Electronic Supplementary Information

Highly Tunable Metal-Free Ring Opening Polymerization of Glycidol into Various Controlled Topologies Catalyzed by Frustrated Lewis Pairs

Si Eun Kim,[a,b] Yu-Ri Lee,[c] Minseong Kim,[d,e] Eunyong Seo,[f] Hyun-Jong Paik,[b] Jin Chul Kim,[a] Ji-Eun Jeong,[a] Young Il Park,[a]* Byeong-Su Kim,[d]* and Sang-Ho Lee[a]*

[a]Center for Advanced Specialty Chemicals, Korea Research Institute of Chemical Technology (KRICT), Ulsan 44412, Republic of Korea

[b]Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Republic of Korea

[c]Materials Architecturing Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

[d]Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea

[e]Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

[f]Department of Chemical Engineering, Ulsan College, Ulsan 44610, Republic of Korea

Correspondence and requests for materials should be addressed to

S.-H.L. (e-mail: slee@krict.re.kr), B.-S.K. (e-mail: bskim19@yonsei.ac.kr), Y.I.P. (e-mail: ypark@krict.re.kr)
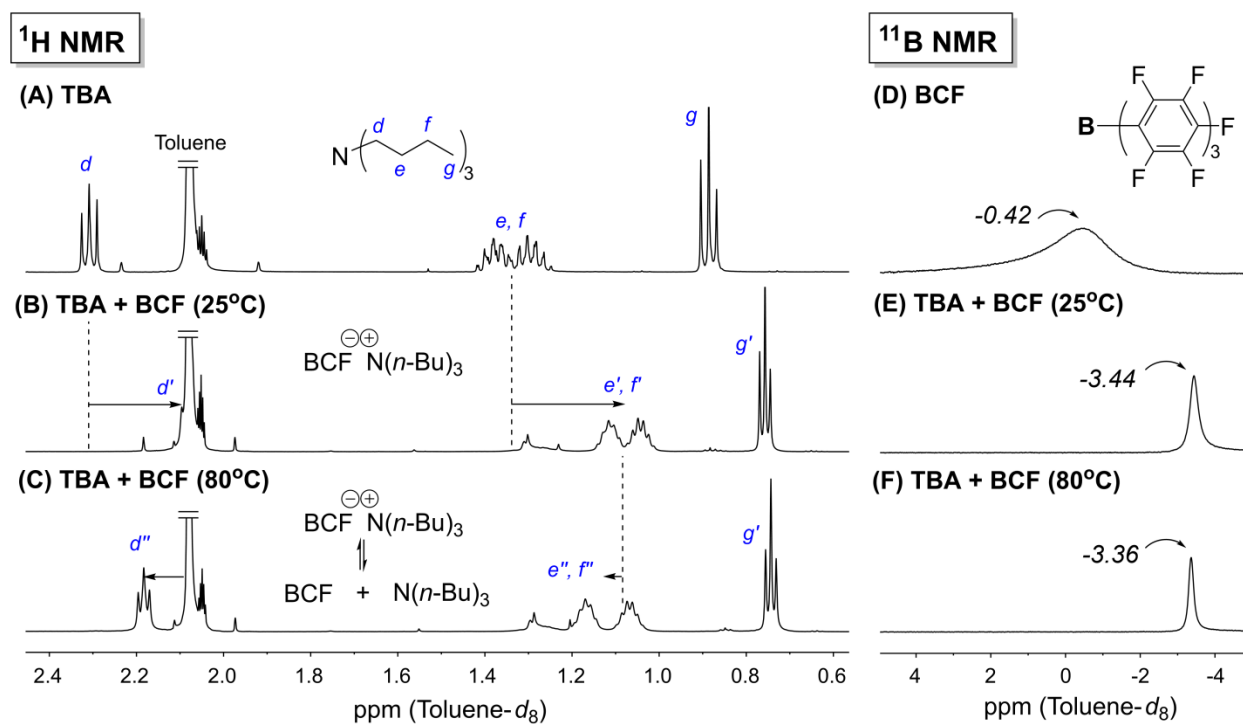
Figure S1. ^{1}H NMR spectra of (A) TBA ([TBA]$_0$ = 40 mM in toluene) at 25 °C, (B) a mixture prepared with a 2:1 ratio ([TBA]$_0$ = 40 mM; [BCF]$_0$ = 20 mM) at 25 °C, and (C) a mixture prepared with a 2:1 ratio ([TBA]$_0$ = 40 mM; [BCF]$_0$ = 20 mM) at 80 °C; ^{11}B NMR spectra of (D) BCF ([BCF]$_0$ = 20 mM) at 25 °C, (E) a mixture prepared with a 2:1 ratio ([TBA]$_0$ = 40 mM; [BCF]$_0$ = 20 mM) at 25 °C, and (F) a mixture prepared with a 2:1 ratio ([TBA]$_0$ = 40 mM; [BCF]$_0$ = 20 mM) at 80 °C.

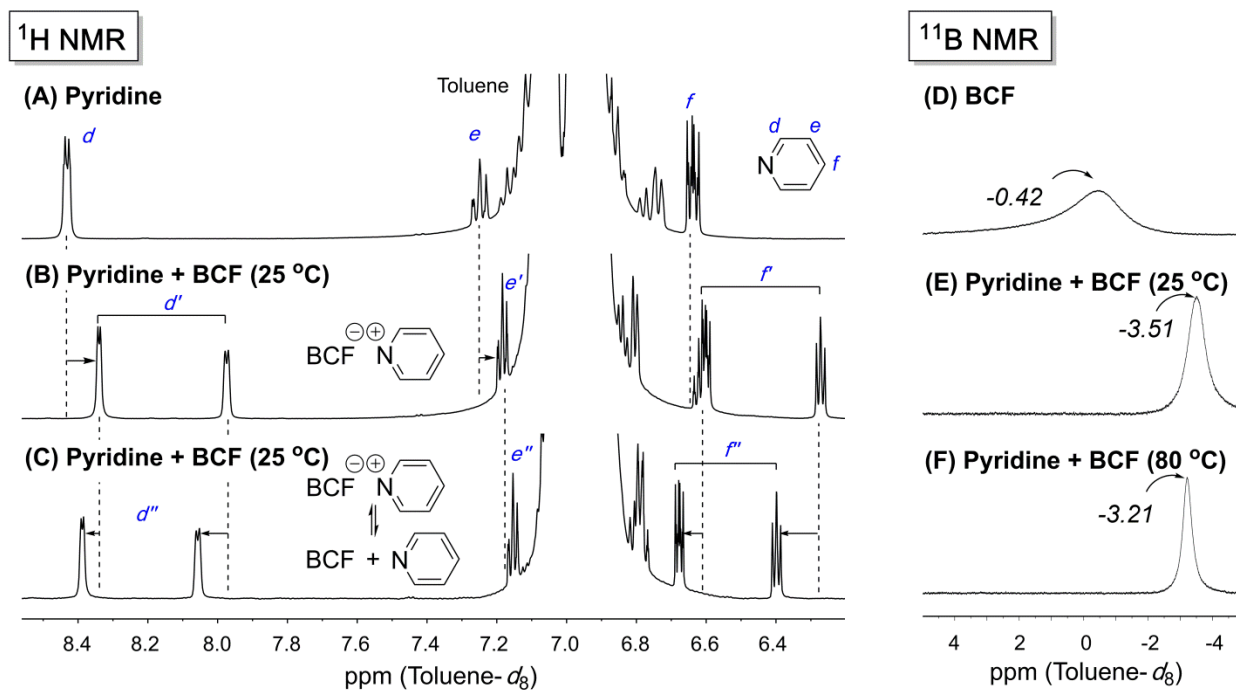**Figure S2.** ^{1}H NMR spectra of (A) Py ($[Py]_0 = 40$ mM in toluene) at 25 °C, (B) a mixture of Py and BCF with a 2:1 ratio ($[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 25 °C, (C) a mixture of Py and BCF with a 2:1 ratio ($[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 80 °C, ^{11}B NMR spectra of (D) BCF ($[BCF]_0 = 20$ mM) at 25 °C, (E) a mixture of Py and BCF with a 2:1 ratio ($[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 25 °C, and (F) a mixture of Py and BCF with a 2:1 ratio ($[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 80 °C.

