Electronic Supplementary Material (ESI) for Materials Advances.

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

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

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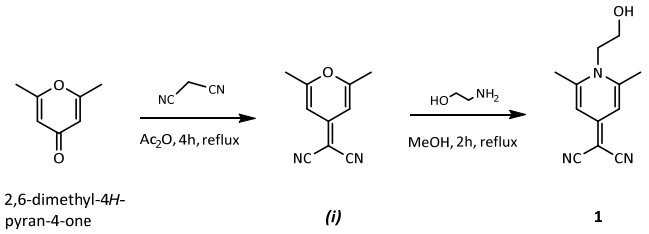
Synthesis of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

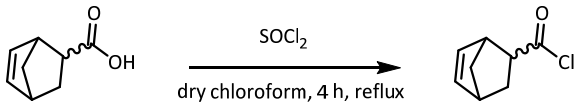


Scheme S1 Synthesis of compound 1

Compound **1** was designed and synthesized as shown in Scheme S1. Initially, 2,6-dimethyl-4*H*-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 %). Furtherly, 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%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.68 (s, 2H, Ar–H), 5.17 (t, J = 5.4 Hz, 1H, OH), 4.17 (t, J = 5.6 Hz, 2H, N–CH_2), 3.70 (q, J = 5.4 Hz, 2H, CH_2–OH), 2.53 (s, 6H, Ar–CH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.40 (C_{Ar}=C(CN)$_2$), 150.92 (C_{Ar} –CH_3), 119.43 (CN), 113.07 (C_{Ar} –H), 59.76 (=C(CN)$_2$ and CH_2–OH), 51.13 (N–CH_2) , 21.03 (Ar–CH_3). MS (ESI) m/z for $C_{12}H_{13}N_3NaO$ $[M+Na]^+$: calc. = 238.0951; found = 238.0950 Elemental analysis $C_{12}H_{13}N_3O$ (%): calc. C 66.96, H 6.09, N 19.52, O 7.43; found: C 66.91, H 6.01, N 19.43 O 7.31

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



(ii)

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%).

^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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

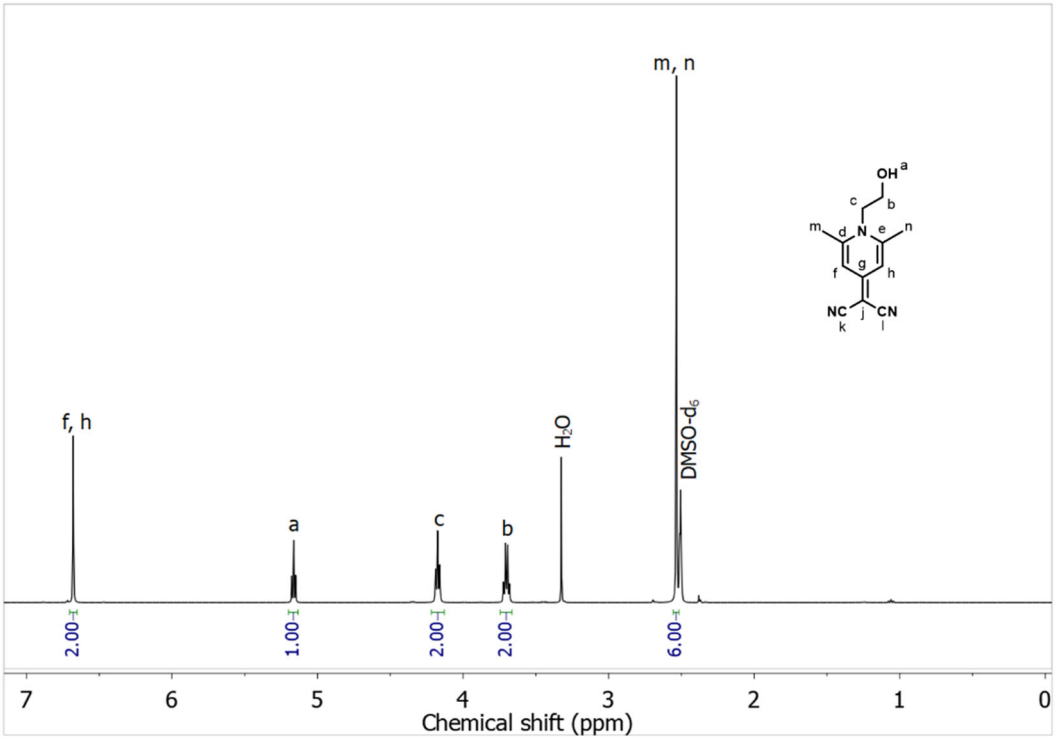


Figure S1 ^{1}H NMR spectrum of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

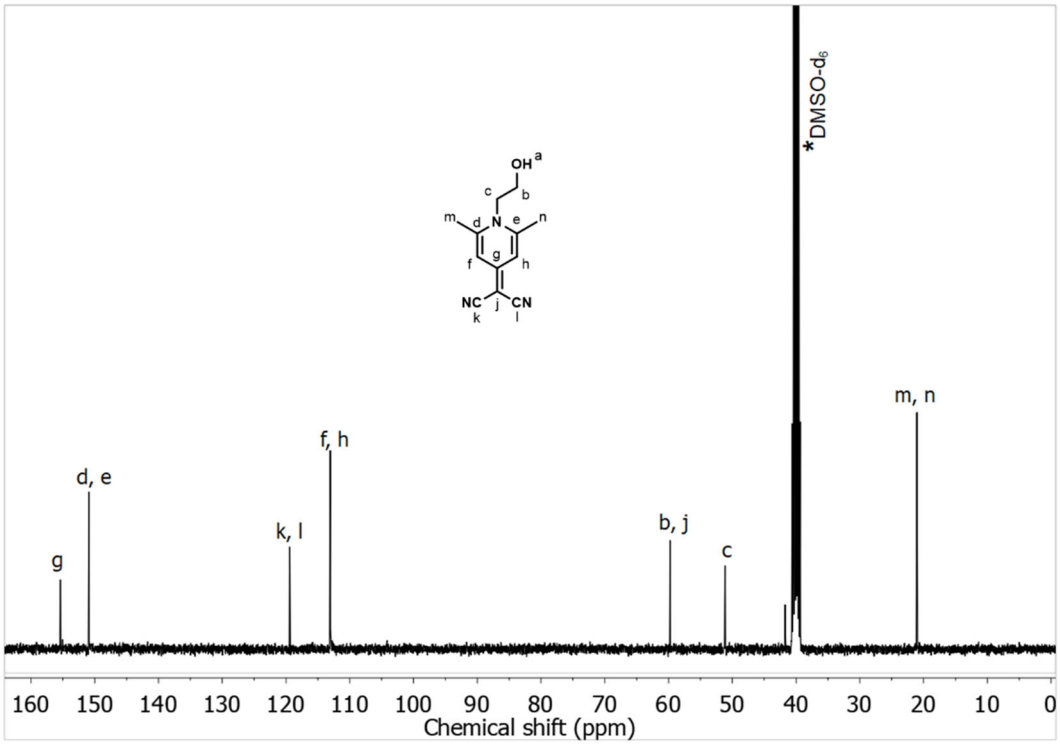


Figure S2 ^{13}C NMR spectrum of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

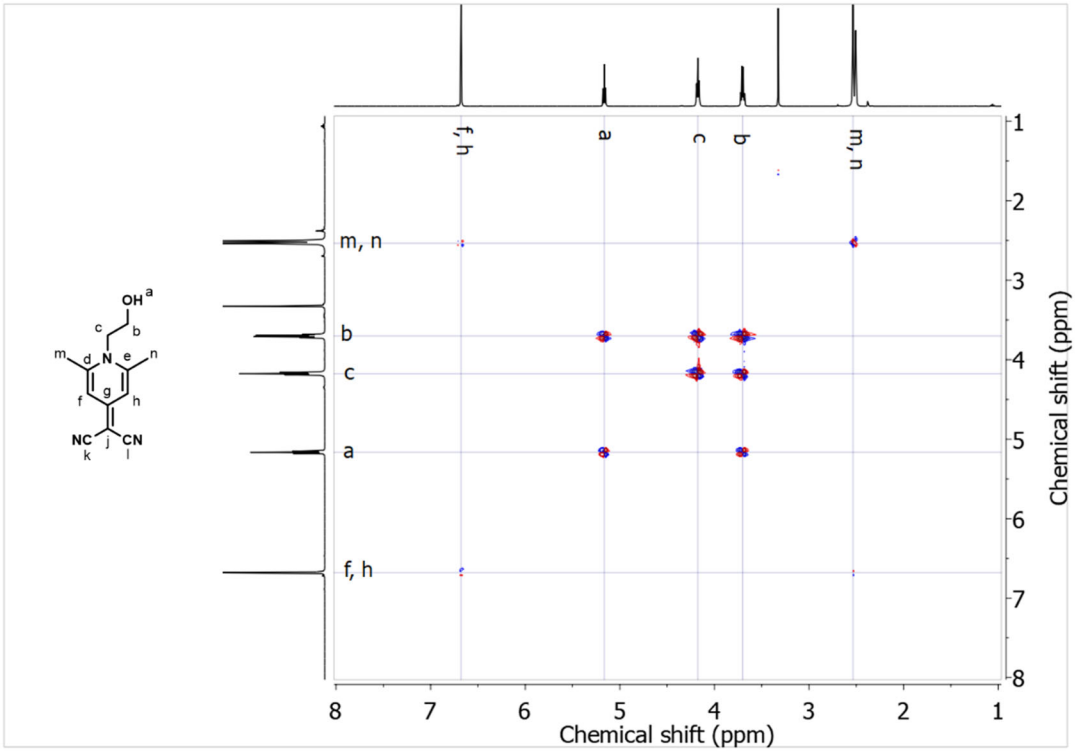


Figure S3 COSY of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

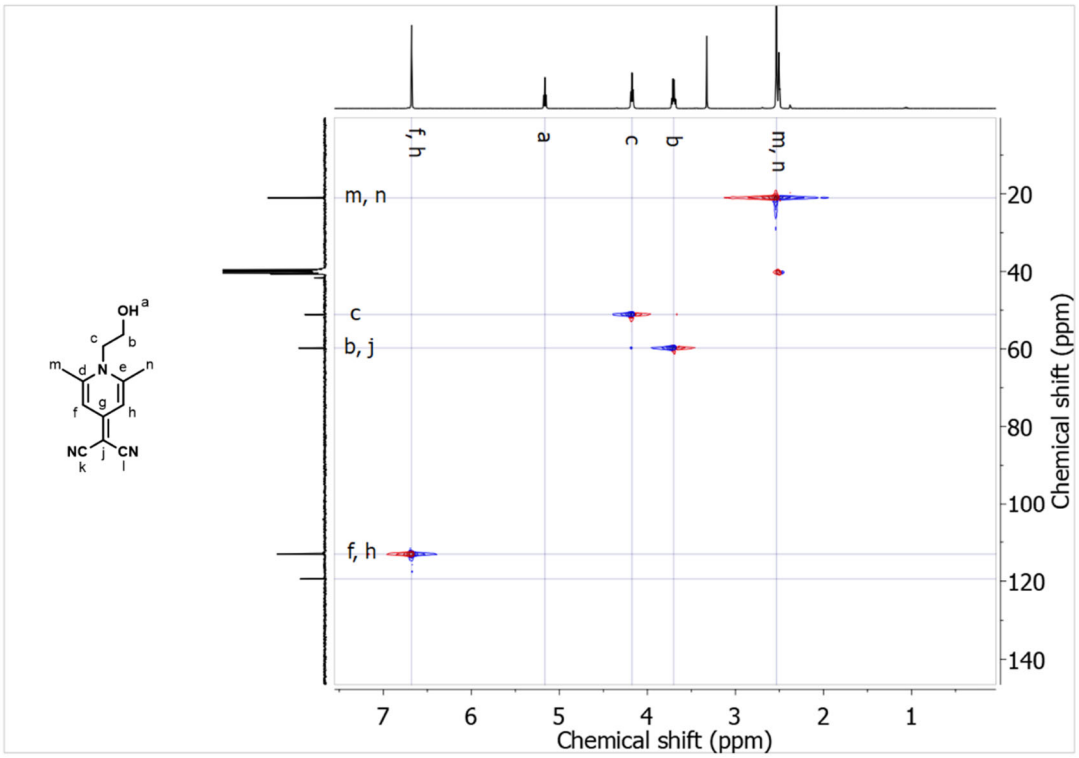


Figure S4 HSQC of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

Eidgenössische Technische Hochschule Zürich

Laboratorium für Organische Chemie

ETH-Hönggerberg - HCI E304 8093 Zürich Tel: 044/633 43 58

Mikroelementaranalyse

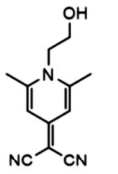
Name: Owusu Francis Gruppe: Opris EMPA
Labor: LA182 Tel: 058/765 48 01

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



$C_{12}H_{13}N_3O$
M= 215.26 g/mol

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			Acquisition Date:	10.10.2019 15:57:20
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

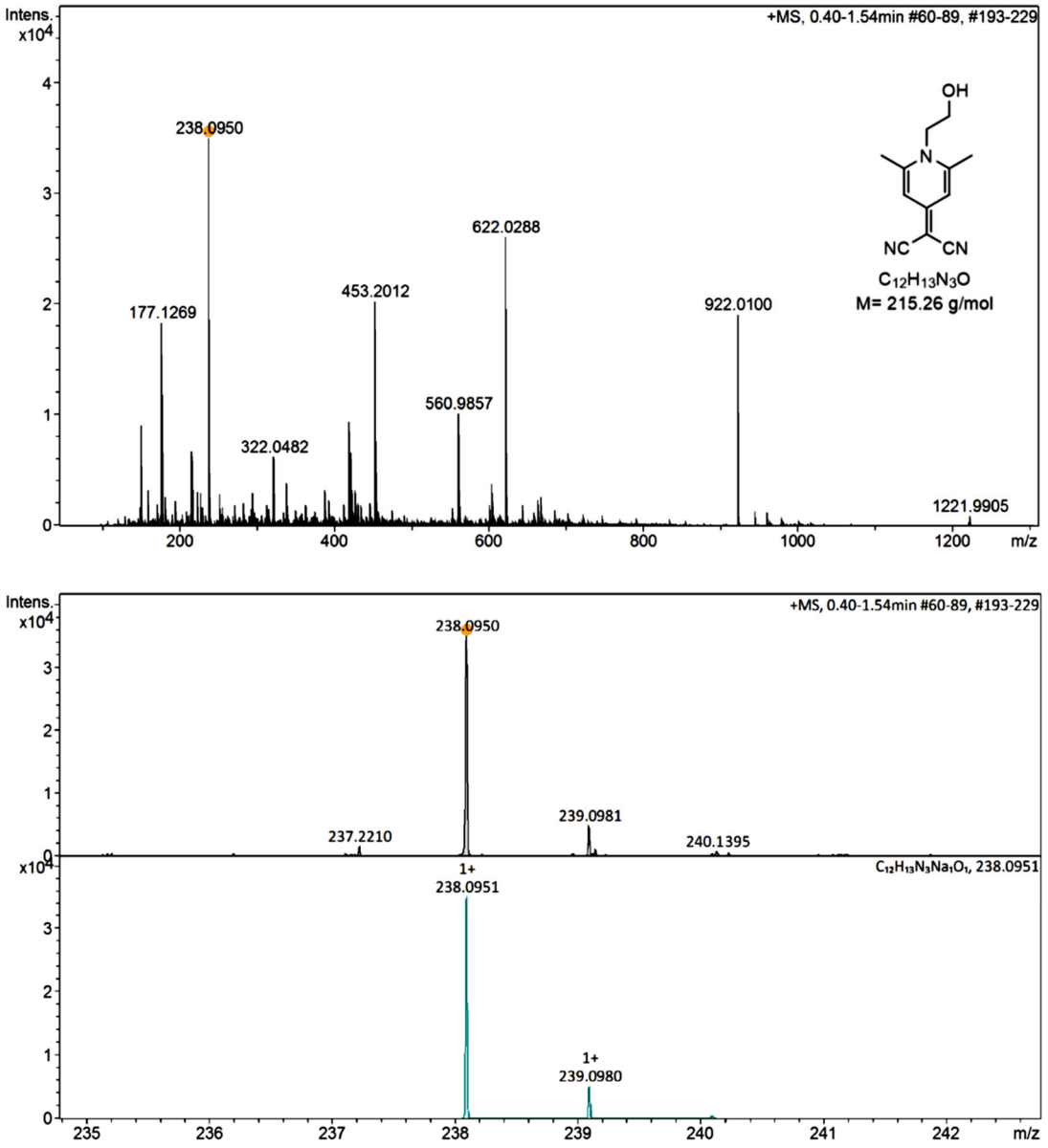


Figure S6 Mass spectra of 2-(1-(2-hydroxyethyl)-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile

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

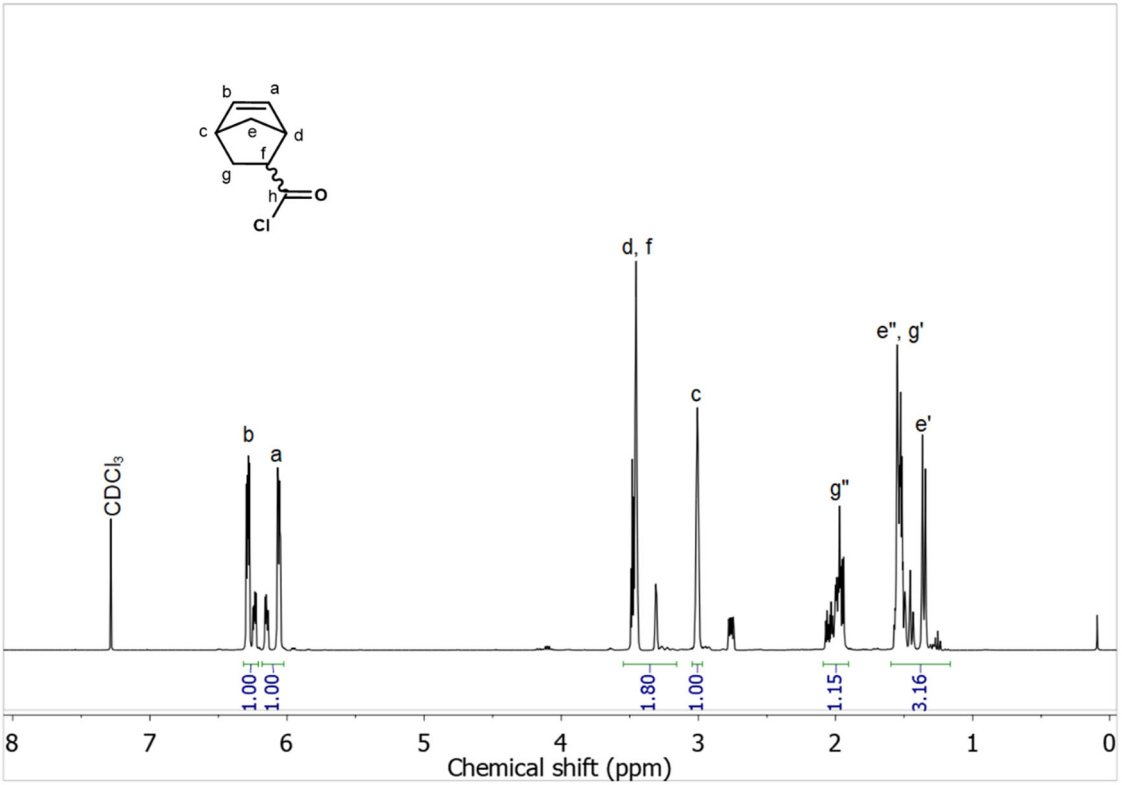


Figure S7 ^{1}H NMR spectrum of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

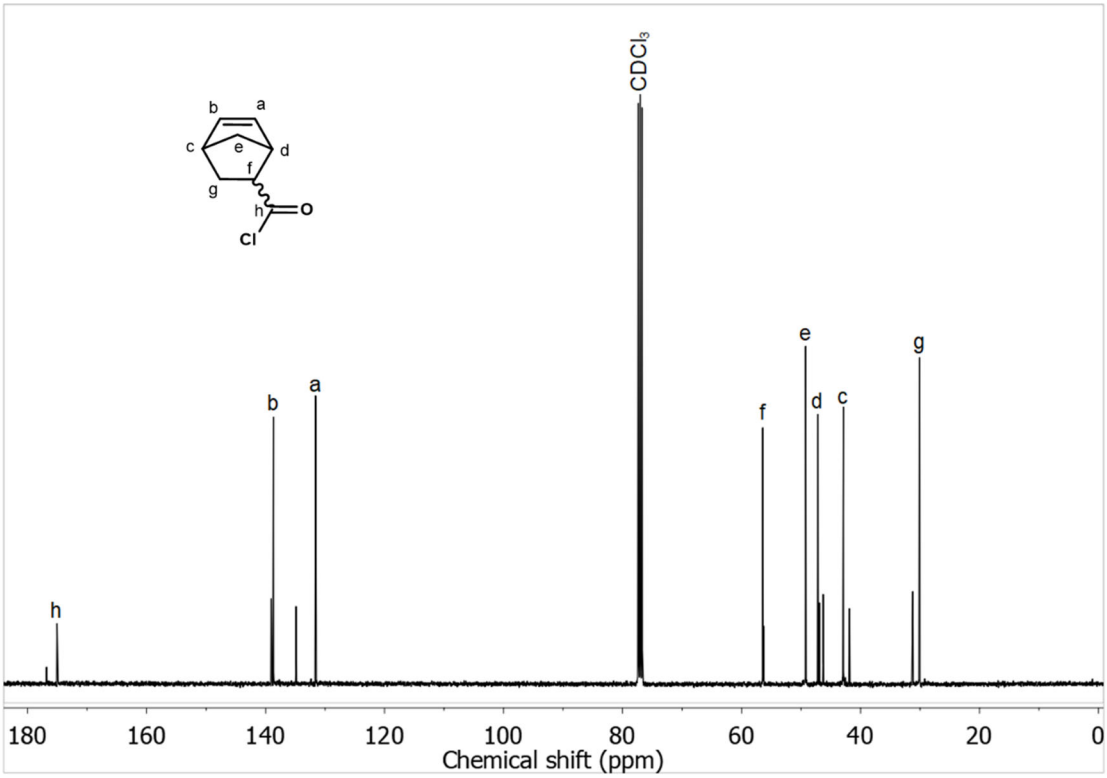


Figure S8 13C NMR spectrum of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

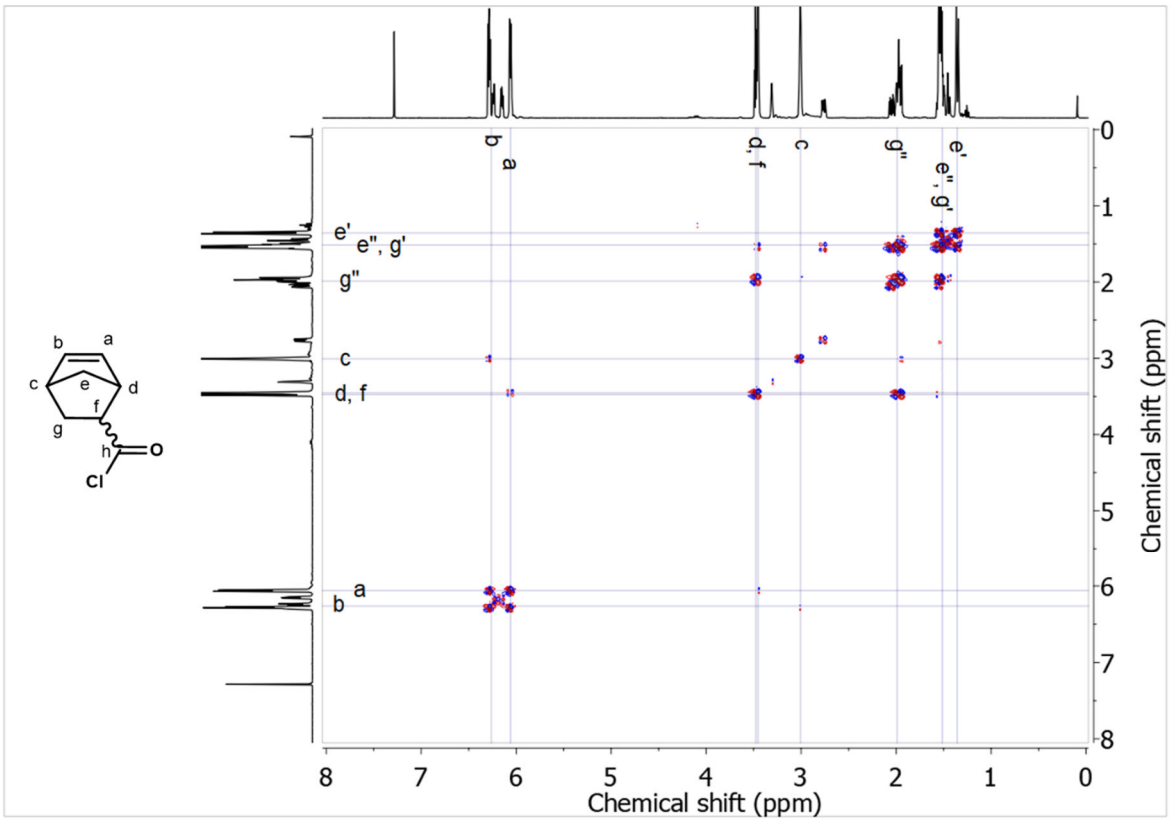


Figure S9 COSY of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

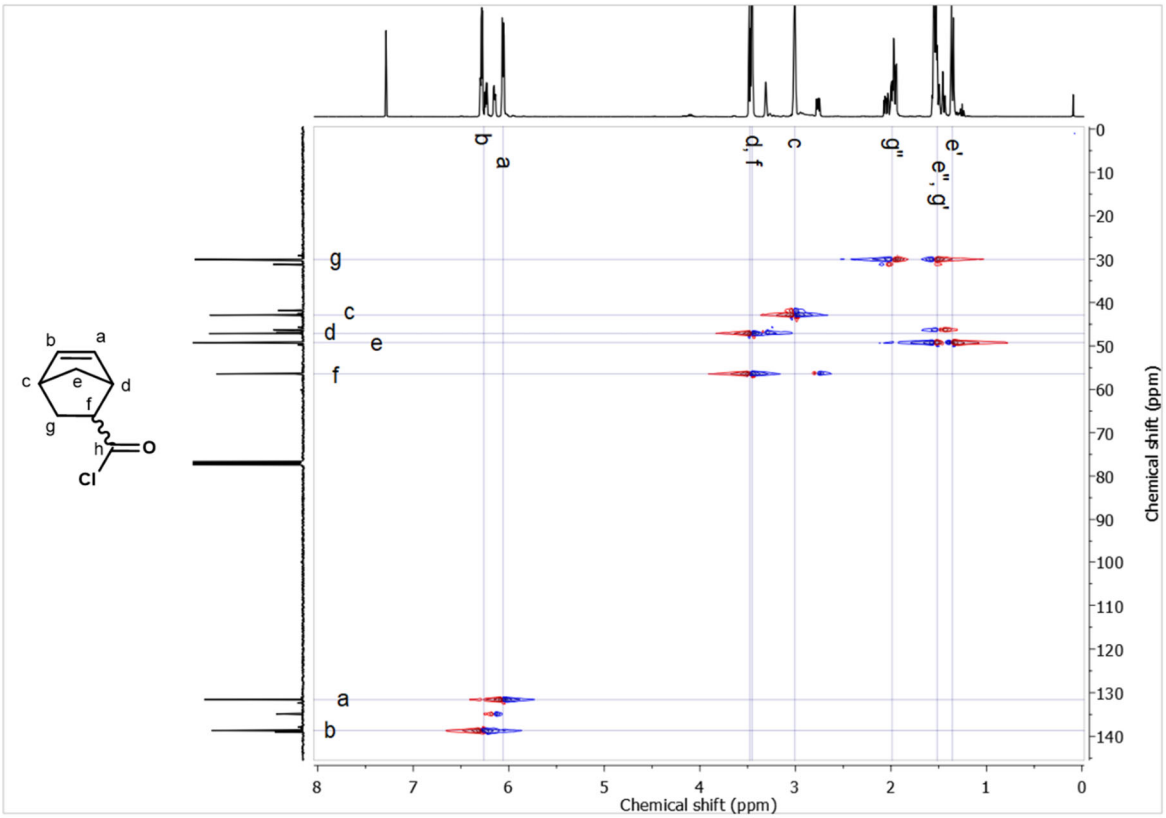


Figure S10 HSQC of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

Structure characterization of monomers

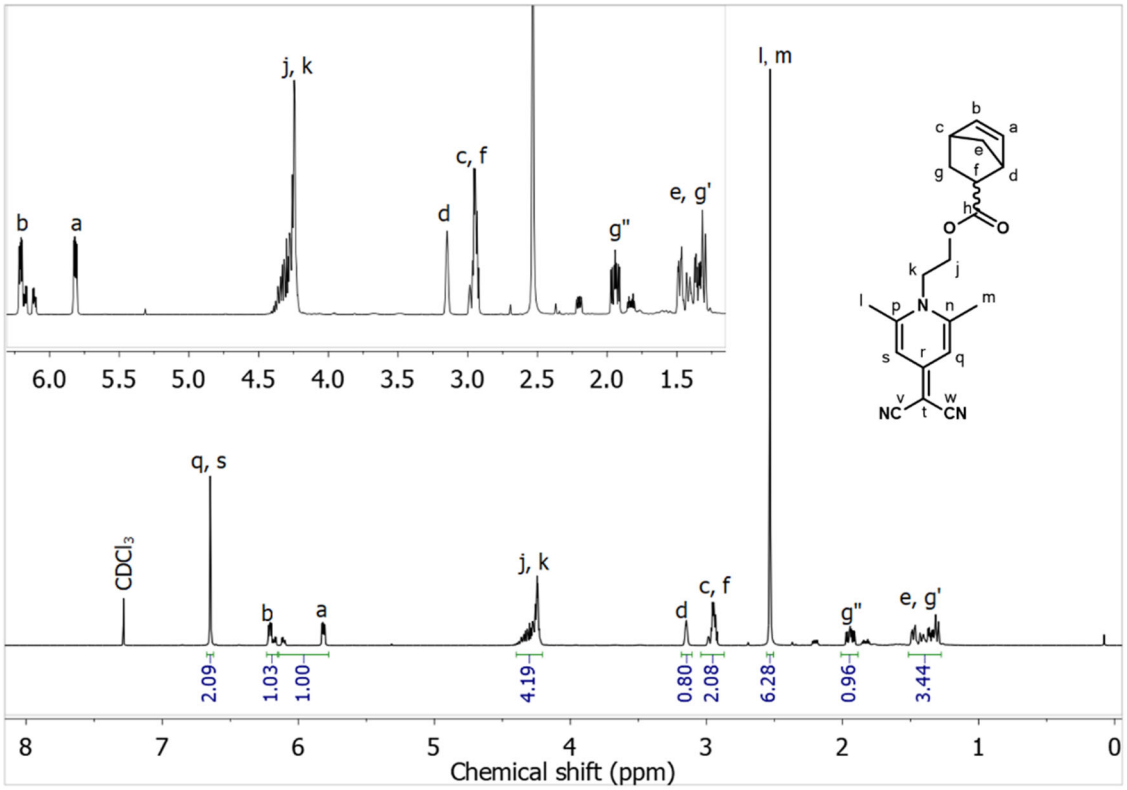


Figure S11 ^{1}H NMR spectrum of **NBE-1**

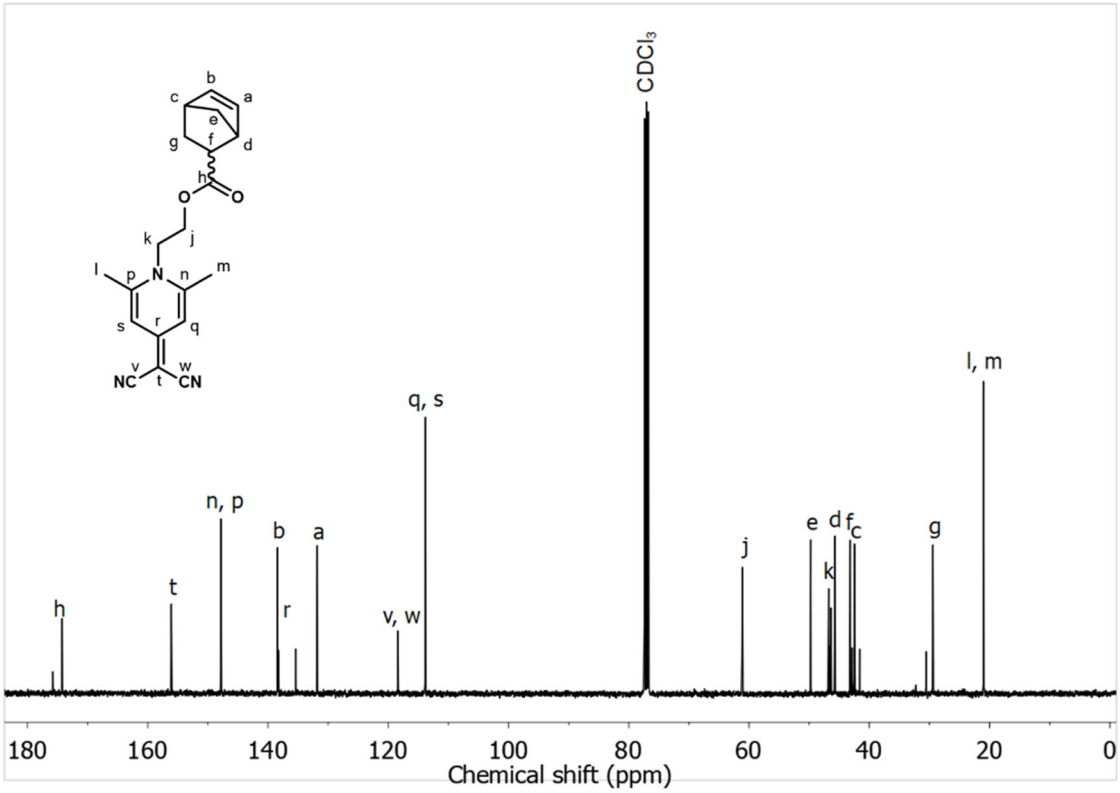


Figure S12 ^{13}C NMR spectrum of **NBE-1**

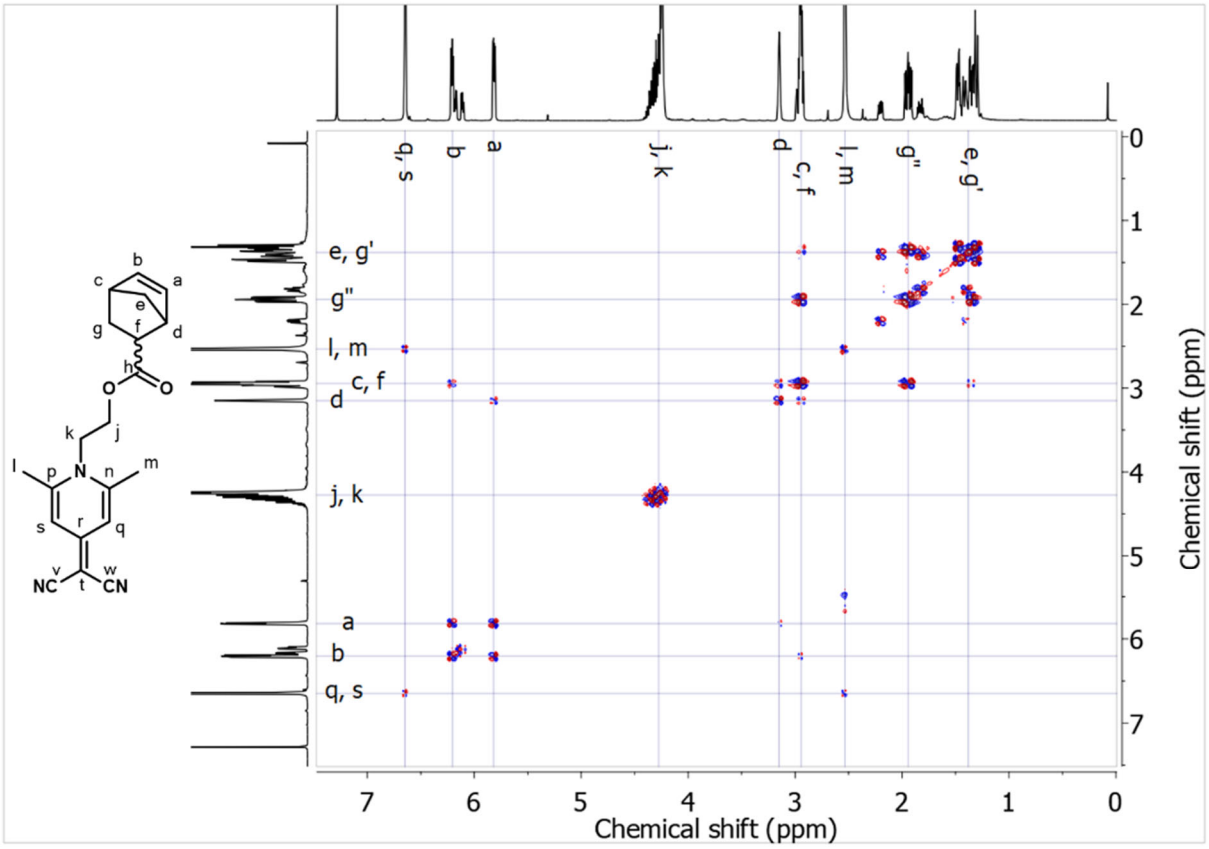


Figure S13 COSY of **NBE-1**

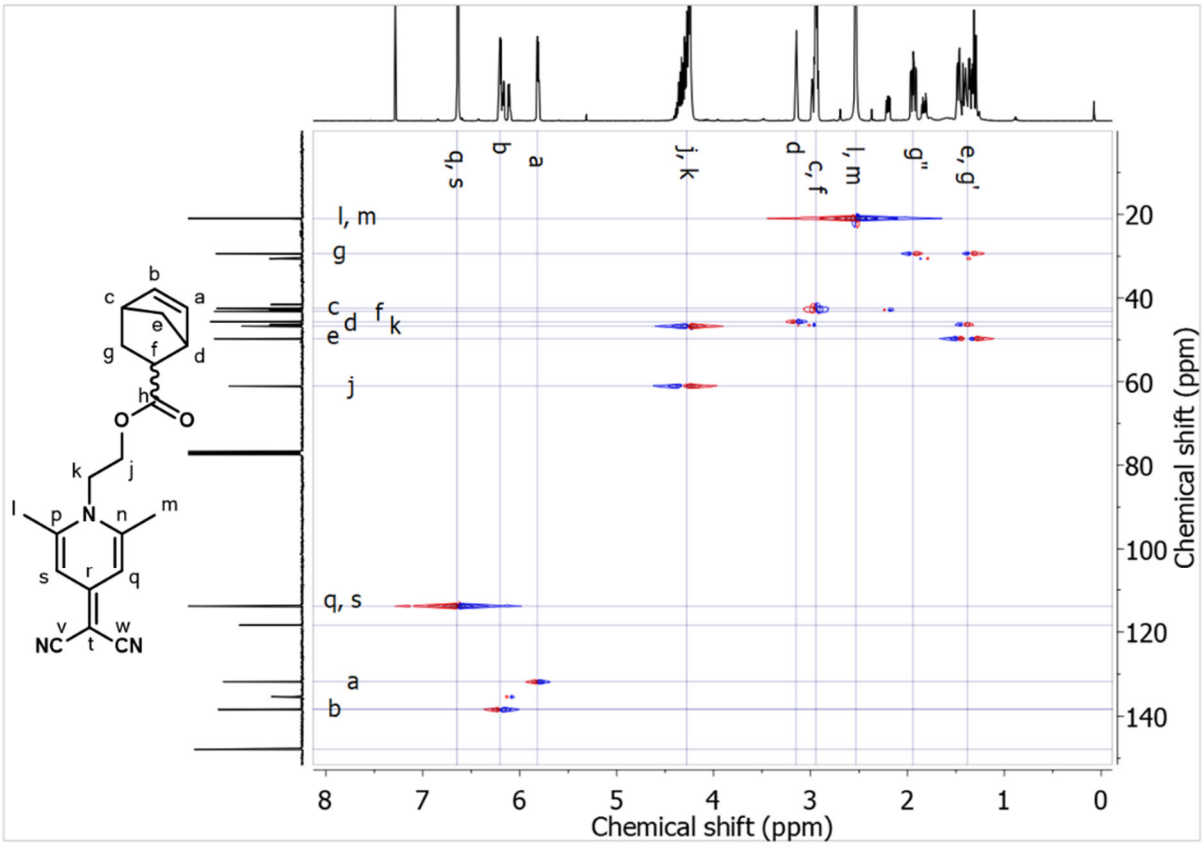


Figure S14 HSQC of **NBE-1**

Eidgenössische Technische Hochschule Zürich

Laboratorium für Organische Chemie

ETH-Hönggerberg - HCI E304 8093 Zürich Tel: 044/633 43 58

Mikroelementaranalyse

Name: Owusu Francis Gruppe: Opris EMPA
Labor: LA182 Tel: 058/765 48 01

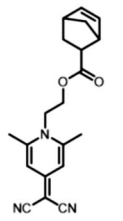
Substanz: NBE-1
Molekularformel: C20 H21 N3 O2 Mr = 335.40g/mol
HV

Schmelzpunkt:
gereinigt: ?????????????????????????? getrocknet:

Bestimmungen: C H N O

Eingang: 19.09.19 Ausgang: 23.09.19

M-166263 Operator: PK



$C_{20}H_{21}N_3O_2$
M = 335.41 g/mol

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

Figure S15 Elemental analysis of **NBE-1**

Acquisition Parameter

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File Name:	D:\Data\bmax0051xx\BMAX005107.d			Operator:	Daniel Wirz
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

