Re-healable Polyimine Thermosets: Polymer Composition and Moisture Sensitivity

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Experimental procedures for preparation of polymer films

*General procedure for preparation of polyimine (**4N1-4NMe**) films*

Terephthaldehyde (**1**, 1.00 g, 7.45 mmol) was added to a 25 mL screw cap vial followed by ethanol (15 mL) and the solution was stirred for 10 minutes. Diamine monomer **2** (3.36 mmol) was added dropwise while stirring. The solution becomes translucent and yellow-to-orange in color. To a tray made from silicone-coated release paper (with approximate dimensions 5 cm x 5 cm x 3 cm) was added tris(2-aminoethyl)amine (**3**, 0.398 g, 2.72 mmol), followed by ethanol (~5 mL or enough to cover most of the surface area of the bottom of the tray). The solution of terephthaldehyde and diamine solution was poured into the tray with gentle mixing. The solution was allowed to evaporate in a fume hood for 24 h. The resulting uncured elastomeric film was first heat pressed for 3 h at 78 ˚C, followed by 1 h at 95 ˚C, and finally 1 h at 105 ˚C using a top platen-heated hand-operated heat press under nominal pressure.

*General procedure for preparation of polyimine (**4C2-4C12**) films*

Terephthaldehyde (**1**, 1.00 g, 7.45 mmol) was added to a 25 mL screw cap vial followed by ethanol (5 mL) and dichloromethane (8 mL). The solution was stirred for 10 minutes. Diamine monomer **2** (3.36 mmol) was added, and DI water (5 mL) was added dropwise while stirring until the solution became homogeneous. The solution becomes translucent and yellow-to-orange in color. To a tray made from silicone-coated release paper (with approximate dimensions 5 cm x 5 cm x 3 cm) was added tris(2-aminoethyl)amine (**3**, 398 mg, 2.72 mmol), followed by dichloromethane (~5 mL or enough to cover most of the surface area of the bottom of the tray). The solution of terephthaldehyde and diamine was poured into the tray with gentle mixing. The solution was allowed to evaporate in a fume hood for 24 h. The resulting uncured elastomeric film was first heat pressed for 3 h at 78 ˚C, followed by 1 h at 95 ˚C, and finally 1 h at 105 ˚C using a top platen-heated hand-operated heat press under nominal pressure.

Note: In order to obtain a homogeneous polyimine film, pure CH_2Cl_2 was used without the addition of DI water in the synthesis of **4C2**.

Characterization of thermal properties of polymers

Determination of T_g through dynamic mechanical analysis (DMA)

The DMA measurement was performed using a DMA instrument (Model Q800, TA Instruments, New Castle, DE, USA). Samples were mounted between film tension fixture and tested under the following parameters: Test Mode DMA Multi-Frequency – Strain; Strain 0.0250 %; Preload force 0.1000N; Force track: 125%; Equilibrate at 40℃; Isothermal for 5.00 min; Ramp 3.00 ℃/min to 160.00 ℃

