

Supporting Information

Structural Insight into the Viscoelastic Behaviour of Elastomeric Polyesters: Effect of the Nature of Fatty Acid Side Chains and Degree of Unsaturation

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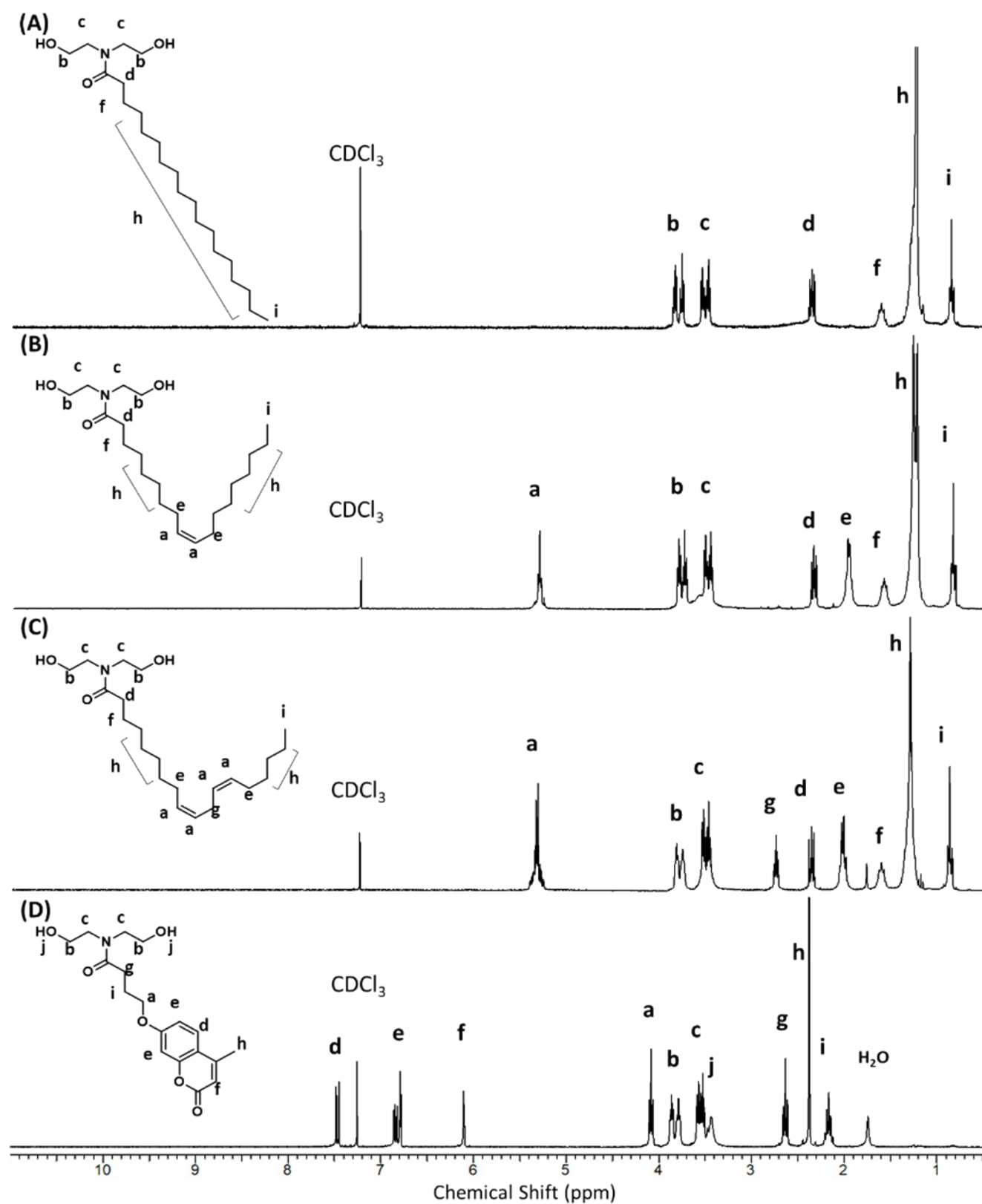


Figure S1. ^1H NMR (CDCl_3) spectra of four diol monomers, (A) **Ste**, (B) **Ole**, (C) **Lin**, and (D) **Cou**.

