Supporting Information

Bio-derived Polymers for Coating Applications: Comparing Poly(limonene carbonate) and Poly(cyclohexadiene carbonate)

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Materials

1,4-Cyclohexadiene (97 %), *meta*-chloroperoxybenzoic acid (mCPBA, ≤77 %), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (99%), (±)-*trans*-1,2-diaminocyclohexane (99%), trimethylolpropane tris(3-mercaptopropionate) (≥ 95%), cobalt(II) acetate tetrahydrate (99%), limonene oxide, and *para*-toluenesulfonic acid monohydrate (≥ 98.5%), Irgacure 819 (phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, 97%) were purchased from Sigma Aldrich and used without further purification. Bis(triphenylphosphoranylidene)ammonium chloride (PPNCl, 97%) was obtained from Sigma Aldrich, re-crystallised from acetonitrile / diethylether, and dried at 40°C over night before use. The commercial mixture of (*R*)-LO was used, which is a mixture of cis and trans isomers (45/55). LO was purified by vacuum distillation after stirring over calcium hydride overnight. The GC is provided in the supporting information of Reference 1 (same batch was used).[1] Other chemicals and solvents were obtained from several commercial suppliers (Sigma Aldrich, Fischer, VWR, Alfa Aesar, Acros Organics) and used as received unless noted differently.

Characterisation

ATR-IR

IR spectra for the synthesis section were recorded on a Perkin Elmer Spectrum 100 (FT-IR) with an AT-IR crystal. Films were recorded on a Varian FT-IR 3100 spectrophotometer equipped with a heat-controlled, single-reflection accessory unit (Golden Gate). All the IR measurements were performed in the reflection mode in a resolution of 4 cm^{-1}.

DMTA

Dynamic mechanical thermal analysis (DMTA) was performed on a Q800 DMTA (TA instruments), equipped with a film fixture for tensile testing. Film tension DMTA measurements were performed on rectangular dry film samples between 20 and 180 °C, with a heating rate of 3 °C x min^{-1}. The tests were performed in the controlled strain mode with a frequency of 1 Hz, an oscillating amplitude of 0.12 μm, and a force track of 125 %.

DSC

Differential scanning calometry (DSC) was performed on a DSC4000 (Perkin Elmer) calorimeter under nitrogen at a heating rate of 10 °C/min. Data from the second heating scan are reported.

EA

Elemental analysis was measured at London Metropolitan University (by Mr Stephen Boyer) using a Carlo Erba Flash 2000 Elemental Analyser.

MALDI-ToF

Mass spectrometry was done on a MALDI micro MX micromass instrument with dithranol as matrix, potassium trifluoroacetic acid as additive, and THF as solvent.

NMR

^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra were measured on a Bruker AV 400 in CDCl$_3$ or deuterated DMSO.[2]

Raman

Raman spectra were recorded on a LabRAM Infinity N°3/81F spectrometer from Horiba Jobin Yvon Ltd. using a He-Ne Laser (633nm, 8 mW) with a pinhole of 200 μm and a magnification of 50x (Olympus LMPlanFl 50x/$_{0.50}$). Acquisition times varied between 180 and 300 seconds and the number of scans was set to 1 or 2 (depending on the quality of the spectra). Accumulated spectra were

smoothed by adjacent averaging (5 points) in Origin and peaks caused by residual radiation were removed before processing ("cosmic peaks"). To determine the conversion, the signal between 2520 and 2620 cm^{-1} was integrated and compared after normalisation of the carbonyl peak at 1750 cm^{-1}. To take the (C=C):(SH) ratio into account, the obtained ratios were multiplied by the theoretical conversion (i. e. the ratios yield values between 1 and 0; the multiplication with the theoretical conversions (25, 50, 100 for 4:1, 2:1, 1:1, respectively) transforms the numbers into meaningful percentages). For all the films, freshly made polymers and new reagents were used; significant background fluorescence was recorded for samples that were casted ca. 6 months after the preparation of the polymers (including samples that were recorded before the curing). However, no changes were detected by ^{1}H NMR, which suggests the stability of the materials. This effect was not further investigated and may be attributed to microstructural changes during the long-term drying process.

Raman spectrum S 21,22,23 and 24 were recorded on a Jobin Yvon (Horiba) spectrometer using a He-Ne laser at a wavelength of 632 nm, which was controlled by a motorised stage. Confocal Raman microscopy depth profiling was performed in air, thus the focus was slightly shifted due to refraction of the transparent polymer films. 100 × magnification objectives (Olympus) with a 400-µm pinhole were used and a laser step increment of 3 µm was set for CRM depth profiling. Small differences in the spectra were detected depending on the spectrometer.

Sample preparation (small scale)
The polymer (40 mg for poly(cyclohexadiene carbonate) (PCHDC) and 67 mg for poly(limonene carbonate) (PLC)) was dissolved in DCM (80 µL) and the curing agent trimethylolpropane tris(3-mercaptopropionate) (for molar ratios (C=C):(SH) = 1:1, 2:1 and 4:1 63, 32 and 16 µL of a stock solution of 121 mg in 0.2 mL), and the initiator Irgacure 819 (24 µL from a stock solution of 10 mg per 0.1 mL) were added. This solution (10 µL) was applied on a glass slide and left to dry overnight, in a well-ventilated fume hood. The obtained films were positioned in a drying tube, which was placed in a heated oil bath (silicon oil), and irradiated for a defined amount of time with a UV lamp (Philips Facial Tanner HB172, 4x15 W) in a distance of ca. 10 cm. All work was done under exclusion of light, mainly by protecting the samples in boxes covered with aluminium foil.

Sample preparation (mechanical testing)
Polymer (1.0 g of PCHDC or 1.4 g of PLC), curing agent (955 mg, 478 and 239 mg for 1:1, 2:1 and 4:1, respectively) and initiator Irgacure 819 (60 mg) were dissolved in chloroform (2 mL). The solution was applied on an aluminium plate (10 cm x 5 cm) with a doctor blade set to 250 µm, in a room designed for work with light-sensitive compounds. The plate was dried in a fume hood overnight, placed on a heating plate, under nitrogen atmosphere, in a self-built device and irradiated for 30 minutes with the UV lamp in a distance of ca. 10 cm. Free-standing films for DMTA were cast on a Teflon surface.

SEC
Molecular weights were determined by size exclusion chromatography (SEC) on an Agilent PL GPC-50 instrument, with HPLC grade THF (flow rate: 1.0 mL/min). Near monodisperse polystyrene standards were used for calibration. Samples were dissolved in THF and filtered through a 2 µm filter before injection. Characterisation by SEC-MALLS was done on a Shimadzu LC-20AD, with two mixed bed PSS SDV linear S columns (flow rate 1.0 mL/min). Dn/dc values were determined with an external RID detector (Knauer) with three different concentrations of the polymer of interest.

Experimental section

Synthesis of Cyclohexadiene oxide (CHDO)[3]

1,4-Cyclohexadiene (25 mL, 265 mmol) was oxidised with mCPBA (59.3 g, 255 mmol) and purified by repeated fractional vacuum distillation. Before use, CHDO was dried overnight over CaH_2, distilled, and stored in the glove box (10.5 mL, 109 mmol, 41%). The ^1H NMR data was in agreement with previously reported data.[3]

The purity was analysed by high-resolution GC-MS:
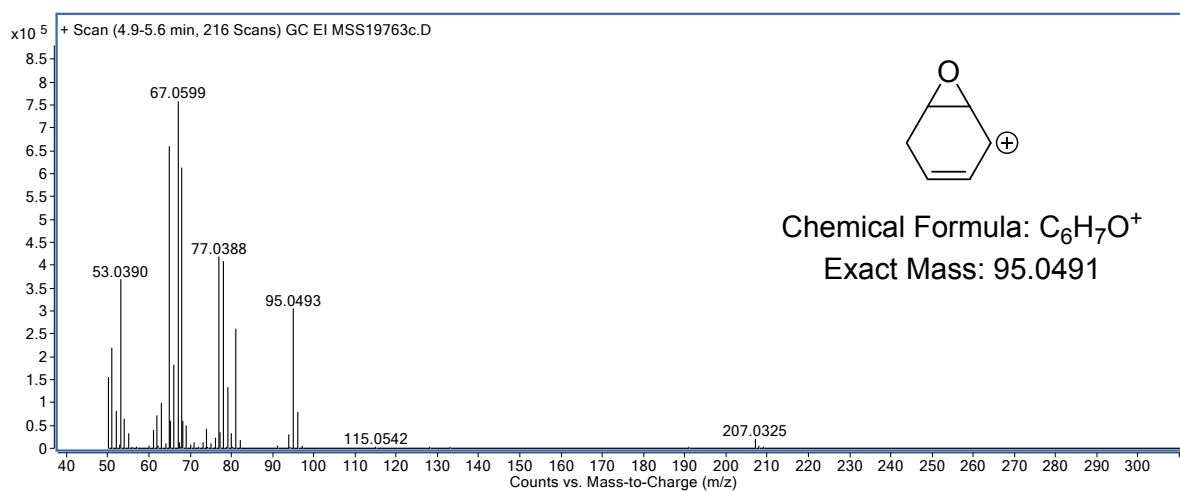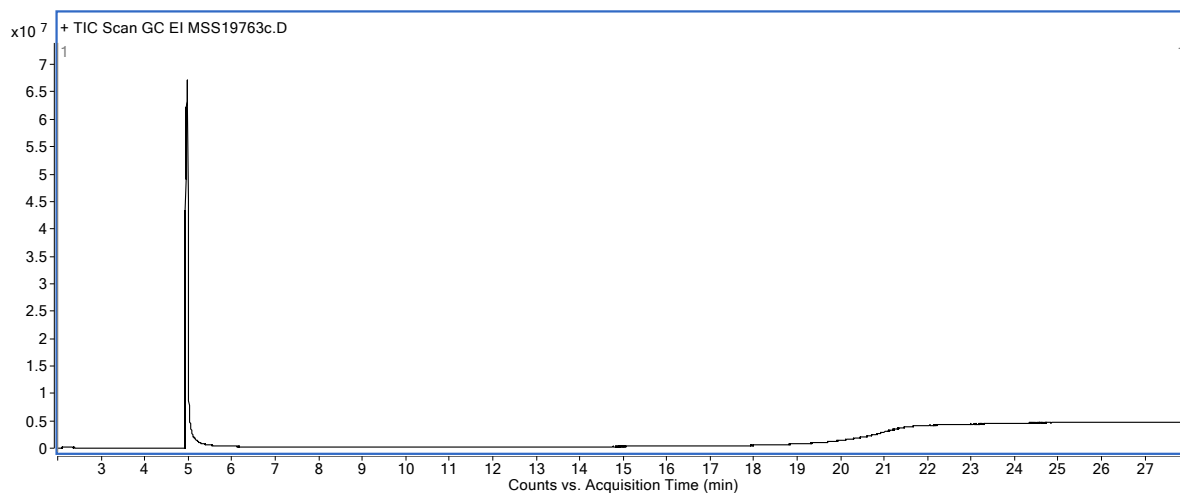
Synthesis of Cobalt(III)-salen catalyst[4-7]
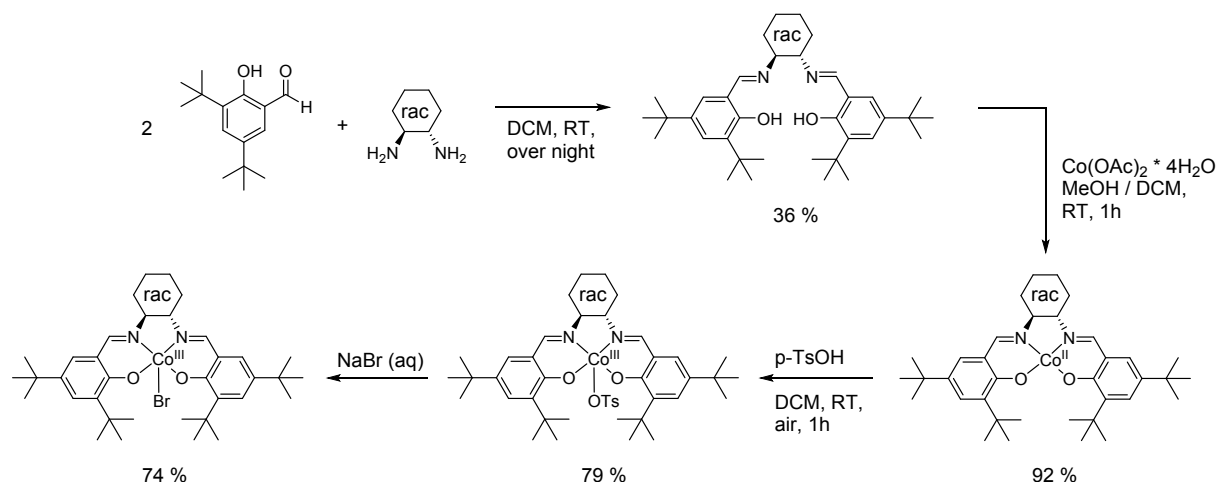
The salen ligand was prepared from the corresponding aldehyde (3.9 g, 16.6 mmol) and diamine (1.0 mL, 8.3 mmol) in 36% yield (3.5 g, 6.4 mmol) according to the reported method.[4] Next, the cobalt(II) complex was prepared in 92% yield (3.0 g, 5.04 mmol) following the reported procedures.[5,6] The Co(II)salen complex (2.0 g, 3.31 mmol) was then oxidised with *para*-toluenesulfonic acid (0.67 g, 3.51 mmol) and the corresponding bromo complex (1.36 g, 1.94 mmol) was obtained according to reported procedures (74% yield).[5-7]

