Supporting Information for:

A Highly Efficient Metal-Free Protocol for the Synthesis of Linear Polydicyclopentadiene

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1. Synthesis

General: The pyrylium tetrafluoroborate (**3**) salt was prepared according to our previous procedure.[1] *endo*-DCPD (*endo*-**1**, containing about 2.6% *exo*-**1**) with BHT stabilizer was used as received from Sigma-Aldrich. *exo*-DCPD (*exo*-**1**, containing about 2.9% *endo*-**1**),[2] *endo*-dihydroDCPD (*endo*-**5**, containing about 3.1% *exo*-**5**),[3] and *exo*-dihydroDCPD (*exo*-**5**, containing about 6.5% *endo*-**5**)[4] were prepared according to literature procedure. Norbornene (**4**) was purchased from Sigma-Aldrich and sublimed prior to use. Dichloromethane (CH_2Cl_2) was dried over 3 Å molecular sieves before use. Other reagents employed were commercially available and used without any further purification. NMR spectra were recorded on Bruker Avance III 400 MHz and Bruker Avance III 500 MHz spectrometers. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio-solvent as an internal standard ($CDCl_3$, δ_H = 7.26 ppm for ^{1}H NMR). All polymerizations were carried out under air in standard 2-dram borosilicate glass vials with PTFE-lined screw cap purchased from Fisher Scientific unless otherwise noted. Irradiation of photoredox mediated ROMP was done using Norman Lamps MR16-4W blue LEDs (450 nm).

Gel permeation chromatography (GPC) was performed using the following setup: an Agilent Technologies Infinity Series II pump, 3 in-line columns, and Wyatt Technology miniDAWN TREOS multi-angle light scattering (MALS) and Optilab T-rEX refractive index (RI) detectors using THF as the mobile phase with a flow rate of 1 mL/min. The absolute Weight-average molecular weight (M_w) was determined by a dn/dc value which was measured by assuming 100% mass recovery of the polymer after passing the columns. The dn/dc of pDCPD was found to be 0.1759 (mL/g).

***General Procedure for MF-ROMP of endo-DCPD*:** A 2-dram glass vial containing a magnetic stir bar and pyrylium (**3**, 0.07 equiv) were added *endo*-DCPD (*endo*-**1**, 10 – 100 equiv) and CH_2Cl_2 (0.88 – 2.60 M) under air. The mixture was stirred at room temperature for 1 – 3 min till the pyrylium salt dissolved. Then ethyl propenyl ether (**2**, 1 equiv) was added via micro-syringe. The vial was sealed with PTFE-lined screw cap and irradiated with blue LED lights (450 nm, 4 W) for indicated period of time (usually 60 min) at varied temperature. One LED light with 1 cm distance from the vial was used at room temperature, while two lights around the cooling bath were used for low temperature set up (Figure S1). Upon completion, a small scoop of hydroquinone (HQ) was added to the reaction mixture, and an aliquot was taken and diluted with $CDCl_3$ for ^{1}H NMR analysis to determine monomer conversion. A second aliquot was taken and diluted with tetrahydrofuran (THF) for analysis of crude molecular weight by GPC. The polymer sample was then diluted with CH_2Cl_2 and passed through basic alumina to remove any remaining **3**. This CH_2Cl_2 mixture was concentrated down to approximately 5 mL and precipitated into cold MeOH (80 mL, 3 ℃). The pure polymer was collected by filtration, washed with MeOH, and dried under reduced pressure to give white powder form solids. The ^{1}H NMR spectra are consistent with the reported ones in literature.[4,5]

***General Procedure for Chain Transfer*:** A 2-dram glass vial containing a magnetic stir bar and pyrylium (**3**, 2.5 mg, 0.0051 mmol, 0.07 equiv) were added *endo*-DCPD (*endo*-**1**, 239 mg, 1.81 mmol, 25 equiv), dried CH_2Cl_2 (1.81 mL) and 1-hexene (**6**, 0 – 50 equiv) or 1-octene (**7**) under air. The mixture was stirred at room temperature for 1 – 3 min till the pyrylium salt dissolved. Then ethyl propenyl ether (**2**, 8 μL, 0.0722 mmol, 1 equiv) was added via micro-syringe. The vial was sealed with PTFE-lined screw cap and irradiated with two blue LED lights (450 nm, 4 W) for 60 min at 3 ℃. Upon completion, a small scoop of hydroquinone (HQ) was added to the reaction mixture, and an aliquot was taken and diluted with $CDCl_3$ for ^{1}H NMR analysis to determine monomer conversion. A second aliquot was taken and diluted with tetrahydrofuran (THF) for analysis of crude molecular weight by GPC. The polymer sample was then diluted with CH_2Cl_2 and passed through basic alumina to remove any remaining **3**. This CH_2Cl_2 mixture was concentrated down to approximately 5 mL and precipitated into cold MeOH (80 mL, 3 ℃). The pure polymer was collected by filtration, washed with MeOH, and dried under reduced pressure to give white powder form solids.

***General Procedure for copolymerization*:** A 2-dram glass vial containing a magnetic stir bar and pyrylium (**3**, 1.2 mg, 0.0025 mmol, 0.07 equiv) were added *endo*-DCPD (*endo*-**1**), norbornene (**4**) (*endo*-**1** + **4** = 1.81 mmol, 50 equiv), and dried CH_2Cl_2 (1.81 mL) under air. The mixture was stirred at room temperature for 1 – 3 min till the pyrylium salt dissolved. Then ethyl propenyl ether (**2**, 4 μL, 0.0361 mmol, 1 equiv) was added via micro-syringe. The vial was sealed with PTFE-lined screw cap and irradiated with two blue LED lights (450 nm, 4 W) for 60 min at 3 °C. Upon completion, a small scoop of hydroquinone (HQ) was added to the reaction mixture, and an aliquot was taken and diluted with $CDCl_3$ for ^{1}H NMR analysis to determine monomer conversion. A second aliquot was taken and diluted with tetrahydrofuran (THF) for analysis of crude molecular weight by GPC. The polymer sample was then diluted with CH_2Cl_2 and passed through basic alumina to remove any remaining **3**. This CH_2Cl_2 mixture was concentrated down to approximately 5 mL and precipitated into cold MeOH (80 mL, 3 °C). The pure polymer was collected by filtration, washed with MeOH, and dried under reduced pressure to give white powder form solids. The ^{1}H NMR spectra are consistent with the reported ones in literature.[4]

Table S1. Results of molecular weight modulation using 1-hexene (6) or 1-octene (7) as CTA.

entry	[*endo*-**1**]$_o$ (M)	CTA	CTA (equiv)[a]	conv (%)[b]	$M_{n,theo}$ (kDa)[c]	$M_{n,exp}$ (kDa)[d]	$M_{w,exp}$ (kDa)[d]	$Đ$[d]	IE (%)[e]
1[f]	0.88	--	0	89	3.03	6.49	9.65	1.5	47
2	0.84	**6**	12.5	69	2.38	1.96	2.96	1.5	122
3	0.79	**6**	25	73	2.51	1.54	2.20	1.4	163
4	0.72	**6**	50	68	2.34	1.00	1.41	1.4	234
5	0.69	**7**	50	53	1.85	1.04	1.47	1.4	178

All reactions were conducted with an initial molar ratio of *endo*-**1**:**2**:**3** = 25:1:0.07 in CH_2Cl_2 at 3 °C for 60 min. [a]Equivalents of CTA relative to **2**. [b]Conversion determined by ^{1}H NMR spectroscopy. [c]Theoretical number-average molecular weight (M_n) based upon [*endo*-**1**]$_o$/[**2**]$_o$ and monomer conversion. [d]Determined by GPC analysis on crude reaction sample using multi-angle light scattering (MALS) and RI detection. Dispersity ($Đ$) = M_w/M_n. [e]Initiation efficiency (IE) = $M_{n,theo}/M_{n,exp}$. [f]Average of three runs. GPC dRI traces of entry 1–4 are shown in Figure S3.

