Enzymatic Synthesis of poly(glycerol sebacate): Kinetics, Chain Growth, and Branching Behavior.

Giovanni B. Perin, Maria I. Felisberti

Supporting Information

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- Polycondensation conditions and characteristics of glycerol-based polyesters prepared *via* CALB catalysis – A short review.

Table S1 summarizes the main reaction conditions employed for the CALB-catalyzed synthesis of glycerol-based polyesters and the structural characteristics of these polyesters reported in the literature.

Table S1: Reaction conditions, mass average molecular weight (M_w), molecular weight dispersity ($Đ$), and structural features of glycerol-based polyesters prepared *via* CALB catalysis

Precursor	Solvent	T (°C)	t (h)	Byproduct removal	M_w (kDa)	$Đ$	Polyester structure	Reference
Vinyl adipate	Bulk	50	24	n.s.*	10.4	2.3	Branched, n° hydroxyl per unit < 1.0	20
Adipic acid	Dioxane	30	72	Molecular sieves	1.7	1.2	Linear	21
Diethyl suberate	Diphenyl ether	80	24	Vacuum	40.0	4.7	Branched-26 mol% dendritic unit	22
Diethyl suberate	Diphenyl ether	40	48	Vacuum	8.9	2.3	Branched-18 mol% dendritic unit	22
Diethyl suberate	Diphenyl ether	60	48	Vacuum	13.3	3.0	Branched-26 mol% dendritic unit	22
Diethyl suberate	Diphenyl ether	80	48	Vacuum	50.0	3.6	Branched-28 mol% dendritic unit	22
Adipic acid	Bulk	80	6	Vacuum	2.7	1.0	Branched-6.3mol% dendritic unit	23
Vinyl sebacate	Bulk	60	8	Argon flow	19.0	5.4	Branched - 16 mol% dendritic unit	24,25
Adipic acid	Bulk	90	44	Vacuum	2.7	1.6	Branched - DB = 58%	27
Vinyl adipate	THF	50	24	Open system	12.6	2.8	n.s.*	28
Oleic diacid	Bulk	90	24	Vacuum	9.1	3.4	Branched - 12.7 % dendritic unit	29
Vinyl adipate	THF	60	8	Open system	7.7	2.1	Branched - presence of dendritic unit	30
Vinyl adipate	THF	40	n.s.*	Open system	n.s.*	n.s.*	Linear	30
Dimethyl adipate	THF	60	48	Low pressure, soxhlet, molecular sieves	4.8	2.4	Branched-8 mol% dendritic unit	30
Vinyl adipate	THF	40	24	Open system	11.4	2.7	Branched-8-10 mol% dendritic unit	31
Vinyl adipate	THF	50	24	Open system	13.0	2.8	Branched-5-9 mol% dendritic unit	31
Vinyl adipate	THF	60	24	Open system	8.9	3.5	Branched-~20 mol% dendritic unit	31
Vinyl adipate	THF	70	24	Open system	5.2	4.2	Branched-~30 mol% dendritic unit	31
Sebacic acid	Bulk	120/90	71	N_2 flow/vacuum	63.9	16.9	n.s.*	40
Succinic acid	sc(CO_2)	40	24	Molecular sieves	10.2	3.0	Branched - DB = 5%	41
Succinic acid	sc(CO_2)	50	24	Molecular sieves	7.1	2.7	Branched - DB = 13%	41
Succinic acid	sc(CO_2)	60	24	Molecular sieves	5.8	3.4	Branched - DB = 11%	41

* n.s. - not specified

- IR spectrum

A representative IR spectrum of PGS is presented in Figure S1.
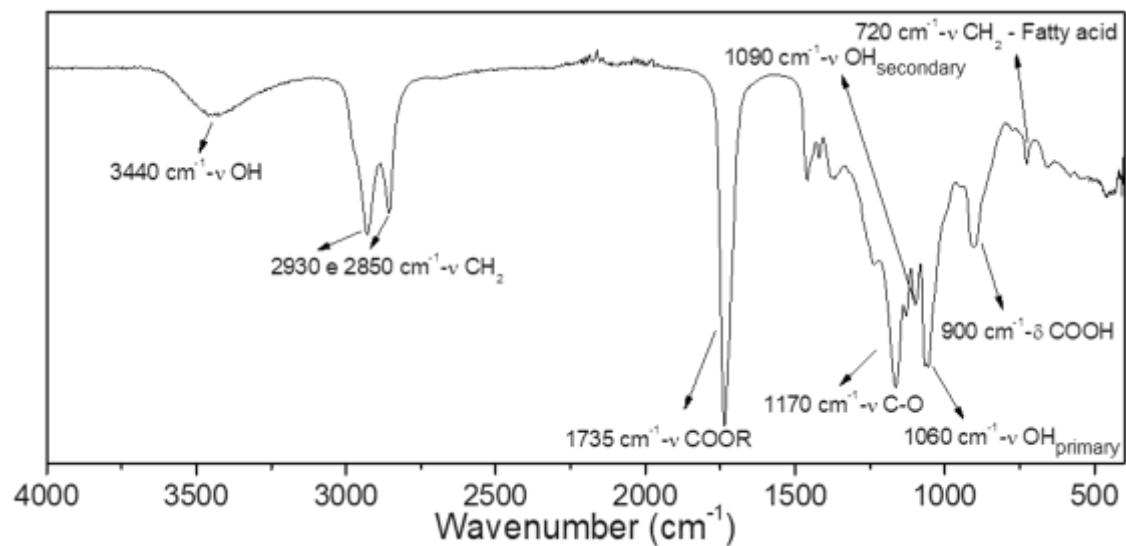
Figure S1. IR spectrum of PGS.