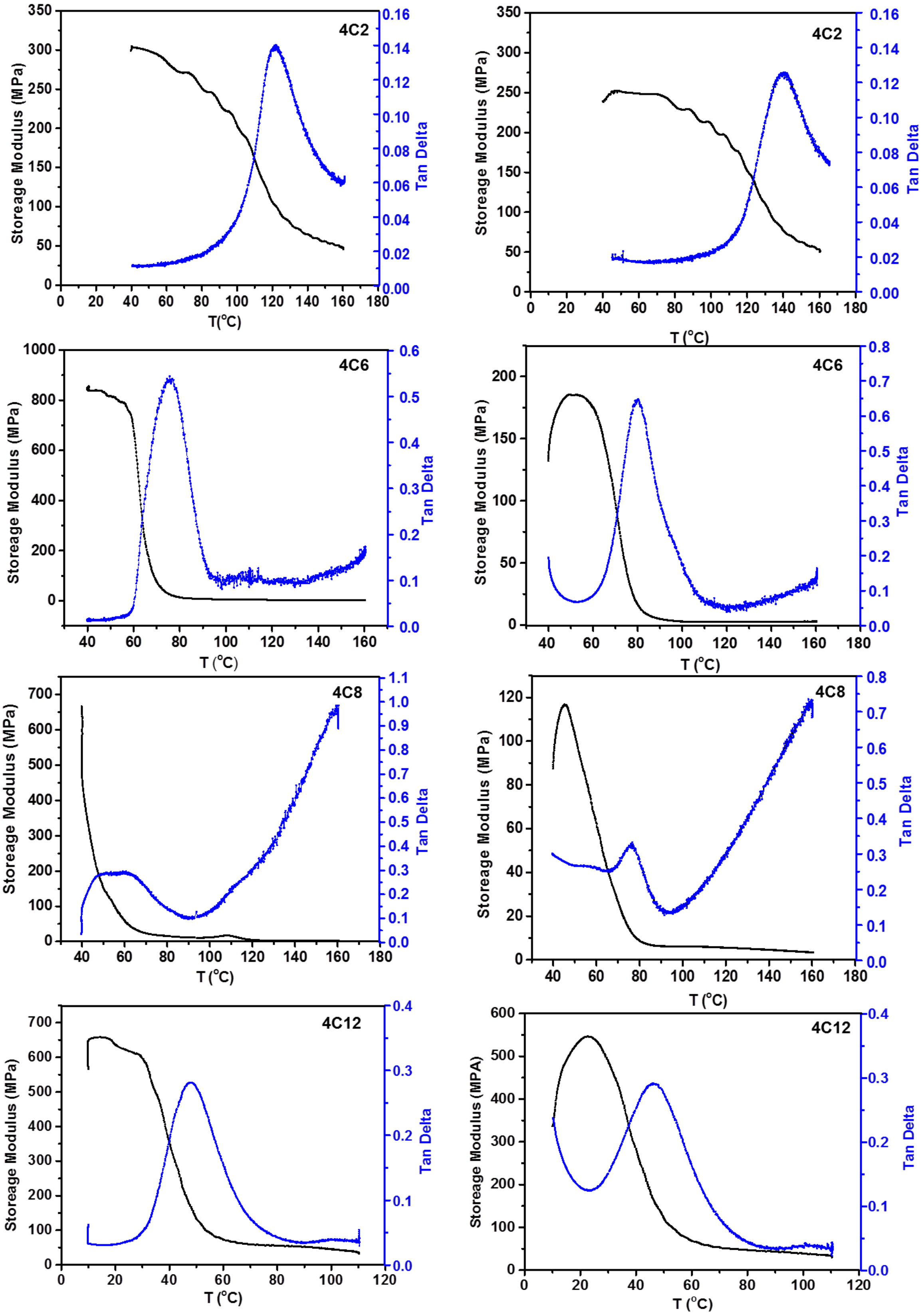


Fig. S1 The DMA scans of polyimines **4N1-4NMe**.

