
Supplementary information

Cleavable comonomers enable degradable, recyclable thermoset plastics

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Cleavable Comonomers Enable Degradable, Recyclable Thermoset Plastics

Peyton Shieh¹, Wenxu Zhang¹, Keith E. L. Husted¹, Samantha L. Kristufek¹, Boya Xiong², David J. Lundberg^{1,3}, Jet Lem^{1,4}, David Veyssset¹, Yuchen Sun^{1,4}, Keith A. Nelson^{1,4}, Desiree L. Plata², Jeremiah A. Johnson^{*1}

Affiliations

¹ Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

² Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

³ Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

⁴ Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

*Correspondence to: jaj2109@mit.edu

Supplementary Information

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Materials and Methods

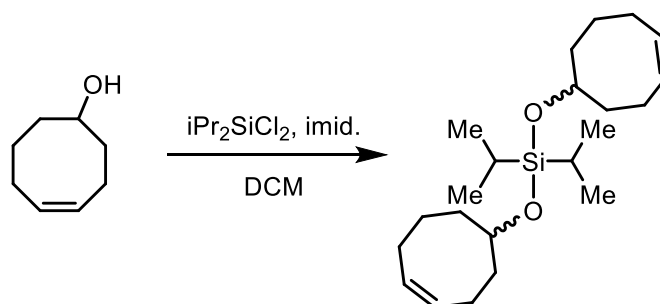
All reagents were purchased from commercial suppliers and were used without further purification unless otherwise noted. Grubbs 2nd Generation catalyst was purchased from Sigma-Aldrich, dissolved in dry dichloromethane, concentrated under vacuum, and finely powdered immediately before use.

¹H nuclear magnetic resonance (¹H-NMR) and ¹³C nuclear magnetic resonance (¹³C-NMR) spectra were acquired at the MIT Department of Chemistry Instrumentation Facility on a Bruker AVANCE III DRX 400 or Neo 500. Chemical shifts are reported in ppm relative to signals from the NMR solvent: for CDCl₃, this corresponds to 7.26 for ¹H and 77.0 for ¹³C spectra. Solid state NMR was performed on a Bruker AVANCE III 501. High-resolution mass spectrometry (HRMS) measurements were obtained on a JEOL AccuTOF system at the MIT Department of Chemistry Instrumentation Facility. Gel permeation chromatography (GPC) analyses were performed on an Agilent 1260 Infinity system with dual Agilent PL1110-6500 columns using a chloroform mobile phase at a flow rate of 1 mL/min. The differential refractive index (dRI) of each compound was monitored using a Wyatt Optilab T-rEX detector and light scattering (LS) for molecular weight analysis was monitored using a Wyatt Dawn Heleos II detector. Specific materials characterization techniques are described in the relevant sections below.

Monomer Synthesis

Dicyclopentadiene was distilled and stored at -20 °C until they were ready to use. **iPrSi** and **EtSi** were prepared following a previously described protocol (28).

Synthesis of Cyclooctene-Functionalized Silyl Ether Crosslinker



5-Hydroxy-1-cyclooctene (2 mmol, 0.252 g) was dissolved in 4 mL of dry dichloromethane. Imidazole (2 mmol, 1 equiv., 0.136 g) was then added and the solution cooled to 0 °C. Finally, dichlorodiisopropylsilane (1 mmol, 0.5 equiv., 0.185 g, 0.180 mL) was added dropwise. A white precipitate formed. The solution was then stirred at RT for 30 minutes. The solids were removed by filtration and the resulting solution was concentrated. The material was concentrated and purified by column chromatography using 20:1 hexanes/ethyl acetate to yield 0.218 (60%) of diastereomeric products as a clear oil.

¹H NMR (400 MHz, Chloroform-d) δ 5.68 (dt, *J* = 10.6, 7.5 Hz, 1H), 5.57 (dt, *J* = 10.5, 7.9 Hz, 1H), 4.00 (td, *J* = 8.6, 4.2 Hz, 1H), 2.47 – 2.30 (m, 1H), 2.21 (dtd, *J* = 13.0, 8.4, 4.1 Hz, 1H), 2.17 – 2.05 (m, 1H), 1.99 (dtd, *J* = 14.1, 6.9, 3.6 Hz, 1H), 1.92 – 1.55 (m, 5H), 1.44 (dtd, *J* = 14.0, 9.7, 9.1, 3.9 Hz, 1H), 1.02 (dd, *J* = 7.1, 1.6 Hz, 7H), 0.99 – 0.81 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 130.23, 129.24, 77.32, 77.00, 76.68, 72.67, 72.49, 72.47, 37.80, 36.32, 36.30, 25.76, 25.75,

25.04, 22.64, 22.63, 17.48, 17.44, 17.17, 12.59, 12.56, 12.55, 12.45, 12.18. HRMS (DART): Calculated for $C_{22}H_{41}O_2Si$ (M+H)⁺ 365.2875, found 365.2779.

Material Synthesis

pDCPD Resin Synthesis (Sheets)

50 μ L of monomer mixture were sandwiched between two glass slides (VWR, Part No. 16004-422), with additional slides used as a spacer between the top and bottom surface. The material was cured at 120 °C for 15 minutes, during which time the pink solution turned into a yellow solid as it polymerized and crosslinked to form pDCPD. The sample was removed from the oven, cooled to room temperature, and the glass slides were removed to yield the free resin. The collected pDCPD samples were cured for another 30 minutes at 120 °C and then stored at room temperature under vacuum until further use.

pDCPD Resin Synthesis (Dogbone)

Dogbones for tensile testing were prepared using custom silicon molds. The mold was prepared by from Mold Max 60 silicone rubber (Smooth-On), which was poured over 2 mm thick aluminum dogbones cut into the 1BB format inside an aluminum tin and cured overnight at RT following manufacturer protocols. 800 μ L of resin precursor was used for each dogbone, and the samples were cured for 30 minutes at 120 °C before tensile testing on the Instron. For dynamic mechanical analysis experiments, the dogbone samples were further cut and sanded down to the requisite bar geometry (1.5 mm x 1.5 mm x 8 mm).

Synthesis of Linear pDCPD

1 g of DCPD was transferred into a nitrogen-filled glovebox and dissolved in 4 mL of toluene. Next, a pill of XiMo Schrock's catalyst (Strem, CAS No. 139220-25-0) was added and the mixture allowed to stir for 24 hours. The remaining material was collected and the soluble fractions were precipitated in methanol and concentrated under vacuum to yield the polymer as a white solid.

Material Characterization

Rheological Measurements

Samples of pDCPD containing 0, 2.5, or 5% **iPrSi** were treated with TBAF to cleave the silyl ether functionalities and then washed with THF to remove residual TBAF and silyl fluoride byproducts. Afterwards, samples were washed with THF and allowed to fully swell.

Frequency sweep rheology experiments were performed on a TA Instruments Discovery Hybrid Rheometer HR-2 rheometer. A parallel-plate geometry (radius = 8 mm) was used and coupled with a bottom plate, with the typical gap of 5.00 mm between the two plates. Frequency sweep experiments were performed from 0.1 to 100 rad/s at 1.0% strain. Experiments were performed at 25 °C and measurements were performed immediately and completed within five minutes to minimize solvent evaporation.

Silicon Quantification by ICP-OES

pDCPD samples were digested in a 37% HNO_3 solution in a 2 mL glass vial, then diluted 50-100x into a solution of 1% HNO_3 . As a reference, **iPrSi** monomer was similarly digested using nitric acid treatment before elemental analysis. Silicon was then quantified using an Agilent 5100 DVD

Inductively Coupled Plasma-Optical Emission Spectrometer. Experiments were performed at the MIT Materials Research Laboratory MRSEC.

Quantification of Polymer Mass as a Function of Time

A 200 mg sample of **iPrSi** doped pDCPD was covered with 5 mL of THF containing 188 μL of 1M TBAF (2 equivalents). At a specific timepoint, the solution was removed and the material was washed with 3 x 5 mL THF. The solid was allowed to sit in 10 mL THF for 1 hour; then it was washed again and allowed to sit in 10 mL THF for another 24 hours. The solvent was removed under vacuum for 48 hours and the mass of the residual solid was measured.

Quantification of Polymer Mass as a Function of Si Doping

200 mg samples of pDCPD containing 0, 2.5, 5, 7.5, or 10% **iPrSi** were covered with 10 mL of 0.5 M TBAF. Each solution was allowed to sit for 24 hours. Then, the liquid fraction was removed and the residual solid was washed with 3 x 5 mL THF and allowed to sit in 10 mL THF for 24 hours. The THF was removed and another 10 mL of THF was added. After another 24 hours, the THF was removed and residual solvent was removed by storing the materials in a vacuum oven for 48 hours. The mass of remaining solids was measured and compared to the initial mass of the pDCPD samples. For **SiXL**-doped pDCPD samples used for mass quantification (Fig. 2b, Fig. S7), an identical protocol was used but samples were treated with TBAF for 17 days.

Swelling Ratio Measurements

Samples of pDCPD were swollen in THF for at least 24 hours. The materials were gently dried with a Kimwipe to remove excess solvent and the mass of the swollen material measured. The resulting solids were then dried under vacuum oven for 24 hours to remove any residual solvent and the mass of the resulting dried material measured. The swelling ratio is reported as the ratio of the mass of the swollen material to that of the dried material.

Confirmation of Silyl Ether Cleavage by Tetrabutylammonium Fluoride

A 1 M solution TBAF in d_8 -THF was prepared by removing solvent from commercially available 1 M TBAF solution in THF followed by dilution in d_8 -THF. This process of solvent removal and dilution in d_8 -THF was repeated two more times to guarantee removal of residual THF. A sample of either **iPrSi** or **SiXL** (15 mg) was dissolved in 0.8 mL d_8 -THF in an NMR tube. 0.2 mL of 1 M TBAF was then added and the reaction was monitored by ^1H NMR after a 30 min incubation.

Surface Mechanical Measurements by Nanoindentation

Mechanical testing was performed on a TriboIndenter (Hysitron) using a Berkovich diamond tip. Indentations were performed using a sequence of 10 s approach, 10 s static hold, and 10 s departure. Indentation depths of 300 and 1000 nm were performed to explore the influence of indentation depth on material mechanical properties. Experiments were performed at the MIT Department of Materials Science and Engineering NanoMechanical Technology Laboratory.

Characterization of Surface Etching of Doped pDCPD by AFM

Surface roughness measurements were performed on a Cypher S AFM (Asylum) fitted with an AC160TS silicon tip. Flat samples were suitable for characterization by AFM were prepared by sandwiching the monomer solution between two glass slides using other glass slides as shims. The samples were cured at 120 $^{\circ}\text{C}$ for 30 minutes. For surface etching, samples were exposed

to 2 M NaOH for 30 minutes before being thoroughly washed with deionized water and drying under high vacuum. RMS roughness values of 0, 10, and 50% **iPrSi**-doped samples are 2.23 nm, 1.550 nm, and .783 nm before etching and 2.08 nm, 3.34 nm, and 3.07 nm after etching, respectively. Experiments were performed at the MIT Department of Materials Science and Engineering NanoMechanical Technology Laboratory.

Characterization of Etching of Doped pDCPD by He-Ion Imaging

pDCPD pellets doped with 0, 2.5, or 5% **iPrSi** were treated with THF or TBAF in THF following the standard workflow. Excess TBAF was removed by soaking the samples in fresh THF over the course of 24 hours. The solvent samples were then cut with a razor blade vertically to expose a cross section of the material, and the samples were dried under vacuum for 48 hours. The samples were then sputter coated with Au/Pd, mounted onto a stage using double-sided carbon tape, and imaged with an Orion He-Ion microscope (Zeiss).

Isolation of Dissolved Material for Solution-State Characterization

200 μ L pellets of doped pDCPD, prepared by the above described protocol, were placed in 5 mL of THF. Next, sufficient amounts of TBAF were added for 2 equivalents relative to silyl ether monomer. The material was allowed to sit for 12 hours, after which time the material almost completely dissolved. The liquid components of the samples were carefully transferred to another vial to separate them from any residual solids and the solutions were concentrated under vacuum. The products (degradation “fragments”) were then analyzed by NMR and GPC. To remove tetrabutylammonium salts, which interfered with DOSY and 2D NMR analysis, a THF solution of the material was incubated with an excess of H^+ -Dowex resin and calcium carbonate and filtered following literature protocol (43).

GPC Analysis of pDCPD Fragments

The fragments were dissolved in $CHCl_3$ at a concentration of 2 mg/mL. The material was then filtered through a 0.2 μ m Teflon filter before analysis. Gel permeation chromatography (GPC) analyses were performed on an Agilent 1260 Infinity system with dual Agilent PL1110-6500 columns using a chloroform mobile phase at a flow rate of 1 mL/min. The differential refractive index (dRI) of each compound was monitored using a Wyatt Optilab T-rEX detector and light scattering (LS) for molecular weight analysis was monitored using a Wyatt Dawn Heleos II detector. dn/dc calculations were performed by injecting known concentrations of 10% pDCPD fragments into the T-rEX detector.

Tensile Testing Experiments

Dogbones were prepared using silicone molds containing a modified 1BB format with larger grips. Silicone molds were prepared from Smooth-On Mold Max 60 poured over aluminum dog bones, cut to the 1BB format, and placed in an aluminum tin. The silicone was cured following manufacturer instructions. 900 μ L of pDCPD mixture were added to each mold and the samples were cured at 120 $^{\circ}$ C for 1 hour. The dogbones were then removed from the mold and kept at room temperature until use. Tensile testing was performed on an 8848 MicroTester (Instron) with an extension rate of 0.1 mm/s using a 2 kN load cell. Experiments were performed at the MIT Department of Materials Science and Engineering NanoMechanical Technology Laboratory.

Thermogravimetric Analysis of Doped pDCPD

Thermogravimetric analysis was performed on ~2-3 mg samples of pDCPD. Analyses were performed on a TGA/DSC 2 STAR System (Mettler-Toledo) equipped with a Gas Controller GC 200 Star System. Studies were performed under a constant stream of nitrogen gas at a temperature ramp of 15 °C/minute.

Dynamic Mechanical Analysis of Doped pDCPD

DMA was performed on a Discovery DMA 850 System (TA). Samples with dimensions ca. 2.2 x 1.5 x 5.5-9 mm (w x t x l) were tested in tension mode. Measurements were recorded at a frequency of 1 Hz and an amplitude of 10 µm from 50–225 °C at a rate of 3 °C min⁻¹ with a data sampling interval of 3 s/pt using a 125% force tracking and 0.01 N preload force. Data were collected using Trios software and exported to Microsoft Excel for analysis. Experiments were performed at the MIT Institute for Soldier Nanotechnologies. Reported modulus values in the main text are measurements made at 50 °C. For T_g calculations, the temperature of the highest tan delta peak was used, which is relevant for 33% and 50% iPrSi-doped samples where an additional smaller tan delta peak was observed at higher temperatures.

Comparison of EtSi vs. iPrSi-Doped pDCPD

10% **EtSi** doped pDCPD was prepared in an analogous manner to that of **iPrSi** doped pDCPD to generate ~200 mg pellets. For dissolution experiments, the material was placed into a 20 mL vial and 10 mL of 15% conc. HCl in THF or 0.5 M TBAF were added. The resulting mixtures were then monitored over time.

Dissolution of iPrSi-Doped pDCPD with HF-pyridine Complex

A ~200 mg pellet of 10% **iPrSi**-doped pDCPD was covered with 2 mL of THF in a 15 mL Falcon tube. Next, 20 µL of HF-pyridine complex was added. The material was allowed to incubate for 24 hours, upon which time the bulk of the material had entirely dissolved.

Techno-Economic Analysis

A systematic search of several synthetic pathways was performed to identify existing literature precedents for transformations performed on scale. Calculations used to calculate the prices for each reagent are shown below:

Calculations for Feedstock Contribution to Price of iPrSi (see Figure S1 for more details)

Isopropylchloride (IPC)

$$\left[\left(\frac{\$1.00}{1 \text{ kg Prop.}} \right) \left(\frac{42.08 \text{ kg}}{1 \text{ kmol Prop.}} \right) \left(\frac{1 \text{ kmol Prop.}}{0.94 \text{ kmol IPC}} \right) + \left(\frac{\$0.50}{1 \text{ kg HCl}} \right) \left(\frac{36.46 \text{ kg}}{1 \text{ kmol HCl}} \right) \left(\frac{1 \text{ kmol HCl}}{0.94 \text{ kmol IPC}} \right) \right]$$

$$= \frac{\$64.16}{1 \text{ kmol IPC}} \text{ or } \frac{\$0.82}{1 \text{ kg IPC}}$$

iPr₂SiCl₂

$$\left[\left(\frac{\$64.16}{1 \text{ kmol IPC}} \right) \left(\frac{2 \text{ kmol IPC}}{1 \text{ kmol } i\text{Pr}_2\text{SiCl}_2} \right) + \left(\frac{\$2.65}{1 \text{ kg Silicon}} \right) \left(\frac{28.09 \text{ kg}}{1 \text{ kmol Silicon}} \right) \left(\frac{1 \text{ kmol Silicon}}{1 \text{ kmol } i\text{Pr}_2\text{SiCl}_2} \right) \right]$$

$$= \frac{\$202.76}{1 \text{ kmol } i\text{Pr}_2\text{SiCl}_2} \text{ or } \frac{\$1.10}{1 \text{ kg } i\text{Pr}_2\text{SiCl}_2}$$

3-Butene-1-ol (3B1O)

$$\left[\left(\frac{\$1.00}{1 \text{ kg Prop.}} \right) \left(\frac{42.08 \text{ kg}}{1 \text{ kmol Prop.}} \right) \left(\frac{1 \text{ kmol Prop.}}{0.88 \text{ kmol 3B1O}} \right) + \left(\frac{\$1.08}{1 \text{ kg CH}_2\text{O}} \right) \left(\frac{30.03 \text{ kg}}{1 \text{ kmol CH}_2\text{O}} \right) \left(\frac{1 \text{ kmol CH}_2\text{O}}{0.88 \text{ kmol 3B1O}} \right) \right]$$

$$= \frac{\$84.67}{1 \text{ kmol 3B1O}} \text{ or } \frac{\$1.17}{1 \text{ kg 3B1O}}$$

2-pentene-1,5-diol (PDO)

$$\left[\left(\frac{\$84.67}{1 \text{ kmol 3B1O}} \right) \left(\frac{1 \text{ kmol 3B1O}}{0.45 \text{ kmol PDO}} \right) + \left(\frac{\$1.08}{1 \text{ kg CH}_2\text{O}} \right) \left(\frac{30.03 \text{ kg}}{1 \text{ kmol CH}_2\text{O}} \right) \left(\frac{1 \text{ kmol CH}_2\text{O}}{0.45 \text{ kmol PDO}} \right) \right]$$

$$= \frac{\$260.23}{1 \text{ kmol PDO}} \text{ or } \frac{\$2.55}{1 \text{ kg PDO}}$$

iPrSi

$$\left[\left(\frac{\$260.23}{1 \text{ kmol PDO}} \right) \left(\frac{1 \text{ kmol PDO}}{0.5 \text{ kmol } i\text{PrSi}} \right) + \left(\frac{\$202.76}{1 \text{ kmol } i\text{Pr}_2\text{SiCl}_2} \right) \left(\frac{1 \text{ kmol } i\text{Pr}_2\text{SiCl}_2}{0.5 \text{ kmol } i\text{PrSi}} \right) \right]$$

$$= \frac{\$925.98}{1 \text{ kmol } i\text{PrSi}} \text{ or } \frac{\$4.32}{1 \text{ kg } i\text{PrSi}}$$

Weathering Experiments

We note that there are no standard methods for the abiotic exposure of plastics to light in marine systems. The closest analog is ASTM D4329-13 “Standard Practice for Fluorescent Ultraviolet (UV) Lamp Apparatus Exposure of Plastics.” The principal differences between this method and the ones used here are as follows:

- 1) The method is for solid plastic coupons rather than aqueous samples, so we deployed our own seawater recipe based on the literature (Parker and Mitch, PNAS 2016).
- 2) The ASTM method has a specific mounting procedure that is not applicable to aqueous experimentation.
- 3) Our areal irradiance is much lower than the ASTM method requires: 0.004 W m⁻² versus 0.7 W m⁻² at 340nm, respectively. This would translate to lower weathering rates (e.g., a worst-case scenario). Thus, we emphasized relative weathering rates for samples with variable iPrSi contributions, rather than absolute ones. Note that due to the much lower irradiance, we opted to avoid the light and dark cycling.
- 4) We do not employ a light and dark cycle. While this avoidance of light and dark cycling is irrelevant to photochemical weathering of dissolved organic compound, it could have a non-linear impact on total weathering of polymers in water.
- 5) The light source spectrum power distribution varies somewhat:
 - a. The percent distribution of total irradiance (290-400nm) for recommended UVA 340 lamps and benchmark solar radiation is (ASTM G154-16):
 - i. 290 < λ < 320, 5.9% - 9.3%; solar: 5.8%
 - ii. 320 < λ < 360, 40.0% - 65.5%; solar: 40%

- iii. $360 < \lambda < 400$, 26.5 – 32.8%; solar: 54.2%
- b. whereas our distributions are 1%, 25% and 75%, respectively.
- 6) Note the ASTM method is also geared toward assessment of visual and mechanical properties of weathered materials, rather than environmental degradation properties. Here, we opted to use a non-purgable total organic carbon measurement (akin to methods that seek to interrogate evolved CO₂ in biodegradation experiments, such as ISO Method 14852).

