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SUPPORTING INFORMATION

Role of the Branched PEG-b-PLLA Chain in Morphological Structures and Thermodynamics for PEG-b-PLLA-g-glucose Copolymers with Different Architectures

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1. Experimental Section

1.1 Gel Permeation Chromatography (GPC).

GPC curves were measured with Malvern Viscotek 270 by using THF as the mobile phase at 40 °C. The flow rate was 1 mL/min, and the injection volume was 100 μL. A refractive index (RI) detector was employed to characterize the number of average molecular weight (M_n) and molecular weight distribution ($Đ$) through conventional calibration by using narrow-distributed polystyrene as an internal standard. The trapping experiments were conducted on Shimadzu LC20-AT Liquid Chromatograph equipped with RI and photodiode array (PDA) detectors.

1.2 Nuclear Magnetic Resonance (NMR).

^{1}H-NMR spectra of copolymers were acquired using a Bruker 600 spectrometer (Bruker Biospin; AVANCE III HD; Switzerland) at 600 MHz and ambient temperature, with $CDCl_3$ and D_2O as the solvent and TMS as the object of reference. The sample solutions were prepared by dissolving 10-15 mg of dried polymers in 1 mL of $CDCl_3$ or D_2O.

1.3 Fourier Transform Infrared Spectroscopy (FTIR).

Fourier transform infrared (FTIR) spectra were measured that were equipped with a DTGS detector. The technique of attenuated total reflectance (ATR) was used for the IR measurements. The spectra were obtained by adding 64 scans at a resolution of 2 cm^{-1}.

1.4 Differential Scanning Calorimetry (DSC).

DSC measurements were performed on a NETZSCH DSC-200F3 differential scanning calorimetry from the instrument (NETZSCH-Gerätebau GmbH, Selb, Germany) equipped with an IC70 intercooler. The sample sealed in an aluminum pan was first heated to 200 °C and held for 3 min to eliminate the thermal history. To investigate the melting behavior, the sample was cooled from 200 to -70 °C and then reheated to 200 °C again under a nitrogen gas flow of 60 mL/min. Both the heating rate and cooling rate were 10 °C/min. To investigate nonisothermal melt crystallization, the sample was cooled from 200 to -70 °C and then reheated to 200 °C again under a nitrogen gas flow of 60 mL/min. Both the heating rate and cooling rate were 10 °C/min.

2. Supplementary Discussion

The degree of polymerization (DP) of MPEG-b-PLLA-OH (**1**), HO-PLLA-b-PEG-b-PLLA-OH (**2**), MPEG-b-PLLA-COOH (**3**), HOOC-PLLA-b-PEG-b-PLLA-COOH (**4**), 1A-MPELAG (**7**), 1A-PELAG (**8**), 3A-MPELAG (**9**), 3A-PELAG (**10**), 5A-MPELAG (**11**), and 5A-PELAG (**12**) were calculated from ^{1}H NMR[1, 2]:

$$DP_{PLLA}(\mathbf{1}) = \frac{A_{5.16\text{ - }5.20}}{A_{5.03\text{ - }5.07}} \qquad \text{(Eq S1)}$$

$$DP_{PEG}(\mathbf{1}) = \frac{A_{3.67} \times \frac{1}{4}}{A_{5.03\text{ - }5.07}} \qquad \text{(Eq S2)}$$

$$DP_{PLLA}(\mathbf{2}) = \frac{A_{5.17\text{ - }5.20}}{A_{5.04\text{ - }5.07} \times \frac{1}{2}} \qquad \text{(Eq}$$

S3)

$$DP_{PEG}(\mathbf{2}) = \frac{A_{3.67}}{A_{5.04\,-\,5.07} \times \frac{1}{2}} \qquad \text{(Eq S4)}$$

$$DP_{PLLA}(\mathbf{1}) = DP_{PLLA}(\mathbf{3}) = DP_{PLLA}(\mathbf{7}) \qquad \text{(Eq S5)}$$

$$DP_{PEG}(\mathbf{1}) = DP_{PEG}(\mathbf{3}) = DP_{PEG}(\mathbf{7}) \qquad \text{(Eq S6)}$$

$$DP_{PLLA}(\mathbf{2}) = DP_{PLLA}(\mathbf{4}) = DP_{PLLA}(\mathbf{8}) \qquad \text{(Eq S7)}$$

$$DP_{PEG}(\mathbf{2}) = DP_{PEG}(\mathbf{4}) = DP_{PEG}(\mathbf{8}) \qquad \text{(Eq S8)}$$

$$DP_{PLLA}(\mathbf{9}) = DP_{PLLA}(\mathbf{1}) \times n_g(\mathbf{9}) \qquad \text{(Eq S9)}$$

$$DP_{PEG}(\mathbf{9}) = DP_{PEG}(\mathbf{1}) \times n_g(\mathbf{9}) \qquad \text{(Eq S10)}$$

$$DP_{PLLA}(\mathbf{10}) = DP_{PLLA}(\mathbf{2}) \times n_g(\mathbf{10}) \qquad \text{(Eq S11)}$$

$$DP_{PEG}(\mathbf{10}) = DP_{PEG}(\mathbf{2}) \times n_g(\mathbf{10}) \qquad \text{(Eq S12)}$$

$$DP_{PLLA}(\mathbf{11}) = DP_{PLLA}(\mathbf{1}) \times n_g(\mathbf{11}) \qquad \text{(Eq S13)}$$

$$DP_{PEG}(\mathbf{11}) = DP_{PEG}(\mathbf{1}) \times n_g(\mathbf{11}) \qquad \text{(Eq S14)}$$

$$DP_{PLLA}(\mathbf{12}) = DP_{PLLA}(\mathbf{2}) \times n_g(\mathbf{12}) \qquad \text{(Eq S15)}$$

$$DP_{PEG}(\mathbf{12}) = DP_{PEG}(\mathbf{2}) \times n_g(\mathbf{12}) \qquad \text{(Eq S16)}$$

where $A_{5.03\text{-}5.07}$and $A_{5.17\text{-}5.20}$ are the integrals at 5.03-5.07 ppm and 5.17-5.20 ppm , respectively.

The number of graft (n_g) of 1A-MPELAG (**7**), 1A-PELAG (**8**), 3A-MPELAG (**9**), 3A-PELAG (**10**), 5A-MPELAG (**11**), and 5A-PELAG (**12**) copolymer was calculated from ^{1}H NMR:

$$n_g(\mathbf{7}) = \frac{A_{3.40} \times \frac{1}{3}}{A_{5.38\,-\,5.41}} \qquad \text{(Eq S17)}$$

$$n_g(\mathbf{8}) = \frac{A_{5.04-5.07}}{A_{5.29-5.33}} \quad \text{(Eq S18)}$$

$$n_g(\mathbf{9}) = \frac{A_{3.40} \times \frac{1}{3}}{A_{5.29-5.33}} \quad \text{(Eq S19)}$$

$$n_g(\mathbf{10}) = \frac{A_{2.64} \times \frac{1}{4}}{A_{5.29-5.33}} \quad \text{(Eq S20)}$$

$$n_g(\mathbf{11}) = \frac{A_{3.40} \times \frac{1}{3}}{A_{5.29-5.33}} \quad \text{(Eq S21)}$$

$$n_g(\mathbf{12}) = \frac{A_{2.64} \times \frac{1}{4}}{A_{5.29-5.33}} \quad \text{(Eq S22)}$$

