Supporting Information for

Fast and Catalyst-Free Hetero-Diels-Alder Chemistry for Cyclable Bonding/Debonding on Demand Material Design

Kim K. Oehlenschlaeger[a], Nathalie K. Guimard[a], Josef Brandt[b], Jan O. Mueller[a], Ching Yeh Lin,[c] Stefan Hilf[d], Albena Lederer[b], Michelle L. Coote,[c,*] Friedrich G. Schmidt[e] and Christopher Barner-Kowollik[a,*]

[a]*Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT),Engesserstr. 18, 76131 Karlsruhe, Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen,, Germany. Fax +49 721 608 45740, E-Mail: christopher.barner-kowollik@kit.edu.*

[b]*Leibniz-Institut für Polymerforschung Dresden, Hohe Strasse 6, D-01069 Dresden, Germany and Technische Universität Dresden, 01062 Dresden, Germany.*

[c]*ARC Centre of Excellence for Free-Radical Chemistry and Biotechnology, Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia, mcoote@rsc.anu.edu.au*

[d]*Evonik Industries AG, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany.*

[e]*Evonik Industries AG Paul-Baumann-Strasse 1, 45764 Marl, Germany.*

Table of Contents

SI - Ultra Fast, Catalyst-Free Hetero-Diels-Alder Chemistry for Cyclable Bonding/Debonding on Demand Material Design

SI - Ultra Fast, Catalyst-Free Hetero-Diels-Alder Chemistry for Cyclable Bonding/Debonding on Demand Material Design

1. Materials and Analytic Instrumentation

ε-Caprolactone (ε-CL, Sigma Aldrich) was distilled from CaH_2 and stored over molecular sieves. Dichloromethane (DCM, VWR) and *N*,*N*-dimethyl formamide (DMF, 99+%, Alfa Aesar) were dried and stored over $CaCl_2$ prior to use. Cyclopentadiene was obtained by cracking and distilling dicyclopentadiene (97% Sigma Aldrich) at 160°C. Acetonitrile (MeCN, LC-MS chromasolve, Fluka), magnesium sulfate (99%, ROTH), methyl-4-(bromomethyl)benzoate (97%, Alfa Aesar), 4-(bromomethyl)benzoate (97%, ABCR), diisobutylaluminium hydride (25% solution in hexane, Alfa Aesar), carbondisulfide (Merck), sodium cyanide (98% ABCR), 1,3-dimethylbutadiene (Merck), tetraethylammoniumbromide (Sigma Aldrich), isophorone diisocyanate (97% Sigma Aldrich), dibutyltin dilaurate (Sigma Aldrich), triethylamine (Sigma Aldrich), tetrahydrofuran (THF, GPC-grade, VWR), trichlorobenzene (TCB, GPC-grade, VWR), toluene (Acros), ethanol (Acros), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Sigma Aldrich) were used as received, Cp_2-P(iBoA-BA) (M_n = 13,000 g•mol^{-1}, $Đ_M$ = 1.6) and isophorone diisocyanate-sorbic alcohol (IPDI-SA) was supplied by Evonik industries.

Electrospray ionization-mass spectrometry (ESI-MS)

ESI-MS spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m*/*z* range 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Sigma-Aldrich). A constant spray voltage of 4.5 kV was used and nitrogen was applied with a dimensionless sweep gas flow-rate of 2 (approx. 3 L·min^{-1}) and a dimensionless sheath gas flow-rate of 12 (approx. 1 L·min^{-1}). The capillary voltage, the tube lens offset voltage and the capillary temperature was set to 60 V, 110 V and 300 °C, respectively. A typical polymer concentration of approximately 3 mg mL^{-1} (in a 3:2 THF/MeOH mixture) was utilized. Data treatment was performed using the procedure outlined in a recent publication.[1]

[1] Junkers, T.; Koo, S. P. S.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromolecules* **2007**, *40*, *8906-8912*.

Molar mass analysis via size exclusion chromatography (SEC)

For the determination of molar mass distributions (MWD) a SEC system (Polymer Laboratories PL-GPC 50 Plus), comprised of an auto injector, a guard column (PLgel Mixed C, 50 × 7.5 mm) followed by three linear columns (PLgel Mixed C, 300 × 7.5 mm, 5 µm bead-size) and a differential refractive index detector, was employed. THF at 40 °C at a flow rate of 1 mL·min^{-1} was used as the eluent. The SEC system was calibrated using narrow poly(methyl methacrylate) standards ranging from 600 to 5105 g·mol^{-1} (Polymer Standards Service (PSS), Mainz, Germany). The resulting molar mass distributions were determined by universal calibration using Mark-Houwink parameters for PiBoA (K = 5 10^{-5} dL g^{-1}, α = 0.745), PS (K = 14 10^{-5} dL g^{-1}, α = 0.7) and PCL (K = 13.95 10^{-5} dL g^{-1}, α = 0.786),[2] respectively.

UV-Vis spectroscopy

UV-visible spectroscopy was performed using a Cary 300 Bio spectrophotometer (Varian) featuring a thermostated sample cell holder. Absorption spectra for samples dissolved in toluene at a ratio of 10 mg mL^{-1} were measured from 200 to 800 nm with a resolution of 1 nm and slit width of 2 nm in a 1 cm UV cuvette. In case of the kinetic measurement, the concentration of the samples was different. 0.2 mL of toluene were placed in the cuvette and 10 mg of the sample were dissolved in 0.5 mL toluene for the measurements. The sample that was taken for repolymerisation analysis had a different concentration, due to the evaporation of toluene which took place during heating.

High temperature dynamic light scattering (HT-DLS)

The HT-DLS experiments have been carried out using a DynaPro NanoStar photospectrometer (WYATT Technology Corporation, USA). A solution of **6** (17 mg mL^{-1} in 1,2,4-triclorobenzene (TCB)) was prepared and filtered through a 0.2 µm PTFE syring filter after 20 minutes of dissolution. In multiple cycles, the temperature has been changed from 30 to 120 °C (heating/cooling rate = 15 °C min^{-1}) and the hydrodynamic radius has been determined continuously (each data point represents an average of 15 single acquisitions (see Figure S4, p. S26)) by light scattering at 658 nm. The control sample (Cp_2-P(iBoA-nBA), 17 mg mL^{-1} in TCB, filtration was not necessary) was measured under identical conditions. In both cases, the solution was kept in the quartz-glass cuvette during the whole experiment to avoid introducing dust or other impurities, thus shaking or stirring for increasing the reaction rate was not possible.

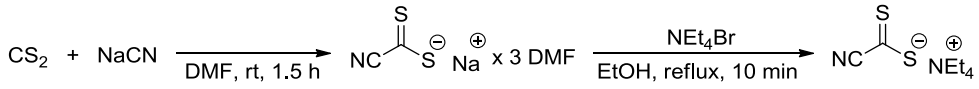
[2] Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *Journal of Polymer Science, Polymer Chemistry Edition* **1982**, *20*, 319.

Nuclear Magnetic Resonance Spectroscopy (NMR and on-line HT-NMR)

^{1}H-NMR spectroscopy was carried out on a Bruker AM 400 MHz spectrometer. The samples were dissolved in DMSO-d_6 and measured with 16 scans for **5,** 100 for **6**, and a relaxation time of 1 s for both. The δ-scale is referenced to tetramethylsilane (δ = 0.00 ppm) as internal standard. For the on-line high temperature measurements the samples were dissolved in toluene-d_8. The temperatures were kept constant by continuous heating with a thermo element (20% heating power), while cooling was performed with a compressed air stream (400 L h^{-1}).

2. Synthetic Procedures

Carbonocyanidodithioate



A suspension of 5.46 g (0.111 mol, 1.1 eq) sodiumcyanide in 20 mL DMF was cooled with an ice-bath to 0°C. Under strong stirring 6.20 mL (7.75 g, 0.102 mol, 1 eq) of carbondisulfide (CS_2), diluted with 13 mL DMF; were added over a period of 10 min. After completion of the CS_2 addition, the ice-bath was removed and the solution was stirred until complete solidification, due to the precipitation of brown needles (ca. 60 min). Isopropanol (150 mL) was added and heated to 90°C, to dissolve the precipitated needles. The warm suspension was filtered to remove the excess of sodiumcyanide. The filtrate was cooled with liquid nitrogen and the reprecipitated solid was filtered and washed with diethylether. The mustard colored powder was recrystallized from an isopropanol /diethylether mixture (1:1). Yield: 90% (30.0 g, 0.090 mol)

The entire obtained mustard colored solid was subsequently heated to reflux in 110 mL ethanol, while – in parallel- 18.9 g (0.090 mol, 1 eq) tetraethylammoniumbromide were heated to reflux in 50 mL ethanol. The two boiling solutions were combined and heated to reflux for an additional 10 min. During the slow cooling to ambient temperature a brown solid crystallized, which was filtered off and recrystallized from ethanol. The final product was a brown lustrous powder which was used without further characterization.

Yield: 48% (10.0 g, 0.043mol)

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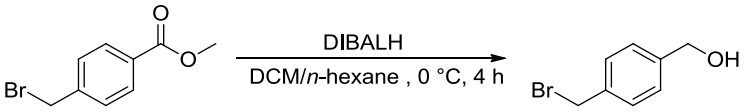
4-(bromomethyl)benzylic alcohol



50 mL of a 25% diisobutylaluminium hydride solution (25% in hexane, 8.17 g, 57.4 mmol, 2 eq) were added to a two neck round bottom flask under an inert atmosphere (N_2). The flask was cooled to 0°C with an ice bath before 6.57 g (28.7 mmol, 1 eq) methyl-4-(bromomethyl)benzoate, dissolved in 30 mL DCM (dry), were added within 30 min. After 4 h reaction time the remaining diisobutylaluminium hydride was quenched with water. To dissolve the white solid, which precipitated during the quenching process, 30 mL HCl (37%) and 30 mL DCM were added. The phases were separated and the aqueous layer was extracted 4 times with 50 mL DCM. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to yield a white solid which was employed without further purification. Yield: 77% (4.40 g, 22.0 mmol), ^{1}H-NMR (DMSO-d^6, 250 MHz) δ (ppm): 7.41-7.38 (d, ^3J = 8.1 Hz, 2H, Ar*H*), 7.31-7.28 (d, ^3J = 8.1 Hz, 2H, Ar*H*), 4.70 (s,, 2H, CH_2Br), 4.49 (s, 2H, CH_2OH).

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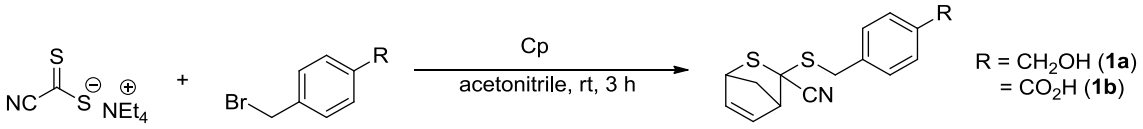
Cp-protected cyanodithioester (1a or 1b)



1a)

5.22 g (22.5 mmol, 1.02 eq) tetraethylammonium carbonocyanidodithioate were dissolved in 120 mL acetonitrile and stirred at ambient temperature. 4.40 g (22.0 mmol, 1 eq) 4-(bromomethyl)benzylic alcohol, dissolved in 80 mL acetonitrile, were added to the solution. After 1 min reaction time 5.22 mL (4.02 g, 60.9 mmol, 2.7 eq) cyclopentadiene were added and the mixture was stirred for 3 h. The solvent was removed under reduced pressure and the obtained yellow oil purified via flash chromatography (silica gel/ hexane:ethylacetate (1:1)-(1:2)). Yield: 32% (2.03 g, 7.04 mmol), MS: found 311.93 *m*/*z*, expected 312.03 *m*/*z*, ^{1}H and ^{13}C NMR data are provided below.

