Supporting Information

Kinetic and Mechanistic Study of Heterogeneous Double Metal Cyanide-Catalyzed Ring-Opening Multibranching Polymerization of Glycidol

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Contents

1. Experimental section

1.1 Materials

Potassium hexacyanocobaltate(III) (K3[Co(CN)6]; ≥97%), diethylmalonate (DEM ; 99%), ethyl acetoacetate (EAA; 99%), anhydrous tert-butyl alcohol (TBA; ≥99.5%), and Pluronic P-123 (molecular weight (MW) = 5800) all purchased from Sigma-Aldrich, anhydrous zinc chloride (>98%) obtained from Alfa Aesar and were used as received. Glycidol (96%) obtained from Sigma-Aldrich was dried over calcium hydride (CaH_2) and distilled in vacuum directly prior to use.

1.2 Preparation of DMC Catalysts

The catalysts used in this work was prepared with the same procedure used in our recent work (Tran, C. H.; Pham, L. T. T.; Lee, Y.; Jang, H. B.; Kim, S.; Kim, I. Mechanistic Insights on Zn(II)−Co(III) Double Metal Cyanide-Catalyzed Ring-Opening Polymerization of Epoxides. J. Catal. 2019, 372, 86−102). A series of DMC catalysts was prepared using $ZnCl_2$ as a metal salt and $K_3[Co(CN)_6]$ as a metal cyanide salt in the presence of P123 as a co-complexing agent (co-CA) and a CA selected from the following β-dicarbonyl compounds such as DEM and EAA. For example, in one sampling bottle, $ZnCl_2$ (1.23 g, 9 mmol) was dissolved in distilled water (2.5 mL), and DEM (2.5 mL, 16.5 mmol) was added (solution 1). In a second sampling bottle, $K_3[Co(CN)_6]$ (0.5 g, 1.5 mmol) was dissolved in distilled water (2.5 mL) (solution 2). Solution 2 was added to solution 1 with vigorous stirring for 30 min at 50 °C. A mixture of DEM (1 mL, 6.6 mmol) and P123 (0.1 g, 0.017 mmol) was then added; the mixture was stirred for 10 min; and the resulting suspension was separated from the solution by centrifugation (×6,000). Alternate re-slurry using water/DEM and DEM/P123, and centrifugation steps were repeated two more times (total amount of DEM is 69 mmol). Then, the obtained catalyst slurry was washed twice with 10 mL of distilled water to remove unreacted $ZnCl_2$ and the wet catalyst cake isolated by centrifugation was dried at 85 °C under vacuum for 6 h to a constant weight. This catalyst is identified as DMC-DEM. Similarly, DMC-EAA and DMC-TBA were prepared using EAA and TBA as CAs, respectively.

For comparison, DMC-pure was prepared by reacting aqueous $ZnCl_2$ with aqueous $K_3Co(CN)_6$ at 50 °C in the absence of both CAs and P123 with a same [*Zn*]/[*Co*] ratio (6:1), respectively.

2. Characterization of Catalysts

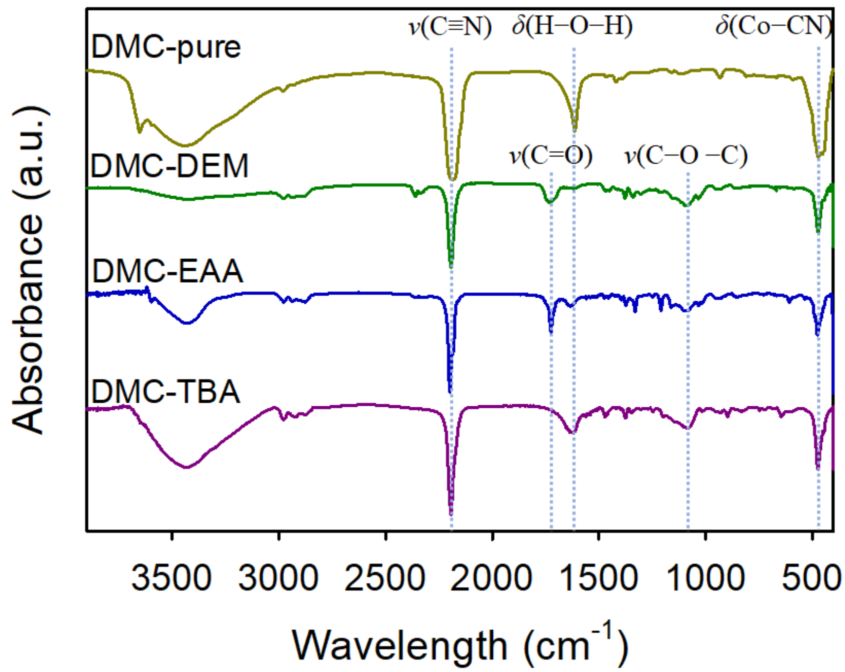

Figure S1. FTIR spectra of the prepared DMC compounds.

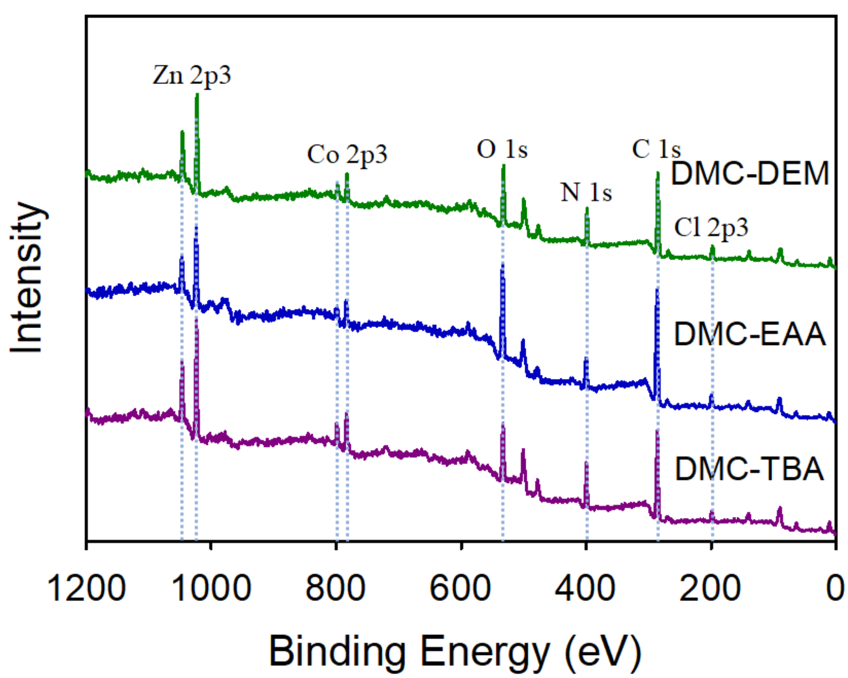

Figure S2. XPS spectra of the prepared DMC catalysts.

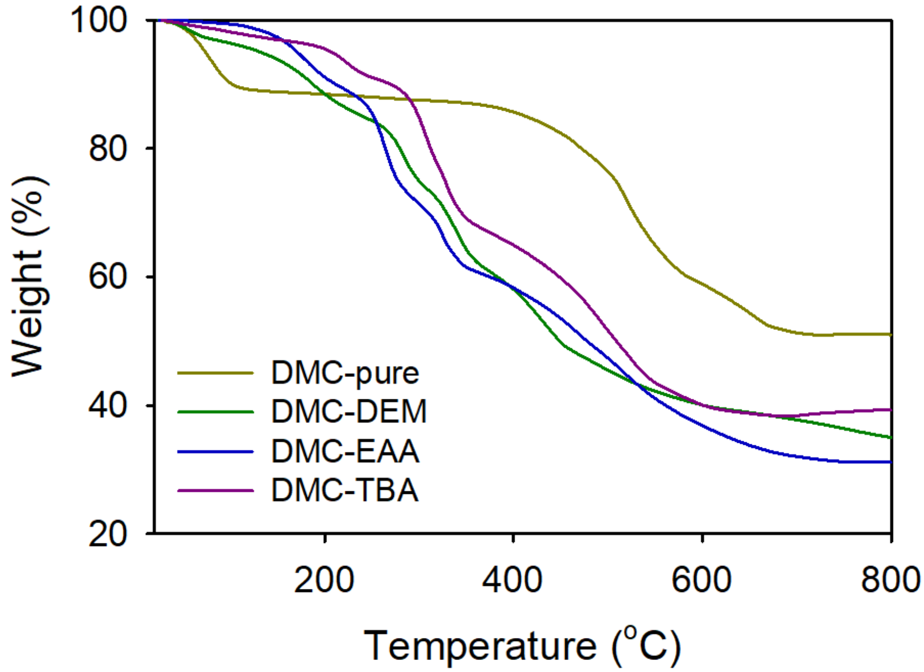

Figure S3. TGA curves of the prepared DMC compounds.

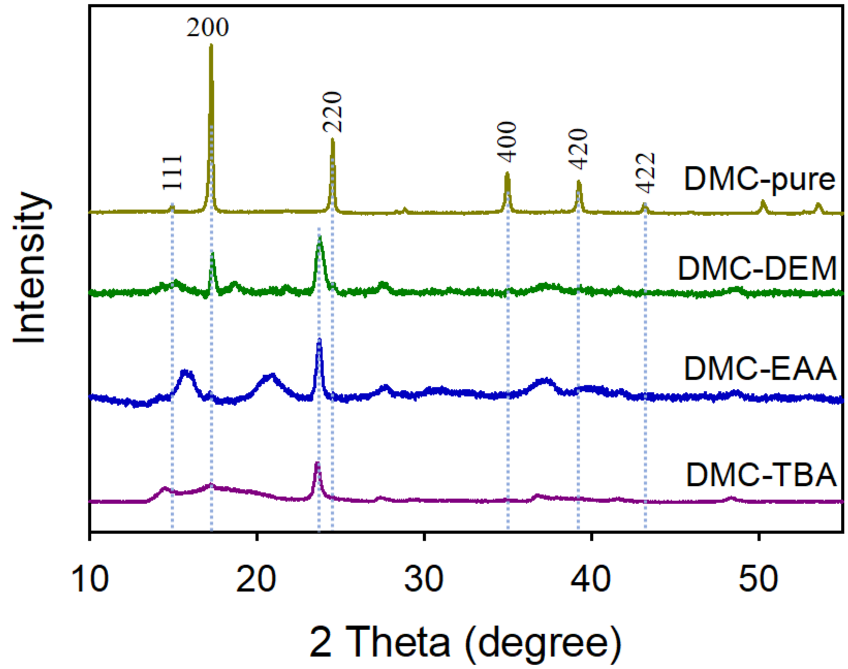

Figure S4. XRD patterns of the prepared DMC compounds.

3. Kinetics and Mechanistic of DMC-Catalyzed ROP of Glycidol

3.1 Polymerization Using Various Catalysts

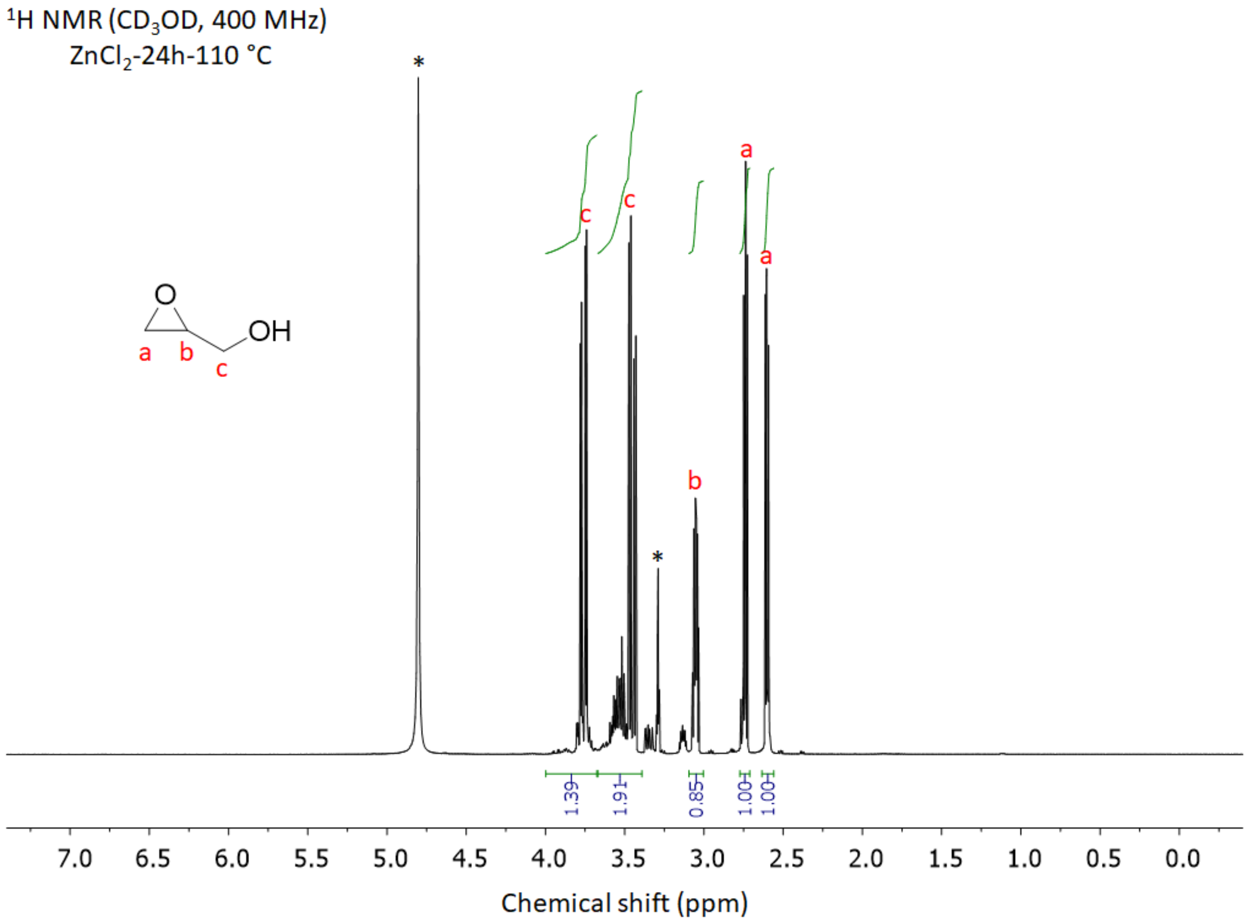

Figure S5. ^{1}H NMR spectra of the crude reaction mixture of the glycidol ROP using $ZnCl_2$ in CD_3OD (Table 1, run 1).

