Supporting Information

3-Methylenephthalide Derivatives Enable Vinyl (Co)polymers Degradable via Simultaneous Main- and Side-Chain Cleavage

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CONTENTS

Methods

Instruments

Flash column chromatography: Silica gel flash chromatography was performed on a Selekt (Biotage) equipped with a column occupied Wakogel C-400HG (20–40 μm, 70% up).

NMR spectroscopy: ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 (99.9 atom % D, Kanto Chemical) and $CDCl_3$ (99.8 atom % D with 0.03vol% TMS, Kanto Chemicals) on AVANCE NEO (Bruker) spectrometers. The chemical shifts were referred to the signal of tetramethylsilane (TMS) or solvent (DMSO and $CHCl_3$).

UV-vis spectroscopy: UV-vis spectra were recorded on a V-730ST spectrometer (JASCO).

IR spectroscopy: IR spectra were recorded on a Cary 630 FTIR spectrometer equipped with a diamond-attenuated total reflection (ATR) accessory.

Size-exclusion chromatography (SEC): Molar mass and its distributions of the polymers soluble in DMF were evaluated by SEC on an EXTREMA chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C (300 mm _7.5 mm), Polymer Laboratories], using *N*,*N*-dimethylformamide (DMF, Wako Pure Chemical Industries, for GPC grade) as an eluent (flow rate = 0.8 mL min^{-1}) at 40 °C. Molar mass and its distributions of the polymers soluble in $CHCl_3$ were evaluated by SEC on an EXTREMA chromatograph (JASCO) equipped with two SEC columns [Shodex HK-404L × 2], using chloroform ($CHCl_3$; Wako Pure Chemical Industries, GPC grade) as an eluent (flow rate = 0.6 mL min^{-1}) at 40 °C. The signals were detected with a UV-4070 detector (JASCO) and calibrated against standard polystyrene (PS) samples (TSK-gel oligomer kit, Tosoh, M_n: 1.03×10^6, 3.89×10^5, 1.82×10^5, 3.68×10^4, 1.36×10^4, 5.32×10^3, 3.03×10^3, 8.73×10^2).

High performance liquid chromatography (HPLC): The purity of products were evaluated by HPLC performed on an EXTREMA chromatograph (JASCO) equipped with LC columns [InertSustain Phenylhexyl (150 mm_2.1 mm), GL Science] at 40 °C, using pure water (90 vol %) and acetonitrile (Yoneyama Yakuhin Kogyo Co., Ltd. for LC grade, 10 vol %) mixed with 0.01 wt% trifluoroacetic acid (Kanto Chemical Co., Inc. for HPLC grade) as the eluent (flow rate: 0.2 mL·min^{-1}). The chemicals were detected using a UV detector (UV-4070, JASCO) at 254 nm.

Thermal and mechanical properties: Thermogravimetric/differential thermal analysis (TG/DTA) was carried out from room temperature to 500 °C at a heating rate of 10 °C min^{-1} with a Rigaku Thermo plus II TG8120 under an N_2 atmosphere. Tensile tests were performed using a Shimadzu Autograph AGS-500NX STD.

Dynamic mechanical analysis (DMA): A film with thickness of 0.25 mm was prepared by hot-pressing at 140 °C for 2 min. A disc-shaped sample with a diameter of 12 mm and approximately 0.25 mm thickness was measured. Temperature-sweep rheology was conducted using a shear-type rheometer, MCR302e (Anton Paar) and disposable 12 mm plate. The frequency was fixed at 1 Hz and a constant strain of 0.1% was applied. Cyclic cooling and heating measurements were performed at a rate of 5 °C/min. Frequency-sweep rheology analysis was performed using a similar set-up at 180 °C.

Materials

Anhydrous DMF was purchased from Kanto Chemical Co., Inc. Oxalyl chloride, malonic acid, *p*-toluenesulfonic acid monohydrate ($TsOH \cdot H_2O$), tetrachloromethane (CCl_4), isopropanol, concentrated HCl aq., and 2,2′-azoisobutyronitrile (AIBN) were purchased from Fujifilm Wako Pure Chemical Co. Phthalic anhydride. Triethyl amine (TEA, GR), methanol, dichloromethane (CH_2Cl_2), sodium hydroxide (NaOH) and magnesium sulfate ($MgSO_4$) were purchased from Yoneyama Yakuhin Kogyo Co., Ltd. 4-Methylphthalic anhydride, *N*-bromosuccinimide (NBS), trimellitic anhydride, isobutyric acid, *n*-octanoic acid, 2-octanol,

decamethylcyclopentasiloxane, and other chemicals were purchased from Tokyo Chemical Industry Co., Ltd.

Synthesis

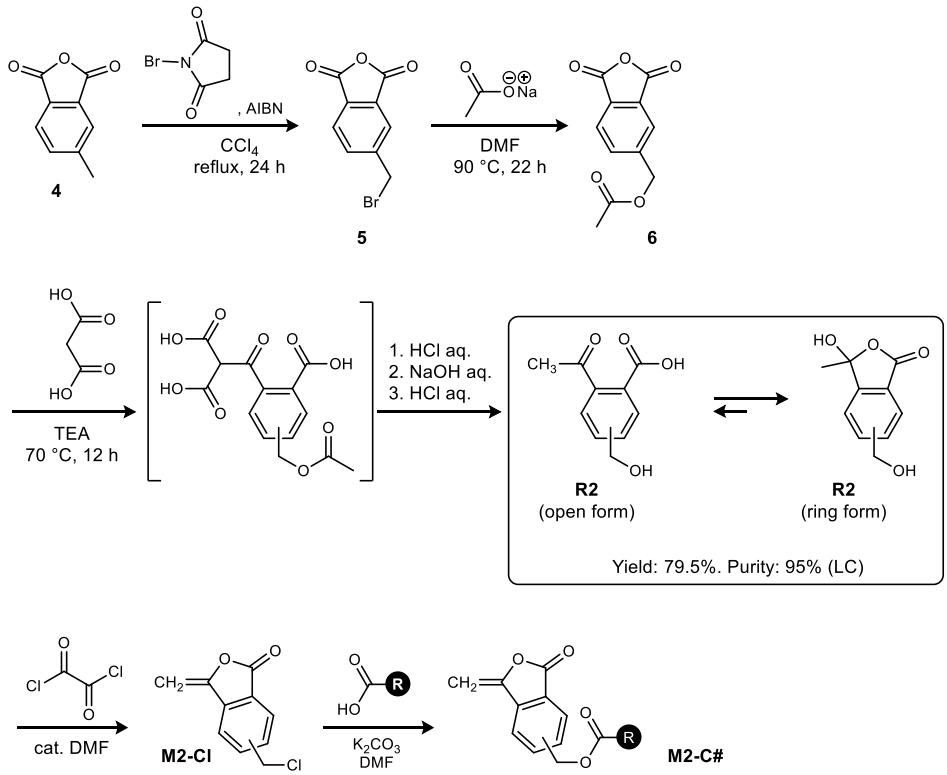


Figure S1: Synthesis route of **M2-#.**

5-(bromomethyl)isobenzofuran-1,3-dione (**5**)

A solution of 4-methyl phthalic anhydride (**4**, 65.6 g, 400 mmol), NBS (71.2 g, 400 mmol), and AIBN (1.97 g, 6.00 mmol) in tetrachloromethane (CCl4, 600 mL) was refluxed for 24 h. After cooling to room temperature, the solution was washed by *conc.* sodium sulfite aq., water, and brine. The organic layer was dried over $MgSO_4$ followed by concentration and drying *in vacuo*. The obtained crude product containing **2** (123 g, purity: 54.6%) was used in the next step without further purification

(1,3-dioxo-1,3-dihydroisobenzofuran-5-yl)methyl acetate (**6**)

A solution of the crude product of **5** (50.0 g, purity: 70.4%) and sodium acetate (3.31 g, 39.8 mmol) in DMF (anhydrous, 33.2 mL) was heated at 90 °C for 22 h, cooled to room temperature, diluted with ethyl acetate (200 mL), and washed with water, *sat.* $NaHCO_3$ aq., and brine. The organic layer was dried over $MgSO_4$, concentrated, and dried in *vacuo* to afford viscous liquid. The crude product was purified by column chromatography using a cosolvent of acetone and hexane (v/v= 0/100 to 40/60) to afford **6** (30.8 g, 87.0% yield) as colorless solids. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$): δ/ppm 8.00 (d, *J* = 8.0 Hz, 1H, aromatic), 7.99 (s, 1H, aromatic), 7.86 (d, *J* = 7.9 Hz, 1H, aromatic), 5.28 (s, $PhCH_2O$), 2.17 (s, Ac).

R2 (isomer mixtures)

Malonic acid (5.67 g, 54.5 g) was added to the suspension of **6** (10.0 g, 45.4 mmol) in TEA (4.41 g, 43.6 mmol) at 70 °C. The mixture was heated at 70 °C for 12 h, cooled to room temperature, and acidified with 1 M HCl aq. (200 mL). The product was extracted with ethyl acetate (50 mL × 3), and the organic layer was washed with 1 M HCl aq. (100 mL × 3) and brine (100 mL × 3), dried over $MgSO_4$,

concentrated, and dried *in vacuo*. The yellow residue was dissolved in 5 wt% NaOH aq. The solution was stirred for 16 h at 25 °C, acidified to pH 2 using *conc.* HCl aq., and extracted with ethyl acetate (50 mL × 3). The combined organic layer was dried over $MgSO_4$, concentrated, and dried *in vacuo*. The yielded viscous liquid was dissolved in ethyl acetate (30 mL) and poured into hexane (200 mL). The precipitate was isolated by decantation and dried in *vacuo* to afford **R2** [7.01 g, Yield: 79.5%, purity: 95.0%(LC)]. ^{1}H NMR spectrum (400 MHz, 25 °C, DMSO-d_6): δ/ppm 7.82–7.38 (3H, aromatic), 5.42 (*s*, 1H, OH), 4.65–4.58 (CH_2), 2.46 (s, 3H, $COCH_3$), 1.75 (s, 3H, CH_3).

M2-Cl (isomer mixture)

A solution of **R2** (4.62 g, 23.8 mmol) in DMF (anhydrous, 14.8 mL) was heated at 60 °C, and oxalyl chloride (6.1 mL, 71 mmol) was added dropwise carefully with keeping the inner temperature below 62 °C. The solution was stirred at 60 °C for 4 h, cooled to room temperature, and poured into water (1.2 L) at 0 °C in several portions. The product was extracted with CH_2Cl_2 (200 mL × 3). The combined organic layer was washed with water (300 mL × 3) and brine (300 mL × 3), dried over magnesium sulfate ($MgSO_4$), and concentrated. The residual liquid was purified by column chromatography using a cosolvent of acetone and hexane (v/v= 0/100 to 30/70) to afford **M2-Cl** (3.26 g, yield: 70.2%) as colorless solids. Melting point: 72.0–77.5 °C. IR spectra (ATR): 3014 cm^{-1} (Ar-H), 1766 cm^{-1} (C=O), 1658 cm^{-1} (C=C). ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$): 7.90 (d, *J* = 0.69 Hz, 1H, Ar), 7.89 (d, *J* = 8.0 Hz, 1H, Ar), 7.77–7.70 (m, 1H+2H, Ar), 5.27–5.24 (m, 2H+2H, C=CH_2), 4.69 (s, 1H, CH_2Cl), 4.68 (s, 1H, CH_2Cl), ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C): δ/ppm 166.36, 151.54, 144.57, 140.59, 139.74, 139.05, 135.06, 130.96, 125.87, 125.26, 125.15, 121.25, 120.63, 92.11, 92.04, 45.22, 45.11.

Synthesis of M2-#

General Procedure: A solution of **M2-Cl**, carboxylic acid (1.1 equimol.), K_2CO_3 (1.1 equimol.), and small amount of 4,4′-methylenebis(2,6-di-tert-butylphenol) as a polymerization inhibitor in DMF (1 mL for 1 mmol of **M2-Cl**) was heated at 95 °C for 1 h. Rapidly cooled by adding water, the product was extracted using ethyl acetate three times, and the combined organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated. The residual liquid was purified by flash column chromatography using a cosolvent of acetone and hexane (v/v= 0/100 to 30/70) as an eluent to afford **M2-#**.

The isomeric mixture of (1-methylene-3-oxo-1,3-dihydroisobenzofuran-5-yl) methyl acetate and (3-methylene-1-oxo-1,3-dihydroisobenzofuran-5-yl)methyl acetate (**M2-C2**)**:** Colorless solids. Yield: 98.0%. Melting point: 64.5–72.6 °C. IR spectra (ATR): *ν*/cm^{-1} 3010 (C-H), 1771 (C=O), 1718 (C=O), 1662 (C=C). ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$): *δ*/ppm 7.90 (d, *J* = 3.2 Hz) and 7.88 (s) (1H, 3-CH), 7.69 (br, 1.41H, 5- and 6-CHs) and 7.54 (d, *J* = 7.8 Hz, 0.59H, 4-CH), 5.25–5.21 (m, 4H, benzyl and vinylidene), 2.15 and 2.13 (s, 3H, CH_3). ^{13}C NMR spectrum (100 MHz, 25 °C, $CDCl_3$): *δ*/ppm 170.55, 166.47, 166.39, 151.55, 143.31, 139.46, 139.22, 138.75, 134.18, 130.07, 125.56, 124.87, 124.44, 120.86, 119.75, 91.71, 65.25, 65.08, 20.89.

The isomeric mixture of (1-methylene-3-oxo-1,3-dihydroisobenzofuran-5-yl) methyl isobutyrate and (3-methylene-1-oxo-1,3-dihydroisobenzofuran-5-yl) methyl isobutyrate (**M2-C4**)**:** Yellow liquid. Yield: 70.7%. IR spectra (ATR): *ν*/cm^{-1} 2975 (C-H), 1780 (C=O), 1731 (C=O), 1661 (C=CH_2). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): *δ*/ppm 7.89–7.87 (m, 1H, 3-CH), 7.71–7.67 (1.53H, 5-CH and 6-CH), 7.53 (d, *J* = 8.3 Hz, 0.47H, 4-CH), 5.23–5.20 (m,4H, benzyl and vinylidene), 2.67–2.58 (m, 1H, CH), 1.20 (d, *J* = 6.8 Hz,) and 1.18 (d, *J* = 6.8 Hz) (3H, methyl). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C): *δ*/ppm 176.75, 176.70, 166.57, 166.49, 151.67, 151.64, 143.77, 139.62, 139.53, 138.77, 134.16, 129.97, 125.65, 125.62, 124.85, 124.34, 120.96, 119.64, 91.72, 91.71, 65.12, 64.99, 34.03, 19.02.

The isomeric mixture of (1-methylene-3-oxo-1,3-dihydroisobenzofuran-5-yl) methyl octanoate and (3-methylene-1-oxo-1,3-dihydroisobenzofuran-5-yl) methyl octanoate (**M2-C8**)**:** Yellow liquid. Yield: 79.2%. IR spectra (ATR): *ν*/cm^{-1} 2985 cm^{-1} (C-H), 2857 cm^{-1} (C-H), 1782 cm^{-1} (C=O), 1735 cm^{-1} (C=O), 1662 cm^{-1} (C=C), ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): *δ*/ppm 7.90–7.88 (m, 1H, 3-CH), 7.72–7.71 (1.43H, 5- and 6-CHs), 7.56 (d, *J* = 7.4 Hz, 0.57H, 4-CH), 5.26–5.22 (m,4H, benzyl and vinylidene), 2.43–2.37 (m, 2H, OCH_2), 1.69–1.63 (m, -$OCOCH_2CH_2$-), 1.30–1.29 (8H, –CH_2–), 0.89–0.85 (3H, –CH_3). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C): *δ*/ppm 173.39, 173.46, 166.50, 166.43, 151.63, 151.60, 143.64, 139.50, 139.48, 138.73, 134.24, 130.07, 125.58, 125.54, 124.80, 124.42, 120.90, 119.74, 91.68, 91.66, 65.06, 64.91, 34.21, 31.68, 28.93, 24.95, 22.62, 14.09.

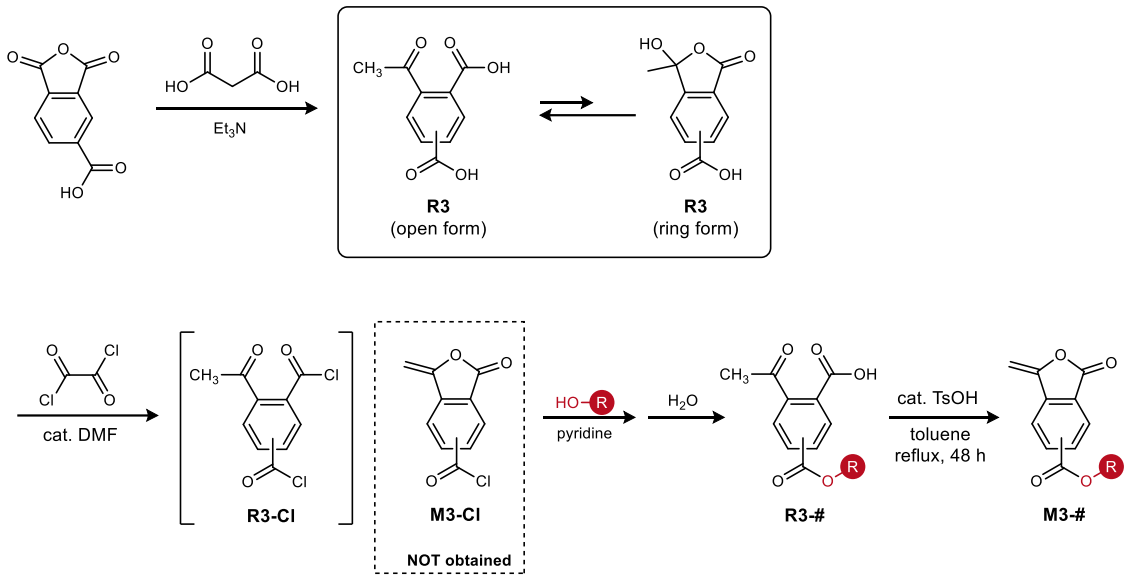


Figure S2: Synthesis route of **R3-#**.

The mixture of 2-acetylisophthalic acid and 4-acetylisophthalic acid (**R3**)
Malonic acid (25.0 g, 240 mmol) was added in small portions to a suspension of trimellitic anhydride (**7**, 38.4 g, 200 mmol) in TEA (55.8 mL, 400 mmol) heated at 70 °C. The mixture was stirred at 70 °C for 18 h and 4 M HCl aq. (200 mL) was added before cooling. The acidified solution was cooled to room temperature and stored in a refrigerator (4–5 °C) overnight. The precipitate was collected by filtration, washed with water, and dried in *vacuo* to afford **R3** (9.64 g, yield: 25.1%). The crude product was used in the next reaction without further purification.

Synthesis of M3-#

General Procedure: A suspension of **R3** (4.00 g, 19.2 mmol) in oxalyl chloride (10 mL) was refluxed for 3 h in the presence of DMF (0.02 mL). After cooling, the resulting solution was concentrated. The residue containing **R3-Cl** was dissolved in CH_2Cl_2 (100 mL) with alcohol (1 equimolar), and a pyridine (2.0 equimolar) solution in CH_2Cl_2 (20 mL) was added at 0 °C. The reaction mixture was stirred at 25 °C for 12 h, washed with 1 M HCl aq. (100 mL × 3) and brine (100 mL × 3). The combined organic layer was dried over $MgSO_4$, concentrated, and dried *in vacuo*. The residue containing **R3-#** (4.10 g) and 4,4'-methylenebis(2,6-di-*tert*-butylphenol), a polymerization inhibitor, were refluxed in toluene (200 mL) with the Dean-Stark apparatus for 15 min. *p*-Toluenesulfonic acid monohydrate (0.301 g, 1.58 mmol) was added to the solution, and the solution was refluxed for 36 h. After cooling, *sat.* $NaHCO_3$ aq. was added to quench the reaction, and the organic layer was concentrated. The residue was dissolved in ethyl acetate (100 mL), washed by *sat.* $NaHCO_3$ aq. (100 mL × 3), water (100 mL × 3), and brine (100 mL × 3), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography using a cosolvent of acetone/hexane (v/v = 0/100 to 20/80) to afford **M3-C#**.

isopropyl 1-methylene-3-oxo-1,3-dihydroisobenzofuran-5-carboxylate (**M3-C3p**): Yellow solid. Yield: 26.2%. Melting point: not observed (polymerized at 102–104 °C). IR spectrum (ATR): ν/cm^{-1} 1773 (C=O), 1708 (C=O), 1661 (C=C). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): δ/ppm 8.56 (s, 1H, 3-CH), 8.49 (d, J = 8.2 Hz, 1H, 5-CH), 7.78 (d, J = 8.2 Hz, 1H, 6-CH), 5.35 (d, J = 3.2 Hz, 1H, -C=C*H*H), 5.34 (d, J = 3.2 Hz, 1H, -C=C*H*H), 5.29 (m, 1H, -C(=O)OC*H*-), 1.40 (d, J = 6.3 Hz, 6H, -CH_3), ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C): δ/ppm 166.13, 164.46, 151.43, 142.22, 135.64, 133.49, 127.02, 125.50, 120.78, 93.61, 69.70, 30.45, 22.04.

isopropyl 3-methylene-1-oxo-1,3-dihydroisobenzofuran-5-carboxylate (**M3-C3m**): Yellow solid. Yield: 12.5%. Melting point: 96-98 °C, IR spectrum (ATR): ν/cm^{-1} 1772 (C=O), 1701 (C=O), 1660 (C=C), ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): δ/ppm 8.36 (s, 1H, 6-CH), 8.23 (dd, J_1 = 8.2 Hz, J_2=1.1 Hz, 1H, 4-CH), 7.96 (dd, J = 8.2 Hz, 1H, 3-CH), 5.34 (d, J = 3.0 Hz, 1H, –C=C*H*H), 5.31 (d, J = 3.0 Hz, 1H, –C=C*H*H), 5.32–5.28 (m, 1H, *O*-CH), 1.41 (d, J = 6.4 Hz, 6H, –CH_3). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C): δ/ppm 166.10, 164.63, 151.41, 139.12, 136.83, 131.50, 128.25, 125.43, 122.12, 92.52, 69.93, 30.43, 22.01.

