

Supplementary information

ALTERNATING RING-OPENING COPOLYMERIZATION OF PHTHALIC ANHYDRIDE WITH EPOXIDES CATALYSED BY SALOPHEN CHROMIUM(III) COMPLEXES. AN EFFECT OF SUBSTITUENTS IN SALOPHEN LIGANDS

K. Bester,^{a*} A. Bukowska,^a B. Myśliwiec,^a K. Hus,^a D. Tomczyk,^b P. Urbaniak^b and W. Bukowski^a

^a*Faculty of Chemistry, Rzeszów University of Technology, Powstańców Warszawy 6, 35-959 Rzeszów, Poland*

^b*Department of Inorganic and Analytical Chemistry, University of Łódź, 91-403, ul. Tamka 12, Poland*

**corresponding author (email address: bester_k@prz.edu.pl)*

1. General information

All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or using the standard Schlenk techniques under dry nitrogen or argon atmosphere.

1.1. Materials

Cyclohexene oxide (Sigma-Aldrich, 98%), 4-vinyl-1-cyclohexene 1,2-epoxide (Sigma-Aldrich, 98%), propylene oxide (Fluka, 97%), 1,2-butylene oxide (Fluka, 99%), styrene oxide (Fluka, 97%), epichlorohydrin (Sigma-Aldrich, 99%), phenyl glycidyl ether (Sigma-Aldrich, 99%) and methylene chloride were stirred with calcium hydride (Sigma-Aldrich, 90%) under argon for 2 days, distilled under vacuum or argon and stored under argon until use. Phthalic anhydride (Sigma-Aldrich, 99%) was refluxed with chloroform (10 g anhydride in 40 ml chloroform) under argon for 1 h followed by hot filtration. The filtrate was evaporate via rotary evaporation and resulted white solid was washed with diethyl ether, filtered off and dried under vacuum for 12 h. Next, freshly recrystallized anhydride was resublimed and stored under argon in the glove box until use. Tetrahydrofuran and toluene were refluxed with sodium/benzophenone under argon until the deep blue colour of benzophenone ketyl formed, and dry solvents were collected directly prior to use. All other chemicals and reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Acros) and used as received.

1.2. Methods

NMR experiments. ^1H and ^{13}C NMR spectra were recorded at 298 K temperature in CDCl_3 solutions using a Bruker Avance 500 MHz spectrometer (^1H , 500 MHz and ^{13}C , 125 MHz). TMS was used as a standard. Samples for analysis were prepared by dissolving 15-30 mg (compounds) or 60-80 mg (polymers) obtained products in *ca.* 0.6 ml of an appropriate solvent.

Infrared experiments. FT-IR spectra were recorded using a Thermo Scientific Nicolet 8700 spectrometer. All measurements were performed by a transmission method in the range of 4000-400 cm^{-1} . Samples were prepared in the form of KBr pellets, by grinding *ca.* 0.2 mg analyzed substances with 200 mg KBr in a mortar and pressing the resulting mixtures in a hydraulic press.

Electronic spectra. The electronic spectra were recorded on Jasco V-670 spectrophotometer in the range 200-800 nm. The samples were diluted to a concentration of 10^{-4} mol/L in dichloromethane. Analysis of results was done using program The Spectra Manager II.

Mass spectroscopy. Laser desorption/ionization (LDI) time-of-flight (ToF) mass spectrometry experiments were performed using a Bruker Autoflex Speed reflectron time-of-flight mass spectrometer equipped with a SmartBeam II laser (352 nm) in the range of 80-2000 m/z . Laser impulse energy and the rate of laser repetition were approximately 60–120 μJ and 1000 Hz, respectively. The first accelerating voltage was held at 19 kV and the second ion-source voltage at 16.7 kV. The reflector voltages applied were 21 kV (first) and 9.55 kV (second). The analytical data were collected and analyzed using the software provided with the Autoflex instrument (FlexAnalysis version 3.3). Mass calibration (typically cubic calibration based on five to seven points) was performed using internal standards (gold ions and clusters from Au^+ to Au_{10}^+ depending on m/z range). The sum of *ca.* 7000 scans was collected for each sample. Analytical samples were prepared by dissolution/suspending *ca.* 0.5 mg analysed substance in 1 mL toluene and placing one drop of resulting solution/suspension on AuNPET.^{S1}

Gel permeation chromatography (GPC). Molecular weight determinations (M_n and M_w) were conducted using an Agilent 1100 HPLC instrument equipped with a RI detector and a MIXED-D 300 x 7.5 mm column. The analytical data were collected and analyzed using the software provided with instrument (ChemStation for LC Rev. A.10.02 with ChemStation GPC Data

Analysis Software Rev. A.02.02). Polystyrene standards (Polymer Laboratories, M_p = 580, 1480, 4490, 10680, 30230, 63350, 170800, 504500 Da) were used to calibrate the system. All analyses were performed at 35°C using THF as eluent at flow rate of 0.5 mL/min. The concentrations of analysed samples were about 0.5 %. The samples were filtered through 0.2 μ m PTFE filters before their injection. The injection volume was 20 μ L.

Differential scanning calorimetry (DSC). DSC measurements were carried out with a Mettler-Toledo DSC-1 instrument. The glass transition temperature (T_g) of polymers were determined from the second heating at a heating rate of 10 °C/min from -50 to +200 °C under nitrogen atmosphere.

ICP-OES analysis. The content of chromium in the synthesized metal complexes were determined using a ICP-OES ULTIMA 2 HORIBA JOBIN YVON spectrometer (λ = 283.563 nm, photomultiplier voltage of 950 V and generator power 1400 W). The samples of the complexes (about 20 mg) were mineralized in conc. nitric acid (5.0 ml) using a *Plazmatronika Uni Claver* // microwave mineralizer and diluted with demineralized water before their analysis.

Melting point measurements. The melting points of the obtained ligands were determined using a SRS OptiMelt MPA100 instrument with the heating rate of 2°C/min.

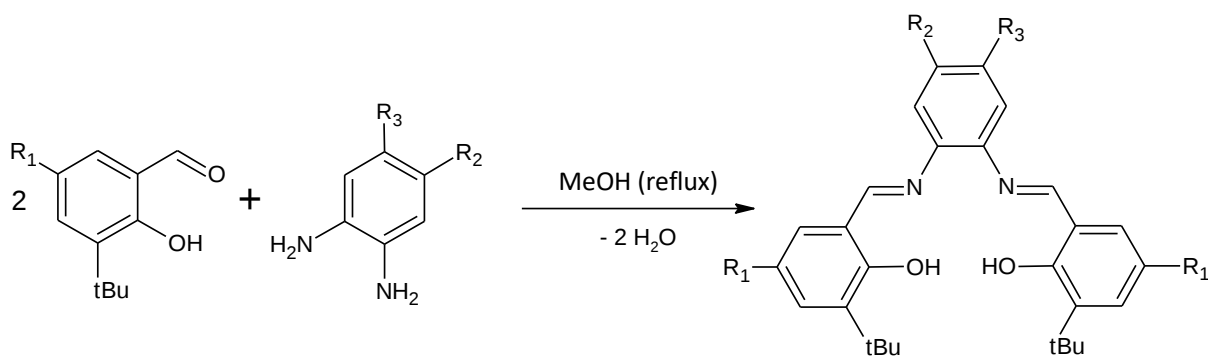
2. Syntheses

2.1. Aldehyde syntheses

All salicylaldehydes used for salophen ligand syntheses were prepared according to literature procedures: 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde,^{S2} 3-*tert*-butyl-2-hydroxybenzaldehyde and 3-*tert*-butyl-5-methoxy-2-hydroxybenzaldehyde.^{S3}

2.2. Salophen ligand syntheses

Salophen ligands **1-10** were prepared in the reactions between the appropriate derivatives of salicylaldehyde and 1,2-phenylenediamine (*Scheme S1*). The procedure described in literature with minor changes was applied.^{S4}



Salophen ligand	R ₁	R ₂	R ₃
1		H	H
2		-(CH) ₄ -	
3		Cl	Cl
4	tBu	F	
5		Cl	
6		Br	H
7		Me	
8	MeO	Cl	Cl
9		Me	H
10	H	Me	H

Scheme S1. Synthesis of the salophen ligands **1-10**.

General synthesis procedure. The solution of phenylenediamine derivative (4 mmol) in 10 ml methanol and few drops of aqueous formic acid (85 %) were added to the refluxing solution of salicylaldehyde (8.8 mmol) in 25 ml of methanol. The resulting mixture was refluxed for several hours (TLC controlled, hexane:ethyl acetate = 90:10). The products of reaction were isolated by filtration and purified by recrystallization from CH₂Cl₂/MeOH.

N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-phenylenediamine

(1): Yield 1.90 g, 88%, orange solid, mp = 193.8-194.5°C; **¹H-NMR** (CDCl₃) δ ppm: 13.53 (s, 2H), 8.66 (s, 2H), 7.43 (d, *J*=2.5 Hz, 2H), 7.33-7.28 (m, 2H), 7.26-7.22 (m, 2H), 7.21 (d, *J*=2.5 Hz, 2H), 1.44 (s, 18H), 1.32 (s, 18H); **¹³C-NMR** (CDCl₃) δ ppm: 164.7, 158.6, 142.8, 140.3, 137.2, 128.2, 127.3, 126.8, 119.8, 118.4, 35.1, 34.2, 31.5, 29.5; **HRMS** (AuNPET LDI-ToF) *m/z*: calculated for C₃₆H₄₈N₂NaO₂⁺ [M+Na]⁺ = 563.3608 found 563.3607, for C₃₆H₄₉N₂O₂⁺ [M+H]⁺ = 541.3789 found 541.3845; **FT-IR** (KBr, cm⁻¹): 2958, 2907, 2870, 1616, 1575, 1467, 1436, 1392, 1362, 1271, 1250, 1200, 1172, 755; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε): 232 (4.48), 281 (4.32), 339 (4.29).

N,N'-Bis(3,5-di-tert-butylsalicylidene)-2,3-naphthalenediamine

(2): Yield 1.95 g, 82%, orange solid, mp = 222.5-224.1°C; **¹H-NMR** (CDCl₃) δ ppm: 13.49 (s, 2H), 8.76 (s, 2H), 7.88-7.82 (m, 2H), 7.56 (s, 2H), 7.50-7.44 (m, 2H), 7.27 (d, *J*=2.5 Hz, 2H), 1.45 (s, 18H), 1.34 (s, 18H); **¹³C-NMR** (CDCl₃) δ ppm: 165.0, 158.7, 143.1, 140.4, 137.2, 132.7, 128.3, 127.6, 126.9, 126.1, 118.5, 116.7, 35.2, 34.2, 31.5, 29.5; **HRMS** (AuNPET LDI-ToF) *m/z*: *calculated for* C₄₀H₅₀N₂NaO₂⁺ [*M*+Na]⁺ = 613.3764 *found* 613.3751, *for* C₄₀H₅₁N₂O₂⁺ [*M*+H]⁺ = 591.3945 *found* 591.4017; **FT-IR** (KBr, cm⁻¹): 2958, 2908, 2870, 1612, 1593, 1578, 1500, 1468, 1436, 1392, 1362, 1271, 1250, 1229, 1202, 1169, 1151, 1100, 877, 773, 747, 477; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε): 232 (4.72), 281 (4.57), 315 (sh), 340 (sh).

N,N'-Bis(3,5-di-tert-butylsalicylidene)-4,5-dichloro-1,2-phenylenediamine

(3): Yield 1.13 g, 46%, orange solid, mp = 264.7-265.5°C; **¹H-NMR** (CDCl₃) δ ppm: 13.15 (s, 2H), 8.63 (s, 2H), 7.46 (d, *J*=2.2 Hz, 2H), 7.33 (s, 2H), 7.22 (d, *J*=2.2 Hz, 2H), 1.42 (s, 18H), 1.34 (s, 18H); **¹³C-NMR** (CDCl₃) δ ppm: 165.6, 158.7, 142.2, 140.7, 137.4, 130.5, 129.0, 127.1, 121.2, 118.1, 35.1, 34.2, 31.4, 29.4; **HRMS** (AuNPET LDI-ToF) *m/z*: *calculated for* C₃₆H₄₆Cl₂N₂NaO₂⁺ [*M*+Na]⁺ = 631.2828 *found* 631.2874, *for* C₃₆H₄₇Cl₂N₂O₂⁺ [*M*+H]⁺ = 609.3009 *found* 609.2810; **FT-IR** (KBr, cm⁻¹): 2955, 2908, 2870, 1613, 1593, 1568, 1469, 1438, 1393, 1362, 1271, 1250, 1201, 1175, 1150, 1139, 879, 866, 772; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε in): 234 (4.31), 287 (4.34), 345 (4.16).