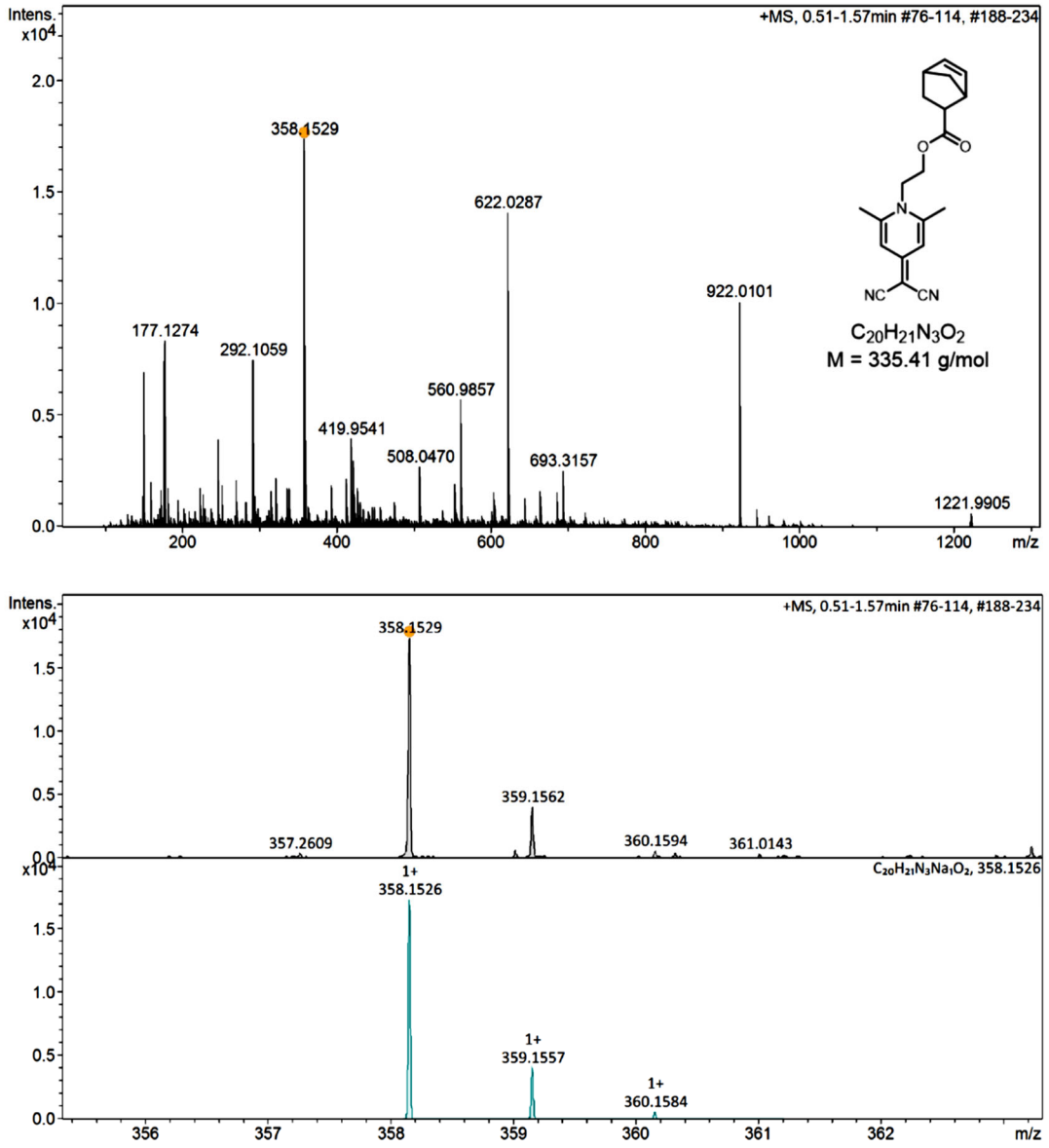

Figure S16 Mass spectra of **NBE-1**

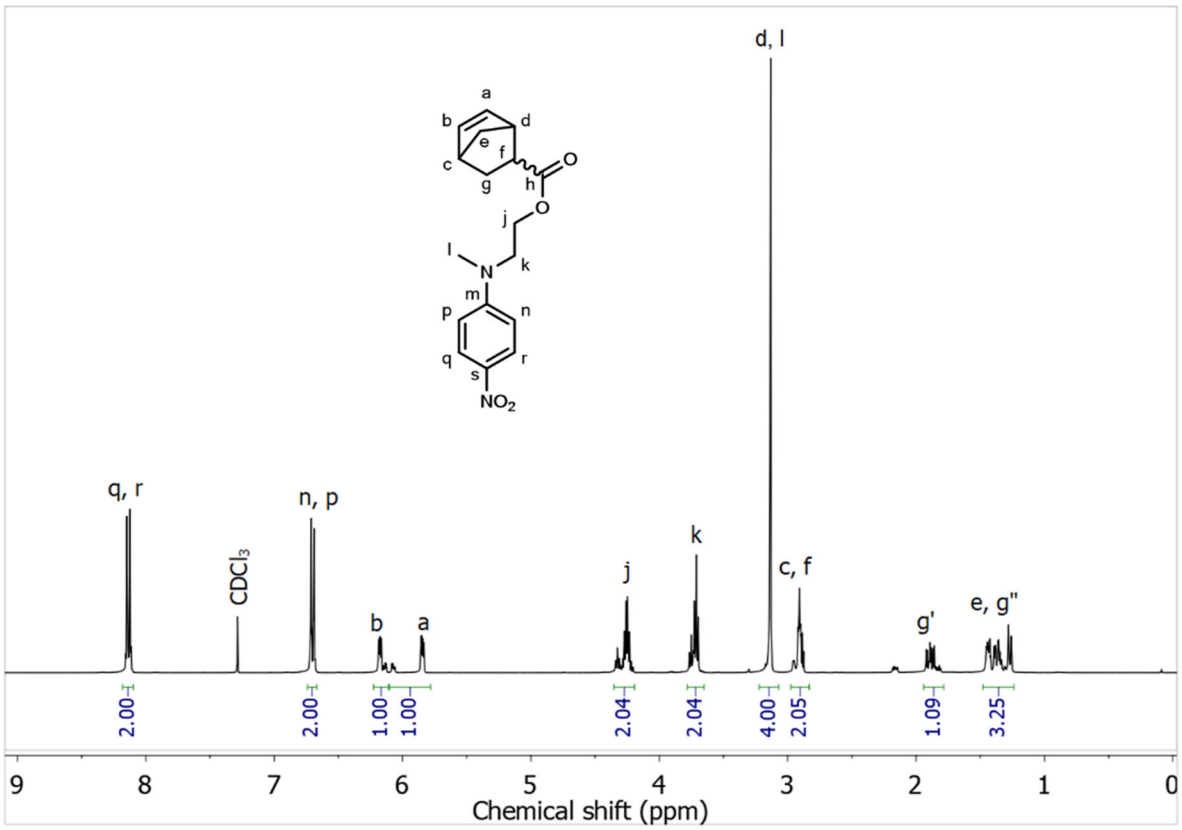

Figure S17 ^{1}H NMR spectrum of **NBE-2**

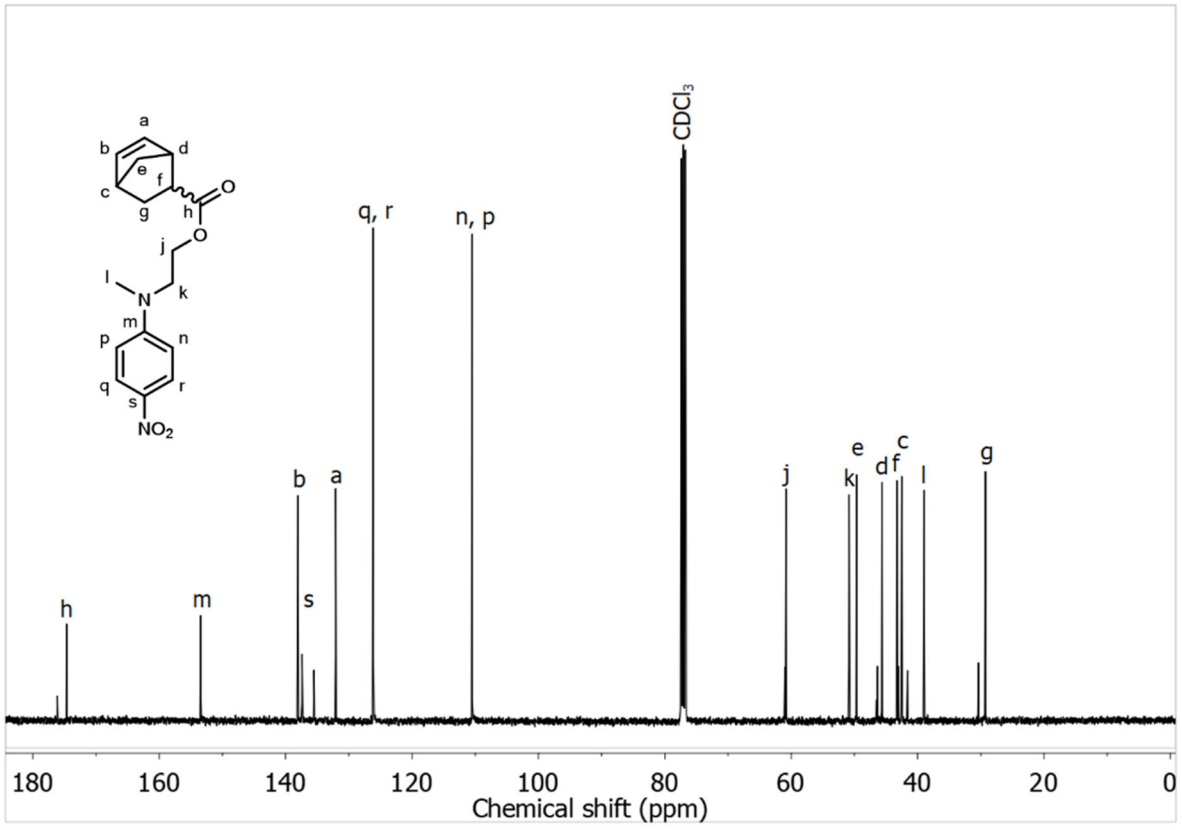

Figure S18 ^{13}C NMR spectrum of **NBE-2**

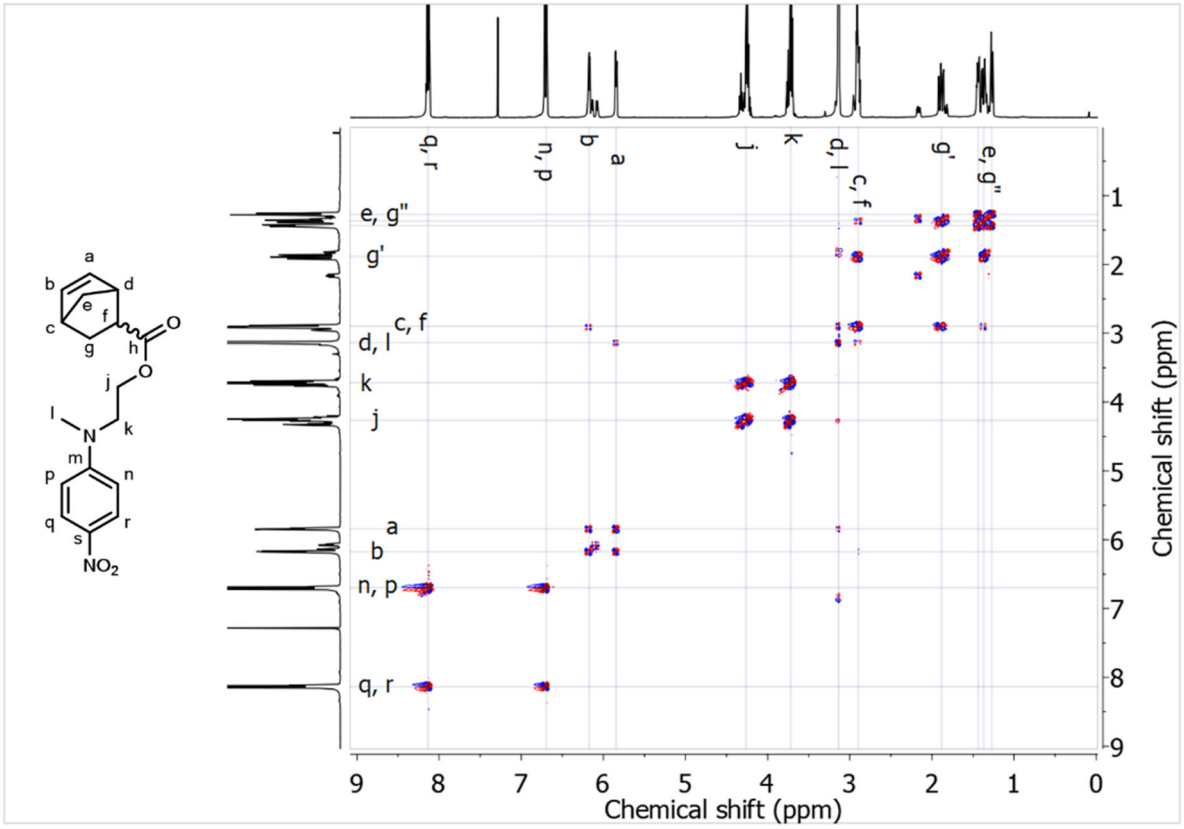

Figure S19 COSY of **NBE-2**

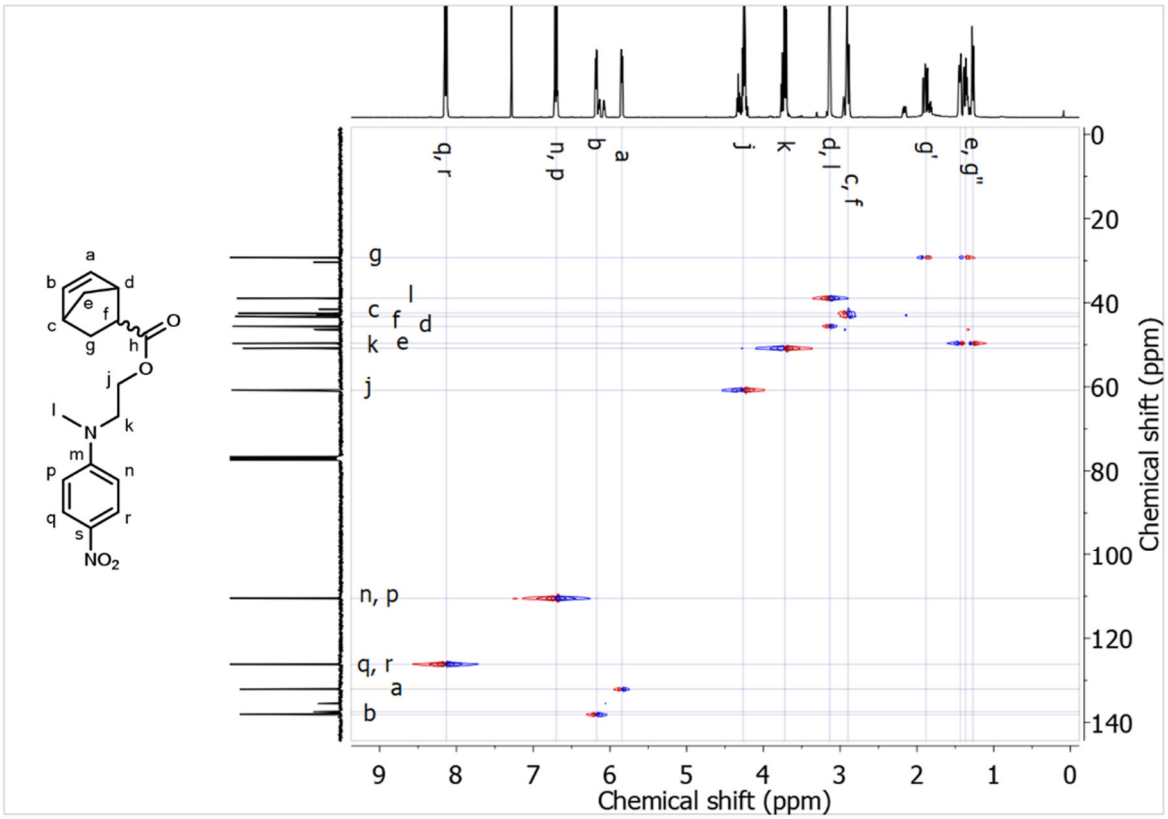

Figure S20 HSQC of **NBE-2**

Eidgenössische Technische Hochschule Zürich

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ETH-Hönggerberg - HCI E304 8093 Zürich Tel: 044/633 43 58

Mikroelementaranalyse

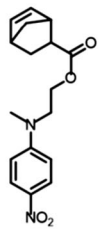
Name: Owusu Francis Gruppe: Opris EMPA
Labor: LA182 Tel: 058/765 48 01

Substanz: NBE-2
Molekularformel: C17 H20 N2 O4 Mr = 316.36g/mol

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

Bestimmungen: C H N

Eingang: 19.09.19 Ausgang: 19.09.19



$C_{17}H_{20}N_2O_4$
M = 316.36 g/mol

M-166262 Operator: PK

Berechnete Gewichtsanteile:

[C] 64.54% [H] 6.37% [N] 8.86% [O] 20.23%

Gefundene Gewichtsanteile:

Einwaage: 0.959mg LECO TruSpec Micro
[C] 64.68% [H] 6.54% [N] 8.92% 19.09.19

Von flüssigen Proben können nur CHN bestimmt werden.

Figure S21 Elemental analysis of **NBE-2**

Acquisition Parameter

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File Name:	D:\Data\bmax0051xx\BMAX005106.d			Operator:	Daniel Wirz
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

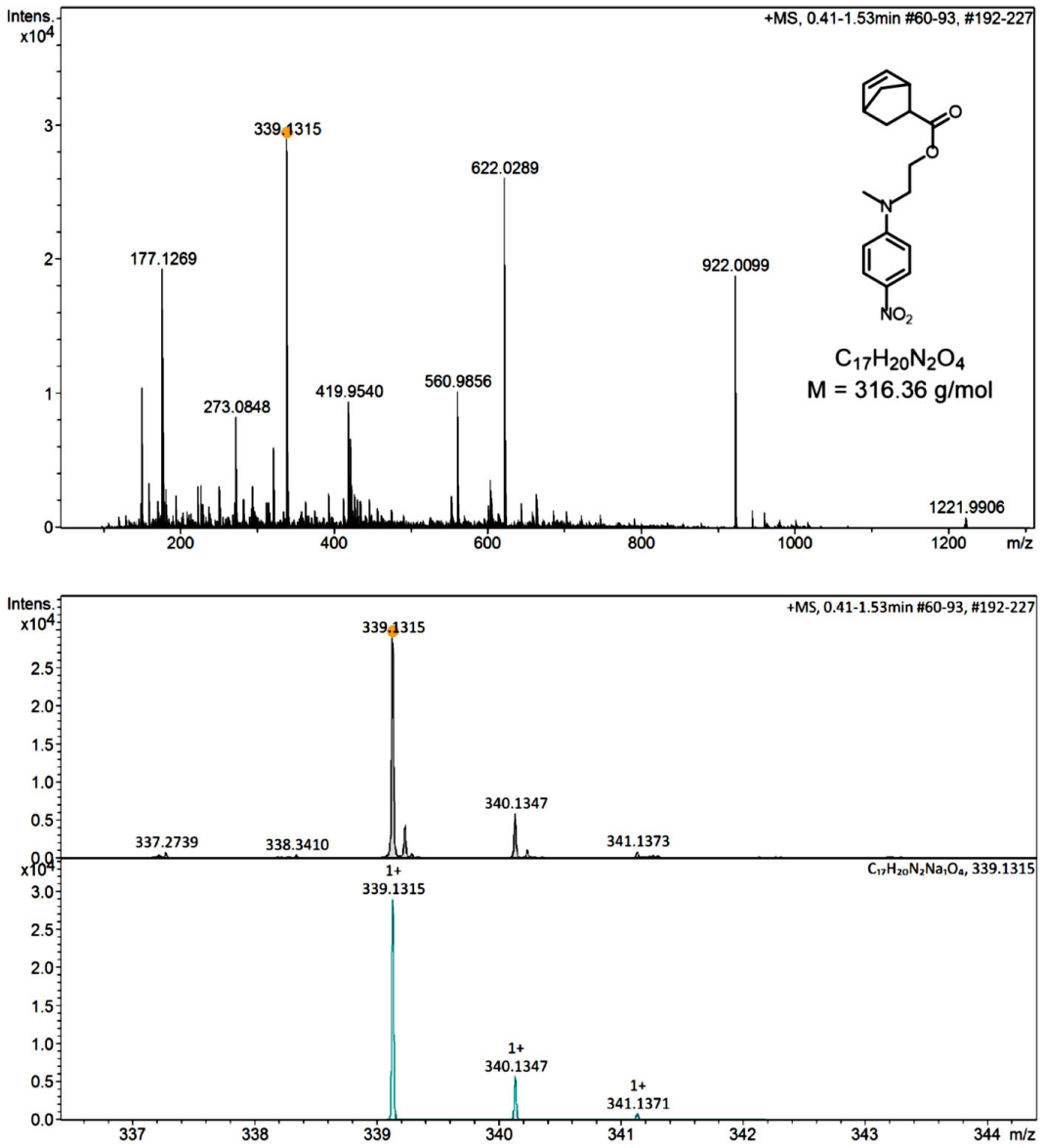


Figure S22 Mass spectra of **NBE-2**

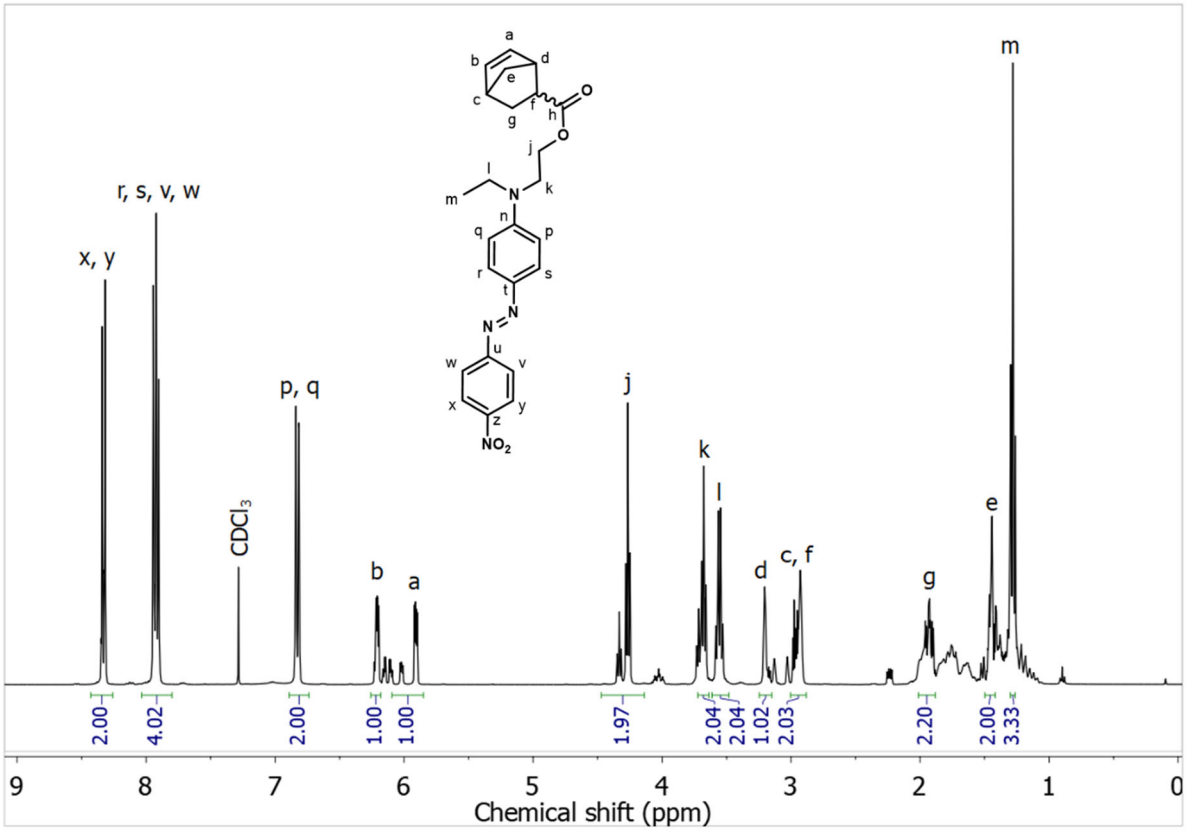


Figure S23 ^{1}H NMR spectrum of **NBE-3**

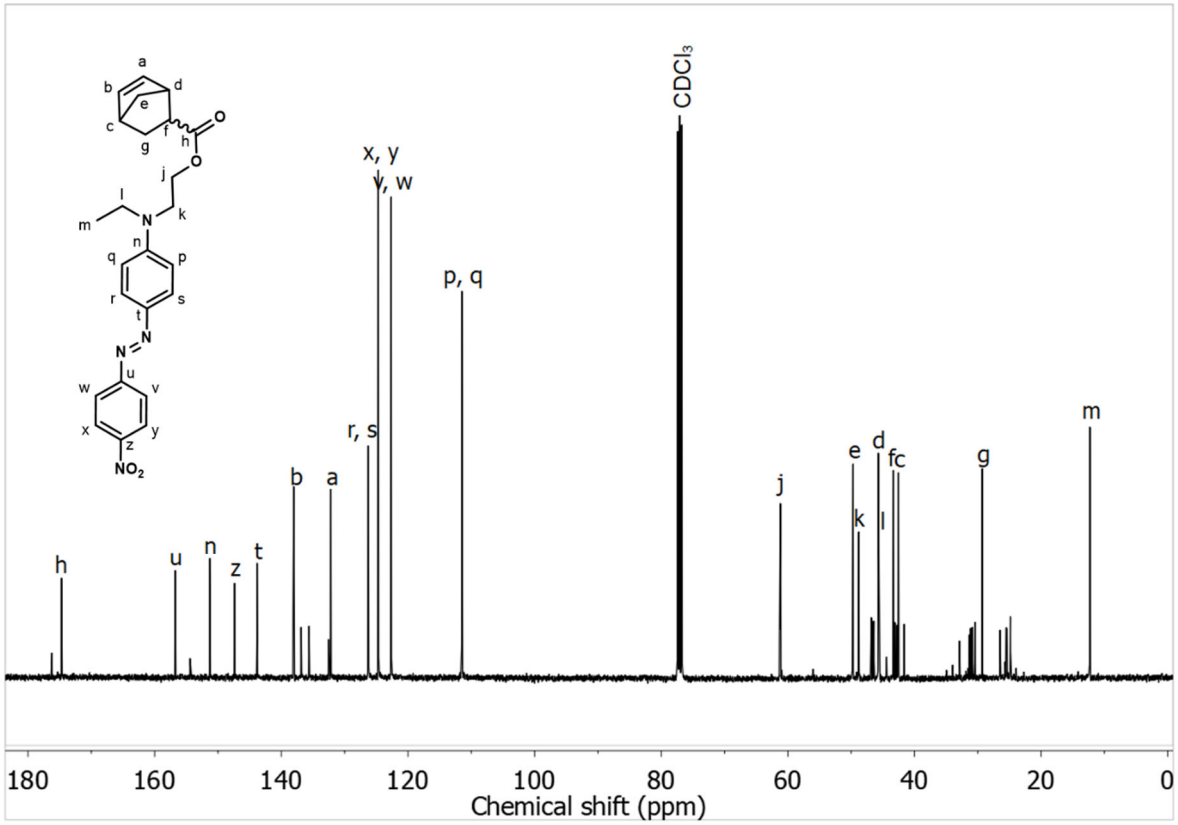


Figure S24 ^{13}C NMR spectrum of **NBE-3**

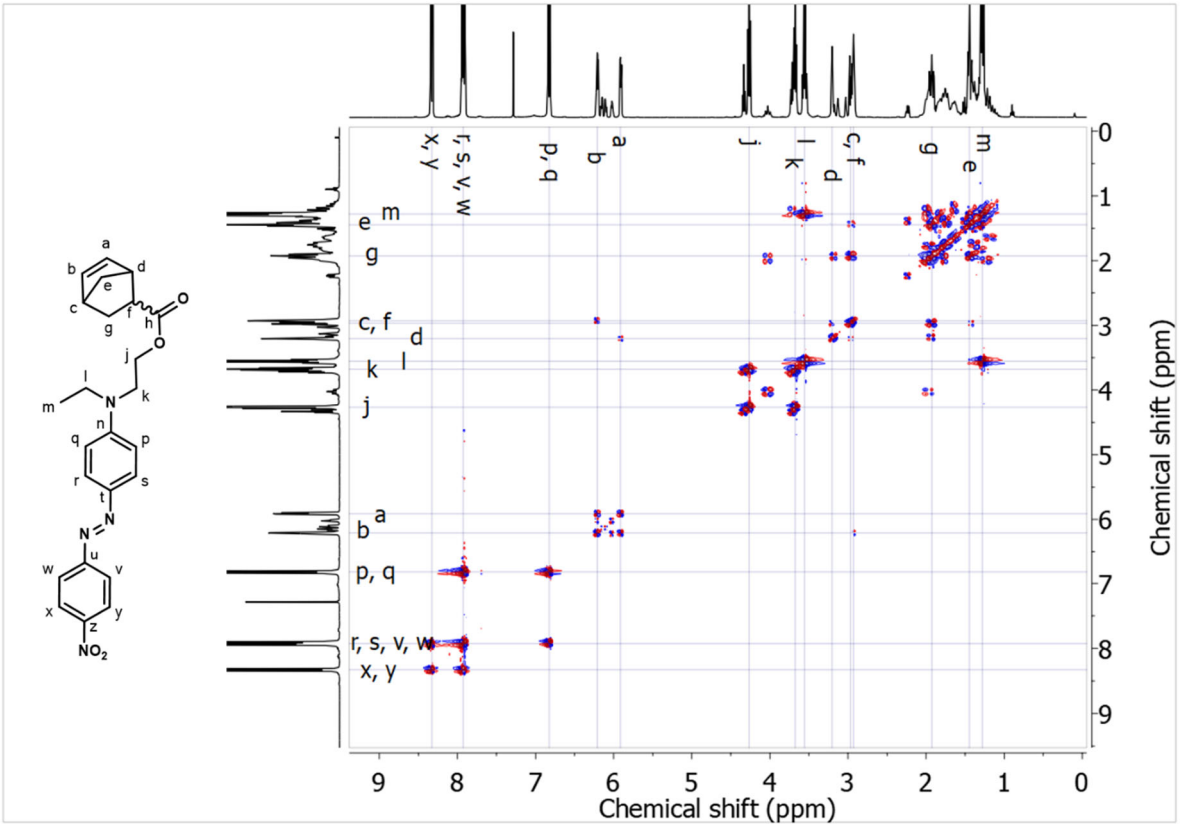


Figure S25 COSY of **NBE-3**

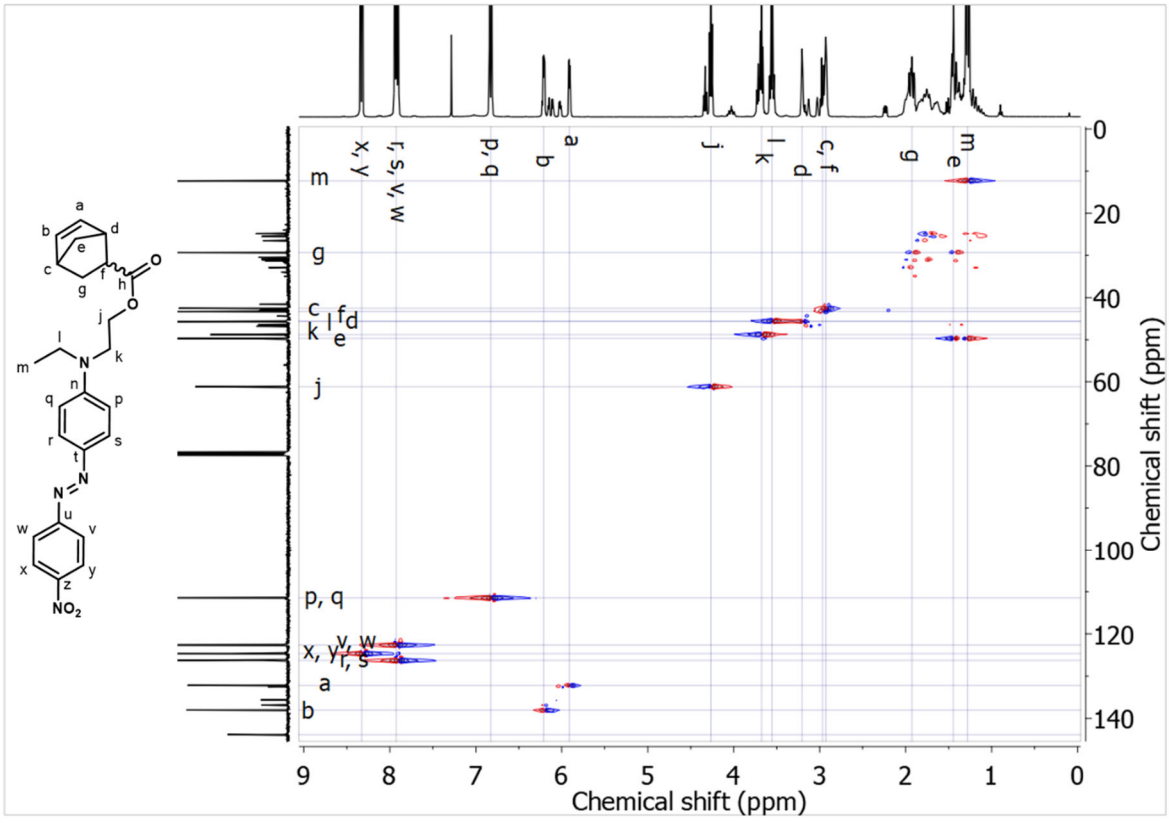


Figure S26 HSQC of **NBE-3**

Eidgenössische Technische Hochschule Zürich

Laboratorium für Organische Chemie

ETH-Hönggerberg - HCI E304 8093 Zürich Tel: 044/633 43 58

Mikroelementaranalyse

Name: Owusu Francis Gruppe: Opris EMPA
Labor: LA182 Tel: 058/765 48 01

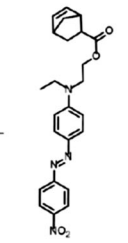
Substanz: NBE-3
Molekularformel: C24 H26 N4 O4 Mr = 434.49g/mol

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

Bestimmungen: C H N

Eingang: 19.09.19 Ausgang: 19.09.19

M-166264 Operator: PK



$C_{24}H_{26}N_4O_4$
M = 434.50 g/mol

Berechnete Gewichtsanteile:

[C] 66.34% [H] 6.03% [N] 12.89% [O] 14.73%

Gefundene Gewichtsanteile:

Einwaage: 0.919mg LECO TruSpec Micro
[C] 68.16% [H] 6.89% [N] 12.13% 19.09.19

Einwaage: 0.910mg LECO TruSpec Micro
[C] 67.97% [H] 6.94% [N] 12.13% 19.09.19

wegen zu grosser Abweichung werden keine weiteren Bestimmungen durchgeführt

Figure S27 Elemental analysis of **NBE-3**

Acquisition Parameter

Method:	ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m			Acquisition Date:	10.10.2019 16:06:14
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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

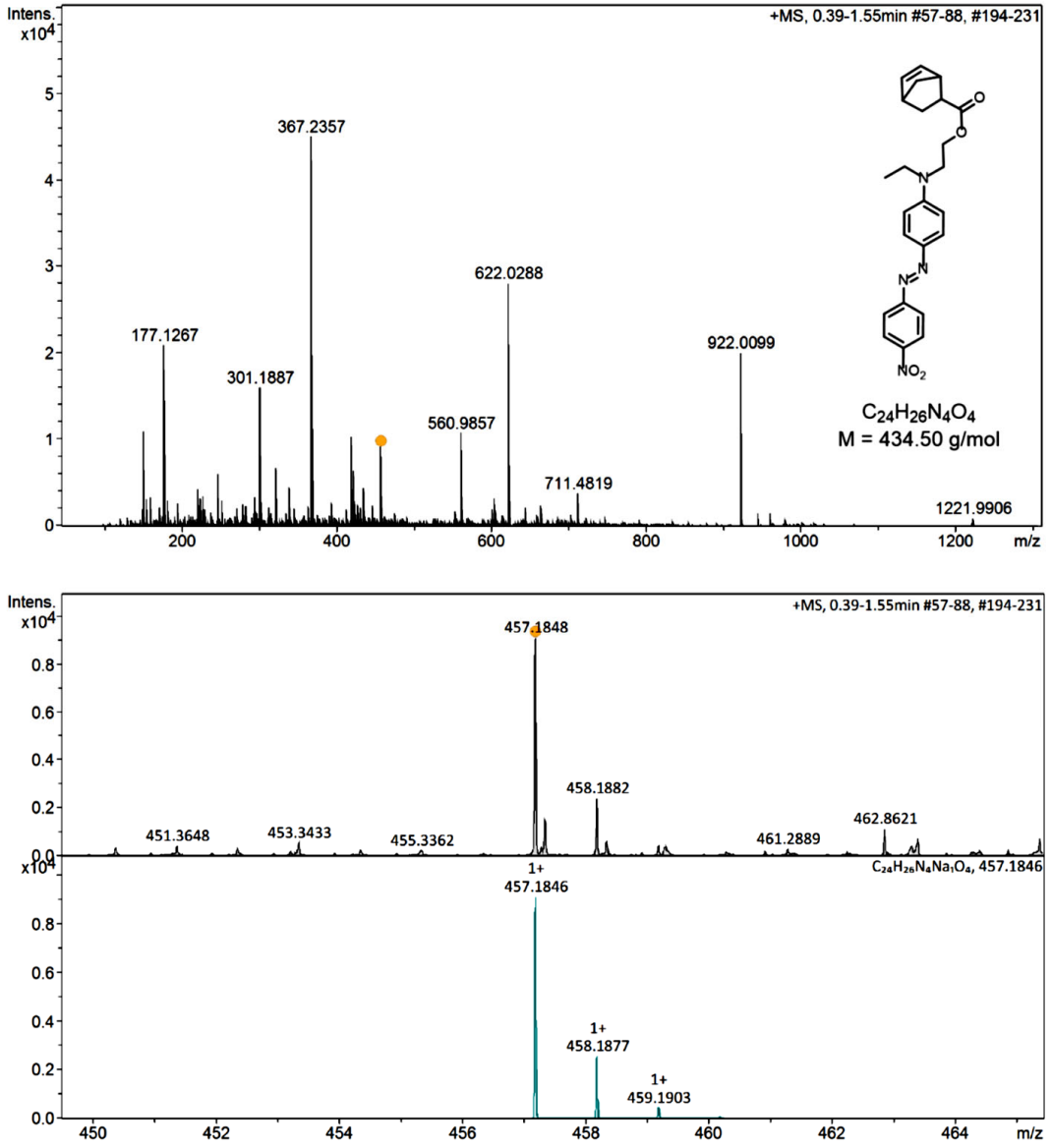


Figure S28 Mass spectra of **NBE-3**

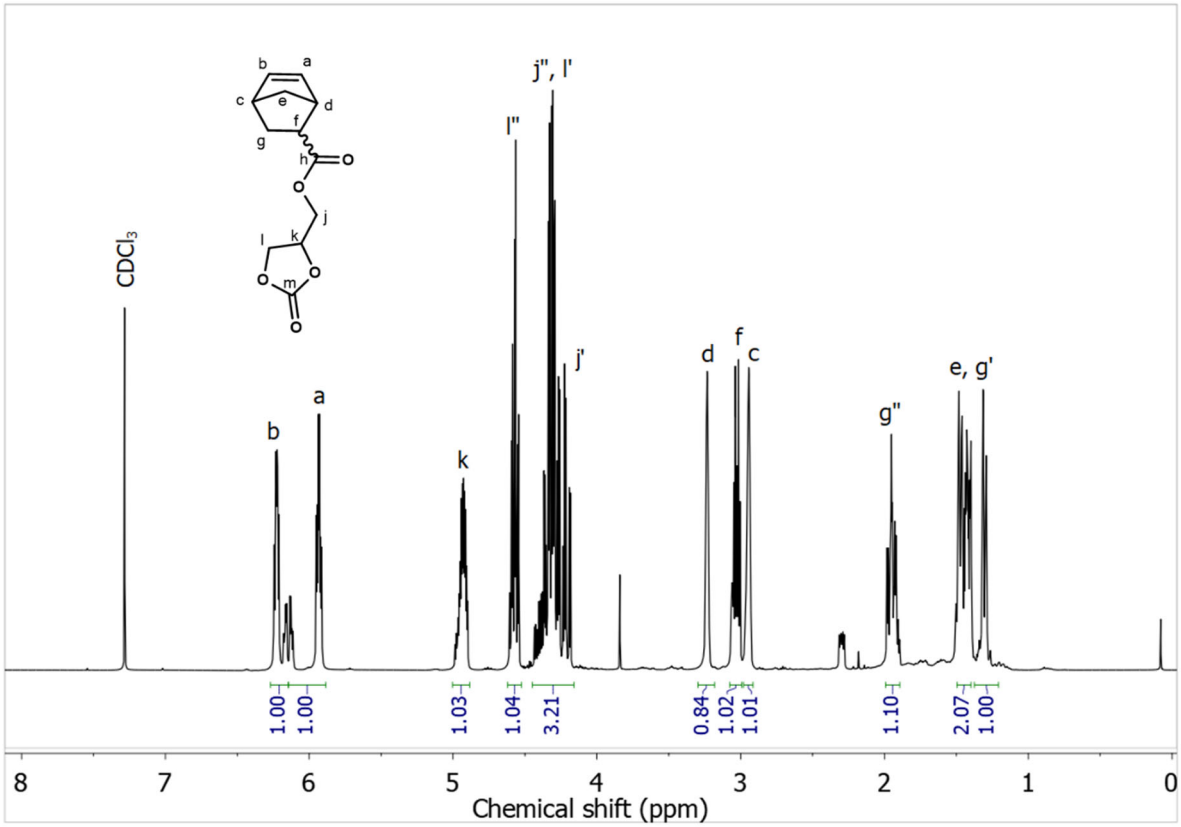


Figure S29 ^{1}H NMR spectrum of **NBE-4**

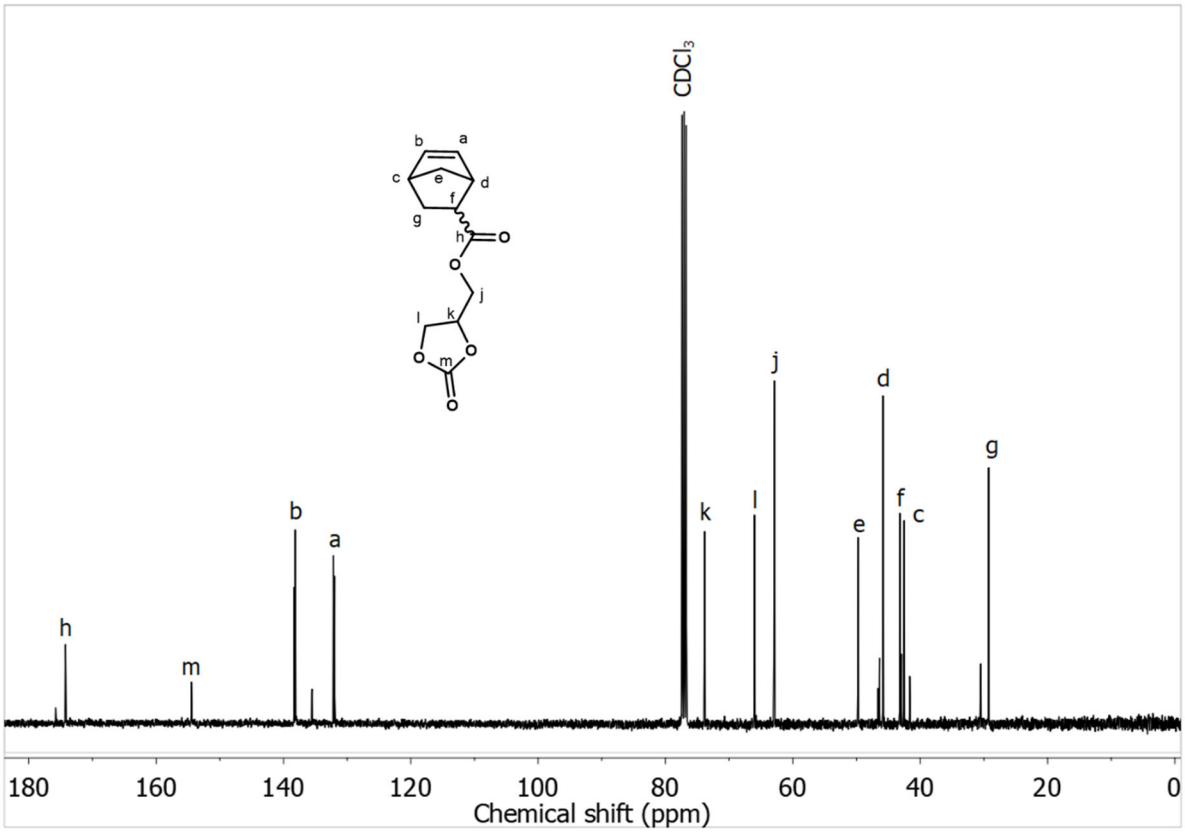


Figure S30 ^{13}C NMR spectrum of **NBE-4**

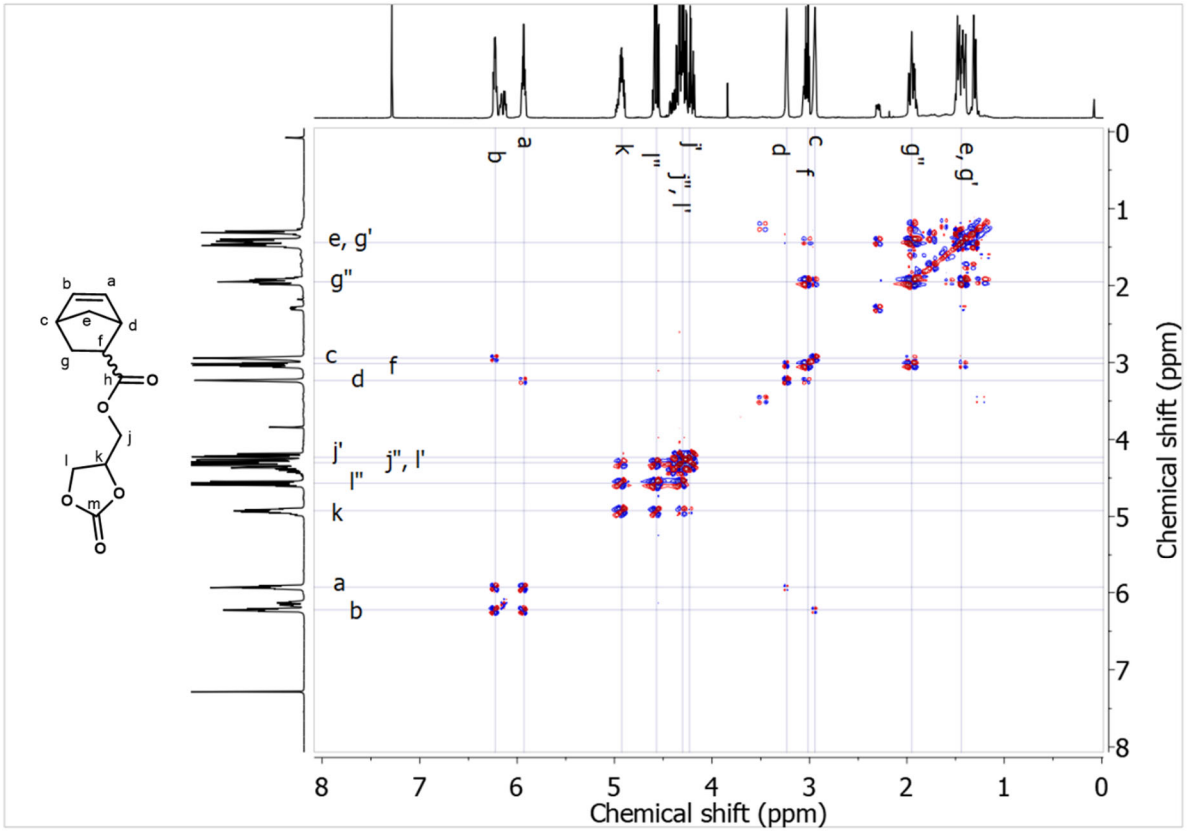


Figure S31 COSY of **NBE-4**

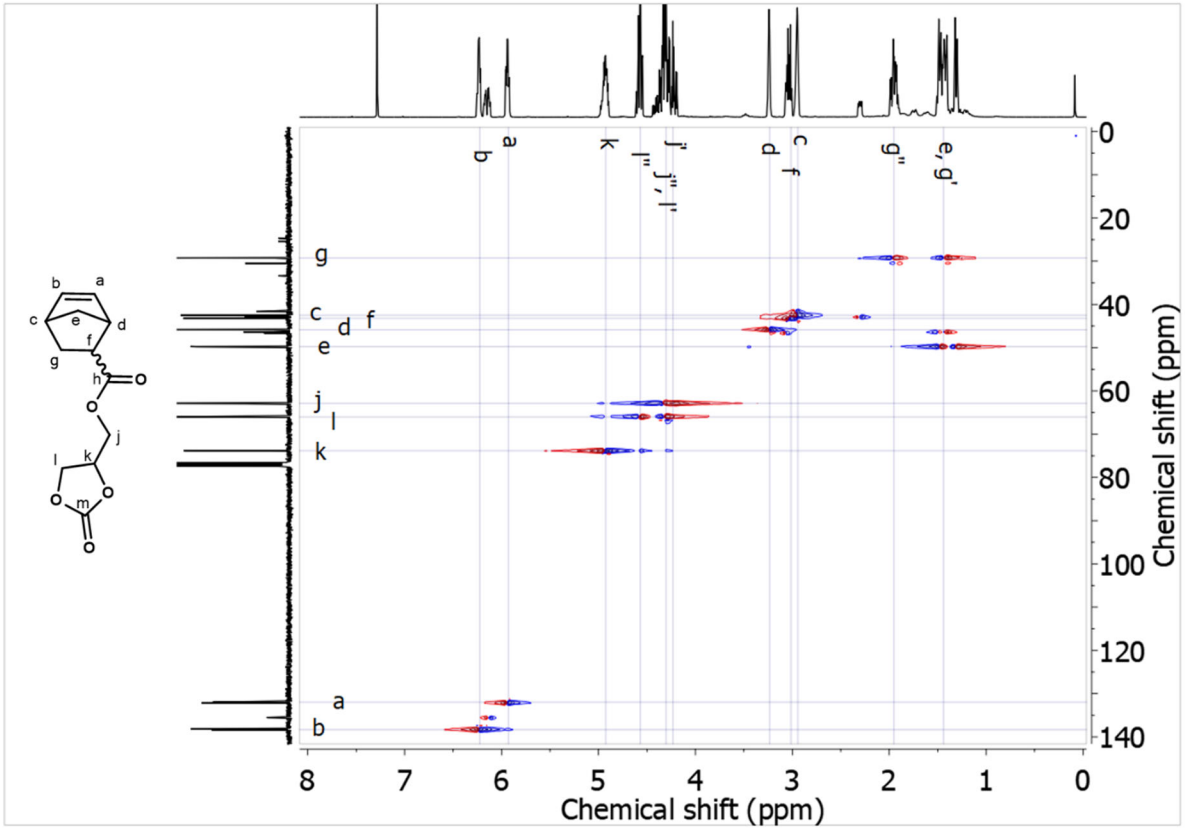


Figure S32 HSQC of **NBE-4**

Eidgenössische Technische Hochschule Zürich

Laboratorium für Organische Chemie

ETH-Hönggerberg - HCI E304 8093 Zürich Tel: 044/633 43 58

Mikroelementaranalyse

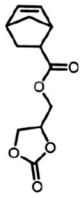
Name: Owusu Francis Gruppe: Opris EMPA
Labor: LA182 Tel: 058/765 48 01

