

Lignin-based Bisguaiacol diisocyanate: a green route for the synthesis of biobased polyurethanes

Sébastien Lemouzy, ^{†a} Aliénor Delavarde, ^{†a} Frédéric Lamaty, ^b Xavier Bantreil, ^{b,c} Julien Pinaud, ^a and Sylvain Caillol ^{*a}

^a ICGM, Université Montpellier, CNRS, ENSCM, 34095 Montpellier, France. E-mail: sylvain.caillol@enscm.fr

^b IBMM, Université de Montpellier, CNRS, ENSCM, Montpellier, France

^c Institut universitaire de France (IUF)

[†]Both authors equally contributed to this study.

General information

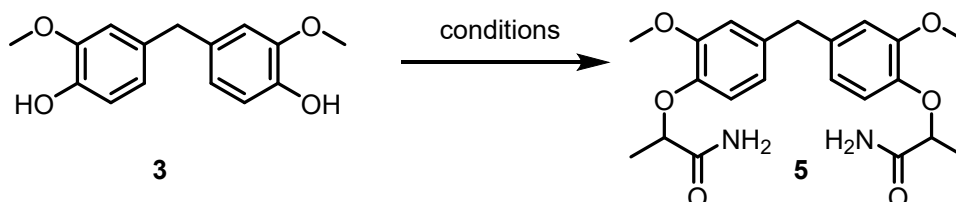
2-methoxyphenol (guaiacol, ≥99%), 4-Hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, 98%), sulfuric acid (H₂SO₄, 99.99%), potassium carbonate (K₂CO₃, ≥99%) potassium iodide (KI, ≥99%), 2-bromopropionamide (99%), hydroxide potassium (KOH, ≥85%), triethylamine (≥99.5%), di-*tert*-butyl dicarbonate (Boc₂O, 99%), 4-(dimethylamino)pyridine (DMAP, ≥99%), methylene diphenyl diisocyanate (MDI, 98 %), 1,3,5-trimethoxybenzene (≥99%), d-chloroform (CDCl₃, 99.5 % D) were supplied by Sigma-Aldrich (Darmstadt, Germany) and used as received. Velvetol® H500 was kindly supplied by WeylChem International GmbH (Frankfurt am Main, Germany) and used as received. Glycerol (≥99.5%) was purchased by Prolabo (Paris, France) and used as received.

Silica gel plates (GF254, coating thickness 0.2-0.25 mm) were employed for thin-layer chromatography (TLC), and 200-300 mesh silica gel was used for flash column chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance™ 400 spectrometer at ambient temperature with CDCl₃ as solvent. Chemical shifts were reported in ppm with tetramethylsilane as an internal standard. The Fourier transform infrared spectra were recorded using a ThermoScientific Nicolet 210 FT-IR spectrometer equipped with a Specac golden gate attenuated total reflection (ATR) heating cell. The characteristic IR spectra were plotted in transmittance mode, then we observed the disappearance of the isocyanate peak. The conversion degree of curing reaction is given by $U = (A_0 - A_t)/A_0$ where A_0 is the peak area of C=O stretching (OCN function) at t_0 and A_t is the peak area of C=O stretching (OCN function) over the time. High resolution mass spectrometry (HRMS) data were obtained on a LC-TOF mass spectrometer (microTOF-Q) using electrospray ionization (ESI) in positive or negative mode. GCMS were analyzed by electrospray ionization (ESI) using Shimadzu QP2010SE mass spectrometer. Thermogravimetric analyses (TGA) of the cured polyurethanes were performed on a Netzsch STA 449 F1 TGA. The protective gas used was nitrogen with a 20 mL·min⁻¹ flow. Approximately 10 mg of sample was placed in an alumina crucible and heated from room temperature to 800 °C with a 10 °C·min⁻¹ heating ramp. Differential scanning calorimetry (DSC) analyses were carried out using a Netzsch DSC 3500 Sirius calorimeter. Nitrogen was used as the purge gas at 40 mL·min⁻¹. Approximately 10 mg of sample was placed in pierced aluminum pans. The melting temperatures were recorded between room temperature and 150°C at 20 °C·min⁻¹. The thermal properties of the thermoset materials were recorded between -100 and 200 °C at 20 °C·min⁻¹ to observe the glass transition temperature. Gelation times were determined using a ThermoFischer Mars 60 rheometer using plate-plate aluminium disposable geometry (25 mm diameter, 0.4 mm gap, 0.2 mL of formulation). Measurements were performed using a multi-frequency program (0.8 Hz, 3 Hz and 7 Hz) at 90°C with a stress of 3 Pa.

The milling reactions were carried out in a vibratory Retsch Mixer Mill 400 (vbm) operated at up to 30 Hz. The microwave reactions were carried out in an Anton Paar Monowave 300 microwave reactor using standard 5 mL glass vials.

1. Experimental section

1.1 General procedure for the synthesis of bis O-Alkylated bisguaicol F



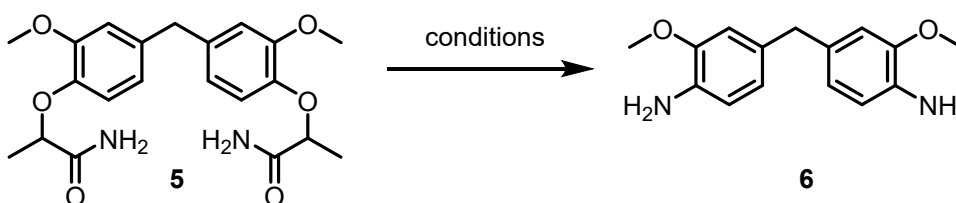
- Thermal procedure

Bisguaicol F (1 equiv., 1.92 mmol, 5 g), potassium iodide (0.1 equiv., 0.19 mmol, 0.32 g), potassium carbonate (3 equiv., 5.77 mmol, 7.96 g) and 2-bromopropionamide (2 equiv., 3.84 mmol, 5.80 g) were taken in a 500 mL round bottomed flask equipped with a magnetic stirrer and a reflux condenser. To the stirring mixture, 150 mL of acetonitrile was added. Then, the reaction mixture was heated to reflux for 24 h, cooled to room temperature, filtrated and concentrated under reduced pressure. The crude product was purified through flash column chromatography on silica gel with dichloromethane-methanol as eluents. After evaporation of the solvents, the isolated bis O-Alkylated bisguaicol F was obtained as a white to yellowish powder with a yield of 94%.

- Mechanochemical procedure

A 20 mL stainless steel milling jar was loaded with bisguaicol F (1 equiv., 0.81 mmol, 0.212 g), potassium iodide (0.1 equiv., 0.08 mmol, 0.014 g), potassium carbonate (3 equiv., 2.41 mmol, 0.333 g), 2-bromopropionamide (2 equiv., 1.62 mmol, 0.245 g) and one 1 cm stainless steel ball. The reactor was then sealed and subjected to vibratory milling at 30 Hz for the set amount of time. The reaction mixture was then dissolved in acetonitrile, filtrated and concentrated under reduced pressure. The obtained bis O-Alkylated bisguaicol F was obtained as a white to yellowish powder with a full conversion.

1.2 General procedure for the synthesis of bisguaicol F diamine (BGA)



- Thermic procedure

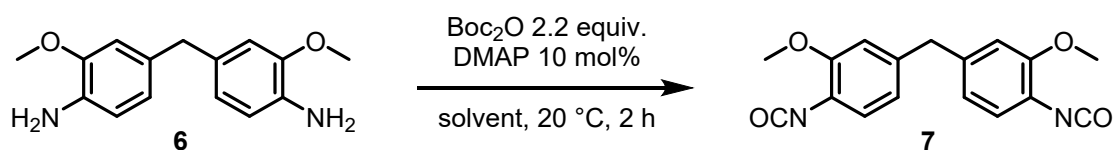
Bis O-Alkylated bisguaicol F (1 equiv., 12.4 mmol, 5 g) and potassium hydroxide (85% purity, 2.4 equiv., 29.8 mmol, 1.67 g) were taken in a 100 mL round bottomed flask equipped with a magnetic stirrer. The reaction mixture was dissolved in 50 mL of dry DMSO and heated at 140 °C for 18 h. The solution was then cooled to room temperature and diluted in water, extracted three times with ethyl acetate. The combined organic layers were washed one time with sat. brine solution and finally dried

over MgSO_4 . The crude product was purified through flash column chromatography on silica gel with cyclohexane/ethyl acetate as eluents containing (0.2%^v of triethylamine). After evaporation of the solvents, the obtained bisguaiacol F diamine was obtained a light brown powder with a yield of 66%.

- *Microwave procedure*

Bis O-Alkylated bisguaiacol F (1 equiv., 1.24 mmol, 0.500 g), potassium hydroxide (85% purity, 5.2 equiv., 6.46 mmol, 0.380 g) and 5 mL of solvent were added in a microwave reactor consisting in a 10 mL vessel tube, a pressure monitor system and a fiber optic temperature probe. The system was irradiated under microwave conditions at different temperature and during different periods. Reaction conversion was monitored by GCMS analysis using 1,3,5-trimethoxybenzene as internal standard.

1.3 General procedure for the synthesis of bisguaiacol F diisocyanate (BGI)



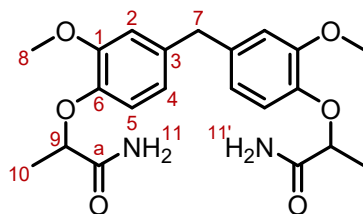
A solution of di-tert-butyl dicarbonate (2.2 equiv., 8.52 mmol, 1.86 g), DMAP (0.1 equiv., 0.39 mmol, 0.047 g) in 10 mL of dry acetonitrile was prepared in a 50 mL round bottomed flask equipped with a magnetic stirrer. A solution of bisguaiacol F diamine (1 equiv., 3.87 mmol, 1 g) in 10 mL of dry acetonitrile was then slowly added to the previous solution. The reaction mixture was stirred at room temperature for 2 h and then concentrated under reduce pressure. The crude product was purified through flash column chromatography on silica gel with cyclohexane/ethyl acetate as eluents. After evaporation of the solvents, a highly pure ($\geq 99\%$) bisguaiacol F diisocyanate was obtained as a white powder with a yield of 70%.