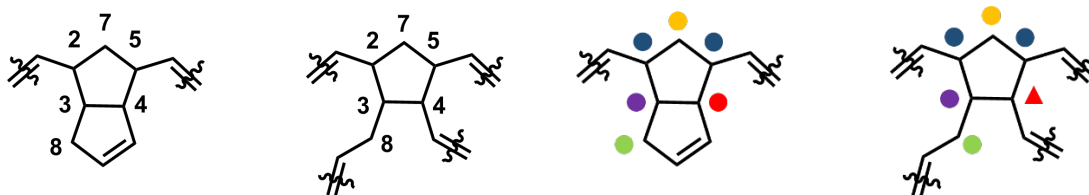
The degradation of these thermosets in the presence of light showed a dependence on the **iPrSi** content (Fig 3i). While the exact origin of this effect is unclear, we note that our doped pDCPD samples absorb light in the UV range due to the presence of residual Ru (Extended Data Fig. 6c). Photo-oxidation of the bulk pDCPD may enhance its aqueous wettability, ultimately promoting the hydrolysis of silyl ether groups.

TEM Characterization of Organic Material Released During Weathering

To characterize the organic material released into solution during weathering, approximately 10 mL of post-irradiation sample was extracted with 5 mL DCM. 2 mL of the organic layer was then collected and the solvent removed. The remaining organic residue was dissolved in 200 μ L of DCM. 5 μ L of sample was cast onto a TEM grid. The samples were then stained with RuO₄ vapor for 5 minutes and imaged by TEM on an FEI Tecnai transmission electron microscope (Fig. S21).

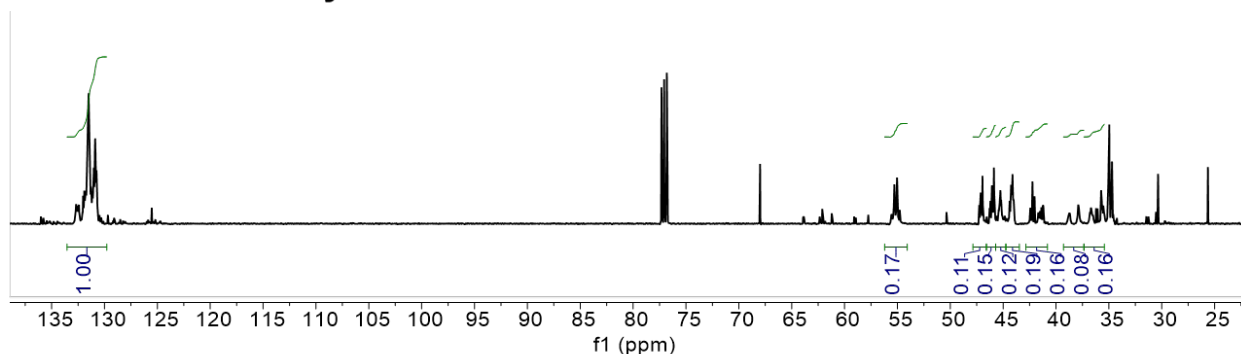
Crosslink Quantification from ¹³C NMR

We assigned the peak at 55 ppm to the allylic carbon of the ring-closed DCPD monomer (red circle, C4). Upon ring opening, the chemical shift of this peak moves upfield to resemble more closely the two bridgehead norbornene carbons (blue circles, C2/C5). HSQC allowed for the assignment of the peaks from 35–40 ppm to the norbornene methylene (yellow circle, C7) and the peaks at 35 ppm to the allylic cyclopentene carbon (green circle, C8). We found that the integral under the 55 ppm C4 peak was lower than expected (only 85%) when compared to the integrations for C7 or C8, suggesting 15% of the cyclopentenones were ring-opened.

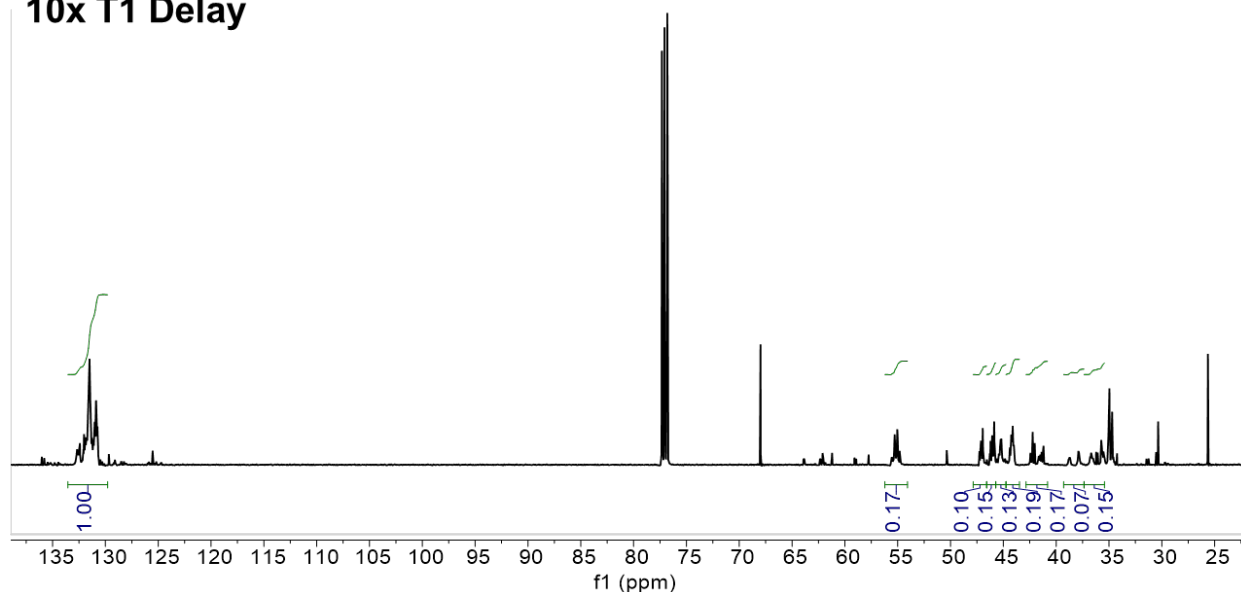


¹³C measurements for integration were acquired on a Bruker Neo 500 in CDCl₃. A total of 2048 scans (300 ms delay time, 1 s overall recycle time, 30–45 degree acquisition pulse) were used for acquisition. Peak integration was performed using MestreNova. As none of the carbons are quaternary, we assume that these acquisition parameters are sufficient to provide accurate integration values in our analysis. To confirm the suitability of these parameters, we performed an additional measurement using a 10 s overall recycle time, which provided identical relative integrations for the peaks under analysis.

Standard T1 Delay



10x T1 Delay



pDCPD Fragment Recycling

Transmission Electron Microscopy

A dilute solution of pDCPD fragments (prepared from TBAF dissolution of 10% **iPrSi**-doped pDCPD followed by Dowex/ CaCO_3 clean-up) in DCM was dropcast onto a copper grid and stained with RuO_4 vapors. The samples were then imaged on an FEI Tecnai transmission electron microscope.

Recycling of pDCPD Fragments

pDCPD fragments derived from 10% **iPrSi**-doped pDCPD were prepared following the standard workflow. 500 mg of the fragments were then dissolved in 1.5 g of DCPD, forming a viscous brown liquid. To this liquid was added 8 mg of finely powdered Grubbs' 2nd generation catalyst. The material was then poured into vials (for forming discs) and silicone molds (for tensile and DMA measurements) and cured at 120 °C for 30 minutes.

Dynamic Mechanical Analysis of Recycled pDCPD

DMA was performed on a TA Discovery DMA 850 system. Samples with dimensions ca. 3.3

x 3.0 x 8-10 mm (w x t x l) were tested in tension mode. Measurements were recorded at a frequency of 1 Hz, an amplitude of 10 μm from 30–225 °C at a rate of 3 °C min⁻¹ with a data sampling interval of 3 s/pt using a 125% force tracking and 0.01 N preload force. DMA data were obtained using Trios software and exported to Microsoft Excel for analysis. Experiments were performed at the MIT Institute for Soldier Nanotechnologies. Reported values are measurements made at 50 °C.

Tensile Testing of Recycled pDCPD

Dogbones were prepared using silicone molds containing a modified 1BB format with larger grips. Silicone molds were prepared from Smooth-On Mold Max 60 poured over aluminum dog bones, cut to the 1BB format, and placed in an aluminum tin. The silicone was cured following manufacturer instructions. 900 μL of pDCPD mixture were added to each mold and the samples were cured at 120 °C for 1 hour. The dogbones were then removed from the mold and kept at room temperature until use. Tensile testing was performed on an 8848 MicroTester (Instron) with an extension rate of 0.1 mm/s using a 2 kN load cell at a sampling rate of 0.2 kHz. Experiments were performed at the MIT Department of Materials Science and Engineering NanoMechanical Technology Laboratory.

Laser Induced Projectile Impact Testing of Recycled pDCPD

The ballistic impact resistance for recycled and native pDCPD bulk samples were tested with LIPIT. 1 mm thick samples of fresh and recycled pDCPD were prepared in silicone mold. The coefficient of restitution was measured at particle impact speeds of 497 ± 15 m/s for 12.5 ± 0.5 μm steel particles. The recycled and control pDCPD exhibit comparable impact resistance within the error of the measurement.

Recovery of Carbon Fiber from pDCPD Composites

Twill-weave carbon fiber (McMaster Carr) was mounted on a piece of tape and cut into a 15 x 15 mm square. The tape was placed into a 20 mL vial and covered with 1 mL of 10% **iPrSi**-doped DCPD precursor (with Grubbs' catalyst, 2 mg/mL). The material was then cured at 120 °C for 30 minutes and the sample removed from the vial. The sample was then placed into a glass chamber and covered with 5 mL of 0.2 M TBAF. After 8 hours, the carbon fiber was carefully removed from the chamber and allowed to dry overnight. Some fraying of the material was observed, which is attributed to loss of the tape used to mount the material over the course of composite synthesis and TBAF dissolution.

Raman Spectroscopy Characterization of Recovered Carbon Fiber

Raman spectra were collected using a Horiba Jobin-Yvon LabRam (Model HR 800) Raman confocal microscope with a 532 nm laser (1.2 μm spot size) excitation and an acquisition time of 3 seconds. Laser intensity was set to 25% for the 532 nm excitation wavelength. Raman spectra were normalized to the G-band (~ 1590 cm^{-1}) and averaged from three individual spectra recorded at different locations on the sample surface.

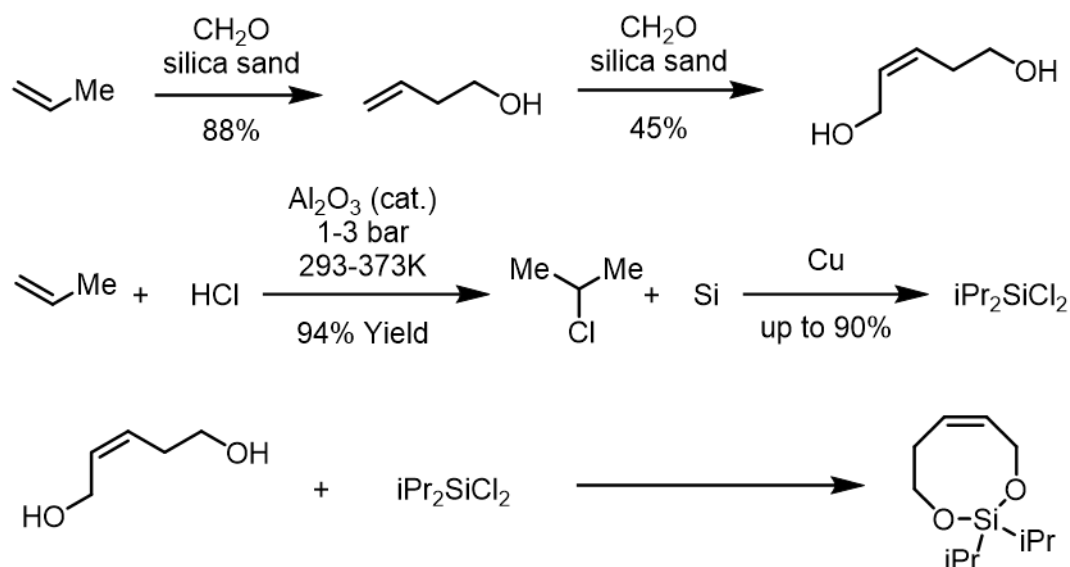


Figure S1. Potential industrial-scale synthesis of **iPrSi** following techno-economic analysis. Although presented at the laboratory scale, both precursors to the final monomer, diisopropyldichlorosilane and 2-pentene-1,5-diol, have the potential to be manufactured from low-cost commodity chemicals at industrially relevant scales. Diisopropyldichlorosilane can be synthesized similarly to other organosilicon compounds, such as dimethyldichlorosilane, a precursor to poly(dimethylsiloxane) that is produced on the megaton scale annually. Initially, isopropyl chloride is formed with 94% selectivity from the gas-phase reaction of propylene and hydrogen chloride over an aluminum oxide catalyst at elevated temperature and pressure (EP1449820A1). Isopropyl chloride (and in general other alkyl halides such as chloromethane or chloroethane) can react in the presence of crushed molecular silicon over a copper catalyst in what is known as the “Direct Process” to form diisopropyldichlorosilane with as high as 90% selectivity (EP1449820A1). 2-pentene-1,5-diol (PDO) can be synthesized through two sequential carbonyl-ene reactions from propylene and formaldehyde, first to 3-buten-1-ol in 88% yield by reaction at elevated temperature and pressure in the presence of a silica sand catalyst (US4288374A). A subsequent catalyst free carbonyl-ene reaction with formaldehyde under supercritical conditions can lead to selective formation of the *cis* alkene product with as high as 45% single-pass yield (CN101928203A, US3692848A). Finally, the silyl ether monomer can be prepared from these two components with yield greater than 50% under dilute conditions. The above yield and selectivity information is based upon identical and/or analogous reactions in the literature and can be used to calculate the costs that feedstocks would contribute towards a final selling price of the silyl ether monomer if it were produced using the presented pathway. Based on the starting material prices listed in Table S1, feedstocks would contribute \$4.32/kg to the final selling price of the silyl ether monomer. Note, this price does not include any process operation or capital costs and is only given to support the claim that production of the silyl ether monomer at scale is feasible from commodity chemical feedstocks.

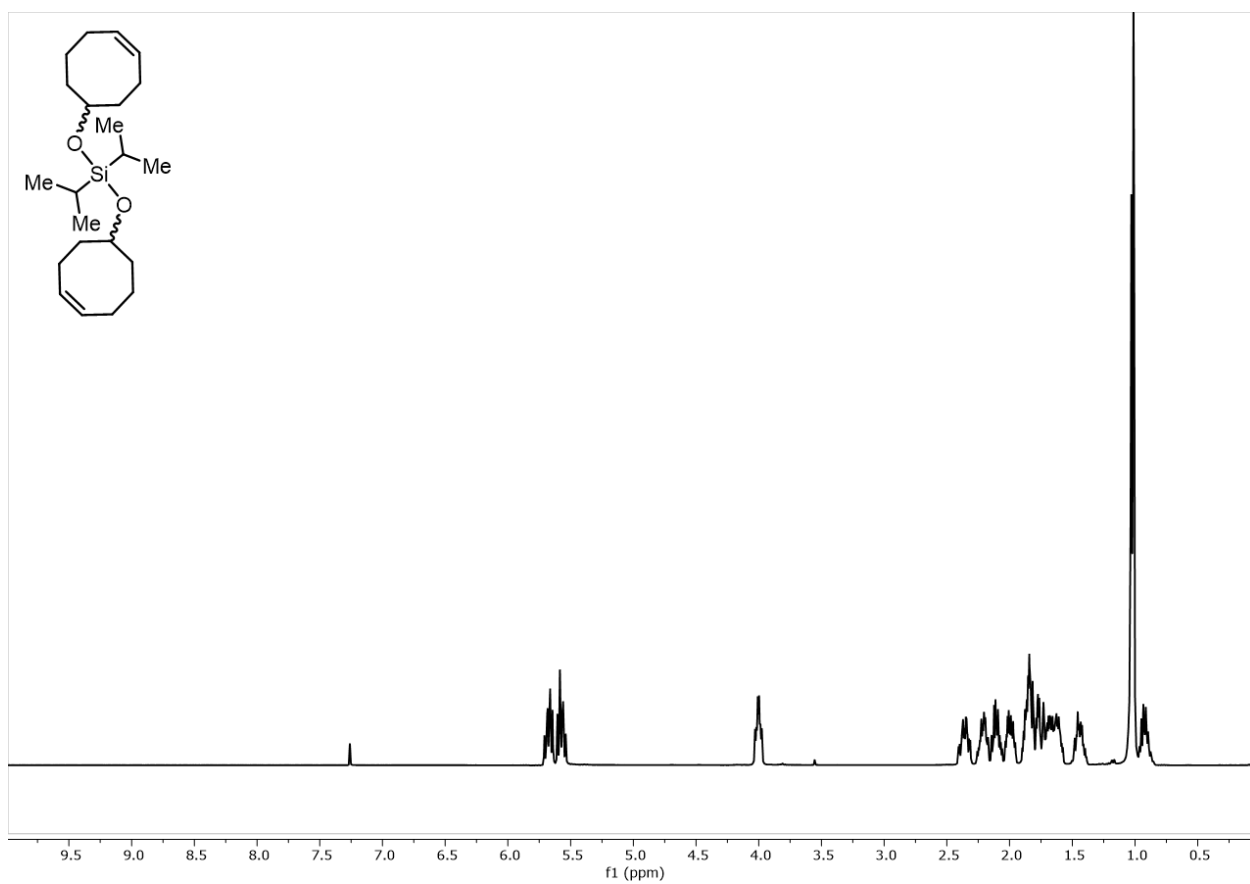


Figure S2. ^1H NMR of silyl ether crosslinker **SiXL**. (CDCl_3 ; 400 MHz)