Substanz: NBE-4
Molekularformel: C12 H14 O5 Mr = 238.24g/mol

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

Bestimmungen: C H N

Eingang: 19.09.19 Ausgang: 20.09.19



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

M-166265 Operator: PK

Berechnete Gewichtsanteile:

[C] 60.50% [H] 5.92% [O] 33.58%

Gefundene Gewichtsanteile:

Einwaage: 0.982mg LECO TruSpec Micro
[C] 60.78% [H] 6.44% 20.09.19

Einwaage: 0.971mg LECO TruSpec Micro
[C] 60.83% [H] 6.22% 20.09.19

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

Figure S33 Elemental analysis of **NBE-4**

Acquisition Parameter

Method:	ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m			Acquisition Date:	10.10.2019 16:09:13
File Name:	D:\Data\bmax0051xx\BMAX005109.d			Operator:	Daniel Wirz
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

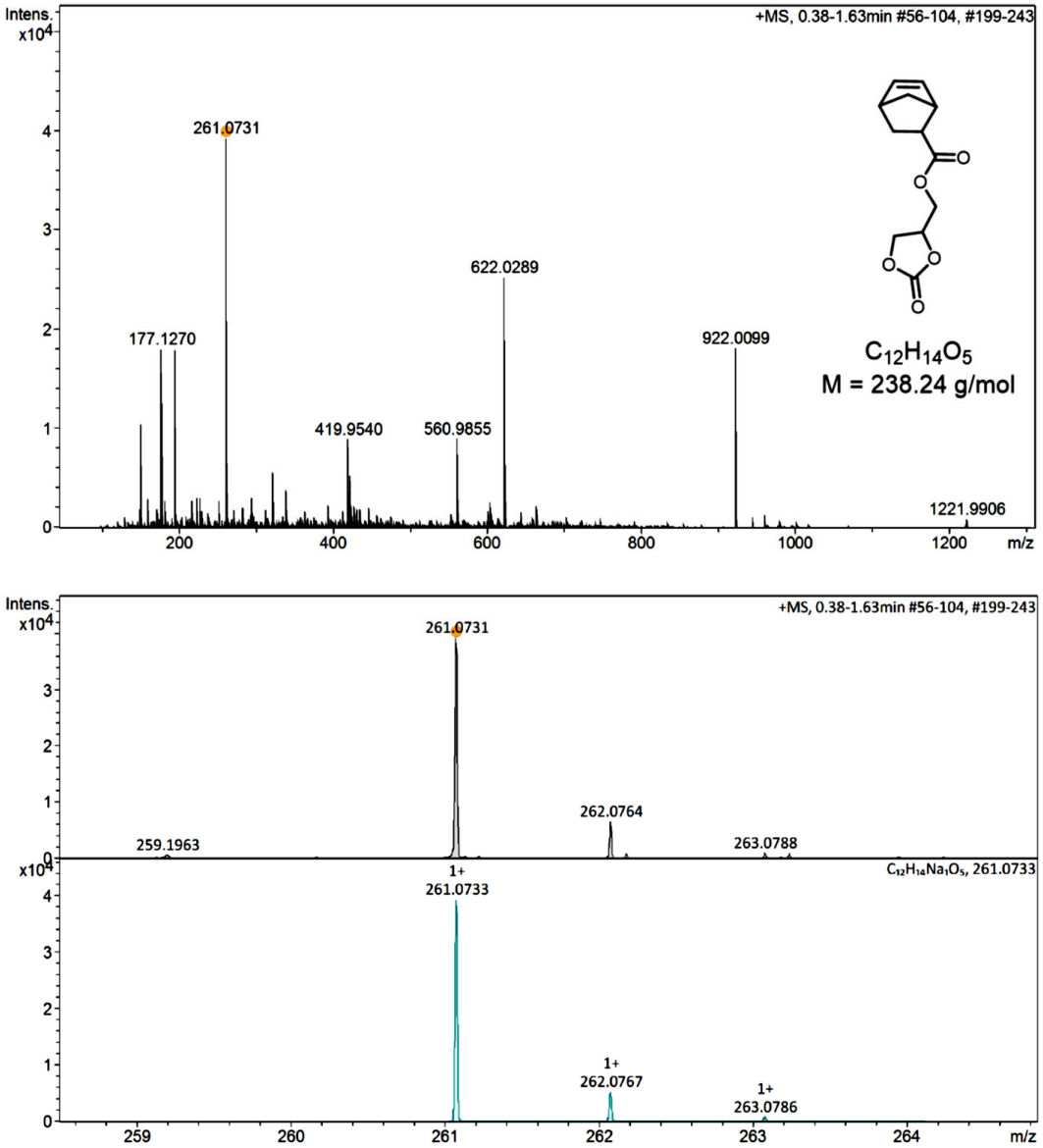


Figure S34 Mass spectra of **NBE-4**

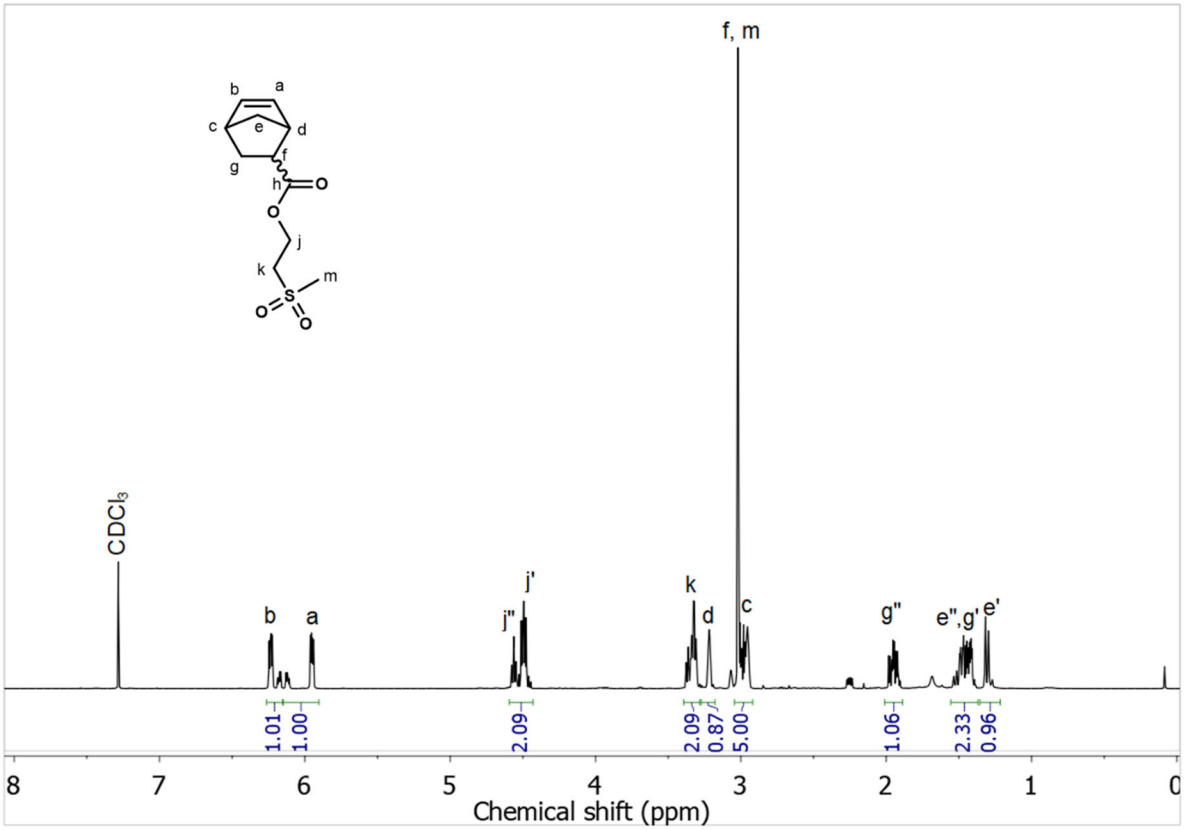


Figure S35 ^{1}H NMR spectrum of **NBE-5**

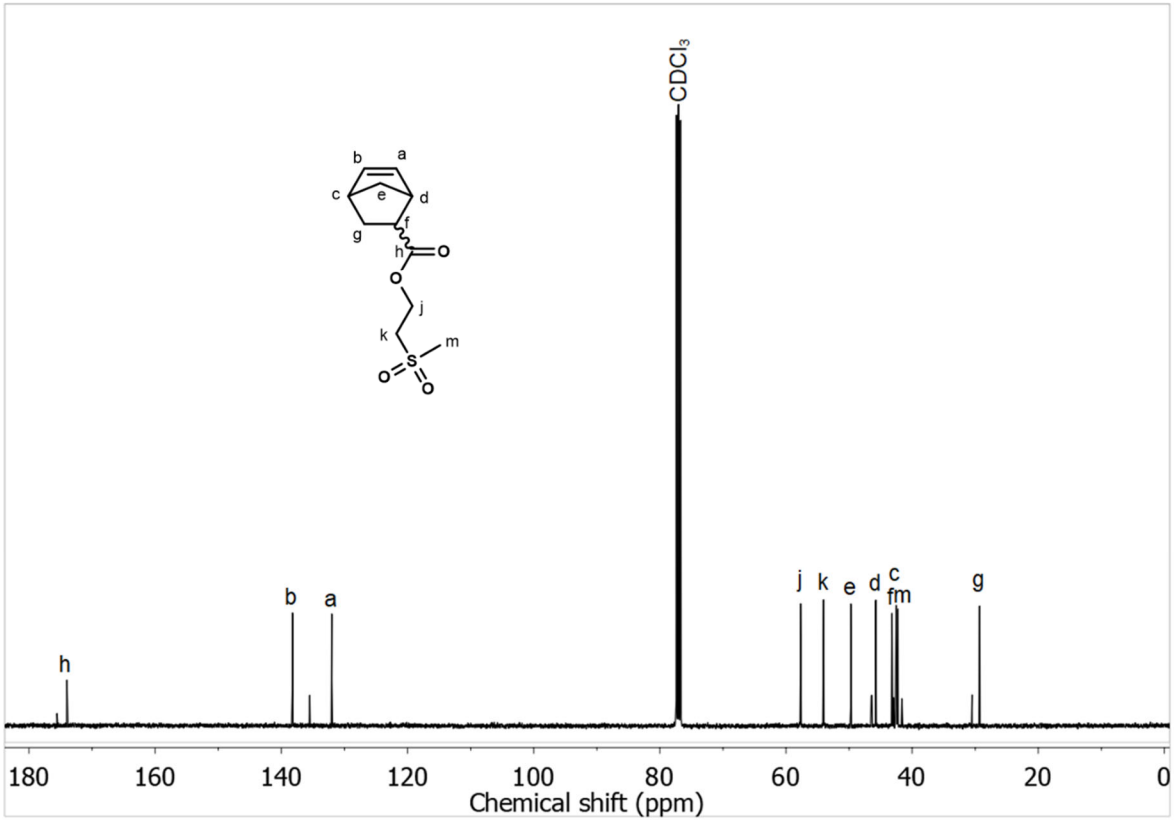


Figure S36 ^{13}C NMR spectrum of **NBE-5**

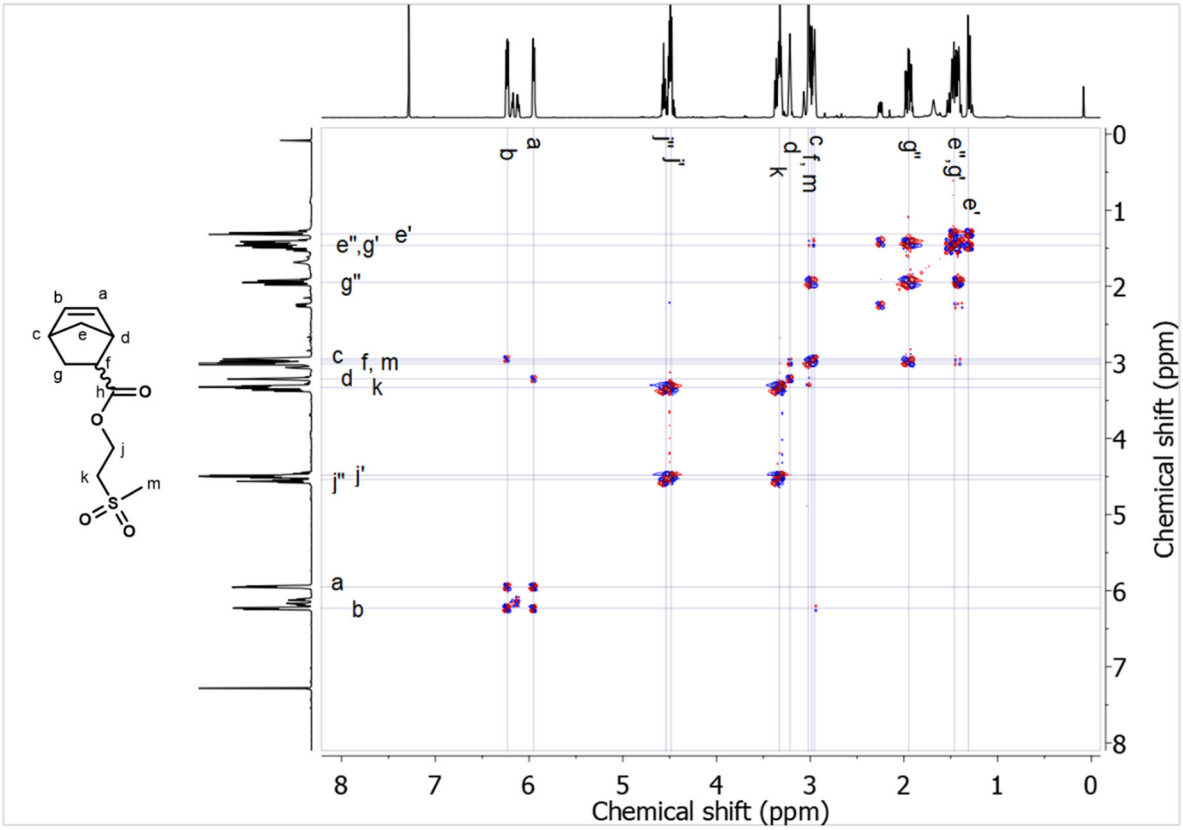


Figure S37 COSY of **NBE-5**

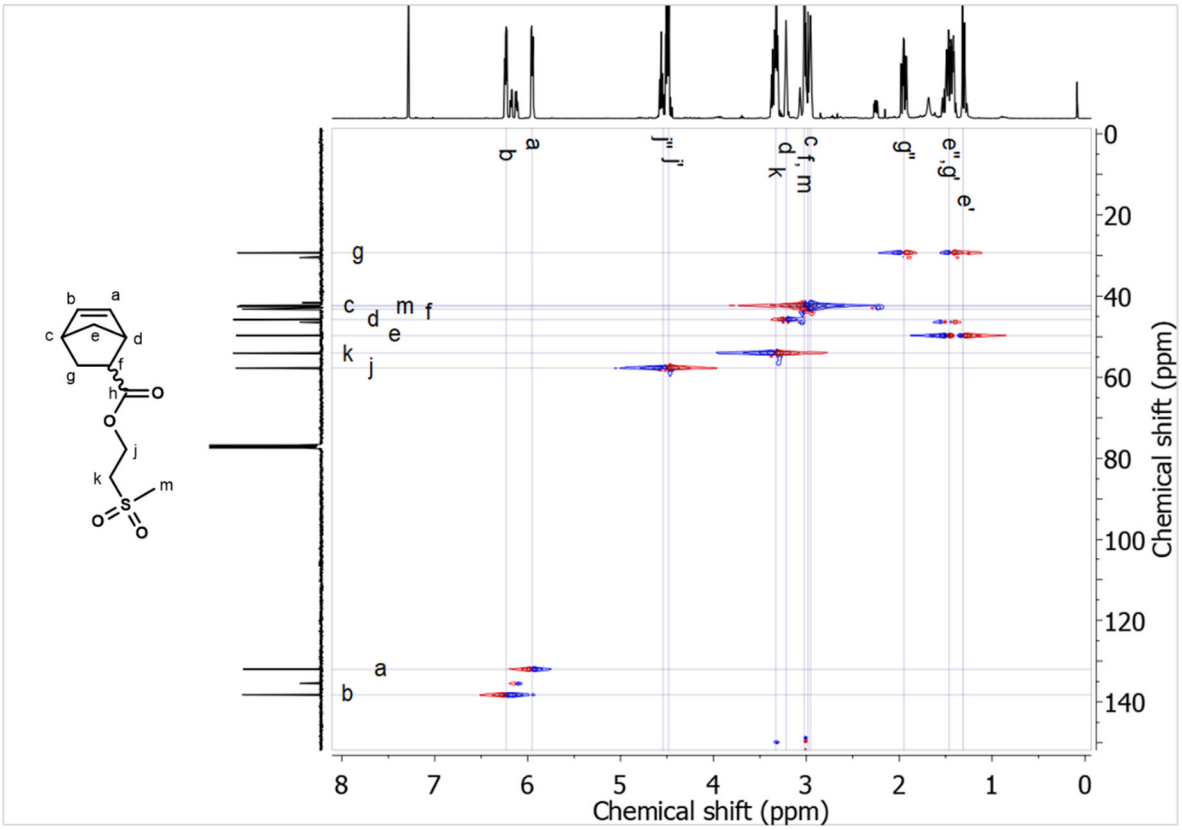


Figure S38 HQSC of **NBE-5**

Acquisition Parameter

Method:	ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m			Acquisition Date:	26.08.2020 13:39:31
File Name:	D:\Data\bmax0096xx\BMAX009630.d			Operator:	Michael Meier
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

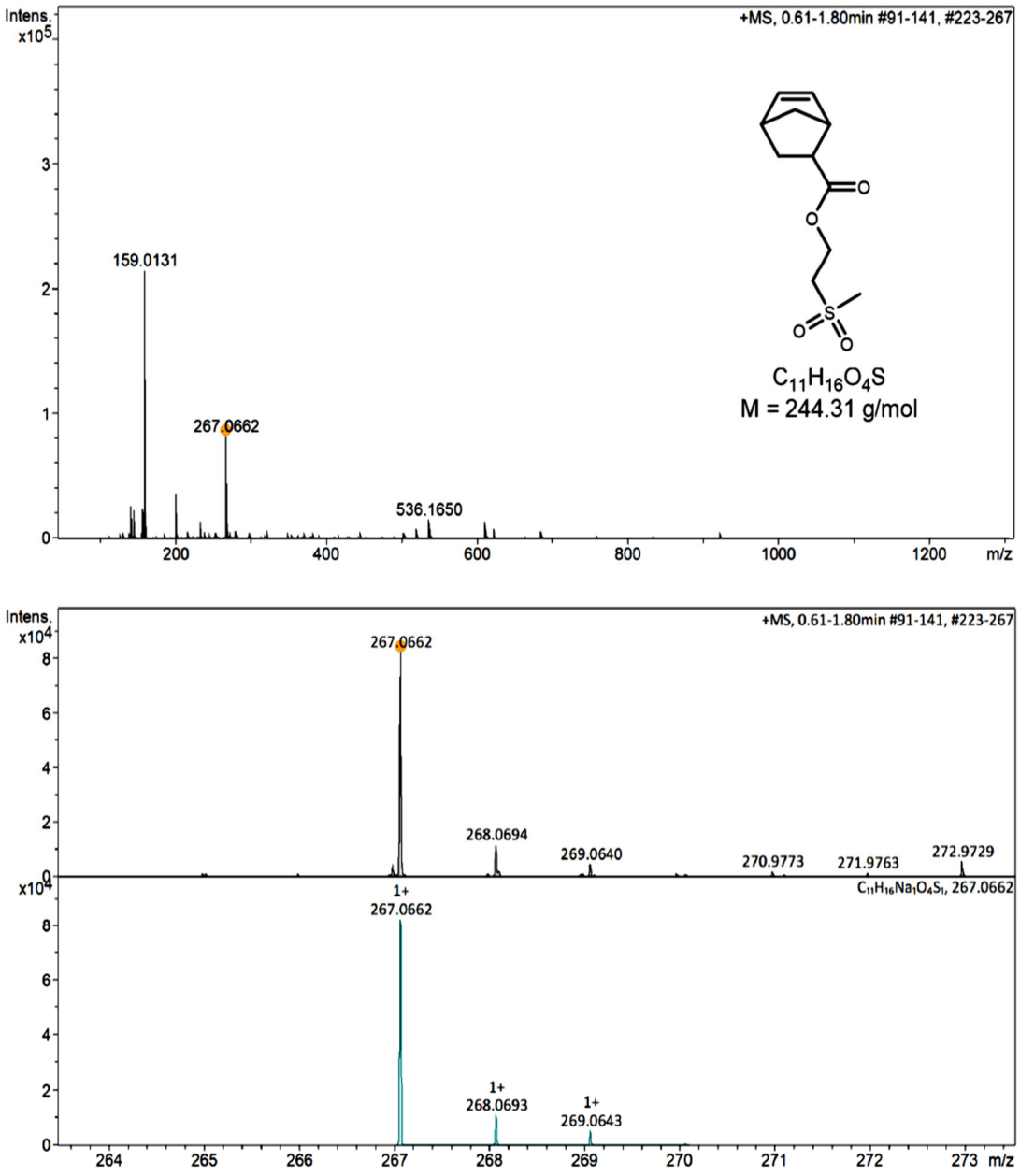


Figure S39 Mass spectra of **NBE-5**

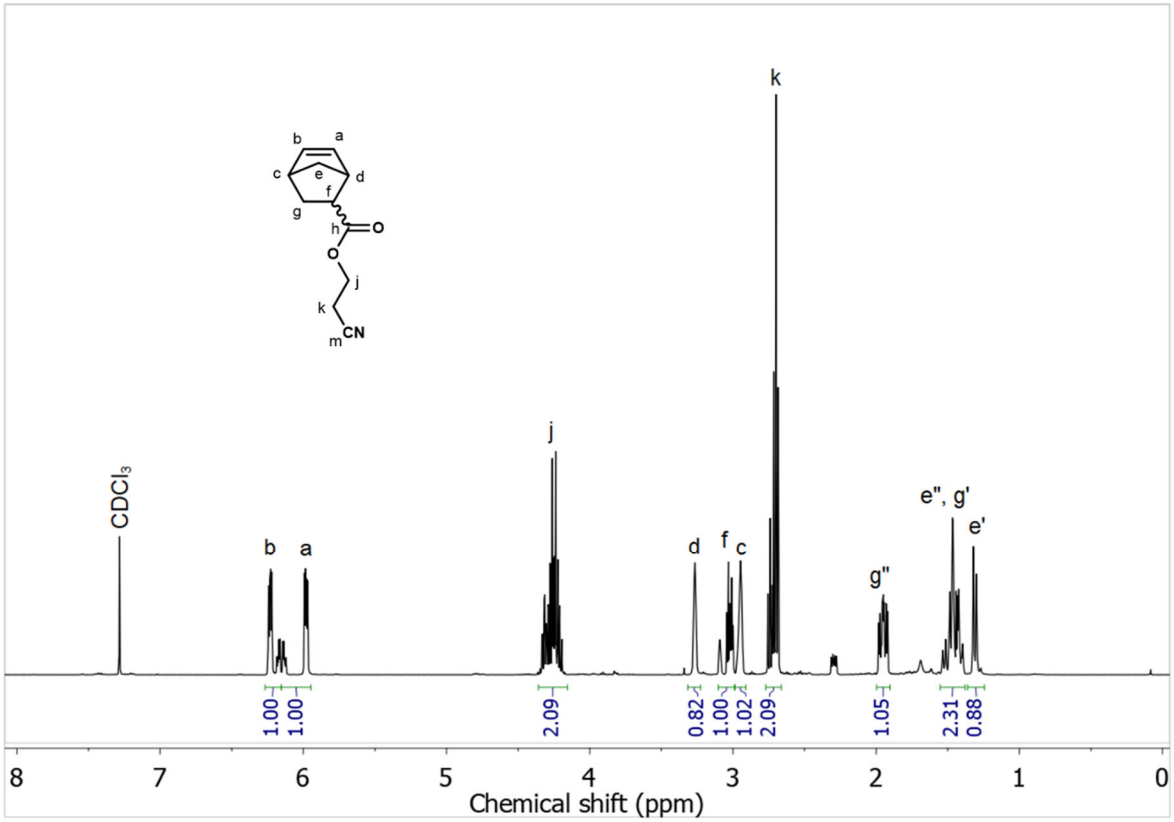


Figure S40 ^{1}H NMR spectrum of **NBE-6**

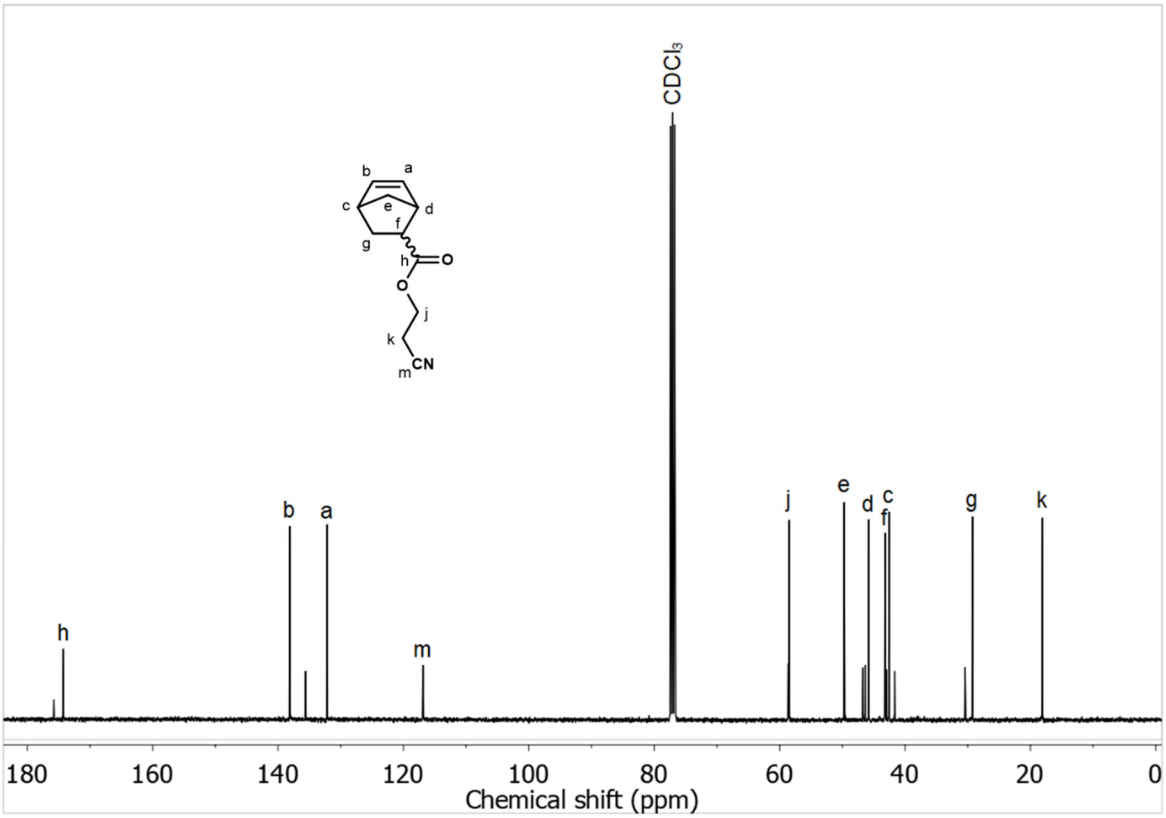


Figure S41 ^{13}C NMR spectrum of **NBE-6**

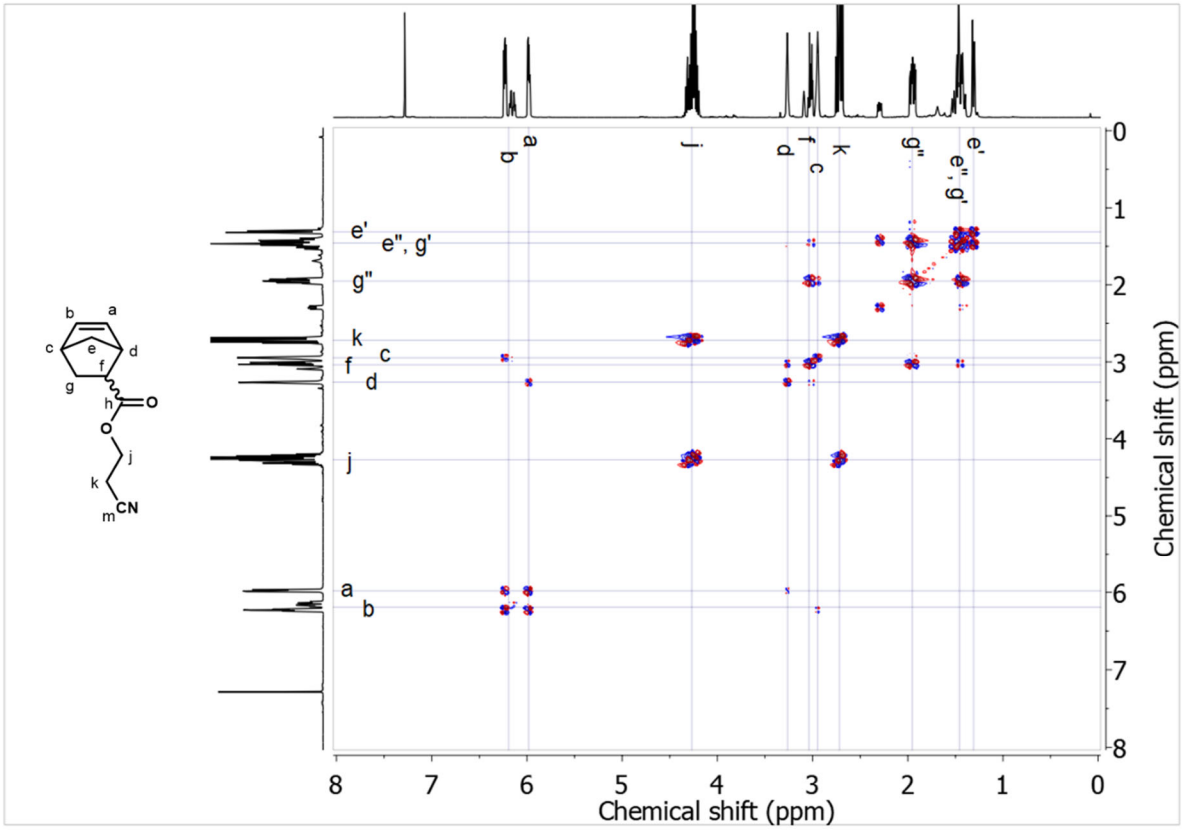


Figure S42 COSY of **NBE-6**

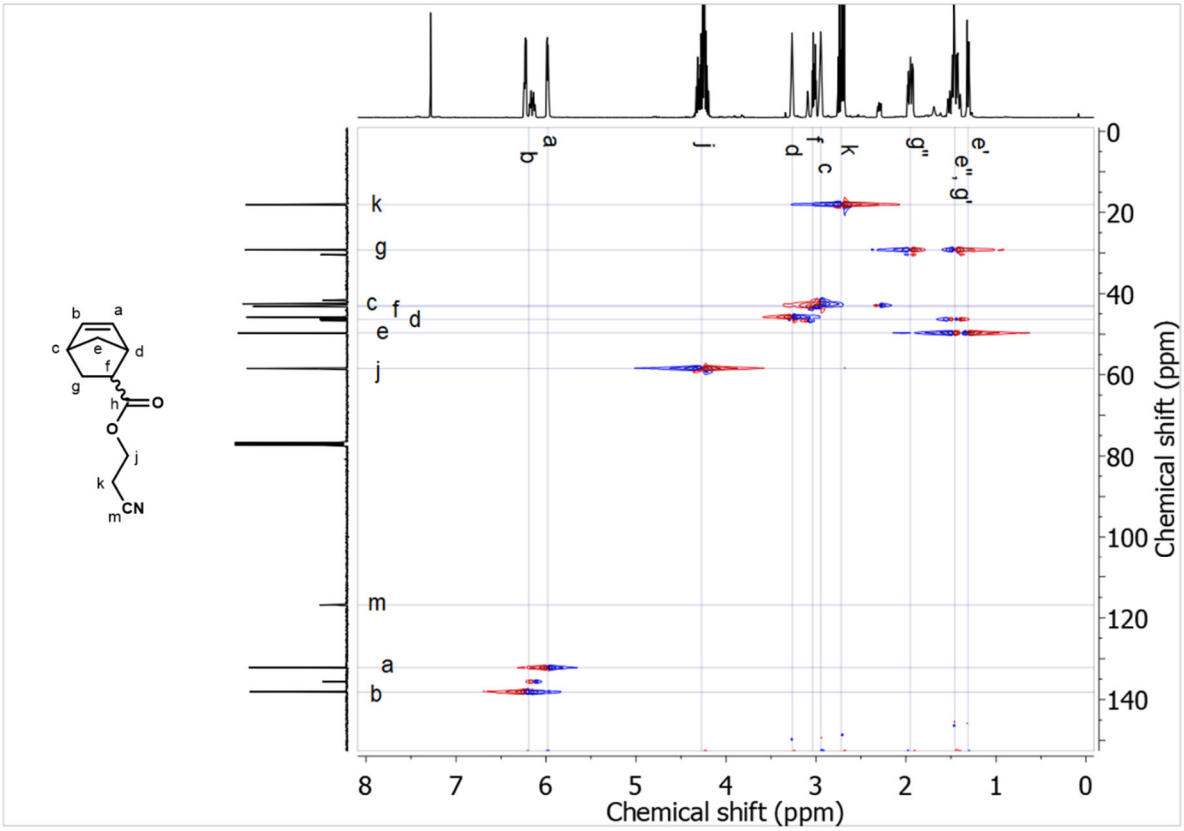


Figure S43 HSQC of **NBE-6**

Acquisition Parameter

Method:	ETH_HyStar_HPLC_QTOF_POS_LowMass_Loop-AS.m			Acquisition Date:	26.08.2020 13:42:29
File Name:	D:\Data\bmax0096xx\BMAX009631.d			Operator:	Michael Meier
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

