Supporting Information

Recyclable Metal-Free Catalytic System for the Cationic Ring-Opening Polymerization of Glycidol under Ambient Conditions

Si Eun Kim,[1,2] Hyun Ji Yang,[1] Soonyoung Choi,[1] Eunbyul Hwang,[1] Minseong Kim[3,4] Hyun-Jong Paik,[2] Ji-Eun Jeong,[1] Young Il Park,[1] Jin Chul Kim,[1] Byeong-Su Kim,[3]* and Sang-Ho Lee[1]**

[1]Center for Advanced Specialty Chemicals, Korea Research Institute of Chemical Technology, Ulsan 44412, Republic of Korea

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

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

[4]Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, 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). J.C.K. (e-mail: jckim81@krict.re.kr)

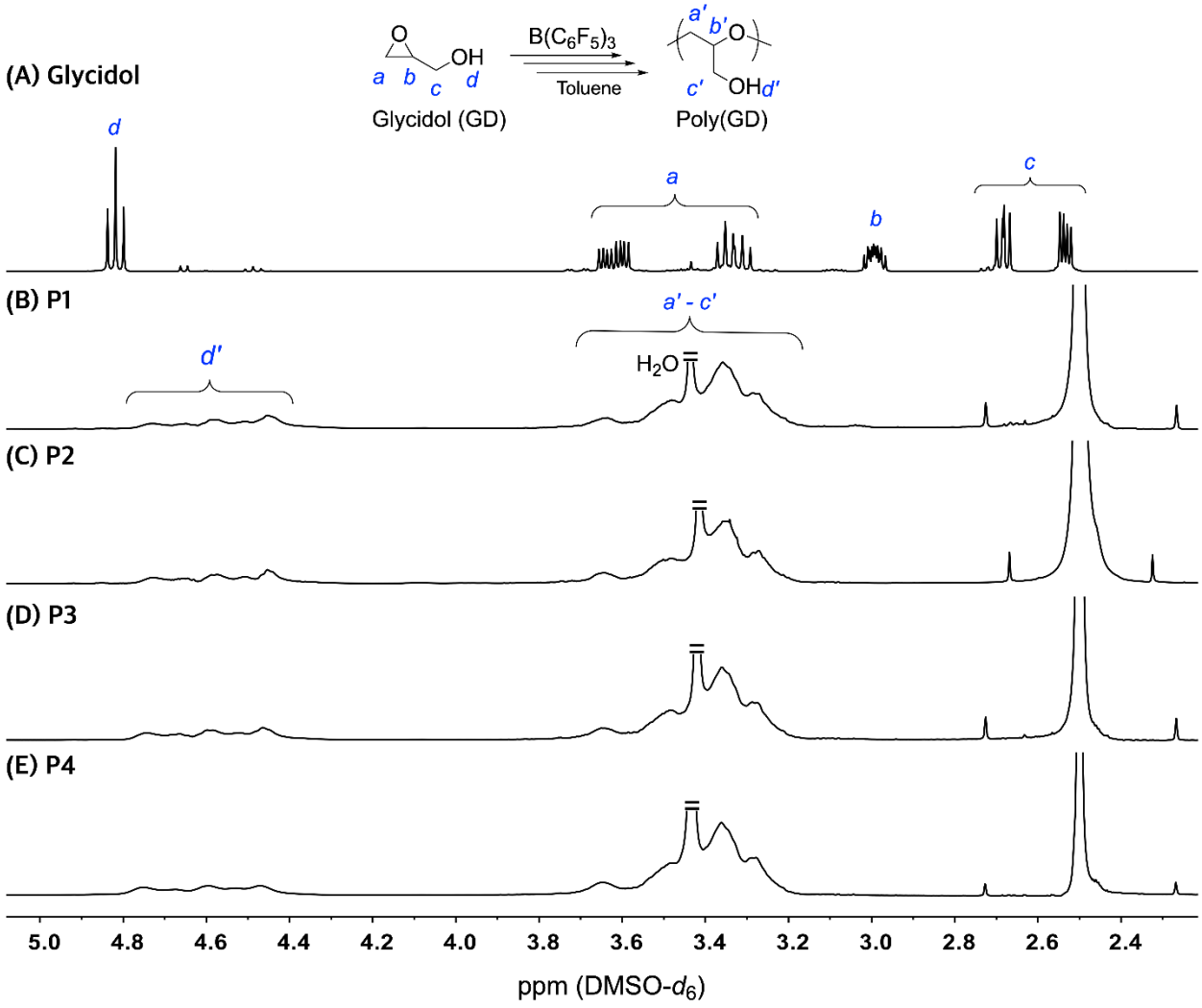

Figure S1. ^{1}H NMR spectra (DMSO-d_6, room temperature) of (A) GD, (B) P1 ($[GD]_0 = 2500$ mM; $[B(C_6F_5)_3]_0 = 1$ mM in toluene), (C) P2 ($[GD]_0 = 2500$ mM; $[B(C_6F_5)_3]_0 = 3$ mM in toluene), (D) P3 ($[GD]_0 = 2500$ mM; $[B(C_6F_5)_3]_0 = 5$ mM in toluene), and (E) P4 ($[GD]_0 = 2500$ mM; $[B(C_6F_5)_3]_0 = 10$ mM in toluene).

