Electronic Supporting Information (ESI) for:

Separation, identification, and confirmation of cyclic and tadpole macromolecules via UPLC-MS/MS

Jason M. O'Neill,[a] Jialin Mao,[a] Farihah M. Haque,[b] Fabienne Barroso-Bujans,[c-e] Scott M. Grayson,[b] and Chrys Wesdemiotis*[a]

[a] Department of Chemistry, The University of Akron, Akron, OH 44325, USA. E-mail: wesdemiotis@uakron.edu

[b] Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

[c] Donostia International Physics Center (DIPC), Paseo Manuel Lardizábal 4, Donostia - San Sebastián 20018, Spain

[d] Materials Physics Center, CSIC-UPV/EHU, Paseo Manuel Lardizábal 5, Donostia - San Sebastián 20018, Spain

[e] IKERBASQUE - Basque Foundation for Science, María Díaz de Haro 3, E-48013 Bilbao, Spain

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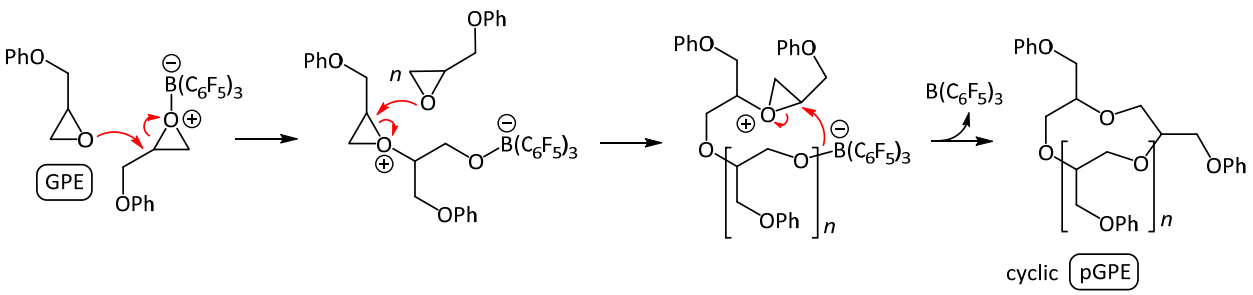
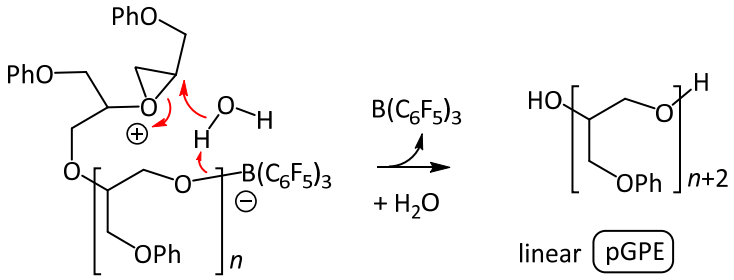
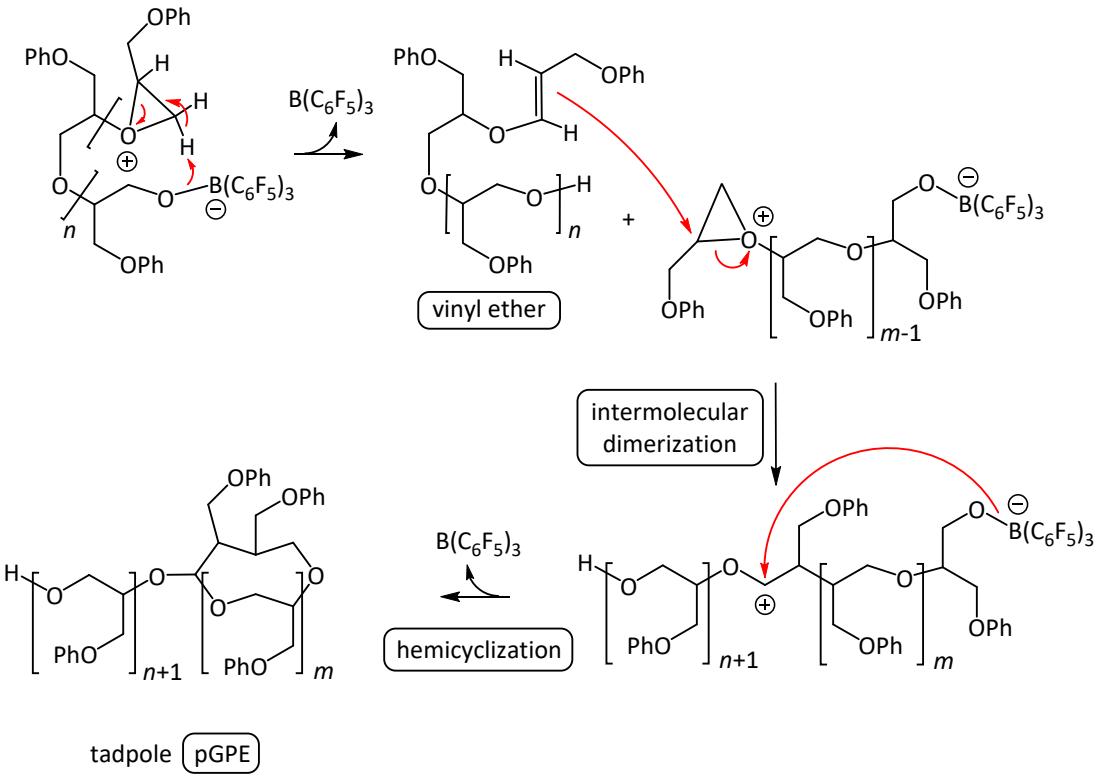
References