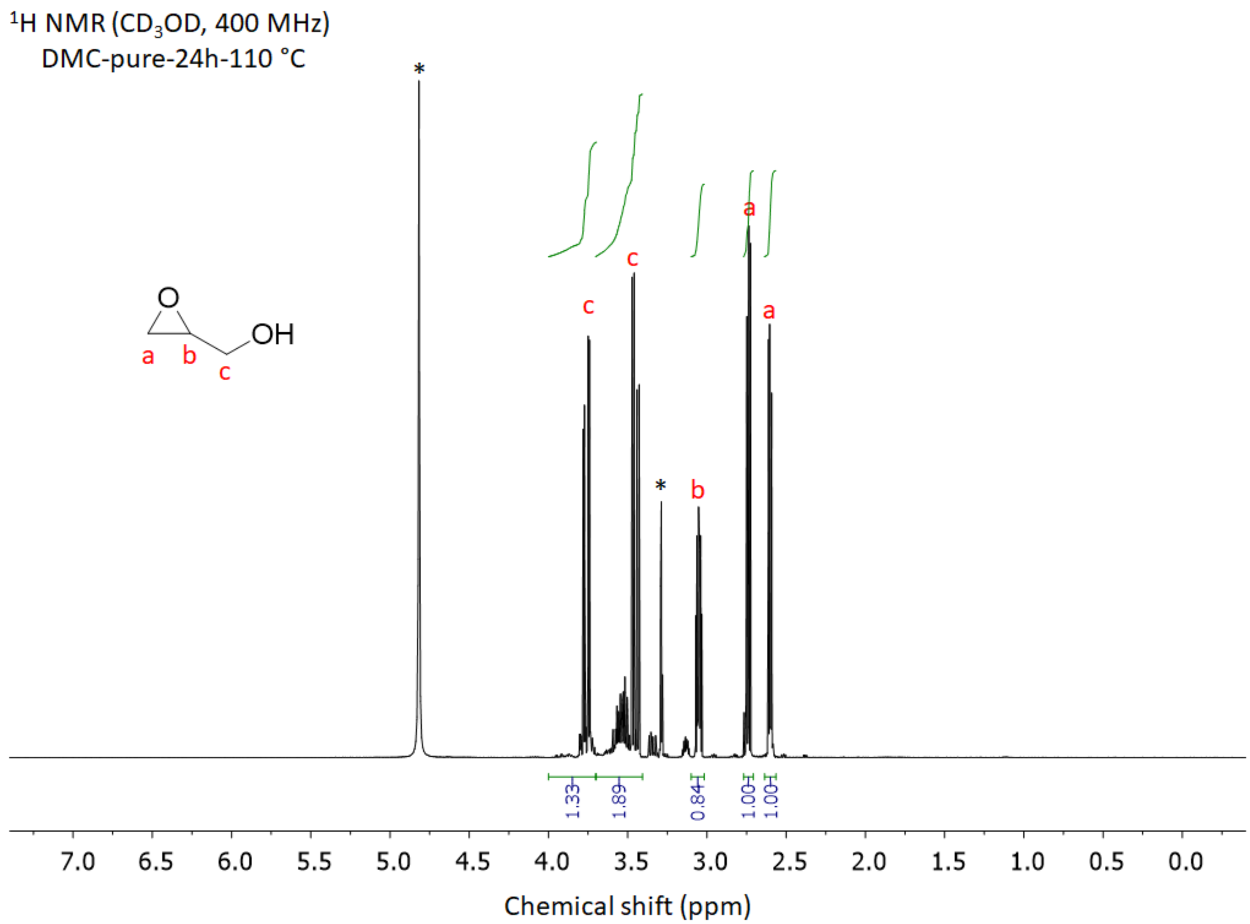

Figure S6. ^{1}H NMR spectra of the crude reaction mixture of the glycidol ROP using DMC-pure in CD_3OD (Table 1, run 3).

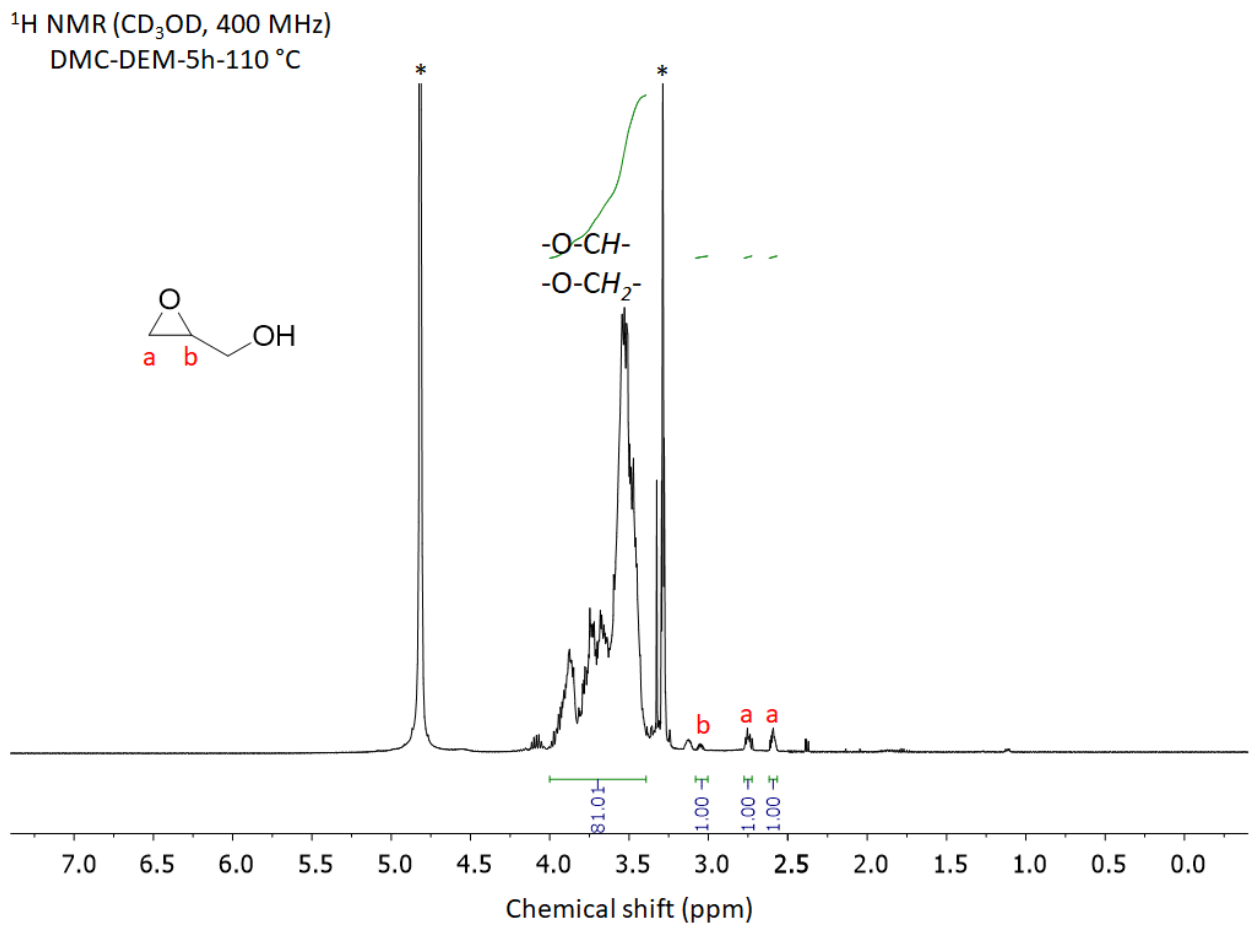

Figure S7. ^{1}H NMR spectra of the crude reaction mixture of the glycidol ROP using DMC-DEM in CD_3OD (Table 1, run 4).

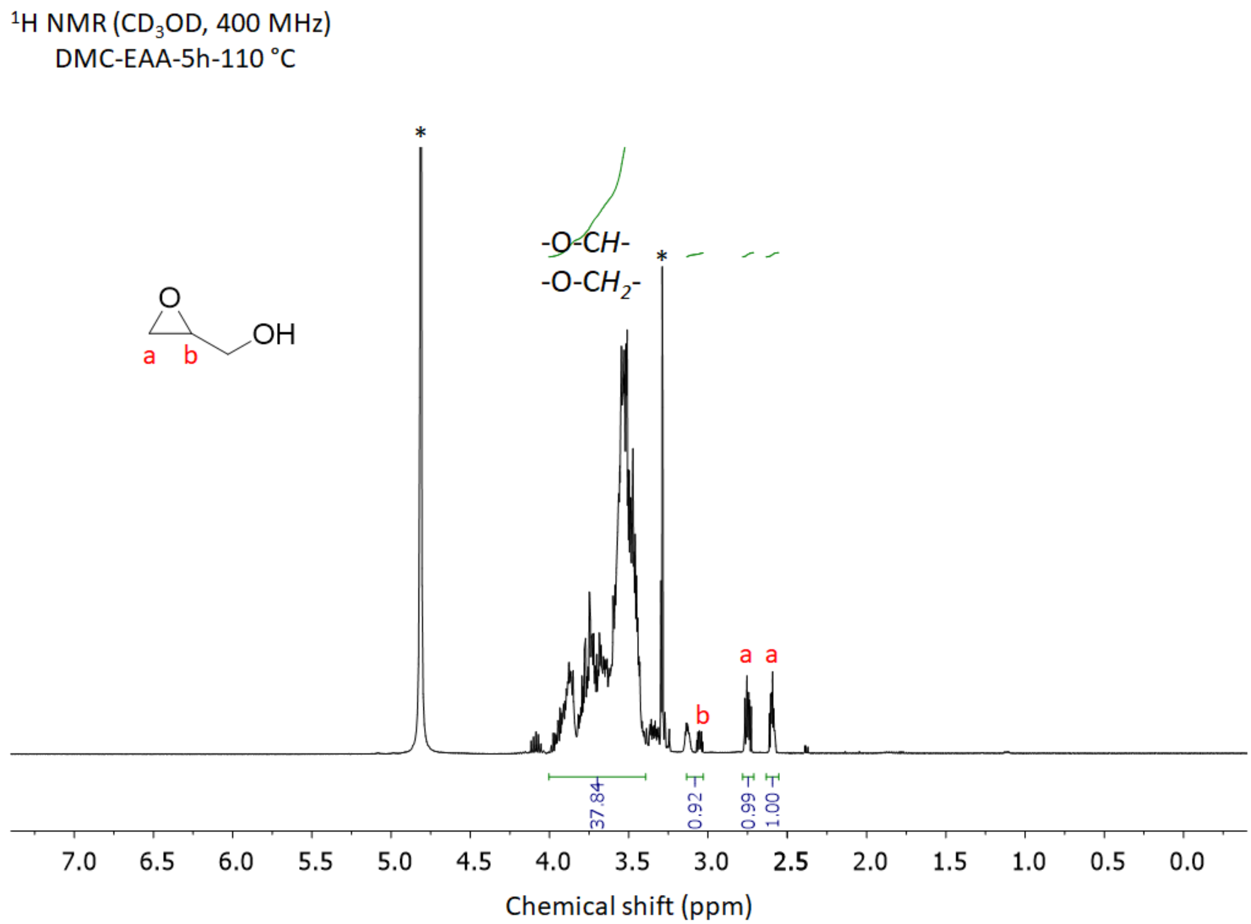

Figure S8. ^{1}H NMR spectra of the crude reaction mixture of the glycidol ROP using DMC-EAA in CD_3OD (Table 1, run 5).

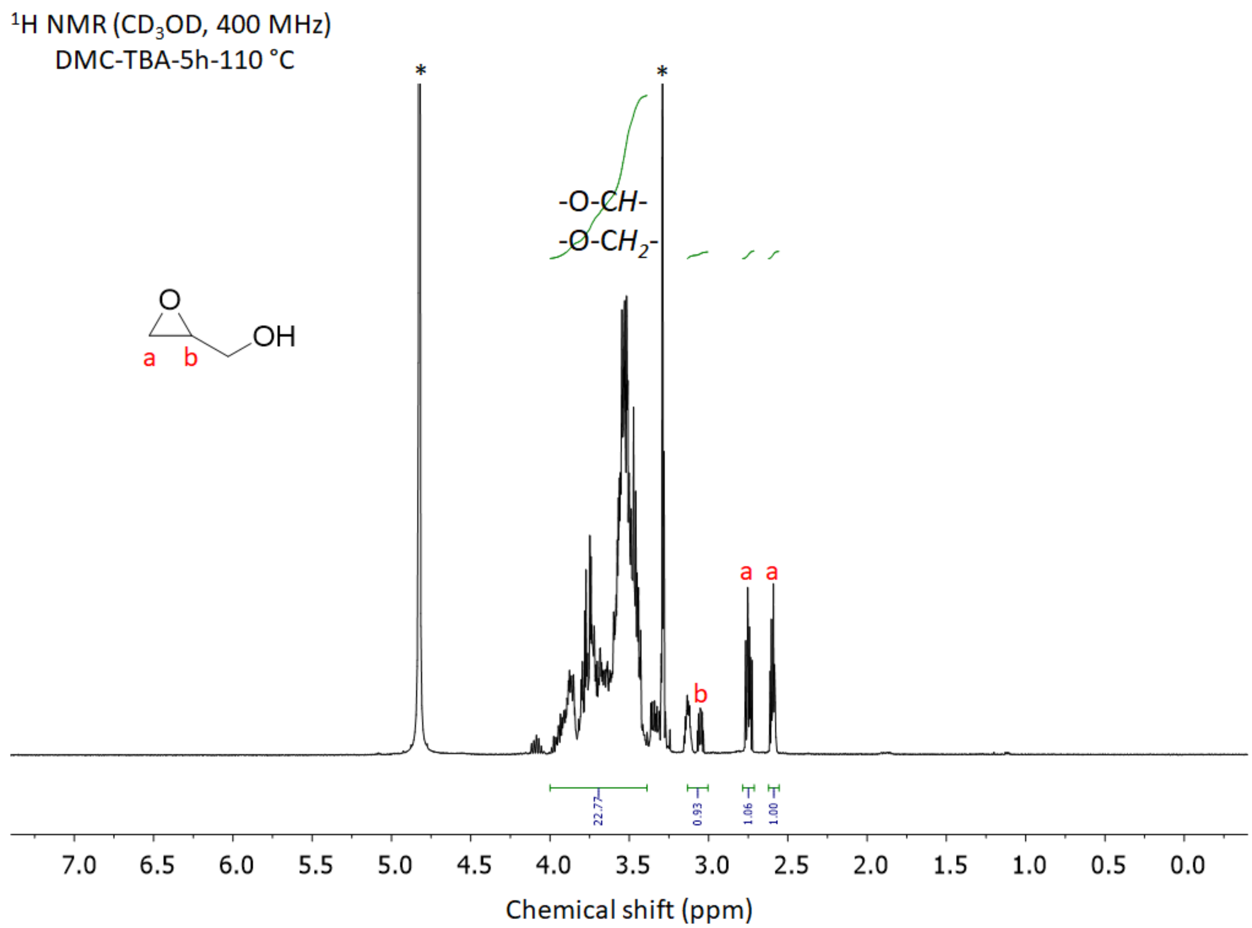

Figure S9. ^{1}H NMR spectra of the crude reaction mixture of the glycidol ROP using DMC-TBA in CD_3OD (Table 1, run 6).

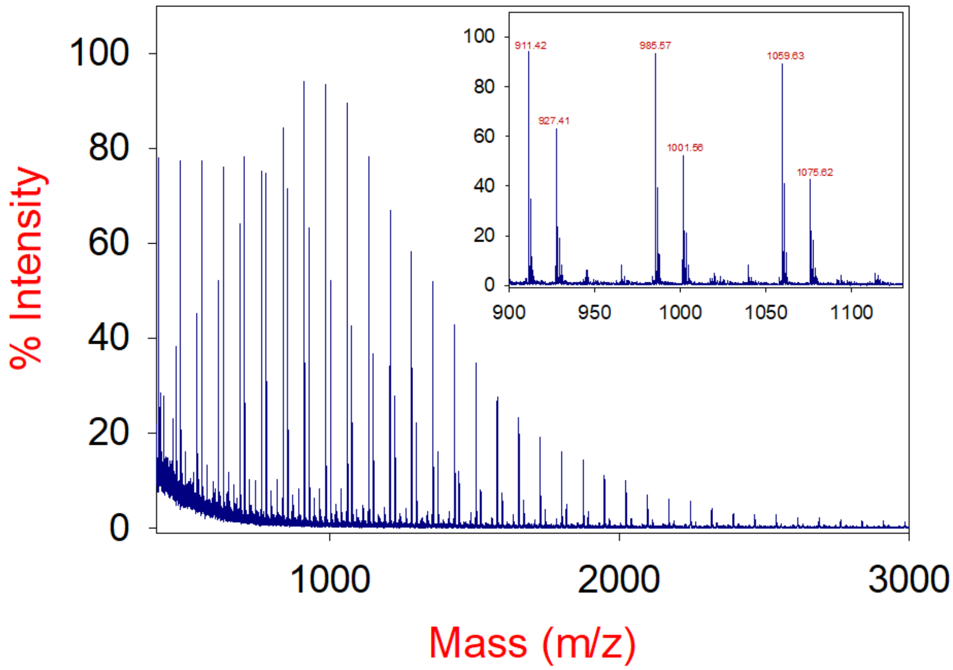

Figure S10. MALDI-TOF spectra of the SBPG produced by DMC-EAA (Table 1, run 5).