The M_n of MPEG-b-PLLA-OH (**1**), HO-PLLA-b-PEG-b-PLLA-OH (**2**), MPEG-b-PLLA-COOH (**3**), HOOC-PLLA-b-PEG-b-PLLA-COOH (**4**), 1A-MPELAG (**7**), 1A-PELAG (**8**), 3A-MPELAG (**9**), 3A-PELAG (**10**), 5A-MPELAG (**11**), and 5A-PELAG (**12**) copolymer were calculated from ^{1}H NMR as follows:

$$M_n(\mathbf{1}) = 14+DP_{PEG\text{-}1}\times62+DP_{PLLA\text{-}1}\times180-(DP_{PEG\text{-}1}+DP_{PLLA\text{-}1}-2)\times18 \quad \text{(Eq S23)}$$

$$M_n(\mathbf{2}) = DP_{PEG\text{-}2}\times62+DP_{PLLA\text{-}2}\times180-(DP_{PEG\text{-}2}+DP_{PLLA\text{-}2}-2)\times18 \quad \text{(Eq S24)}$$

$$M_n(\mathbf{3}) = 14+DP_{PEG\text{-}3}\times62+DP_{PLLA\text{-}3}\times180-(DP_{PEG\text{-}3}+DP_{PLLA\text{-}3}-2)\times18+100 \quad \text{(Eq S25)}$$

$$M_n(\mathbf{4}) = DP_{PEG\text{-}4}\times62+DP_{PLLA\text{-}4}\times180-(DP_{PEG\text{-}4}+DP_{PLLA\text{-}4}-2)\times18+100\times2 \quad \text{(Eq S26)}$$

$$M_n(\mathbf{7}) = 14+DP_{PEG\text{-}7}\times62+DP_{PLLA\text{-}7}\times180-(DP_{PEG\text{-}7}+DP_{PLLA\text{-}7}-2)\times18+100\times n_g(\mathbf{7})+260 \quad \text{(Eq S27)}$$

$$M_n(\mathbf{8}) = DP_{PEG\text{-}8}\times62+DP_{PLLA\text{-}8}\times180-(DP_{PEG\text{-}8}+DP_{PLLA\text{-}8}-2)\times18+100\times2\times n_g(\mathbf{8})+260\times2 \quad \text{(Eq S28)}$$

$M_n(\mathbf{9}) = 14+DP_{PEG-9}\times62+ DP_{PLLA-9}\times180-(DP_{PEG-9}+ DP_{PLLA-9}-2)\times18+100\times n_g(\mathbf{9})+220$ (Eq S29)

$M_n(\mathbf{10}) = DP_{PEG-10}\times62+ DP_{PLLA-10}\times180-(DP_{PEG-10}+ DP_{PLLA-10}-2)\times18+100\times2\times n_g(\mathbf{10})+220\times3$ (Eq S30)

$M_n(\mathbf{11}) = 14+DP_{PEG-11}\times62+ DP_{PLLA-11}\times180-(DP_{PEG-11}+ DP_{PLLA-11}-2)\times18+100\times n_g(\mathbf{11})+180$ (Eq S31)

$M_n(\mathbf{12}) = DP_{PEG-12}\times62+ DP_{PLLA-12}\times180-(DP_{PEG-12}+ DP_{PLLA-12}-2)\times18+100\times2\times n_g(\mathbf{12})+180\times5$ (Eq S32)

where $M_{n,CH2-} = 14$, $M_{n, SA} =100$, $M_{n, ODG} = 260$, $M_{n, MG} = 220$, $M_{n, Glu} = 180$.

The MPEG/PEG weight fraction of PEG-b-PLLA-g-glucose copolymers (ω_{PEG}) were determined from ^{1}H NMR:

$$\omega_{PEG}(\mathbf{1}) = \frac{DP_{PEG}(1) \times 62 + 14}{M_n(1)}$$ (Eq S33)

$$\omega_{PEG}(\mathbf{2}) = \frac{DP_{PEG}(2) \times 62}{M_n(2)}$$ (Eq S34)

$$\omega_{PEG}(\mathbf{3}) = \omega_{PEG}(\mathbf{7}) = \omega_{PEG}(\mathbf{9}) = \omega_{PEG}(\mathbf{11}) = \frac{DP_{PEG}(3) \times 62 + 14}{M_n}$$ (Eq S35)

$$\omega_{PEG}(\mathbf{4}) = \omega_{PEG}(\mathbf{8}) = \omega_{PEG}(\mathbf{10}) = \omega_{PEG}(\mathbf{12}) = \frac{DP_{PEG}(4) \times 62}{M_n}$$ (Eq S36)

The PLLA weight fraction of PEG-b-PLLA-g-glucose copolymers (ω_{PLLA}) were determined from ^{1}H NMR:

$$\omega_{PLLA}(\mathbf{1}) = \frac{DP_{PLLA}(1) \times (180 - 18)}{M_n(1)}$$

(Eq S37)

$$\omega_{PLLA}(\mathbf{2}) = \frac{DP_{PLLA}(2) \times (180 - 18)}{M_n(2)}$$

(Eq S38)

$$\omega_{PLLA}(\mathbf{3}) = \omega_{PLLA}(\mathbf{7}) = \omega_{PLLA}(\mathbf{9}) = \omega_{PLLA}(\mathbf{11}) = \frac{DP_{PLLA}(3) \times (180 - 18)}{M_n}$$

(Eq S39)

$$\omega_{PLLA}(\mathbf{4}) = \omega_{PLLA}(\mathbf{8}) = \omega_{PLLA}(\mathbf{10}) = \omega_{PLLA}(\mathbf{12}) = \frac{DP_{PLLA}(4) \times (180 - 18)}{M_n}$$

(Eq S40)

The crystallinities of X_{PEG} and X_{PLLA} in PEG-b-PLLA-g-glucose copolymers were calculated as:

$$X_{PEG} = \frac{\Delta H_{m,PEG}}{\omega_{PEG} \times 197\ J/g}$$

(Eq S41)

$$X_{PLLA} = \frac{\Delta H_{m,PLLA}}{\omega_{PLLA} \times 94\ J/g}$$

(Eq S42)

The $\Delta H_{m,PEG}$ and $\Delta H_{m,PLLA}$ (fusion enthalpy) were calculated from the DSC second heating thermograms, and X_{PEG} and X_{PLLA} were referred to their weight fraction. 94 J/g is the reported value of fusion enthalpy for 100% (ΔH0 m) crystallized PLLA and 197 J/g is that for PEG[3, 4].

