Supporting Information

Quasilinear Polyglycidols by Triethylborane-Controlled Anionic Polymerization of Unprotected Glycidol

Prakash Alagi, Yves Gnanou,*† and Xiaoshuang Feng*,†

†Physical Sciences and Engineering Division, King Abdullah University of Science and

Technology (KAUST), Thuwal 23955, Saudi Arabia

Corresponding author: *yves.gnanou@kaust.edu.sa; fxs101@gmail.com*

Table of Content

Experimental Section:

1. Materials and characterization

2. Polymer synthesis

Table S1. Characterization of PGs obtained from mono-functional initiator (ABA) with slow addition (0.3mL/hour).

Table S2. Interpretation of ^{13}C NMR with relative integral value for dendritic, linear and terminal units for PGM, PGT, PGMS, PGE and PGB.

Table S3. Characterization of PGEs with degradable ester units obtained from mono-functional (ABA) initiator and excess of TEB using slow monomer addition (0.1mL/hour) process.

Table S4. Characterization of PGB with PPO units obtained from mono-functional (ABA)/ATA (di-functional terphthalic acid based) initiator and excess of TEB using slow monomer addition (0.1mL/hour) process.

Scheme S1. Mechanism of anionic polymerization of glycidol in absence of TEB.

Scheme S2. One pot synthesis of PG-based di-block and tri-block copolymers using ABA/ATA as an initiator and TEB as activator.

Figure S1. (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGM-1, PGM-2, and PGM-4 respectively.

Figure S2. (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGM-5 (DP-20), PGM-6 (DP-50) and PGM-7 (DP-500).

Figure S3. . (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGT-9 and PGT-11 respectively.

Figure S4. (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, (C) DSC curves, and (D) GPC traces for PGT-10.

Figure S5. (A) ^{1}H NMR spectra, (B) GPC traces for PGM-3 and PGM-8 respectively.

Figure S6. Characterization of PGs obtained from mono-functional initiator (ABA) with slow addition (0.3mL/hour).

Figure S7. (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGMS-5 and PGMS-6 where glycidol added at once.

Figure S8. Chemical shift variations of proton for glycidol in the absence and in the presence of TEB (1.0 equivalent) in THF-d_8.

Figure S9. Inverse gated ^{13}C NMR spectra of (A) PGE-1, (B) PGE-2, (C) PGE-3, and (D) PGE-4.

Figure S10. GPC traces (RI and UV detector) of (A) PGE-1, (B) PGE-2, (C) PGE-3, and (D) PGE-4 respectively.

Figure S11. (A) GPC traces and (B) ^{1}H NMR of PGE-3 before and after degradation (Insight region to show the acid peak).

Figure S12. (A) Inverse gated ^{13}C NMR spectra for di- and tri-block copolymers, (B) GPC traces for di-block, and (C) GPC traces for tri-block copolymer (Note: di-block and tri-block samples were esterified to have comparable GPC traces in THF.

Figure S13. Dosy NMR spectra for PGB-1 (after dialysis) and PGB-2 (after precipitation in toluene) indicating the formation of block copolymer structure.

Experimental section

1. Materials and Characterization

Glycidol (GLY, Aldrich, 96%) was distilled over CaH_2 prior to use under reduced pressure. 1,4 dioxane was distilled over CaH_2. Triethyl borane (TEB) in THF solution (c=1M) was purchased from Aldrich and used without further purifications. Benzoic acid (99.5%, Aldrich) and trimesic acid (95%, Aldrich) dried over P_2O_5 under argon. Tributylamine (NBu_3 Aldrich, 99%) was distilled over CaH_2 before using as deprotonating agent. Phthalic anhydride (99%, PA, Aldrich) was recrystallized in chloroform (10 g/100 mL), sublimed three times, and dried over P_2O_5 under argon immediately prior to use. Terephthalic acid (98%, Aldrich) was dried over P_2O_5 under argon. The Spectra/Por dialysis membrane with molecular weight cut off (MWCO) 1kD was purchased from Spectrum Laboratories, Inc. USA.

All ^1H NMR and Inverse gated (quantitative carbon) ^{13}C NMR spectra (ZGIG30 pulse program) were conducted on either a 950 MHz Bruker AV NEO or 800 MHz Bruker AV NEO NMR spectrometers with relaxation delay of 25 seconds and 3000 scans. This is to ensured full relaxation for quantitative measurement to calculate precise degree of branching in each polyglycidols (PGs). The 950 MHz NMR spectrometer is equipped with a TXO cryogenic probe providing best sensitivity for ^{13}C- detected spectra with a ^{13}C signal-to-noise (SINO) ratio of 2877 on a standard 40% Dioxane in Benzene-D6 (ASTM) sample in a single scan experiment. The 800 MHz NMR spectrometer is equipped with a TCI cryogenic probe with a ^{13}C SINO ratio of 2067 on a standard ASTM sample in a single scan experiment. Both instruments provide utmost ^{13}C NMR sensitivity for optimal quantitative measurements on relatively small amounts of sample. Gel permeation chromatography (GPC) was performed in DMF at a flow rate of 1.0 mL min^{-1} on an Agilent liquid chromatography system fitted with refractive index (RID) and UV-Vis detectors, using two

identical Aligent PLgel-Mixed C columns (5 µm) in connected series. The column and flow path temperatures were controlled at 40°C. Data analysis was performed using SEC-Addon for ChemStation software from Agilent. A calibration curve to determine the molecular weight was obtained using a PMMA standard. MALDI-TOF MS experiments were carried out by using 2,5-dihydroxybenzoic acid (DHB) as the matrix in methanol and Na-TFA as ionizing agent on a Bruker Ultrafex III MALDI-TOF mass spectrometer (Bruker Daltonik, Bremen, Germany). The thermal behavior of PGs were performed on differential scanning calorimetry (DSC) in the temperature range –80 to 150°C at a heating rate of 10 °C /min in a nitrogen atmosphere.

2. Polymer synthesis

2.1. General procedure for polymerization of PGs using tributyl ammonium salt of benzoic acid (ABA)/ tributyl ammonium salt of trimesic acid (ATMA) initiator

Considering entry PGM-4 in table 1 as a reference for PGs, the experimental procedure is described below. The polymerization was conducted by applying Schlenk technique under argon atmosphere. Using glovebox, benzoic acid (11 mg, 0.09 mmol) was placed in Schlenk flask followed by tributylamine (17µL, 0.072 mmol) as a deprotonating agent and the reaction mixture was stirred for few minute (1-2 min) to obtain ABA initiator. To this reaction mixture 5.0 equivalent 1.0 M TEB (0.45 mmol, in THF) solution was added. The flask was sealed with rubber septum. In a glass syringe the mixture of glycidol (18 mmol, 1.2 mL) and 1,4 dioxane (1.2 mL) were taken and the slow addition of reaction mixture was carried out at 0.1mL/hr for a time period of 24 hours at 80 °C using a precision dosing pump. After completion of addition of reaction mixture the schlenk flask was cooled at room temperature and reaction mixture was quenched with few drops of methanol (containing 5% HCl) to terminate the reaction and the reaction mixture was diluted with excess of methanol. The polymer was precipitated twice in hexane and finally dried

at 50 °C in a vacuum oven. Similar experiment (PGM-8) were carried out in absence of TEB to see the effect on properties of resulting PGs. Also similar experimental procedure were used for tri-functional initiator (ATMA) to obtain PGs.