1.4 General procedure for the synthesis of polyurethane thermosets through a two-step method

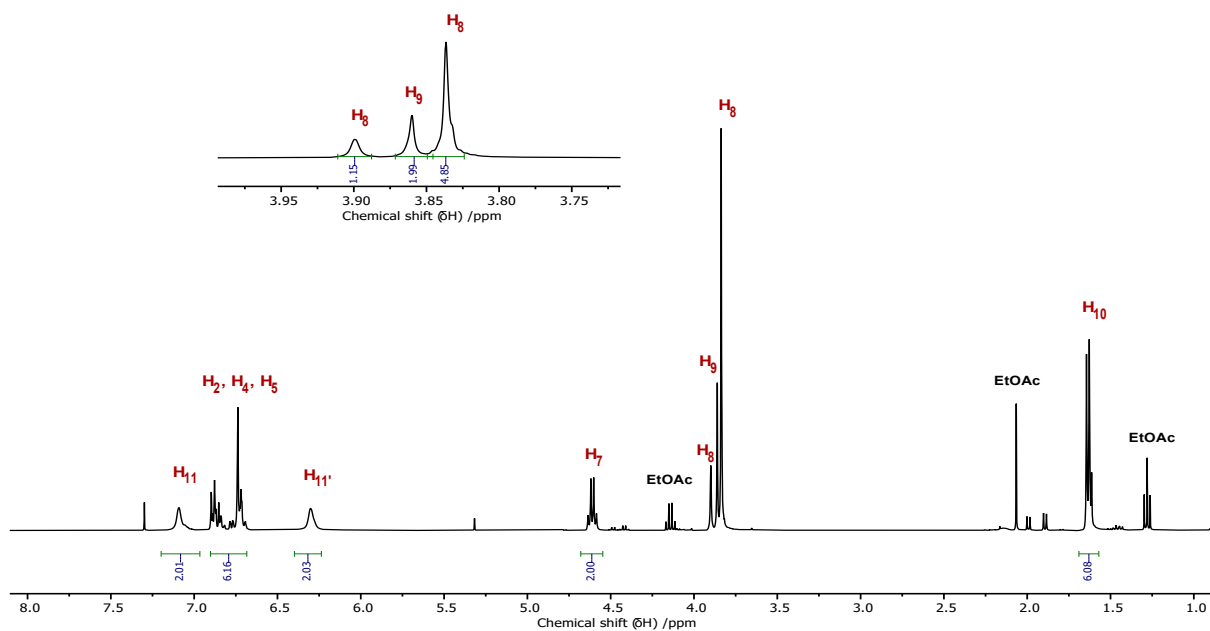
As a representative example, 2.40 g of BGI (2.5 equiv., 0.77 mol) was introduced in a 10 mL two necks round-bottom flask, equipped with a mechanical stirrer. The system was purged with nitrogen for 10 min and then heated up to 90 °C. Afterwards, 1.60 g of Velvetol[®] H500 (1 equiv., 2.72 mmol) were added with a syringe driver for one hour. The mixture was mechanically stirred for 4 h at 90 °C. Finally, 2.60 g of the obtained prepolymer was poured into a PP flask, and 0.187 g of glycerol was added. The mixture was mixed at 2500 rpm for 3 mins in a PP flask with a SpeedMixer[™], poured into a silicon mould, and cured at 90 °C for 24 h in oven.

2. Characterization of the products and the polyurethane materials

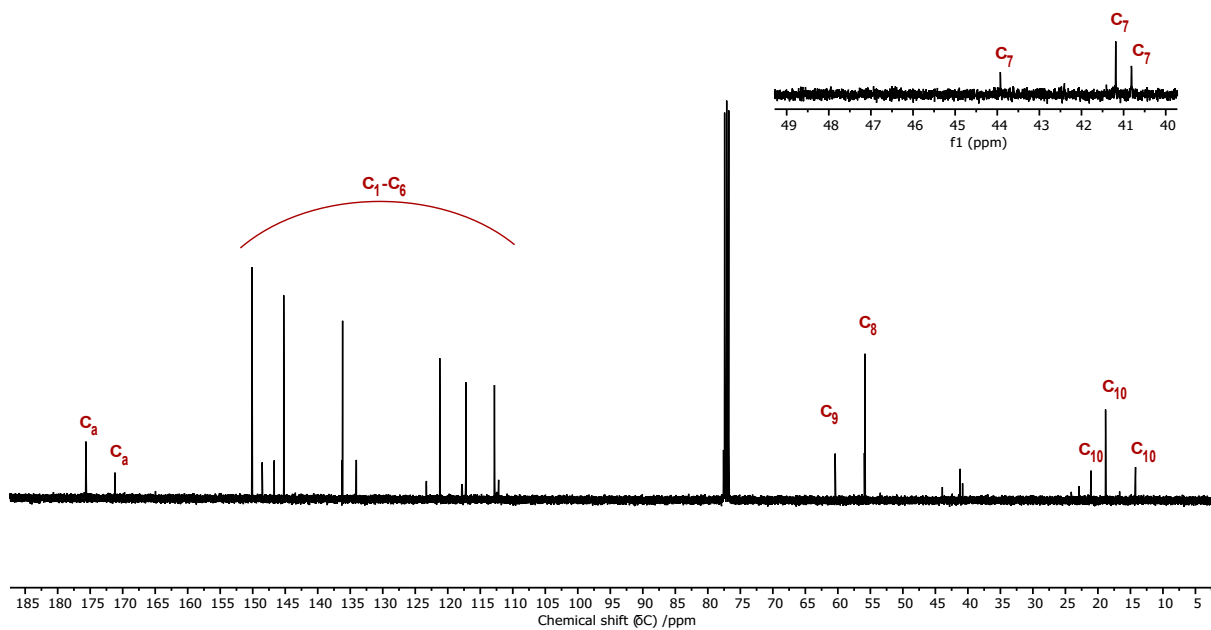
2.1 O-bis Alkylated BGF characterizations



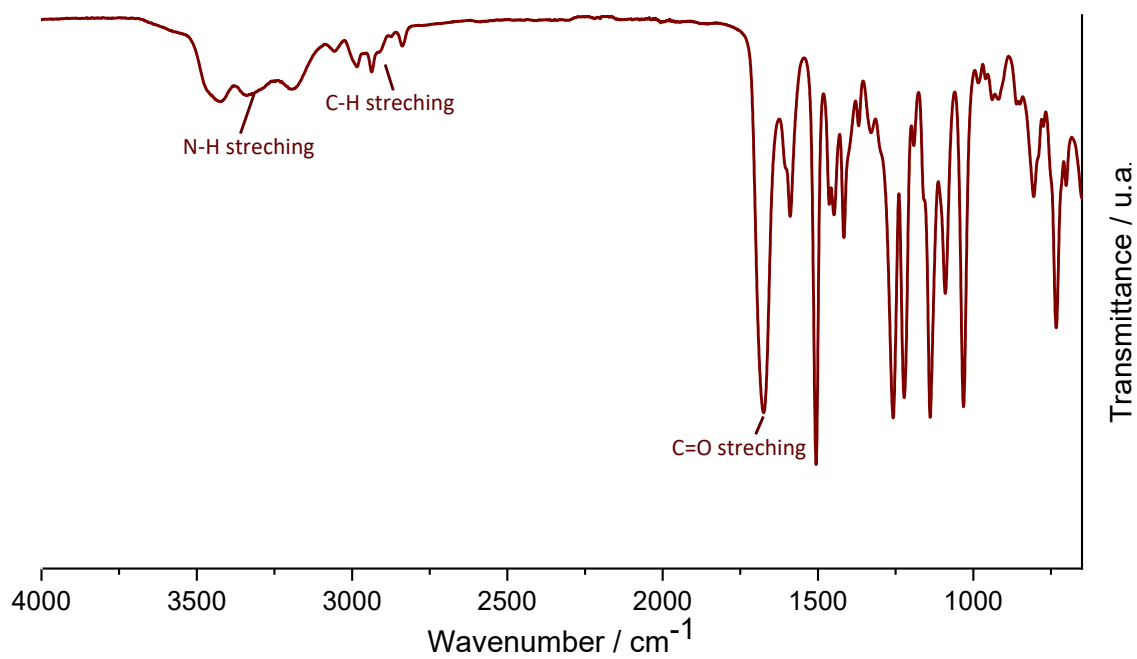
S1. Molecular structure assignment of O-bis Alkylated BGF



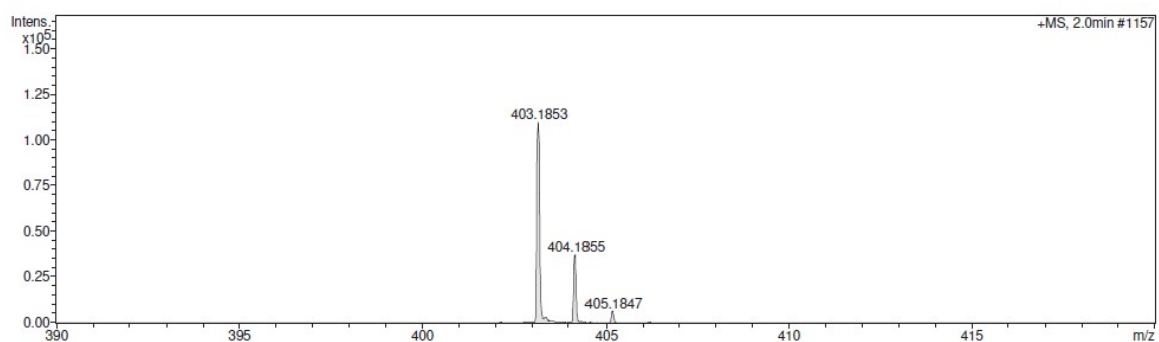
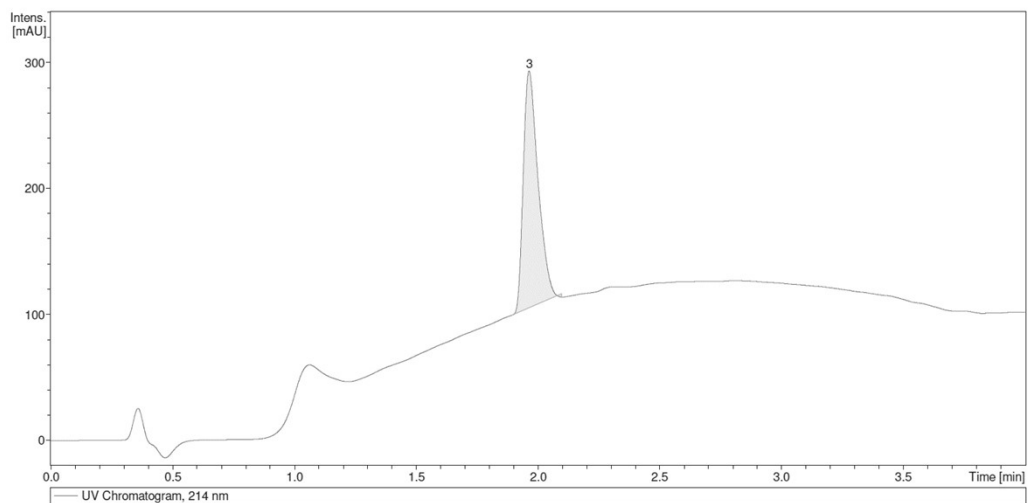
S2. ¹H NMR spectrum of O-bis Alkylated BGF (in CDCl₃)



S3. ^{13}C NMR spectrum of O-bis Alkylated BGF (in CDCl_3)

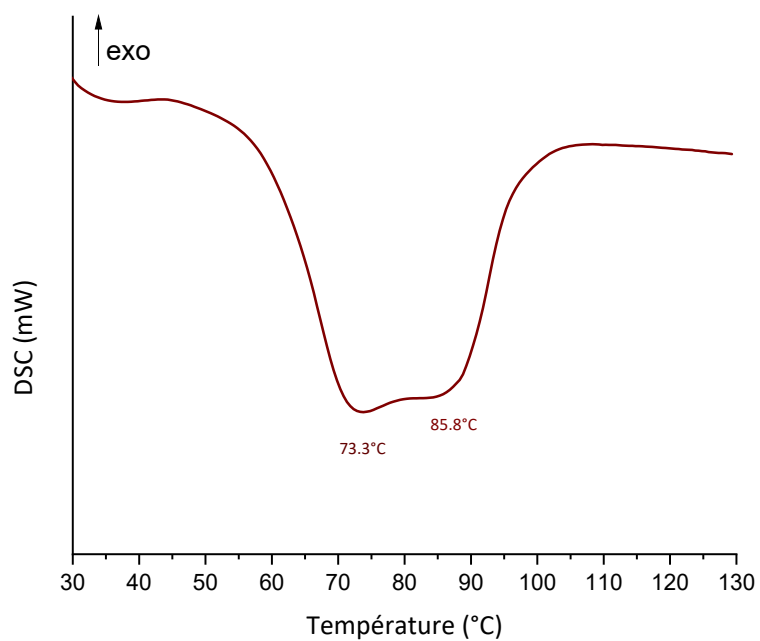


S4. FTIR spectrum of O-bis Alkylated BGF



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
403.1853	1	C ₂₁ H ₂₇ N ₂ O ₆	403.1864	2.6	50.1	1	100.00	9.5	even	ok