- ¹³C NMR

Figure S2 presents the ¹³C NMR spectrum of PGS prepared via CALB-catalyzed polycondensation in acetone at 30 °C for 24 h.
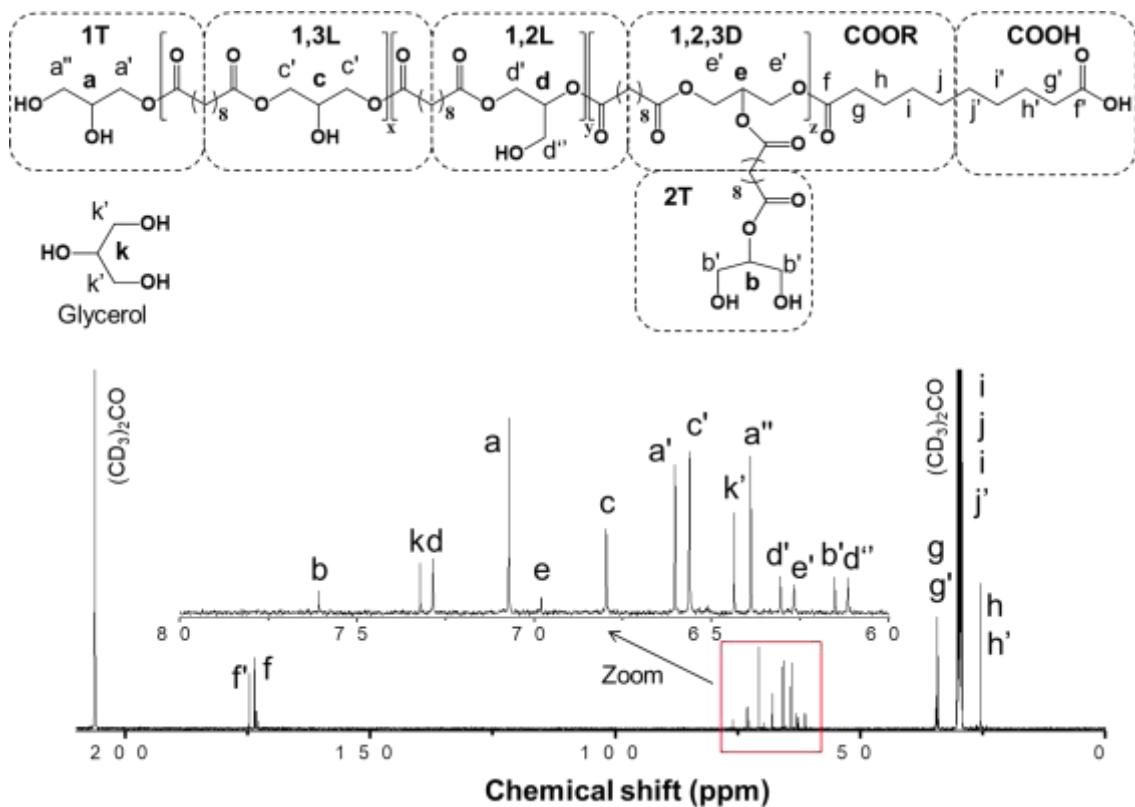
Figure S2. ¹³C NMR spectrum of PGS in $(CD_3)_2CO$.

- ^{1}H-^{13}C HSQC contour map

Figure S3 presents the ^{1}H-^{13}C HSQC contour map of PGS prepared via CALB-catalyzed polycondensation in acetone at 40 °C for 24 h.
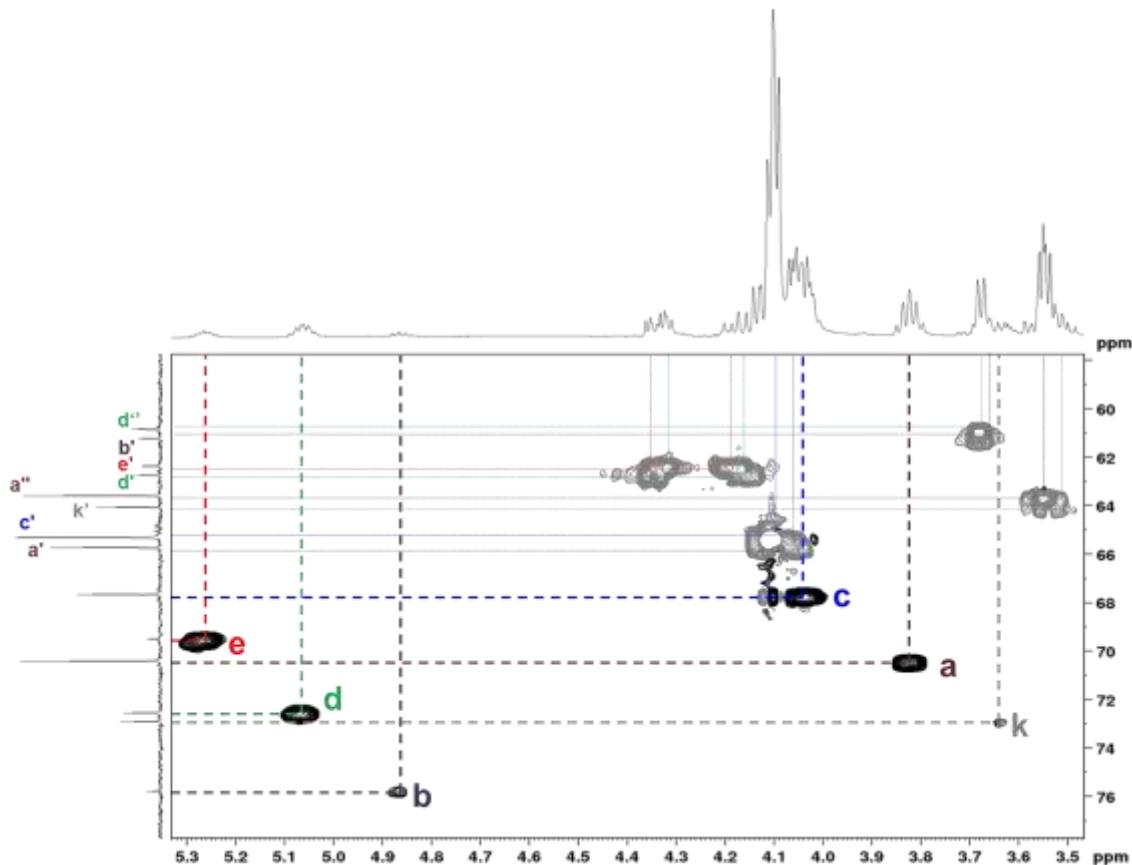
Figure S3. Contour map from HSQC single bond proton-carbon correlation spectra of PGS in (CD$_3$)$_2$CO. The black and dark gray cross-peaks relates to methine and methylene groups, respectively.