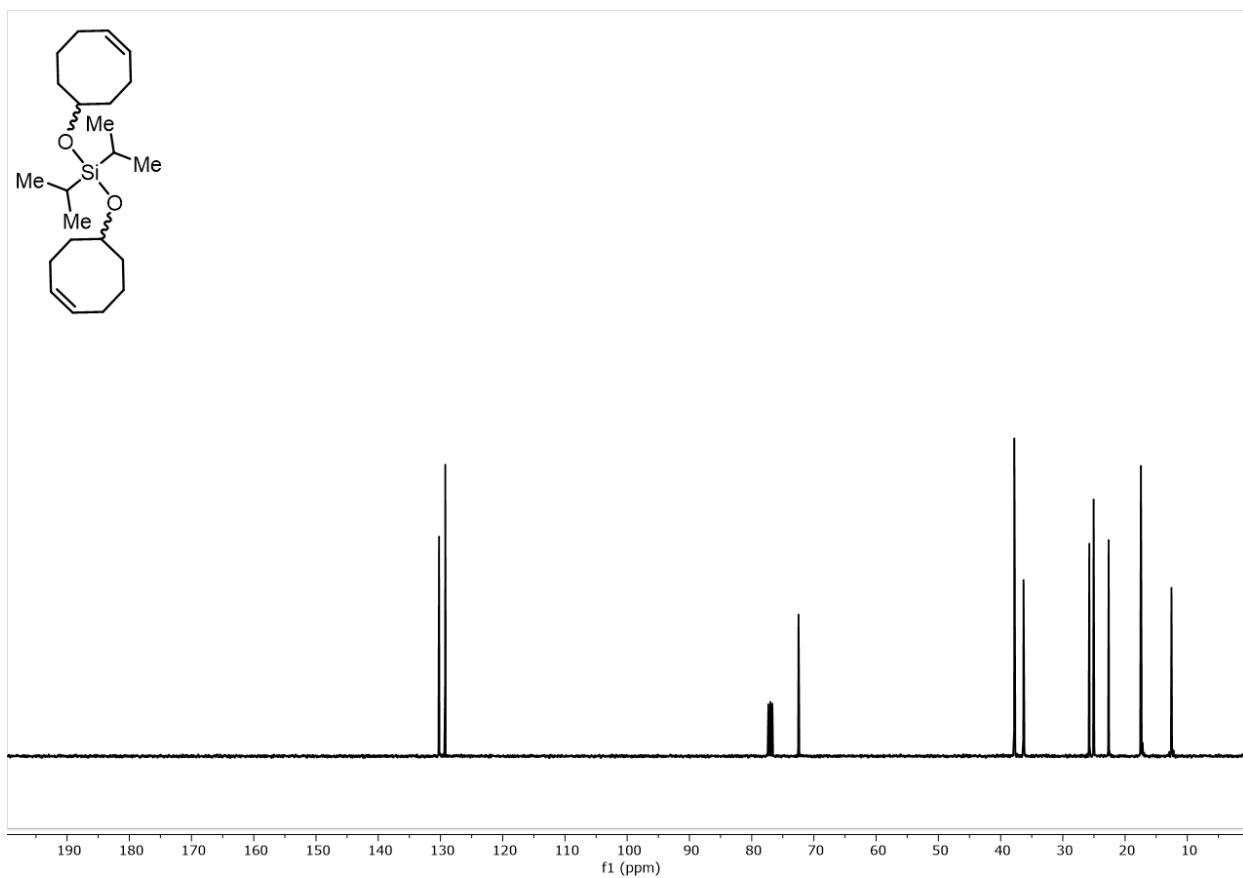


Figure S3. ^{13}C NMR of control silyl ether crosslinker **SiXL**. (CDCl₃; 101 MHz)

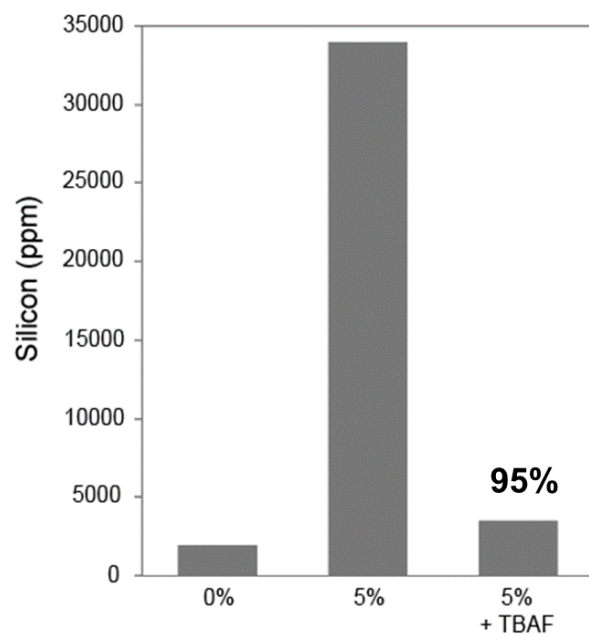


Figure S4. ICP-OES data on solid 0% and 5% **iPrSi** doped pDCPD samples before and after TBAF treatment. These results demonstrate that at least 95% of the silyl ether groups in the material are cleaved under our conditions. The residual silicon signal in the 0% sample, which is expected to show no silicon in ICP-OES analysis in theory, is likely derived from environmental sources of silicon such as the glass used to prepare and digest the material.

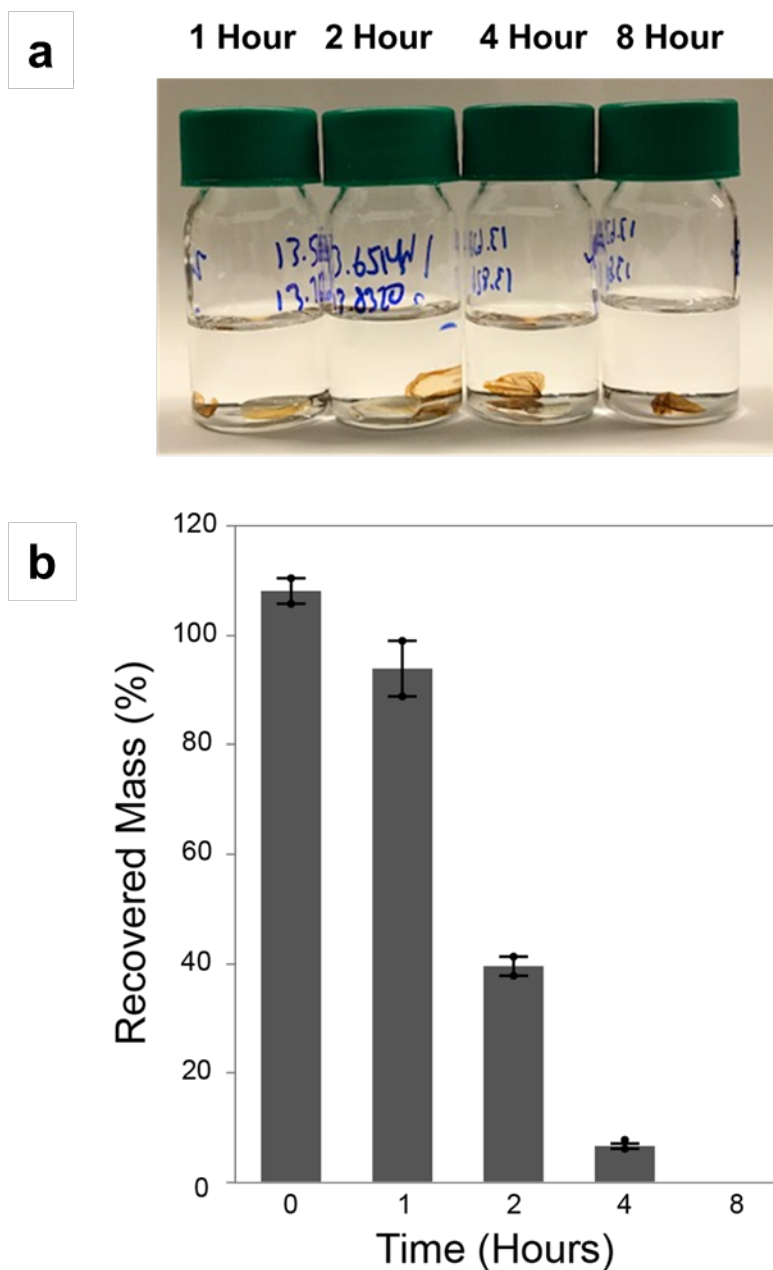


Figure S5. Dissolution of **iPrSi** doped pDCPD as a function of time. 10% **iPrSi** doped pDCPD was incubated with TBAF at 1, 2, 4, or 8 hours in the presence of 200 mol % TBAF. **a.** Images of samples after treatment with TBAF for various times, followed by washing with THF to remove unreacted TBAF and to stop the reaction. **b.** Quantification of residual solid mass as a percentage of initial sample mass. Minimal swelling of the material was visually observed, suggesting that degradation of the material proceeds via surface erosion and that diffusion of TBAF into the material is rate-limiting.

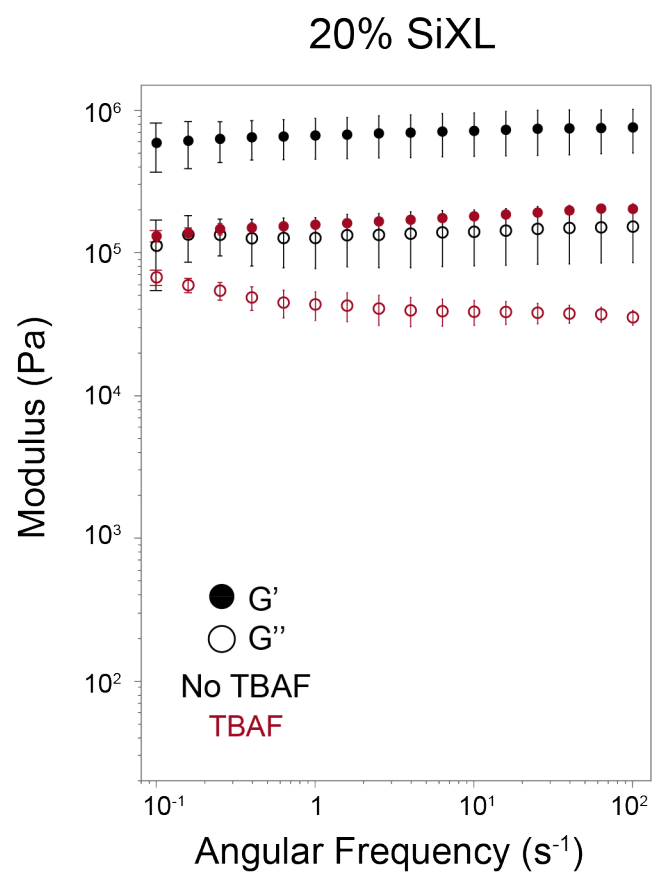


Figure S6. Frequency sweep rheology of THF swollen samples containing 20% v/v of **SiXL**.

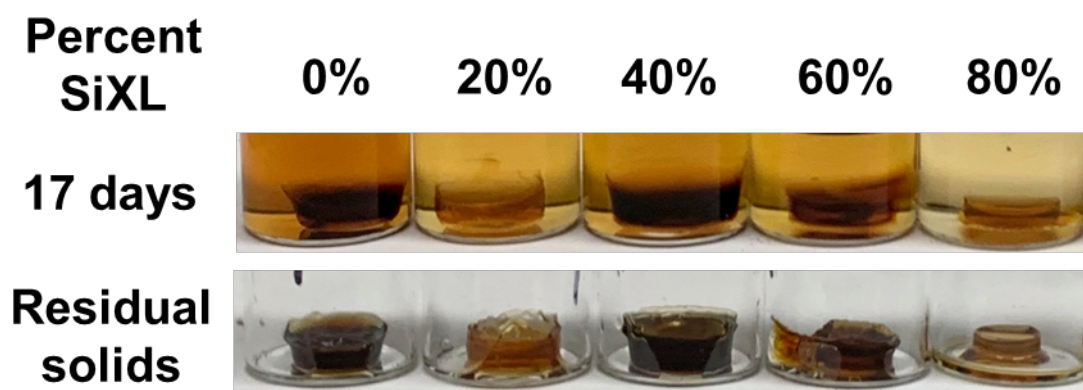


Figure S7. Images of **SiXL**-doped samples after treatment with TBAF for 17 days.

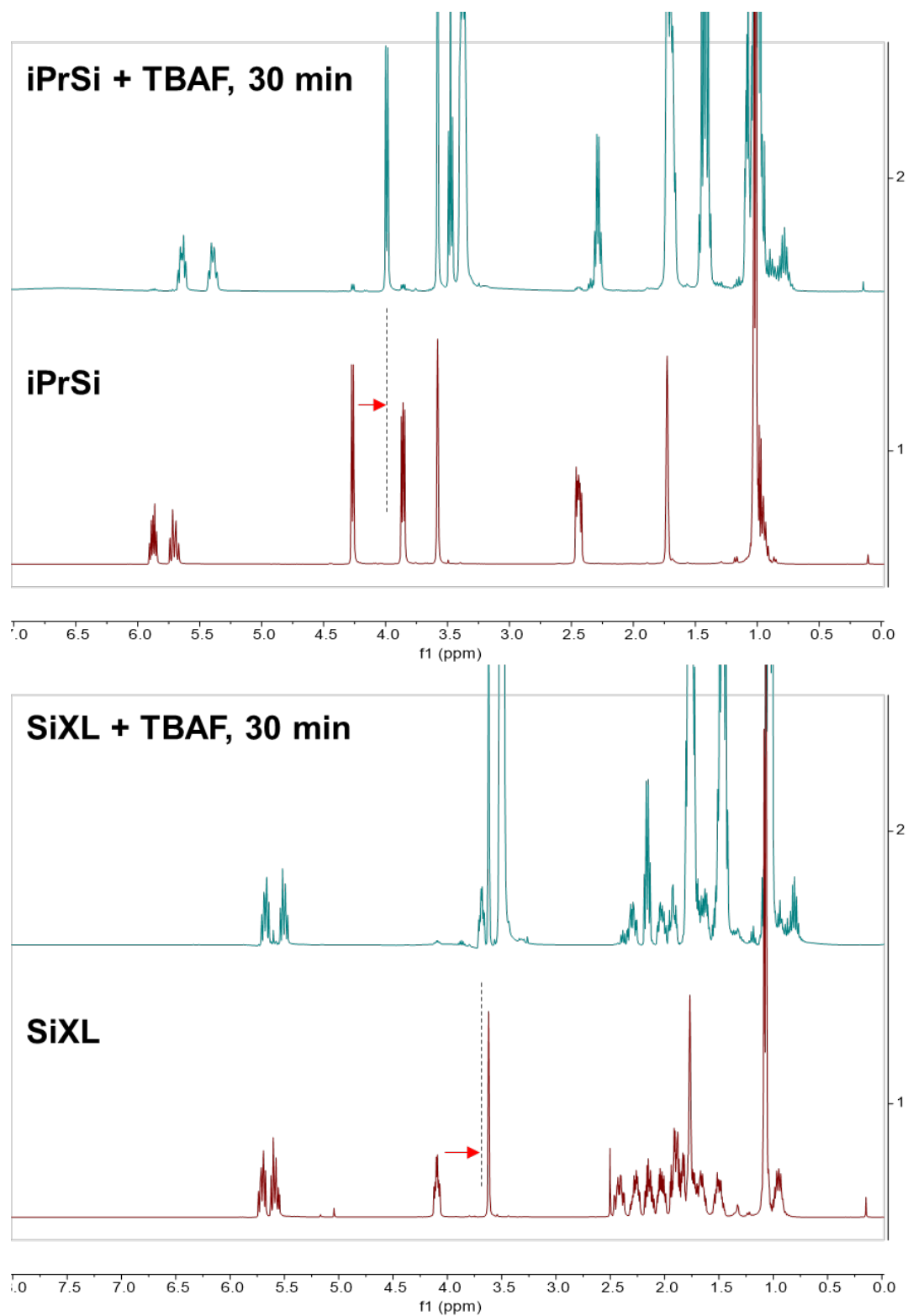


Figure S8. ¹H NMR (*d*₈-THF, 400 MHz) shows 0.2 M tetrabutylammonium fluoride efficiently cleaves silyl ether groups within one hour.

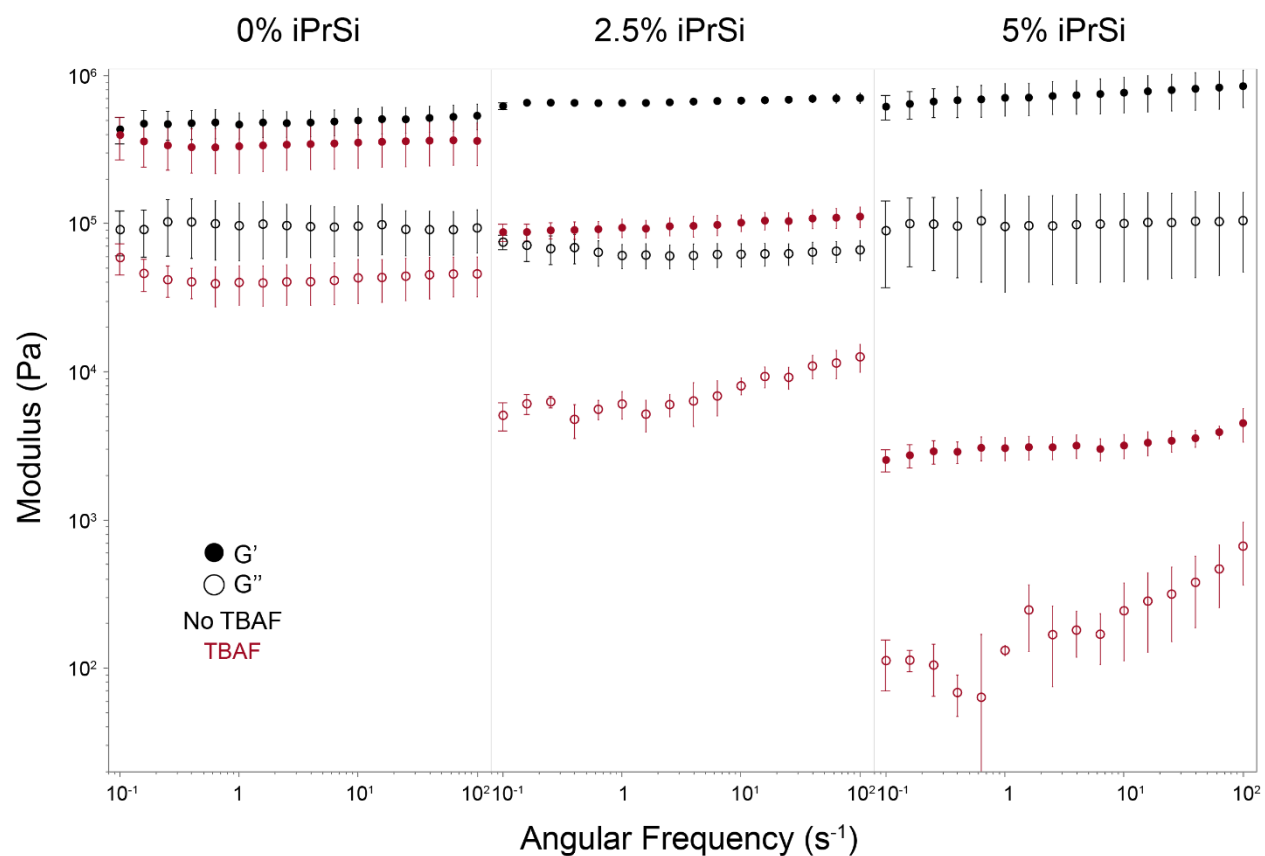


Figure S9. Frequency sweep rheology of THF swollen samples of degraded pDCPD samples showing decreasing moduli after TBAF treatment with increasing **iPrSi**. In contrast, all three samples show similar moduli in the absence of TBAF.

