Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Diels-Alder Reaction between Cyanates and Cyclopentadienone-Derivatives – A New Class of Crosslinkable Oligomers

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1. General methods

Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q 1000 from TA Instruments. The curves were recorded between -80 °C to 200 °C or 360/370 °C, respectively. A scan rate of 10 K/min was used for all measurements. Per scan, 3-6 mg of sample were weighted into an aluminum pan and subsequently measured in nitrogen atmosphere. The cyclic program has two heating and one cooling phases. For the data treatment the software PYRIS 4.01 and both heating phases were used.

Gel permeation chromatography measurements were carried out using a Waters Alliance HPCL system with a 300x7.5 mm MIXED-B-LS column and 10 µm PSgel from Agilent Technologies. Chloroform was used as eluent at a flow rate of 1 ml/min. The RI detector series1100 from Agilent Technologies was calibrated using PS-standards. The samples were filtered with a 0.2 µm syringe filter prior to the measurements.

Infrared spectroscopy (FT-IR) was measured with a Bruker Vertex 80v. The samples were measured as powders with a golden gate diamond ATR unit (SPECAC) and an MTC-detector. The spectra were recorded between 4000 and 600 cm^{-1}, with a resolution of 4 cm^{-1} and 100 scans per measurement.

Kinetic determination was done in a nitrogen filled high temperature cell (SPECAC) and a DLaTGS-detector on a Bruker Vertex 70. The samples were measured in KBr pellets with around 1 mg substance per 400 mg pellet. To compensate temperature dependence of the bands, a background was recorded for every temperature. The spectra were recorded between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and 100 scans per measurement, and a heating rate of 10 K/min.

Nuclear magnetic resonance (NMR) measurements were carried out on a Bruker Avance III 500 NMR spectrometer operating at 500.13 MHz for ^{1}H and at 125.75 MHz for ^{13}C. Deuterated chloroform ($CDCl_3$) was used as a solvent for all experiments and the solvent peaks, $\delta(^{1}H)$ = 7.26 ppm and $\delta(^{13}C)$ = 77.00 ppm, were used for internal calibration. To support the signal assignments HSQC, HMBC and HSQC-TOCSY spectra were measured using standard pulse sequences of the TOPSPIN 3.1 software (Bruker).

The ^{1}H-^{13}C cross polarization (CP)/MAS spectrum was recorded using a Bruker Avance III 500 NMR spectrometer with a BL3.2 HXY MAS NMR probe in double resonance mode. The experiment was carried out with a $\pi/2$ pulse duration of 3 μs for ^{1}H, a contact time of 1 ms, heteronuclear decoupling (TPPM) and 2750 scans at a MAS spinning rate of 12 kHz.

UV/Vis spectra were recorded using a Perkin Elmer Lambda 800. The samples were measured in a diphenyl ether solution and disposable cuvettes. Spectra were collected between 370 and 800 nm.

Thermogravimetric analysis (TGA) measurements were recorded using a TGA Q5000 from TA-Instruments. The thermal mass degradation was measured with 5 to 6 mg of sample in aluminum pans. The heating rate was set to 10 K/min. Nitrogen was used as the flushing gas. For the data treatment the software PYRIS 4.01 and both heating phases was used.

Variable angle spectroscopic ellipsometry (VASE) was measured at a J.A. Woollam Company M 2000. Three angles were measured (65°, 70° and 75°) over a wavelength range of 400 to 1600 nm. The properties were fit using a Chauchy layer (because of the transparent nature of the oligomer and cured resin) on top of a native SiO_x layer on Si. The native SiO_x was determined measuring a blank wafer treated in the same way as the sample wafers.

2. Materials

All chemicals (Table S1) were used as received by the suppliers. Only the diphenyl ether was additionally purified by distillation and passing through a basic Al_2O_3 column. Afterwards it was stored over molecular sieve. The BADCY monomer was kindly provided by Prof. Bauer (PYCO Berlin).

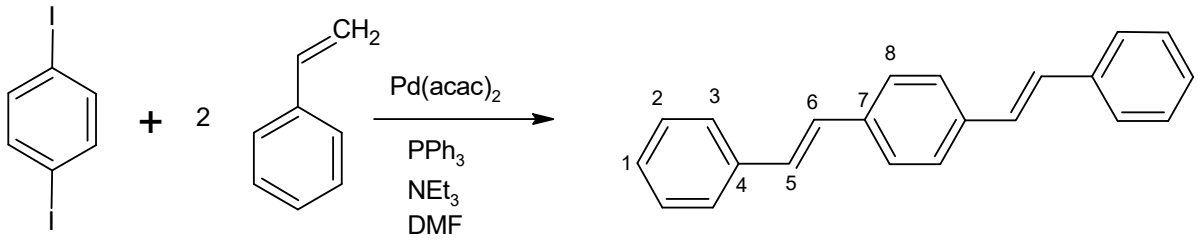
Table S1. Overview of used chemicals

Chemical	CAS Number	Purity [%]	Supplier
Aluminium chloride	7446-70-0	98.5	Acros Organics
Bisphenol A cyanate ester	1156-51-0	98.0	-
1,2-Dichlorobenzene	95-50-1	99	Acros Organics
1,3-Diphenylacetone	102-04-5	99	Acros Organics
1,4-Diiodobenzene	624-38-4	98	Acros Organics
Bis(triphenylphosphine)palladium(II) dichloride	13965-03-2	98	Acros Organics
Dimethyl formamide over molar sieve	68-12-2	99.8	Acros Organics
Dimethyl sulfoxide	67-68-5	99.7	Acros Organics
2,4-Dinitrophenylhydrazine	119-26-6	Min. 30	Acros Organics
Diphenyl ether	101-84-8	99	Acros Organics
Hydrobromic acid solution (48 % in water)	10035-10-6	-	Acros Organics
Iodine	7553-56-2	99	ABCR
Palladium on activated carbon (5 wt%)	440-05-3	-	Acros Organics
Palladium(II) acetate	3375-31-3	98	Acros Organics
Palladium(II) acetylacetonate	14024-61-4	99	Sigma Aldrich
Phenylacetylene	536-74-3	98	ABCR
Sodium thiosulfate	7772-98-7	99	Acros Organics
Styrene	100-42-5	99	Sigma Aldrich
Tetraphenylcyclopentadienone	479-33-4	98	Sigma Aldrich
Triethylamine	121-44-8	99	Acros Organics

3. Synthetic procedures

3.1. Monomer synthesis

3.1.1. 1,4-Bis(phenylethenyl)benzene



9.9 g (30 mmol) of 1,4-diidobenzene, 91.4 mg (0.3 mmol) of palladium(II) acetylacetonate and 157.4 mg (0.6 mmol) of triphenylphosphine were dissolved in a mixture of 150 ml N,N-dimethylformamide (DMF) and 15.2 g (150 mmol) of trimethylamine under argon. After the addition of 7.24 g (34.8 mmol) of styrene, the reaction mixture was heated to 70 °C and another 7.24 g (34.8 mmol) of styrene were added dropwise. Afterwards, the solution was heated to 80 °C and stirred under reflux for 24 hours. After cooling to room temperature, the precipitated product was collected by filtration. The crude product was washed with acetone and used for the next reaction step without further purification. If desired, a recrystallisation in toluene/isopropyl alcohol yields a yellow-green solid.

