

Next-Generation High-Performance Bio-Based Naphthalate Polymers Derived from Malic Acid for Sustainable Food Packaging

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Supplementary Information

- Number of pages (including cover): 7
- Number of figures: 9

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- Bio-based precursors (2,7-N and THN) synthesis
- Polymer synthesis pathway
- IV results
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- Mechanical Tensile Testing

Dimethyl 1,2,3,4-tetrahydronaphthalene-2,7-dicarboxylate (THN)

A solution of methyl coumalate (644 mg, 4.2 mmol) in 10 mL of methanol was slowly added to a solution of methyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1-carboxylate (1.14 g, 5.5 mmol) in 2 mL of methanol at ambient temperature. The mixture was stirred for 2 h and quenched with 1M HCl solution. The mixture was extracted with ethyl acetate 3 times and dried by Na_2SO_4 . Purification by column chromatography afforded the product as light yellow oil.

Dimethyl naphthalene-2,7-dicarboxylate (2,7-N)

To a solution of Dimethyl 1,2,3,4-tetrahydronaphthalene-2,7-dicarboxylate (THN) (99.4 g, 0.4 mol) in 1.2 L of chloroform at room temperature under argon, N-Bromosuccinimide (146 g, 0.82 mol) and Azobisisobutyronitrile (660 mg, 4 mmol) was added, and argon was sweeping through the mixture for 20 minutes. The solution was stirred under reflux for 8 h. After cooling down to room temperature, triethylamine (230 mL, excess) was added, and was stirred for additional 2 h. 1.5 M HCl solution was added to neutralize the amine. The mixture was extracted by DCM then dried over Na_2SO_4 . The crude oil was recrystallized from hexane twice to afford the product as light yellow crystal.

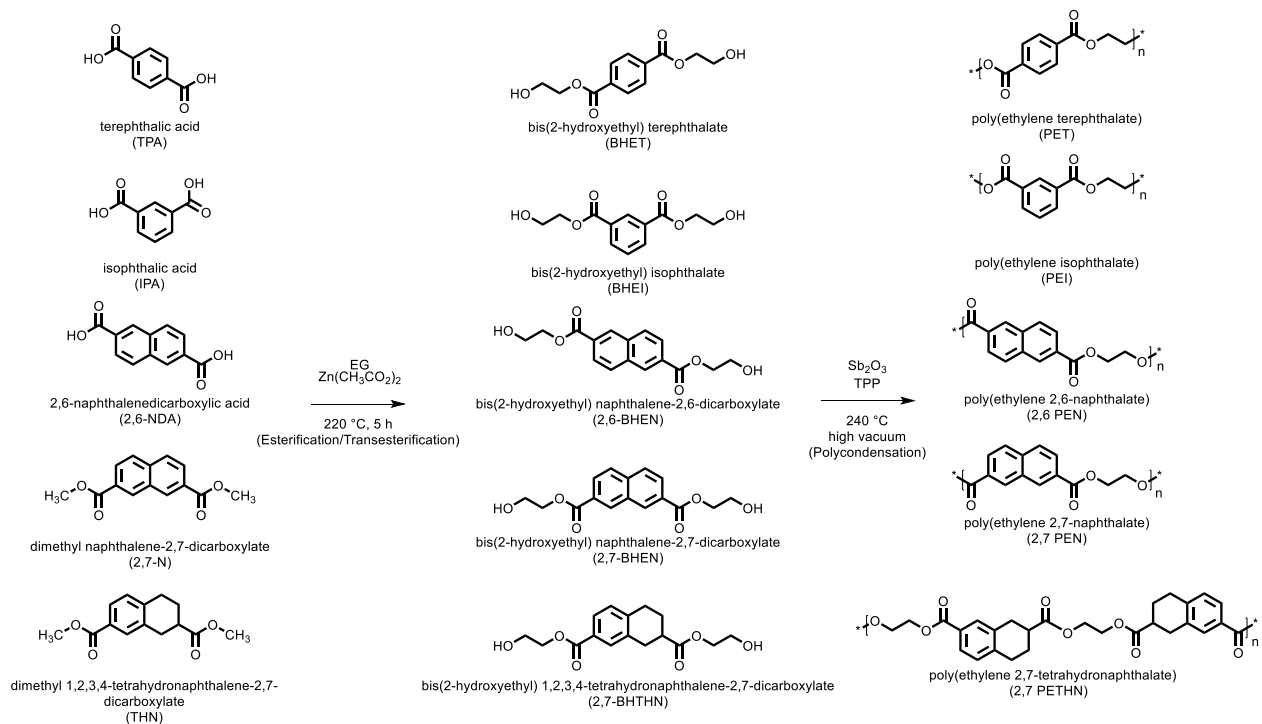


Figure S1: Step-growth polycondensation of PET and naphthalate-based polymers via two-step polymerization