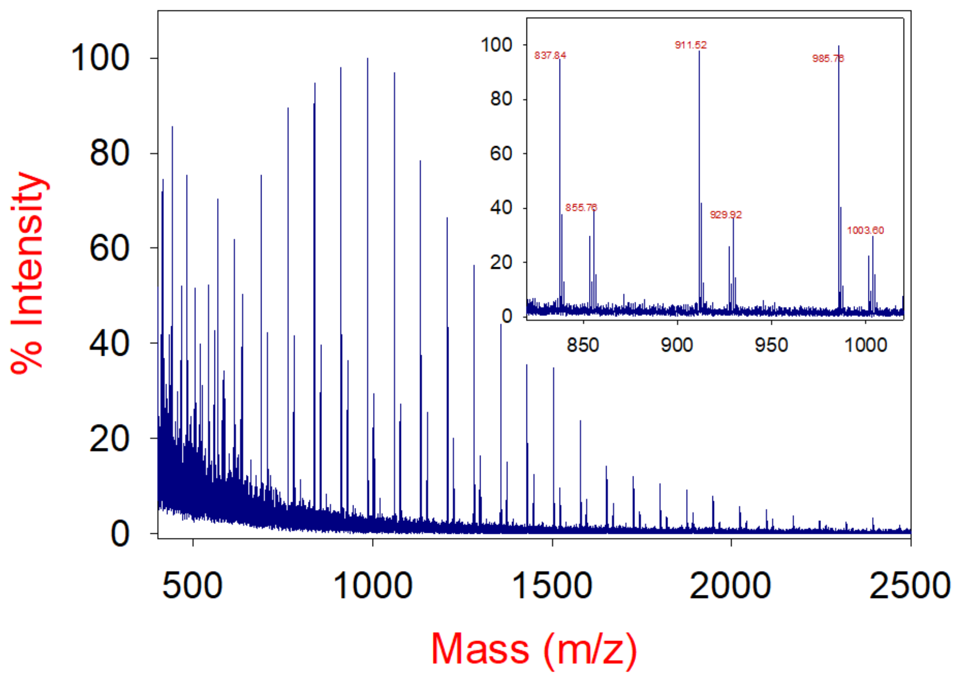

Figure S11. MALDI-TOF spectra of the SBPG produced by DMC-TBA (Table 1, run 6).

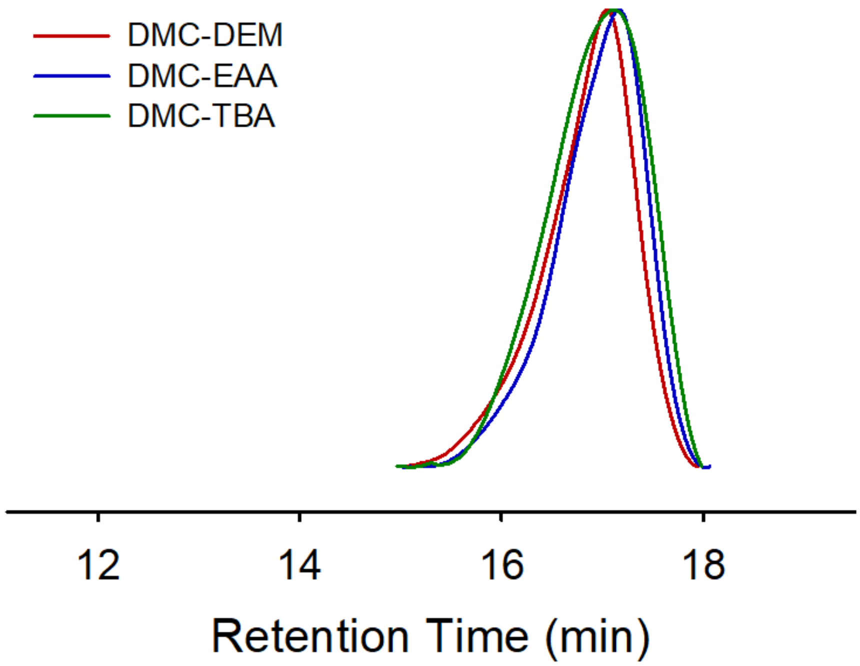

Figure S12. GPC curves of the SBPGs produced by DMC catalysts. Conditions: [Zn] = 15 × 10^{-3} M; [G] = 15 M; reaction temperature: 110 °C.

3.2 Kinetic Studies

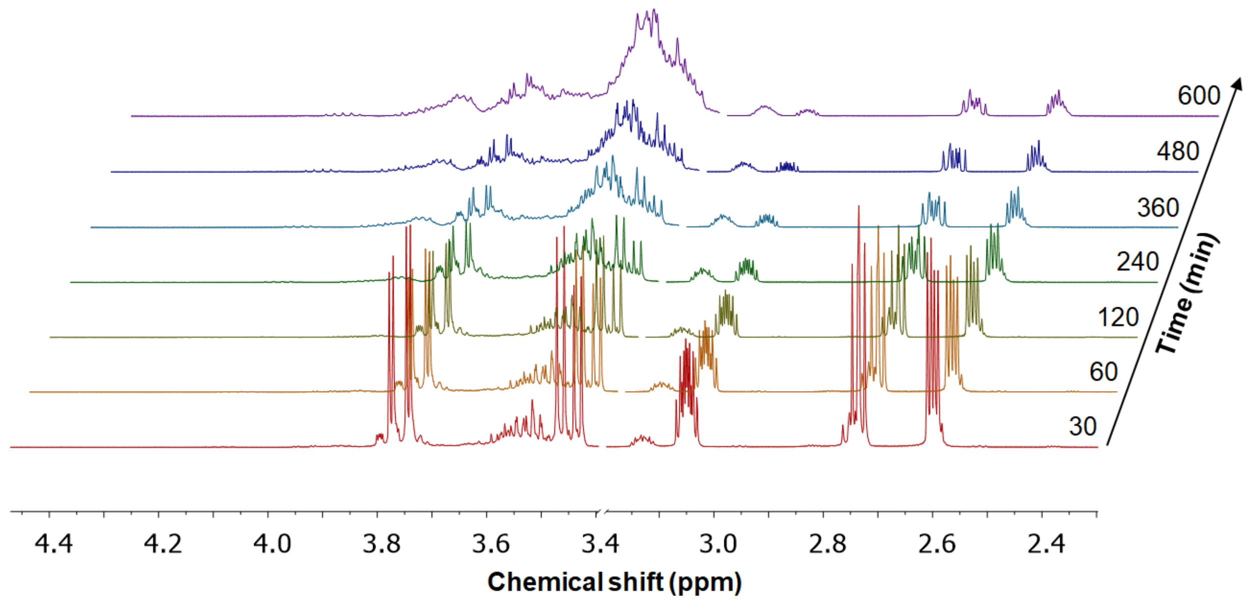

Figure S13. In situ ^{1}H NMR (400 MHz, CD_3OD) spectra of the batch polymerization of glycidol at 90 °C. Conditions: $[Zn] = 15 \times 10^{-3}$ M, $[G] = 15$ M. The peak corresponding to methanol at 3.29 ppm was omitted for clarity.

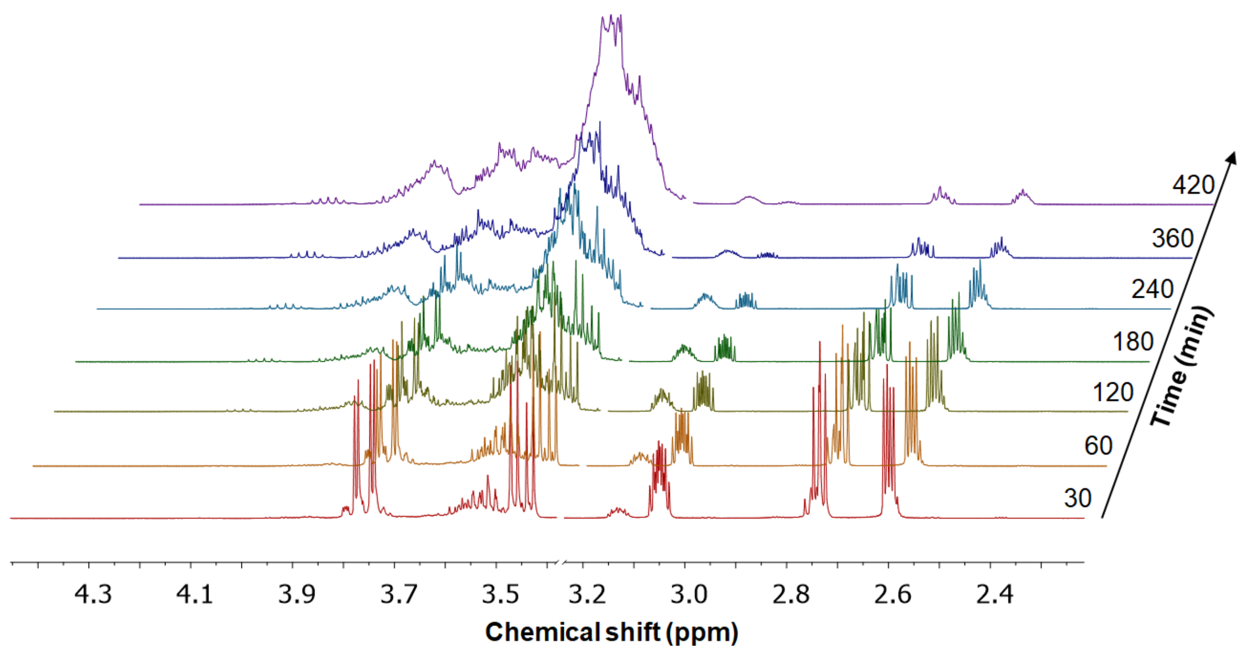

Figure S14. In situ ^{1}H NMR (400 MHz, CD_3OD) spectra of the batch polymerization of glycidol at 100 °C. Conditions: $[Zn] = 15 \times 10^{-3}$ M, $[G] = 15$ M. The peak corresponding to methanol at 3.29 ppm was omitted for clarity.

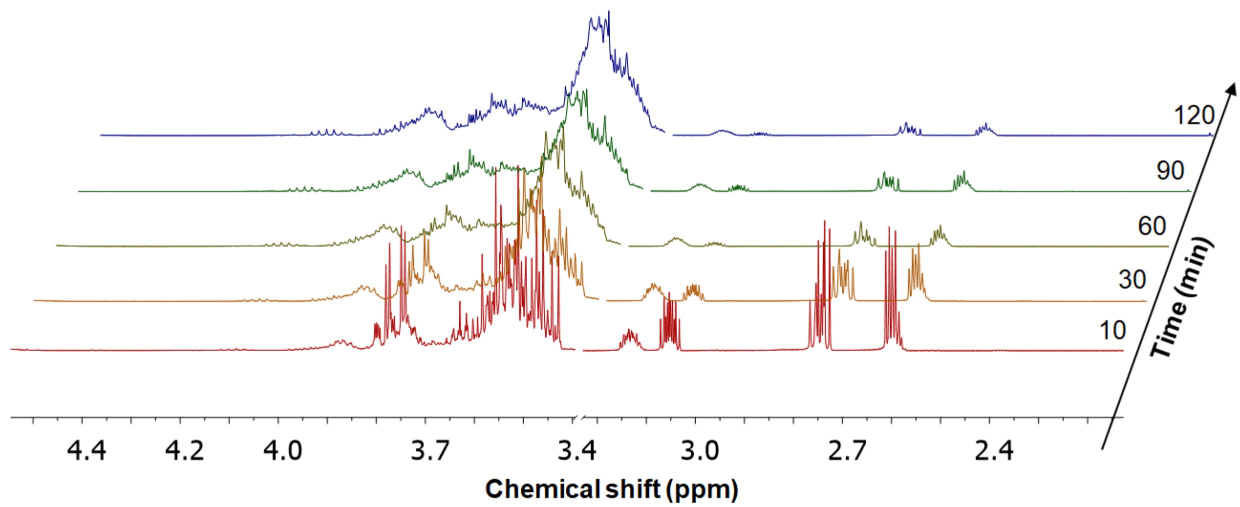

Figure S15. In situ [1]H NMR (400 MHz, CD_3OD) spectra of the batch polymerization of glycidol at 120 °C. Conditions: [*Zn*] = 15 × 10^{-3} M, [*G*] = 15 M. The peak corresponding to methanol at 3.29 ppm was omitted for clarity.

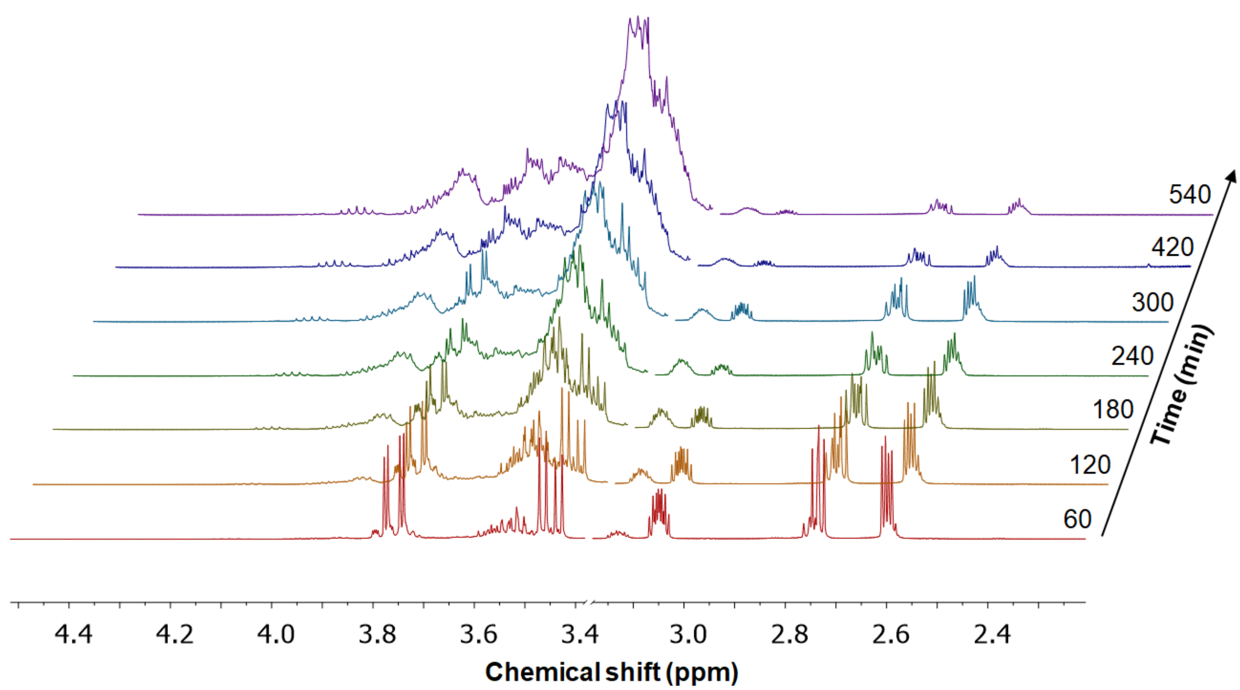

Figure S16. In situ [1]H NMR (400 MHz, CD_3OD) spectra of the batch polymerization of glycidol at 110 °C. Conditions: [*Zn*] = 3 × 10^{-3} M, [*G*] = 15 M. The peak corresponding to methanol at 3.29 ppm was omitted for clarity.