N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-fluoro-1,2-phenylenediamine

(4): Yield 1.89 g, 85%, light yellow solid, mp = 214.5°C; **¹H-NMR** (CDCl₃) δ ppm: 13.42 (s, 1H), 13.28 (s, 1H), 8.631 (s, 1H), 8.626 (s, 1H), 7.45 (d, *J*=2.5 Hz, 1H), 7.44 (d, *J*=2.5 Hz, 1H), 7.23-7.17 (m, 3H), 1.429 (s, 9H), 1.426 (s, 9H), 1.32 (s, 9H), 1.32 (s, 9H), 1.31 (s, 9H); **¹³C-NMR** (CDCl₃) δ ppm: 165.5, 164.6, 161.7, (d, ¹*J*_{C-F} = 245.7 Hz), 158.7, 158.5, 143.9 (d, ³*J*_{C-F} = 8.4 Hz), 140.6, 140.4, 139.2 (d, ⁴*J*_{C-F} = 2.8 Hz), 137.3, 137.2, 128.7, 128.3, 127.0, 126.8, 120.7 (d, ³*J*_{C-F} = 9.1 Hz), 118.3, 118.1, 113.8 (d, ²*J*_{C-F} = 22.6 Hz), 106.9 (d, ²*J*_{C-F} = 23.6 Hz), 35.1, 34.2, 31.47, 31.45, 29.4; **HRMS** (AuNPET LDI-ToF) *m/z*: *calculated for* C₃₆H₄₇FN₂NaO₂⁺ [*M*+Na]⁺ = 581.3514 *found* 581.3450, *for* C₃₆H₄₈FN₂O₂⁺ [*M*+H]⁺ = 559.3694 *found* 559.3703; **FT-IR** (KBr, cm⁻¹): 2958, 2908, 2869, 1617, 1582, 1494, 1483, 1440, 1362, 1270, 1251, 1167, 1152, 966, 855, 817, 774; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε): 232 (4.48), 282 (4.44), 341 (4.29).

N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-chloro-1,2-phenylenediamine

(5): Yield 1.79 g, 78%, orange solid, mp = 202.3-202.8°C; **¹H-NMR** (CDCl₃) δ ppm: 13.36 (s, 1H), 13.26 (s, 1H), 8.64 (s, 1H), 8.63 (s, 1H), 7.45 (d, *J*=2.5 Hz, 1H), 7.44 (d, *J*=2.5 Hz, 1H), 7.27 (dd, *J*=8.25 Hz, *J*=2.5 Hz, 1H), 7.23 (d, *J*=2.5 Hz, 1H), 7.23 (d, *J*=2.5 Hz, 1H), 7.20 (d, *J*=2.5 Hz, 1H), 7.17 (d, *J*=8.5 Hz, 1H), 1.42 (s, 18H), 1.32 (s, 9H), 1.31 (s, 9H); **¹³C-NMR** (CDCl₃) δ ppm: 165.5, 164.9, 158.7, 158.6, 143.7, 141.4, 140.6, 140.5, 137.31, 137.29, 132.5, 128.7, 128.5, 127.0, 126.9, 120.8, 119.9, 118.3, 118.2, 35.1, 34.2, 31.5, 29.4; **HRMS** (AuNPET LDI-ToF) *m/z*: calculated for C₃₆H₄₇ClN₂NaO₂⁺ [M+Na]⁺ = 597.3218 found 597.3264, for C₃₆H₄₈ClN₂O₂⁺ [M+H]⁺ = 575.3399 found 575.3414; **FT-IR** (KBr, cm⁻¹): 2955, 2908, 2870, 1615, 1594, 1570, 1482, 1468, 1439, 1393, 1362, 1273, 1249, 1200, 1173, 808, 772; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε) 233 (4.27), 284 (4.26), 341 (4.10).

N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-bromo-1,2-phenylenediamine

(6): Yield 1.82 g, 73%, orange solid, mp = 205.1-206.0°C; **¹H-NMR** (CDCl₃) δ ppm: 13.34 (s, 1H), 13.24 (s, 1H), 8.632 (s, 1H), 8.629 (s, 1H), 7.45 (d, *J*=2.5 Hz, 1H), 7.44 (d, *J*=2.5 Hz, 1H), 7.41 (dd, *J*=8.5 Hz, *J*=2.5 Hz, 1H), 7.40 (d, *J*=2.5 Hz, 1H), 7.22 (d, *J*=2.5 Hz, 1H), 7.20 (d, *J*=2.5 Hz, 1H), 7.10 (d, *J*=8.5 Hz, 1H), 1.42 (s, 18H), 1.32 (s, 9H), 1.31 (s, 9H); **¹³C-NMR** (CDCl₃) δ ppm: 165.5, 164.9, 158.7, 158.6, 143.7, 141.4, 140.6, 140.5, 137.32, 137.28, 132.5, 128.7, 128.5, 127.0, 126.9, 120.8, 119.9, 118.25, 118.18, 35.1, 34.2, 31.5, 29.4; **HRMS** (AuNPET LDI-ToF) *m/z*: calculated for C₃₆H₄₇BrN₂NaO₂⁺ [M+Na]⁺ = 641.2713, found 641.2563; for C₃₆H₄₈BrN₂O₂⁺ [M+H]⁺ = 619.2894 found 619.2445; **FT-IR** (KBr, cm⁻¹): 2954, 2907, 2869, 1614, 1593, 1568, 1481, 1468, 1438, 1393, 1362, 1273, 1249, 1200, 1173, 806, 772; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε in): 232 (4.50), 285 (4.49), 342 (4.34).

N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-methyl-1,2-phenylenediamine

(7): Yield 1.85 g, 83%, orange solid, mp = 184.9-186.0°C; **¹H-NMR** (CDCl₃) δ ppm: 13.61 (s, 1H), 13.57 (s, 1H), 8.65 (s, 2H), 7.43 (d, *J*=2.5 Hz, 1H), 7.42 (d, *J*=2.5 Hz, 1H), 7.21 (d, *J*=2.5 Hz, 1H), 7.20 (d, *J*=2.5 Hz, 1H), 7.17-7.13 (m, 1H), 7.13-7.08 (m, 1H), 7.06-7.02 (m, 1H), 1.44 (s, 9H), 1.43 (s, 9H), 1.320 (s, 9H), 1.317 (s, 9H); **¹³C-NMR** (CDCl₃) δ ppm: 164.6, 163.9, 158.6, 158.5, 142.6, 140.26, 140.24, 140.16, 137.4, 137.2, 137.1, 128.1, 127.9, 126.8, 126.7, 120.5, 119.4, 118.45, 118.40, 35.1, 34.2, 31.5, 29.5, 21.1; **HRMS** (AuNPET LDI-ToF) *m/z*: calculated for C₃₇H₅₀N₂NaO₂⁺ [M+Na]⁺ = 577.3764 found 577.3870, for C₃₇H₅₁N₂O₂⁺ [M+H]⁺ = 555.3945

found 555.4090; **FT-IR** (KBr, cm^{-1}): 2954, 2908, 2869, 1617, 1581, 1468, 1439, 1393, 1361, 1273, 1250, 1200, 1173, 857, 807, 773; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 233 (4.22), 281 (4.17), 342 (4.06).

N,N'-Bis(3-tert-butyl-5-methoxysalicylidene)-4,5-dichloro-1,2-phenylenediamine

(8): Yield 1.91 g, 83%, orange solid, mp = 189.2-190.0 °C; **$^1\text{H-NMR}$** (CDCl_3) δ ppm: 13.00 (s, 2H), 8.60 (s, 2H), 7.35 (s, 2H), 7.06 (d, $J=3.0$ Hz, 2H), 6.71 (d, $J=3.0$ Hz, 2H), 3.79 (s, 6H), 1.41 (s, 18H); **$^{13}\text{C-NMR}$** (CDCl_3) δ ppm: 164.9, 155.7, 151.6, 141.9, 139.8, 130.7, 121.2, 120.6, 118.0, 111.8, 55.8, 35.1, 29.2; **HRMS** (AuNPET LDI-ToF) m/z : calculated for $\text{C}_{30}\text{H}_{34}\text{Cl}_2\text{N}_2\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$ = 579.1788 found 579.1811 for $\text{C}_{30}\text{H}_{35}\text{Cl}_2\text{N}_2\text{O}_4^+$ $[\text{M}+\text{H}]^+$ = 557.1968 found 557.1845; **FT-IR** (KBr, cm^{-1}): 2996, 2957, 2911, 2870, 2832, 1616, 1589, 1567, 1466, 1446, 1429, 1391, 1360, 1336, 1314, 1281, 1265, 1230, 1211, 1197, 1167, 1153, 1141, 1060, 980, 885, 869, 858, 793, 765; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 246 (4.49), 288 (4.47), 342 (4.23).

N,N'-Bis(3-tert-butyl-5-methoxysalicylidene)-4-methyl-1,2-phenylenediamine

(9): Yield 1.90 g, 92%, orange solid, mp = 160.1-162.5 °C; **$^1\text{H-NMR}$** (CDCl_3) δ ppm: 13.43 (s, 1H), 13.39 (s, 1H), 8.62 (s, 2H), 7.19-7.14 (m, 1H), 7.14-7.10 (m, 1H), 7.05 (br. s, 1H), 7.03 (d, $J=3.0$ Hz, 1H), 7.02 (d, $J=3.0$ Hz, 1H), 6.72 (d, $J=3.0$ Hz, 1H), 6.71 (d, $J=3.0$ Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 2.42 (s, 3H), 1.42 (s, 9H), 1.41 (s, 9H); **$^{13}\text{C-NMR}$** (CDCl_3) δ ppm: 163.9, 163.2, 155.6, 155.5, 151.4, 142.3, 139.8, 139.54, 139.49, 137.6, 128.1, 120.5, 119.6, 119.43, 119.41, 118.46, 118.40, 111.82, 111.79, 55.8, 35.07, 29.2, 21.1; **HRMS** (AuNPET LDI-ToF) m/z : calculated for $\text{C}_{31}\text{H}_{39}\text{N}_2\text{O}_4^+$ $[\text{M}+\text{H}]^+$ = 503.2904 found 503.3253; **FT-IR** (KBr, cm^{-1}): 2998, 2950, 2911, 2868, 2833, 1618, 1575, 1461, 1447, 1429, 1360, 1332, 1314, 1279, 1231, 1210, 1195, 1150, 1060, 858, 835, 806, 795, 776, 763; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 243 (4.59), 282 (4.51), 346 (sh), 368 (4.38).

N,N'-Bis(3-tert-butyl-salicylidene)-4-methyl-1,2-phenylenediamine

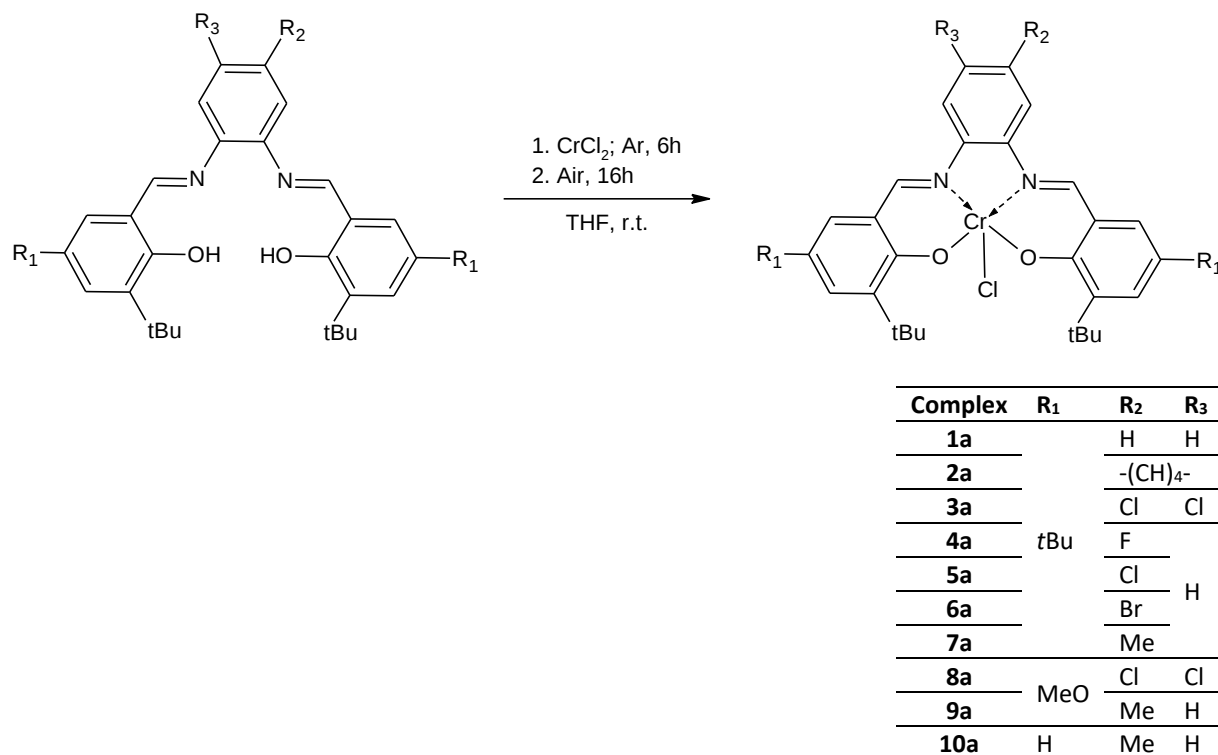
(10): Yield 1.33 g, 75%, orange solid, mp = 117.1-118.8 °C; **$^1\text{H-NMR}$** (CDCl_3) δ ppm: 13.80 (s, 1H), 13.75 (s, 1H), 8.643 (s, 1H), 8.639 (s, 1H), 7.40-7.33 (m, 2H), 7.26-7.20 (m, 2H), 7.18-7.09 (m, 2H), 7.05 (br. s, 1H), 6.88-6.80 (m, 2H), 2.42 (s, 3H), 1.44 (s, 9H), 1.43 (s, 9H); **$^{13}\text{C-NMR}$** (CDCl_3) δ ppm: 160.8, 160.7, 142.4, 139.9, 137.81, 137.77, 137.6, 130.7, 130.6, 130.4, 130.2, 128.1, 120.4, 119.3, 119.2, 118.10, 118.07, 34.9, 29.3, 29.2, 21.1; **HRMS** (AuNPET LDI-ToF)

m/z : calculated for $C_{29}H_{34}N_2NaO_2^+$ $[M+Na]^+ = 465.2512$ found 465.2270, for $C_{29}H_{35}N_2O_2^+$ $[M+H]^+ = 443.2693$; found 443.2470; **FT-IR** (KBr, cm^{-1}): 2953, 2913, 2870, 1609, 1573, 1564, 1502, 1484, 1470, 1428, 1392, 1363, 1311, 1276, 1192, 1143, 1116, 1085, 965, 856, 836, 809, 751, 743, 488; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 231 (4.50), 278 (4.48), 341 (4.41).

