Supporting Information for

An Energy Efficient, Rapid Synthesis of High Molecular Weight Polyesters using Ketenes

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This supporting information includes:

- Materials and Methods
- Synthesis
- Figure S1-S5
- References

Materials and Methods

All commercially obtained solvents and reagents were used without further purification except as noted below. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. *N*,*N*-dimethylformamide (DMF) was obtained from Aldrich Chemical Company, Inc. as anhydrous, 99+% grade. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F254 glass plate and flash column chromatography was performed either on Merck silica gel 60 (70 - 230 mesh) or on a Biotage SP1 Flash Purification System using FLASH 40+M cartridges and FLASH 40+ sample cartridges. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 500 (500 MHz for ^{1}H, and 125 MHz for ^{13}C), or Bruker DMX-500 (500 MHz for ^{1}H, and 125 MHz for ^{13}C) spectrometer. Chemical shifts are reported relative to tetramethylsilane peak (δ 0.00) or solvent peak (δ 7.27 for $CDCl_3$ in ^{1}H NMR, δ 77.2 for $CDCl_3$ in ^{13}C NMR). IR spectra were obtained using either a Thermo-Nicholet Avartar-330 IR spectrometer with a single-bounce attenuated total reflection (ATR) (Ge crystal) accessory (Smart MIRacle) or a Perkin-Elmer Spectrum 100 IR spectrometer in a single bounce ATR mode (diamond). Size exclusion chromatography (SEC) for **P1** was performed in DMF on a Waters 2695 Separation Module equipped with a Waters 2414 Refractive Index Detector and a Waters 2998 Photodiode Array Detector having two columns: 1)Viscotek I-MBHMW-3078, I-Series Mixed Bed High Molecular Weight, (30cm x 7.8mm id.); 2) Viscotek IMBLMW-3078, I-Series Mixed Bed Low Molecular Weight GPC/SEC Columns (30cm x 7.8mm id). For **P2-P5** SEC was measured at 80 ^{o}C using HPLC-grade ortho-dichlorobenzene on a Polymer-Lab GPC 120 high temperature chromatographer using an RI detector and a Midas autosampler. The column was a PL-mixed C 380 + 7.5 mm having a precolumn in front of it. Flow speed was 1 mL/min and an injection volume of 100 microliter. Molecular weights of the polymers were calculated relative to linear polystyrene standards. Mass spectral data were collected on a Micromass QTOF2 Quadrupole/Time-of Flight Tandem mass spectrometer (ESI-MS). TGA and TGA-MS data were collected on a Mettler 851e TG coupled with a Pfeiffer ThermoStar Mass Spectrometer. Differential Scanning Calorimetry was measured on a TA Instruments Q2000 MDSC (modulated differential scanning calorimeter) with 50 position autosampler and mass flow control. Temperature: from – 90 °C to 400 °C. Refrigerated Cooling System (RCS90). Cooling rate for the experiments were 10 ^{o}C/min, while the data from the second heating/cooling curve was taken as the reported value.

Synthesis

Bis-Meldrum's acid benzyl (3). 1,4-Bis(chloromethyl)benzene **1** (3.7 g, 21 mmol, 1 eq), potassium carbonate (2.96 g, 21.1 mmol, 1 eq) and 2,2,5-trimethyl-1,3-dioxane-4,6-dione **2** (10 g, 33 mmol, 3 eq) were added to dry *N,N*-dimethylformamide (50 mL) and stirred at 50 ^{o}C under and inert atmosphere. After 17 hours 200 mL 1N HCl was added and the aqueous layer was extracted with hot ethyl acetate (3 × 250 mL). The hot organic layers were combined and dried with $MgSO_4$, filtered hot, and the solvent was evaporated. The residue was refluxed in toluene overnight, after which the solvent was evaporated. The crude was recrystallized from EtOAc to obtain 6.26 g (71 %) of a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.05 (s, 4H, Ar-H); 3.26 (s, 4H, benzylic-H); 1.70 (s, 6H, CH_3), 1.60 (s, 6H, CH_3); 1.06 (s, 6H, CH_3)

^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.6; 134.7; 130.3; 105.1; 51.7; 44.6; 29.4; 28.4; 25.5

FT-IR υ (cm^{-1}): 2990, 2942, 1769, 1727, 1518, 1454, 1438, 1426, 1392, 1376, 1324, 1271, 1250, 1200, 1133, 1101, 1060, 979, 970, 938, 895, 854, 813, 777, 730, 682

High Res- Mass Spectrometry mass found: 441.1517 $[M+ Na]^+$ (441.1525 $C_{22}H_{26}O_8Na$)

The compound decomposed before melting.

Crystal Structure data CCDC number: 833163

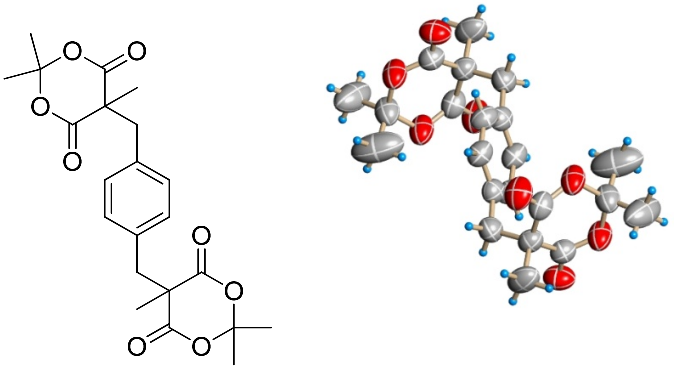
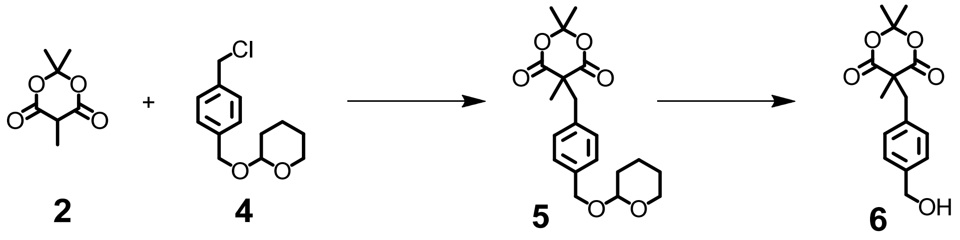