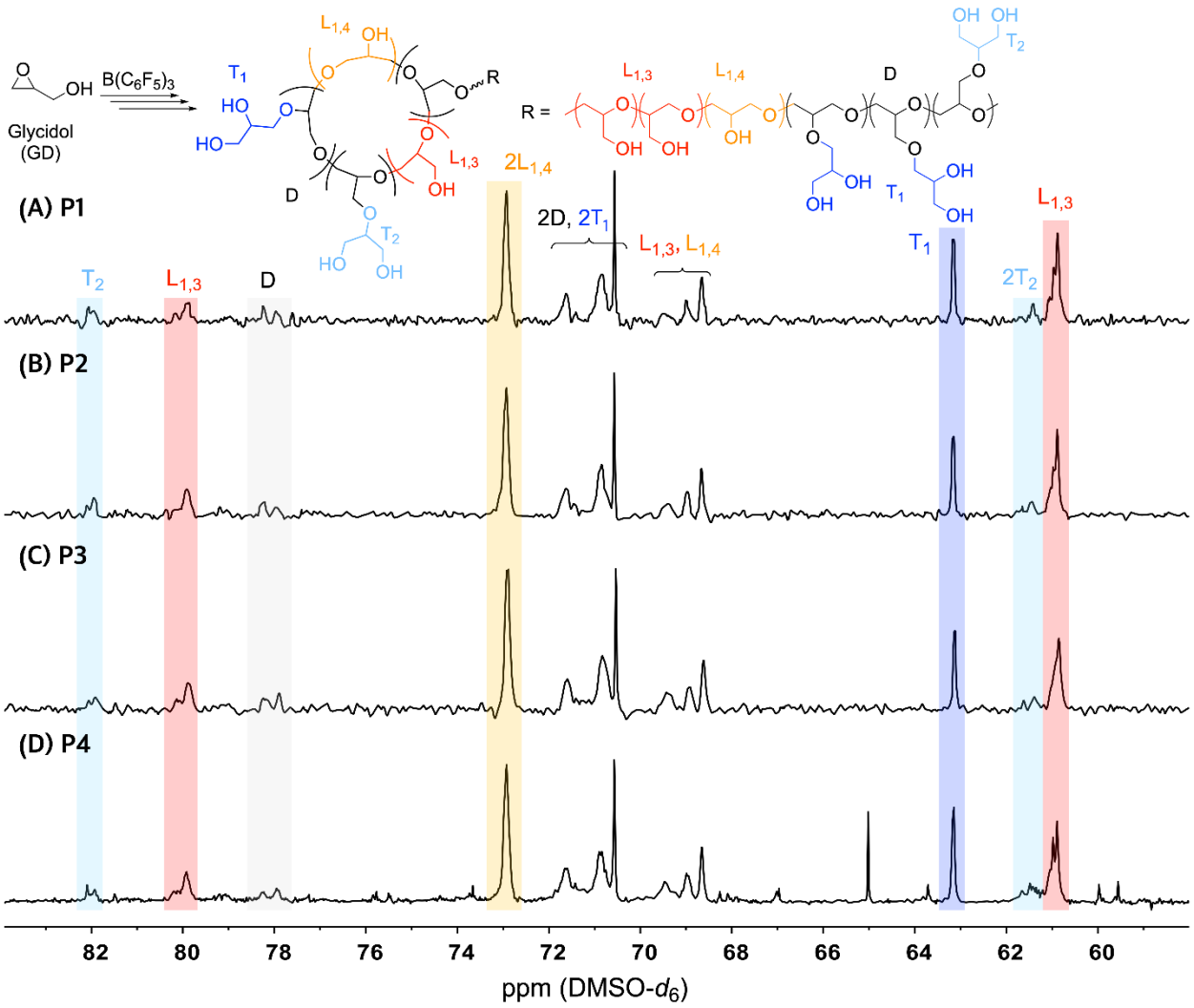

Figure S2. Inverse-gated ^{13}C NMR spectra (DMSO-d_6, room temperature) of (A) P1 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 1 mM in toluene), (B) P2 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 3 mM in toluene), (C) P3 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene), and (D) P4 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 10 mM in toluene).

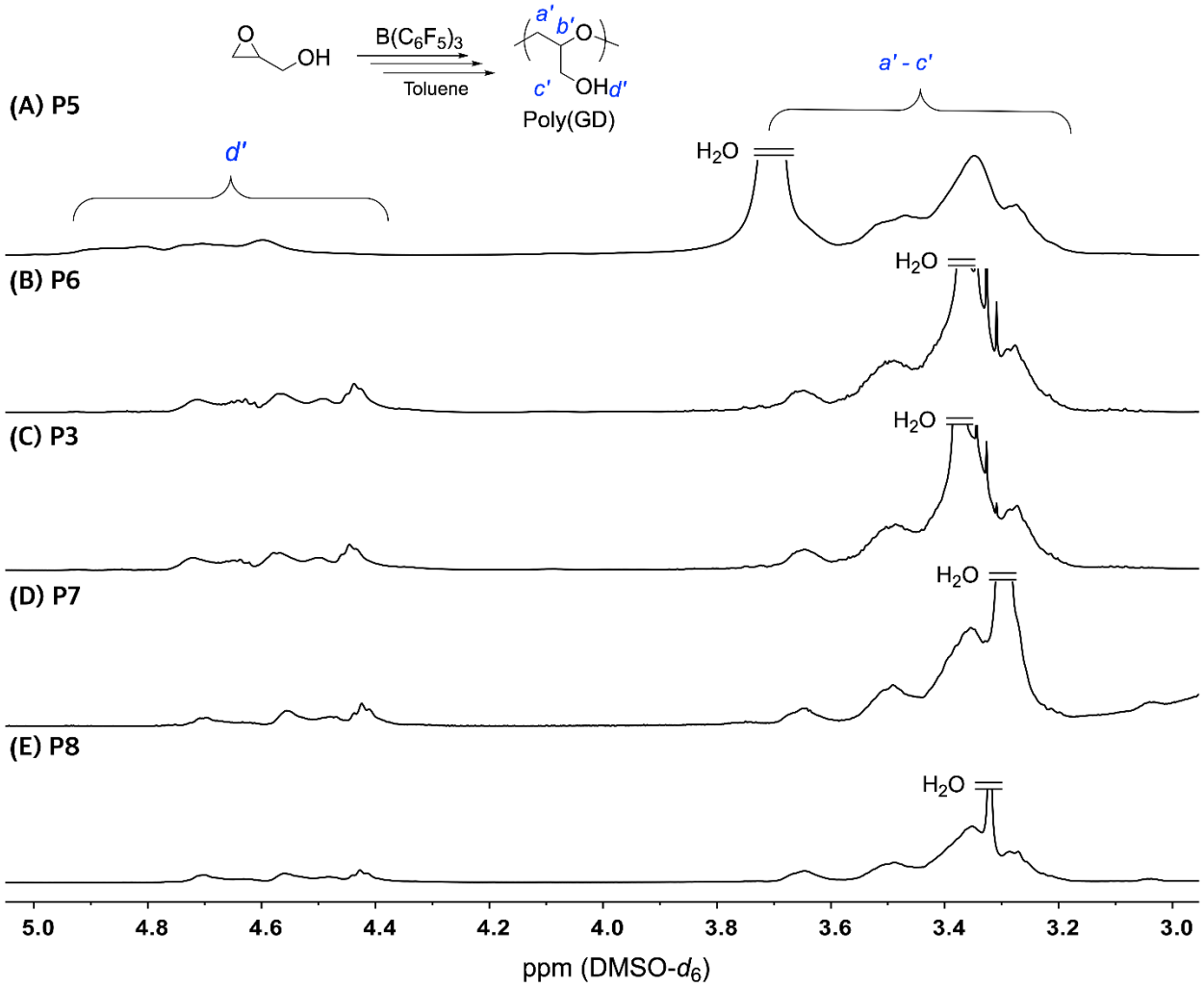

Figure S3. ^{1}H NMR spectra (DMSO-d_6, room temperature) of (A) P5 ($[GD]_0$ = 500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene), (B) P6 ($[GD]_0$ = 1000 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene), (C) P3 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene), (D) P7 ($[GD]_0$ = 5000 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene), and (E) P8 ($[GD]_0$ = 10000 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene).