2.3. Syntheses of salophen chromium(III) complexes

Chromium(III) complexes were prepared in the reaction between the salophen ligands and anhydrous $CrCl_2$ with the subsequent oxidation (*in situ*) of chromium(II) to chromium(III) ions (Scheme S2). Reactions conditions were selected according to literature method.^{S4-S6}

The structures of the chromium(III) complexes were determined based on the results of FT-IR, HRMS and ICP-OES analyses. The results of elementary analysis showed that the resulting salophen chromium(III) complexes **1a-10a** contain the molecule of THF coordinated additionally to the metal center. The HRMS spectra provided the peaks with the values corresponding to $(salophen)CrCl^+$ or $(salophen)Cr^+$ ions, without THF which is lost during analysis.



Scheme S2. Synthesis of the salophen chromium(III) complexes **1.1 – 10.1**.

General synthesis procedure. Salophen ligand (1.0 mmol) and CrCl₂ (1.3 mmol) were transferred to the Schlenk tube under argon and 30 ml of anhydrous THF was added. The resulting mixture having deep red colour was stirred at ambient temperature for 6 hrs under argon. Then, the tube was opened and the mixture was allowed to stir under air for additional 16 hrs. After the addition of 50 ml diethyl ether, the organic layer was washed with the saturated aqueous solutions of NH₄Cl (3 x 50 ml) and NaCl (1 x 50 ml) and dried over Na₂SO₄. The organic solvent was evaporate under reduced pressure to yield dark red-brown solid. It was then re-suspended in pentane and the resulting mixture was cooled to -20°C. The final product was filtered off and dried under vacuum.

[N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-phenylenediamine]chromium(III) chloride

(1a): Yield 0.69, 99%, red-brown solid, **FT-IR** (KBr, cm⁻¹): 2955, 2904, 2868, 1604, 1578, 1526, 1485, 1462, 1427, 1387, 1360, 1256, 1196, 1173, 750, 540; **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* C₃₆H₄₆ClCrN₂O₂⁺ [M]⁺ = 625.2647 *found* [M]⁺ = 625.2664; **Elemental analysis** *calculated (%) for* C₃₆H₄₆ClCrN₂O₂ **(1a)** Cr 8.30, *for* C₄₀H₅₄ClCrN₂O₃ **(1a · THF)** Cr 7.45 *found* Cr 7.44; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε): 245 (3.98), 318 (sh), 345 (4.38), 404 (sh), 498 (4.47).

[N,N'-Bis(3,5-di-tert-butylsalicylidene)-2,3-naphthalenediamine]chromium(III) chloride

(2a): Yield 0.63 g, 84%, red-brown solid, **FT-IR** (KBr, ν_{max}/cm⁻¹): 2954, 2904, 2867, 1597, 1576, 1526, 1546, 1526, 1503, 1462, 1423, 1388, 1360, 1339, 1254, 1198, 1172, 1148, 1133, 867, 786, 539, 506; **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* C₄₀H₄₈ClCrN₂O₂⁺ [M]⁺ = 675.2804 *found* 675.2675, *for* [M-Cl]⁺ = 640.3115 *found* 640.2936; **Elemental analysis** *calculated (%) for* C₄₀H₄₈ClCrN₂O₂ **(2a)** Cr 7.69, *for* C₄₄H₅₆ClCrN₂O₃ **(2a · THF)** Cr 6.95 *found* Cr 6.65; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ε): 239 (4.36), 332 (4.24), 406 (sh), 510 (3.82).

[N,N'-Bis(3,5-di-tert-butylsalicylidene)-4,5-dichloro-1,2-phenylenediamine]chromium(III) chloride

(3a): Yield 0.75 g, 98%, red-brown solid, **FT-IR** (KBr, cm⁻¹): 2956, 2904, 2868, 1597, 1575, 1548, 1525, 1468, 1422, 1387, 1358, 1257, 1197, 1173, 1131, 892, 841, 786, 544, 485; **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* C₃₆H₄₄Cl₂CrN₂O₂⁺ [M-Cl]⁺ = 658.2179 *found* 658.2151; **Elemental analysis** *calculated (%) for* C₃₆H₄₄Cl₃CrN₂O₂ **(3a)** Cr 7.48, *for* C₄₀H₅₂Cl₃CrN₂O₃

(3a·THF) Cr 6.78 *found* Cr 6.42; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ϵ): 234 (4.43), 246 (sh), 316 (4.35), 352 (4.36), 412 (3.97), 514 (3.98).

[N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-fluoro-1,2-phenylenediamine]chromium(III) chloride
(4a): Yield 0.53 g, 74%, red-brown solid, **FT-IR** (KBr, cm⁻¹): 2956, 2905, 2869, 1610, 1583, 1526, 1495, 1462, 1424, 1386, 1360, 1274, 1262, 1251, 1173, 843, 786, 542, 510; **HRMS** (AuNPET LDI-ToF) *m/z*: *calculated for* C₃₆H₄₅ClFCrN₂O₂⁺ [M]⁺ = 643.2553 *found* [M]⁺ = 643.2514, *for* C₃₆H₄₅FCrN₂O₂⁺ [M-Cl]⁺ = 608.2865 *found* 608.2812; **Elemental analysis** *calculated (%) for* C₃₆H₄₅ClFCrN₂O₂ **(4a)** Cr 8.07, *for* C₄₀H₅₃ClFCrN₂O₃ **(4a·THF)** Cr 7.26 *found* Cr 7.29; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ϵ): 237 (4.45), 313 (4.32), 347 (4.35), 400 (sh), 505 (3.96).

[N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-chloro-1,2-phenylenediamine]chromium(III) chloride
(5a): Yield 0.70 g, 96%, red-brown solid, **FT-IR** (KBr, cm⁻¹): 2956, 2905, 2868, 1599, 1575, 1548, 1526, 1483, 1462, 1424, 1386, 1360, 1256, 1196, 1173, 786, 541; **HRMS** (AuNPET LDI-ToF) *m/z*: *calculated for* C₃₆H₄₅ClCrN₂O₂⁺ [M-Cl]⁺ = 624.2569 *found* 624.2382; **Elemental analysis** *calculated (%) for* C₃₆H₄₅Cl₂CrN₂O₂ **(5a)** Cr 7.87, *for* C₄₀H₅₃Cl₂CrN₂O₃ **(5a·THF)** Cr 7.10 *found* Cr 6.92; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ϵ): 237 (4.51), 315 (4.41), 348 (4.42), 400 (sh), 507 (4.02).

[N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-bromo-1,2-phenylenediamine]chromium(III) chloride
(6a): Yield 0.51 g, 66%, red-brown solid, **FT-IR** (KBr, cm⁻¹): 2955, 2904, 2867, 1597, 1573, 1547, 1525, 1481, 1462, 1423, 1379, 1359, 1256, 1195, 1173, 839, 786, 541; **HRMS** (AuNPET LDI-ToF) *m/z*: *calculated for* C₃₆H₄₅ClBrCrN₂O₂⁺ [M]⁺ = 703.1752 *found* 703.2047, *for* C₃₆H₄₅BrCrN₂O₂⁺ [M-Cl]⁺ = 668.2064 *found* 668.1824; **Elemental analysis** *calculated (%) for* C₃₆H₄₅ClBrCrN₂O₂ **(6a)** Cr 7.37, *for* C₄₀H₅₃ClBrCrN₂O₃ **(6a·THF)** Cr 6.69 *found* Cr 6.64; **UV-Vis** (CH₂Cl₂) λ_{max} in nm (log ϵ): 235 (4.42), 316 (4.33), 350 (4.35), 406 (sh), 510 (2.96).

[N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-methyl-1,2-phenylenediamine]chromium(III) chloride
(7a): Yield 0.70 g, 98%, red-brown solid, **FT-IR** (KBr, cm⁻¹): 2954, 2904, 2867, 1612, 1585, 1526, 1497, 1462, 1426, 1385, 1359, 1259, 1195, 1173, 785, 542; **HRMS** (AuNPET LDI-ToF) *m/z*: *calculated for* C₃₇H₄₈ClCrN₂O₂⁺ [M]⁺ = 639.2804 *found* 639.2797; *for* C₃₇H₄₈CrN₂O₂⁺

$[M-Cl]^+ = 604.3115$ found 604.3045; **Elemental analysis** calculated (%) for $C_{37}H_{48}ClCrN_2O_2$ (**7a**) Cr 8.12, for $C_{41}H_{56}ClCrN_2O_3$ (**7a**·THF) Cr 7.30 found Cr 7.38; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 236 (4.43), 245 (4.43), 327 (4.32), 341 (4.32), 398 (sh), 502(3.92).

[N,N'-Bis(3-tert-butyl-5-methoxysalicylidene)-4,5-dichloro-1,2-phenylenediamine]chromium(III) chloride

(8a): Yield 0.44 g, 62%, purple solid, **FT-IR** (KBr, cm^{-1}): 3093, 2956, 2908, 1694, 1597, 1533, 1471, 1410, 1387, 1359, 1309, 1282, 1226, 1208, 1194, 1159, 1058, 826; **HRMS** (AuNPET LDI-ToF) m/z: calculated for $C_{30}H_{32}Cl_3CrN_2O_4^+$ $[M]^+ = 641.0833$ found 641.0832, for $C_{30}H_{32}Cl_2CrN_2O_4^+$ $[M-Cl]^+ = 606.1139$ found 606.0981; **Elemental analysis** calculated (%) for $C_{30}H_{32}Cl_3CrN_2O_4$ (**8a**) Cr 8.09, for $C_{34}H_{40}Cl_3CrN_2O_5$ (**8a**·THF) Cr 7.27 found Cr 6.90; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 234 (4.43), 312 (4.17), 344 (4.16), 520 (3.65).

[N,N'-Bis(3-tert-butyl-5-methoxysalicylidene)-4-methyl-1,2-phenylenediamine]chromium(III) chloride

(9a): Yield 0.50 g, 76%, dark red solid, **FT-IR** (KBr, cm^{-1}): 2954, 2910, 1611, 1590, 1535, 1499, 1464, 1415, 1387, 1360, 1317, 1225, 1211, 1186, 1170, 1154, 1112, 1059, 824, 778, 568, 406; **HRMS** (AuNPET LDI-ToF) m/z: calculated for $C_{31}H_{36}CrN_2O_4^+$ $[M-Cl]^+ = 552.2075$ found 552.1942; **Elemental analysis** calculated (%) for $C_{31}H_{36}ClCrN_2O_4$ (**9a**) Cr 8.84, for $C_{35}H_{44}ClCrN_2O_5$ (**9a**·THF) Cr 7.88 found Cr 7.97; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 233 (4.40), 298 (4.24), 328 (sh), 406 (3.74), 523 (3.66).

[N,N'-Bis(3-tert-butyl-salicylidene)-4-methyl-1,2-phenylenediamine]chromium(III) chloride

(10a): Yield 0.59 g, 98%, brown solid, **FT-IR** (KBr, cm^{-1}): 2954, 2867, 1611, 1602, 1588, 1536, 1501, 1463, 1417, 1382, 1355, 1338, 1255, 1185, 1147, 1087, 870, 814, 750, 561, 507; **HRMS** (AuNPET LDI-ToF) m/z: calculated for $C_{29}H_{32}ClCrN_2NaO_2^+$ $[M+Na]^+ = 550.1445$ found 550.1440, for $C_{29}H_{32}CrN_2O_2^+$ $[M-Cl]^+ = 492.1863$ found 492.1883; **Elemental analysis** calculated (%) for $C_{29}H_{32}ClCrN_2O_2$ (**10a**) Cr 9.85, for $C_{33}H_{40}ClCrN_2O_3$ (**10a**·THF) Cr 8.66 found Cr 8.29; **UV-Vis** (CH_2Cl_2) λ_{max} in nm (log ϵ): 240 (4.48), 314 (sh), 339 (4.36), 404 (sh), 484 (3.99).

