

Water Resistant Boronic Ester Vitrimer with Hydrophobic Side Chain Protection

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Materials. 2,3-dihydroxypropyl acrylate (90.0 %, BOC Sciences, USA), 2,2,2-trifluoroethyl acrylate (>98.0 %, TCI), tetrahydrofuran (\geq 99.9 %, Aldrich, USA), 1,4-dioxane (>99.0 %, TCI), ethyl acrylate (>99.0 %, TCI), 2,2'-azobis(isobutyronitrile) (>98.0 %, TCI), and 1,4-phenylenediboronic acid (>98.0 %, TCI) were used as received without any further purification.

Characterization. ^1H nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform (CDCl_3 , 99.9% D, Cambridge Isotope Laboratories, USA) and dimethyl sulfoxide (DMSO-d_6 , 99.9% D, Cambridge Isotope Laboratories, USA) on a JEOL 500MHz spectrometer. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on Perkin Elmer Spectrum 2000 FT-IR Spectrometer. Analytical Gel Permeation Chromatography (GPC). GPC analysis using THF as an eluent was performed on an Agilent 1260 Infinity II equipped with a refractive index detector. The flow rate was 1.0 mL/min. Thermogravimetric analysis (TGA) was done via TA Instruments Q500. Approximately 5 mg of sample was placed in ceramic pan and heated from 35 to 100 °C, isothermal for 10 mins and heated to 600 °C with a ramp rate of 20 °C / min in nitrogen at a flow rate of 60 mL / min. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 calorimeter. Approximately 5 mg of sample was placed in an aluminium hermetic pan. The sample was first scan from -40 to 80 °C, isothermal for 10 min, followed by cooling to -40 °C to erase any thermal history, then heated to 80 °C. The heating and cooling rate were set at 10 °C / min under a nitrogen flow of 50 mL / min. Dynamic Mechanical Analysis (DMA) was performed on a TA Instruments Q800. The samples ($15 \times 5 \times 0.5 \text{ mm}^3$) were measured using a tension mode from -40 to 80 °C at a frequency of 1 Hz, amplitude of 15 μm , and a temperature ramp of 3 °C min^{-1} . The storage modulus (E')

and tan delta (δ) were recorded as a function of temperature. Stress relaxation experiments were also performed on the TA Instruments Q800 in “stress relaxation mode”, where a 10 % relaxation strain was applied at temperature of 25, 35, 40, 45, and 50 °C, respectively. Tensile strength analysis was done on a Instron 5569 Table Universal testing machine in accordance with ISO 527, samples were stretched at a crosshead speed of 30 mm min⁻¹ at ambient temperature. The swelling ratio and gel content of FV1 was determined by immersing samples of FV1 ($m_0 \sim 200$ mg) in chloroform, ethyl acetate, diethyl ether, and THF (4 mL) for 72 h, after which the solvent was removed, and the samples were dried with a paper towel and recording its mass (m_1). The samples were then dried in a 60 °C oven for 24 h before recording

its mass again (m_2). Swelling ratio was determined by $\frac{m_1 - m_0}{m_0} \times 100 \%$, while gel content

was determined by $\frac{m_2}{m_0} \times 100 \%$.

Synthesis of 20% poly(2,2,2 trifluoroethyl acrylate/2,3-dihydroxypropyl acrylate) random copolymer (LP1). A mixture of 2,3-dihydroxyethyl acrylate (2.00 g, 13.7 mmol), 2,2,2-trifluoroethyl acrylate (8.44 g, 54.7 mmol) and azobisisobutyronitrile (0.22 g, 1.37 mmol) in anhydrous dioxane (30 mL), was bubbled under constant nitrogen flow for 5 min. The mixture was then stirred at 65 °C for 6 h under nitrogen atmosphere. The solution was then allowed to cool and added dropwise to a mixture of 1:4 diethyl ether:hexane in a plastic beaker under constant stirring. The product was then washed with 1:4 diethyl ether:hexane and redissolved in dioxane and reprecipitation was repeated to obtain pure LP15. (9.60 g, Yield: 92 %). ¹H NMR (500 MHz, 24 °C, CDCl₃,

ppm): δ = 4.58 (brs, 2H, CH_2-CF_3), 4.12 (brs, 2H, CH_2-CHOH), 3.81 (brs, 2H, $CHOH-CH_2$), 3.54 (brs, 2H, $CH_2OH-CHOH$).

Synthesis of cross-linked LP1 (FV1). A solution of LP1 (2 g) and 1,4-phenylenebisboronicacid (0.1516 g, 2:1 C-OH: B-OH ratio) was prepared in THF (15 mL). The mixture was heated to 60 °C and temperature was maintained under constant stirring for 6 h. Temperature was then increased to 80 °C for 10 min to concentrate the solution and poured onto a silicon mold. The silicon mold was placed in a vacuum oven at 80 °C for further drying and curing for 12 h before being hot-pressed at 80 °C and 5 bar for 5 min to form a film of FV1.

Synthesis of 30% poly(2,2,2 trifluoroethyl acrylate/2,3-dihydroxypropyl acrylate) random copolymer (LP2). A mixture of 2,3-dihydroxyethyl acrylate (3.00 g, 20.5 mmol), 2,2,2-trifluoroethyl acrylate (7.38 g, 47.9 mmol) and azobisisobutyronitrile (0.22 g, 1.37 mmol) in anhydrous dioxane (30 mL), was bubbled under constant nitrogen flow for 5 min. The mixture was then stirred at 65 °C for 6 h under nitrogen atmosphere. The solution was then allowed to cool and added dropwise to a mixture of 1:4 diethyl ether:hexane in a plastic beaker under constant stirring. The product was then washed with 1:4 diethyl ether:hexane and redissolved in dioxane and reprecipitation was repeated to obtain pure LP2. (9.03 g, Yield: 87 %). 1H NMR (500 MHz, 24 °C, $CDCl_3$, ppm): δ = 4.57 (brs, 2H, CH_2-CF_3), 4.15 (brs, 2H, CH_2-CHOH), 3.85 (brs, 2H, $CHOH-CH_2$), 3.56 (brs, 2H, $CH_2OH-CHOH$).

Synthesis of cross-linked LP2 (FV2). A solution of LP2 (2 g) and 1,4-phenylenebisboronicacid (0.1093 g, 3:1 C-OH:B-OH ratio) was prepared in THF (15

mL). The mixture was heated to 60 °C and temperature was maintained under constant stirring for 6 h. Temperature was then increased to 80 °C for 10 min to concentrate the solution and poured onto a silicon mold. The silicon mold was placed in a vacuum oven at 80 °C for further drying and curing for 12 h before being hot-pressed at 80 °C and 5 bar for 5 min to form a film of FV2.

Synthesis of 40% poly(2,2,2 trifluoroethyl acrylate/2,3-dihydroxypropyl acrylate) random copolymer (LP3). A mixture of 2,3-dihydroxyethyl acrylate (4.00 g, 27.4 mmol), 2,2,2-trifluoroethyl acrylate (6.33 g, 41.1 mmol) and azobisisobutyronitrile (0.22 g, 1.37 mmol) in anhydrous dioxane (30 mL), was bubbled under constant nitrogen flow for 5 min. The mixture was then stirred at 65 °C for 6 h under nitrogen atmosphere. The solution was then allowed to cool and added dropwise to a mixture of 1:4 diethyl ether:hexane in a plastic beaker under constant stirring. The product was then washed with 1:4 diethyl ether:hexane and redissolved in dioxane and reprecipitation was repeated to obtain pure LP3. (9.19 g, Yield: 89 %). ¹H NMR (500 MHz, 24 °C, CDCl₃, ppm): δ = 4.61 (brs, 2H, CH₂-CF₃), 4.15 (brs, 2H, CH₂-CHOH), 3.86 (brs, 2H, CHOH-CH₂), 3.58 (brs, 2H, CH₂OH-CHOH).

Synthesis of cross-linked LP3 (FV3). A solution of LP3 (2 g) and 1,4-phenylenebisboronicacid (0.1098 g, 4:1 C-OH:B-OH ratio) was prepared in THF (15 mL). The mixture was heated to 60 °C and temperature was maintained under constant stirring for 6 h. Temperature was then increased to 80 °C for 10 min to concentrate the solution and poured onto a silicon mold. The silicon mold was placed

in a vacuum oven at 80 °C for further drying and curing for 12 h before being hot-pressed at 80 °C and 5 bar for 5 min to form a film of FV3.

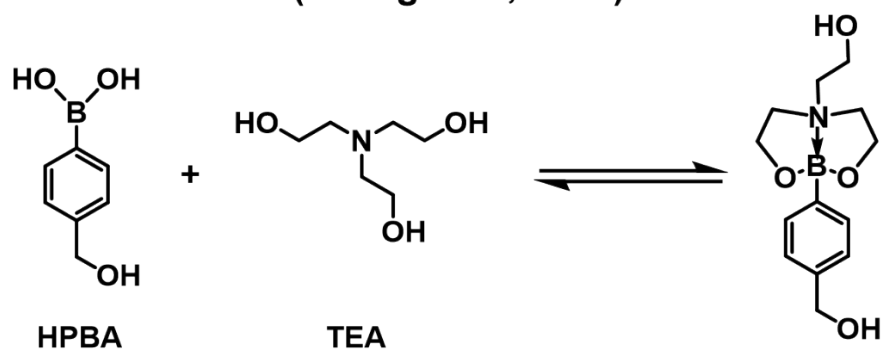
Synthesis of 20% poly(ethyl acrylate/2,3-dihydroxypropyl acrylate) random copolymer (HP1). A mixture of 2,3-dihydroxyethyl acrylate (1.50 g, 15.0 mmol), ethyl acrylate (9.23 g, 59.9 mmol) and azobisisobutyronitrile (0.22 g, 1.37 mmol) in anhydrous dioxane (30 mL), was bubbled under constant nitrogen flow for 5 min. The mixture was then stirred at 65 °C for 6 h under nitrogen atmosphere. The solution was then allowed to cool and added dropwise to a mixture of 1:4 diethyl ether:hexane in a plastic beaker under constant stirring. The product was then washed with 1:4 diethyl ether:hexane and redissolved in dioxane and reprecipitation was repeated to obtain pure HP1. (9.66 g, Yield: 90 %). ¹H NMR (500 MHz, 24 °C, CDCl₃, ppm): δ = 4.13 (brs, 2H, CH₂-CH₃), 4.13 (brs, 2H, CH₂-CHOH), 3.84 (brs, 2H, CHOH-CH₂), 3.58 (brs, 2H, CH₂OH-CHOH), 1.27 (brs, 2H, CH₃-CH₂).

Synthesis of cross-linked HP1 (HV1). A solution of HP1 (2 g) and 1,4-phenylenebisboronicacid (0.0837 g, 1:2 C-OH:B-OH ratio) was prepared in THF (15 mL). The mixture was heated to 60 °C and temperature was maintained under constant stirring for 6 h. Temperature was then increased to 80 °C for 10 min to concentrate the solution and poured onto a silicon mold. The silicon mold was placed in a vacuum oven at 80 °C for further drying and curing for 12 h before being hot-pressed at 80 °C and 5 bar for 5 min to form a film of HV1.

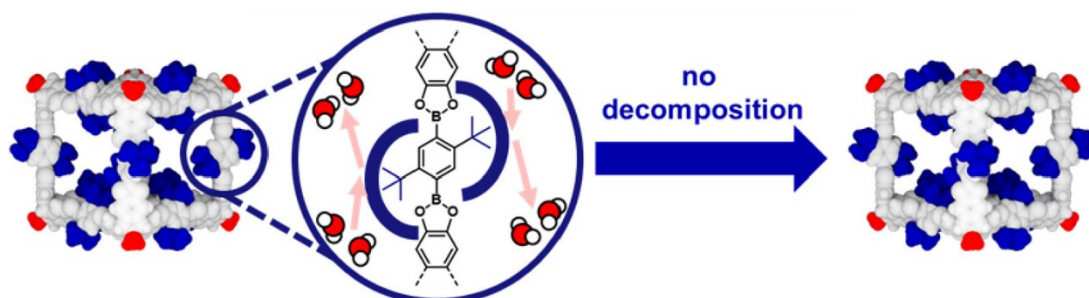
Self-healing of FV1. Self-healing of bulk FV1 was demonstrated by cutting a 2 x 0.5 cm sample of FV1 in half and joint together and left to heal at 25 °C for 2 h before being hand-stretched to test its recovery. Tensile tests were conducted on 1 x 0.5 cm samples of FV1 which were cut in half and joint together in a similar fashion and left to heal at 25 °C for 3 h and 6 h respectively before being analysed by a Instron 5569 Table Universal testing machine.

Mechanical reprocessing and chemical recycling of FV1. Mechanical reprocessing of FV1 was demonstrated by cutting a 2 g sample of FV1 into small pieces and hot-pressed using a Collin hot press at 25 °C and 20 bar for 15 min or 100 °C and 20 bar for 5 min to yield the reformed FV1. Chemical recycling of FV1 was demonstrated by dialysis of a 2 g sample of FV1 in methanol at room temperature for 24 h, with methanol replaced and repeated for 3 cycles to obtain LP1 and 1,4-phenylenediboronic acid. which can be reformed into FV1 by addition of cross-linker 1,4-phenylenebisboronic acid.

a) B-N coordination (Zhang et al, 2020)



b) Steric hindrance at o-position (Kirchner et al, 2024)



c) Hydrophobic protection (This work)

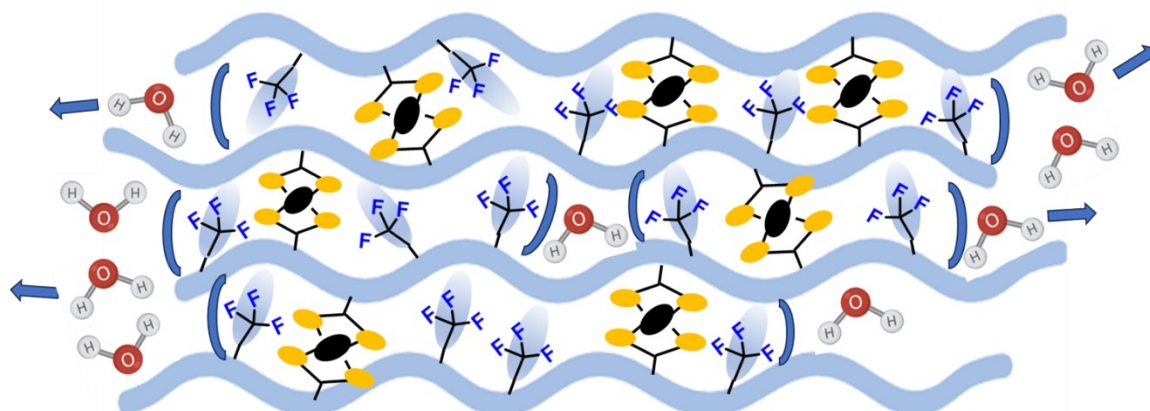


Fig. S1 Previous and this work of improving the hydrolytic stability of boronic esters in polymers (a) Previous work on introducing nitrogen coordination bonds affording enhanced hydrolytic stability¹; (b) Previous work on using ortho-substituted crosslinkers as steric hindrances to protect the boronic ester linkages²; (c) This work on protection afforded by fluorinated side chains of polymer