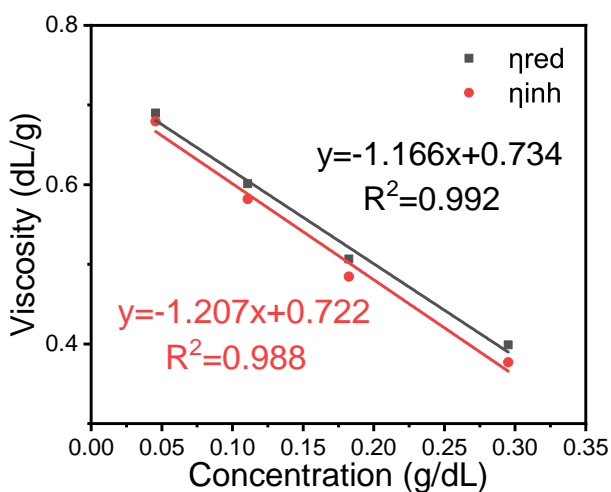


Figure S2: Illustrative example of intrinsic viscosity plot of PET using phenol/1,1,2,2-tetrachloroethane (60/40) as solvent with solution concentrations of roughly 0.05 g/dL, 0.11 g/dL, 0.18 g/dL and 0.30 g/dL, respectively

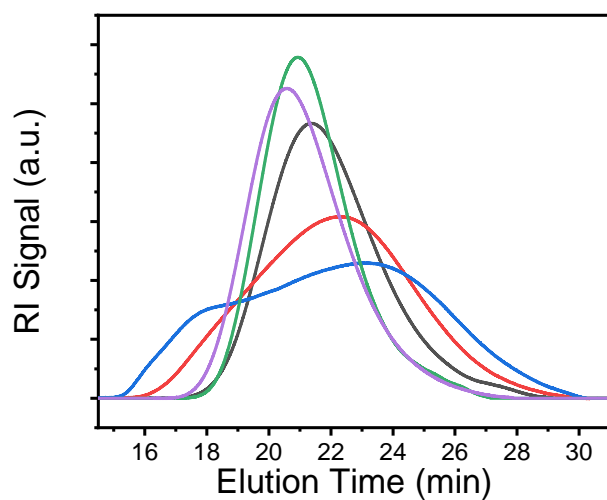


Figure S3: GPC analysis of various polymers produced in this study: PET (black); 2,7 PEN (red); 2,7 PETHN (blue); PEI (green); and 2,6 PEN (purple)