^{1}H NMR (DMSO-d_6, 400.0 MHz, 298 K): 7.81 (s, 2H), 7.47 (s, 2H), 7.44 (s, 2H), 2.08-1.79 (m, 6H), 1.74 (s, 18H), 1.65-1.47 (m, 4H), 1.30 (s, 18H) ppm; ^{13}C{^{1}H} NMR (DMSO-d_6, 400.0 MHz, 298 K): 164.6, 162.0, 141.8, 135.9, 129.2, 128.8, 118.6, 69.3, 35.8, 33.5, 31.5, 30.4, 29.5, 24.3 ppm; MS(ES-ToF): M$^+$(-Br) found (calcd for $C_{36}H_{52}CoN_2O_2$): 603.3378 (603.3361) m/z; IR: 2865, 2952, 1590, 1521, 1461, 1389, 1359, 1336, 1310, 1251, 1200, 1175, 1033, 916, 876, 834, 812, 782 cm^{-1}; Elemental Analysis: Calcd. (%): C, 63.25; H, 7.67; N, 4.10. Found (%): C, 63.00; H, 7.62; N, 4.16.

Polymerisation of CHDO

In a Schlenk flask, CHDO (6 mL, 64.7 mmol), the cobalt(III)-salen catalyst (83 mg, 0.13 mmol), PPNCl (74 mg, 0.13 mmol), and *n*-PrOH (0.11 mL, 1.55 mmol) were mixed and injected in a 20 mL high pressure Parr Reactor, at 25 °C. The reactor was then pressurised to 20 bar with carbon dioxide and stirred at 30°C overnight. The crude polymer was dissolved in DCM, hexanoic acid (1 mL) was added, and the solution was stirred for 2 hours at room temperature. After concentration, the residue was dissolved in acetonitrile and extracted with hexane. The solution was then evaporated to dryness, dissolved in DCM, and precipitated in methanol (two times) and the pure polymer was obtained after drying under high vacuum at 40 °C (4.89 g).

^{1}H and ^{13}C{^{1}H} NMR data were reported previously (see also Fig. S 1).[8] Elemental Analysis: Calcd. (%): C, 60.00; H, 5.75. Found (%): C, 59.96; H, 5.96.

Selectivities and conversion were based on known ^{1}H NMR data of CHDO, the corresponding cyclic carbonate, and PCHDC (Fig. S 2).[8,9] For GPC traces and dn/dc values for SEC-MALLS, see Fig. S 3. End groups were determined by MALDI (Fig. S 4) and hydroxyl groups were further analysed by the ^{31}P{^{1}H} shift after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane to distinguish between primary, secondary and tertiary alcohol (Fig. S 5).[10]
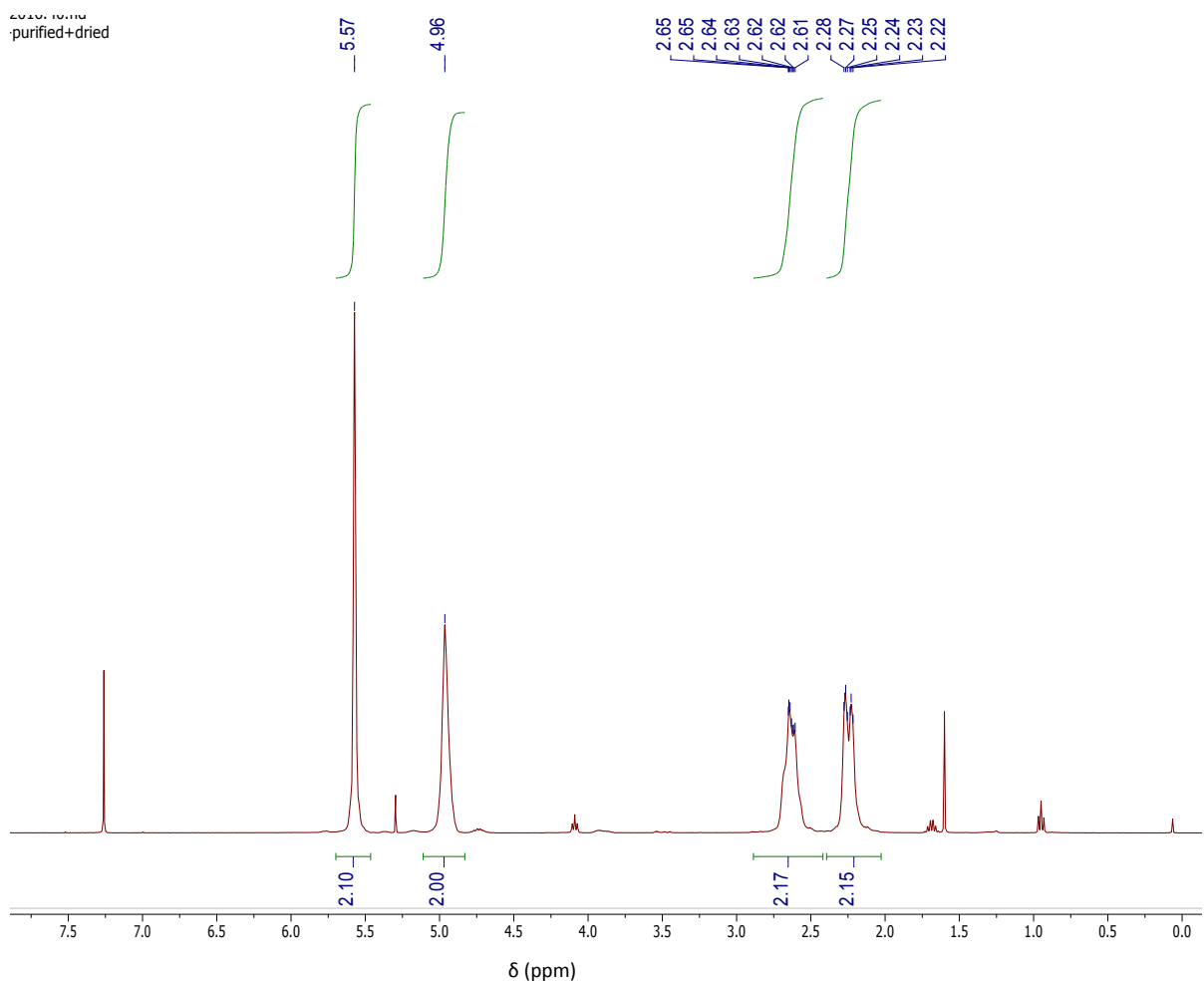
Fig. S 1 ¹H NMR (400 MHz, CDCl₃, 298 K) of PCHDC.

