Supplementary Data

Influence of Polyol Impurities on Transesterification Kinetics, Molecular Structures and Properties of Isosorbide Polycarbonate

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GC-MS curves of isosorbide samples A and B

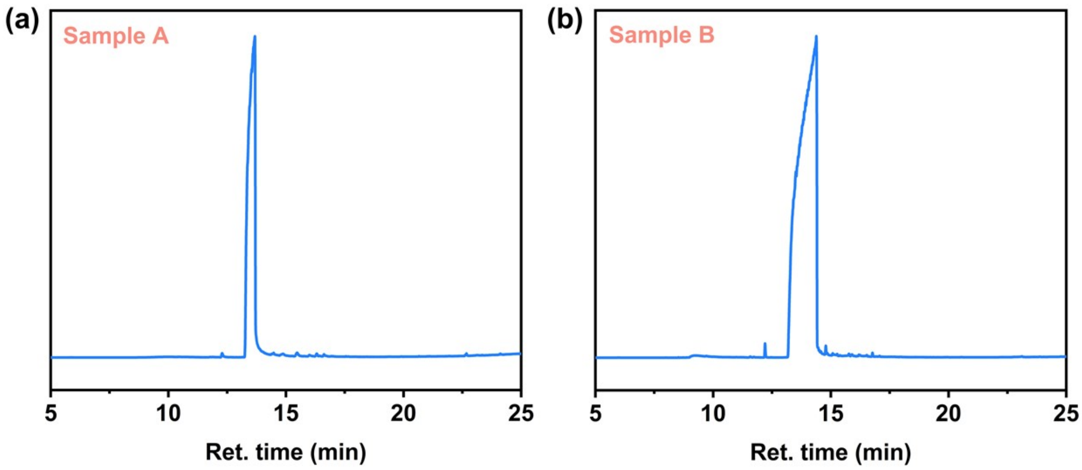

Figure S1. GC-MS curves of isosorbide samples A (a) and B (b).

Standard curve of phenol

Different mass concentrations of phenol-acetonitrile solutions with equal gradient dilution were first prepared and then tested and analyzed using HPLC. Different scattered points were obtained according to the phenol peak area of different HPLC curves, and the scattering points were fitted to a straight line, which was the standard curve of phenol solution (Figure S2). The correlation coefficient (R^2) corresponding to the line was greater than 0.99, indicating that it had a good fit degree. The measurement conditions were as follows: the above samples were dissolved in acetonitrile solvent to form a concentration of 0.01 $g \cdot mL^{-1}$ solution under test, detector wavelength 245 nm, column temperature 40 °C, the mobile phase was acetonitrile and water (flow rate ratio 30:70), and injection volume 20 μL.

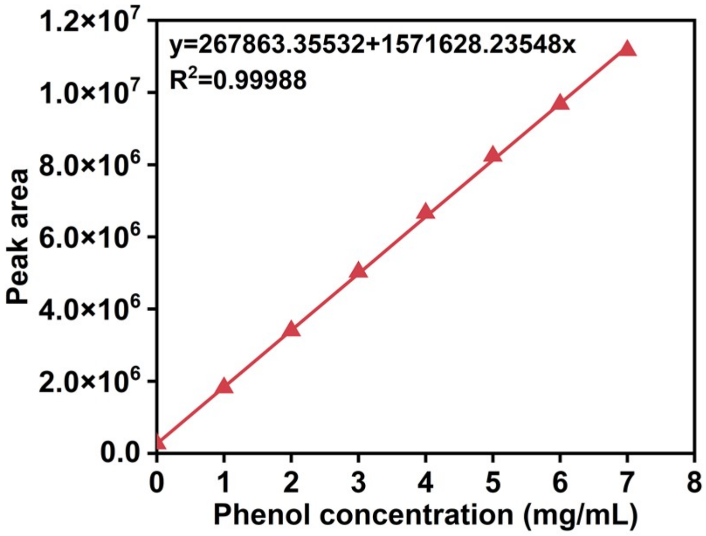

Figure S2. Standard curve equation of peak area and phenol concentration.

