Supporting Information for

Aromatic Copolyesters with Enhanced Crystallizability and Mechanical Property by Adding the Renewable Nipagin-based Composition

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1. Experimental Section

![Scheme S1 Synthetic routes for the preparation of the nipagin and eugenol-based dimethyl esters.](image)

**Synthesis of Nipagin and Eugenol-based Dimethyl Esters**

**Synthesis of 4,4'-[1,4-Butanediyl-Bisox] Bis-1,1'-Dimethyl Benzoate (N2).**

Nipagin (12.90 g, 84 mmol), 1,4-dibromobutane (8.64 g, 40 mmol), anhydrous K$_2$CO$_3$ (11.70 g, 84 mmol), KI (0.32 g, 2 mmol) and 300 mL anhydrous CH$_3$CN were added into a 500 mL three-necked round bottom flask equipped with a magnetic stirrer (Scheme S1). Subsequently, the mixture was refluxed at 82 °C for 24 hours under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, the suspension was cooled to room temperature. A modified method was used for the post-process. First, the cooled suspension was immediately concentrated under vacuum to afford a white solid, which was subjected to recrystallization twice from methanol to obtain 13.18 g N2 as a white solid. Yield 92%; mp 146-148 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.02-7.95 (m, 4H; Ar-H), 6.95-6.86 (m, 4H; Ar-H), 4.15-4.03 (m, 4H; ArO-CH$_2$-), 3.88 (s, 6H; ArCO-CH$_3$), 2.06-1.95 (m, 4H; ArOCH$_2$-CH$_2$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ 166.84 (Ar-CO-), 162.74 (Ar-C), 131.62 (Ar-C), 122.63 (Ar-C), 114.09 (Ar-C), 67.61 (ArO-CH$_2$-), 51.84 (ArCOO-CH$_3$), 25.88 (ArOCH$_2$-CH$_2$) ppm (Fig. S1-S2); HRMS (ESI) m/z: [M+H]$^+$ calc'd for C$_{20}$H$_{22}$O$_6$: 359.1495; found: 359.1492. [M+Na]$^+$ calc'd for C$_{20}$H$_{22}$NaO$_6$: 381.1314; found: 381.1311.

**Synthesis of 2-Methoxy-4-[3-(2-Methoxy-2-Oxoethyl)]thiopropyl Phenol (P1).**

Eugenol (13.24 g, 80 mmol), methyl thioglycolate (10.28 g, 96 mmol), and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 0.1028 g, 0.4 mmol) as the photoinitiator, were added into a 50 mL quartz tube and thoroughly mixed into a homogeneous solution (Scheme S1). Then the reaction mixture was irradiated with four 6W ultraviolet lamps ($\lambda = 365$ nm). The reaction was detected by TLC until eugenol completely disappearing. The crude product was directly purified by column chromatography ($V_{petroleum~ether}: V_{ethyl~acetate} = 5 : 1$) to afford 10.24 g P1 as a light yellow oil. Yield 95%; bp 183-185 °C (5 mmHg).

S2
400 MHz, £OCH3, 3.71 (s, 3H; -COO-CH3), 3.22 (s, 2H; -S-CH2-CO-), 2.61-2.66 (m, 4H; -S-CH2-CH2-CH2-), 1.93-1.85 (q, J = 7.3 Hz, 2H; -SCH2-CH2-) ppm; 13C NMR (100.6 MHz, CDCl3): δ 171.07 (-SCH2-CO-), 146.61 (Ar-C), 143.94 (Ar-C), 133.20 (Ar-C), 121.03 (Ar-C), 114.46 (Ar-C), 111.28 (Ar-C), 55.92 (ArO-CH3), 52.32(-COO-CH3), 34.27 (-S-CH2-CO-), 33.43 (Ar-CH2-), 32.05 (-S-CH2-CH2-), 30.79 (-SCH2-CH2-) ppm (Fig. S3-S4); HRMS (ESI) m/z: [M-H]’ 269.0848; found: 269.0852.