M3-C8 (isomer mixture): Yellow liquid. Yield: 8.5%. IR spectrum (ATR): ν/cm^{-1} 1772 (C=O), 1701 (C=O), 1660 (C=CH_2). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): δ/ppm 8.53 (br, 0.66H, 3-CH), 8.38 (dd, J_1 = 8.3 Hz, J_2 = 1.4 Hz, 0.66H, 5-CH), 8.34 (br, 0.34H, 6-CH), 8.21 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 0.34H, 4-CH), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 0.6 Hz, 0.34H, 3-CH), 7.77 (dd, J_1 = 8.3 Hz, J_2 = 0.7 Hz, 1H, 6-CH), 5.33–5.28 (m, 2H, CH_2=), 5.20–5.15 (m, 1H, *O*-CH), 1.78-1.57 (m, 2H, –OCOCHC*H*$_2$–), 1.39–1.26 (m, 10H, –CH_2–),

0.85 (t, J = 6.6 Hz, 3H, CH_3). ^{13}C NMR spectrum (100 MHz, 25 °C, $CDCl_3$): 165.97, 165.93, 164.60, 164.42, 151.28, 142.07, 139.00, 136.73, 135.51, 133.34, 131.35, 128.11, 126.79, 125.35, 125.30, 121.99, 120.69, 93.45, 92.37, 73.20, 72.96, 53.45, 35.97, 35.93, 31.70, 29.10, 25.40, 20.02, 20.00.

Radical polymerization

A general procedure: AIBN (2 mol%) was added to a monomer solution in DMF (1.0 M), and the solution was degassed using a freeze-pump-thaw cycle three times. The solution was stirred at 65 °C for 18 h and was poured into methanol (100 mL). The precipitate was collected by filtration and dried *in vacuo* to afford the corresponding polymers.

Cationic polymerization

A typical example (**Table S2**, entry 3): CH_2Cl_2 and 1-isobutoxyethyl acetate (IBEA) were used after vacuum distillation followed by drying over CaH_2. **M1** (0.731 g, 5.0 mmol) was placed in a 50 mL flask equipped with a three-way cock and displaced with dry nitrogen. A CH_2Cl_2 solution of IBEA (0.530 M, 0.19 mL, 0.10 mmol) and CH_2Cl_2 (8.1 mL) was introduced by syringe. The reaction system was cooled at 0 °C, and a CH_2Cl_2 solution of $BF_3{\cdot}OEt_2$ (0.478 M, 0.21 mL, 0.10 mmol) was added to initiate polymerization. After 2 h, methanol (0.75 mL) was added to stop the polymerization. The reaction mixture was diluted with $CHCl_3$ and washed with 1 M aq. HCl (20 mL, two times) and H_2O (20 mL). The organic layer was concentrated. The resulting white solid was dissolved in DMSO, then reprecipitated in acetone for purification (Yield: 29%, M_n = 59300 g/mol, $Đ$ = 7.23).

Polymer Degradation

A general procedure: 10 M NaOH aq. (3.0 equimolar to the ester bonds) was added to a polymer (100 mg) solution in DMSO (1.0 mL). The solution was stirred at 25 or 70 °C. A small portion was sampled at the predetermined time and quenched using acetic acid for the SEC measurement. The reaction mixture was finally quenched using 1 M HCl aq. until the pH became below 7, and the product was extracted with ethyl acetate (10 mL, three times). In the case of **P2-C2$_{50}$C8$_{50}$,** the concentrated organic layer was further washed with hexane to separate the *n*-octanoic acid derived from the C8 pendant. *n*-octanoic acid was isolated by drying the hexane layer following washing with water.

Additional figures, charts, and schemes

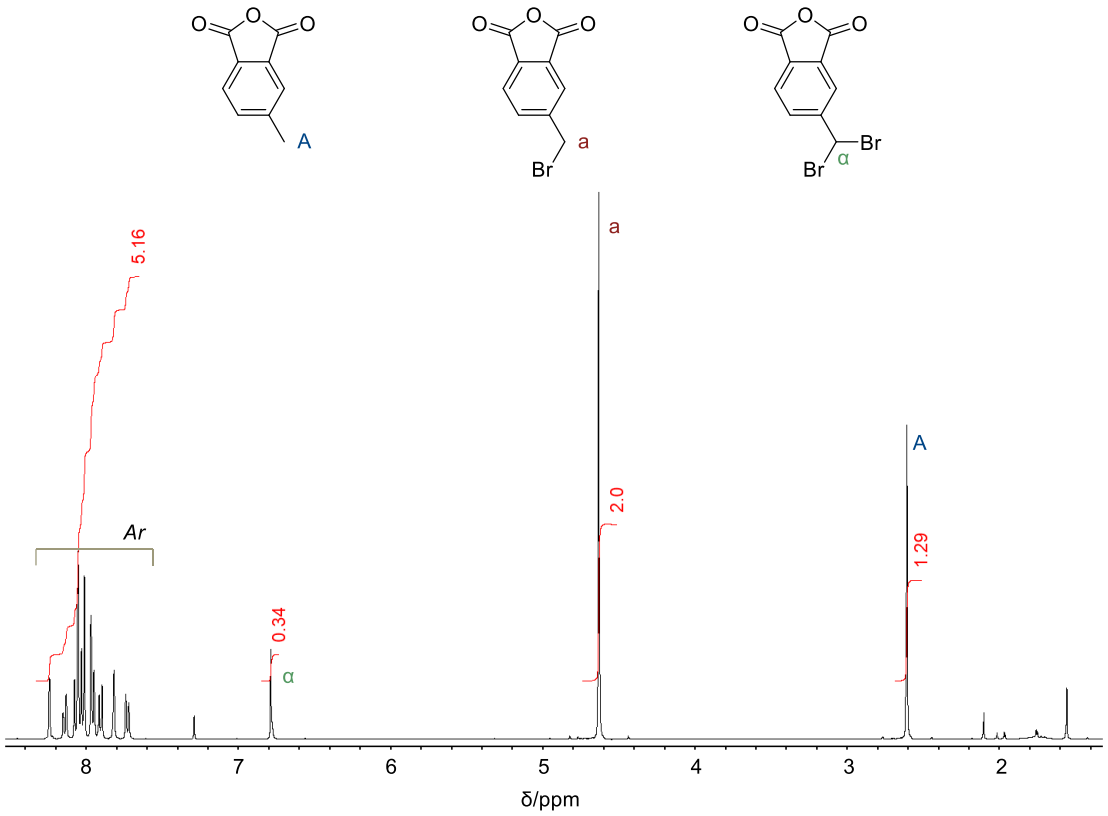


Figure S3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of crude product containing **5.**

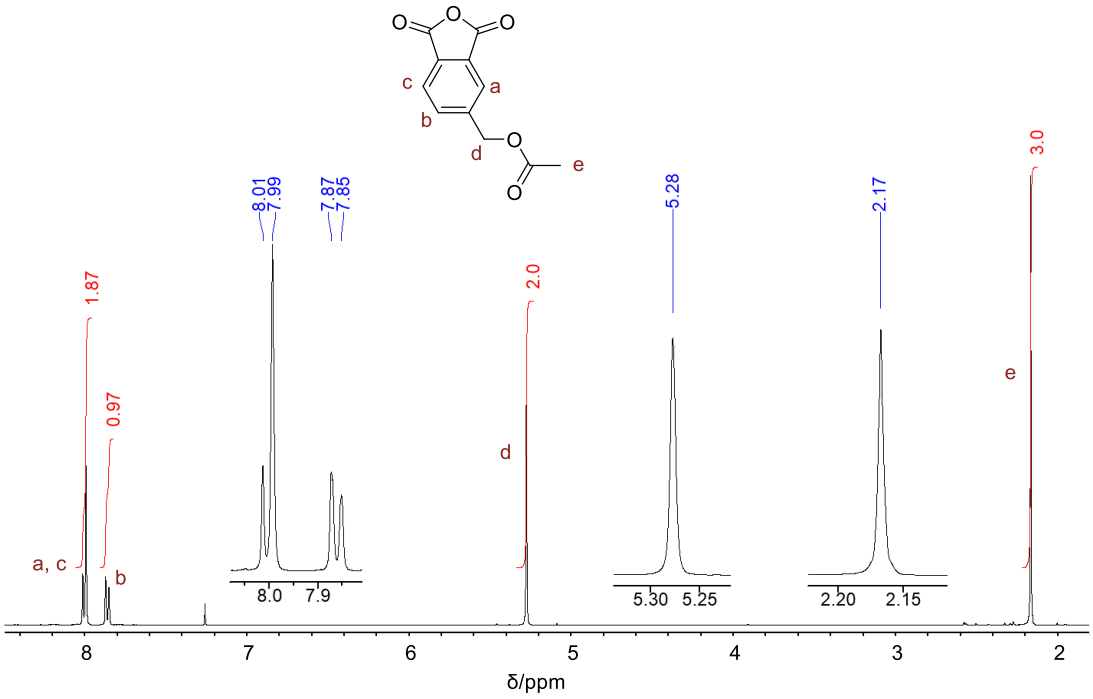


Figure S4: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **6.**

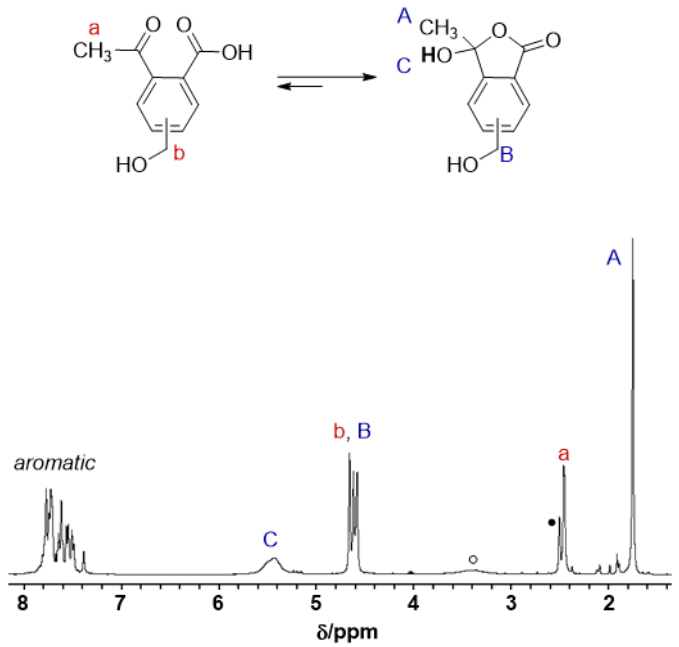


Figure S5: ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of crude **R2.** ●: DMSO

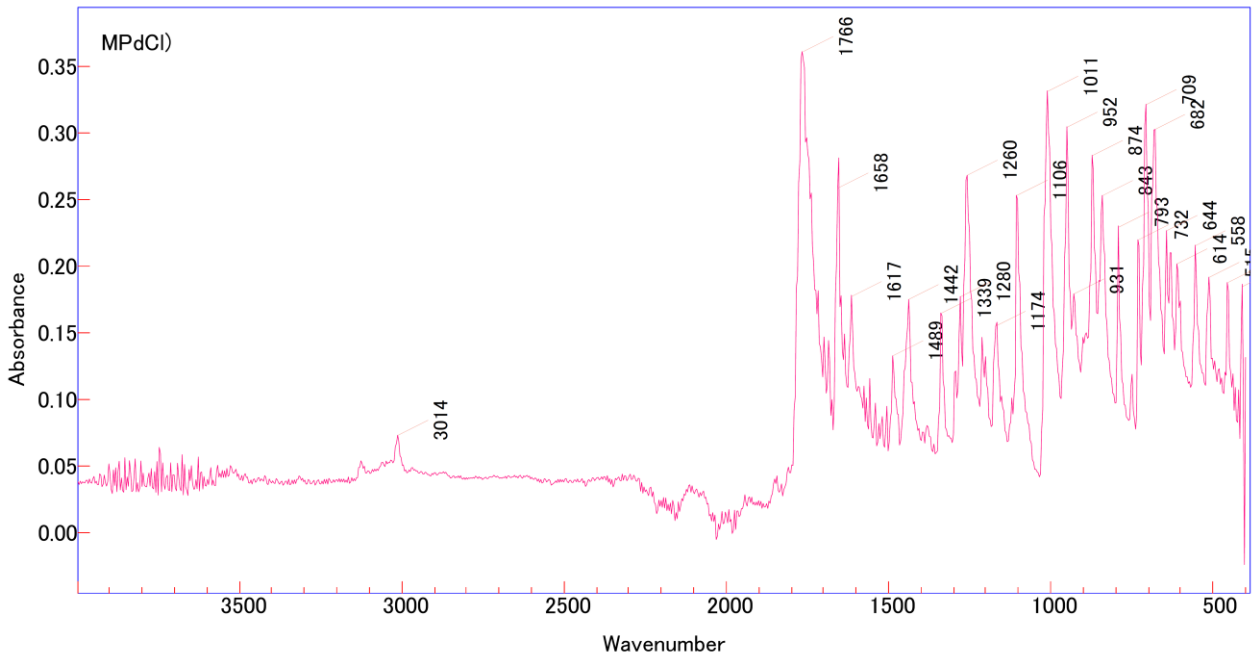


Figure S6: IR spectrum of **M2-Cl** (ATR).

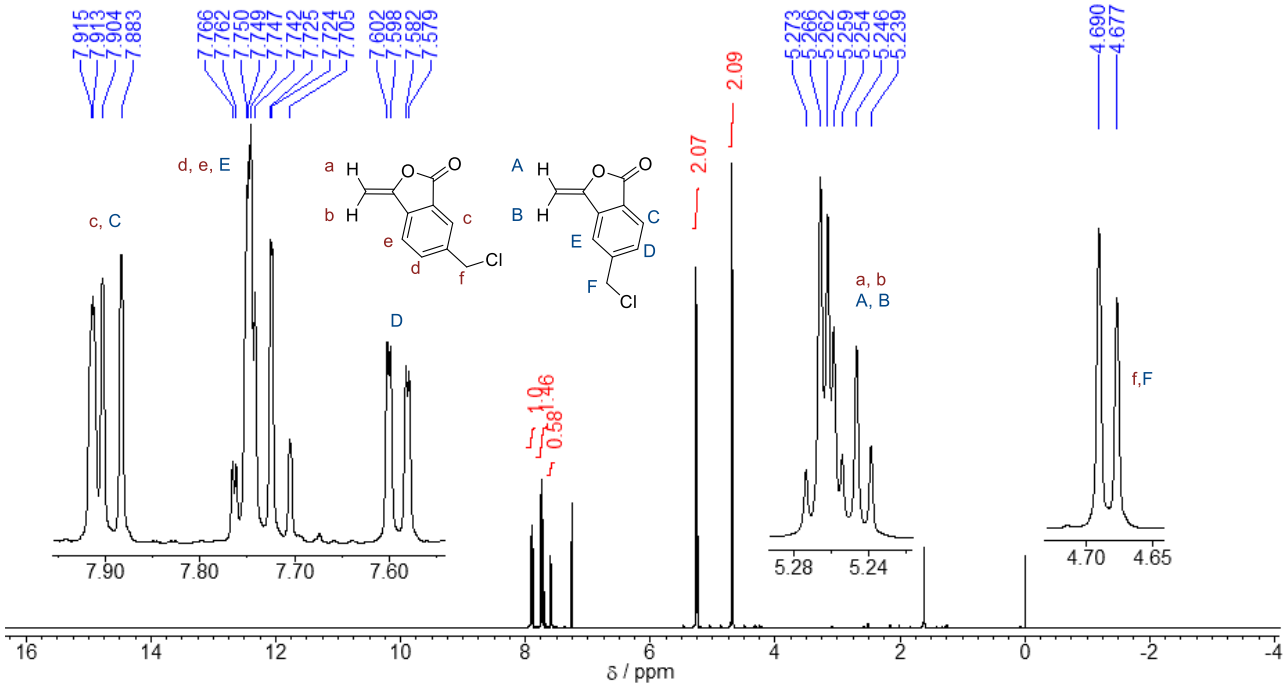


Figure S7: ^{1}H NMR spectrum of **M2-Cl** (400 MHz, $CDCl_3$, 25 °C).

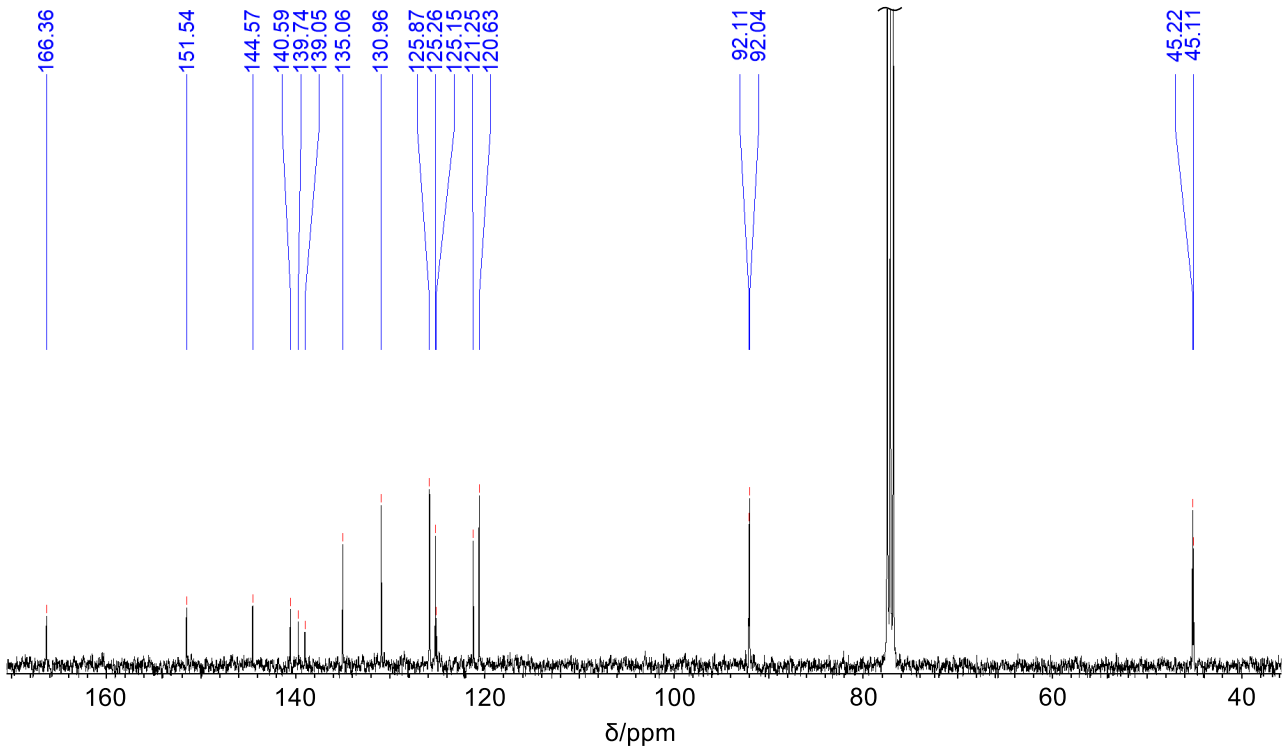


Figure S8: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **M2-Cl**.

