Supplementary Information

End Group Characterization of Poly(phthalaldehyde): Surprising Discovery of a Reversible, Cationic Macrocyclization Mechanism

Joshua A. Kaitz, Charles E. Diesendruck, and Jeffrey S. Moore[*]

Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign.

*To whom all correspondence should be addressed. Phone: (217) 244-1646. Fax: (217) 244-8024. E-mail: jsmoore@illinois.edu

Table of Contents

I.	General Experimental Details	S2
II.	Synthetic Procedures	S3
III.	NMR Spectra	S8
IV.	GPC Data	S16
V.	MALDI-TOF MS Data	S23
VI.	Thermal Characterization Data	S29
VII.	In Situ FTIR Characterization Data	S31
VIII.	References for Supporting Information	S32

I. General Experimental Details

Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. Anhydrous tetrahydrofuran and dichloromethane were obtained from an Anhydrous Solvent Delivery System (SDS) equipped with activated alumina columns. *o*-Phthalaldehyde (98%, Alfa-Aesar) was purified according to a literature procedure.[1] 1,6-hexanediol (99% Aldrich) was dissolved in THF over CaH_2, filtered after stirring overnight, and collected by evaporation of the solvent.[2] All reactions were performed in oven dried glassware under N_2 atmosphere unless otherwise indicated.

^{1}H, ^{19}F, and ^{13}C NMR spectra were obtained with a Varian 400 or Varian 500 MHz spectrometer in the School of Chemical Sciences NMR laboratory at the University of Illinois at Urbana-Champaign. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak. Coupling constants (J) are expressed in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), and b (broad).

Analytical gel permeation chromatography (GPC) analyses were performed on either of two systems. Most GPC analyses were performed on a system composed of a Waters 515 HPLC pump, a Thermoseparations Trace series AS100 autosampler, a series of three Waters HR Styragel columns (7.8' 300 mm, HR3, HR4, and HR5), and a Viscotek TDA Model 300 triple detector array, in HPLC grade THF (flow rate = 0.9 mL/min) at 25 °C. The GPC was calibrated using a series of monodisperse polystyrene standards. Cationic/anionic of similar weight comparison was carried out in Waters 1515 Isocratic HPLC pump, with a Waters (2707) 96-well autosampler, and a series of 4 Waters HR Styragel columns (7.8 X 300mm, HR1, HR3, HR4, and HR5) in THF at 30 °C, coupled to 4 detectors in sequence: Waters (2998) Photodiode Array Detector, a Waters (2414) Refractive Index Detector, Wyatt mini-DAWN TREOS multi-angle laser light-scattering, and a Wyatt Viscostar II viscometer. Analysis of the data was done using Wyatt's Astra 6 software. PPA dndc was calculated online to be 0.1515 as an average of three 100% mass-recovery experiments and was used for all samples.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done using a Mettler-Toledo TGA/DSC1 LF. Scans were collected in the range of 25 °C 300 °C with a ramping rate of 10 °C/min under a dry nitrogen atmosphere.

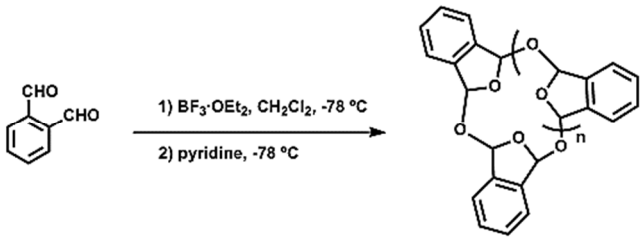
MALDI-TOF mass spectra were obtained with a Bruker Daltonics UltrafleXtreme MALDI TOF at the Mass Spectrometry Facility, SCS, University of Illinois at Urbana-Champaign. The instrument was operated in reflectron mode and positive ions were detected. The ions were accelerated under a potential of 20 kV. External mass calibration was used (PEG 1500, Sigma-Aldrich). Samples were prepared by mixing 10 μL of polymer sample (at 10 mg/mL in THF) with 10 μL of NaI (at 10 mg/mL in THF) and 1 μL spotted on the MALDI sample plate and air dried. Then, 1 μL of 2,5-dihydroxybenzoic acid (DHB, at 10 mg/mL in methanol) was spotted on top of the polymer/salt mixture and air-dried. Note that if DHB is

dissolved in THF and mixed with polymer samples prior to spotting, appreciable hydrolysis results and a second major peak series is observed from the linear hydrolysis product (cyclic + 18 mass units).

Infrared spectra (FTIR) were recorded on a Perkin Elmer Spectrum BX spectrophotometer equipped with a Mettler-Toledo ReactIR^{TM} probe for in situ reaction monitoring. Background was taken as monomer solution in dichloromethane prior to addition of initiator. Scans were collected at eight second intervals.

II. Synthetic Procedures

General cationic polymerization.



o-Phthalaldehyde (*o*-PA) is purified according to a literature procedure[1] and dried under high vacuum for 24 hours. *o*-PA (1.00 g, 7.5 mmol) is weighed into a Schlenk flask and dissolved in dichloromethane (10 mL). The solution is cooled to -78 °C and boron trifluoride etherate is added (0.02 mL, 0.16 mmol). The reaction is left stirring at -78 °C for 2 h, then pyridine (0.12 mL, 1.5 mmol) is added. The mixture is left stirring 2 h at -78 °C, then brought to room temperature and the polymer precipitated by pouring into methanol (100 mL). The product is collected by filtration, then further purified by dissolving in dichloromethane and re-precipitating from methanol/diethyl ether (0.84 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.15 ppm (br, 4H, aromatic), 7.15-6.25 ppm (br, 2H, acetal). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 138.8 ppm, 130.2 ppm, 123.5 ppm, 105.0-101.8 ppm.

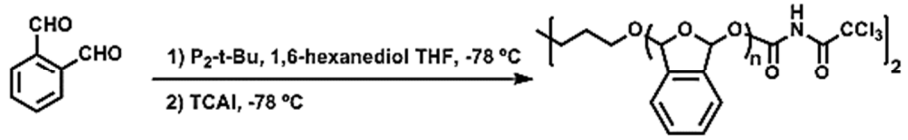
Table S1 | Cationic polymerization samples.

Entry	*[o-PA]*	$[M]_0/[I]_0$	*Yield*	M_n *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]
1	1.0 M	10 / 1	86%	36.1	158	4.5
2	0.7 M	7 / 1	99%	109	199	2.5
3	0.5 M	10 / 1	77%	6.7	10.1	2.4
4	0.1 M	10 / 1	48%	14.9	54.1	3.5
5[b]	0.2 M	10 / 1	63%	10.5	22.0	2.2
6[c]	0.7 M	6 / 1	76%	15.4	73.7	4.4
7[d]	0.7 M	8 / 1	99%	51.5	107	2.0
8[e]	0.2 M	6 / 1	68%	25.0	71.4	2.8

9	0.9 M	20 / 1	94%	104	218	2.3
10[f]	0.9 M	20 / 1	92%	88.6	158	2.2
11[g]	0.9 M	20 / 1	86%	89.4	181	2.3
12[h]	0.8 M	20 / 1	92%	26.2	57.2	2.3

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [b]3-fluoropyridine used in place of pyridine. [c]No pyridine added. Polymer precipitated directly at -78 °C in diethyl ether and washed in diethyl ether and methanol. [d]Precipitation and washing conducted in hexanes and diethyl ether only. [e]Addition of 1-pyrene methanol following reaction and precipitation into diethyl ether. [f]Triethyloxonium tetrafluoroborate initiator. [g]Tin(IV) chloride initiator. [h]Triphenylcarbenium tetrafluoroborate initiator.

General anionic polymerization.



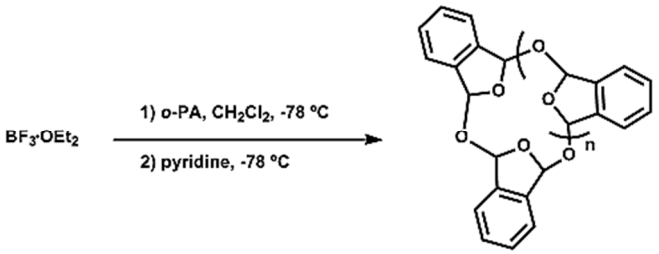
In a glovebox, purified *o*-PA (0.20 g, 1.5 mmol) is weighed into a Schlenk flask and dissolved in THF (2 mL). The solution is removed from the glovebox and degassed by three freeze-pump-thaw cycles. Then, 1,6-hexanediol in THF (0.10 mL of a 0.03 M solution, 3 μmol) is added, and the solution stirred 2 minutes then cooled to -78 °C. Finally, P_2-t-Bu phosphazene base in THF (0.03 mL of a 0.20 M solution, 6 μmol) is added to initiate polymerization. The reaction is left stirring at -78 °C for 2.5 h, then the polymer is end-capped by adding trichloroacetyl isocyanate (0.05 mL, 0.4 mmol) and allowing the mixture to stir an additional 2 h at -78 °C. The reaction mixture is then brought to room temperature and polymer precipitated by pouring into methanol (100 mL) and collected by filtration. If necessary, the polymer is further purified by dissolving in dichloromethane and re-precipitating from methanol/diethyl ether (0.18 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.15 (b, 4H, aromatic), 7.15-6.25 (b, 2H, acetal), 3.80-3.30 (b, initiator), 1.85-0.75 (b, initiator).

***Table S2 | Anionic polymerization samples**:*

Entry	*[o-PA]*	$[M]_0/[I]_0/[P_2]_0$[a]	*Yield*	M_n *(kDa)*[b]	M_p *(kDa)*[b]	*PDI*[b]
1	0.7	125 / 1 / 2	83%	4.4	5.4	1.8
2	0.7	250 / 1 / 2	92%	6.3	8.1	3.0
3	0.7	625 / 1 / 2	92%	9.0	11.5	2.1
4	0.7	2500 / 1 / 3	36%	16.1	26.5	2.7
5	0.7	5000 / 1 / 3	34%	20.4	40.9	2.0

[a]Initial monomer-to-initiator-to catalyst ratio.[2] [b]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

Inverse addition cationic polymerization.



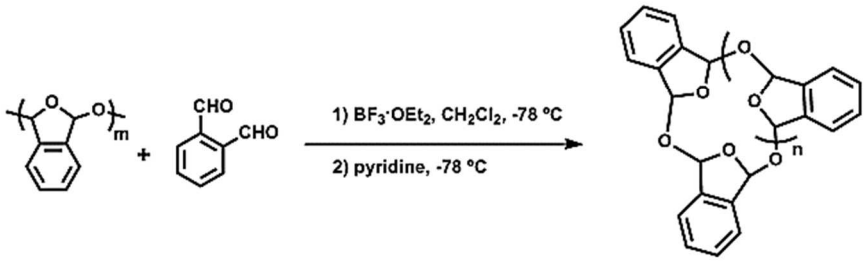
In a clean, dry Schlenk flask, boron trifluoride etherate (0.15 mL, 1.2 mmol) is dissolved in dichloromethane (3 mL). The solution is cooled to -78 °C and *o*-PA (0.30 g, 2.2 mmol) in dichloromethane (2 mL) is added dropwise to the stirring mixture. The reaction is left stirring at -78 °C for 10 minutes, then pyridine (0.15 mL, 1.9 mmol) is added. The mixture is left stirring 10 minutes at -78 °C, then brought to room temperature and the polymer precipitated by pouring into methanol (100 mL). The product is collected by filtration, then further purified by dissolving in dichloromethane and re-precipitating from methanol/diethyl ether (0.25 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.15 ppm (br, 4H, aromatic), 7.15-6.25 ppm (br, 2H, acetal).

Table S3 | Inverse addition cationic polymerization samples.

Entry	*[o-PA]*	*$[M]_0/[I]_0$*	*Yield*	*M_n (kDa)[a]*	*M_p (kDa)[a]*	*PDI[a]*
1	0.6 M	5 / 1	99%	61.3	124.6	2.5
2	0.4 M	2 / 1	83%	25.8	165.3	4.5
3[b]	0.1 M	1 / 2	17%	2.7	2.5	1.6

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [b]Low yield attributed to low monomer concentration and use of excess initiator.

Cationic repolymerization reactions (polymers correspond to Figure 4).



Poly(phthalaldehyde) [PPA] (0.20 g) is weighed into a Schlenk flask and dissolved in dichloromethane (2 mL). The solution is cooled to -78 °C and boron trifluoride etherate is added (0.02 mL, 0.16 mmol). Then, *o*-PA (0.20 g, 1.5 mmol) in dichloromethane (2 mL) is added dropwise to the stirring mixture. The

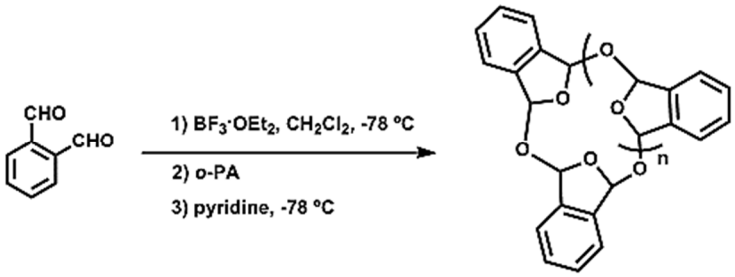
reaction is left stirring at -78 °C for 2 h, then pyridine (0.12 mL, 1.5 mmol) is added. The mixture is left stirring 2 h at -78°C, then brought to room temperature and then the polymer precipitated by pouring into methanol (100 mL). The product is collected by filtration, then further purified by dissolving in dichloromethane and re-precipitating from methanol/diethyl ether (0.29 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.15 ppm (br, 4H, aromatic), 7.15-6.25 ppm (br, 2H, acetal).

Table S4 | Repolymerization samples.

Entry	*[o-PA]*	*$[M]_0/[I]_0$*	*Yield*	*Initial Polymer M_p (kDa)*	*Final Polymer M_n (kDa)[a]*	*Final Polymer M_p (kDa)[a]*	*PDI[a]*
1	0.1 M	6 / 1	21%	- -	4.0	5.1	1.6
2[b]	0.6 M	18 / 1	86%	5.1	12.5	67.4	5.1
3[c]	0.6 M	18 / 1	86%	67.4	16.8	45.6	2.7
4	0.7 M	7 / 1	99%	- - -	109	199	2.5
5[d]	0.5 M	4 / 1	77%	199	6.7	10.1	2.4
6[e]	0.4 M	5 / 1	52%	10.1	7.9	9.1	1.7

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [b]Repolymerization of Entry 1. [c]Repolymerization of Entry 2. [d]Repolymerization of Entry 4. [e]Repolymerization of Entry 5.

Second batch monomer addition reactions (polymers correspond to Figure 5a).



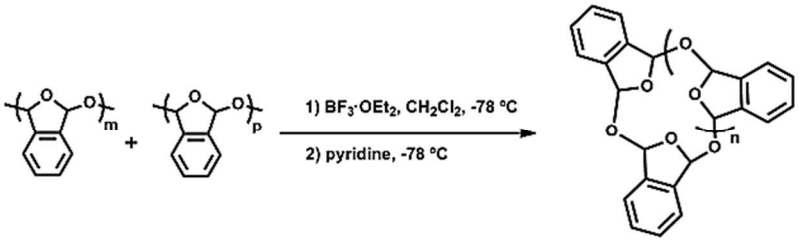
o-PA (0.10 g, 0.7 mmol) is weighed into a Schlenk flask and dissolved in dichloromethane (0.7 mL). The solution is cooled to -78 °C and boron trifluoride etherate is added (0.02 mL, 0.16 mmol). The reaction is left stirring at -78 °C for 1 h, then *o*-PA (0.10 g, 0.7 mmol) in dichloromethane (14 mL) is added dropwise. After stirring for another 1 h at -78 °C, pyridine (0.12 mL, 1.5 mmol) is added. Finally, the mixture is stirred 2 h at -78 °C, then brought to room temperature and the polymer precipitated by pouring into methanol (100 mL). The product is collected by filtration, then further purified by dissolving in dichloromethane and re-precipitating from methanol/diethyl ether (96 mg, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.15 ppm (br, 4H, aromatic), 7.15-6.25 ppm (br, 2H, acetal).

Table S5 | Second batch monomer addition samples.

Entry	*[o-PA]*	*$[M]_0/[I]_0$*	*Yield*	*M_n (kDa)[a]*	*M_p (kDa)[a]*	*PDI[a]*
1	1.0 M	10 / 1	86%	36.1	158	4.5
2	0.1 M	10 / 1	48%	14.9	54.1	3.5
3[b]	1.0 → 0.1 M	10 / 1	48%	11.8	48.6	4.1

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [b]Initial monomer concentration of 1.0 M, total concentration after addition of second batch of monomer 0.1 M.

Polymer mixing reactions (polymers correspond to Figure 5b).



High molecular weight PPA (75 mg, M_p = 199 kDa) and low molecular weight PPA (75 mg, M_p = 30 kDa) are weighed into a Schlenk flask and dissolved in dichloromethane (2.2 mL). The solution is cooled to -78°C and boron trifluoride etherate is added (0.03 mL, 0.24 mmol). The reaction is left stirring at -78 °C for 2 h, then pyridine (0.10 mL, 1.2 mmol) is added. The mixture is left stirring 2 h at -78 °C, then brought to room temperature and then the polymer precipitated by pouring into methanol (100 mL). The product is collected by filtration, then further purified by dissolving in dichloromethane and re-precipitating from methanol/diethyl ether (0.13 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.15 ppm (br, 4H, aromatic), 7.15-6.25 ppm (br, 2H, acetal).

Table S6 | Polymer mixing samples.

Entry	*[o-PA]*	*$[M]_0/[I]_0$*	*Yield*	*M_n (kDa)[a]*	*M_p (kDa)[a]*	*PDI[a]*
1	0.7 M	7 / 1	99%	109	199	2.5
2	0.5 M	14 / 1	83%	11.7	29.5	2.1
3[b]	0.5 M	5 / 1	87%	8.3	6.0	1.6
4[c,d]	0.5 M	- - -	99%	10.5	30.7, 155	7.8
5[e]	0.7 M	125 / 1	83%	4.4	5.4	1.8
6	1.0 M	10 / 1	86%	36.1	158	4.5
7[f]	0.6 M	3 / 1	90%	7.5	32.9	2.2

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [b]Polymers 1 and 2 mixed and initiator added. [c]Control reaction; polymers 1 and 2 mixed, no initiator added. [d]Bimodal molecular weight distribution. [e]Polymer prepared by anionic polymerization. [f]Polymers 5 and 6 mixed and initiator added.