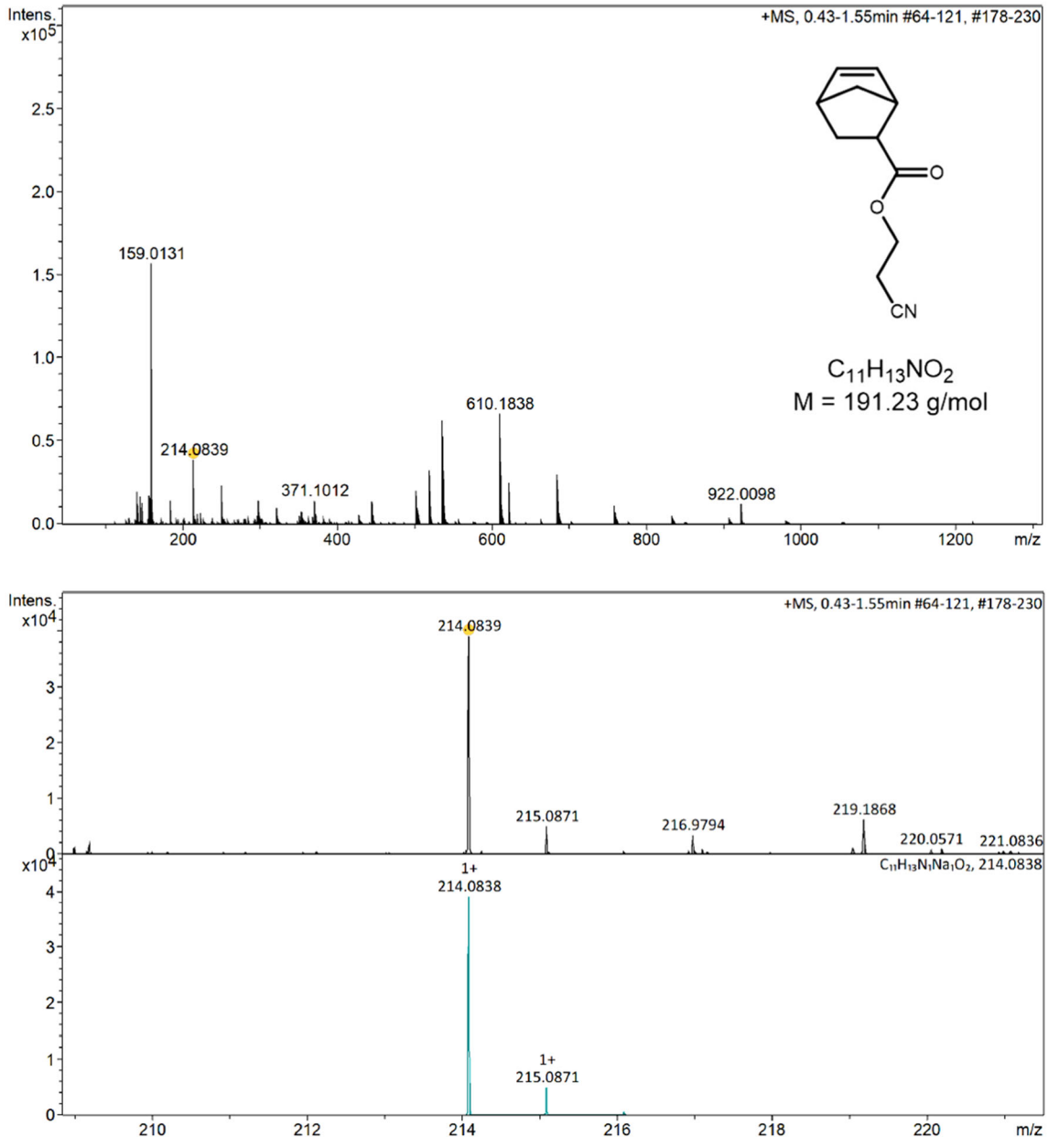


Figure S44 Mass spectra of **NBE-6**

Structure characterization of polymers

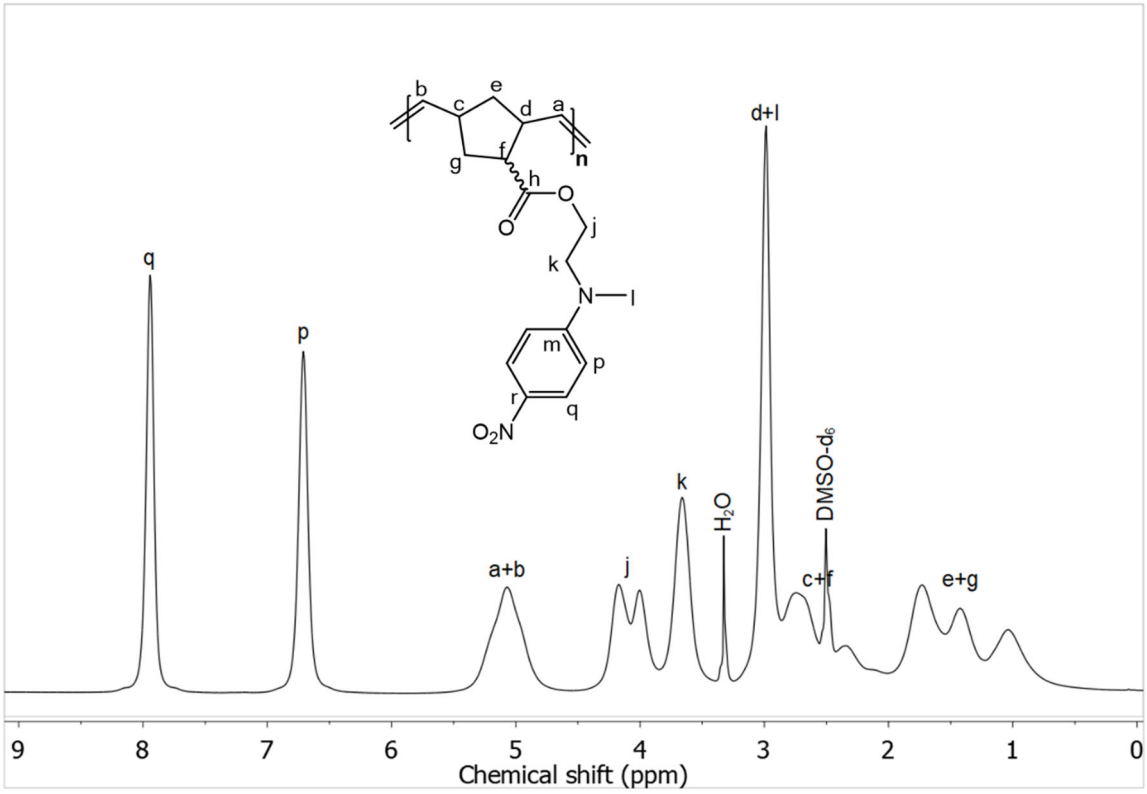


Figure S45 ^{1}H NMR spectrum of **PNBE-2**

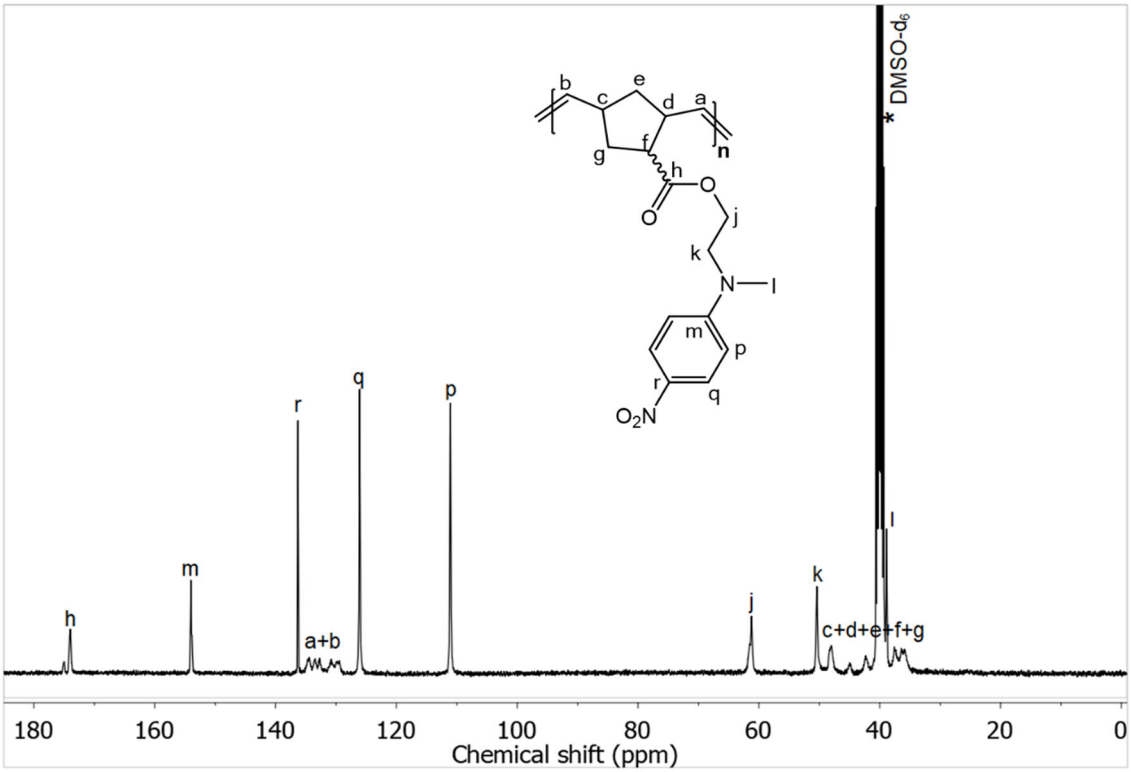


Figure S46 ^{13}C NMR spectrum of **PNBE-2**

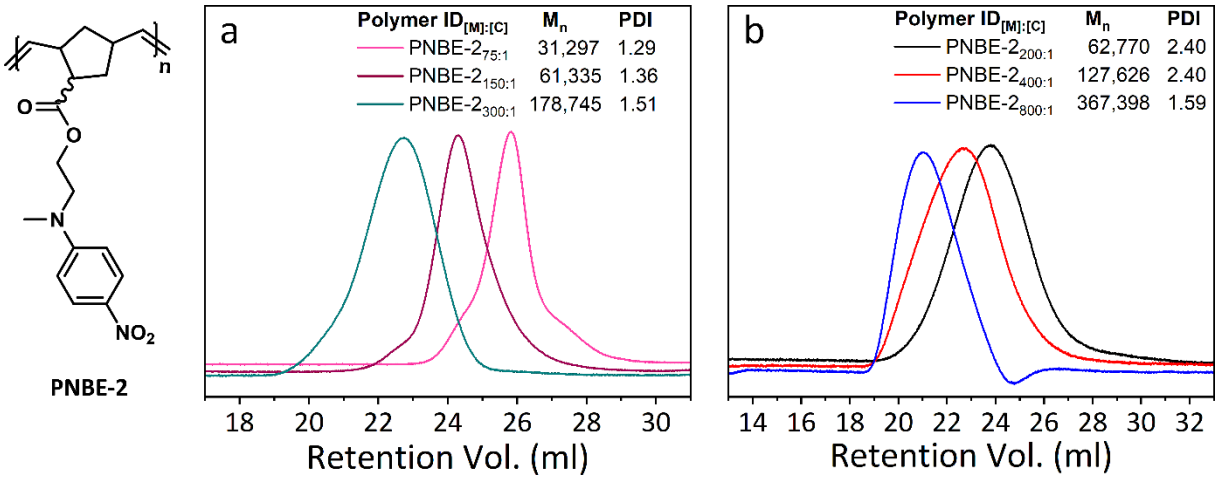


Figure S47 GPC elugrams of **PNBE-2** synthesized by (a) Grubb's first- and (b) third generation catalyst; in HFIP + 20 mM sodium trifluoroacetate

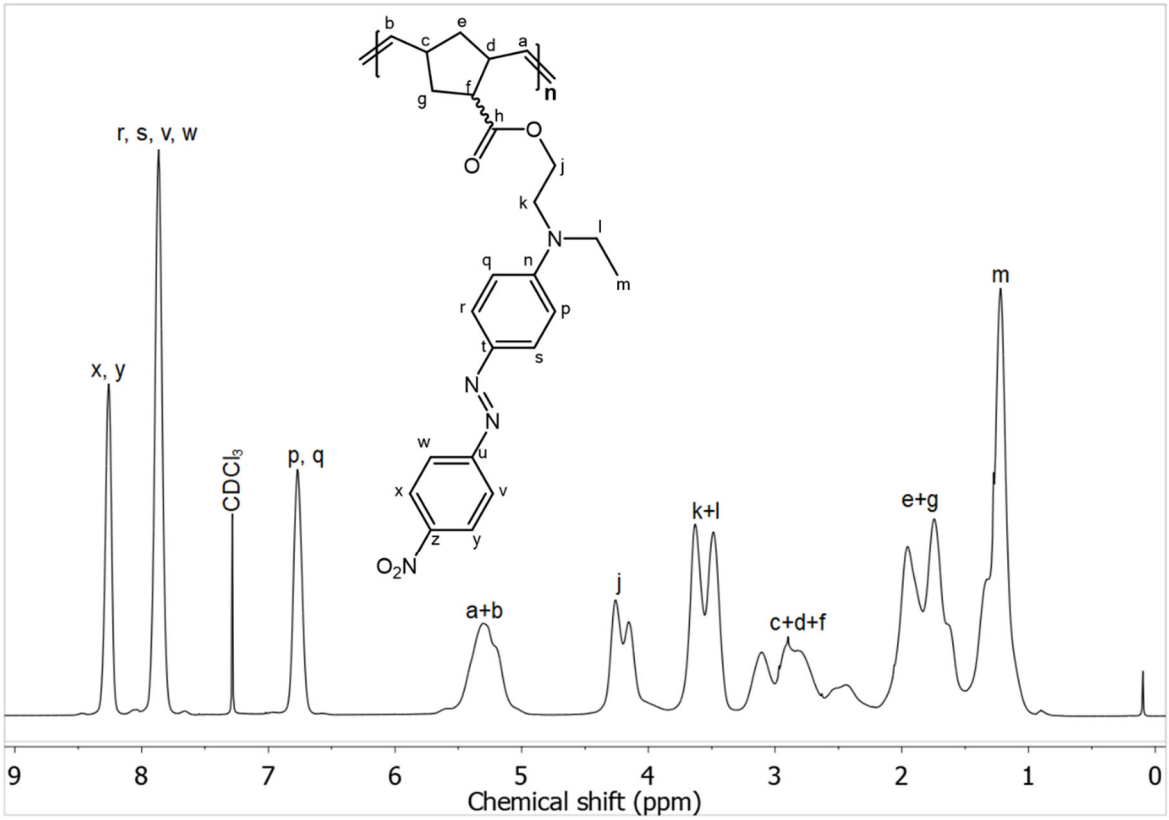


Figure S48 ^{1}H NMR spectrum of **PNBE-3**

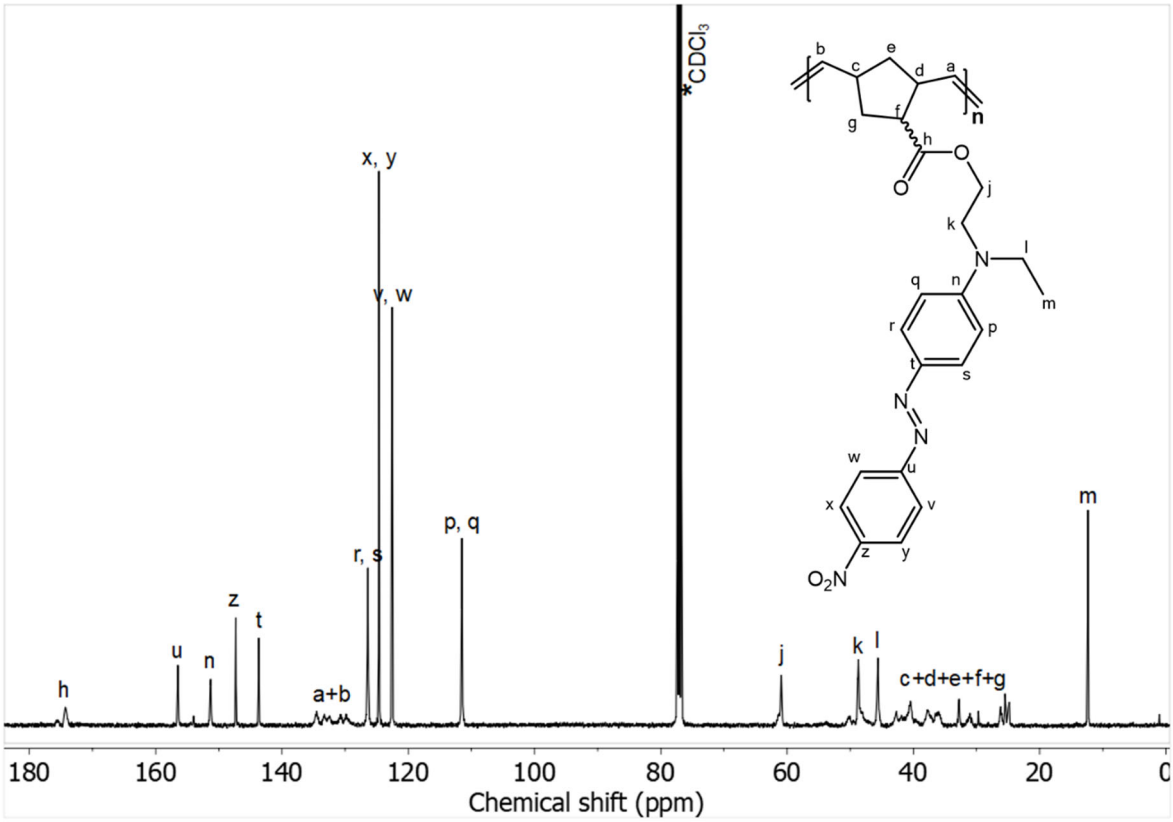


Figure S49 ^{13}C NMR spectrum of **PNBE-3**

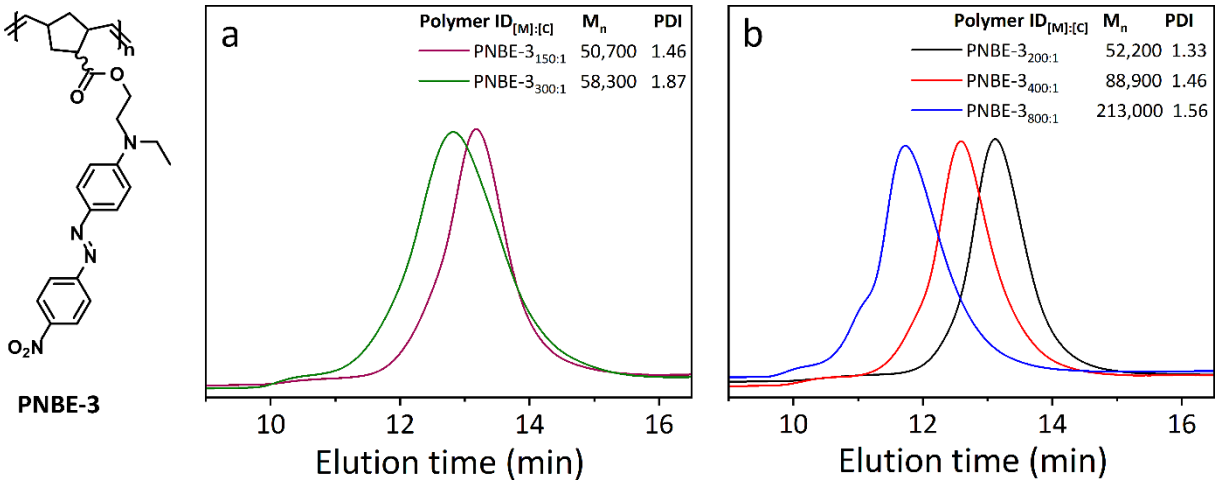


Figure S50 GPC elugrams of **PNBE-3** synthesized by (a) Grubb's first- and (b) third generation catalyst; in THF

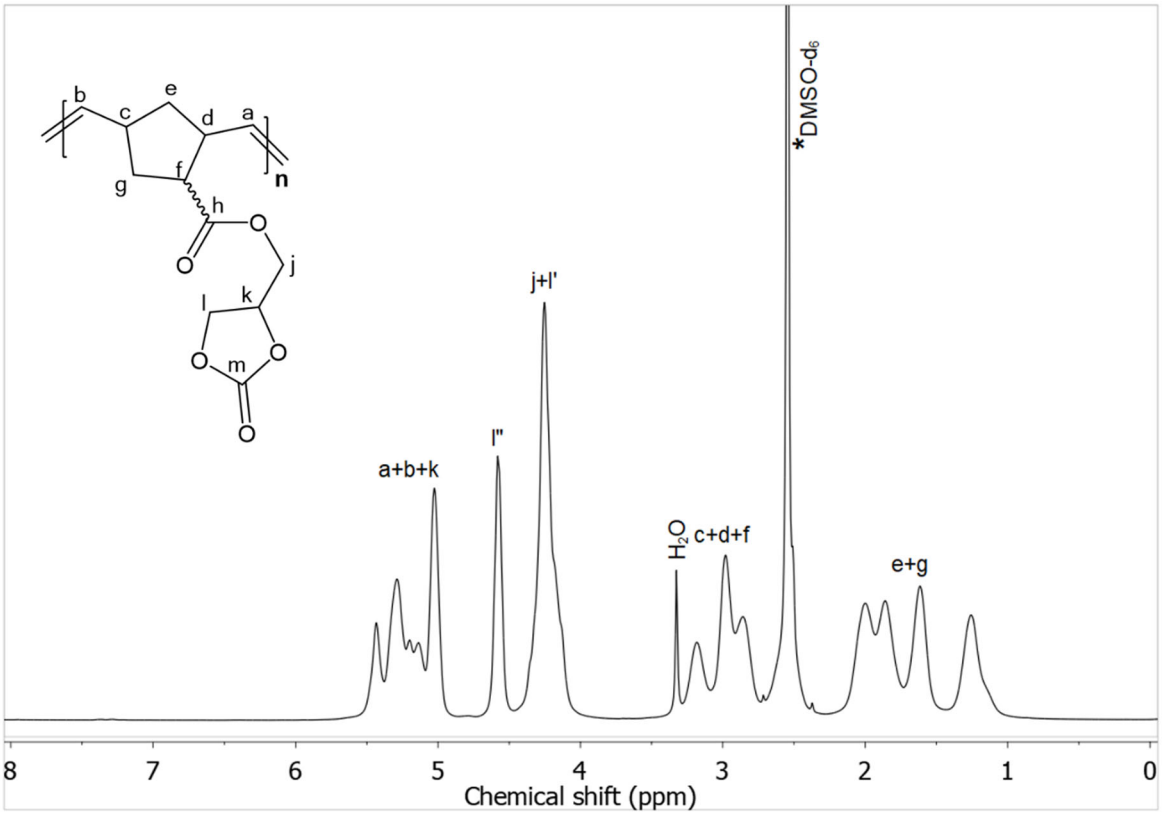


Figure S51 ^{1}H NMR spectrum of **PNBE-4**

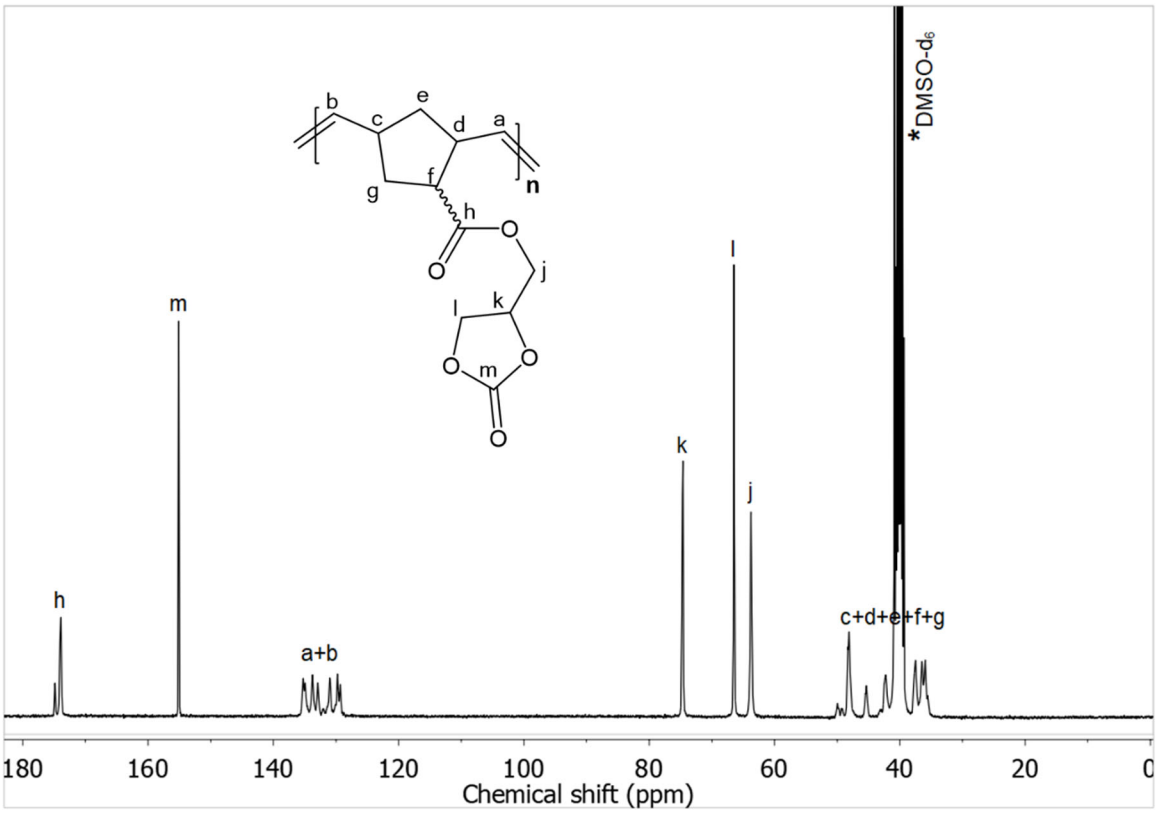


Figure S52 ^{13}C NMR spectrum of **PNBE-4**

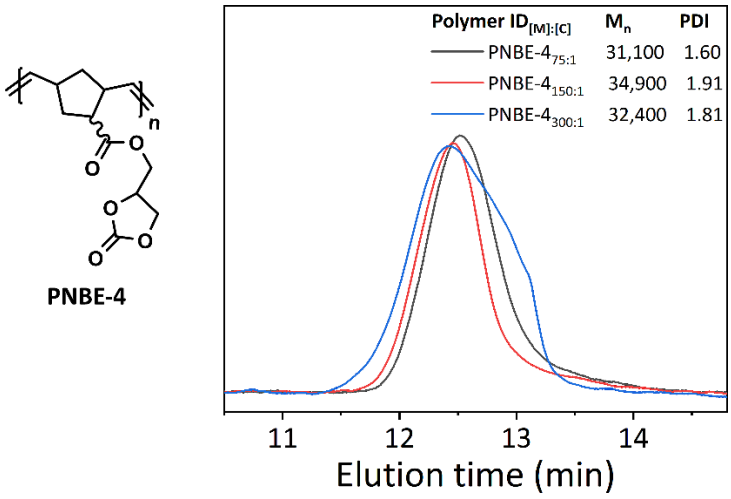


Figure S53 GPC elugrams of **PNBE-4** in HFIP

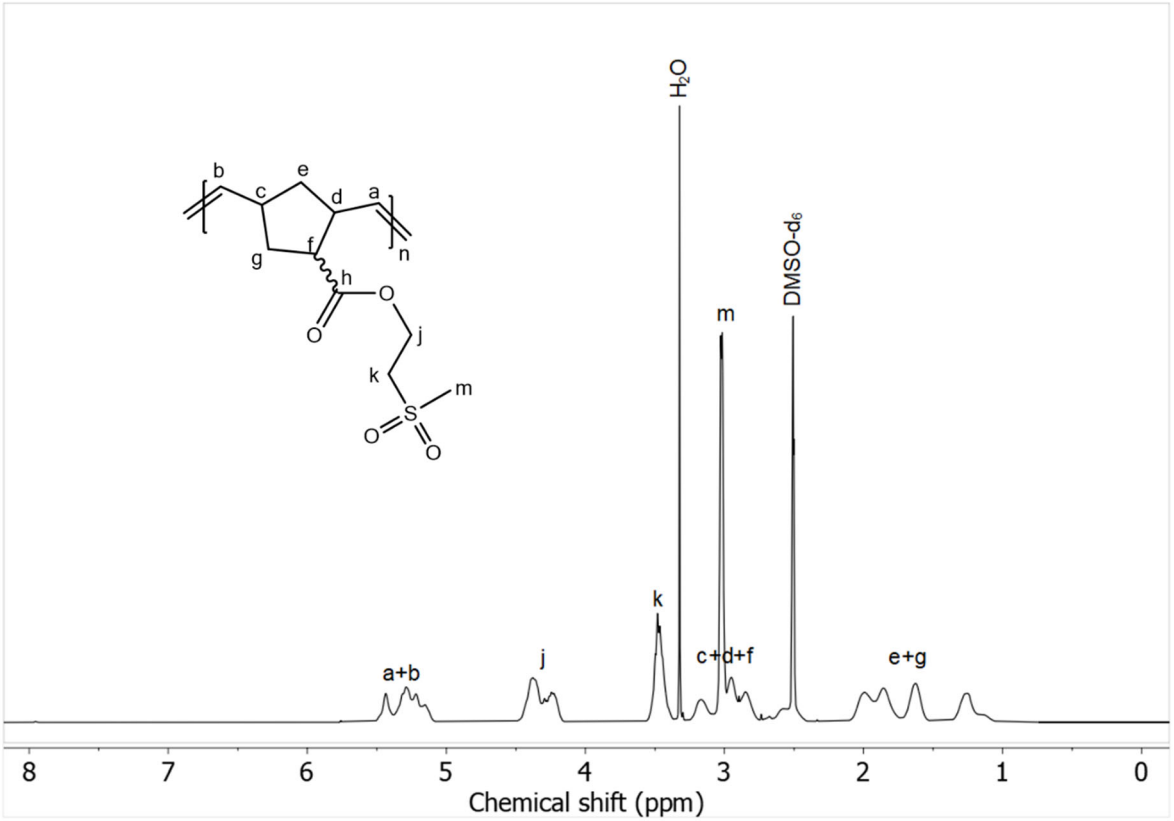


Figure S54 ^{1}H NMR spectrum of **PNBE-5**

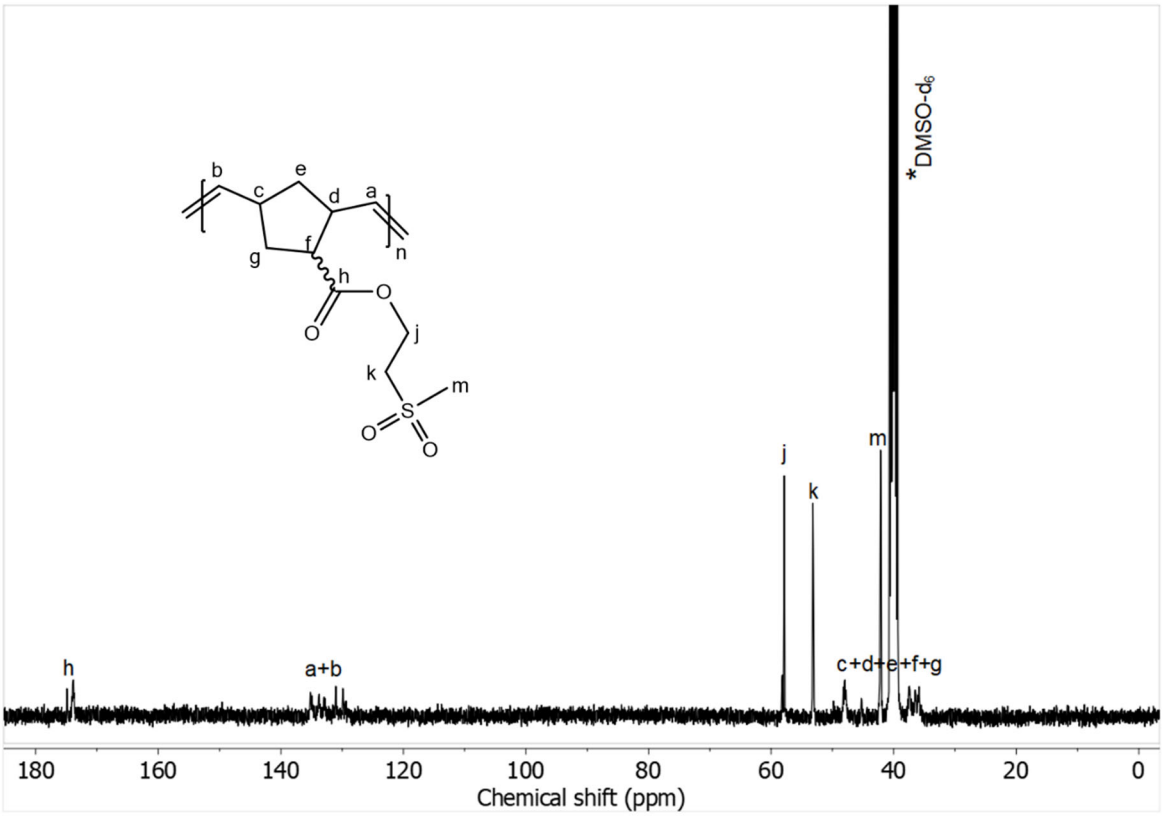


Figure S55 ^{13}C NMR spectrum of **PNBE-5**

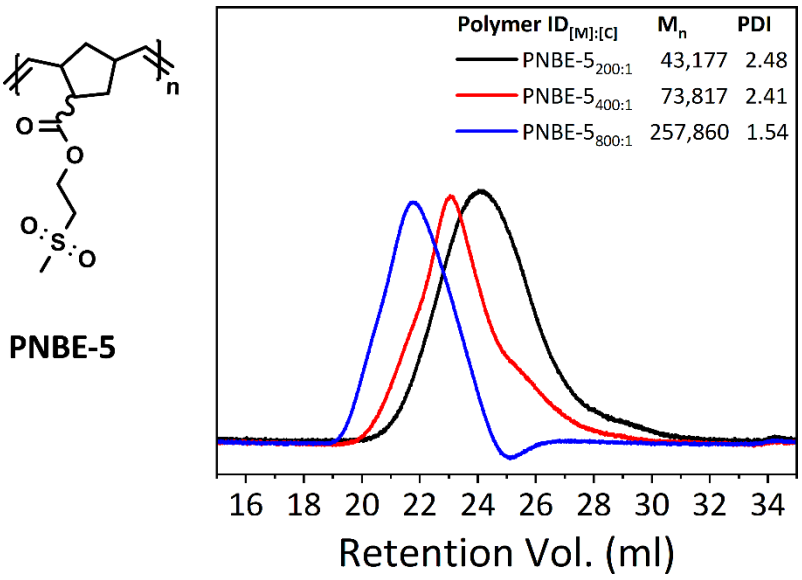


Figure S56 GPC elugrams of **PNBE-5** in HFIP + 20 mM sodium trifluoroacetate

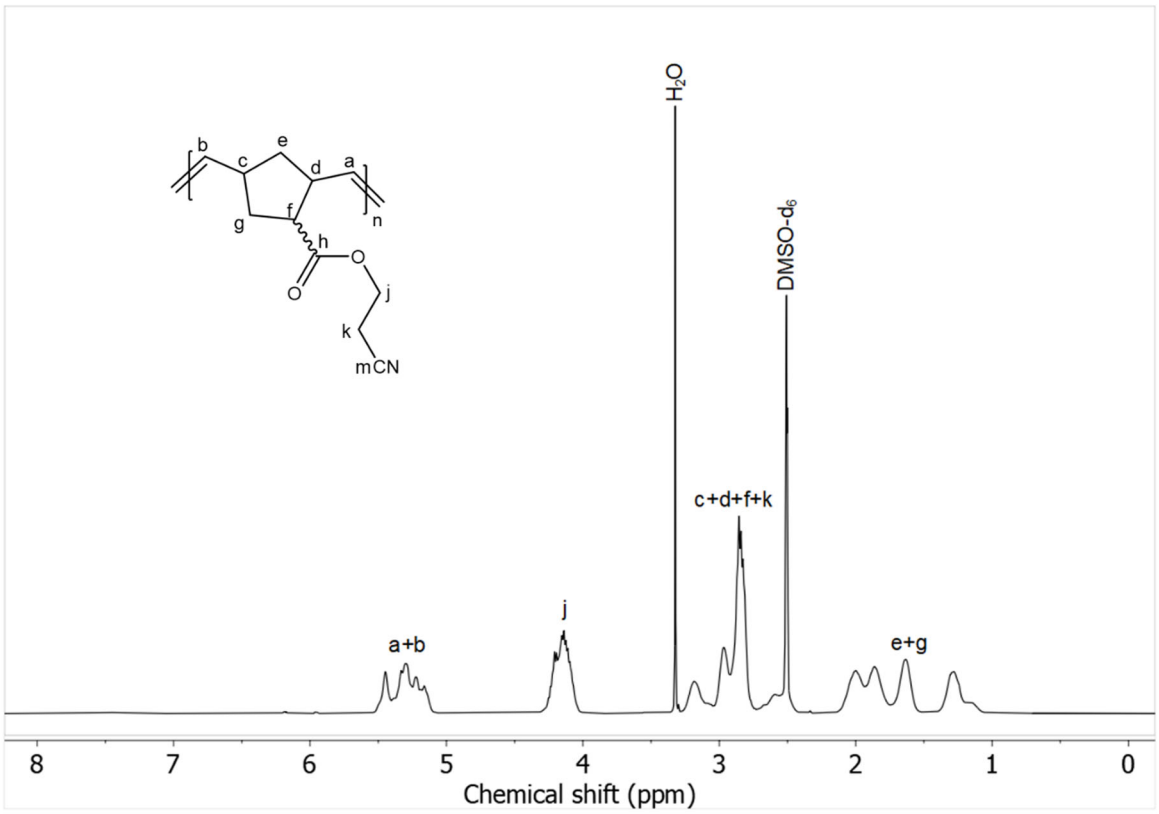


Figure S57 ^{1}H NMR spectrum of **PNBE-6**

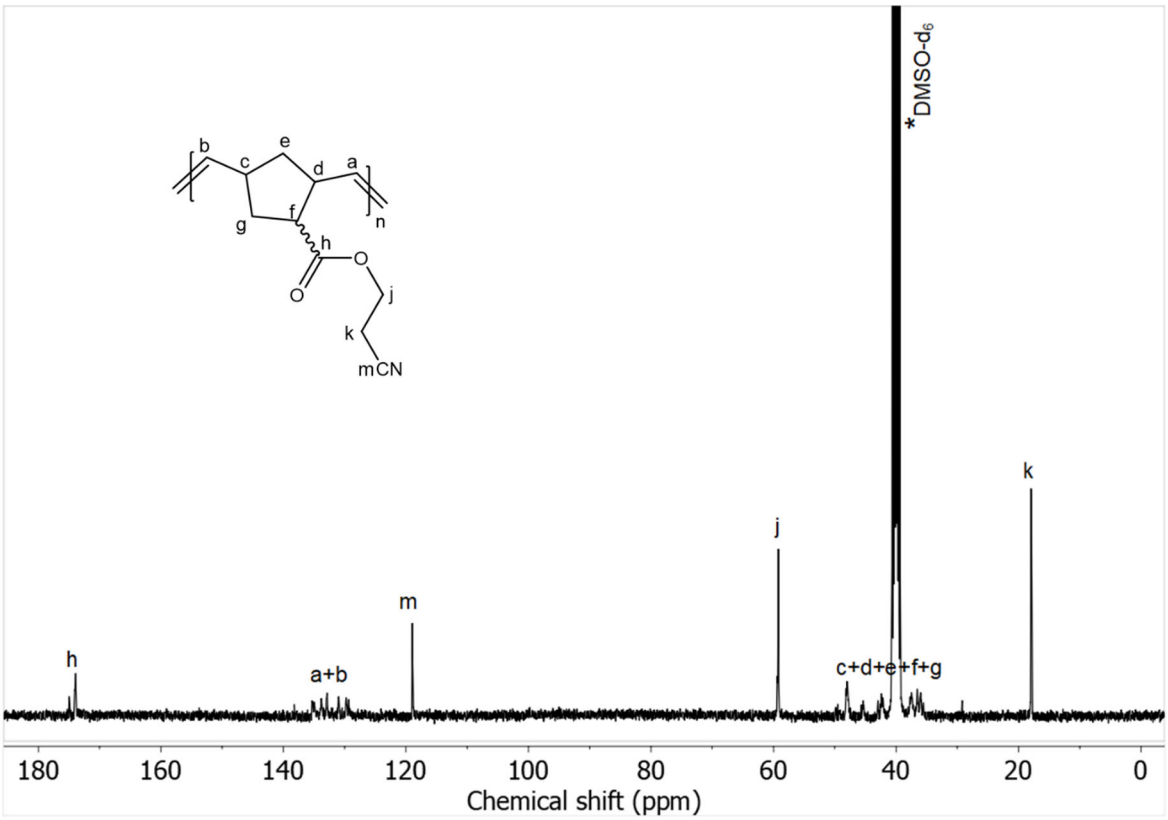


Figure S58 ^{13}C NMR spectrum of **PNBE-6**

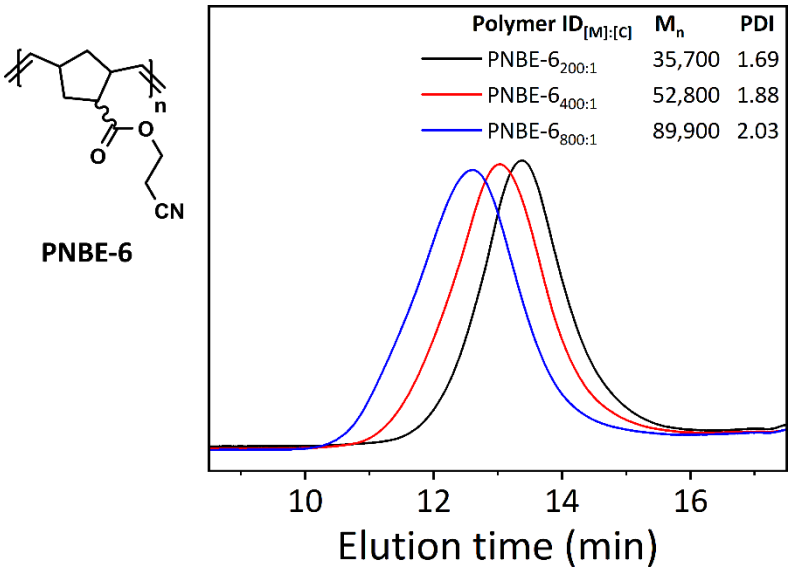
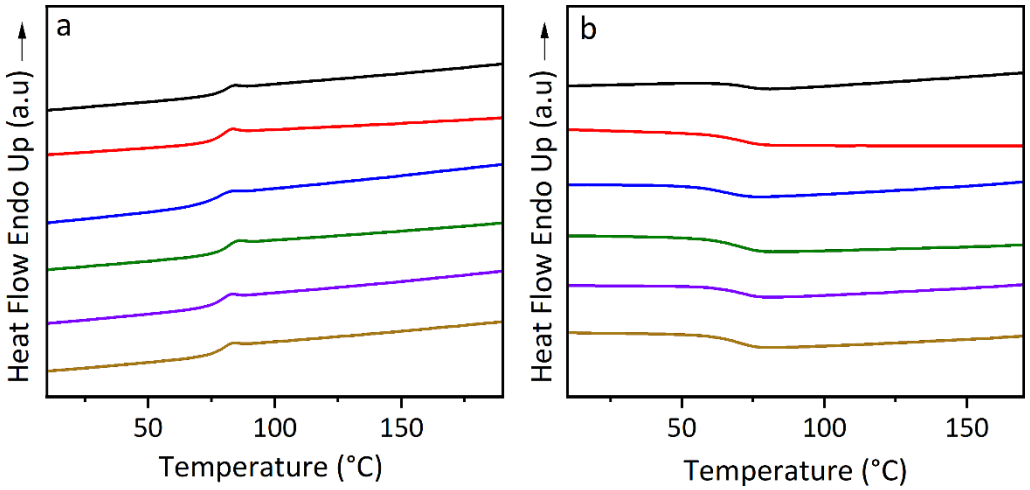


Figure S59 GPC elugrams of **PNBE-6** in THF

Thermal behaviour of polymers



Polymer ID$_{[M]:[C]}$	T_g (°C) 2nd heating cycle (a)	1st cooling cycle (b)
PNBE-2$_{75:1}$	79	73
PNBE-2$_{150:1}$	78	69
PNBE-2$_{200:1}$	75	64
PNBE-2$_{300:1}$	80	68
PNBE-2$_{400:1}$	77	68
PNBE-2$_{800:1}$	78	70

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

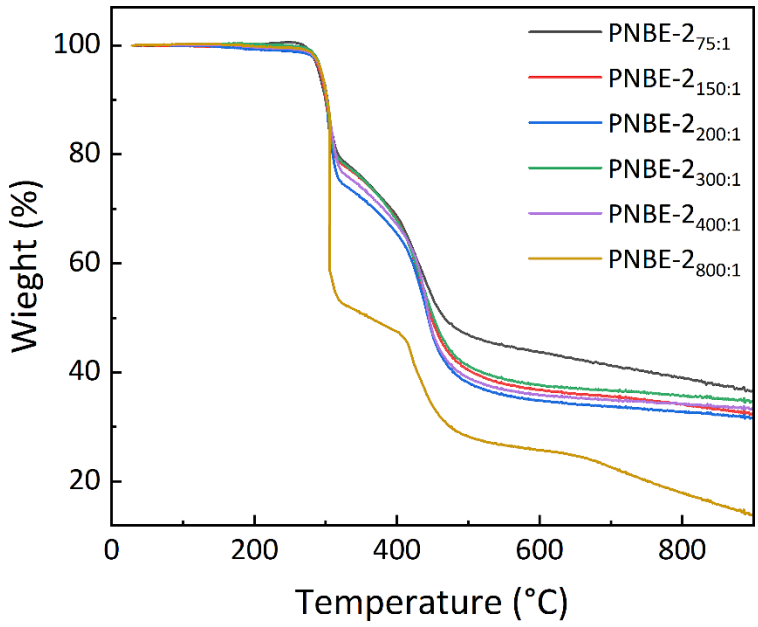
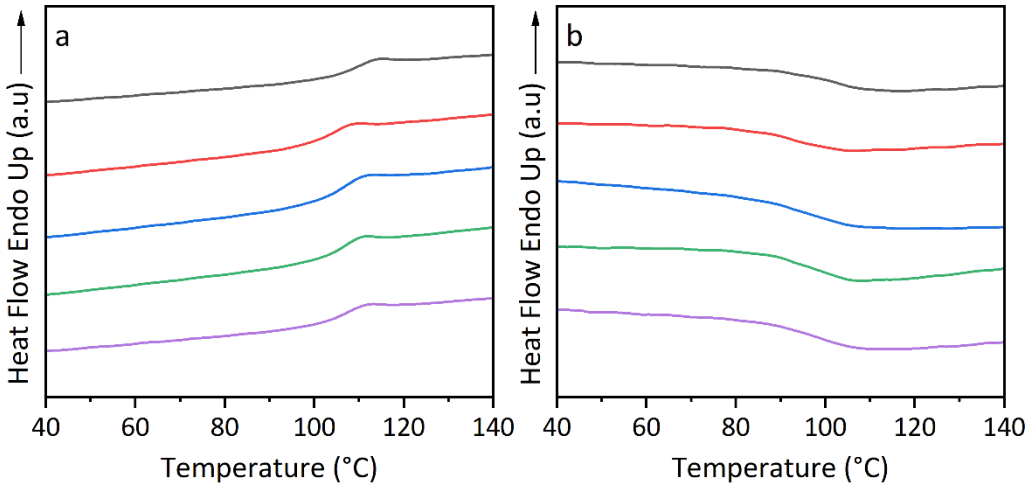


Figure S61 TGA curves for **PNBE-2** polymer sets



Polymer ID$_{[M]:[C]}$	T_g (°C)	
	2nd heating cycle [a]	1st cooling cycle [b]
PNBE-3$_{150:1}$	108	99
PNBE-3$_{200:1}$	103	92
PNBE-3$_{300:1}$	106	95
PNBE-3$_{400:1}$	106	96
PNBE-3$_{800:1}$	106	95