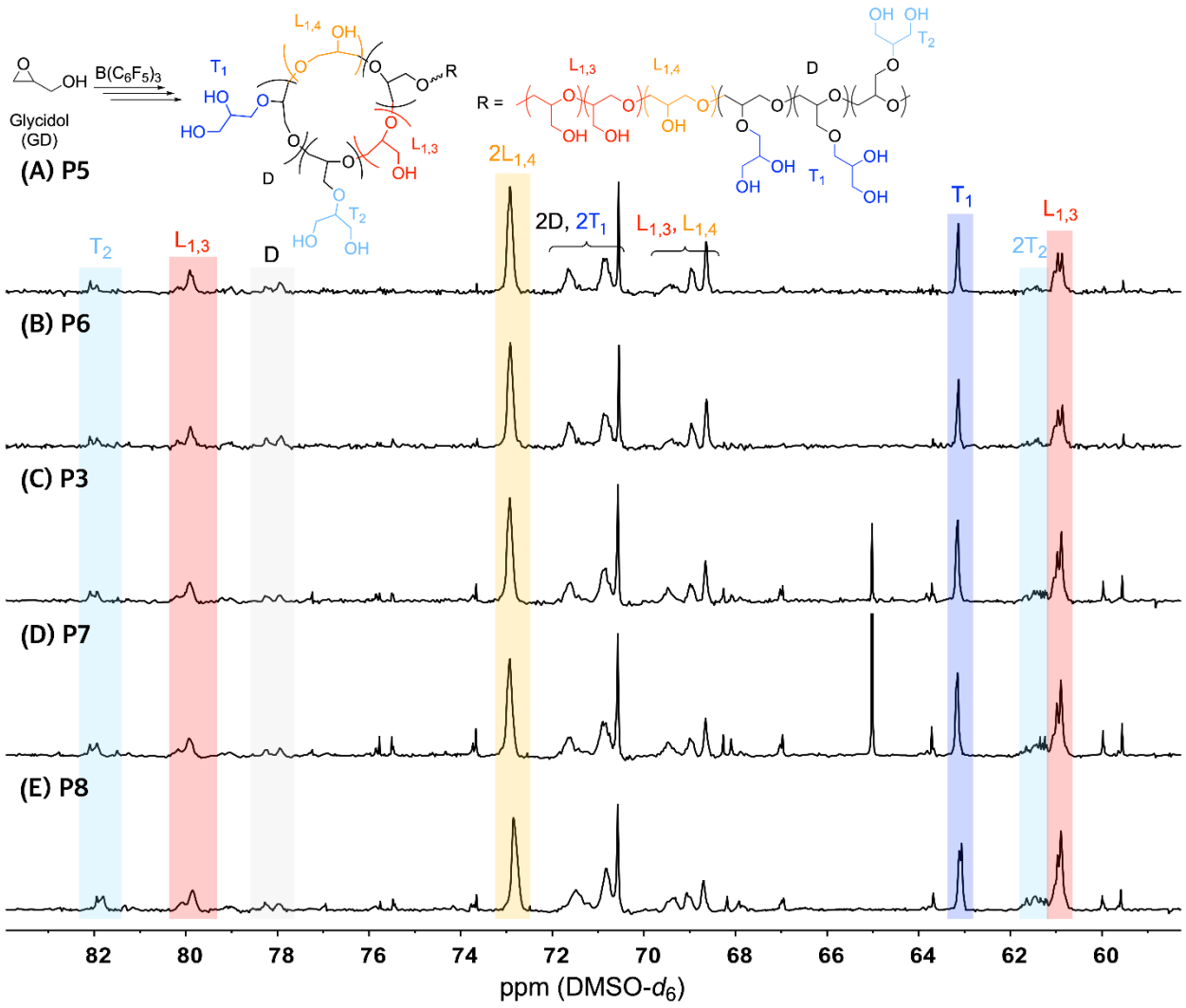

Figure S4. Inverse-gated ^{13}C NMR spectra (DMSO-d_6, room temperature) of (A) P5 ($[GD]_0 = 500$ mM; $[B(C_6F_5)_3]_0 = 5$ mM in toluene), (B) P6 ($[GD]_0 = 1000$ mM; $[B(C_6F_5)_3]_0 = 5$ mM in toluene), (C) P3 ($[GD]_0 = 2500$ mM; $[B(C_6F_5)_3]_0 = 5$ mM in toluene), (D) P7 ($[GD]_0 = 5000$ mM; $[B(C_6F_5)_3]_0 = 5$ mM in toluene), and (E) P8 ($[GD]_0 = 10000$ mM; $[B(C_6F_5)_3]_0 = 5$ mM in toluene).

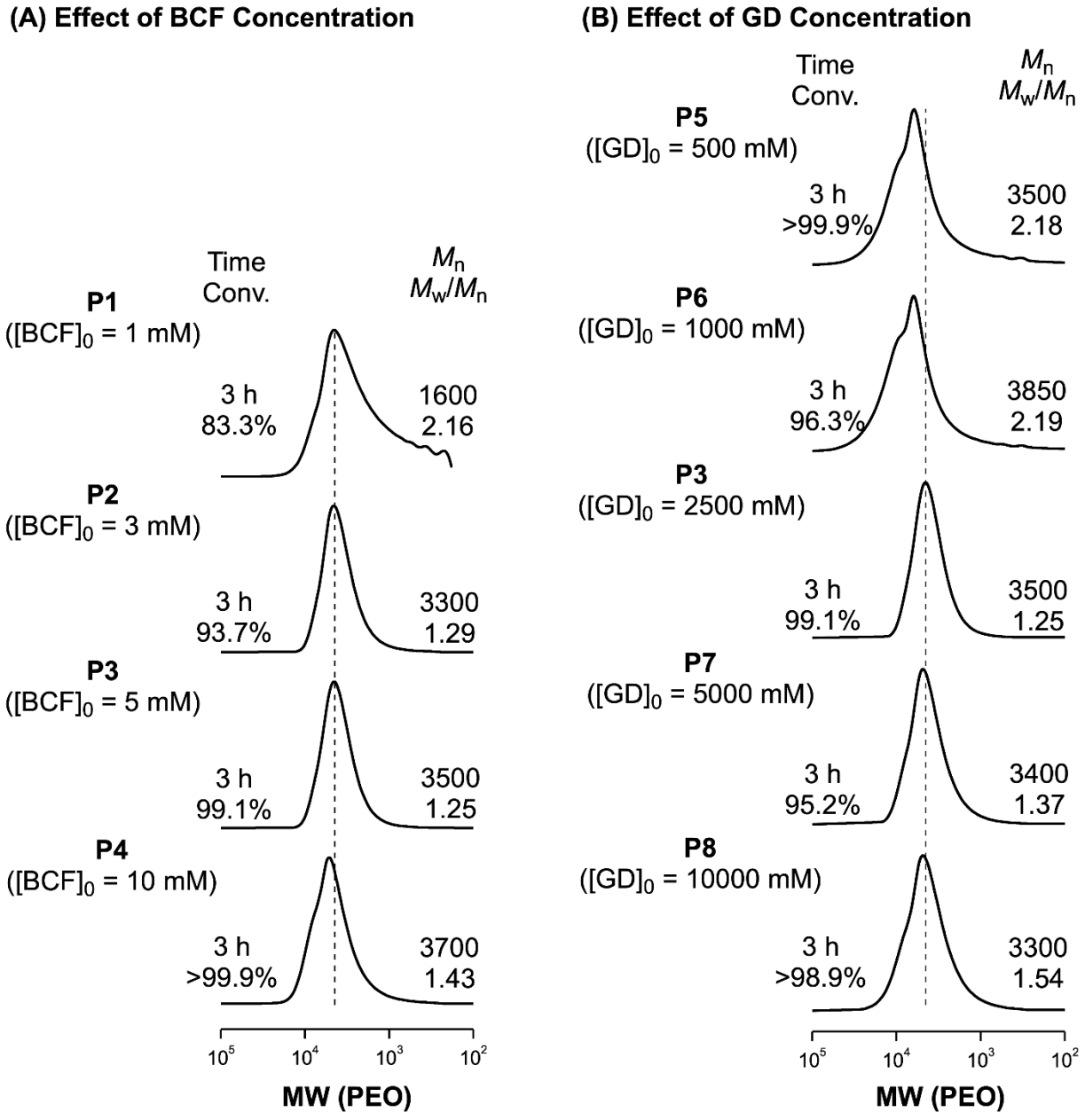

Figure S5. SEC curves of BC-PGDs obtained via the metal-free CROP of GD for studying the effects of the polymerization parameters: (A) BCF concentration ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 1, 3, 5, or 10 mM in toluene at −40 °C) and (B) GD concentration ($[GD]_0$ = 500, 1000, 2500, 5000, or 10,000 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene at −40 °C).