3. Supplementary Figures and Tables

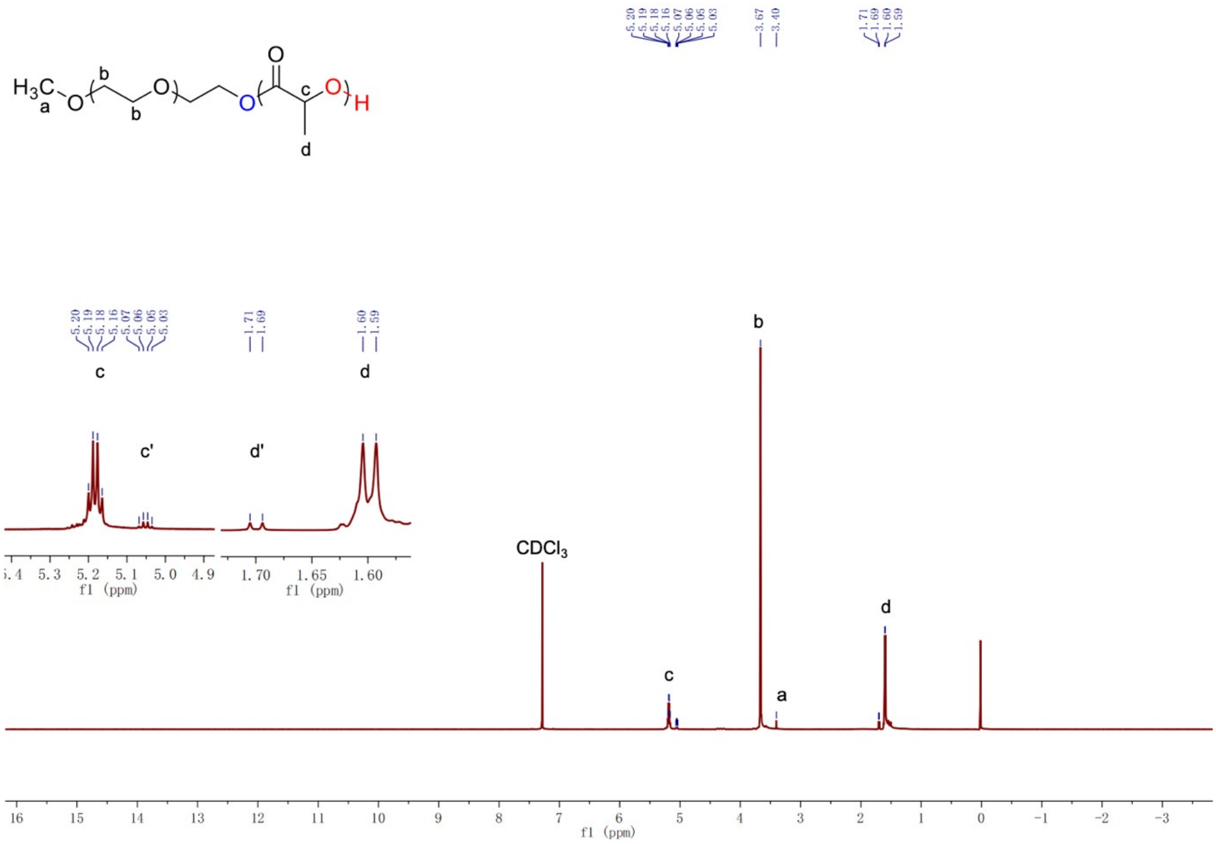

Figure S1. ^{1}H NMR spectra of MPEG-b-PLLA-OH (**1**) in $CDCl_3$.

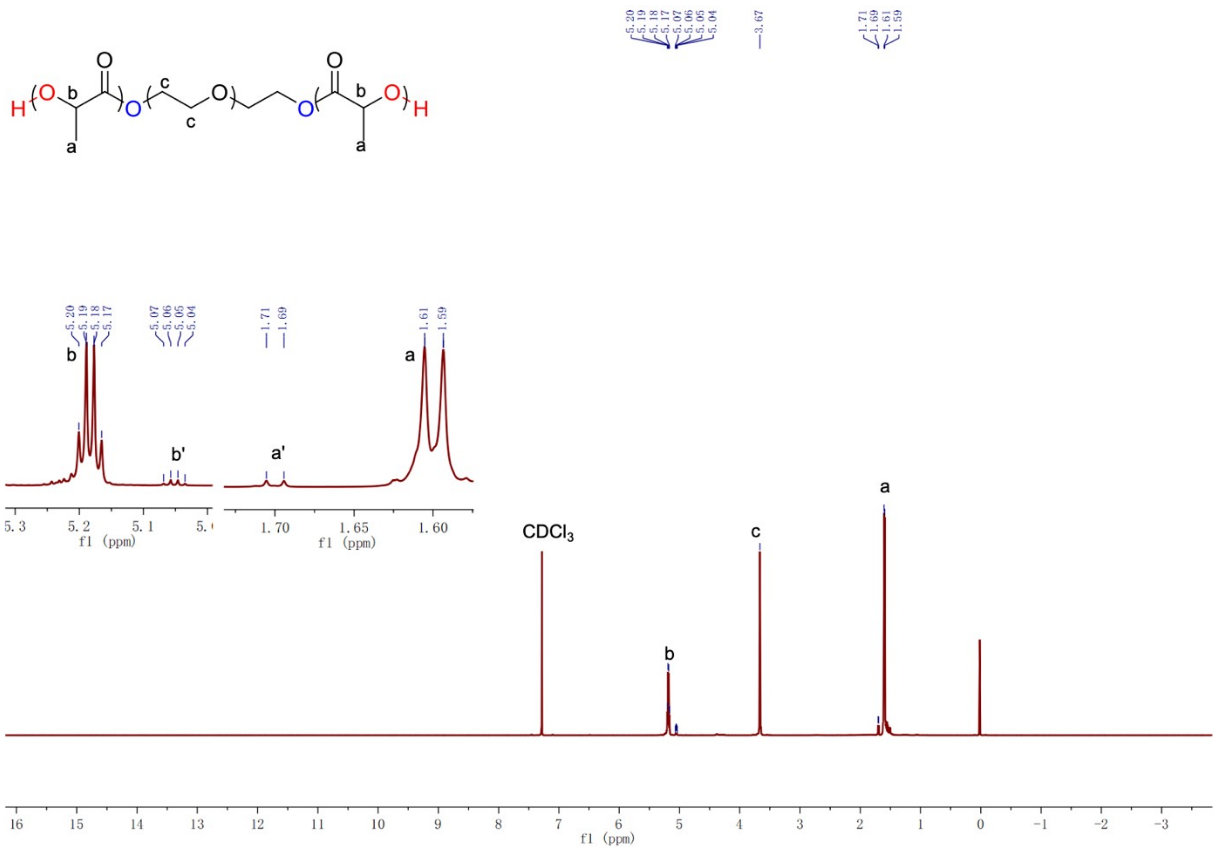

Figure S2. ^{1}H NMR spectra of HO-PLLA-b-PEG-b-PLLA-OH (**2**) in $CDCl_3$.

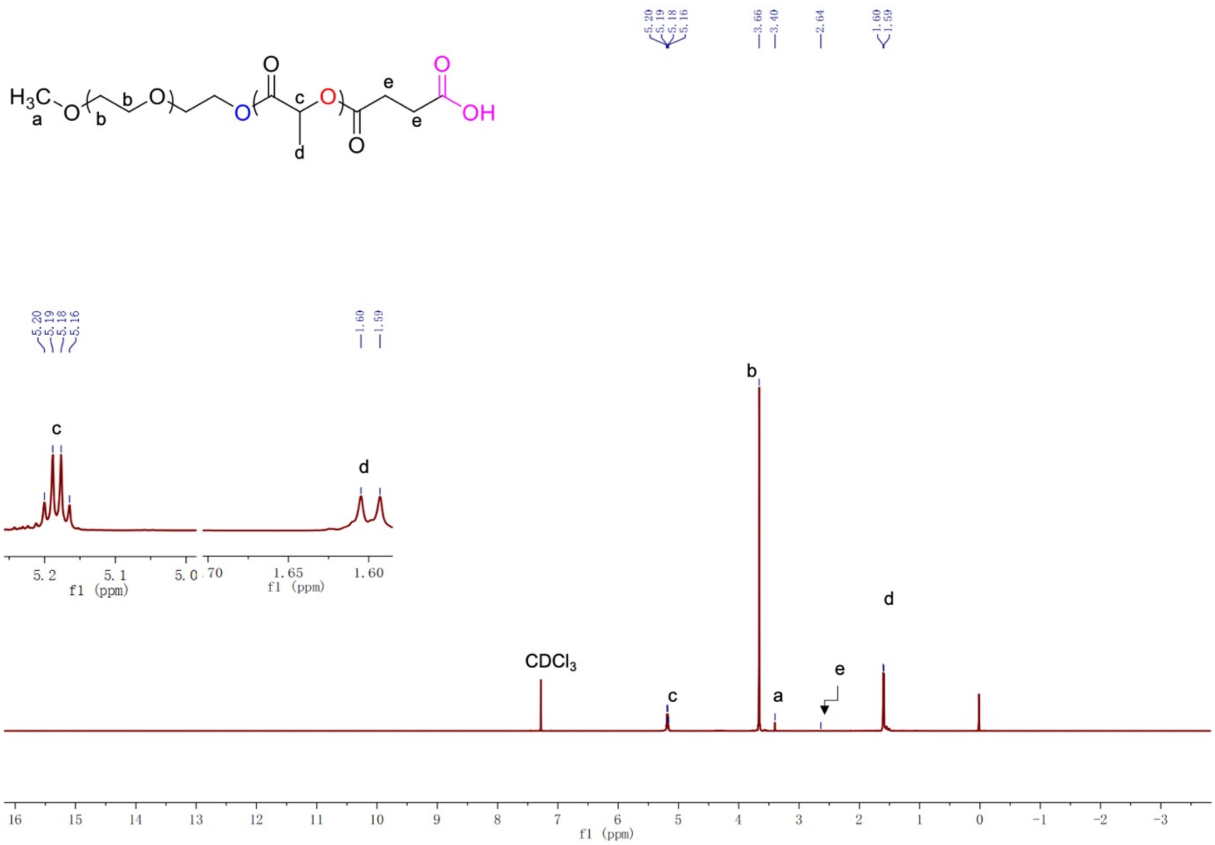

Figure S3. ^{1}H NMR spectra of MPEG-b-PLLA-COOH (**3**) in $CDCl_3$.