Figure S1. *Crystal structure of **3***

Table S1. *Crystal data and structure refinement for **3***

Empirical formula	C22 H26 O8
Formula weight	418.43
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.089(3) A alpha = 90 deg.
	b = 10.451(3) A beta = 110.965(5) deg.
	c = 12.182(4) A gamma = 90 deg.
Volume	1080.6(6) A^3
Z, Calculated density	2, 1.286 Mg/m^3
Absorption coefficient	0.098 mm^-1
F(000)	444
Crystal size	0.25 x 0.25 x 0.2 mm
Theta range for data collection	2.40 to 26.37 deg.
Limiting indices	-11<=h<=11, -13<=k<=12, -14<=l<=15
Reflections collected / unique	8493 / 2174 [R(int) = 0.0283]
Completeness to theta =	26.37 98.4 %
Absorption correction	Multi scan
Max. and min. transmission	1 and 0.838
Refinement method	Full-matrix least-squares on F^2

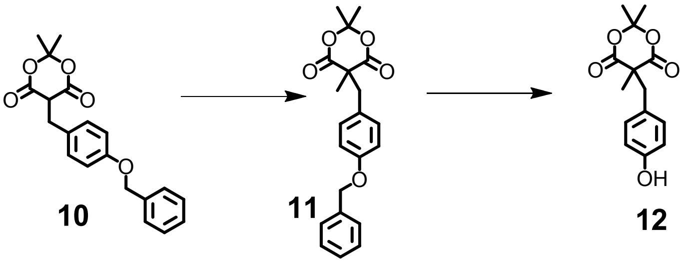
Data / restraints / parameters	2174 / 8 / 141
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0588, wR2 = 0.1626
R indices (all data)	R1 = 0.0832, wR2 = 0.1435
Extinction coefficient	0.264(16)
Largest diff. peak and hole	0.295 and -0.248 e.A^-3



***Scheme S1.** Synthetic scheme towards monomer **6**. Compound **4** was prepared as reported by Pyun, et al.*[S1]

2,2,5-trimethyl-5-(4-(((tetrahydro-2H-pyran-2-yl)oxy)methyl)benzyl)-1,3-dioxane-4,6-dione (5) – A round-bottom flask was charged with 2,2,5-trimethyl-1,3-dioxane-4,6-dione (**2**) (2.000 g, 12.64 mmol, 1 eq), 2-((4-(chloromethyl)benzyl)oxy)tetrahydro-2H-pyran (**4**) (3.805 g, 15.80 mmol, 1.25 eq), potassium carbonate (2.622 g, 18.97 mmol, 1.5 eq) and *N*,*N*-dimethylformamide (25 mL). The solution was stirred under argon for 24 hours, and allowed to cool to RT. 100 mL of pH 7 buffer solution was added to the reaction, and the aqueous phase was extracted with dichloromethane. The organic phase was combined, and washed with saturated sodium bicarbonate, water and brine. The organic phase was dried over magnesium sulfate and concentrated. The resulting solid was purified by flash chromatography (70:30 hexanes/ethyl acetate) and dried to give a crystalline white solid (3.40g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.25 (d, 2H, J = 8 Hz), 7.15 (d, 2H, J = 8 Hz), 4.88 (m, 1H), 4.60 (s, 2H), 3.87 (m, 1H, CH_2), 3.52 (m, 1H, CH_2), 3.27 (s, 2H),1.70-1.53 (m, 6H), 1.73 (s, 3H), 1.54 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ169.4, 138.8, 133.5, 130.4, 126.4, 105.9, 94.8, 69.1, 64.9, 44.1, 31.8, 29.6, 28.5, 26.7, 25.6, 20.4. TOF-MS (ESI) calculated [M+Na]: 385.16; Found: 385.16.

5-(4-(hydroxymethyl)benzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (6) – Compound **5** (3.10 g, 8.56 mmol) was dissolved in tetrahydrofuran (20 mL) and methanol (40 mL). Dowex acidic resin (~5 g) was added and the reaction was stirred in ambient conditions for 6 hours. The resin was removed by filtration, and the crude product was isolated as an off-white solid after evaporation of the solvent. This solid was purified by flash chromatography (50:50 hexanes/ethyl acetate) and dried to give a crystalline white solid (2.24 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 8, Hz 2H), 7.12 (d, J = 8 Hz, 2H), 4.60 (s ,2H), 3.29 (s, 2H), 1.71 (s, 3H), 1.58 (s, 3H), 0.94 (2, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.9, 140.6, 134.5, 130.3, 127.2, 105.2, 64.7, 52.1, 44.7, 29.4, 28.3, 25.7. TOF-MS (ESI) calculated [M+Na]: 301.10; Found: 301.11. IR (ATR, neat): 3326, 3031, 3001, 1774, 1732, 1380, 1330.