**Synthesis of Methyl 2-(2-Methoxy-4-[3-(2-Methoxy-2-Oxoethyl)]thiopropyl)phenoxy Acetate (E1).**

Precursor P1 (10.80 g, 40 mmol), methyl chloroacetate (10.64 g, 80 mmol), anhydrous K2CO3 (11.04 g, 80 mmol), KI (0.33 g, 2 mmol) and 200 mL anhydrous CH3CN were added into a 500 mL three-necked round bottom flask equipped with a magnetic stirrer (Scheme S1). The reaction mixture was refluxed at 82 °C for 6 hours under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After finish of the reaction, the suspension was cooled to room temperature, white solid was filtered off. The filtrate was concentrated under vacuum to obtain a viscous oil, which was dissolved in 350 mL dichloromethane and successively washed by distilled water (2 × 120 mL) and saturated NaCl solution (2 × 120 mL). The organic phase was dried over anhydrous magnesium sulphate and concentrated under vacuum. The resulting residue was purified by column chromatography (Vpetroleum ether : Vethyl acetate = 3 : 1) to afford 11.84 g E1 as a light yellow viscous oil. Yield 88%; bp 196-197 °C (5 mmHg).

1H NMR (400 MHz, CDCl3): δ 6.78-6.66 (m, 3H; Ar-H), 4.66 (s, 2H; ArO-CH2-CO-), 3.87 (s, 3H; ArO-CH3), 3.78 (s, 3H; ArOCH2COO-CH3), 3.71 (s, 3H; -SCH2COO-CH3), 3.22 (s, 2H; -S-CH2-CO-), 2.68-2.61 (m, 4H; -S-CH2-CH2-CH2-), 1.94-1.86 (q, J = 7.4 Hz, 2H; -SCH2-CH2-CH2-) ppm; 13C NMR (100.6 MHz, CDCl3): δ 170.85 (-SCH2-CO-), 169.54 (ArOCH2-CO-), 149.58 (Ar-C), 145.52 (Ar-C), 135.82 (Ar-C), 120.28 (Ar-C), 114.74 (Ar-C), 112.57 (Ar-C), 66.67 (ArO-CH2-CO-), 55.85 (ArO-CH3), 52.23 (-CH2COO-CH3), 52.01 (-SCH2COO-CH3), 34.16 (-SCH2-CO-), 33.35 (-SCH2-CH2-CH2-), 31.97 (-SCH2-CH2-CH2-), 30.50 (-S-CH2-CH2-CH2-) ppm (Fig. S5-S6); HRMS (ESI) m/z: [M+Na]+ calcd for C13H17O3S: 365.1035; found: 365.1035.

**Synthesis of 1,4-Bis[2-Methoxy-4-[3-(2-Methoxy-2-Oxoethyl)]thiopropyl]phenoxy Butane (E2).**

Precursor P1 (22.68 g, 84 mmol), 1,4-dibromobutane (8.72 g, 40 mmol), anhydrous K2CO3 (12.12 g, 88 mmol), KI (0.33 g, 2 mmol) and 300 mL anhydrous CH3CN were added into a 500 mL three-necked round bottom flask equipped with a magnetic stirrer (Scheme S1). The reaction mixture was refluxed at 82 °C for 48 hours under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After finish of the reaction, the suspension was cooled to room temperature, white solid was filtered off. The filtrate was concentrated under vacuum to obtain a viscous oil, which was dissolved in 400 mL dichloromethane and successively washed by water (2 × 150 mL) and saturated NaCl solution (2 × 150 mL). The organic phase was dried over anhydrous magnesium sulphate and concentrated under vacuum. The resulting residue was directly purified by twice-recrystallization from methanol to afford 9.74 g E2 as a white crystalline solid. Yield 86%; mp 78-79 °C.

