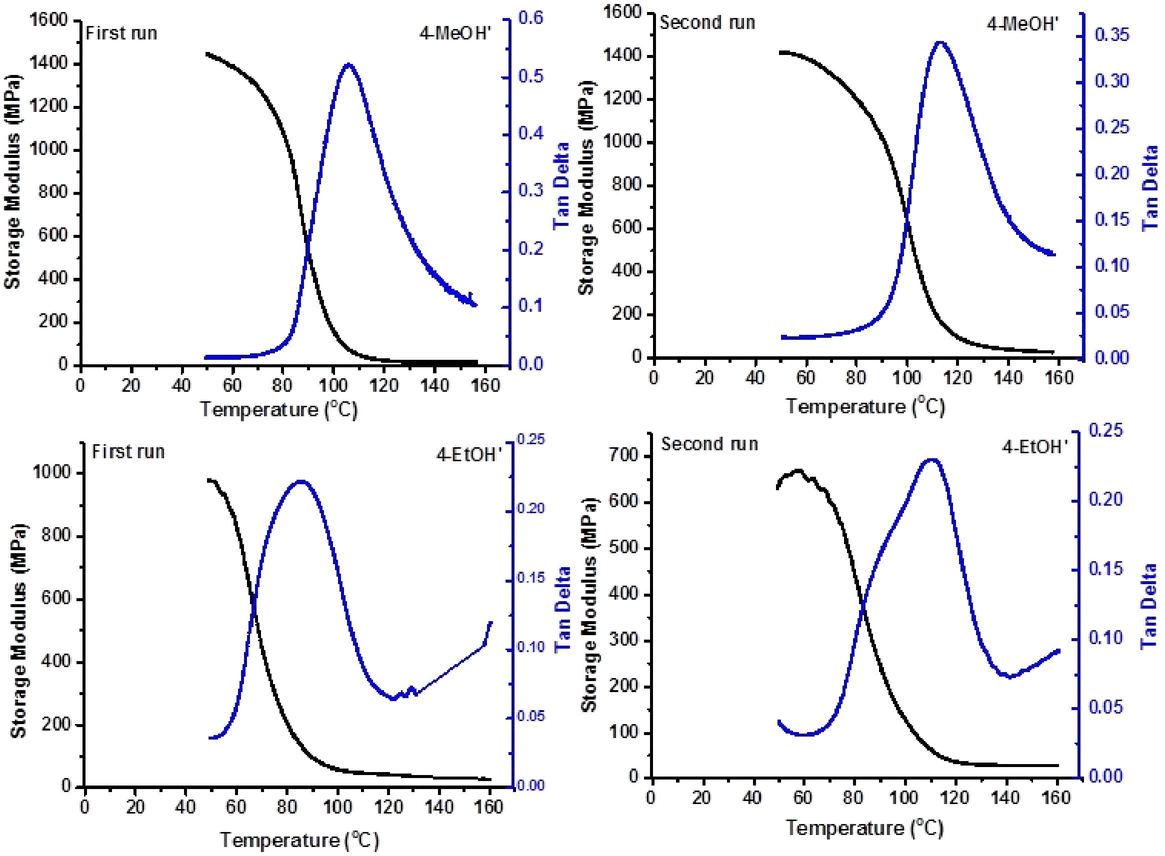


Figure S2. The DMA scans of polyimines.

Thermal Gravimetric Analysis of polyimines

Samples were run on a TA Instrument Q-500 series thermal gravimetric analyzer with samples held in a platinum pan under nitrogen atmosphere. A 10 K min^{-1} ramp rate was used.

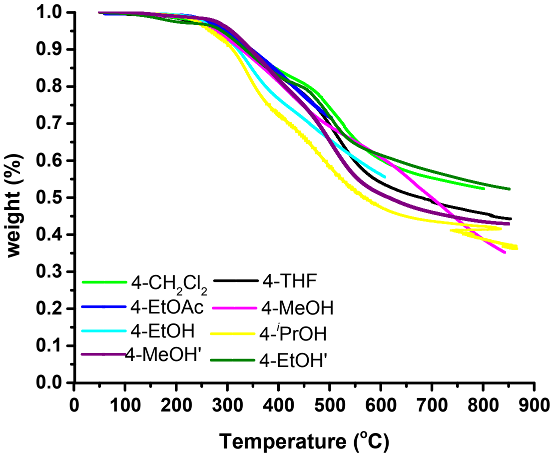


Figure S3. TGA plots of polyimines.