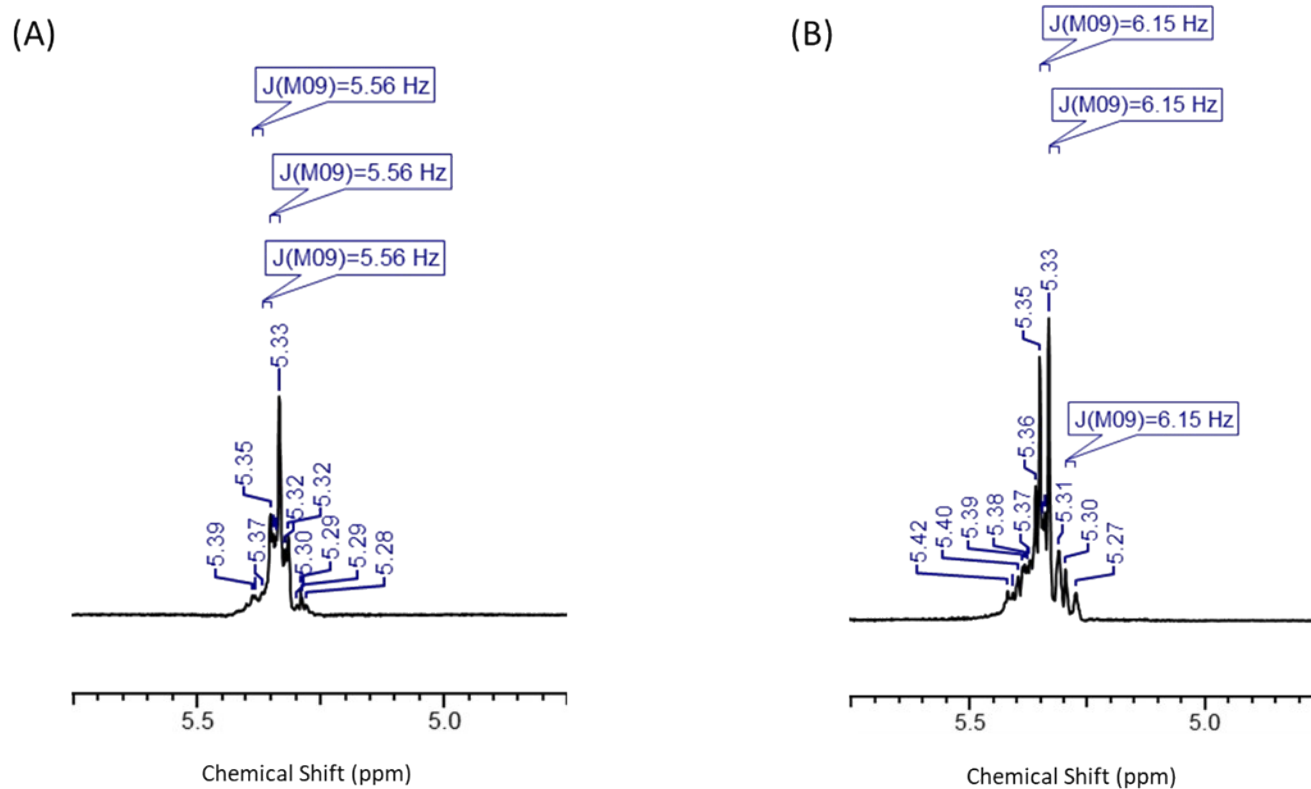


Figure S2. Zoom-in ^1H NMR spectra of (A) **Ole** and (B) **Lin**.