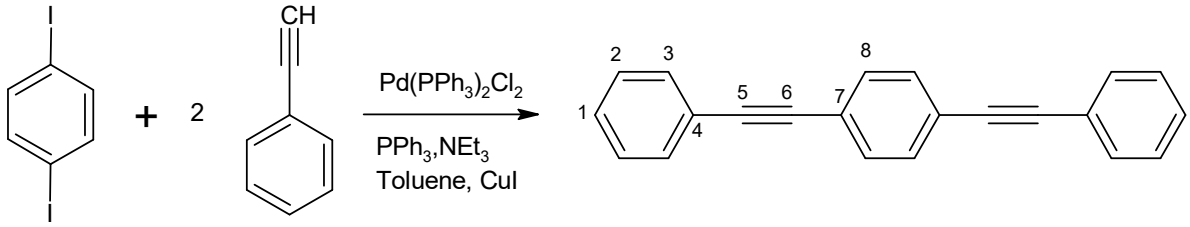
Yield: 6.5015 g (23 mmol); 76.75 %

^{1}H NMR ($CDCl_3$): δ = 7.12 (AB system, $H_{5,6}$), 7.26 (t, H_1), 7.37 (t, H_2), 7.52 (s, H_8), 7.54 (d, H_3) ppm

^{13}C NMR ($CDCl_3$): δ = 126.25 (C_3), 126.85 (C_8), 127.64 (C_1), 128.30 (C_6), 128.63 (C_5), 128.70 (C_2), 136.74 (C_7), 137.36 (C_4) ppm

FT-IR: v = 688 and 741 (s, $_{oop}$ mono-substitution), 812 (s, δ_{oop} para-substitution), 960 (s, δ C=C), 1569 and 1593 (m, aromatic v C=C), 1673 (w, v C=C) 3057 and 3081 (s, v C-H) cm^{-1}

3.1.2. 1,4-Bis(phenylethynyl)benzene



4.95 g (15 mmol) of 1,4-diidobenzene, 0.53 g (0.75 mmol) of bis(triphenylphosphine)palladium(II) dichloride, 0.29 g (1.5 mmol) of copper(I) iodide and 0.39 g (1.5 mmol) of triphenylphosphine were dissolved in a mixture of 100 mL toluene and 70 mL of trimethylamine under argon. The mixture was heated to 60 °C for 10 minutes before 3.22 g (31.5 mmol) of ethynylbenzene were added. After the addition, the suspension was heated at 90 °C for 4 hours under reflux. Subsequently, the solvent was removed under low pressure and the remaining solid was dissolved in dichloromethane (DCM). The organic phase was washed with 0.1 M HCl, aq. Na_2CO_3 (10 %) and brine and eventually dried over $MgSO_4$. Afterwards, the solvent was removed and the reddish solid was washed with ethyl acetate (EA) to yield the white product.

Yield: 3.7406 g (13.4 mmol); 89,59 %

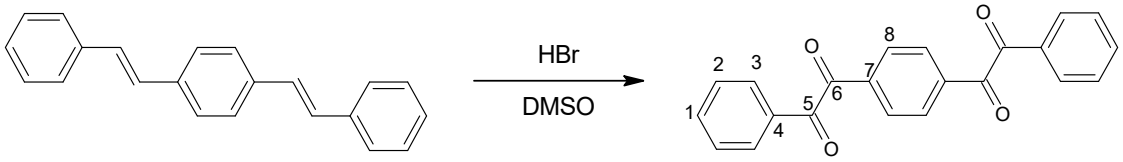
^{1}H NMR ($CDCl_3$): δ = 7.35 (m, H_1), 7.37 (m, H_2), 7.52 (s, H_8), 7.54 (m, H_3) ppm

^{13}C NMR ($CDCl_3$): δ = 89.12 (C_6), 91.24 (C_5), 123.07 (C_4), 123.12 (C_7), 128.38 (C_2), 128.44 (C_1), 131.53 (C_8), 131.63 (C_3) ppm

FT-IR: v = 688 and 750 (s, δ_{oop} mono-substitution), 837 (s, δ_{oop} para-substitution), 1511 and 1595 (m, aromatic v C=C), 2163 (w, v C≡C), 3055 and 3024 (s, v C-H) cm^{-1}

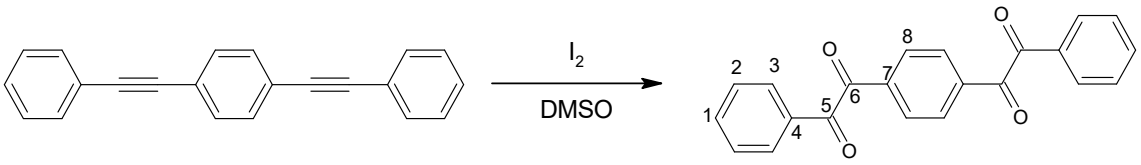
3.1.3. 1,4-Bis(phenylglyoxaloyl)benzene

(a)



13 g (45 mmol) of 1,4-bis(phenylethenyl)benzene were suspended in 450 mL of dimethyl sulfoxide (DMSO). 45 mL of hydrobromic acid were added into this dispersion and the mixture was heated at 100 °C under reflux for 11 hours. Afterwards, the reaction was diluted with 500 mL of water and extracted three times with 250 mL of diethyl ether. The combined organic phases were washed with 500 mL of water and brine and eventually dried over $MgSO_4$. Afterwards, the solvent was removed and the crude product was purified by column chromatography with silica gel using EA/hexane (1:5), resulting in a yellow solid.

(b)



9.4 g (33.8 mmol) of 1,4-bis(phenylethynyl)benzene and 18 g (71 mmol) of iodine were dispersed in 500 mL of dimethyl sulfoxide (DMSO). The mixture was stirred at 155 °C under reflux for 2 hours. After cooling, the reaction was diluted with 500 mL of sodium thiosulfate solution (5 wt%) and extracted three times with 250 mL of ethyl acetate (EA). The combined organic phases were washed with 250 mL of sodium thiosulfate solution (5 wt%) and brine and eventually dried over $MgSO_4$. Afterwards, the solvent was removed and the resulting solid was used for the next reaction step without further purification. If desired, a recrystallisation in alcohol produces fine yellow needles.

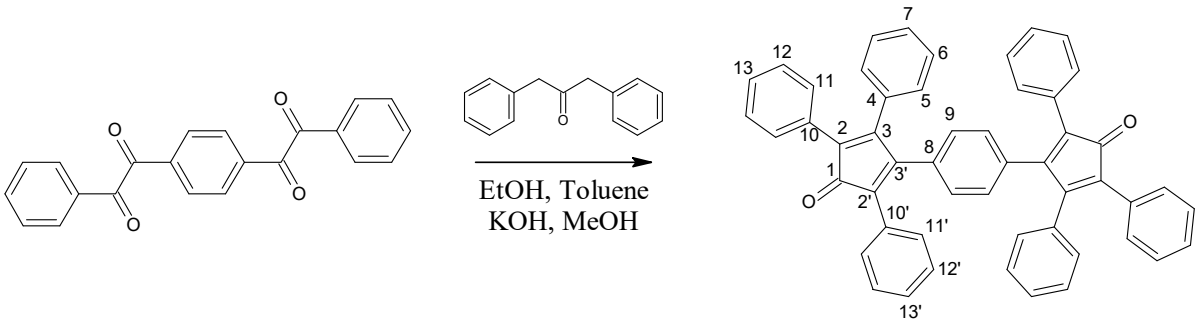
Yield: (a) 5.41 g (15.8 mmol); 35.1 % (b) 11.1 g (32.4 mmol); 95.9 %

^{1}H NMR ($CDCl_3$): δ = 7.54 (t, H_2), 7.69 (t, H_1), 7.97 (d, H_3), 8.11 (s, H_8) ppm

^{13}C NMR ($CDCl_3$): δ = 129.14 (C_2), 129.96 (C_3), 130.23 (C_8), 132.60 (C_4), 135.22 (C_1), 137.15 (C_7), 193.24 (C_6), 193.39 (C_5) ppm

FT-IR: v = 707 and 786 (w, δ_{oop} mono-substitution), 827 (w, δ_{oop} para-substitution), 1500 and 1595 (m, aromatic v C=C), 1663 and 3326 (s, δ C=O), 3005 and 3057 (s, v C-H) cm^{-1}

3.1.4. 3,3'-(1,4-Phenylene)bis(2,4,5-triphenylcyclopentadienone) (1)



3.44 g (10 mmol) of 1,4-bis(phenylglyoxaloyl)benzene and 5.29 g of 1,3-diphenylacetone were suspended in a mixture of 40 mL ethanol and 4 mL toluene. After heating to 130 °C a solution of 750 mg (13.3 mmol) potassium hydroxide in 4 mL methanol was added dropwise into the reaction mixture. The reaction was stirred for one hour under reflux at 130 °C. After cooling to 0 °C, the precipitated solid was collected and washed with ethanol and acetone to yield the blackish purple product.