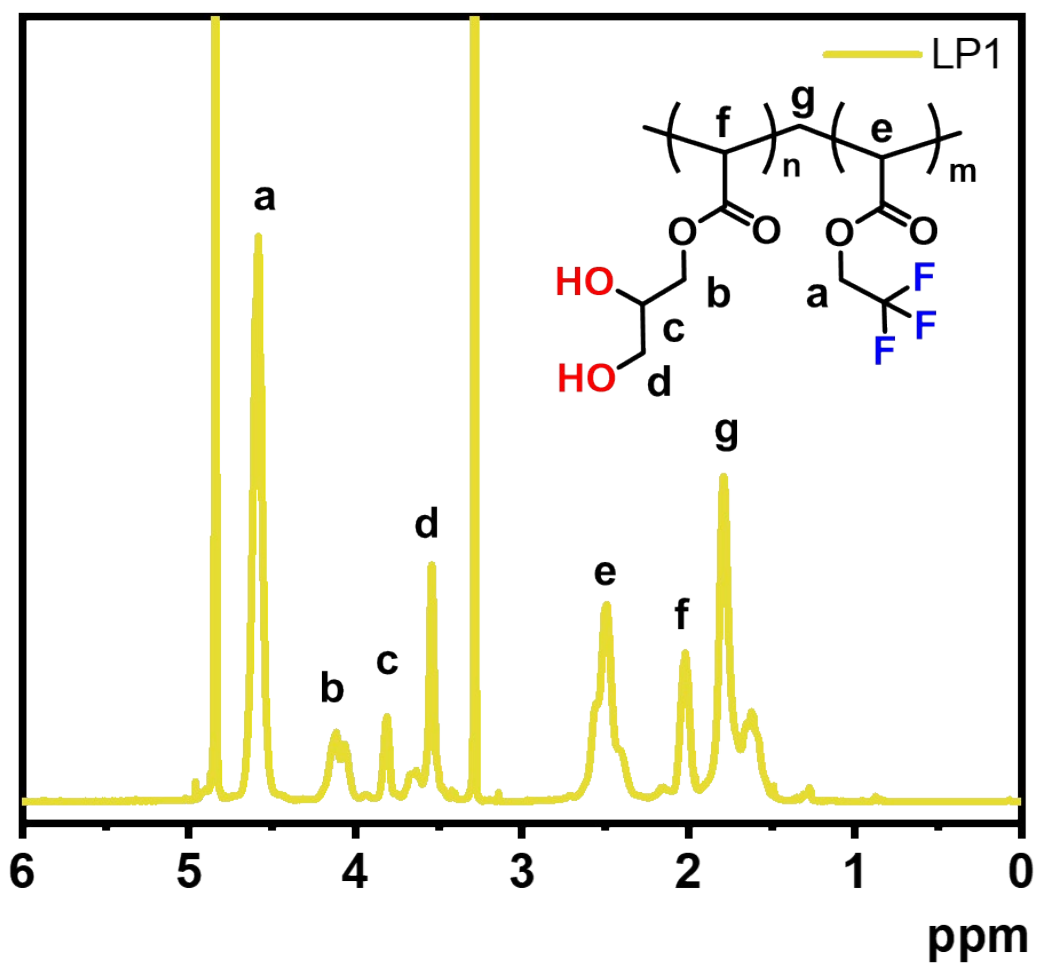


Fig. S2 ¹H NMR spectrum of LP1 in methanol-D₄ with proton signals annotated

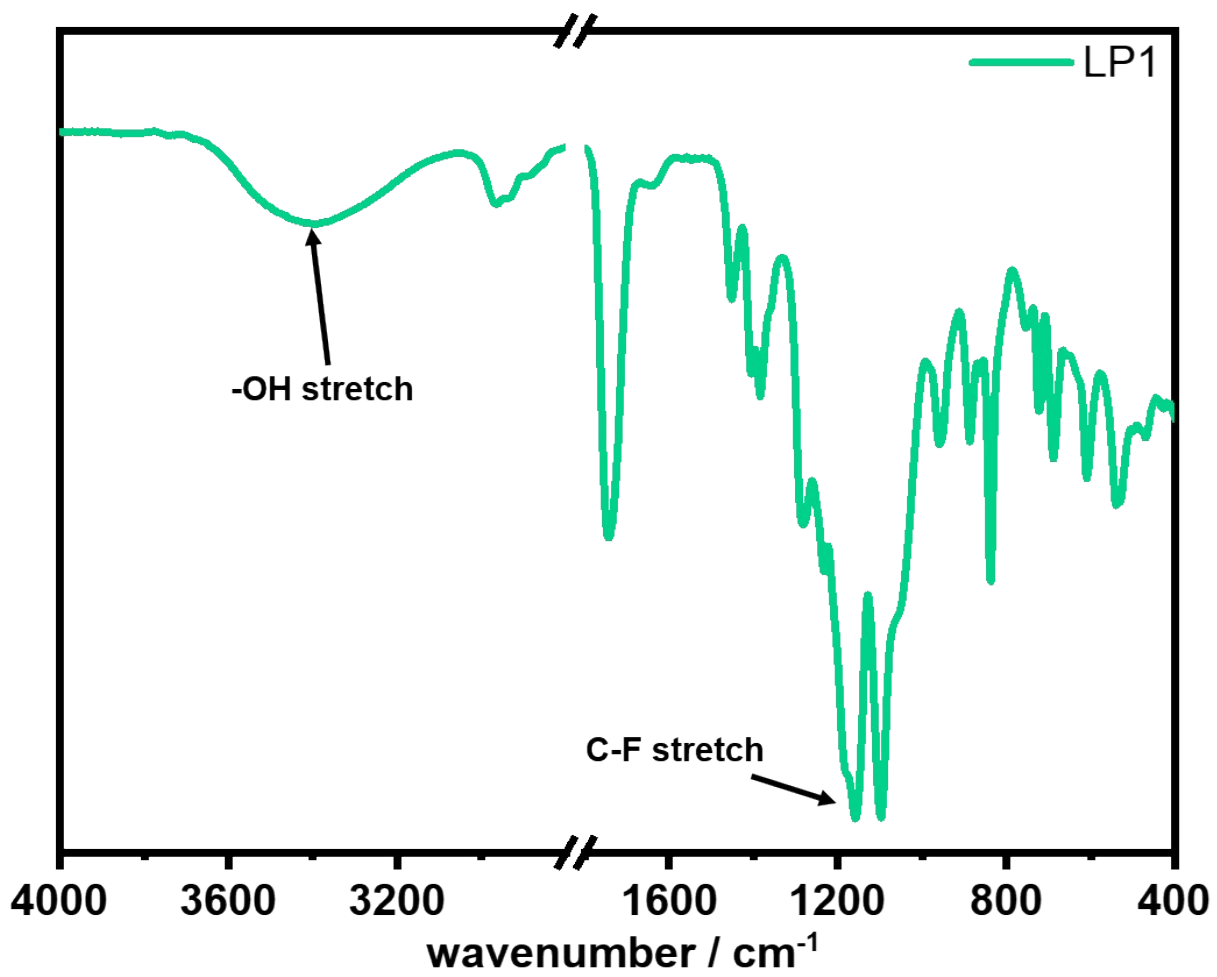


Fig. S3 FTIR spectrum of LP1 with signals annotated

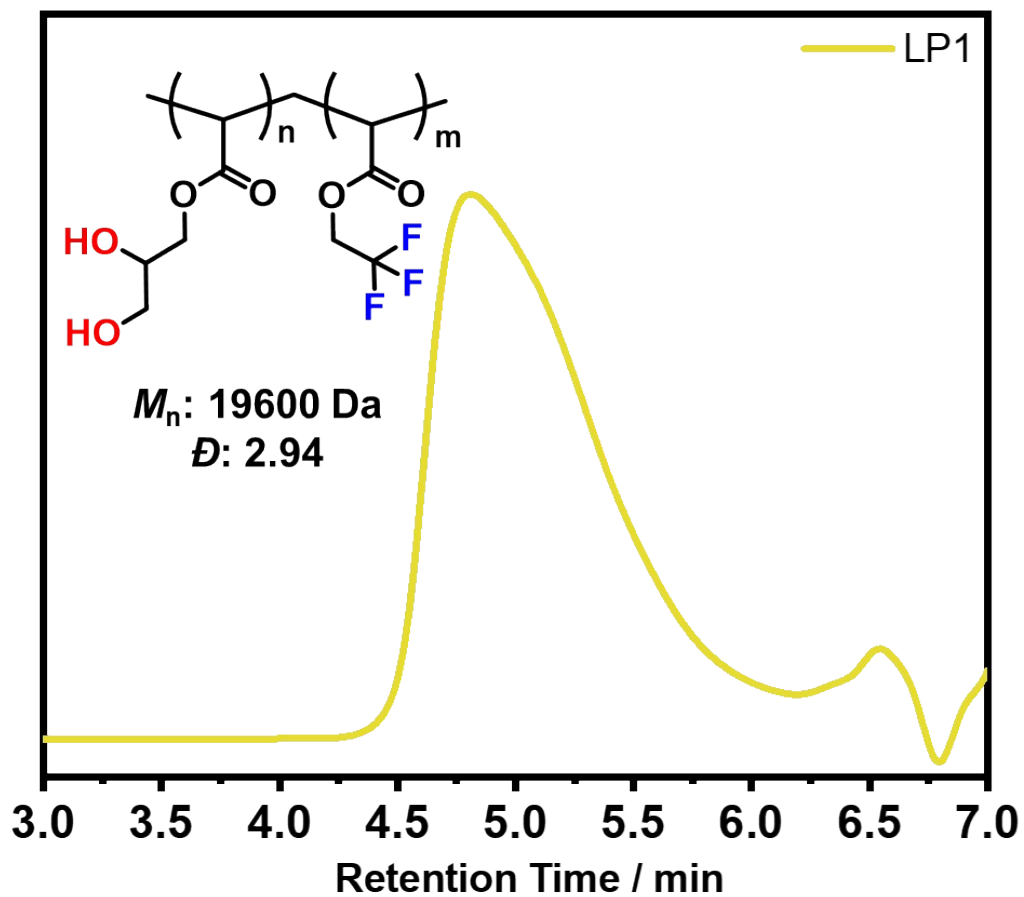


Fig. S4 GPC trace of LP1 with average molecular weight and polydispersity

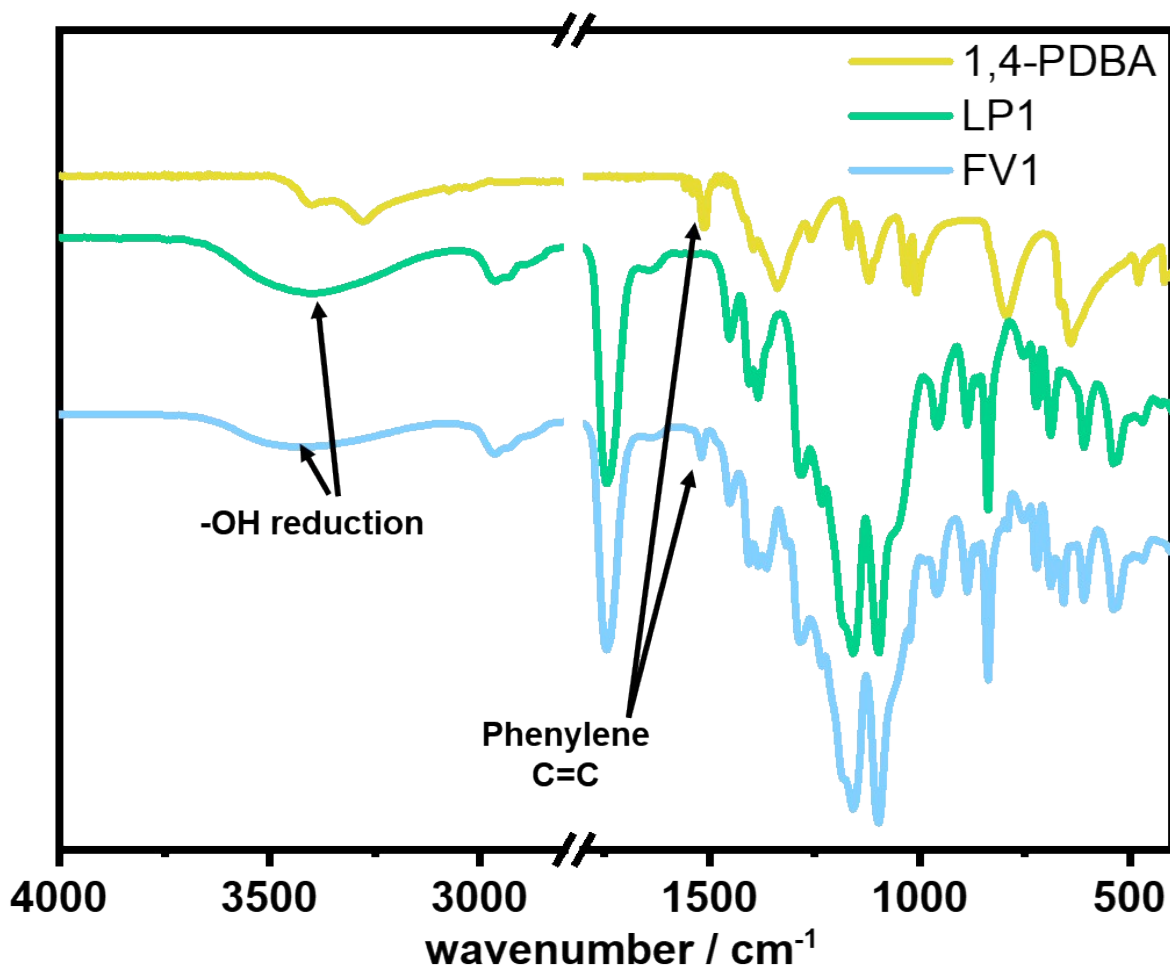


Fig. S5 Stacked FTIR spectrum of 1,4-phenylenediboronic acid, LP1 and FV1

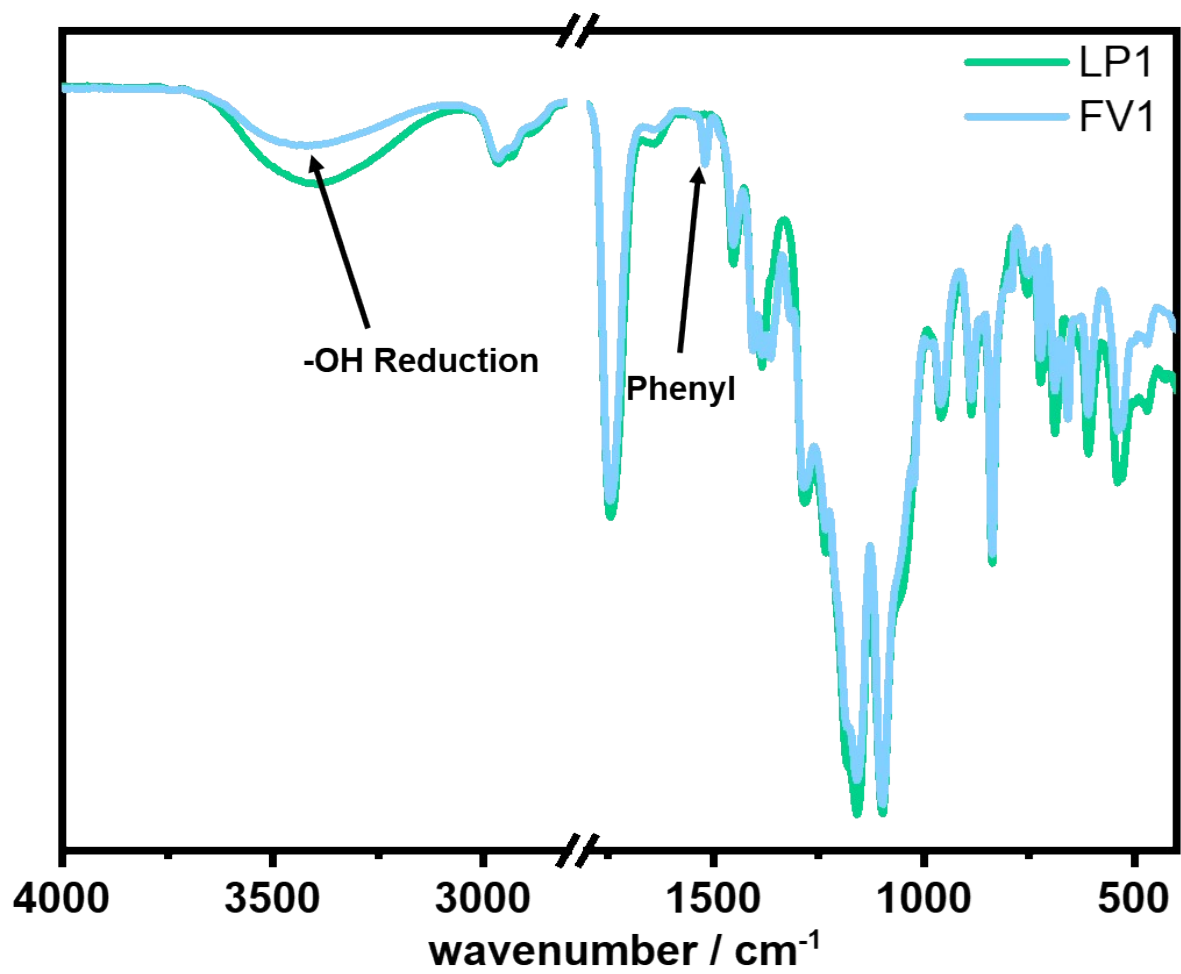


Fig. S6 Overlapping FTIR spectrum of of LP1 and FV1 with annotation.

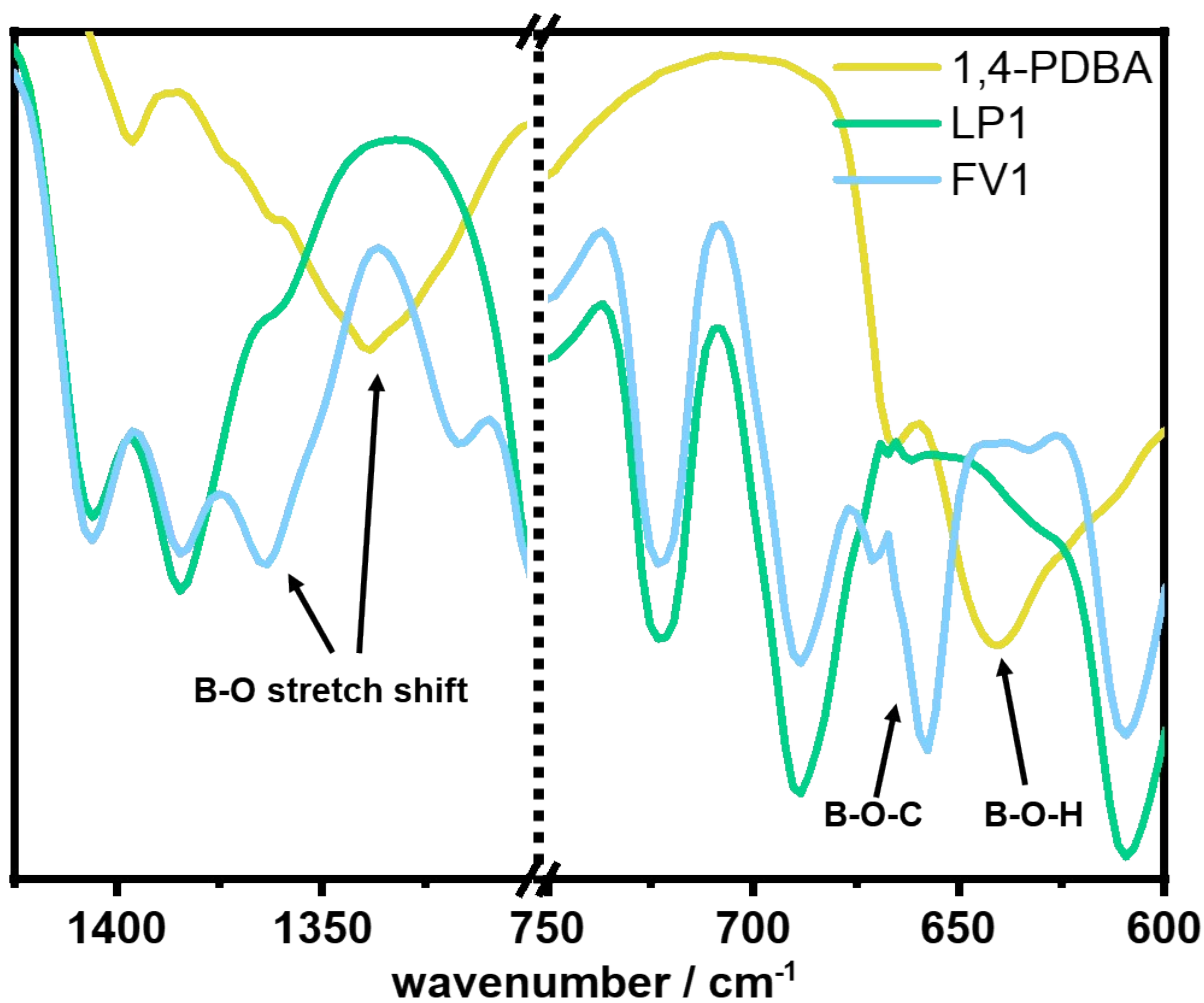


Fig. S7 Overlaid zoomed in (600-750 & 1300-1450 cm^{-1}) FTIR spectrum of 1,4-phenylenediboronic acid, LP1 and FV1 showing the shift of B-O stretch and after crosslinking and shift from B-O-H to B-O-C

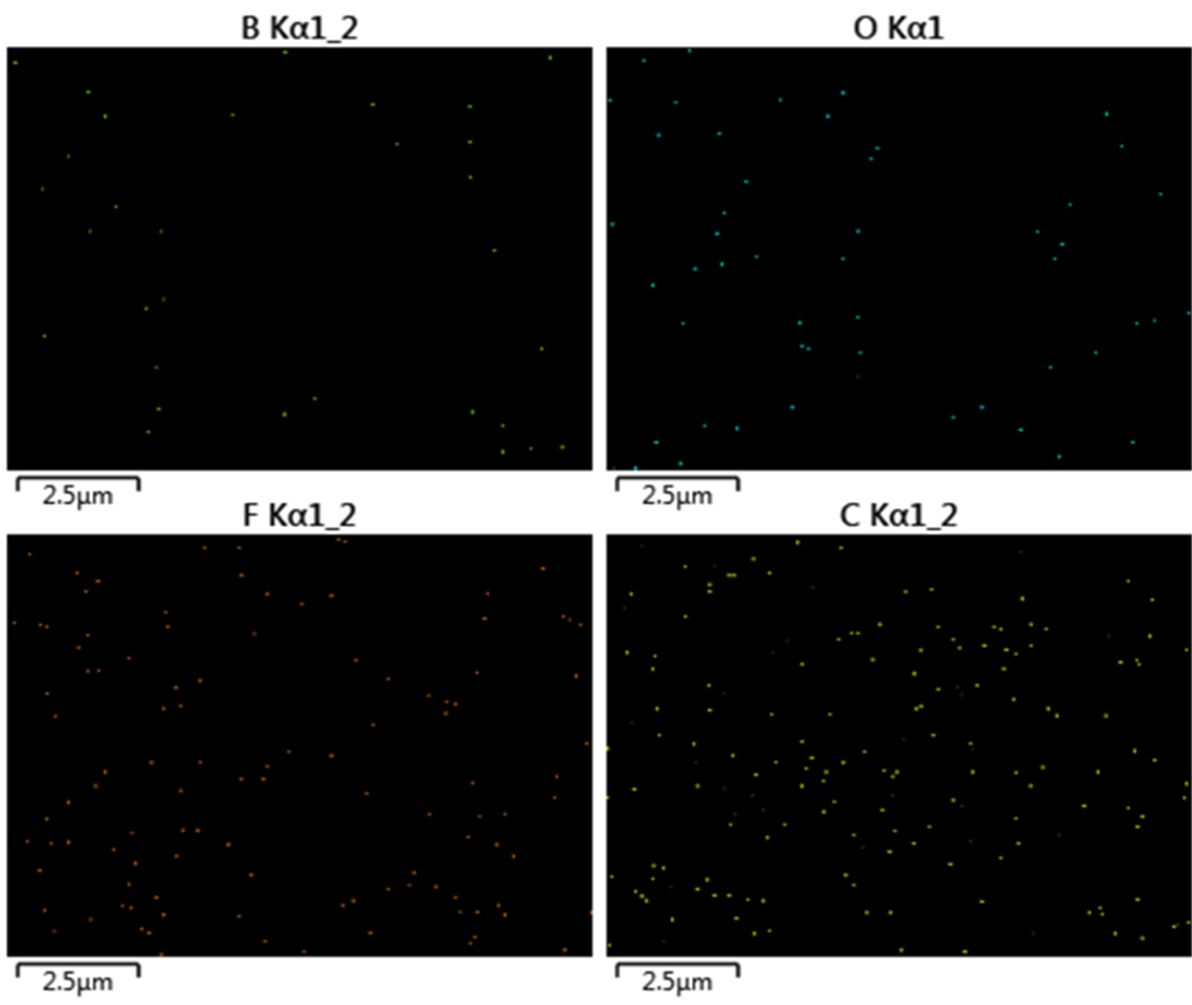


Fig. S8 SEM-EDX analysis of FV1 sample with specific elements (Green: Boron, Teal: Oxygen, Orange: Fluorine, Yellow: Carbon).

