

Supplementary Information

Solution [2 + 2] photopolymerization of biomass-derived nonrigid biscinnamate monomers enabled by energy transfer catalysis

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1. General Methods

Unless stated otherwise, all polymerization were carried out under an atmosphere of argon using standard Schlenk techniques. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. Chromatographic purification of monomers was accomplished by flash chromatography on silica gel. The monomers spots on the thin layer chromatography (TLC) was identified/visualized by fluorescence quenching or potassium permanganate stains. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz and 100 MHz) or a Bruker Avance 500 (500 MHz and 126 MHz) instrument at 298 K, and are internally referenced to solvent residual signals (note: CDCl_3 referenced at 7.26 and 77.16 ppm respectively). Data for ^1H NMR were reported as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in ppm with the internal chloroform signal at 77.16 ppm as a standard. GPC analysis of crude samples were carried out on a Waters 1515 gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive-index detector, using a Styragel HR 3 THF (7.8 \times 300 mm) column and a HR 4 THF(7.8 \times 300 mm) column with measurable molecular weights ranging from 10^2 to 10^6 $\text{g}\cdot\text{mol}^{-1}$. HPLC grade THF was as eluent at a flow rate of 1.0mL/min at 35 $^\circ\text{C}$ and samples were injected manually. The system was calibrated with Shodex Polystyrene standards. Analysis of isolated polymer molecular weights was performed via gel permeation chromatography (GPC) coupled with multi-angle laser light scattering (MALLS), using an Agilent HPLC and two Shodex GPC KD-806M gel permeation columns (8.0 mm ID \times 300 mm L), a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology DAWN EOS multi-angle light scattering detector, using THF as the eluent at a flow rate of 1.0 mL/min. GC measurements were performed on a GCMS-QP2010SE from SHIMADZU. UV/Vis/NIR spectra were recorded on a perkins Elmer Lambda 900 spectrometer equipped with a PTP-1 Peltier temperature controller and steady-state emission spectra were acquired using

Edinburgh Instruments, FLS920 spectrometer. IR spectra were determined in the range 4000-500 cm^{-1} on a Nicolet IS50 Fourier transform infrared (FT/IR) spectrometer. Decomposition onset temperatures (T_d) and maximum decomposition temperatures (T_{max}) of precipitated and dried polymer samples were measured by thermal gravimetric analysis (TGA) on a TA Instruments Q500 Thermogravimetric Analyzer. Polymer samples were heated from ambient temperatures to 600 °C at a heating rate of 10 °C/min. Values of T_d (temperature at 5% weight loss) were obtained from wt % vs. temperature (°C) plots, and values of T_{max} were obtained from plots of derivative (wt %/°C) vs. temperature (°C). Glass-transition temperature (T_g) of precipitated and dried polymer samples were measured using differential scanning calorimetry (DSC) on a TA Instruments Q2000. Heat flow were obtained from the second heating scan after the thermal history was removed. All heating and cooling rates were 10 °C/min. Tensile stress and strain of polymer films were measured to the point of break at room temperature using an extension speed of 20.0 mm/min on a Drick instruments DRK 101D. Measurements were repeated for at least 3 specimens and the values reported are averaged from the measured data.

2. General Polymerization Procedures

General Polymerization Procedure for catalyst screen

A 5 mL Shclenk tube equipped with a magnetic stir bar was charged with 0.25 mmol monomers, 1 mol % photocatalyst and 0.5 mL DMF. This system was deoxygenated by five freeze-pump-thaw cycles. The reaction mixture was irradiated with blue light emitting diode (LED, $\lambda_{\text{max}} = 465 \text{ nm}$) reactor at room temperature for 300 min. To analyze the progress of a polymerization at a given time point (60 min and 300 min), one (about 0.02 mL) and two drop of reaction solution were removed in glove box for GPC analysis and ^1H NMR spectra analysis respectively.

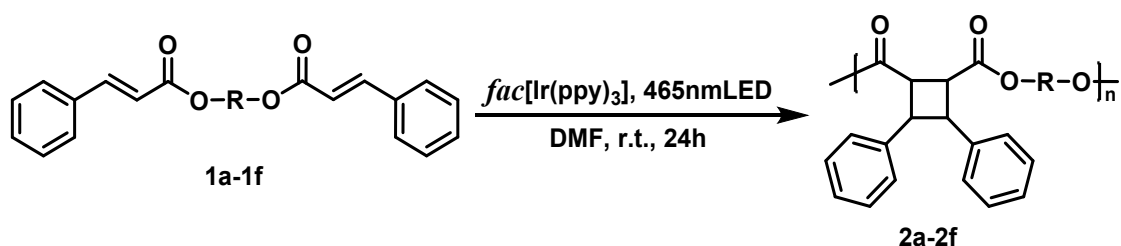
General Polymerization Procedure for monomer concentration and photocatalyst content screen

A 5 mL Schlenk tube equipped with a magnetic stir bar was charged with 0.25-0.1 mmol monomers, 0.01-1 mol % photocatalyst and 0.5 mL DMF. This system was deoxygenated by five freeze-pump-thaw cycles. The reaction mixture was irradiated with blue light emitting diode (LED, $\lambda_{\text{max}} = 465$ nm) reactor at room temperature for 270 min. To analyze the progress of a polymerization at a given time point, one (about 0.02mL) and two drop of reaction solution were removed in glove box for GPC analysis and ^1H NMR spectra analysis respectively.

General Polymerization Procedure for Kinetics

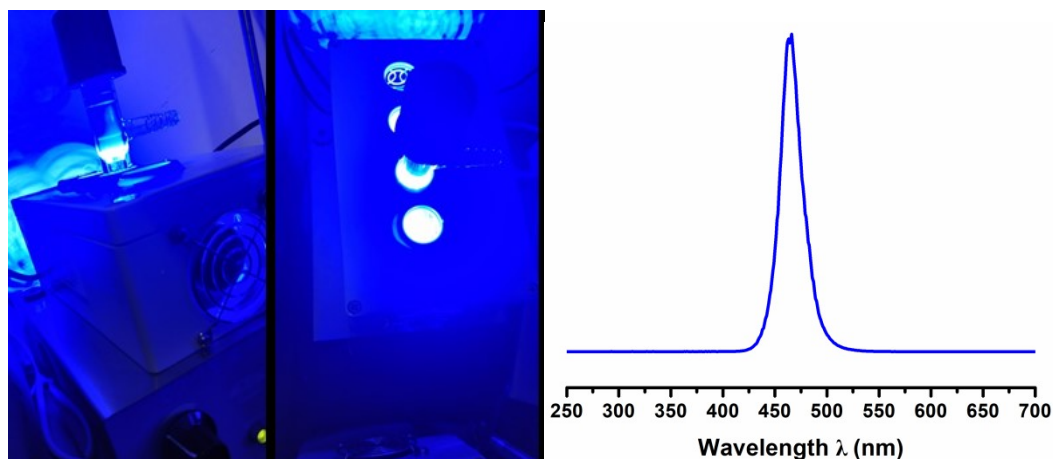
A 5 mL Schlenk tube equipped with a magnetic stir bar was charged with 1.5 mmol monomers, 0.01-1 mol% photocatalyst and 1.0 mL DMF. This system was deoxygenated by five freeze-pump-thaw cycles. The reaction mixture was irradiated with blue light emitting diode (LED, $\lambda_{\text{max}} = 465$ nm) reactor at room temperature for 72 h. To analyze the progress of a polymerization at a given time point, one (about 0.02mL) and two drop of reaction solution were removed in glove box for GPC analysis and ^1H NMR spectra analysis respectively.

General Polymerization Procedure for Substrate Scope Study and Solvent Screen

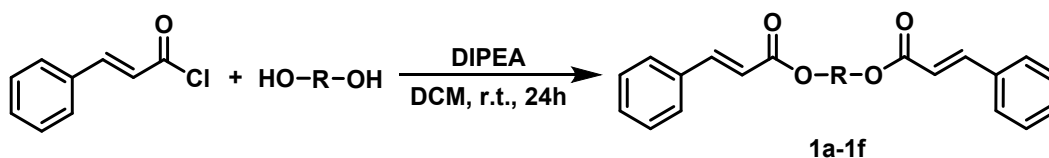


A 5 mL Schlenk tube equipped with a magnetic stir bar was charged with 0.1 or 0.3 mmol monomers, 1 mol % photocatalyst and 0.2 mL DMF or other solvent. This system was deoxygenated by five freeze-pump-thaw cycles. The reaction mixture was irradiated with blue light emitting diode (LED, $\lambda_{\text{max}} = 465$ nm) reactor at room temperature for 24 h. The reaction mixtures were added directly to 50 mL methanol at ambient temperature to precipitate the polymers (2a-2f).

Reaction Setup: Reactions were conducted in an 18 W photo-reactor (Model: H106062, GeAo chemical, Wuhan, China) as shown below. One place/hole with three 3W blue LED beads ($\lambda_{\text{max}} = 465 \text{ nm}$) on both side, and the distance between the Schlenk tube and LED beads is ca. 2 cm. The light intensity is 66.6 mW/cm^2 .



3. Preparation of Dicinnamates Monomers



General procedure for the preparation monomer 1a-1f

Excessive cinnamoyl chloride (3.65 g, 22 mmol) were dissolved in 10 mL CH_2Cl_2 , and then added dropwise to a solution of diol (10 mmol) and *N,N*-diisopropylethylamine (DIPEA) (2.84 g, 22 mmol) in 15 mL CH_2Cl_2 . The reaction mixture was continuously stirred at room temperature for 24h. The resulting solution was washed with dilute hydrochloric acid and water, dried with anhydrous magnesium sulfate. The white crystals was obtained by column chromatography on silica gel and following recrystallization from ethanol.

Ethylene dicinnamate (1a) was prepared following the general procedure for the preparation of monomers, and the used diol is ethylene glycol (0.62g, 10mmol).

Purification via flash chromatography (silica gel and eluting with dichloromethane/petroleum ether = 1:3→2:1; R_f = 0.25 at dichloromethane/petroleum ether = 2:1) and recrystallization from ethanol yielded **1a** as a white crystalline solid (yield = 72%): ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 16.0 Hz, 2H), 7.55-7.52 (m, 4H), 7.40-7.38 (m, 6H), 6.49 (d, J = 16.0 Hz, 2H), 4.50 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.86, 145.61, 134.44, 130.57, 129.05, 128.31, 117.70, 62.53;

Isopropylene dicinnamate (1b) was prepared following the general procedure for the preparation of monomers, and the used diol is isopropylene glycol (0.76g, 10mmol). Purification via flash chromatography (silica gel and eluting with dichloromethane/petroleum ether = 1:3→2:1; R_f = 0.32 at dichloromethane/petroleum ether = 2:1) and recrystallization from ethanol yielded **1b** as a white solid (yield = 68%): ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 16.0Hz, 2H), 7.54-7.51 (m, 4H), 7.39-7.37 (m, 6H), 6.46 (d, J = 16.0 Hz, 2H), 5.38-5.35 (m, 1H), 4.38-4.30 (m, 2H), 1.39 (d, J = 6.3Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.79, 166.46, 145.53, 145.27, 134.52, 134.45, 130.53, 130.47, 129.02, 128.30, 128.27, 118.24, 117.73, 68.64, 66.40, 16.82;

Pentylene dicinnamate (1c) was prepared following the general procedure for the preparation of monomers, and the used diol pentylene glycol (1.04g, 10mmol). Purification via flash chromatography (silica gel and eluting with dichloromethane/petroleum ether = 1:3→2:1; R_f = 0.28 at dichloromethane/petroleum ether = 2:1) and recrystallization from ethanol yielded **1c** as a white solid (yield = 71%): ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 16.0 Hz, 2H), 7.53-7.51 (m, 4H), 7.38-7.36 (m, 6H), 6.44 (d, J = 16.0 Hz, 2H), 4.24 (t, J = 6.3Hz, 4H), 1.82-1.75 (m, 4H), 1.57-1.51(m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.17, 144.87, 134.58, 130.39, 129.02, 128.21, 118.30, 64.48, 28.56, 22.76;

Hexylene dicinnamate (1d) was prepared following the general procedure for the preparation of monomers, and the used diol is hexylene glycol (1.18g, 10mmol). Purification via flash chromatography (silica gel and eluting with dicholomethane/petroleum ether = 1:3→2:1; R_f = 0.3 at dicholomethane/petroleum ether = 2:1) and recrystallization from ethanol yielded 1f as a white crystalline solid (73%): ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 16.0 Hz, 2H), 7.53-7.50 (m, 4H), 7.38-7.36 (m, 6H), 6.44 (d, J = 16.0 Hz, 2H), 4.22 (t, J = 6.4Hz, 4H), 1.77-1.71 (m, 4H), 1.50-1.46 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.10, 144.72, 134.53, 130.30, 128.94, 128.14, 118.30, 64.55, 28.74, 25.79;

1,4-Butendiol dicinnamate (1e) was prepared following the general procedure for the preparation of monomers, and the used diol is 1,4-butendiol (0.88g, 10mmol). Purification via flash chromatography (silica gel and eluting with dicholomethane/petroleum ether = 1:3→2:1; R_f = 0.29 at dicholomethane/petroleum ether = 2:1) and recrystallization from ethanol yielded 1g as a white solid (yield = 66%): ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 16.0 Hz, 2H), 7.54-7.51 (m, 4H), 7.39-7.37 (m, 6H), 6.45 (d, J = 16.0 Hz, 2H), 6.00-5.85 (m, 2H), 4.91-4.76 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.77, 145.39, 134.48, 130.51, 129.04, 128.26, 117.85, 60.29;

1,4-Benzenedimethanol dicinnamate (1f) was prepared following the general procedure for the preparation of monomers, and the used diol is 1,4-benzenedimethanol (1.38g, 10mmol). Purification via flash chromatography (silica gel and eluting with dicholomethane/petroleum ether = 1:3→2:1; R_f = 0.34 at dicholomethane/petroleum ether = 2:1) and recrystallization from ethanol yielded 1j as a white crystalline solid (yield = 73%): ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 16.0 Hz, 2H), 7.54-7.51 (m, 4H), 7.44 (s, 4H), 7.40-7.37 (m, 6H), 6.49 (d, J = 16.0 Hz, 2H), 5.26 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.87, 145.43, 136.32, 134.48, 130.52, 129.05, 128.66, 128.26, 117.94, 66.13;

4. General Dimerization Procedures of Ethyl Cinnamates

A 5 mL Shlenk tube equipped with a magnetic stir bar was charged with 0.25 mmol (44.5 mg) ethyl cinnamates, 1 mol % (5.0 mg) photocatalyst *fac*-[Ir(ppy)₃] and 0.5 mL DMF. This system was deoxygenated by five freeze-pump-thaw cycles. The reaction mixture was irradiated with blue light emitting diode (LED, $\lambda_{\text{max}} = 465 \text{ nm}$) reactor at room temperature for 24 h. Then the reaction mixture was saturated with brine (5 mL) and extracted with ethyl acetate (3 x 10 mL). After drying the combined organic layers on Na₂SO₄, the resulting solution was concentrated in vacuo. Purification by a short silica-gel column using hexanes and ethyl acetate as eluents afforded cycloaddition product.