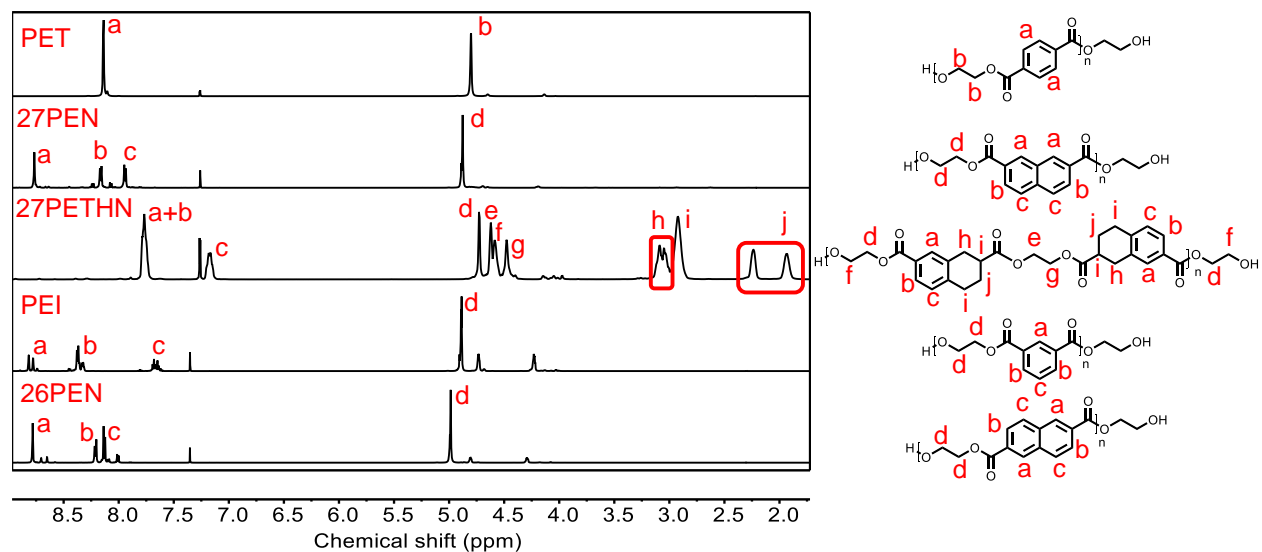


Figure S4: ^1H NMR spectra of PET and naphthalate-based polymers

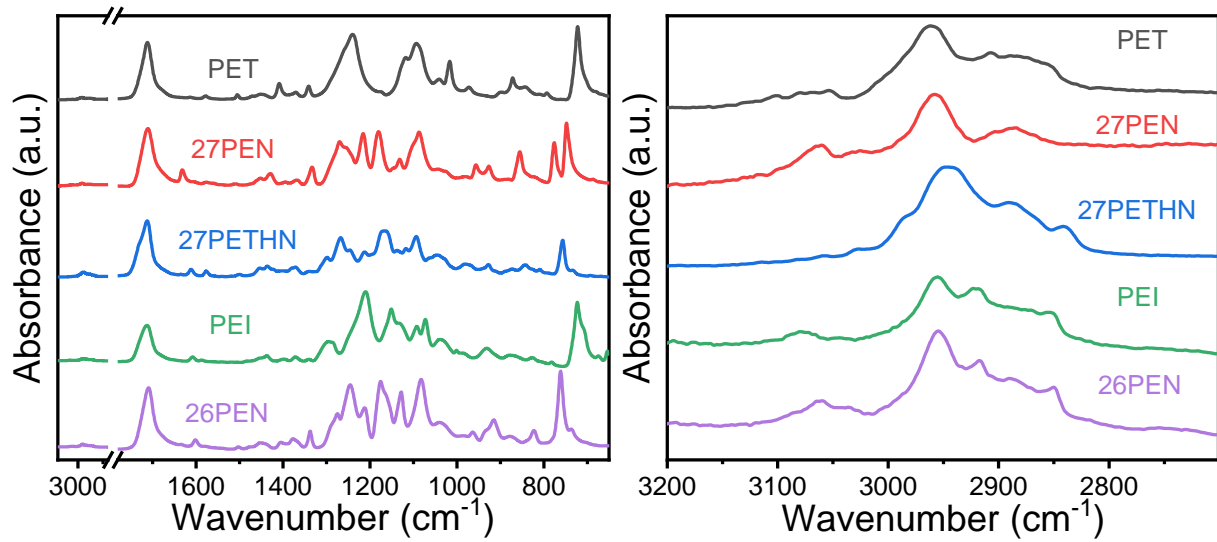


Figure S5: ATR-FTIR spectra of PET, PEI, and