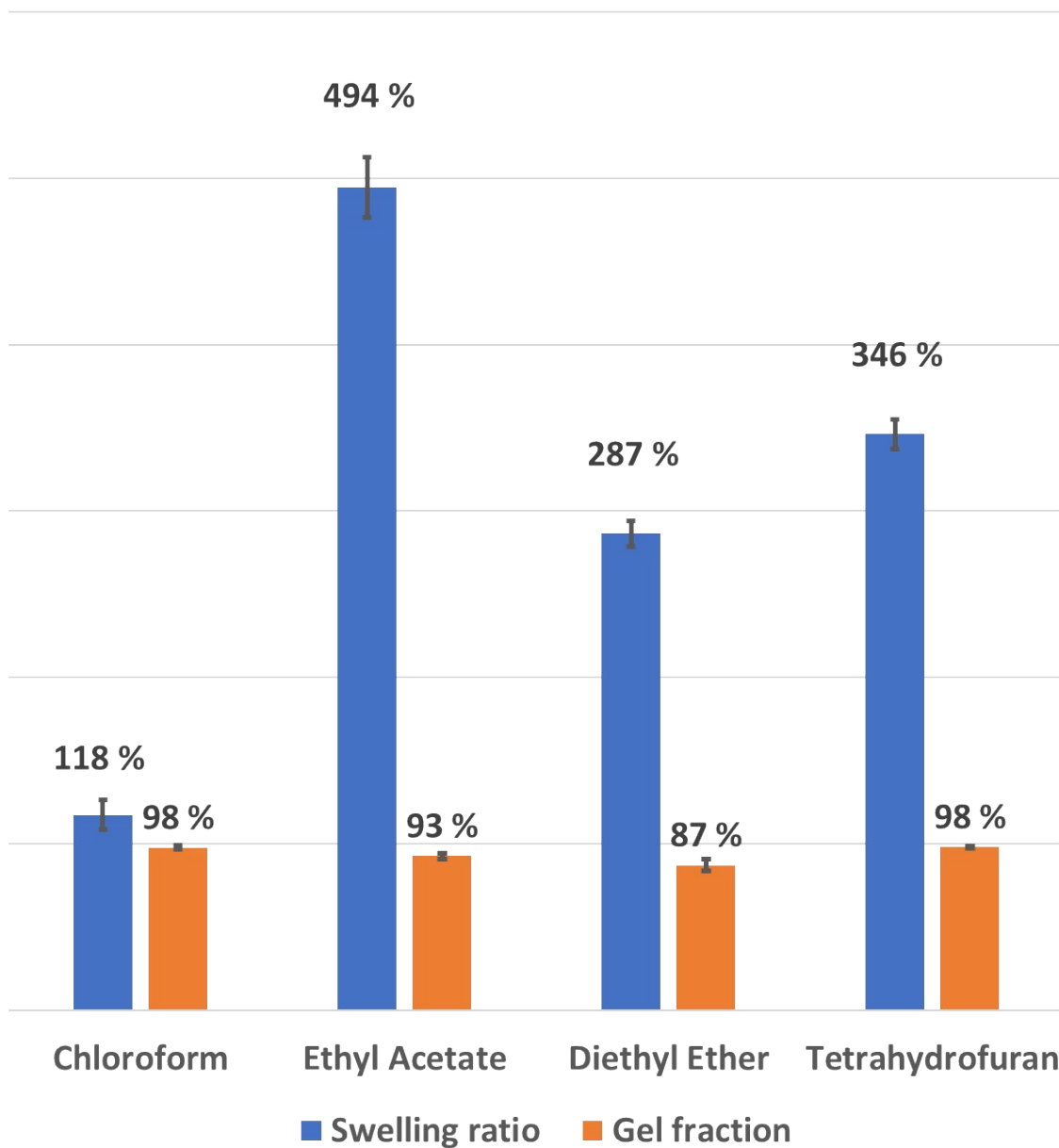


Fig. S9 Results of swelling and gel content analysis conducted for FV1 in chloroform, ethyl acetate, diethyl ether and tetrahydrofuran.

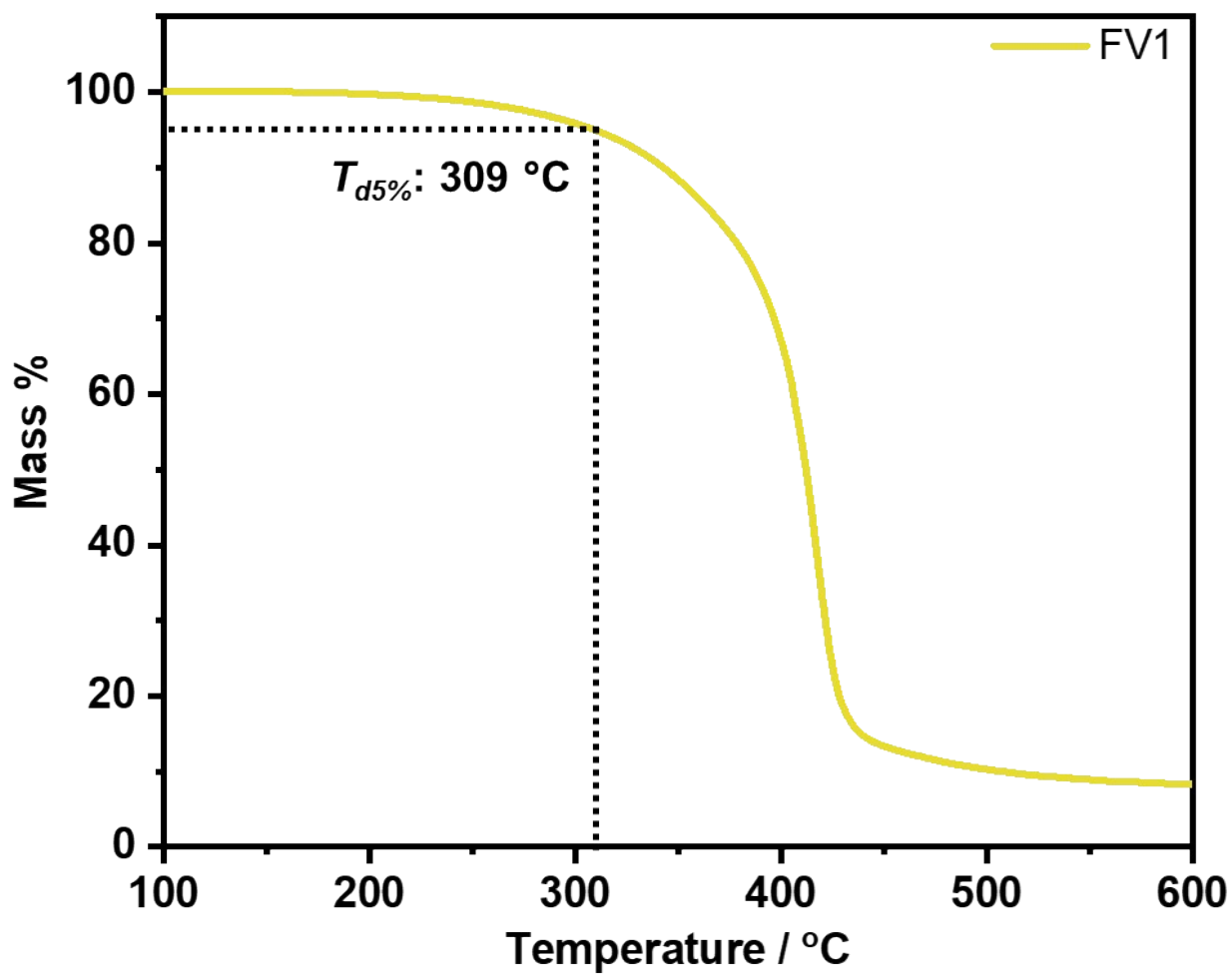


Fig. S10 TGA thermogram of FV1 under N₂ atmosphere

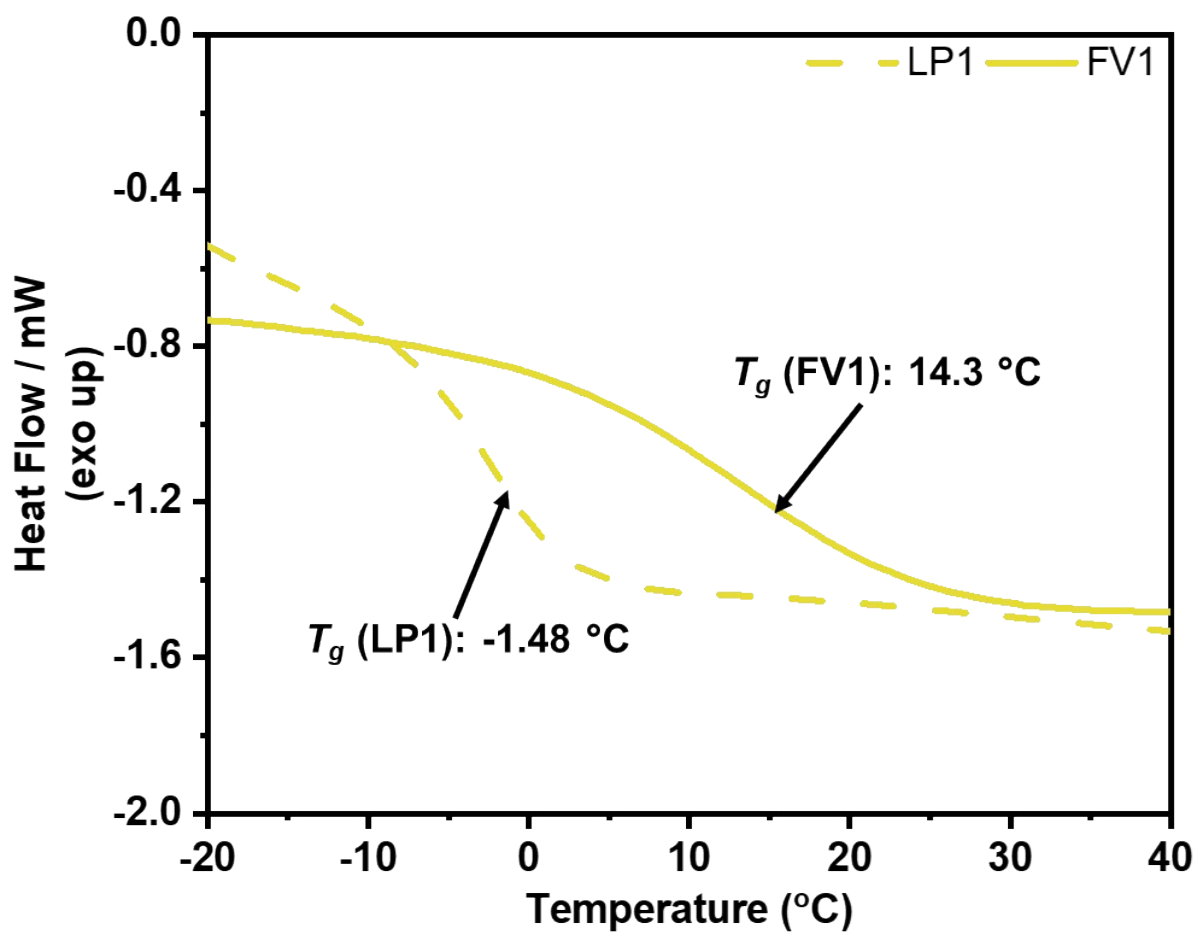


Fig. S11 DSC thermogram of LP1 (dash line) and FV1 (solid line)

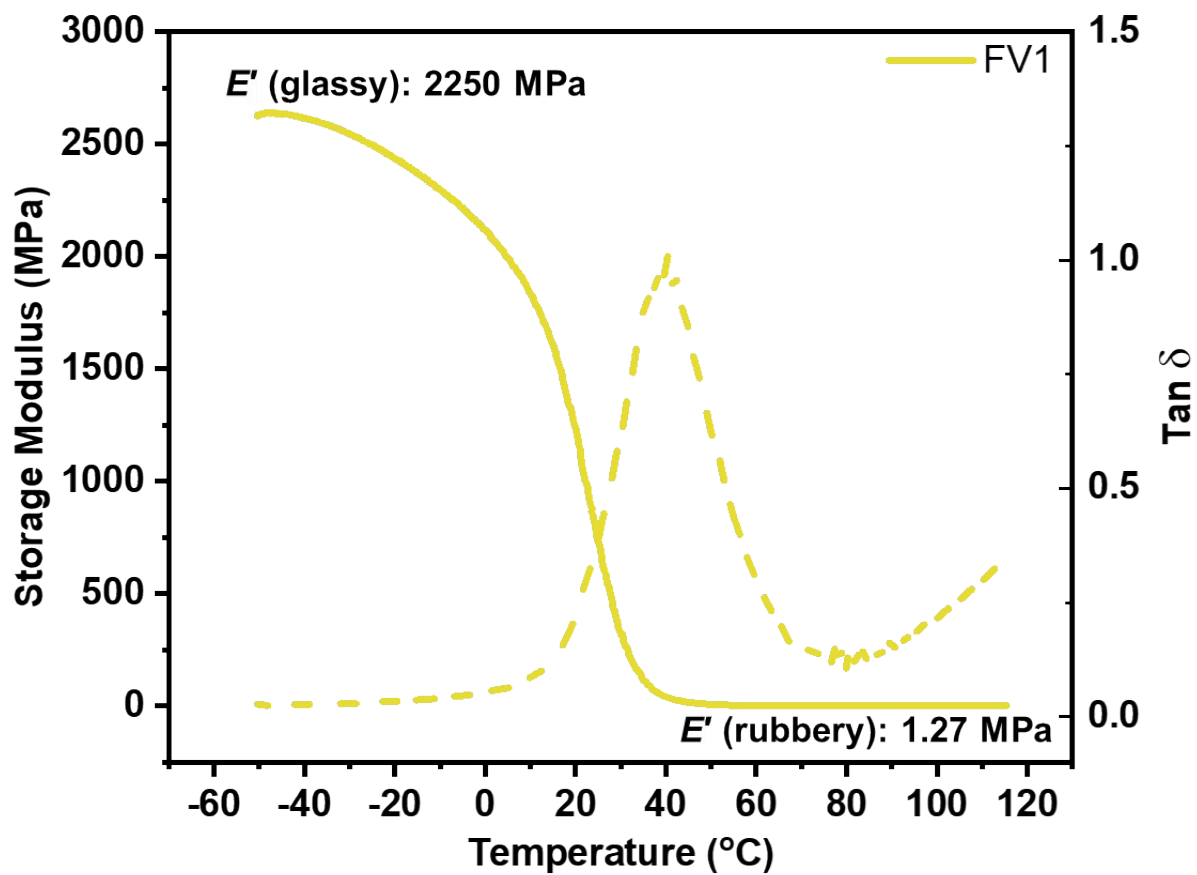


Fig. S12 Plot of storage modulus (solid line) and $\tan \delta$ (dash line) against temperature for FBE15

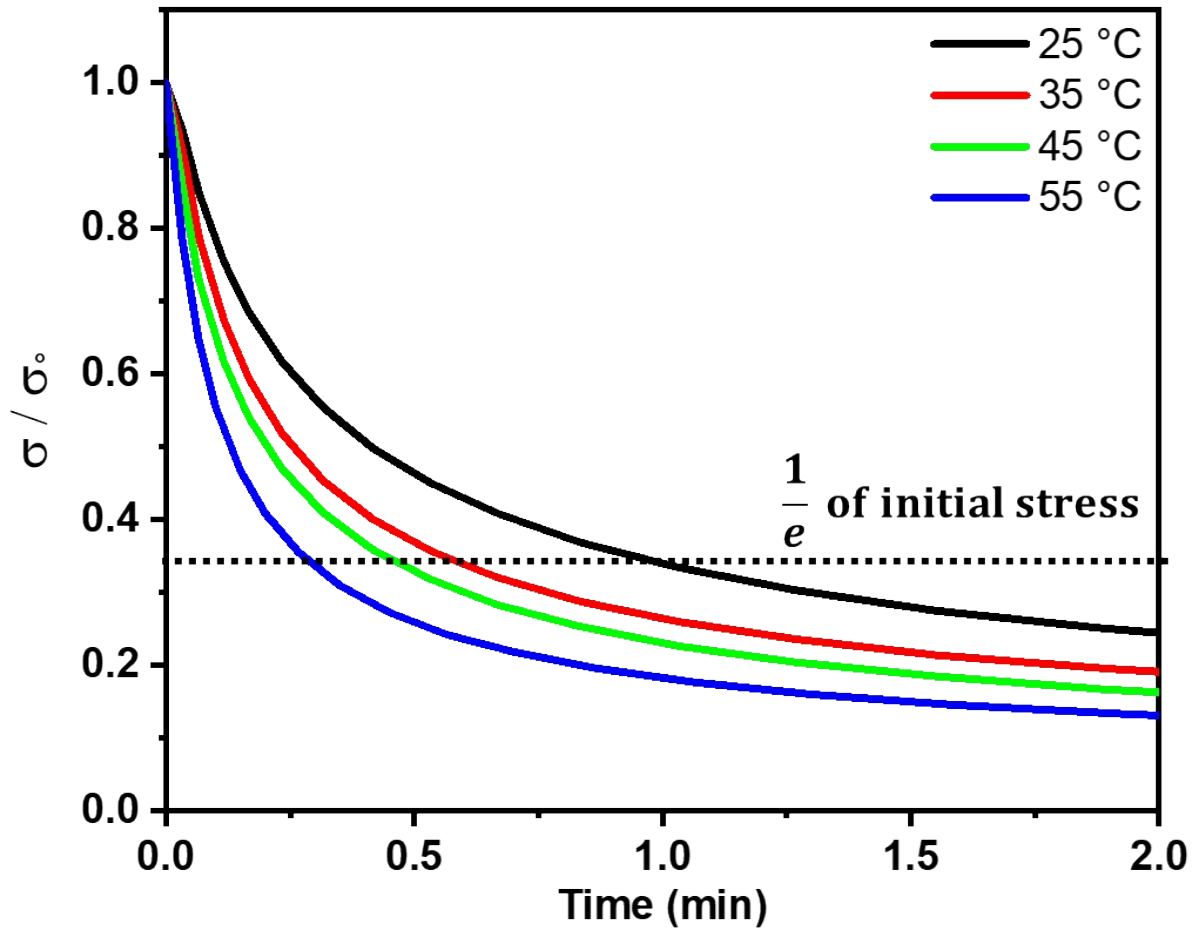


Fig. S13 Stress relaxation curve of FBE15 at varying temperatures from 25 °C to 55 °C

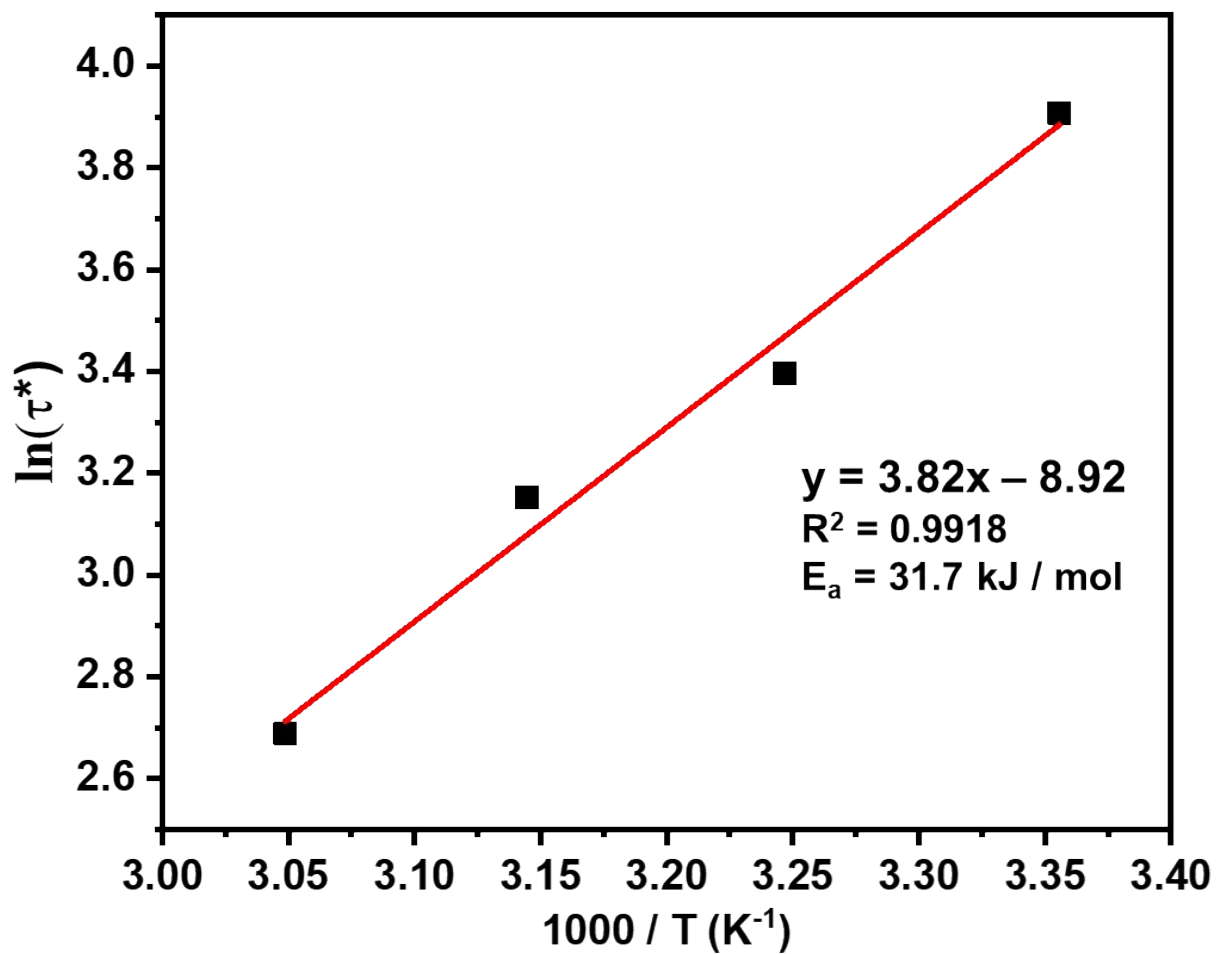


Fig. S14 Arrhenius fitted curve of relaxation time against $1000/T$ with E_a of 31.7