S5. (LC)-HRMS of O-bis Alkylated BGF



S6. DSC thermogram of O-bis Alkylated BGF

2.2 BGF diamine characterizations

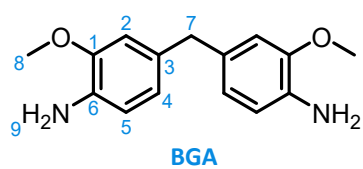
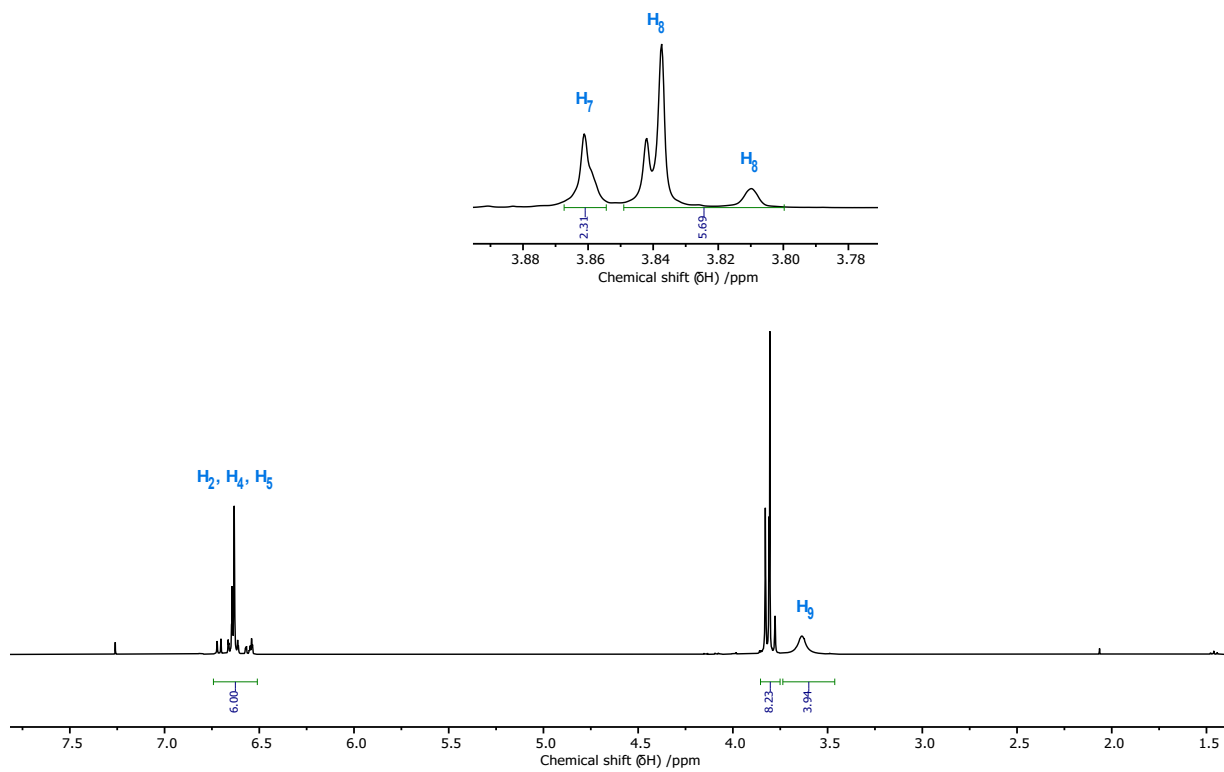
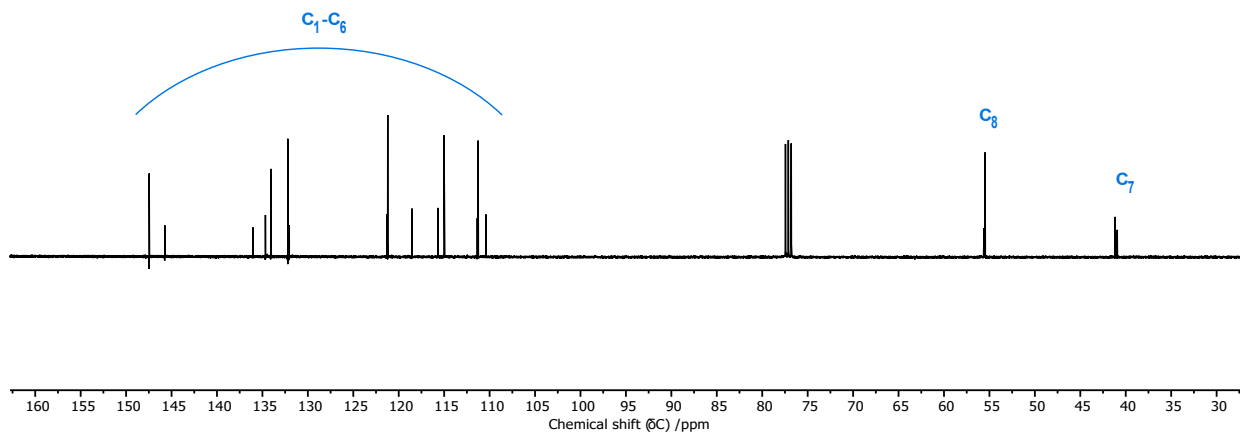


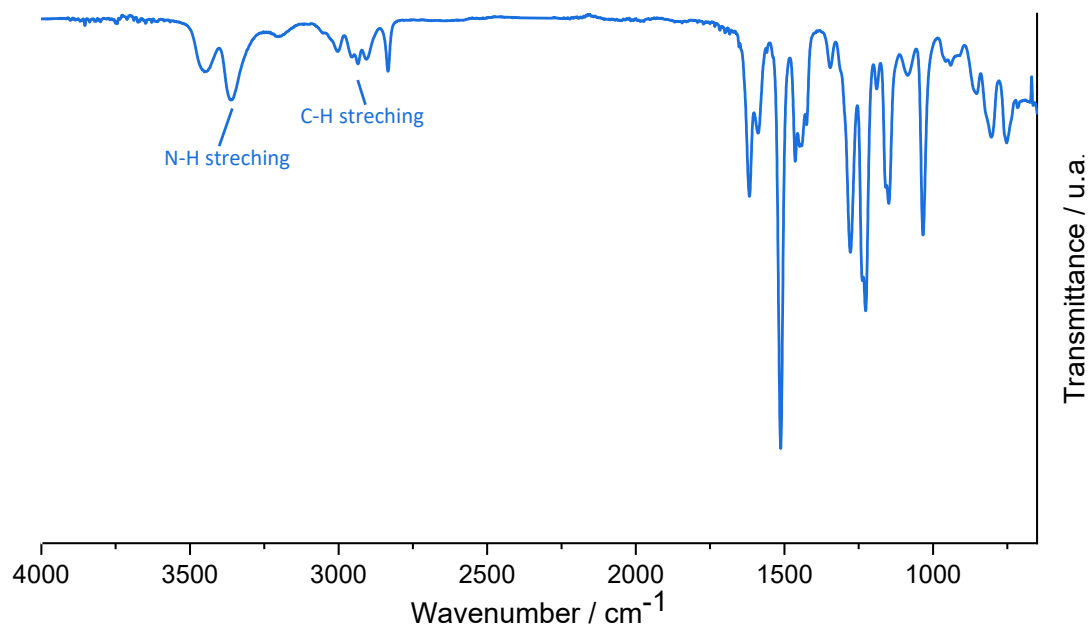
Figure S7. Molecular structure assignment of BGF diamine



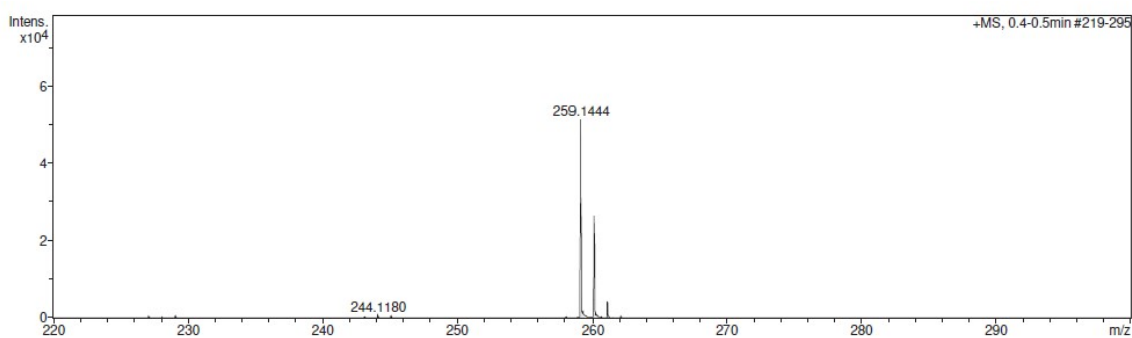
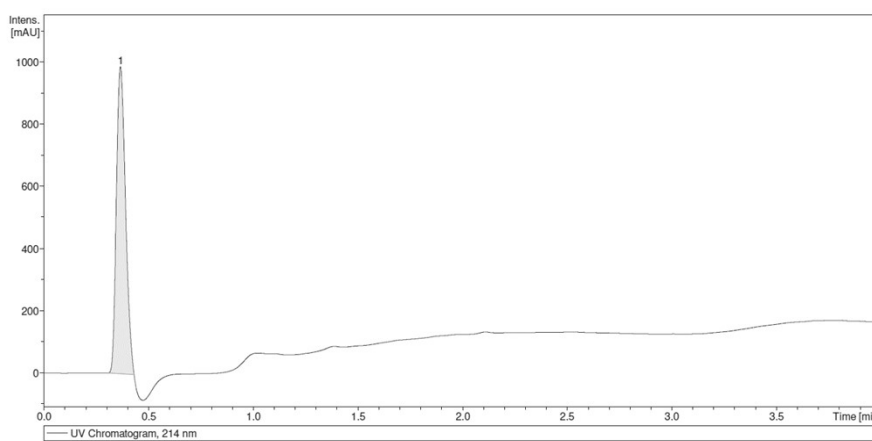
S8. ^1H NMR spectrum of BGF diamine



S9. ^{13}C NMR spectrum of BGF diamine

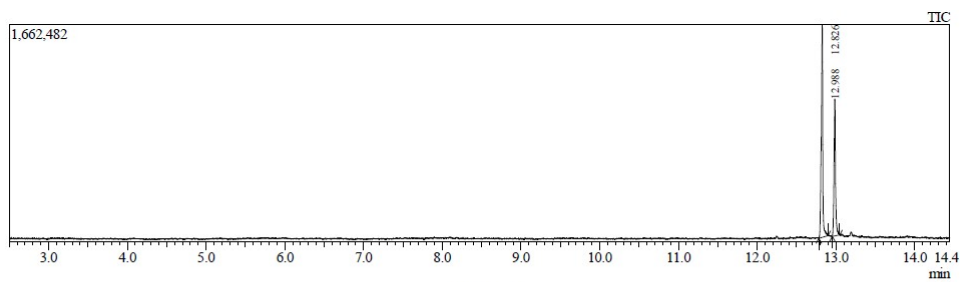


S10. FTIR spectrum of BGF diamine



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
259.1444	1	C ₁₅ H ₁₉ N ₂ O ₂	259.1441	-1.0	201.1	1	100.00	7.5	even	ok

