

Electronic Supplementary Information (ESI)

Synthesis and water absorption of galactose-containing amphiphilic triblock copolymers based on PLA

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Experimental

Materials

Methacryloyl chloride (Aladdin, 95%) and α -bromoisobutyryl bromide (Aladdin, 98%) were distilled under reduced pressure. L-lactic acid was purchased from Aladdin Chemical Reagent. Tetrahydrofuran was refluxed for 24 h over sodium and distilled before use. 6-*O*-Methacryloyl-1,2,3,4-di-*O*-isopropylidene-D-galactopyranose (MalpGP) was prepared as reported,^{1,2} and its ¹H NMR (400 MHz, CDCl₃, δ , ppm): 1.33–1.54 (m, 12H, –CH₃), 1.90–2.02 (s, 3H, –CH₃), 4.01–4.18, 4.24–4.33, 4.59–4.66, and 5.54 (7H, sugar moiety), 5.50–5.63 and 6.02–6.10 (s, 2H, =CH₂). All other reagents of analytical grade were purchased from Sinopharm Chemical Reagent and used without further purification.

Synthesis of Double-hydroxyl-terminated Polylactide (HO-PLA-OH)

HO-PLA-OH were synthesized by condensation polymerization. 50g L-lactic acid (0.55 mol) was added into a reaction flask (100 mL) containing a stirring bar under a dry nitrogen atmosphere. The solution was heated to 80 °C and pressure to 250 mm Hg for 2 h in order to remove free water in L-lactic acid. 1,4-Butylene glycol and Sn(ot)₂ were then added through the rubber stopper with a syringe and stainless steel capillary.³⁹ The mixture was stirred and heated to 180 °C under the pressure of 10 mm Hg for another 5 h. The polymer was then selectively precipitated in a large volume of cold hexane, filtrated, and dried under reduced pressure until constant weight. ¹H NMR (400 MHz, CDCl₃, δ ppm): 5.12–5.19 (CH, PLA), 3.72 (terminal CH, PLA), 1.50–1.56 (CH₃, PLA), 1.21–1.28 (terminal CH₃, PLA), 4.34 (terminal CH₂, initiator), 4.14 (middle CH₂, initiator).

Synthesis of α -Bromoisobutyrate Polylactide Macroinitiator (Br-PLA-Br)

The HO-PLA-OH was quantitatively converted into ATRP initiator (Br-PLA-Br) via esterification with α -bromoisobutyryl bromide using a known procedure. For instance, PLA (7.46g, 1.00 mmol) and excess of triethylamine (0.51 mL, 4.00 mmol) were

dissolved in dichloromethane (20 mL). The flask was placed in an ice-water bath. Then α -bromoisobutyryl bromide (0.97 mL, 8.00 mmol) was added dropwise during 1 h under dry nitrogen, subsequently the temperature was allowed to room temperature. The reaction was continued under stirring for 18 h. The solution was filtered, half of the solvent was evaporated, and the Br-PLA-Br macroinitiator was precipitated in cold hexane, followed by filtration and drying in vacuum until constant weight. ^1H NMR (400 MHz, CDCl_3 , δ ppm): 5.12-5.19 (CH, PLA), 1.90 ($\text{C}(\text{Br})(\text{CH}_3)_2$), 1.50-1.56 (CH_3 , PLA), 4.34 (terminal CH_2 , initiator), 4.14 (middle CH_2 , initiator).