kJ/mol

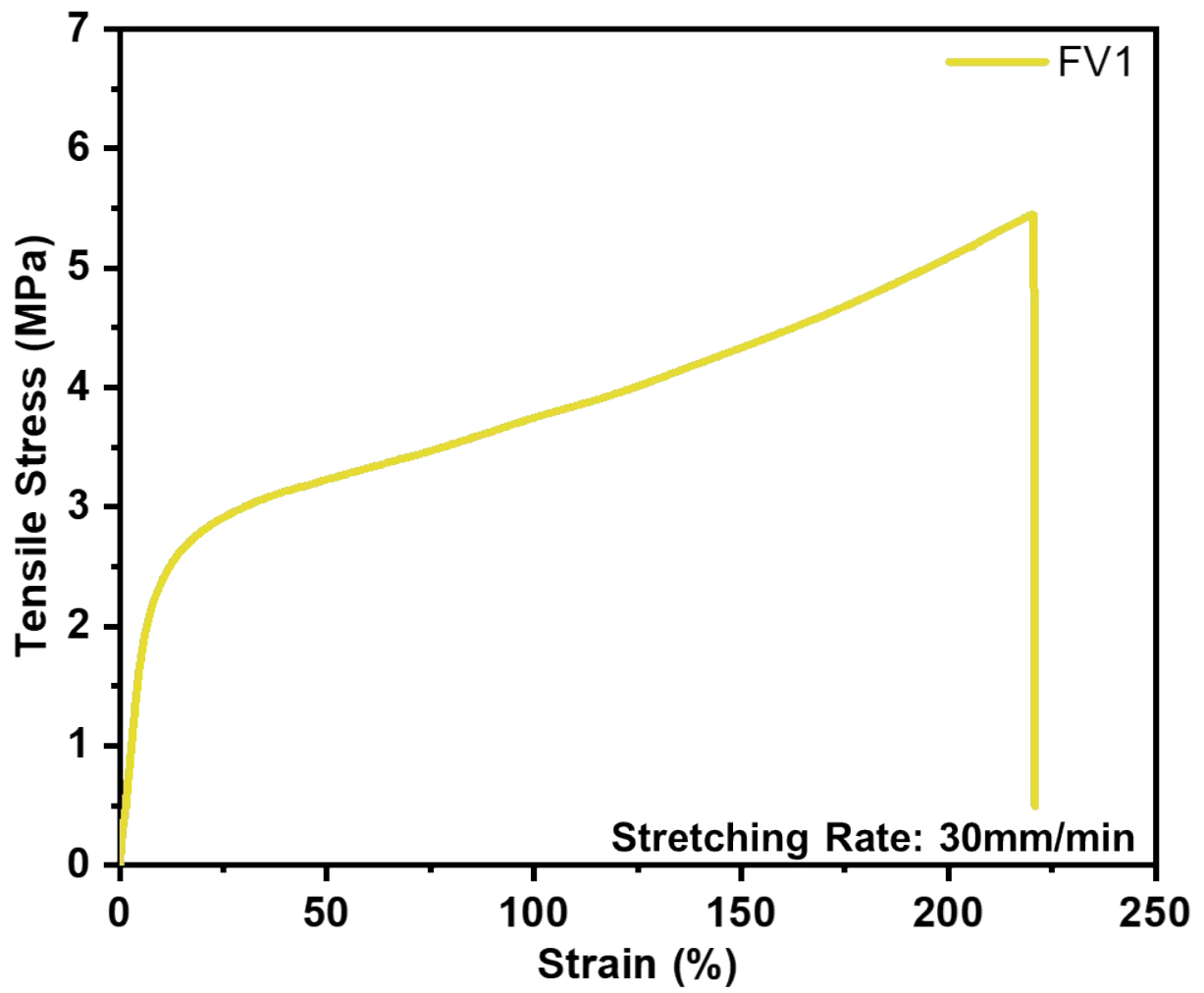


Fig. S15 Stress-strain curve of FV1 when pulled at a rate of 30 mm/min

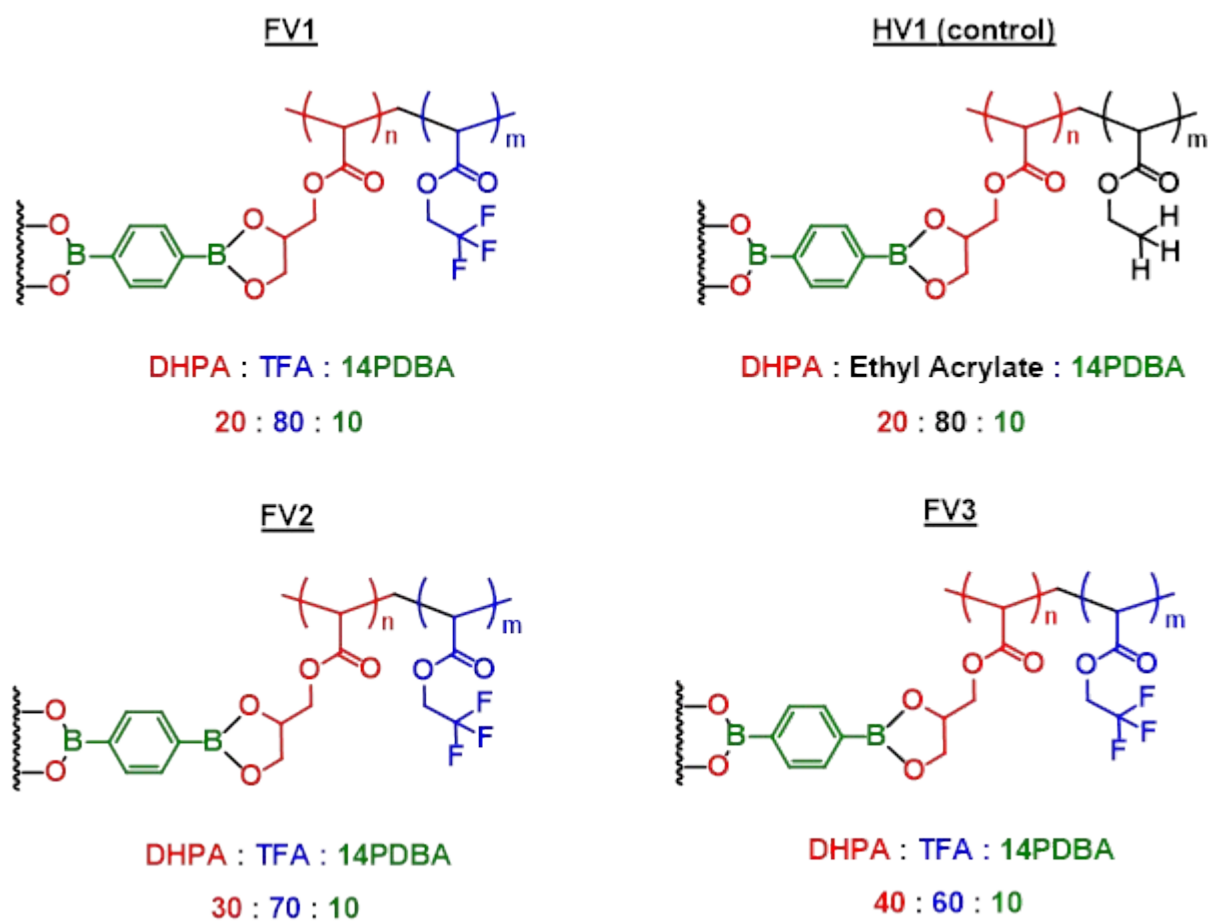


Fig. S16 Structure comparison of FV1, HV1, FV2 and FV3 with the various monomer and crosslinker ratio.

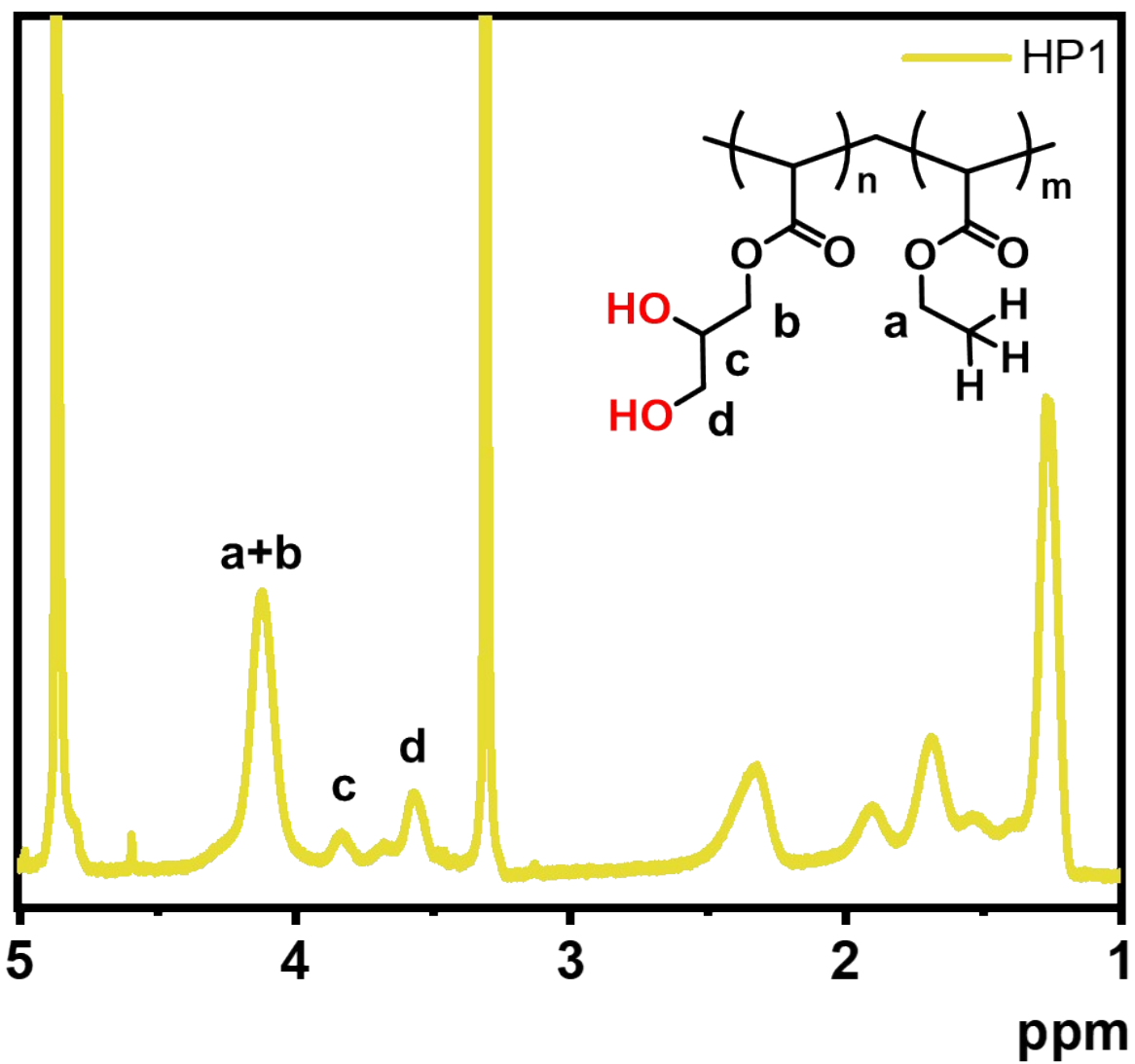


Fig. S17 ^1H NMR spectrum of HP1 in methanol- D_4 solvent with proton signals annotated.

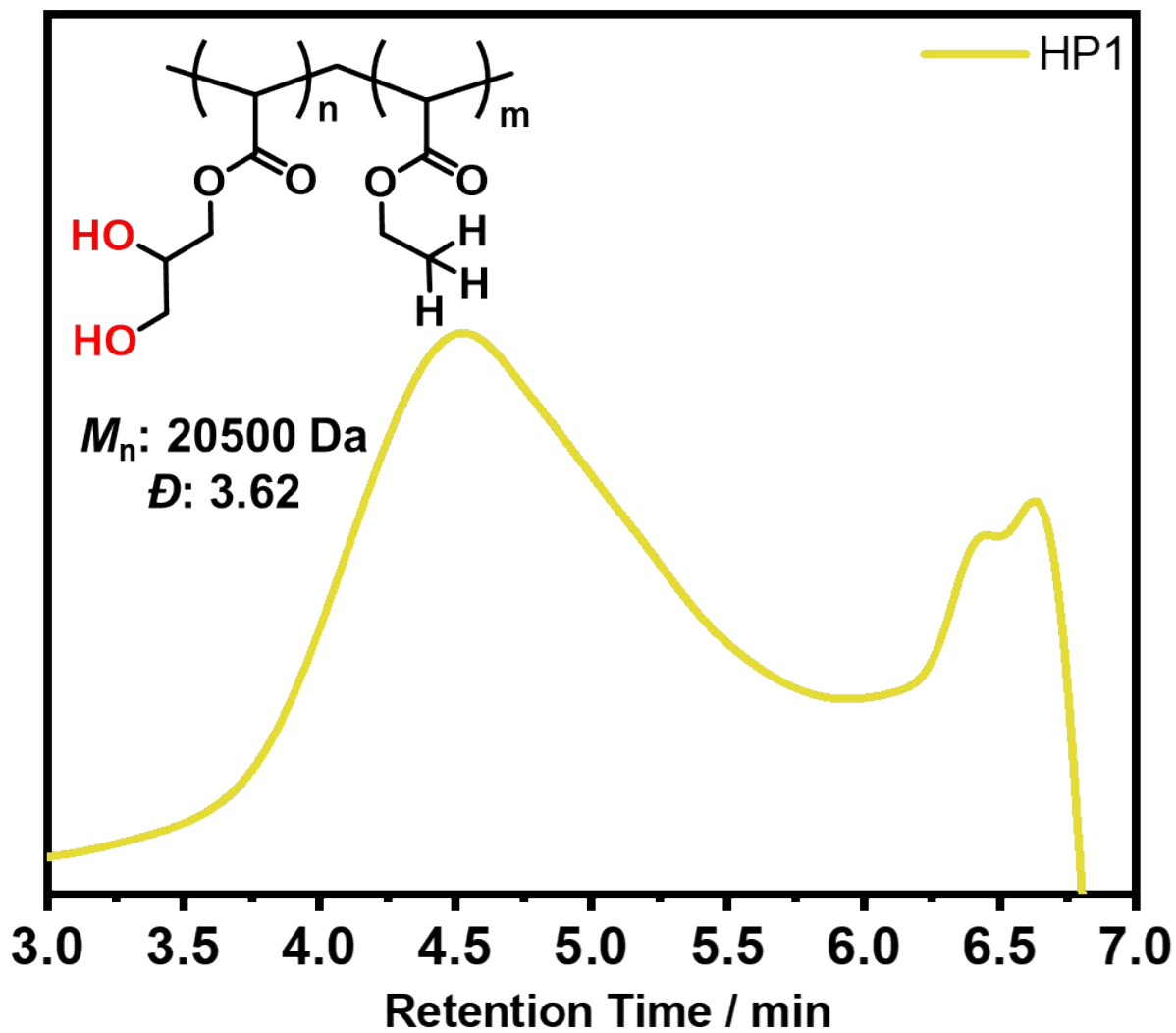


Fig. S18 GPC trace of HP1 with average molecular weight and polydispersity.

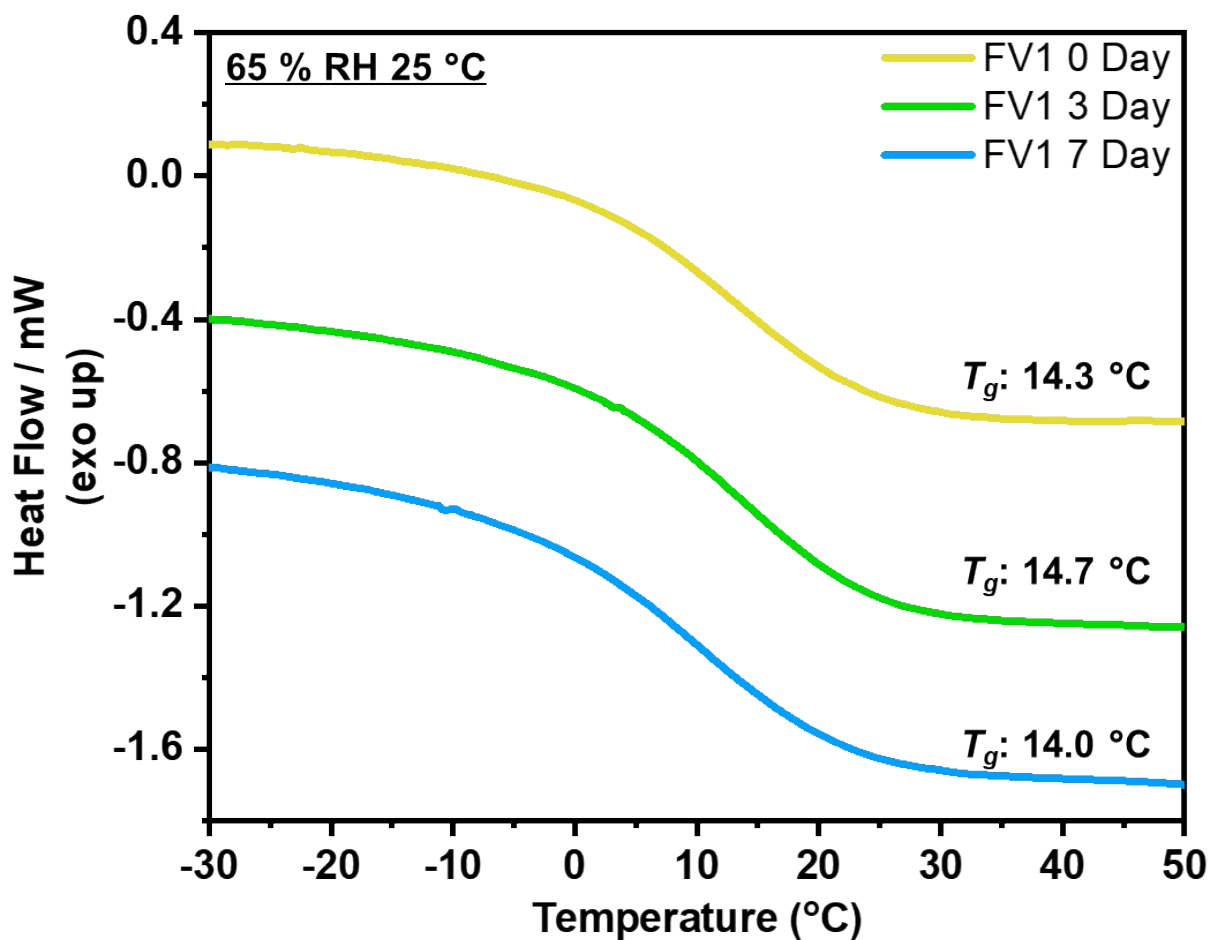


Fig. S19 DSC thermogram of FV1 after being kept in a RH 65 % at 25 °C environment for 0, 3 and 7 days.

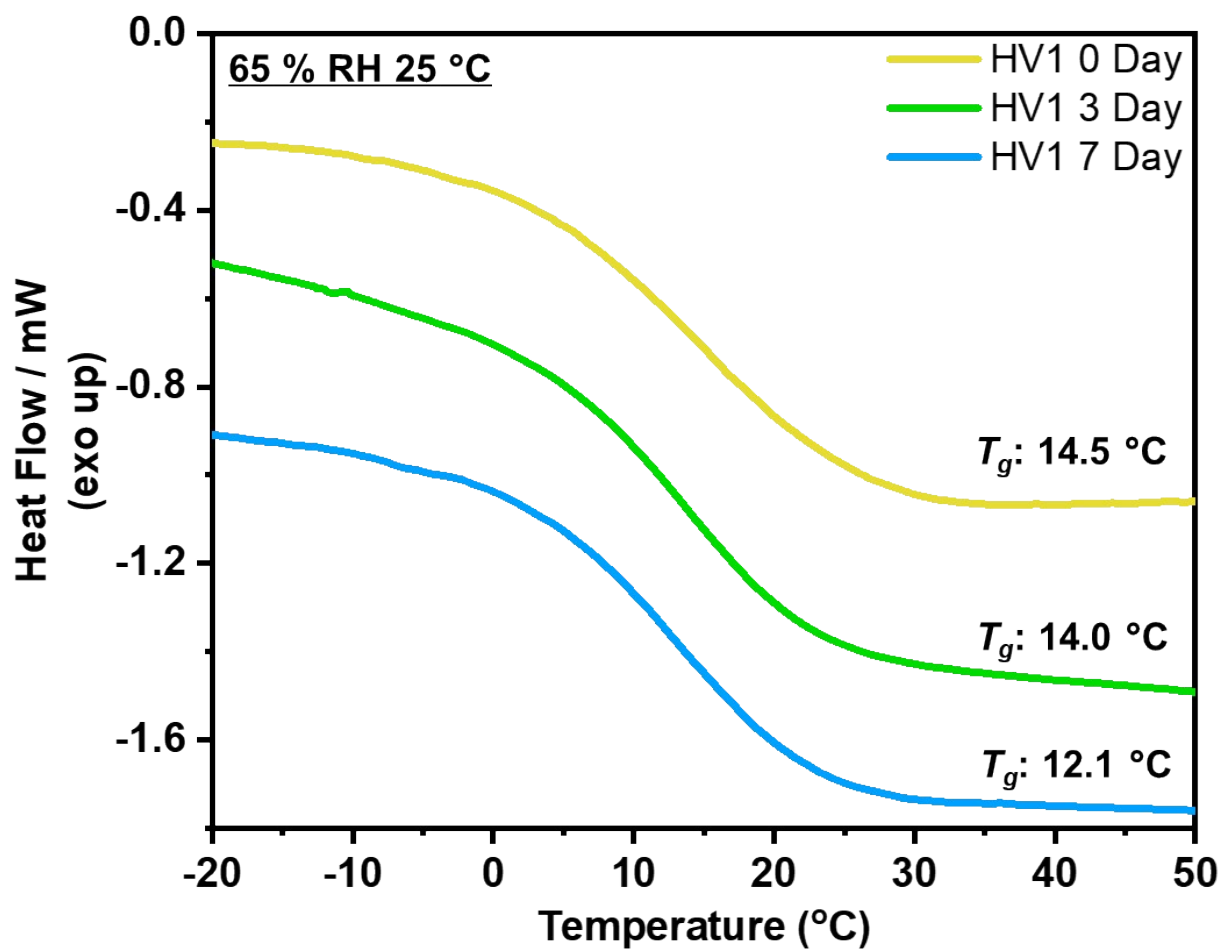


Fig. S20 DSC thermogram of HV1 after being kept in a RH 65 % 25 °C environment for 0, 3 and 7 days.