Moisture sensitivity of polyimines

Pristine polyimine films were prepared in the manner describe above. The swelling study was performed by placing a dog-bone shape pre-tared sample of each polyimine in a 20 mL screw cap vial filled with DI water. Samples were soaked in DI water for 24 h. Upon removal of the samples from the water, the samples were blotted dry and weighed within 1 minute to minimize the ambient drying of the swollen polymer films. Total five samples were examined for each polyimine prepared in a different solvent.

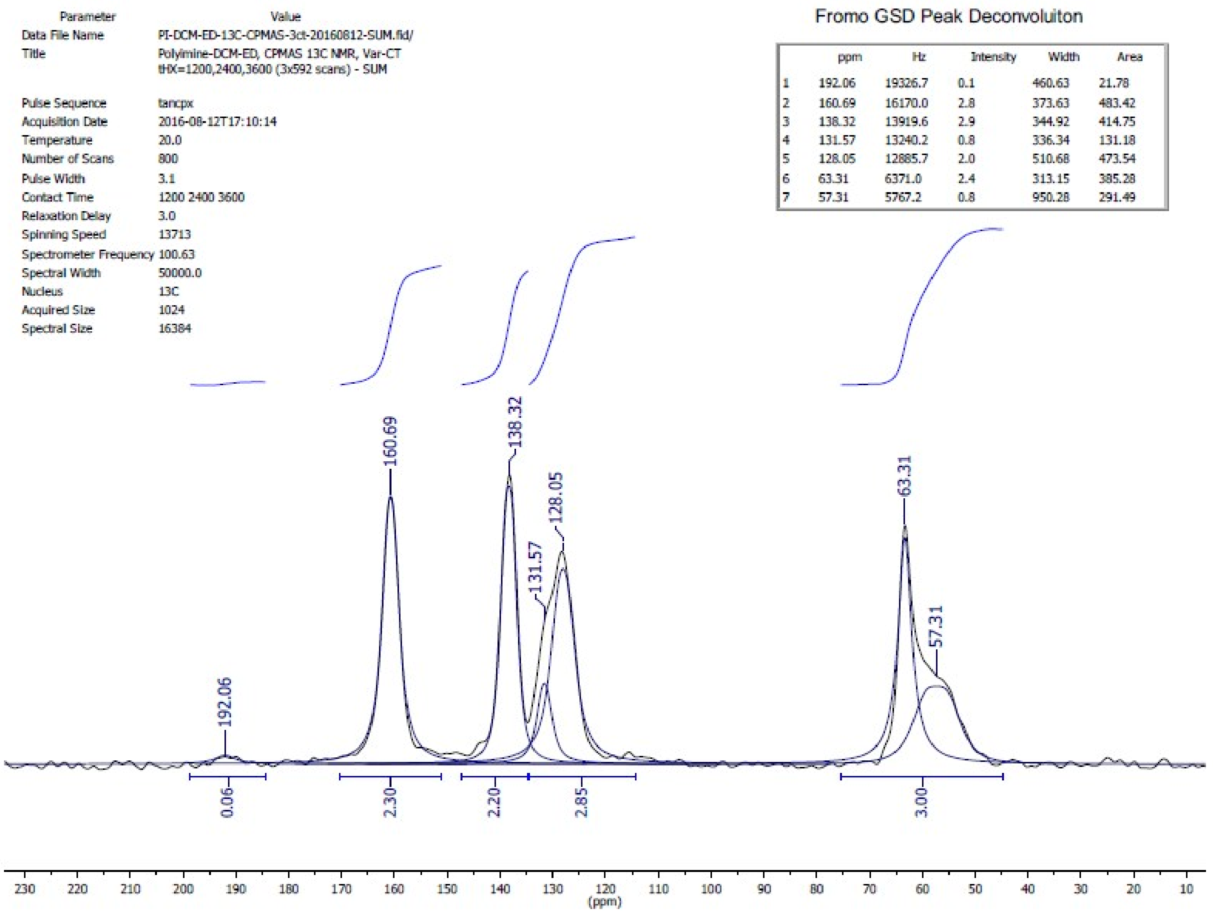
Table S1. Summary of mechanical properties of polyimines.