Table S2. Conversion and molecular weight data for *endo*-1 and 4 copolymerization.

entry	*endo*-**1**:**4**	[*endo*-**1**]$_o$ (M)	[**4**]$_o$ (M)	%*endo*-**1** (feed)[a]	%*endo*-**1** (polymer)[b]	*endo*-**1** conv (%)[c]	**4** conv (%)[c]	total conv (%)[c]	$M_{n,exp}$ (kDa)[d]	$M_{w,exp}$ (kDa)[d]	$Đ$[d]	IE (%)[e]
1[f]	50:0	0.88	0	100	100	70	0	70	8.89	13.5	1.5	53
2	40:10	0.71	0.18	80	74	75	92	78	8.86	13.6	1.5	56
3	25:25	0.45	0.45	50	46	84	97	91	10.1	16.2	1.6	51
4	10:40	0.025	0.72	20	19	93	99	98	9.77	15.5	1.6	52
5	0:50	0	0.91	0	0	0	99	99	9.79	15.8	1.6	49

All reactions were conducted in CH_2Cl_2 at 3 °C for 60 min. [a]Mole fraction of *endo*-**1** in the initial monomer mixture. [b]Mole fraction of *endo*-**1** in purified polymer determined by ^{1}H NMR spectroscopy. [c]Conversion determined by ^{1}H NMR spectroscopy. [d]Determined by GPC analysis on crude reaction sample using MALS and RI detection. $Đ = M_w/M_n$. [e]IE = $M_{n,theo}/M_{n,exp}$. [f]Average of three runs.

Table S3. Conversion, molecular weight data and thermal property for linear pDCPD.

entry	scale (mmol)	$[endo\text{-}\mathbf{1}]_o$ (M)	*endo*-**1**:**6**:**2**:**3**	temp (°C)	time (min)	conv (%)[a]	$M_{n,exp}$ (kDa)[b]	$M_{w,exp}$ (kDa)[b]	$Đ$[b]	T_d (°C)[c]	T_g (°C)[d]
1[e]	1.806	0.69	25:50:1:0.07	3	60	53	1.26	1.58	1.3	432.8	40.3
2	1.806	0.72	25:50:1:0.07	3	60	68	1.25	1.57	1.3	435.8	42.9
3	1.806	0.79	25:25:1:0.07	3	60	73	1.52	2.01	1.3	436.0	63.5
4	1.806	0.88	25:12.5:1:0.07	3	60	65	2.07	2.88	1.4	436.9	82.3
5	2.250	0.84	25:12.5:1:0.07	3	60	69	2.11	3.00	1.4	435.6	84.2
6	2.709	0.88	15:0:1:0.05	3	60	65	2.30	3.10	1.3	437.9	89.1
7	2.709	0.88	15:0:1:0.06	3	120	79	2.79	3.95	1.4	436.9	103.9
8	1.806	0.88	20:0:1:0.05	3	60	78	3.51	5.01	1.4	437.9	109.7
9	1.806	0.88	25:0:1:0.05	3	60	76	4.34	5.89	1.4	436.9	114.9
10	1.129	0.88	25:0:1:0.07	3	60	90	4.97	9.66	1.9	435.9	122.3
11	1.129	0.88	25:0:1:0.07	3	60	90	6.69	11.7	1.7	434.9	129.7
12	4.064	0.87	75:0:1:0.07	3	60	42	7.82	10.4	1.3	435.6	133.6
13	1.129	0.88	25:0:1:0.07	3	60	94	8.50	14.2	1.7	436.3	131.5
14	4.515	0.88	100:0:1:0.07	3	60	36	8.55	11.7	1.4	437.8	134.4
15	1.806	0.88	50:0:1:0.07	3	60	70	9.86	14.7	1.5	434.2	135.9
16	1.806	0.88	40:0:1:0.07	-18	90	86	12.6	18.6	1.5	436.5	141.0
17	2.258	0.88	50:0:1:0.07	-20	90	75	12.7	17.4	1.4	436.2	141.2
18	2.709	0.88	60:0:1:0.07	-20	90	72	13.0	18.0	1.4	437.8	141.4
19	2.709	0.88	75:0:1:0.08	-23	90	59	14.6	20.7	1.4	436.8	144.4
20	2.709	0.88	100:0:1:0.07	-30	60	47	15.6	22.0	1.4	437.2	144.1
21	3.610	0.88	100:0:1:0.08	-23	110	51	16.0	23.7	1.5	436.9	144.2
22	4.064	0.87	150:0:1:0.13	-22	90	40	16.1	22.8	1.4	437.2	145.6

[a]Conversion determined by ^{1}H NMR spectroscopy. [b]Determined by GPC analysis on purified polymer sample using MALS and RI detection. $Đ = M_w/M_n$. [c]T_d of each purified polymer was determined by the onset of the weight loss from TGA thermogram under nitrogen. [d]T_g of each purified polymer was determined by the midpoint of DSC curve during the second heating cycle under nitrogen. [e]1-Octene (**7**) was used as CTA instead of 1-hexene (**6**).

Table S4. DP of *endo*-DCPD oligomers characterized by GPC and NMR analysis.

entry	*endo*-**1**:**6**:**2**[a]	$M_{n,exp}$ (kDa)[b]	DP[c]	DP[d]
1	25:12.5:1	2.11	15	20
2	25:25:1	1.52	11	13
3	25:50:1	1.25	9	9

[a]Initial molar ratio of *endo*-**1**, **6**, and **2**. [b]Determined by GPC analysis on purified polymer sample using MALS and RI detection. [c]Degree of polymerization (DP) determined from GPC. [d]DP determined from NMR spectra by comparing the integration of oligomer and chain end.

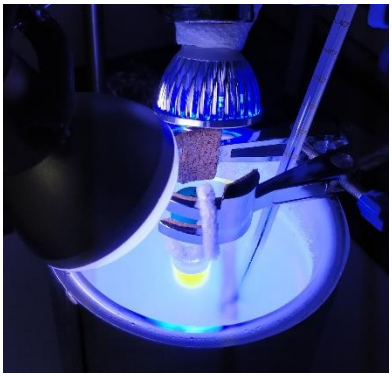

Figure S1. Setup of MF-ROMP at low temperature.

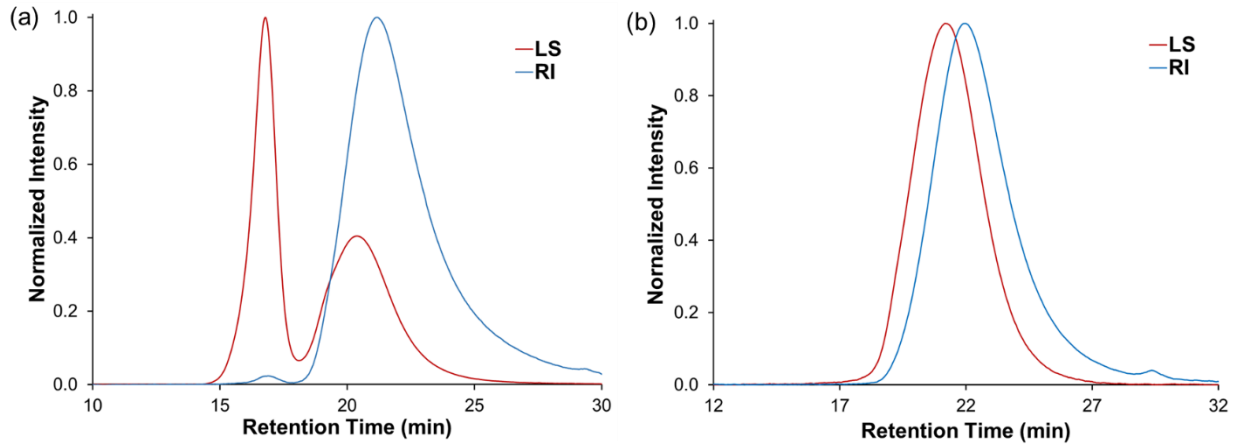

Figure S2. Normalized GPC traces of linear pDCPD prepared using 50:1 ([*endo*-**1**]$_o$:[**2**]$_o$) loading ratio at (a) -29 ℃ (Table 1, entry 5) and (b) -11 ℃ (Table 2, entry 4), respectively.