Figure S11. (LC)-HRMS of BGF diamine



Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Name
1	12.826	12.783	12.900	2135753	60.30	1629111	BGF diamine isomer 1
2	12.988	12.953	13.047	1405934	39.70	1050088	BGF diamine isomer 2
				3541687	100.00	2679199	

Spectrum

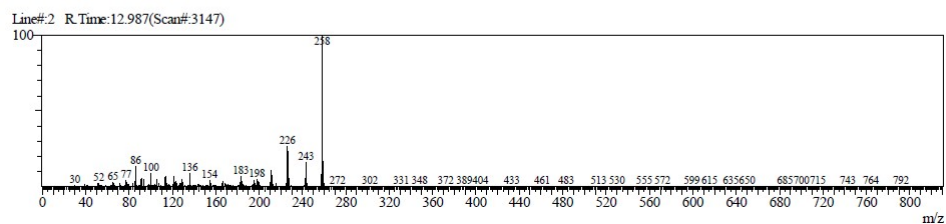
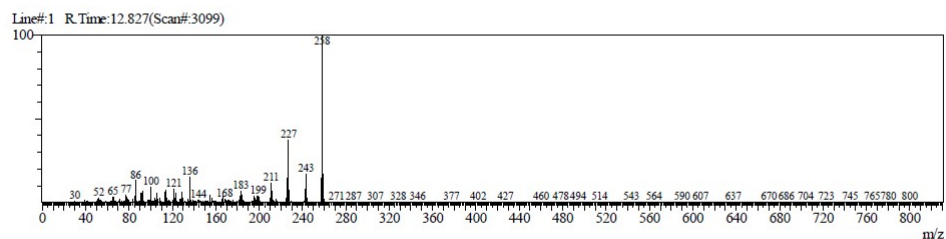