5. General Calculating Method for Monomer Conversion

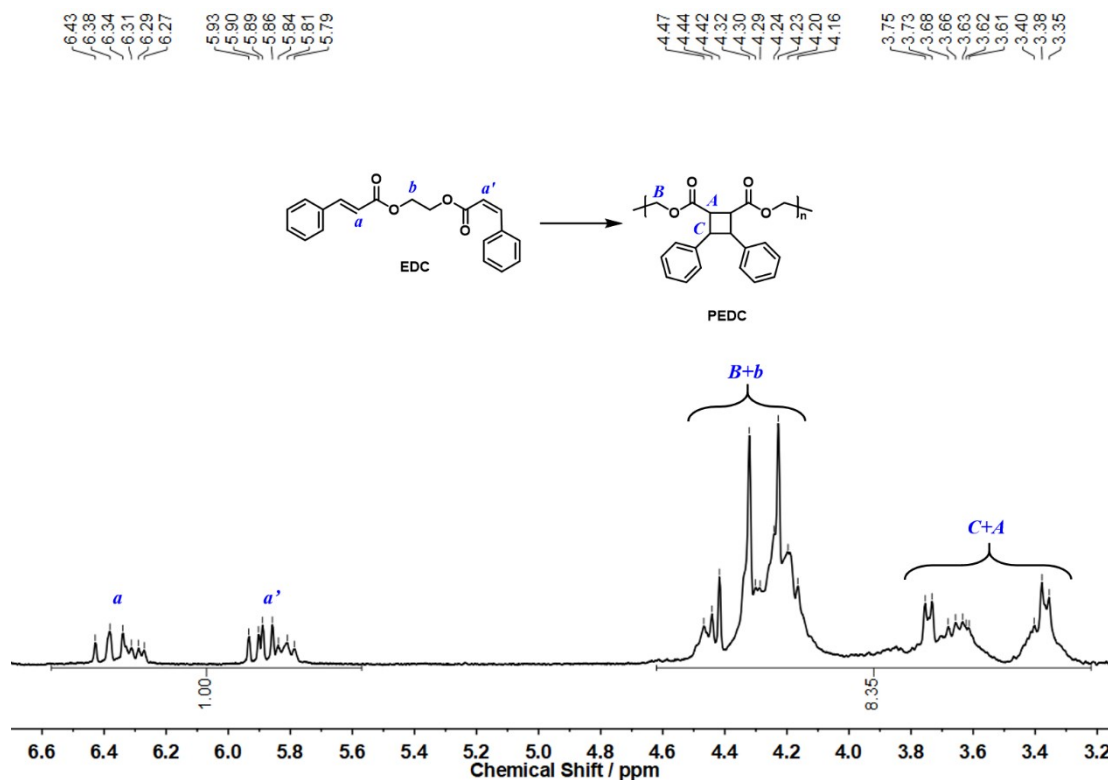


Figure S1 ^1H NMR spectra of EDC polymerization catalyzed by 1% *fac*[Ir(ppy) $_3$]
(0.5M, 300 min)

$C+A$

$$\begin{aligned} &= \frac{(C + A) + (B + b) - b}{2} = \frac{(C + A) + (B + b) - 2(a + a')}{2} = \frac{8.35 - 2 * 1}{2} = 3.175 \\ \text{Conv.} &= \frac{C + A}{C + A + 2(a + a')} = \frac{3.175}{3.175 + 2} = 61\% \end{aligned}$$

The letters represent the integration in the ^1H NMR spectrum. The conversion percentage mentioned in this paper all calculated from this method.

6. Monomer Concentration and Catalyst Dosage Screen

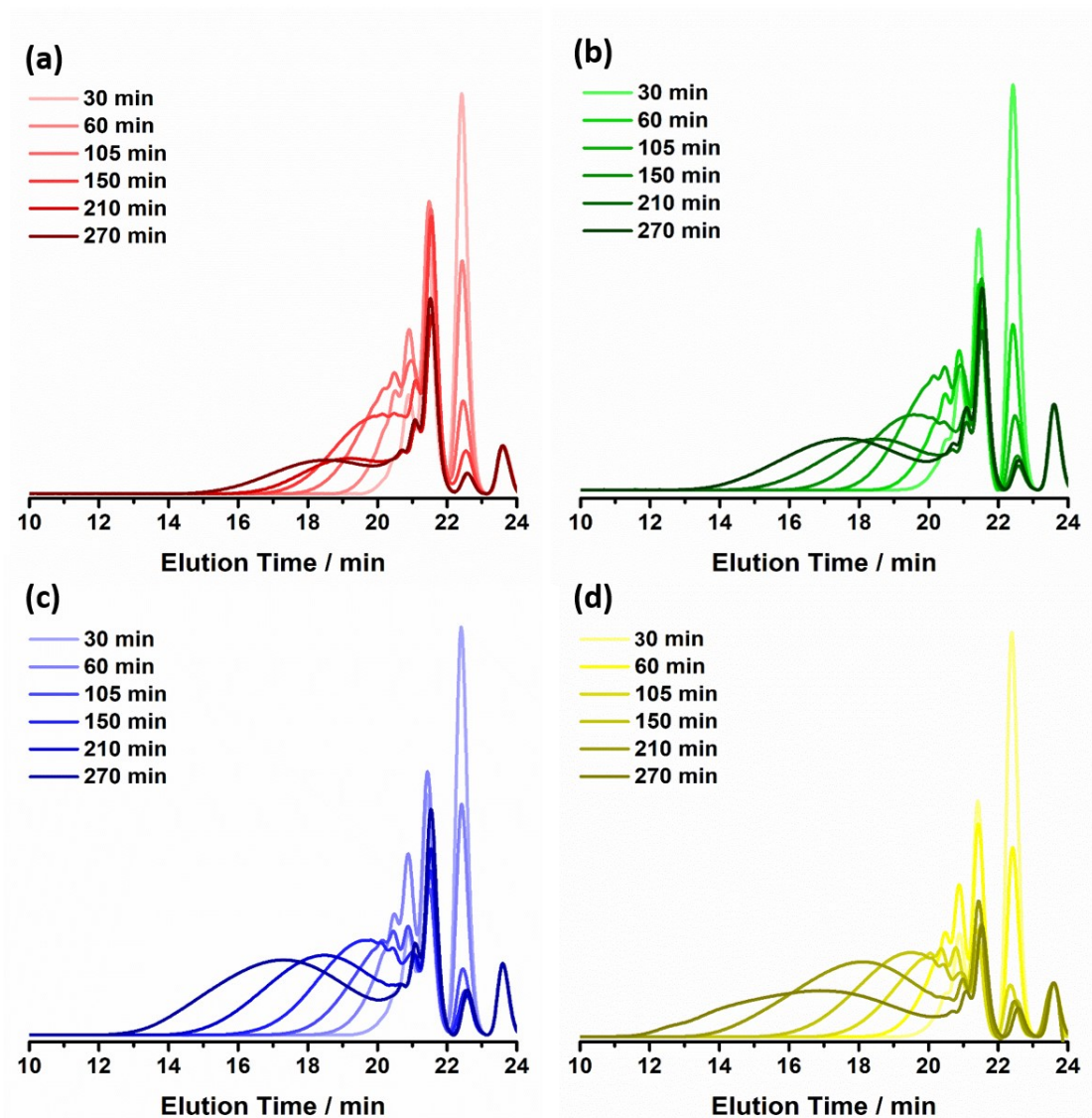


Figure S2 Overlaying GPC traces of crude aliquots that were taken at different time intervals (from 30-270 min) in different monomer concentration, (a) 0.5M, (b) 1.0M, (c) 1.5M, (d) 2.0M.

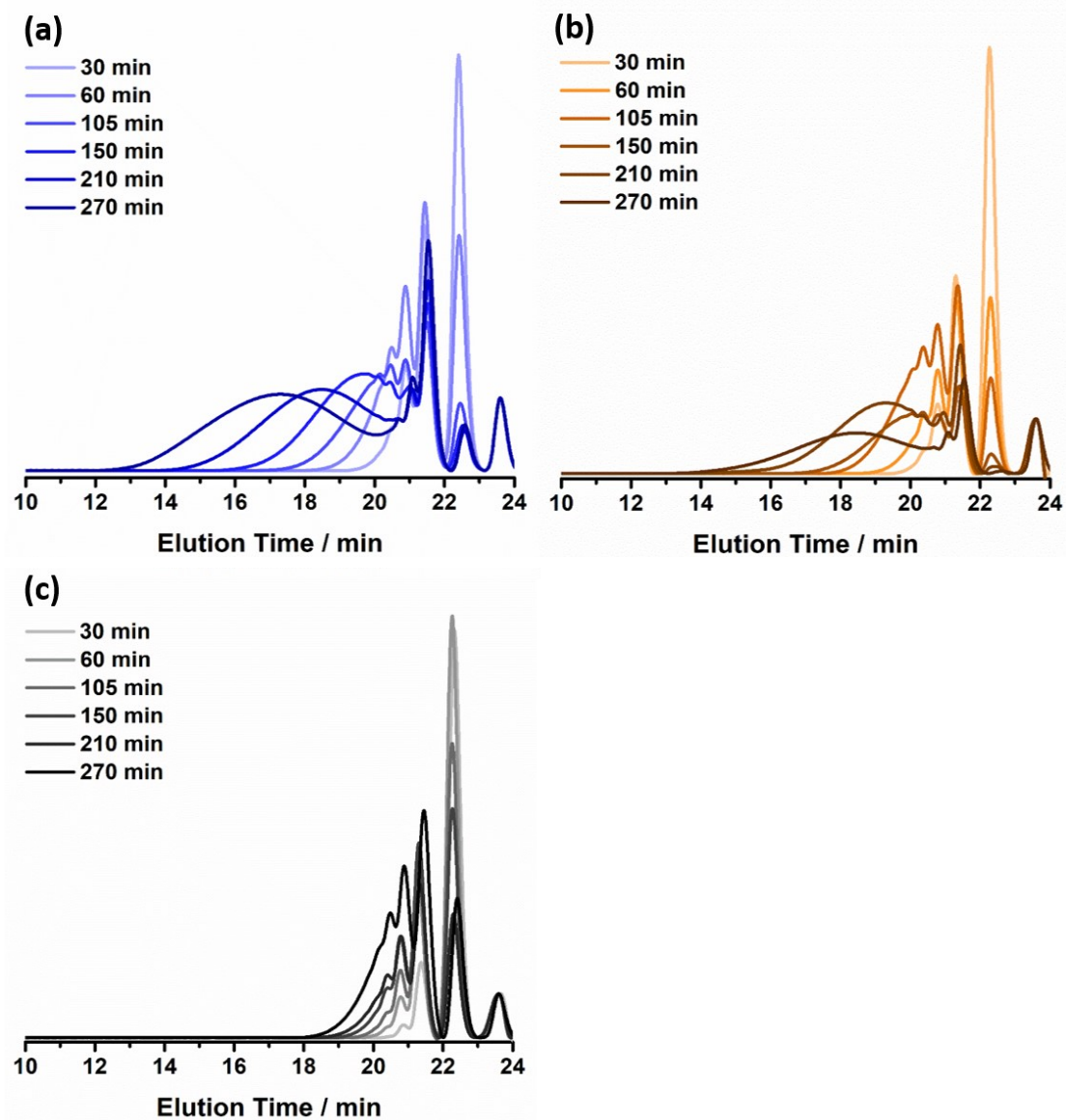


Figure S3 Overlaying GPC traces of crude aliquots that were taken at different time intervals (from 30-270 min) in different catalyst dosage, (a) 1 mol %, (b) 0.1 mol %, (c) 0.01 mol %.

7. Polymerization Solvent Screen

Solvent	Yield(%) ^a	M_w (kDa) ^b	M_n (kDa) ^b	M_w/M_n ^b
DMF	71.6	31.8	9.6	3.29
DMA	55.3	23.9	7.1	3.38
Toluene	66.7	18.9	6.9	2.72
DCM	43.7	28.5	8.9	3.20
THF	65.8	25.7	8.1	3.17
1,4-Dioxane	65.0	21.8	7.8	2.79
DMSO	56.0	24.6	7.4	3.35

[a] The yield of polymer is isolated yield. [b] The GPC data is determined through calibration column method (standard PS).

Table S1 Polymerization solvent screen

8. Dependence of Polymerization Result on Time

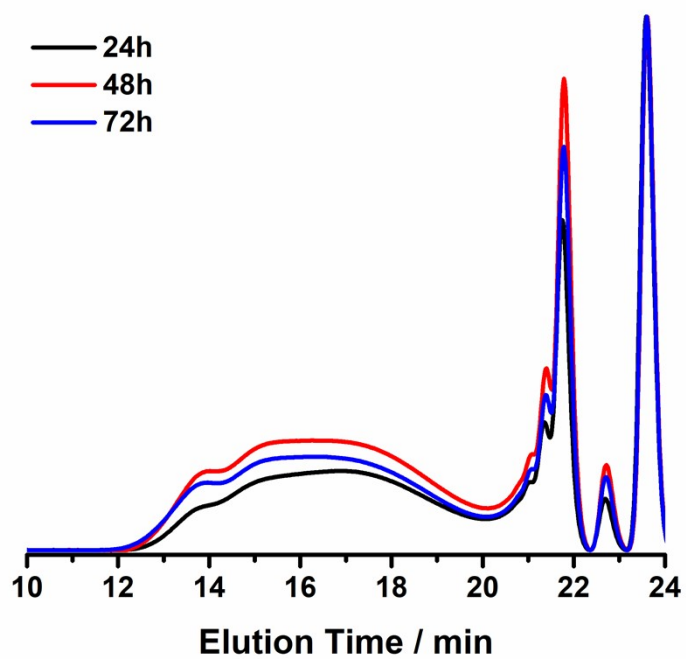


Figure S4 Overlaying GPC traces of prolonging polymerization time (crude sample)

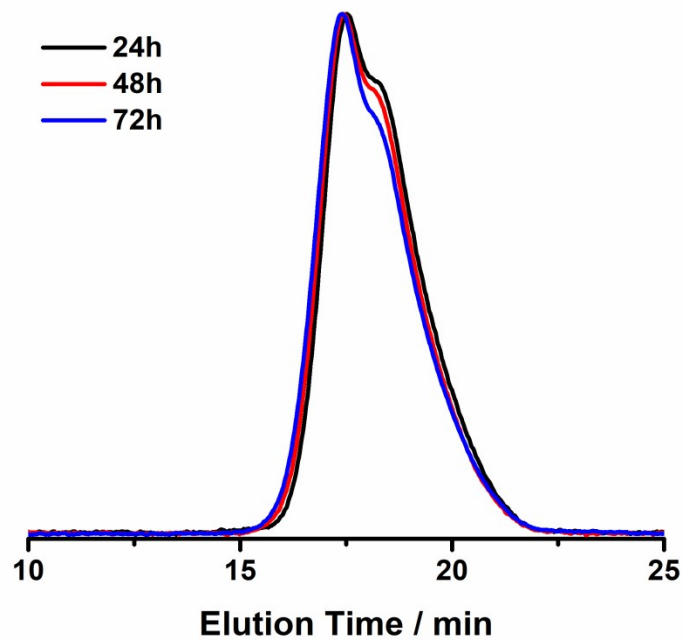


Figure S5 Overlaying MALS signal of prolonging polymerization time (isolated polymer, detector scattering angle: 90°)

9. GC-MS Spectra of Dimerization of Ethyl Cinnamates

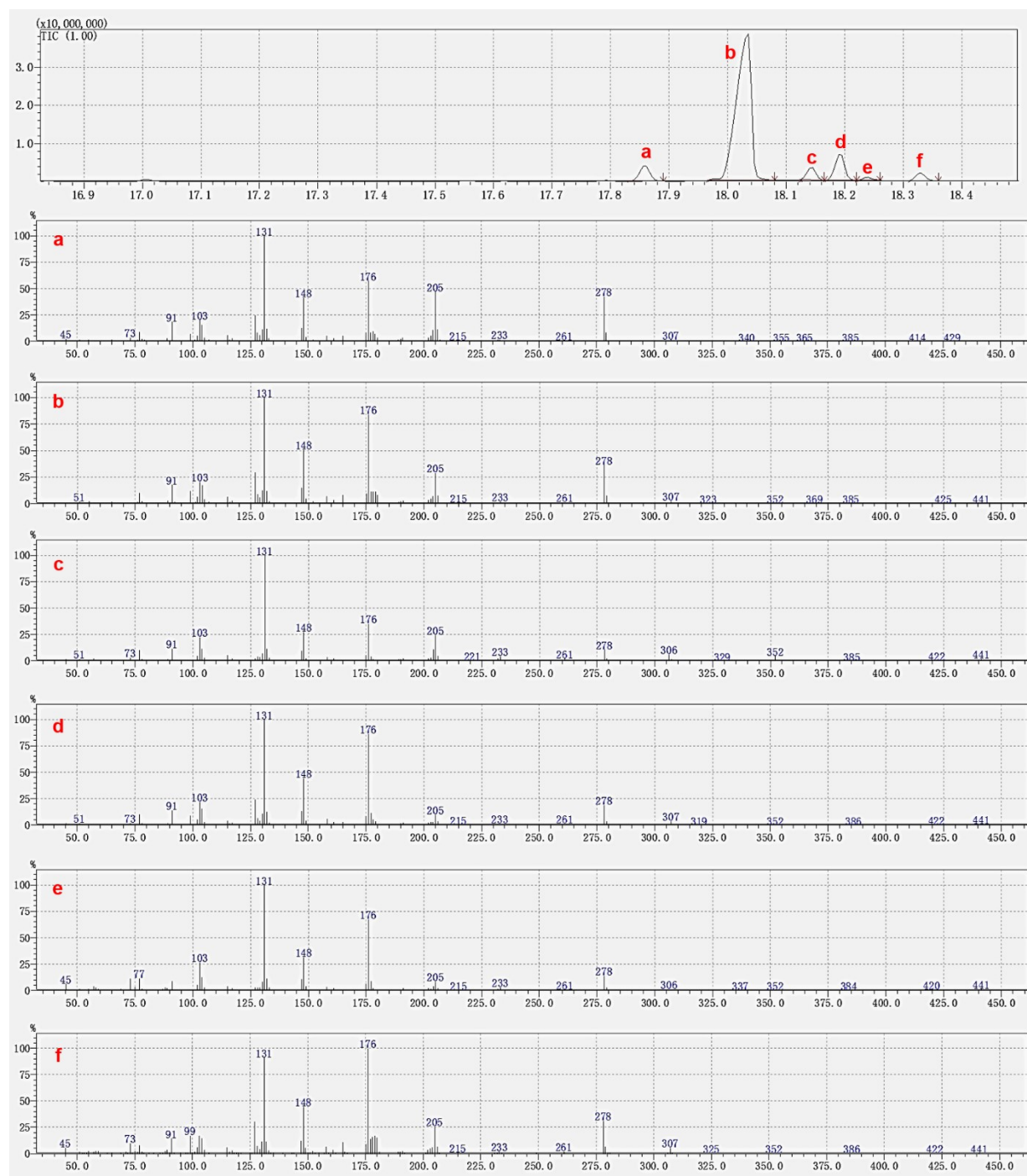


Figure S6 GC-MS spectra of dimerization of ethyl cinnamates and the fragment peak of six cyclobutane isomer

Peak	Retention time (min)	Peak Area	Content (%)
a	17.86	4912802	5.7
b	18.03	67440154	77.8
c	18.14	3392204	3.9
d	18.19	7788478	9.0
e	18.24	901912	1.0
f	18.33	2286275	2.6

Table S2 GC-MS spectra peak data

10. GPC Analysis Details

GPC was used to determine number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (M_w / M_n). Some polymer (solvent screen) was calibrated using narrow molecular weight polystyrene standards and isolated polymer was determined using multi-angle light scattering (Wyatt DAWN EOS) detector. Mobile phase was HPLC grade THF. MALS analysis reports are provided for the key polymer samples.