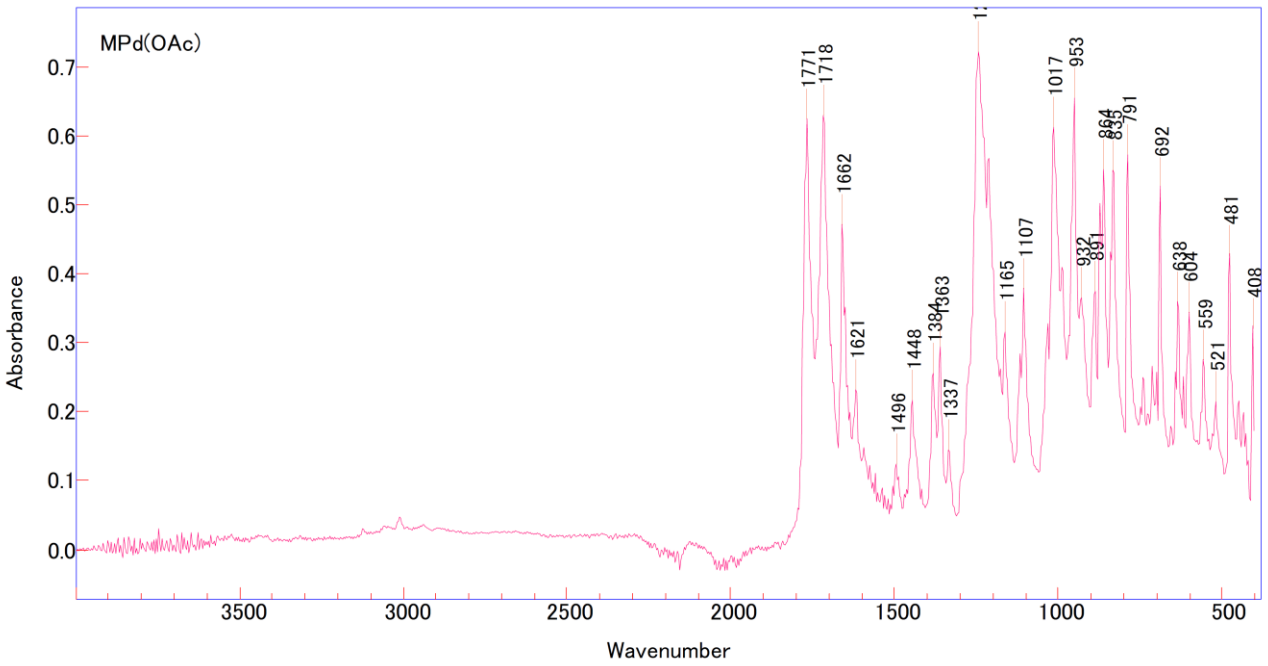


Figure S9: IR spectrum of **M2-C2** (ATR).

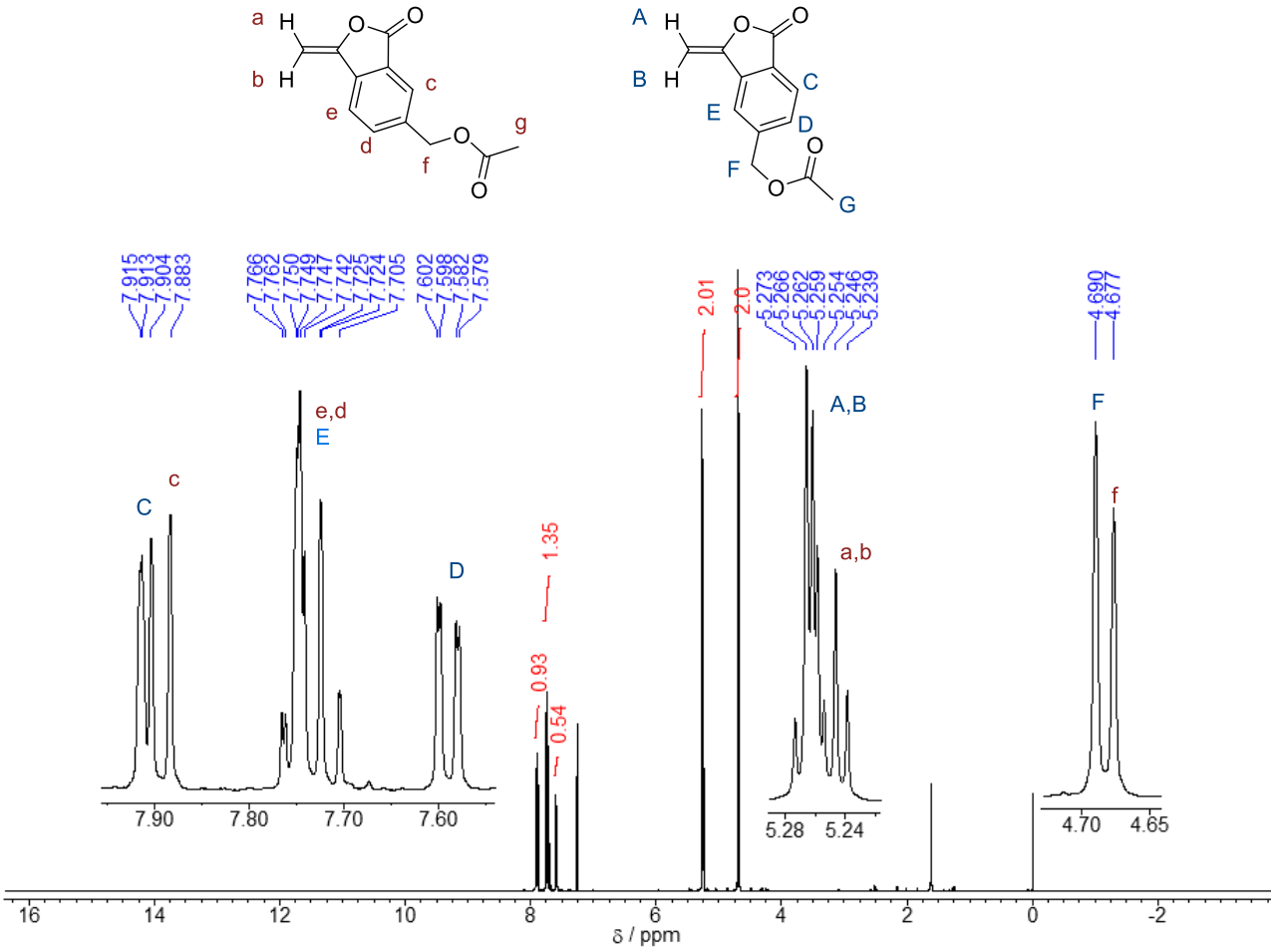


Figure S10: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **M2-C2.**

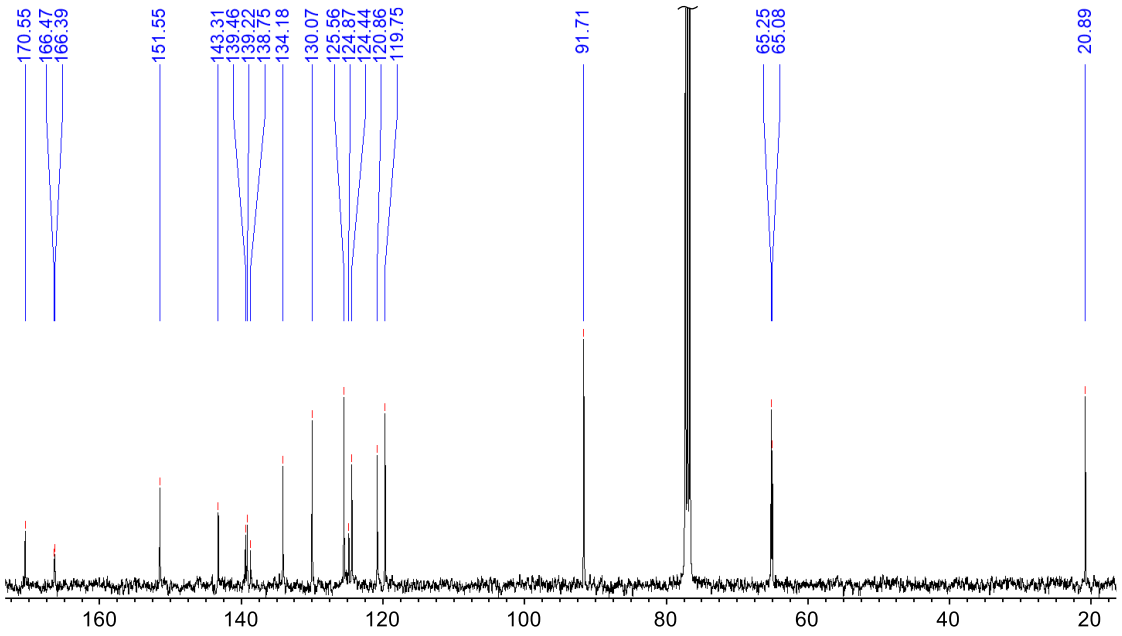


Figure S11: ^{13}C NMR spectrum of **M2-C2** (100 MHz, $CDCl_3$, 25 °C).

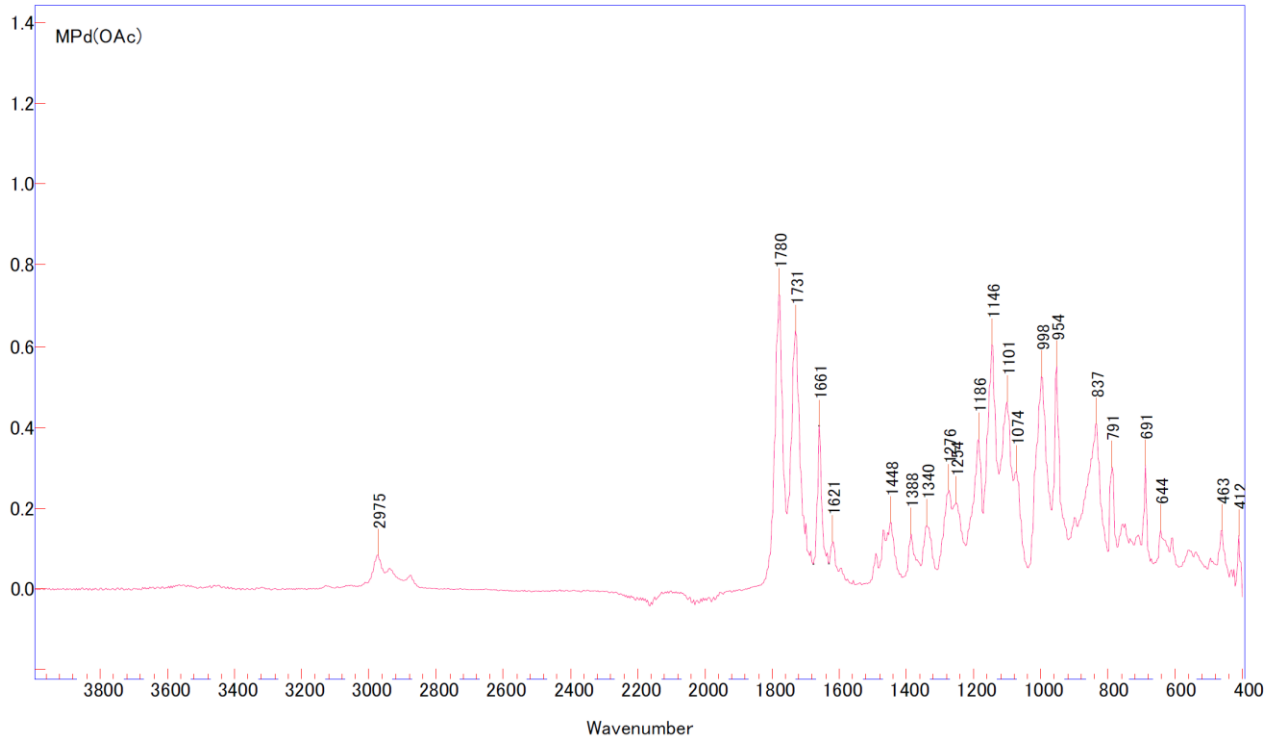


Figure S12: IR spectrum of **M2-C4** (ATR).

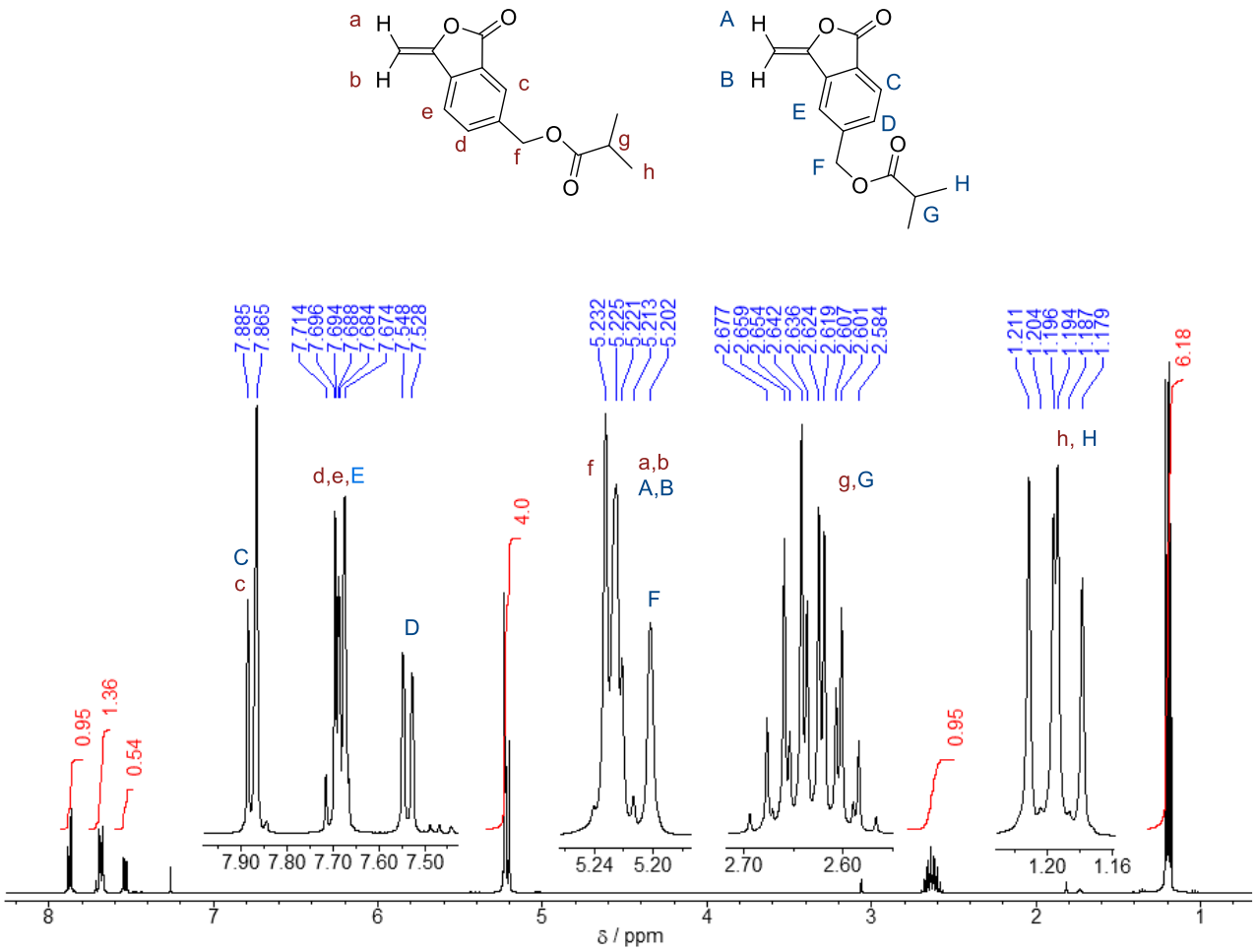


Figure S13: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **M2-C4.**

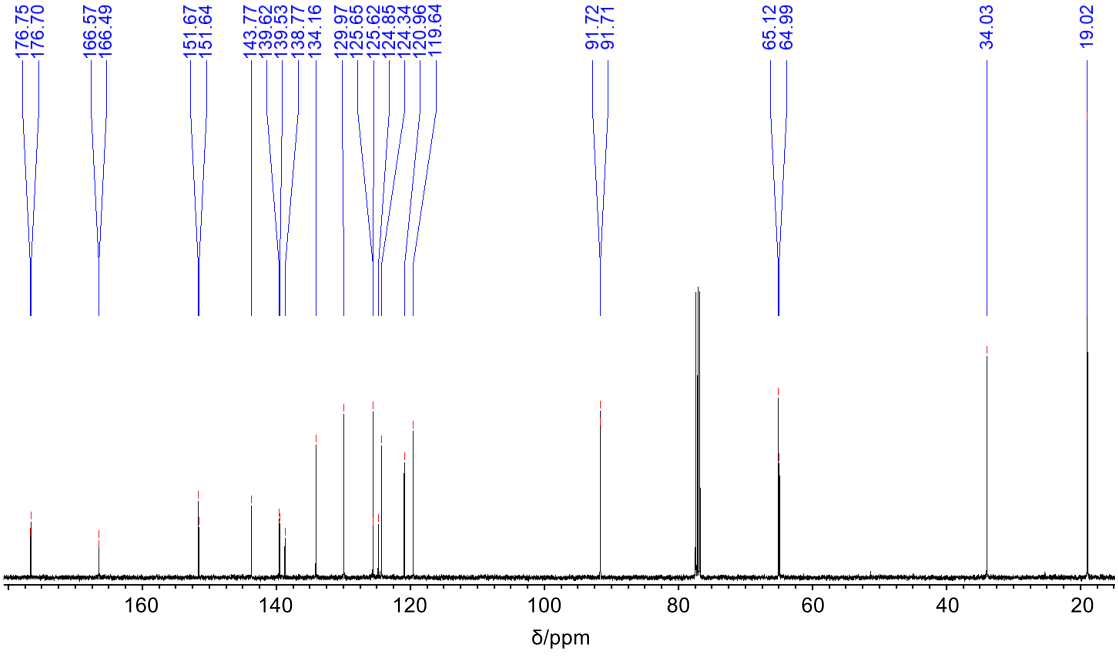


Figure S14: ^{13}C NMR spectrum of **M2-C4** (100 MHz, $CDCl_3$, 25 °C).

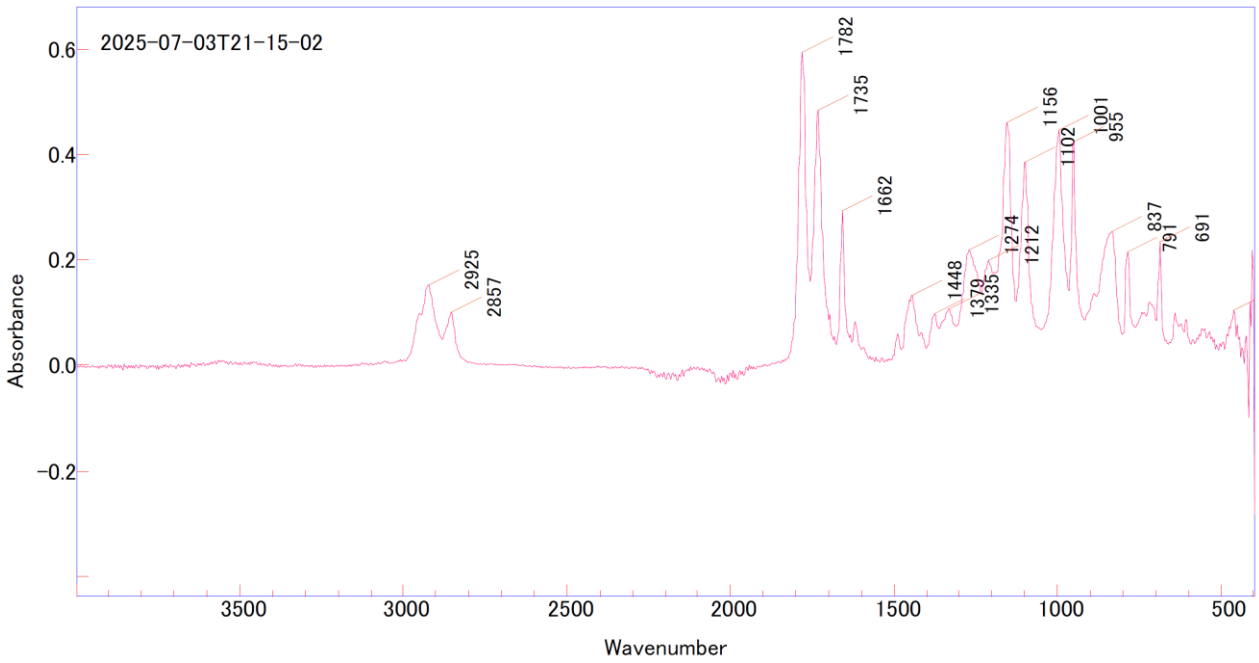


Figure S15: IR spectrum of **M2-C8** (ATR).