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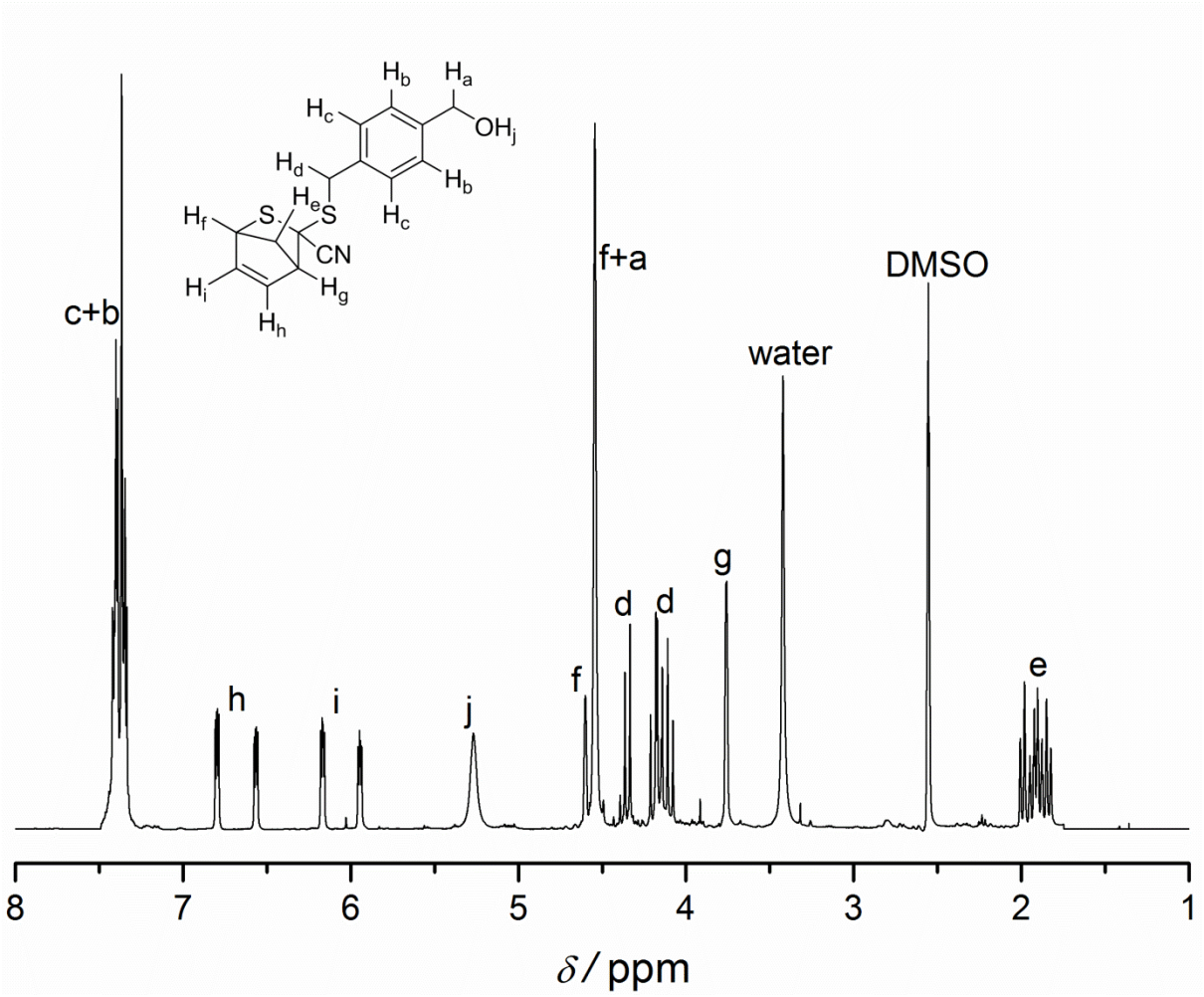

^{1}H-NMR (DMSO-d^{6}, 250 MHz) δ (ppm): 7.37-7.28 (m, 4H, Ar*H*), 6.76-6.73 (dd, *J* = 5.4, 2.9 Hz, 0.4H, C=C*H*$_{exo}$), 6.53-6.50 (dd, *J* = 5.4, 2.9 Hz, 0.45H, C=C*H*$_{endo}$), 6.12-6.10 (dd, *J* = 5.4, 3.2 Hz, 0.4H, C=C*H*$_{exo}$), 5.88-6.86 (dd, *J* = 5.4, 3.2 Hz, 0.45H, C=C*H*$_{endo}$), 5.20 (br, 1H, CH$_2$O*H*), 4.55 (s, 0.5H, C*H*SC), 4.49 (s, 2.5H, C*H*SC + C*H*$_2$OH), 4.31-4.28 (d, *J* = 12 Hz, 0.5H, SC*H*$_2$Ar), 4.23-4.13 (m, 1.5H, SC*H*$_2$Ar), 3.70 (s, 1H, C*H*CCN), 1.95-1.77 (d+ddt+d, *J* = 10.2, 18.1, 10.2, 2.1, 10.4Hz, 1.75H, bridge C*H*$_2$).

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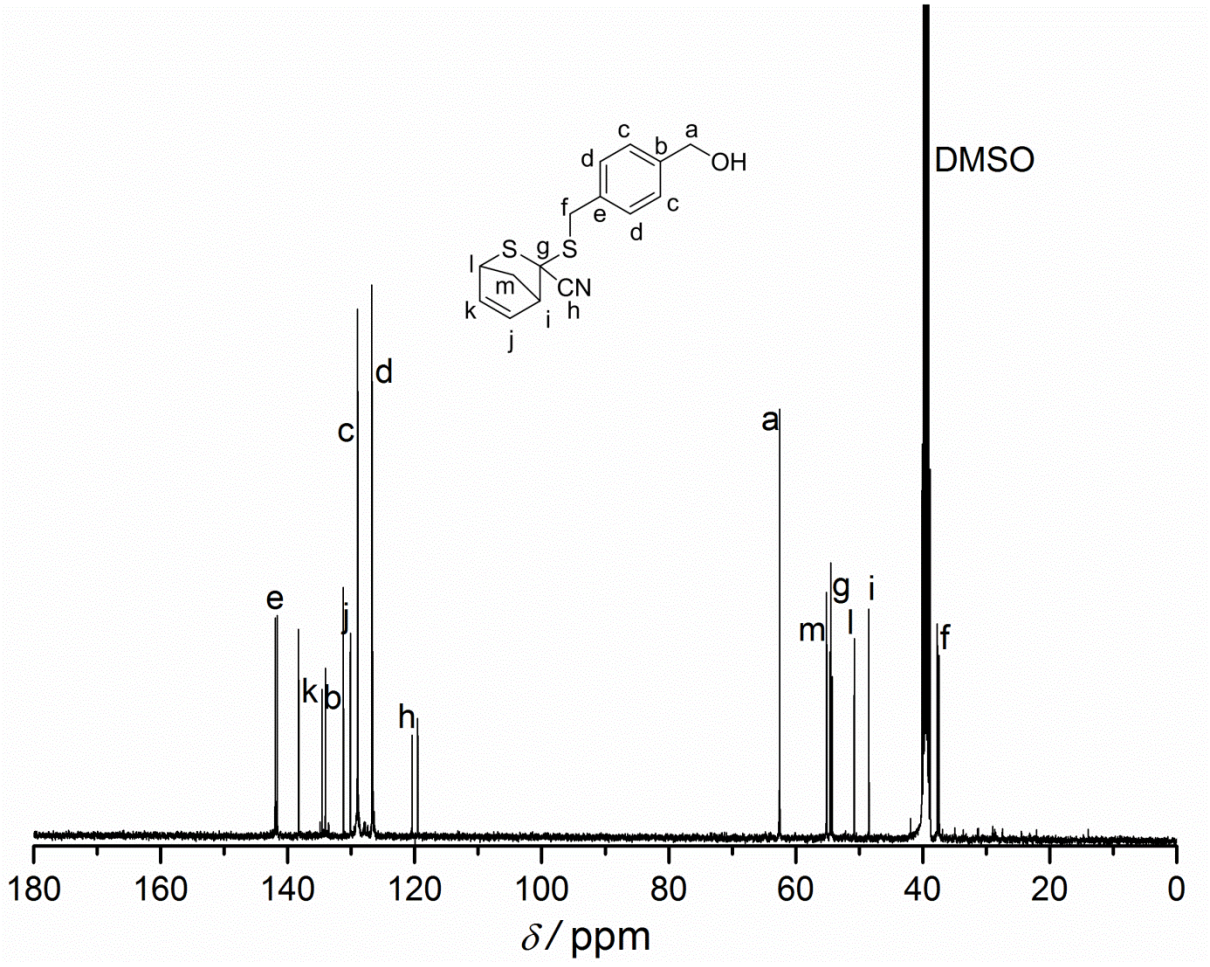

^{13}C-NMR (DMSO-d^{6}, 100 MHz) δ (ppm): 142.0 (e), 141.69 (e), 138.31 (k), 134.61 (k), 134.10 (b), 131.27 (j), 130.17 (j), 129.02 (c), 128.97 (c), 126.78 (d), 126.70 (d), 120.74 (h), 119.56 (h), 62.58 (a), 55.21 (m), 55.19 (m), 54.64 (l), 54.55 (g), 54.51 (g), 54.31 (l), 50.84 (i), 48.54 (i), 37.75 (f), 37.48 (f).

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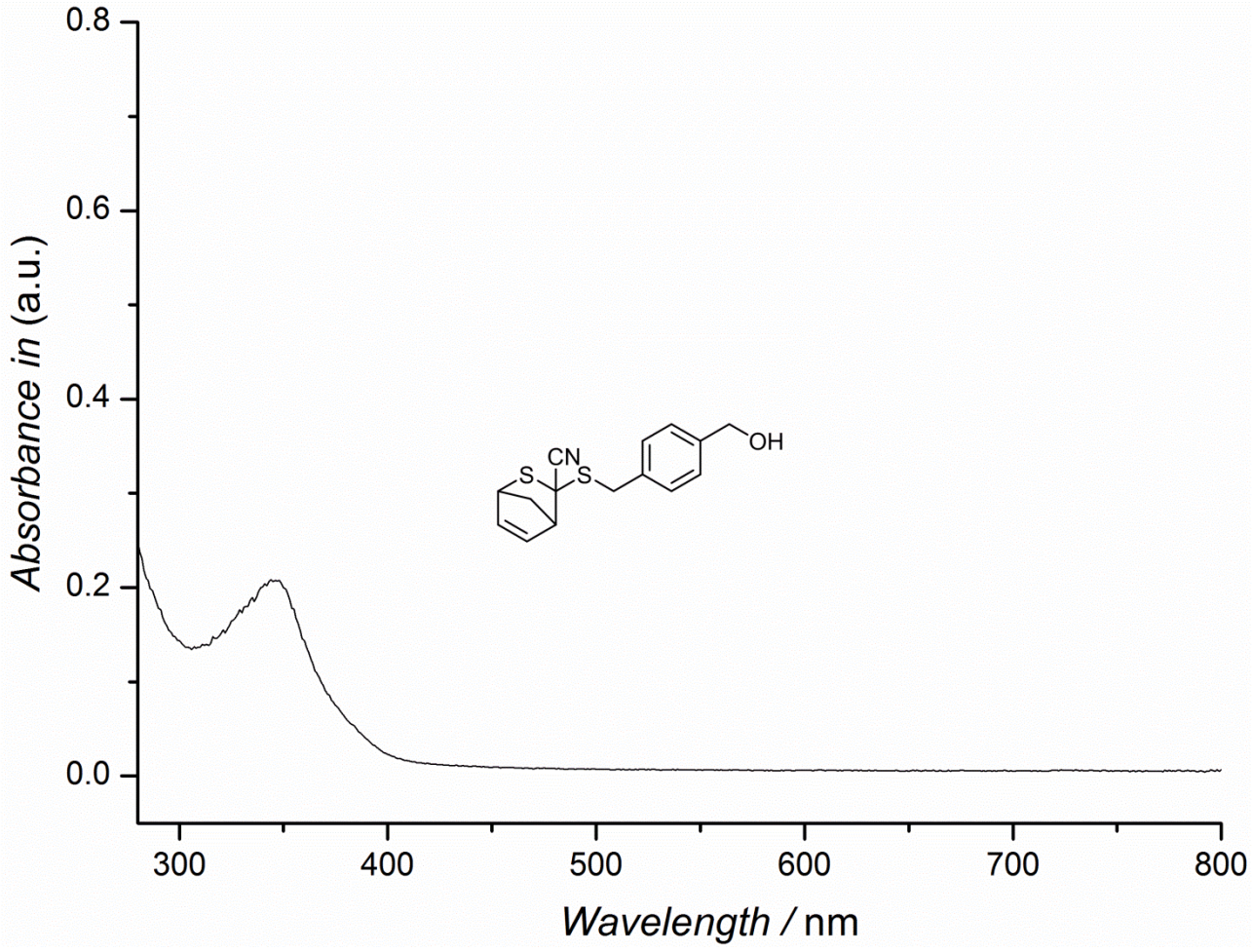

1b)

3.88 g (16.7 mmol, 1.1 eq) tetraethylammonium carbonocyanidodithioate, dissolved in 80 mL acetonitrile, were placed in a 100 mL round bottom flask and stirred at ambient temperature. 3.24 g (15.2 mmol, 1 eq) 4-(bromomethyl)benzoic acid, suspended in 70 mL acetonitrile, were added to the solution. After 1 min reaction time, 3.80 mL (3.01 g, 45.4 mmol, 3 eq) cyclopentadiene were added and the mixture was stirred for 24 h. The solvent was removed under reduced pressure and final purification, of the yellow oil, was performed via flash chromatography (silica gel/ dichloromethane:methanol (19:1)). Yield: 32% (2.03 g, 7.04 mmol), MS: found 326.00 *m/z*, expected 326.03 *m/z*, ^{1}H and ^{13}C NMR data are provided below.