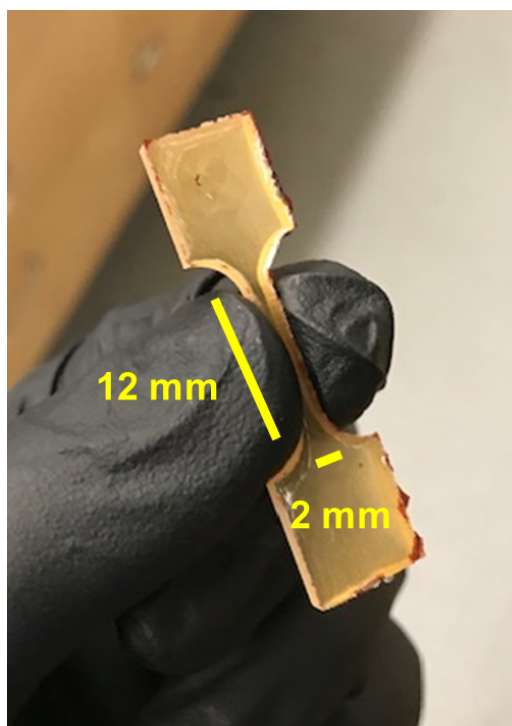


Figure S10. Representative image of a pDCPD dogbone used for tensile testing experiments.

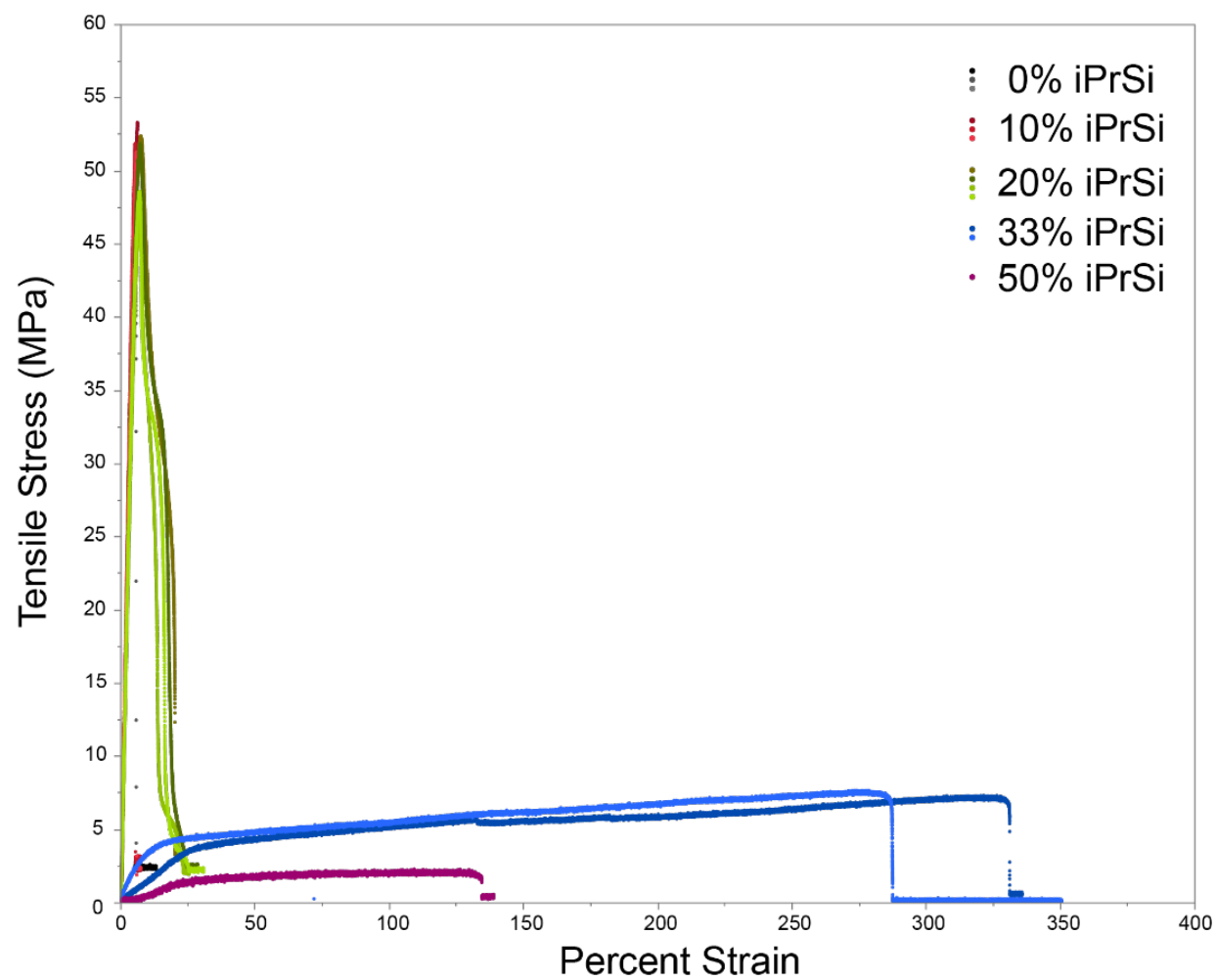


Figure S11. Full stress-strain curves from pDCPD samples containing different levels of **iPrSi**.

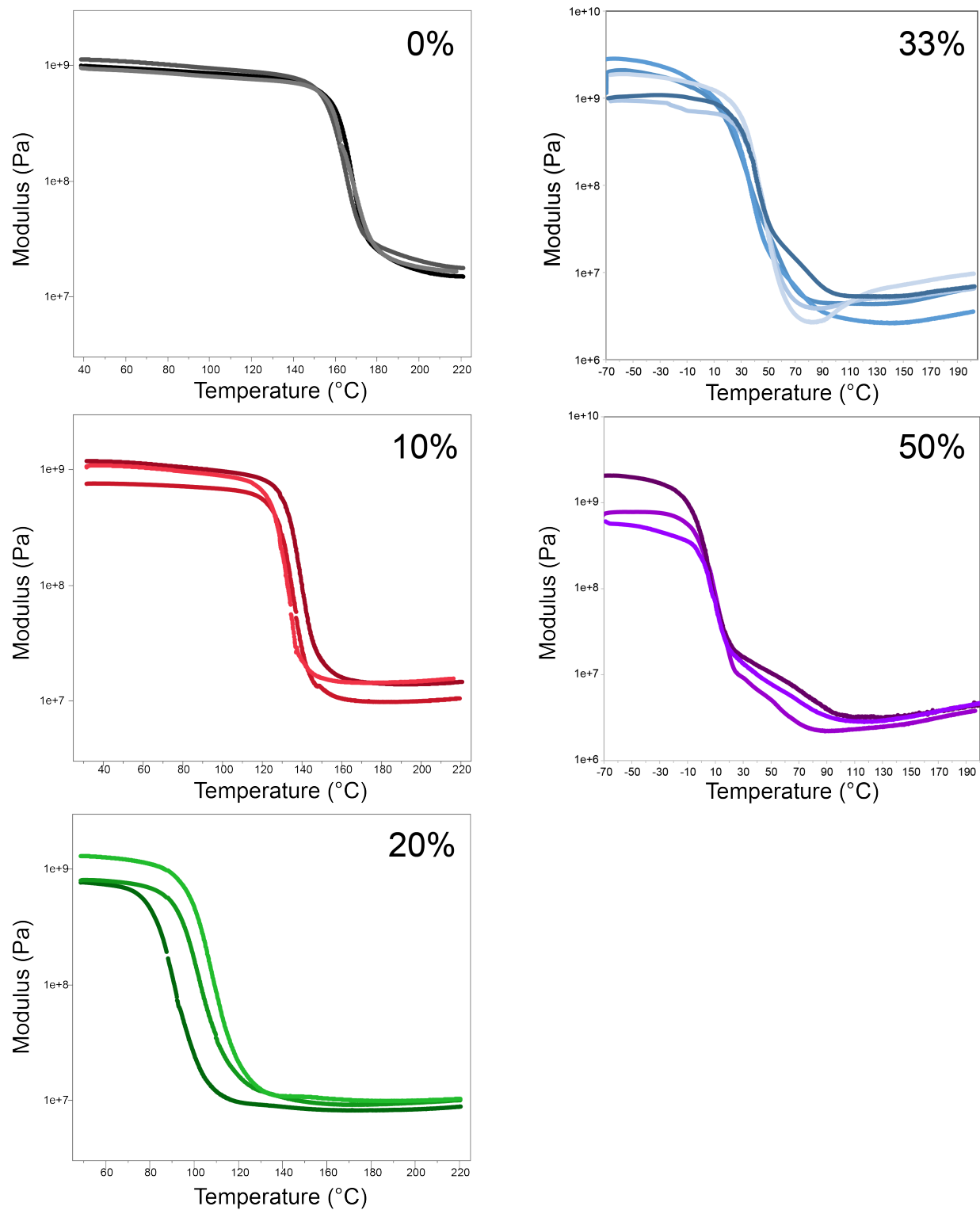


Figure S12. DMA traces from pDCPD samples containing different amounts of iPrSi.

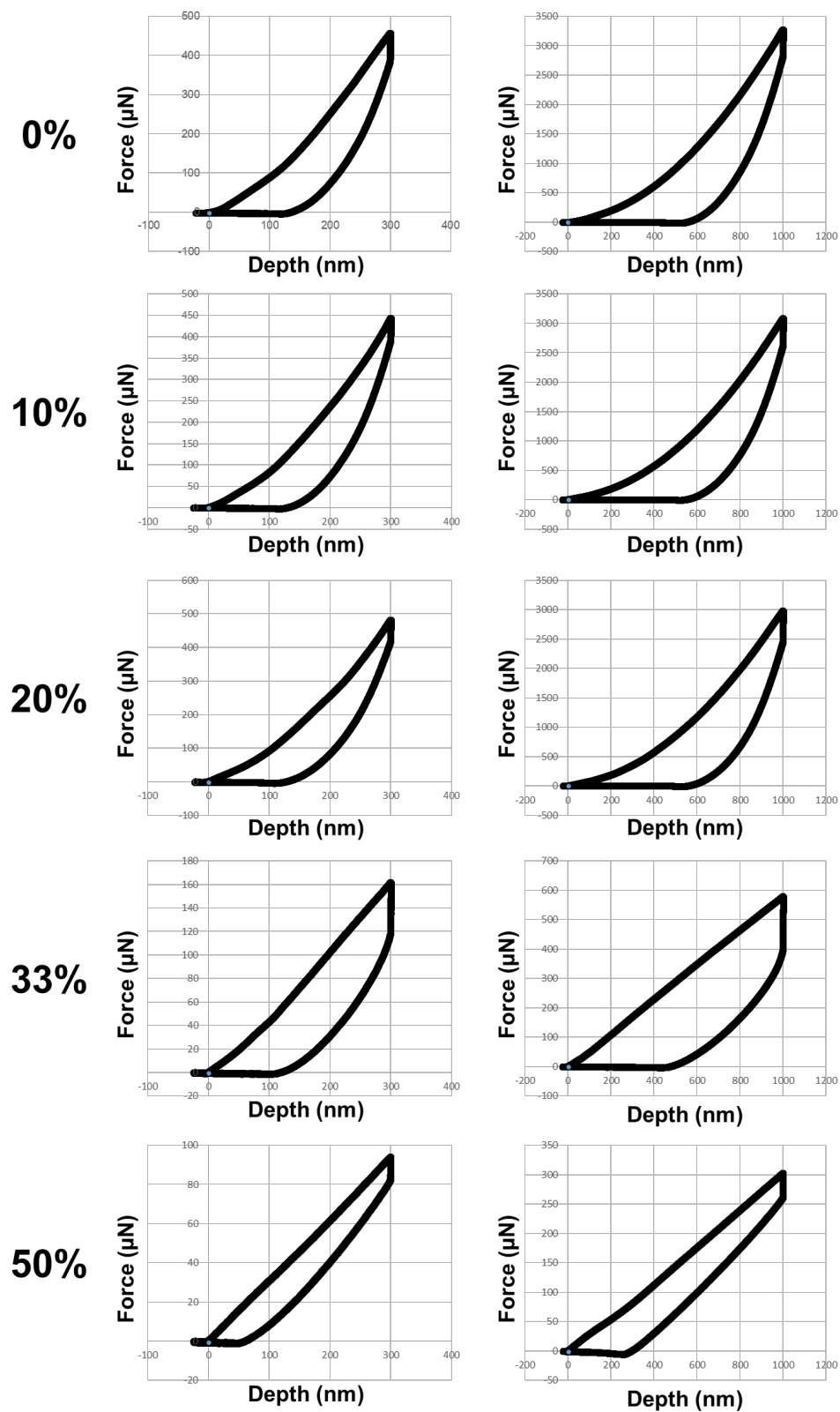


Figure S13. Representative nanoindentation traces from pDCPD samples containing different amounts of iPrSi.

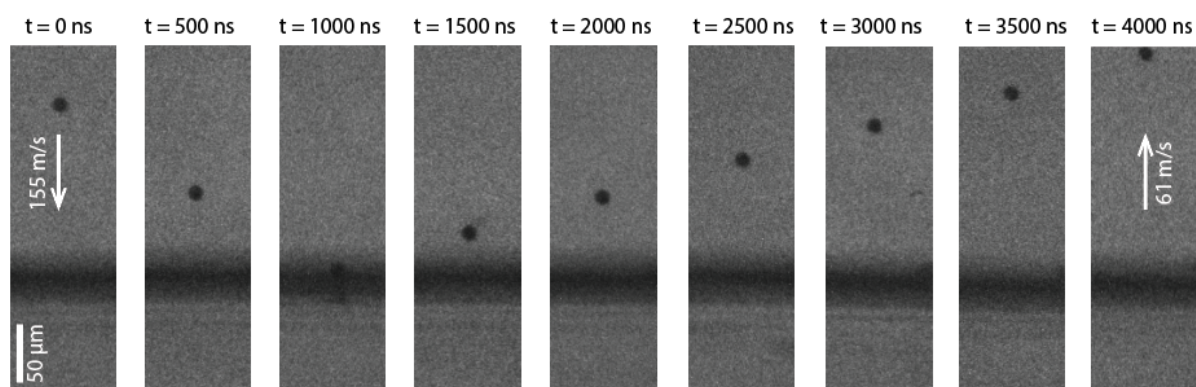


Figure S14. A representative LIPIT image sequence from a 0% iPrSi-doped pDCPD sample showing particle rebound.

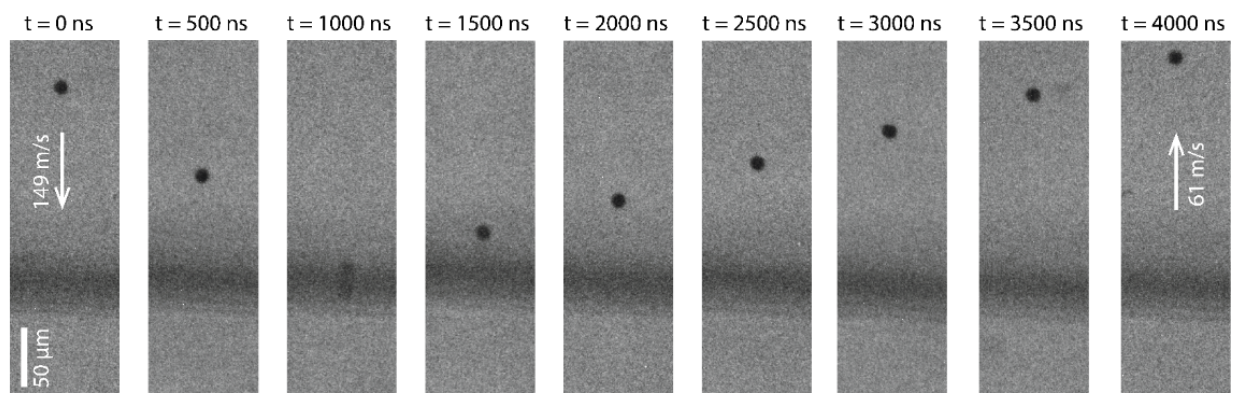


Figure S15. A representative LIPIT image sequence from a 10% **iPrSi**-doped pDCPD sample showing particle rebound.

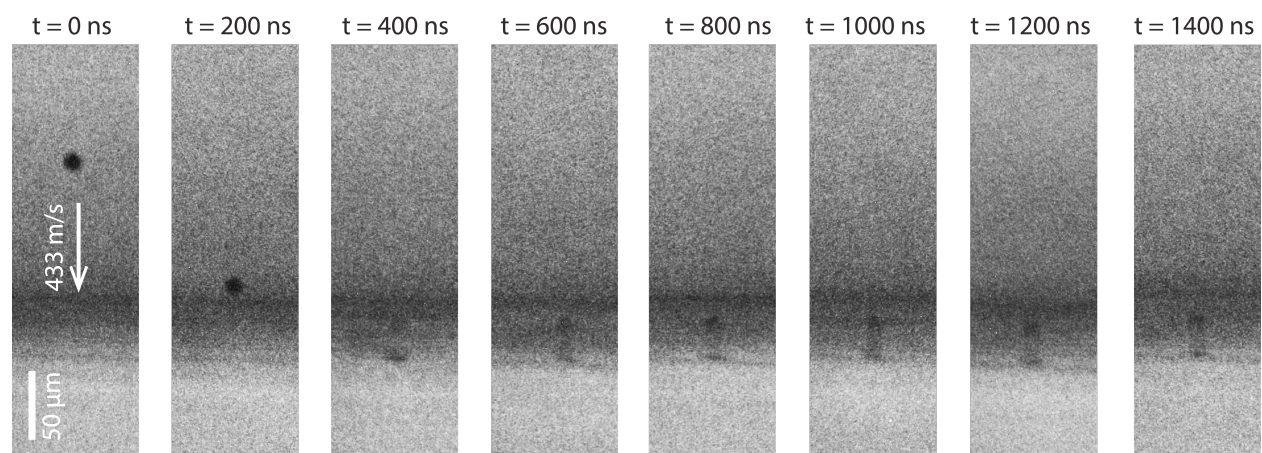


Figure S16. A representative LIPIT image sequence from a 10% iPrSi-doped pDCPD sample showing particle embedment.

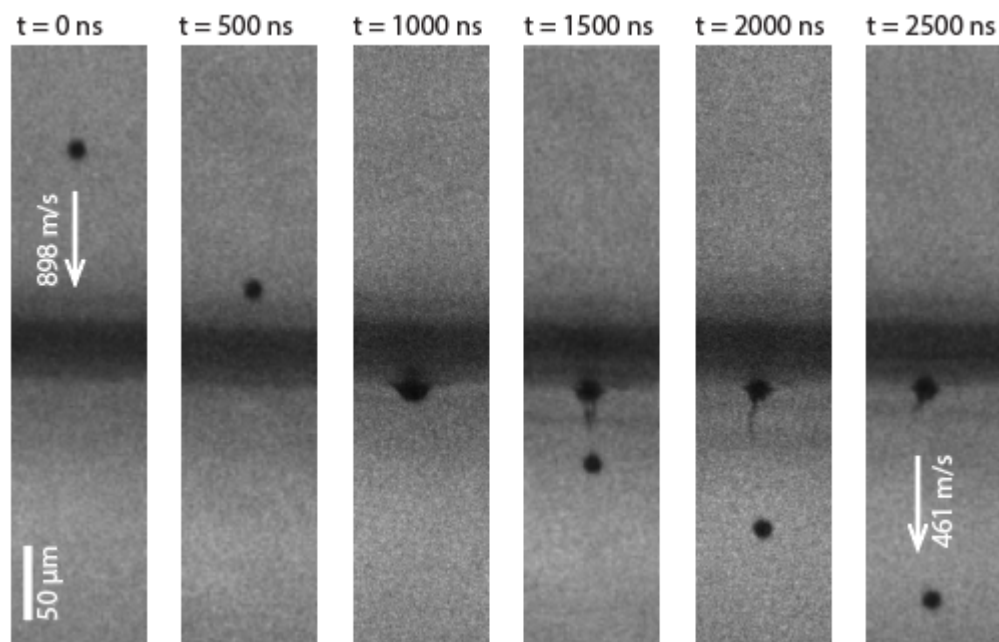


Figure S17. A representative LIPIT image sequence from a 10% iPrSi-doped pDCPD sample showing particle perforation.