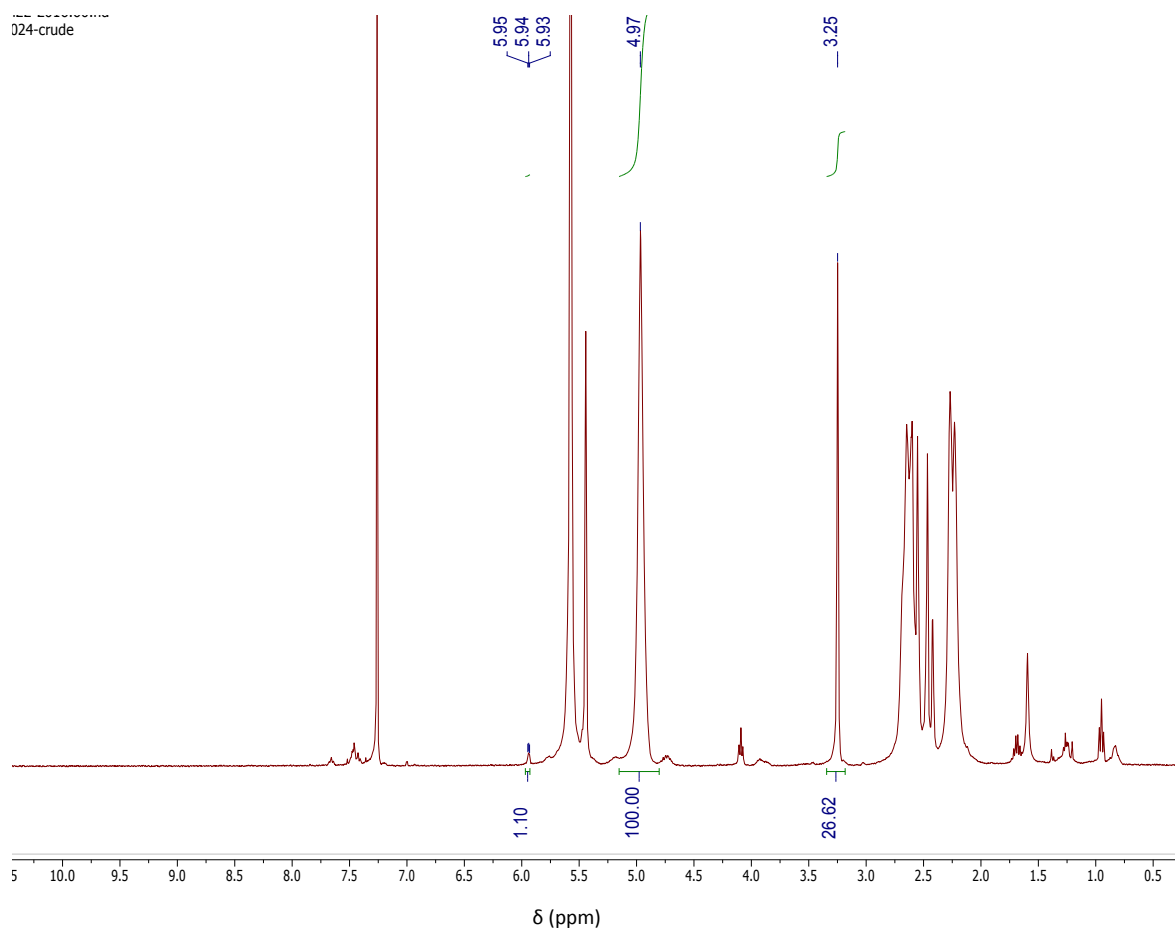**Fig. S 2**   ^{1}H NMR of crude PCHDC (400 MHz, CDCl$_3$, 298 K). The signals at 5.94, 4.97, and 3.25 ppm are characteristic for the cyclic carbonate, PCHDC and CHDO, respectively. No signal was found at 3.45 ppm (polyether signal).
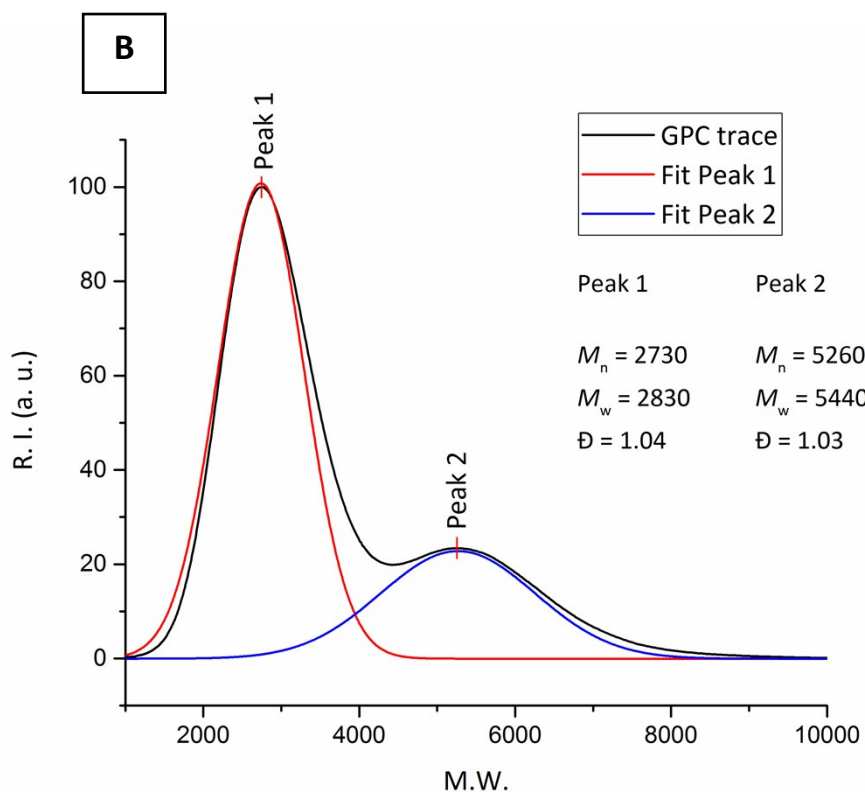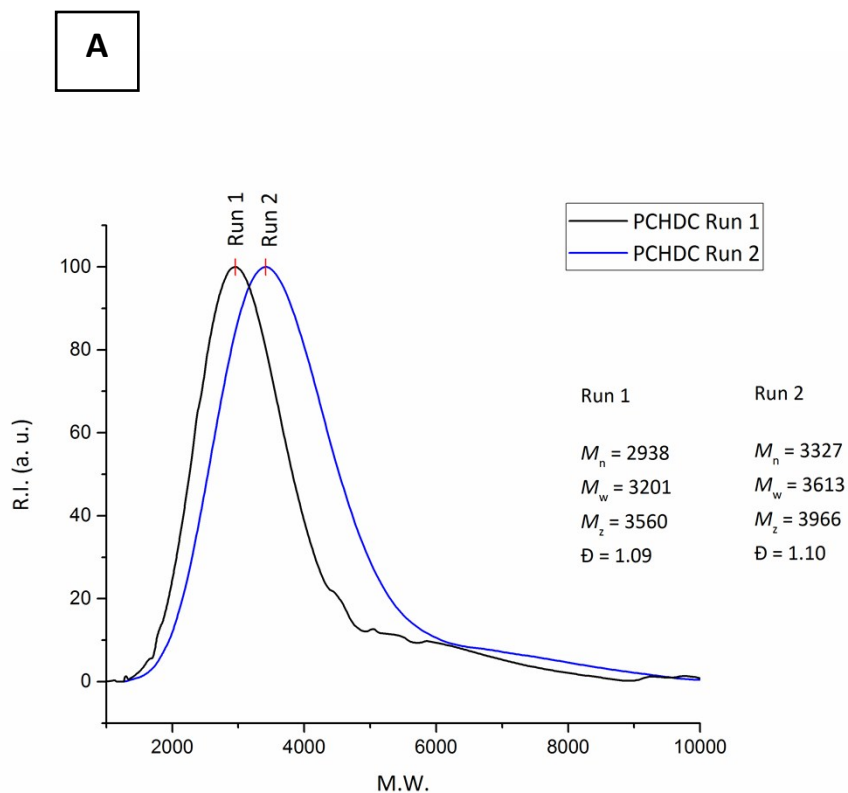
Fig. S 3 (PS)-SEC traces of PCHDC. A: monomodal traces; B: bimodal traces. Fit function for peak 1: f(x) = -0.03838 + (139830/(1106*sqrt(PI/2)))*exp(-2*((x-2740)/1106)^2); peak 2: f(x) = -0.03838 + (56666/(1981*sqrt(PI/2)))*exp(-2*((x-5265)/1981)^2). M_n if both peaks were not considered separately: 2850 g mol^{-1} (1.12). For SEC-MALLS, dn/dc was determined to be 0.0851 mL/g (not shown).
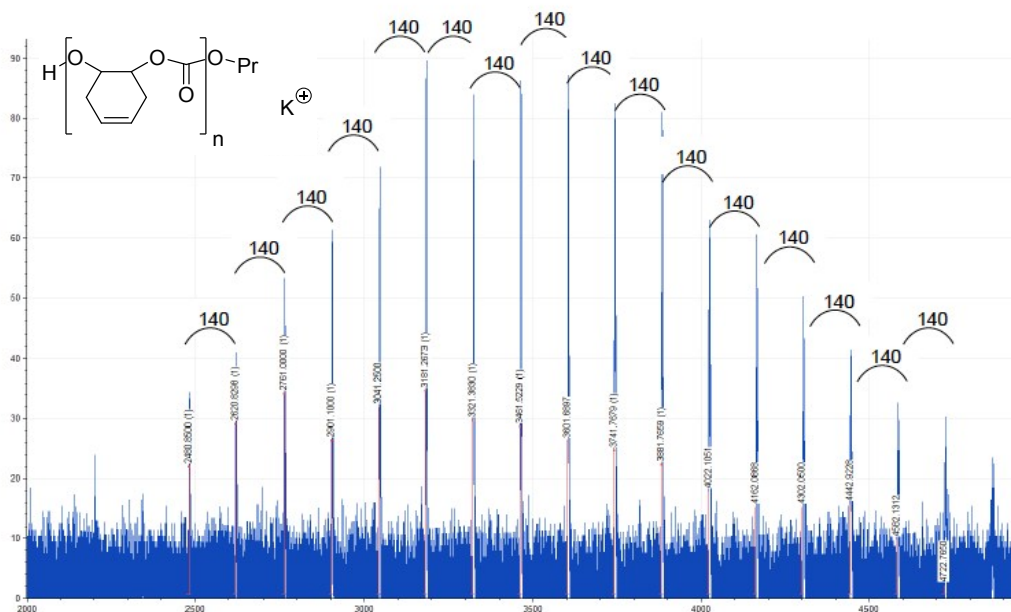
Fig. S 4 MALDI-ToF spectrum of poly(cyclohexadiene carbonate). The series shows m/z = [60.06 (propanol) + (140.05 x n) (PCHDC) + 38.96 (K$^+$)] (n = 17 ~ 33). Y-Axis: Intensity (a. u.), x-axis: m/z.

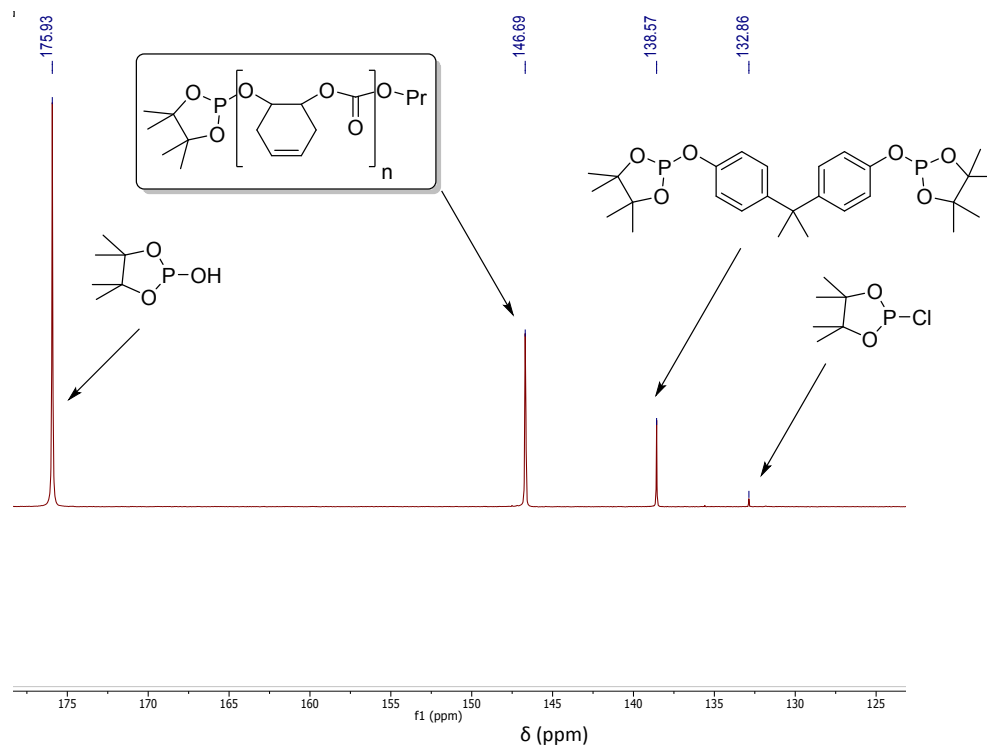**Fig. S 5** ^{31}P{^{1}H} NMR spectrum (400 MHz, CDCl$_3$, 298 K) of PCHDC after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane (bisphenol A used as an internal standard). The peaks

at 175.9, 146.7, 138.6, 132.9 ppm correspond to the phosphorus agent, the OH end-group (after the reaction), bisphenol A and the hydrolysed phosphorus agent, respectively.

Polymerisation of (R)-limonene oxide[11]

(R)-Limonene oxide (108 mL, 0.66 mol), the Al complex (0.5 mol%, 3.3 mmol, 1.7 g), PPNCl (0.95 g, 1.65 mmol, 0.25 mol%) and water (0.47 mL, 0.026 mmol, 4 mol%) were transferred into a 250 mL stainless steel Büchi reactor. The reactor was sealed, pressurised with 15 bar CO_2 and allowed to react for 48 hours at 45 °C. The final monomer conversion was determined by ^{1}H NMR to be 67%. The reaction mixture was dissolved in a small amount of dichloromethane and precipitated with a large excess of methanol. The polymer was washed with methanol to remove the catalyst and the unreacted epoxide and dried *in vacuo* (65 g, 0.33 mol, 50%).