III. NMR Spectra

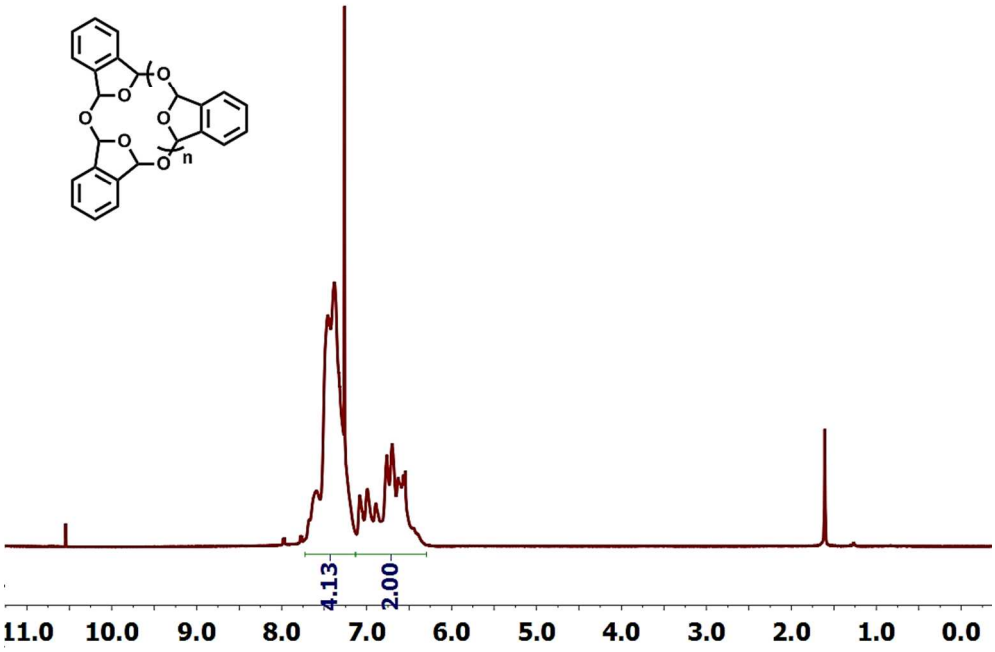


Figure S1 | ^{1}H NMR spectra of cyclic PPA*: NMR spectra of M_n = 5.9 kDa PPA prepared by cationic polymerization in $CDCl_3$. No end-groups are observed. Additional peaks correspond to water (1.6 ppm) and residual* o*-phthalaldehyde monomer.*

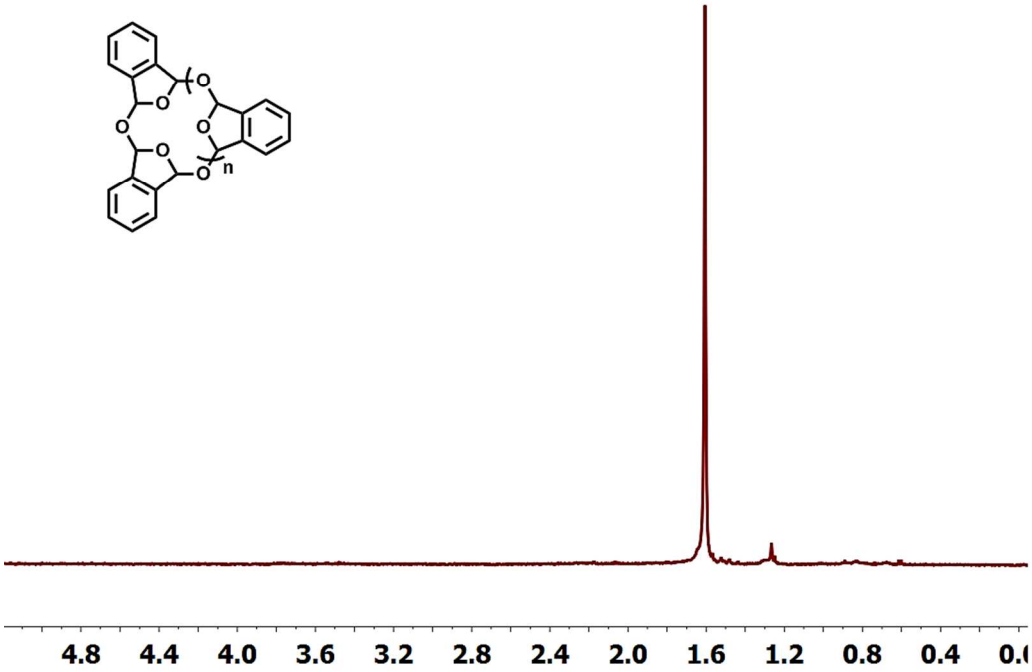


Figure S2 | Zoomed Region of ^{1}H NMR spectra of cyclic PPA (Figure S1)*: NMR spectra of M_n = 5.9 kDa PPA prepared by cationic polymerization in $CDCl_3$. Peak corresponds to water (1.6 ppm).*

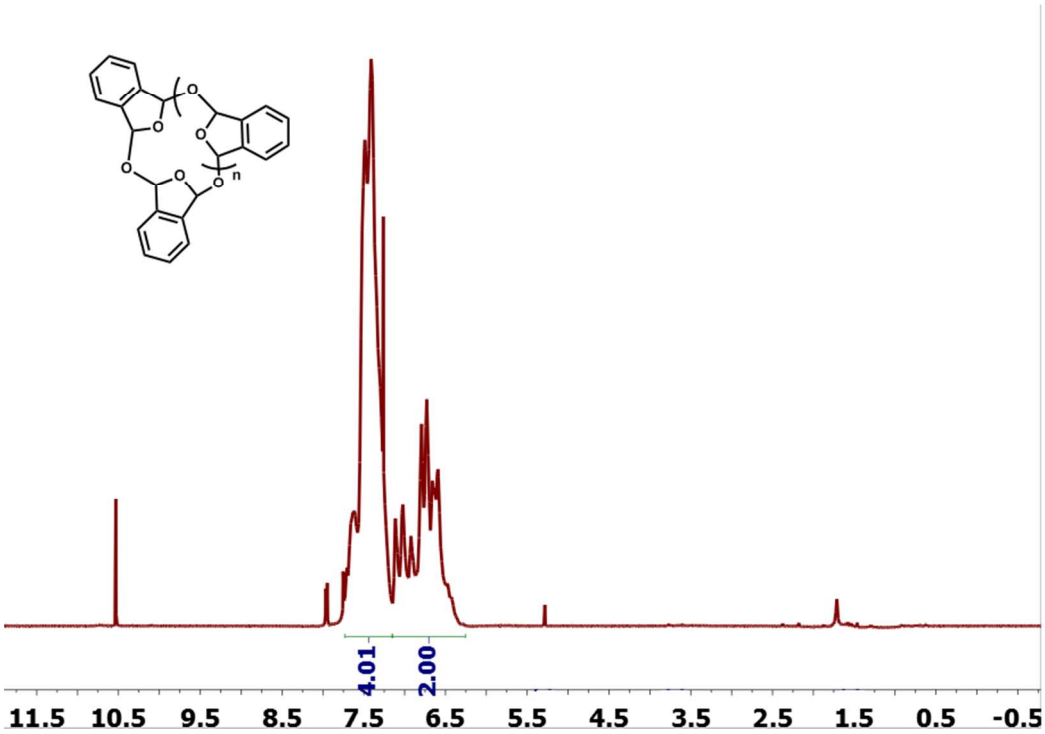


Figure S3 | ^{1}H NMR spectra of cyclic PPA*: NMR spectra of M_n = 12 kDa PPA prepared by cationic polymerization in $CDCl_3$. No end-groups are observed. Additional peaks correspond to water (1.6 ppm), dichloromethane (5.3 ppm), and residual* o*-phthalaldehyde monomer.*

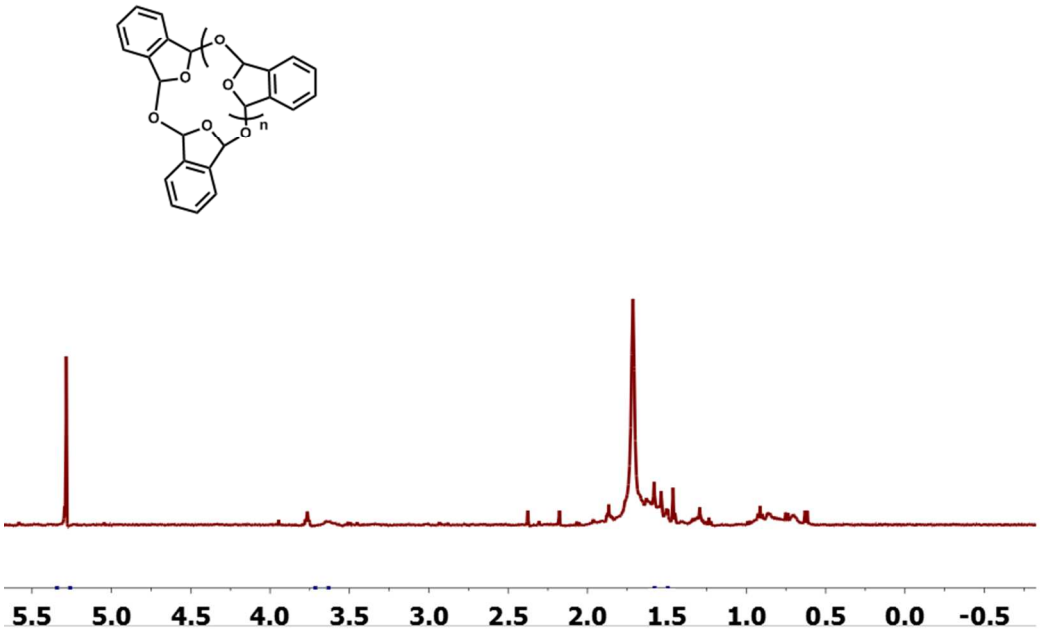


Figure S4 | Zoomed Region of ^{1}H NMR spectra of cyclic PPA (Figure S3)*: NMR spectra of M_n = 12 kDa PPA prepared by cationic polymerization in $CDCl_3$. Peaks correspond to water (1.6 ppm) and dichloromethane (5.3 ppm).*

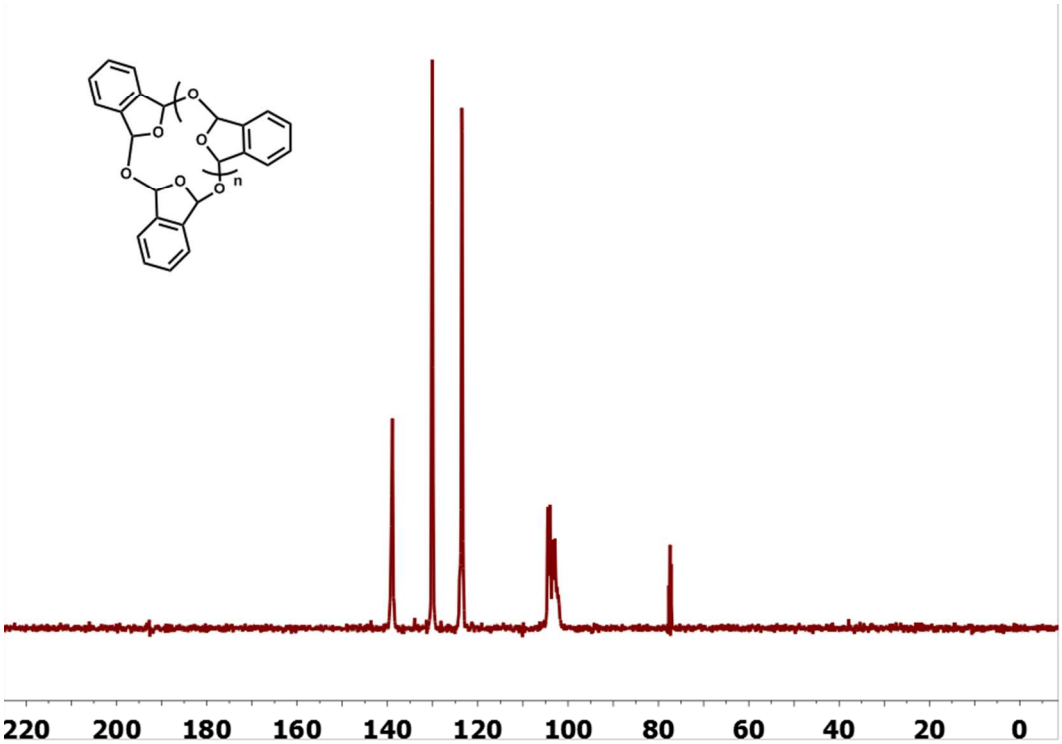


Figure S5 | ^{13}C NMR spectra of cyclic PPA*: NMR spectra of M_n = 12 kDa PPA prepared by cationic polymerization in $CDCl_3$.*

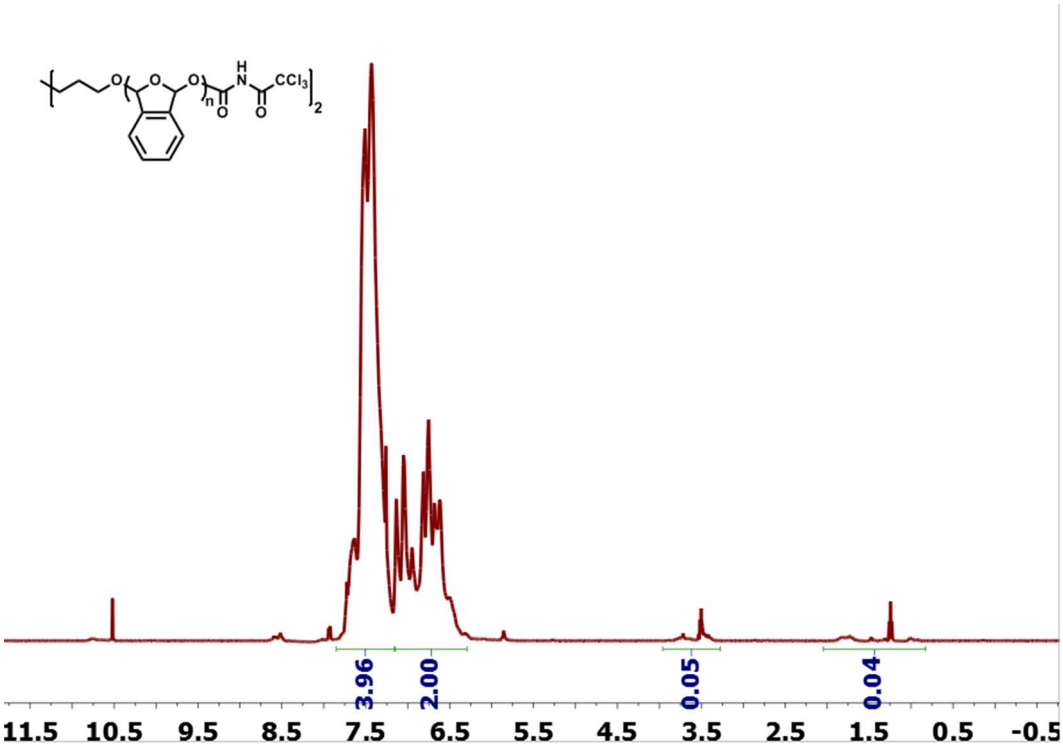


Figure S6 | ^{1}H NMR spectra of linear PPA*: NMR spectra of M_n = 6 kDa PPA prepared by anionic polymerization in $CDCl_3$. Residual* o*-phthalaldehyde monomer remains even after three successive precipitations.*

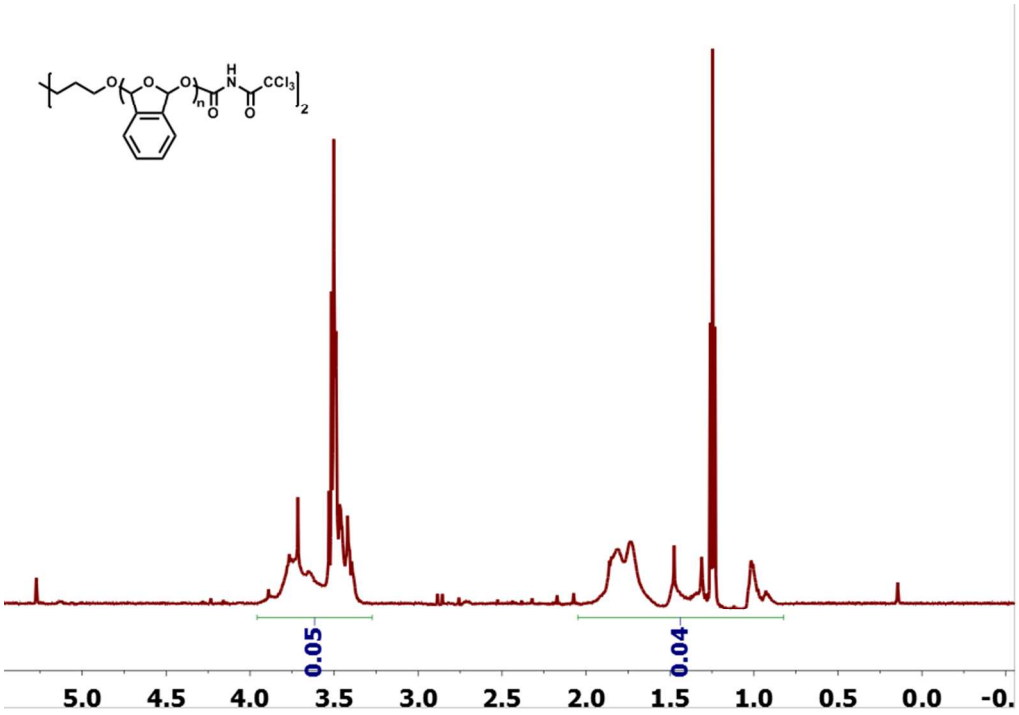


Figure S7 | Zoomed Region of ^{1}H NMR spectra of linear PPA (Figure S6)*: NMR spectra of M_n = 6 kDa PPA prepared by anionic polymerization in $CDCl_3$. Residual diethyl ether washing solvent remains after storage on vacuum.*