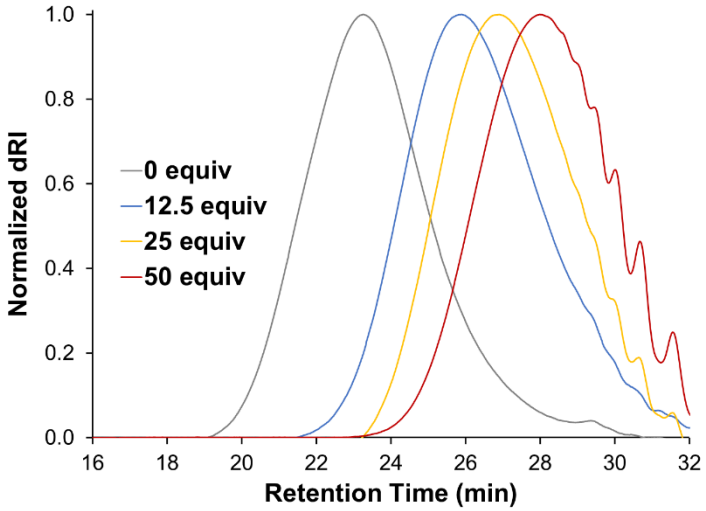

Figure S3. Normalized GPC dRI traces of linear *endo*-DCPD polymers and oligomers prepared via MF-ROMP using 1-hexane (**6**) as CTA with varied equivalents relative to initiator **2** at 3 ℃ (Table S1, entry 1–4).

2. Tracking Monomer Conversion vs. Time

***General Procedure for homopolymerization*:** A 2-dram glass vial containing a magnetic stir bar and pyrylium (**3**, 2.5 mg, 0.0051 mmol, 0.07 equiv) were added monomer (25 equiv) and CH_2Cl_2 (1.81 mL, 0.88 M) under air. The mixture was stirred at room temperature for 1 – 3 min till the pyrylium salt dissolved. Then ethyl propenyl ether (**2**, 8 μL, 0.0722 mmol, 1 equiv) was added via micro-syringe. The vial was sealed with PTFE-lined screw cap and thermally equilibrated at 3 °C for 2 min. The reaction was irradiated with two blue LED lights (450 nm, 4 W) as shown in Figure S1 for indicated period of time. Stopped irradiation at t = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 30, 45, 60, 75 min. At each time points, the vial was removed from the cooling bath and warmed up to room temperature. Then aliquots were taken and diluted with $CDCl_3$ containing hydroquinone (HQ) for ^{1}H NMR analysis to determine monomer conversion.

***General Procedure for copolymerization*:** A 2-dram glass vial containing a magnetic stir bar and pyrylium (**3**, 1.2 mg, 0.0025 mmol, 0.07 equiv) were added *endo*-DCPD (*endo*-**1**, 119 mg, 0.900 mmol, 25 equiv), norbornene (**4**, 85 mg, 0.90 mmol, 25 equiv) and CH_2Cl_2 (1.81 mL, 0.88 M) under air. The mixture was stirred at room temperature for 1 – 3 min till the pyrylium salt dissolved. Then ethyl propenyl ether (**2**, 4 μL, 0.0361 mmol, 1 equiv) was added via micro-syringe. The vial was sealed with PTFE-lined screw cap and thermally equilibrated at 3 °C for 2 min. The reaction was irradiated with two blue LED lights (450 nm, 4 W) as shown in Figure S1 for indicated period of time. Stopped irradiation at t = 5, 10, 15, 20, 30, 40, 50, 60 min. At each time points, the vial was removed from the cooling bath and warmed up to room temperature. Then aliquots were taken and diluted with $CDCl_3$ containing hydroquinone (HQ) for ^{1}H NMR analysis to determine monomer conversion.

Conversions of homopolymerization and copolymerization were determined by ^{1}H NMR ($CDCl_3$) as shown below in detail:

Polymerization of *endo*-**1**: the monomer signal at δ 5.99 – 5.92 ppm (2H) was integrated against the polymer signal at δ 5.68 ppm (1H).

Polymerization of *exo*-**1**: the monomer signal at δ 6.10 – 6.03 ppm (2H) was integrated against the region from δ 5.78 to 5.59 ppm (1H from poly(*exo*-**1**) and 1H from monomer *exo*-**1**).

Polymerization of *endo*-**5**: the monomer signal at δ 6.11 ppm (2H) was integrated against the region from δ 2.95 to 2.24 ppm (4H from poly(*endo*-**5**) and 4H from monomer *endo*-**5**).

Polymerization of *exo*-**5**: the monomer signal at δ 6.08 ppm (2H) was integrated against the sum of two peaks at δ 2.39 – 2.21 and 2.02 – 1.84 ppm (2H from poly(*exo*-**5**) in total and 3H from monomer *exo*-**5**).

Copolymerization of *endo*-**1** and **4**: the monomer (*endo*-**1**) signal at δ 5.94 – 5.92 ppm (1H) was integrated against the polymer signal at δ 5.68 ppm (1H) to calculate conversion of *endo*-**1**; the monomer (**4**) signal at δ 5.99 ppm (2H) was integrated against the polymer signal at δ 1.88 – 1.76 ppm (3H) to calculate conversion of **4**; the monomer signal at δ 5.99 – 5.92 ppm (2H from monomer *endo*-**1** and 2H from monomer **4**) was integrated against the region from δ 3.00 to 2.07 ppm (2H from poly(**4**), 5H from pDCPD and 3H from monomer *endo*-**1**) to calculate total conversion.

Table S5. Conversion vs. time data for monomer *endo*-1, *exo*-1, *endo*-5 and *exo*-5.

time (min)	 *endo*-**1**	 *exo*-**1**	 *endo*-**5**	 *exo*-**5**
0	0	0	0	0
1	7%	6%	7%	24%
2	12%	18%	12%	54%
3	17%	30%	16%	74%
4	21%	40%	22%	88%
5	27%	47%	26%	95%
6	30%	55%	32%	97%
7	34%	61%	37%	98%
8	38%	67%	42%	99%
9	41%	72%	46%	99%
10	43%	75%	50%	100%
15	53%	84%	61%	100%
20	59%	89%	68%	99%
30	68%	91%	78%	100%
45	75%	93%	81%	100%
60	77%	93%	82%	100%
75	78%	92%	80%	100%

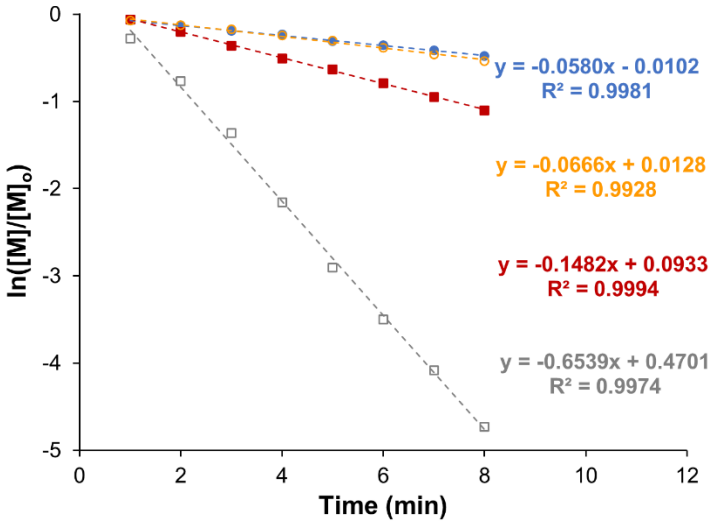

Figure S4. Plot of ln([M]/[M]$_o$) vs. time for MF-ROMP of *endo*-**1** (●), *exo*-**1** (■), *endo*-**5** (○) and *exo*-**5** (□) (CH_2Cl_2, 3 °C, [M]$_o$ = 0.88 M, [M]$_o$/[I]$_o$ = 25:1). Linear regressions can be found in Table S6.

Table S6. Linear regressions and molecular weight data for kinetic trials under optimized conditions.

monomer	k_{obs} (min^{-1})	R^2	$M_{n,theo}$ (kDa)[a]	$M_{n,exp}$ (kDa)[b]	$M_{w,exp}$ (kDa)[b]	$Đ$[b]	IE (%)[c]
endo-**1**	0.058	0.9981	2.69	7.70	14.3	1.9	35
exo-**1**	0.15	0.9994	3.14	9.56	18.5	1.9	33
endo-**5**	0.067	0.9928	2.78	8.25	13.8	1.7	34
exo-**5**	0.65	0.9974	3.44	7.05	9.81	1.4	49

[a]Theoretical M_n based upon [M]$_o$/[I]$_o$ and monomer conversion. [b]Determined by GPC analysis on crude reaction sample using MALS and RI detection. Dispersity ($Đ$) = M_w/M_n. [c]Initiation efficiency (IE) = $M_{n,theo}/M_{n,exp}$.

