

## Supporting Information

### Synthesis of highly branched poly( $\delta$ -valerolactone)s: A comparative study between comb and linear analogues

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Table S1. Molecular weight and degree of epoxidation of macroinitiators

| sample | $M_n^a$ (Da) | $M_w^a$ (Da) | $D^a$ | $E^b$ (mol%) |
|--------|--------------|--------------|-------|--------------|
| L-HPB  | 6100         | 6600         | 1.08  | 23.7         |
| S-HPB  | 12400        | 13800        | 1.11  | 12.3         |

<sup>a</sup>Measured by GPC in THF. <sup>b</sup>Degree of epoxidation. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

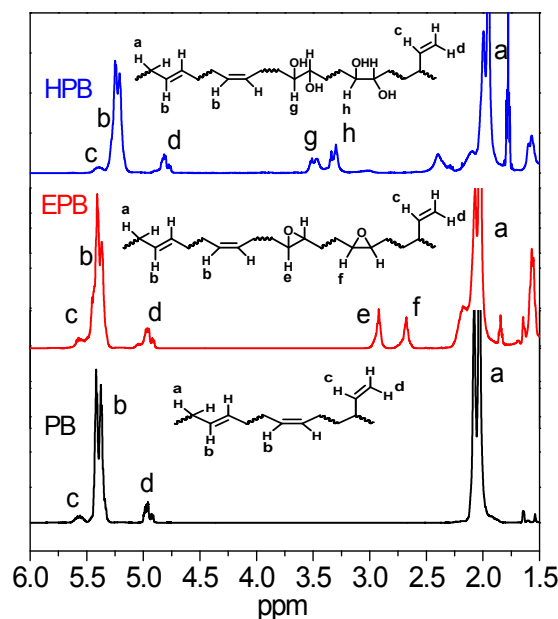


Figure S1. <sup>1</sup>H-NMR spectra of polybutadiene, epoxidized polybutadiene (E 23.7 mol %), and hydroxylated polybutadiene.

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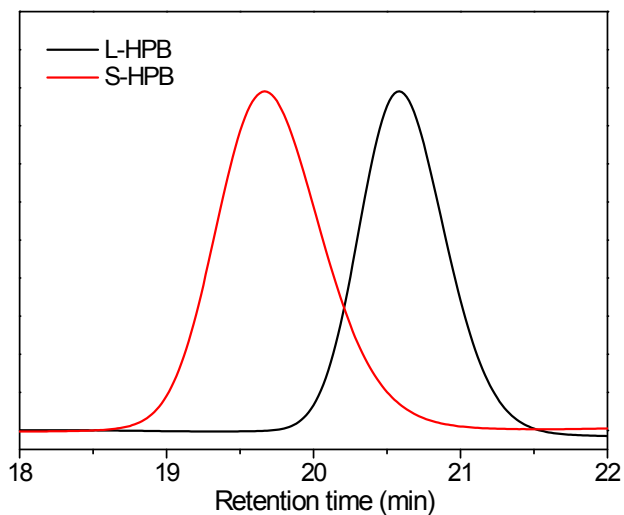


Figure S2. GPC curves of linear and star hydroxylated polybutadienes.