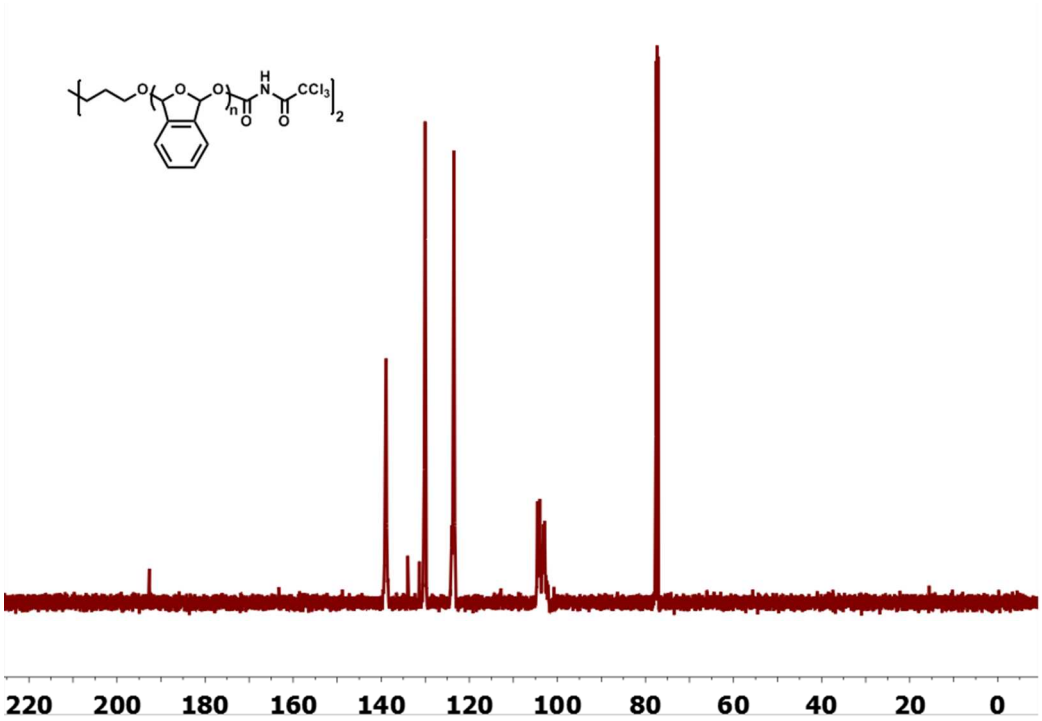


Figure S8 | ^{13}C NMR spectra of linear PPA*: NMR spectra of M_n = 6 kDa PPA prepared by anionic polymerization in $CDCl_3$. Residual* o*-phthalaldehyde monomer remains even after three successive precipitations.*

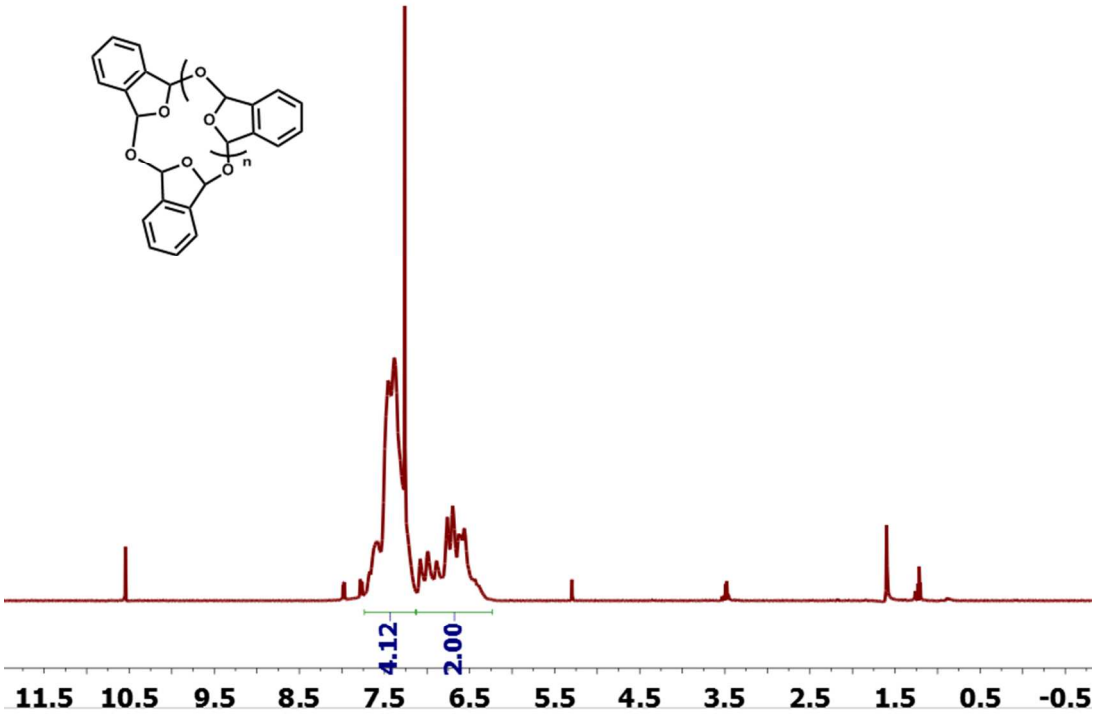


Figure S9 | ^{1}H NMR spectra of cyclic PPA*: NMR spectra of M_n = 51 kDa PPA prepared by cationic polymerization washed in hexanes and diethyl ether only (no methanol) in $CDCl_3$. Additional peaks correspond to residual* o*-phthalaldehyde monomer, water, and remaining solvent after 3 days storage on vacuum.*

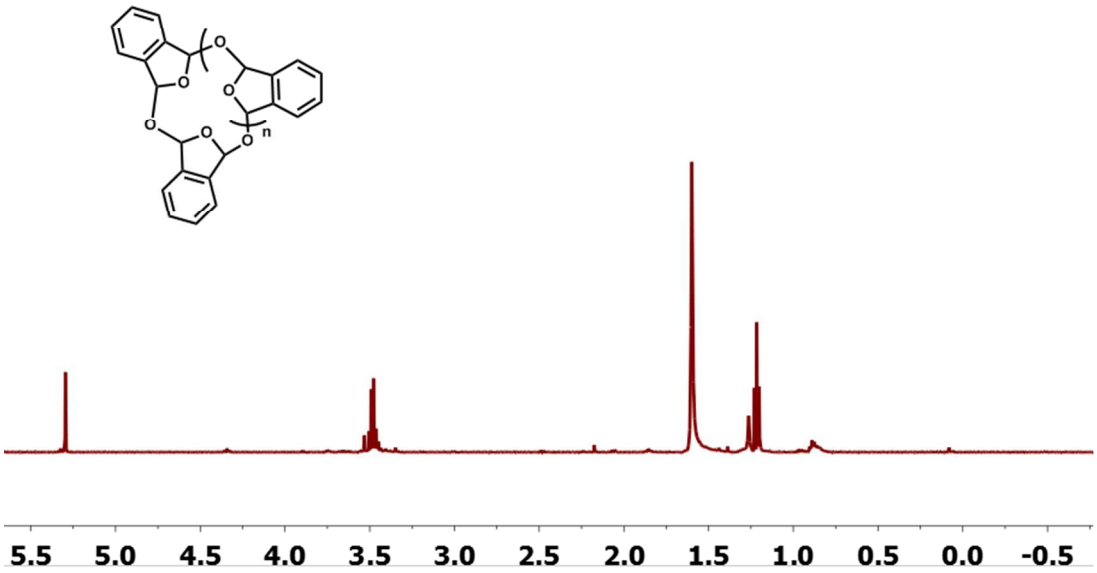


Figure S10 | Zoomed Region of ^{1}H NMR spectra of cyclic PPA*: NMR spectra of M_n = 51 kDa PPA prepared by cationic polymerization washed in hexanes and diethyl ether only (no methanol) in $CDCl_3$. Additional peaks correspond to water and dichloromethane, diethyl ether, and hexanes remaining after 3 days storage on vacuum.*

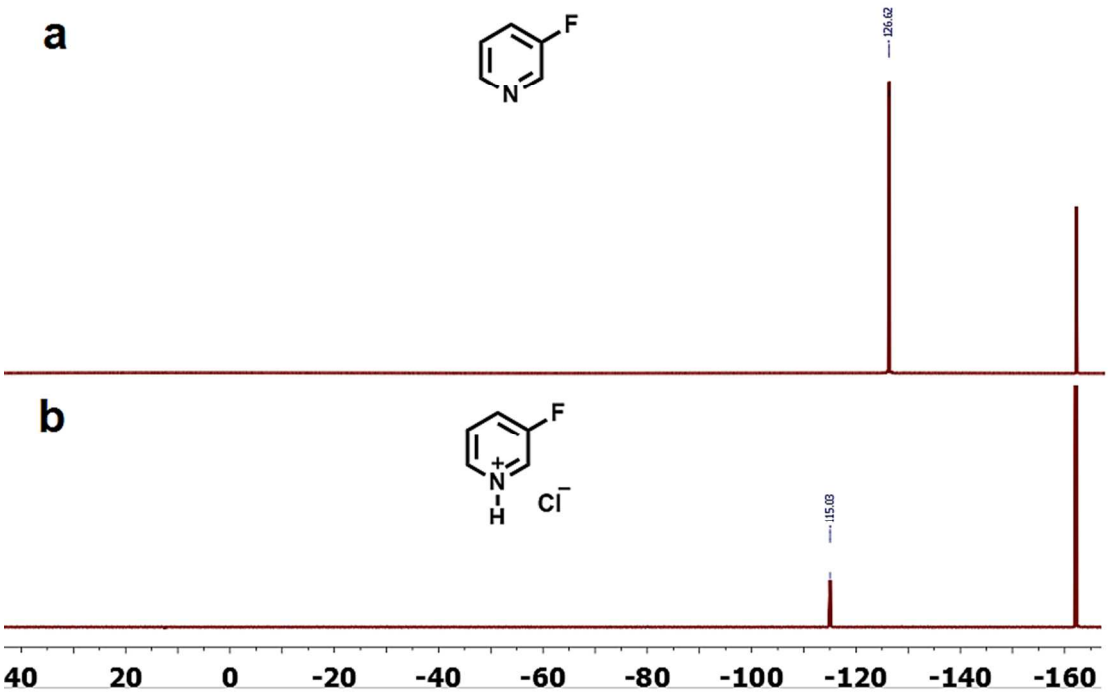


Figure S11 | (a) ^{19}F NMR spectra of 3-fluoropyridine (δ -126.6 ppm), and (b) ^{19}F NMR spectra of 3-fluoropyridium hydrochloride salt (δ -115.0 ppm) in $CDCl_3$. *Peak at -164 ppm corresponds to hexafluorobenzene internal standard.*

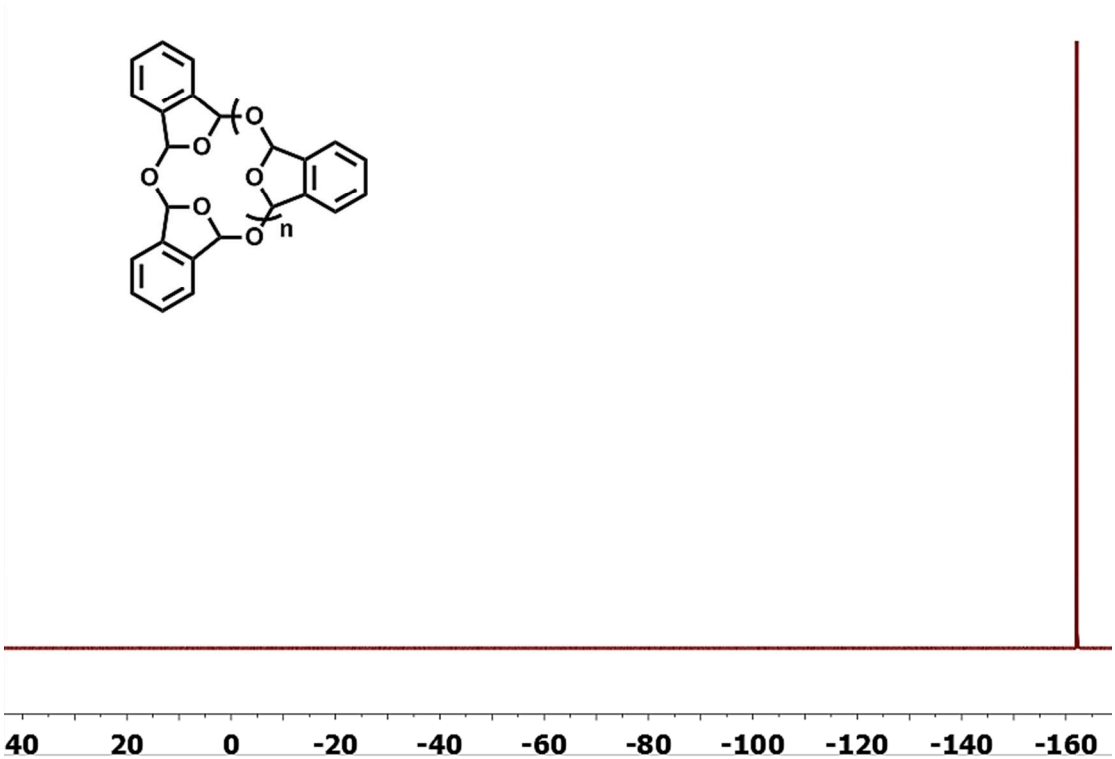


Figure S12 | ^{19}F NMR spectra of cyclic PPA quenched with 3-fluoropyridine*: NMR spectra of M_n = 10.5 kDa PPA prepared by cationic polymerization quenched with 3-fluoropyridine in $CDCl_3$ (polymer concentration 50 mg/mL). Peak at -164 ppm corresponds to hexafluorobenzene internal standard.*

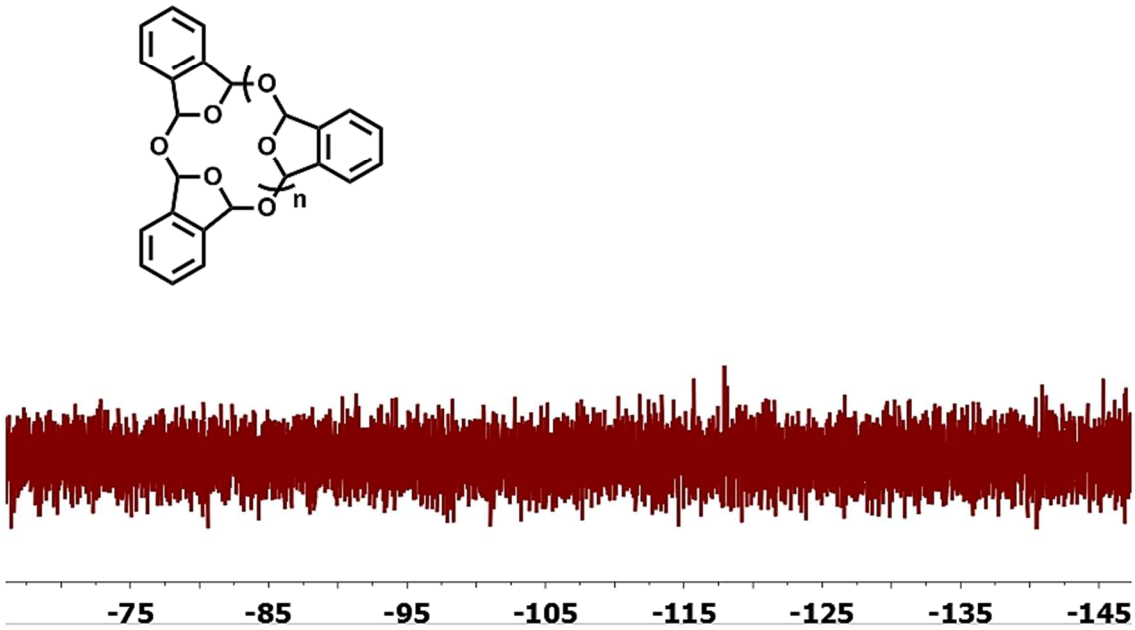


Figure S13 | Zoomed Region of ^{19}F NMR spectra of cyclic PPA quenched with 3-fluoropyridine*: NMR spectra of M_n = 10.5 kDa PPA prepared by cationic polymerization quenched with 3-fluoropyridine in $CDCl_3$. No peaks observed for 3-fluoropyridine or salts thereof (polymer concentration 50 mg/mL).*

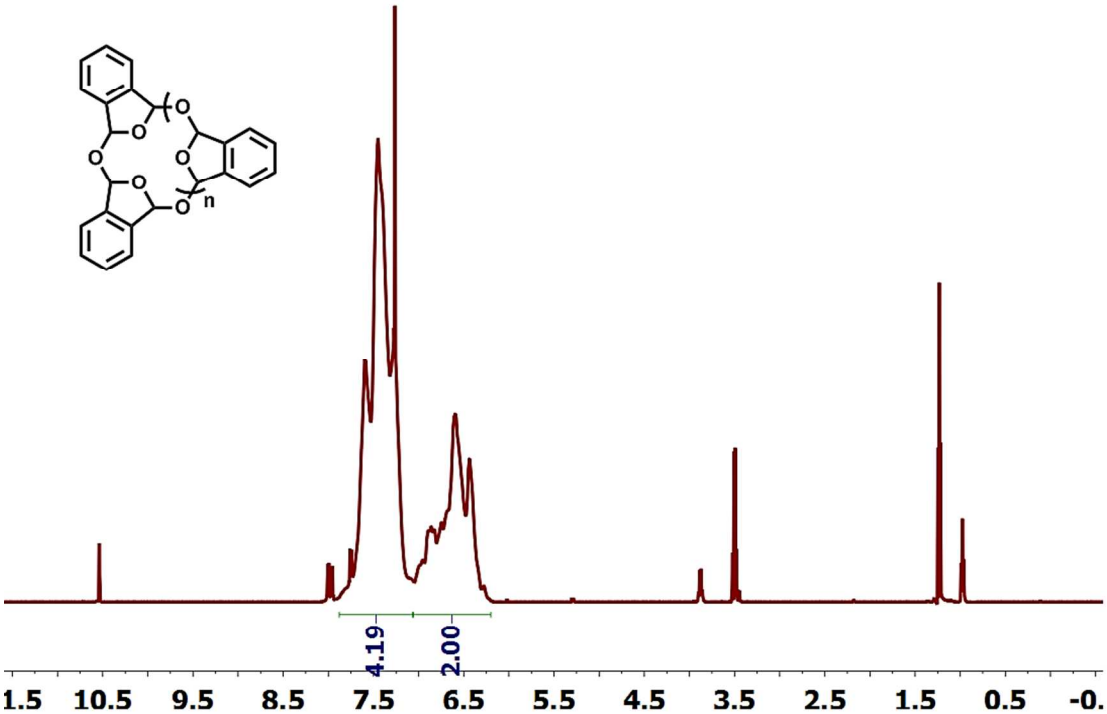


Figure S14 | ^{1}H NMR spectra of cyclic PPA prepared with triethyloxonium tetrafluoroborate*: NMR spectra of M_n = 89 kDa PPA prepared by cationic polymerization with triethyloxonium tetrafluoroborate in $CDCl_3$. No end-groups are observed. Additional peaks correspond to diethyl ether (1.2 ppm and 3.5 ppm) and residual salt and* o*-phthalaldehyde monomer.*