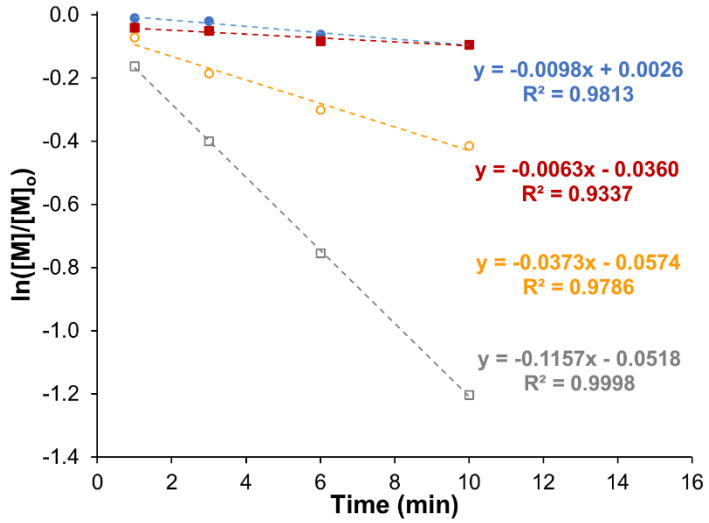

Figure S5. Plot of ln([M]/[M]$_o$) vs. time for MF-ROMP of *endo*-**1** (●), *exo*-**1** (■), *endo*-**5** (○) and *exo*-**5** (□) (CH_2Cl_2, room temperature, [M]$_o$ = 1.73 M, [M]$_o$/[I]$_o$ = 100:1). Linear regressions can be found in Table S7.

Table S7. Linear regressions and molecular weight data for kinetic trials under unoptimized conditions from previous report.[4]

monomer	k_{obs} (min^{-1})	R^2	$M_{n,theo}$ (kDa)[a]	$M_{n,exp}$ (kDa)[b]	$M_{w,exp}$ (kDa)[b]	$Đ$[b]	IE (%)[c]
endo-**1**	0.0098	0.9813	2.99	5.10	7.60	1.5	59
exo-**1**	0.0063	0.9337	2.99	10.8	14.8	1.4	28
endo-**5**	0.037	0.9786	7.33	16.4	20.6	1.3	45
exo-**5**	0.12	0.9998	13.0	17.2	22.8	1.3	75

[a]Theoretical M_n based upon [M]$_o$/[I]$_o$ and monomer conversion. [b]Determined by GPC analysis on crude reaction sample using MALS and RI detection. Dispersity ($Đ$) = M_w/M_n. [c]Initiation efficiency (IE) = $M_{n,theo}/M_{n,exp}$.

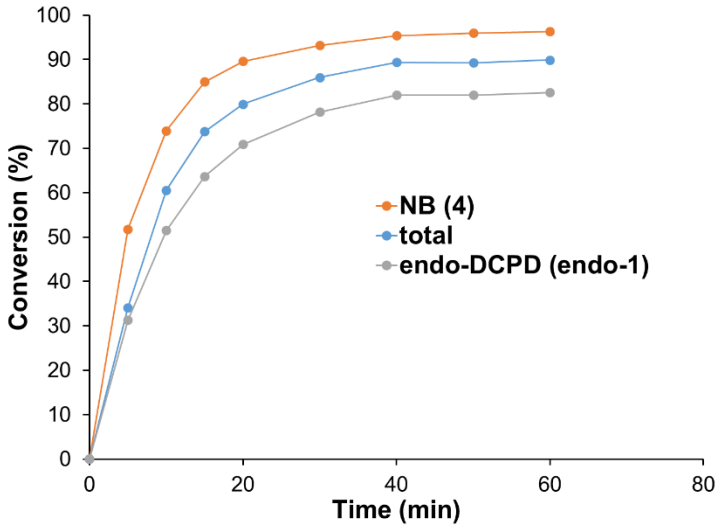

Figure S6. Plot of monomer conversion vs. time for the statistical copolymerization of *endo*-**1** and **4** with 1:1 molar feed ratio (CH_2Cl_2, 3 °C, [*endo*-**1**]$_o$ = [**4**]$_o$ = 0.45 M, *endo*-**1**:**4**:**2** = 25:25:1).

4. MALDI-TOF Mass Spectroscopy

Mass spectral data were collected using a Bruker-Daltonics Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) Autoflex III mass spectrometer in reflector mode with positive ion detection. Typical sample preparation for MALDI-TOF MS data was performed by making stock solutions in THF of matrix (50 mg/ml), polymer analyte (2 mg/ml), and an appropriate cation source (2 mg/ml). The data herein were acquired using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix, and CuBr and AgTFA were used as cation sources. With the Ag^+ cation, the stock solutions were mixed in a 4/2/1 ratio (matrix/analyte/cation). With the Cu^+ cation, the stock solutions were mixed in a 2/1/4 ratio for the 1-hexene (**6**) initiated *endo*-DCPD oligomer; a ratio of 4/2/3 was used for the 1-octene (**7**) initiated *endo*-DCPD oligomer. The prepared solutions were vortexed and deposited onto the MALDI target plate and allowed to evaporate via the dried droplet method. MALDI-TOF MS data were calibrated against poly(ethylene glycol) methyl ether (M_n = 550 Da) from Sigma Aldrich and SpheriCal dendritic calibrants from Polymer Factory (Stockholm, Sweden). M_n and $Đ$ of the resultant spectra were calculated using Polytools software.

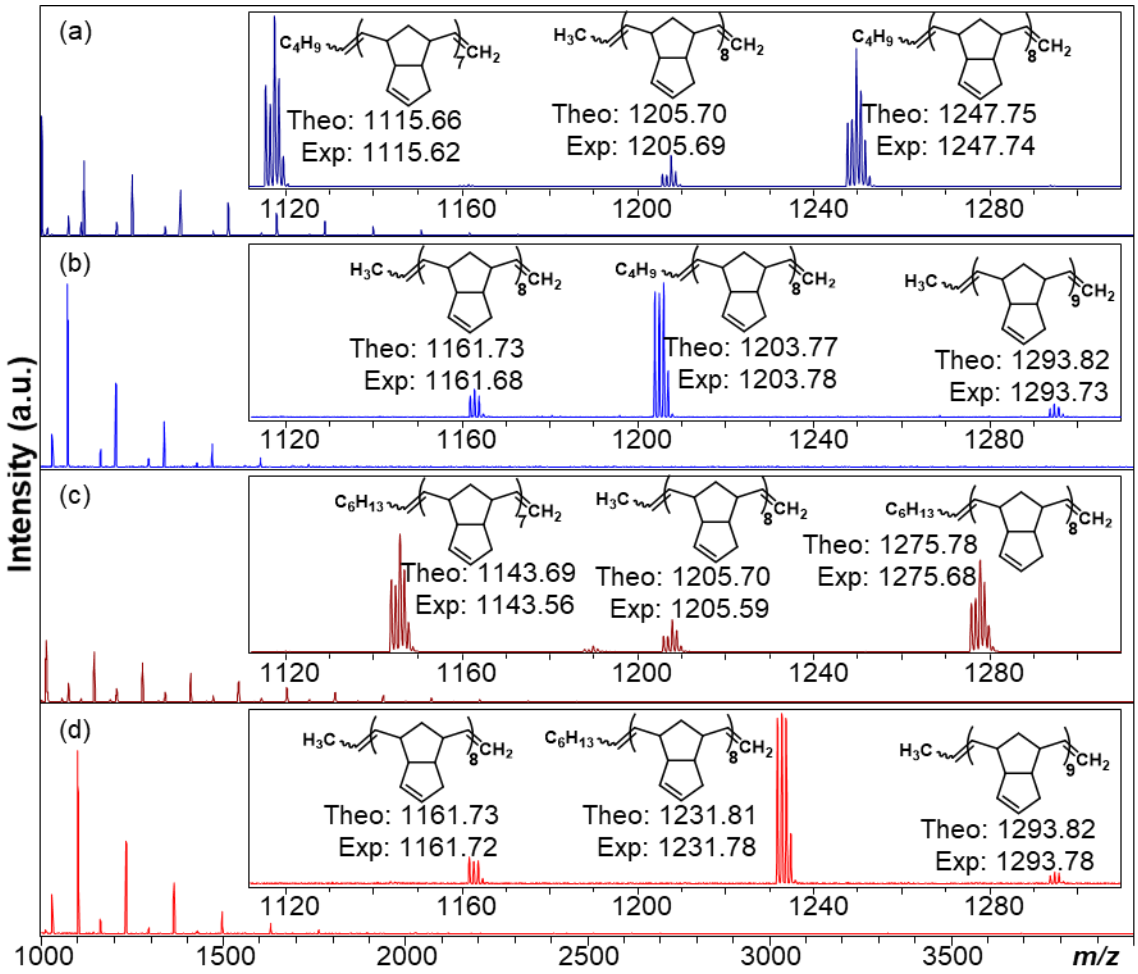

Figure S7. MALDI-TOF mass spectra with insert spectra from *m/z* = 1110 to 1310 showing *endo*-DCPD oligomers prepared with **6** or **7** as CTA, and the ionization mode for each sample. (a) **6** as CTA, ionized with $^{107}Ag^+$; (b) **6** as CTA, ionized with $^{63}Cu^+$; (c) **7** as CTA, ionized with $^{107}Ag^+$; (d) **7** as CTA, ionized with $^{63}Cu^+$. The spectra were taken in positive reflector mode.