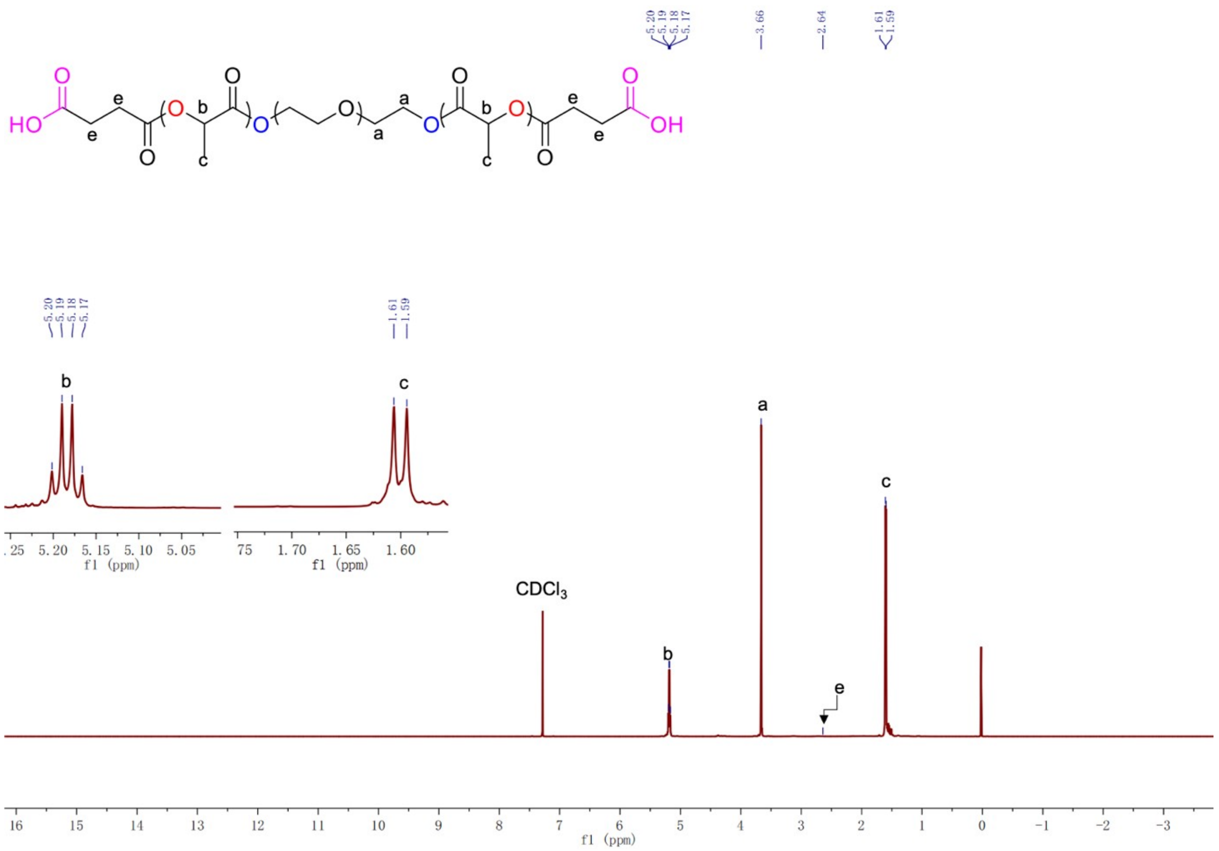

Figure S4. ^{1}H NMR spectra of HOOC-PLLA-b-PEG-b-PLLA-COOH (**4**) in $CDCl_3$.

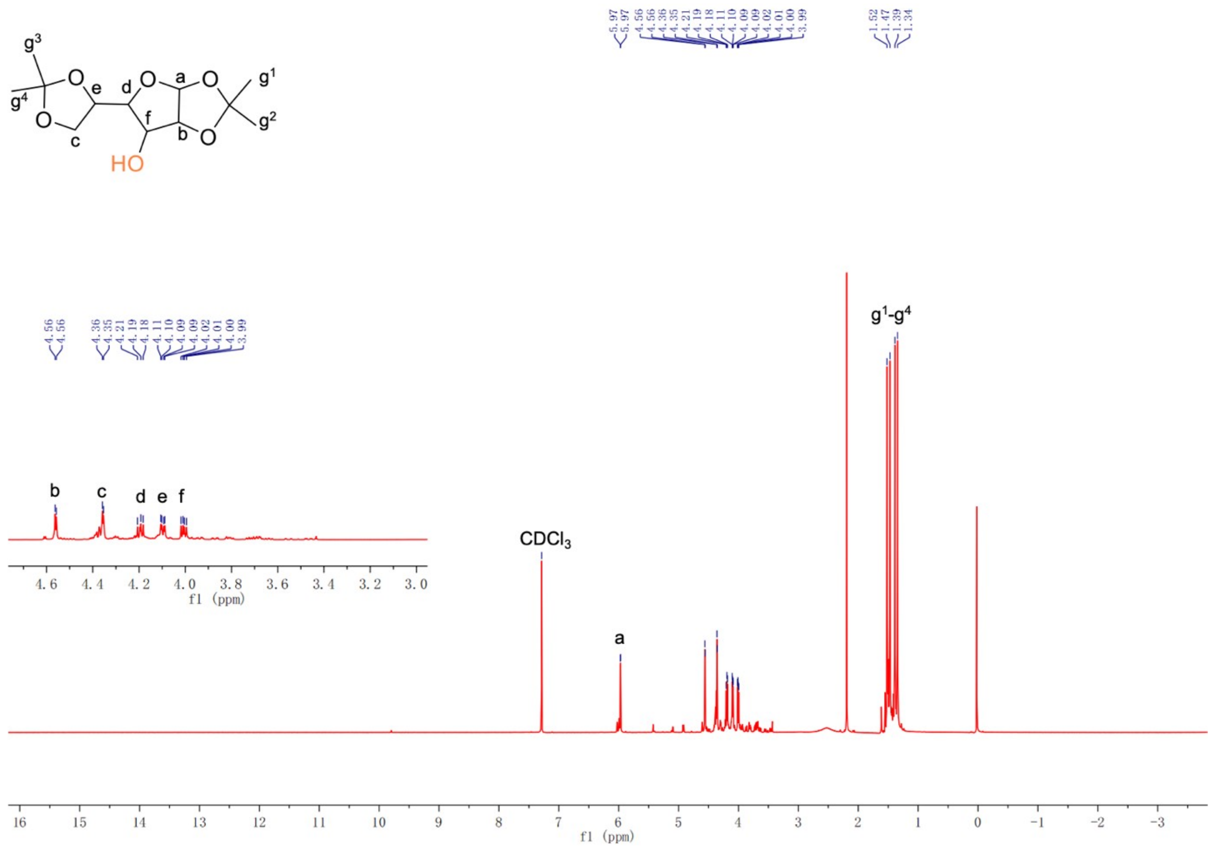

Figure S5. ^{1}H NMR spectra of ODG (**5**) in $CDCl_3$.