Multi-angle Light Scattering (MALS) GPC

The differential index of refraction (dn/dc) was determined using batch method by plotting the refractive index of the polymer solution versus varying solution concentrations. The sample PEDC (2a) was dissolved in HPLC grade THF, for dn/dc determination and subsequent MALS analysis was HPLC grade THF.¹

Entry	Concentration (mg/mL)	Differential Refractive Index (10^{-4})
1	0.411	0.576
2	1.028	1.45
3	2.056	3.56
4	3.084	5.55
5	4.111	6.83
6	6.167	10.7

Table S3 dn/dc calculation data of polymer for THF

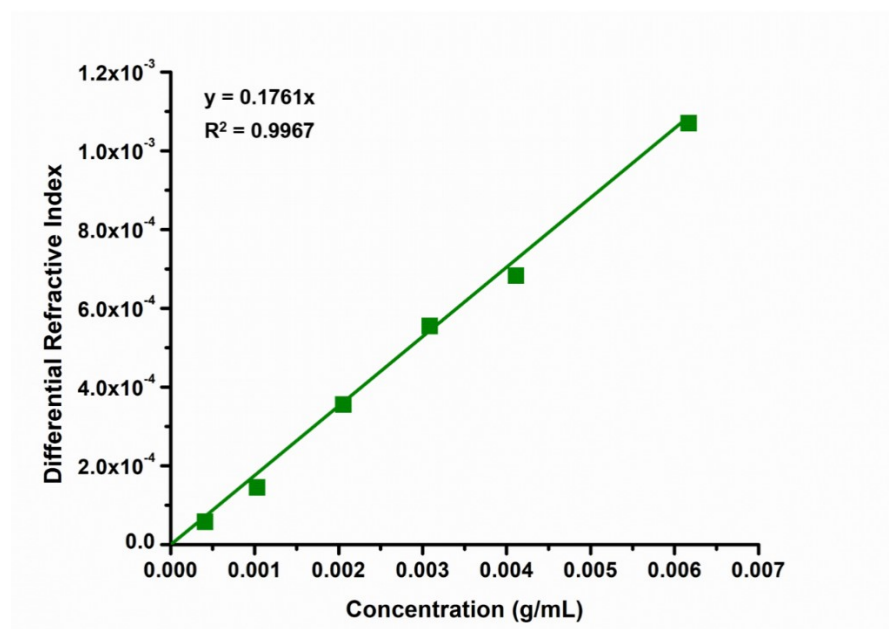


Figure S7 Polymer Concentration vs Differential Refractive Index plot to calculate dn/dc

Polymer	Yield(%)^a	M_w (kDa)	M_n (kDa)	M_w/M_n
PEDC (2a)	71.6	38.6	12.1	3.20
PIPDC (2b)	68.8	61.3	19.4	3.16
PPDC (2c)	50.3	14.7	6.7	2.19
PHDC (2d)	46.7	18.6	7.1	2.61
PBDC (2e)	67.9	60.5	22.5	2.69
PBMDC (2f)	58.2	25.3	13.8	1.84

[a] The yield of polymer is isolated yield.

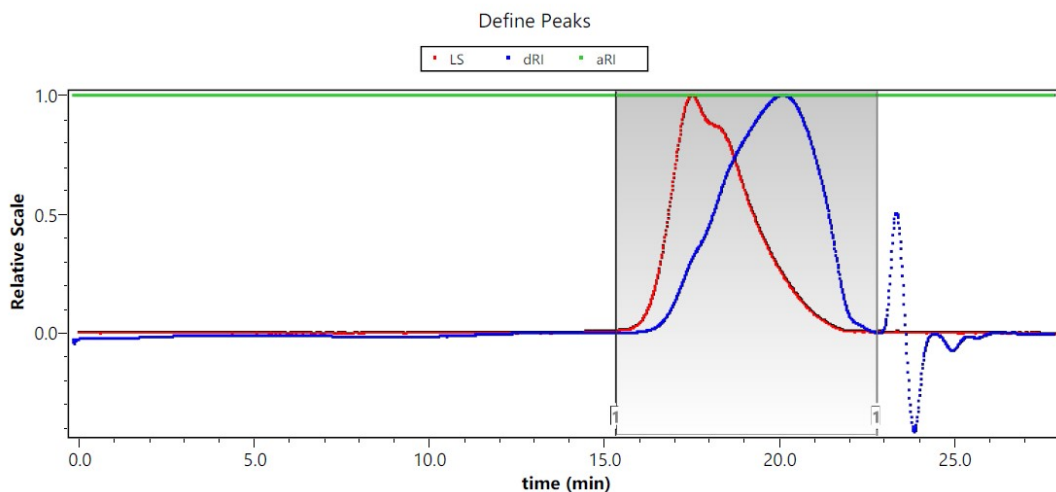
Table S4 The information of polymers from different monomers

GPC-MALS Analysis Reports

Polymer PEDC (2a)



Sample: E004



Configuration

Concentration Source: RI
Flow Rate: 1.000 mL/min

Light Scattering Instrument: DAWN EOS
Physical Instrument Name: DAWN EOS on COM3
Wavelength: 690.0 nm
Calibration Constant: 9.3437×10^{-6} 1/(V cm)

Detector	Refractive Index	Corrected Scattering Angle	Gain	Normalization Coefficient
1	n/a		101	1.000
2	16.9°		101	1.487
3	23.2°		101	1.162
4	31.4°		101	1.166
5	38.8°		101	1.349
6	45.8°		101	0.695
7	53.8°		101	0.812
8	61.6°		101	0.897
9	70.4°		101	1.119
10	80.2°		101	1.100
11	90.0°		101	1.000
12	99.8°		101	0.968
13	109.6°		101	0.933
14	119.5°		101	0.822
15	129.6°		101	0.868
16	138.8°		101	65.771
17	147.4°		101	1.383
18	155.4°		101	1.041

RI Instrument: rEX
Temperature: 35.0 °C
Physical Instrument Name: Optilab T-rEX
Calibration Constant: 3.4484×10^{-5} RIU/pixel

Solvent: thf
Temperature Correction Enabled: yes
Refractive Index: 1.401

Processing

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	15.350 - 22.816
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1761
A2 (mol mL/g ²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

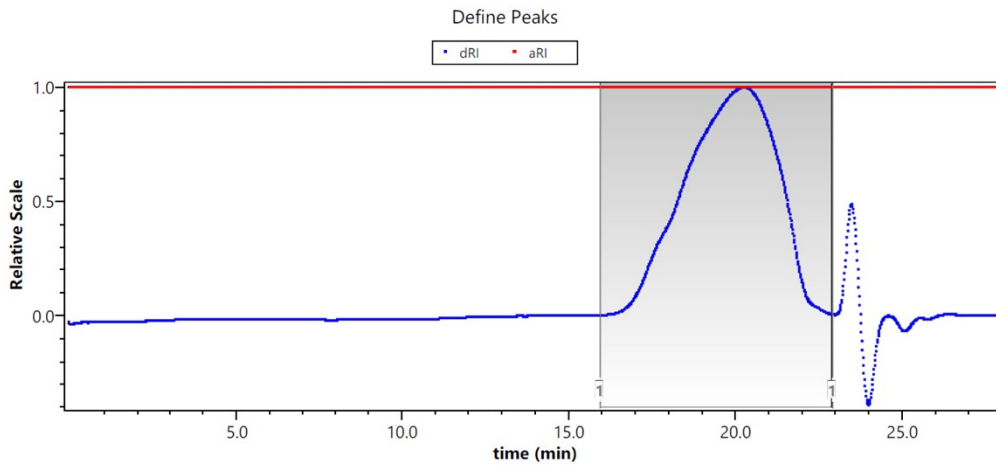
Results

Peak Results

	Peak 1
Masses	
Injected Mass (μg)	0.00
Calculated Mass (μg)	314.00
Mass Recovery (%)	n/a
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	1.382×10^4 ($\pm 3.562\%$)
Mp	1.472×10^4 ($\pm 0.729\%$)
Mv	n/a
Mw	4.726×10^4 ($\pm 0.551\%$)
Mz	1.428×10^5 ($\pm 1.127\%$)
Polydispersity	
Mw/Mn	3.419 ($\pm 3.605\%$)
Mz/Mn	10.328 ($\pm 3.736\%$)
rms radius moments (nm)	
rn	n/a
rw	6.9 ($\pm 148.8\%$)
rz	10.7 ($\pm 21.3\%$)

Polymer PEDC (2a, PS standard)

Sample: E004


Configuration

 Concentration Source: RI
 Flow Rate: 1.000 mL/min

RI Instrument: rEX

 Band Broadening Correction: Yes (Instrumental: 1.000 μ L, Mixing: 50.000 μ L)
 Wavelength: 658.0 nm

Column: column calibration file-PS-1019

Flow Marker: 24.029 mL

Mark-Houwink-Sakurada a: 0.000

Mark-Houwink-Sakurada K: 0.000 mL/g

Conventional Calibration Function Fit Standard Error: 0.0467658

Universal Calibration Function Fit Standard Error: 0

Calibration Technique: Conventional

 Conventional Calibration Function: $\log(\text{Molar Mass}) = 33.6631 - 3.99736 v + 0.20139 v^2 - 0.00376164 v^3$

Solvent: THF

Refractive Index: 1.397

Processing

Peak settings:

Peak	Peak Name	dn/dc	Viscometry Model	Huggins Equation Parameter	Kraemers Equation Parameter
1	Peak 1	0.1850	Huggins	0	0

Results

Peak Results

Peak 1

Molar mass moments (g/mol)

Mn	8.236×10^3	($\pm 11.369\%$)
Mp	1.119×10^4	($\pm 11.369\%$)
Mw	3.594×10^4	($\pm 11.369\%$)
Mz	1.089×10^5	($\pm 25.423\%$)
M(avg)	7.221×10^2	($\pm 1.174\%$)

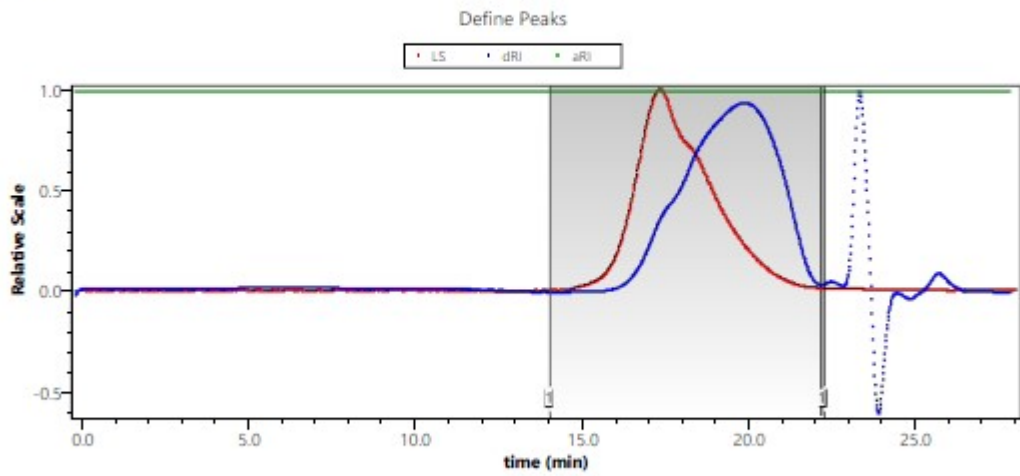
Polydispersity

Mw/Mn	4.364	($\pm 16.079\%$)
Mz/Mn	13.226	($\pm 27.849\%$)

Polymer PIPDC (2b)



Sample: F146



Configuration

Concentration Source: RI
 Flow Rate: 1.000 mL/min

Light Scattering Instrument: DAWN EOS
 Physical Instrument Name: DAWN EOS on COM3
 Wavelength: 690.0 nm
 Calibration Constant: 9.3437×10^{-6} 1/(V cm)

Detector	Refractive Index	Corrected Scattering Angle	Gain	Normalization Coefficient
1	n/a		101	1.000
2	16.9°		101	1.487
3	23.2°		101	1.162
4	31.4°		101	1.166
5	38.8°		101	1.349
6	45.8°		101	0.695
7	53.8°		101	0.812
8	61.6°		101	0.897
9	70.4°		101	1.119
10	80.2°		101	1.100
11	90.0°		101	1.000
12	99.8°		101	0.968
13	109.6°		101	0.933
14	119.5°		101	0.822
15	129.6°		101	0.868
16	138.8°		101	65.771
17	147.4°		101	1.383
18	155.4°		101	1.041

RI Instrument: rEX
 Temperature: 35.0 °C
 Physical Instrument Name: Optilab T-rEX
 Calibration Constant: 3.4484×10^{-5} RIU/pixel

Solvent: thf
 Temperature Correction Enabled: yes
 Refractive Index: 1.401

Processing

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	14.027 - 22.226
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1761
A2 (mol mL/g ²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

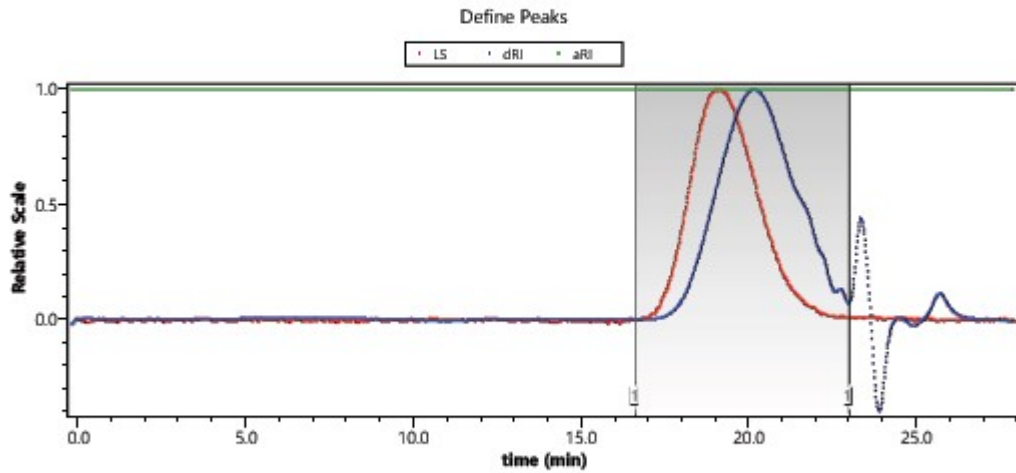
Results

Peak Results

	Peak 1
Masses	
Injected Mass (µg)	300.00
Calculated Mass (µg)	256.35
Mass Recovery (%)	85.5
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	1.940×10 ⁴ (±1.321%)
Mp	1.843×10 ⁴ (±0.450%)
Mv	n/a
Mw	6.132×10 ⁴ (±0.300%)
Mz	2.147×10 ⁵ (±0.883%)
Polydispersity	
Mw/Mn	3.161 (±1.355%)
Mz/Mn	11.069 (±1.589%)
rms radius moments (nm)	
rn	19.7 (±16.9%)
rw	15.7 (±14.7%)
rz	13.9 (±7.5%)