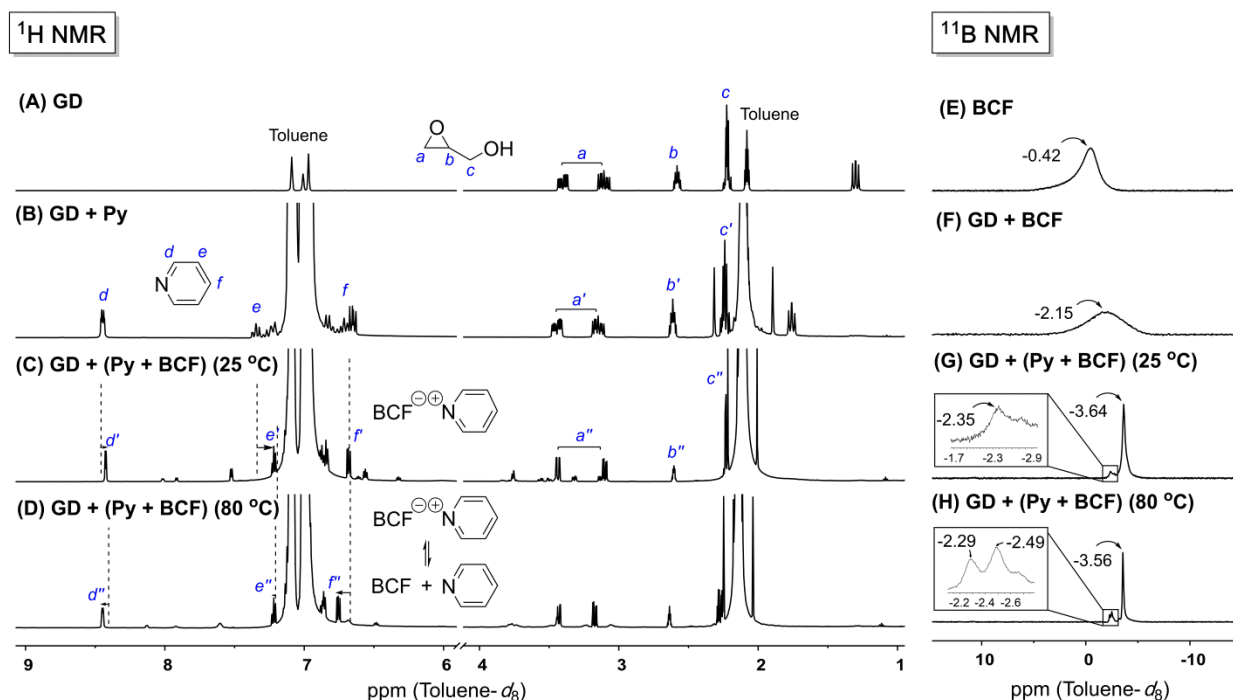**Figure S3.** ^1H NMR spectra of (A) ($[GD]_0 = 40$ mM in toluene) at 25 °C, (B) a mixture of GD and Py with a 1:1 ratio ($[GD]_0 = 40$ mM; $[Py]_0 = 40$ mM) at 25 °C, (C) a mixture of GD and BCF-Py ($[GD]_0 = 40$ mM; $[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 25 °C, (D) a mixture of GD and BCF-Py ($[GD]_0 = 40$ mM; $[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 80 °C; ^{11}B NMR spectra of (E) BCF ($[BCF]_0 = 20$ mM) at 25 °C, (F) a mixture of Py and BCF with a 2:1 ratio ($[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 25 °C, (G) a mixture of GD and BCF-Py ($[GD]_0 = 40$ mM; $[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 25 °C, and (H) a mixture of GD and BCF-Py ($[GD]_0 = 40$ mM; $[Py]_0 = 40$ mM; $[BCF]_0 = 20$ mM) at 80 °C.
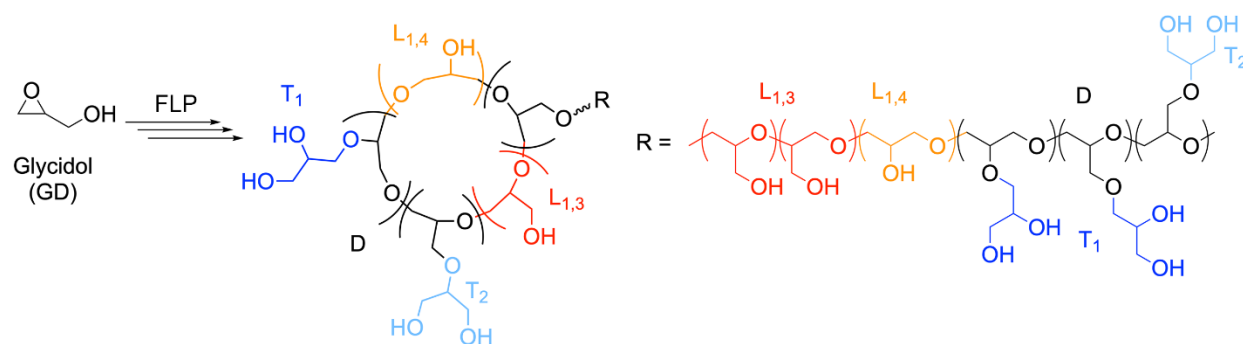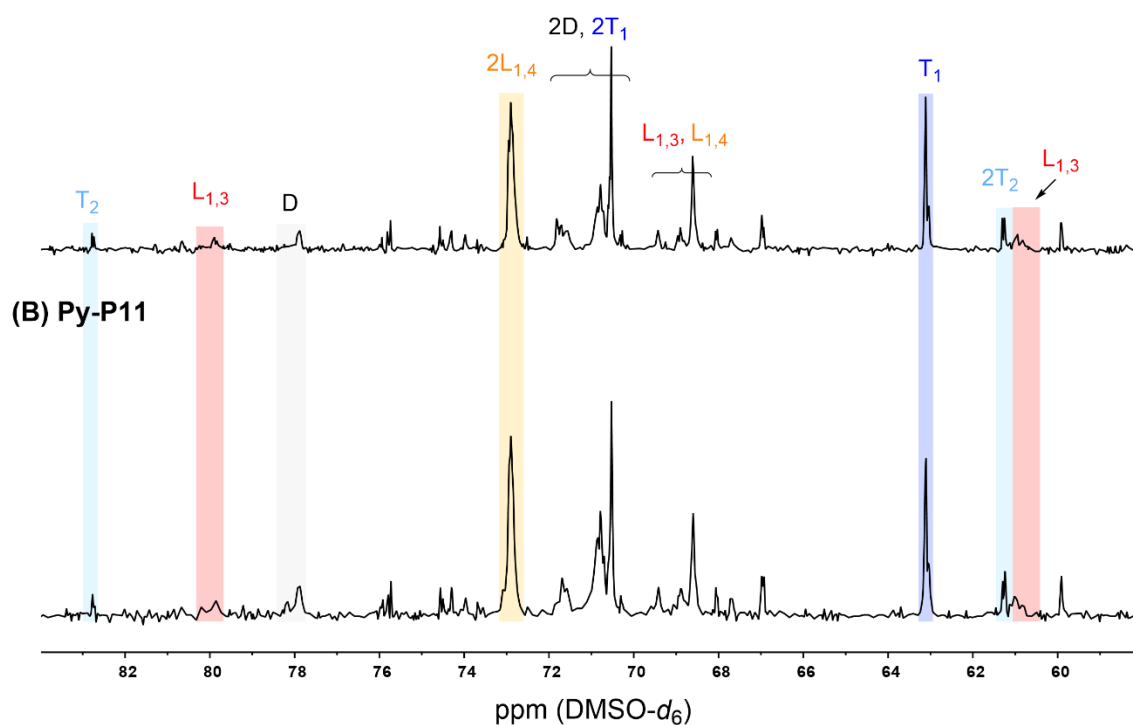
Figure S4. Inverse-gated ^{13}C NMR spectra (DMSO-d_6, room temperature) of (A) TBA-P15 ([GD]$_0$ = 2500 mM; [B(C$_6$F$_5$)$_3$]$_0$ = 3 mM; [TBA]$_0$ = 12 mM in toluene), and (B) Py-P11 ([GD]$_0$ = 2500 mM; [B(C$_6$F$_5$)$_3$]$_0$ = 3 mM; [Py]$_0$ = 6 mM in toluene).