Synthesis of PMAIpGP-PLA-PMAIpGP

The triblock copolymers were synthesized by ATRP of MAIpGP using the Br-PLA-Br samples as macroinitiators and $\text{CuBr}/\text{Me}_6\text{TREN}$ as catalyst system. The synthesis of PMAIpGP-PLA-PMAIpGP was given below as a typical example. Br-PLA-Br (386.50 mg, 0.05 mmol), MAIpGP (328.00 mg, 1.00 mmol), CuBr (15.00 mg, 0.10 mmol), Me_6TREN (28.00 μL , 0.20 mmol), and anisol (2 mL) were added to a 10 mL Schlenk flask, immediately the mixture was frozen in liquid nitrogen, and a vacuum was applied. After three freeze-pump-thaw cycles, the flask was sealed in vacuum and placed in an oil bath preheated at 90 °C. The reaction lasted 10 h and the reaction was stopped by dilution with THF. Then the mixture was passed through a neutral aluminum column to remove the catalyst. The polymer was purified three times by precipitation in excess of hexane, collected by filtration, and dried in a vacuum oven for 24 h.

Synthesis of PMAGP-PLA-PMAGP

The triblock copolymer PMAIpGP-PLA-PMAIpGP (1.0 g) was dissolved in 10 mL of $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ (9/1 V/V), the mixture was stirred at room temperature overnight, precipitated in absolute methanol, and dried in vacuum at room temperature. The product was obtained in 92% yield as a white powder. All other copolymers were treated in the same manner.

Preparation of polymers films

The hydrophilic properties of polymers were studied on cast films obtained by

evaporation using polymer solutions in *N,N*-dimethylformamide at room temperature. Equiweight amounts of HO-PLA-OH, PMAGP₈-b-PLA₁₀₀-b-PMAGP₈, PMAGP₁₃-b-PLA₁₀₀-b-PMAGP₁₃, PMAGP₁₆-b-PLA₁₀₀-b-PMAGP₁₆, PMAGP₂₄-b-PLA₁₀₀-b-PMAGP₂₄, and PMAGP₂₈-b-PLA₁₀₀-b-PMAGP₂₈ were dissolved in *N,N*-dimethylformamide with an identical concentration, then cast on a glass petri dish surface.

Characterization

¹H NMR spectra were measured using a Bruker 400 MHz spectrometer at room temperature. Chemical shifts were referenced to tetramethyl silane (TMS). The static contact angle of water drop deposited onto film surface was measured using a drop shape analysis system OCA40 at room temperature.

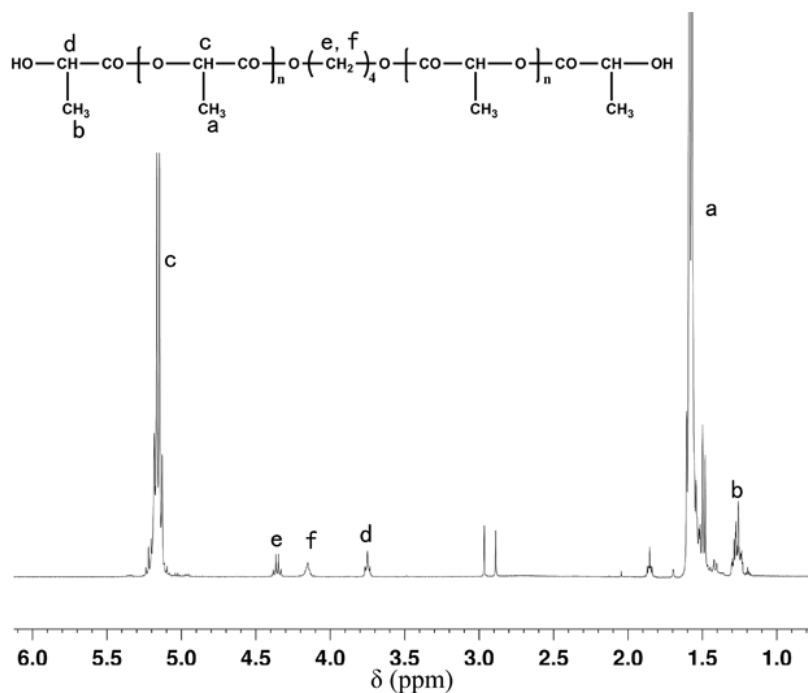


Fig. S1 ¹H NMR spectrum of HO-PLA-OH recorded in CDCl₃.