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

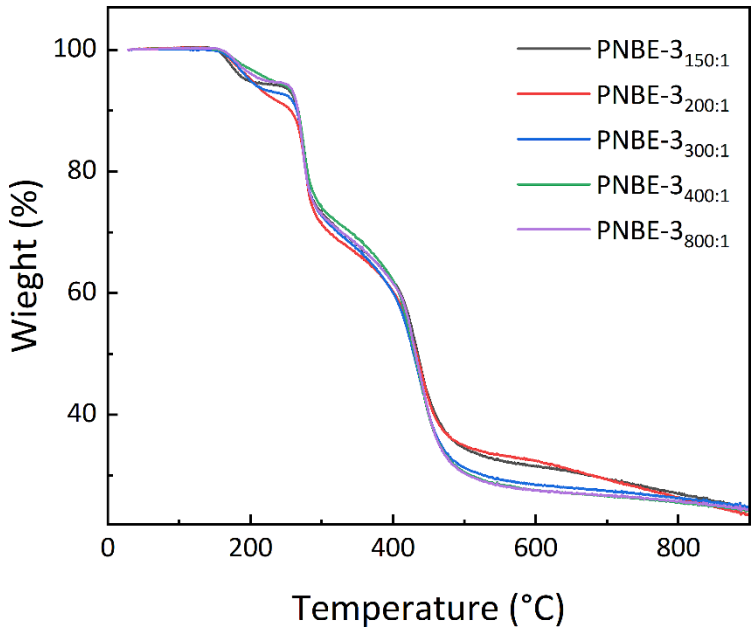
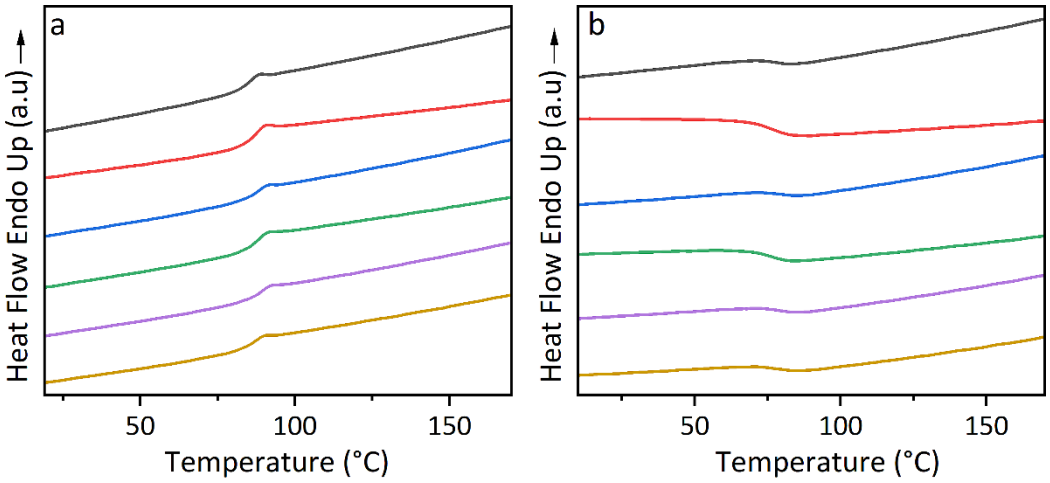


Figure S63 TGA curves for **PNBE-3** polymer sets



Polymer ID$_{[M]:[C]}$	T_g (°C)	
	2nd Heating cycle $^{(a)}$	1st cooling cylce $^{(b)}$
PNBE-4$_{75:1}$	84	79
PNBE-4$_{150:1}$	86	76
PNBE-4$_{200:1}$	87	80
PNBE-4$_{300:1}$	87	76
PNBE-4$_{400:1}$	88	80
PNBE-4$_{800:1}$	86	80

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

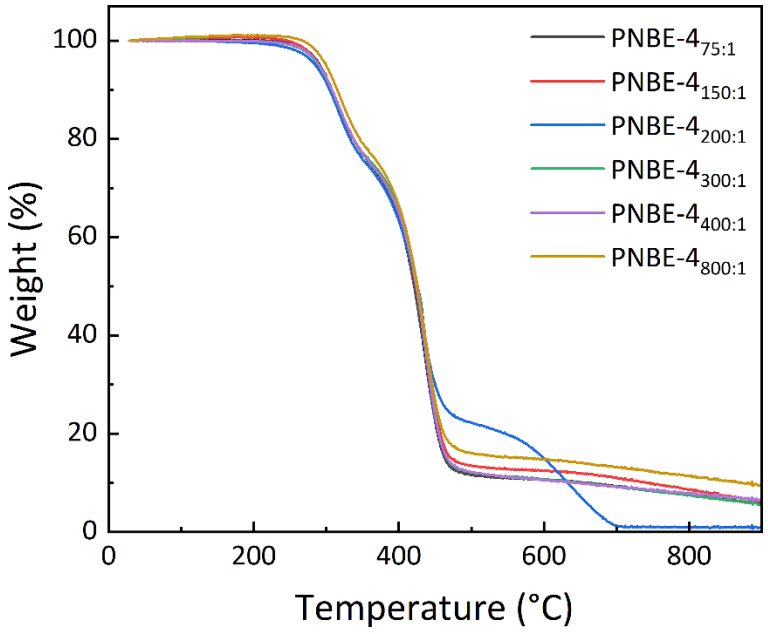
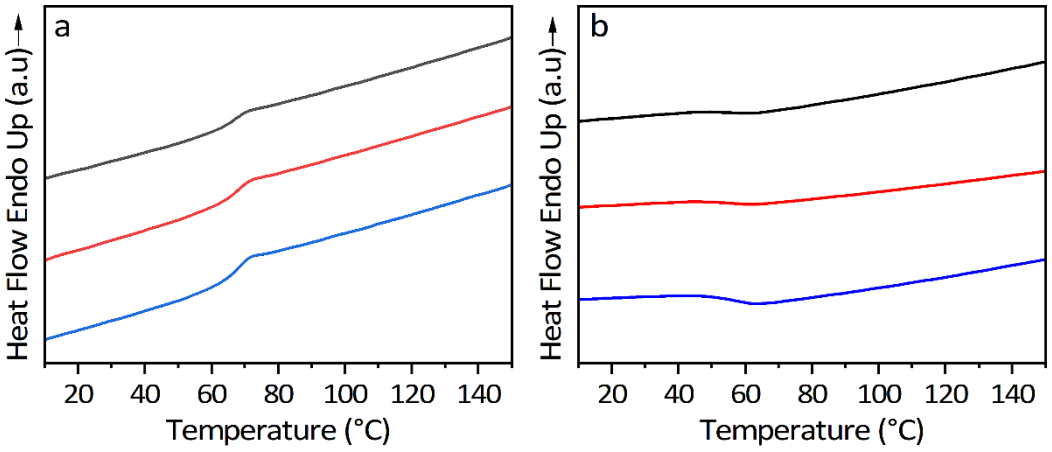


Figure S65 TGA curves for **PNBE-2** polymer sets



Polymer ID$_{[M]:[C]}$	T_g (°C)	
	2nd heating cycle (a)	1st cooling cycle (b)
PNBE-5$_{200:1}$	66	56
PNBE-5$_{400:1}$	68	56
PNBE-5$_{800:1}$	67	57

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

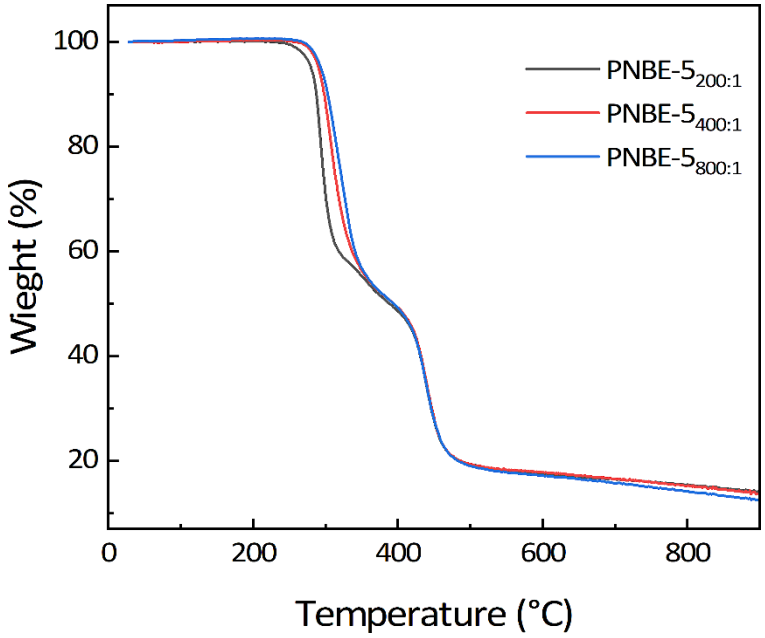
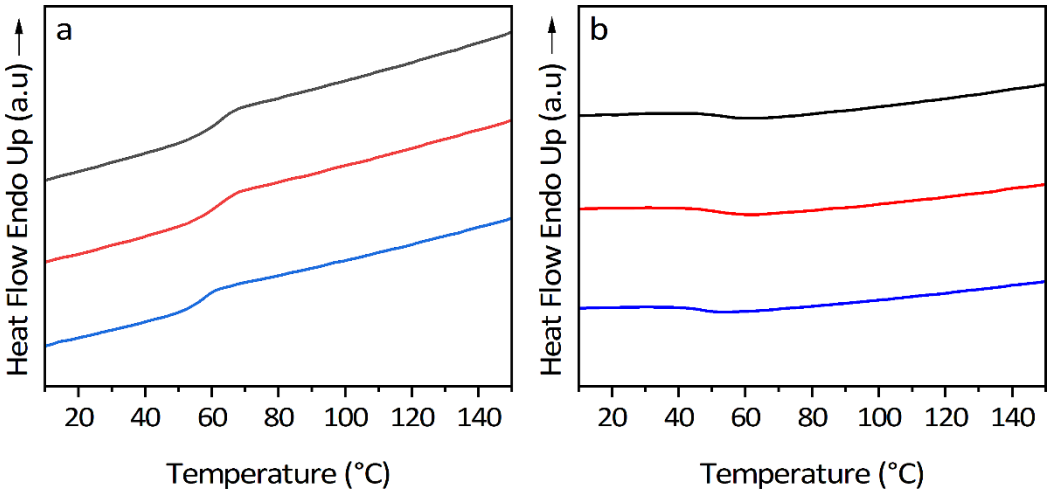


Figure S67 TGA curves for **PNBE-5** polymer sets



Polymer ID$_{[M]:[C]}$	T_g (°C)	
	2nd heating cycle $^{(a)}$	1st cooling cycle $^{(b)}$
PNBE-6$_{200:1}$	62	55
PNBE-6$_{400:1}$	62	52
PNBE-6$_{800:1}$	58	48

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

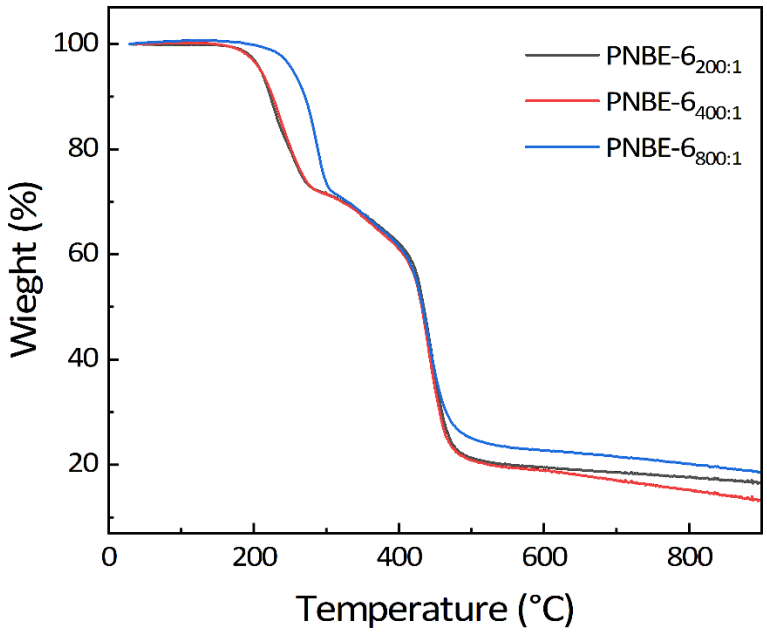


Figure S69 TGA curves for **PNBE-6** polymer sets

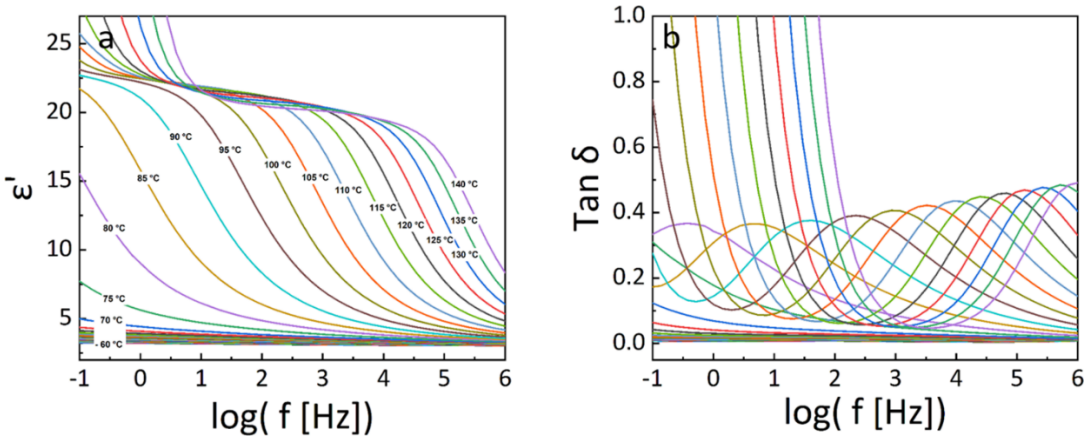


Figure S70 Isothermal dielectric response of **PNBE-2**; (a) real permittivity, ε'; (b) tangent loss Tan δ; of the complex dielectric function vs frequency

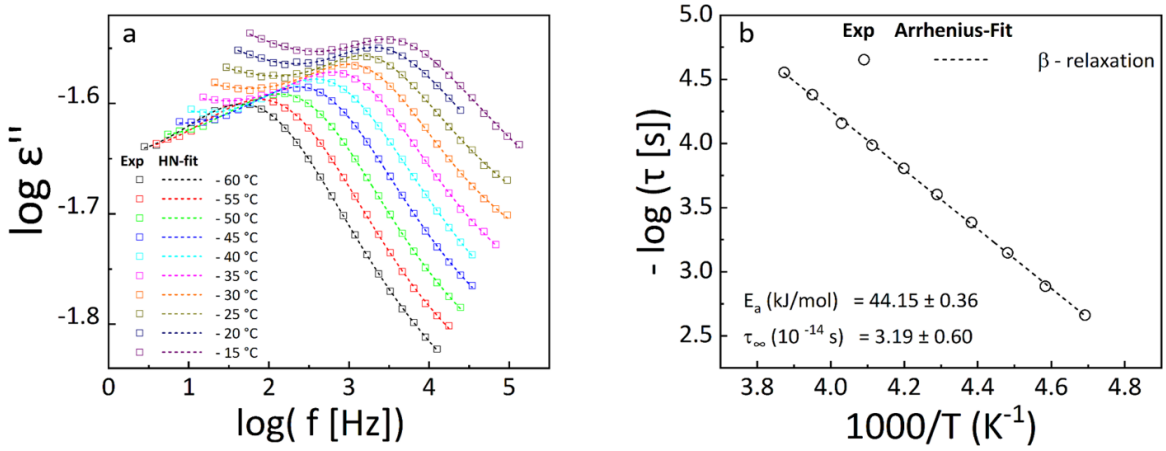


Figure S71 β-relaxation processes in **PNBE-2**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Arrhenius plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented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

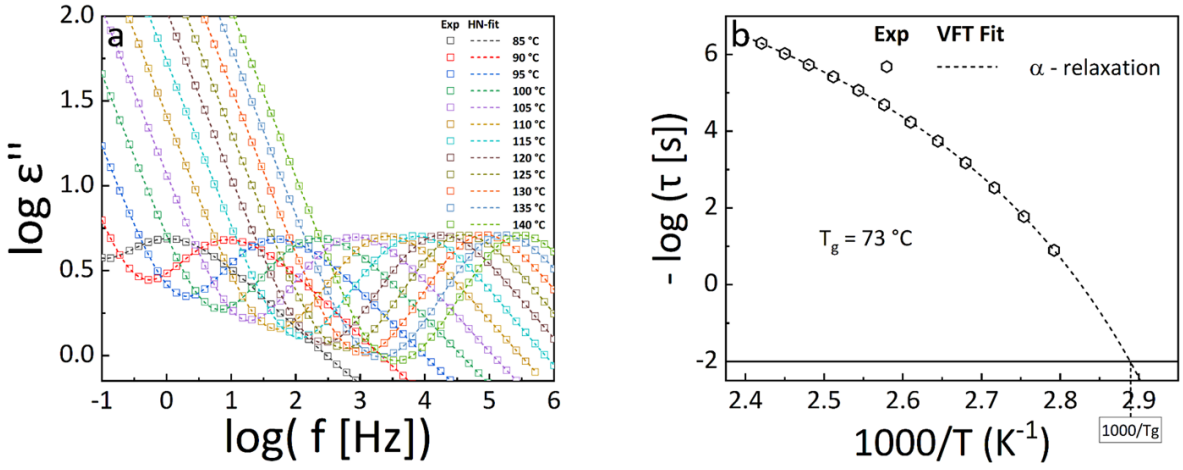


Figure S72 α-relaxation processes in **PNBE-2**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Vogel-Fulcher-Tammann (VFT) plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental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

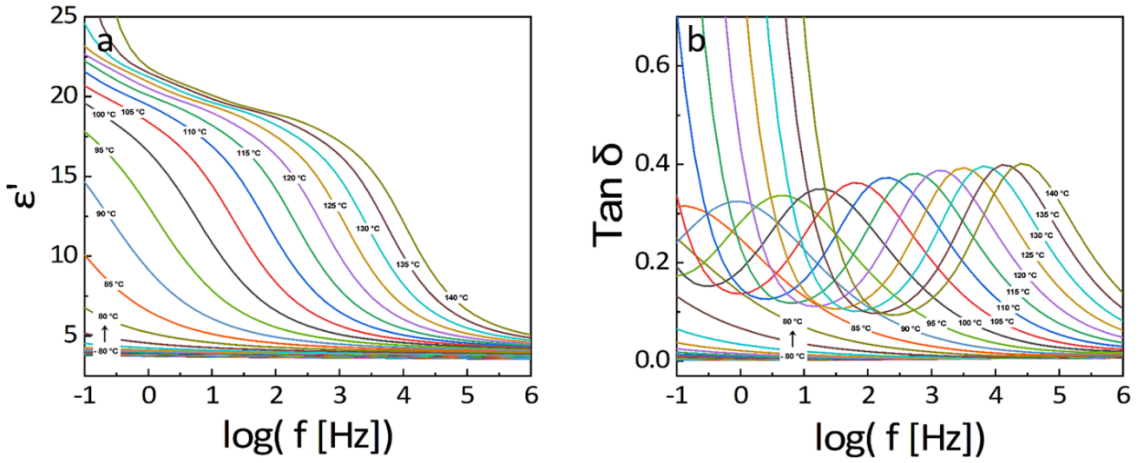


Figure S73 Isothermal dielectric response of **PNBE-3**; (a) real permittivity, ε'; (b) tangent loss Tan δ; of the complex dielectric function vs frequency

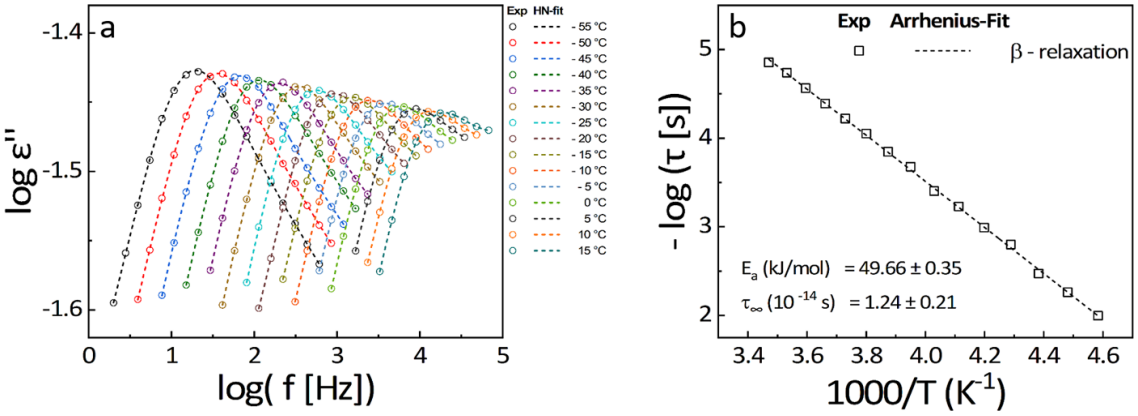


Figure S74 β-relaxation processes in **PNBE-3**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Arrhenius plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented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

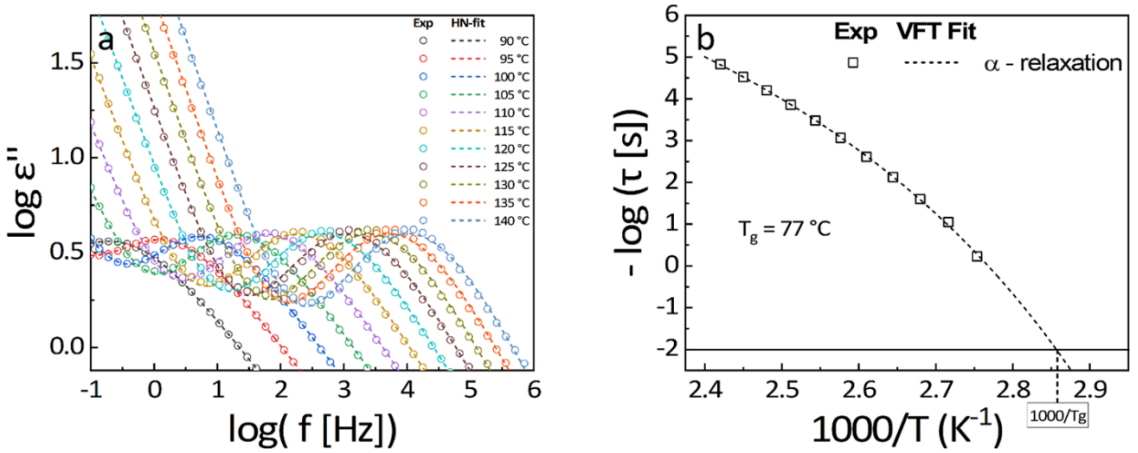


Figure S75 α-relaxation processes in **PNBE-3**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Vogel-Fulcher-Tammann (VFT) plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental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

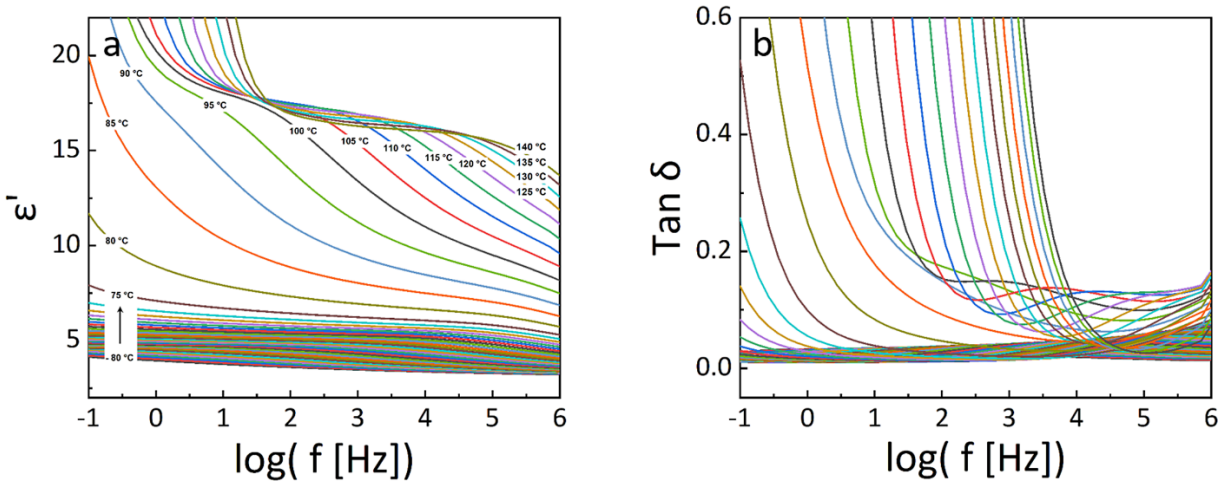


Figure S76 Isothermal dielectric response of **PNBE-4**; (a) real permittivity, ε'; (b) tangent loss Tan δ; of the complex dielectric function vs frequency

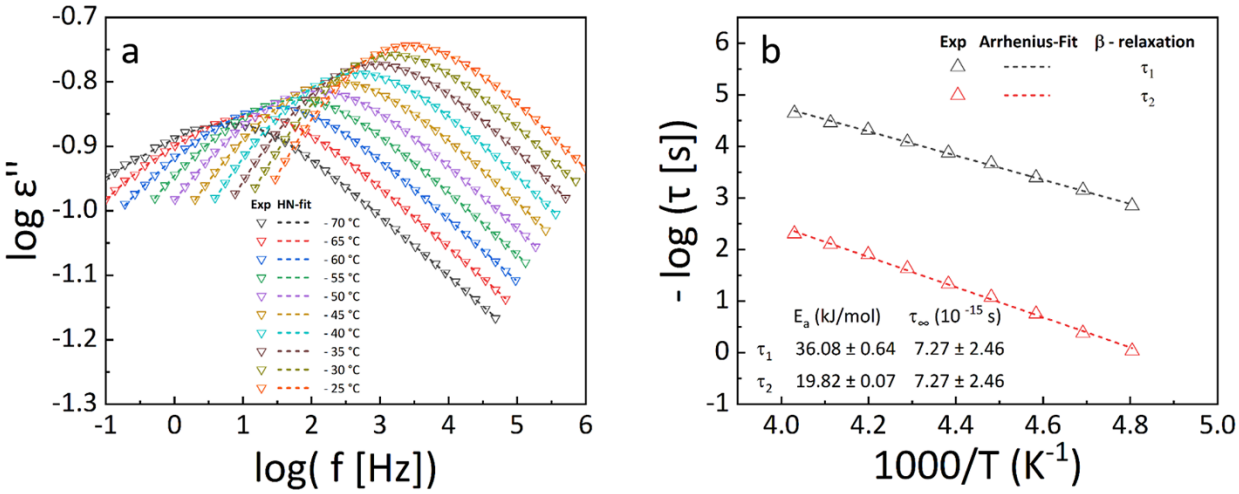


Figure S77 β-relaxation processes in **PNBE-4**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Arrhenius plots of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented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

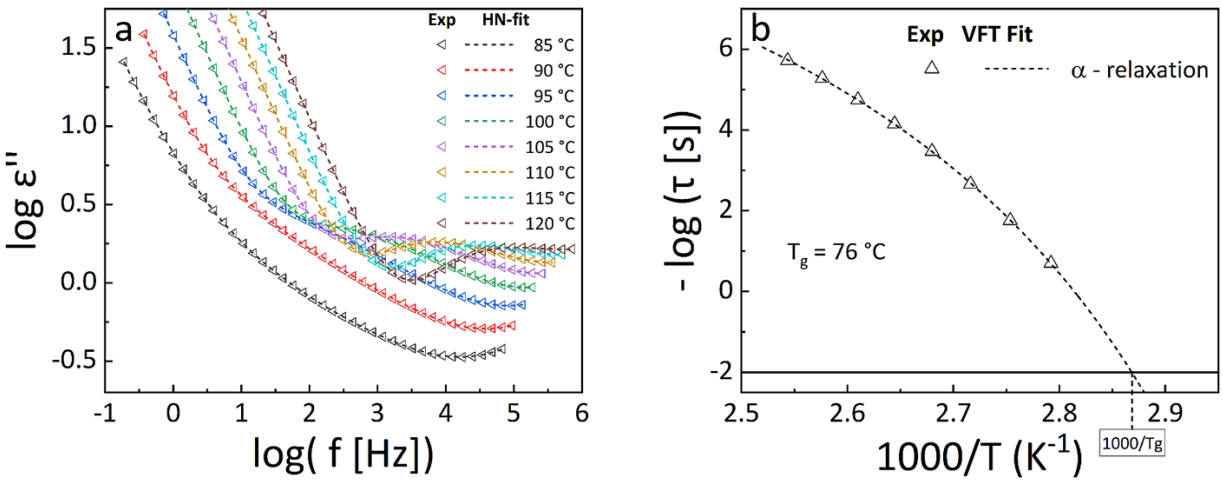


Figure S78 α-relaxation processes in **PNBE-4**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Vogel-Fulcher-Tammann (VFT) plot of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus the inverse of temperature. The experimental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

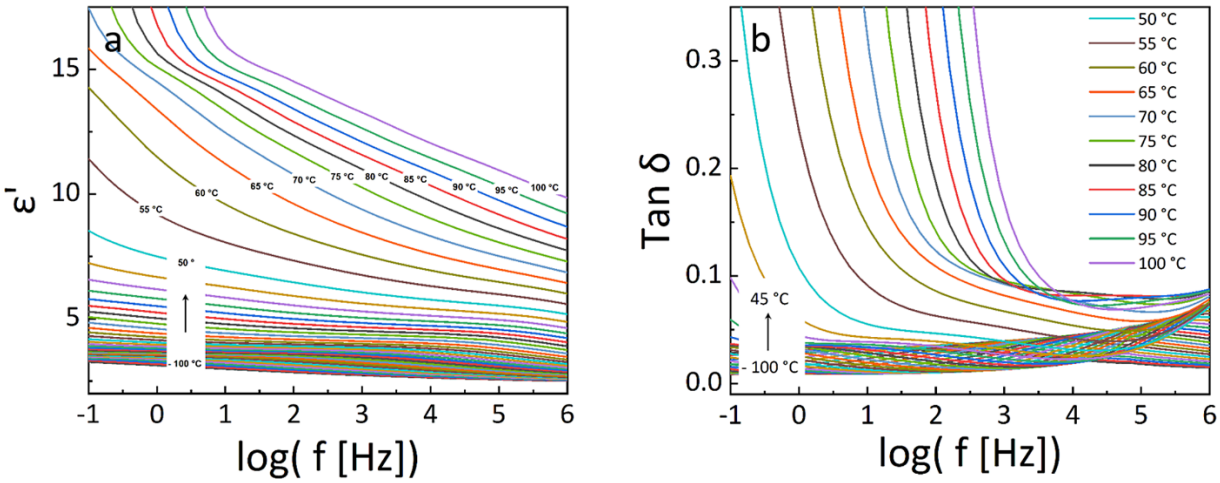


Figure S79 Isothermal dielectric response of **PNBE-5**; (a) real permittivity, ε'; (b) tangent loss Tan δ; of the complex dielectric function vs frequency

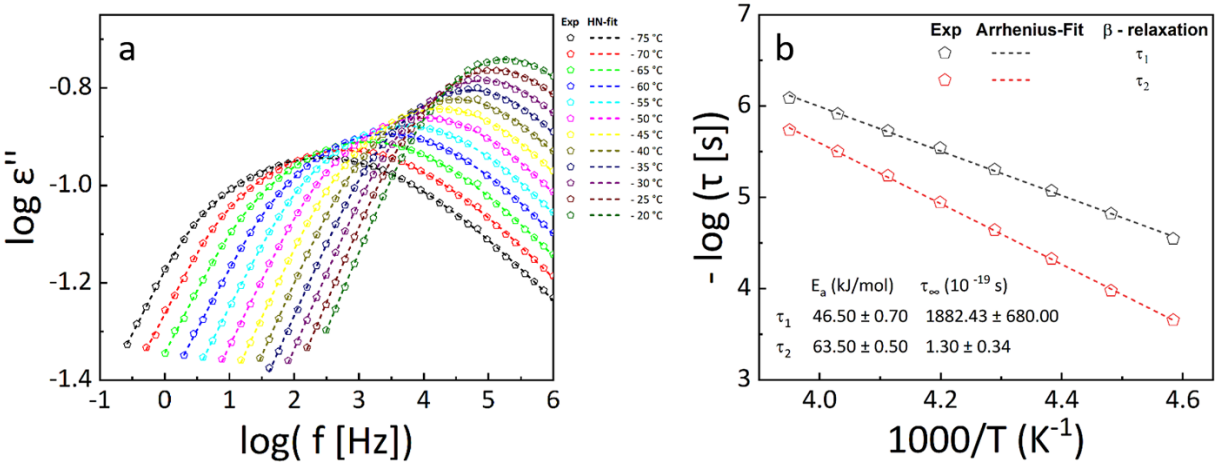


Figure S80 β-relaxation processes in **PNBE-5**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Arrhenius plots of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented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

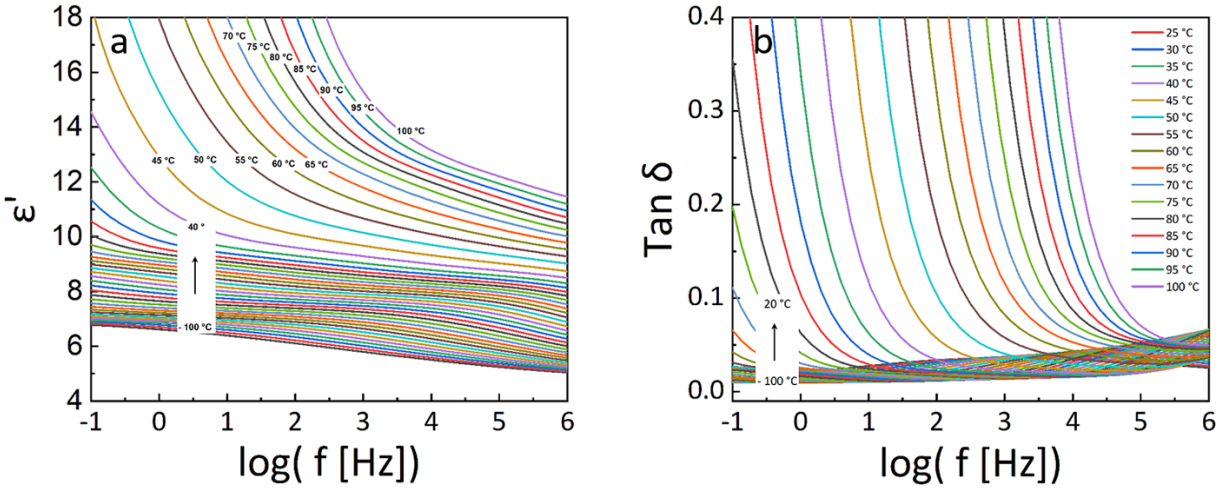


Figure S81 Isothermal dielectric response of **PNBE-6**; (a) real permittivity, ε'; (b) tangent loss Tan δ; of the complex dielectric function vs frequency

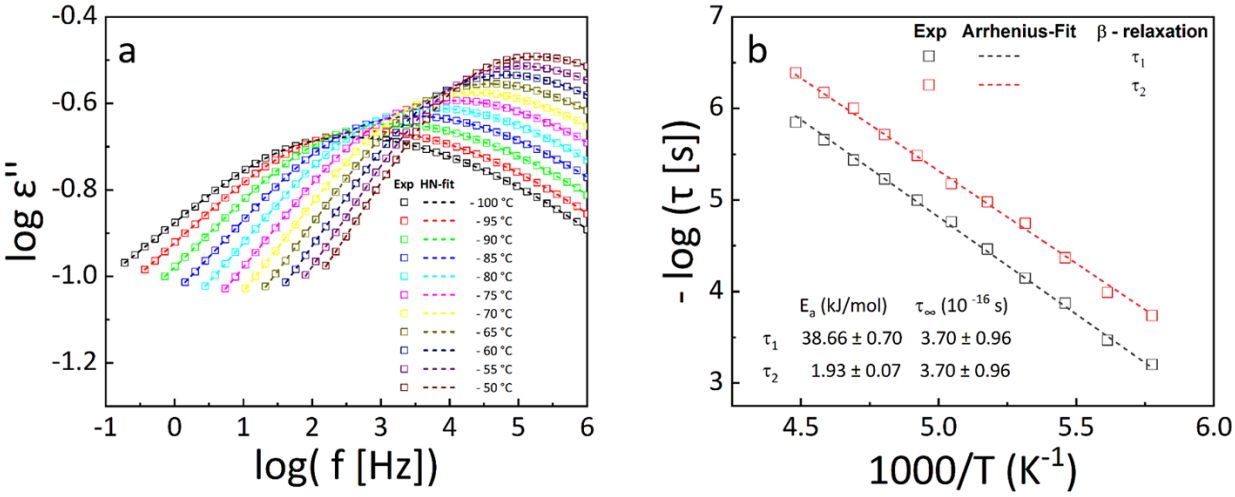


Figure S82 β-relaxation processes in **PNBE-6**: (a) isothermal plot of imaginary part ε'' of the complex dielectric permittivity versus frequency (b) Arrhenius plots of corresponding relaxation times obtained from Havriliak-Negami (HN)-fit versus inverse of temperature. The experimental data are represented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

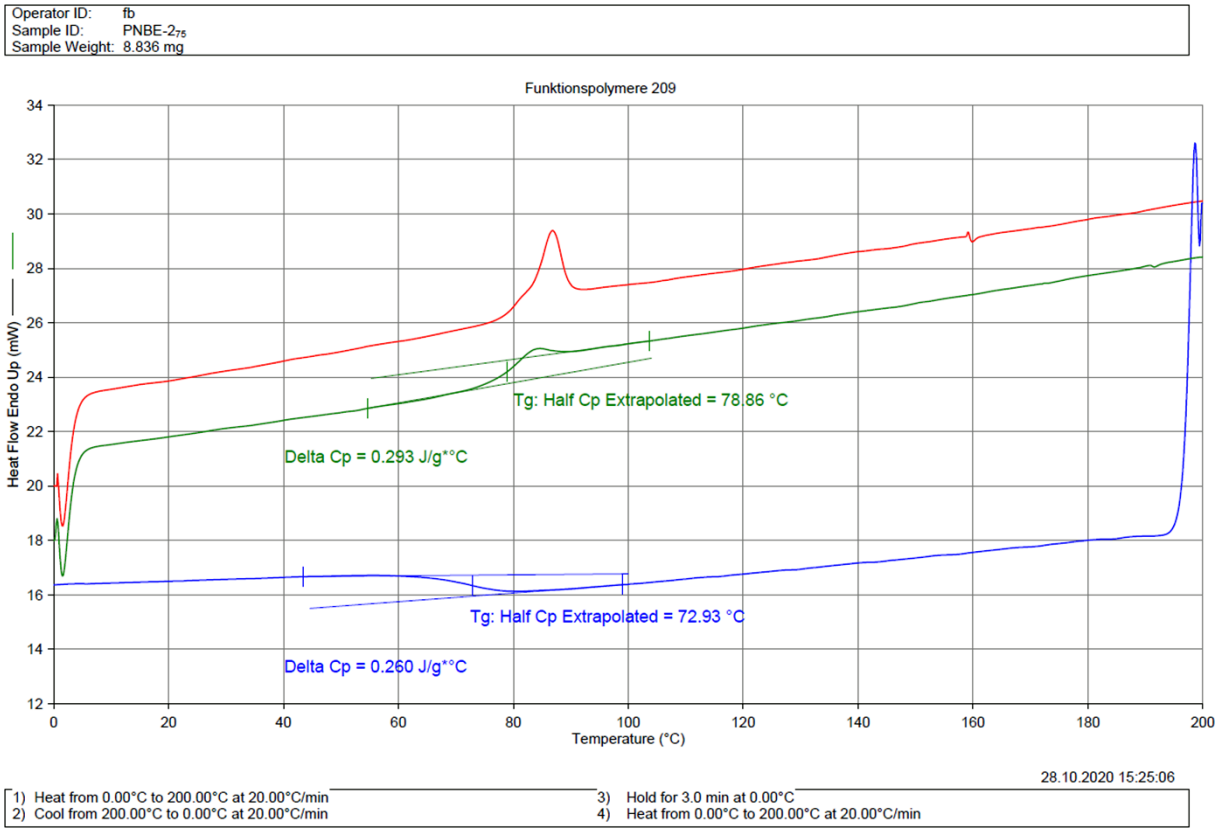
$$\mu_2^2 = \frac{27 \cdot M_2 \cdot k_B \cdot T}{4\pi \cdot \rho_1 \cdot (\varepsilon_1 + 2)^2 \cdot N_A} \cdot \left(\frac{\partial \varepsilon_{12}}{\partial x_2} - (n_2^2 - n_1^2) \right) \qquad (Eq\ 1).$$

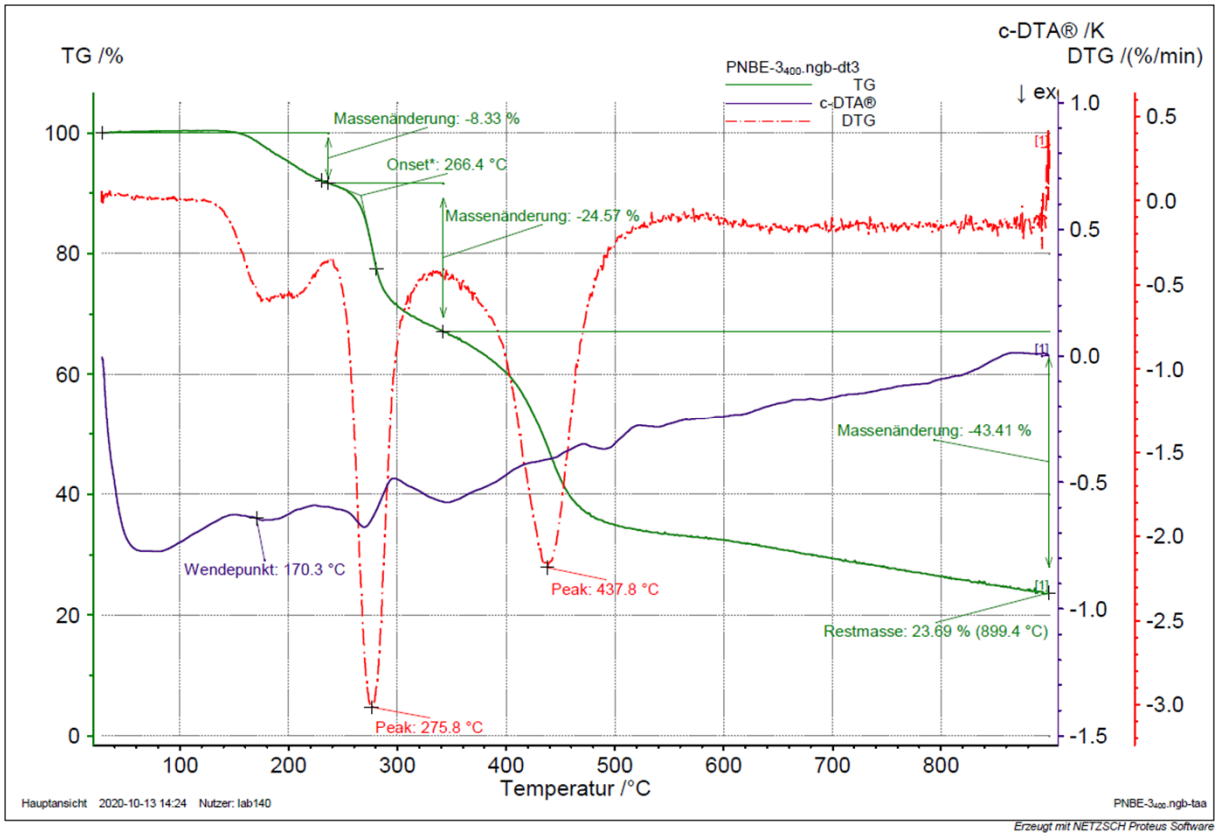
$$\varepsilon_{12} = 1 + \frac{4\pi}{3} \frac{\varepsilon_{12}(2\varepsilon_{12}+1)(n_1^2+2)^2}{3(2\varepsilon_{12}+n_1^2)^2} \frac{\mu_1^2}{k_B T} N_1 + \frac{4\pi}{3} \frac{\varepsilon_{12}(2\varepsilon_{12}+1)(n_2^2+2)^2}{3(2\varepsilon_{12}+n_2^2)^2} \frac{\mu_2^2}{k_B T} N_2 + 3\frac{N_1}{N_A} R_1 \frac{\varepsilon_{12}(n_1^2+2)}{2\varepsilon_{12}+n_1^2} + 3\frac{N_2}{N_A} R_2 \frac{\varepsilon_{12}(n_2^2+2)}{2\varepsilon_{12}+n_2^2} \qquad (Eq\ 2).$$