Determination of phenol concentration and conversion of diphenyl carbonate in transesterification reaction

The products of transesterification reaction taken out at regular intervals were dissolved in acetonitrile solvent to prepare 0.01 g·mL^{-1} sample to be tested, and the samples were measured and analyzed under the set measurement conditions by HPLC. The measurement conditions were as follows: the above samples were dissolved in acetonitrile solvent to form a concentration of 0.01 g·mL^{-1} solution under test, detector wavelength 245 nm, column temperature 40 °C, the mobile phase was acetonitrile and water (flow rate ratio 30:70), and injection volume 20 μL. Based on the standard curve equation of phenol concentration versus peak area (Figure S2), the phenol concentration ($C_{\text{ph-OH}}$) in the products of the transesterification reaction at different times was calculated. Then the phenol concentration (C_{p}) in the molten state of the reaction system could be calculated by substituting $C_{\text{ph-OH}}$ into Eq. (S1).[1, 2]

$$C_P = \frac{C_{Ph-OH} \times (M_{IS} + M_{DPC})}{C_0 \times M_{Ph-OH} \times (V_{IS} + V_{DPC})} \tag{S1}$$

where C_0 is the concentration of the extracted melt acetonitrile solution, M_{IS}, M_{DPC}, and $M_{\text{Ph-OH}}$ are the molar mass of isosorbide, diphenyl carbonate and phenol, respectively, V_{IS} and V_{DPC} are the molar volume of isosorbide and diphenyl carbonate, respectively.

The transesterification reaction of isosorbide and diphenyl carbonate was sampled at equilibrium and the amount of phenol at equilibrium was tested by HPLC. Then the conversion of diphenyl carbonate could be calculated from Eq. (S2).

$$z = \frac{n}{n_0} \times 100\% = \frac{n}{2n_{DPC}} \times 100\% \tag{S2}$$

where n is the amount of phenol at the equilibrium of the transesterification reaction, n_0 is the theoretical molar amount of phenol produced, and n_{DPC} is the initial molar amount of diphenyl carbonate.

Cross-linking occurred in PIC containing 2-deoxy-$_{\mathrm{D}}$-ribose impurity

Figure S3. Severe cross-linking of PIC occurred when isosorbide contained 1.5 mol% 2-deoxy-$_{\mathrm{D}}$-ribose impurity, as well as a gel produced by solubilization in $CHCl_3$.

Supplementary description ^{1}H NMR

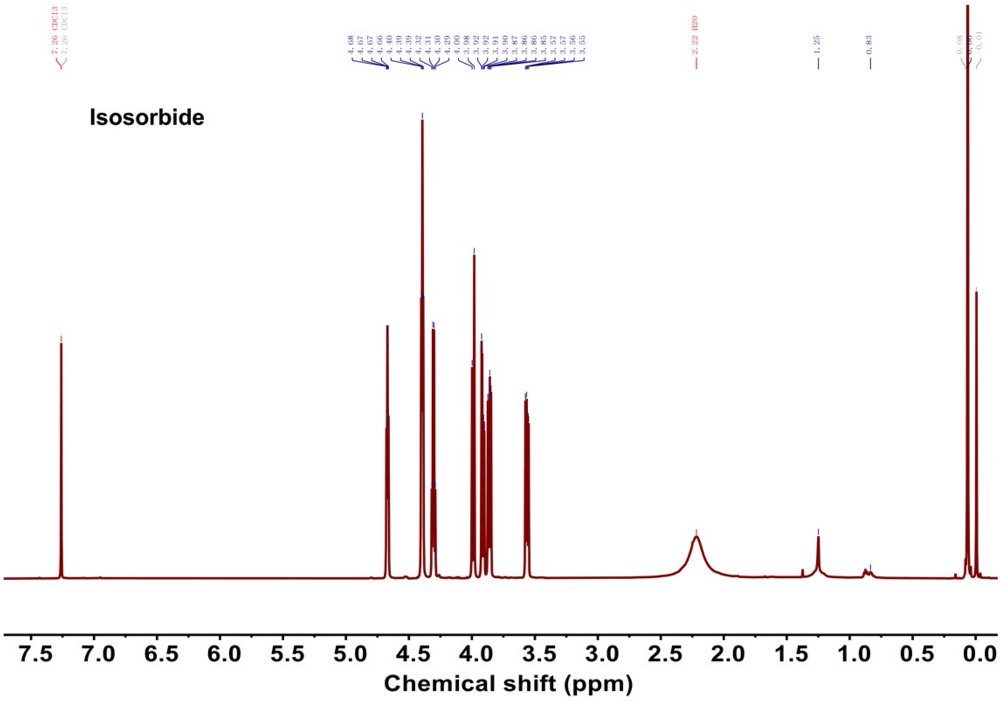

Figure S4. ^{1}H NMR spectrum of isosorbide.

