## **Supporting Information**

 Table S1 Thermal parameters of PDLA-PCVL-PDLA triblock copolymers and the

 corresponding supramolecular polymers derived from DSC scans

Table S2 Thermal parameters of PLLA/supramolecular polymer blends derived from

DSC scans

Fig. S1 XRD patterns of PLLA/SMP blends: (a) PLLA/SMP0.49; (b) PLLA/SMP1.04

Fig. S2 Variation of storage modulus (G') and loss modulus (G'') as function of frequency for the

neat PLLA melted at 175°C

Fig. S3 Variation of loss tangent (tanδ) as function of frequency for the neat PLLA melted at 175°C

Fig. S4 Variation of complex viscosity ( $\eta^*$ ) as function of frequency for the neat PLLA melted at 175°C

|                    |   | Coc                             | oling                                 |                                 |                        | Re-heating                                      |                                       |   |                                 |                                   |                                 |  |  |  |  |
|--------------------|---|---------------------------------|---------------------------------------|---------------------------------|------------------------|---|---------------------------------------|---|---------------------------------|-----------------------------------|---------------------------------|--|--|--|--|
| Sample             | <i>T<sub>c</sub>, <sub>PCVL</sub></i><br>(°С) | $\Delta H_c$ ,<br>PCVL<br>(J/g) | <i>Т<sub>с,PDL</sub></i><br>А<br>(°С) | $\Delta H_c$ ,<br>pdla<br>(J/g) | Т <sub>g</sub><br>(°С) | <i>T<sub>cold,PCV</sub></i><br><i>L</i><br>(°С) | ΔH <sub>cold</sub> ,<br>PCVL<br>(J/g) | <i>T<sub>m</sub>, <sub>PCVL</sub></i><br>(°С) | $\Delta H_m$ ,<br>PCVL<br>(J/g) | <i>Т<sub>m,PDLA</sub></i><br>(°С) | $\Delta H_m$ ,<br>PDLA<br>(J/g) |  |  |  |  |
| PDLA-PCVL-PDLA0.49 | 3.8/11.<br>6                                  | 47.3                            |                                       |                                 |                        |   |                                       | 30.2/35.4                                     | 46.7                            |                                   |                                 |  |  |  |  |
| PDLA-PCVL-PDLA1.04 | 7.9   | 30.1                            | 72.4                                  | 8.9                             |                        |   |                                       | 29.2/34.7                                     | 30.0                            | 108.9/127.9                       | 8.7                             |  |  |  |  |
| SMP0.49            | -16.3   | 11.6                            |                                       |                                 | -54.1                  | -12.9   | 24.6                                  | 28.9  | 38.5                            |                                   |                                 |  |  |  |  |
| SMP1.04            |   |                                 |                                       |                                 | -45.6                  |   |                                       |   |                                 | 117.3                             | 3.3                             |  |  |  |  |

Table S1 Thermal parameters of PDLA-PCVL-PDLA triblock copolymers and the corresponding supramolecular polymers derived from DSC scans

Notes:  $T_{c,PCVL}$  and  $T_{c,PDLA}$  denote the crystallization temperatures of PCVL and PDLA blocks in the cooling run, respectively;  $\Delta H_{c,PCVL}$  and  $\Delta H_{c,PDLA}$  represent the crystallization enthalpy of PCVL

and PDLA block in the cooling run;  $T_g$  represents the glass transition temperature;  $T_{cold, PCVL}$  and  $\Delta H_{cold, PCVL}$  are cold crystallization temperature and cold crystallization enthalpy of PCVL block in

heating run, respectively;  $T_{m,PCVL}$  and  $T_{m,PDLA}$  are melting temperatures of PCVL and PDLA blocks, respectively;  $\Delta H_{m,PCVL}$  and  $\Delta H_{m,PDLA}$  are the melting enthalpy of PCVL and PDLA blocks in the

heating run.