2.2. General procedure for polymerization of poly(glycidol-*co*-ester) using ABA and TEB initiating system

Considering entry PGE-3 in table S3 as a reference for PGEs, the experimental procedure is described below. The polymerization was conducted by applying Schlenk technique under argon atmosphere. Using glovebox, benzoic acid (12.5 mg, 0.10 mmol) was placed in Schlenk flask followed by tributylamine (19μL, 0.08 mmol) as a deprotonating agent and 0.5 mL of 1,4 dioxane. The reaction mixture was stirred for few minute (1-2 min). To this reaction mixture 5.0 equivalent 1.0 M TEB (0.5 mmol, in THF) solution was added. The flask was sealed with rubber septum. In a glass syringe the mixture of glycidol (18 mmol, 1.2 mL), phthalic anhydride (0.295 g, 2.0 mmol), and 1,4 dioxane (1.2 mL) were taken and the slow addition of reaction mixture was carried out at 0.1mL/hr for a time period of 24 hours at 60 °C using a precision dosing pump. After completion of addition of reaction mixture the schlenk flask was cooled at room temperature and reaction mixture was quenched with few drops of methanol (containing 5% HCl) to terminate the reaction and the reaction mixture was diluted with excess of methanol. The polymer was precipitated twice in hexane and finally dried at 50 °C in a vacuum oven. Similar experiment (PGE-5) were carried out in absence of TEB to see the effect on properties of resulting PGEs.

2.3. General procedure for degradation of poly(glycidol-*co*-ester)

20 mg of a pure polymer is dissolved in 2 mL deionized water, to this solution 3 mL 0.5 M NaOH solution is added and stirred at 60 ∘C until complete degradation is achieved (24h). An aliquot of

the above solution is neutralized with 10% HCl in H_2O and the degraded polymer is extracted by freeze drying. The resultant product were characterized by ^{1}H NMR and GPC.

2.4. General procedure for polymerization of PPO-b-PG diblock copolymers using ABA as monofunctional initiator and TEB as activator

Considering entry PGB-1 in table S4, the experimental procedure is described below. The polymerization was conducted by applying Schlenk technique under argon atmosphere. In a glovebox, benzoic acid (122 mg, 1.0 mmol) was introduced in a Schlenk flask followed by tributylamine (0.19 mL, 0.8 mmol) as a deprotonating agent and 0.5 mL of THF. The reaction mixture was stirred for few minutes (1-2 min). To this reaction mixture 3.0 equivalent of 1.0 M TEB (3.0 mmol, in THF) solution was added. To this reaction mixture 20 equiv. of propylene oxide (1.4 mL, 20 mmol) added and the flask was sealed; the reaction was carried out for a time period of 12 hours at 40 °C. In the same reaction flask additional 2 equiv. of TEB was added. The flask was covered with rubber septum. In a glass syringe a mixture of glycidol (1.34 mL, 20 mmol) and 1,4 dioxane (1.4 mL) were taken and a slow addition of the reaction mixture was carried out at 0.1mL/hr for a time period of 24 hours at 80 °C using a precision dosing pump. After completion of addition of the reaction mixture the schlenk flask was cooled at room temperature and the reaction mixture was quenched with few drops of methanol (containing 5% HCl) to terminate the reaction; the reaction mixture was then diluted with excess of methanol. The polymer was precipitated twice using hexane and finally dried at 50 °C in a vacuum oven. For further purification of the diblock copolymer dialysis was used. In a general procedure, the diblock copolymer (0.1 g) was dissolved in 1.0 mL deionized water, transferred to dialysis membrane

(MWCO 1 kD) and dialyzed against a large excess of deionized water for 8 hours. Water was replaced every two hours during the 8-hour dialysis time.

2.5. General procedure for polymerization of PG-b-PPO-b-PG triblock copolymers using tributyl ammonium salt of terephthalic acid (ATA) as difunctional initiator and TEB as activator

Considering entry PGB-2 in table S4, the experimental procedure is described below. The polymerization was conducted by applying Schlenk technique under argon atmosphere. Using glovebox, terephthalic acid (166 mg, 1.0 mmol) was introduced in a Schlenk flask followed by tributylamine (0.38 mL, 1.6 mmol) as a deprotonating agent and 0.5 mL of THF. The reaction mixture was stirred for few minutes (1-2 min). To this reaction mixture 6.0 equivalent 1.0 M TEB (6.0 mmol, in THF) solution was added. To this reaction mixture 20 equiv. of propylene oxide (1.4 mL, 20 mmol) was added and the flask was sealed; the reaction was carried out for a time period of 12 hours at 40 °C. In the same reaction flask additional 4 equiv. TEB was added. The flask was covered with a rubber septum. In a glass syringe a mixture of glycidol (1.34 mL, 20 mmol) and 1,4 dioxane (1.4 mL) were taken and a slow addition of the reaction mixture was carried out at 0.1mL/hr for a time period of 24 hours at 80 °C using a precision dosing pump. After completion of addition of the reaction mixture, the schlenk flask was cooled at room temperature and the reaction mixture was quenched with few drops of methanol (containing 5% HCl) to terminate the reaction; the reaction mixture was then diluted with an excess of methanol. The polymer was precipitated twice using hexane and finally dried at 50 °C in a vacuum oven. For further purification, the triblock copolymer was dissolved in methanol and washed with toluene. This procedure was repeated 3 times.

Table S1. Characterization of PGMS samples obtained from monofunctional initiator (ABA) with moderate rate of monomer addition (0.3mL/hour).

Entry	[ABA/ [TEB]/[Gly]	Temperature (°C)	Mn theoretical [a]	Mn (^{1}H NMR) [b]	Mn/PDI GPC [c]	Degree of branching [d]	L_{13} [e] (%)	L_{14} [f] (%)	D [g] (%)	T [h] (%)
PGMS-1	1/-/200	90	15000	18700	4200/2.24	0.56	10.79	28.55	25.04	35.62
PGMS-2	1/1/200	90	15000	16000	12800/1.80	0.19	31.95	42.81	8.95	16.29
PGMS-3	1/3/200	90	15000	13400	11800/1.43	0.12	40.82	42.86	5.71	10.61
PGMS-4	1/5/200	90	15000	13500	13200/1.45	0.10	41.58	43.45	4.57	10.40
PGMS-5[i]	1/5/200	90	15000	-	2900/1.20	0.03	20.10	59.40	1.00	19.50
PGMS-6[j]	1/-/200	90	15000	-	3600/1.40	0.31	8.19	43.49	11.71	36.61
PGMS-7[h]	1/-/20	80	1600	2200	2400/1.54	0.57	11.64	25.96	25.26	37.14

[a] Theoretical molar mass calculated assuming linear PG structure, Mn(theoretical) = [(Glycidol/Initiator) × 74.08 × conversion + Mol. wt. of initiator + H]; [b] Calculated from ^{1}H NMR spectra by comparison of repeating unit signal intensity to the initiator signal intensity; [c] determined via SEC-RI in DMF using linear PMMA standards; [c]Degree of branching were calculated according to equation described by Frey et.al; (DB=2D/(2D+L_{13}+L_{14})); [e]Content of linear 1-3 connected units; [f]Content of linear 1-4 connected units; [g]Ratio of dendritic unit: [h]Ratio of terminal unit; [i] Polymerization performed in a single batch using TEB (5.0 equivalent); [j] Polymerization performed in a single batch without TEB. [h]Polymerization performed without TEB (20 DP) with 0.1 mL/hr addition of glycidol.

Table S2. Interpretation of ^{13}C NMR with relative integral value for dendritic, linear and terminal units for PGM, PGT, PGMS, PGE and PGB.