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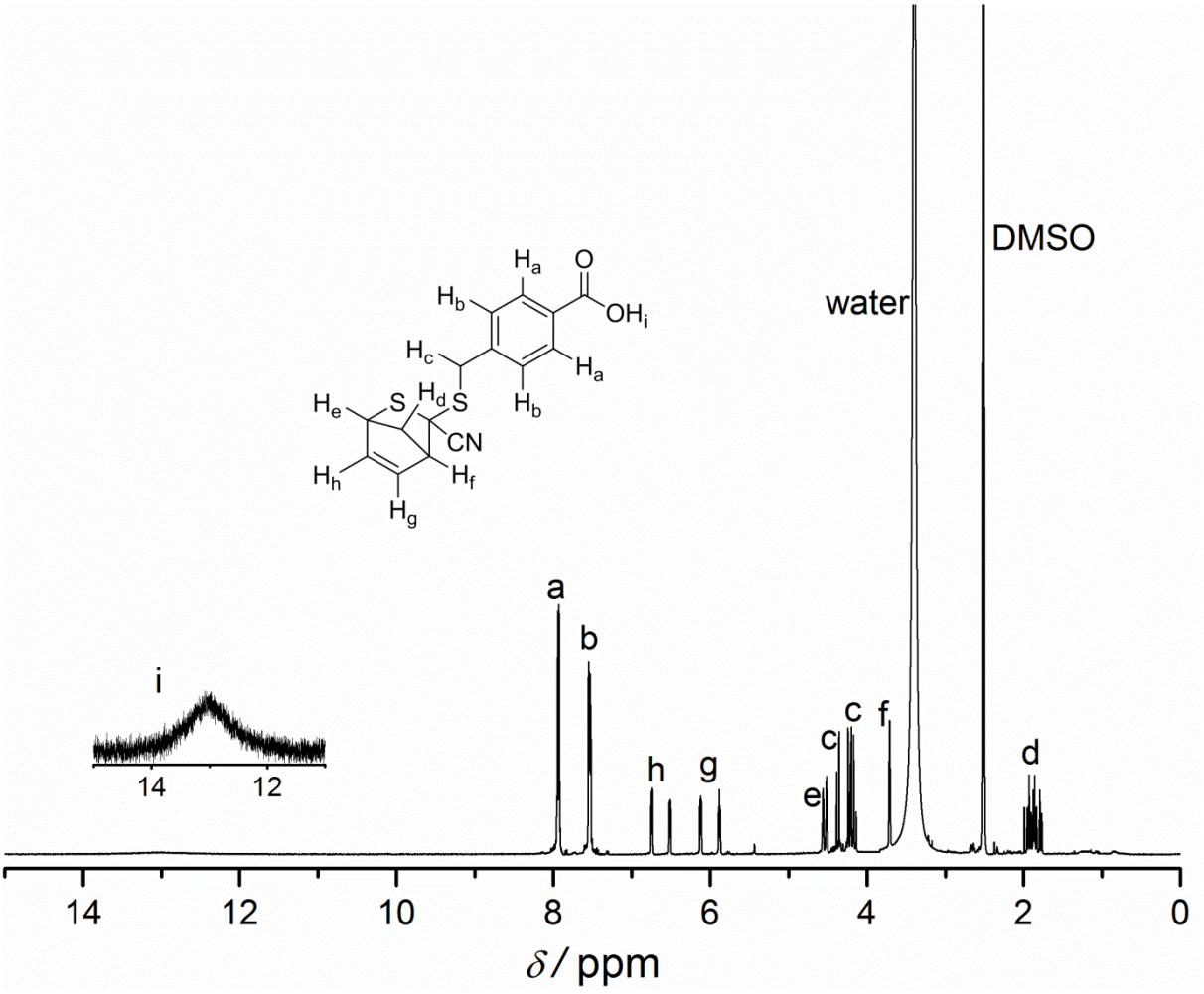

^{1}H-NMR (DMSO-d^{6}, 250 MHz) δ (ppm): 13.01 (br, 1H, CO_2H), 7.94-7.91 (dd, *J* = 8.3, 1.7 Hz, 2H, Ar*H*), 7.54-7.51 (dd, *J* = 8.3, 3.9 Hz, 2H, Ar*H*), 6.76-6.73 (dd, *J* = 5.4, 2.9 Hz, 0.4H, C=C*H*), 6.53-6.50 (dd, *J* = 5.4, 2.9 Hz, 0.45H, C=C*H*), 6.13-6.09 (dd, *J* = 5.4, 3.2 Hz, 0.4H, C=C*H*), 5.91-6.87 (dd, *J* = 5.4, 3.2 Hz, 0.45H, C=C*H*), 4.55 (s, 0.5H, C*H*SC), 4.50 (s, 0.5H, C*H*SC), 4.38-4.35 (d, *J* = 12.6 Hz, 0.5H, SCH_2Ar), 4.16-4.02 (m, 1.5H, SCH_2Ar), 3.70 (s, 1H, C*H*CCN), 1.95-1.77 (d+ddt+d, *J* = 10.2, 18.1, 10.2, 2.1, 10.4 Hz, 1.75H, bridge CH_2).

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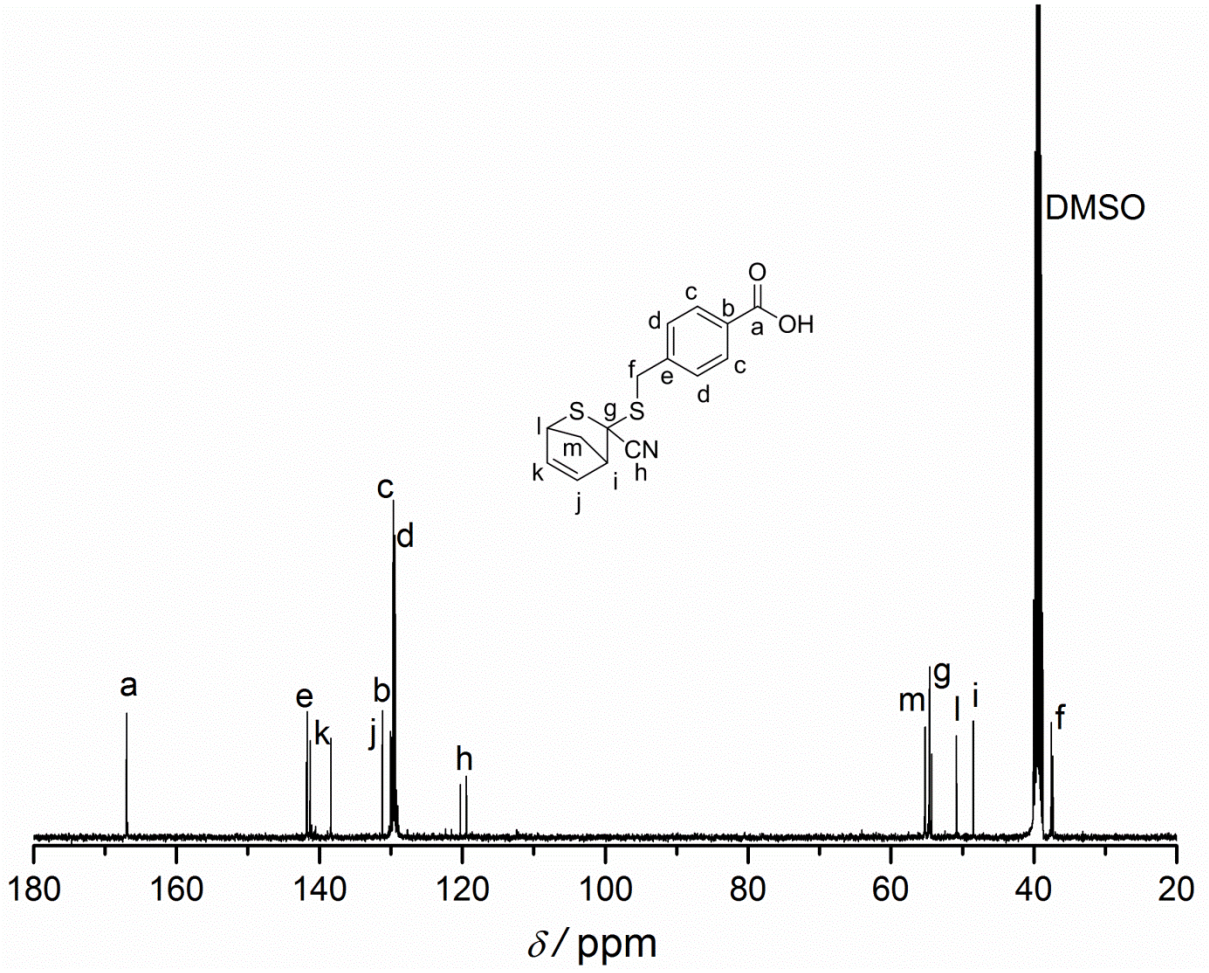

^{13}C-NMR (DMSO-d^{6}, 100 MHz) δ (ppm): 167.10 (a), 141.92 (e), 141.81 (e), 141.41 (k), 138.50 (k), 131.29 (b),130.13 (j), 130.00 (j), 129.78 (c), 129.75 (c), 129.54 (d), 129.50 (d), 120.39 (h), 119.53 (h), 55.39 (m), 55.33 (m), 54.77 (l), 54.70 (g), 54.69 (g), 54.41 (l), 50.95 (i), 48.59 (i), 37.68 (f), 37.46 (f).

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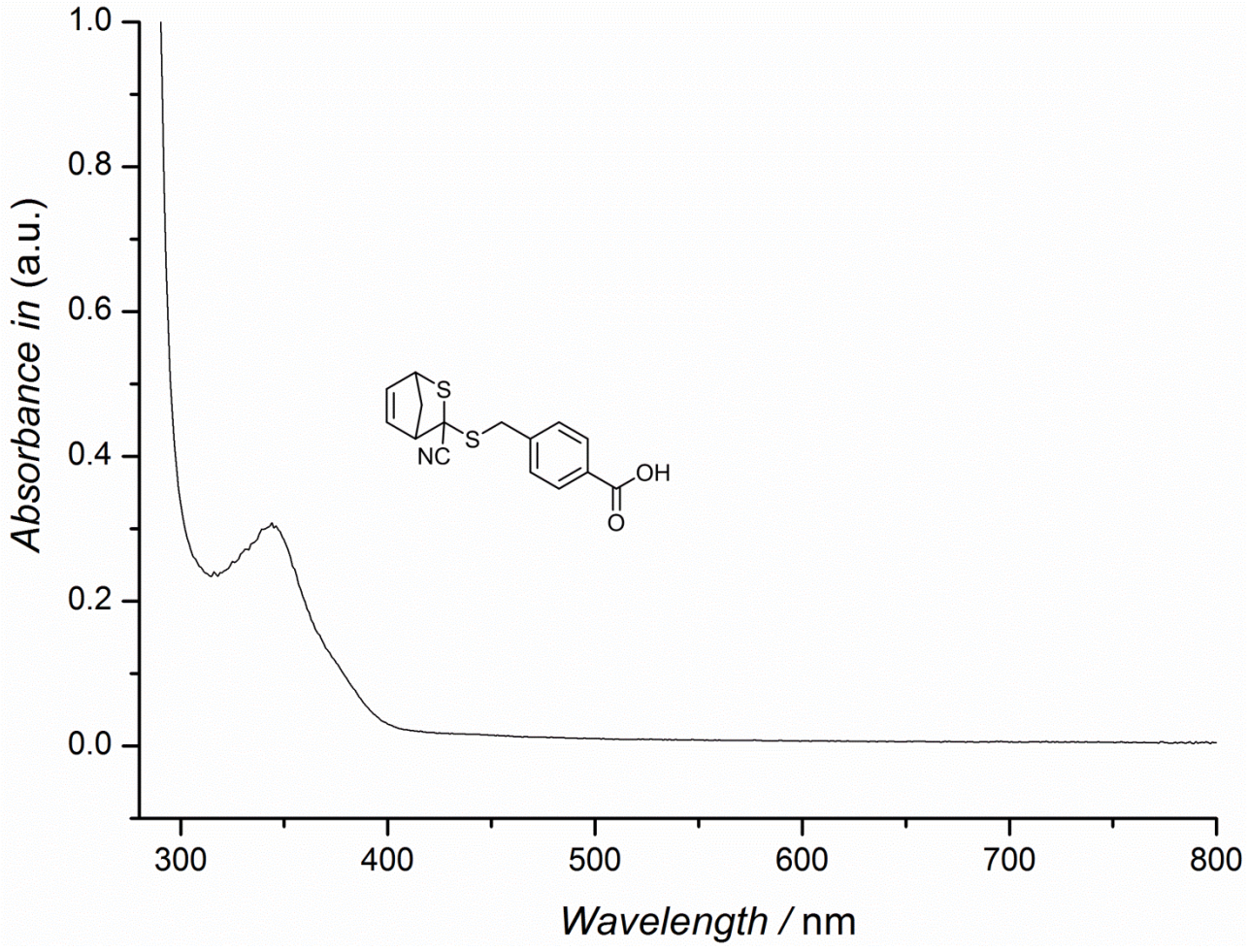