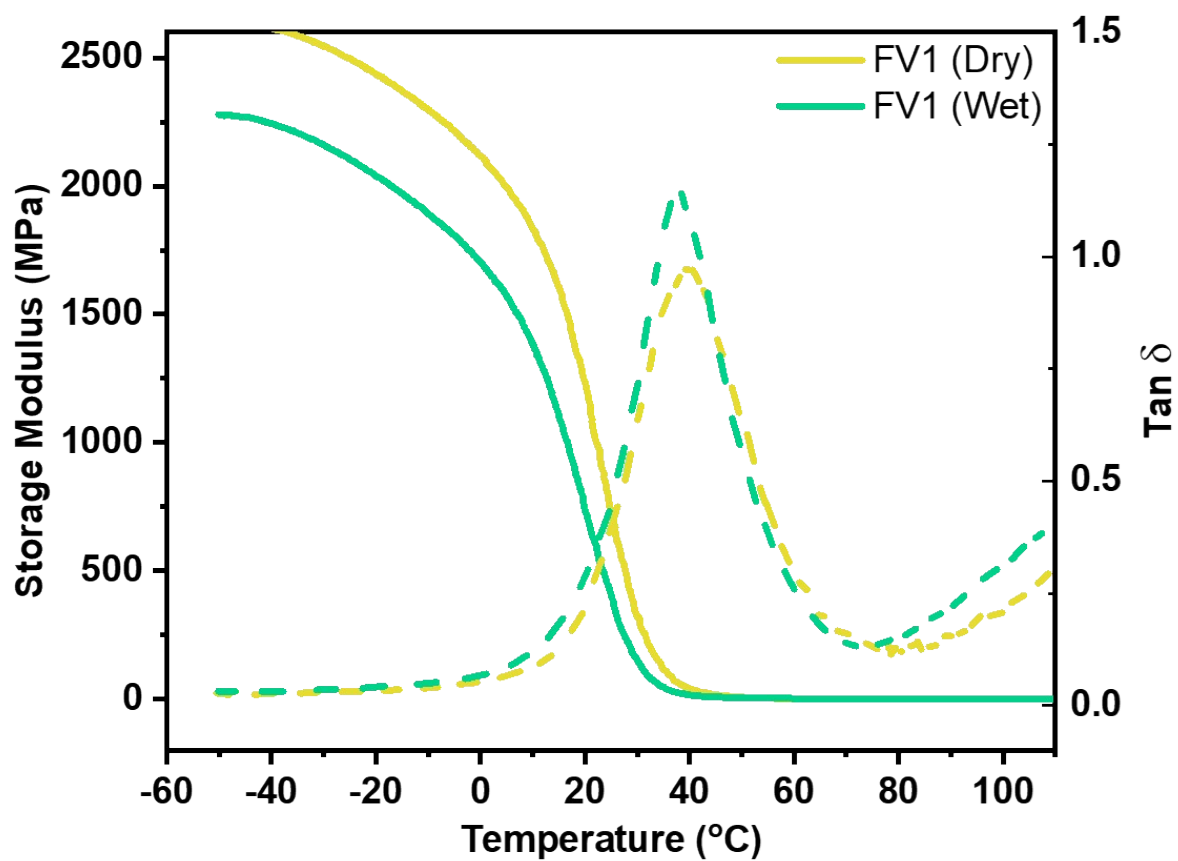


Fig. S21 DMA analysis of fluorinated FV1 from -40 °C to 100 °C before and after immersion in water for 30 min

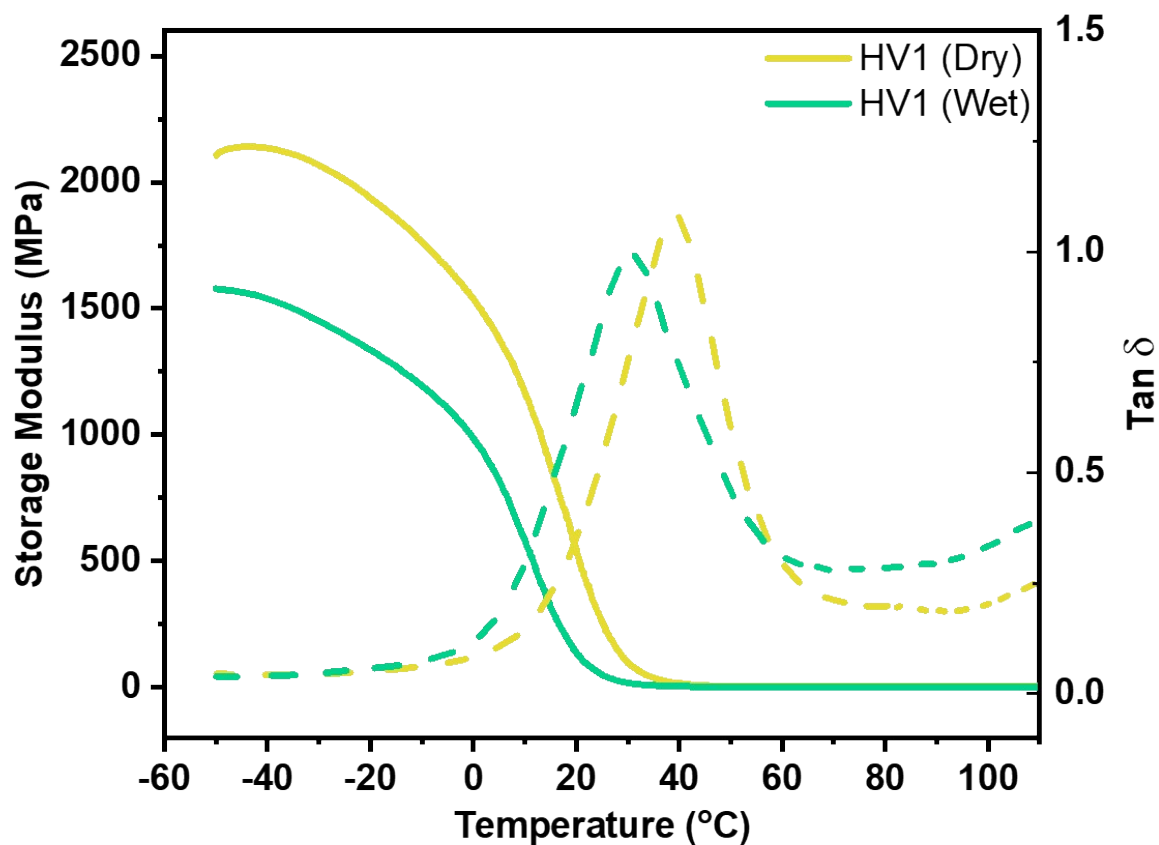


Fig. S22 DMA analysis of non-fluorinated HV1 from -40 °C to 100 °C before and after immersion in water for 30 min

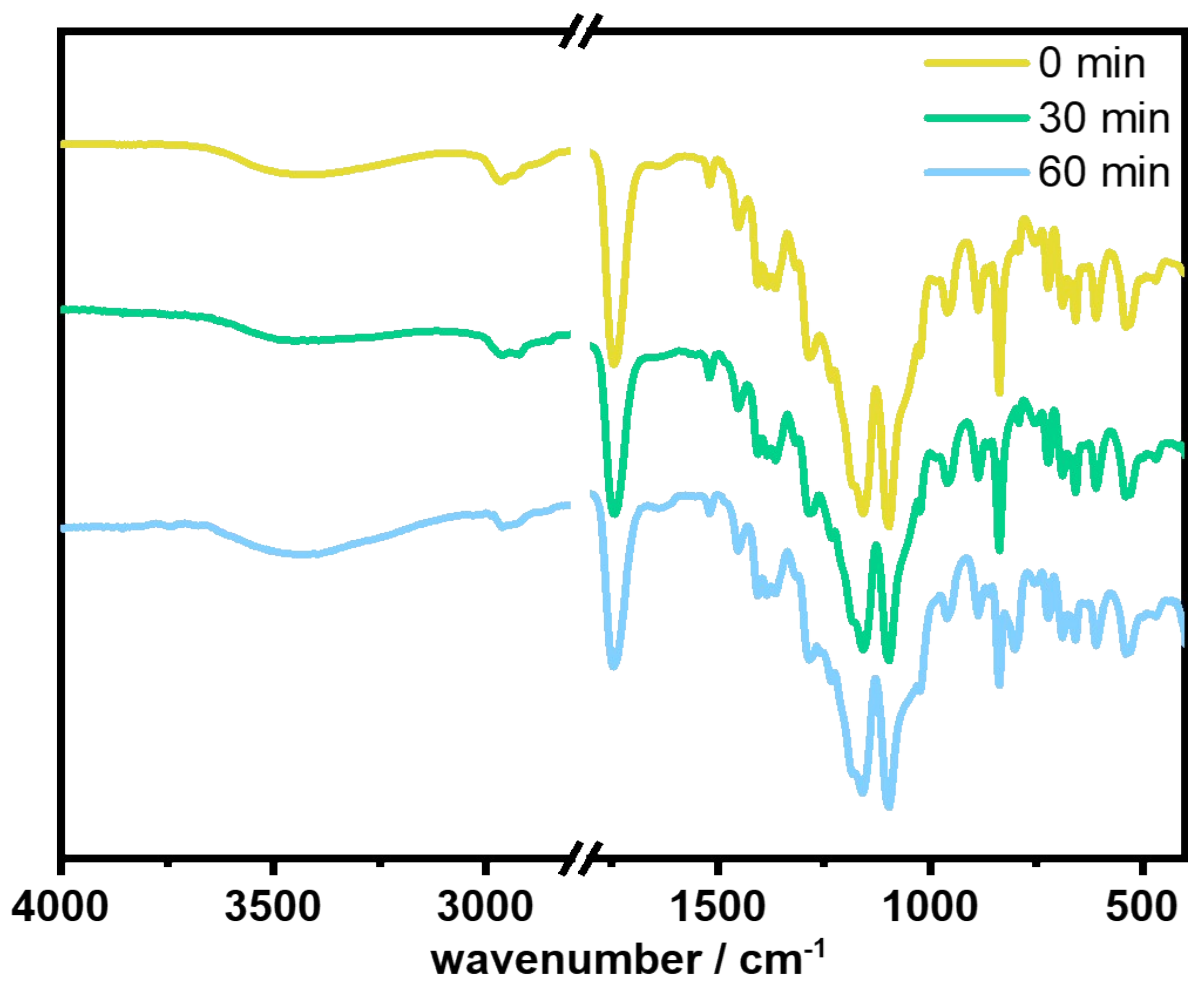


Fig. S23 FTIR spectra of FV1 immersed in water after 0 min (yellow), 30 min (green) and 60 min (blue).

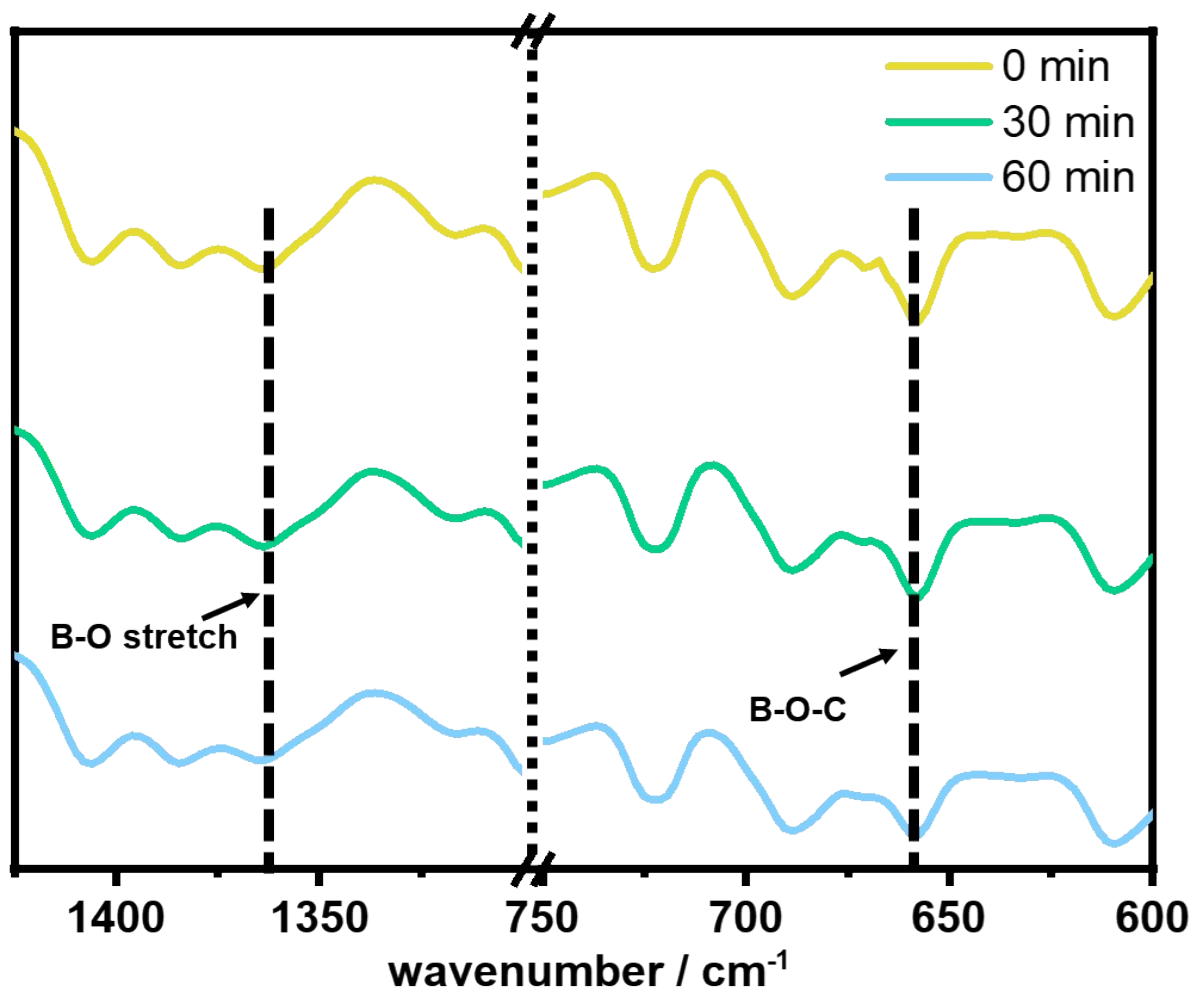


Fig. S24 Zoomed-in FTIR spectra ($600\text{-}750$ & $1300\text{-}1450$ cm^{-1}) of FV1 immersed in water after 0 min (yellow), 30 min (green) and 60 min (blue).

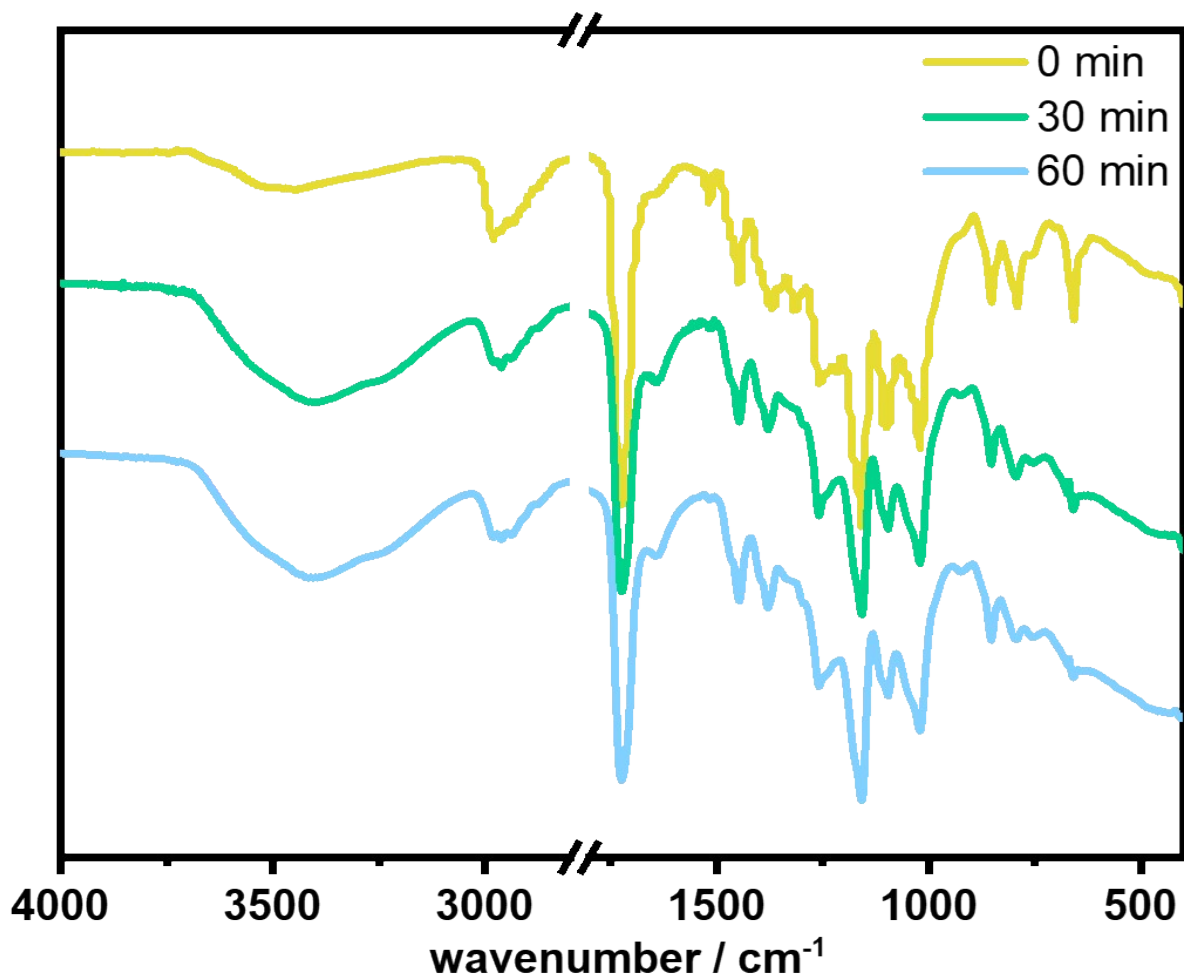


Fig. S25 FTIR spectra of HV1 immersed in water after 0 min (yellow), 30 min (green) and 60 min (blue).

