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Zwitterionic Polymerization of Glycidyl Monomers to Cyclic Polyethers with $B(C_6F_5)_3$

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Experimental section

Synthesis of cyclic poly(glycidyl phenyl ether)

Reagents were manipulated and transferred either by distillation or under Argon in a vacuum line. Glycidyl phenyl ether (GPE), dichloromethane and deuterated chloroform (Aldrich) were dried over CaH_2, degassed and distilled in the vacuum line. $B(C_6F_5)_3$ (Aldrich) was sublimed in vacuo at 50ºC and transferred to the reaction flask in the glove box. All polymerization reactions were performed under Argon at room temperature. Bulk polymerization with a monomer/catalyst ratio of 943/1 was carried out by mixing 2 mg (3.9 µmol) of $B(C_6F_5)_3$ and 0.5 mL (3.68 mmol) of GPE. Special care must be taken because this reaction can be violent and very exothermic if high amounts of catalyst are used in bulk conditions (i.e. monomer/catalyst ratio of 94/1). In solution polymerization, similar amounts of borane were first dissolved in 1 mL of dry solvent, followed by the addition of GPE. Other reagent concentrations were investigated as specified in Table 1. To end, 0.1 mL of dry methanol or acetonitrile was added to the reaction. The mixture was precipitated in methanol. In the case of bulk polymerization, the viscous reaction mixture was first dissolved in CH_2Cl_2 before precipitation. Polymers were dried in a vacuum oven at 40 ºC until they reached a constant weight.

Synthesis of cyclic poly(glycidol) and cyclic poly(glycidyl octafluoropentyl ether)

Polymerization reactions were done in 20 mL glass bottles at room temperature in argon atmosphere for 3h. All chemicals were used as received. First, 2 mg of $B(C_6F5)_3$ was dissolved in 1 mL of dichloromethane. Then, 0.5 mL of glycidol or glycidyl octafluoropentyl ether was added to the solution under stirring. Purification of poly(glycidol) was done by precipitation in THF and that of poly(glycidyl octafluoropentyl ether) [poly(GOFPE)] was done by precipitation in hexane. The products were dried at 40 ºC in a vacuum oven.

Synthesis of linear poly(GPE)

Linear poly(PGE) was synthesized by using the method of Endo et al.[1] All reagents were manipulated and transferred either by distillation or under inert gas in a vacuum line. Tetrabutylammonium fluoride (1M) in THF solution (0.7 mL) was added to a schlenk under Argon. THF was evaporated under vacuum, and GPE (2 mL) was added. The polymerization was conducted at 60 °C for 6 h under argon. The reaction was terminated by the addition of methanol. The resulting polymer was precipitated twice from THF to methanol. Poly(GPE) with Mn = 3.4 kg/mol and PDI = 1.1 was obtained. To prepare a linear poly(GPE) of higher molecular weight, a similar protocol was used but after 6h of reaction, 2 mL more of GPE was added. The reaction was left for 6h more. As a result, linear poly(GPE) with Mn = 4.3 kg/mol and PDI = 1.1 was obtained. These samples were used in DSC experiments.

Size exclusion chromatography

The molecular weight and molecular weight distribution were determined by size exclusion chromatography (SEC) on an Agilent G-1310A HPLC pump equipped with PLgel 5 µm Guard and PLgel 5 µm Mixed-C columns at a flow rate of 1 mL/min THF. A calibration curve based on linear PS standards was used in conjunction with a differential refractive index (RI) detector (Optilab rEX Wyatt refractometer).

MALDI-TOF mass spectrometry

MALDI-TOF MS measurements were performed on a Bruker Autoflex Speed system (Bruker, Germany) equipped with a 355 nm NdYAG laser. Spectra were acquired in the positive reflectron mode. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malonitrile (DCTB, Fluka) was used as a matrix. Sodium iodide (Aldrich) was added as the cationic ionization agent (~10 mg/ml dissolved in THF). In case of using a different cationic ionization agent and detection mode, it is specified in the text. The matrix was also dissolved in THF at a concentration of 20 mg/ml. Poly(GPE) and poly(GOFPE) were dissolved in THF and poly(glycidol) was dissolved in methanol at a concentration of ~10 mg/ml. In a typical MALDI experiment, the matrix, salt and polymer solutions were premixed at a 20:1:3 ratio. Approximately 0.5 µL of the obtained mixture were hand spotted on the ground steel target plate. For each spectrum 1000 laser shots were accumulated. Polytools software (Bruker) was used to identify the molar masses and end-group structures of the polymer chains.