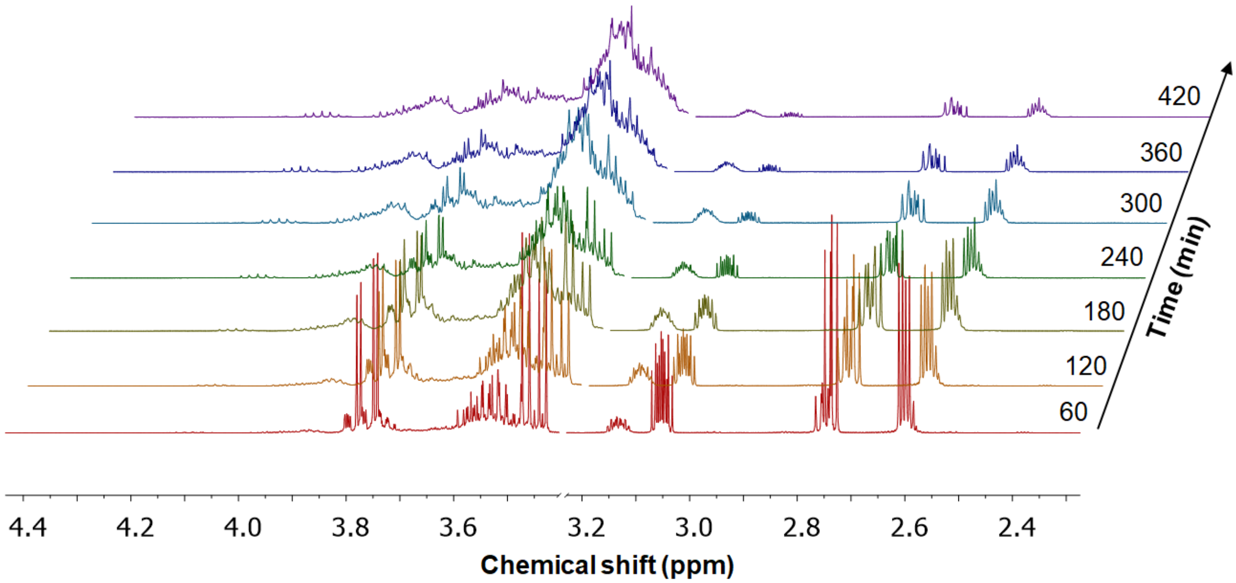

Figure S17. In situ ^{1}H NMR (400 MHz, CD_3OD) spectra of the batch polymerization of glycidol at 110 °C. Conditions: $[Zn] = 6 \times 10^{-3}$ M, $[G] = 15$ M. The peak corresponding to methanol at 3.29 ppm was omitted for clarity.

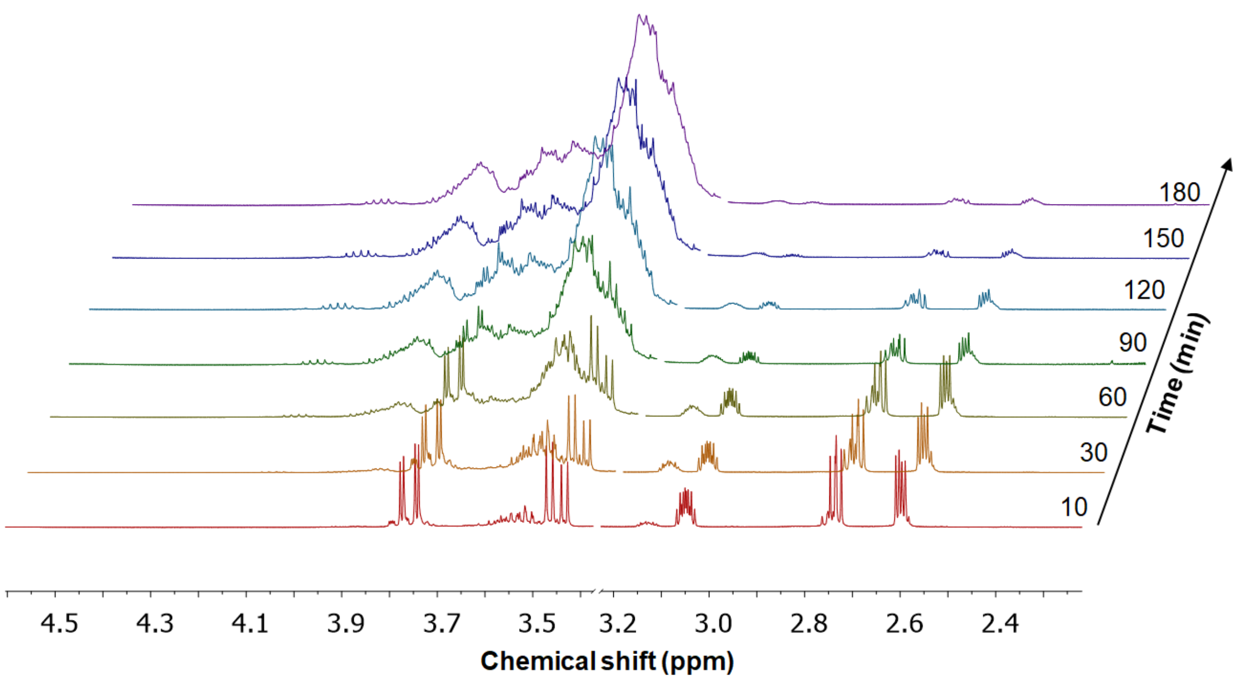

Figure S18. In situ ^{1}H NMR (400 MHz, CD_3OD) spectra of the batch polymerization of glycidol at 110 °C. Conditions: $[Zn] = 30 \times 10^{-3}$ M, $[G] = 15$ M. The peak corresponding to methanol at 3.29 ppm was omitted for clarity.

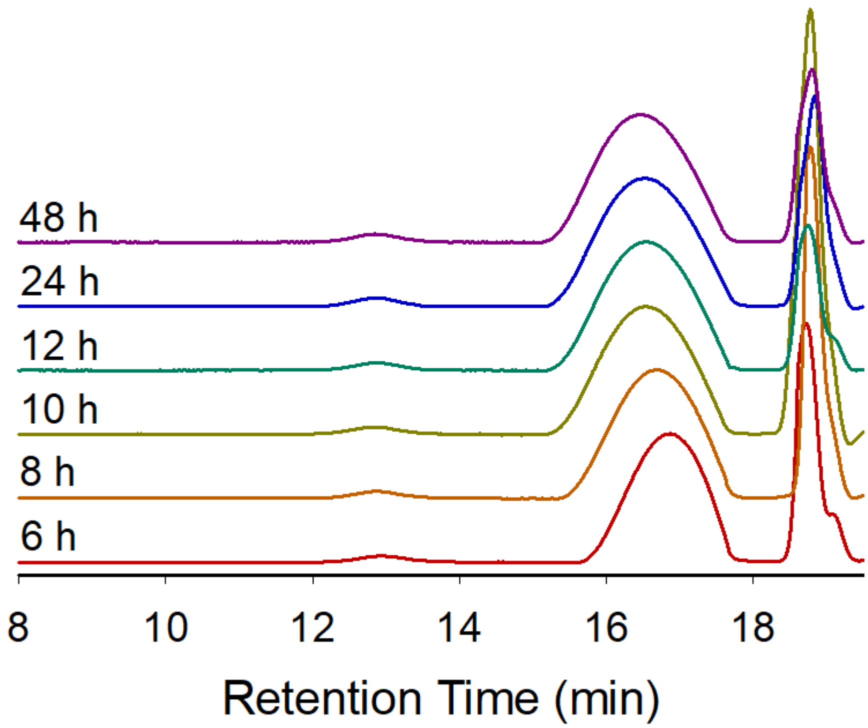

Figure S19. GPC curves of SBPGs collected at different intervals via batch polymerization of glycidol. Conditions: [*Zn*] = 1.5 × 10^{-3} M, [*G*] = 15 M.

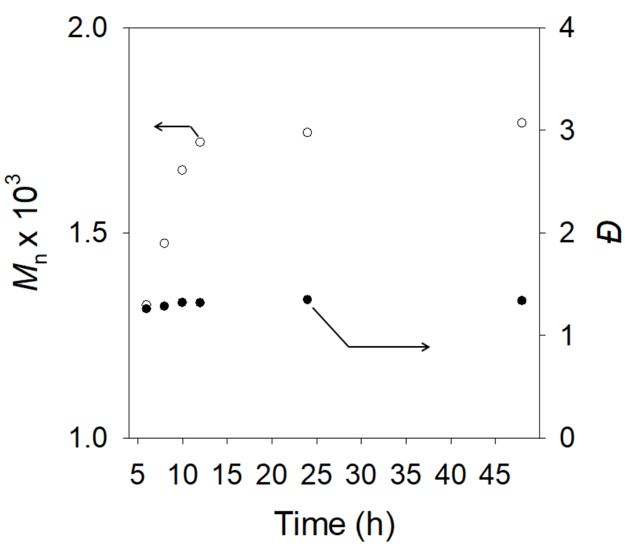

Figure S20. Dependence of M_n and PDI on the reaction time of the low molecular weight fractions obtained from Figure S21. Conditions: [*Zn*] = 1.5 × 10^{-3} M, [*G*] = 15 M.

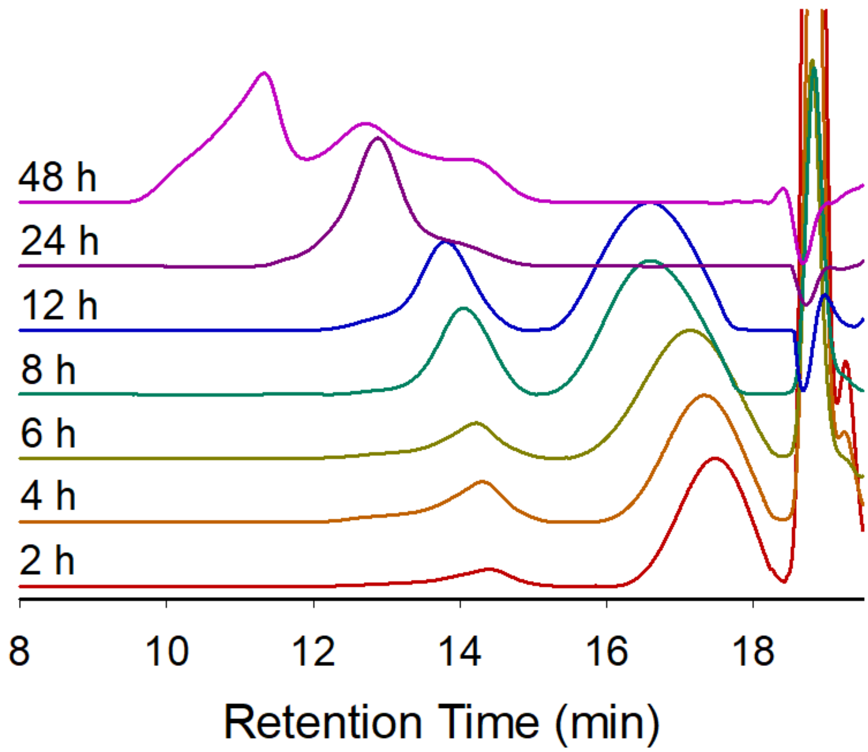

Figure S21. GPC curves of SBPGs collected at different intervals via batch polymerization of glycidol. Conditions: $[Zn] = 6 \times 10^{-4}$ M, $[G] = 15$ M.

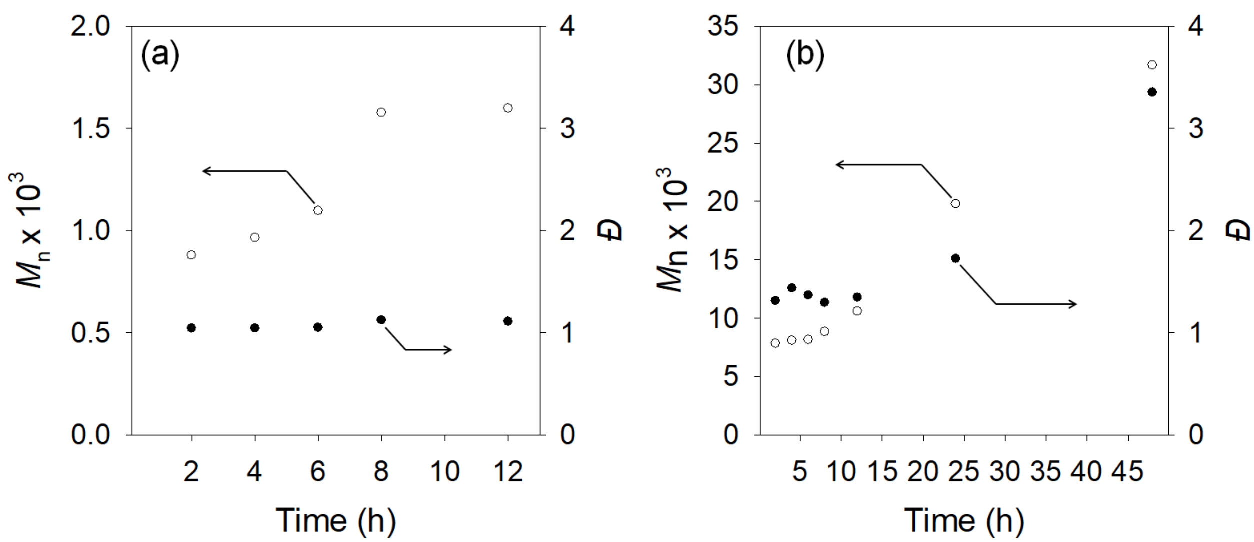

Figure S22. Dependence of M_n and PDI of (a) low molecular weight fractions and (b) high molecular weight fractions on the reaction time obtained from Figure S21. Conditions: $[Zn] = 6 \times 10^{-4}$ M, $[G] = 15$ M.