Scheme S2. *Synthetic scheme towards monomer* ***12*** *Compound* ***10*** *was prepared as reported by Frost, et al.*[S2]

5-(4-(benzyloxy)benzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (11) – A round bottom flask was charged with 5-(4-(benzyloxy)benzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**10**) (2.50 g, 7.34 mmol, 1 eq), methyl iodide (1.56 g, 11.0 mmol, 1.5 eq), potassium carbonate (1.522 g, 11.01 mmol, 1.5 eq), and *N*,*N*-dimethylformamide (20 mL). The resulting solution was stirred at 50 °C for 24 hours, and then allowed to cool to RT. 100 mL of pH 7 buffer solution was added to the reaction, and the aqueous phase was extracted with dichloromethane. The organic phase was combined, and washed with saturated sodium bicarbonate, water and brine. The organic phase was dried over magnesium sulfate and concentrated. The resulting solid was purified by flash chromatography (70:30 hexanes/ethyl acetate) and dried to give a crystalline white solid (2.54 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.45-7.30 (5H, m), 7.23 (2H, d, *J* = 9 Hz), 6.92 (2H, d, *J* = 9 Hz), 5.05 (2H, s), 3.30 (2H, s), 1.74 (3H, s), 1.51 (3H), 0.95 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 168.9, 158.3, 137.3, 131.4, 129.8, 129.0, 128.4, 127.9, 115.3, 105.7, 70.0, 55.7, 43.6, 28.9, 27.8, 24.1. TOF-MS (ESI) calculated [M+Na]: 377.14; Found: 377.16.

5-(4-hydroxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (12)– Compound **11** (2.20 g, 6.21 mmol) was dissolved in THF in a round bottom flask. To this solution was added Pd/C (100 mg) directly. The flask was fitted with a balloon containing hydrogen gas and stirred for twelve hours at RT, and monitored by TLC. Upon complete conversion of starting material, the Pd/C was removed by filtration and the solvent evaporated to give the crude product as a white solid. The resulting solid was purified by flash chromatography (40:60 hexanes : ethyl acetate) and dried to give a white powder (1.52 g, 93%). ^{1}H-NMR (500 MHz, $CDCl_3$) *δ* 7.01 (2H, d, *J* = 8.5 Hz), 6.88 (1H, b), 6.75 (2H, d, *J* = 8.5 Hz), 3.26 (2H, s), 1.72 (3H, s), 1.61 (3H, s), 0.99 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* 171.7, 170.2, 156.0, 126.8, 115.6, 105.4, 60.6, 52.4, 44.2, 29.3, 28.4, 21.0, 14.1. IR (neat, ATR) 3241, 3002, 1775, 1731, 1698, 1602, 1474, 1387, 1332.

TOF-MS (ESI) calculated [M+Na]: 287.09; Found: 287.09. The compound decomposed prior to melting.

General procedure for the polymerization yielding P1-P3.

An ampoule was charged with a stoichiometric amount of the respective diol and **3** (100 mg). The ampoule was put in an oil bath that was preheated to 190 °C for 20 minutes, after which it was heated to 250 °C and kept there for 10 min. These ampoules were open to air and the monomers were not extensively dried prior to the polymerization. **P1**, **P3** were obtained as waxy yellowish solids, while **P2** was a crystalline off white solid.

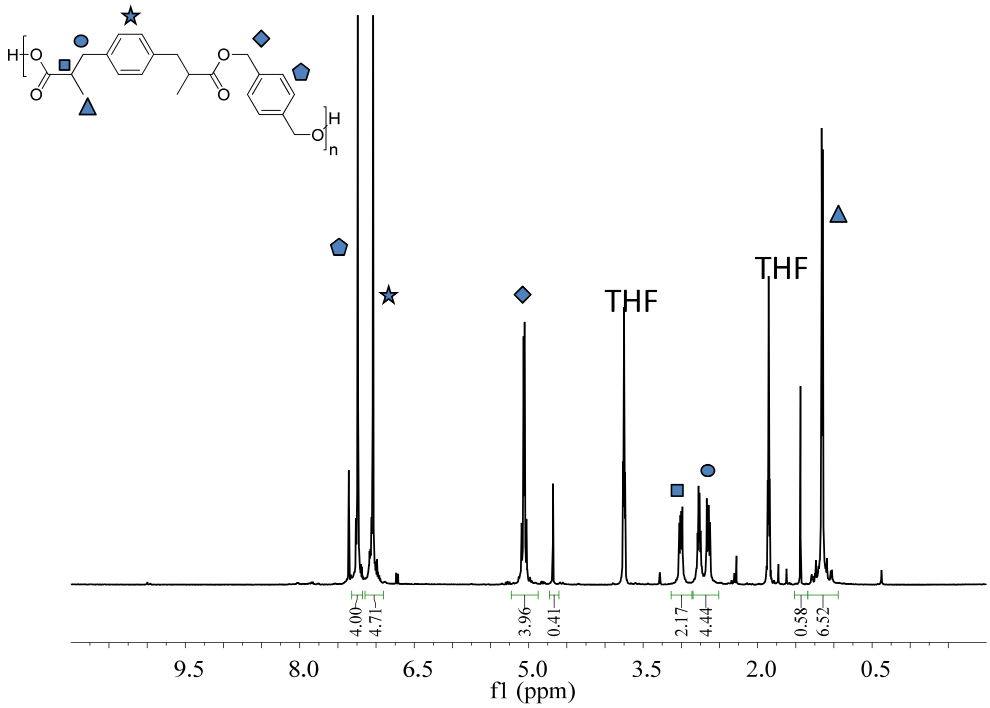
General procedure for the polymerization yielding P4, P5.