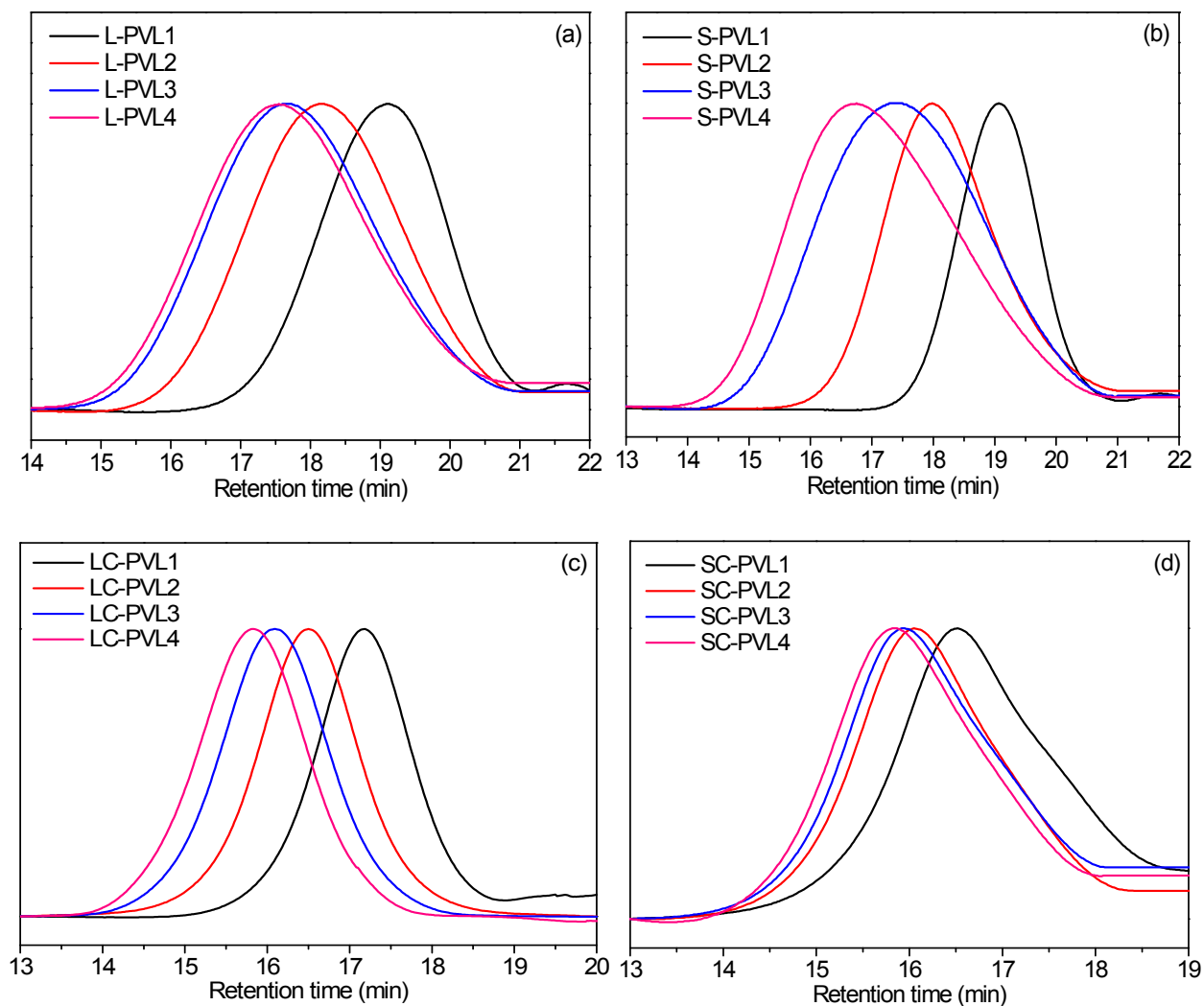


Figure S3. GPC curves of (a) linear poly( $\delta$ -valerolactone)s, (b) star poly( $\delta$ -valerolactone)s, (c) linear-comb poly( $\delta$ -valerolactone)s, and (d) star-comb poly( $\delta$ -valerolactone)s.

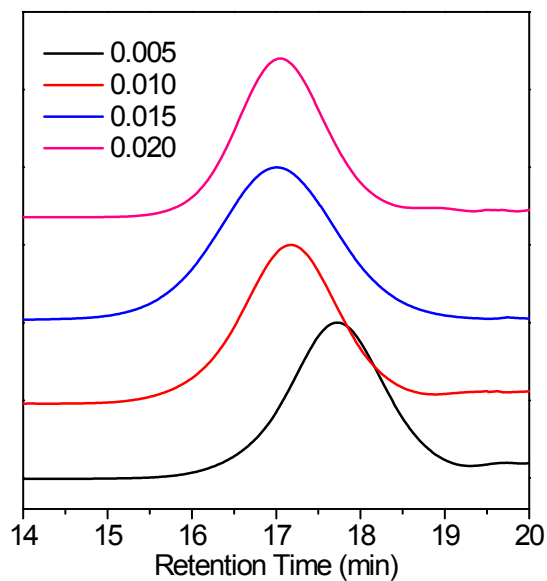


Figure S4. GPC curves of LC-PVLs synthesized with different catalyst loadings.