PGs/PGE/ PGB	L_{13} (80-81ppm)	D (78-79 ppm	$2L_{14}$ (73-74 ppm)	T (T_1+T_2) (63-64 and 82-83 ppm)
PGM-1	1.0	0.06	1.99	0.20
PGM-2	1.0	0.09	2.03	0.21
PGM-3	1.0	0.10	2.00	0.25
PGM-4	1.0	0.11	2.20	0.27
PGM-5	1.0	0.04	2.59	0.28
PGM-6	1.0	0.09	2.14	0.32
PGM-7	1.0	0.14	2.20	0.27
PGM-8	1.0	2.71	6.30	4.24
PGT-9	1.0	0.10	2.98	0.58
PGT-10	1.0	0.11	2.28	0.30
PGT-11	1.0	0.13	2.05	0.23
PGMS-1	1.0	2.32	5.29	3.30
PGMS-2	1.0	0.28	2.68	0.51
PGMS-3	1.0	0.14	2.10	0.26
PGMS-4	1.0	0.11	2.09	0.25
PGMS-5	1.0	0.05	5.91	0.97
PGMS-6	1.0	1.43	10.62	4.47
PGMS-7	1.0	2.17	4.46	3.19
PGE-1	1.0	0.08	2.86	0.56
PGE-2	1.0	0.11	2.27	0.42
PGE-3	1.0	0.12	2.15	0.39
PGE-4	1.0	0.14	2.56	0.46
PGB-1	1.0	2.48	1.24	0.33
PGB-2	1.0	0.18	2.98	0.36

Table S3. Characterization of PGE samples including degradable ester units obtained from monofunctional (ABA) initiator and an excess of TEB using slow monomer addition (0.1mL/hour) process. All PGE samples correspond to full conversion of glycidol and phthalic anhydride.

Entry	[ABA]/ [TEB]/[Gly]/[PA]	Temperature (°C)	Mn theoretical [a]	Mn [b] (^{1}H NMR)	Mn/PDI GPC [c]	Degree of branching [d]	L_{13} [e] (%)	L_{14} [f] (%)	D [g] (%)	T [h] (%)
PGE-1	1/5/27/3	60	2600	2500	4100/1.29	0.06	32.57	46.58	2.61	18.24
PGE-2	1/5/45/5	60	4200	4500	8300/1.50	0.09	37.52	42.59	4.13	15.76
PGE-3	1/5/180/20	60	16400	16100	16300/1.80	0.10	38.68	41.59	4.64	15.09
PGE-4	1/5/180/20	80	16400	14600	15900/8.7	0.11	34.72	44.44	4.86	15.97

[a] Theoretical molar mass calculated assuming linear PG structure, Mn(theoretical) = [(74.08×Glycidol/Initiator) + (148.1×PA/Initiator) × conversion + Mol. wt. of initiator + H]; [b] Calculated from ^{1}H NMR spectra by comparison of repeating unit signal intensity of glycidol and PA to the initiator signal intensity; [c] determined via GPC-RI in DMF using linear PMMA standards; [d] Degree of branching were calculated according to equation described by Frey et.al; (DB=2D/(2D+L_{13}+L_{14})); [e] Content of linear 1-3 connected monomers; [f] Content of linear 1-4 connected monomers; [g] Content of dendritic unit: [h] Content of terminal unit.

Table S4. Characterization of PGB block copolymer samples including both PPO and PG blocks obtained from monofunctional (ABA) and difunctional terephthalic acid (ATA) initiators and an excess of TEB using slow monomer addition (0.1mL/hour) process.

Entry	[ABA/ATA] [TEB]/[PO]/[Gly]	Temperature (°C)	Mn theoretical [a]	Mn [b] (^{1}H NMR)	Mn/PDI GPC [c]	Degree of branching [d]	L_{13} [e] (%)	L_{14} [f] (%)	D [g] (%)	T [h] (%)
PGB-1	1/5/20/10	80	2800	4100	2600/1.32	0.14	36.23	44.93	6.88	11.96
PGB-2	1/5/20/10	80	2800	4200	3100/1.34	0.13	33.00	49.18	5.94	11.88