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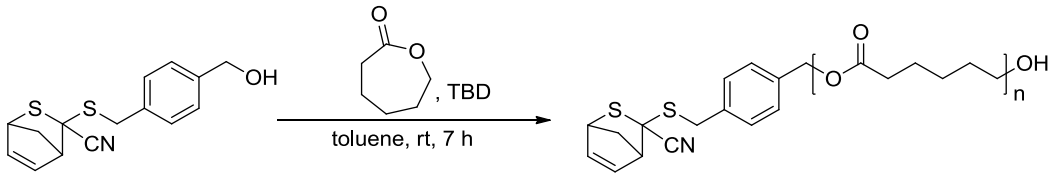
Trapped cyanodithioester end-capped poly(ε-caprolactone) (2)



1a **2**

Alcohol **1a** (200 mg, 0.690 mmol, 1 eq) and TBD (9.60 mg, 0.069 mmol, 0.1 eq) were dissolved in toluene (4 mL) under inert atmosphere. ε-CL (2.22 mg, 19.0 mmol, 20 eq) was added and the solution was stirred under argon atmosphere at ambient temperature for 7 h. The reaction was quenched with benzoic acid (50.0 mg, 0.40 mmol, 0.6 eq) and the polymer was precipitated in cold hexane/Et_2O (1:1 v/v, 200 mL) to yield 1.4 g of **2** (M_n = 2000 g·mol^{-1} and $Đ$ = 1.20). ESI-MS data are provided below.

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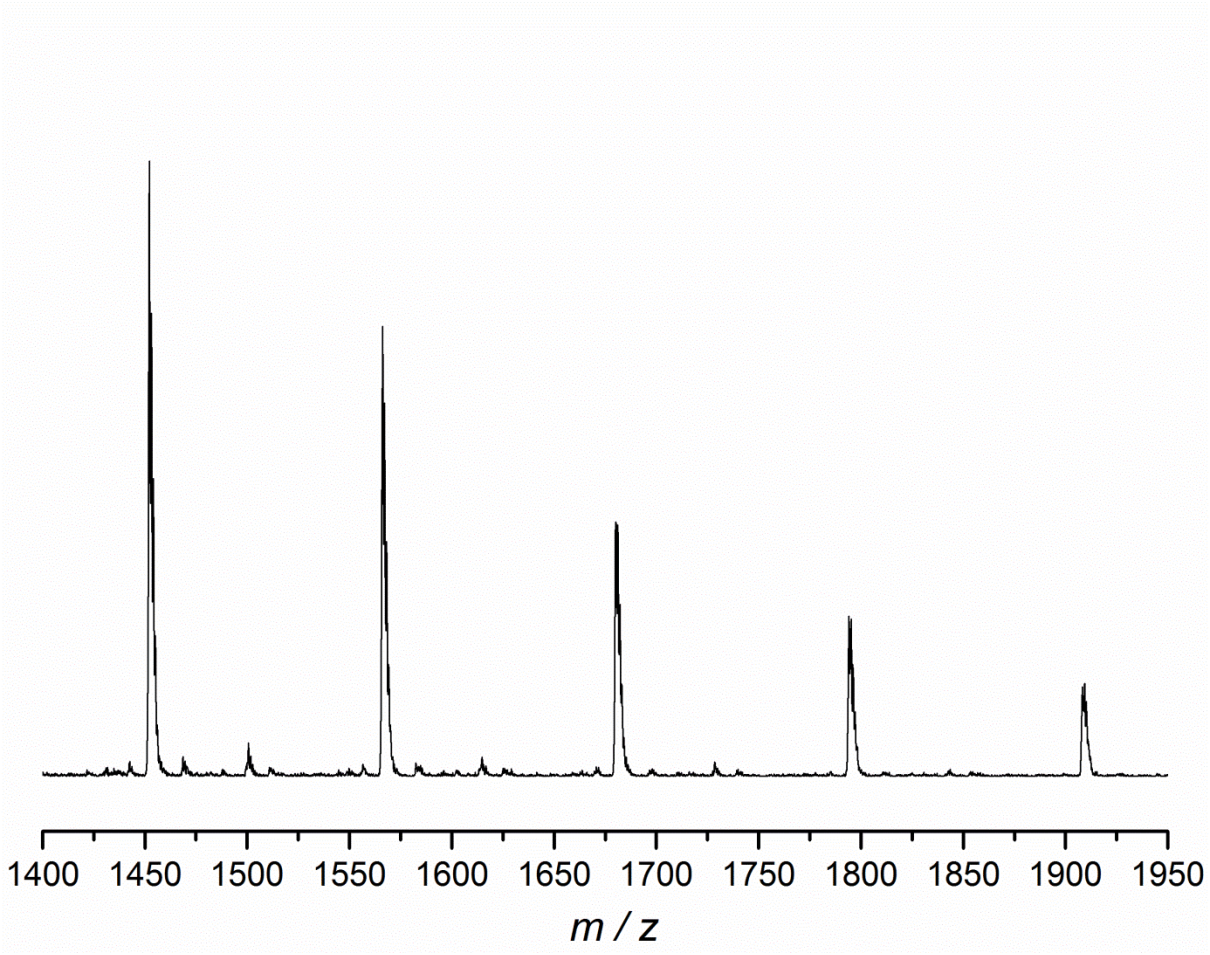

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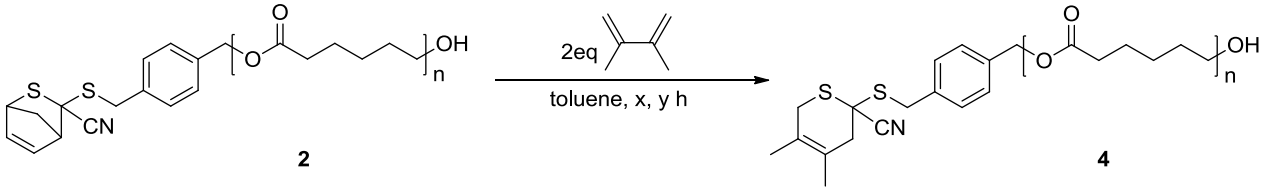
Diene exchange of cyanodithioester end-capped poly(ε-caprolactone) (4)



CDTE end-capped PCL **2** (27.0 mg, 0.013 mmol, 1 eq) was placed in a two neck flask and dissolved in 2 mL toluene. 3.00 µL (2.21 µg, 0.026 mmol, 2 eq) DMBD were added and the mixture was heated to the desired temperature (80°C, 100°C or 120°C) with a rubber septum on one neck and a reflux condenser on the other. For the kinetic studies, samples were taken after pre-defined time, and cooled to ambient temperature. The solvent was removed and the residue was dissolved in THF for ESI-MS analysis. The reaction conversion was calculated by comparing the product's and starting material's peak intensities of the first signal of the isotopic pattern. To prevent the error of chain length depended ionization, the 3 most intensive repeating units were averaged. Figure S2 (p. S24) depicts the resulting kinetic plots.

	PCL-Cp DA product	**PCL-unprotected CDTE**	**PCL-DMBD DA product**
Measured mass values	**1338.09**	**1386.66**	**1354.67**
Theoretical mass values	**1338.17**	**1386.61**	**1354.76**

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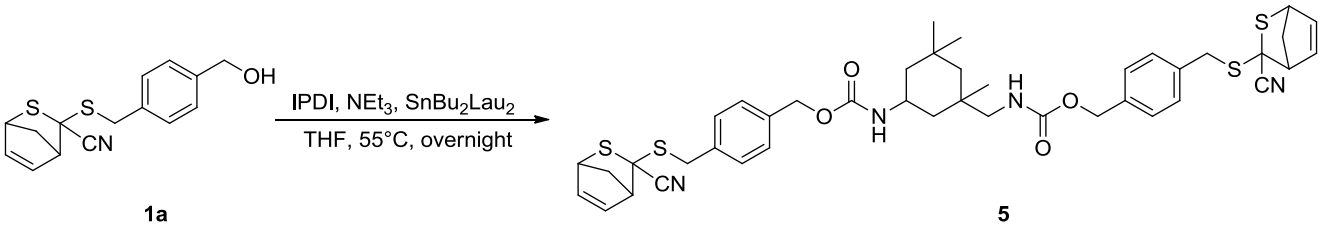
Trapped cyanodithioester di-linker (5)



1a 5

Alcohol 1a (1.00 g, 3.40 mmol, 2.3 eq), isophorone diisocyanate (0.33 mg, 1.50 mmol, 1 eq) and dibutyltin dilaurate (1,00 mg, 0.015 mmol, 0.01 eq) were placed in a two neck flask under nitrogen atmosphere. 4 mL dry THF were added and the mixture was heated to 55 °C. 0.5 mL (0.362 mg, 3.50 mmol, 2.3 eq) triethylamine were added and the reaction mixture was stirred overnight at 55°C. To cease the reaction, the mixture was exposed to air and cooled to ambient temperature. THF was removed under reduced pressure and the residue was dissolved in 40 mL DCM. The organic layer was washed with 1 M NaOH (2 • 30 mL), 1 M HCl (2 • 30 mL), and brine. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to gain 1.40 g of a dark solid. The crude product was purified by flash chromatography (silica gel/ ethylacetate:hexane (2:1)). Yield: 53% (0.700 g, 0.8 mmol), MS: found 823.00 *m*/*z*, expected 323.23 *m*/*z*. ^{1}H and ^{13}C NMR data are provided below.