Polymer PPDC (2c)

Sample: F153



Configuration

Concentration Source: RI

Flow Rate: 1.000 mL/min

Light Scattering Instrument: DAWN EOS

Physical Instrument Name: DAWN EOS on COM3

Wavelength: 690.0 nm

Calibration Constant: 9.3437×10^{-6} 1/(V cm)

Detector	Refractive Index	Corrected Scattering Angle	Gain	Normalization Coefficient
1	n/a		101	1.000
2	16.9°		101	1.487
3	23.2°		101	1.162
4	31.4°		101	1.166
5	38.8°		101	1.349
6	45.8°		101	0.695
7	53.8°		101	0.812
8	61.6°		101	0.897
9	70.4°		101	1.119
10	80.2°		101	1.100
11	90.0°		101	1.000
12	99.8°		101	0.968
13	109.6°		101	0.933
14	119.5°		101	0.822
15	129.6°		101	0.868
16	138.8°		101	65.771
17	147.4°		101	1.383
18	155.4°		101	1.041

RI Instrument: rEX

Temperature: 35.0 °C

Physical Instrument Name: Optilab T-rEX

Calibration Constant: 3.4484×10^{-5} RIU/pixel

Solvent: thf

Temperature Correction Enabled: yes

Refractive Index: 1.401

Processing

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	16.636 - 22.977
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1761
A2 (mol mL/g ²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results

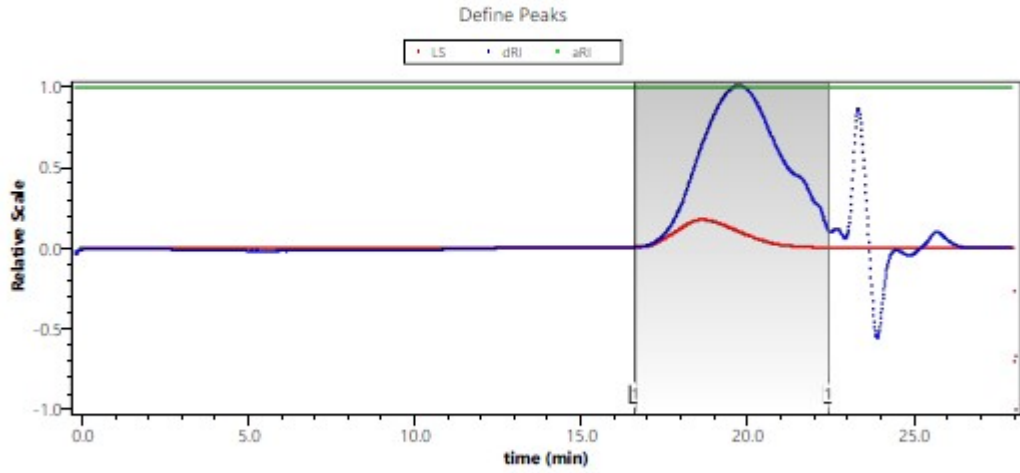
Peak Results

	Peak 1
Masses	
Injected Mass (µg)	300.00
Calculated Mass (µg)	260.77
Mass Recovery (%)	86.9
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	6.739×10 ³ (±5.378%)
Mp	1.096×10 ⁴ (±0.639%)
Mv	n/a
Mw	1.472×10 ⁴ (±1.124%)
Mz	3.075×10 ⁴ (±3.943%)
Polydispersity	
Mw/Mn	2.185 (±5.495%)
Mz/Mn	4.563 (±6.669%)
rms radius moments (nm)	
rn	n/a
rw	n/a
rz	5.5 (±163.7%)

Polymer PHDC (2d)



Sample: F148



Configuration

Concentration Source: RI
 Flow Rate: 1.000 mL/min

Light Scattering Instrument: DAWN EOS
 Physical Instrument Name: DAWN EOS on COM3
 Wavelength: 690.0 nm
 Calibration Constant: 9.3437×10^{-6} 1/(V cm)

Detector	Refractive Index	Corrected Scattering Angle	Gain	Normalization Coefficient
1	n/a		101	1.000
2	16.9°		101	1.487
3	23.2°		101	1.162
4	31.4°		101	1.166
5	38.8°		101	1.349
6	45.8°		101	0.695
7	53.8°		101	0.812
8	61.6°		101	0.897
9	70.4°		101	1.119
10	80.2°		101	1.100
11	90.0°		101	1.000
12	99.8°		101	0.968
13	109.6°		101	0.933
14	119.5°		101	0.822
15	129.6°		101	0.868
16	138.8°		101	65.771
17	147.4°		101	1.383
18	155.4°		101	1.041

RI Instrument: rEX
 Temperature: 35.0 °C
 Physical Instrument Name: Optilab T-rEX
 Calibration Constant: 3.4484×10^{-5} RIU/pixel

Solvent: thf
 Temperature Correction Enabled: yes
 Refractive Index: 1.401

Processing

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	16.635 - 22.460
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1761
A2 (mol mL ² g ⁻²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results

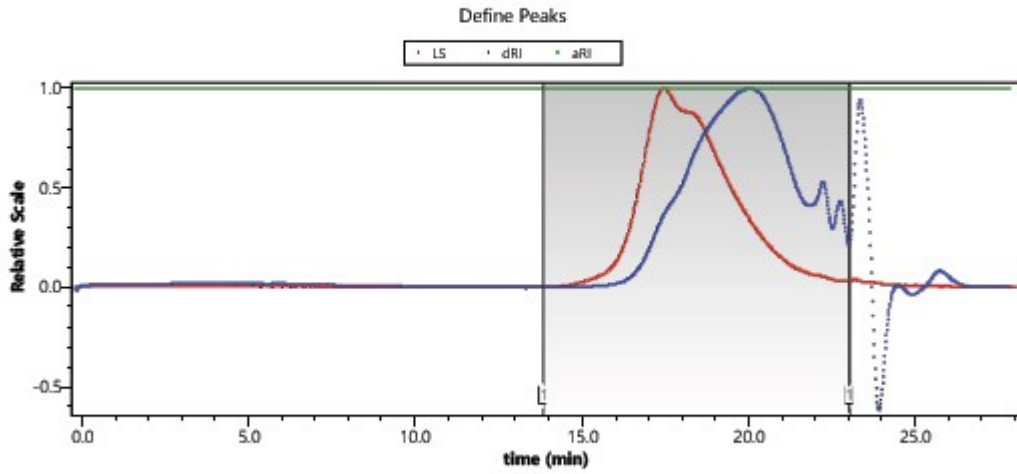
Peak Results

	Peak 1
Masses	
Injected Mass (µg)	300.00
Calculated Mass (µg)	236.14
Mass Recovery (%)	78.7
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	7.126×10 ³ (±10.589%)
Mp	1.368×10 ⁴ (±0.716%)
Mv	n/a
Mw	1.859×10 ⁴ (±1.164%)
Mz	3.758×10 ⁴ (±2.367%)
Polydispersity	
Mw/Mn	2.609 (±10.653%)
Mz/Mn	5.274 (±10.850%)
rms radius moments (nm)	
rn	n/a
rw	n/a
rz	n/a

Polymer PBDC (2e)



Sample: F150



Configuration

Concentration Source: RI
Flow Rate: 1.000 mL/min

Light Scattering Instrument: DAWN EOS
Physical Instrument Name: DAWN EOS on COM3
Wavelength: 690.0 nm
Calibration Constant: 9.3437×10^{-6} 1/(V cm)

Detector	Refractive Index	Corrected Scattering Angle	Gain	Normalization Coefficient
1	n/a		101	1.000
2	16.9°		101	1.487
3	23.2°		101	1.162
4	31.4°		101	1.166
5	38.8°		101	1.349
6	45.8°		101	0.695
7	53.8°		101	0.812
8	61.6°		101	0.897
9	70.4°		101	1.119
10	80.2°		101	1.100
11	90.0°		101	1.000
12	99.8°		101	0.968
13	109.6°		101	0.933
14	119.5°		101	0.822
15	129.6°		101	0.868
16	138.8°		101	65.771
17	147.4°		101	1.383
18	155.4°		101	1.041

RI Instrument: rEX
Temperature: 35.0 °C
Physical Instrument Name: Optilab T-rEX
Calibration Constant: 3.4484×10^{-5} RIU/pixel

Solvent: thf
Temperature Correction Enabled: yes
Refractive Index: 1.401

Processing

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	13.872 - 23.040
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1761
A2 (mol mL/g ²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results

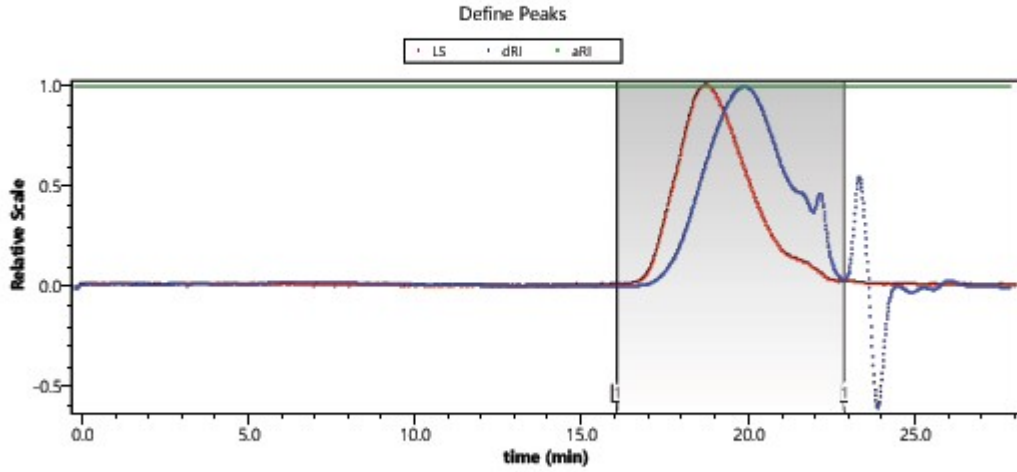
Peak Results

	Peak 1
Masses	
Injected Mass (µg)	300.00
Calculated Mass (µg)	317.72
Mass Recovery (%)	105.9
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	2.251×10 ⁴ (±1.234%)
Mp	2.530×10 ⁴ (±0.481%)
Mv	n/a
Mw	6.054×10 ⁴ (±0.335%)
Mz	1.784×10 ⁵ (±1.009%)
Polydispersity	
Mw/Mn	2.690 (±1.279%)
Mz/Mn	7.926 (±1.594%)
rms radius moments (nm)	
rn	6.6 (±132.6%)
rw	9.5 (±34.5%)
rz	13.1 (±9.4%)

Polymer PBMDc (2f)



Sample: F154



Configuration

Concentration Source: RI
 Flow Rate: 1.000 mL/min

Light Scattering Instrument: DAWN EOS
 Physical Instrument Name: DAWN EOS on COM3
 Wavelength: 690.0 nm
 Calibration Constant: 9.3437×10^{-6} 1/(V cm)

Detector	Refractive Index	Corrected Scattering Angle	Gain	Normalization Coefficient
1	n/a		101	1.000
2	16.9°		101	1.487
3	23.2°		101	1.162
4	31.4°		101	1.166
5	38.8°		101	1.349
6	45.8°		101	0.695
7	53.8°		101	0.812
8	61.6°		101	0.897
9	70.4°		101	1.119
10	80.2°		101	1.100
11	90.0°		101	1.000
12	99.8°		101	0.968
13	109.6°		101	0.933
14	119.5°		101	0.822
15	129.6°		101	0.868
16	138.8°		101	65.771
17	147.4°		101	1.383
18	155.4°		101	1.041

RI Instrument: rEX
 Temperature: 35.0 °C
 Physical Instrument Name: Optilab T-rEX
 Calibration Constant: 3.4484×10^{-5} RIU/pixel

Solvent: thf
 Temperature Correction Enabled: yes
 Refractive Index: 1.401

Processing

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	16.072 - 22.880
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1761
A2 (mol mL/g ²)	0.000
UV Ext. Coef. (mL/mg cm)	0.000

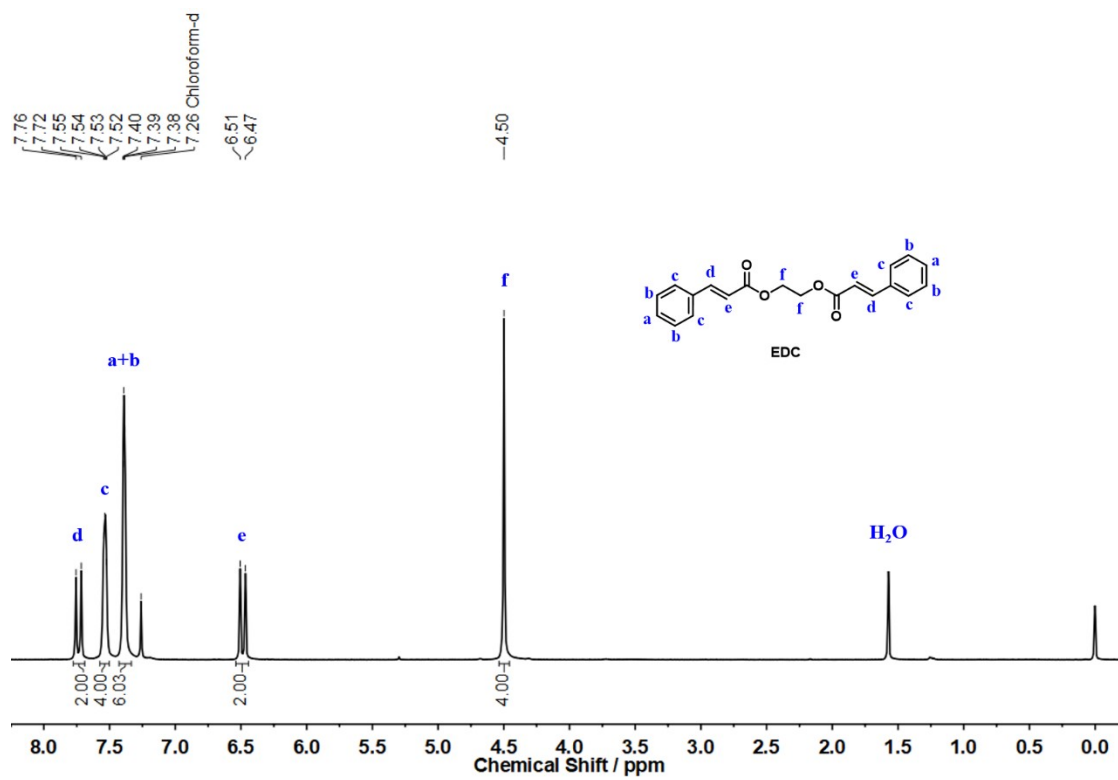
Results

Peak Results

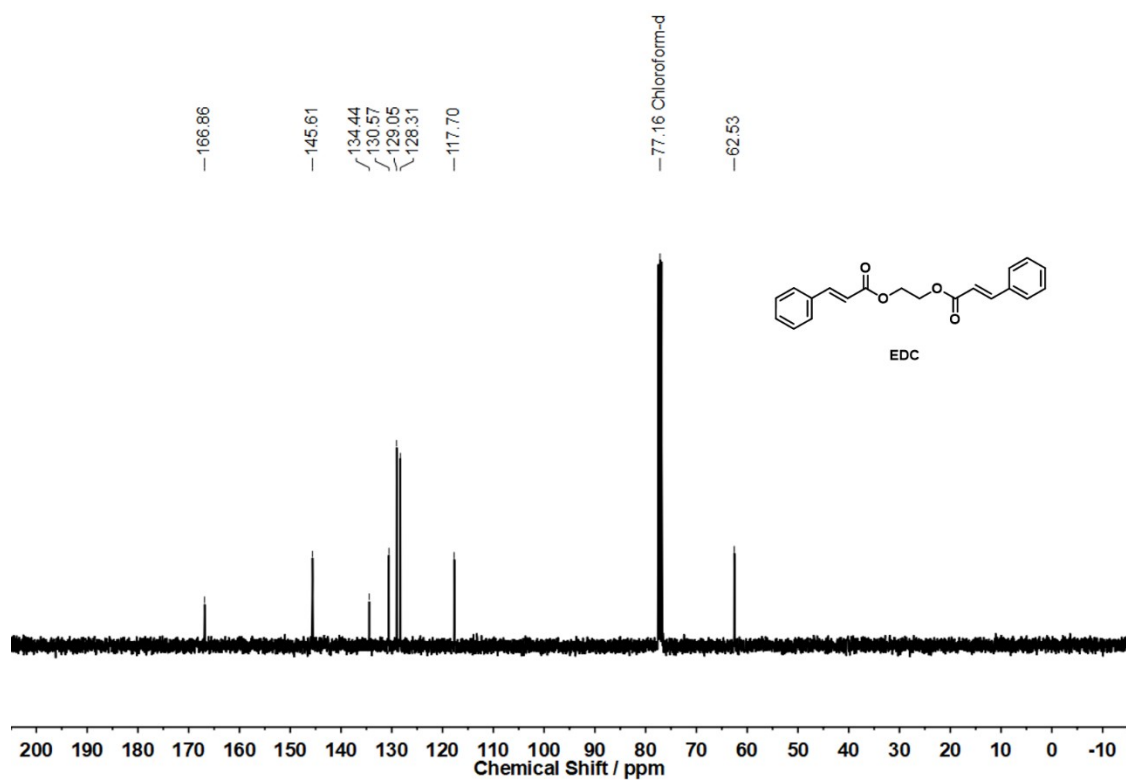
	Peak 1
Masses	
Injected Mass (µg)	300.00
Calculated Mass (µg)	283.84
Mass Recovery (%)	94.6
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	1.377×10 ⁴ (±2.010%)
Mp	1.730×10 ⁴ (±0.623%)
Mv	n/a
Mw	2.533×10 ⁴ (±0.806%)
Mz	5.501×10 ⁴ (±3.096%)
Polydispersity	
Mw/Mn	1.840 (±2.165%)
Mz/Mn	3.996 (±3.691%)
rms radius moments (nm)	
rn	23.8 (±17.7%)
rw	19.4 (±16.7%)
rz	16.9 (±14.2%)