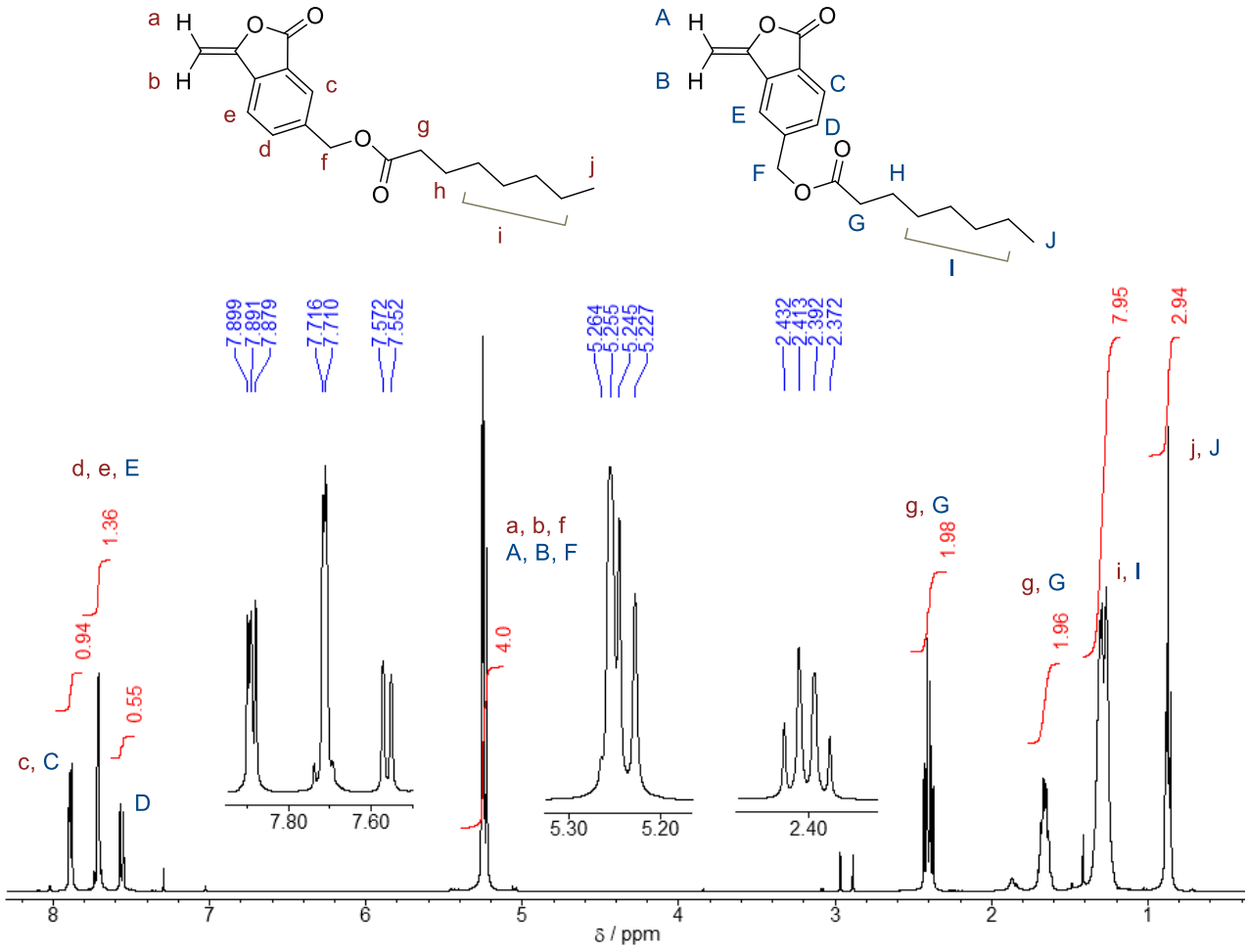


Figure S16: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **M2-C8.**

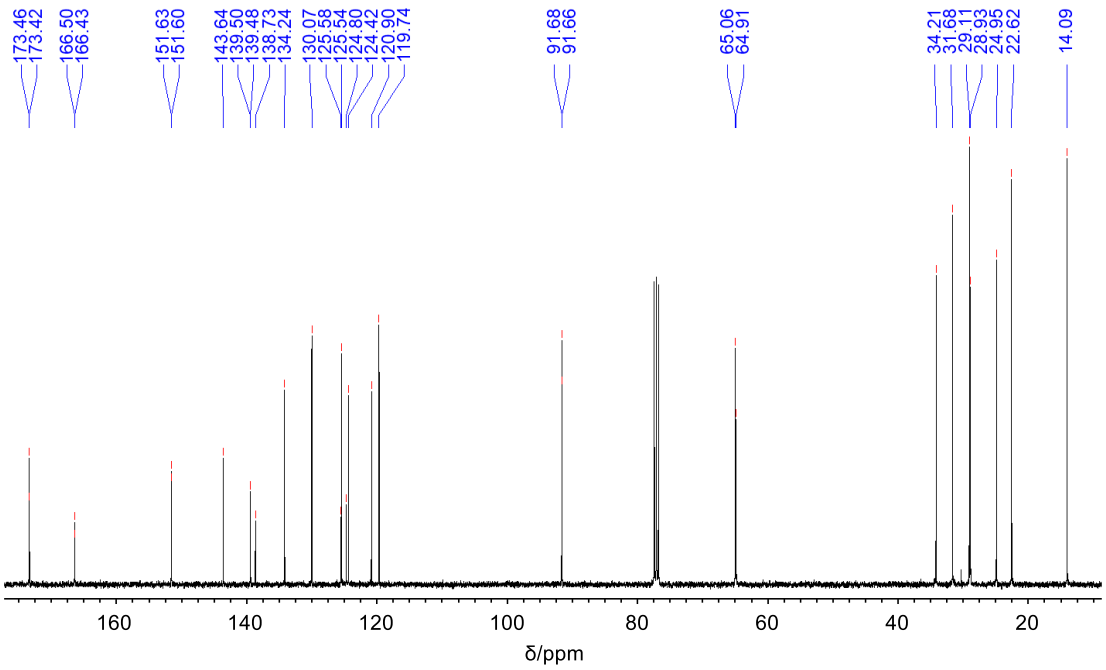


Figure S17: ^{13}C NMR spectrum of **M2-C8 (100 MHz, $CDCl_3$, 25 °C).**

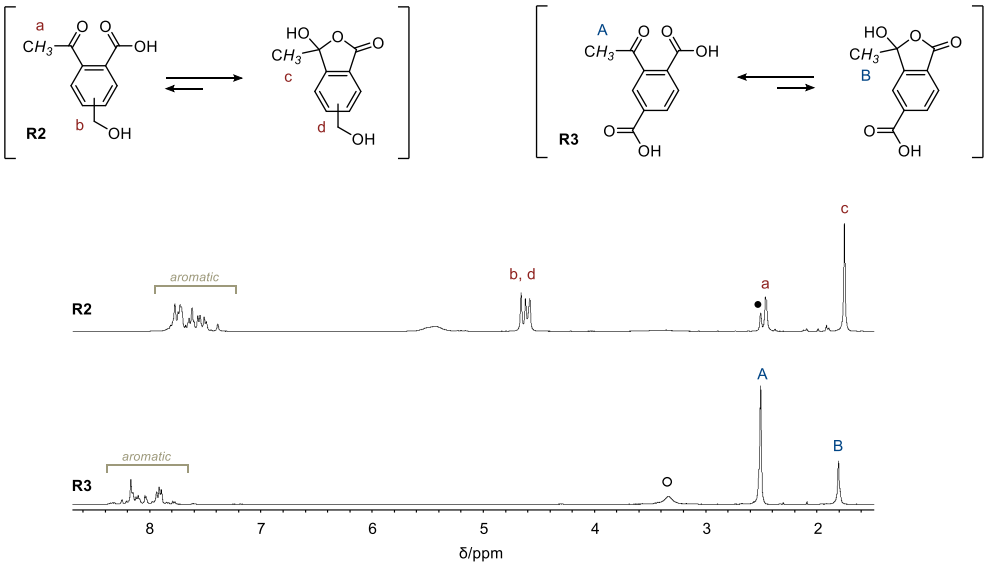


Figure S18: ^{1}H NMR spectra of **R2** and **R3** (400 MHz, DMSO-d_6, 25 °C). ○: H_2O. ●: DMSO.

Table S1. Mono-esterification of R3-C3 with ROH at −40 °C.

Entry	ROH	Base	Composition[a] [%]	
			R3-C3	byproduct
1	*tert*-butanol	Lutidine	*Not proceeded*	*Not proceeded*
2		Pyridine	*Not proceeded*	*Not proceeded*
3	Isopropanol	Lutidine	42	58
4		Pyridine	48	52

Reaction was conducted with equimolar amounts of **R3-C3**, ROH, and base in CH_2Cl_2 (0.1 M) at -40 °C for 24 h, followed by quenching with H_2O. [a] The composition of crude products was determined by ^{13}C NMR spectrum.

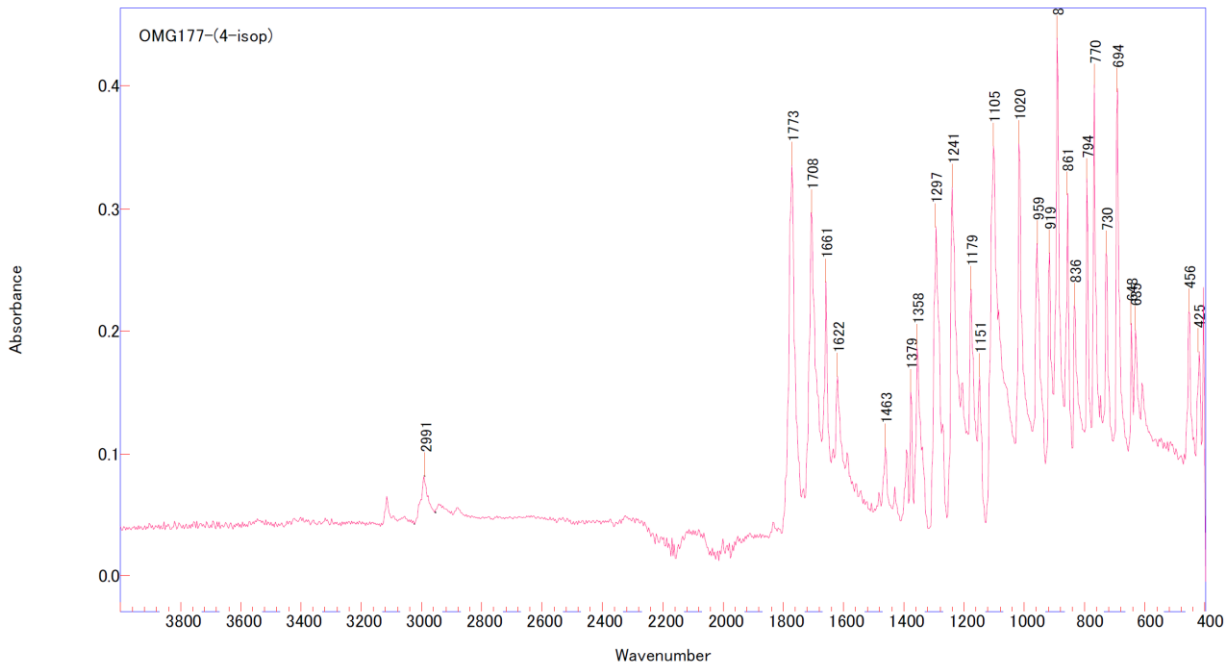


Figure S19: IR spectrum of **M3-C3p** (ATR).

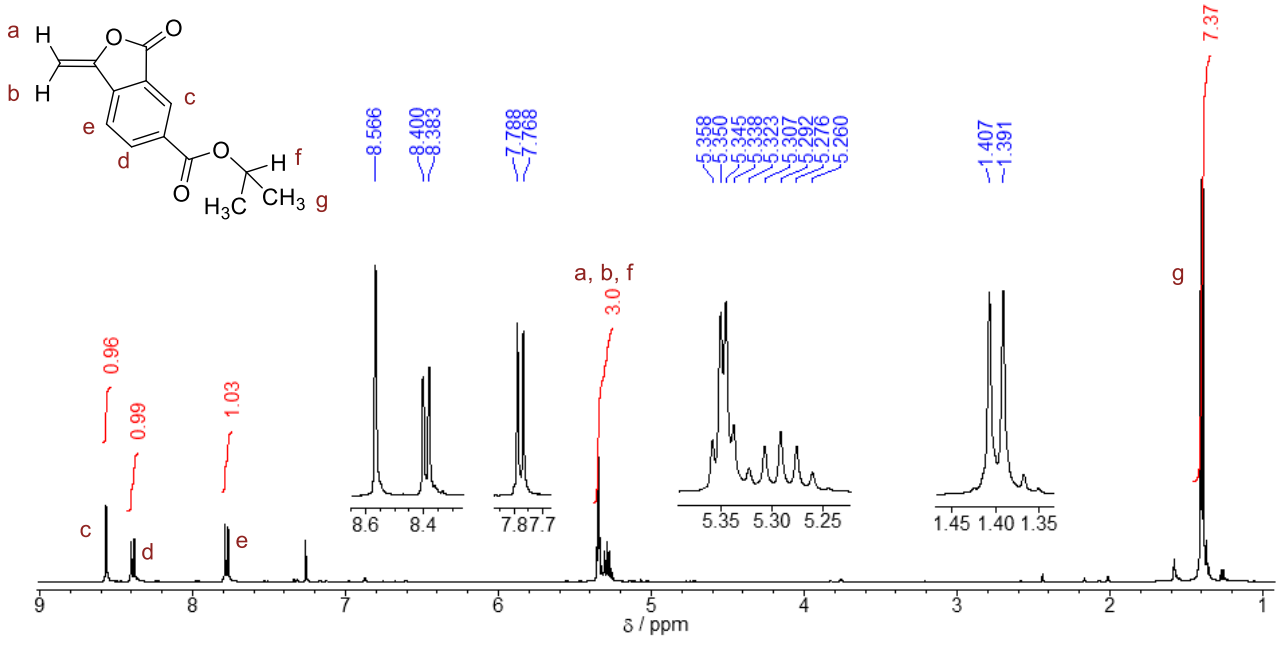


Figure S20: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **M3-C3p.**

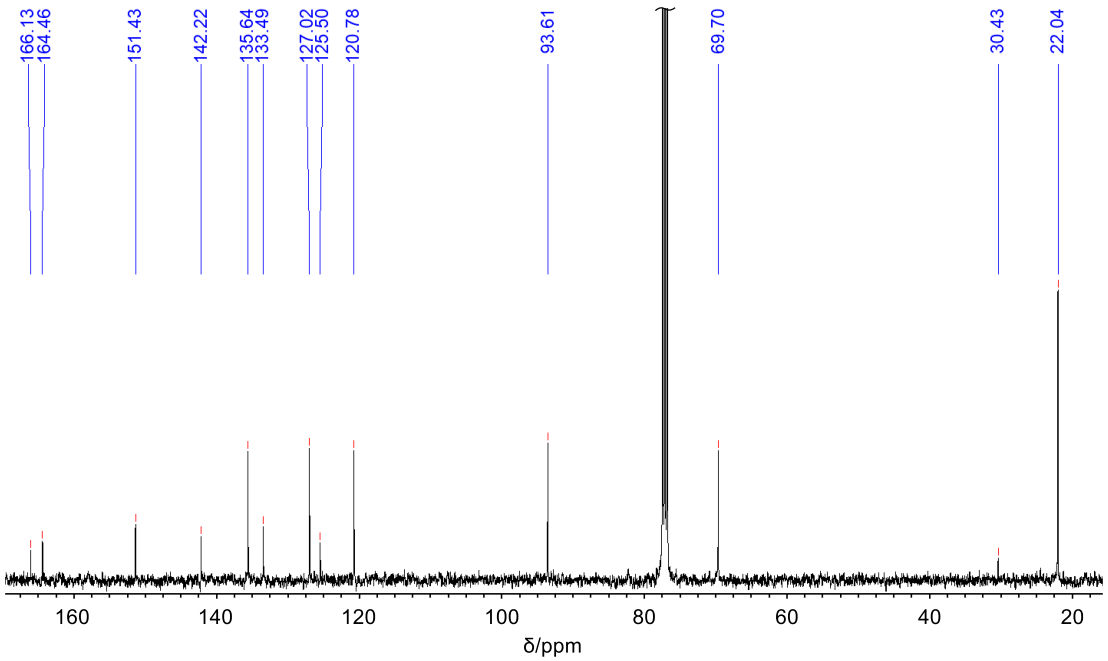


Figure S21: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **M3-C3p.**

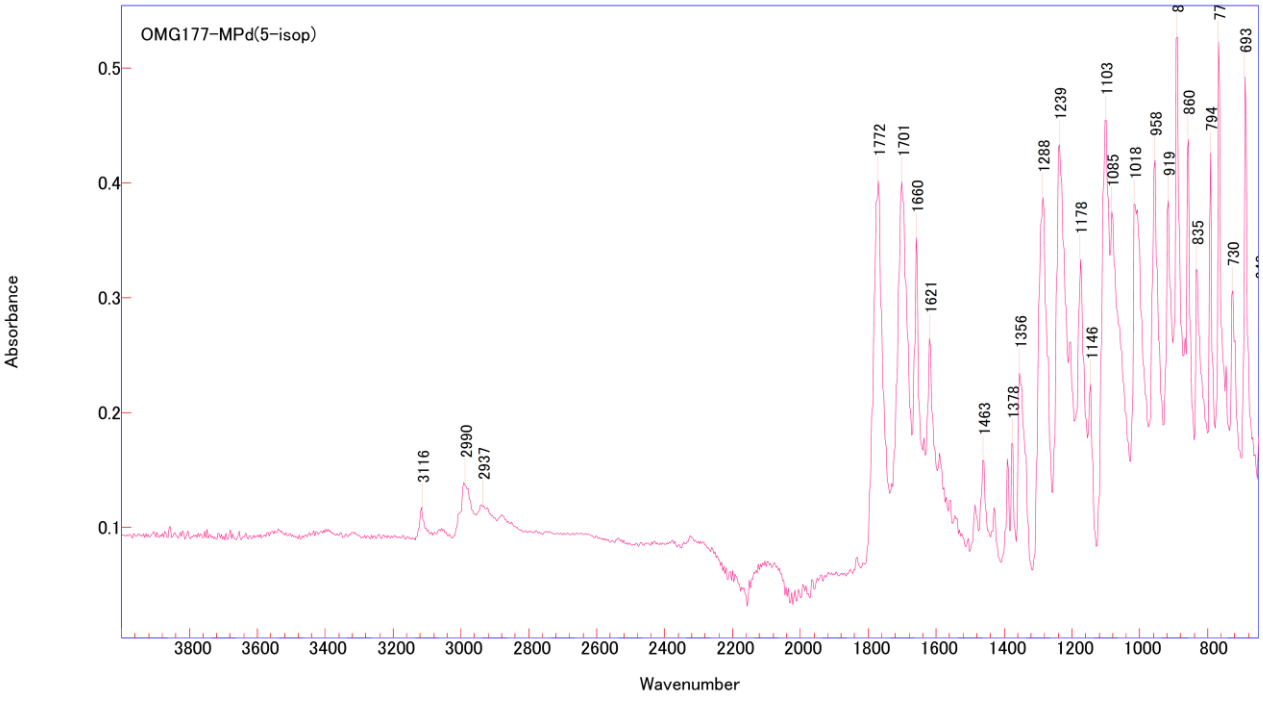


Figure S22: IR spectrum of **M3-C3m** (ATR).