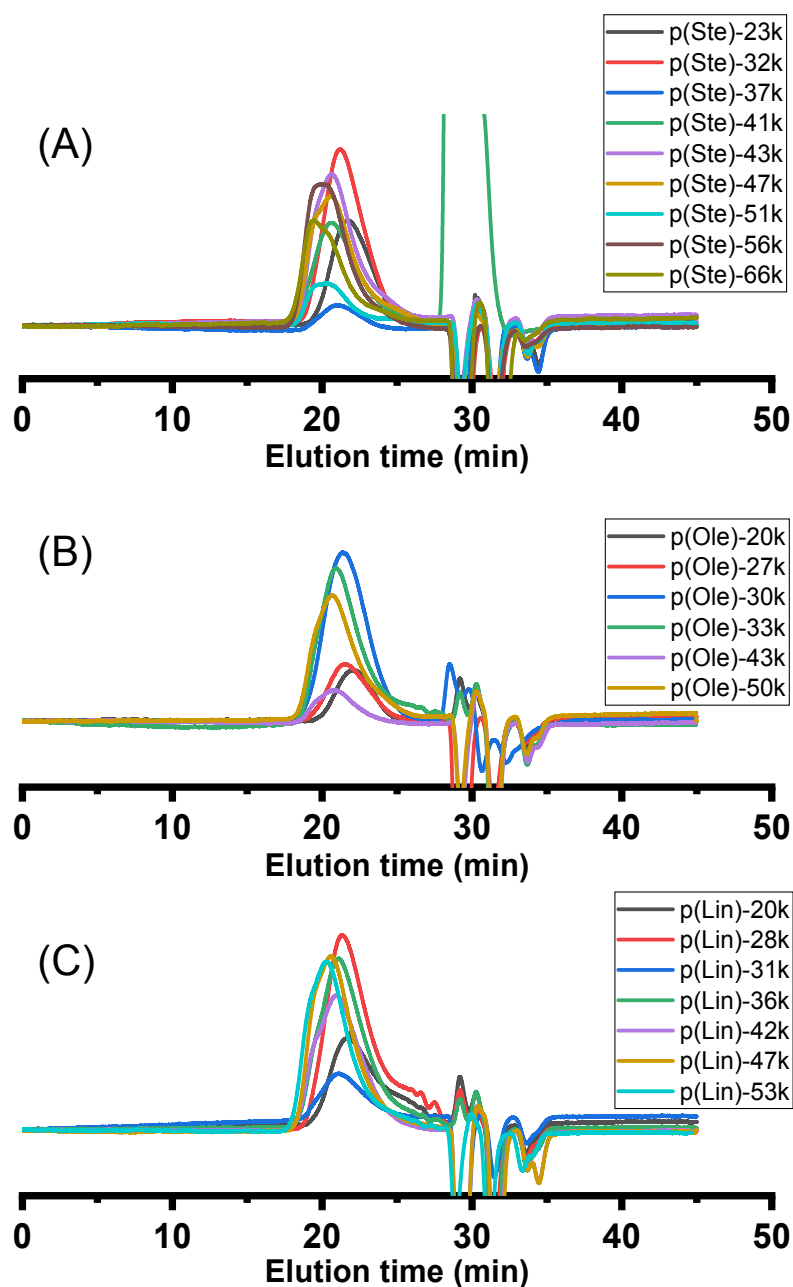


Figure S3. Raw GPC traces of (A) **p(Ste)**, (B) **p(Ole)** and (C) **p(Lin)** using DMF (with 25 mM LiBr) as the eluent and polystyrene as the standard.