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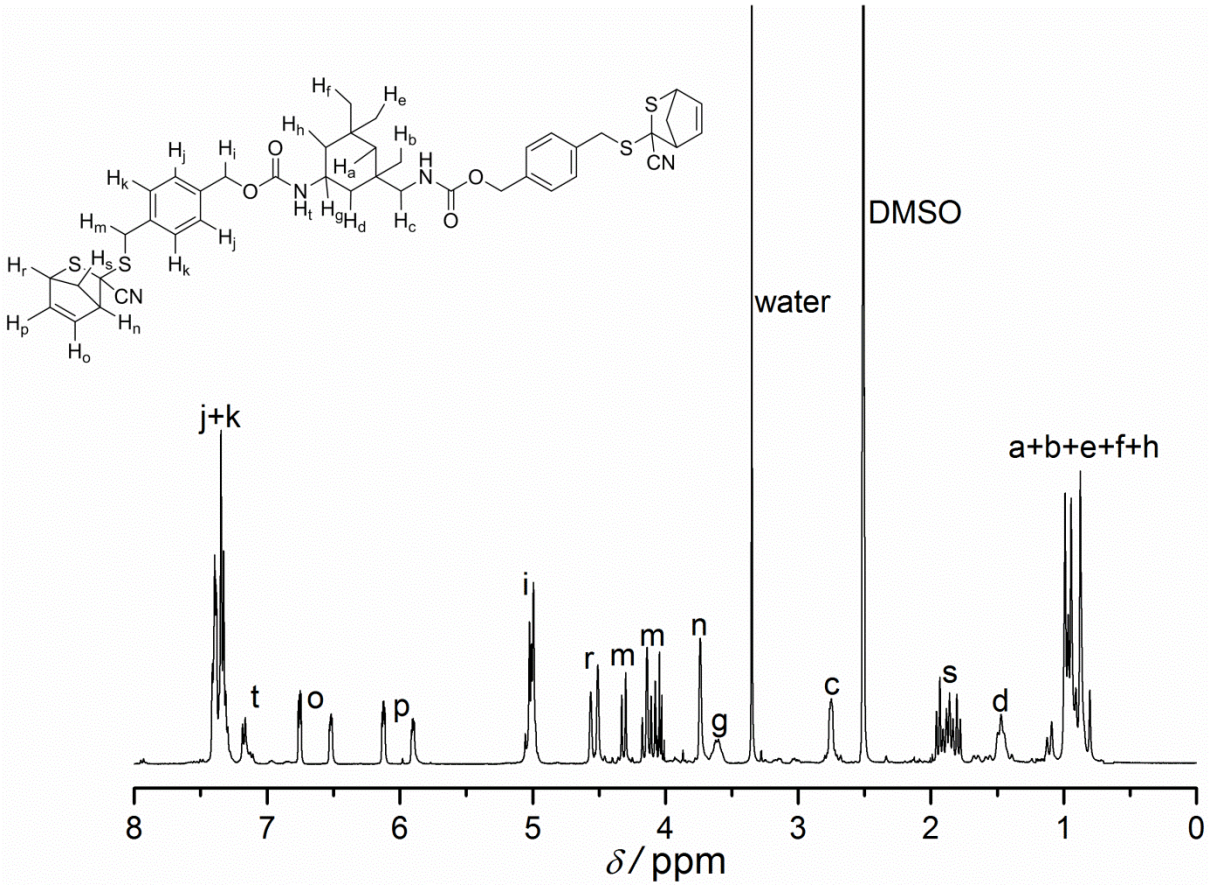

^{1}H-NMR (DMSO-d^{6}, 250 MHz) δ (ppm): 7.40-7.29 (m, 8H, Ar*H*), 7.18-7.10 (m, 1 H, N*H*), 6.76-6.74 (dd, *J* = 5.4, 2.9 Hz, 1H, C=C*H*), 6.52-6.50 (dd, *J* = 5.1, 2.9 Hz, 1H, C=C*H*), 6.13-6.10 (dd, *J* = 5.3, 3.2 Hz, 1H, C=C*H*), 5.90-5.88 (dd, *J* = 5.0, 3.4 Hz, 1H, C=C*H*), 5.05-4-95 (m, 4H, NCOOCH_2), 4.55 (s, 1H, C*H*SC), 4.50 (s, 1H, C*H*SC), 4.32-4.29 (d, *J* = 12.1 Hz, 1H, SCH_2Ar), 4.17-4.02 (m, 3H, SCH_2Ar), 3.73 (s, 2H, C*H*CCN), 3.60 (br, 1H, OOCNC*H*), 2.74 (br, 2H, OOCNCH_2) 1.95-1.77 (m, 4H, bridge CH_2), 1.46 (br, 2H, CH2) 1.12-0.79 (m, 13H, three CH_3 groups and two CH_2 groups from the cyclohexane fragment).

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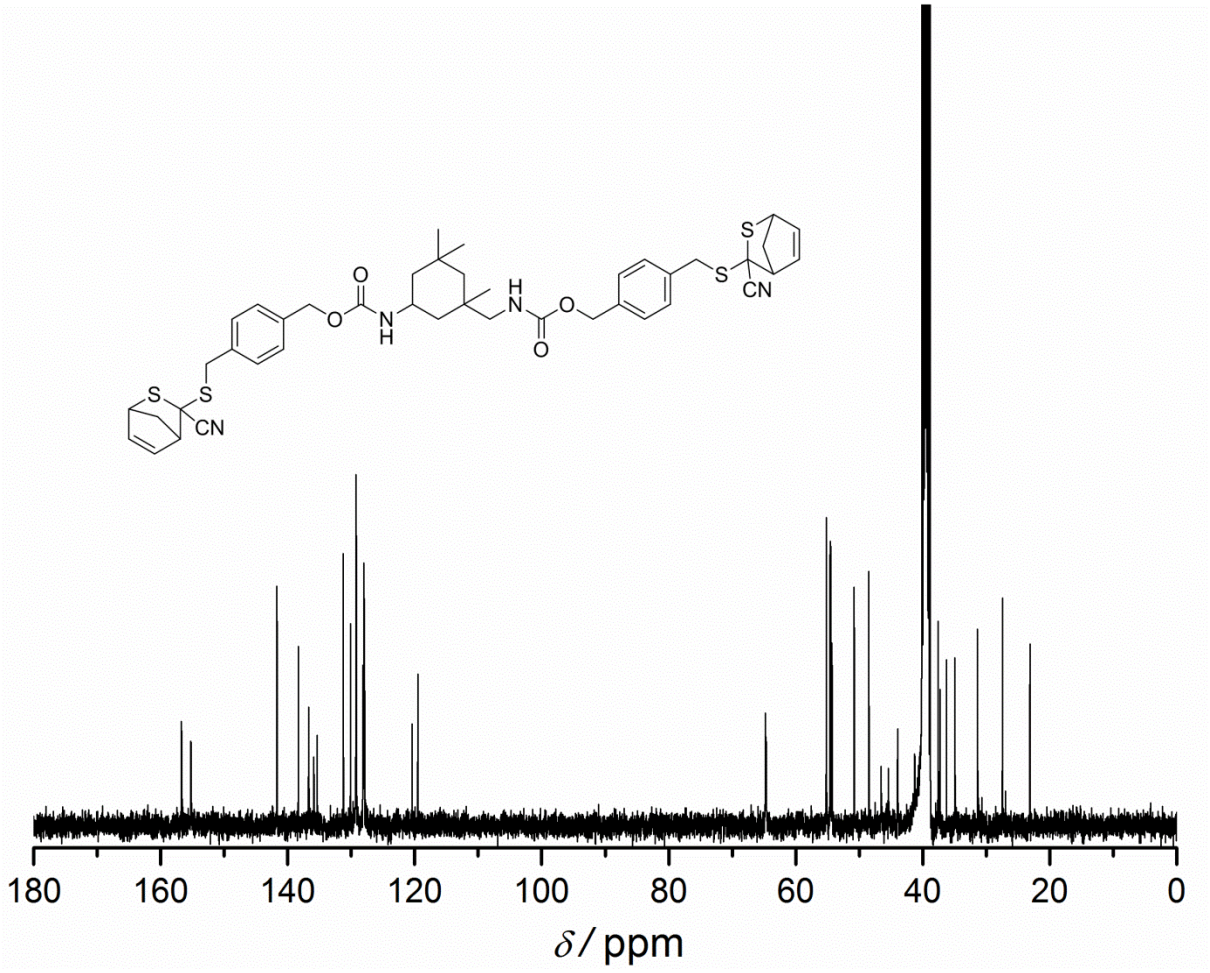

^{13}C-NMR (DMSO-d^{6}, 100 MHz) δ (ppm): 156.74, 155.26, 141.71, 138.35, 135.90, 135.39, 131.27, 130.14, 129.27, 129.22, 128.18, 128.11, 128.00, 127.93, 120.44, 119.54, 64.81, 64.71, 59.76, 55. 22, 54.61, 54.59, 54.53, 54.33, 50.84, 48.53, 46.60, 45.44, 44.00, 37.62, 37.34, 36.30, 34.98, 31.42, 27.50, 23.18.

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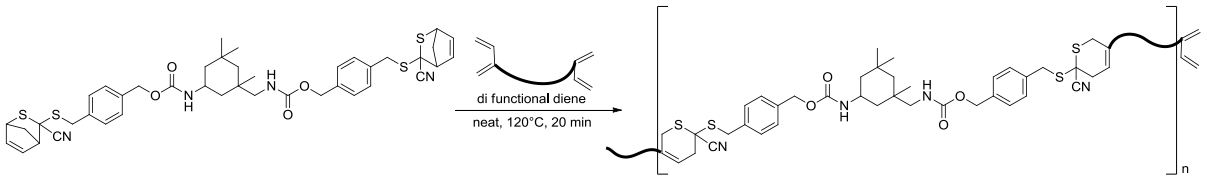
Polymerization reactions



5 **6 , IPDI-SA + 5**

Di-linker **5** and a molar equivalent amount of the suitable diene di-linker Cp_2-P(iBoA-BA) or IPDI-SA were dissolved in DCM and stirred for 5 min. After the solids were dissolved, the solution was transferred to a 5 mL flask. The flask was coated with a thin layer of starting material mixture by removing the solvent under reduced pressure. The flask was subsequently placed in an oil bath and heated to 120°C. After 20-60 min reaction time the oil bath was removed and the obtained polymer was analyzed via SEC.

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3. Additional Data (SI Figures)

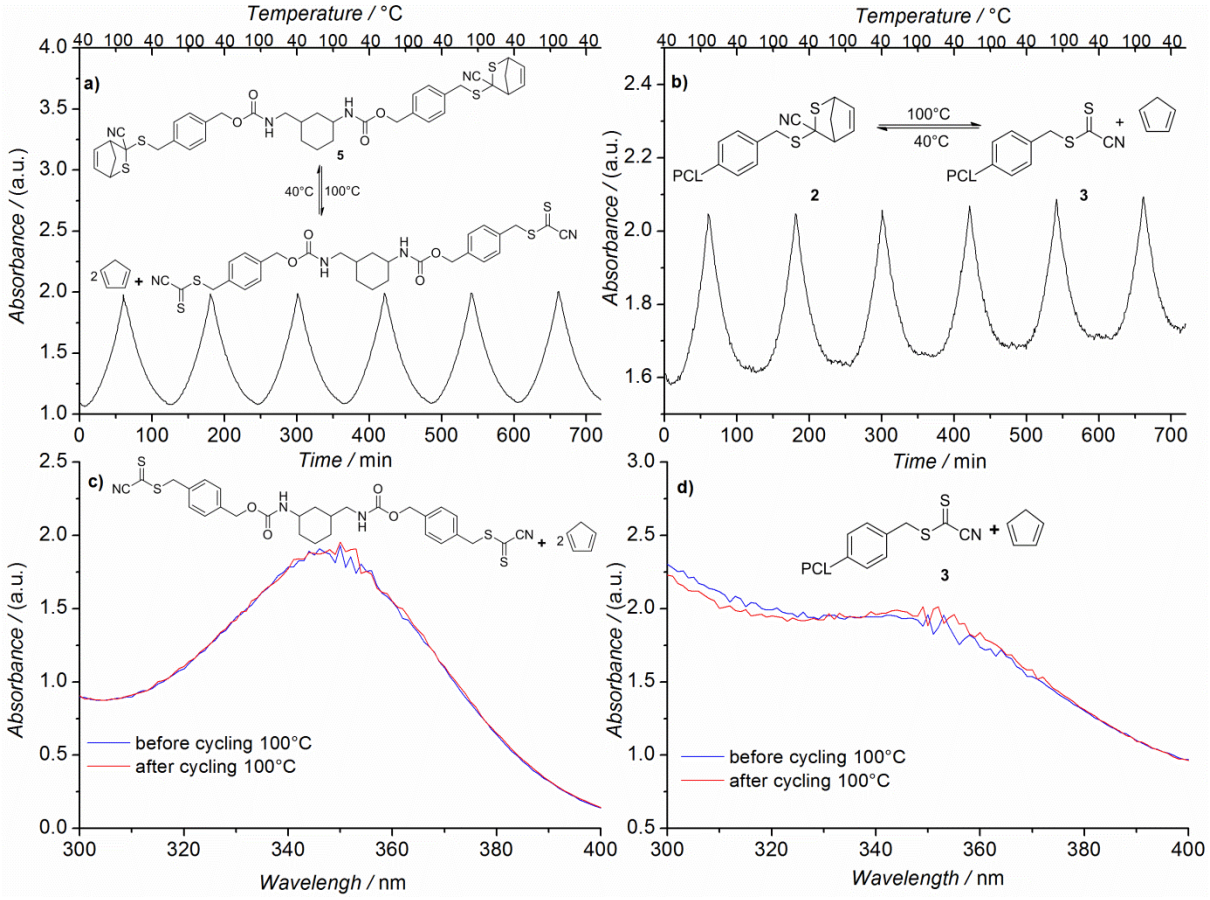

Figure S1. a) and b) show the raw data (without baseline correction) of the temperature cycling experiments of di-linker 5 and PCL end capped CDTE 2. The absorbtion at 347 nm was recorded. c) and d) depict the samples absorption spectra prior (blue) and after (red) the heat cycling experiment. Evaporated toluene was refilled after the cycling, to ensure an identical concentration as before the cycling experiment.