[a] Theoretical molar mass calculated assuming linear PG structure, Mn(theoretical) = [(58×PO/Initiator) + (74.08×Glycidol/Initiator) × conversion + Mol. wt. of initiator + H]; [b] Calculated from ^{1}H NMR spectra by comparison of repeating unit signal intensity of glycidol and PO to the initiator signal intensity; [c] determined via GPC-RI in THF using linear PS standards; [d] Degree of branching were calculated according to equation described by Frey et.al; (DB=2D/(2D+L_{13}+L_{14})); [e] Content of linear 1-3 connected monomers; [f] Content of linear 1-4 connected monomers; [g] Content of dendritic unit: [h] Content of terminal unit.
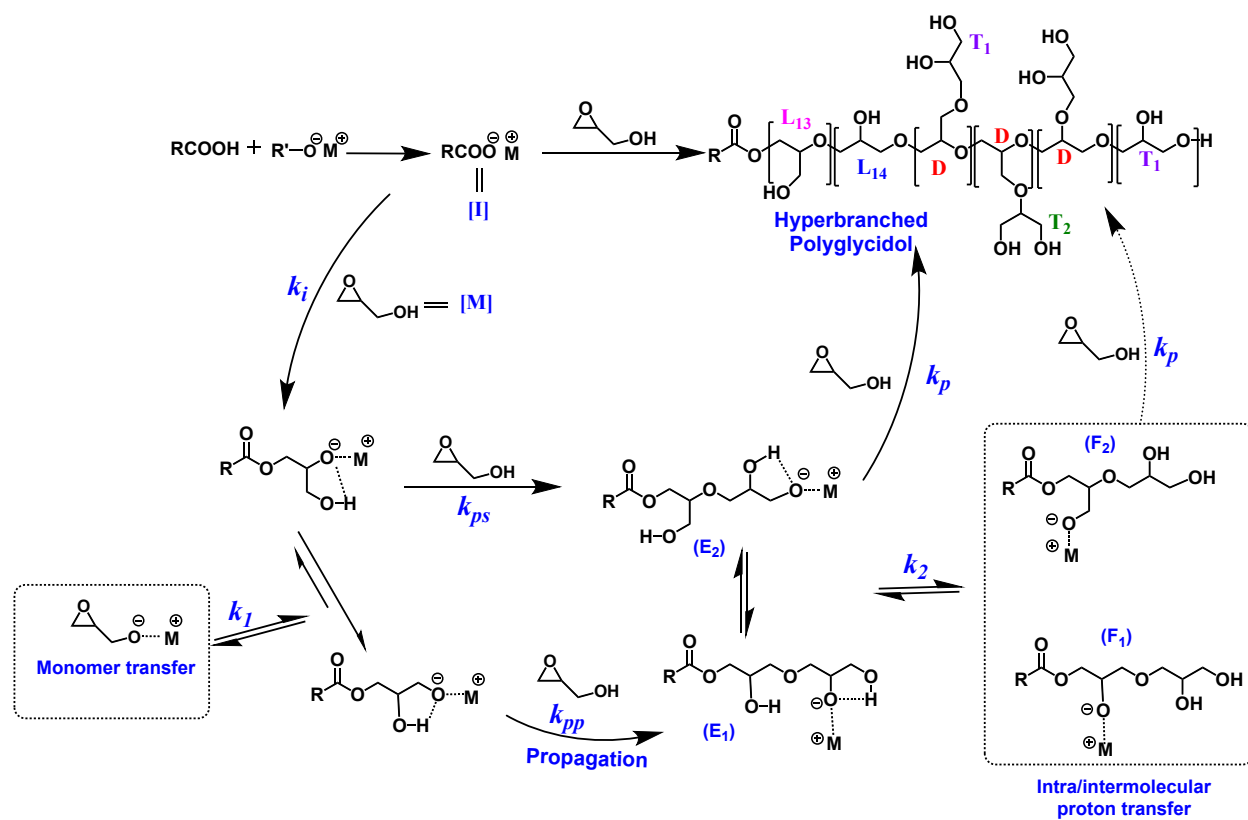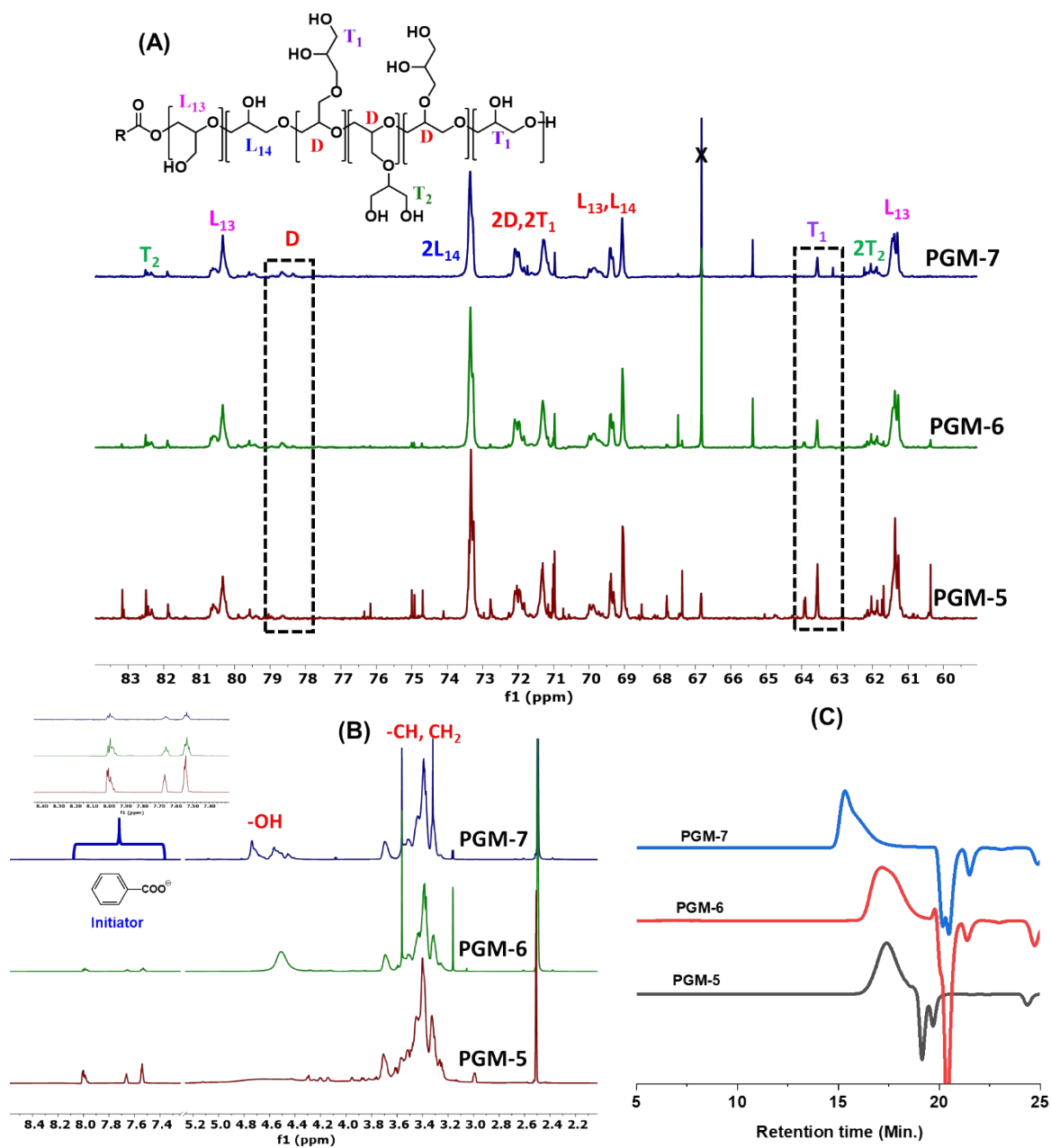
**Scheme S1.** Mechanism of anionic polymerization of glycidol in absence of TEB.
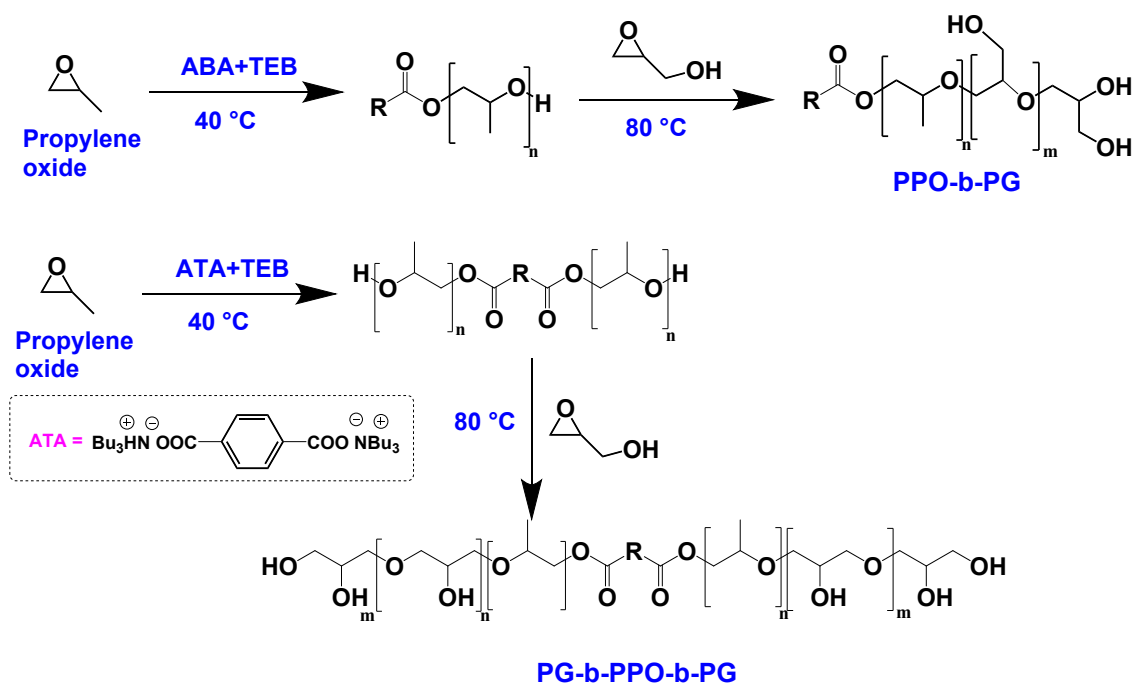
Scheme S2. One-pot synthesis of PG-based diblock and triblock copolymers using ABA/ATA as initiators and TEB as activator.
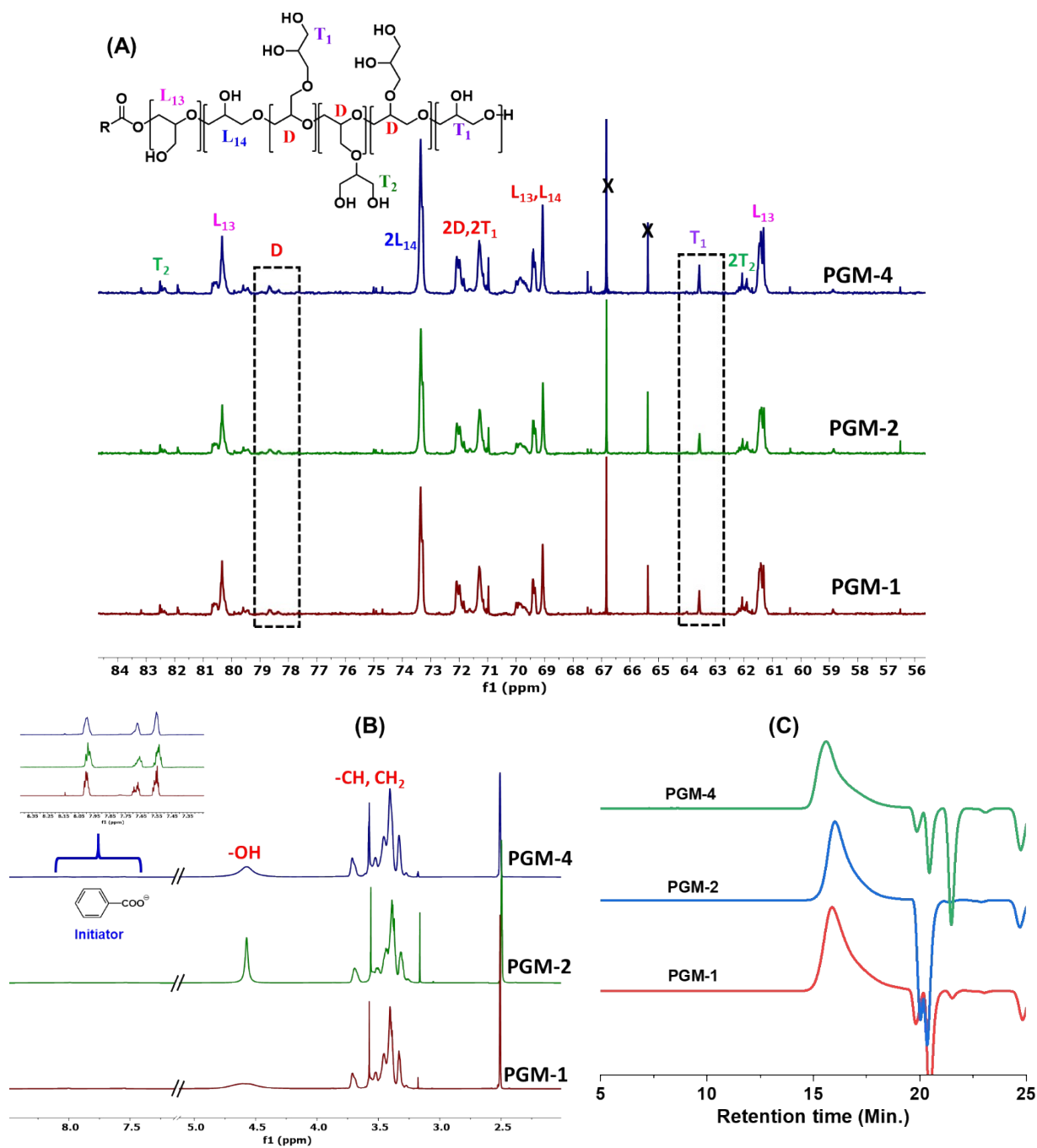
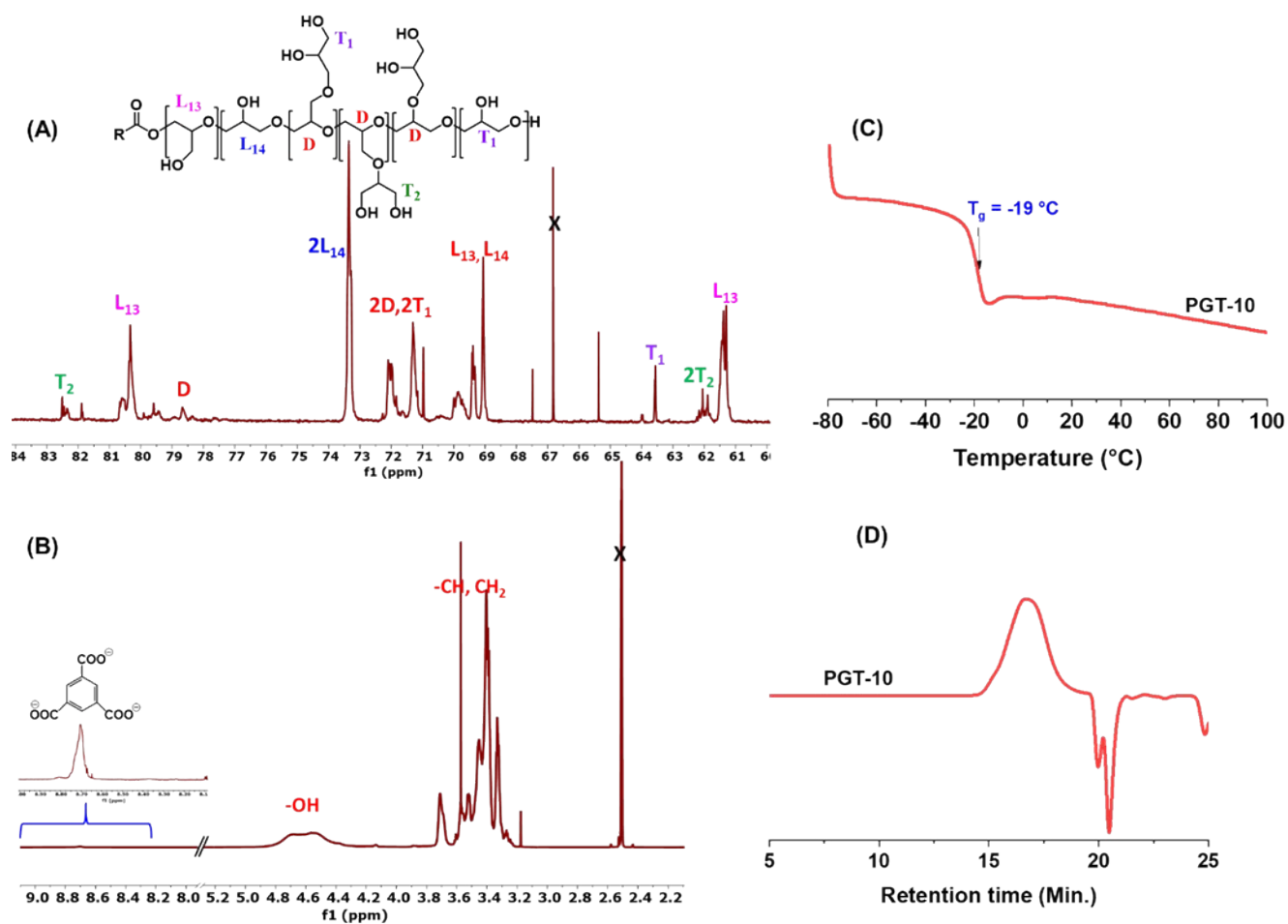**Figure S1.** (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGM-1, PGM-2, and PGM-4, respectively.