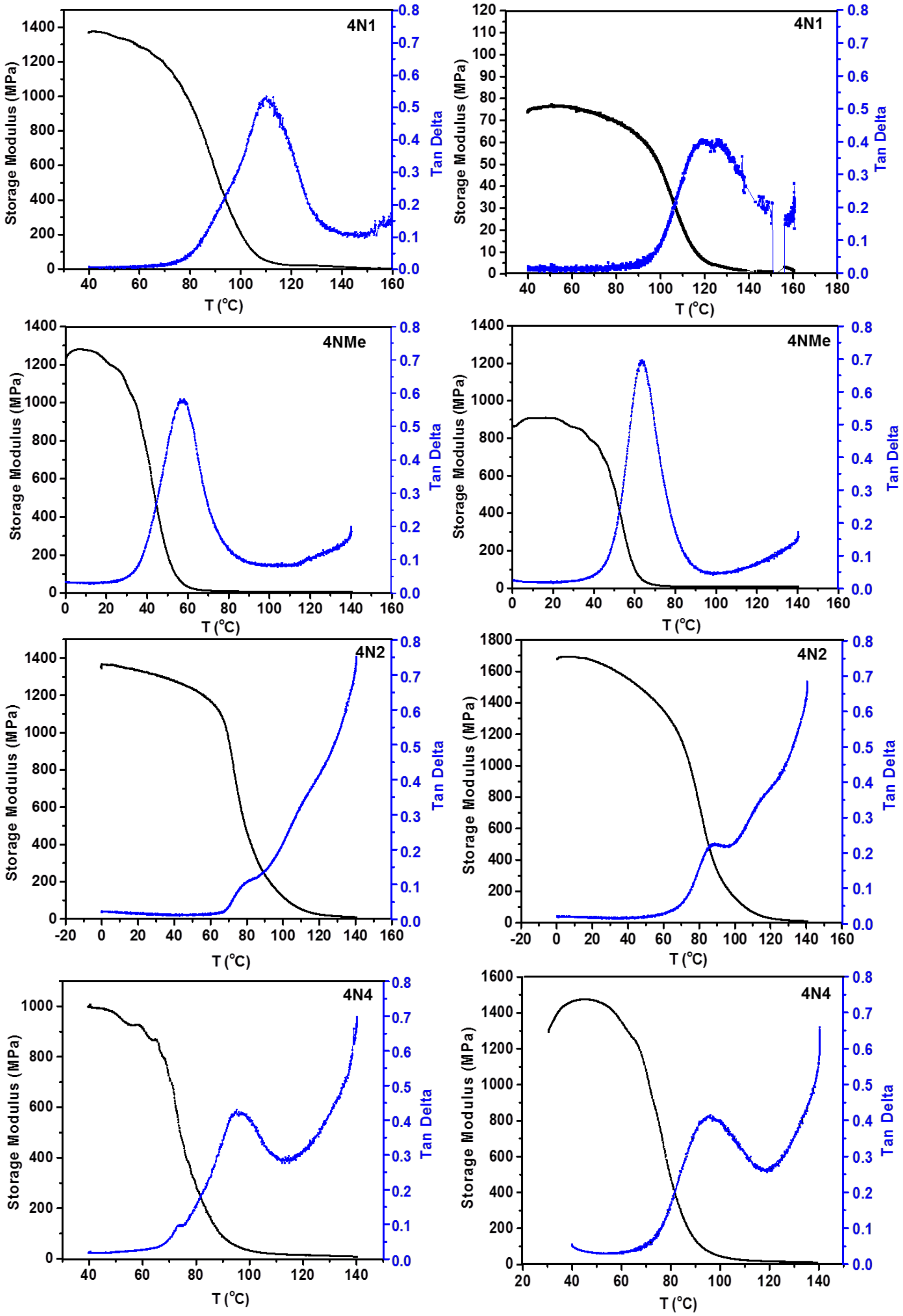


Fig. S2 The DMA scans of polyimines **4C2-4C12**.

Table S1. T_g of polyimines **4N1-4C12** obtained from Tan delta peak in DMA scans.

Polyimines T_g (^{o}C)	**4N1**	**4N2**	**4N4**	**4NMe**	**4C2**	**4C6**	**4C8**	**4C12**
First Run	110	80	95	57	120	76	61	47
Second Run	122	88	96	64	135	80	76	46

Thermal Gravimetric Analysis

Samples were run on a TA Instruments 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. The results are shown below in Fig. S2.