^{1}H NMR (400 MHz, CDCl3): δ 5.15 – 5.03 (m, 1H), 4.74 – 4.67 (m, 2H), 2.40 (m, 1H), 2.22 (m, 1H), 1.94 - 1.72 (m, 3H), 1.70 (br s, 3H), 1.60 (m, 1H), 1.50 (m, 3H), 1.37 (m, 1H) ppm.

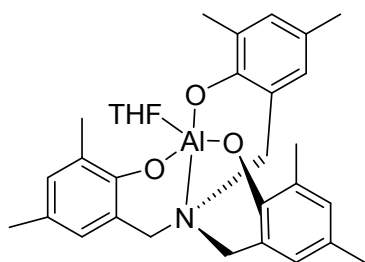Elemental Analysis: Calcd. (%):C, 67.32; H, 8.22. Found (%): C, 67.42; H, 8.30.

Fig. S 6   Aluminium catalyst, first reported by Kleij and co-workers, which was used in the PLC synthesis.[11]
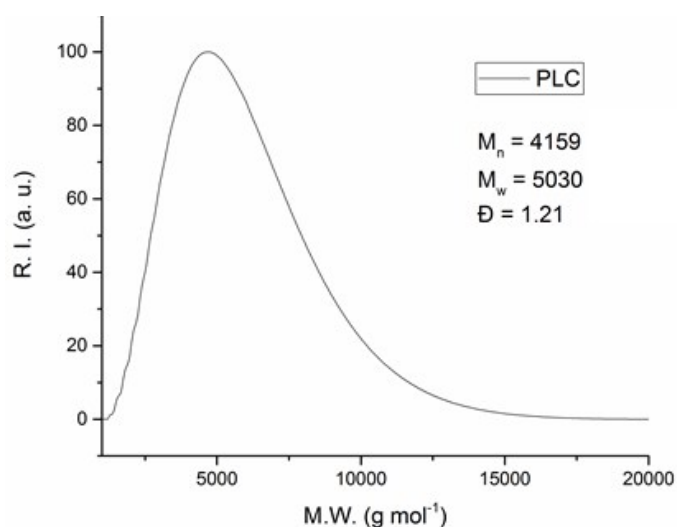

Fig. S 7   (PS)-SEC trace of PLC. For SEC-MALLS, dn/dc was determined to be 0.0804 mL/g (not shown).
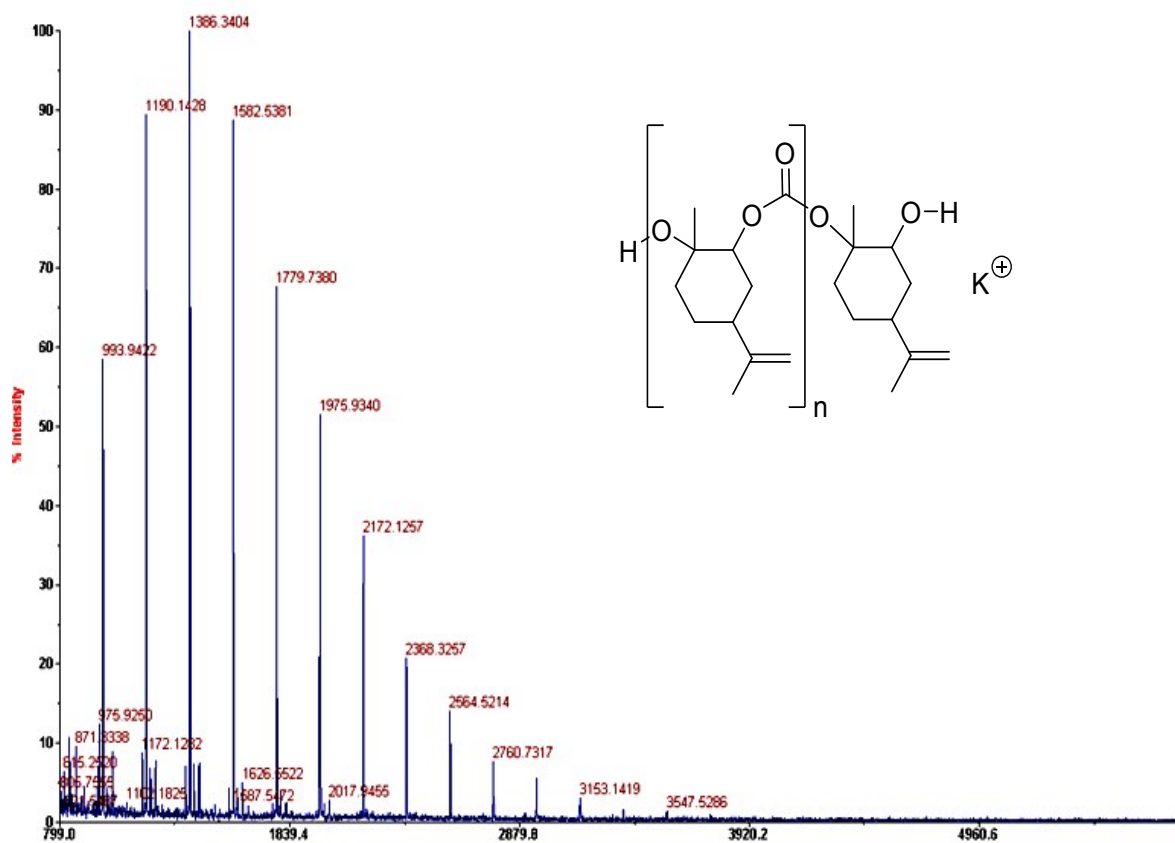
Fig. S 8 MALDI-ToF spectrum of poly(limonene carbonate). The series shows m/z = [18.01 (water) + limonene oxide (152.12) + (196.11 x n) (PLC) + 38.96 (K⁺)] (n = 4 ~15).
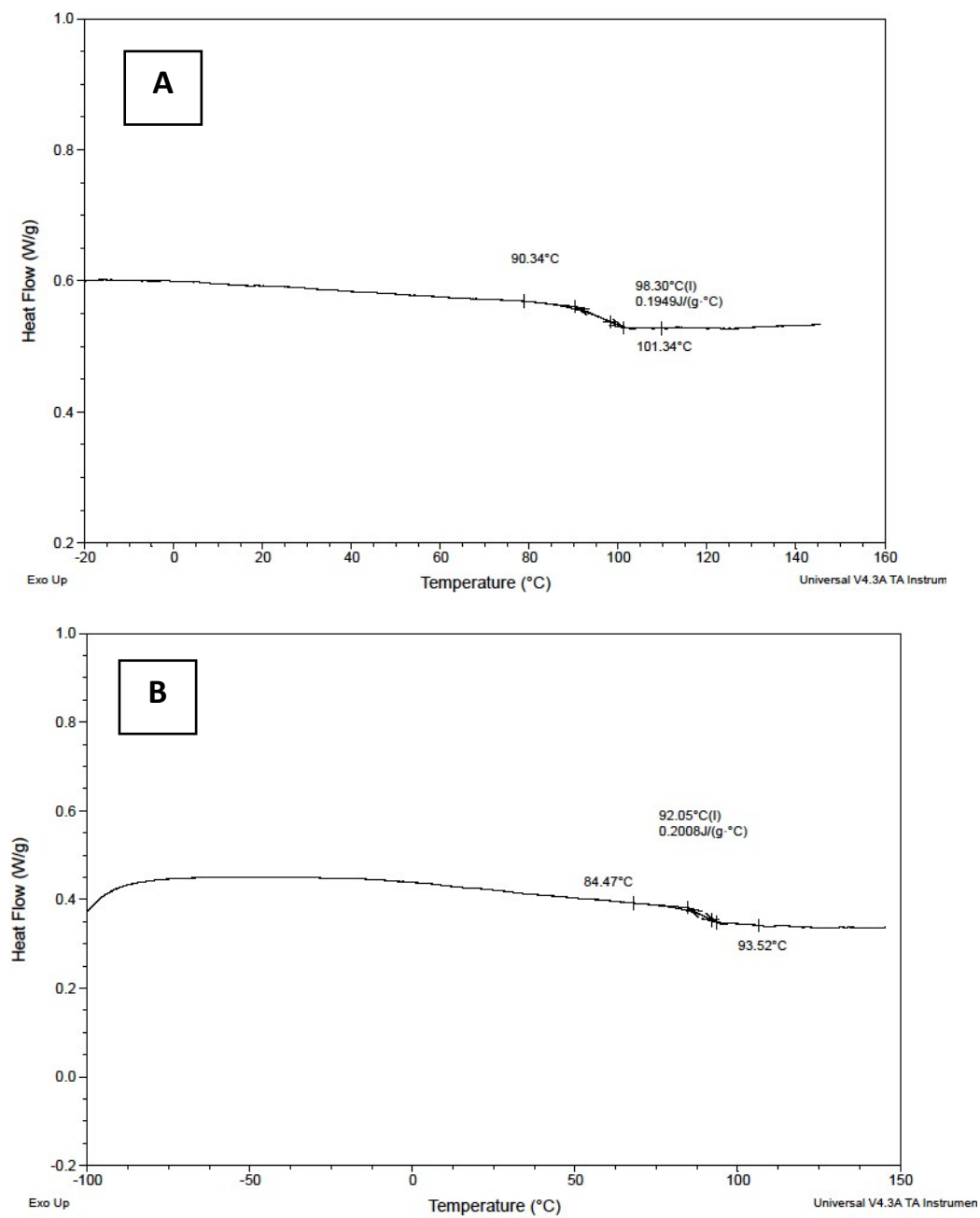
DSC results