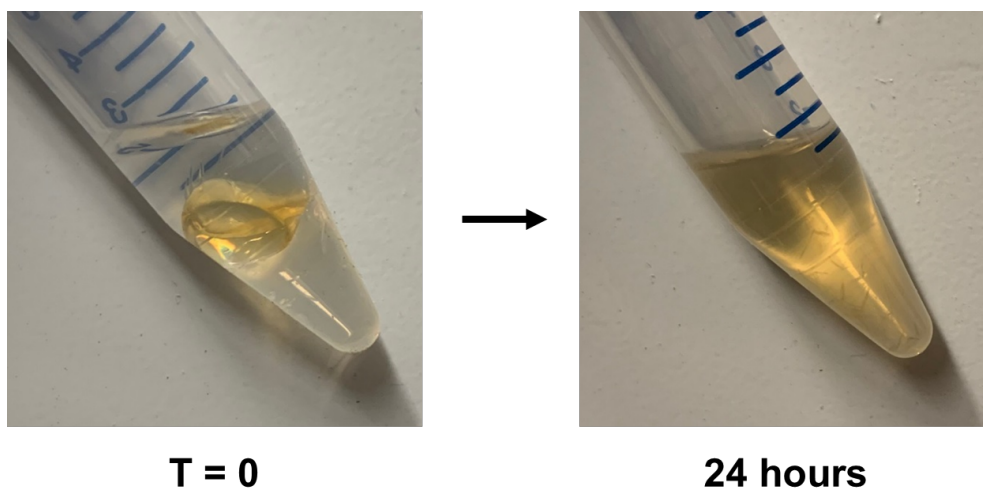


Figure S18. 10% **iPrSi** doped pDCPD readily dissolves in the presence of hydrogen fluoride-pyridine complex in THF.

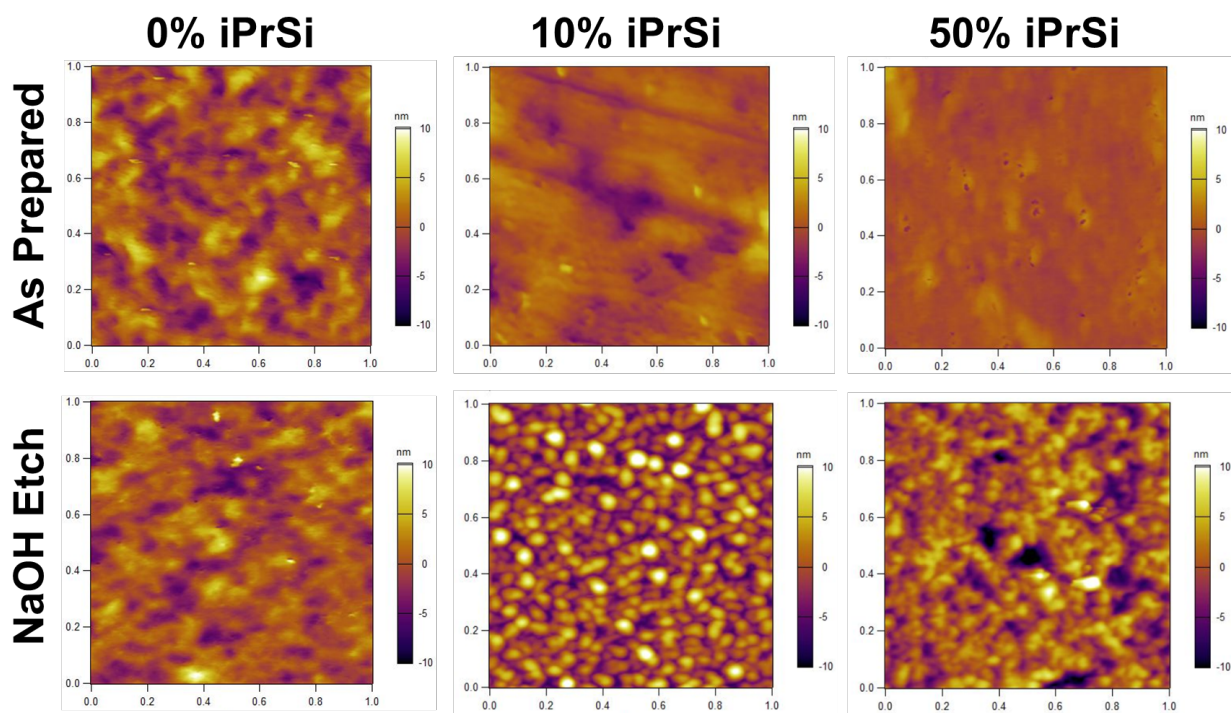


Figure S19. iPrSi doped samples display distinct surface morphologies following exposure to aqueous NaOH as assessed by atomic force microscopy, suggesting base-mediated etching of silyl ether groups at the surface of the material.

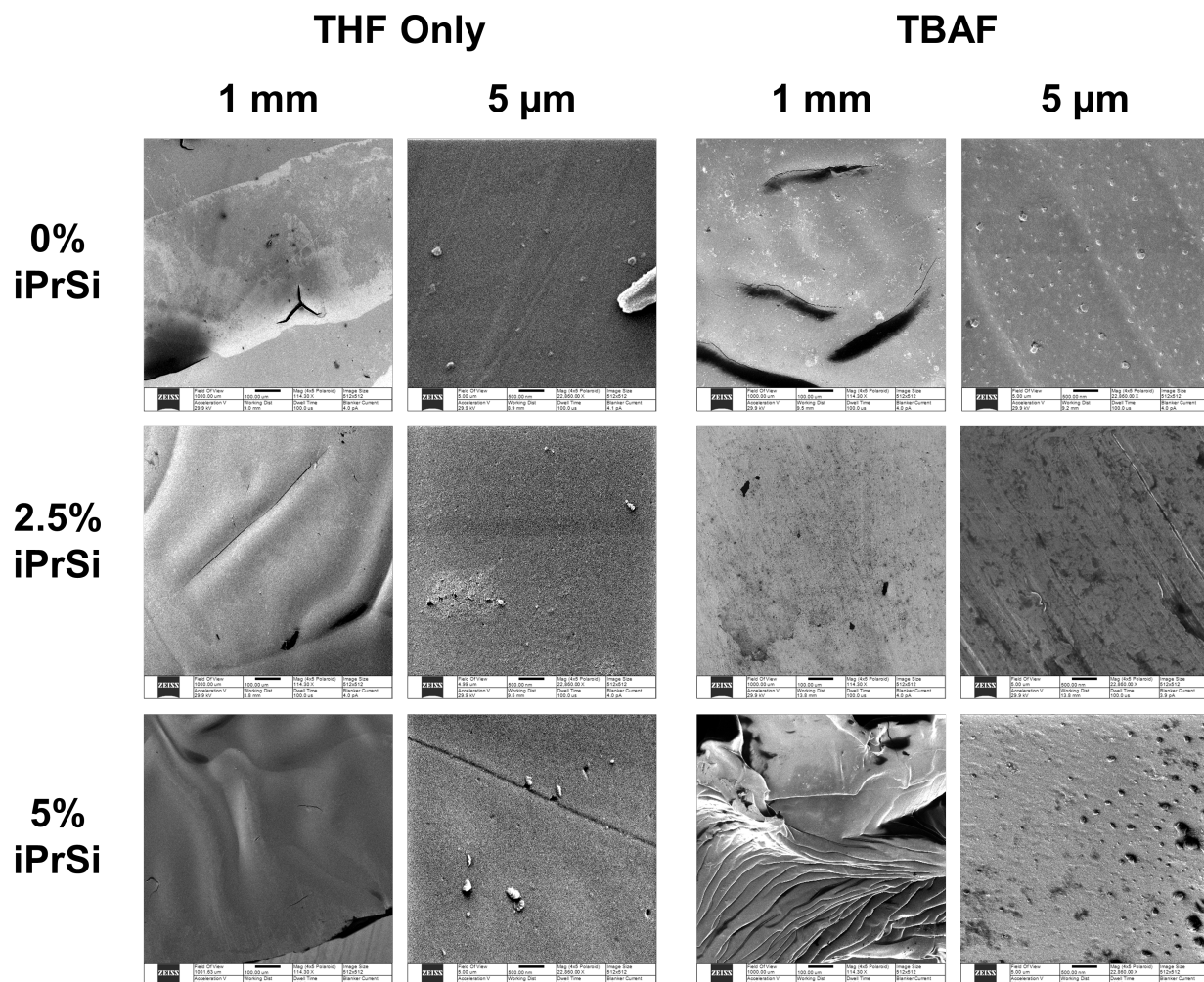


Figure S20. Images of samples of pDCPD containing 0, 2.5, or 5% **iPrSi** treated with TBAF for 12 hours or swollen in THF for 12 hours, then dried. Samples were sputter coated with AuPd alloy before He-ion imaging. Buckling of the THF-only samples is attributed to deformations induced by swelling and drying of the material. The 5% **iPrSi** sample, after TBAF treatment and drying, is significantly deformed (as evidenced in the 1 mm image). No microporosity was observed in the TBAF-treated samples (no pores observed at 5 μ m), consistent with full collapse of the partially degraded polymer networks upon solvent removal.

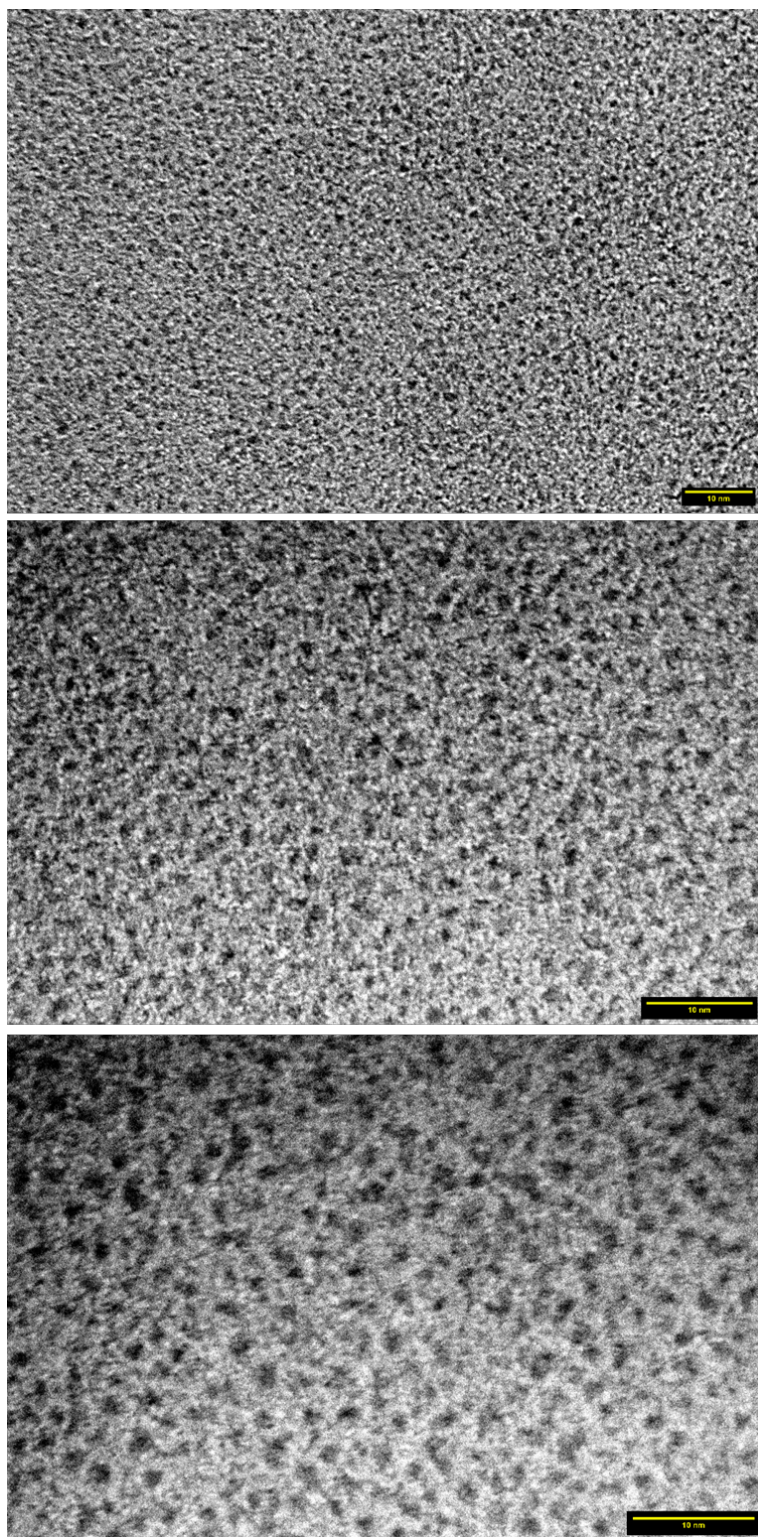
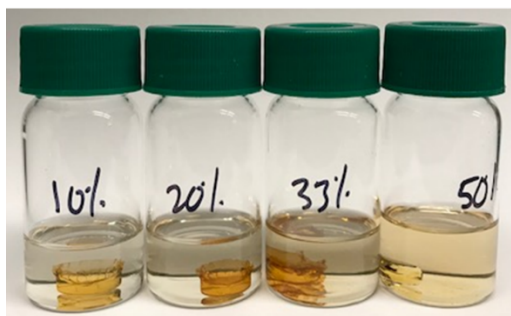


Figure S21. TEM images of organic extracts from weathered samples. Scale bars are 10 nm for all images.

15 Minutes

10% 20% 33% 50%



12 Hours

10% 20% 33% 50%



Figure S22. Samples of pDCPD containing 10, 20, 33, and 50% **iPrSi** dissolve in the presence of 2 equivalents of TBAF in THF at room temperature.

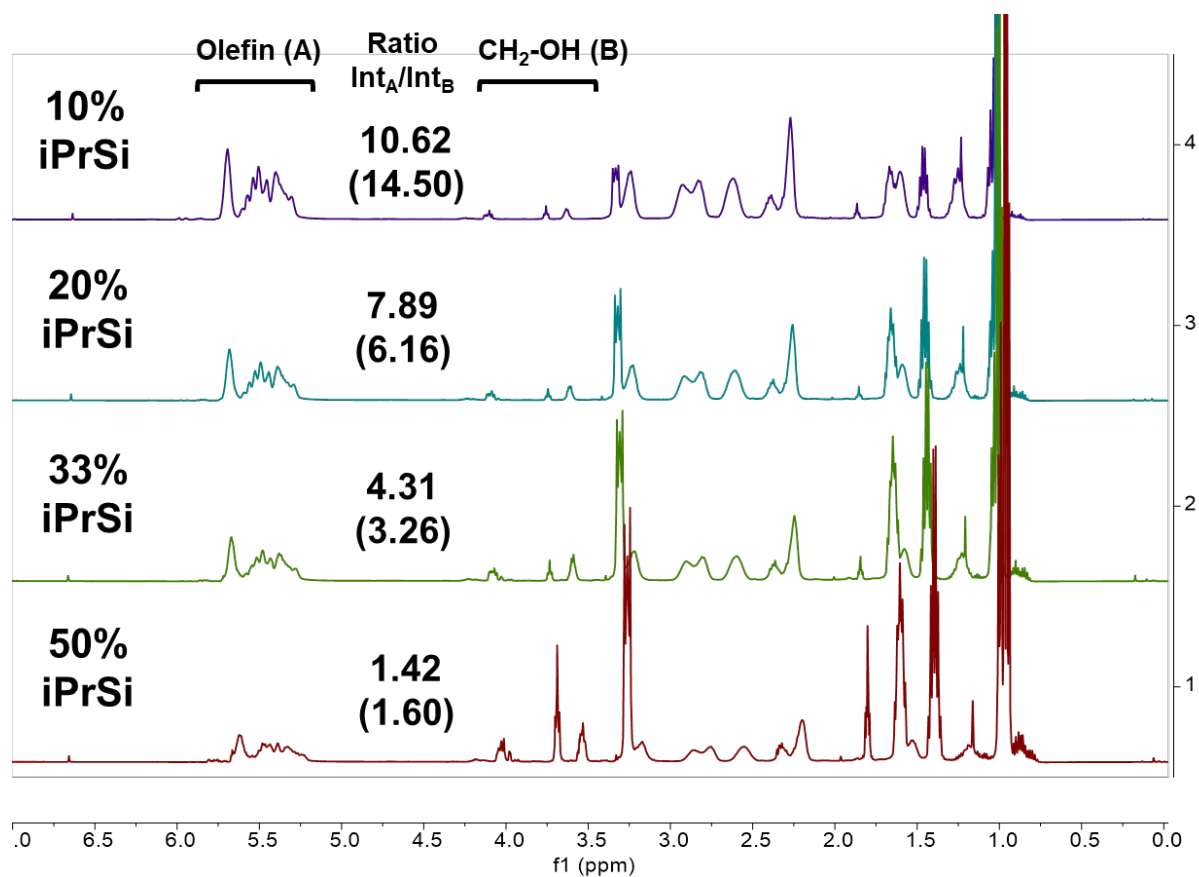


Figure S23. ^1H NMR (CDCl_3 ; 500 MHz.) of soluble fragments derived from materials with different amounts of hydroxyl groups, showing increased levels of silyl ether-derived fragments from pDCPD doped with more **iPrSi**. In parentheses are the theoretical integration values assuming equal addition of equal volumes of the two materials. These results also indicate full consumption of the norbornene component of DCPD in our materials, as the sharp peaks corresponding to unreacted DCPD are absent.

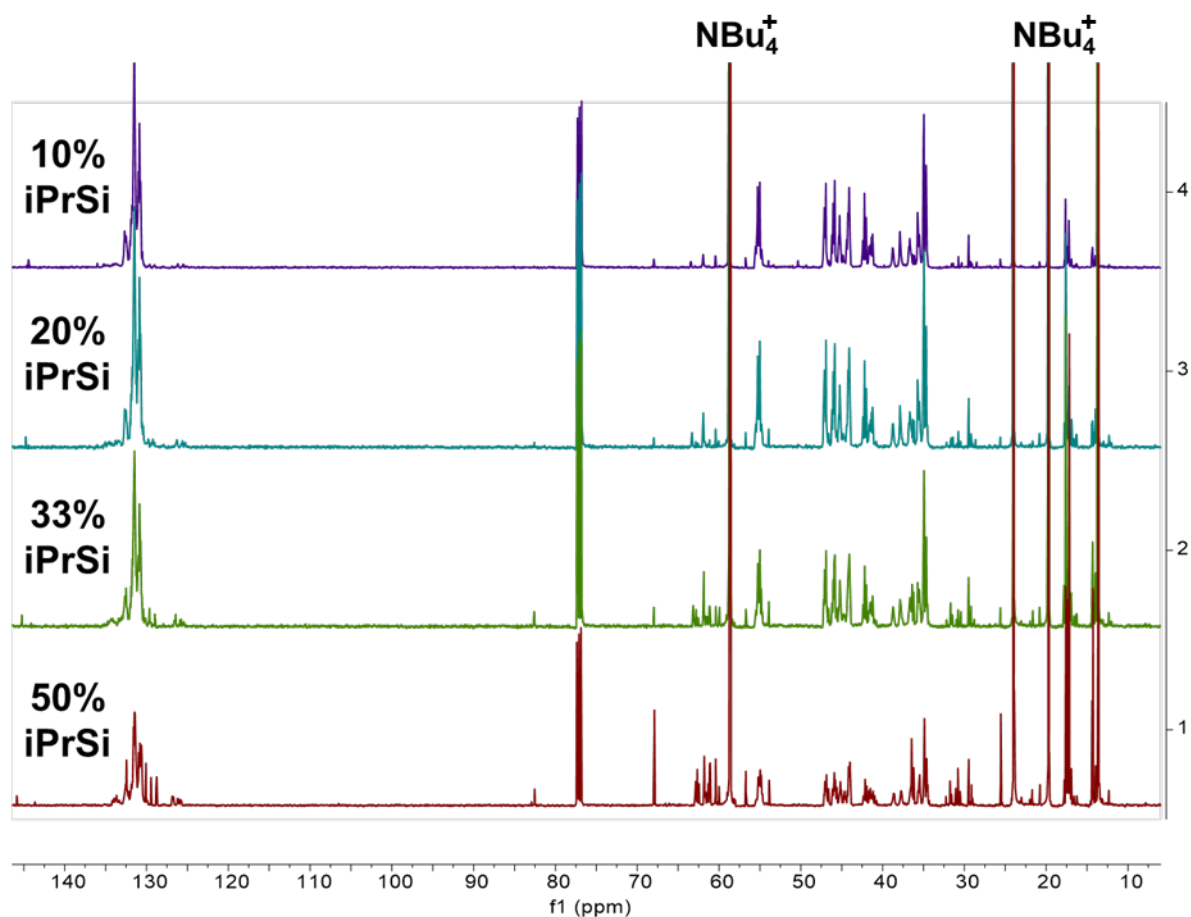


Figure S24. Full solution-phase ^{13}C NMR spectra (CDCl_3 ; 500 MHz) of the degradation solution, enabling characterization of crosslink density within the parent pDCPD material.