In the above equations,

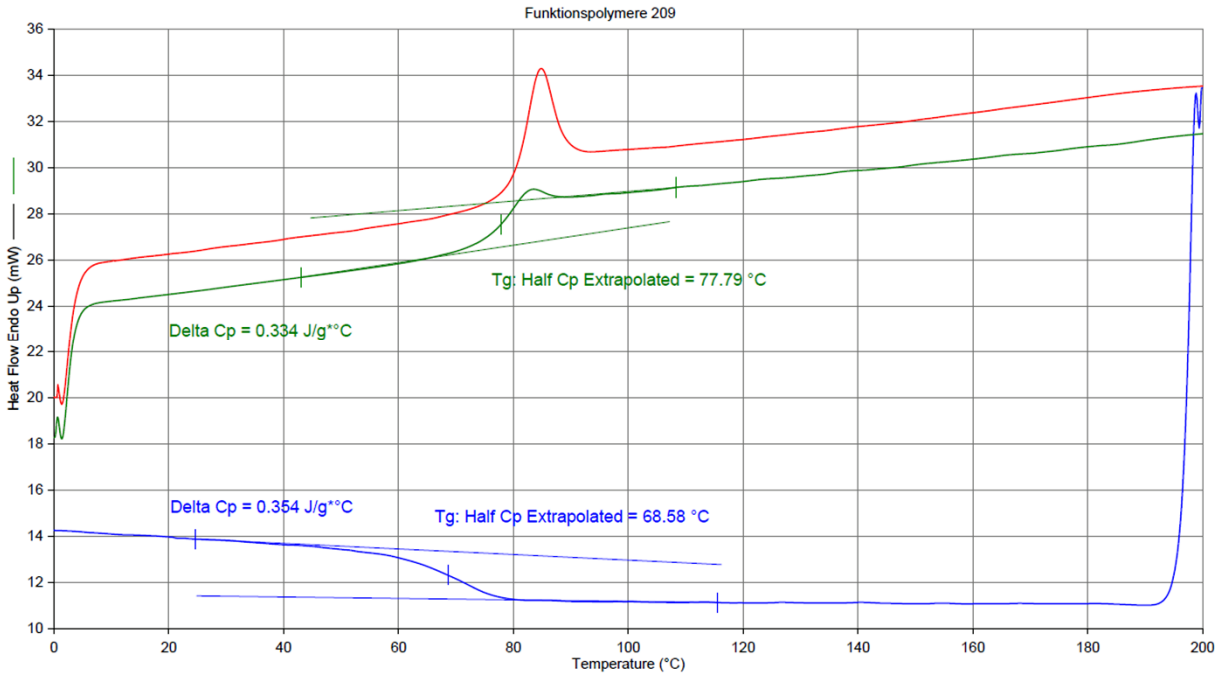
μ_1	dipole moment of the solvent
μ_2	dipole moment of NBE-X monomer
M_2	molar mass of NBE-X monomer
N_A	Avogadro's constant
k_B	Boltzmann's constant
T	Temperature
ρ_1	density of the solvent
ε_1	dielectric permittivity of the solvent
ε_{12}	dielectric permittivity of the solution
x_2	molar fraction of 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 $R_i = \frac{M_i}{\rho_i} \frac{(n_i^2-1)}{(n_i^2+2)}$

Appendices


Operator ID: fb
Sample ID: PNBE-2$_{75}$
Sample Weight: 8.836 mg
Funktionspolymere 209
Heat Flow Endo Up (mW)
Temperature (°C)
Tg: Half Cp Extrapolated = 78.86 °C
Delta Cp = 0.293 J/g*°C
Tg: Half Cp Extrapolated = 72.93 °C
Delta Cp = 0.260 J/g*°C
28.10.2020 15:25:06
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

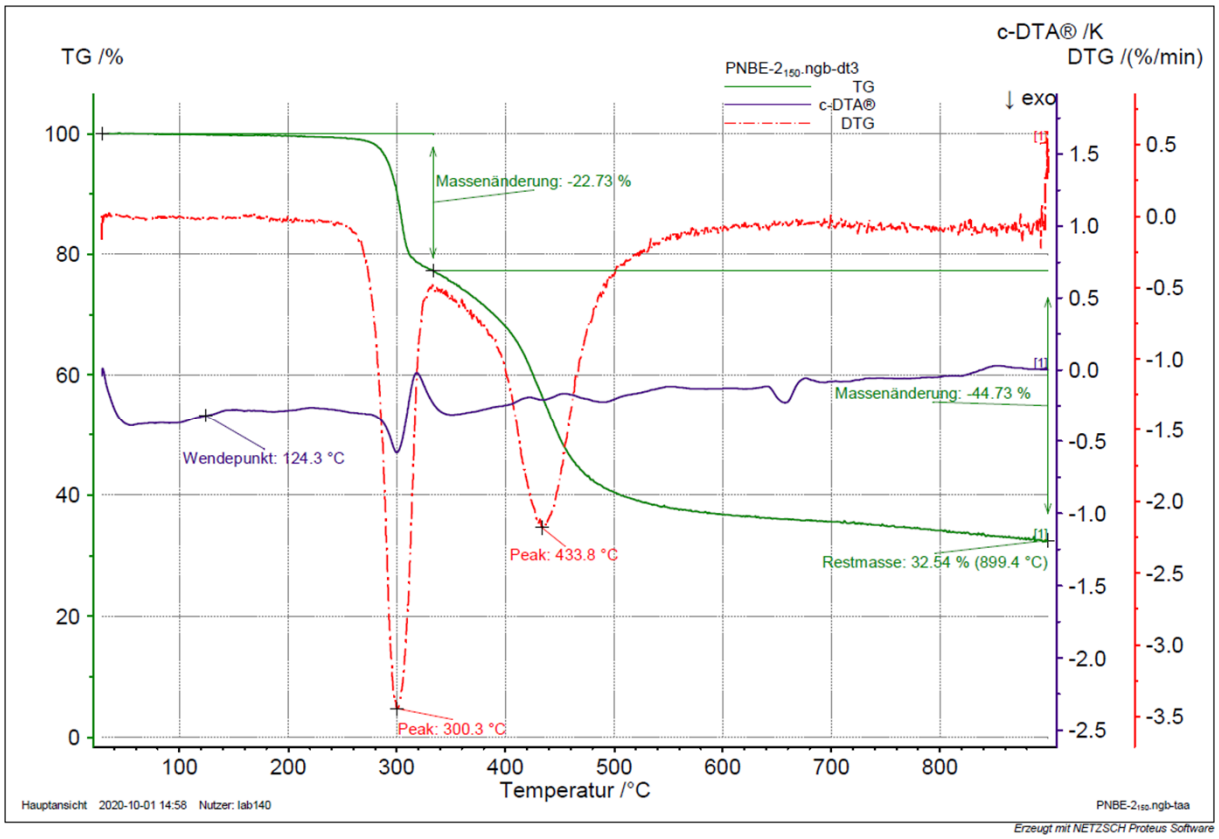

TG /%
c-DTA® /K
DTG /(%/min)
PNBE-3$_{400}$.ngb-dt3
TG
c-DTA®
DTG
↓ ex
Massenänderung: -8.33 %
Onset*: 266.4 °C
Massenänderung: -24.57 %
Massenänderung: -43.41 %
Wendepunkt: 170.3 °C
Peak: 437.8 °C
Peak: 275.8 °C
Restmasse: 23.69 % (899.4 °C)
Temperatur /°C
Hauptansicht 2020-10-13 14:24 Nutzer: lab140
PNBE-3$_{400}$.ngb-taa
Erzeugt mit NETZSCH Proteus Software

Operator ID: fb
Sample ID: PNBE-2_{150}
Sample Weight: 17.526 mg

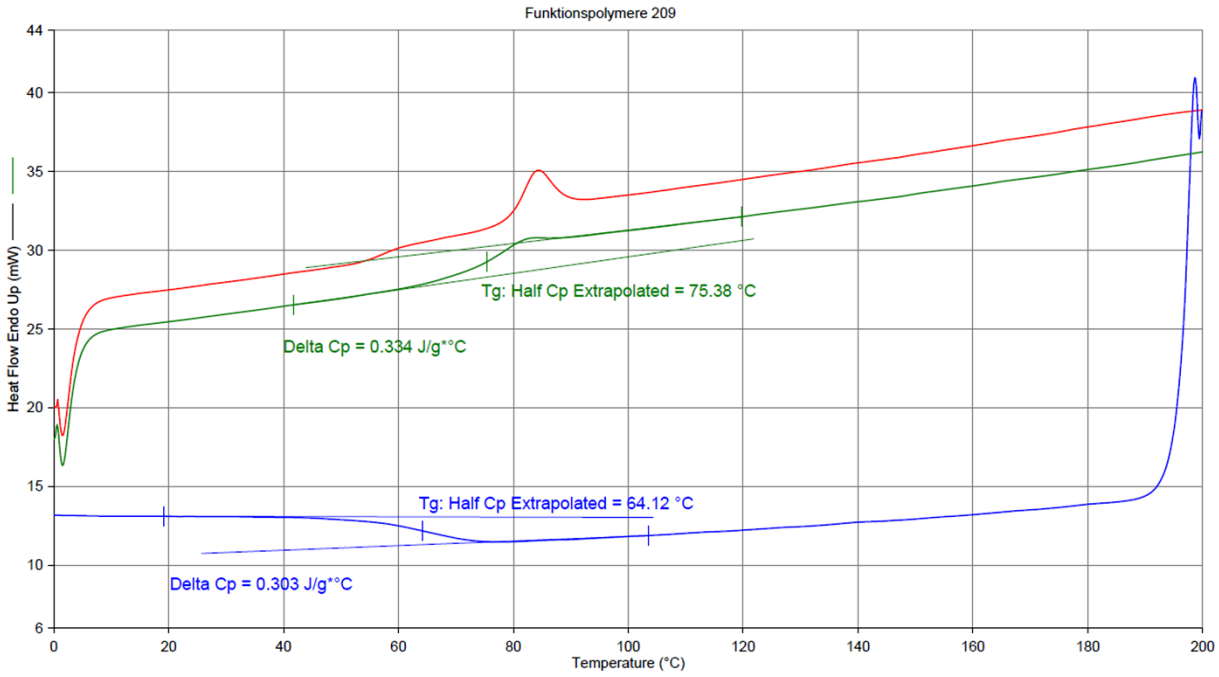


23.10.2020 15:15:01

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

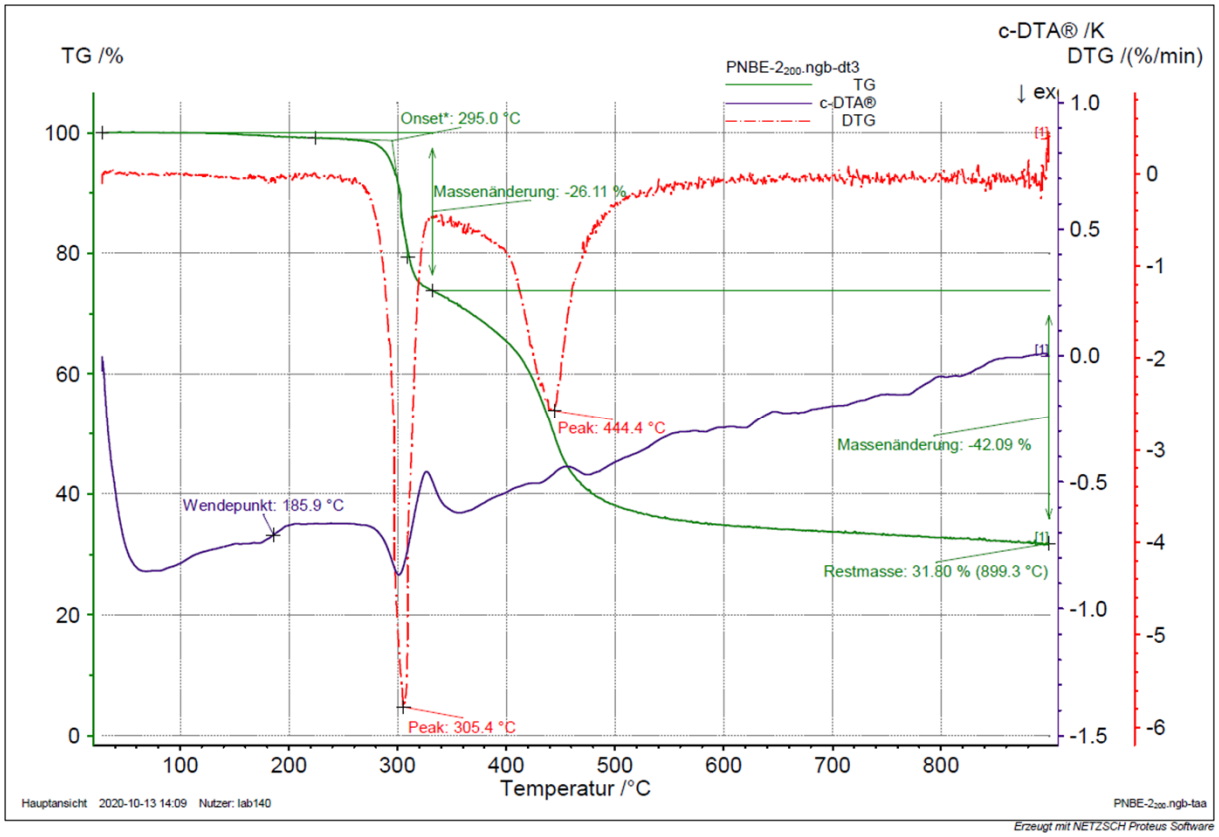


Operator ID: fb
Sample ID: PNBE-2_{200}
Sample Weight: 17.442 mg

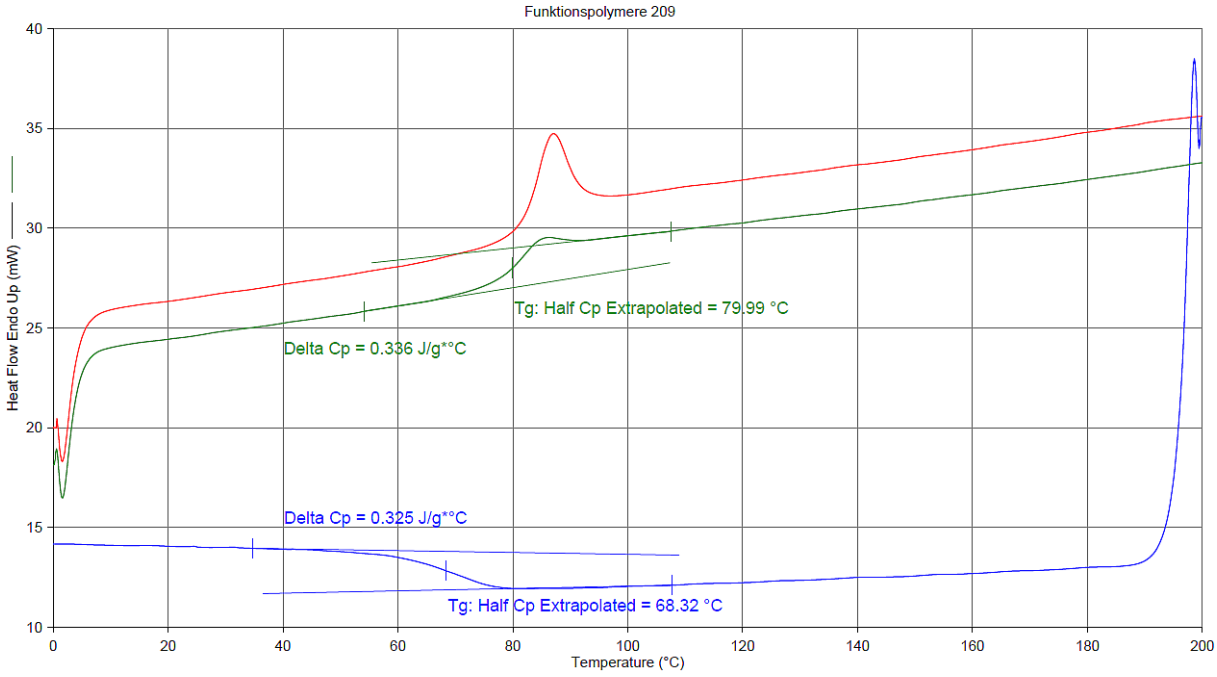


28.10.2020 13:26:30

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

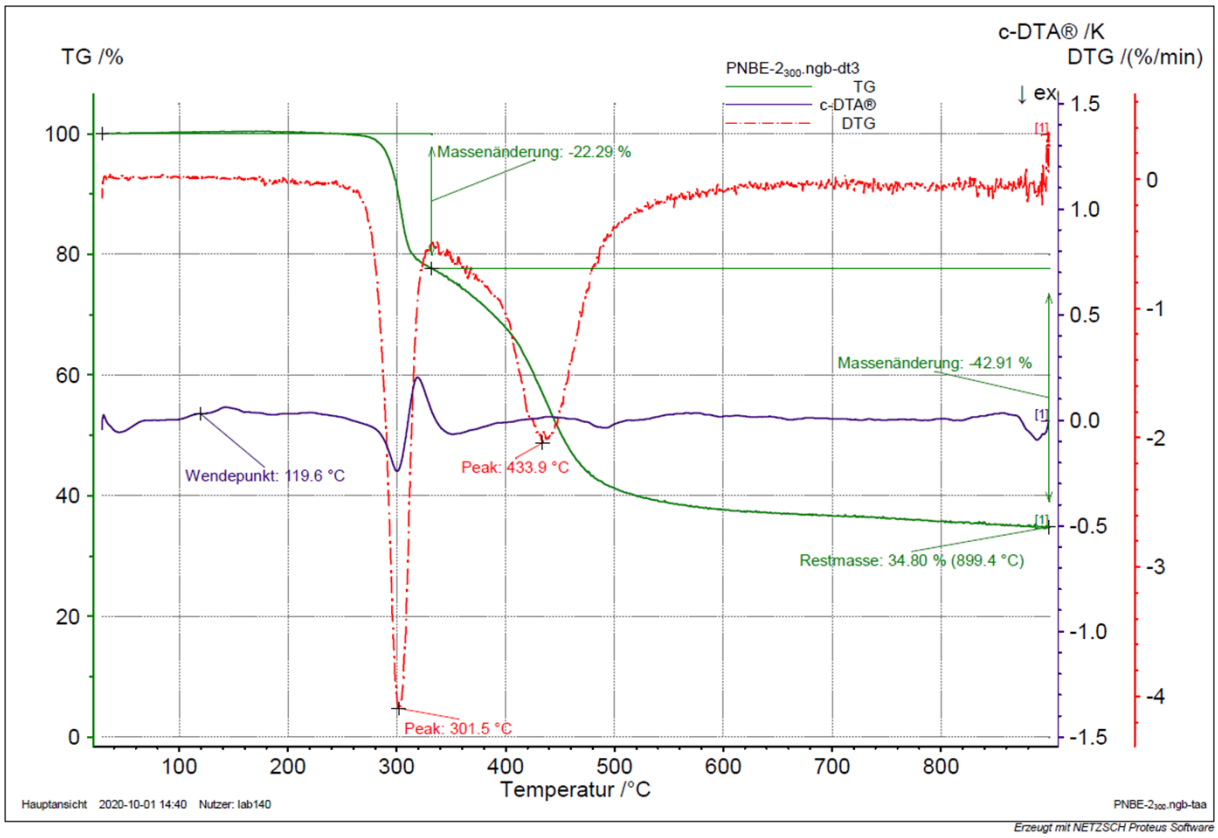


Operator ID: fb
Sample ID: PNBE-2_{300}
Sample Weight: 17.766 mg

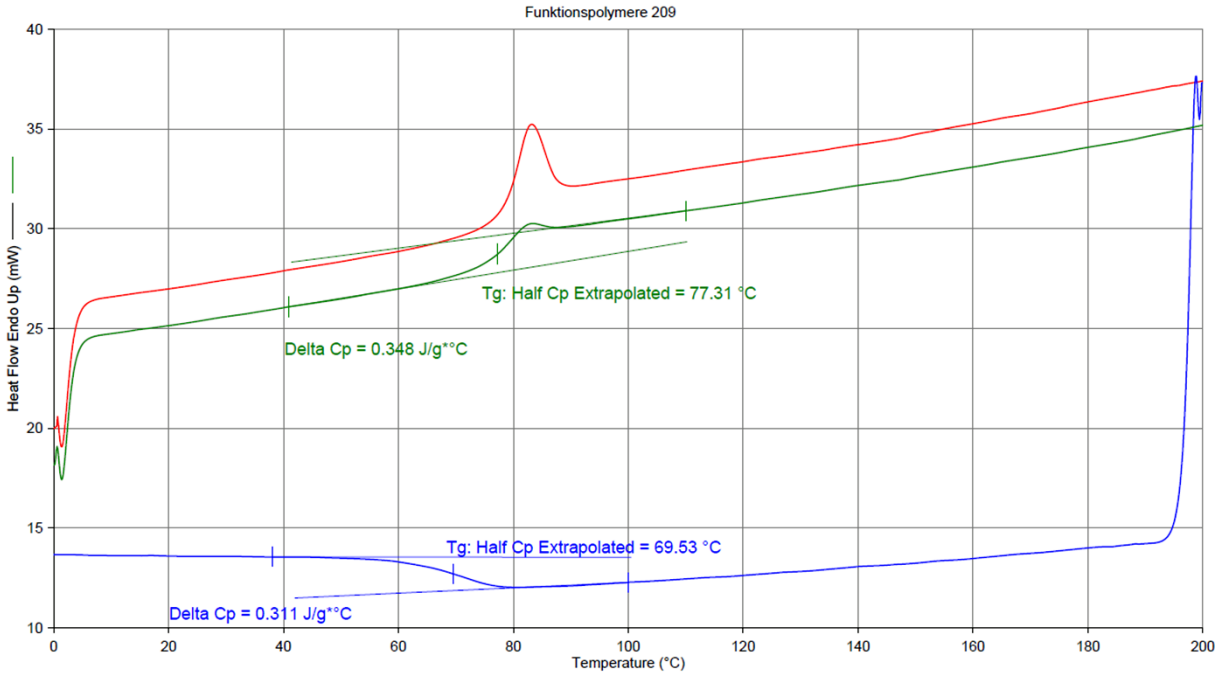


28.10.2020 15:23:26

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

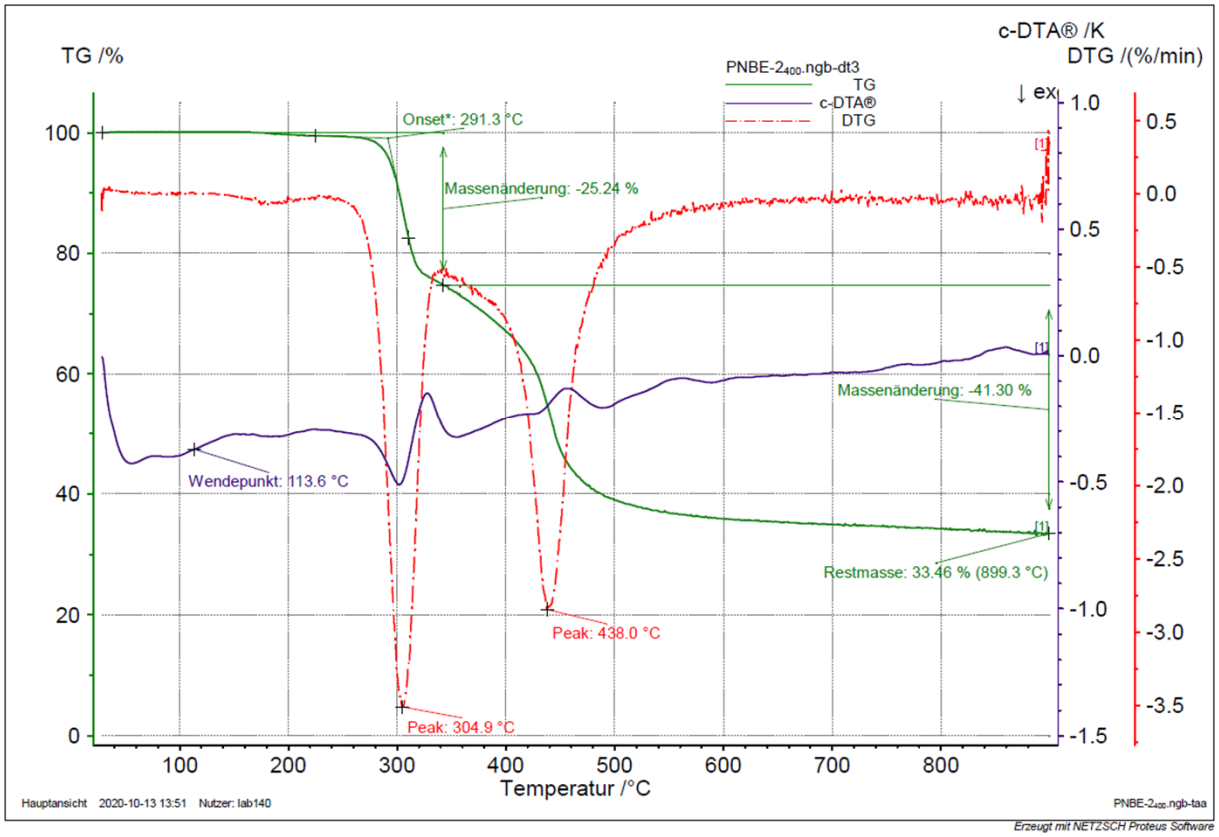


Operator ID: fb
Sample ID: PNBE-2_{400}
Sample Weight: 16.168 mg

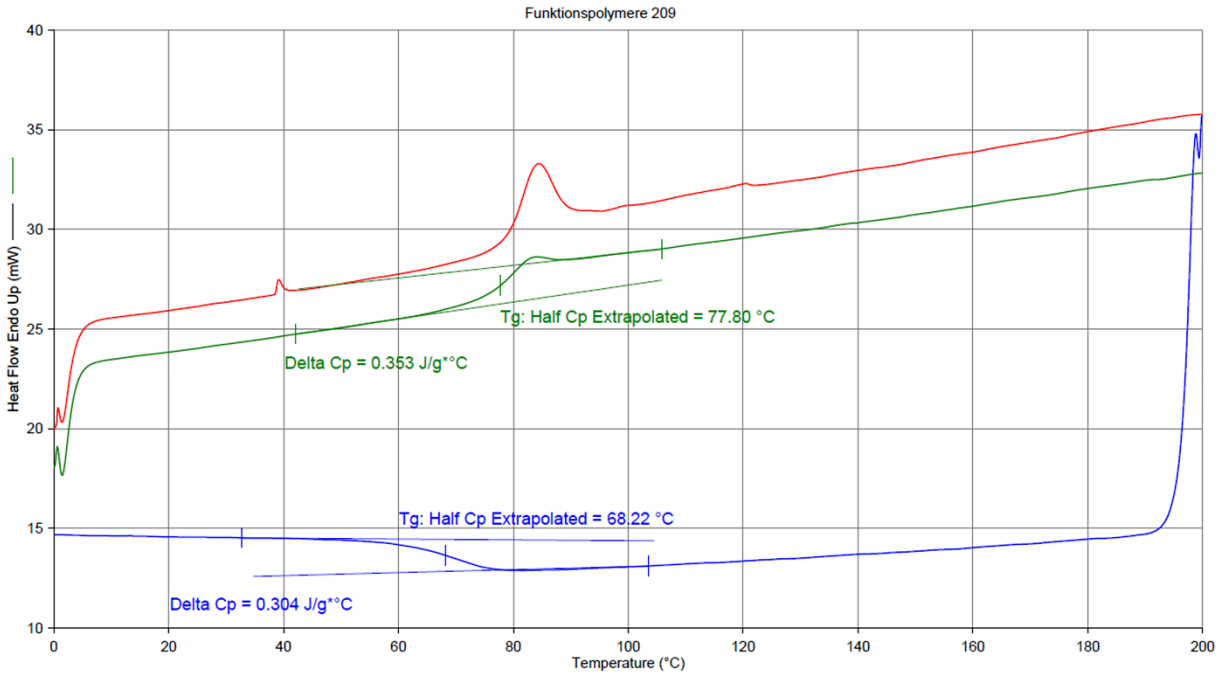


28.10.2020 13:19:57

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

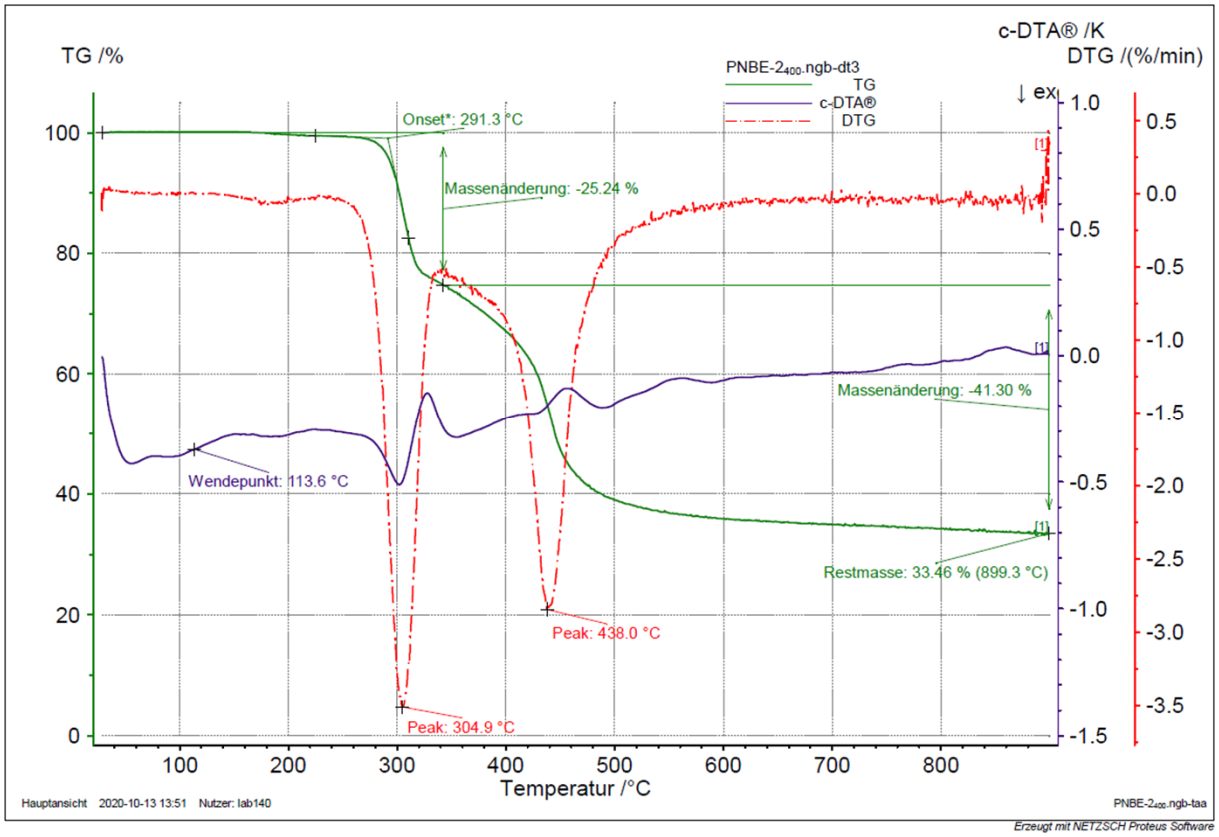


Operator ID: fb
Sample ID: PNBE-2_{800}
Sample Weight: 15.874 mg

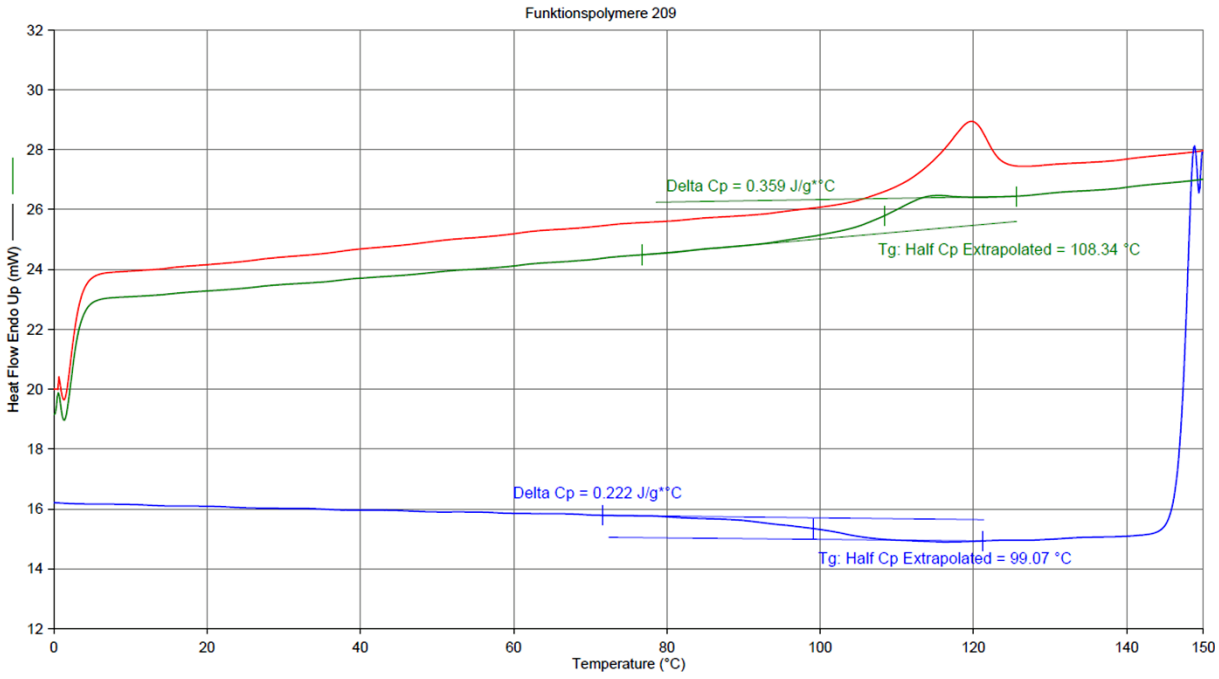


28.10.2020 13:09:14

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

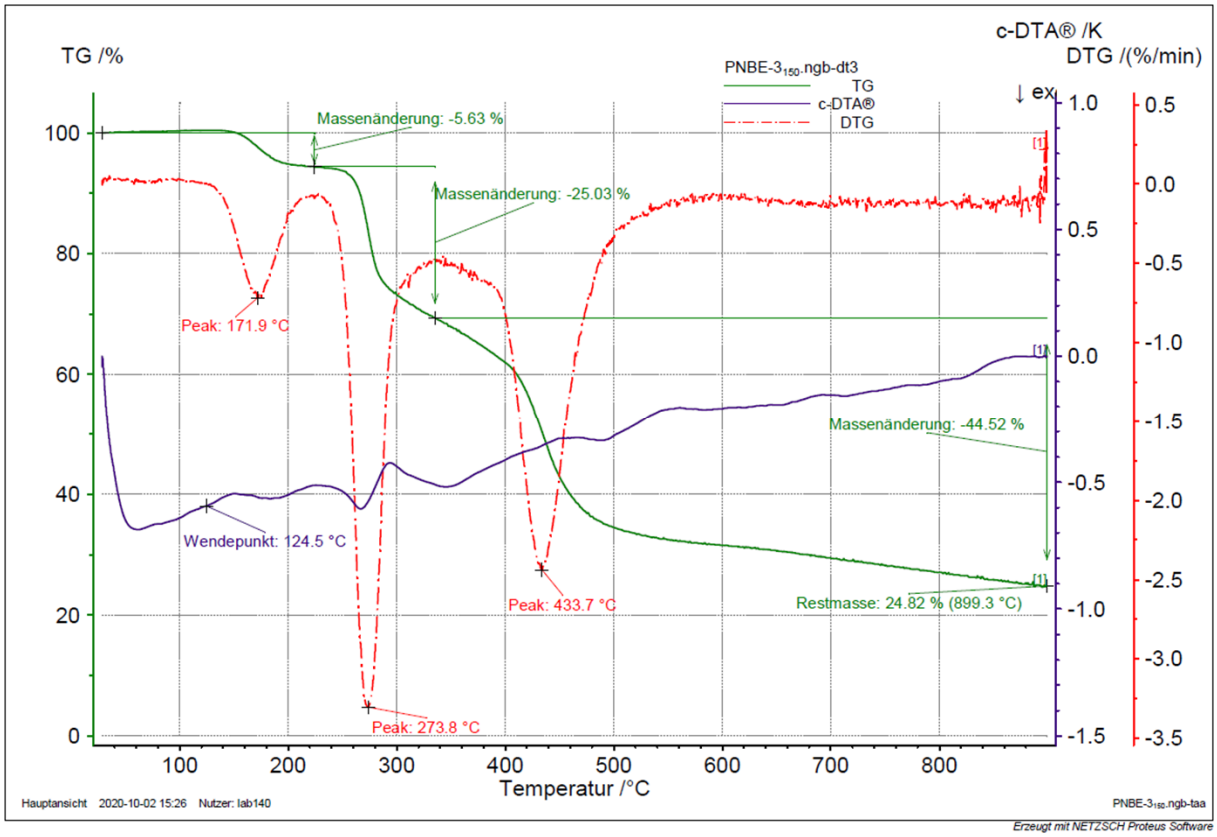


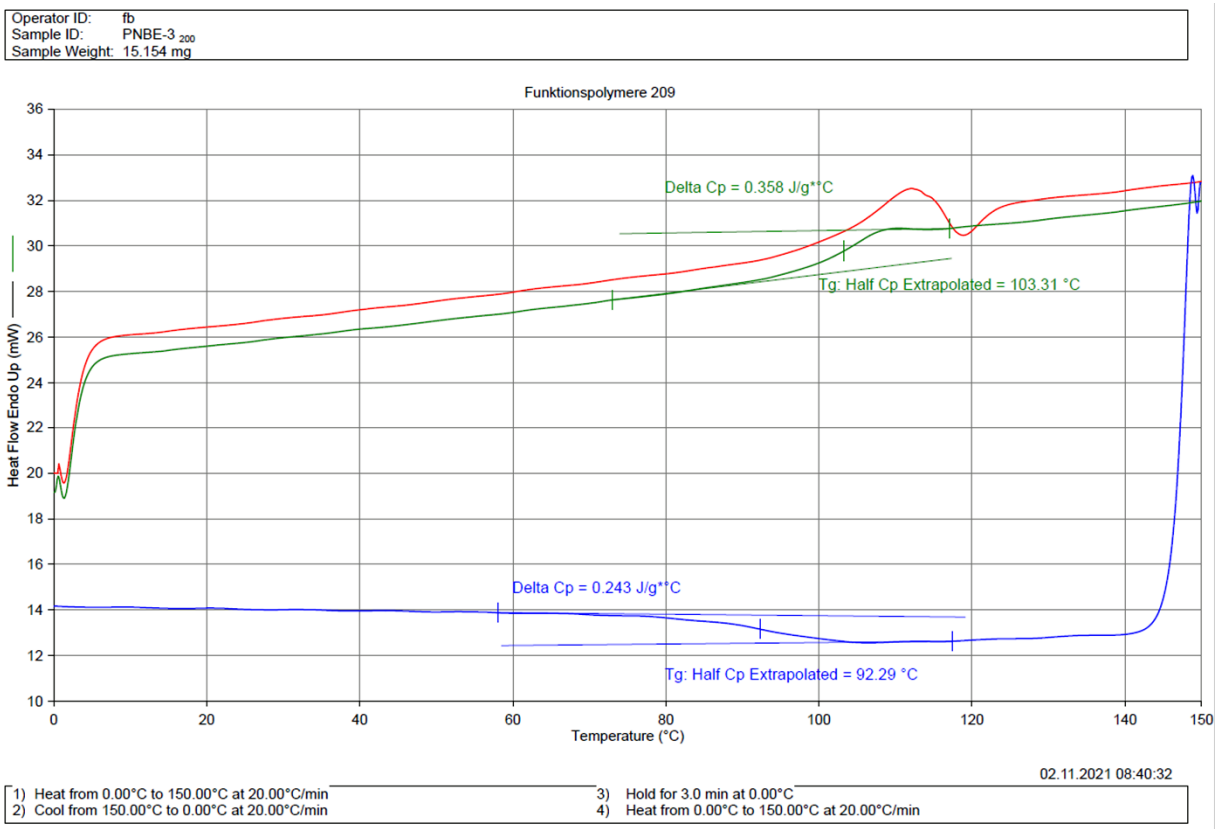
Operator ID: fb
Sample ID: PNBE-3 $_{150}$
Sample Weight: 9.736 mg