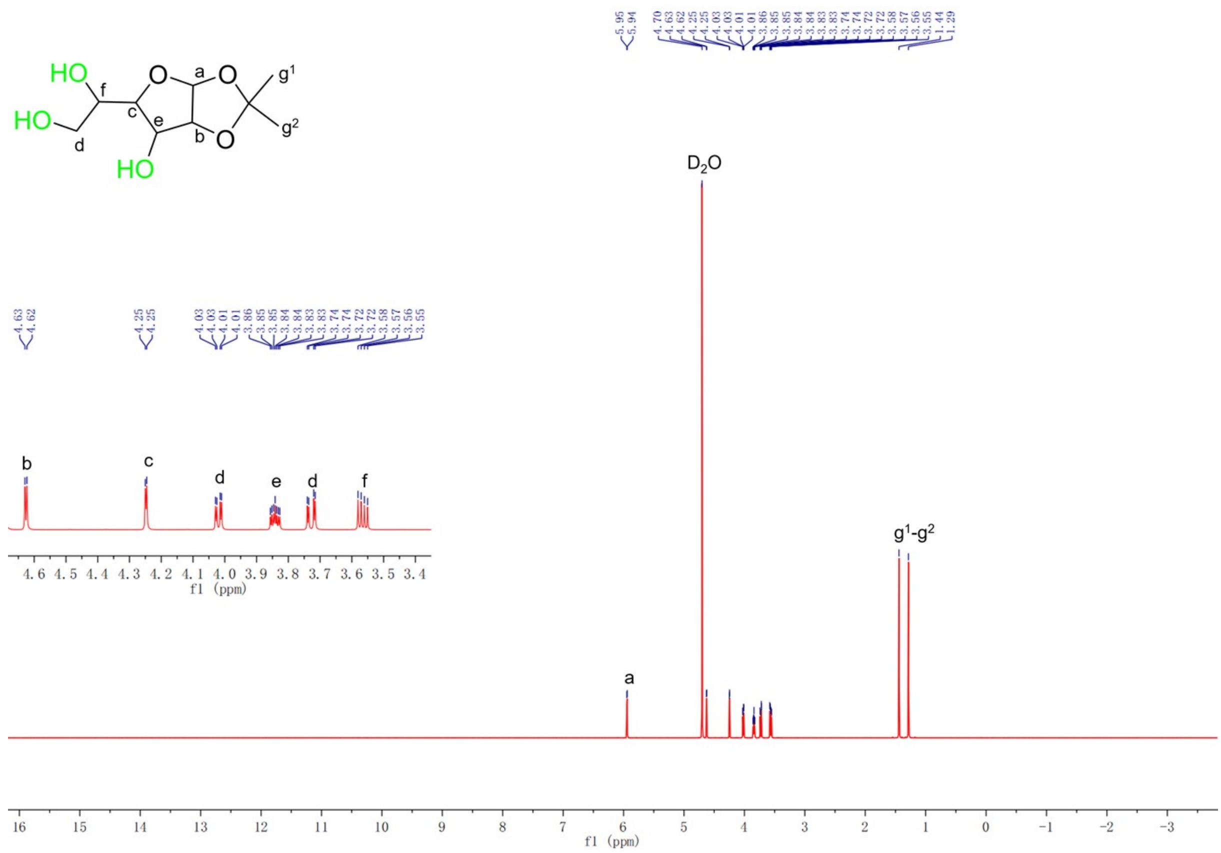

Figure S6. ^{1}H NMR spectra of MG (**6**) in D_2O.

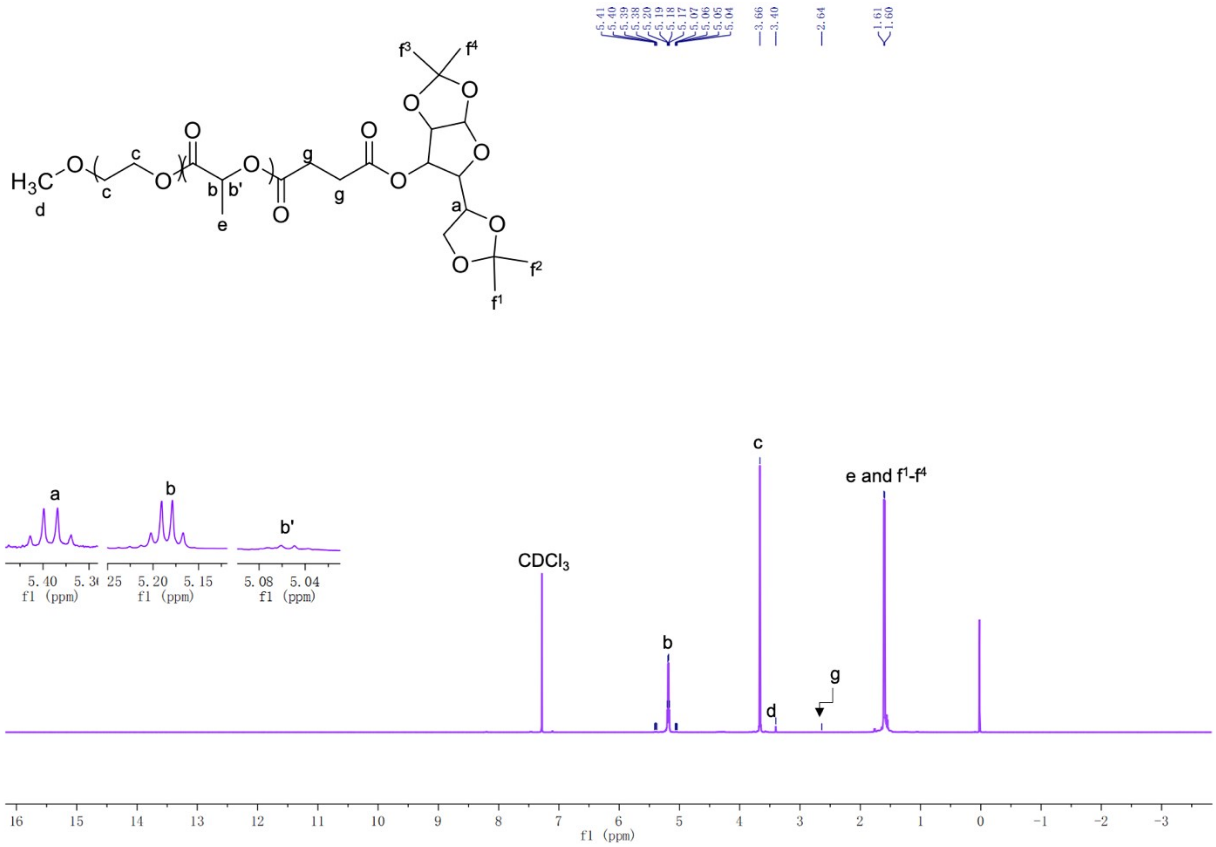

Figure S7. ^{1}H NMR spectra of 1A-MPELAG (**7**) in $CDCl_3$.