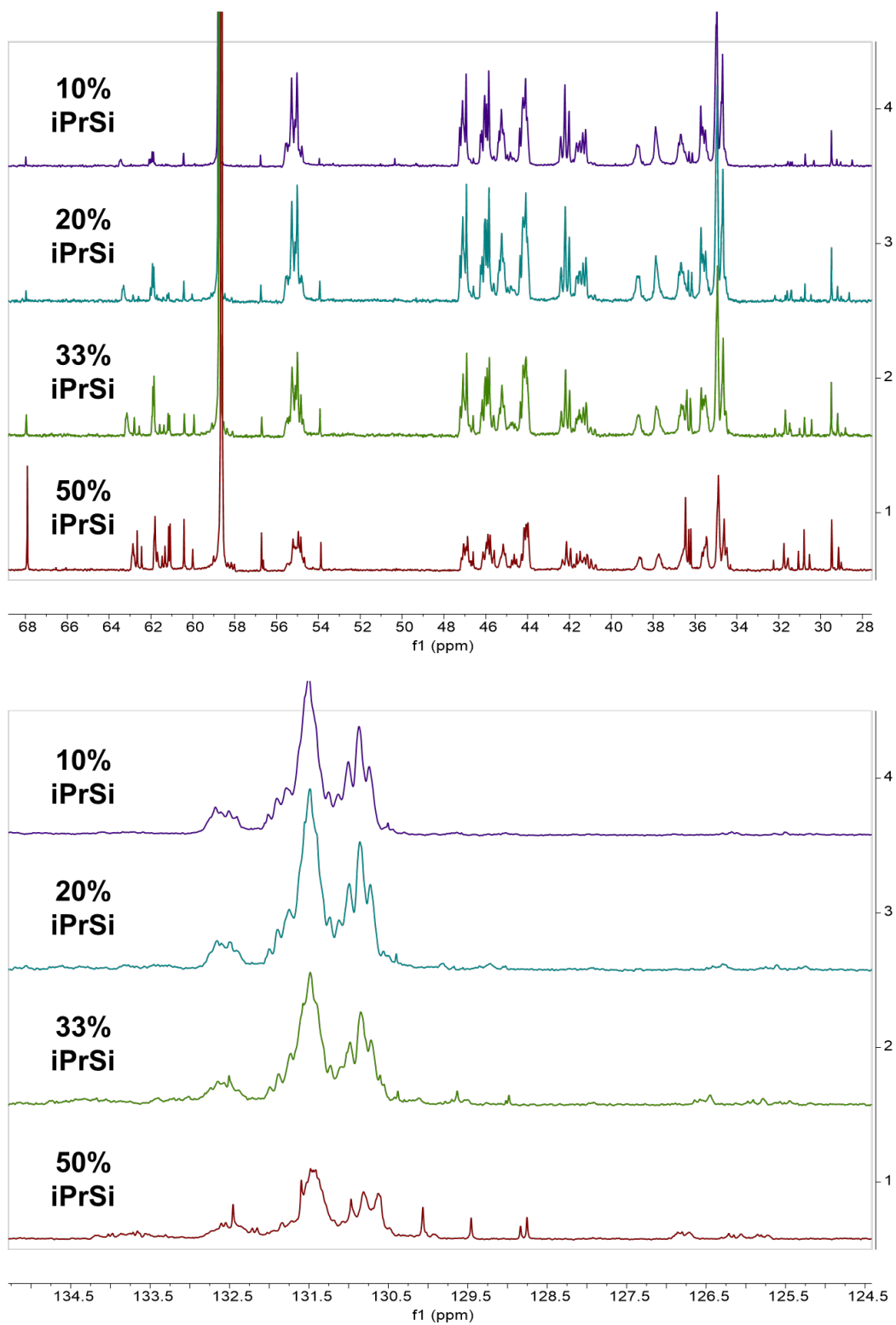


Figure S25. ^{13}C NMR spectra (CDCl_3 ; 125 MHz) of pDCPD fragments with different amounts of iPrSi doping.

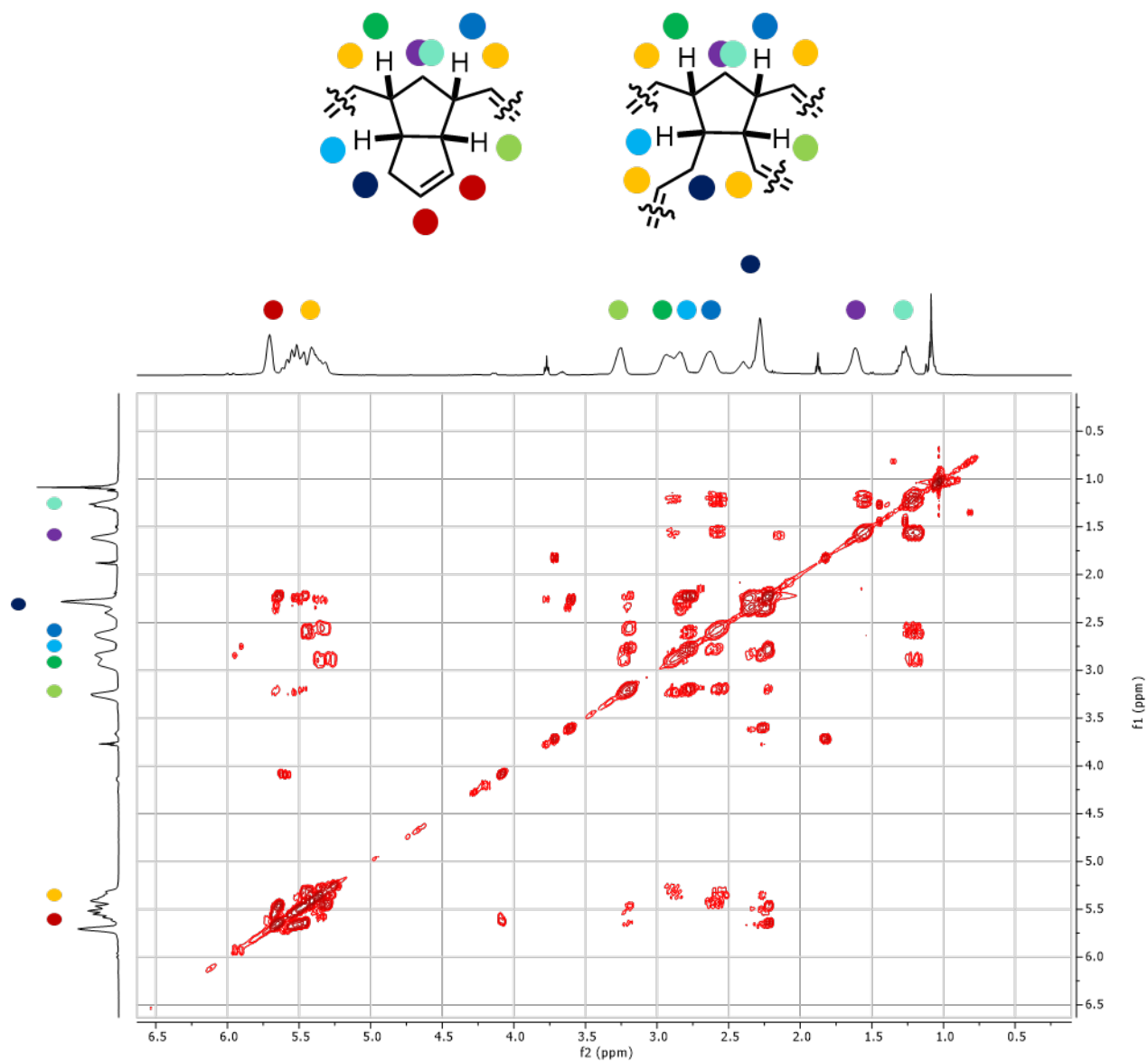


Figure S26. Solution-phase COSY spectrum (CDCl₃; 500 MHz) of the degradation solution derived from 10% **iPrSi** doped pDCPD.

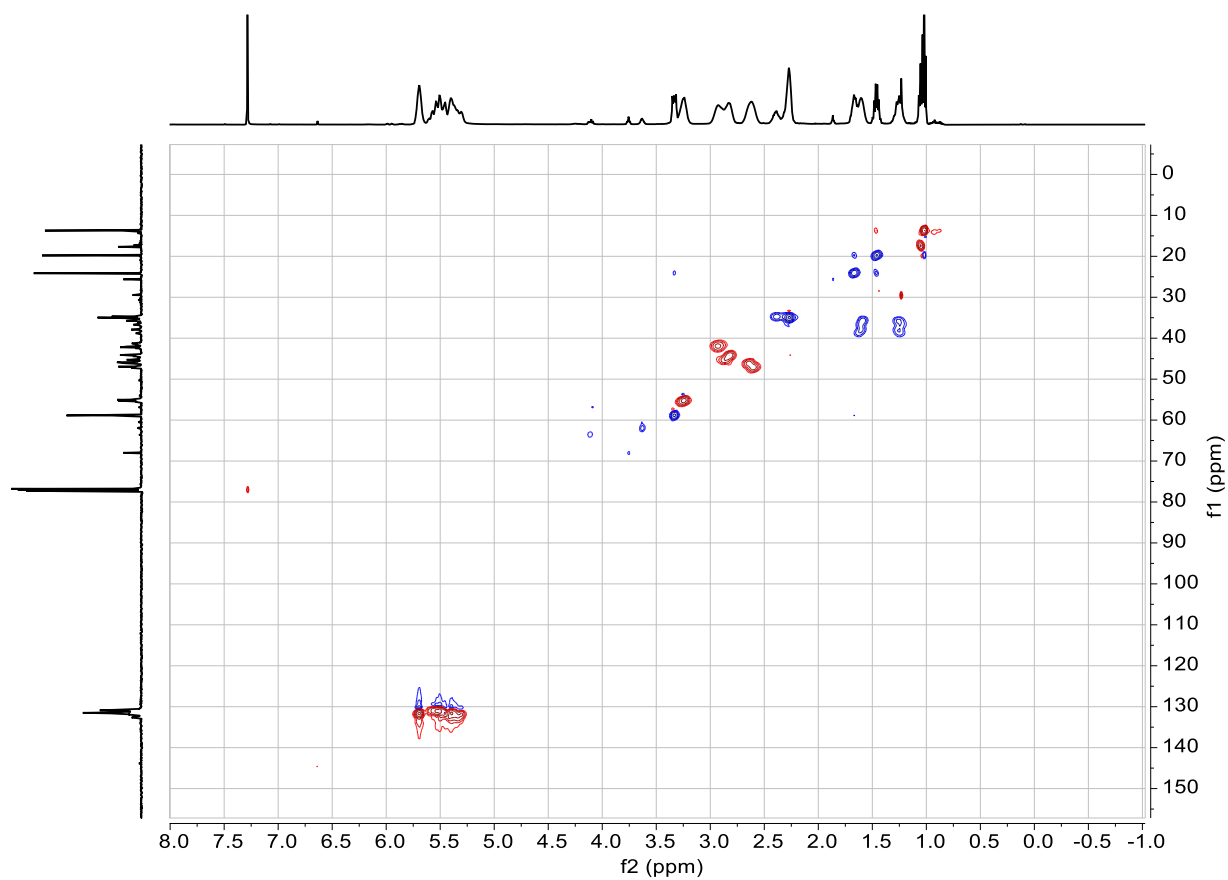


Figure S27. Solution-phase HSQC spectrum (CDCl_3 ; 500 MHz) of the degradation solution derived from 10% **iPrSi** doped pDCPD.

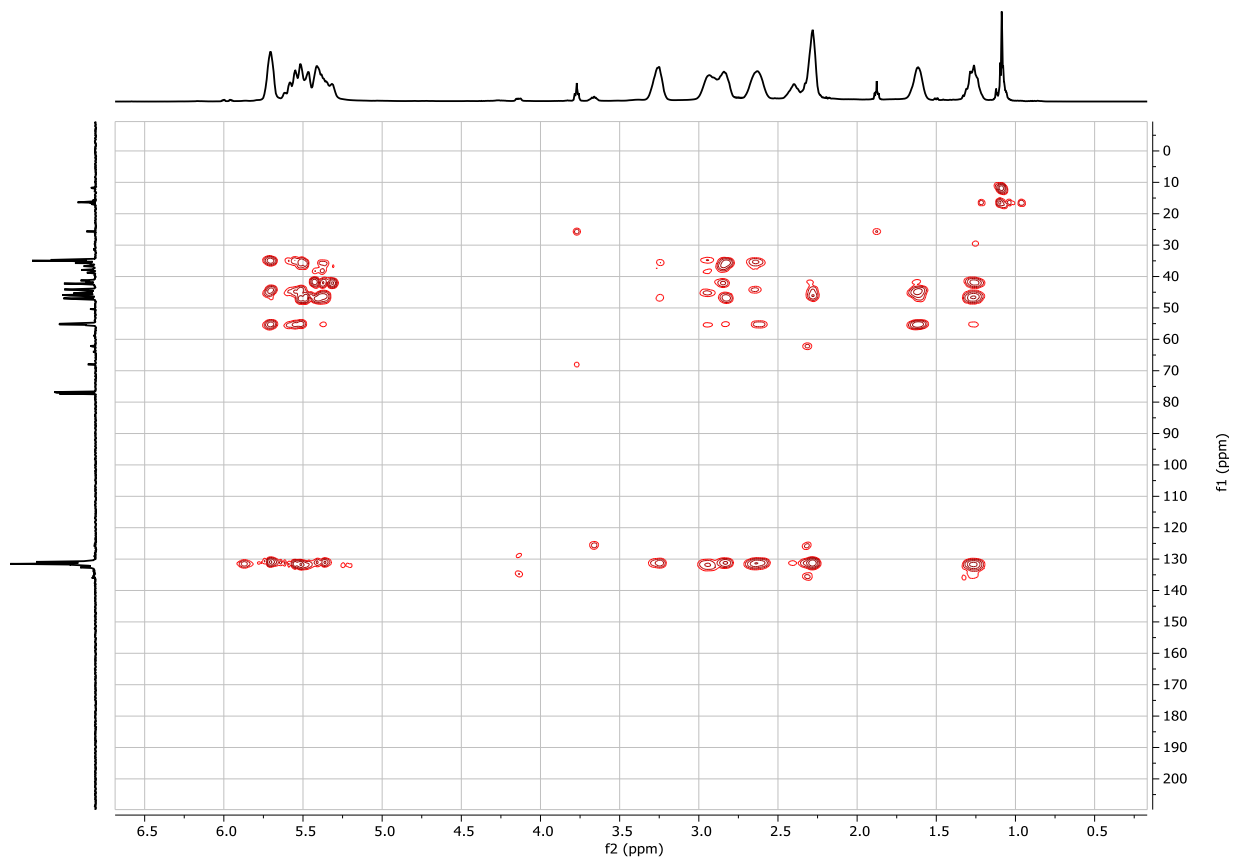


Figure S28. Solution-phase HMBC spectrum (CDCl_3 ; 500 MHz) of the degradation solution derived from 10% **iPrSi** doped pDCPD.

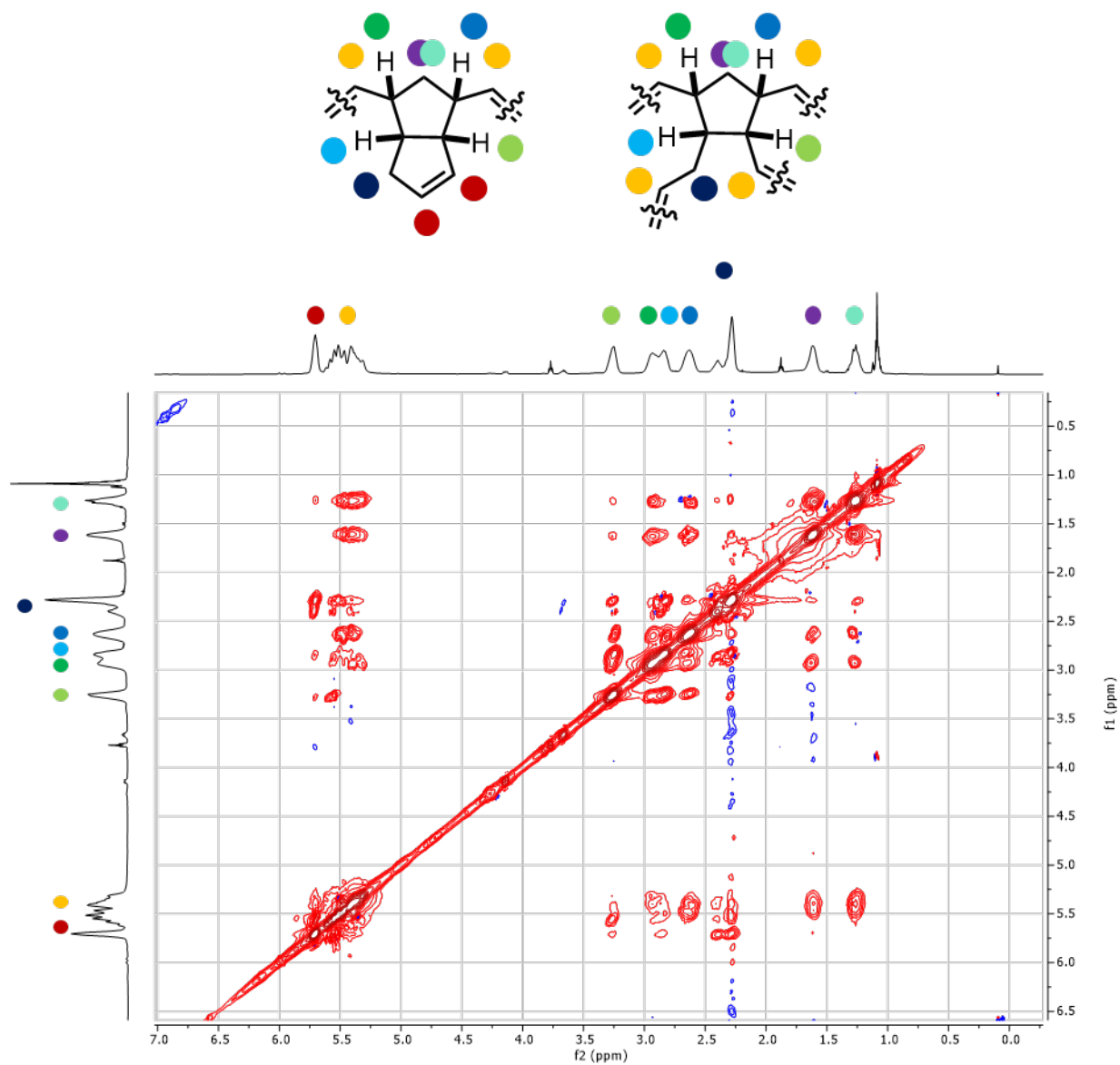


Figure S29. Solution-phase NOESY spectrum (CDCl_3 ; 500 MHz) of the degradation solution from 10% iPrSi-doped pDCPD.