Yield: 4.33 g (6.27 mmol); 62.7 %

^{1}H NMR ($CDCl_3$): δ = 6.79 (s, H_9), 6.92 (d, H_5), 7.20 (t, H_6), 7.21-7.26 ($H_{11\text{-}13,}$ $H_{11'\text{-}13'}$), 7.28 (t, H_7) ppm

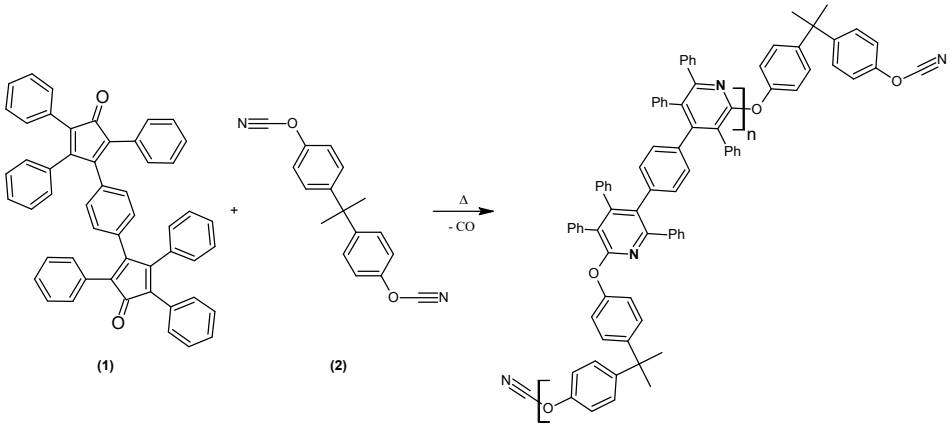
^{13}C NMR ($CDCl_3$): δ = 125.27 (C_2), 125.56 ($C_{2'}$), 127.56 and 127.60 ($C_{13/13'}$), 127.98 (C_6), 128.00 and 128.05 ($C_{12/12'}$), 128.55 (C_7), 129.04 (C_9), 129.25 (C_5), 130.04 ($C_{11/11'}$), 130.60 ($C_{10/10'}$), 132.94 (C_4), 133.54 (C_8), 153.90 ($C_{3'}$), 154.07 (C_3), 200.05 (C_1) ppm

FT-IR: v = 686 and 736 (w, δ_{oop} mono-substitution), 856 (w, δ_{oop} para-substitution), 1488 and 1597 (m, aromatic v C=C), 1707 and 3394 (s, δ C=O), 3022 and 3053 (s, v C-H) cm^{-1}

3.2. Polymer synthesis

The polymerisation was carried out in diphenyl ether under inert atmosphere at 230 °C. The monomer concentration was kept around 0.1 mol L^{-1} but varied because of different glassware used in the metal bath. After the polymerisation was stopped (after 5-36 hours) the solution was precipitated in ethanol, washed with ethanol and dried. To purify the polymer the solid was dissolved in chloroform and again precipitated and washed with ethanol. The reaction conditions for the different polymers can be found in the main text in Table 1.

3.2.1. Polymerisation of the A_2 and BADCY monomers



3.2.2. Example: PL-3-200

0.250 g (0.36 mmol) of 3,3‘-(1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (5) and 0.403 g (1.45 mmol) of 2,2-bis-(4-cyanatophenyl)propane were suspended in 5 mL diphenyl ether. The mixture was heated to 200 °C and subsequently stirred for 24 hours. After the reaction was stopped, the solution was precipitated and washed with ethanol. The raw product was dissolved in chloroform and precipitated with ethanol. The solid was filtered and washed with ethanol to yield the whitish beige product.

Yield: 318 mg; 71.2 %

FT-IR: v = 3054 (m), 3028 (m), 2966 (m), 2870 (w), 2266 (m), 2235 (m), 1551 (m), 1497 (s), 1365(s), 1213 (s), 1169 (s), 1074 (m), 1014 (m), 946 (m), 916 (w), 829 (m), 754 (m), 694 (s) cm^{-1}

3.3. Preparation of thin films

The thin polymer films were cast onto 2x2 cm silicon wafers with a natural oxide layer via spin coating. Prior to the coating, the wafer had to be cleaned by the following procedure. The wafer and tools used were washed with Millipore water and dried with pressurised air. Afterwards, they were immerged in Millipore water and treated 20 minutes in an ultra-sonic bath. Subsequently, the wafers were cleaned for 5 minutes in an 80 °C RCA-1 solution (1:1:5, H_2O_2/NH_4OH/Millipore water) under continuous ultra-sonication. After another rinsing with Millipore water, the wafers were ultra-sonicated for 5 minutes in an 80 °C RCA-2 solution (1:1:5, H_2O_2/HCl/Millipore water). Finally, the wafers were rinsed once more and treated for 30 minutes in 80 °C hot Millipore water. In the end, everything was dried with pressurised air.

In order to cast thin films, a 5 wt% solution of polymer in dichlorobenzene was prepared. Prior to the coating, the solution was filtered through a syringe filter (PTFE, 0.2 µm). After the filtration, 100 µl of the solution was applied onto the wafer with an Eppendorf pipette. The films were spun for 45 seconds at 500 rpm with a 100 rpm/min ramp and for 20 seconds at 5000 rpm with a 1000 rpm/min ramp. After the coating, the wafers were dried at 50 °C in a vacuum oven over night. Afterwards the thickness of the homogenous films was determined to be in the range 110 to 160 nm depending on the sample.

The thin films were cured for 12 hours at 200 °C in air after the ellipsometric measurement of the oligomer films. During the curing the thickness of the films did not change.

4. Characterisation of the oligomers

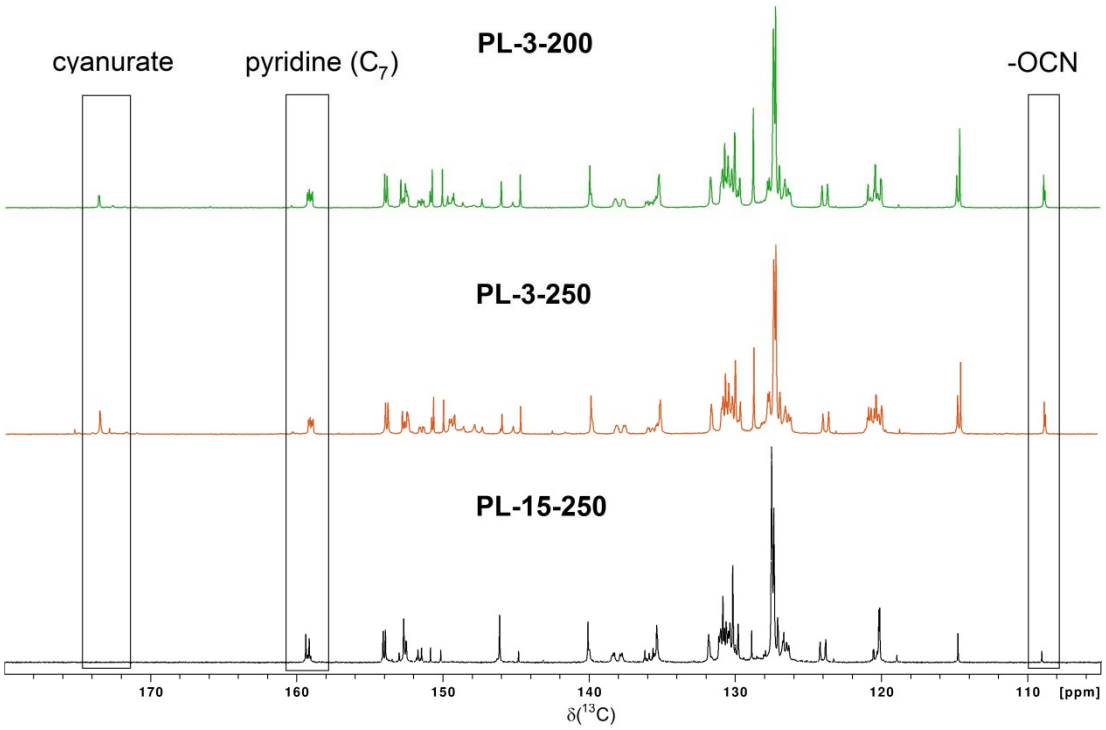


Fig. S1. Characteristic cyanurate and pyridine signals and the –OCN signal in ^{13}C NMR spectra of different oligomers synthesised at different temperatures.