5. Thermogravimetric Analysis (TGA)

TGA was performed on a TA TGA Q50 under nitrogen or air from room temperature to 600 °C at 10 °C/min. The decomposition temperature (T_d) of each sample was determined by the onset of the weight loss from TGA thermogram.

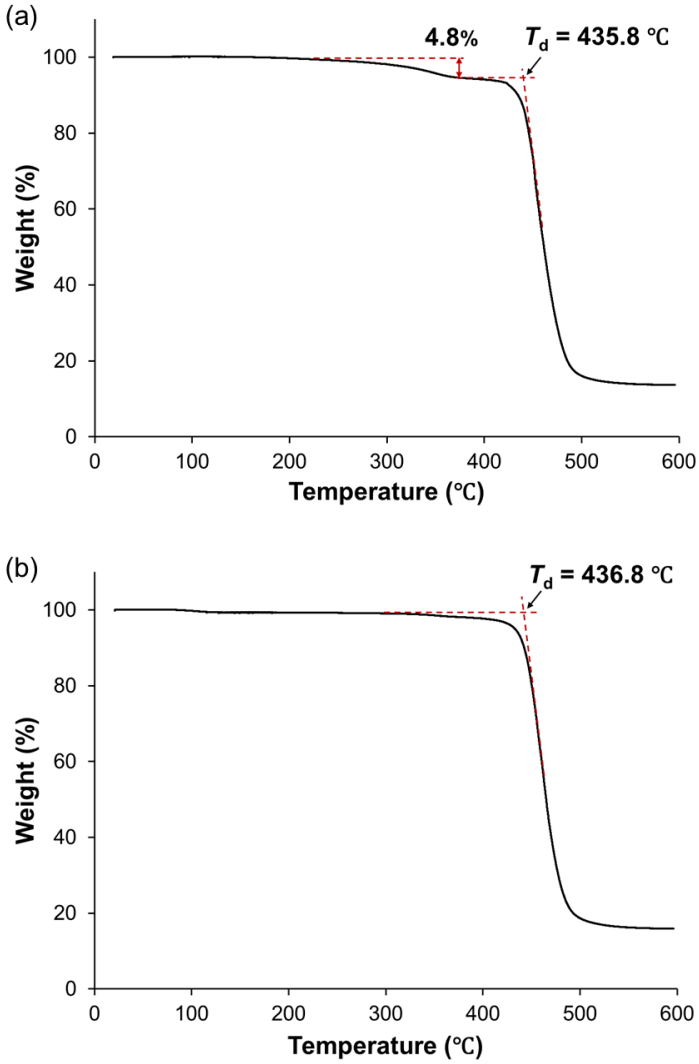

Figure S8. Representative TGA thermograms of (a) *endo*-DCPD oligomer (M_n = 1.25 kDa, Table S3, entry 2) and (b) pDCPD (M_n = 14.6 kDa, Table S3, entry 19) under nitrogen.

Table S8. Comparison of the chain ends weight percent and the minor weight loss around 310 − 330 °C determined by TGA for representative *endo*-DCPD oligomers and polymers.

entry	CTA	M_n (kDa)[a]	wt % of chain ends	weight loss around 310 − 330 °C from TGA
1	**7**	1.256	6.8%	5.5%
2	**6**	1.250	4.6%	4.8%
3	**6**	1.521	3.8%	3.7%
4	**6**	2.065	2.8%	2.8%
5	**6**	2.114	2.7%	2.7%
6	wo	2.298	2.6%	3.1%
7	wo	2.791	2.2%	2.9%
8	wo	3.514	1.7%	2.3%
9	wo	4.344	1.4%	2.1%
10	wo	4.966	1.2%	1.4%
11	wo	6.692	0.9%	1.0%
12	wo	16.10	0.4%	0.8%

[a]Determined by GPC analysis on purified polymer sample using MALS and RI detection.

6. Differential Scanning Calorimetry (DSC)

DSC was performed on a TA DSC Q250 calorimeter under nitrogen atmosphere. A powder sample sealed in an aluminum pan was subjected to heating-cooling cycles with rates at 10 °C/min. Thermal history of the sample was removed in the first heating cycle. Heat flow as watts from first cooling and the second heating were recorded and reported after normalizing by mass of the sample (W/g). For oligomers with M_n < 2 kDa, the samples were heated from -10 to 90 °C and cooled to -10 °C. For oligomers with M_n between 2 and 3 kDa, the samples were heated from 0 to 150 °C and cooled to 0 °C. For polymers with M_n > 3 kDa, the samples were heated from 0 to 190 °C and cooled to 0 °C. The glass transition temperature (T_g) of each sample was determined by the midpoint of DSC curve during the second heating cycle.

For thermal curing under nitrogen atmosphere experiments, the *endo*-DCPD oligomer (M_n = 1.25 kDa, Table S3, entry 2) and polymer (M_n = 14.6 kDa, Table S3, entry 19) sample was each purged inside a 2-dram vial with nitrogen for 20 min before curing at 150 °C for 1 h. During thermal curing, the powder-like oligomer rapidly liquified and formed transparent beads, while the polymer formed milky solids. When these annealed samples were subjected to DSC, no exothermic peaks were observed during the first heating. All samples after thermal curing in a 2-dram vial or under DSC measurement were characterized by GPC to determine the changes in molecular weights.

Table S9. Results of *endo*-DCPD oligomer (M_n = 1.25 kDa) after thermal curing.

entry	description	$M_{n,exp}$ (kDa)[b]	$M_{w,exp}$ (kDa)[b]	$Đ$[b]	T_g (°C)[c]
1	original sample	1.25	1.57	1.3	42.9
2	thermal curing in a vial	1.25	1.62	1.3	44.7
3	only DSC measurement	1.18	1.55	1.3	--
4[a]	vial + DSC measurement	1.10	1.15	1.4	--

[a]Sample after thermal curing under nitrogen in a 2-dram vial was subjected to DSC. [b]Determined by GPC analysis using MALS and RI detection. Dispersity ($Đ$) = M_w/M_n. [c]T_g of each polymer sample was determined by the midpoint of DSC curve during the second heating cycle under nitrogen.

Table S10. Results of *endo*-DCPD polymer (M_n = 14.6 kDa) after thermal curing.

entry	description	$M_{n,exp}$ (kDa)[b]	$M_{w,exp}$ (kDa)[b]	$Đ$[b]	T_g (°C)[c]
1	original sample	14.6	20.7	1.4	144.4
2	thermal curing in a vial	14.8	36.4	2.5	152.0
3[a]	only DSC measurement	34.9	119.6	3.4	--

[a]The original polymer sample was subjected to DSC. [b]Determined by GPC analysis using MALS and RI detection. Dispersity ($Đ$) = M_w/M_n. [c]T_g of each polymer sample was determined by the midpoint of DSC curve during the second heating cycle under nitrogen.