Figure S12. (GC)-MS of BGF diamine

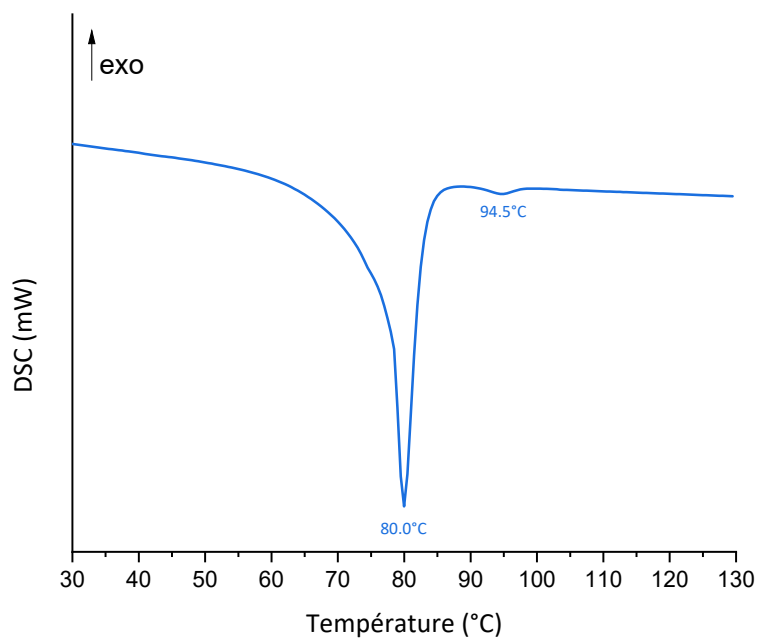


Figure S13. DSC thermogram of BGF diamine

2.3 BGF diisocyanate characterizations

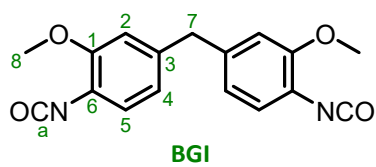


Figure S14. Molecular structure assignment of BGF diisocyanate

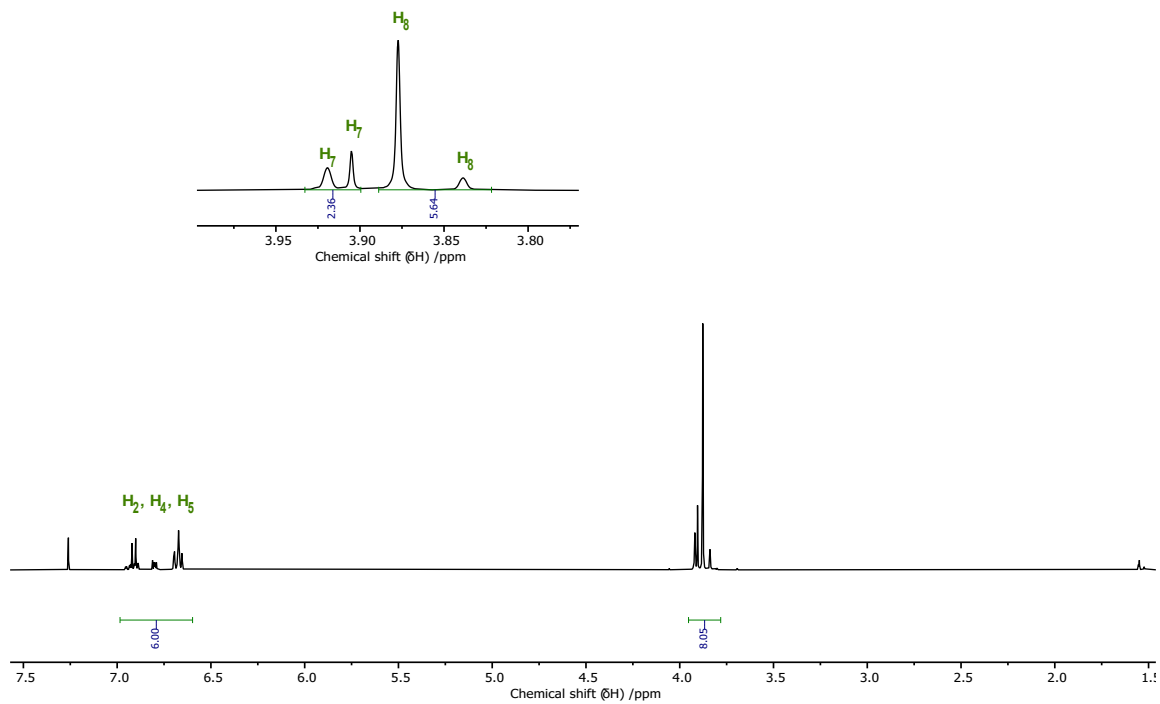


Figure S15. ¹H NMR spectrum of BGF diisocyanate

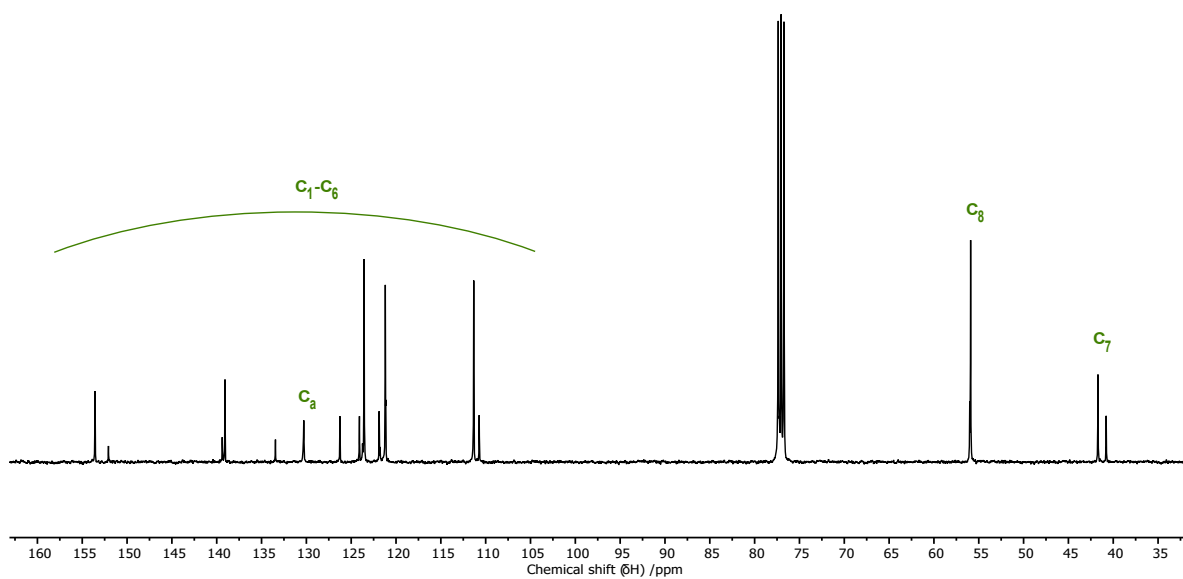


Figure S16. ¹³C NMR spectrum of BGF diisocyanate

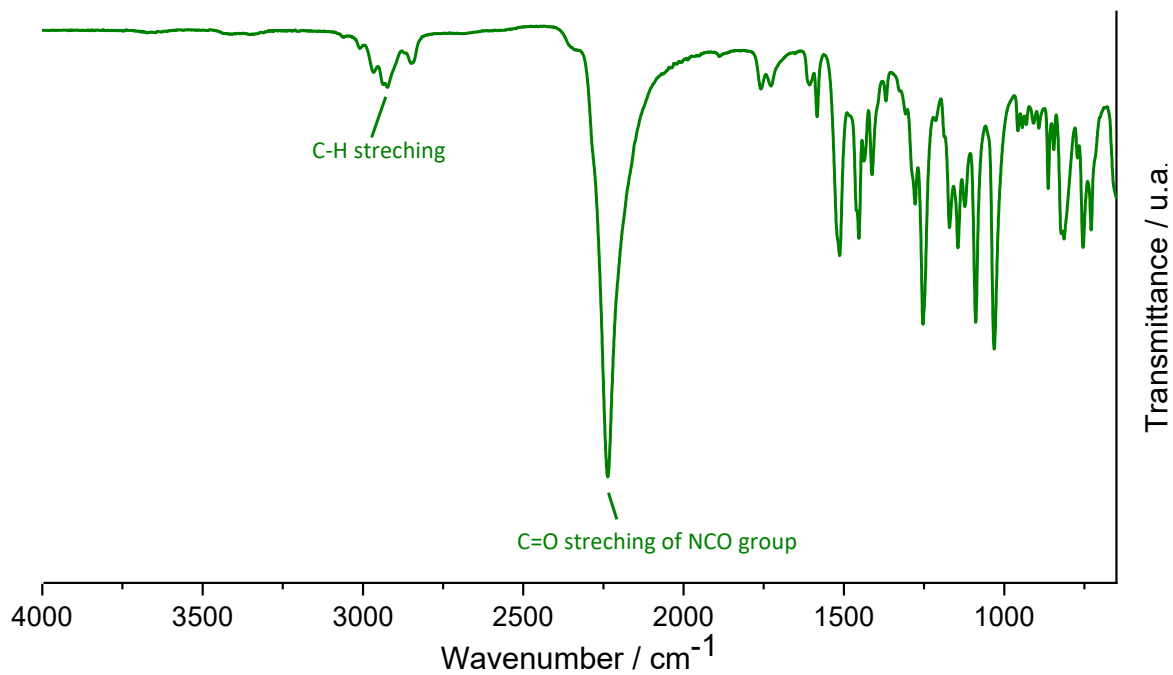


Figure S17. FTIR spectrum of BGF diisocyanate

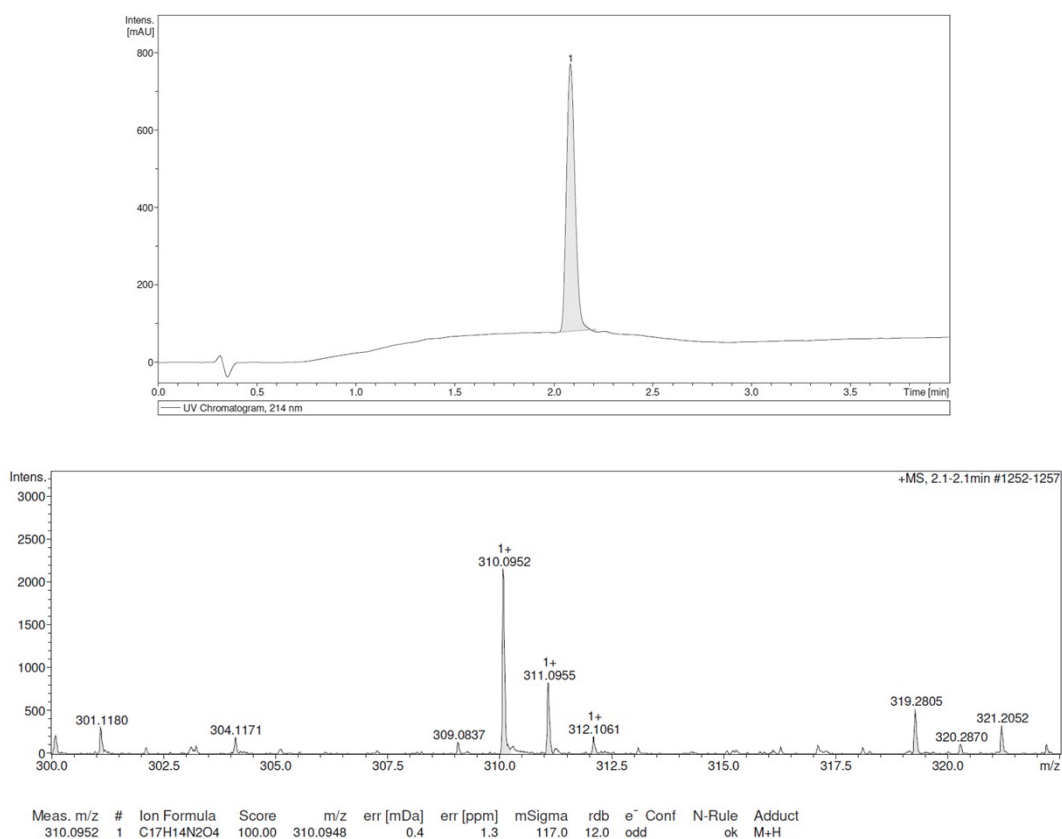


Figure S18. (LC)-HRMS of BGF diisocyanate

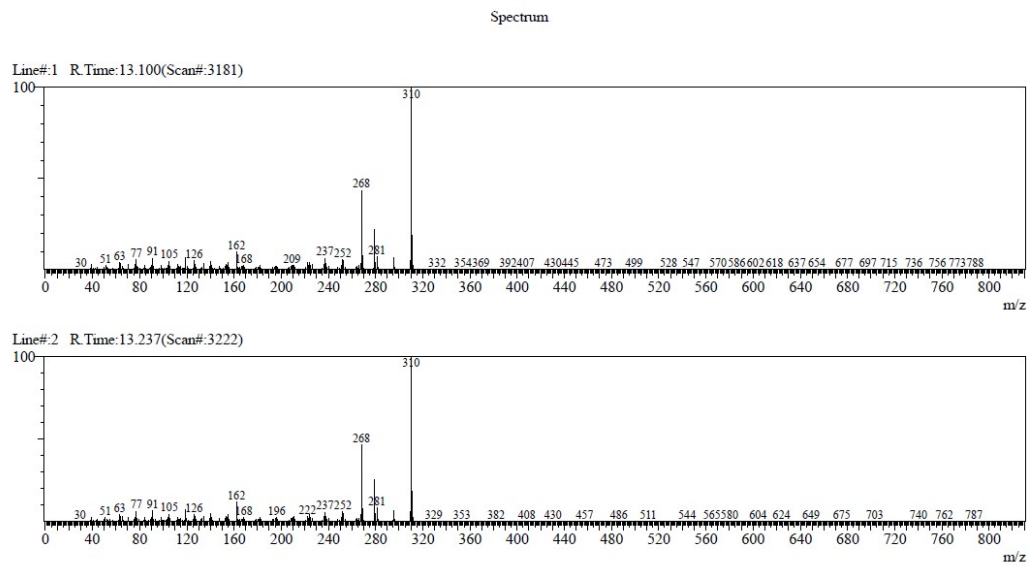
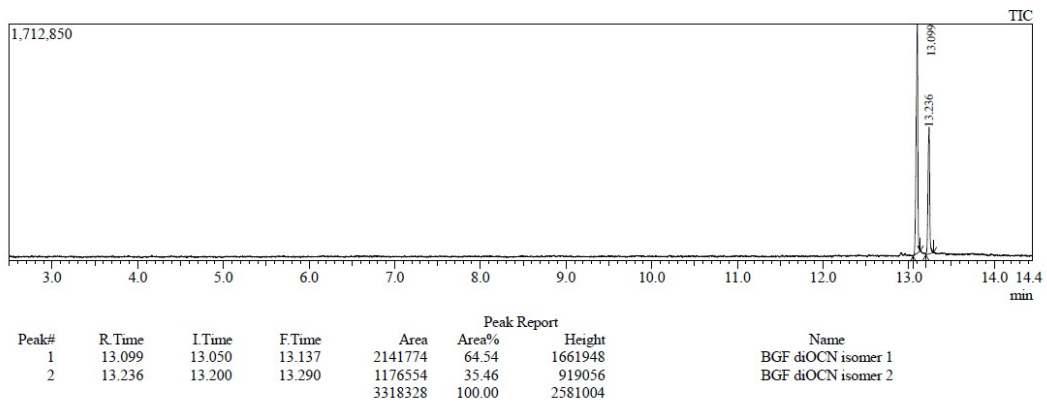