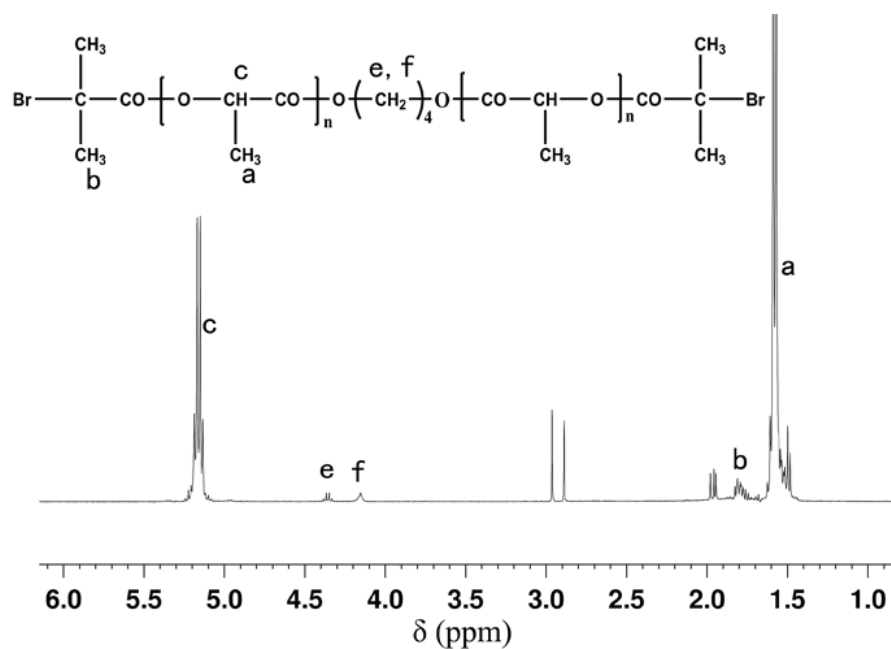


Fig. S2 ^1H NMR spectrum of Br-PLA-Br recorded in CDCl_3 .

Table S1 Macromolecular Characteristics of PLA and PMAIpGP-PLA-PMAIpGP.

sample	$[\text{PLA}]_0/[\text{MAIpGP}]_0^a$	$M_{n,\text{NMR}}^b$	$[\text{PLA}]/[\text{MAIpGP}]^c$
PLA ₁₀₀	1:0	7460	-
PMAIpGP ₈ -PLA ₁₀₀ -PMAIpGP ₈	1:20	12710	100:16
PMAIpGP ₁₃ -PLA ₁₀₀ -PMAIpGP ₁₃	1:30	15980	100:26
PMAIpGP ₁₆ -PLA ₁₀₀ -PMAIpGP ₁₆	1:40	17956	100:32
PMAIpGP ₂₄ -PLA ₁₀₀ -PMAIpGP ₂₄	1:50	23204	100:48
PMAIpGP ₂₈ -PLA ₁₀₀ -PMAIpGP ₂₈	1:60	25828	100:56

^a $[\text{PLA}]_0/[\text{MAIpGP}]_0$ represents the feed molar ratio of PLA and MAIpGP

^b Determined by ^1H NMR (g/mol)

^c Determined by ^1H NMR, $[\text{PLA}]/[\text{MAIpGP}]$ represents the repeat units molar ratio of $[\text{OCCH}(\text{CH}_3)\text{O}]$ and MAIpGP in the resultant polymers.