11. ^1H and ^{13}C NMR Spectra

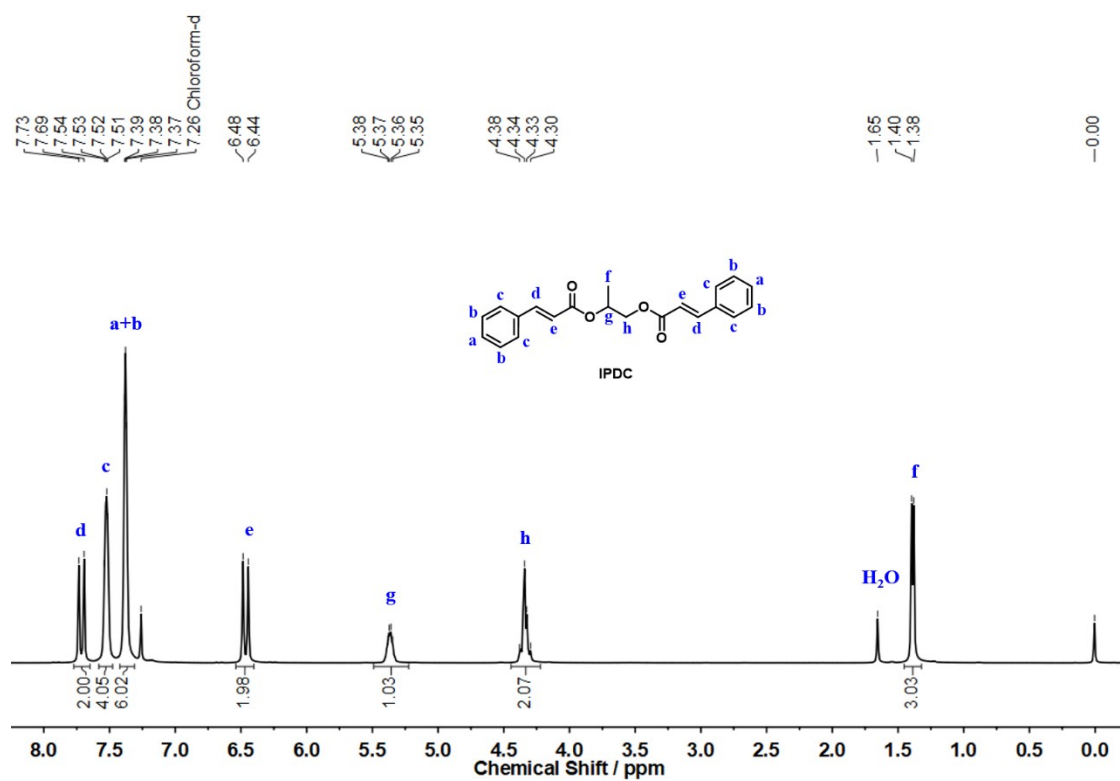
^1H NMR (400 MHz, CDCl_3) spectrum of product 1a



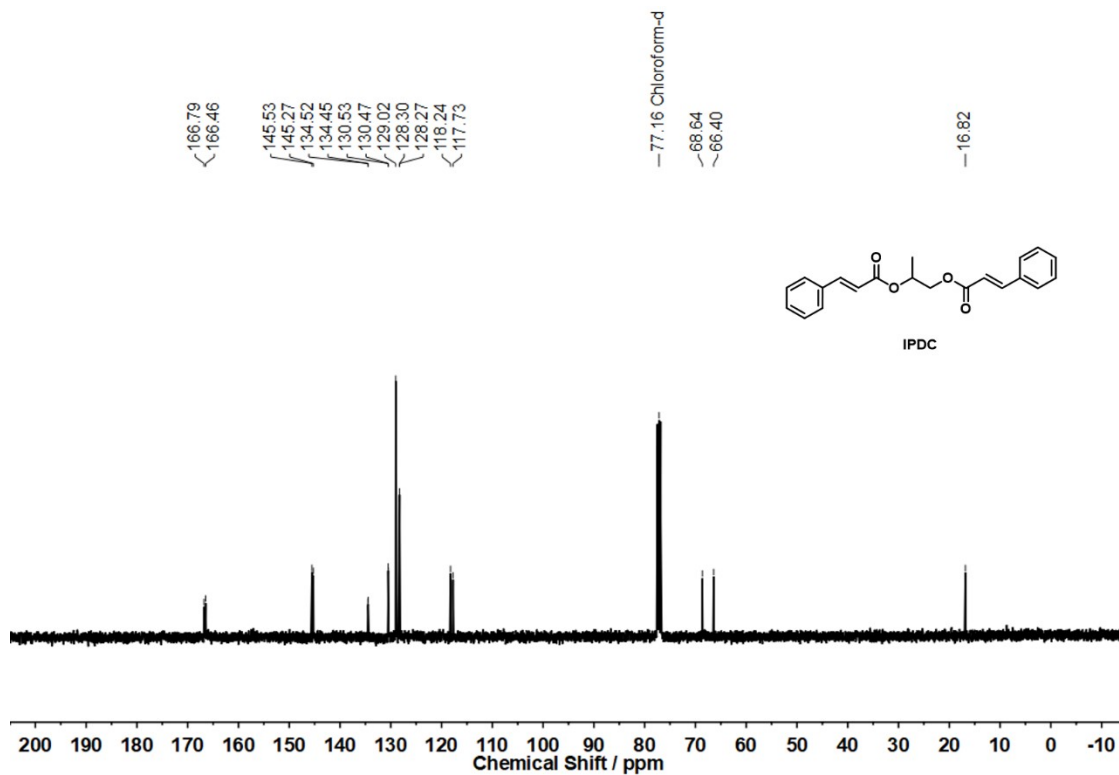
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 1a



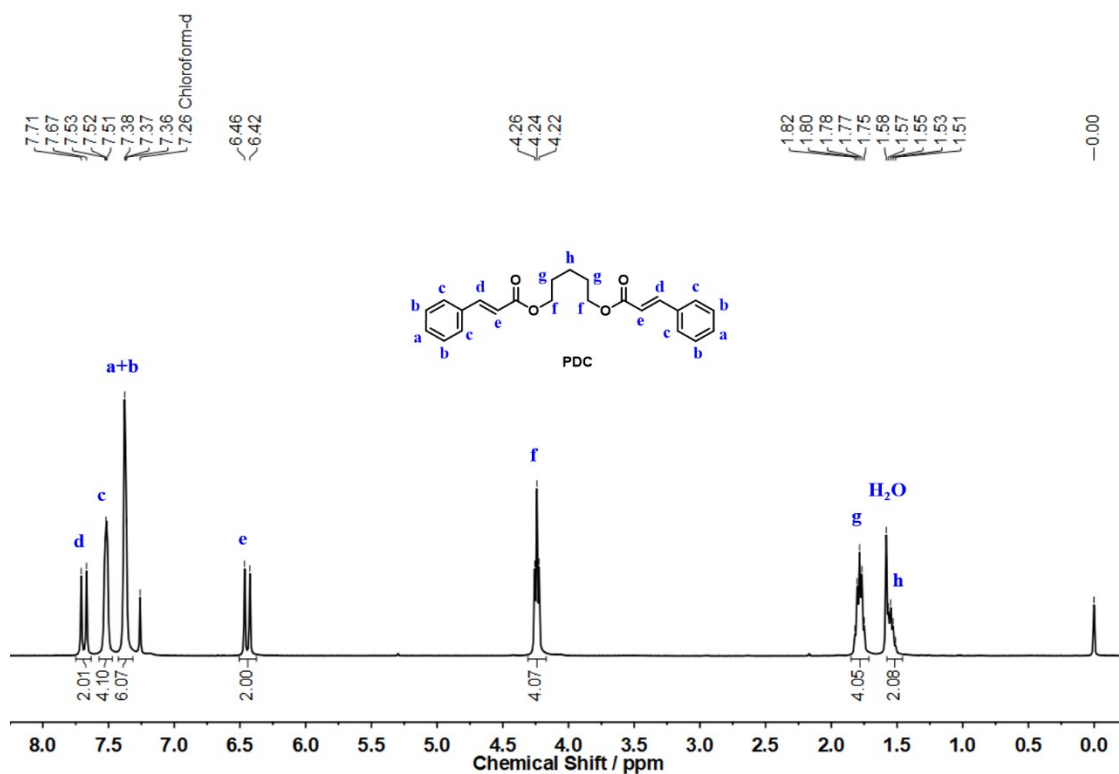
¹H NMR (400 MHz, CDCl₃) spectrum of product 1b



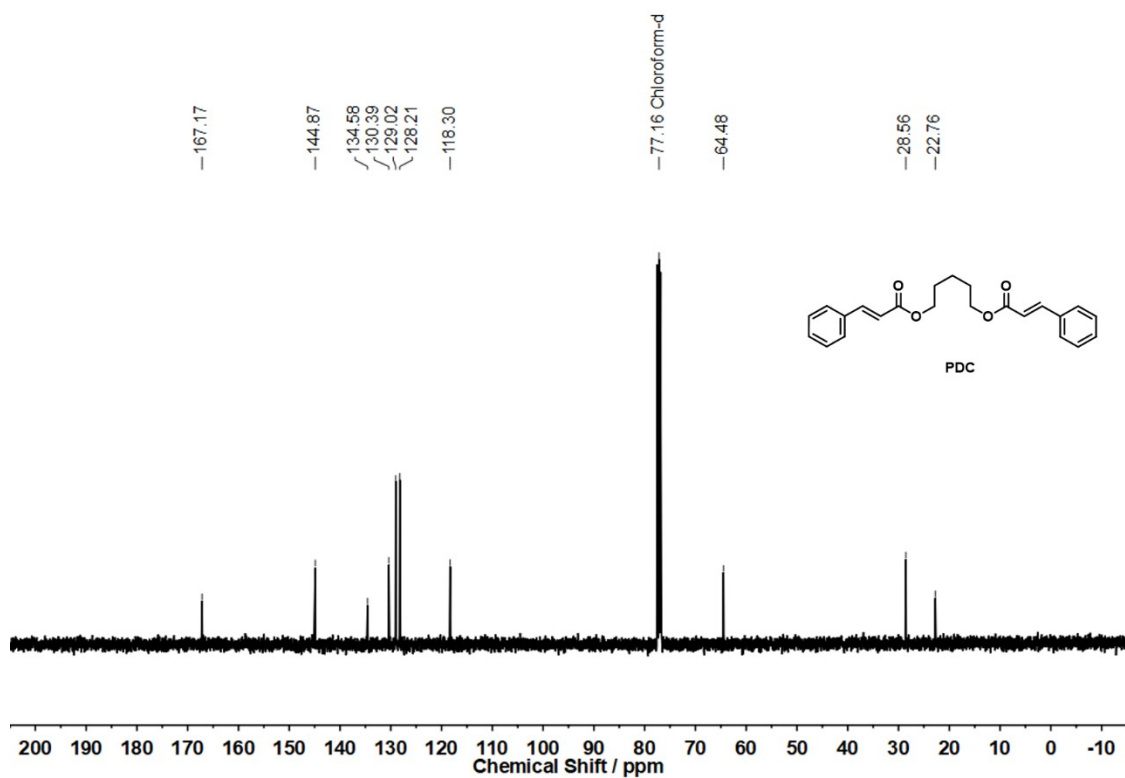
¹³C NMR (100 MHz, CDCl₃) spectrum of product 1b



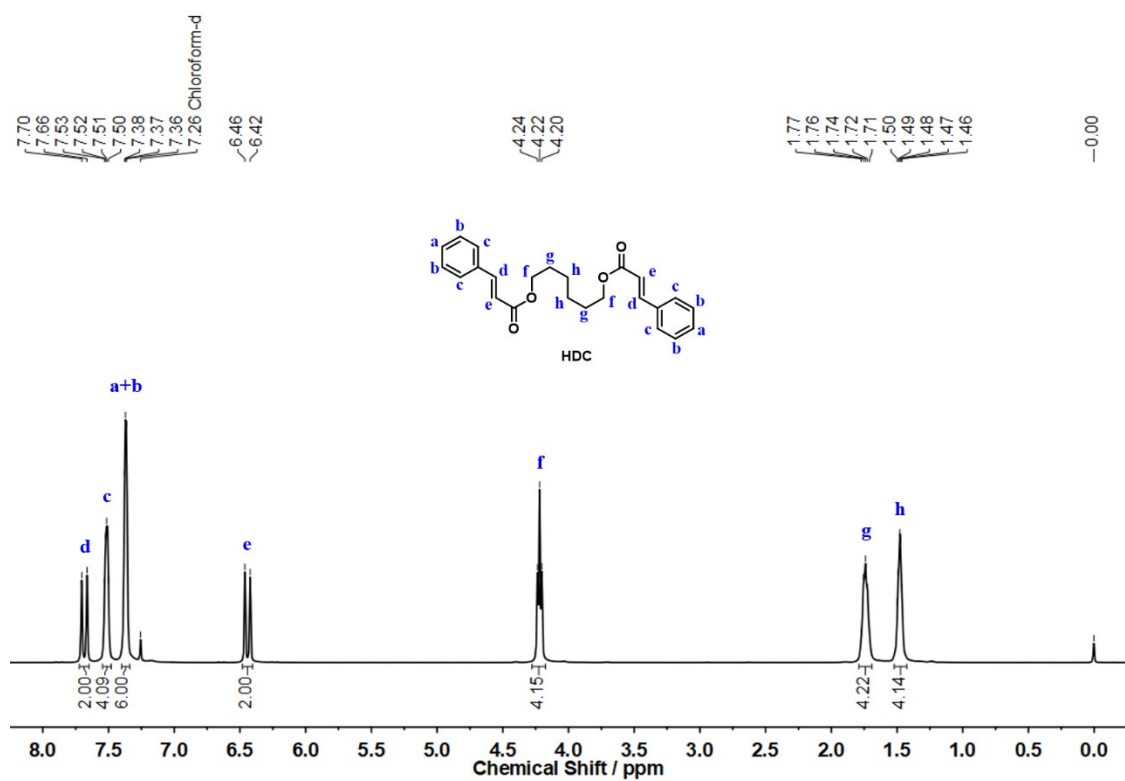
¹H NMR (400 MHz, CDCl₃) spectrum of product 1c