Fig. S 9 DSC thermograms of (A) PCHDC and (B) PLC. All DSC thermograms, the heat flow (W/g, y-axis) is displayed versus the temperature (°C, x-axis).
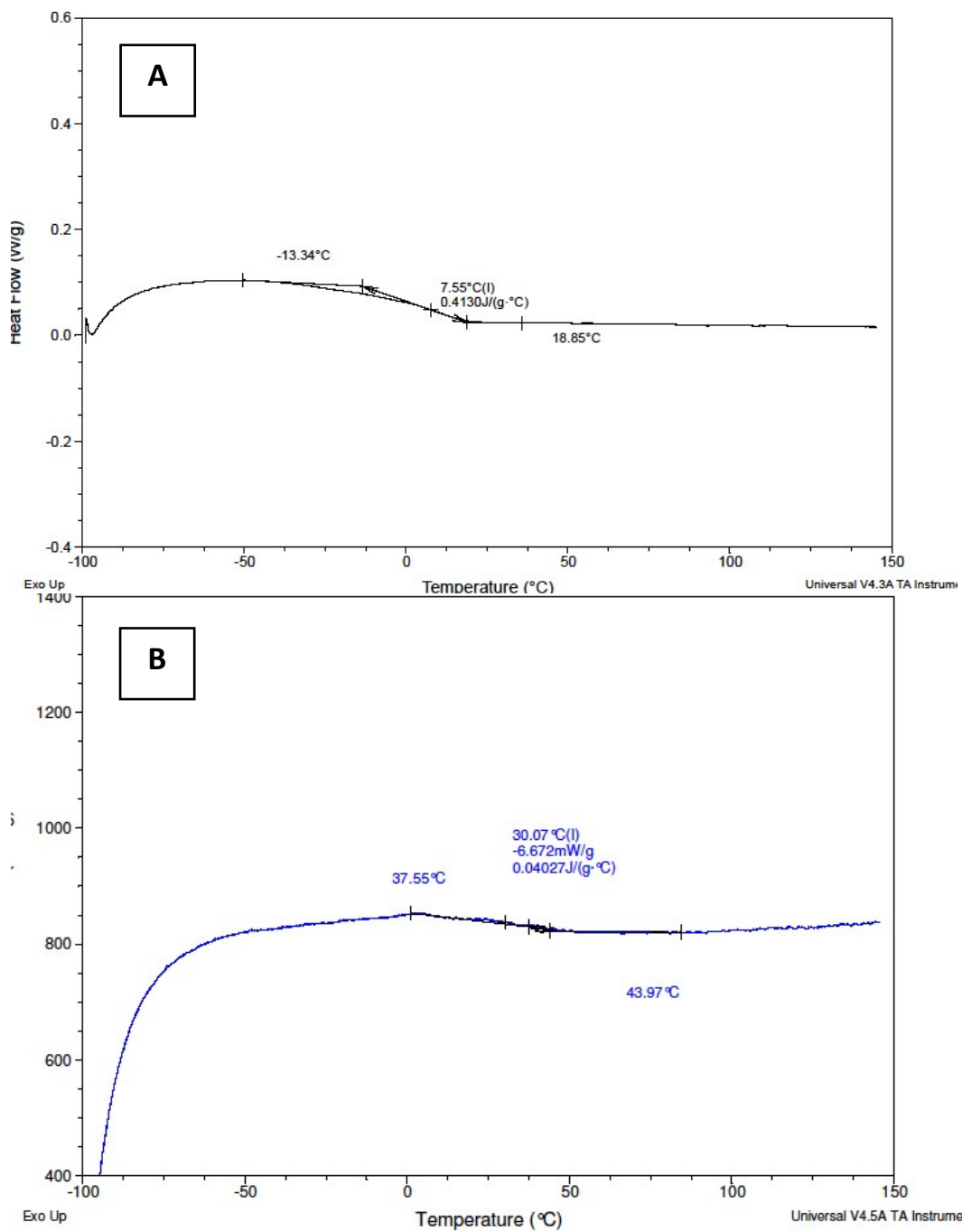
Fig. S 10   DSC thermograms of uncured (C=C):(SH) = 1:1 films for PCHDC (A) and (B) PLC.
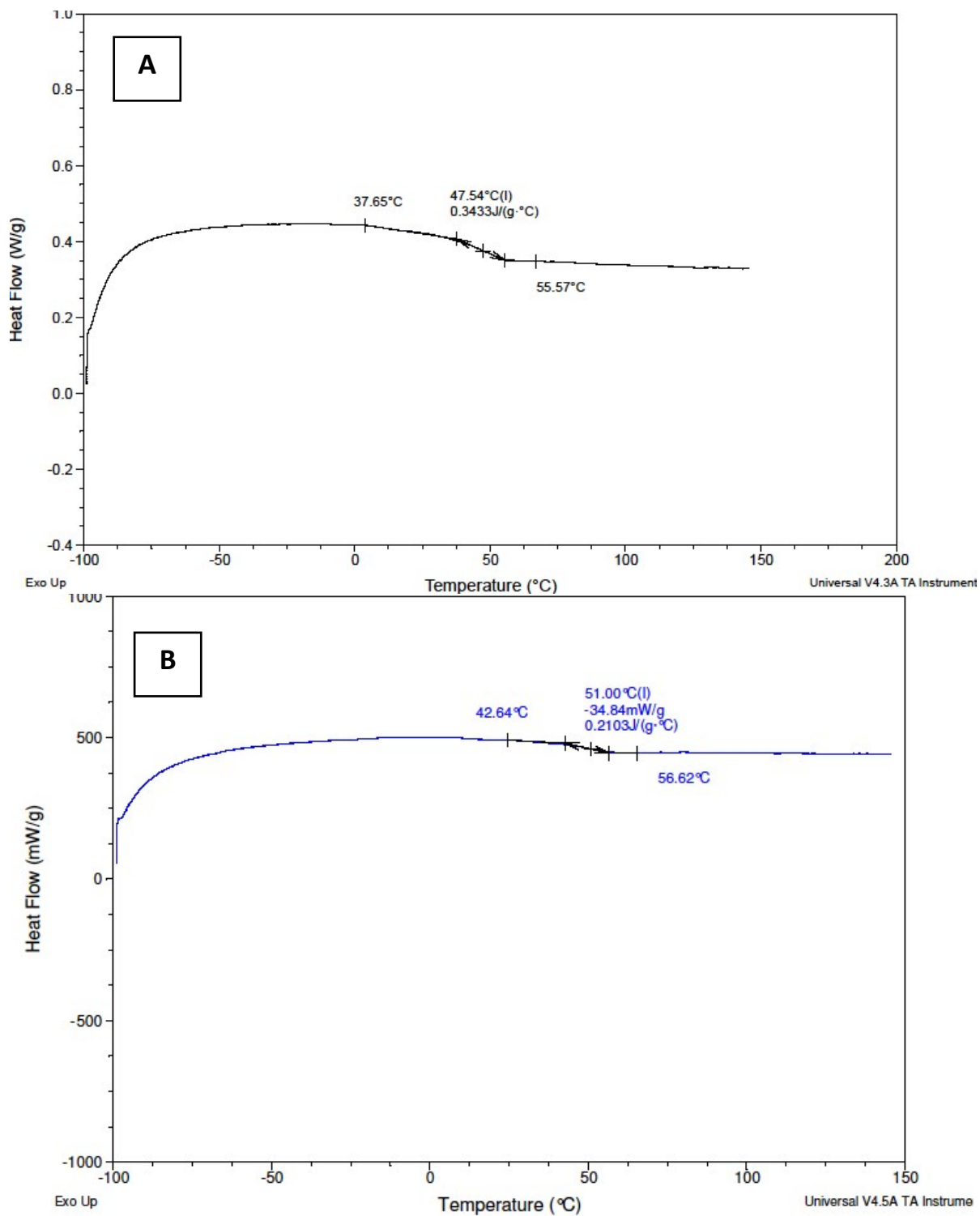
Fig. S 11 DSC thermograms of uncured (C=C):(SH) = 2:1 films for PCHDC (A) and (B) PLC.
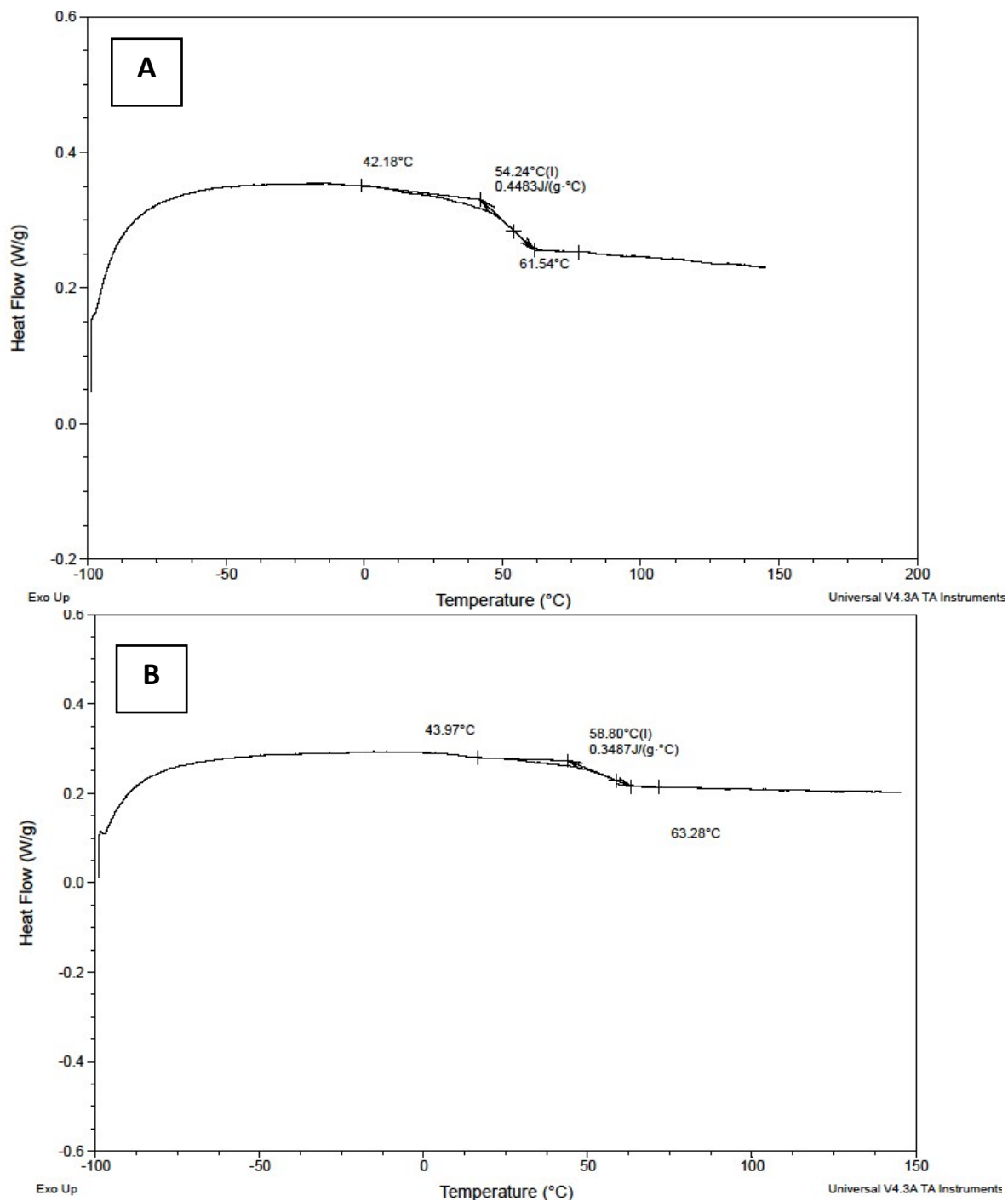
Fig. S 12 DSC thermograms of uncured (C=C):(SH) = 4:1 films for PCHDC (A) and (B) PLC films.