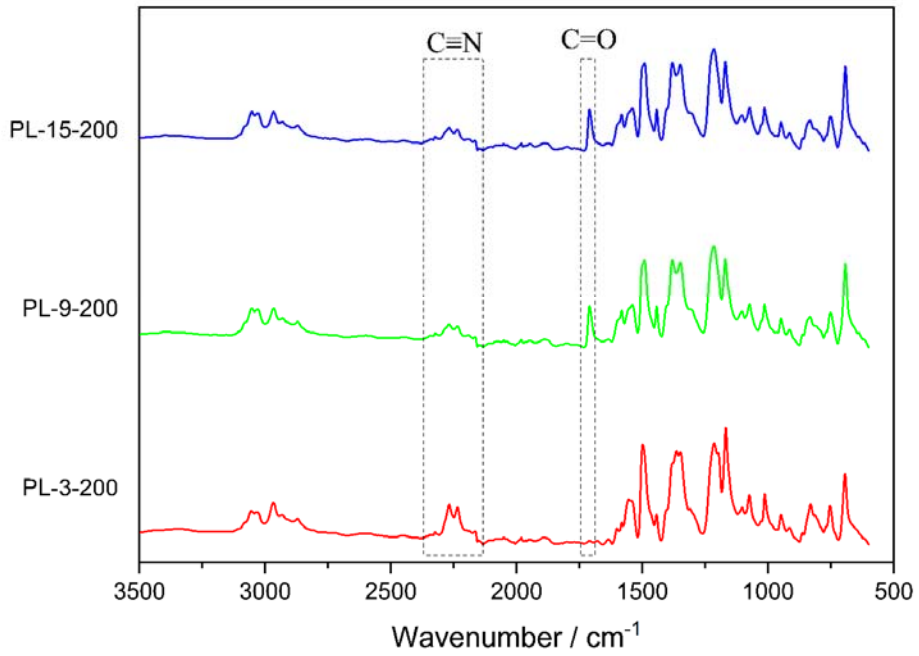


Fig. S2. Infrared spectra of the three different oligomers; C≡N and C=O bands are highlighted. For further assignments see Table S2.

Table S2. Infrared spectroscopy correlation table for the oligomers

Band [cm^{-1}]	Bond type	Related molecule
3060	Aromatic C-H	all
2970	Aliphatic C-H	BADCY, Oligomer
2270	C≡N	BADCY
1710	C=O	A_2
1560	O-C-N	Oligomer
1500	Aromatic C-C	all
1370	C-N	Oligomer
1210	Ar-O-Ar	Oligomer
1175	Phenyl C-O	BADCY
1070	Alkoxy C-O	BADCY
830	Para-subst. Aromatic C-H	BADCY
697	Mono-subst. Aromatic C-H	A_2

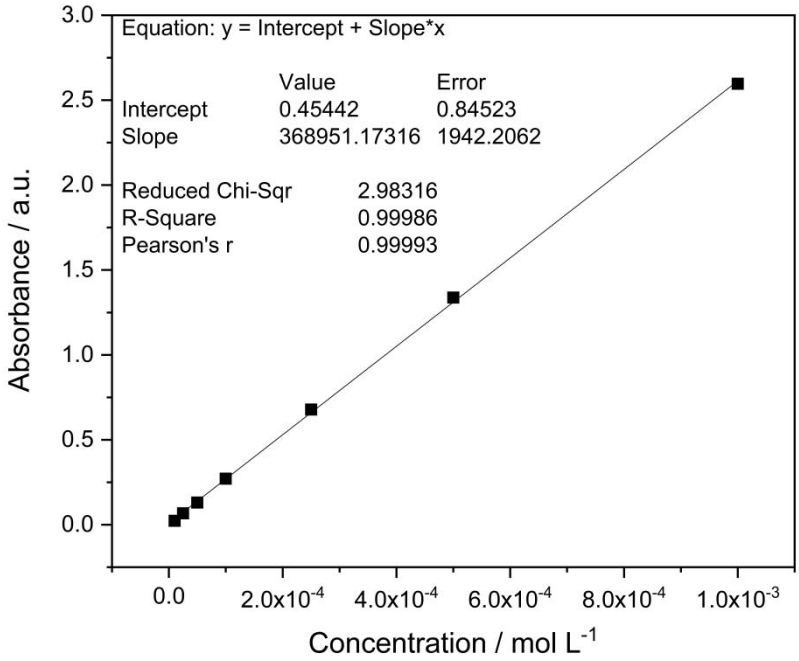


Fig. S3. Calibration for the UV/Vis measurement; absorbance at 515 nm for different concentrations.

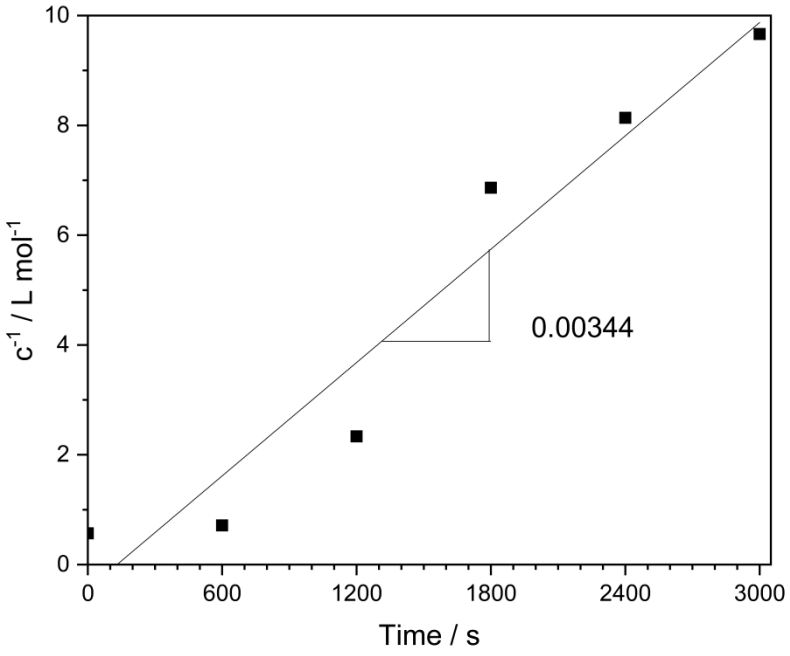


Fig. S4. Second order rate law fit for the Diels-Alder reaction.