Table S1. Calculated value of $10Dq$ base on electronic spectra of salophen ligands and their chromium(III) complexes **1a-10a**

Complex	$10Dq$ [cm^{-1}]
1a	20080
2a	19610
3a	19455
4a	19800
5a	19725
6a	19610
7a	19920
8a	19230
9a	19120
10a	20660

3. Spectra

3.1. NMR spectra of the obtained polymers

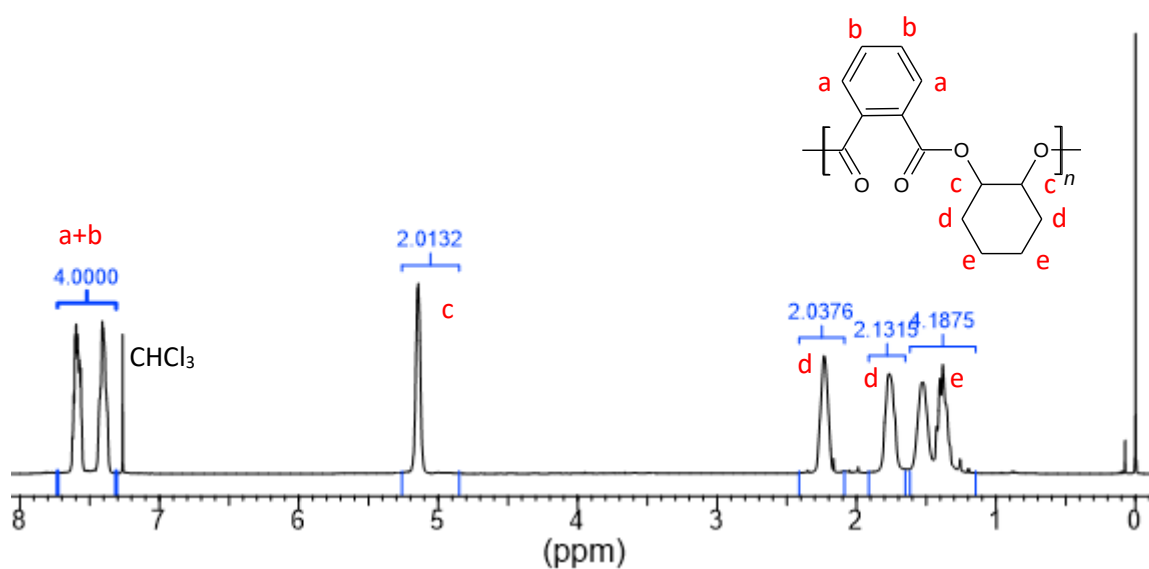


Fig. S1. 1H -NMR ($CDCl_3$) spectra of the obtained poly(cyclohexene phthalate),

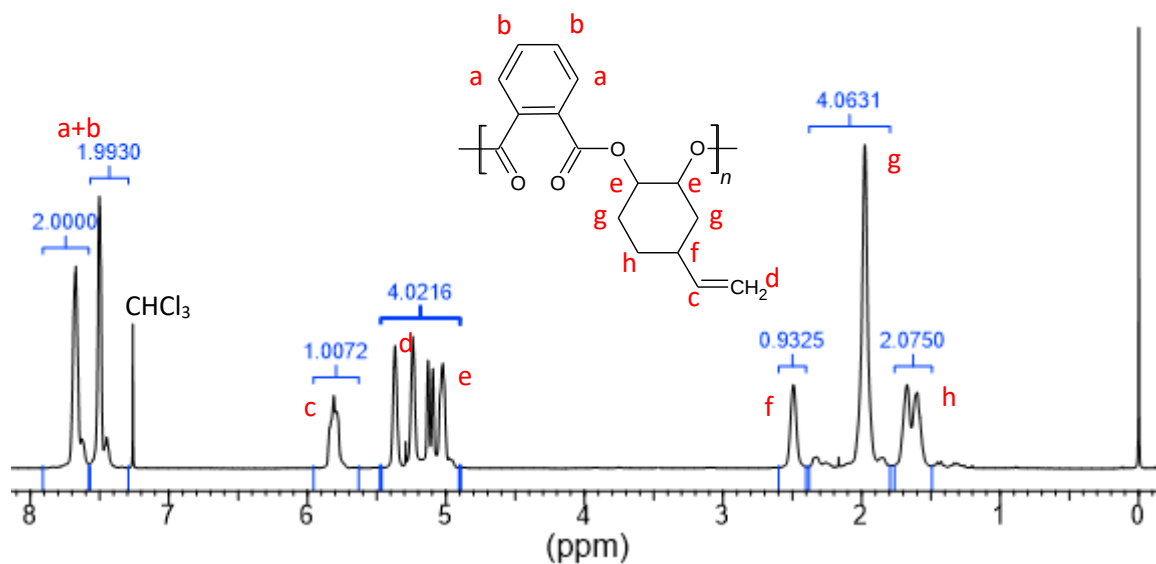


Fig. S2. $^1\text{H-NMR}$ (CDCl_3) spectra of the obtained poly(4-vinylcyclohexen phthalate).

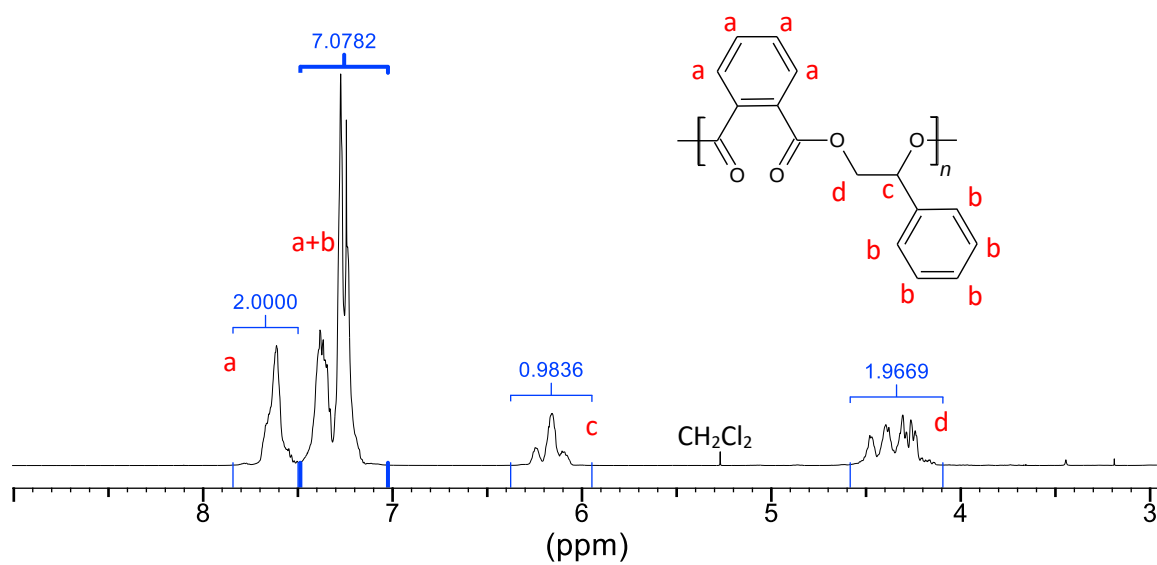


Fig. S3. $^1\text{H-NMR}$ (CDCl_3) spectra of the obtained poly(phenylethylene phthalate).

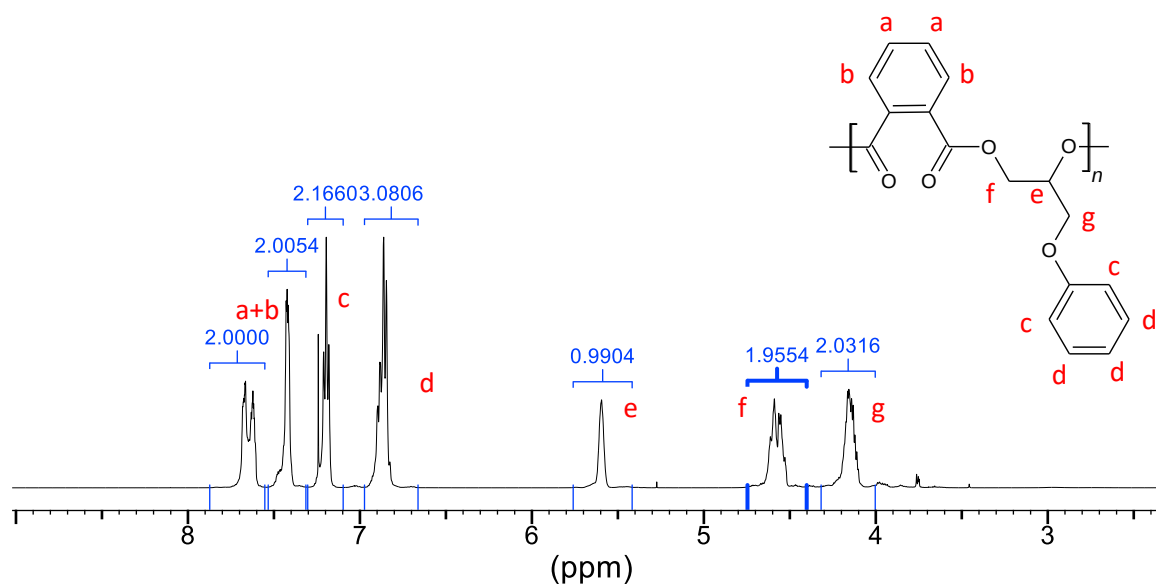


Fig. S4. ¹H-NMR (CDCl₃) spectra of the obtained poly(phenoxyethylene phthalate).

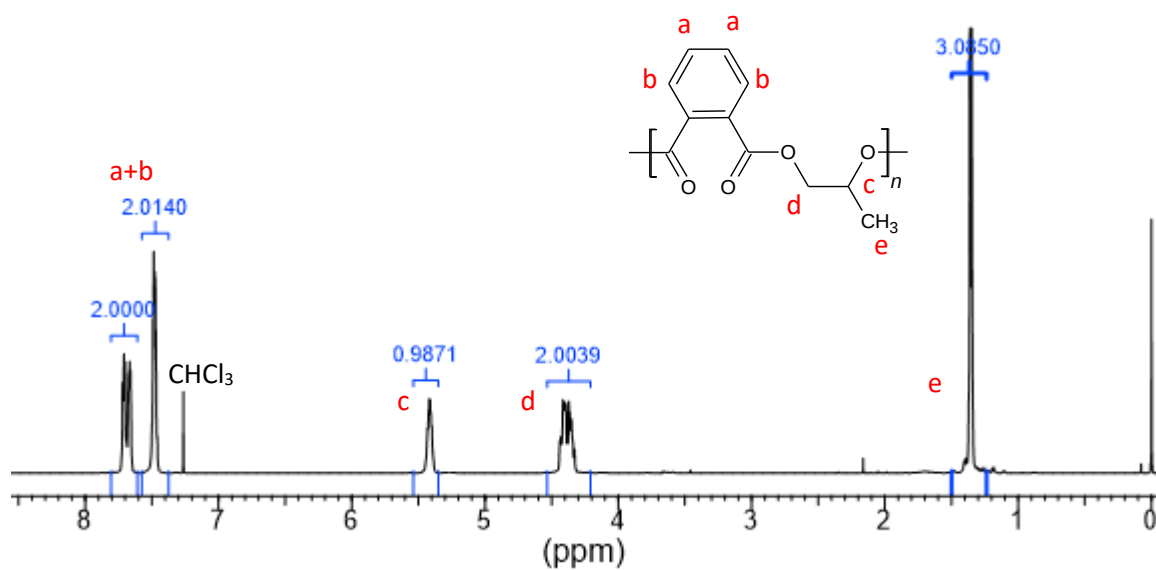


Fig. S5. ¹H-NMR (CDCl₃) spectra of the obtained poly(propylene phthalate).

