Supporting Information

Solvent Assisted Anionic Ring Opening Polymerization of Glycidol towards Medium and High Molecular Weight Hyperbranched Polyglycerols

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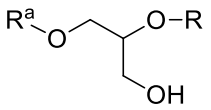
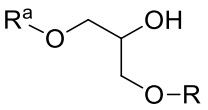
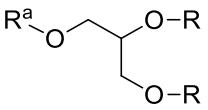
Table S1. Degree of branching (DB) and relative abundance of different structural units determined from ^{13}C NMR. [a]Integral data determined by IG ^{13}C NMR in D_2O.
b. HPG synthesized in 1,4-dioxane; c- HPG synthesized in THP; d- HPG synthesized in EGDE



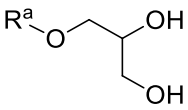
Linear 1,3 (L_{13})



Linear 1,4 (L_{14})



Dendritic (D)



Terminal (T)

region	shift (ppm)	1,4-dioxane (Mn- 100 g/mol)[b]	THP (Mn-100 g/mol)[c]	EGDE (Mn-75 g/mol)[d]
L_{13}	81.3, 81.5	1.0	1.0	1.0
D	79.7, 80.0	3.03	2.71	3.37
$2L_{14}$	73.8	7.45	5.98	7.20
2 D, 2 T	72.0-73.0	12.58	10.93	14.18
L_{13},L_{14}	70.5, 70.8	4.61	4.03	5.13
T	64.2, 64.3	3.36	3.12	3.89
L_{13}	62.6	0.88	0.94	1.30
Structural Units	**Error**	**relative abundance (%)**		
linear 1,3 (L_{13})	± 2%	9	11	11
dendritic (D)	± 1%	25	23	29
terminal (T)	± 2%	32	34	32
linear 1,4 (L_{14})	± 2%	34	32	28
DB	± 0.05%	0.56	0.57	0.58

Table S2. Ratio between Linear 1,3 (L_{13}) and Linear 1,4 (L_{14}) units determined from integrals values by IG ^{13}C NMR in D_2O. Molecular weight characteristics determined by GPC-MALLS in 0.1 N $NaNO_3$ solution. [a]HPG synthesized in EGDE has Molecular weight of 75 g/mol.

b. HPG synthesized in 1,4-dioxane; c- HPG synthesized in THP; d- HPG synthesized in EGDE

Polymers (KDa)	**1,4-dioxane[b] (L_{13}:L_{14})**	**THP[c] (L_{13}:L_{14})**	**EGDE[d] (L_{13}:L_{14})**
HPG-8	1 : 3.15	1 : 2.93	1 : 2.61
HPG-100[a]	1 : 3.71	1 : 2.91	1 : 2.54
HPG-500	1 : 3.01	1 : 2.82	1 : 2.75

Table S3. [a]Reaction solvents; [b]Molecular weight characteristics determined by GPC-MALLS; [c]Radius of hydration (R_h), [d]radius of gyration (R_g) and intrinsic viscosity [η] determined by viscometry (Viscotek) in 0.1 N $NaNO_3$ solution.

Polymer	Solvent[a]	M_n (g.mol^{-1})[b]	M_w/M_n[b]	R_h[c] (nm)	R_g[d] (nm)	[η][d] (dL/g)
1	Dioxane	104	1.4	4.85	6.32	0.0552
2	THP	113	1.4	5.18	6.75	0.0587
3	EGDE	75	1.5	4.85	6.32	0.0569