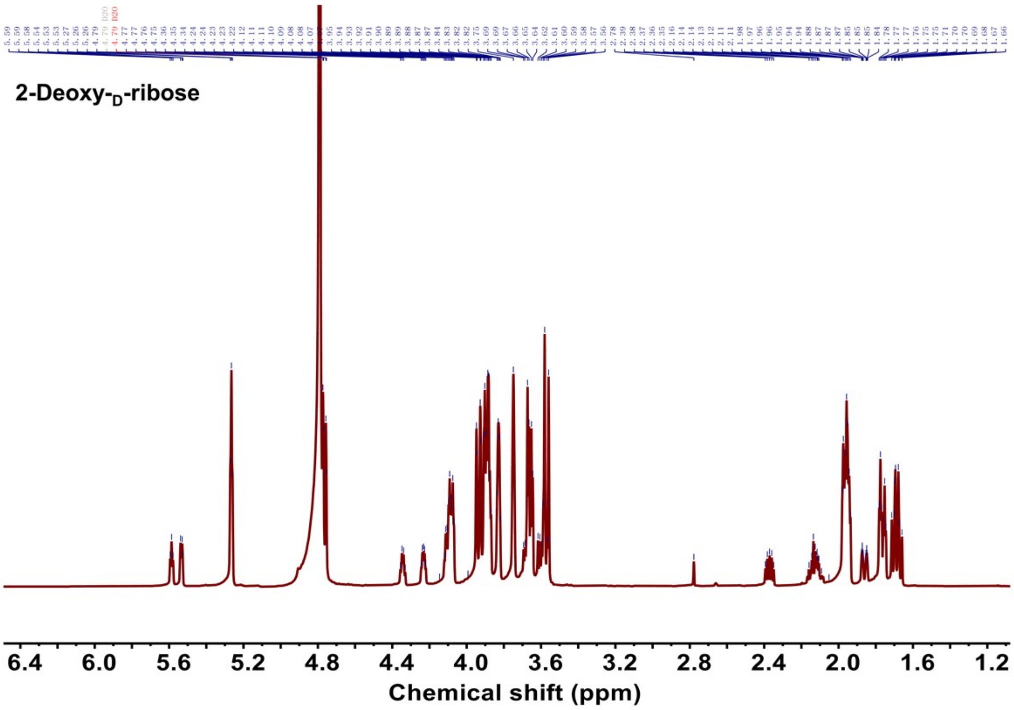

Figure S5. ^{1}H NMR spectrum of 2-deoxy-$_\mathrm{D}$-ribose.