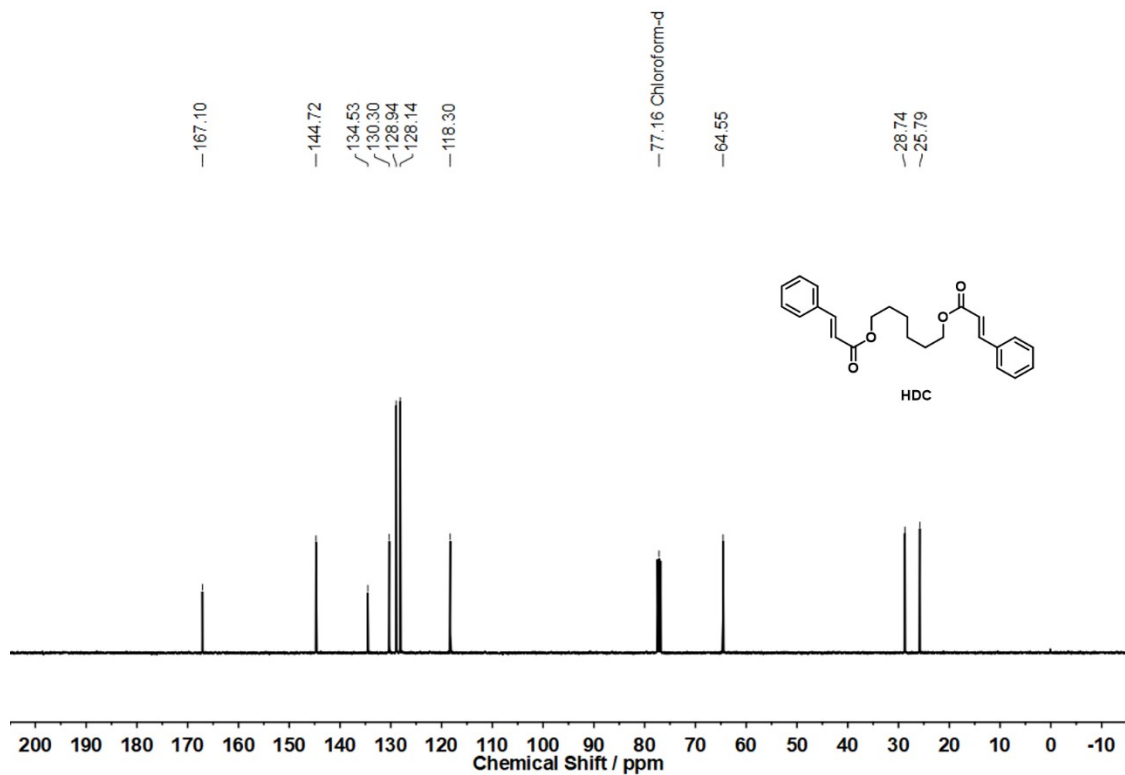
¹³C NMR (100 MHz, CDCl₃) spectrum of product 1c



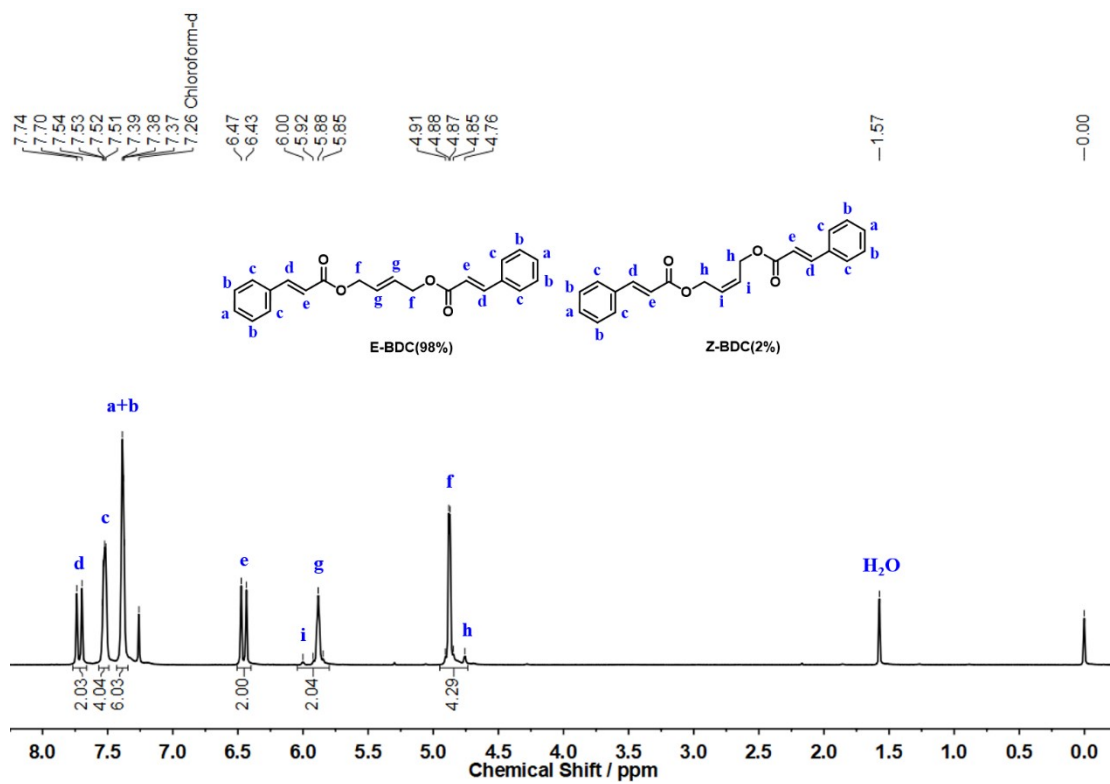
¹H NMR (400 MHz, CDCl₃) spectrum of product 1d



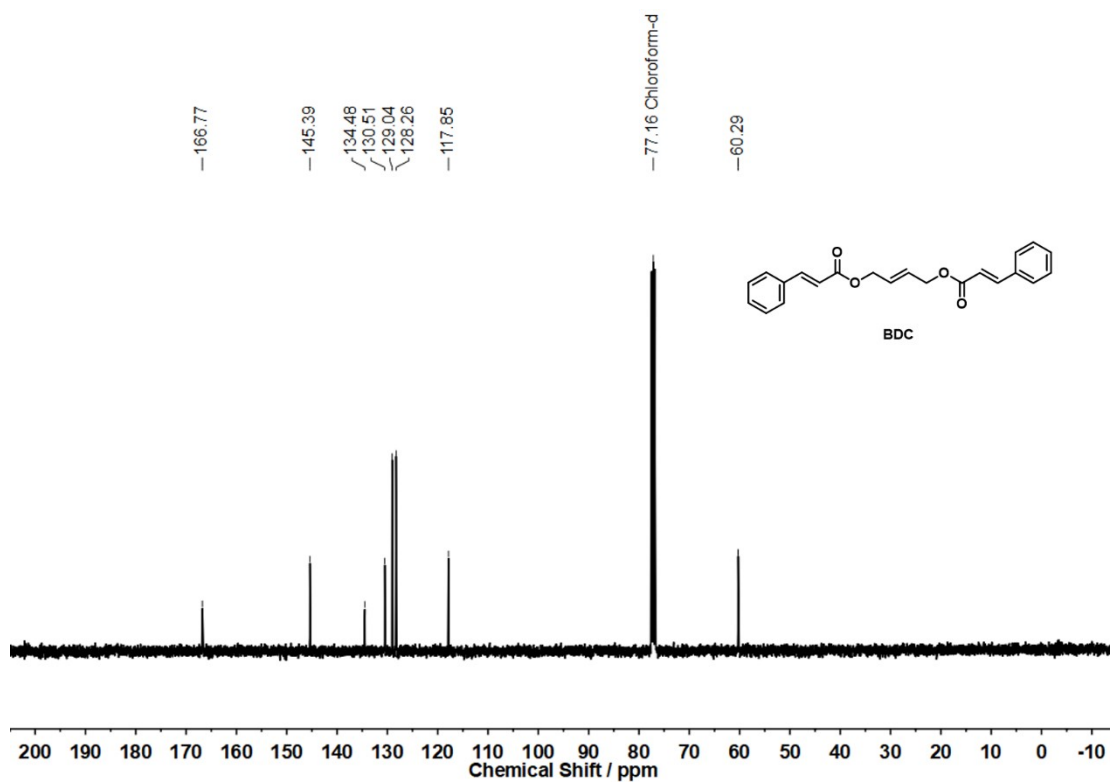
¹³C NMR (100 MHz, CDCl₃) spectrum of product 1d



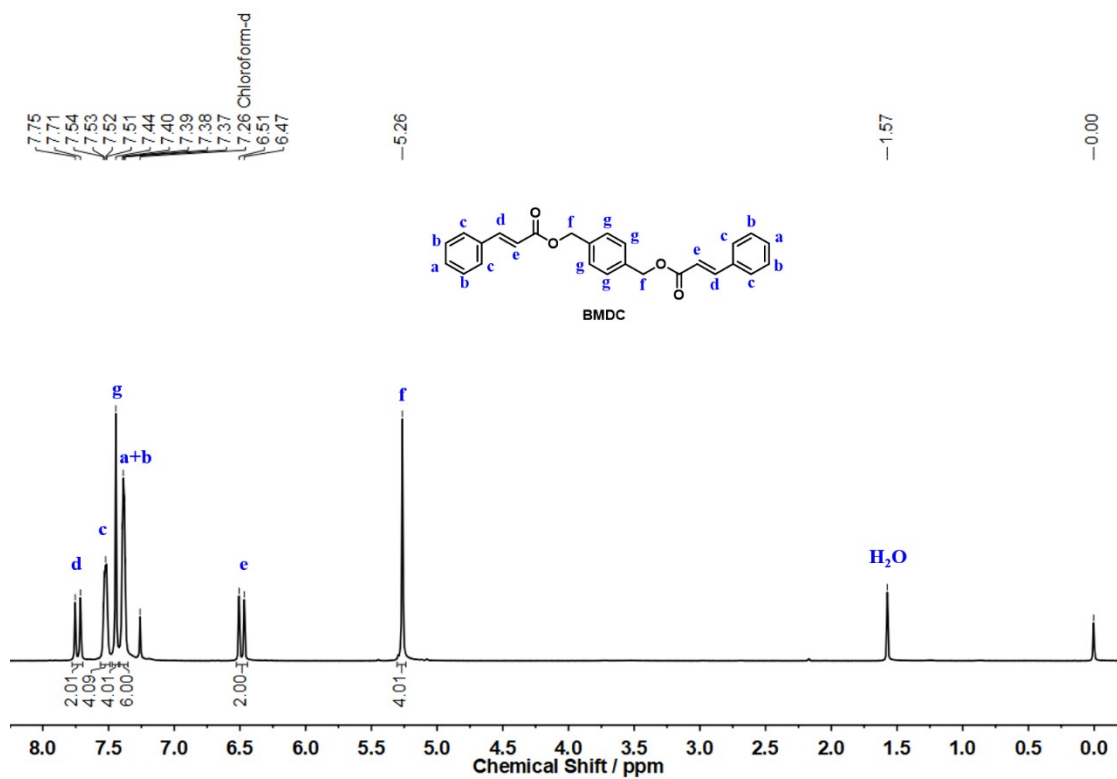
¹H NMR (400 MHz, CDCl₃) spectrum of product 1e



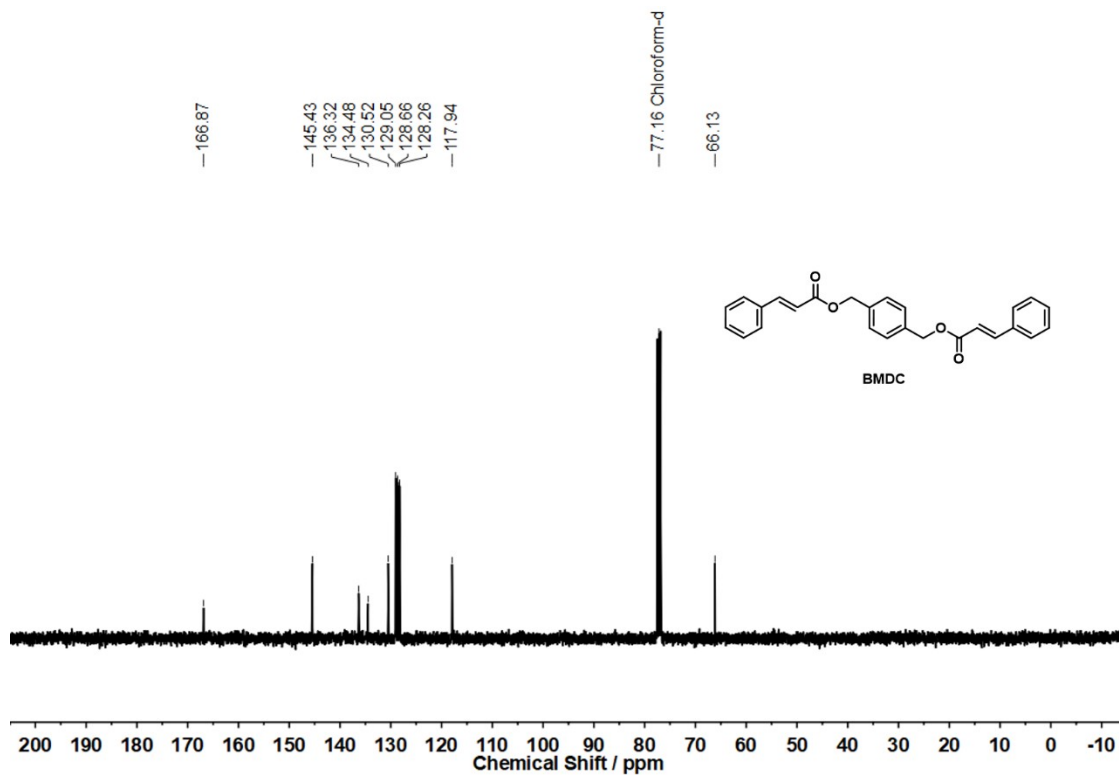
¹³C NMR (100 MHz, CDCl₃) spectrum of product 1e



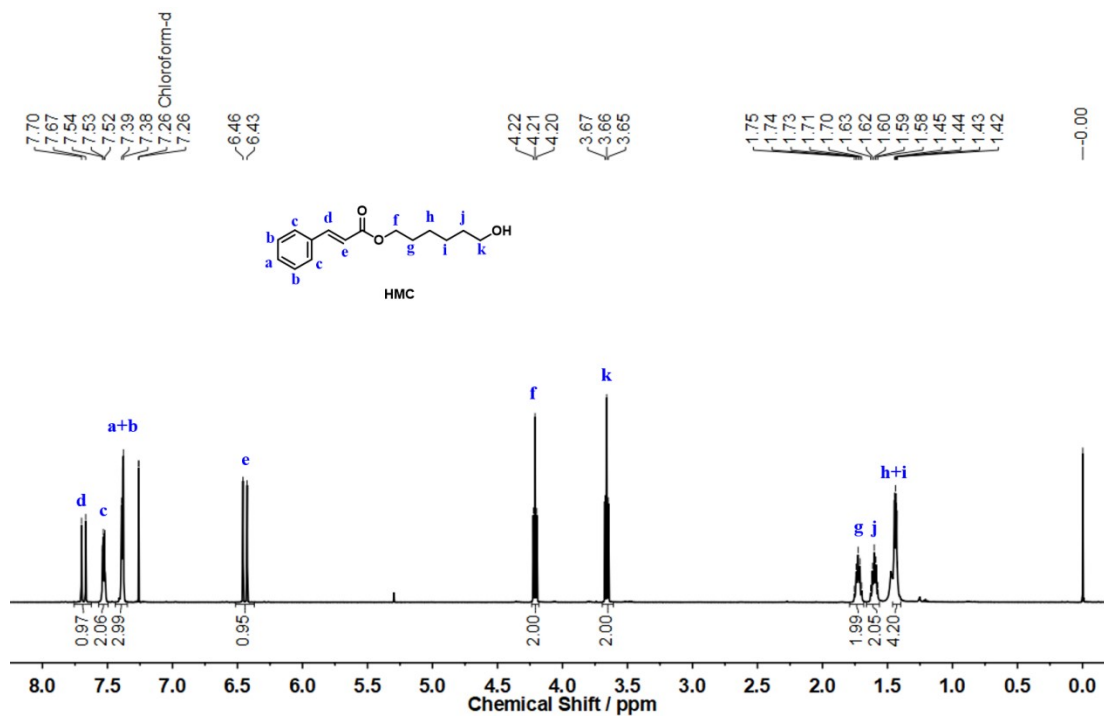
¹H NMR (400 MHz, CDCl₃) spectrum of product 1f