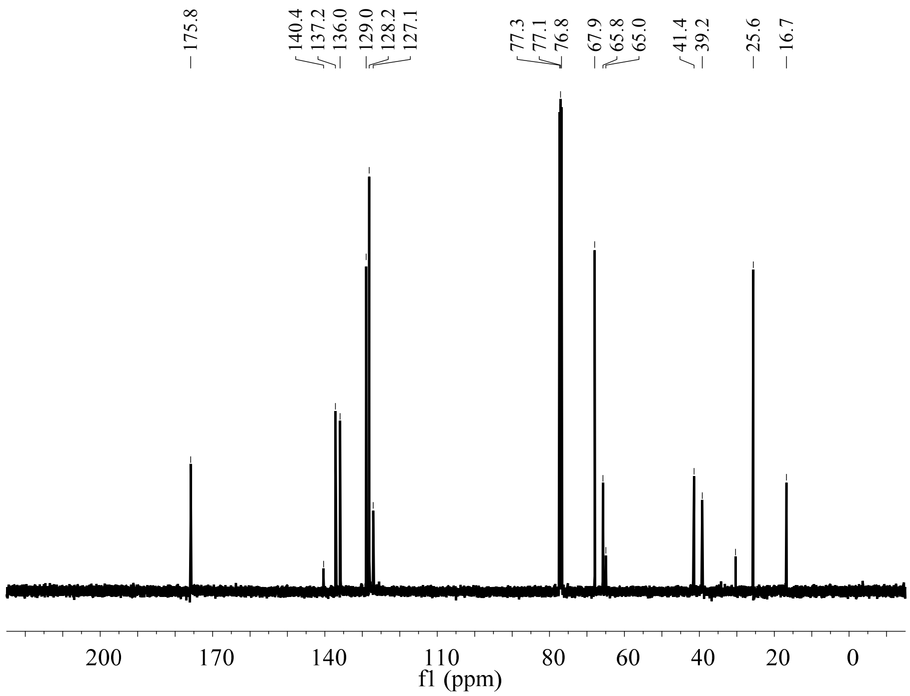
An ampoule was charged with the monomer and heated for 10 minutes in an oil bath that was preheated to 220 °C. These ampoules were open to air and the monomers were not extensively dried prior to the polymerization. **P4** was obtained as waxy yellowish solid, while **P2** was a crystalline off white solid

Characterization of polymers P1-P5

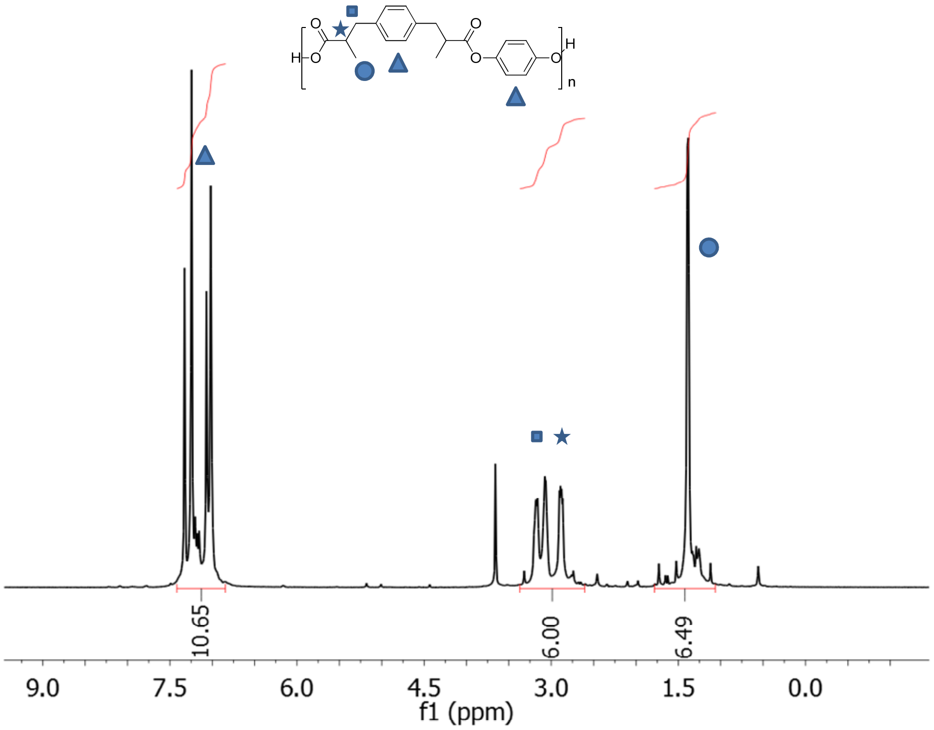
^{1}H and ^{13}C NMR of **P1** through **P5**.