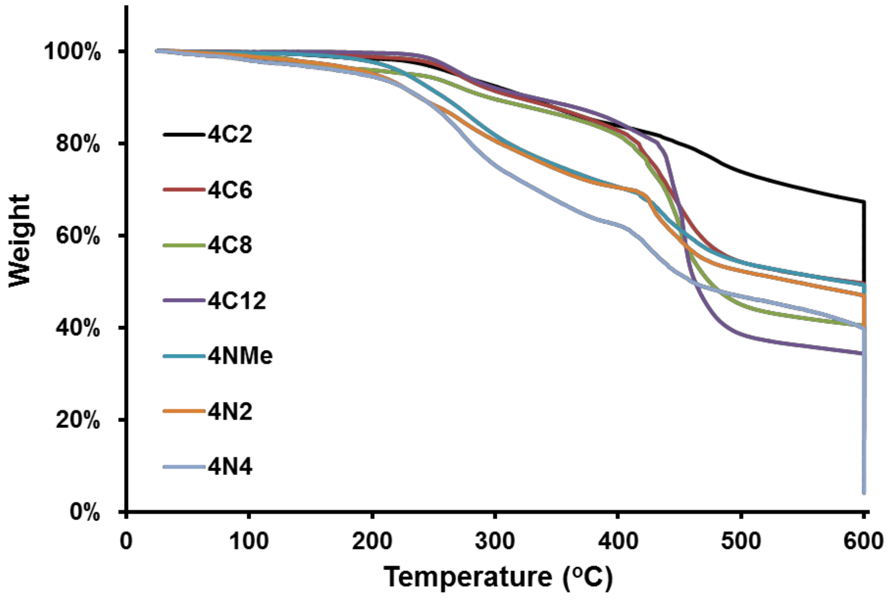


Fig. S3 TGA plot for polyimine polymers. Scan rate is 5 °C/min.

Mechanical testing of polymer 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 (26 ^{o}C locally). All the samples were trimmed into a uniform size of 12 mm × 3 mm × 1.1 mm, and then stretched under a constant loading rate (2 MPa/min) until broken. For the wet tensile measurements, pre-cut samples were immersed in DI water for 24 h. After being removed from the water, each sample was blotted dry, loaded into the DMA instrument, and tested within 2 minutes to minimize the ambient drying of the films.

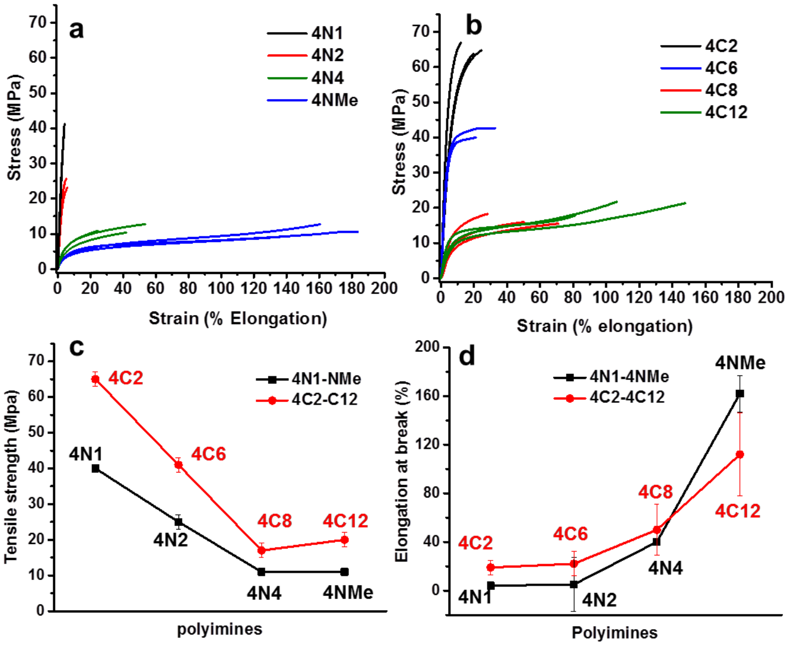


Fig. S4 Comparison of mechanical properties of dry polyimine samples.