Figure S19. (GC)-MS of BGF diisocyanate

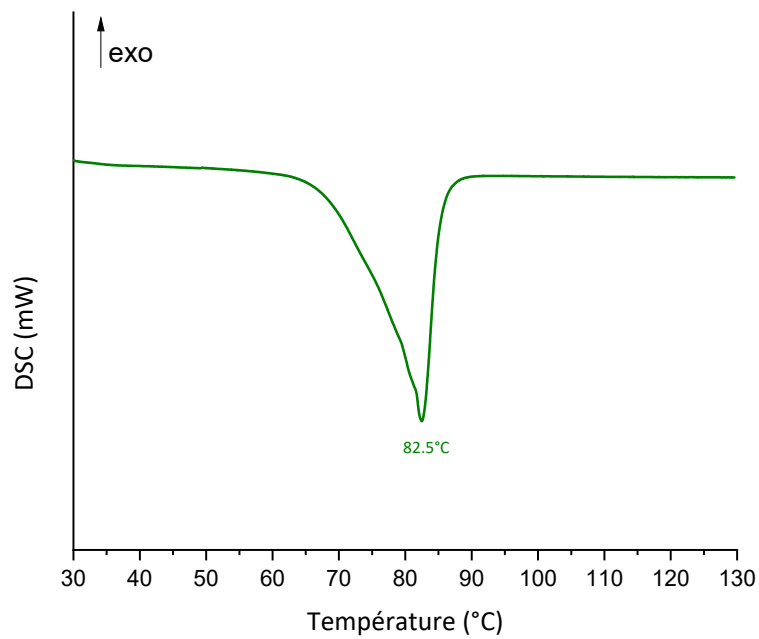


Figure S20. DSC thermogram of BGF diisocyanate

2.4 MDI-based prepolymer characterization

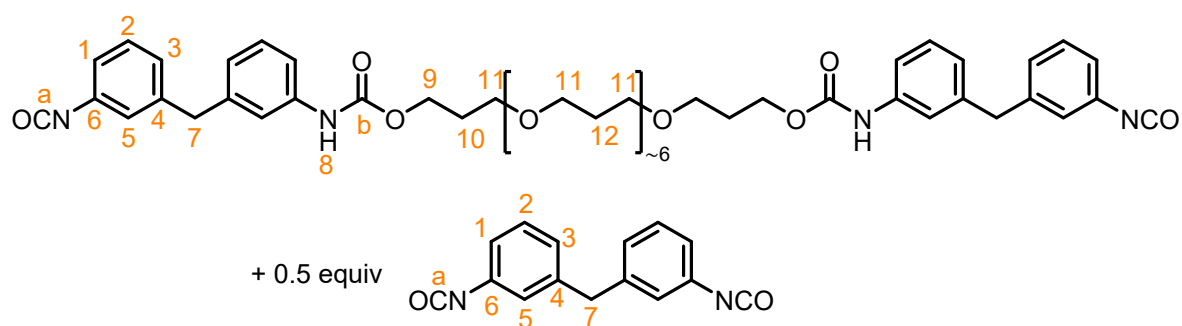


Figure S21. Molecular structure assignment of MDI-based prepolymer

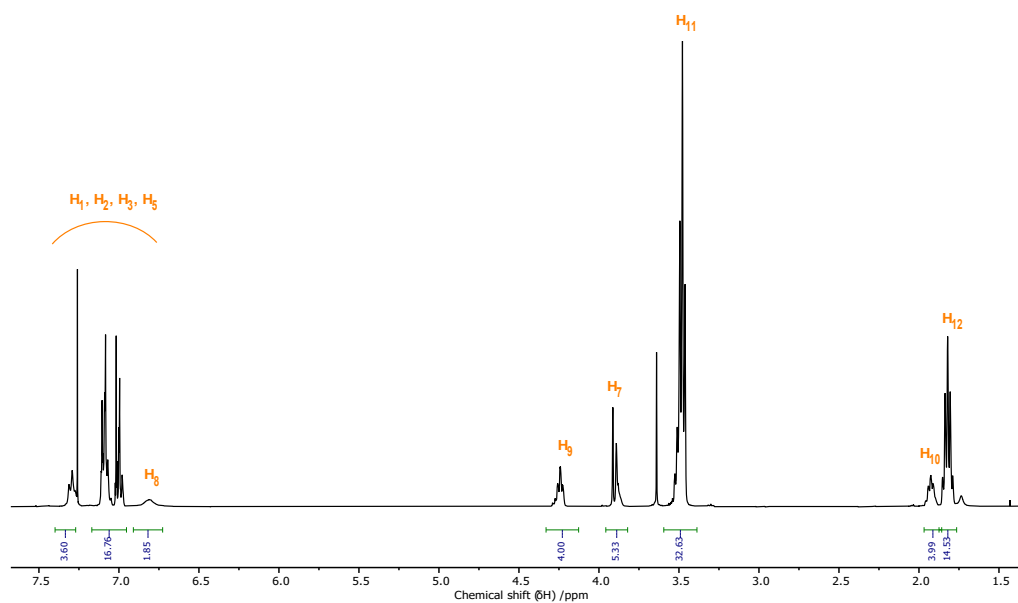


Figure S22. ^1H NMR spectrum of MDI-based prepolymer

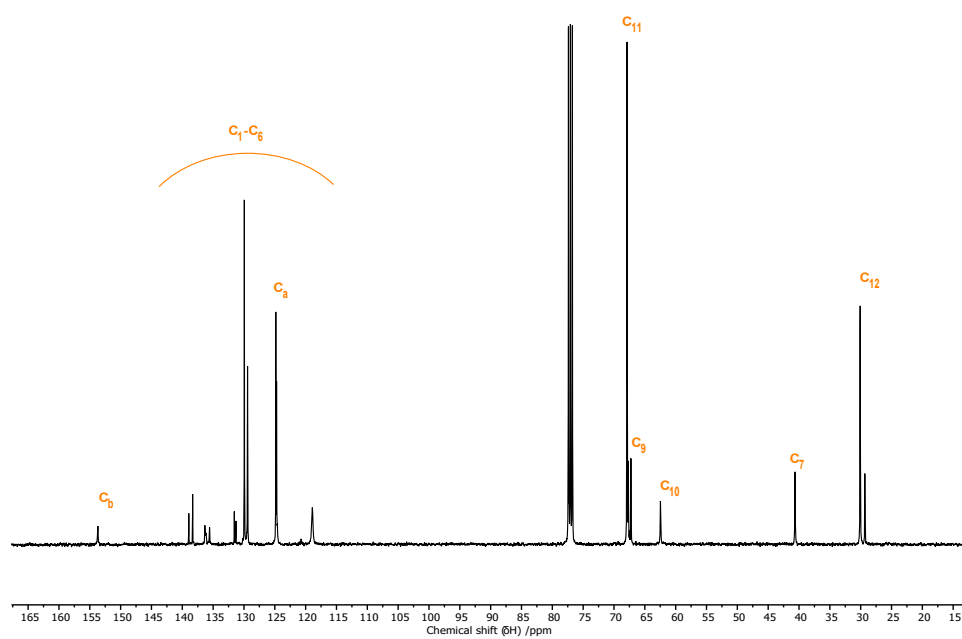


Figure S23. ^{13}C NMR spectrum of MDI-based prepolymer

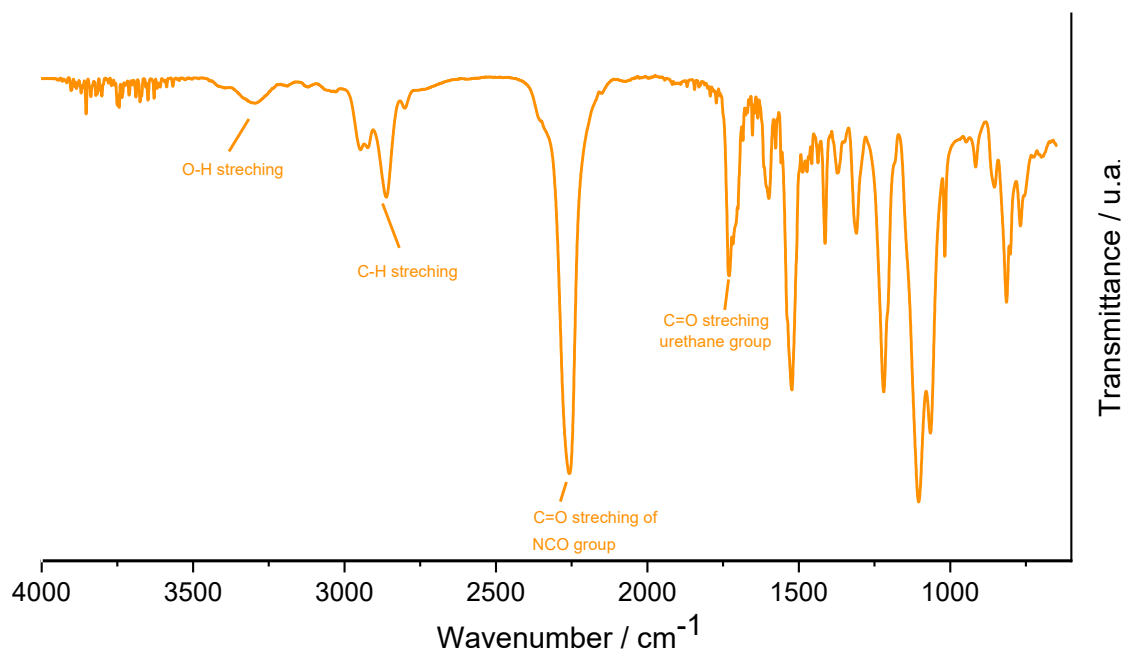


Figure S24. FTIR spectrum of MDI-based prepolymer

2.5 BGI-based prepolymer characterization

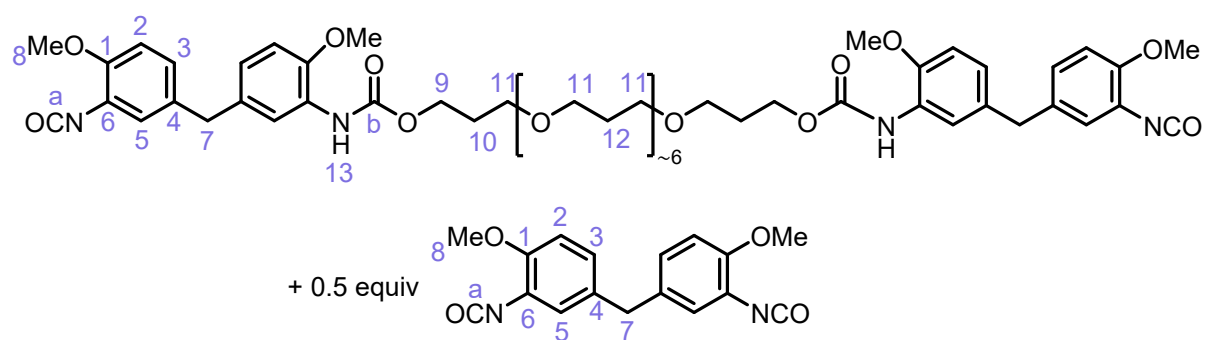


Figure S25. Molecular structure assignment of BGI-based prepolymer

