Supporting Information

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

Xinhao Liu, Tanmay Jain, Qianhui Liu and Abraham Joy*

a Department of Polymer Science, The University of Akron, Akron, OH 44325, USA

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Figure S1. $^1$H NMR (CDCl$_3$) spectra of four diol monomers, (A) Ste, (B) Ole, (C) Lin, and (D) Cou.
Figure S2. Zoom-in $^1$H 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).

<table>
<thead>
<tr>
<th>Polyester</th>
<th>$M_n^a$ (kDa)</th>
<th>$M_w^a$ (kDa)</th>
<th>$D^b$</th>
<th>$M_w^b$ (kDa)</th>
<th>$dn/dc^c$ (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(Ste)-32k</td>
<td>19.7</td>
<td>32.5</td>
<td>1.65</td>
<td>26.0</td>
<td>0.0905</td>
</tr>
<tr>
<td>p(Ole)-30k</td>
<td>17.5</td>
<td>30.0</td>
<td>1.72</td>
<td>24.4</td>
<td>0.0920</td>
</tr>
<tr>
<td>p(Lin)-31k</td>
<td>18.1</td>
<td>31.9</td>
<td>1.76</td>
<td>25.4</td>
<td>0.0876</td>
</tr>
<tr>
<td>p(Ste)-41k</td>
<td>20.8</td>
<td>41.8</td>
<td>2.00</td>
<td>33.1</td>
<td>0.0918</td>
</tr>
</tbody>
</table>

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

$^b$The 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.

$^c$The $dn/dc$ 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 short vertical dotted 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 \textbf{p(Ste)-32k}, \textbf{p(Ole)-30k}, and \textbf{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.

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

<table>
<thead>
<tr>
<th>Polyester</th>
<th>(M_0) (mg)</th>
<th>(M_s) (mg)</th>
<th>(M_d) (mg)</th>
<th>Gel fraction (%)</th>
<th>Swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{p(Ste)-32k}</td>
<td>28.1±1.3</td>
<td>179.9±8.9</td>
<td>4.0±0.4</td>
<td>14.18±0.85</td>
<td>532.28±31.62</td>
</tr>
<tr>
<td>\textbf{p(Ole)-30k}</td>
<td>27.0±0.7</td>
<td>176.4±5.7</td>
<td>4.0±0.2</td>
<td>14.89±0.62</td>
<td>551.79±7.82</td>
</tr>
<tr>
<td>\textbf{p(Lin)-31k}</td>
<td>27.0±0.5</td>
<td>184.1±12.3</td>
<td>4.1±0.2</td>
<td>15.29±0.60</td>
<td>567.79±26.98</td>
</tr>
</tbody>
</table>

\(^a\)M_{0} is the initial weight of initial dry film (5 × 5 × 1 mm)
\(^b\)M_{s} is the weight of swollen film after 48 h.
\(^c\)M_{d} is the weight of dried film after 48h.
\(^d\)Gel fraction = \(M_d\)/\(M_0\)*100%
\(^e\)Swelling = \((M_s\ - \ M_0)/\ M_0\)*100%

\textbf{Entanglement molecular weight calculation for \textbf{p(Ste)}}

The \(M_e\) of \textbf{p(Ste)} was determined as follows,

\[
M_e = \frac{\rho RT G_0^0 N}{G_N^0} = \frac{1.12 \times 10^3 \text{kg} \cdot \text{m}^{-3} \cdot 8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298.15K}{8.7 \times 10^4 \text{Pa}} = 32.0 \text{kg} \cdot \text{mol}^{-1}
\]

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

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

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

\(T = 298.15 \text{K}\)

\textbf{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, \( \eta_{0R} \) is Rouse zero shear viscosity, \( N \) is the number of repeating unit, \( l_k \) is Kuhn length, \( \tau_0 \) is elemental time scale for chain segment, \( \zeta \) is friction coefficient, \( G_R \) is Rouse modulus and \( \tau_q \) is the relaxation time of the Rouse segments. \(^4\)

In our case, the \( \eta_{0R} \) follows the trend \( p(\text{Ste}) > p(\text{Ole}) > p(\text{Lin}) \) 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 \( p(\text{Lin}) \) 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 \( p(\text{Ste}) < p(\text{Ole}) < p(\text{Lin}) \). Therefore, based on Equation 2\(^4\) and the observed zero-shear viscosity trend, the \( p \) value trend can be estimated to be \( p(\text{Ste}) < p(\text{Ole}) < p(\text{Lin}) \).

Reference