Nuclear magnetic resonance

Polymerization reactions were monitored by ^{1}H NMR on a Bruker Avance spectrometer at 400 MHz. Appropriate amounts of GPE, $CDCl_3$ and finally $B(C_6F_5)_3$ were transferred into an NMR tube, which was immediately introduced into the NMR probe at 25 ºC. The monomer conversion was calculated from the integrals of epoxide and the aromatic signals of GPE.

Differential Scanning Calorimetry

DSC measurements were carried out on ~10 mg specimens using a Q2000 TA Instruments in standard mode. Measurements were performed by placing the samples in sealed aluminum pans, equilibrating the temperature at 100 ºC, cooling to -100 ºC at 10 ºC/min and heating back to 100 ºC at 10ºC/min. This procedure was repeated once again at the same cooling and heating rates. A helium flow rate of 25 mL/min was used throughout.

Computational Details

Computations were performed using the Gaussian 09[2] software package in a Linux multiprocessor environment. For the initial model studies, all structures were optimized using the functional B3LYP[3-5] and the 6-31G* basis sets. Single-points calculation and vibration analysis were performed using the M06[6] DFT functional, as described by Zhao and Truhlar, and with the triple-zeta, diffuse, polarized 6-311G+(d,p) basis set with the self-consistent reaction field (SCRF). The CPCM solvent model ($CHCl_3$)[7] was used. All calculations were performed with the overall molecular charges being zero (Charge = 0) and singlet ground state multiplicities (Multiplicity = 1). Electronic energies (not ZPE corrected), enthalpies (298.15K) and free energies (298.15K) were obtained from the frequency files under default parameters. All numbers in plots were referenced with respect to the origin point in their respective domain (i.e. energy, enthalpy or free energy) and plotted in kcal/mol (1 hartree =627.51 kcal/mol).

Results

Characterization by ^{1}H NMR

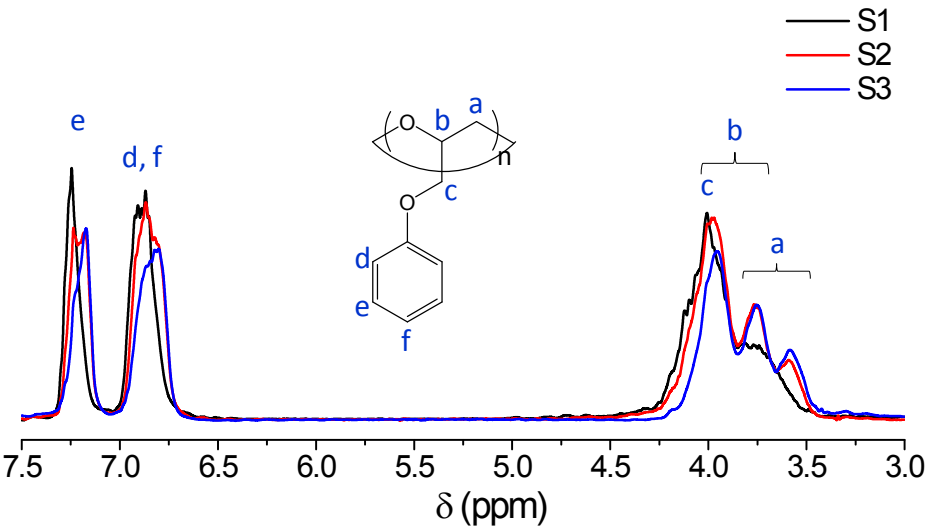


Figure S1. ^{1}H NMR spectra of poly(GPE) reported in Table 1. Solvent: $CDCl_3$. Spectra are referenced to TMS.

