

Synthesis of polar polynorbornenes with high dielectric relaxation strength as candidate materials for dielectric applications

Francis Owusu,^{a,b} Martin Tress,^c Frank A. Nüesch,^{a,b,d} Sandro Lehner,^e and Dorina M. Opris^{a*}

^a Swiss Federal Laboratories for Materials Science and Technology Empa, Laboratory for Functional Polymers, Überlandstr. 129, CH-8600, Dübendorf, Switzerland

^b Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL, Station 6, CH-1015 Lausanne, Switzerland

^c Leipzig University, Peter Debye Institute for Soft Matter Physics, Linne'straße 5, 04103 Leipzig, Germany

^d École Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux, Station 12, CH 1015, Lausanne, Switzerland.

^e Swiss Federal Laboratories for Materials Science and Technology Empa, Laboratory for Advanced Fibers, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland

* Correspondence and requests for materials should be addressed to e-mail:dorina.opris@empa.ch

Contents	Page
Synthesis of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile	2
Synthesis of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride.....	3
Structure characterization of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile	4
Structure characterization of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride.....	8
Structure characterization of monomers	10
Structure characterization of polymers	32
Thermal behaviour of polymers.....	40
Dielectric properties of polymers	45
Dipole moments of monomers	50
Appendices	51

2,6-dimethyl-4H-pyran-4-one

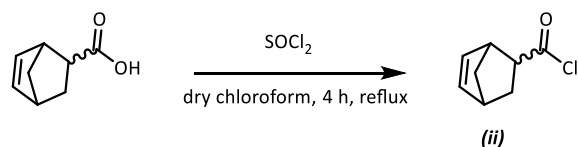
(i)

1

Compound **1** was designed and synthesized as shown in Scheme S1. Initially, 2,6-dimethyl-4H-pyran-4-one (20.00 g, 161.10 mmol), malononitrile (10.64 g, 161.10 mmol), and acetic anhydride (80 ml) were charged into a 200 ml round bottom flask. The system was refluxed at 130 °C for 4 hours to obtain crude of *compound (i)* intermediate. The intermediate was purified by washing with warm water and recrystallizing from heptane to produce a dark brown powder (yield, 87 %). Further, a 200 ml round bottom flask was charged *compound (i)* intermediate (15.00 g, 87.11 mmol), ethanolamine (44.7 ml, 740.46 mmol) and methanol (100 ml). The reaction was then refluxed at 70 °C for 2 hours and left to stand overnight. The separated solid was collected by filtration, dried, and recrystallized in ethanol to produced compound **1** as brown flakes (yield, 60%).

S-2

Synthesis of bicyclo[2.2.1]het-5-ene-2-carbonyl chloride



Scheme 2 Synthesis of compound (ii)

A 2-necked round bottom flask was charged with 5-norbornene-2-carboxylic acid (15 g, 108.56 mmol), thionyl chloride (19.37 g, 162.84 mmol), and anhydrous chloroform (10 ml). The reaction mixture was refluxed for 4 hours under argon protection. The solvent was then evaporated and the residue was distilled at 1 mbar (40 °C) to give the corresponding acyl chloride as colorless oily liquid (yield, 83%).

¹H NMR (400 MHz, CDCl₃) δ 6.26 (ddd, *J* = 19.1, 5.7, 3.1 Hz, 1H), 6.06 (dd, *J* = 5.8, 2.5 Hz, 1H), 3.48 (dd, *J* = 7.9, 4.2 Hz, 1H), 3.45 (s, 1H), 3.01 (dt, *J* = 4.2, 2.3 Hz, 1H), 2.09 – 1.92 (m, 1H), 1.60 – 1.40 (m, 2H), 1.36 (d, *J* = 8.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.81, 175.04, 139.04, 138.69, 134.88, 131.61, 77.23, 56.43, 56.32, 49.22, 47.16, 46.90, 46.29, 42.89, 41.85, 31.22, 30.09.

Structure characterization of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

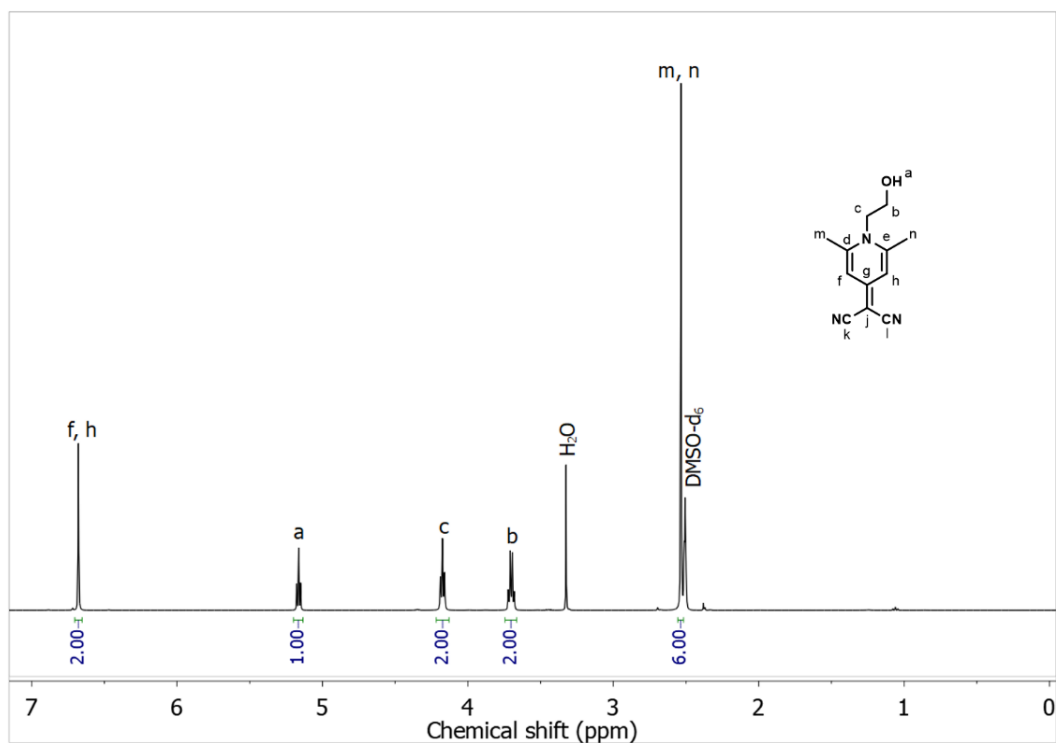


Figure S1 ¹H NMR spectrum of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

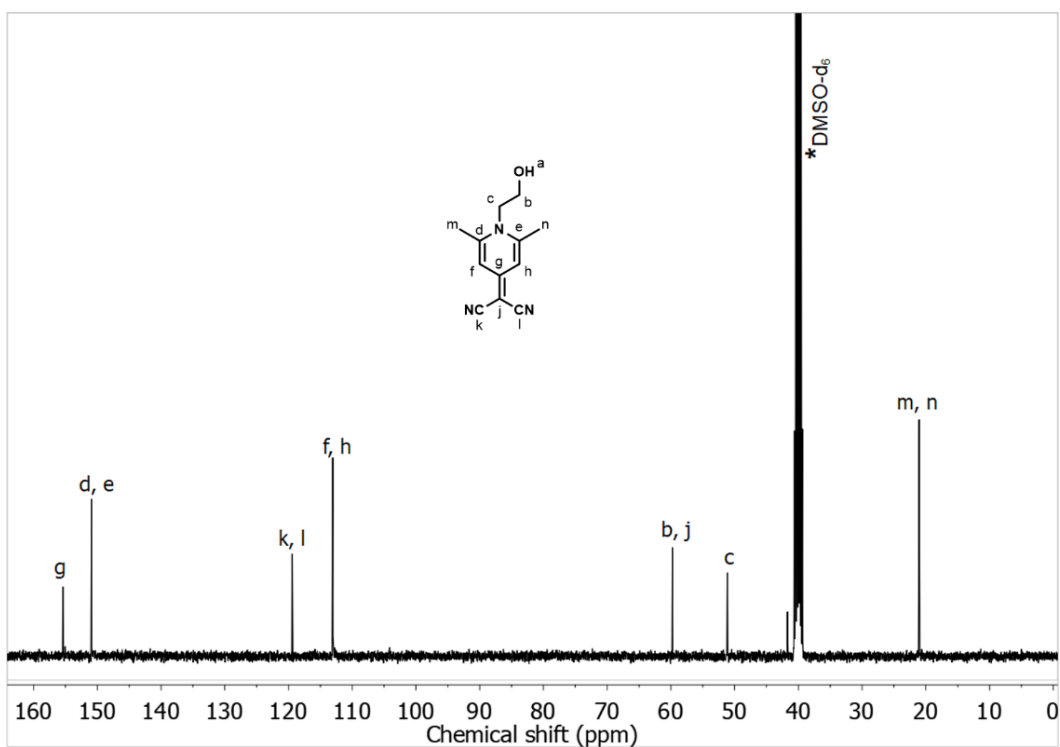


Figure S2 ¹³C NMR spectrum of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

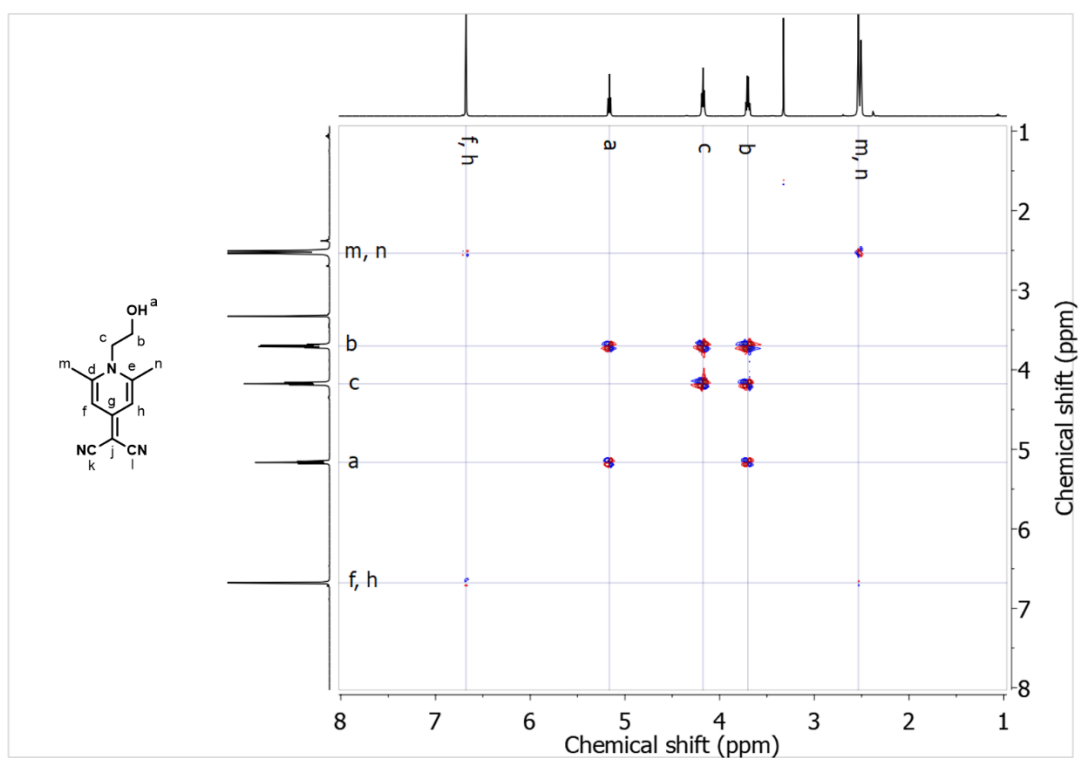


Figure S3 COSY of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

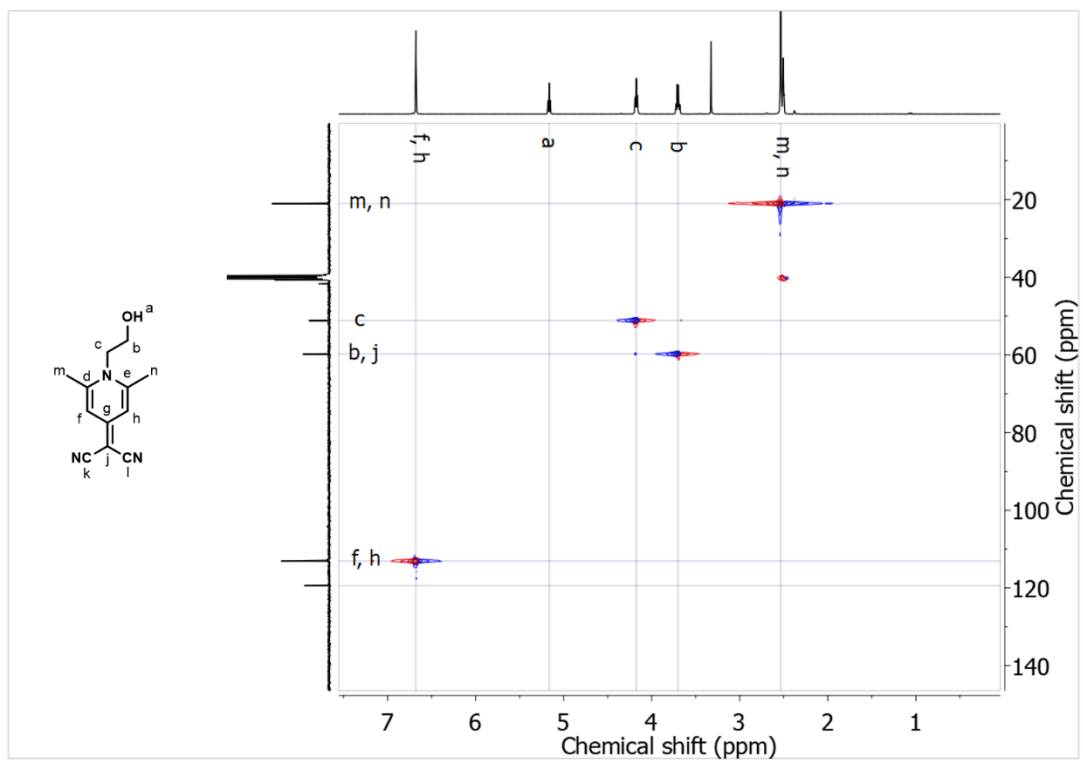


Figure S4 HSQC of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

Eidgenössische Technische Hochschule Zürich
Laboratorium für Organische Chemie

ETH-Hönggerberg - HCI E304

8093 Zürich

Tel: 044/633 43 58

Mikroelementaranalyse

Name: Owusu Francis
 Labor: LA182

Gruppe: Opris EMPA
 Tel: 058/765 48 01

Substanz: 1

Molekularformel: C₁₂ H₁₃ N₃ O

Mr = 215.25g/mol

Schmelzpunkt:

gereinigt: ?????????????????????? getrocknet: HV

Bestimmungen: C H N O

Eingang: 19.09.19

Ausgang: 23.09.19

M-166261

Operator: PK

Berechnete Gewichtsanteile:

[C] 66.96% [H] 6.09% [N] 19.52% [O] 7.43%

Gefundene Gewichtsanteile:

Einwaage: 0.910mg

LECO TruSpec Micro

[C] 66.91% [H] 6.01%

[N] 19.43%

19.09.19

Einwaage: 1.048mg

LECO RO-628

[O] 7.31%

23.09.19

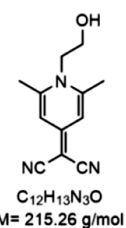


Figure S5 Elemental analysis of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

Acquisition Parameter

Method: ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m
File Name: D:\Data\bmax0051xx\BMAX005105_44666.d
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 1300 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 200.0 Vpp

Acquisition Date: 10.10.2019 15:57:20
Operator: Daniel Wirz
Set Nebulizer: 1.6 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 8.0 l/min
Set Divert Valve: Source

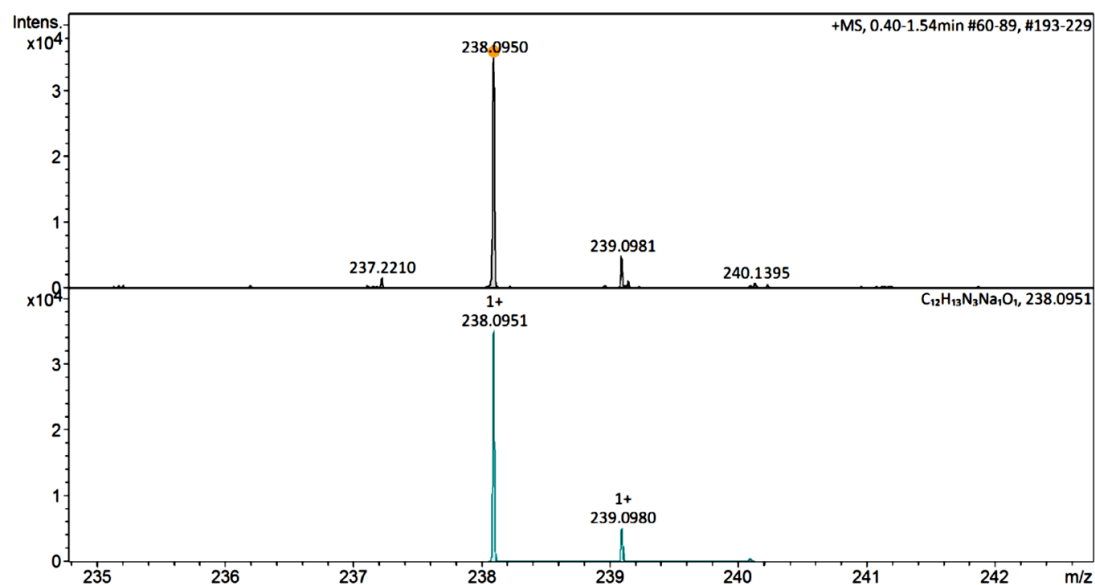
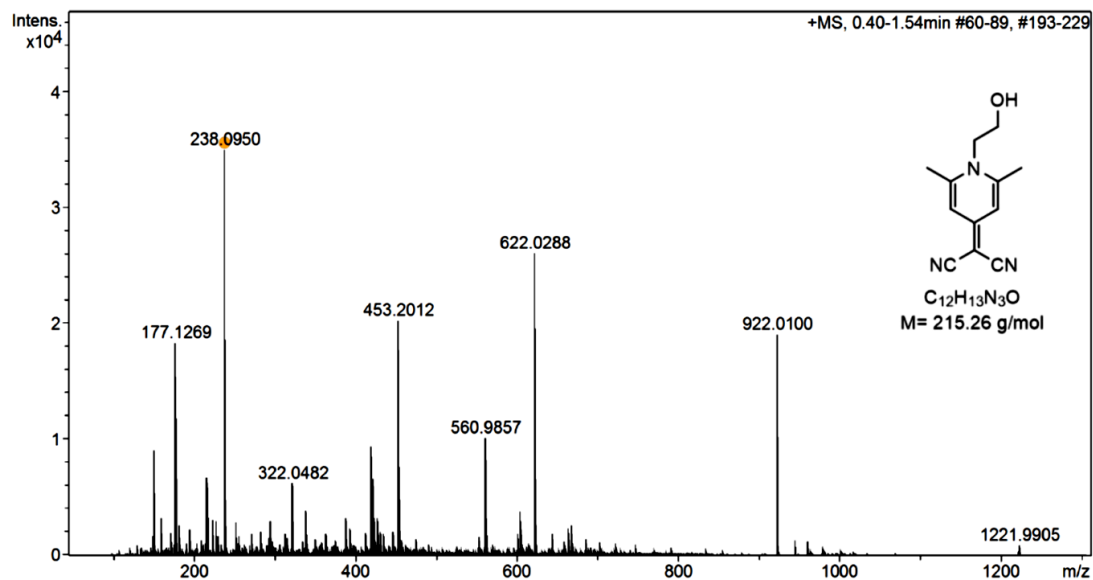


Figure S6 Mass spectra of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

Structure characterization of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

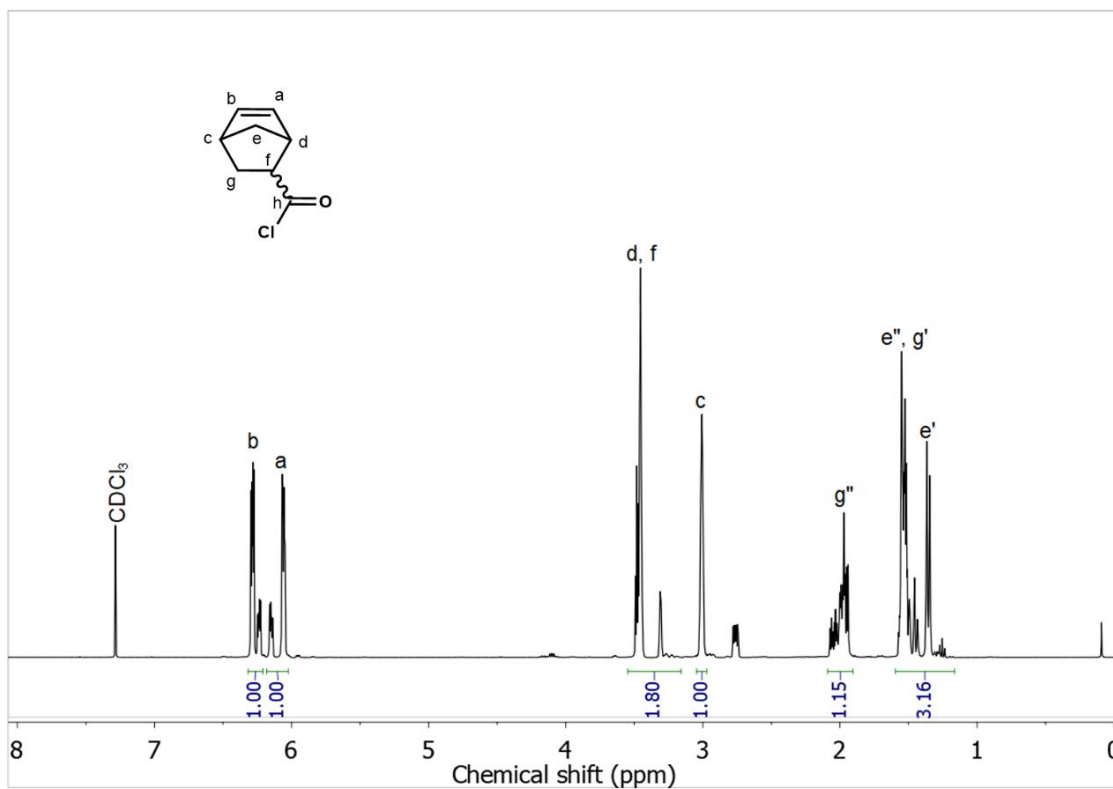


Figure S7 ^1H NMR spectrum of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

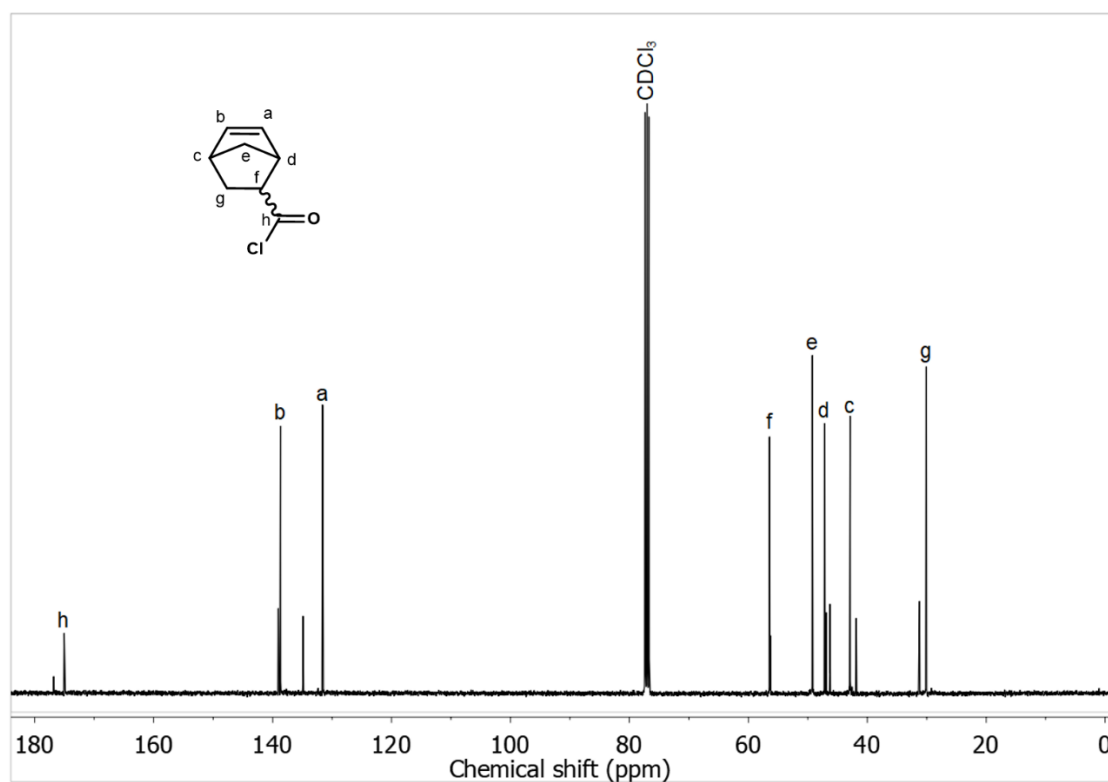


Figure S8 ^{13}C NMR spectrum of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

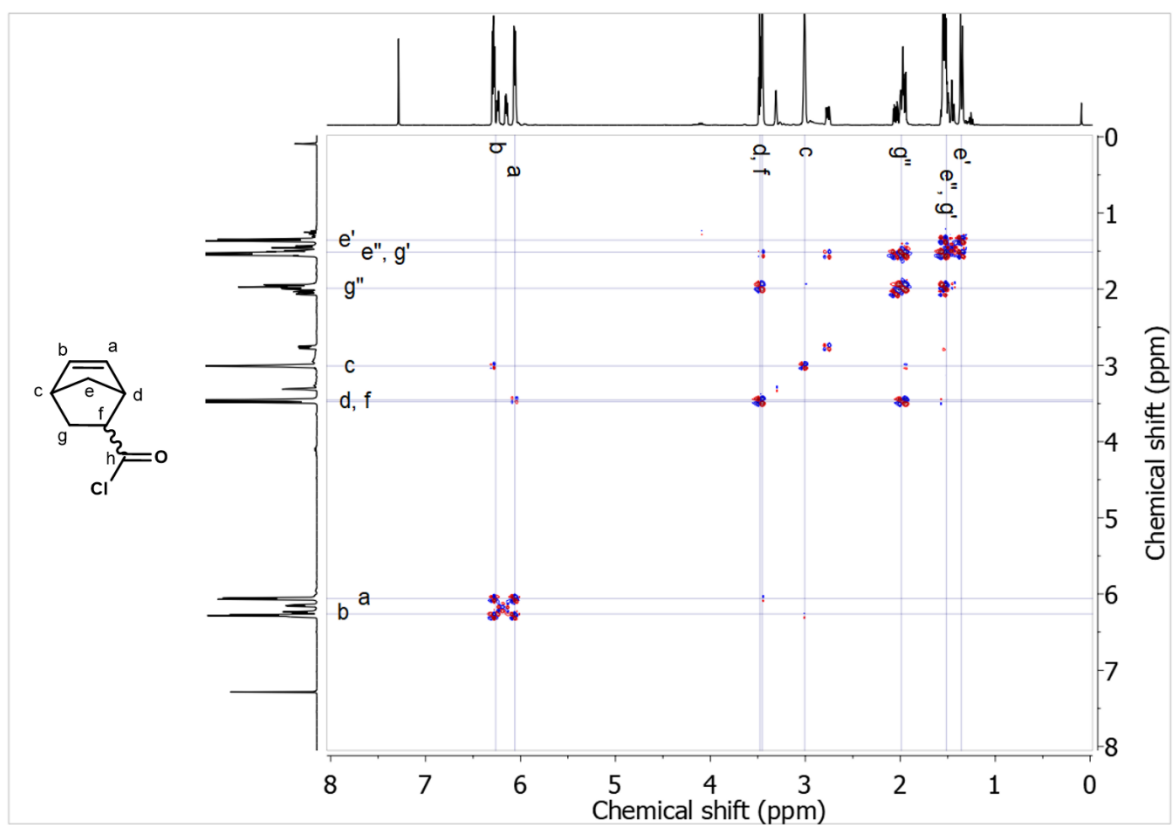


Figure S9 COSY of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

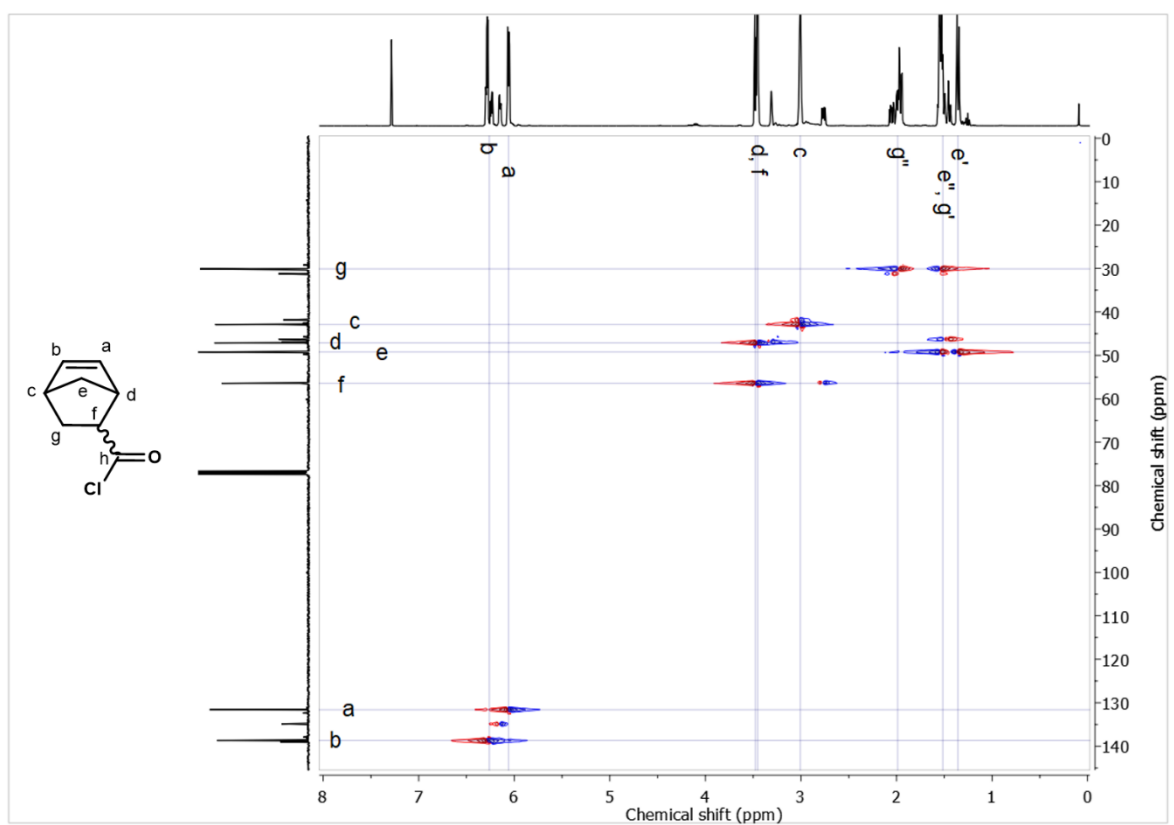


Figure S10 HSQC of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

Structure characterization of monomers

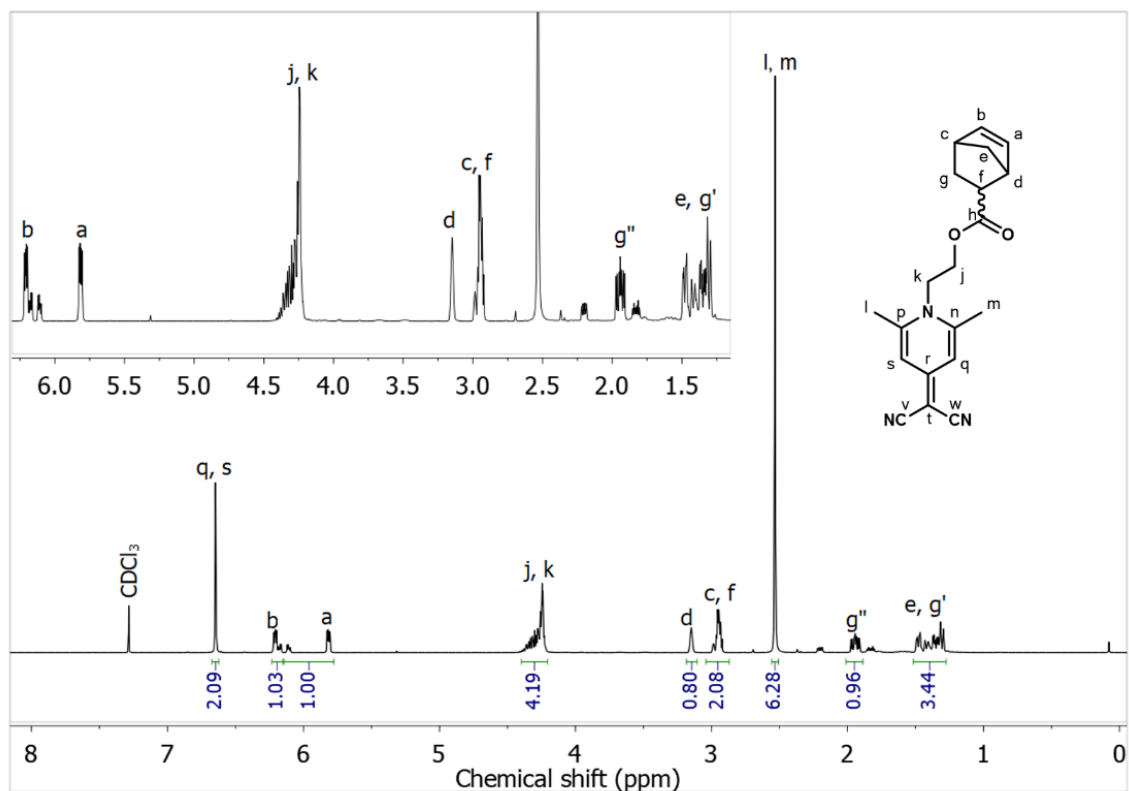


Figure S11 ^1H NMR spectrum of **NBE-1**

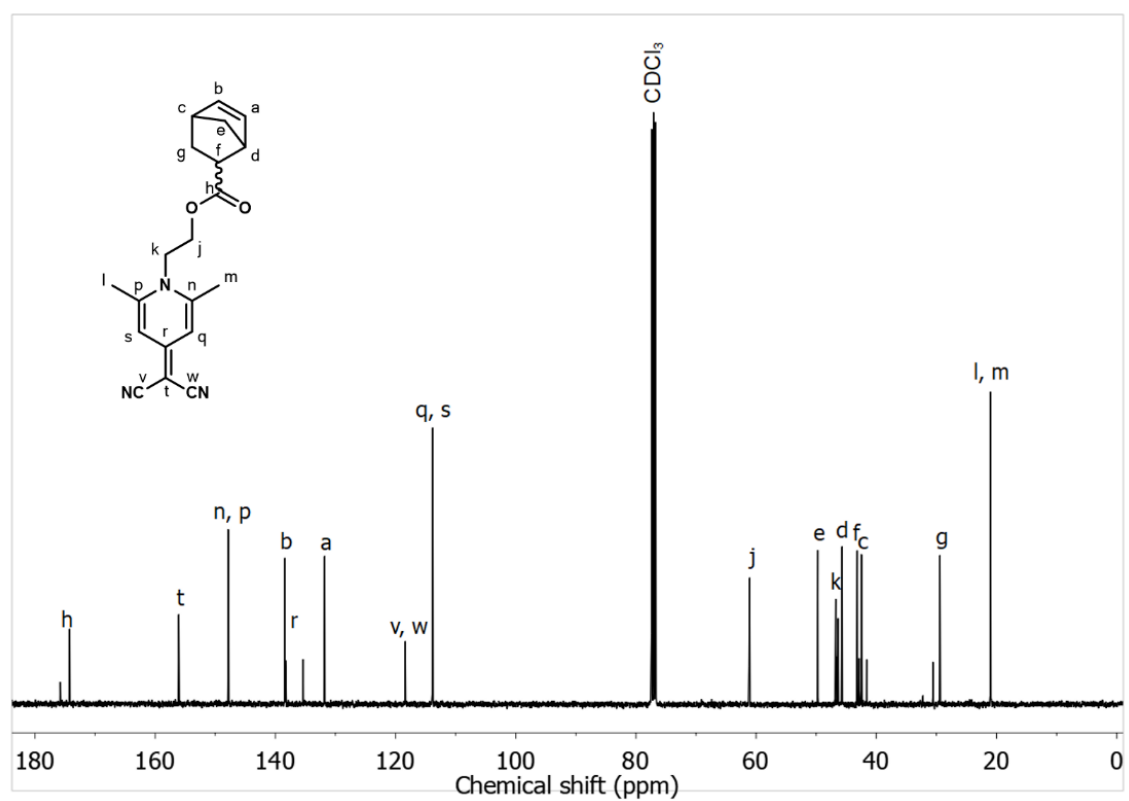


Figure S12 ^{13}C NMR spectrum of **NBE-1**

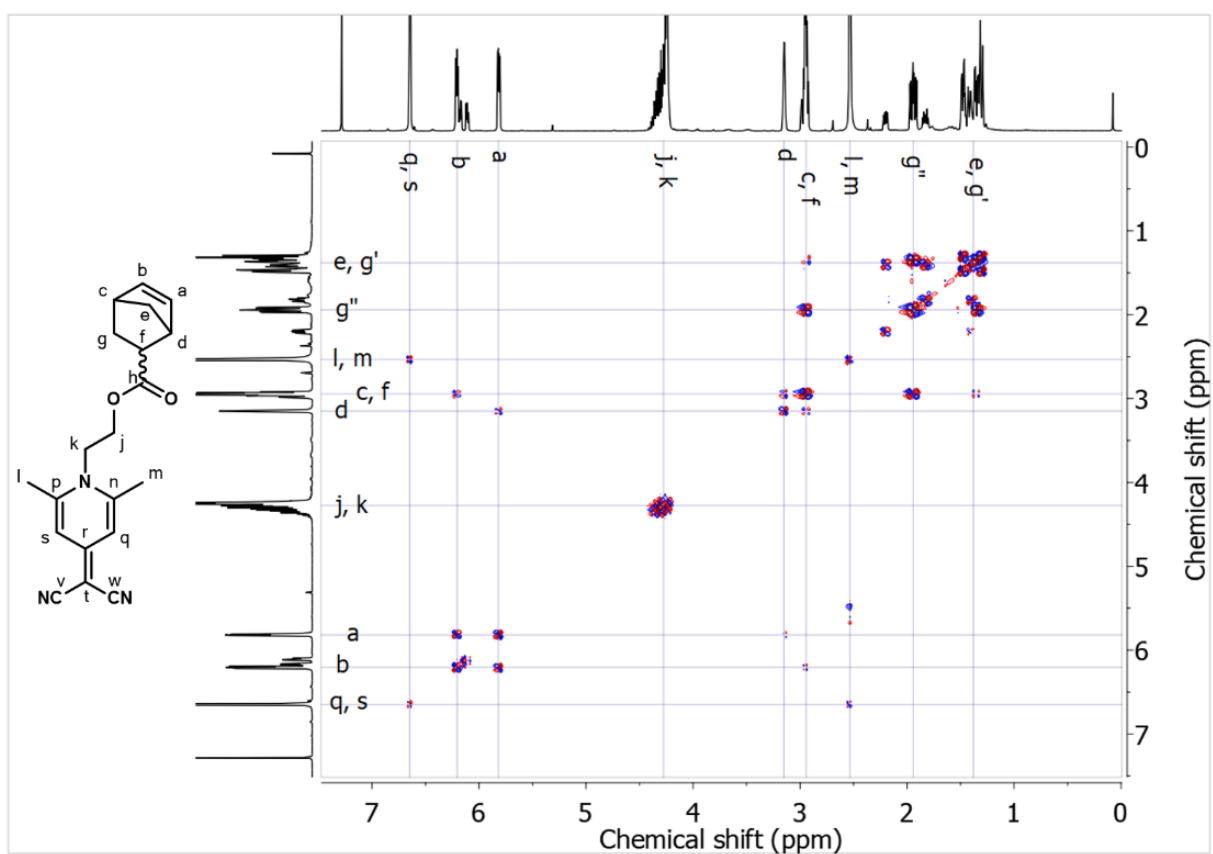


Figure S13 COSY of NBE-1

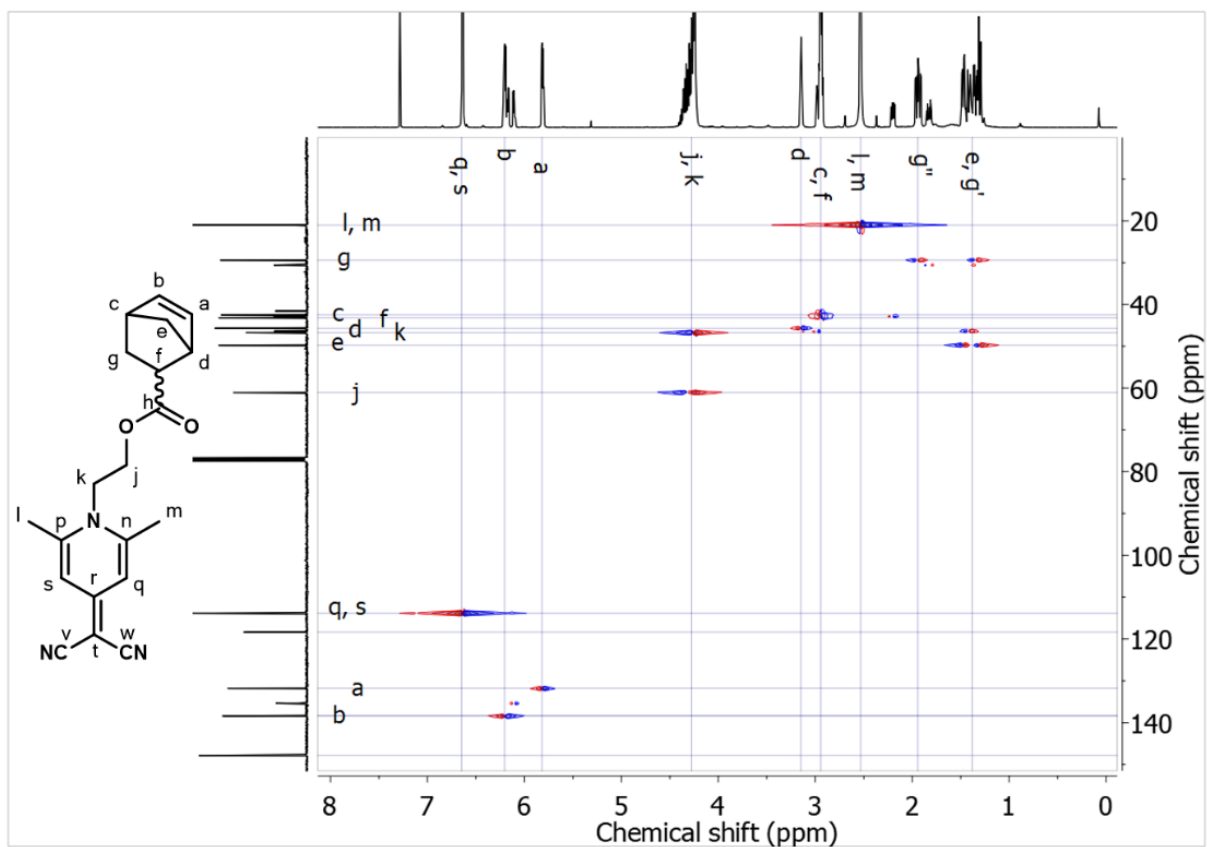


Figure S14 HSQC of NBE-1

Eidgenössische Technische Hochschule Zürich
Laboratorium für Organische Chemie

ETH-Hönggerberg - HCI E304

8093 Zürich

Tel: 044/633 43 58

Mikroelementaranalyse

Name: Owusu Francis
 Labor: LA182

Gruppe: Opris EMPA
 Tel: 058/765 48 01

Substanz: NBE-1

Molekularformel: C₂₀ H₂₁ N₃ O₂

Mr = 335.40g/mol

HV

Schmelzpunkt:

gereinigt: ??? getrocknet:

Bestimmungen: C H N O

Eingang: 19.09.19

Ausgang: 23.09.19

M-166263

Operator: PK

Berechnete Gewichtsanteile:

[C]	71.62%	[H]	6.31%	[N]	12.53%	[O]	9.54%
-----	--------	-----	-------	-----	--------	-----	-------

Gefundene Gewichtsanteile:

Einwaage: 0.886mg

LECO TruSpec Micro

[C]	71.47%	[H]	6.37%
-----	--------	-----	-------

[N]	12.53%
-----	--------

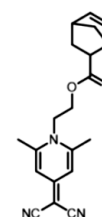
19.09.19

Einwaage: 0.990mg

LECO RO-628

[O]	9.26%
-----	-------

23.09.19



C₂₀H₂₁N₃O₂
 M = 335.41 g/mol

Figure S15 Elemental analysis of NBE-1

Acquisition Parameter

Method: ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m
File Name: D:\Data\lmax0051xx\BMAX005107.d
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 1300 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 200.0 Vpp

Acquisition Date: 10.10.2019 16:03:16
Operator: Daniel Wirz
Set Nebulizer: 1.6 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 8.0 l/min
Set Divert Valve: Source

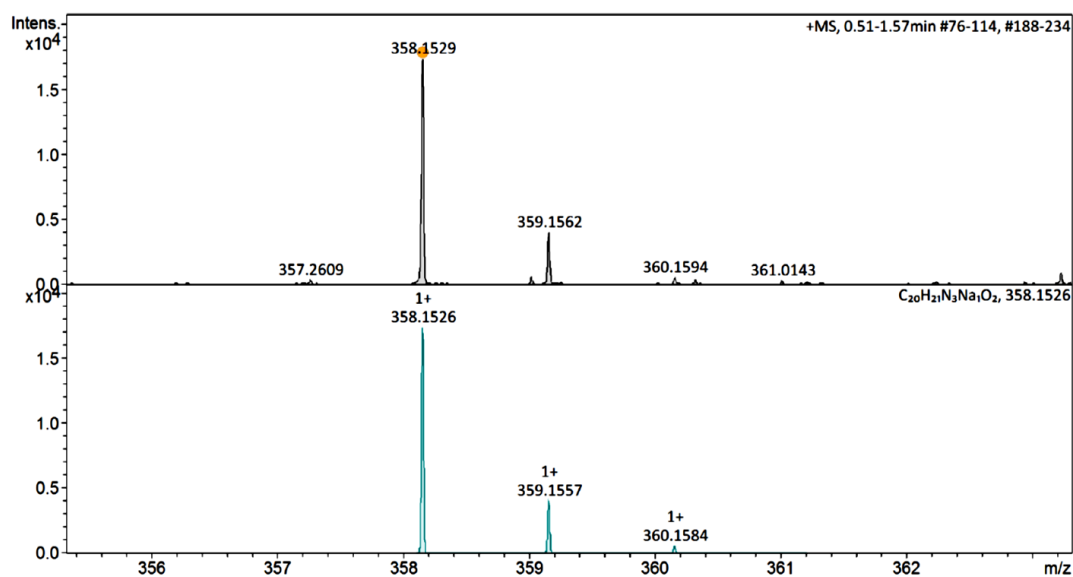
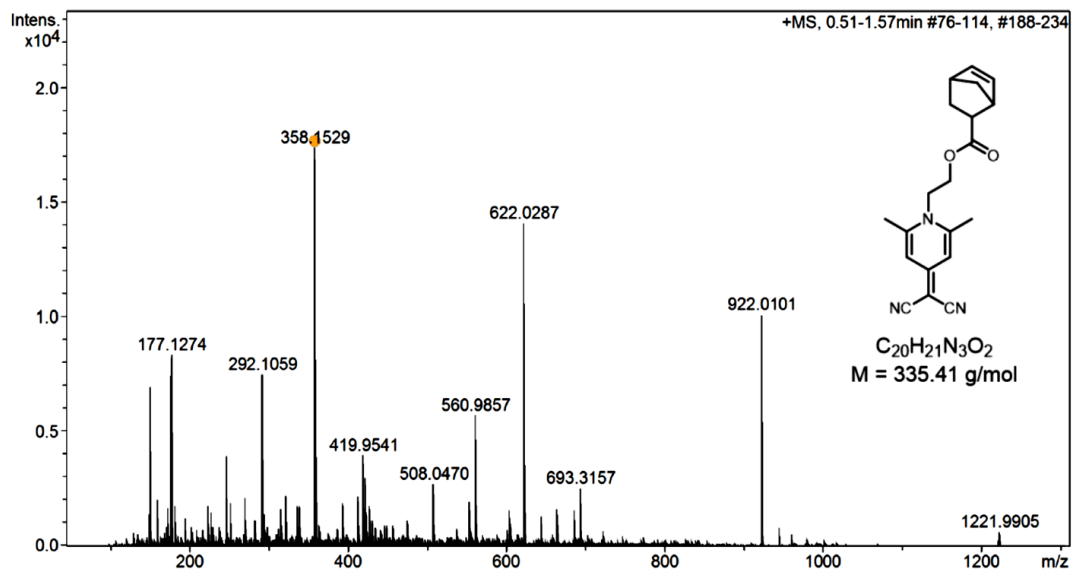


Figure S16 Mass spectra of NBE-1

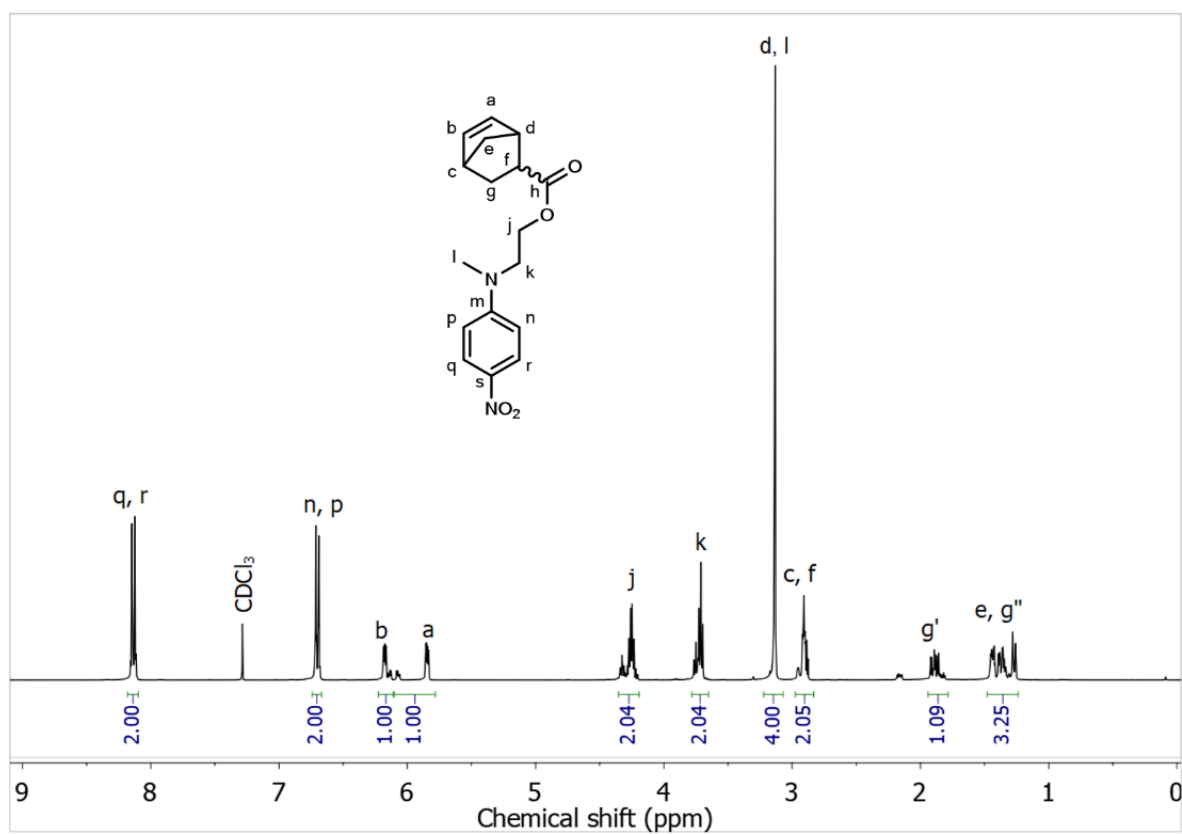


Figure S17 ¹H NMR spectrum of NBE-2

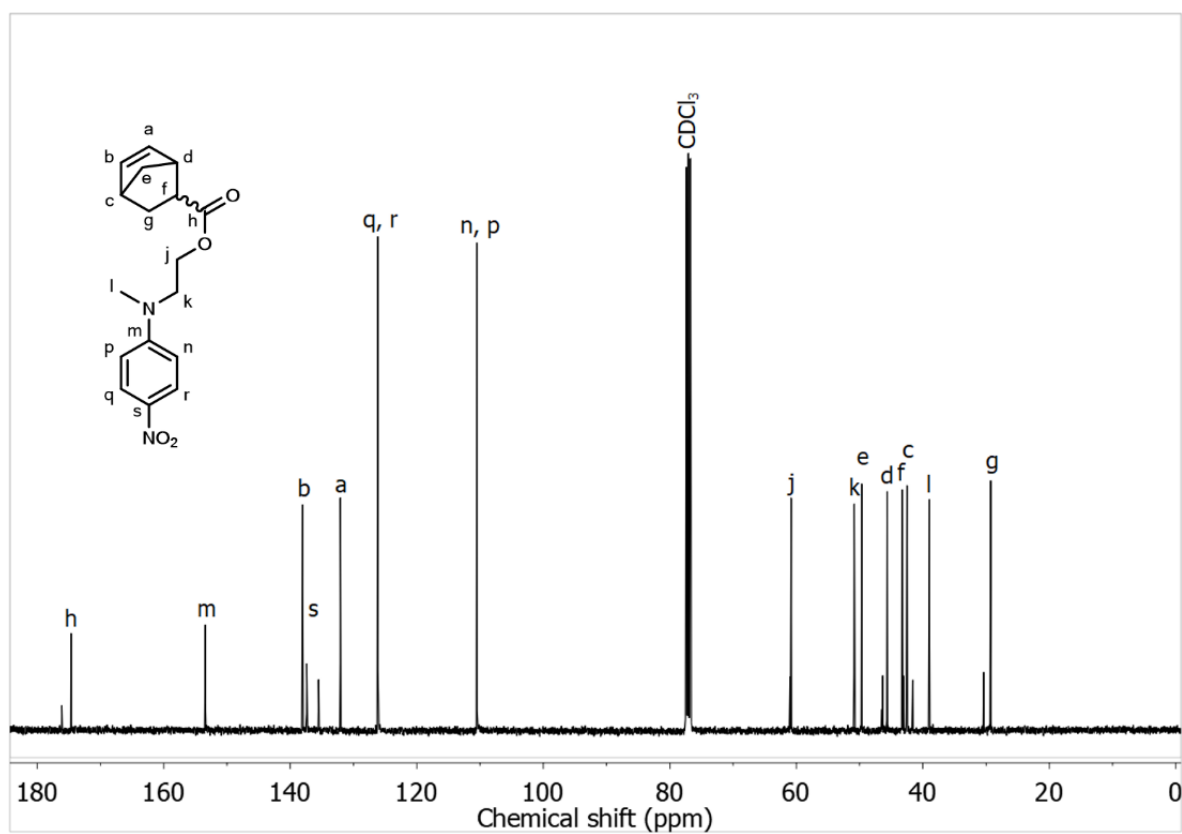


Figure S18 ¹³C NMR spectrum of NBE-2

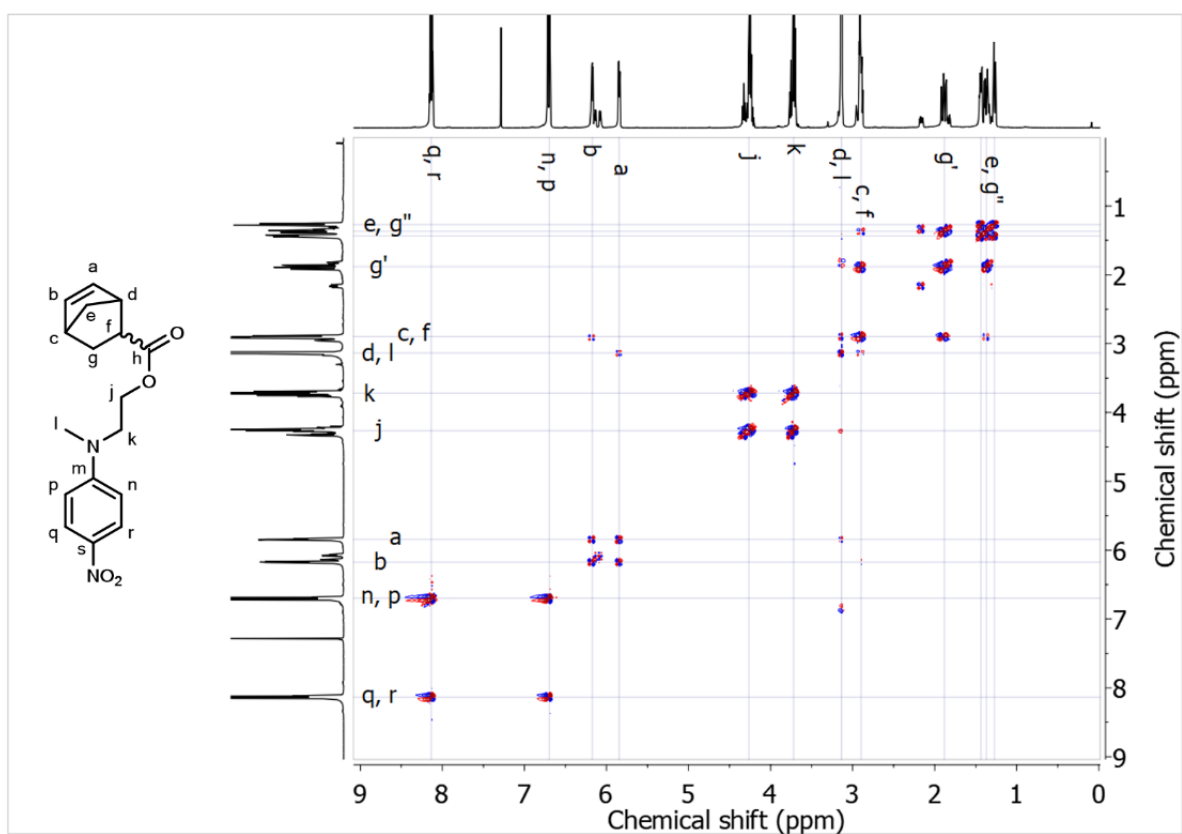


Figure S19 COSY of NBE-2

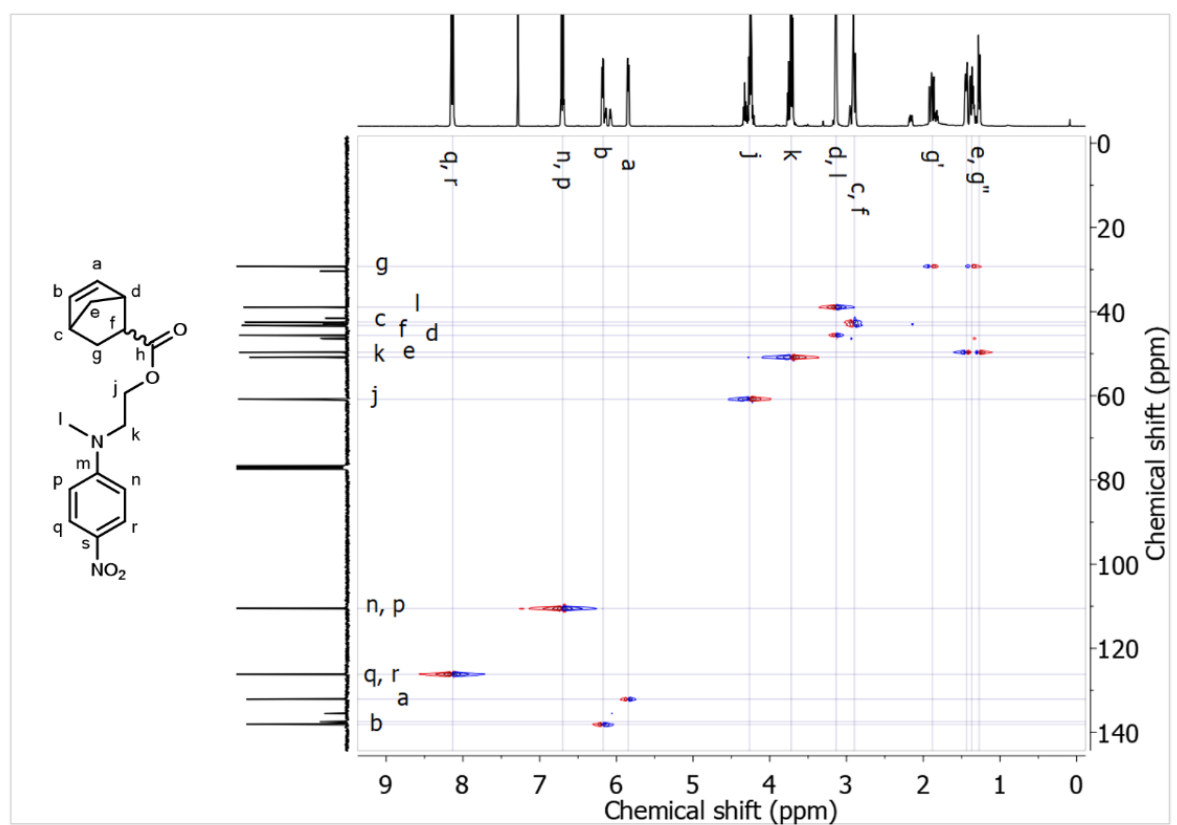


Figure S20 HSQC of NBE-2

Acquisition Parameter

Method: ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m
File Name: D:\Data\bmax0051xx\BMAX005106.d
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 1300 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 200.0 Vpp

Acquisition Date: 10.10.2019 16:00:19
Operator: Daniel Wirz
Set Nebulizer: 1.6 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 8.0 l/min
Set Divert Valve: Source

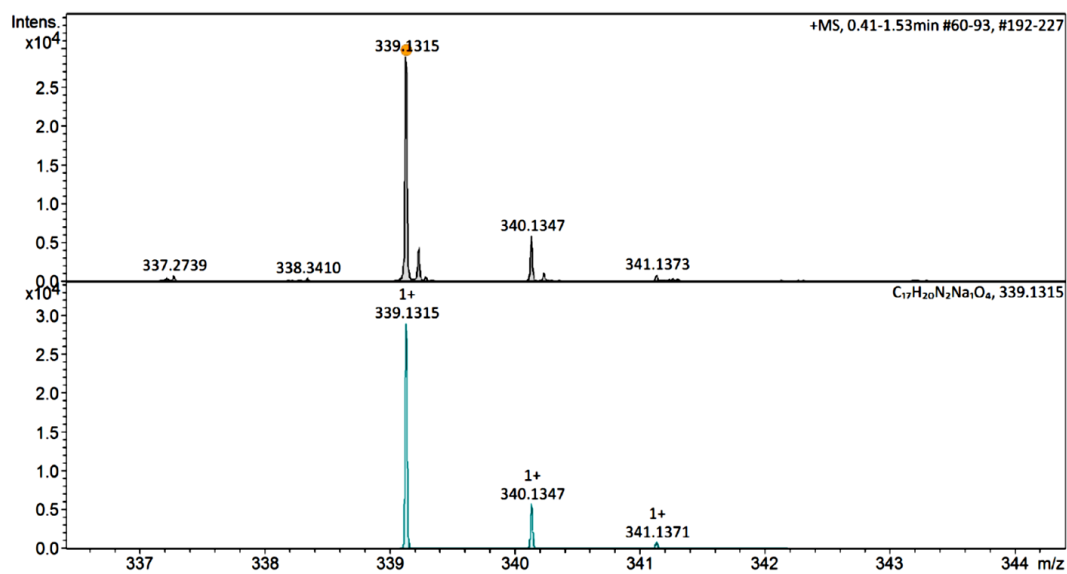
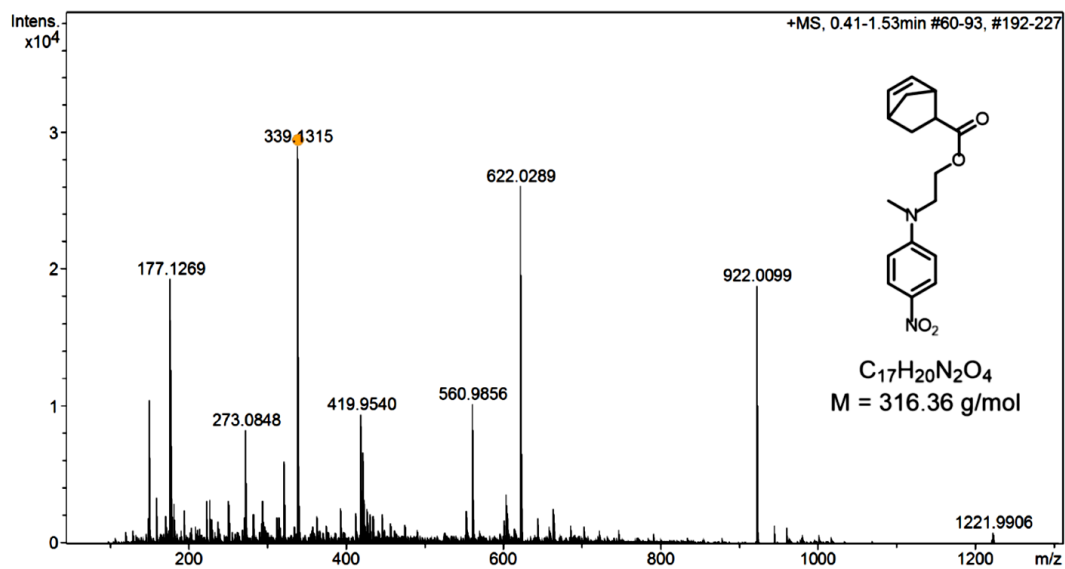


Figure S22 Mass spectra of NBE-2

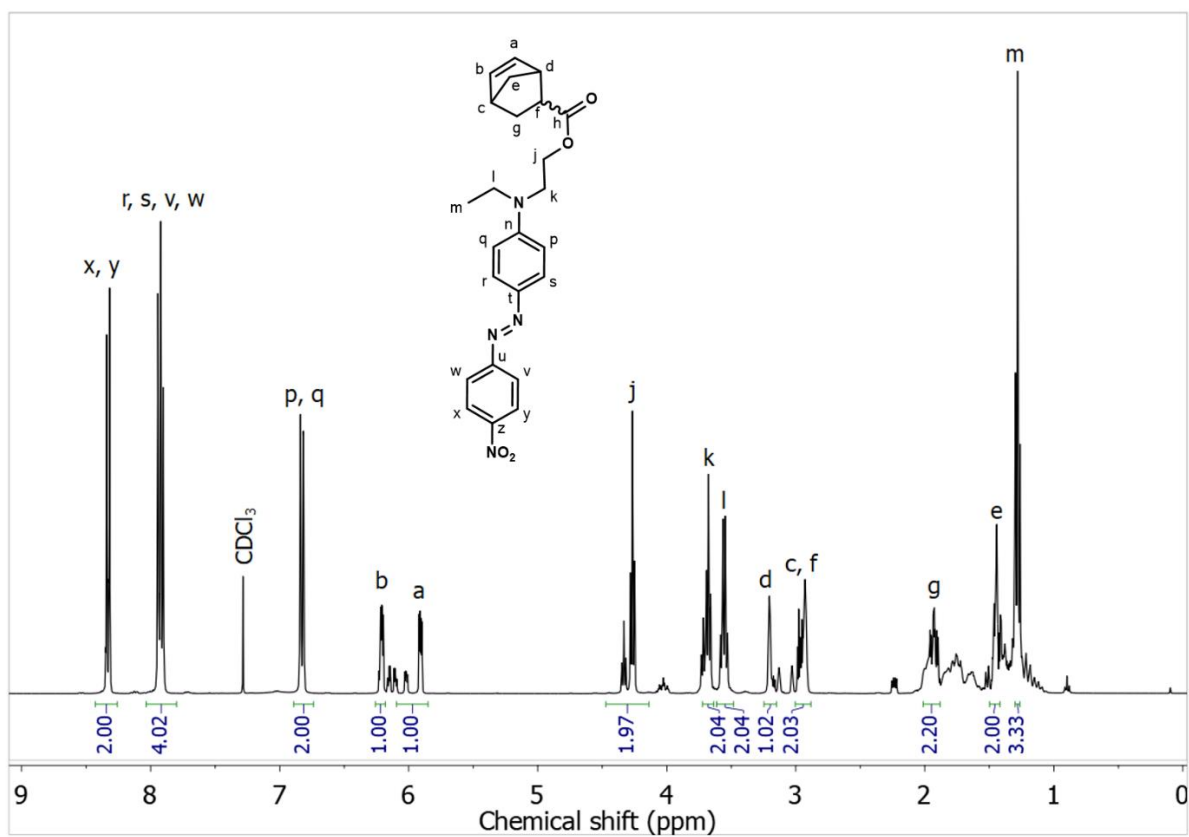


Figure S23 ^1H NMR spectrum of **NBE-3**

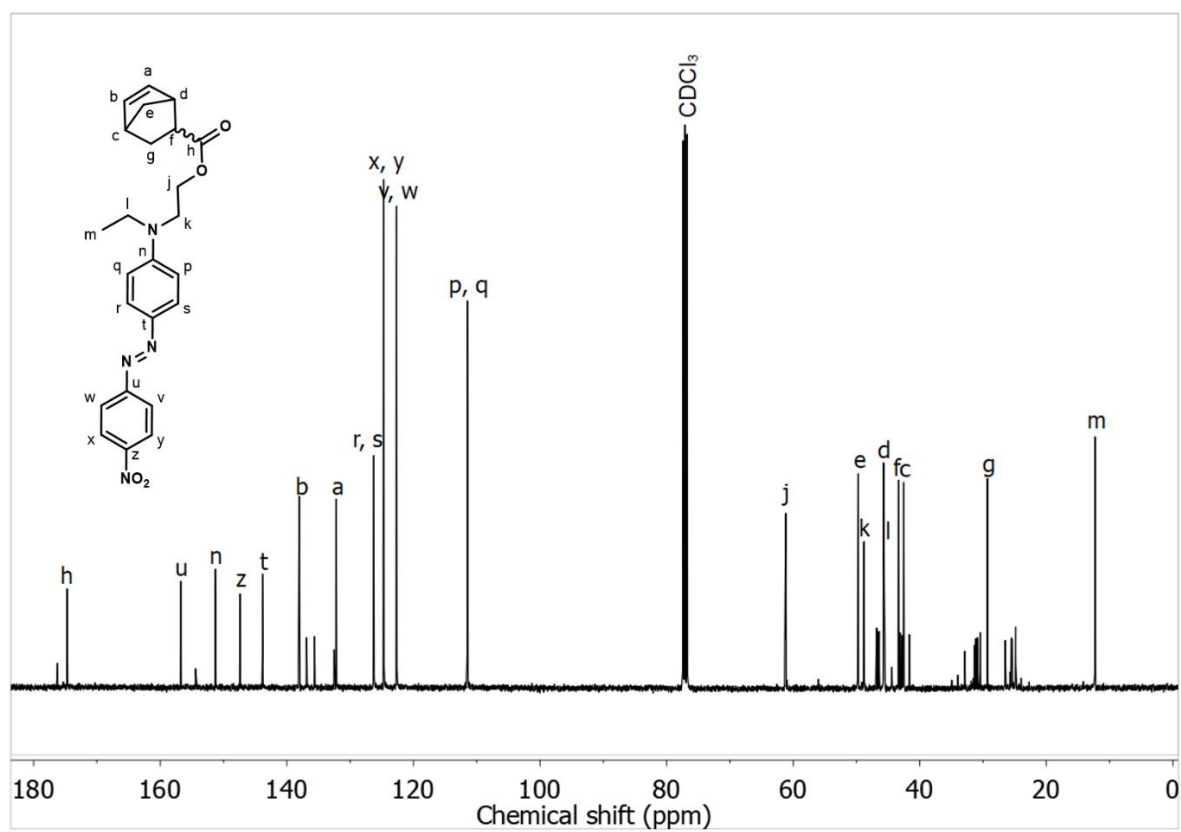


Figure S24 ^{13}C NMR spectrum of **NBE-3**

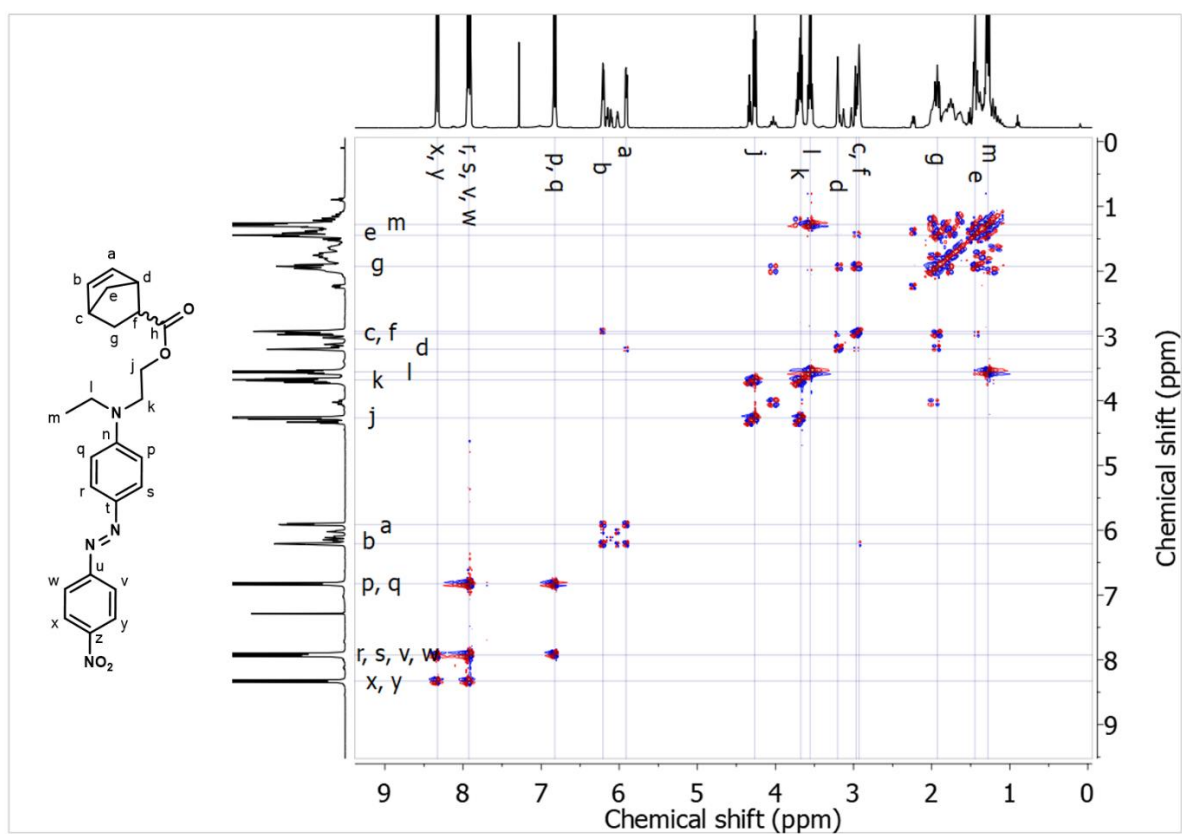


Figure S25 COSY of NBE-3

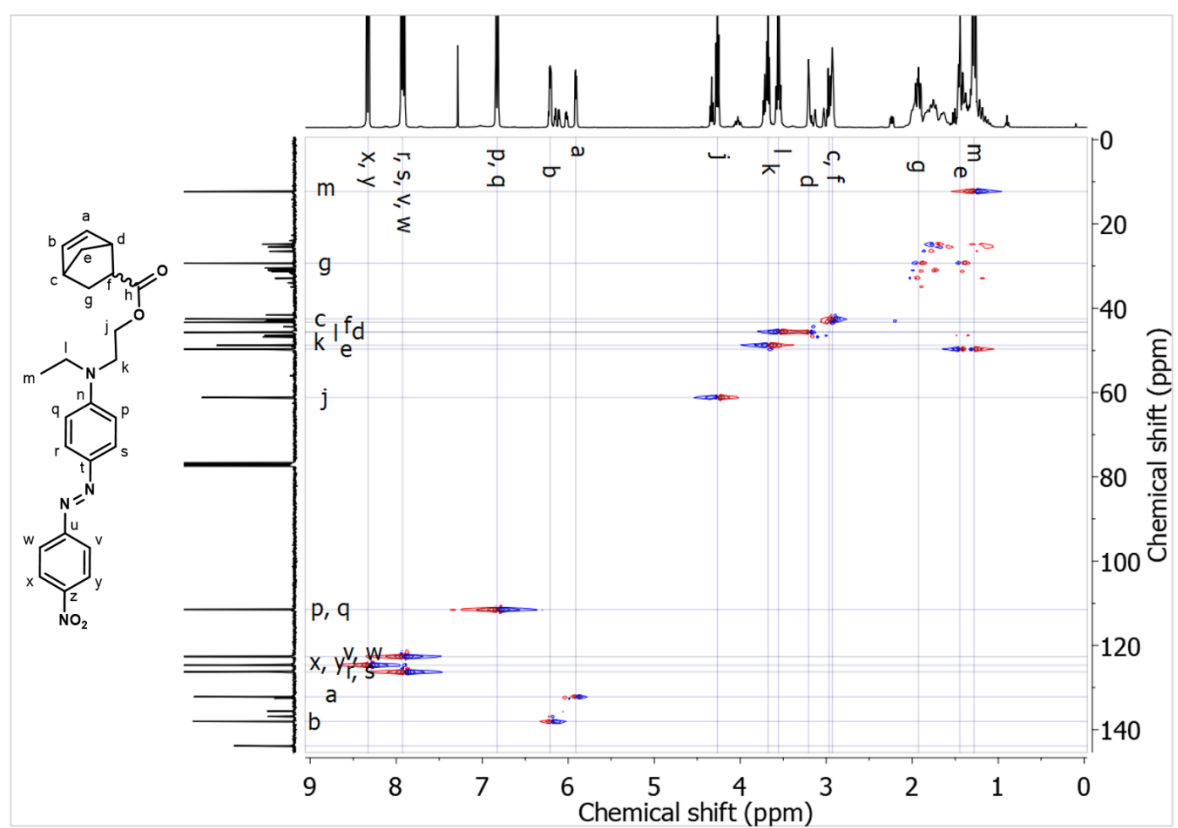


Figure S26 HSQC of NBE-3

Acquisition Parameter

Method: ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m
File Name: D:\Data\lmax0051xx\BMAX005108.d
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 1300 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 200.0 Vpp

Acquisition Date: 10.10.2019 16:06:14
Operator: Daniel Wirz
Set Nebulizer: 1.6 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 8.0 l/min
Set Divert Valve: Source

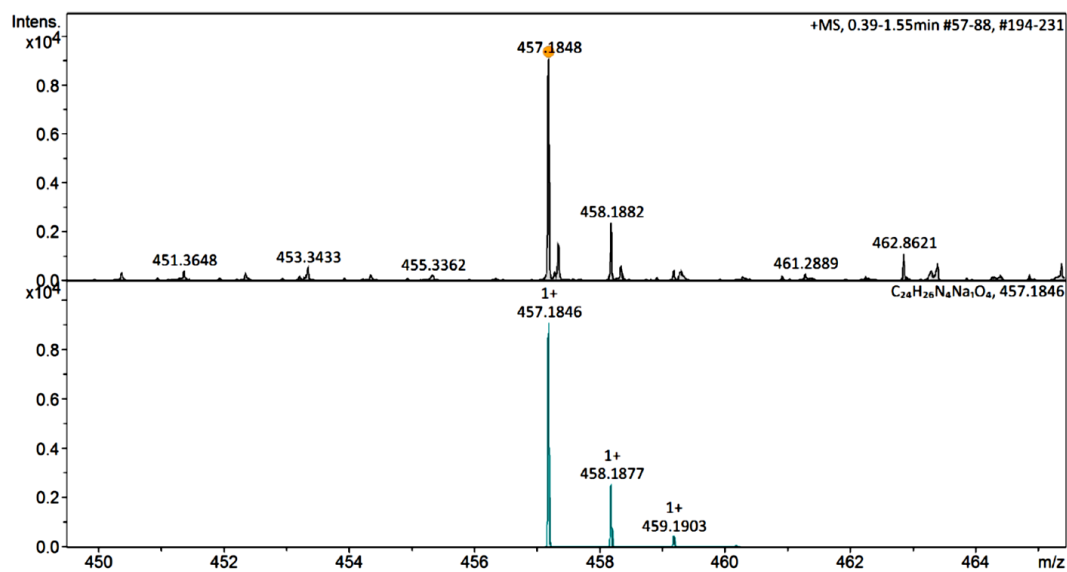
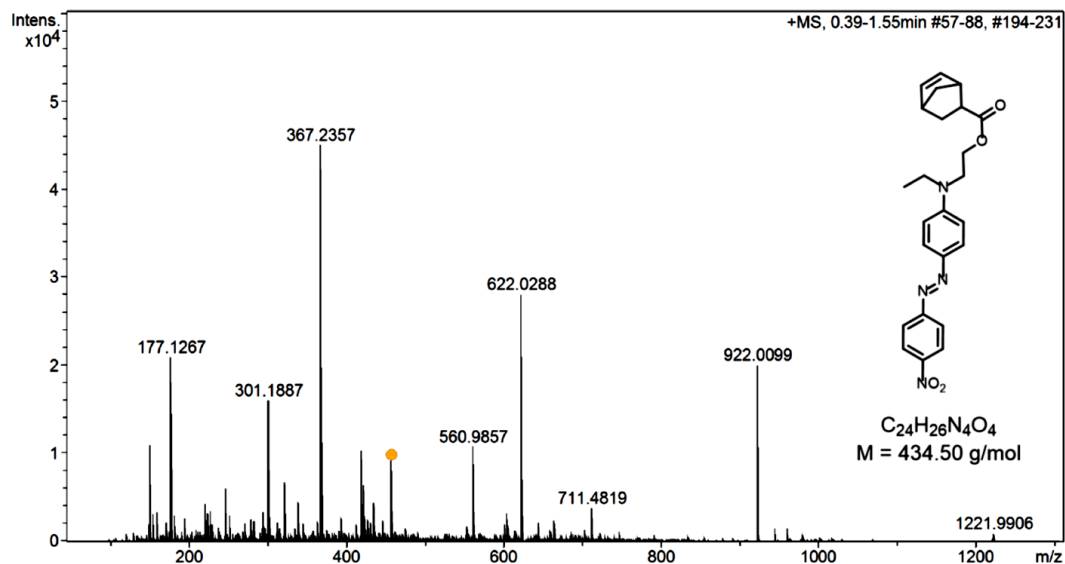