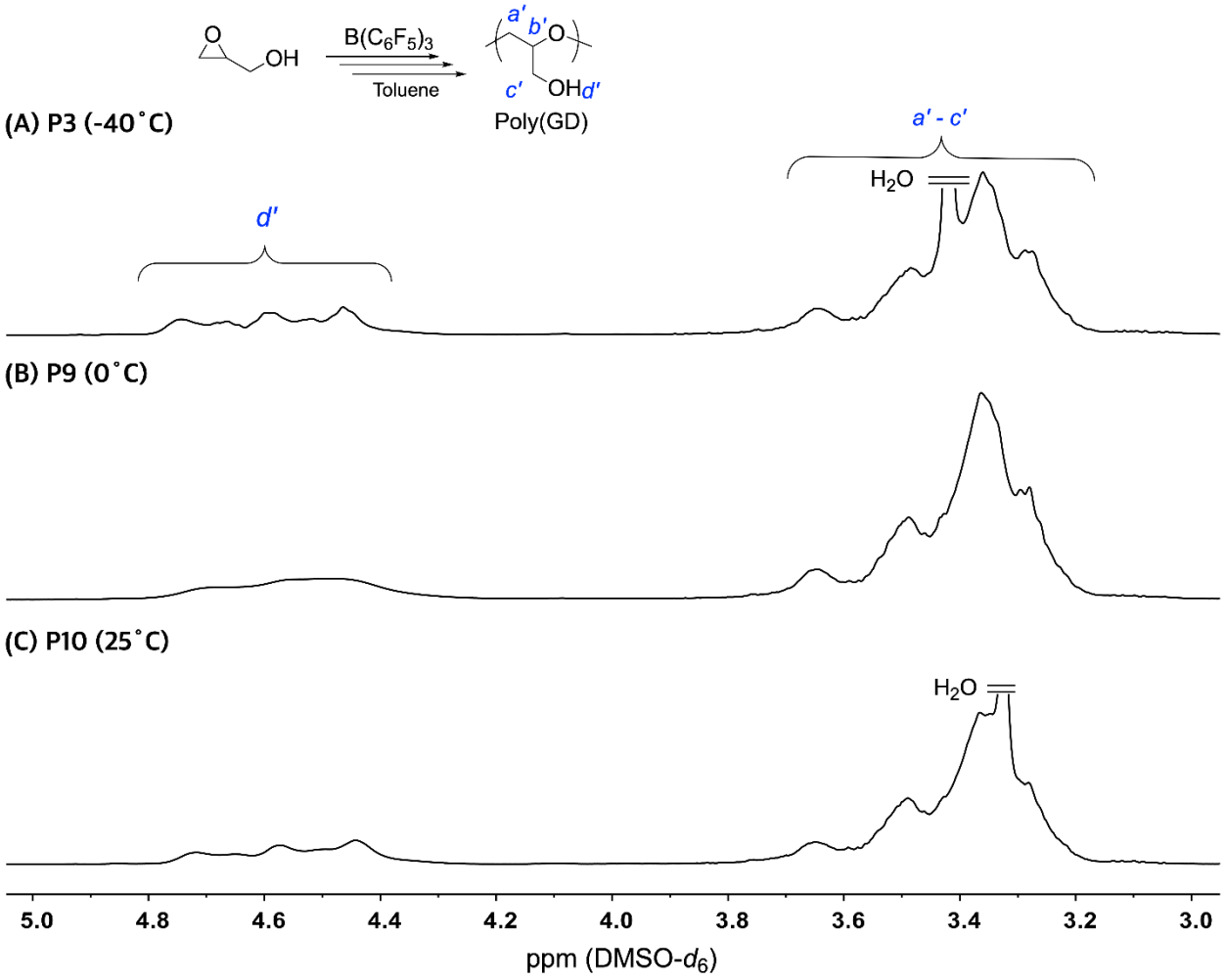

Figure S6. ^{1}H NMR spectra (DMSO-d_6, room temperature) of (A) P3 ([GD]$_0$ = 2500 mM; [B(C$_6$F$_5$)$_3$]$_0$ = 5 mM in toluene at −40 °C), (B) P9 ([GD]$_0$ = 2500 mM; [B(C$_6$F$_5$)$_3$]$_0$ = 5 mM in toluene at 0 °C), and (C) P10 ([GD]$_0$ = 2500 mM; [B(C$_6$F$_5$)$_3$]$_0$ = 5 mM in toluene at 25 °C).

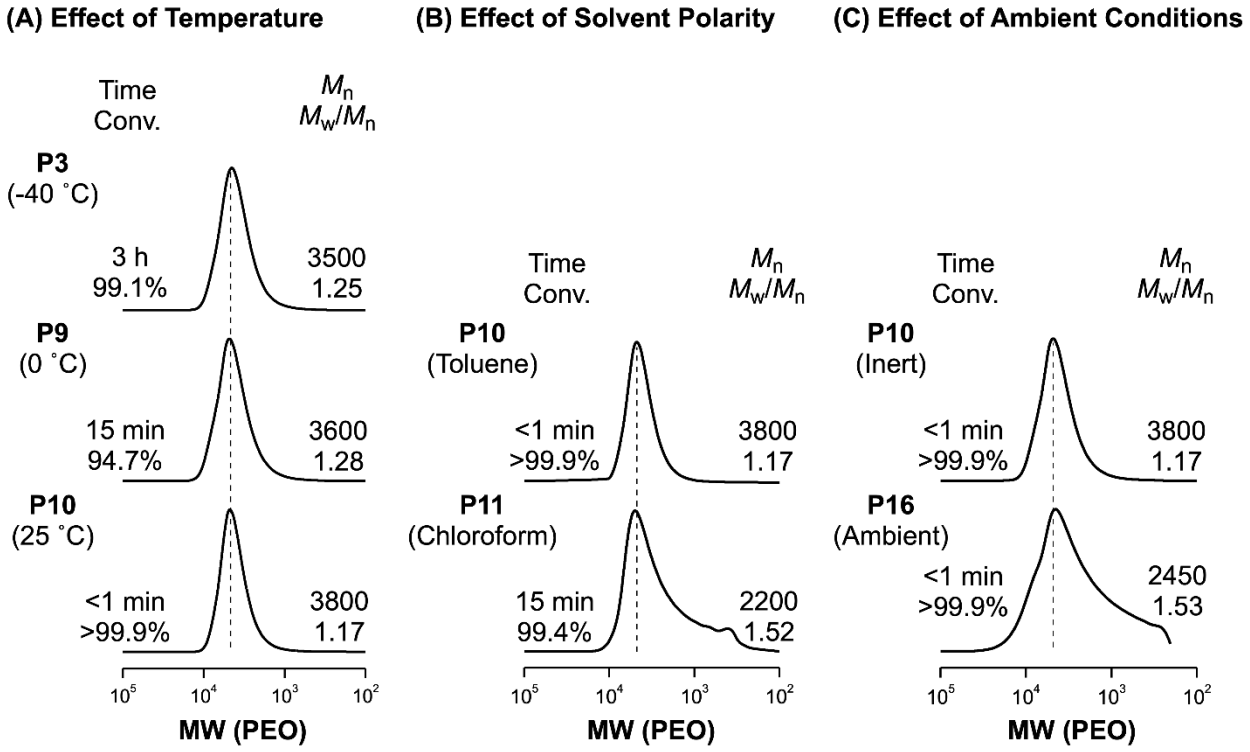

Figure S7. SEC curves of BC-PGDs obtained via the metal-free CROP of GD for studying the effects of the polymerization parameters: (A) reaction temperatures ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene at −40, 0, 25 °C), (B) solvent polarity ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene or chloroform at 25 °C), and (C) ambient conditions ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene at 25 °C under inert atmosphere using purified GD and toluene or under ambient conditions using unpurified GD and toluene).

