

## Electronic Supplementary Information

### **Stereocomplex formation in stereoblock copolymer networks composed of 4-armed star-shaped lactide oligomers and 2-armed $\epsilon$ -caprolactone oligomer**

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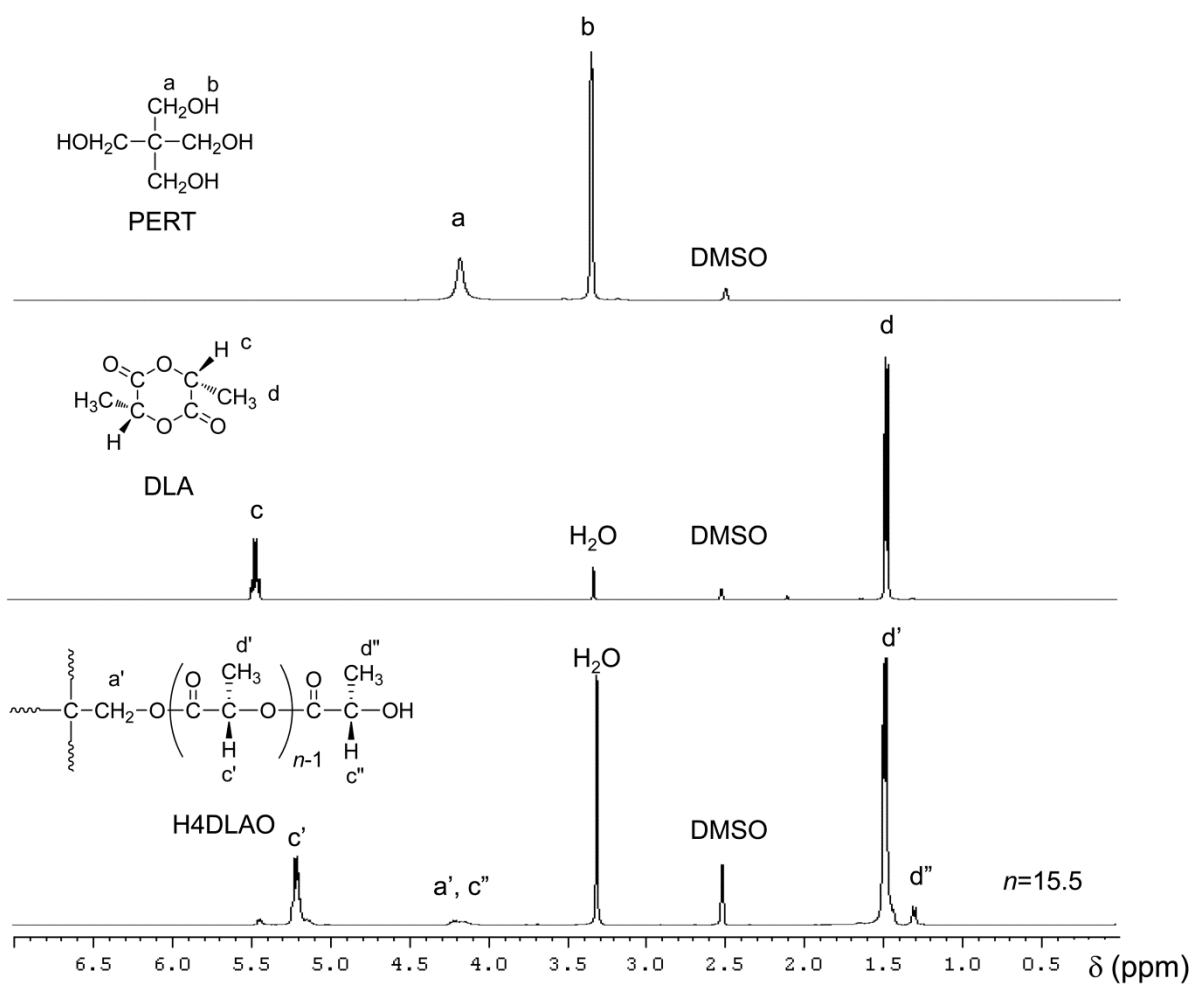
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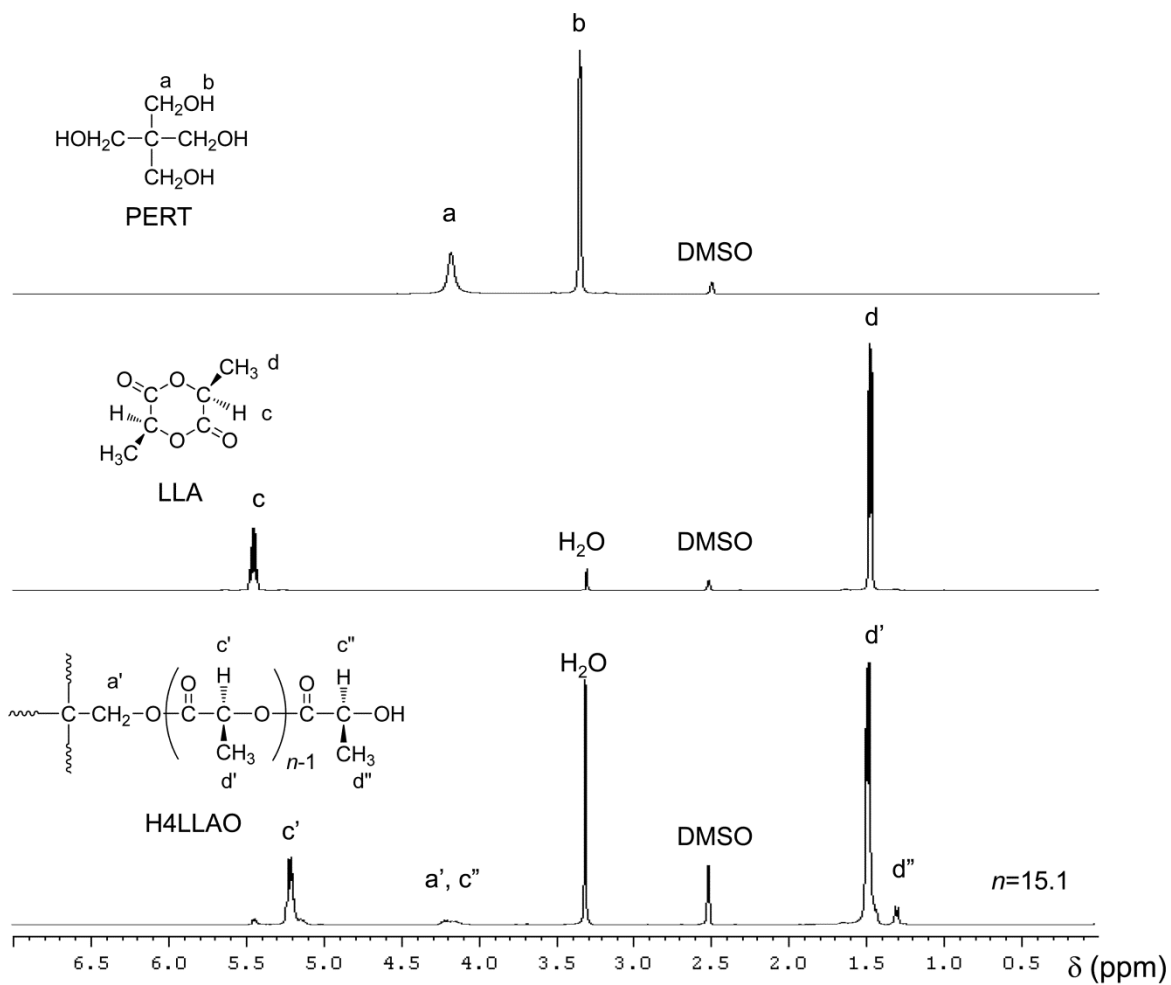
E-mail: [mitsuhiro.shibata@p.chibakoudai.jp](mailto:mitsuhiro.shibata@p.chibakoudai.jp) (M.Shibata);