3.3 Mechanistic study

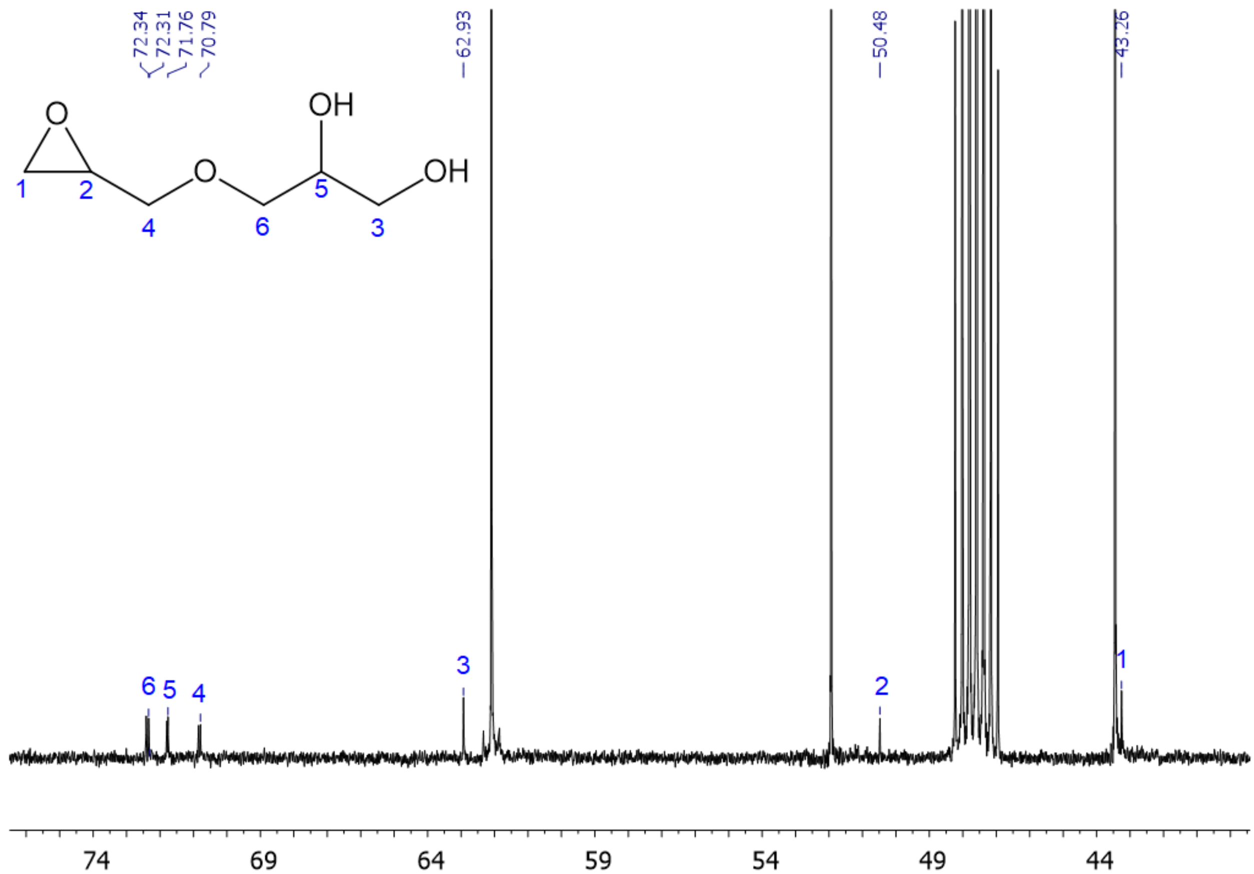

Figure S23. ^{13}C NMR of the SBPG intermediate collected after 30 seconds of the batch polymerization at 120 °C. Conditions: [Zn] = 15 × 10−3 M, [G] = 15 M.

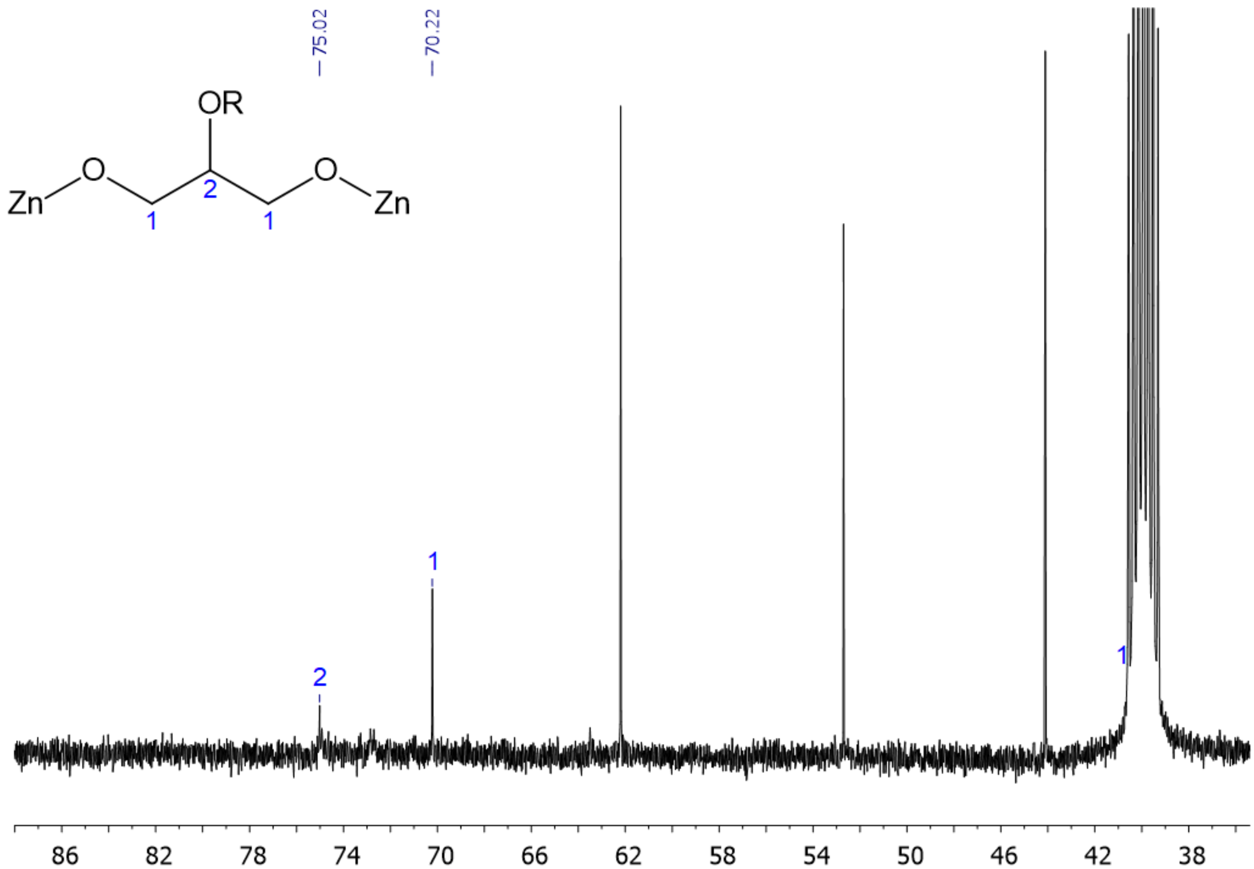

Figure S24. ^{13}C NMR of the HBPG intermediate collected after 30 seconds of the semi-batch polymerization at 120 °C. Conditions: [Zn] = 15 × 10−3 M, [G] = 15 M.

4. Characterization of the Resultant Polyglycidols

4.1 SBPGs obtained via batch ROP of glycidol

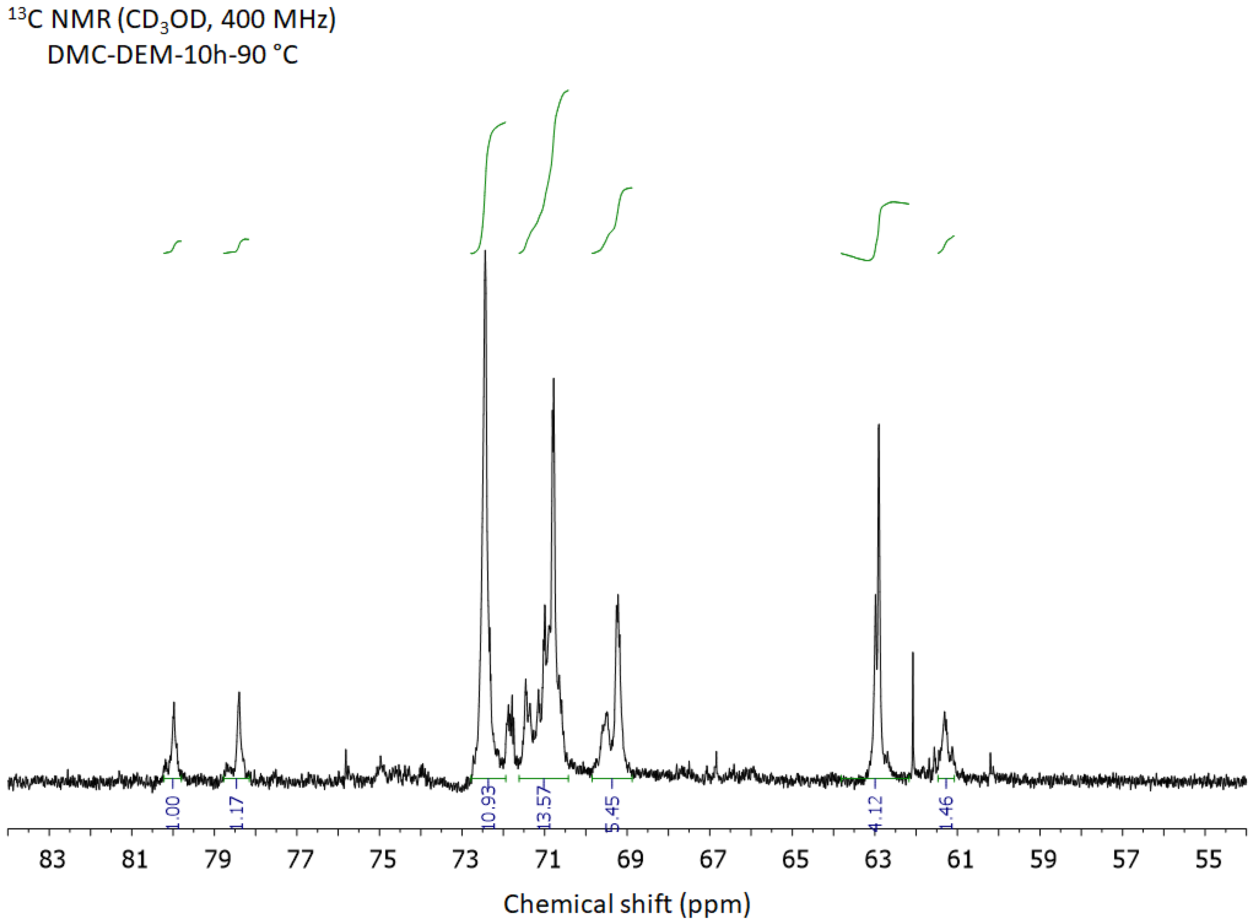

Figure S25. ^{13}C NMR of the SBPG produced by DMC-DEM at 90 °C. Conditions: [*Zn*] = 15 × 10^{-3} M, [*G*] = 15 M (Table 2).

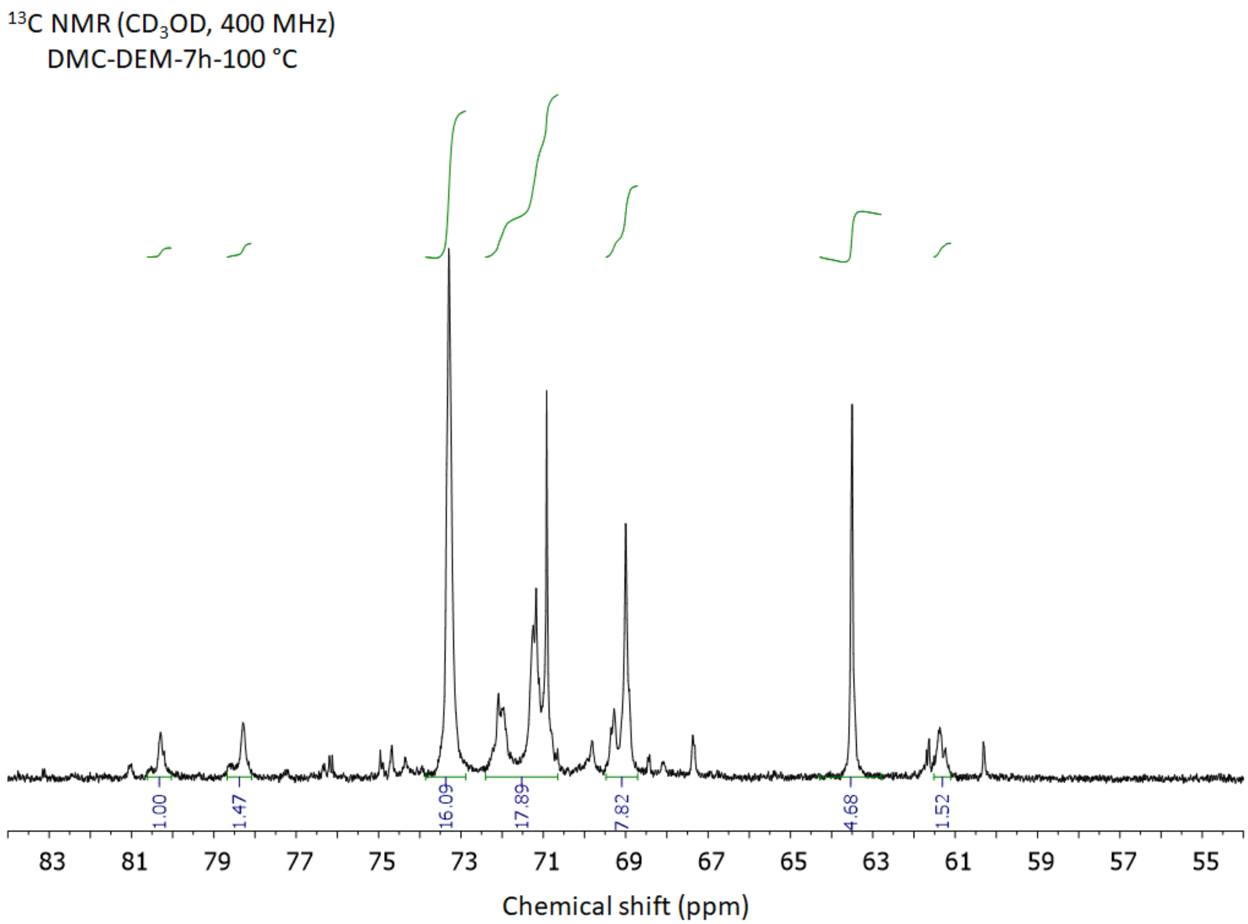

Figure S26. ^{13}C NMR of the SBPG produced by DMC-DEM at 100 °C. Conditions: $[Zn] = 15 \times 10^{-3}$ M, $[G] = 15$ M (Table 2).

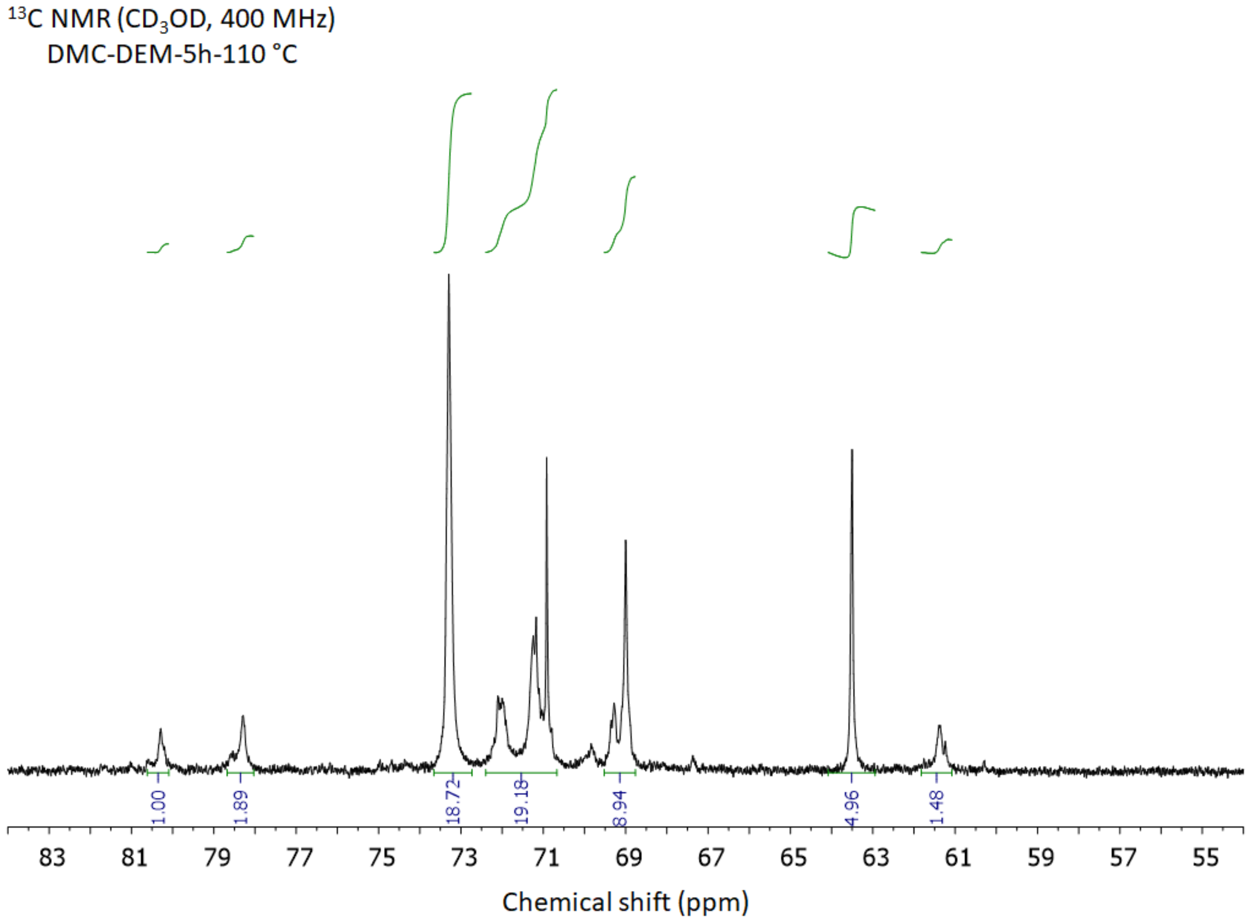

Figure S27. ^{13}C NMR of the SBPG produced by DMC-DEM at 110 °C. Conditions: [*Zn*] = 15 × 10^{-3} M, [*G*] = 15 M (Table 2).