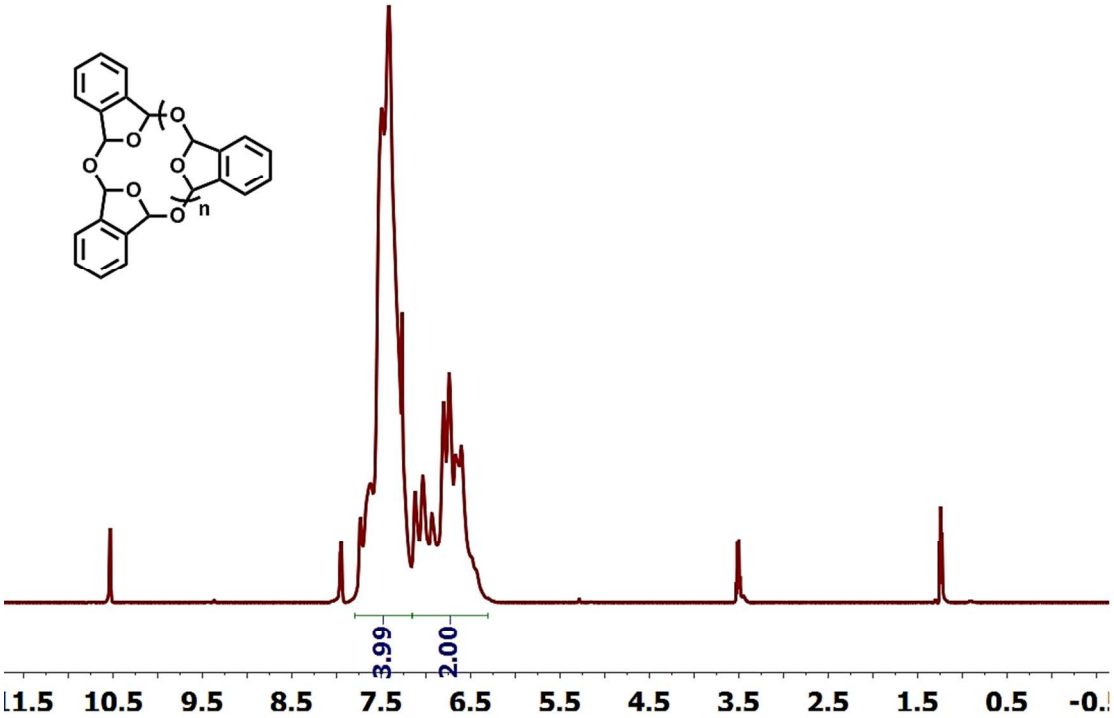


Figure S15 | ^{1}H NMR spectra of cyclic PPA prepared with tin chloride*: NMR spectra of M_n = 89 kDa PPA prepared by cationic polymerization with tin(IV) chloride in $CDCl_3$. No end-groups are observed. Additional peaks correspond to diethyl ether (1.2 ppm and 3.5 ppm) and residual* o*-phthalaldehyde monomer.*

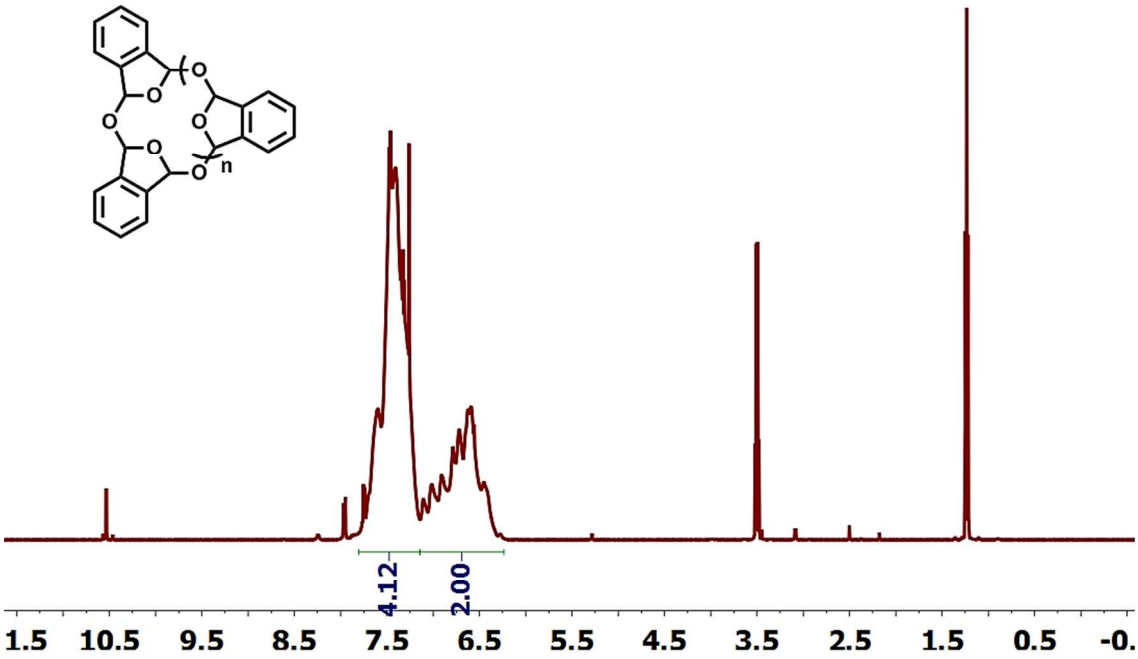


Figure S16 | ^{1}H NMR spectra of cyclic PPA prepared with triphenylcarbenium tetrafluoroborate*: NMR spectra of M_n = 26 kDa PPA prepared by cationic polymerization with triphenylcarbenium tetrafluoroborate in $CDCl_3$. No end-groups are observed. Additional peaks correspond to diethyl ether (1.2 ppm and 3.5 ppm) and residual* o*-phthalaldehyde monomer.*

IV. GPC Data

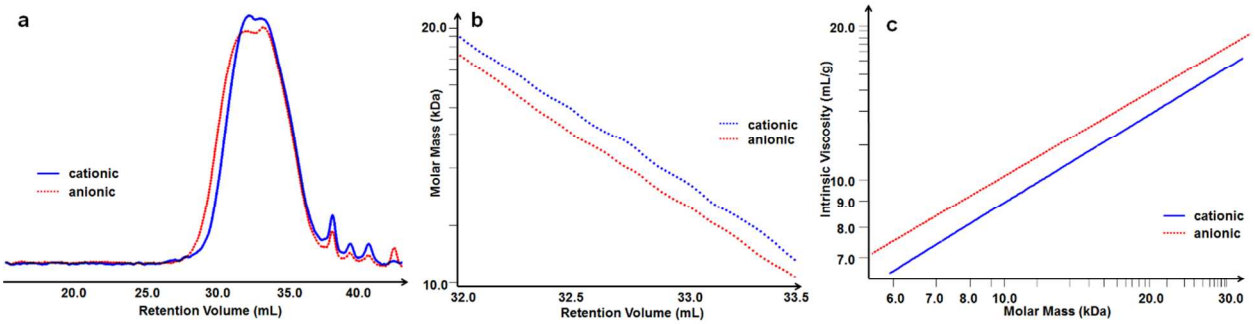


Figure S17 | Comparison of the physical properties of PPA produced by cationic and anionic polymerization*: a) Normalized GPC chromatograms of PPA made by cationic (blue) and anionic (red) polymerization of comparable molecular weight; b) Plot of molecular weight (logarithmic axis) versus retention volume; c) Mark-Houwink-Sakurada double log plot of intrinsic viscosity (IV) versus molecular weight.* M*olecular weights are summarized in Table S7.*

Table S7 | Comparison of PPA prepared by anionic and cationic polymerizations*.*

Sample	M_n *(kDa)*[a]	M_w *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]
Cationic	11.2	16.8	17.3	1.5
Anionic	11.7	19.7	11.3	1.7

[a]Average molecular weights and polydispersity determined absolutely by triple detector GPC analysis.

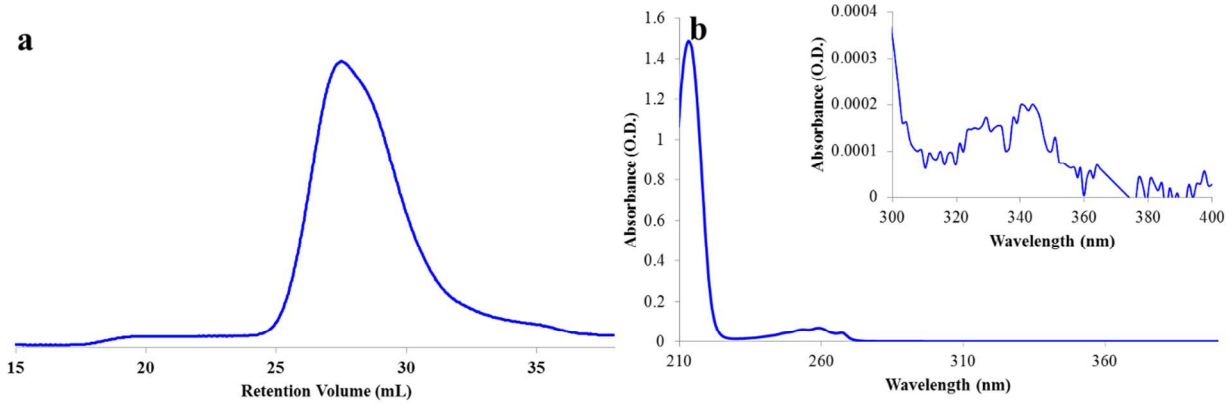


Figure S18 | GPC Chromatogram and UV detector trace of cPPA precipitated with 1-pyrene methanol*: a) GPC chromatogram of cPPA (blue) precipitated with 1-pyrene methanol (Table S1, Entry 8); b) UV spectrum at retention volume 28 mL. Pyrene peaks are notably absent during polymer elution (see zoom in at 345 nm where pyrene absorbs strongly),[3] indicating that pyrene is not incorporated into the polymer.* M*olecular weight data is summarized in Table S8.*

Table S8 | Absolute molecular weight data of cPPA mixed with 1-pyrene methanol*.*

Sample	M_n *(kDa)*[a]	M_w *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]
Cationic	25.0	70.4	71.4	2.8

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

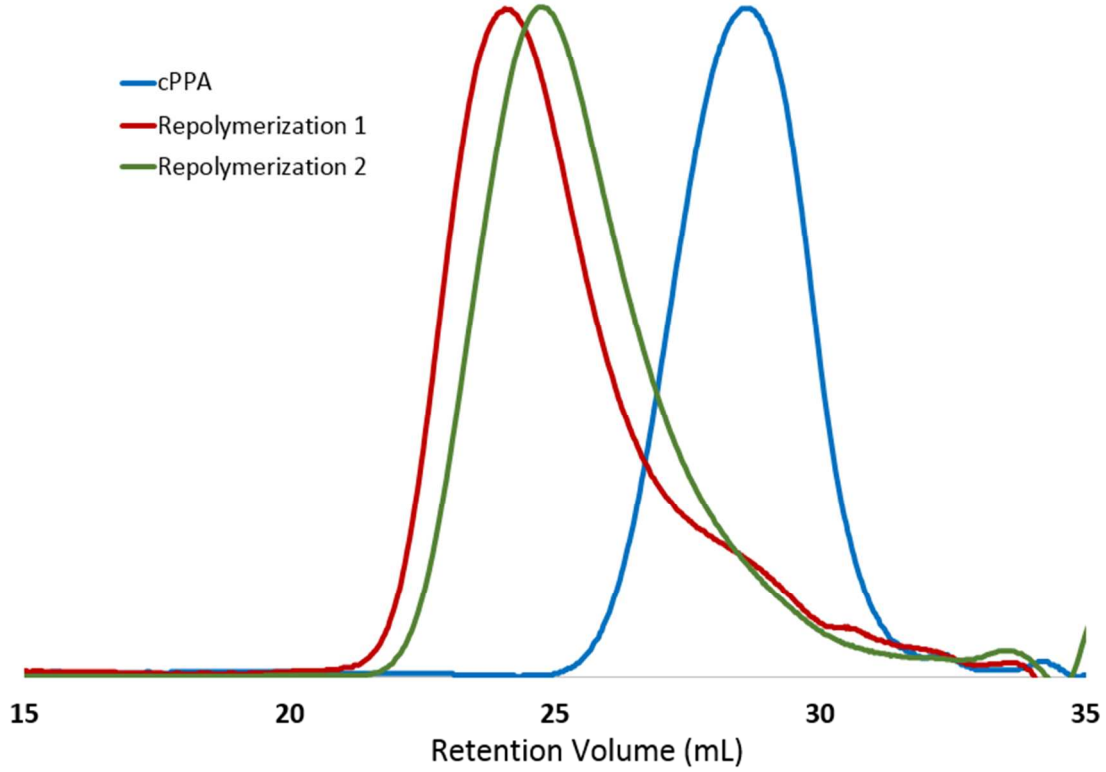


Figure S19 | GPC Chromatograms of cPPA after repolymerization experiments*: Normalized GPC traces of cPPA (blue) repolymerized to higher molecular weight at a total monomer concentration of 0.6 M (red) and repolymerized a second time at 0.6 M (green). Experimental conditions and molecular weights are summarized in Table S9.*

Table S9 | Repolymerization samples*.*

Sample	*[o-PA]*	*$[M]_0/[I]_0$*	*Yield*	*M_n (kDa)*[a]	*M_p (kDa)*[a]	*PDI*[a]
cPPA	0.1 M	6 / 1	21%	4.0	5.1	1.6
Repolymerization 1	0.6 M	18 / 1	86%	12.5	67.4	5.1
Repolymerization 2	0.6 M	18 / 1	86%	16.8	45.6	2.7

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

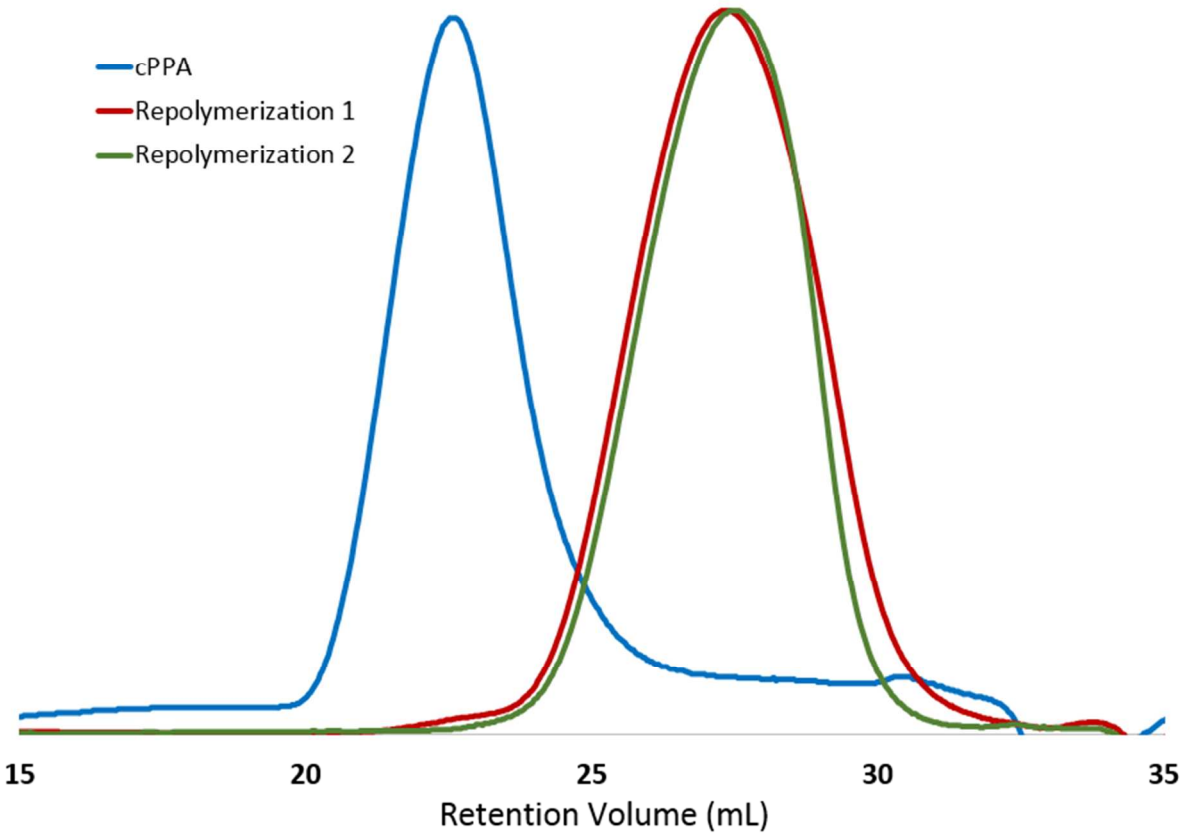


Figure S20 | GPC Chromatograms of cPPA after repolymerization experiments*: Normalized GPC traces of cPPA (blue) repolymerized to lower molecular weight at a total monomer concentration of 0.5 M (red) and repolymerized a third time at 0.5 M (green). Experimental conditions and molecular weights are summarized in Table S10.*

Table S10 | Repolymerization samples*.*

Sample	*[o-PA]*	$[M]_0/[I]_0$	*Yield*	M_n *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]
cPPA	0.7 M	7 / 1	99%	109	199	2.5
Repolymerization 1	0.5 M	4 / 1	77%	6.7	10.1	2.4
Repolymerization 2	0.4 M	5 / 1	52%	7.9	9.1	1.7