Figure S2. (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGM-5 (DP-20), PGM-6 (DP-50) and PGM-7 (DP-500).
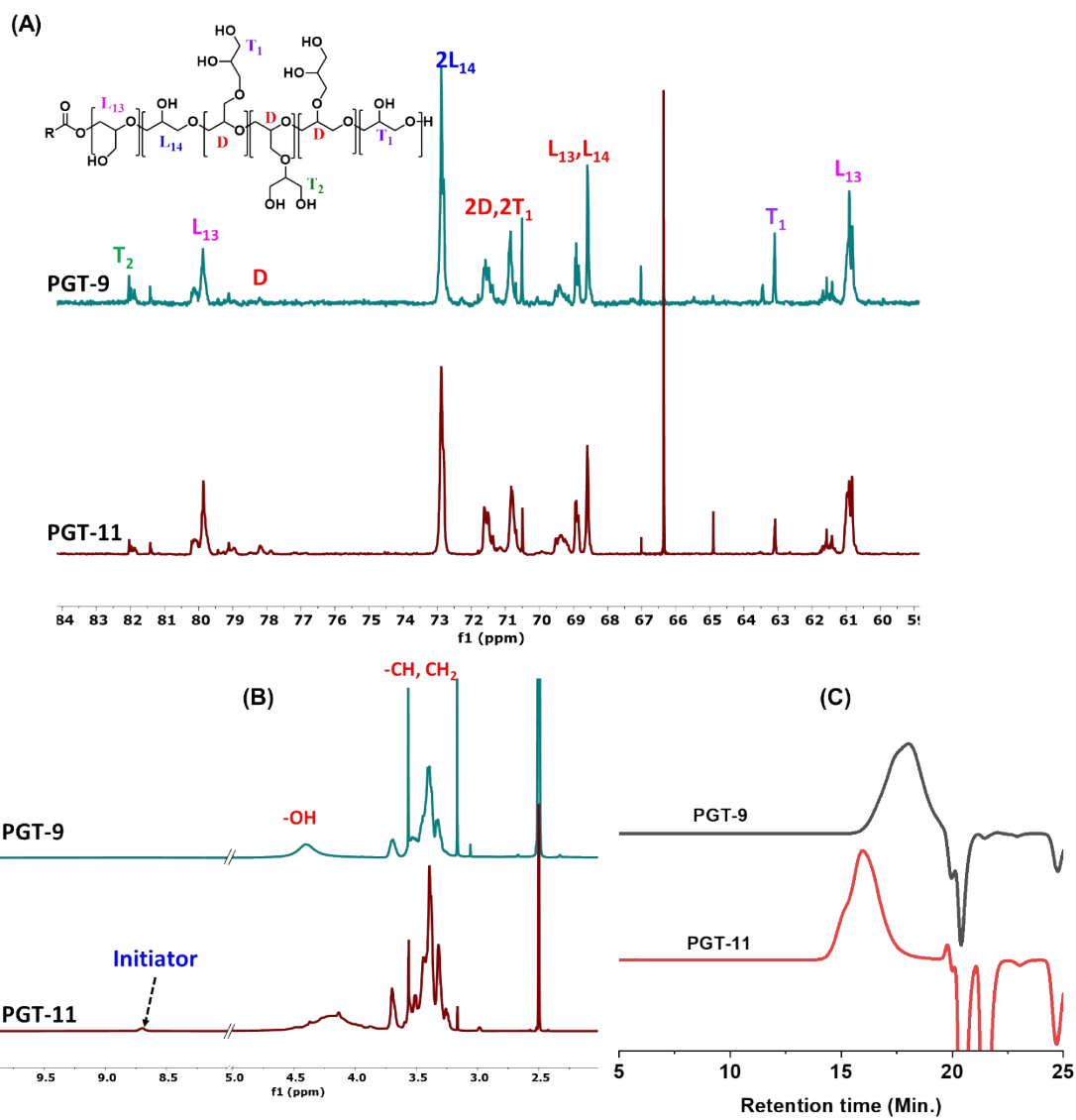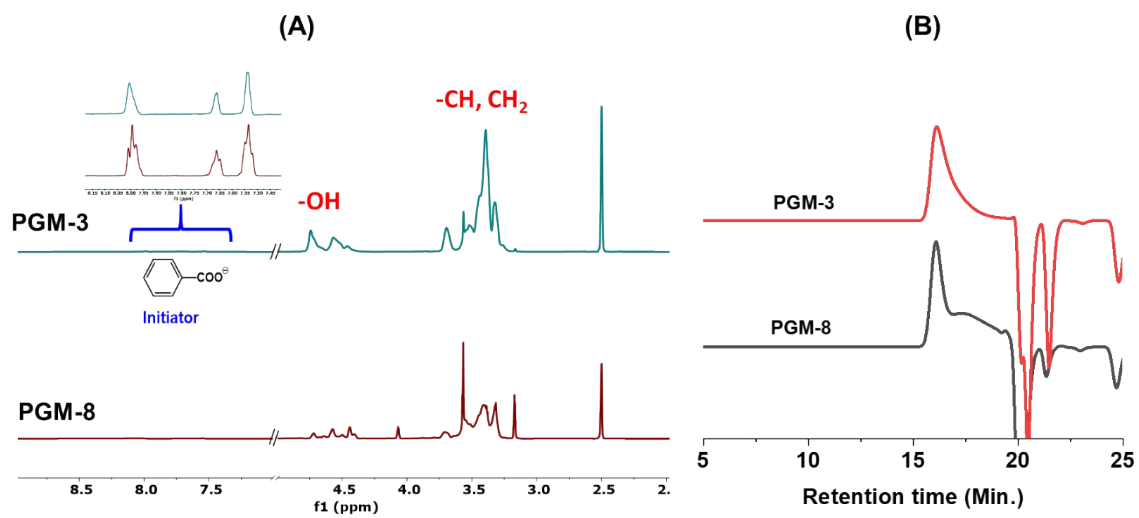
Figure S3. (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGT-9 and PGT-11, respectively. As show the values of molar masses for entries PGT-9, PGT-10 and PGT-11 in Table 1, the technique of slow monomer addition allowed a rather good control of molar masses by minimizing initiation by the hydroxyl function of the monomer. The broader distribution of molar masses in the latter case compared to values seen for monofunctional initiation may be explained by the slow rate of initiation of the carboxylate functions of the trifunctional initiator (ATMA).