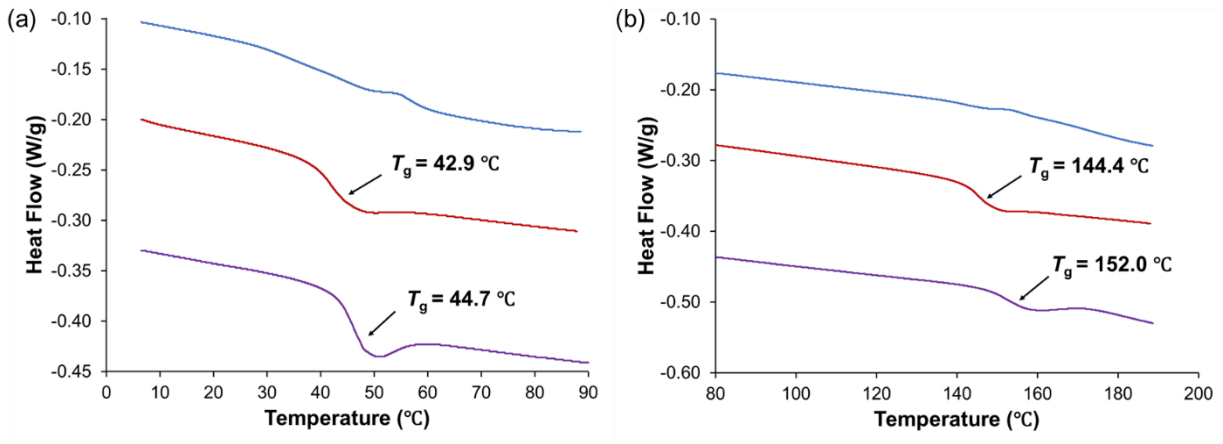

Figure S9. Representative DSC thermograms of (a) *endo*-DCPD oligomer (M_n = 1.25 kDa, Table S3, entry 2) and (b) pDCPD (M_n = 14.6 kDa, Table S3, entry 19) during first heating (blue), second heating (red), and after thermal curing in a 2-dram vial at 150 °C for 1 h under nitrogen (purple).

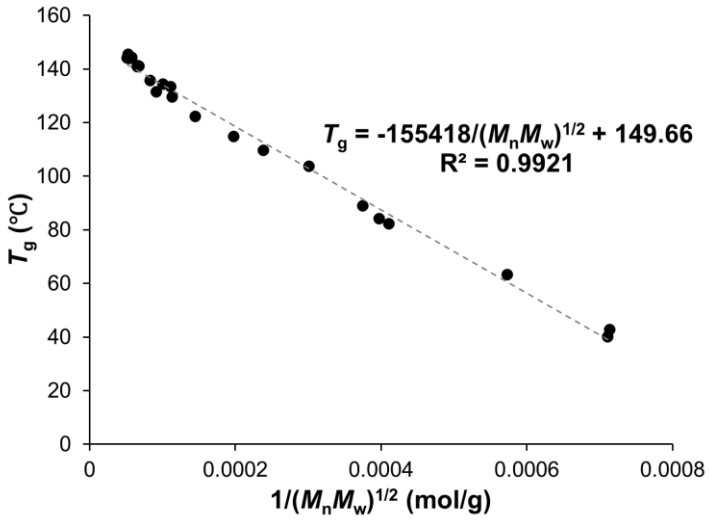

Figure S10. Plot of T_g vs. $(M_nM_w)^{-1/2}$ for polymeric and oligomeric *endo*-DCPD samples using equation 2 to determine $T_{g,\infty}$.

7. Representative Polymer ^{1}H NMR Spectra

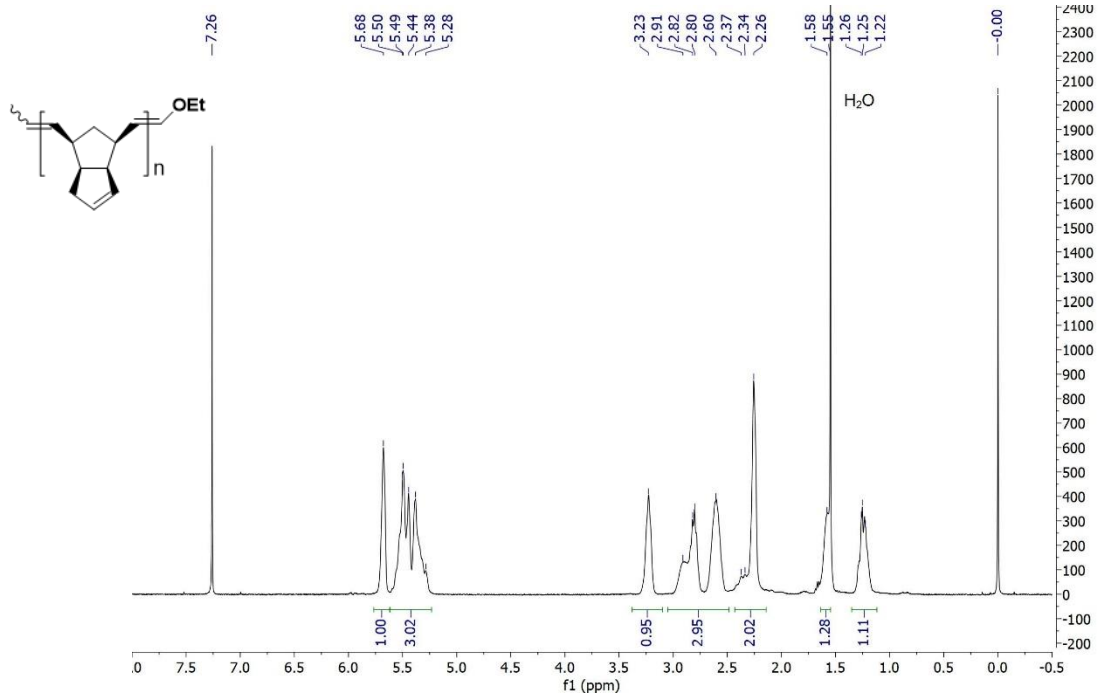

Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of pDCPD with M_n = 13.9 kDa. Condition: [*endo*-**1**]$_o$:[**2**]$_o$ = 50:1, -29 ℃ (Table 1, entry 5).

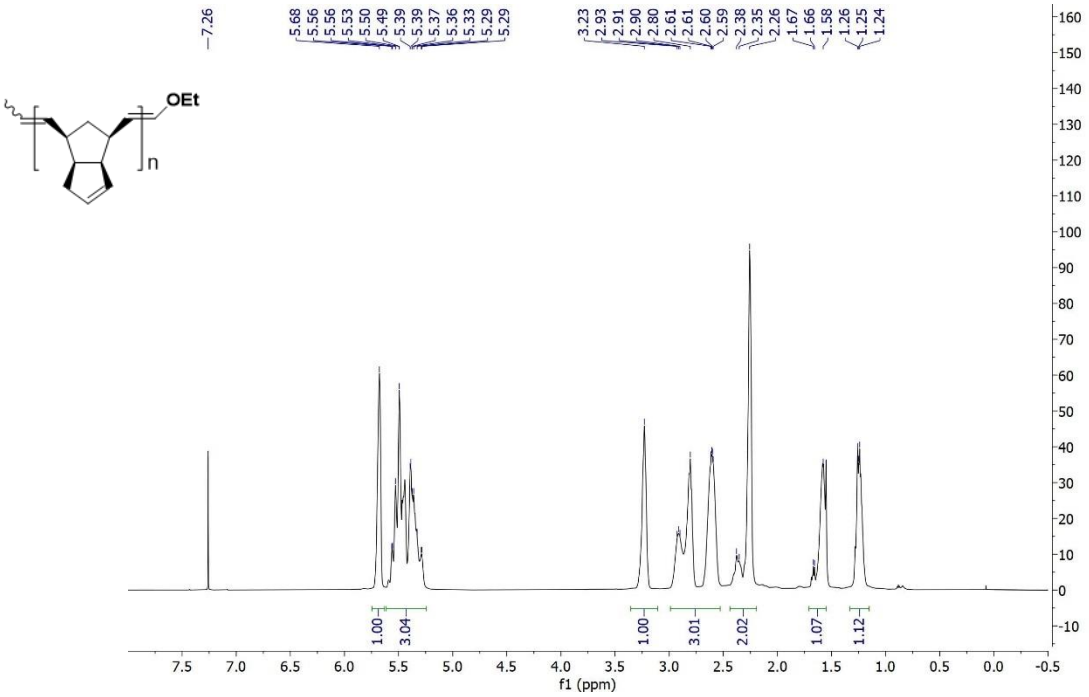

Figure S12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of pDCPD with M_n = 9.86 kDa. Condition: [*endo*-**1**]$_o$:[**2**]$_o$ = 50:1, 3 ℃ (Table 2, entry 7).