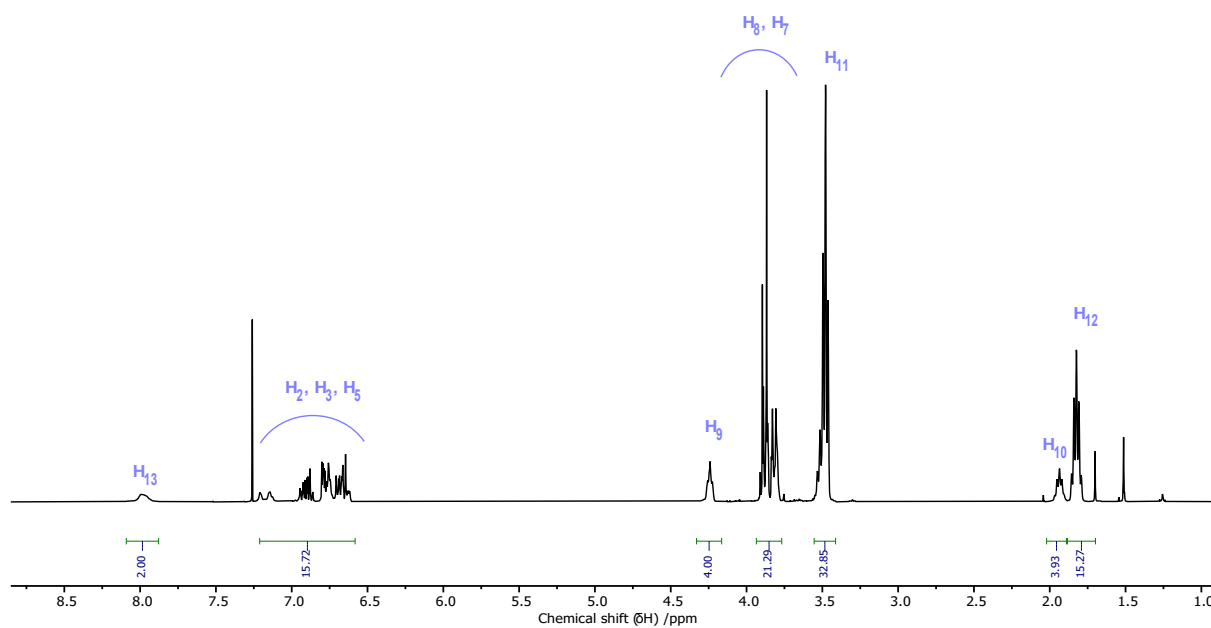


Figure S26. ^1H NMR spectrum of BGI-based prepolymer

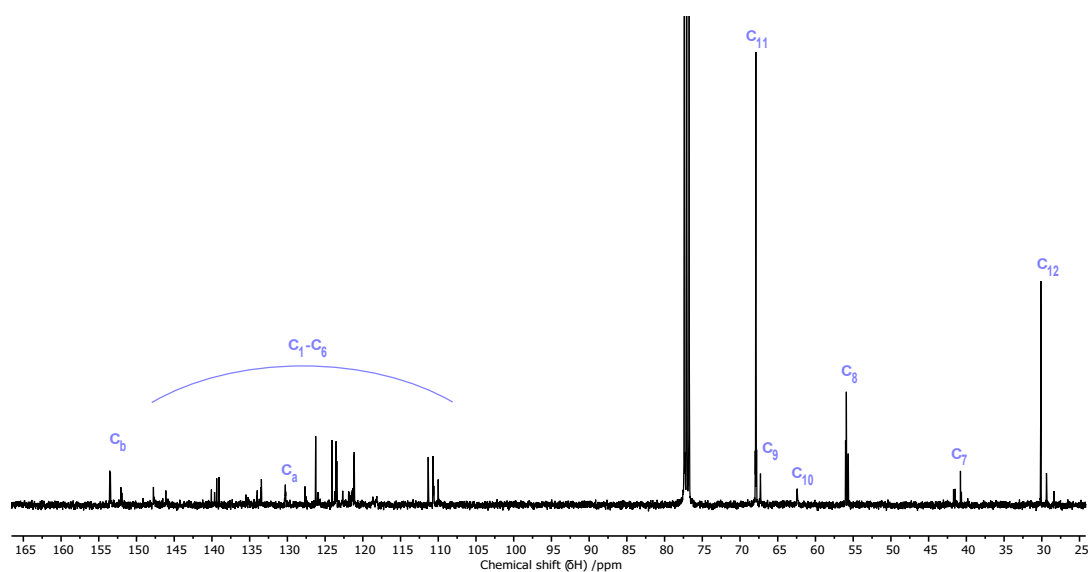


Figure S27. ^{13}C NMR spectrum of BGI-based prepolymer

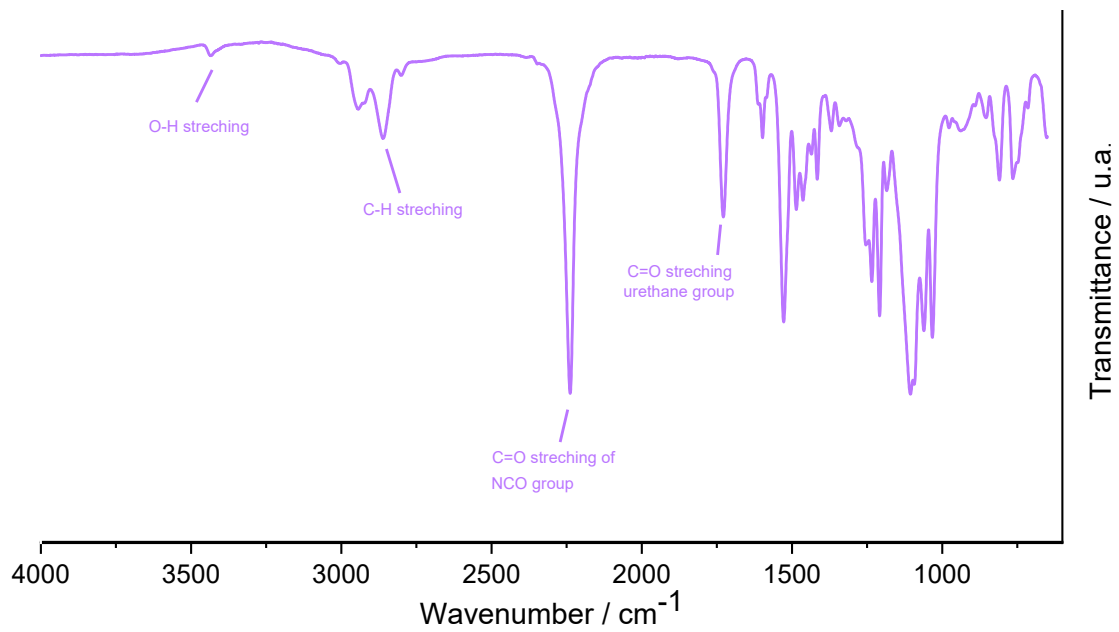


Figure S28. FTIR spectrum of BGI-based prepolymer

2.6 MDI-based cured material characterizations

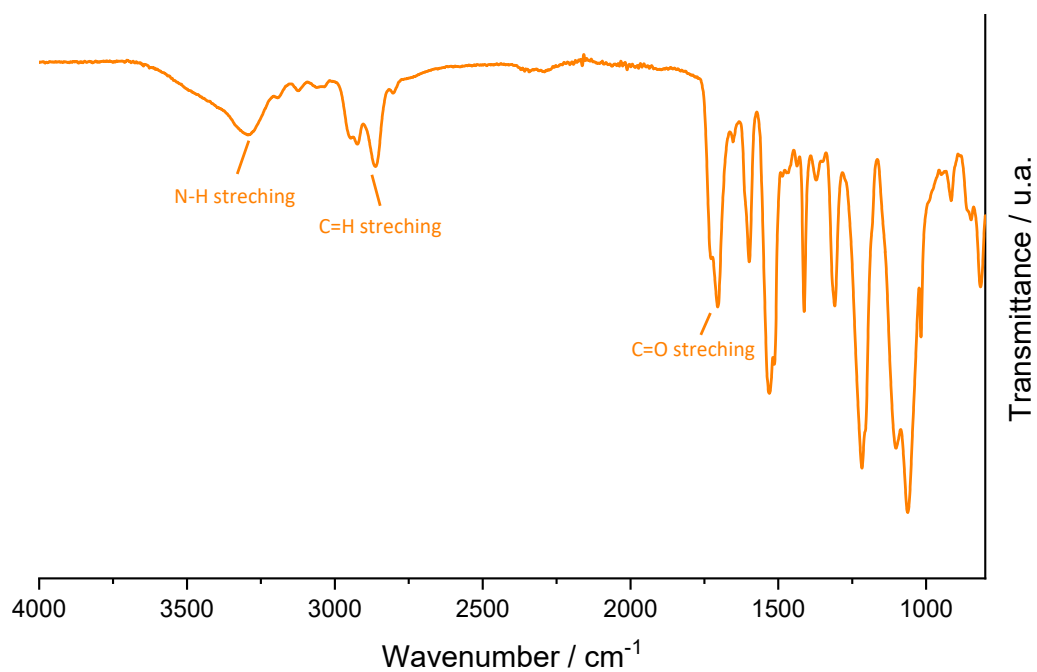


Figure S29. FTIR spectrum of MDI-based thermoset

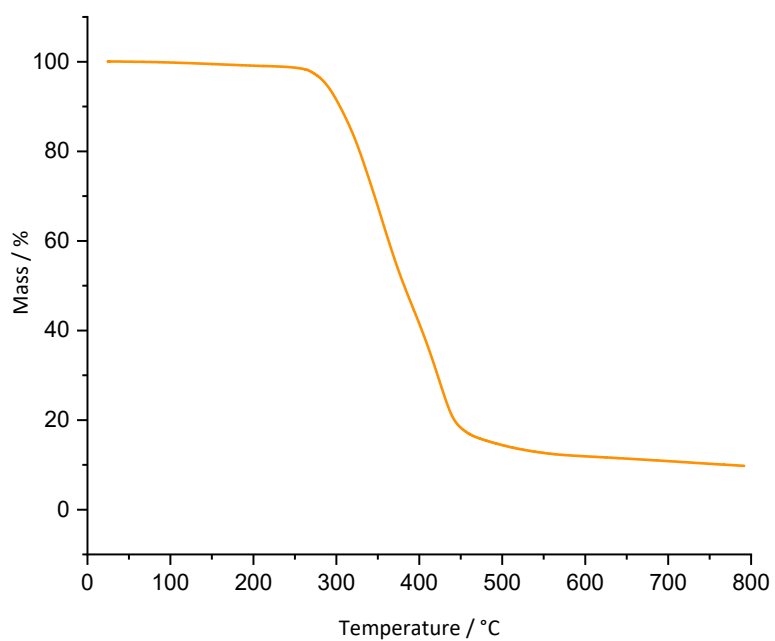


Figure S30. TGA thermogram of MDI-based thermoset

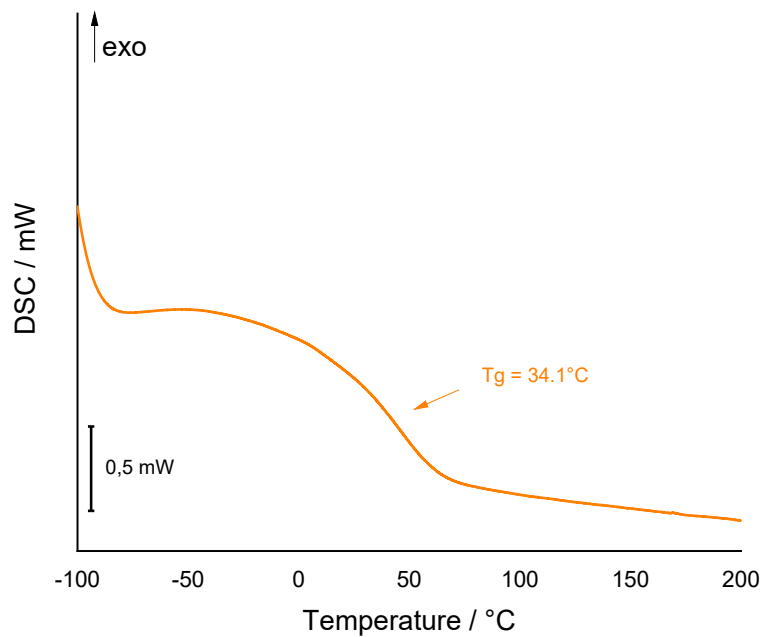


Figure S31. DSC thermogram of MDI-based thermoset

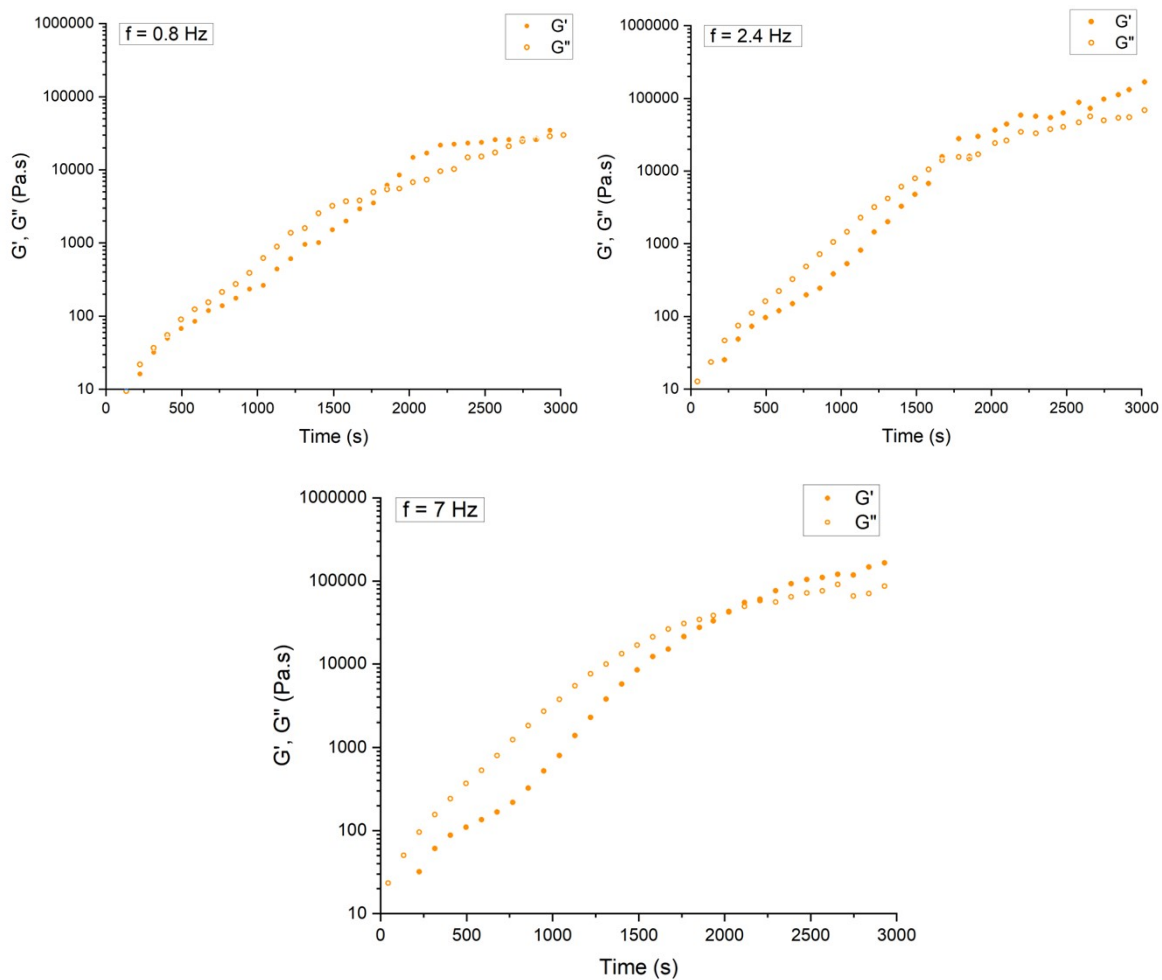


Figure S32. Gelation time determination of MDI-based thermoset at 90°C (f=0.8 Hz, 2.4 Hz, 8 Hz)