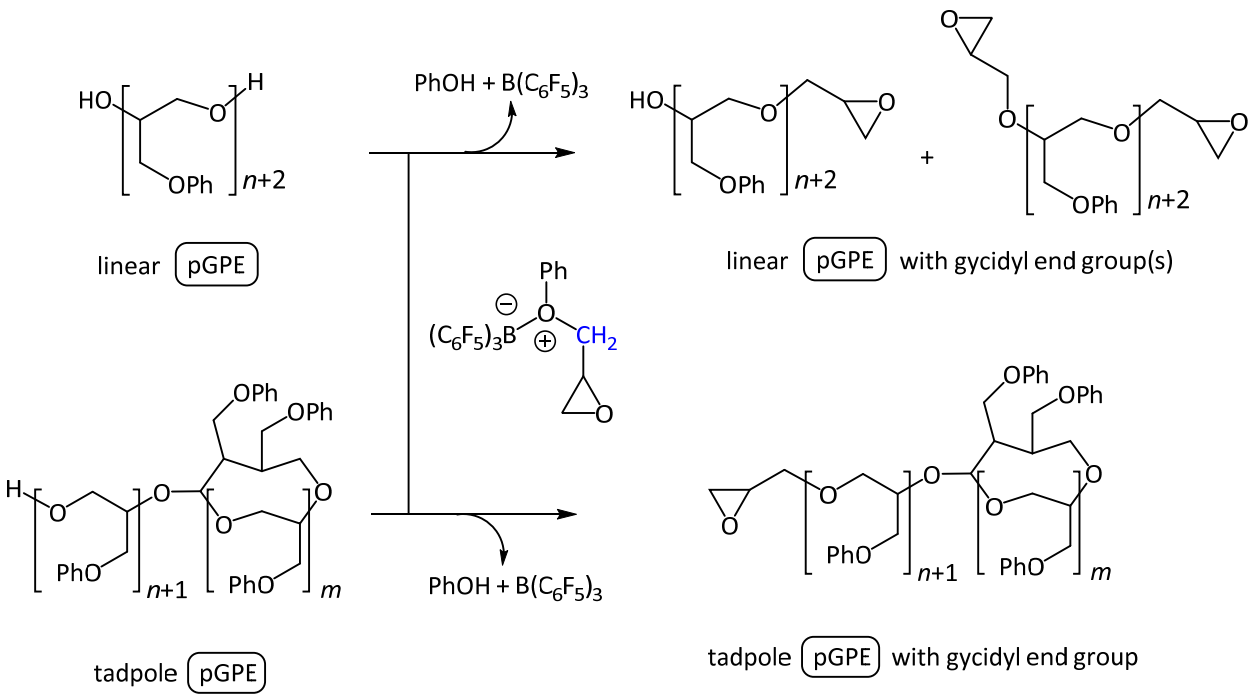
Scheme S1. Formation of cyclic poly(glycidyl phenyl ether), pGPE, by zwitterionic ring expansion polymerization (ZREP) of glycidyl phenyl ether (GPE).[1-3] Initiation proceeds by activation of the monomer via complexation with $B(C_6F_5)_3$ catalyst, which generates a zwitterionic complex that readily undergoes ring opening by nucleophilic insertion of an uncomplexed GPE monomer. This step transfers the cationic charge to the newly added monomer, maintaining a zwitterionic structure that facilitates the continuous insertion of monomers and formation of a polymer chain that is kept cyclized through electrostatic interactions between the positive and negative charges. Termination by a backbiting reaction (intramolecular nucleophilic ring opening) that expels the $B(C_6F_5)_3$ catalyst ultimately leads to a macrocyclic product. Alternative termination steps and other side reactions are possible, however, giving rise to byproducts with distinct architectures, cf. Schemes S2-S5.[2,3]