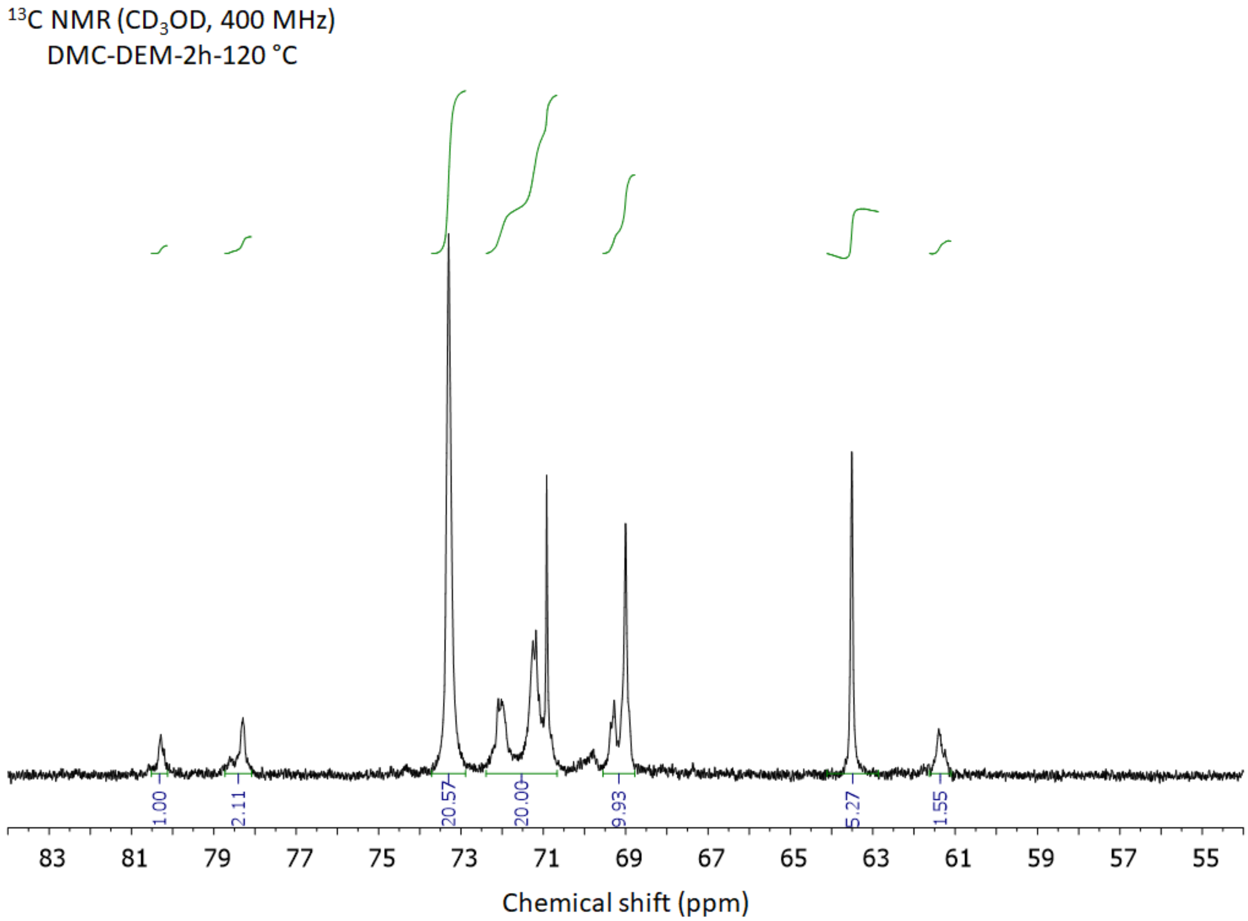

Figure S28. ^{13}C NMR of the SBPG produced by DMC-DEM at 120 °C. Conditions: [*Zn*] = 15 × 10^{-3} M, [*G*] = 15 M (Table 2).

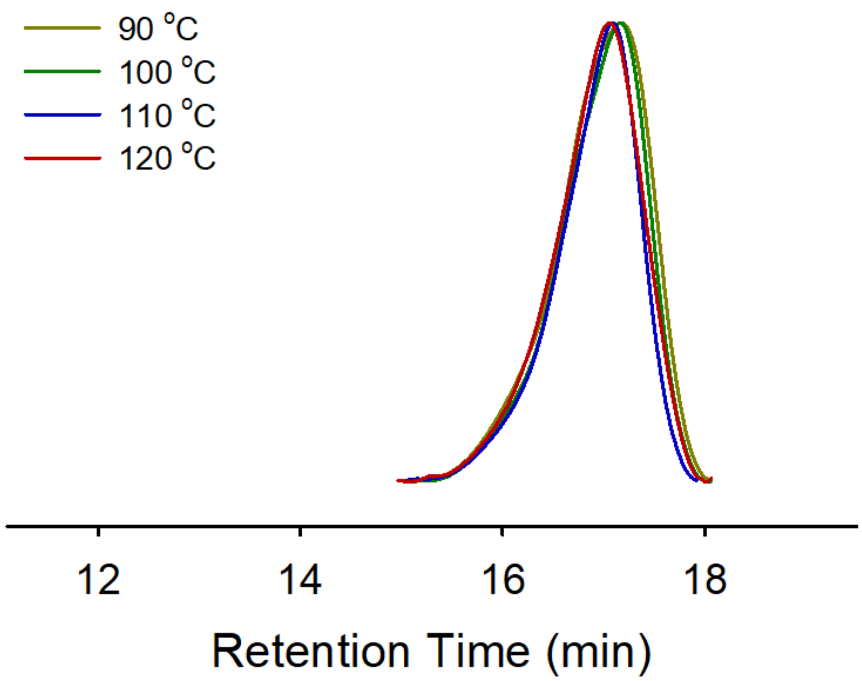

Figure S29. GPC curves of the SBPGs produced by DMC-DEM at different temperatures. Conditions: [*Zn*] = 15 × 10^{-3} M; [*G*] = 15 M.

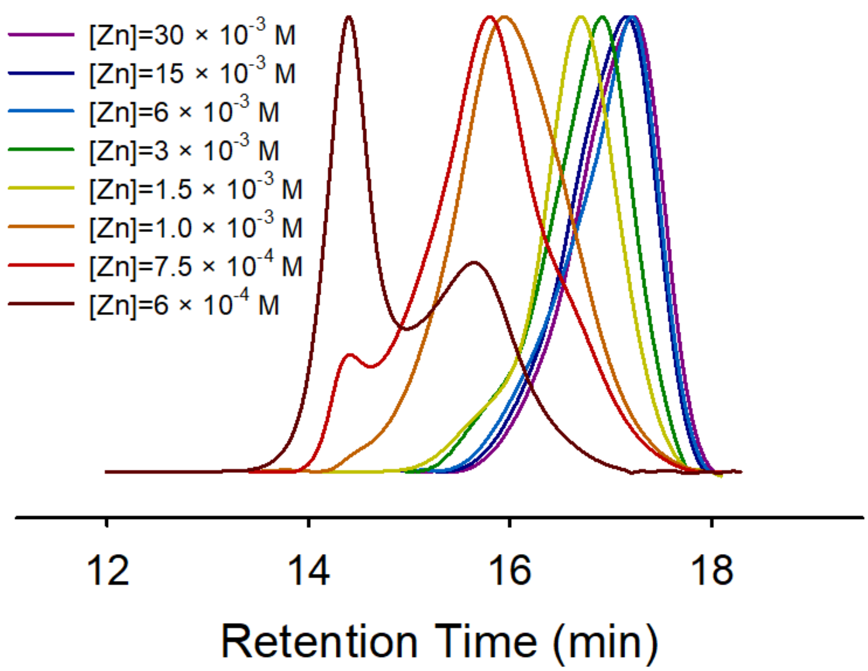

Figure S30. GPC curves of the SBPGs produced by different DMC-DEM amounts ([*Zn*]). Conditions: [*G*] = 15 M, reaction temperature: 110 °C.

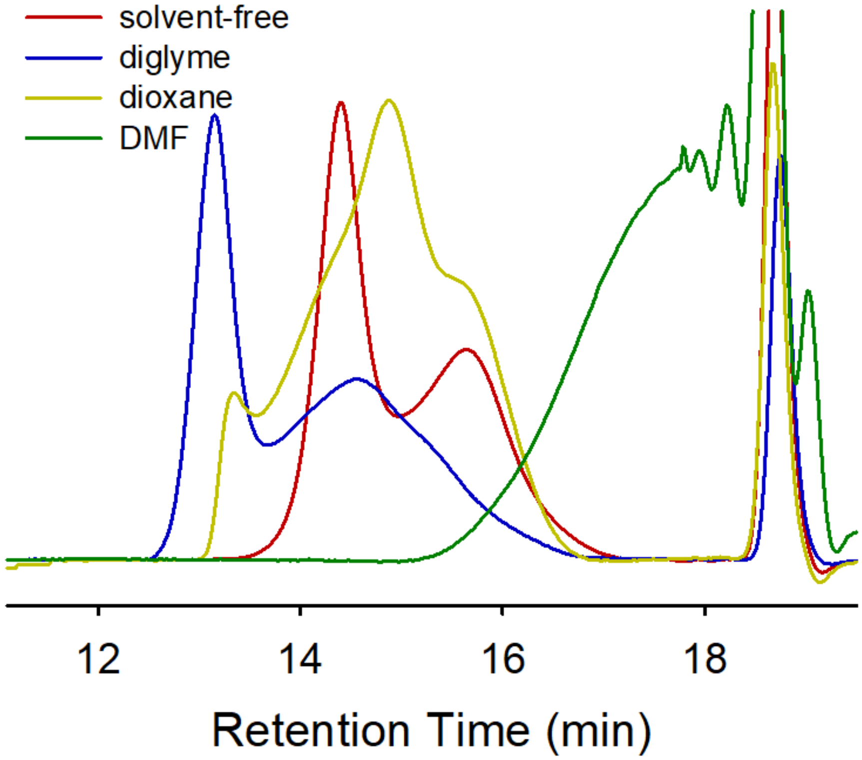

Figure S31. GPC curves of the SBPGs produced by different solvent. Conditions: [*Zn*] = 3 × 10^{-3} mmol, [*G*] = 7.5 M, solvent: 5mL, reaction temperature: 110 °C.

4.2 HBPGs obtained via semi-batch ROP of glycidol

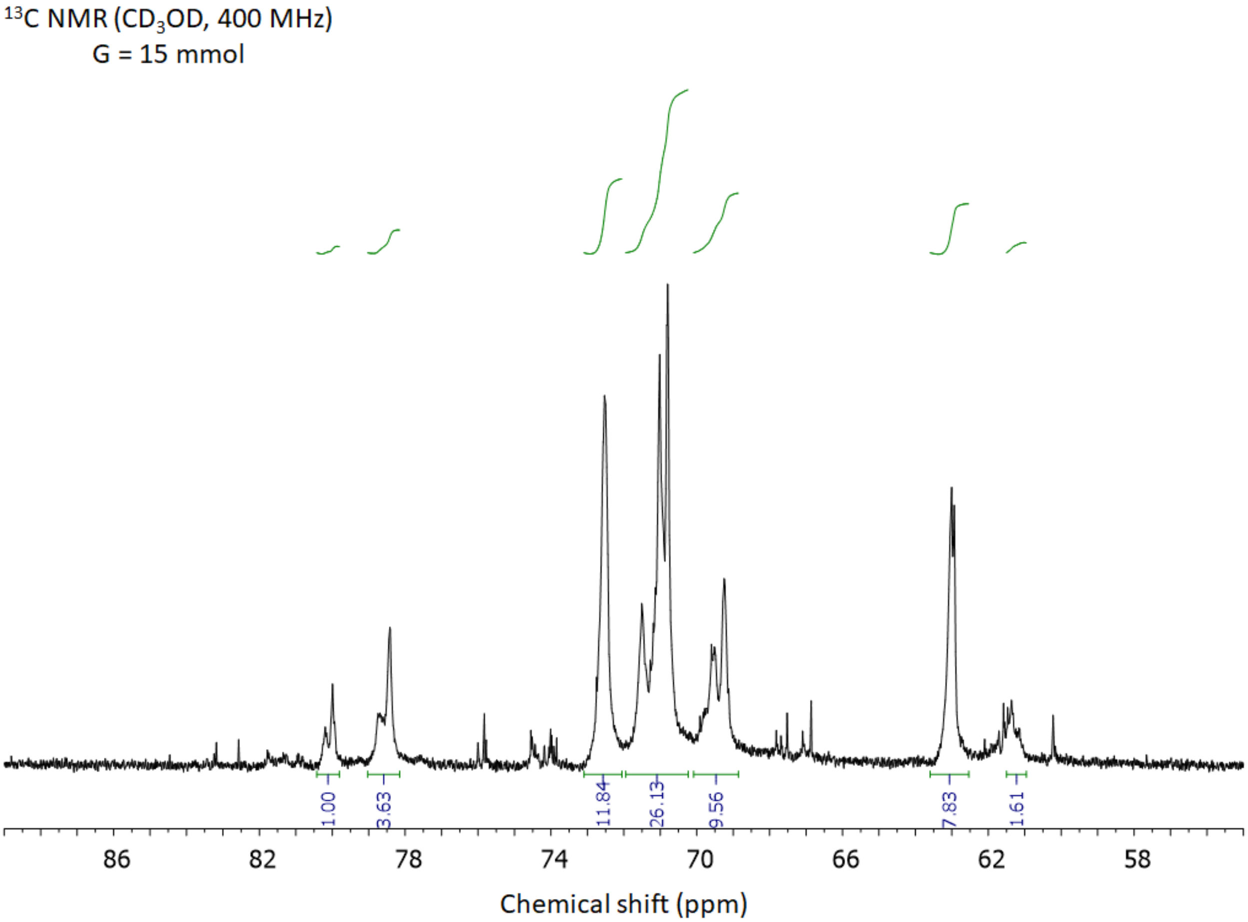

Figure S32. ^{13}C NMR of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3×10^{-3} mmol, G = 15 mmol (Table 5).