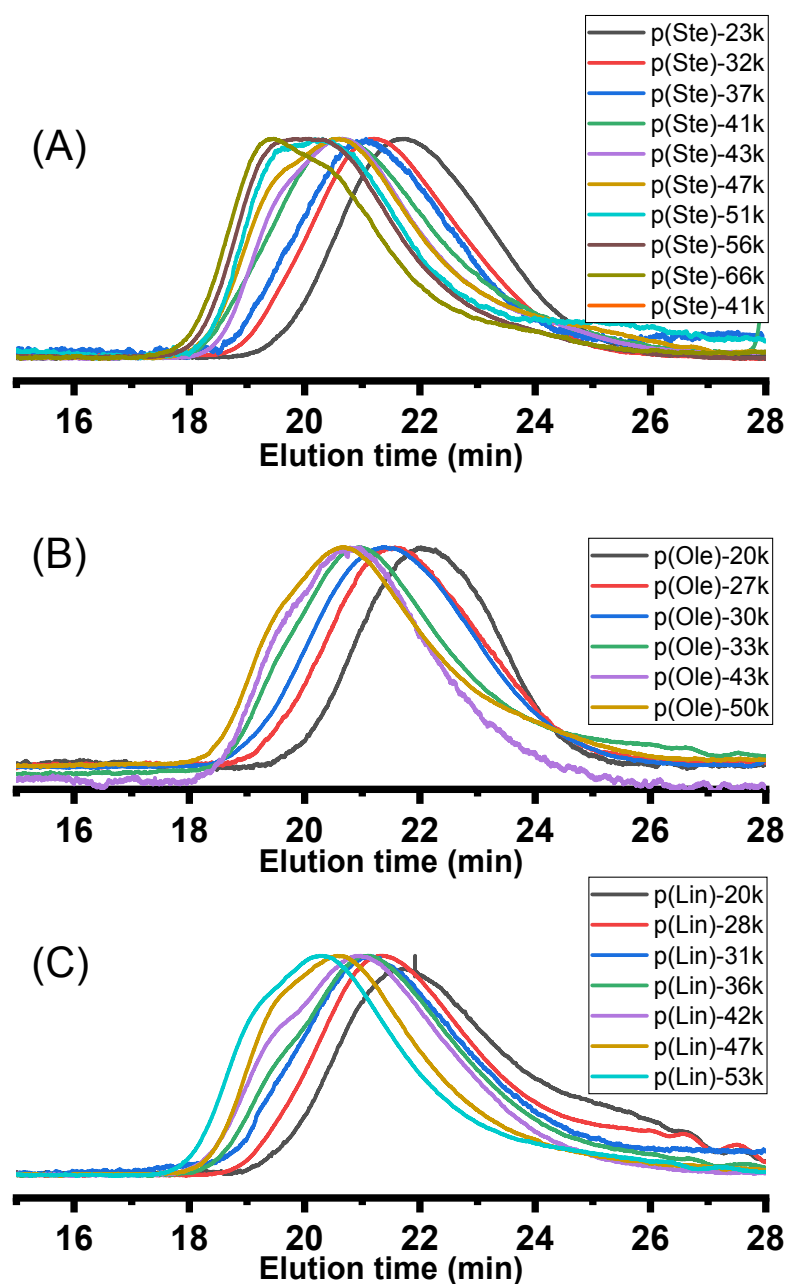


Figure S4. Normalized GPC traces of (A) **p(Ste)**, (B) **p(Ole)** and (C) **p(Lin)** using DMF (with 25 mM LiBr) as the eluent and polystyrene as the standard.