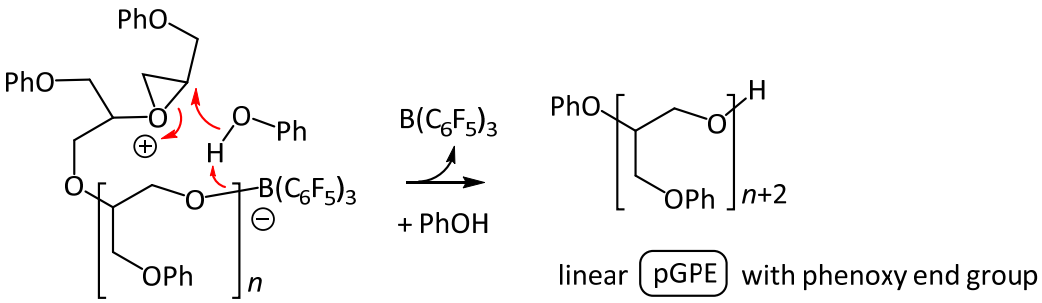
Scheme S2. Termination of the ZREP of GPE by the addition of water, which expels the catalyst and produces a linear polyether with HO- and -H end groups (18 Da).[2,3]



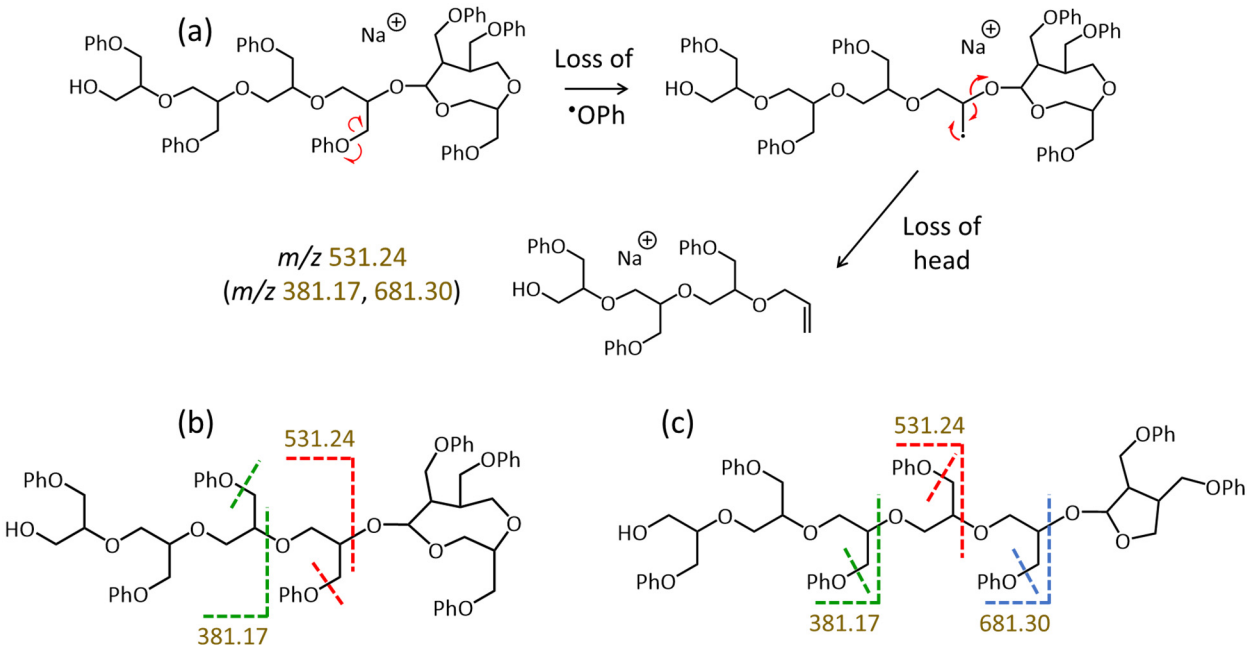
Scheme S3. Termination of the ZREP of GPE by dimerization, proceeding via hydrogen abstraction to yield a vinyl ether, intermolecular dimerization between the vinyl ether and propagating polymer, and hemicyclization via backbiting that gives rise to a polyether with tadpole architecture.[2,3]