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

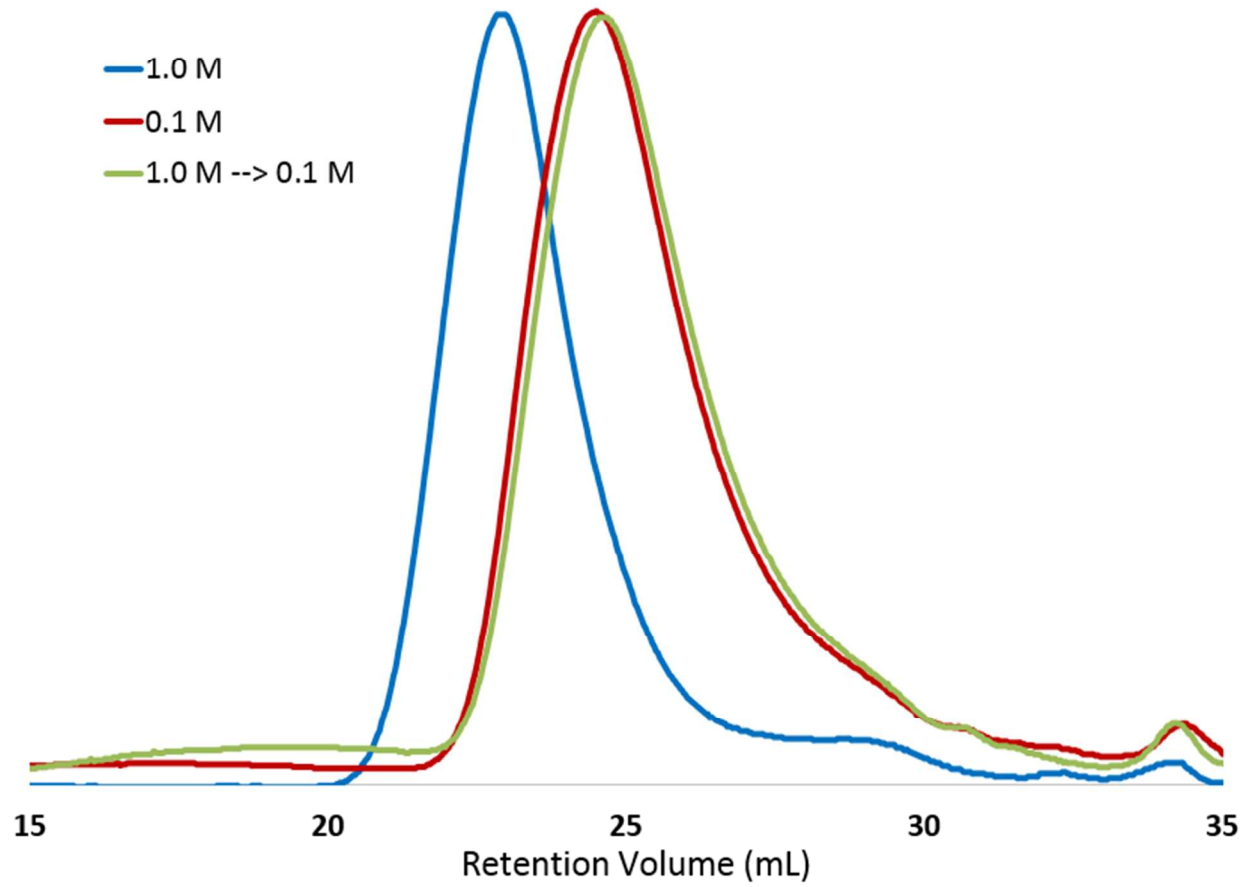


Figure S21 | GPC Chromatograms after second batch monomer addition experiment*: Normalized GPC traces of cPPA polymerized at monomer concentrations of 1.0 M (blue), 0.1 M (red), and an initial [o-PA] of 1.0 M followed by addition of a second batch of o-PA to final concentration of 0.1 M (green). Experimental conditions and molecular weights are summarized in Table S11.*

Table S11 | Second batch monomer addition samples*.*

Sample	*[o-PA]*	$[M]_0/[I]_0$	*Yield*	M_n *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]
Blue	1.0 M	10 / 1	86%	36.1	158	4.5
Red	0.1 M	10 / 1	48%	14.9	54.1	3.5
Green	1.0 → 0.1 M	10 / 1	48%	11.8	48.6	4.1

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

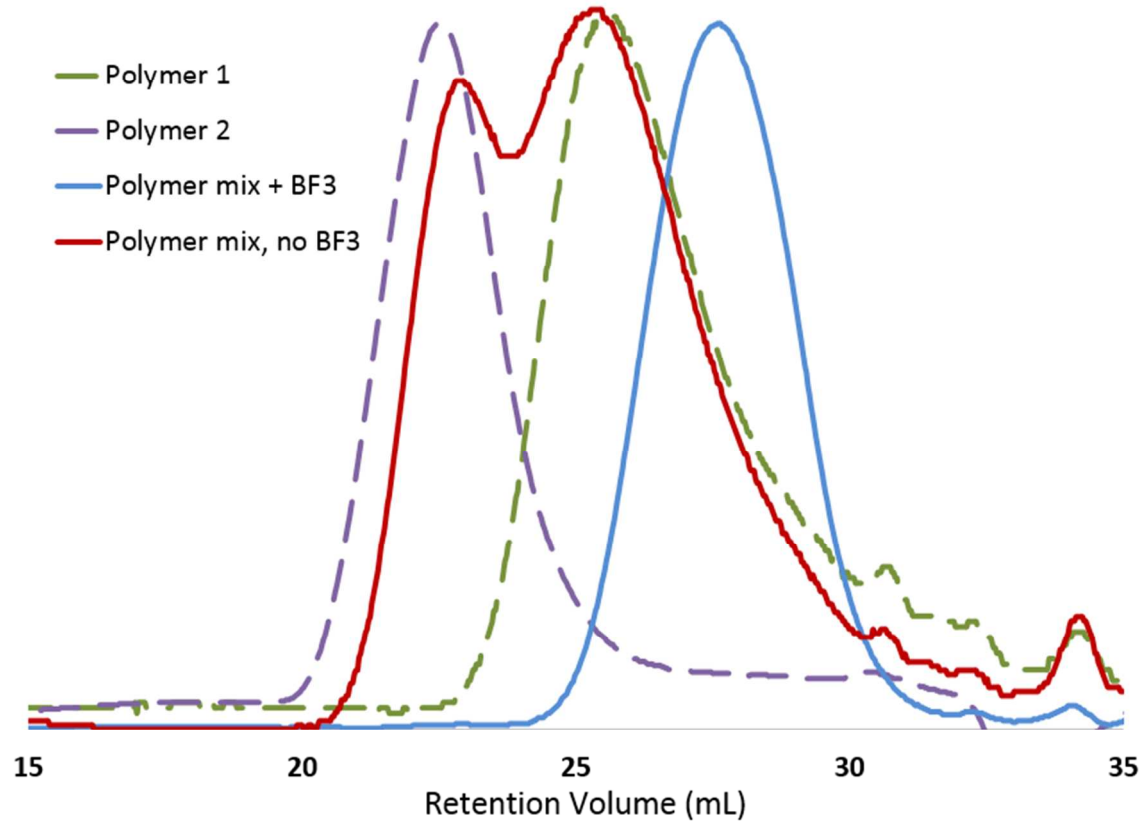


Figure S22 | GPC Chromatograms after polymer mixing experiment*: Normalized GPC traces of two cPPA polymers (green and purple, dashed lines) and blends of the two polymers in the presence (blue) and absence (red) of initiator. Experimental conditions and molecular weights are summarized in Table S12.*

Table S12 | Polymer mixing samples*.*

Sample	*[o-PA]*	$[M]_0/[I]_0$	*Yield*	M_n *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]
Purple	0.7 M	7 / 1	99%	109	199	2.5
Green	0.5 M	14 / 1	83%	11.7	29.5	2.1
Blue[b]	0.5 M	5 / 1	87%	8.3	6.0	1.6
Red[c,d]	0.5 M	- - -	99%	10.5	30.7, 155	7.8

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [b]Polymers mixed and initiator added. [c]Control reaction, no initiator added. [d]Bimodal molecular weight distribution.

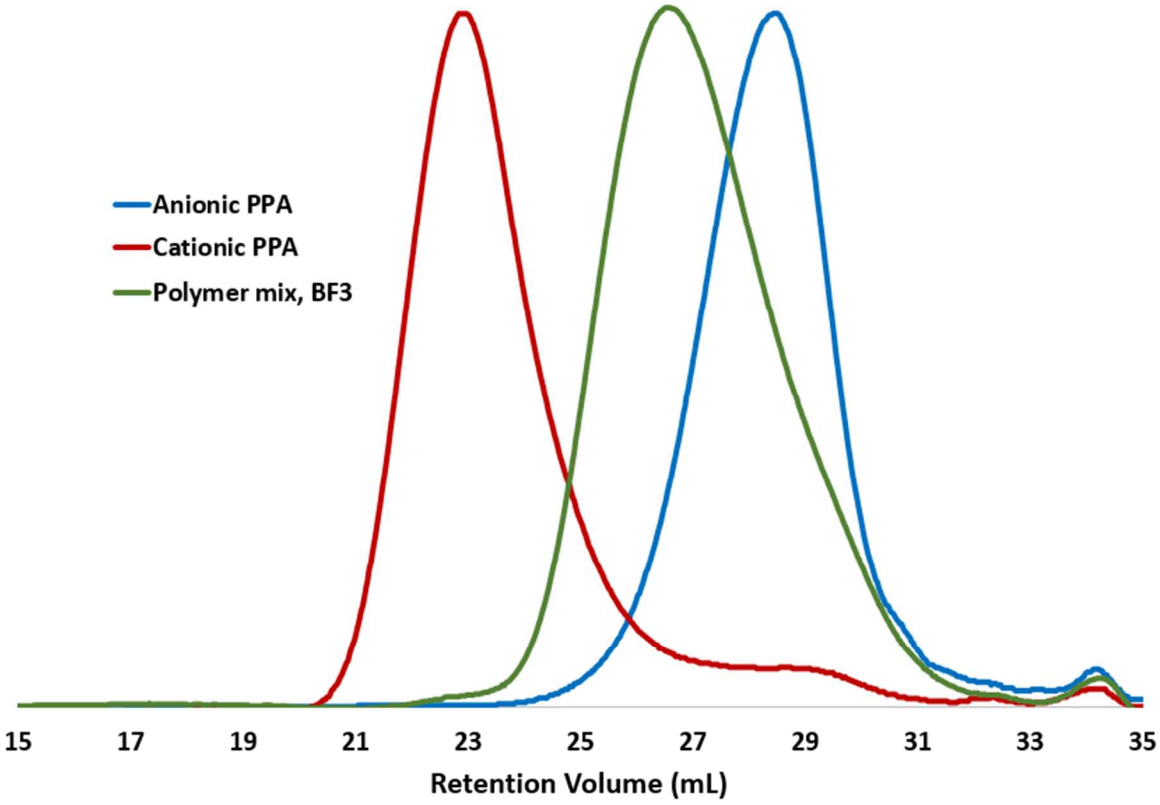


Figure S23 | GPC Chromatograms after polymer mixing experiment*: Normalized GPC traces of linear PPA (blue), cPPA (red) and a blend of the two polymers in the cationic polymerization conditions (green). Experimental conditions and molecular weights are summarized in Table S13.*

Table S13 | Polymer mixing samples*.*

Sample	*[o-PA]*	*Yield*	M_n *(kDa)*[a]	M_w *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]
Anionic	0.7 M	83%	4.4	7.7	5.4	1.8
Cationic	1.0 M	86%	36.1	164	158	4.5
Blend[b]	0.6 M	90%	7.5	16.6	32.9	2.2

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [b]Polymers mixed and initiator added at -78 °C.

V. MALDI-TOF MS Data

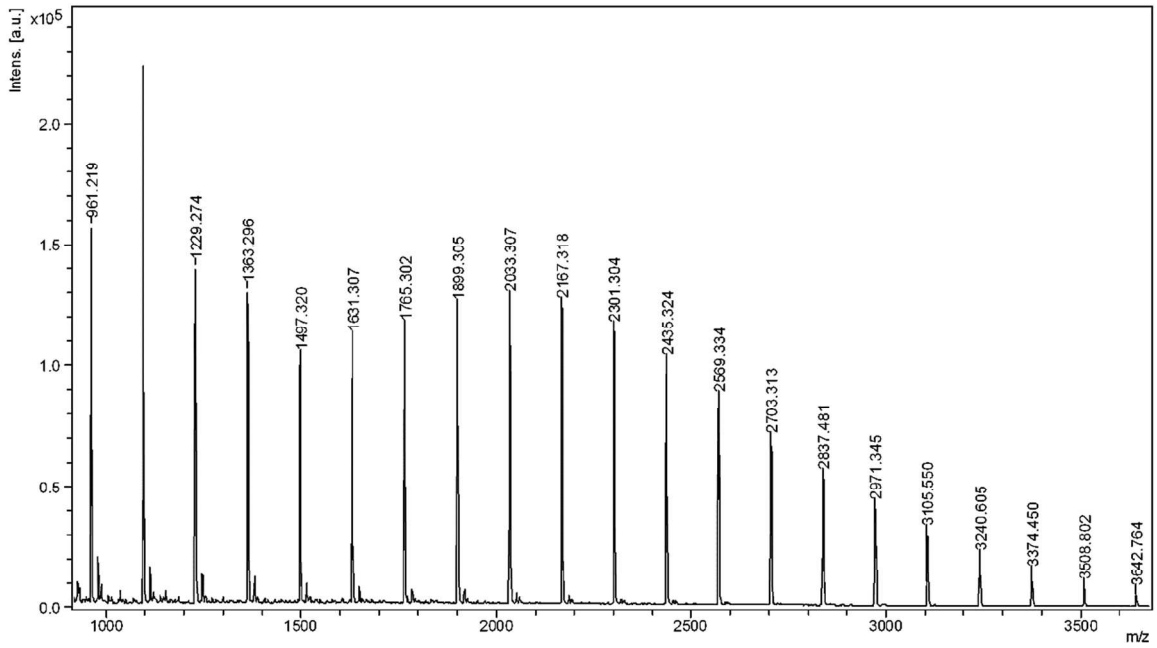


Figure S24 | MALDI-TOF MS spectrum of cPPA*: Peaks match sodium adduct of cPPA (GPC M_n = 2.7 kDa); minor secondary peaks match sodium and water adduct of PPA, presumably PPA with hemiacetal groups from reaction with MALDI matrix (+18 mass units).*

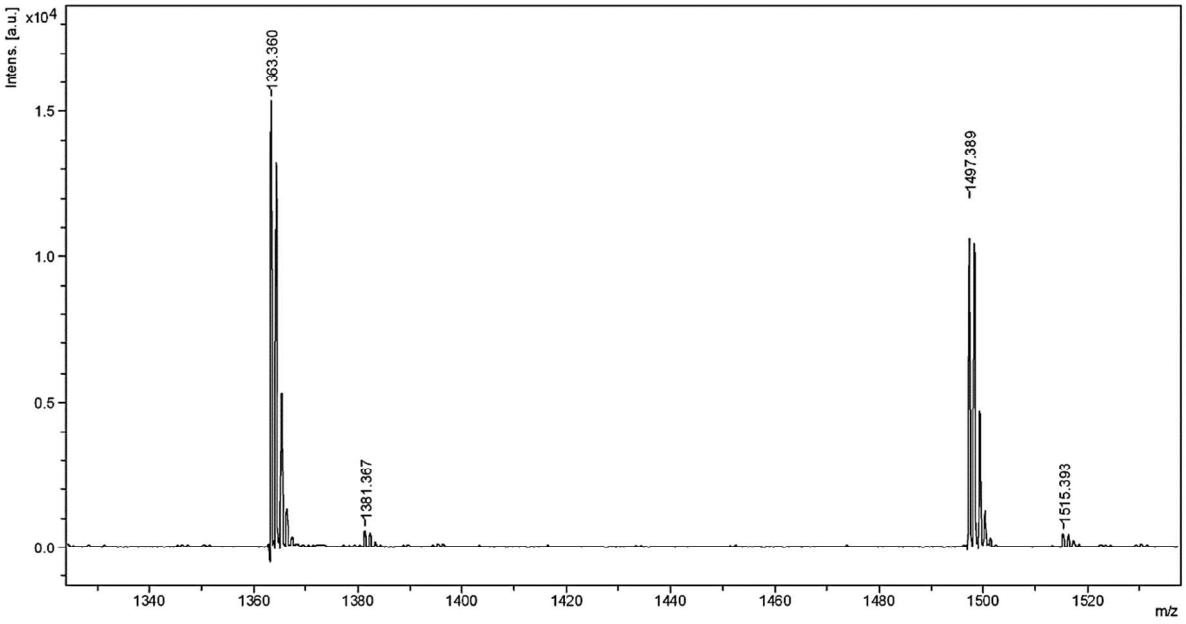


Figure S25 | Expansion of MALDI-TOF MS spectrum of cPPA*: Expansion of peaks matching sodium adduct of cPPA 10-mer and 11-mer (GPC M_n = 11.8 kDa); minor secondary peaks match sodium and*

water adduct of PPA, presumably PPA with hemiacetal groups from reaction with MALDI matrix (+18 mass units).