- ^{1}H-^{1}H COSY contour map

COSY contour map from the proton homonuclear correlation spectroscopy spectrum of PGS prepared in acetone at 40 °C for 24 h is presented in Figure S4.
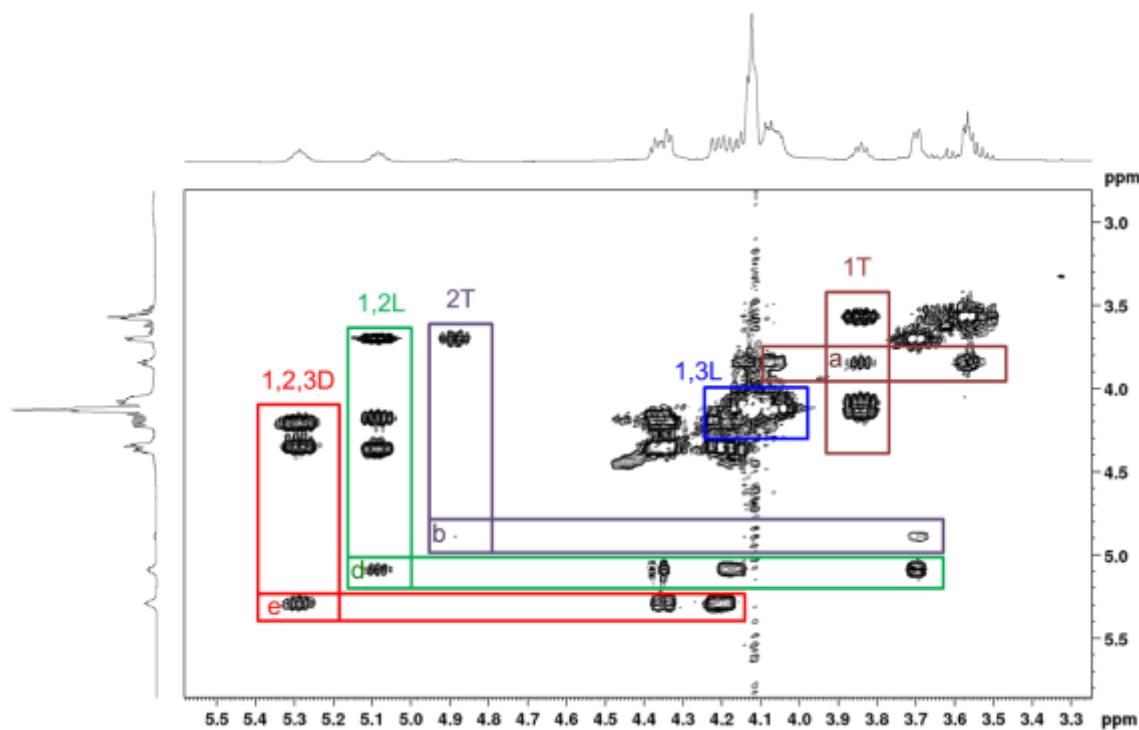
Figure S4. Contour map from the COSY proton homonuclear correlation spectroscopy spectrum of PGS in $(CD_3)_2CO$.

- Temporal evolution of ^{1}H NMR spectra signals

^{1}H NMR spectra of PGS are divided into the three main regions: (i) the region from 2.2 to 2.4 ppm related to the evolution of the signals of the methylene protons adjacent to the carbonyl of sebacic acid/ester (Figure S5a); (ii) the region from 3.4 to 4.4 ppm mainly related to the evolution of the protons signals of the non-reacted glycerol (Glyc) and the 1T and 1,3L glyceridic units (Figure S5b), and (iii) the region from 4.8 to 5.4 ppm related to the evolution of the signals of the methine protons of the 2T, 1,2L, and 1,2,3D glyceridic units, Figure S5c.
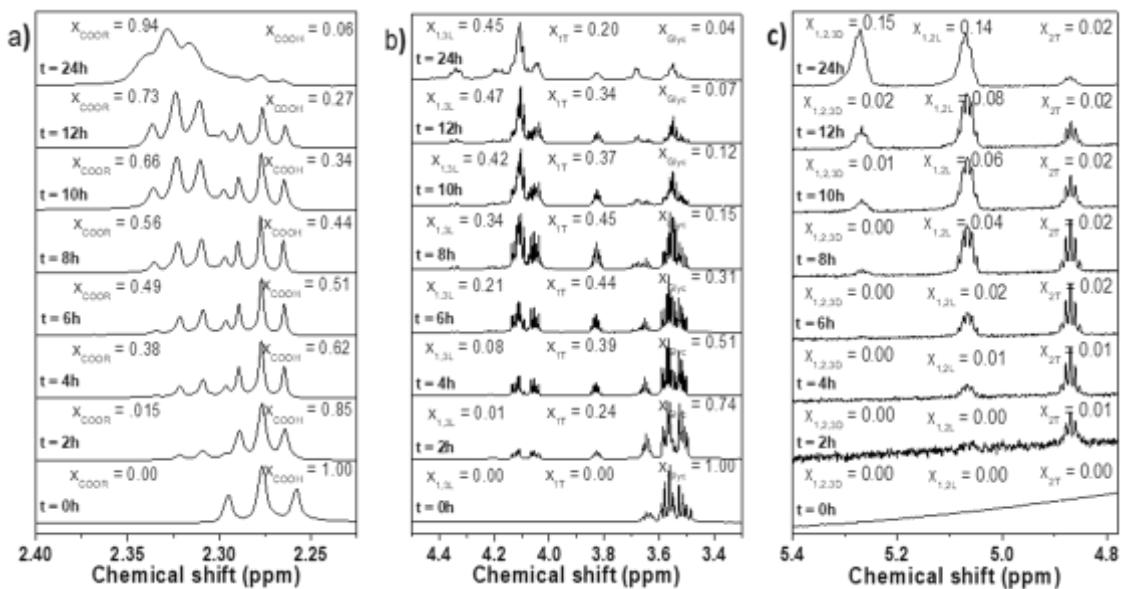
Figure S5. ^{1}H NMR spectra of the reaction medium as a function of reaction time during the polymerization in acetone at 30 °C. The average molar fraction of each species are given for the three mains regions: (a) signals of the methylene protons adjacent to the carbonyl of sebacic acid/ester, (b) signals of the protons from non-reacted glycerol (Glyc), and from 1T and 1,3L units; and (c) signals of the methine protons of the 2T, 1,2L, and 1,2,3D glyceridic units. The signals intensity of each spectrum was normalized.