Figure S4. (A) Inverse gated ^{13}C NMR spectra, (B) ^1H NMR spectra, (C) DSC curves, and (D) GPC traces for PGT-10.

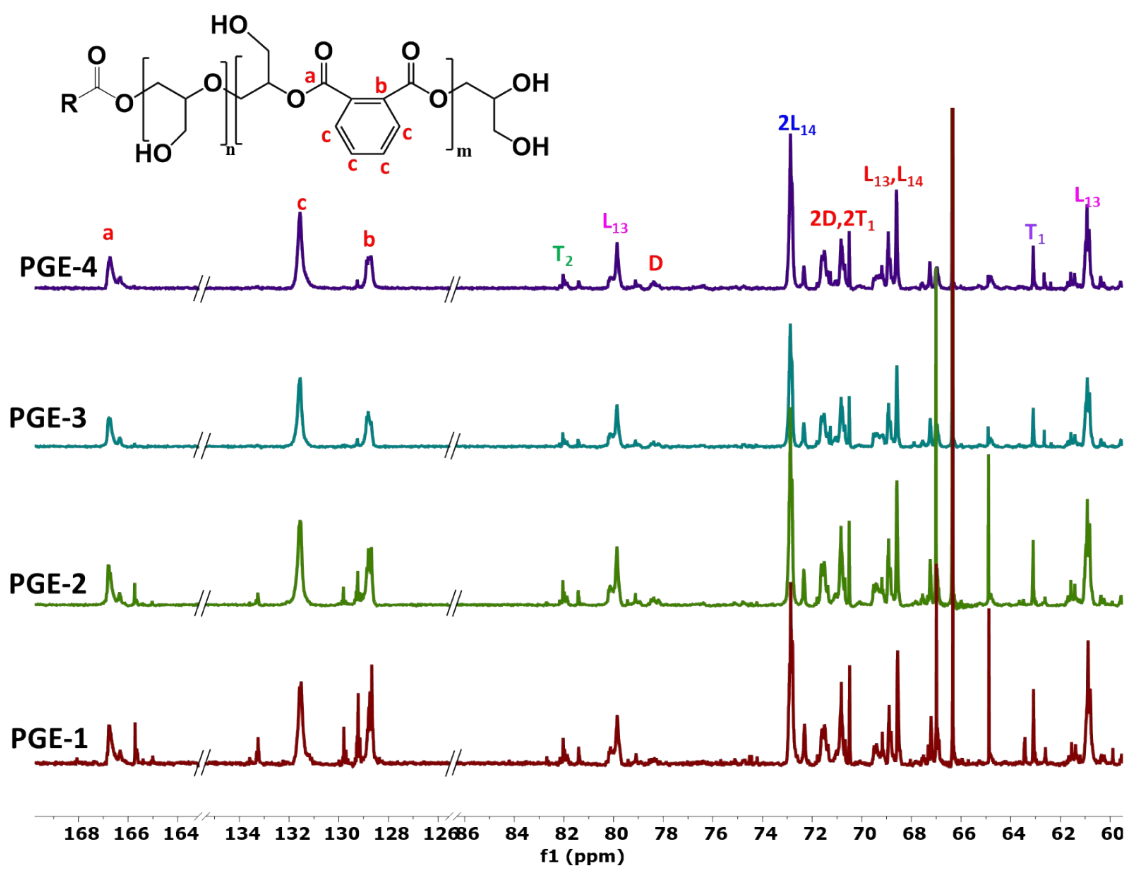**Figure S5.** (A) ^{1}H NMR spectra, (B) GPC traces for PGM-3 and PGM-8 respectively.