	Pristine samples		**After soaking in DI water**		
polyimines	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Weight gain (%)**	**Tensile strength (MPa)**	**Elongation at break (%)**
4-CH$_2$Cl$_2$	69±6	6.4±1.3	6.5±1.8	29±1	2.3±0.3
4-THF	42±1	4.6±0.2	14±3	9.7±0.4	2.9±0.5
4-EtOAc	3.8±0.7	2.3±0.3	138±18	1.6±0.1	1.9±0.3
4-MeOH	6.6±0.8	3.8±0.5	59.3±4.3	3.8±0.5	2.2±0.1
4-EtOH	1.2±0.1	1.42±0.08	106.45±6.5	0.85±0.1	1.65±0.15
4-^{i}PrOH	0.23±0.01	0.7±0.1	262±19	0.185±0.15	1.1±0.1
4-MeOH’	39±5	0.087±0.050	12.2±1.0	20±2	0.11±0.04
4-EtOH’	33±1	1.11±0.03	23±2	11.4±1.6	0.2±0.07

NMR spectra of selected compounds

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-State, Cross-Polarization Magic Angle Spinning (CPMAS), ^{13}C NMR spectroscopy was performed using a

Varian INOVA-400 spectrometer (Agilent Technologies, Inc.) operating at 100.63 MHz for ^{13}C observation. The probe incorporates a 5 mm Magic Angle spinning module and coil assembly designed and constructed by Revolution NMR, Inc. (Fort Collins, CO), capable of spinning up to 13 KHz with Zirconia rotors (also from Revolution NMR, Inc.). Spectra were acquired using cross-polarization spin-lock and decoupling R_f field of 80.5 KHz, and TPPM (Time Proportional Phase Modulation) decoupling was applied during signal acquisition. Chemical shifts were referenced using the absolute, calibrated spectrometer configuration frequency and magnetic field offset, such that the aldehyde carbon peak appears at 191 ppm. Sample spinning frequencies from 10.5-11.57 KHz were employed with the sample oriented at the magic angle (54.736 degrees, relative to the magnetic field axis, calibrated using the ^{79}Br spinning sideband pattern of KBR). To effect the uniform cross-polarization of ^{1}H magnetization to all ^{13}C nuclei, spectra were acquired using multiple cross-polarization contact times among 1.2, 2.4 and 3.6 mSec and these were summed to yield the final spectra. These optimal contact times were determined using variable contact-time experiments and were chosen to obtain uniform excitation across all carbon atoms in the molecules of polyimine samples.