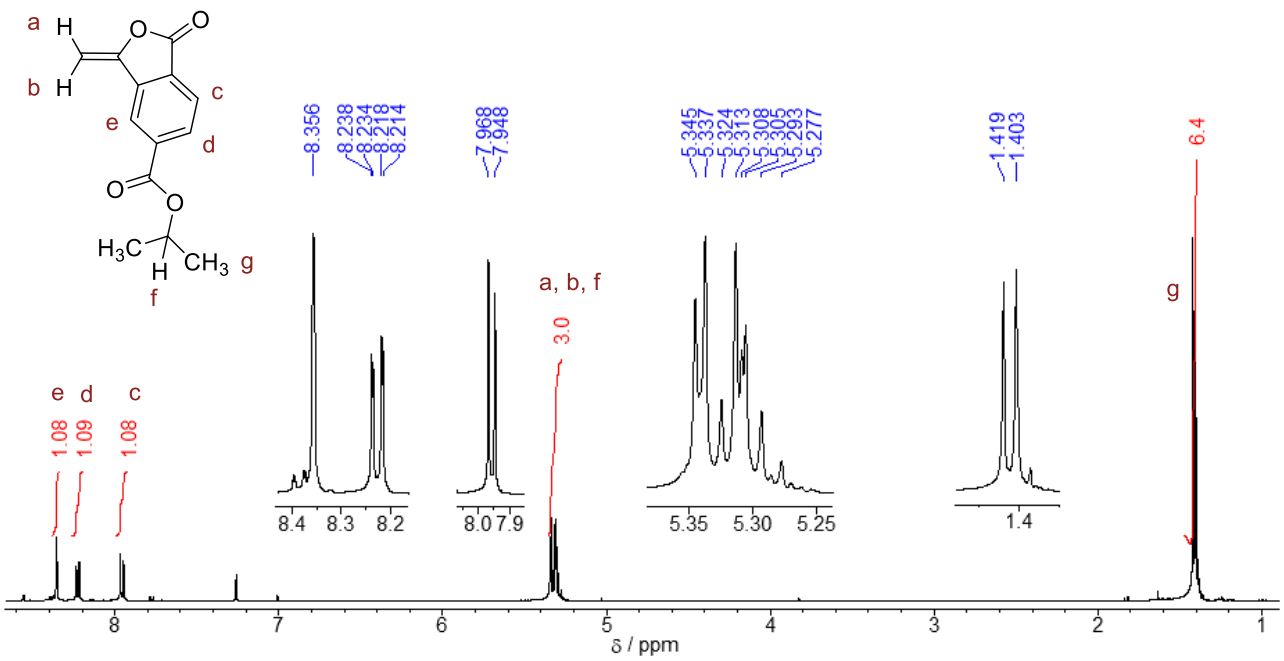


Figure S23: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **M3-C3m.**

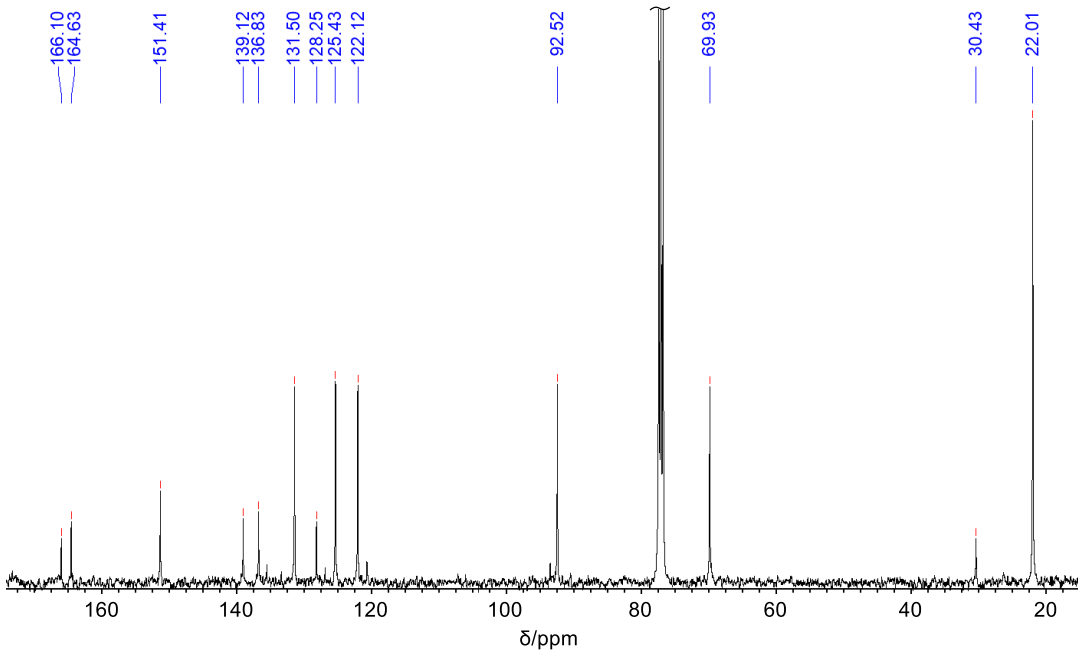


Figure S24: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **M3-C3m.**

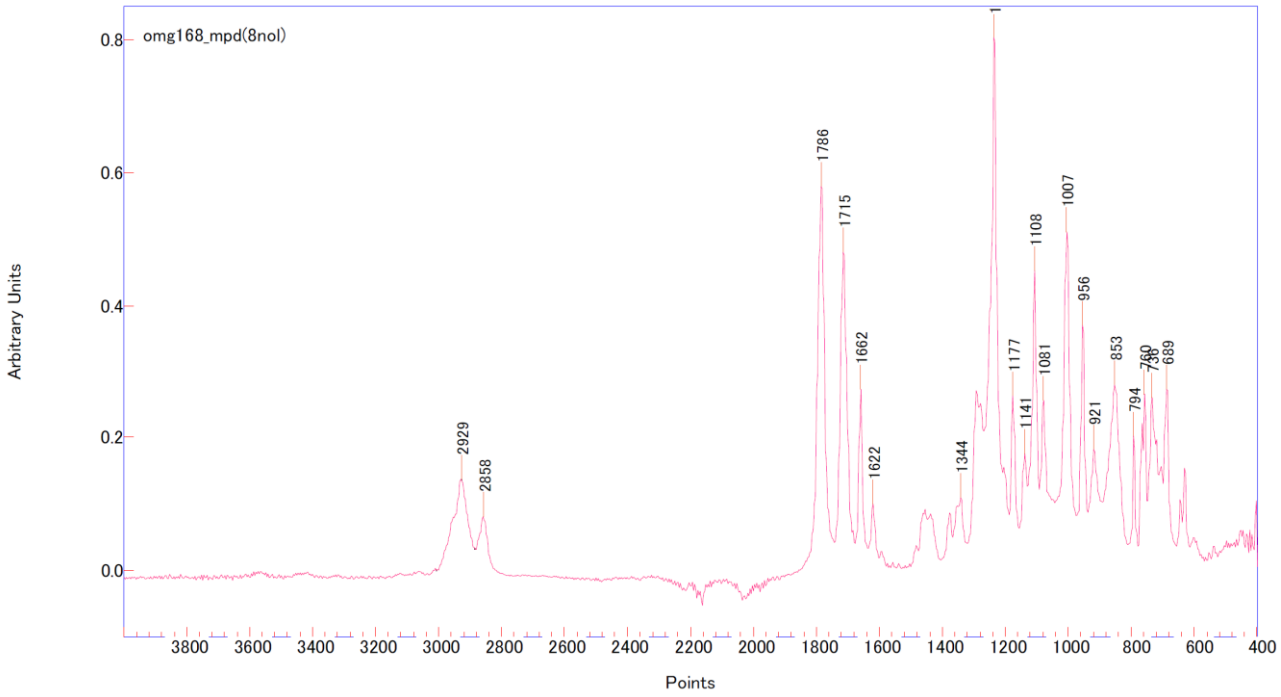


Figure S25: IR spectrum of **M3-C8** (ATR).

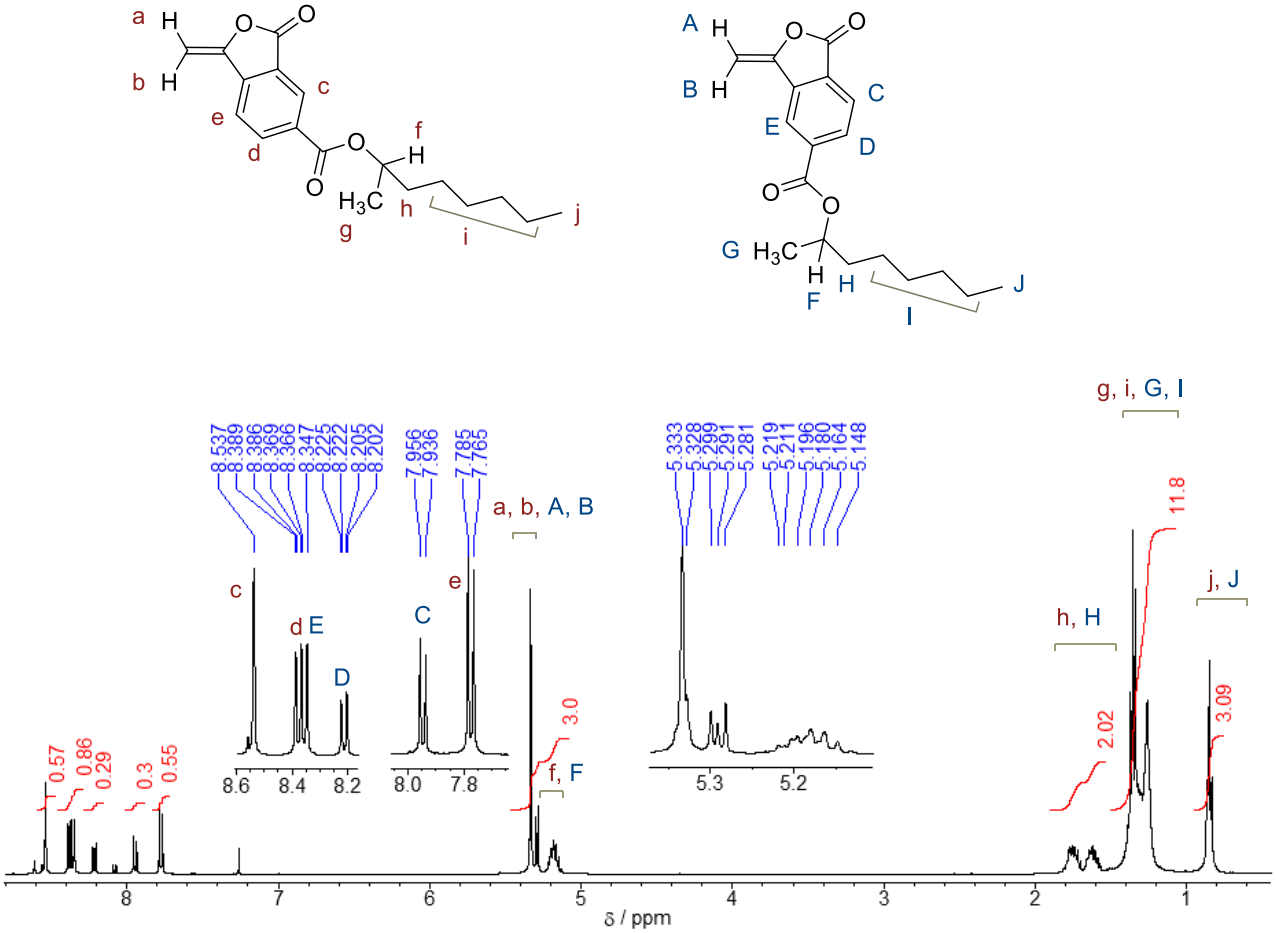


Figure S26: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **M3-C8.**

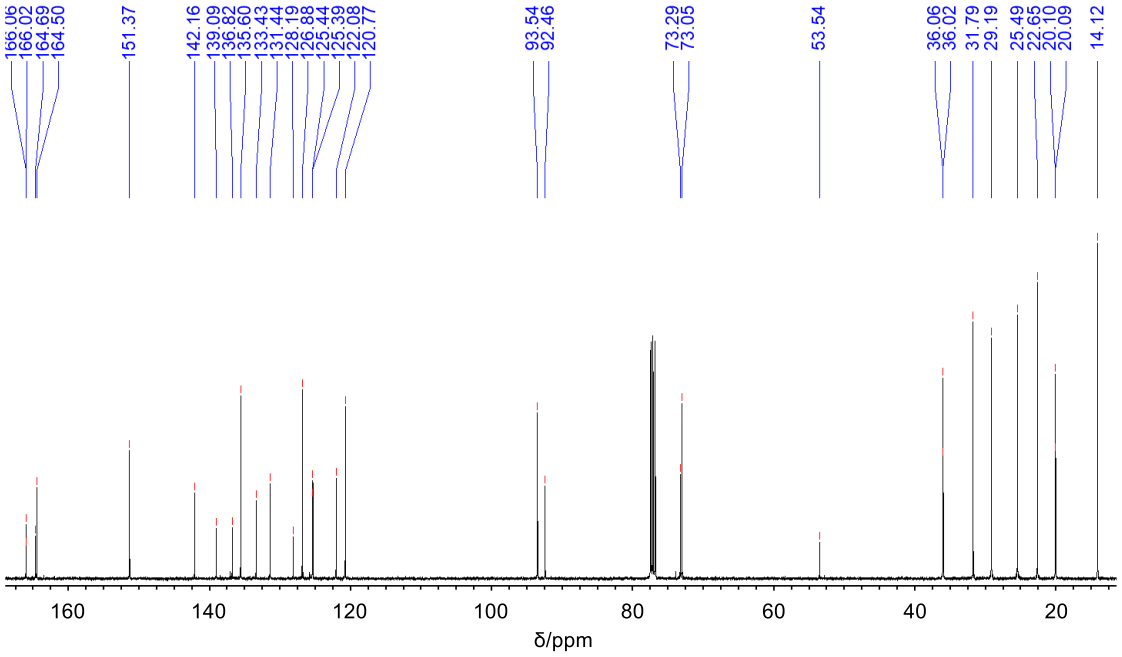


Figure S27: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **M3-C8.**

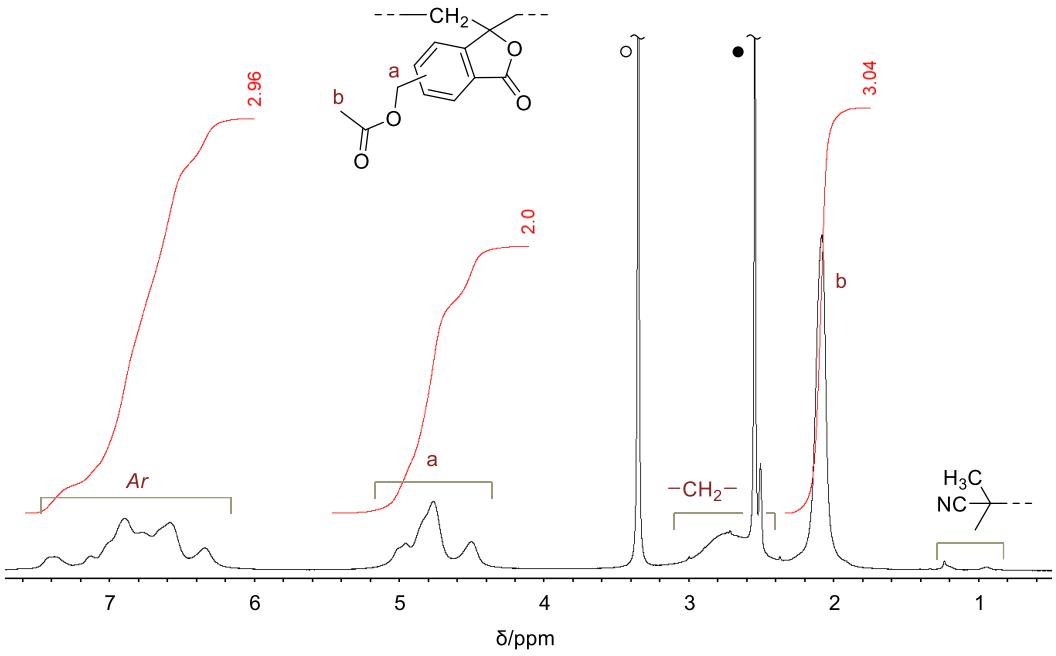


Figure S28. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of **P2-C2.** ○: H_2O. ●: DMSO.

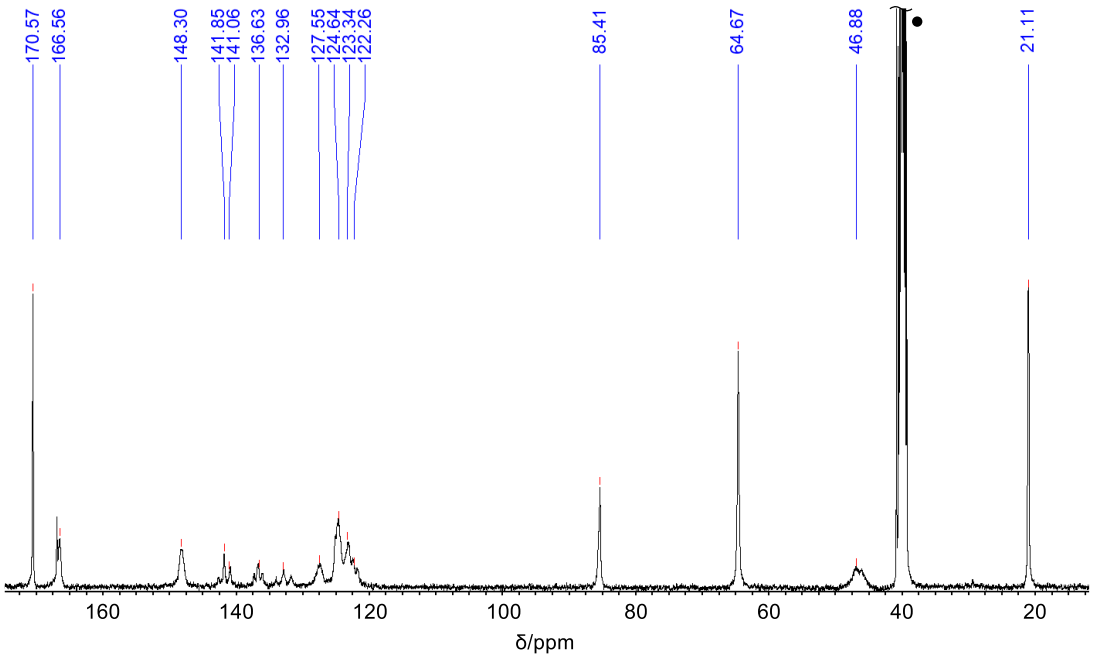


Figure S29: ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 25 °C) of **P2-C2**. ●: DMSO.

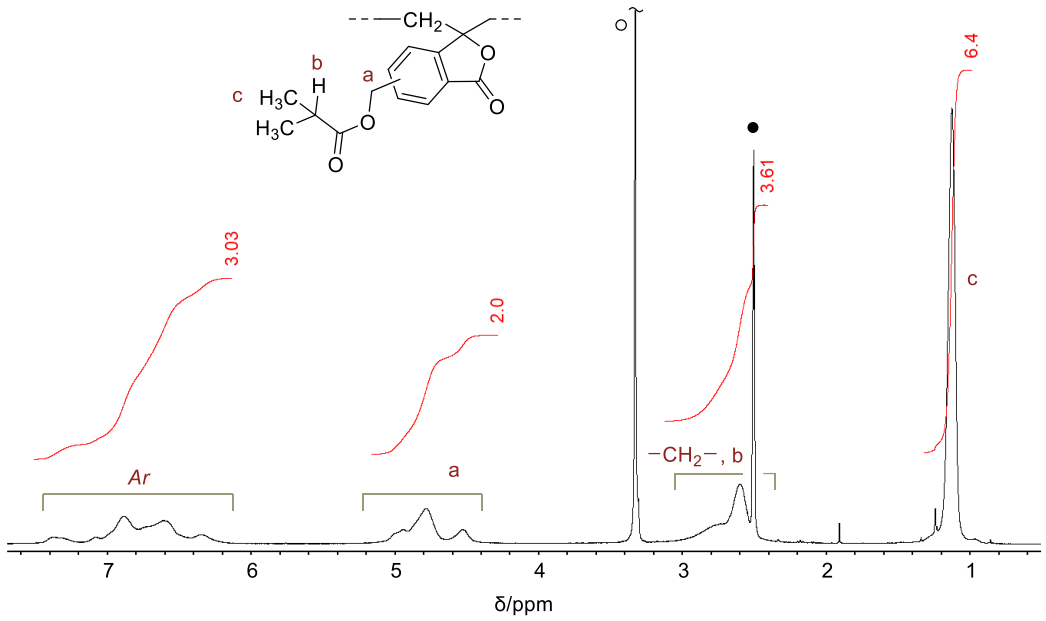


Figure S30: ^{1}H NMR spectra (400 MHz, DMSO-d_6, 25 °C) of **P2-C4**. ○: H_2O. ●: DMSO.