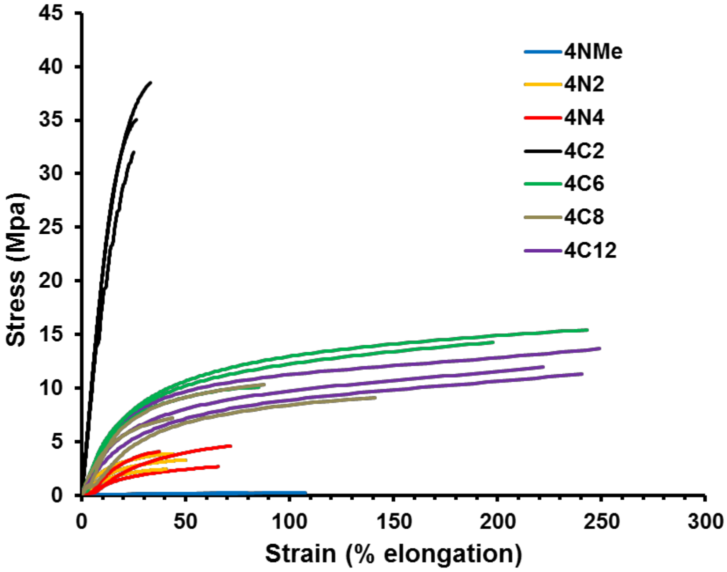


Fig. S5 Tensile test results of wet polyimines after 24 h swelling.

Characterizing the interaction of the polymer films with moisture

Pristine polyimine films were prepared in the manner described above. The swelling study was performed by placing a pre-tared sample (approx. 1 cm x 1 cm) of each formulation in a 25 mL screw cap vial filled with DI water. Upon removal of the sample from the water, the samples were blotted dry and massed on a digital balance (with 0.0001 g resolution) within 1 minute to minimize the ambient drying of the swollen polymer films.

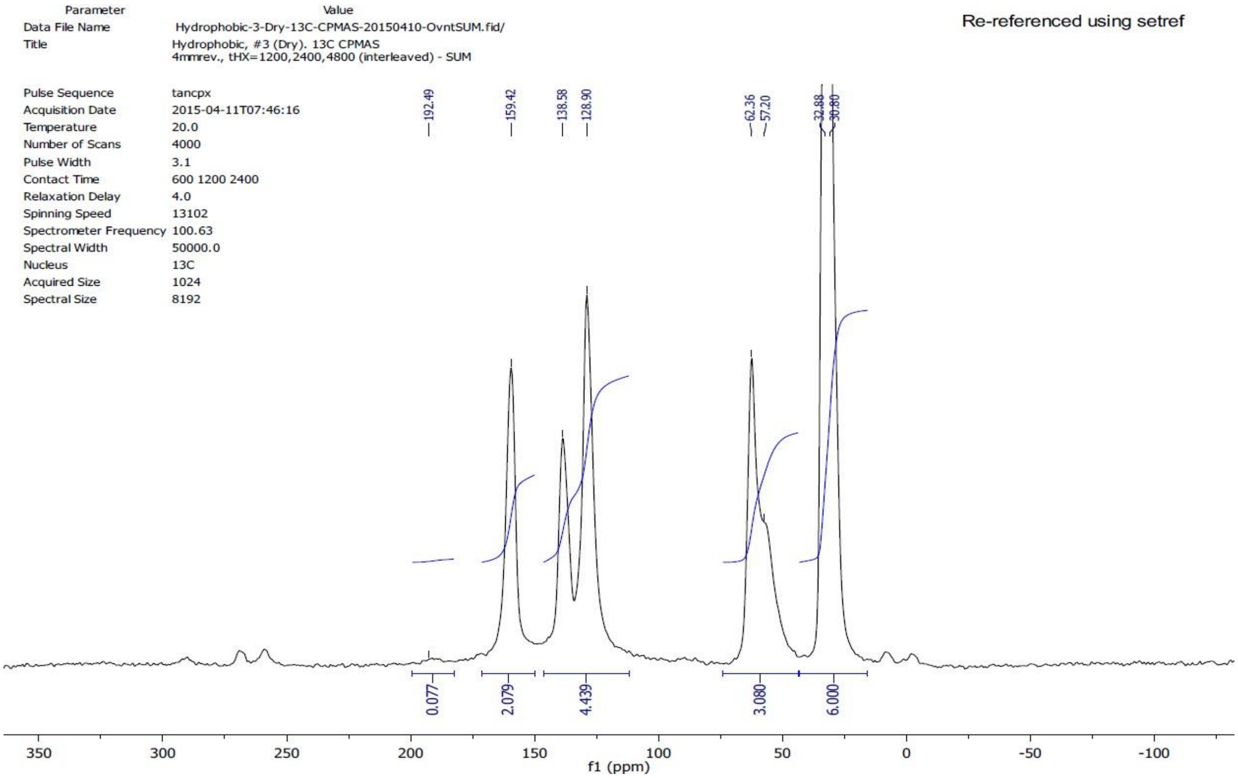
Table S2. Summary of mechanical properties of dry and wet samples of polyimines.