5. NMR characterisation

5.1. BADCY

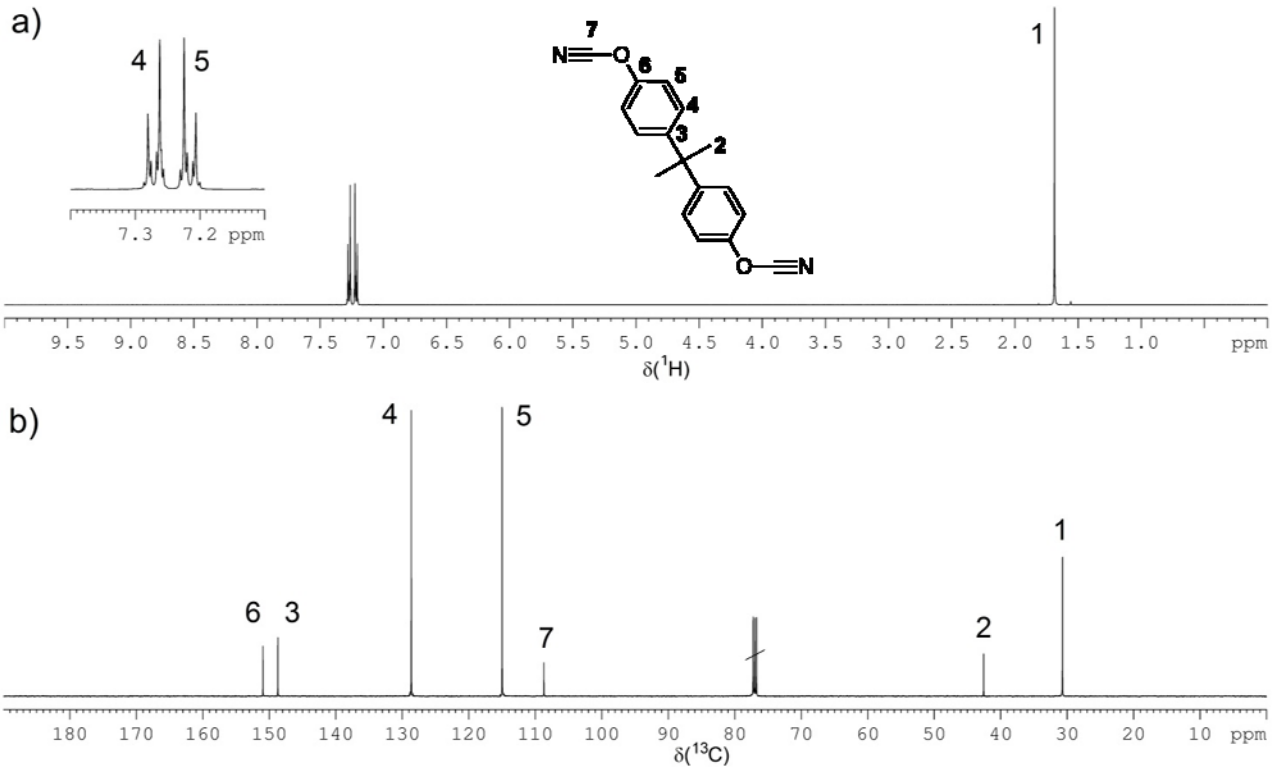


Fig. S5. ^{1}H (a) and ^{13}C NMR (b) spectra of BADCY monomer (solvent $CDCl_3$).

^{1}H NMR ($CDCl_3$): δ = 7.27 (d, H_4), 7.22 (d, H_5), 1.69 (s, H_2) ppm

^{13}C NMR ($CDCl_3$): δ = 150.97 (C_6), 148.72 (C_3), 128.65 (C_4), 115.00 (C_5), 108.70 (C_7), 42.56 (C_2), 30.70 (C_1) ppm

5.2. BADCY prepolymer

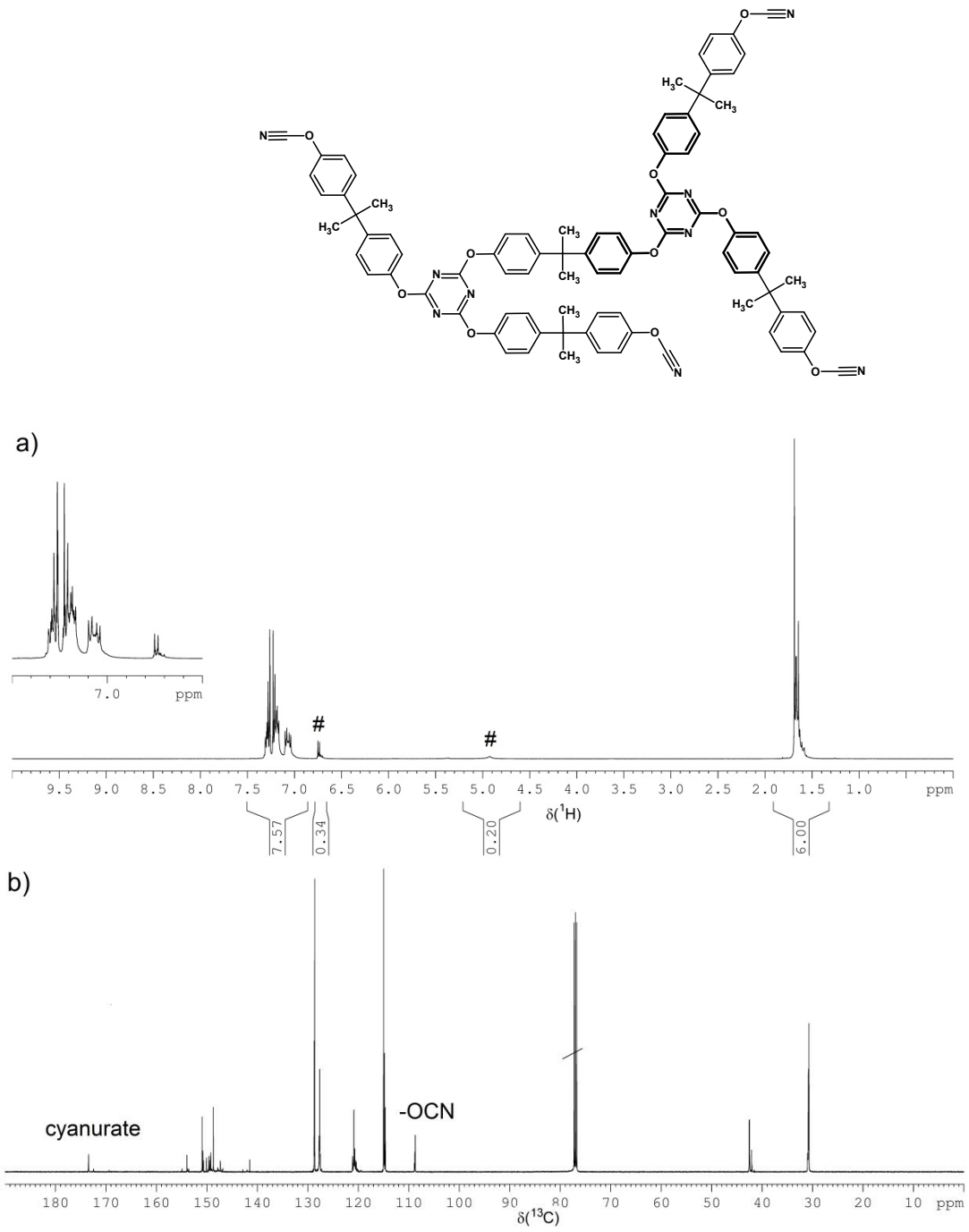


Fig. S6. ^{1}H (a) and ^{13}C NMR (b) spectrum of a BADCY prepolymer with about 35% conversion of –OCN groups (solvent $CDCl_3$). Signals of phenolic groups are marked with #.

Partial cyclotrimerisation of BADCY to phenyl-substituted cyanurate results in new signals both in the ^{1}H and ^{13}C NMR spectrum. The *ortho*-protons of the phenoxy moiety result in the signal group at 7.1 – 7.0 ppm. Further signals in the ^{1}H NMR spectrum point to a small content of phenolic groups. A characteristic ^{13}C NMR signal appears at 173.5 ppm for the cyanurate carbon. Signals of the CH carbons of the new phenoxy moiety were observed at 120.9 ppm (*ortho* to O) and at 127.7 ppm (*meta* to O). The multitude of the aromatic carbons' signals results from different substitution pattern within the oligomers. The sample still contains unreacted BADCY.

5.3. Model substance

To get reference values for the ^{1}H and ^{13}C chemical shifts of the fivefold-substituted pyridine moiety and of the linking 2,2-diphenylpropane unit of the synthesised oligomers, tetraphenylcyclopentadienone was reacted with BADCY monomer in a 2:1 ratio (Fig. S7). The isolated compound could be proved as **T1** by NMR spectroscopy.