Parameter	Value
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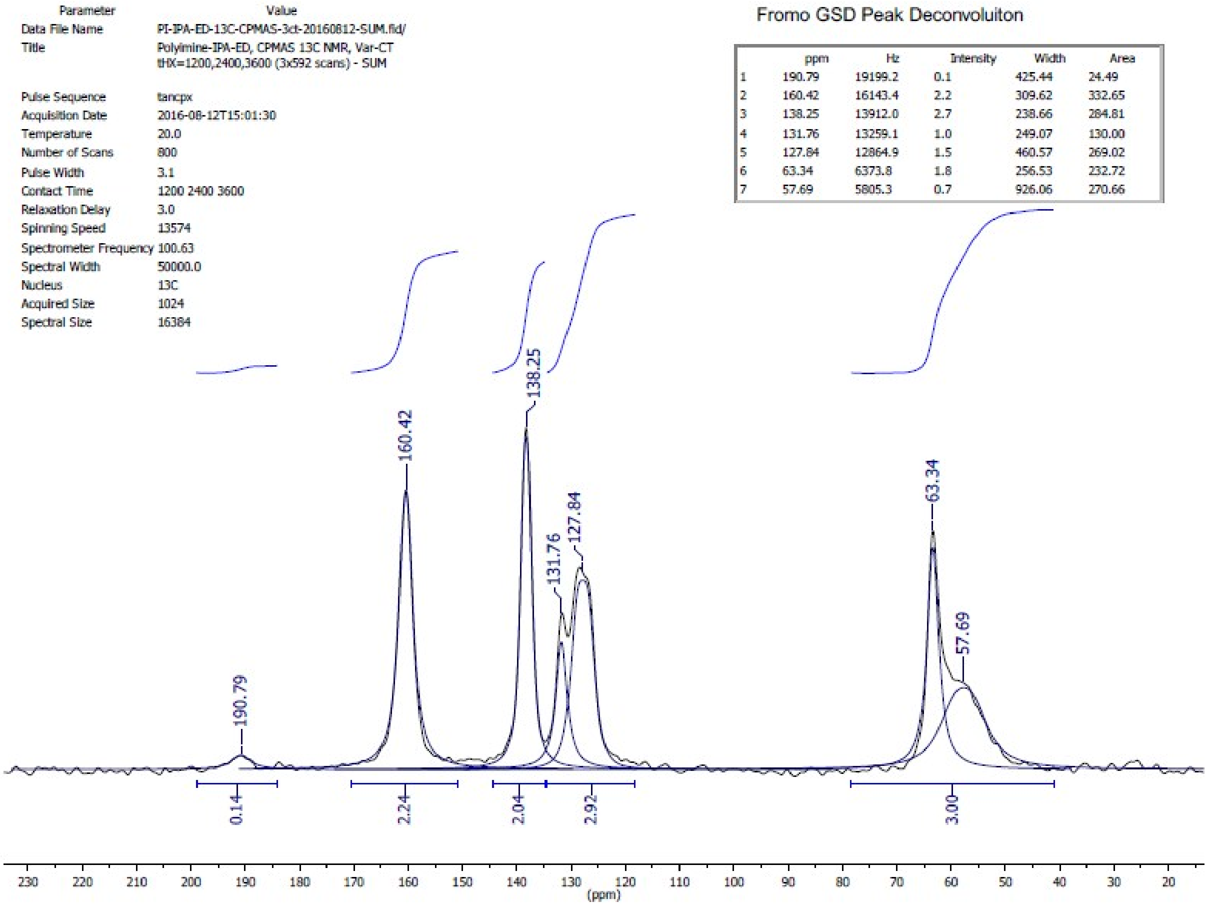
Acquisition Date	2016-08-12T17:10:14
Temperature	20.0
Number of Scans	800
Pulse Width	3.1
Contact Time	1200 2400 3600
Relaxation Delay	3.0
Spinning Speed	13713
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	16384

Fromo GSD Peak Deconvoluiton

	ppm	Hz	Intensity	Width	Area
1	192.06	19326.7	0.1	460.63	21.78
2	160.69	16170.0	2.8	373.63	483.42
3	138.32	13919.6	2.9	344.92	414.75
4	131.57	13240.2	0.8	336.34	131.18
5	128.05	12885.7	2.0	510.68	473.54
6	63.31	6371.0	2.4	313.15	385.28
7	57.31	5767.2	0.8	950.28	291.49

Figure S4. ^{13}C NMR spectrum of **4-CH_2Cl_2** dry sample.



Parameter	Value
Data File Name	PI-IPA-ED-13C-CPMAS-3ct-20160812-SUM.fid/
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Pulse Sequence	tancpx
Acquisition Date	2016-08-12T15:01:30
Temperature	20.0
Number of Scans	800
Pulse Width	3.1
Contact Time	1200 2400 3600
Relaxation Delay	3.0
Spinning Speed	13574
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	16384

Fromo GSD Peak Deconvoluiton

	ppm	Hz	Intensity	Width	Area
1	190.79	19199.2	0.1	425.44	24.49
2	160.42	16143.4	2.2	309.62	332.65
3	138.25	13912.0	2.7	238.66	284.81
4	131.76	13259.1	1.0	249.07	130.00
5	127.84	12864.9	1.5	460.57	269.02
6	63.34	6373.8	1.8	256.53	232.72
7	57.69	5805.3	0.7	926.06	270.66

Figure S5. ^{13}C NMR spectrum of **4-^{i}PrOH** dry sample.