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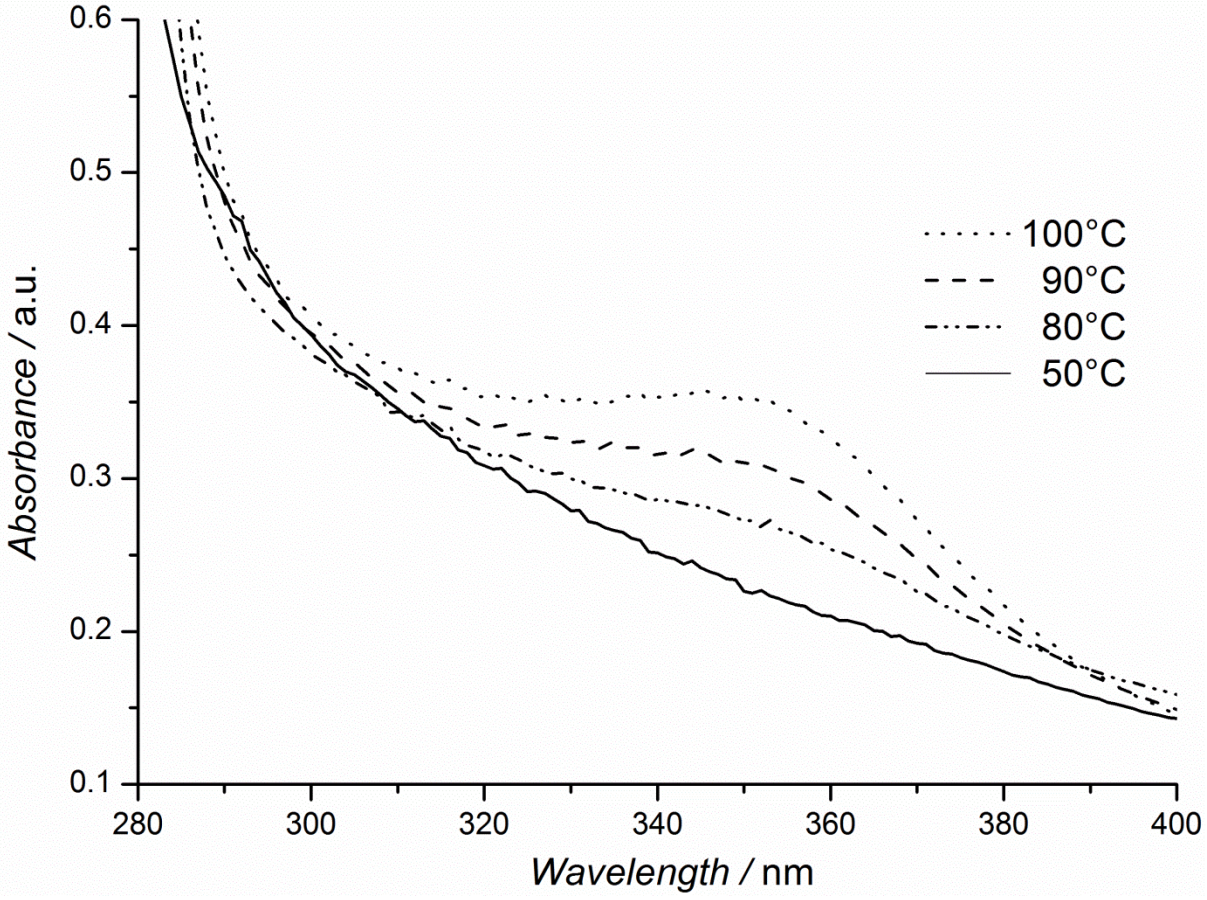

Figure S2. Absorption spectrum of CDTE end-capped PCL 2 at different temperatures. With increasing temperature, the DA equilibrium is shifted to the diene/dienophile side which results in more free CDTE 3 featuring the typical dithioester π-π* transition.

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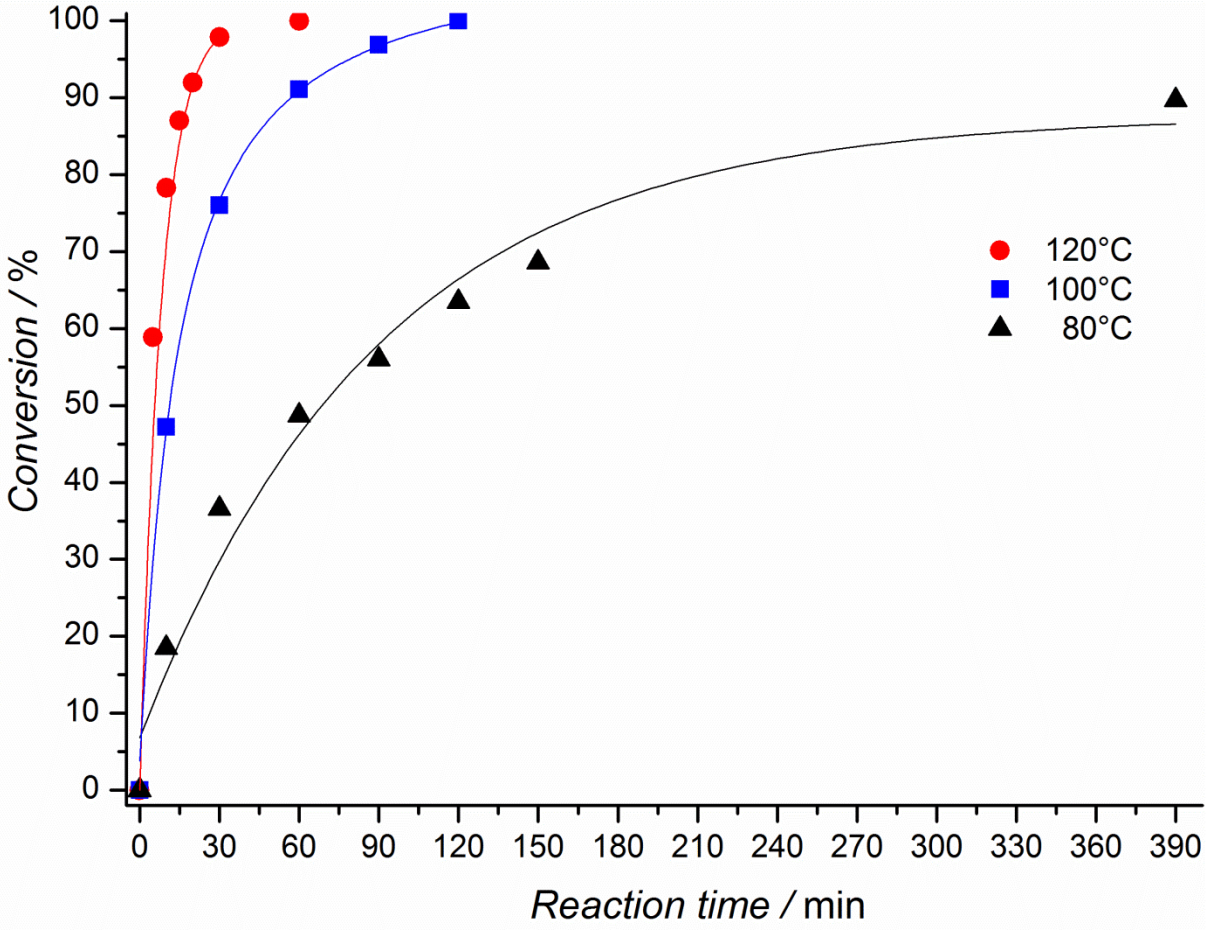

Figure S3. Kinetic plot of the diene exchange reaction between 2 and DMBD at 80°C, 100°C, and 120°C in toluene.

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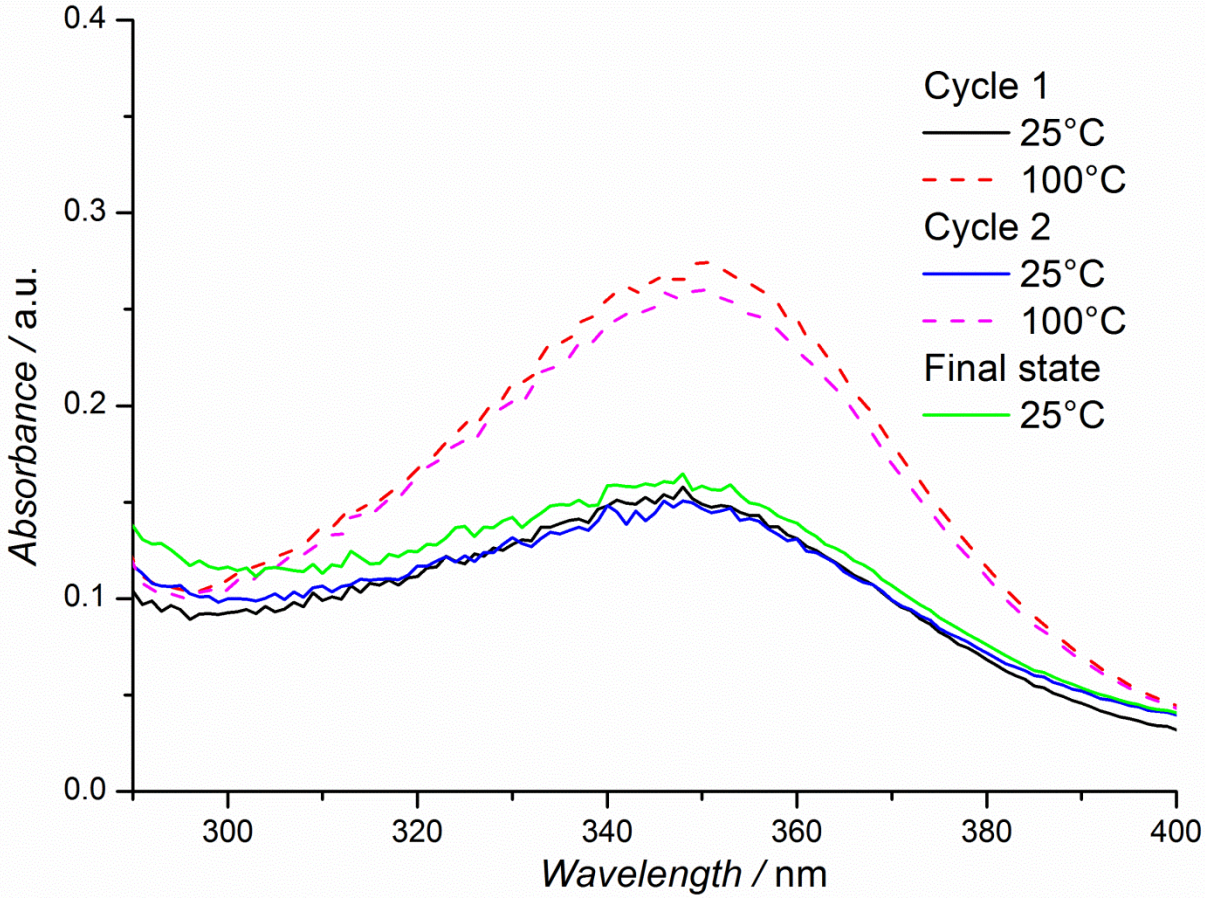

Figure S4. UV/Vis traces of the polymer 6 at 25°C and 100°C in toluene. The polymer was cycled two times between these temperatures.