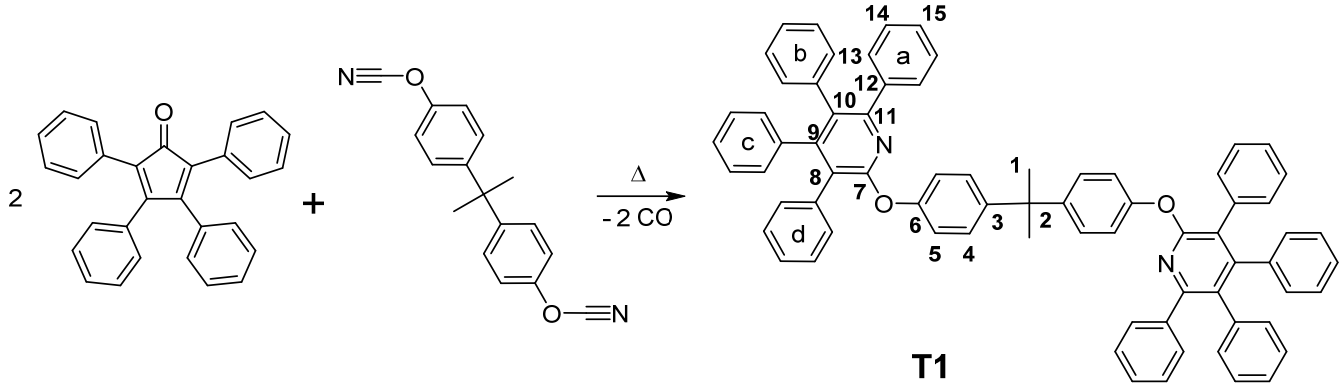


Fig. S7: Synthesis of the model compound **T1**

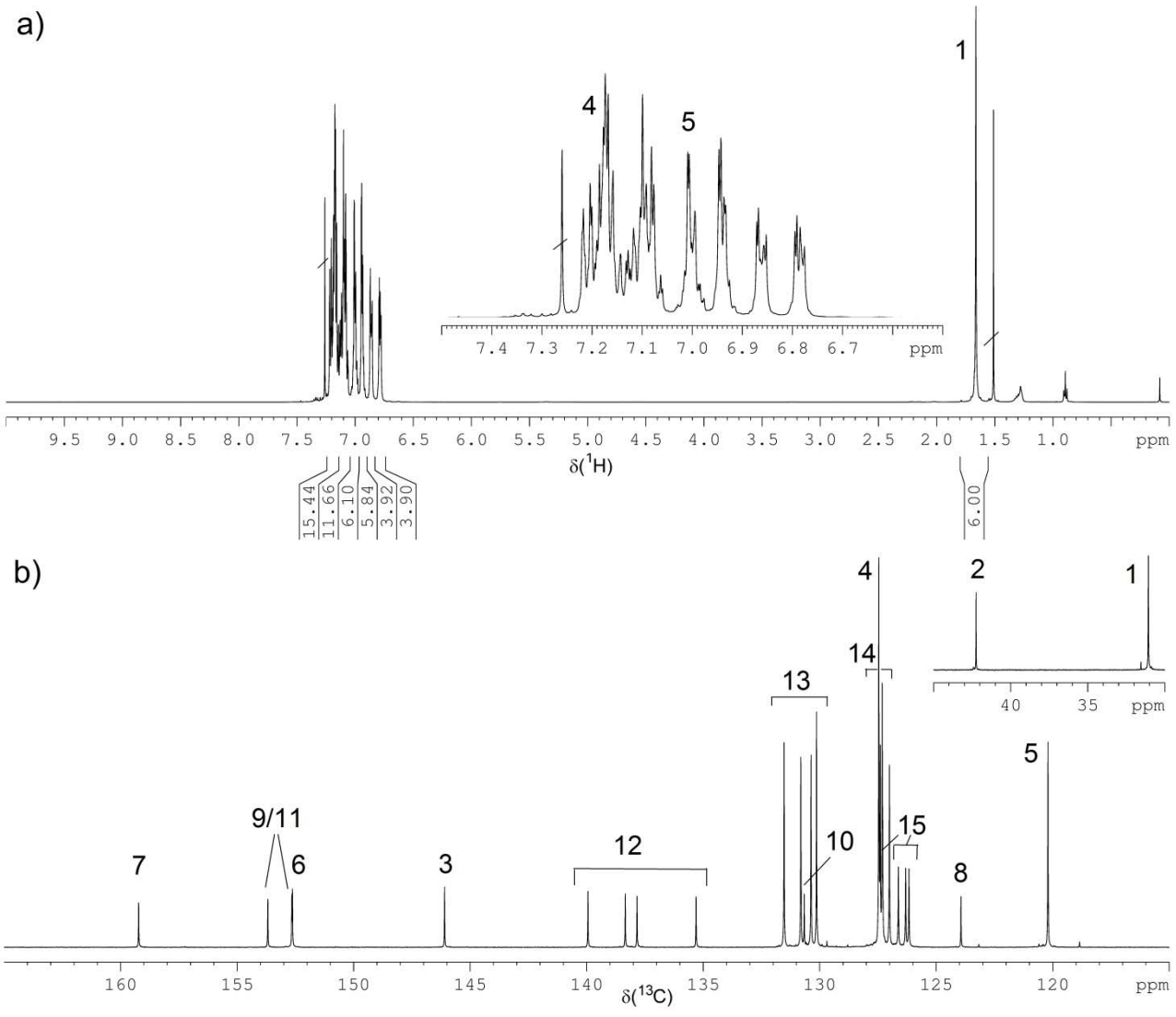


Fig. S8. ^{1}H (a) and ^{13}C NMR (b) spectrum of **T1** (solvent $CDCl_3$).

A detailed signal assignment is rather complex and not the aim. The methyl group signal can be well assigned in the ^{1}H NMR spectrum and the chemical shifts of H_4 and H_5 result from a HSQC spectrum (Fig. S8). The proton signals of the four phenyl rings a – d overlap in a complex manner. The HSQC-TOCSY spectrum (Fig. S9) give some correlations allowing few assignments. The signals of the 2,2-diphenylpropane unit can be well assigned in the ^{13}C NMR spectrum based on HSQC and HMBC correlations. This also applies for the pyridine carbons C_7 – C_{11}, where C_9 and C_{11} cannot be distinguished unequivocally.

^{1}H NMR ($CDCl_3$): δ = 7.25 – 6.75 (H_{13} – H_{15} of a – d), 7.19 (d, H_4), 7.09 (d, H_5), 1.66 (s, H_2) ppm

^{13}C NMR ($CDCl_3$): δ = 159.22 (C_7), 153.68 and 152.65 (C_9 and C_{11}), 152.62 (C_1), 146.09 (C_4), 139.95, 138.34, 137.84 and 135.31 (C_{12} of a -d), 131.53, 130.82, 130.37 and 130.14 (C_{13} of a – d), 130.66 (C_{10}), 127.46 (C_4), 127.42, 127.40, 127.32 and 127.01 (C_{14} of a – d), 127.30, 126.63, 126.37 and 126.17 (C_{15} of a – d), 120.21 (C_5), 42.25 (C_2), 31.08 (C_1) ppm

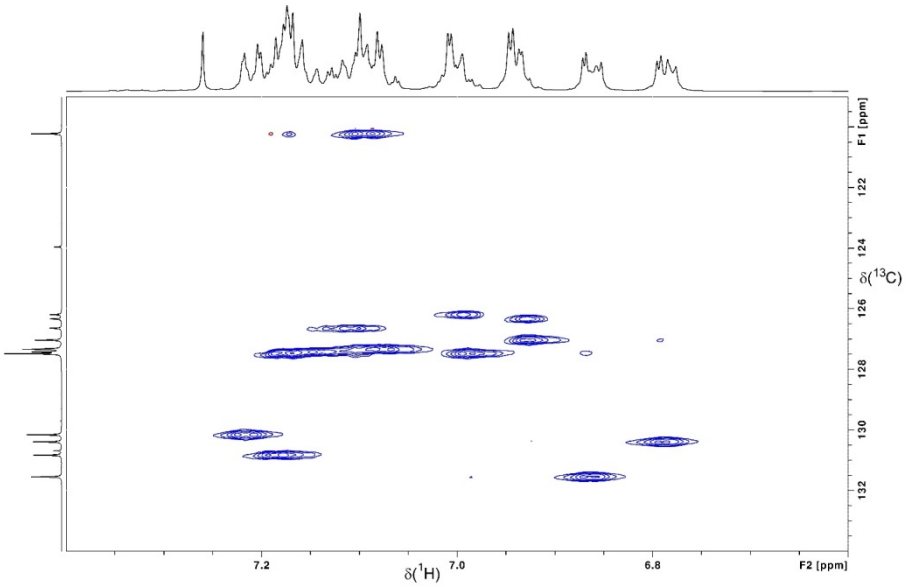


Fig. S9. HSQC spectrum (region) of **T1** (solvent $CDCl_3$).