	Tensile (Mpa)		Modulus (Mpa)		Elongation (%)		Weight gain (%)
	dry	Wet	dry	wet	dry	wet	
4N1	40 ± 1	3.4	1000		4 ± 0.2	79	63
4N2	25 ± 1	3.2	930	0.3	5 ± 1	45	71
4N4	11 ± 1	3.8	210	0.2	40 ± 15	58	90
4NMe	11 ± 2	0.2	13	0.06	162 ± 22	73	52
4C2	65 ± 2	35	1050	185	19 ± 6	28	7
4C6	41 ± 2	13	1010	0.5	22 ± 10	175	11
4C8	17 ± 2	9	14	0.3	50 ± 21	91	6
4C12	20 ± 2	12	27	0.5	112 ± 34	237	6

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 (Agilent Technologies, Inc.) spectrometer operating at 100.63 MHz for ^{13}C observation. The probe incorporates a 5mm Magic Angle spinning module and coil assembly designed and constructed by Revolution NMR, Inc. (Fort Collins, CO), capable of spinning up to 13KHz with Zirconia rotors (also from Revolution NMR, Inc.). Spectra were acquired using cross-polarization spin-lock and decoupling R_f fields 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 methyl carbons of hexamethylbenzene appear at 17.3 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 between 500 and 1000 μsec 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 the dry and hydrated samples. Spectra were the result of between 2,016 and 5,600 scans, yielding adequate signal-to-noise ratios.