(A) TBA-P15 (Hyperbranched)

2336.48 (n = 31) 2410.53 (n = 32) 2484.61 (n = 33) 2558.66 (n = 34, 2558.36)

GD

$[\blacktriangle = \bullet + 18]$

Mass (m/z)

Mass (m/z)

(B) Py-P11 (Branched Cyclic)

2318.45 (n = 31) 2392.59 (n = 32) 2466.52 (n = 33) 2540.59 (n = 34, 2540.36)

GD

Mass (m/z)

Mass (m/z)

(C) Linear PG

2353.57 (n = 30) 2427.68 (n = 31) 2501.70 (n = 32) 2575.78 (n = 33, 2574.46)
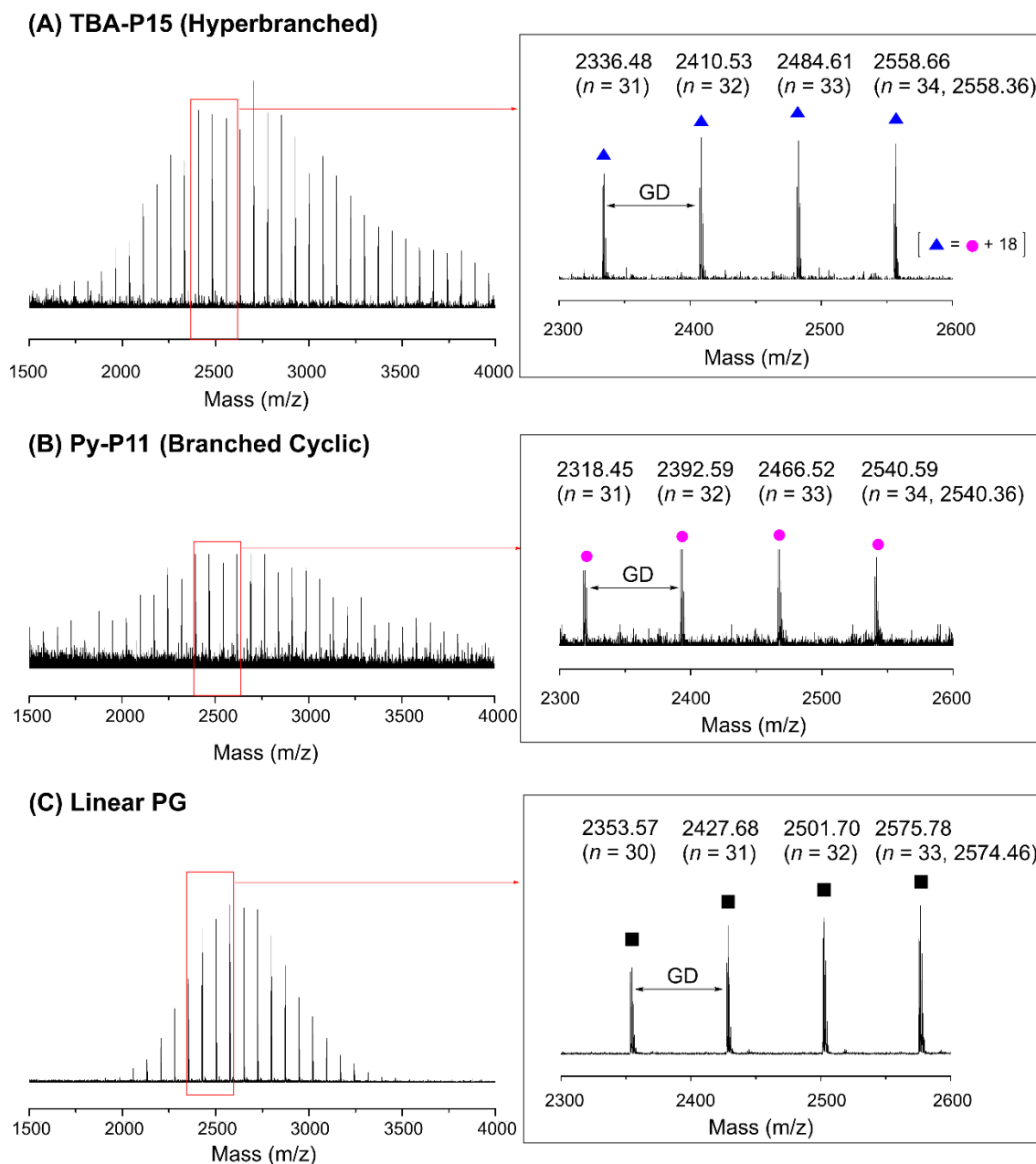
GD