Figure S28 Mass spectra of NBE-3

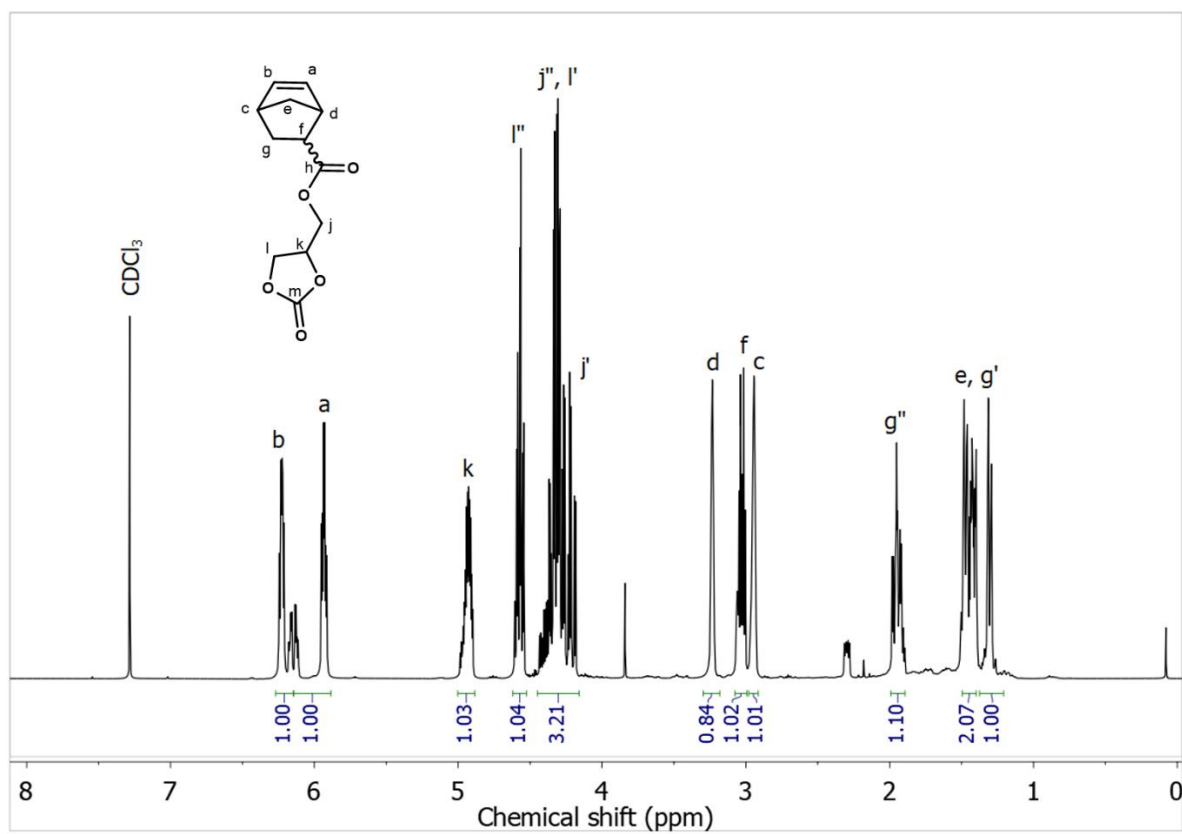


Figure S29 ^1H NMR spectrum of NBE-4

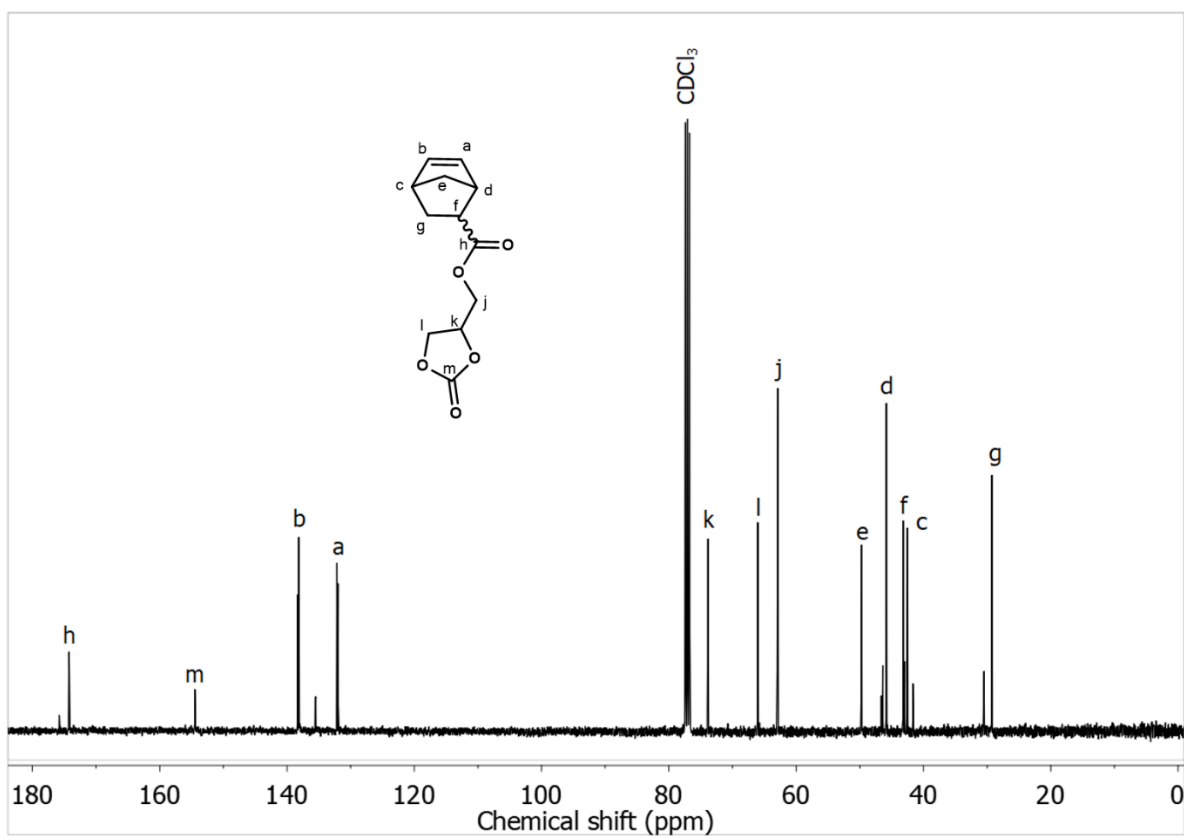


Figure S30 ^{13}C NMR spectrum of NBE-4

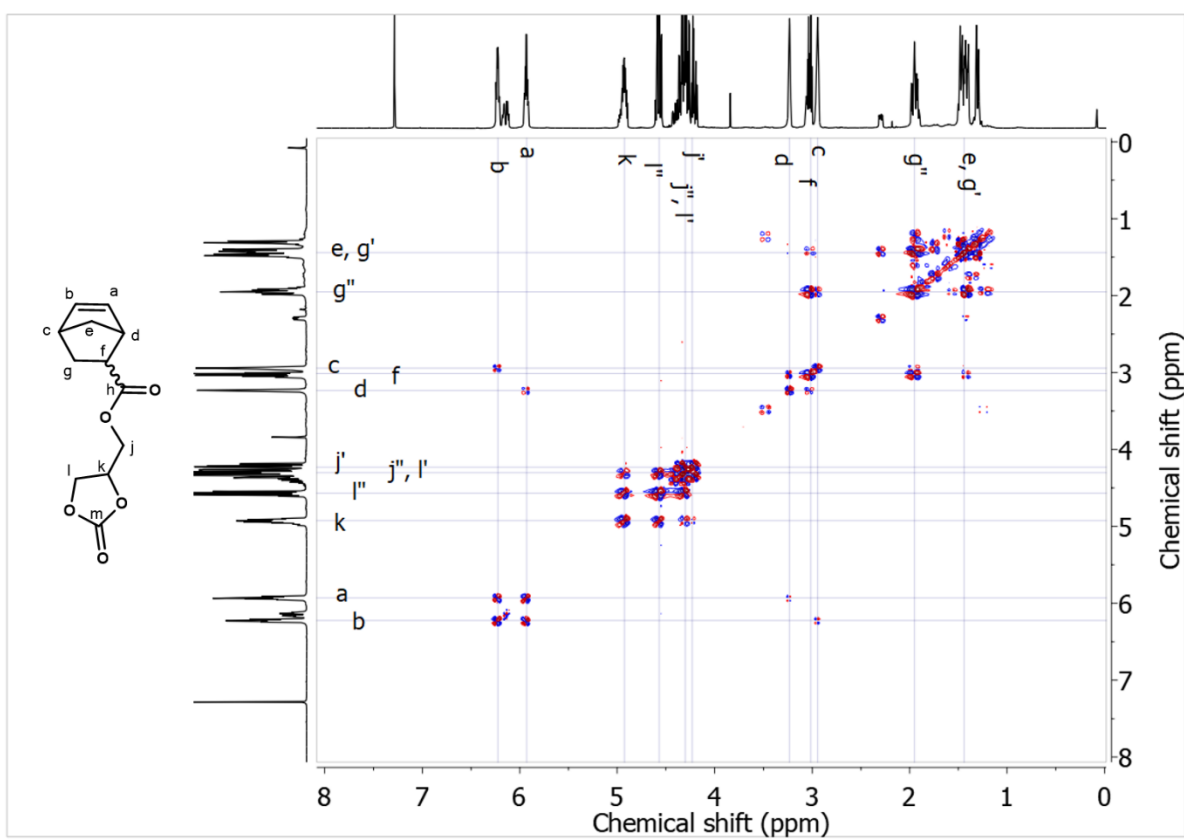


Figure S31 COSY of NBE-4

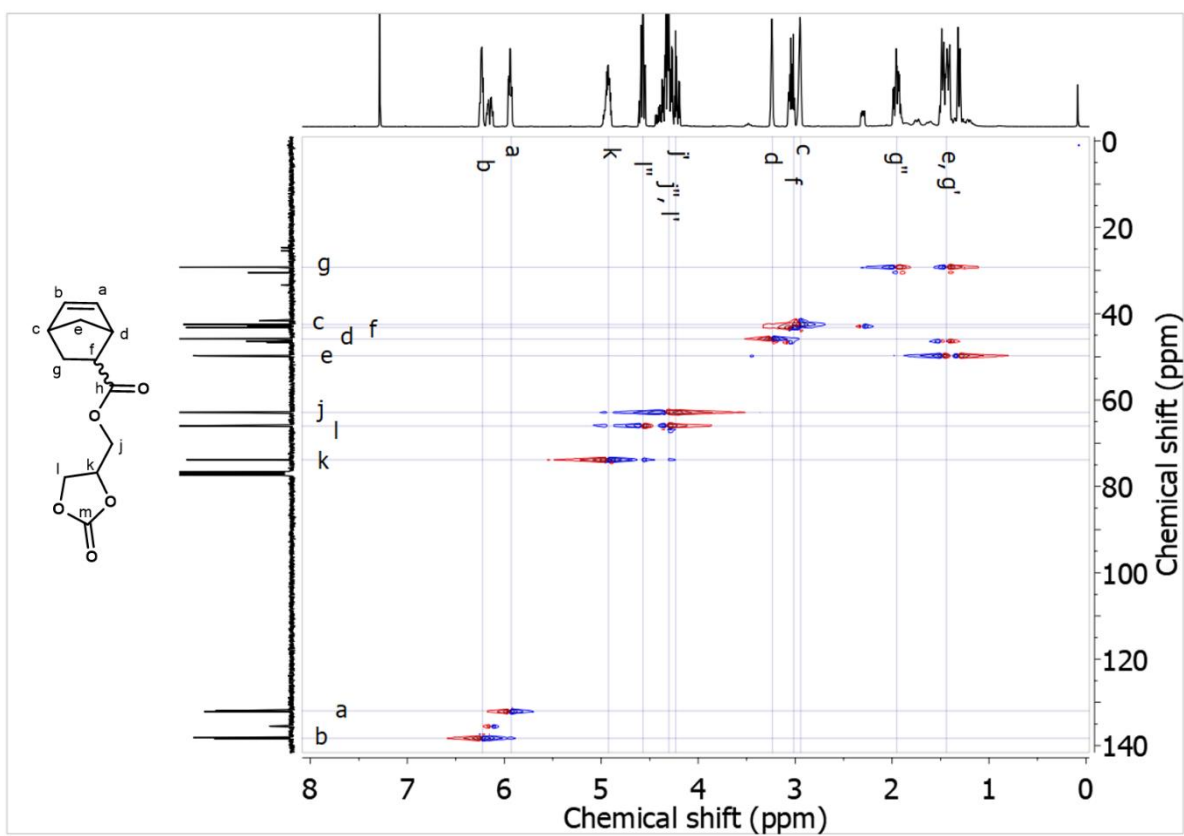


Figure S32 HSQC of NBE-4

Laboratorium für Organische Chemie

Tel: 044/633 43 58

Mikroelementaranalyse

Tel: 058/765 48 01

$$M_r = 238.24 \text{ g/mol}$$

```
gereinigt: ?????????????????????? getrocknet: HV
```

Bestimmungen: C H N

Ausgang: 20.09.19

Operator: PK

Berechnete Gewichtsanteile:

O=C1OC(=O)C1OCC(=O)C2=CC=CC=C2

$C_{12}H_{14}O_5$
M = 238.24 g/mol

Gefundene Gewichtsanteile:

20.09.19

20.09.19

Von flüssigen Proben können nur CHN bestimmt werden. Probe ist nicht homogen (Flüssig+Kristalle)

Figure S33 Elemental analysis of NBE-4

Acquisition Parameter

Method: ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m
File Name: D:\Data\lmax0051xx\BMAX005109.d
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 1300 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 200.0 Vpp

Acquisition Date: 10.10.2019 16:09:13
Operator: Daniel Wirz
Set Nebulizer: 1.6 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 8.0 l/min
Set Divert Valve: Source

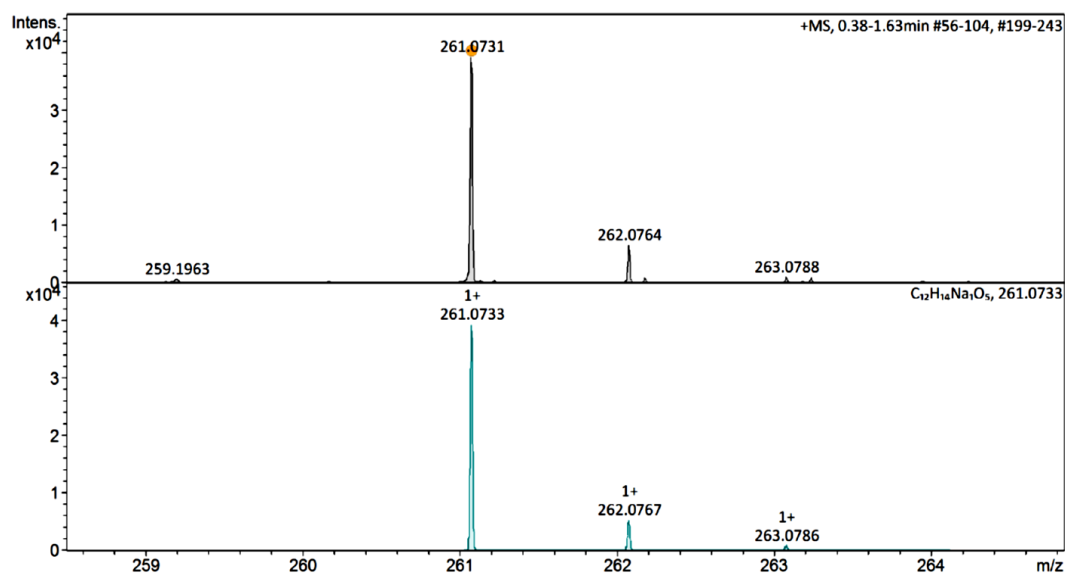
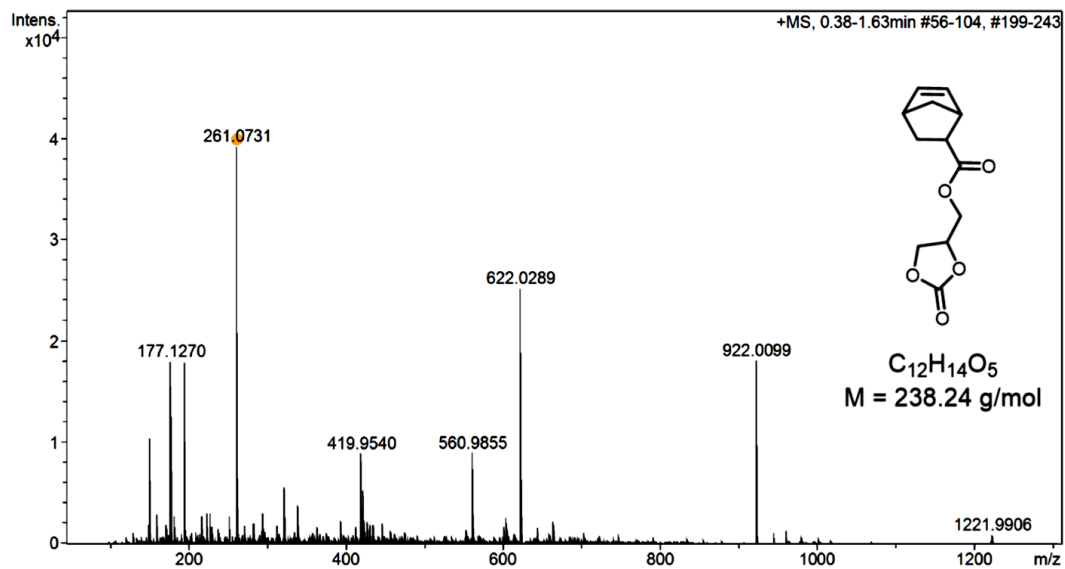


Figure S34 Mass spectra of NBE-4

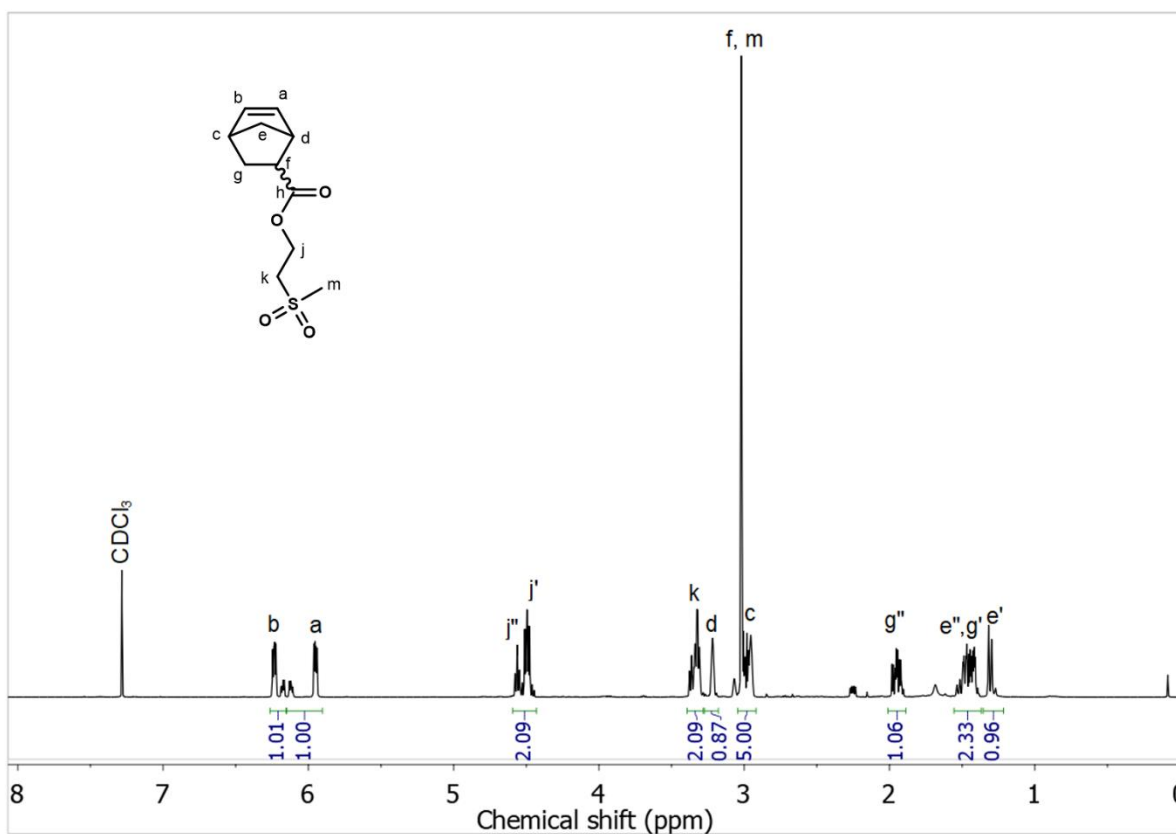


Figure S35 ¹H NMR spectrum of NBE-5

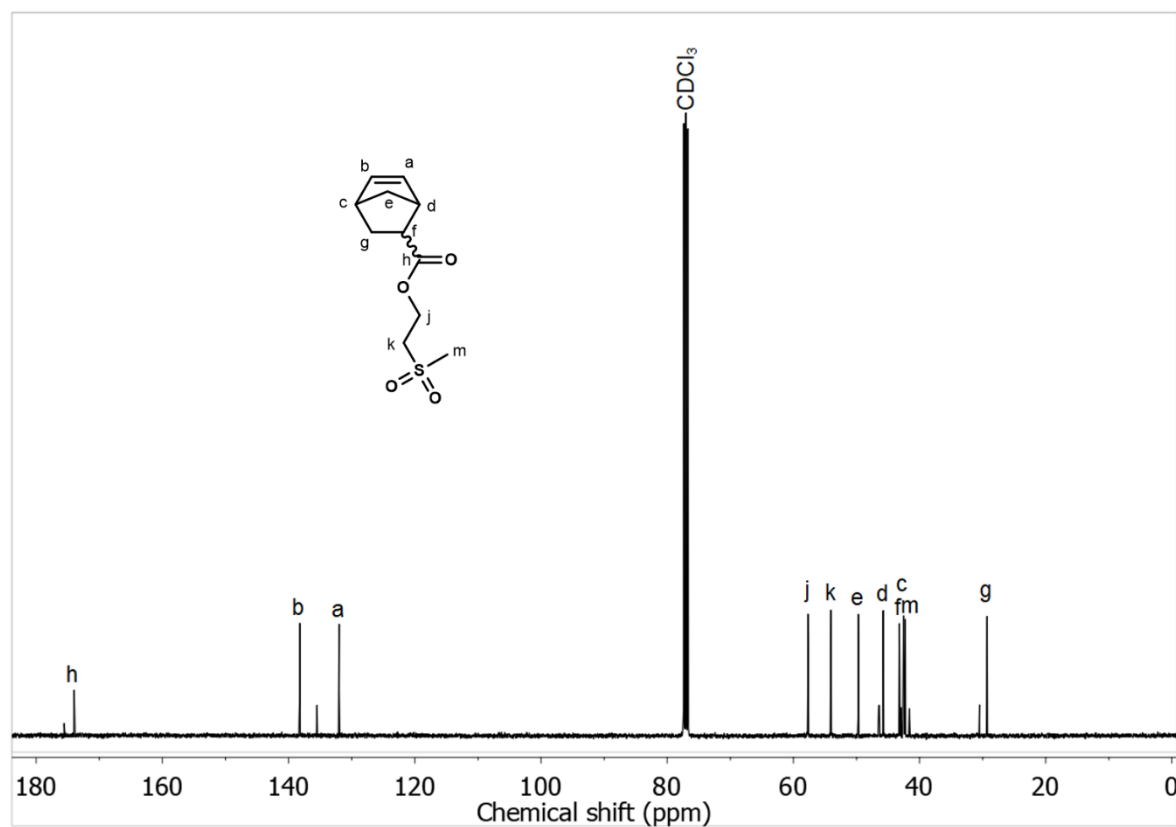


Figure S36 ¹³C NMR spectrum of NBE-5

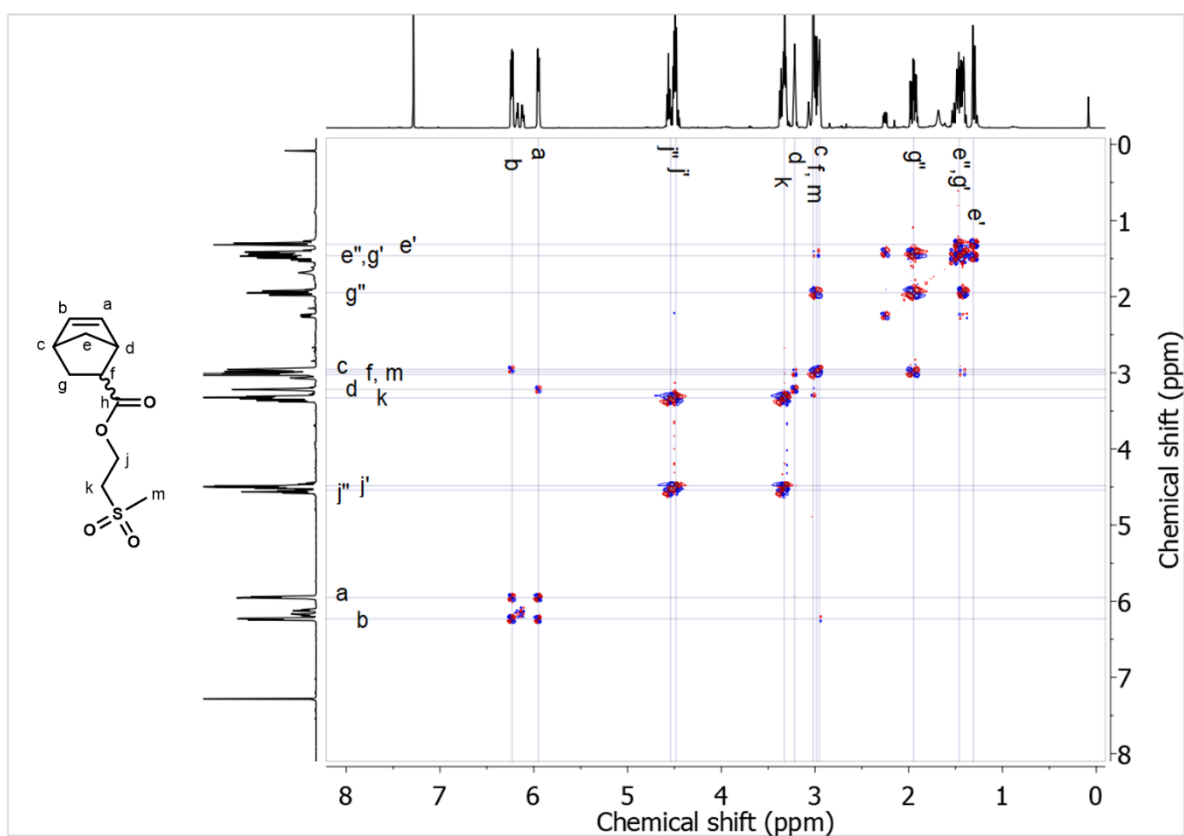


Figure S37 COSY of NBE-5

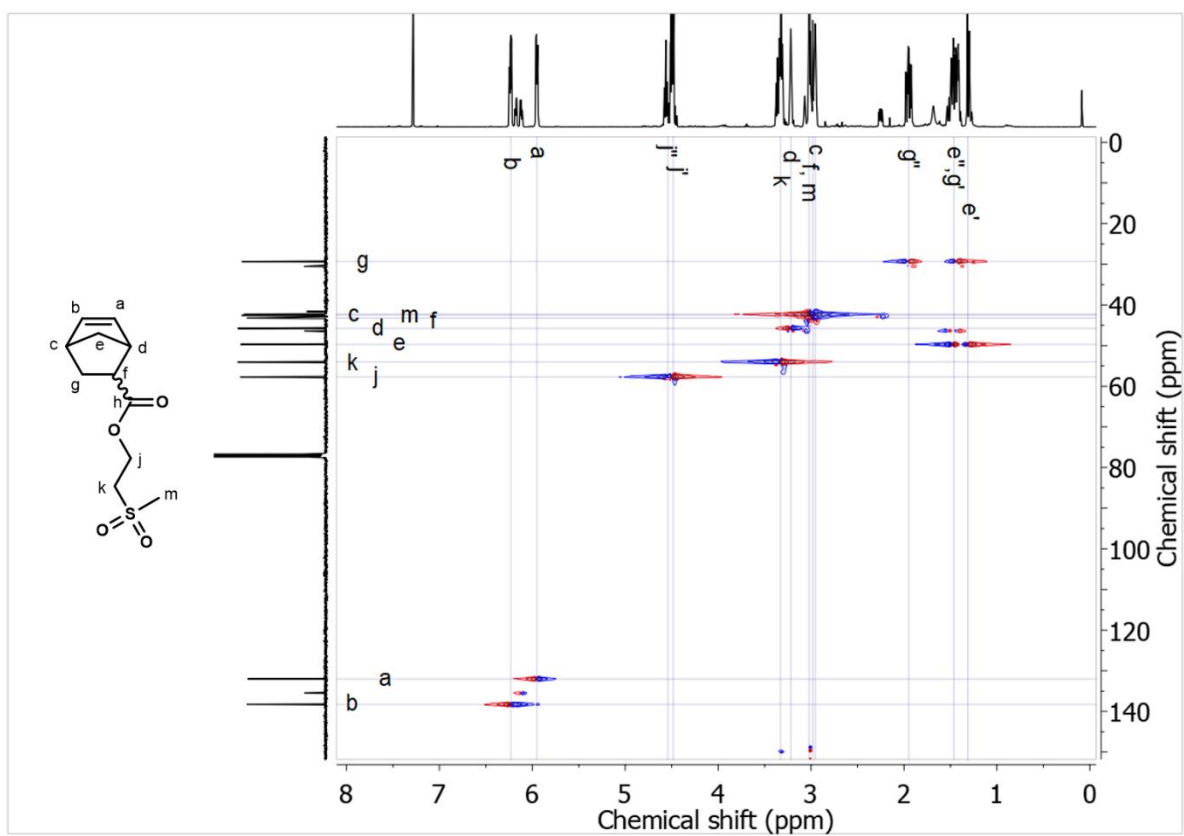


Figure S38 HMQC of NBE-5

Acquisition Parameter

Method: ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m
File Name: D:\Data\lmax0096xx\BMAX009630.d
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 1300 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 200.0 Vpp

Acquisition Date: 26.08.2020 13:39:31
Operator: Michael Meier
Set Nebulizer: 1.6 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 8.0 l/min
Set Divert Valve: Source

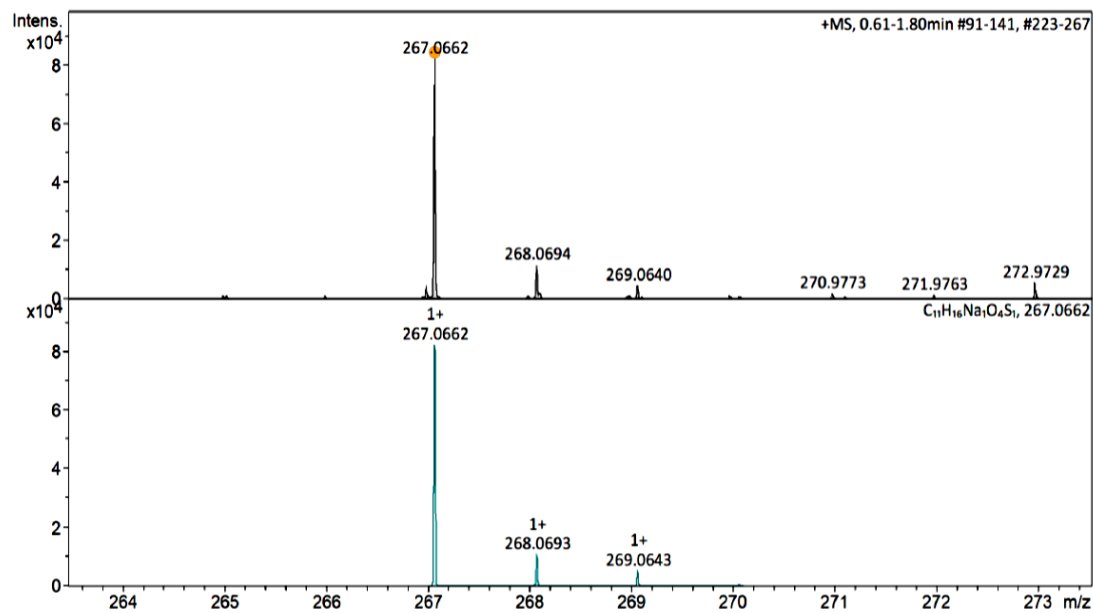
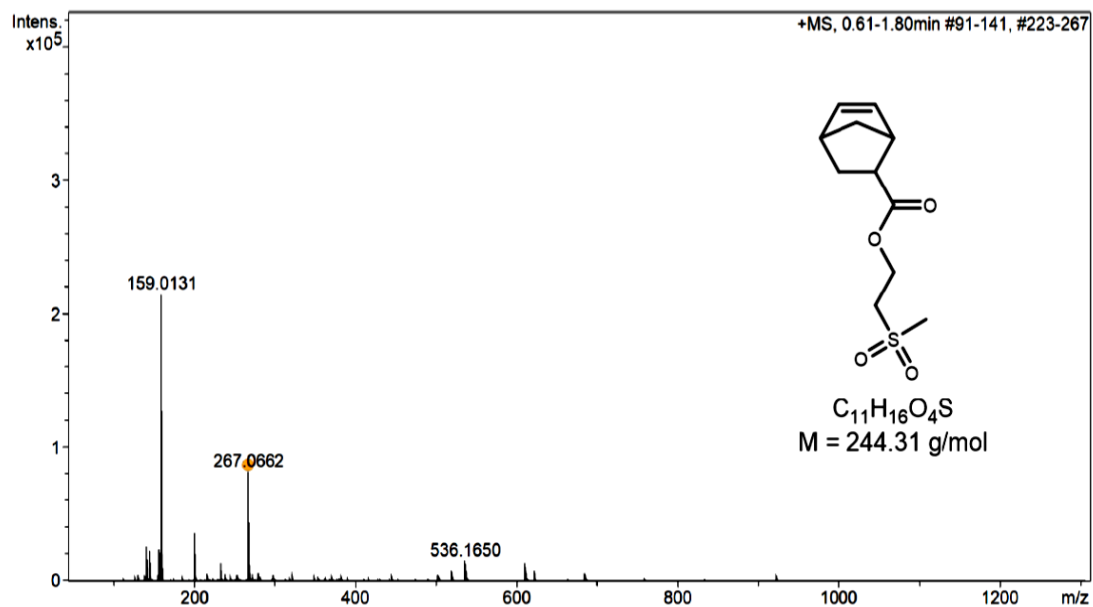


Figure S39 Mass spectra of NBE-5

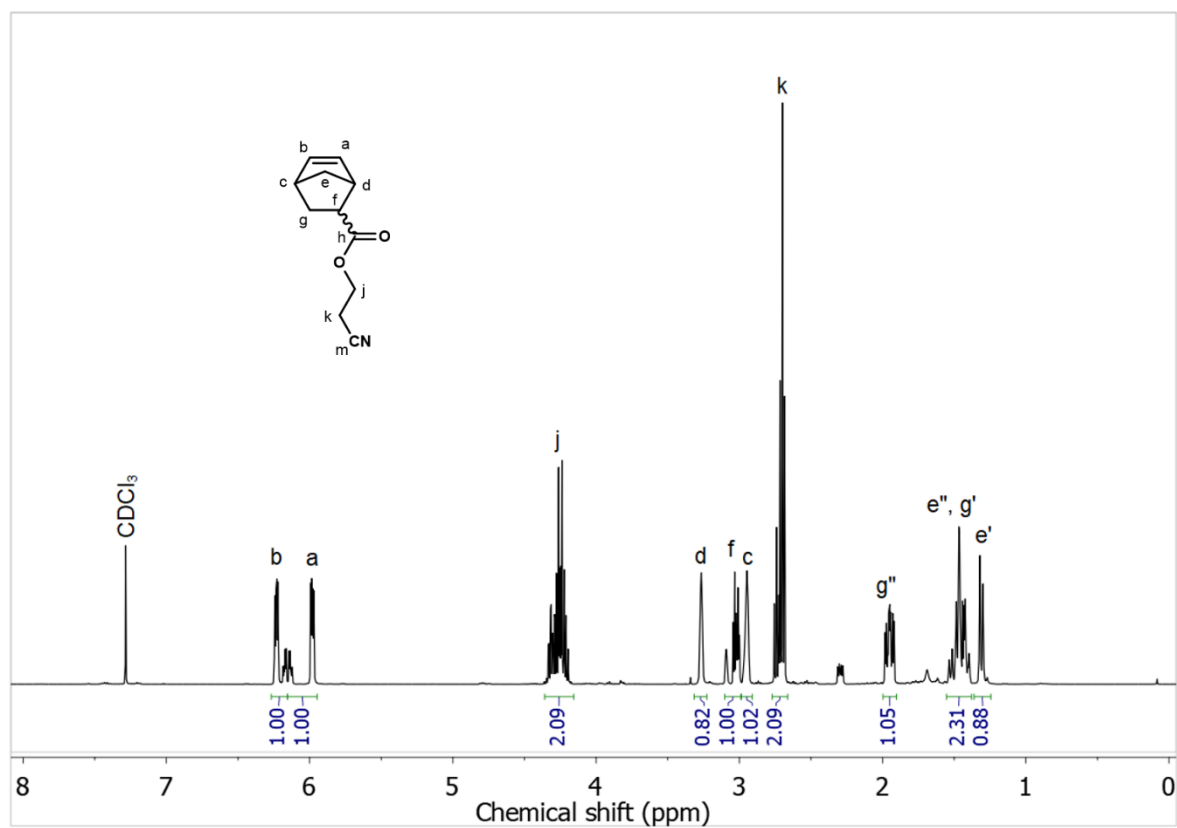


Figure S40 ¹H NMR spectrum of **NBE-6**

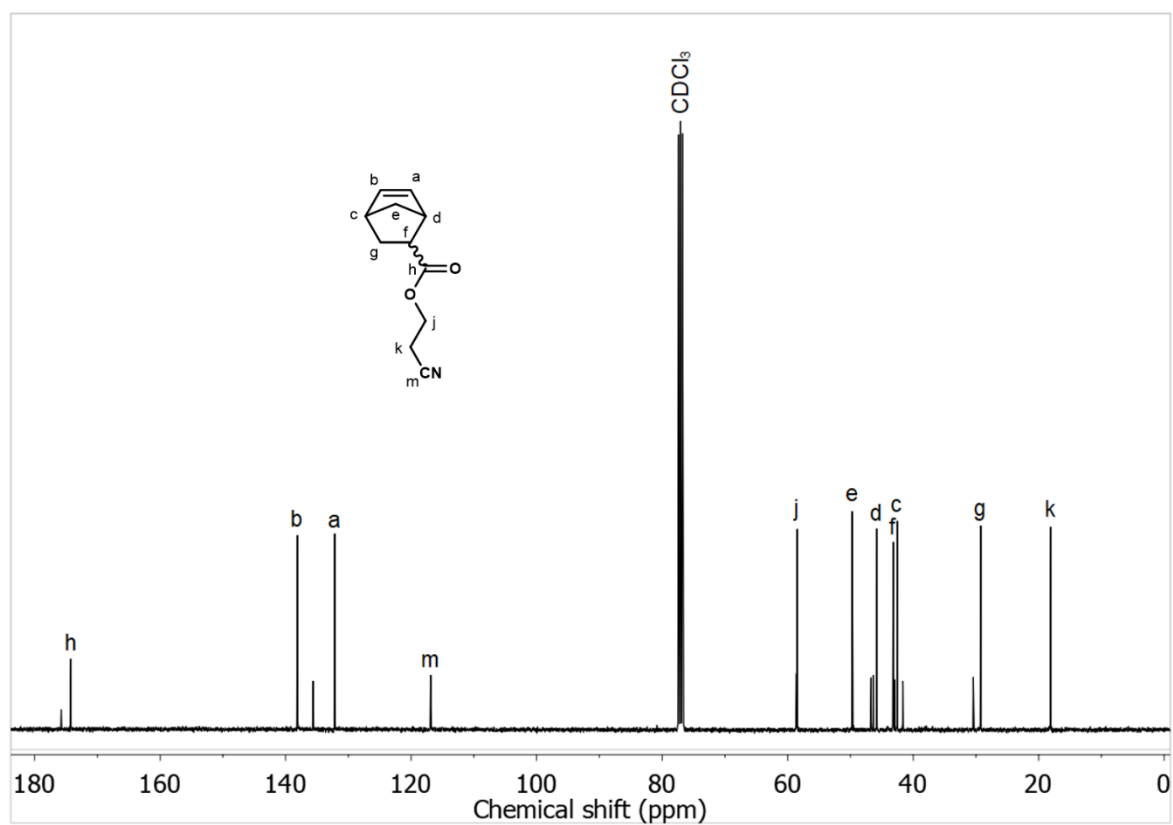


Figure S41 ¹³C NMR spectrum of **NBE-6**

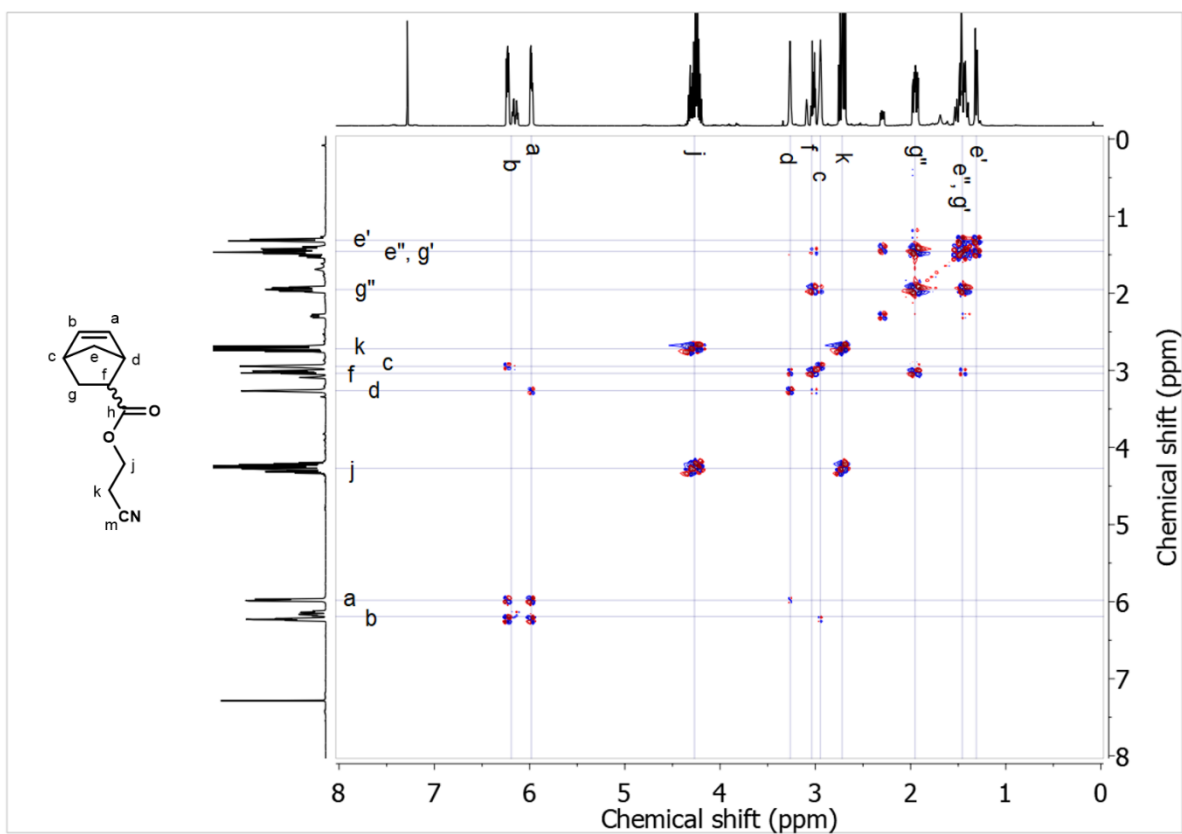


Figure S42 COSY of NBE-6

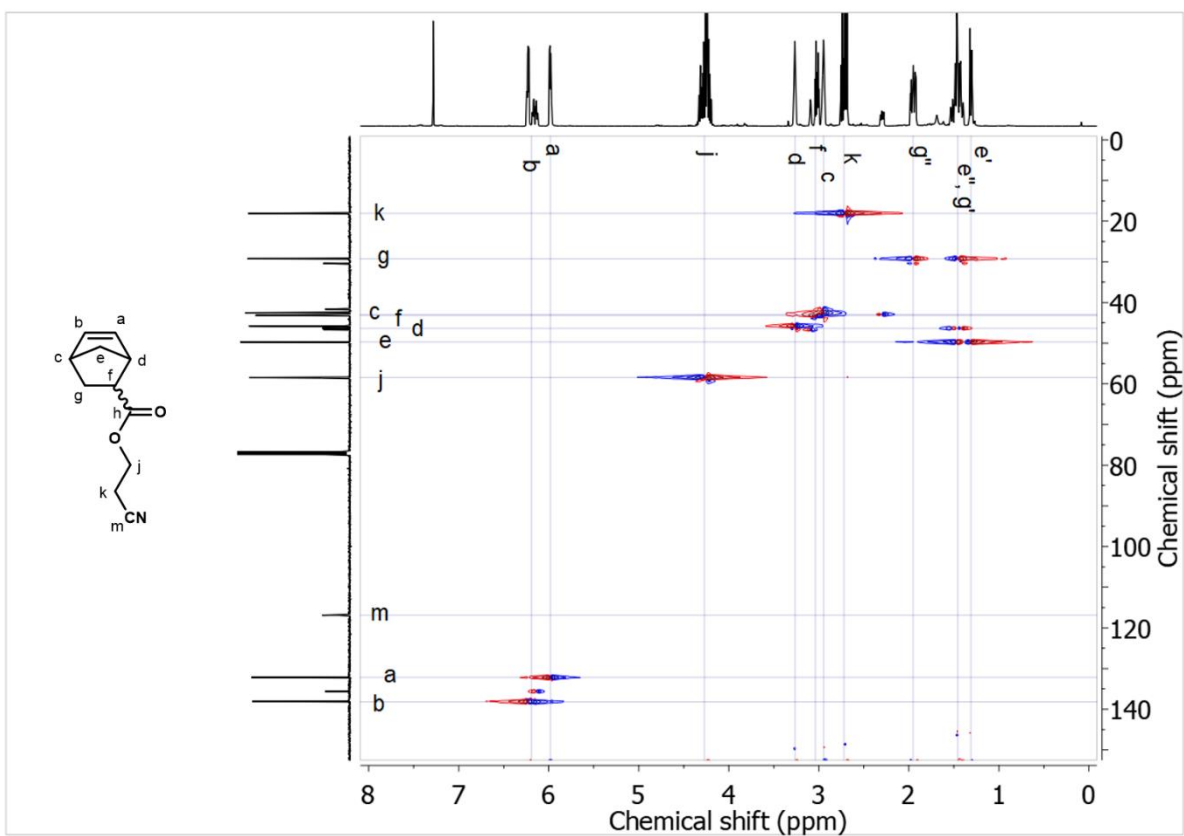


Figure S43 HSQC of NBE-6

Acquisition Parameter

Method: ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m
 File Name: D:\Data\lmax0096xx\BMAX009631.d
 Source Type: ESI
 Focus: Not active
 Scan Begin: 50 m/z
 Scan End: 1300 m/z
 Ion Polarity: Positive
 Set Capillary: 4500 V
 Set End Plate Offset: -500 V
 Set Collision Cell RF: 200.0 Vpp

Acquisition Date: 26.08.2020 13:42:29
 Operator: Michael Meier
 Set Nebulizer: 1.6 Bar
 Set Dry Heater: 200 °C
 Set Dry Gas: 8.0 l/min
 Set Divert Valve: Source

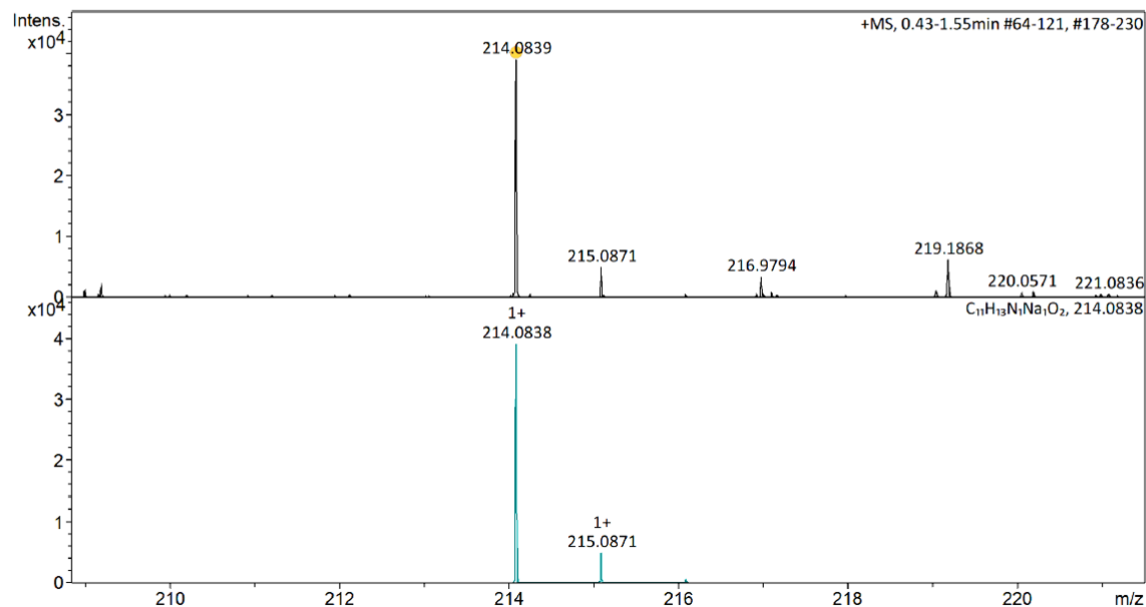
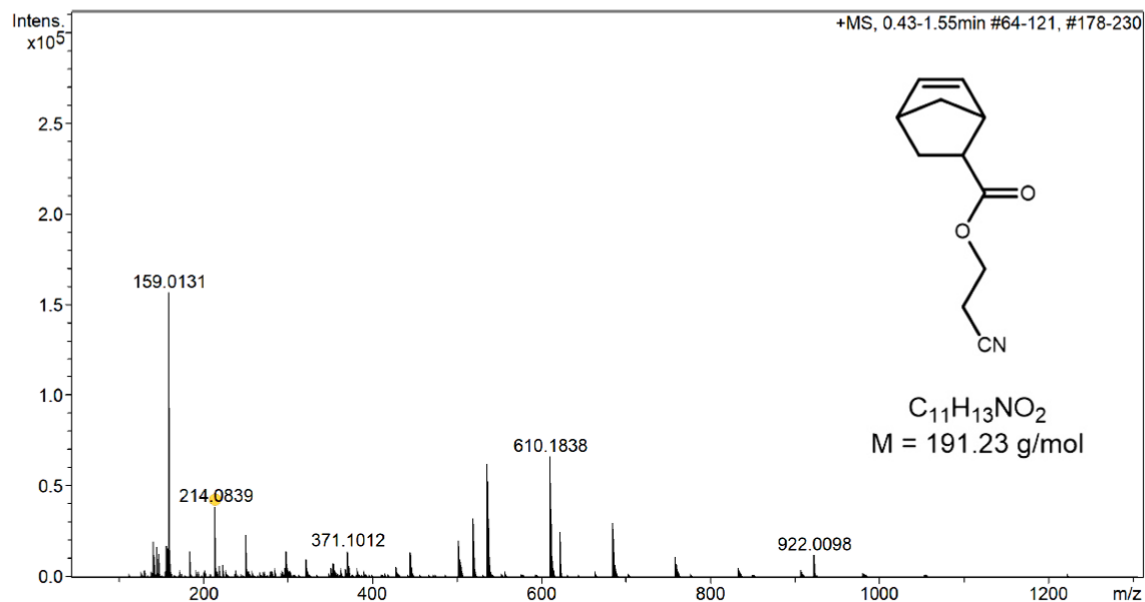