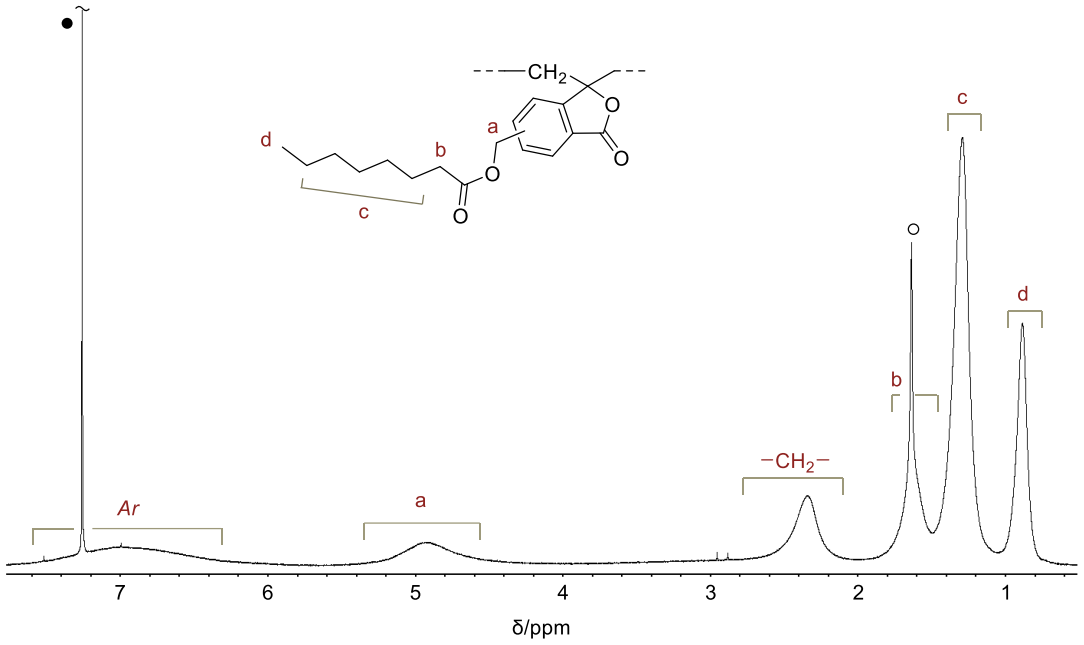


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **P2-C8.** ○: H_2O. ●: $CHCl_3$.

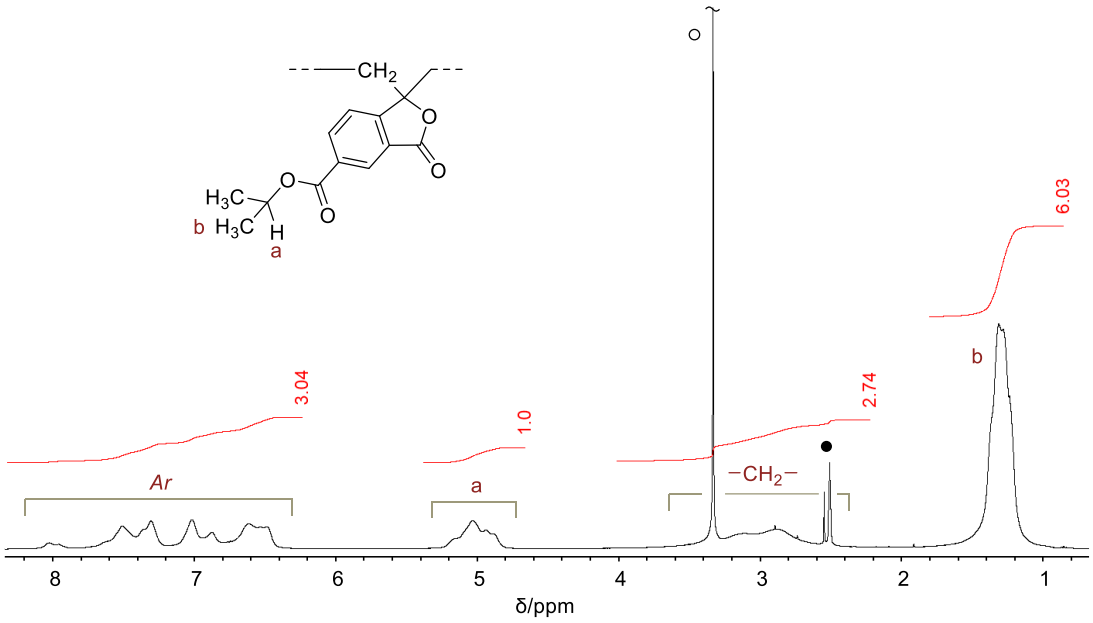


Figure S32. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of **P3-C3p.** ○: H_2O. ●: DMSO.

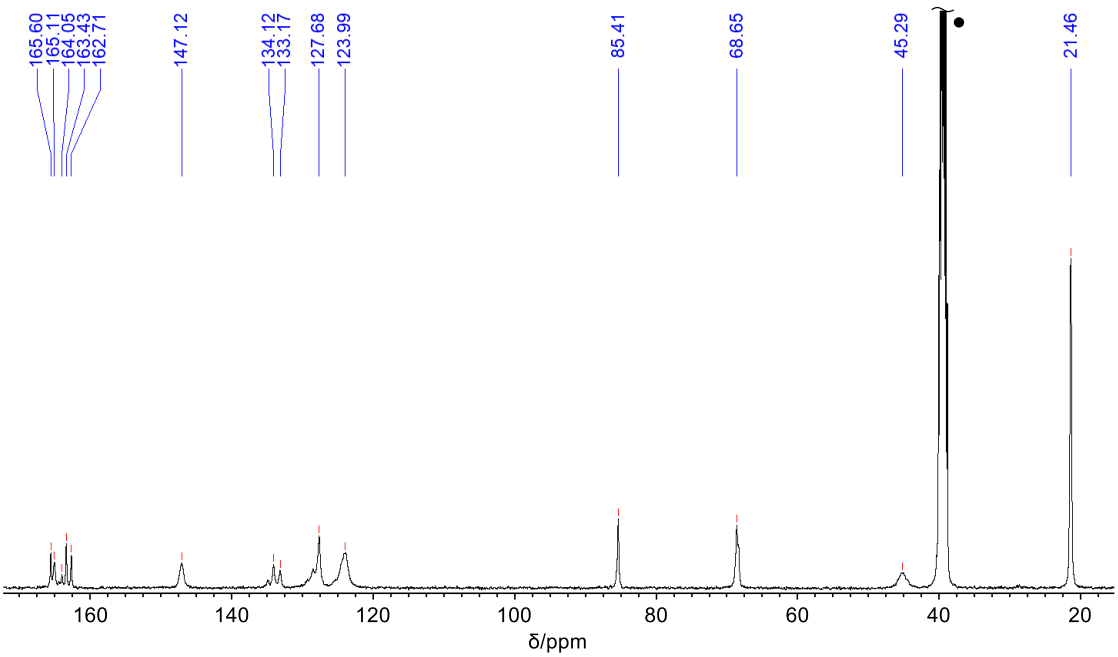


Figure S33: ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 25 °C) of **P3-C3p.** ●: DMSO.

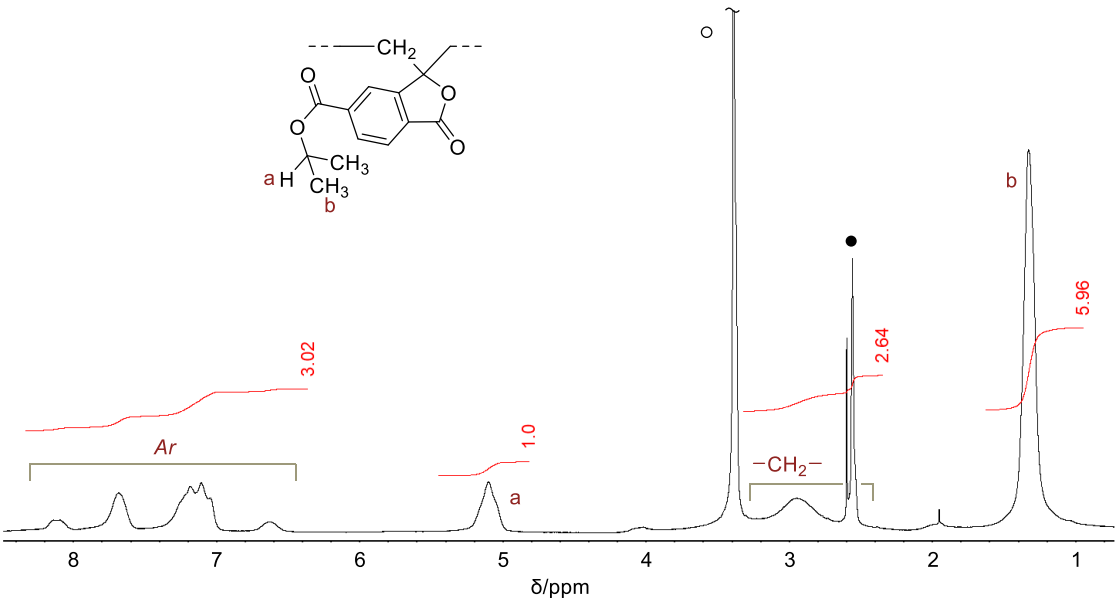


Figure S34: ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of **P3-C3m**.○: H_2O. ●: DMSO.

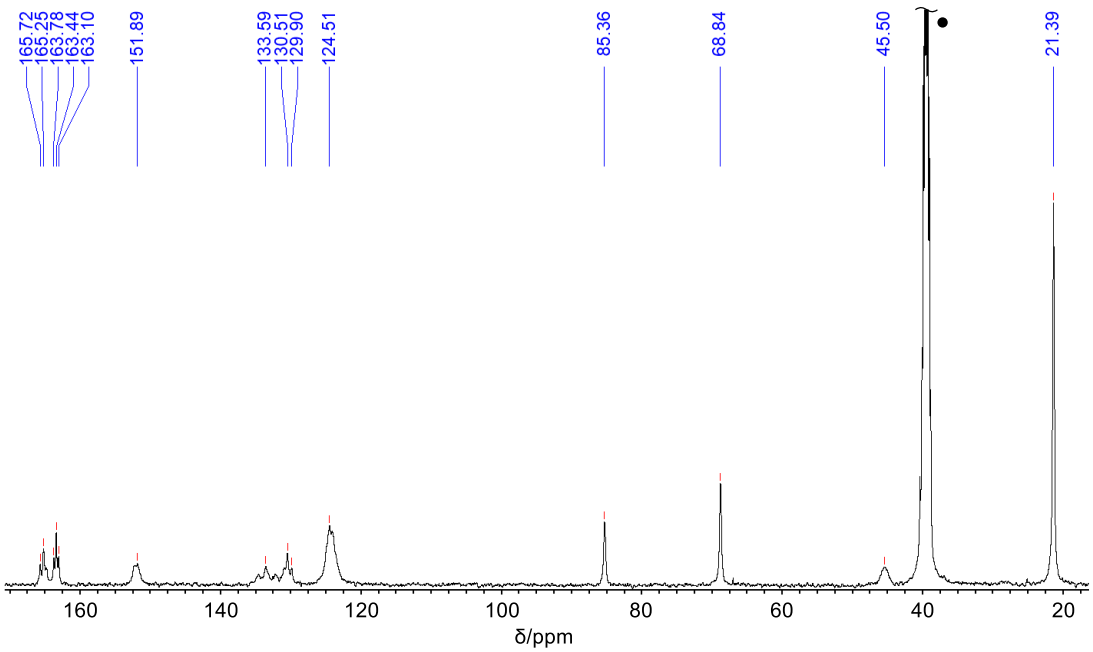


Figure S35. ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 25 °C) of **P3-C3m.** ●: DMSO.

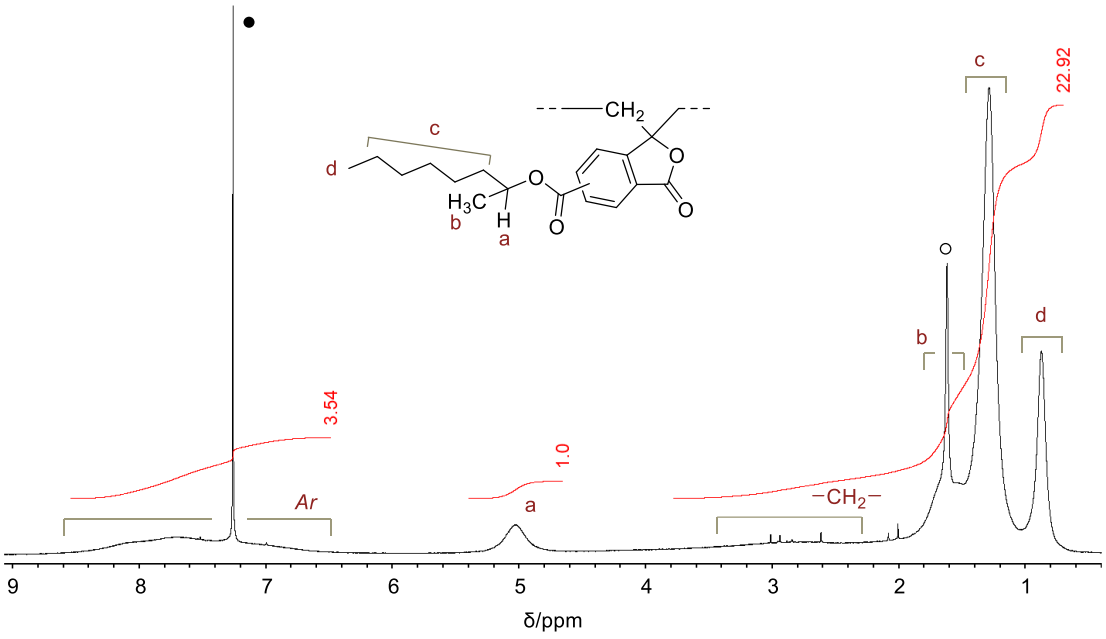


Figure S36: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **P3-C8**. ○: H_2O. ●: $CHCl_3$**.**

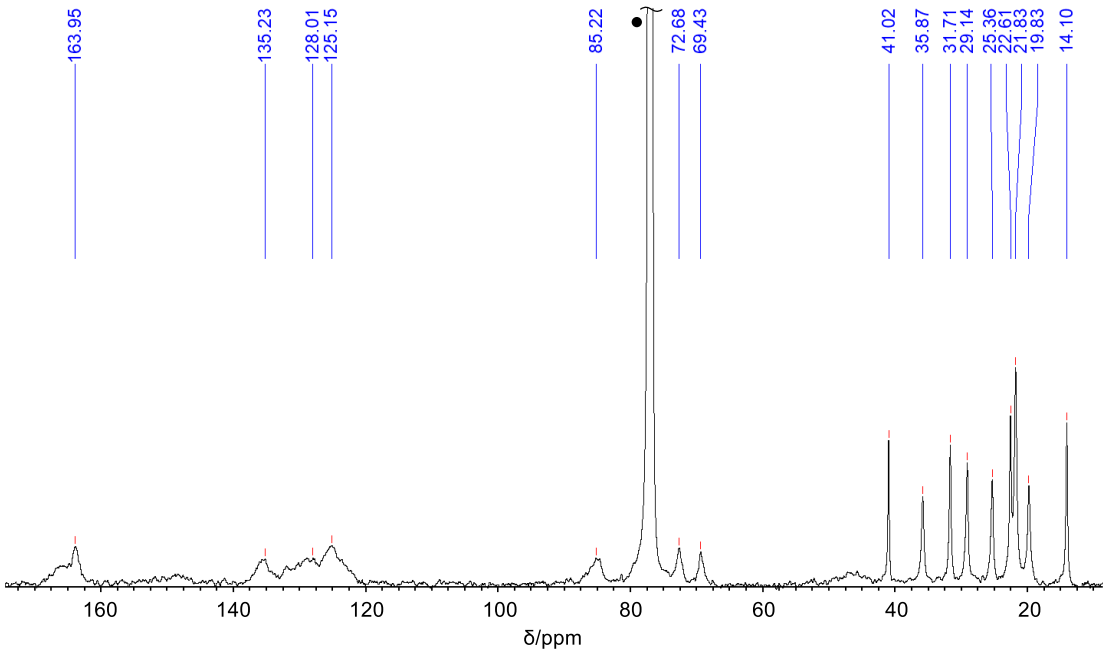


Figure S37: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **P3-C8.** ●: $CHCl_3$.

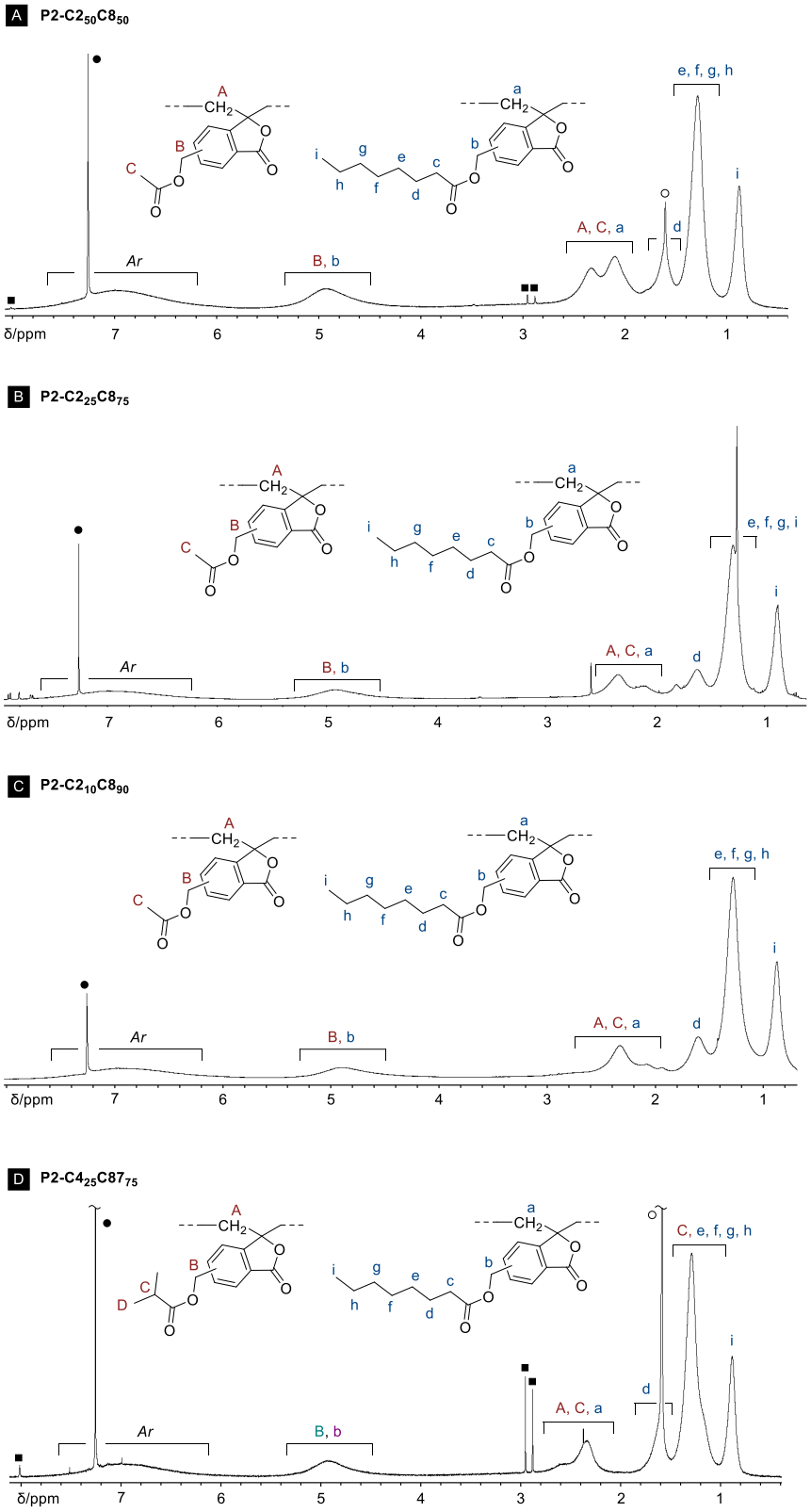


Figure S38: ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of the copolymers prepared from **M2-#.** ○: H_2O. ●:$CHCl_3$. ■: DMF used for polymerization.