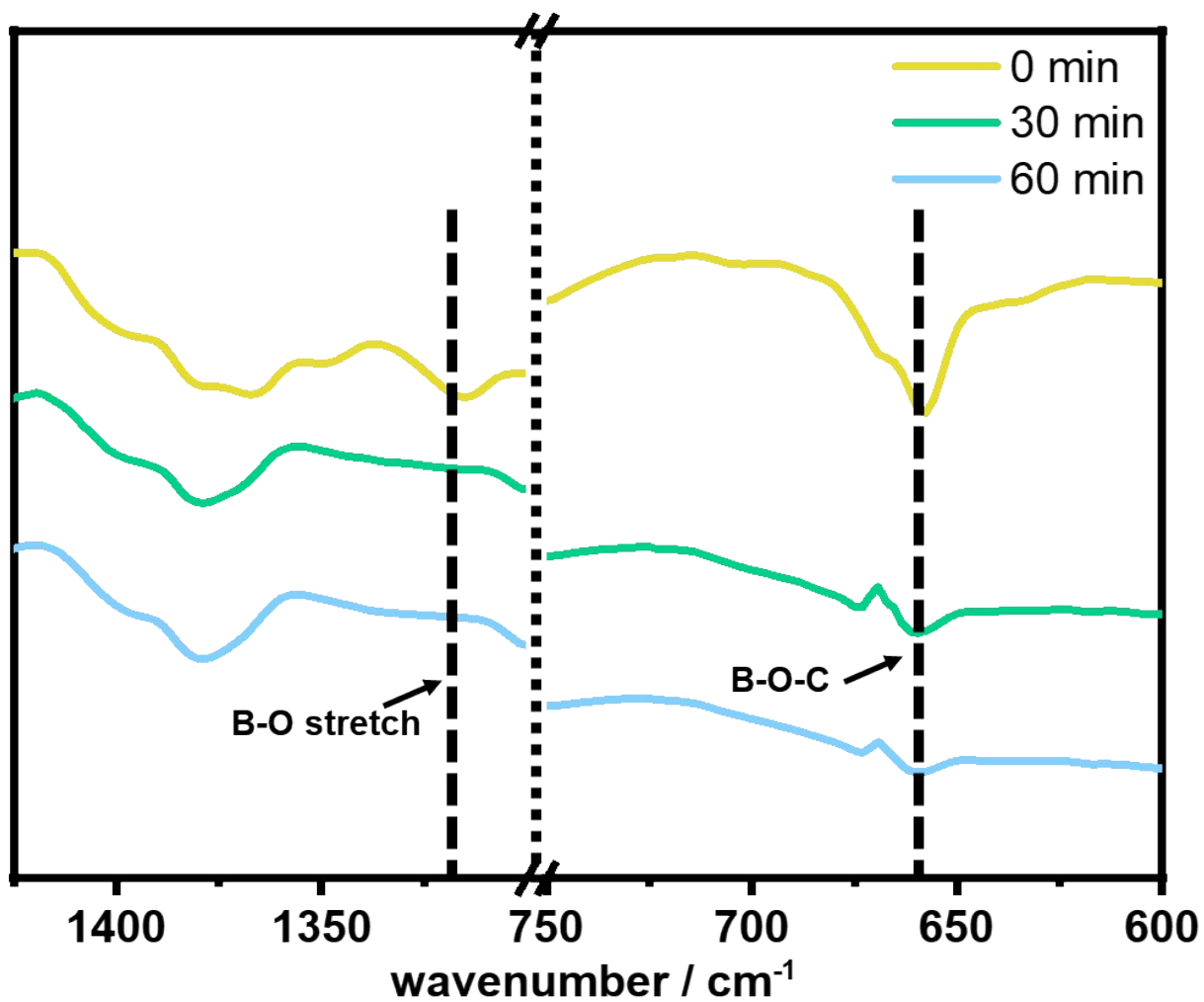


Fig. S26 Zoomed-in FTIR spectra ($600\text{-}750$ & $1300\text{-}1450$ cm^{-1}) of HV1 immersed in water after 0 min (yellow), 30 min (green) and 60 min (blue).

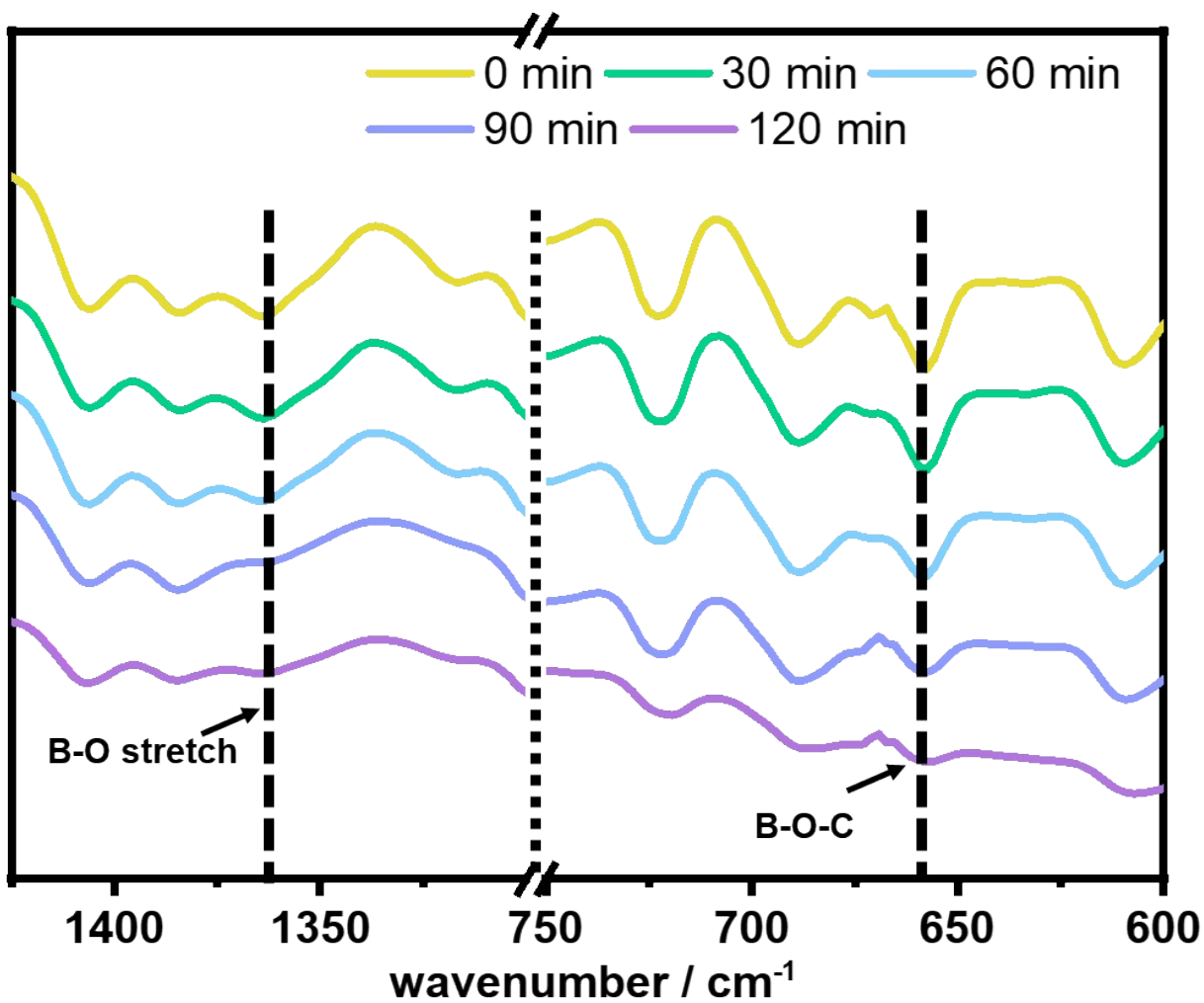


Fig. S27 Zoomed-in FTIR spectra (600-750 & 1300-1450 cm^{-1}) of FV1 immersed in water after 0 min (yellow), 30 min (green), 60 min (blue), 90 min (purple) and 120 min (violet).

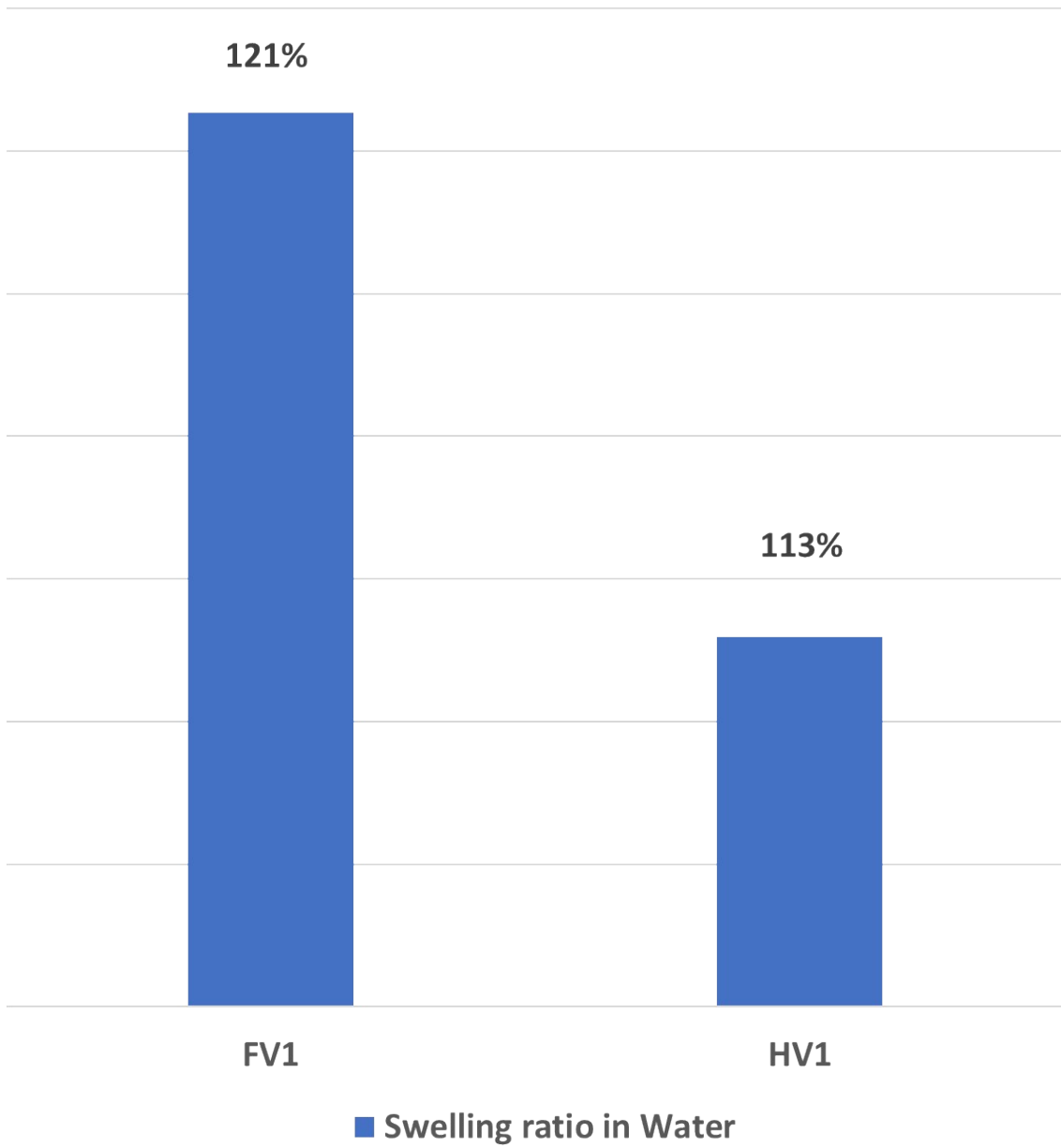


Fig. S28 Results of swelling ratio analysis conducted for FV1 and HV1.

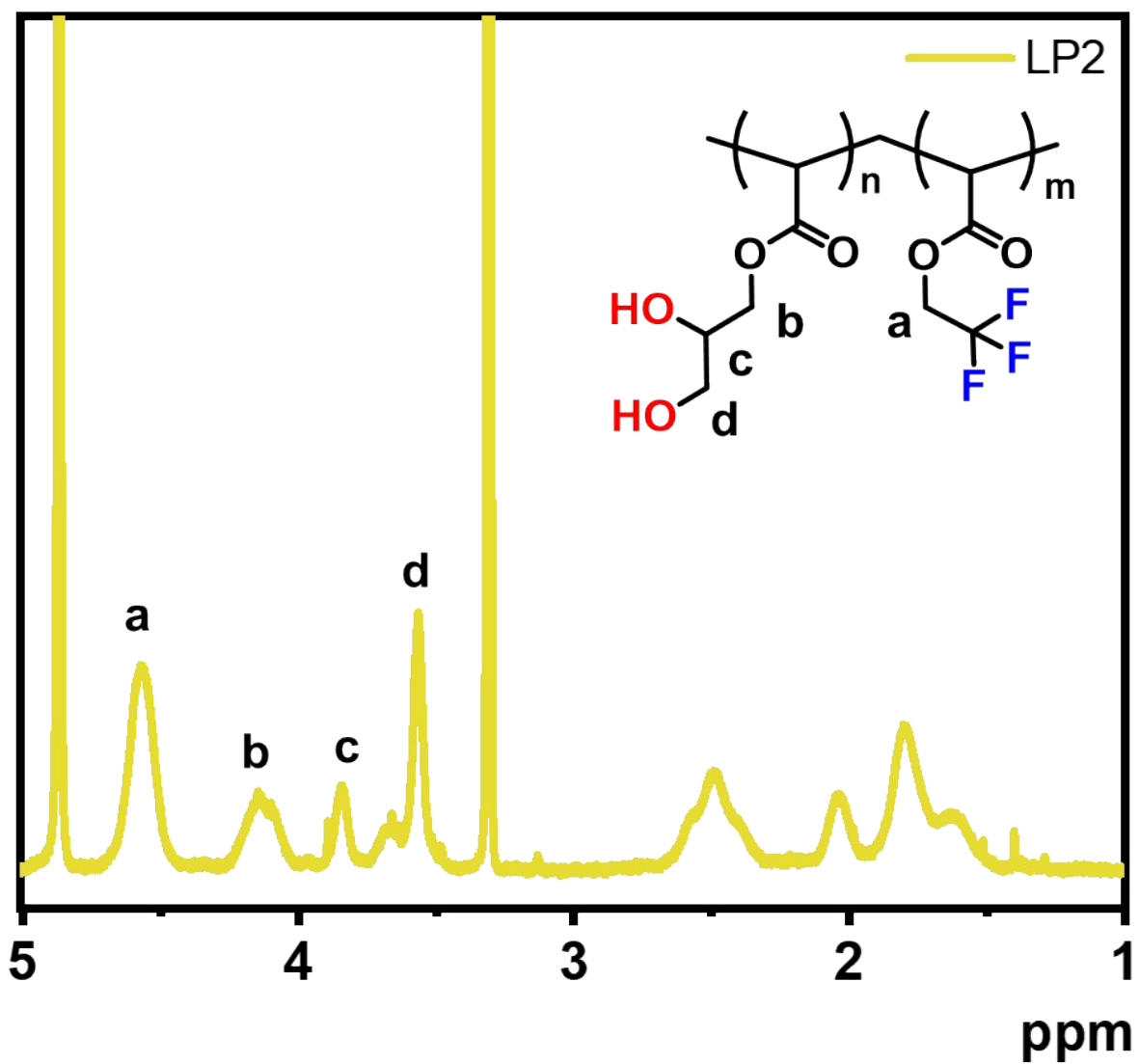


Fig. S29 ¹H NMR spectrum of LP2 in methanol-D₄ solvent with proton signals annotated.

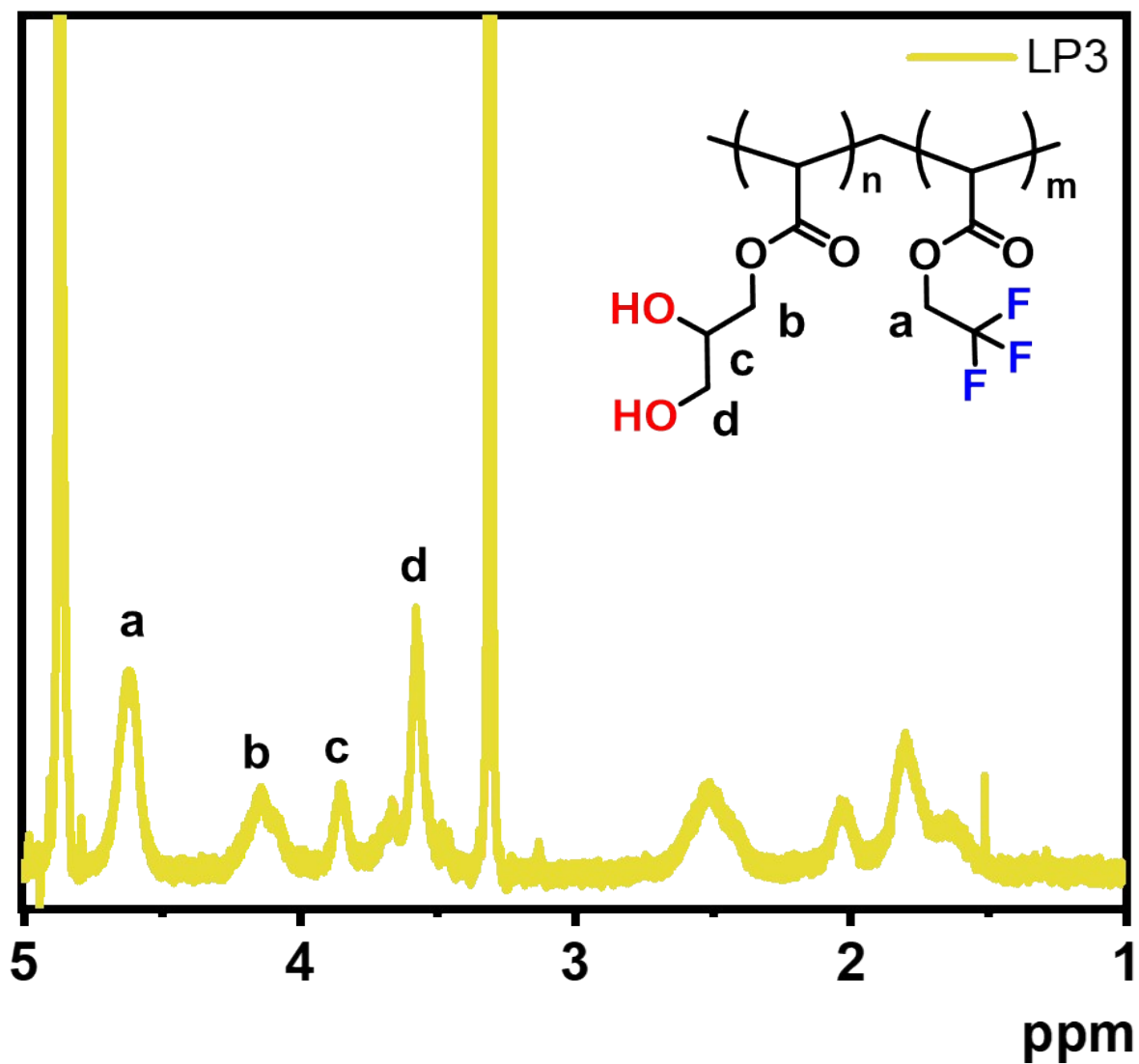


Fig. S30 ¹H NMR spectrum of LP3 in methanol-D₄ solvent with proton signals annotated.