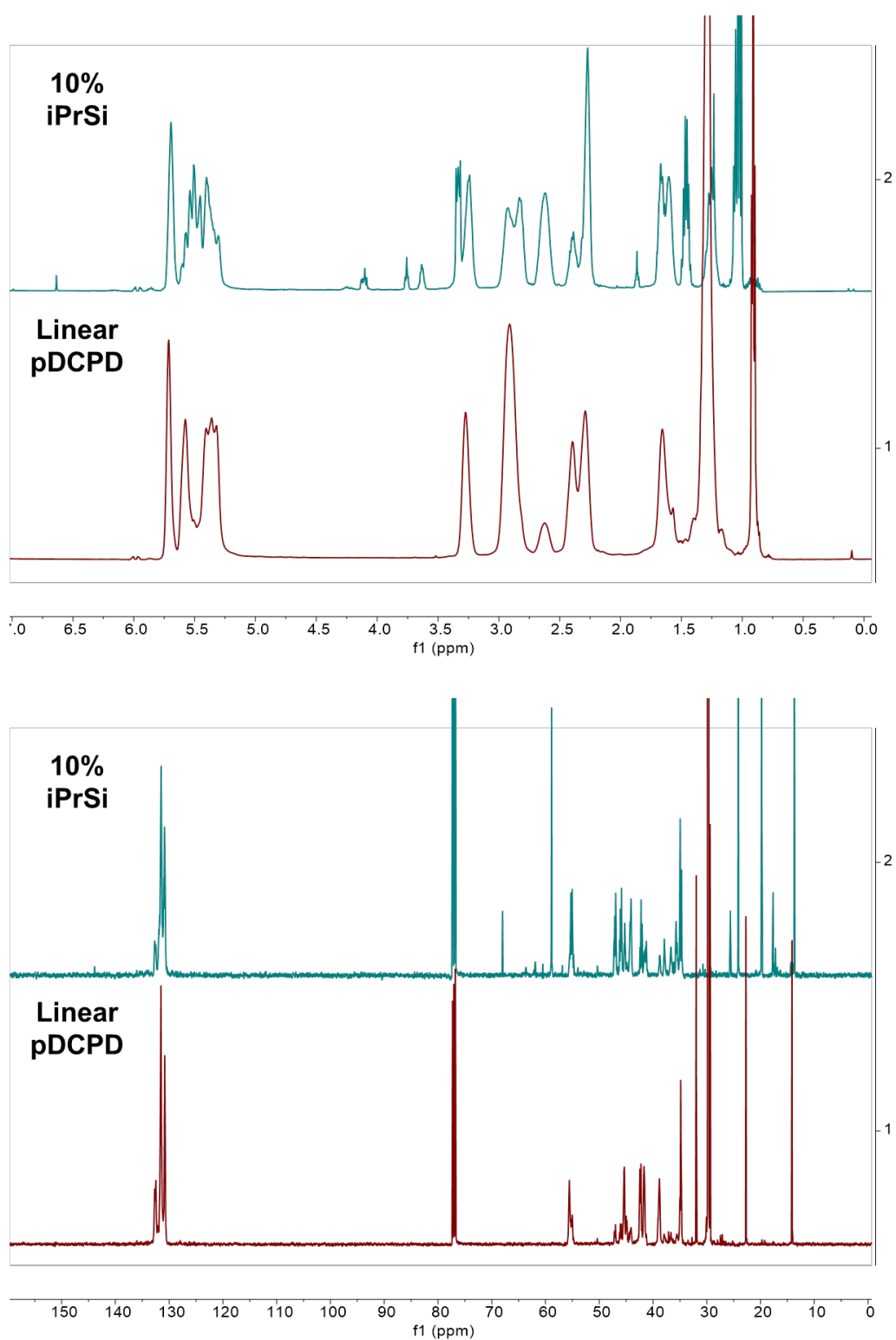


Figure S30. Comparison of ¹H NMR spectra (CDCl₃; 500 MHz/125 MHz) from our pDCPD fragments and independently synthesized linear pDCPD. Linear pDCPD was synthesized through the polymerization of DCPD with Schrock's Mo-catalyst (XiMo).

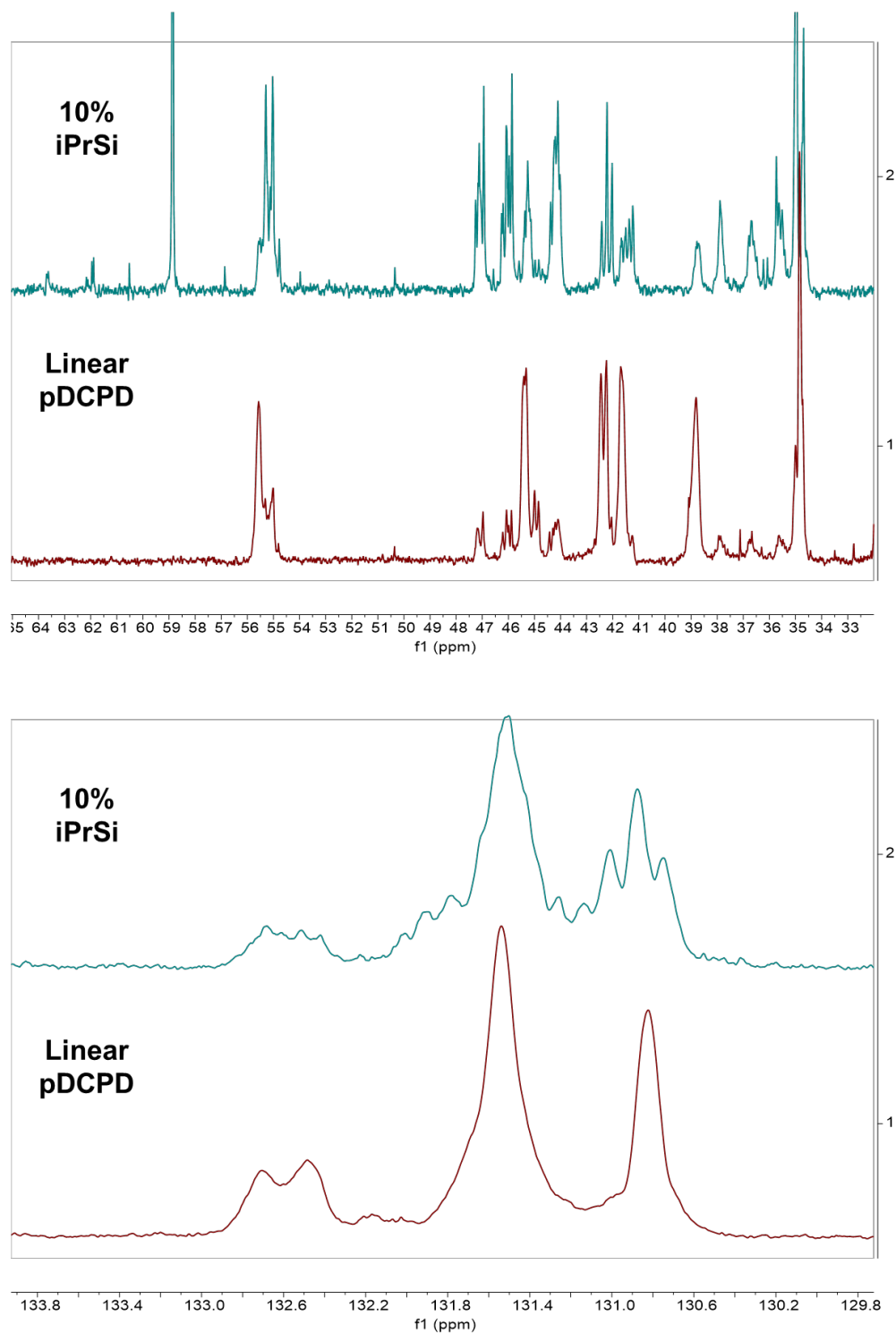


Figure S31. ^{13}C spectra comparing our pDCPD fragments to linear pDCPD (CDCl_3 ; 125 MHz). ^{13}C spectra, zoomed into the olefinic region, to highlight differences between pDCPD fragments and linear pDCPD. We assign some of the differences in the olefinic region to pDCPD crosslinks.

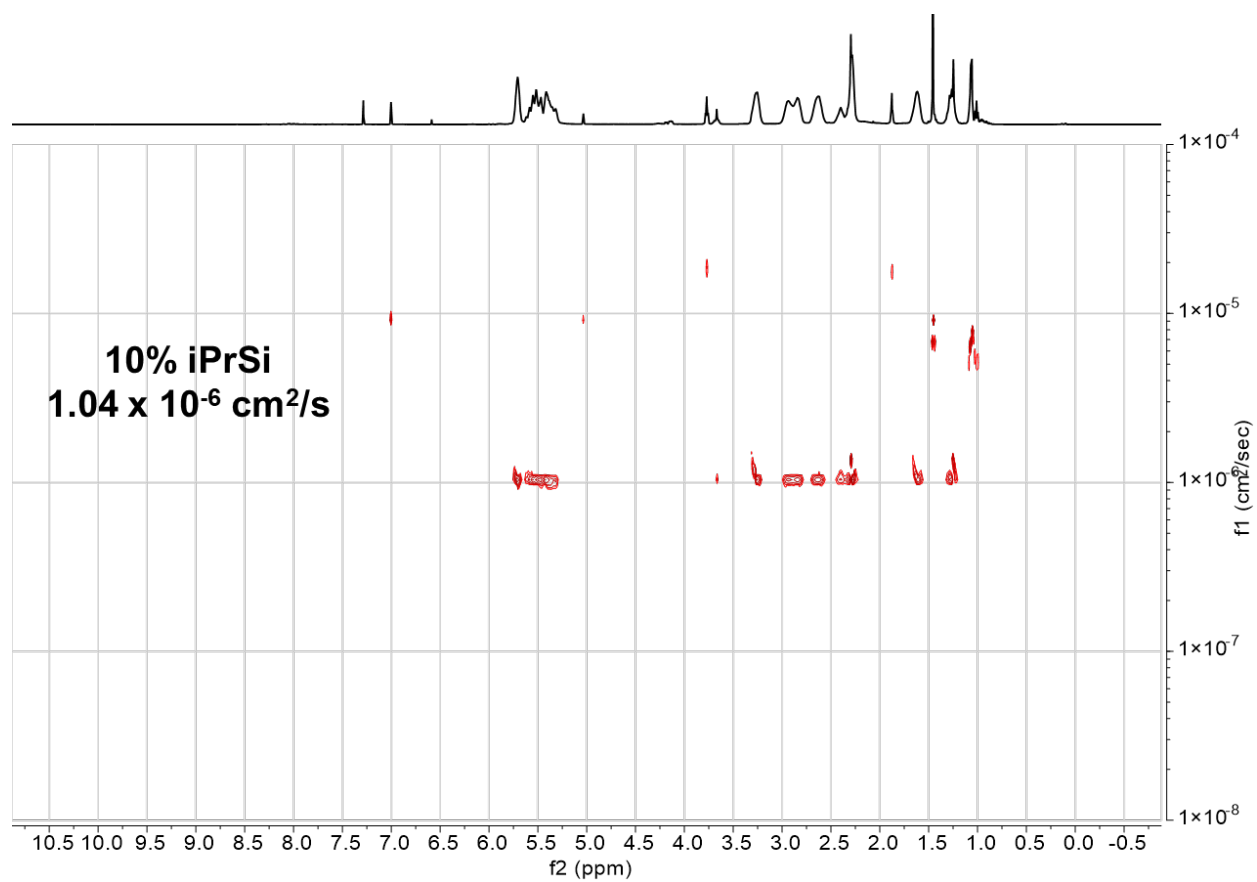


Figure S32. DOSY spectrum (CDCl_3 ; 500 MHz) of the degradation solution from pDCPD doped with 10% iPrSi.

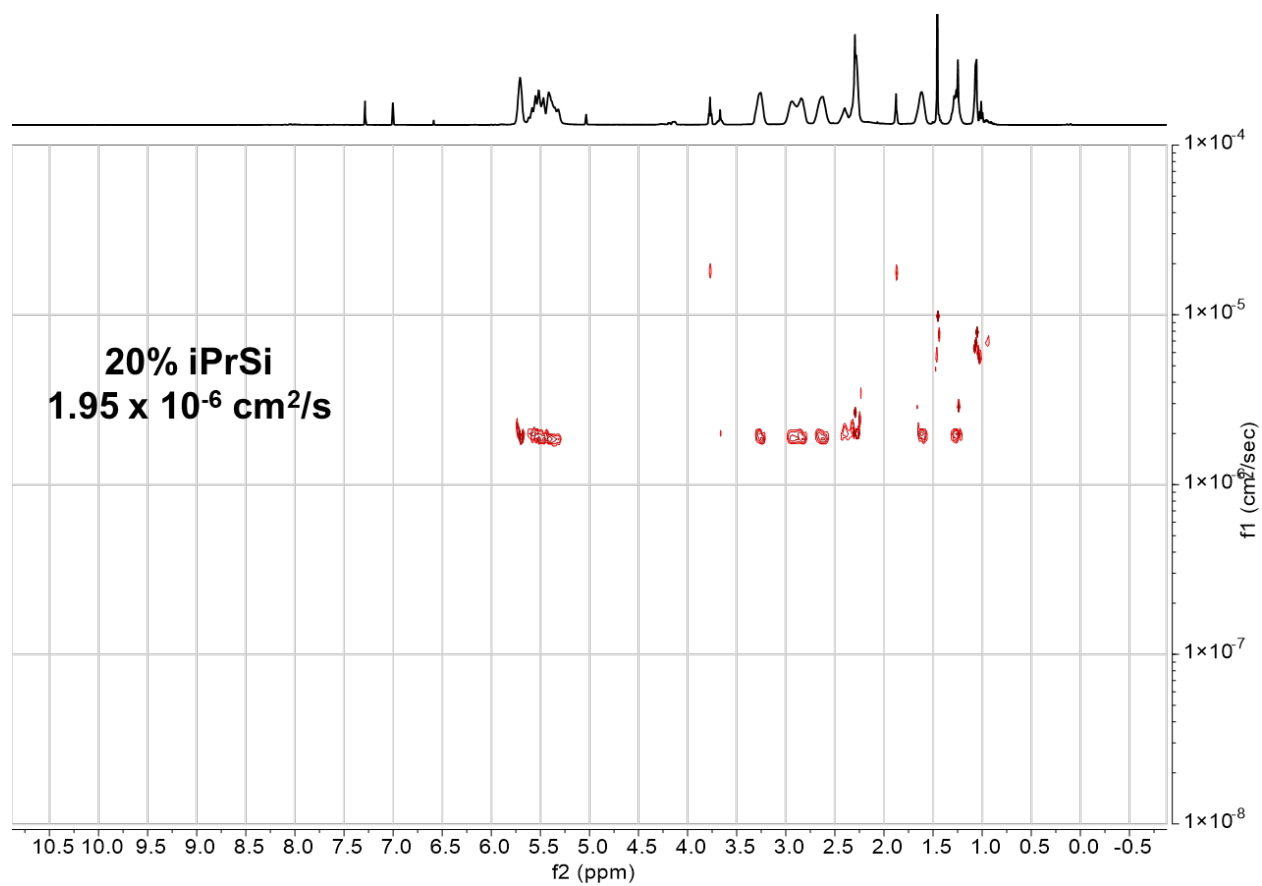


Figure S33. DOSY spectrum (CDCl_3 ; 500 MHz) of the degradation solution from pDCPD doped with 20% iPrSi.

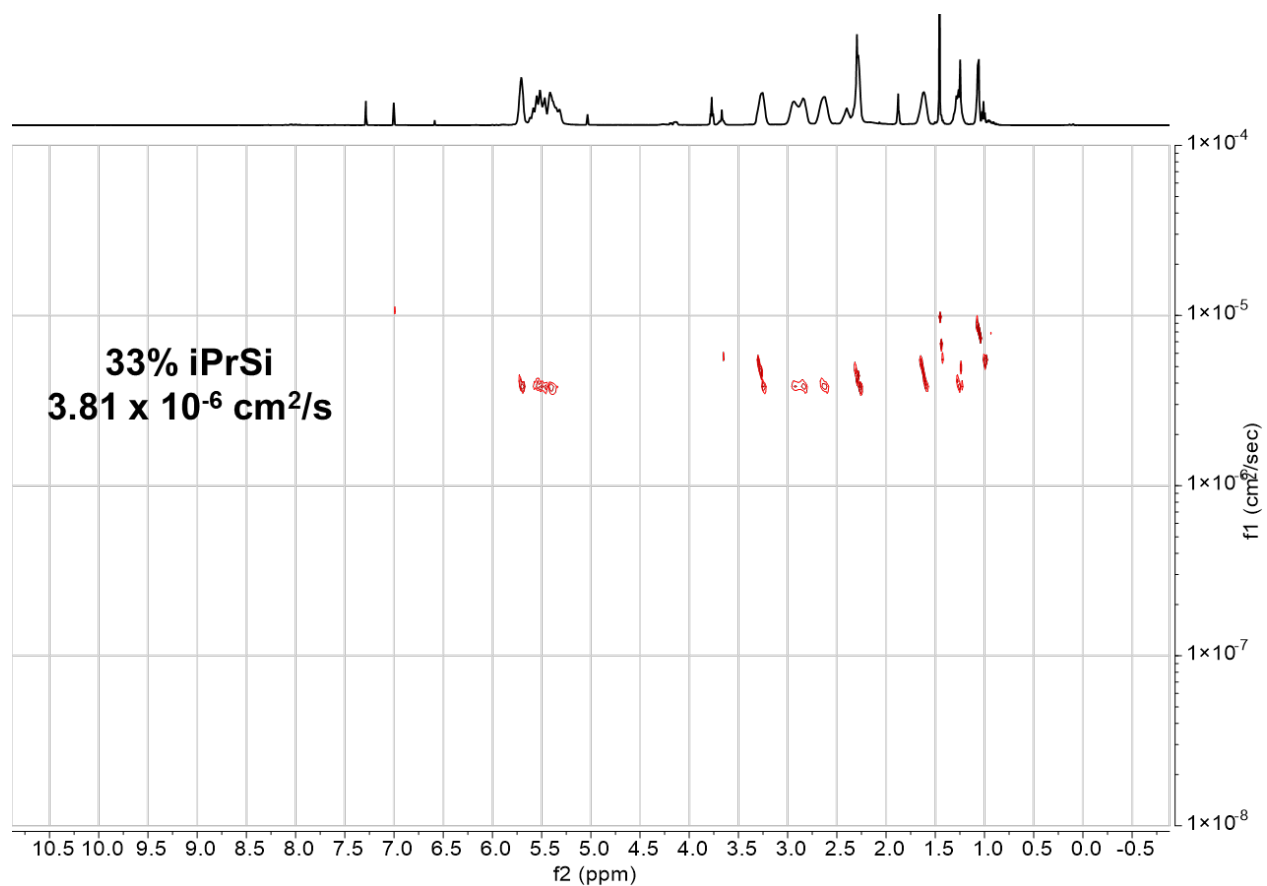


Figure S34. DOSY spectrum (CDCl_3 ; 500 MHz) of the degradation solution from pDCPD doped with 33% iPrSi.