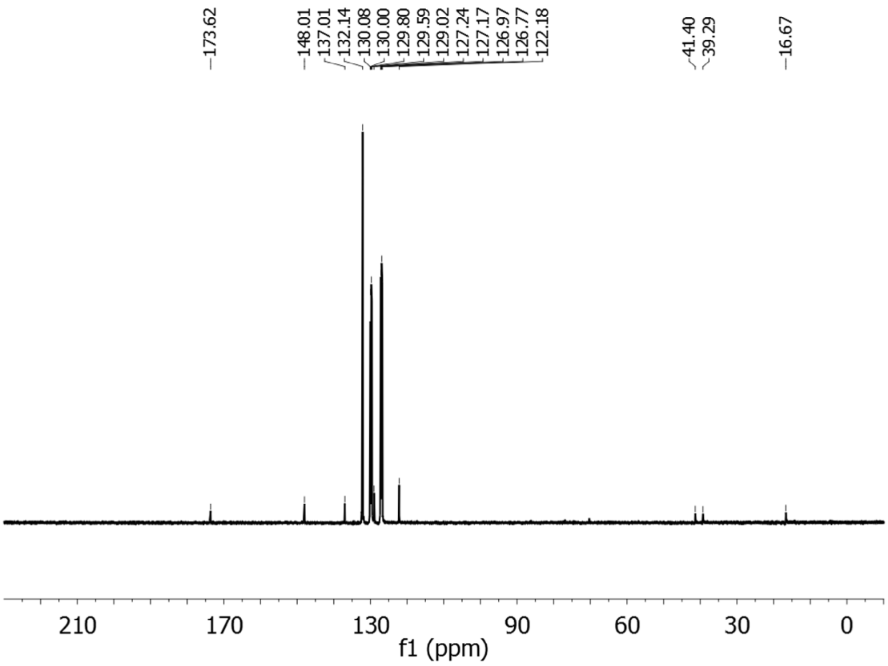
P1 (CDCl$_3$, 500 MHz for proton and 125 MHz for carbon)



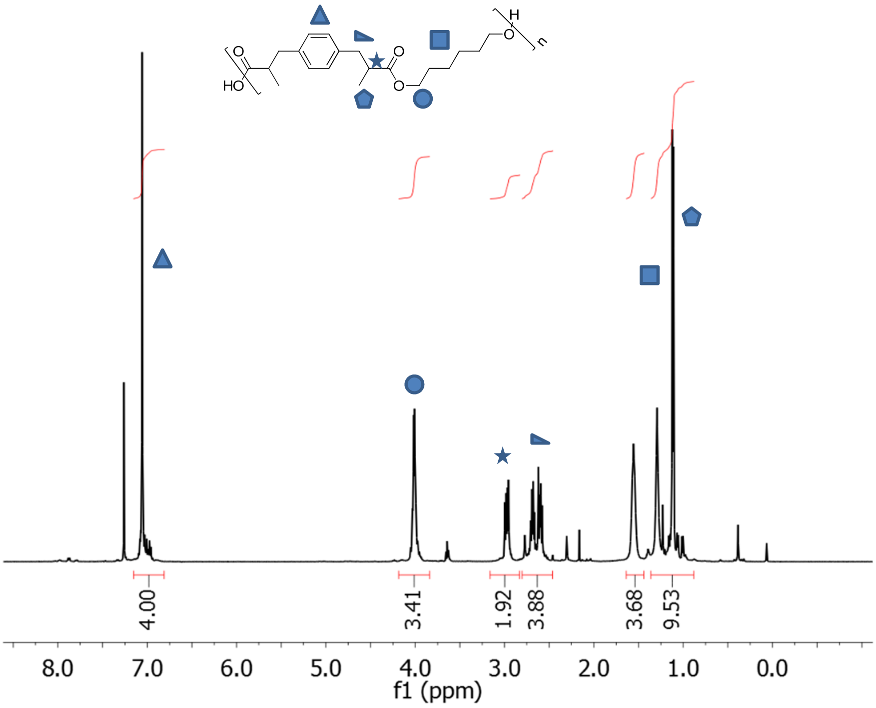


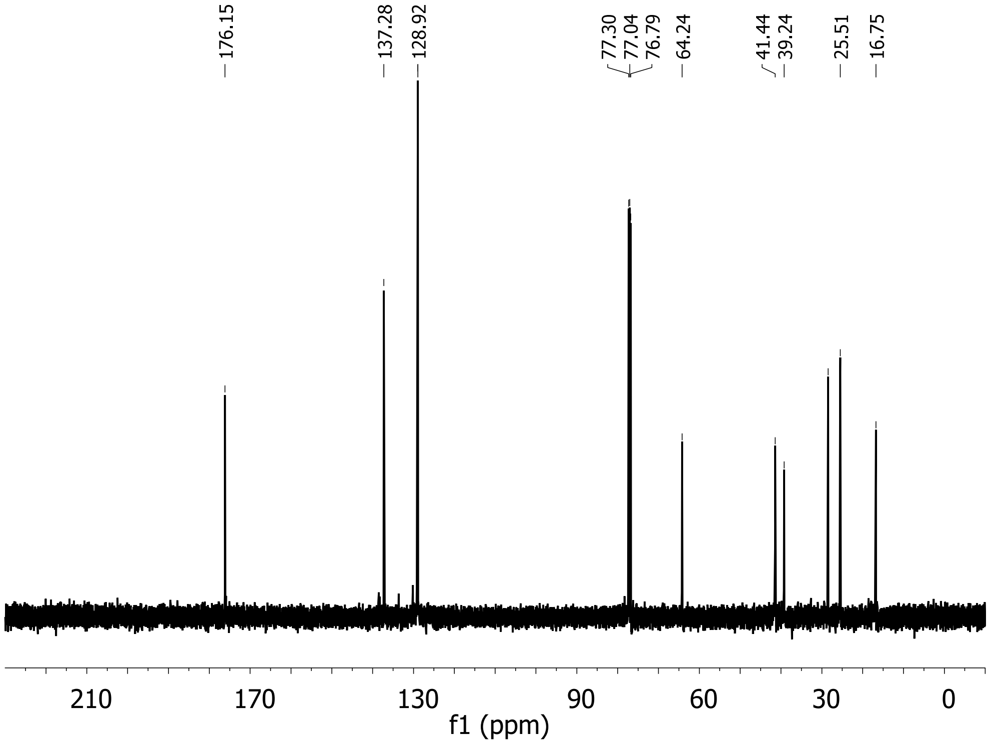
P2 (ortho-dichlorobenzene-d4, 500 MHz for proton, and 125 MHz for carbon)