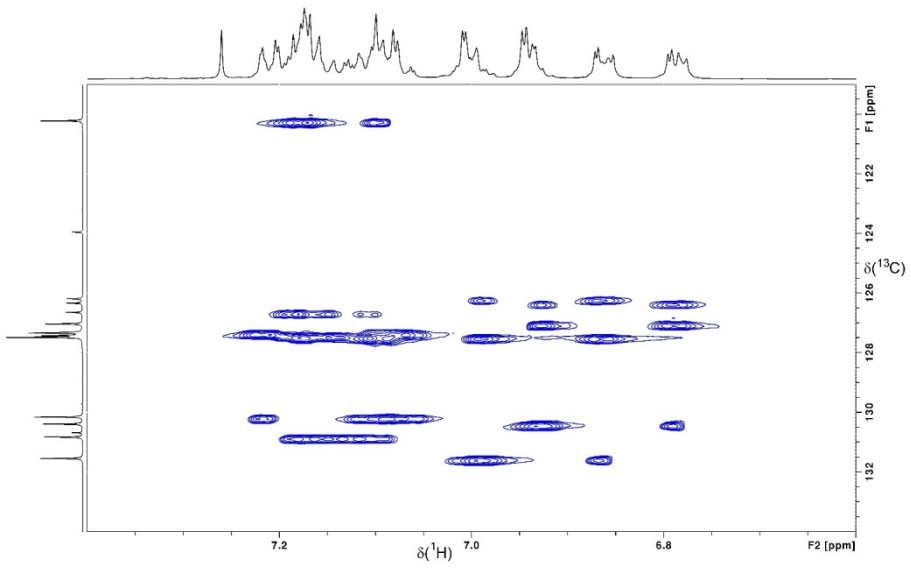


Fig. S10. HSQC-TOCSY spectrum (region) of **T1** (solvent $CDCl_3$).

5.4. 2D NMR spectra of oligomer PL-3-200 and isomer content of the samples

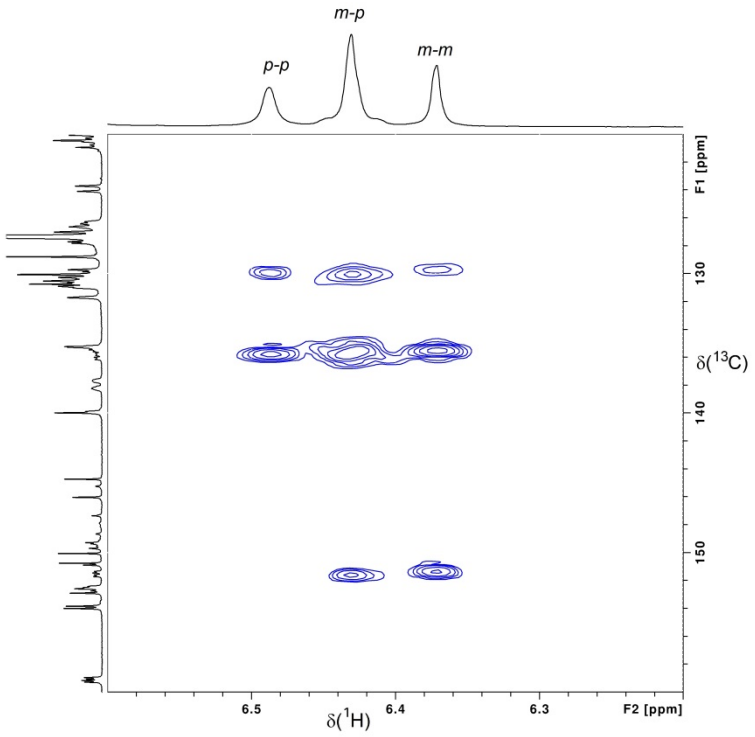


Fig. S11. HMBC spectrum of PL-3-200 (region) (solvent $CDCl_3$).

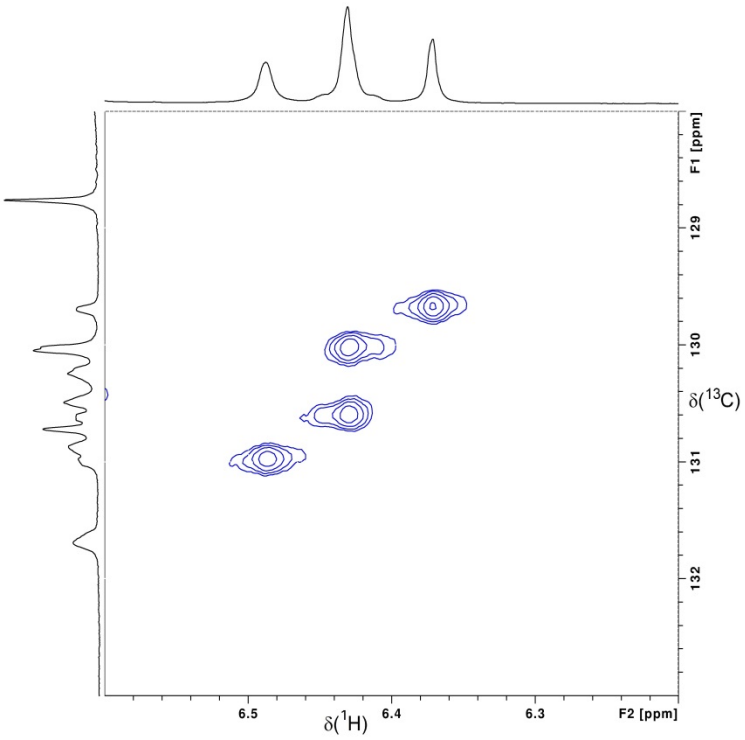


Fig. S12. HSQC spectrum of PL-3-200 (region) (solvent $CDCl_3$).

Table S3. Fraction of catenation isomers for different samples calculated from ^{1}H NMR signal integrals

Sample	Content (mol%)		
	para - para	***para-meta***	***meta-meta***
PL-3-200	0.26	0.48	0.26
PL-3-250	0.24	0.50	0.26
PL-3-270	0.24	0.50	0.26
PL-15-250	0.24	0.50	0.26
PL-L-250	0.23	0.50	0.27

6. Characterisation of the curing process

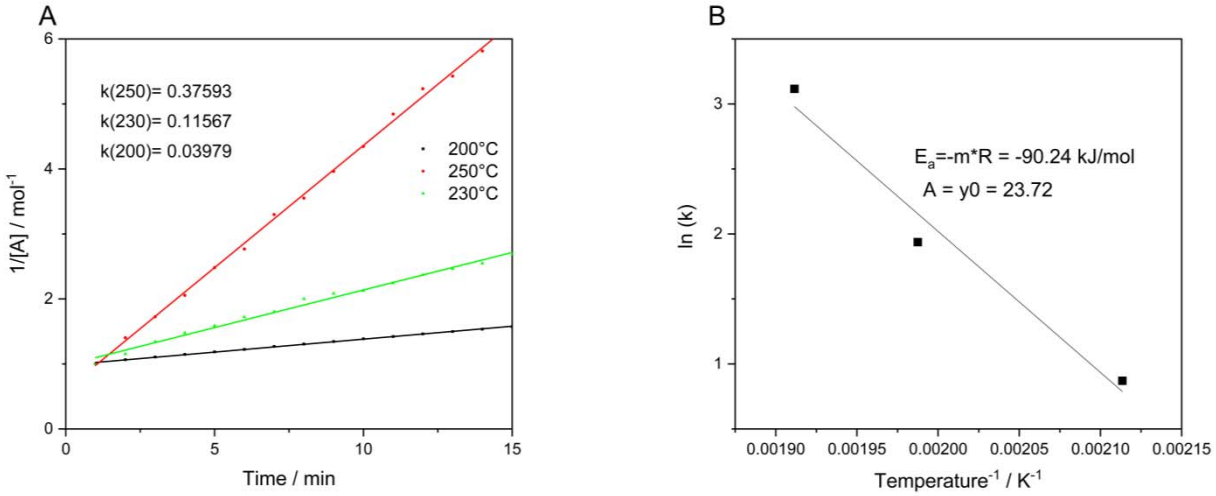


Fig. S13. A: Second order fit for the curing of the oligomer for three different temperatures. B: Arrhenius fit for these three temperatures.