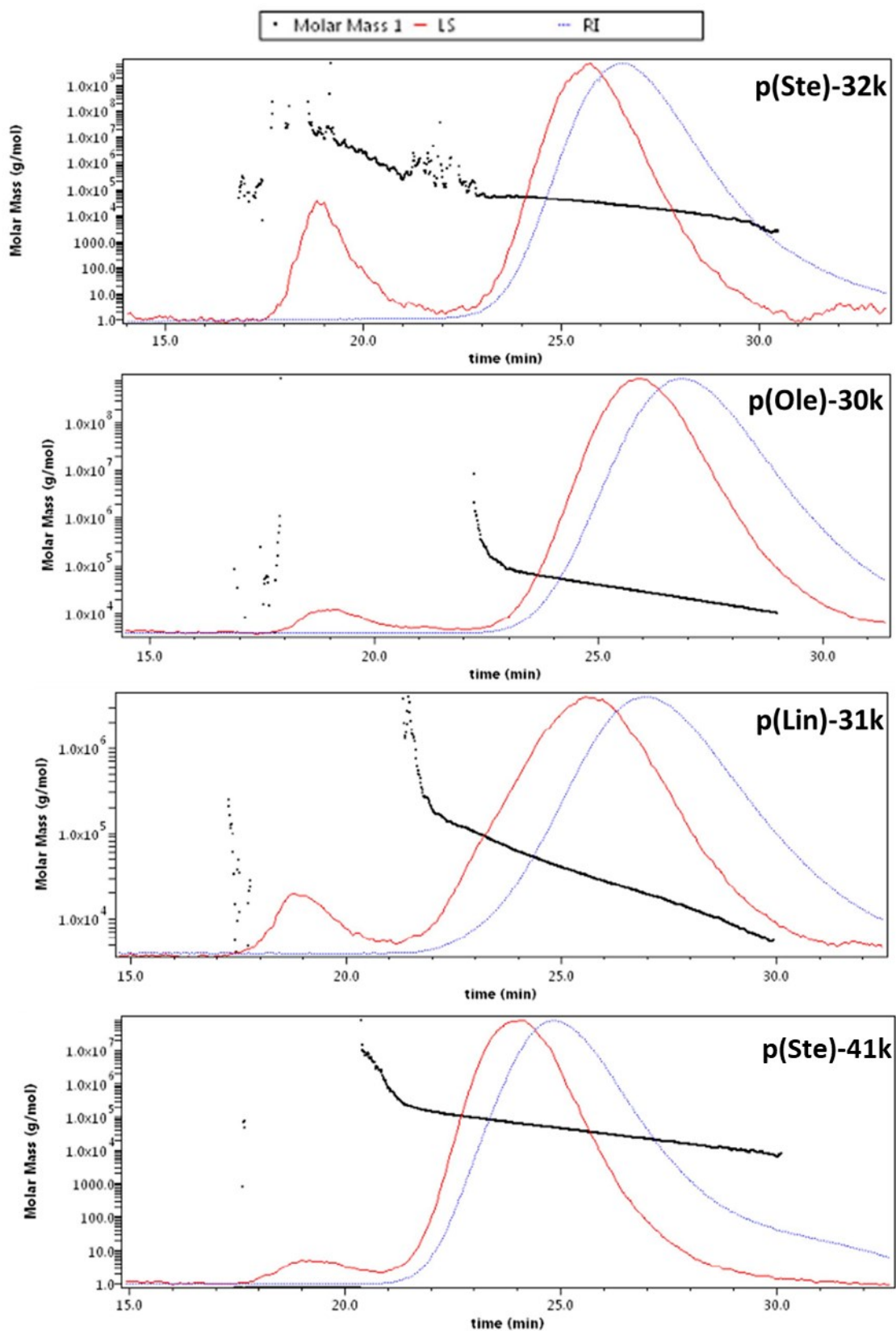


Figure S5. Light scattering data and fitting molecular weight curves of four polymers for absolute molecular weight determination.

Table S1. The summary of molecular characterizations of **p(Ste)**, **p(Ole)**, and **p(Lin)**.

Polyester	M_n^a (kDa)	M_w^a (kDa)	$\bar{D}^a$	M_w^b (kDa)	dn/dc^c (mL/g)
p(Ste)-32k	19.7	32.5	1.65	26.0	0.0905
p(Ole)-30k	17.5	30.0	1.72	24.4	0.0920
p(Lin)-31k	18.1	31.9	1.76	25.4	0.0876
p(Ste)-41k	20.8	41.8	2.00	33.1	0.0918

^aDetermined by GPC equipped with RI detector using DMF (with 25mM LiBr) as the eluent and PS as the standard.

^bThe absolute M_w was determined by GPC using multiangle laser light scattering (MALLS) detector and DMF (with 0.1M LiBr) as the eluent at 30 °C.

^cThe dn/dc of the polymer in DMF (with 0.1M LiBr) was measured at 30 °C using waters 2410 RI detector.

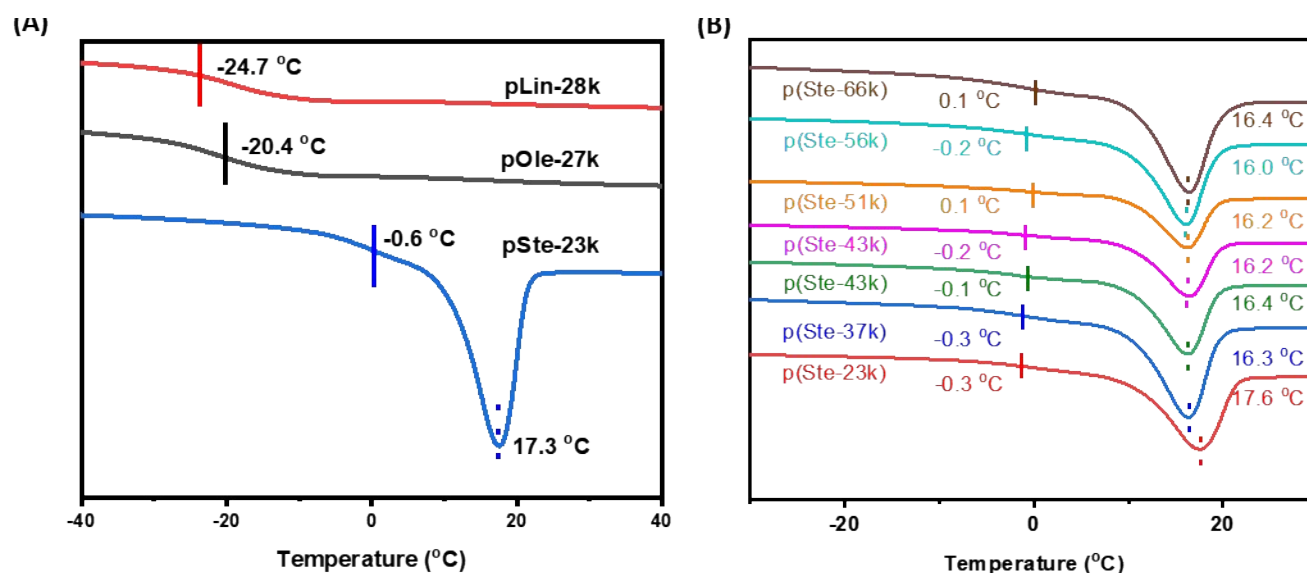


Figure S6. (A) DSC traces of **p(Ste)-23k**, **p(Ole)-27k**, and **p(Lin)-28k** at a heating rate of 10 °C/min. (B) DSC traces of **p(Ste)** with different weight average molecular weights at a heating rate of 10 °C/min. Glass transition temperatures are indicated by short vertical solid lines and melting temperatures are indicated by dotted vertical lines.