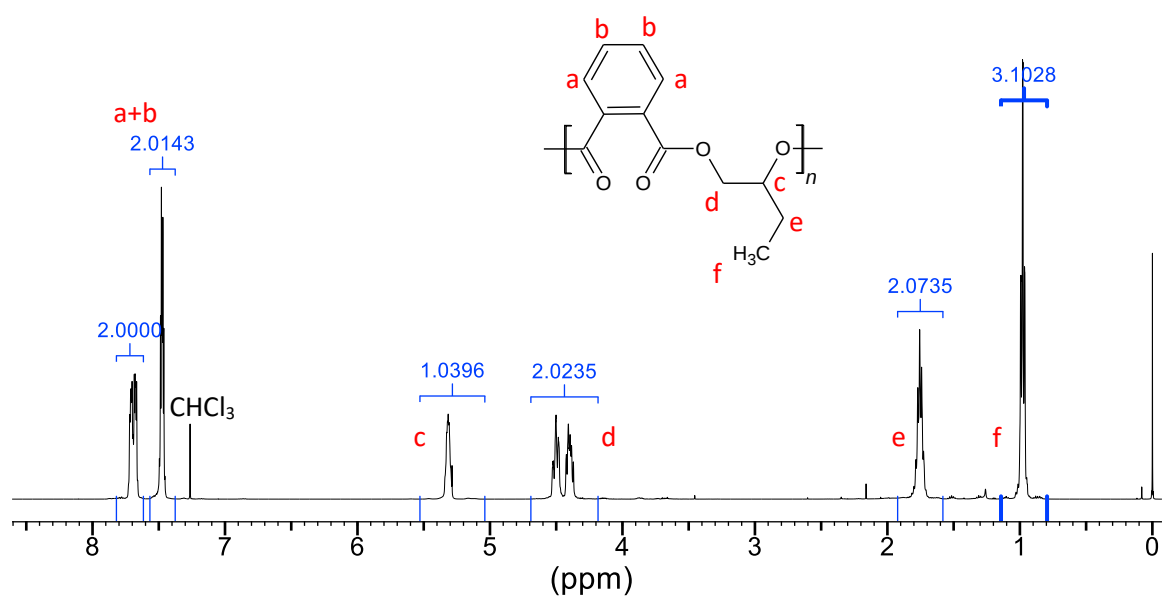


Fig. S6. ^1H -NMR (CDCl_3) spectra of the obtained poly(butylene phthalate).

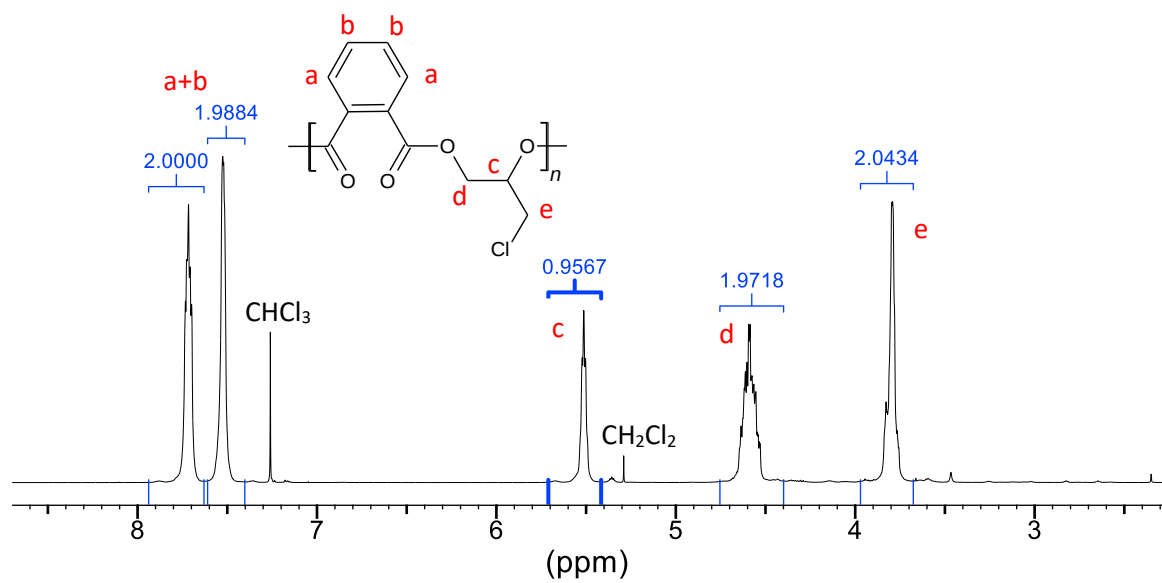


Fig. S7. ^1H -NMR (CDCl_3) spectra of the obtained poly(chloromethylethylene phthalate).

3.2. FTIR spectra of the obtained polyesters

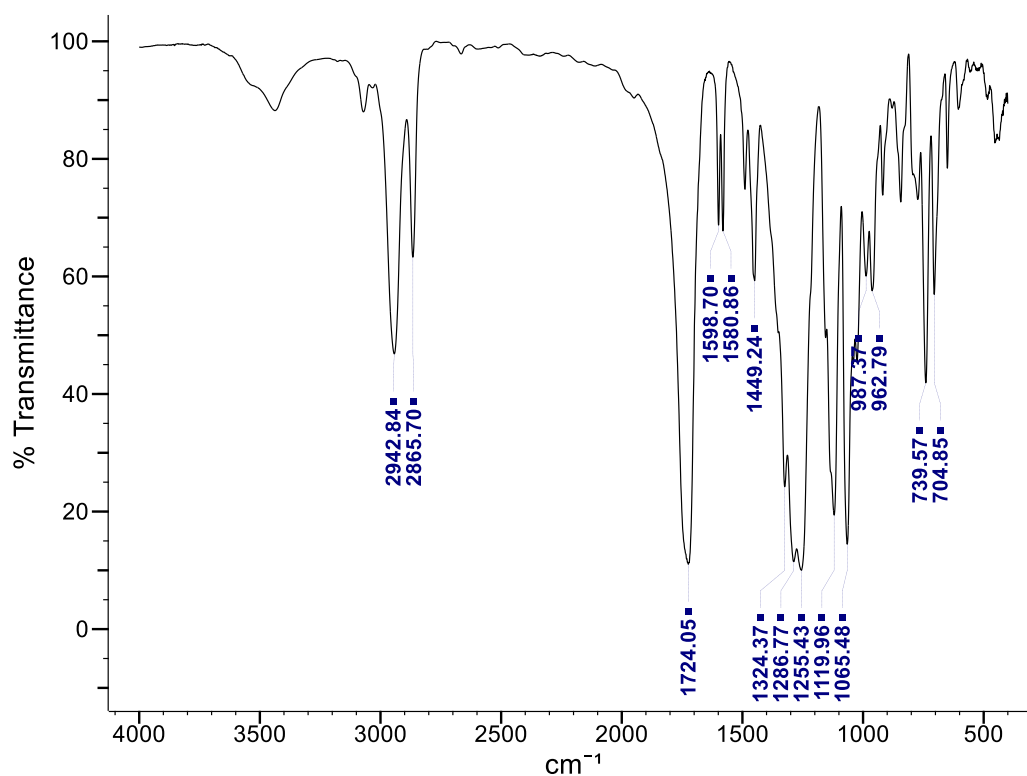


Fig. S8. FT-IR (KBr) spectra of the obtained poly(cyclohexene phthalate).

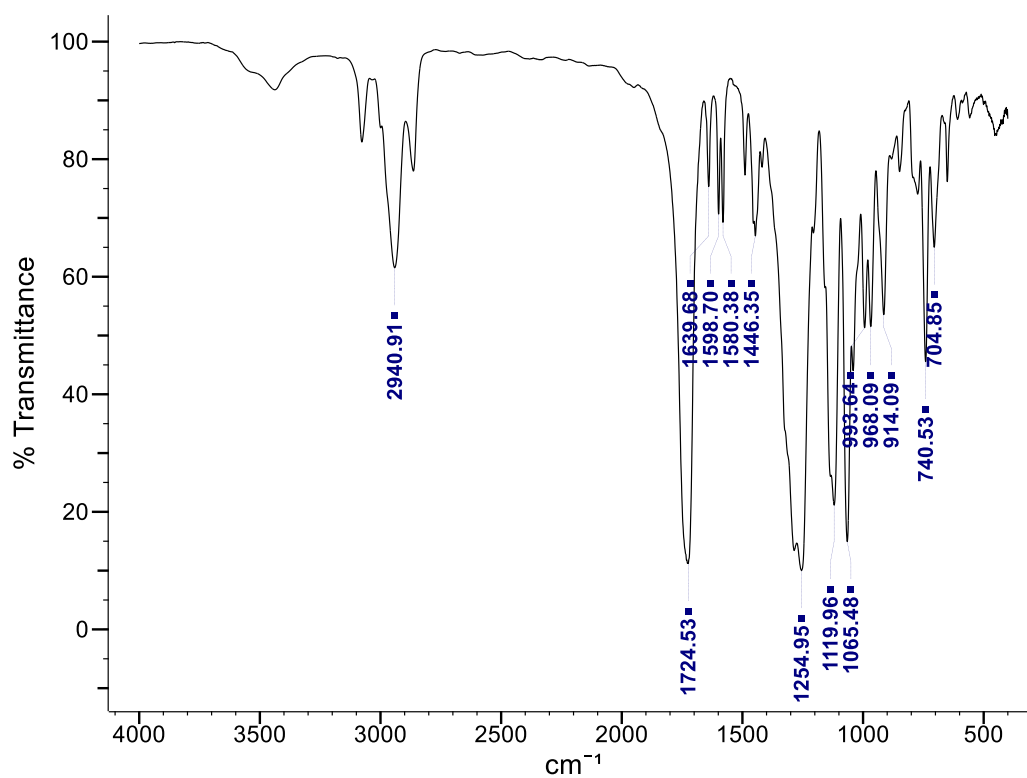


Fig. S9. FT-IR (KBr) spectra of the obtained poly(4-vinylcyclohexene phthalate).

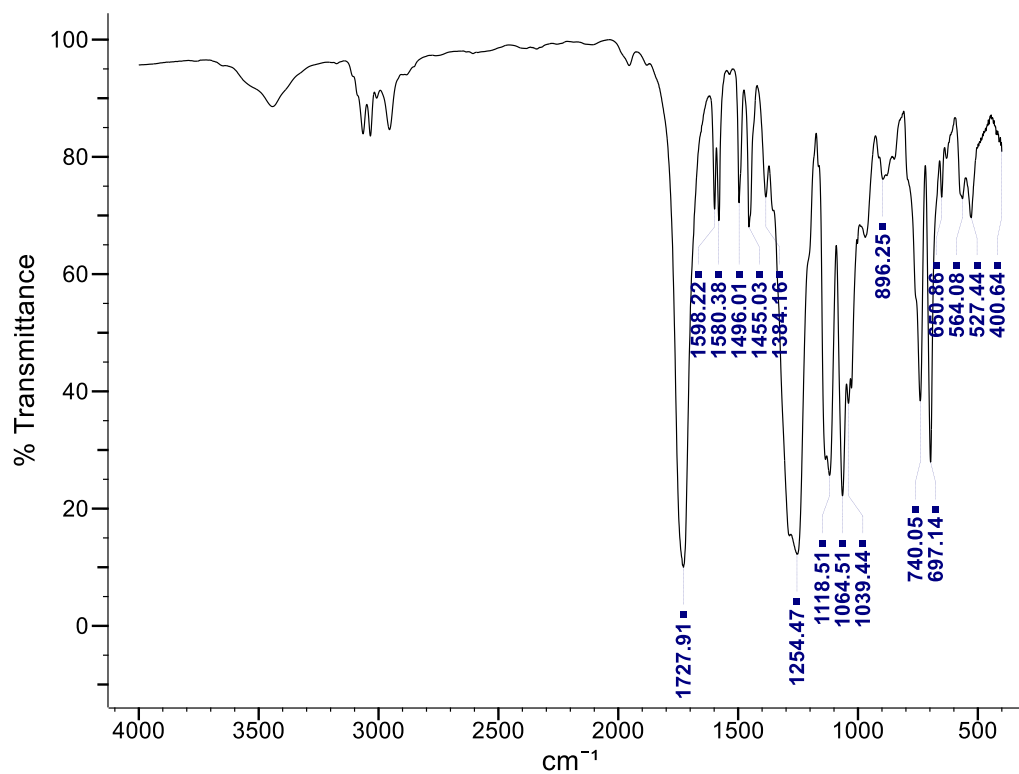


Fig. S10. FT-IR (KBr) spectra of the obtained poly(phenylethylene phthalate).