Figure S44 Mass spectra of NBE-6

Structure characterization of polymers

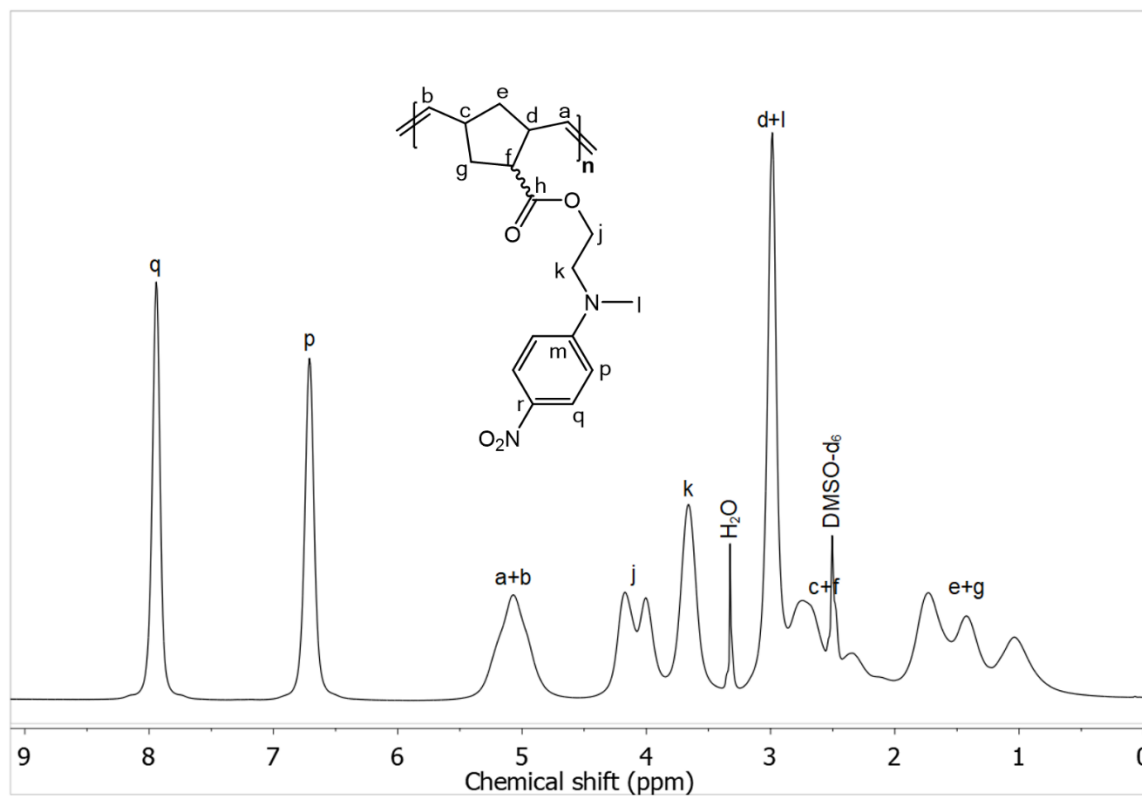


Figure S45 ^1H NMR spectrum of PNBE-2

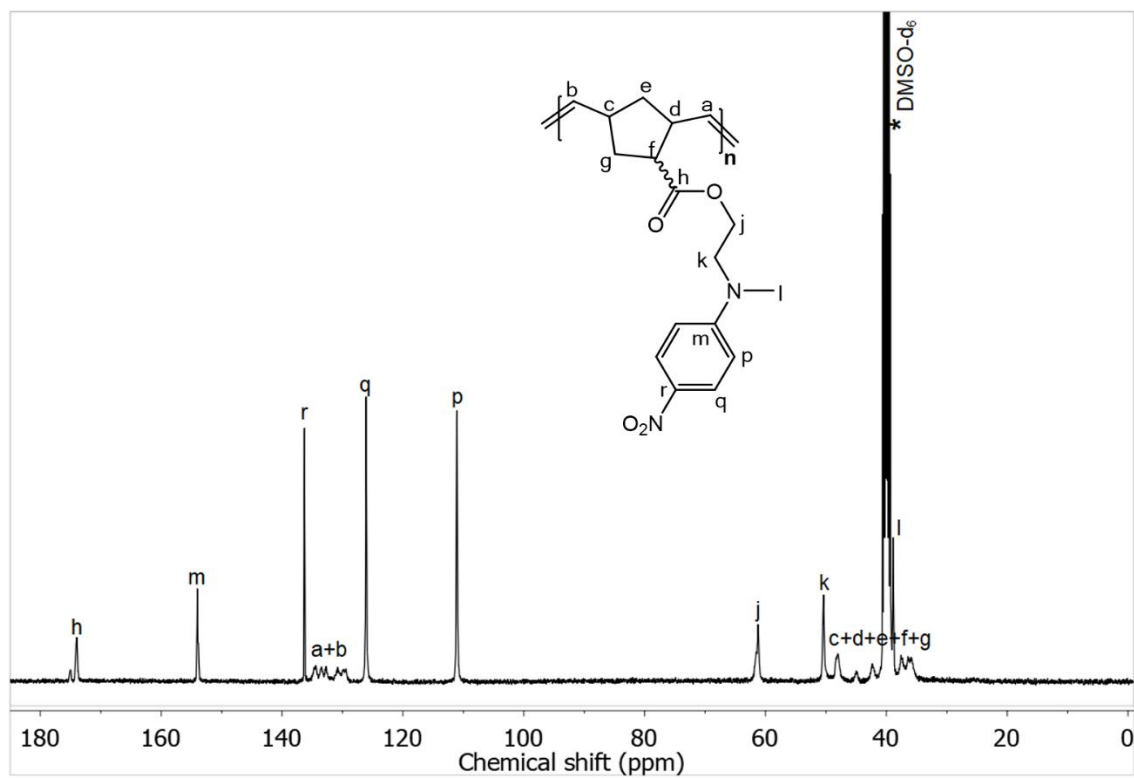


Figure S46 ^{13}C NMR spectrum of PNBE-2

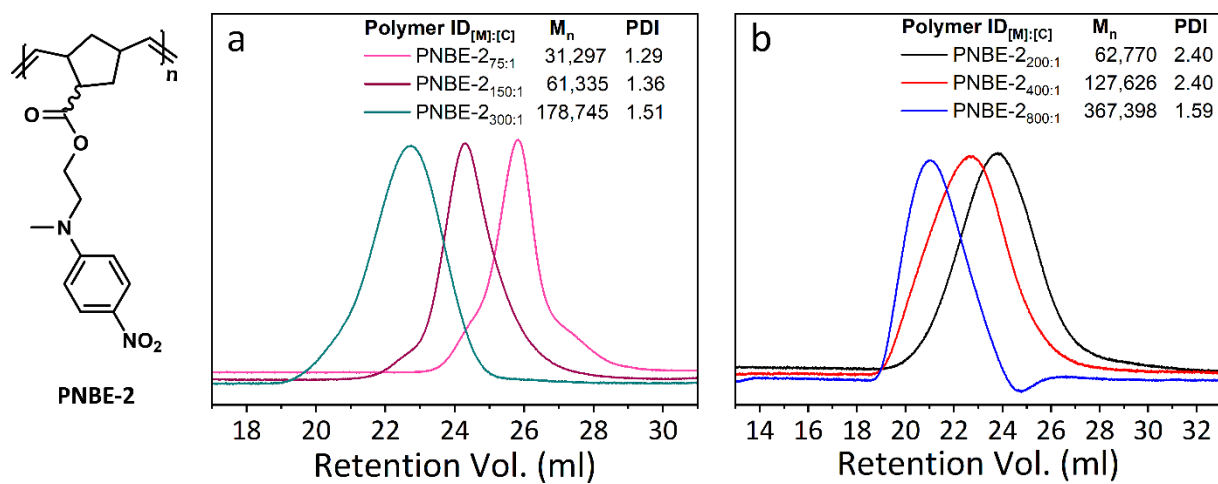


Figure S47 GPC elugrams of **PNBE-2** synthesized by (a) Grubb's first- and (b) third generation catalyst; in HFIP + 20 mM sodium trifluoroacetate

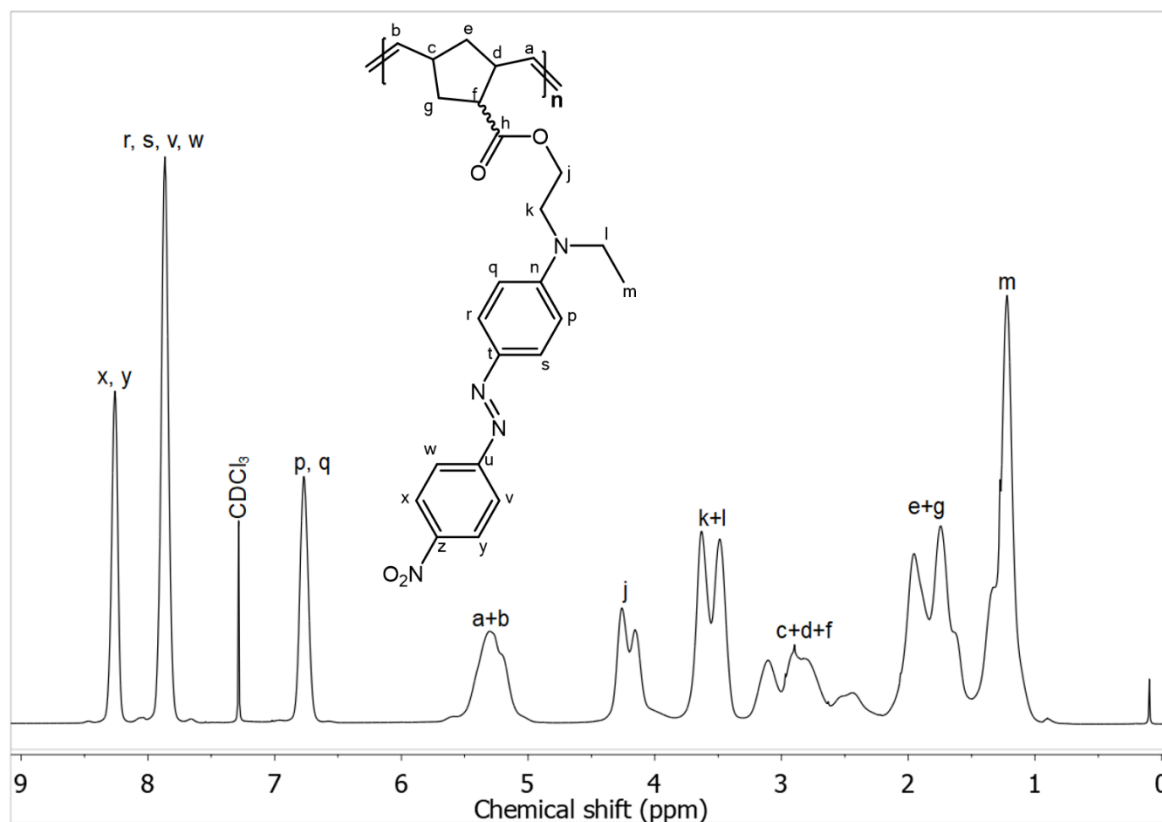


Figure S48 ^1H NMR spectrum of **PNBE-3**

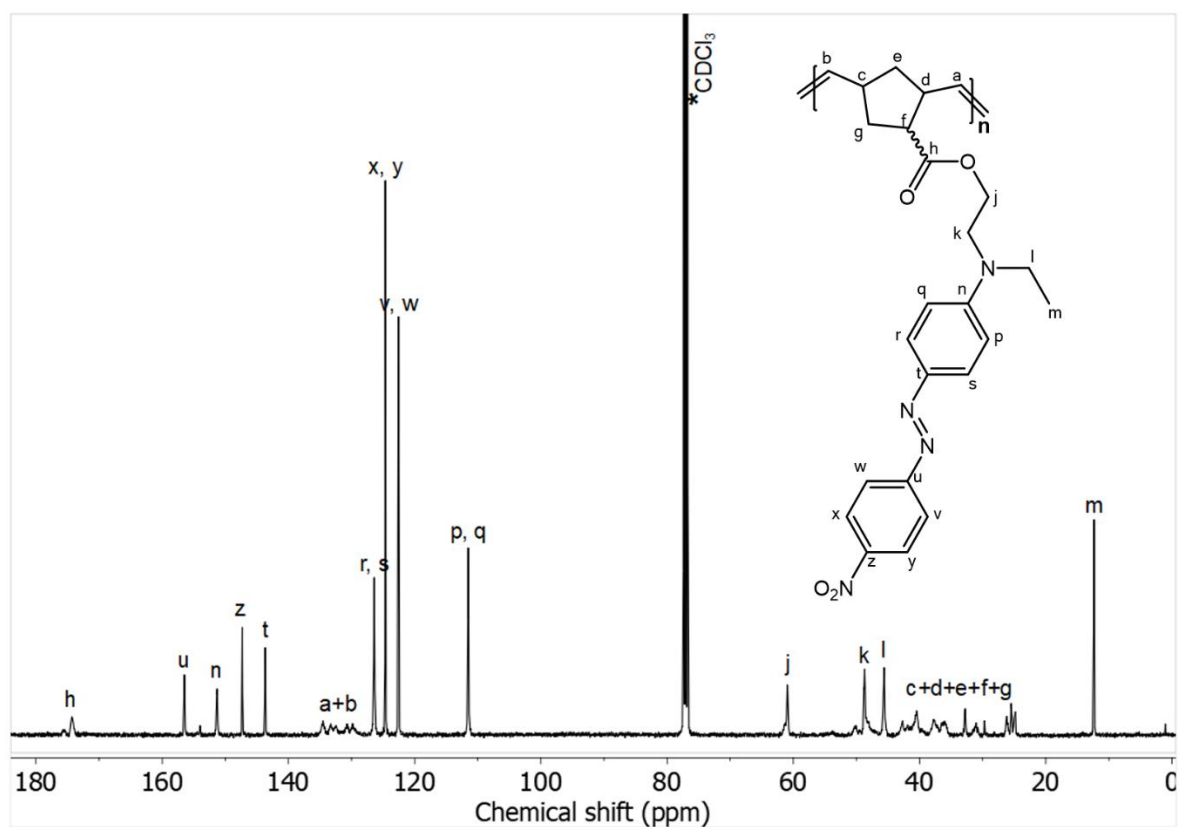


Figure S49 ^{13}C NMR spectrum of PNBE-3

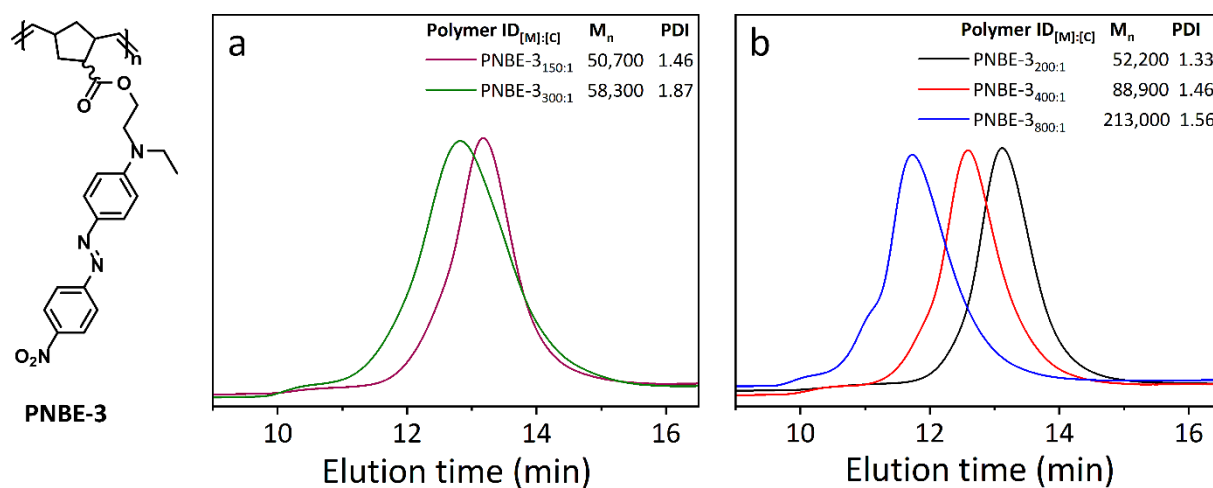


Figure S50 GPC elugrams of PNBE-3 synthesized by (a) Grubb's first- and (b) third generation catalyst; in THF

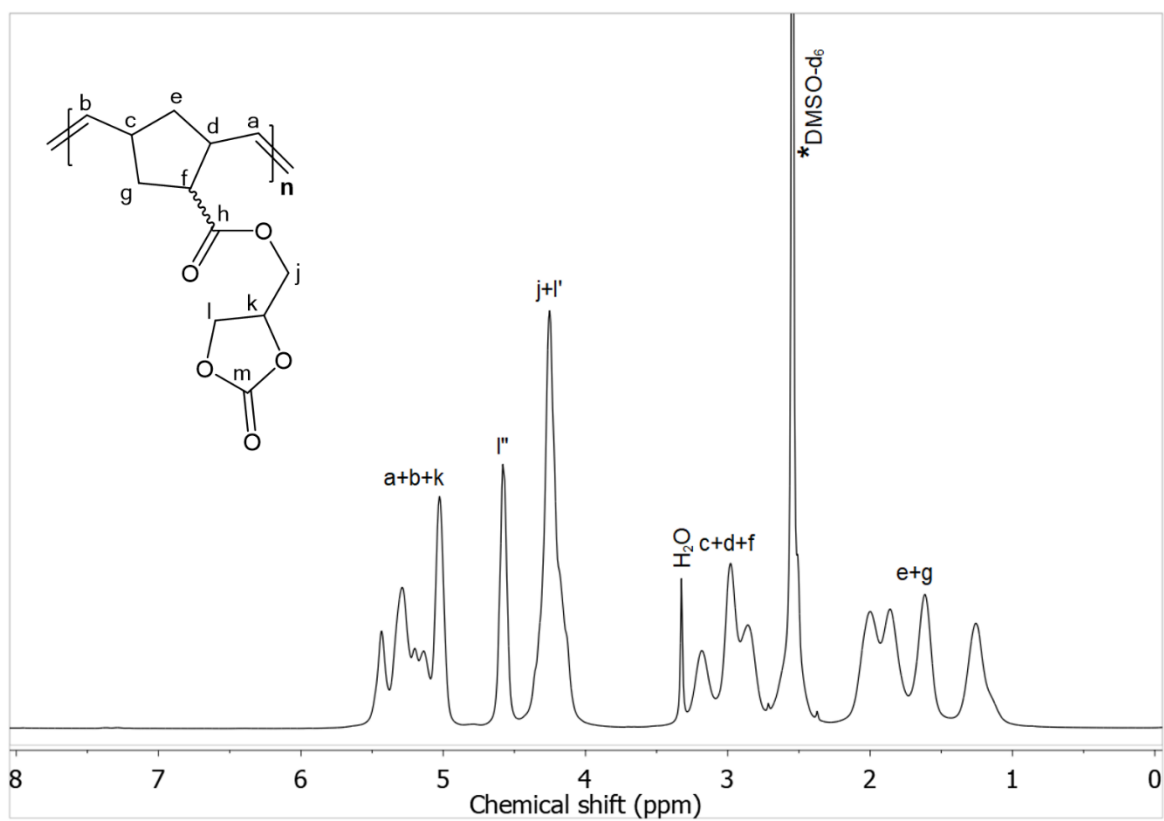


Figure S51 ^1H NMR spectrum of PNBE-4

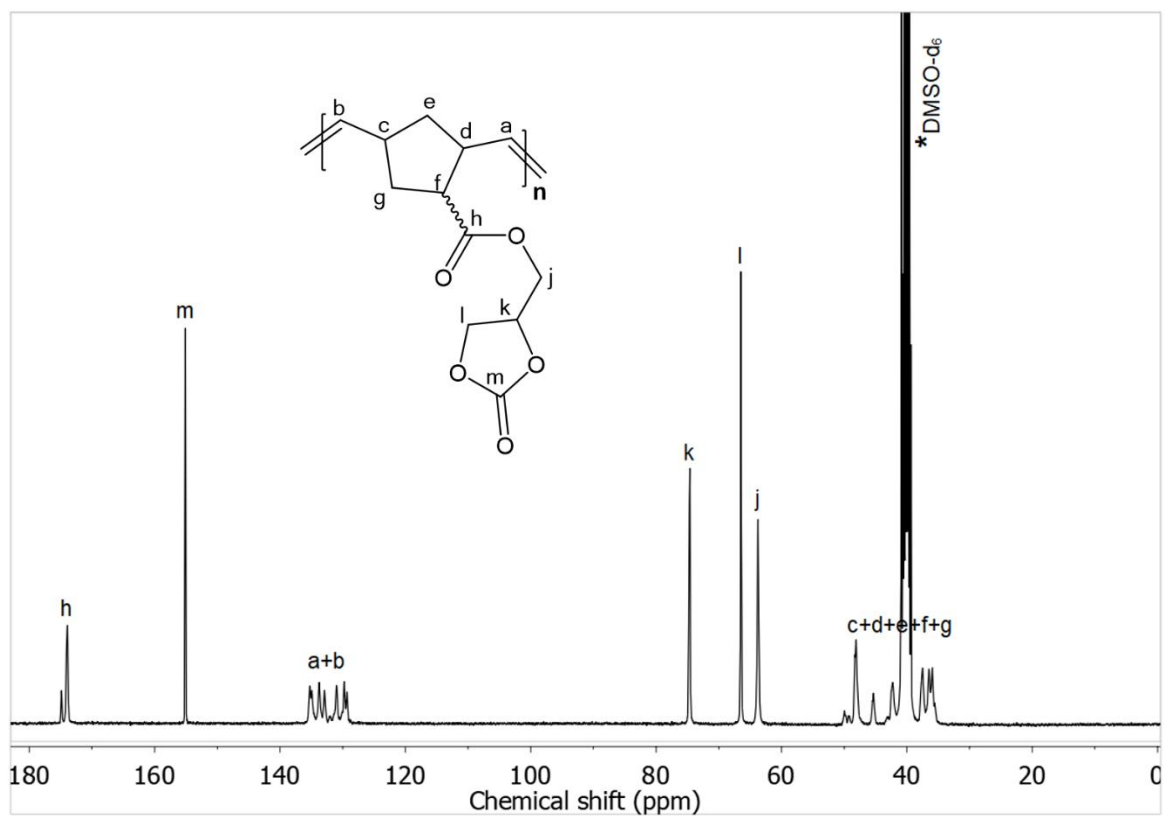


Figure S52 ^{13}C NMR spectrum of PNBE-4

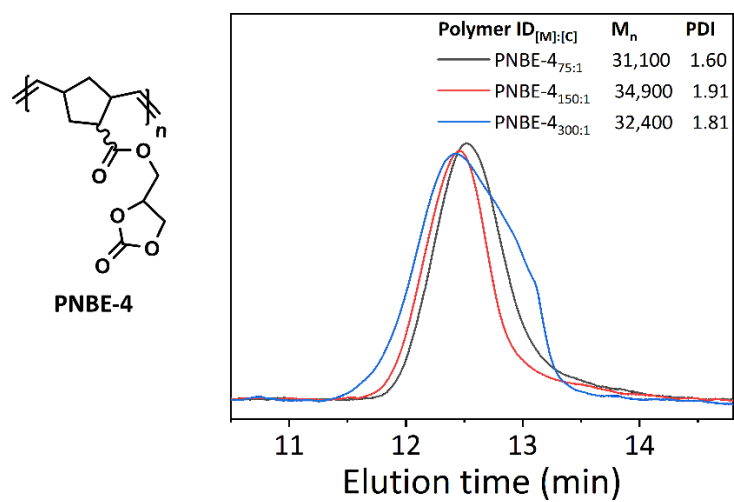


Figure S53 GPC elograms of **PNBE-4** in HFIP

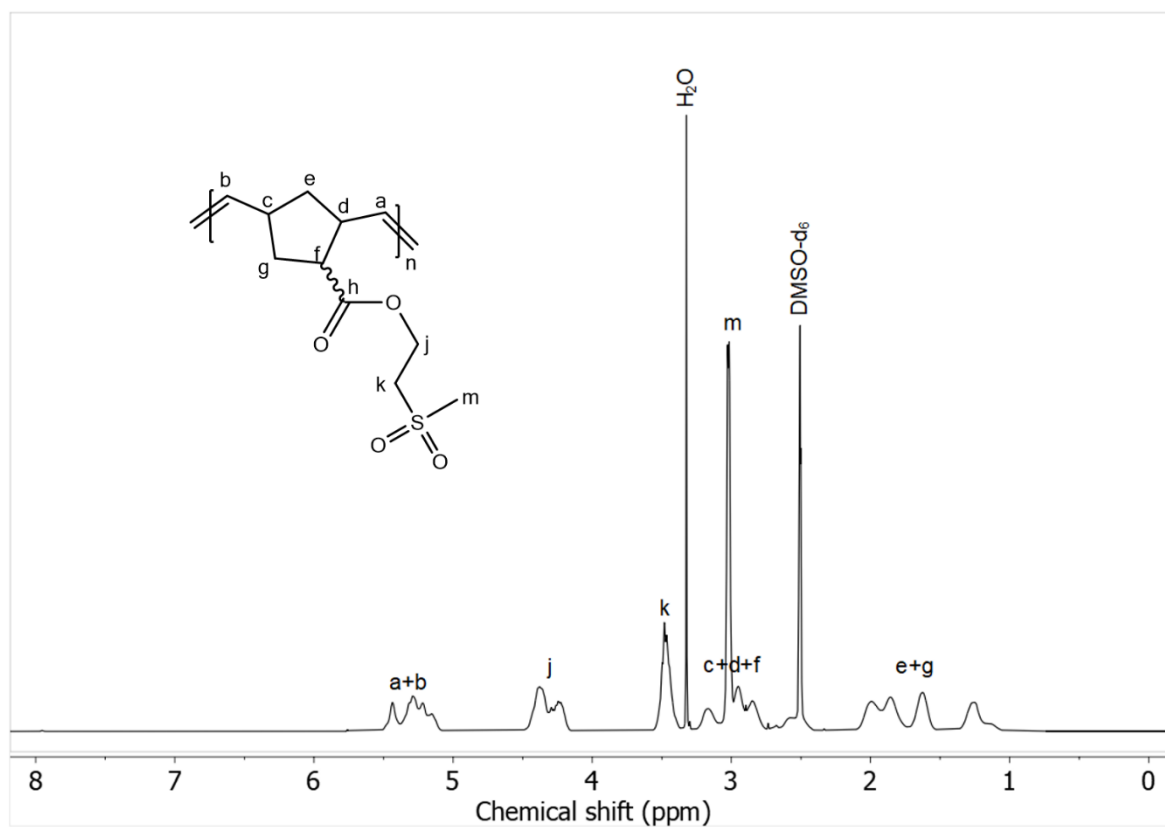


Figure S54 ^1H NMR spectrum of **PNBE-5**

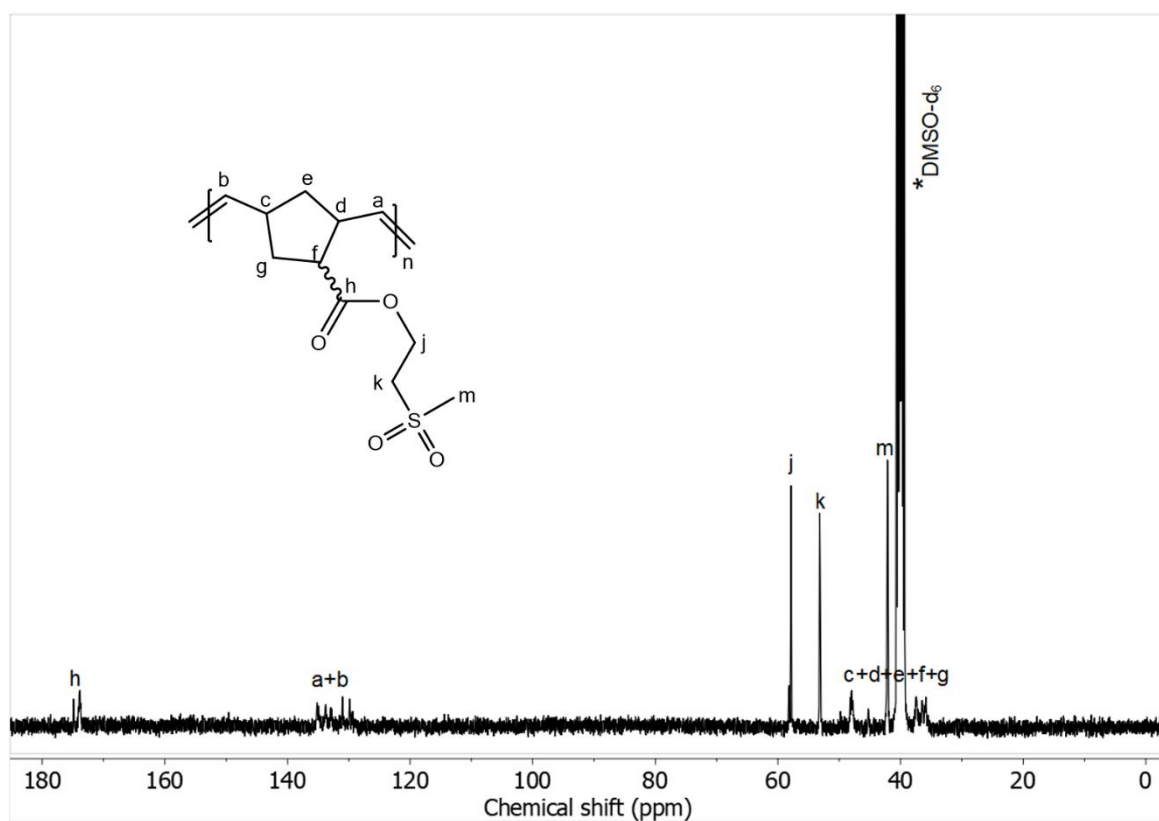


Figure S55 ^{13}C NMR spectrum of **PNBE-5**

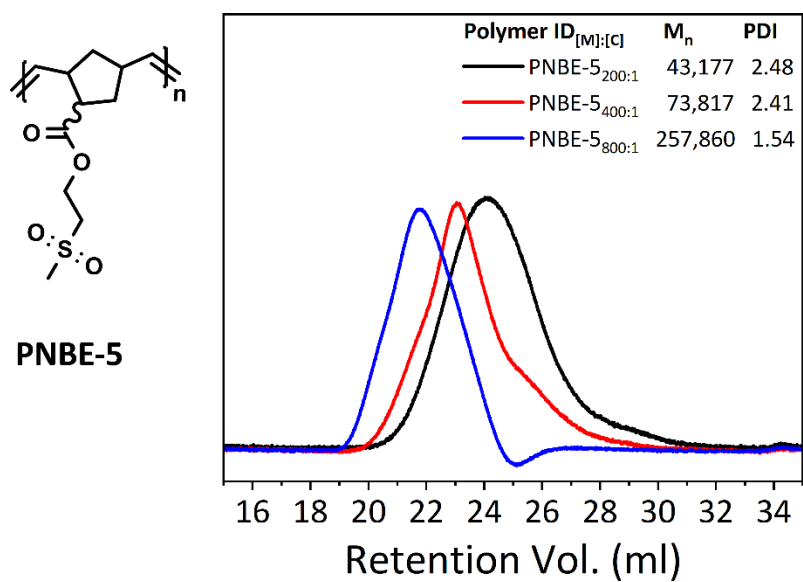


Figure S56 GPC elugrams of **PNBE-5** in HFIP + 20 mM sodium trifluoroacetate

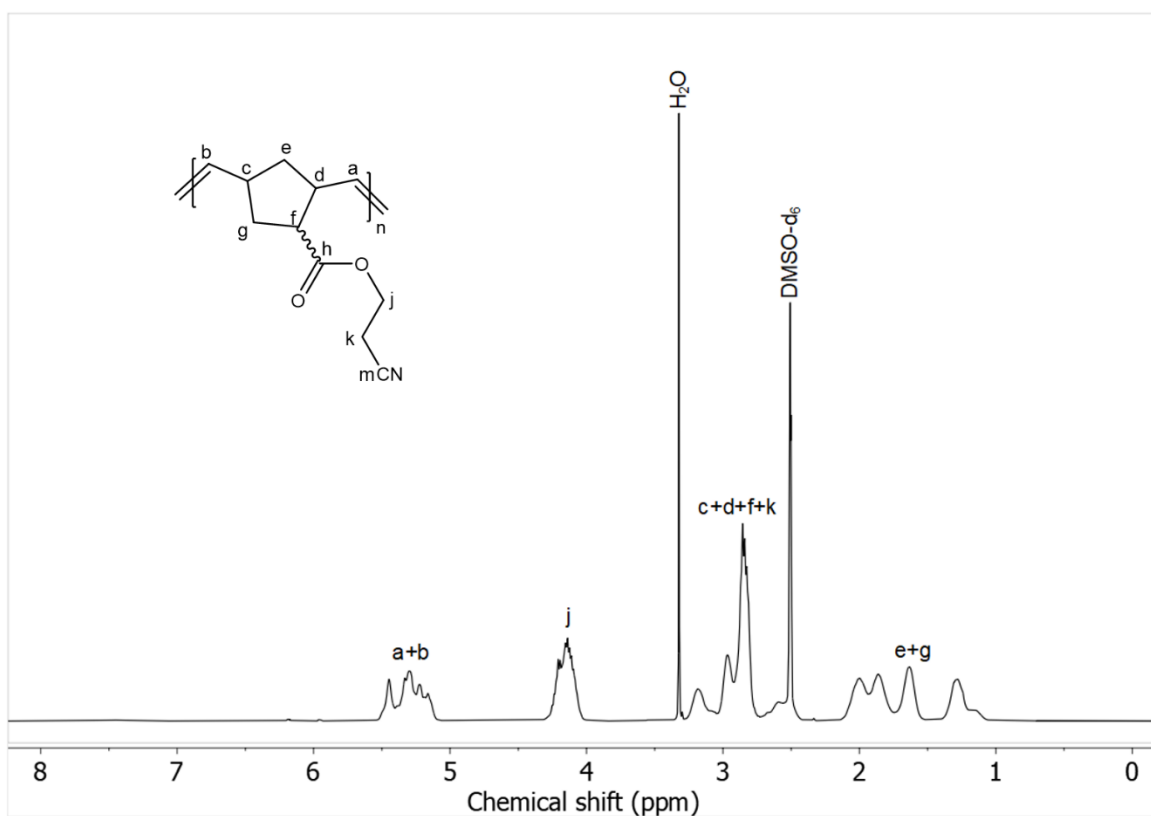


Figure S57 ¹H NMR spectrum of PNBE-6

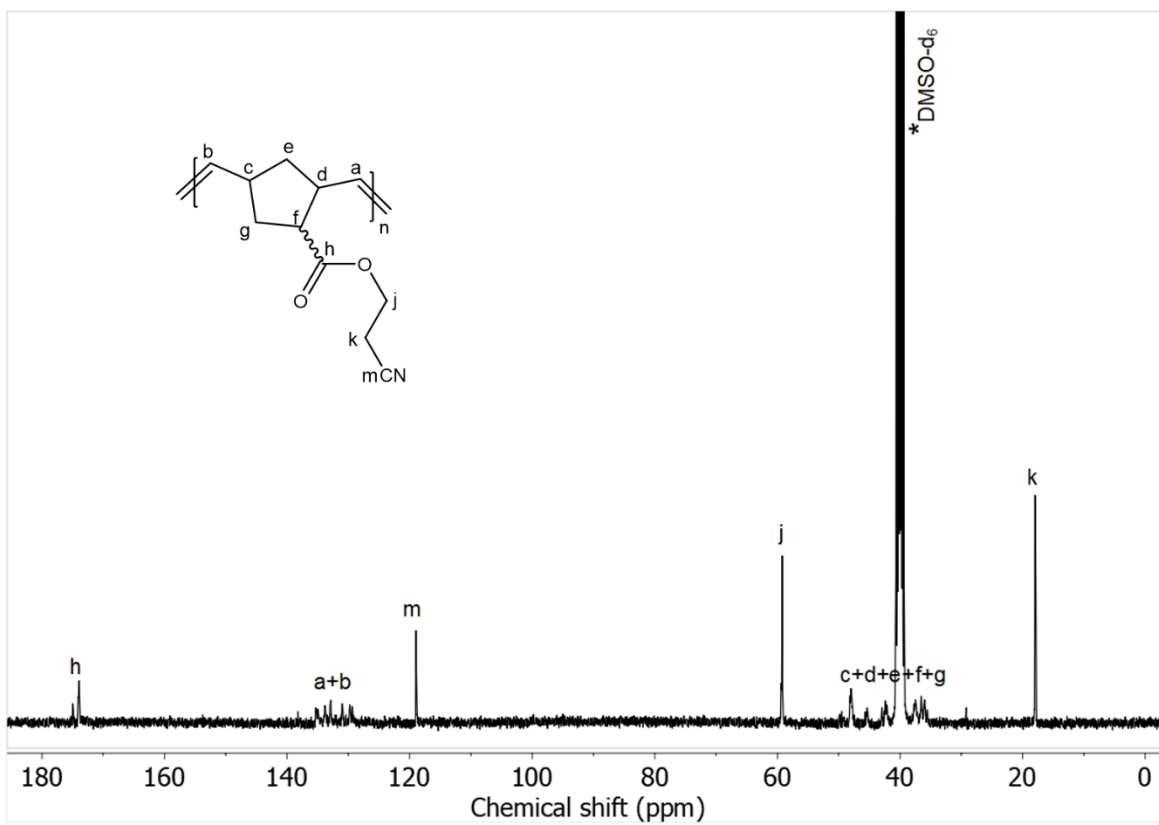


Figure S58 ¹³C NMR spectrum of PNBE-6

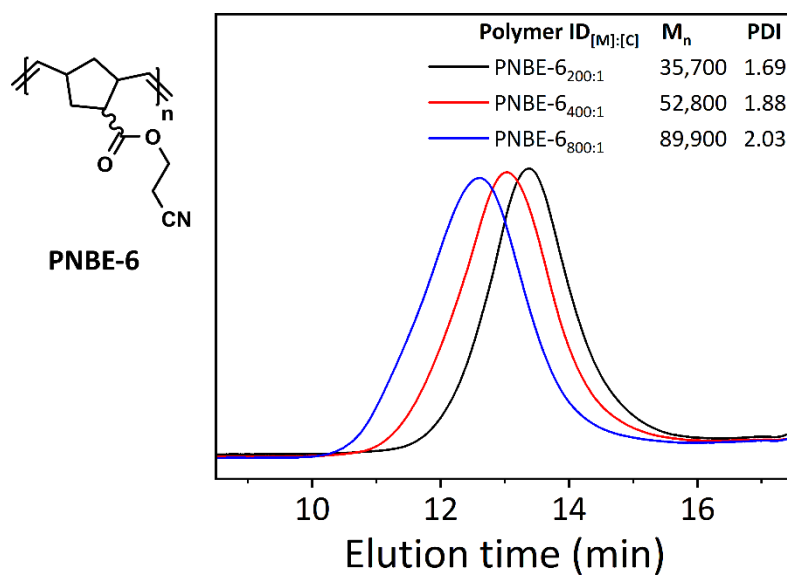


Figure S59 GPC elugrams of **PNBE-6** in THF

Thermal behaviour of polymers

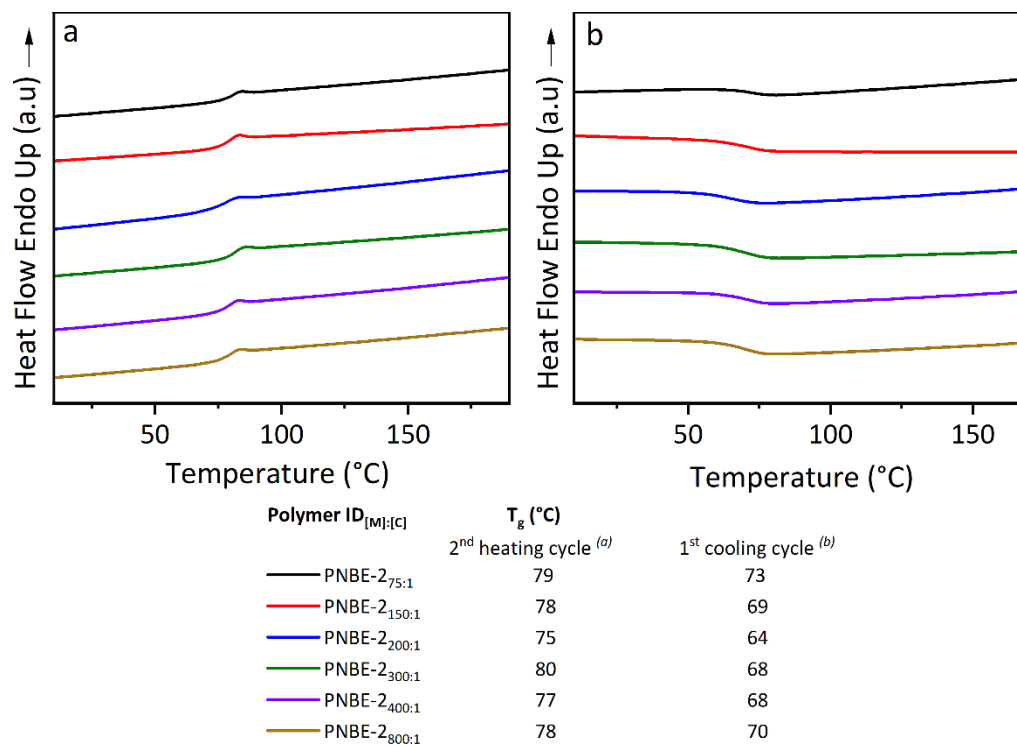


Figure S60 DSC thermograms for **PNBE-2** polymer sets in (a) second heating and (b) first cooling cycle

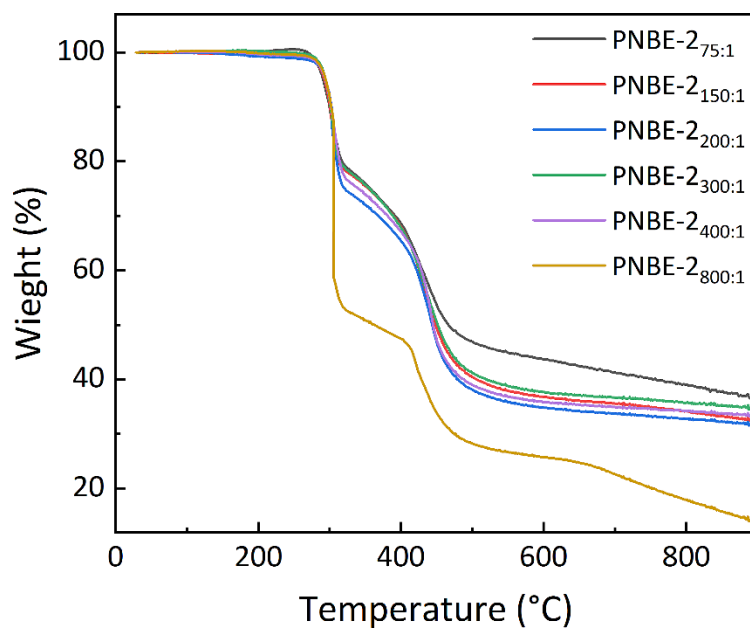


Figure S61 TGA curves for **PNBE-2** polymer sets

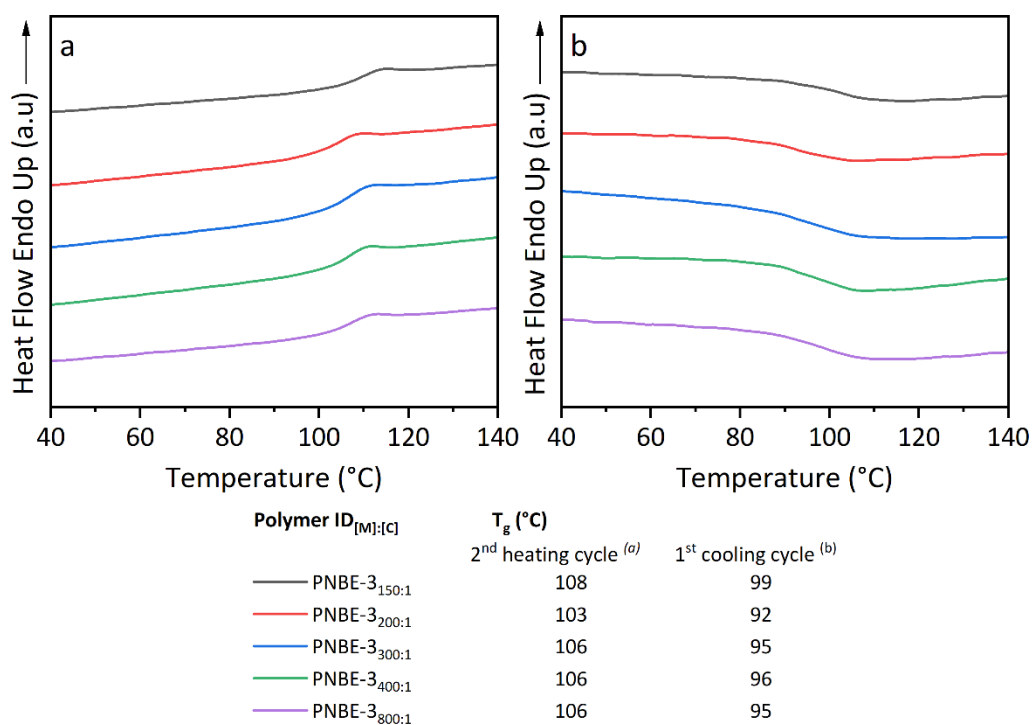


Figure S62 DSC thermograms for **PNBE-3** polymer sets in (a) second heating and (b) first cooling cycle