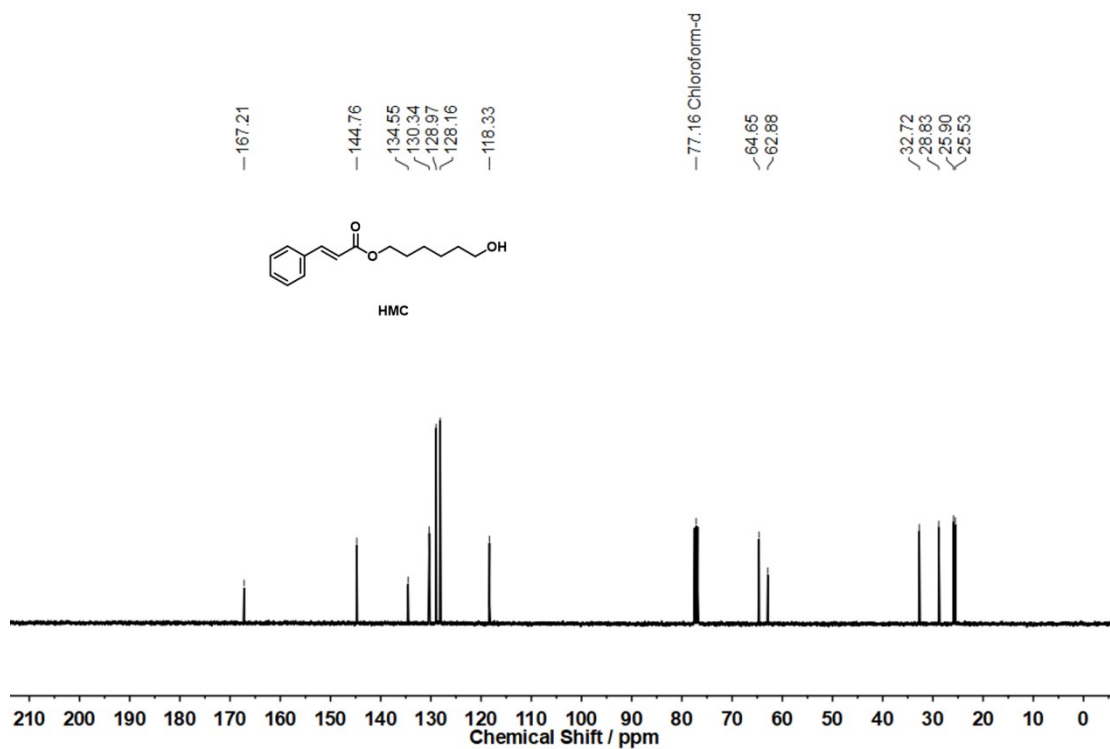
¹³C NMR (100 MHz, CDCl₃) spectrum of product 1f



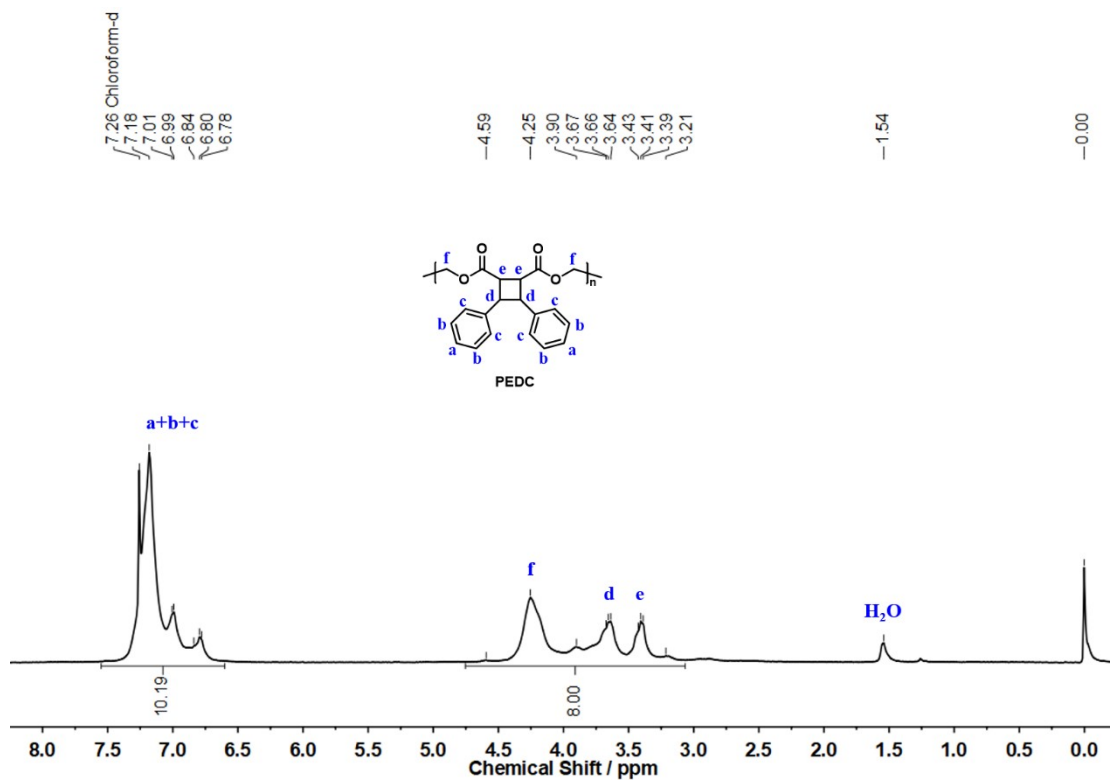
¹H NMR (400 MHz, CDCl₃) spectrum of HMC



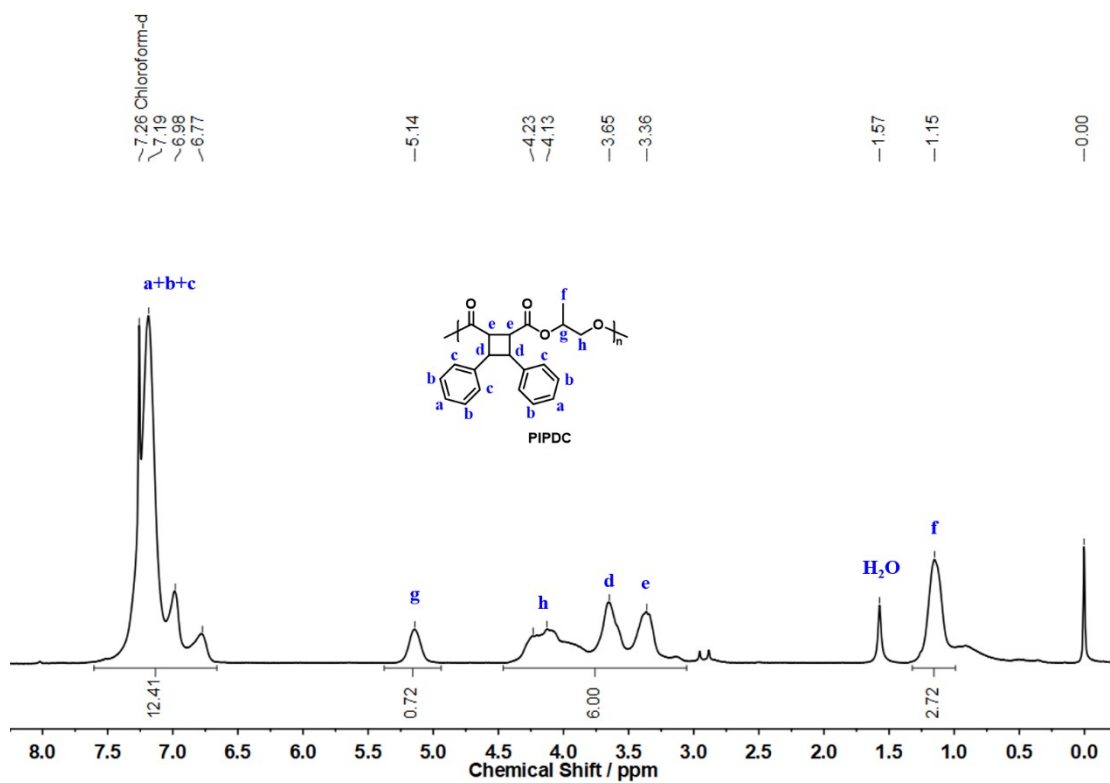
¹³C NMR (100 MHz, CDCl₃) spectrum of HMC



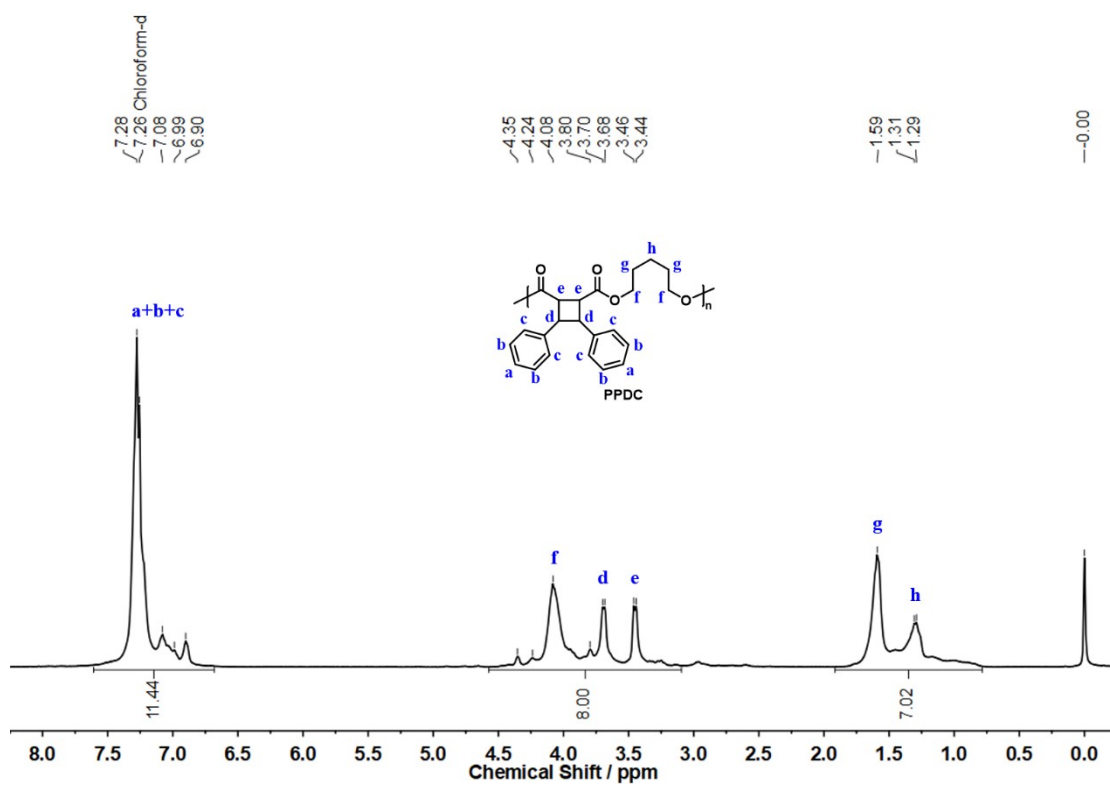
¹H NMR (400 MHz, CDCl₃) spectrum of polymer 2a



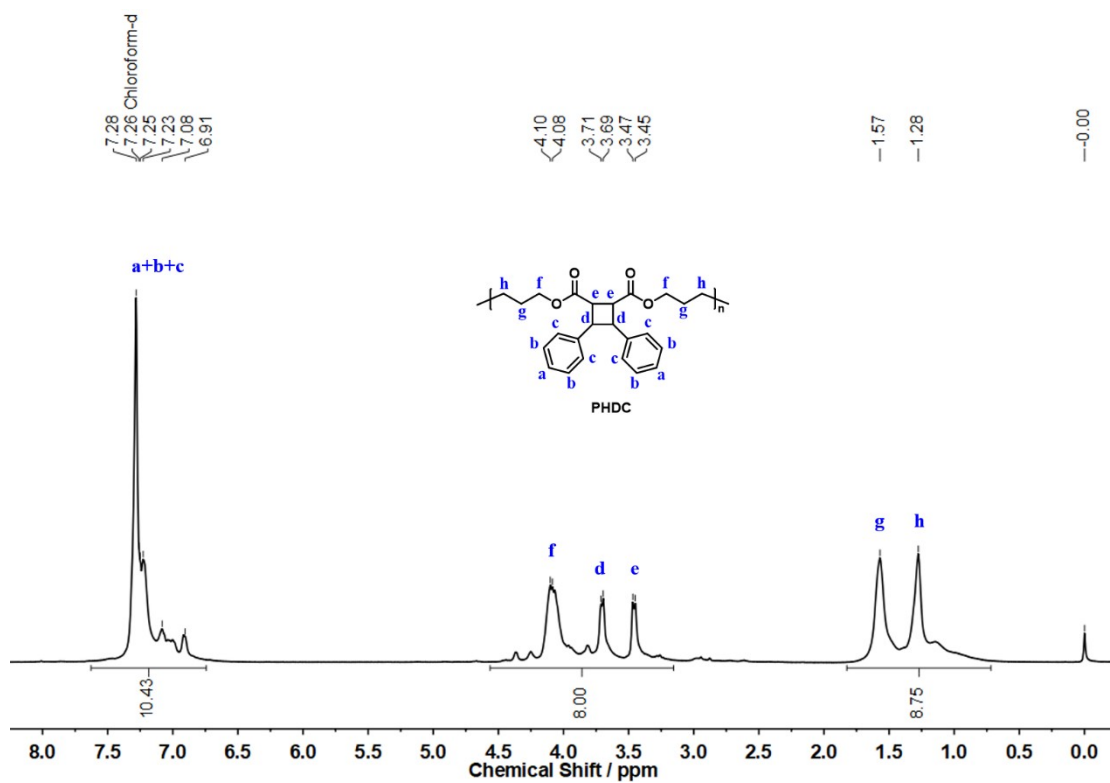
¹H NMR (400 MHz, CDCl₃) spectrum of polymer 2b



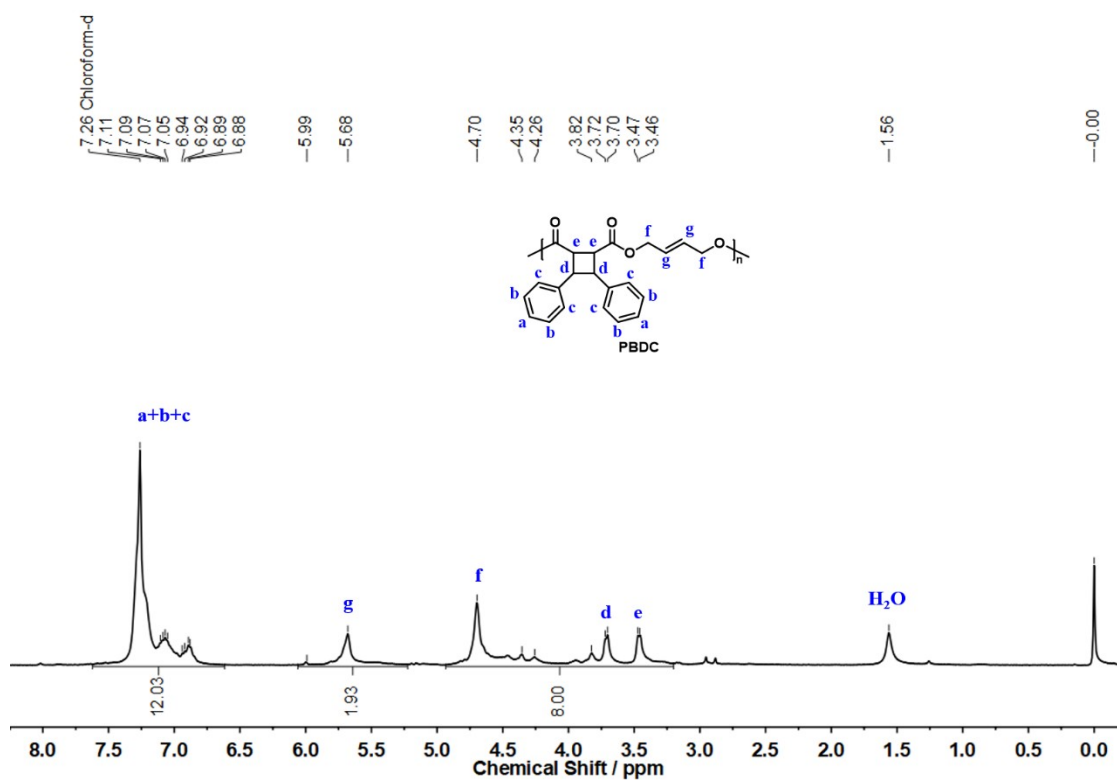
¹H NMR (400 MHz, CDCl₃) spectrum of polymer 2c