1H NMR (400 MHz, CDCl3): δ 6.82-6.67 (m, 3H; Ar-H), 4.06 (m, 4H; ArO-CH2-), 3.84 (s, 6H; ArO-CH3), 3.72 (s, 6H; -SCH2COO-CH3), 3.22 (s, 4H; -S-CH2-CO-), 2.67-2.62 (m, 8H; -S-CH2-CH2-), 2.01 (m, 4H; -OCH2-CH2-), 1.94-1.87 (q, J = 7.2 Hz, 4H; -SCH2-CH2-)
ppm; \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): δ 170.96 (\(-\text{SCH}_2\text{-CO-}\)), 149.47 (Ar-C), 146.83 (Ar-C), 134.14 (Ar-C), 120.41 (Ar-C), 113.48 (Ar-C), 112.45 (Ar-C), 68.88 (ArO-CH\(_2\)), 56.00 (ArO-CH\(_3\)), 52.33 (\(-\text{SCH}_2\text{COO-CH}_2\)), 34.23 (\(-\text{SCH}_2\text{CH}_2\text{-CH}_2\)), 32.10 (\(-\text{SCH}_2\text{CH}_2\text{-CH}_2\)), 30.68 (\(-\text{SCH}_2\text{CH}_2\text{-CH}_2\)), 26.10 ppm (Fig. S5, Fig. S7); HRMS (ESI) m/z: [M+Na]\(^+\) calcld for C\(_{30}\)H\(_{42}\)O\(_8\)NaS\(_2\): 617.2219; found: 617.2218.

2. Characterization Section

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<th>Copolyester</th>
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\(^a\) The diffraction angles measured in powder diffraction patterns for samples coming directly from synthesis. Intensities visually estimated as follows: m, medium; s, strong; w, weak. \(^b\) Crystallinity index calculated as the quotient between crystalline area and total area. Crystalline and amorphous areas in the X-ray diffraction pattern were quantified using PeakFit v4.12 software.
Fig. S1 $^1$H NMR spectrum of N2.

Fig. S2 $^{13}$C NMR spectrum of N2.

Fig. S3 $^1$H NMR spectrum of P1.

Fig. S4 $^{13}$C NMR spectrum of P1.
Fig. S5 $^1$H NMR spectra of E1 and E2.

Fig. S6 $^{13}$C NMR spectrum of E1.

Fig. S7 $^{13}$C NMR spectrum of E2.
Fig. S8 SEC traces of the corresponding copolyesters carried out in CHCl₃.

Fig. S9 SEC traces of the corresponding copolyesters carried out in THF.
Fig. S10 $^1$H NMR spectra of PDN2$_{x}$E1$_{x}$ copolyesters.

Fig. S11 $^{13}$C NMR spectra of PDN2$_{x}$E1$_{x}$ copolyesters.
Fig. S12 $^1$H NMR spectra of PDN$_{21-x}$E$_x$ copolyesters.

Fig. S13 $^{13}$C NMR spectra of PDN$_{21-x}$E$_x$ copolyesters.
Fig. S14 FTIR spectra of PDN2$_{1-x}$E1$_x$ copolyesters.

Fig. S15 FTIR spectra of PDN2$_{1-x}$E2$_x$ copolyesters.
Fig. S16 The splitting situations of the methylenes adjacent to the hydroxy-oxygens with the indications of the dyads to which they are assigned in PDN21,E2x copolyesters.
Fig. S17 TGA curves of PDN2₁-E₁ copolyesters.

Fig. S18 TGA derivative curves of PDN2₁-E₁ copolyesters.
Fig. S19 TGA curves of PDN21_xE2_x copolyesters.

Fig. S20 TGA derivative curves of PDN21_xE2_x copolyesters.
Fig. S21 Second heating DSC curves of the copolyesters coming from samples after precipitation from methanol carried out from -30 to 210 °C at a heating / cooling rate of 10 °C min\(^{-1}\).
**Fig. S22** Isothermal crystallization of PDN2_{80\% E1_{20\%}} and PDN2_{80\% E2_{20\%}} at the indicated temperature. Relative crystallinity versus time plots (A) and Ln[-Ln(1-X_t)] versus Ln(t-t_0) plots (B).
Fig. S23 Storage modulus as a function of temperature for PDN2₁ₓE₂ₓ copolyesters.

Fig. S24 Tan δ as a function of temperature for PDN2₁ₓE₂ₓ copolyesters.