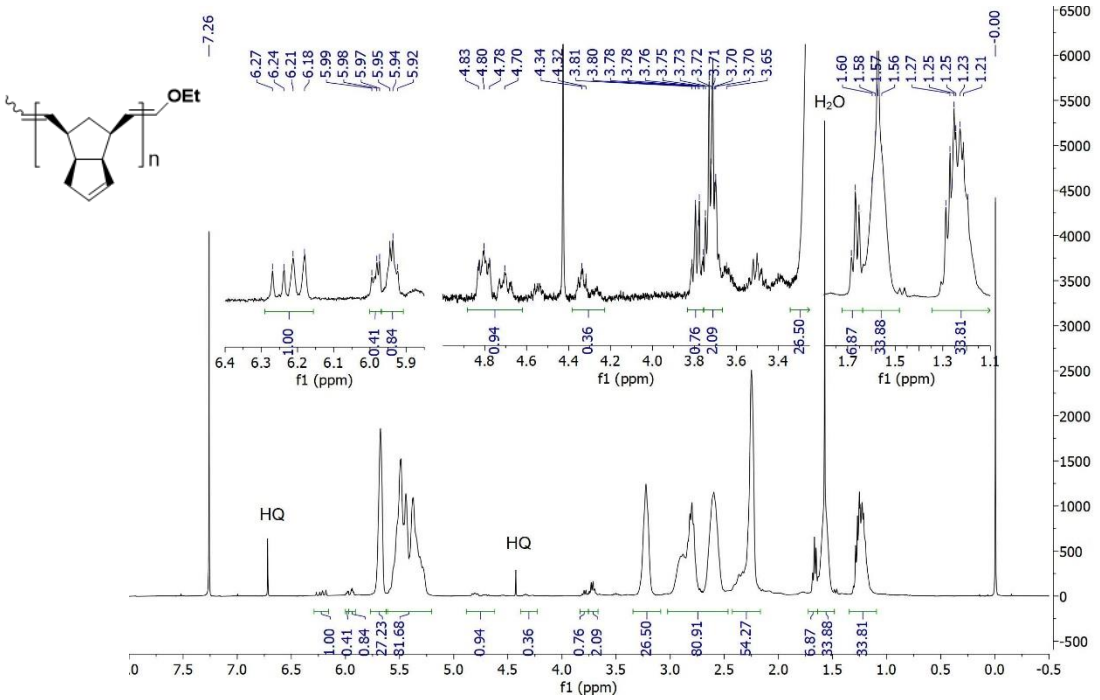

Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *endo*-DCPD oligomer (M_n = 2.30 kDa) with enol ether end group visible. Condition: [*endo*-**1**]$_o$:[**2**]$_o$ = 15:1, 3 °C (Table S3, entry 6).

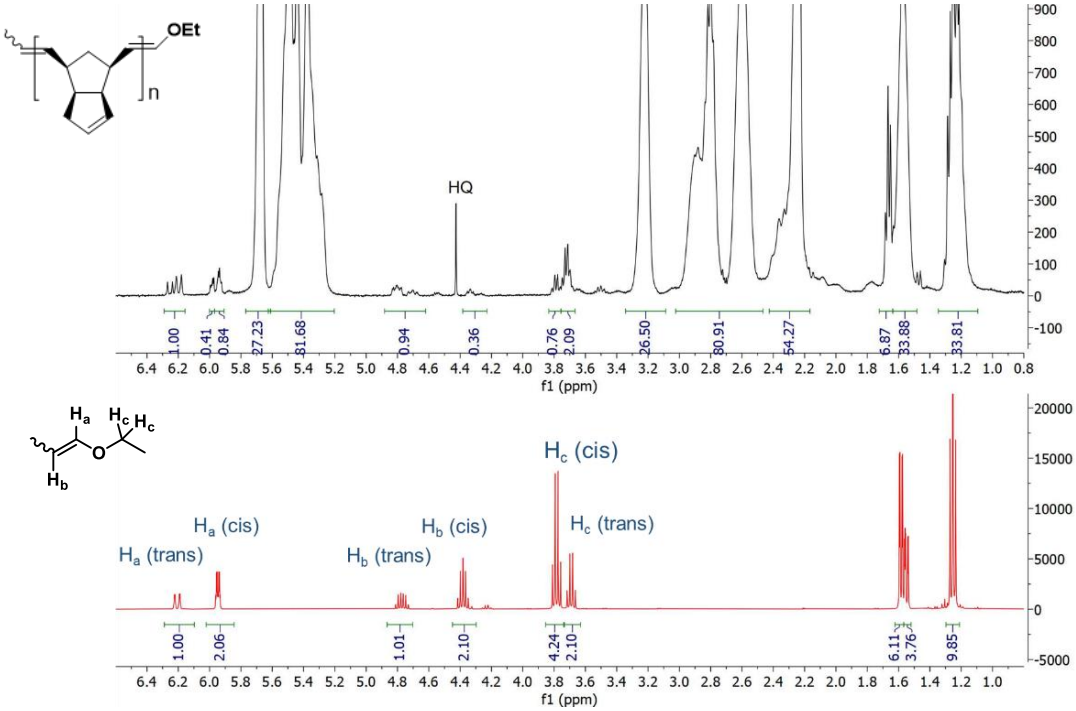

Figure S14. Comparison of ^{1}H NMR spectra of *endo*-DCPD oligomer (M_n = 2.30 kDa, top, black) end group with ethyl-1-propenyl ether (**2**) (bottom, red). Initiator **2** exists as a mixture of *cis*:*trans* (ca. 2:1). The end group of the oligomer shows multiple *cis* and *trans* enol ether species, which cannot be fully assigned. The multiplet at δ = 1.67 ppm may come from impurities.

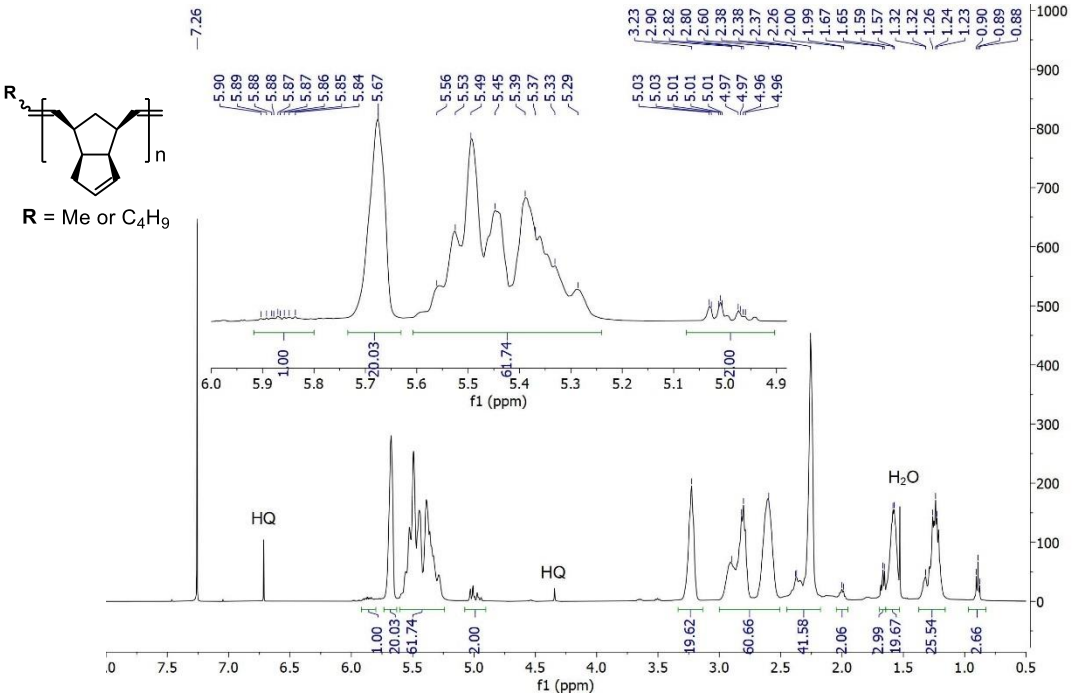

Figure S15. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *endo*-DCPD oligomer (M_n = 2.11 kDa) prepared by chain transfer with end group visible. Condition: [*endo*-**1**]$_o$:[**6**]$_o$:[**2**]$_o$ = 25:12.5:1, 3 °C (Table S1, entry 2).