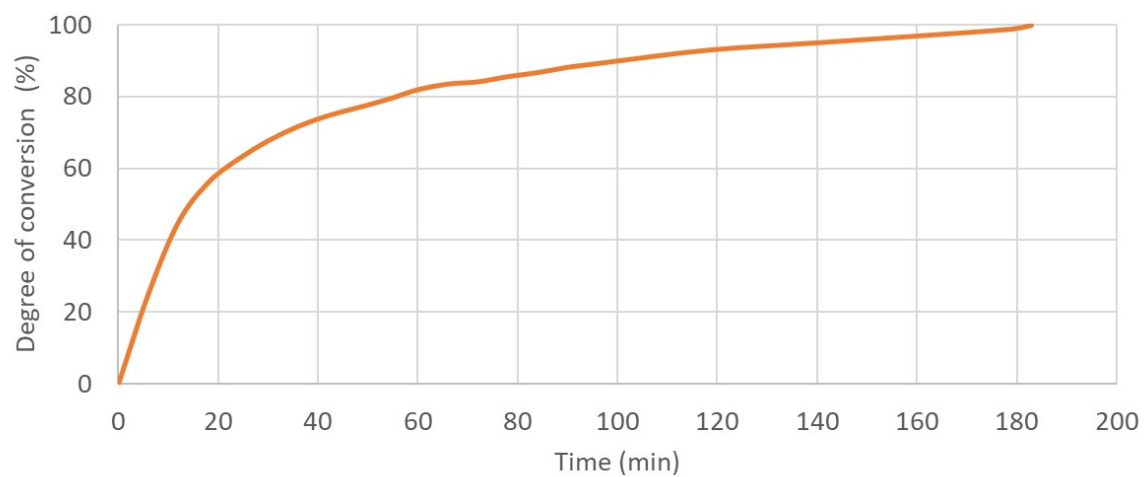
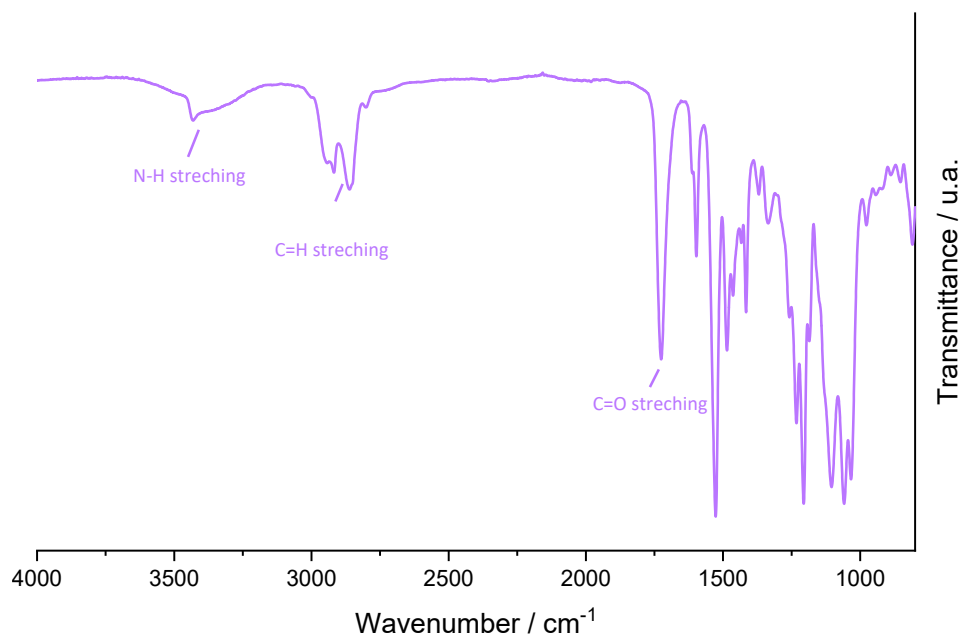


Figure S33. Curing conversion of MDI-based thermoset monitoring by FTIR spectroscopy at 90 °C

2.7 BGI-based cured material characterization



S34. FTIR spectrum of BGI-based thermoset

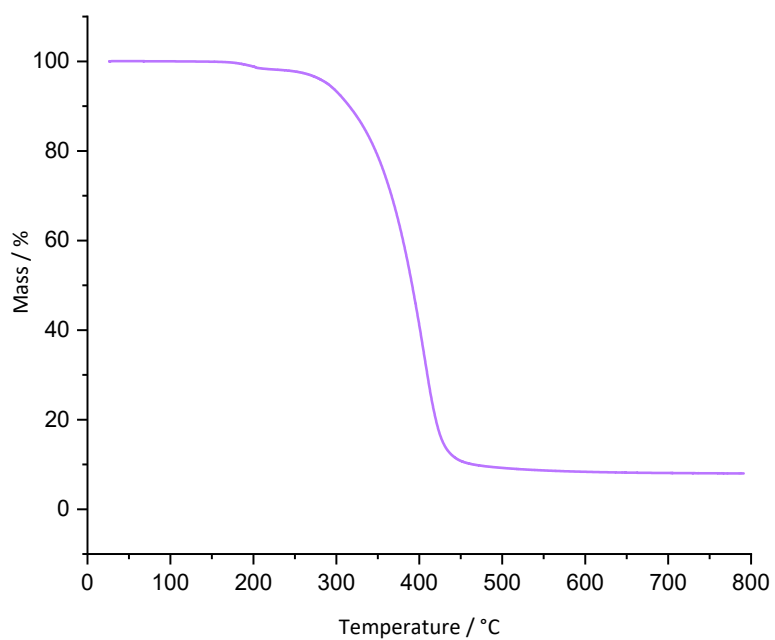


Figure S35. TGA thermogram of BGI-based thermoset

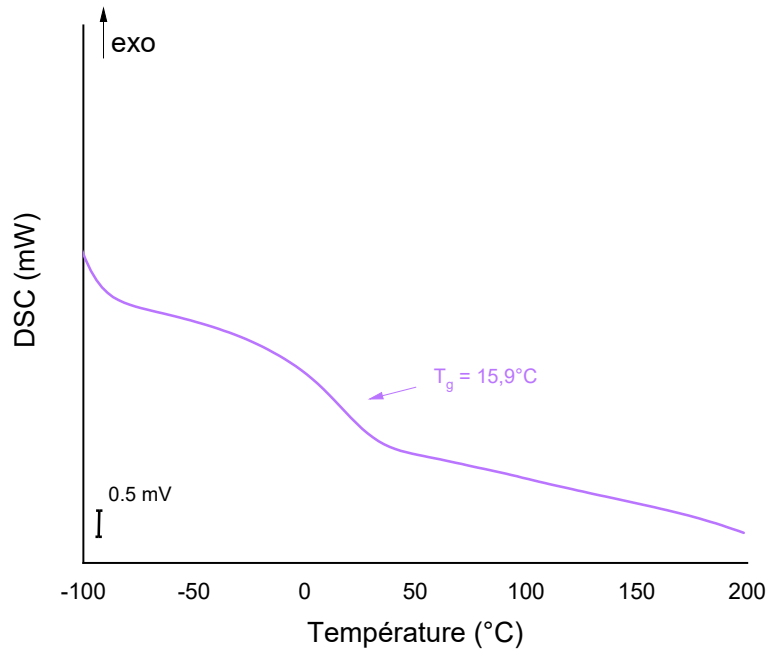


Figure S36. DSC thermogram of BGI-based thermoset

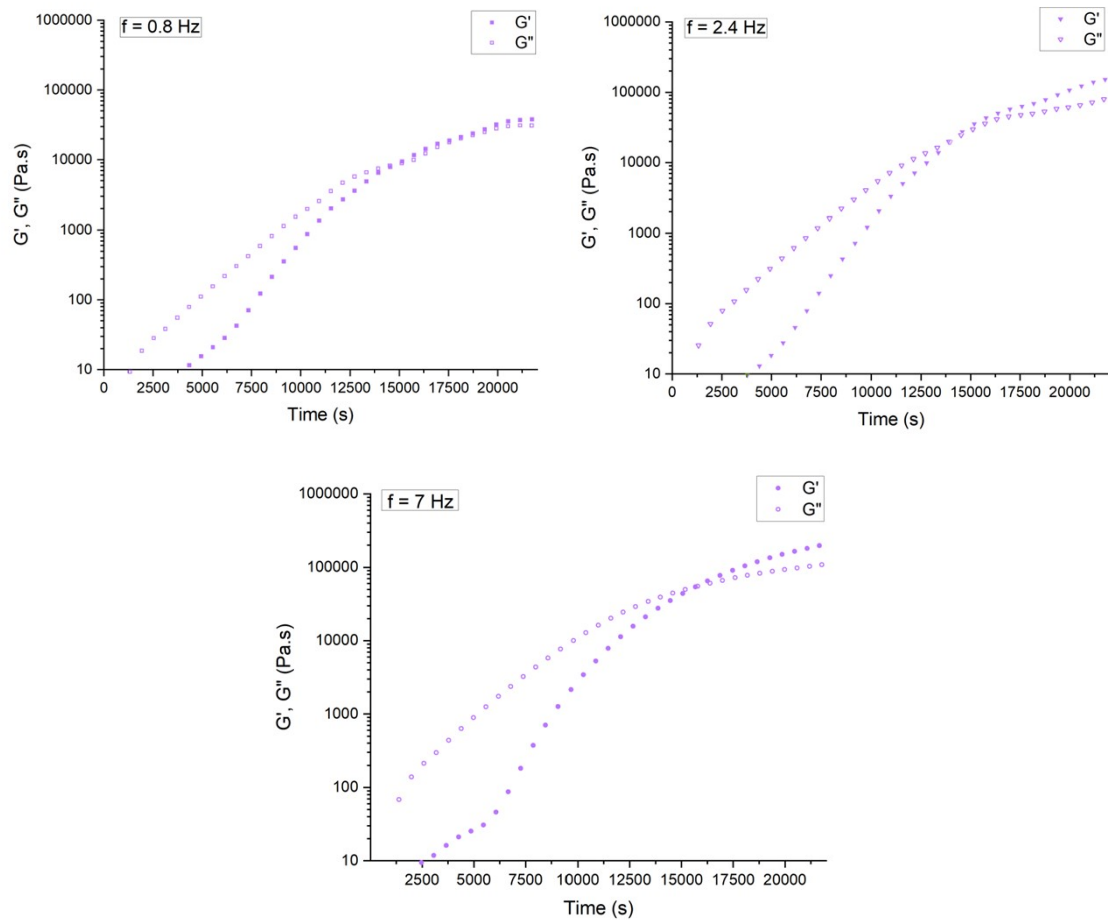


Figure S37. Gelation time determination of BGI-based thermoset at 90°C ($f=0.8 \text{ Hz}$, 2.4 Hz , 8 Hz)

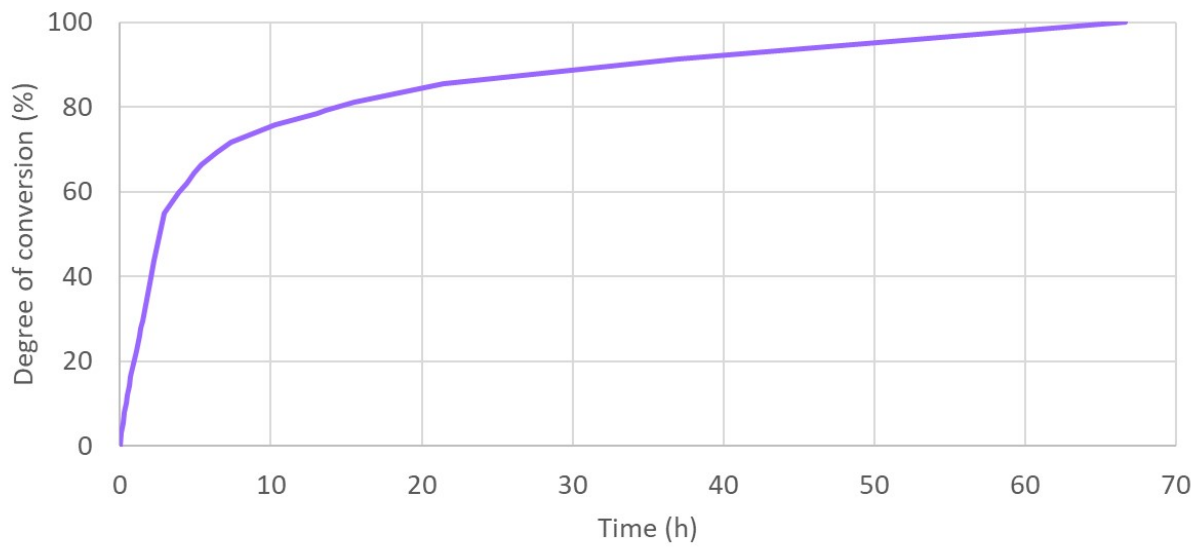


Figure S38. Curing conversion of BGI-based thermoset monitoring by FTIR spectroscopy at 90 °C