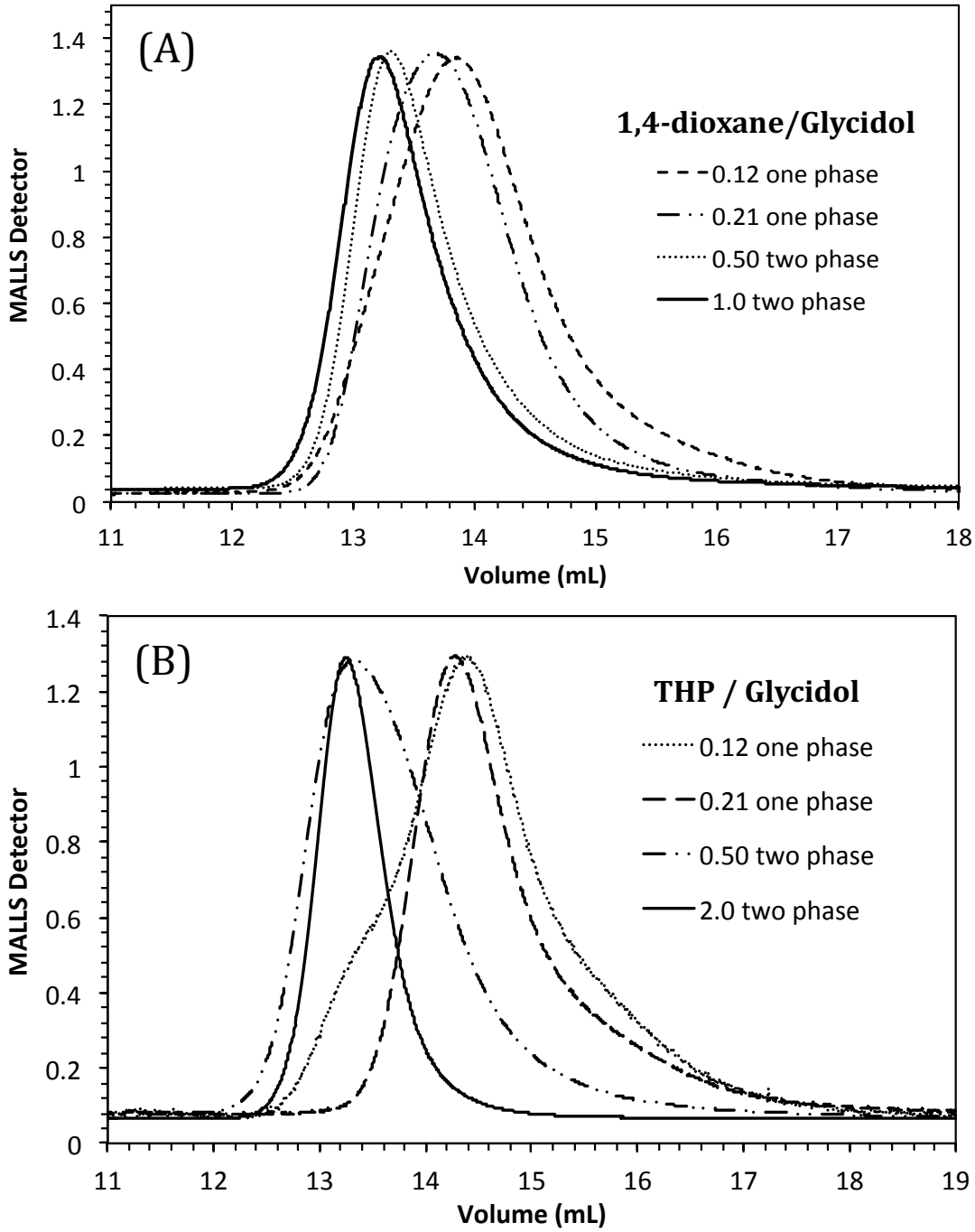


Figure S1. A)- MALLS chromatograms of molecular weights distributions of HPGs obtained with different 1, 4-dioxane/glycidol ratios at constant initiator/glycidol ratio. B)- MALLS chromatograms of molecular weight distributions of HPGs obtained with different tetrahydropyran/glycidol ratios at constant initiator/glycidol ratio. Molecular weight

characteristics determined by GPC-MALLS in 0.1N $NaNO_3$, TMP (0.125 g) and polymerization time (15h).