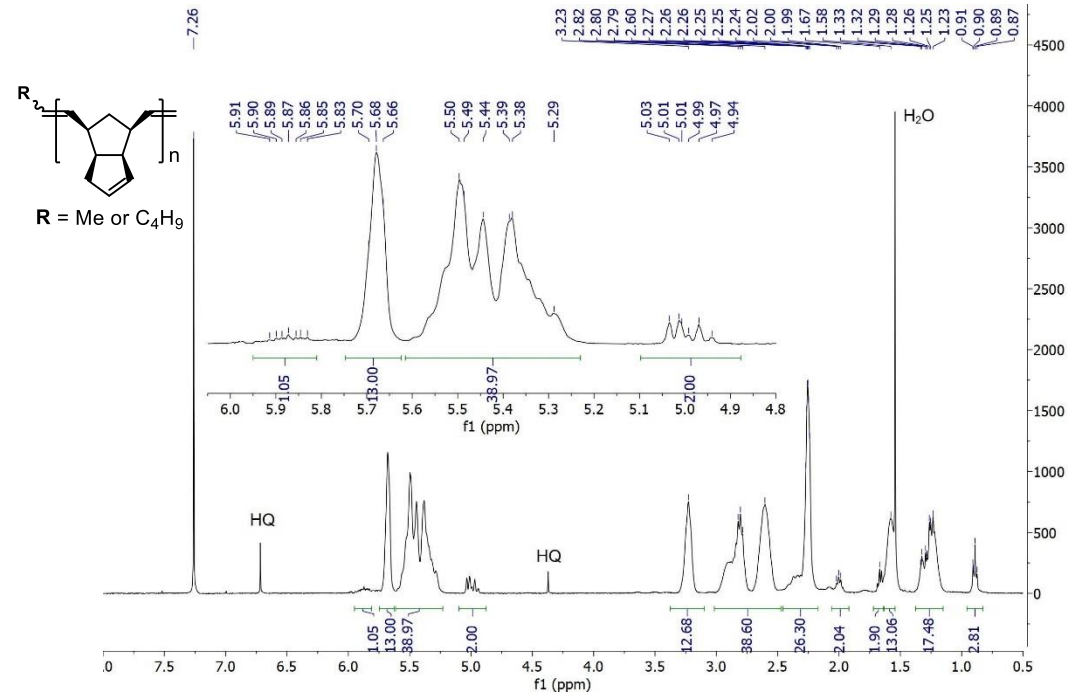

Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *endo*-DCPD oligomer (M_n = 1.52 kDa) prepared by chain transfer with end group visible. Condition: [*endo*-**1**]$_o$:[**6**]$_o$:[**2**]$_o$ = 25:25:1, 3 °C (Table S1, entry 3).

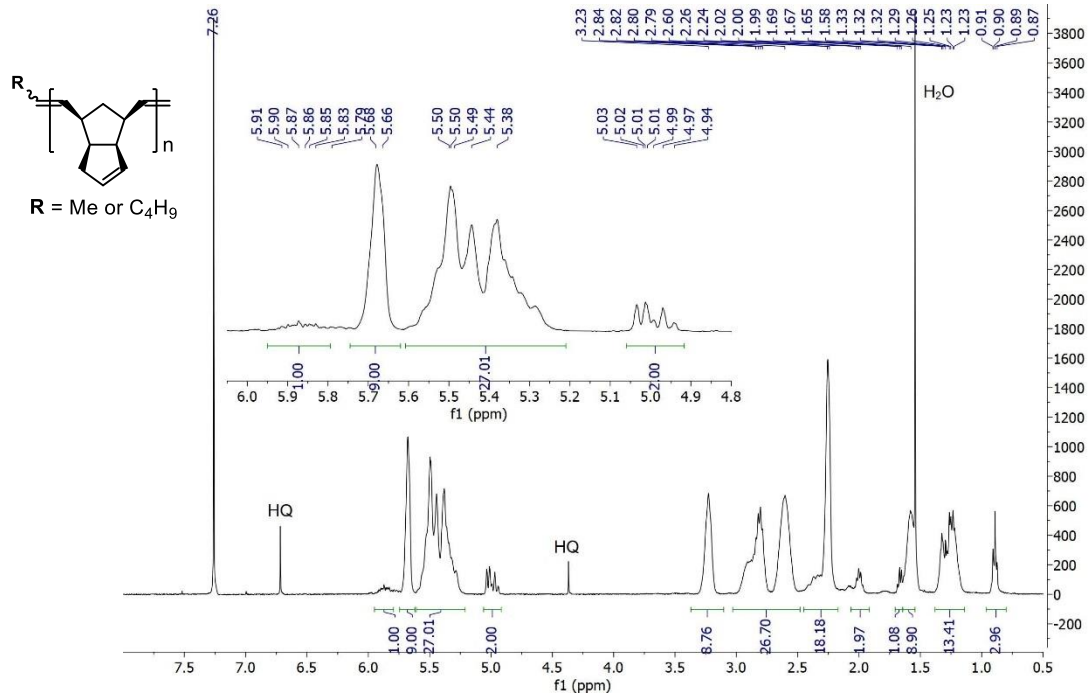

Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *endo*-DCPD oligomer (M_n = 1.25 kDa) prepared by chain transfer with end group visible. Condition: [*endo*-**1**]$_o$:[**6**]$_o$:[**2**]$_o$ = 25:50:1, 3 °C (Table S1, entry 4).

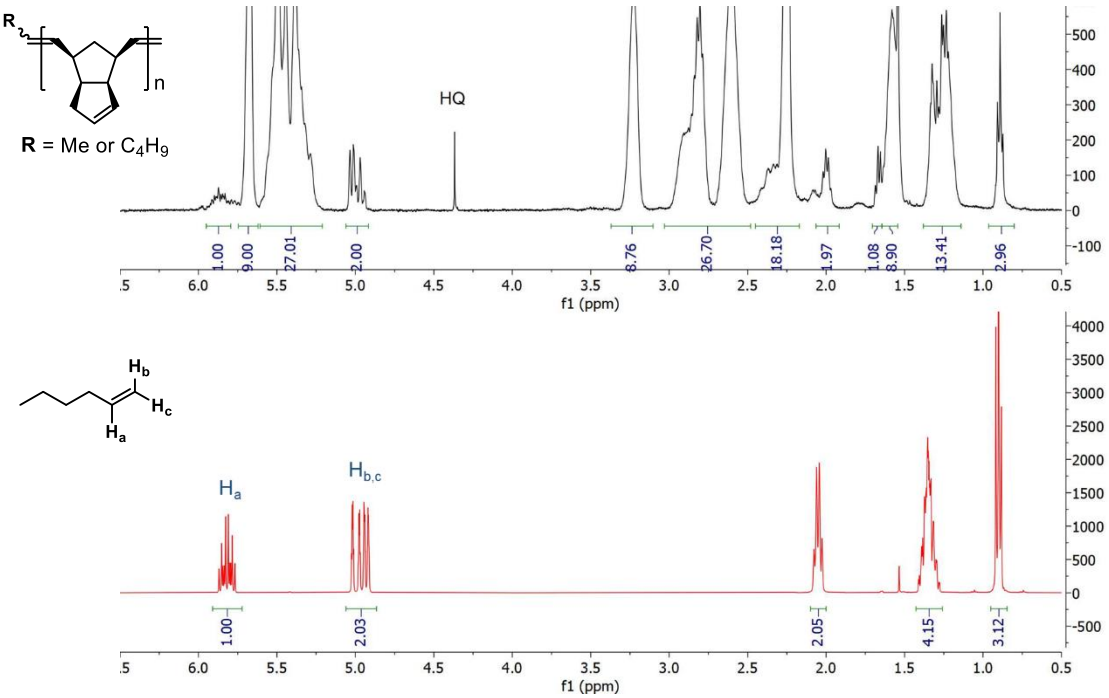

Figure S18. Comparison of ^{1}H NMR spectra of *endo*-DCPD oligomer (M_n = 1.25 kDa, top, black) end group with 1-hexene (**6**) (bottom, red). The multiplet at δ = 1.67 ppm may come from impurities.

8. References

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