Mass (m/z)

Mass (m/z)

Figure S5. Representative MALDI-ToF spectra for (A) TBA-P15 (*hb*-PG), (B) Py-P11 (*bc*-PG) and (C) linear PG (*lin*-PG) from 1500 to 4500 Da.
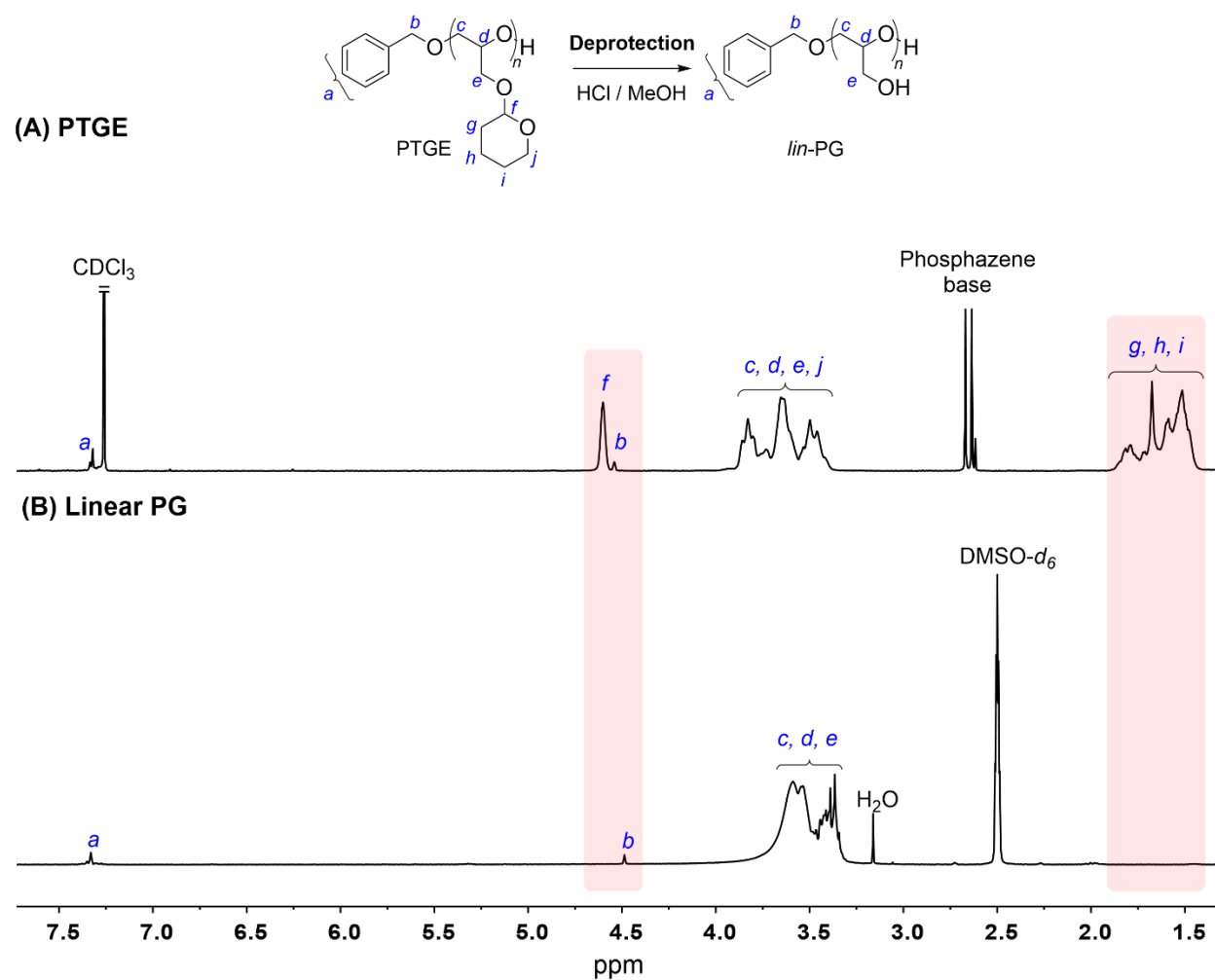
Figure S6. ^{1}H NMR spectra of (A) poly(TGE) ([benzyl alcohol]$_0$ = 65 mM; [t-BuP$_4$]$_0$ = 84.5 mM; [TGE]$_0$ = 2340 mM in toluene at 25 °C for 24 h) and (B) lin-PG (a solution of poly(TGE) (0.5 