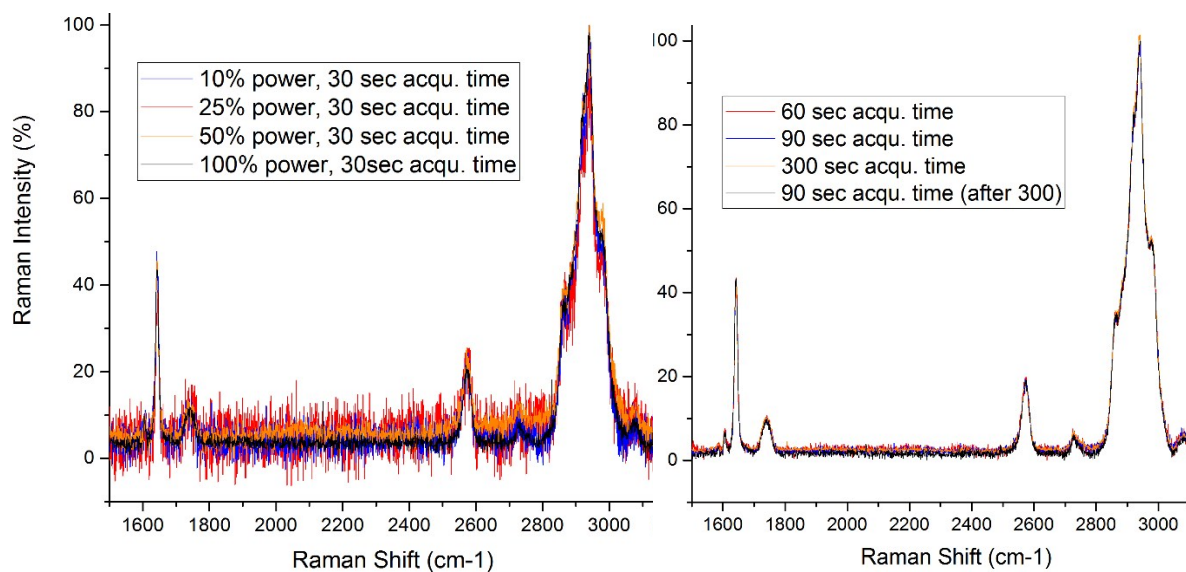# Control experiments (Raman spectroscopy)

Fig. S 13   Stability of PLC films (including TMP-SH [1:1] and 2 mol% Irgacure 819) with Laser Power (left) and acquisition time at 100% intensity (right).
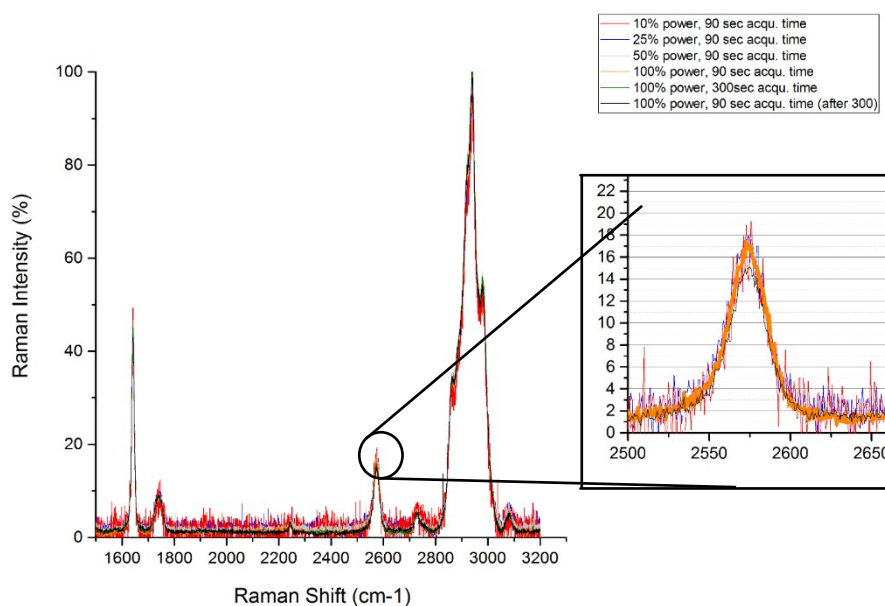
Fig. S 14   Stability of PLC films depending on laser power and acquisition time. The enlarged section shows the thiol signal.

UV / VIS spectrum of Irgacure 819
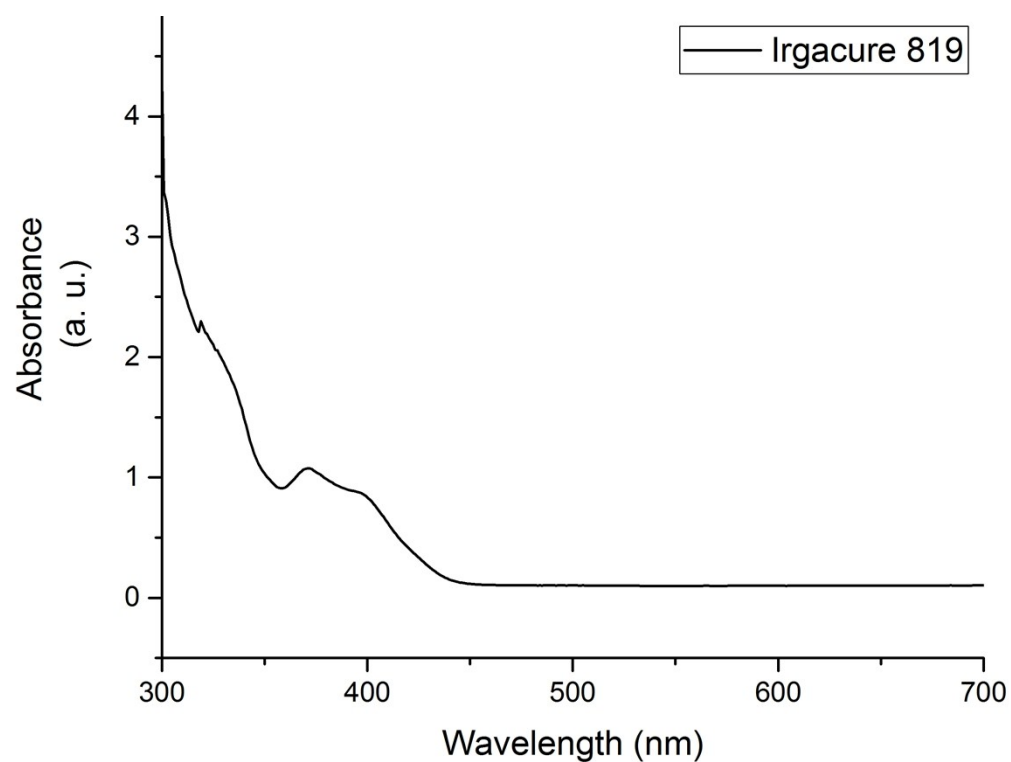
Fig. S 15 UV/VIS spectrum of Irgacure 819. It should be noted, that no absorbance is observed at the operating wavelength of the laser (633 nm).

Temperature optimization (Raman spectroscopy)
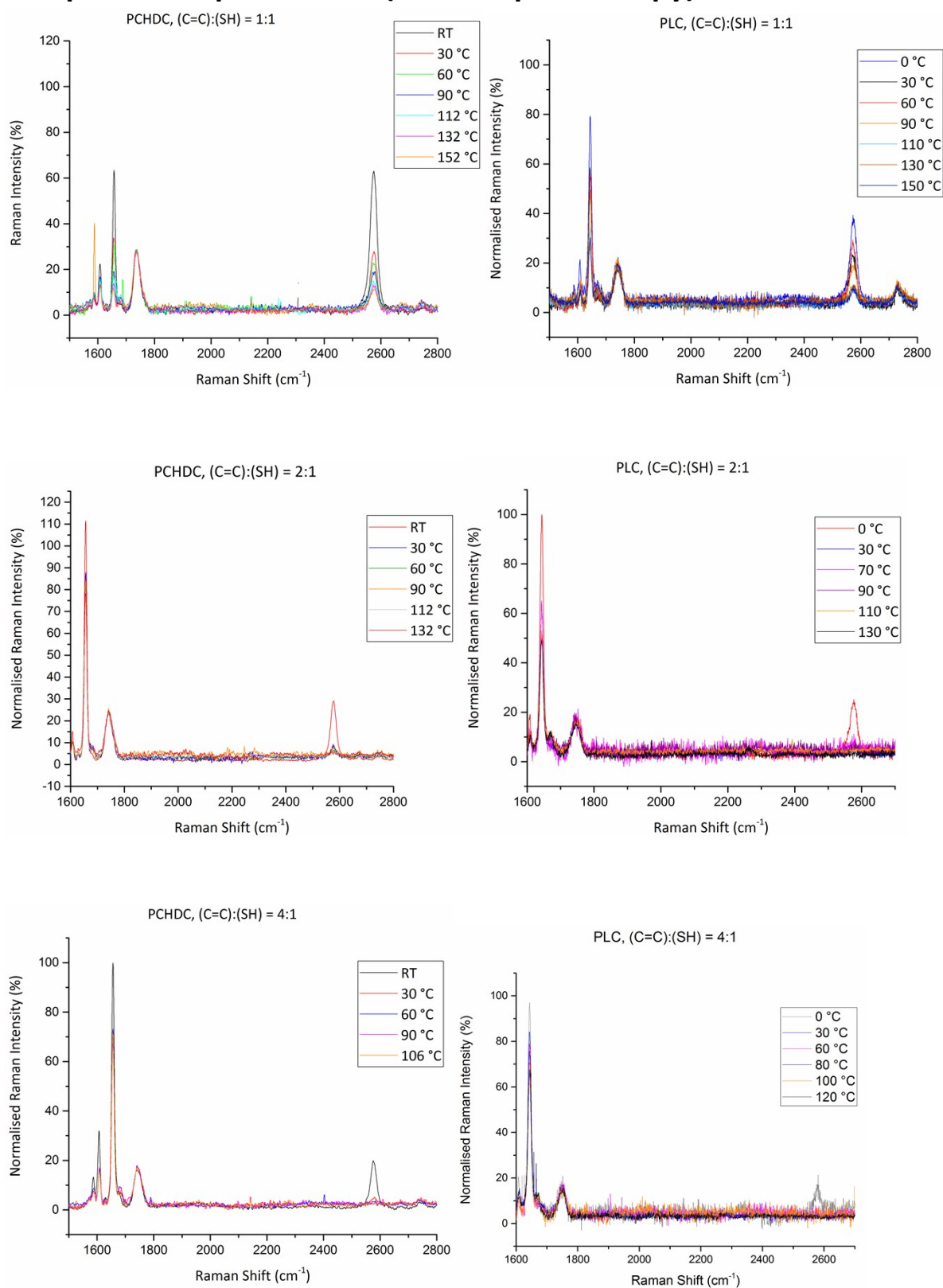
Fig. S 16 Temperature optimization for various PLC and PCHDC films. For PCHDC, absolute temperatures are given; for PLC temperatures above T_g are shown).

Kinetics PLC (Raman spectroscopy)
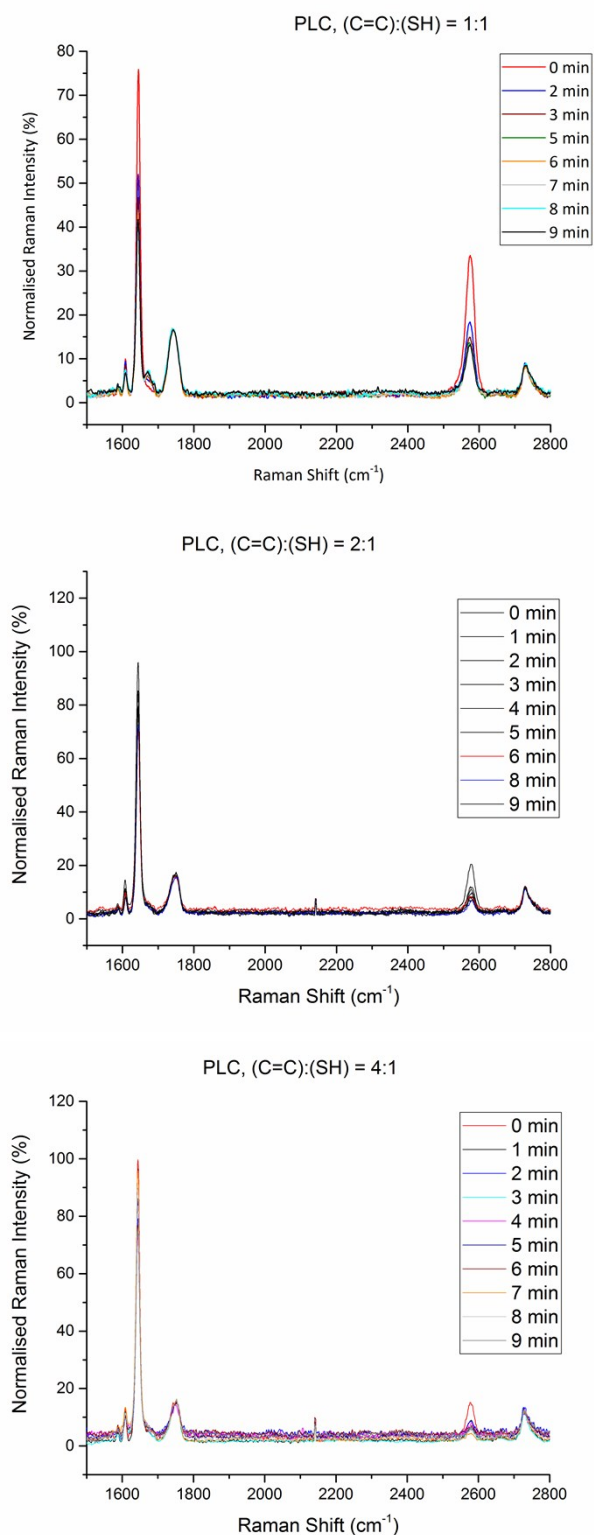
Fig. S 17   Kinetic analyses of the cross-linking of various PLC films at optimized temperatures (see Table 2 for values).