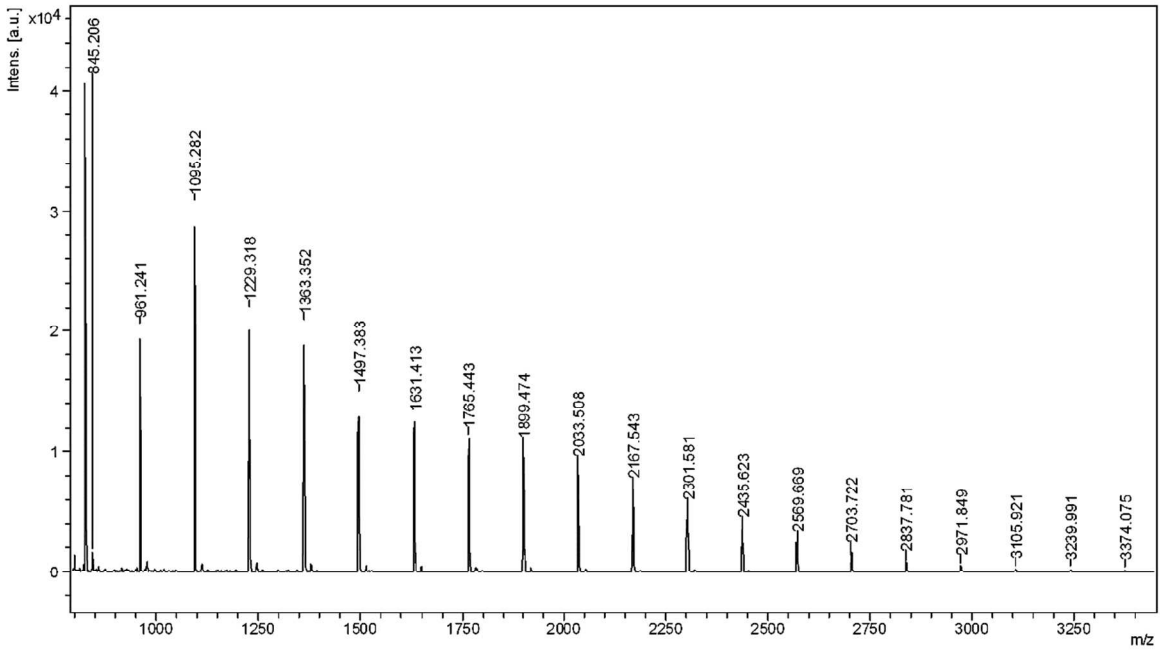


***Figure S26 | MALDI-TOF MS spectrum of cPPA**: Peaks match sodium adduct of cPPA (GPC M_n = 11.8 kDa); minor secondary peaks match sodium and water adduct of PPA, presumably PPA with hemiacetal groups from reaction with MALDI matrix (+18 mass units).*

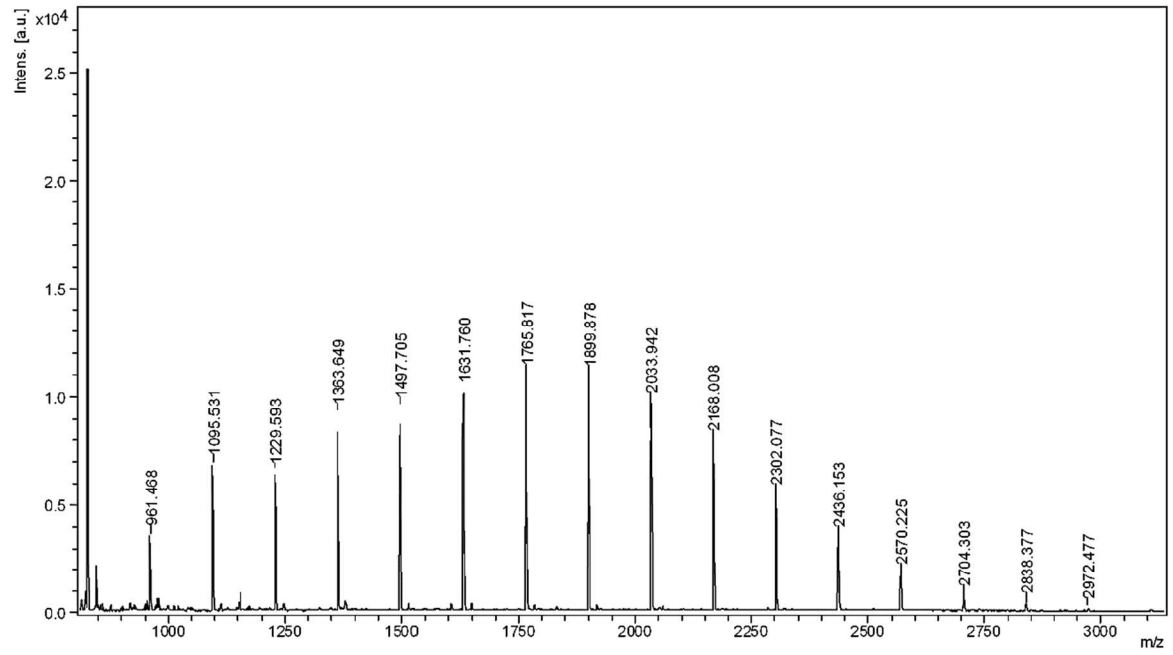


***Figure S27 | MALDI-TOF MS spectrum of cPPA**: Peaks match sodium adduct of cPPA (GPC M_n = 25.0 kDa).*

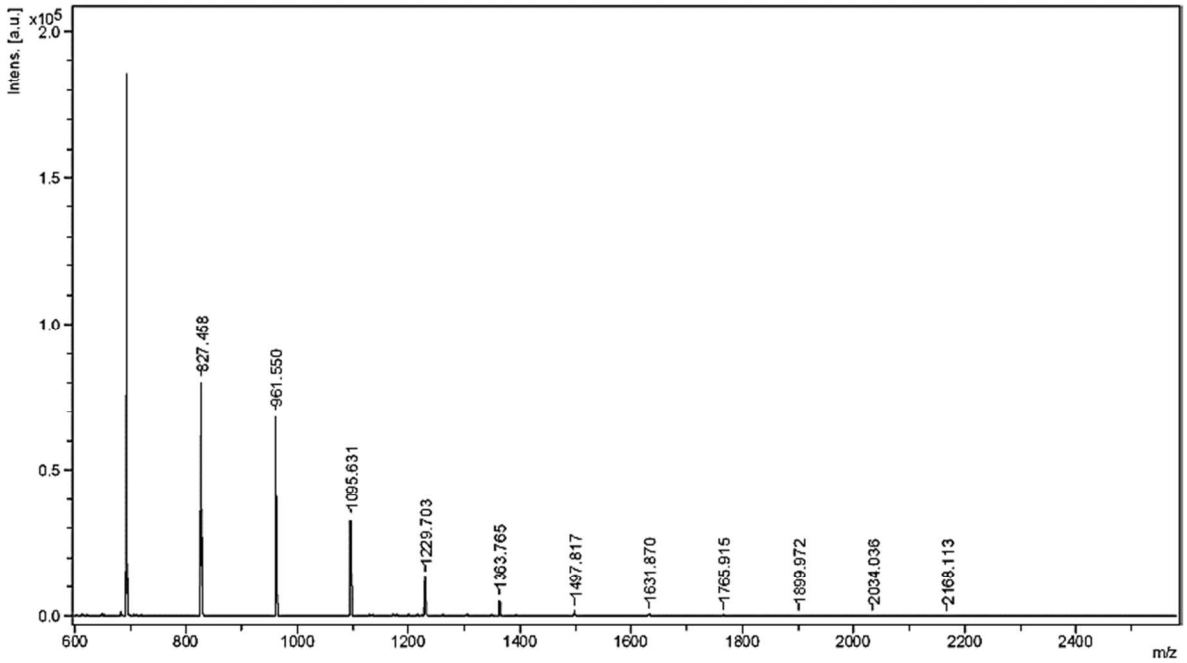


Figure S28 | MALDI-TOF MS spectrum of cPPA prepared with triethyloxonium tetrafluoroborate*: Peaks match sodium adduct of cPPA (GPC M_n = 89 kDa).*

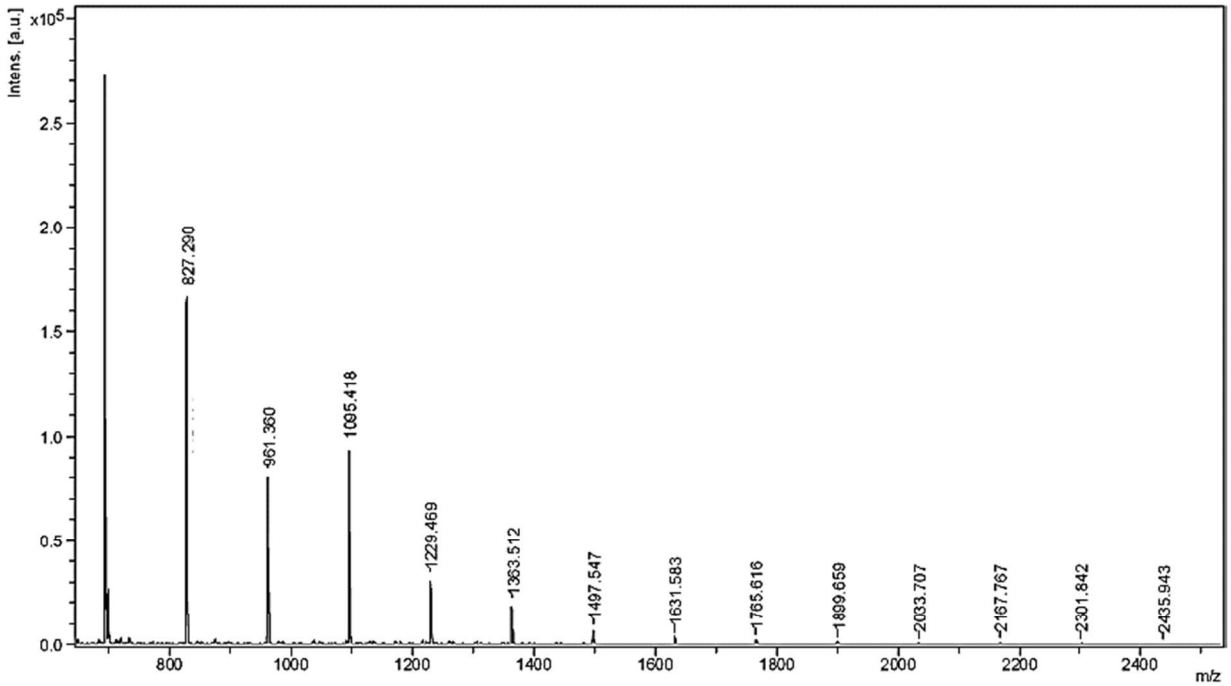


Figure S29 | MALDI-TOF MS spectrum of cPPA prepared with tin(IV) chloride*: Peaks match sodium adduct of cPPA (GPC M_n = 89 kDa).*

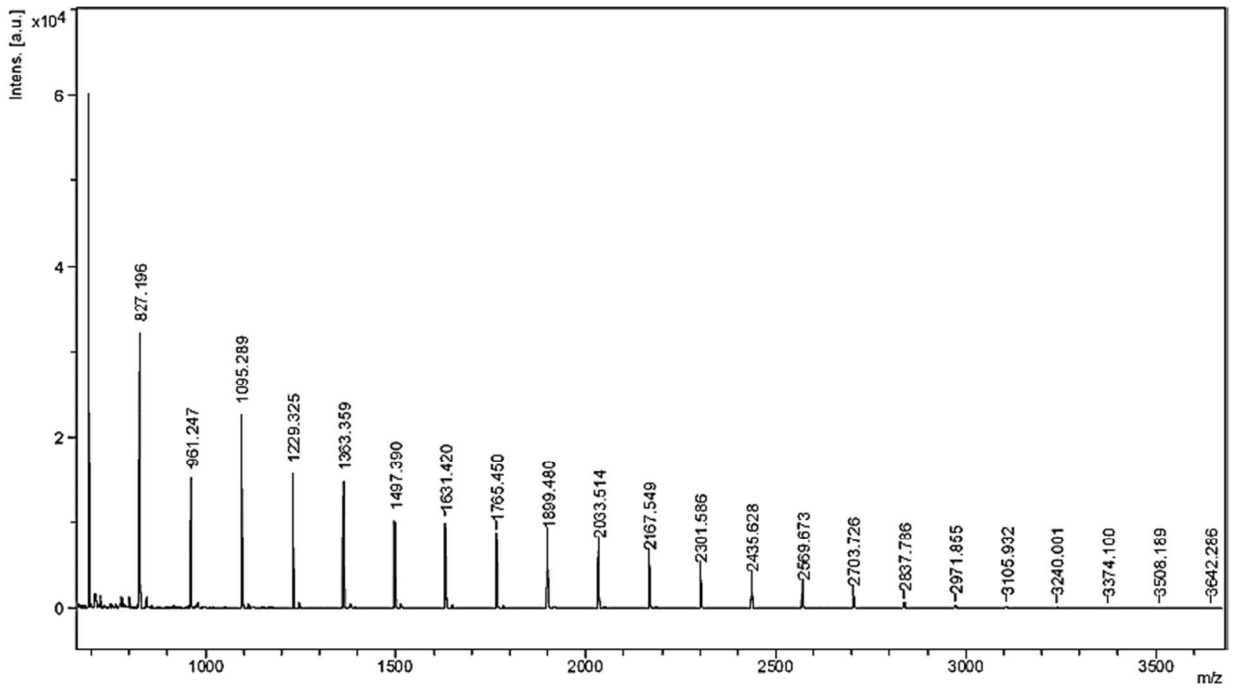


Figure S30 | MALDI-TOF MS spectrum of cPPA prepared with triphenylcarbenium tetrafluoroborate*: Peaks match sodium adduct of cPPA (GPC M_n = 26 kDa).*

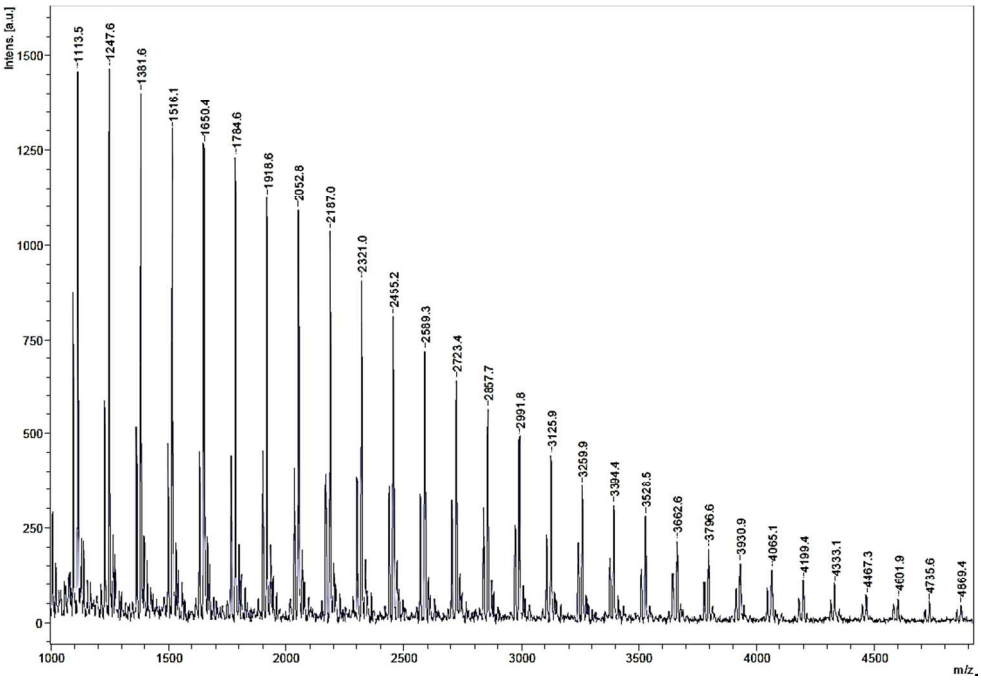


Figure S31 | MALDI-TOF MS spectrum of hydrolyzed cPPA*: Sample prepared by mixing DHB matrix with polymer in THF prior to spotting. Major peaks match sodium and water adduct of PPA, presumably PPA with hemiacetal groups from reaction with MALDI matrix; secondary peaks match sodium adduct of cyclic PPA (-18 mass units).*

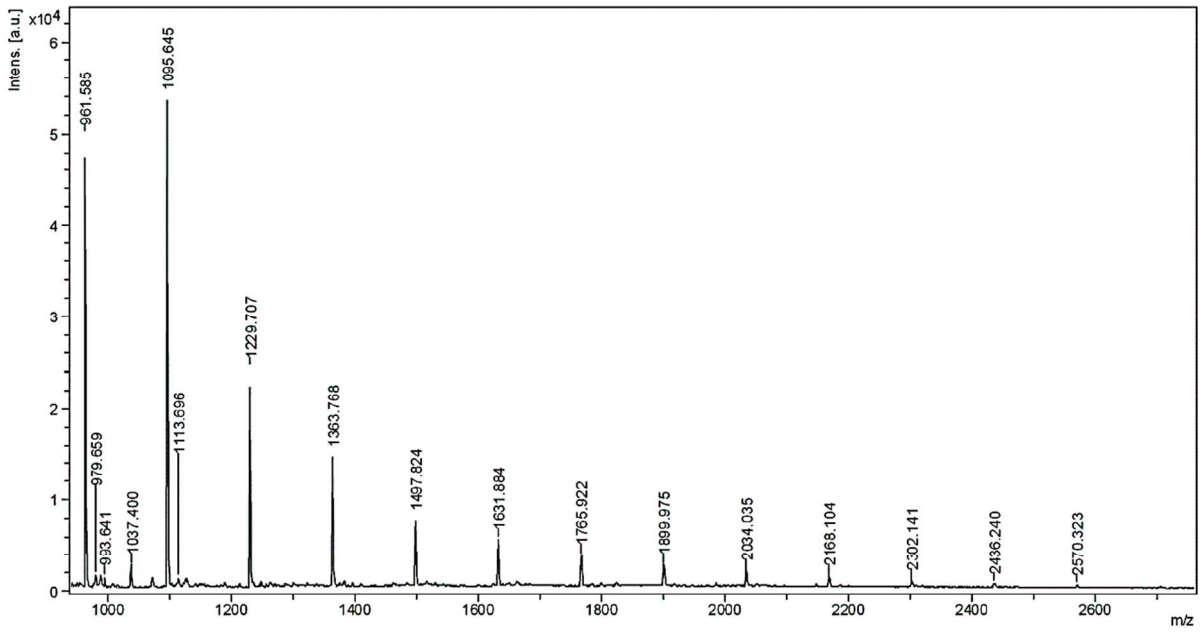


Figure S32 | MALDI-TOF MS spectrum of linear PPA "repolymerization" samples*: Polymers prepared by subjecting linear PPA to cationic polymerization conditions. Peaks match sodium adduct of cPPA (GPC M_n = 7.5 kDa).*

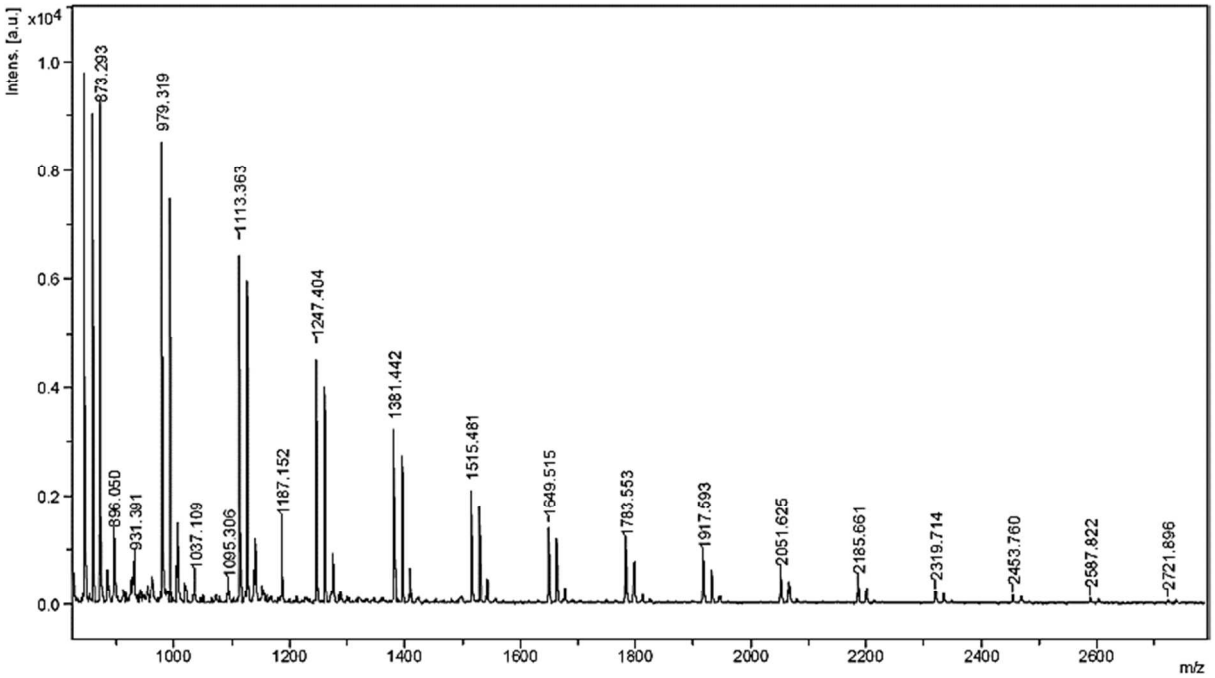


Figure S33 | MALDI-TOF MS spectrum of PPA prepared by anionic initiation*: PPA prepared by anionic polymerization (GPC M_n = 6.3 kDa; Table S2, Entry 2). Fine spacing of 14 m/z units (presumably –CH_2- units in initiator) observed within oligomer clusters.*