Scheme S4. Attachment of the $B(C_6F_5)_3$ Lewis acid at the phenoxy O atom of GPE creates an electrophilic CH_2 center next to the oxonium ion, which can react with the nucleophilic OH groups in the linear and tadpole pGPE, derivatizing them into glycidyl ether moieties. Phenol and the Lewis acid are released in this process. The O-H → O-glycidyl conversion increases the mass by 56 Da.



Scheme S5. Termination of the ZREP of GPE by the addition of phenol (formed as shown in Scheme S4), which expels the catalyst and produces a linear polyether with PhO- and -H end groups (94 Da).



Scheme S6. (a) Fragmentation pathway to the fragment ion series $[150n + 58 + Na]^+$, illustrated for the formation of the fragment at *m/z* 531.24 from a tadpole 7-mer with 3 repeat units in its cyclic head; similar fragmentation pathways in 7-mers with (b) three or (c) two repeat units in their cyclic heads account for all ions observed within the $[150n + 58 + Na]^+$ series.

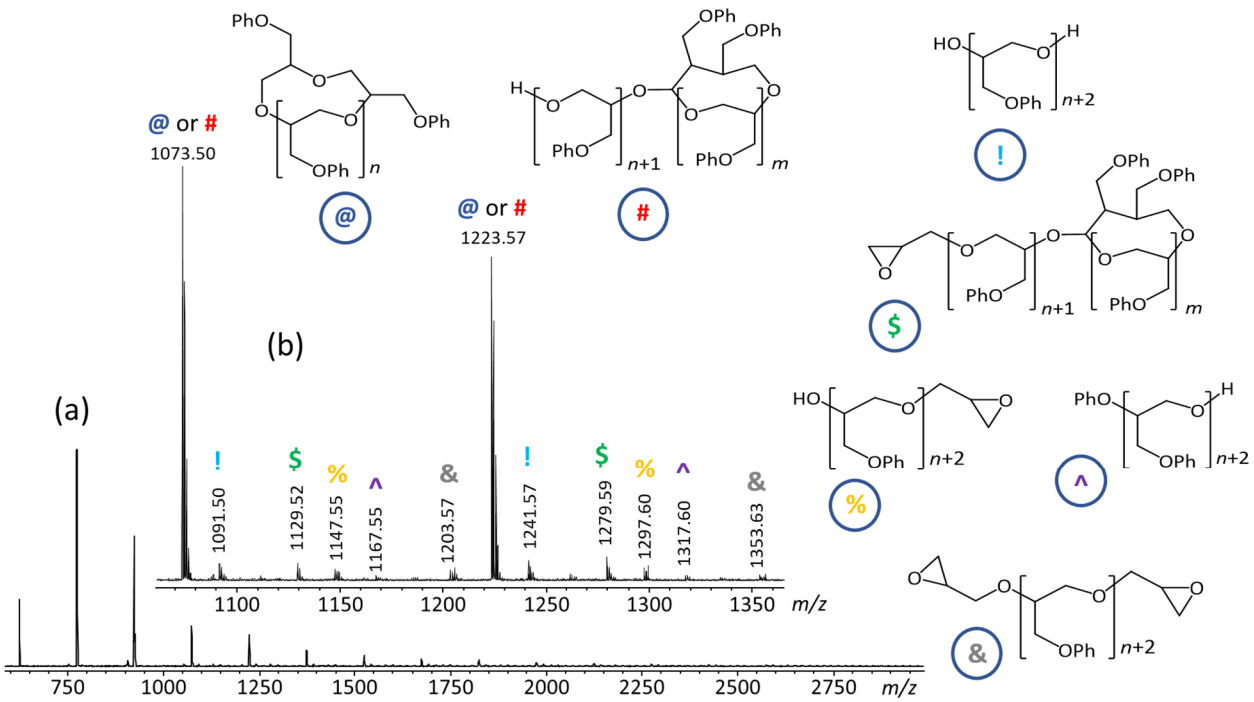


Fig. S1. (a) Matrix-assisted laser desorption/ionization (MALDI) MS spectrum of pGPE, prepared by ZREP of GPE ($C_9H_{10}O_2$, 150 Da). (b) Expanded view of the *m/z* 1050-1360 region, showing the products observed within two repeat units. All ions are sodiated species, $[M + Na]^+$. The main series (marked with **@** or **#**) arises from