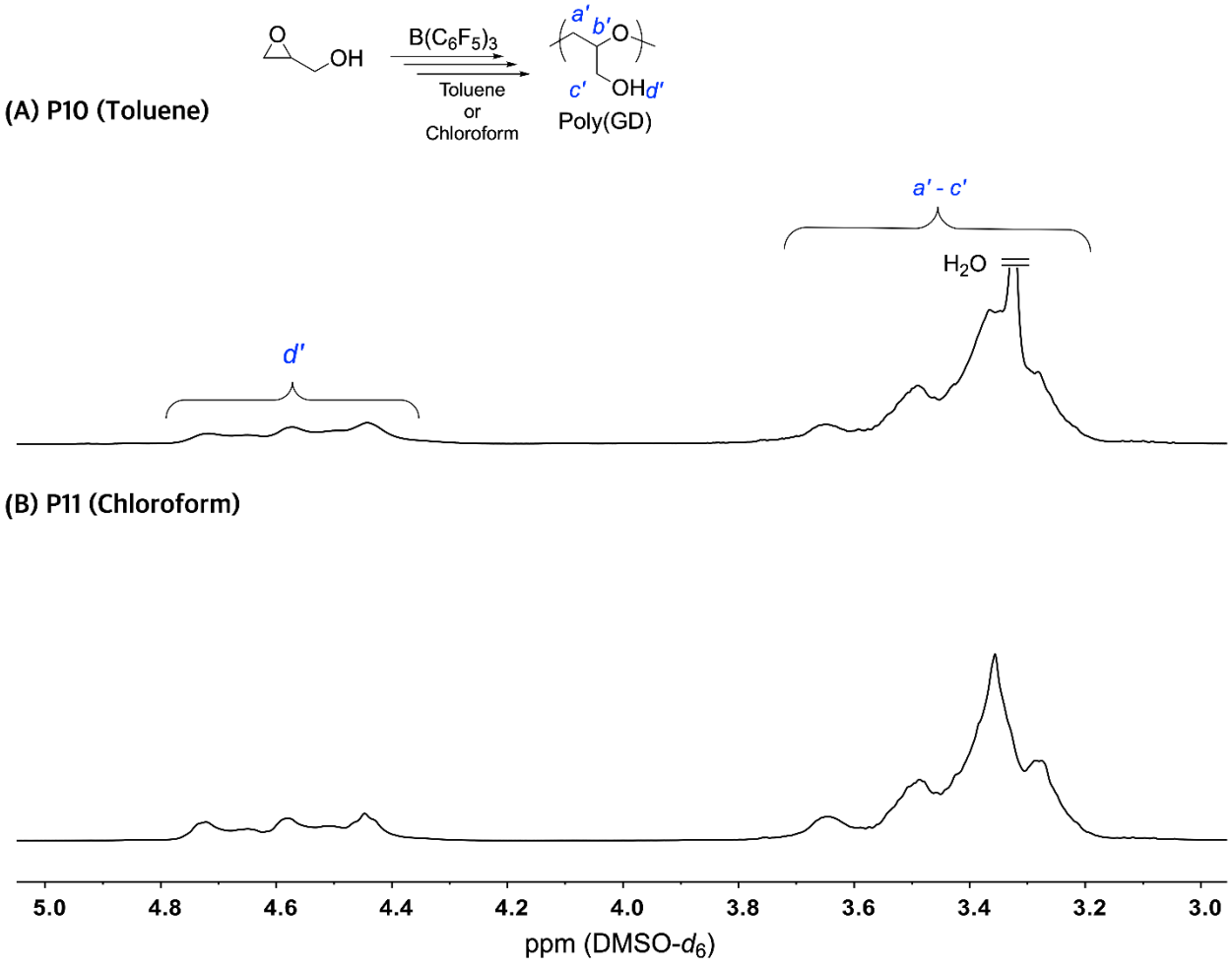

Figure S8. ^{1}H NMR spectra (DMSO-d_6, room temperature) of (A) P10 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene at 25 °C) and (B) P11 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in chloroform at 25 °C).

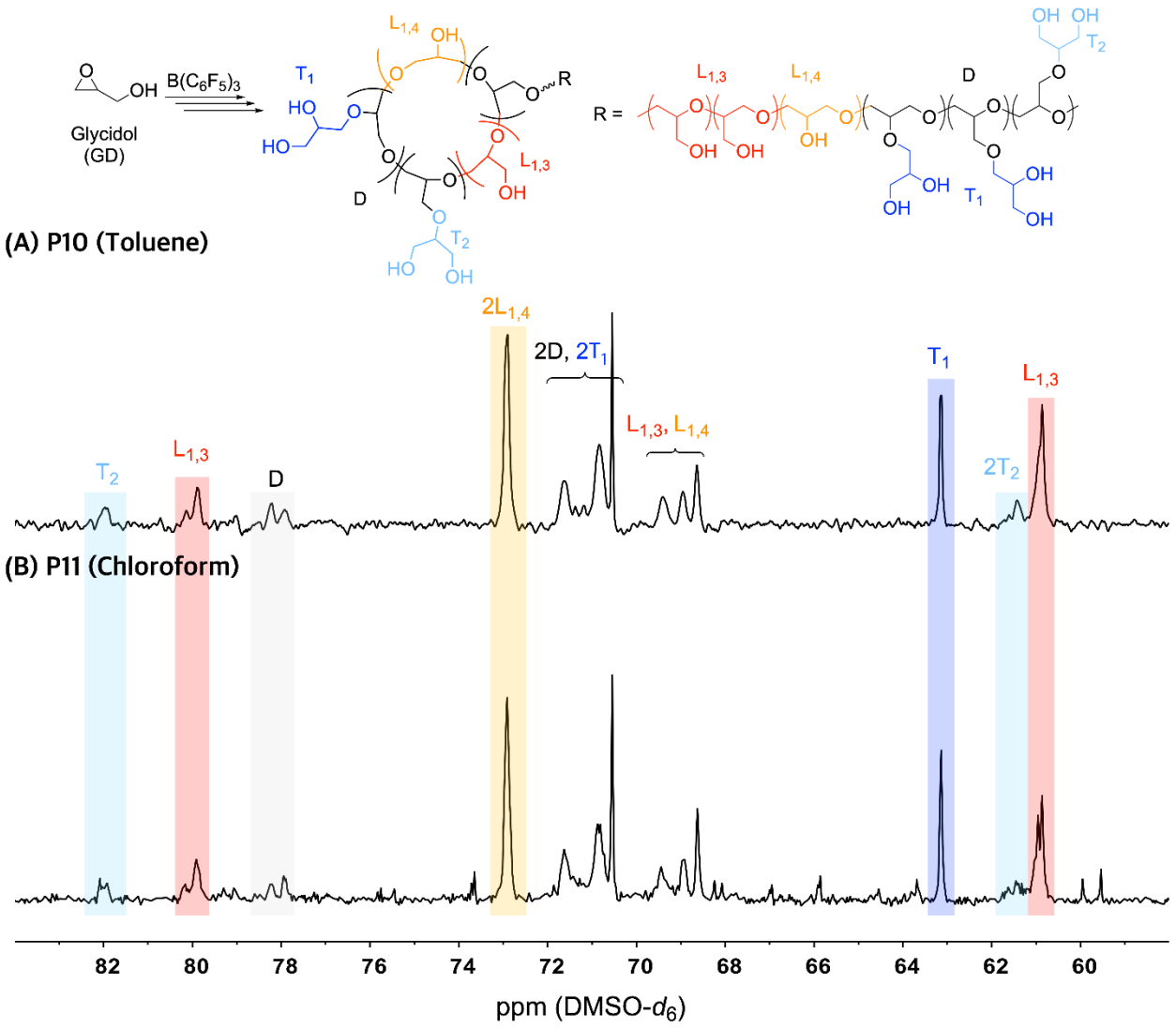

Figure S9. Inverse-gated ^{13}C NMR spectra (DMSO-d_6, room temperature) of (A) P10 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene at 25 °C) and (B) P11 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in chloroform at 25 °C).