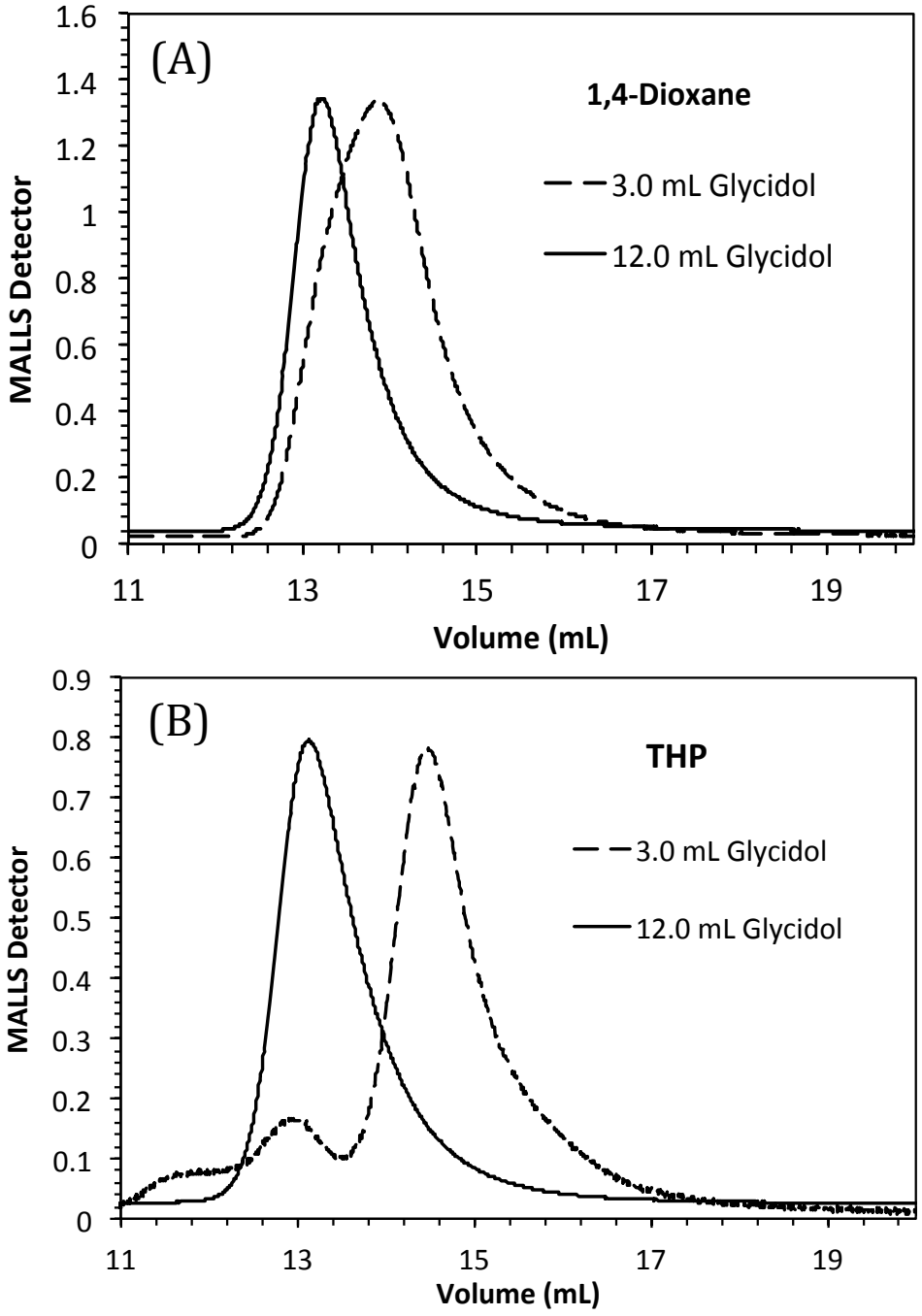


Figure S2. A)- MALLS detector chromatograms of HPGs obtained with different glycidol concentrations at constant 1,4-dioxane/glycidol ratio. B)- MALLS detectors of chromatograms of molecular weight distributions of HPGs obtained with different glycidol concentrations at a

constant tetrahydropyran/glycidol ratio. Molecular weight characteristics determined by GPC-MALLS in 0.1N $NaNO_3$, TMP (0.125 g) and polymerization time (15h), solvent/glycidol ~1.5.