macrocyclic (**@**) or tadpole (**#**) isomers, both of which have the composition $(C_9H_{10}O_2)_n$ with no nominal end groups and overlap at the same *m/z* value. The other series originate from the linear or tadpole structures depicted at right, which contain end groups that endow unique *m/z* ratios to the corresponding $[M + Na]^+$ species. (This spectrum was acquired with a Bruker UltraFlex III MALDI tandem time-of-flight (ToF/ToF) mass spectrometer, using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix.)

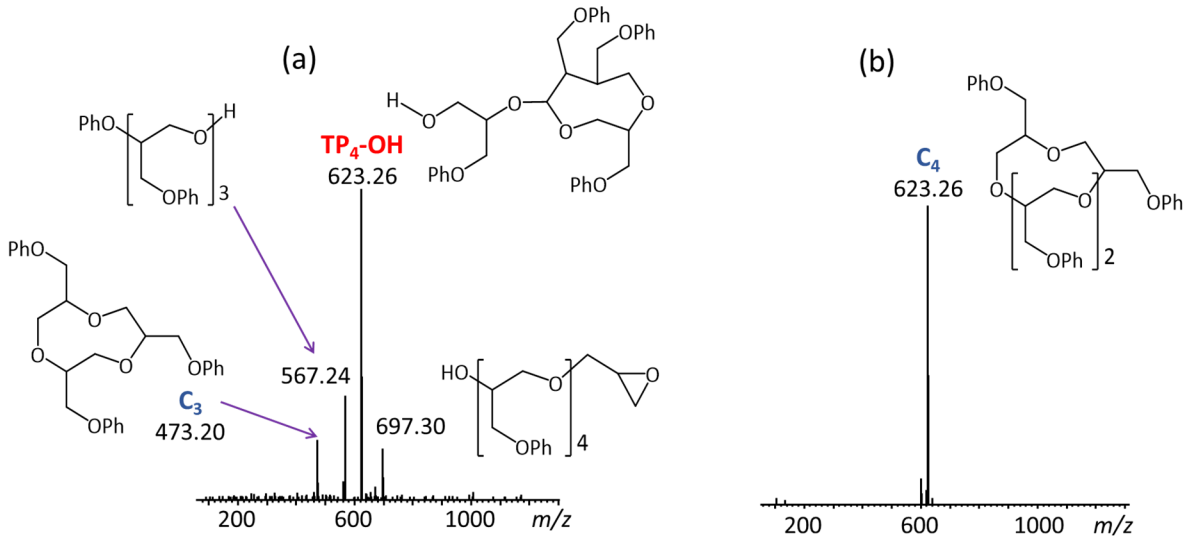


Fig. S2. LC-MS spectra acquired at (a) 4.88 and (b) 5.63 min (maxima of LC peaks in Fig. 2), illustrating separation according to degree of polymerization and polarity. Polarity increases with decreasing degree of polymerization (due to the hydrophobic nature of the monomer) and with hydroxylation (due to the higher polarity of alcohol vs. ether groups). A higher polarity lowers the retention time in reversed-phase LC. Consequently, the more polar cyclic trimer (C_3) elutes before the cyclic tetramer (C_4); similarly, the tadpole tetramer (TP_4-OH) elutes earlier that the isomeric cyclic tetramer (C_4) tetramer. The separate elution of isomers (identical *m/z*) with distinct polarities is more clearly displayed in extracted ion chromatograms (XICs), as discussed in the main text.