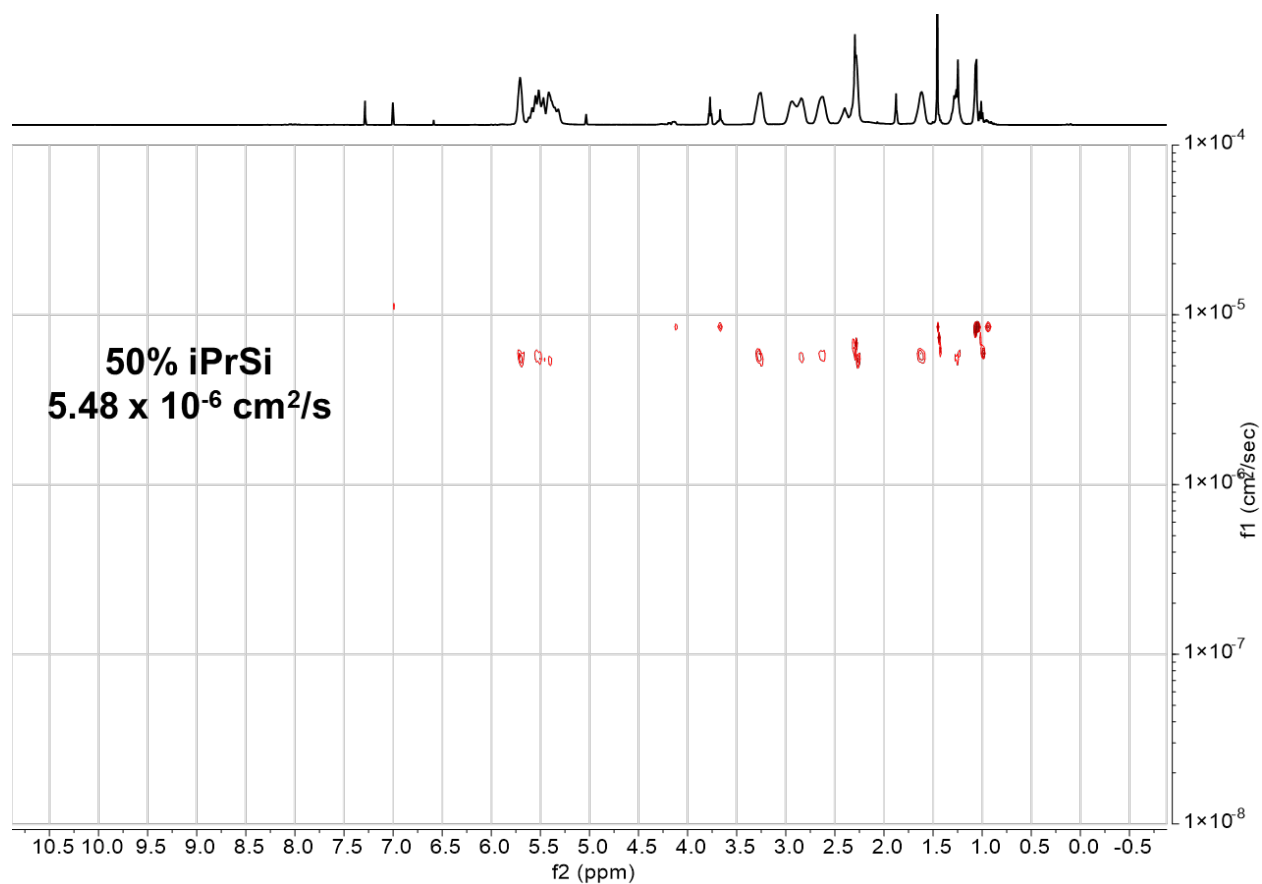


Figure S35. DOSY spectrum (CDCl_3 ; 500 MHz) of the degradation solution from pDCPD doped with 50% iPrSi.

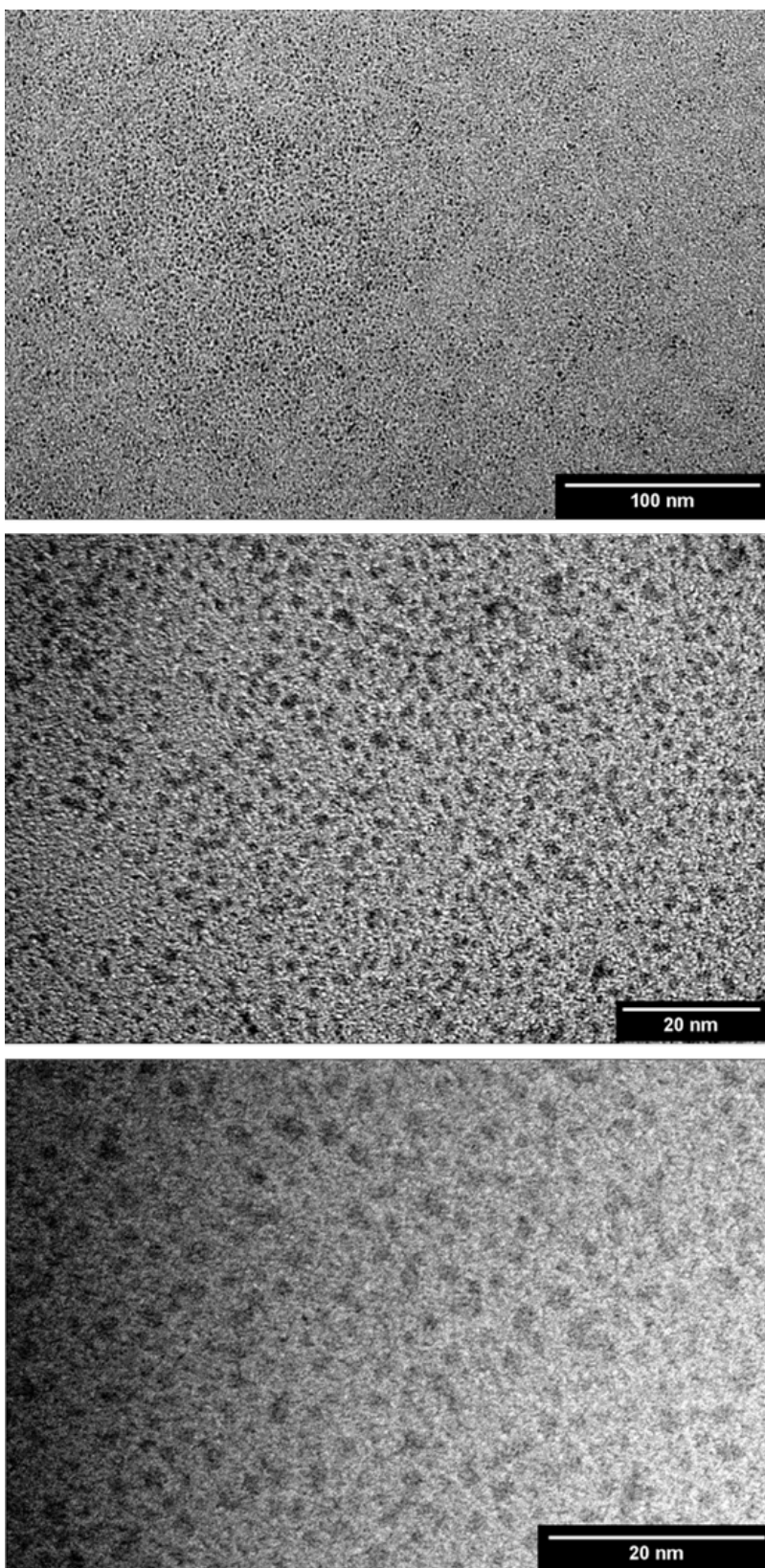


Figure S36. Additional TEM images of fragments derived from 10% **iPrSi**-doped pDCPD.

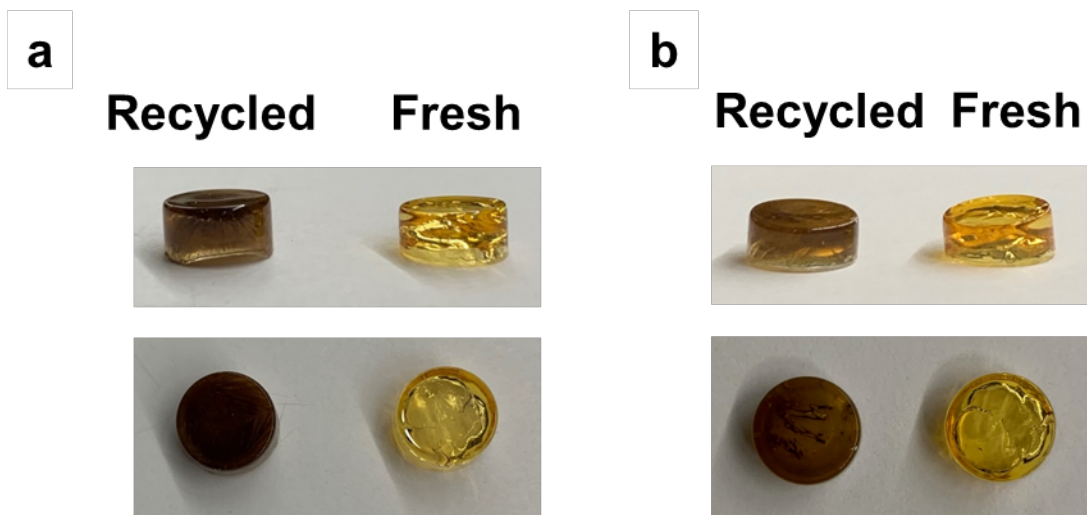


Figure S37. Images of recycled pDCPD (containing 25% w/w pDCPD fragments) and fresh pDCPD samples. **a.** Samples prepared using fragments from the TBAF dissolution method. **b.** Samples prepared using fragments from the HF-pyridine dissolution method.

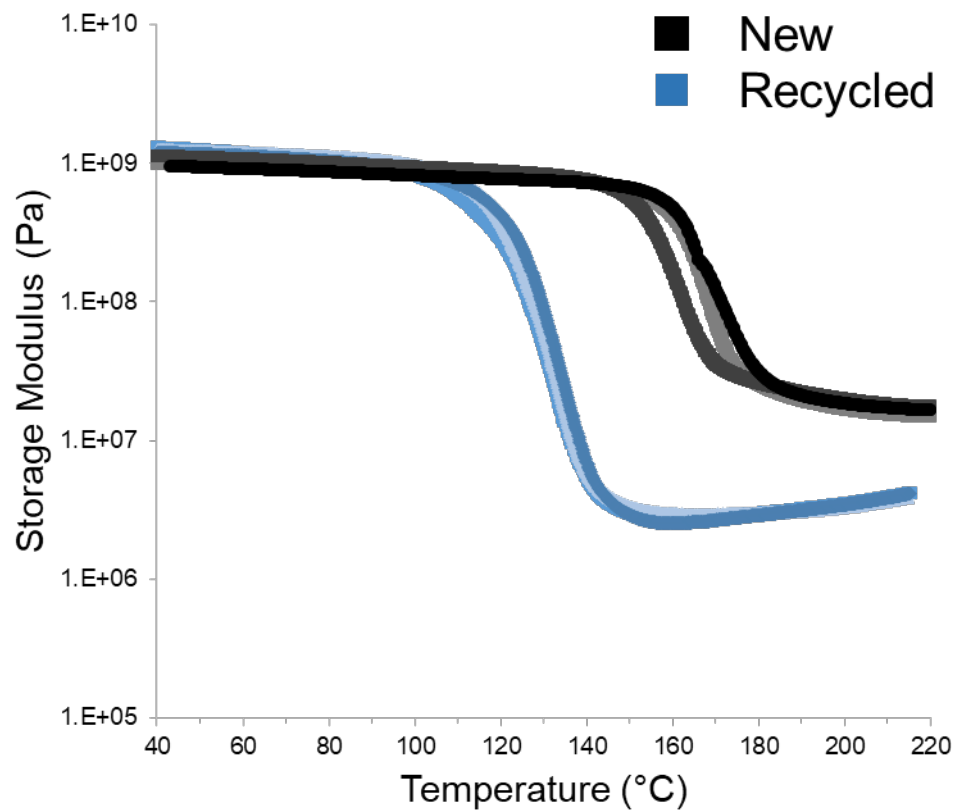


Figure S38. DMA traces of recycled pDCPD (containing 25% pDCPD fragments).

Table 1. Feedstock prices for economic analysis (July 2019)

<i>Starting Material</i>	<i>Price (\$/kg)</i>	<i>Citation/Source</i>
<i>Propylene</i>	1.00	Dang, T.; <i>Olefins - Propylene</i> ; Americas Chemicals Outlook 2017; ICIS. Ng, J.; <i>Olefins – Propylene</i> ; Asia Chemicals Outlook 2019; ICIS.
<i>Hydrogen Chloride</i>	0.50	Bowen, B.; US hydrochloric acid prices jump higher on outages, ICIS June 8, 2017. https://www.icis.com/explore/resources/news/2017/06/08/10114252/us-hydrochloric-acid-prices-jump-higher-on-outages/ (accessed Aug 30, 2019).
<i>Silicon Metal</i>	2.65	Garside, M.; Average silicon prices in the US by type 2014-2018, Statista March 25, 2019. https://www.statista.com/statistics/301564/us-silicon-price-by-type/ (accessed Aug 30, 2019).
<i>Formaldehyde</i>	1.08	Global Chemical Price. Formaldehyde Weekly Report Jan 2017. http://www.globalchemicalprice.com/chemical-market-reports/formaldehyde-weekly-report-7-jan-2017 . (accessed Sep 5, 2019).

Table 2. LIPIT Data for 0% iPrSi-doped pDCPD.

Impact Velocity m/s	Uncertainty	Post- Impact Velocity m/s	Uncertainty	Coefficient of Restitution	Uncertainty	Particle Diameter (μm)	Film Thickness (μm)
718	14.36	0	0	0	0	13.2	21.75
820	16.4	154	3.08	0.187805	0.005312	12.5	22.5
675	13.5	0	0	0	0	12.5	23.25
895	17.9	310	6.2	0.346369	0.009797	12.2	23.25
851	17.02	342	6.84	0.40188	0.011367	12.7	22.75
949	18.98	512	10.24	0.539515	0.01526	12.2	22.75
841	16.82	291	5.82	0.346017	0.009787	12.9	22.5
606	12.12	0	0	0	0	12.3	21
910	18.2	530	10.6	0.582418	0.016473	12.7	22.5
855	17.1	322	6.44	0.376608	0.010652	11.8	24.75
691	13.82	0	0	0	0	12.7	24
593	11.86	0	0	0	0	12.9	24
155	3.1	-61	-1.22	-0.39355	-0.01113	12.8	25.5
488	9.76	-38	-0.76	-0.07787	-0.0022	13.2	27
572	11.44	0	0	0	0	13.2	24.75
567	11.34	0	0	0	0	13.1	24.75
376	7.52	-51.7	-1.034	-0.1375	-0.00389	13.2	24.75
328	6.56	-63	-1.26	-0.19207	-0.00543	13.6	24.75
430	8.6	0	0	0	0	13.9	21
255	5.1	-79	-1.58	-0.3098	-0.00876	13.4	23.25
261	5.22	-67	-1.34	-0.2567	-0.00726	13.2	24.75
300	6	-81	-1.62	-0.27	-0.00764	12.5	24.75
395	7.9	-56	-1.12	-0.14177	-0.00401	13.3	23.25
307	6.14	-73	-1.46	-0.23779	-0.00673	12.9	23.25
443	8.86	-70	-1.4	-0.15801	-0.00447	12.5	23.25
469	9.38	-37	-0.74	-0.07889	-0.00223	12.8	23.25

Table 3. LIPIT Data for 10% iPrSi-doped pDCPD.

Impact Velocity m/s	Uncertainty	Post-Impact Velocity m/s	Uncertainty	Coefficient of Restitution	Uncertainty	Particle Diameter (μm)	Film Thickness (μm)
656	13.12	0	0	0	0	12.9	20.25
677	13.54	0	0	0	0	12.2	22.5
149	2.98	-61	-1.22	0.409396	0.011579	12.5	23.5
235	4.7	-75	-1.5	0.319149	0.009027	12.9	23.5
243	4.86	-77	-1.54	0.316872	0.008963	12.5	23.5
364	7.28	-78	-1.56	0.214286	0.006061	11.8	24.05
507	10.14	0	0	0	0	12.9	24.05
537	10.74	0	0	0	0	12.9	24.05
433	8.66	0	0	0	0	12.9	24
427	8.54	-58	-1.16	0.135831	0.003842	12.5	23.5
344	6.88	-75	-1.5	0.218023	0.006167	12.6	24.5
289	5.78	-77	-1.54	0.266436	0.007536	12.4	25.5
879	17.58	367	7.34	-0.41752	-0.01181	12.2	18
936	18.72	492	9.84	-0.52564	-0.01487	13.0	21
936	18.72	504	10.08	-0.53846	-0.01523	13.1	21
898	17.96	461	9.22	-0.51336	-0.01452	12.9	21
880	17.6	422	8.44	-0.47955	-0.01356	12.5	21
718	14.36	42	0.84	-0.0585	-0.00165	12.7	21
726	14.52	0	0	0	0	12.9	21
725	14.5	0	0	0	0	12.2	22
570	11.4	0	0	0	0	12.7	21
829	16.58	375	7.5	-0.45235	-0.01279	13.3	21
739	14.78	219	4.38	-0.29635	-0.00838	13.2	21
781	15.62	266	5.32	-0.34059	-0.00963	12.3	24
661	13.22	0	0	0	0	13.1	24
615	12.3	0	0	0	0	13.0	24

Table 4. Statistical analysis of weathering experiments.

<i>Comparative group</i>	<i>Test</i>	<i>n</i>	<i>P value (0.05 significance level)</i>
<i>Light 0% vs 10% iPrSi</i>	Two sample t-Test	3	7.4×10^{-4}
<i>Light 0% vs 20% iPrSi</i>	Two sample t-Test	3	0.001
<i>Light 10% vs 20% iPrSi</i>	Two sample t-Test	3	0.005
<i>Light 10% EtSi vs 10% iPrSi</i>	Two sample t-Test	3	0.001
<i>Dark 0% vs 10% iPrSi</i>	Two sample t-Test	3	0.02
<i>Dark 0% vs 20% iPrSi</i>	Two sample t-Test	3	0.001
<i>Dark 10% vs 20% iPrSi</i>	Two sample t-Test	3	0.06
<i>Dark 10% EtSi vs 10% iPrSi</i>	Two sample t-Test	3	0.26
<i>Light vs Dark</i>	Two sample t-Test	12	2.9×10^{-7}
<i>0% iPrSi Light vs Dark</i>	Two sample t-Test	3	2.9×10^{-4}
<i>10% iPrSi Light vs Dark</i>	Two sample t-Test	3	1.4×10^{-4}
<i>20% iPrSi Light vs Dark</i>	Two sample t-Test	3	4.3×10^{-4}
<i>10% EtSi Light vs Dark</i>	Two sample t-Test	3	2.6×10^{-5}

Table 5. Mass of carbon released into seawater matrix during 16 days of UV light exposure.

<i>Doped pDCPD</i>	<i>Light</i>		<i>Dark</i>	
	g C released / g C in polymer	Standard deviation	g C released / g C in polymer	Standard deviation
0% <i>iPrSi</i>	0.0033	0.0003	0.0005	0.0002
10% <i>iPrSi</i>	0.0052	0.0001	0.0015	0.0003
20% <i>iPrSi</i>	0.0081	0.0007	0.0023	0.0002
10% <i>EtSi</i>	0.0073	0.0003	0.0019	0.0002

Seawater matrix blank has an organic carbon content of 0.73 +/- 0.06 mg/L and was subtracted when presenting the dissolved carbon in sample incubated with pDCPD pellets. All samples were measured in triplicate.

Table 6. Calculated Fragment Molecular Weights from GPC-MALS

Sample	M_w	M_n	M_w/M_n
10% iPrSi	7.70 x 10 ³	3.41 x 10 ³	2.26
20% iPrSi	5.72 x 10 ³	2.13 x 10 ³	2.69
33% iPrSi	3.19 x 10 ³	1.95 x 10 ³	1.63
50% iPrSi	1.91 x 10 ³	1.38 x 10 ³	1.38