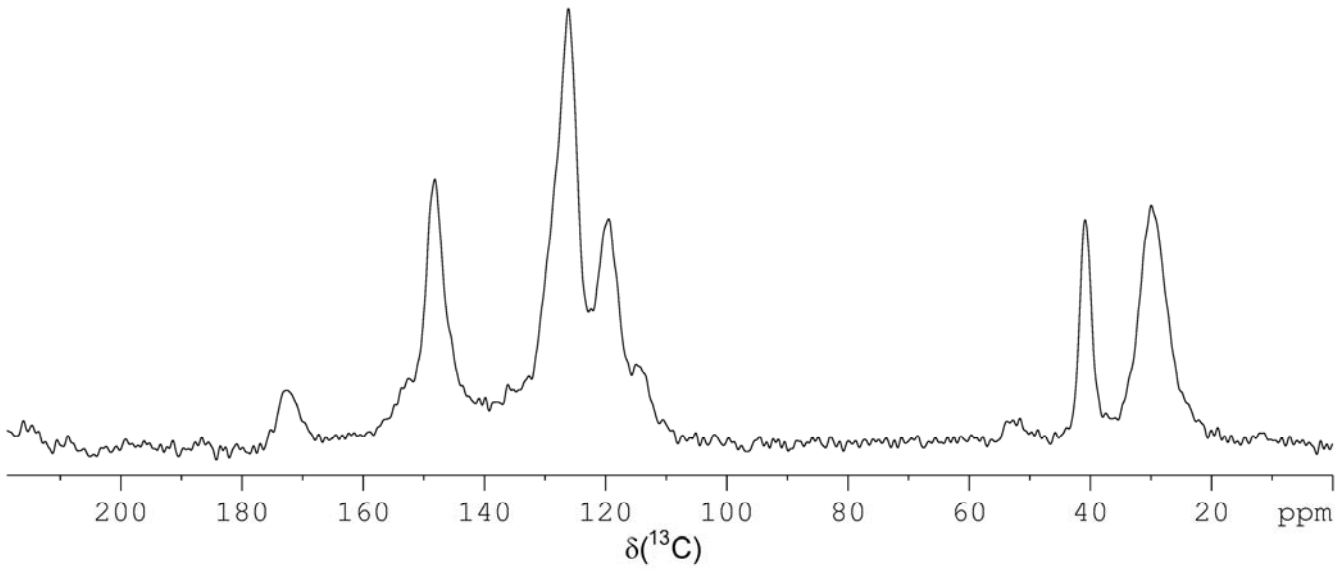


Fig. S14. ^{13}C {^{1}H} CP/MAS NMR spectrum of the cured resin produced from PL-3-270.

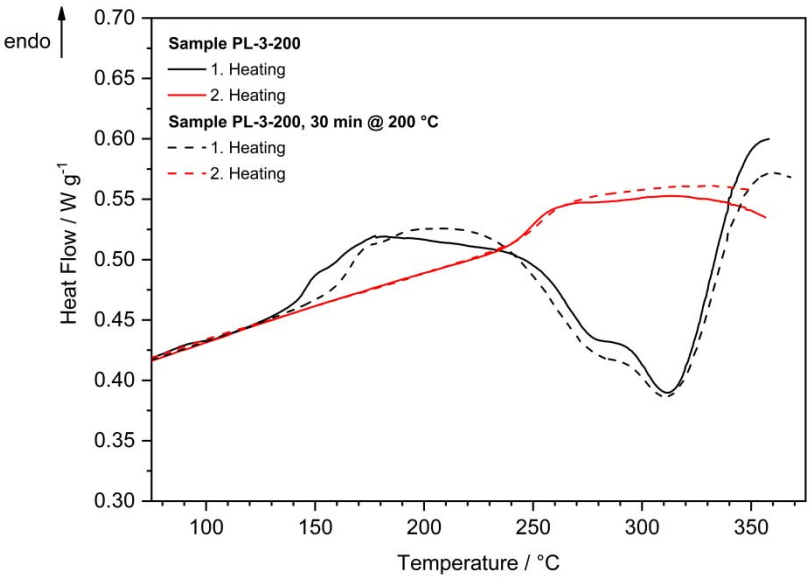


Fig. S15. DSC curves of PL-3-200 with (dashed) and without (bold) a precuring at 200 °C for 30 minutes prior to the main measurement cycle. A shift towards a higher T_g and a higher curing onset (195 °C) can be observed.

Table S4. TGA results for PL-3-200, PL-15-250 and PL-3-250-C, the corresponding curves can be found in the main paper, Fig. 7

Sample	mass [mg]	T_{max} Decomposition [°C]	T_{end} dec. step [°C]	Δm at T_{end} dec. step [%]	Residual mass at 800 °C [%]
PL-3-200	6.491	75	100	0.3	41
		145	195	1.0	
		270	285	0.4	
		310	330	0.3	
		448	485	15.1	
		533	690	39.2	
PL-3-250-C	5.458	163	290	4.7	43
		446	490	20.2	
		533	690	28.8	
		738		2.7	
PL-15-250	5.304	162	250	0.6	37
		348	485	5.3	
		532	715	55.2	

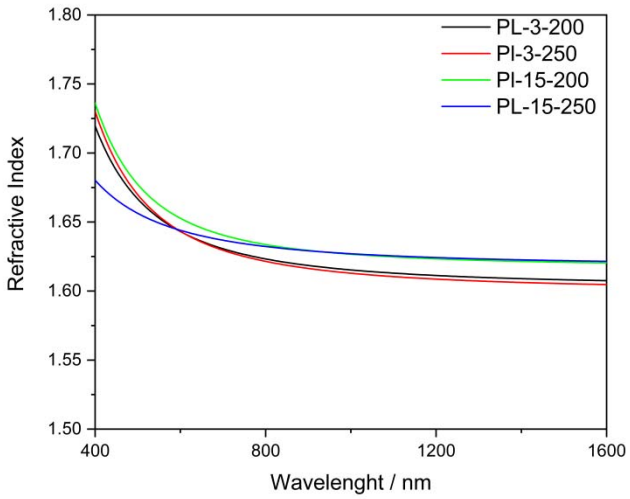


Fig. S16. Refractive index versus wavelength obtained from ellipsometric measurements for different samples prepared at different temperatures

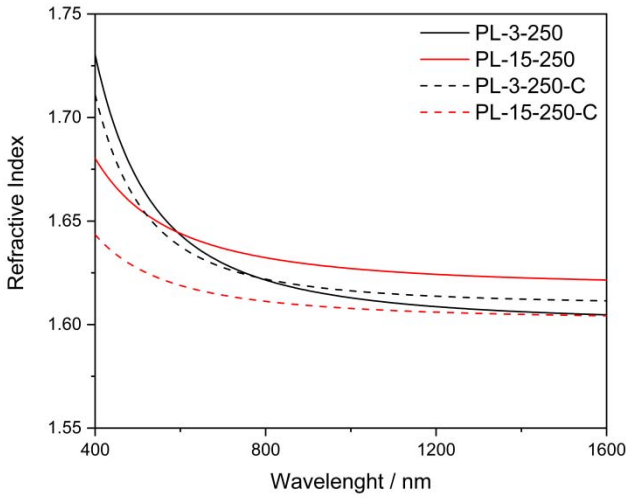


Fig. S17. Refractive index versus wavelength obtained from ellipsometric measurements for samples before (bold) and after (dashed) curing.

Table S5 Refractive index of the oligomers and cured resins at different wavelengths

Sample	n_D[a]		n_{1550}[b]	
	pristine	after curing	pristine	after curing
PL-3-200	1.64	1.62	1.61	1.58
PL-3-250	1.65	1.64	1.61	1.61
PL-15-200	1.65	1.65	1.62	1.62
PL-15-200-C	1.62	1.61	1.58	1.56
PL-15-250	1.65	1.62	1.62	1.60

[a] refractive index at 589.3 nm (Fraunhofer D line); [b] refractive index at 1550 nm