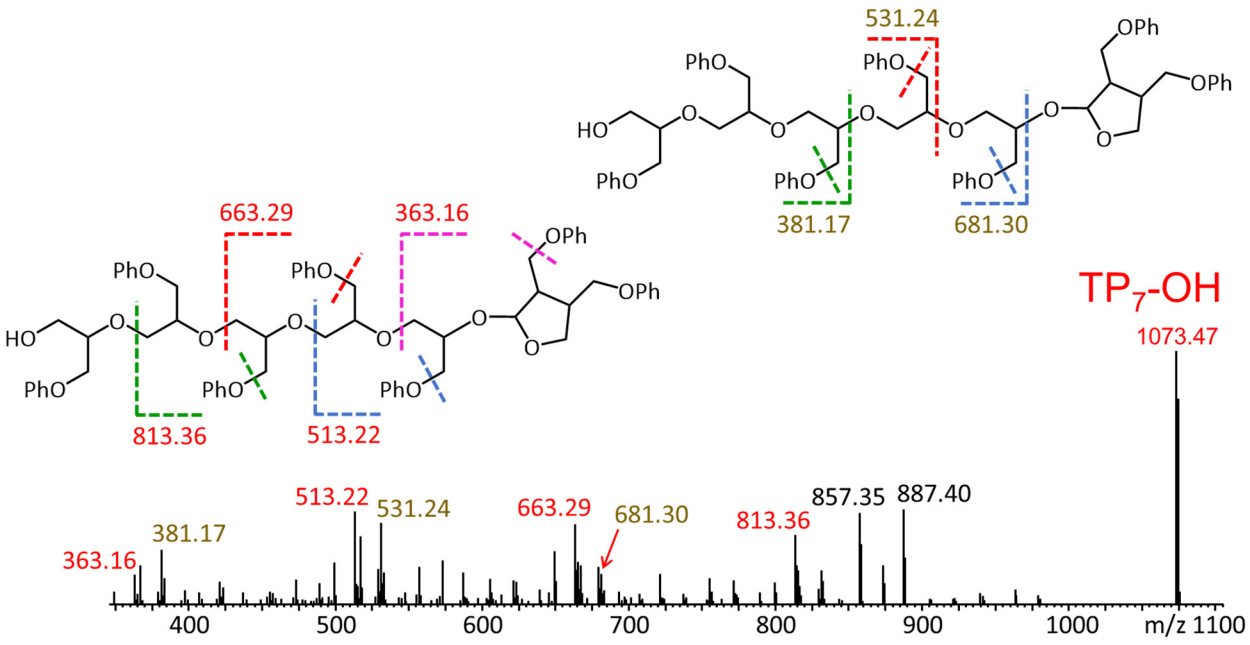


Fig. S3. LC-MS/MS spectrum of sodiated TP_7-OH (*m/z* 1073.47) displaying all detectable fragment ions (the spectra in Fig. 5 were acquired over a smaller mass range, viz. *m/z* 400-1100, as C_7 formed no detectable fragments below *m/z* 400). The structures on top of the spectrum indicate the bonds being cleaved to form fragment ion series $[150n + 40 + Na]^+$ (red *m/z*) and $[150n + 58 + Na]^+$ (brown *m/z*) from tadpole 7-mers with 2 repeat units in their cyclic head.