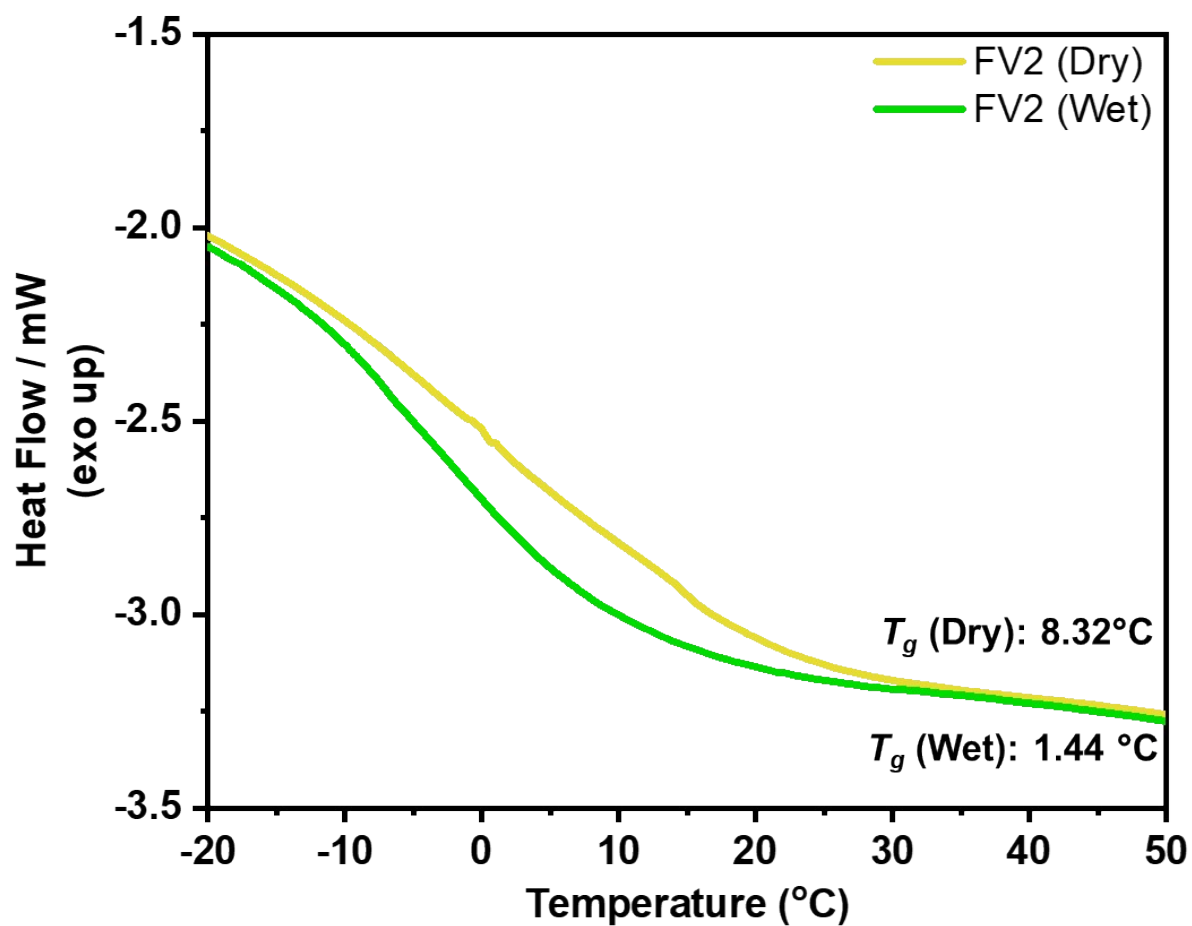


Fig. S31 DSC thermogram of FV2 before and after immersion in water for 30 min

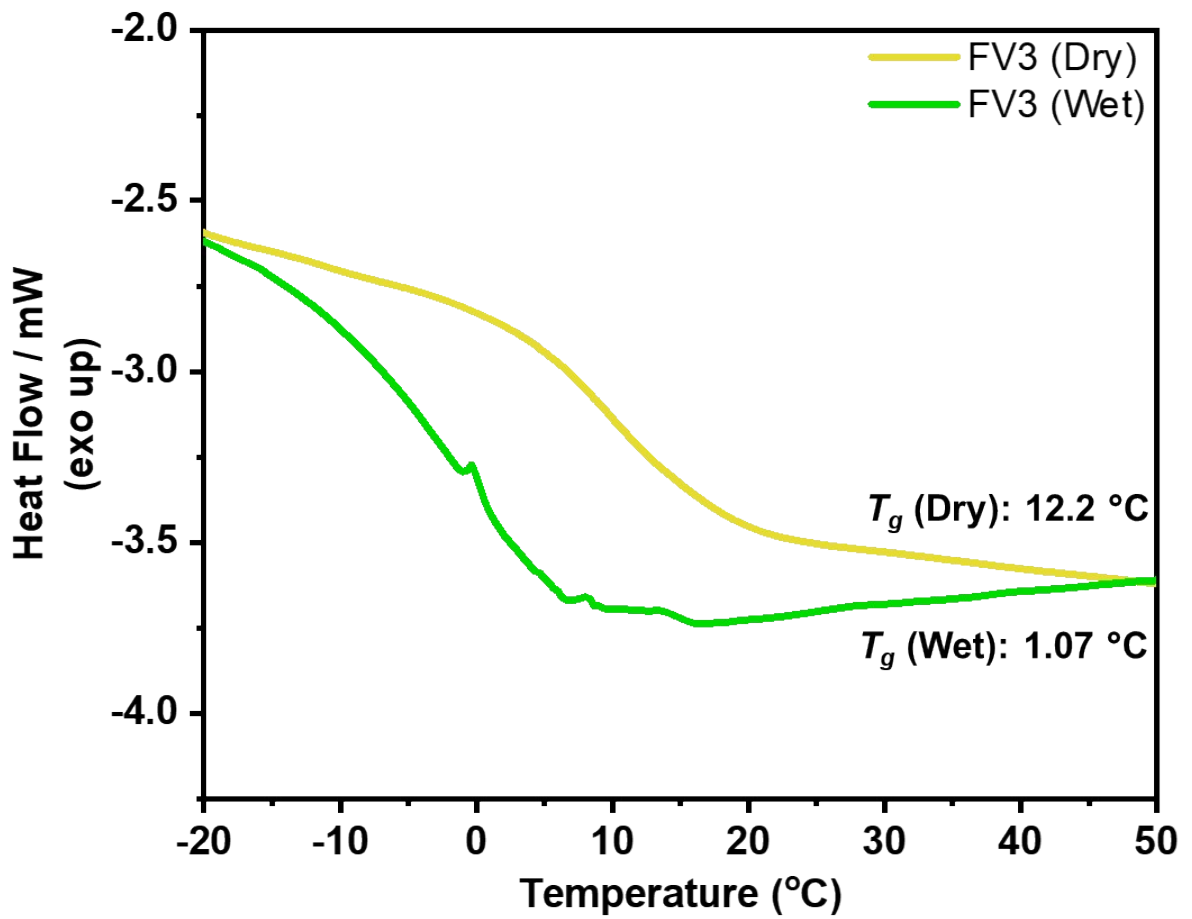


Fig. 32 DSC thermogram of FV3 before and after immersion in water for 30 min

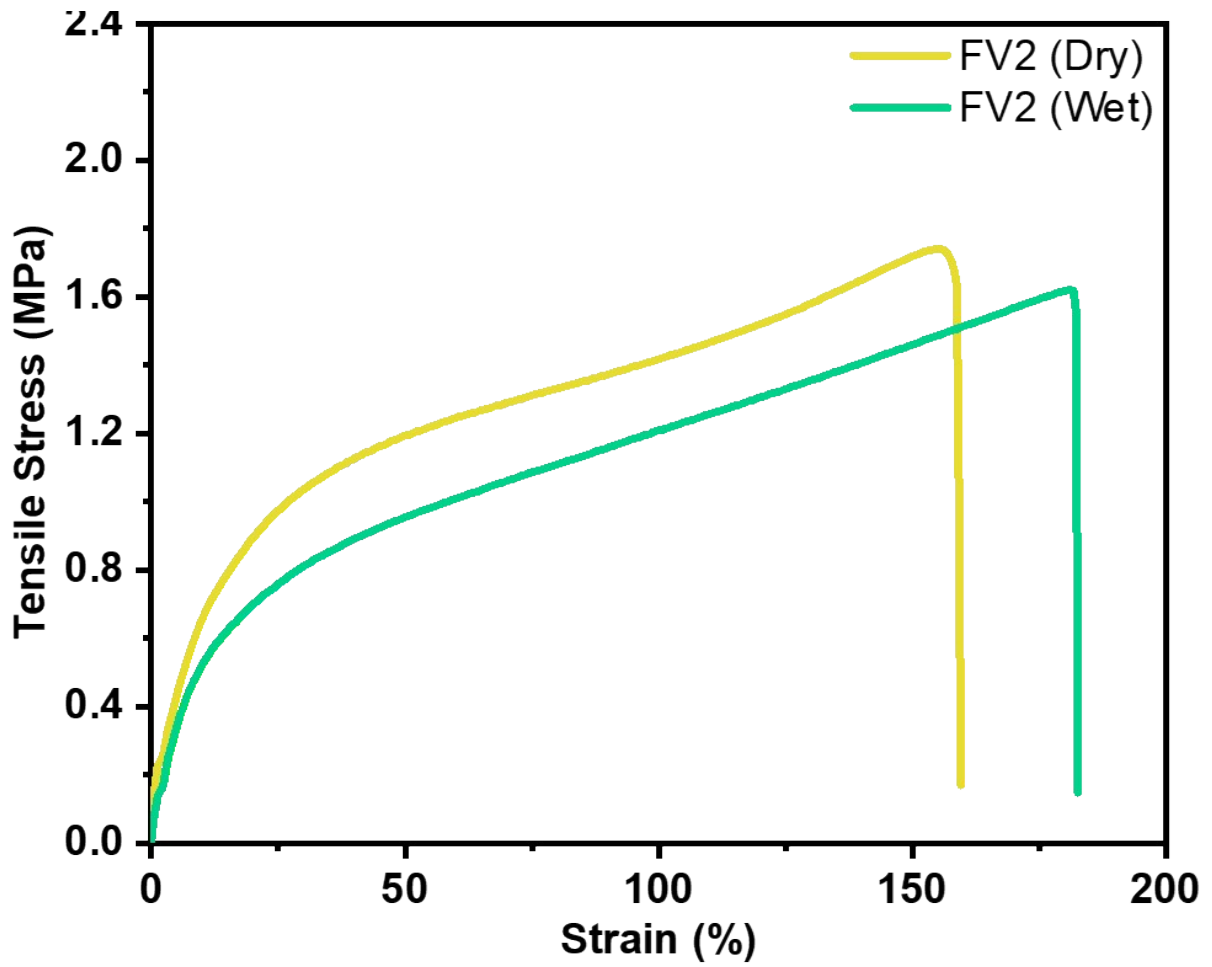


Fig. 33 Tensile test of FV2 before and after immersion in water for 30 min (stretching rate 30 mm/min)

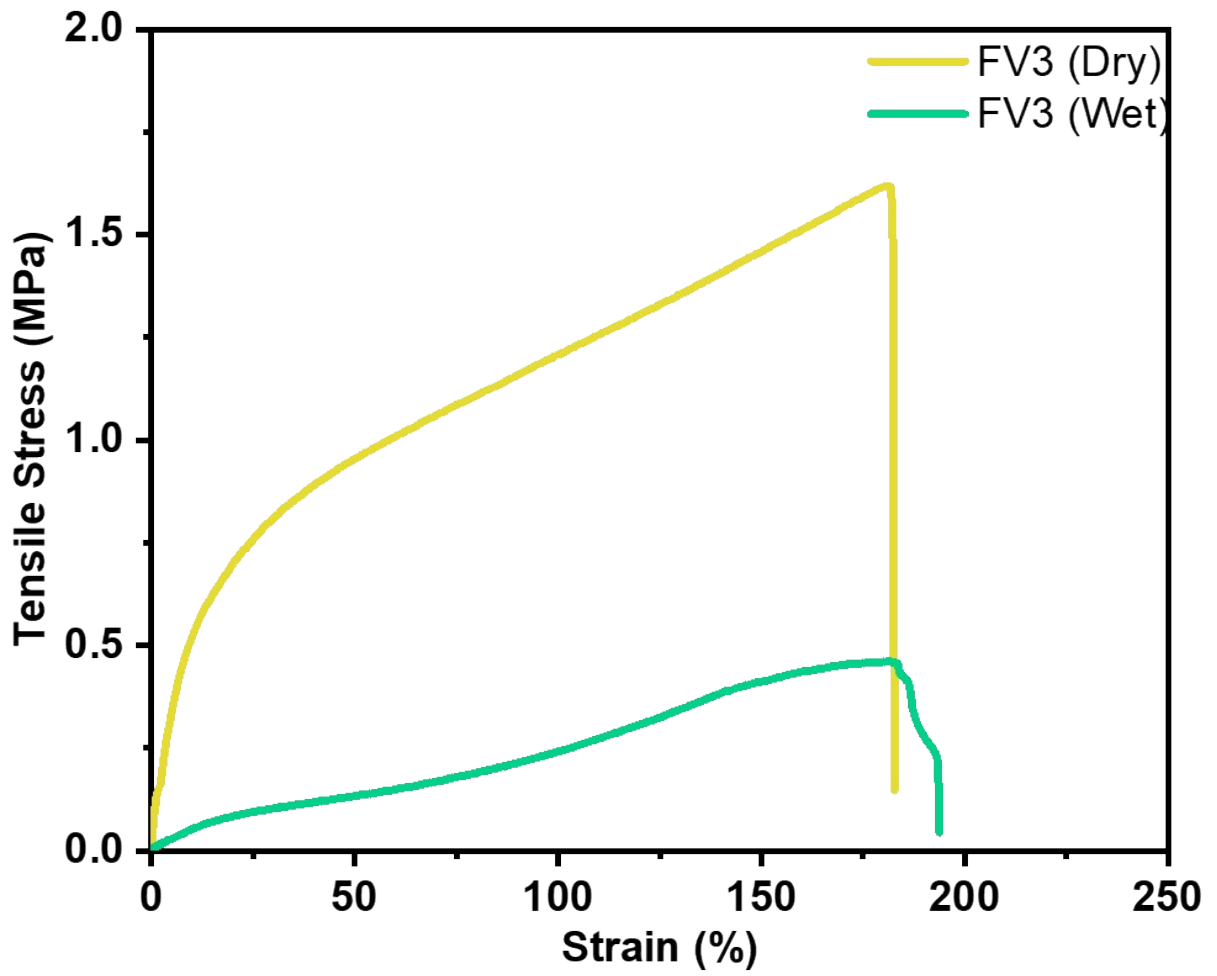


Fig. 34 Tensile test of FV3 before and after immersion in water for 30 min (stretching rate 30 mm/min)

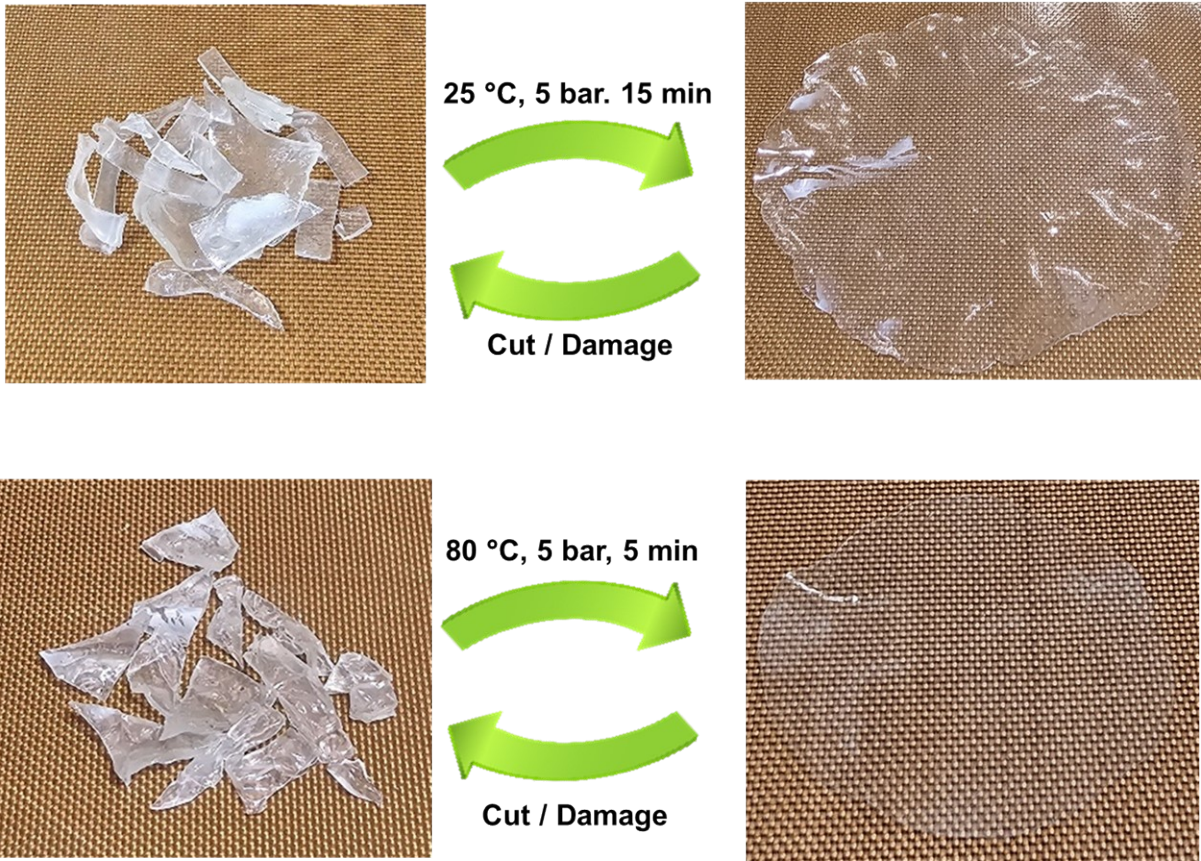


Fig. S35 Mechanical reprocessing of FV1 via hot-press at RT and 100 °C

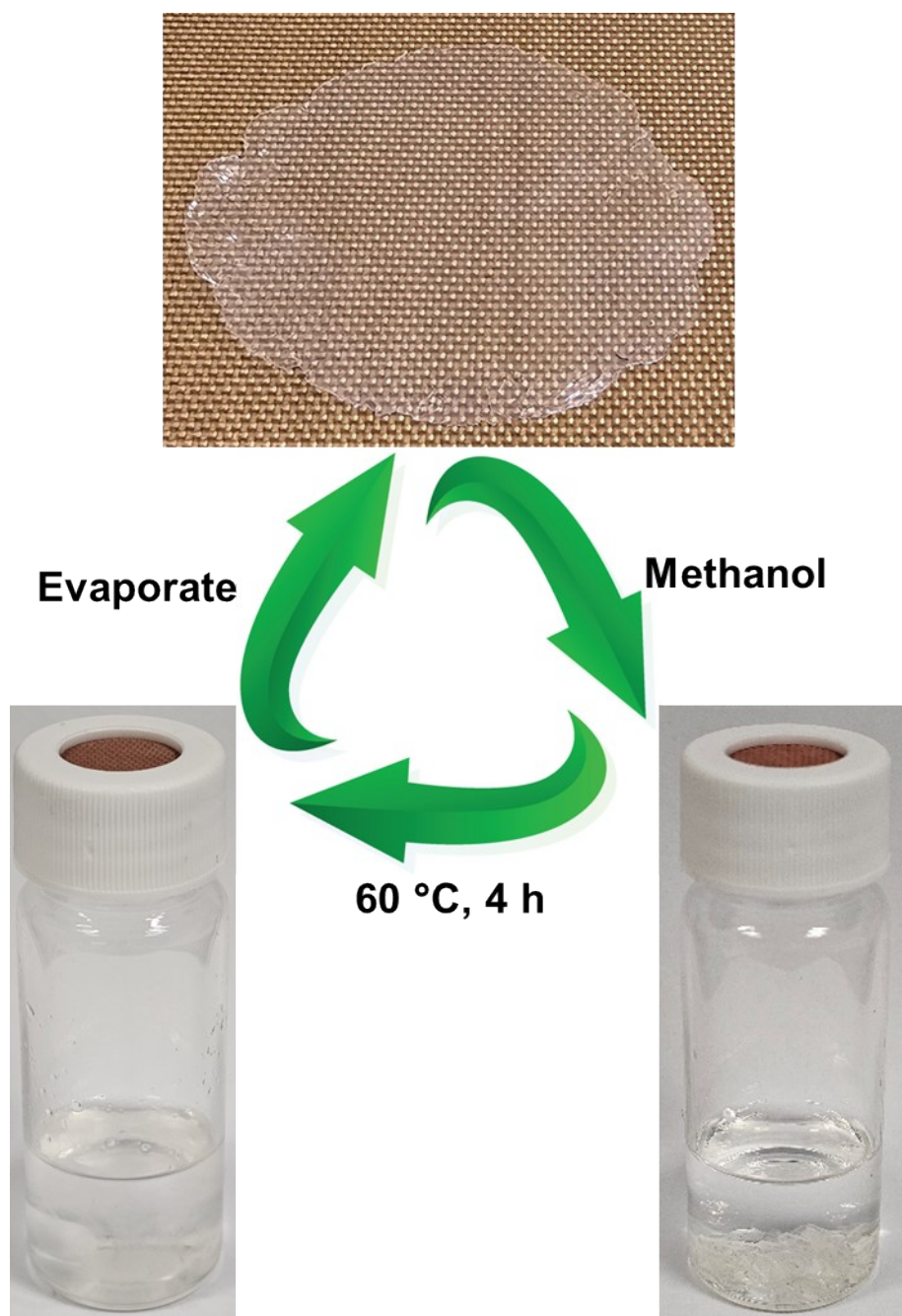


Fig. S36 Chemical recycling of FV1 by stirring in methanol at 60 °C

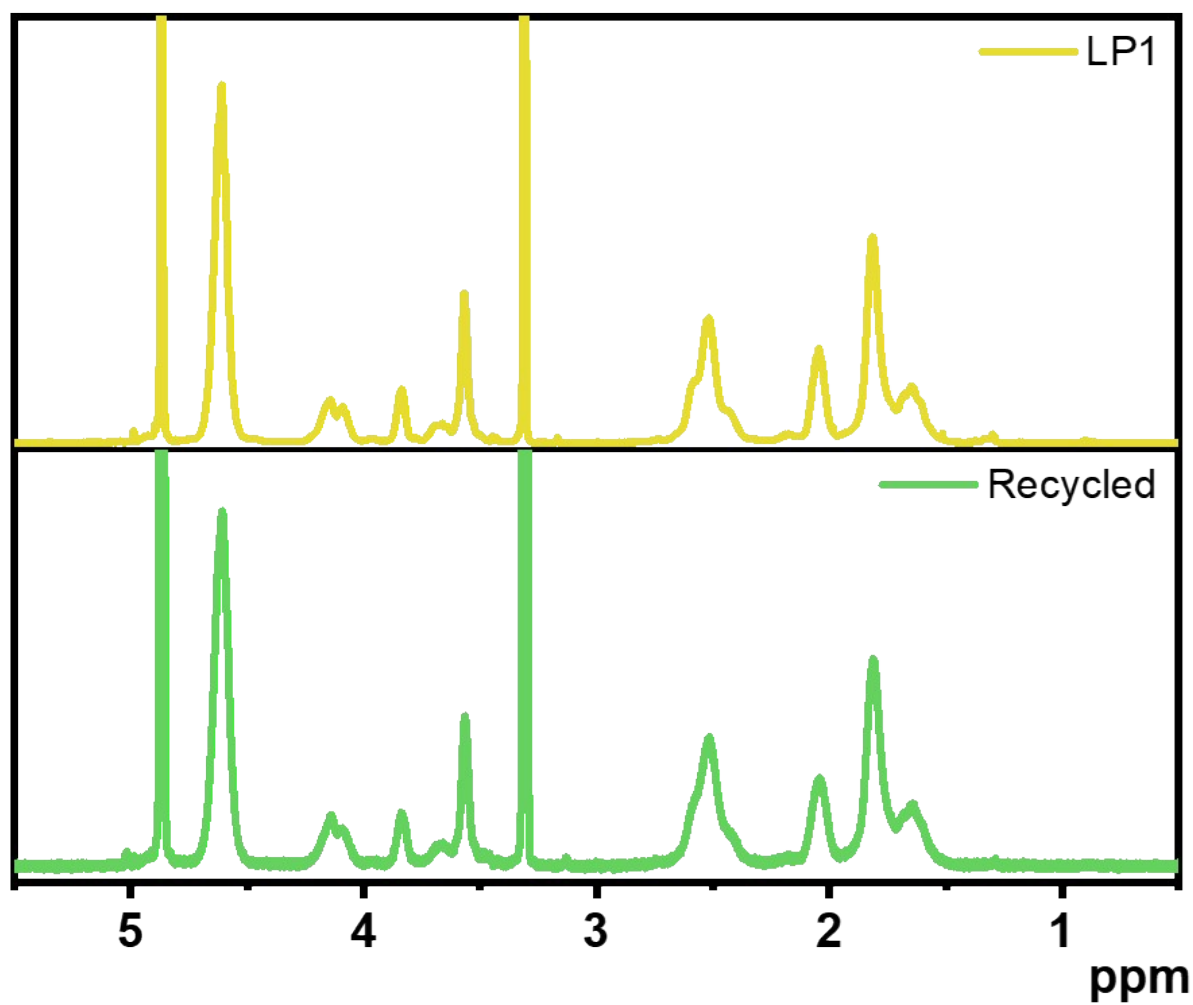


Fig. S37. ¹H NMR spectrum of original LP1 and recycled LP1 in methanol-D₄ solvent.