Kinetics PCHDC (Raman spectroscopy)
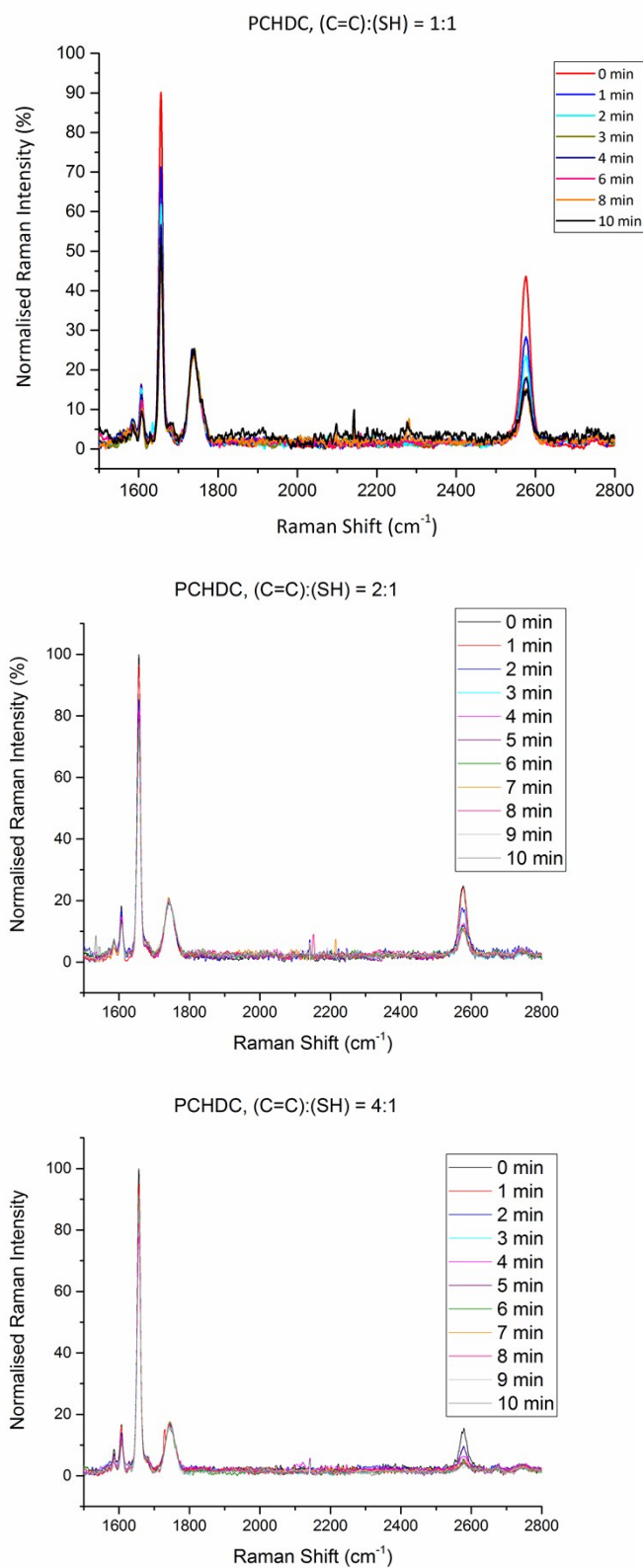
Fig. S 18   Kinetic analyses of the cross-linking of various PCHDC films at optimized temperatures (see Table 2 for values).

Drying under nitrogen and air
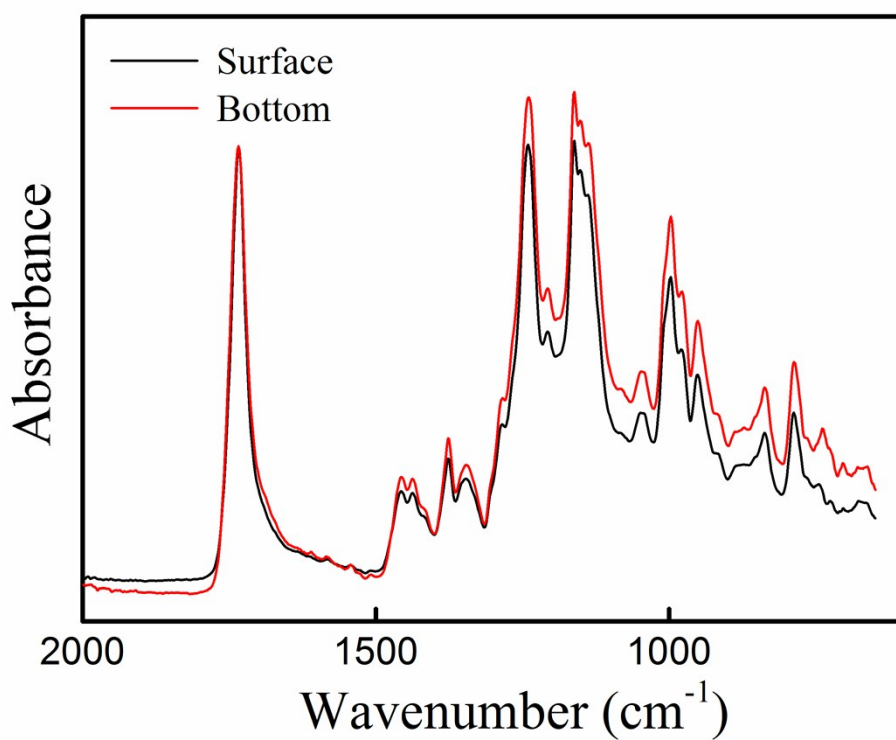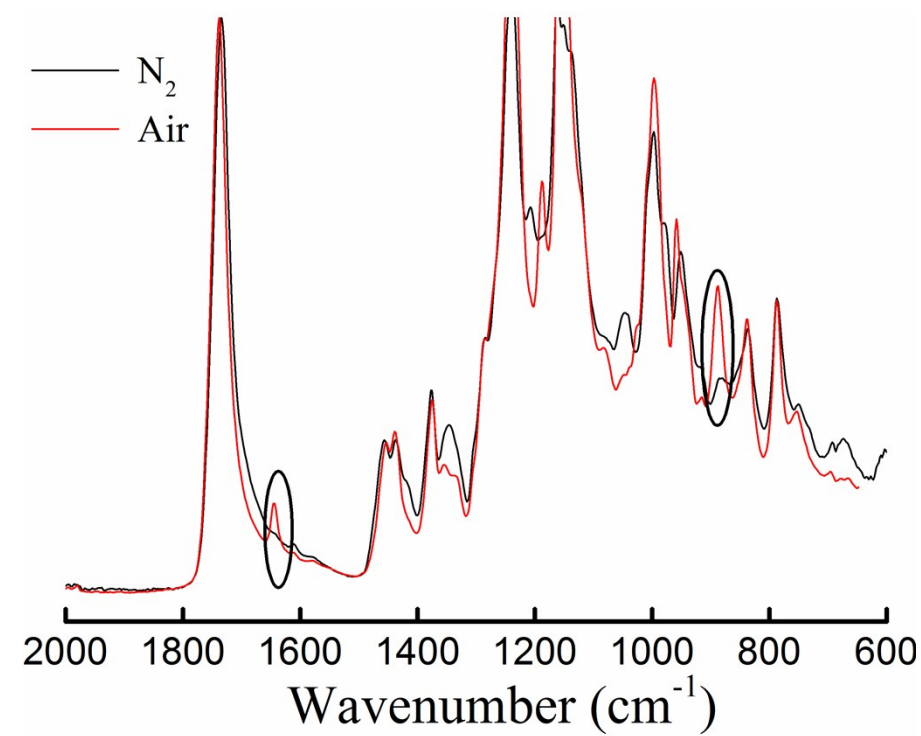
Fig. S 19   ATR-IR spectra of PLC films dried under nitrogen and under air; the circles are indicative signals for C=C of the polymer (top). IR spectra of the surface and the bottom of a film dried under nitrogen (bottom; note: thiol was consumed at both sides).
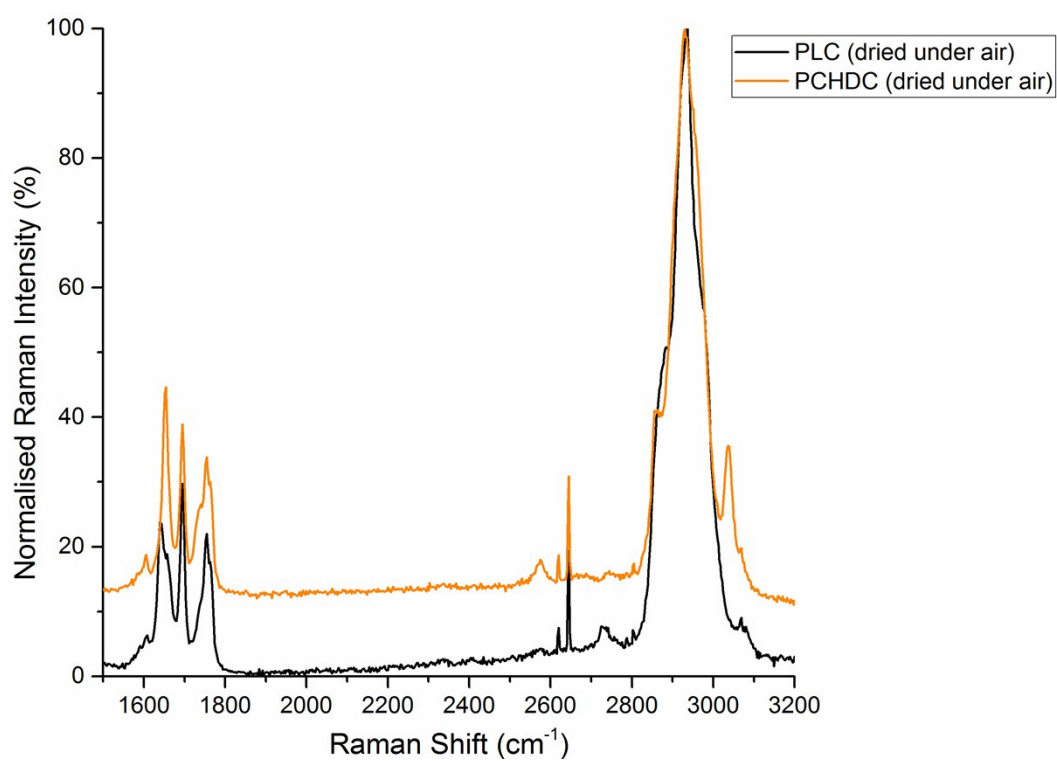
Fig. S 20 Raman spectra of PLC and PCHDC film used for mechanical testing (subtle differences to the spectra shown in the previous sections were a result of a different spectrometer; the peak at ~ 2650 cm^{-1} was considered as an artefact ("cosmic peak") of the instrument).
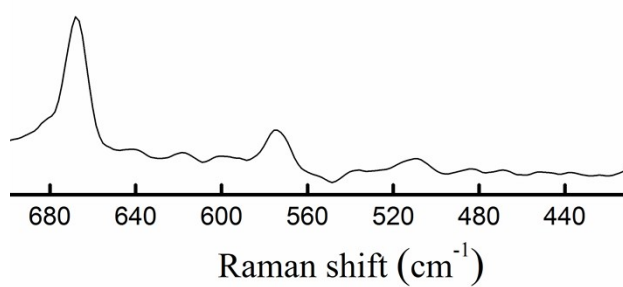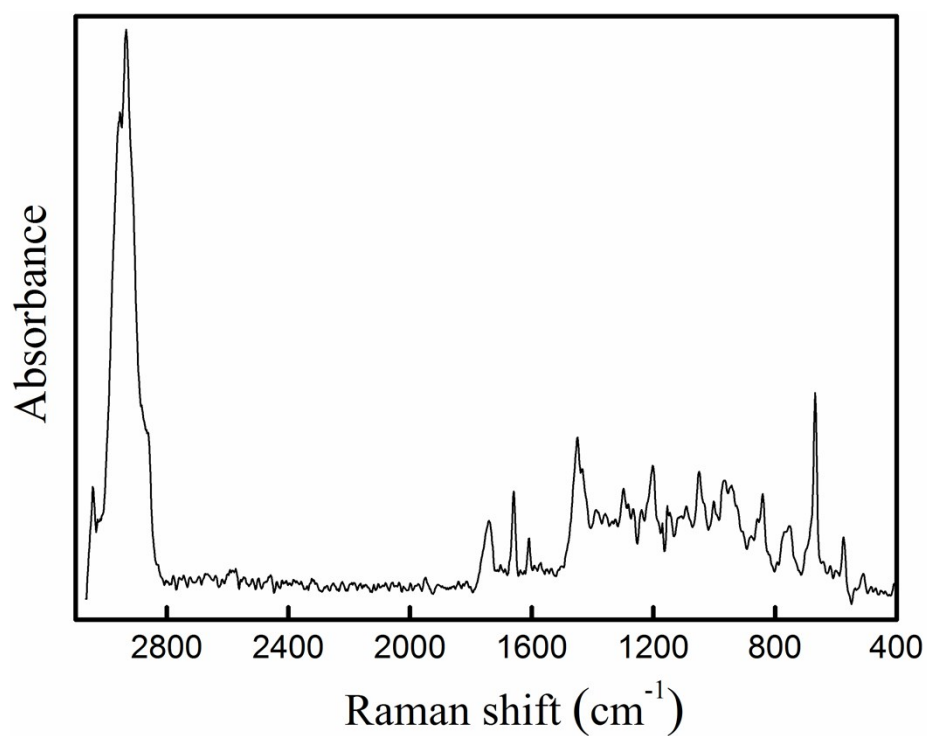
Fig. S 21   Raman spectra of a cured PCHDC film (full region, top; relevant region for S-S bonds, bottom).
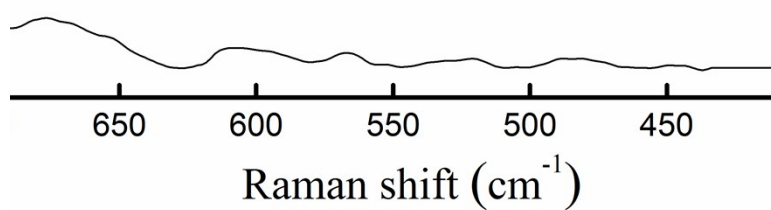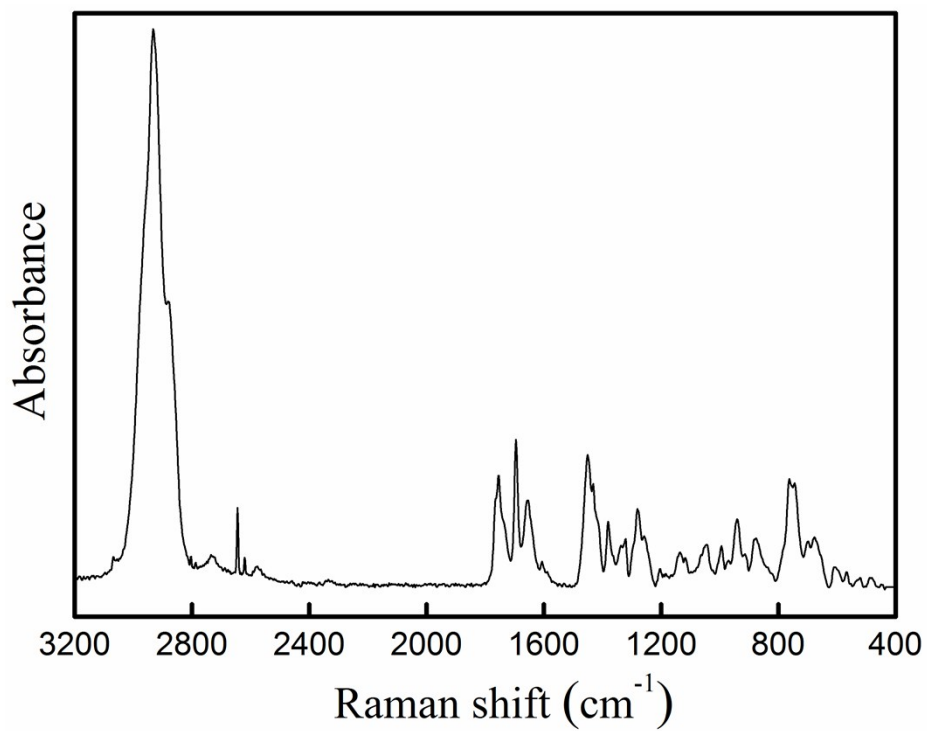
Fig. S 22 Raman spectra of a cured PLC film (full region, top; relevant region for S-S bonds, bottom).