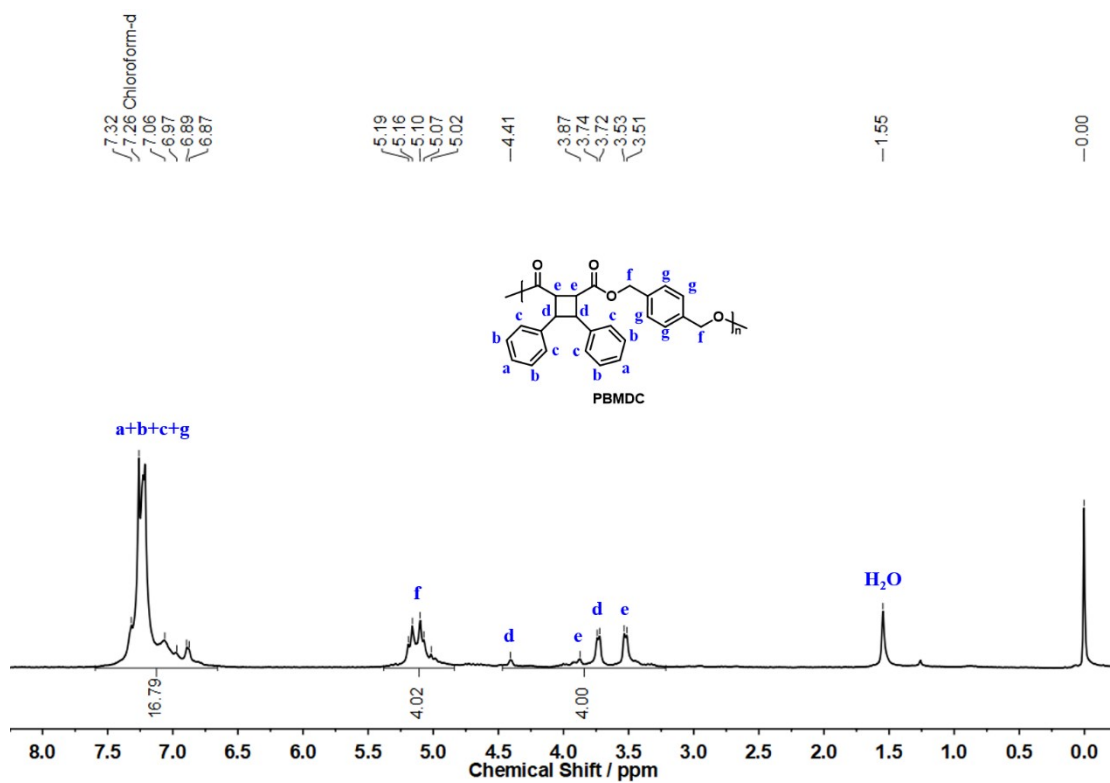
¹H NMR (400 MHz, CDCl₃) spectrum of polymer 2d



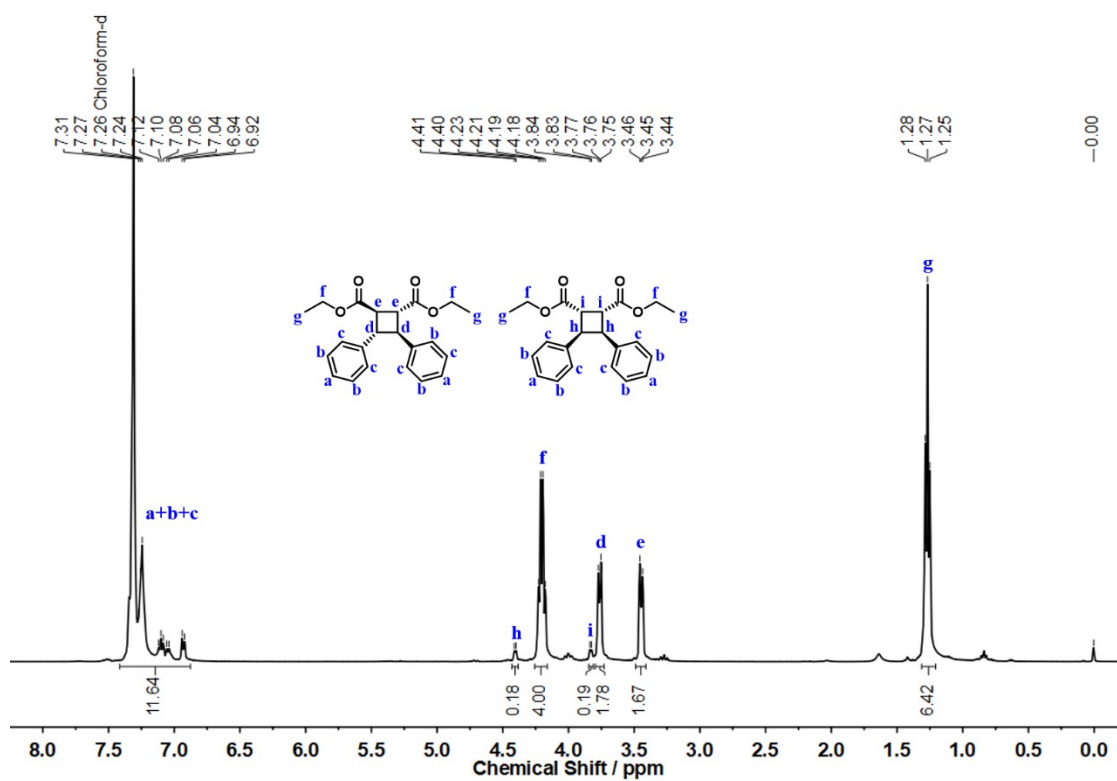
¹H NMR (400 MHz, CDCl₃) spectrum of polymer 2e



¹H NMR (400 MHz, CDCl₃) spectrum of polymer 2f



¹H NMR (400 MHz, CDCl₃) spectrum of dimer of Ethyl Cinnamates



12. Thermal Stability Analyses

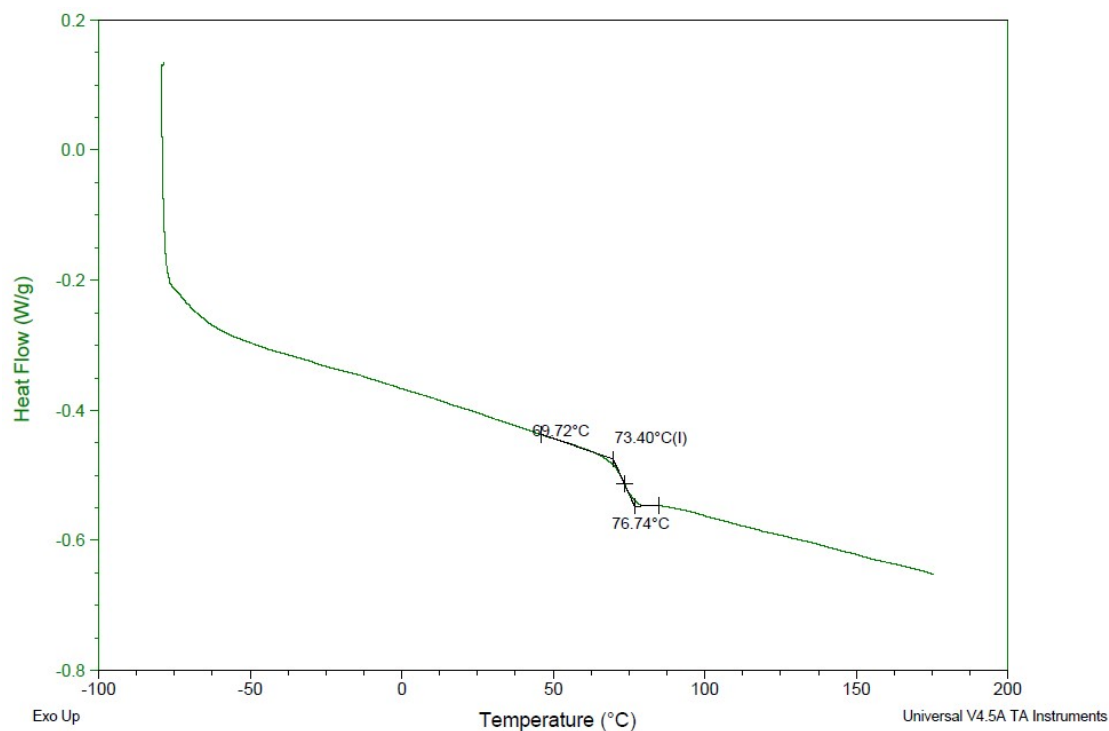


Figure S8 Representative DSC curves for isotactic PEDC during the second heat at a temperature ramp rate of 10 °C/min.

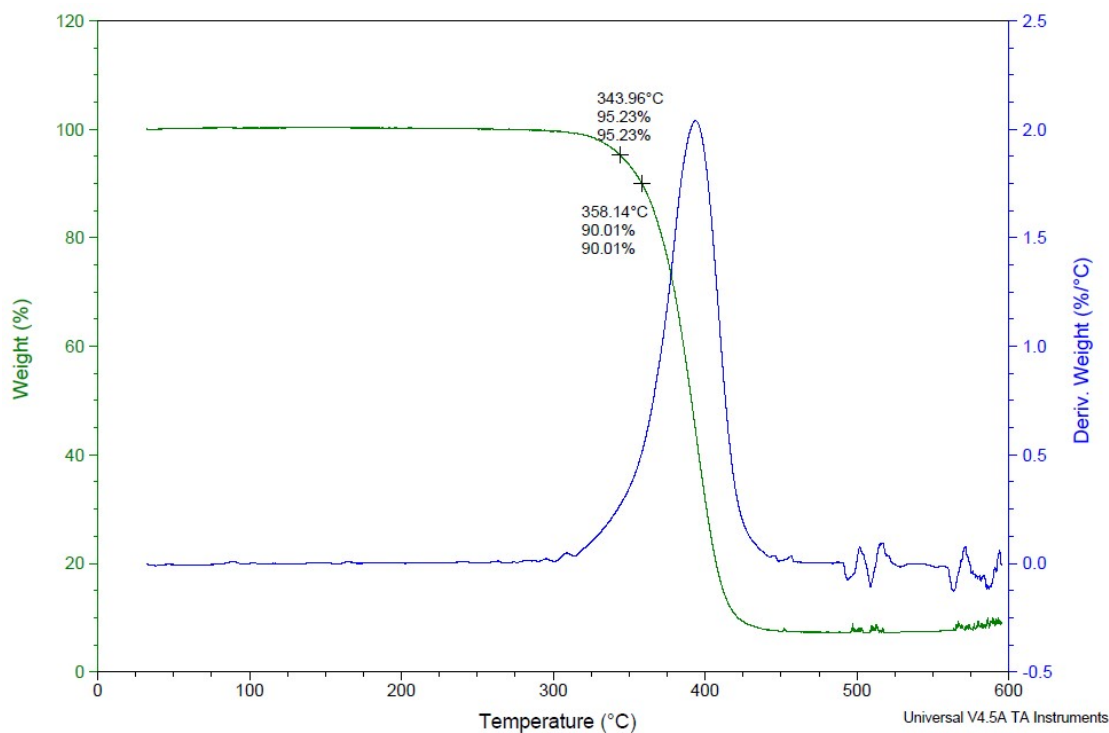


Figure S9 Representative TGA and DTG curves for isotactic PEDC

13. Preparation of Polymer Thin Films

The copolymers were dried in a vacuum oven at 100 °C for 1 h. The dry copolymer was then placed in a flat mold (thickness, 0.7 mm) between two Kapton films. These films were then placed between two steel plates. Subsequently, the two steel plates were placed under a plate vulcanizer at 100 °C and the film was formed using a pressure of 2 MPa. After hot-pressing, the mold was quickly quenched in cold water to produce the transparent copolyester film with a thickness of $0.7 \pm 0.01\text{mm}$.²⁻³

14. Tensile Properties and Process of Polymer Films

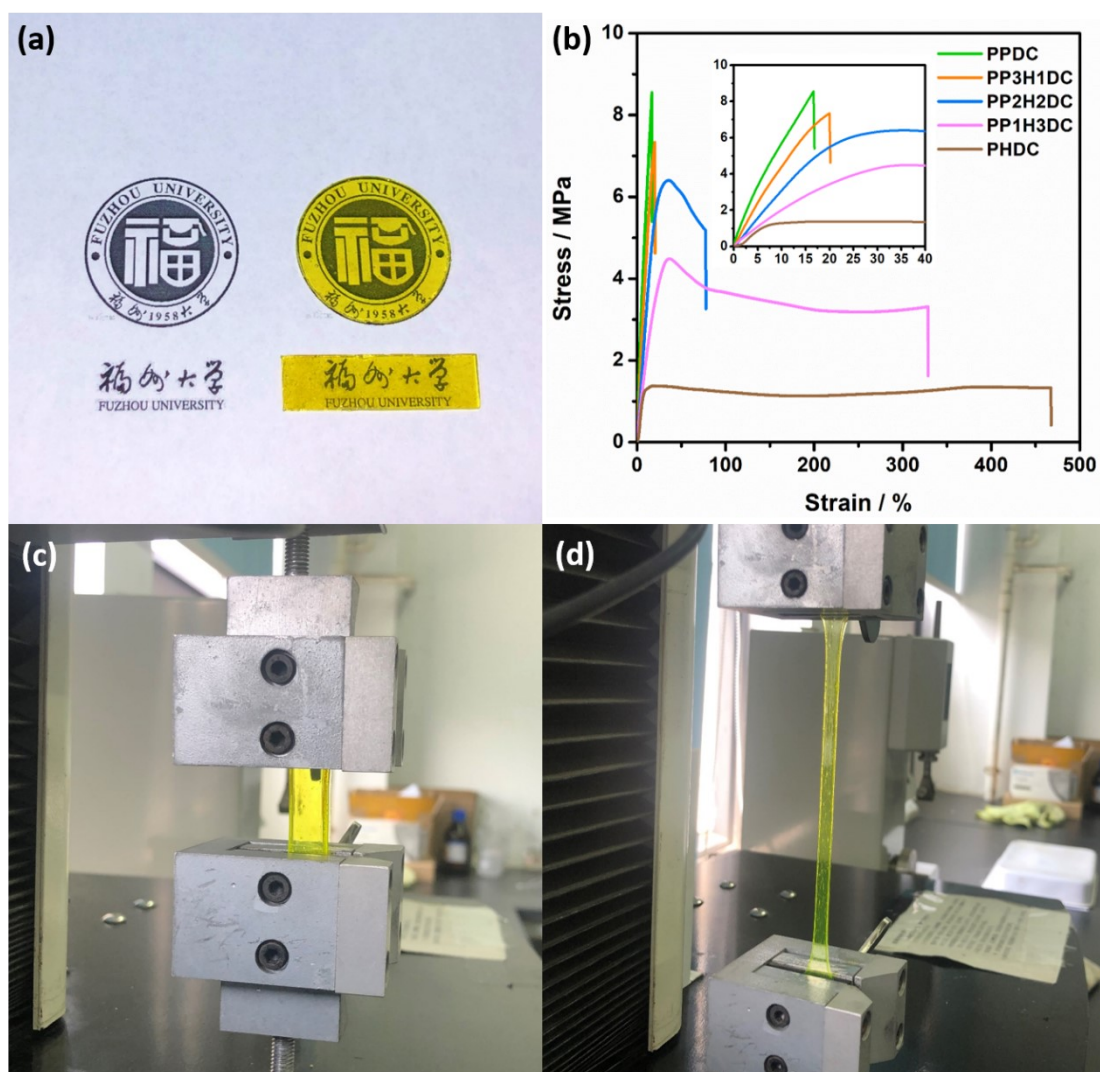


Figure S10 the tensile process of poly (hexylene glycol dicinnamate) (PHDC).

Copolymer	Young's modulus (E , MPa)	Maximum tensile strength (σ_m , MPa)	Elongation at break (ε_b , %)
PPDC	48.5±4.3	8.6±1.2	16.6±3.0
PP3H1DC	37.3±2.3	7.4±1.3	20.0±6.5
PP2H2DC	29.0±3.2	6.4±2.4	77.3±12.6
PP1H3DC	15.6±1.8	4.5±0.8	328.5±34.6
PHDC	16.9±2.7	1.4±0.4	468.8±58.7

Table S5 Tensile properties of polymer

15. Reference

1. Dong, J., Sharpless, K. B., Kwisnek, L., Oakdale, J. S. & Fokin, V. V. SuFEx-based synthesis of polysulfates. *Angew. Chem., Int. Ed.* **53**, 9466-9470 (2014).
2. Teator, A. J. & Leibfarth, F. A. Catalyst-controlled stereoselective cationic polymerization of vinyl ethers. *Science* **363**, 1439-1443 (2019).
3. Ding, L., Liu, L., Chen, Y., Du, Y., Guan, S., Bai, Y. & Huang, Y. Modification of poly(ethylene terephthalate) by copolymerization of plant-derived α -truxillic acid with excellent ultraviolet shielding and mechanical properties. *Chem. Eng. J.* **374**, 1317-1325 (2019).