Kinetic experiments by ^{1}H NMR

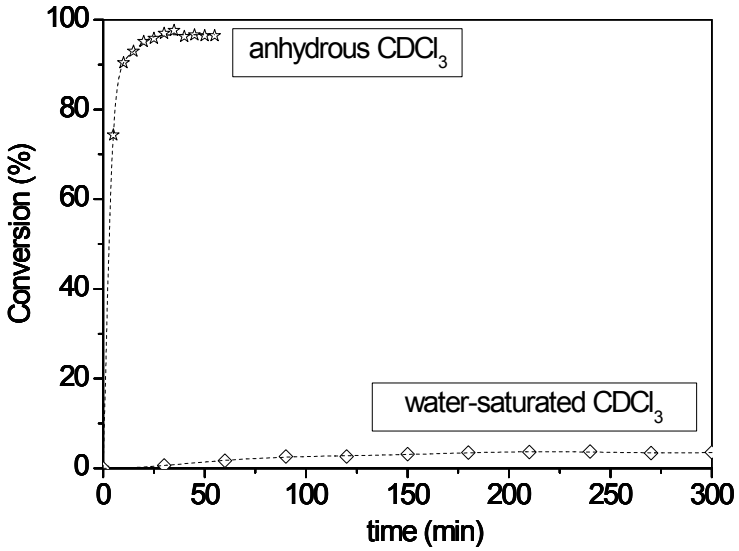


Figure S2. Time evolution of GPE conversion during ZROP catalyzed by $B(C_6F_5)_3$ in dry and water-saturated $CDCl_3$ as determined by ^{1}H NMR measurements. In all cases [GPE]=2.5 mol/L and $[B(C_6F_5)_3]$=0.026 mol/L.

Synthesis of poly(GPE) in different solvents

Table 1. ZROP of GPE at 25ºC in dry solvents after 4h of reaction time. In all cases [GPE]=2.5 mol/L and $[B(C_6F_5)_3]$=0.0026 mol/L. The yields were calculated gravimetrically from polymers precipitated in methanol.

	ε	Mp[a] (g/mol)	PDI	Yield (wt%)
CH_2Cl_2	8.93	3100	1.9	70
THF[b]	7.52	67500	1.7	33
$CHCl_3$	4.81	1900	1.4	67
toluene	2.38	2100	1.7	77
benzene	2.28	2300	1.3	8
CCl_4	2.24	2100	1.5	26
1,4-dioxane[b]	2.21	2600	1.3	5

[a]HMW peak, [b]GPE copolymerizes with THF and 1,4-dioxane.

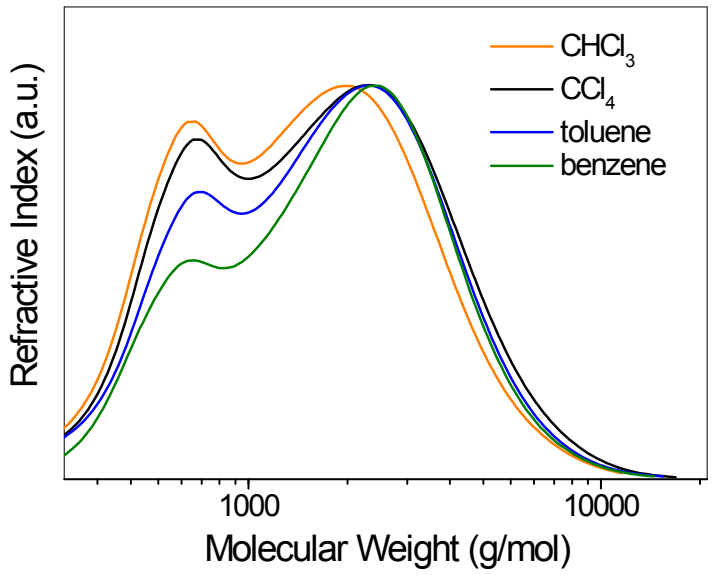


Figure S3. SEC traces of poly(GPE) obtained in different solvents.