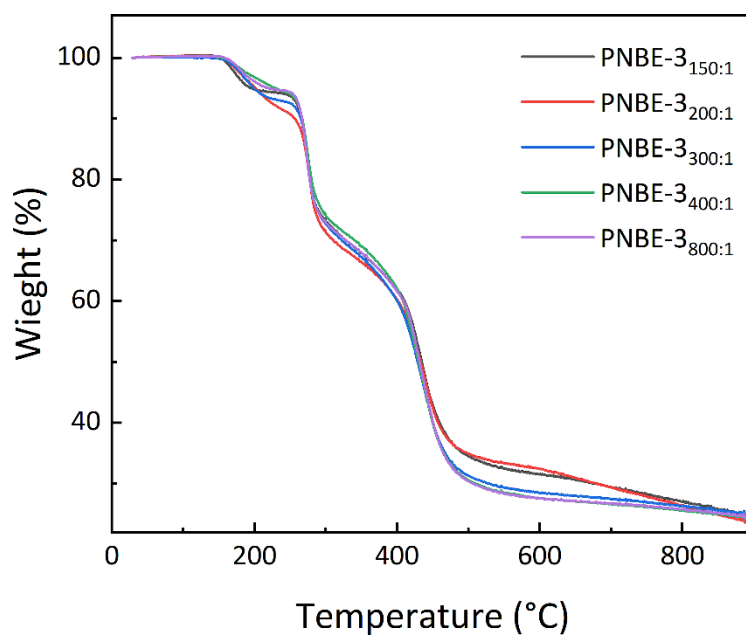


Figure S63 TGA curves for **PNBE-3** polymer sets

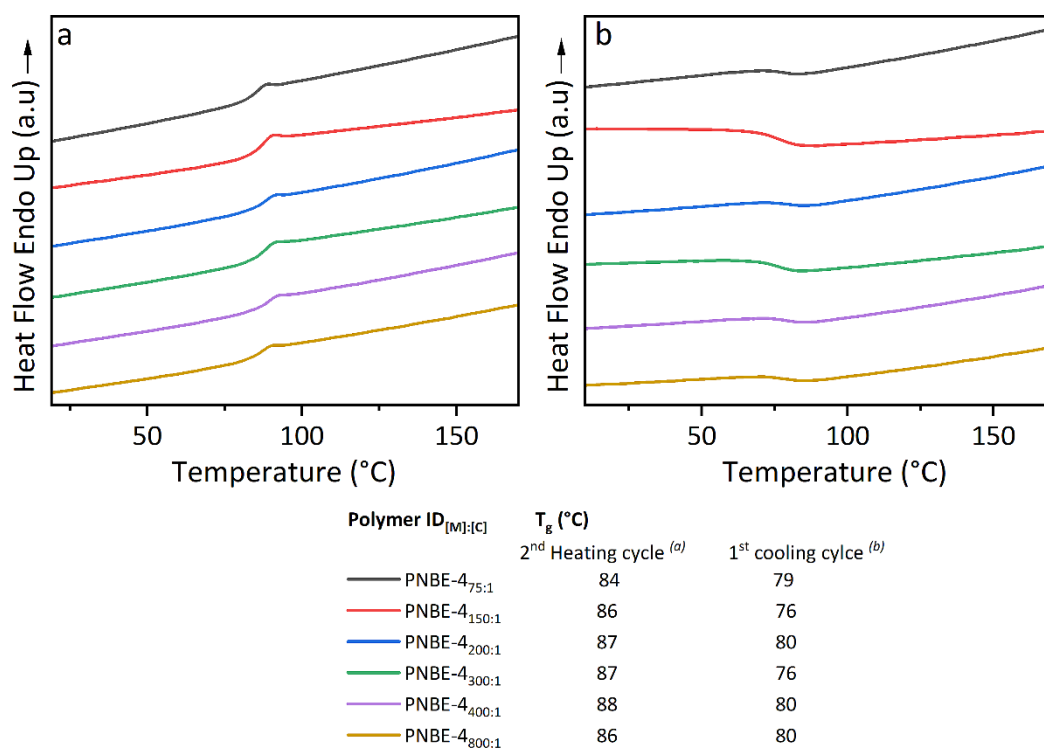


Figure S64 DSC thermograms for **PNBE-4** polymer sets in (a) second heating and (b) first cooling cycle

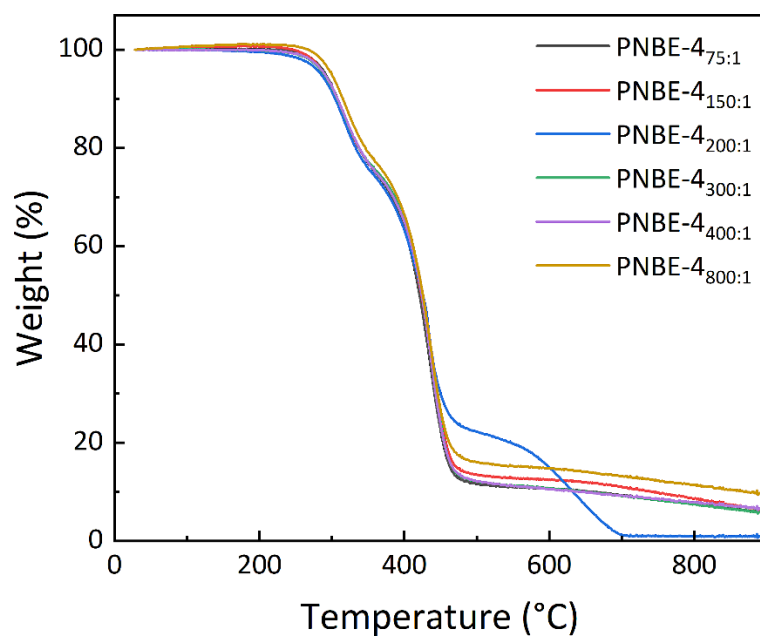


Figure S65 TGA curves for **PNBE-2** polymer sets

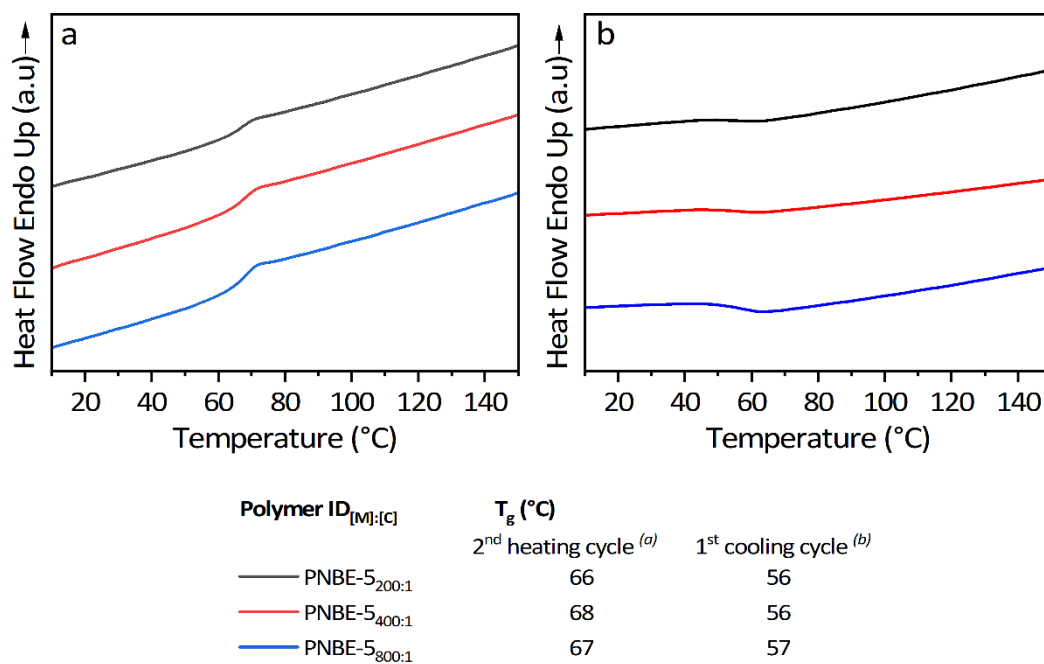


Figure S66 DSC thermograms for **PNBE-5** polymer sets in (a) second heating and (b) first cooling cycle

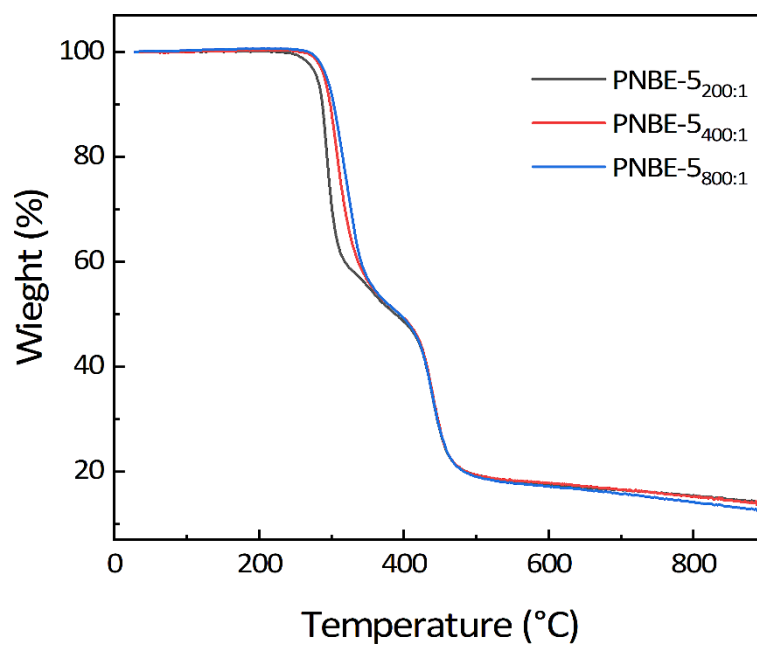


Figure S67 TGA curves for **PNBE-5** polymer sets

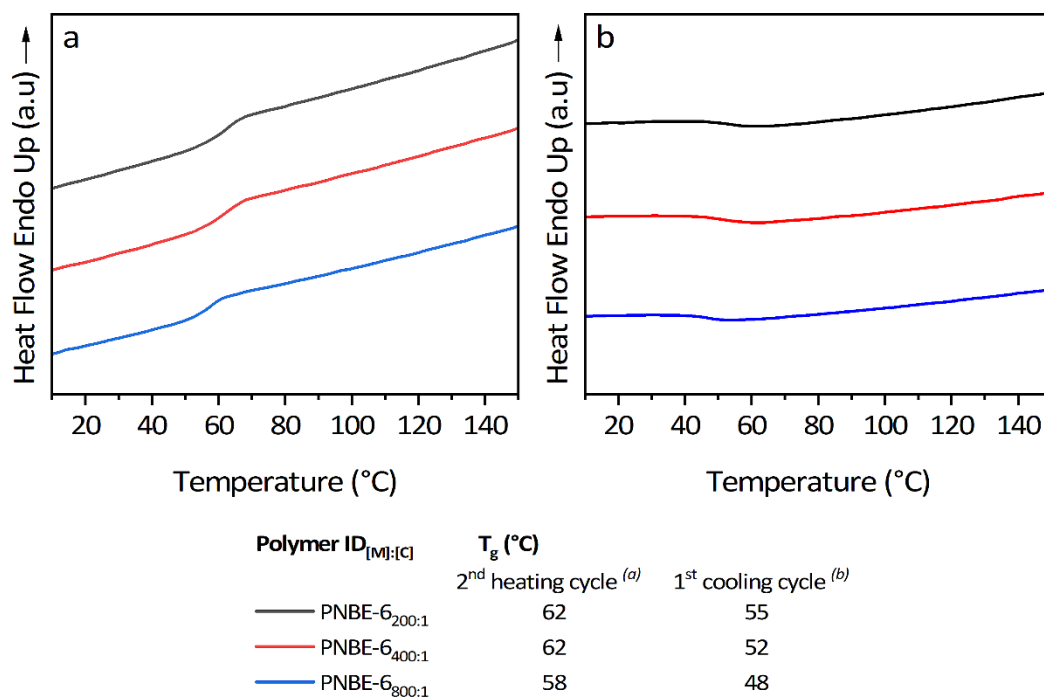


Figure S68 DSC thermograms for **PNBE-6** polymer sets in (a) second heating and (b) first cooling cycle

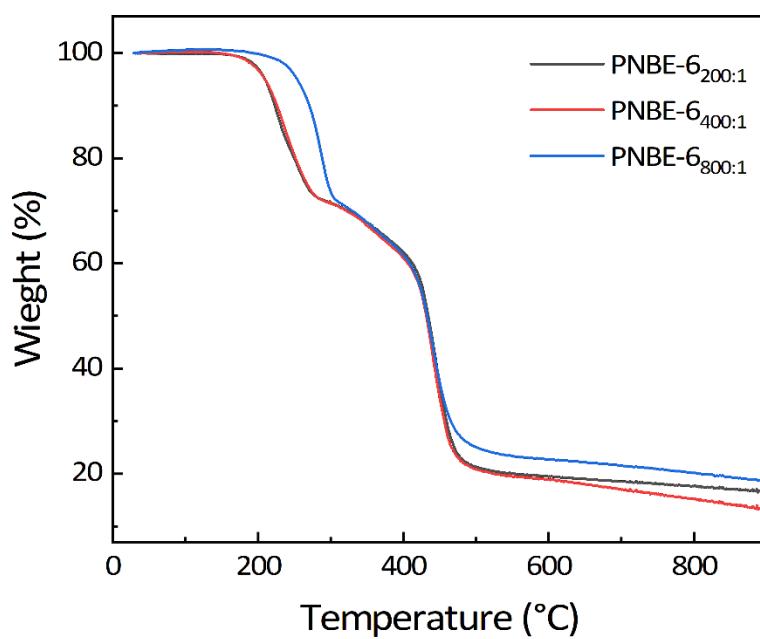


Figure S69 TGA curves for **PNBE-6** polymer sets

Dielectric properties of polymers

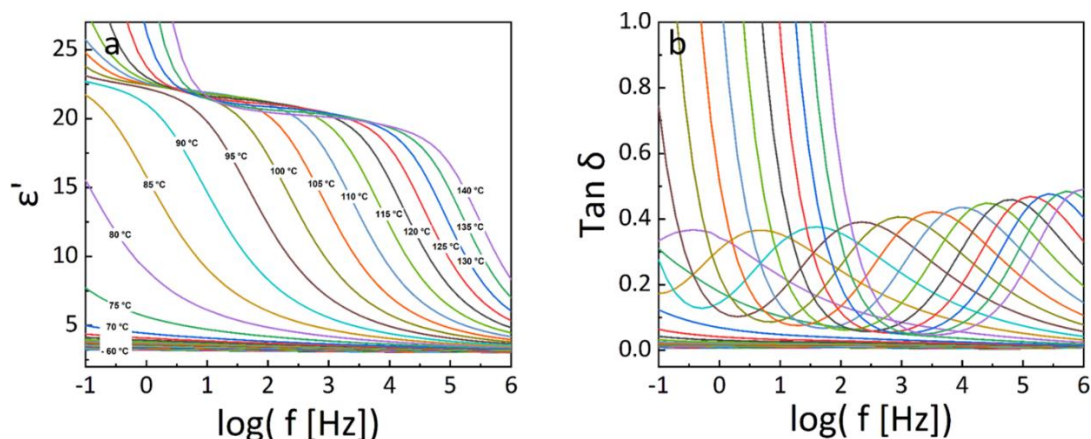


Figure S70 Isothermal dielectric response of **PNBE-2**; (a) real permittivity, ϵ' ; (b) tangent loss $\tan \delta$; of the complex dielectric function vs frequency

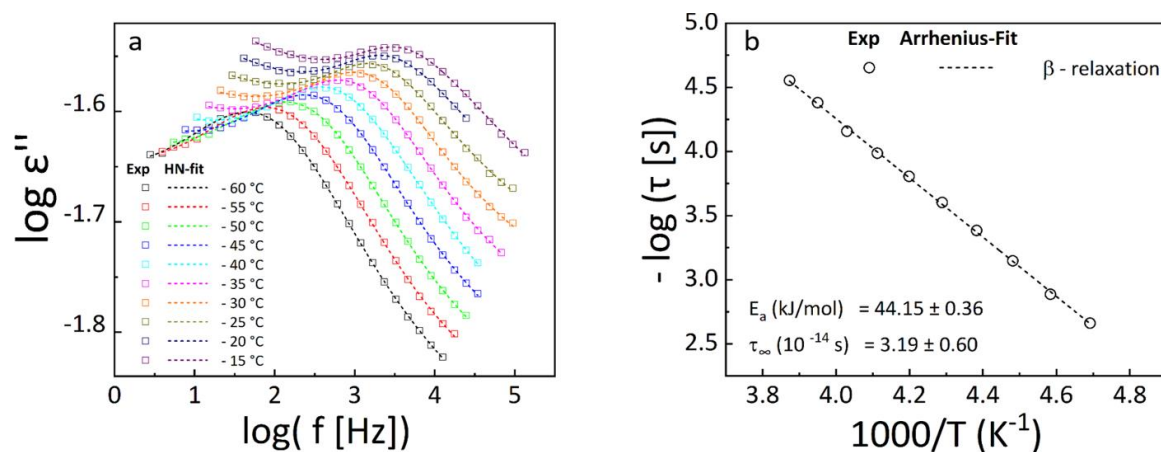


Figure S71 β -relaxation processes in **PNBE-2**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Arrhenius plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

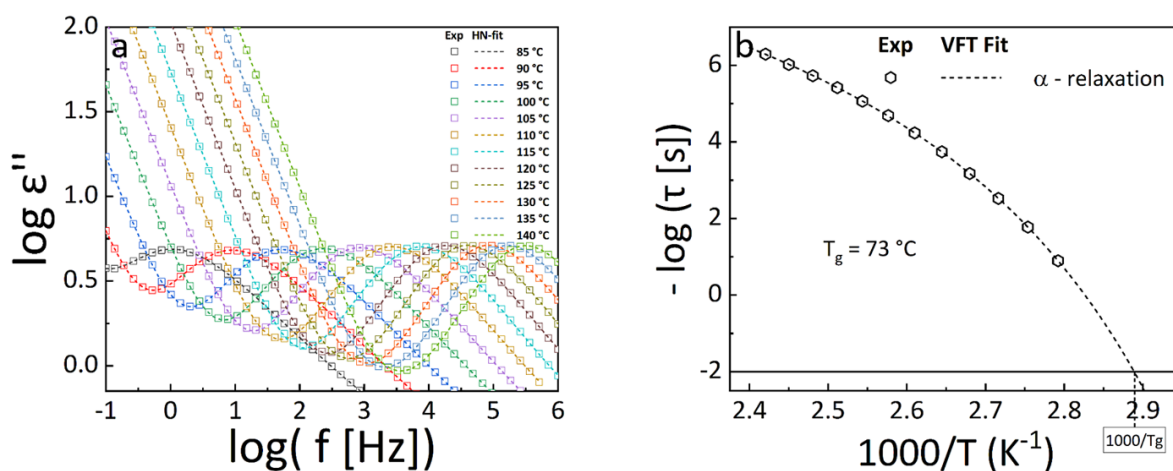


Figure S72 α -relaxation processes in **PNBE-2**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Vogel-Fulcher-Tammann (VFT) plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

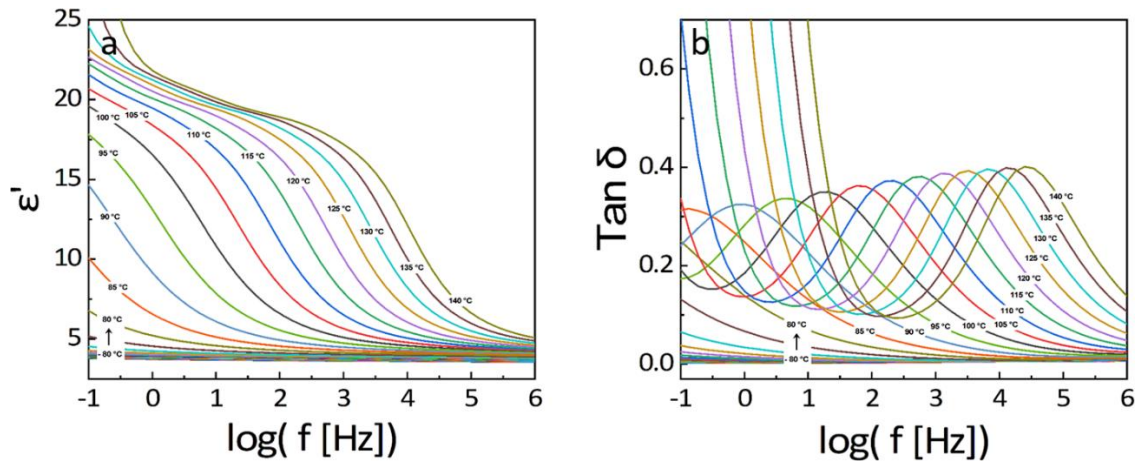


Figure S73 Isothermal dielectric response of **PNBE-3**; (a) real permittivity, ϵ' ; (b) tangent loss $\text{Tan } \delta$; of the complex dielectric function vs frequency

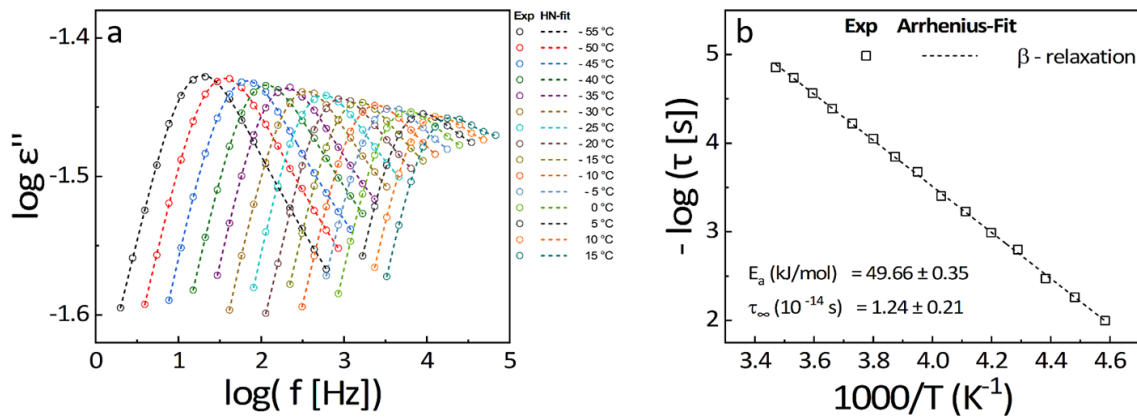


Figure S74 β -relaxation processes in **PNBE-3**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Arrhenius plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

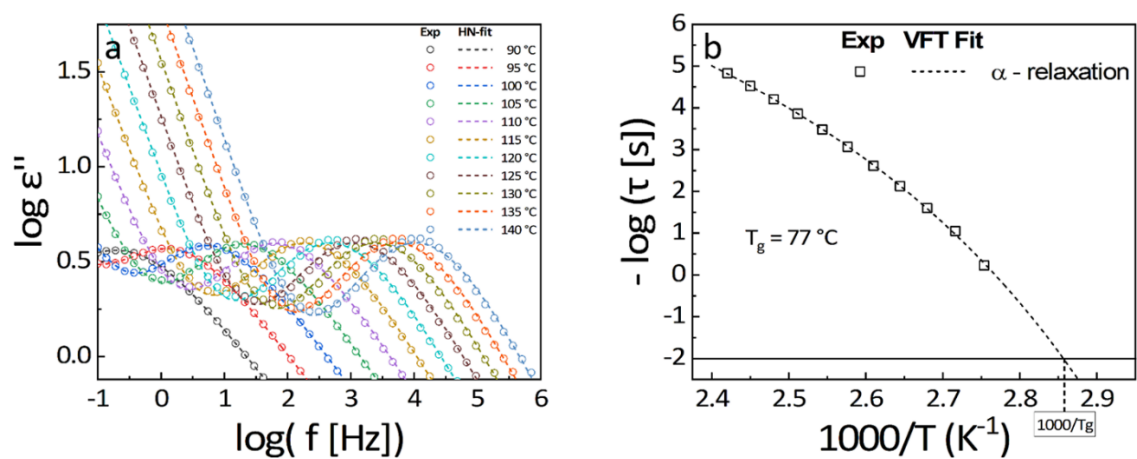


Figure S75 α -relaxation processes in **PNBE-3**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Vogel-Fulcher-Tammann (VFT) plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

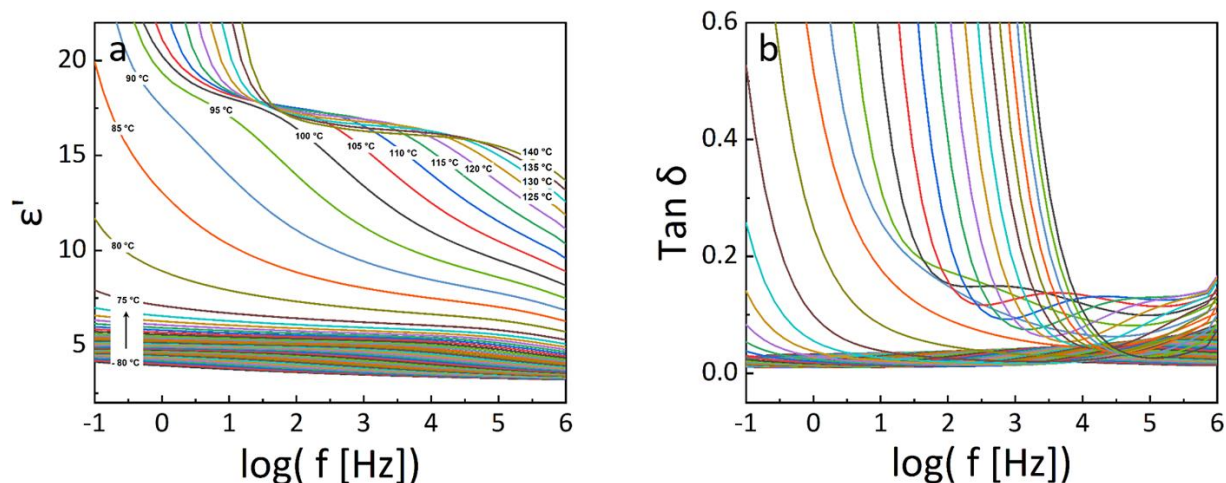


Figure S76 Isothermal dielectric response of **PNBE-4**; (a) real permittivity, ϵ' ; (b) tangent loss $\tan \delta$; of the complex dielectric function vs frequency

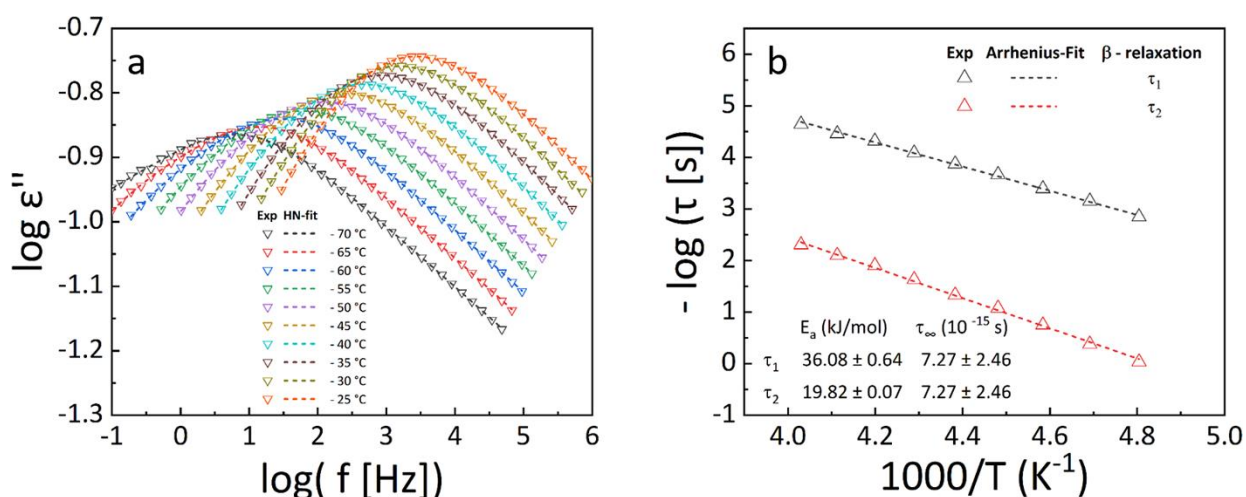


Figure S77 β -relaxation processes in **PNBE-4**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Arrhenius plots of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

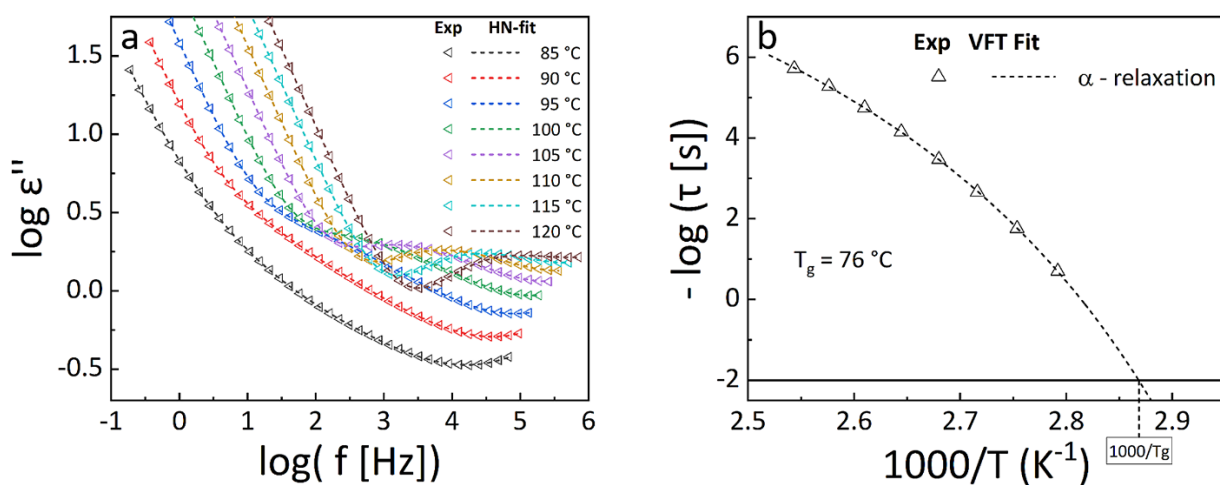


Figure S78 α -relaxation processes in **PNBE-4**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Vogel-Fulcher-Tammann (VFT) plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus the inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

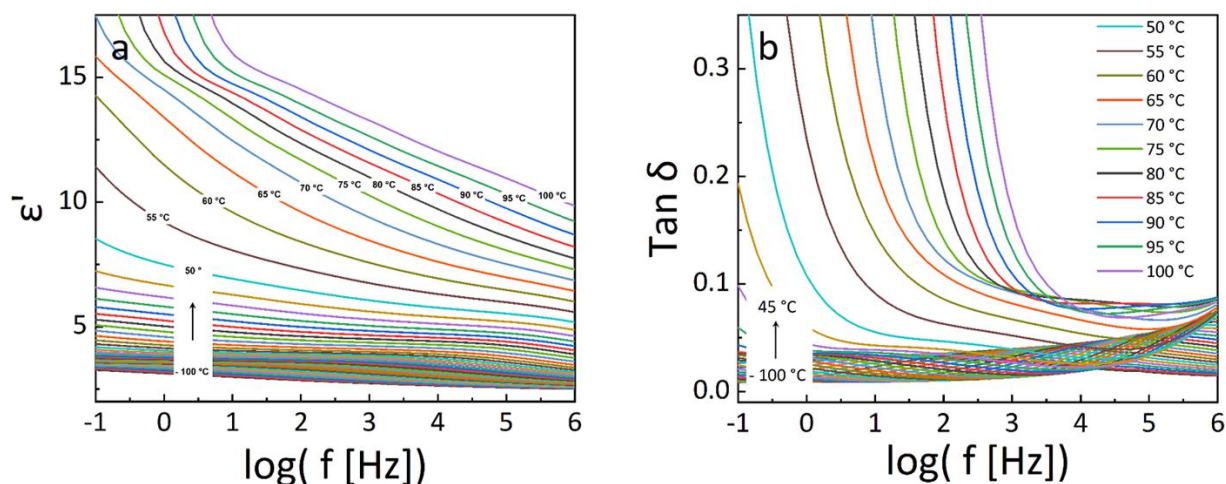


Figure S79 Isothermal dielectric response of **PNBE-5**; (a) real permittivity, ϵ' ; (b) tangent loss $\tan \delta$; of the complex dielectric function vs frequency

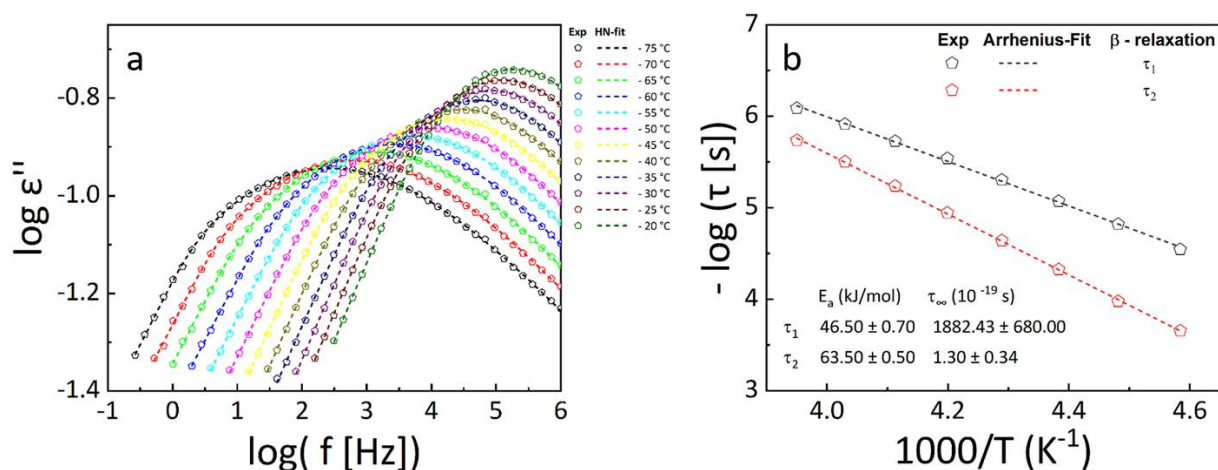


Figure S80 β -relaxation processes in **PNBE-5**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Arrhenius plots of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

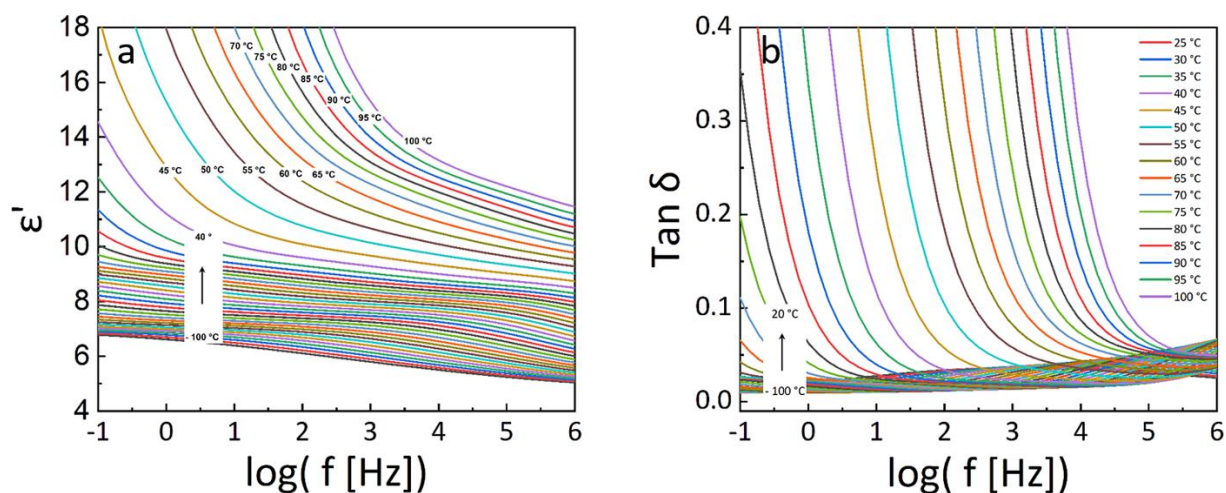


Figure S81 Isothermal dielectric response of **PNBE-6**; (a) real permittivity, ϵ' ; (b) tangent loss $\tan \delta$; of the complex dielectric function vs frequency

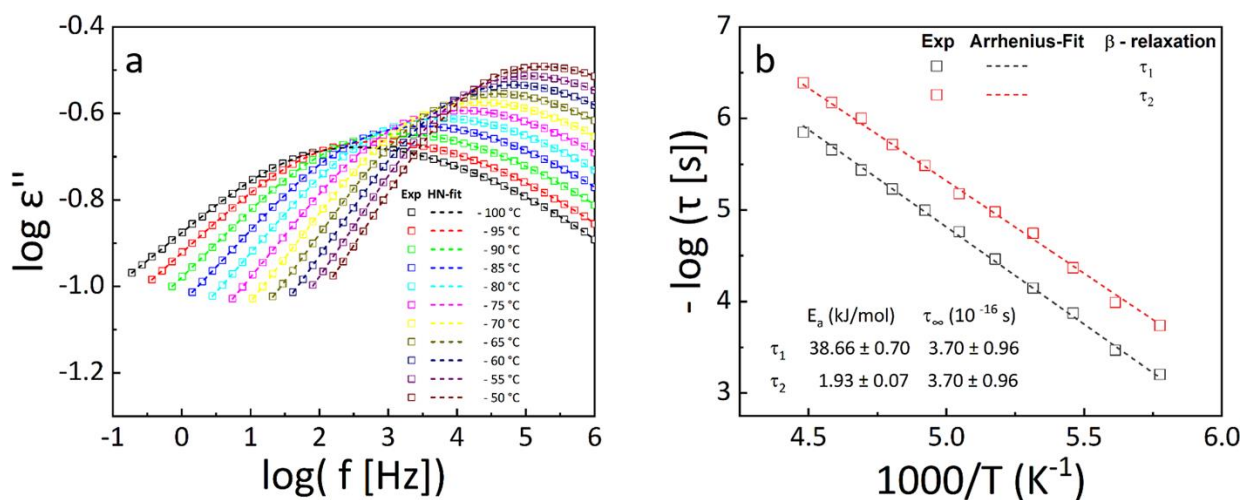


Figure S82 β -relaxation processes in **PNBE-6**: (a) isothermal plot of imaginary part ϵ'' of the complex dielectric permittivity versus frequency (b) Arrhenius plots of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented by scattered dots and the fit functions are represented by short-dashed lines.

Dipole moments of monomers

NBE-X solutions of different concentrations were prepared by dissolving in chloroform. Dilute solutions of **NBE-X** were used to avoid antiparallel orientation of dipoles. Dielectric measurements on the solutions were performed using a high-resolution ALPHA analyzer (Novocontrol, Montabaur, Germany) using a liquid parallel plate sample cell BDS 1308 to avoid errors related to solvent evaporation during measurement. The dielectric permittivity ϵ' was recorded at a frequency of 10^5 Hz at ambient temperature. The liquid cell BDS 1308 was calibrated using chloroform.