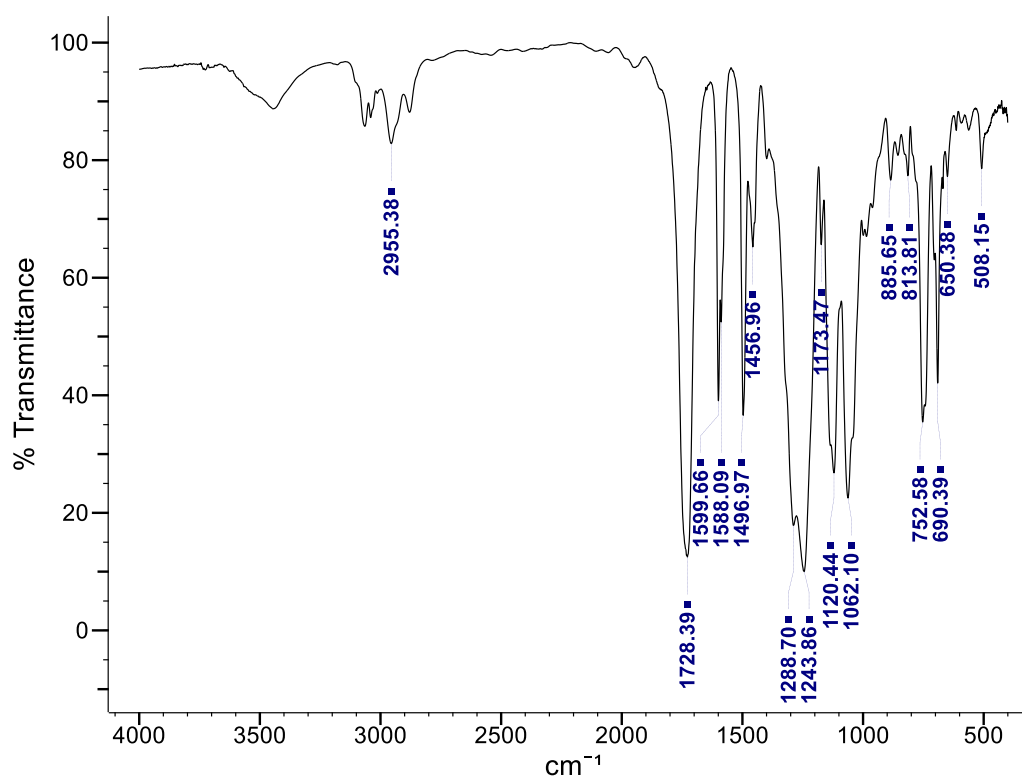


Fig. S11. FT-IR (KBr) spectra of the obtained poly(phenoxyethylene phthalate).

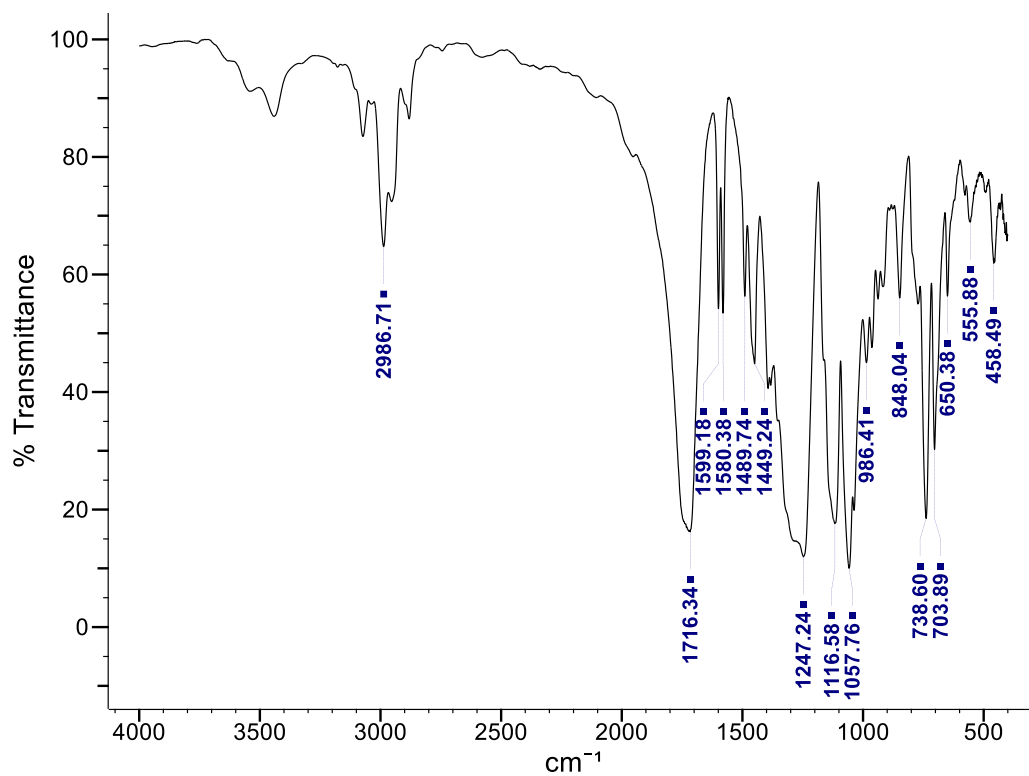


Fig. S12. FT-IR (KBr) spectra of the obtained poly(propylene phthalate).

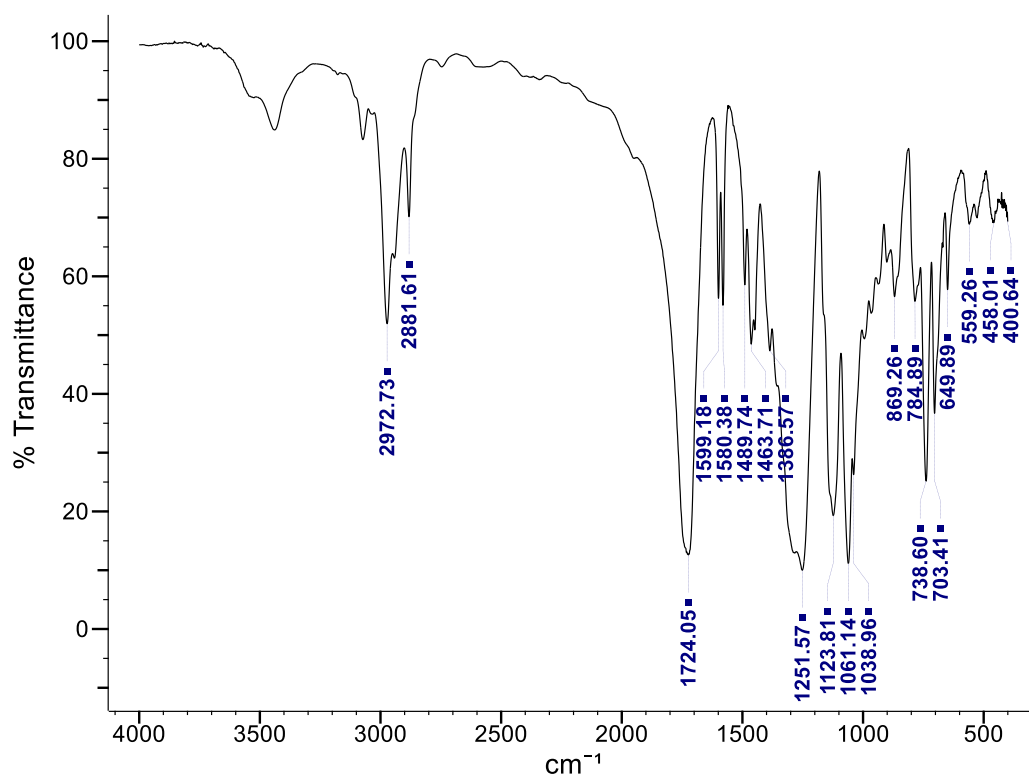


Fig. S13. FT-IR (KBr) spectra of the obtained poly(buthylene phthalate).

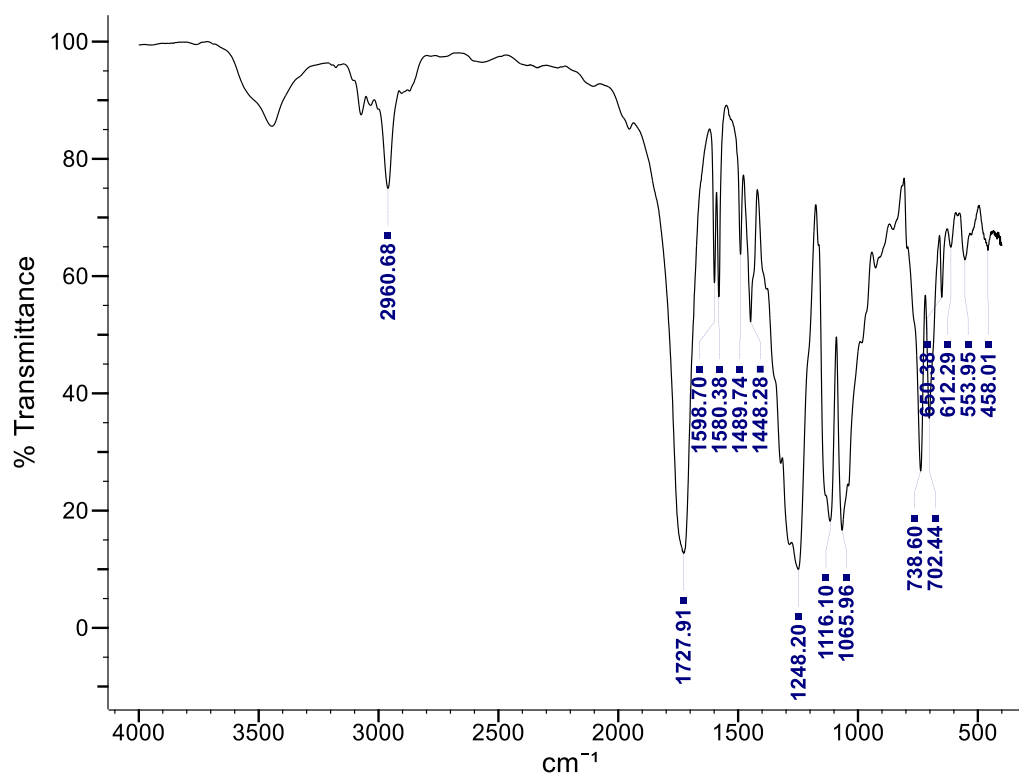


Fig. S14. FT-IR (KBr) spectra of the obtained poly(chloromethylethylene phthalate).

4. DSC thermograms

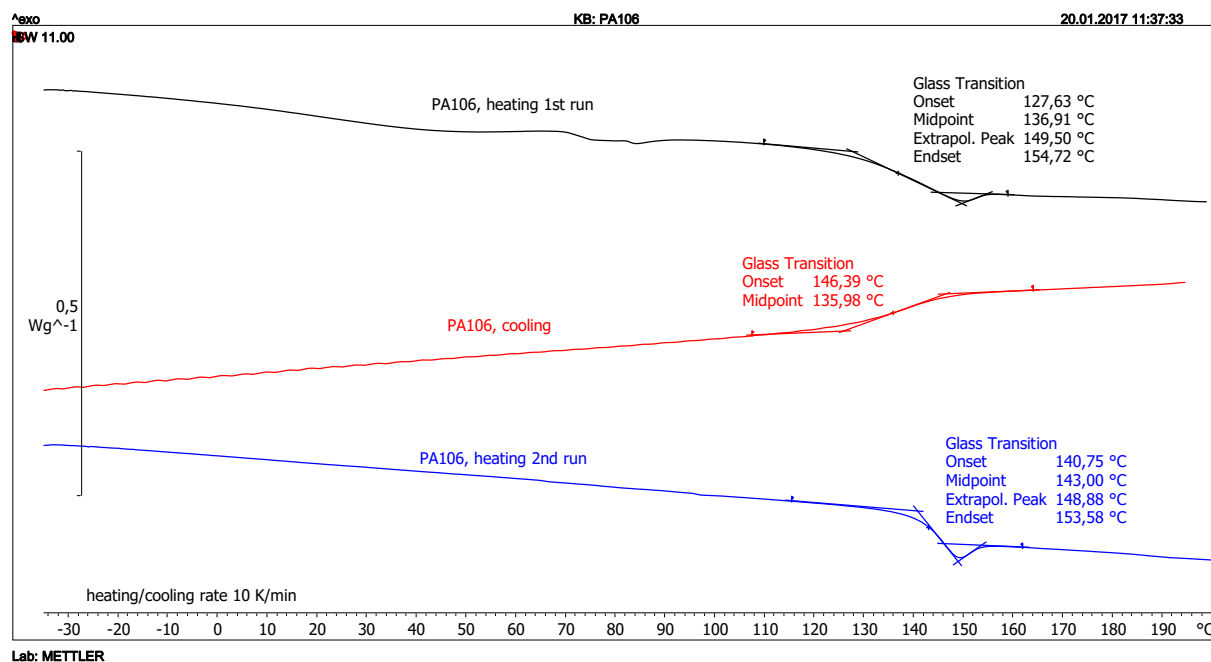


Fig. S15. DSC thermograms of the obtained poly(cyclohexene phthalate).