MALDI-TOF mass spectrometry

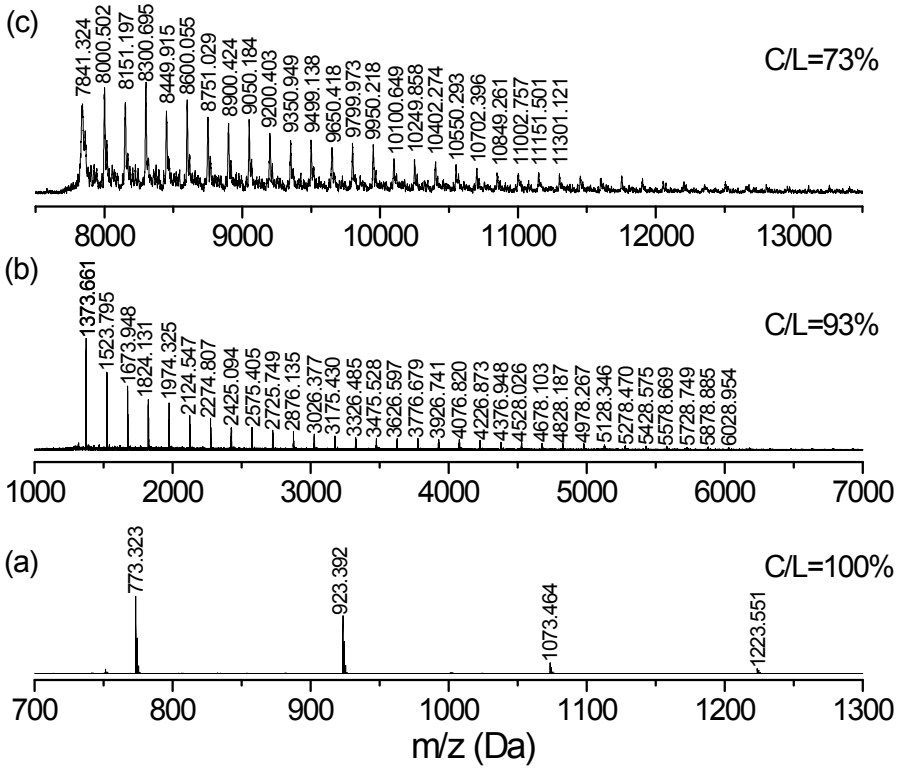


Figure S4. MALDI-TOF spectra of sample B in the low (a), medium (b) and high (c) molecular weight ranges. To acquire spectra (b) and (c), the ions below 1300 Da and 8000 Da were deflected. Spectra (a) and (b) were obtained by using NaI as the cationic ionization agent and detection in positive reflectron mode, as detailed in the experimental section. Instead, spectrum (c) was obtained by

using potassium trifluoroacetate (KTFA) as the cationic ionization agent and detection in positive linear mode. The percentage ratio of cycles to linear chains (C/L) was calculated in each range of molecular weights.

DFT calculations

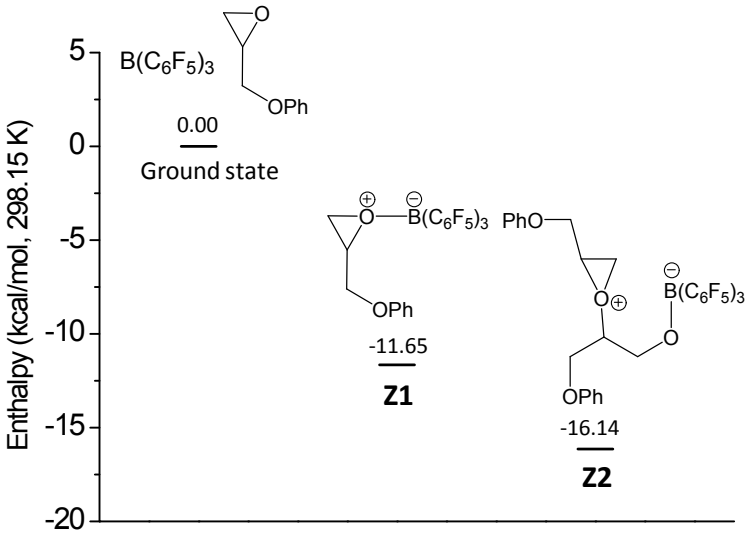
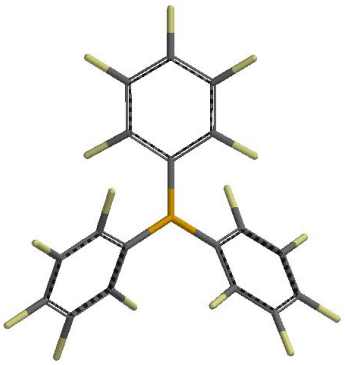


Figure S5. Enthalpy from DFT calculations for the zwitterionic intermediates Z1 and Z2 respect to free borane and GPE.