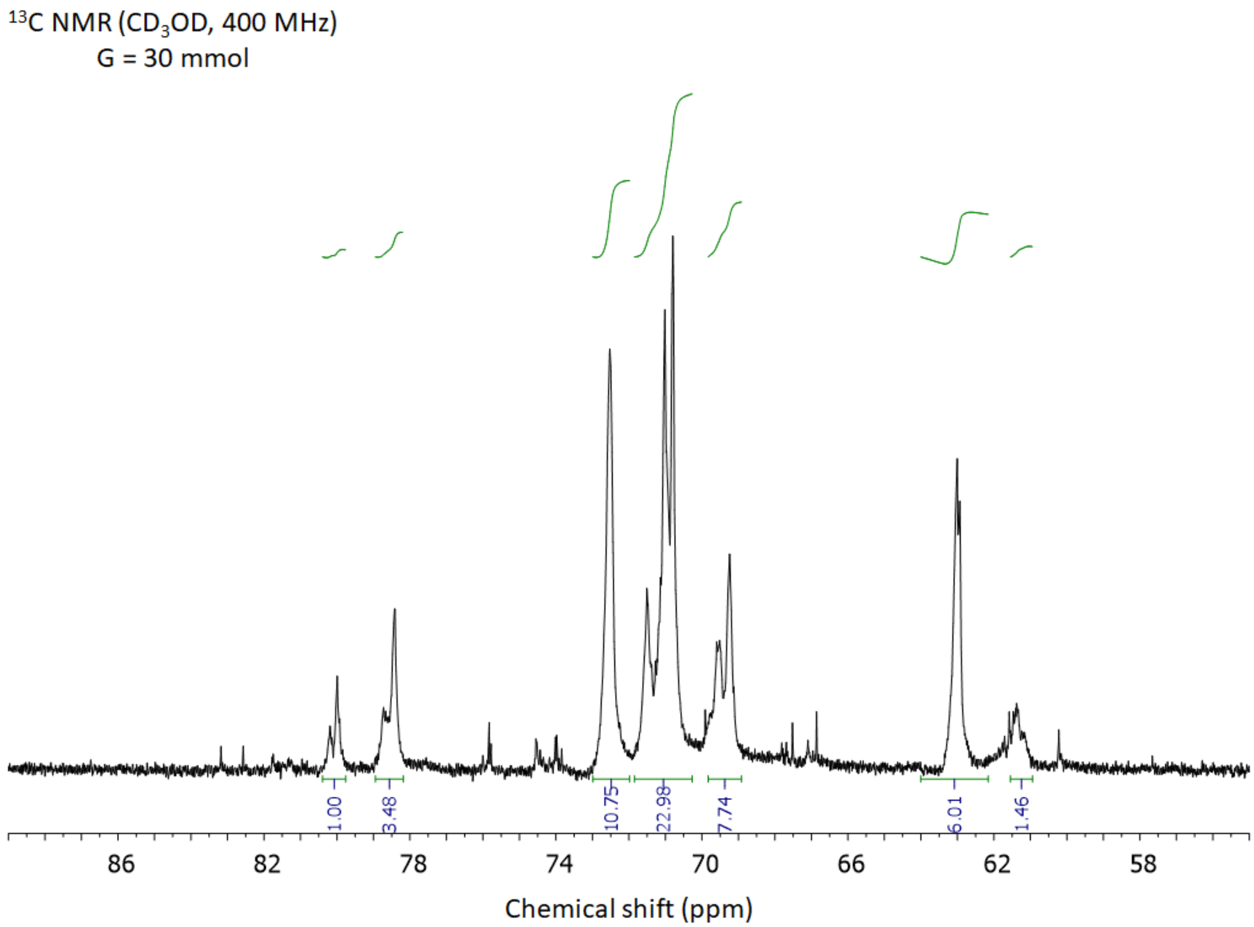

Figure S33. ^{13}C NMR of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3×10^{-3} mmol, G = 30 mmol (Table 5).

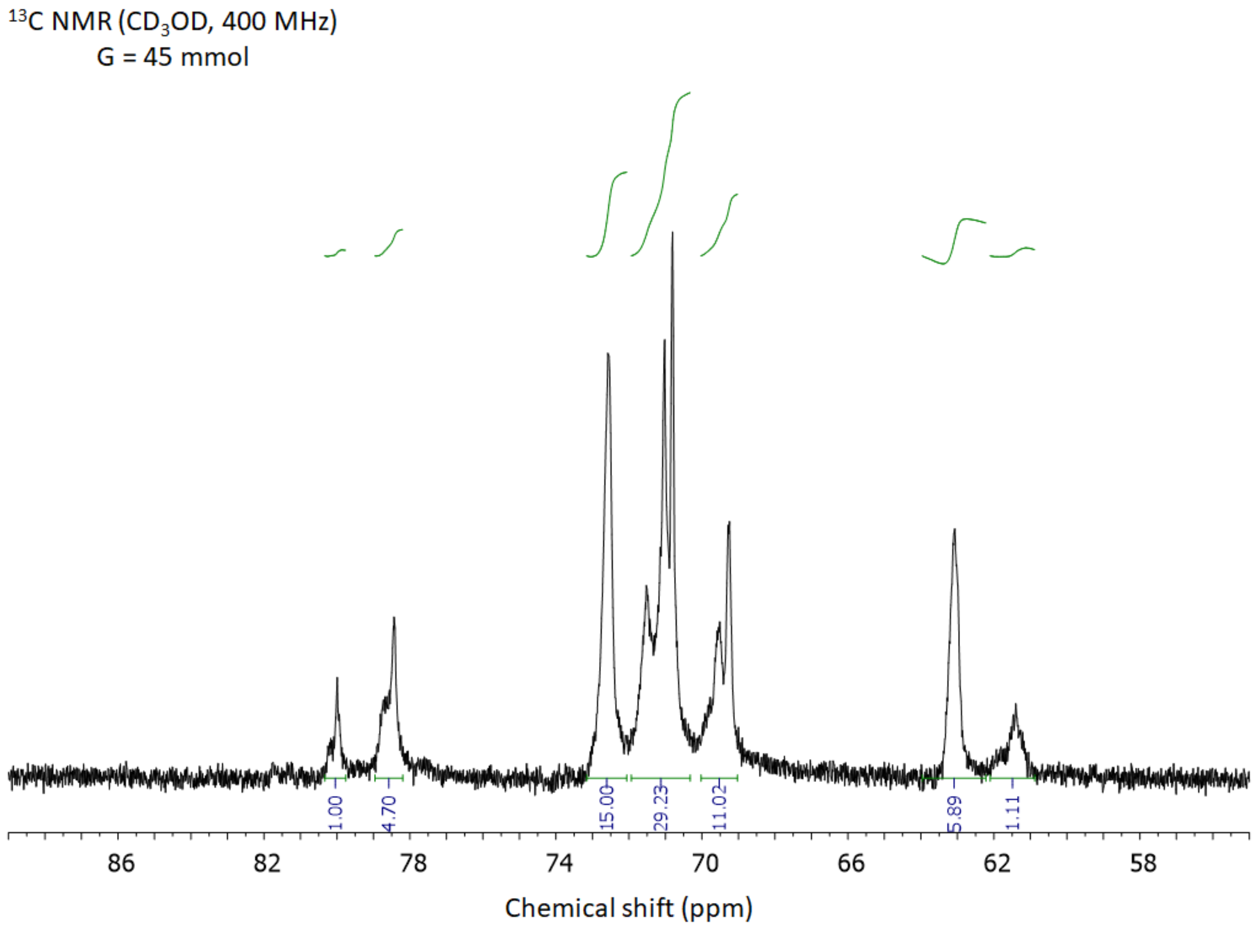

Figure S34. ^{13}C NMR of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3×10^{-3} mmol, G = 45 mmol (Table 5).

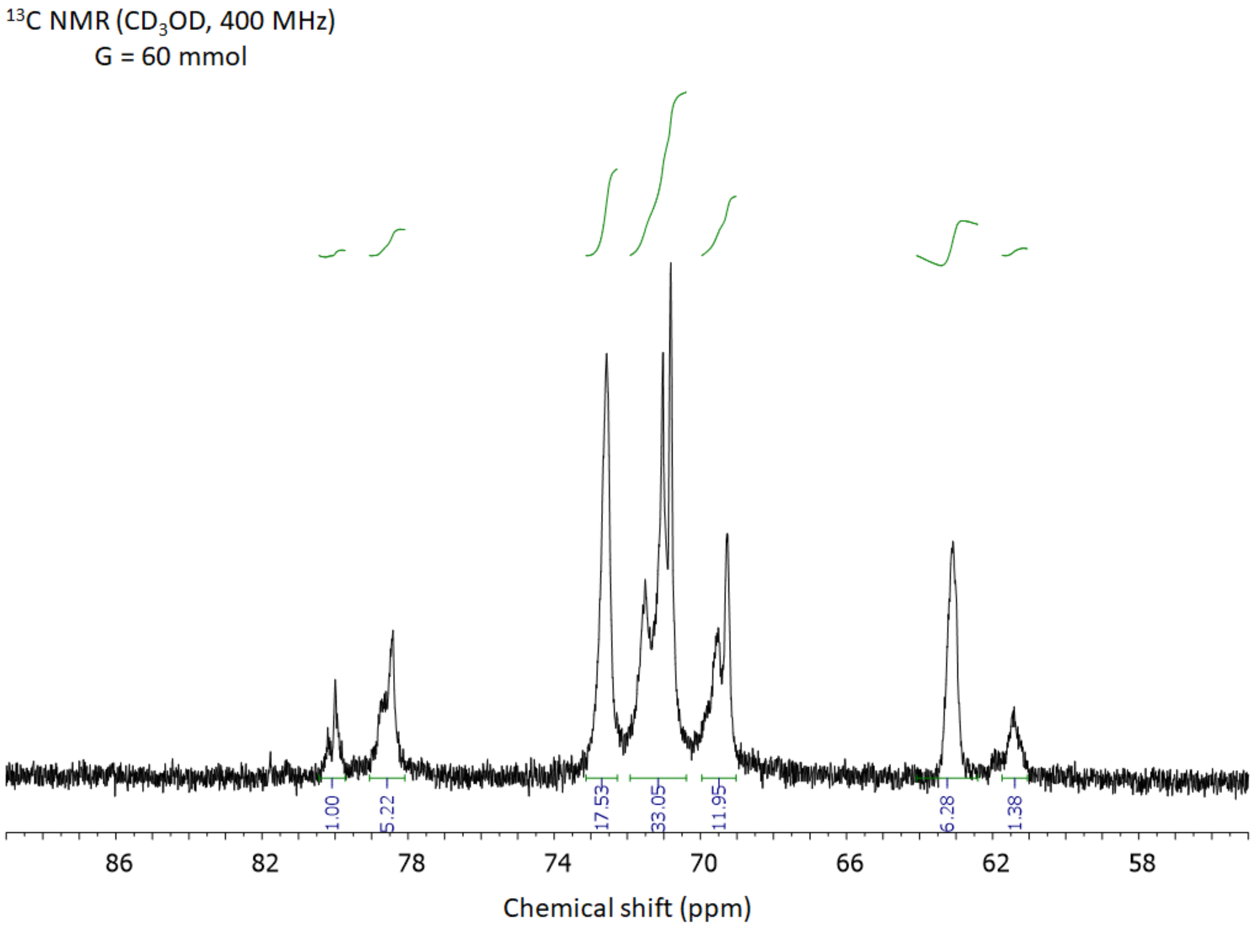

Figure S35. ^{13}C NMR of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3 × 10^{-3} mmol, G = 60 mmol (Table 5).

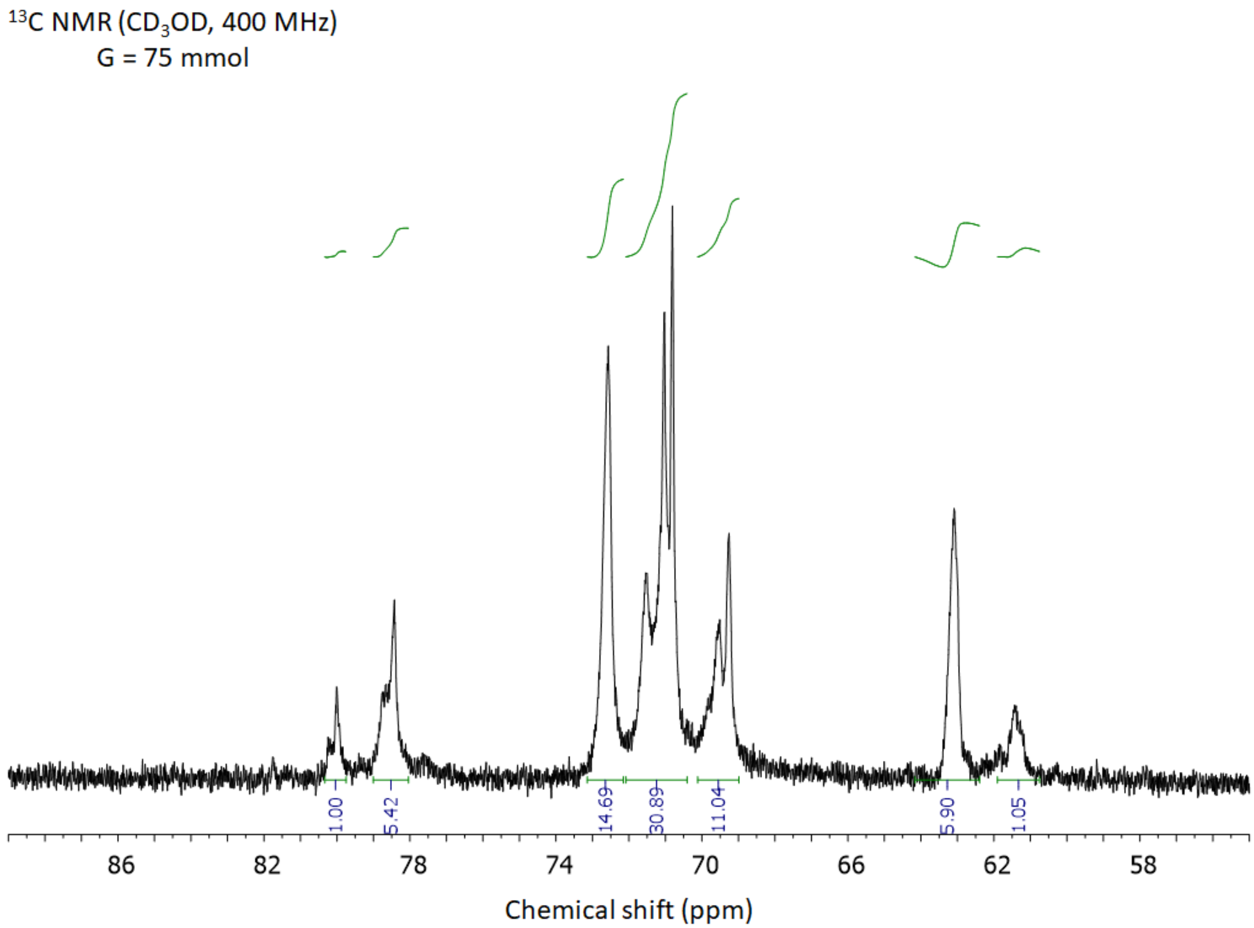

Figure S36. ^{13}C NMR of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3 × 10^{-3} mmol, G = 75 mmol (Table 5).