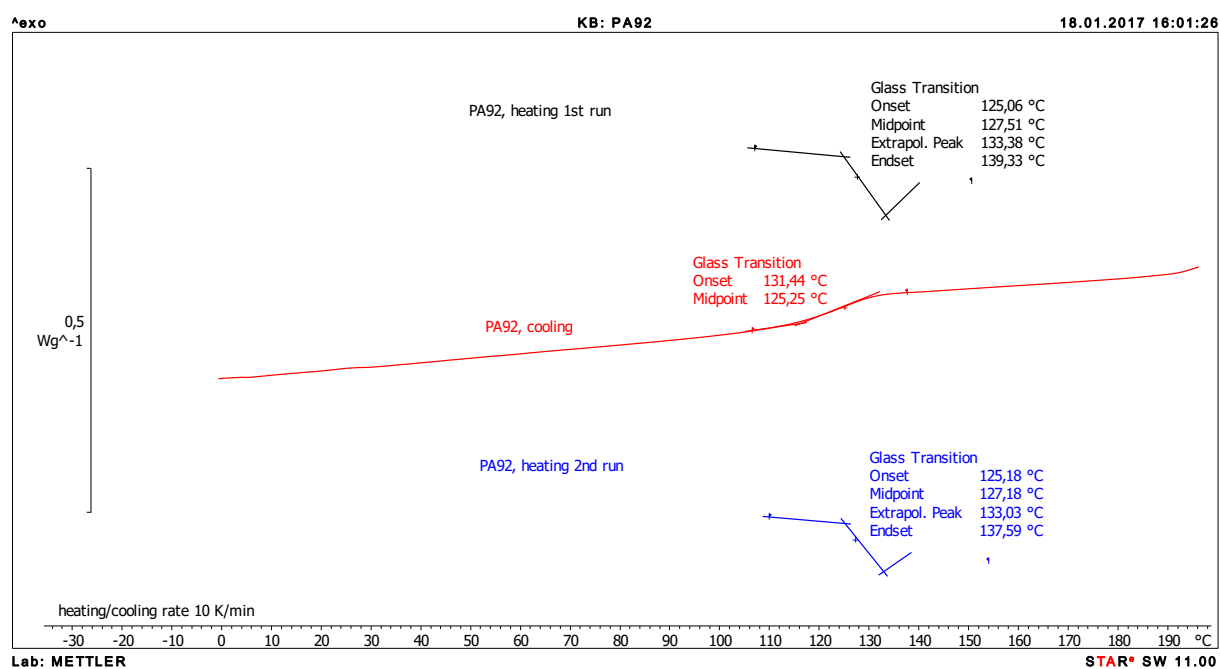


Fig. S16. DSC thermograms of the obtained poly(4-vinylcyclohexene phthalate).

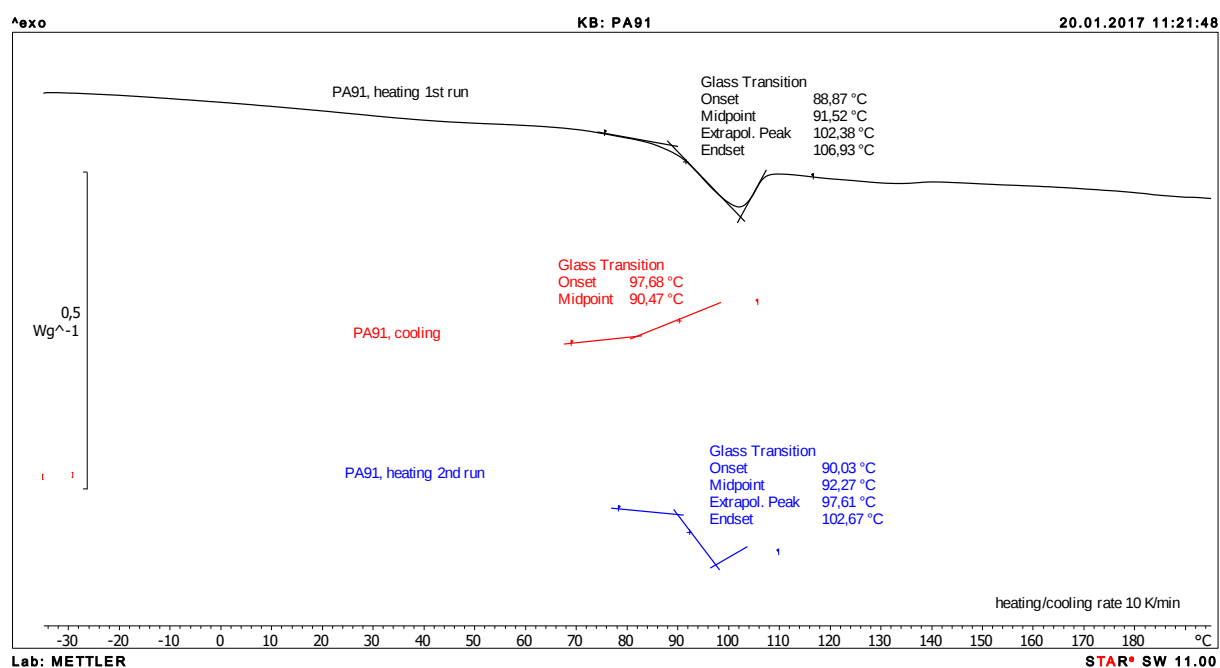


Fig. S17. DSC thermograms of the obtained poly(phenylethylene phthalate).

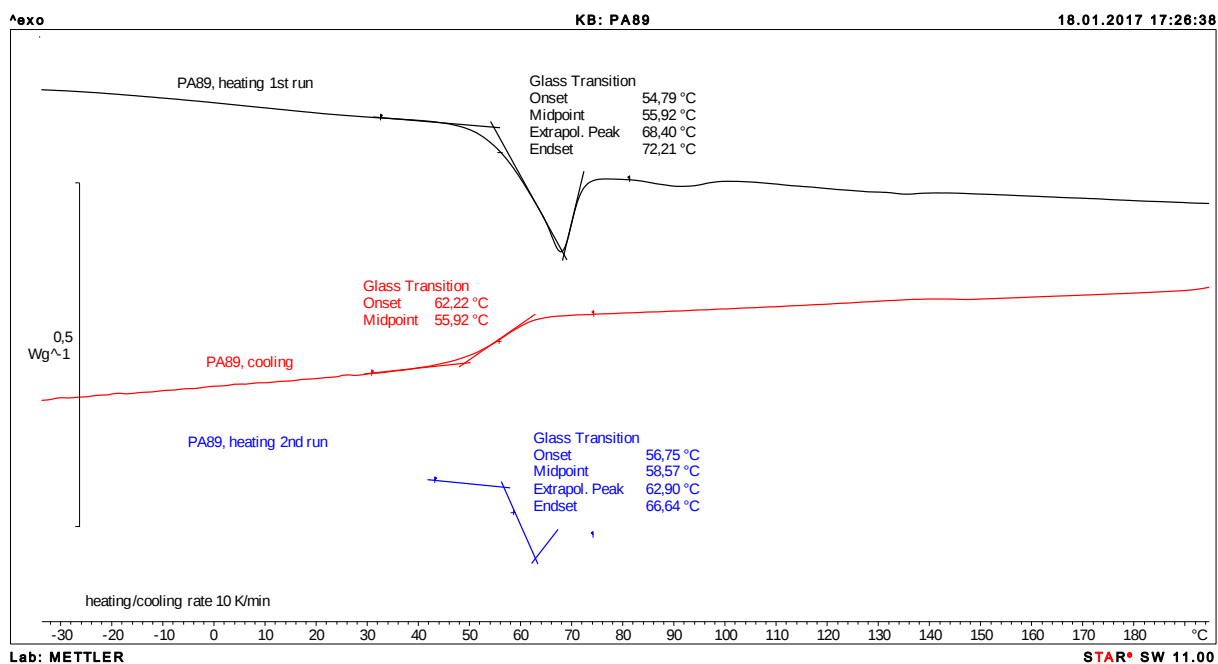


Fig. S18. DSC thermograms of poly(phenoxy methylethylene phthalate).

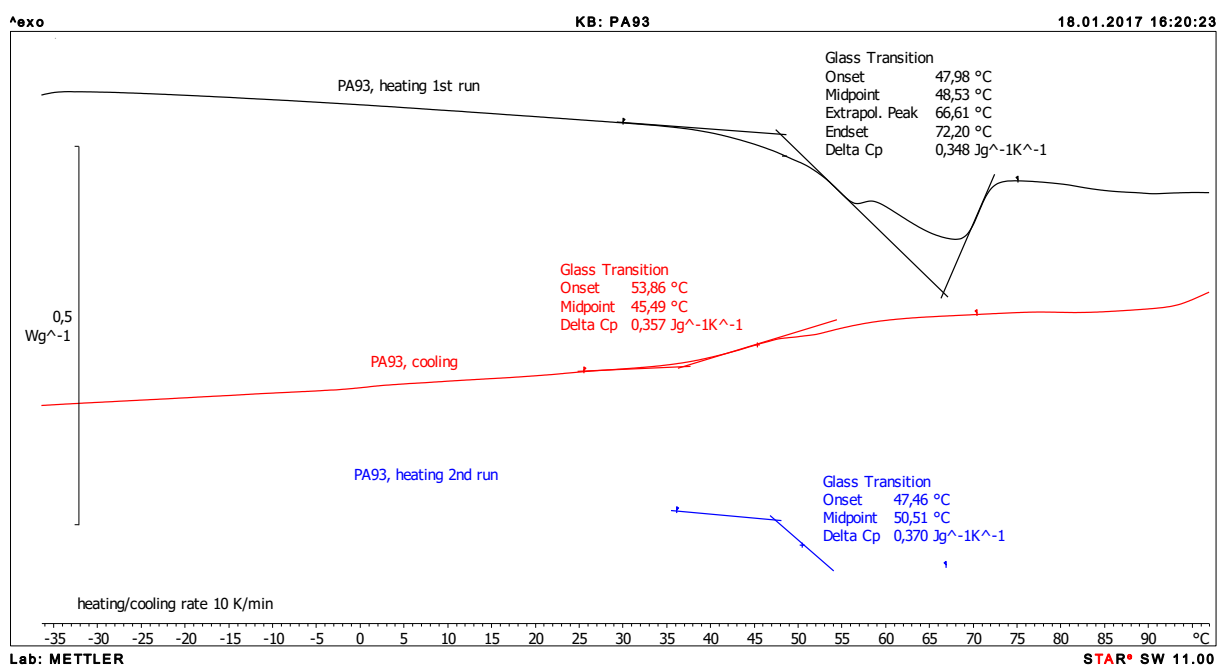


Fig. S19. DSC thermograms of the obtained poly(propylene phthalate).

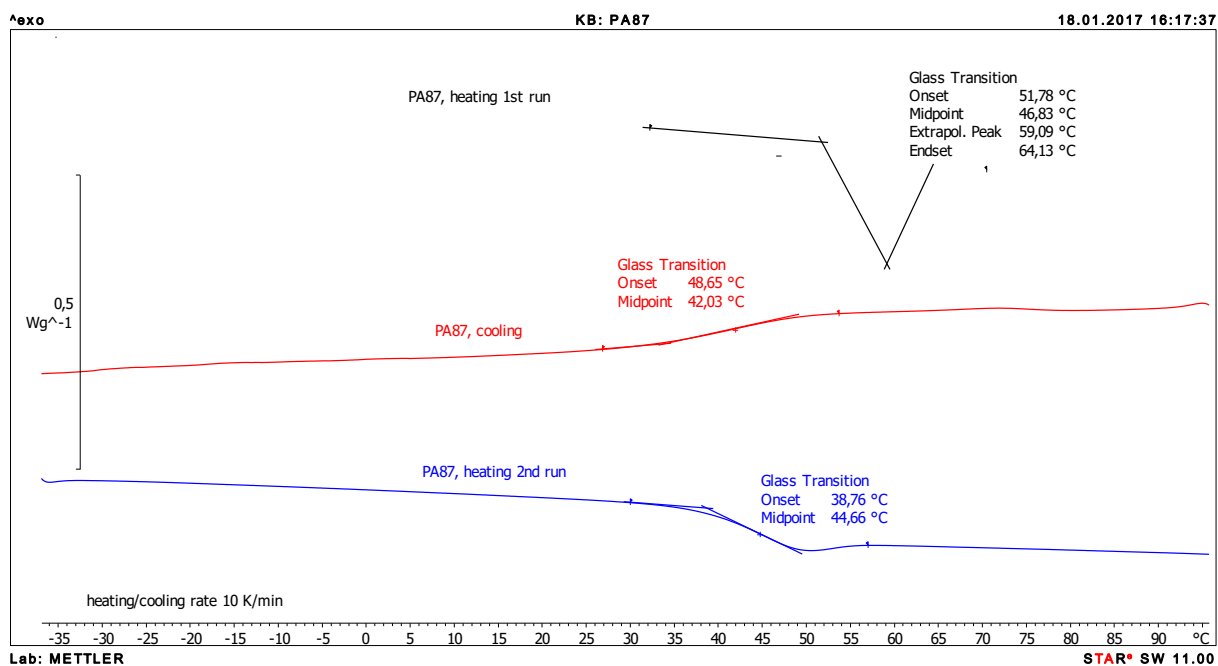


Fig. S20. DSC thermogram of the obtained poly(buthylene phthalate).