The Figure S5a shows that the conversion of the carboxylic acid into ester during the polymerization shifts and broadens the signals of the methylene protons adjacent to carbonyl from 2.28 to 2.33 ppm (signals g and g' in Figure 1, respectively). Despite these signals being overlapped, the average molar fraction of ester (x_{COOR}) and carboxylic acid groups (x_{COOH}) were estimated by non-linear fitting using the software

Topspin (Bruker). As presented in Figure S5b, the intensity of the methine and methylene protons signals of nonreacted glycerol (chemical shift region from 3.4 to 3.7 ppm) tends to decrease with the reaction progression, while the intensity of the signals of methine and methylene protons of esterified glycerol (in the range from 3.8 to 4.4 ppm) increases. It is also observed an increase in the intensity of the signal of the methine protons of glyceridic units with esterified secondary hydroxyl in the region from 4.8 to 5.3 ppm, Figure S5c.

An illustrative example of the curve-fitted signals in the region of the methylene protons adjacent to the carbonyl of the sebacic acid/ester is presented in Figure S6.
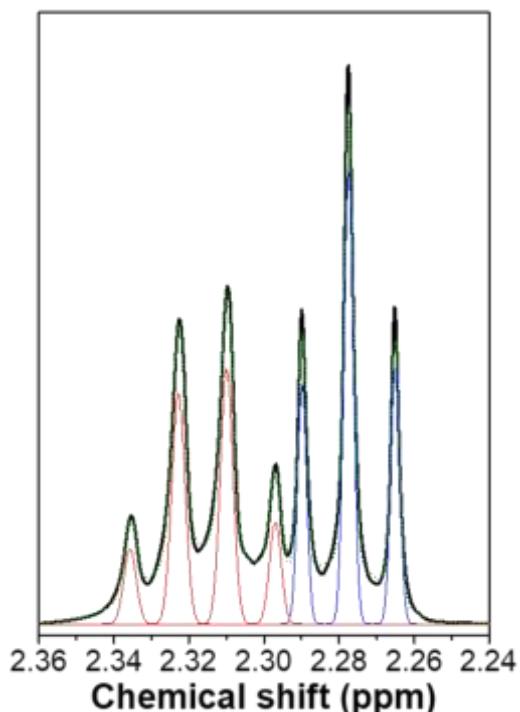
Figure S6. A representative curve-fitted signals related to the ^{1}H NMR spectra shown in Figure S5a for the polycondensation performed in acetone at t = 8h: **black** line - experimental data; **blue** line - related to the protons signals of the methylene group adjacent to the carboxylic acid (f'); **red** line - related to the protons signals of the methylene group adjacent to the carbonyl ester (f), and the **green** dash line - related to the overall fit model.

- Structural parameters

The average molar fraction of nonreacted glycerol (x_{Glyc}) could be estimated by Equation S1.

$$x_{Glyc} = \frac{I_{3.45-3.79ppm} - (I_{a''}) + (I_{b'}) + (I_{d''})}{5} = \frac{I_{3,45-3,79ppm} - (2I_a) + (4I_b) + (2I_d)}{5} = \frac{(I_k + I_{k'})}{5}$$

Equation S1

where $I_{3.45-3.79ppm} = I_{a''} + I_{b'} + I_{d''} + I_k + I_{k'}$ is the integral of the signals in the chemical shift region from 3.45 to 3.79 ppm (Fig. 1 and Fig.S5b).

The molar fraction of the 1,3L unit could be determined by using Equation S2.

$$x_{1,3L} = \frac{I_{4.0-4.5ppm} - (I_{a'}) + (I_{d'}) + (I_{e'})}{5} = \frac{I_{4.0-4.5ppm} - [(2I_a) + (2I_d) + (4I_e)]}{5} = \frac{(I_c + I_{c'})}{5}$$ Equation S2

where $I_{4.0-4.5ppm} = I_{a'} + I_{d'} + I_{e'} + I_c + I_{c'}$ is the integral of the signals in the chemical shift region from 4.0 to 4.5 ppm (Fig. 1 and Fig.S5b).

The molar fraction of the 1,3L unit can also be determined by Equation S3.

$$x_{1,3L} = 1.00 - (x_{1T} + x_{2T} + x_{1,2L} + x_{1,2,3D} + x_{Glyc})$$ Equation S3

The carboxylic acid conversion (p_{COOH}) was calculated using Equation S4.

$$p_{COOH} = \frac{I_f}{I_f + I_{f'}}$$ Equation S4

The relative molar fraction of each glyceridic unit in PGS (y_i) was calculated by Equation S5.

$$y_i = \frac{x_i}{\sum x_i} 100 \quad x_i \neq x_{Glycerol}$$ Equation.S5

The number average degree of polymerization (Dp_n) of PGS was calculated by Equation S6.

$$Dp_n = \frac{\frac{1}{2}(x_{1T} + x_{2T} + x_{COOH} - x_{1,2,3D}) + x_{COOR}}{\frac{1}{2}(x_{1T} + x_{2T} + x_{COOH} - x_{1,2,3D})}$$ Equation S6

8

The number average molecular weight (M_n) was determined from Dp_n by Equation S7.

$$M_{n\,RMN} = Dp_n M_o \qquad \text{Equation S7}$$

where $M_0 = 258.34$ g mol^{-1} is the average molecular weight of the repetitive units.