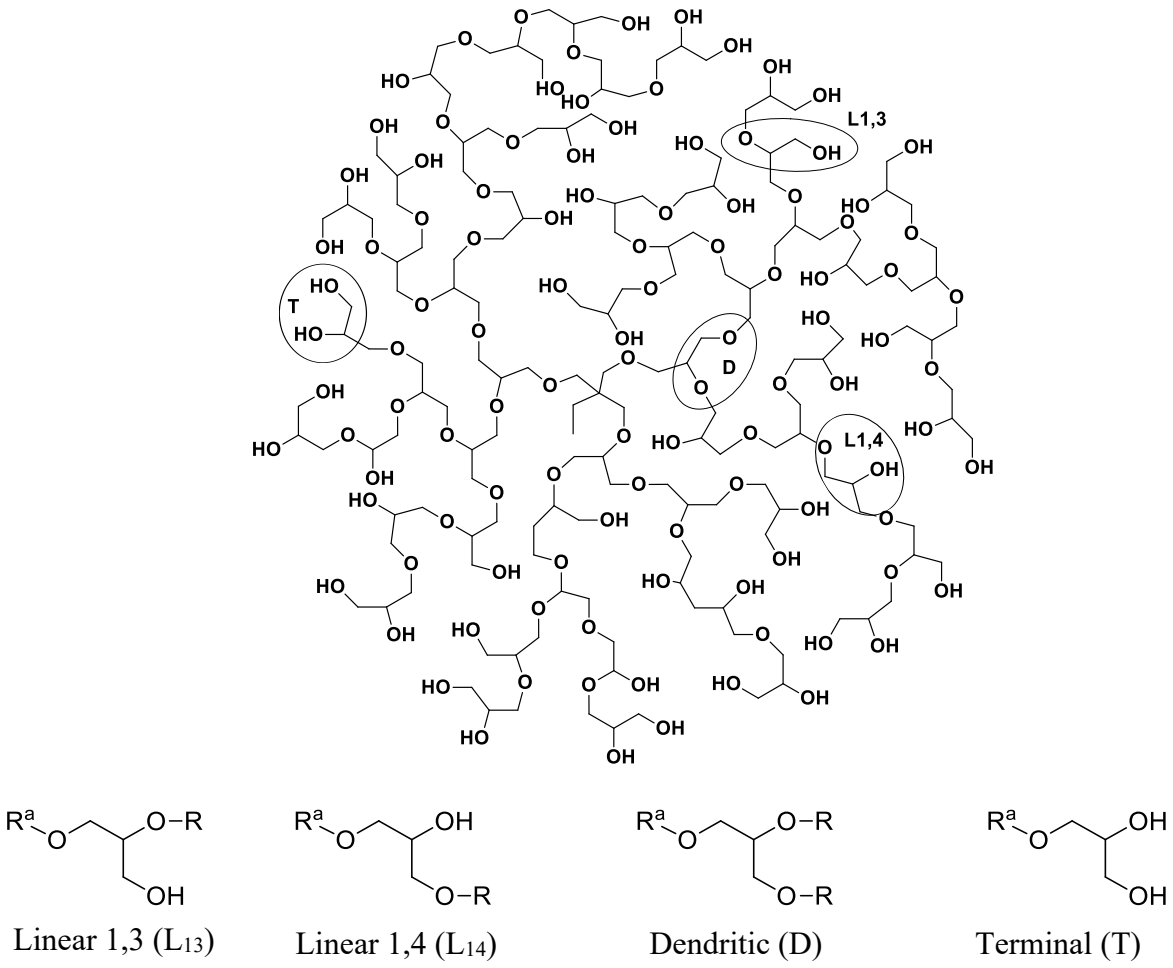


Figure S3. HPG representing different structural units of branching. Several environments within the structure exist, including linear (L), dendritic (D), and terminal (T). Linear units are formed from either secondary hydroxyls ($L_{1,3}$) or primary hydroxyls ($L_{1,4}$).

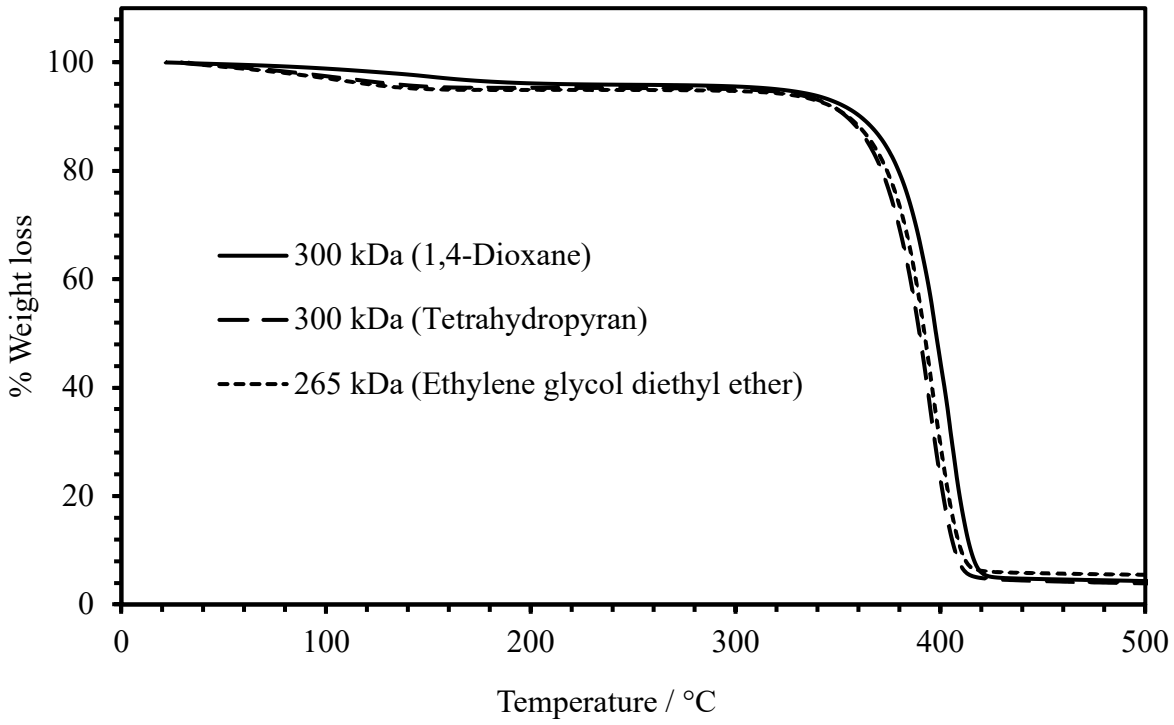


Figure S4. Thermogravimetric analysis of HPGs synthesized using three different solvents.