naphthalate-based polymers

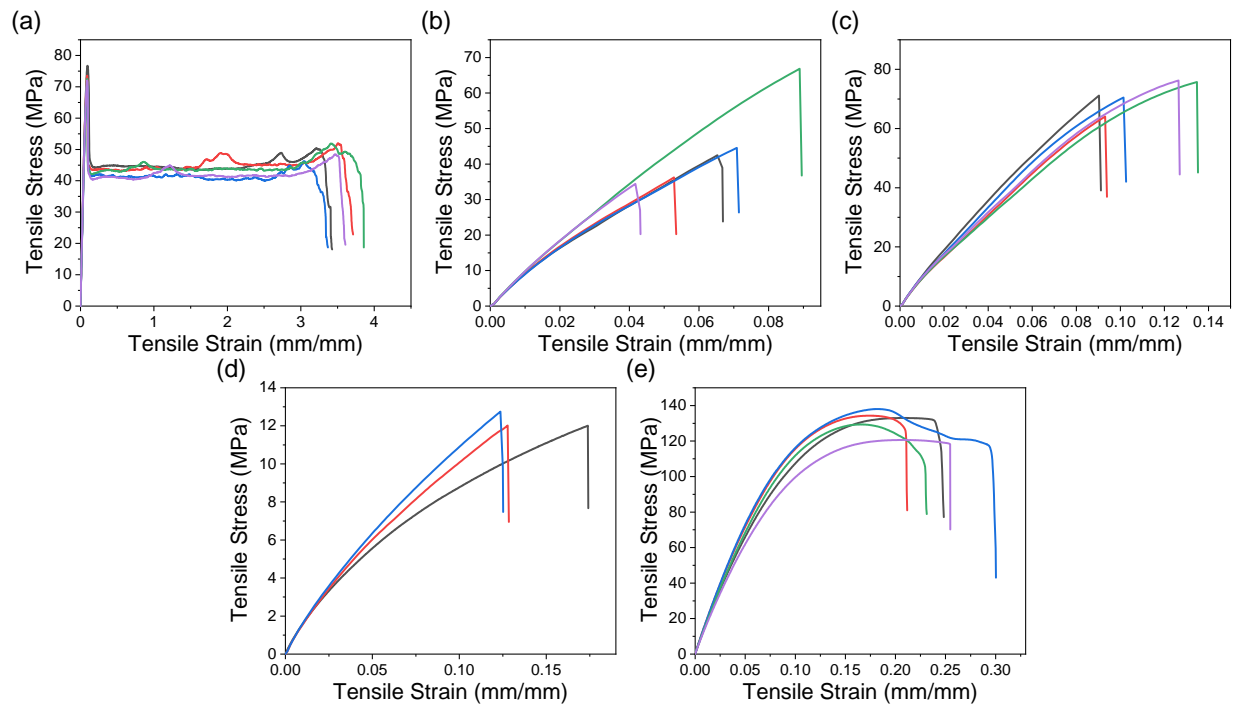


Figure S6: Stress–strain curves at room temperature: (a) PET; (b) 2,7 PEN; (c) 2,7 PETHN; (d) PEI; and (e) 2,6 PEN