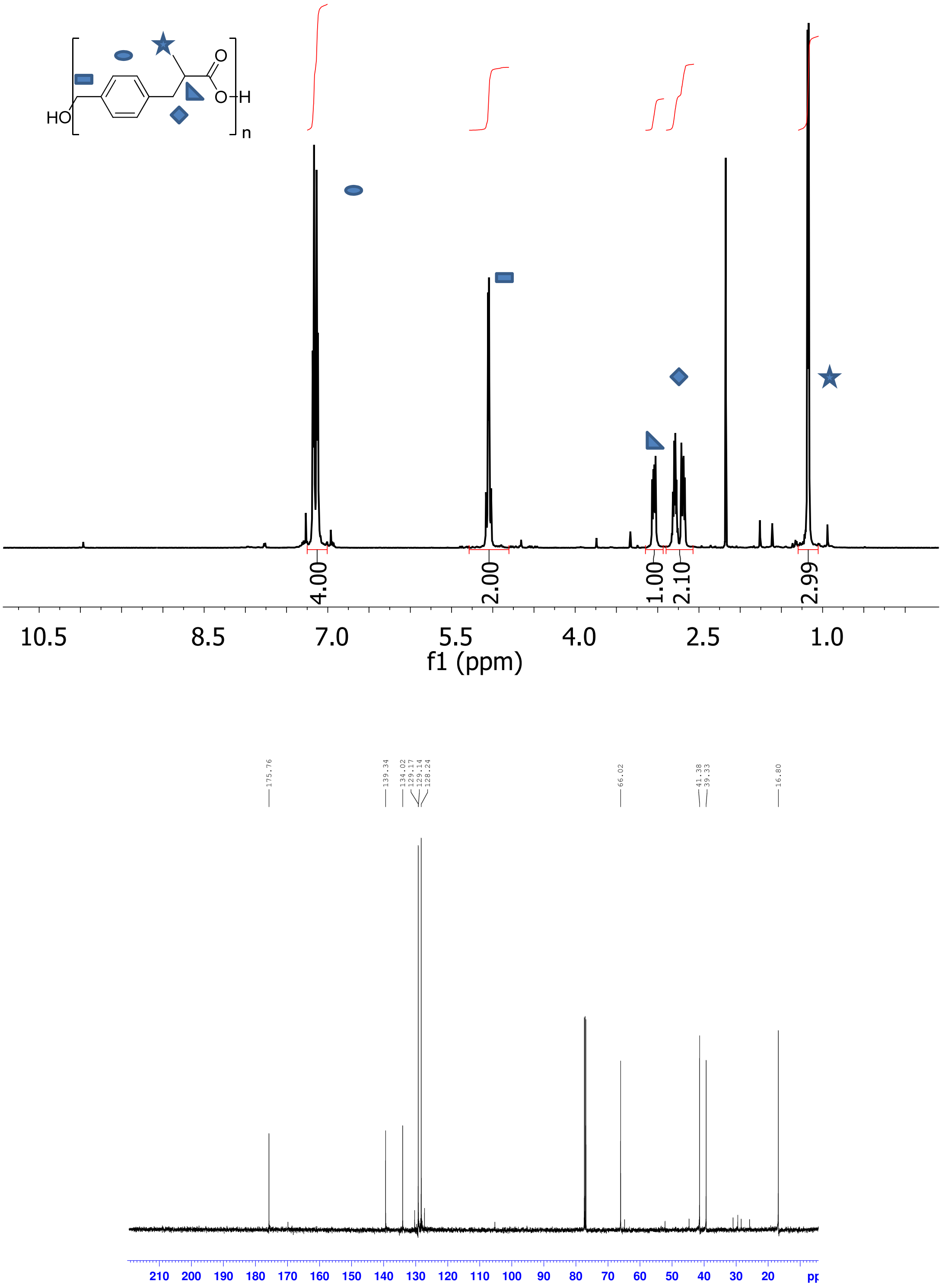


P3 (CDCl$_3$. 500 MHz for proton and 125 MHz for Carbon)