| Sample           | Cooling                   |  |                            |                                 | Re-heating                        |                                |                        |                             |                                    |                           |                          |                                 |                         | XcPULA |
|------------------|---------------------------|--|----------------------------|---------------------------------|-----------------------------------|--------------------------------|------------------------|-----------------------------|------------------------------------|---------------------------|--------------------------|---------------------------------|-------------------------|--------|
|                  | Т <sub>с,hc</sub><br>(°С) | ∠ <i>H<sub>c,h</sub></i><br>c<br>(J/g) | Т <sub>с, sc</sub><br>(°С) | ΔH <sub>c,s</sub><br>c<br>(J/g) | <i>Т<sub>т,РСVL</sub></i><br>(°С) | $\Delta H_{m,PCV}$ $L$ $(J/g)$ | Т <sub>g</sub><br>(°С) | T <sub>cold,hc</sub><br>(℃) | ΔH <sub>cold,h</sub><br>c<br>(J/g) | Т <sub>т,hc</sub><br>(°С) | $\Delta H_{m,h}$ c (J/g) | <i>Т<sub>т,sc</sub></i><br>(°С) | $\Delta H_{m,sc}$ (J/g) | (%)    |
| PLLA             | 99.4                      | 7.4                                    |                            |                                 |                                   |                                | 60.0                   | 112.2                       | 24.5                               | 161.6/166.9               | 35.6                     |                                 |                         | 11.9   |
| PLLA/SMP0.49-10% | 99.3                      | 0.5                                    |                            |                                 | 30.5                              | 3.2                            | 59.8                   | 113.3                       | 29.3                               | 162.5/169.1               | 29.6                     |                                 |                         | 0.4    |
| PLLA/SMP0.49-30% |                           |  |                            |                                 | 29.9                              | 5.3                            | 58.9                   | 112.9                       | 21.3                               | 161.0/167.9               | 21.3                     | 181.2                           | 0.4                     | 0      |
| PLLA/SMP0.49-50% |                           |  |                            |                                 | 29.8                              | 11.3                           | 58.6                   | 114.5                       | 16.3                               | 161.7/168.7               | 16.0                     | 183.0                           | 0.7                     | 0      |
| PLLA/SMP1.04-10% | 96.5                      | 2.4                                    | 137.6                      | 1.1                             |                                   |                                | 58.7                   | 112.2                       | 18.9                               | 161.0/166.9               | 23.8                     | 182.0                           | 0.3                     | 5.8    |
| PLLA/SMP1.04-30% | 98.6                      | 8.5                                    | 141.0                      | 1.8                             | 27.9                              | 0.8                            | 58.7                   | 109.8                       | 9.6                                | 160.2/166.0               | 22.6                     | 182.3                           | 1.3                     | 19.8   |
| PLLA/SMP1.04-50% | 110.1                     | 12.9                                   | 142.8                      | 4.8                             | 26.5/33.2                         | 9.0                            |                        |                             |                                    | 156.0/164.3               | 13.7                     | 183.3                           | 3.8                     | 29.2   |

Table S2 Thermal parameters of PLLA/supramolecular polymer blends derived from DSC scans

Notes:  $T_{c,hc}$  and  $T_{c,sc}$  denote the crystallization temperatures of homo-crystallization and stereocomplex crystallization in the cooling run, respectively;  $\Delta H_{c,hc}$  and  $\Delta H_{c,sc}$  represent the crystallization enthalpy of homo-crystallization and stereocomplex crystallization in the cooling run, respectively;  $T_{m,PCVL}$  and  $\Delta H_{m,PCVL}$  are melting temperature and melting enthalpy of PCVL block, respectively;  $T_g$  represents the glass transition temperature;  $T_{cold,hc}$  and  $\Delta H_{cold,hc}$  are cold crystallization temperature and cold crystallization enthalpy of homo-crystallization in heating run, respectively;  $T_{m,hc}$  and

 $T_{m,sc}$  are melting temperatures of homo-crystallized PLLA and stereocomplex in the heating run, respectively;  $\Delta H_{m,hc}$  and  $\Delta H_{m,sc}$  are the melting enthalpy of homo-crystallized PLLA and stereocomplex; respectively;  $X_{c,PLLA}(\%) = (\Delta H_{m,hc} - \Delta H_{cold,hc})/([1-P] \times \Delta H_{m,PLLA}^0)$ ,  $\Delta H_{m,PLLA}^0 = 93.6$  J/g,P denotes the mass fraction of supramolecular polymer in the blends.



Fig. S1 XRD patterns of PLLA/SMPs blends: (a) PLLA/SMPs0.49; (b) PLLA/SMPs1.04



Fig. S2 Variation of storage modulus (G') and loss modulus (G'') as function of frequency for the neat

PLLA melted at 175°C



Fig. S3 Variation of loss tangent (tan $\delta$ ) as function of frequency for the neat PLLA melted at 175°C



Fig. S4 Variation of complex viscosity ( $\eta^*$ ) as function of frequency for the neat PLLA melted at 175°C