Figure S6. Characterization of PGMS samples obtained from monofunctional initiator (ABA) with slow addition (0.3mL/hour).
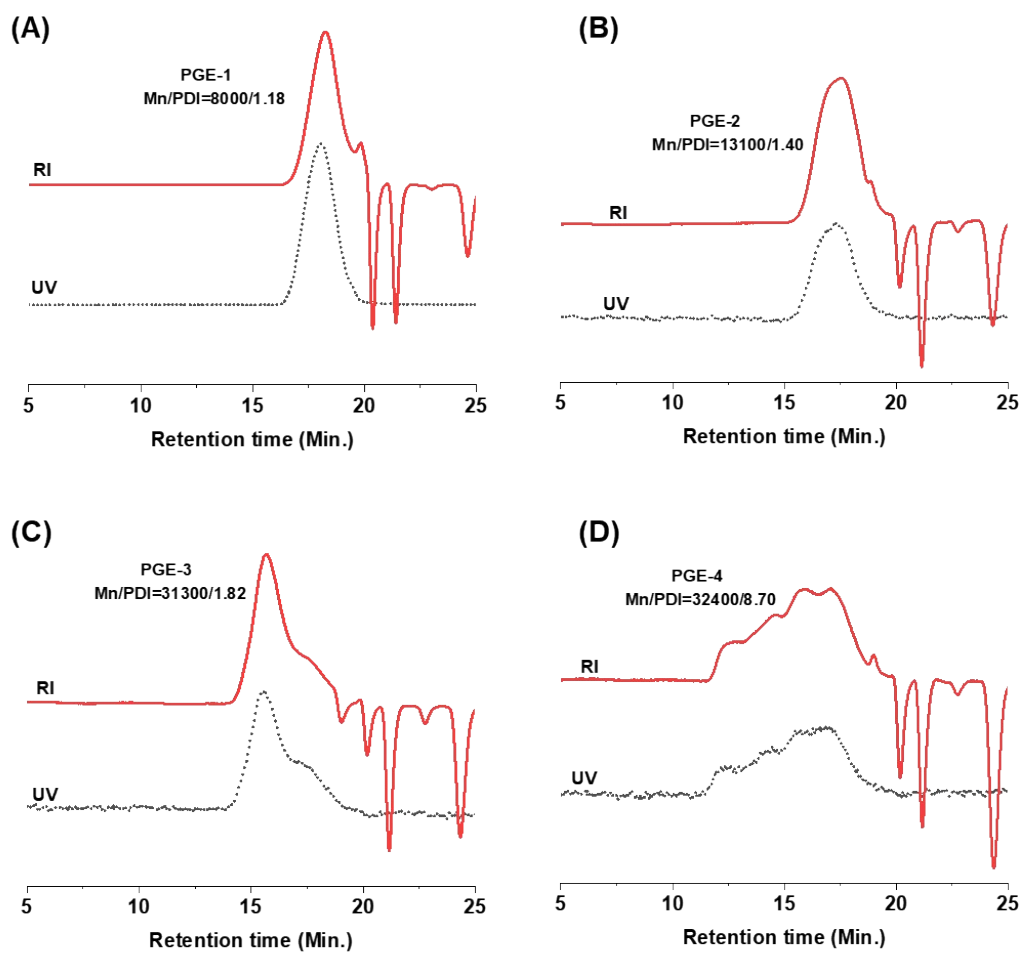
Figure S7. (A) Inverse gated ^{13}C NMR spectra, (B) ^{1}H NMR spectra, and (C) GPC traces for PGMS-5 and PGMS-6 where glycidol added at once.
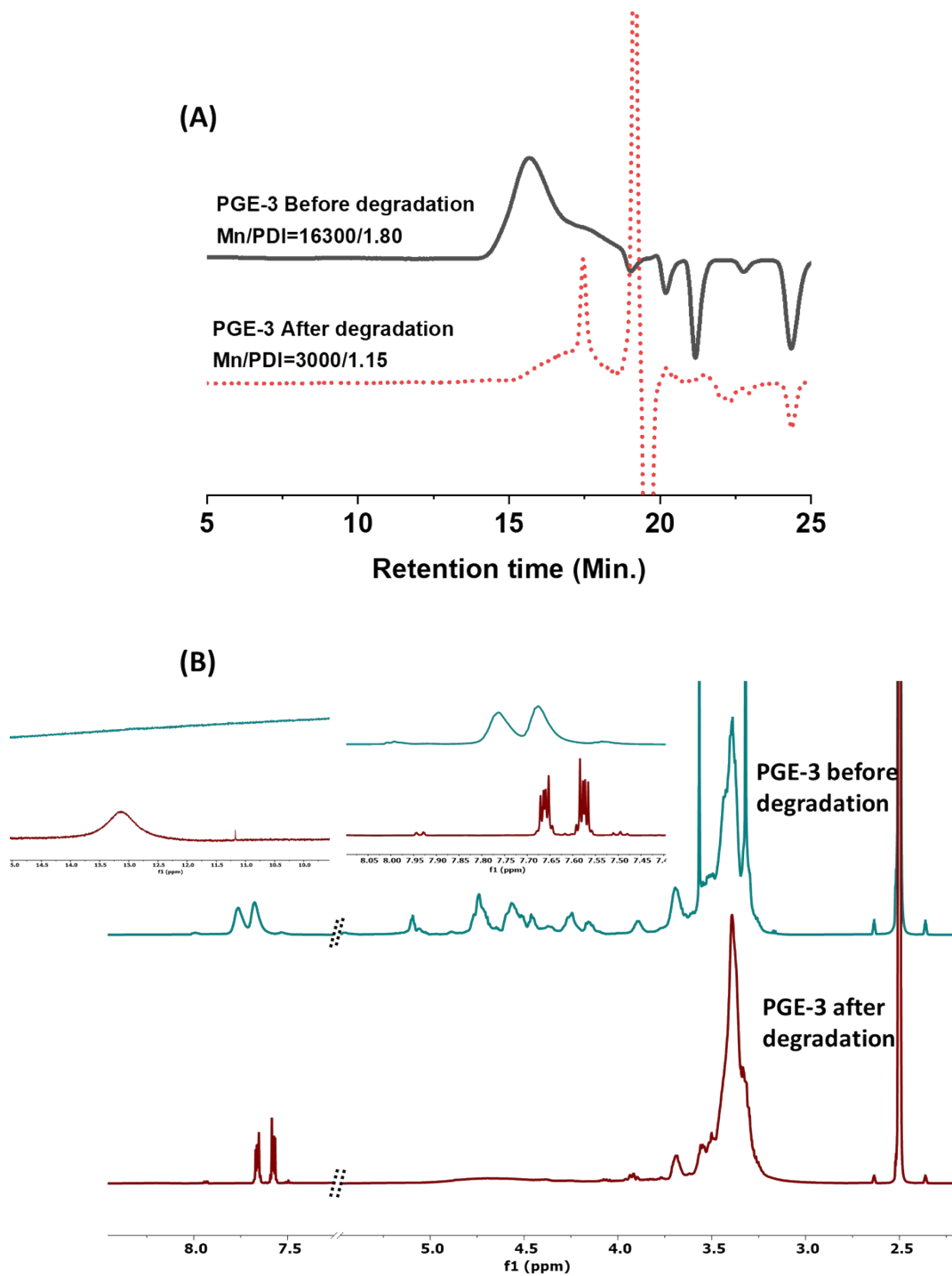
Figure S8. Chemical shift variations of proton for glycidol in the absence and in the presence of TEB (1.0 equivalent) in THF-d_8.