The dipole moments of **NBE-X** were experimentally estimated according to the Hedestrand-Guggenheim – Smith equation (Eq 1) and the modified Onsager equation according to Böttcher (Eq 2):

$$\mu_2^2 = \frac{27 \cdot M_2 \cdot k_B \cdot T}{4\pi \cdot \rho_1 \cdot (\epsilon_1 + 2)^2 \cdot N_A} \cdot \left(\frac{\partial \epsilon_{12}}{\partial x_2} - (n_2^2 - n_1^2) \right) \quad (\text{Eq 1}).$$

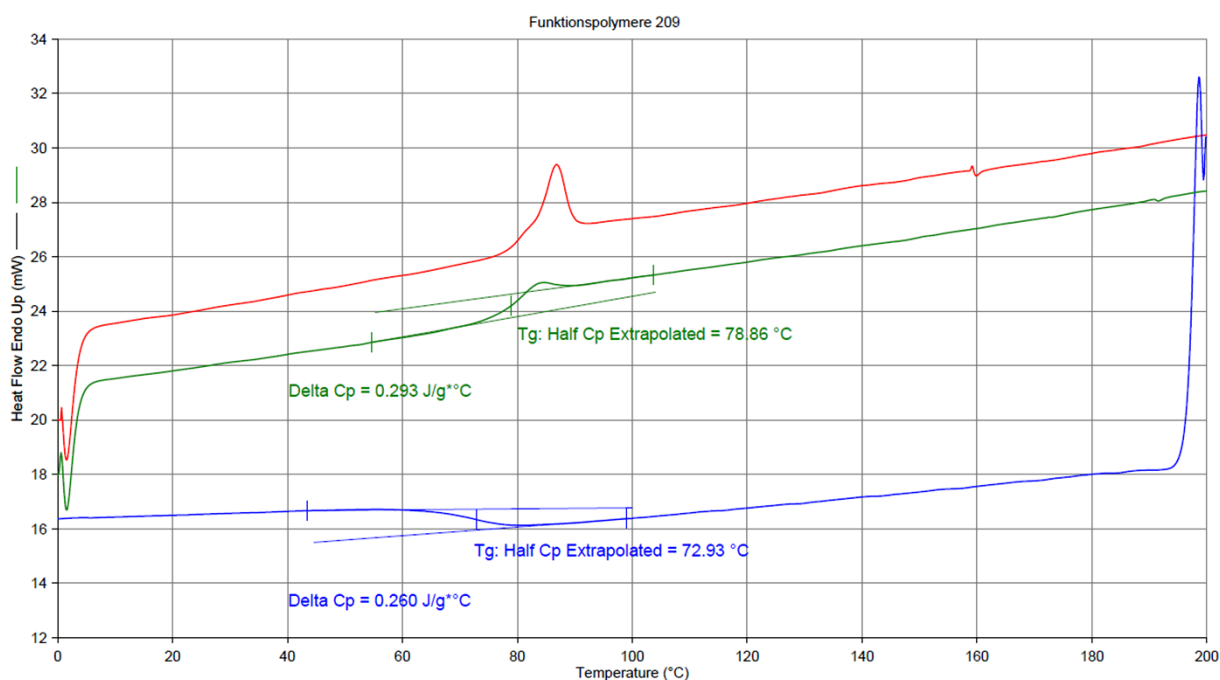
$$\begin{aligned} \epsilon_{12} = 1 + \frac{4\pi}{3} \frac{\epsilon_{12}(2\epsilon_{12} + 1)(n_1^2 + 2)^2}{3(2\epsilon_{12} + n_1^2)^2} \frac{\mu_1^2}{k_B T} N_1 + \frac{4\pi}{3} \frac{\epsilon_{12}(2\epsilon_{12} + 1)(n_2^2 + 2)^2}{3(2\epsilon_{12} + n_2^2)^2} \frac{\mu_2^2}{k_B T} N_2 \\ + 3 \frac{N_1}{N_A} R_1 \frac{\epsilon_{12}(n_1^2 + 2)}{2\epsilon_{12} + n_1^2} + 3 \frac{N_2}{N_A} R_2 \frac{\epsilon_{12}(n_2^2 + 2)}{2\epsilon_{12} + n_2^2} \end{aligned} \quad (\text{Eq 2}).$$

In the above equations,

μ_1	dipole moment of the solvent
μ_2	dipole moment of NBE-X monomer
M_2	molar mass of NBE-X monomer
N_A	Avogadro's constant
k_B	Boltzmann's constant
T	Temperature
ρ_1	density of the solvent
ϵ_1	dielectric permittivity of the solvent
ϵ_{12}	dielectric permittivity of the solution
x_2	molar fraction of NBE-X monomer
n_1	refractive index of the solvent
n_2	refractive index of NBE-X monomer
N_i	number density of dipoles expressed as $N_i = \frac{\rho_i}{M_i} N_A$
R_i	molecular refraction in the limit of infinite wavelength expressed as $R_i = \frac{M_i (n_i^2 - 1)}{\rho_i (n_i^2 + 2)}$

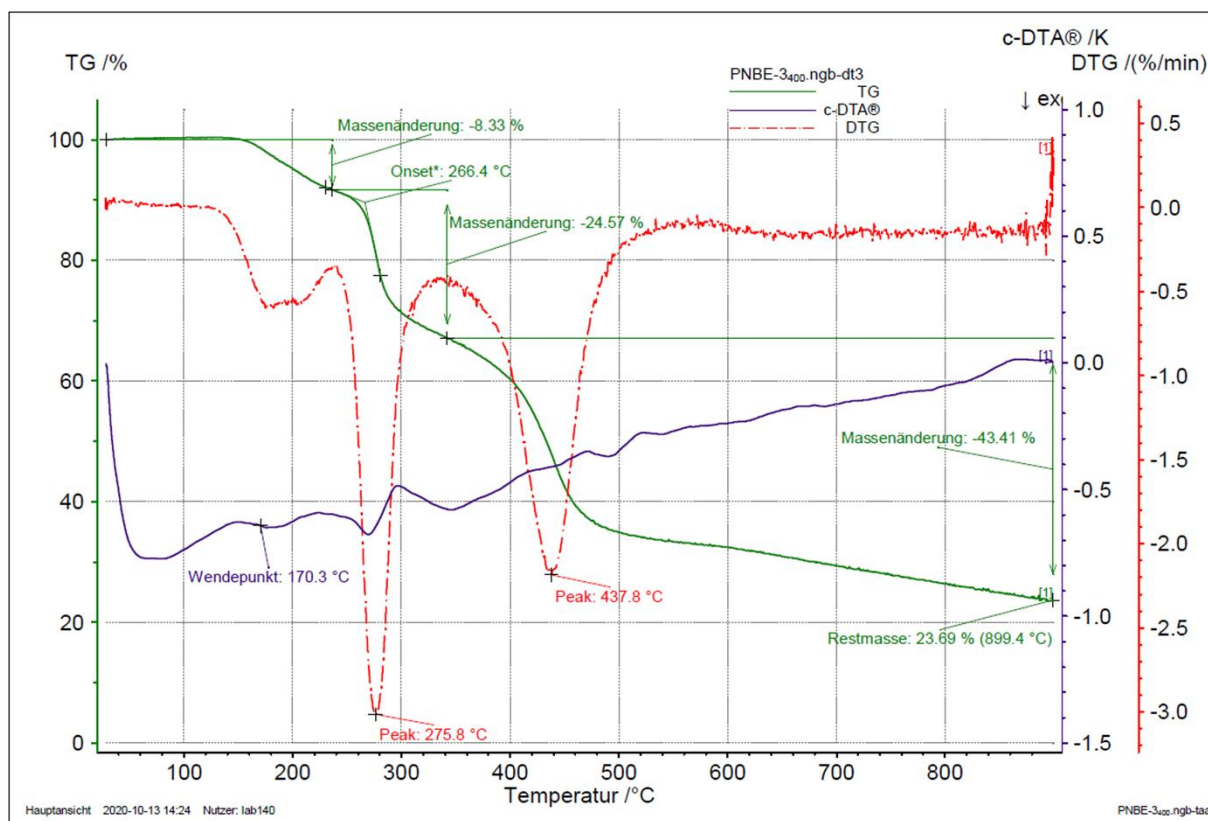
Appendices

Operator ID: fb
Sample ID: PNBE-2₇₅
Sample Weight: 8.836 mg

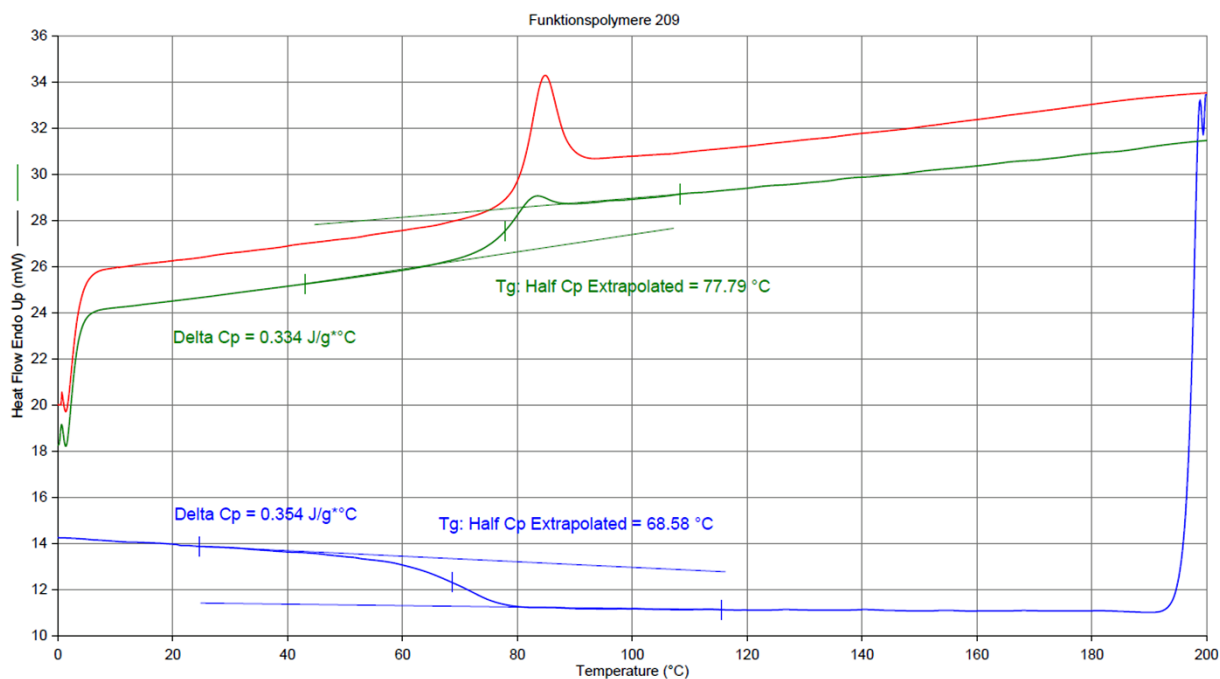


28.10.2020 15:25:06

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

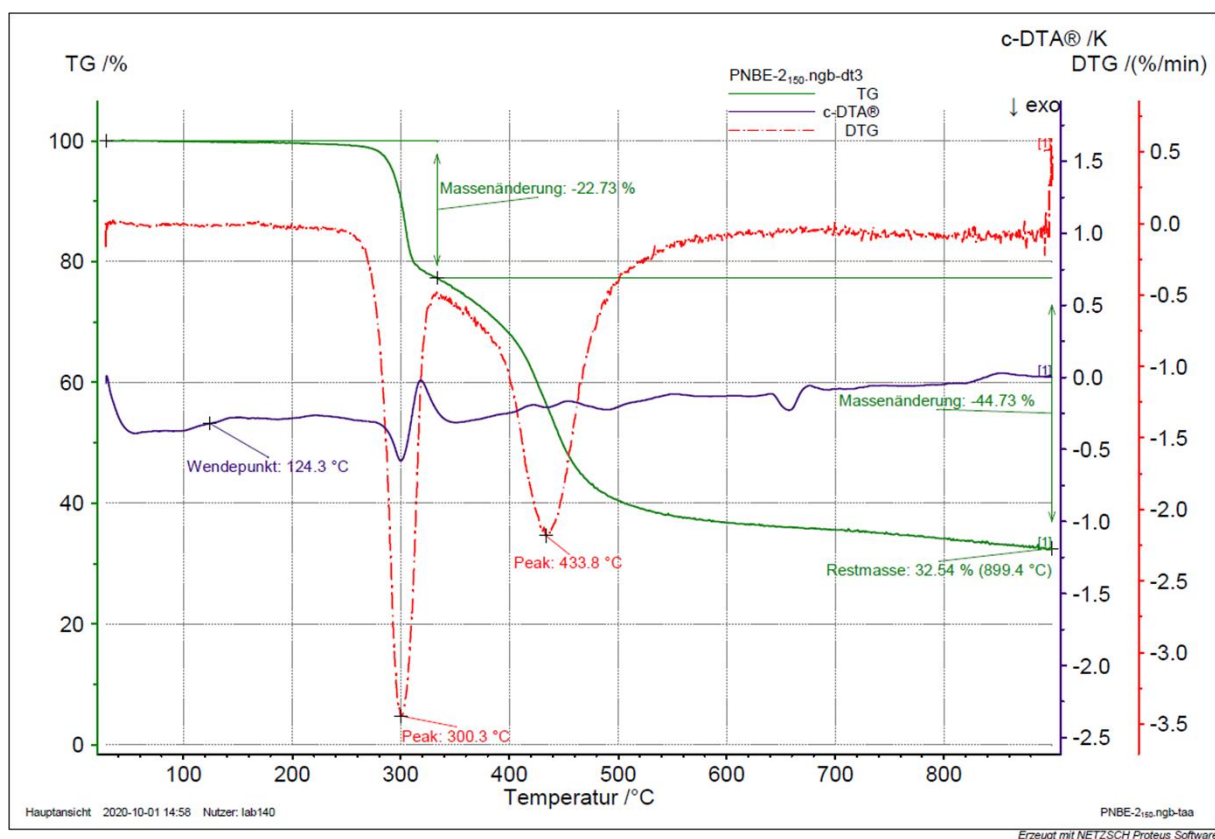


Operator ID: fb
Sample ID: PNBE-2₁₅₀
Sample Weight: 17.526 mg

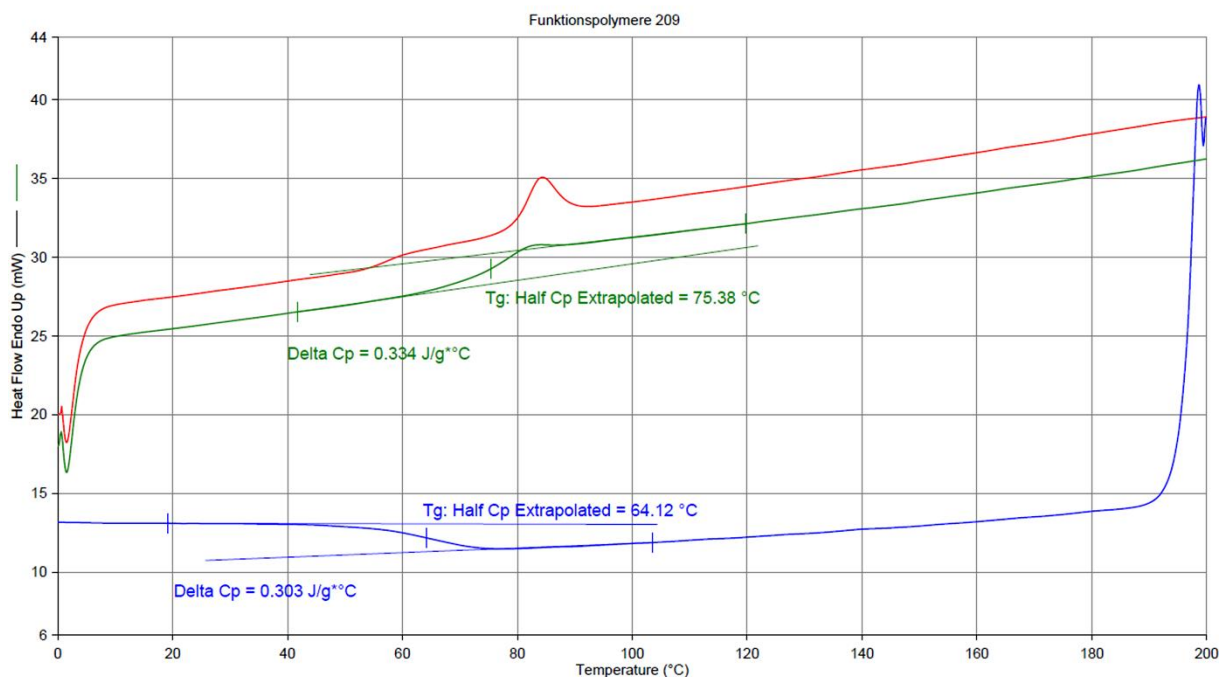


23.10.2020 15:15:01

- 1) Heat from 0.00°C to 200.00°C at 20.00°C/min
- 2) Cool from 200.00°C to 0.00°C at 20.00°C/min
- 3) Hold for 3.0 min at 0.00°C
- 4) Heat from 0.00°C to 200.00°C at 20.00°C/min

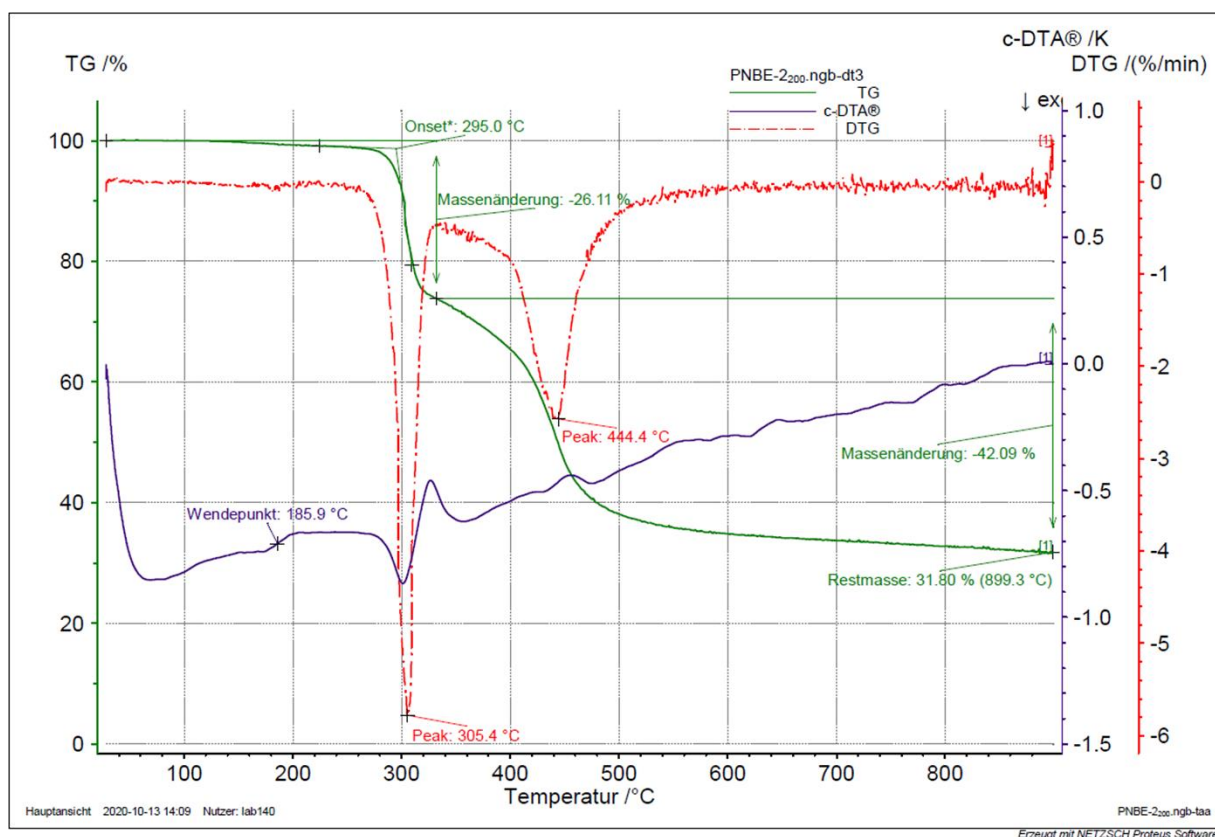


Operator ID: fb
Sample ID: PNBE-2₂₀₀
Sample Weight: 17.442 mg

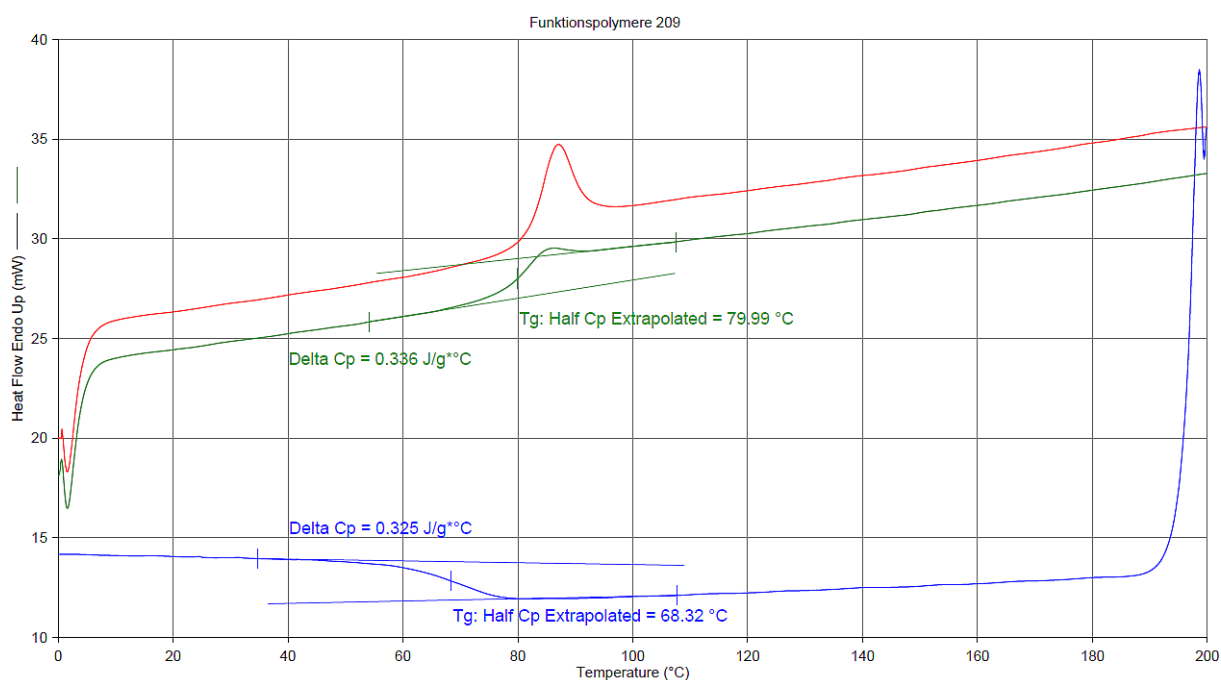


28.10.2020 13:26:30

- 1) Heat from 0.00°C to 200.00°C at 20.00°C/min
- 2) Cool from 200.00°C to 0.00°C at 20.00°C/min
- 3) Hold for 3.0 min at 0.00°C
- 4) Heat from 0.00°C to 200.00°C at 20.00°C/min

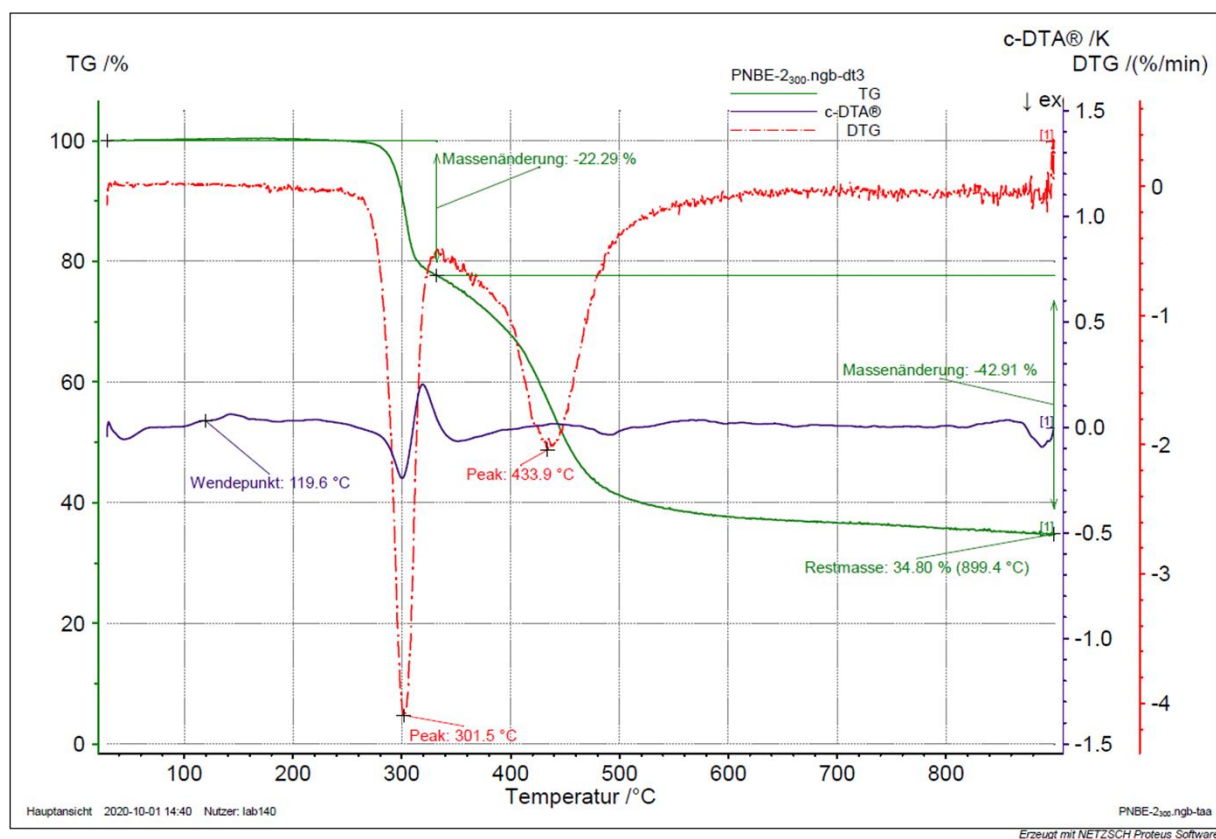


Operator ID: fb
Sample ID: PNBE-2₃₀₀
Sample Weight: 17.766 mg

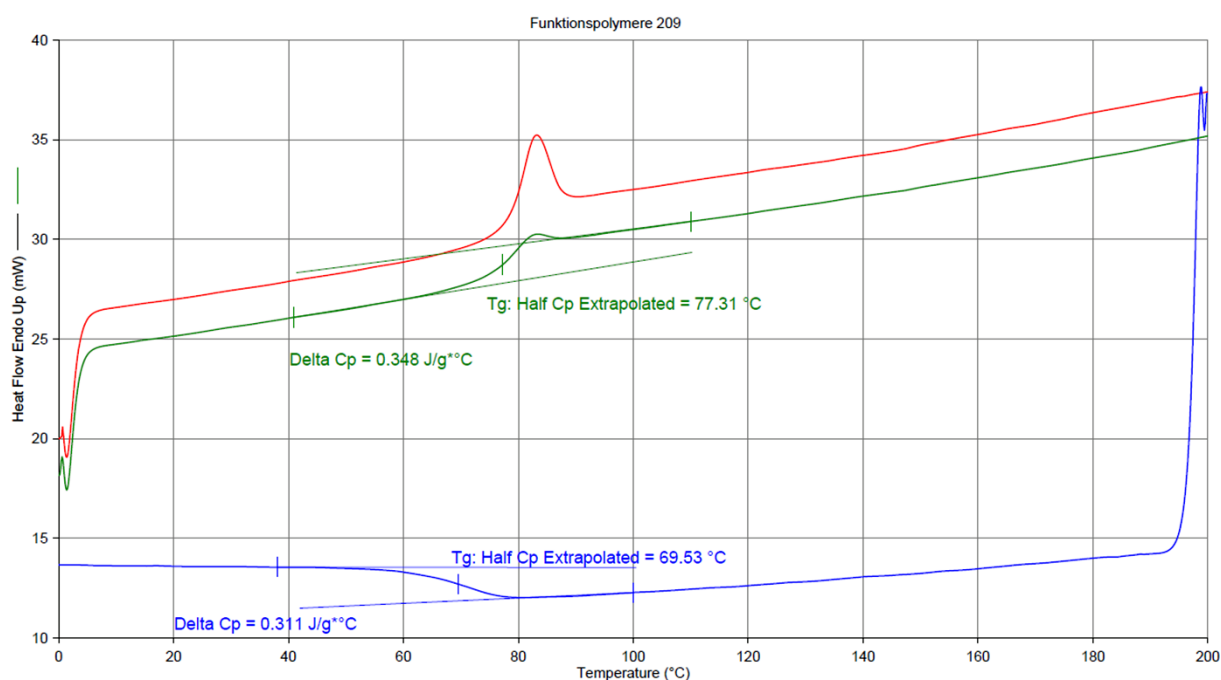


28.10.2020 15:23:26

- 1) Heat from 0.00°C to 200.00°C at 20.00°C/min
- 2) Cool from 200.00°C to 0.00°C at 20.00°C/min
- 3) Hold for 3.0 min at 0.00°C
- 4) Heat from 0.00°C to 200.00°C at 20.00°C/min

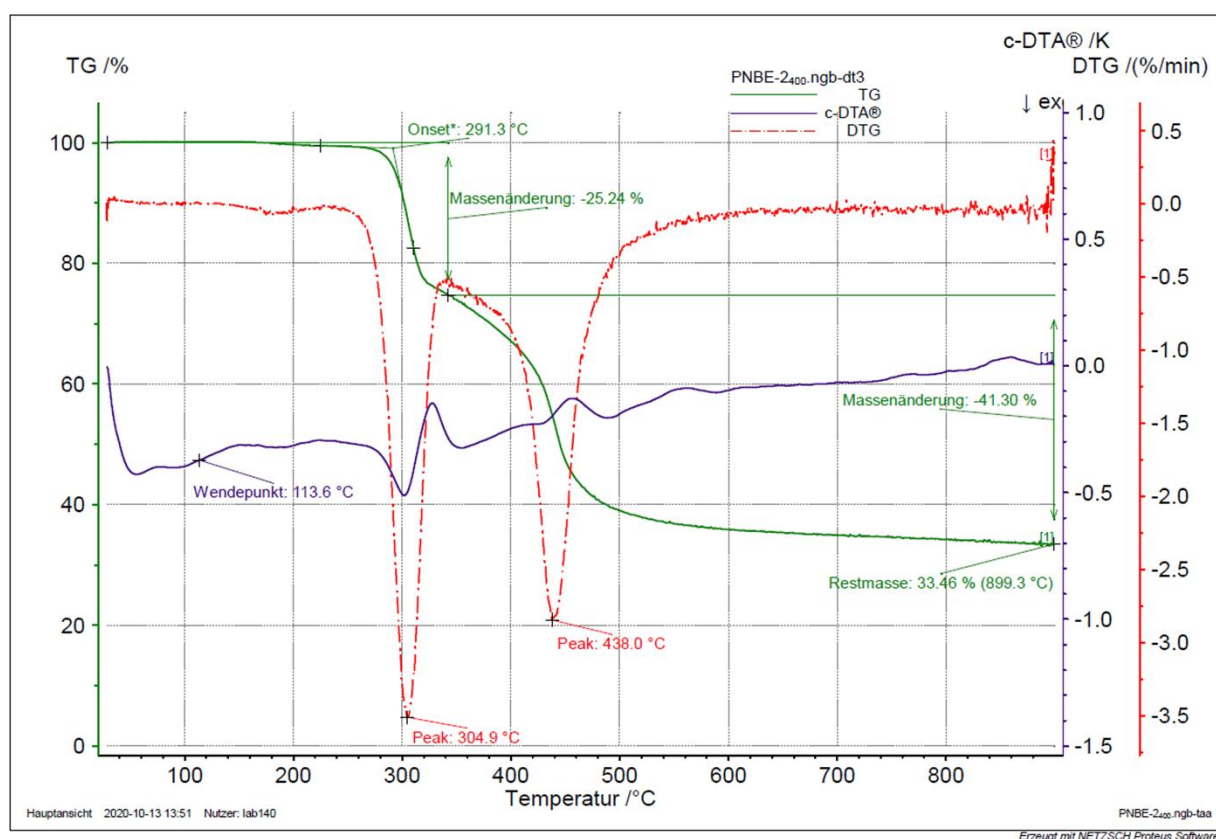


Operator ID: fb
Sample ID: PNBE-2₄₀₀
Sample Weight: 16.168 mg

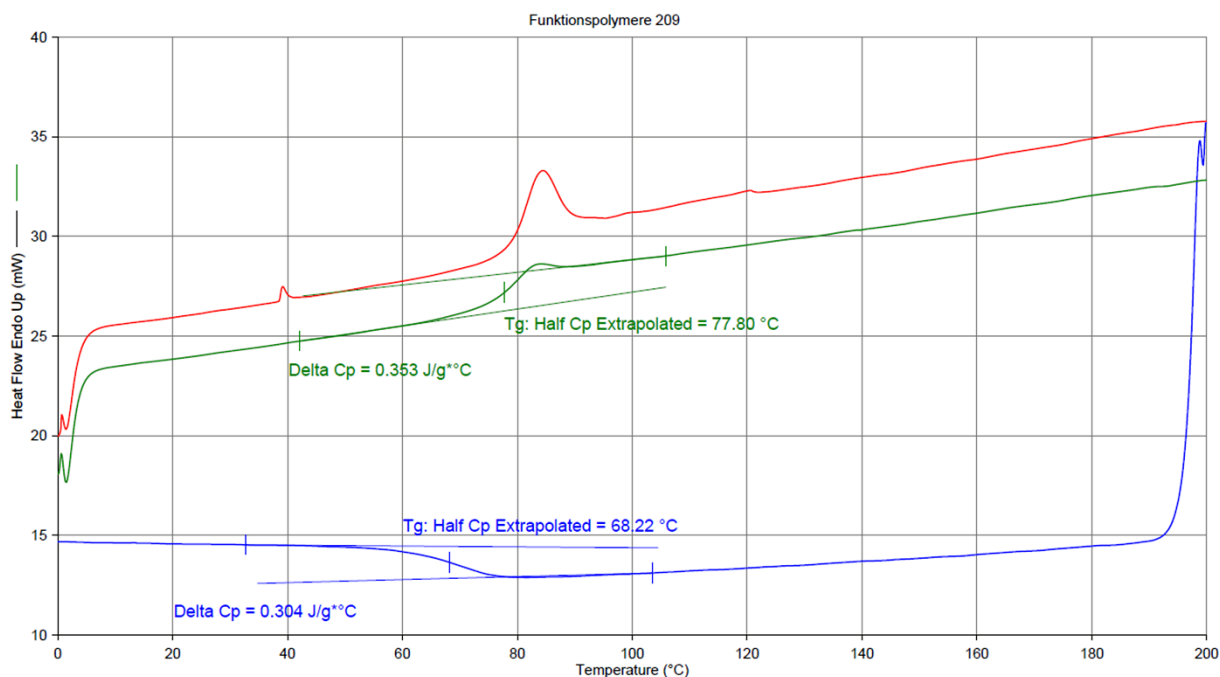


28.10.2020 13:19:57

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

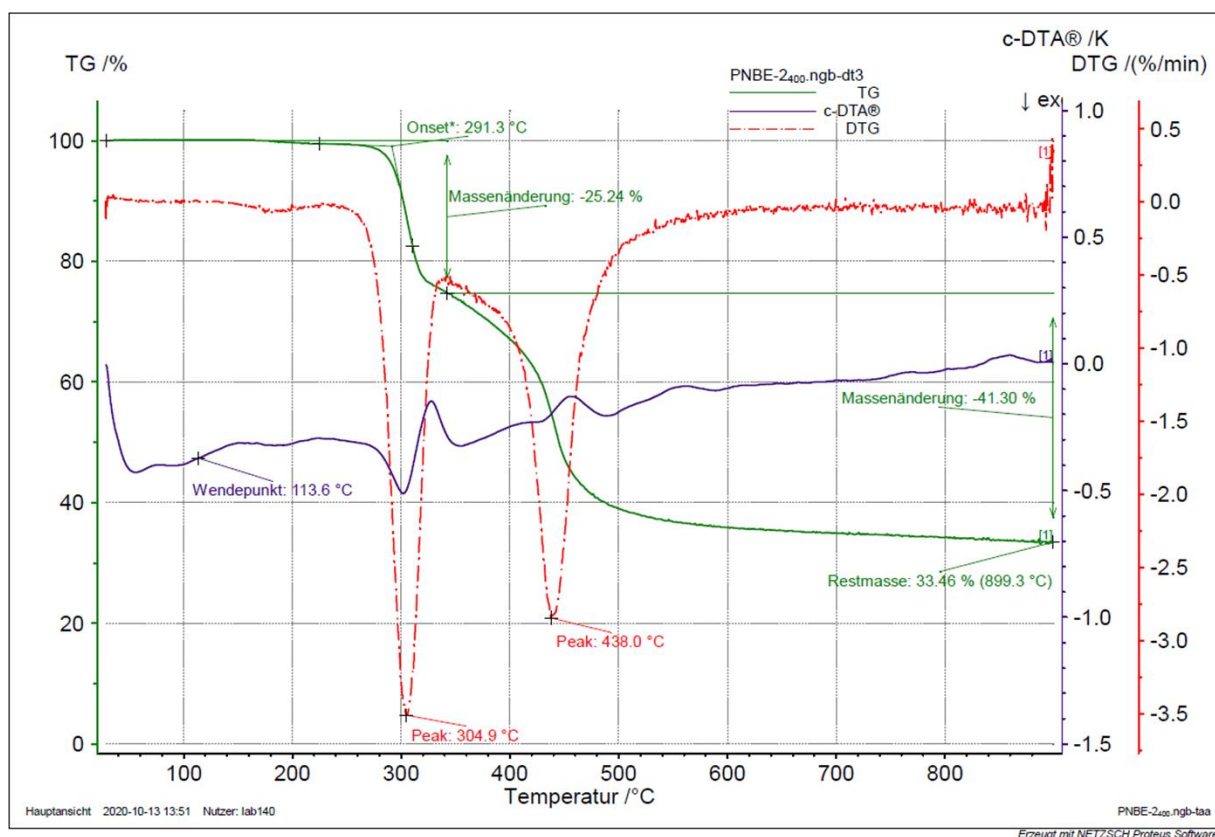


Operator ID: fb
Sample ID: PNBE-2₉₀₀
Sample Weight: 15.874 mg

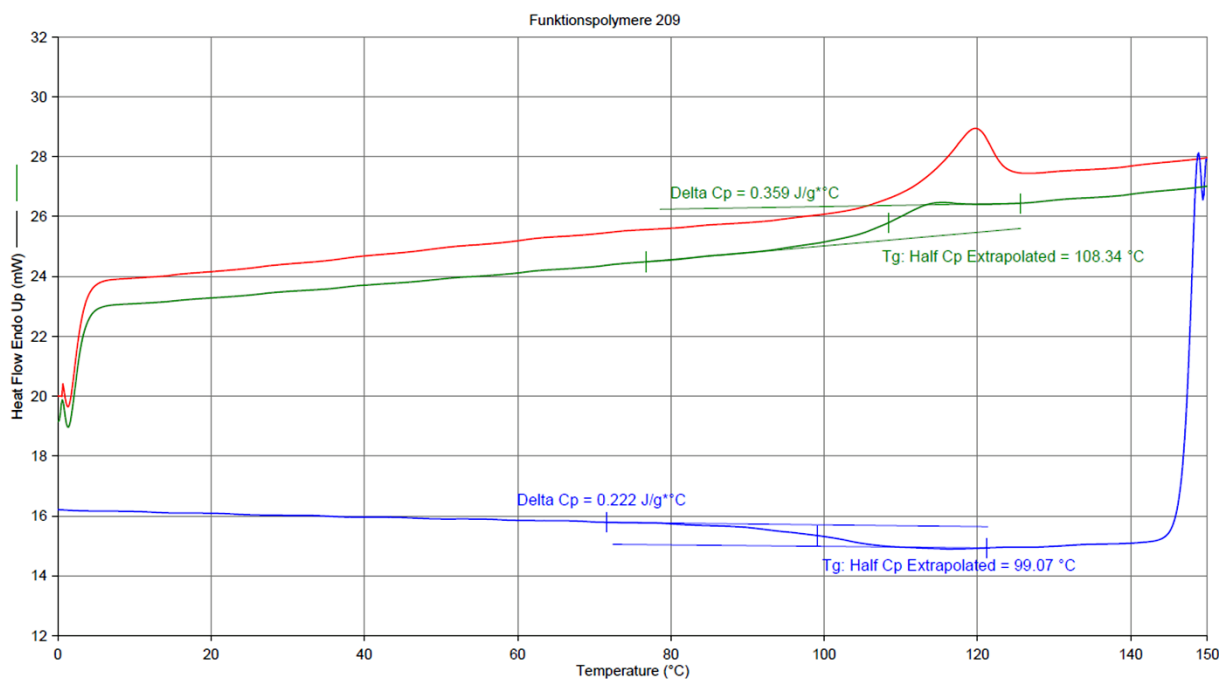


28.10.2020 13:09:14

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

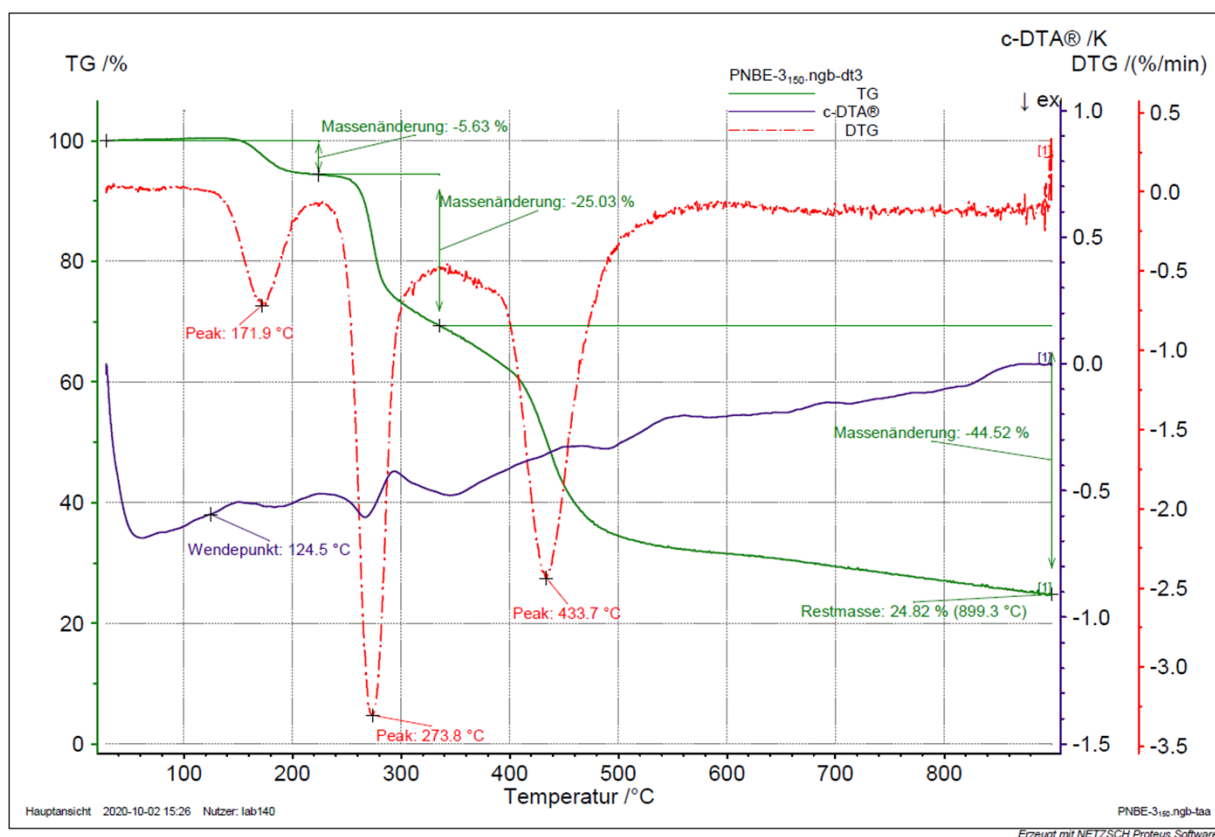


Operator ID: fb
 Sample ID: PNBE-3₁₅₀
 Sample Weight: 9.736 mg

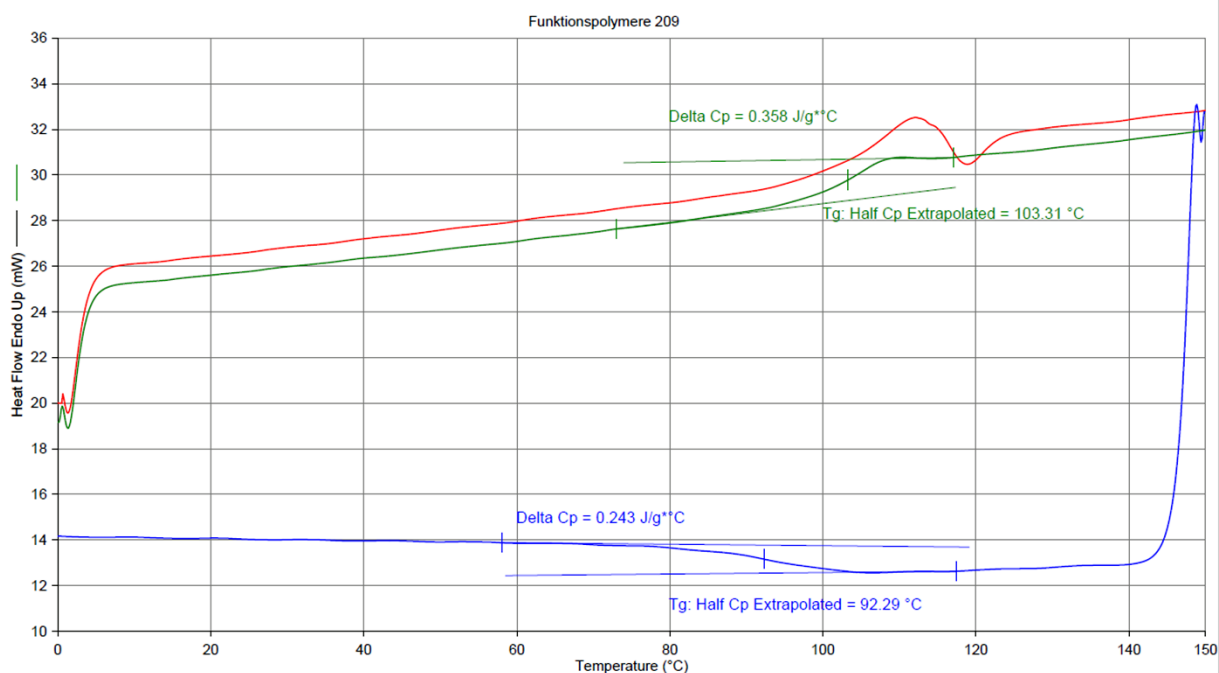


02.11.2021 07:55:07

- | | |
|--|--|
| 1) Heat from 0.00°C to 150.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 150.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 150.00°C at 20.00°C/min |