The average number of each glyceridic unit per PGS chain (n_i) was determined by Equation S8.

$$n_i = Dp_n\left(\frac{y_i}{100}\right) \qquad \text{Equation S8}$$

The glycerol degree of substitution (DS) was calculated by Equation S9.

$$DS = \frac{x_{1T} + x_{2T} + 2.x_{1,3L} + 2.x_{1,2L} + 3.x_{1,2,3D}}{x_{1T} + x_{2T} + x_{1,3L} + x_{1,2L} + x_{1,2,3D}} \qquad \text{Equation S9}$$

The hydroxyl conversion (p_{OH}) was calculated by Equation S10.

$$p_{OH} = {DS}/{3} \qquad \text{Equation S10}$$

- Comparison of results from ^{1}H NMR and quantitative ^{13}C NMR spectra

Table S2: Average molar fractions (x_i) of each glyceridic unit of the PGS and conversion (p_i) determined from ^{1}H NMR and quantitative ^{13}C NMR spectra for the sample prepared in tetrahydrofuran at 40 °C and reaction time of 6 h and 8h.

| | | x_i | | | | | | | |
Sample	Technique	1T	2T	1,3L	1,2L	1,2,3D	Glycerol	p_{COOH}	p_{OH}
6 h	^{1}H NMR	0.28	0.02	0.48	0.12	0.05	0.05	0.85	0.58
6 h	^{13}C NMR	0.29	0.04	0.47	0.09	0.03	0.07	0.77	0.56
8 h	^{1}H NMR	0.27	0.02	0.46	0.13	0.07	0.05	0.84	0.59
8 h	^{13}C NMR	0.31	0.04	0.43	0.10	0.03	0.09	0.74	0.55

- General data from the ^{1}H NMR and GPC analyses for PGS prepared in different solvents

The general data from the ^{1}H NMR and GPC analyses of the reaction media for the kinetics studies of CALB-catalyzed polycondensation of glycerol and sebacic acid in tetrahydrofuran, t-butanol, acetone, and acetonitrile at the temperature range from 30 to 70 °C are presented in Table S3, S4, S5, and S6, respectively.

Table S3. Number average molecular weight (M_n), molecular weight dispersity ($Đ$), number average degree of polymerization (Dp_n), the average molar fraction of glyceridic species in the reaction medium (x_i), carboxylic acid conversion (p_{COOH}), glycerol degree of substitution (DS), hydroxyl conversion (p_{OH}) and degree of branching (DB) of PGS synthesized using CALB as the catalyst, and tetrahydrofuran as solvent at different temperatures and reaction times

T (°C)	t (h)	GPC M_n (Da)	$Đ$	Dp_n	x_{Glyc}	x_{1T}	x_{2T}	$x_{1,3L}$	$x_{1,2L}$	$x_{1,2,3D}$	p_{COOH}	DS	p_{OH}	DB (%)
	2	681	1.62	2.3	0.13	0.47	0.02	0.35	0.03	0.00	0.59	1.44	0.48	0
	4	980	1.75	3.5	0.07	0.34	0.02	0.47	0.08	0.02	0.75	1.63	0.54	7
40	6	753	1.78	5.3	0.05	0.28	0.02	0.48	0.12	0.05	0.85	1.74	0.58	14
	8	679	1.67	5.4	0.05	0.27	0.02	0.46	0.13	0.07	0.84	1.77	0.59	19
	10	1285	2.59	5.5	0.05	0.27	0.03	0.43	0.13	0.09	0.84	1.78	0.59	24
	24	1840	5.60	12.5	0.07	0.22	0.02	0.36	0.17	0.16	0.92	1.91	0.64	38
	2	551	1.62	2.6	0.10	0.41	0.02	0.40	0.06	0.01	0.64	1.53	0.51	4
	4	731	1.77	3.9	0.07	0.31	0.02	0.47	0.10	0.03	0.76	1.68	0.56	10
	6	471	1.74	4.3	0.05	0.27	0.02	0.47	0.12	0.07	0.76	1.77	0.59	19
50	8	504	1.97	7.0	0.05	0.25	0.02	0.44	0.14	0.10	0.88	1.82	0.61	26
	10	802	2.65	6.6	0.05	0.26	0.03	0.40	0.15	0.11	0.87	1.81	0.60	29
	12	589	2.33	6.5	0.05	0.27	0.03	0.40	0.15	0.10	0.88	1.79	0.60	27
	24	1693	5.39	11.5	0.09	0.22	0.03	0.32	0.17	0.17	0.91	1.91	0.64	41
	2	744	1.50	2.5	0.13	0.46	0.02	0.34	0.04	0.01	0.63	1.45	0.48	2
	4	994	1.65	3.5	0.08	0.35	0.03	0.43	0.09	0.03	0.74	1.63	0.54	9
	6	1168	1.86	4.1	0.08	0.31	0.03	0.41	0.11	0.05	0.78	1.69	0.56	15
60	8	1368	2.15	4.6	0.08	0.30	0.03	0.39	0.13	0.07	0.81	1.72	0.57	20
	10	1487	2.34	5.2	0.08	0.28	0.03	0.37	0.14	0.10	0.82	1.77	0.59	25
	12	1280	2.85	5,0	0.09	0.28	0.04	0.35	0.14	0.11	0.81	1.77	0.59	27
	24	1614	4.58	7.3	0.07	0.26	0.03	0.32	0.16	0.15	0.87	1.84	0.61	34

Table S4. Number average molecular weight (M_n), molecular weight dispersity (Đ), number average degree of polymerization (Dp$_n$), the average molar fraction of glyceridic species in the reaction medium (x_i), carboxylic acid conversion (p_{COOH}), glycerol degree of substitution (DS), hydroxyl conversion (p_{OH}) and degree of branching (DB) of PGS synthesized using CALB as the catalyst, and t-butanol as solvent at different temperatures and reaction times