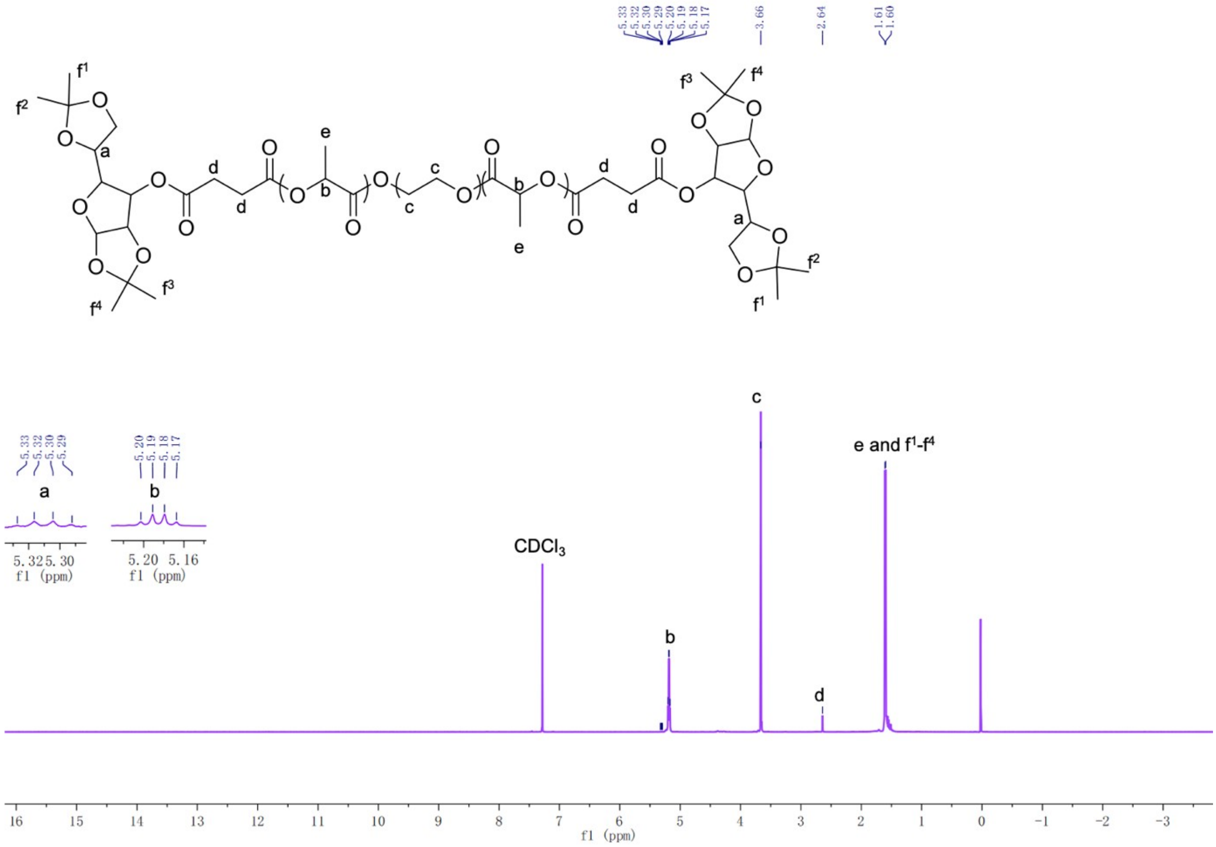

Figure S8. ^{1}H NMR spectra of 1A-PELAG (**8**) in $CDCl_3$.

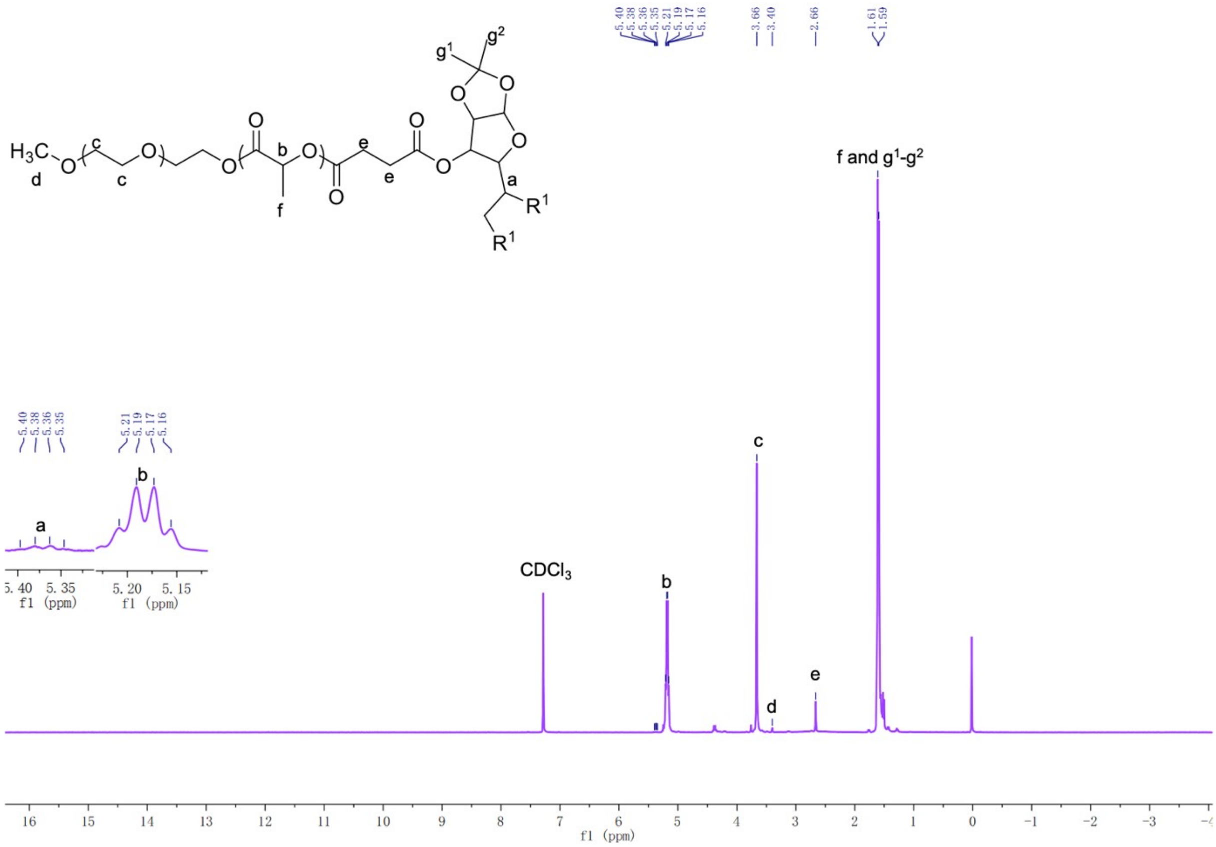

Figure S9. ^{1}H NMR spectra of 3A-MPELAG (**9**) in $CDCl_3$.

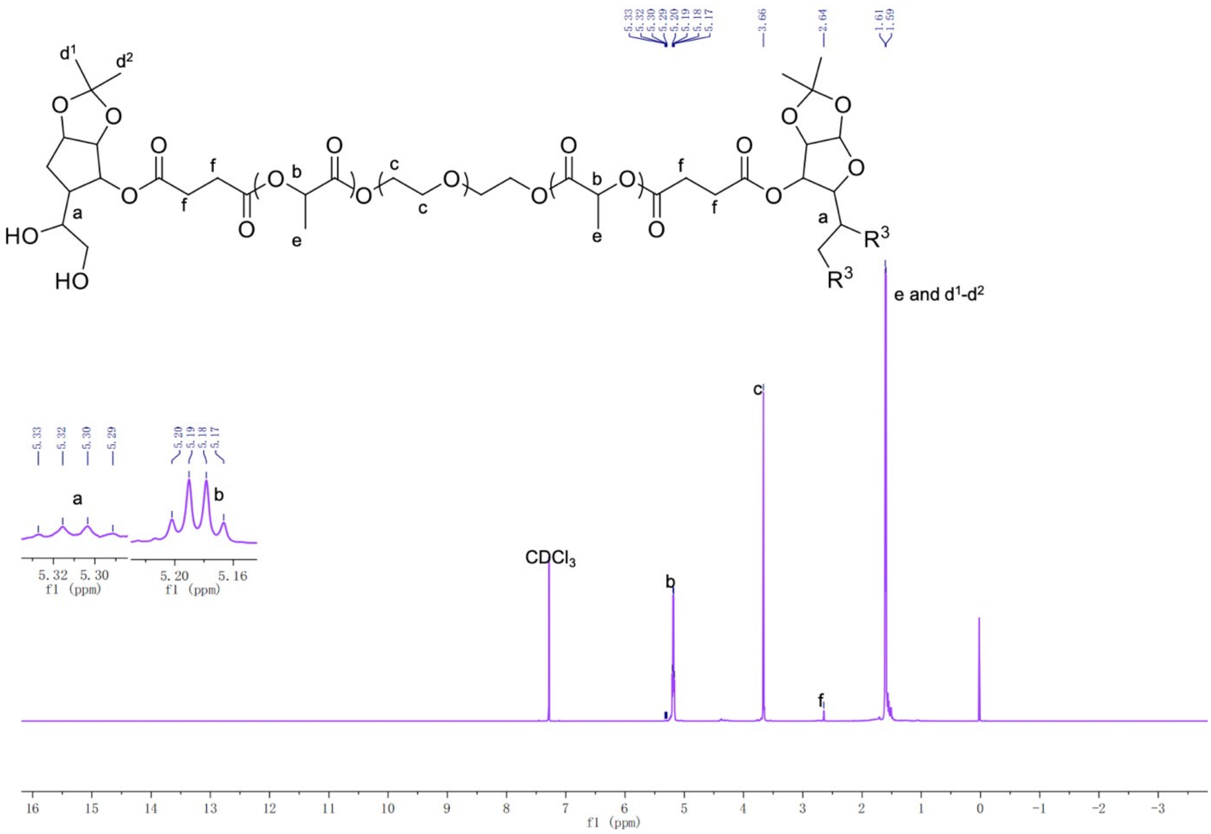

Figure S10. ^{1}H NMR spectra of 3A-PELAG (**10**) in $CDCl_3$.