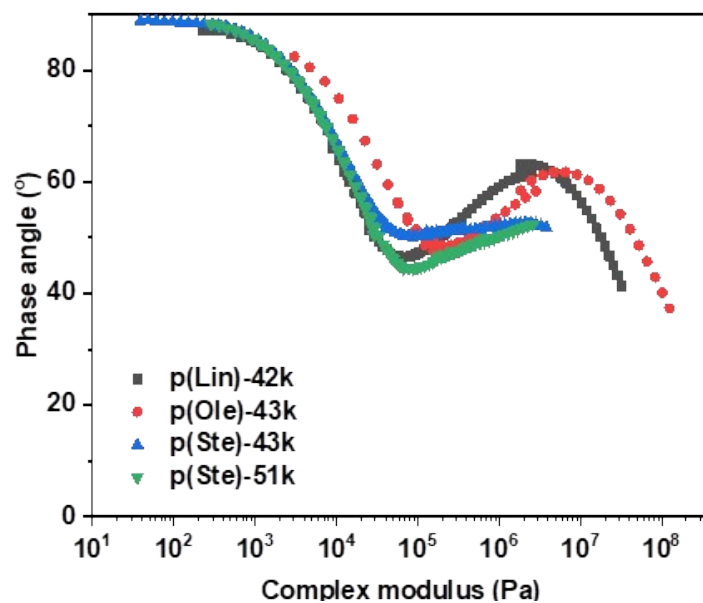


Figure S7. Van Gurp-Palmen plots of **p(Ste)-51k**, **p(Ste)-43k**, **p(Ole)-43k**, and **p(Lin)-42k**.