g, $M_{n, NMR}$ = 5650) in HCl/MeOH (1.25 M, 0.13 mL) at room temperature for 24 h).
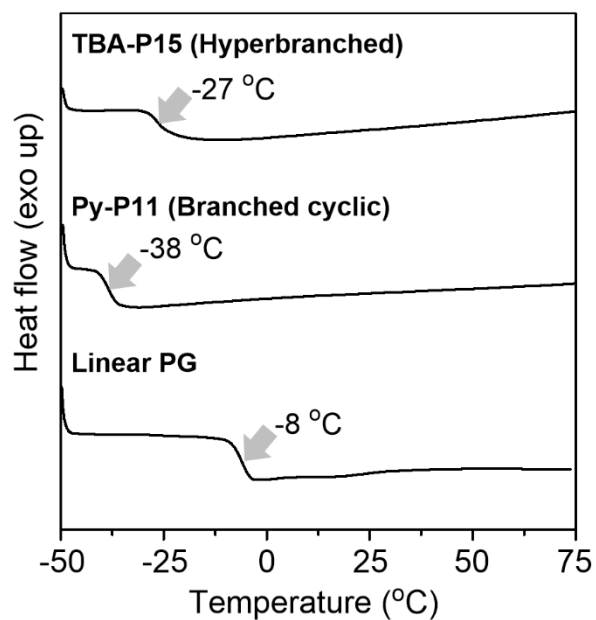
Figure S7. DSC profiles (heating, 10 °C/min) of topology-controlled PGs (TBA-P15 (hyperbranched), Py-P11 (branched cyclic), and linear PG).
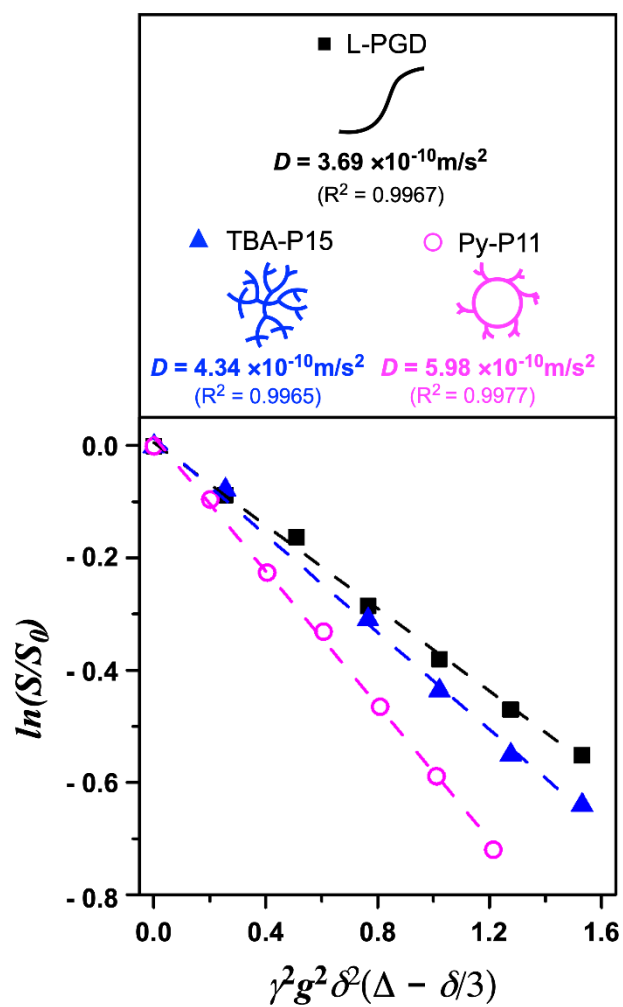
Figure S8. Stejskal–Tanner plot obtained from ^{1}H DOSY spectra and the determined diffusion coefficient (D) values.