Table S 1   Comparison of mechanical parameters of cured coatings dried, under air, and, under nitrogen.

Dried under	Sample (molar ratio)	Acetone resistance	Thickness (μm)	Pencil hardness	König hardness (s)	Impact
Air	PLC, (C=C):(SH) = 1:1	+	29	2H	109	-
	PLC, (C=C):(SH) = 2:1	+	155	H	96	-
	PLC, (C=C):(SH) = 4:1	-	25	H	102	-
	PCHDC, (C=C):(SH) = 1:1	+	148 and 255	H	113 and 107	-
	PCHDC, (C=C):(SH) = 2:1	-	35	2H	139	-
	PCHDC, (C=C):(SH) = 4:1	-	40	2H	144	-
Nitrogen	PLC, (C=C):(SH) = 1:1	+	40	H	103	-
	PLC, (C=C):(SH) = 2:1	+	36	2H	110	-
	PLC, (C=C):(SH) = 4:1	+/-	32	2H	114	-
	PCHDC, (C=C):(SH) = 1:1	+	60	2H	123	-
	PCHDC, (C=C):(SH) = 2:1	+	40	2H	151	-
	PCHDC, (C=C):(SH) = 4:1	+/-	38	H	159	-

Legend:
- ▲ PLC, (C=C):(SH) = 1:1
- —— Gauss Fit PLC, (C=C):(SH) = 1:1
- ● PCHDC, (C=C):(SH) = 1:1
- —— Gauss Fit PCHDC, (C=C):(SH) = 1:1
- ▲ PLC, (C=C):(SH) = 2:1
- —— Gauss Fit PLC, (C=C):(SH) = 2:1
- ● PCHDC, (C=C):(SH) = 2:1
- —— Gauss Fit PCHDC, (C=C):(SH) = 2:1
- ● PCHDC, (C=C):(SH) = 4:1
- —— Gauss Fit PCHDC, (C=C):(SH) = 4:1

PCHDC 4:1

Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	3.59308E-4		
Adj. R-Square	0.99337		
		Value	Standard Error
E	y0	0.04111	6.92276E-4
E	xc	68.49241	0.04118
E	w	30.20344	0.09213
E	A	27.84697	0.08652
E	sigma	15.10172	0.04606
E	FWHM	35.56183	0.10847
E	Height	0.73563	0.0018

PCHDC 2:1

Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	0.00112		
Adj. R-Square	0.9698		
		Value	Standard Error
E	y0	0.03511	0.00119
E	xc	73.65595	0
E	w	28.62212	0.18821
E	A	21.92543	0.14514
E	sigma	14.31106	0.0941
E	FWHM	33.69997	0.2216
E	Height	0.6112	0.00326

PCHDC 1:1

Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	7.53807E-4		
Adj. R-Square	0.94074		
		Value	Standard Error
E	y0	0.04685	0.00104
E	xc	111.72129	0.13682
E	w	33.30007	0.31148
E	A	14.05671	0.13647
E	sigma	16.65003	0.15574
E	FWHM	39.20783	0.36673
E	Height	0.3368	0.0025

PLC 2:1

Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	1.86935E-4		
Adj. R-Square	0.9896		
		Value	Standard Error
Tan Delta	y0	0.0273	5.22206E-4
Tan Delta	xc	89.72298	0
Tan Delta	w	38.11473	0.14137
Tan Delta	A	19.1686	0.07525
Tan Delta	sigma	19.05737	0.07069
Tan Delta	FWHM	44.87667	0.16646
Tan Delta	Height	0.40127	0.00117

PLC 1:1

Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	0.00137		
Adj. R-Square	0.89323		
		Value	Standard Error
E	y0	0.06074	0.00136
E	xc	101.39307	0
E	w	35.26497	0.4404
E	A	14.52267	0.18841
E	sigma	17.63249	0.2202
E	FWHM	41.52133	0.51853
E	Height	0.32858	0.00328

Fig. S 23   Peak analysis of DMTA data. All data points were fitted by a single peak fit using Gauss functions.

Pictures of PLC- and PCHDC-based Coatings

Fig. S 24   A typical picture of a PLC-based coating.

Fig. S 25   A typical picture of a PCHDC-based coating.

Calculation of Crosslink-Density

The crosslink-density ν_e is defined as the "number of crosslinks per unit volume in a polymer network" (IUPAC).[12] For cross-linked films, the crosslink-density can be calculated based on the storage modulus E' in the rubbery plateau (measured by DMTA):[13,14]

$$E' = 3\nu_e RT,$$

with ν_e as the cross-link density, R as the universal gas constant ($8.314 \ \frac{J}{mol \ K}$) and T as the onset temperature of the rubbery plateau in Kelvin. The onset of the rubbery plateau was determined from the Storage Modulus vs. Temperature graph from DMTA once two data points had a difference of less than 0.11% in storage modulus.

Entry	Polymer, Ratio (C=C) : (SH)	$T_{Rubbery}$ (°C)	$E'_{Rubbery}$ (MPa)	$\nu_e \left(10^{-3} \frac{mol}{cm^3}\right)$
1	PCHDC, 1:1	149.1	27.0	2.5
2	PCHDC, 2:1	131.5	10.8	1.1
3	PCHDC, 4:1	135.5	2.7	0.26
4	PLC, 1:1	136.6	18.0	1.76
5	PLC, 2:1	138.2	6.2	0.6
6 (Reference)[14]	Acrylic/MF clearcoat	108	33	3.47

Table S 2 – Determination of Crosslink-Density.

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