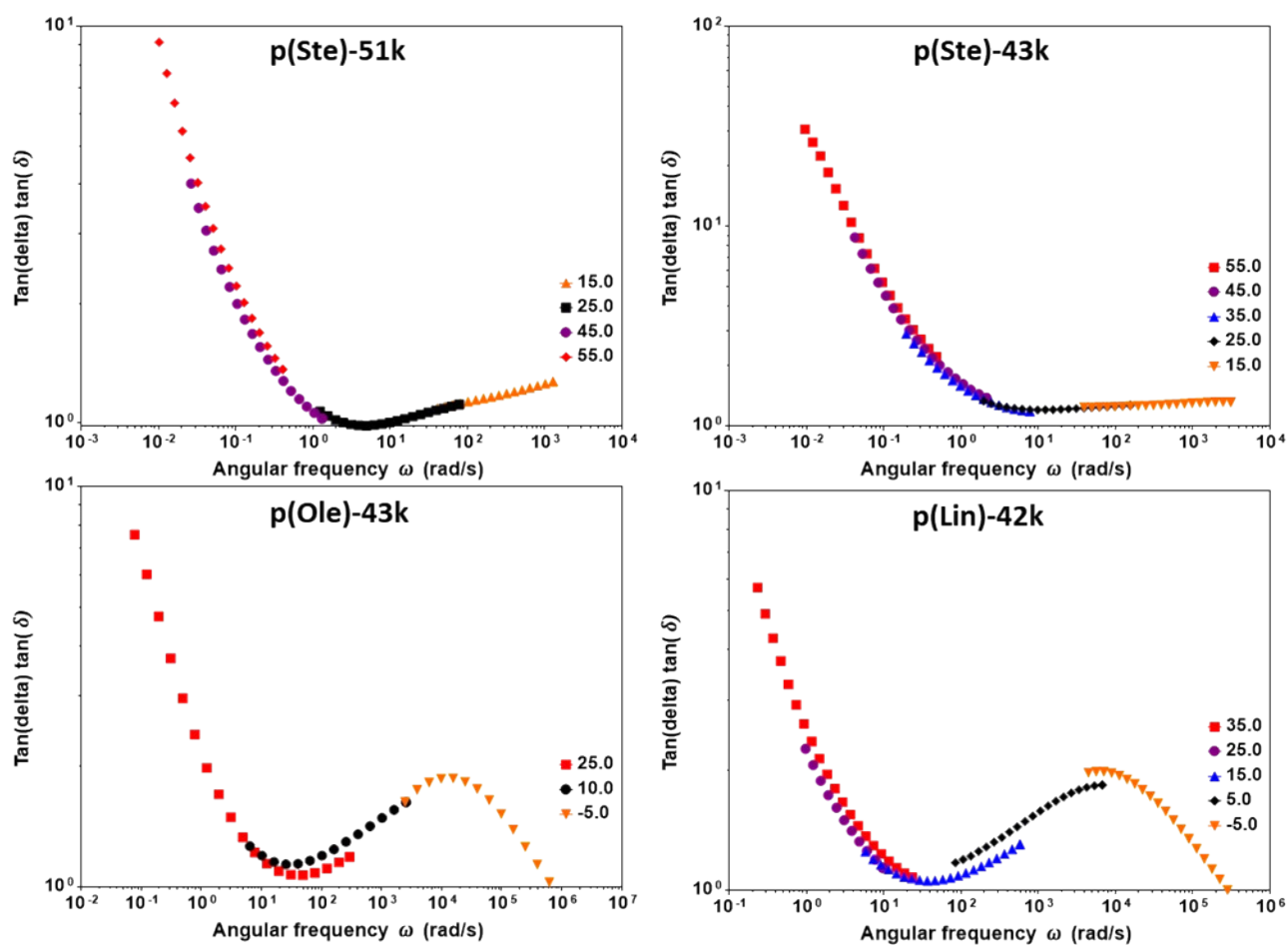


Figure S8. Tan (delta) versus angular frequency plots of **p(Ste)-51k**, **p(Ste)-43k**, **p(Ole)-43k**, and **p(Lin)-42k**.

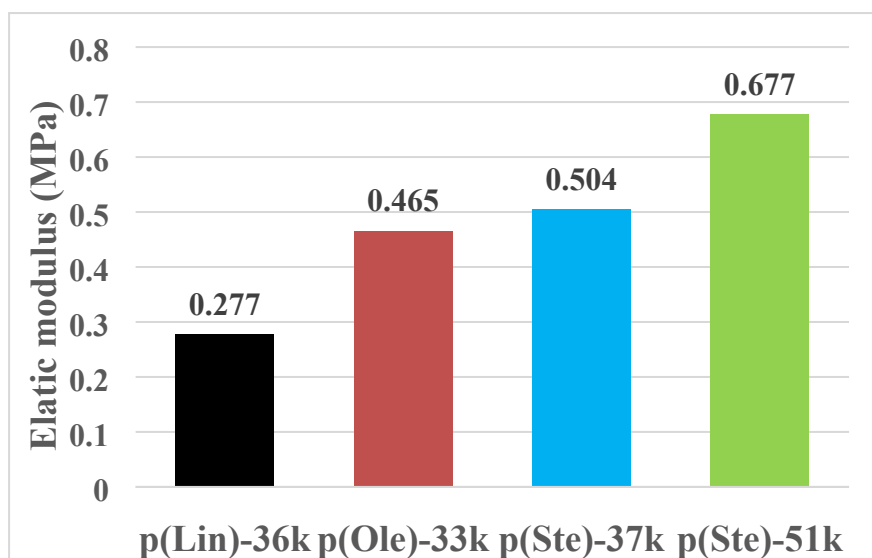


Figure S9. Elastic modulus of p(Ste)-51k, p(Ste)-37k, p(Ole)-33k and p(Lin)-36k.

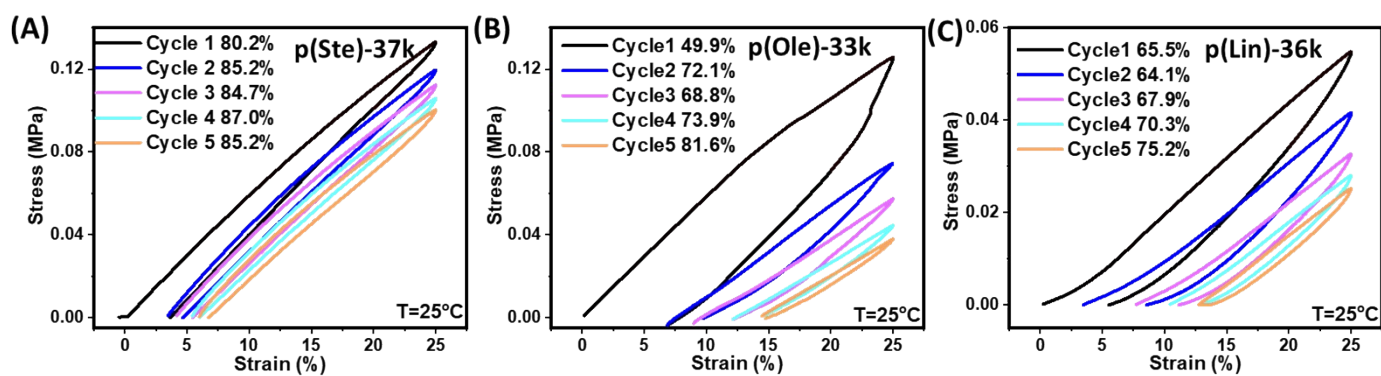


Figure S10. Cyclic tensile test results of (A) p(Ste)-37k, (B) p(Ole)-33k, and (C) p(Lin)-36k at 25 °C.