**Table S1** Tensile properties of MH-4scLAO/2CLOs (100/0, 75/25, 50/50, 25/75 and 0/100).

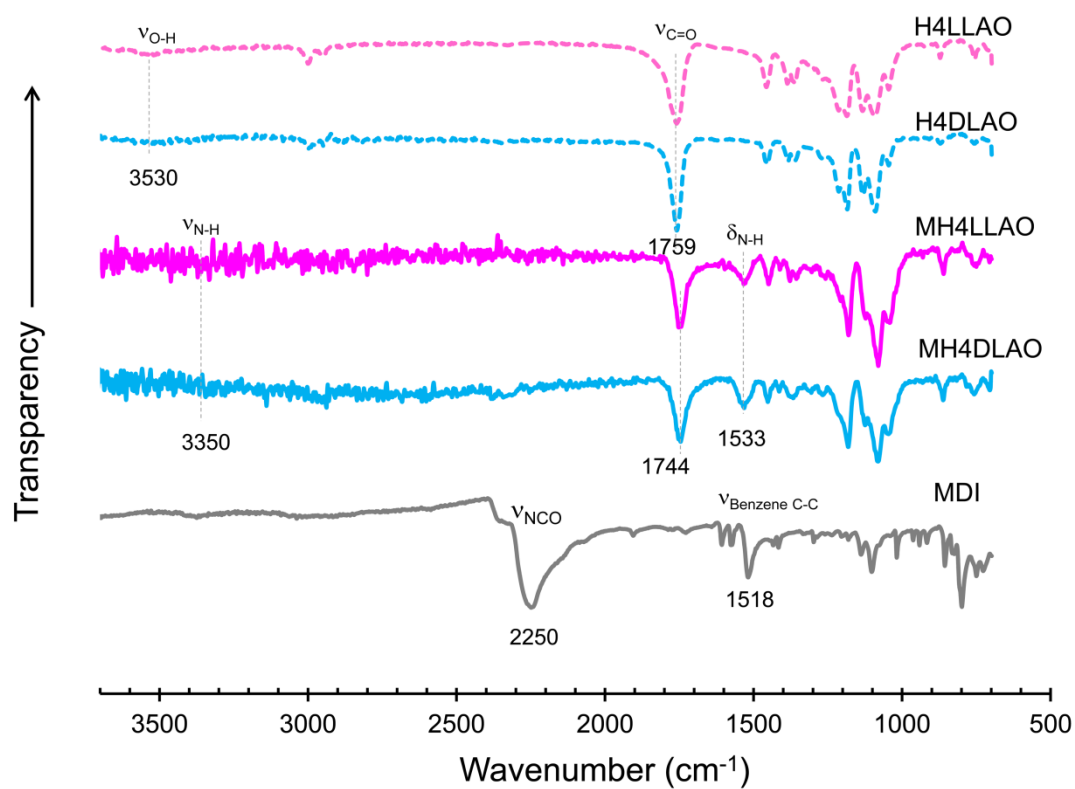
| Sample               | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) | Tensile toughness (MJ m <sup>-3</sup> ) |
|----------------------|------------------------|-----------------------|-------------------------|---|
| MH4LLAO              | 28.3 ± 9.2             | 2355 ± 224            | 1.8 ± 0.6               | 0.32 ± 0.20                             |
| MH4DLAO              | 39.6 ± 11.8            | 2716 ± 463            | 6.1 ± 4.3               | 1.10 ± 0.52                             |
| MH4scLAO             | 34.7 ± 10.2            | 1695 ± 169            | 2.9 ± 1.0               | 0.66 ± 0.34                             |
| MH-4scLAO/2CLO 75/25 | 13.8 ± 3.2             | 632 ± 78              | 32.6 ± 10.9             | 4.13 ± 2.01                             |
| MH-4scLAO/2CLO 50/50 | 7.1 ± 0.5              | 68.6 ± 17.5           | 142 ± 13                | 7.82 ± 0.52                             |
| MH-4scLAO/2CLO 25/75 | 8.3 ± 1.1              | 132.8 ± 32.4          | 155 ± 51                | 1.10 ± 0.93                             |
| MH2CLO               | 9.3 ± 1.3              | 103.2 ± 4.8           | 884 ± 207               | 10.9 ± 3.3                              |



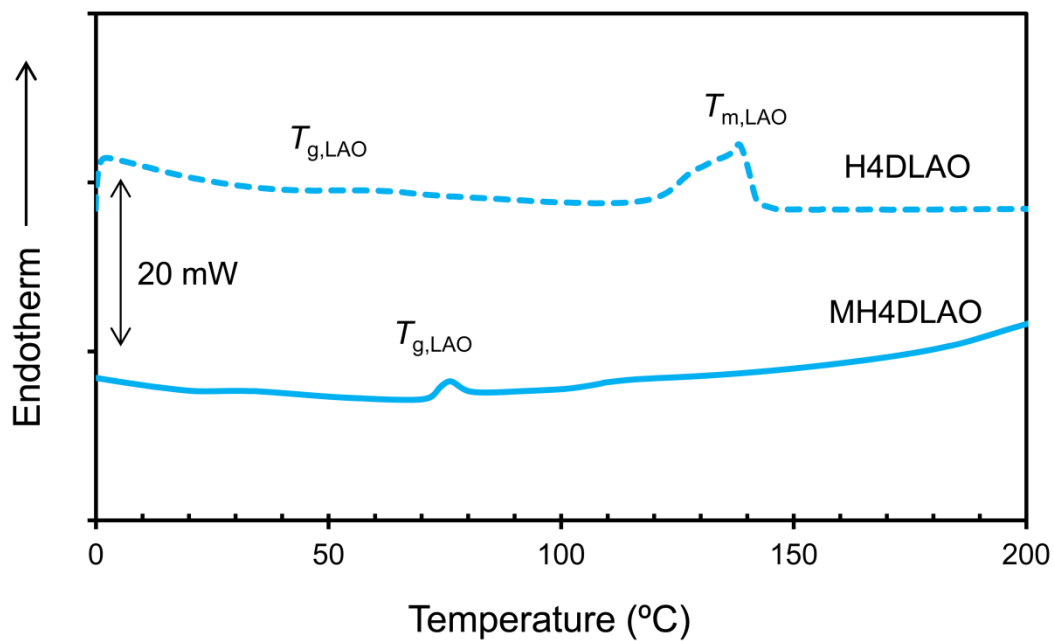
**Figure S1.** 400 MHz  $^1\text{H}$ -NMR spectrum of H4DLAO in  $\text{DMSO-}d_6$ .



**Figure S2.**  $^1\text{H-NMR}$  spectra of PERT, DLA, and H4DLAO in  $\text{DMSO-}d_6$ .



**Figure S3.** FT-IR spectra of H4LLAO, H4DLAO, MH4LLAO, MH4DLAO and MDI.



**Figure S4.** The first heating DSC curves of H4DLAO and MH4DLAO.