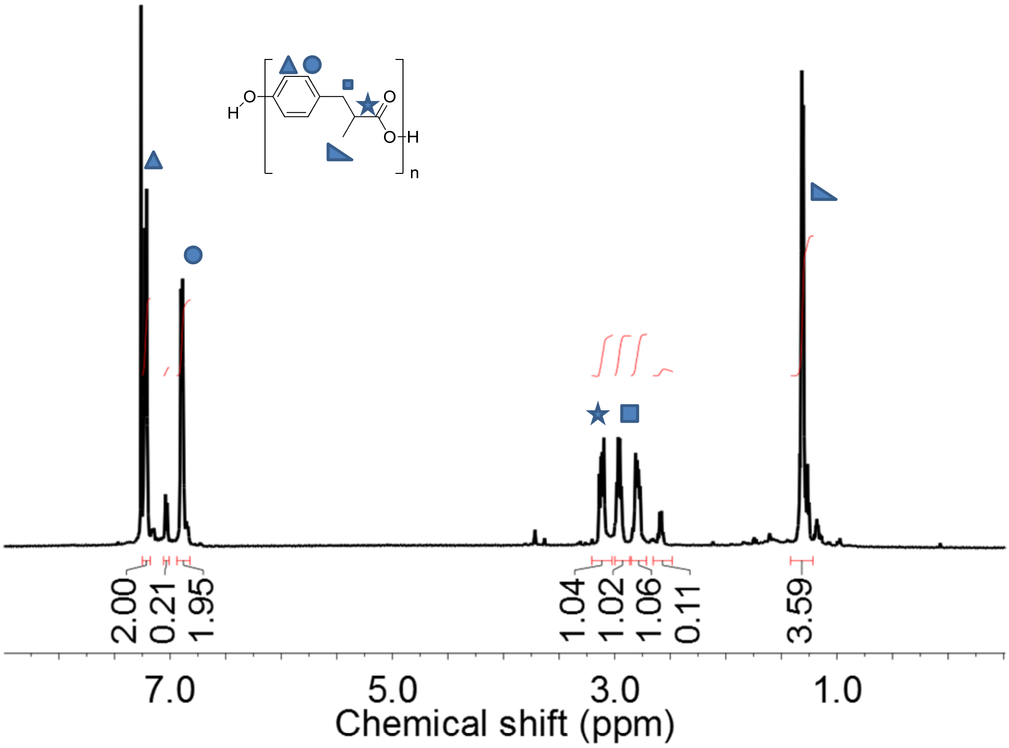


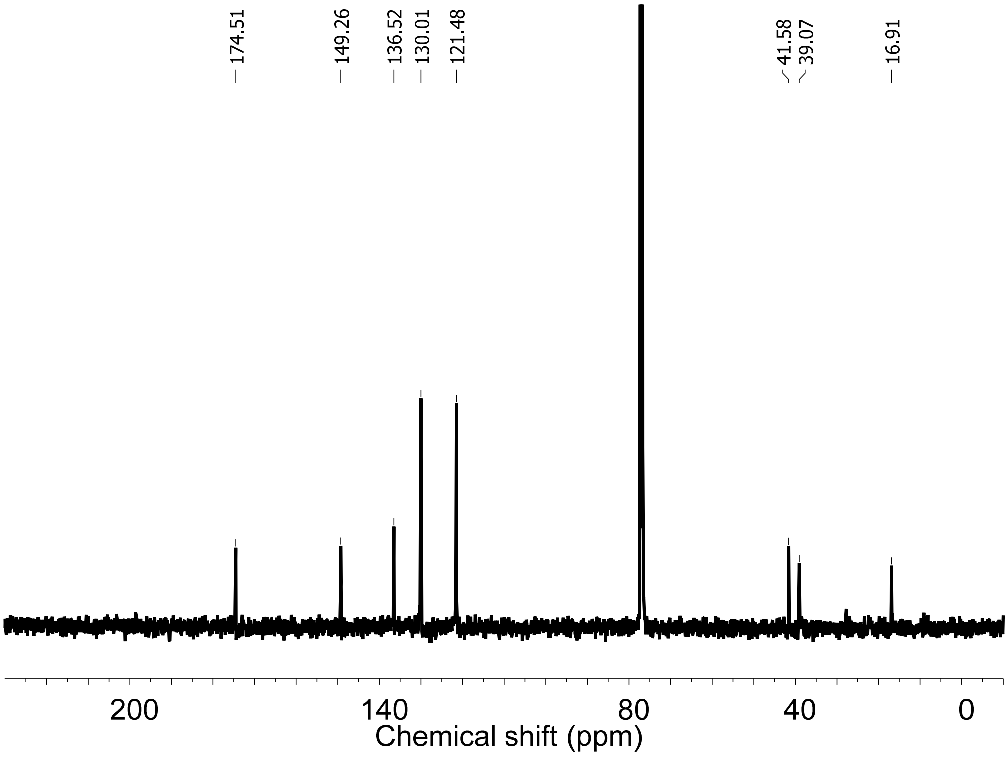


P4 ($CDCl_3$. 500 MHz for proton and 125 MHz for Carbon)



P5 ($CDCl_3$. 500 MHz for proton and 125 MHz for Carbon)


O
H
O
O
H
n
2.00
0.21
1.95
1.04
1.02
1.06
0.11
3.59
7.0
5.0
3.0
1.0
Chemical shift (ppm)


174.51
149.26
136.52
130.01
121.48
41.58
39.07
16.91
200
140
80
40
0
Chemical shift (ppm)

FT-IR

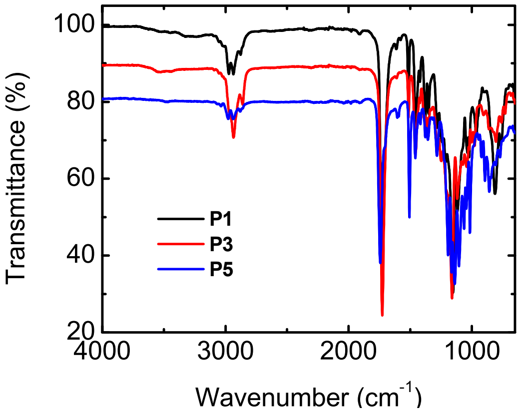


Figure S2. *FT-IR data for some of the synthesized polymers **P1** (black), **P3** (red), **P5** (blue)*