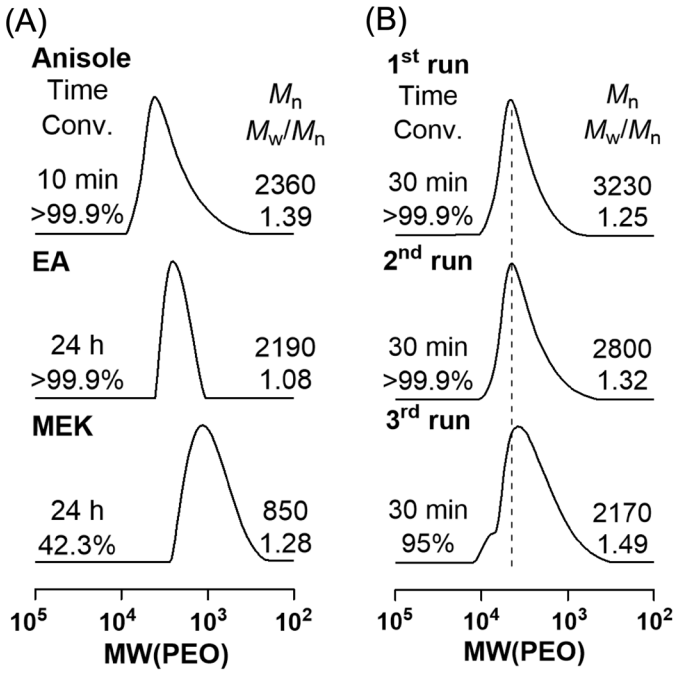

Figure S10. SEC curves of (A) BC-PGDs obtained via the metal-free CROP of GD in green solvents and (B) recyclable polymerization in anisole (1^{st} polymerization: $[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM at 25 °C; 2^{nd}-3^{rd} polymerization: $[GD]_{add}$ = 2500 mM).

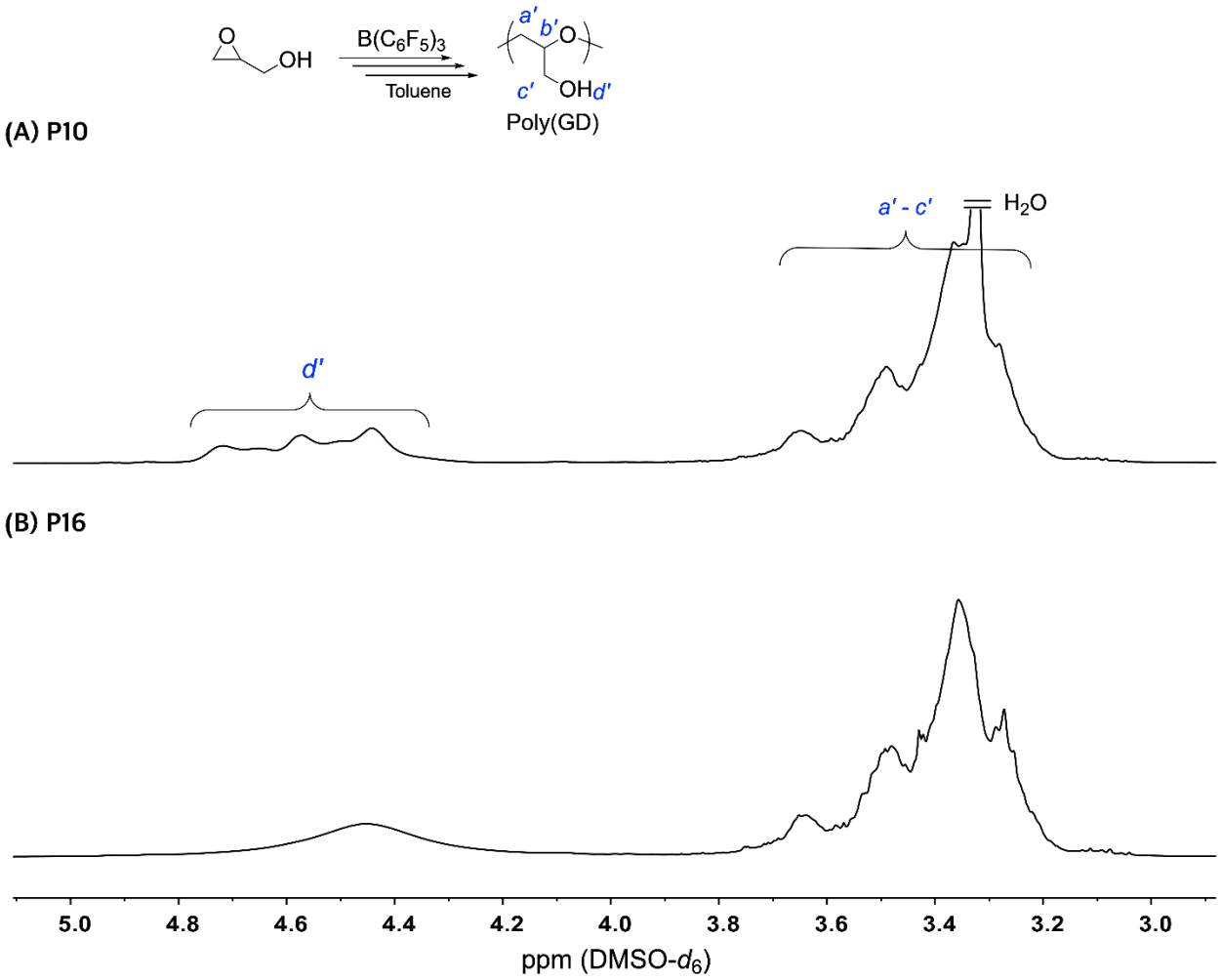

Figure S11. ^{1}H NMR spectra (DMSO-d_6, room temperature) of (A) P10 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene under inert conditions) and (B) P16 ($[GD]_0$ = 2500 mM; $[B(C_6F_5)_3]_0$ = 5 mM in toluene under ambient conditions using unpurified GD and toluene).