T (°C)	t (h)	GPC M_n (Da)	Đ	Dp$_n$	x_{Glyc}	x_{1T}	x_{2T}	$x_{1,3L}$	$x_{1,2L}$	$x_{1,2,3D}$	p_{COOH}	DS	p_{OH}	DB (%)
	2	593	1.54	2.2	0.16	0.47	0.03	0.28	0.05	0.01	0.56	1.42	0.47	6
	4	649	1.98	2.3	0.10	0.42	0.04	0.33	0.09	0.02	0.56	1.51	0.50	9
	6	845	1.72	3.1	0.09	0.36	0.03	0.38	0.11	0.03	0.70	1.60	0.53	11
40	8	893	1.83	3.3	0.08	0.34	0.03	0.38	0.13	0.04	0.71	1.64	0.55	13
	10	837	1.81	3.6	0.08	0.35	0.04	0.35	0.13	0.05	0.75	1.63	0.54	17
	12	831	1.87	3.3	0.09	0.35	0.04	0.34	0.13	0.05	0.71	1.63	0.54	17
	24	1003	2.12	3.9	0.09	0.31	0.04	0.32	0.16	0.08	0.76	1.70	0.57	25
	2	890	1.57	2.6	0.14	0.41	0.03	0.32	0.08	0.02	0.63	1.51	0.5	9
	4	1143	1.66	3.5	0.06	0.35	0.03	0.41	0.12	0.03	0.76	1.63	0.54	10
	6	1246	1.81	3.7	0.07	0.31	0.03	0.39	0.14	0.06	0.74	1.70	0.57	18
50	8	1123	1.70	3.7	0.08	0.32	0.03	0.41	0.12	0.04	0.75	1.66	0.55	13
	10	1118	1.67	3.6	0.09	0.34	0.04	0.35	0.13	0.05	0.75	1.64	0.55	17
	12	1105	1.71	3.6	0.09	0.33	0.04	0.35	0.13	0.06	0.74	1.66	0.55	20
	24	1338	2.05	4.3	0.07	0.31	0.04	0.32	0.17	0.09	0.79	1.72	0.57	24
	2	768	1.38	2.4	0.17	0.42	0.04	0.28	0.07	0.02	0.59	1.47	0.49	7
	4	862	1.50	2.8	0.11	0.39	0.04	0.32	0.11	0.03	0.66	1.55	0.52	10
	6	963	1.59	3.1	0.10	0.36	0.04	0.33	0.13	0.04	0.70	1.60	0.53	13
60	8	1042	1.70	3.6	0.08	0.34	0.04	0.34	0.14	0.06	0.74	1.65	0.55	18
	10	1127	1.80	3.8	0.09	0.32	0.04	0.33	0.15	0.07	0.75	1.68	0.56	20
	12	1200	1.91	3.8	0.09	0.32	0.04	0.32	0.15	0.08	0.75	1.69	0.56	22
	24	1339	2.66	5.3	0.06	0.28	0.04	0.34	0.17	0.11	0.83	1.78	0.59	28
	2	823	1.43	2.6	0.15	0.40	0.04	0.30	0.09	0.02	0.62	1.50	0.50	7
	4	944	1.53	3,0	0.13	0.37	0.04	0.31	0.09	0.04	0.68	1.58	0.53	13
	6	1019	1.62	3.4	0.12	0.33	0.04	0.33	0.13	0.05	0.72	1.64	0.55	15
70	8	1088	1.73	3.9	0.10	0.31	0.04	0.34	0.14	0.07	0.76	1.69	0.56	19
	10	1103	1.84	3.8	0.07	0.32	0.04	0.34	0.15	0.08	0.75	1.70	0.57	22
	12	1179	1.94	4.1	0.08	0.31	0.04	0.34	0.15	0.08	0.78	1.71	0.57	22
	24	1311	2.67	5.4	0.07	0.27	0.04	0.34	0.17	0.11	0.83	1.78	0.59	28

Table S5. Number average molecular weight (M_n), molecular weight dispersity ($Đ$), number average degree of polymerization (Dp_n), the average molar fraction of glyceridic species in the reaction medium (x_i), carboxylic acid conversion (p_{COOH}), glycerol degree of substitution (DS), hydroxyl conversion (p_{OH}) and degree of branching (DB) of PGS synthesized using CALB as the catalyst, and acetone as solvent at different temperatures and reaction times

T (°C)	t (h)	GPC M_n (Da)	$Đ$	Dp_n	x_{Glyc}	x_{1T}	x_{2T}	$x_{1,3L}$	$x_{1,2L}$	$x_{1,2,3D}$	p_{COOH}	DS	p_{OH}	DB (%)
	2	341	1.31	1.3	0.74	0.24	0.01	0.01	0.00	0.00	0.15	1.03	0.34	0
	4	422	1.31	1.7	0.51	0.39	0.01	0.08	0.01	0.00	0.38	1.18	0.39	0
	6	512	1.40	2.0	0.31	0.44	0.02	0.21	0.02	0.00	0.49	1.34	0.45	0
30	8	649	1.59	2.2	0.15	0.45	0.02	0.34	0.04	0.00	0.56	1.45	0.48	0
	10	810	1.78	2.8	0.12	0.37	0.02	0.42	0.06	0.01	0.66	1.57	0.52	3
	12	1006	2.04	3.4	0.07	0.34	0.02	0.47	0.08	0.02	0.73	1.63	0.54	6
	24	2018	6.46	14.9	0.04	0.20	0.02	0.45	0.14	0.15	0.94	1.93	0.64	34
	2	798	2.14	2.6	0.10	0.44	0.02	0.39	0.04	0.01	0.64	1.50	0.50	4
	4	1289	2.05	4.3	0.04	0.28	0.02	0.50	0.10	0.06	0.77	1.75	0.58	17
	6	1720	2.62	7.9	0.03	0.23	0.02	0.48	0.13	0.11	0.88	1.86	0.62	27
40	8	1974	3.55	11.0	0.04	0.21	0.02	0.45	0.14	0.14	0.91	1.91	0.64	32
	10	2054	5.04	11.7	0.05	0.21	0.02	0.41	0.15	0.16	0.90	1.93	0.64	36
	12	2061	6.51	14.1	0.05	0.21	0.02	0.40	0.15	0.17	0.92	1.94	0.65	38
	24	2590	6.80	36.2	0.05	0.19	0.03	0.36	0.17	0.20	0.97	1.98	0.66	41
	2	844	1.64	2.8	0.10	0.42	0.02	0.39	0.05	0.02	0.67	1.53	0.51	8
	4	1350	2.03	4.9	0.04	0.29	0.02	0.47	0.11	0.07	0.82	1.75	0.58	20
	6	1924	2.61	7.8	0.03	0.25	0.02	0.45	0.13	0.12	0.89	1.84	0.61	29
50	8	2211	3.72	8.5	0.05	0.24	0.03	0.38	0.15	0.15	0.88	1.87	0.62	36
	10	2890	4.42	16.0	0.03	0.22	0.02	0.40	0.16	0.17	0.94	1.93	0.64	38
	12	3461	5.45	16.5	0.03	0.22	0.03	0.37	0.17	0.18	0.95	1.93	0.64	40
	24	3030	6.70	18.9	0.06	0.21	0.03	0.33	0.21	0.20	0.94	1.96	0.65	42