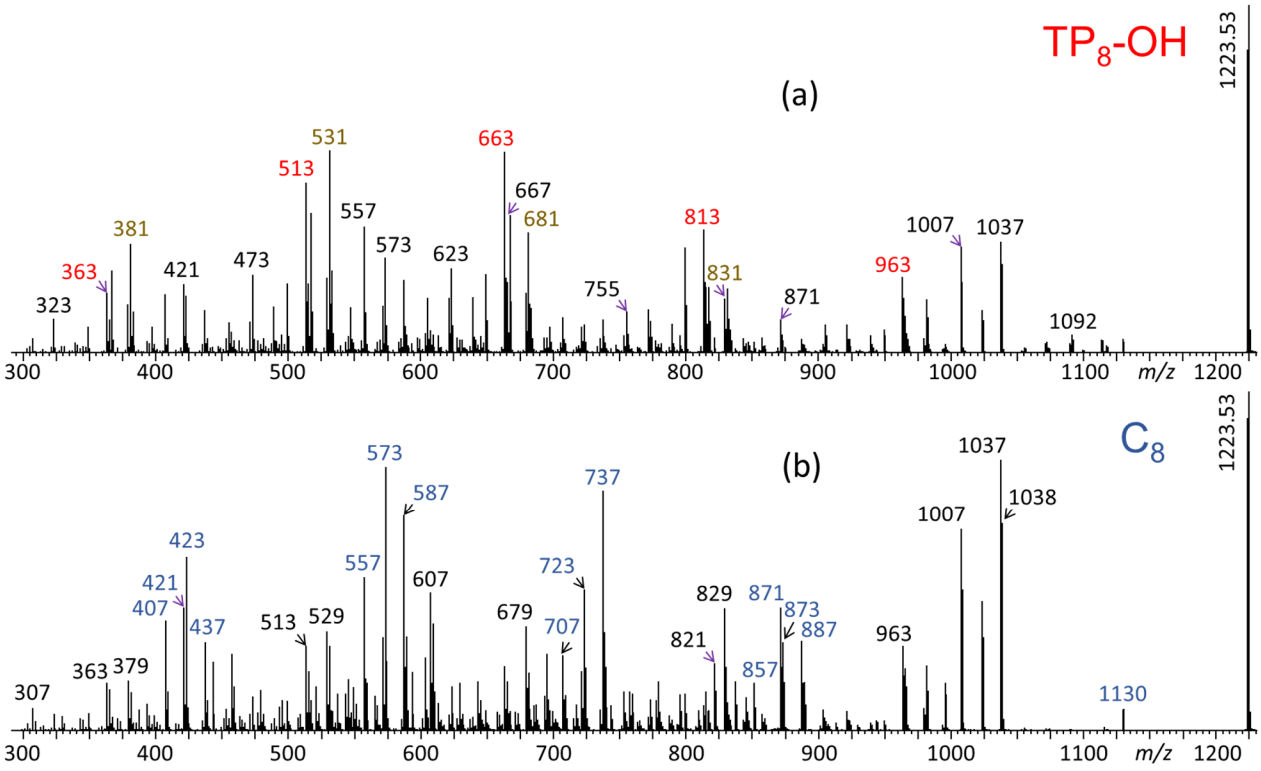


Fig. S4. LC-MS/MS spectra of the sodiated 8-mers (*m/z* 1223.53) eluting at (a) 8.60 and (b) 9.32 min (cf. Fig. 4 and Table S1). Based on the elution order in RPLC, these eluates correspond to (a) TP_8-OH and (b) C_8, respectively. Fragments formed from the tadpole architecture according to the pathways depicted in Schemes 1 and S6 are marked with red and brown *m/z* values, whereas fragments formed from the macrocyclic architecture according to Schemes 2-4 are marked with blue *m/z* values. The two spectra mirror the differences observed for the corresponding 7-mers (Fig. 5).

Table S1. Retention times and peak areas of the tadpole and macrocyclic oligomers in the extracted ion chromatograms (XICs) of poly(glycidyl phenyl ether) (pGPE) in Fig. 4[a]

pGPE oligomer (*n*)	Architecture	Retention time (min)	Peak area (a.u.)[a]
4	tadpole (TP_4-OH)	4.91	84
	cyclic (C_4)	5.63	1735
5	tadpole (TP_5-OH)	5.92	102
	cyclic (C_5)	6.80	1445
6	tadpole (TP_6-OH)	7.06	97
	cyclic (C_6)	7.75	359
7	tadpole (TP_7-OH)	7.84	119
	cyclic (C_7)	8.57	192
8	tadpole (TP_8-OH)	8.60	60
	cyclic (C_8)	9.32	85
9	tadpole (TP_9-OH)	9.28	41
	cyclic (C_9)	9.93	23
10	tadpole (TP_{10}-OH)	9.91	37
	cyclic (C_{10})	10.57	4
11	tadpole (TP_{11}-OH)	10.44	22
	cyclic (C_{11})	11.02	2
12	tadpole (TP_{12}-OH)	10.95	14
	cyclic (C_{12})	-	0
13	tadpole (TP_{13}-OH)	11.36	7
	cyclic (C_{13})	-	0

[a] Based on the summed peak areas of the XICs, the pGPE sample analyzed contains 87% macrocyclic and 13% tadpole chains, corroborating that electrophilic ZREP predominantly yields macrocyclic product.

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