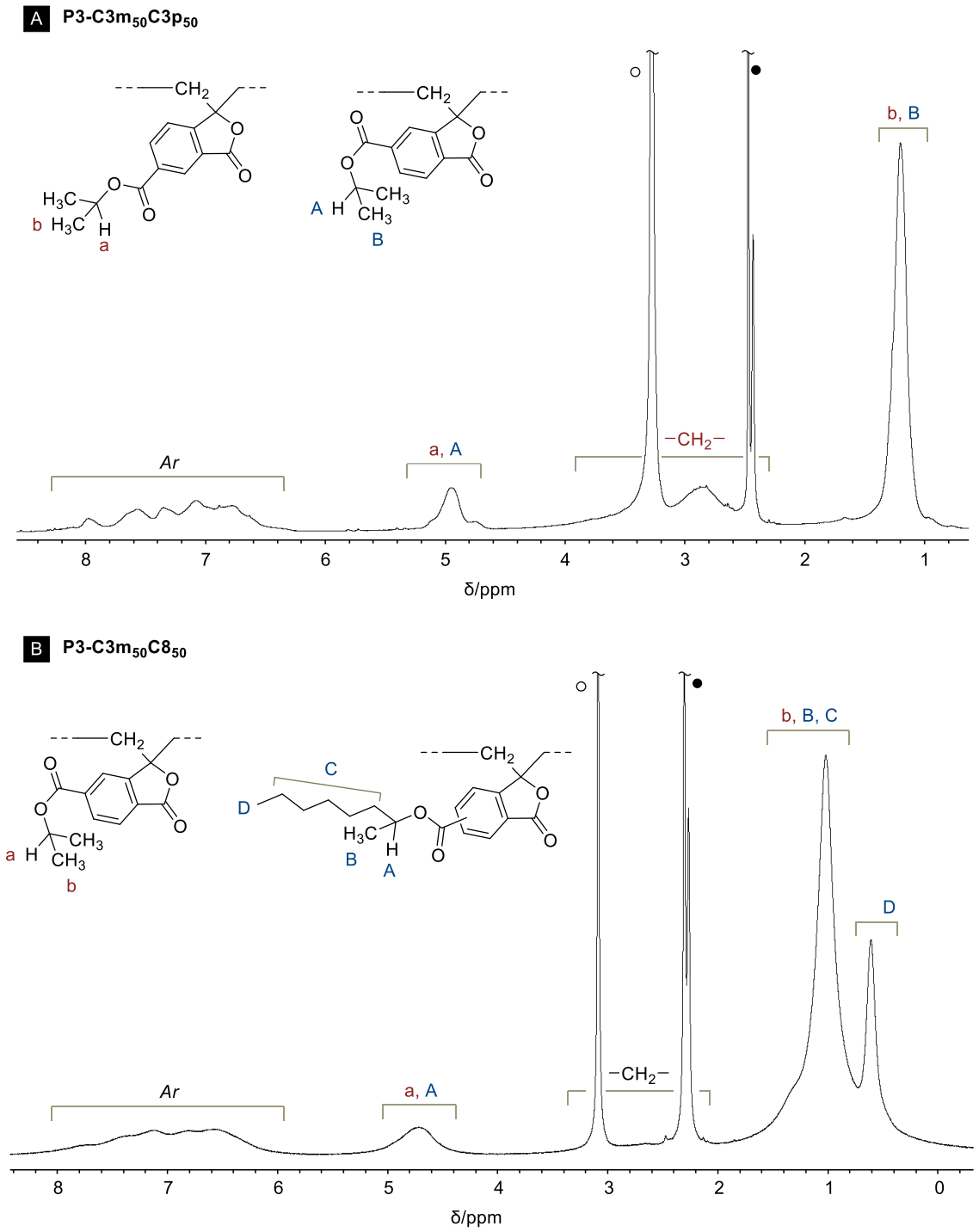


Figure S39: ^{1}H NMR spectra (400 MHz, DMSO-d_6, 25 °C) of the copolymers prepared from **M3-#.** ○: H_2O. ●: DMSO.

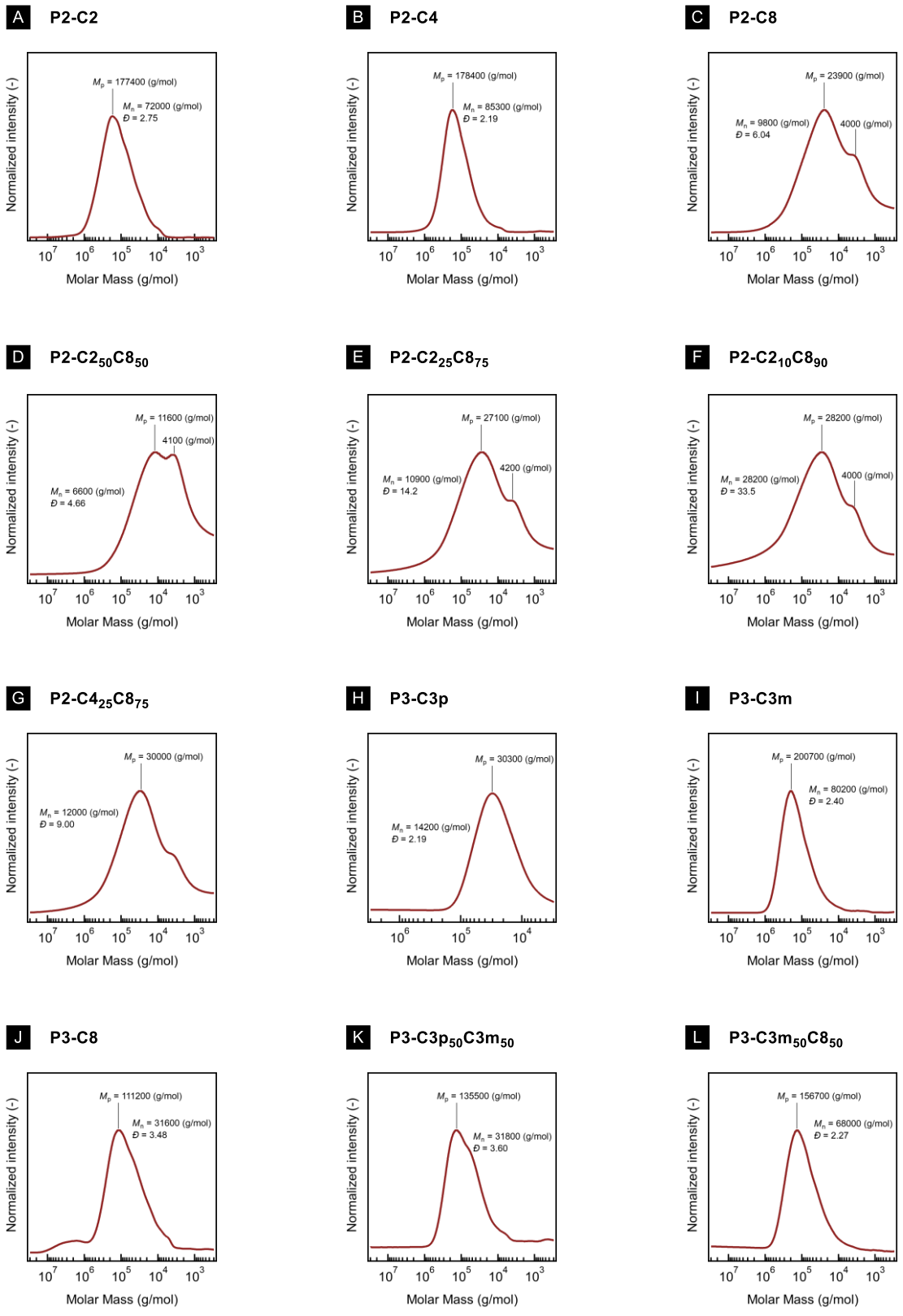


Figure S40: SEC curves of obtained (co)polymers (40 °C, polystyrene standard). Eluent: DMF for A, B, H, I. J, K, L. $CHCl_3$ for others.

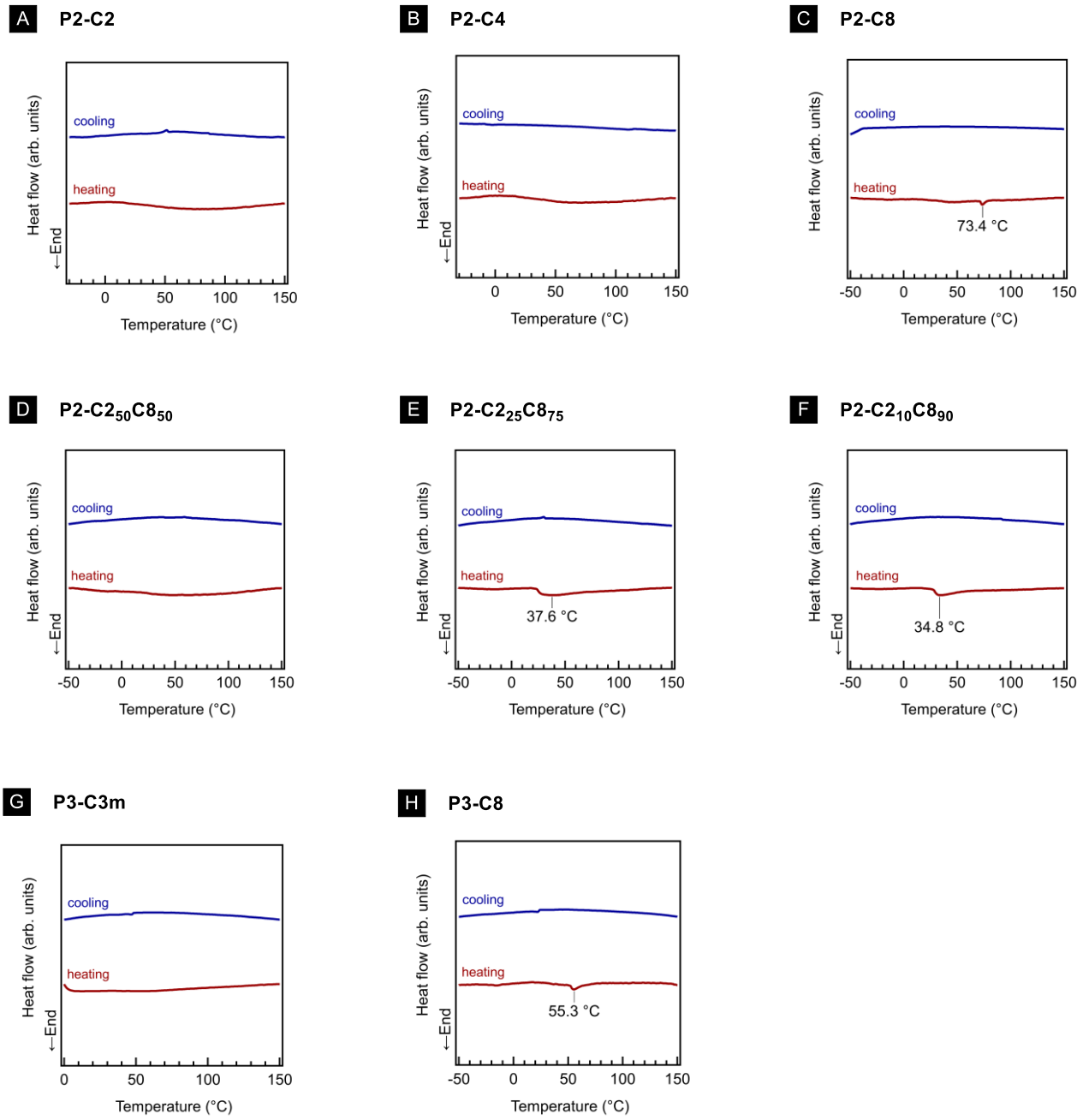


Figure S41. DSC curves (N_2 flow, heating: 10 °C/min, cooling: 20 °C/min) for the polymers.

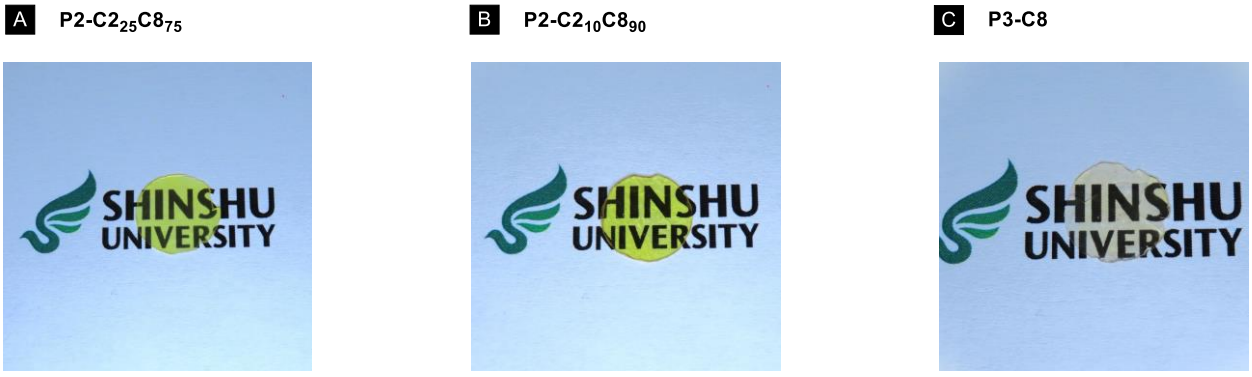


Fig S42. Photographs of the films prepared by hot-pressing. (A) **P2-C2$_{25}$C8$_{75}$** (B) **P2-C2$_{10}$C8$_{90}$** (C) **P3-C8**

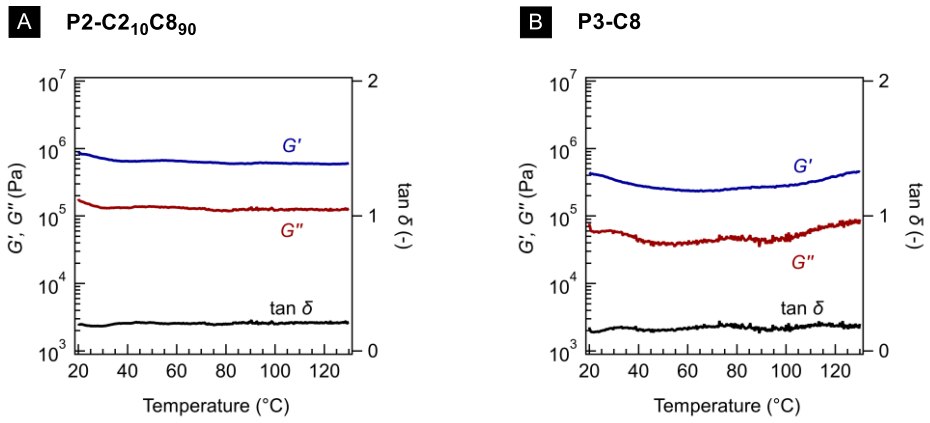


Fig S43. DMA curves for (A) **P2-C2$_{10}$C8$_{90}$** and (B) **P3-C8**.

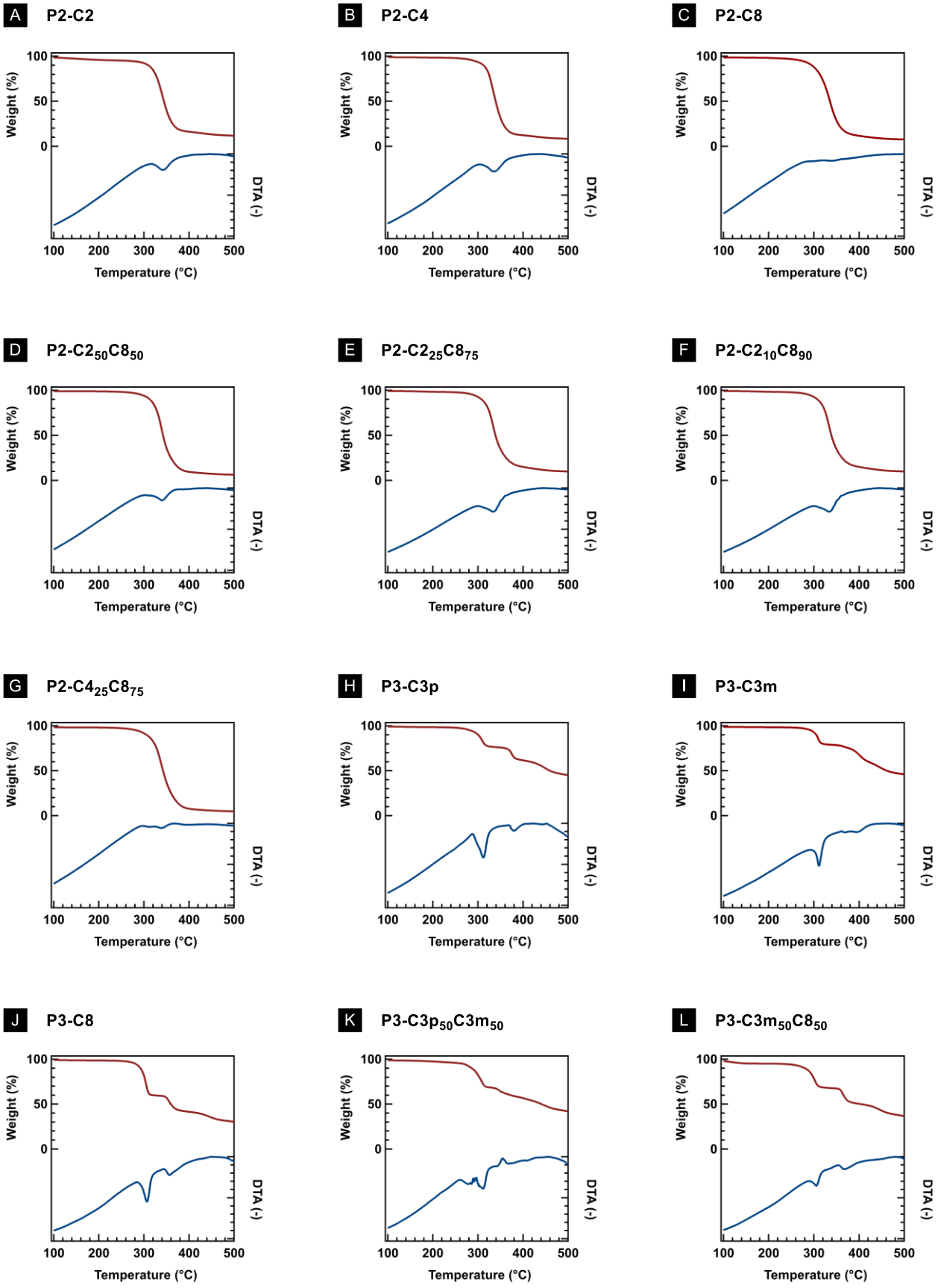


Figure S44. TG-DTA curves (N_2 flow, 10 °C/min) for the polymers.