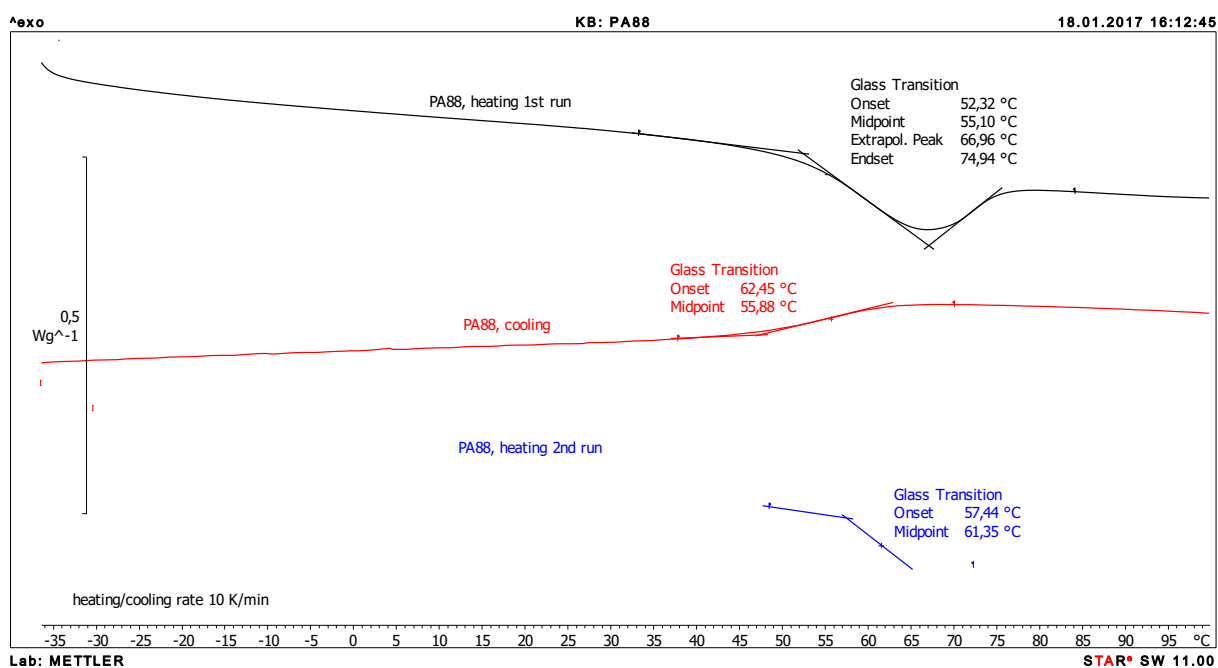


Fig. S21. DSC thermogram of the obtained poly(chloromethylethylene phthalate).

5. Representative GPC traces

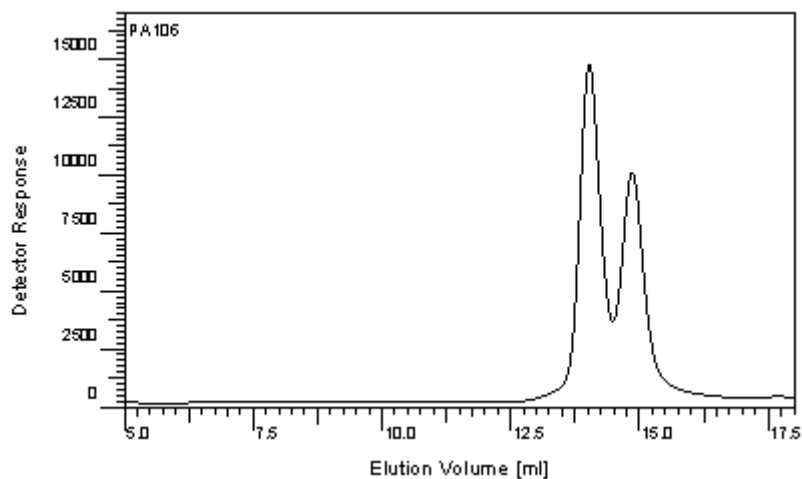


Fig. S22. Representative GPC trace for poly(cyclohexene phthalate) with $M_n = 13.7$ g/mol, $M_w = 15.9$ g/mol, $\bar{D} = 1.16$.

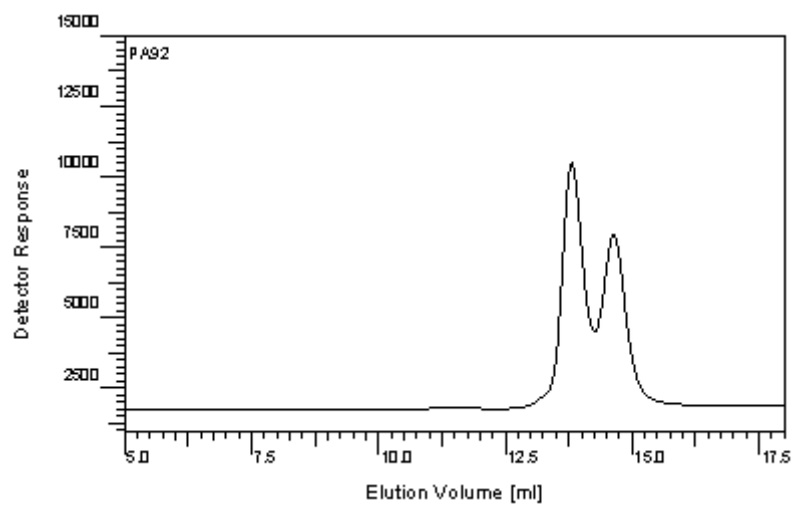


Fig. S23. Representative GPC trace for poly(4-vinyl cyclohexene phthalate) with $M_n = 19.1$ g/mol, $M_w = 22.5$ g/mol, $\bar{D} = 1.18$.

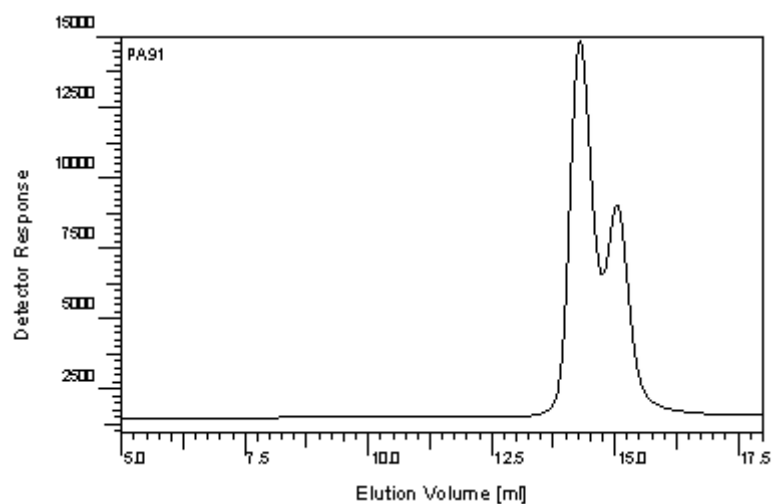


Fig. S24. Representative GPC trace for poly(phenylethylene phthalate) with $M_n = 13.5$ g/mol, $M_w = 15.8$ g/mol, $\bar{D} = 1.17$.

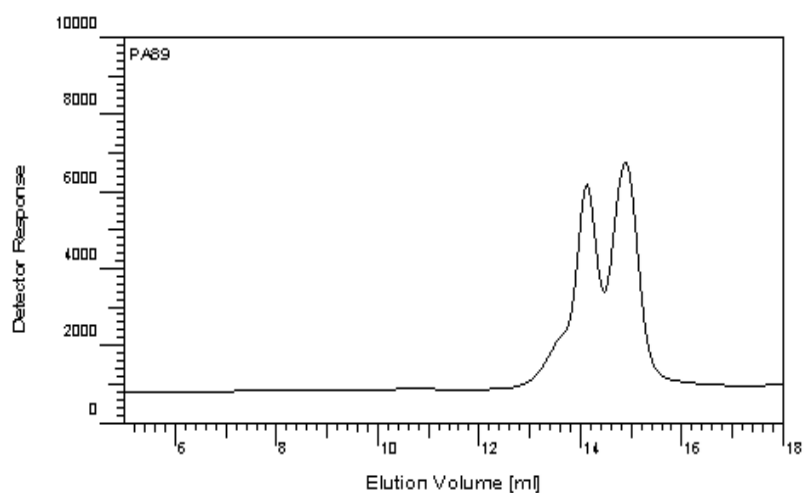


Fig. S25. Representative GPC trace for poly(phenoxyethylene phthalate) with $M_n = 14.6$ g/mol, $M_w = 22.2$ g/mol, $\bar{D} = 1.52$.

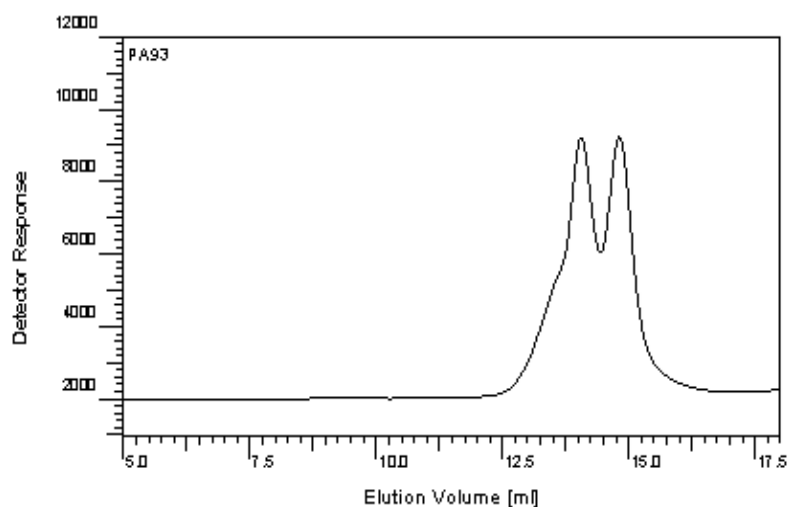


Fig. S26. Representative GPC trace for poly(propylene phthalate) with $M_n = 16.0$ g/mol, $M_w = 21.7$ g/mol, $\bar{D} = 1.36$.

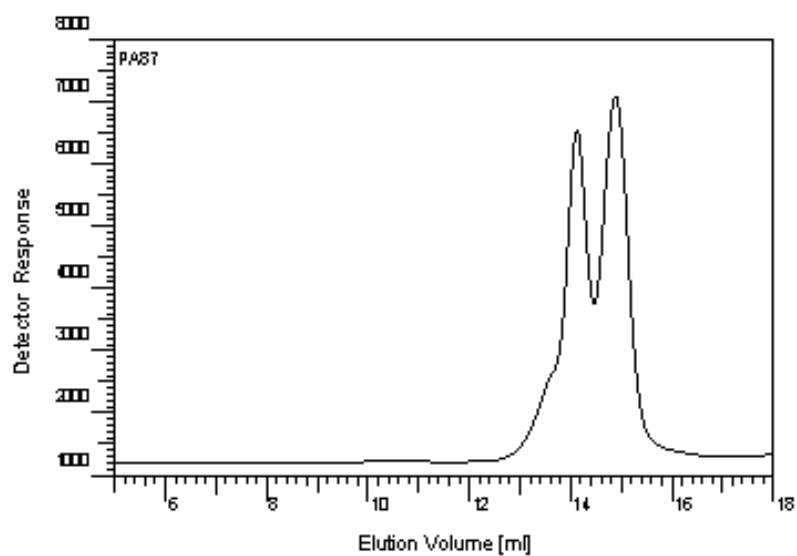


Fig. S27. Representative GPC trace for poly(butylene phthalate) with $M_n = 14.7$ g/mol, $M_w = 18.5$ g/mol, $\bar{D} = 1.26$.

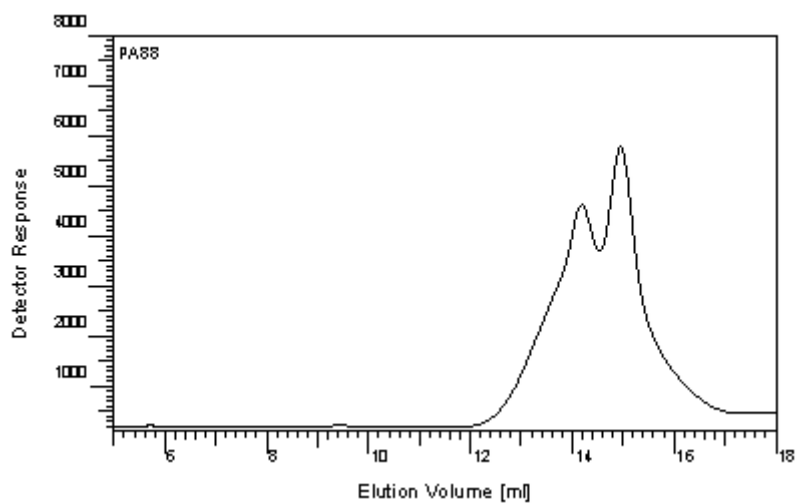


Fig. S28. Representative GPC trace for poly(chloromethylethylene phthalate) with $M_n = 12.4$ g/mol, $M_w = 20.0$ g/mol, $\bar{D} = 1.61$.

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