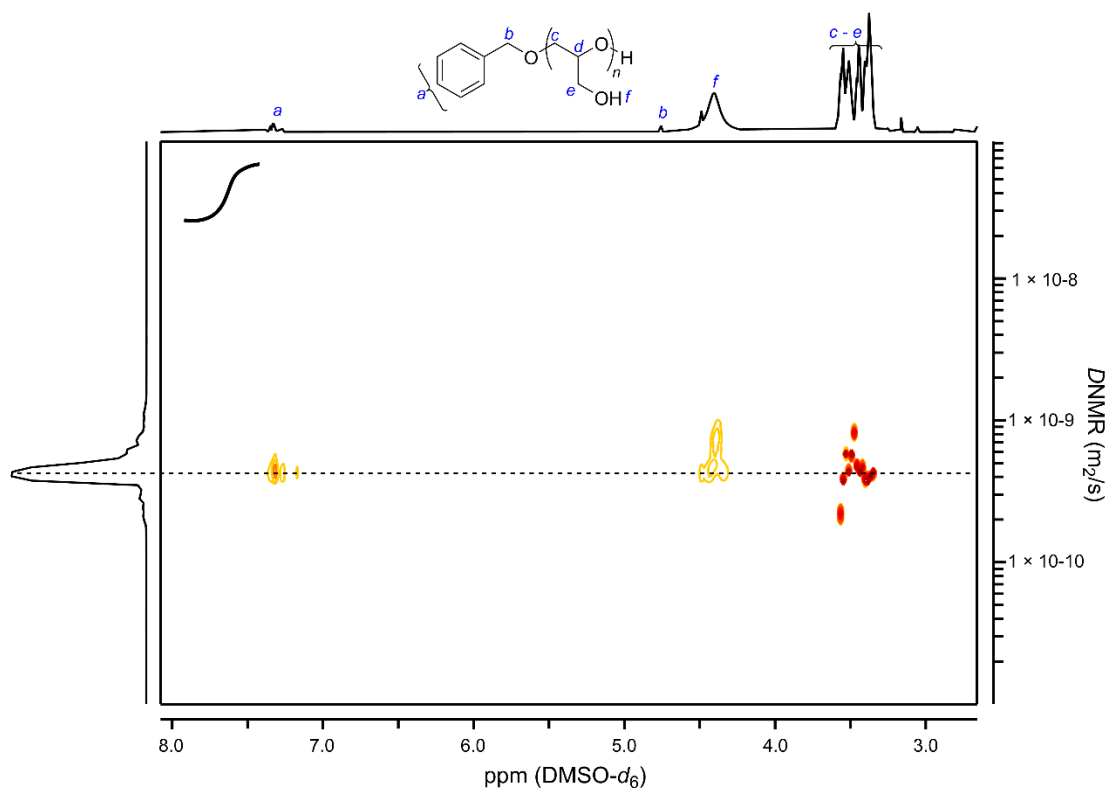
Figure S9. ^{1}H DOSY spectra (DMSO-d_6, room temperature) of *lin*-PG.
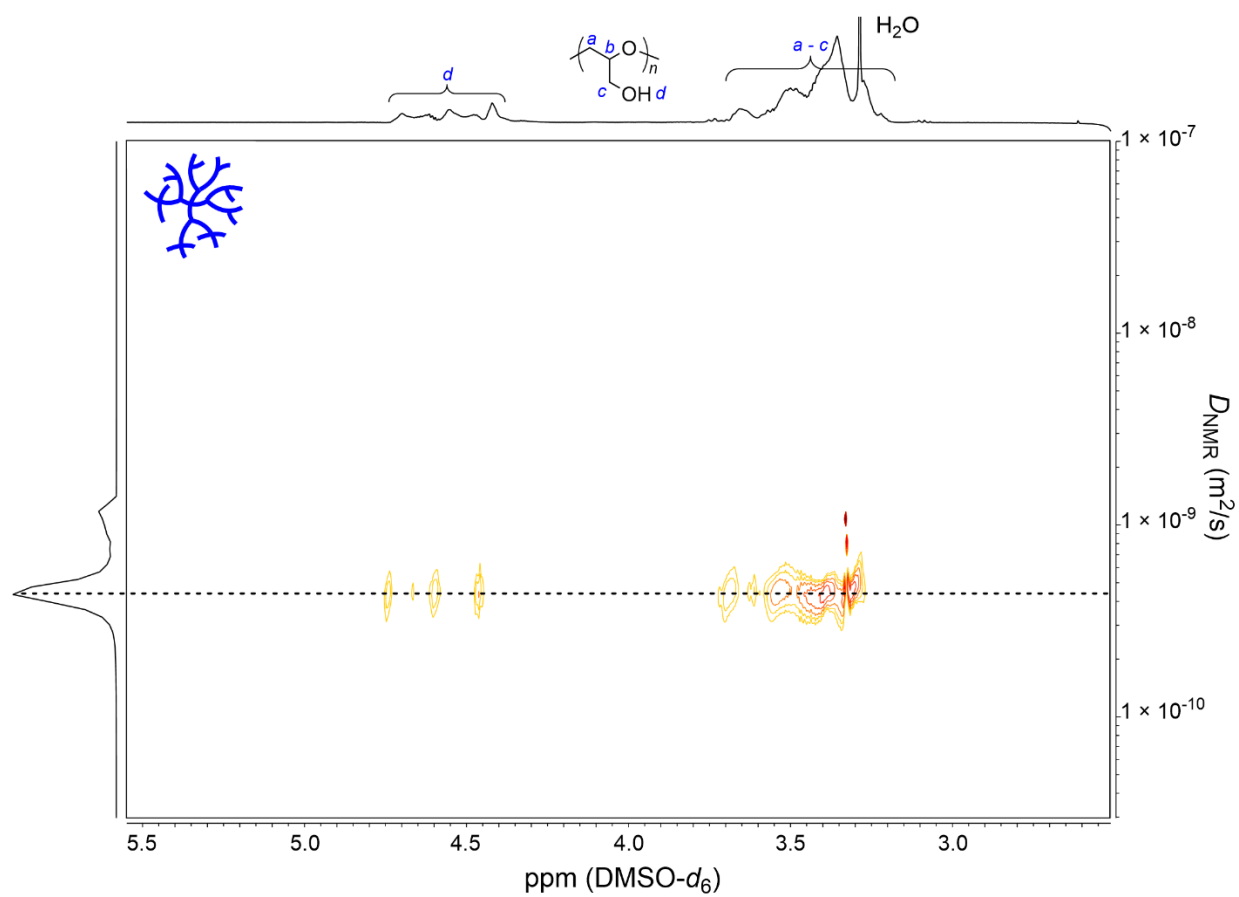
Figure S10. ^{1}H DOSY spectra (DMSO-d_6, room temperature) of TBA-P15 (hyperbranched).
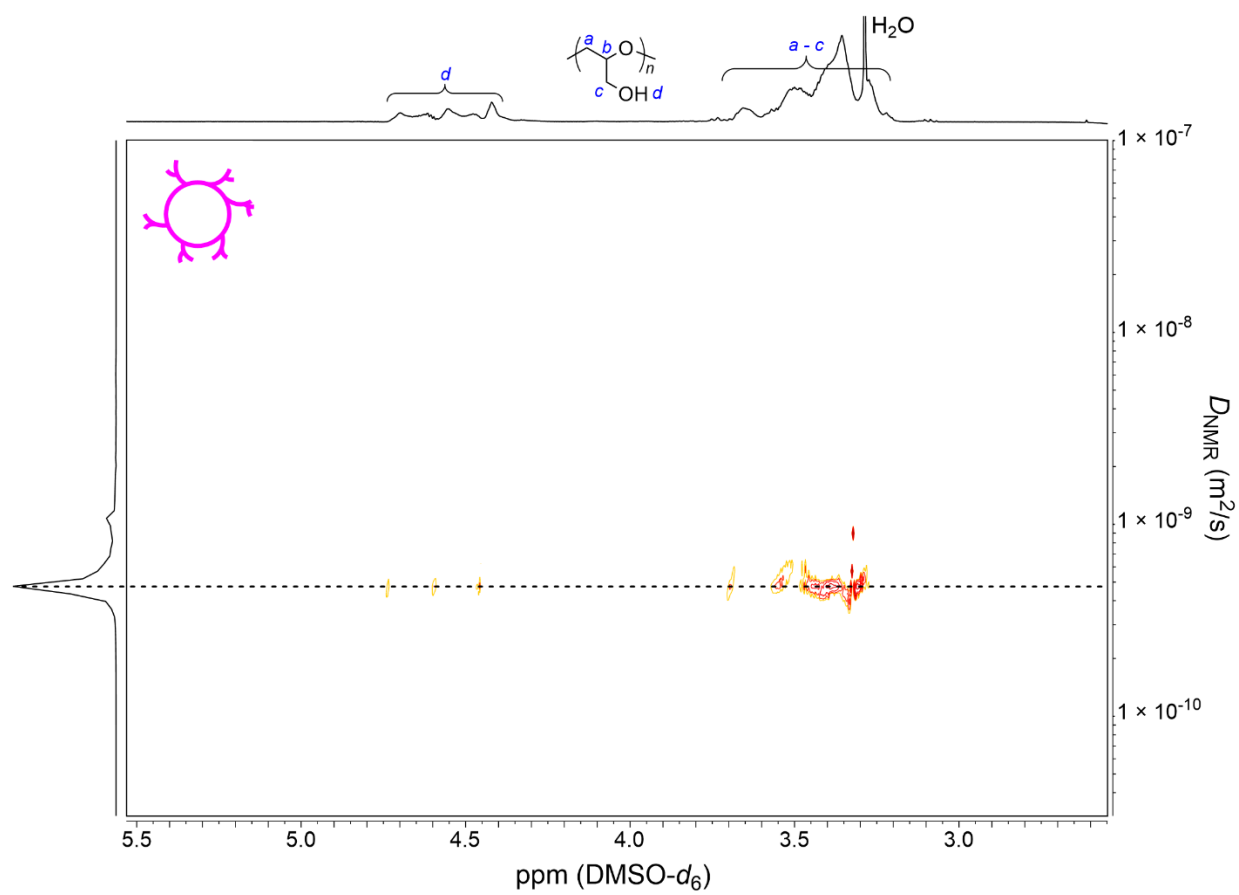
Figure S11. ^{1}H DOSY spectra (DMSO-d_6, room temperature) of Py-P11 (branched cyclic).