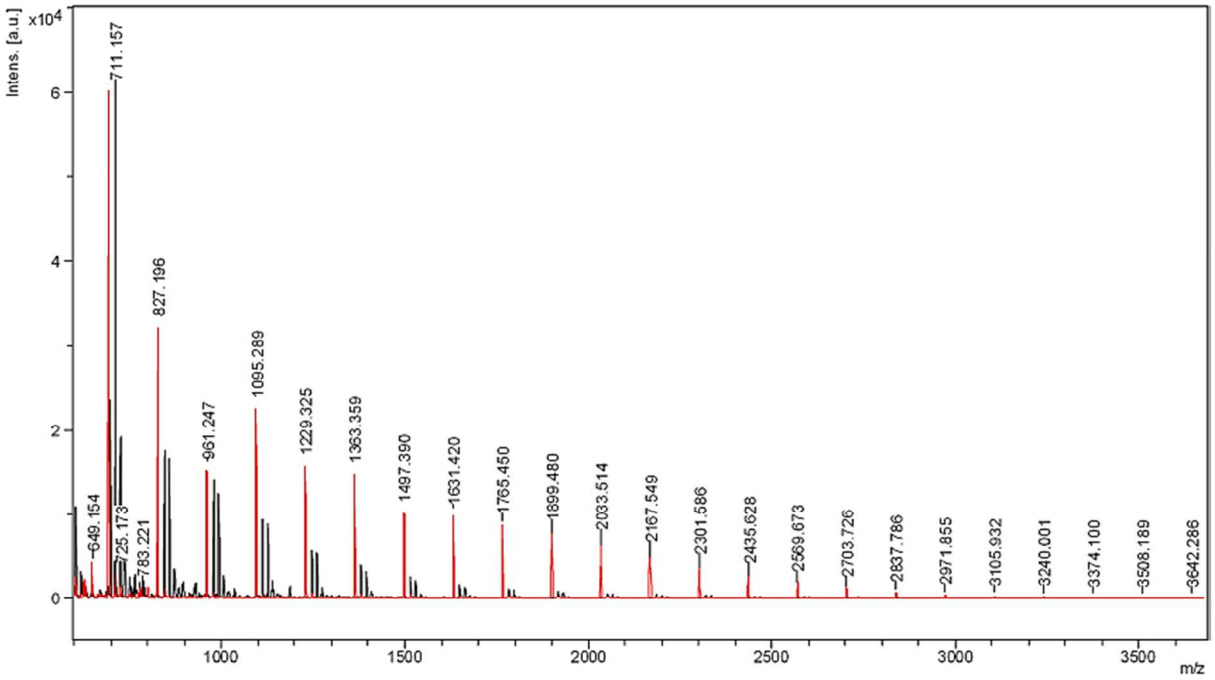


Figure S34 | MALDI-TOF MS spectra overlay of cPPA and PPA prepared by anionic initiation*: PPA prepared by anionic polymerization (black trace; GPC M_n = 6.3 kDa) overlayed with cPPA (red trace; GPC M_n = 11.8 kDa); clear microstructural differences observed.*

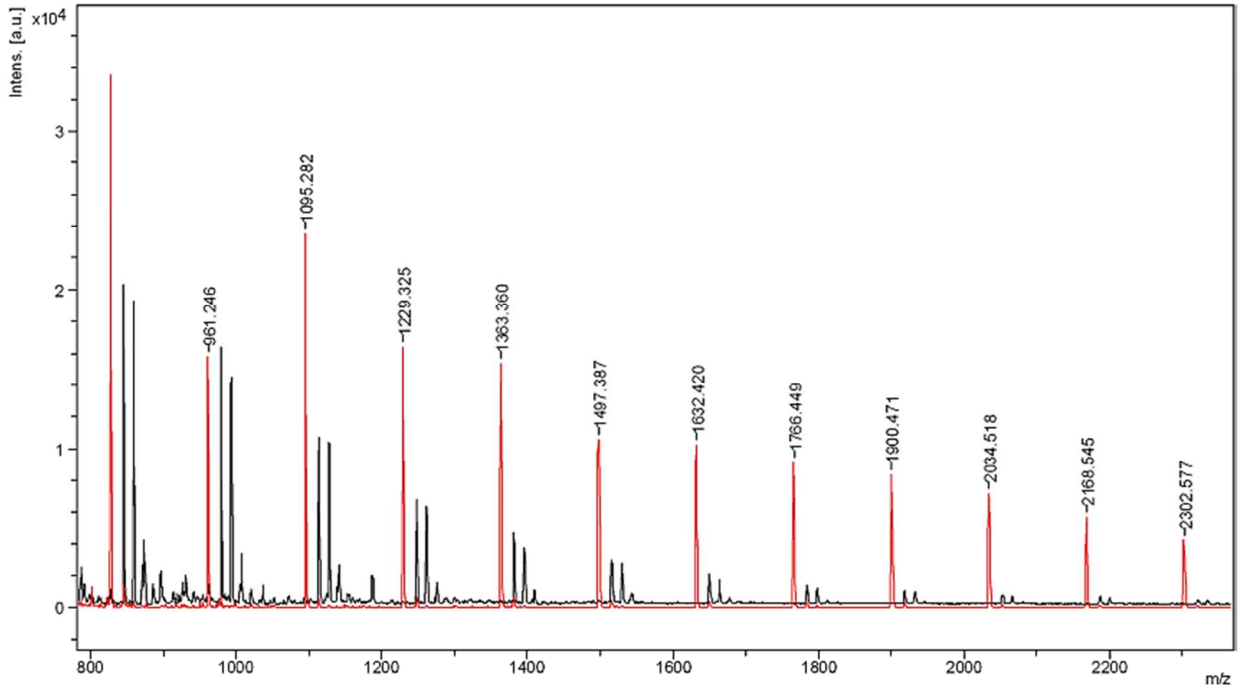


Figure S35 | Zoom of MALDI-TOF MS spectra overlay of cPPA and PPA prepared by anionic initiation*: PPA prepared by anionic polymerization (black trace; GPC M_n = 6.3 kDa) overlayed with cPPA (red trace; GPC M_n = 11.8 kDa); clear microstructural differences observed.*

VI. Thermal Characterization

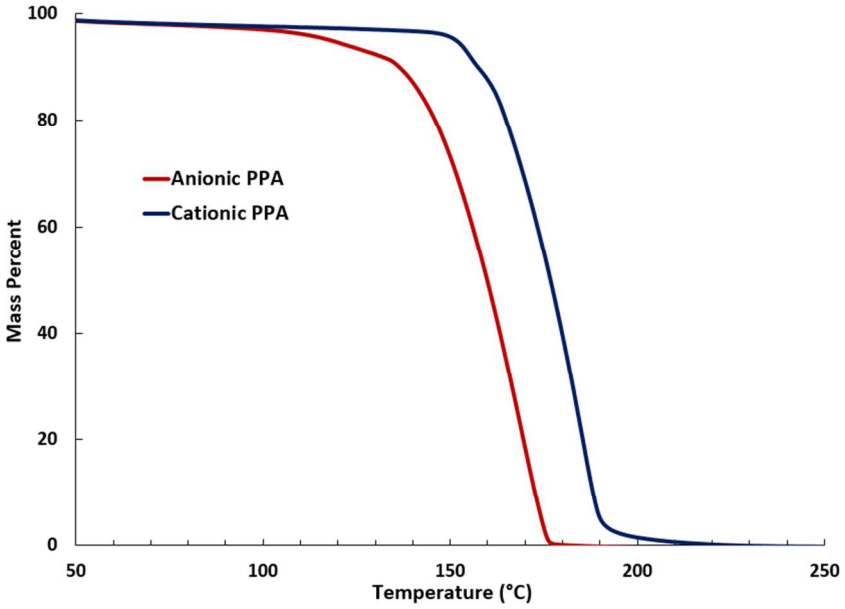


Figure S36 | TGA of linear and cyclic PPA*: Normalized TGA curves of representative samples of linear (red) and cyclic (blue) PPA. Molecular weight data and depolymerization temperatures are summarized in Table S14.*

Table S14 | TGA Samples. *Molecular weight and depolymerization data for linear and cyclic PPA.*

Entry	*Polymerization*	M_n *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]	*Onset Temp (°C)*	*Endset Temp (°C)*	*Residue at 300 °C*
1	Cationic	6.7	10.1	2.4	159	236	3.6%
2	Cationic	7.9	9.1	1.7	156	211	2.4%
3	Cationic	11.8	48.6	4.1	157	186	4.5%
4	Cationic	14.9	54.1	3.5	148	204	2.3%
5	Cationic	36.1	158	4.5	139	199	2.0%
6	Cationic	37.1	79.8	2.2	158	195	1.1%
Cationic Averages					153 ± 8 °C		2.6 ± 1.2%
7	Anionic	4.4	5.4	1.8	150	199	3.6%
8	Anionic	6.3	8.1	3.0	141	190	3.2%
9	Anionic	9.0	11.5	2.1	132	193	2.1%
10	Anionic	16.1	26.5	2.7	135	185	2.6%
11	Anionic	20.4	40.9	2.0	138	200	2.4%
12	Anionic	22.6	35.5	1.6	136	177	0.5%
Anionic Averages					139 ± 6 °C		2.4 ± 1.1%

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

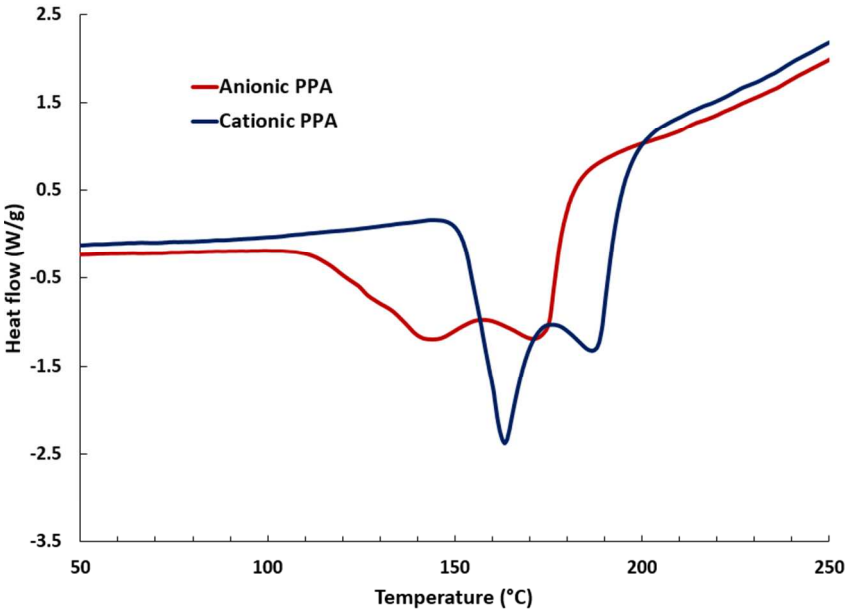


Figure S37 | DSC of linear and cyclic PPA*: Normalized DSC curves of representative samples of linear (blue) and cyclic (red) PPA. Molecular weight data and depolymerization temperatures are summarized in Table S15.*

Table S15 | DSC Samples*. Molecular weight and enthalpic data for linear and cyclic PPA.*

Entry	*Polymerization*	M_n *(kDa)*[a]	M_p *(kDa)*[a]	*PDI*[a]	*Enthalpy (J/g)*
1	Cationic	6.7	10.1	2.4	-540
2	Cationic	7.9	9.1	1.7	-520
3	Cationic	11.8	48.6	4.1	-540
4	Cationic	14.9	54.1	3.5	-580
5	Cationic	36.1	158	4.5	-590
6	Cationic	37.1	79.8	2.2	-520
Cationic Averages					-550 ± 30 J/g
7	Anionic	4.4	5.4	1.8	-590
8	Anionic	6.3	8.1	3.0	-580
9	Anionic	9.0	11.5	2.1	-570
10	Anionic	16.1	26.5	2.7	-530
11	Anionic	20.4	40.9	2.0	-580
12	Anionic	22.6	35.5	1.6	-520
Anionic Averages					-560 ±30 J/g

[a]Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

Author's note: Trace elemental analysis of samples characterized by TGA and DSC was inconclusive. Thermal analysis of linear and cyclic polymers may be influenced by residual contaminants.

VII. In Situ FTIR Characterization Data.

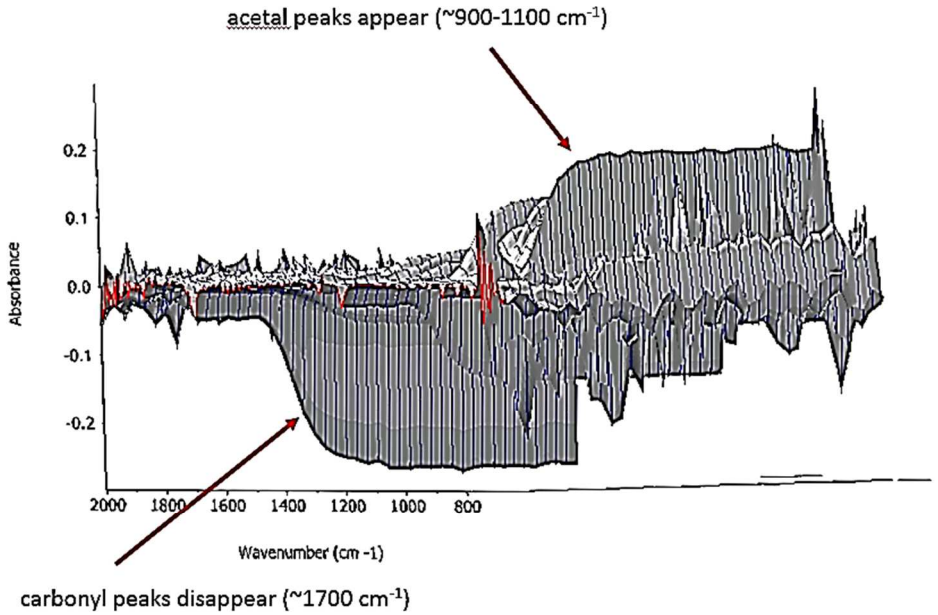


Figure S38 | In situ FTIR monitoring of cPPA polymerization*: Disappearance of carbonyl peaks and appearance of acetal peaks observed as reaction progresses. Polymerization conducted at 0.7 M monomer concentration and 10 / 1 ratio of monomer to initiator. Measurements recorded at intervals of 8 seconds.*

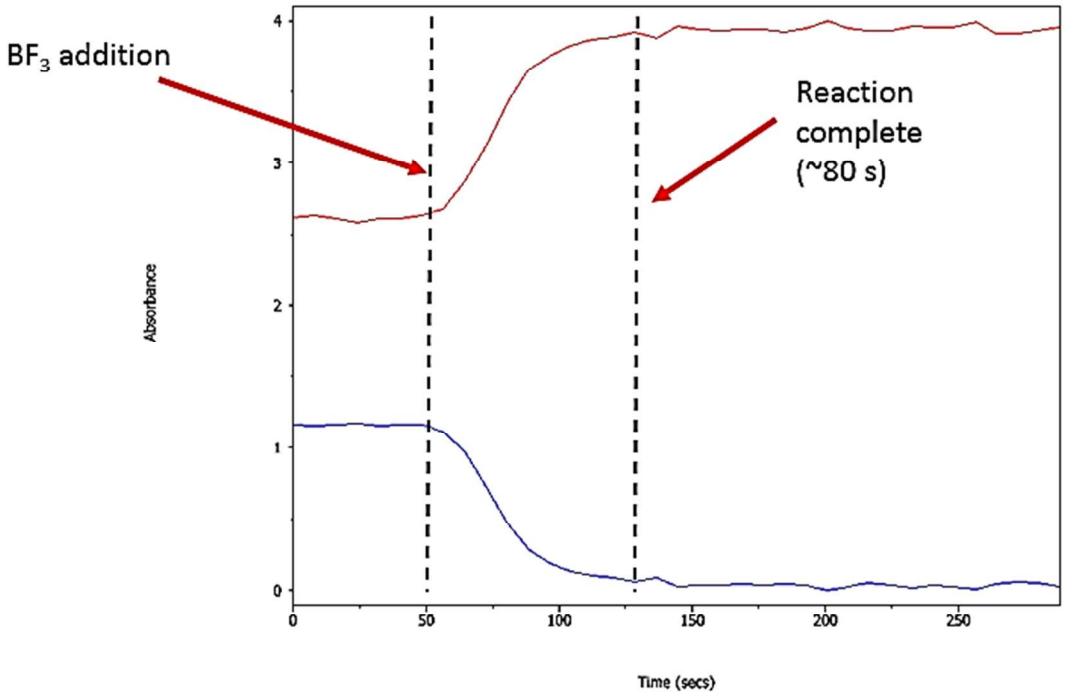


Figure S39 | Reaction progress monitored by in situ FTIR*: Disappearance of carbonyl peaks (blue trace) and appearance of acetal peaks (red trace) tracked over time. Monomer conversion to polymer plateaus after several minutes.*

VIII. References for Supporting Information

(1) Dilauro, A. M.; Robbins, J. S.; Phillips, S. T. *Macromolecules*, **2013**, 46, 2963-2968.

(2) Coulembier, O.; Knoll, A.; Pires, D.; Gotsmann, B.; Duerig, U.; Frommer, J.; Miller, R. D.; Dubois, P.; Hedrick, J. L. *Macromolecules* **2010**, 43, 572-574.

(3) Potisek, S. L.; Davis, D. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *J. Am. Chem. Soc.*, **2007**, 129, 13808-13809.

Addendum A: Data for GPC comparisons of linear and cyclic PPAs (Figures 3 and S17).