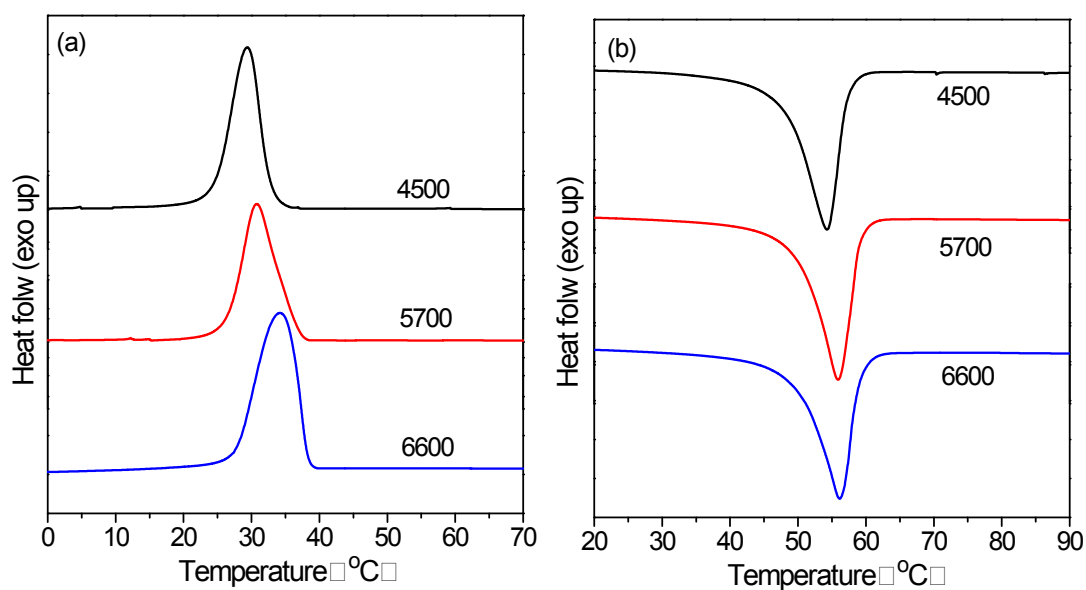


Figure S5. (a) Crystallization curves of SC-PVLs with different side chain length. (b) Melting curves of SC-PVLs with different side chain length.

Table S2. Thermal parameters of SC-PVLs with different side chain length

| sample | $M_n^a$ (KDa) | $M_n^{*b}$ (Da) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) |
|--------|---------------|-----------------|------------|--------------------|------------|--------------------|
| 6-1    | 71            | 4500            | 54.3       | 70.9               | 29.4       | 70.6               |
| 6-2    | 147           | 5700            | 55.9       | 78.4               | 30.9       | 79.6               |
| 6-3    | 134           | 6600            | 56.1       | 80.9               | 34.2       | 85.9               |

<sup>a</sup>Measured by GPC in THF.

<sup>b</sup> $M_n^*$  means the molecular weight of single arm. Measured by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

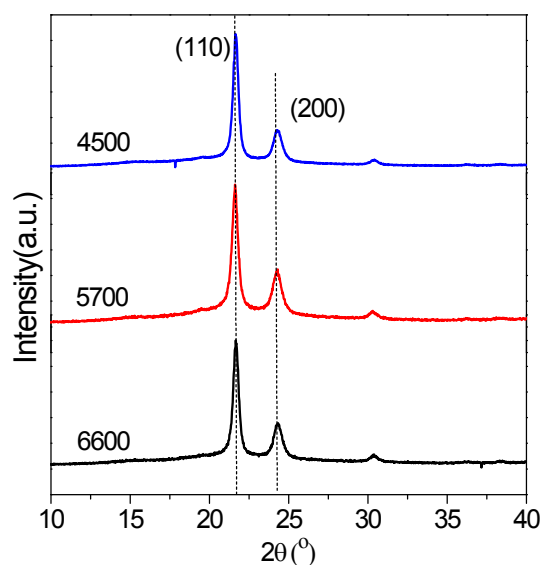


Figure S6. WAXD patterns of SC-PVLs with different side chain length.

Table S3. Crystallite size of  $L_{110}$  and  $L_{200}$  and crystallinity of SC-PVLs with different side chain length

| sample | $M_n^*$ (Da) | $L_{110}$   |           |                | $L_{200}$   |           |                | $X_c^d$ (%) |
|--------|--------------|-------------|-----------|----------------|-------------|-----------|----------------|-------------|
|        |              | $2\theta^b$ | $\beta^c$ | $d_{hkl}$ (nm) | $2\theta^b$ | $\beta^c$ | $d_{hkl}$ (nm) |             |
| 6-1    | 4500         | 21.65       | 0.375     | 22.4           | 24.28       | 0.638     | 12.9           | 71.2        |
| 6-2    | 5700         | 21.60       | 0.413     | 22.1           | 24.24       | 0.696     | 12.3           | 75.3        |
| 6-3    | 6600         | 21.66       | 0.379     | 20.2           | 24.32       | 0.640     | 11.8           | 78.6        |

<sup>a</sup> $M_n^*$  means the molecular weight of single arm. Measured by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

<sup>b</sup>Bragg angle.

<sup>c</sup>Measured half-width of the experimental profile.

<sup>d</sup>Crystallinities were measured by XRD.