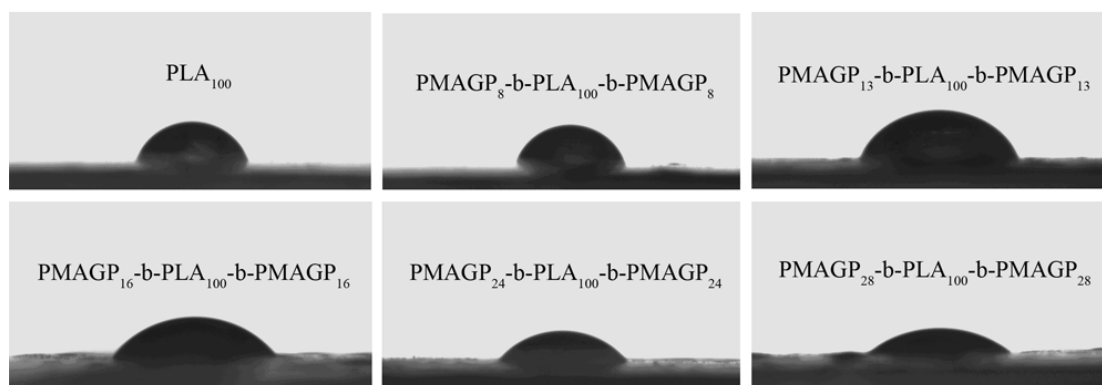


Fig. S3 Recorded images of water drops ($10 \mu\text{L}$) deposited on the surface of films of PLA_{100} , $\text{PMAGP}_8\text{-b-PLA}_{100}\text{-b-PMAGP}_8$, $\text{PMAGP}_{13}\text{-b-PLA}_{100}\text{-b-PMAGP}_{13}$, $\text{PMAGP}_{16}\text{-b-PLA}_{100}\text{-b-PMAGP}_{16}$, $\text{PMAGP}_{24}\text{-b-PLA}_{100}\text{-b-PMAGP}_{24}$ and $\text{PMAGP}_{28}\text{-b-PLA}_{100}\text{-b-PMAGP}_{28}$.

Table S2 Water contact angle and water absorption of the polymer films

Sample	Water contact angle ($^\circ$)				Water absorption(%)
PLA_{100} film	78.5	77.6	79.1	78.1	39.2
$\text{PMAGP}_8\text{-b-PLA}_{100}\text{-b-PMAGP}_8$ film	71.6	72.3	72.1	70.5	64.3
$\text{PMAGP}_{13}\text{-b-PLA}_{100}\text{-b-PMAGP}_{13}$ film	69.4	68.8	67.4	68.3	80.0
$\text{PMAGP}_{16}\text{-b-PLA}_{100}\text{-b-PMAGP}_{16}$ film	66.4	65.3	66.5	65.8	127.7
$\text{PMAGP}_{24}\text{-b-PLA}_{100}\text{-b-PMAGP}_{24}$ film	49.6	51.1	50.3	51.7	131.3
$\text{PMAGP}_{28}\text{-b-PLA}_{100}\text{-b-PMAGP}_{28}$ film	40.1	39.3	39.1	40.3	138.5

Dyeing Procedure

The films of PLA and the copolymer (P1, P2, P3, P4, and P5) were soaked in beet red aqueous solution for 2 h at room temperature, and then washed the residual dye on the surface of films by deionized water before observation.

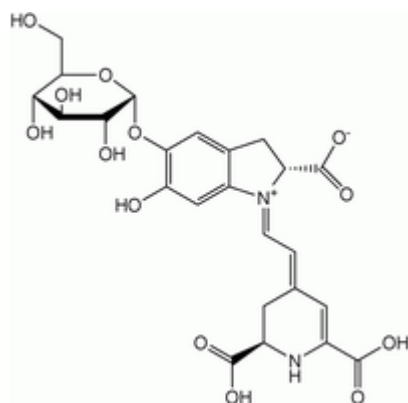


Fig. S4 Molecular structure of beet red.

References

1. J. Q. Meng, F. S. Du, Y. S. Li and Z. C. Li, *J. Polym. Sci. Part A: Polym. Chem.*, 2005, **43**, 752.
2. Y. M. Chen and G. Wulff, *Macromol. Rapid Commun.*, 2002, **23**, 59.