Figure S9. Inverse gated ^{13}C NMR spectra of (A) PGE-1, (B) PGE-2, (C) PGE-3, and (D) PGE-4.
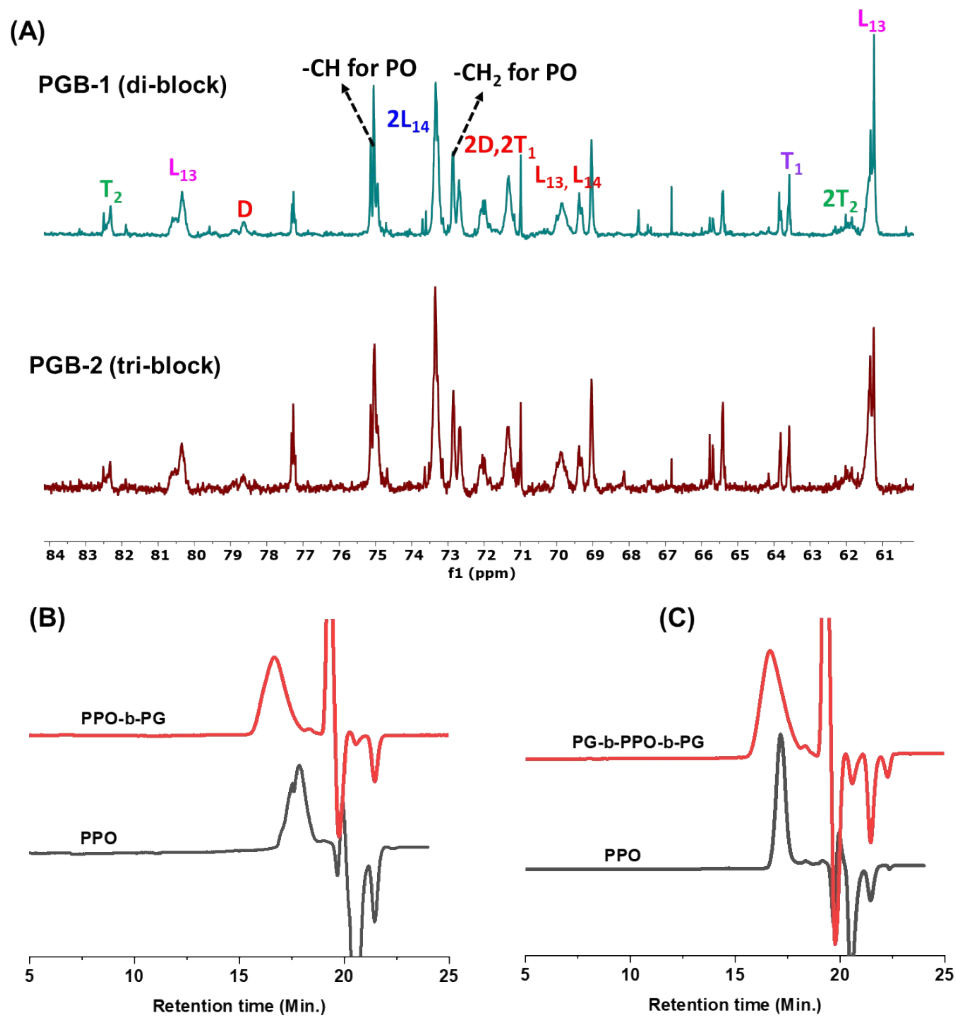
Figure S10. GPC traces (RI and UV detector) of (A) PGE-1, (B) PGE-2, (C) PGE-3, and (D) PGE-4 respectively.

Figure S11. (A) GPC traces and (B) ^{1}H NMR of PGE-3 before and after degradation (Insight region to show the acid peak).

Figure S12. (A) Inverse gated ^{13}C NMR spectra for di- (PGB-1) and triblock (PGB-2) copolymers, (B) GPC traces for diblock, and (C) GPC traces for triblock copolymer (Note: di-block and triblock samples were esterified to have comparable GPC traces in THF). The slight hump in the high molar mass region for the first PPO block (B) is due to the adventitious presence of small amount of water.
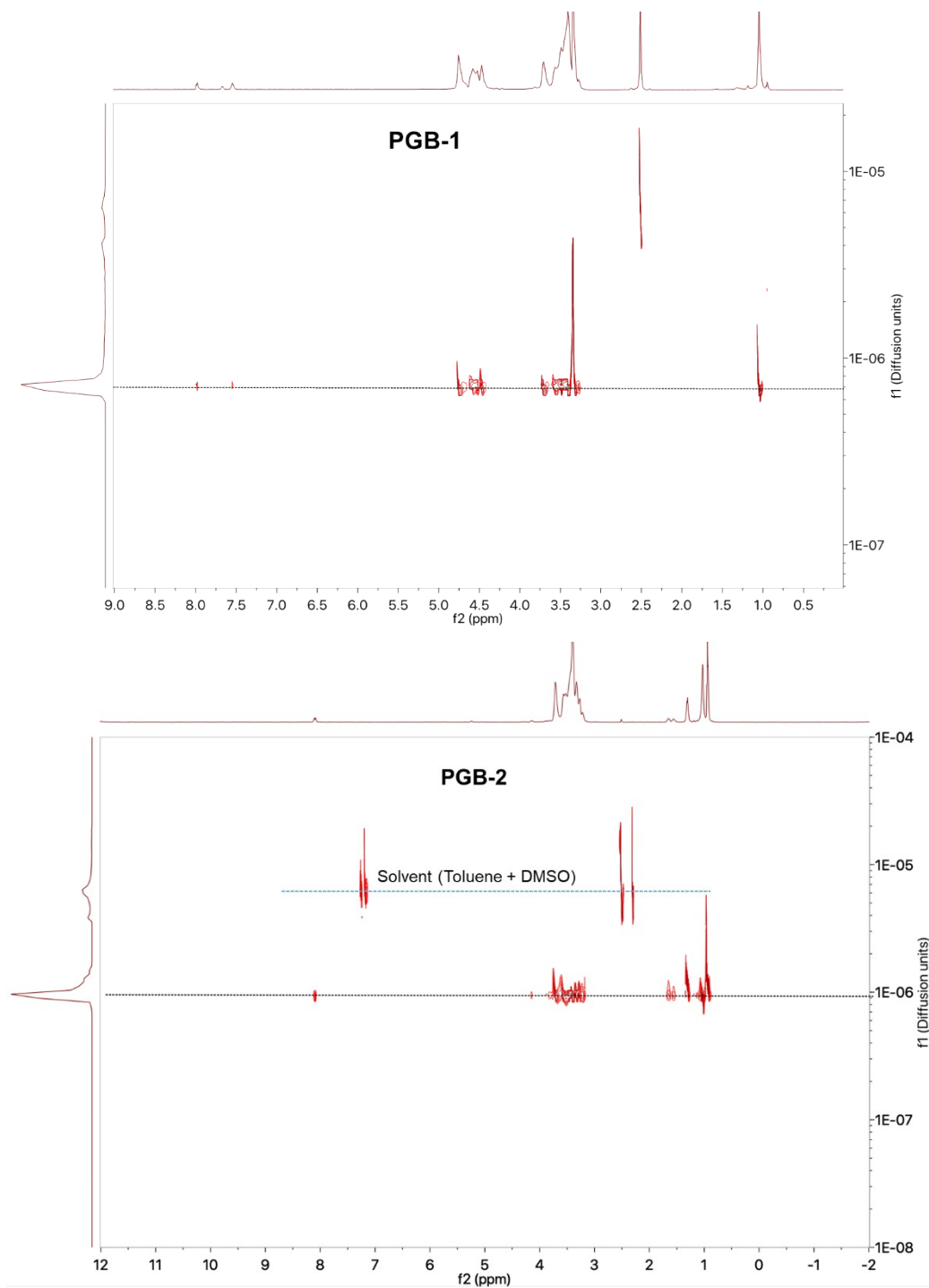
Figure S13. DOSY NMR spectra for PGB-1 (after dialysis) and PGB-2 (after precipitation in toluene) indicating the formation of a block copolymer structure.