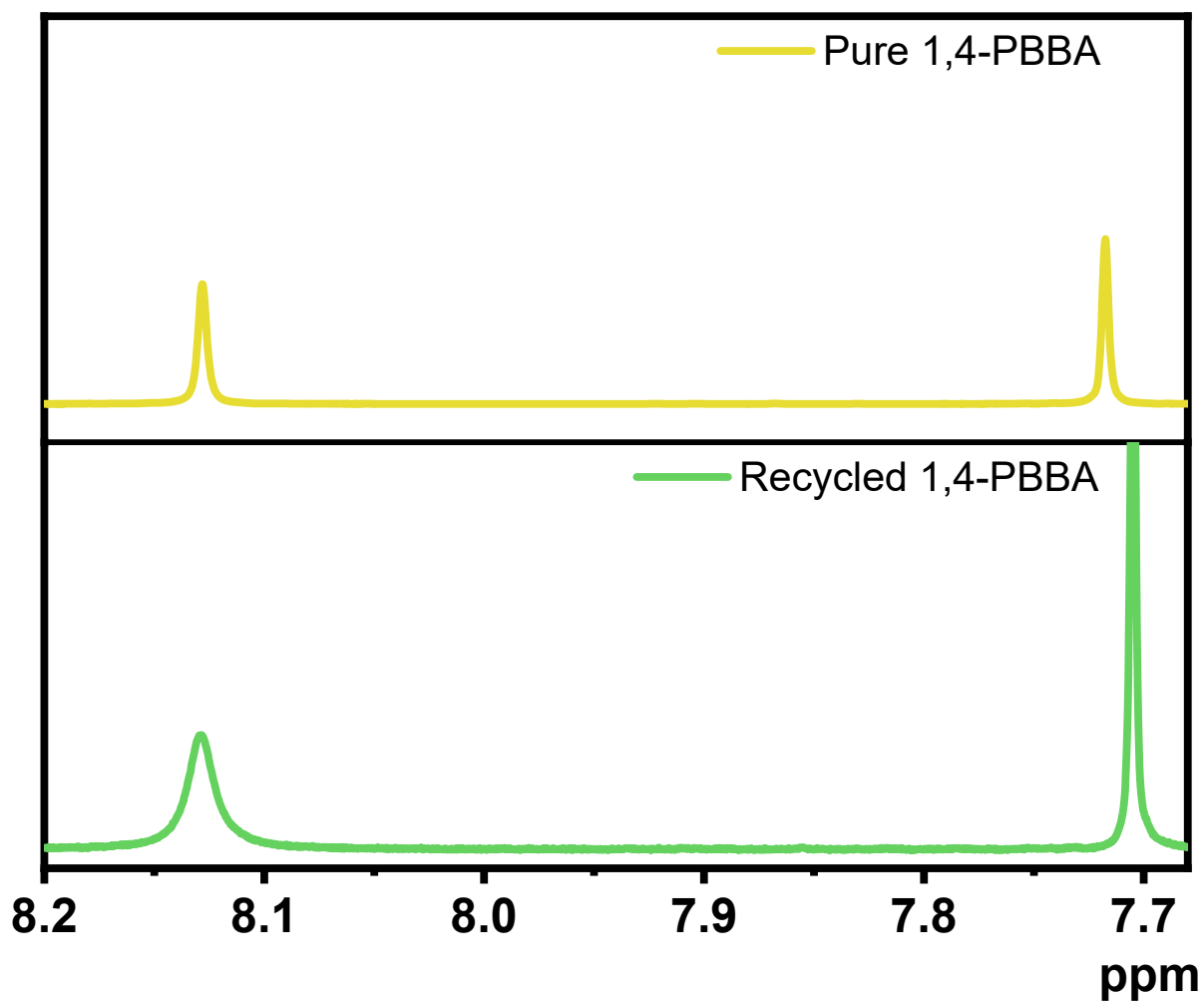


Fig. S38. ¹H NMR spectrum of original 1,4-phenylenediboronic acid and recycled 1,4-phenylenediboronic acid in CDCl₃ solvent.

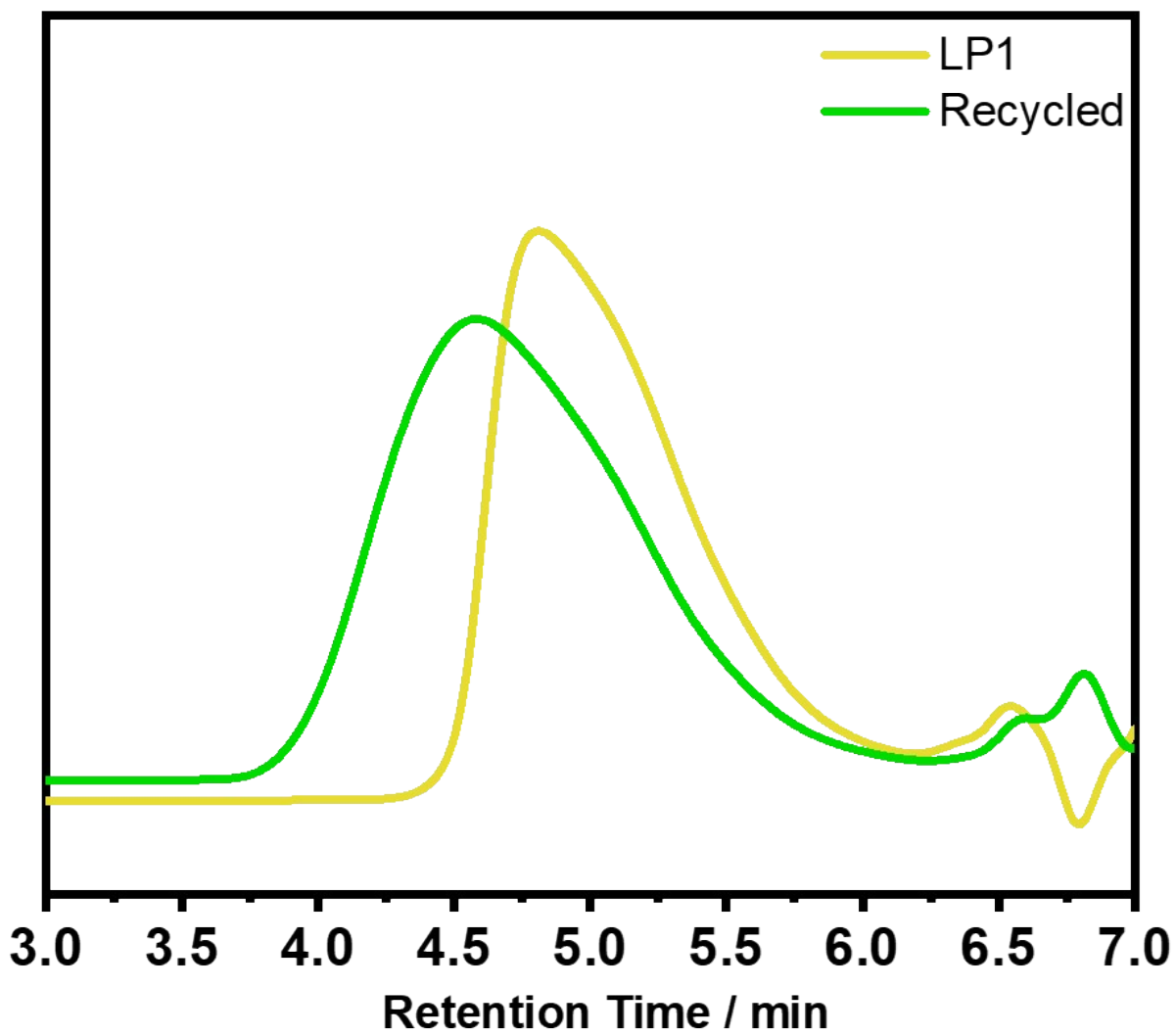


Fig. S39 GPC trace of original LP1 and recycled LP1

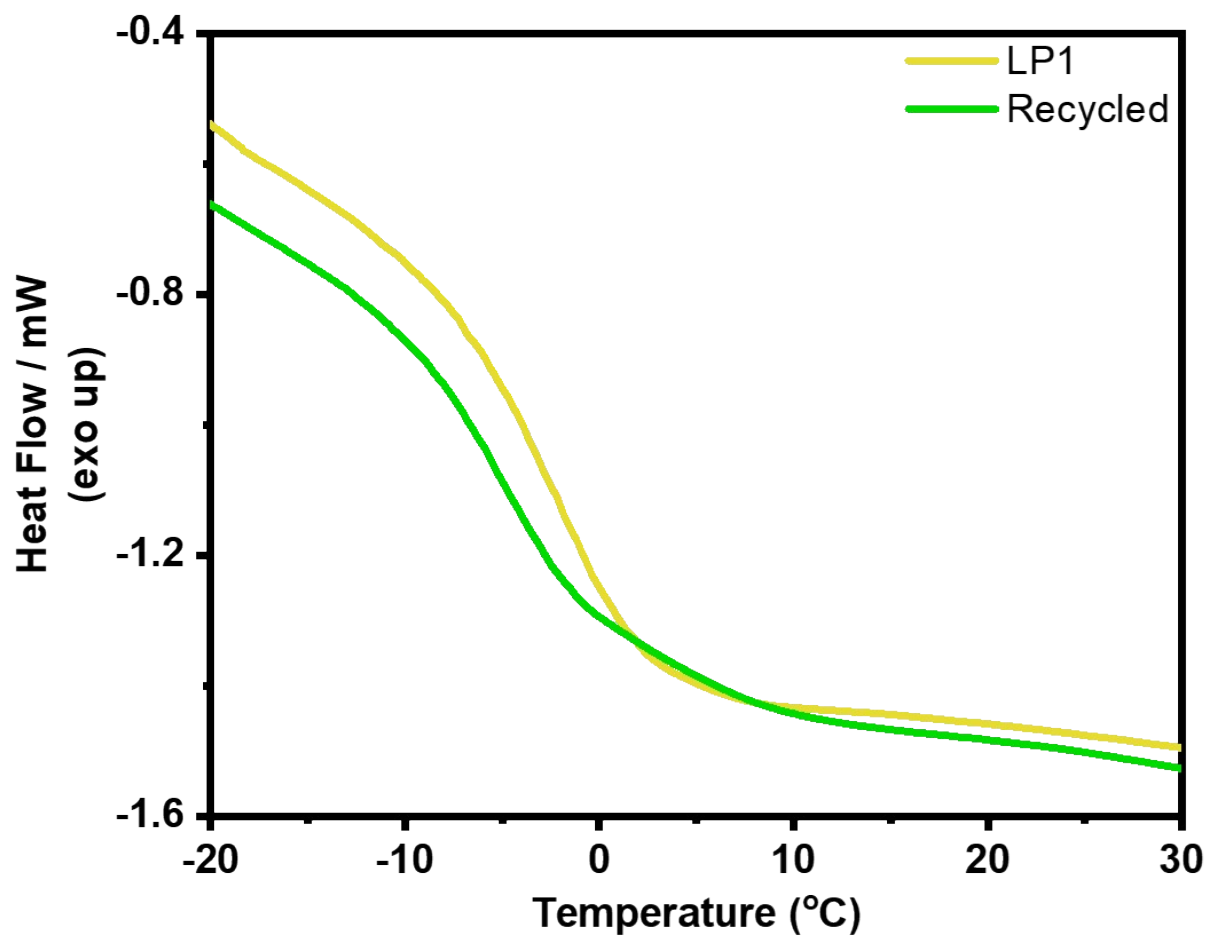


Fig. 40 DSC thermogram of original LP1 and recycled LP1

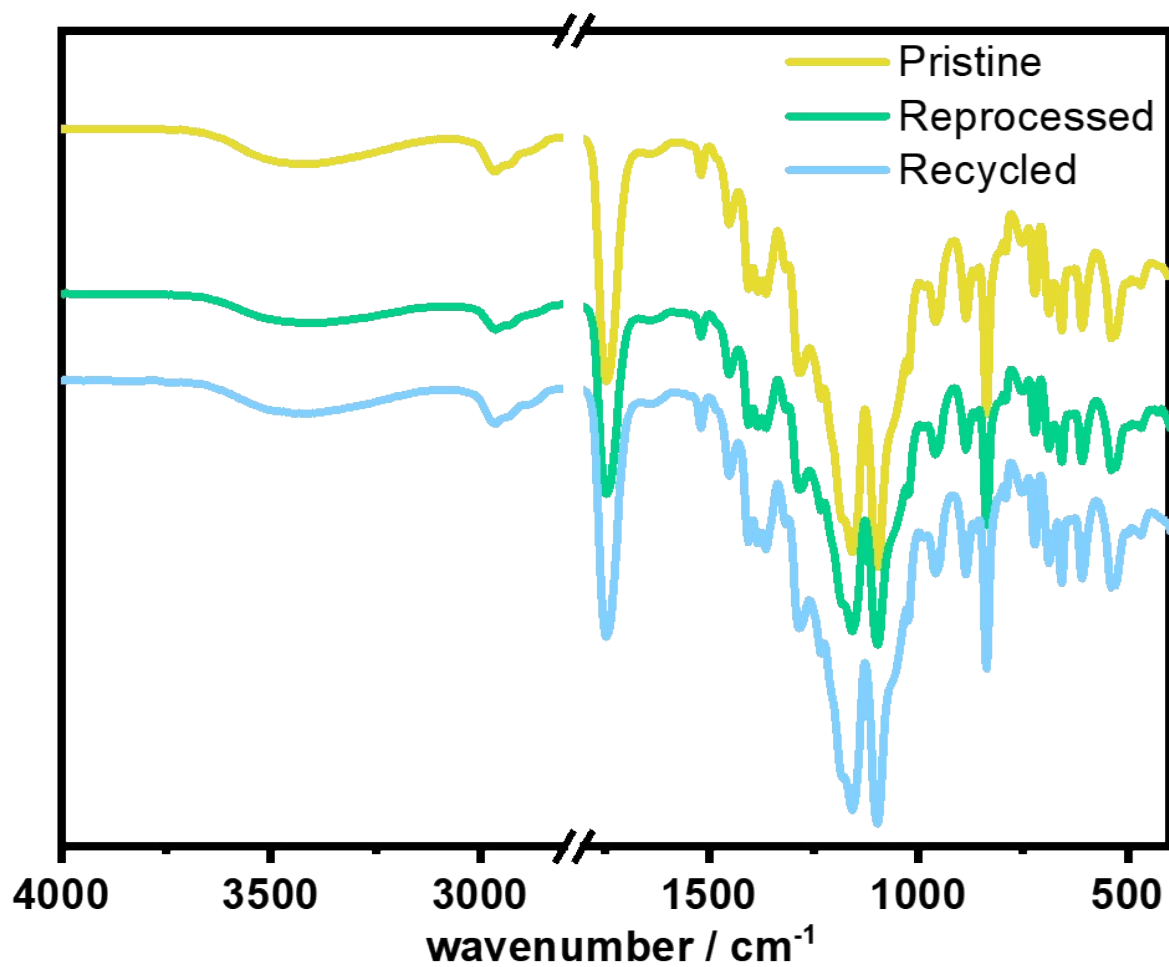


Fig. S41 FTIR spectra of pristine, reprocessed and recycled FV1

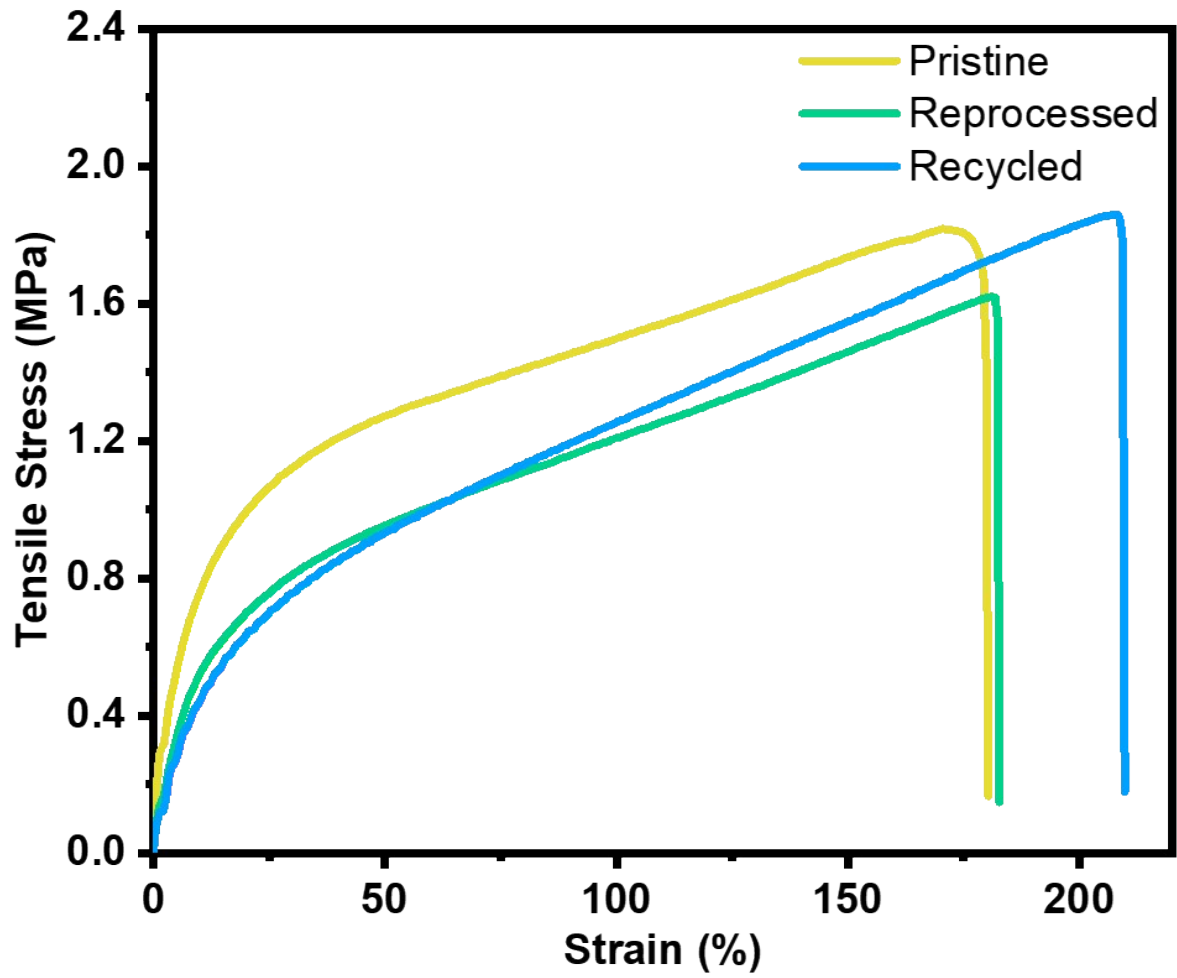


Fig. S42 Tensile test of of pristine, reprocessed and recycled FV1.