Thermogravimetric analysis

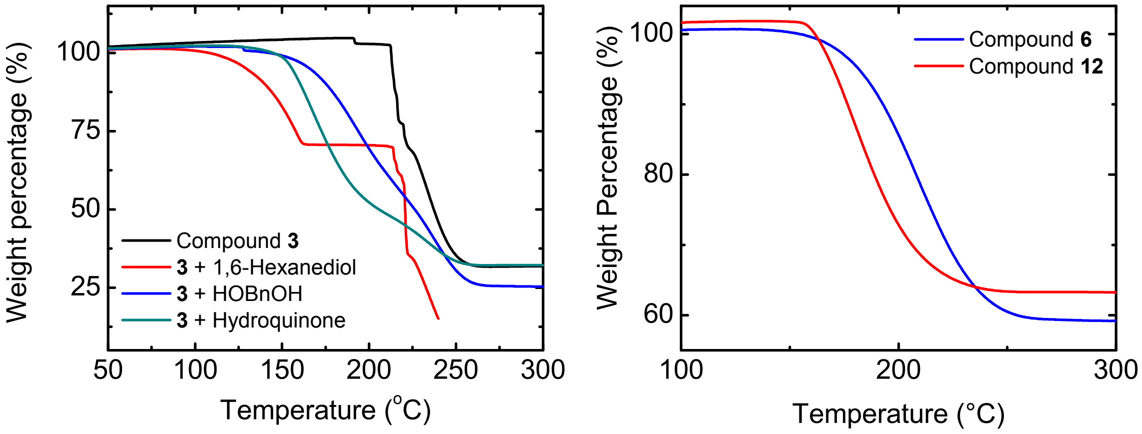


Figure S3. *Thermogravimetric data for **3** and its mixtures (left graph, pure **3** (black), mixed with 1,6-hexanediol (red), 1,4-benzenedimethanol (blue) and hydroquinone (green)) and for compounds **6** (blue) and **12** (red) (right graph).*

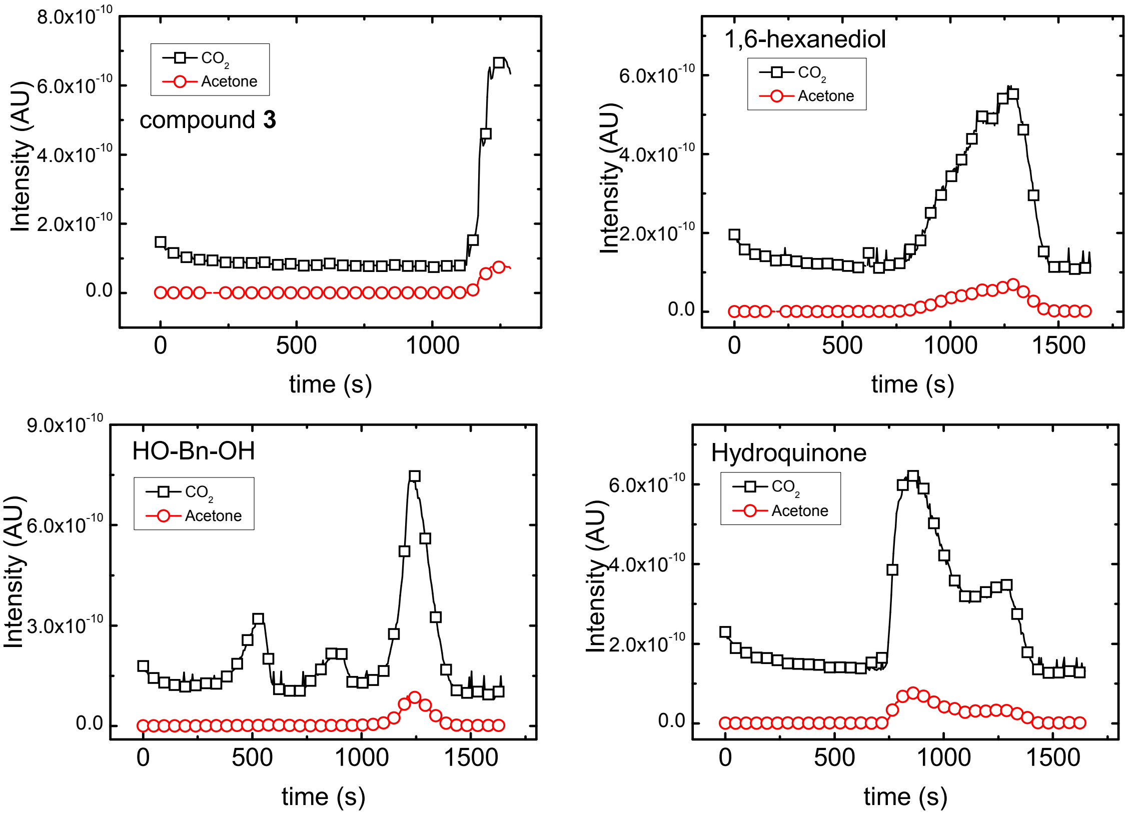


Figure S4. *Simultaneous mass spectrometry during of the gaseous products formed during the thermogravimeteric analysis as shown in Figure S1 left. The masses analyzed correspond to carbon dioxide (black squares) and acetone (red circles).*

Size Exclusion Chromatography

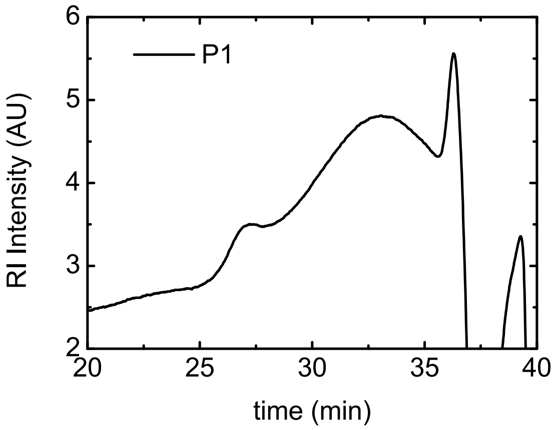


Figure S5. *SEC measurement of* ***P1*** *in DMF at room temperature.*

S1 Pyun, J.; Tang, C. Kowalewski, T.; Fréchet, J. M. J.; Hawker, C. J., *Macromolecules* **2005**, *38*, 2674-2685.
S2 Frost, C. G.; Hartley, B. C., *J. Org. Chem.* **2009**, *74*, 3599–3602.