Parameter	Value
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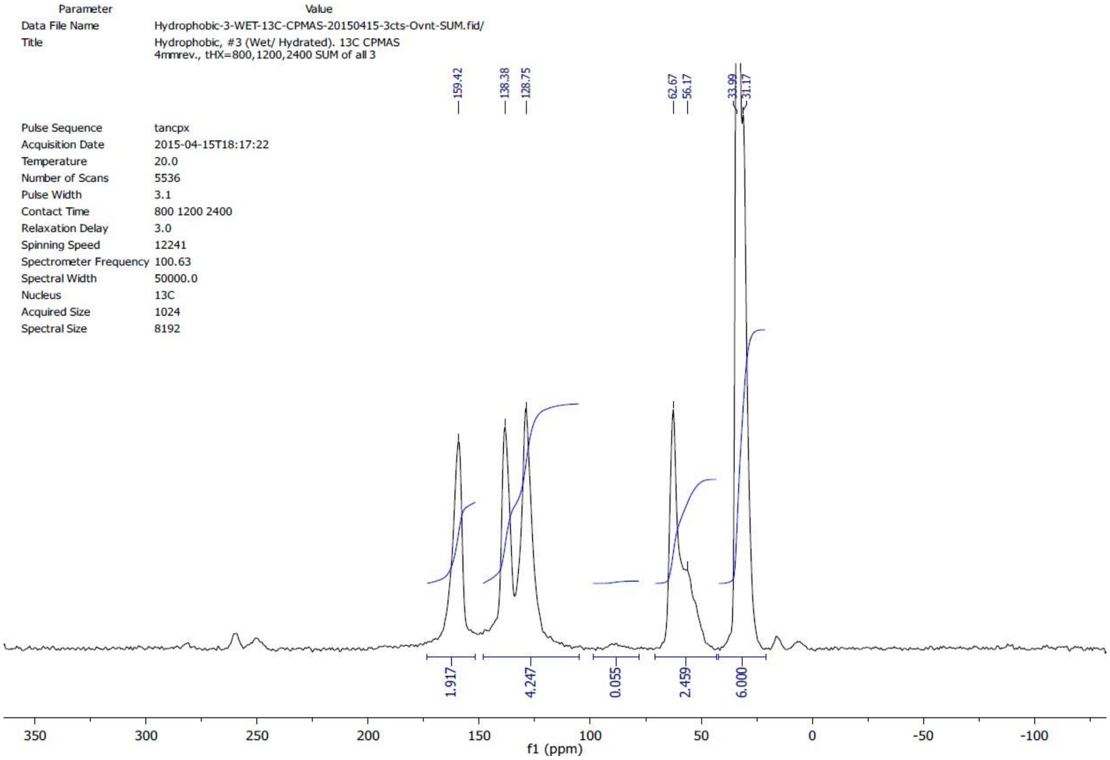
Acquisition Date	2015-04-11T07:46:16
Temperature	20.0
Number of Scans	4000
Pulse Width	3.1
Contact Time	600 1200 2400
Relaxation Delay	4.0
Spinning Speed	13102
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	8192

Fig. S6 ^{13}C NMR spectrum of **4C12** dry sample.



Parameter	Value
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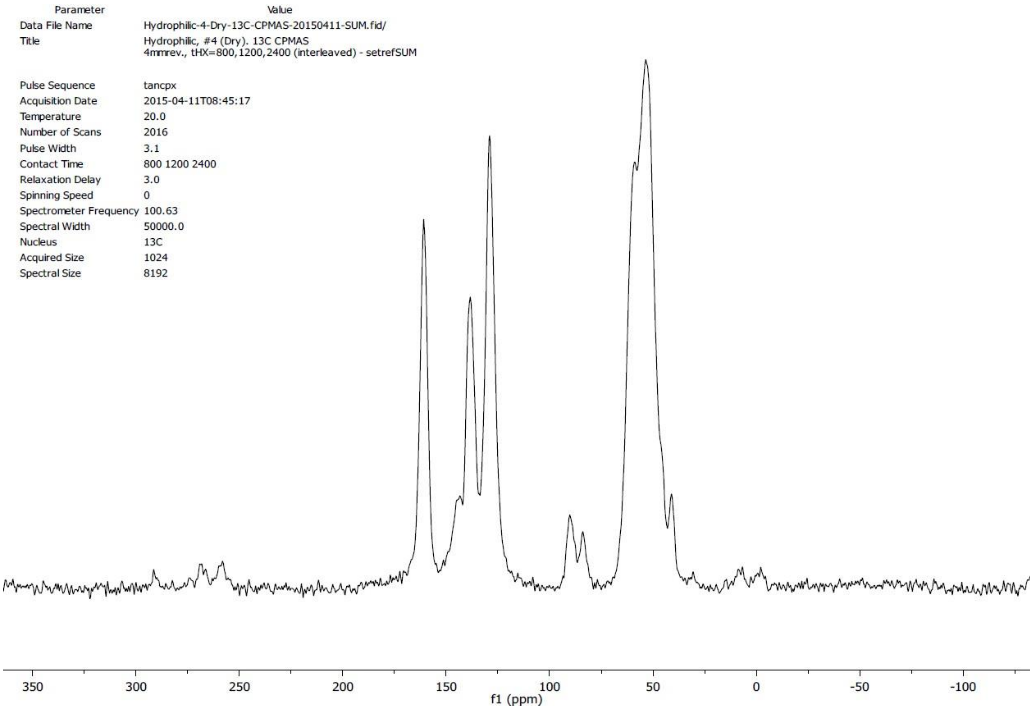
Pulse Sequence	tancpx
Acquisition Date	2015-04-15T18:17:22
Temperature	20.0
Number of Scans	5536
Pulse Width	3.1
Contact Time	800 1200 2400
Relaxation Delay	3.0
Spinning Speed	12241
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	8192

Fig. S7 ^{13}C NMR spectrum of **4C12** wet sample.