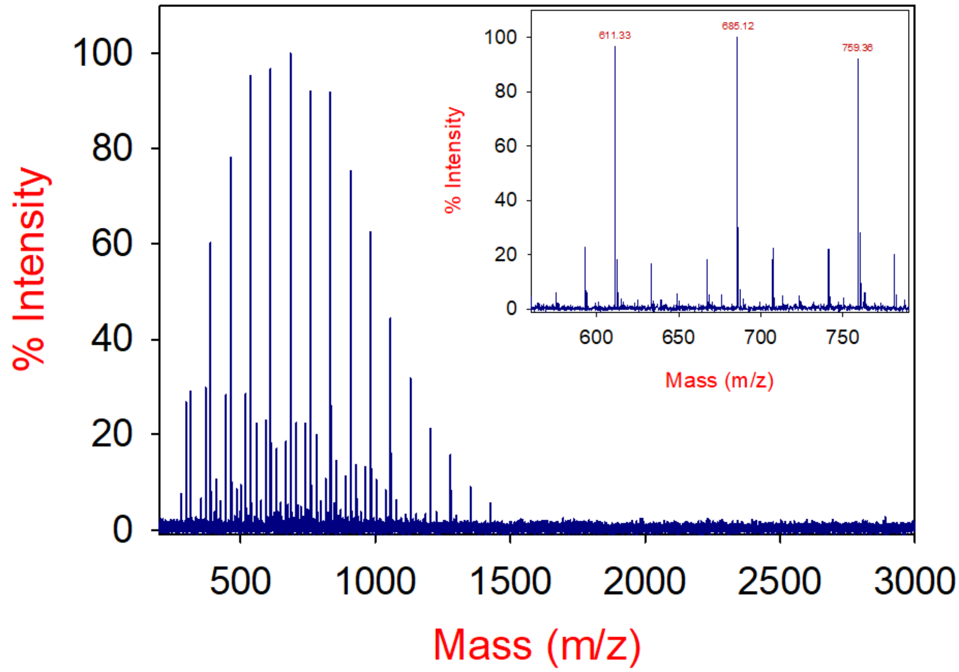

Figure S37. MALDI-TOF spectra of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3 × 10^{-3} mmol, G = 15 mmol (Table 6, run 1).

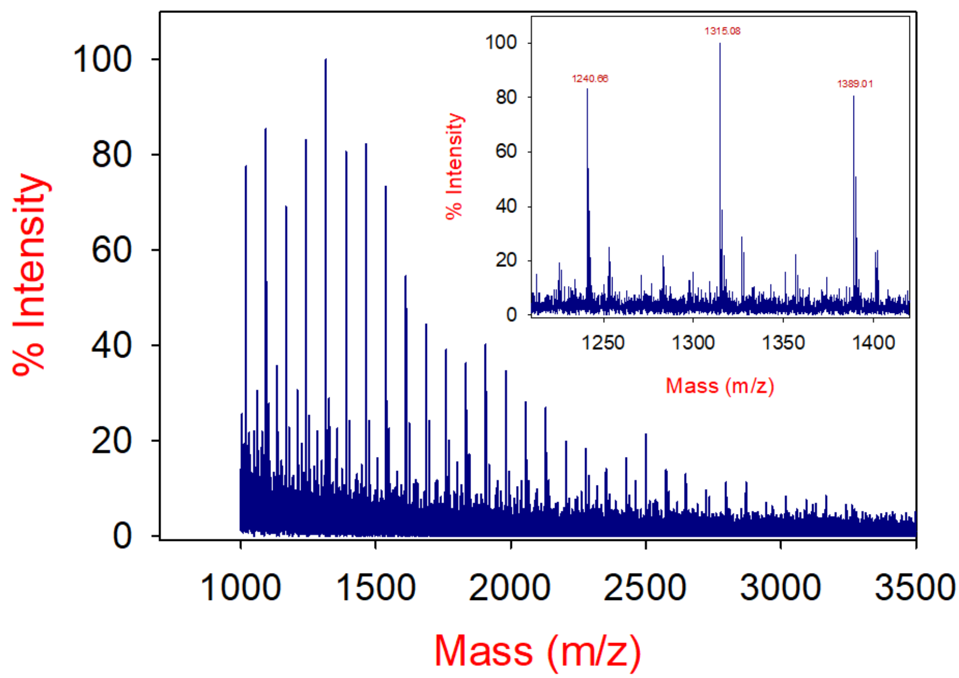

Figure S38. MALDI-TOF spectra of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3 × 10^{-3} mmol, G = 30 mmol (Table 6, run 2).

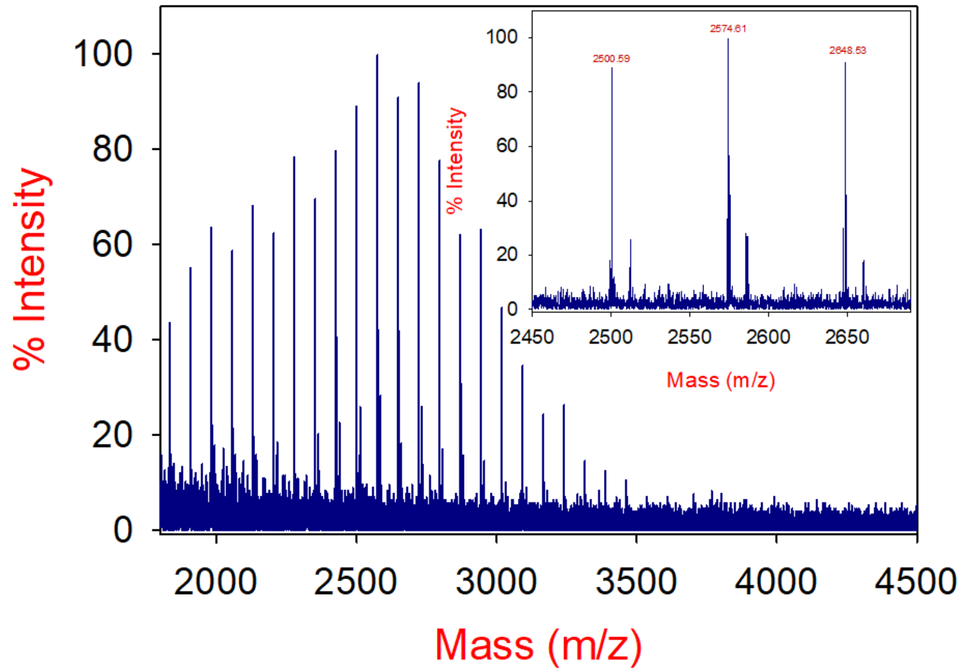

Figure S39. MALDI-TOF spectra of the HBPG produced by semi-batch polymerization at 120 °C. Conditions: Zn = 3 × 10^{-3} mmol, G = 45 mmol (Table 6, run 3).

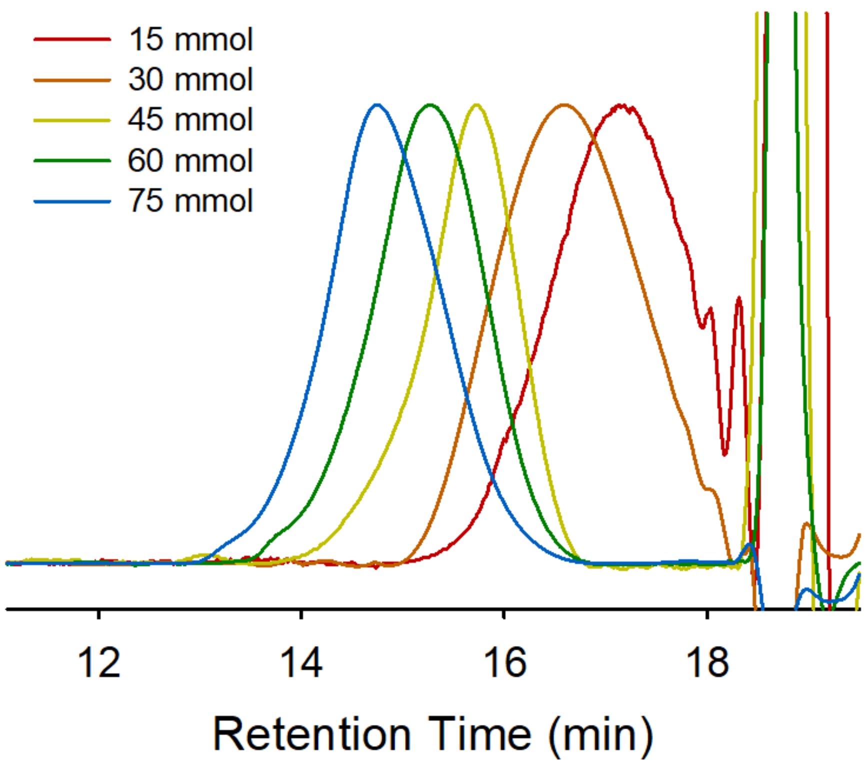

Figure S40. GPC curves of the HBPGs produced by semi-batch polymerization at 120 °C, injection rate of monomer: 0.1−0.5 mL h^{-1} (Table 6, run 1−5).

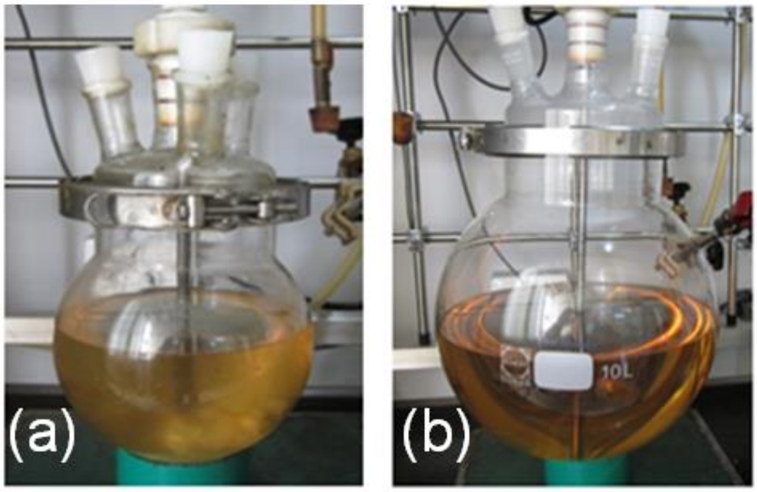

Figure S41. Results of scale-ups (1 L (a) and 10 L (b)) of the DMC-DEM-catalyzed ROMBPs of glycidol at 120 °C.

Table S1. Summary of the FTIR of the prepared DMC compounds

DMC compounds	ν(C≡N) (cm^{-1})	ν(C=O) (cm^{-1})	δ(O−H)	ν(C−O −C)	δ(Co−CN)
DMC-pure	2184	−	1615	−	463
DMC-DEM	2194	1732	1620	1090	473
DMC-EAA	2194	1725, 1709	1622	1090	473
DMC-TBA	2194	−	1620	1090	473

Table S2. Elemental analysis of the DMC catalysts

Catalyst	ICP-Mass (wt %)		Elemental analysis (wt %)			TGA (wt %)			Estimated catalyst formulation
	Zn	Co	C	H	N	CA	P123	H_2O	
DMC-DEM	21.3	9.4	29.8	2.9	14.0	13.1	23.1	2.4	$Zn_{2.04}Co(CN)_{6.27}\cdot 0.51DEM \cdot 0.03P123\cdot 0.83H_2O\cdot 0.53Cl^-$
DMC-EAA	21.5	10.1	30.5	3.0	14.6	14.8	25.2	0.8	$Zn_{1.92}Co(CN)_{6.10}\cdot 0.66EAA \cdot 0.03P123\cdot 0.26H_2O\cdot 0.07Cl^-$
DMC-TBA	23.9	10.7	29.3	3.3	16.3	7.2	24.1	1.9	$Zn_{2.01}Co(CN)_{6.41}\cdot 0.53TBA \cdot 0.02P123\cdot 0.58H_2O\cdot 0.29Cl^-$

Table S3. GPC results of SBPGs produced by batch polymerization using various catalysts obtained from Figure S12

Run	Catalyst	Zn		Glycidol		PMMA			PEG		
		$n_{Zn} \times 10^3$ (mmol)	$[Zn] \times 10^3$ (M)	n_G (mmol)	$[G]$ (M)	M_n	M_w	PDI	M_n	M_w	PDI
1	DMC-DEM	15.00	15.00	15.00	15.00	2340	2850	1.21	1390	1600	1.15
2	DMC-EAA	15.00	15.00	15.00	15.00	2160	2572	1.19	1400	1620	1.16
3	DMC-TBA	15.00	15.00	15.00	15.00	2110	2510	1.19	1369	1584	1.16

Table S4. GPC results of SBPGs produced by batch polymerization using DMC-DEM obtained from Figure S29 and 30

Run	Zn		Glycidol		React. Temp. (°C)	PMMA			PEG		
	$n_{Zn} \times 10^3$ (mmol)	$[Zn] \times 10^3$ (M)	n_G (mmol)	$[G]$ (M)		M_n	M_w	PDI	M_n	M_w	PDI
1	30.00	30.00	15.00	15.00	110	2020	2360	1.16	1310	1500	1.14
2	15.00	15.00	15.00	15.00	90	2130	2580	1.21	1380	1630	1.18
3	15.00	15.00	15.00	15.00	100	2160	2580	1.19	1400	1620	1.16
4	15.00	15.00	15.00	15.00	110	2150	2520	1.18	1390	1600	1.15
5	15.00	15.00	15.00	15.00	120	2300	2820	1.23	1480	1762	1.19
6	6.00	6.00	15.00	15.00	110	2170	2590	1.20	1400	1630	1.17
7	3.00	3.00	15.00	15.00	110	2530	3040	1.20	1620	1890	1.17
8	3.00	1.50	30.00	15.00	110	2650	3280	1.24	1690	2030	1.20
9	3.00	1.00	45.00	15.00	110	3310	4760	1.43	2090	2840	1.36
10	3.00	0.75	60.00	15.00	110	3680	5610	1.52	2300	3300	1.43
11	3.00	0.60	75.00	15.00	110	5810	8430	1.45	3500	4810	1.37

Table S5. GPC results of SBPGs produced by batch polymerization using various solvents obtained from Figure S31

Run	Solvent		Zn		Glycidol		PMMA			PEG		
		V (mL)	$n_{Zn} \times 10^3$ (mmol)	$[Zn] \times 10^3$ (M)	n_G (mmol)	$[G]$ (M)	M_n	M_w	PDI	M_n	M_w	PDI
1	−	−	3.00	0.60	75.00	15.00	5810	8430	1.45	3500	4810	1.37
2	Diglyme	5.00	3.00	0.30	75.00	7.50	8930	15080	1.69	5230	8170	1.56
3	Dioxane	5.00	3.00	0.30	75.00	7.50	7700	11590	1.51	4540	6440	1.42
4	DMF	5.00	3.00	0.30	75.00	7.50	1250	1720	1.37	850	1110	1.31

Table S6. GPC results of HBPGs produced by semi-batch polymerization using DMC-DEM obtained from Figure S40

Run	Zn		Glycidol		$V_{Diglyme}$ (mL)	PMMA			PEG		
	$n_{Zn} \times 10^3$ (mmol)	$[Zn] \times 10^3$ (M)	n_G (mmol)	V_G (mL)		M_n	M_w	PDI	M_n	M_w	PDI
1	3.00	3.00	15.00	1.00	1.00	1630	2090	1.28	1090	1340	1.23
2	3.00	1.50	30.00	2.00	2.00	2090	2800	1.34	1360	1750	1.28
3	3.00	1.00	45.00	3.00	3.00	6170	7770	1.26	3690	4490	1.22
4	3.00	0.75	60.00	4.00	4.00	6890	9370	1.36	4090	5310	1.30
5	3.00	0.60	75.00	5.00	5.00	8330	12090	1.45	4900	6700	1.37