Mark-Houwink-Sakurada				Molecular weight vs. Retention time		
	Cationic		Anionic			
Mw (Da)	Intrinsic Viscosity (mL/g)	Mw (Da)	Intrinsic Viscosity (mL/g)	Retention Volume (mL)	Cationic Mw (Da)	Anionic Mw (Da)
3709.68	5.12	4144.64	6.19	32.01	18944.42	18076.33
3713.61	5.13	4166.22	6.21	32.03	18799.45	17949.16
3714.46	5.13	4205.18	6.24	32.05	18658.66	17824.60
3723.42	5.14	4220.26	6.26	32.06	18523.93	17701.70
3729.11	5.14	4258.46	6.29	32.08	18394.89	17580.25
3735.29	5.14	4261.41	6.29	32.10	18271.42	17461.69
3755.83	5.16	4261.85	6.29	32.11	18154.91	17347.75
3755.88	5.16	4273.23	6.30	32.13	18046.63	17238.04
3792.77	5.19	4278.85	6.31	32.15	17944.74	17129.51
3795.45	5.19	4290.57	6.32	32.16	17843.90	17018.38
3796.78	5.19	4302.46	6.33	32.18	17738.94	16902.66
3841.34	5.23	4304.00	6.33	32.20	17628.94	16782.86
3863.84	5.25	4309.38	6.33	32.21	17517.51	16661.10
3868.26	5.25	4325.54	6.35	32.23	17409.33	16539.71
3904.22	5.28	4336.36	6.36	32.25	17306.20	16420.21
3949.84	5.32	4339.80	6.36	32.26	17205.17	16302.79
3970.18	5.33	4341.48	6.36	32.28	17099.54	16186.30
3980.44	5.34	4355.58	6.37	32.30	16983.31	16069.14
4041.34	5.39	4375.23	6.39	32.31	16856.30	15950.65
4062.76	5.40	4378.79	6.39	32.33	16725.08	15832.31
4087.54	5.42	4380.50	6.39	32.35	16598.44	15717.54
4132.51	5.46	4386.14	6.40	32.37	16481.93	15609.69
4142.85	5.47	4390.93	6.40	32.38	16376.19	15509.33
4196.23	5.51	4397.76	6.41	32.40	16279.14	15413.32
4215.14	5.52	4400.24	6.41	32.42	16188.79	15317.14
4219.95	5.53	4400.64	6.41	32.43	16103.92	15218.47
4275.27	5.57	4405.40	6.41	32.45	16022.75	15117.72
4278.99	5.57	4406.88	6.41	32.47	15941.27	15015.73
4302.63	5.59	4409.09	6.42	32.48	15853.63	14912.06
4314.51	5.60	4414.05	6.42	32.50	15755.14	14806.43
4314.74	5.60	4416.96	6.42	32.52	15645.44	14701.45
4398.66	5.66	4417.94	6.42	32.53	15528.38	14603.01
4502.74	5.74	4420.83	6.43	32.55	15409.19	14516.40
4595.64	5.81	4422.94	6.43	32.57	15292.42	14441.49
4657.19	5.85	4424.40	6.43	32.58	15182.48	14372.55
4681.93	5.87	4425.81	6.43	32.60	15083.89	14302.96
4683.69	5.87	4426.75	6.43	32.62	14998.22	14229.12
4685.50	5.87	4429.82	6.43	32.63	14921.50	14149.96
4703.71	5.89	4430.55	6.43	32.65	14847.39	14064.46
4739.38	5.91	4435.16	6.44	32.67	14773.78	13971.74
4782.41	5.95	4444.24	6.45	32.68	14704.45	13873.03
4823.93	5.98	4449.30	6.45	32.70	14642.58	13772.54
4864.24	6.00	4456.01	6.46	32.72	14583.75	13676.35
4907.98	6.04	4458.42	6.46	32.74	14517.32	13590.04
4953.16	6.07	4462.83	6.46	32.75	14434.85	13515.34
4988.96	6.09	4464.81	6.46	32.77	14335.97	13447.28
4990.00	6.10	4468.78	6.47	32.79	14226.50	13376.02
4990.51	6.10	4474.57	6.47	32.80	14112.63	13293.38
4996.96	6.10	4477.02	6.47	32.82	13997.85	13198.51
4997.53	6.10	4483.49	6.48	32.84	13883.82	13097.01
5005.13	6.11	4489.71	6.48	32.85	13772.89	12995.24
5005.82	6.11	4520.69	6.51	32.87	13669.02	12896.74
5016.10	6.11	4526.23	6.51	32.89	13575.98	12803.02
5048.89	6.14	4533.47	6.52	32.90	13494.62	12715.50
5096.80	6.17	4557.22	6.54	32.92	13421.62	12635.20
5157.74	6.21	4560.52	6.54	32.94	13351.63	12561.48
5228.40	6.26	4585.51	6.56	32.95	13281.17	12492.41
5305.92	6.32	4586.89	6.56	32.97	13209.81	12426.44

5386.82	6.37	4592.88	6.57	32.99	13137.57	12362.56
5464.42	6.43	4599.13	6.57	33.00	13062.40	12299.34
5529.39	6.47	4602.00	6.58	33.02	12981.09	12234.65
5546.64	6.48	4602.97	6.58	33.04	12891.66	12165.94
5549.92	6.49	4603.03	6.58	33.06	12794.30	12090.85
5561.40	6.49	4612.70	6.58	33.07	12690.98	12008.65
5566.09	6.50	4614.06	6.59	33.09	12584.90	11922.18
5572.66	6.50	4634.91	6.60	33.11	12480.33	11837.50
5583.95	6.51	4640.62	6.61	33.12	12382.64	11760.55
5589.74	6.51	4643.12	6.61	33.14	12297.02	11693.26
5591.75	6.52	4663.72	6.63	33.16	12225.46	11632.31
5628.13	6.54	4668.79	6.63	33.17	12164.72	11571.62
5657.86	6.56	4671.80	6.63	33.19	12107.68	11506.55
5670.11	6.57	4676.81	6.64	33.21	12047.75	11435.93
5672.42	6.57	4709.71	6.66	33.22	11982.29	11360.75
5673.15	6.57	4752.22	6.70	33.24	11912.65	11281.95
5674.63	6.57	4792.85	6.73	33.26	11841.78	11199.96
5692.17	6.58	4830.21	6.76	33.27	11771.69	11115.36
5720.47	6.60	4863.01	6.79	33.29	11702.03	11029.38
5752.55	6.62	4889.46	6.81	33.31	11630.73	10944.10
5781.44	6.64	4909.86	6.82	33.32	11555.85	10862.40
5804.38	6.66	4929.01	6.84	33.34	11476.86	10786.93
5824.15	6.67	4954.59	6.86	33.36	11394.28	10718.42
5846.40	6.69	4992.41	6.89	33.38	11308.92	10655.42
5874.92	6.71	5043.04	6.93	33.39	11221.44	10595.91
5909.03	6.73	5102.89	6.98	33.41	11132.23	10538.74
5945.40	6.75	5167.28	7.03	33.43	11041.88	10483.20
5981.45	6.78	5232.25	7.08	33.44	10951.64	10427.79
6016.25	6.80	5295.63	7.13	33.46	10863.21	10370.04
6048.74	6.82	5358.13	7.17	33.48	10777.97	10308.03
6077.62	6.84	5422.30	7.22	33.49	10696.42	10242.18
6103.49	6.86	5488.88	7.27	33.51	10618.66	10174.93
6129.84	6.88	5554.75	7.32			
6161.01	6.90	5614.78	7.37			
6199.70	6.92	5665.47	7.41			
6246.06	6.95	5707.46	7.44			
6298.43	6.99	5745.93	7.47			
6354.33	7.02	5787.64	7.50			
6411.14	7.06	5836.09	7.53			
6466.93	7.09	5889.03	7.57			
6521.03	7.13	5940.68	7.61			
6573.48	7.16	5986.46	7.65			
6623.70	7.19	6026.24	7.67			
6669.07	7.22	6063.31	7.70			
6705.60	7.25	6100.58	7.73			
6731.38	7.26	6138.03	7.76			
6749.80	7.27	6173.61	7.78			
6768.36	7.29	6206.18	7.81			
6794.29	7.30	6237.77	7.83			
6831.47	7.33	6272.88	7.85			
6880.45	7.36	6314.55	7.88			
6939.43	7.39	6360.50	7.92			
7005.49	7.43	6403.58	7.95			
7075.93	7.48	6436.59	7.97			
7149.53	7.52	6457.23	7.98			
7226.62	7.57	6469.59	7.99			
7307.23	7.62	6481.17	8.00			
7388.68	7.67	6497.61	8.01			
7465.68	7.72	6519.85	8.03			
7533.89	7.76	6546.74	8.05			
7592.62	7.79	6579.95	8.07			
7643.32	7.82	6624.29	8.10			
7686.39	7.85	6682.18	8.14			
7721.25	7.87	6748.66	8.19			
7749.32	7.89	6812.75	8.23			
7775.75	7.90	6863.88	8.27			
7808.00	7.92	6897.93	8.29			
7852.27	7.95	6918.49	8.31			
7911.13	7.98	6933.28	8.32			
7982.98	8.02	6949.26	8.33			

8063.22	8.07	6970.78	8.34
8146.28	8.12	7000.96	8.36
8228.16	8.17	7042.44	8.39
8307.73	8.21	7096.30	8.43
8386.08	8.26	7160.92	8.47
8464.62	8.30	7231.92	8.52
8543.87	8.35	7302.79	8.57
8622.80	8.40	7366.39	8.61
8698.50	8.44	7417.48	8.65
8767.25	8.48	7454.68	8.67
8827.51	8.51	7480.60	8.69
8882.08	8.54	7500.31	8.70
8936.02	8.57	7519.22	8.71
8992.68	8.60	7541.29	8.73
9052.05	8.64	7569.21	8.75
9112.16	8.67	7604.86	8.77
9170.84	8.70	7648.73	8.80
9226.16	8.73	7699.06	8.83
9276.94	8.76	7752.82	8.87
9323.99	8.79	7807.76	8.90
9370.53	8.81	7863.80	8.94
9420.18	8.84	7922.33	8.98
9474.09	8.87	7984.53	9.02
9530.90	8.90	8049.79	9.06
9589.72	8.93	8115.24	9.10
9652.70	8.97	8177.05	9.14
9723.63	9.01	8232.58	9.18
9803.86	9.05	8281.94	9.21
9889.90	9.10	8327.84	9.24
9974.71	9.14	8374.17	9.27
10050.74	9.18	8424.46	9.30
10111.65	9.22	8480.37	9.34
10153.31	9.24	8540.99	9.37
10176.11	9.25	8603.89	9.41
10186.93	9.26	8666.58	9.45
10197.28	9.26	8727.14	9.49
10217.67	9.27	8783.67	9.52
10253.04	9.29	8834.06	9.56
10302.44	9.32	8877.05	9.58
10361.63	9.35	8913.81	9.61
10426.26	9.38	8948.38	9.63
10493.92	9.42	8986.26	9.65
10564.33	9.45	9032.29	9.68
10638.09	9.49	9089.28	9.71
10715.54	9.53	9157.54	9.76
10796.64	9.58	9234.96	9.80
10881.22	9.62	9317.18	9.85
10968.63	9.66	9398.30	9.90
11057.50	9.71	9473.03	9.95
11146.27	9.76	9539.71	9.99
11233.86	9.80	9601.22	10.02
11319.72	9.84	9662.49	10.06
11403.46	9.89	9726.82	10.10
11484.42	9.93	9794.43	10.14
11561.86	9.97	9863.40	10.18
11635.36	10.00	9931.42	10.22
11705.47	10.04	9997.37	10.26
11774.07	10.07	10061.87	10.30
11843.10	10.11	10126.46	10.33
11912.87	10.14	10192.06	10.37
11981.44	10.18	10257.94	10.41
12045.94	10.21	10321.91	10.45
12105.10	10.24	10382.08	10.48
12161.38	10.27	10438.48	10.52
12220.97	10.30	10493.06	10.55
12290.62	10.33	10548.01	10.58
12373.67	10.37	10604.64	10.61
12468.59	10.42	10663.69	10.65
12570.72	10.47	10726.36	10.68
12674.96	10.52	10794.51	10.72

12777.10	10.57	10869.35	10.76
12873.95	10.61	10950.04	10.81
12963.45	10.66	11034.04	10.86
13045.10	10.70	11118.64	10.90
13120.42	10.73	11201.87	10.95
13192.21	10.77	11282.57	11.00
13262.69	10.80	11360.16	11.04
13332.29	10.83	11434.20	11.08
13401.33	10.87	11503.84	11.12
13472.34	10.90	11568.12	11.15
13549.89	10.94	11628.11	11.19
13637.75	10.98	11688.10	11.22
13736.38	11.03	11753.81	11.26
13843.12	11.08	11828.61	11.30
13954.25	11.13	11911.09	11.34
14066.97	11.18	11996.00	11.39
14179.45	11.23	12077.55	11.43
14289.05	11.28	12152.63	11.47
14390.94	11.33	12221.41	11.51
14479.43	11.37	12285.88	11.55
14552.21	11.40	12348.43	11.58
14613.74	11.43	12411.18	11.61
14673.16	11.46	12475.64	11.65
14737.65	11.49	12542.85	11.68
14807.89	11.52	12614.18	11.72
14880.60	11.55	12691.36	11.76
14954.69	11.59	12775.36	11.81
15033.96	11.62	12865.68	11.85
15123.50	11.66	12961.07	11.90
15224.95	11.71	13060.14	11.96
15335.73	11.76	13160.17	12.01
15451.56	11.81	13256.08	12.06
15568.18	11.86	13342.26	12.10
15681.05	11.91	13417.07	12.14
15785.60	11.96	13485.44	12.18
15879.38	12.00	13556.07	12.22
15963.96	12.04	13635.76	12.26
16044.10	12.07	13725.82	12.30
16124.93	12.11	13822.67	12.35
16209.76	12.15	13920.75	12.40
16300.17	12.19	14015.14	12.45
16397.47	12.23	14103.16	12.50
16503.59	12.28	14184.57	12.54
16620.02	12.33	14260.27	12.58
16745.42	12.38	14331.24	12.61
16874.03	12.44	14399.50	12.65
16997.74	12.49	14469.62	12.68
17111.02	12.54	14547.59	12.72
17214.59	12.58	14636.94	12.76
17314.23	12.62	14736.01	12.81
17416.09	12.67	14839.58	12.87
17522.76	12.71	14943.00	12.92
17632.42	12.76	15044.59	12.97
17740.64	12.81	15144.68	13.02
17843.98	12.85	15243.35	13.07
17943.26	12.89	15339.91	13.11
18043.57	12.93	15434.56	13.16
18149.99	12.98	15529.99	13.21
18264.33	13.03	15630.23	13.25
18385.47	13.08	15737.63	13.31
18512.09	13.13	15851.20	13.36
18644.22	13.18	15967.74	13.42
18782.19	13.24	16084.23	13.47
18924.42	13.30	16199.50	13.53
19066.88	13.36	16314.28	13.58
19205.54	13.41	16430.07	13.64
19339.03	13.47	16547.85	13.69
19468.85	13.52	16667.39	13.75
19597.55	13.57	16787.20	13.81
19727.37	13.63	16905.06	13.86

19859.87	13.68	17018.98	13.92
19995.44	13.73	17128.39	13.97
20133.26	13.79	17235.27	14.02
20272.33	13.85	17343.26	14.07
20412.07	13.90	17455.27	14.12
20551.74	13.96	17571.74	14.17
20690.05	14.01	17691.11	14.23
20826.43	14.07	17811.99	14.29
20962.46	14.12	17934.46	14.34
21101.49	14.17	18059.36	14.40
21246.69	14.23	18186.62	14.46
21399.17	14.29	18314.48	14.51
21557.83	14.35	18440.78	14.57
21720.46	14.42	18565.16	14.63
21885.06	14.48	18689.79	14.68
22050.49	14.54	18817.34	14.74
22216.22	14.61	18948.61	14.80
22381.59	14.67	19082.75	14.86
22545.74	14.73	19219.21	14.92
22708.34	14.80	19359.02	14.98
22869.91	14.86	19503.65	15.05
23030.74	14.92	19653.16	15.11
23189.92	14.98	19805.55	15.18
23346.23	15.04	19958.36	15.25
23500.16	15.10	20110.48	15.31
23654.65	15.15	20262.26	15.38
23813.22	15.21	20413.96	15.45
23977.09	15.28	20564.46	15.51
24143.82	15.34	20712.03	15.58
24308.68	15.40	20856.72	15.64
24467.80	15.46	21001.40	15.70
24620.65	15.51	21149.67	15.76
24770.18	15.57	21302.72	15.83
24920.91	15.62	21458.62	15.89
25076.74	15.68	21614.27	15.96
25239.78	15.74	21767.86	16.03
25410.07	15.80	21919.72	16.09
25586.03	15.87	22071.72	16.15
25766.07	15.93	22226.32	16.22
25950.10	16.00	22385.67	16.28
26139.39	16.07	22550.58	16.35
26334.75	16.14	22719.75	16.42
26535.37	16.21	22890.04	16.49
26739.09	16.28	23058.19	16.56
26943.08	16.35	23222.74	16.63
27144.44	16.43	23384.66	16.70
27342.03	16.50	23546.72	16.76
27538.89	16.57	23712.18	16.83
27742.20	16.64	23883.00	16.90
27958.57	16.71	24058.71	16.97
28187.64	16.79	24237.02	17.04
28420.33	16.87	24415.89	17.12
28646.03	16.95	24595.20	17.19
28860.48	17.03	24777.26	17.26
29067.78	17.10	24965.83	17.34
29275.24	17.17	25164.01	17.41
29487.43	17.24	25372.14	17.50
29705.00	17.32	25587.40	17.58
29927.18	17.39	25805.27	17.67
30153.71	17.47	26021.79	17.75
30383.77	17.55	26235.10	17.84
30612.62	17.62	26445.35	17.92
30829.49	17.70	26653.15	18.00
31022.42	17.76	26858.16	18.08
31189.02	17.82	27059.75	18.16
31342.72	17.87	27258.36	18.23
31505.96	17.92	27455.43	18.31
31695.69	17.99	27652.43	18.38
31914.47	18.06	27850.81	18.46
32153.34	18.14	28052.42	18.53

32400.86	18.22	28258.10	18.61
32649.90	18.30	28466.35	18.69
32898.79	18.38	28674.25	18.77
33148.38	18.46	28880.47	18.85
33398.71	18.55	29087.35	18.92
33647.98	18.63	29299.84	19.00
33894.36	18.71	29521.80	19.08
34138.63	18.78	29753.39	19.17
34384.84	18.86	29992.01	19.26
34638.39	18.95	30235.05	19.35
34902.95	19.03	30480.64	19.44
35178.05	19.12	30725.82	19.53
35458.56	19.21	30965.58	19.61
35735.82	19.29	31195.67	19.70
		31416.60	19.78
		31633.94	19.86
		31854.08	19.93
		32080.17	20.02