$(C_6F_5)_3$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	0.000000	-0.010818
2	6	0	0.377205	1.302548	-0.787395

3	6	0	1.060120	3.651008	-2.174698
4	6	0	1.116953	1.273291	-1.968386
5	6	0	0.000000	2.565026	-0.332229
6	6	0	0.317067	3.728404	-1.007556
7	6	0	1.469201	2.418323	-2.657726
8	6	0	0.000000	0.000000	1.552151
9	6	0	0.000000	0.000000	4.362211
10	6	0	0.980426	0.660052	2.288120
11	6	0	-0.980426	-0.660052	2.288120
12	6	0	-1.002555	-0.660588	3.670026
13	6	0	1.002555	0.660588	3.670026
14	6	0	-0.377205	-1.302548	-0.787395
15	6	0	-1.060120	-3.651008	-2.174698
16	6	0	-1.116953	-1.273291	-1.968386
17	6	0	0.000000	-2.565026	-0.332229
18	6	0	-0.317067	-3.728404	-1.007556
19	6	0	-1.469201	-2.418323	-2.657726
20	9	0	-0.073471	4.906160	-0.555175
21	9	0	-0.714015	2.689336	0.780951
22	9	0	1.380166	4.749224	-2.824326
23	9	0	2.186402	2.354411	-3.764924
24	9	0	1.541893	0.117392	-2.465003
25	9	0	-1.541893	-0.117392	-2.465003
26	9	0	0.714015	-2.689336	0.780951
27	9	0	0.073471	-4.906160	-0.555175
28	9	0	-2.186402	-2.354411	-3.764924
29	9	0	-1.380166	-4.749224	-2.824326
30	9	0	-1.960255	-1.282050	4.334157
31	9	0	0.000000	0.000000	5.678306
32	9	0	1.962635	1.303338	1.666613
33	9	0	1.960255	1.282050	4.334157
34	9	0	-1.962635	-1.303338	1.666613

Rotational constants (GHZ): 0.1193512 0.1187735 0.0687834
Standard basis: 6-311G(d,p) (5D, 7F)

SCF Done: E(RM06) = -2207.87872705 A.U. after 1 cycles
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NROrb= 612 NOA= 124 NOB= 124 NVA= 488 NVB= 488

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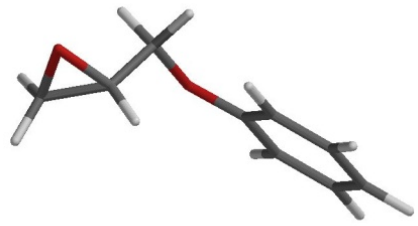
Sum of electronic and thermal Energies= -2207.693934
Sum of electronic and thermal Enthalpies= -2207.692989
Sum of electronic and thermal Free Energies= -2207.781179

Glycidyl phenyl ether (GPE)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	-3.321840	-0.316572	0.898640
4	1	0	-3.600920	-1.310452	0.548090
5	1	0	-3.560080	-0.099752	1.938380
6	6	0	-1.506740	-0.276171	-0.904150
7	1	0	-1.206720	0.469089	-1.654000
8	1	0	-2.201230	-0.969041	-1.389350
9	8	0	-0.401450	-1.048411	-0.487220
10	6	0	0.782410	-0.432551	-0.233390
11	6	0	3.308500	0.614320	0.318570
12	6	0	1.833160	-1.278210	0.119990
13	6	0	0.999380	0.939910	-0.308890
14	6	0	2.263440	1.450190	-0.033350
15	6	0	3.082440	-0.756220	0.394020
16	1	0	1.635940	-2.344260	0.168810
17	1	0	0.200249	1.621489	-0.577920
18	1	0	2.421769	2.522740	-0.094810
19	1	0	3.891490	-1.426820	0.667510
20	1	0	4.290220	1.022620	0.533920
21	8	0	-3.548250	0.738748	-0.013030

Rotational constants (GHZ): 3.1454859 0.5578072 0.5119018
Standard basis: 6-311G(d,p) (5D, 7F)

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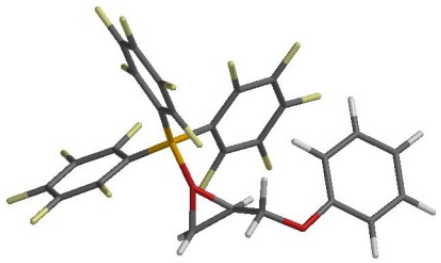
Sum of electronic and thermal Free Energies= -499.017407

Zwitterion Z1



Standard orientation:

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4	6	0	-2.071923	1.633486	-1.186244
5	6	0	-0.957671	2.575587	0.646727
6	6	0	-1.505172	3.816327	0.356058
7	6	0	-2.637625	2.851845	-1.512422
8	6	0	0.556801	-0.513848	-0.794758
9	6	0	2.846057	-1.337598	-2.247491
10	6	0	1.236862	0.339256	-1.657818
11	6	0	1.089020	-1.797775	-0.707525
12	6	0	2.202172	-2.227278	-1.403394
13	6	0	2.353858	-0.055125	-2.381345
14	6	0	-1.928943	-1.083697	0.297956
15	6	0	-4.241023	-2.679834	0.597201
16	6	0	-2.828004	-0.909343	1.343622
17	6	0	-2.259422	-2.084560	-0.607321
18	6	0	-3.387166	-2.878250	-0.473148
19	6	0	-3.961327	-1.684674	1.516959
20	9	0	2.990588	0.809424	-3.158338
21	9	0	0.875894	1.609940	-1.814806
22	9	0	3.937050	-1.699911	-2.890996
23	9	0	2.670217	-3.454164	-1.254635
24	9	0	0.541279	-2.685821	0.133917
25	9	0	-2.331558	0.606457	-2.000341
26	9	0	-3.431435	2.976235	-2.563211

27	9	0	-2.880964	5.131298	-1.013538
28	9	0	-1.215759	4.871016	1.102938
29	9	0	-0.117839	2.547489	1.688987
30	9	0	-1.505814	-2.312368	-1.679015
31	9	0	-3.658381	-3.821149	-1.360062
32	9	0	-5.316163	-3.432191	0.738352
33	9	0	-4.772935	-1.483720	2.543196
34	9	0	-2.612719	0.045806	2.256071
35	6	0	0.116062	-1.027390	2.710356
36	1	0	-0.283370	-0.709078	3.669539
37	1	0	-0.144185	-2.025917	2.369608
38	6	0	1.303579	-0.383751	2.157612
39	6	0	2.073180	0.722985	2.829508
40	1	0	2.021374	1.631928	2.217960
41	1	0	1.644474	0.961702	3.806866
42	8	0	3.395402	0.310086	3.054542
43	6	0	4.264451	0.297463	1.998296
44	6	0	6.199985	0.173001	-0.000335
45	6	0	5.540613	-0.179383	2.288415
46	6	0	3.956096	0.714573	0.707765
47	6	0	4.932414	0.649033	-0.282913
48	6	0	6.498442	-0.238172	1.294837
49	1	0	5.750663	-0.495517	3.304977
50	1	0	2.975137	1.103127	0.450145
51	1	0	4.685738	0.976323	-1.289419
52	1	0	7.490011	-0.610604	1.532357
53	1	0	6.951969	0.121952	-0.780072
54	1	0	1.873753	-0.956439	1.428175
55	8	0	-0.009743	-0.006369	1.703847

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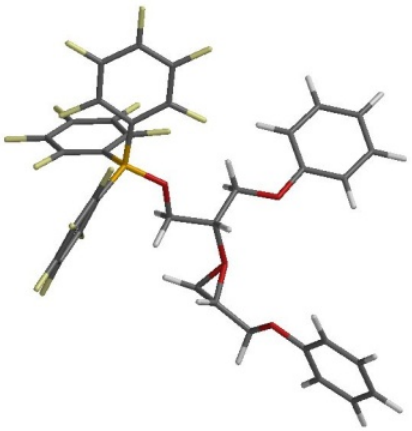

Standard orientation:

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5	6	0	3.457520	-0.299550	1.966190
6	6	0	4.059481	0.294300	3.074300
7	6	0	2.583181	2.159870	2.833890
8	6	0	1.869650	-1.999730	-0.294050
9	6	0	1.881300	-4.855200	-0.527880
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23	9	0	0.580681	1.842900	-2.025220
24	9	0	1.965411	3.198530	-3.809620
25	9	0	3.965960	-1.500990	1.619230
26	9	0	5.063830	-0.322900	3.720110
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28	9	0	2.142561	3.364710	3.238230