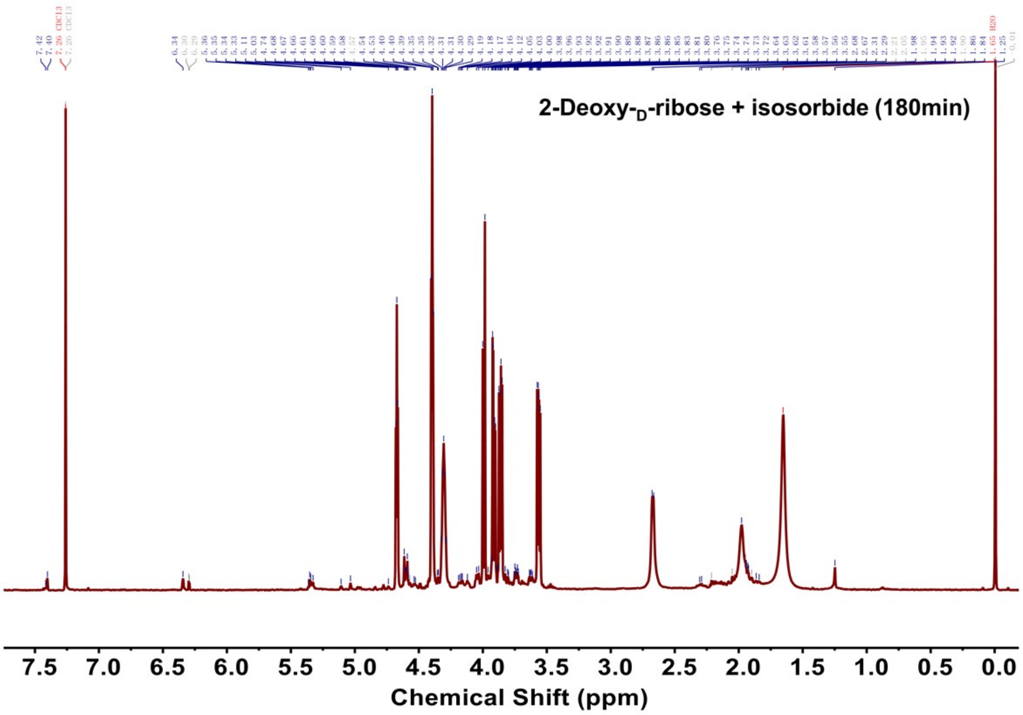

Figure S6. ^{1}H NMR of the product of isosorbide and the impurity 2-deoxy-$_\mathrm{D}$-ribose stirred at 130 °C for 3h (the ratio of the two substances is 1:1).

Performance parameters of PIC with impurities of different types and additions

Table S1. Performance parameters of PIC with impurities of different types and additions

polyol impurities		[η] (mL·g^{-1})	M_η (g·mol^{-1})	L*	a*	b*	ΔC	T_g (°C)
type	addition (mol%)							
glycerol	0	67.6	41218	99.6	-0.06	1.08	0.14	174.6
	0.1	63.8	38413	99.6	-0.29	1.83	0.79	173.9
	0.5	49.5	28216	99.8	-0.27	1.98	0.99	172.3
	1	47.8	27055	99.6	-0.24	2.10	1.01	171.8
	2	43.3	23961	99.6	-0.25	2.14	1.04	168.8
	3	31.1	15974	99.6	-0.37	2.50	1.29	165.6
	4	27.3	13663	99.2	-0.45	2.75	1.49	160.5
	5	22.0	10464	99.6	-0.28	1.80	0.84	157.6
2-deoxy-$_\mathrm{D}$-ribose	0.1	68.9	42175	98.7	-0.61	4.92	3.31	175.0
	0.3	77.0	48348	97.8	-0.85	6.27	4.27	175.9
	0.5	77.7	48877	99.0	-0.58	6.50	2.20	175.4
	1	91.8	59873	98.1	-1.01	6.75	4.85	176.1
	1.5	-	-	97.8	-0.98	8.45	-	176.5

Colors of PIC containing different types of impurities

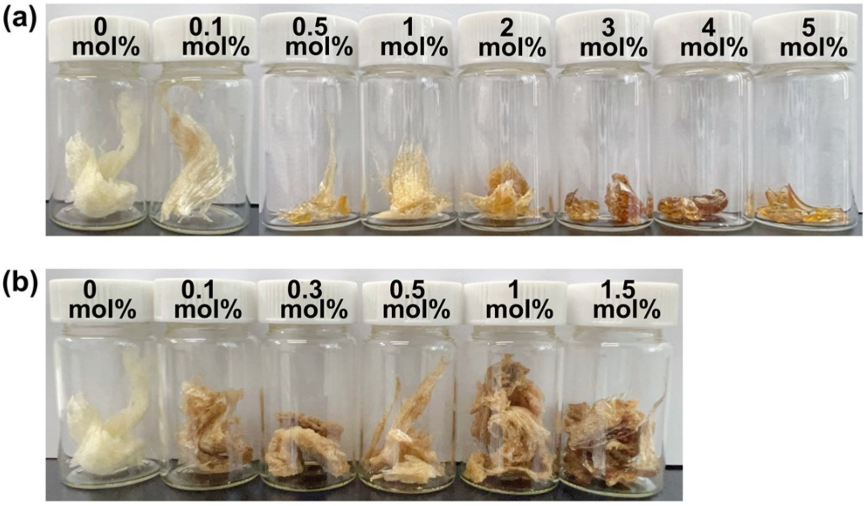

Figure S7. Colors of PIC containing glycerol impurity (a) and 2-deoxy-D-ribose impurity (b).