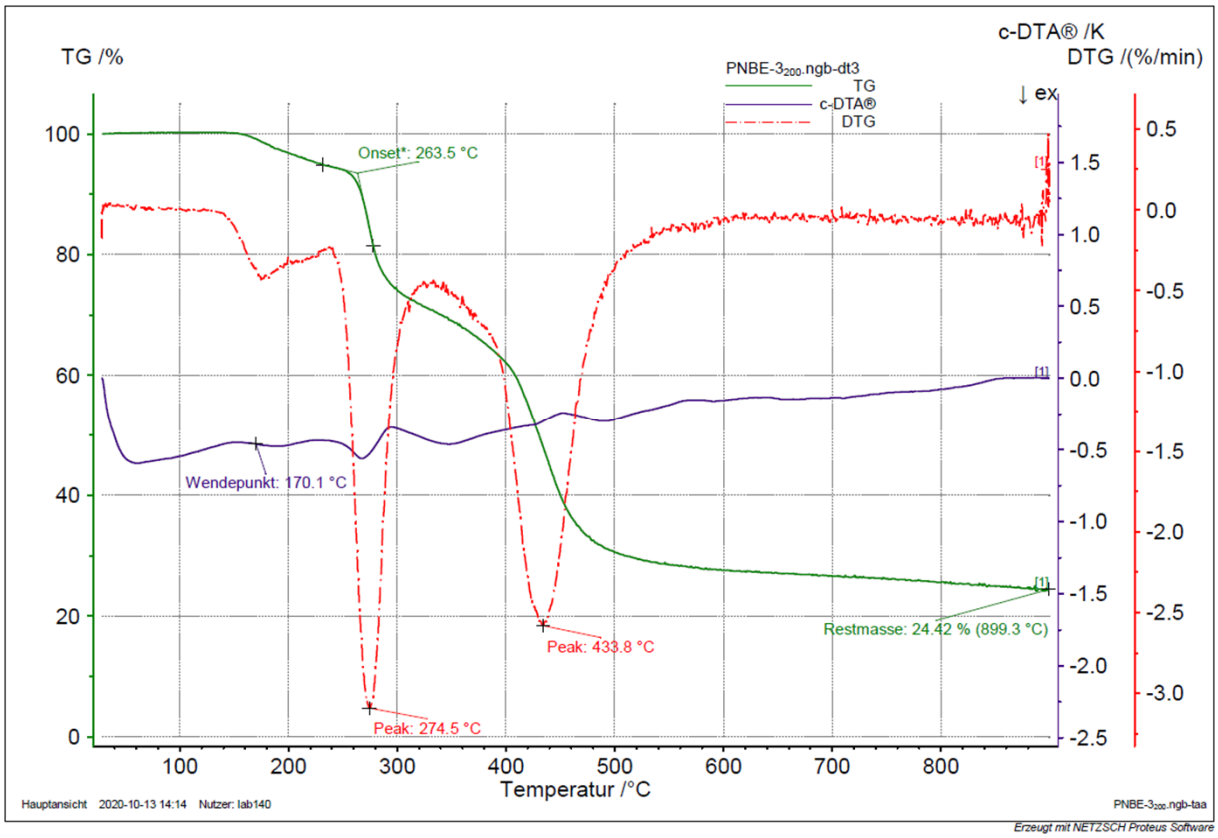


02.11.2021 07:55:07

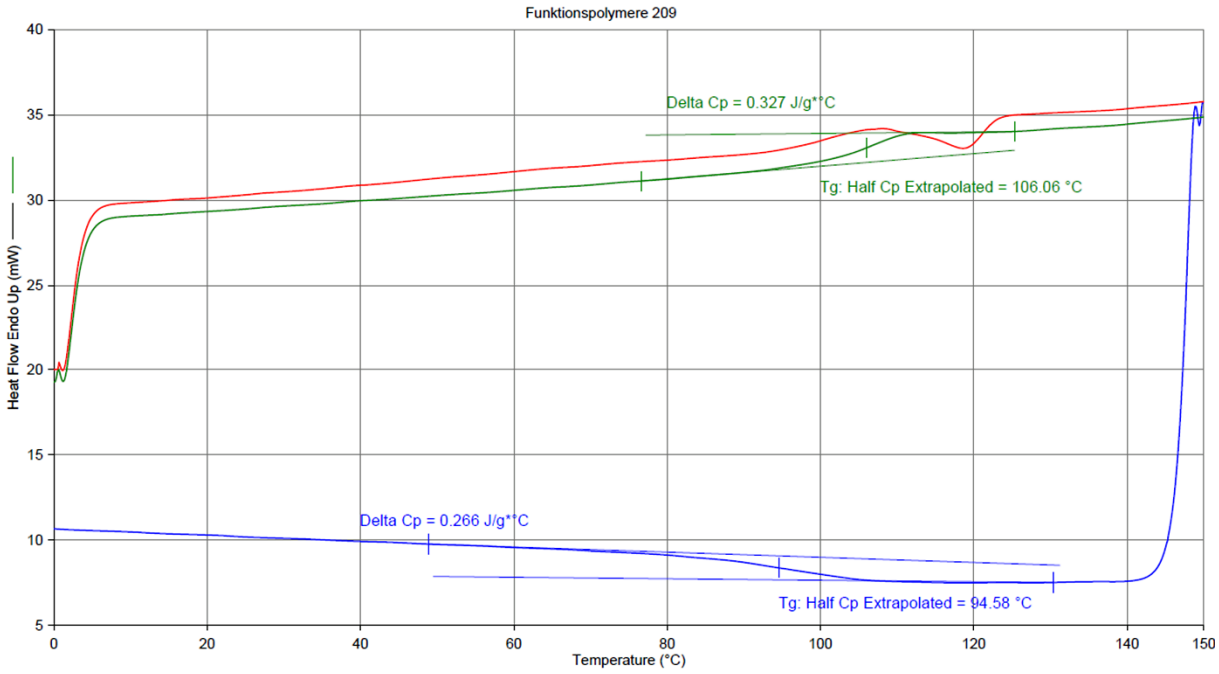
1) Heat from 0.00°C to 150.00°C at 20.00°C/min
2) Cool from 150.00°C to 0.00°C at 20.00°C/min
3) Hold for 3.0 min at 0.00°C
4) Heat from 0.00°C to 150.00°C at 20.00°C/min



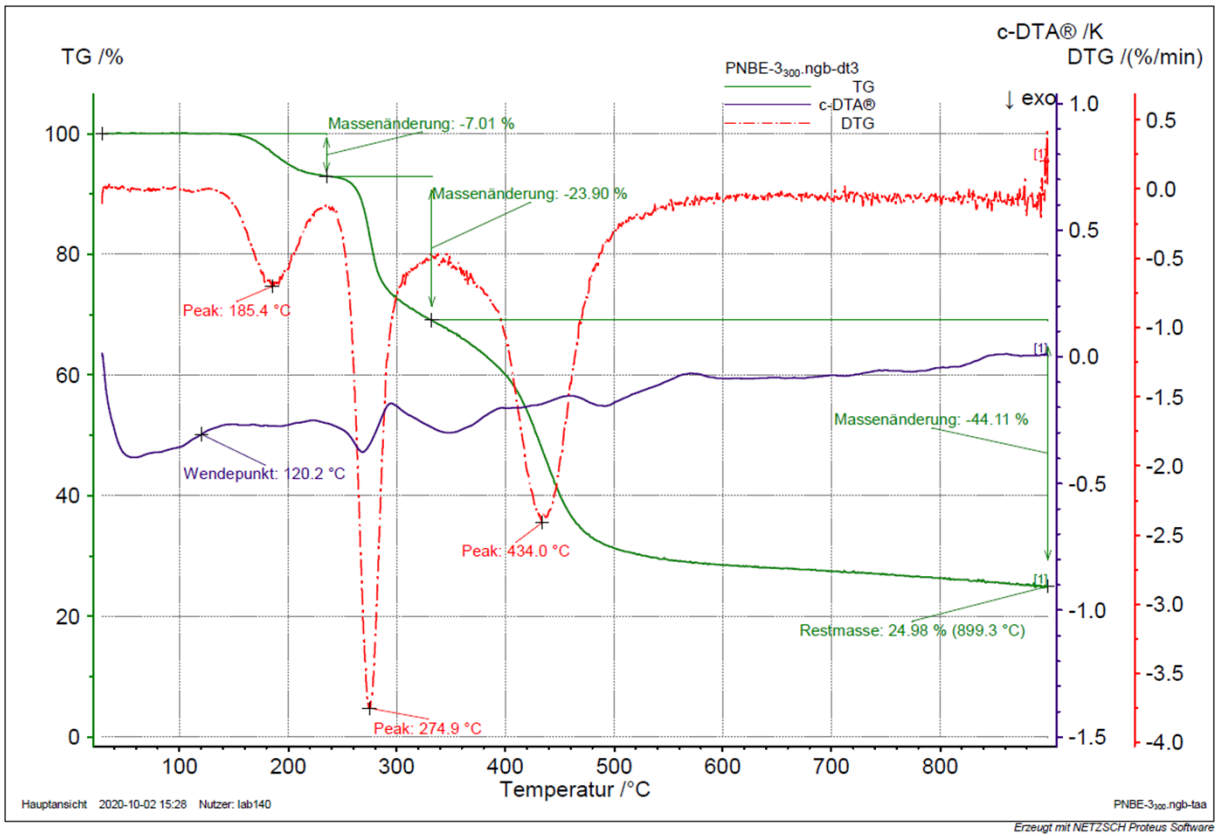

Operator ID: fb
Sample ID: PNBE-3 200
Sample Weight: 15.154 mg
Funktionspolymere 209
Delta Cp = 0.358 J/g**C
Tg: Half Cp Extrapolated = 103.31 °C
Delta Cp = 0.243 J/g**C
Tg: Half Cp Extrapolated = 92.29 °C
Heat Flow Endo Up (mW)
Temperature (°C)
02.11.2021 08:40:32
1) Heat from 0.00°C to 150.00°C at 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


TG /%
c-DTA® /K
DTG /(%/min)
PNBE-3200.ngb-dt3
TG
c-DTA®
DTG
↓ ex
Onset*: 263.5 °C
Wendepunkt: 170.1 °C
Peak: 433.8 °C
Peak: 274.5 °C
Restmasse: 24.42 % (899.3 °C)
Temperatur /°C
Hauptansicht 2020-10-13 14:14 Nutzer: lab140
PNBE-3200.ngb-taa
Erzeugt mit NETZSCH Proteus Software

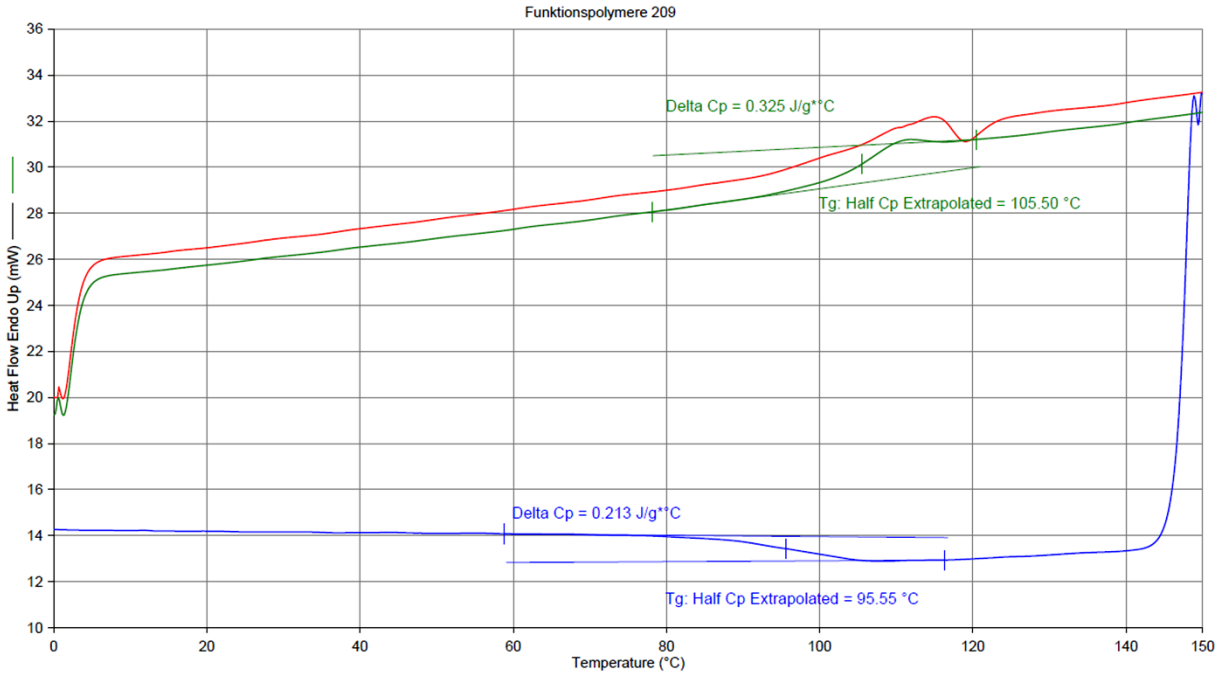
Operator ID: fb
Sample ID: PNBE-3 300
Sample Weight: 15.836 mg



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

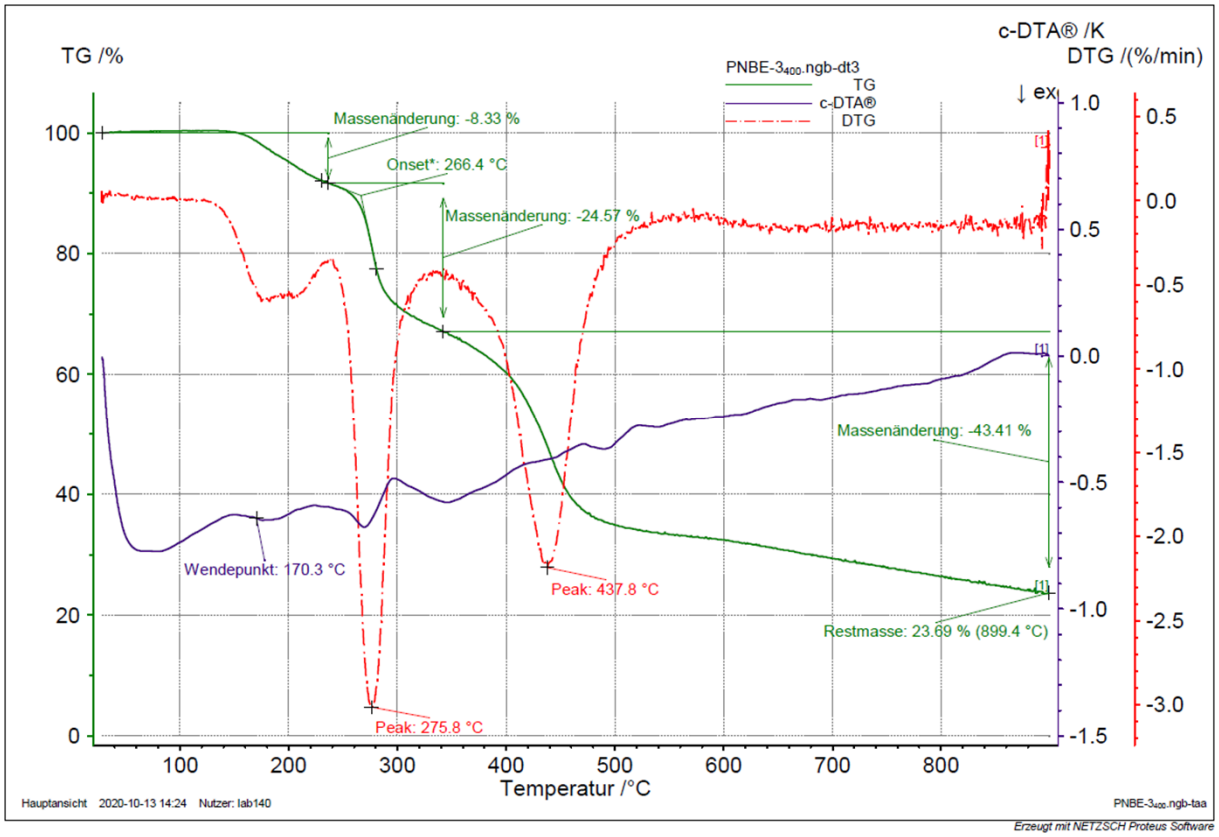


Operator ID: fb
Sample ID: PNBE-3 400
Sample Weight: 15.128 mg

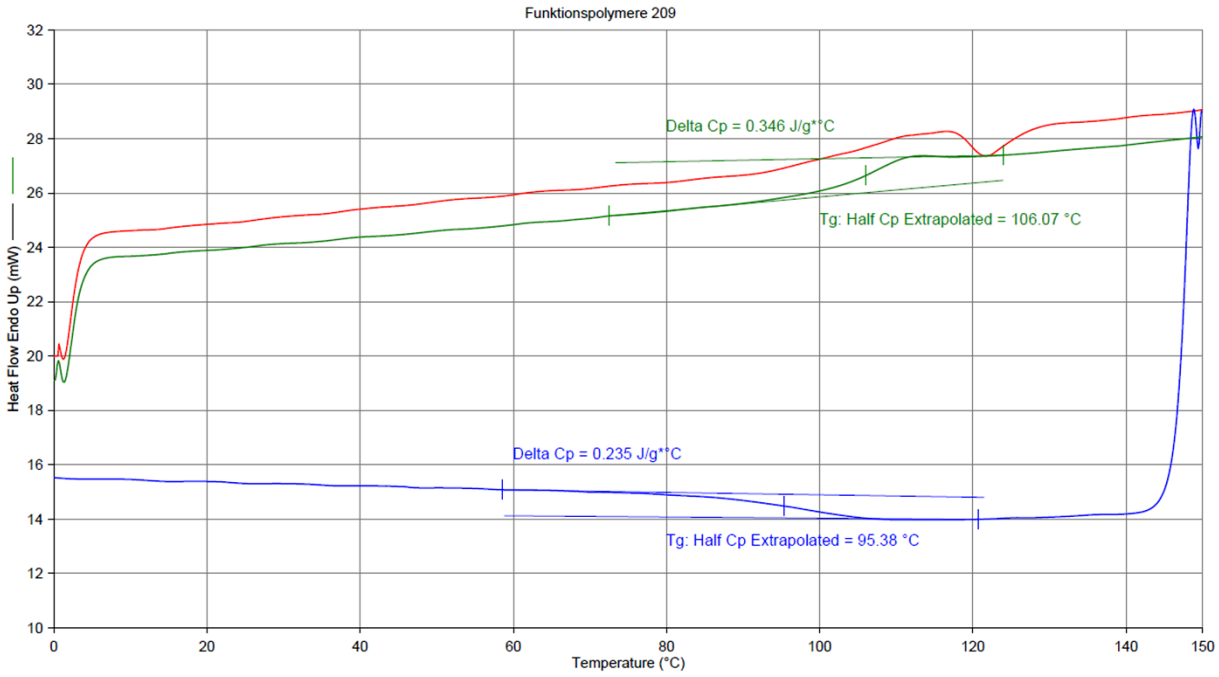


02.11.2021 08:51:07

1) Heat from 0.00°C to 150.00°C at 20.00°C/min
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