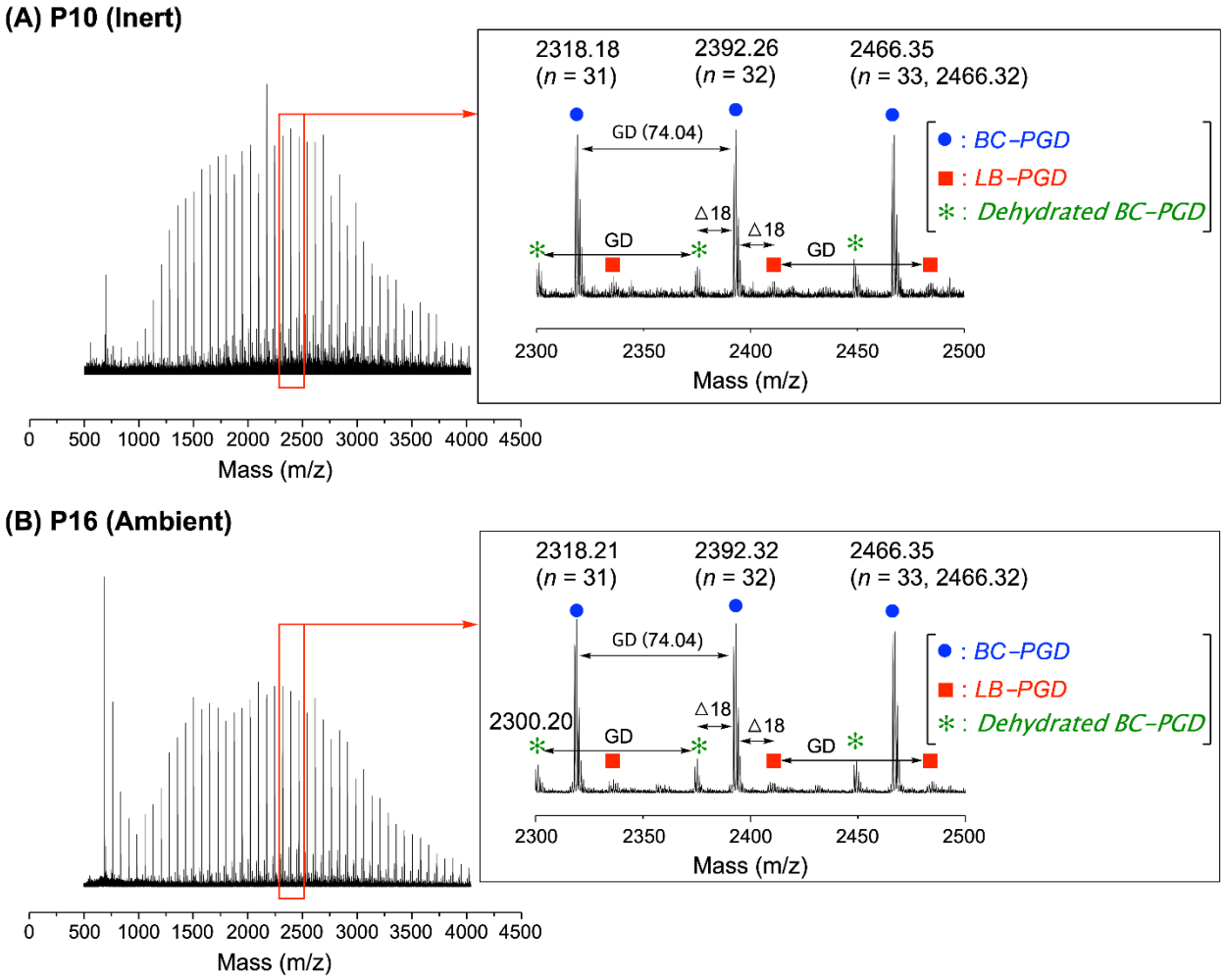

Figure S12. MALDI-TOF mass spectrum of (A) P10 (prepared under inert conditions with purified GD and solvent) and (B) P16 (prepared under ambient conditions using unpurified GD and solvent).

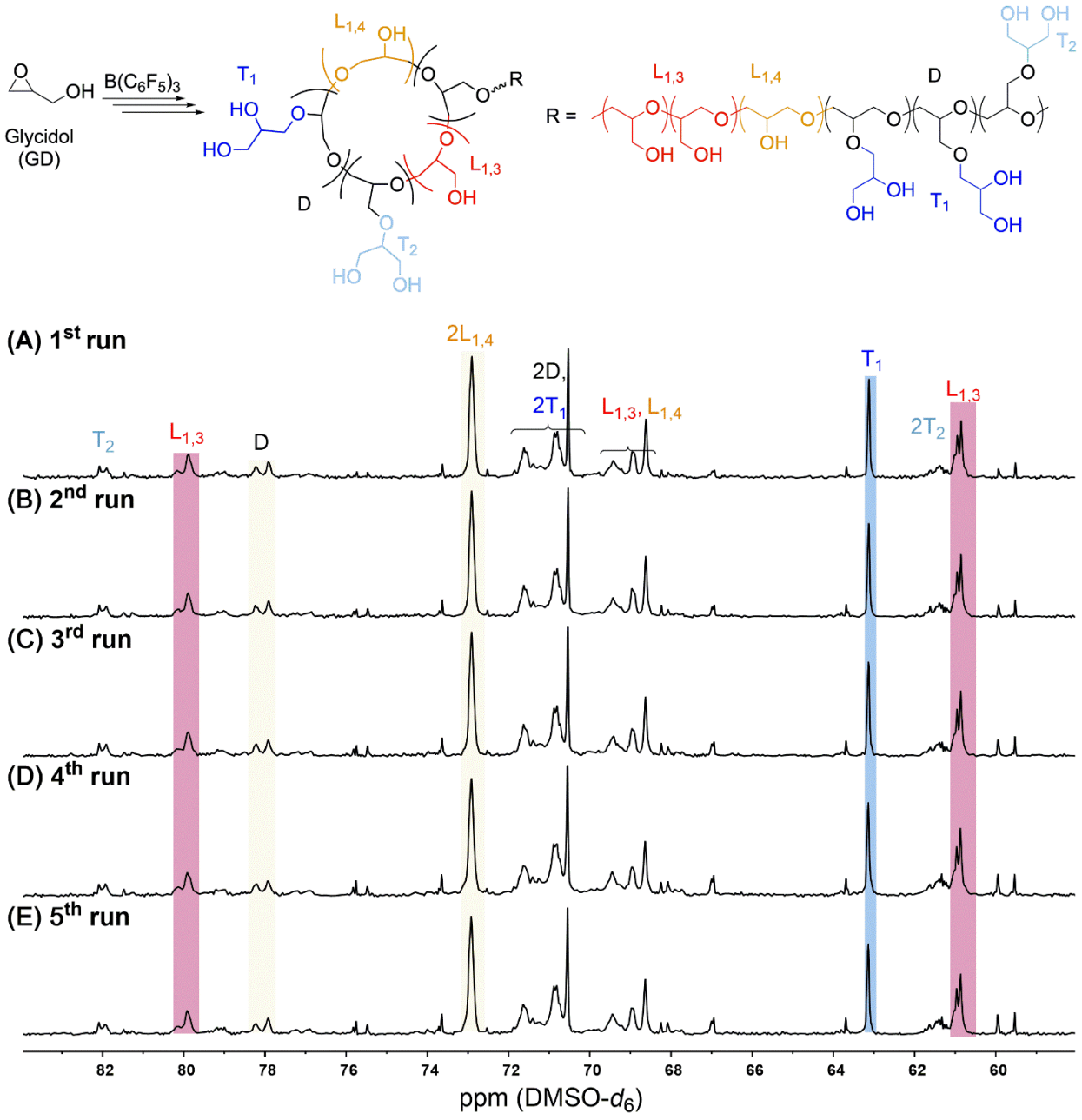

Figure S13. Inverse-gated ^{13}C NMR spectra (DMSO-d_6, room temperature) of the obtained PGDs from the (A) first, (B) second, and (C) third polymerizations under ambient conditions using unpurified GD and solvent.

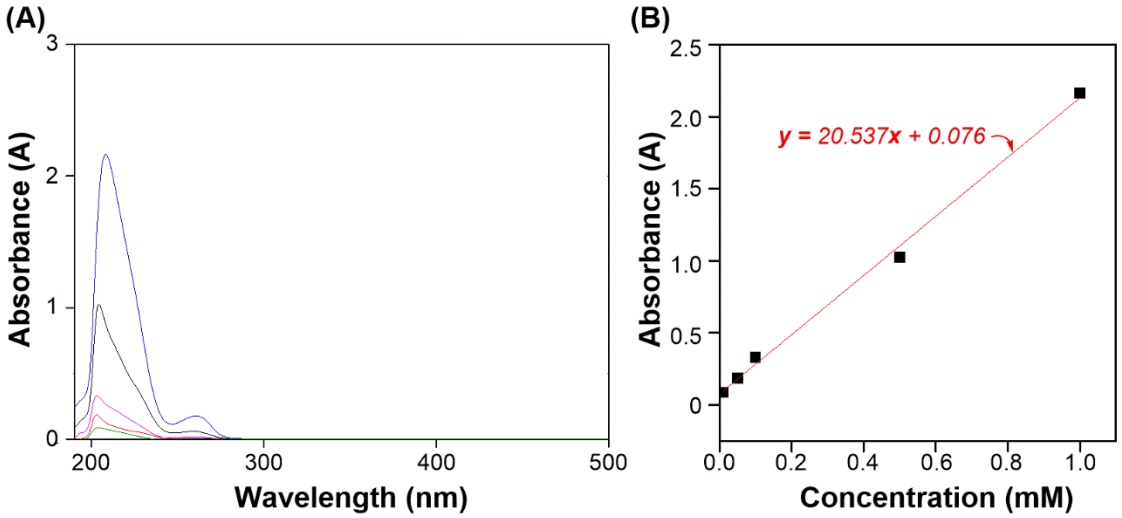

Figure S14. (A) Absorption spectra of BCF solution from 0.005 mM to 0.1 mM in methanol and (B) the calibration curve depending on the BCF concentration.