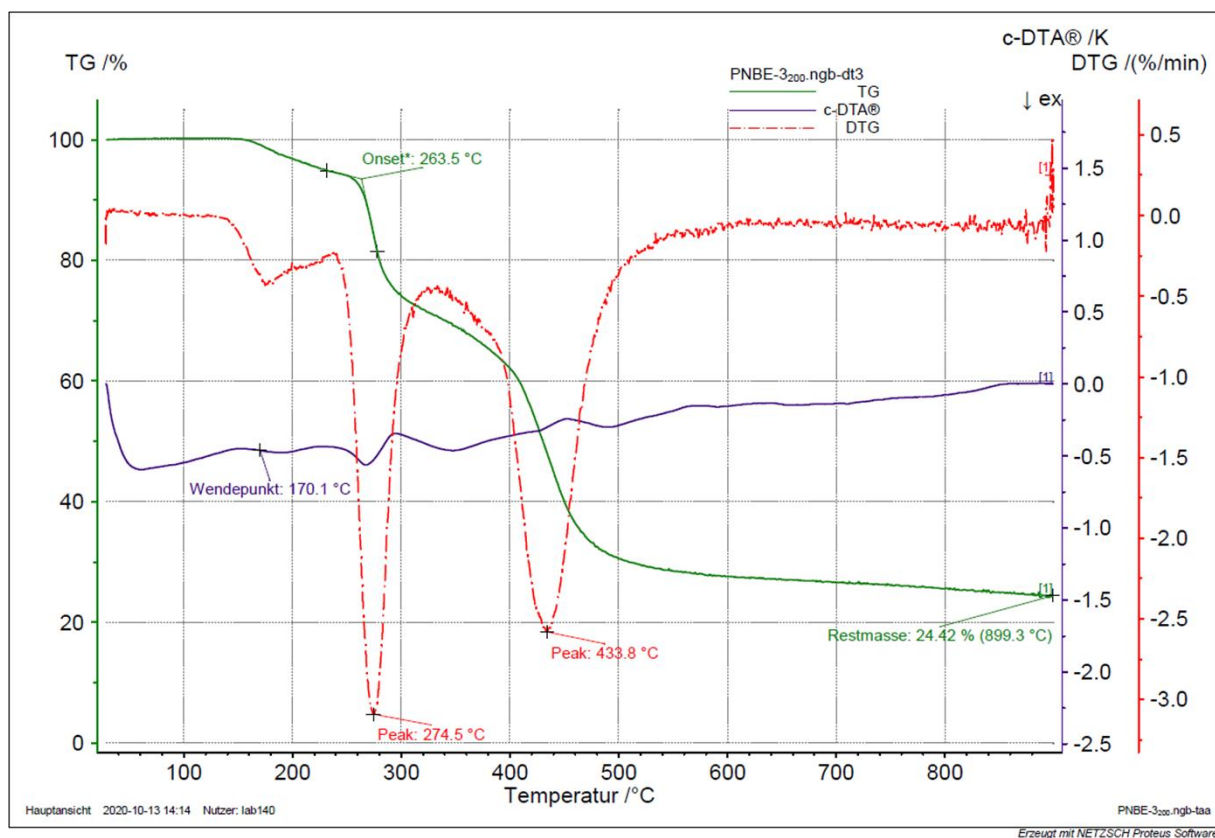


Operator ID: fb
 Sample ID: PNBE-3₂₀₀
 Sample Weight: 15.154 mg

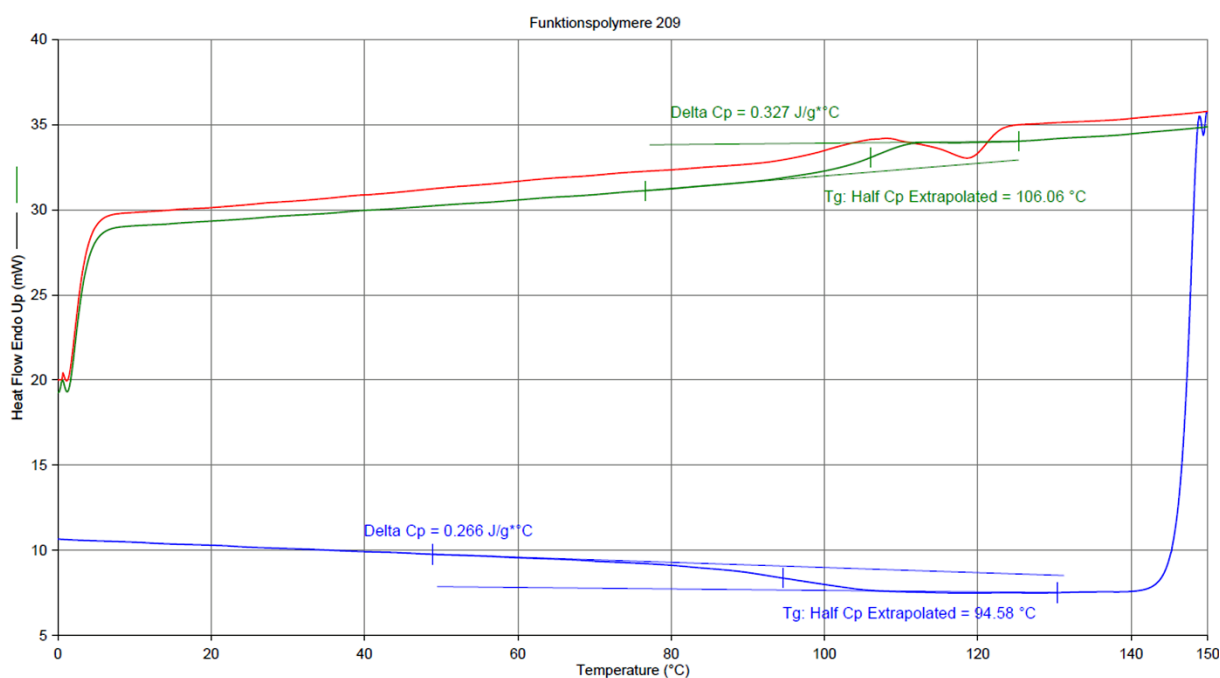


02.11.2021 08:40:32

- | | |
|--|--|
| 1) Heat from 0.00°C to 150.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 150.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 150.00°C at 20.00°C/min |

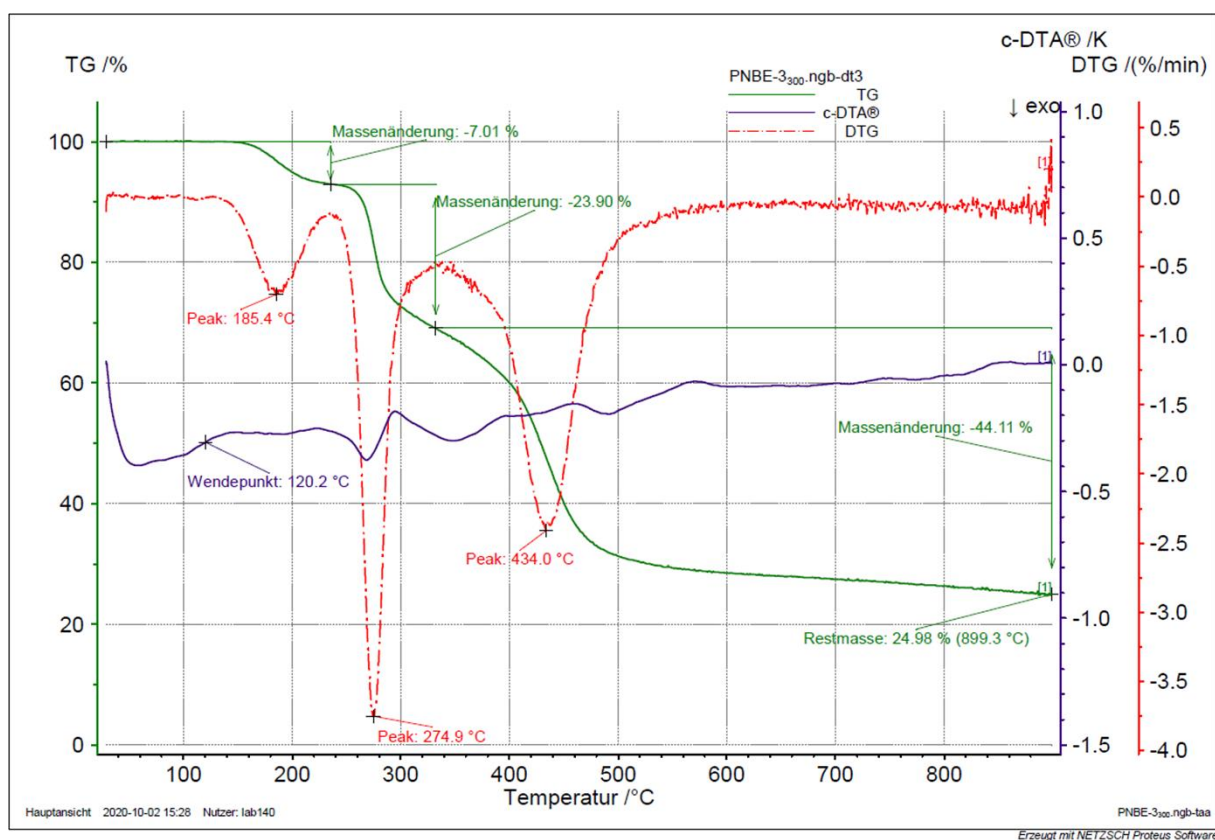


Operator ID: fb
Sample ID: PNBE-3₃₀₀
Sample Weight: 15.836 mg

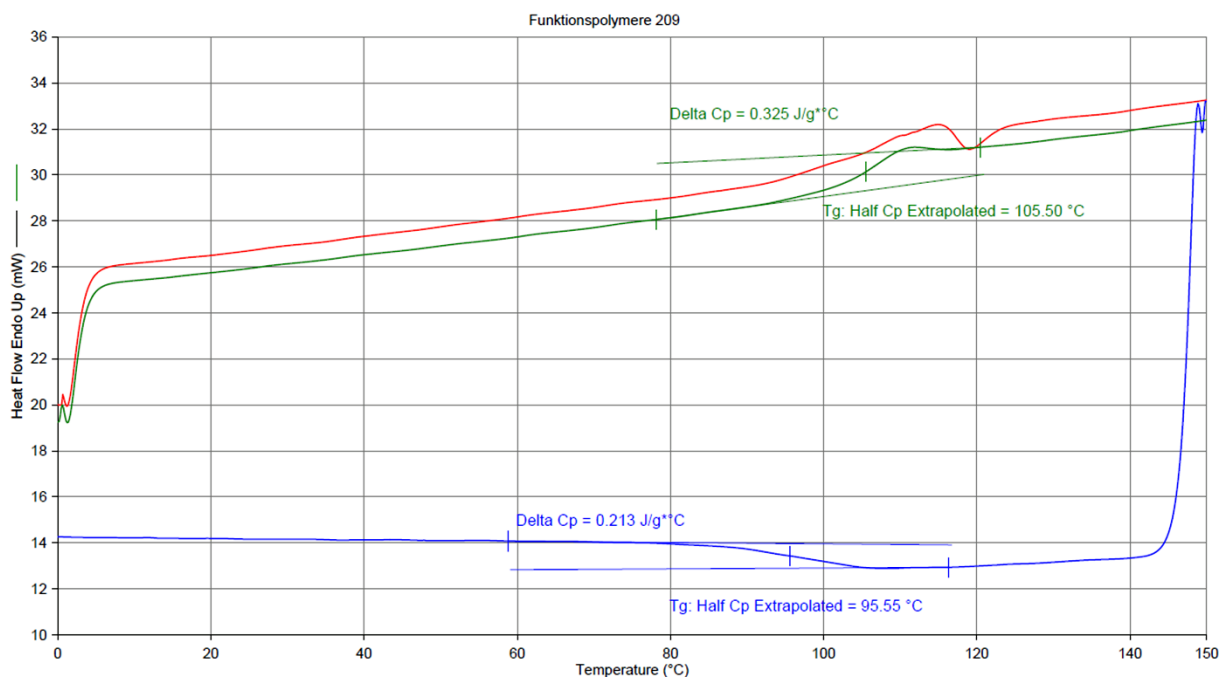


02.11.2021 07:50:38

- | | |
|--|--|
| 1) Heat from 0.00°C to 150.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 150.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 150.00°C at 20.00°C/min |

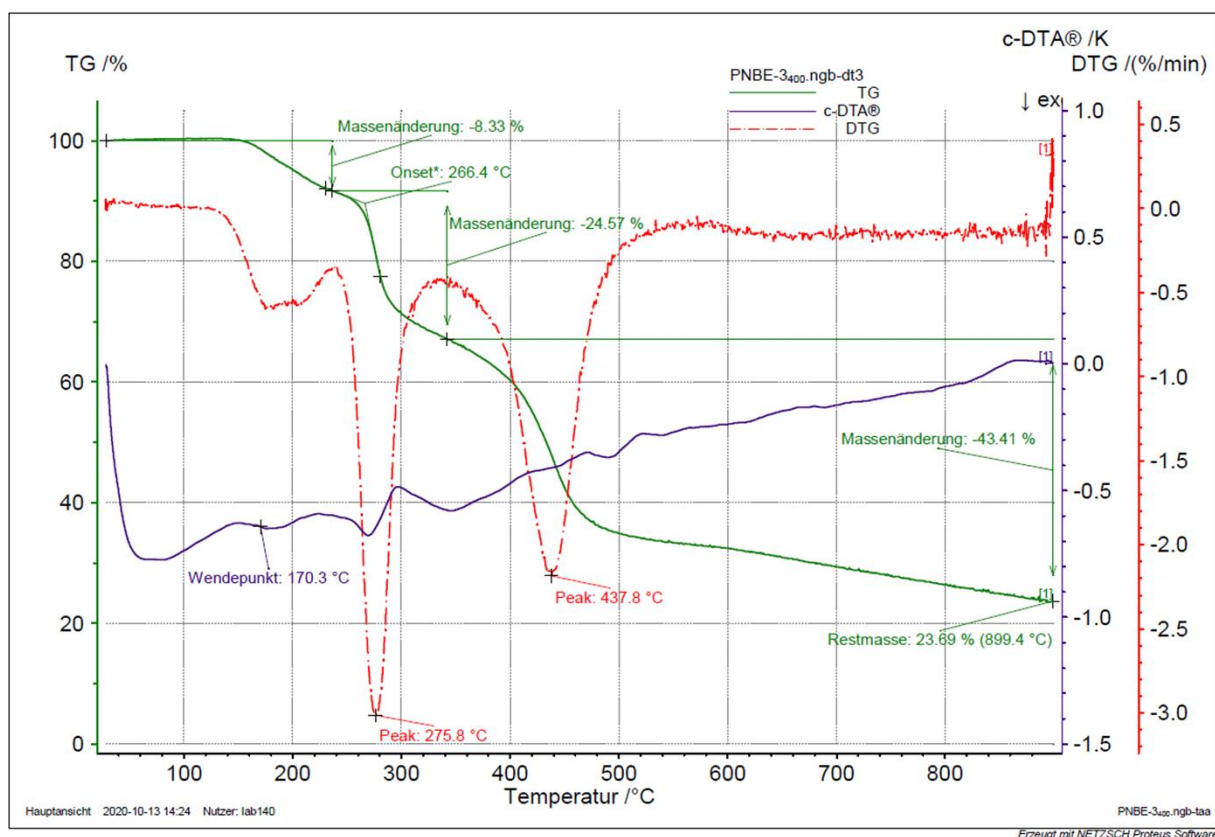


Operator ID: fb
Sample ID: PNBE-3₄₀₀
Sample Weight: 15.128 mg

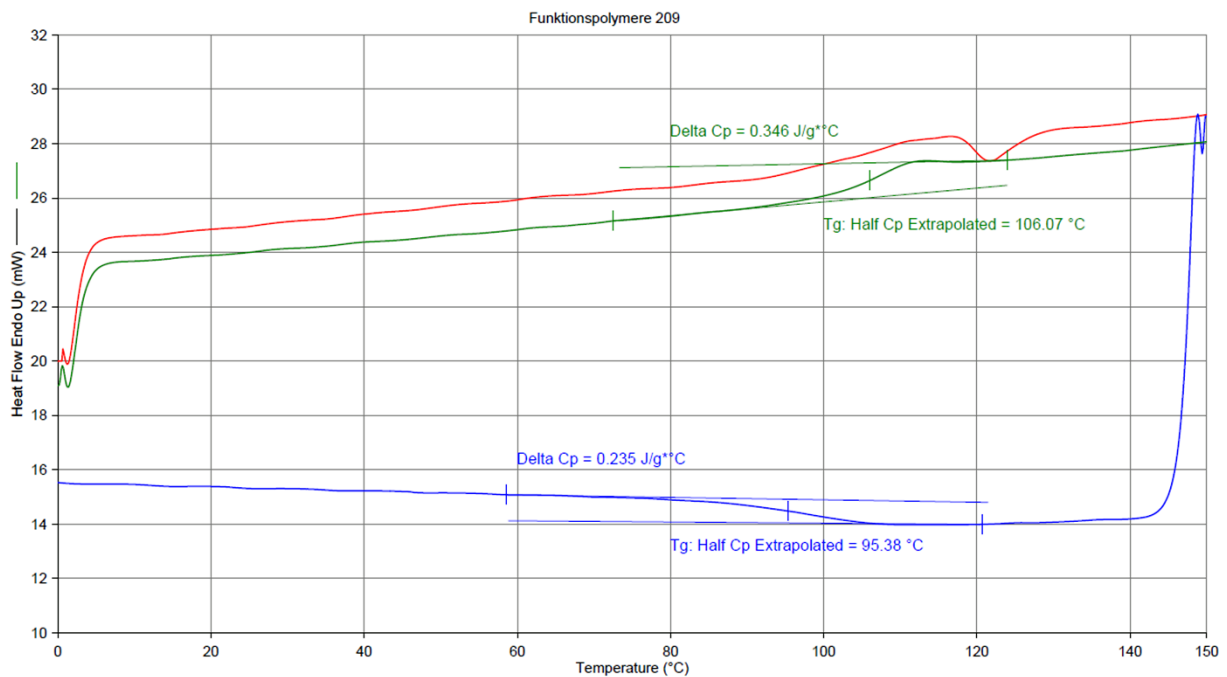


02.11.2021 08:51:07

- | | |
|--|--|
| 1) Heat from 0.00°C to 150.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 150.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 150.00°C at 20.00°C/min |

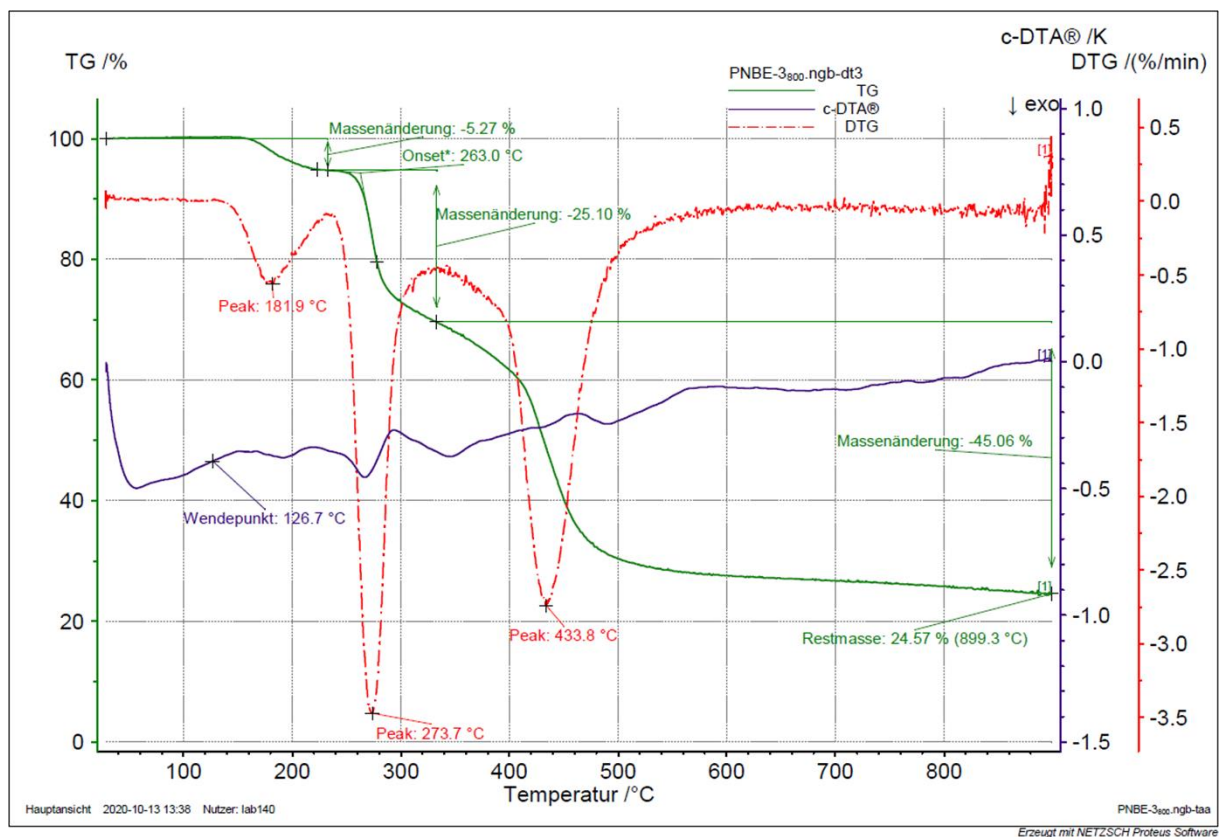


Operator ID: fb
 Sample ID: PNBE-3₈₀₀
 Sample Weight: 11.110 mg

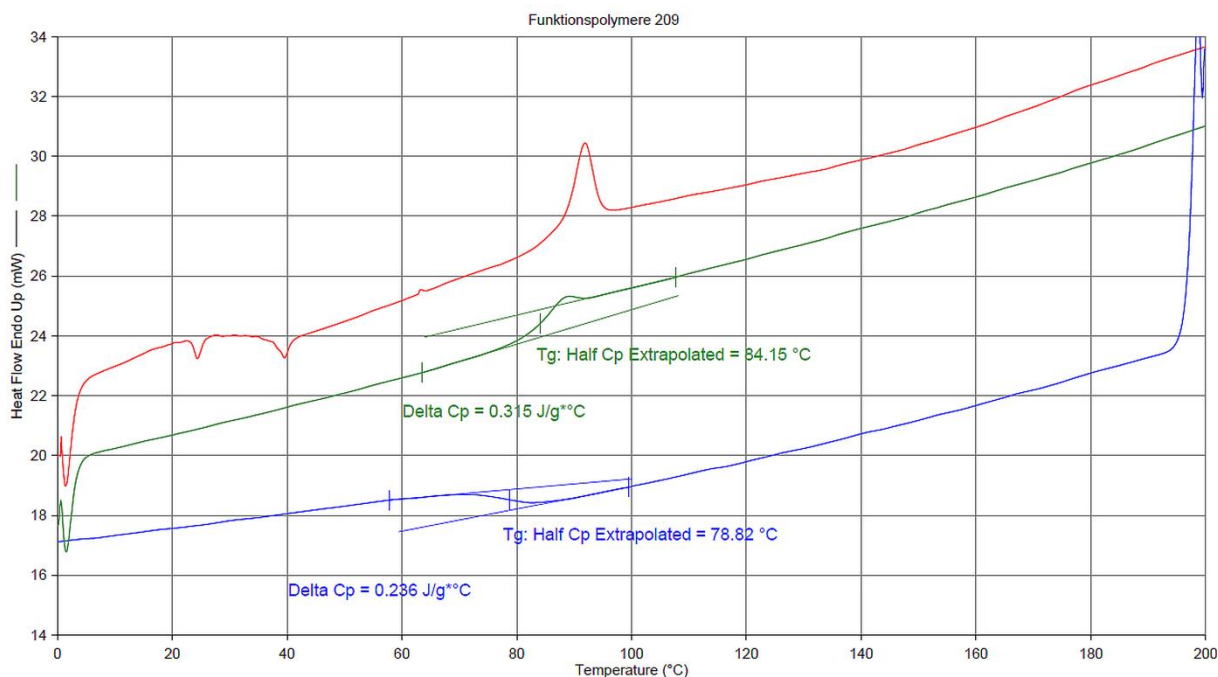


02.11.2021 08:04:25

- 1) Heat from 0.00°C to 150.00°C at 20.00°C/min
- 2) Cool from 150.00°C to 0.00°C at 20.00°C/min
- 3) Hold for 3.0 min at 0.00°C
- 4) Heat from 0.00°C to 150.00°C at 20.00°C/min

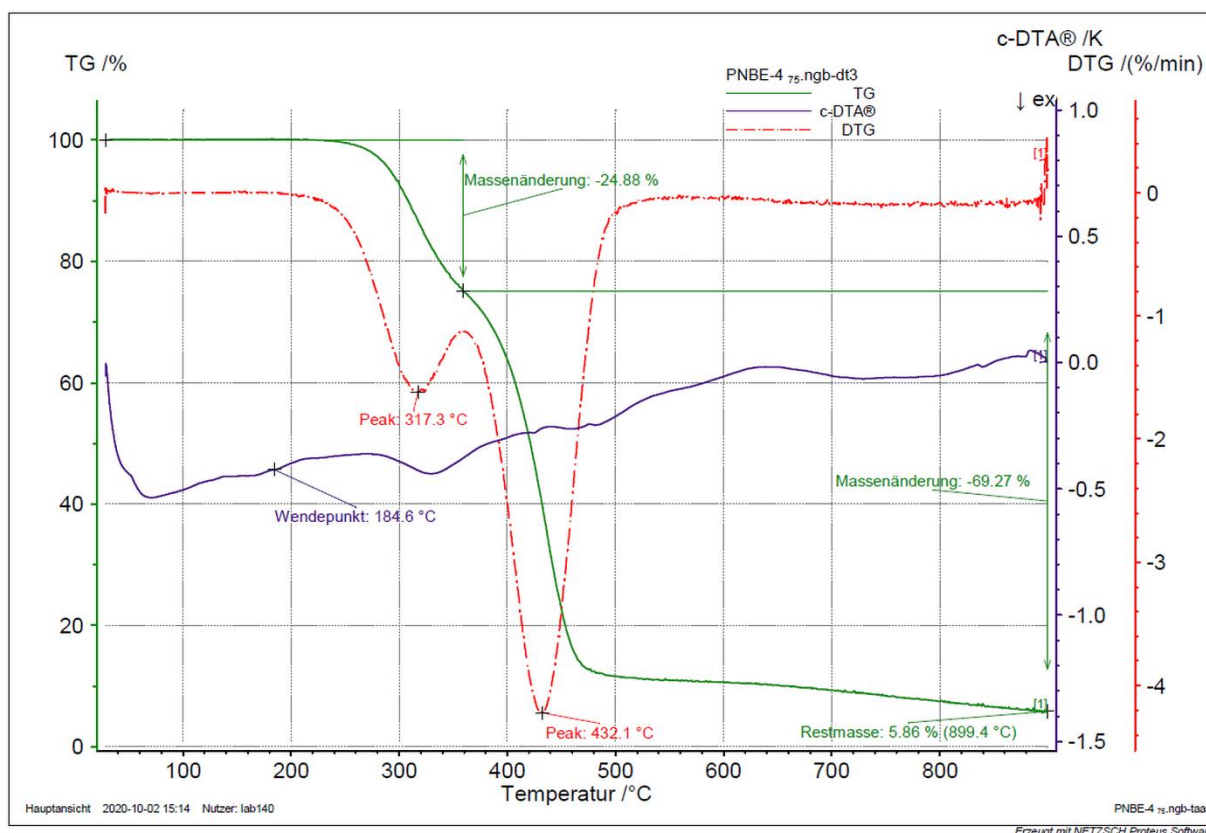


Operator ID: fb
Sample ID: PNBE-4₇₅
Sample Weight: 8.780 mg

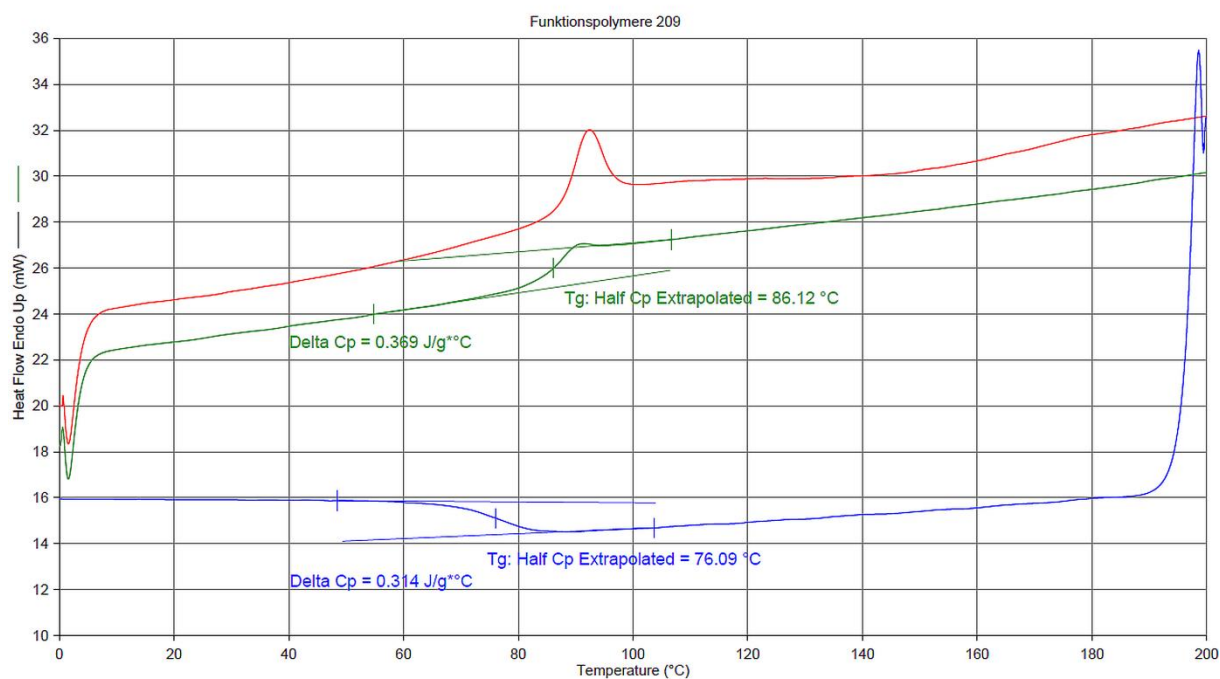


28.10.2020 15:28:54

- 1) Heat from 0.00°C to 200.00°C at 20.00°C/min
- 2) Cool from 200.00°C to 0.00°C at 20.00°C/min
- 3) Hold for 3.0 min at 0.00°C
- 4) Heat from 0.00°C to 200.00°C at 20.00°C/min