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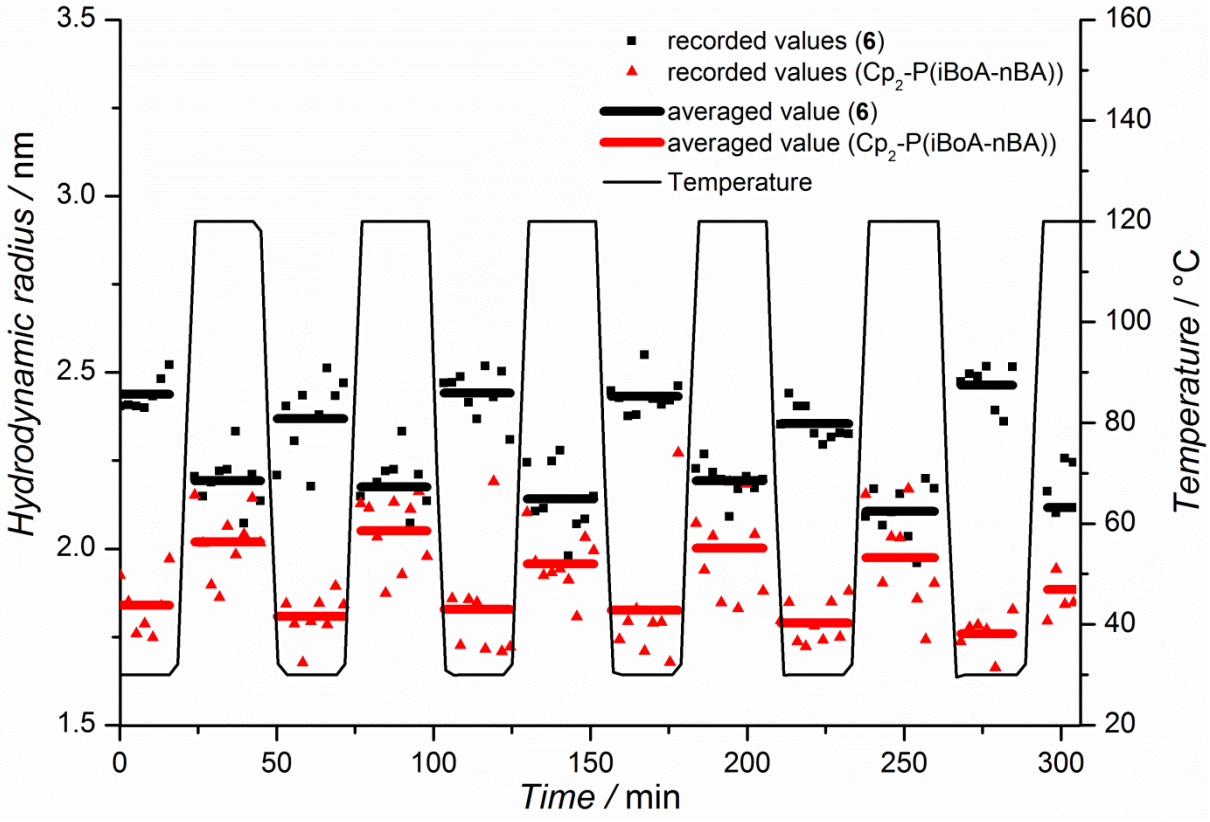

Figure S5. Raw data of the temperature dependent DLS experiment of DA polymer 6 and Cp_2-P(iBoA-nBA) in trichlorobenzene (refer to Figure 5b in the main manuscript text).

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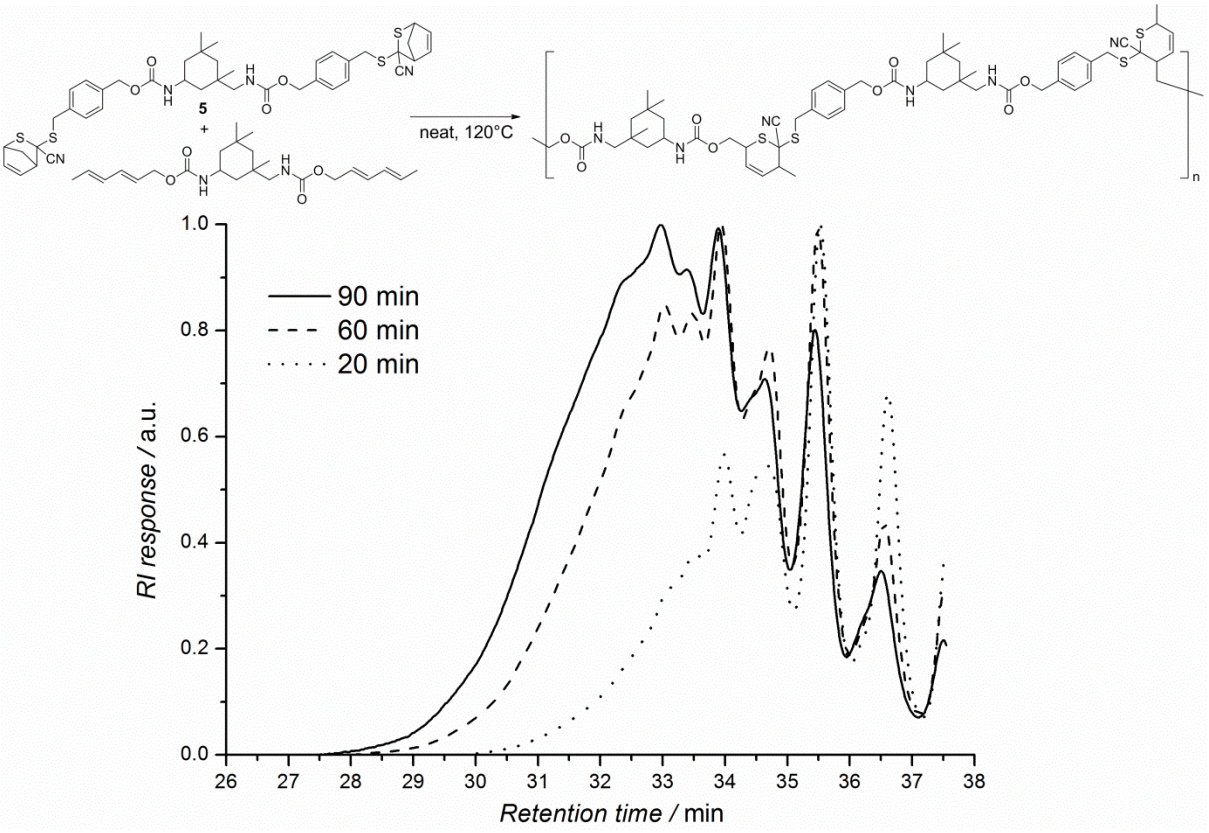

Figure S6. SEC traces of the polymerization reaction between 5 and the sorbic alcohol derivative of IPDI after 20, 60, and 90 min at 120°C.

Reaction time	M_p (g mol^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	$Đ_M$
20 min	**1400**	**1700**	**2800**	**1.7**
60 min	**3000**	**2500**	**4600**	**1.9**
90 min	**4800**	**3000**	**5900**	**2.0**

SEC evaluation used the Mark-Houwink parameters for polystyrene. K = 14 dL g^{-1} and α = 0.7.

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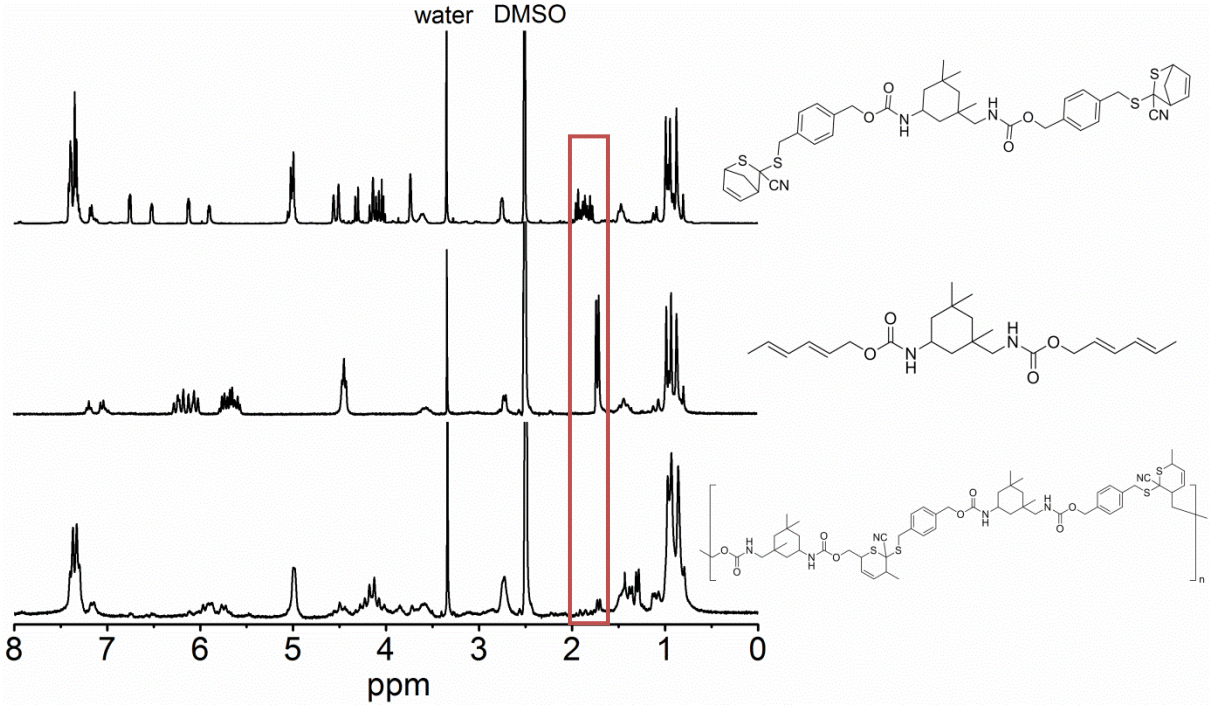

Figure S7. ^{1}H NMR analysis of the obtained polymer from **5** and the sorbic alcohol derivative of IPDI. As can be seen in the marked red zone, the resonances of the bridge-head protons of the Cp DA product (top) vanish in the polymer spectrum (bottom), as well as the signals of the terminal methyl groups (middle) of the sorbic alcohol. Moreover, a significant change in the double bond region evidences the generation of the DA product.

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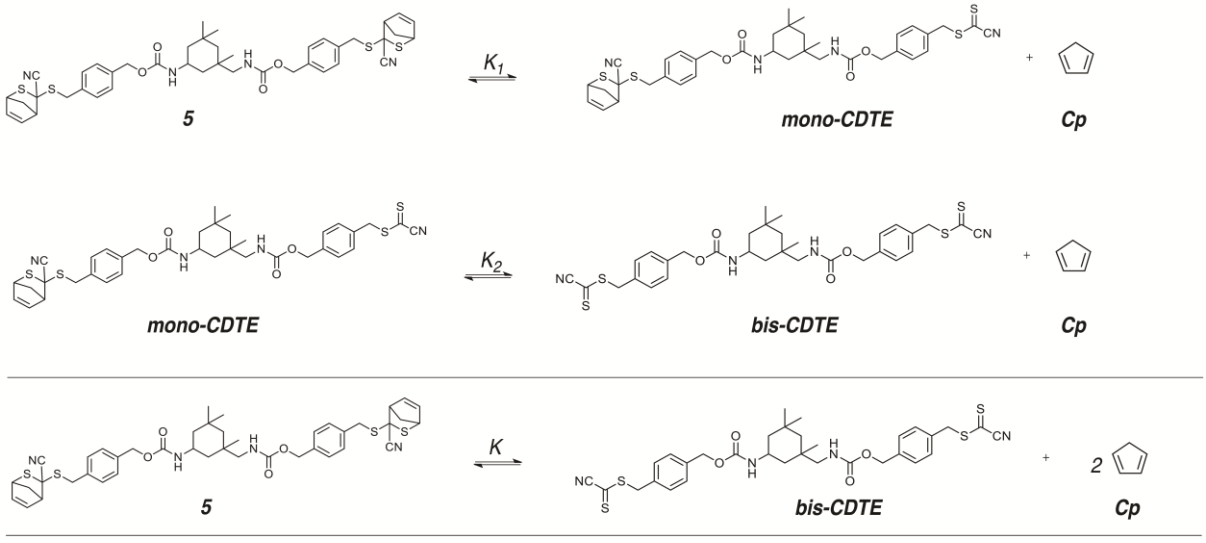
4. Computational Study

4.1 Relationship Between Equilibrium Concentrations and Equilibrium Constants

The reversible two-step Diels-Alder reaction in which the isophorone diisocyanate-cyanodithioester **5** decomposed into free Cp and CDTE was studied using high-level *ab initio* computational chemistry so as to determine the equilibrium constants for each step as a function of temperature.