(A) TBA-P15
(*hb*-PG, $M_{n, MALDI}$ = 2850)

Time		M_n
Conv.		M_w/M_n
6 h		1790
99.7%		1.92

(B) Py-P11
(*bc*-PG, $M_{n, MALDI}$ = 2730)

| 6 h | | 1370 |
| 92.3% | | 1.67 |

(C) Linear PG
(*lin*-PG, $M_{n, MALDI}$ = 2660)

| 24 h | | 4420 |
| > 99.9% | | 1.04 |

$10^5 \quad 10^4 \quad 10^3 \quad 10^2 \quad 10^1$

Figure S12. SEC curves of (A) TBA-P15 (*hb*-PG), (B) Py-P11 (*bc*-PG) and (C) linear PG (*lin*-PG).

Table S1. Structural control of PGs via BCF catalyst with $(n\text{-Bu})_3\text{N}$ as Lewis base [a]

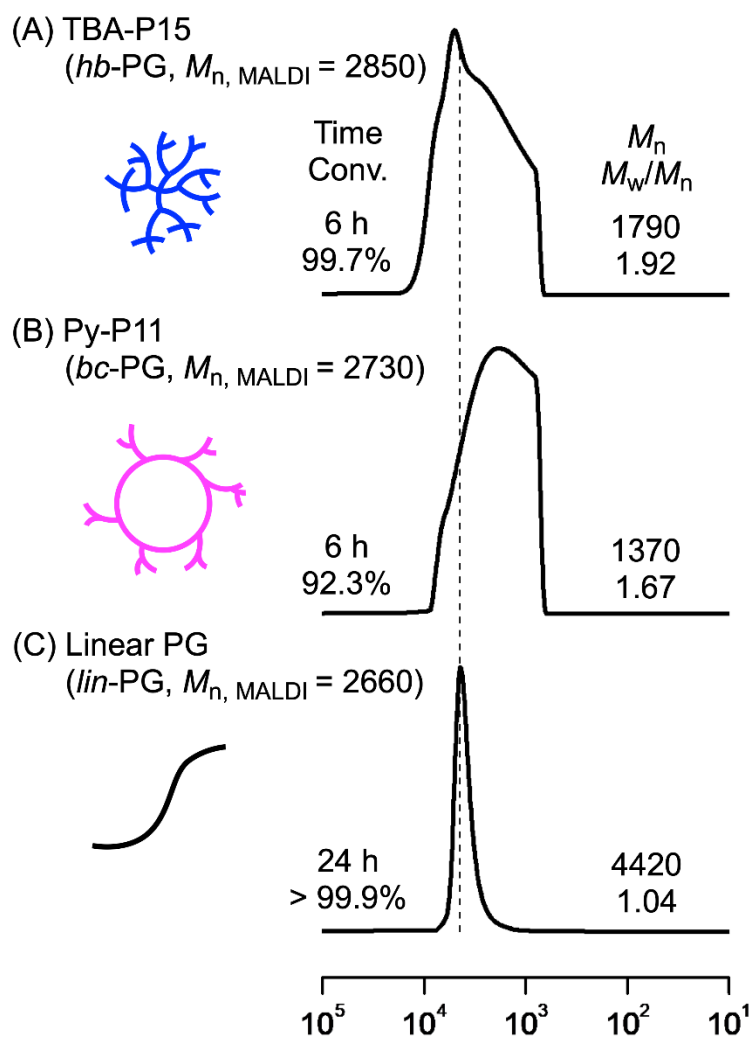| Polymer code	$[\text{B}(\text{C}_6\text{F}_5)_3]_0$ (mM)	$[(n\text{-Bu})_3\text{N}]_0$ (mM)	Temp. (°C)	Time	Conv. (%)[b]	M_n[c]	M_w/M_n[c]	DB[d]
BCF-P1	3	0	25	15 min	94.7	2720	1.55	0.38
TBA-P2	0	12	25	72 h	55.0	n/d[e]	n/d[e]	n/d[e]
TBA-P3	0	12	100	6 h	99.7	1620	1.53	0.67
TBA-P4	3	3	0	24 h	<5	n/d[e]	n/d[e]	n/d[e]
TBA-P5	3	3	25	24 h	<5	n/d[e]	n/d[e]	n/d[e]
TBA-P6	3	3	80	24 h	99.8	1950	1.65	0.51
TBA-P7	3	3	100	24 h	99.8	1830	1.48	0.49
TBA-P8	3	6	0	24 h	<5	n/d[e]	n/d[e]	n/d[e]
TBA-P9	3	6	25	72 h	44.7	n/d[e]	n/d[e]	n/d[e]
TBA-P10	3	6	80	6 h	93.3	1600	1.87	0.50
TBA-P11	3	6	100	3 h	96.4	1420	1.74	0.50
TBA-P12	3	12	0	72 h	49.6	n/d[e]	n/d[e]	n/d[e]
TBA-P13	3	12	25	72 h	97.4	1500	1.60	0.46
TBA-P14	3	12	80	6 h	99.8	1640	1.73	0.49
TBA-P15	3	12	100	6 h	99.7	1790	1.92	0.51

[a]$[\text{GD}]_0 = 2500$ mM in toluene. [b]Conversion was determined by ^1H NMR with tetralin as an internal standard. [c]Measured by size-exclusion chromatography calibrated with PEO standards in DMF (50 mM LiBr, 45 °C, flow rate 1.0 mL/min). [d]Degree of branching (DB) was calculated by inverse-gated ^{13}C NMR using the following equation: $(D + T)/(D + T + L)$ (D = dendritic unit; T = terminal unit; L = linear unit). [e]Not determined.

Table S2. Structural control of PGs using BCF catalyst with pyridine as Lewis base[a]

Polymer code	$[B(C_6F_5)_3]_0$ (mM)	$[Pyridine]_0$ (mM)	Temp. (°C)	Time	Conv. (%)[b]	M_n[c]	M_w/M_n[c]	DB[d]
BCF-P1	3	0	25	15 min	94.7	2720	1.55	0.38
Py-P2	0	6.0	0	24 h	< 1.0	n/d[e]	n/d[e]	n/d[e]
Py-P3	0	6.0	100	24 h	99.5	1670	1.50	0.50
Py-P4	3	3.0	0	12 d	49.03	n/d[e]	n/d[e]	n/d[e]
Py-P5	3	3.0	25	12 d	50.41	n/d[e]	n/d[e]	n/d[e]
Py-P6	3	3.0	80	12 d	>99.9	3210	1.10	0.44
Py-P7	3	3.0	100	6 d	>99.9	1480	1.99	0.45
Py-P8	3	6.0	0	18 h	<1.0	n/d[e]	n/d[e]	n/d[e]
Py-P9	3	6.0	25	6 d	91.6	1190	1.18	0.48
Py-P10	3	6.0	80	18 h	97.98	1430	1.60	0.49
Py-P11	3	6.0	100	18 h	92.3	1370	1.67	0.49

[a]$[GD]_0 = 2500$ mM in toluene. [b]Conversion was determined by ^{1}H NMR with tetralin as an internal standard. [c]Measured by size-exclusion chromatography calibrated with PEO standards in DMF (50 mM LiBr, 45 °C, flow rate 1.0 mL/min). [d]Degree of branching (DB) was calculated by inverse-gated ^{13}C NMR with following equation: $(D + T)/(D + T + L)$ (D = dendritic unit; T = terminal unit; L = linear unit). [e]Not determined.

Table S3. Structural control of PGs using BCF catalyst with (n-Bu)$_3$N as Lewis base at different polymerisation temperatures [a, b]

Region	Chemical shift (ppm)	BCF-P1	TBA-P3	TBA-P13	TBA-P14	TBA-P15
$L_{1,3}$	60.6–61.2	2.32	1.09	0.75	1.56	1.62
$2T_2$	61.2–61.8	0.83	0.91	1.54	0.00	1.57
T_1	63.0–63.3	1.41	2.62	3.89	4.82	6.13
$L_{1,3}$, $L_{1,4}$	68.5–69.7	2.60	4.36	6.54	7.57	8.35
$2D$, $2T_1$	70.4–72.0	5.47	9.54	12.91	16.15	21.01
$2L_{1,4}$	72.7–73.2	3.44	1.60	11.56	11.61	13.50
D	77.7–78.9	0.57	1.57	1.76	2.19	2.48
$L_{1,3}$	79.7–80.4	1.00	1.00	1.00	1.00	1.00
T_2	81.5–82.2	0.42	0.00	0.00	0.00	0.00
Structure units (%) [c]						
D units		**9**	**26**	**15**	**15**	**15**
L units		**63**	**31**	**53**	**51**	**49**
($L_{1,3}$ units)		(36)	(18)	(6)	(11)	(9)
($L_{1,4}$ units)		(27)	(13)	(47)	(40)	(40)
T units		**28**	**43**	**32**	**34**	**36**
(T_1 units)		(22)	(43)	(32)	(34)	(36)
(T_2 units)		(6)	(0)	(0)	(0)	(0)
Degree of Branching [d]		0.37	0.69	0.47	0.49	0.51

[a][GD]$_0$ = 2500 mM, [B(C$_6$F$_5$)$_3$]$_0$ = 3 mM or/and [TBA]$_0$ = 12 mM in toluene at 25, 80, and 100 °C. [b]Obtained by inverse gated ^{13}C NMR. [c]The structure units (%) were calculated from the following equation: integration ratio of each structure region / ($D + T + L$) × 100. [d]Degree of branching (DB) = ($D + T$)/($D + T + L$).