Crosslinking density measurement by swelling equilibrium method

The polyesters **p(Ste)-32k**, **p(Ole)-30k**, and **p(Lin)-31k** (see Figure S5 and Table S1 for molecular characterization) were vacuum pressed into films and irradiated with UV light in the same way as those used for tensile test sample preparations. Three replicates of pre-weighed dry film (5 × 5 × 1 mm) were cut from each polymer film, weighed and immersed into 15 mL dichloromethane (DCM) at 25 °C. The DCM was removed by pipette and refilled every 12h. After 48h, the film was taken out, blotted with filter paper, and weighed. The samples were dried in oven (110 °C) until constant weight values were attained and compared to the initial weight.

The crosslinking density cannot be calculated due to the lack of the polymer-dichloromethane interaction parameters.¹

Table S2. The summary of the swelling experiment data of **p(Ste)-32k**, **p(Ole)-30k**, and **p(Lin)-31k**.

Polyester	M ₀ (mg)	M _s (mg)	M _d (mg)	Gel fraction (%)	Swelling (%)
p(Ste)-32k	28.1±1.3	179.9±8.9	4.0±0.4	14.18±0.85	532.28±31.62
p(Ole)-30k	27.0±0.7	176.4±5.7	4.0±0.2	14.89±0.62	551.79±7.82
p(Lin)-31k	27.0±0.5	184.1±12.3	4.1±0.2	15.29±0.60	567.79±26.98

^aM₀ is the initial weight of initial dry film (5 × 5 × 1 mm)

^bM_s is the weight of swollen film after 48 h.

^cM_d is the weight of dried film after 48h.

^dGel fraction = M_d/ M₀*100%

^eSwelling = (M_s- M₀)/ M₀*100%

Entanglement molecular weight calculation for **p(Ste)**

The M_e of **p(Ste)** was determined as follows,

$$M_e = \frac{\rho RT}{G_N^0} = \frac{1.12 * 10^3 \text{ kg} \cdot \text{m}^{-3} * 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} * 298.15 \text{ K}}{8.7 * 10^4 \text{ Pa}} = 32.0 \text{ kg} \cdot \text{mol}^{-1}$$

(Eq. S1)

$G_N^0 = |G^*|_{\delta-\min} = 8.7 * 10^4 \text{ Pa}$, $|G^*|_{\delta-\min}$ is the value of complex modulus at the minimum $\tan\delta$ of **p(Ste)-51k** in Van-Gurp plots (Figure S4).¹⁻³

$\rho = 1.12 * 10^3 \text{ kg} \cdot \text{m}^{-3}$, the density here is measured for polyesters made from soybean oil, a mixture of different fatty acids. The actual density of **p(Ste)** will be higher than the density of polyesters made from soybean oil.

$$R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

$$T = 298.15 \text{ K}$$

Trend of packing length of three polyesters

$$\eta_{0R} = G_R \sum_{q=1}^N \tau_q = (\rho RT/M) \sum_{q=1}^N \frac{\tau_1}{q^2} = (\rho RT/M) \tau_1 \sum_{q=1}^N \frac{1}{q^2} = (\rho RT/M) \tau_0 N^2 \sum_{q=1}^N \frac{1}{q^2} = \zeta N/18p$$

(Eq. S2)

Where, η_{0R} is Rouse zero shear viscosity, N is the number of repeating unit, l_k is Kuhn length, τ_0 is elemental time scale for chain segment, ζ is friction coefficient, G_R is Rouse modulus and τ_q is the relaxation time of the Rouse segments.⁴

In our case, the η_{0R} follows the trend **p(Ste) > p(Ole) > p(Lin)** for similar molecular weights or N . Based on the energy recovery or resilience plots shown in Fig. 5, the highest energy dissipation or lowest resilience is seen for **p(Lin)** which has the highest degree of unsaturation. Since the energy dissipation is directly related to the intermolecular friction, the trend for molecular friction coefficient trend can be estimated to be **p(Ste) < p(Ole) < p(Lin)**. Therefore, based on Equation 2⁴ and the observed zero-shear viscosity trend, the p value trend can be estimated to be **p(Ste) < p(Ole) < p(Lin)**.

Reference

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