Dissolution-precipitation experiments

Since all the proton signals of 1,4-anhydrosorbitol could not be clearly identified, we probed whether the substance causing the yellowing of PIC was located in the macromolecular chain by a simple dissolution-precipitation experiment. It was found that the synthesized PIC was dissolved in the good solvent chloroform followed by precipitated in the bad solvent methanol to give a colorless methanol solution and white PIC (Figure S8a-c). Subsequently, PIC performed an alcoholysis experiment in NaOH-methanol alcoholizing agent and obtained a yellow coloration of the alcoholized solution (Figure S8d). The formula for the alcoholysis reaction is shown in Figure S8e.[3] The above phenomenon indicated that the substance X causing the yellowing of PIC should be located on the macromolecular chain rather than between the molecular chains wrapped by macromolecular entanglements.

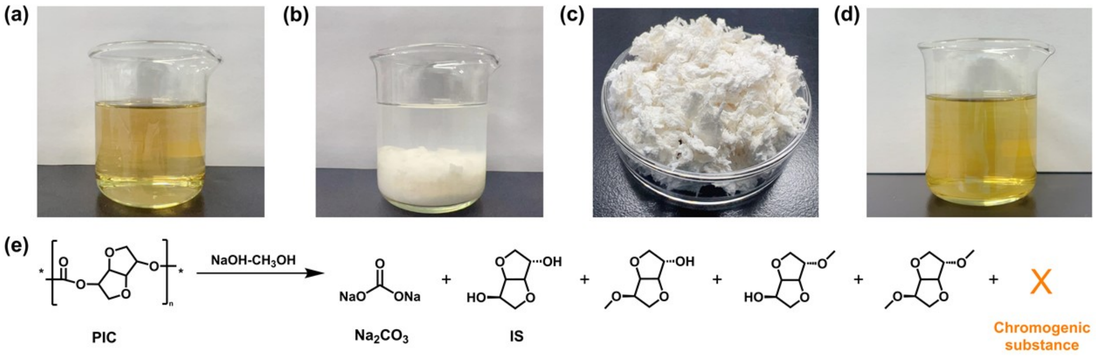

Figure S8. Dissolution-precipitation and alcoholysis of PIC prepared with the presence of 1% 2-deoxy-D-ribose impurity: (a) the solution of PIC dissolved in $CHCl_3$; (b) precipitation of PIC in methanol after dissolution in $CHCl_3$; (c) PIC product after dissolution-precipitation and drying; (d) alcoholysis of PIC in NaOH-methanol solution; and (e) alcoholysis reaction equation of PIC.

The influence of different polyol impurities on T_g

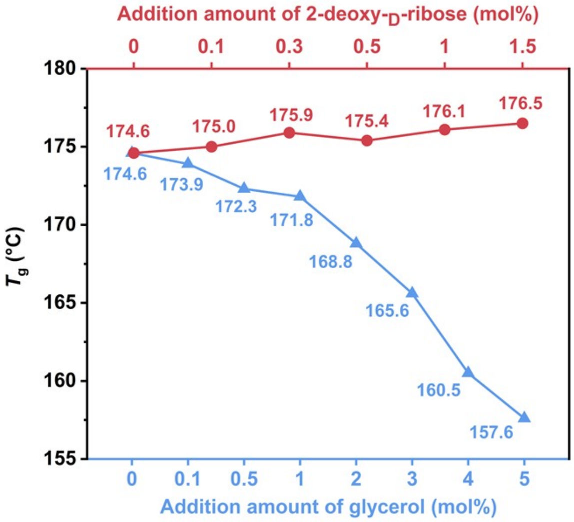

Figure S9. The relationship between T_g and the amount of different polyol impurities added.

References

1. Y. Wang, J. Wu, C. E. Koning and H. Wang, *Green Chem.*, 2022, **24**, 8637-8670.
2. C. Ma, F. Xu, W. Cheng, X. Tan, Q. Su and S. Zhang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 2684-2693.
3. T. Abe, R. Takashima, T. Kamiya, C. P. Foong, K. Numata, D. Aoki and H. Otsuka, *Green Chem.*, 2021, **23**, 9030-9037.