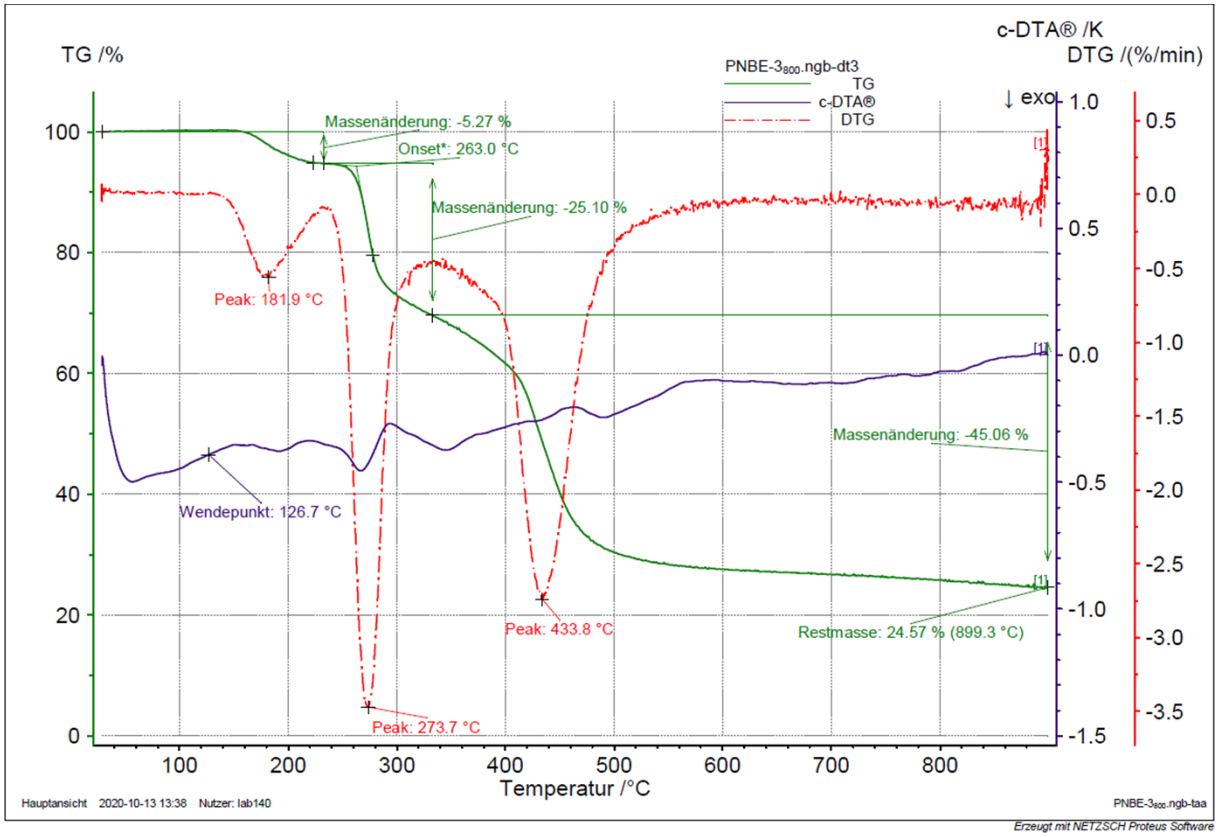


Operator ID: fb
Sample ID: PNBE-3 800
Sample Weight: 11.110 mg

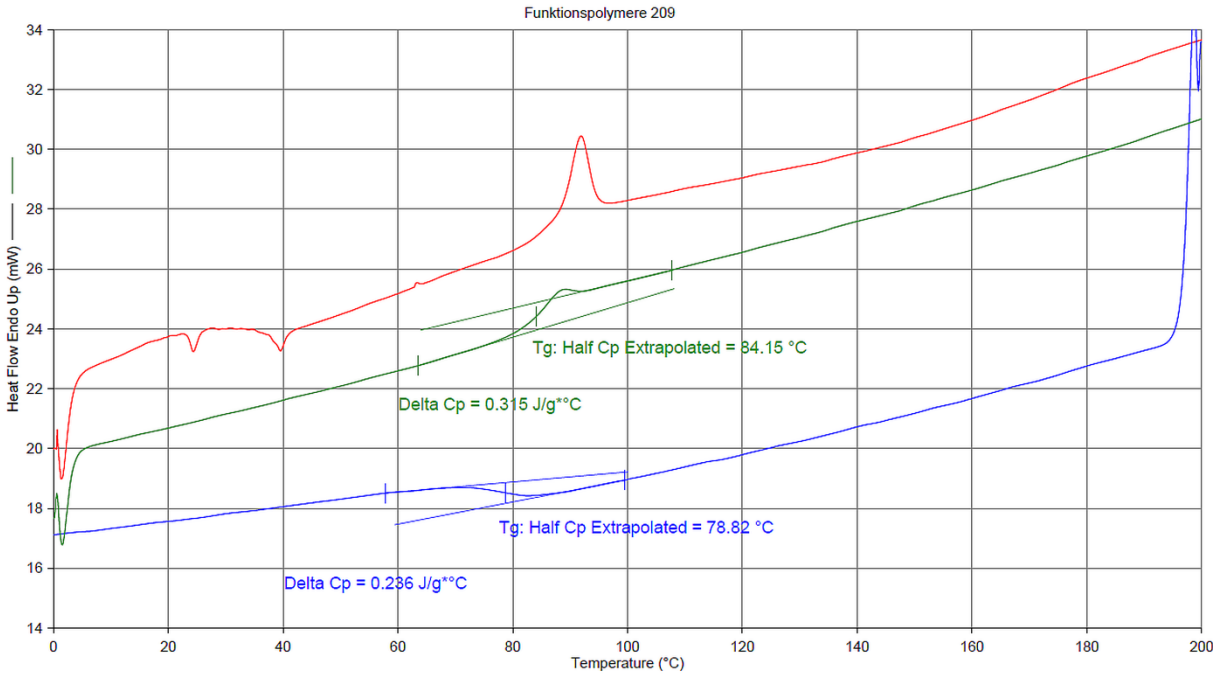


02.11.2021 08:04:25

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

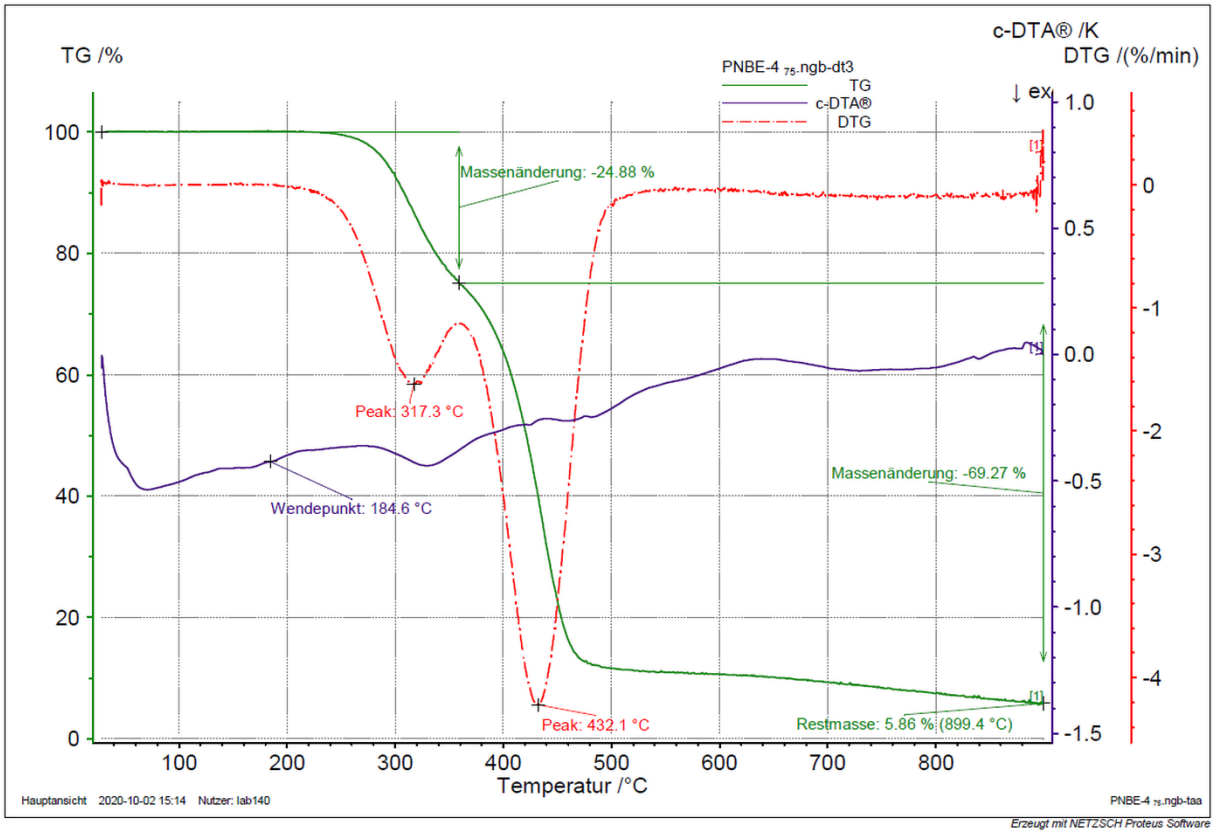


Operator ID: fb
Sample ID: PNBE-4 $_{75}$
Sample Weight: 8.780 mg

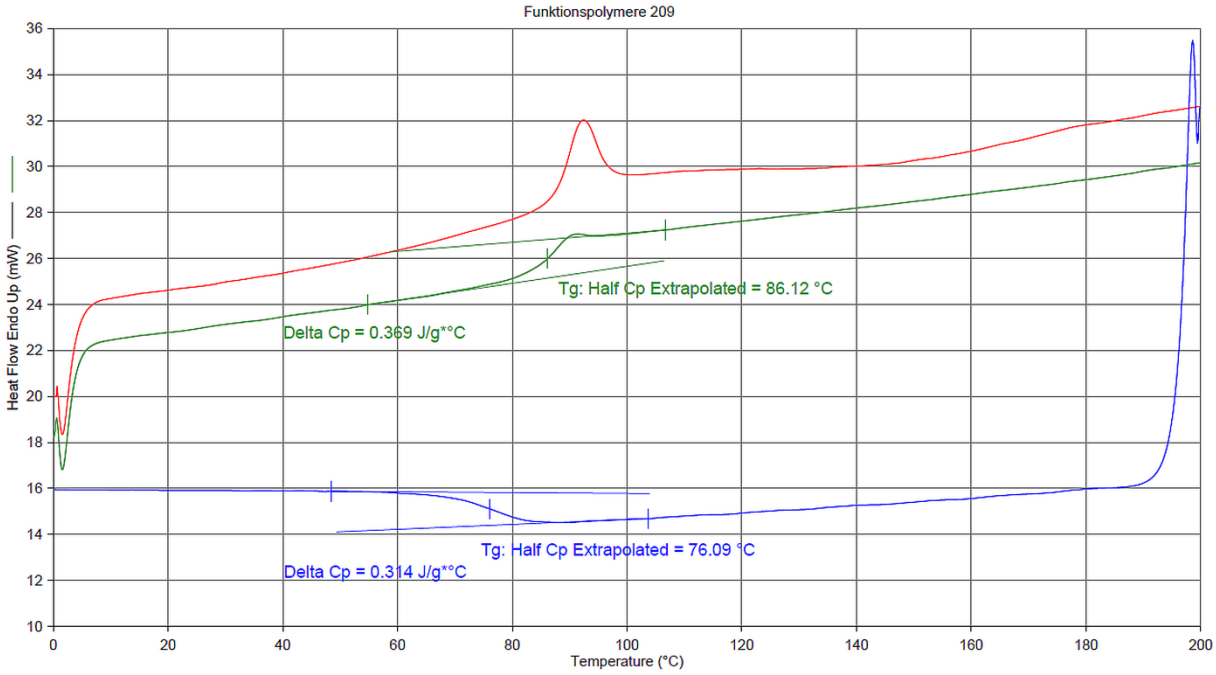


28.10.2020 15:28:54

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

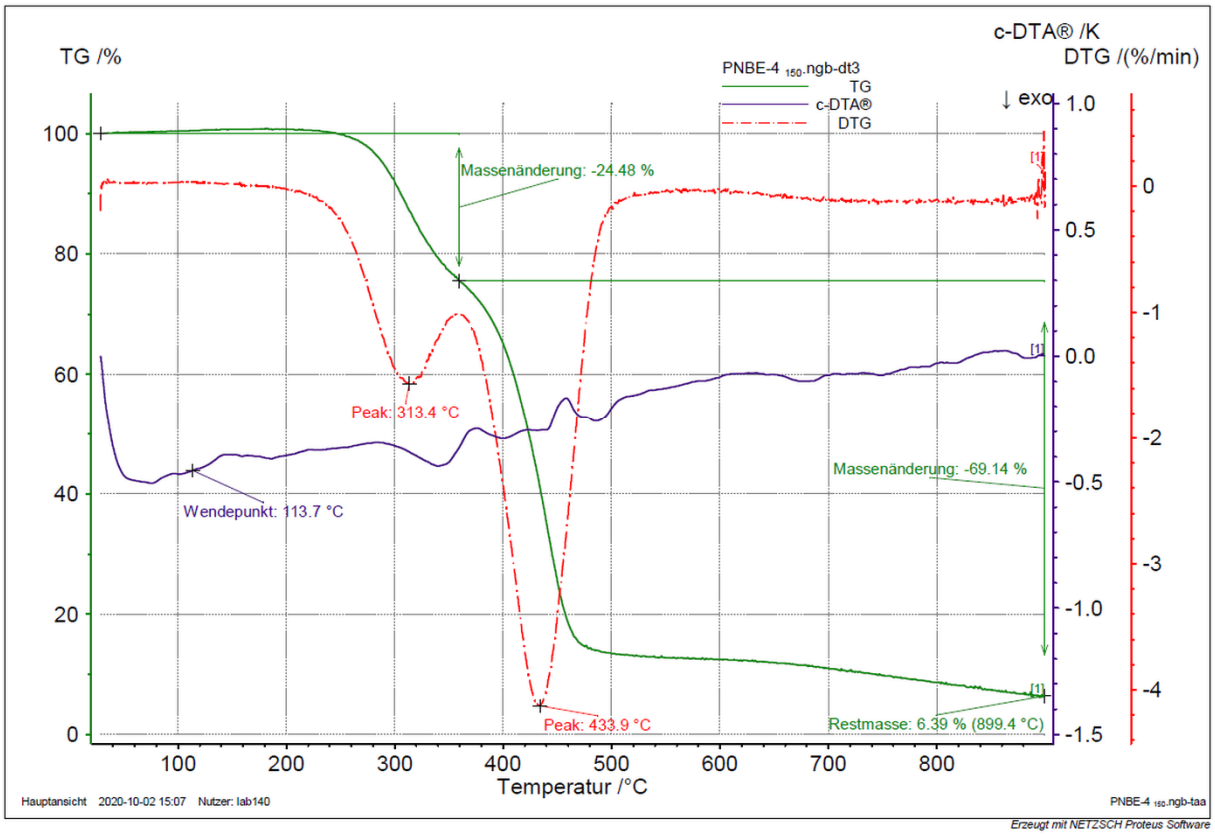


Operator ID: fb
Sample ID: PNBE-4 $_{150}$
Sample Weight: 13.672 mg

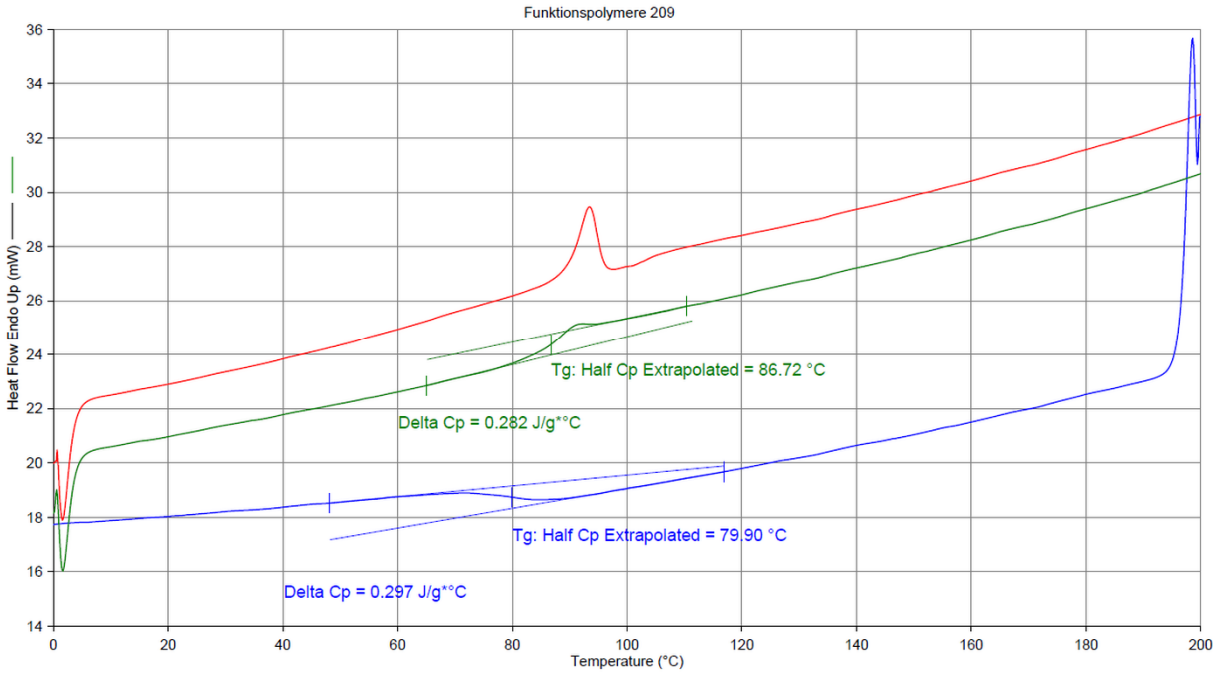


28.10.2020 15:03:39

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

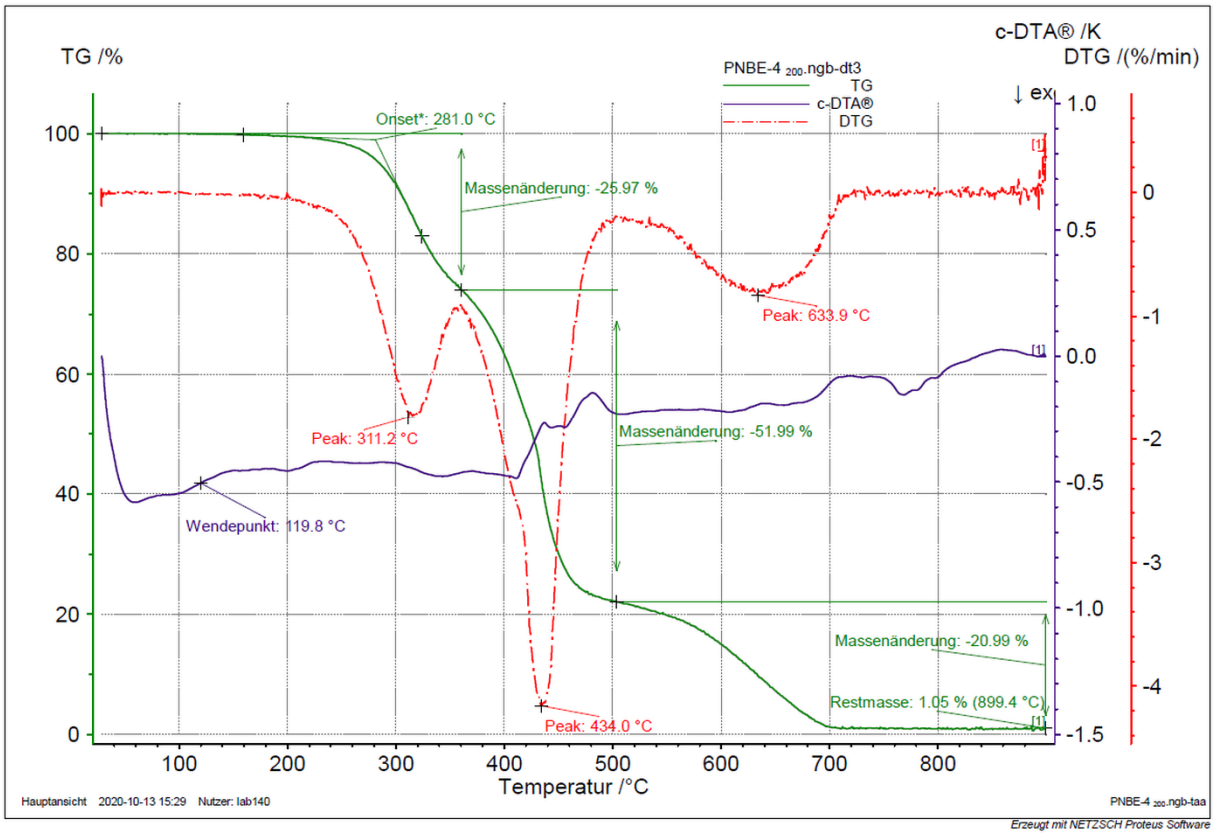


Operator ID: fb
Sample ID: PNBE-4 $_{200}$
Sample Weight: 8.328 mg

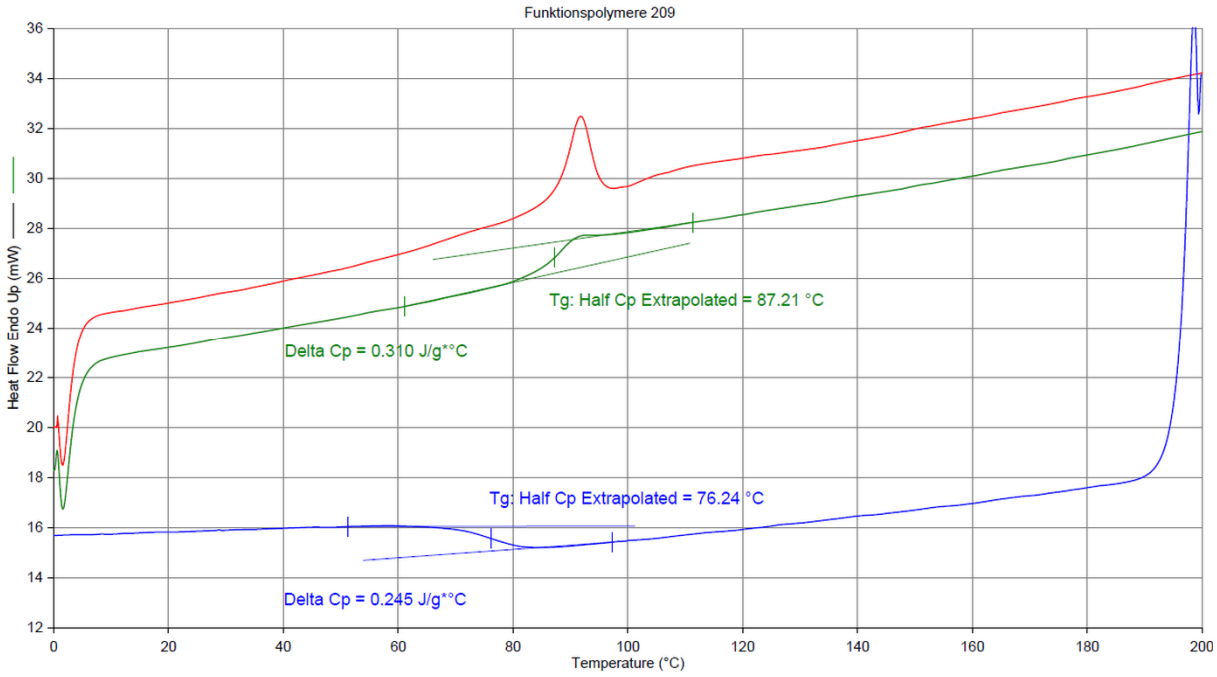


29.10.2020 13:22:40

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

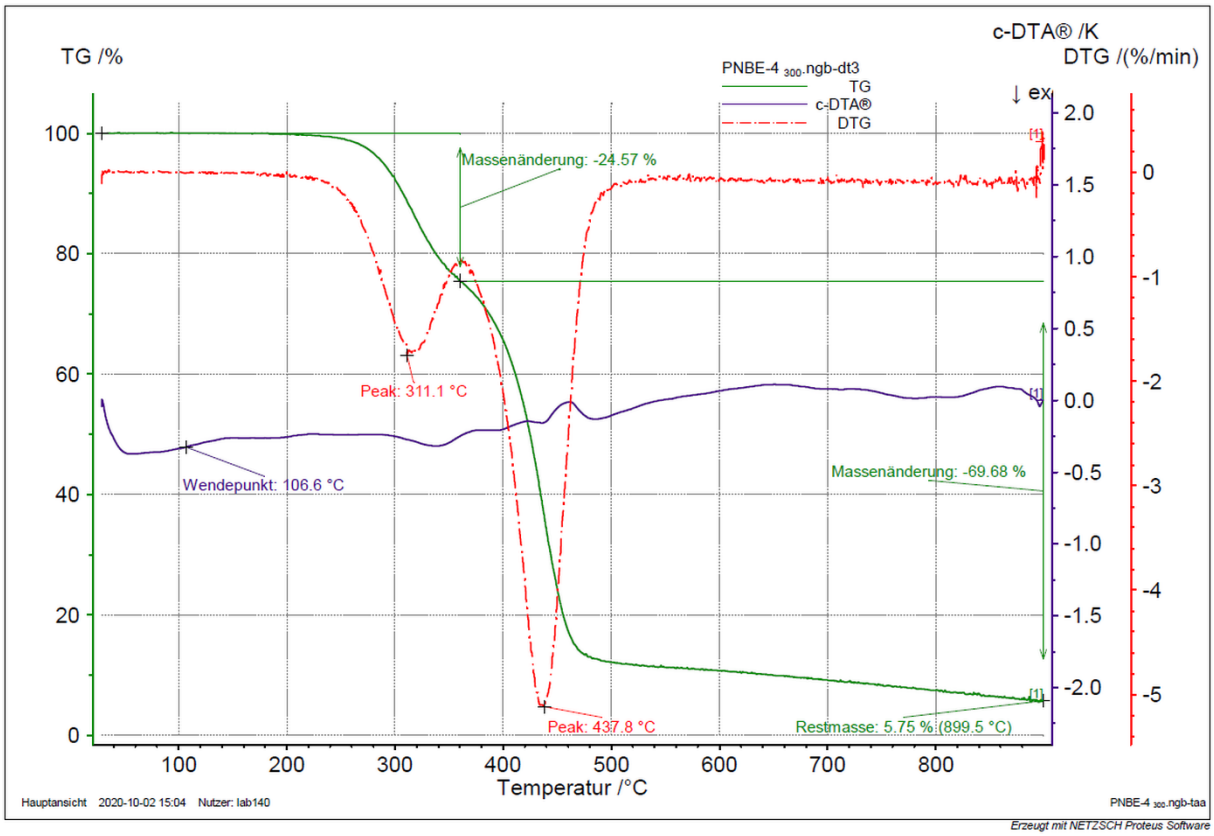


Operator ID: fb
Sample ID: PNBE-4 300
Sample Weight: 12.060 mg

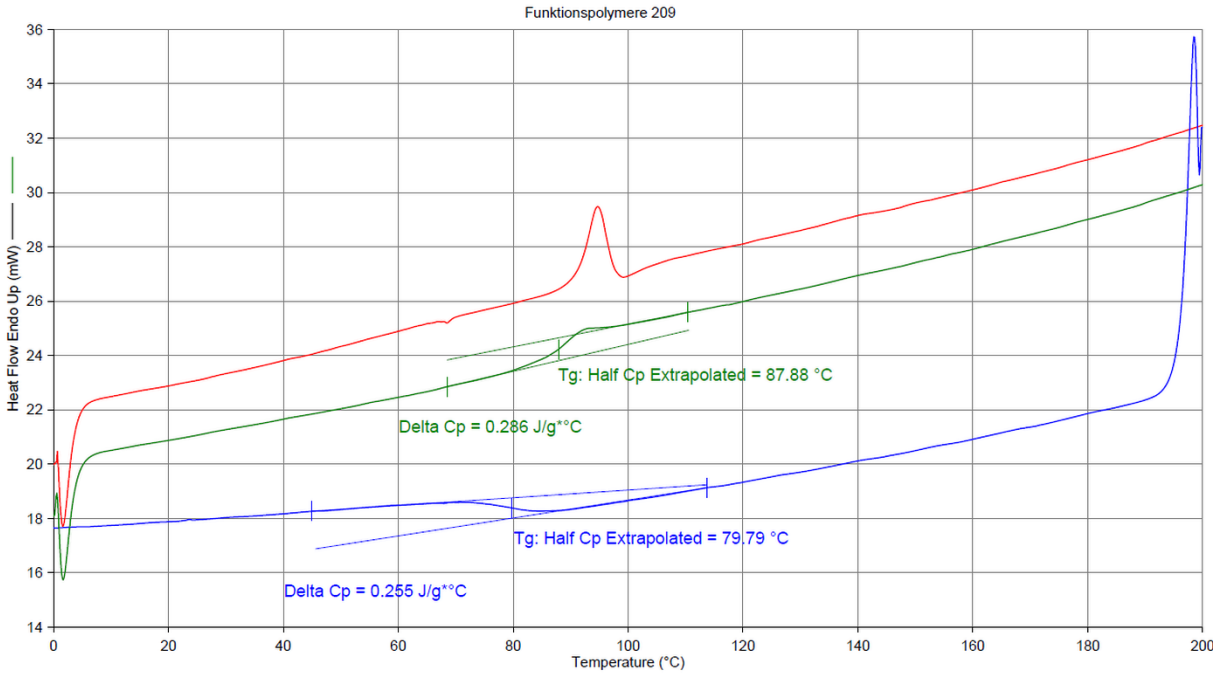


23.10.2020 15:42:09

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

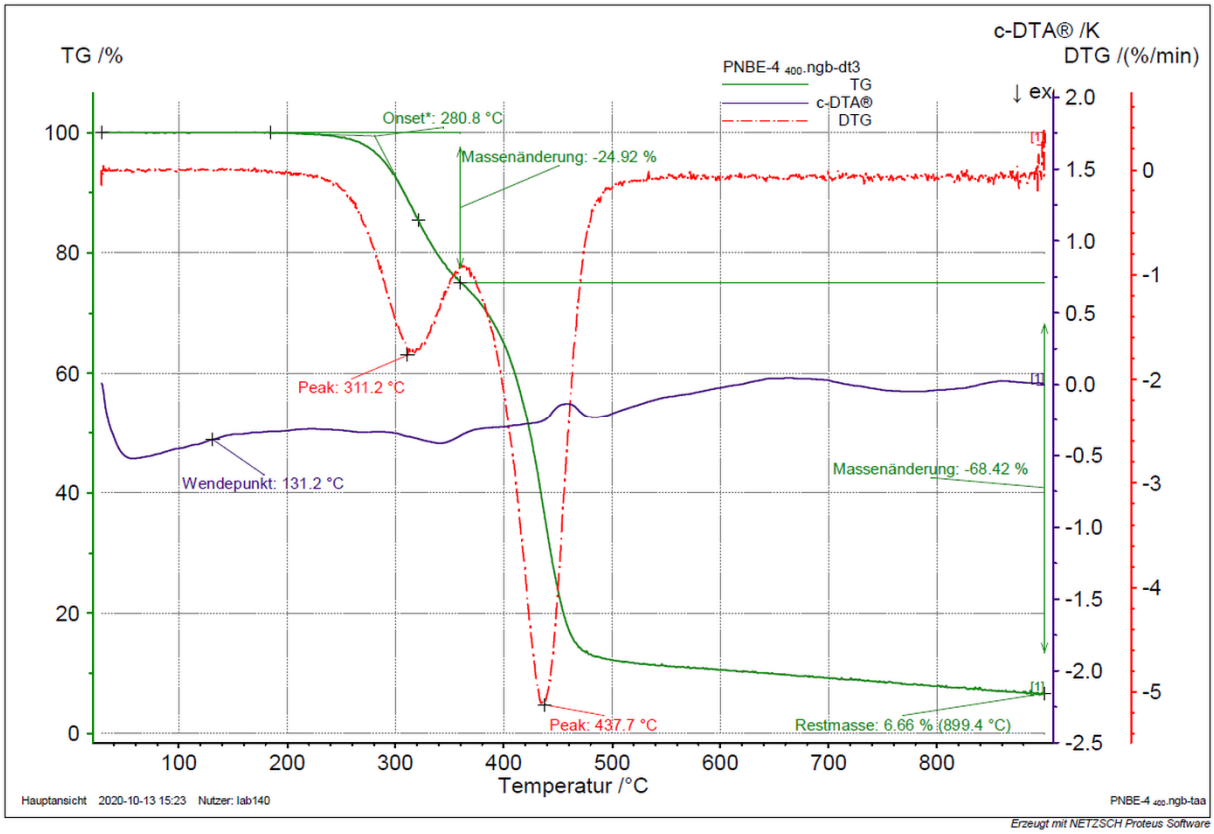


Operator ID: fb
Sample ID: PNBE-4 400
Sample Weight: 8.786 mg

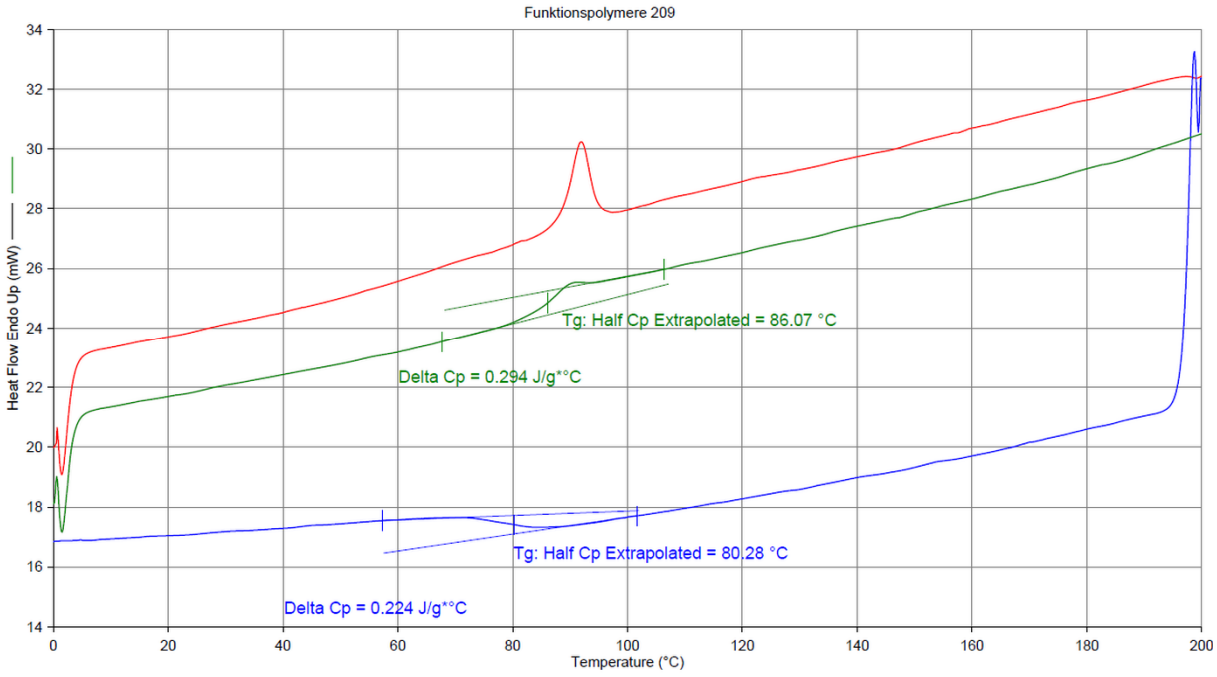


28.10.2020 14:56:35

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

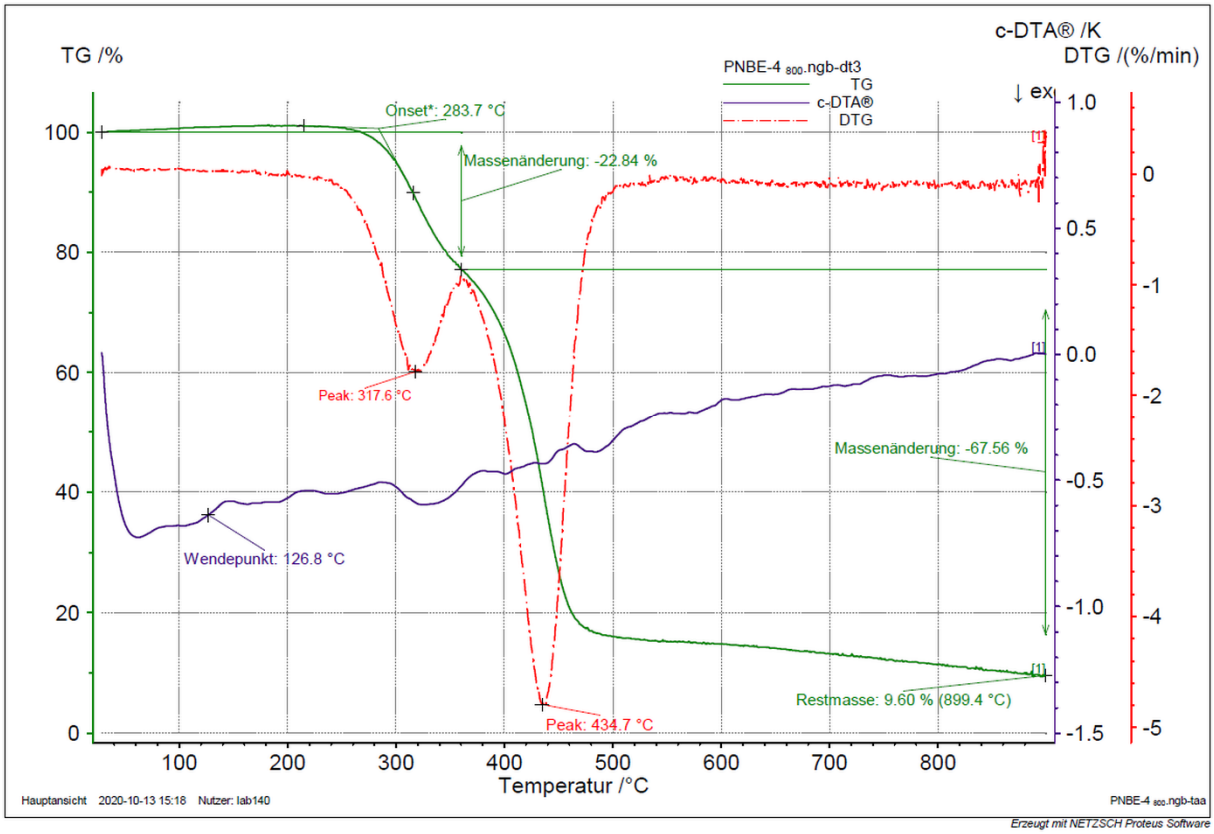


Operator ID: fb
Sample ID: PNBE-4 800
Sample Weight: 8.220 mg

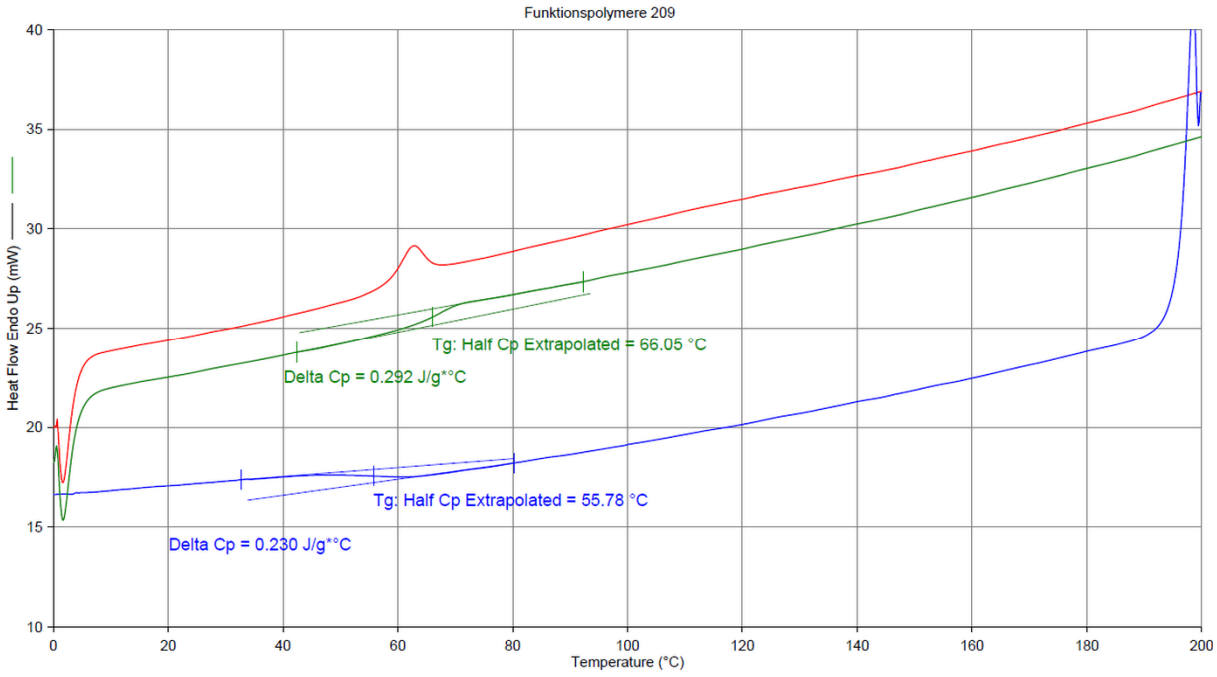


28.10.2020 16:04:11

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

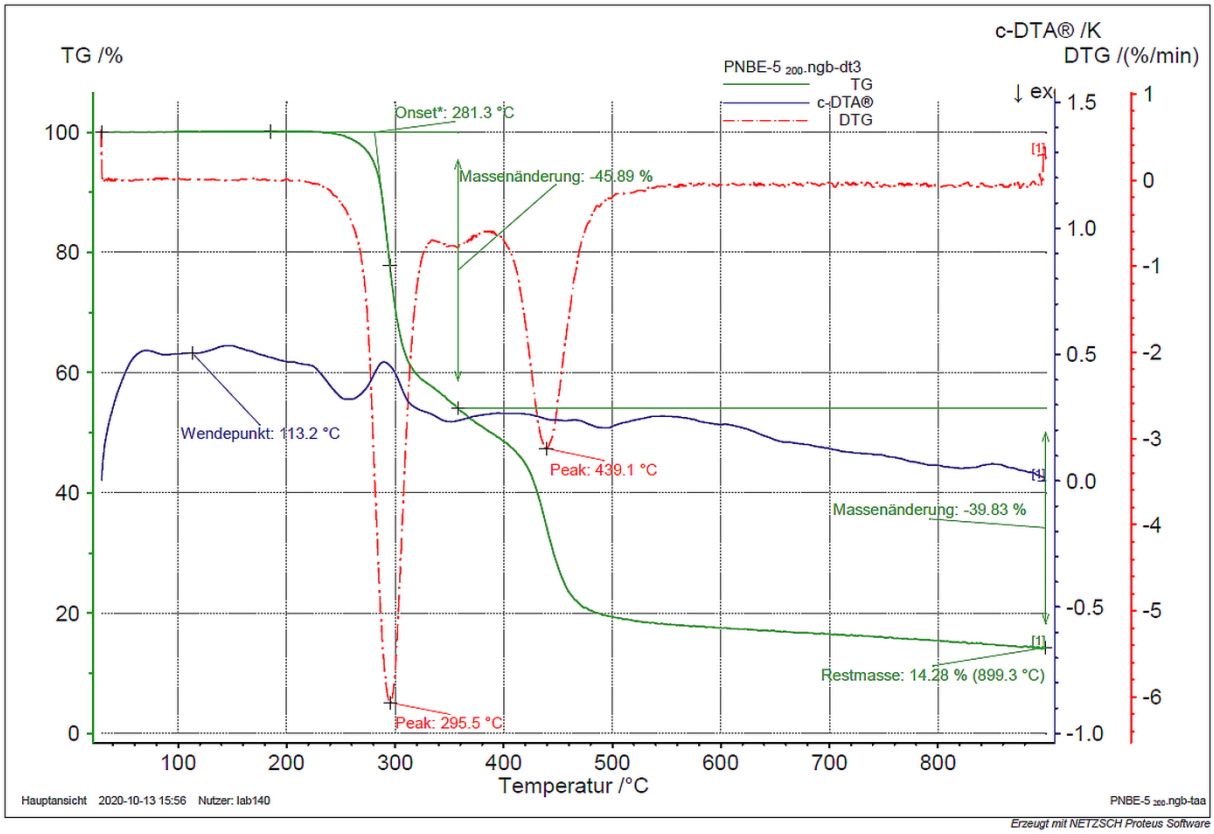


Operator ID: fb
Sample ID: PNBE-5 200
Sample Weight: 8.594 mg

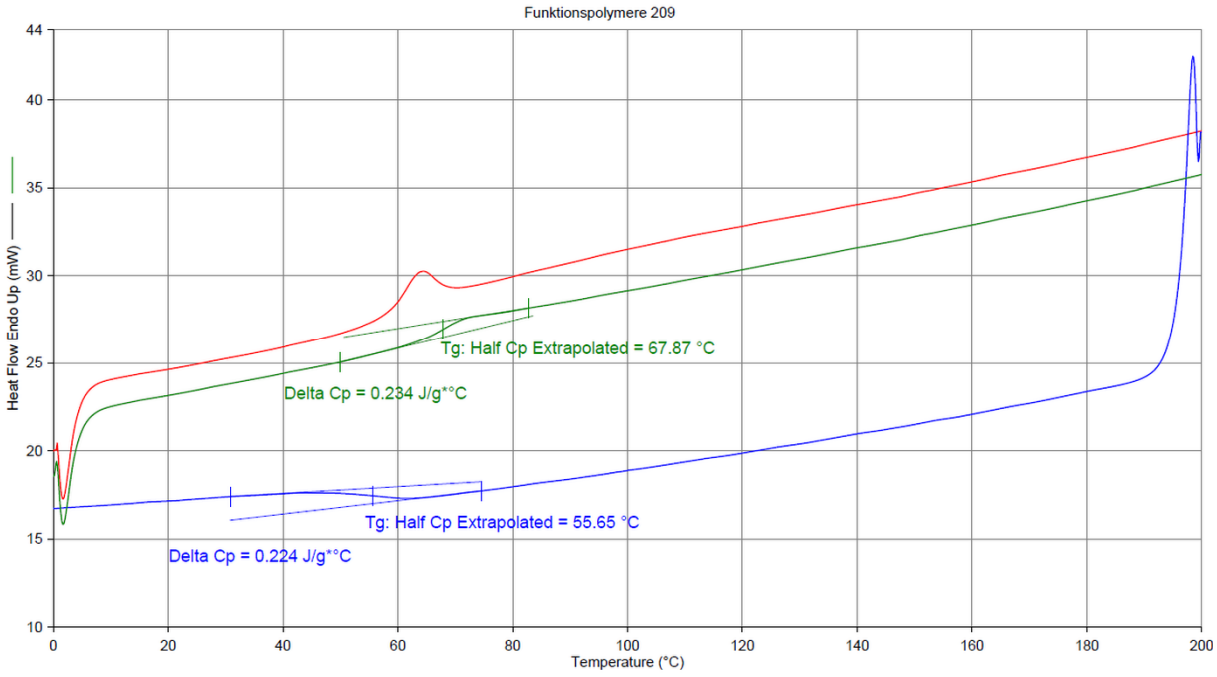


29.10.2020 13:47:33

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

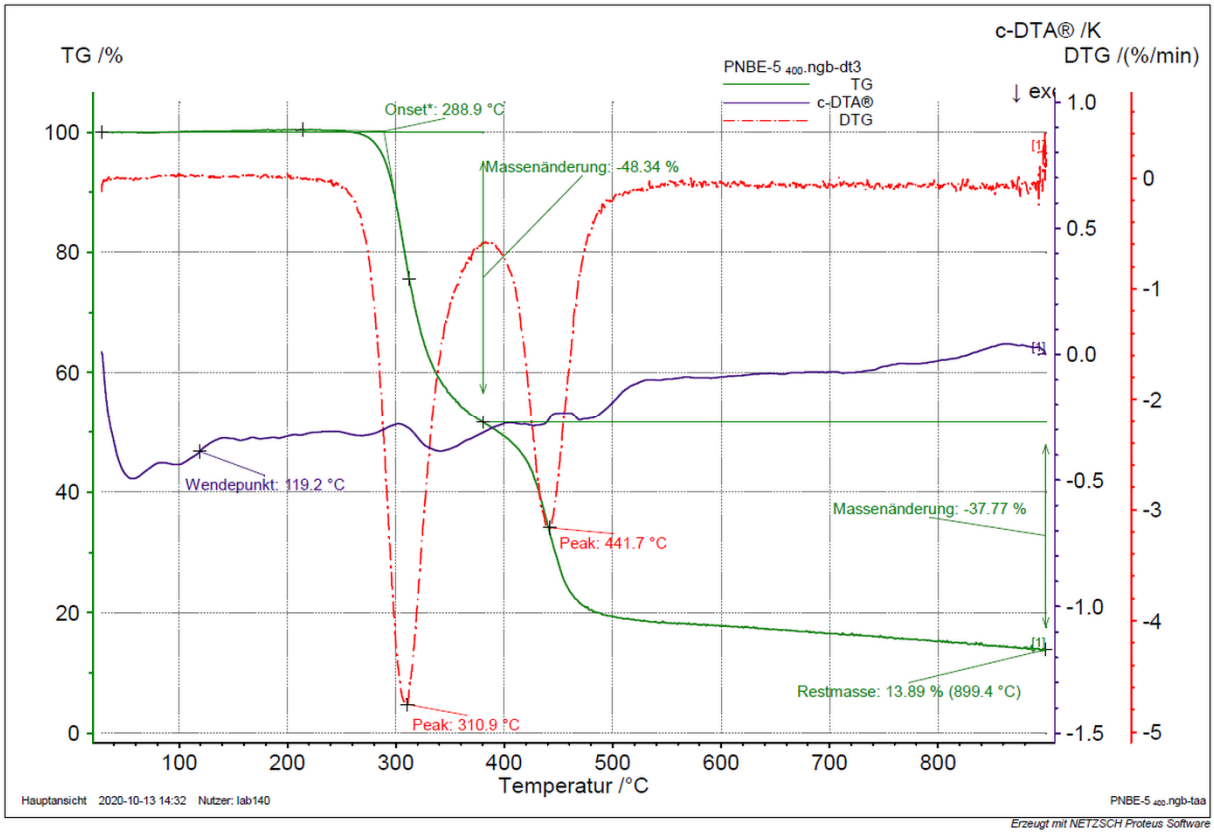


Operator ID: fb
Sample ID: PNBE-5 400
Sample Weight: 11.710 mg

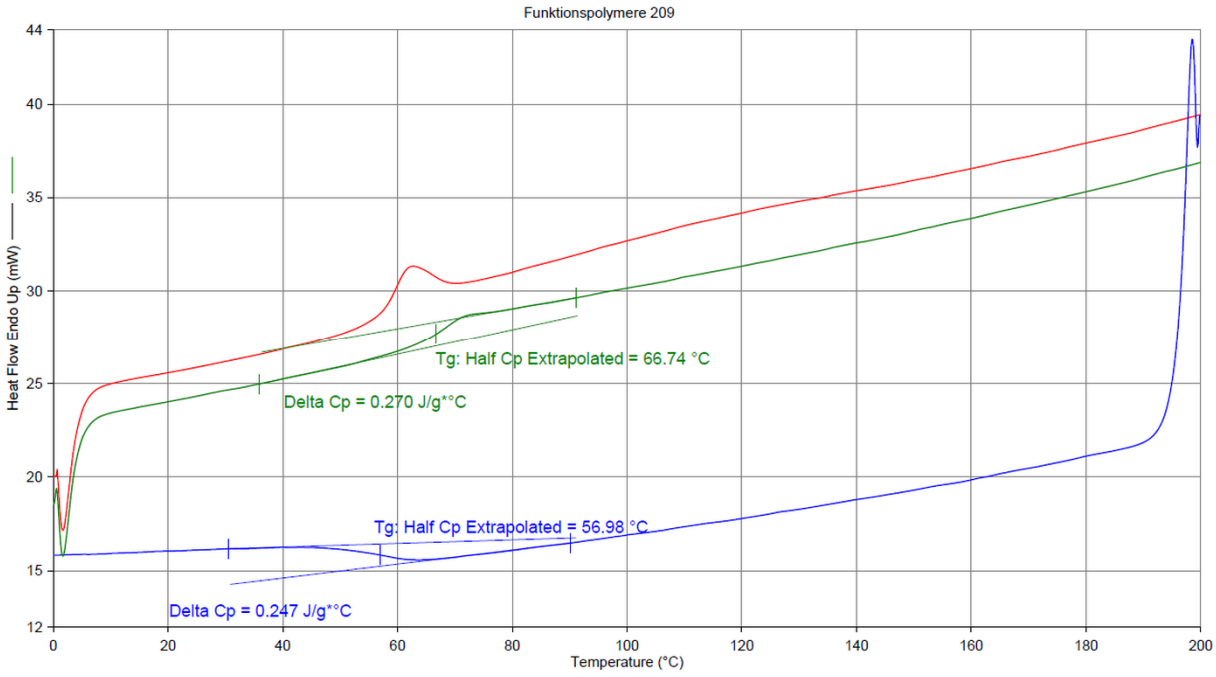


28.10.2020 15:00:40

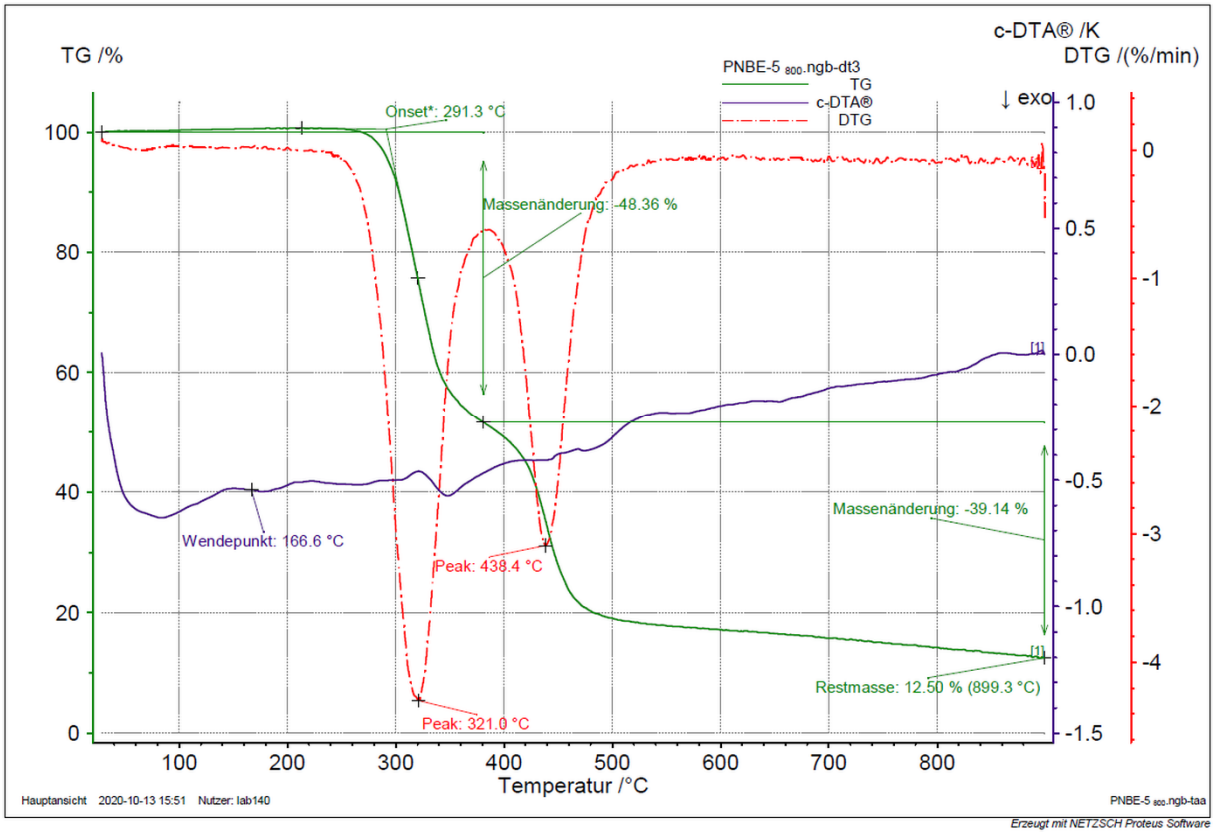
1) Heat from 0.00°C to 200.00°C at 20.00°C/min
2) Cool from 200.00°C to 0.00°C at 20.00°C/min
3) Hold for 3.0 min at 0.00°C
4) Heat from 0.00°C to 200.00°C at 20.00°C/min



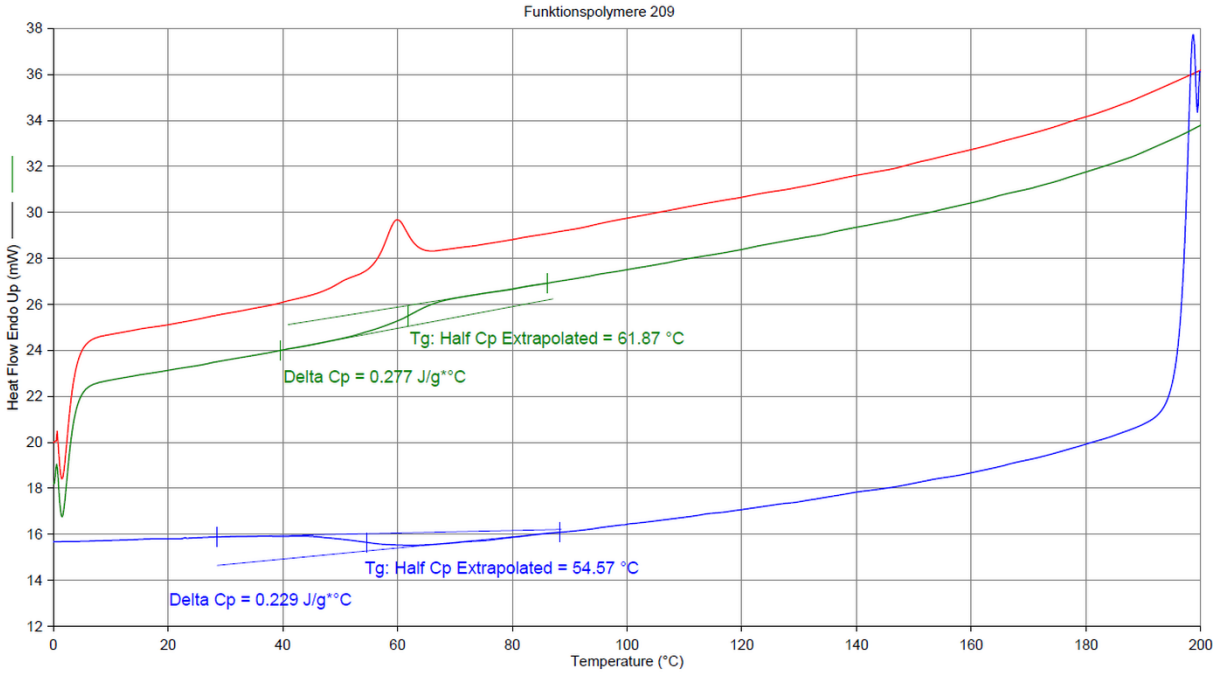
Operator ID: fb
Sample ID: PNBE-5 800
Sample Weight: 14.408 mg



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

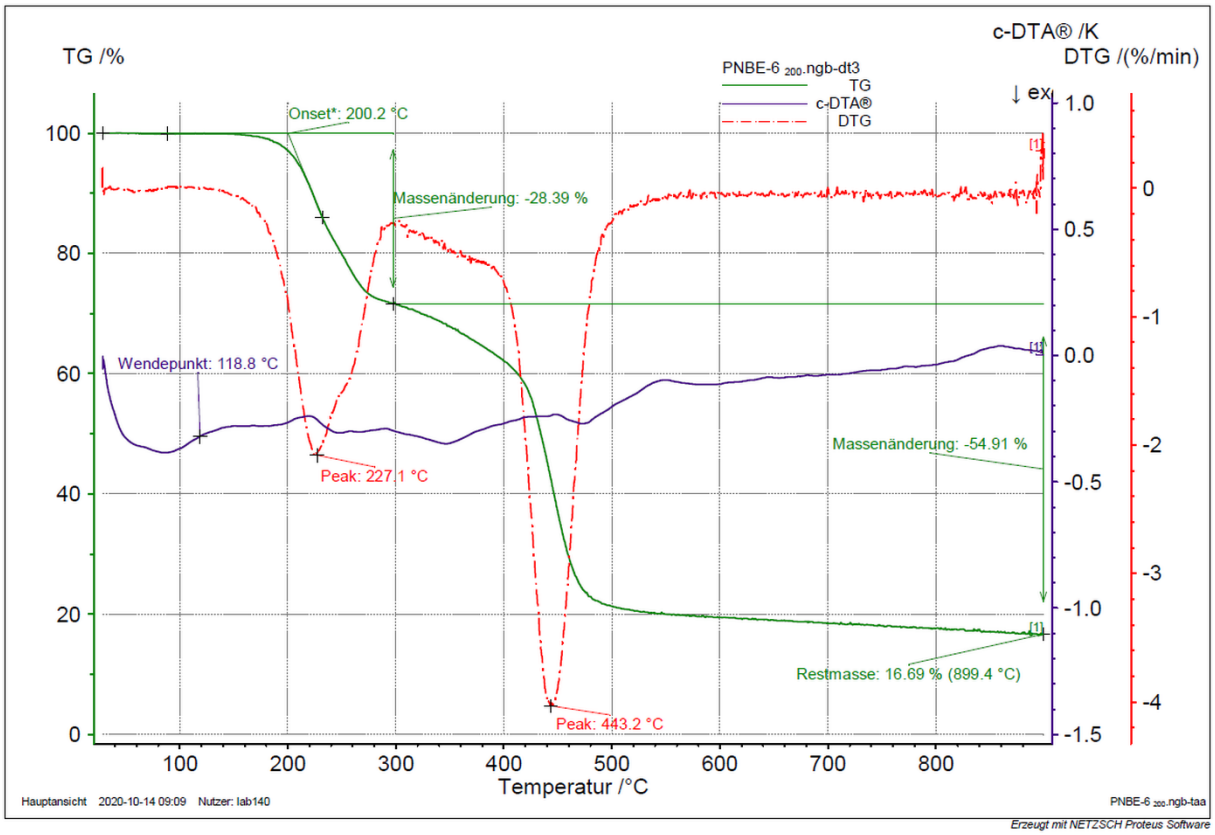


Operator ID: fb
Sample ID: PNBE-6 200
Sample Weight: 9.854 mg

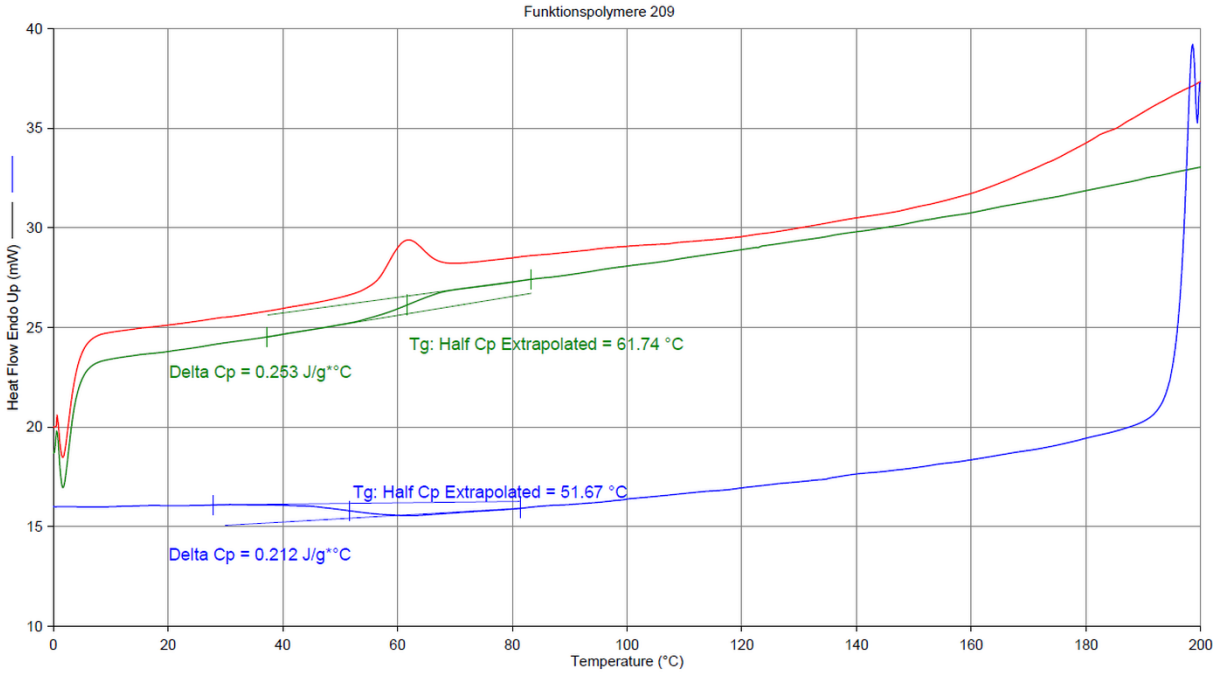


29.10.2020 14:15:44

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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

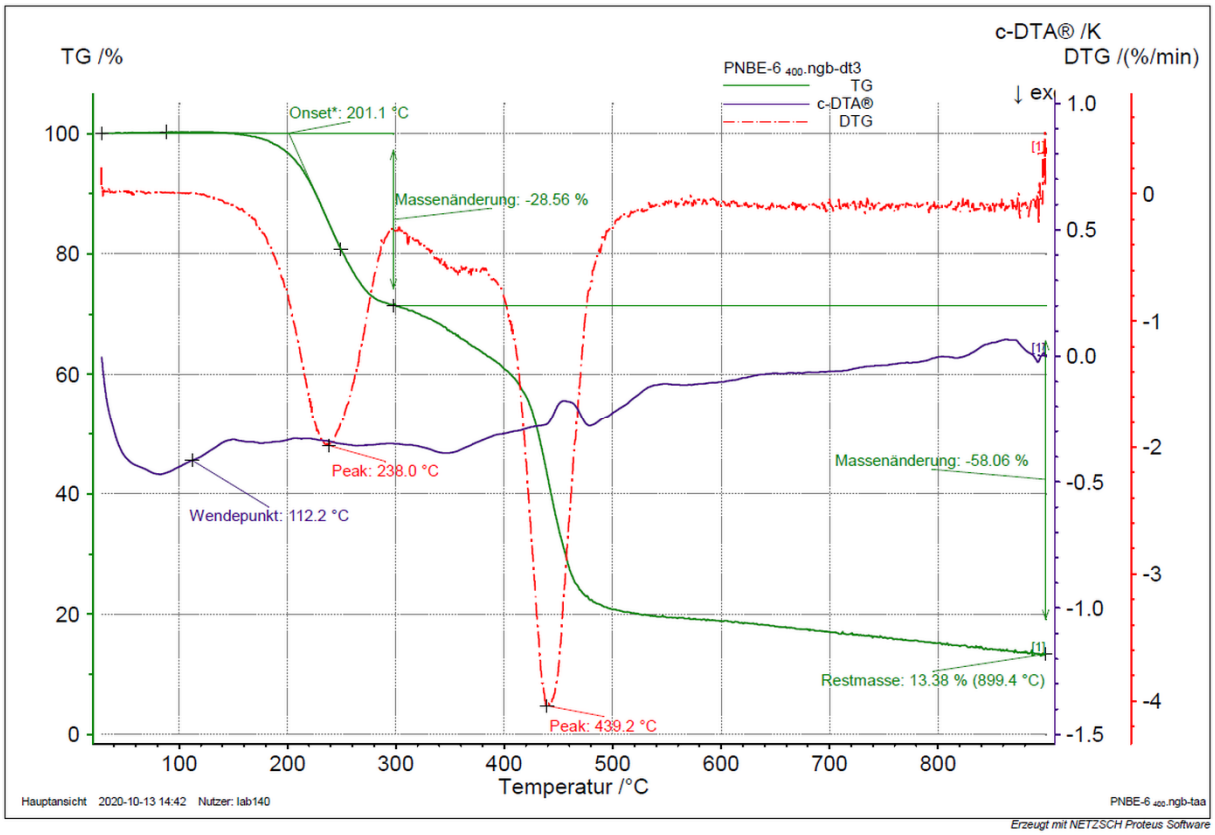


Operator ID: fb
Sample ID: PNBE-6 400
Sample Weight: 10.556 mg

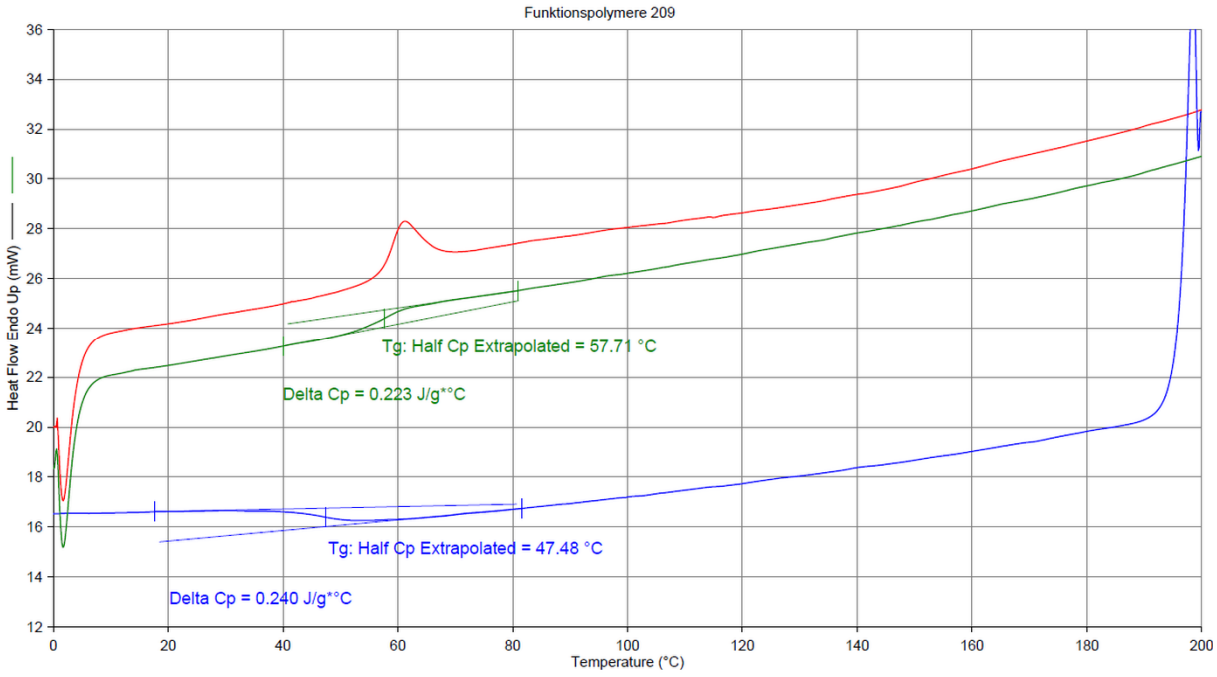


28.10.2020 14:28:49

1) Heat from 0.00°C to 200.00°C at 20.00°C/min
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-6 800
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
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