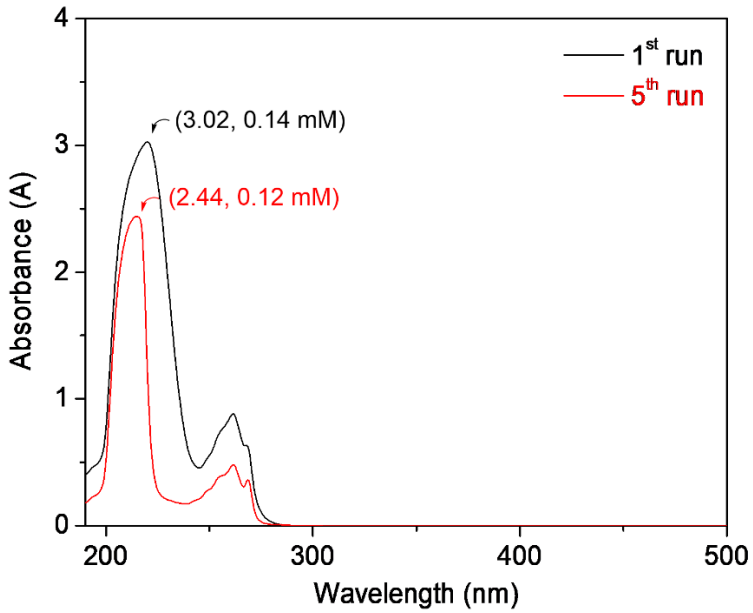

Figure S15. Absorption spectra of the obtained PGDs from the first and fifth polymerizations (10 mg/mL in methanol).

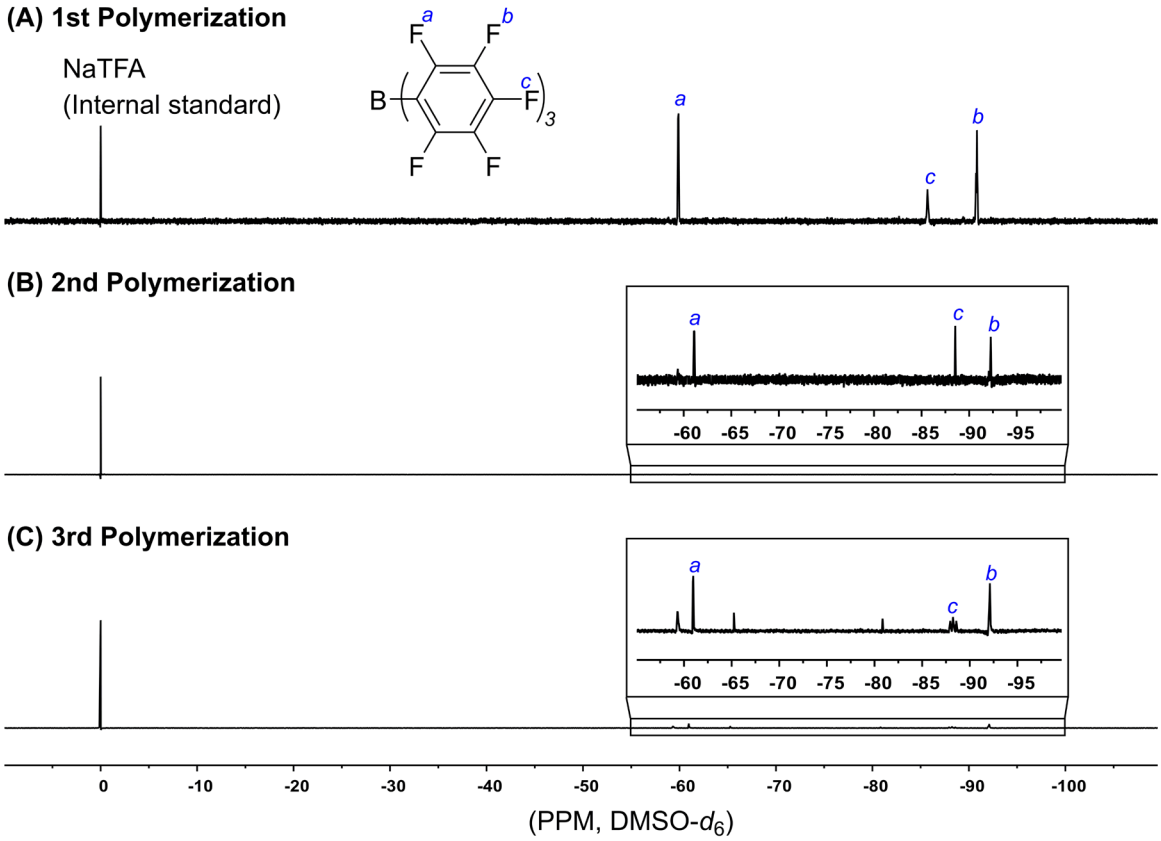

Figure S16. ^{19}F NMR spectra of PGDs collected from recyclable polymerization (200 mg/mL PGD with 0.29 mM Na-TFA).

Table S1. Effects of reaction temperature and ambient conditions on the polymer structure.[a, b]

Region	Chemical shift (ppm)	P3 (−40 °C)	P9 (0 °C)	P10 (25 °C)	P16 (25 °C)[c]
$L_{1,3}$	60.6–61.2	6.23	4.64	4.53	4.21
$2T_2$	61.2–61.8	1.23	1.99	1.43	2.23
T_1	63.0–63.3	3.33	2.51	2.35	2.32
$L_{1,3}$, $L_{1,4}$	68.5–69.7	6.02	5.56	5.84	5.15
2D, $2T_1$	70.4–72.0	13.82	12.21	11.49	11.02
$2L_{1,4}$	72.7–73.2	10.28	6.39	5.70	5.28
D	77.7–78.9	1.64	1.64	1.88	1.41
$L_{1,3}$	79.7–80.4	2.72	2.73	2.21	2.11
T_2	81.5–82.2	1.00	1.00	1.00	1.00
Structure units (%)[d]					
D units		**9**	**12**	**14**	**12**
L units		**66**	**61**	**59**	**59**
($L_{1,3}$ units)		(36)	(36)	(36)	(36)
($L_{1,4}$ units)		(30)	(25)	(23)	(23)
T units		**25**	**27**	**27**	**29**
(T_1 units)		(18)	(19)	(19)	(20)
(T_2 units)		(7)	(8)	(8)	(9)
Degree of Branching[e]		**0.34**	**0.39**	**0.41**	**0.41**

[a]$[GD]_0$ = 2500 mM, $[B(C_6F_5)_3]_0$ = 5 mM in toluene. [b]Obtained by inverse-gated ^{13}C NMR. [c]The polymerization was performed under ambient conditions using unpurified monomer and solvent. [d]The structure units (%) were calculated using the following equation: integration ratio of each structure region/$(D + T + L) \times 100$. [e]Degree of branching = $(D + T)/(D + T + L)$.

Table S2. Influence of the recycled polymerization solution in ambient conditions on the polymer structure.[a, b, c]

	1st run	2nd run	3rd run	4th run	5th run
Structure units (%)[d]					
D units	**11**	**10**	**11**	**11**	**11**
L units	**61**	**62**	**61**	**62**	**61**
($L_{1,3}$ units)	(32)	(34)	(32)	(32)	(31)
($L_{1,4}$ units)	(29)	(28)	(29)	(30)	(30)
T units	**28**	**28**	**28**	**27**	**28**
(T_1 units)	(23)	(23)	(22)	(22)	(22)
(T_2 units)	(5)	(5)	(5)	(5)	(6)
Degree of Branching[e]	**0.40**	**0.39**	**0.39**	**0.37**	**0.39**

[a] $[GD]_0$ = 500 mM, $[B(C_6F_5)_3]_0$ = 5 mM in toluene. [b] Obtained by inverse-gated ^{13}C NMR. [c] The polymerization was performed under ambient conditions using the unpurified monomer and solvent. [d] The structure units (%) were calculated using the following equation: integration ratio of each structure region/($D + T + L$) × 100. [e] Degree of branching (DB) = ($D + T$)/($D + T + L$).