Table S4. Structural control of PGs via BCF with different concentration of $(n\text{-Bu})_3\text{N}$ [a, b]

Region	Chemical shift (ppm)	BCF-P1	TBA-P3	TBA-P7	TBA-P11	TBA-P15
$L_{1,3}$	60.6–61.2	2.32	1.09	1.89	1.56	1.62
$2T_2$	61.2–61.8	0.83	0.91	1.44	1.64	1.57
T_1	63.0–63.3	1.41	2.62	9.49	6.88	6.13
$L_{1,3}$, $L_{1,4}$	68.5–69.7	2.60	4.36	11.52	10.11	8.35
$2D$, $2T_1$	70.4–72.0	5.47	9.54	23.34	23.30	21.01
$2L_{1,4}$	72.7–73.2	3.44	1.60	20.74	16.01	13.50
D	77.7–78.9	0.57	1.57	2.22	2.83	2.48
$L_{1,3}$	79.7–80.4	1.00	1.00	1.00	1.00	1.00
T_2	81.5–82.2	0.42	0.00	0.05	0.00	0.00
Structure units (%) [c]						
D units		**9**	**26**	**9**	**15**	**15**
L units		**63**	**31**	**51**	**49**	**49**
(L$_{1,3}$ units)		(36)	(18)	(8)	(8)	(9)
(L$_{1,4}$ units)		(27)	(13)	(43)	(41)	(40)
T units		**28**	**43**	**40**	**36**	**36**
(T$_1$ units)		(22)	(43)	(40)	(36)	(36)
(T$_2$ units)		(6)	(0)	(0)	(0)	(0)
Degree of Branching [d]		0.37	0.69	0.49	0.50	0.51

[a]$[GD]_0 = 2500$ mM, $[B(C_6F_5)_3]_0 = 3$ mM or/and $[TBA]_0 = 3, 6,$ and 12 mM in toluene at 100 °C. [b]Obtained by inverse-gated ^{13}C NMR. [c]The structure units (%) were calculated from the following equation: integration ratio of each structure region $/(D + T + L) \times 100$. [d]Degree of branching (DB) $= (D + T)/(D + T + L)$.

Table S5. Structural control of PGs using BCF catalyst with pyridine as Lewis base at different polymerisation temperatures [a, b]

Region	Chemical shift (ppm)	BCF-P1	Py-P3	Py-P9	Py-P10	Py-P11
$L_{1,3}$	60.6–61.2	2.32	0.70	0.88	1.37	1.17
$2T_2$	61.2–61.8	0.83	0.58	0.00	0.86	2.82
T_1	63.0–63.3	1.41	1.52	6.18	6.27	23.78
$L_{1,3}$, $L_{1,4}$	68.5–69.7	2.60	2.37	9.56	8.47	20.30
$2D$, $2T_1$	70.4–72.0	5.47	5.01	17.25	18.69	64.02
$2L_{1,4}$	72.7–73.2	3.44	3.27	19.02	15.55	55.84
D	77.7–78.9	0.57	0.85	1.90	1.47	3.57
$L_{1,3}$	79.7–80.4	1.00	1.00	1.00	1.00	1.00
T_2	81.5–82.2	0.42	0.00	0.00	0.00	0.00
Structure units (%) [c]						
D units		**9**	**18**	**10**	**9**	**6**
L units		**63**	**50**	**56**	**54**	**52**
($L_{1,3}$ units)		(36)	(15)	(5)	(8)	(2)
($L_{1,4}$ units)		(27)	(35)	(51)	(46)	(50)
T units		**28**	**32**	**34**	**37**	**42**
(T_1 units)		(22)	(32)	(34)	(37)	(42)
(T_2 units)		(6)	(0)	(0)	(0)	(0)
Degree of Branching [d]		0.37	0.50	0.44	0.46	0.48

[a]$[GD]_0 = 2500$ mM, $[B(C_6F_5)_3]_0 = 3$ mM or/and $[pyridine]_0 = 6$ mM in toluene at 25, 80, and 100 °C. [b]Obtained by inverse-gated ^{13}C NMR. [c]The structure units (%) were calculated from the following equation: integration ratio of each structure region / $(D + T + L) \times 100$. [d]Degree of branching $(DB) = (D + T)/(D + T + L)$.

Table S6. Structural control of PGDs using BCF with different concentration of pyridine [a, b]

Region	Chemical shift (ppm)	BCF-P1	Py-P3	Py-P7	Py-P11
$L_{1,3}$	60.6–61.2	2.32	0.70	2.15	1.17
$2T_2$	61.2–61.8	0.83	0.58	0.89	2.82
T_1	63.0–63.3	1.41	1.52	4.08	23.78
$L_{1,3}$, $L_{1,4}$	68.5–69.7	2.60	2.37	4.05	20.30
$2D$, $2T_1$	70.4–72.0	5.47	5.01	9.03	64.02
$2L_{1,4}$	72.7–73.2	3.44	3.27	7.94	55.84
D	77.7–78.9	0.57	0.85	0.40	3.57
$L_{1,3}$	79.7–80.4	1.00	1.00	1.00	1.00
T_2	81.5–82.2	0.42	0.00	0.60	0.00
Structure units (%)[c]					
D units		**9**	**18**	**4**	**6**
L units		**63**	**50**	**54**	**52**
($L_{1,3}$ units)		(36)	(15)	(19)	(2)
($L_{1,4}$ Units)		(27)	(35)	(35)	(50)
T units		**28**	**32**	**42**	**42**
(T_1 units)		(22)	(32)	(37)	(42)
(T_2 units)		(6)	(0)	(5)	(0)
Degree of Branching[d]		0.37	0.50	0.45	0.48

[a]$[GD]_0 = 2500$ mM, $[B(C_6F_5)_3]_0 = 3$ mM or/and $[pyridine]_0 = 3$ and 6 mM in toluene at 100 °C. [b]Obtained by inverse-gated ^{13}C NMR. [c]The structure units (%) were calculated from the following equation: integration ratio of each structure region $/(D + T + L) \times 100$. [d]Degree of branching (DB) $= (D + T)/(D + T + L)$.