Table S6. Number average molecular weight (M_n), molecular weight dispersity ($Đ$), number average degree of polymerization (Dp_n), the average molar fraction of glyceridic species in the reaction medium (x_i), carboxylic acid conversion (p_{COOH}), glycerol degree of substitution (DS), hydroxyl conversion (p_{OH}) and degree of branching (DB) of PGS synthesized using CALB as the catalyst, and acetonitrile as solvent at different temperatures and reaction times

T (°C)	t (h)	GPC M_n (Da)	$Đ$	Dp_n	x_{Glyc}	x_{1T}	x_{2T}	$x_{1,3L}$	$x_{1,2L}$	$x_{1,2,3D}$	p_{COOH}	DS	p_{OH}	DB (%)
	2	1007	1.94	3.9	0.07	0.35	0.03	0.42	0.09	0.04	0.79	1.63	0.54	14
	4	1275	3.94	5.7	0.05	0.28	0.02	0.44	0.12	0.09	0.85	1.49	0.50	24
	6	1394	2.65	6.7	0.04	0.26	0.03	0.42	0.14	0.11	0.88	1.81	0.60	28
40	8	1443	2.92	7.9	0.06	0.24	0.02	0.42	0.15	0.11	0.89	1.84	0.61	28
	10	1372	3.07	7.3	0.05	0.25	0.03	0.40	0.15	0.12	0.88	1.83	0.61	30
	12	1357	3.15	7.5	0.05	0.25	0.03	0.40	0.15	0.12	0.89	1.83	0.61	30
	24	1095	3.13	5.3	0.07	0.30	0.03	0.33	0.15	0.12	0.82	1.77	0.59	33
	2	2460	1.32	4,0	0.05	0.32	0.03	0.44	0.10	0.06	0.78	1.69	0.56	17
	4	3368	1.45	5.3	0.05	0.29	0.03	0.39	0.14	0.10	0.83	1.77	0.59	26
	6	3848	1.55	5.8	0.05	0.28	0.03	0.39	0.14	0.11	0.84	1.79	0.60	28
50	8	3484	1.62	5.2	0.08	0.28	0.03	0.37	0.13	0.11	0.81	1.78	0.59	28
	10	5391	1.68	7.8	0.05	0.24	0.02	0.42	0.15	0.12	0.88	1.85	0.62	28
	12	5113	1.62	7.4	0.04	0.24	0.02	0.44	0.15	0.11	0.87	1.84	0.61	26
	24	4484	1.66	5.9	0.06	0.28	0.03	0.36	0.15	0.12	0.84	1.80	0.60	30
	2	1196	1.88	5.4	0.07	0.30	0.02	0.47	0.09	0.05	0.87	1.71	0.57	14
	4	1431	2.41	6.6	0.07	0.27	0.02	0.39	0.14	0.11	0.87	1.81	0.60	27
	6	1503	2.81	8.1	0.06	0.26	0.03	0.37	0.15	0.13	0.90	1.83	0.61	31
60	8	1574	3.04	9.2	0.05	0.24	0.03	0.39	0.16	0.13	0.92	1.85	0.62	30
	10	1557	3.15	9.4	0.05	0.25	0.03	0.36	0.17	0.14	0.92	1.85	0.62	33
	12	1496	3.26	8.5	0.07	0.26	0.03	0.33	0.17	0.14	0.91	1.84	0.61	33
	24	1422	3.37	10.3	0.07	0.26	0.03	0.35	0.16	0.13	0.95	1.83	0.61	31

- DLS analyses and CAC estimation

Dynamic light scattering (DLS) experiments were performed on a Zetasizer Nano:Malvern 3600 Zetasizer equipment, by using a light source He-Ne LASER (632.8 nm) and detector angle of 173°. The influence of concentration on polymer aggregation was studied by using the PGS synthesized in acetone at 40 °C for 24 h, suspended in tetrahydrofuran at a concentration range from 0.01 to 10 mg mL^{-1}. The solutions were analyzed at 40 °C.

The size distribution profile from DLS analyses performed at 40 °C for PGS in tetrahydrofuran at concentrations from 0.01 to 10 mg mL^{-1} is presented in Fig. S7a. Critical aggregation concentration (CAC) was determined by plotting the mean scattering intensity as a function of PGS concentration, Figure S7b.
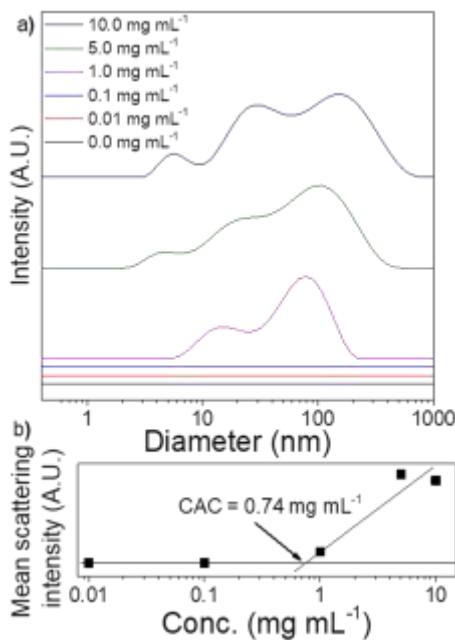

Figure S7. (a) Particle size distribution curve of PGS solutions at different concentrations in THF at 40 °C; and (b) mean scattering intensity as a function of PGS concentration.