29	9	0	1.033711	2.234050	1.109820
30	9	0	1.352860	-2.354320	2.011990
31	9	0	1.393420	-5.005400	1.784550
32	9	0	1.888239	-6.191970	-0.638810
33	9	0	2.334390	-4.621080	-2.835200
34	9	0	2.285440	-1.977590	-2.651050
35	8	0	0.268460	-0.048450	-0.237580
36	6	0	-0.597920	-0.438959	0.769810
37	1	0	-0.733280	-1.533739	0.811180
38	1	0	-0.263140	-0.112170	1.767980
39	6	0	-1.891229	1.734421	0.495530
40	1	0	-1.650159	2.073111	1.511610
41	8	0	-3.148409	2.233591	0.069760
42	6	0	-3.302819	3.597391	0.004770
43	6	0	-3.826098	6.338951	-0.189230
44	6	0	-2.293939	4.518771	0.306190
45	6	0	-4.570719	4.042601	-0.392990
46	6	0	-4.825729	5.406841	-0.488800
47	6	0	-2.568449	5.886851	0.204920
48	1	0	-1.305529	4.193651	0.608580
49	1	0	-5.334339	3.306651	-0.623030
50	1	0	-5.810319	5.743821	-0.799640
51	1	0	-1.781848	6.598561	0.437550
52	1	0	-4.027548	7.402671	-0.265110
53	1	0	-1.078419	2.039261	-0.171850
54	6	0	-1.931429	0.228171	0.432270
55	1	0	-2.325760	-0.114669	-0.524910
56	6	0	-2.860060	-1.033579	2.628480
57	1	0	-3.415570	-0.609339	3.457460
58	6	0	-7.757720	-1.968018	0.591930
59	6	0	-8.281890	-1.945068	-2.156000
60	6	0	-9.068560	-2.091528	0.117840
61	6	0	-6.713410	-1.833518	-0.326390
62	6	0	-6.972720	-1.821018	-1.702130
63	6	0	-9.338380	-2.081118	-1.248660
64	1	0	-9.878840	-2.195588	0.833170
65	1	0	-6.141920	-1.713718	-2.391600
66	1	0	-10.358420	-2.177038	-1.606210
67	1	0	-8.477710	-1.934918	-3.223910
68	6	0	-3.562410	-1.605729	1.476500
69	8	0	-3.050460	-0.188019	1.404100
70	1	0	-1.834630	-1.323289	2.820560
71	8	0	-5.385520	-1.705829	0.023490
72	1	0	-7.575390	-1.978128	1.660090
73	6	0	-5.054400	-1.702939	1.396230
74	1	0	-5.521780	-0.867229	1.932590
75	1	0	-5.348620	-2.640369	1.892000
76	1	0	-3.000620	-2.265429	0.820690

Rotational constants (GHZ): 0.0507222 0.0314531 0.0266942
Standard basis: 6-311G(d,p) (5D, 7F)

SCF Done: E(RM06) = -3206.23732820 A.U. after 1 cycles
Convg = 0.3776D-08 -V/T = 2.0029
Range of M.O.s used for correlation: 1 1128
NBasis= 1128 NAE= 204 NBE= 204 NFC= 0 NFV= 0
NROrb= 1128 NOA= 204 NOB= 204 NVA= 924 NVB= 924

Sum of electronic and zero-point Energies= -3205.739426
Sum of electronic and thermal Energies= -3205.690887
Sum of electronic and thermal Enthalpies= -3205.689943