Parameter	Value
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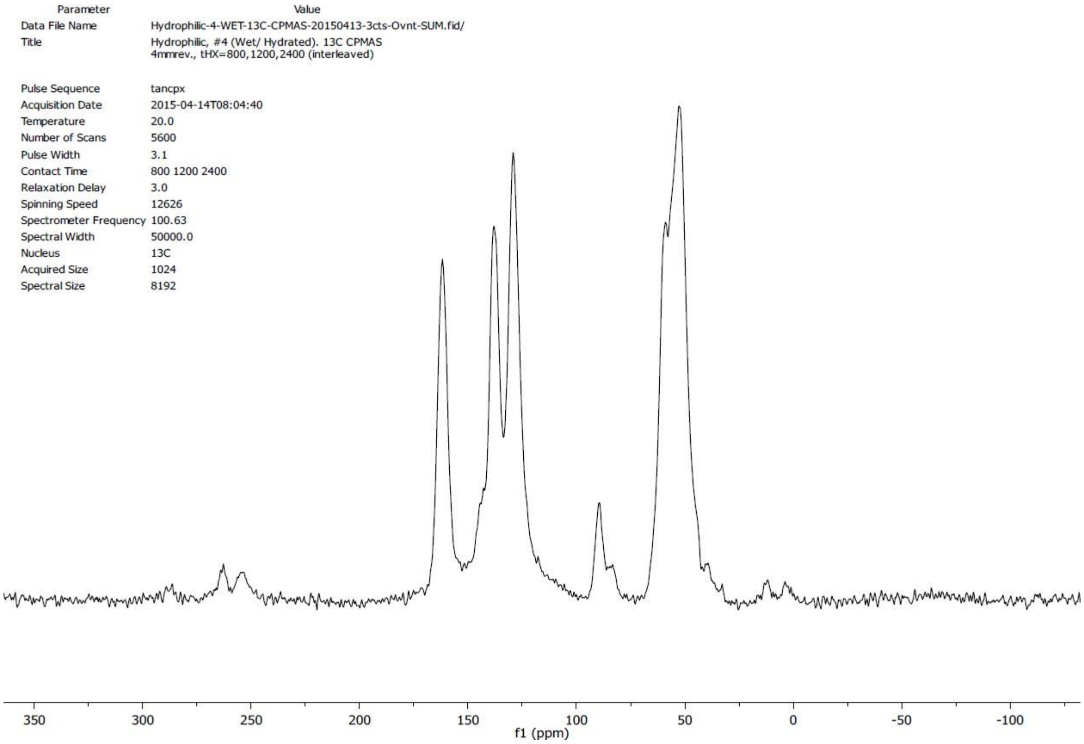
Temperature	20.0
Number of Scans	2016
Pulse Width	3.1
Contact Time	800 1200 2400
Relaxation Delay	3.0
Spinning Speed	0
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	8192

Fig. S8 ^{13}C NMR spectrum of **4N4** dry sample.



Parameter	Value
Data File Name	Hydrophilic-4-WET-13C-CPMAS-20150413-3cts-Ovnt-SUM.fid/
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Acquisition Date	2015-04-14T08:04:40
Temperature	20.0
Number of Scans	5600
Pulse Width	3.1
Contact Time	800 1200 2400
Relaxation Delay	3.0
Spinning Speed	12626
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	8192

Fig. S9 ^{13}C NMR spectrum of **4N4** wet sample