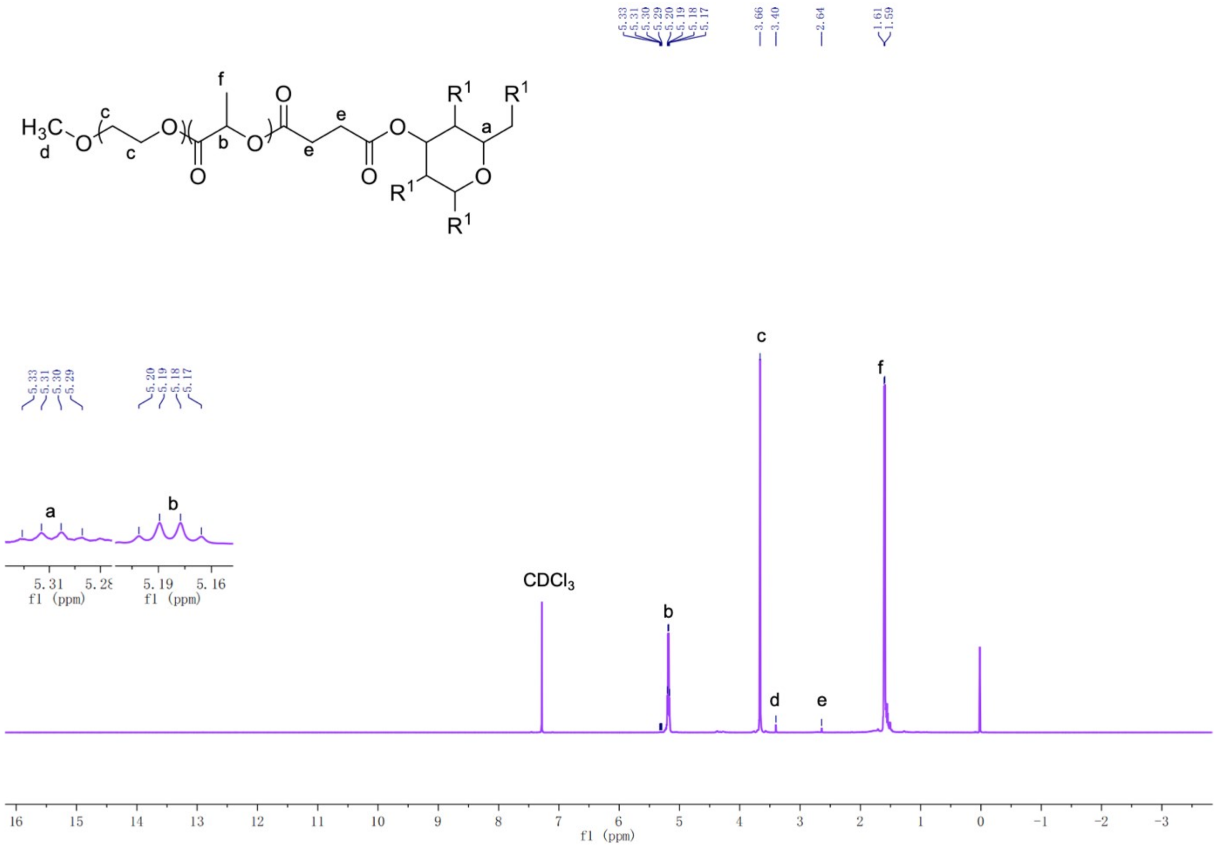

Figure S11. ^{1}H NMR spectra of 5A-MPELAG (**11**) in $CDCl_3$.

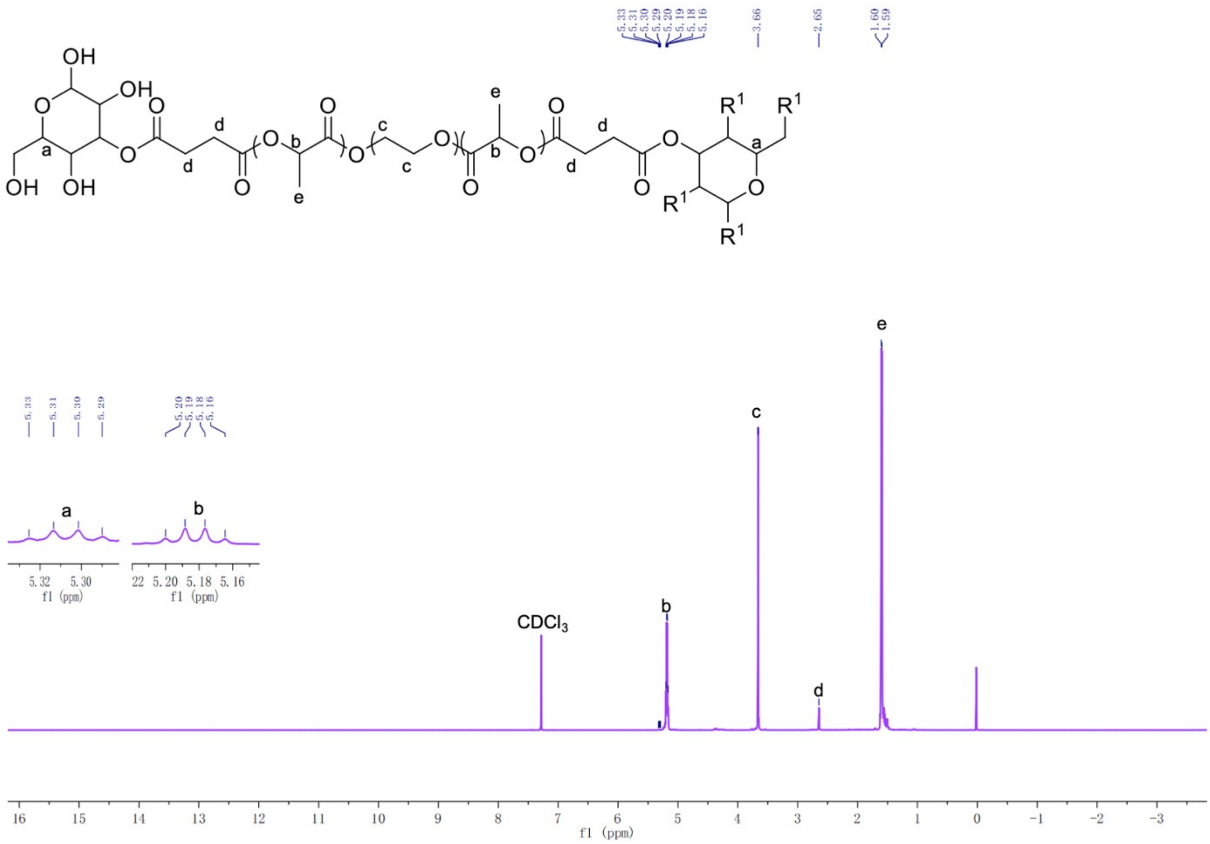

Figure S12. ^{1}H NMR spectra of 5A-PELAG (**12**) in $CDCl_3$.