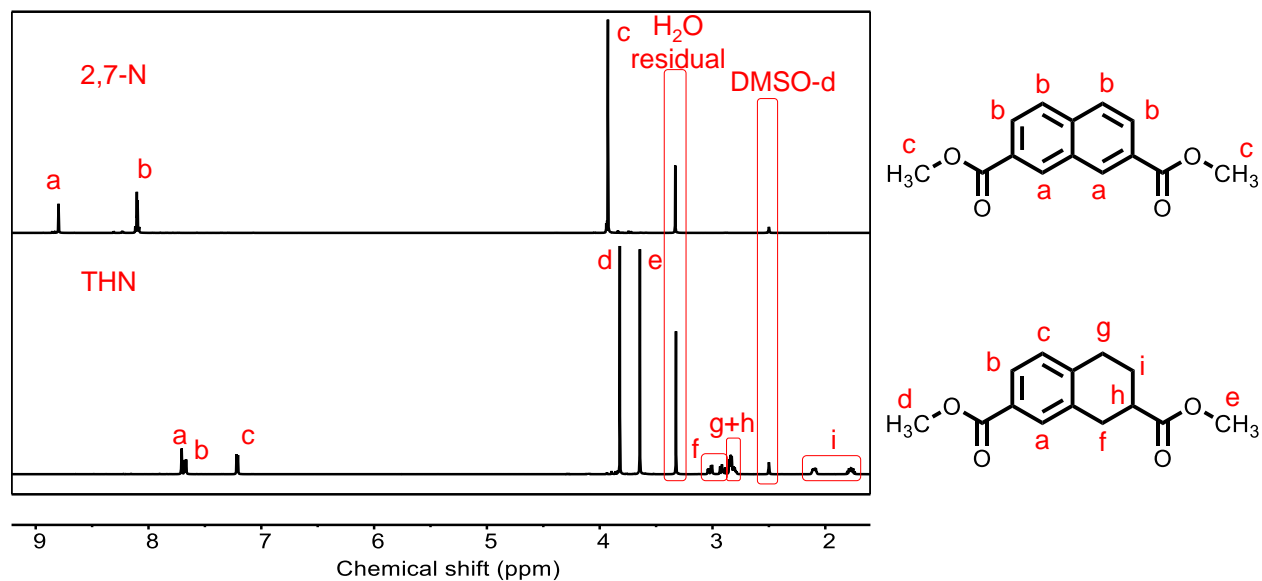


Figure S7: ^1H NMR spectra of naphthalate-based precursors

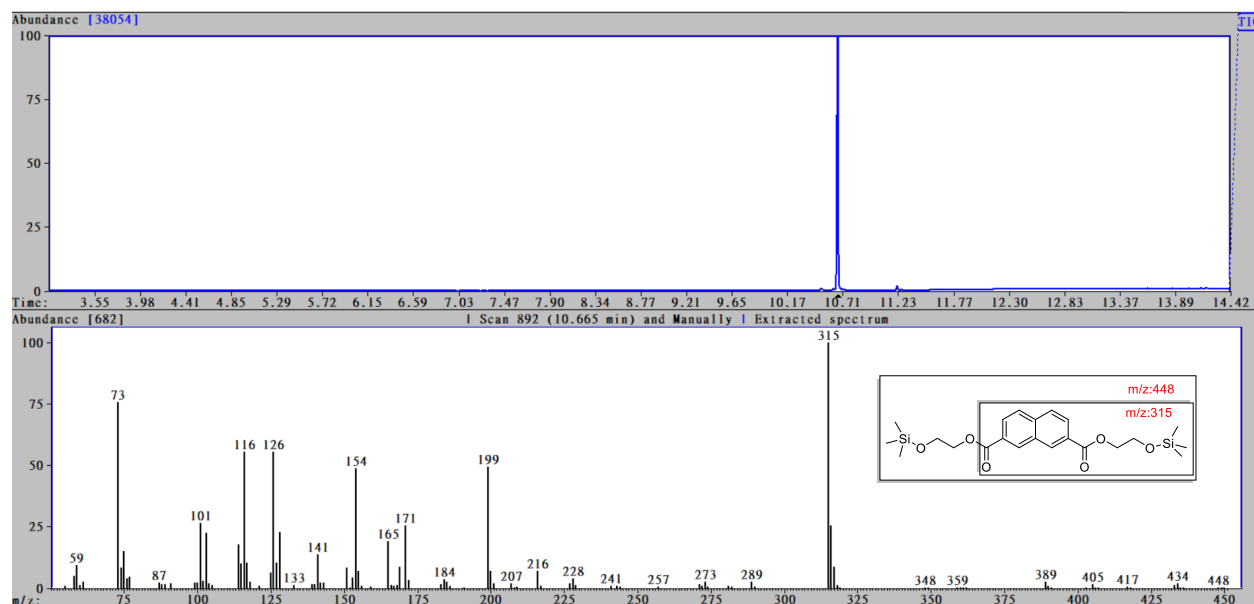


Figure S8: GC-MS data for showing high purity of 27BHEN (the hydroxyl end group was capped by silane agent)

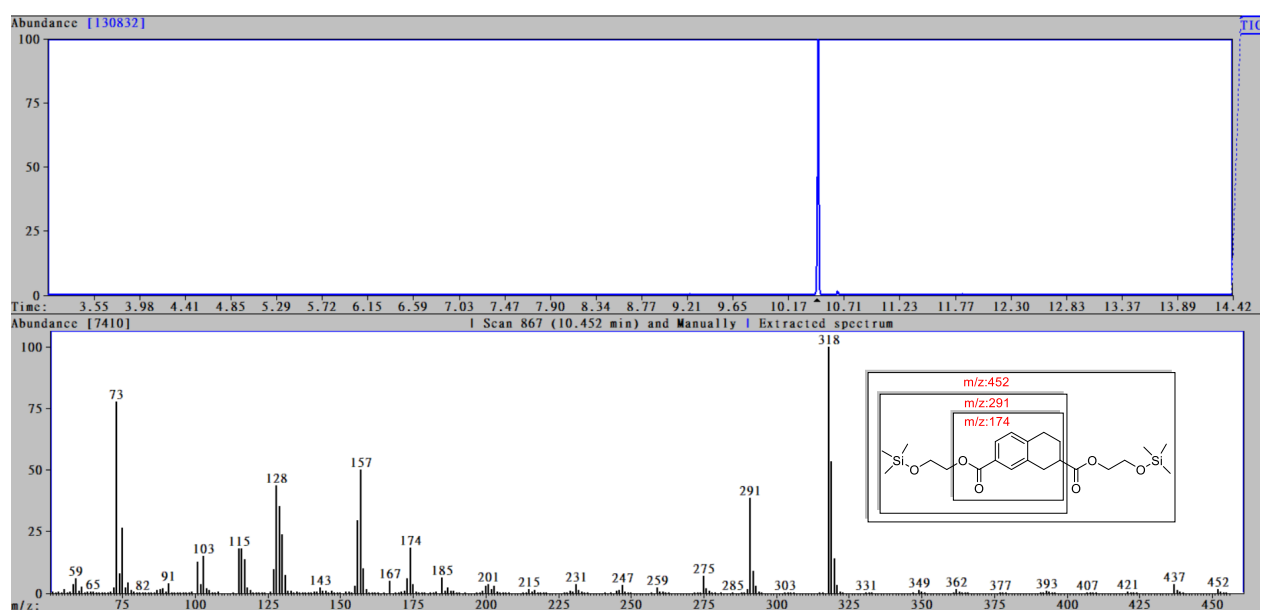


Figure S9: GC-MS data for showing high purity of 27BHTHN (the hydroxyl end group was capped by silane agent)