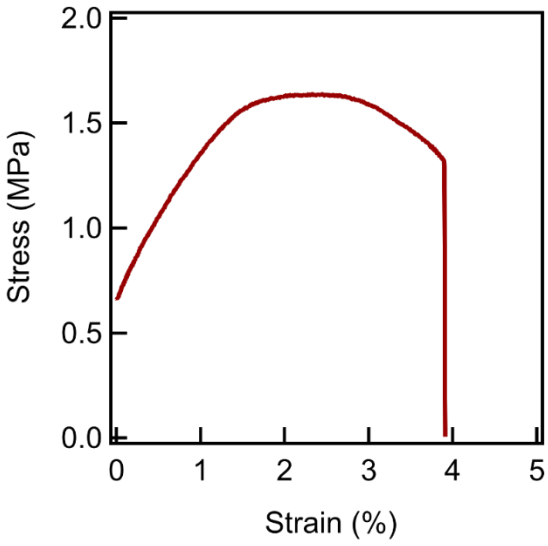


Figure S45: Stress-strain curve of **P2-C4$_{25}$C8$_{75}$.**

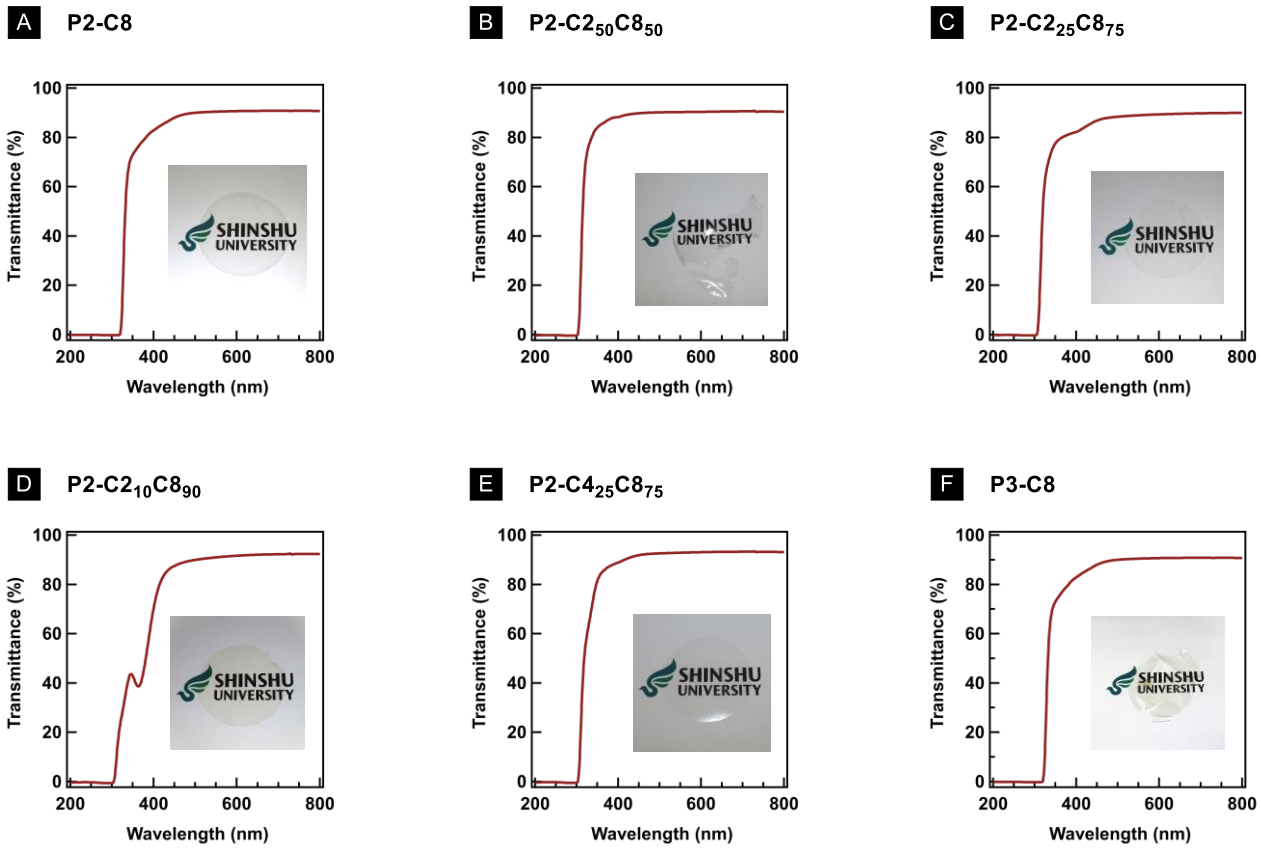
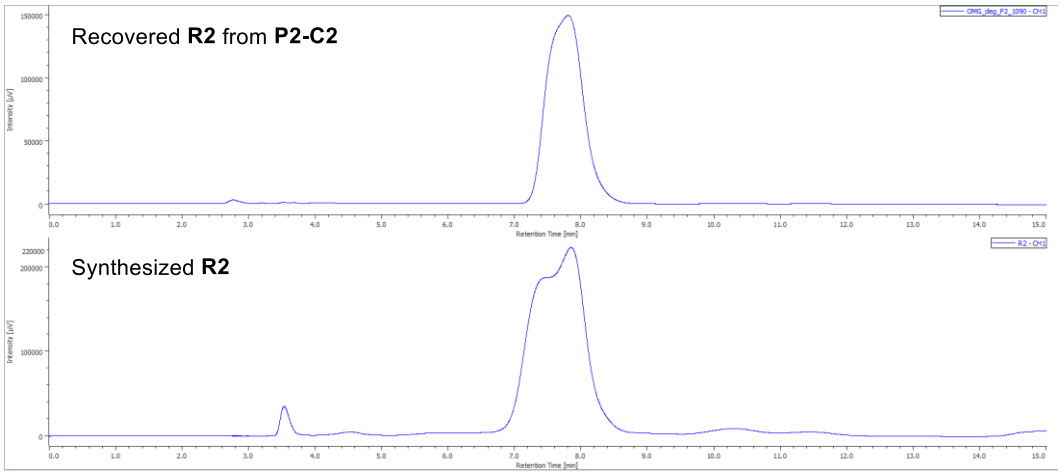


Figure S46: UV-vis spectra of the films prepared from the (co)polymers with images of films.

A **R2**



B **R3**

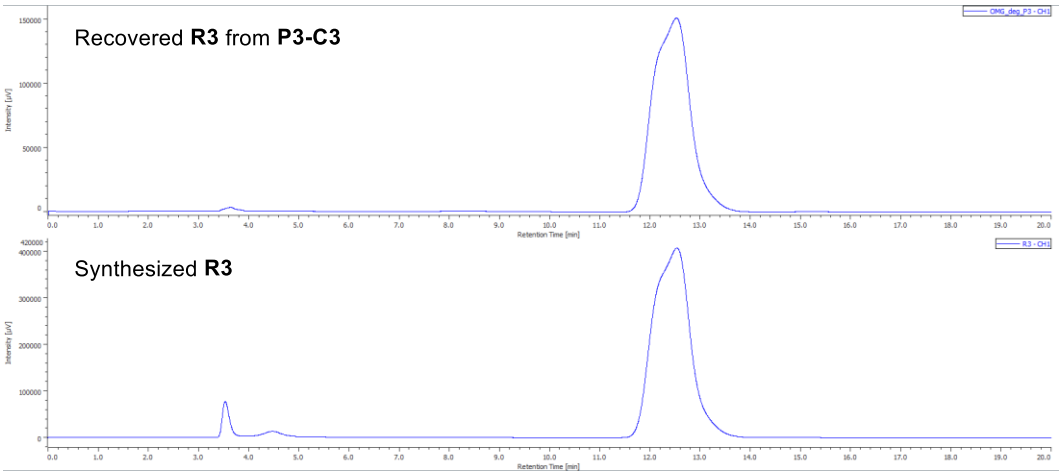


Figure S47: HPLC charts (acetonitrile/H_2O mixed 0.01% TFA =1/9) of (A) recovered **R2** from **P2-C2** and synthesized **R2**, (B) recovered **R3** from **P3-C3** and synthesized **R3**.

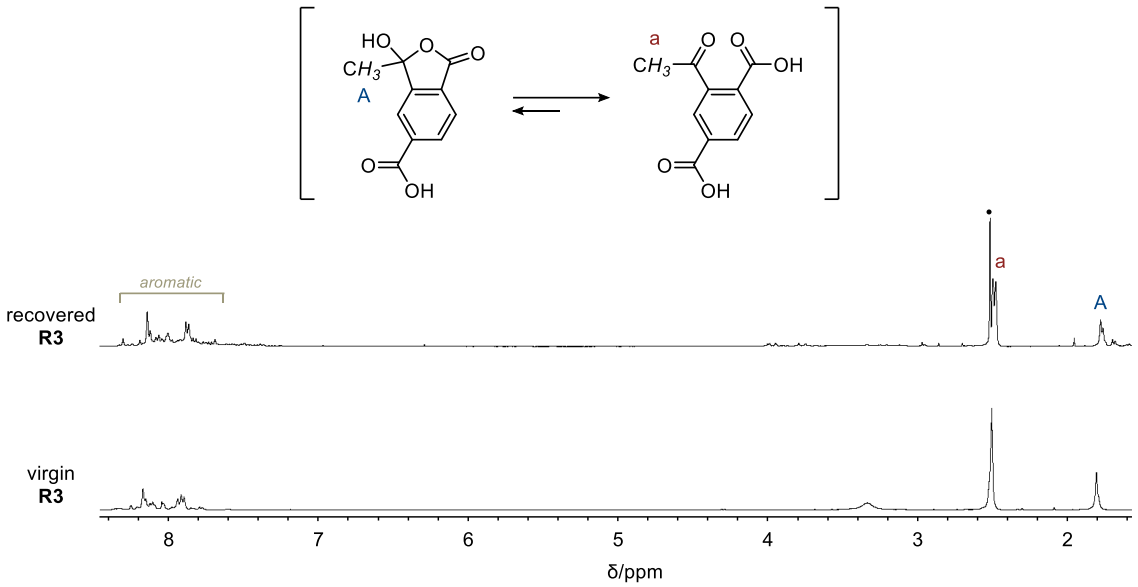


Figure S48: ^{1}H NMR spectra of recovered **R3** and virgin **R3** (400 MHz, DMSO-d_6, 25 °C). ●: DMSO.

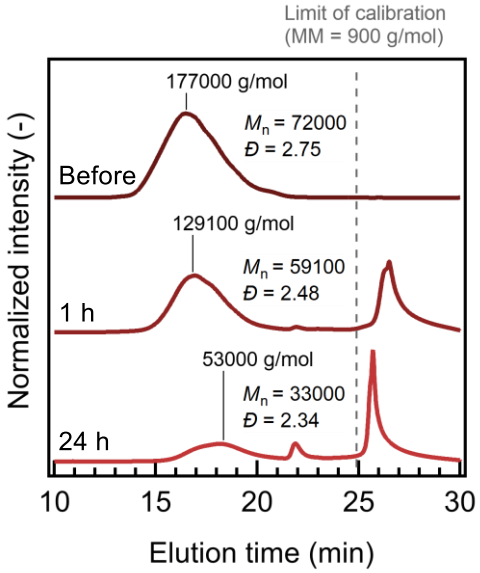


Figure S49: SEC curves changes (40 °C, DMF, polystyrene standard) during the degradation of **P2-C2** at 25 °C.

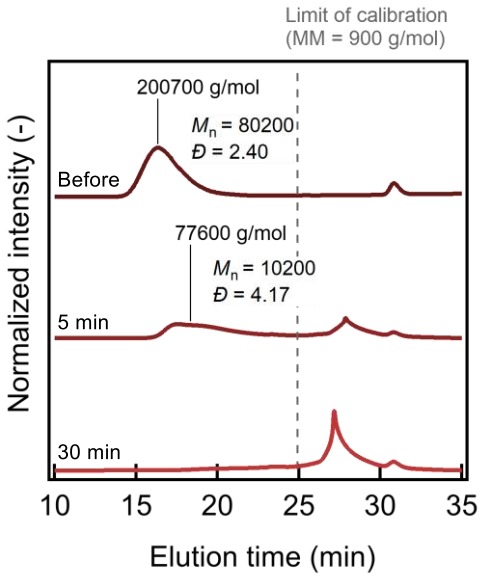


Figure S50: SEC curve changes (40 °C, DMF, polystyrene standard) in the degradation of **P3-C3m** at 25 °C.

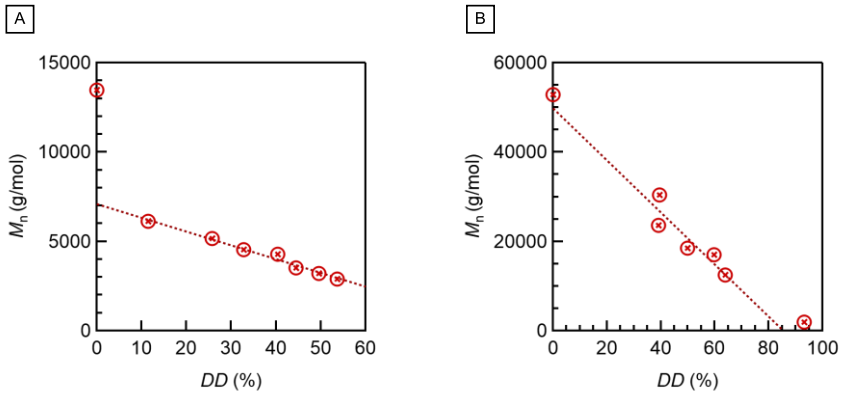


Figure S51. *DD* vs M_n plot for the degradation test of **P1** with 3 molar equiv. of 10 M aq. NaOH in DMSO at RT. (A) **P1** synthesized via free radical polymerization (M_n = 15000, *Đ* = 2.28), (B) **P1** synthesized via cationic polymerization (M_n = 59300, *Đ* = 7.23).

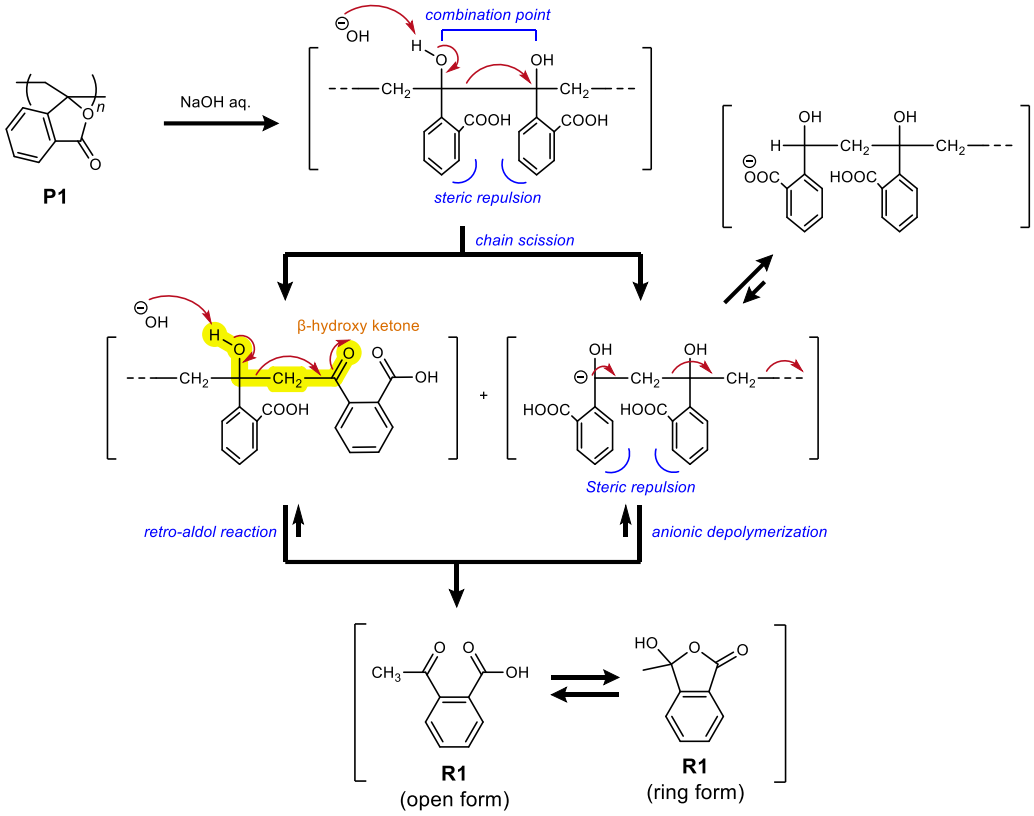


Figure S52: Proposed degradation mechanism of **P1** synthesized via free radical depolymerization.[1]

Table S2. Cationic polymerization of **M1**.

Entry[a]	Initiator	Temp. (°C)	Time (h)	Solvent	Conv.[b] (%)	Yield (%)	M_n[c]	$Đ$[c]
1[d]	$BF_3{\cdot}OEt_2$	0	2	$CHCl_3$	83.3	16	83600	7.92
2	IBEA + $BF_3{\cdot}OEt_2$	−25	2	CH_2Cl_2	27	27	52500	6.25
3	IEBA + $BF_3{\cdot}OEt_2$	0	2	CH_2Cl_2	24	29	59300	7.23
4	IEBA + $BF_3{\cdot}OEt_2$	25	2	CH_2Cl_2	25	22	41700	8.86
5[e]	IEBA + $EtAlCl_2$	0	4.5	$CHCl_3$	0	0	-	-
6[e]	CEB + $EtAlCl_2$	0	6	$CHCl_3$	22	10	44100	3.56
7[e]	CEB+ $EtAlCl_2$	0	6	$CHCl_3$	24	52	76000	3.22
8[e]	CEB + $EtAlCl_2$	−40	6	$CHCl_3$	45	39	60000	3.25
9[e]	CEB + $EtAlCl_2$	40	6	$CHCl_3$	23	30	42700	4.03

[a] [**M1**]/[IBEA]/[$BF_3{\cdot}OEt_2$] = 50/1/1. [b] Determined using ^{1}H NMR spectroscopy. [c] Determined using SEC (DMF, 40 °C, polystyrene standards). [d] [**M1**]/[$BF_3{\cdot}OEt_2$] = 50/1. [e] [**M1**]/[IEVA or CEB]/[$EtAlCl_2$] = 200-/10/1.

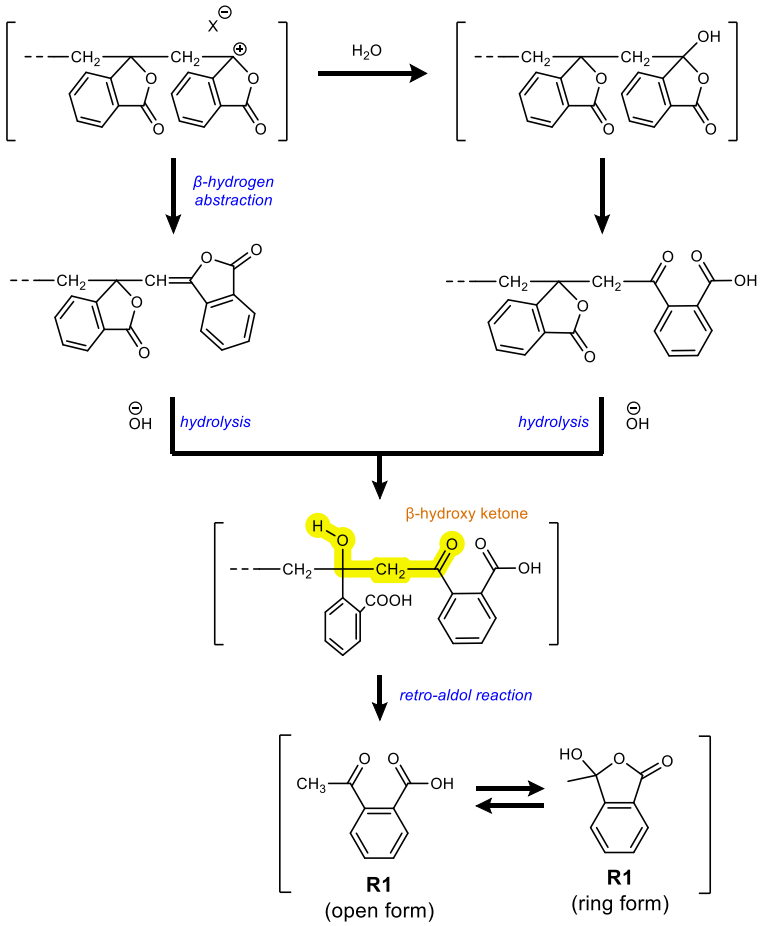


Figure S53: Proposed degradation mechanism of **P1** synthesized by cationic polymerization.

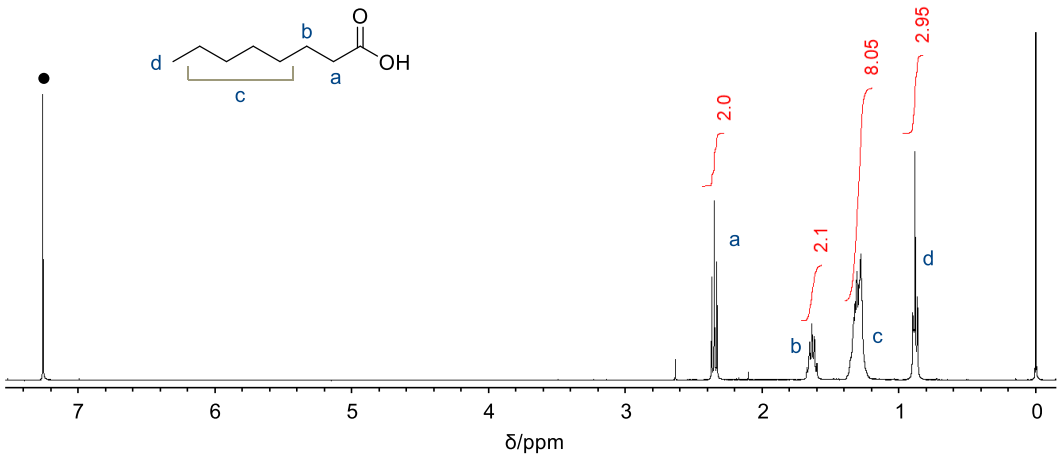


Figure S54. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of recovered *n*-octanoic acid derived from **C8** pendant in the decomposition of **P2-C2$_{50}$C8$_{50}$**. ●: $CHCl_3$.

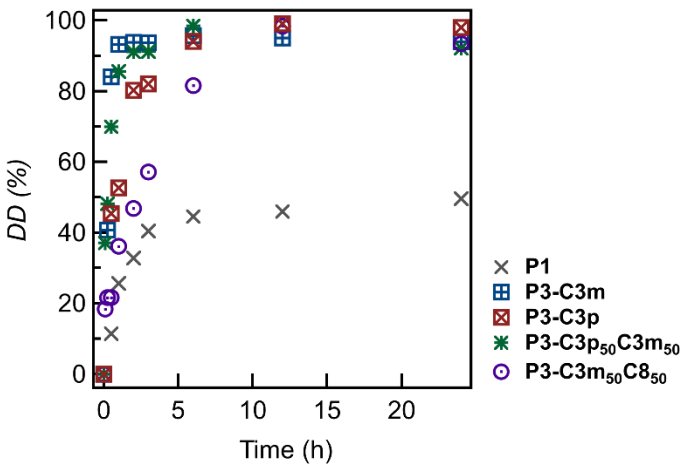


Figure S55. Degree of degradation (*DD*) growth during the reaction at 25 °C.

(1) Chiba, Y.; Kawatani, R.; Kohsaka, Y. Chemically Recyclable Vinyl Polymers by Free Radical Polymerization of Cyclic Styrene Derivatives. *ACS Macro Lett.* **2023**, *12* (12), 1672–1676.