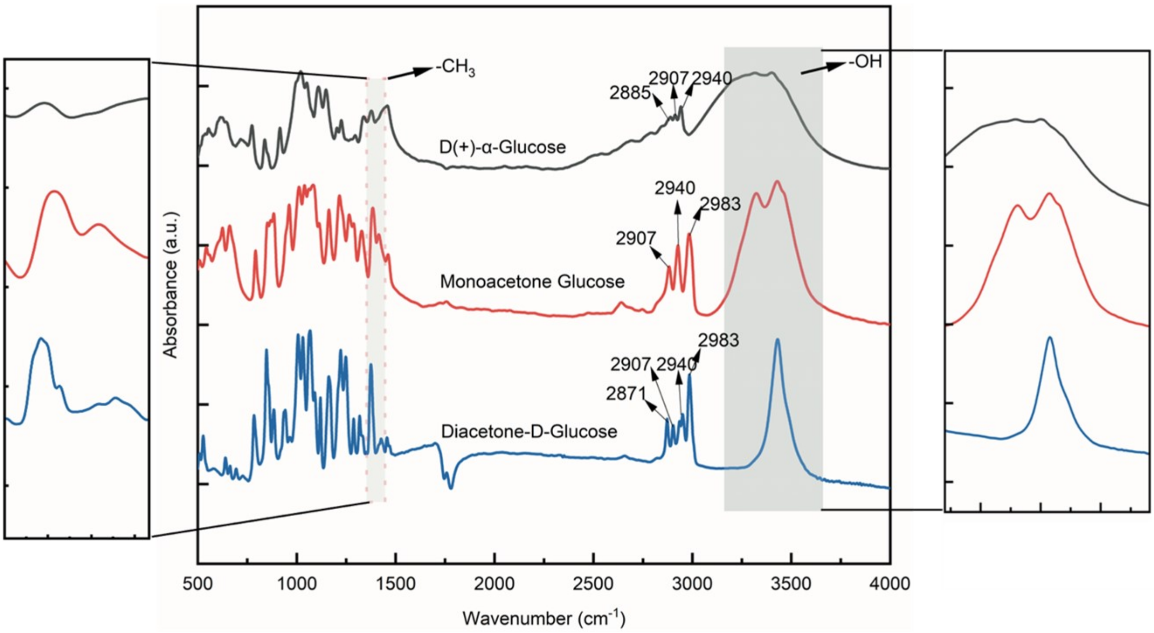

Figure S13. FTIR spectra of D(+)-α-Glucose, Monoacetone Glucose (**5**), and Diacetone-D-Glucose (**6**).

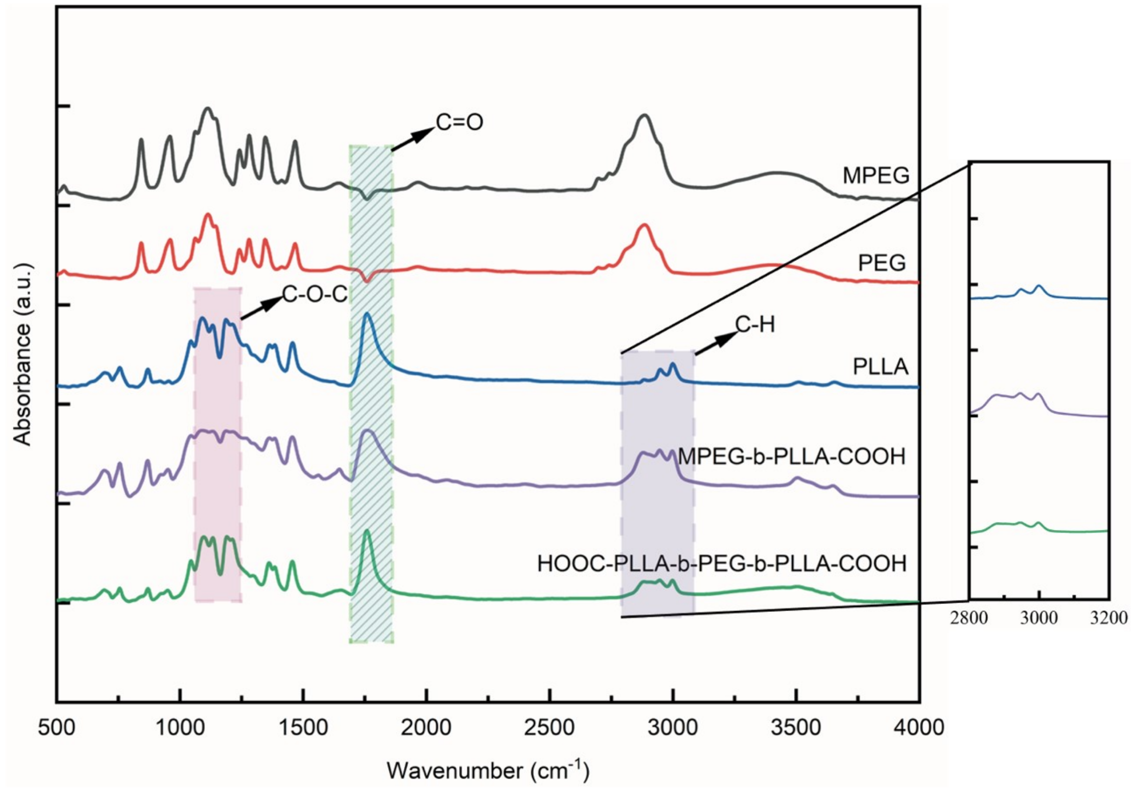

Figure S14. FTIR spectra of MPEG, PEG, PLLA, MPEG-b-PLLA-COOH (**3**), and HOOC-PLLA-b-PEG-b-PLLA-COOH (**4**).

Table S1. The molecular characterization of PEG-b-PLLA-g-glucose copolymers.

	weight fraction		NMR data of samples				
sample	ω_{PEG}[a](%)	ω_{PLLA}[b](%)	DP_{PLLA}[c]	DP_{PEG}[d]	n_g[e]	M_n[f](g·mol^{-1})	Yield[g](%)
1	24.73	75.27	41	49	—	8848	92.4
2	13.70	86.30	82	48	—	15432	90.0
3	24.30	74.43	41	49	—	8948	95.2
4	13.63	85.21	82	48	—	15632	97.5
7	23.61	72.33	41	49	1	9208	86.2
8	13.19	82.47	82	48	1	16152	88.7
9	23.90	73.23	123	147	3	26964	80.6
10	23.60	72.44	142	170	3	31780	84.1
11	24.20	74.13	205	245	5	44720	79.3
12	23.35	72.58	229	271	5	51138	82.9

[a]The MPEG/PEG weight fraction of PEG-b-PLLA-g-glucose copolymers (ω_{PEG}) was calculated by Eq S33-S36. [b]The PLLA weight fraction of PEG-b-PLLA-g-glucose copolymers (ω_{PLLA}) was calculated by Eq S37. [c]The average degree of polymerization (DP_{PLLA}) of PLLA, calculated from ^{1}H NMR. [d]The average degree of polymerization (DP_{PEG}) of MPEG/PEG, calculated from ^{1}H NMR. [e]The number of graft (n_g) of copolymers, calculated from ^{1}H NMR using Eq S17-S22. [f]The number-average molecular weight (M_n) of copolymers was calculated by ^{1}H NMR from Eq S23-S32. [g]The yield of copolymers were calculated as follows: yield(%)= M_P / (M_R− M_{water})×100, where M_P, M_{water}, and M_R are the weight of Products, Water, and Reactants, respectively.

4. References

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2. G. Wu, S. C. Chen, Q. Zhan and Y. Z. Wang, *Macromolecules*, 2011, **44**, 999-1008.

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4. P. Pan, L. Han, J. Bao, Q. Xie, G. Shan and Y. Bao, *The Journal of Physical Chemistry B*, 2015, **119**, 6462-6470.