Glass transition

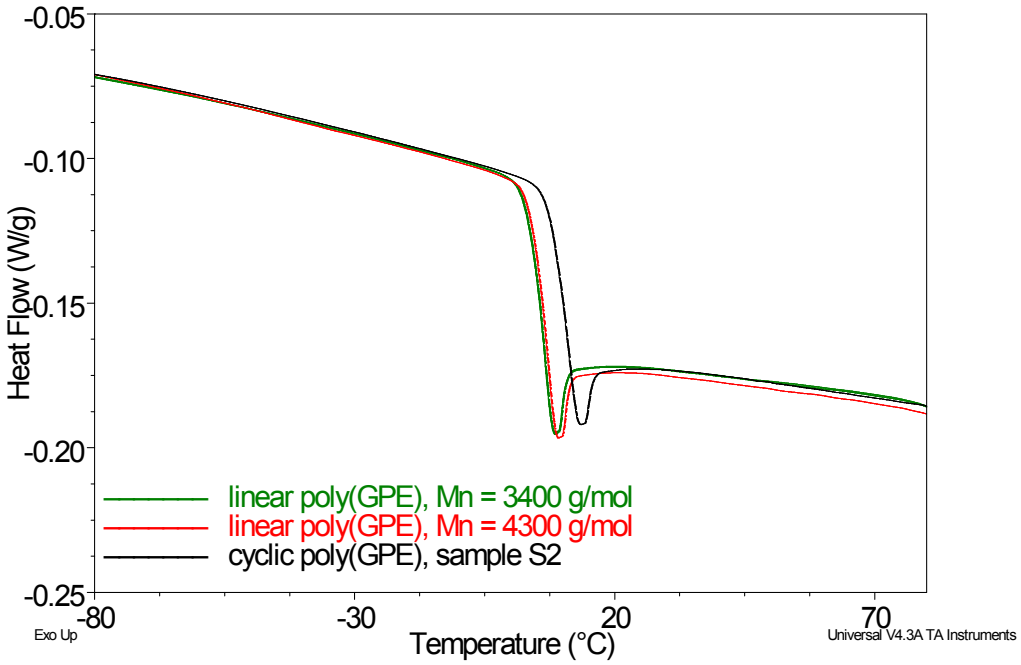

Figure S6. DSC profiles of cyclic and linear poly(GPE) specimens measured during heating at a rate of 10 ºC/min.

Polyglycidol and poly(glycidyl octafluoropentyl ether)

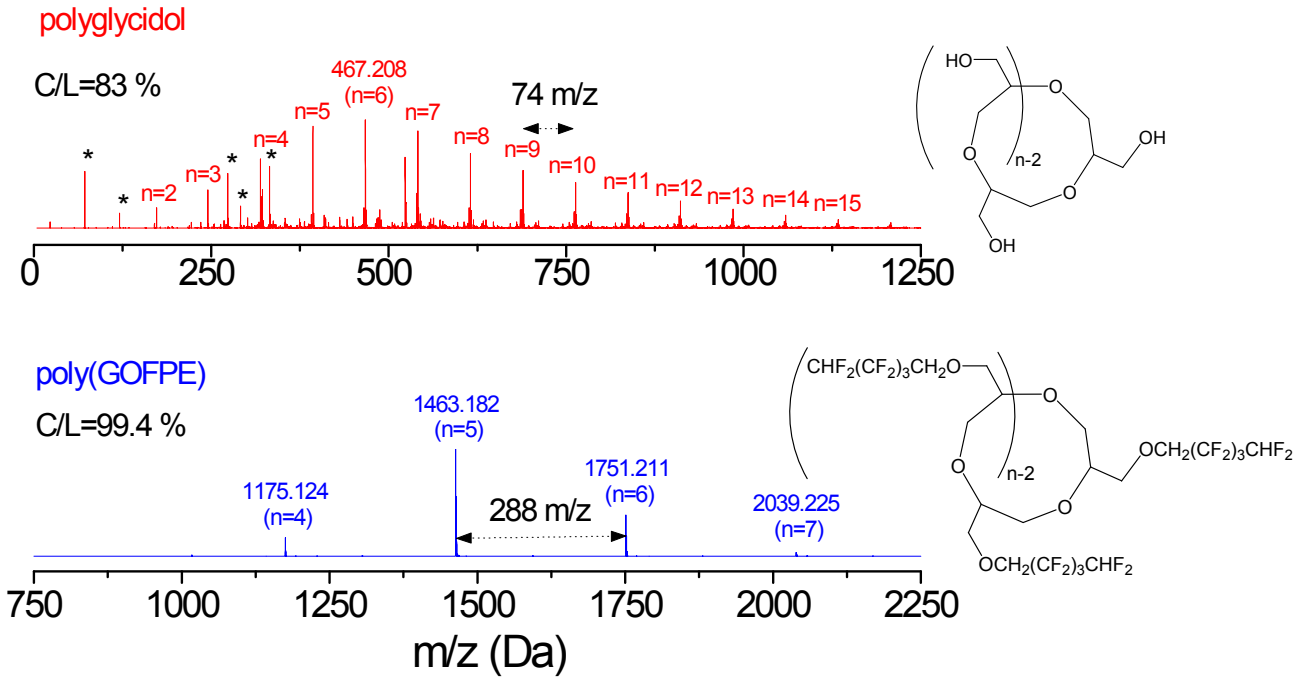

Figure S7. MALDI-TOF spectra of cyclic poly(glycidol) and cyclic poly(GOFPE). C/L values are included. *Signals coming from the matrix.

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