Supporting Information

Intra-molecular interactions dominating dehydration of poly(2-isopropyl-2-oxazoline)-based densely grafted polymer comb in aqueous solution and hysteretic liquid-liquid phase separation

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Figure S1. (a) DSC curve and (b) optical micrographs of comb-PiPOx aqueous solution (20 wt%) at different temperatures during the LLPS processes.

Figure S2. Variable-temperature FTIR spectra of linear-PiPOx in D2O (5 wt%) upon heating from 18 to 55 °C with an interval of 1 °C in the spectral regions 3020-2860 and 1670-1560 cm⁻¹.
Figure S3. PCMW synchronous and asynchronous spectra of comb-PiPOx in D2O (5 wt%). Warm colors (red) are defined as positive intensities and cool colors (blue) are defined as negative intensities.

**Bands assignments.**

Some of the characteristic bands of comb-PiPOx can be assigned according to previous FTIR studies on PiPOx-based system, such as those of CH-CH$_3$, N-CH$_2$CH$_2$-N and C=O$_A$ groups on side chains.$^{1-3}$ In addition to this, poly(oligo(ethylene glycol)methacrylate) (POEGMA) is commonly considered as an analogue to poly(oligo(2-isopropyl-2-oxazoline)methacrylate) (POiPOxMA, i.e., comb-PiPOx).$^4$ POEGMA and POiPOxMA are both comb-shaped with PMA backbone, and the (N-CH$_2$CH$_2$-N)$_n$-CH$_3$ side chain of POiPOxMA is fairly similar to the (O-CH$_2$CH$_2$-O)$_n$-CH$_3$ side chain of POEGMA. Consulting the band assignments of POEGMA,$^5$-9 we attribute the wavenumbers at 1734, 1717 and 1709 cm$^{-1}$ to free C=O$_E$ (dehydrated), dehydrating C=O$_E$ and hydrated C=O$_E$, respectively, and the band at 2993 cm$^{-1}$ is assigned to the side chain end methyl group (N-CH$_3$).

**Rules for analyzing PCMW and 2Dcos contour maps.**

PCMW technique is suited to analyze the spectral variation with S shaped and anti-S shaped intensity change. In synchronous map, the positive synchronous correlation reflects a spectral intensity increment and the negative one means a spectral intensity decrement, and the temperature coordinate of the cross-correlation peak is the transition temperature of the corresponding wavenumber (inflection-point temperature of the S or anti-S shaped intensity change). In asynchronous map, the positive and negative asynchronous correlations represent a convex spectral intensity change and a concave one, respectively. A pair of cross-correlation peaks with the same wavenumber coordinate reveals the initial and end temperatures of a transition (turning points of the S or anti-S shaped curves).

As proposed by Noda, the 2Dcos spectra can be interpreted via the following rule: if the synchronous and asynchronous cross-correlation peaks at ($v_1$, $v_2$) ($v_1 > v_2$) have the same symbol (both positive or both negative), the vibration mode at $v_1$ takes places earlier response to external perturbation than the one at $v_2$; otherwise, if the two cross-correlation peaks exhibit opposite symbol (one positive and the other one negative), the vibration mode at $v_1$ takes place later response to external perturbation than the one at $v_2$.