Let [***5***], [Cp], [mono-CDTE] and [bis-CDTE] refer to the molar concentrations of the respective species at equilibrium. We can thus write the following equilibrium expressions for each Diels-Alder reaction and also the overall process:

$$K_1 = \frac{[\text{mono-CDTE}][\text{Cp}]}{[\boldsymbol{5}]}$$

$$K_2 = \frac{[\text{bis-CDTE}][\text{Cp}]}{[\text{mono-CDTE}]}$$

$$K = K_1 K_2 = \frac{[\text{Cp}]^2[\text{bis-CDTE}]}{[\boldsymbol{5}]}$$

If we define x as the molar concentration of reacted substrate ***5*** at equilibrium and $[\boldsymbol{5}]_0$ is the initial concentration of substrate ***5***, we obtain:

$[\boldsymbol{5}] = [\boldsymbol{5}]_0 - x$

Applying a simple mass balance, the total amount of [mono-CDTE] and [bis-CDTE] produced at equilibrium has to equal *x*. Thus:

x = [mono-CDTE] + [bis-CDTE]

As one mole of Cp is released when one mole of mono-CDTE is produced from ***5***, while two moles of Cp are released when one mole of bis-CDTE is produced from ***5***, we can also write

[Cp] = [mono-CDTE] + 2[bis-CDTE]

From the two equations above, we obtain:

[bis-CDTE] = [Cp] – x

[mono-CDTE] = 2x – [Cp]

Now we substitute these two expressions into the equations for K_1, K_2 and K to obtain:

$$K_1 = \frac{(2x - [\mathrm{Cp}])[\mathrm{Cp}]}{[\boldsymbol{5}]_0 - x}$$

$$K_2 = \frac{([\mathrm{Cp}] - x)[\mathrm{Cp}]}{2x - [\mathrm{Cp}]}$$

$$K = \frac{[\mathrm{Cp}]^2([\mathrm{Cp}] - x)}{[\boldsymbol{5}]_0 - x}$$

Any pair of these three equations is linearly independent and can be solved simultaneously to obtain x and [Cp]:

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$$[Cp] \to -\frac{K_1}{3} - \left(2^{1/3}\left(3K - 3[5]_0 K_1 - K_1^2\right)\right) \Big/ \left(3\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3}\right) +$$

$$\frac{1}{3\times 2^{1/3}}\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3},$$

$$x \to \frac{1}{-4K + K_1^2}\left(\frac{4KK_1}{3} + \frac{[5]_0 K_1^2}{3} - \frac{K_1^3}{3} - \left(2^{2/3}K^2K_1\right) \Big/ \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{2/3} +$$

$$\left(2\,2^{2/3}[5]_0 KK_1^2\right) \Big/ \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{2/3} -$$

$$\left(2^{2/3}[5]_0{}^2 K_1^3\right) \Big/ \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{2/3} +$$

$$\left(2\times 2^{2/3}KK_1^3\right) \Big/ \left(3\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{2/3}\right) -$$

$$\left(2\,2^{2/3}[5]_0 K_1^4\right) \Big/ \left(3\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{2/3}\right) -$$

$$\left(2^{2/3}K_1^5\right) \Big/ \left(9\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{2/3}\right) +$$

$$\left(2\times 2^{1/3}K^2\right) \Big/ \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3} -$$

$$\left(2\,2^{1/3}[5]_0 KK_1\right) \Big/ \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3} -$$

$$\left(4\times 2^{1/3}KK_1^2\right) \Big/ \left(3\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3}\right) +$$

$$\left(2\,2^{1/3}[5]_0 K_1^3\right) \Big/ \left(3\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3}\right) +$$

$$\left(2\times 2^{1/3}K_1^4\right) \Big/ \left(9\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3}\right) -$$

$$\frac{1}{3}2^{2/3}K\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3} +$$

$$\frac{1}{9}2^{2/3}K_1^2\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{1/3} -$$

$$1/\left(9\times 2^{2/3}\right)K_1\left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3 + \sqrt{4\left(3K - 3[5]_0 K_1 - K_1^2\right)^3 + \left(54[5]_0 K + 9KK_1 - 9[5]_0 K_1^2 - 2K_1^3\right)^2}\right)^{2/3}\Bigg)$$

There are two other solutions but both contain imaginary parts, so they are ignored. The solutions seem complicated, but once we substitute into numerical values of $[\boldsymbol{5}]_0$ (which equals 0.02 mol L^{-1} in the experimental system), K and K_1 calculated from *ab initio* molecular orbital theory, we obtain simple quantitative predictions of the concentrations of every species at the temperature at which K and K_1 is calculated. This can then be repeated for K and K_1 values calculated at other temperatures.

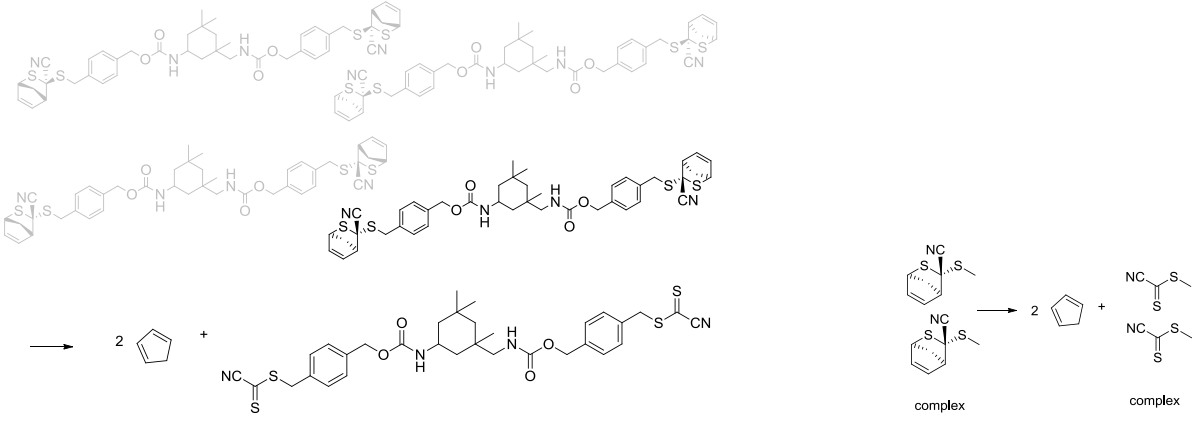
We are interested in the percentage of debonding which can be expressed as the ratio of free Cp to the total Cp available (i.e. free and bound to the IPDI-CDTE ***5***) and hence:

$$\%debonding = \frac{[\mathrm{Cp}]}{2[\boldsymbol{5}]_0} \times 100\%$$

Because K and K_1 are temperature dependent, we can plot the molar concentration of all species and the overall %mole concentration vs T in Figure 3b of the manuscript.

4.2 Theoretical Procedures

To obtain K_1, K_2 and K as a function of temperature, theoretical calculations were performed using Gaussian09[1] and MOLPRO 10.[2] Optimized geometries and harmonic frequencies were obtained at the B3LYP/6-31G* level of theory.[3] The lowest energy conformer for the diene and the product was located using the energy directed tree search (EDTS) algorithm[4], also at the B3LYP/6-31G* level. There are a number of possible diastereomers for the diene and the Diels-Alder product, and all calculations are based on the lowest energy diastereomer (as shown in Scheme S1). The gas phase reaction energies were obtained at the G3(MP2) level with RI-ROMP2/G3MP2Large level where RIMP2-cc-pVTZ was used as the auxiliary basis set.[5] Due to the large size of the full system, ONIOM approximation[6] was used in which the isodesmic full reaction was calculated at the B3LYP/6-31G* level. (see Scheme S1). The temperature-dependent solvation free energies of each species in toluene were calculated using the COSMO-RS model[7] at the BP/TZP level of theory as implemented in the ADF program.[8]



Scheme S1 Reactions studied and the ONIOM core definition.

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4.3 Temperature dependent equilibrium constant (K) for the overall retro-Diels Alder reaction of *5* in toluene solution

T (C)	T (K)	log K	ΔG_{soln} kJ/mol	$\Delta H(g)$ kJ/mol	$\Delta S(g)$ J/mol.K	ΔG^*solv kJ/mol
25	298.15	-14.29	81.55	179.45	414.75	9.90
50	323.15	-11.94	73.85	179.35	414.43	10.80
75	348.15	-9.93	66.16	179.19	413.96	11.68
100	373.15	-8.19	58.49	178.98	413.38	12.53
125	398.15	-6.67	50.85	178.72	412.70	13.36
150	423.15	-5.34	43.23	178.41	411.95	14.18
175	448.15	-4.15	35.64	178.06	411.15	14.97
200	473.15	-3.10	28.07	177.67	410.31	15.75
300	573.15	0.18	-1.94	175.81	406.78	18.68
400	673.15	2.45	-31.56	173.58	403.21	21.37

4.4 Temperature dependent equilibrium constant (K_1) for the first retro-Diels Alder reaction of *5* in toluene solution

T (C)	T (K)	log K_1	ΔG_{soln} kJ/mol	$\Delta H(g)$ kJ/mol	$\Delta S(g)$ J/mol.K	ΔG^*solv kJ/mol
25	298.15	-6.26	35.76	104.83	237.28	-6.26
50	323.15	-5.05	31.25	104.79	237.15	-5.71
75	348.15	-4.01	26.74	104.72	236.93	-5.19
100	373.15	-3.11	22.23	104.62	236.66	-4.69
125	398.15	-2.33	17.73	104.49	236.33	-4.21
150	423.15	-1.63	13.23	104.34	235.97	-3.75
175	448.15	-1.02	8.73	104.17	235.58	-3.30
200	473.15	-0.47	4.24	103.98	235.17	-2.86
300	573.15	1.24	-13.62	103.06	233.42	-1.25
400	673.15	2.43	-31.32	101.95	231.64	0.20

4.5 B3-LYP/6-31G(d) optimized geometries of all species

Cp

```
1\1\GINC-D18\FOpt\RB3LYP\Gen\C5H6\CYL509\04-Mar-2013\0\\#B3LYP/gen 6D
OPT IOP(2/17=4) Freq=noraman
maxdisk=536870912\\1.freq\\0,1\C,-0.7319546296,2.5841220621,0.01208475
16\C,-1.902627708,1.6356892618,0.0050366675\C,-1.4423892877,0.36771009
43,-0.0042668991\C,0.0272263491,0.3839303643,-0.0042714593\C,0.4593665
369,1.6617587888,0.0050293383\H,-0.7391945017,3.2403294588,0.896263174
5\H,-0.7393775894,3.256424202,-0.8597056059\H,-2.9389705436,1.95349243
08,0.0074256949\H,-2.0451828507,-0.534718938,-0.0106114119\H,0.6497909
716,-0.5049742877,-0.0106197743\H,1.4884425437,2.0023581574,0.00741195
68\\Version=EM64L-G09RevC.01\State=1-A'\HF=-194.1010577\RMSD=5.472e-09
```

\RMSF=6.641e-05\Dipole=-0.0019009,0.1722248,0.0018398\Quadrupole=0.599
133,1.6382062,-2.2373392,-0.0114696,-0.0003201,0.0282006\PG=CS
[SG(C1H2),X(C4H4)]\\@

bis-CDTE

1\1\GINC-D12\Freq\RB3LYP\Gen\C32H36N4O4S4\CYL509\04-Mar-2013\0\\#B3LYP
/gen 6D Freq=(noraman)
maxdisk=3489660928\\r.a0f2h2i2.freq\\0,1\C,4.6941395385,-3.4499103571,
1.4773710669\C,3.6470949368,-2.3280341268,1.3813897341\C,3.2598267619,
-2.0729647283,-0.082933465\C,2.7014007393,-3.3305651501,-0.7924282442\
C,3.6747399081,-4.5230762556,-0.5777932288\C,4.2223119468,-4.785686892
,0.8530950517\C,2.6646308356,-3.084153783,-2.3285746747\N,4.1135559993
,-1.0914719924,2.0021216237\N,1.8761319397,-1.9420425262,-2.7621696345
\C,0.6699245118,-2.0622829903,-3.3821603991\C,3.7539187621,-0.72612028
76,3.2621767896\O,4.3894595558,0.4323042392,3.6090959493\O,2.976702127
,-1.3317761355,3.9824876885\O,0.2470693435,-0.8320470904,-3.7954991812
\O,0.0574755292,-3.1041994441,-3.5503244515\C,1.2645419604,-3.62884679
51,-0.3194915245\C,5.4342090049,-5.7323331323,0.7296442017\C,3.1919924
789,-5.4783337581,1.7722889003\C,3.9898884122,1.0036669546,4.878808432
5\C,-1.0993037755,-0.7699009856,-4.3275637991\C,2.756645561,1.86455712
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