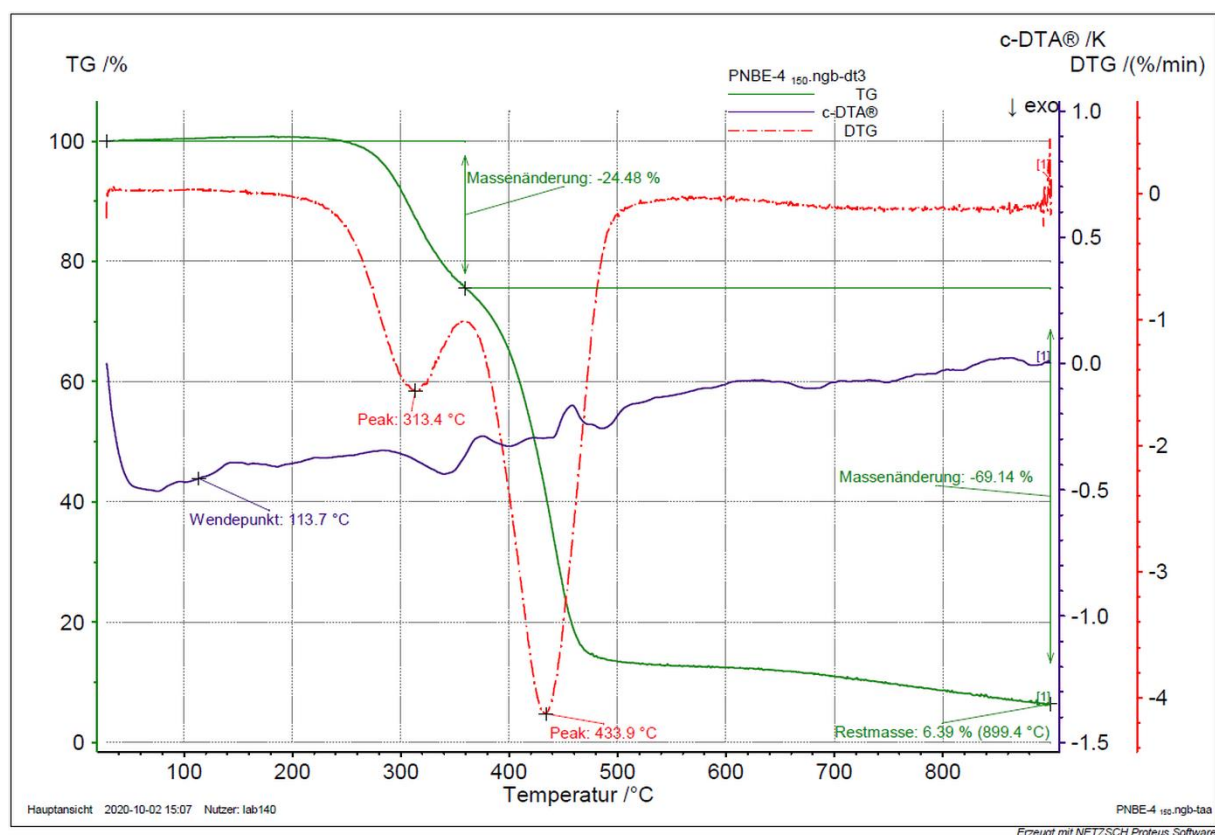


Operator ID: fb
Sample ID: PNBE-4₁₅₀
Sample Weight: 13.672 mg

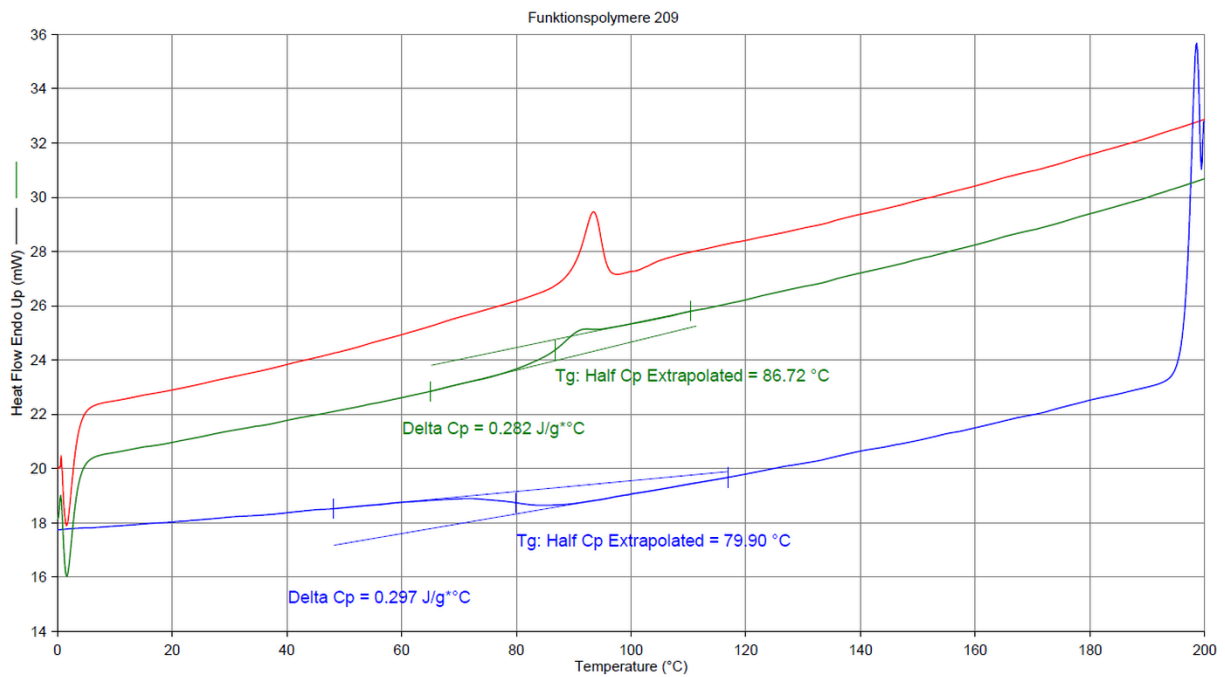


28.10.2020 15:03:39

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

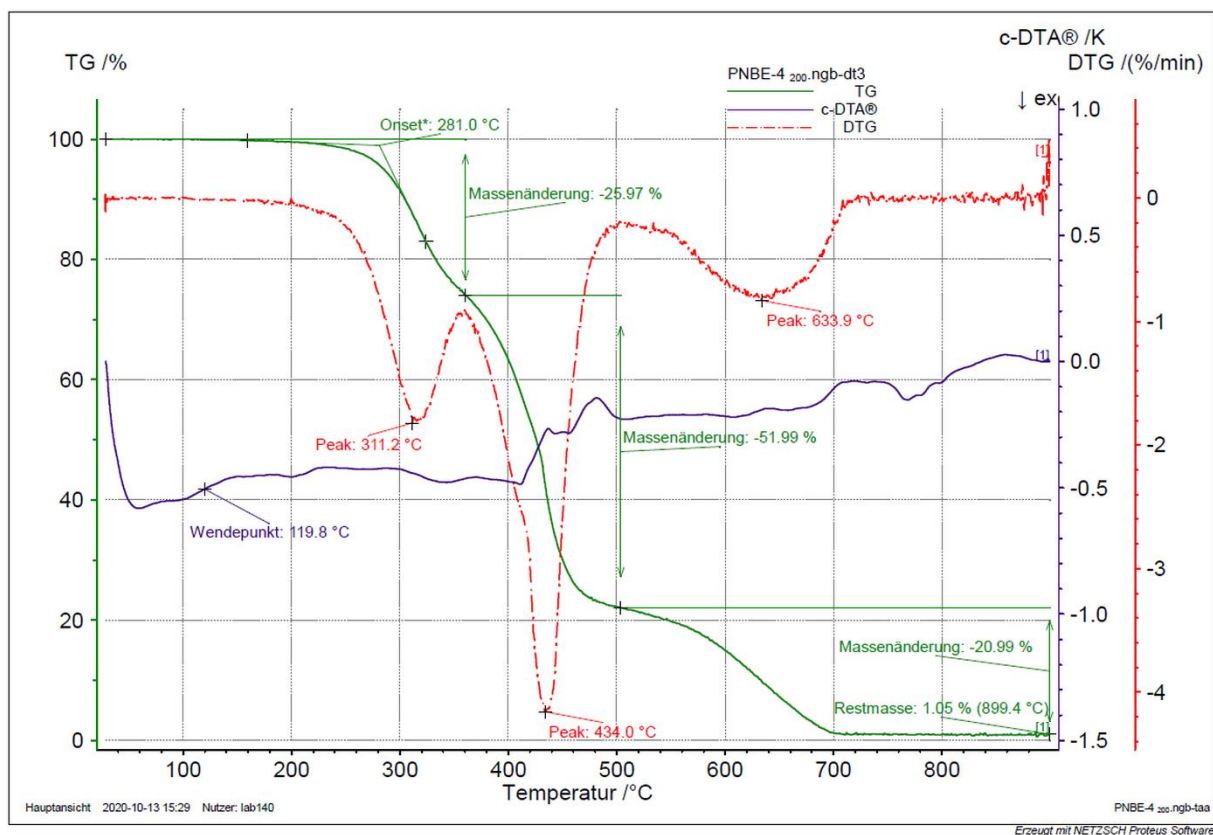


Operator ID: fb
 Sample ID: PNBE-4₂₀₀
 Sample Weight: 8.328 mg

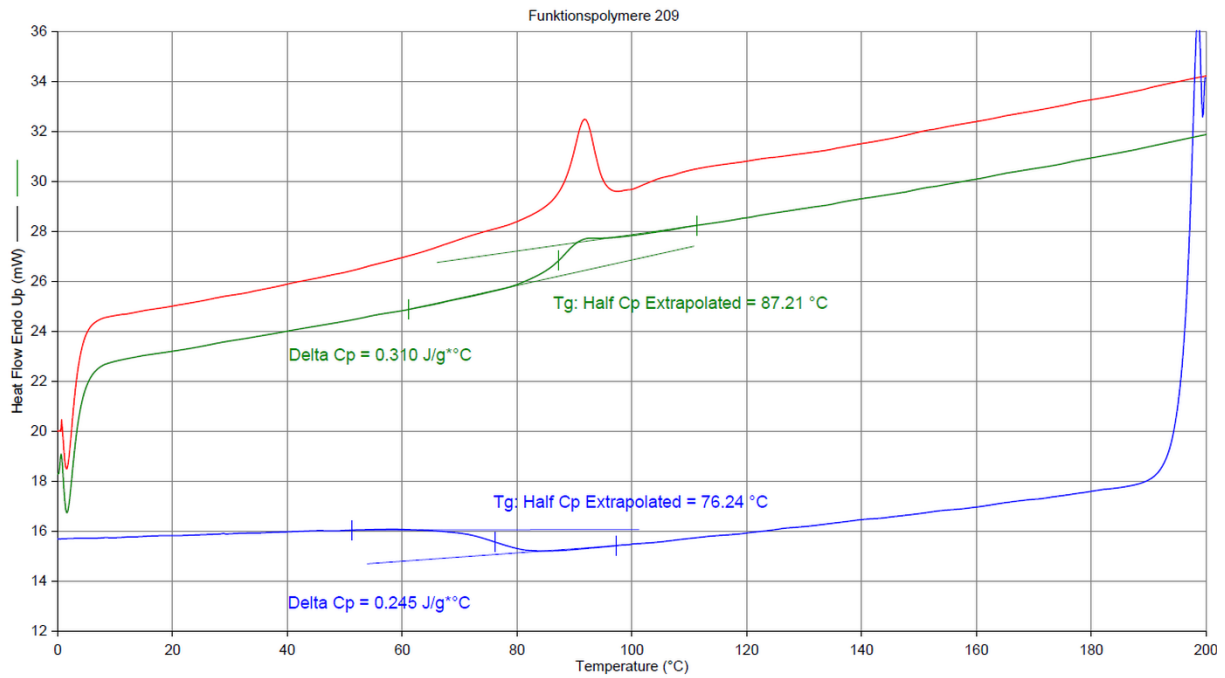


29.10.2020 13:22:40

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

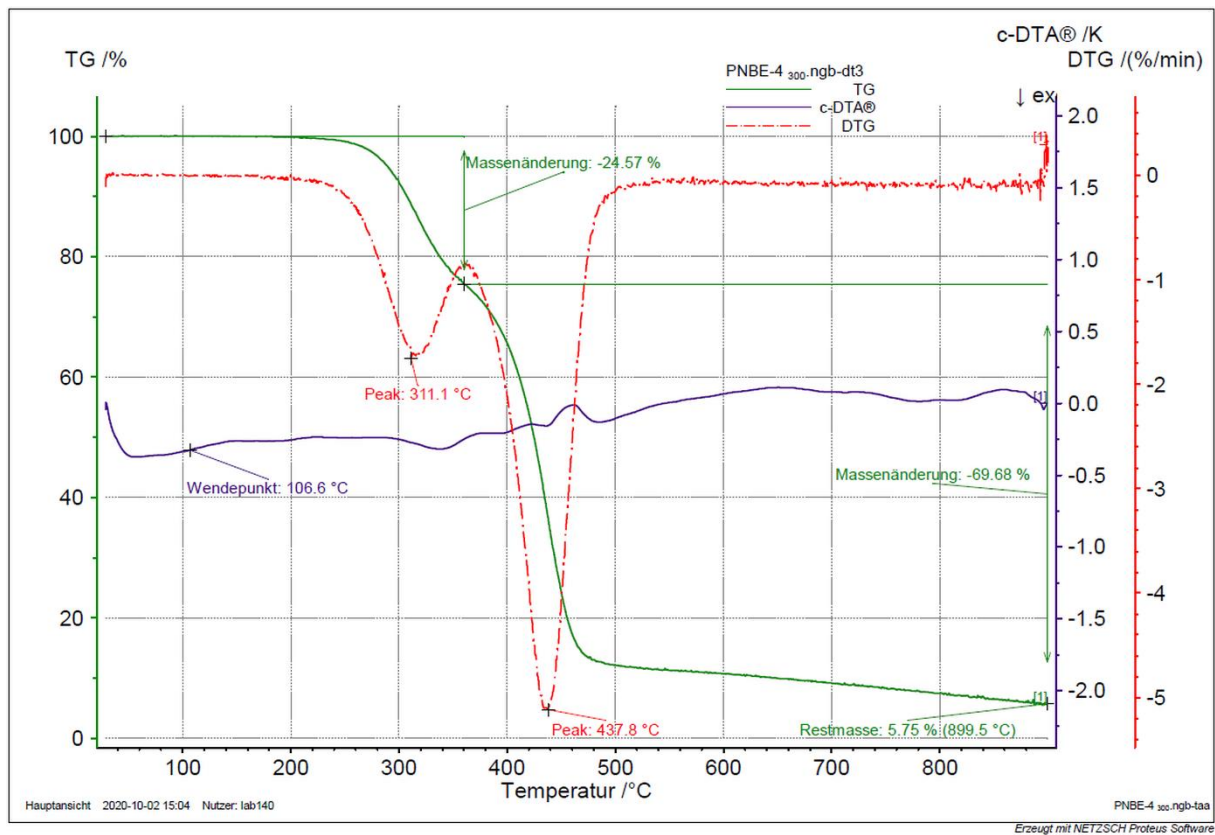


Operator ID: fb
Sample ID: PNBE-4₃₀₀
Sample Weight: 12.060 mg

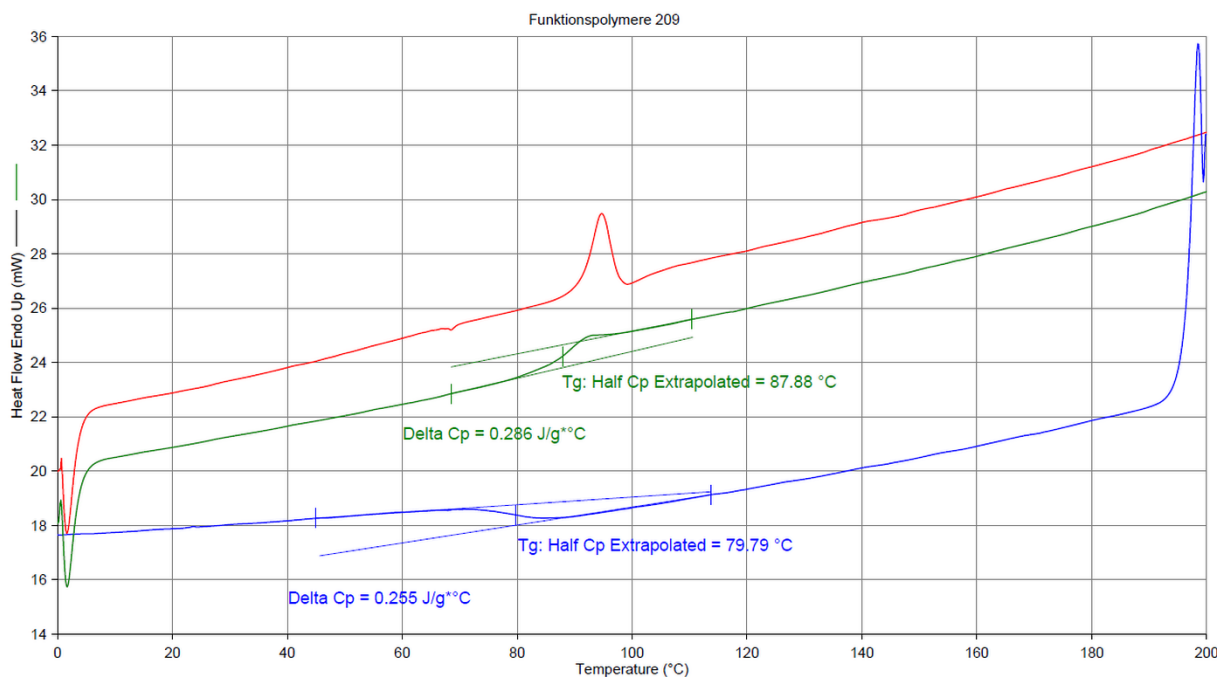


23.10.2020 15:42:09

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

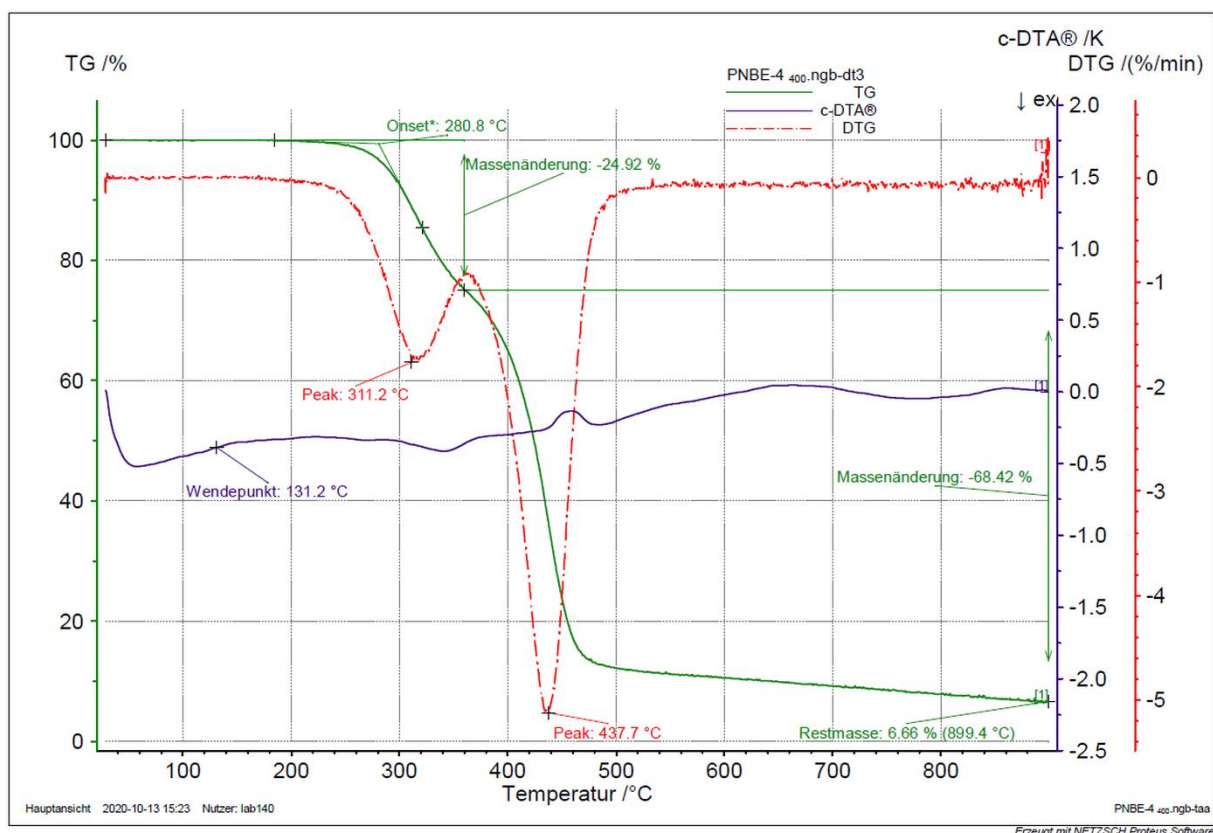


Operator ID: fb
 Sample ID: PNBE-4₄₀₀
 Sample Weight: 8.786 mg

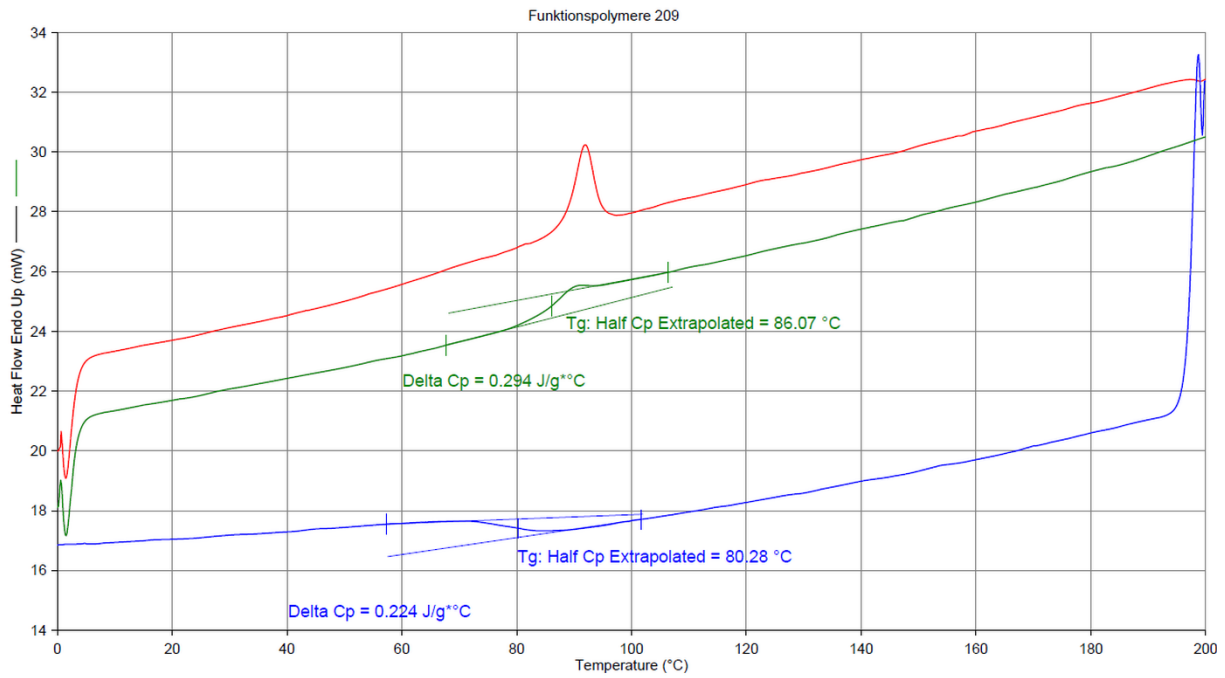


28.10.2020 14:56:35

- 1) Heat from 0.00°C to 200.00°C at 20.00°C/min
- 2) Cool from 200.00°C to 0.00°C at 20.00°C/min
- 3) Hold for 3.0 min at 0.00°C
- 4) Heat from 0.00°C to 200.00°C at 20.00°C/min

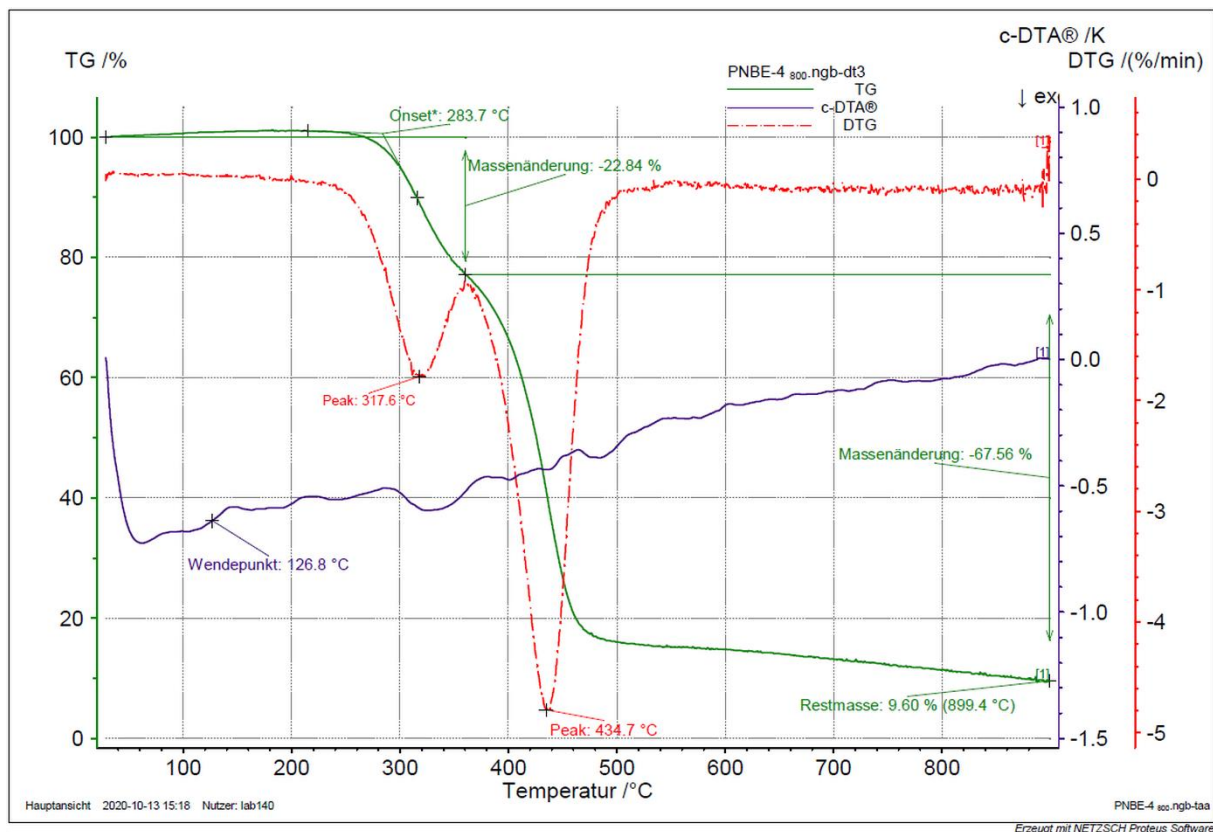


Operator ID: fb
 Sample ID: PNBE-4₈₀₀
 Sample Weight: 8.220 mg

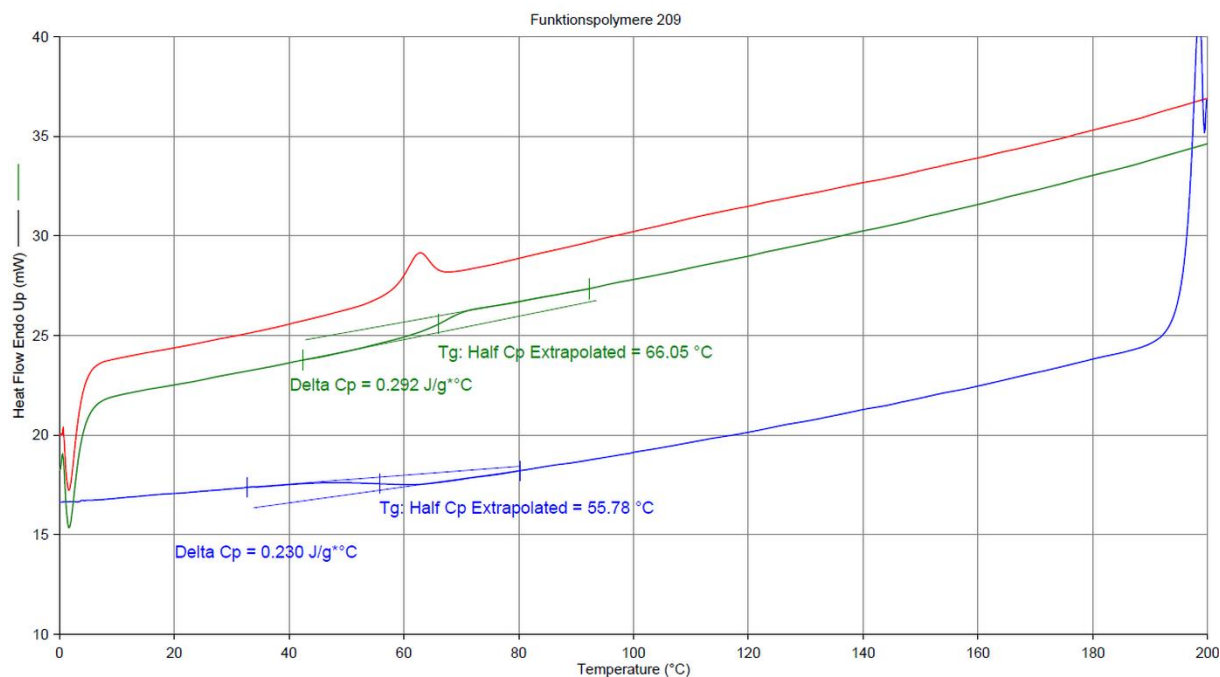


28.10.2020 16:04:11

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

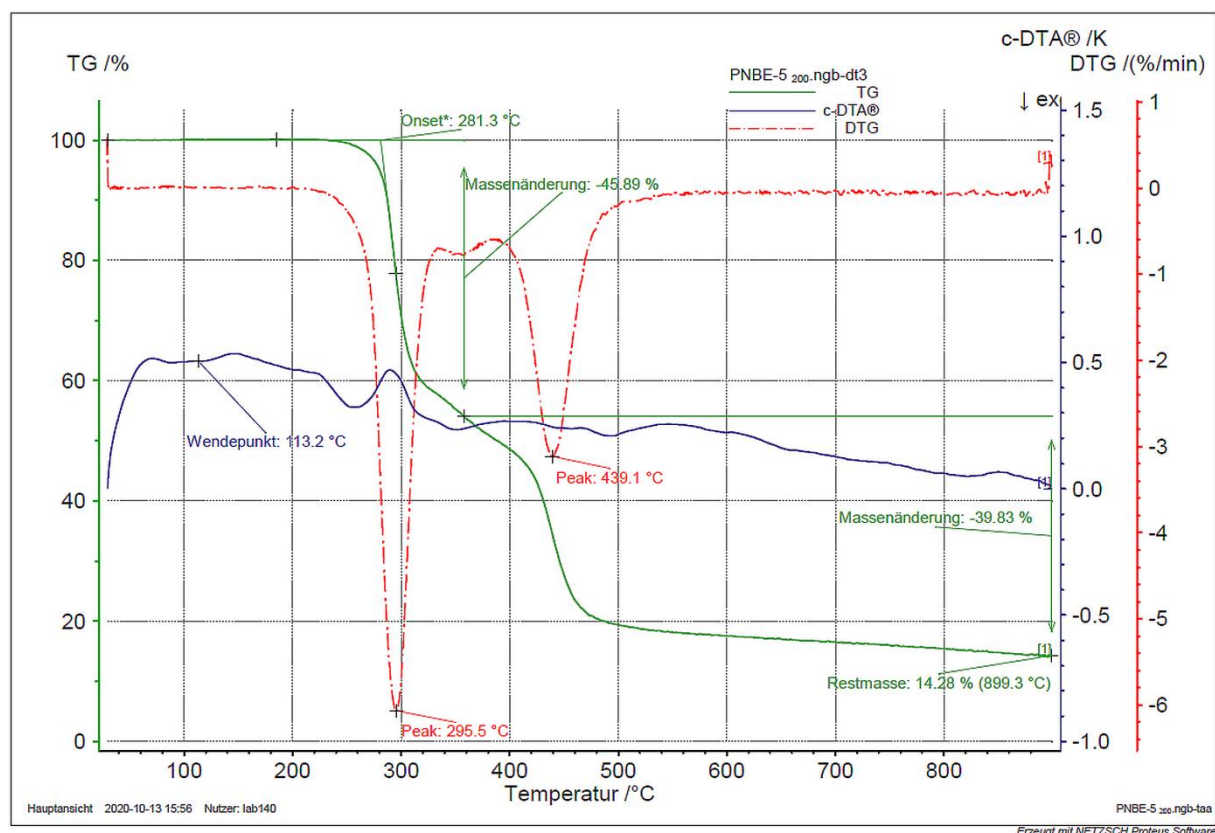


Operator ID: fb
 Sample ID: PNBE-5₂₀₀
 Sample Weight: 8.594 mg

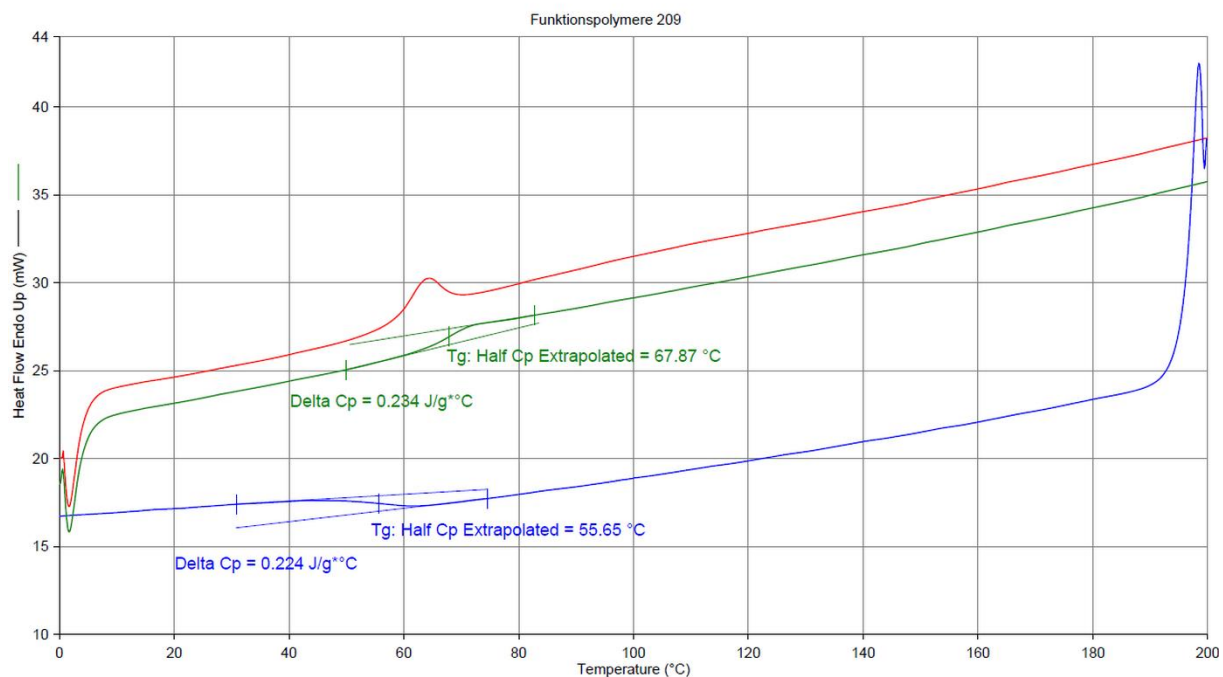


29.10.2020 13:47:33

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

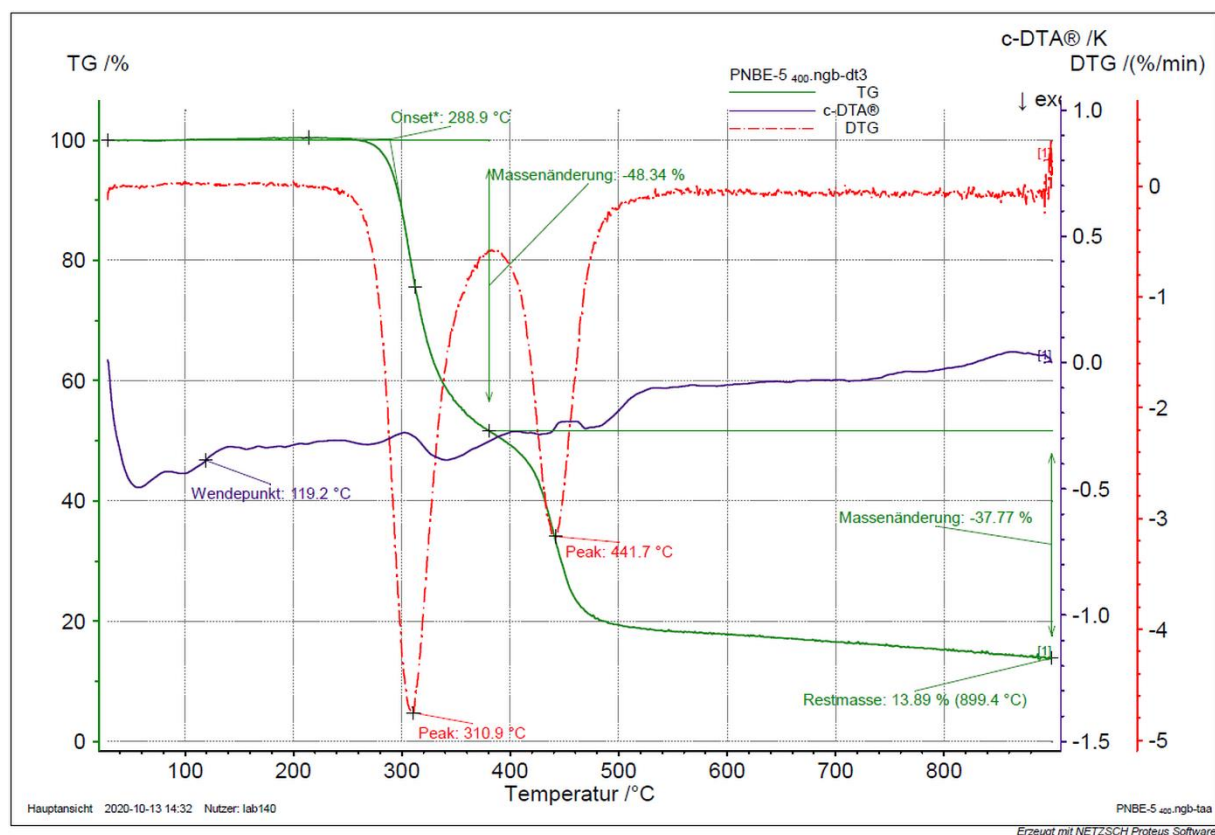


Operator ID: fb
Sample ID: PNBE-5₄₀₀
Sample Weight: 11.710 mg

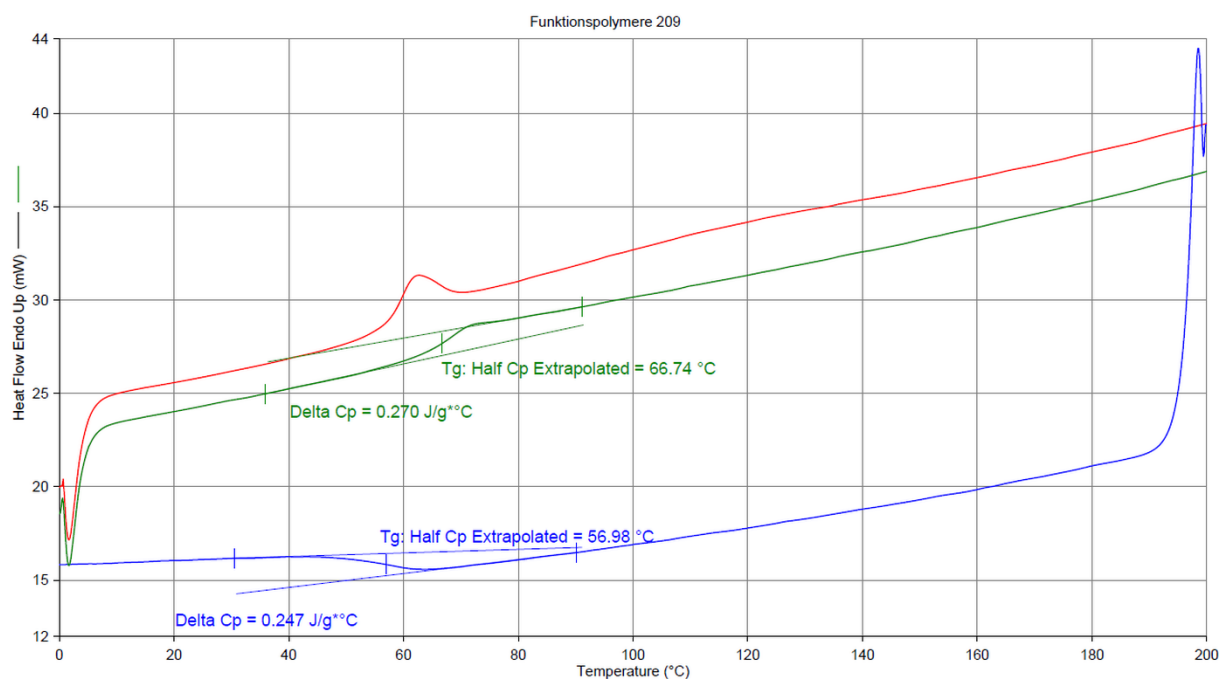


28.10.2020 15:00:40

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

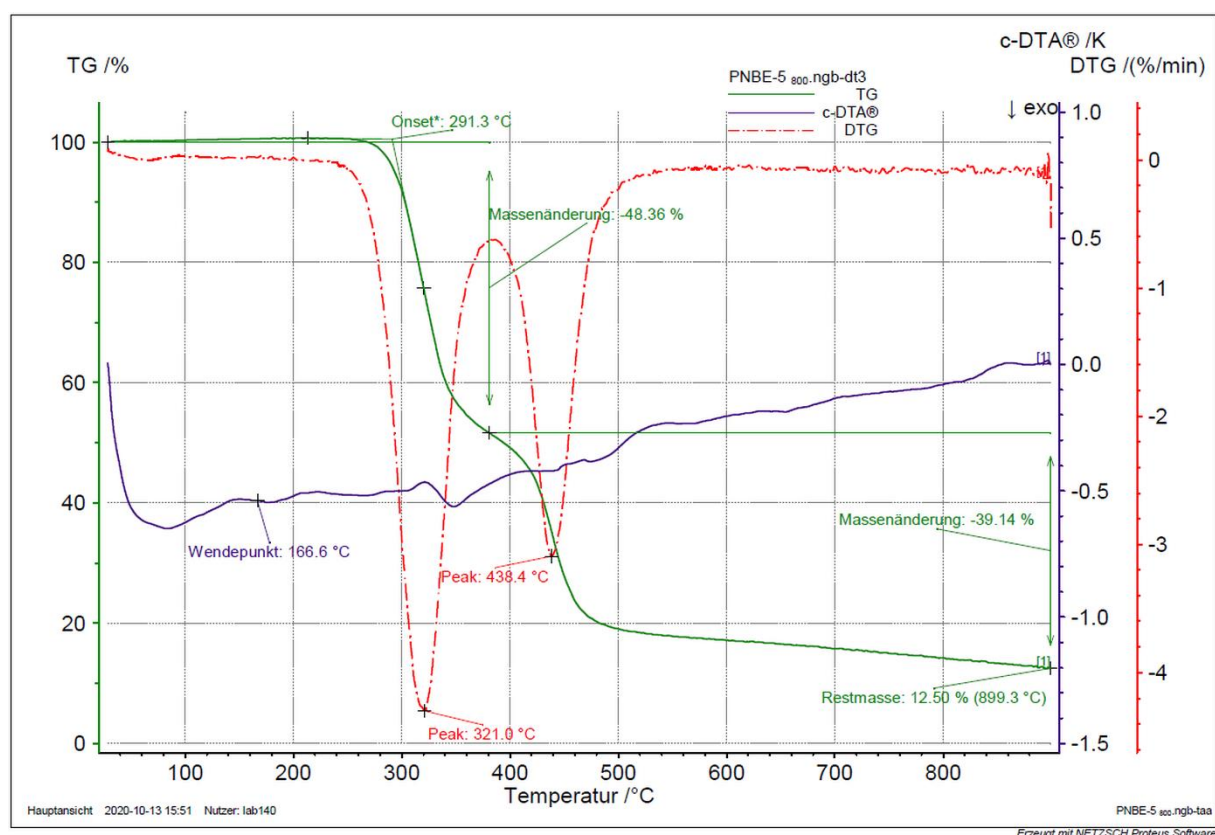


Operator ID: fb
 Sample ID: PNBE-5₈₀₀
 Sample Weight: 14.408 mg

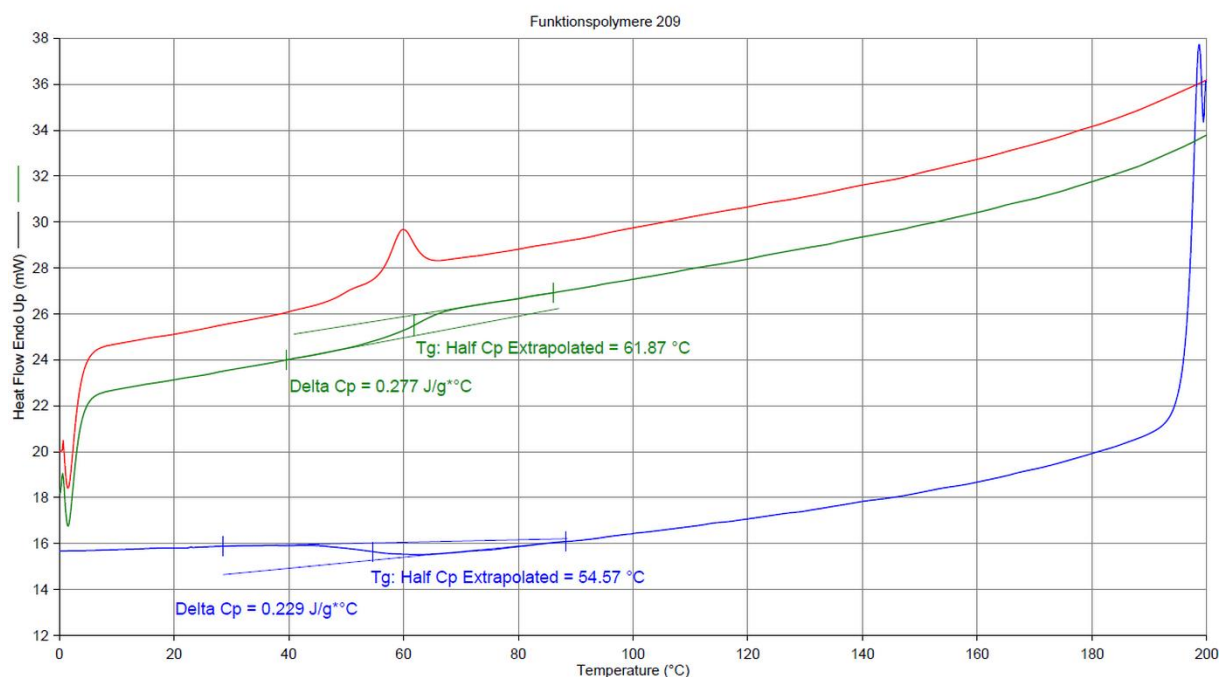


29.10.2020 13:44:10

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

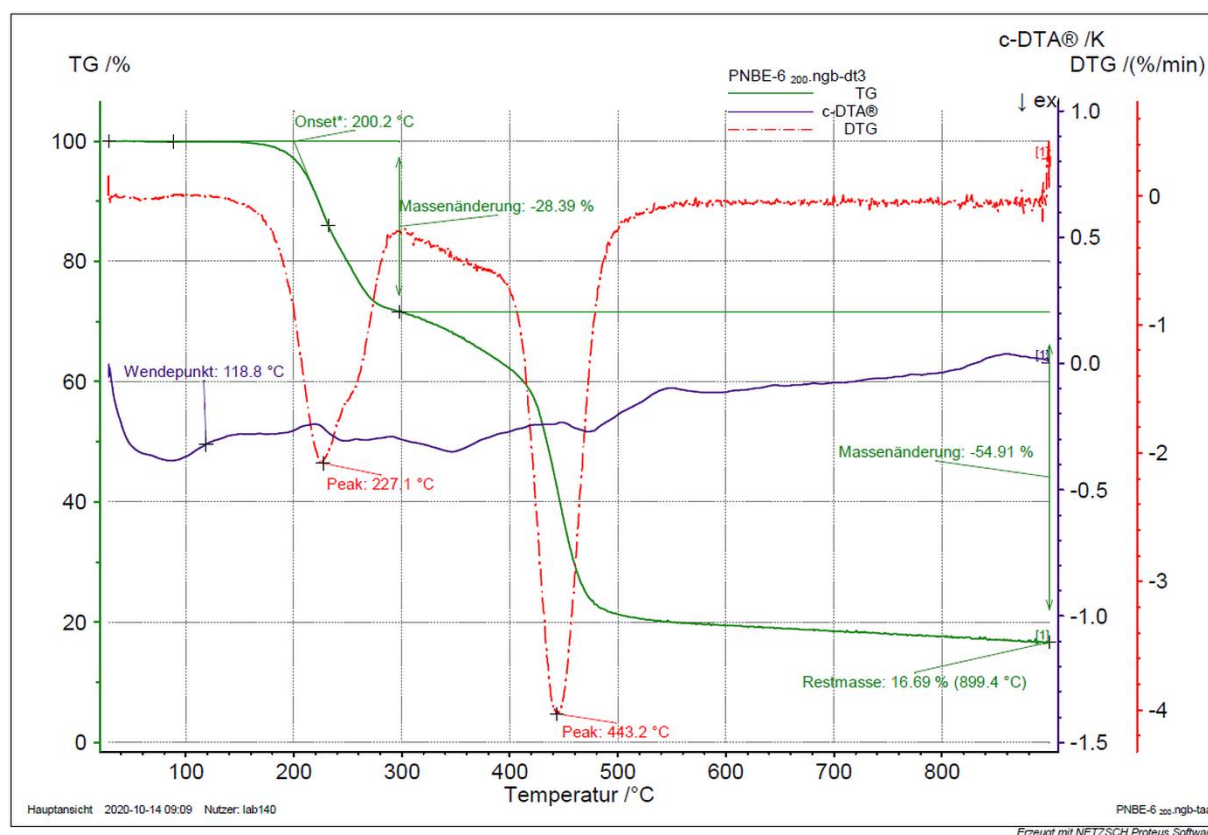


Operator ID: fb
 Sample ID: PNBE-6₂₀₀
 Sample Weight: 9.854 mg

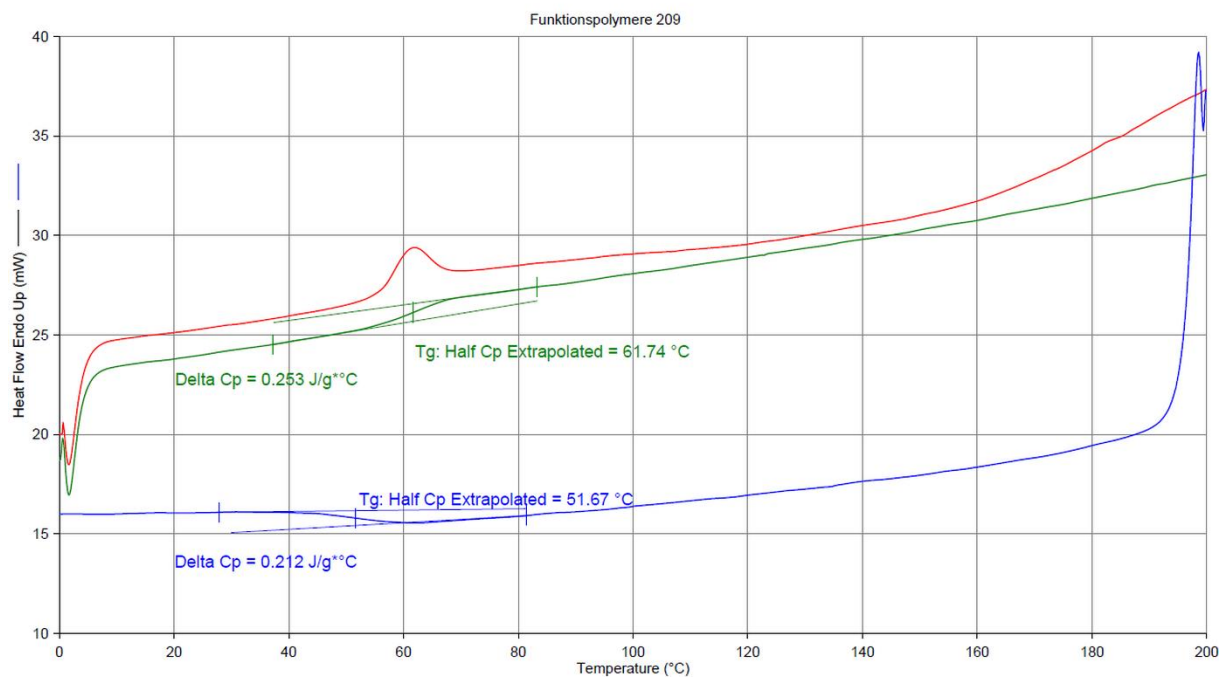


29.10.2020 14:15:44

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

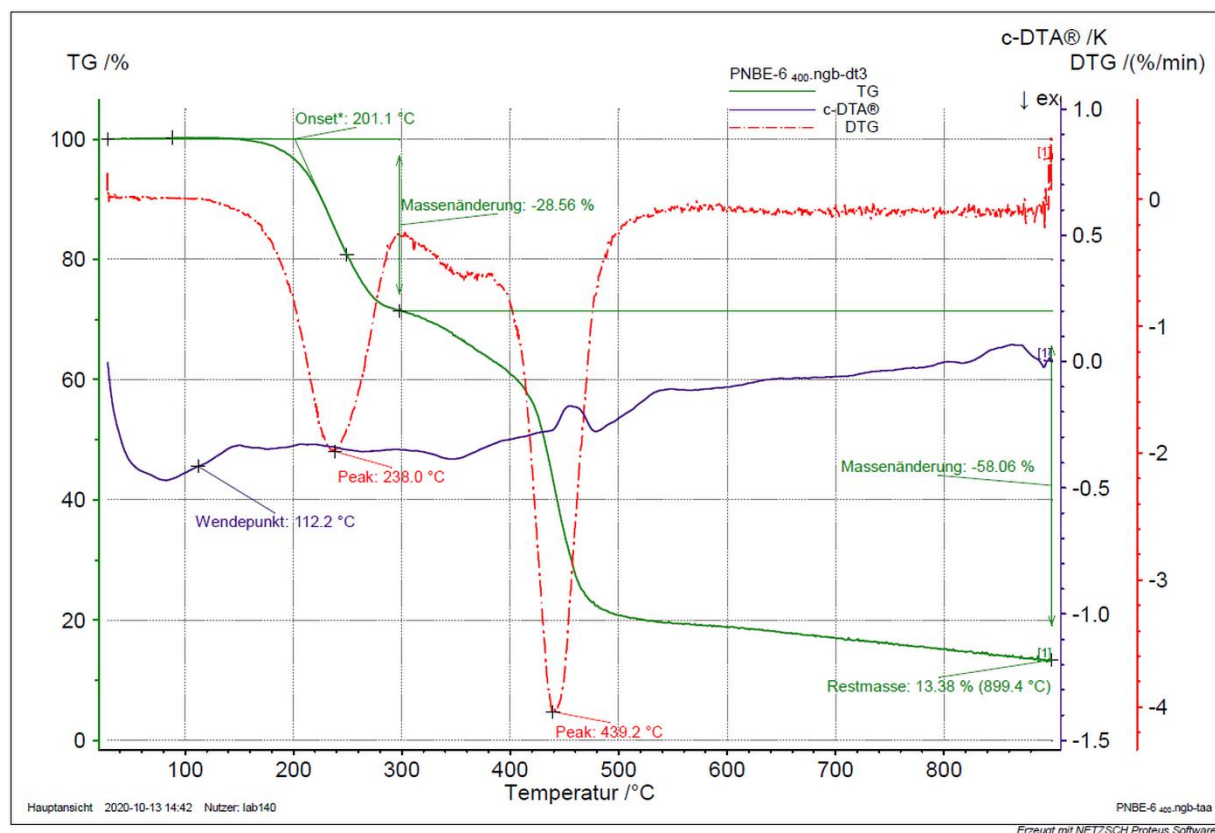


Operator ID: fb
 Sample ID: PNBE-6₄₀₀
 Sample Weight: 10.556 mg

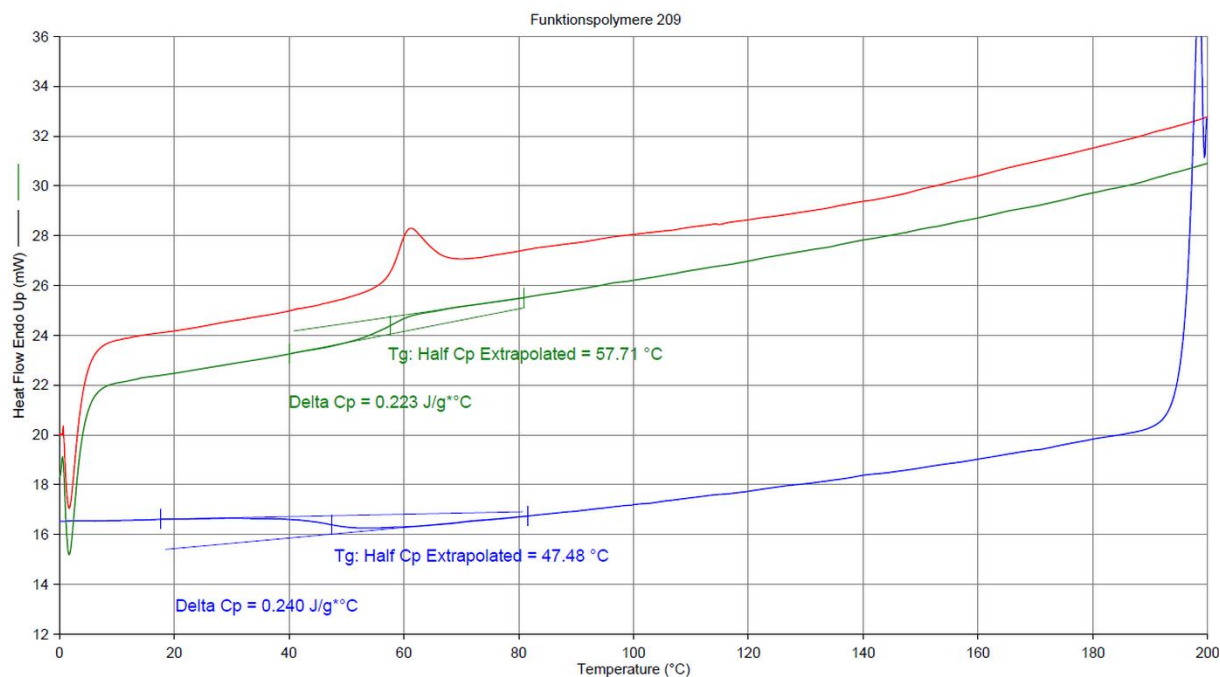


28.10.2020 14:28:49

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |



Operator ID: fb
Sample ID: PNBE-6₈₀₀
Sample Weight: 9.226 mg



29.10.2020 14:10:16

- | | |
|--|--|
| 1) Heat from 0.00°C to 200.00°C at 20.00°C/min | 3) Hold for 3.0 min at 0.00°C |
| 2) Cool from 200.00°C to 0.00°C at 20.00°C/min | 4) Heat from 0.00°C to 200.00°C at 20.00°C/min |