The diameter of the aggregates of the PSG in solution was determined by DLS analyses performed at 40 °C in acetone, acetonitrile, and t-butanol at a concentration of 1 mg mL^{-1}, Figure S8.
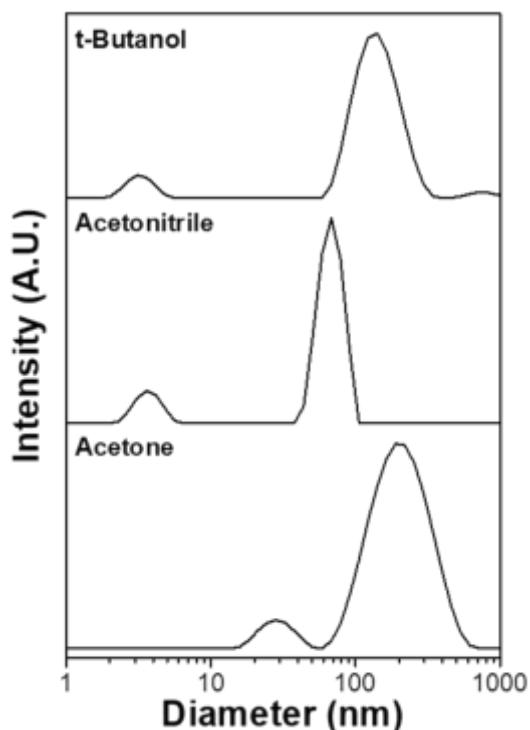

Figure S8. The particle size distribution curve of the PGS solutions at a concentration of 1 mg mL^{-1} in acetone, acetonitrile, and t-butanol at 40 °C.

- x_{1T}/x_{2T} and $x_{1,3L}/x_{1,2L}$ ratios

The x_{1T}/x_{2T} and $x_{1,3L}/x_{1,2L}$ ratios plotted as a function of reaction time for the studied conditions are presented in Figure S9.
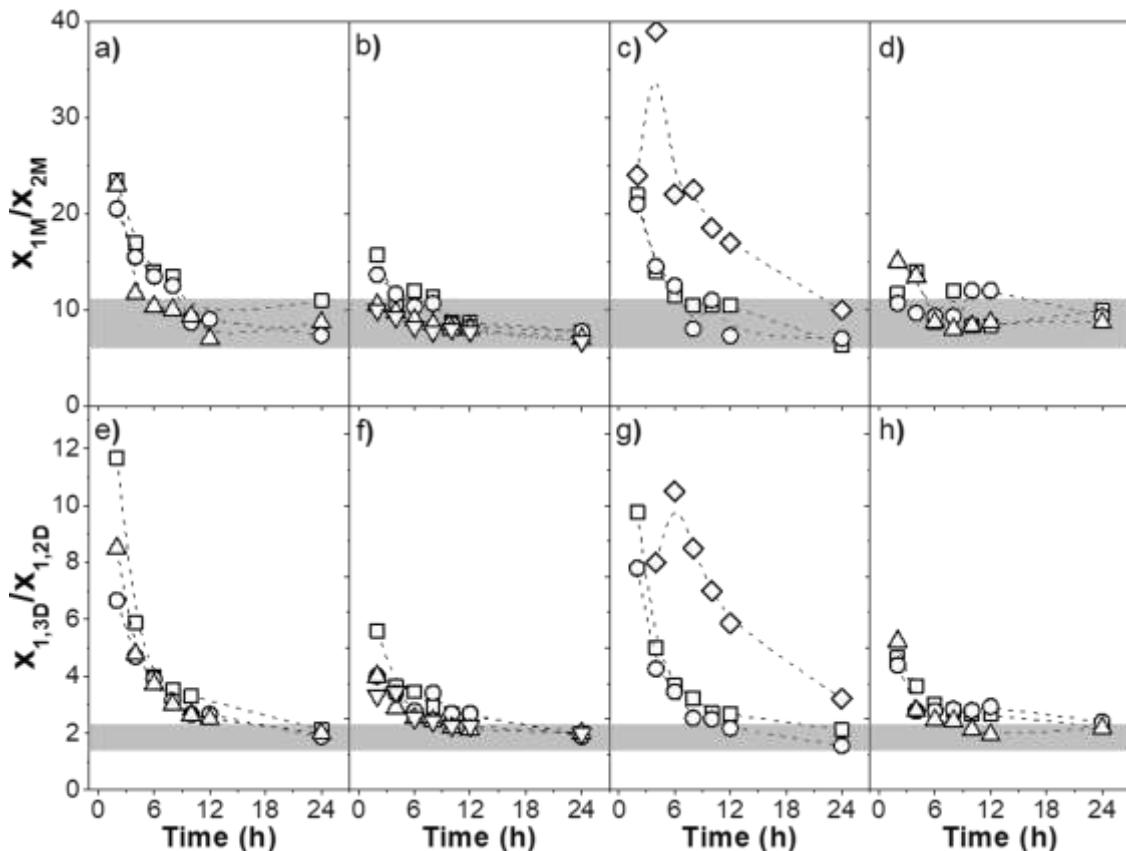

Figure S9. x_{1T}/x_{2T} and $x_{1,3L}/x_{1,2L}$ ratios as a function of time for reactions performed in tetrahydrofuran (a and e), t-butanol (b and f), acetone (c and g), and acetonitrile (d and h), respectively, at 30 °C (◊), 40 °C (□), 50 °C (○), 60 °C (Δ), and 70 °C (▽).

- Acyl migration experiment

The acyl migration experiment was performed by preparing solutions of 0.15 mmol of PGS with different degrees of branching and 0.45 mmol of triethylamine in 2 mL of tetrahydrofuran in the presence of 200 mg of molecular sieves. The solution was gently stirred for 24 h at 40 °C. The reaction media was filtered, tetrahydrofuran, and triethylamine were stripped off under nitrogen flow and PGS was dried in vacuum previously to ^{1}H NMR analysis.

Table S7 shows the ratios x_{1T}/x_{2T} and $x_{1,3L}/x_{1,2L}$ and the difference in the average molar fraction of 1,2,3D units before and after the acyl migration experiment $(\Delta x_{1,2,3T})$.

Table S7. PGS molar fractions before and after the acyl migration experiment

	Before acyl migration		After acyl migration		
DB (%)	x_{1T}/x_{2T}	$x_{1,3L}/x_{1,2L}$	x_{1T}/x_{2T}	$x_{1,3L}/x_{1,2L}$	$\Delta x_{1,2,3D}$ (%)*
31	10.0	3.3	10.3	2.3	0.02
34	9.0	3.4	8.7	2.2	0.01
38	11.0	3.0	9.0	2.3	-0.01
47	8.0	2.2	9.6	1.9	0.00
Mean ± Std deviation	9.5 ± 1	3.0 ± 0.5	9.4 ± 0.6	2.2 ± 0.2	0.01± 0.01

* $\Delta x_{1,2,3T} = x_{1,2,3D}$ after acyl migration $-$ $x_{1,2,3D}$ before acyl migration